

SUPPORTING INFORMATION**Carbopalladation of Nitriles: Synthesis of Benzocyclic Ketones and Cyclopentenones via
Pd-Catalyzed Cyclization of ω -(2-Iodoaryl)alkanenitriles and Related Compounds**

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Reagents. *o*-Iodobenzyl bromide was obtained from Lancaster Synthesis Ltd. Isobutyronitrile, cyclohexanecarbonitrile, cyclopropanecarbonitrile, cyclobutanecarbonitrile, butyronitrile, diphenylacetonitrile, 4,5-dimethoxybenzyl alcohol, *o*-iodobenzoic acid, 5-bromo-2-iodobenzoic acid, methyl *o*-iodobenzoate, 2,2'-diiodobiphenyl, *n*-butyllithium, diisopropylamine and triethylamine were obtained from Aldrich Chemical Co., Inc. (*Z*)-3-Bromo-1-iodo-1,2-diphenylpropene, (*Z*)-3-bromo-1-iodo-2-methyl-1-phenylpropene, (*Z*)-1-bromo-3-iodo-2-butene, (*Z*)-3-bromo-1-iodo-1-phenylpropene, (*Z*)-3-bromo-1-iodo-2-phenylpropene, (*Z*)-1-bromo-3-iodo-2-phenyl-2-butene,¹ as well as 2-iodophenethyl mesylate and 2-iodophenethyl iodide,² were prepared as previously described.

Synthesis of ω -(2-Iodoaryl)alkanenitriles and related starting materials.

General procedure for the α -alkylation of aliphatic nitriles. Compounds **1a-e**, **1g**, **1h**, **1o**, **1q**, **7a**, **7c**, **8**, **11a-f** and **13** were prepared by a procedure reported by Taber *et al.*³ A hexane solution of 3.62 mmol of *n*-BuLi was added to a solution of 3.45 mmol of *i*-Pr₂NH in 10 mL of THF at -78 °C under an Ar atmosphere. After 5 min, 3 mmol (9 mmol if not tertiary) of the nitrile was added (dissolved in THF if the nitrile is a solid). The reaction mixture was stirred at -78 °C for 1 h, after which a solution of 3.6 mmol of *o*-iodobenzyl bromide in 4 mL of THF was added at once and the reaction mixture was stirred with warming to room temperature for about 1.5 h, then diluted with water and extracted with ether. The ethereal extracts were dried with Na₂SO₄, the solvent was evaporated, and the residue was separated by column chromatography on silica gel with a proper eluant. The following compounds were prepared using the above procedure:

3-(2-Iodophenyl)-2,2-dimethylpropanenitrile (1a). Obtained in a 94% yield from the alkylation of isobutyronitrile with *o*-iodobenzyl bromide after column chromatography using 10:1 hexanes/ethyl acetate: white solid, mp 59-61 °C (hexanes); ¹H NMR (CDCl₃) δ 1.43 (s, 6H), 3.08 (s, 2H), 6.96 (td, *J* = 7.5, 1.2 Hz, 1H), 7.35 (td, *J* = 7.5, 1.2 Hz, 1H), 7.51 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.87 (dd, *J* = 7.5, 1.5 Hz, 1H); ¹³C NMR (CDCl₃) δ 26.6, 34.3, 48.7, 102.6, 124.6, 128.4, 129.0, 130.7, 139.0, 139.9; IR (neat) 3072, 2995, 2928, 2232 cm⁻¹; HRMS *m/z* 285.00180 (calcd for C₁₁H₁₂IN, 285.00145).

1-(2-Iodobenzyl)cyclohexanecarbonitrile (1b). Obtained in a 96% yield from the alkylation of cyclohexanecarbonitrile with *o*-iodobenzyl bromide after column chromatography using 10:1 hexanes/ethyl acetate: white solid, mp 58-60 °C (hexanes); ¹H NMR (CDCl₃) δ 1.19-1.22 (m, 1H), 1.45-1.76 (m, 7H), 1.92 (d, *J* = 11.4 Hz, 2H), 3.08 (s, 2H), 6.94 (td, *J* = 7.5, 1.5 Hz, 1H), 7.33 (td, *J* = 7.5, 1.5 Hz, 1H), 7.51

(1) (a) Allylic alcohol preparation: Larock, R. C.; Doty, M. J.; Han, X. *J. Org. Chem.* **1999**, *64*, 8770. (b) Alcohol-to-bromide conversion: Uenishi, J.; Tanaka, T.; Nishiwaki, K.; Wakabayashi, S.; Oae, S.; Tsukube, H. *J. Org. Chem.* **1993**, *58*, 4382.

(2) Ripa, L.; Hallberg, A. *J. Org. Chem.* **1996**, *61*, 7147.

(3) Taber, D. F.; Bhamidipati, R. S.; Yet, L. *J. Org. Chem.* **1995**, *60*, 5537.

(dd, $J = 7.5, 1.5$ Hz, 1H), 7.85 (dd, $J = 7.5, 1.5$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 16.3, 22.9, 25.1, 35.4, 41.0, 48.8, 102.8, 122.9, 128.3, 128.9, 130.9, 138.6, 139.8; IR (neat) 3062, 2935, 2860, 2228 cm^{-1} ; HRMS m/z 325.03330 (calcd for $\text{C}_{14}\text{H}_{16}\text{IN}$, 325.03275).

1-(2-Iodobenzyl)cyclobutanecarbonitrile (1c). Obtained in a 74% yield from the alkylation of cyclobutanecarbonitrile with *o*-iodobenzyl bromide after column chromatography using 10:1 hexanes/ethyl acetate: white solid, mp 29-30 °C (hexanes/ethyl acetate); ^1H NMR (CDCl_3) δ 2.07-2.20 (m, 2H), 2.25-2.32 (m, 2H), 2.47-2.54 (m, 2H), 3.23 (s, 2H), 6.96 (td, $J = 7.6, 1.6$ Hz, 1H), 7.31-7.35 (m, 1H), 7.38-7.41 (m, 1H), 7.86 (dd, $J = 8.0, 1.6$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 17.1, 31.7, 36.4, 45.9, 102.1, 124.4, 128.4, 128.8, 129.7, 139.0, 139.8; IR (neat) 3059, 2991, 2946, 2229 cm^{-1} ; HRMS m/z 297.00187 (calcd for $\text{C}_{12}\text{H}_{12}\text{IN}$, 297.00145).

1-(2-Iodobenzyl)cyclopropanecarbonitrile (1d). Obtained as a colorless oil in a 93% yield from the alkylation of cyclopropanecarbonitrile with *o*-iodobenzyl bromide after column chromatography using 10:1 hexanes/ethyl acetate: ^1H NMR (CDCl_3) δ 1.00-1.03 (m, 2H), 1.29-1.32 (m, 2H), 3.01 (s, 2H), 6.96 (td, $J = 8.0, 1.6$ Hz, 1H), 7.35 (td, $J = 7.6, 1.2$ Hz, 1H), 7.45 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.84 (dd, $J = 8.0, 1.2$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 9.4, 13.6, 43.5, 101.2, 123.1, 128.5, 128.8, 129.5, 139.3, 139.6; IR (neat) 3062, 3010, 2928, 2232 cm^{-1} ; HRMS m/z 282.98628 (calcd for $\text{C}_{11}\text{H}_{10}\text{IN}$, 292.98580).

3-(2-Iodophenyl)-2-methyl-2-phenylpropanenitrile (1e). Obtained as a colorless oil in a 78% yield from the alkylation of 2-phenylpropanenitrile with *o*-iodobenzyl bromide after column chromatography using 10:1 hexanes/ethyl acetate: ^1H NMR (CDCl_3) δ 1.79 (s, 3H), 3.32-3.46 (m, 2H), 6.91-6.97 (m, 1H), 7.24-7.27 (m, 2H), 7.33-7.42 (m, 3H), 7.46-7.49 (m, 2H), 7.84 (dt, $J = 8.4, 0.6$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 25.5, 43.5, 50.7, 103.1, 123.1, 125.9, 128.0, 128.2, 128.9, 129.1, 130.8, 138.3, 139.7, 139.8; IR (neat) 3067, 3031, 2985, 2928, 2238 cm^{-1} ; HRMS m/z 347.01747 (calcd for $\text{C}_{16}\text{H}_{14}\text{IN}$, 347.01710).

2-(2-Iodobenzyl)butanenitrile (1g). Obtained as a colorless oil in an 87% yield from the alkylation of butyronitrile with *o*-iodobenzyl bromide after column chromatography using 10:1 hexanes/ethyl acetate: ^1H NMR (CDCl_3) δ 1.16 (t, $J = 7.5$ Hz, 3H), 1.71-1.77 (m, 2H), 2.85-2.98 (m, 1H), 3.01 (d, $J = 0.9$ Hz, 2H), 6.94-7.00 (m, 1H), 7.33 (dd, $J = 5.1, 0.9$ Hz, 2H), 7.84 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 11.5, 25.4, 33.9, 42.7, 100.2, 115.3, 121.1, 128.6, 129.1, 130.7, 139.7; IR (neat) 3062, 2969, 2933, 2876, 2238 cm^{-1} ; HRMS m/z 285.00180 (calcd for $\text{C}_{11}\text{H}_{12}\text{IN}$, 285.00145).

Methyl 2-cyano-3-(2-iodophenyl)-2-methylpropanoate (1h). Obtained in a 40% yield from the alkylation of methyl 2-cyanopropanoate with *o*-iodobenzyl bromide after column chromatography using 4:1 hexanes/ethyl acetate: white solid, mp 37-39 °C (hexanes/ethyl acetate); ^1H NMR (CDCl_3) δ 1.68 (s, 3H), 3.36-3.46 (m, 2H), 3.82 (s, 3H), 6.98 (td, $J = 8.0, 2.0$ Hz, 1H), 7.34 (td, $J = 7.6, 1.6$ Hz, 1H), 7.39 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.88 (dd, $J = 8.0, 1.2$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 22.9, 44.6, 45.9, 53.7, 102.2,

119.3, 128.5, 129.4, 130.2, 137.3, 140.0, 169.1; IR (neat) 3057, 3008, 2955, 2848, 2250, 1745 cm^{-1} ; HRMS m/z 328.99176 (calcd for $\text{C}_{12}\text{H}_{12}\text{INO}_2$, 328.99128).

3-(2-Iodo-4,5-dimethoxyphenyl)-2,2-dimethylpropanenitrile (1o). Obtained in a 100% yield from the alkylation of isobutyronitrile with 2-iodo-4,5-dimethoxybenzyl bromide (prepared in two steps from 4,5-dimethoxybenzyl alcohol)⁴ after column chromatography using 2:1 hexanes/ethyl acetate: white solid, mp 67-68 °C (hexanes/ethyl acetate); ¹H NMR (CDCl_3) δ 1.43 (s, 6H), 3.00 (s, 2H), 3.87 (s, 3H), 3.90 (s, 3H), 7.10 (s, 1H), 7.24 (s, 1H); ¹³C NMR (CDCl_3) δ 26.3, 34.4, 48.5, 55.8, 55.9, 90.0, 112.8, 121.5, 124.9, 131.4, 148.4, 149.0; IR (neat) 2974, 2933, 2840, 2233 cm^{-1} ; HRMS m/z 345.02315 (calcd for $\text{C}_{13}\text{H}_{16}\text{INO}_2$, 345.02258).

3-(5-Bromo-2-iodophenyl)-2,2-dimethylpropanenitrile (1q). Obtained in a 48% yield from the alkylation of isobutyronitrile with 5-bromo-2-iodobenzyl bromide (prepared in two steps from 5-bromo-2-iodobenzoic acid)^{2,1b} after column chromatography using 4:1 hexanes/ethyl acetate: white solid, mp 61-63 °C (hexanes/ethyl acetate); ¹H NMR (CDCl_3) δ 1.45 (s, 6H), 3.04 (s, 2H), 7.12 (dd, $J = 8.4, 2.4$ Hz, 1H), 7.62 (d, $J = 2.4$ Hz, 1H), 7.72 (d, $J = 8.4$ Hz, 1H); ¹³C NMR (CDCl_3) δ 26.6, 34.1, 48.5, 100.5, 122.7, 124.2, 132.2, 133.5, 141.1 (1 sp^2 carbon missing due to overlap); IR (neat) 3072, 2985, 2238 cm^{-1} ; HRMS m/z 362.91250 (calcd for $\text{C}_{11}\text{H}_{11}\text{INBr}$, 362.91196).

4-(2-Iodophenyl)-2,2-dimethylbutanenitrile (7a). Obtained as a colorless oil in a 38% yield from the alkylation of isobutyronitrile with 2-iodophenethyl mesylate after column chromatography using 10:1 hexanes/ethyl acetate: ¹H NMR (CDCl_3) δ 1.45 (s, 6H), 1.78 (m, 2H), 2.91 (m, 2H), 6.88-6.94 (m, 1H), 7.24-7.30 (m, 2H), 7.80 (dd, $J = 8.1, 1.2$ Hz, 1H); ¹³C NMR (CDCl_3) δ 26.5, 32.1, 36.8, 41.3, 100.1, 124.7, 128.1, 128.6, 129.5, 139.5, 143.3; IR (neat) 3057, 2985, 2933, 2866, 2233 cm^{-1} ; HRMS m/z 299.01767 (calcd for $\text{C}_{12}\text{H}_{14}\text{IN}$, 299.01710).

1-(2-Iodophenethyl)cyclohexanecarbonitrile (7c). Obtained as a colorless oil in a 31% yield from the alkylation of cyclohexanecarbonitrile with *o*-iodophenethyl iodide after column chromatography using 10:1 hexanes/ethyl acetate: ¹H NMR (CDCl_3) δ 1.17-1.39 (m, 2H), 1.60-1.79 (m, 8H), 2.05-2.10 (m, 2H), 2.90-2.95 (m, 2H), 6.87-6.93 (m, 1H), 7.22-7.29 (m, 2H), 7.80 (dd, $J = 7.8, 0.9$ Hz, 1H); ¹³C NMR (CDCl_3) δ 23.1, 25.4, 35.5, 36.0, 38.8, 40.8, 100.1, 123.3, 128.1, 128.6, 129.5, 139.5, 143.6; IR (neat) 3056, 2938, 2856, 2228 cm^{-1} ; HRMS m/z 339.04893 (calcd for $\text{C}_{15}\text{H}_{18}\text{IN}$, 339.04840).

5-(2-Iodophenyl)-2,2-dimethylpentanenitrile (8). To a solution of 2-iodophenethyl mesylate (0.736 g, 2.26 mmol) in 5 mL of MeCN were added KCN (0.9 g, 13.85 mmol) and a catalytic amount of 18-crown-6. The reaction mixture was refluxed with stirring for 24 h, the amount of solvent was reduced on a

(4) Ahmad-Junan, S. A.; Whiting, D. A. *J. Chem. Soc., Perkin Trans. 1* **1992**, 675.

rotary evaporator, and the mixture was diluted with water and extracted with CH_2Cl_2 . The extracts were dried (Na_2SO_4), evaporated and chromatographed using 4:1 hexanes/ethyl acetate to afford a 70% yield of 3-(2-iodophenyl)propanenitrile, which was dissolved in 2 mL of MeOH and added to 1M aq KOH solution (15 mL). The mixture was refluxed overnight, cooled, acidified with aq HCl, and extracted with ether. Upon evaporation, 3-(2-iodophenyl)propanoic acid was obtained in a 100% yield. The acid was converted to 1-iodo-3-(2-iodophenyl)propane (85% yield),² and the latter was used for the alkylation of isobutyronitrile to afford **8** as a colorless oil in a 72% yield after column chromatography using 10:1 hexanes/ethyl acetate: ^1H NMR (CDCl_3) δ 1.35 (s, 6H), 1.60-1.64 (m, 2H), 1.76-1.82 (m, 2H), 2.73-2.77 (m, 2H), 6.90 (td, $J = 7.6, 1.6$ Hz, 1H), 7.20-7.26 (m, 1H), 7.27-7.31 (m, 1H), 7.82 (dd, $J = 8.0, 1.2$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 25.8, 26.5, 26.6, 32.2, 40.4, 100.4, 124.9, 127.8, 128.3, 129.2, 139.4, 143.9; IR (neat) 3057, 2985, 2939, 2233 cm^{-1} ; HRMS m/z 313.03332 (calcd for $\text{C}_{13}\text{H}_{16}\text{IN}$, 313.03275).

(E)-5-Iodo-2,2-dimethyl-4,5-diphenyl-4-pentenitrile (11a). Obtained in a 61% yield from the alkylation of isobutyronitrile with (*E*)-3-bromo-1-iodo-1,2-diphenylpropene after column chromatography using 10:1 hexanes/ethyl acetate: light yellow solid, mp 90-92 $^\circ\text{C}$; ^1H NMR (CDCl_3) δ 1.36 (s, 6H), 3.24 (s, 2H), 7.03-7.11 (m, 10H); ^{13}C NMR (CDCl_3) δ 27.3, 32.4, 53.6, 105.2, 123.8, 127.3, 127.4, 127.6, 128.1, 129.4, 129.6, 138.2, 144.1, 144.4; IR (neat) 3060, 2976, 2933, 2234 cm^{-1} ; HRMS m/z 387.04910 (calcd for $\text{C}_{19}\text{H}_{18}\text{IN}$, 387.04840).

(Z)-5-Iodo-2,2,4-trimethyl-5-phenyl-4-pentenitrile (11b). Obtained as a colorless oil in a 17% yield from the alkylation of isobutyronitrile with (*Z*)-3-bromo-1-iodo-2-methyl-1-phenylpropene after column chromatography using 10:1 hexanes/ethyl acetate: ^1H NMR (CDCl_3) δ 1.55 (s, 6H), 1.91 (s, 3H), 2.83 (s, 2H), 7.19-7.26 (m, 3H), 7.31-7.37 (m, 2H); ^{13}C NMR (CDCl_3) δ 19.9, 27.2, 31.8, 53.2, 100.9, 125.5, 127.8, 128.2, 128.4, 138.9, 144.7; IR (neat) 3063, 2982, 2925, 2232, 1444 cm^{-1} ; HRMS m/z 325.03330 (calcd for $\text{C}_{14}\text{H}_{16}\text{IN}$, 325.03275).

(E)-5-Iodo-2,2-dimethyl-4-phenyl-4-hexenenitrile (11c). Obtained as a colorless oil in a 21% yield from the alkylation of isobutyronitrile with (*Z*)-1-bromo-3-iodo-2-phenyl-2-butene after column chromatography using 10:1 hexanes/ethyl acetate: ^1H NMR (CDCl_3) δ 1.30 (s, 6H), 2.50 (t, $J = 0.8$ Hz, 3H), 3.01 (q, $J = 0.8$ Hz, 2H), 7.19-7.22 (m, 2H), 7.32-7.37 (m, 3H); ^{13}C NMR (CDCl_3) δ 27.2, 32.1, 32.4, 53.9, 103.8, 123.9, 127.9, 128.5, 128.7, 137.8, 141.5; IR (neat) 3057, 2980, 2918, 2233, 1439 cm^{-1} ; HRMS m/z 325.03330 (calcd for $\text{C}_{14}\text{H}_{16}\text{IN}$, 325.03275).

(E)-5-Iodo-2,2-dimethyl-4-phenyl-4-pentenitrile (11d). Obtained as a yellow oil in a 36% yield from the alkylation of isobutyronitrile with (*Z*)-3-bromo-1-iodo-2-phenylpropene after column chromatography using 10:1 hexanes/ethyl acetate: ^1H NMR (CDCl_3) δ 1.32 (s, 6H), 3.05 (s, 2H), 6.64 (s, 1H), 7.32-7.36 (m, 5H); ^{13}C NMR (CDCl_3) δ 27.2, 32.3, 46.3, 84.4, 124.1, 126.9, 128.6, 128.7, 140.6,

147.9; IR (neat) 3057, 2980, 2928, 2232, 1444 cm^{-1} ; HRMS m/z 311.01772 (calcd for $\text{C}_{13}\text{H}_{14}\text{IN}$, 311.01710).

(Z)-5-Iodo-2,2-dimethyl-4-hexenenitrile (11e). Obtained as a light yellow oil in a 66% yield from the alkylation of isobutyronitrile with (Z)-1-bromo-3-iodo-2-butene after column chromatography using 10:1 hexanes/ethyl acetate: ^1H NMR (CDCl_3) δ 1.37 (s, 6H), 2.37-2.39 (m, 2H), 2.58 (dd, $J = 2.4, 1.2$ Hz, 3H), 5.55-5.60 (m, 1H); ^{13}C NMR (CDCl_3) δ 26.3, 32.1, 33.9, 47.4, 105.4, 124.6, 129.5; IR (neat) 2980, 2918, 2238, 1650, 1264 cm^{-1} ; HRMS m/z 249.00175 (calcd for $\text{C}_8\text{H}_{12}\text{IN}$, 249.00145).

(Z)-5-Iodo-2,2-dimethyl-5-phenyl-4-pentenitrile (11f). Obtained as a yellow oil in a 36% yield from the alkylation of isobutyronitrile with (Z)-3-bromo-1-iodo-1-phenylpropene after column chromatography using 10:1 hexanes/ethyl acetate: ^1H NMR (CDCl_3) δ 1.45 (s, 6H), 2.61 (d, $J = 6.8$ Hz, 2H), 6.02 (t, $J = 6.8$ Hz, 1H), 7.29-7.33 (m, 3H), 7.45-7.48 (m, 2H); ^{13}C NMR (CDCl_3) δ 26.5, 32.4, 48.4, 109.4, 124.6, 128.3, 128.6, 128.7, 132.6, 142.7; IR (neat) 3062, 2980, 2933, 2233, 1444 cm^{-1} ; HRMS m/z 311.01772 (calcd for $\text{C}_{13}\text{H}_{14}\text{IN}$, 311.01710).

(E)-2-Ethyl-5-iodo-4,5-diphenyl-4-pentenitrile (13). Obtained as a yellow oil in a 74% yield from the alkylation of butyronitrile with (E)-3-bromo-1-iodo-1,2-diphenylpropene after column chromatography using 10:1 hexanes/ethyl acetate: ^1H NMR (CDCl_3) δ 1.07 (t, $J = 7.2$ Hz, 3H), 1.69 (quintet, $J = 7.2$ Hz, 2H), 2.48-2.56 (m, $J = 7.2$ Hz, 1H), 3.05-3.10 (m, 1H), 3.26-3.31 (m, 1H), 6.98-7.14 (m, 10H); ^{13}C NMR (CDCl_3) δ 11.6, 24.9, 31.5, 46.3, 103.5, 120.9, 127.31, 127.33, 127.6, 128.2, 128.9, 129.5, 137.9, 144.0, 144.2; IR (neat) 3052, 3021, 2969, 2933, 2238, 1440 cm^{-1} ; HRMS m/z 387.04880 (calcd for $\text{C}_{19}\text{H}_{18}\text{IN}$, 387.04840).

3-(2-Iodophenyl)-2,2-diphenylpropanenitrile (1f) was prepared according to the procedure of Parham.⁵ A solution of diphenylacetone nitrile (0.97 g, 5.0 mmol) in 2 mL of DMF was added to a mixture of NaH (0.144 g, 6.0 mmol), 2 mL of DMF and 1 mL of benzene at 0 °C. The reaction mixture was stirred at 0 °C for 30 min, then a solution of *o*-iodobenzyl bromide (1.78 g, 6.0 mmol) in 1 mL of DMF was added. The resulting mixture was allowed to warm up to room temperature, poured into water and extracted with CH_2Cl_2 , dried over Na_2SO_4 , evaporated, and recrystallized from ethyl acetate to afford 1.96 g (96%) of the desired compound **1f**: white solid, mp 122-123 °C; ^1H NMR (CDCl_3) δ 3.89 (s, 2H), 6.91 (td, $J = 5.7, 1.2$ Hz, 1H), 6.98 (dd, $J = 5.7, 1.2$ Hz, 1H), 7.15 (td, $J = 5.7, 1.2$ Hz, 1H), 7.32-7.37 (m, 10H), 7.80 (dd, $J = 5.7, 1.2$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 48.4, 52.0, 103.3, 121.8, 127.6, 127.8, 128.1, 128.7, 129.0, 130.8, 137.6, 139.5, 139.7; IR (neat) 3067, 3046, 3031, 2964, 2938, 2238 cm^{-1} ; HRMS m/z 409.03323 (calcd for $\text{C}_{21}\text{H}_{16}\text{IN}$, 409.03275).

(5) Parham, W. R.; Jones, L. D. *J. Org. Chem.* **1976**, *41*, 1187.

3-(2-Iodo-4,5-dimethoxyphenyl)-2,2-diphenylpropanenitrile (1p) was prepared according to the procedure for **1f** from diphenylacetoneitrile and 2-iodo-4,5-dimethoxybenzyl bromide (prepared in two steps from 4,5-dimethoxybenzyl alcohol)^{4,1b} in an 81% yield after recrystallization from ethyl acetate: white solid, mp 155-156 °C; ¹H NMR (CDCl₃) δ 3.47 (s, 3H), 3.81 (s, 3H), 3.84 (s, 2H), 6.24 (s, 1H), 7.19 (s, 1H), 7.31-7.40 (m, 10H); ¹³C NMR (CDCl₃) δ 28.0, 52.2, 55.3, 55.9, 91.0, 113.1, 121.4, 121.6, 127.6, 128.0, 128.7, 129.6, 139.6 (2 sp² carbons missing due to overlap); IR (neat) 3093, 3062, 3005, 2943, 2912, 2840, 2248 cm⁻¹; HRMS *m/z* 469.05450 (calcd for C₂₃H₂₀INO₂, 469.05388).

4-(2-Iodophenyl)-2,2-diphenylbutanenitrile (7b) was prepared in a 90% yield according to the procedure for **1f** from diphenylacetoneitrile and 2-iodophenethyl iodide: white solid, mp 98-99 °C (hexanes/ethyl acetate); ¹H NMR (CDCl₃) δ 2.57-2.63 (m, 2H), 2.79-2.85 (m, 2H), 6.80-6.88 (m, 1H), 7.15-7.37 (m, 8H), 7.42-7.46 (m, 4H), 7.73-7.76 (m, 1H); ¹³C NMR (CDCl₃) δ 37.0, 39.9, 51.4, 99.9, 122.0, 126.8, 126.9, 127.9, 128.2, 128.5, 128.8, 128.9, 129.7, 129.9, 132.3, 139.5, 139.6, 143.3; IR (neat) 3062, 3036, 2964, 2933, 2238 cm⁻¹; HRMS *m/z* 423.04889 (calcd for C₂₂H₁₈IN, 423.04840).

2-Cyano-3-(2-iodophenyl)-2-methylpropanenitrile (1i) was prepared according to a procedure by Diez-Barra.⁶ A neat mixture of malononitrile (0.66 g, 10.0 mmol), MeI (0.31 mL, 5.0 mmol), and *n*-Bu₄NBr (0.064 g, 0.2 mmol) was stirred for 30 min at room temperature and cooled to 0 °C. Upon addition of dry K₂CO₃ (0.69 g, 5.0 mmol), the reaction mixture was stirred at 0 °C for 15 min, extracted with CH₂Cl₂, and the organic layer was dried with Na₂SO₄. 2-Methylpropanedinitrile (0.22 g, 2.75 mmol, 55%) was isolated after column chromatography using CH₂Cl₂. The nitrile (0.22 g, 2.75 mmol) was mixed with *o*-iodobenzyl bromide (0.90 g, 3.03 mmol), *n*-Bu₄NBr (0.035 g, 0.11 mmol) and benzene (0.5 mL), stirred for 30 min at room temperature, dry K₂CO₃ (0.42 g, 3.03 mmol) was added, and stirring was continued for 5 h. The reaction mixture was extracted with CH₂Cl₂, the extract was dried (Na₂SO₄), the solvent was evaporated and the mixture was separated by column chromatography using 2:1 hexanes/ethyl acetate to afford 0.506 g (34%) of **1i**: white solid, mp 51-52 °C (hexanes/ethyl acetate); ¹H NMR (CDCl₃) δ 1.89 (s, 3H), 3.50 (s, 2H), 7.07 (td, *J* = 7.6, 1.6 Hz, 1H), 7.41 (td, *J* = 7.2, 1.2 Hz, 1H), 7.54 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.93 (dd, *J* = 8.0, 1.2 Hz, 1H); ¹³C NMR (CDCl₃) δ 24.4, 32.6, 46.7, 102.3, 115.7, 128.9, 130.4, 130.6, 135.2, 140.4; IR (neat) 3062, 3005, 2938, 2248 cm⁻¹; HRMS *m/z* 295.98160 (calcd for C₁₁H₉IN₂, 295.98105).

3-(2-Iodo-4-nitrophenyl)-2,2-dimethylpropanenitrile (1r) and **3-(2-iodo-5-nitrophenyl)-2,2-dimethylpropanenitrile (1s)**. To a solution of **1a** (0.88 g, 3.09 mmol) in 3 ml of acetic anhydride at 0 °C was added 1.5 ml of white fuming nitric acid. The reaction mixture was allowed to warm up to room temperature and stirred overnight, poured into ice-water, and extracted with ether. The combined ethereal

(6) Diez-Barra, E.; De la Hoz, A.; Moreno, A.; Sanchez-Verdu, P. *J. Chem. Soc., Perkin Trans. I* **1991**, 2589.

extracts were washed successively with aq NaHCO₃ and water, and dried over Na₂SO₄. The solvent was removed and the residue chromatographed using 4:1 hexanes/ethyl acetate to afford 0.415 g (41%, R_f = 0.40) of **1r** and 0.165 g (16%, R_f = 0.26) of **1s**. Nitrile **1r**: light yellow solid, mp 115-117 °C (4:1 hexanes/ethyl acetate); ¹H NMR (CDCl₃) δ 1.50 (s, 6H), 3.19 (s, 2H), 7.83 (dd, *J* = 8.7, 2.7 Hz, 1H), 8.11 (d, *J* = 8.7 Hz, 1H), 8.30 (d, *J* = 2.7 Hz, 1H); ¹³C NMR (CDCl₃) δ 26.8, 34.1, 48.8, 110.6, 123.3, 123.7, 124.8, 141.1, 148.1 (1 sp² carbon missing due to overlap); IR (neat) 3068, 2984, 2934, 2226, 1524, 1343 cm⁻¹; HRMS *m/z* 329.98693 (calcd for C₁₁H₁₁IN₂O₂, 329.98653). Nitrile **1s**: light yellow solid, mp 59-60 °C (4:1 hexanes/ethyl acetate); ¹H NMR (CDCl₃) δ 1.49 (s, 6H), 3.27 (s, 2H), 7.48-7.55 (m, 2H), 7.71-7.75 (m, 1H); ¹³C NMR (CDCl₃) δ 26.7, 34.4, 49.3, 93.8, 123.3, 124.1, 129.1, 133.0, 142.7 (1 sp² carbon missing due to overlap); IR (neat) 3072, 2983, 2235, 1528, 1350 cm⁻¹; HRMS *m/z* 329.98693 (calcd for C₁₁H₁₁IN₂O₂, 329.98653).

3-(4-Cyano-2-iodophenyl)-2,2-dimethylpropanenitrile (1t). A solution of SnCl₂ (1.05 g, 5.5 mmol) in 5 mL of a 5:4:1 DME-EtOH-AcOH solvent mixture was added dropwise, with stirring, to a solution of **1r** (0.23 g, 0.7 mmol) in 3 mL of the same solvent mixture under Ar at room temperature. The reaction mixture was stirred at room temperature for 5 min, and then heated at 60 °C until the starting material was consumed (about 1.5 h). The reaction mixture was then poured into aq NaHCO₃ and extracted with ether. The extracts were dried (Na₂SO₄), evaporated, and chromatographed using 1:1 hexanes/ethyl acetate to afford 0.21 g (100%) of 3-(4-amino-2-iodophenyl)-2,2-dimethylpropanenitrile, which was immediately converted to **1t** according to a procedure by Rapaport.⁷ A solution of NaNO₂ (0.046 g, 0.67 mmol) in 0.3 mL of water was added, with stirring, to a cold (0 °C) solution of 3-(4-amino-2-iodophenyl)-2,2-dimethylpropanenitrile (0.2 g, 0.67 mmol) in 2 mL of concentrated HCl and 1 mL of ice-water. The mixture was stirred at 0 °C for 30 min, and the cold solution of the resulting diazonium salt was neutralized by addition of solid Na₂CO₃ and added slowly, with stirring, to a suspension of CuCN (0.064 g, 0.71 mmol) and NaCN (0.069 g, 1.41 mmol) in 0.5 mL of H₂O at 0 °C. The reaction mixture was stirred for 1 h at room temperature, the precipitate was dissolved in CH₂Cl₂, the aqueous layer was discarded, and the organic layer was washed with water, dried over Na₂SO₄ and evaporated to afford 0.108 g (52%) of **1t**: yellow solid, mp 135-136 °C (hexanes/ethyl acetate); ¹H NMR (CDCl₃) δ 1.47 (s, 6H), 3.12 (s, 2H), 7.23-7.28 (m, 1H), 7.32 (d, *J* = 1.8 Hz, 1H), 8.04 (d, *J* = 7.5 Hz, 1H); ¹³C NMR (CDCl₃) δ 26.6, 34.0, 48.5, 108.6, 112.6, 117.7, 123.8, 131.6, 133.2, 140.8, 141.0; IR (neat) 3055, 2985, 2924, 2228 cm⁻¹; HRMS *m/z* 309.99725 (calcd for C₁₂H₁₁IN₂, 309.99670).

(7) Ikan, R.; Rapaport, E. *Tetrahedron* **1967**, 23, 3823.

3-(2-Iodophenyl)-2,2-dimethyl-3-(trimethylsilyloxy)propanenitrile (1j) was prepared according to the procedure of Silverman.⁸ To a solution of the lithium salt of isobutyronitrile prepared from 0.77 mL (8.5 mmol) of the nitrile according to the procedure of Taber *et al.*³ in 10 mL of THF at -78 °C under Ar was added a solution of *o*-iodobenzaldehyde (2.0 g, 8.62 mmol) in 3 mL of THF. The reaction mixture was stirred for 45 min at -78 °C, then Me₃SiCl (1.72 mL, 13.6 mmol) was added, followed by MeOH (2 mL) 10 min later. The reaction mixture was allowed to warm up to room temperature, the solvent was evaporated, and the residue was taken up into ethyl acetate, washed with water, and dried over Na₂SO₄. The solvent was removed and the residue was chromatographed using 10:1 hexanes/ethyl acetate to afford a 69% yield of **1j**: white solid, mp 65-66 °C; ¹H NMR (CDCl₃) δ 0.02 (s, 9H), 1.26 (s, 3H), 1.52 (s, 3H), 4.83 (s, 1H), 7.00-7.04 (td, *J* = 7.6, 1.2 Hz, 1H), 7.38-7.42 (td, *J* = 7.6, 1.2 Hz, 1H), 7.74-7.76 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.80-7.83 (m, 1H); ¹³C NMR (CDCl₃) δ -0.0, 22.8, 25.2, 41.1, 81.2, 99.9, 123.5, 128.5, 129.5, 130.1, 139.2, 142.1; IR (neat) 3067, 2949, 2235 cm⁻¹; HRMS *m/z* 373.03653 (calcd for C₁₄H₂₀INOSi, 373.03589).

3-Hydroxy-3-(2-iodophenyl)-2,2-dimethylpropanenitrile (1k). Compound **1j** (1.84 g, 4.93 mmol) was dissolved in 40 mL of THF containing 6 mL of a 1M solution of *n*-Bu₄NF. The reaction mixture was stirred for 5 h at room temperature, concentrated, diluted with brine, and extracted with CH₂Cl₂. The organic extracts were washed with brine, dried (Na₂SO₄), evaporated, and the residue was chromatographed with 4:1 hexanes/ethyl acetate to afford 1.37 g (93 %) of **1k** as a very viscous bright yellow oil: ¹H NMR (CDCl₃) δ 1.27 (s, 3H), 1.61 (s, 3H), 2.60 (d, *J* = 4.0 Hz, 1H), 4.94 (d, *J* = 4.0 Hz, 1H), 7.03-7.07 (m, 1H), 7.44 (td, *J* = 8.0, 1.6 Hz, 1H), 7.79 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.85 (dd, *J* = 8.0, 1.2 Hz, 1H); ¹³C NMR (CDCl₃) δ 23.0, 25.3, 40.3, 100.2, 123.2, 128.4, 128.9, 130.5, 139.6, 141.6; IR (neat) 3448, 3067, 2986, 2940, 2242 cm⁻¹; HRMS *m/z* 300.99726 (calcd for C₁₁H₁₂INO, 300.99637).

3-(2-Iodophenyl)-3-methoxy-2,2-dimethylpropanenitrile (1l). Compound **1k** was methylated according to a procedure by Melder.⁹ To a stirred suspension of NaH (0.025 g, 1.05 mmol) in 2 mL of THF at 0 °C under Ar was added a solution of **1k** (0.301 g, 1.0 mmol) in 3 mL of THF. After stirring for 45 min at room temperature, MeI (0.125 mL, 2.0 mmol) was added and stirring was continued overnight at room temperature. The reaction mixture was then quenched with satd aq NH₄Cl, diluted with water and extracted with ether. The extracts were dried (Na₂SO₄), evaporated, and the residue was chromatographed using 4:1 hexanes/ethyl acetate to afford 0.262 g (83%) of **1l**: colorless oil; ¹H NMR (CDCl₃) δ 1.25 (s, 3H), 1.59 (s, 3H), 3.22 (s, 3H), 4.47 (s, 1H), 7.04-7.10 (m, 1H), 7.42-7.48 (m, 1H), 7.67-7.70 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.85-7.88 (m, 1H); ¹³C NMR (CDCl₃) δ 23.0, 25.4, 39.5, 57.1, 89.0, 101.7, 123.1, 128.5,

(8) Zhou, J. J. P.; Zhong, B.; Silverman, R. B. *J. Org. Chem.* **1995**, *60*, 2261.

(9) Kozikowski, A. P.; Fauq, A. H.; Powis, G.; Melder, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 4528.

128.8, 130.4, 138.9, 139.5; IR (neat) 3061, 2986, 2938, 2821, 2234 cm^{-1} ; HRMS m/z 315.01242 (calcd for $\text{C}_{12}\text{H}_{14}\text{INO}$, 315.01202).

3-Acetoxy-3-(2-iodophenyl)-2,2-dimethylpropanenitrile (1m) was prepared according to a published procedure.¹⁰ Compound **1k** (0.452 g, 1.5 mmol), DMAP (0.046 g, 0.375 mmol) and Ac_2O (0.21 mL, 2.25 mmol) were dissolved in 0.3 mL of Et_3N , and the reaction mixture was stirred overnight at room temperature. Methanol was added to remove excess acetic anhydride, then the mixture was concentrated on a rotary evaporator, the residue was dissolved in ether, washed with water, dilute aq HCl, dilute aq NaHCO_3 , and brine, and dried over Na_2SO_4 . The solvent was evaporated and the residue was recrystallized from 4:1 hexanes/ethyl acetate to afford 0.398 g (77%) of **1m**: beige solid, mp 127-128 $^\circ\text{C}$; ^1H NMR (CDCl_3) δ 1.34 (s, 3H), 1.58 (s, 3H), 2.14 (s, 3H), 5.93 (s, 1H), 7.03-7.09 (m, 1H), 7.39-7.45 (m, 1H), 7.68 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.86 (dd, $J = 7.8, 1.2$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 20.8, 23.3, 25.4, 38.9, 81.0, 100.7, 122.3, 128.2, 128.8, 130.6, 138.6, 139.7, 169.3; IR (neat) 3071, 2999, 2989, 2236, 1745 cm^{-1} ; HRMS m/z 343.00693 (calcd for $\text{C}_{13}\text{H}_{14}\text{INO}_2$, 343.00736).

3-(2-Iodophenyl)-2,2-dimethyl-3-oxopropanenitrile (1n) was prepared according to the general procedure for the alkylation of aliphatic nitriles using isobutyronitrile (0.18 mL, 2.0 mmol) and methyl *o*-iodobenzoate (0.55 g, 2.1 mmol) instead of *o*-iodobenzyl bromide. The residue was chromatographed using 4:1 hexanes/ethyl acetate to afford 0.431 g (72 %) of **1n** as a yellow oil: ^1H NMR (CDCl_3) δ 1.73 (s, 6H), 7.16-7.22 (m, 1H), 7.41-7.49 (m, 2H), 7.92 (dd, $J = 7.2, 0.9$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 24.9, 43.7, 90.9, 121.2, 126.4, 127.7, 131.6, 139.8, 143.1, 199.6; IR (neat) 3060, 2938, 2238, 1714 cm^{-1} ; HRMS m/z 298.98164 (calcd for $\text{C}_{11}\text{H}_{10}\text{INO}$, 298.98072).

3-(4-{3-Bromopyridyl})-3-hydroxy-2,2-dimethylpropanenitrile (3) was prepared according to the general procedure for the alkylation of aliphatic nitriles using isobutyronitrile (0.181 mL, 2.0 mmol) and 3-bromopyridine-4-carbaldehyde (0.378 g, 2.03 mmol) instead of *o*-iodobenzyl bromide. The residue was chromatographed using 2:1 hexanes/ethyl acetate to afford 0.203 g (40%) of **3**: white solid, mp 125-127 $^\circ\text{C}$; ^1H NMR (CDCl_3) δ 1.27 (s, 3H), 1.59 (s, 3H), 4.73 (br s, 1H), 5.03 (s, 1H), 7.76 (d, $J = 4.8$ Hz, 1H), 8.45 (d, $J = 4.8$ Hz, 1H), 8.56 (s, 1H); ^{13}C NMR (CDCl_3) δ 22.6, 24.8, 39.8, 74.5, 121.9, 122.6, 124.1, 148.2, 148.4, 151.4; IR (neat) 3407, 3087, 2938, 2238 cm^{-1} ; HRMS m/z 254.00592 (calcd for $\text{C}_{10}\text{H}_{11}\text{BrN}_2\text{O}$, 254.00547).

2-Cyano-2'-iodobiphenyl (4) was prepared by modifying the procedure of Grinham.¹¹ A mixture of 2,2'-diiodobiphenyl (0.406 g, 1 mmol), CuCN (0.09 g, 1 mmol) and pyridine (2 mL) was heated at 150 $^\circ\text{C}$

(10) (a) McMurry, J. E.; Musser, J. H.; Ahmad, M. S.; Blaszczyk, L. C. *J. Org. Chem.* **1975**, *40*, 1829. (b) Höfle, G.; Stegliah, W.; Vorbrüggen, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 569.

(11) Barton, J. W.; Grinham, A. R. *J. Chem. Soc., Perkin Trans. 1* **1972**, 634.

for 6 h, cooled to room temperature, dissolved in benzene and washed with a 1:1 NH₄OH (aq., 30%)/water mixture. The benzene extract was dried (Na₂SO₄), evaporated, and chromatographed using 4:1 hexanes/ethyl acetate to afford 0.092 g (30 %) of the target biaryl **4** as a white solid: mp 71-72 °C (lit.¹¹ mp 73-74 °C), along with unreacted starting material (25%) and 2,2'-dicyanobiphenyl (29%); ¹H NMR (CDCl₃) δ 7.13 (td, *J* = 7.8, 1.5 Hz, 1H), 7.30-7.53 (m, 4H), 7.63-7.70 (m, 1H), 7.74-7.77 (m, 1H), 7.97 (dd, *J* = 8.1, 1.5 Hz, 1H); ¹³C NMR (CDCl₃) δ 98.3, 112.8, 117.6, 128.2, 128.3, 129.8, 130.2, 130.6, 132.3, 132.7, 139.4, 143.0, 143.7; IR (neat) 3059, 2225 cm⁻¹.

General Procedure for the Pd-Catalyzed Cyclization of ω-(2-Iodoaryl)alkanenitriles. All reactions were performed under an Ar atmosphere. 0.25 Mmol of the ω-(2-iodoaryl)alkanenitrile, 0.025 mmol (10 mol %) of Pd(OAc)₂, and 0.05 mmol (20 mol %) of Ph₃P were dissolved in 4.5 mL of DMF and 0.5 mL of water, and 0.3 mmol (1.2 equiv) of Et₃N were added to the solution. The reaction mixture was stirred at 130 °C for the appropriate amount of time. Then, the reaction mixture was allowed to cool to room temperature and poured into 25 mL of diethyl ether. The ether solution was washed with aq NH₄Cl and dried over Na₂SO₄. The identity of all known products was established by GC-mass spectrometry and ¹H NMR spectroscopy of the reaction mixtures. The yields of known products were determined by ¹H NMR spectroscopy by integration of the appropriate outstanding signals using 1,4-dimethoxybenzene as an internal standard. New products were isolated by column chromatography on a silica gel column.

Spiro[cyclobutane-1,2'-indan]-1'-one (2c) was obtained as a colorless oil in an 83% isolated yield from **1c** according to the general procedure after column chromatography using 10:1 hexanes/ethyl acetate: ¹H NMR (CDCl₃) δ 2.00-2.20 (m, 4H), 2.47-2.54 (m, 2H), 3.30 (s, 2H), 7.33-7.43 (m, 2H), 7.57 (td, *J* = 7.5, 1.2 Hz, 1H), 7.76 (dd, *J* = 7.5, 1.6 Hz, 1H); ¹³C NMR (CDCl₃) δ 16.1, 31.6, 42.2, 50.7, 124.0, 126.2, 127.3, 134.6, 135.9, 152.3, 209.3; IR (neat) 3077, 2933, 2845, 1702, 1604 cm⁻¹; HRMS *m/z* 172.08900 (calcd for C₁₂H₁₂O, 172.08882).

2-Cyano-2-methyl-1-indanone (2i) was obtained as a light yellow oil in an 89% isolated yield from **1i** according to the general procedure after column chromatography using 4:1 hexanes/ethyl acetate: ¹H NMR (CDCl₃) δ 1.67 (s, 3H), 3.24 (d, *J* = 13.2 Hz, 1H), 3.76 (d, *J* = 13.2 Hz, 1H), 7.47-7.52 (m, 2H), 7.70-7.74 (m, 1H), 7.83-7.86 (m, 1H); ¹³C NMR (CDCl₃) δ 23.7, 40.5, 43.2, 120.6, 125.9, 126.9, 129.0, 133.0, 136.7, 150.5, 198.5; IR (neat) 3058, 2982, 2934, 2241, 1724 cm⁻¹; HRMS *m/z* 171.06867 (calcd for C₁₁H₉NO, 171.06841).

3-Acetoxy-2,2-dimethyl-1-indanone (2m) was obtained as a colorless oil in an 80% isolated yield from **1m** according to the general procedure (reaction time 40 h) after column chromatography using 4:1 hexanes/ethyl acetate: ¹H NMR (CDCl₃) δ 1.14 (s, 3H), 1.33 (s, 3H), 2.18 (s, 3H), 6.09 (s, 1H), 7.53 (td, *J* = 7.6, 0.4 Hz, 1H), 7.59 (dd, *J* = 7.6, 0.4 Hz, 1H), 7.69 (td, *J* = 7.6, 1.2 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H);

^{13}C NMR (CDCl_3) δ 19.6, 20.8, 24.0, 49.7, 78.5, 123.9, 126.6, 129.9, 135.0, 135.3, 149.3, 170.9, 207.5; IR (neat) 3078, 2969, 2933, 2872, 1728, 1604 cm^{-1} ; HRMS m/z 218.09456 (calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3$, 218.09429).

5,6-Dimethoxy-2,2-diphenyl-1-indanone (2p) was obtained in an 84% isolated yield from **1p** according to the general procedure after recrystallization from ethyl acetate: off-white solid, mp 172-174 $^\circ\text{C}$; ^1H NMR (CDCl_3) δ 3.83 (s, 2H), 3.91 (s, 3H), 4.00 (s, 3H), 6.94 (s, 1H), 7.18-7.32 (m, 11H); ^{13}C NMR (CDCl_3) δ 44.8, 56.1, 56.3, 62.9, 105.3, 106.7, 126.6, 128.0, 128.1, 128.2, 128.3, 143.7, 147.3, 149.7, 155.9, 203.9; IR (neat) 3080, 3066, 2984, 2834, 1699 cm^{-1} ; HRMS m/z 344.14185 (calcd for $\text{C}_{23}\text{H}_{20}\text{O}_3$, 344.14124).

5-Bromo-2,2-dimethyl-1-indanone (2q) was obtained as a colorless oil in a 64% isolated yield from **1q** according to the general procedure after column chromatography using 4:1 hexanes/ethyl acetate: ^1H NMR (CDCl_3) δ 1.24 (s, 6H), 2.99 (s, 2H), 7.50-7.53 (m, 1H), 7.61-7.63 (m, 2H); ^{13}C NMR (CDCl_3) δ 25.2, 42.5, 45.7, 125.7, 129.9, 130.1, 131.1, 134.2, 153.8, 210.0; IR (neat) 3063, 2965, 2927, 2867, 1716, 1591 cm^{-1} ; HRMS m/z 237.99971 (calcd for $\text{C}_{11}\text{H}_{11}\text{BrO}$, 237.99933).

6-Cyano-2,2-dimethyl-1-indanone (2t) was obtained in a 43% yield from **1t** according to the general procedure. This product could not be separated from the reduced starting material by column chromatography; its yield was determined by ^1H NMR spectroscopy performed on the crude compound by integrating the methylene signal at 3.06 ppm (2H) and the dimethyl signal at 1.26 ppm (6H).

2,2-Diphenyl-1-tetralone (9b) was obtained in a 55% isolated yield from **7b** according to the general procedure after column chromatography using 10:1 hexanes/ethyl acetate: white solid, mp 99-101 $^\circ\text{C}$ (hexanes/ethyl acetate); ^1H NMR (CDCl_3) δ 2.85-2.95 (m, 4H), 7.12-7.15 (m, 5H), 7.22-7.33 (m, 7H), 7.40-7.46 (m, 1H), 8.19 (dd, $J = 7.8, 1.5$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 26.4, 35.1, 59.9, 126.7, 126.9, 128.1, 128.4, 128.6, 133.0, 133.2, 142.0, 143.3, 198.8 (1 sp^2 carbon missing due to overlap); IR (neat) 3061, 3026, 2934, 1685 cm^{-1} ; HRMS m/z 298.13629 (calcd for $\text{C}_{22}\text{H}_{18}\text{O}$, 298.13577).

3,5,5-Trimethyl-2-phenylcyclopent-2-en-1-one (12b), a known compound, was obtained as a light yellow oil in a 72% isolated yield from **11b** according to the general procedure after column chromatography using 10:1 hexanes/ethyl acetate: ^{13}C NMR (CDCl_3) δ 18.2, 25.2, 43.3, 48.9, 127.4, 128.1, 129.1, 132.1, 137.4, 168.2, 211.6; HRMS m/z 200.12051 (calcd for $\text{C}_{14}\text{H}_{16}\text{O}$, 200.12012). Other spectral properties were identical to those previously reported.¹²

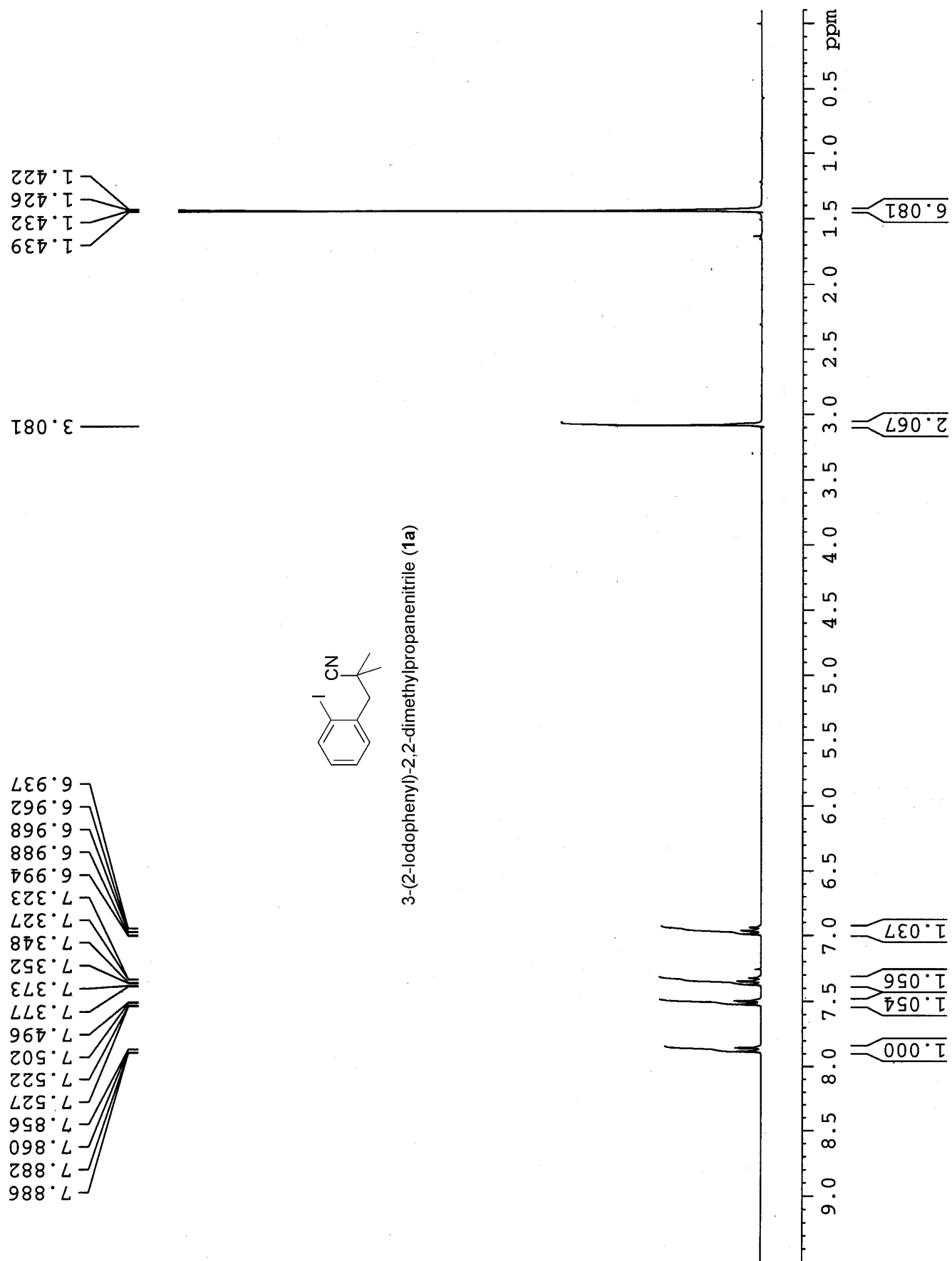
2,5,5-Trimethyl-3-phenylcyclopent-2-en-1-one (12c) was obtained as a colorless oil in an 82% isolated yield from **11c** according to the general procedure after column chromatography using 10:1 hexanes/ethyl acetate: ^1H NMR (CDCl_3) δ 1.20 (s, 6H), 1.99 (t, $J = 2.0$ Hz, 3H), 2.79 (q, $J = 2.0$ Hz, 2H),

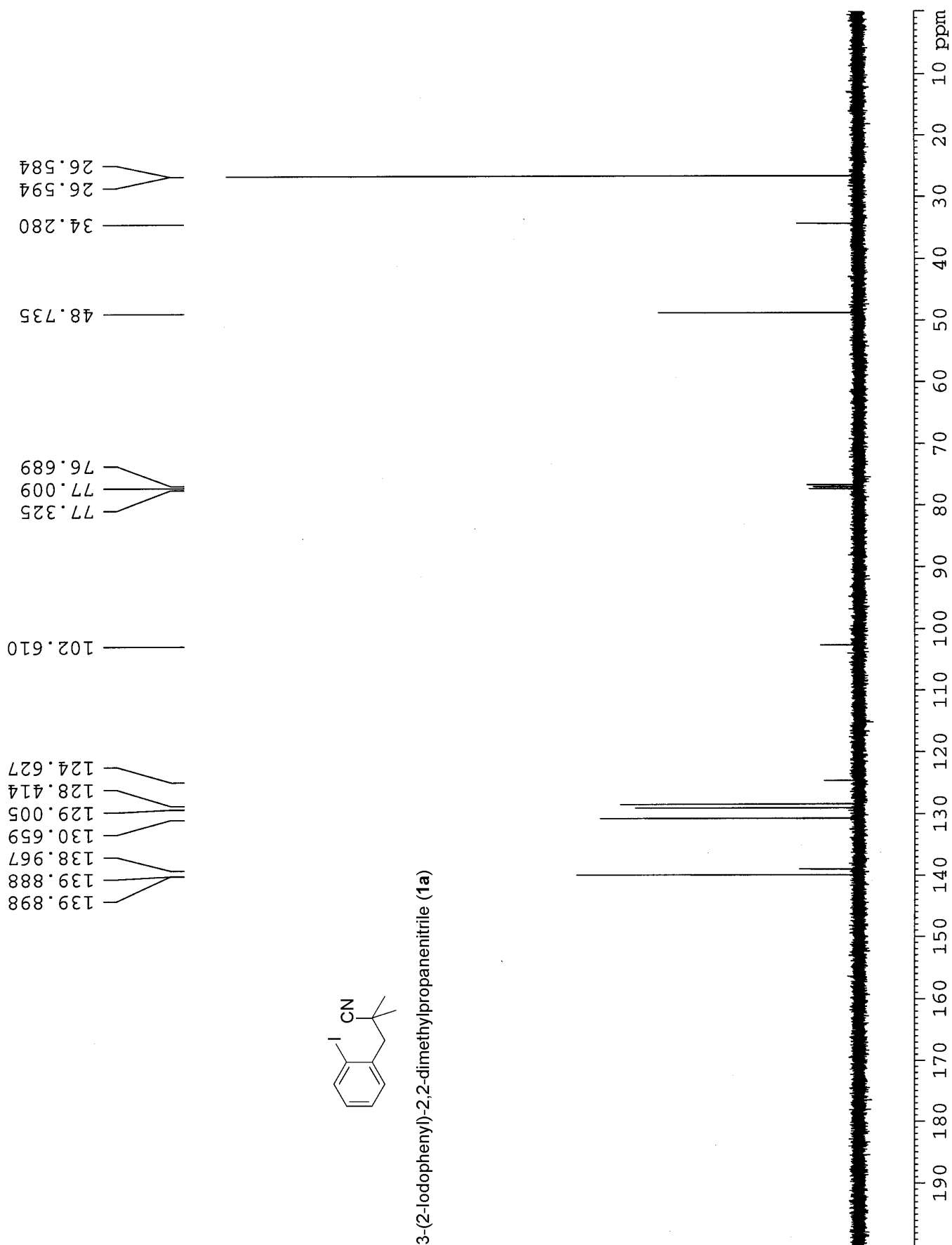
(12) Prempre, P.; Siwapinyoyos, T.; Thebtaranonth, C.; Thebtaranonth, Y. *Tetrahedron Lett.* **1980**, *21*, 1169.

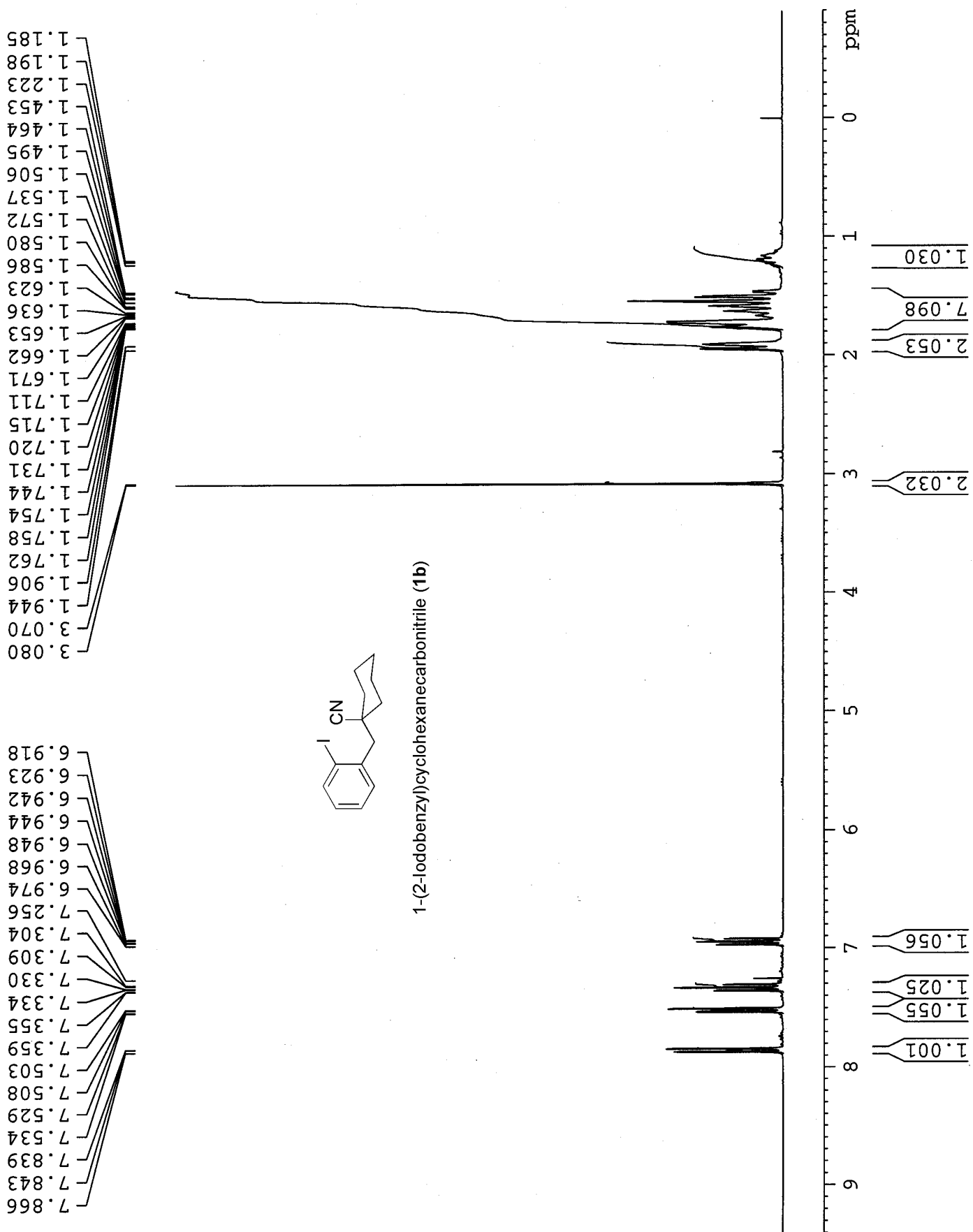
7.40-7.48 (m, 3H), 7.52-7.55 (m, 2H); ^{13}C NMR (CDCl_3) δ 10.3, 25.4, 42.6, 46.3, 127.6, 128.5, 129.4, 133.6, 136.3, 163.1, 214.0; IR (neat) 3057, 2959, 2923, 2866, 1697 cm^{-1} ; HRMS m/z 200.12051 (calcd for $\text{C}_{14}\text{H}_{16}\text{O}$, 200.12012).

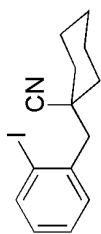
5-Ethyl-2,3-diphenylcyclopent-2-en-1-one (14) was obtained as an amber oil in a 63% isolated yield from **13** according to the general procedure after column chromatography using 10:1 hexanes/ethyl acetate: ^1H NMR (CDCl_3) δ 1.06 (t, $J = 7.2$ Hz, 3H), 1.52-1.65 (m, 1H), 1.95-2.05 (m, 1H), 2.60-2.65 (m, 1H), 2.72 (dd, $J = 18.0, 2.8$ Hz, 1H), 3.22 (dd, $J = 18.0, 6.8$ Hz, 1H), 7.19-7.32 (m, 10H); ^{13}C NMR (CDCl_3) δ 11.5, 24.9, 36.1, 46.9, 127.7, 128.1, 128.4, 129.4, 129.5, 129.7, 132.4, 135.7, 139.2, 166.5, 209.4; IR (neat) 3088, 3052, 2959, 2933, 1697, 1346 cm^{-1} ; HRMS m/z 262.13617 (calcd for $\text{C}_{19}\text{H}_{18}\text{O}$, 262.13577).

2-Cyano-3,4-dihydronaphthalene (6) was obtained in a 58% isolated yield from **1d** according to the general procedure after column chromatography using 4:1 hexanes/ethyl acetate. The 64% yield determined by ^1H NMR spectroscopy was obtained straight from the reaction mixture. Compound **6**: white solid, mp 58-59 $^\circ\text{C}$ (lit.¹³ 58-59 $^\circ\text{C}$); ^1H NMR (CDCl_3) δ 2.51 (td, $J = 8.0, 1.6$ Hz, 2H), 2.88 (t, $J = 8.0$ Hz, 2H), 7.11-7.20 (m, 3H), 7.22-7.29 (m, 2H); ^{13}C NMR (CDCl_3) δ 24.7, 26.7, 109.7, 119.7, 127.1, 127.9, 128.0, 130.2, 131.2, 135.4, 141.7; IR (neat) 3067, 3019, 2944, 2894, 2206, 1622, 1452 cm^{-1} ; HRMS m/z 155.073718 (calcd for $\text{C}_{11}\text{H}_9\text{N}$, 155.07350).

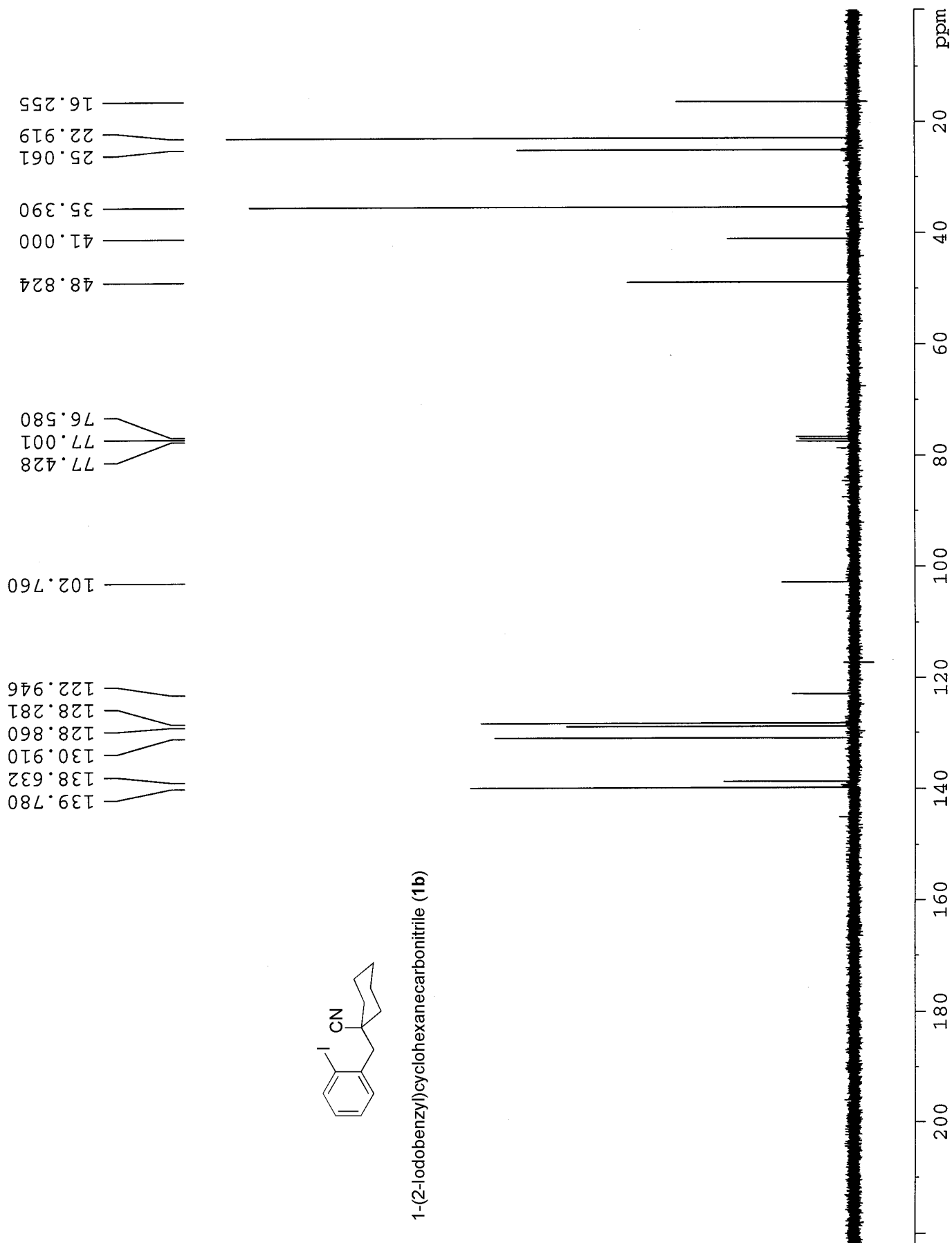


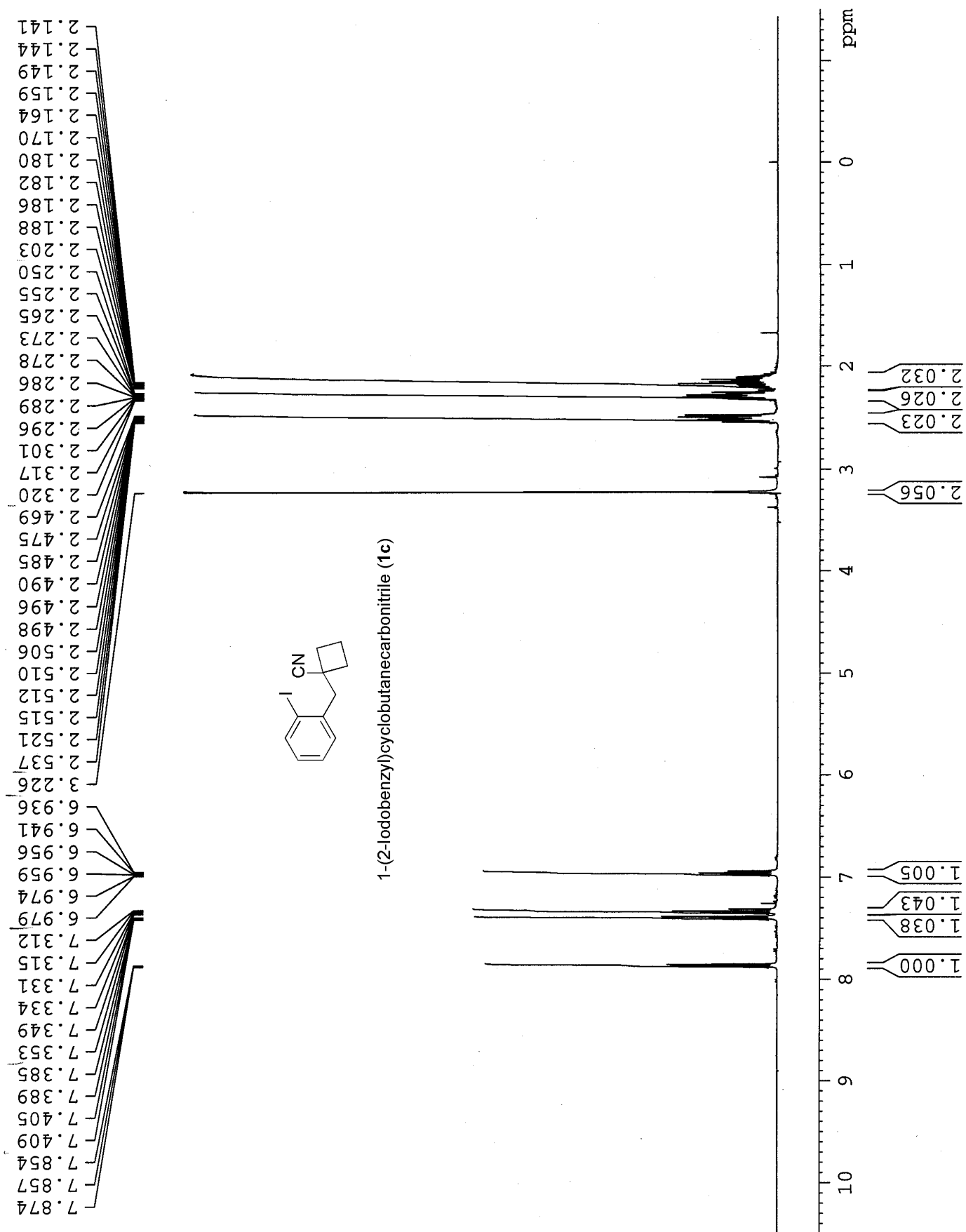


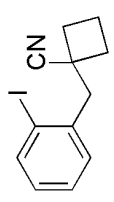




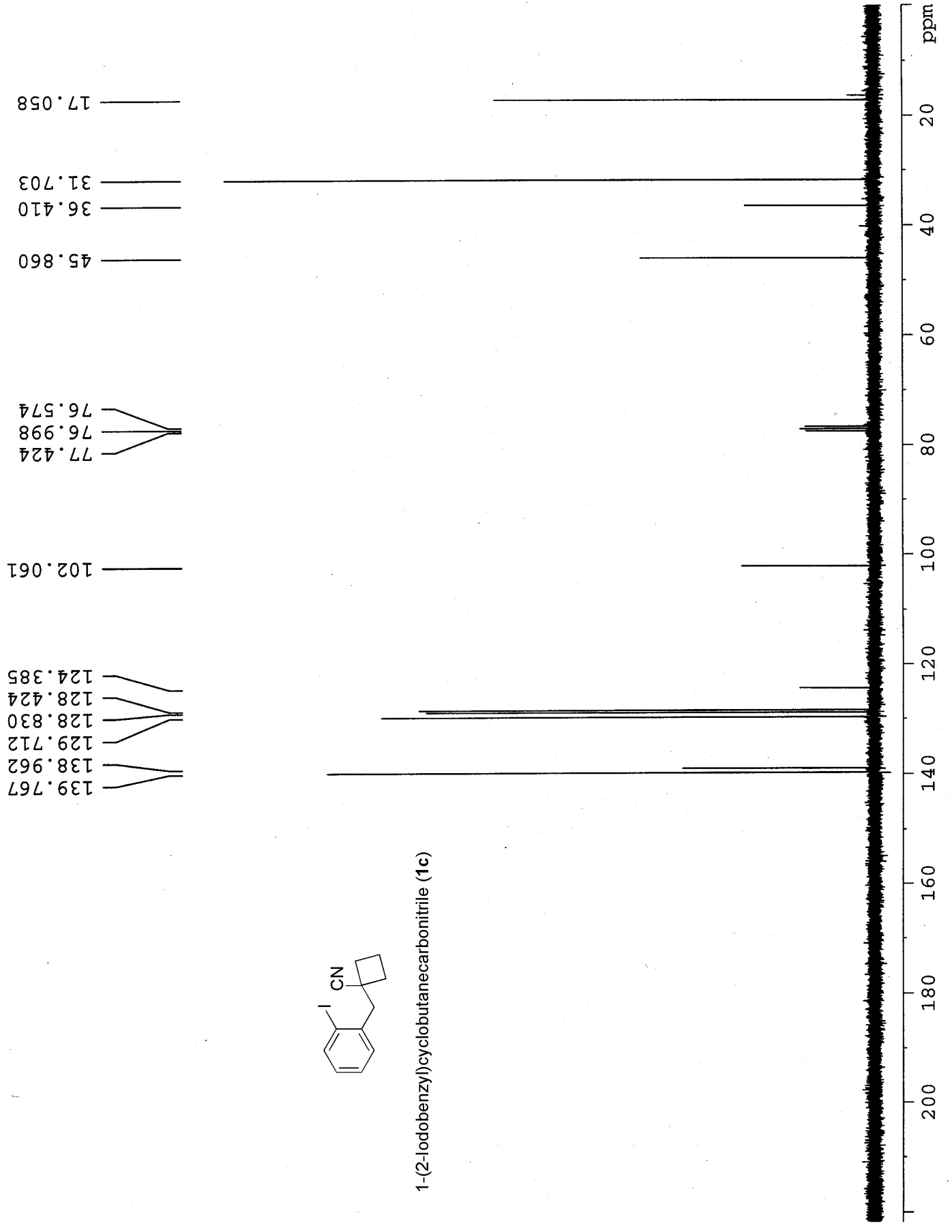
1-(2-iodobenzyl)cyclohexanecarbonitrile (**1b**)

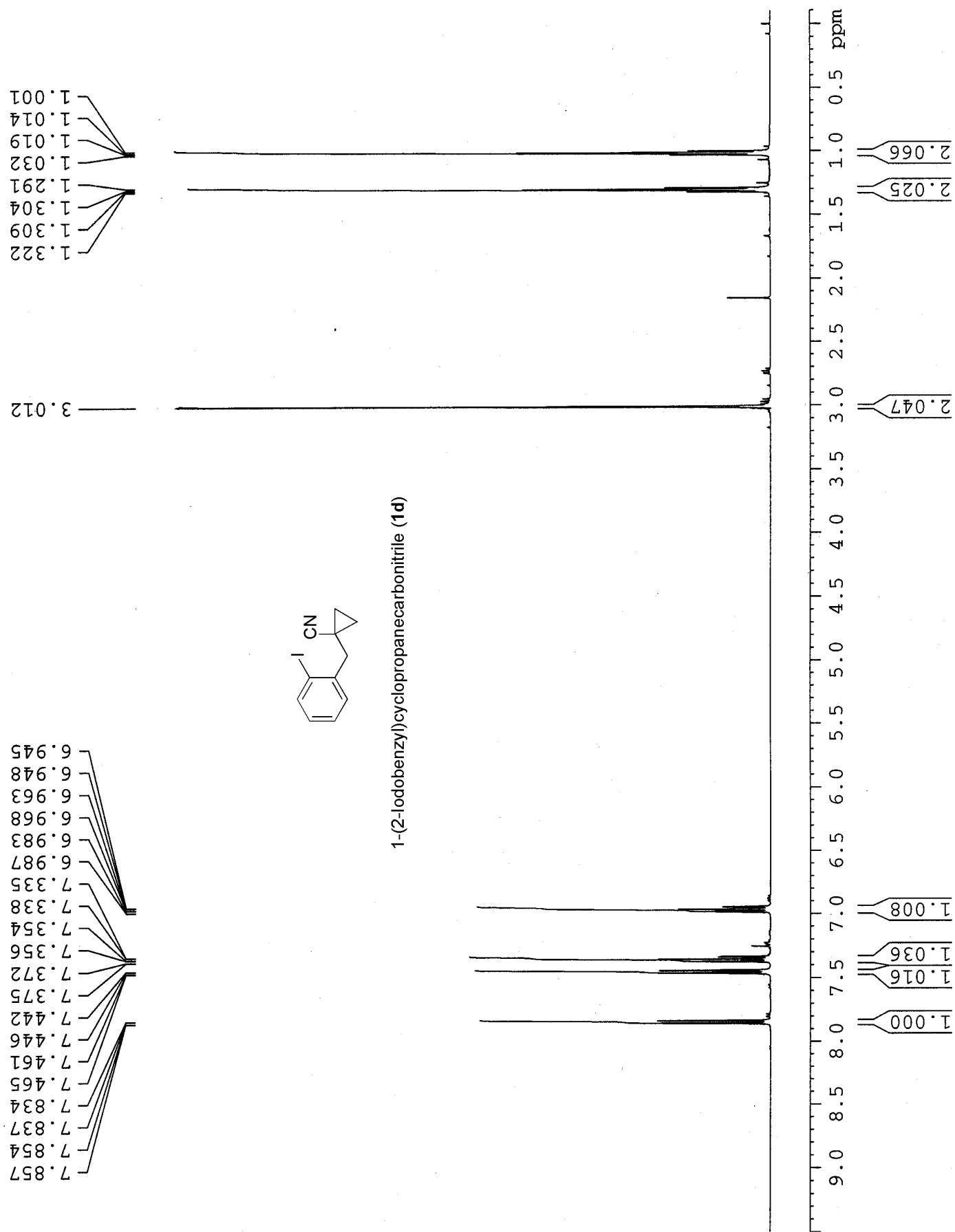


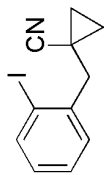




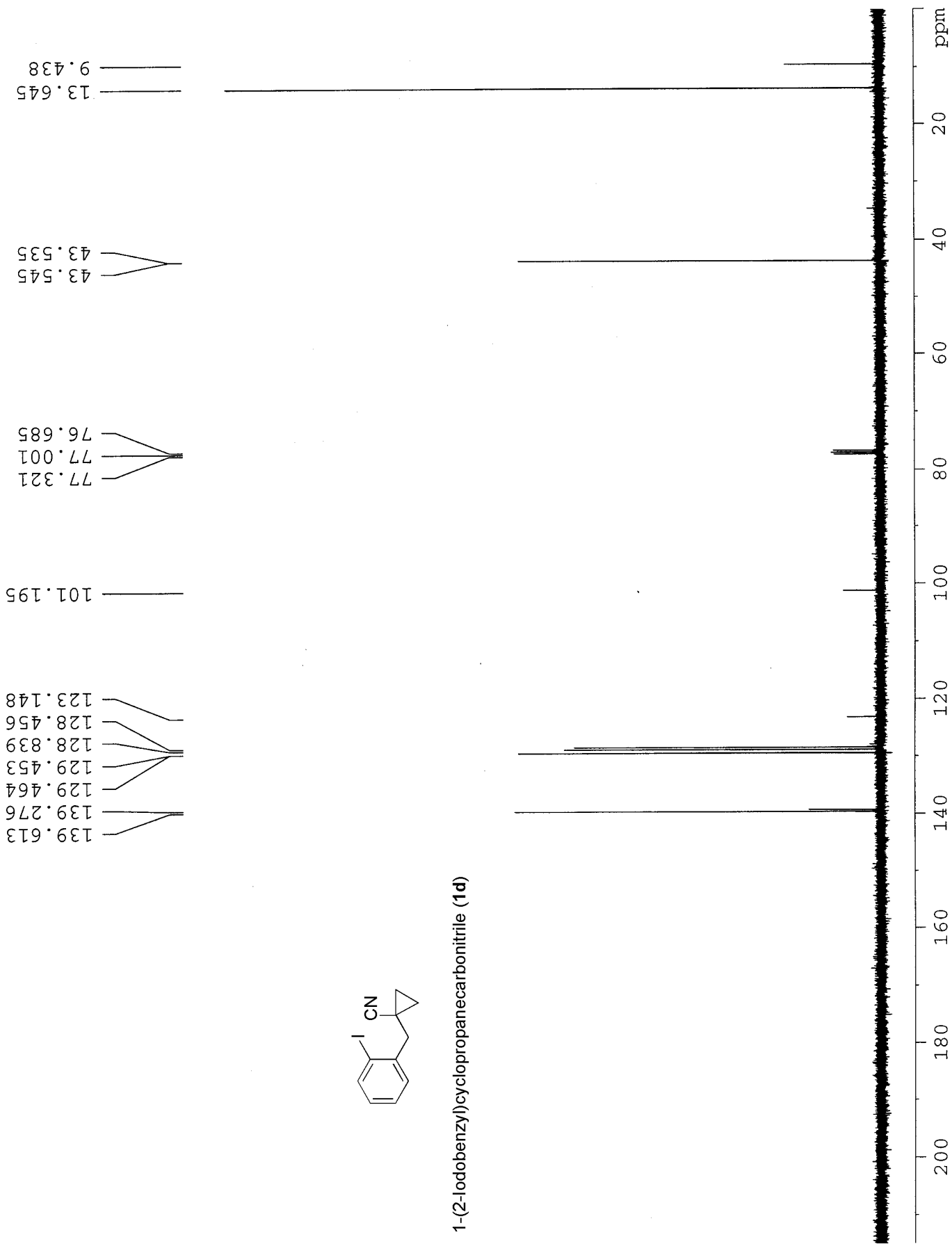
1-(2-iodobenzyl)cyclobutanecarbonitrile (1c)

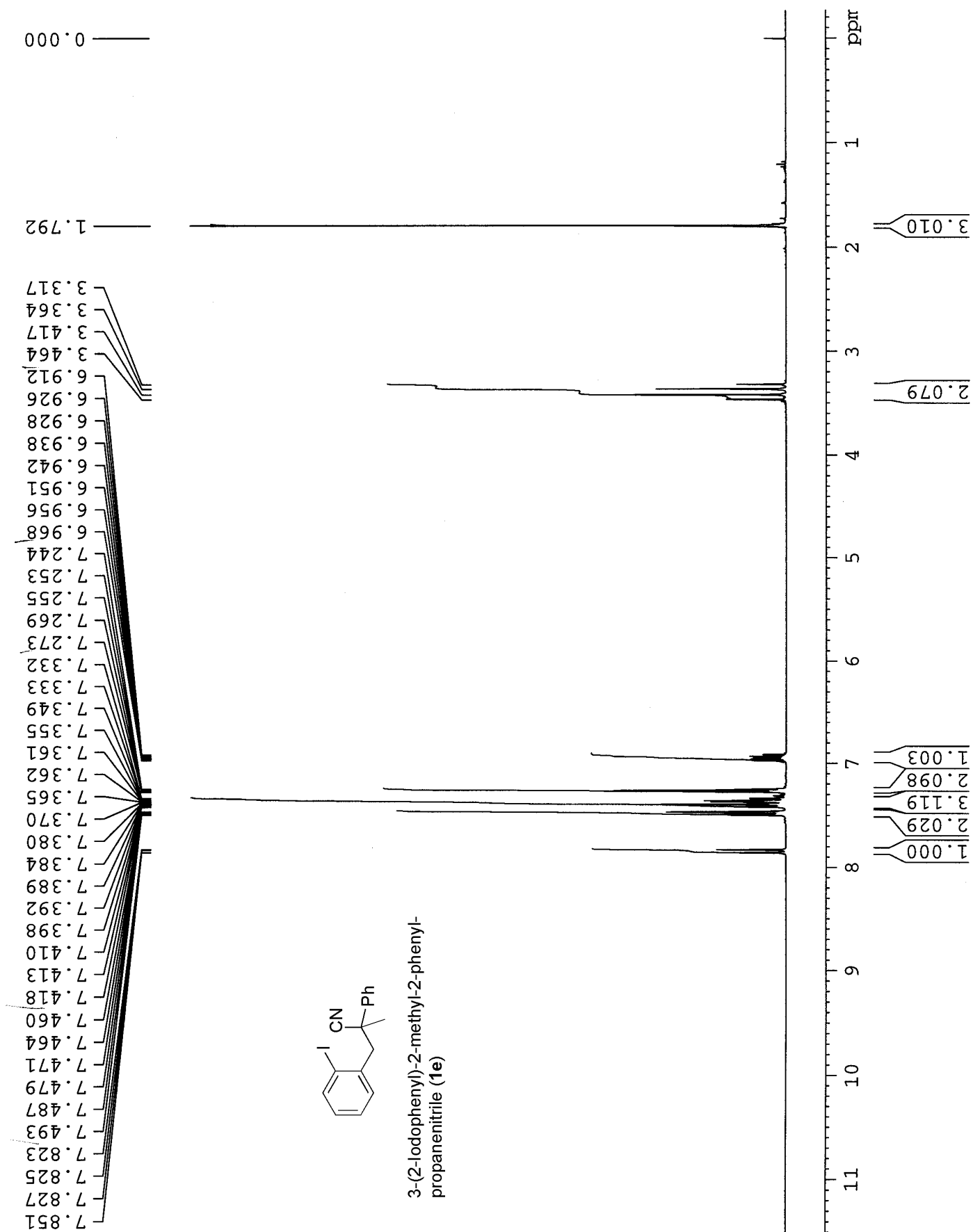


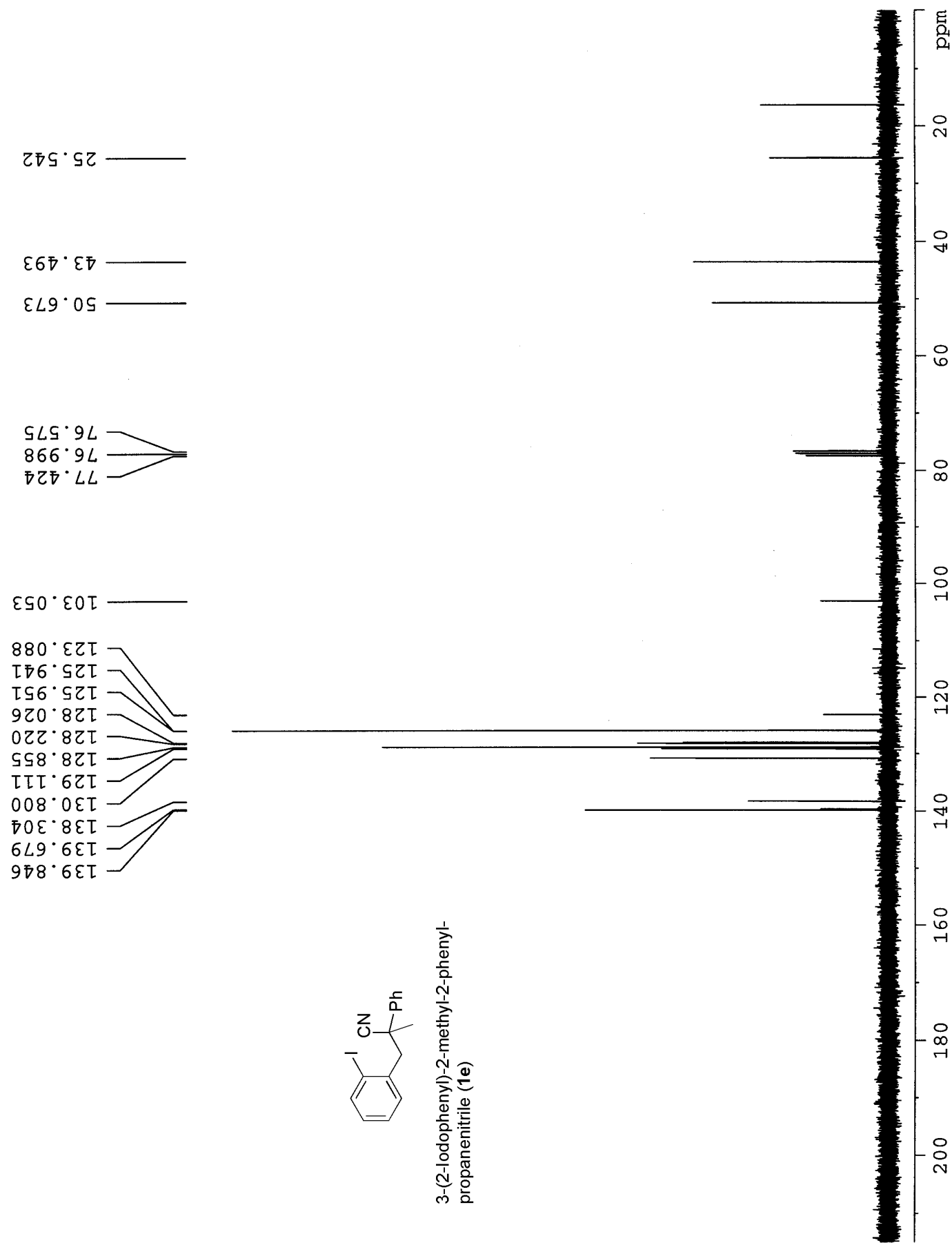


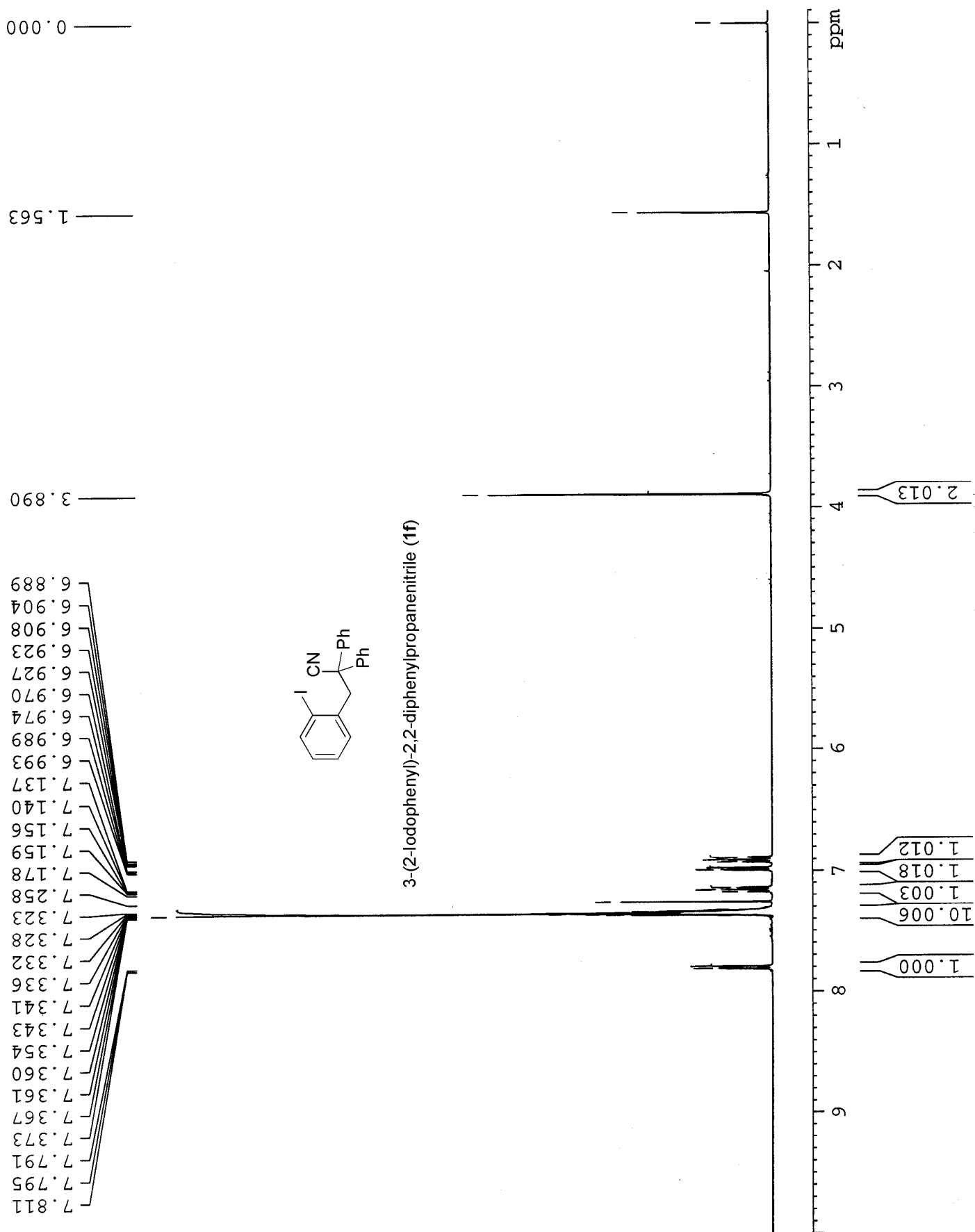


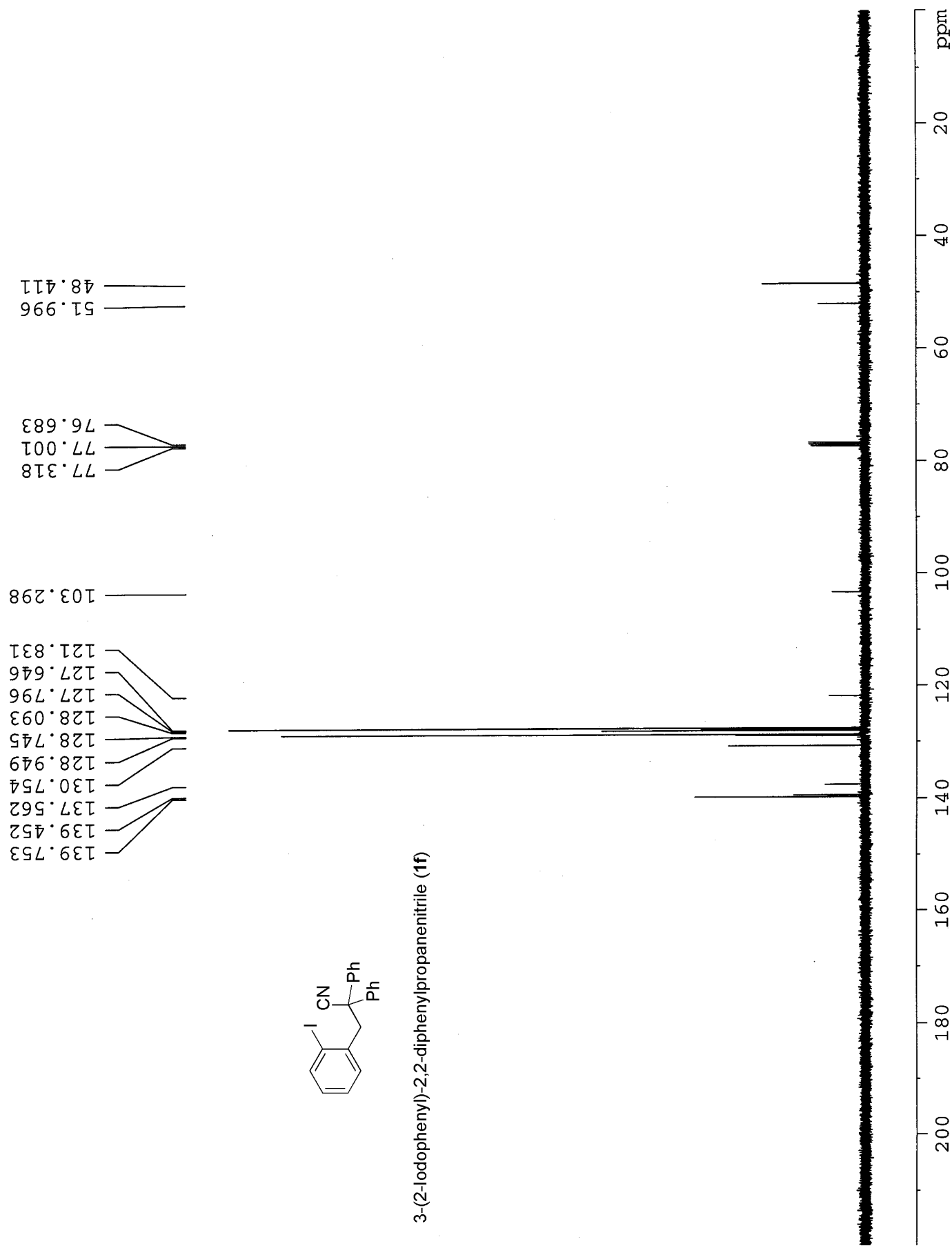
1-(2-Iodobenzyl)cyclopropanecarbonitrile (**1d**)

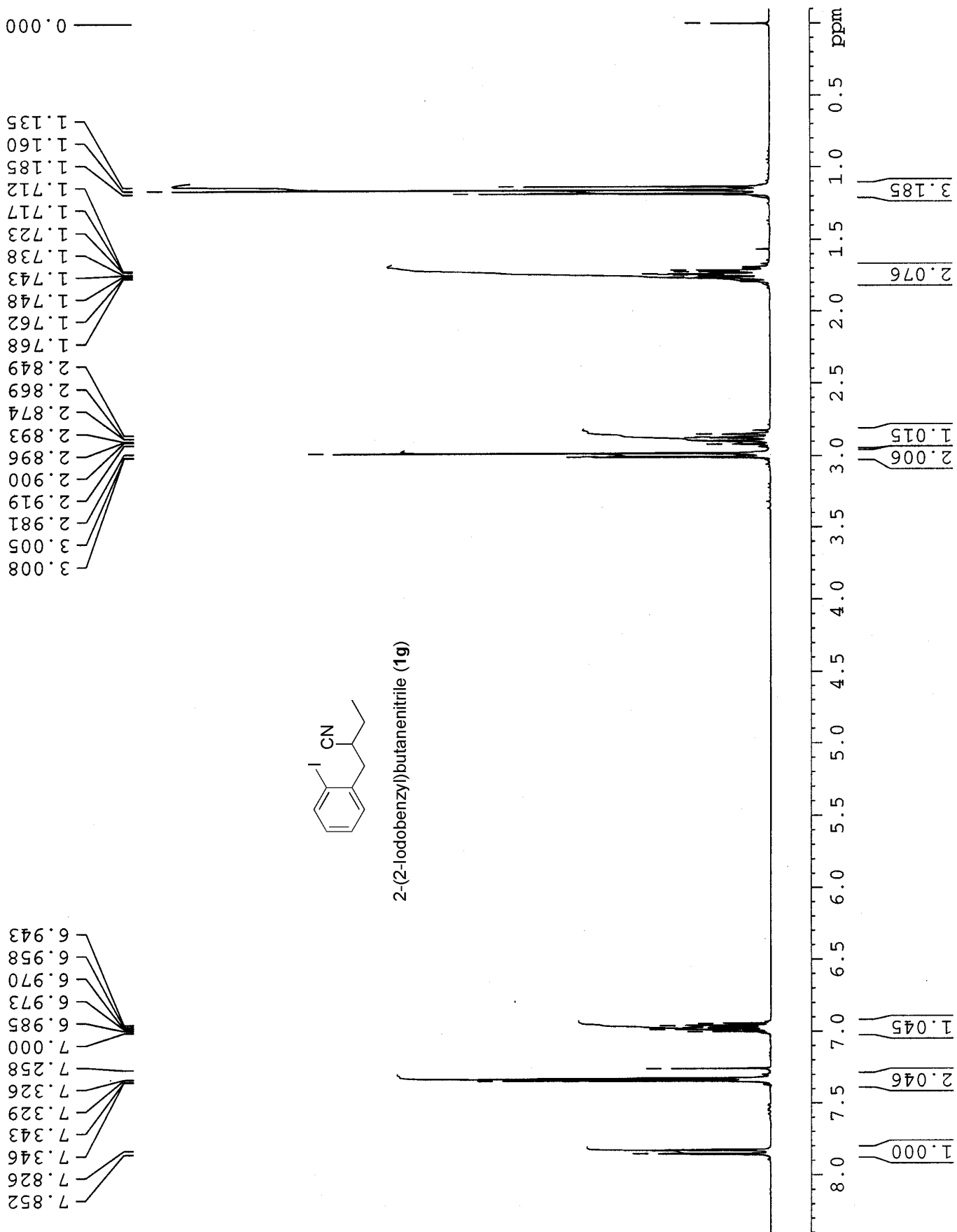


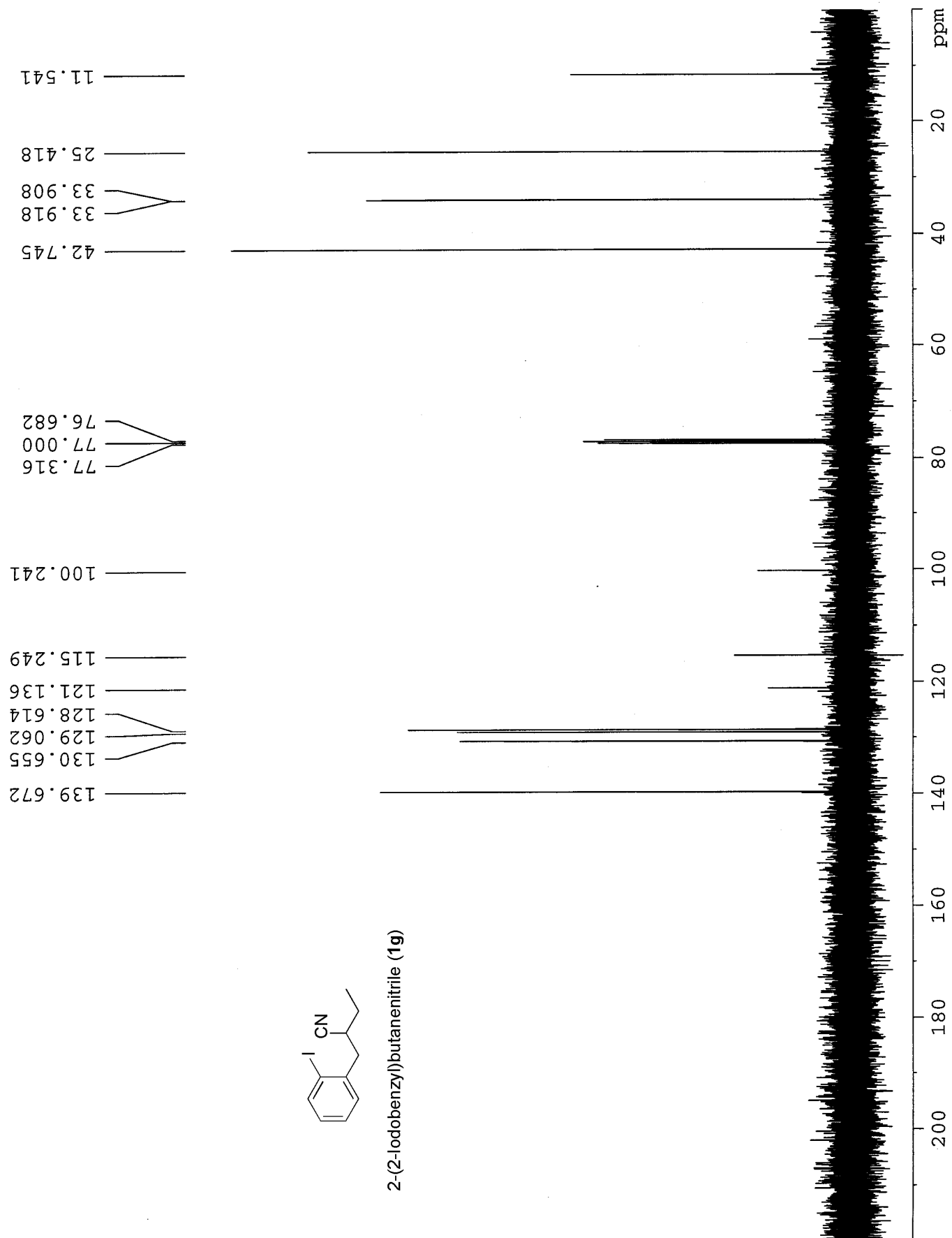


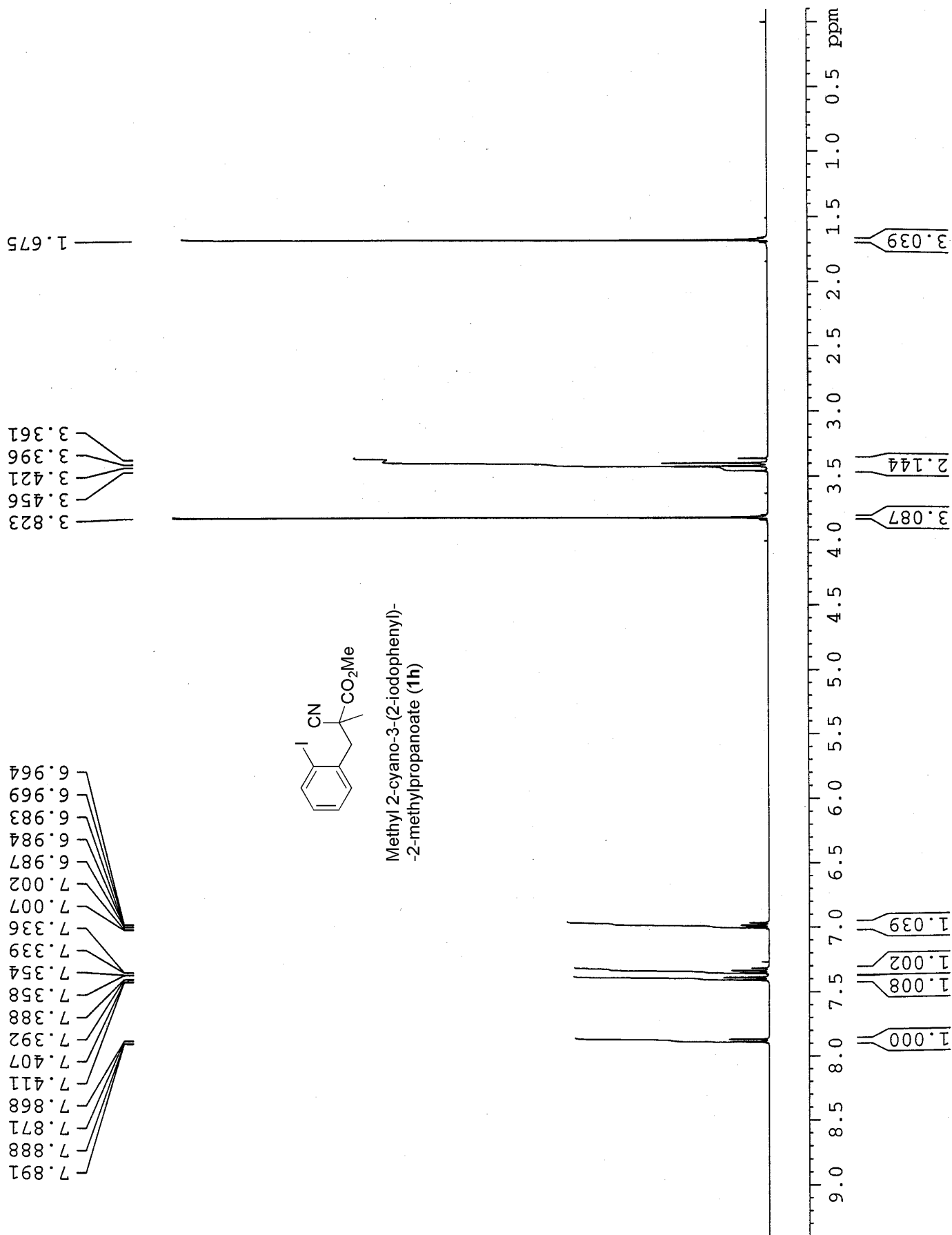


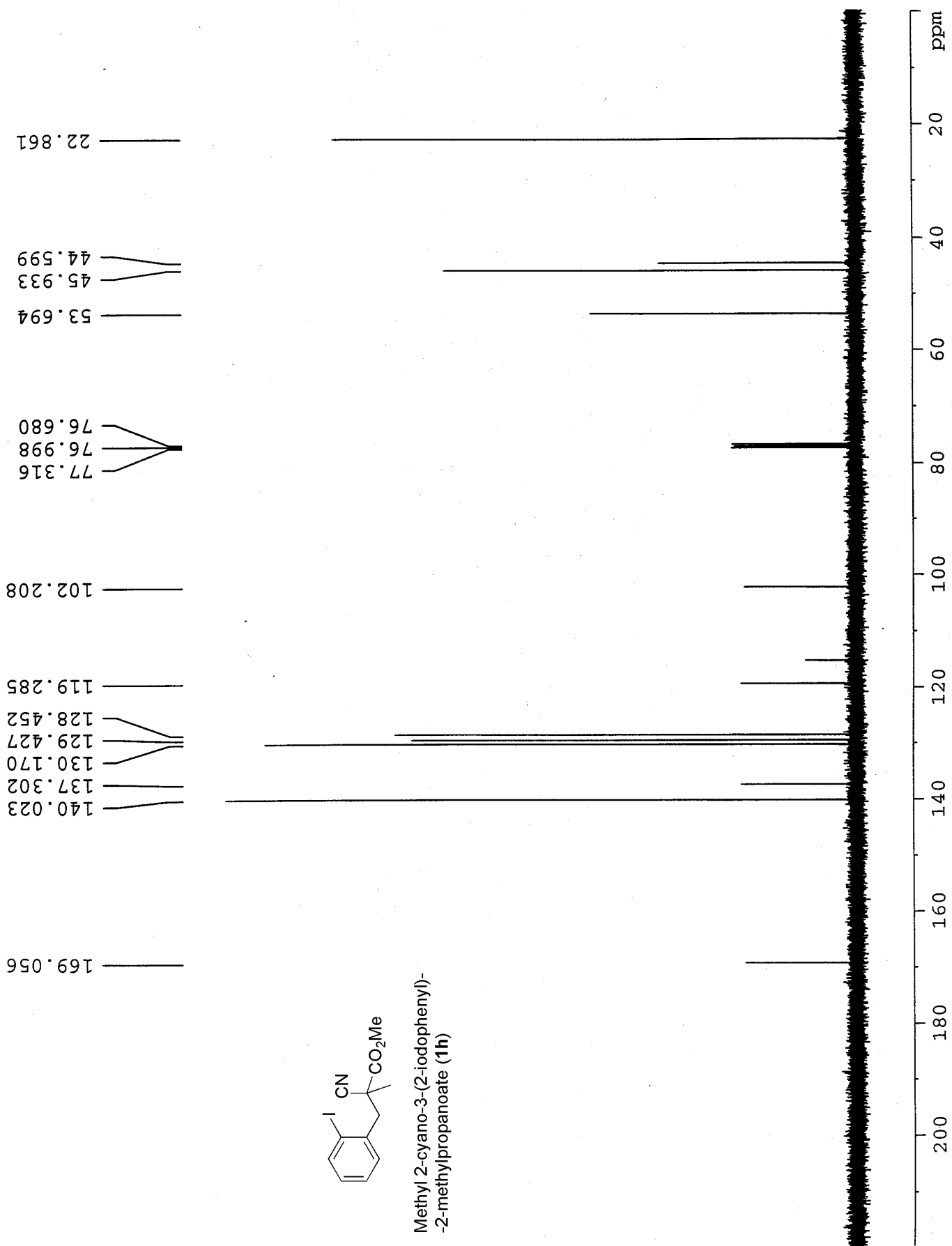


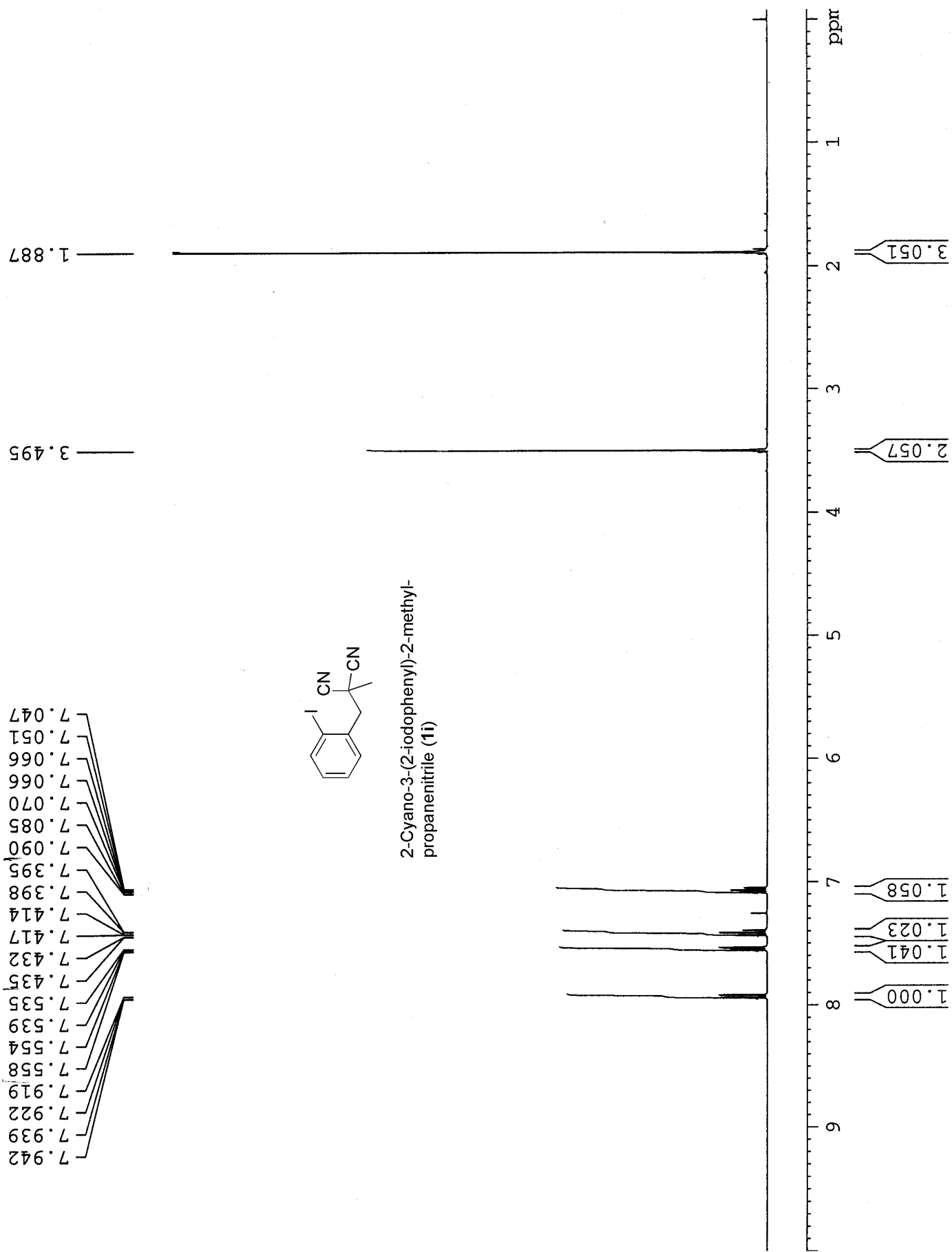


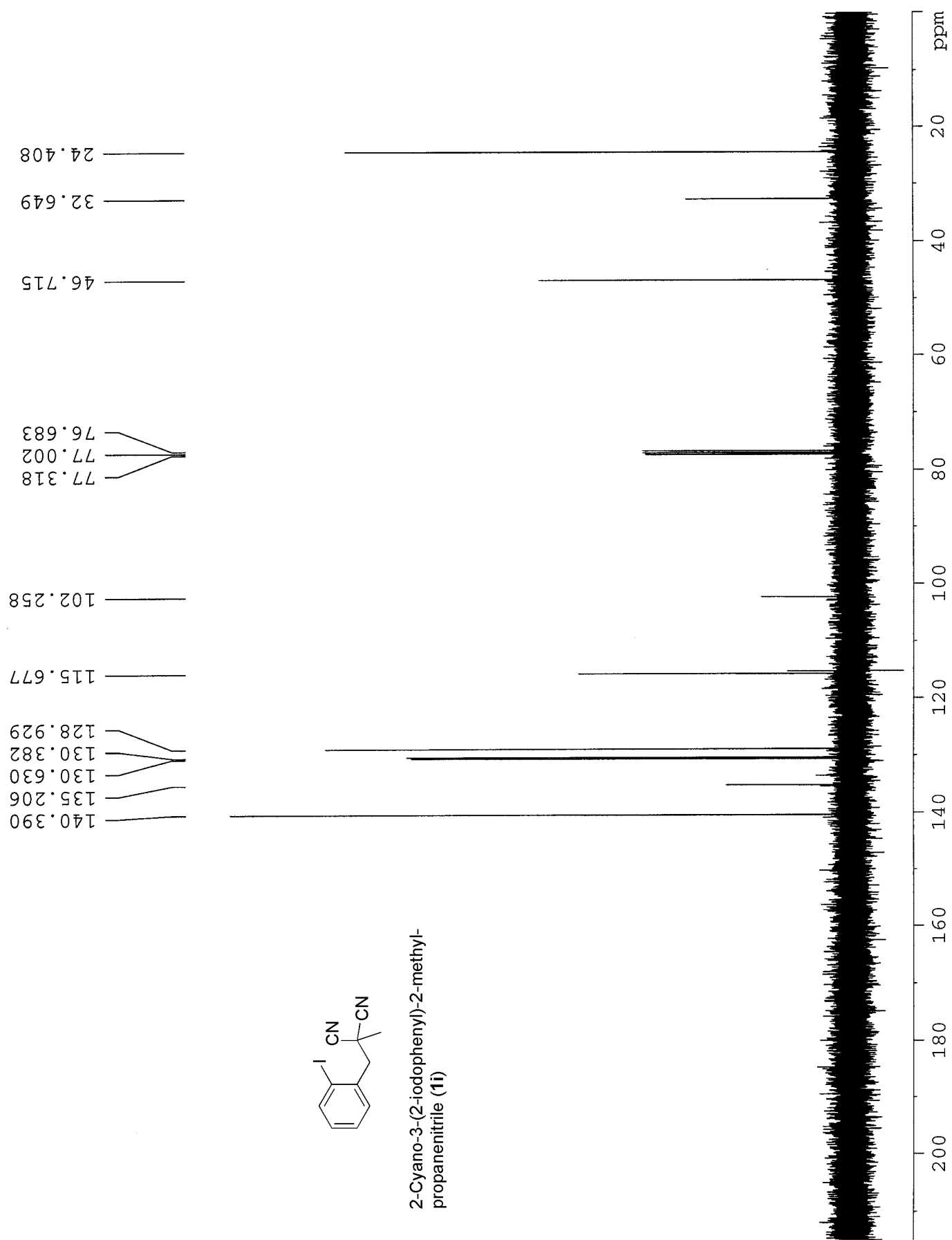


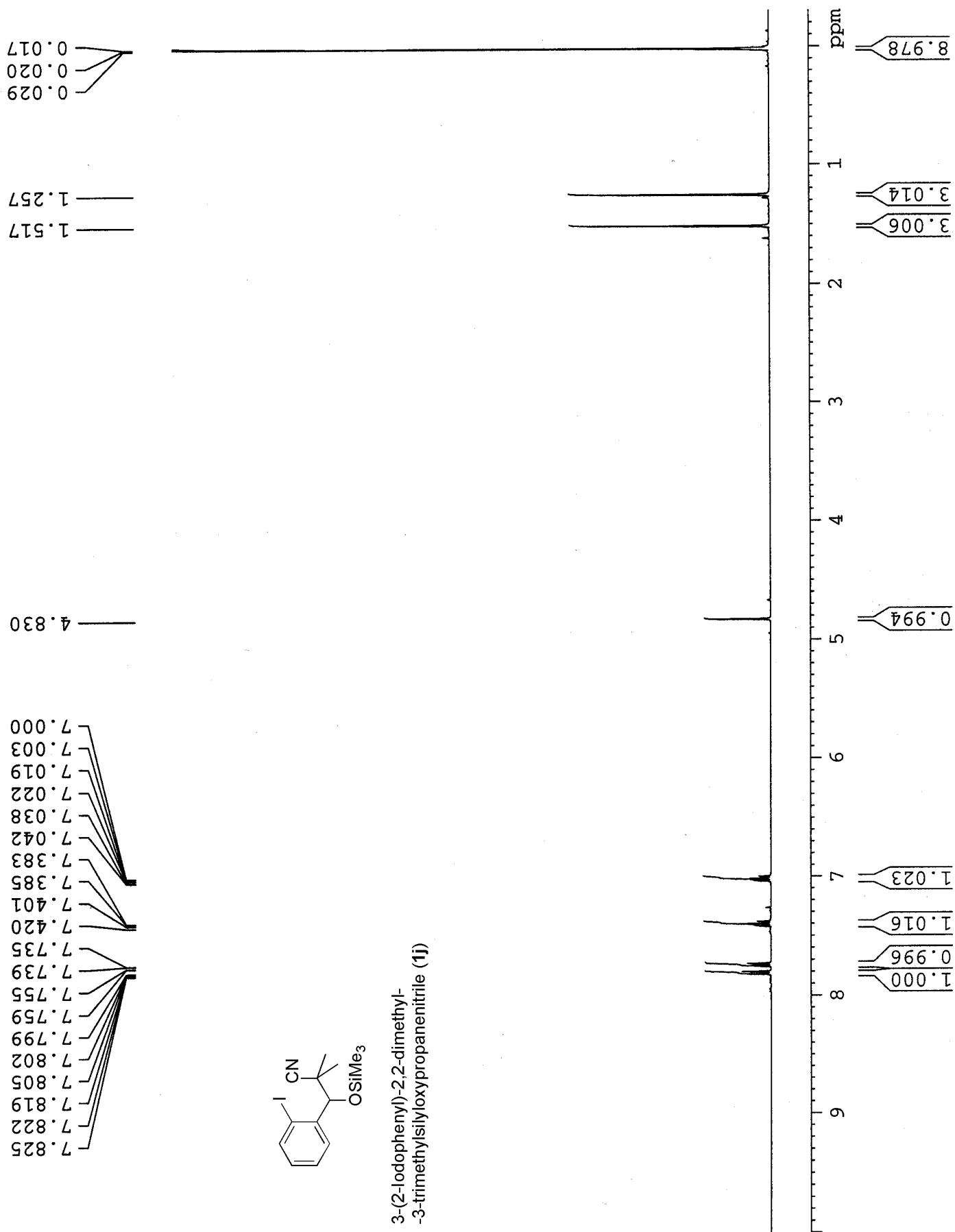


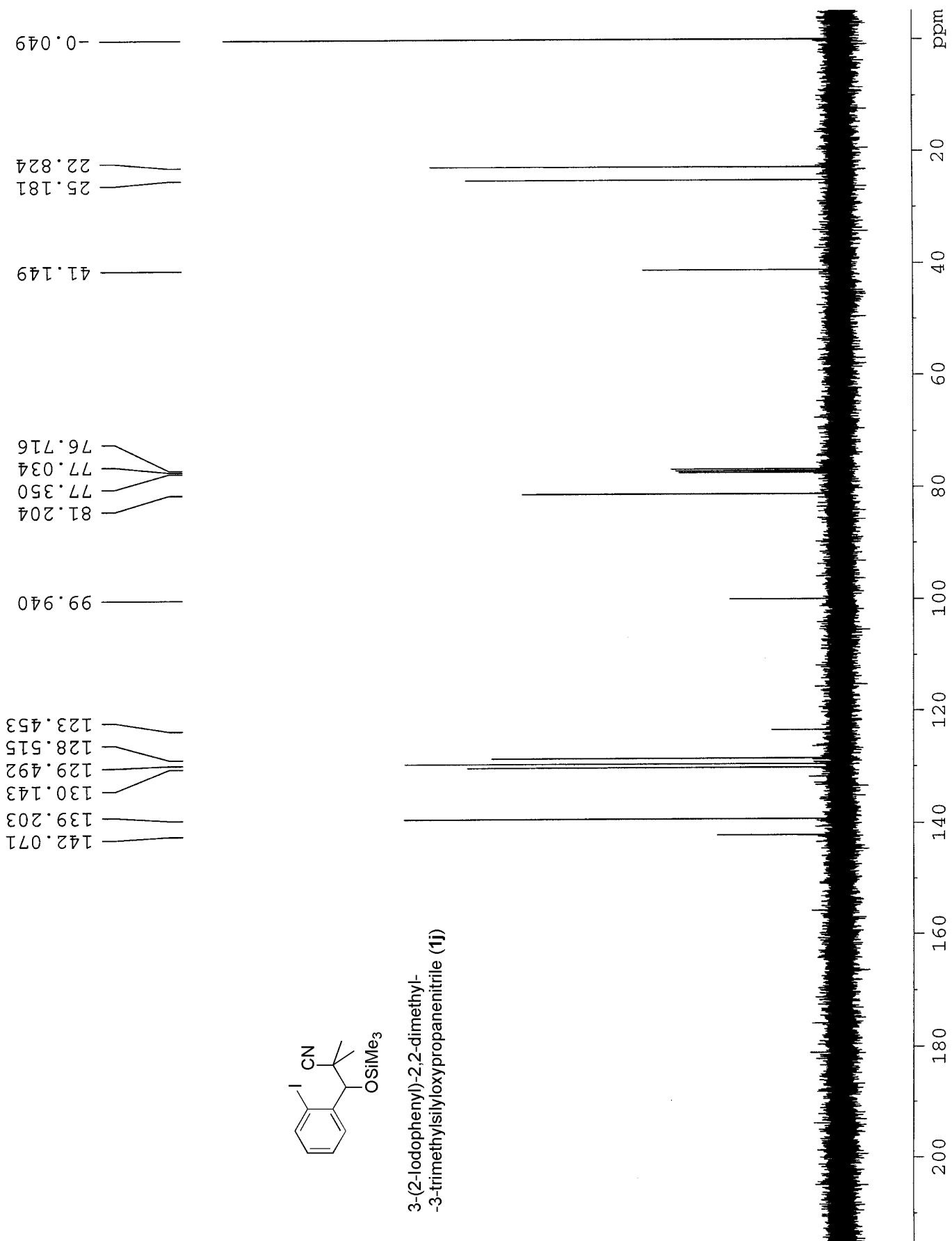


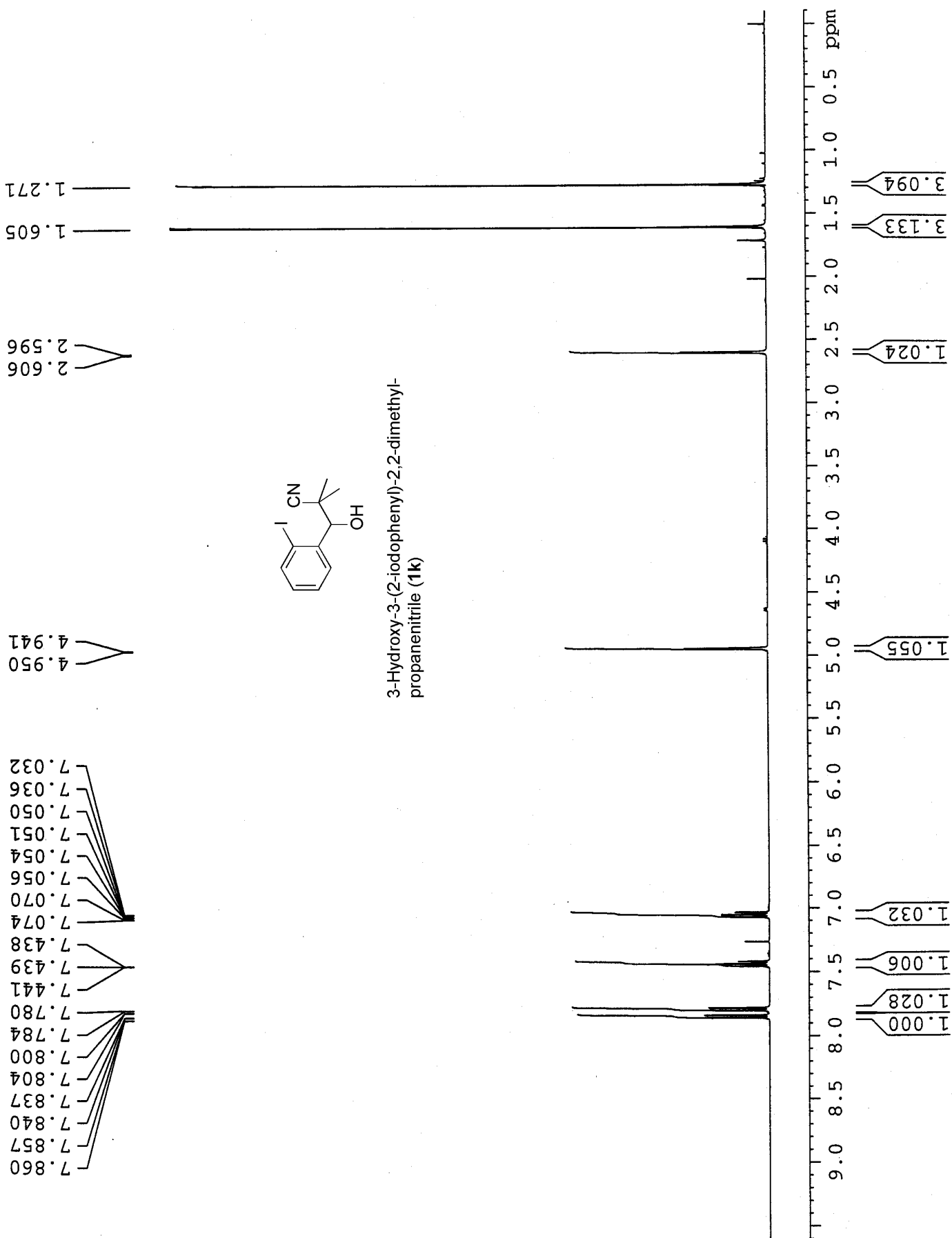


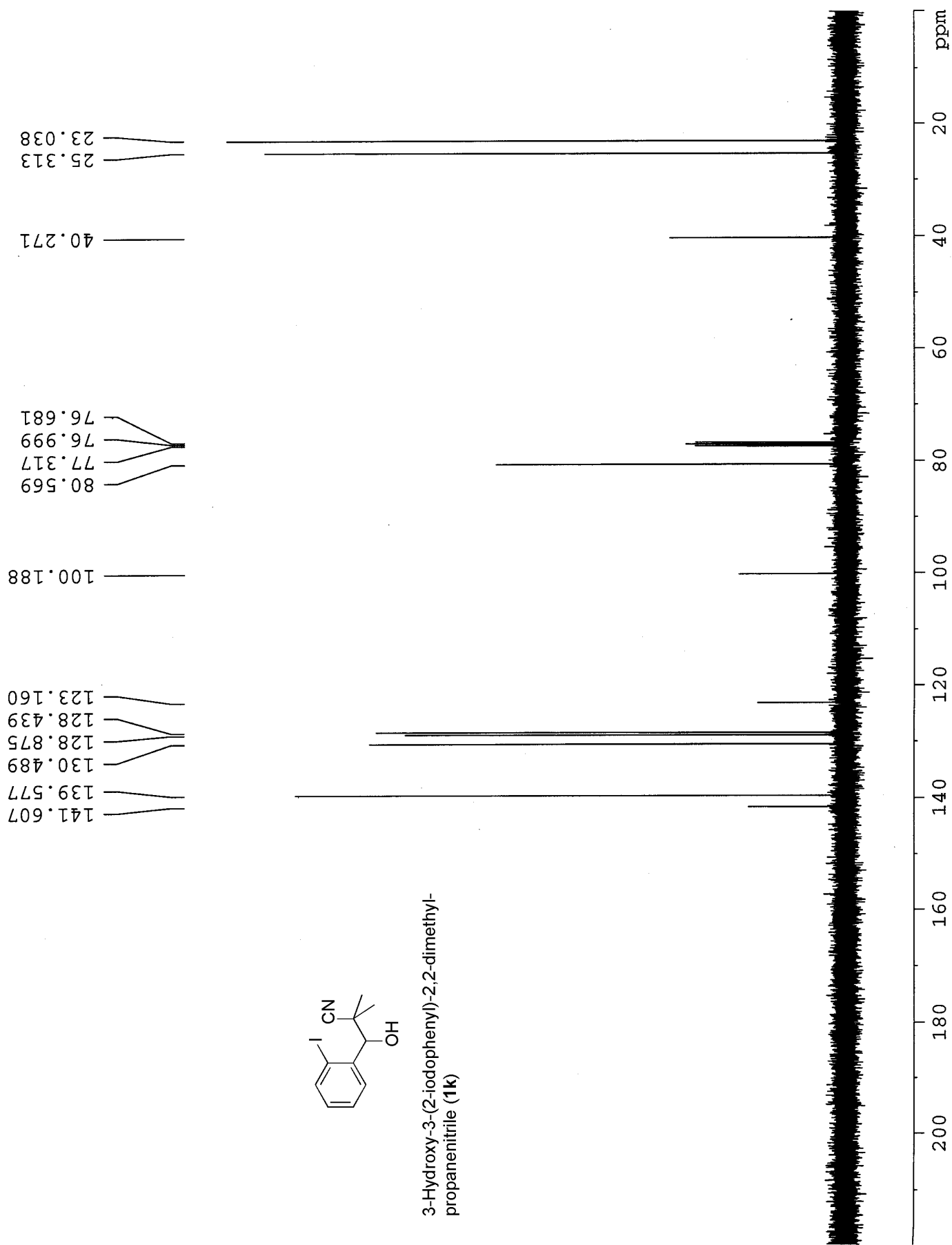


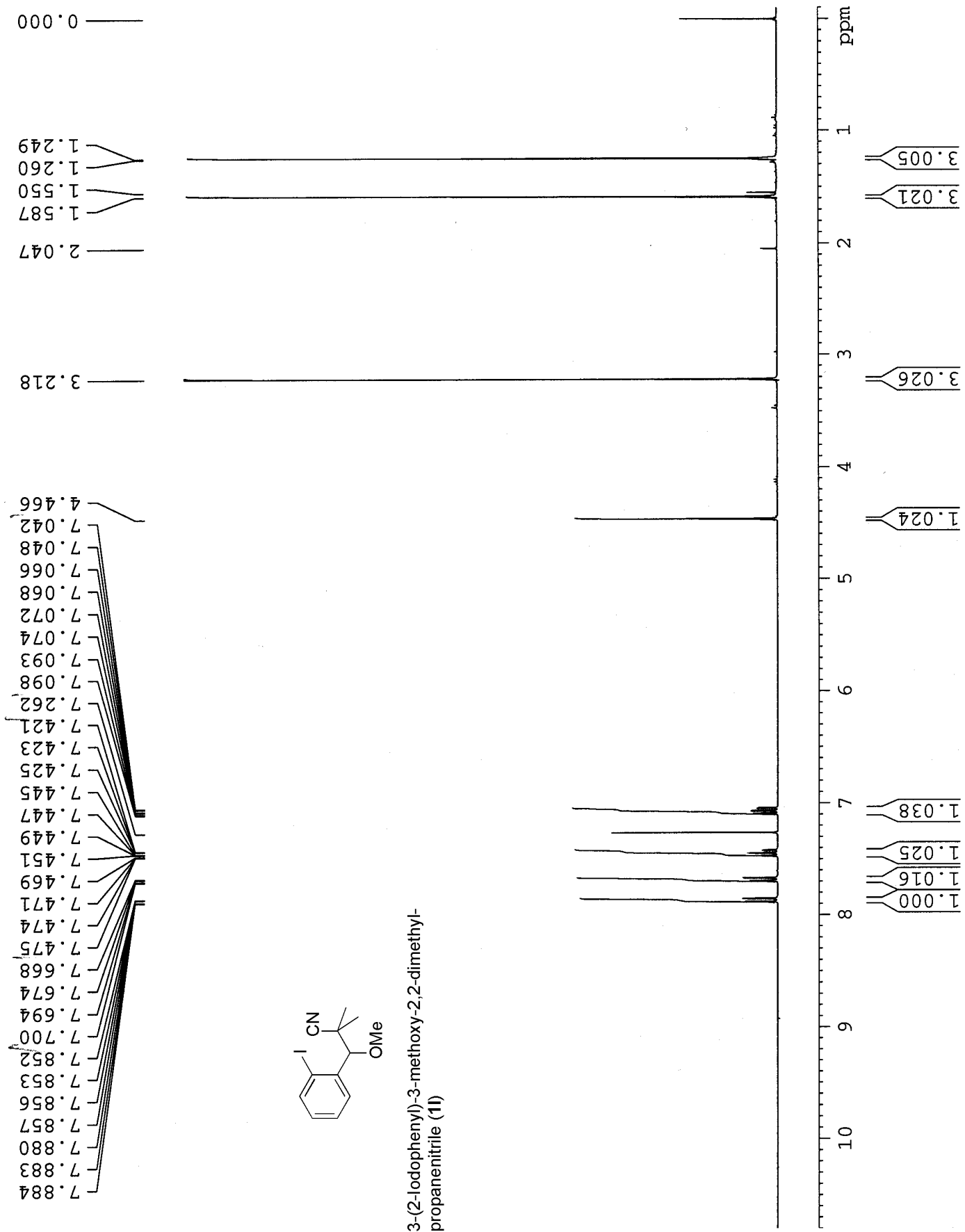


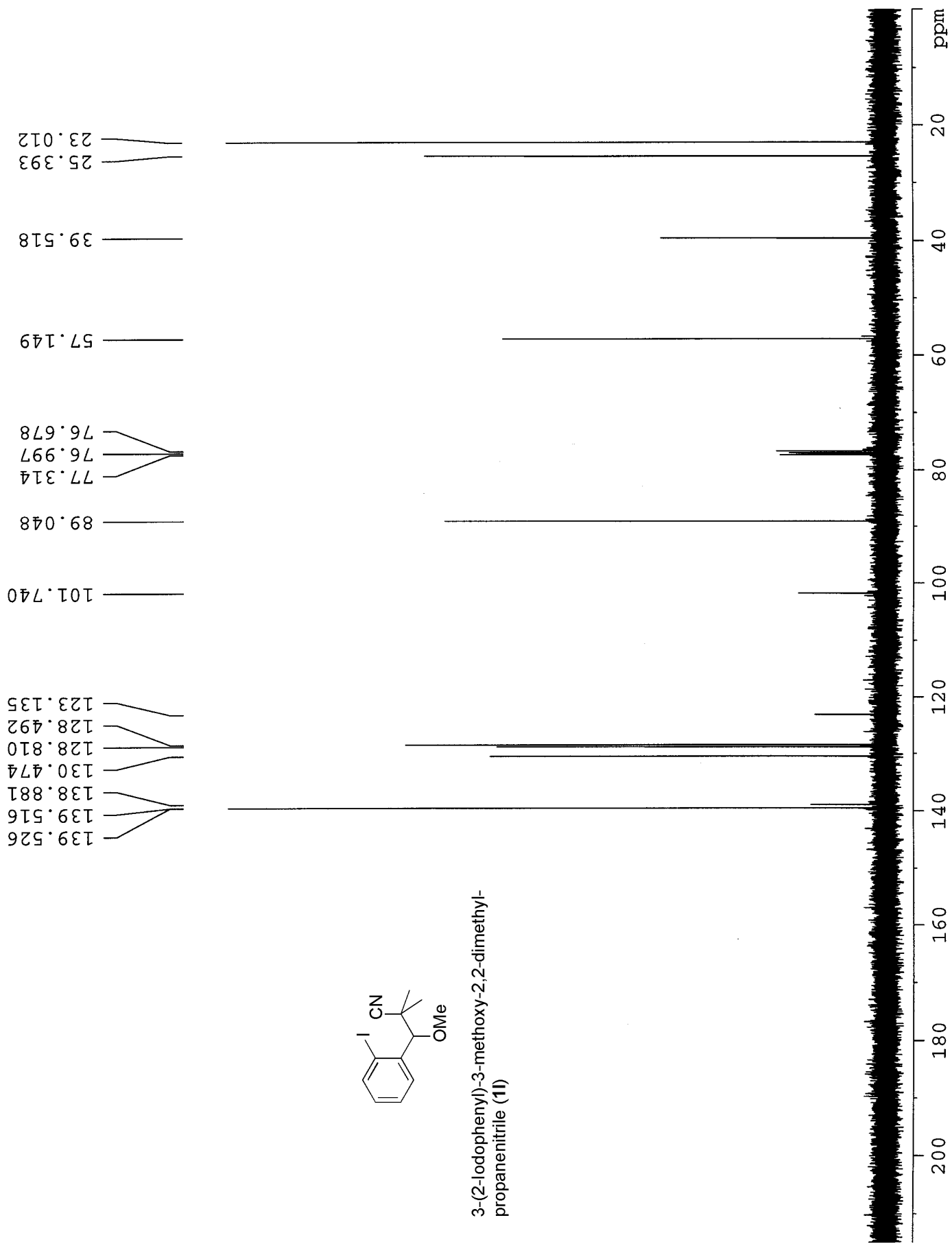


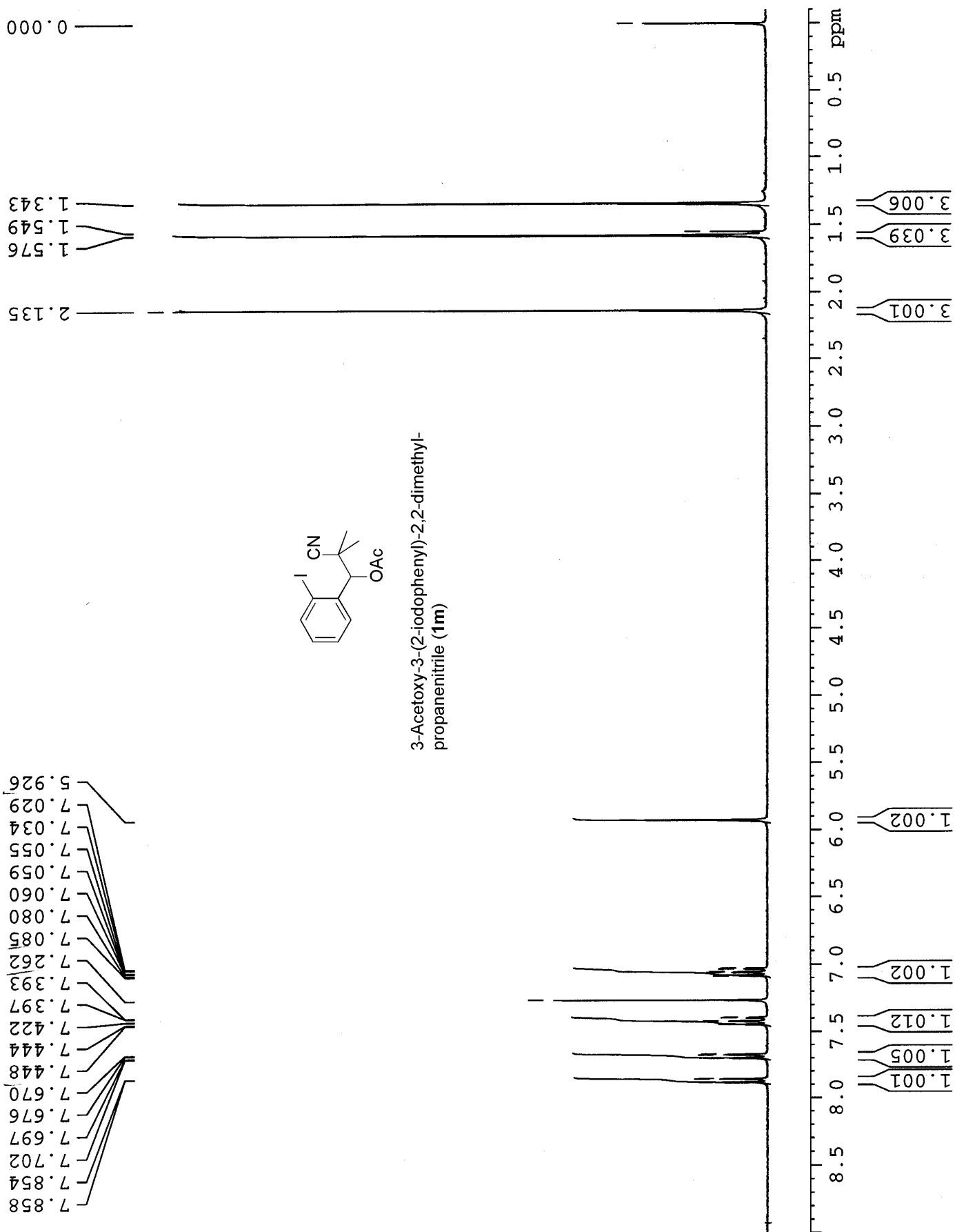


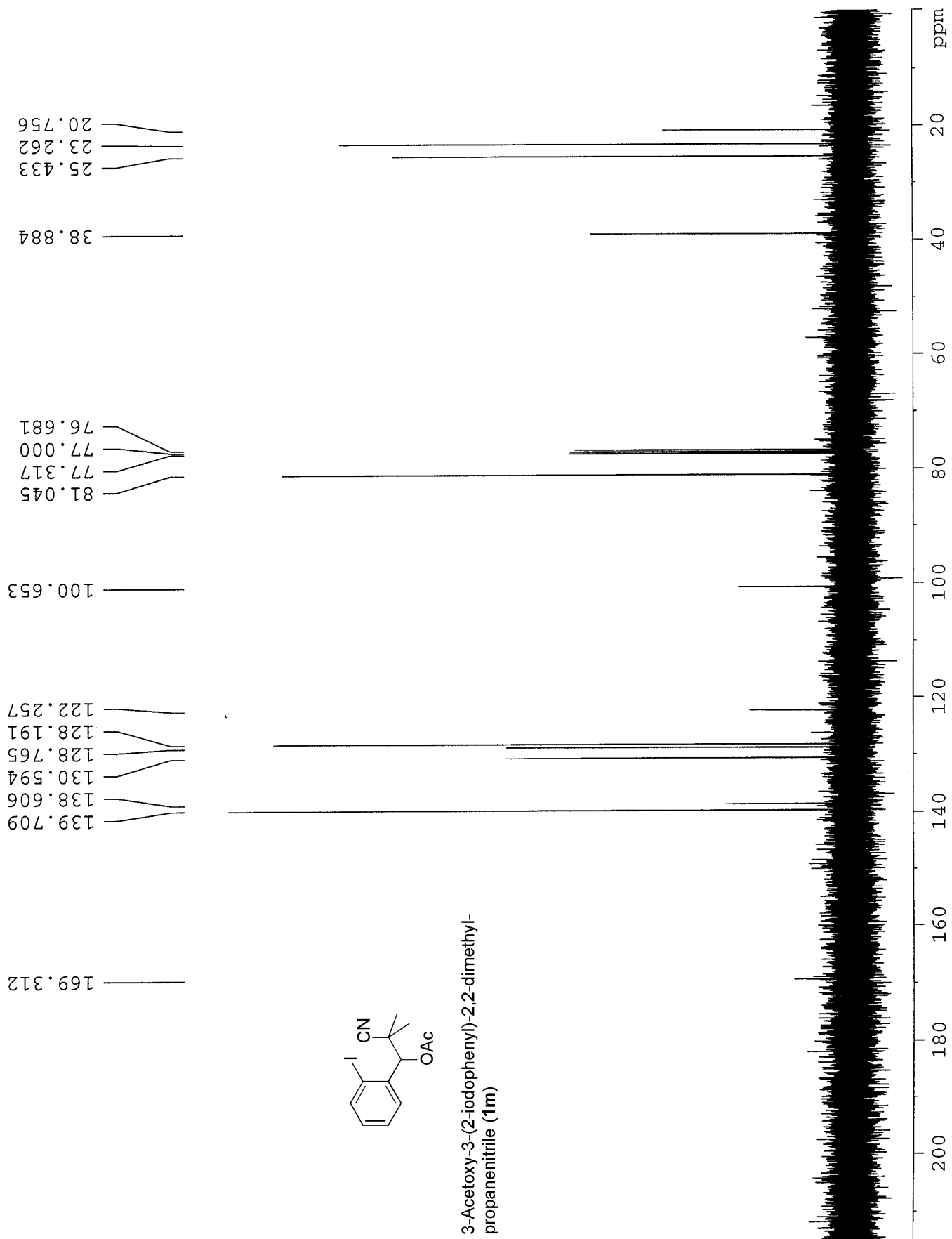


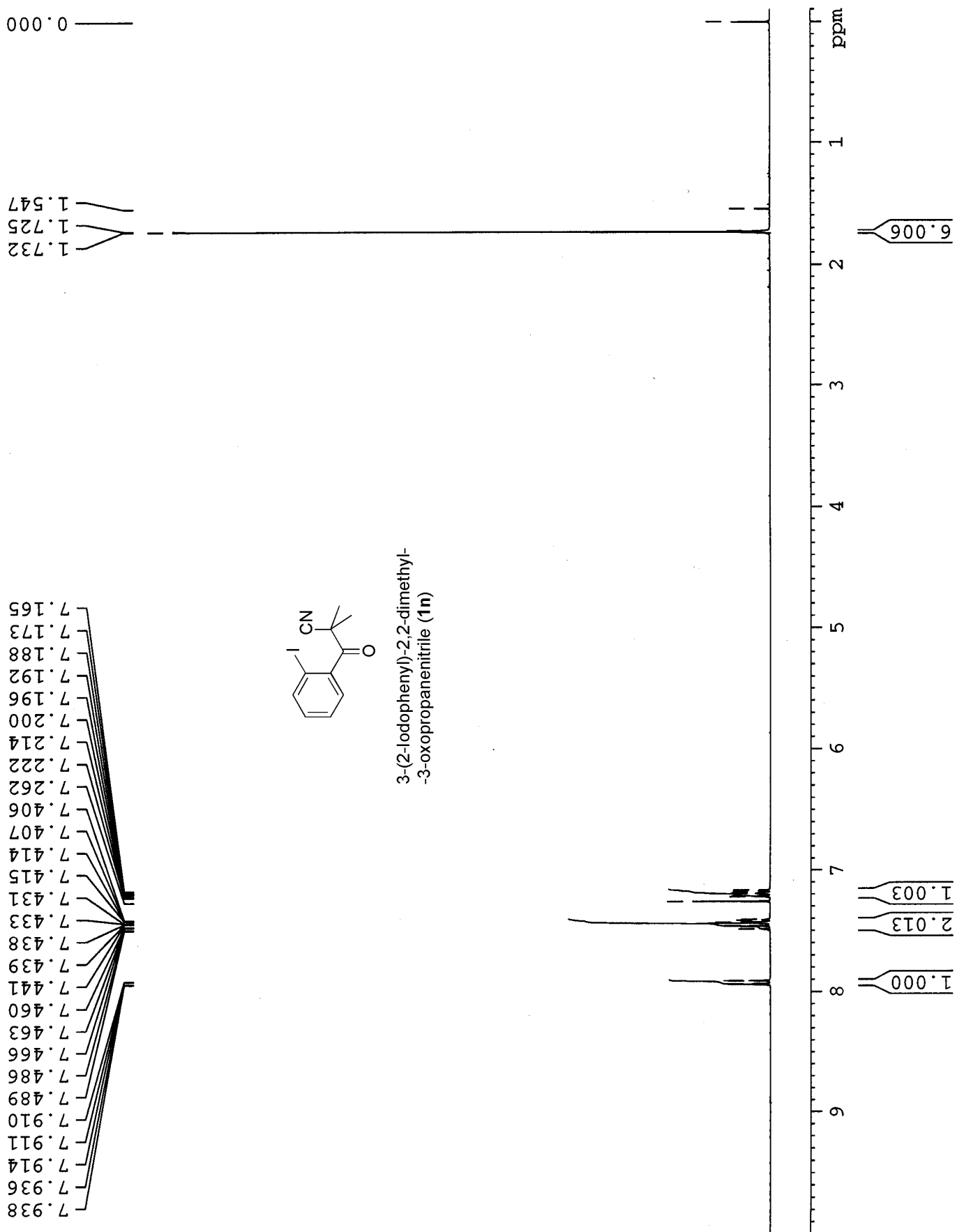


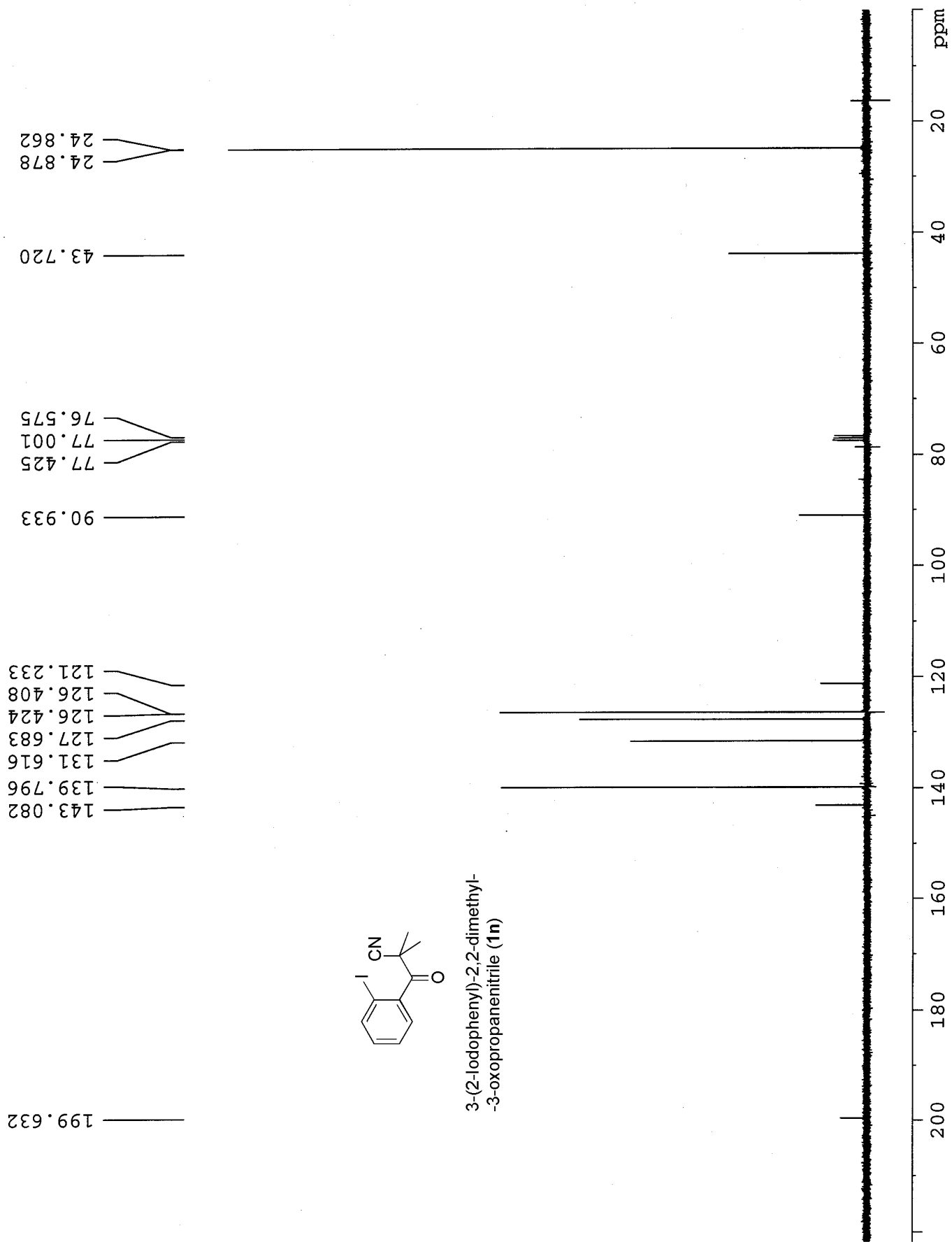


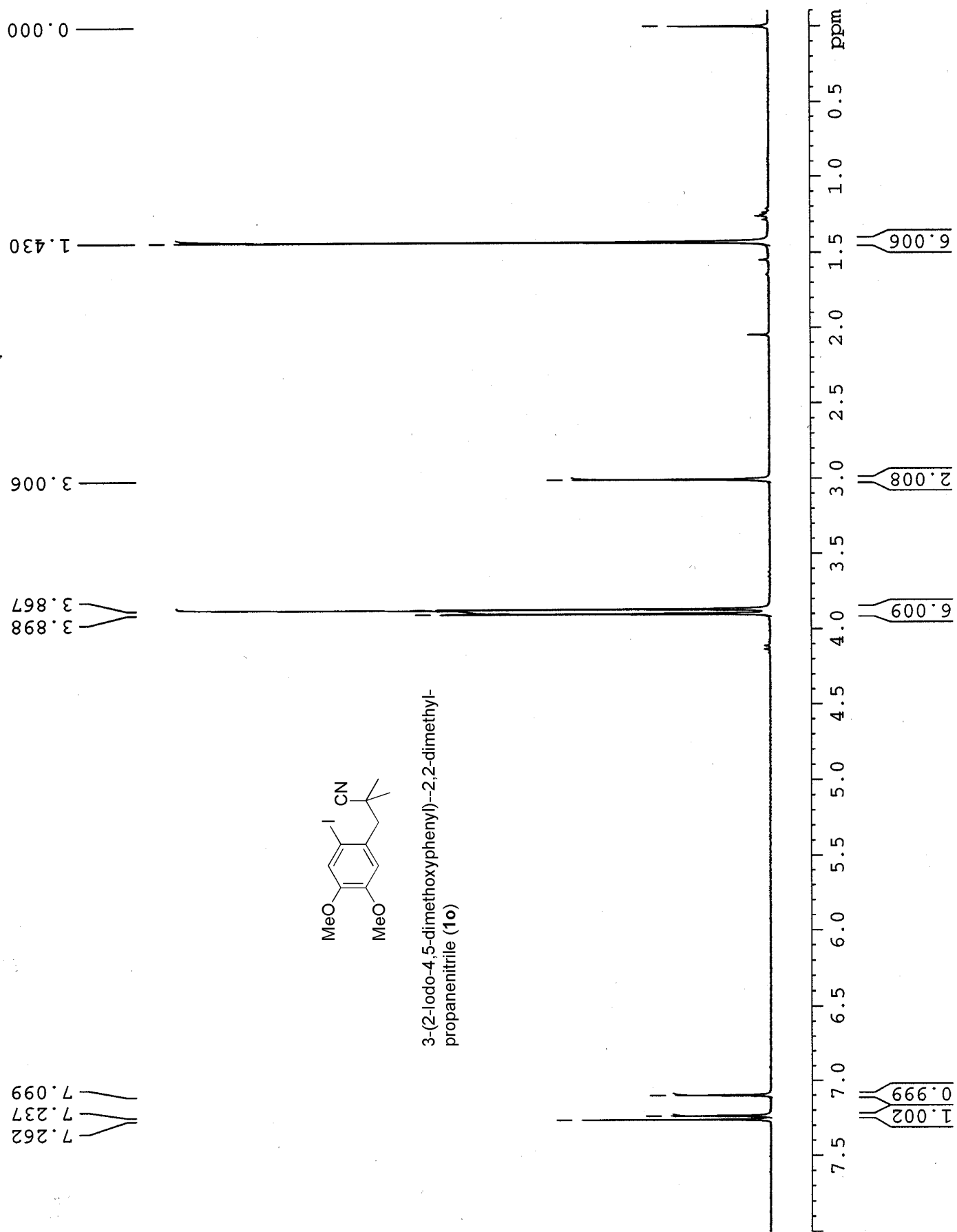


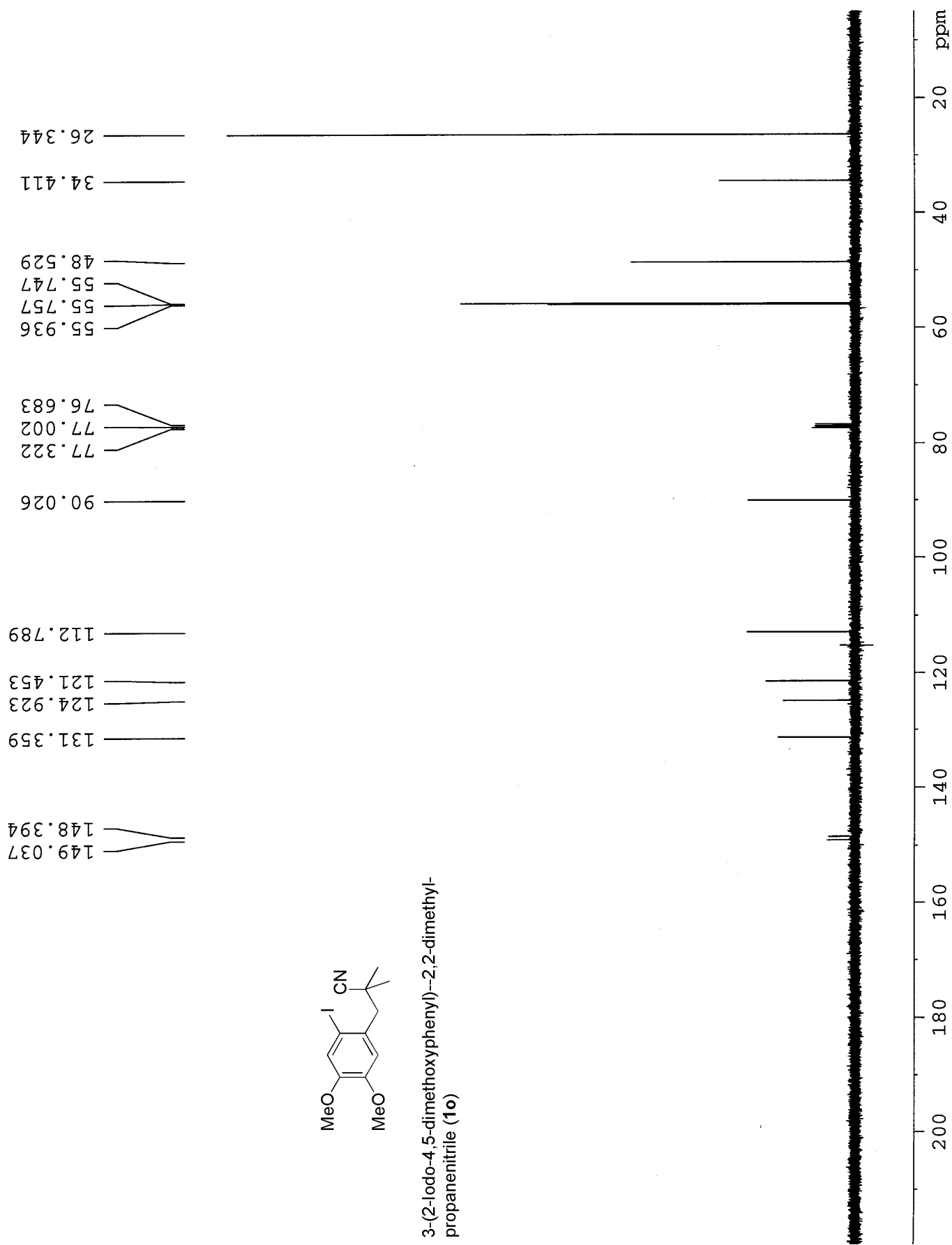


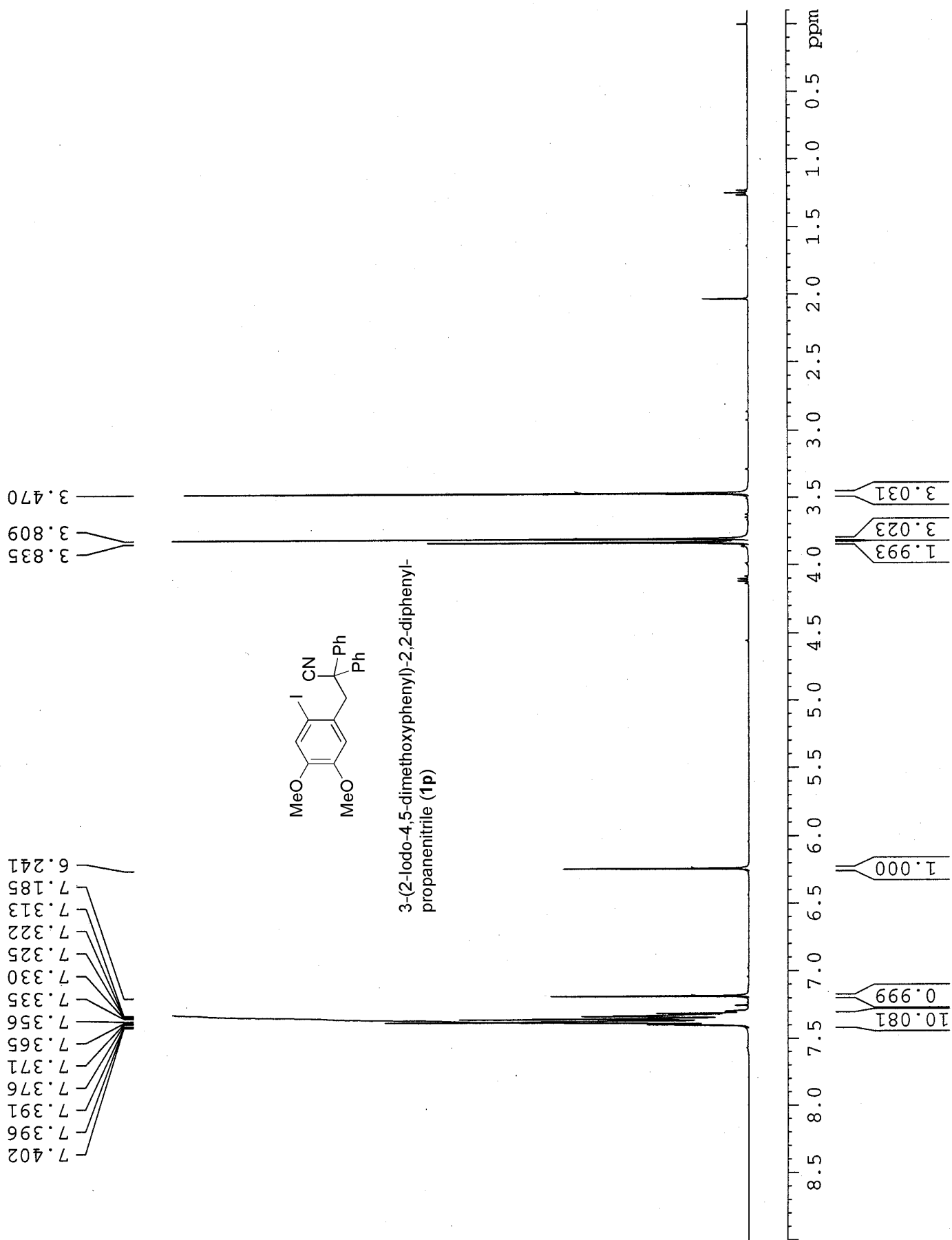


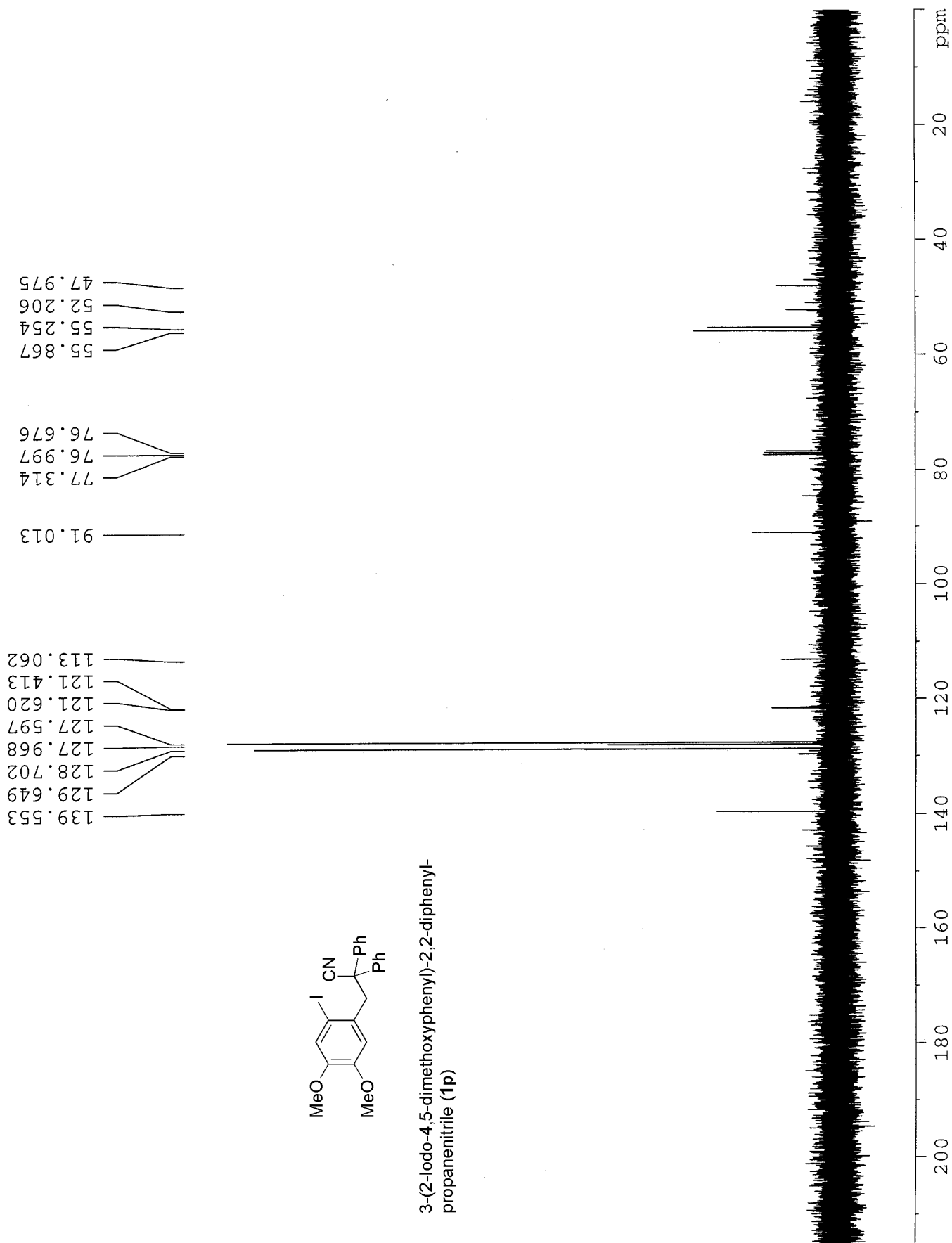


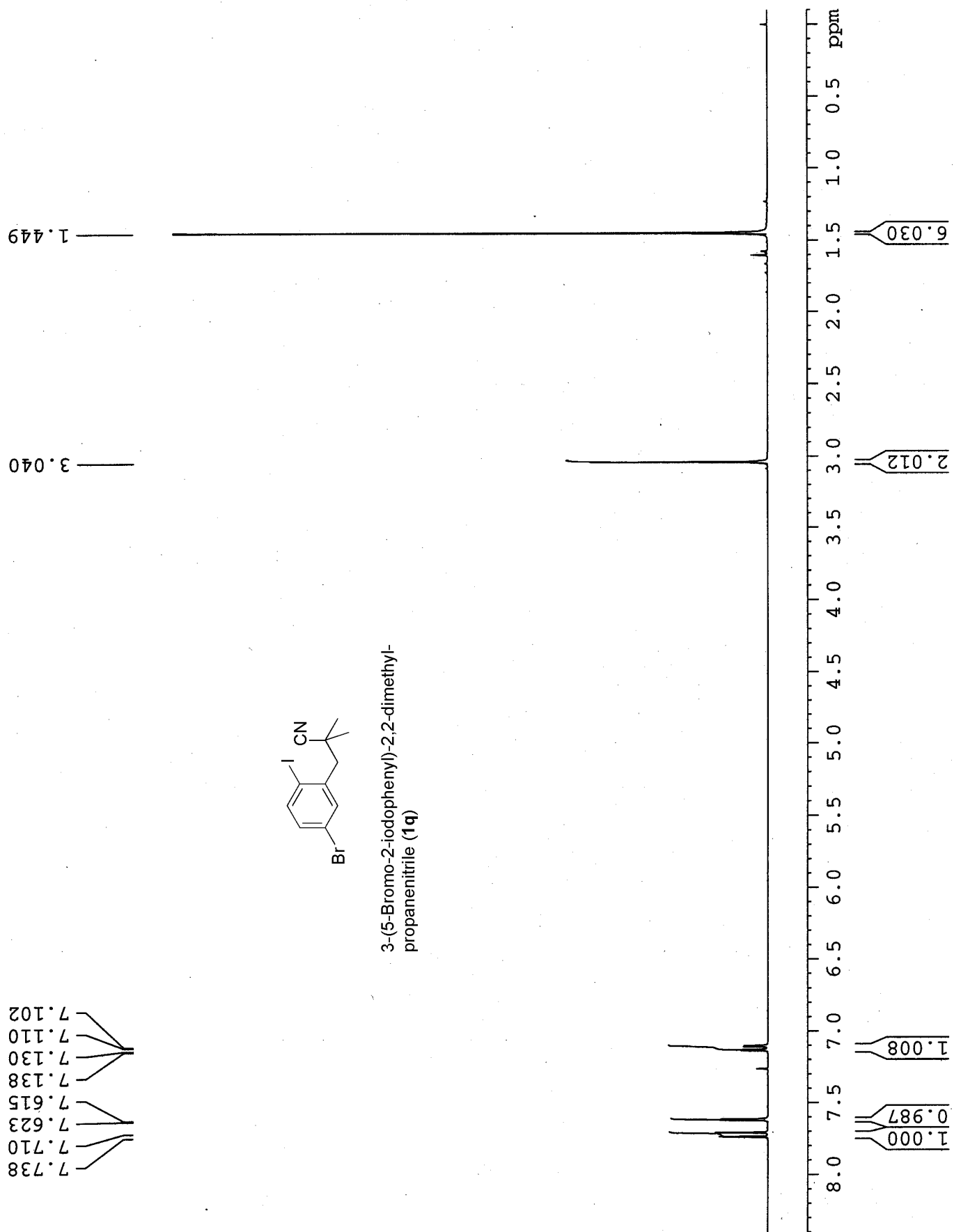


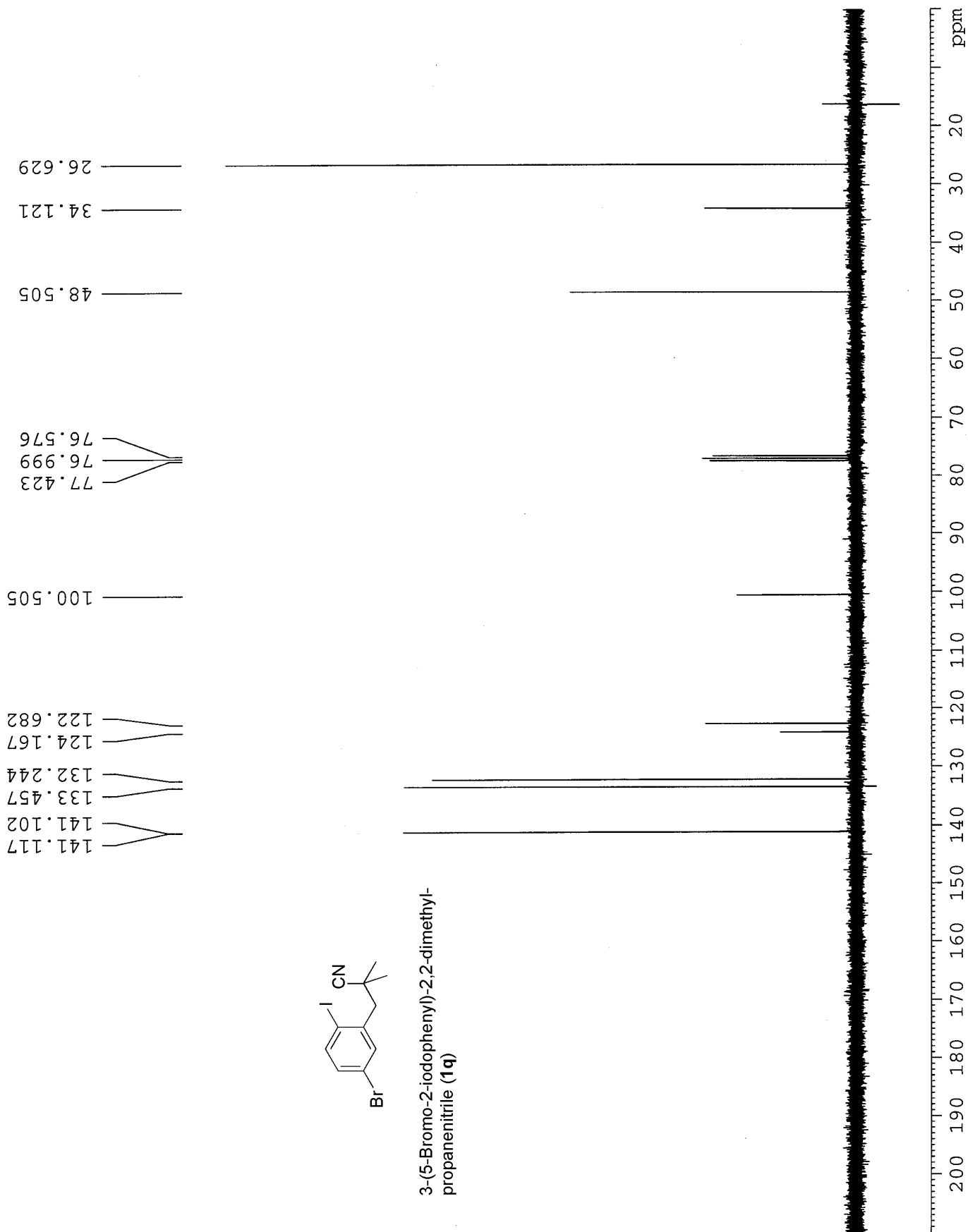


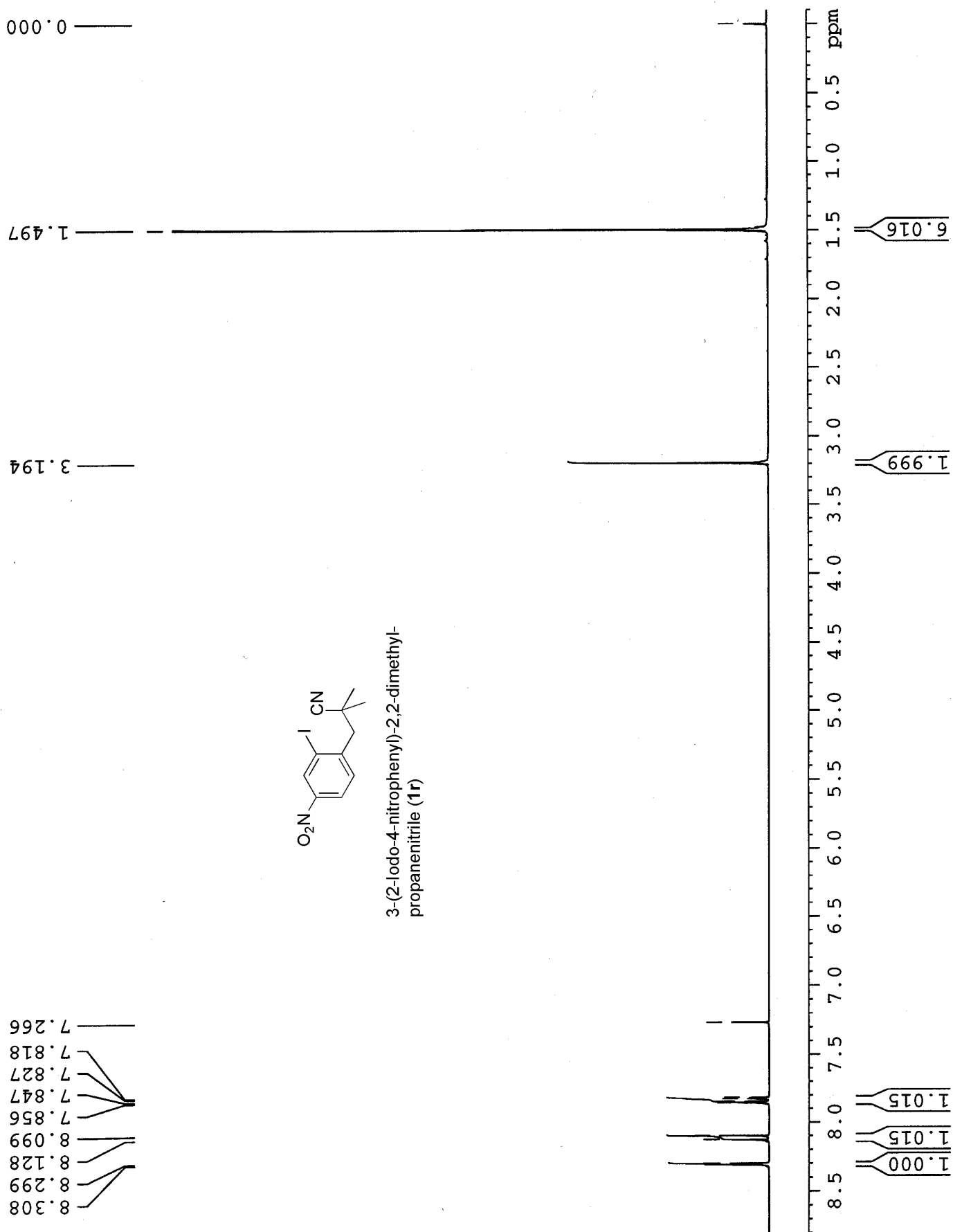


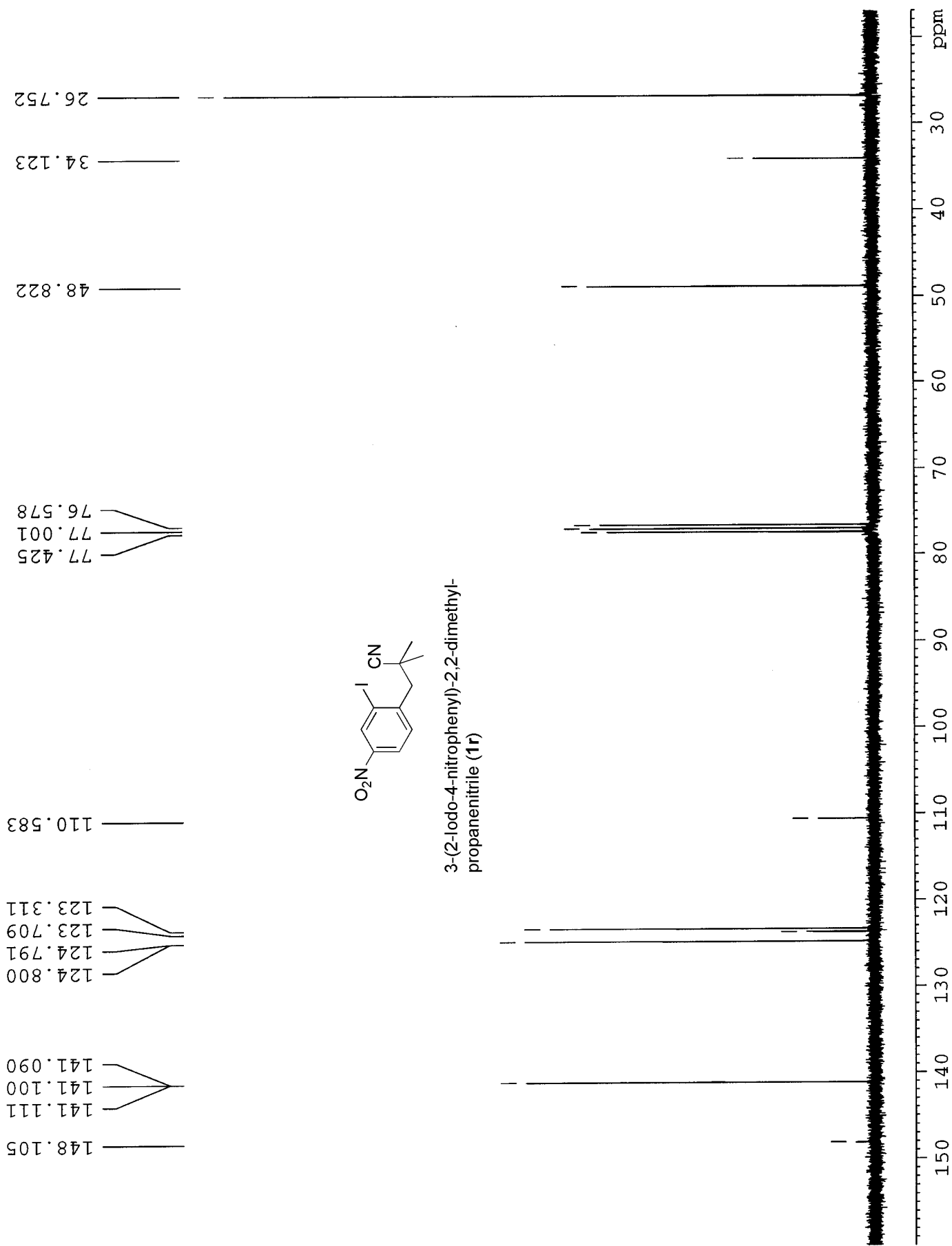


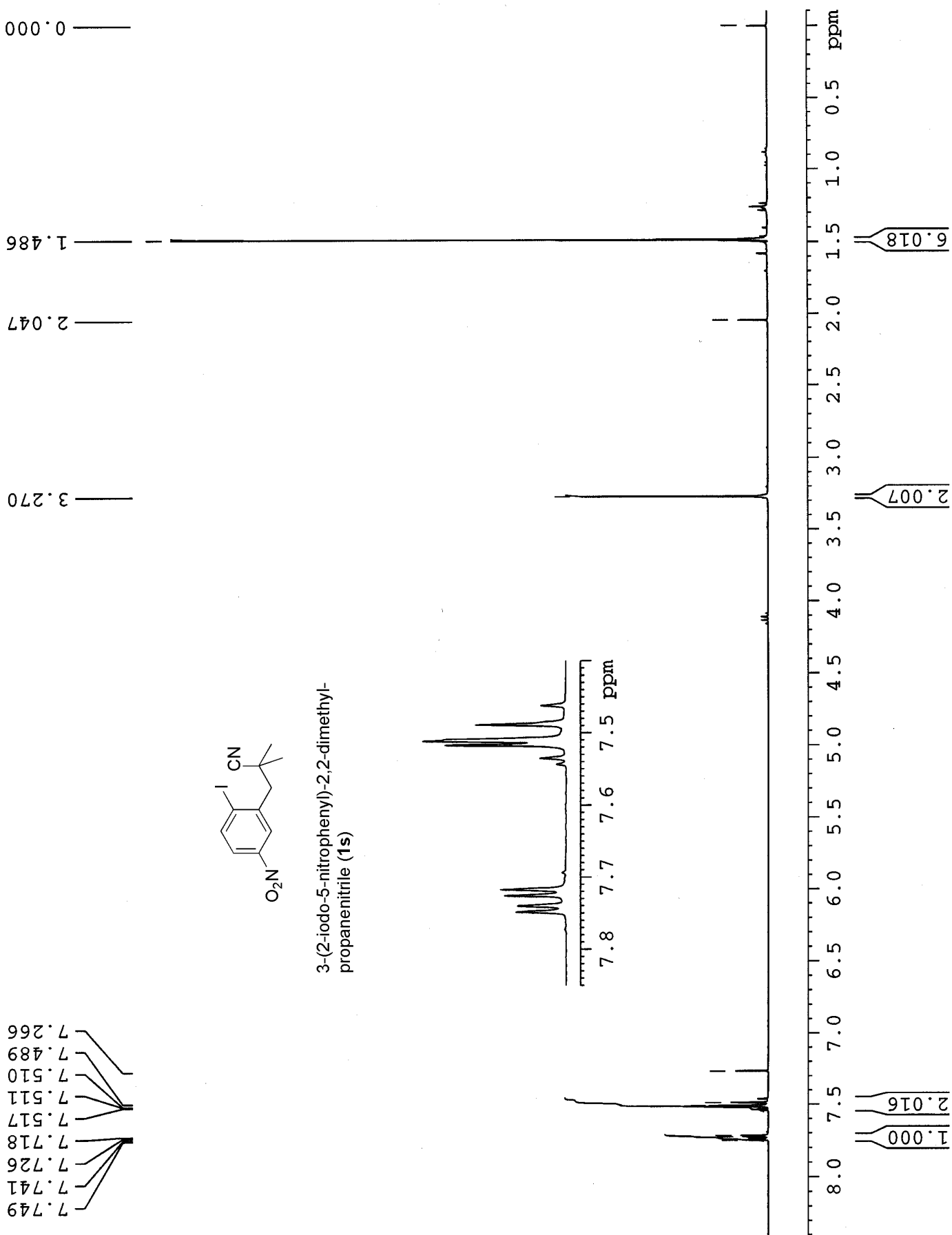


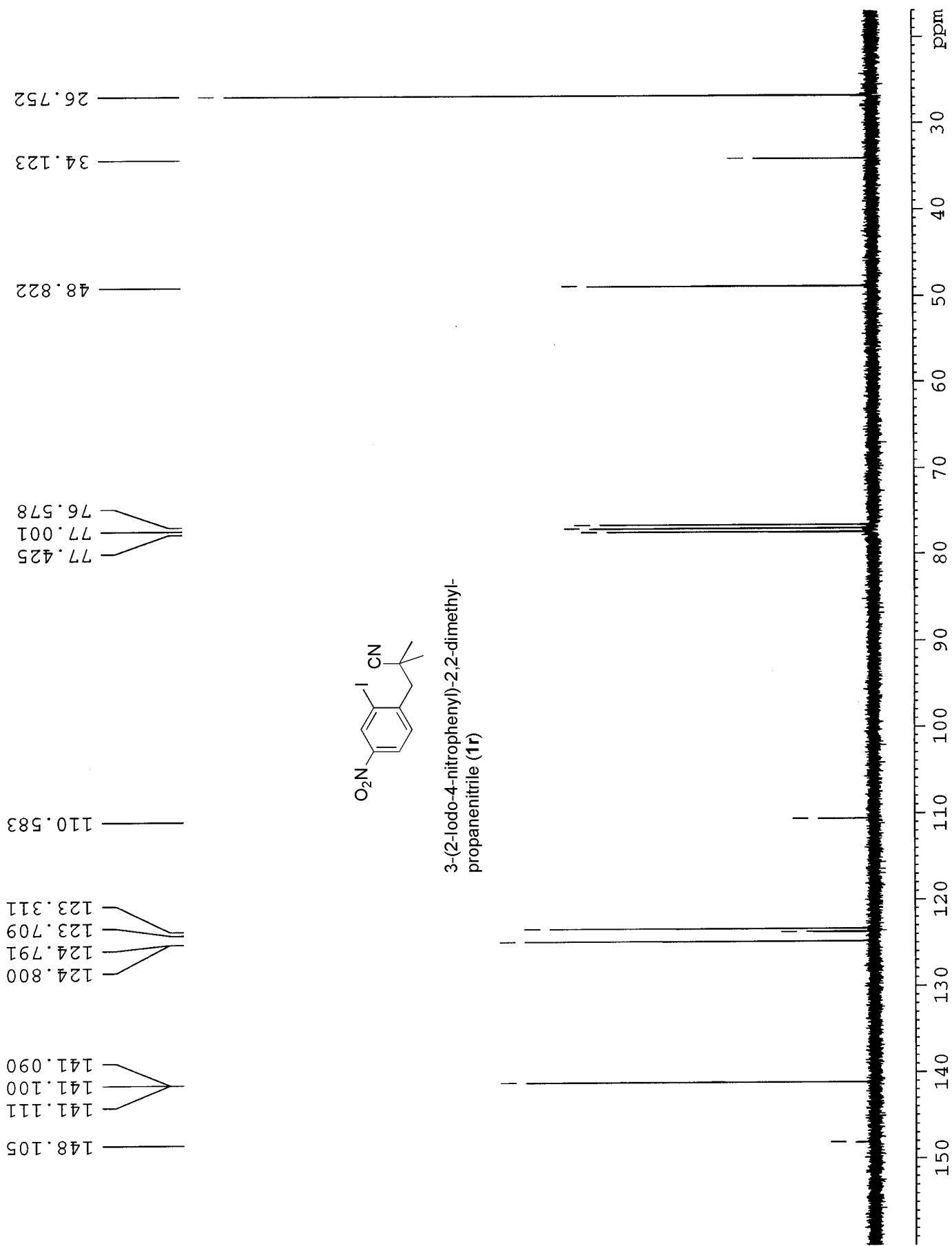


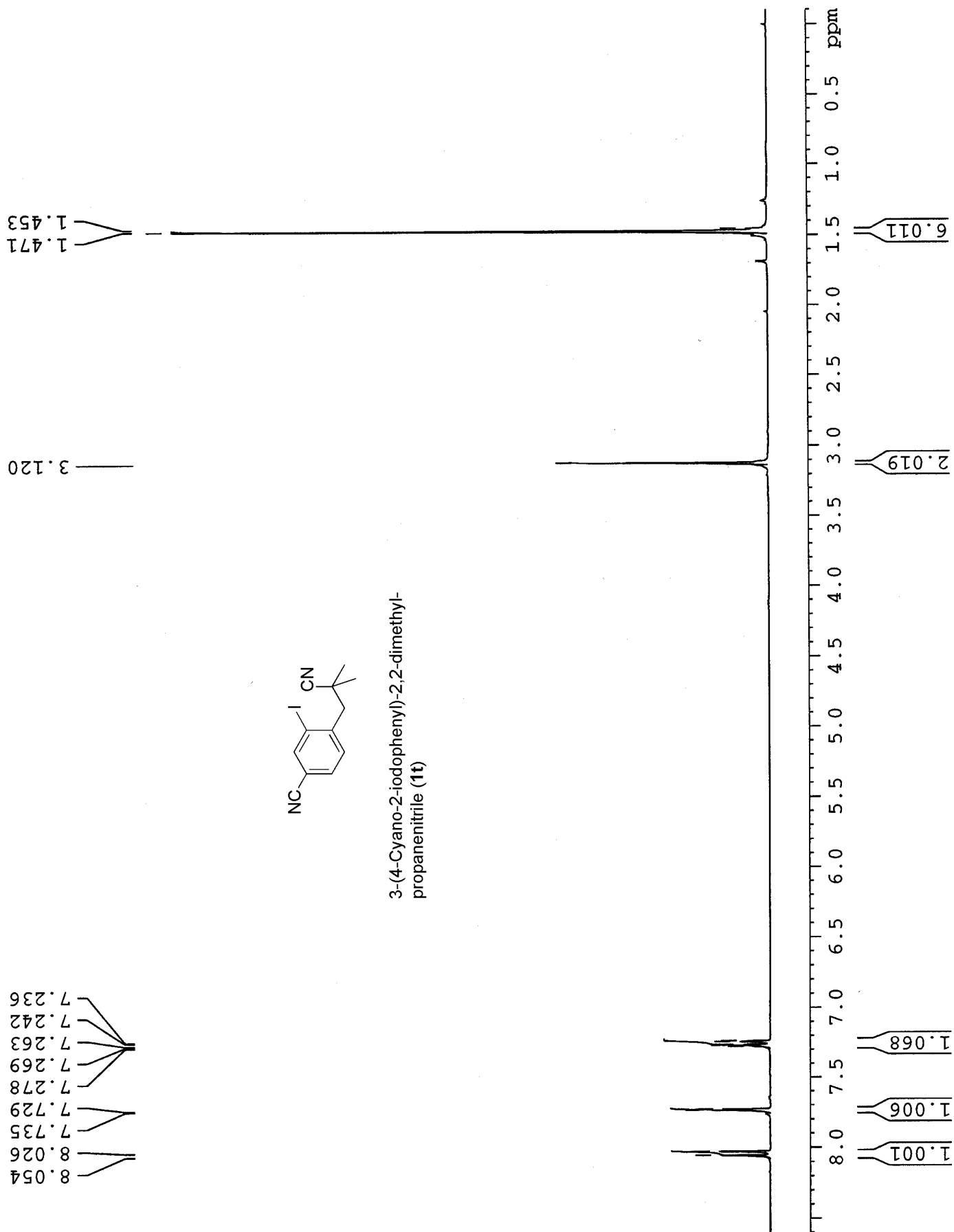


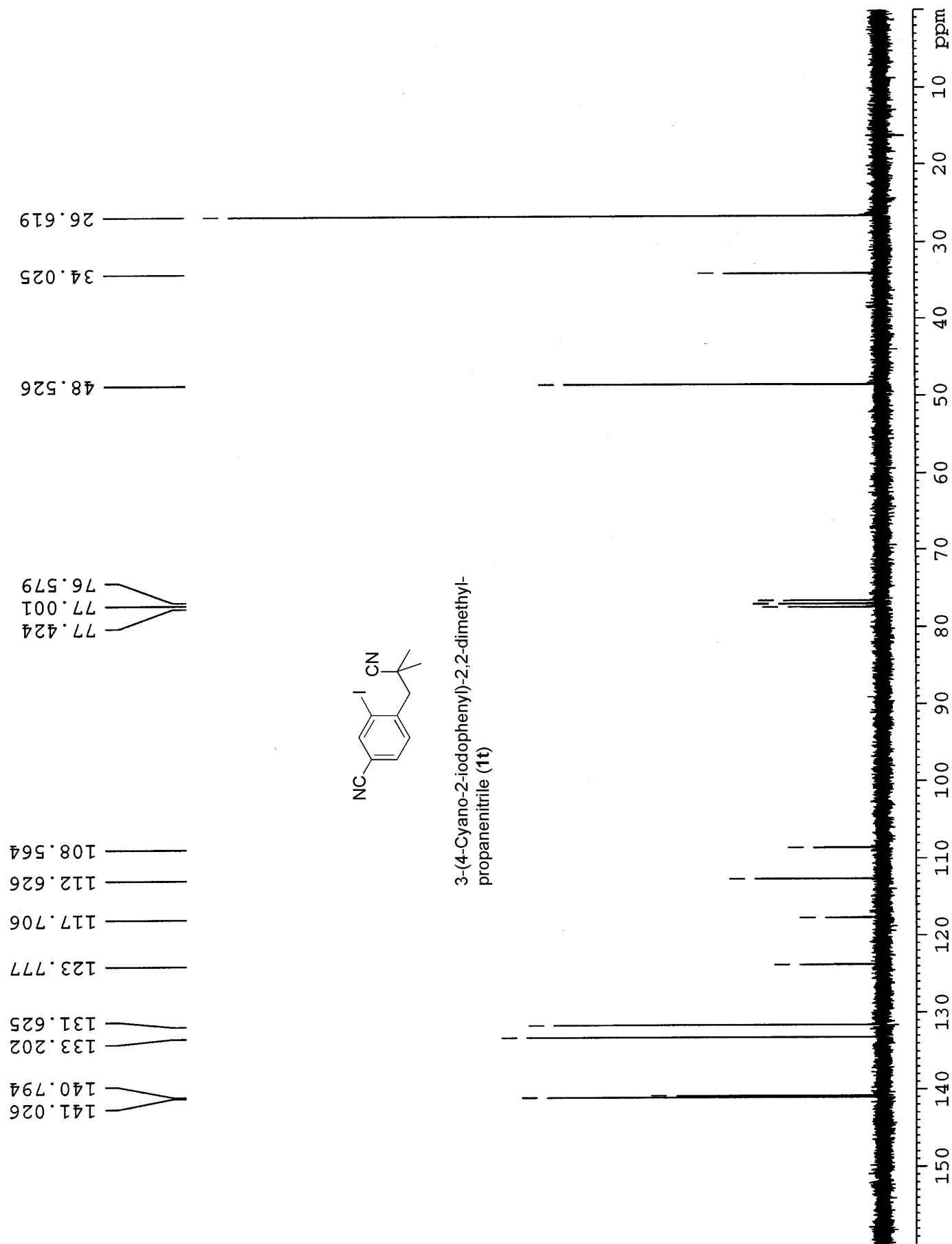


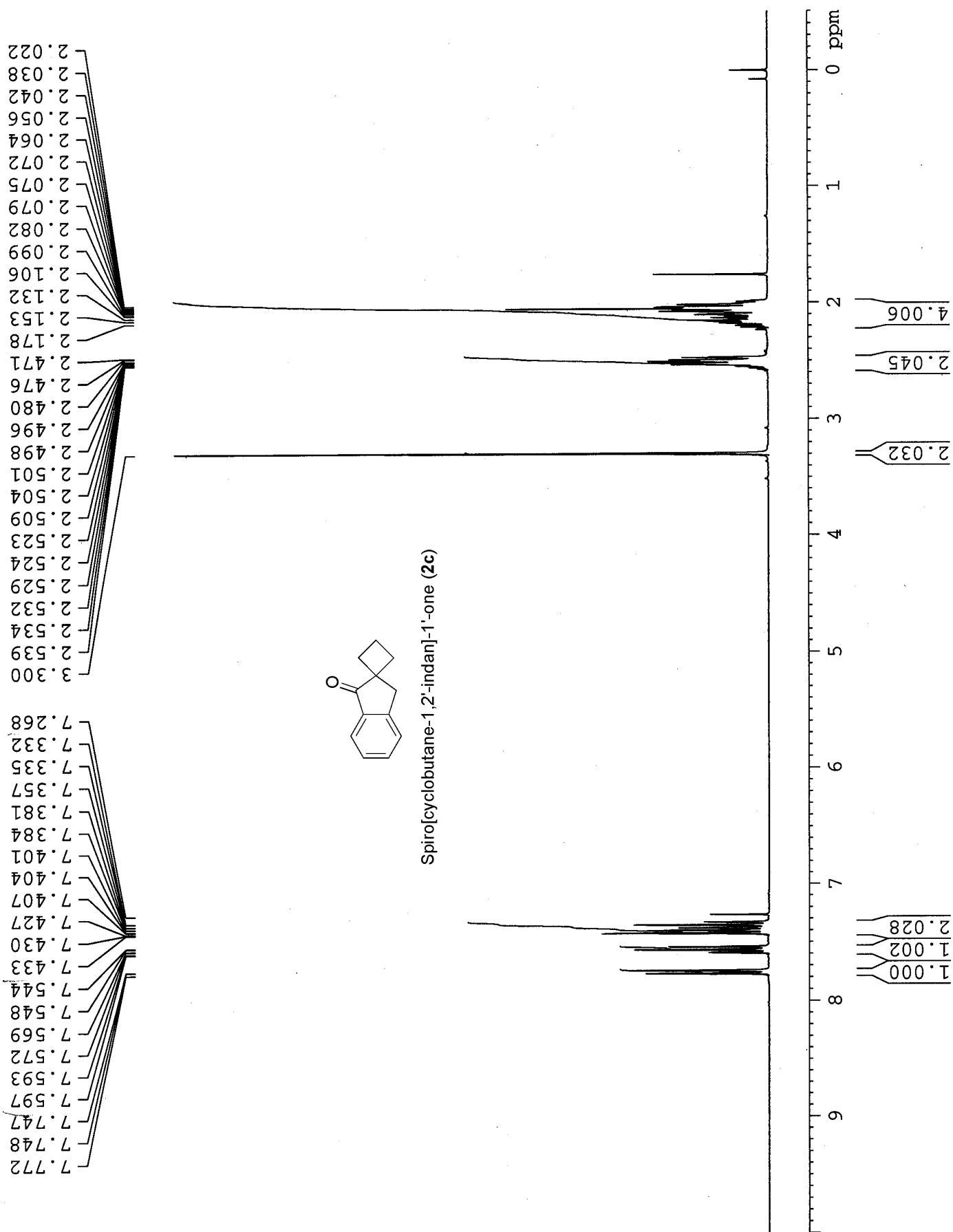


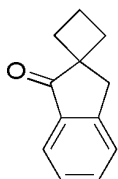
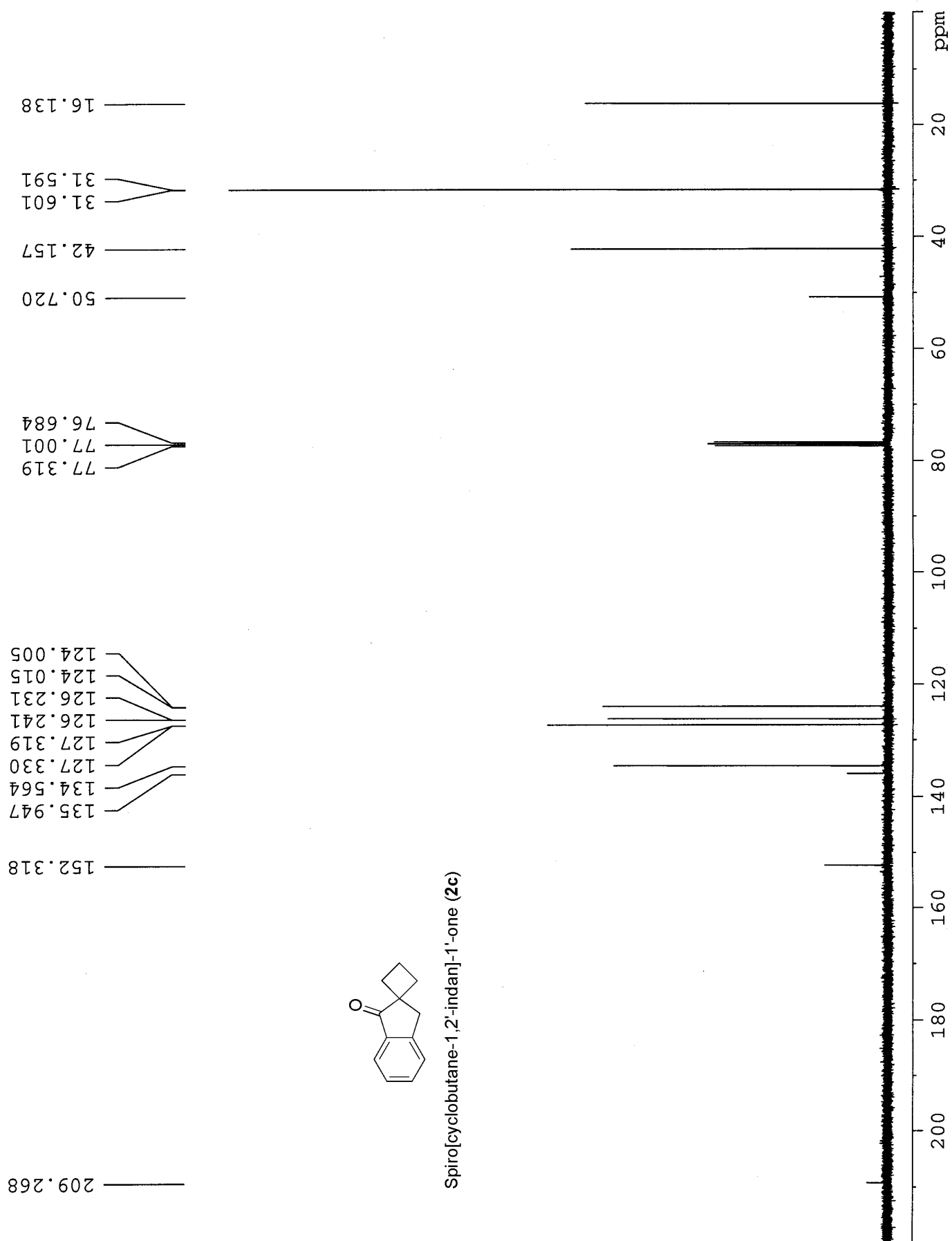




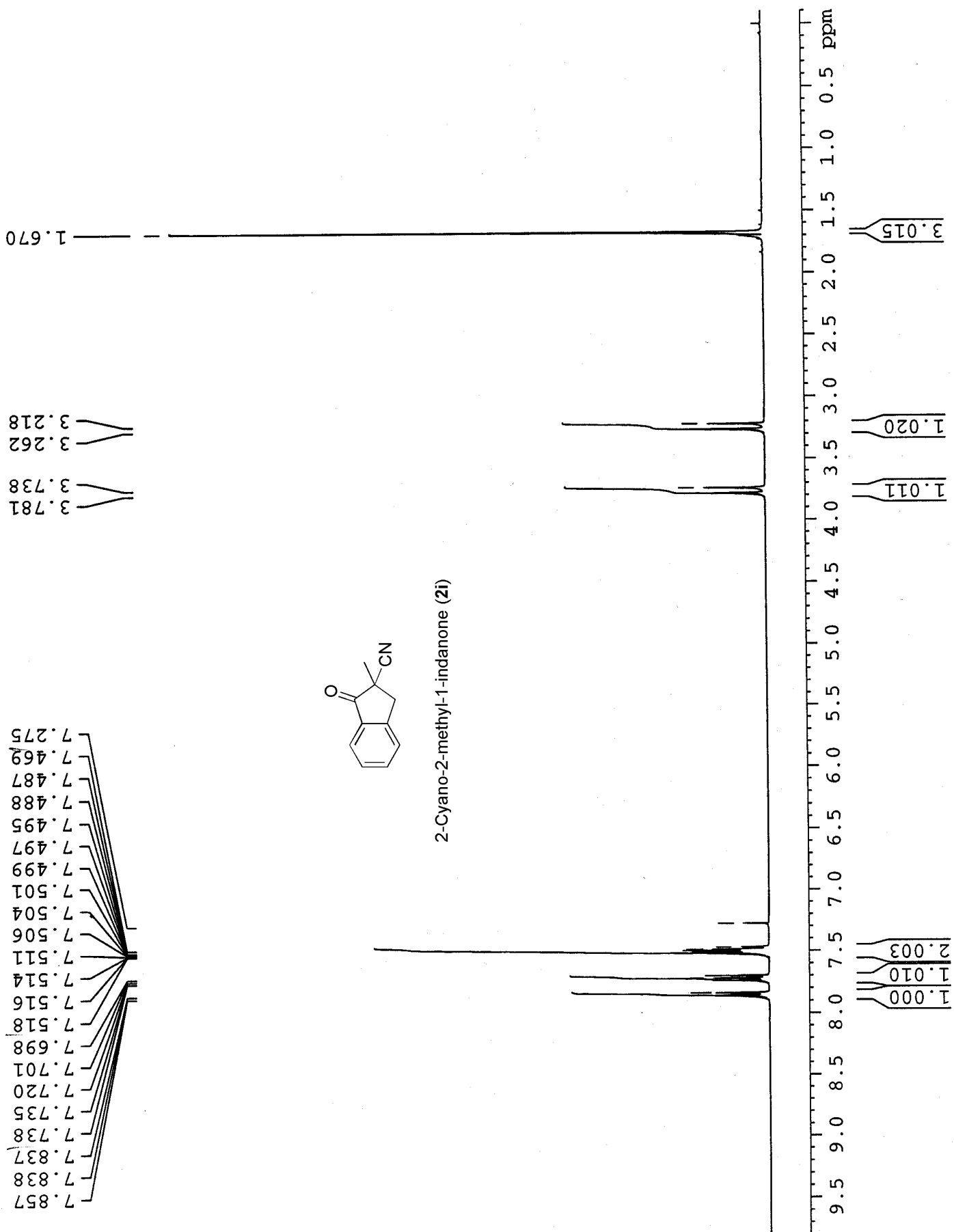


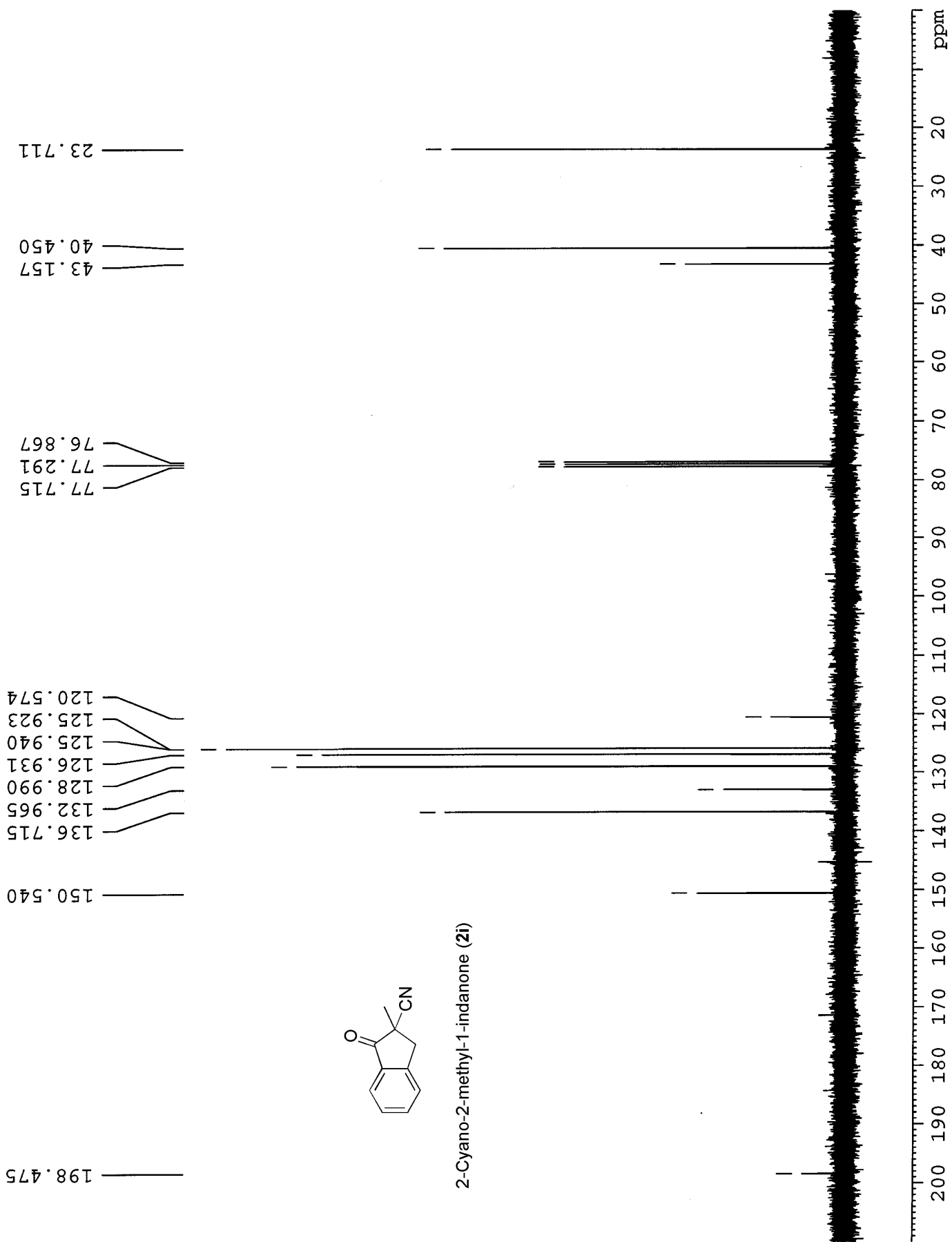


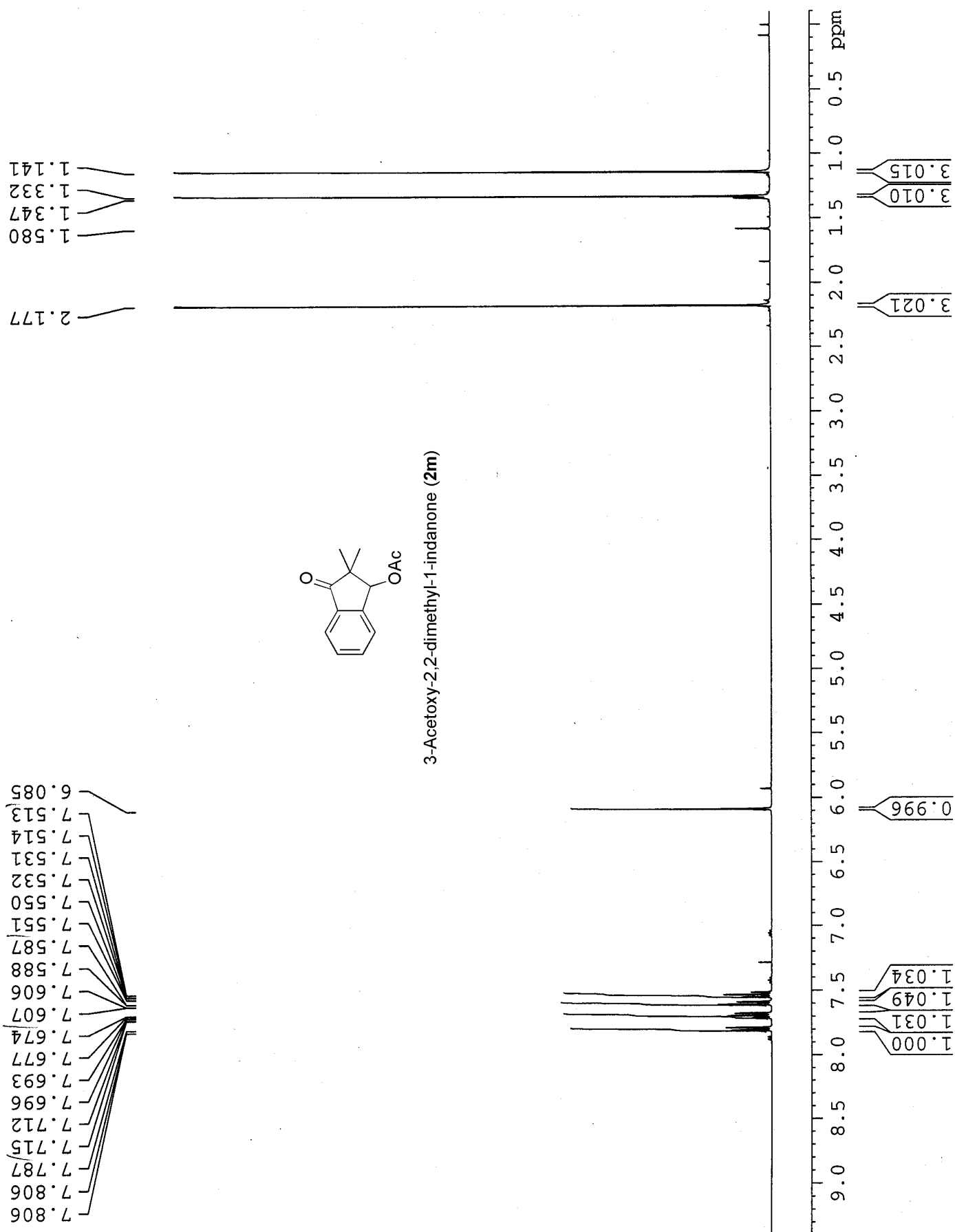


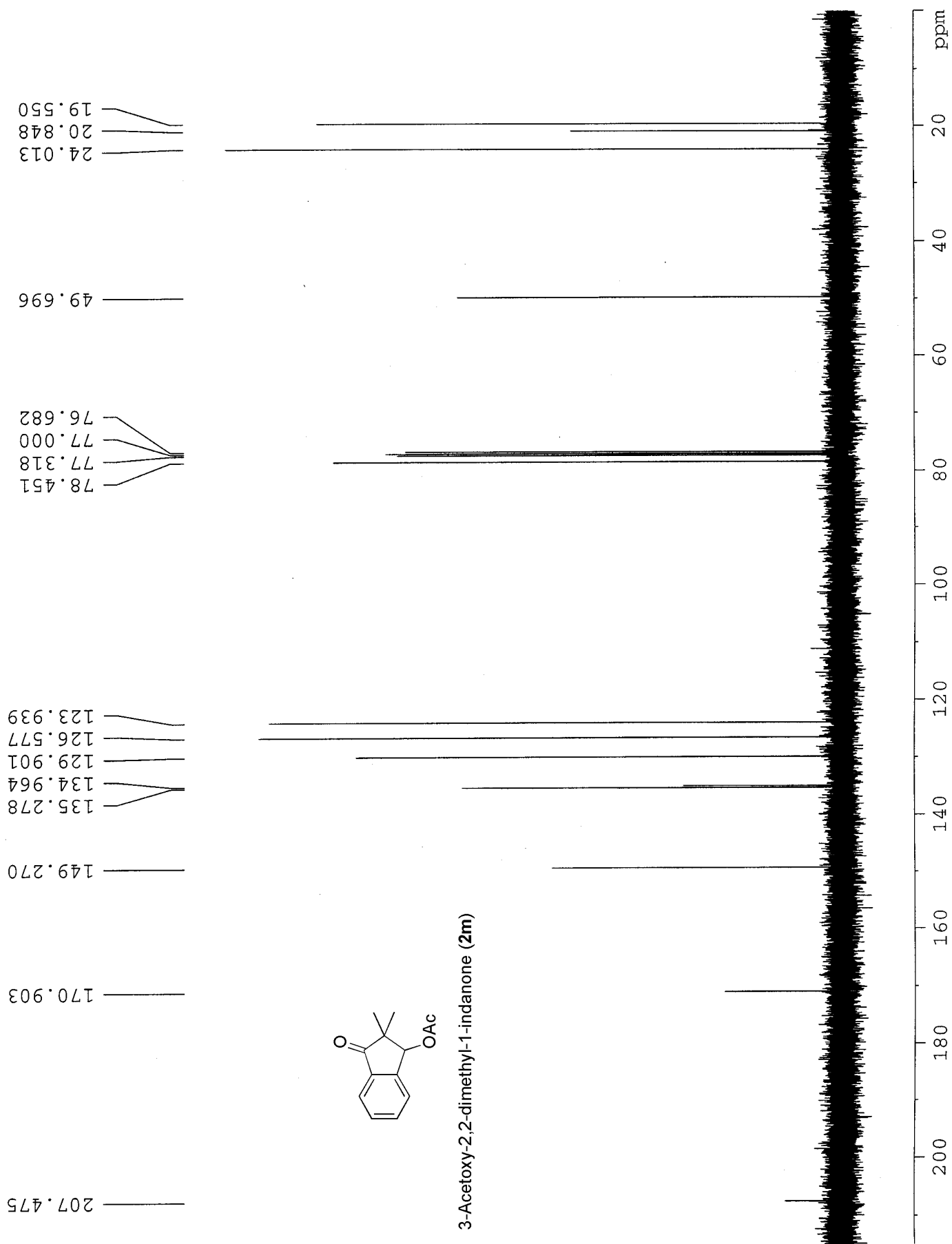


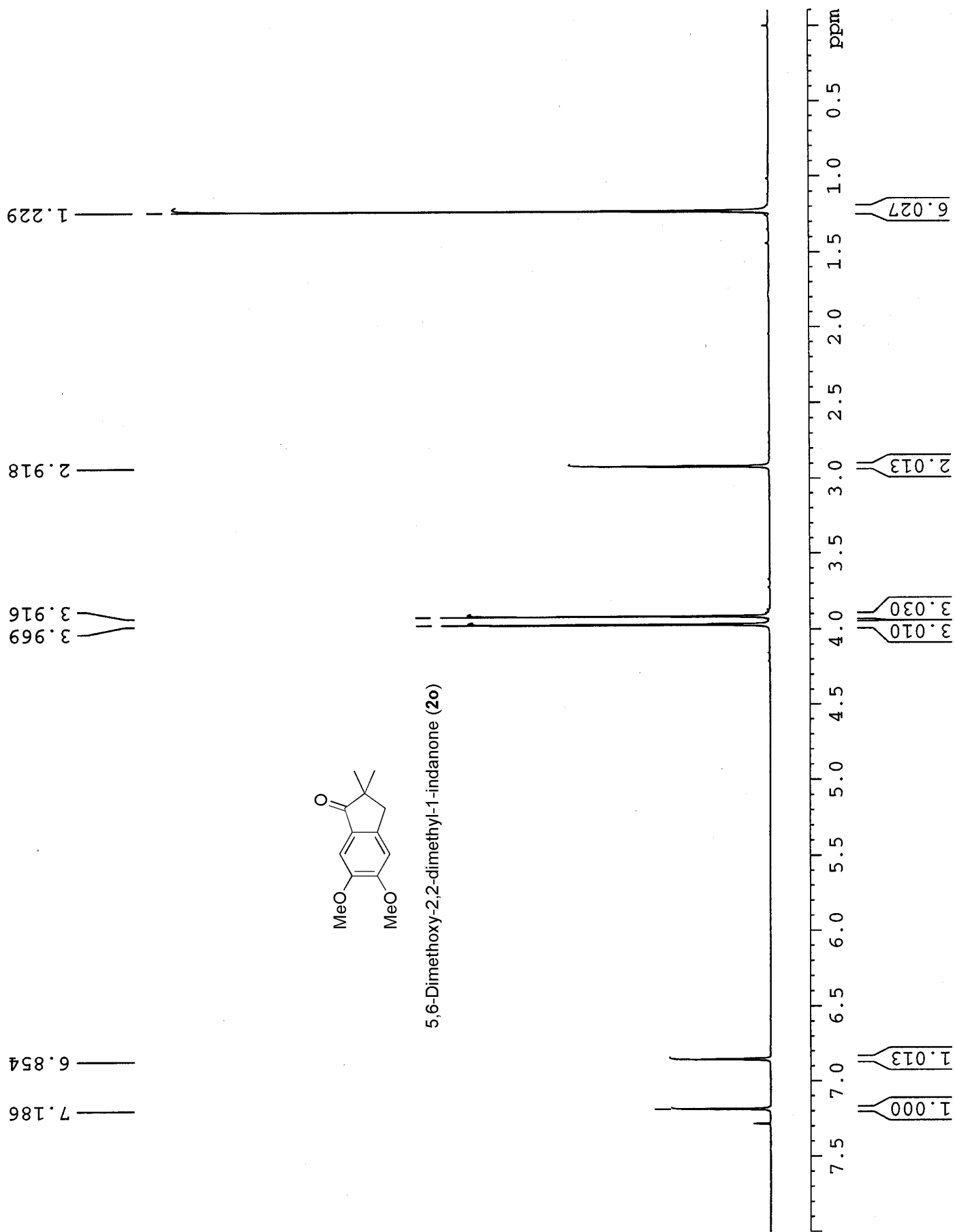
Spiro[cyclobutane-1,2'-indan]-1'-one (2c)

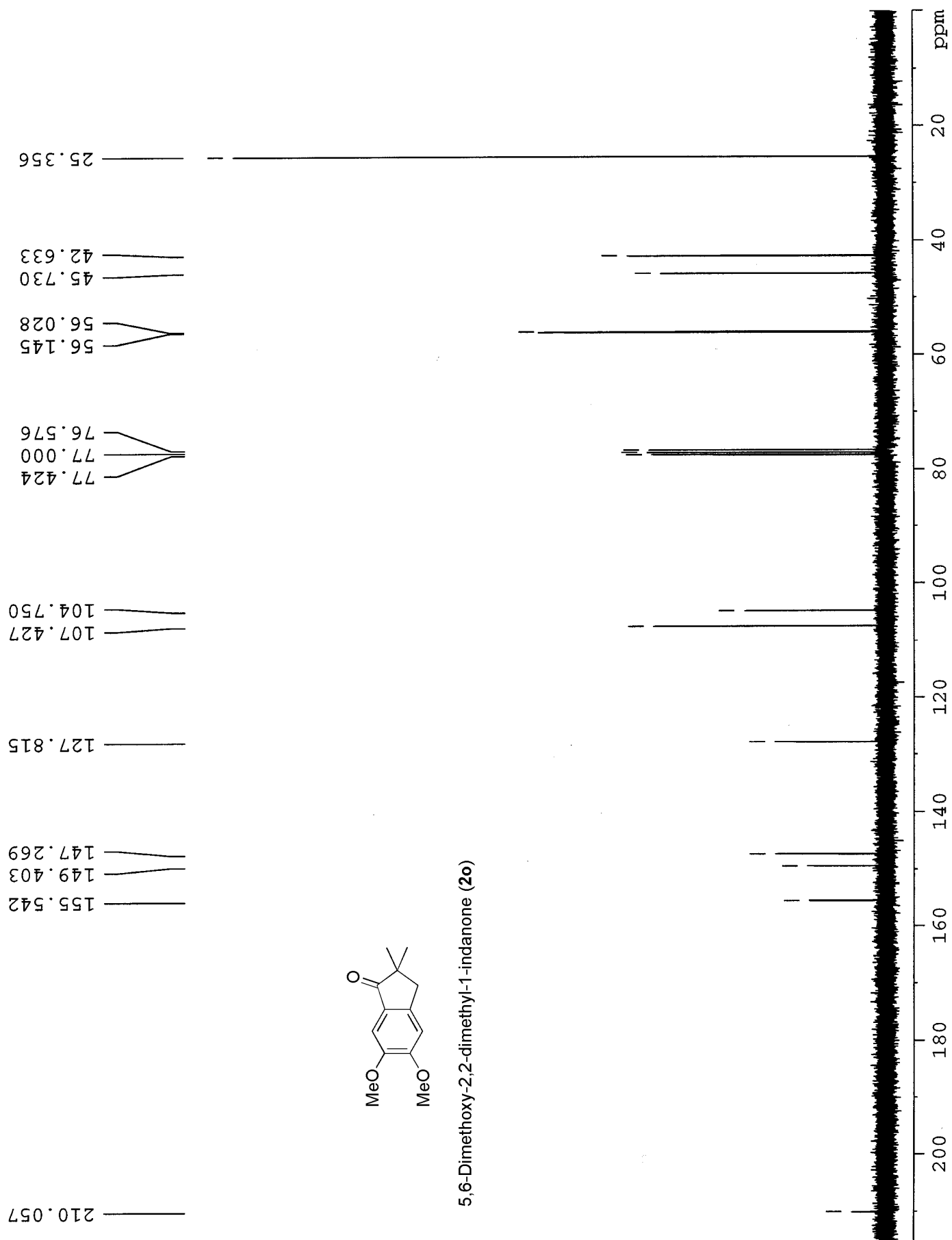


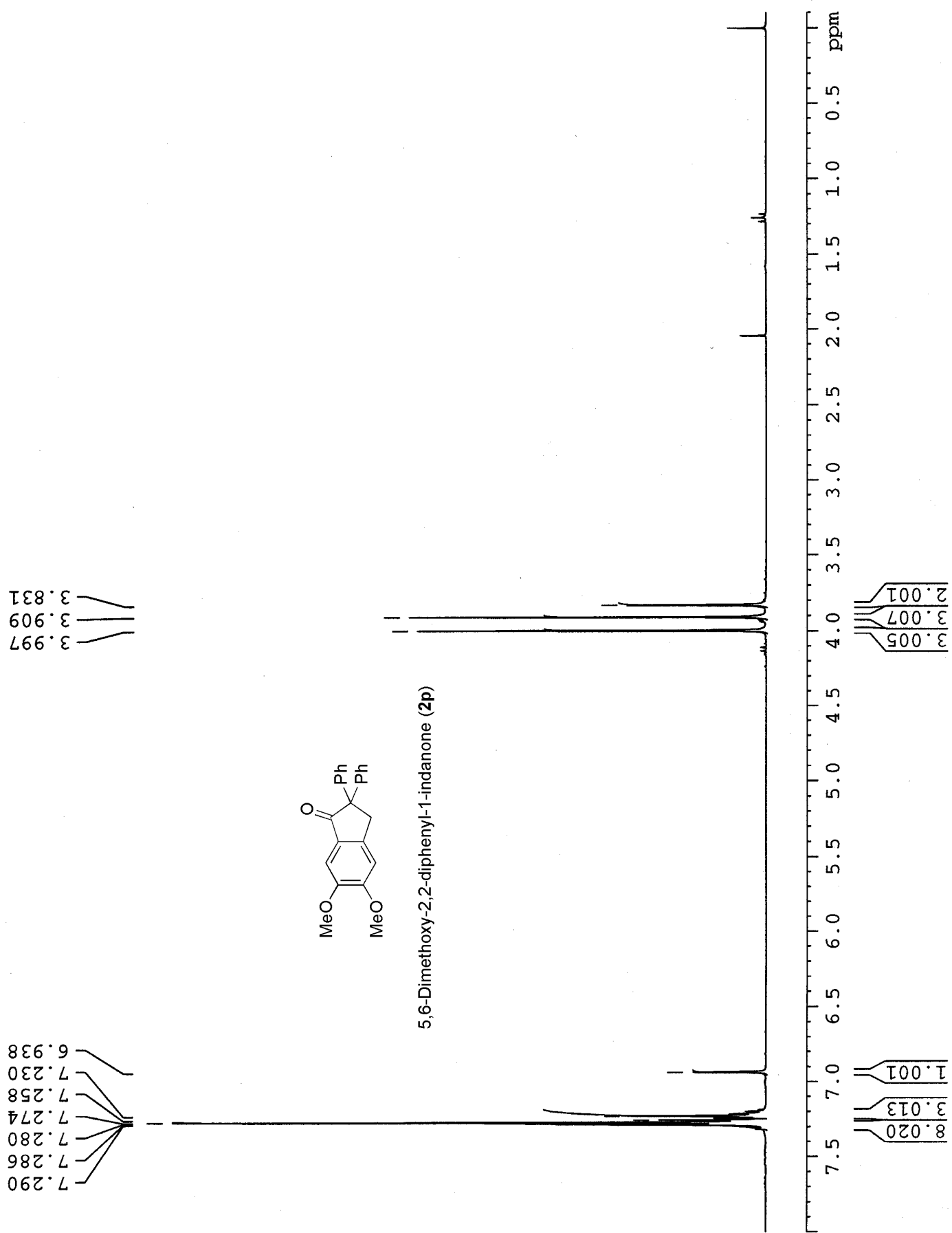


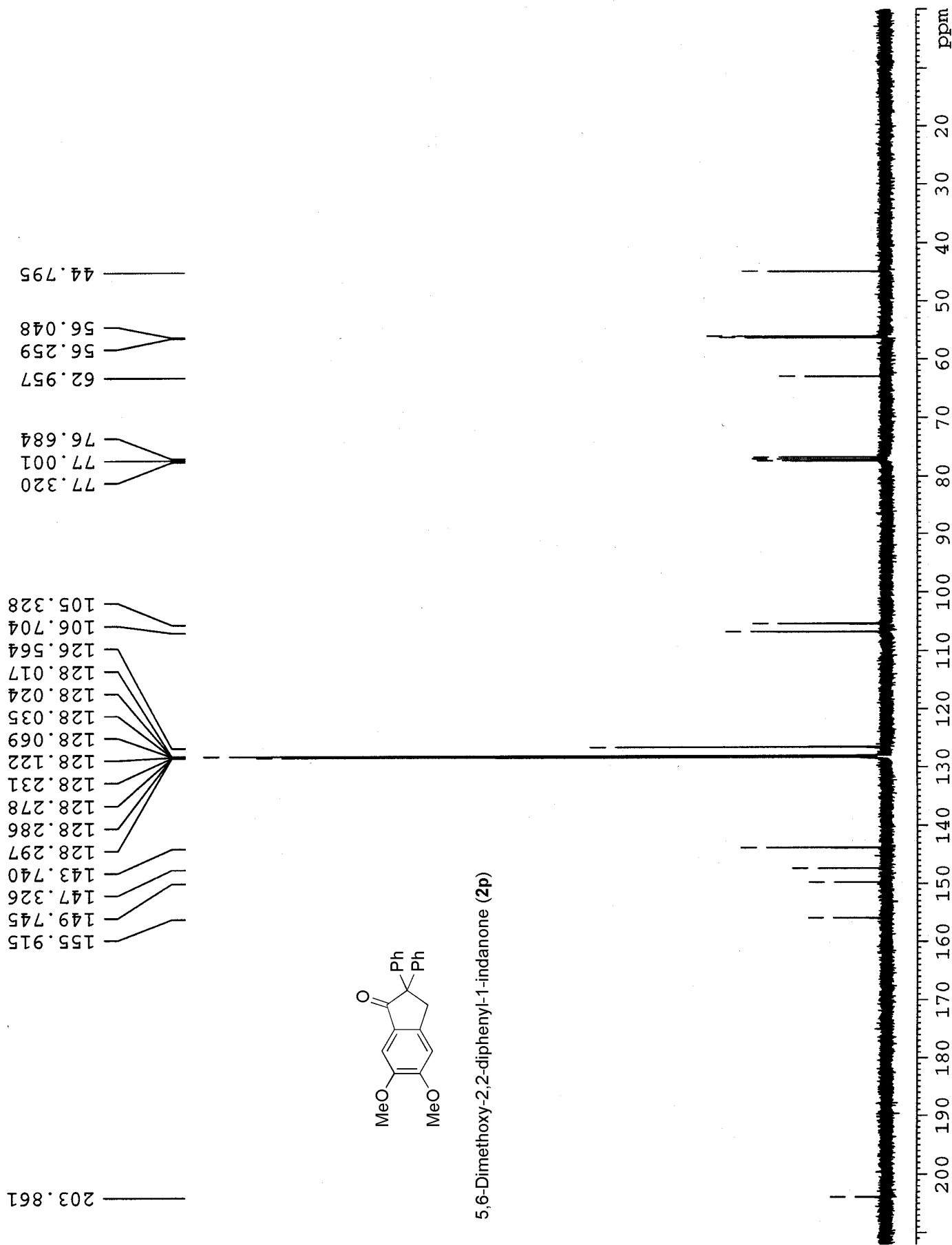


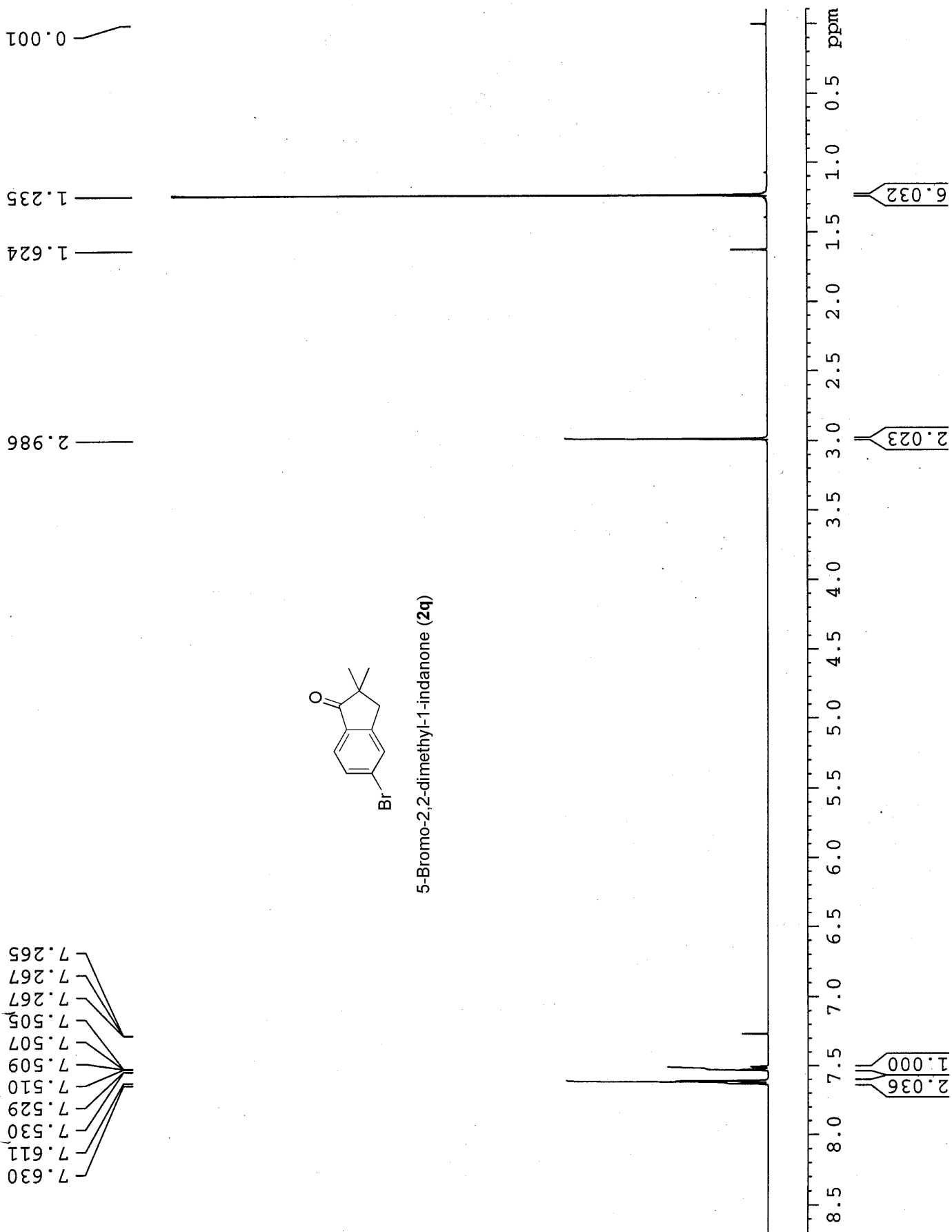


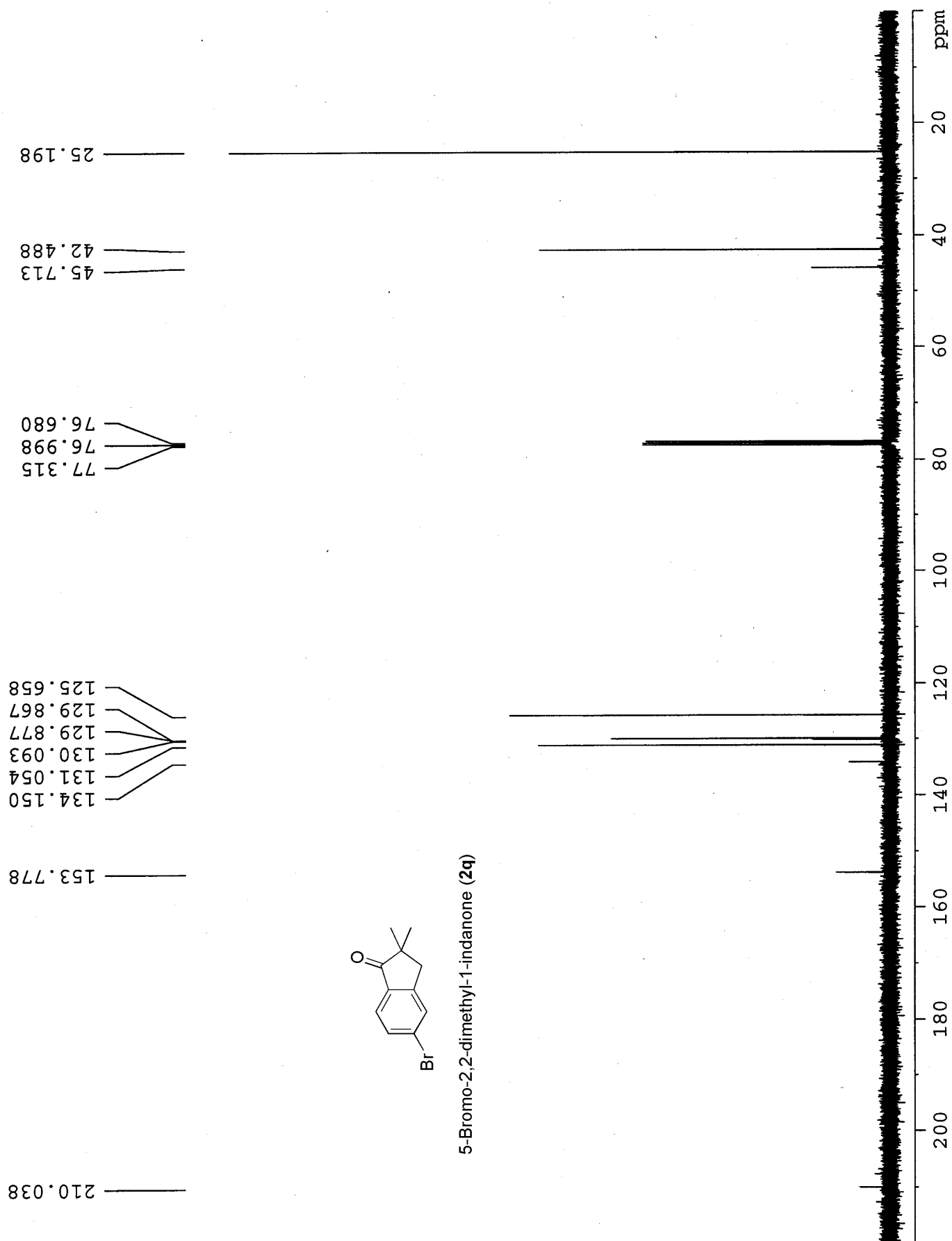


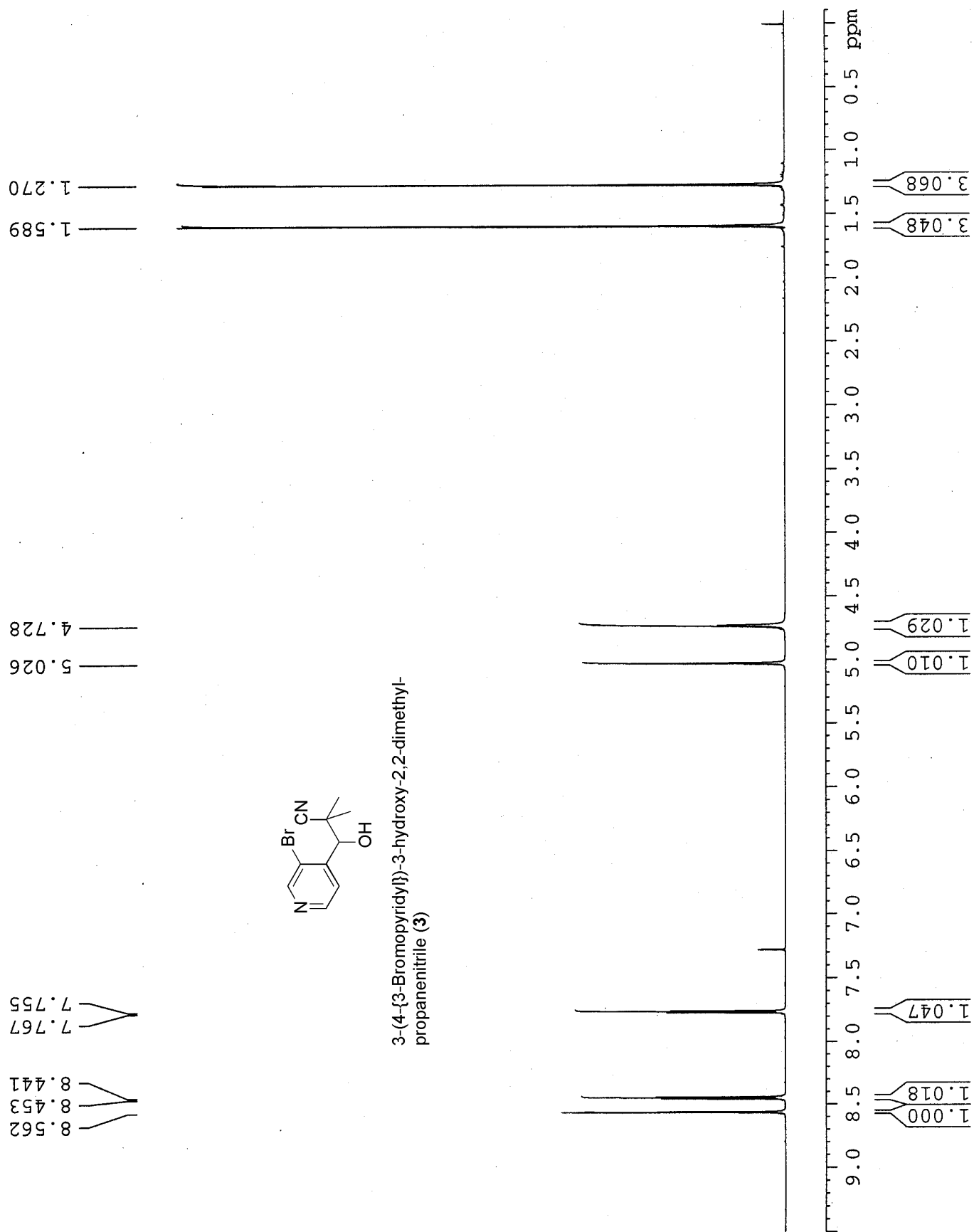


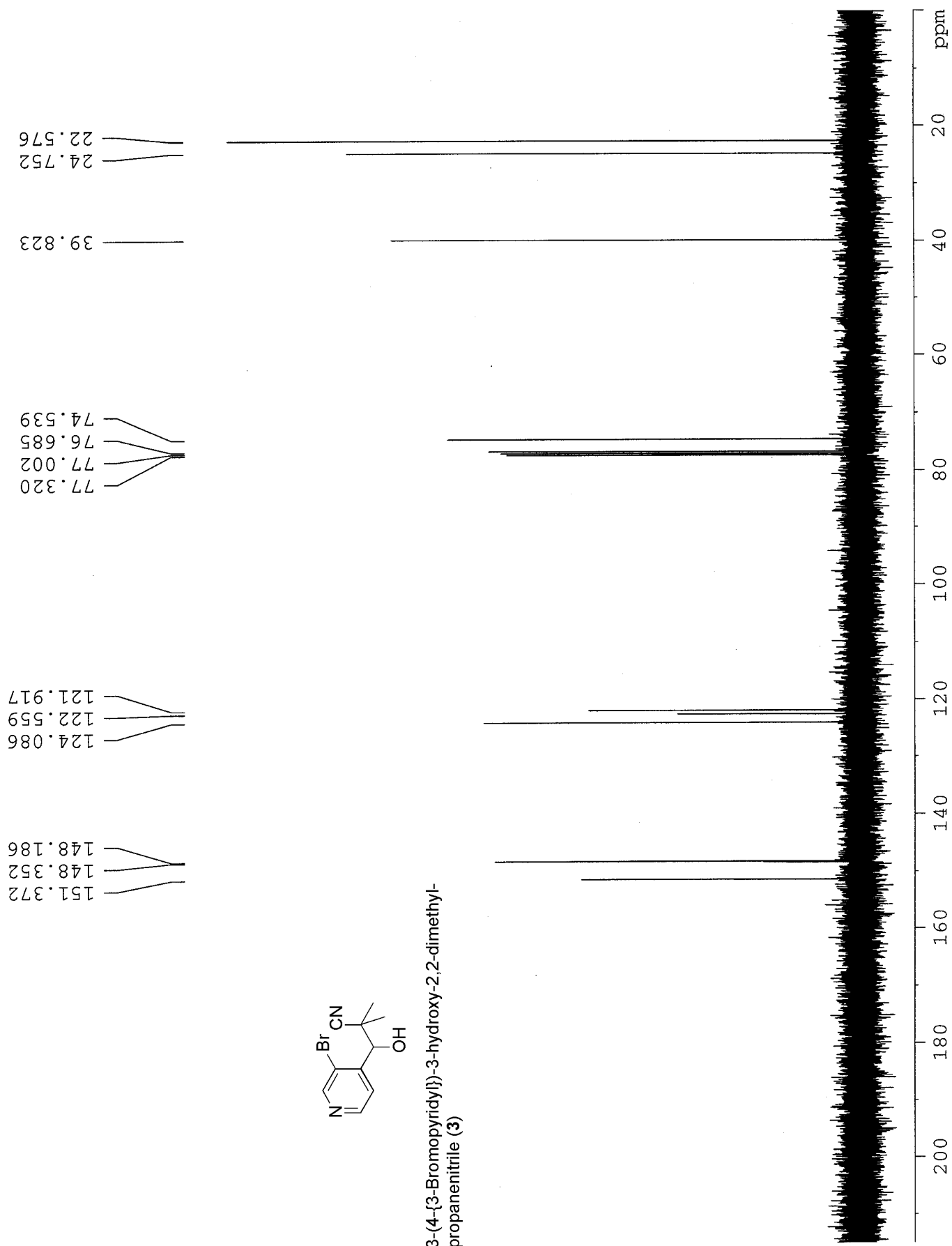


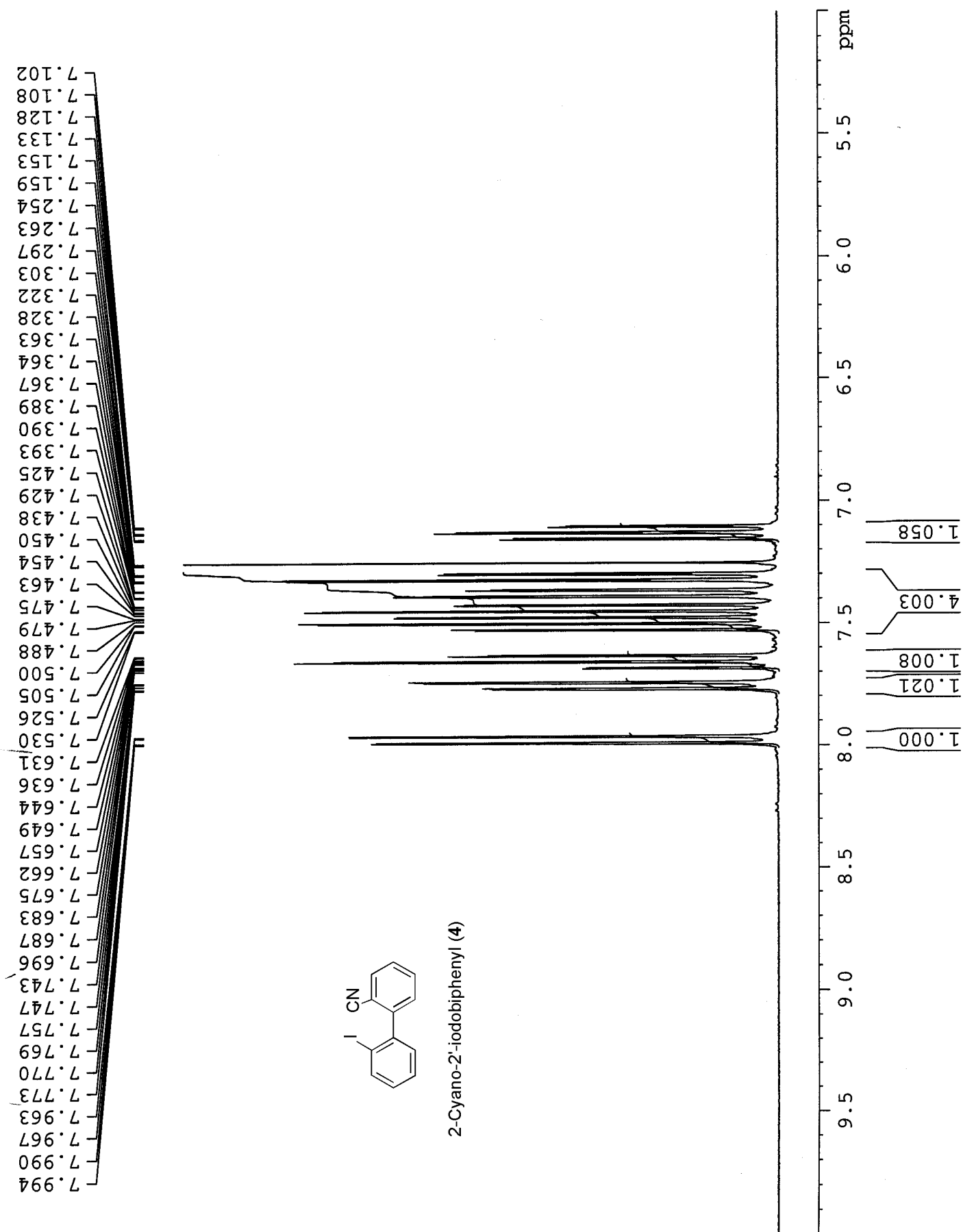


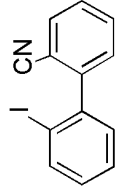




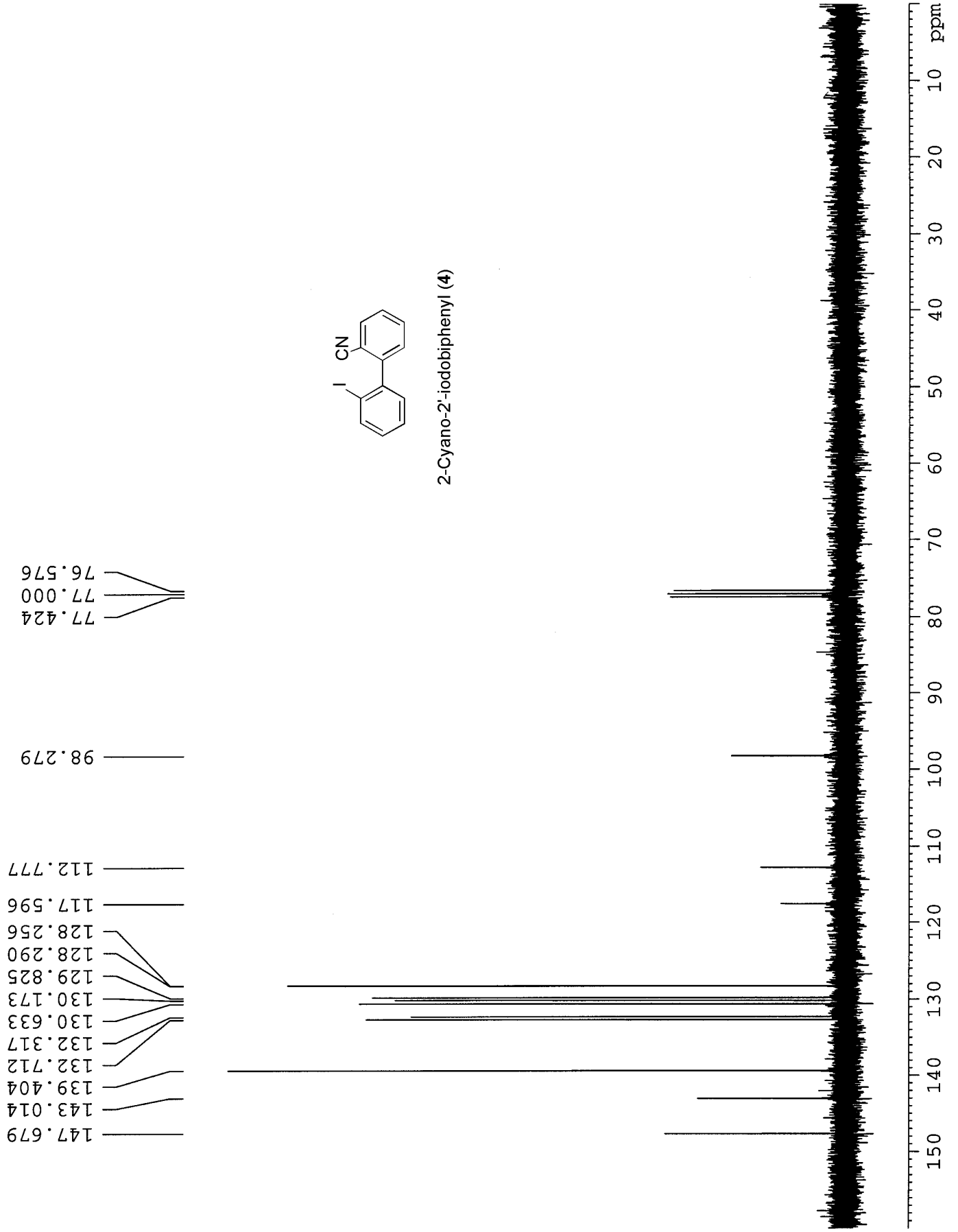


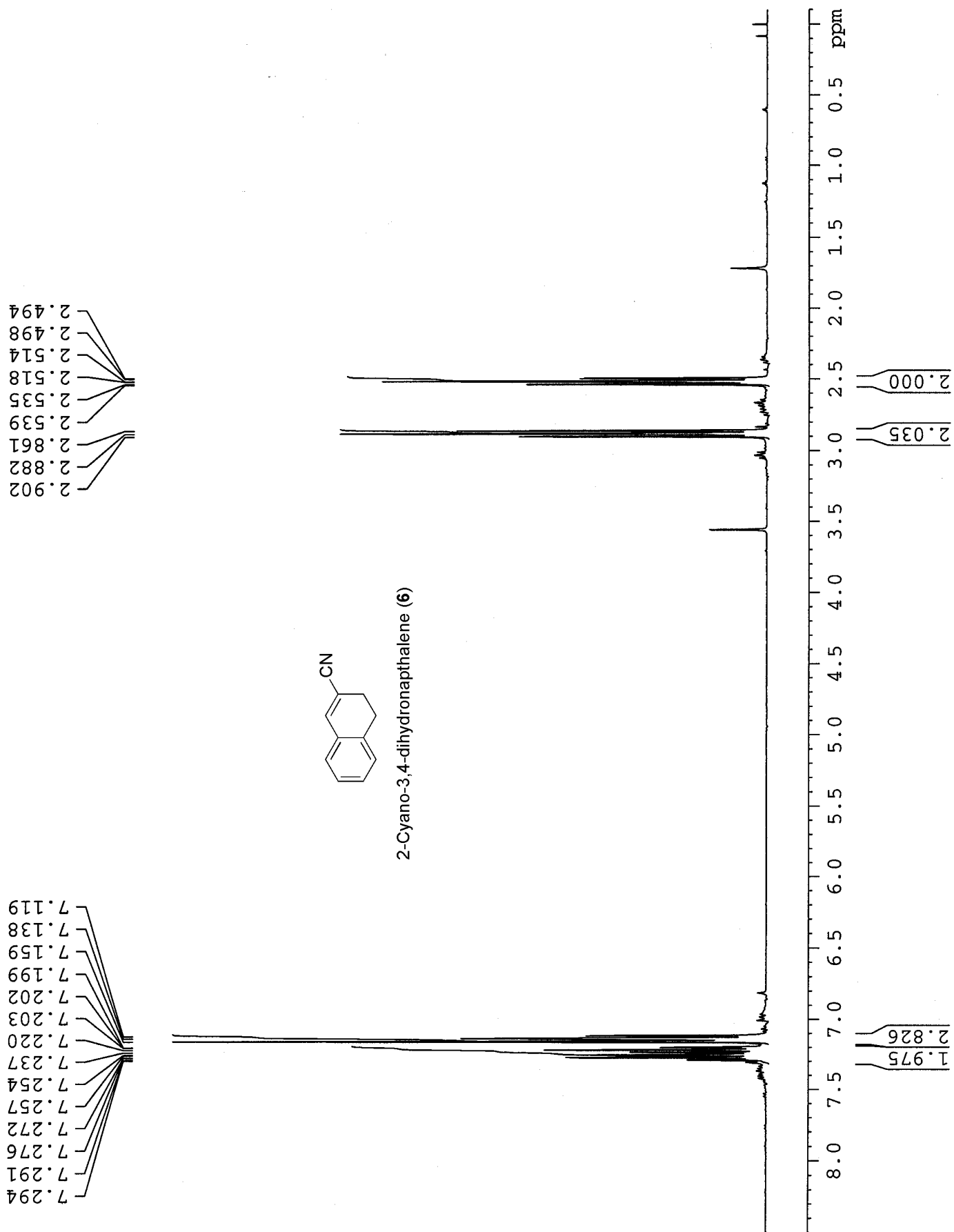


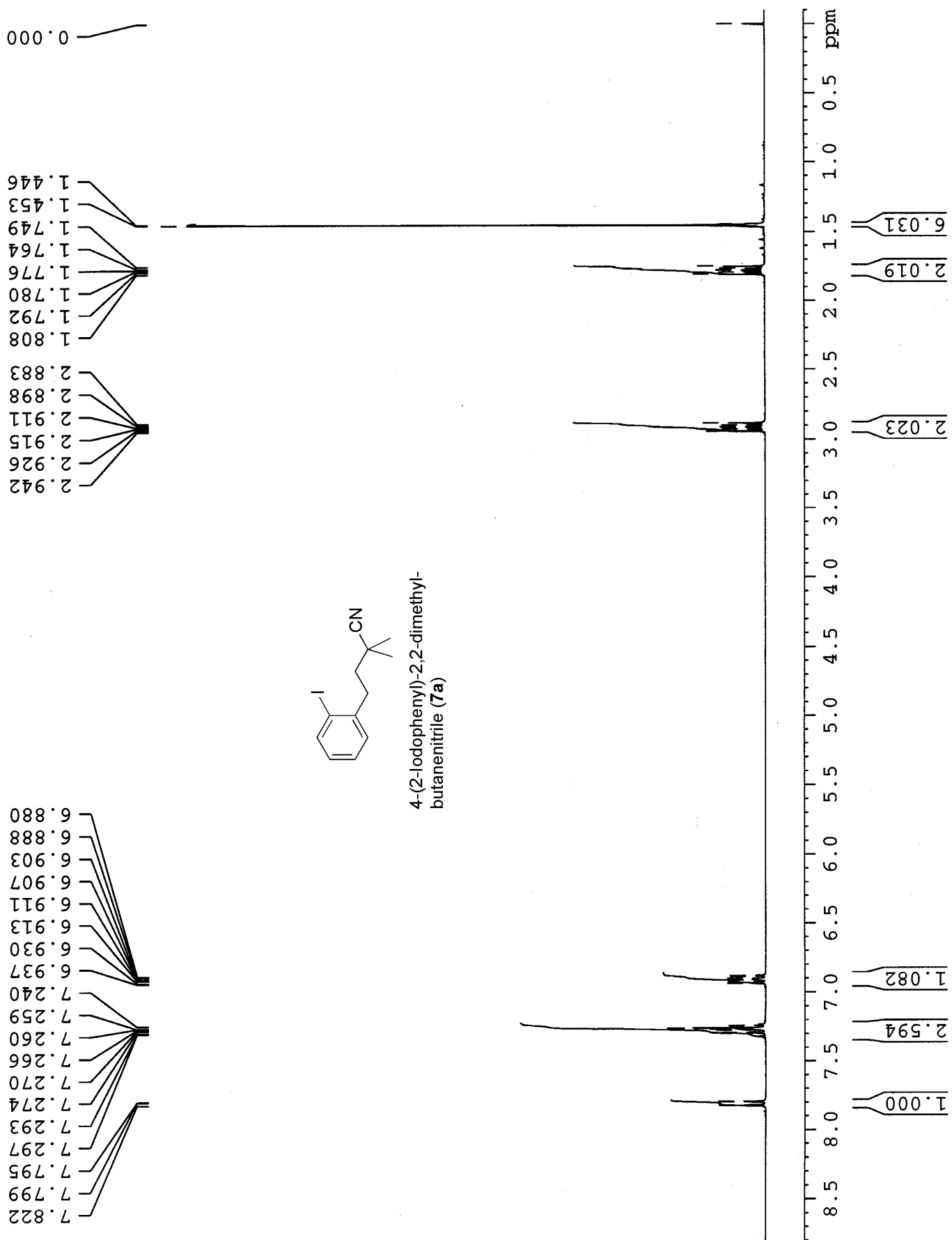


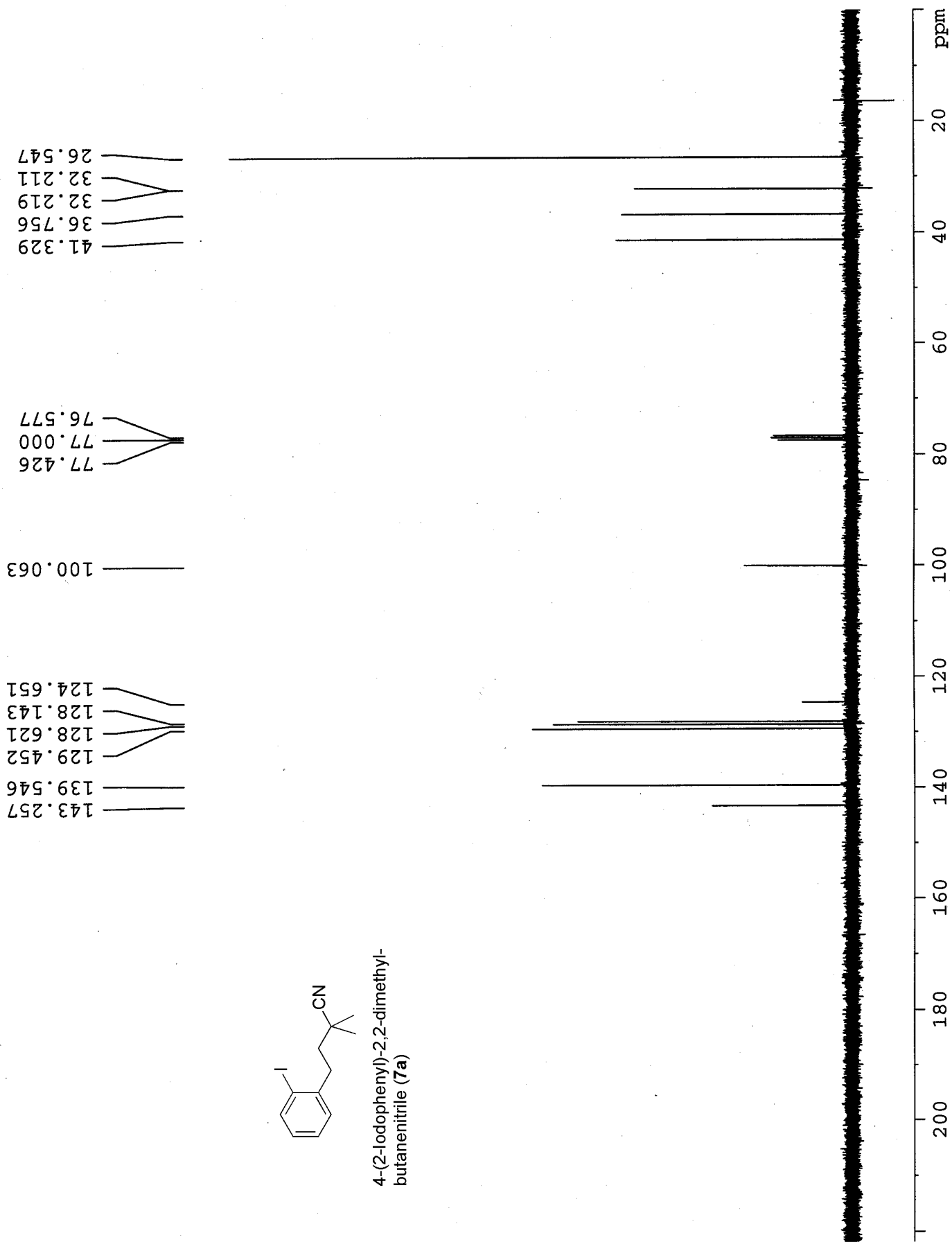


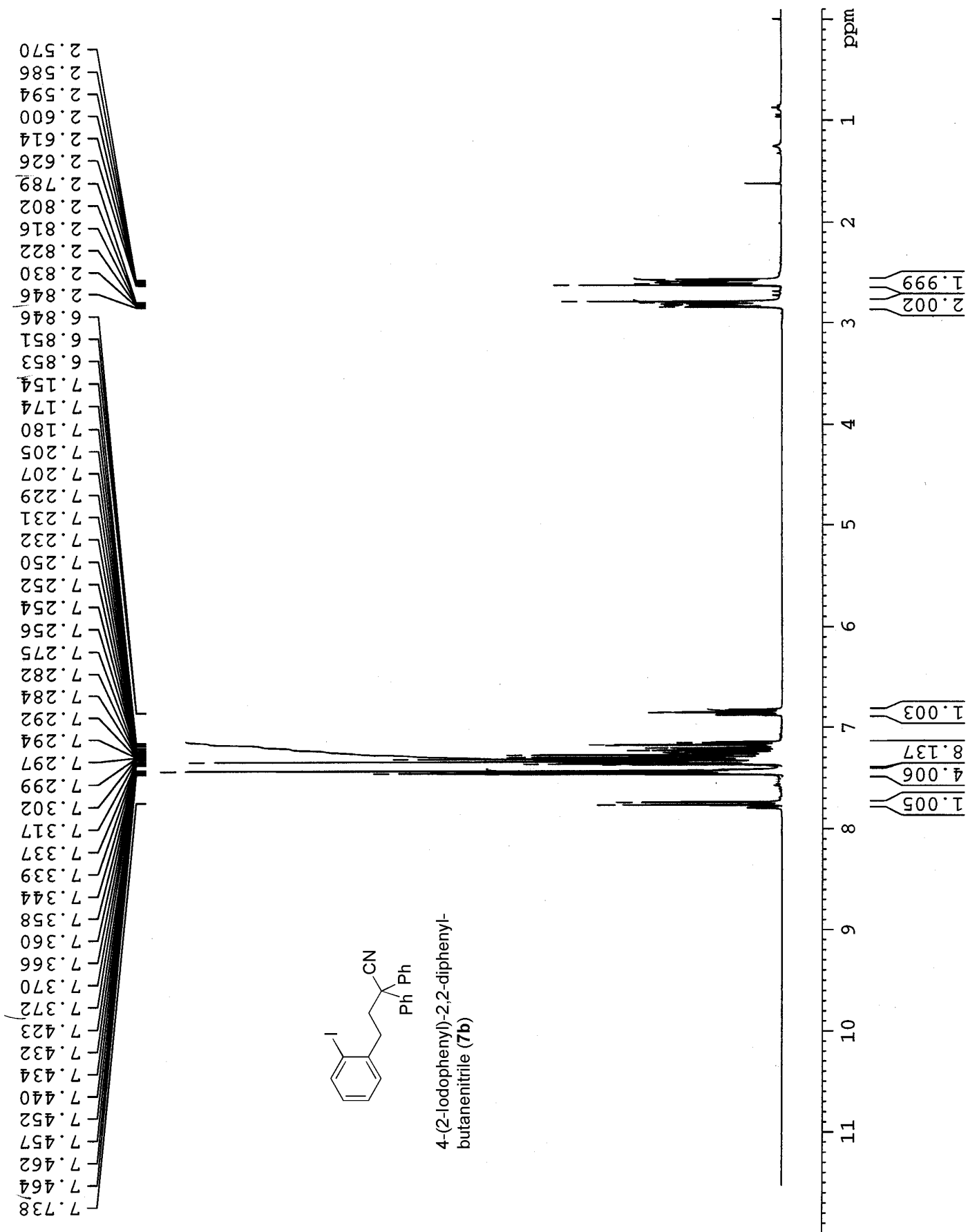
2-Cyano-2'-iodobiphenyl (4)

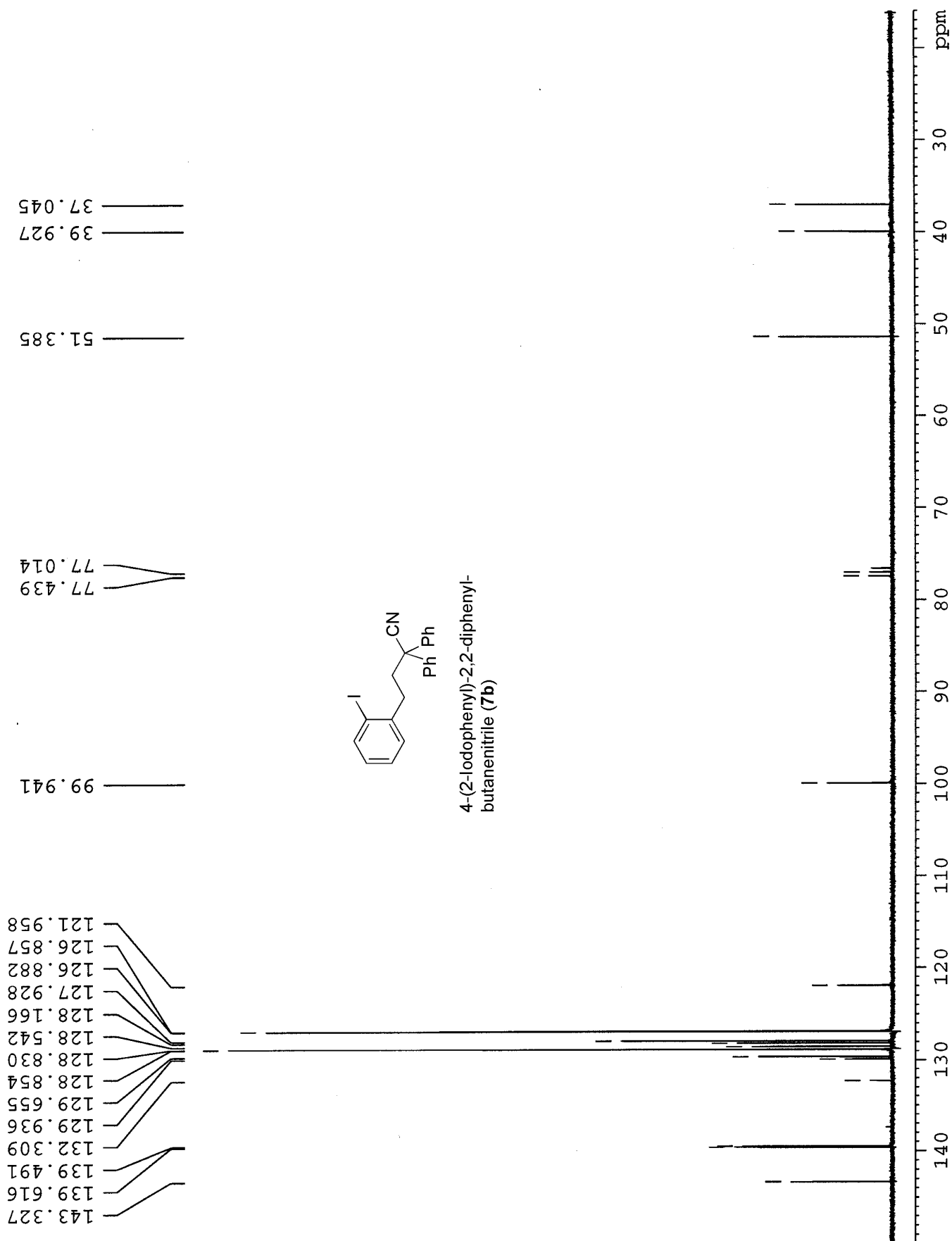


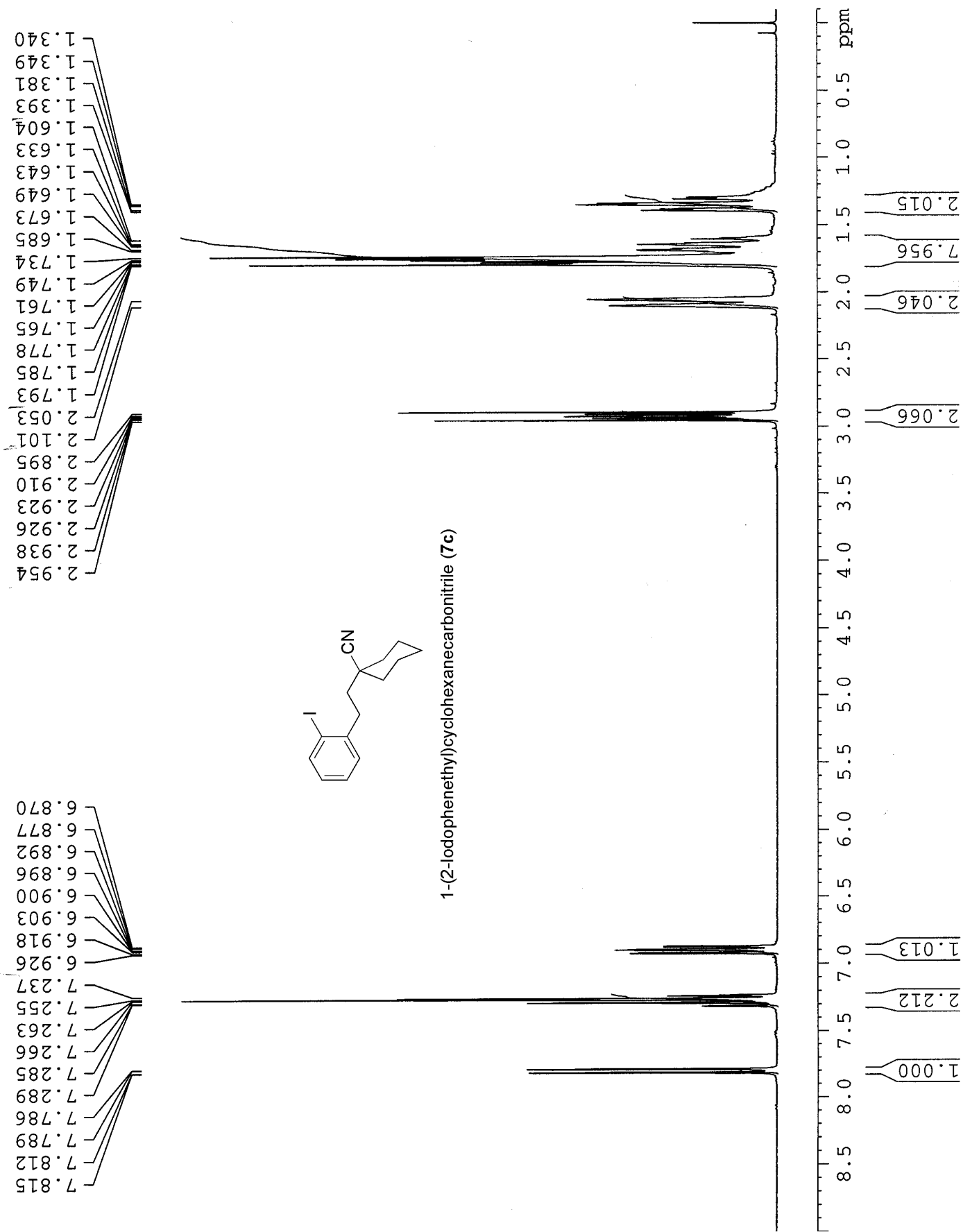


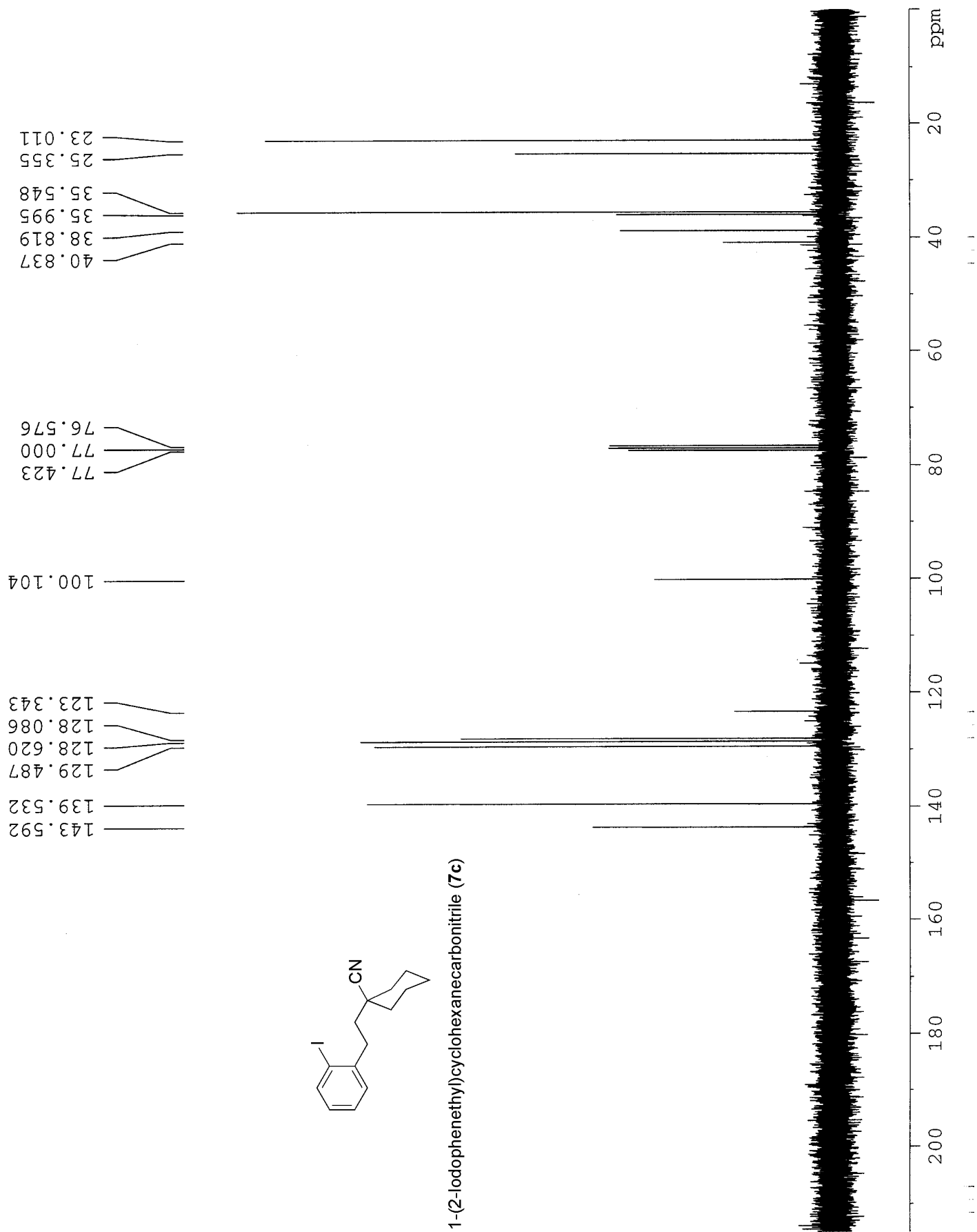


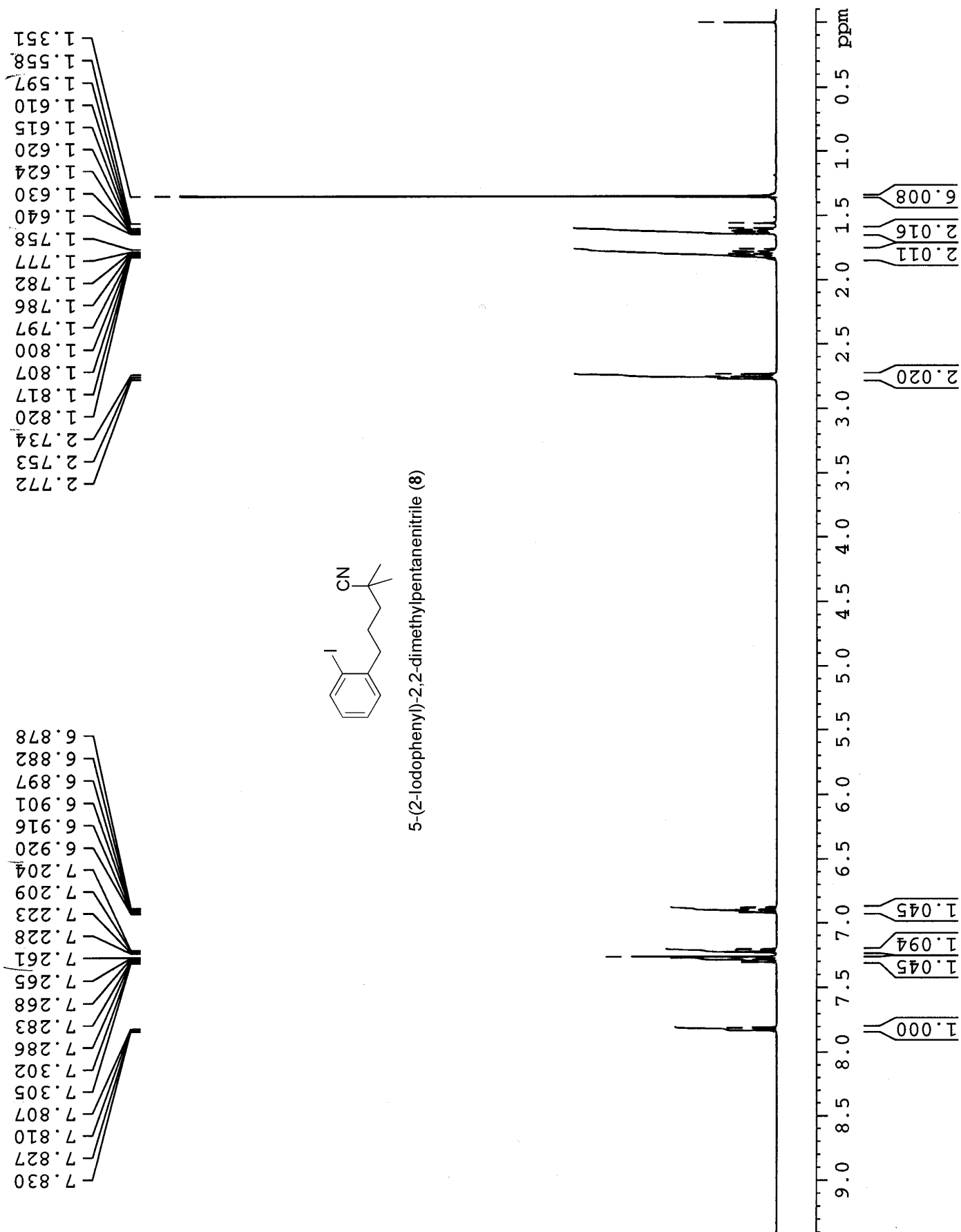






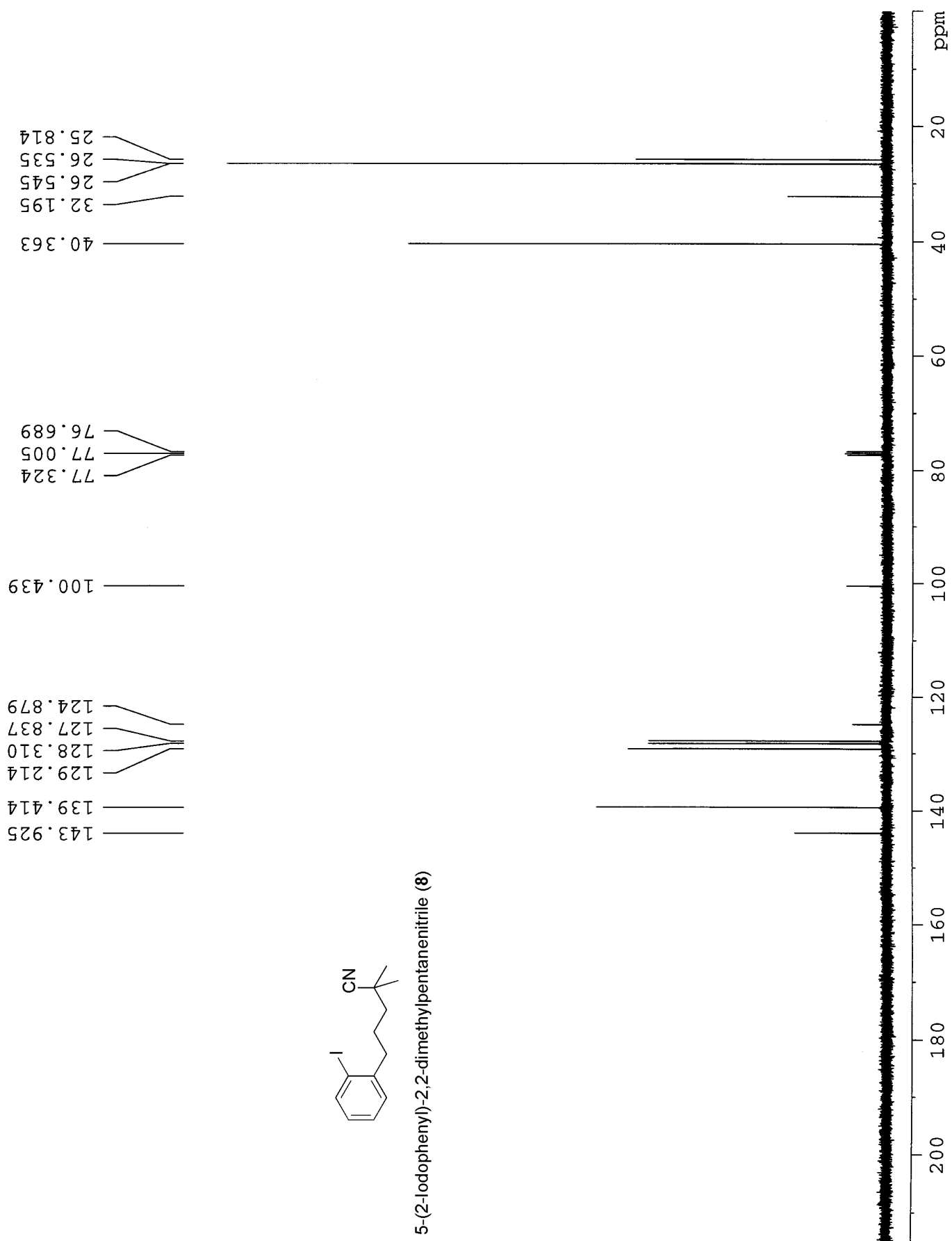


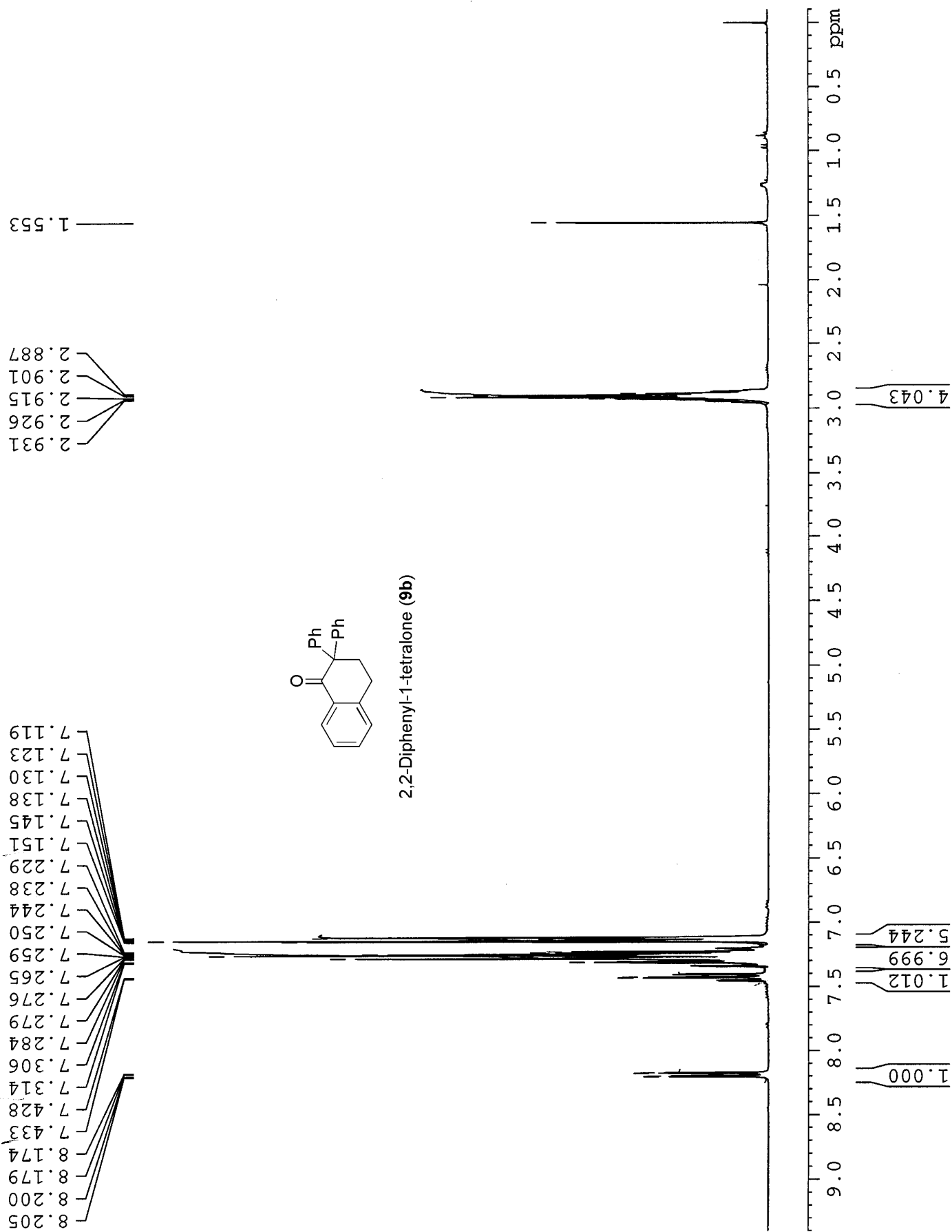


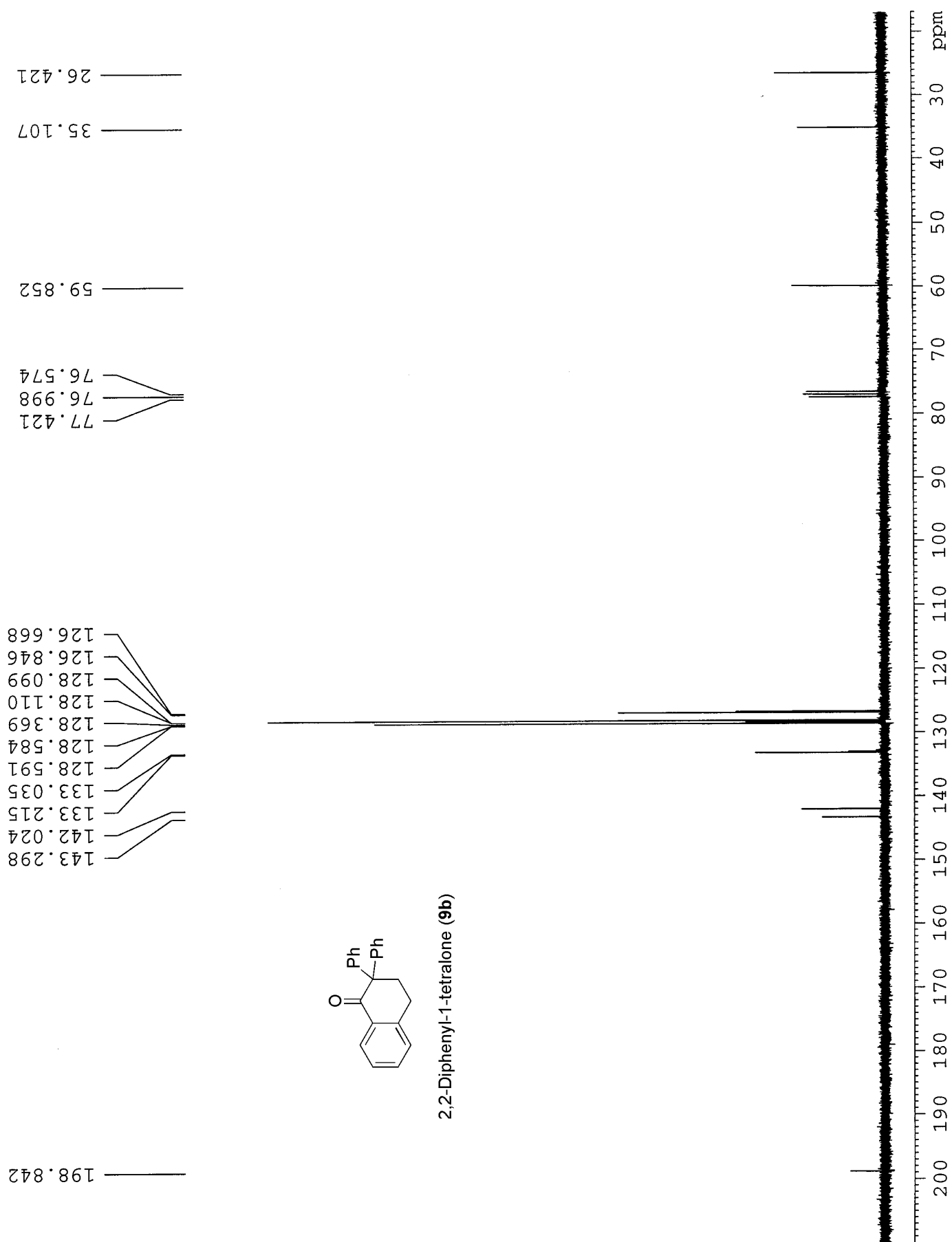


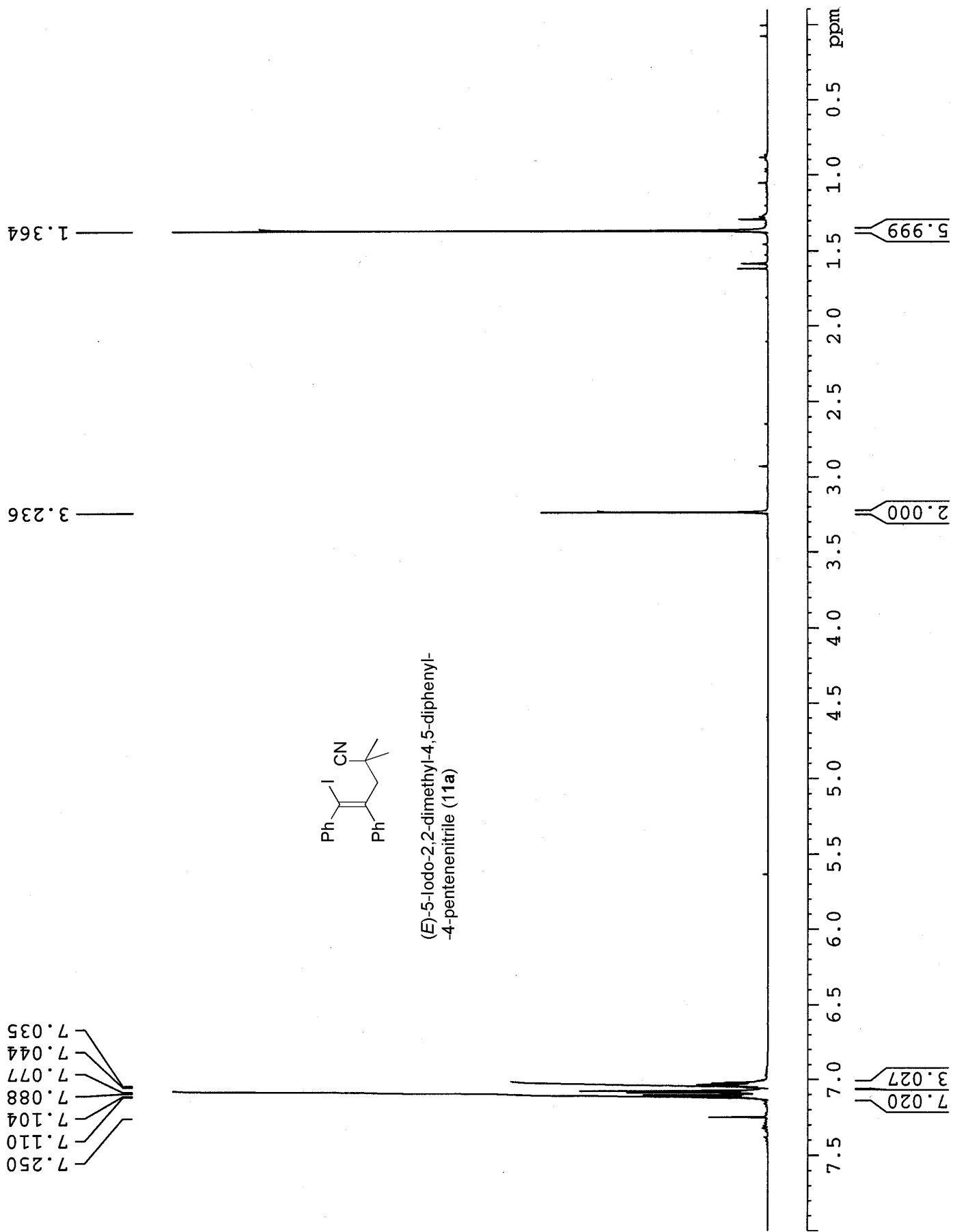


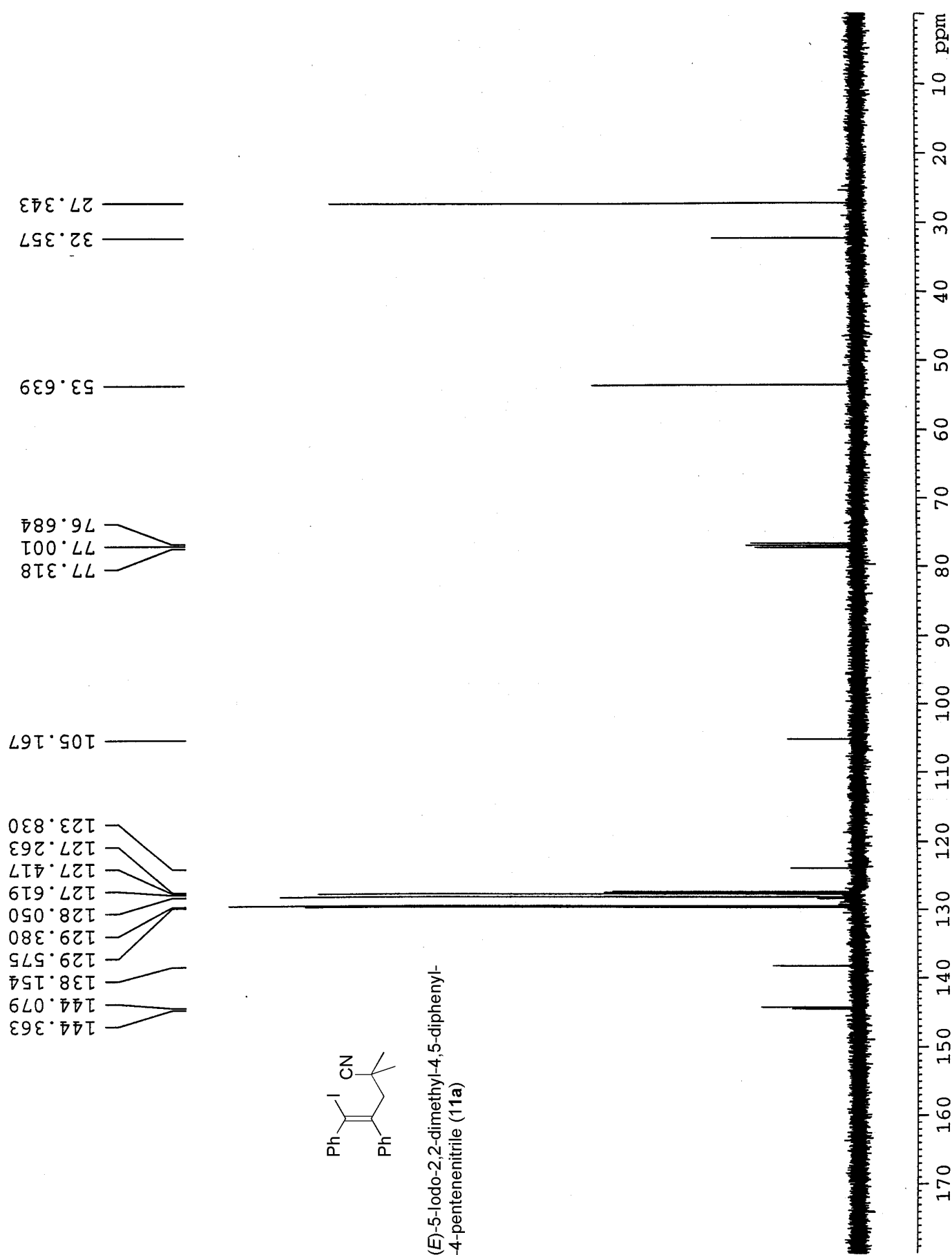
5-(2-Iodophenyl)-2,2-dimethylpentanenitrile (8)

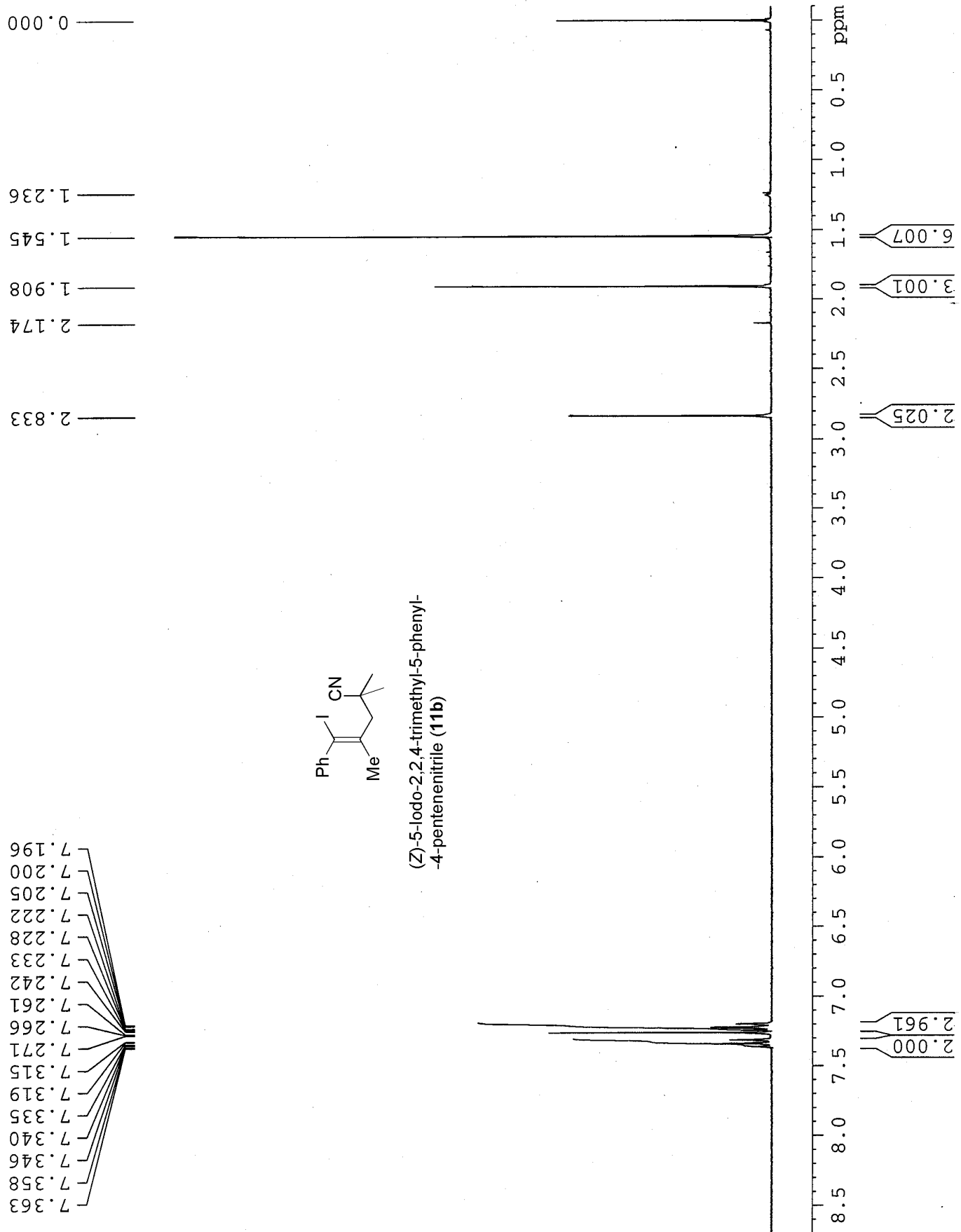


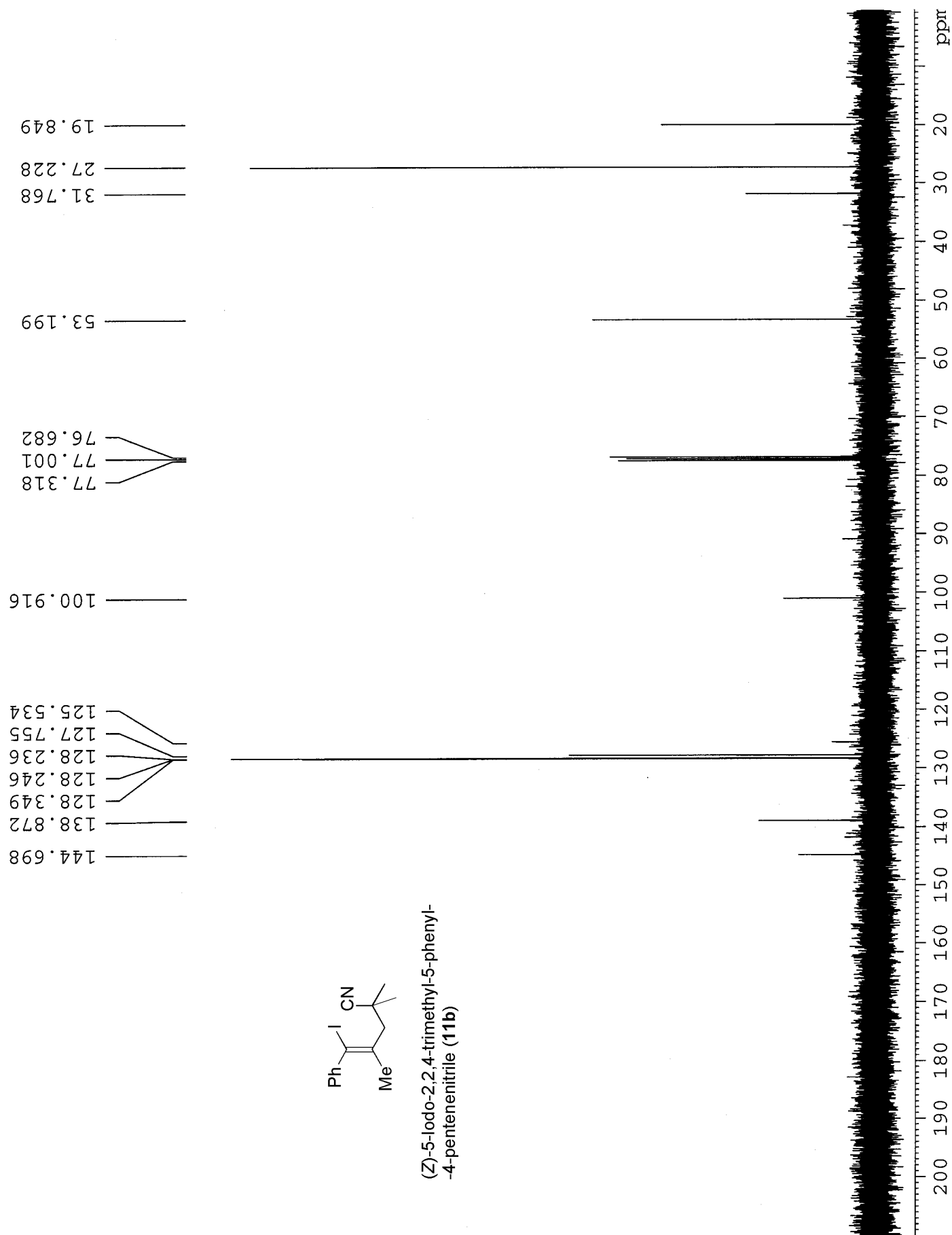


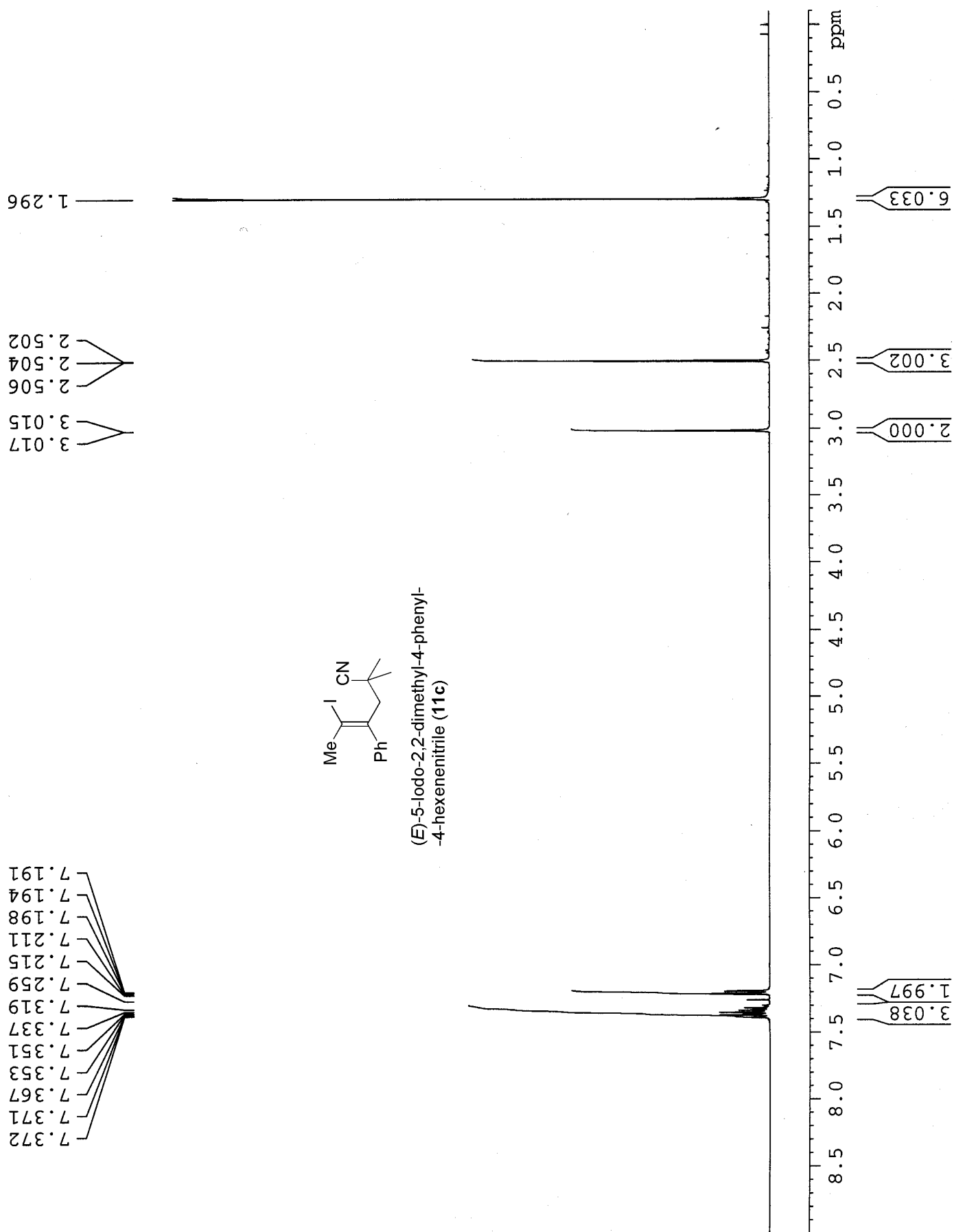


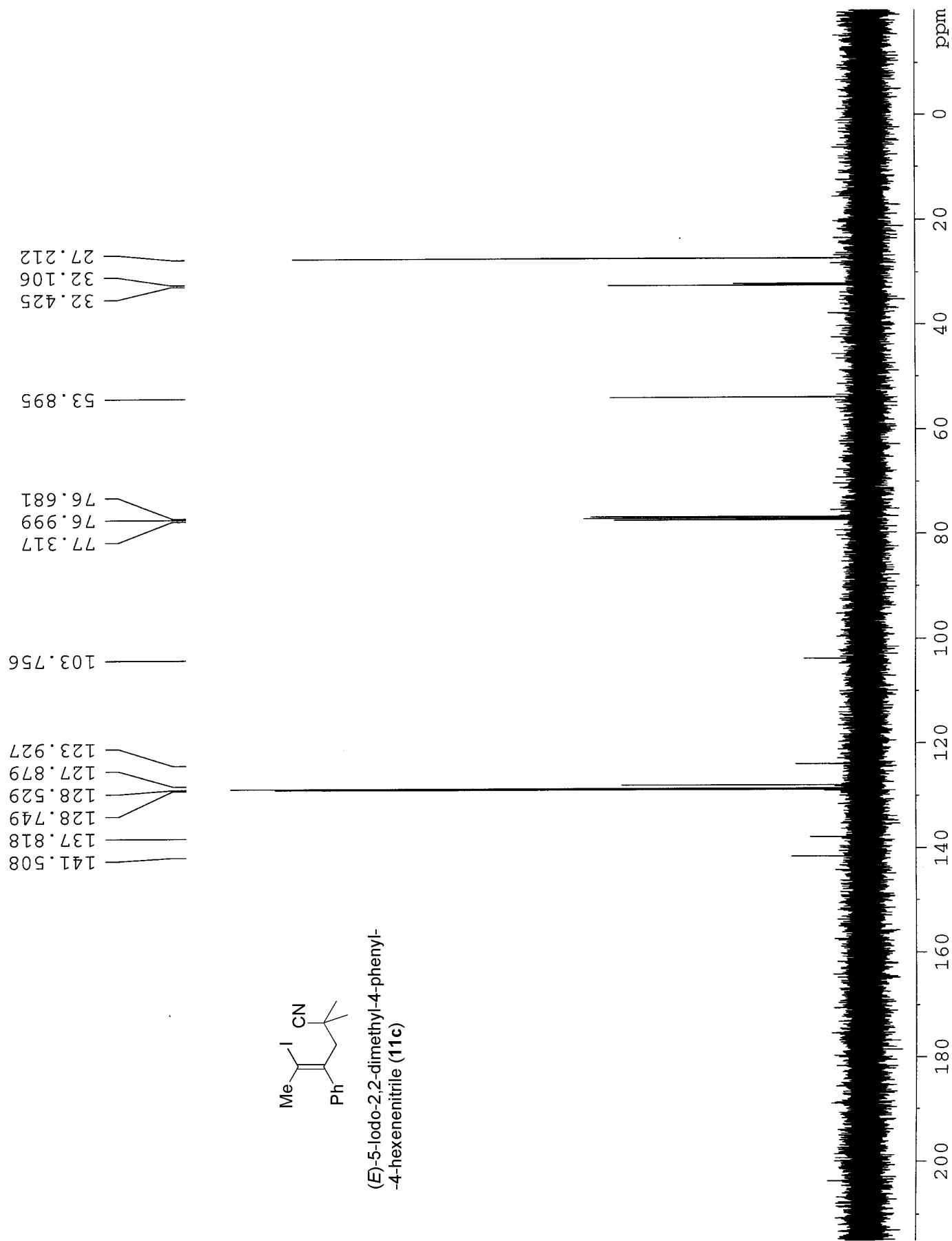


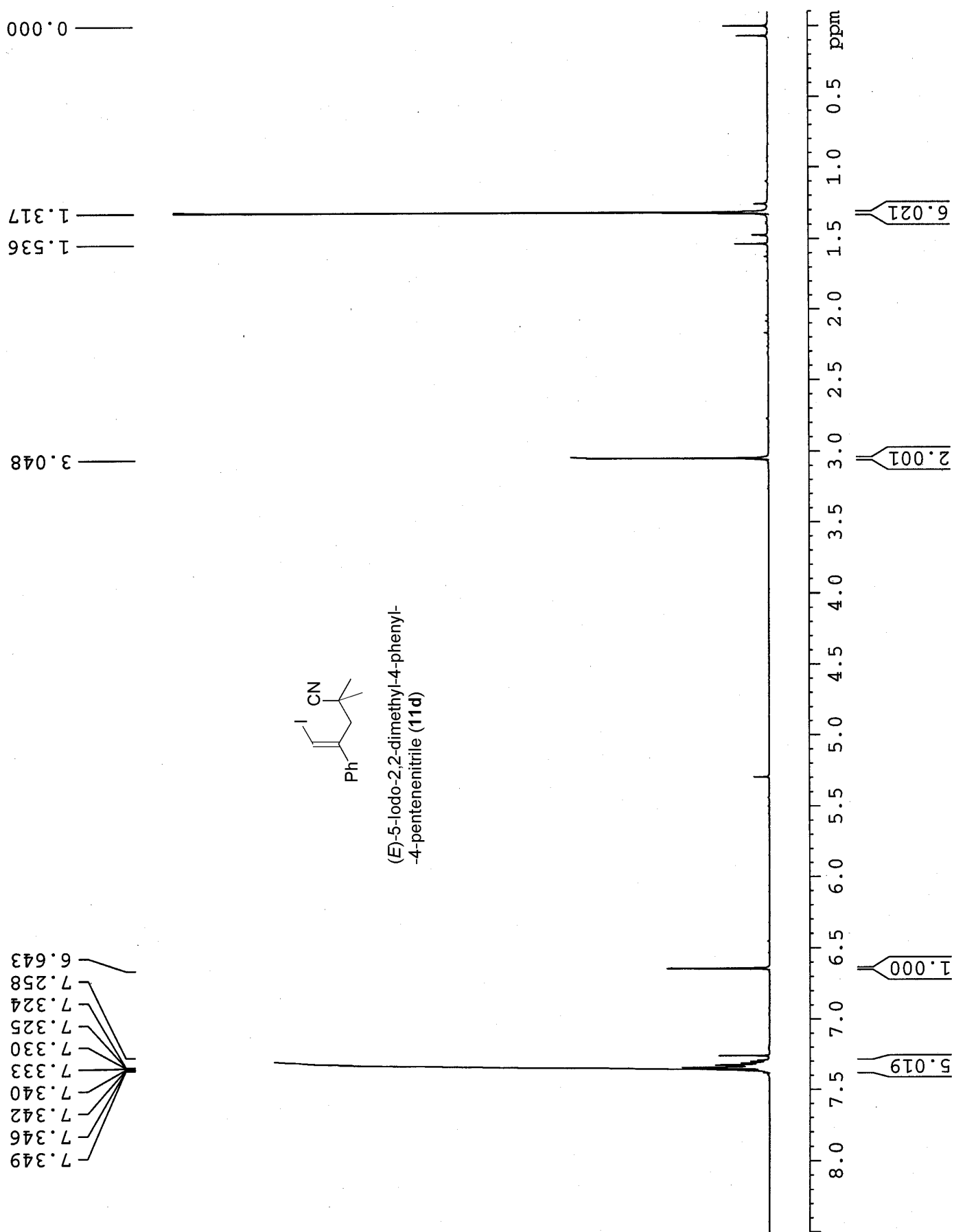


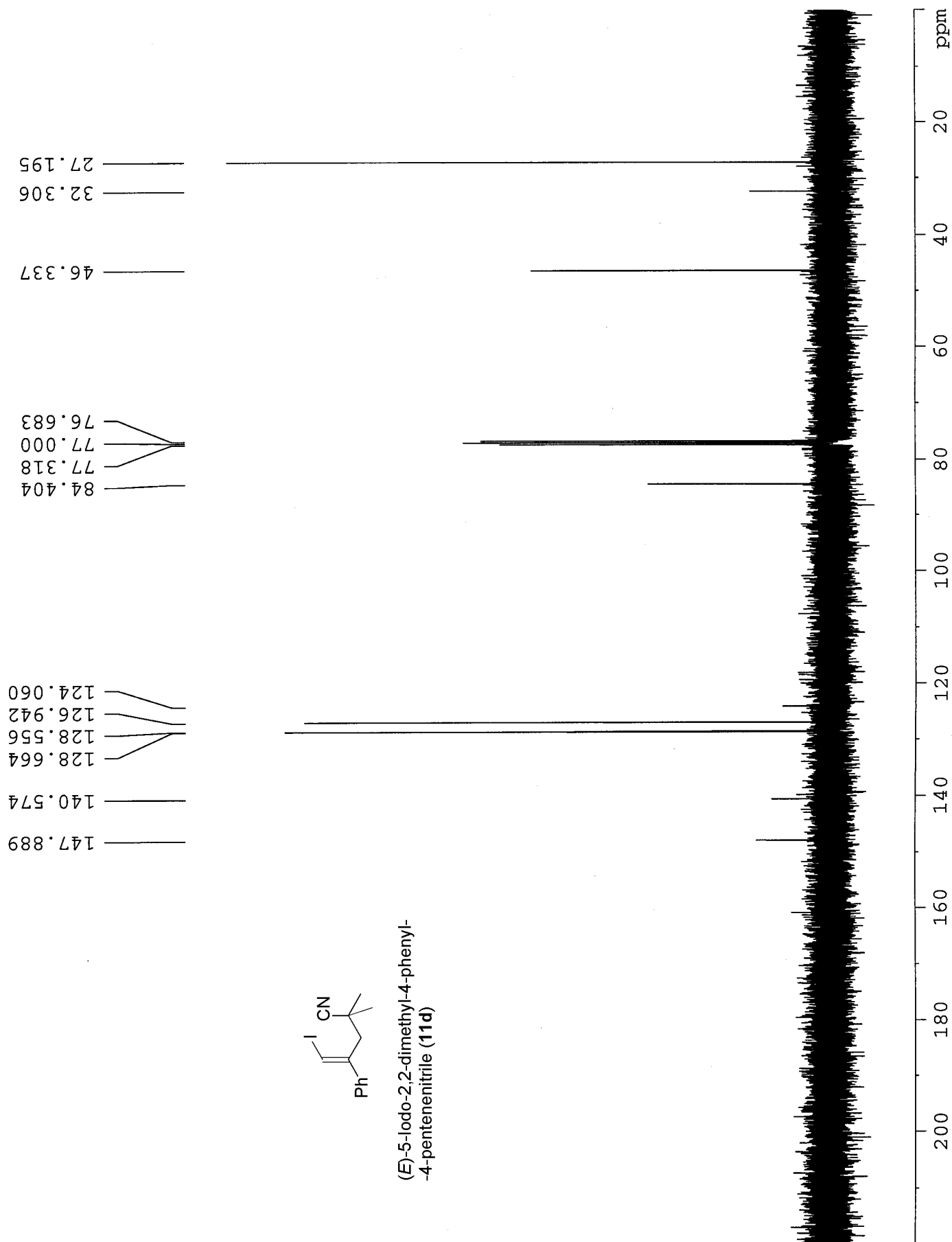


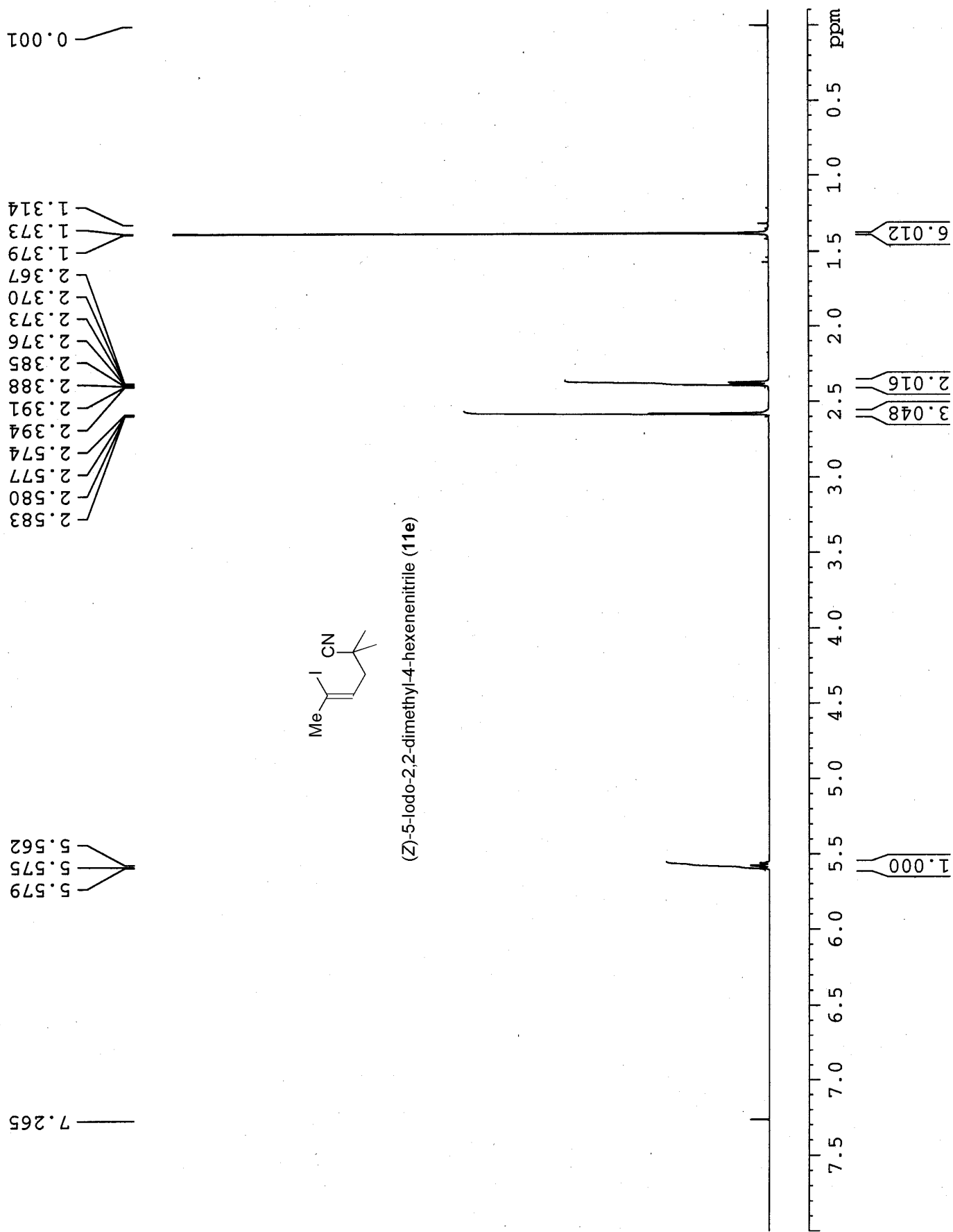


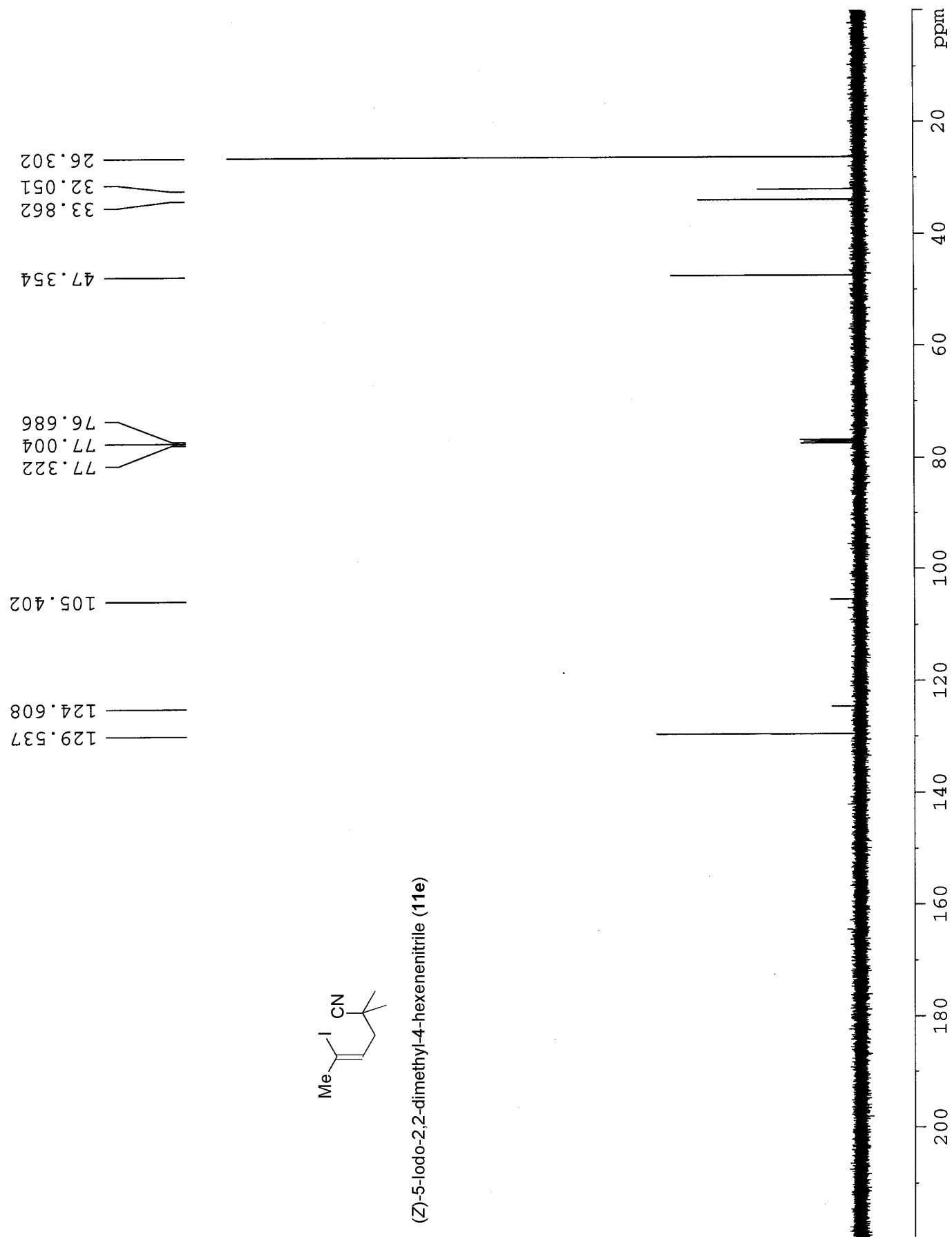


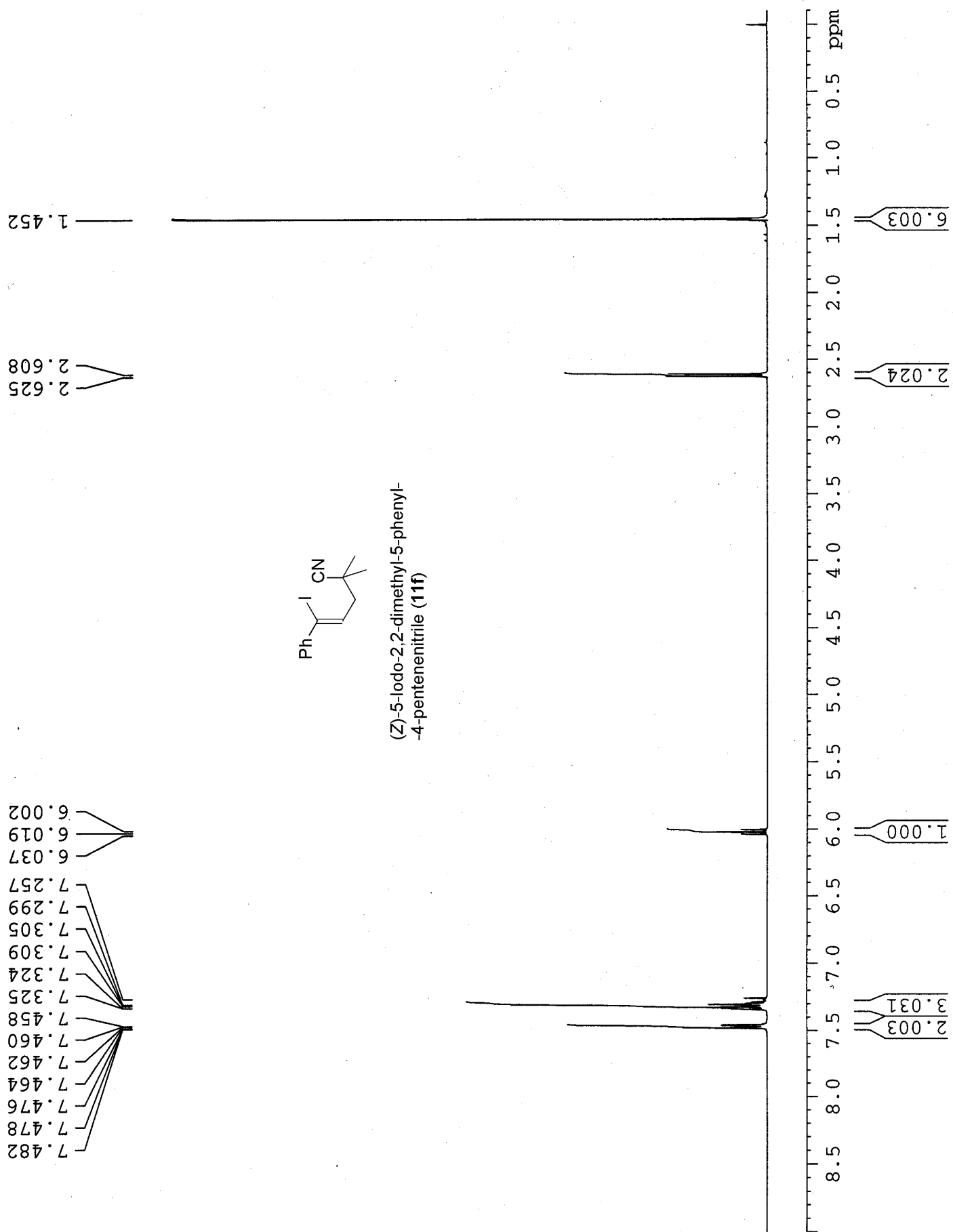


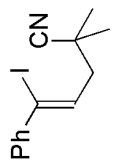




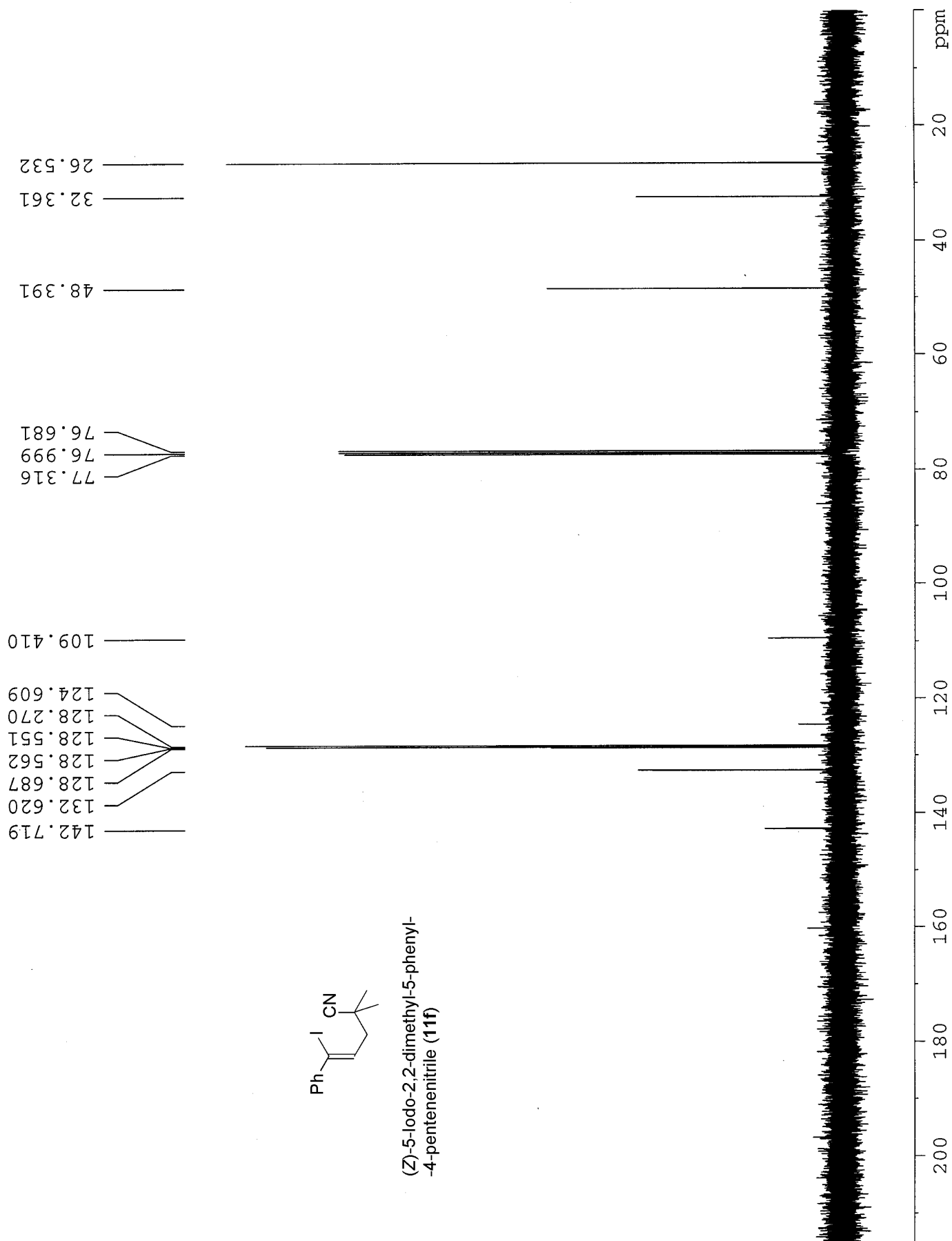


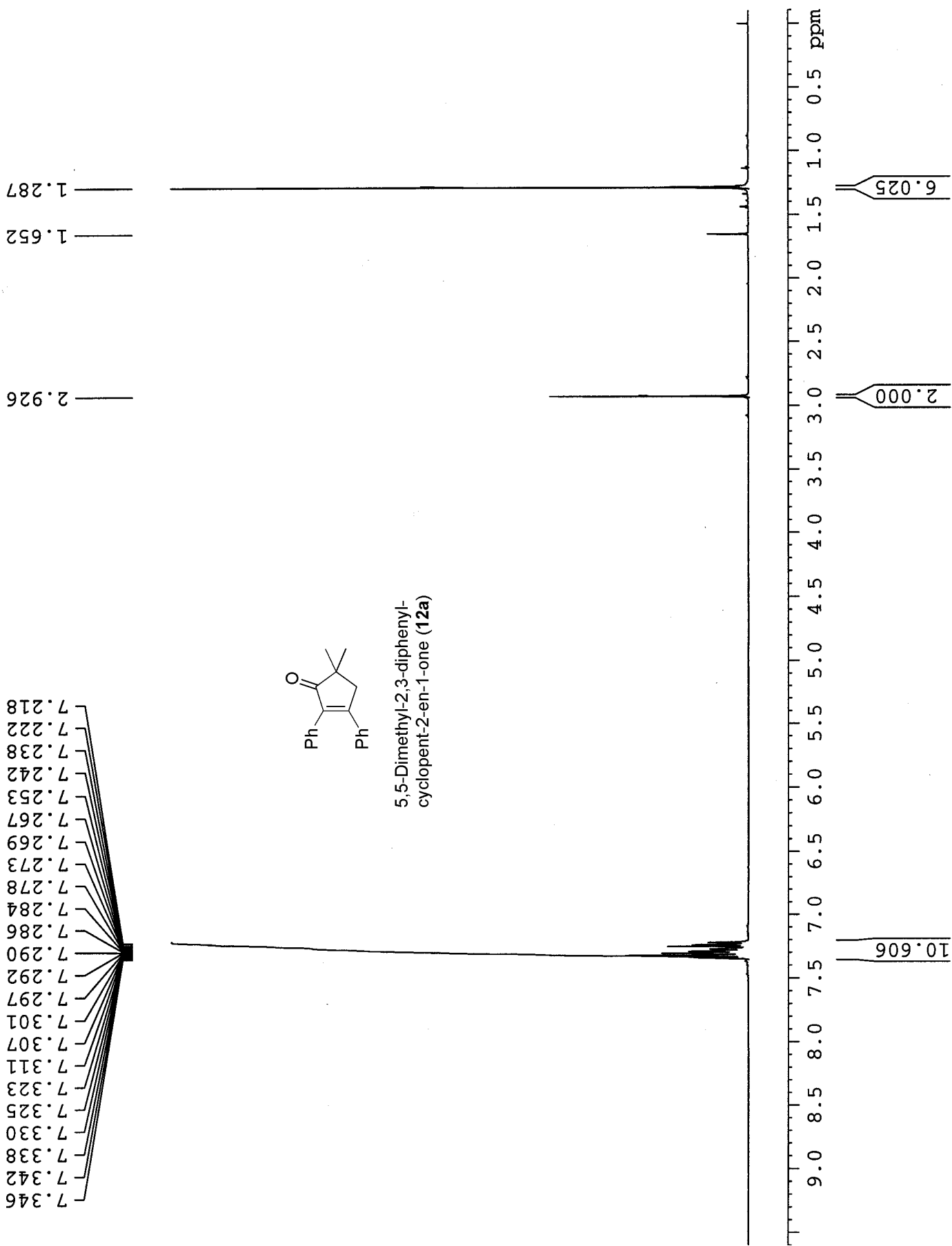


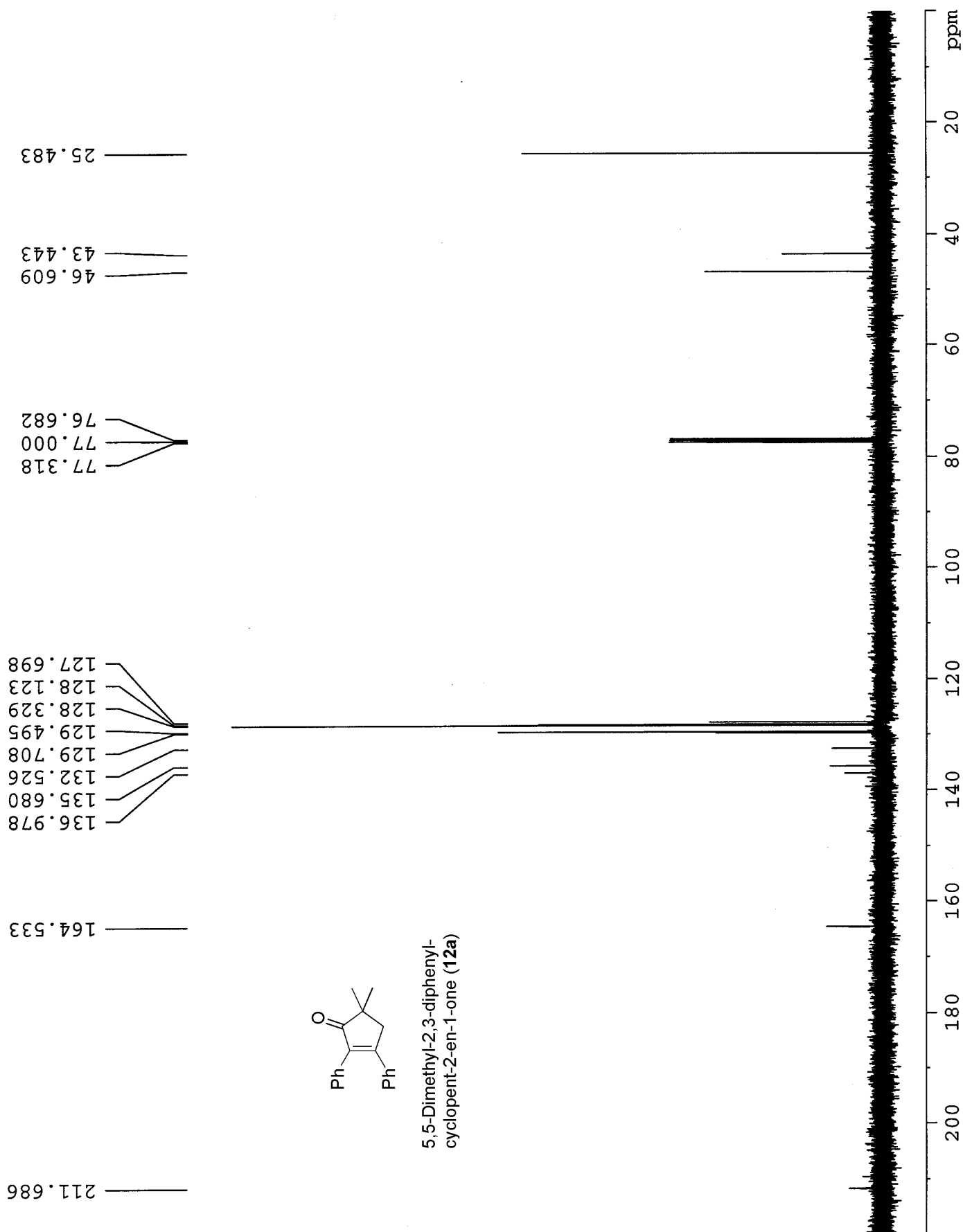


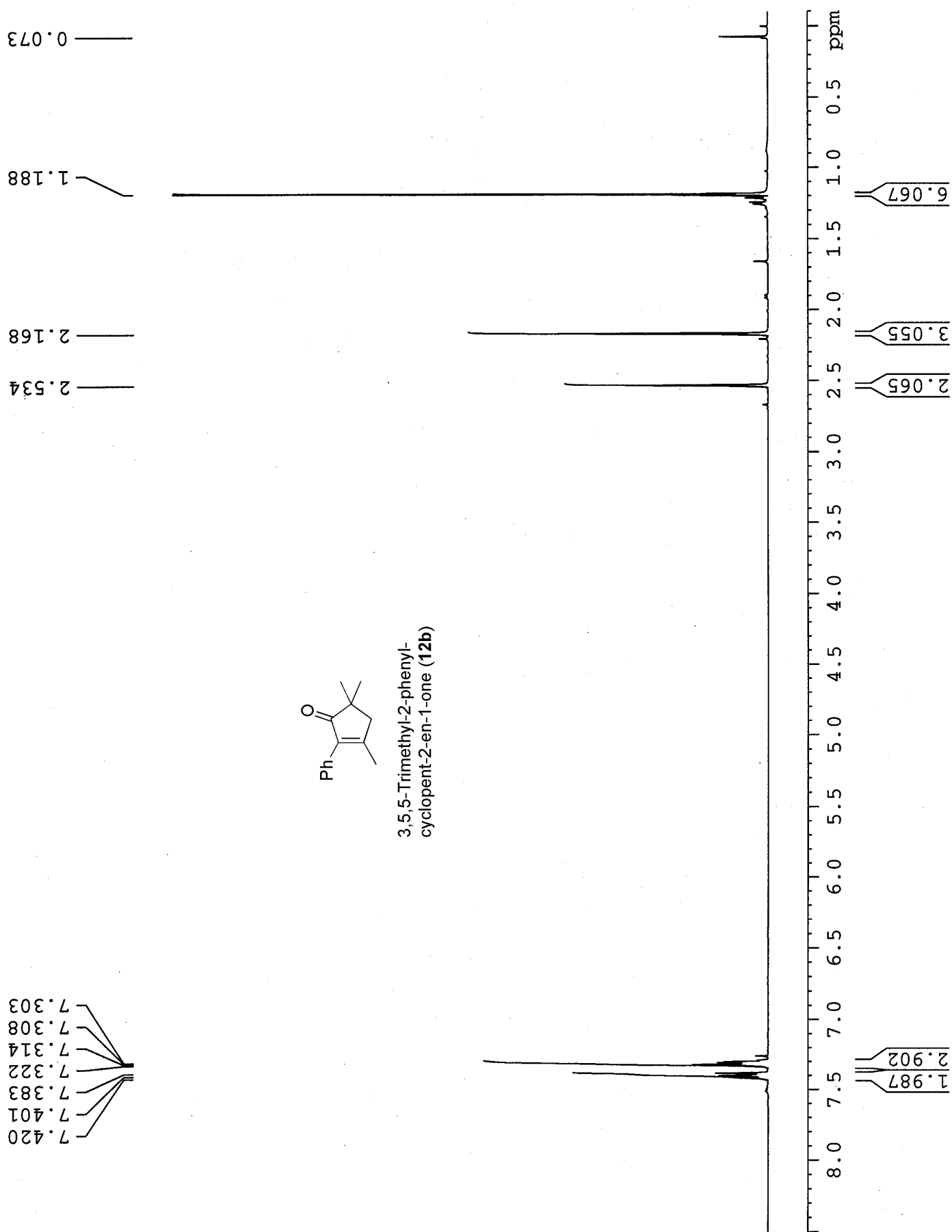


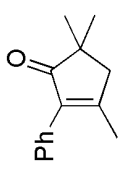
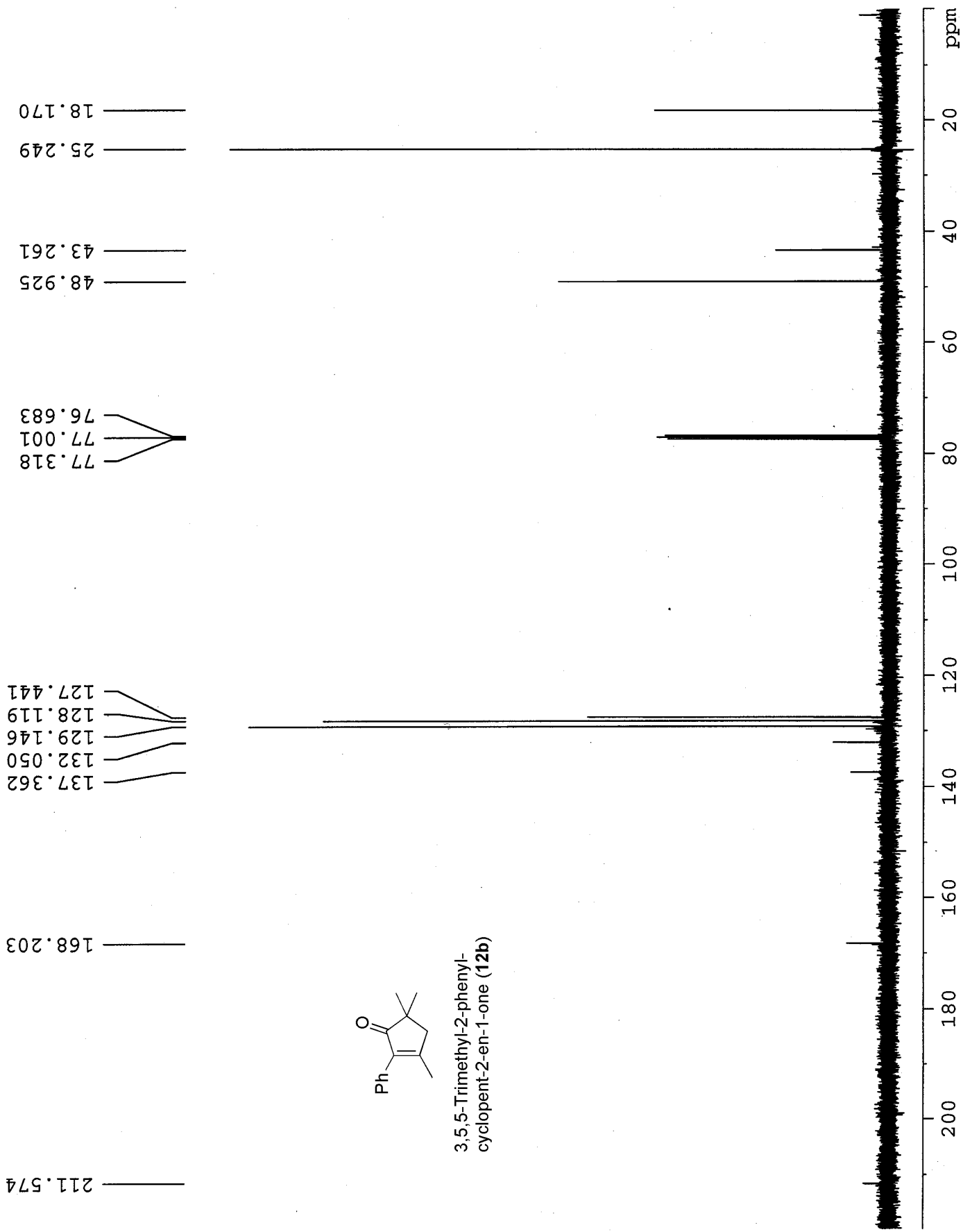
(Z)-5-iodo-2,2-dimethyl-5-phenyl-4-pentenitrile (**11f**)



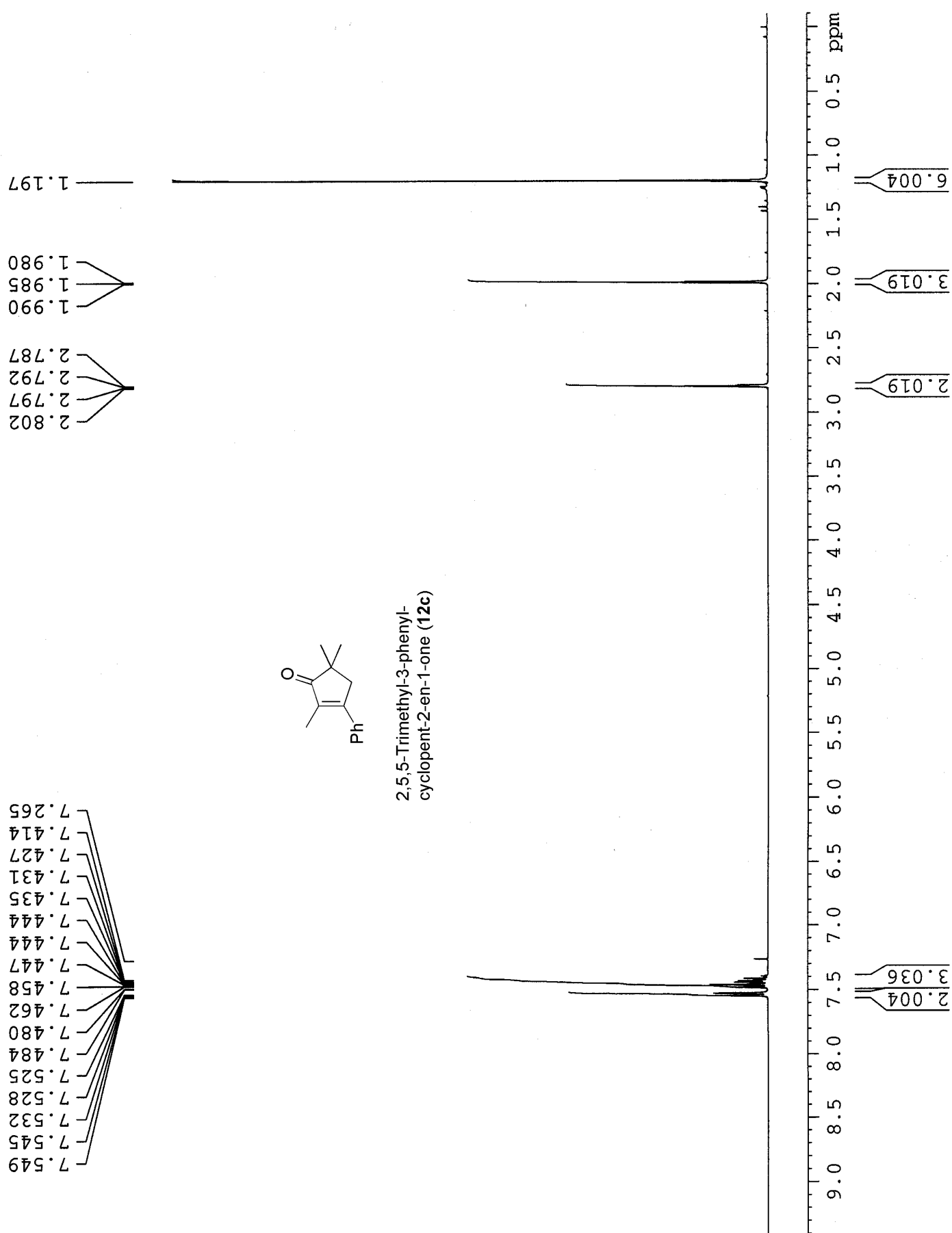


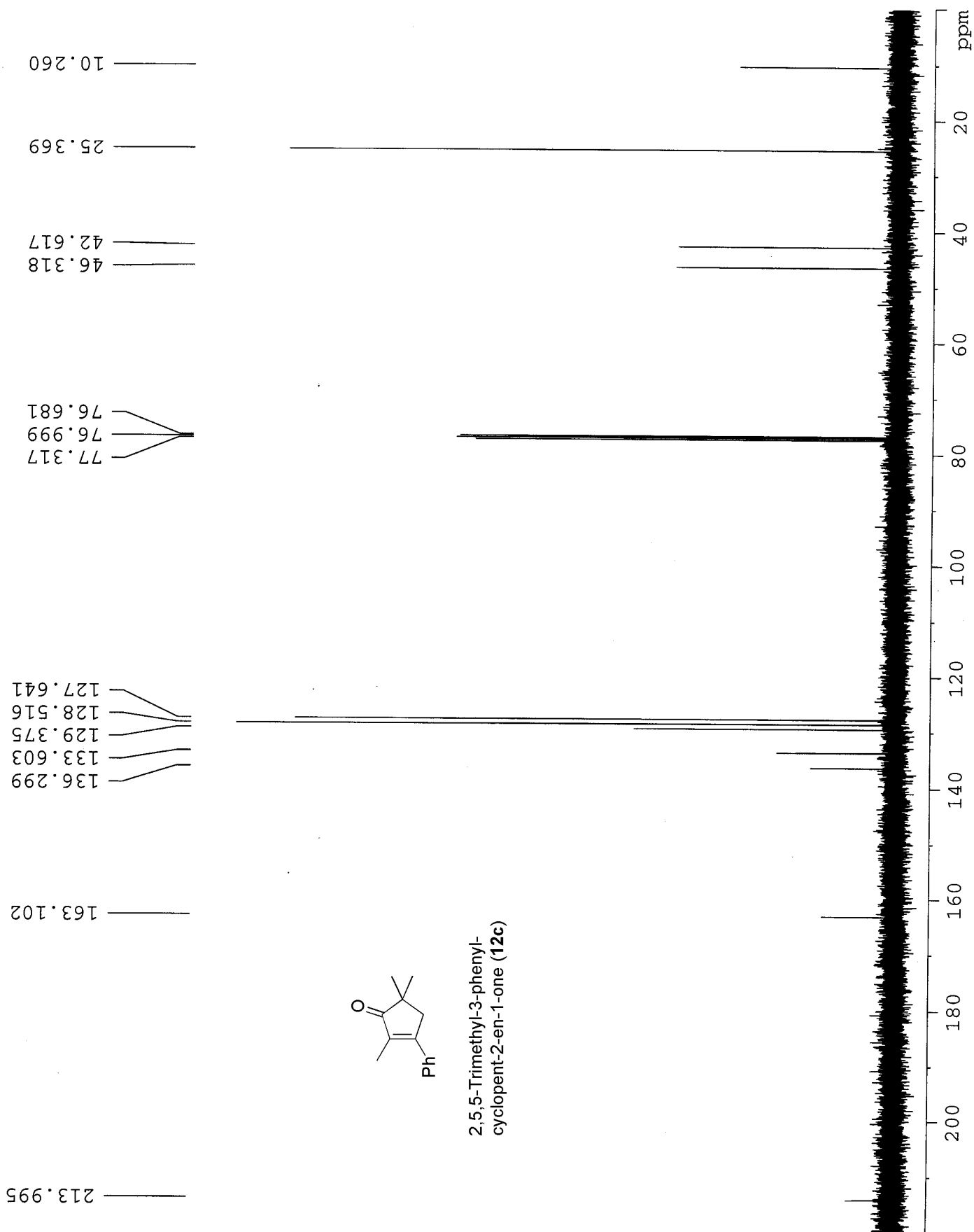


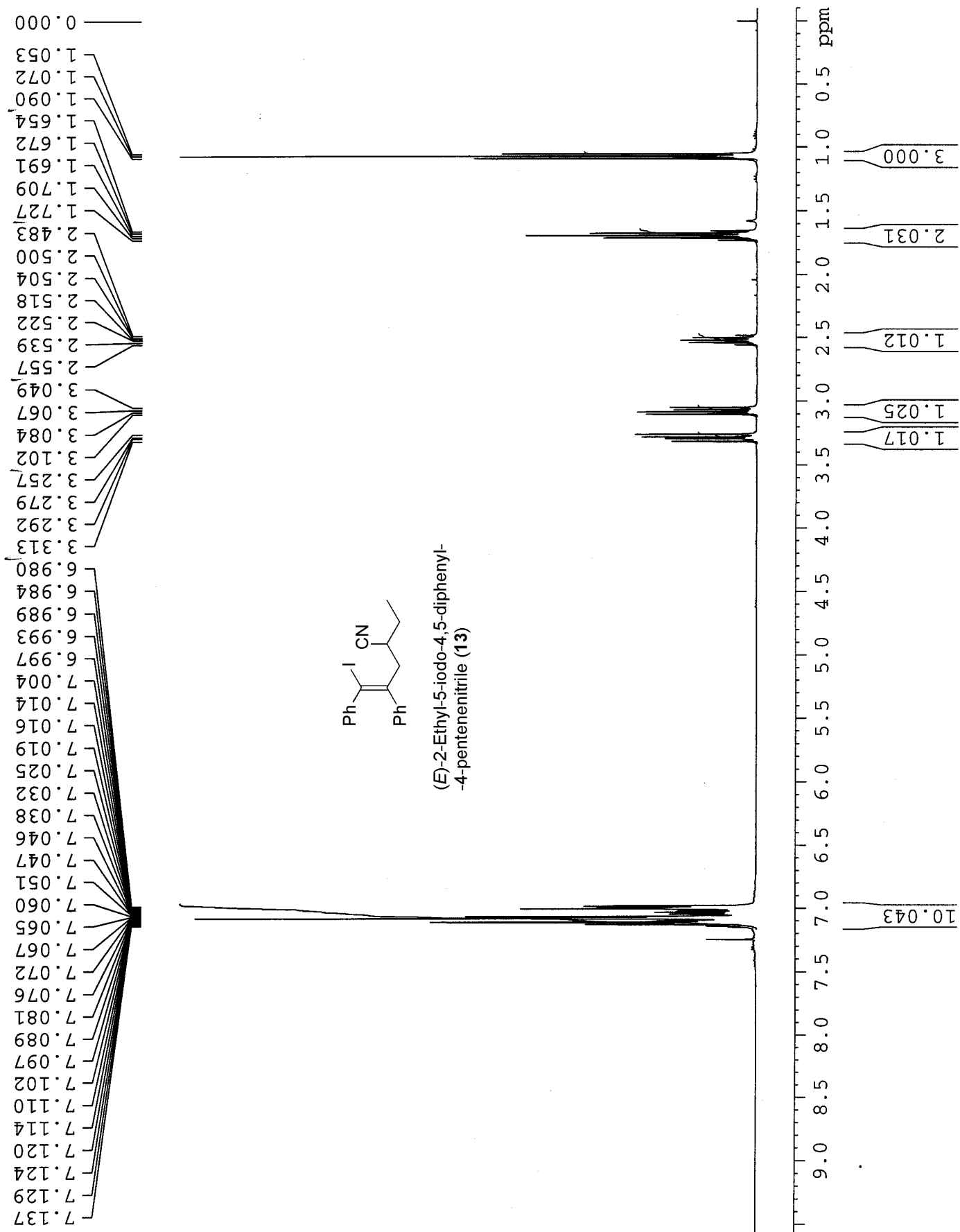


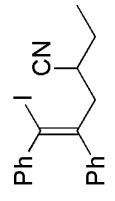


3,5-Trimethyl-2-phenyl-
cyclopent-2-en-1-one (12b)









(E)-2-Ethyl-5-iodo-4,5-diphenyl-4-pentenitrile (13)

