

A highly efficient and green synthesis of 3,4-dihydropyrimidin-2-ones in low melting mixtures

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Supporting Information

Table of Contents:

| | |
|---|---------|
| General Information | S2 |
| General Procedure for the formation of 3,4-dihydropyrimidin-2-ones | S2 |
| Characterization data for compounds | S2-S11 |
| Copy of ¹ H NMR and ¹³ C NMR spectra of compounds | S12-S71 |

General Information

^1H NMR spectra were recorded on 300 MHz and 400 MHz. ^{13}C NMR spectra were recorded on 75 and 100 MHz. Chemical shifts are expressed in δ units relative to tetramethylsilane (TMS) signal as internal reference in DMSO- d_6 , CDCl_3 or MeOD. FT-IR spectra's were recorded in CHCl_3 , or neat. Column chromatography was performed on silica gel (60-120 mesh) using ethyl acetate and hexane as eluent.

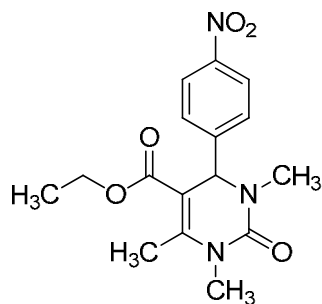
General Procedure for the formation of 3,4-dihydropyrimidin-2-ones:

In a typical experiment, 1.5 g of L-(+)-tartaric acid-DMU (30:70) mixture was heated to 70 °C to obtain a clear melt. To this melt, 1 mmol of aldehyde and 1 mmol of ethyl acetoacetate were added at 70 °C. The reaction was monitored by thin layer chromatography. The reaction mixture was quenched by adding water while still hot. The reaction mixture was cooled to room temperature and the solid separated was filtered out and washed with water (3×5 mL), dried under vacuum and recrystallized from ethanol to afford pure product.

Experimental Section

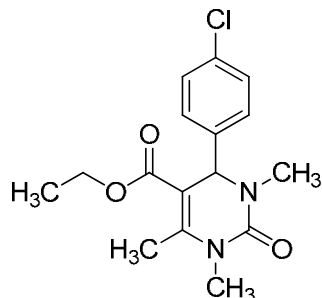
Spectral data of the 3,4-dihydropyrimidin-2-ones and thiones obtained by the condensation of aldehydes, 1,3-dicarbonyls and urea:

2a. Ethyl 1,3,6-trimethyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



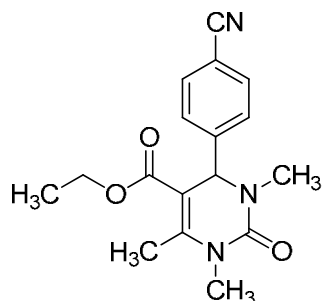
Yellow solid; Yield 96%; M.p. 104-106 °C; IR (neat): 1725, 1609, 1523 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.26 (t, 3H, $J = 6.9$ Hz), 2.49 (s, 3H), 2.93 (s, 3H), 3.27 (s, 3H), 4.16 (q, 2H, $J = 6.6$ Hz), 5.36 (s, 1H), 7.40 (d, 2H, $J = 8.7$ Hz), 8.16 (d, 2H, $J = 8.8$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 14.3, 16.8, 31.2, 34.7, 60.4, 60.5, 102.6, 124.0, 127.5, 147.6, 148.3, 150.4, 153.5, 165.6; HRMS, calcd. for ($\text{M}^+ + 1$) 334.1403, found 334.1415.

2b. Ethyl 4-(4-chlorophenyl)-1,3,6-trimethyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



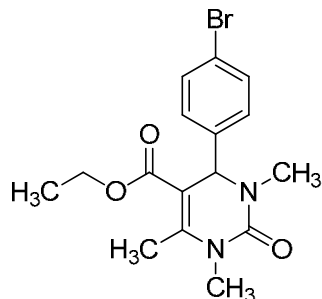
Pale yellow oil; Yield 90%; IR (neat): 1664, 1596 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.23 (t, 3H, $J = 6.9$ Hz), 2.46 (s, 3H), 2.88 (s, 3H), 3.24 (s, 3H), 4.11 (q, 2H, $J = 7.2$ Hz), 5.20 (s, 1H), 7.12–7.17 (m, 2H), 7.23 (s, 1H), 7.33 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 14.3, 16.7, 31.1, 34.5, 60.3, 60.4, 103.3, 128.0, 128.8, 133.6, 139.6, 149.6, 153.6, 165.8; HRMS, calcd. for $\text{C}_{16}\text{H}_{19}\text{ClN}_2\text{O}_3$ (M^+) 322.1084, found 322.1087.

2c. Ethyl 4-(4-cyanophenyl)-1,3,6-trimethyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



Pale yellow solid; Yield 97%; M.p. 85–87 $^\circ\text{C}$; IR (neat): 2110, 1687, 1606 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.21 (t, 3H, $J = 6.9$ Hz), 2.45 (s, 3H), 2.88 (s, 3H), 3.23 (s, 3H), 4.10 (q, 2H, $J = 6.9$ Hz), 5.27 (s, 1H), 7.28–7.34 (m, 2H), 7.55 (d, 2H, $J = 8.1$); ^{13}C NMR (75 MHz, CDCl_3): δ 14.3, 16.8, 31.2, 34.6, 60.4, 60.6, 102.6, 111.8, 118.6, 127.4, 132.6, 146.3, 150.2, 153.5, 165.6; HRMS, calcd. for $\text{C}_{17}\text{H}_{19}\text{N}_3\text{O}_3$ (M^+) 313.1426, found 313.1424.

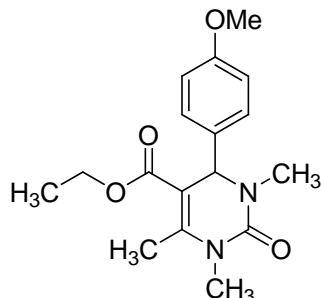
2d. Ethyl 4-(4-bromophenyl)-1,3,6-trimethyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



Pale yellow solid; Yield 84%; M.p. 65–66 $^\circ\text{C}$; IR (neat): 1684, 1611 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.24 (t, 3H, $J = 7.2$ Hz), 2.47 (s, 3H), 2.89 (s, 3H), 3.25 (s, 3H), 4.09–4.17 (m, 2H), 5.20 (s, 1H), 7.07–7.12 (m, 2H), 7.39–7.43 (m, 2H); ^{13}C NMR (75 MHz,

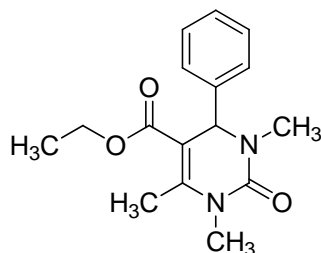
CDCl₃): δ 14.3, 16.7, 31.2, 34.5, 60.3, 60.4, 103.2, 121.8, 128.4, 131.8, 140.1, 149.6, 153.7, 165.8; HRMS, calcd. for C₁₆H₁₉BrN₂O₃ (M⁺) 366.0579, found 366.0575.

2e. Ethyl 4-(4-methoxyphenyl)-1,3,6-trimethyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



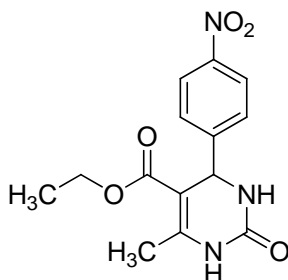
Yellow solid, Yield 98%; M.p. 82–84 °C; IR (neat): 1690, 1635 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 1.21 (t, 3H, *J* = 7.2 Hz), 2.46 (s, 3H), 2.87 (s, 3H), 3.24 (s, 3H), 3.75 (s, 3H), 4.06–4.14 (m, 2H), 5.16 (s, 1H), 6.77–6.81 (m, 2H), 7.11–7.14 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 14.3, 16.7, 31.1, 34.3, 55.3, 60.2, 60.4, 103.8, 113.9, 127.9, 133.2, 149.0, 153.8, 159.2, 166.1; HRMS, calcd. for C₁₇H₂₂N₂O₄ (M⁺) 318.1580, found 318.1577.

2f. Ethyl 1,3,6-trimethyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



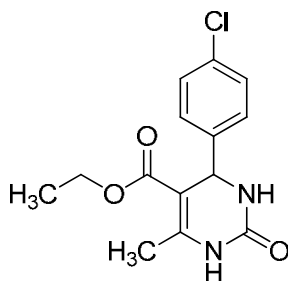
Colorless solid, Yield 97%; M.p. 52–54 °C; IR (neat): 3217, 1705, 1618 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 1.24 (m, 3H), 2.48 (s, 3H), 2.91 (s, 3H), 3.26 (s, 3H), 4.08–4.18 (m, 2H), 5.24 (s, 1H), 7.19–7.32 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ 14.3, 16.7, 31.1, 34.5, 60.2, 60.9, 103.6, 126.7, 127.9, 128.7, 141.1, 149.3, 153.9, 166.0; HRMS, calcd. for C₁₆H₂₁N₂O₃ (M⁺+1) 289.1552, found 289.1561.

3a. Ethyl 6-methyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



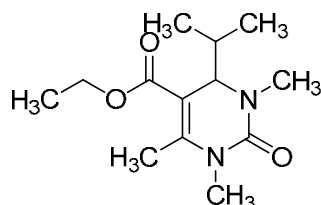
Colorless solid; Yield 91%; M.p. 212–213 °C; IR (neat): 3105, 1707, 1600, 1522, 1043 cm^{-1} ; ^1H NMR (300 MHz, DMSO-d_6): δ 1.09 (t, 3H, $J = 6.9$ Hz), 2.26 (s, 3H), 3.98 (q, 2H, $J = 7.2$ Hz), 5.27 (d, 1H, $J = 3.3$ Hz), 7.49–7.52 (m, 2H), 7.89–7.91 (m, 1H), 8.20–8.23 (m, 2H), 9.36 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 14.0, 17.8, 53.6, 59.3, 98.1, 123.8, 127.6, 146.6, 149.3, 151.7, 151.9, 154.9, 165.0; HRMS, calcd. for $\text{C}_{14}\text{H}_{16}\text{N}_3\text{O}_5$ (M^++1) 306.1090, found 306.1085.

3b. Ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



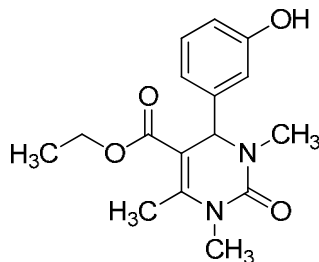
Solid; Yield 83%; M.p. 212–214 °C; IR (neat): 3243, 1713, 1664 cm^{-1} ; ^1H NMR (300 MHz, MeOD): δ 1.15 (t, 3H, $J = 7.2$ Hz), 2.33 (s, 3H), 4.10 (q, 2H, $J = 7.8$ Hz), 5.30 (s, 1H), 7.26–7.33 (m, 4H); ^{13}C NMR (75 MHz, MeOD): δ 14.6, 18.2, 55.8, 61.2, 101.7, 129.4, 129.7, 134.5, 144.7, 149.4, 167.4; HRMS, calcd. for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_3\text{Cl}$ (M^++1) 295.0849, found 295.0854.

5a. Ethyl 4-isopropyl-1,3,6-trimethyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



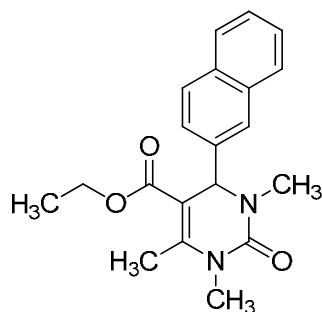
Colorless oil; Yield 98%; IR (neat): 1671, 1213 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 0.83 (dd, 6H, $J = 6.8, 2.8$ Hz), 1.28 (t, 2H, $J = 8.0$ Hz), 1.82–1.95 (m, 1H), 2.39 (s, 3H), 3.04 (s, 3H), 3.12 (s, 3H), 4.09–4.24 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 14.4, 16.4, 18.3, 18.8, 31.0, 33.8, 37.1, 60.1, 62.5, 102.4, 149.6, 154.7, 166.9; HRMS, calcd. for $\text{C}_{13}\text{H}_{23}\text{N}_2\text{O}_3$ (M^++1) 255.1709, found 255.1700.

7a. Ethyl 4-(3-hydroxyphenyl)-1,3,6-trimethyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



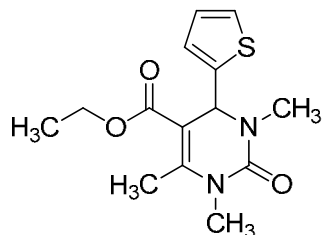
Colorless solid; Yield 92%; M.p. 161-163 °C; IR (neat): 1665, 1597, 1036 cm^{-1} ; ^1H NMR (300 MHz, MeOD): δ 1.22 (t, 3H, $J = 6.9$ Hz), 2.50 (s, 3H), 2.87 (s, 3H), 3.24 (s, 3H), 4.10 (q, 2H, $J = 6.9$ Hz), 5.20 (s, 1H), 6.67–6.72 (m, 3H), 7.08–7.14 (m, 1H); ^{13}C NMR (75 MHz, MeOD): δ 14.6, 16.7, 31.4, 34.8, 61.4, 62.2, 105.2, 114.5, 116.1, 119.0, 130.8, 143.7, 150.6, 155.7, 159.0, 167.4; HRMS, calcd. for $\text{C}_{16}\text{H}_{21}\text{N}_2\text{O}_4$ ($\text{M}^+ + 1$) 305.1501, found 305.1504.

9a. Ethyl 1,3,6-trimethyl-4-(naphthalen-2-yl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



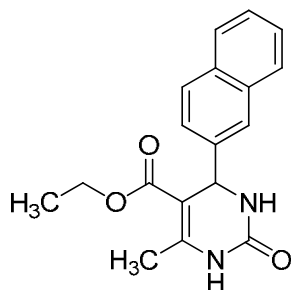
Colorless oil; Yield 93%; IR (neat): 1681, 1623 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.26 (t, 3H, $J = 6.9$ Hz), 2.40 (s, 3H), 2.96 (s, 3H), 3.31 (s, 3H), 4.14 (q, 2H, $J = 7.2$ Hz), 5.42 (s, 1H), 7.34–7.48 (m, 3H), 7.64 (bs, 1H), 7.76–7.84 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 14.3, 16.8, 31.1, 34.6, 60.2, 61.2, 103.5, 124.6, 125.6, 126.0, 126.3, 127.7, 128.0, 128.8, 133.0, 133.1, 138.3, 149.4, 153.9, 166.1; HRMS, calcd. For $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_3$ (M^+) 338.1630, found 338.1629.

11a. Ethyl 1,3,6-trimethyl-2-oxo-4-(thiophen-2-yl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



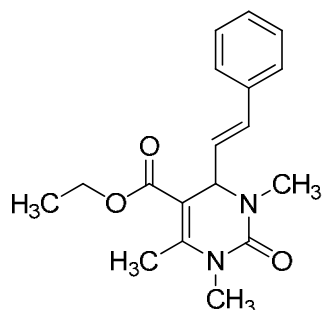
Pale yellow oil; Yield 99%; IR (neat): 1680, 1643 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.26 (t, 3H, $J = 6.9$ Hz), 2.47 (s, 3H), 2.99 (s, 3H), 3.22 (s, 3H), 4.12–4.21 (m, 2H), 5.49 (s, 1H), 6.85–6.89 (m, 2H), 7.14 (dd, 2H, $J = 4.5, 1.2$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 14.3, 16.4, 31.1, 34.6, 56.3, 60.3, 103.8, 124.5, 124.8, 126.5, 143.8, 150.0, 153.9, 165.5; HRMS, calcd. for $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$ (M^+) 294.1038, found 294.1036.

12a. Ethyl 6-methyl-4-(naphthalen-2-yl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



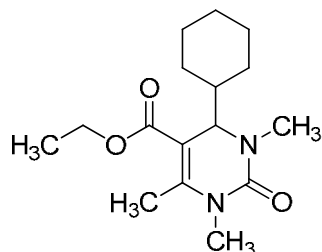
Colorless solid; Yield 70%; M.p. 243-244 °C; IR (neat): 3240, 1697, 1645, 1091 cm^{-1} ; ^1H NMR (300 MHz, MeOD): δ 1.12 (t, 3H, $J = 7.2$ Hz), 2.37 (s, 3H), 4.03 (q, 2H, $J = 7.2$ Hz), 5.49 (s, 1H), 7.43–7.49 (m, 3H), 7.71 (d, 1H, $J = 1.5$ Hz), 7.79–7.83 (m, 3H); ^{13}C NMR (75 MHz, MeOD): δ 14.6, 18.3, 56.7, 61.1, 102.0, 125.8, 126.5, 127.1, 127.3, 128.7, 129.1, 129.7, 134.5, 134.8, 136.5, 143.0, 149.2, 167.6; HRMS, calcd. for $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_3$ ($\text{M}^+ + 1$) 311.1396, found 311.1399.

14a. (E)-Ethyl 1,3,6-trimethyl-2-oxo-4-styryl-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



Colorless oil; Yield 72%; IR (neat): 1671, 1038 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 1.31 (t, 3H, $J = 7.2$ Hz), 2.47 (s, 3H), 3.02 (s, 3H), 3.22 (s, 3H), 4.10–4.26 (m, 2H), 4.78 (d, 1H, $J = 7.2$ Hz), 6.02 (dd, 1H, $J = 15.6, 6.8$ Hz), 6.39 (d, 1H, $J = 15.6$ Hz), 7.20–7.43 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): δ 14.5, 16.6, 31.2, 34.5, 56.0, 60.3, 101.8, 125.5, 126.7, 128.0, 128.7, 130.6, 136.4, 150.2, 154.3, 165.9; HRMS, calcd. for $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}_3$ ($\text{M}^+ + 1$) 315.1709, found 315.1709.

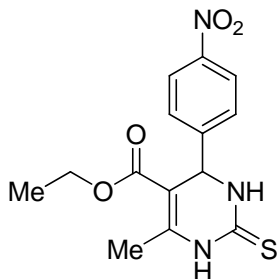
16a. Ethyl 4-cyclohexyl-1,3,6-trimethyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



Colorless solid; Yield 95%; M.p. 57-60 °C; IR (neat): 1671, 1626, 1457 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 0.80–1.18 (m, 5H), 1.27 (t, 3H, $J = 7.2$ Hz), 1.45–1.55 (m, 2H), 1.55–1.64 (m, 2H), 1.64–1.74 (m, 2H), 2.38 (s, 3H), 3.02 (s, 3H), 3.11 (s, 3H), 4.09–4.22 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 14.4, 16.4, 26.2, 26.3, 26.4, 28.6, 29.0,

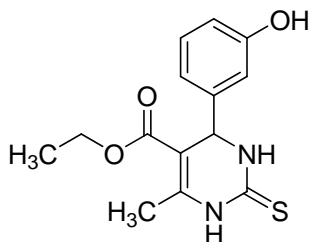
31.0, 37.2, 43.9, 60.1, 61.9, 102.6, 149.5, 154.8, 166.9; HRMS, calcd. for $C_{12}H_{21}N_2O_4$ (M^++1) 295.2022, found 295.2020.

17a. Ethyl 6-methyl-4-(4-nitrophenyl)-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



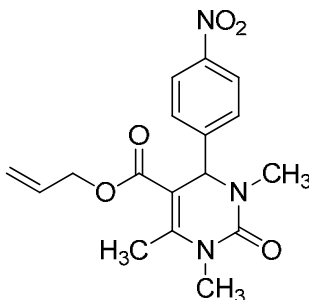
Solid; Yield 85%; M.p. 106–108 °C; IR (neat): 3106, 1705, 1609, 1527 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$): δ 1.20 (t, 3H, $J = 6.9$ Hz), 2.38, (s, 3H), 4.08–4.15 (m, 2H), 5.51 (d, 1H, $J = 2.1$ Hz), 7.47 (d, 2H, $J = 8.7$ Hz), 7.92 (s, 1H), 8.17 (d, 2H, $J = 8.7$ Hz), 8.27 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 18.6, 55.4, 61.0, 102.2, 124.3, 127.8, 128.4, 143.7, 147.8, 148.9, 164.9; HRMS, calcd. for $C_{14}H_{16}N_3O_4S$ (M^++1) 322.0862, found 302.0859.

18a. Ethyl 4-(3-hydroxyphenyl)-6-methyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



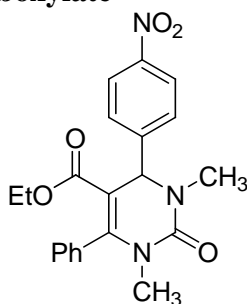
Pale yellow solid; Yield 86%; M.p. 186–188 °C; IR (neat): 3384, 1680, 1638, 1589 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$): δ 1.18 (t, 3H, $J = 8.4$ Hz), 2.33 (s, 3H), 4.05–4.14 (m, 2H), 5.34 (s, 1H), 6.72–6.82 (m, 3H), 7.11–7.17 (m, 1H), 7.61 (s, 1H), 7.98 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 18.5, 55.9, 60.7, 102.9, 113.7, 115.6, 118.9, 130.2, 142.8, 143.7, 143.8, 156.2, 165.4; HRMS, calcd. for $C_{14}H_{17}N_2O_3S$ (M^++1) 293.00960, found 293.0965.

20a. Allyl 1,3,6-trimethyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



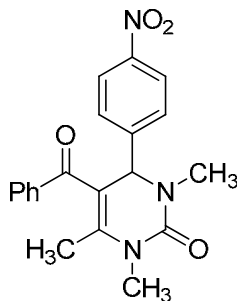
Pale yellow solid; Yield 83%; M.p. 213-215 °C; IR (neat): 1706, 1602, 1532 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 2.46 (s, 3H), 2.88 (s, 3H), 3.23 (s, 3H), 4.55 (d, 2H, $J = 5.7$ Hz), 5.15–5.22 (m, 2H), 5.34 (s, 1H), 5.77–5.91 (m, 1H), 7.36 (d, 2H, $J = 9.0$ Hz), 8.09 (d, 2H, $J = 9.0$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 16.8, 31.2, 34.7, 60.3, 65.2, 102.1, 118.6, 124.0, 127.6, 128.3, 132.1, 147.5, 148.2, 150.9, 153.4, 165.2; HRMS, calcd. for $\text{C}_{17}\text{H}_{20}\text{N}_3\text{O}_5$ (M^++1) 346.1403, found 346.1419.

22a. Ethyl 1,3-dimethyl-4-(4-nitrophenyl)-2-oxo-6-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate



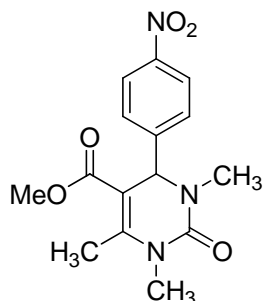
Pale yellow solid; Yield 94%; M.p. 159-161 °C; IR (neat): 1674, 1600, 1522 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 0.74 (t, 2H, $J = 6.8$ Hz), 2.86 (s, 3H), 3.02 (s, 3H), 3.79 (t, 2H, $J = 6.4$ Hz), 5.47 (s, 1H), 7.02–7.22 (m, 2H), 7.32–7.49 (m, 3H), 7.57 (d, 2H, $J = 8.4$ Hz), 8.22 (d, 2H, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 13.5, 33.5, 34.9, 60.3, 60.7, 103.6, 124.3, 127.3, 127.5, 128.4, 128.6, 129.0, 129.2, 134.6, 147.8, 148.4, 151.5, 153.9, 165.4; HRMS, calcd. for $\text{C}_{12}\text{H}_{22}\text{N}_3\text{O}_5$ (M^++1) 396.1559, found 396.1555.

24a. 5-Benzoyl-1,3,6-trimethyl-4-(4-nitrophenyl)-3,4-dihydropyrimidin-2(1H)-one:



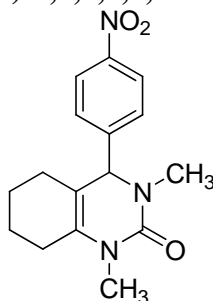
Yellow solid; Yield 95%; M.p. 158-160 °C; IR (neat): 1667, 1623 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.80 (s, 3H), 3.0 (s, 3H), 3.24 (s, 3H), 5.55 (s, 1H), 7.35–7.42 (m, 5H), 7.48–7.53 (m, 2H), 8.13–8.16 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 19.0, 31.1, 34.9, 61.3, 112.2, 124.3, 127.0, 128.3, 128.9, 132.4, 140.5, 145.9, 147.6, 147.9, 153.8, 195.3; HRMS, calcd. for $\text{C}_{20}\text{H}_{20}\text{N}_3\text{O}_4$ (M^++1) 366.1454, found 366.1447.

26a. Methyl 1,3,6-trimethyl-4-(4-nitrophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



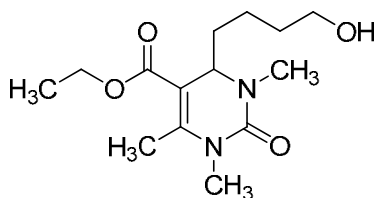
Pale yellow solid; Yield 97%; M.p. 142-144 °C; IR (neat): 1671, 1521, 1026 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 2.46 (s, 3H), 2.91 (s, 3H), 3.25 (s, 3H), 3.68 (s, 3H), 5.34 (s, 1H), 7.37 (d, 2H, $J = 8.0$ Hz), 8.09–8.15 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 16.8, 31.3, 34.7, 51.5, 60.3, 102.3, 124.1, 127.5, 147.5, 148.2, 150.7, 153.5, 166.0; HRMS, calcd. for $\text{C}_{15}\text{H}_{18}\text{N}_3\text{O}_5$ (M^++1) 320.1246, found 320.1255.

28a. 1,3-Dimethyl-4-(4-nitrophenyl)-3,4,5,6,7,8-hexahydroquinazolin-2(1H)-one:



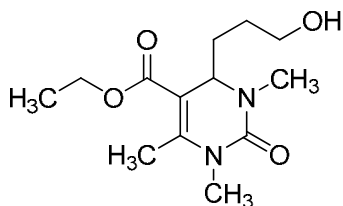
Yellow oil; Yield 70%; IR (neat): 1621 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3): δ 1.38–1.47 (m, 1H), 1.57–1.69 (m, 4H), 1.85–1.92 (m, 1H), 2.21–2.27 (m, 2H), 2.77 (s, 3H), 3.15 (s, 3H), 4.54 (s, 1H), 7.35–7.40 (m, 2H), 8.16–8.19 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 21.7, 22.5, 25.4, 25.9, 29.5, 34.1, 66.6, 106.6, 124.1, 127.7, 131.5, 147.7, 148.7, 154.1; HRMS, calcd. for $\text{C}_{16}\text{H}_{20}\text{N}_3\text{O}_3$ (M^++1) 302.1505, found 302.1511.

30a. Ethyl 4-(4-hydroxybutyl)-1,3,6-trimethyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



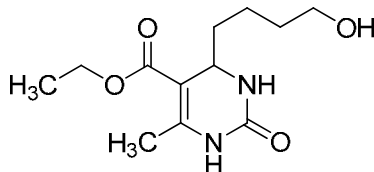
Colorless oil; Yield 97%; IR (neat): 3432, 1661, 1465 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 1.24–1.37 (m, 5H), 1.48–1.58 (m, 4H), 1.77–1.84 (s, 1H), 2.41 (s, 3H), 3.0 (s, 3H), 3.15 (s, 3H), 3.58 (t, 2H, $J = 6.4$ Hz), 4.12–4.26 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 14.5, 16.5, 21.2, 31.1, 32.9, 33.2, 35.4, 56.9, 60.2, 62.7, 103.3, 150.1, 154.5, 166.4; HRMS, calcd. for $\text{C}_{14}\text{H}_{25}\text{N}_2\text{O}_4$ (M^++1) 285.1814, found 285.1813.

32a. Ethyl 4-(3-hydroxypropyl)-1,3,6-trimethyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate:

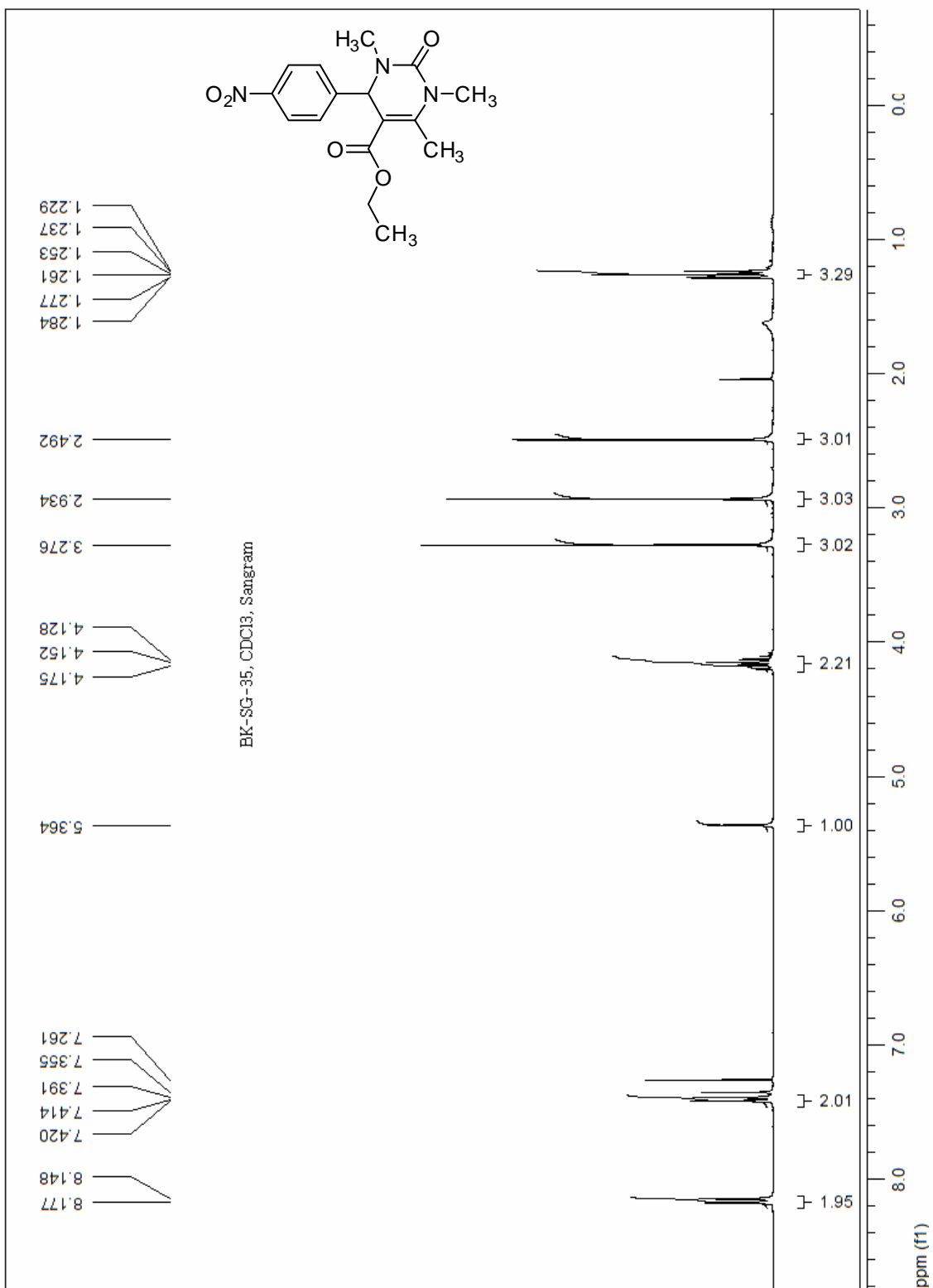


Colorless solid; Yield 94%; M.p. 49-51 °C; IR (neat): 3243, 1664, 1060 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 1.27 (t, 3H, $J = 7.2$ Hz), 1.40–1.62, (m, 4H), 1.91–1.99 (s, 1H), 2.41 (s, 3H), 2.99 (s, 3H), 3.14 (s, 3H), 3.57 (t, 3H, $J = 6.4$ Hz), 4.11–4.20 (m, 2H), 4.27 (t, 2H, $J = 5.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 14.4, 16.5, 27.8, 29.6, 31.1, 35.2, 56.7, 60.2, 62.8, 102.9, 150.2, 154.4, 166.4; HRMS, calcd. for $\text{C}_{13}\text{H}_{23}\text{N}_2\text{O}_4$ ($\text{M}^+ + 1$) 271.1658, found 271.1653.

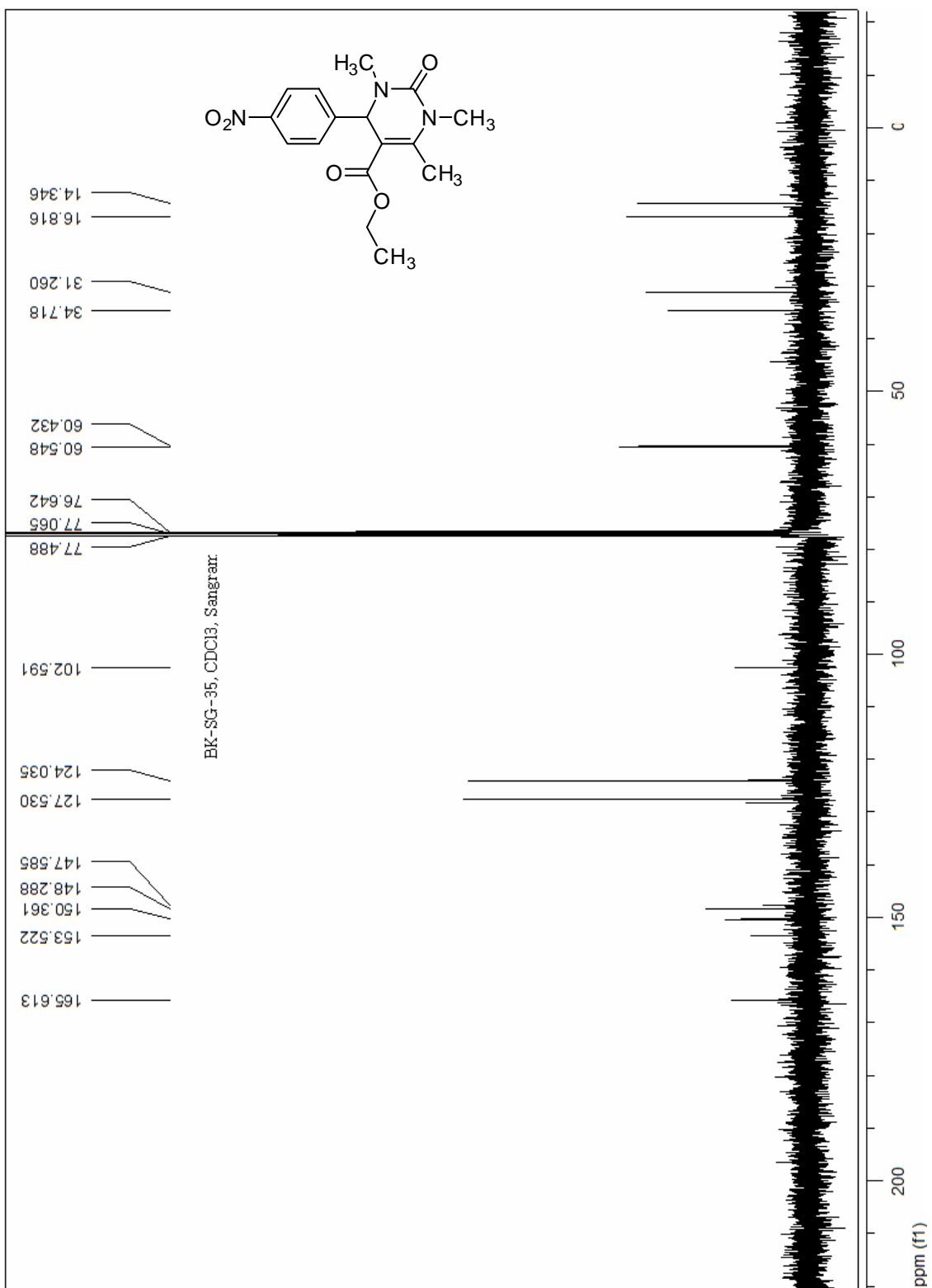
33a. Ethyl 4-(4-hydroxybutyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate:



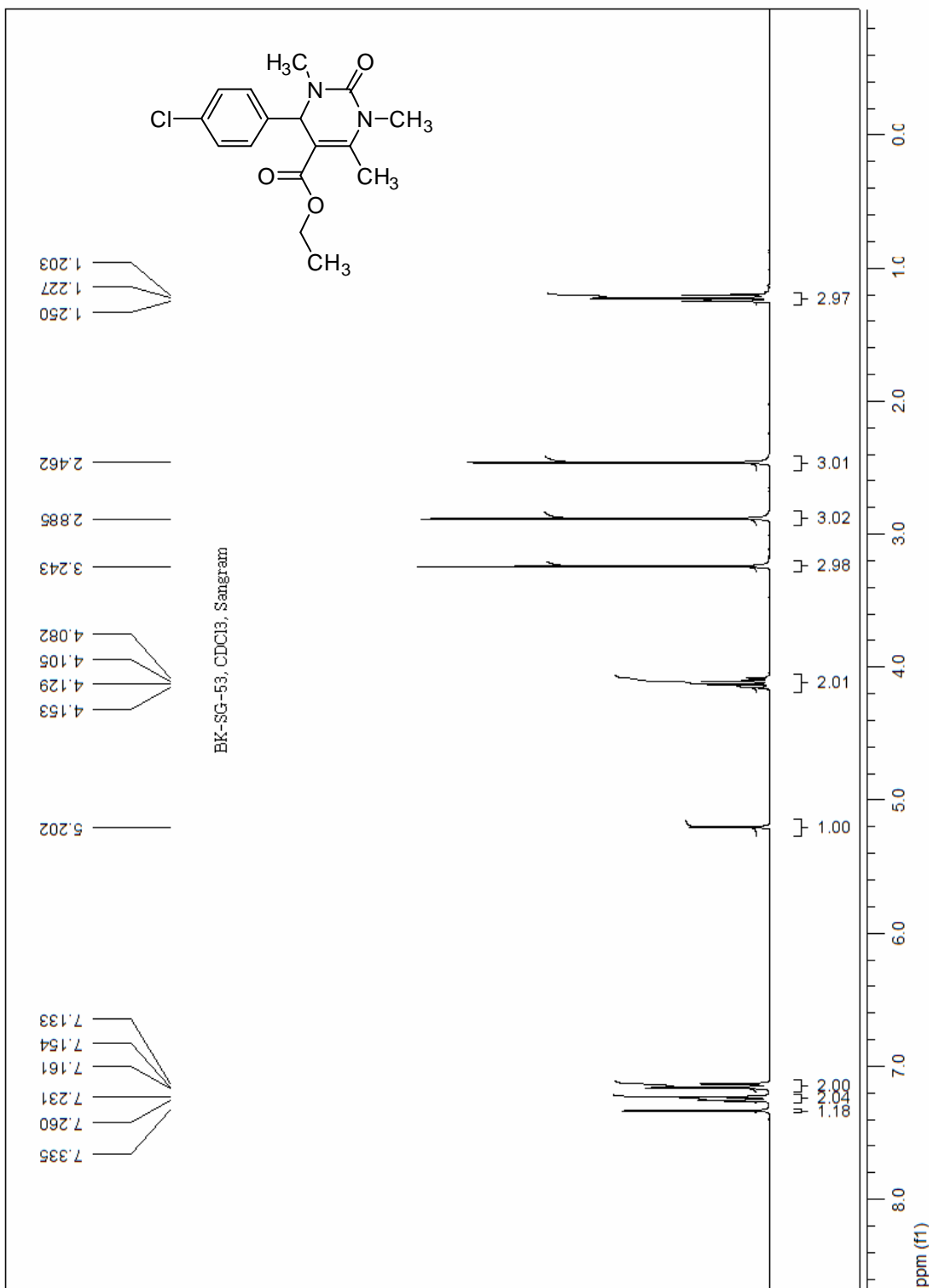
Colorless solid; Yield 87%; M.p. 140-142 °C; IR (neat): 3420, 1696, 1087 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 1.26 (t, 3H, $J = 7.2$ Hz), 1.40–1.68, (m, 6H), 2.26 (s, 3H), 2.47 (s, 1H), 3.14 (s, 1H), 3.54–3.70 (m, 2H), 4.09–4.22 (m, 2H), 4.27–4.38 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 14.5, 18.6, 20.7, 32.0, 36.5, 51.1, 60.1, 62.4, 101.7, 146.9, 155.1, 166.1; HRMS, calcd. for $\text{C}_{12}\text{H}_{21}\text{N}_2\text{O}_4$ ($\text{M}^+ + 1$) 257.1501, found 257.1503.



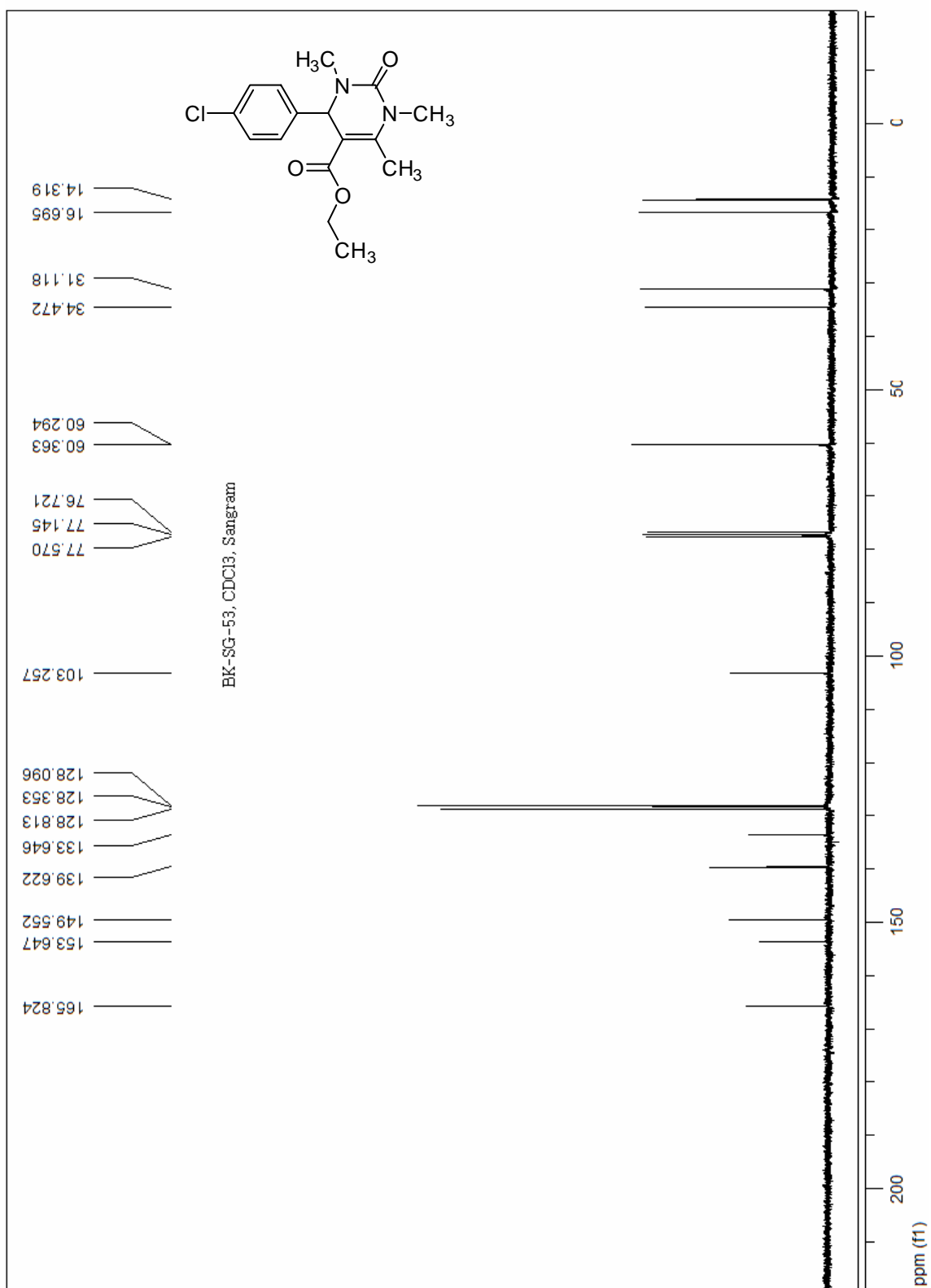
¹H NMR spectra of compound **2a**

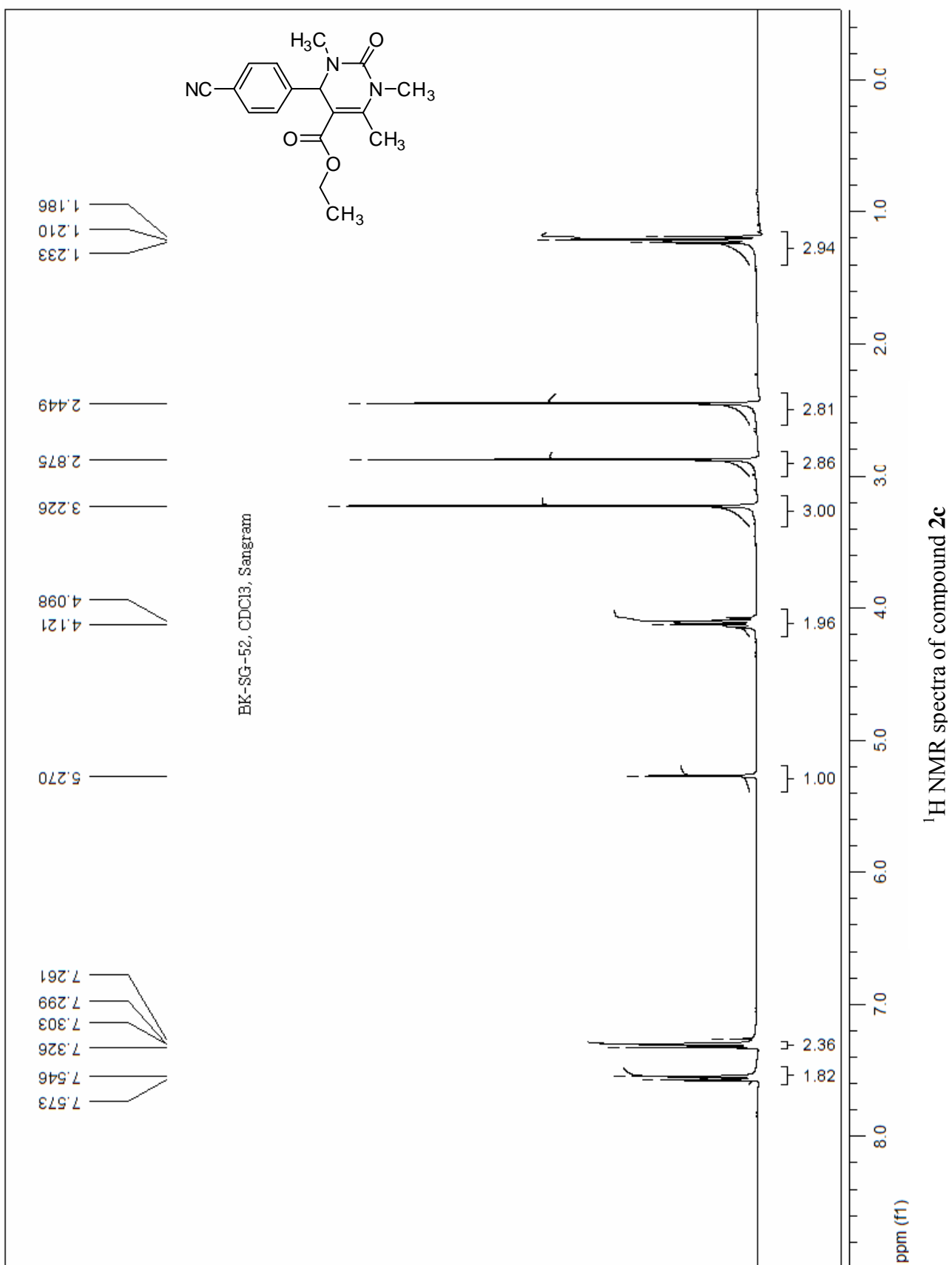


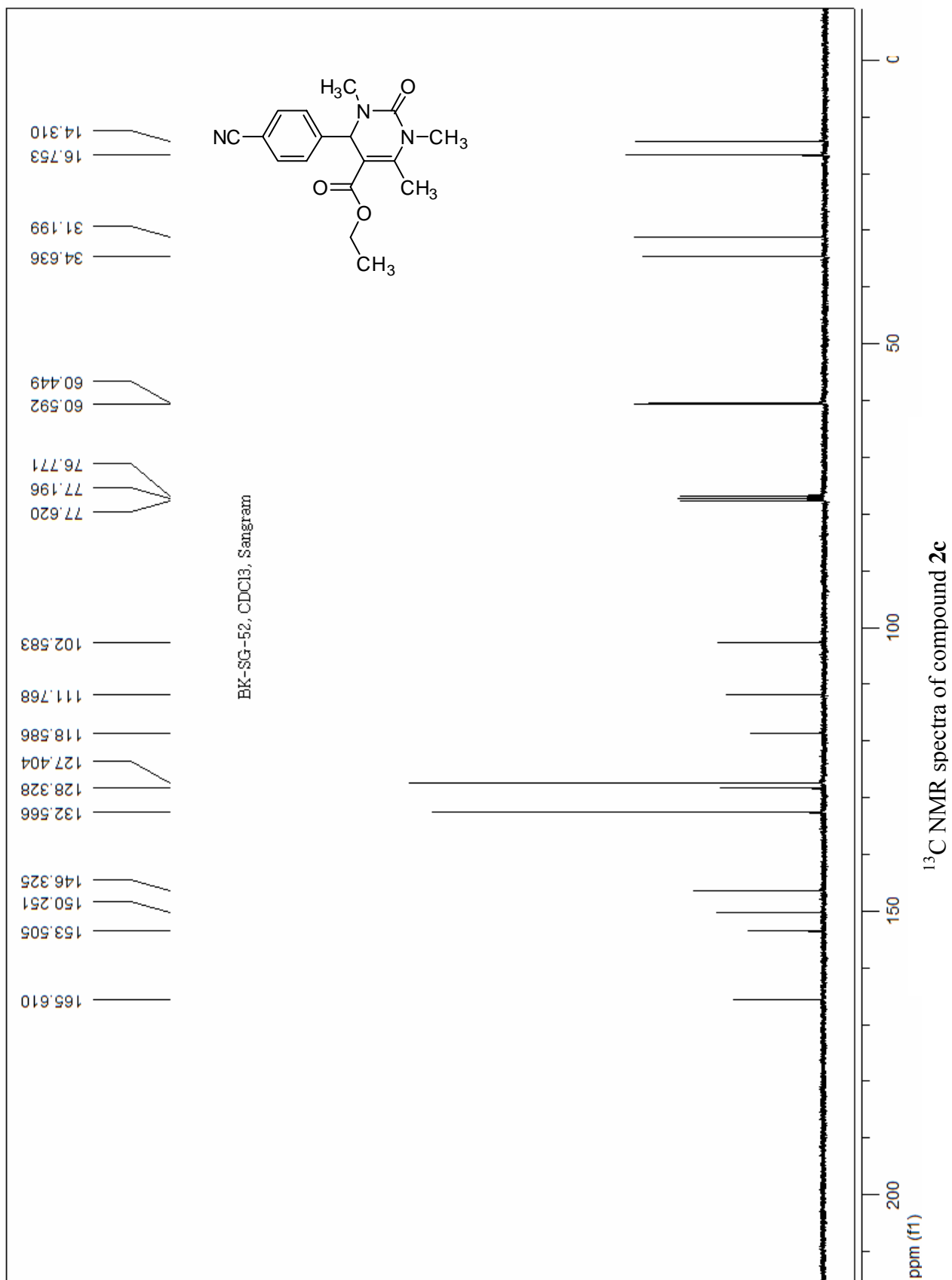
¹³C NMR spectra of compound 2a

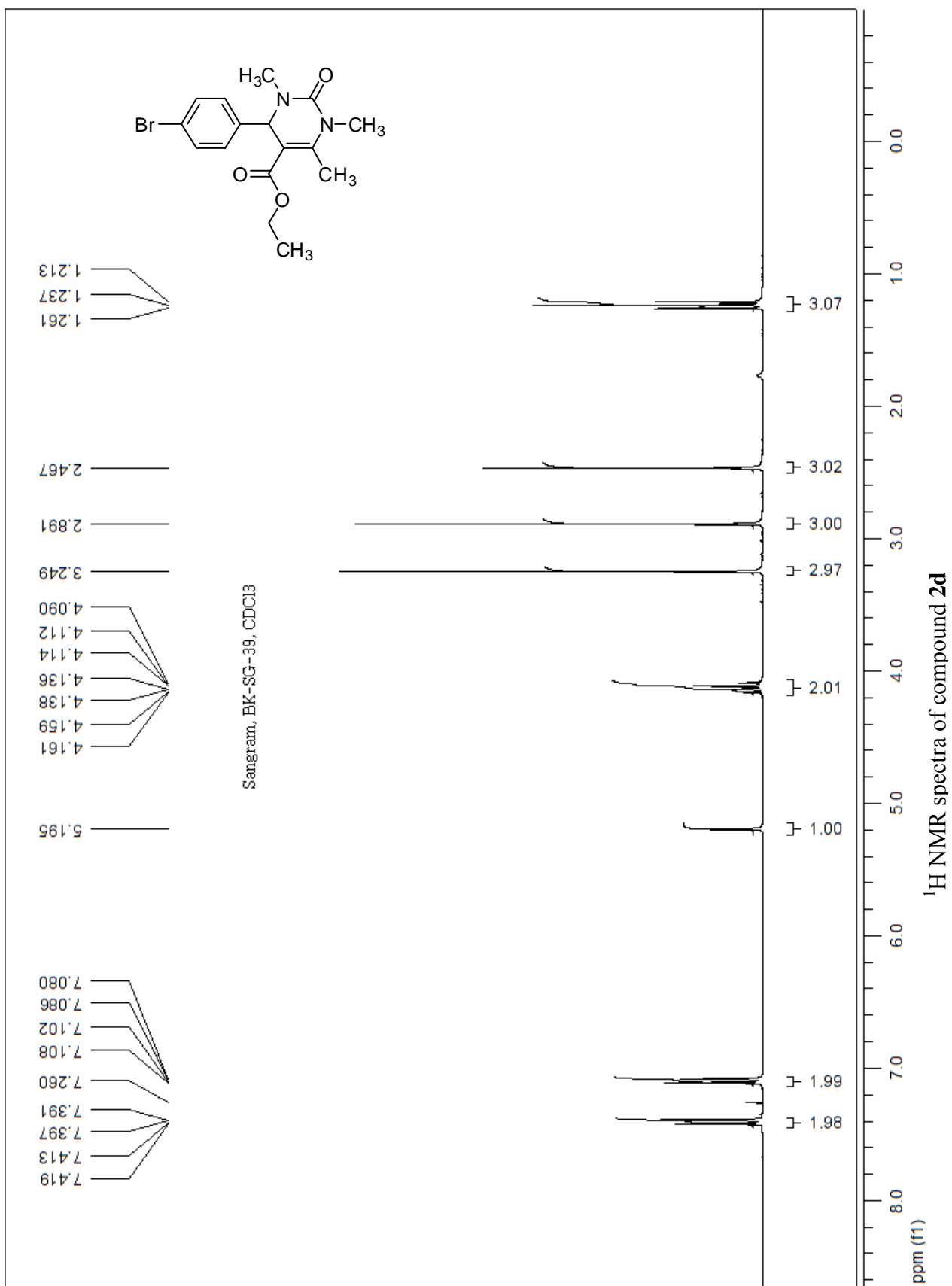


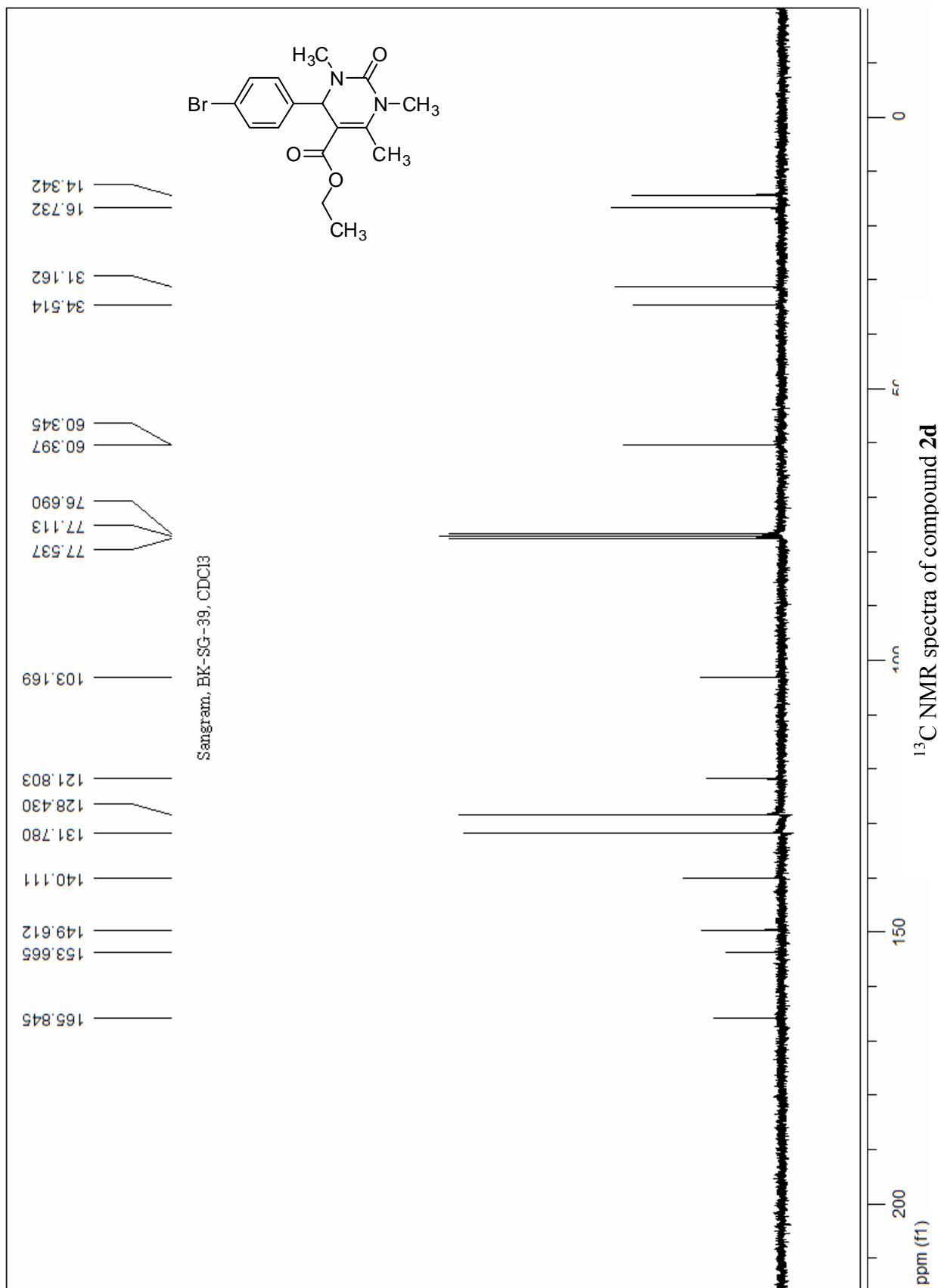
¹H NMR spectra of compound **2b**

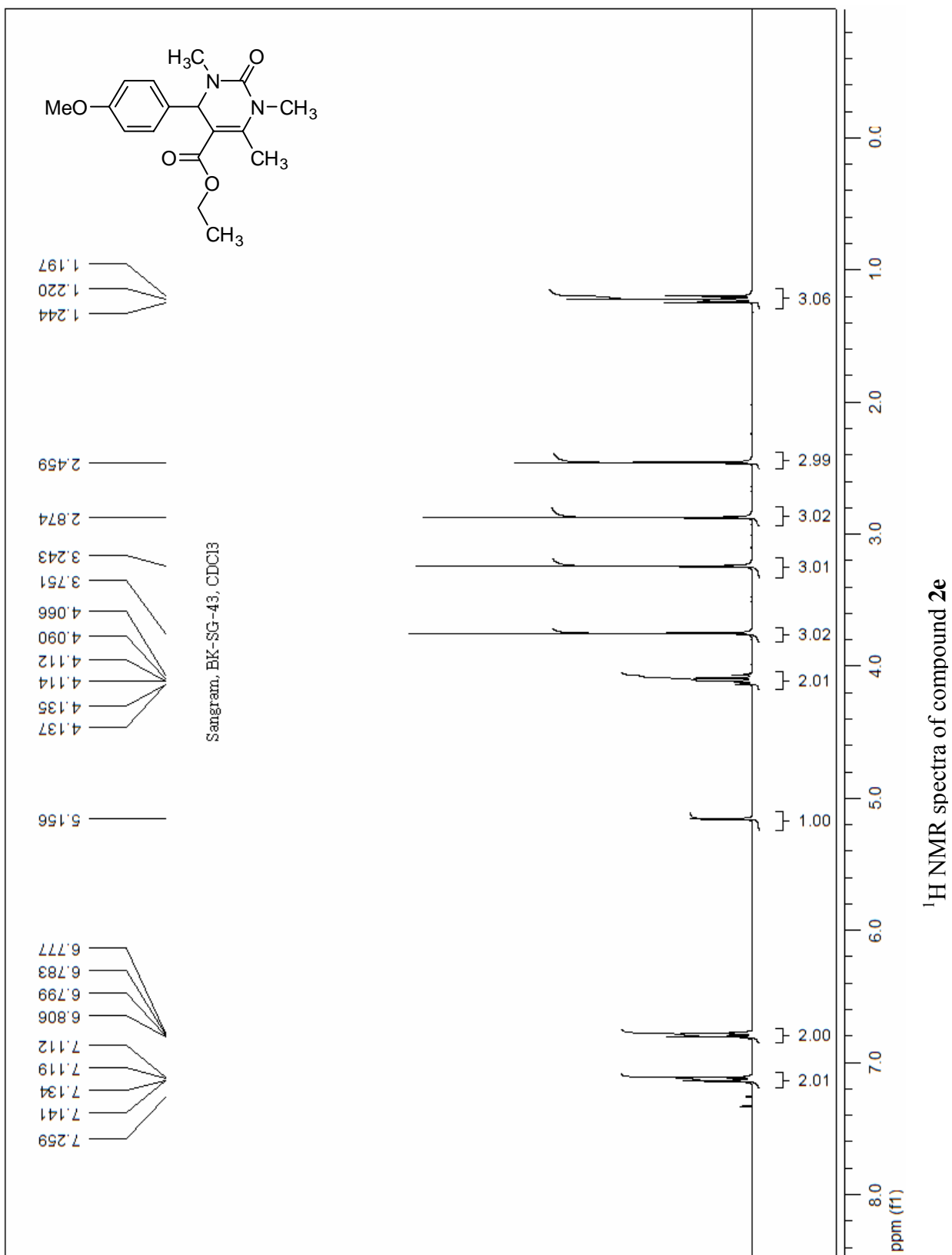


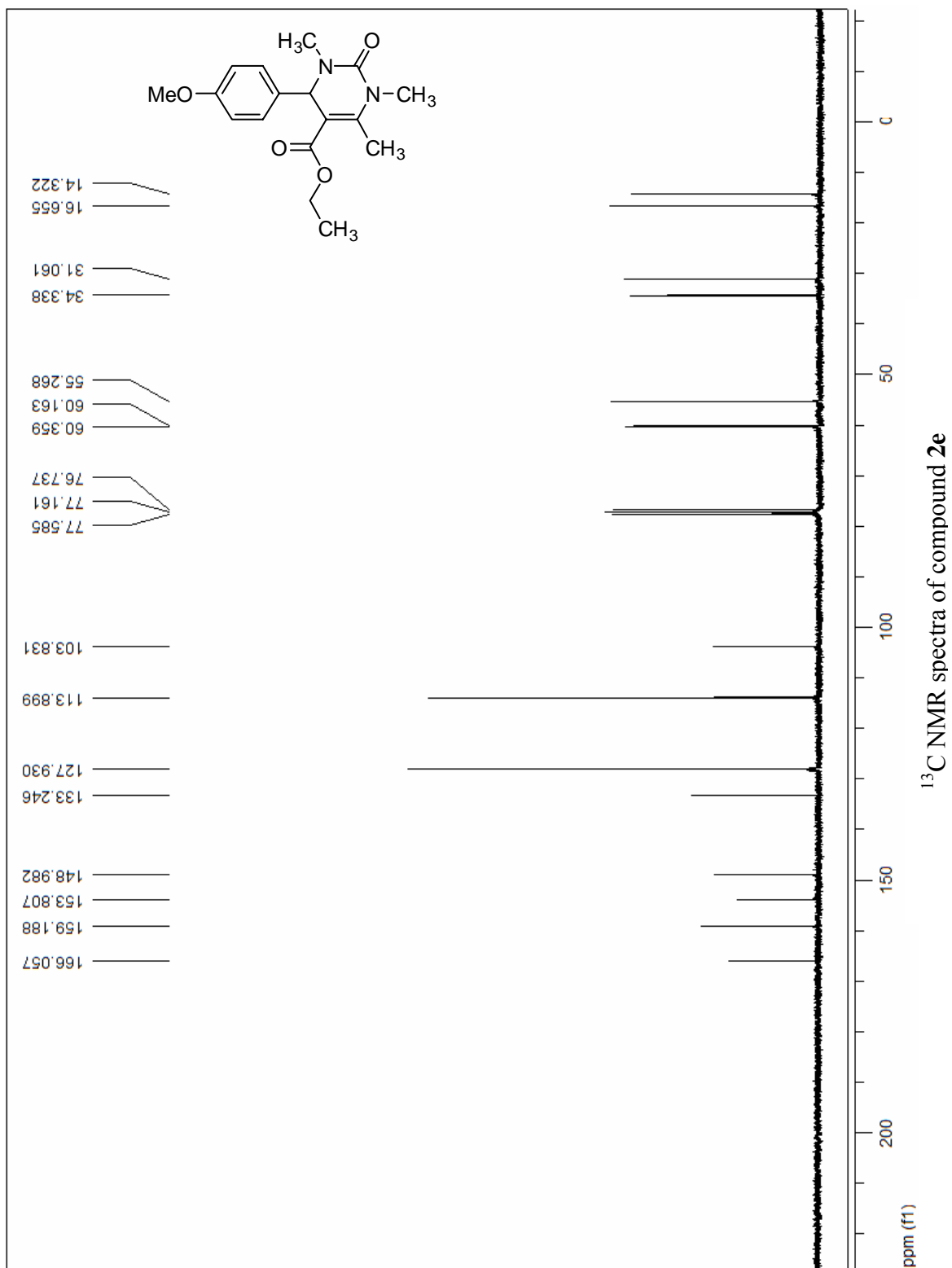


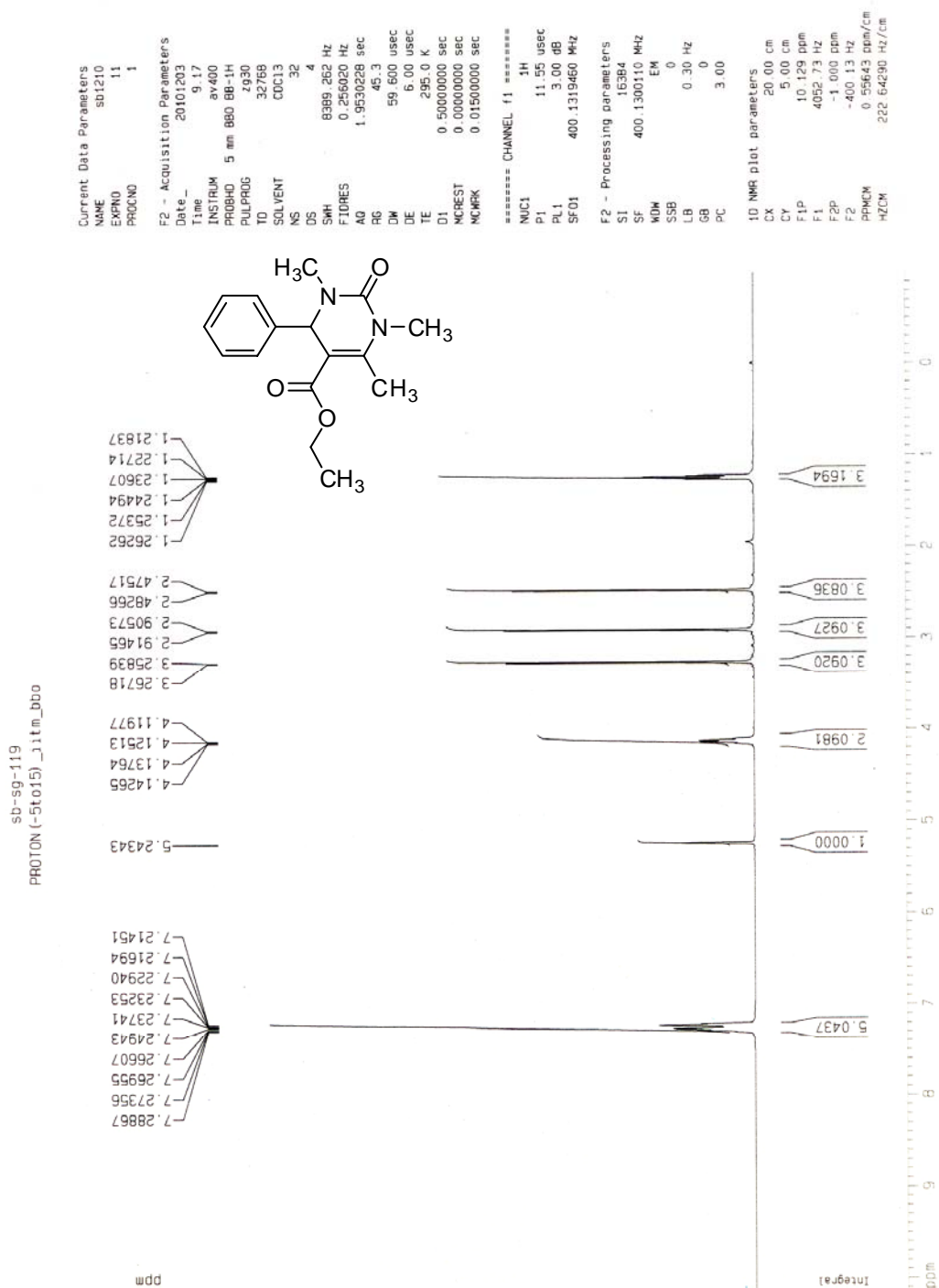




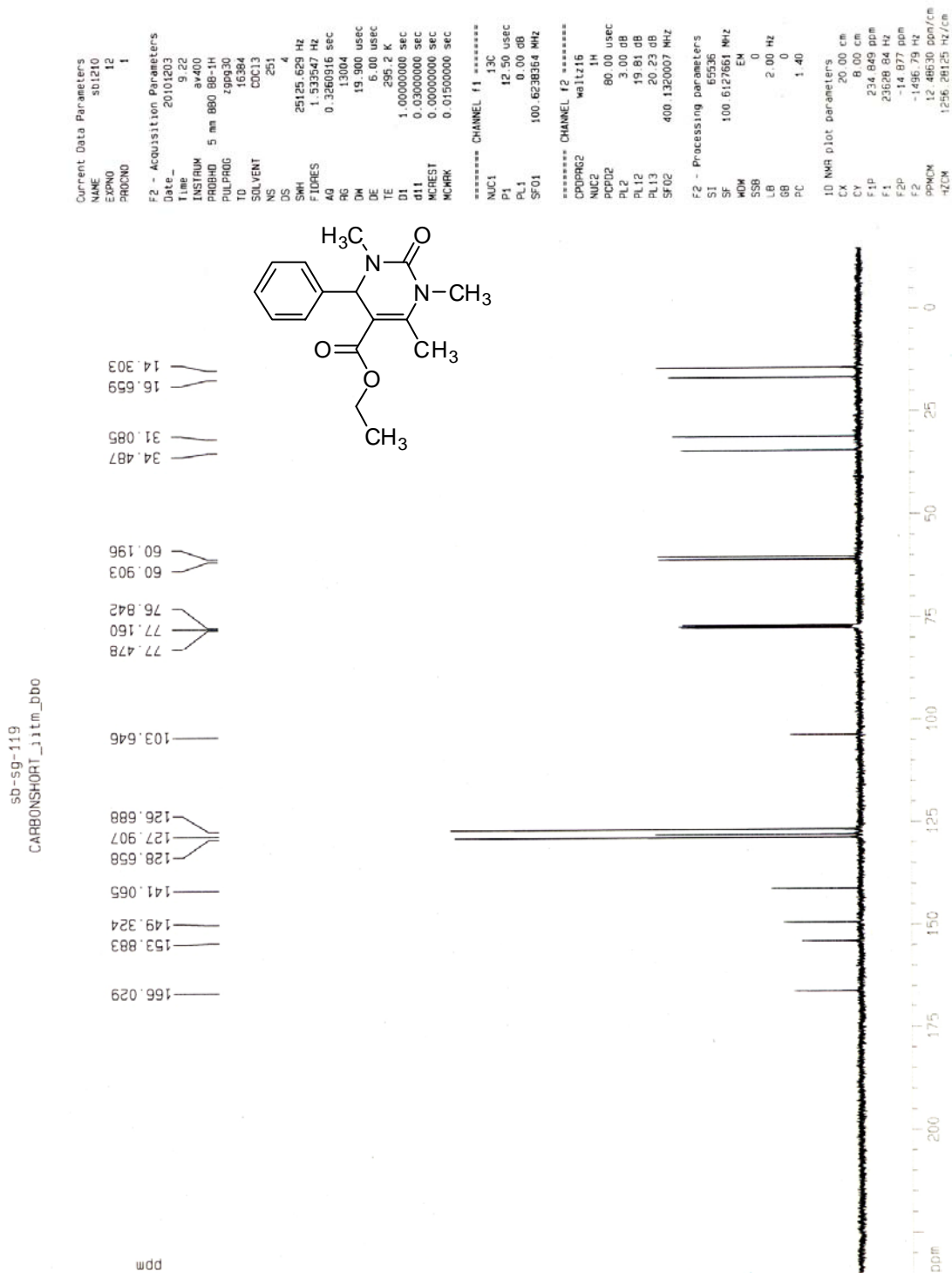




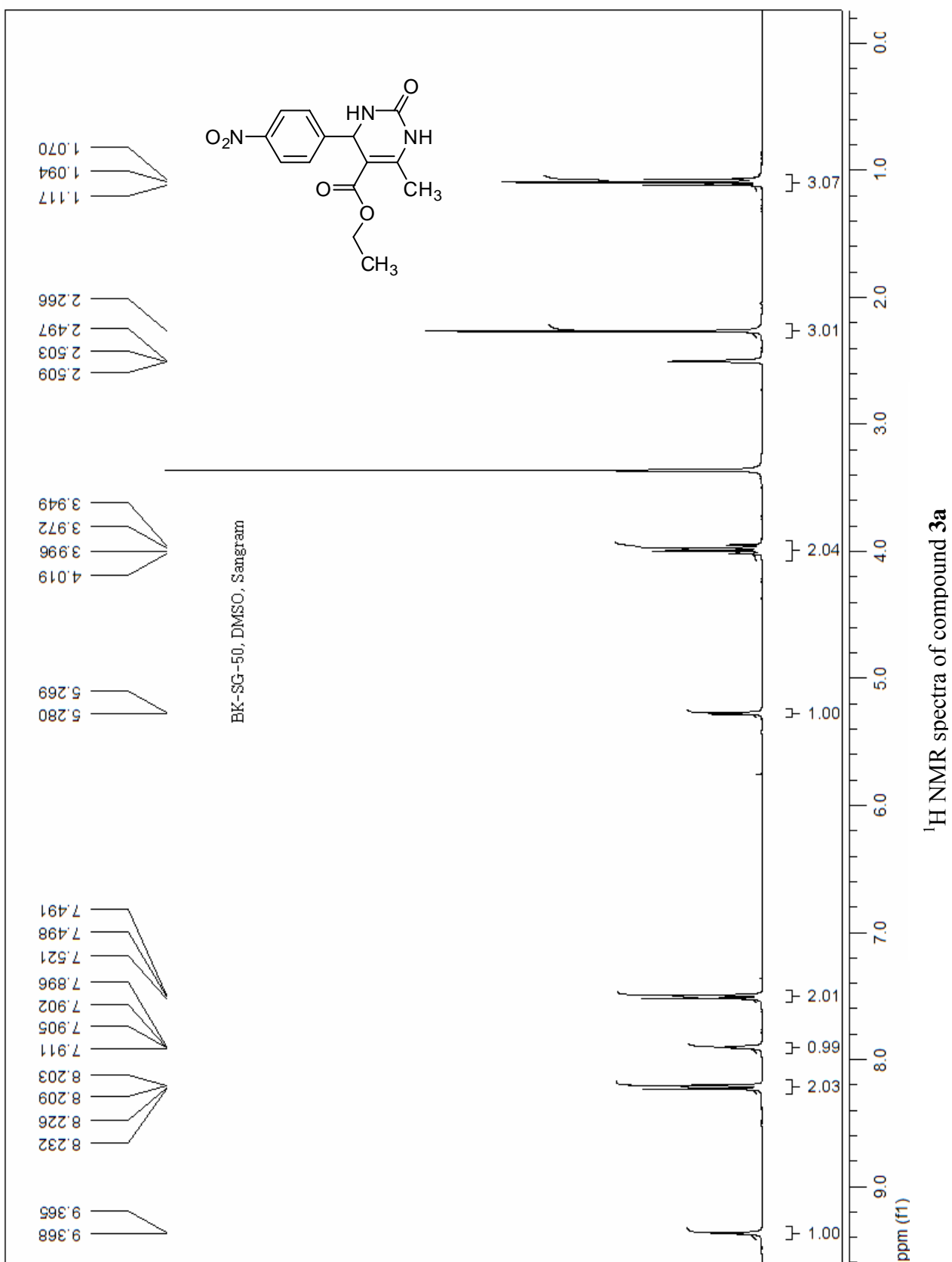


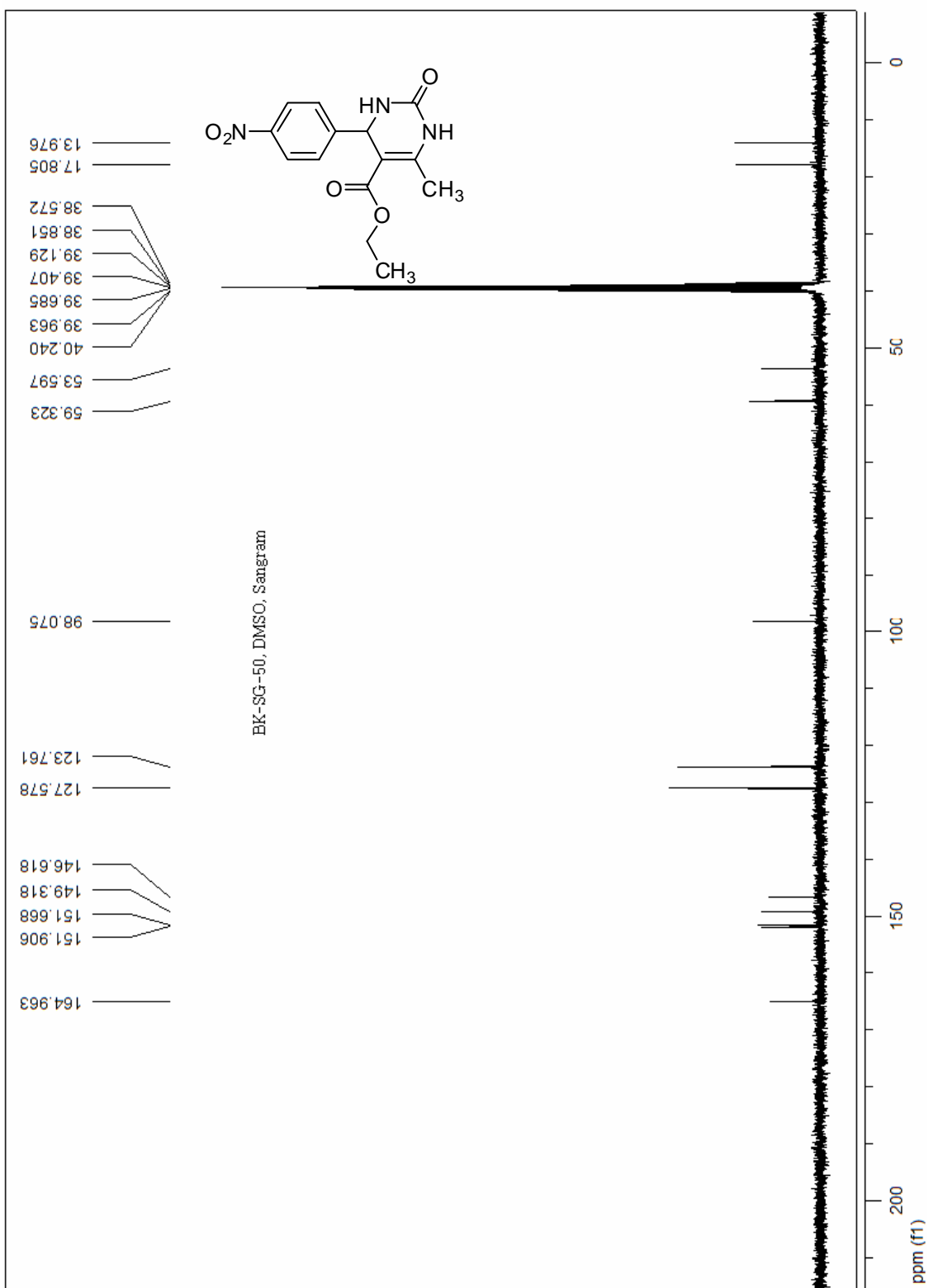


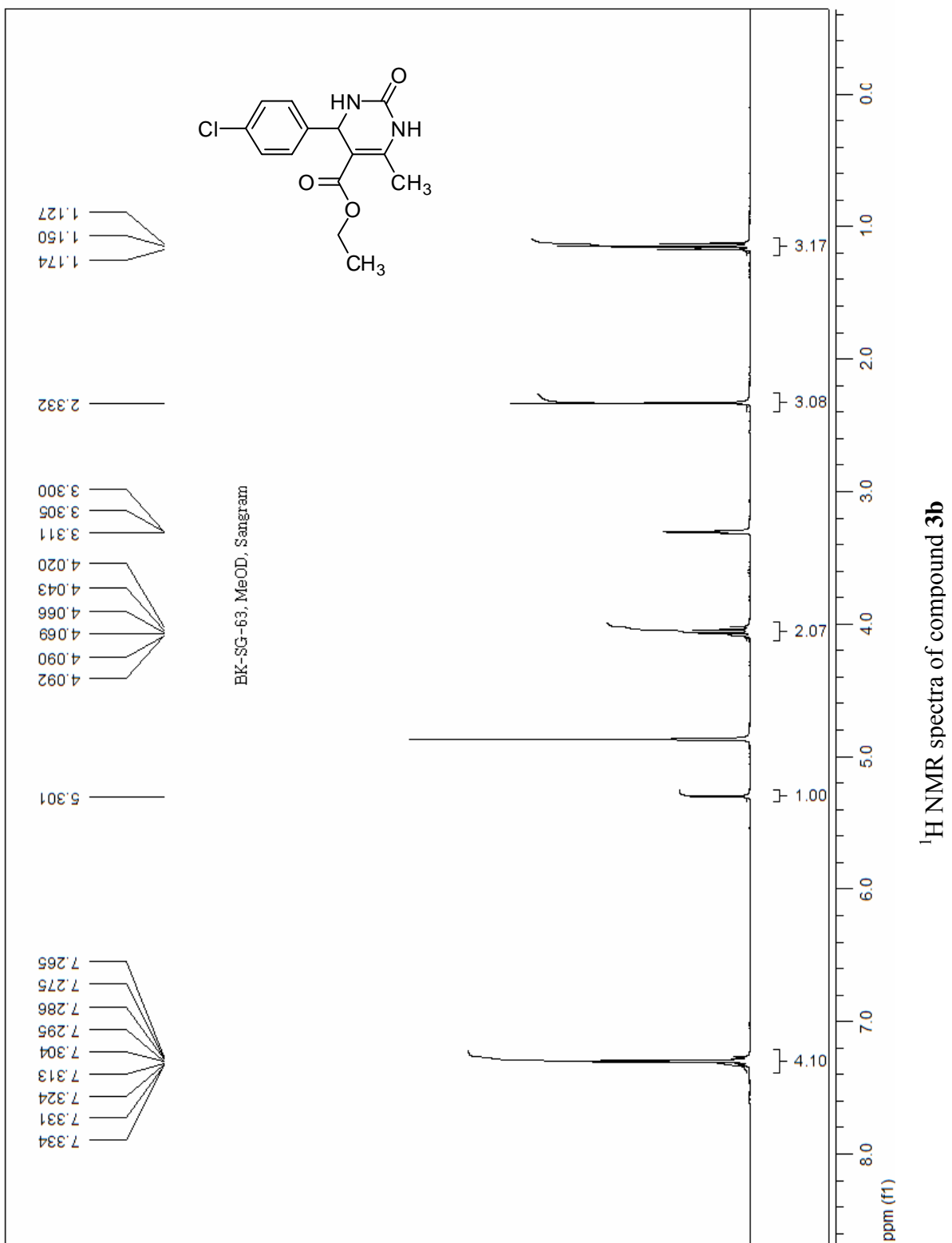
¹H NMR spectra of compound 2f

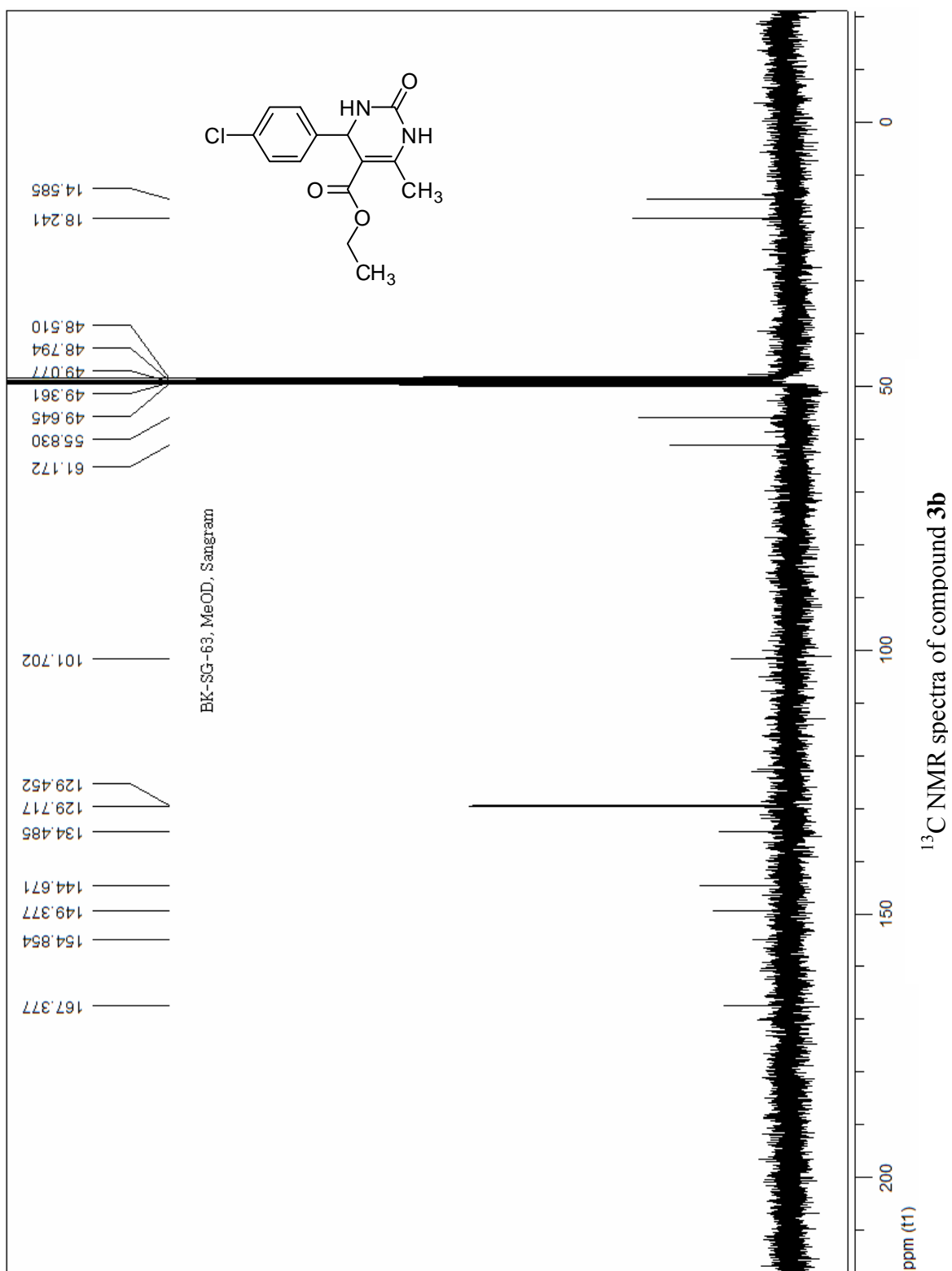


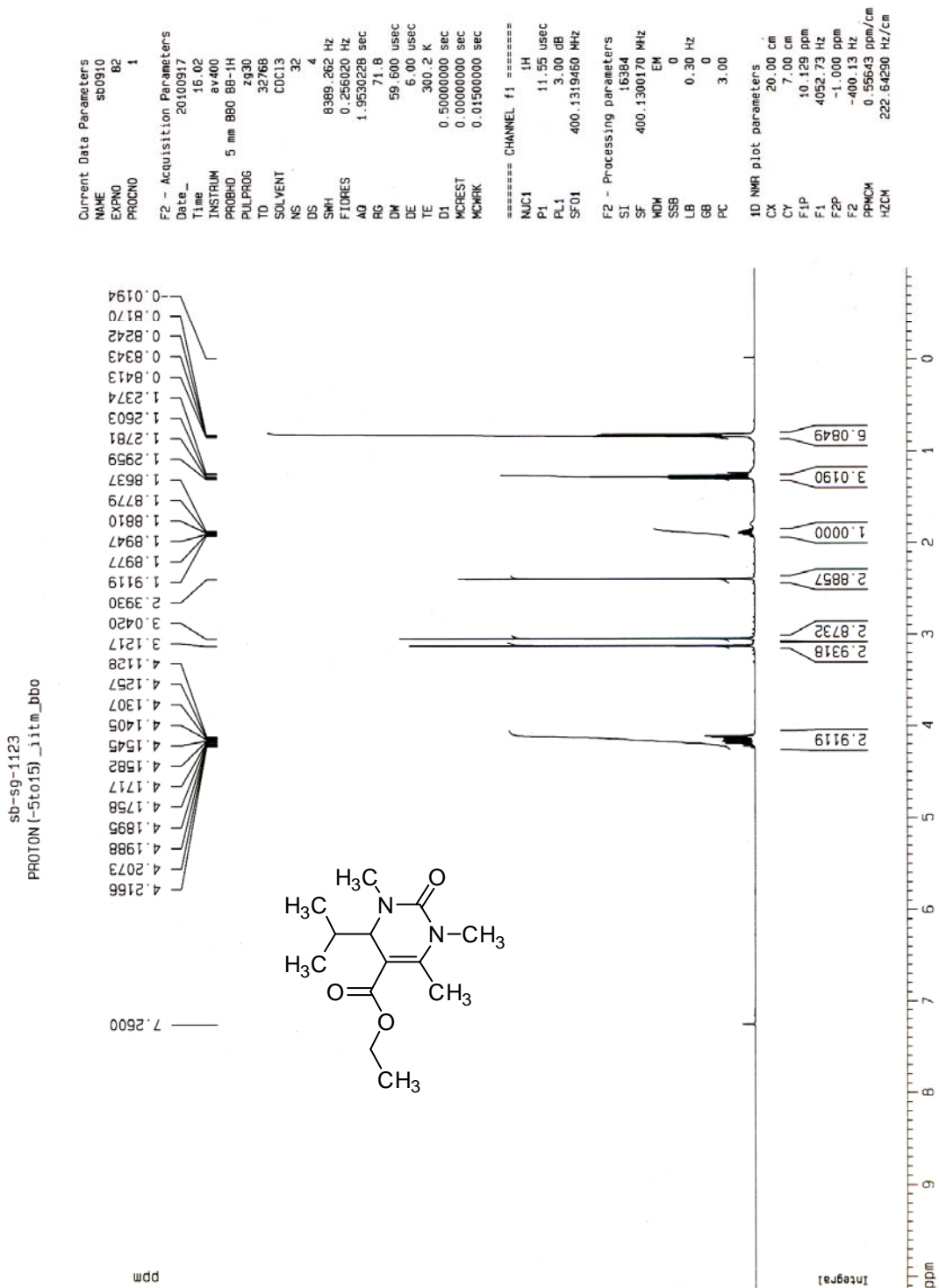
¹³C NMR spectra of compound 2f



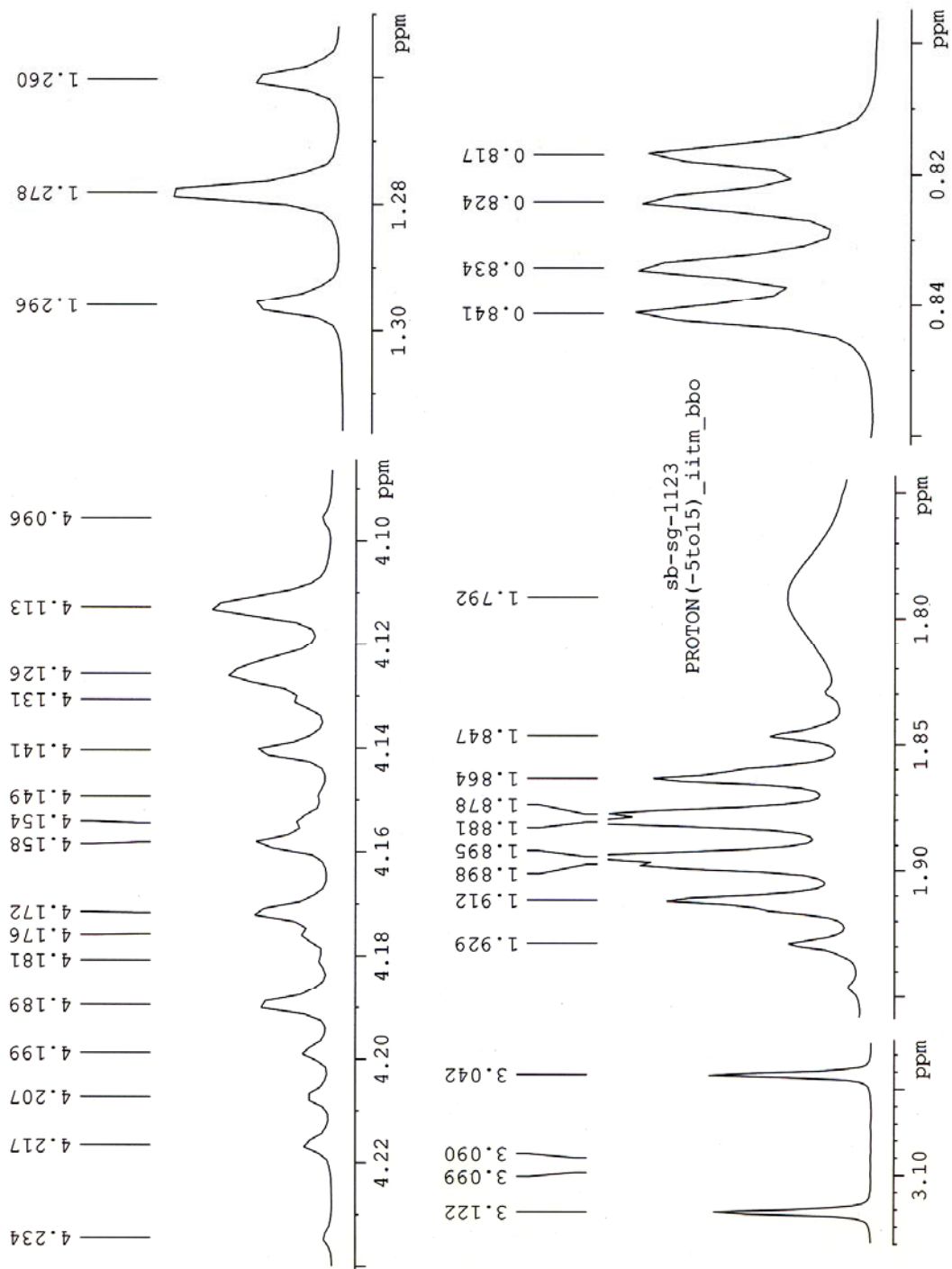






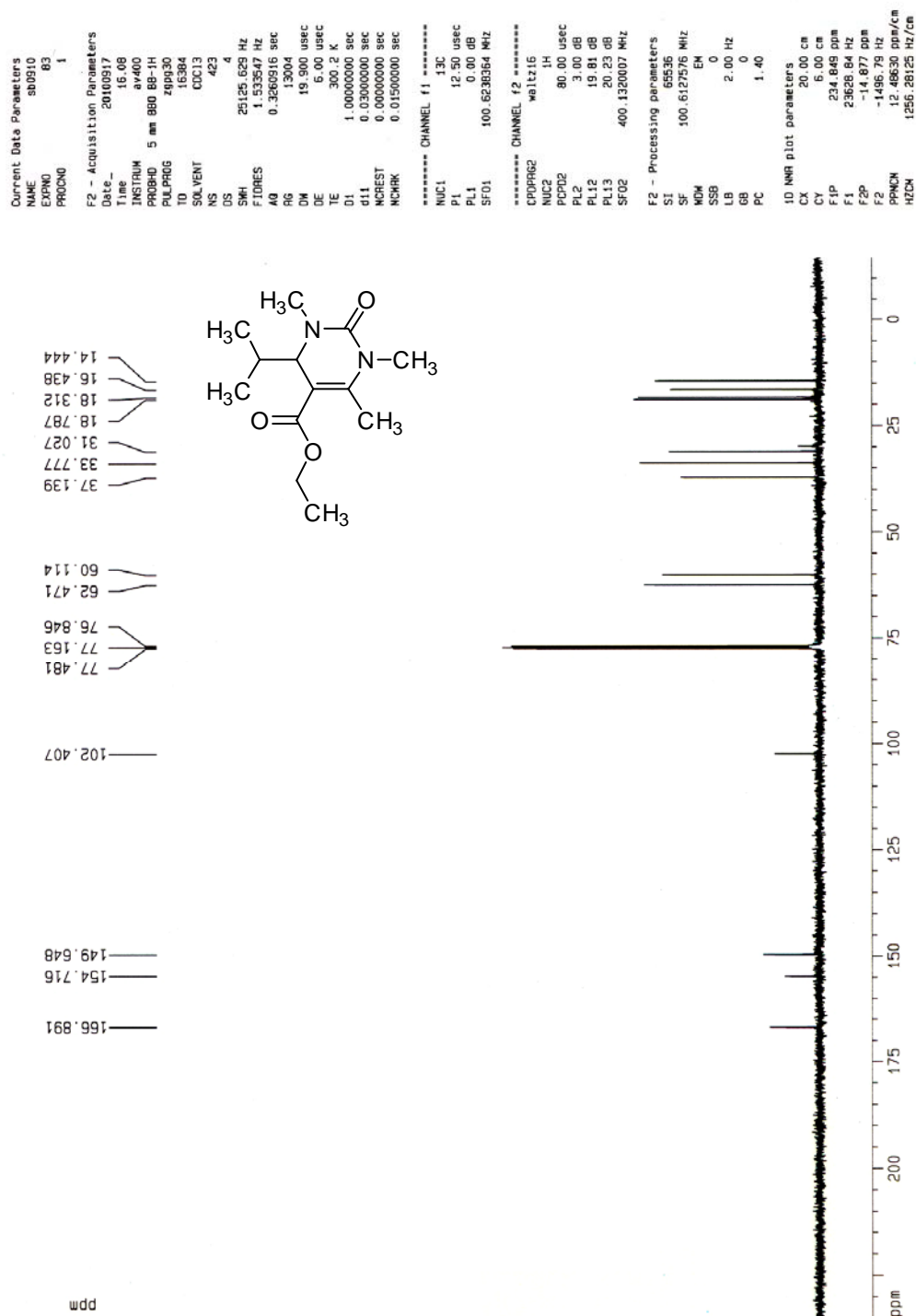


¹H NMR spectra of compound 5a

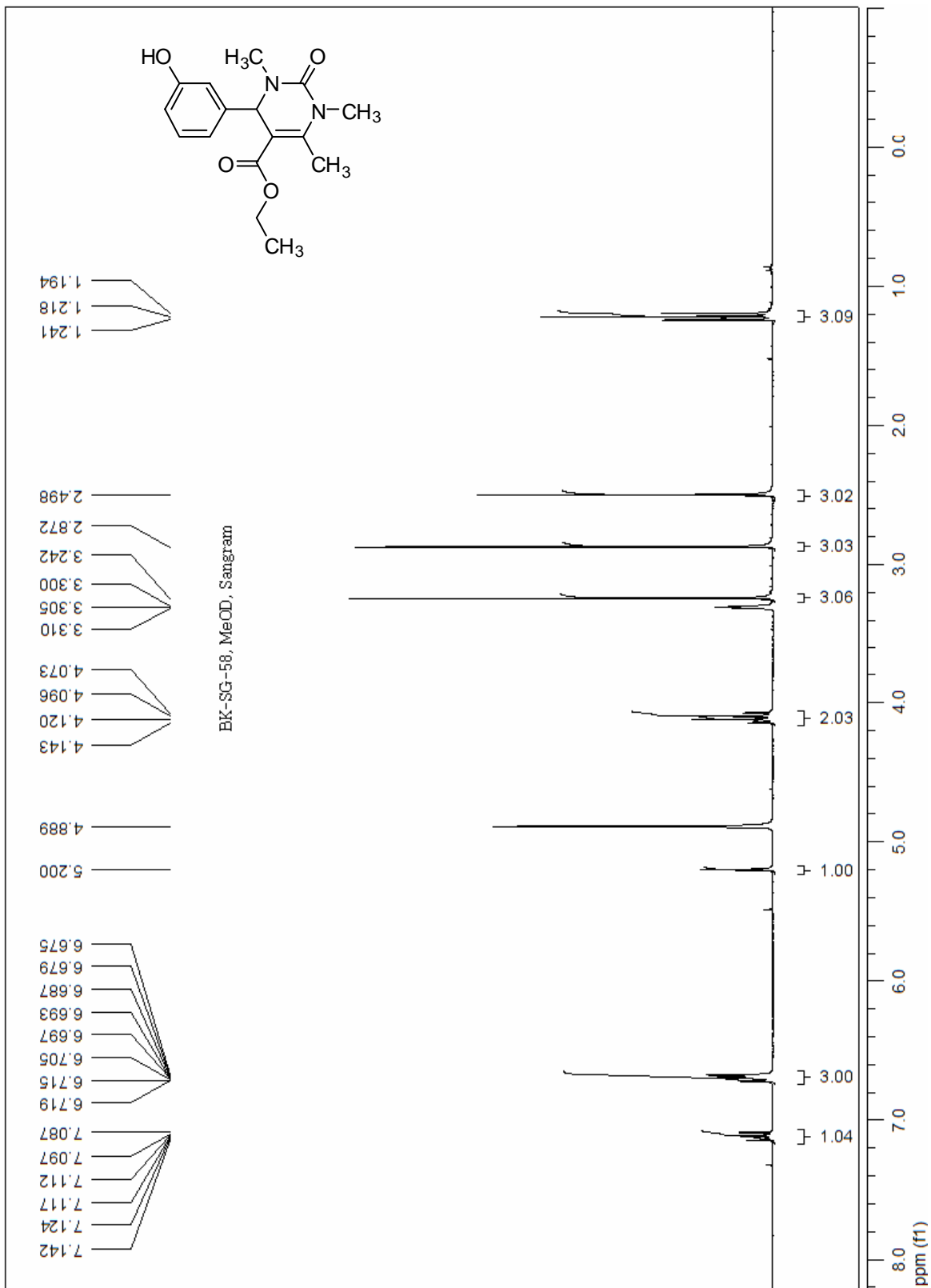


Expanded ^1H NMR spectra of compound **5a**

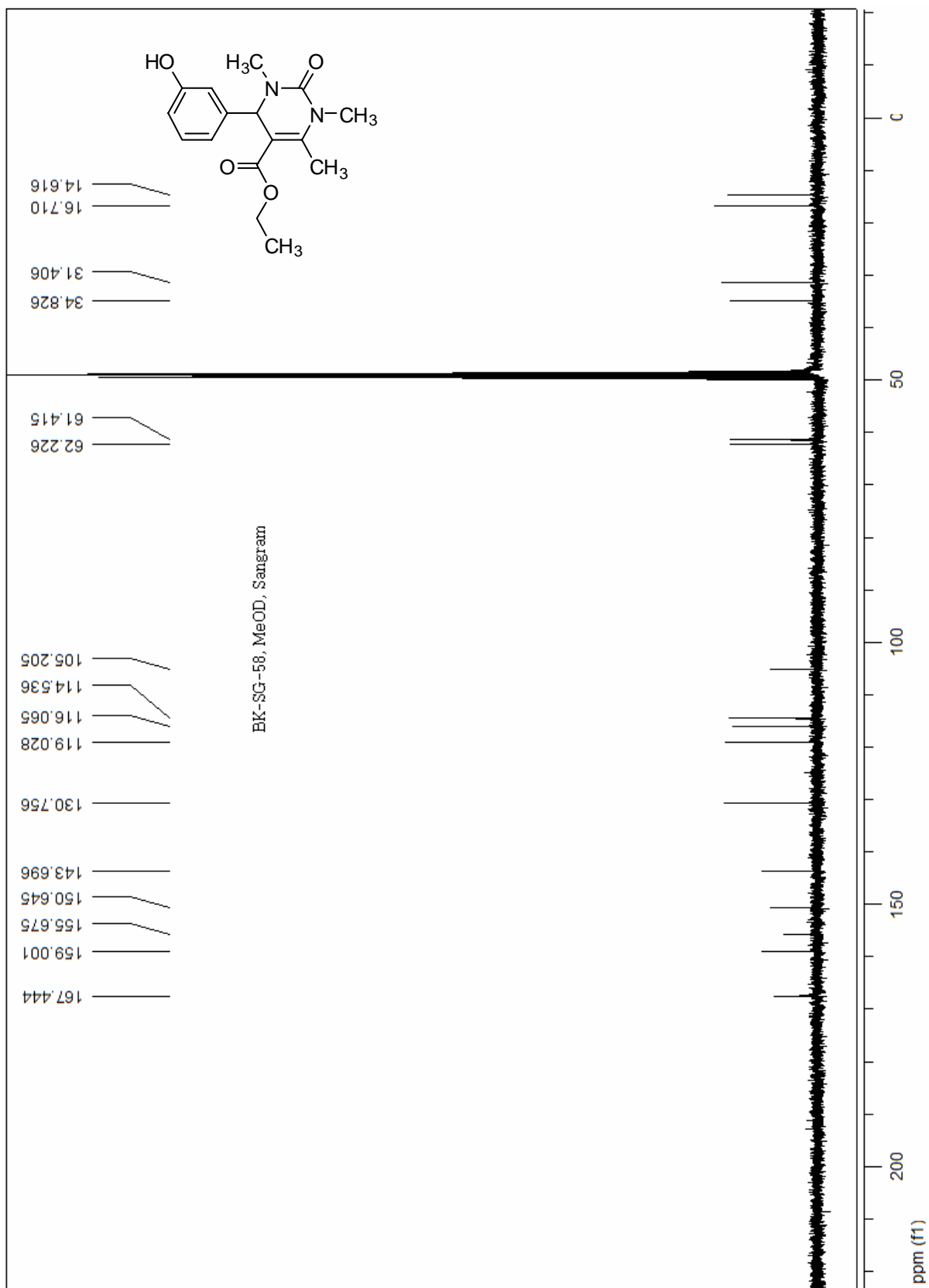
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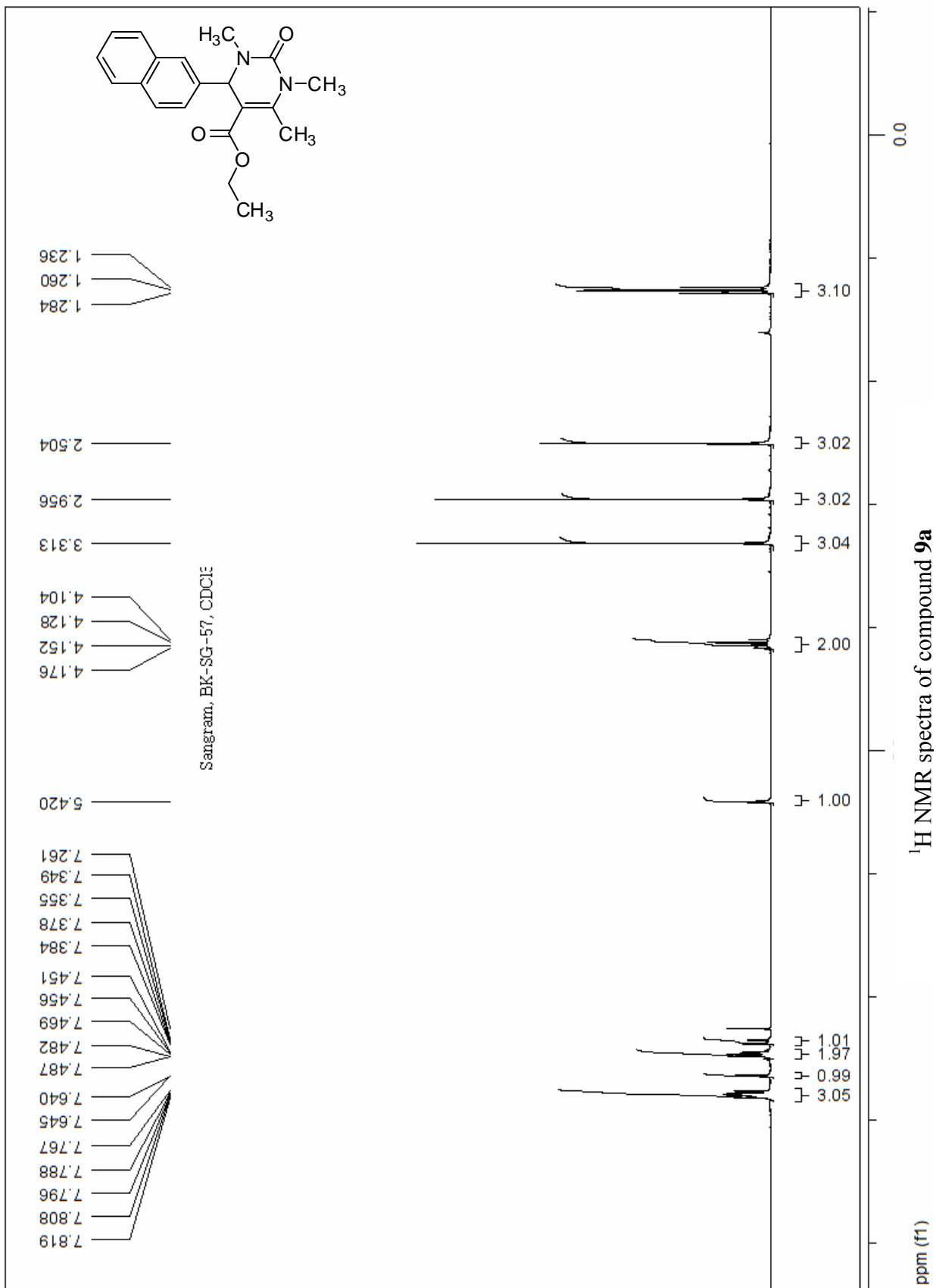
¹³C NMR spectra of compound 5a

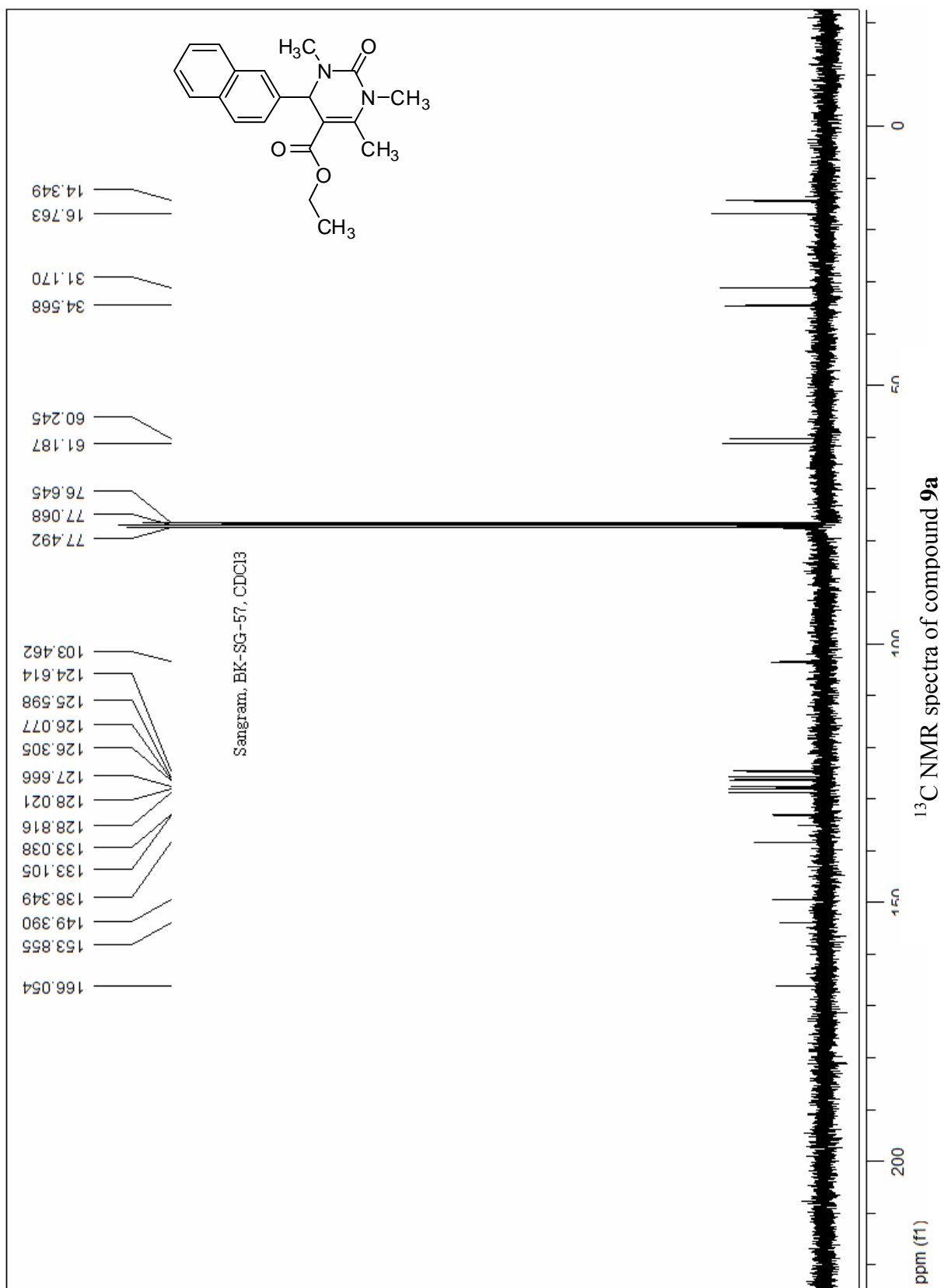


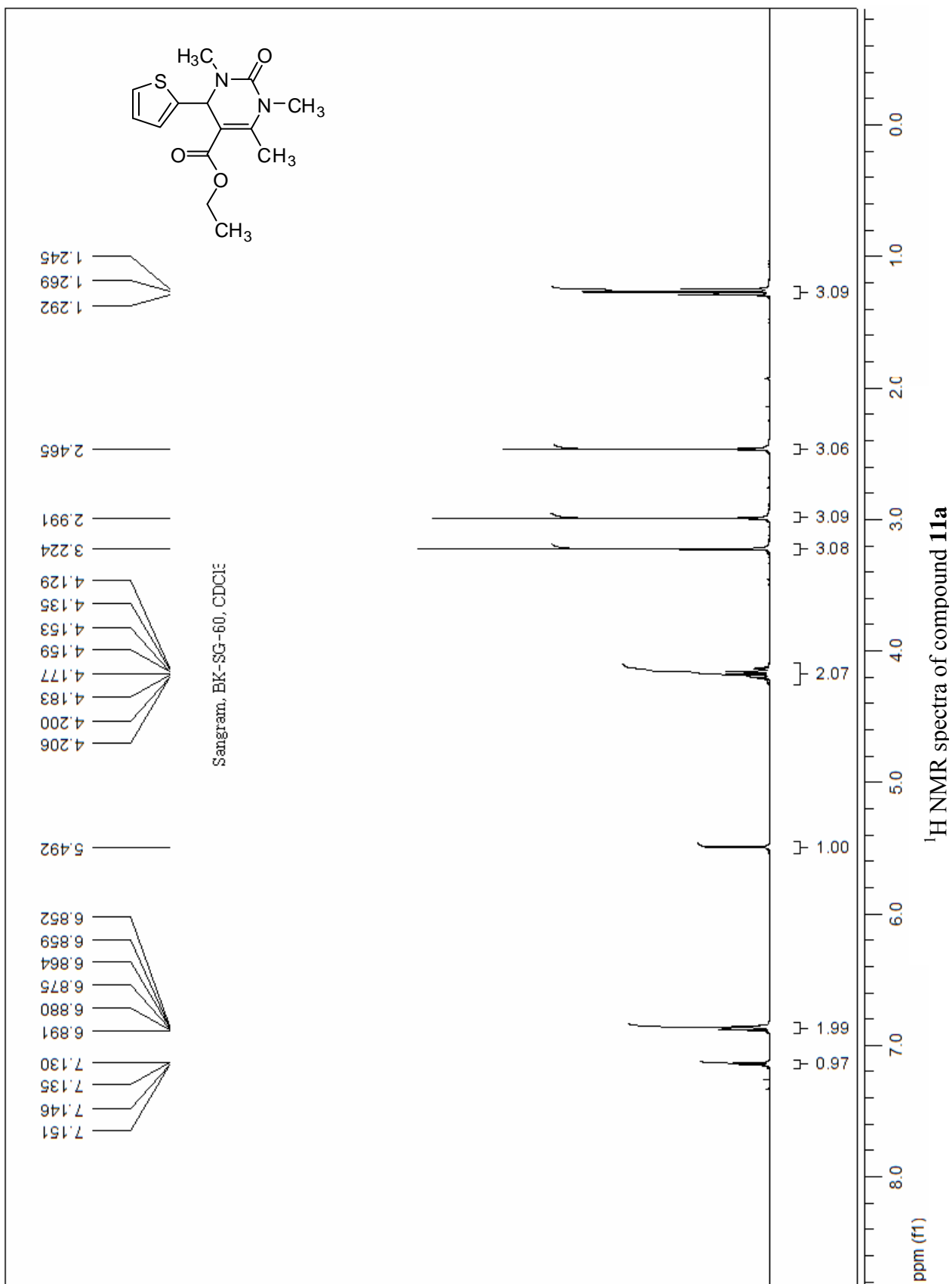
^1H NMR spectra of compound **7a**

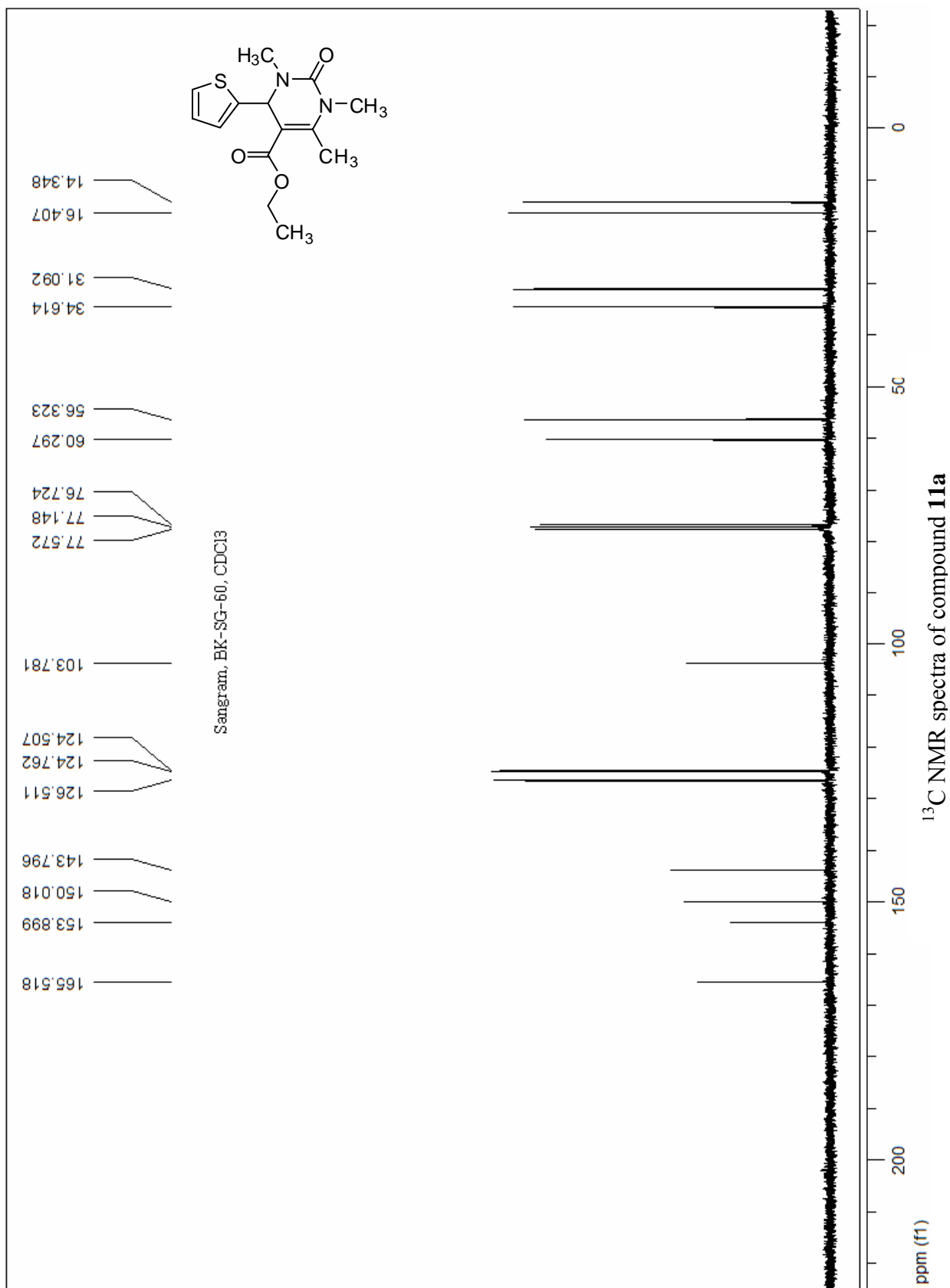


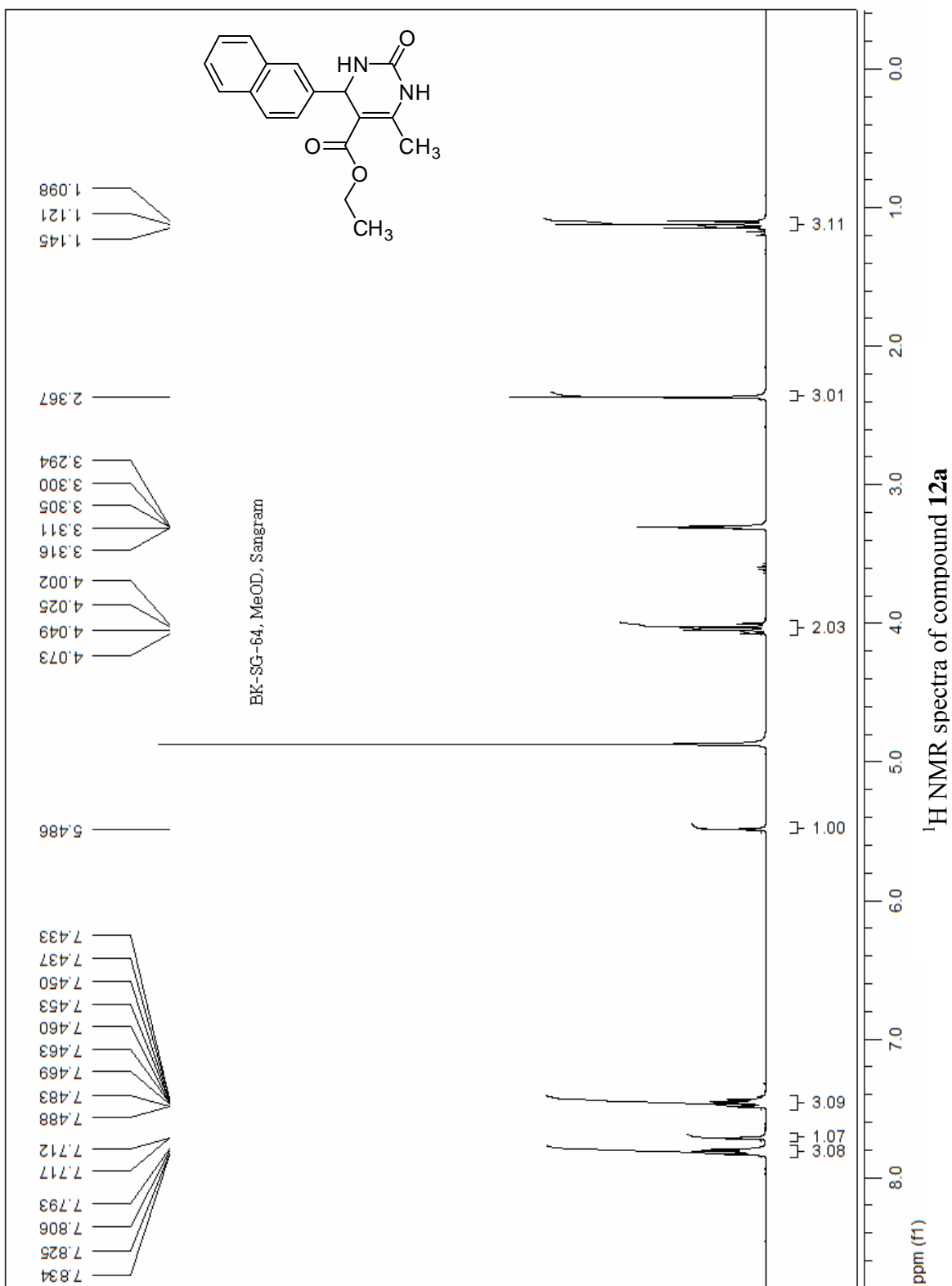
¹³C NMR spectra of compound 7a

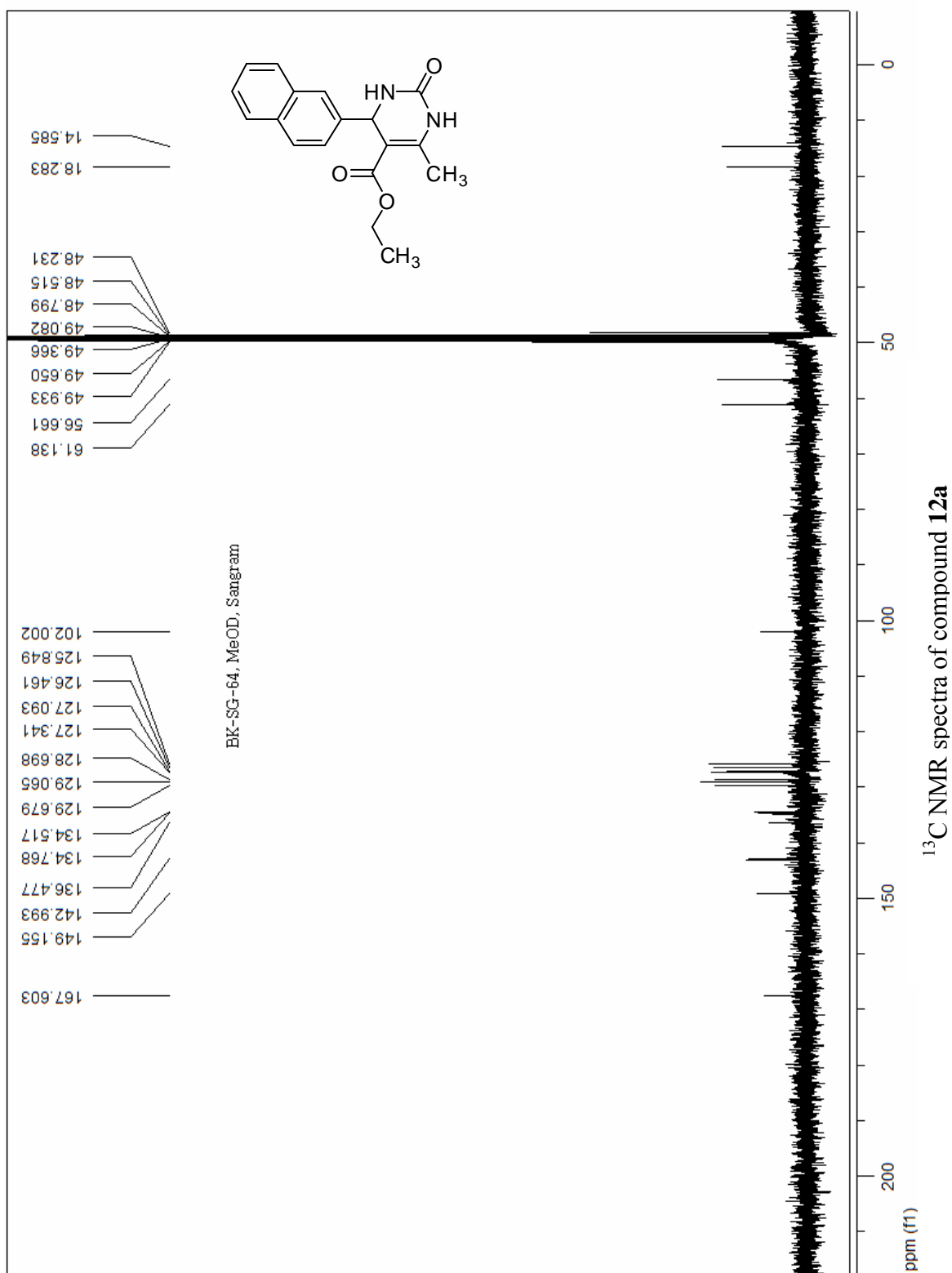


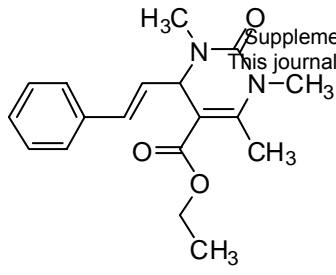












Supplementary Material (ESI) for Green Chemistry
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Current Data Parameters
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 EXPNO 23
 PROCNO 1

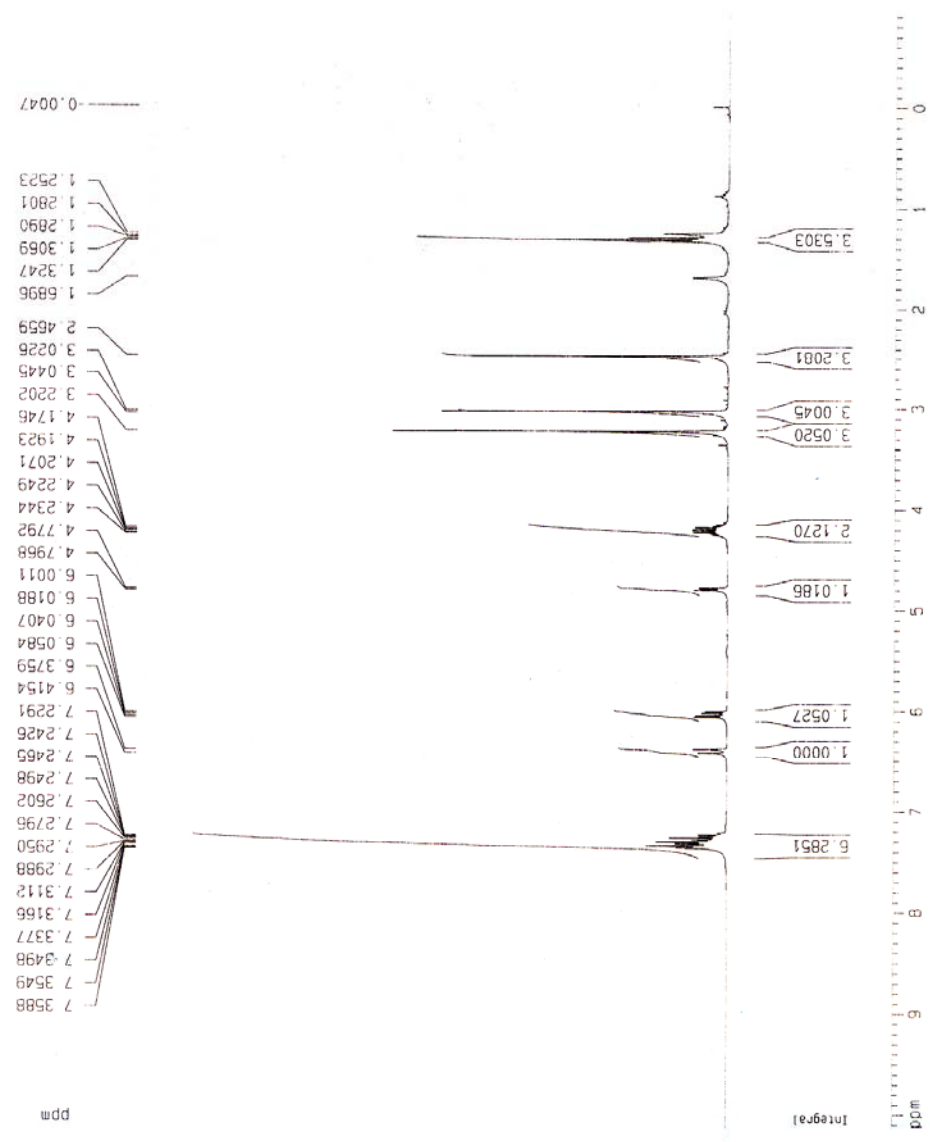
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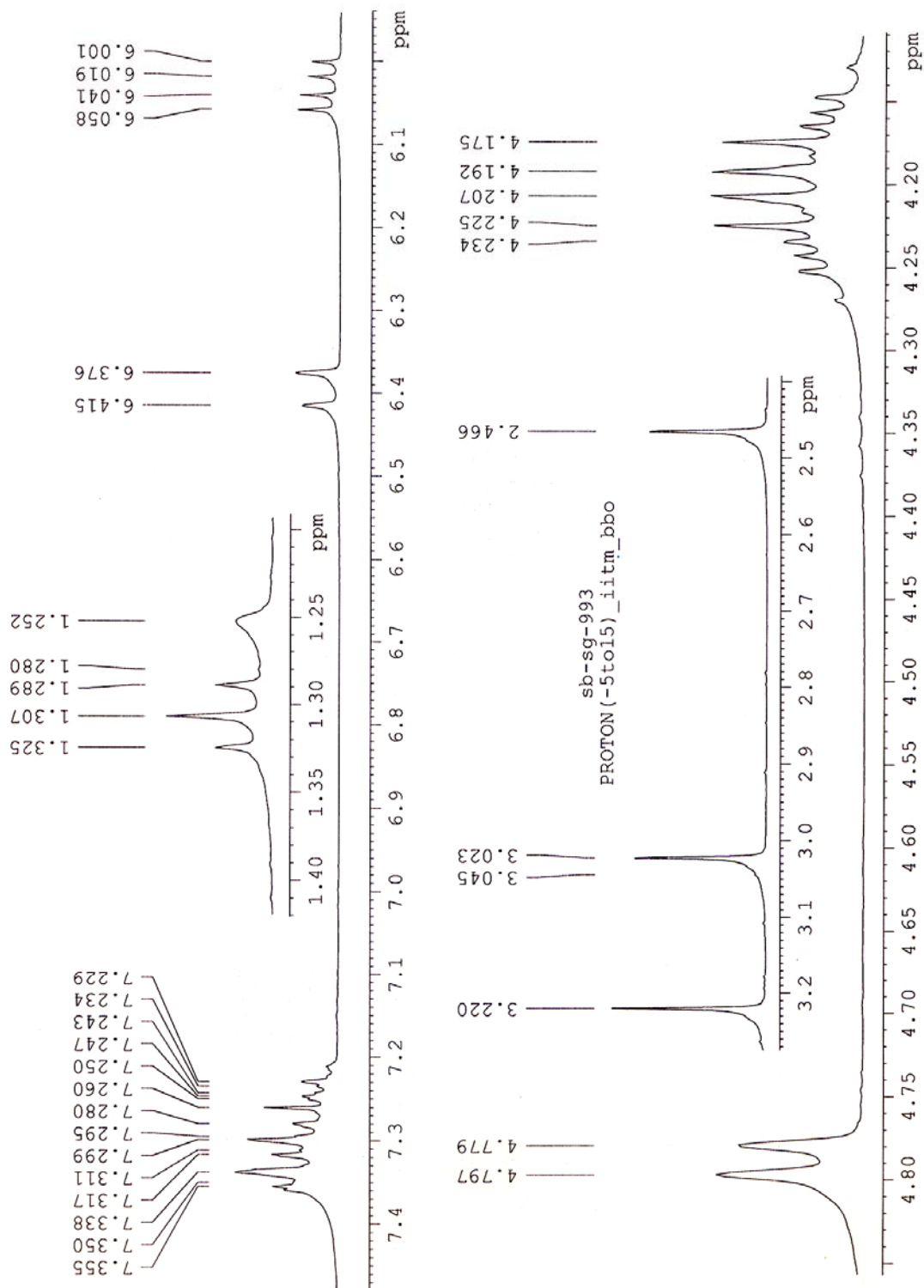
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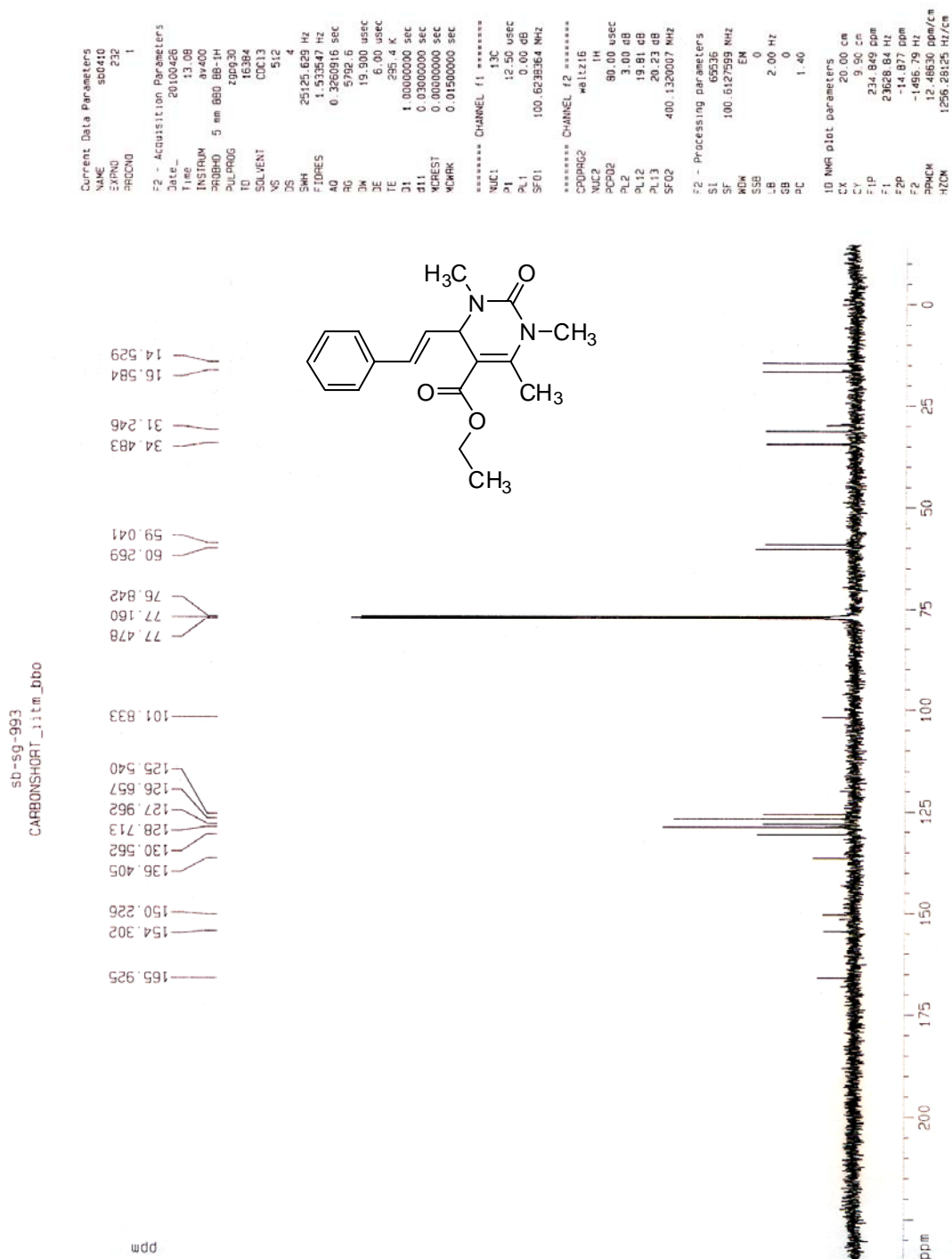
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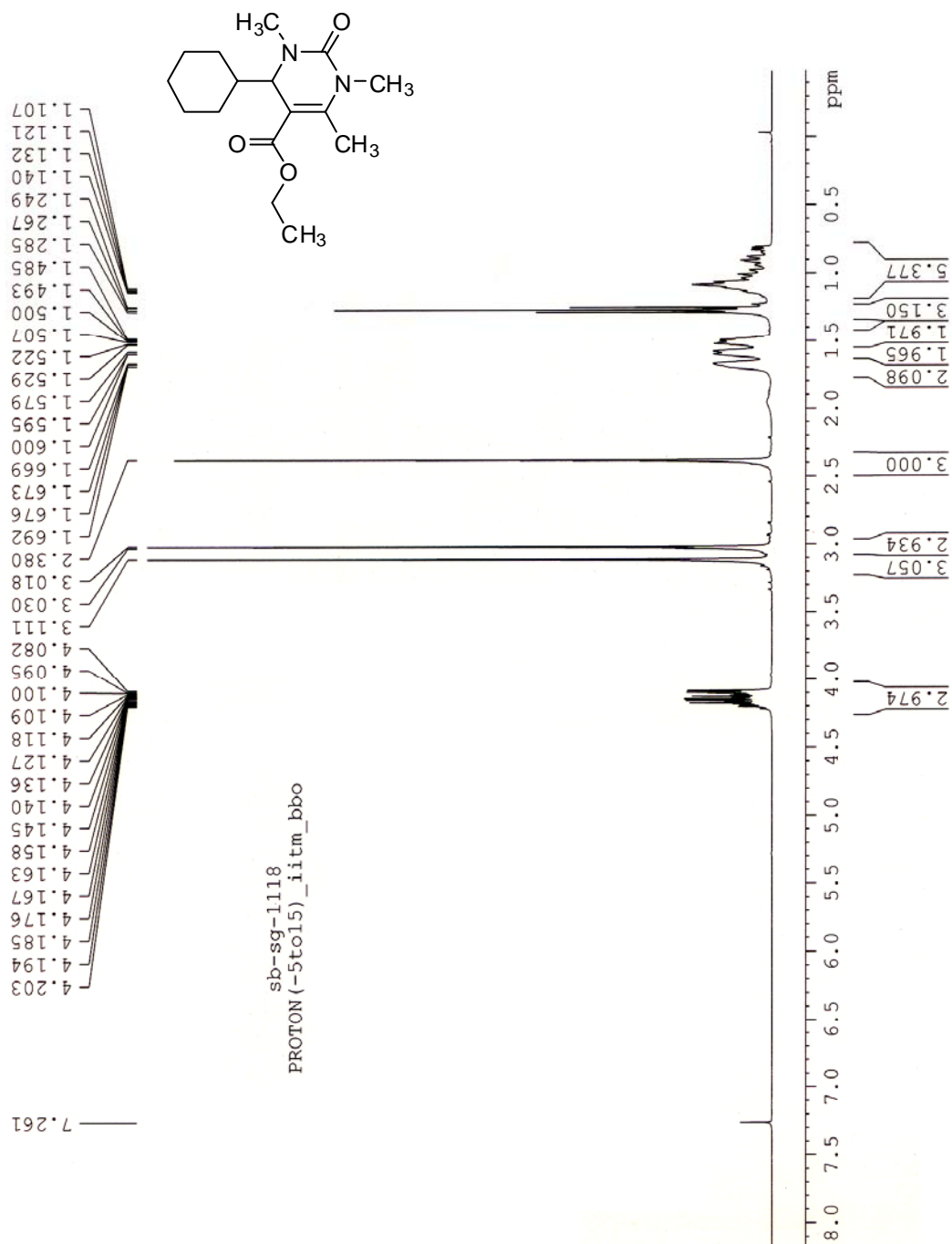
¹H NMR spectra of compound 14a



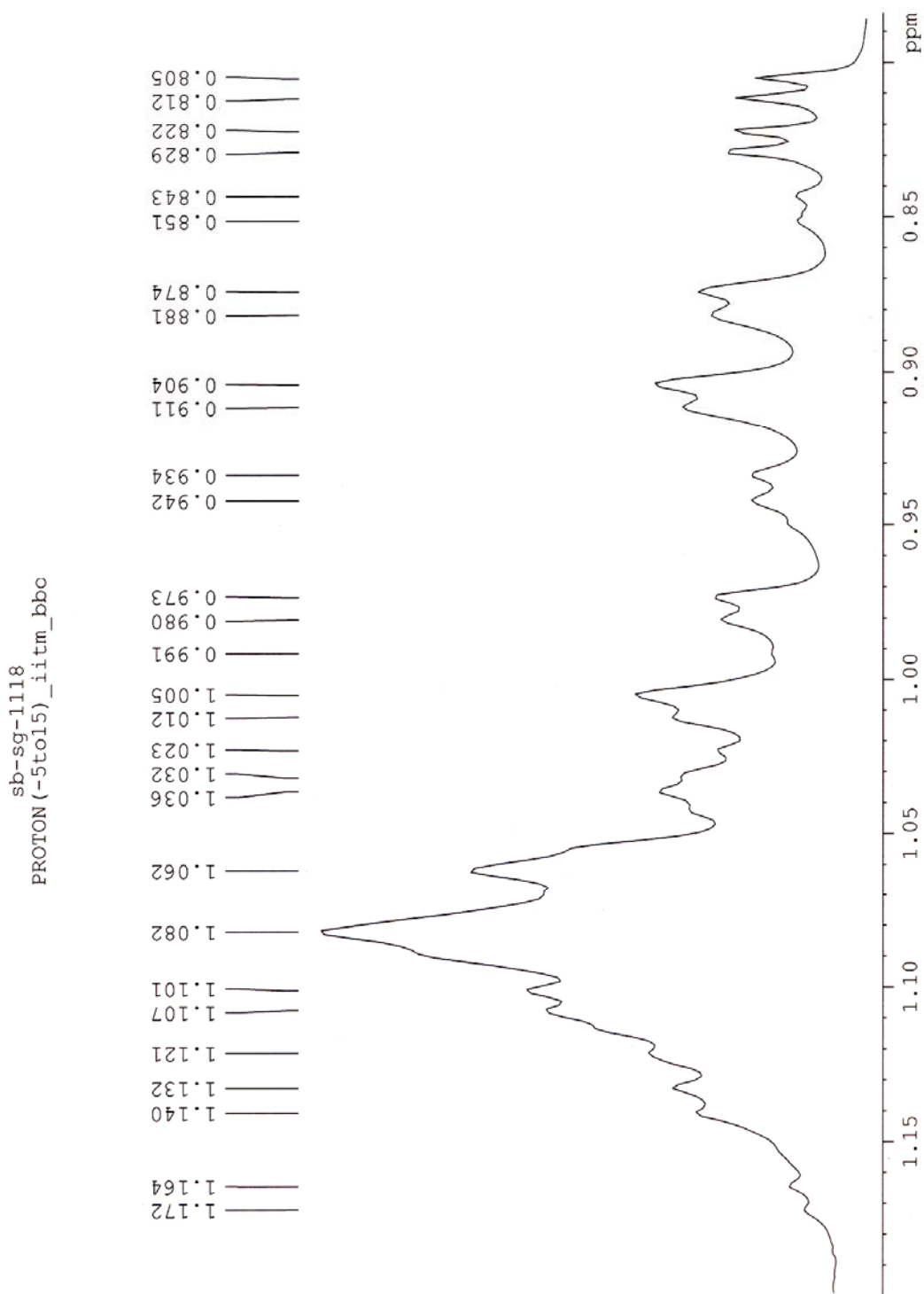
Expanded ¹H NMR spectra of compound 14a



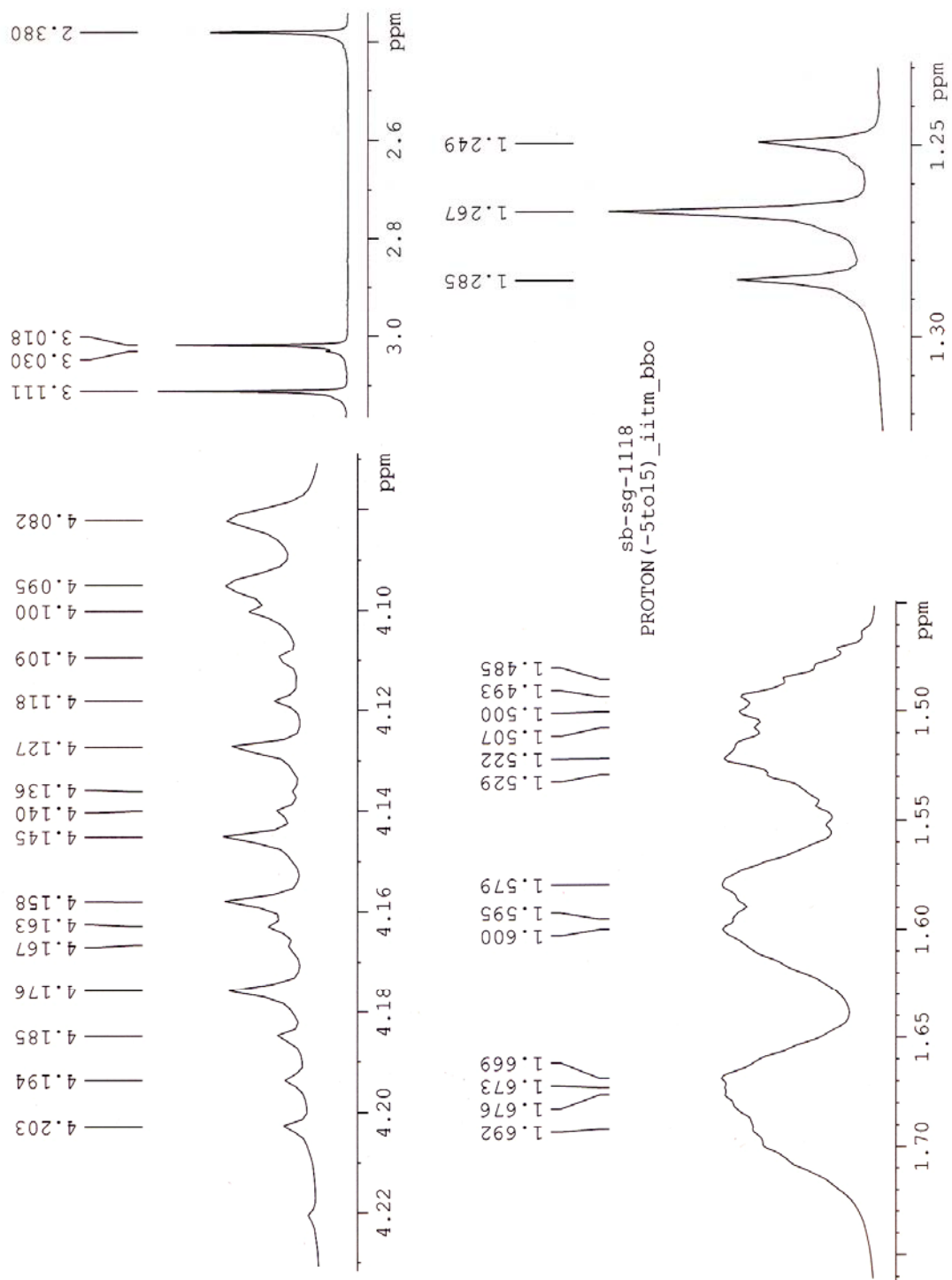
¹³C NMR spectra of compound 14a



¹H NMR spectra of compound **16a**



Expanded ¹H NMR spectra of compound **16a**



Expanded ^1H NMR spectra of compound **16a**

SD-SQ-1118
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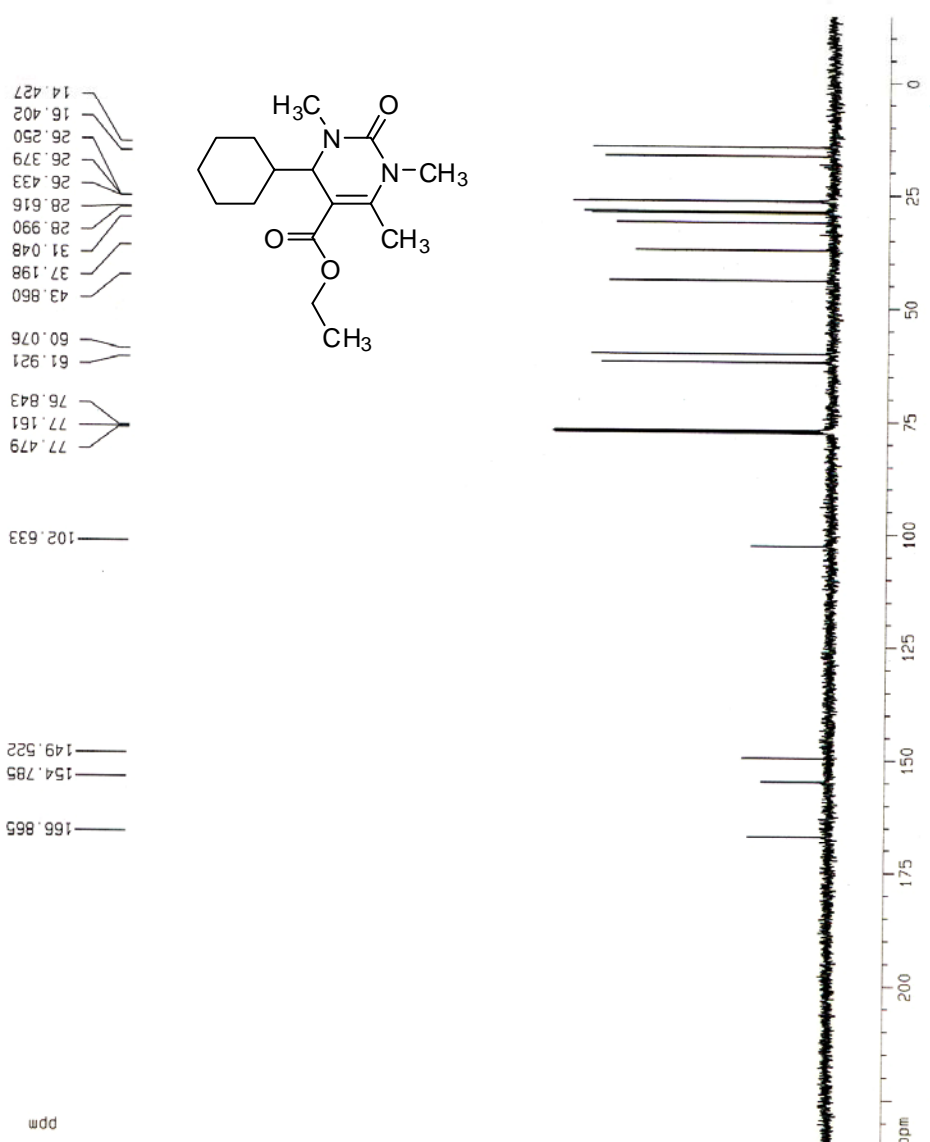
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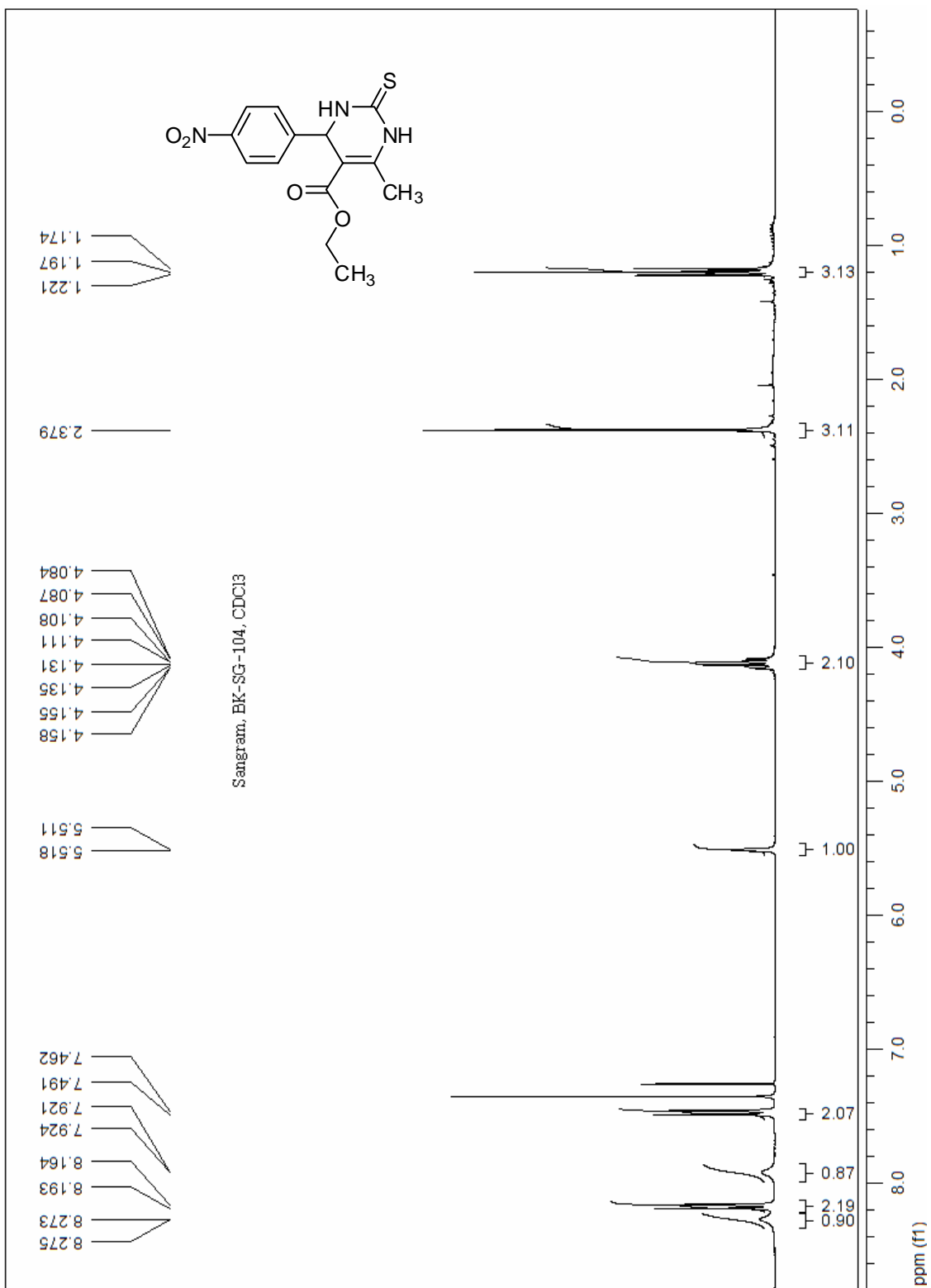
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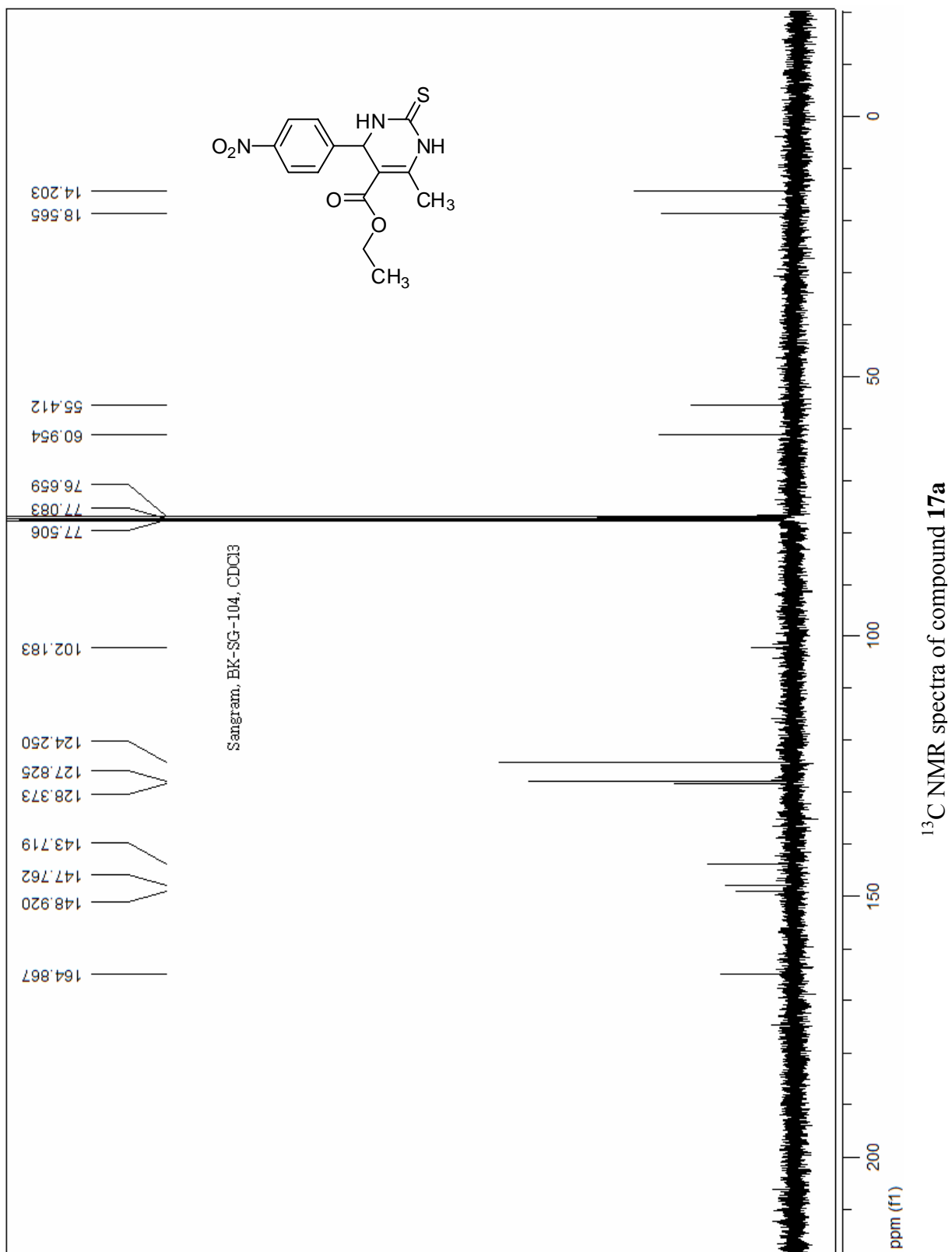
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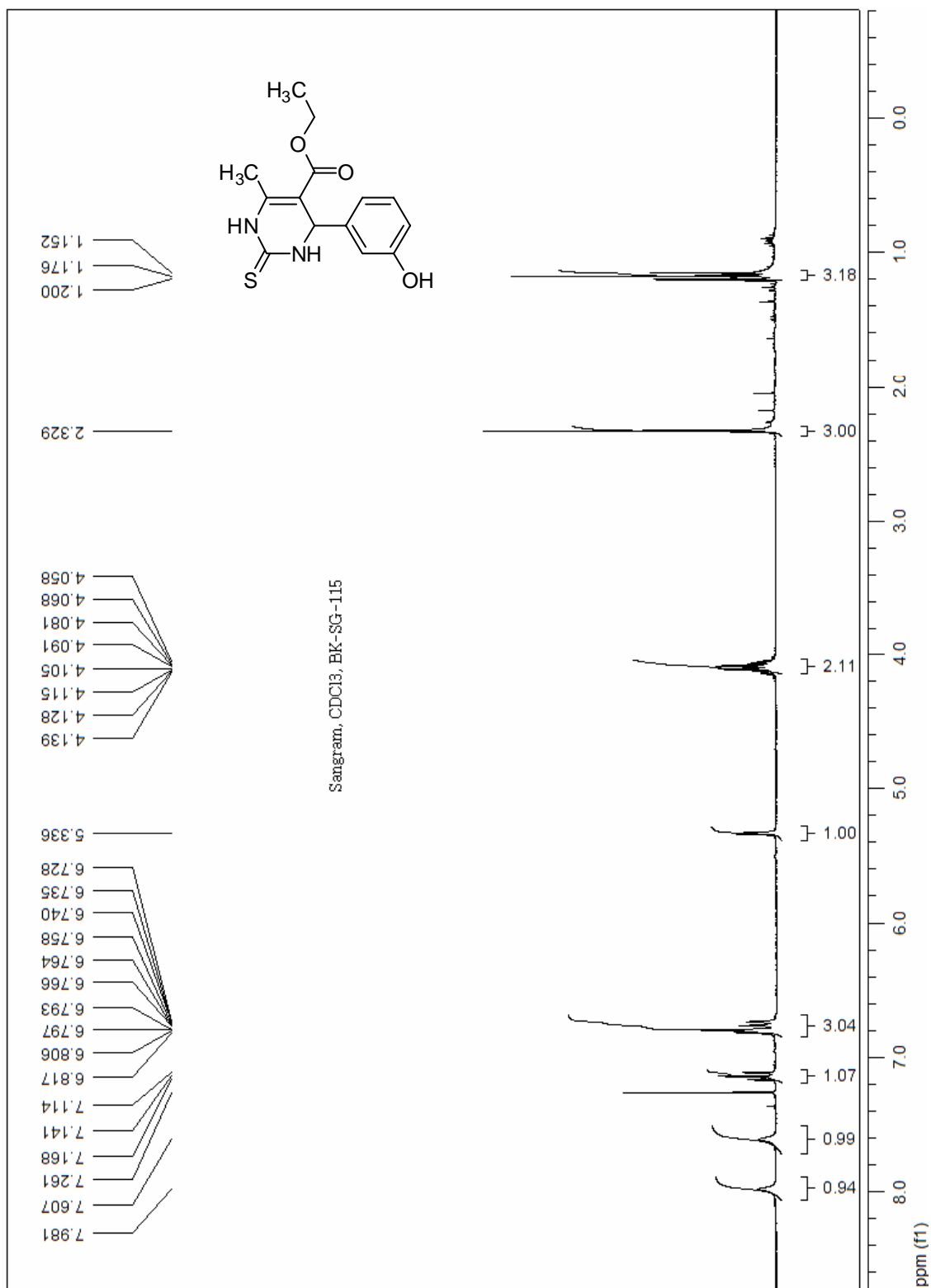


¹³C NMR spectra of compound **16a**

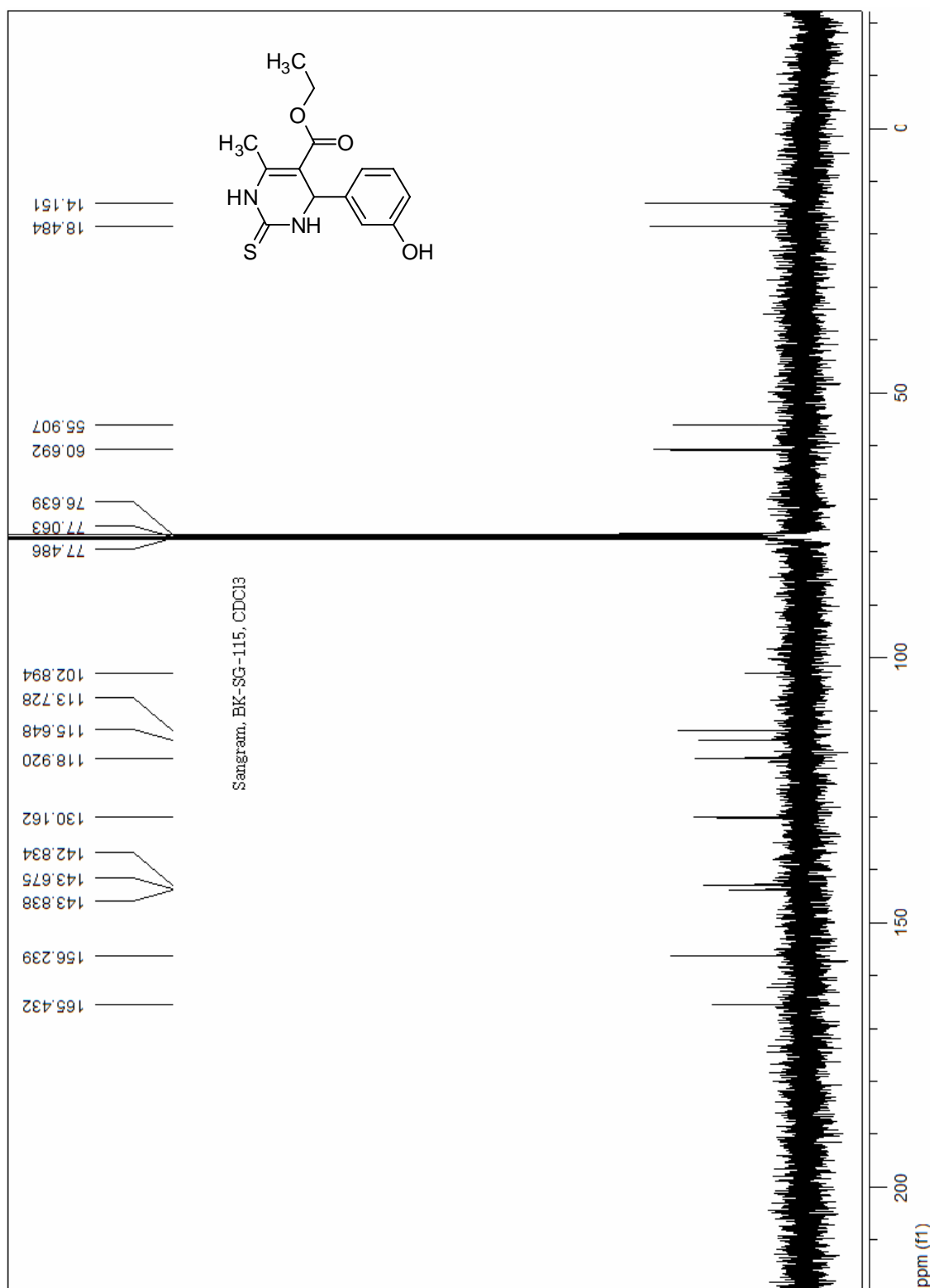


¹H NMR spectra of compound 17a

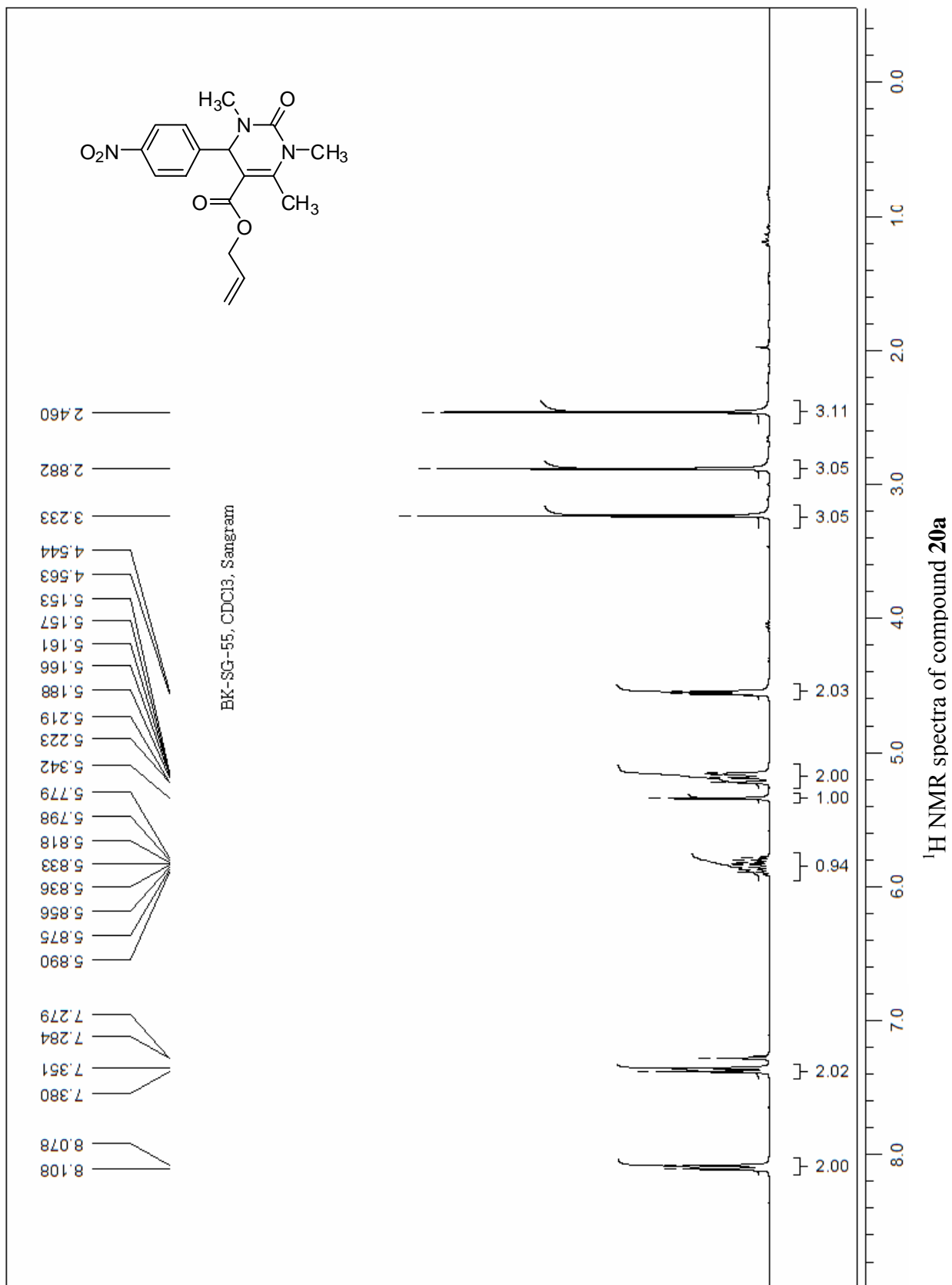


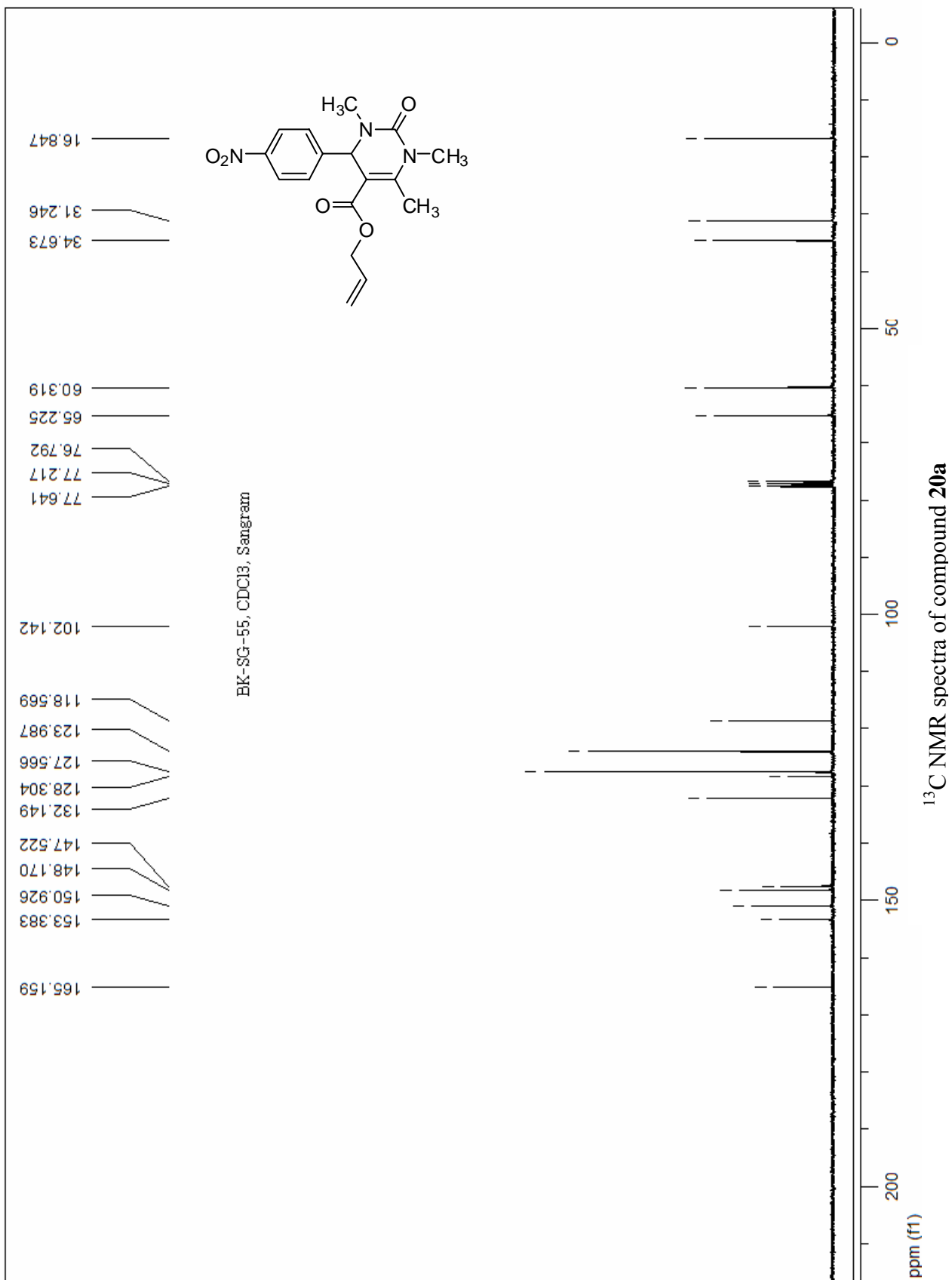


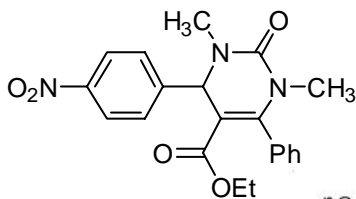
¹H NMR spectra of compound 18a



¹³C NMR spectra of compound **18a**







sb-sg-1132
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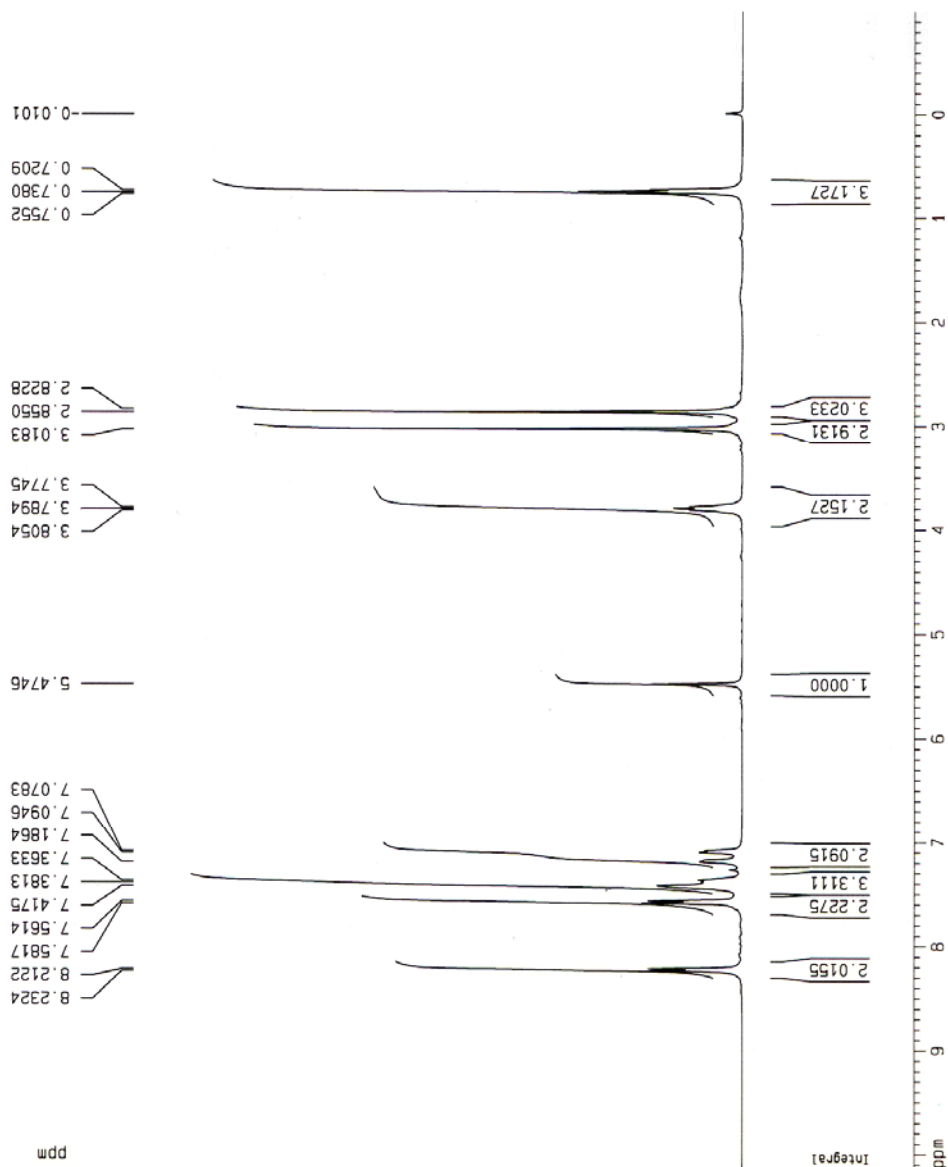
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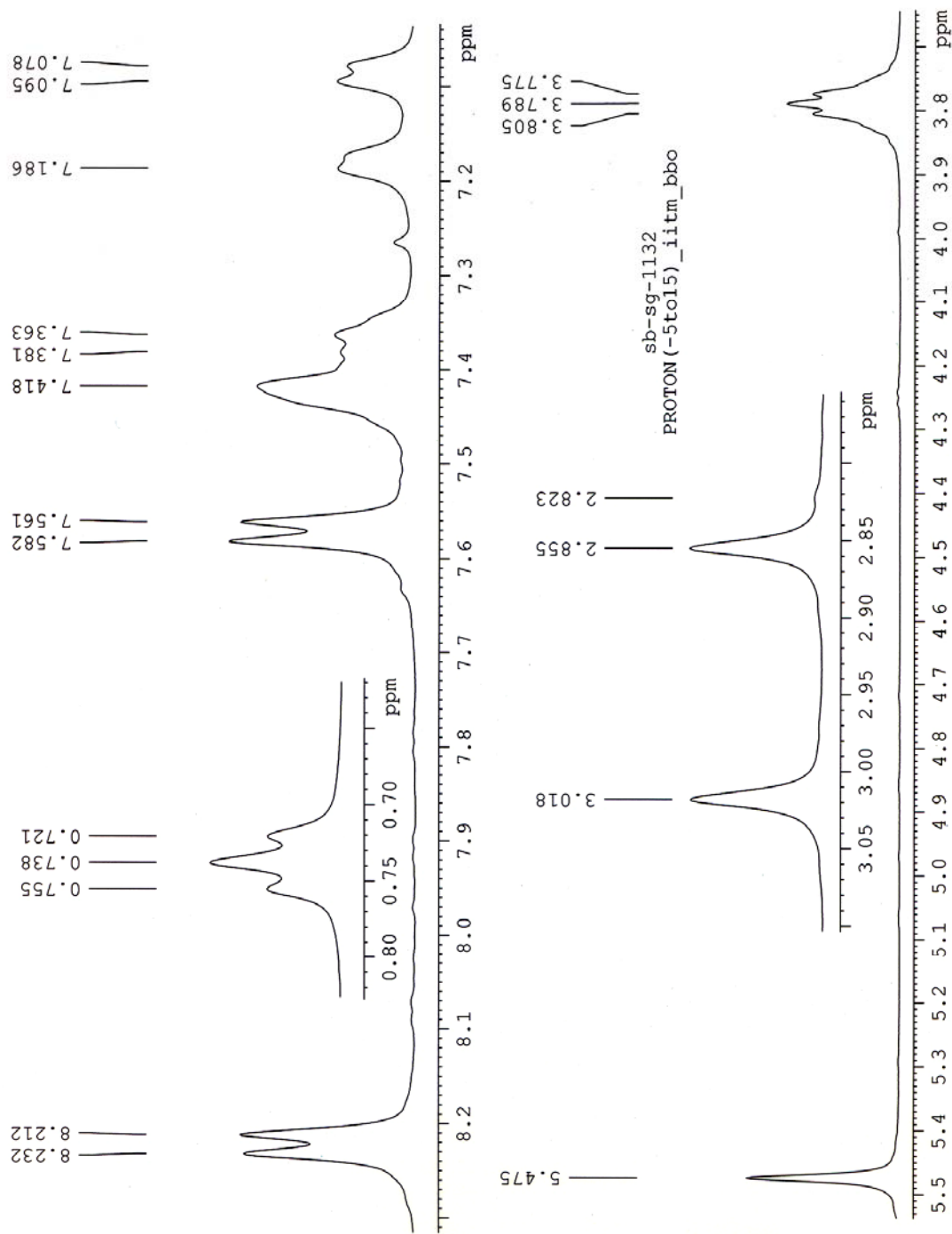
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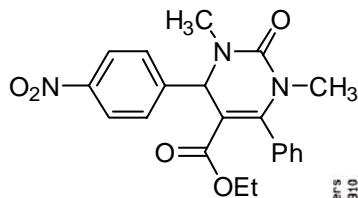
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¹H NMR spectra of compound 22a



Expanded ¹H NMR spectra of compound 22a



```

Current Data Parameters
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PROCNO   1

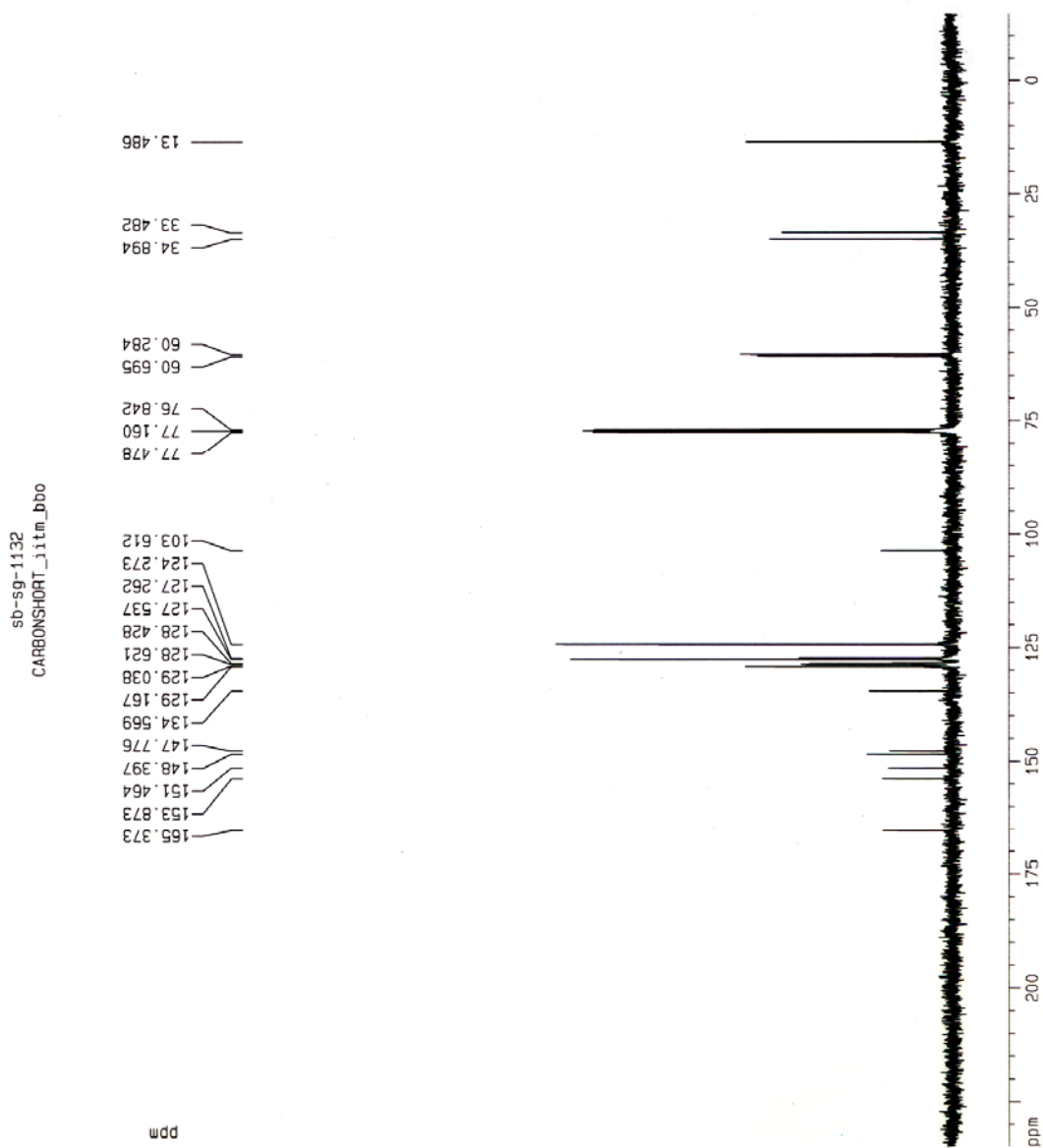
F2 - Acquisition Parameters
Date_    20100920
Time     11.15
INSTRUM  sxt400
PROBHD   5 mm BBO BB-1H
PULPROG  zgpg30
TO       16364
SOLVENT  CDCl3
NS       309
DS       4
SFO1     25125.629 Hz
FIDRES   1.533547 Hz
AQ       0.3560916 sec
RG       13004
DM       19.900 usec
DE       6.00 usec
TE       299.7 K
D1       1.0000000 sec
d11      0.0300000 sec
INCRST   0.0000000 sec
NDCMRK   0.0150000 sec

***** CHANNEL f1 *****
NUC1     13C
P1       12.50 usec
PL1      0.00 dB
SFO1     100.6236364 MHz

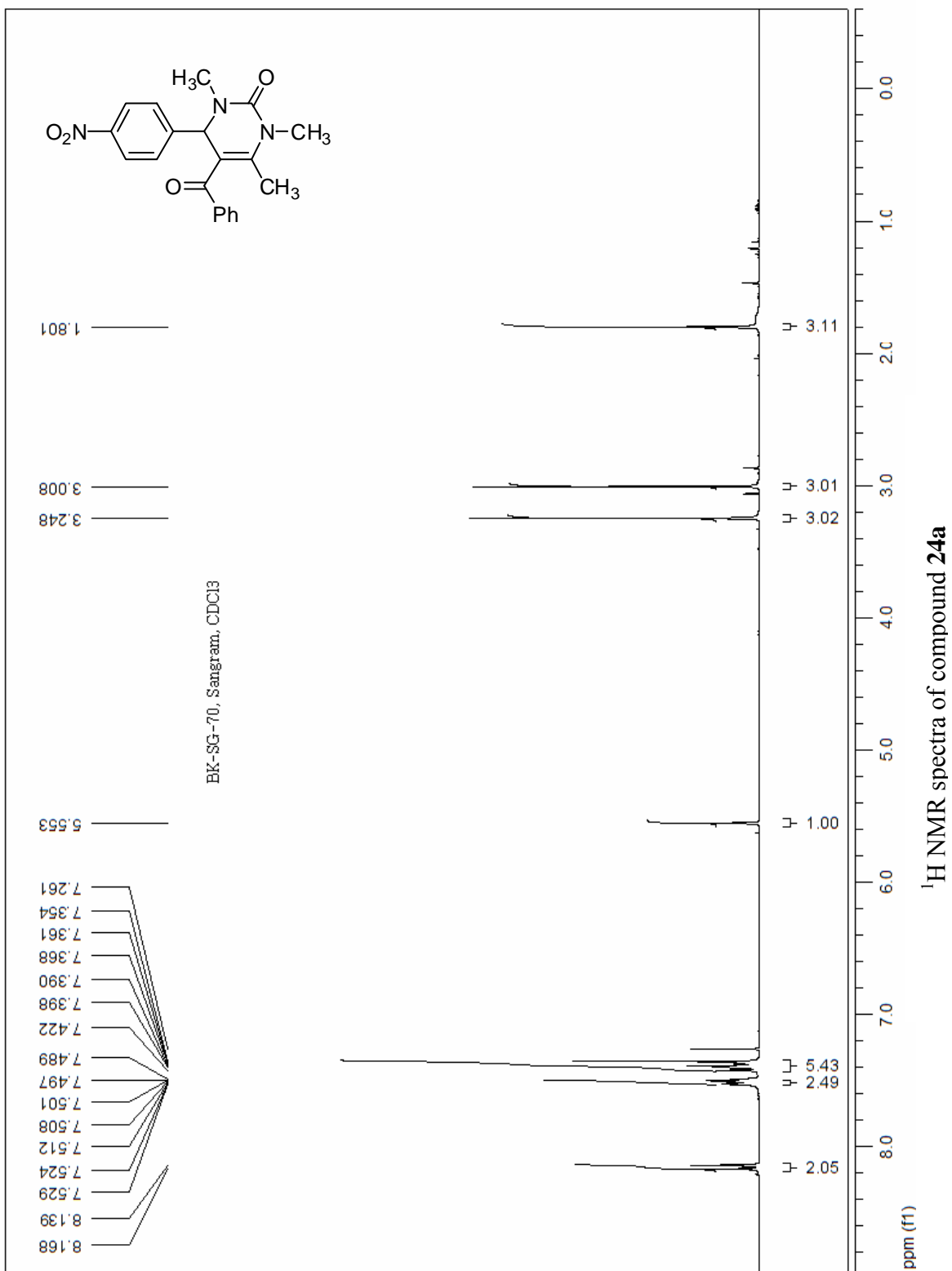
***** CHANNEL f2 *****
CPDPRG2  waltz16
NUC2     1H
P2       80.00 usec
PL2      3.00 dB
PL3      19.81 dB
PL4      20.23 dB
SFO2     400.1320007 MHz

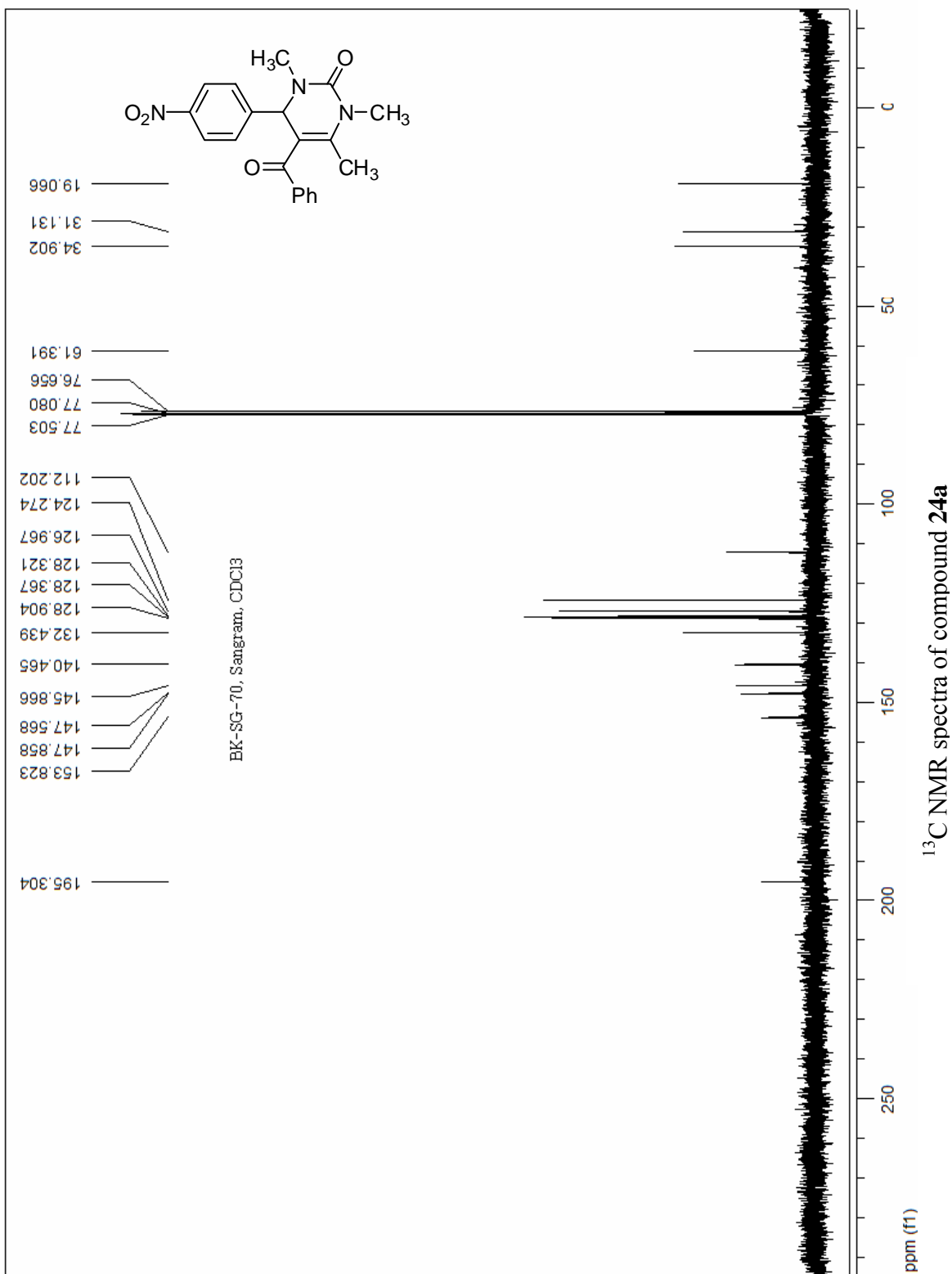
F2 - Processing parameters
SI       65536
SF       100.6127610 MHz
WDW      EM
SSB      0
LB       2.00 Hz
GB       0
BB       0
PC       1.40

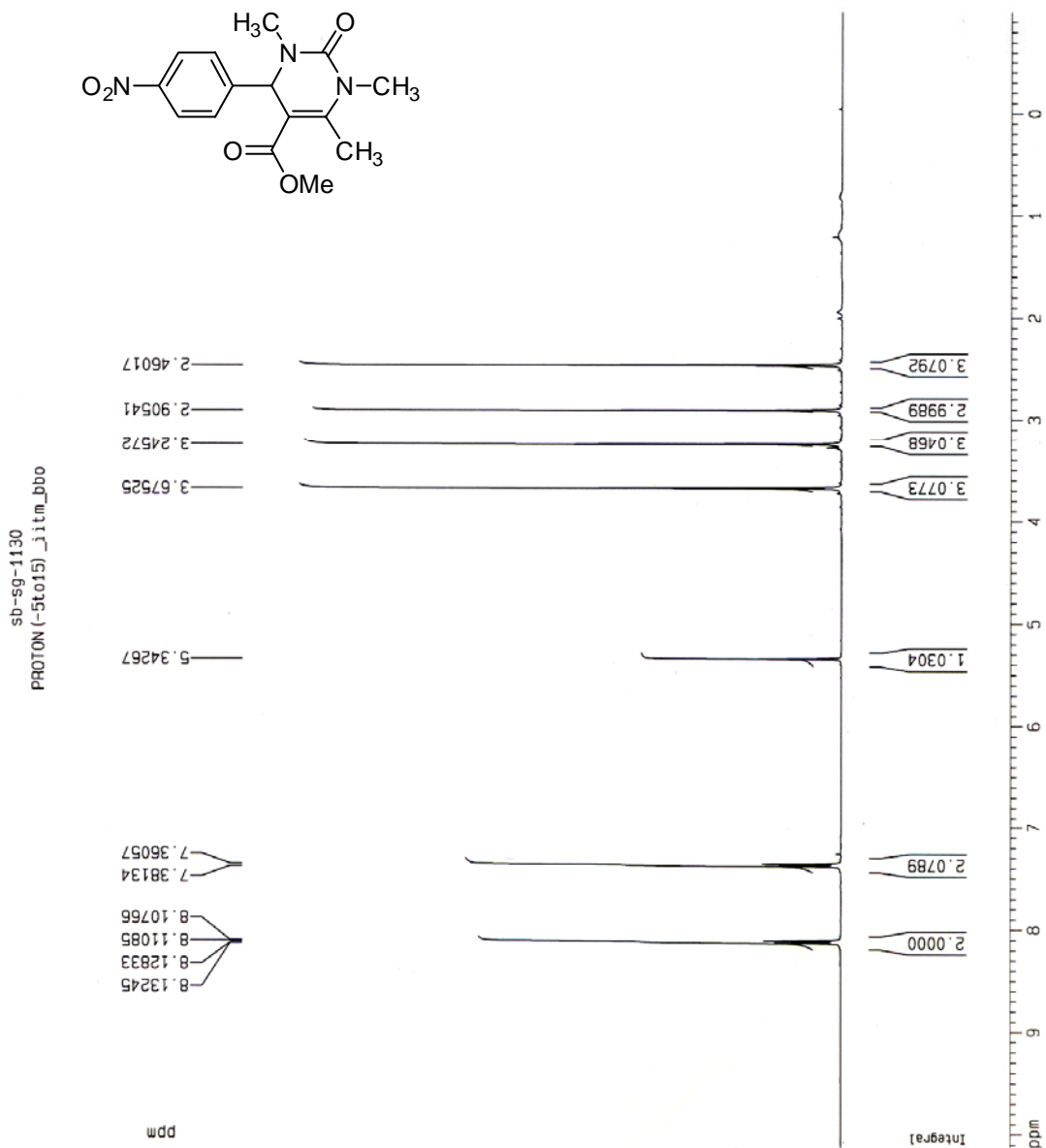
ID NMR plot parameters
CX       20.00 cm
CY       7.00 cm
F1P      234.849 ppm
F1       23626.84 Hz
F2P      -14.877 ppm
F2       -1496.79 Hz
PPMCON   12.46830 ppm/cm
HZCON    1256.26125 Hz/cm
    
```

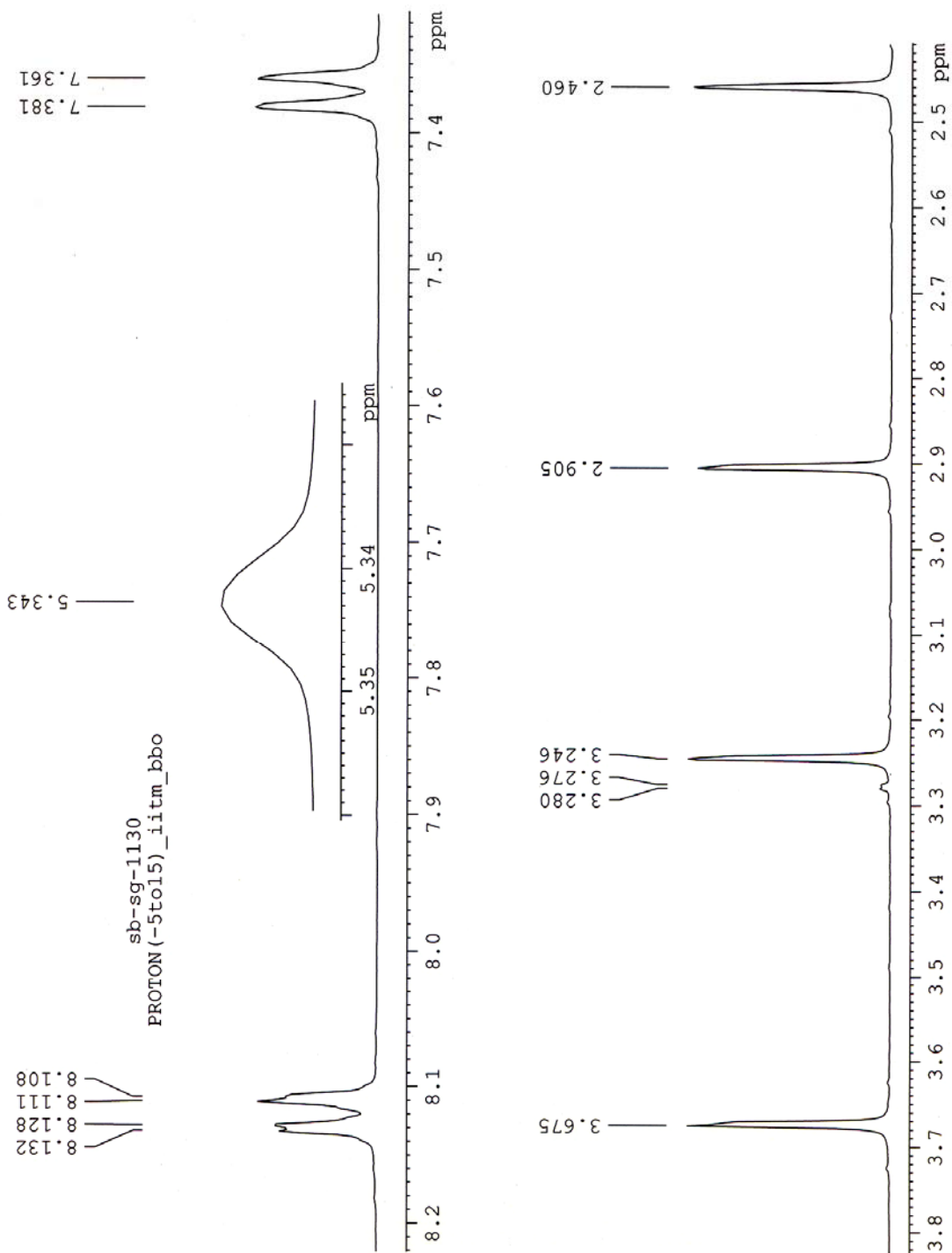


¹³C NMR spectra of compound 22a

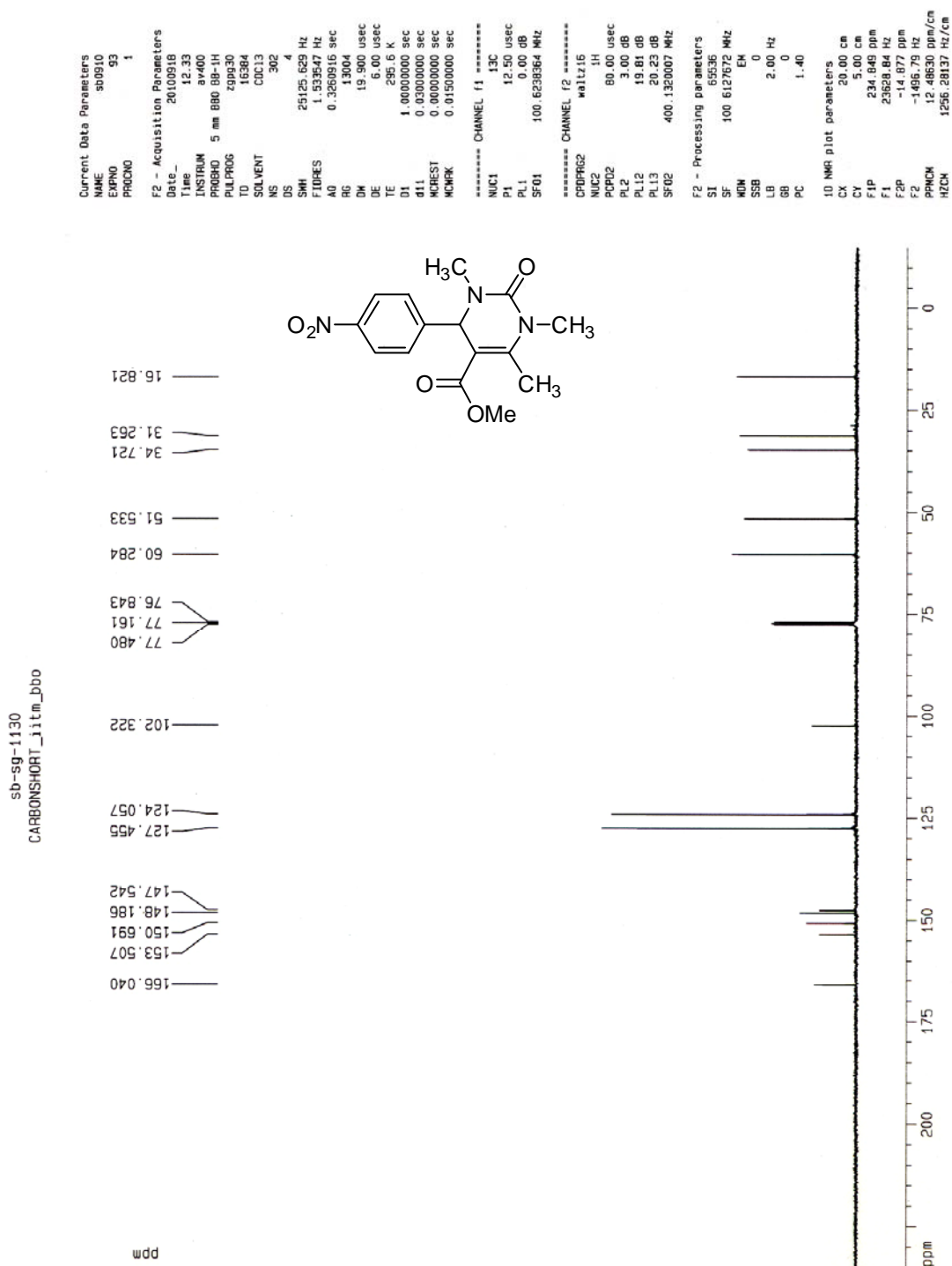


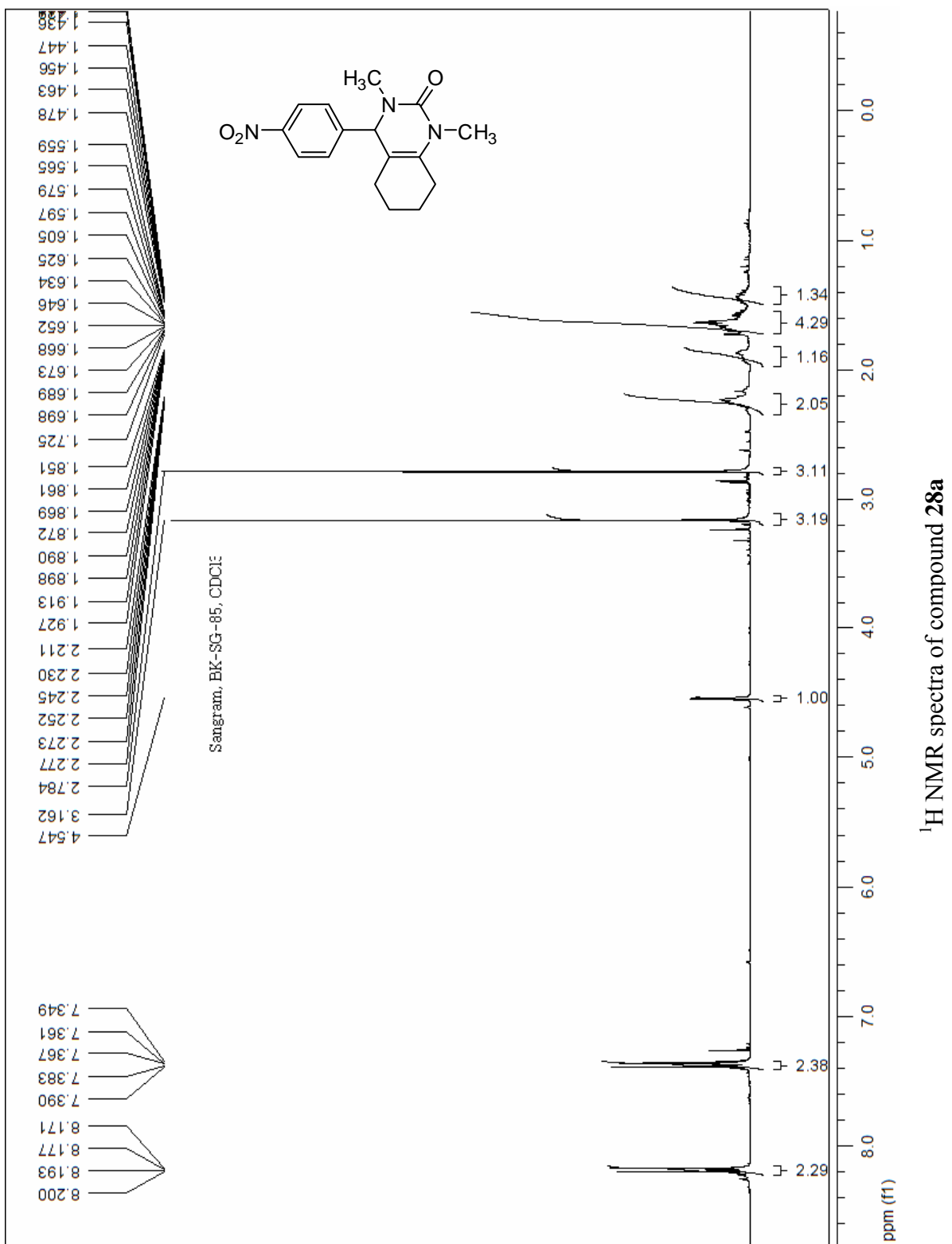


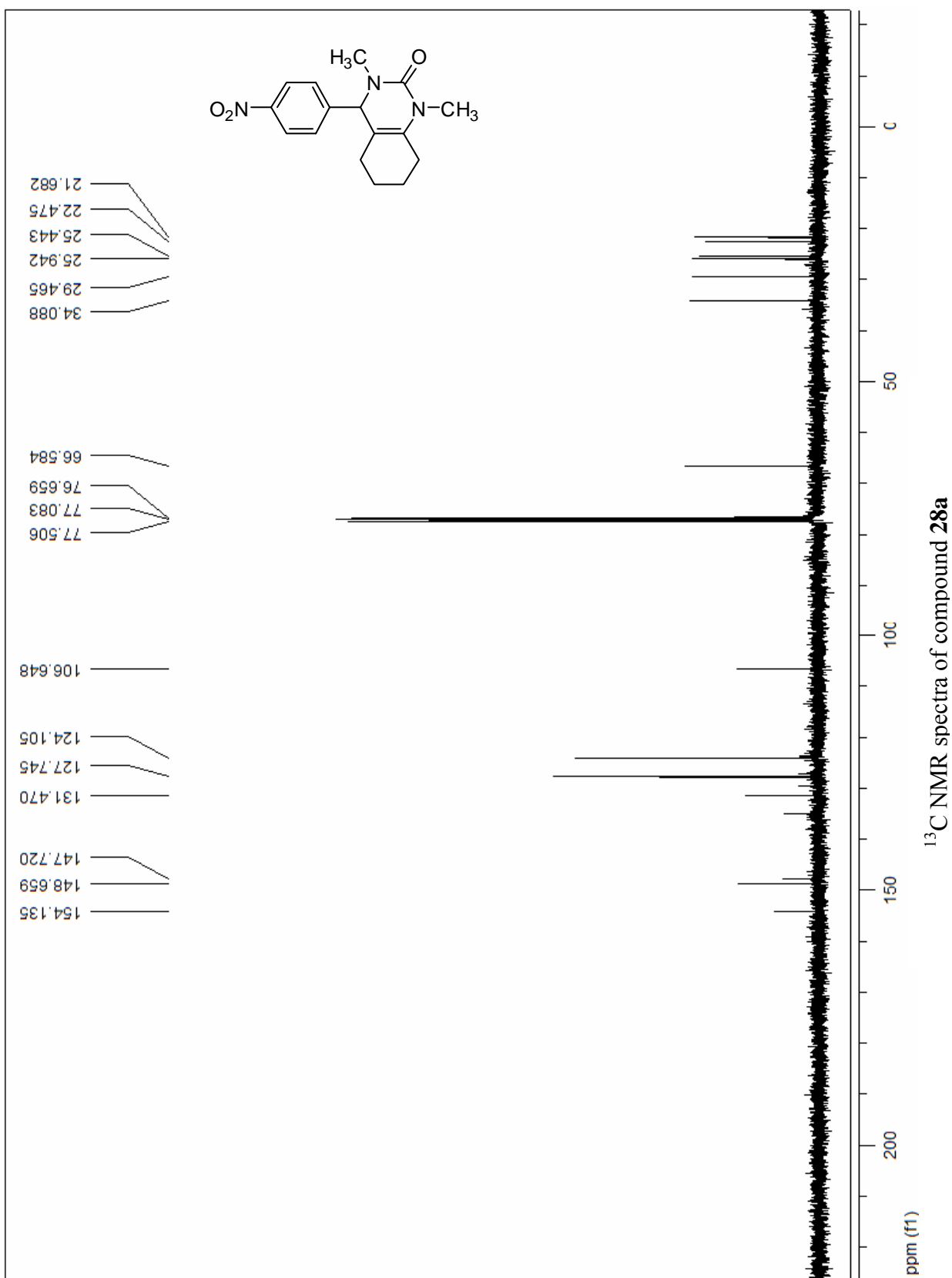


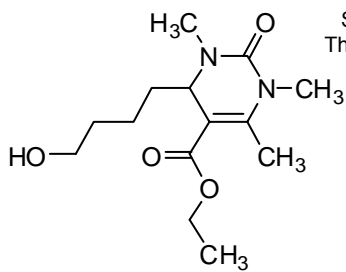


Expanded ¹H NMR spectra of compound **26a**









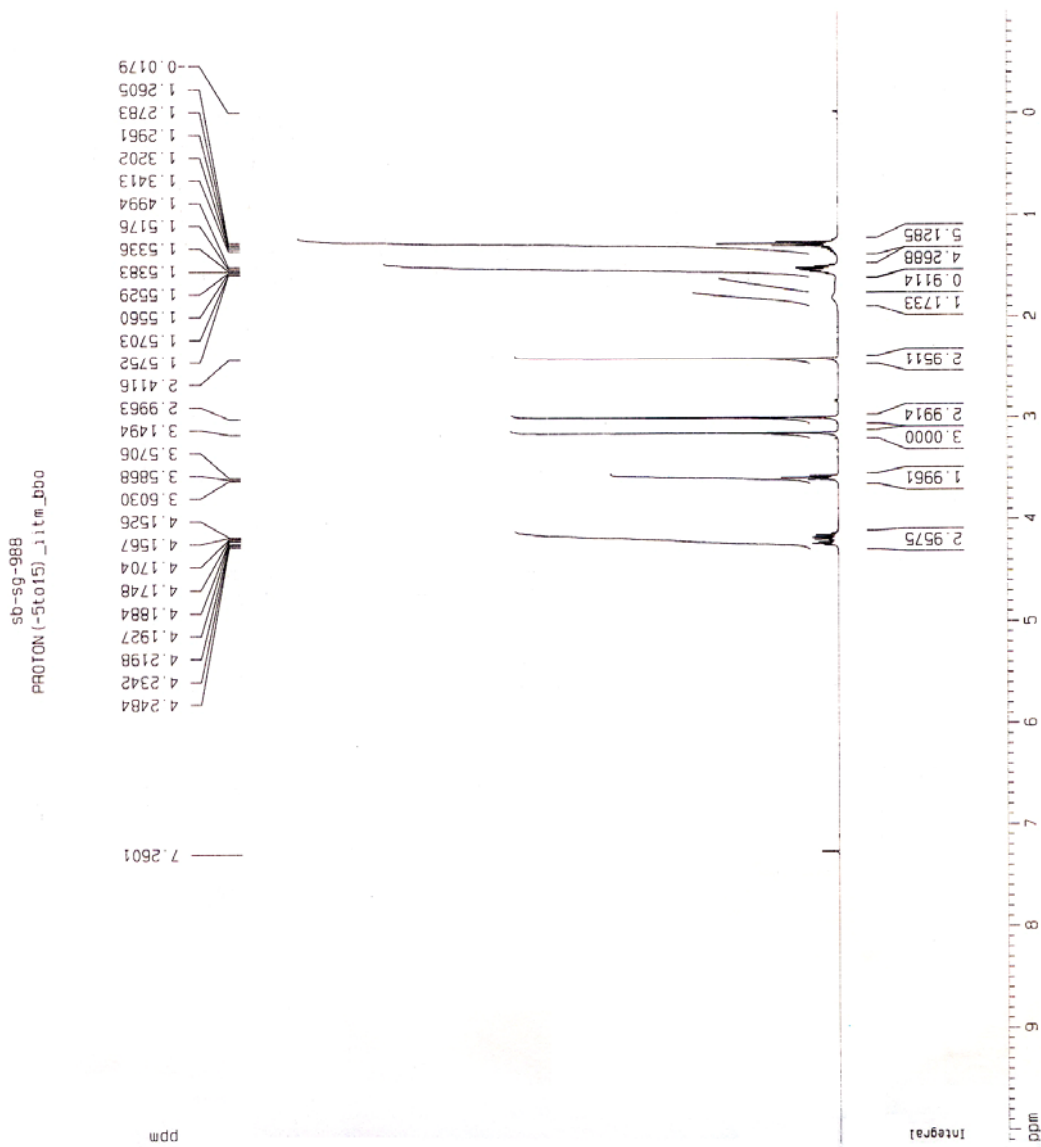
```
Current Data Parameters
NAME      SB0410
EXPNO     207
PROCNO    1

F2 - Acquisition Parameters
Date_     20100423
Time      11:23
INSTRUM   av400
PROBHD    5 mm BBO BB-1H
PULPROG   zg30
TD         32768
SOLVENT   COC13
NS         32
DS         4
SWH        8389.262 Hz
FIDRES     0.256020 Hz
AQ         1.9530228 sec
RG         101.6
CM         59.600 usec
DE         6.00 usec
TE         300.2 K
IC1        0.50000000 sec
MCHREST    0.00000000 sec
MCMRK      0.01500000 sec

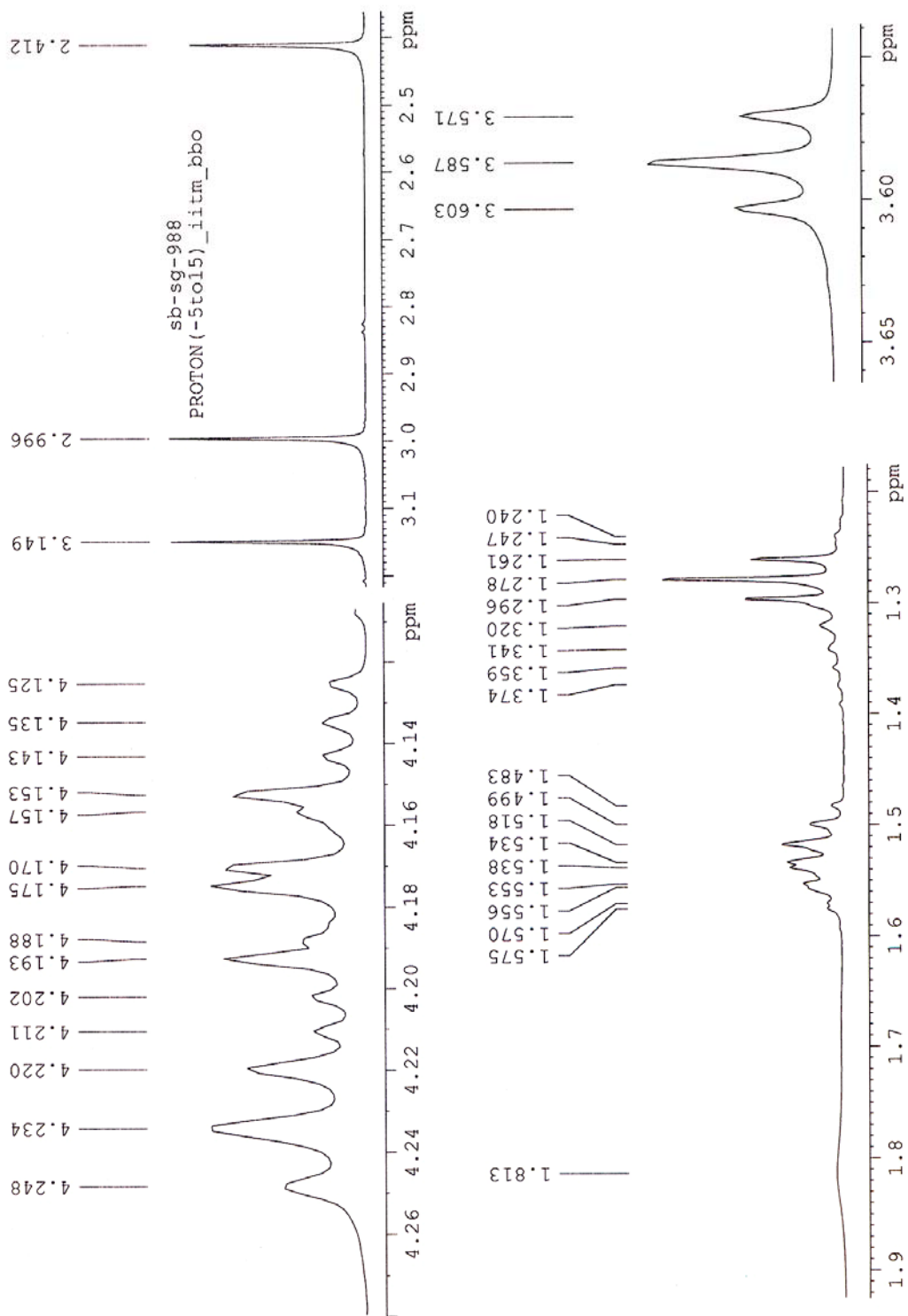
***** CHANNEL f1 *****
NUC1       1H
P1         11.55 usec
PL1        3.00 dB
SFO1       400.1319460 MHz

F2 - Processing parameters
SI         16384
SF         400.1300170 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         3.00

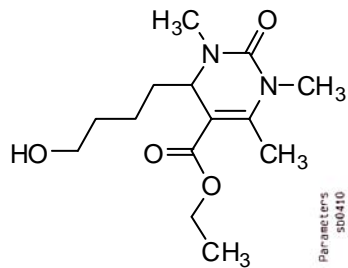
ID: NMR plot parameters
CX         20.00 cm
CY         4.00 cm
FIP        10.129 ppm
F1         4052.73 Hz
F2P        -1.000 ppm
F2         -400.13 Hz
PRNCM      0.55643 ppm/cm
HZCM       222.64290 Hz/cm
```



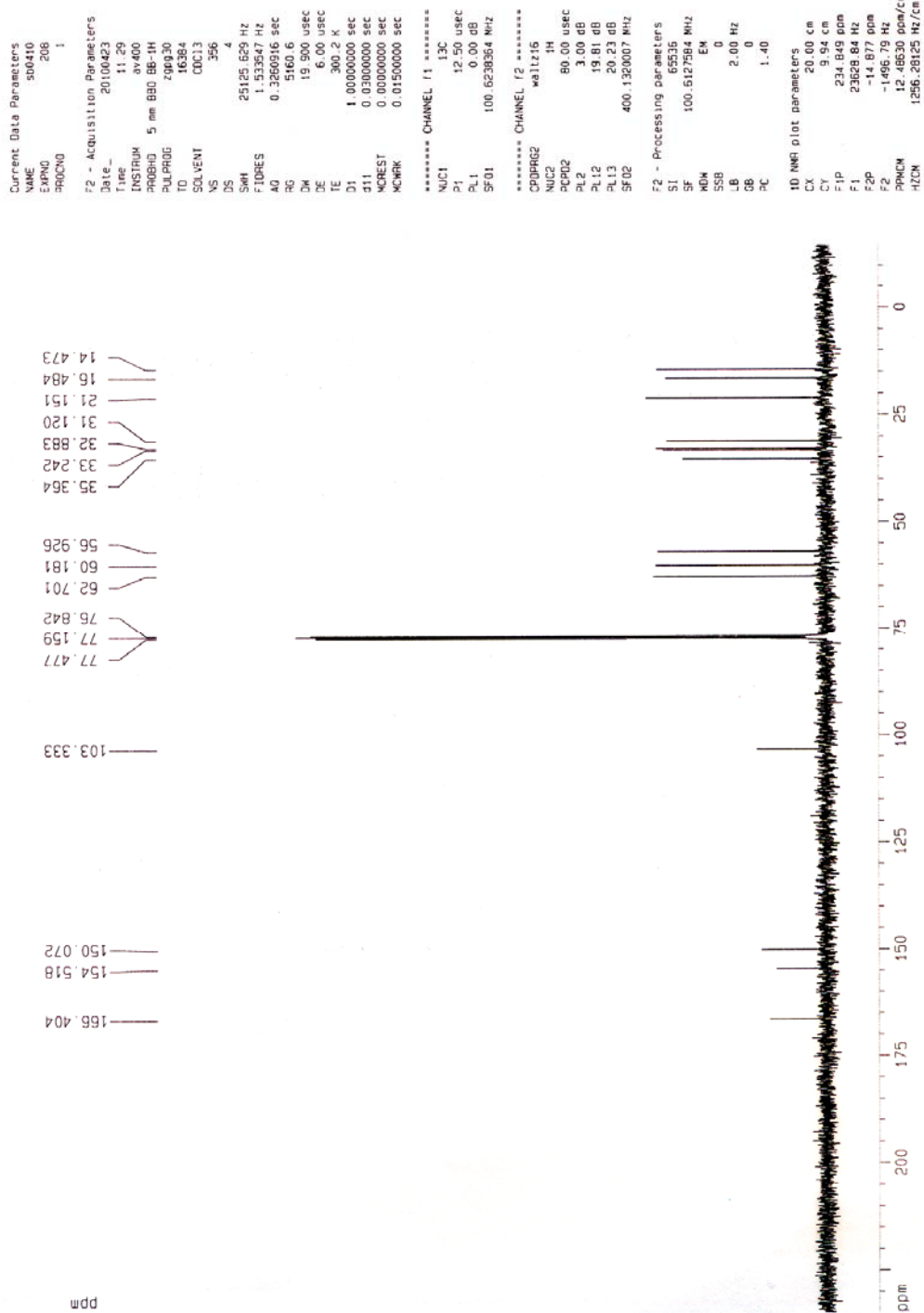
¹H NMR spectra of compound **30a**



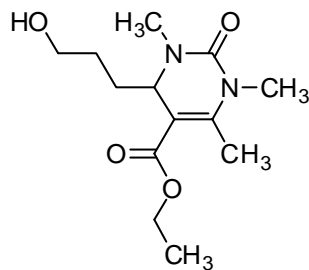
Expanded ^1H NMR spectra of compound **30a**



sb-sg-988
CARBONSHORT_11tm_bbo



¹³C NMR spectra of compound 30a



```

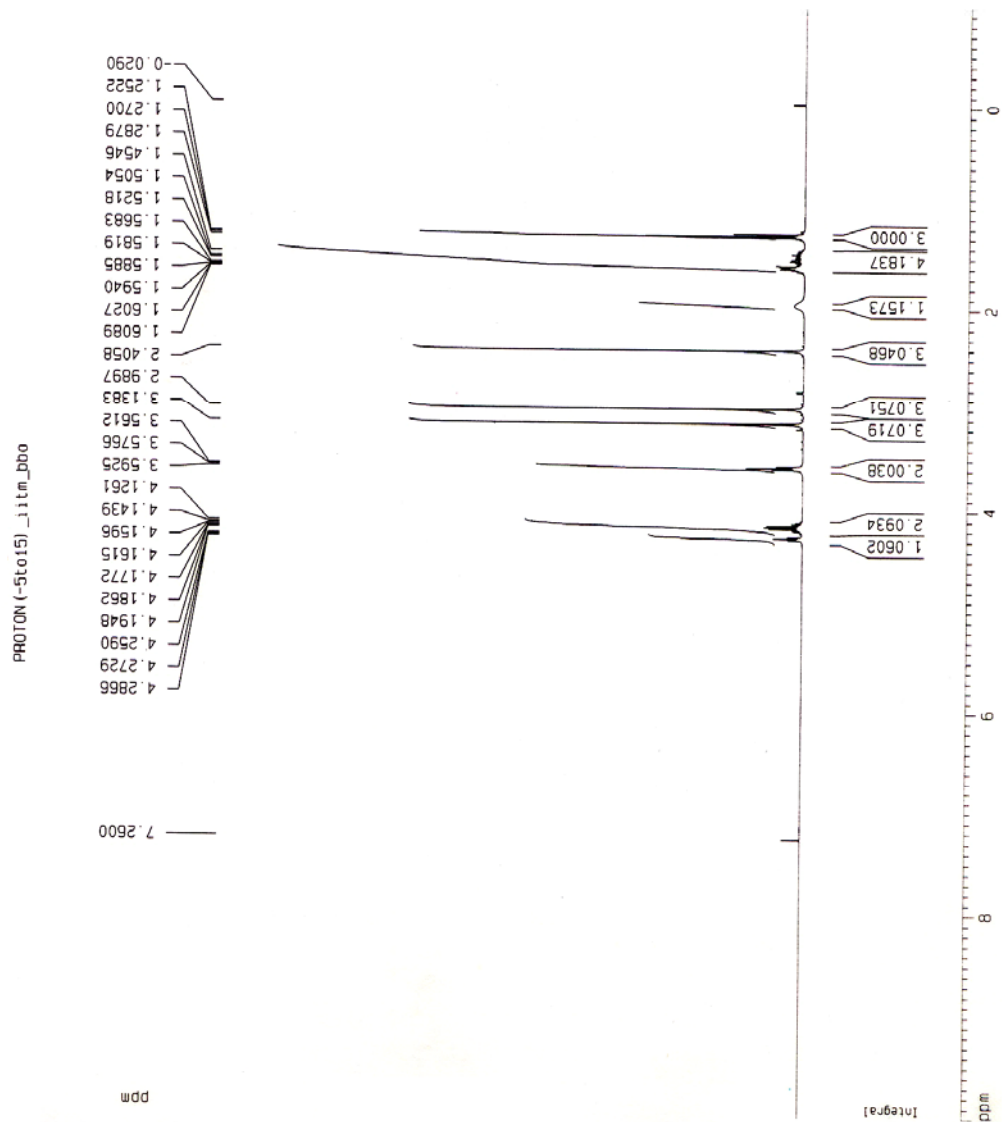
Current Data Parameters
NAME      sb0610
EXPNO    18
PROCNO    1

F2 - Acquisition Parameters
Date_     20100604
Time      10.10
INSTRUM   sv400
PROBHD    5 mm BBO BB-1H
PULPROG   zg30
TD         32768
SOLVENT   CDCl3
NS         32
DS         4
SWH        8389.262 Hz
FIDRES     0.256020 Hz
AQ         1.9530228 sec
RG         57
AQ         59.600 usec
DE         6.00 usec
TE         295.9 K
D1         0.50000000 sec
MCHRG1    0.00000000 sec
MCHRG2    0.01500000 sec

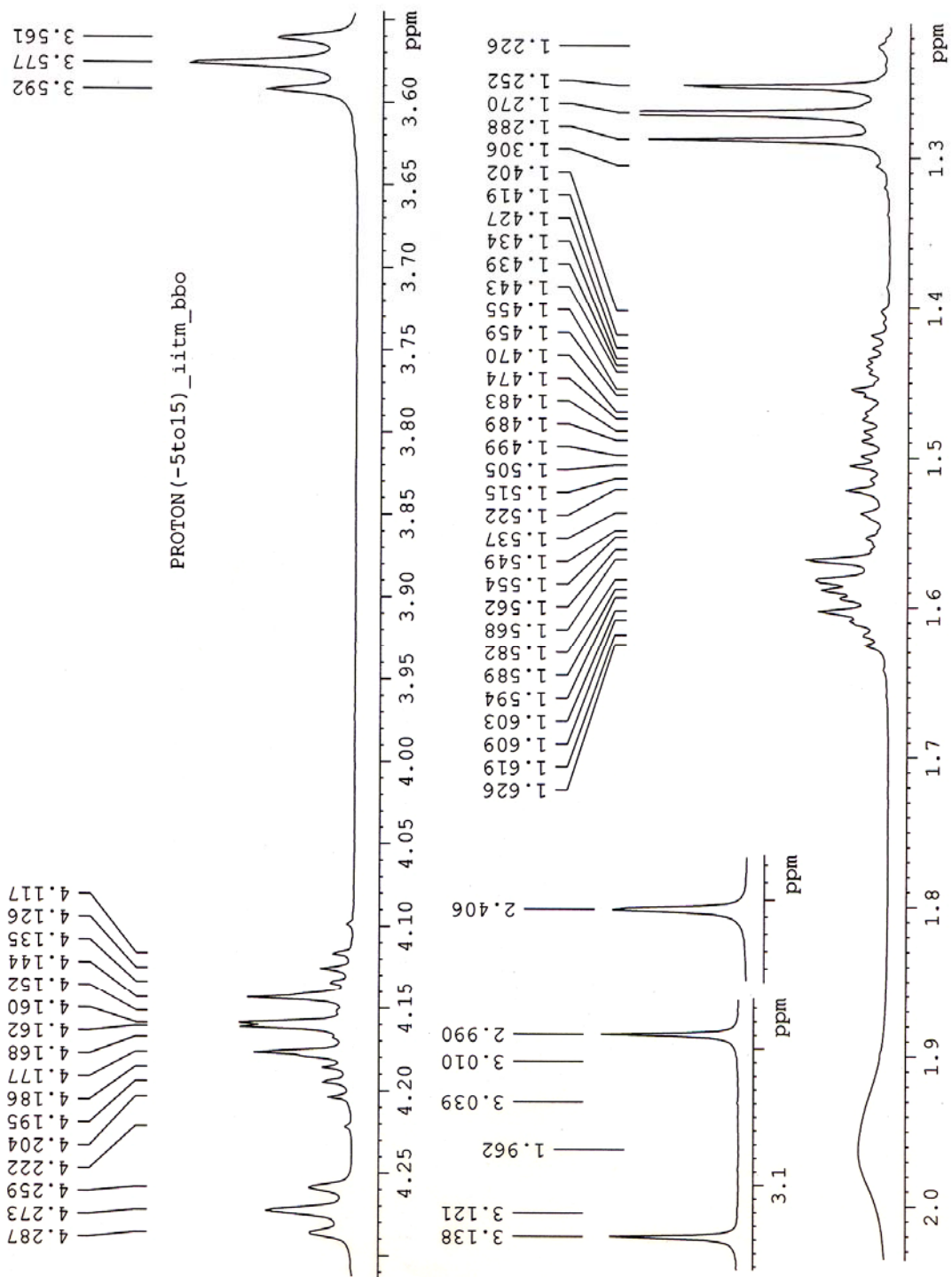
***** CHANNEL f1 *****
NUC1      1H
P1        11.55 usec
PL1       3.00 dB
SFO1      400.1319460 MHz

F2 - Processing parameters
SI         16384
SF         400.1300170 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         3.00

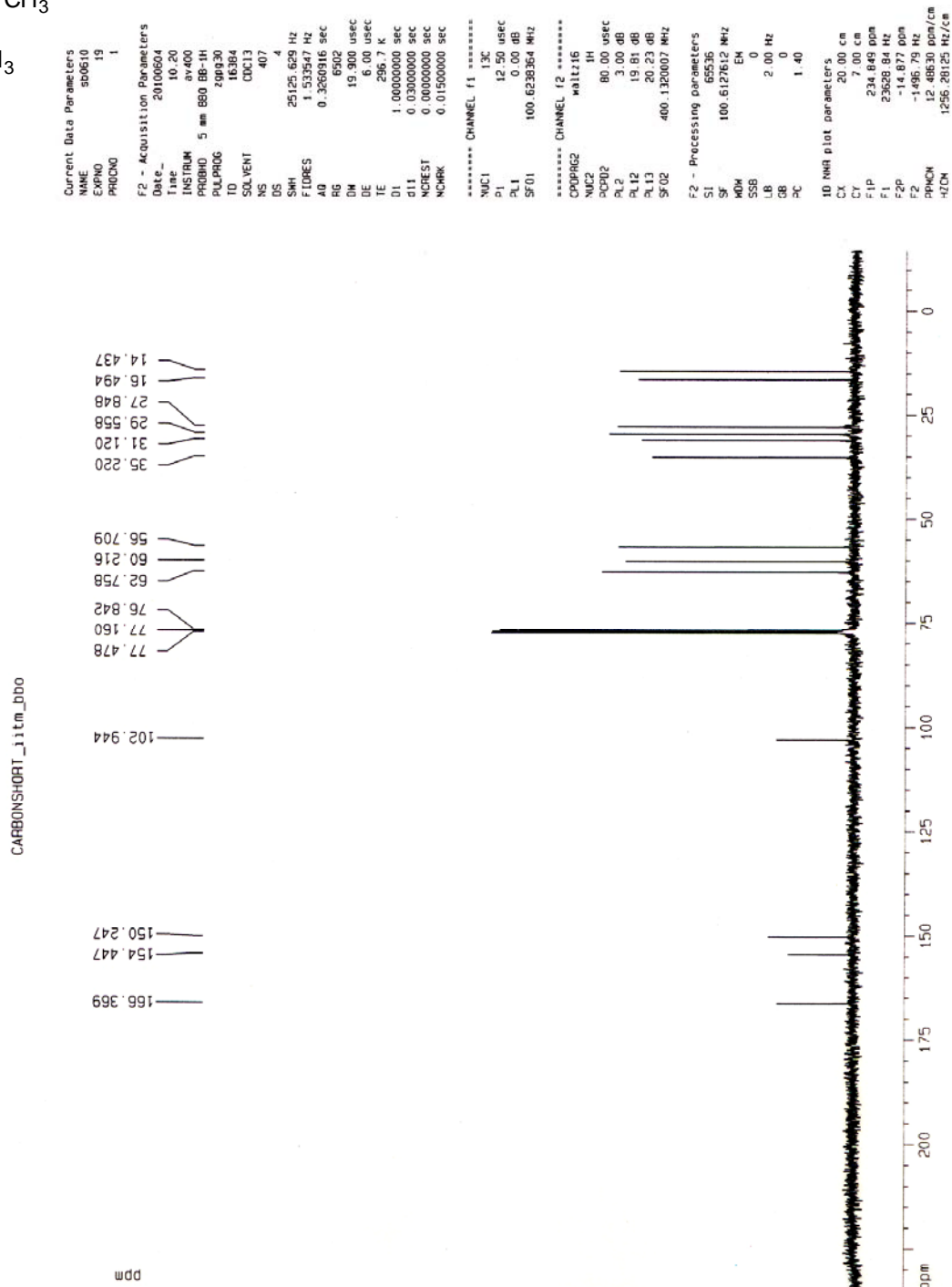
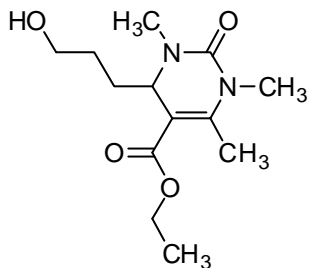
ID NMR plot parameters
CX         20.00 cm
CY         6.00 cm
FIP        10.000 ppm
F1         4001.30 Hz
F2         -1.000 ppm
FZ         -400.13 Hz
PPHCH      0.55000 ppm/cm
HZDM       220.07150 Hz/cm
    
```



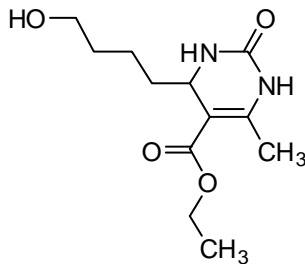
¹H NMR spectra of compound **32a**



Expanded ¹H NMR spectra of compound 32a



¹³C NMR spectra of compound 32a



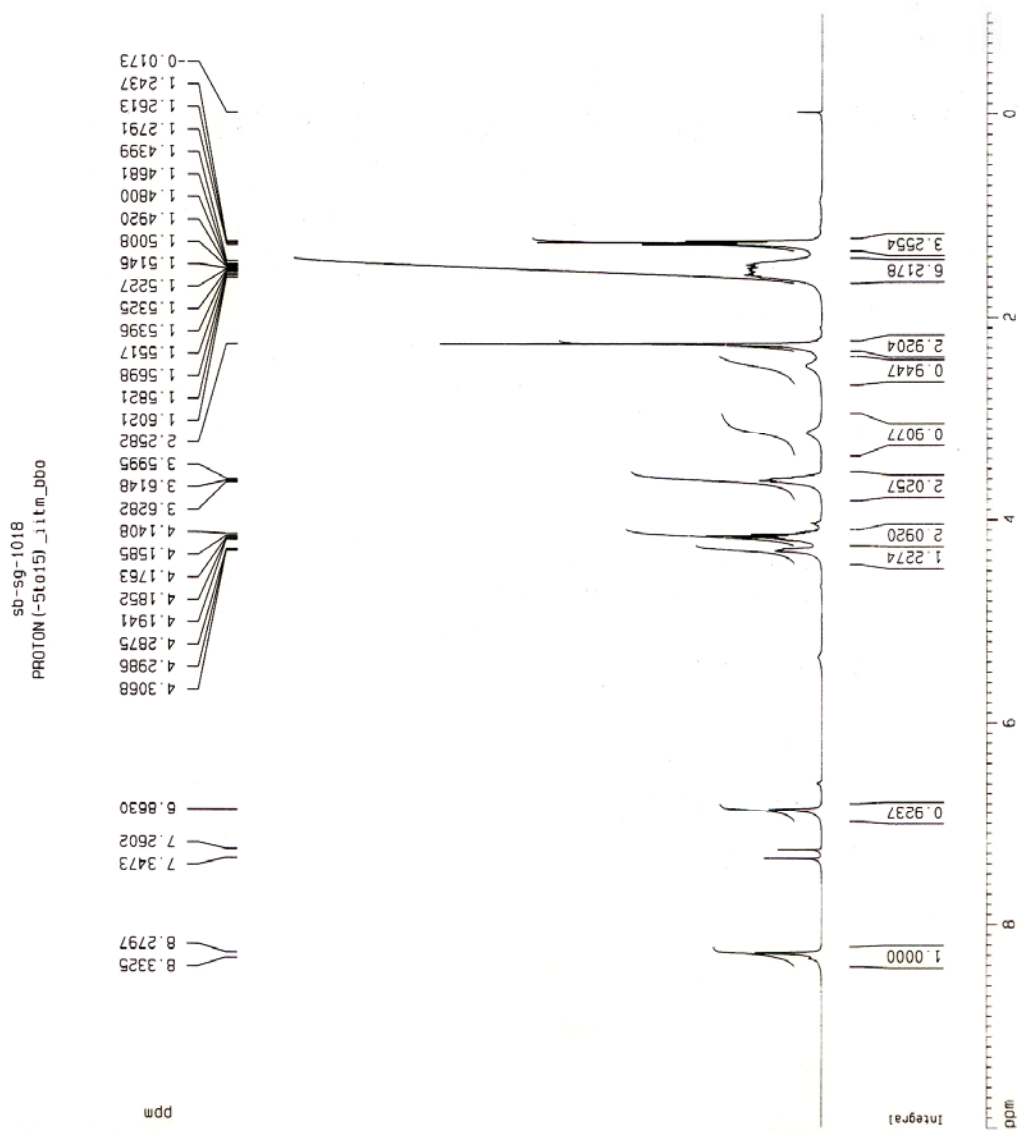
Current Data Parameters
 NAME sb0610
 EXPNO 43
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20100605
 Time 20.36
 INSTRUM av400
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 32
 DS 4
 SWH 8385.262 Hz
 FIDRES 0.256020 Hz
 AQ 1.9530228 sec
 RG 80.6
 DM 59.600 usec
 DE 6.00 usec
 TE 294.2 K
 D1 0.50000000 sec
 MCREST 0.00000000 sec
 MCPRK 0.01500000 sec

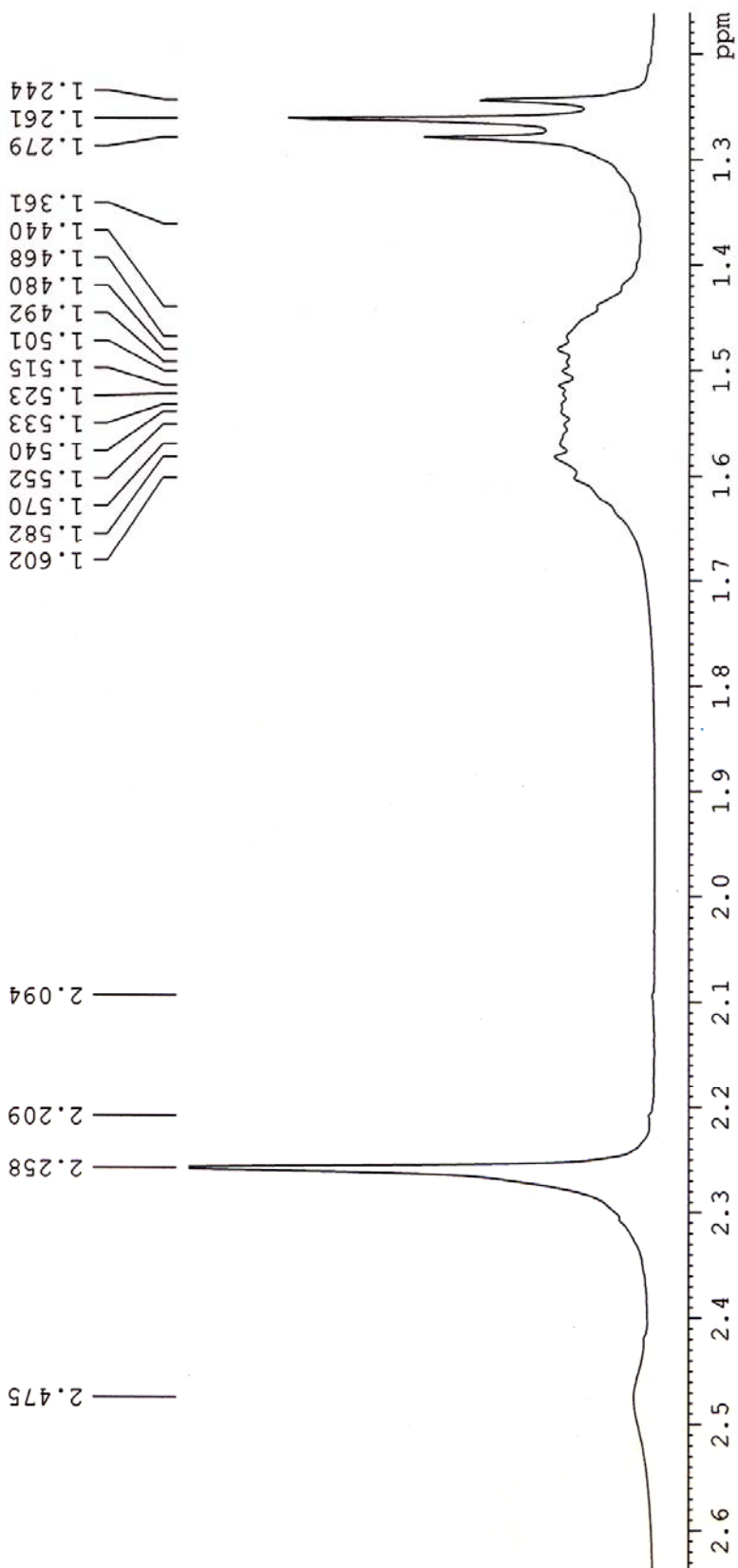
***** CHANNEL f1 *****
 NUC1 1H
 P1 11.55 usec
 PL1 3.00 dB
 SF01 400.1319460 MHz

F2 - Processing parameters
 SI 16384
 SF 400.1300165 MHz
 MDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 3.00

1D NMR plot parameters
 CX 20.00 cm
 CY 7.00 cm
 FIP 10.000 ppm
 F1 4001.30 Hz
 F2P -1.000 ppm
 F2 -400.13 Hz
 PRACH 0.55000 ppm/cm
 HZCM 220.07150 Hz/cm

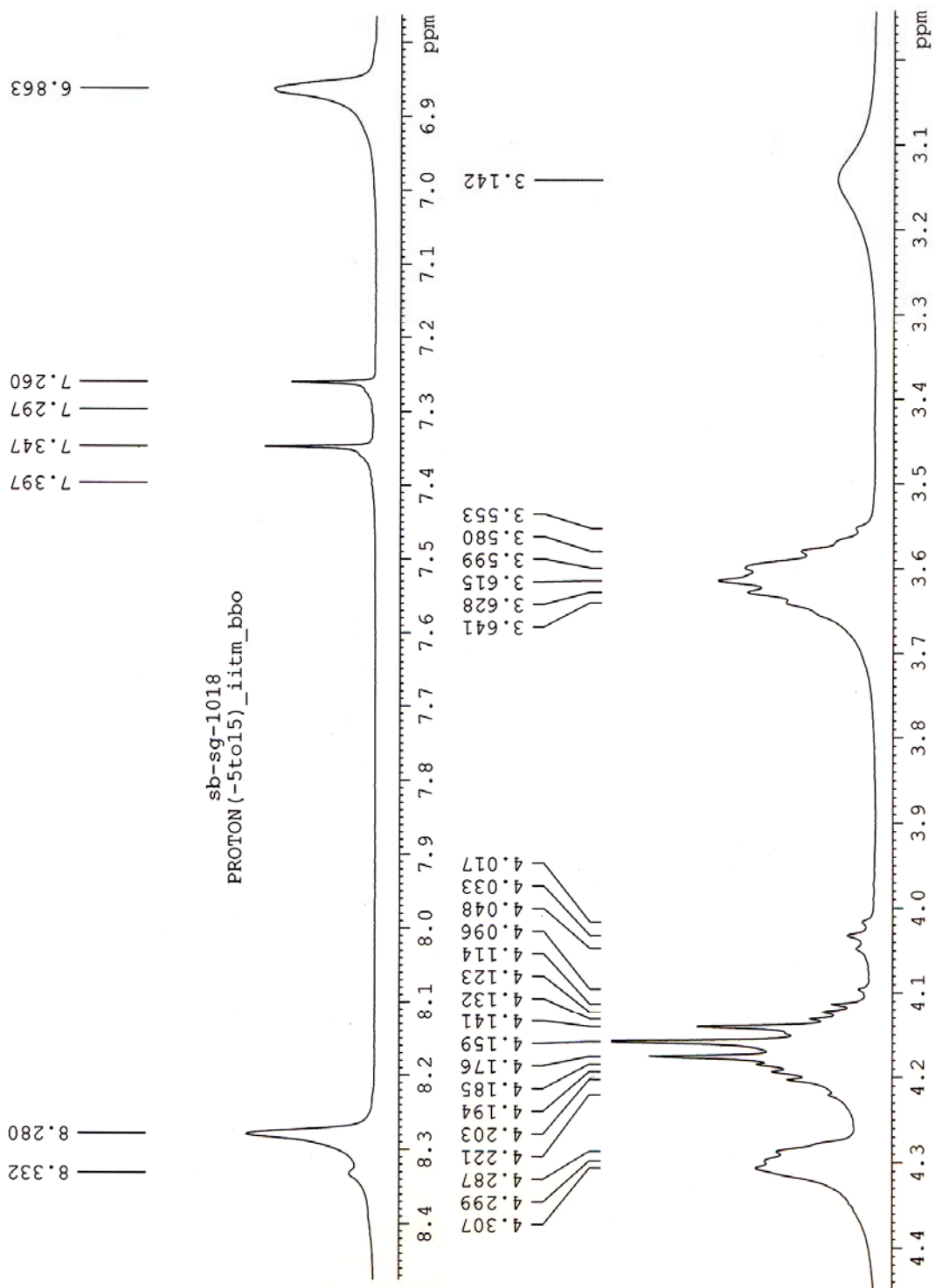


¹H NMR spectra of compound 33a

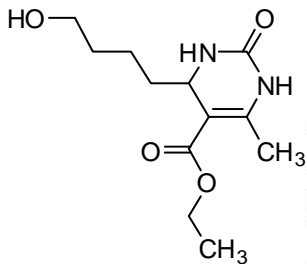


sb-sg-1018
PROTON (-5to15)_iitm_bbo

Expanded ¹H NMR spectra of compound 33a



Expanded ¹H NMR spectra of compound **33a**



sb-sg-1018
 CARBONSHORT_11tm_bbo

```

Current Data Parameters
NAME          SB0510
EXPNO        44
PROCNO       1

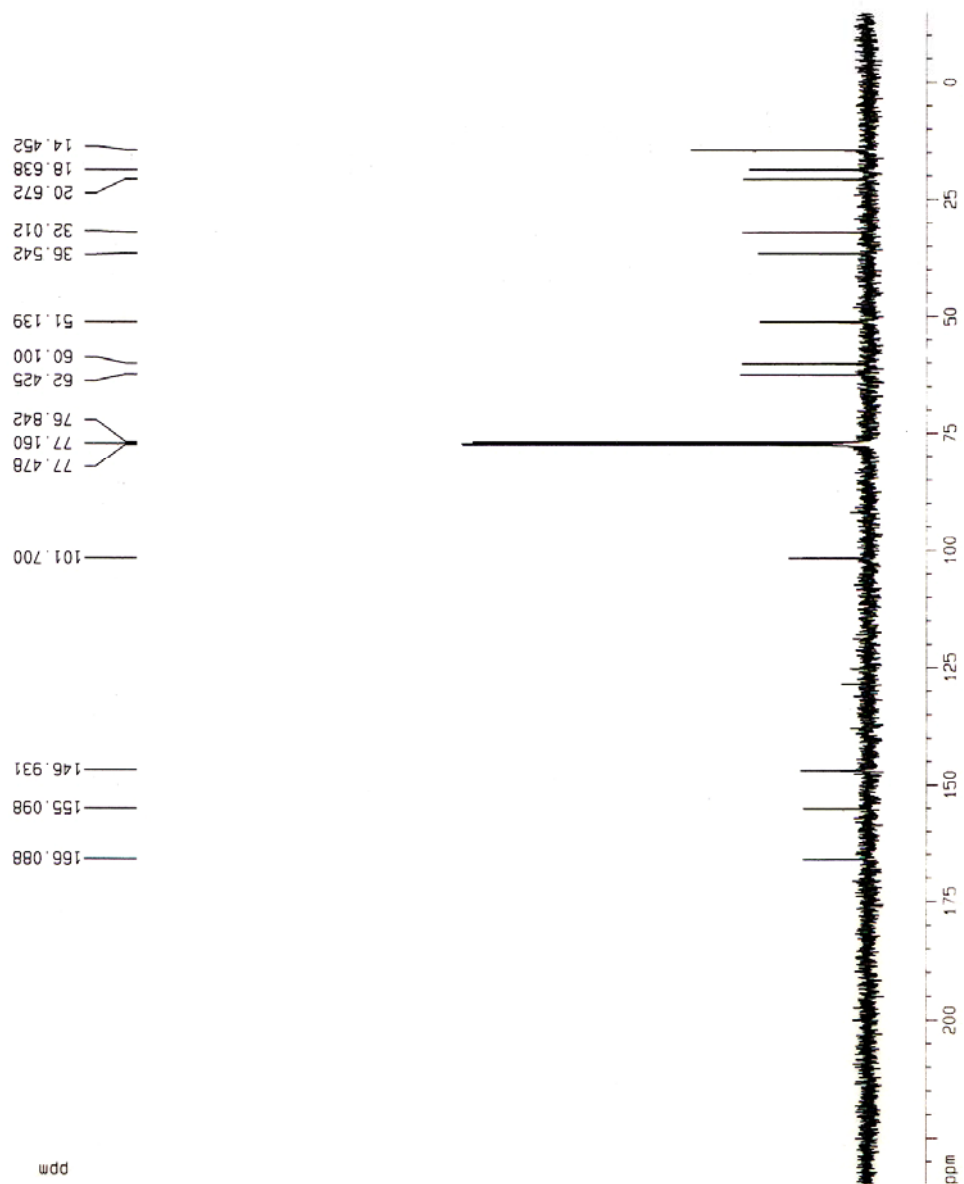
F2 - Acquisition Parameters
Date_        20100805
Time         20.44
INSTRUM      av400
PROBHD       5 mm BBO BB-1H
PULPROG      zgpg30
TD           16384
SOLVENT      CDCl3
NS           282
DS           4
SWH          25125.629 Hz
FIDRES       1.533547 Hz
AQ           0.3260916 sec
RG           8192
DM           19.900 usec
DE           6.00 usec
TE           294.9 K
D1           1.00000000 sec
d11          0.03000000 sec
XCFRES       0.00000000 sec
XCFWRK       0.01500000 sec

***** CHANNEL f1 *****
NUC1         13C
P1           12.50 usec
PL1          0.00 dB
SFO1         100.6238364 MHz

***** CHANNEL f2 *****
CPDPRG2      waltz16
NUC2         1H
PCPD2        80.00 usec
PL2          3.00 dB
PL12         19.81 dB
PL13         20.23 dB
SFO2         400.1320007 MHz

F2 - Processing parameters
SI           65536
SF           100.6127695 MHz
WDW          EM
SSB          0
GB           0
CB           0
PC           1.40

1D NMR plot parameters
CX           20.00 cm
CY           7.00 cm
FIP          234.849 ppm
F1           23628.84 Hz
F2           -14.877 ppm
F2           -1496.79 Hz
PCNCHN      12.48630 ppm/cm
HZCN        1256.28125 Hz/cm
    
```



¹³C NMR spectra of compound 33a