

## Supporting Information

### Transition-Metal Free N-Arylation of Cyanamides by Diaryliodonium Triflates in Aqueous Media

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## General information

Melting points (M.p.) were recorded using microscopic melting point apparatus and are uncorrected.

Infrared spectra were recorded on a Bruke-TENSOR27 FT-IR spectrometer.

Proton NMR ( $^1\text{H}$ ) spectra were recorded at 500 MHz on a Bruker AC-500 spectrometer. Carbon NMR ( $^{13}\text{C}$ ) spectra were similarly recorded at 125. Proton NMR ( $^1\text{H}$  NMR) and carbon NMR ( $^{13}\text{C}$  NMR) chemical shifts ( $\delta$ ) are reported in parts per million (ppm) relative to residual proton signals in  $\text{CDCl}_3$  ( $\delta=7.26, 77.00$ ),  $\text{CD}_3\text{OD}$  ( $\delta= 3.31, 49.00$ ),  $\text{CD}_3\text{CN}$  ( $\delta= 1.94, 1.32$ ) and  $\text{DMSO-d}_6$  ( $\delta= 2.50, 39.52$ ).

Coupling constants ( $J$ ) are reported in Hertz (Hz) and refer to apparent multiplicities. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, qu: quintet, sept: septet, m: multiplet, bs: broad signal.

Mass spectra were obtained either from an LCMS-IT-TOF (ESI or APCI) using positive or negative electron spray ( $\text{ES}^+$  or  $\text{ES}^-$ ) for the high resolution mass spectra (HRMS).

Flash chromatography was performed using SDS silicagel 60 (35-70  $\mu\text{m}$ ). Preparative thin layer chromatography (TLC) was carried out on 20 x 20 cm plates with a layer thickness of 0.5 mm (SDS Silicage l60 F254).

All reagents were obtained from commercial suppliers unless otherwise stated. When necessary, organic solvents were routinely dried and/or distilled prior to use and stored over molecular sieves under argon.

The starting material cyanamides and diaryliodonium triflate are known and were prepared according to the procedure reported in reference (1) and (2) respectively.

## References

(1) a) J. Li and L. Neuville *Org. Lett.*, 2013, **15**, 6124–6127; b) S. K. Sahoo, L. Jamir, S. Guin and B. K. Patel, *Adv. Synth. Catal.*, 2010, **352**, 2538 – 2548; c) V. Kumar, M. P. Kaushik and A. Mazumdar *Eur. J. Org. Chem.*, 2008, 1910–1916.

(2) M. Bielawski, M. Zhu, and B. Olofsson *Adv. Synth. Catal.*, 2007, **349**, 2610 – 2618.

## Experimental procedures:

### General procedures for the synthesis of disubstituted cyanamides through transition-metal free N-Arylation of cyanamides with diaryliodonium triflates.

**Procedure A-1.** Cyanamides (0.2 mmol, 1.0 equiv),  $\text{Na}_2\text{CO}_3$  (0.4 mmol, 2.0 equiv) and diaryliodonium triflates (0.2 mmol, 1 equiv) were added to 0.8 mL  $\text{H}_2\text{O}$  (or toluene) in a round flask (10 mL) with refluxing condenser, heated to 80  $^\circ\text{C}$  and kept it stirring for 2 h. The mixture was cooled to room temperature, extracted with  $\text{EtOAc}$ ; the organic layers were

combined, washed by brine, dried by  $\text{MgSO}_4$  and concentrated under reduced pressure to give a residue which was purified by preparative TLC.

**Procedure A-2.** Cyanamides (1.25 mmol, 1.0 equiv),  $\text{Na}_2\text{CO}_3$  (2.5 mmol, 2.0 equiv) and diaryliodonium triflates (1.25 mmol, 1 equiv) were added to 5 mL  $\text{H}_2\text{O}$  in a round flask (25 mL) with refluxing condenser, heated to 80 °C and kept it stirring for 2 h. The mixture was cooled to room temperature, extracted with EtOAc; the organic layers were combined, washed by brine, dried by  $\text{MgSO}_4$  and concentrated under reduced pressure to give a residue which was purified by column chromatography for 1.25 mmol to give 223 mg phenyl(p-tolyl)cyanamide (yield: 86%) and 196 mg p-tolyl iodide (yield: 72%).

$^1\text{H}$  NMR of p-tolyl iodide (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (d,  $J = 8.0$  Hz, 2H), 6.94 (d,  $J = 7.9$  Hz, 2H), 2.31 (s, 3H).

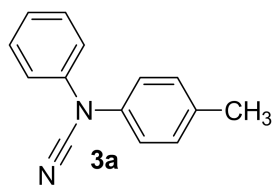
#### **General procedures for the synthesis of N,N-disubstituted ureas through hydrolyzation of disubstituted cyanamides promoted by trifluoroacetic acid in toluene.**

**Procedure B.** Disubstituted cyanamides (0.2 mmol, 1 equiv), trifluoroacetic acid (0.4 mmol, 2 equiv) and  $\text{H}_2\text{O}$  were added to a round flask (10 mL), heated to 80 °C and kept it stirring for 24 h. The mixture was cooled to room temperature, extracted with EtOAc; the organic layers were combined, washed by brine, dried by  $\text{MgSO}_4$  and concentrated under reduced pressure to give a residue which was purified by preparative TLC.

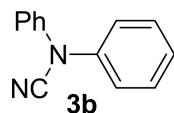
#### **General procedures for one-pot synthesis of N,N-disubstituted ureas through sequential N-arylation and hydrolyzation between cyanamides and diaryliodonium triflate in toluene.**

**Procedure C.** Cyanamides (0.2 mmol, 2.0 equiv),  $\text{Na}_2\text{CO}_3$  (0.4 mmol, 2.0 equiv) and diaryliodonium triflates (0.2 mmol 1 equiv) were added to 0.8 mL  $\text{H}_2\text{O}$  (or toluene) in a round flask (10 mL), heated to 80 °C and kept it stirring for 2 h, then trifluoroacetic acid (0.4 mmol, 2 equiv) and  $\text{H}_2\text{O}$  (1 mmol) were added to the mixture and stirred it 80 °C for 24 h. The mixture was cooled to room temperature, quenched the reaction with  $\text{H}_2\text{O}$ , extracted with EtOAc, the organic layers were combined, washed by brine, dried by  $\text{MgSO}_4$  and concentrated under reduced pressure to give a residue which was purified by preparative TLC.

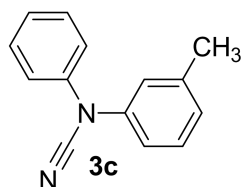
#### **Spectroscopic data of 3a-3j, 3l-3p and 4a-4d**



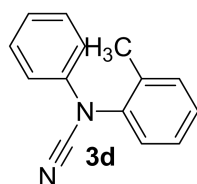
Following the general procedure **A-1**, the title compound was obtained as colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36-7.43 (m, 2H), 7.15-7.25 (m, 7H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  139.66, 136.83, 136.06, 130.46, 129.67, 125.52, 122.42, 120.00, 112.75, 20.88. IR ( $\text{cm}^{-1}$ ): 3037.5, 2923.3, 2223.5, 1593.9, 1593.9, 1508.8, 1492.1, 1264.2, 913.3, 747.5. HRMS (ESI): calcd for  $\text{C}_{14}\text{H}_{13}\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ): 209.1070, found: 209.1067.



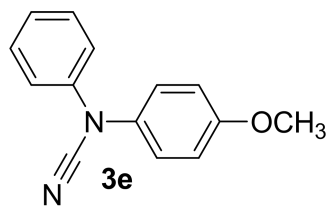
Following the general procedure **A-1**, the title compound was obtained as white solid (36 mg, 93%), **MP**: 68-70 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 – 7.40 (m, 4H), 7.27 (m, 6H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  139.04, 129.83, 126.26, 121.29, 112.57. IR ( $\text{cm}^{-1}$ ): 3475.0, 3058.2, 2924.1, 2223.8, 1590.8, 1490.8, 1262.9, 753.9, 692.1. HRMS (ESI): calcd for  $\text{C}_{13}\text{H}_{11}\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ): 195.0917, found: 195.0912.



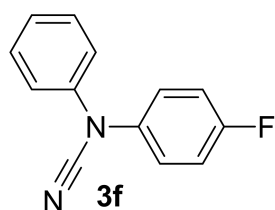
Following the general procedure **A-1**, the title compound was obtained as colorless oil (38 mg, 91%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.40 (dd,  $J=8.4$ , 7.0 Hz, 2H), 7.28 (t,  $J=7.9$  Hz, 1H), 7.23-7.26 (m, 3H), 7.06-7.09 (m, 2H), 7.04 (dd,  $J=9.0$ , 2.0 Hz, 1H), 2.35 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  140.10, 139.16, 138.85, 129.75, 129.57, 127.14, 126.06, 122.03, 121.09, 118.51, 112.68, 21.29. IR ( $\text{cm}^{-1}$ ): 3449.7, 3044.3, 2922.8, 2221.1, 1609.5, 1491.3, 1260.0, 1029.7, 753.8, 691.0. HRMS (ESI): calcd for  $\text{C}_{14}\text{H}_{13}\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ): 209.1070, found: 209.1065.



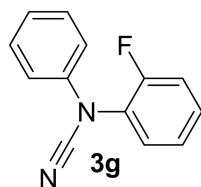
Following the general procedure **A-1**, the title compound was obtained as colorless oil (37 mg, 91%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.29 (m, 6H), 7.11 (tt,  $J=7.4$ , 0.9 Hz, 1H), 6.95 – 6.97 (m, 2H), 2.28 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  140.57, 136.39, 135.41, 132.01, 129.62, 129.57, 128.10, 127.90, 123.74, 115.77, 112.03, 17.43. IR ( $\text{cm}^{-1}$ ): 3472.9, 3086.4, 2925.2, 2222.2, 1596.8, 1492.1, 1266.6, 751.3, 721.7. HRMS (ESI): calcd for  $\text{C}_{14}\text{H}_{13}\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ): 209.1070, found: 209.1068.



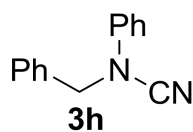
Following the general procedure **A-1**, the title compound was obtained as colorless oil (41 mg, 93%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.36 (dt, *J*=7.5, 1Hz, 2H), 7.25-7.27 (m, 2H), 7.17 (t, *J*=7.4Hz, 1H), 7.13 (dd, *J*=8.7, 1Hz, 2H), 6.98 (dd, *J*=8.9, 2.2 Hz, 2H), 3.85 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 158.87, 140.44, 130.73, 129.56, 125.73, 124.69, 118.25, 115.20, 112.80, 55.55. IR (cm<sup>-1</sup>): 3476.4, 3007.7, 2934.5, 2838.2, 2222.7, 1595.3, 1507.9, 1245.6, 1031.3, 833.4, 752.4. HRMS (ESI): calcd for C<sub>14</sub>H<sub>13</sub>N<sub>2</sub>O ([M +H]<sup>+</sup>): 225.1022, found: 225.1020.



Following the general procedure **A-1**, the title compound was obtained as white solid (40 mg, 89%), MP: 49-51 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.39-7.43 (m, 2H), 7.23-7.29 (m, 3H), 7.18-7.20 (m, 2H), 7.12-7.16 (m, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 160.99 (d, *J*=247.8Hz), 139.46, 134.70, 129.85, 125.87, 124.41 (d, *J* = 8.6 Hz), 120.00, 116.90 (d, *J*=23.2 Hz), 112.44. IR (cm<sup>-1</sup>): 3478.6, 3073.6, 2926.7, 2225.2, 1594.9, 1504.3, 1258.6, 1222.0, 1157.0, 836.1, 752.9. HRMS (ESI): calcd for C<sub>13</sub>H<sub>10</sub>FN<sub>2</sub> ([M +H]<sup>+</sup>): 213.0823, found: 213.0824.

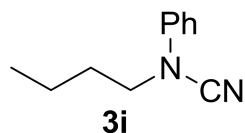


Following the general procedure **A-1**, the title compound was obtained as colorless oil (41 mg, 91%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.48 – 7.41 (m, 2H), 7.39 – 7.33 (m, 2H), 7.31 – 7.23 (m, 2H), 7.19 – 7.16 (tt, *J*=7.5, 1.0 Hz, 1H), 7.10 – 7.03 (d, *J*=8.1Hz, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 157.46 (d, *J*=262.2 Hz), 140.00, 130.66 (d, *J* = 7.8 Hz, 8H), 129.57, 128.35, 125.48 (d, *J* = 4.1 Hz, 8H), 124.95 (d, *J* = 11.8 Hz), 124.60, 117.52 (d, *J* = 19.0 Hz, 8H), 116.66, 111.64. IR (cm<sup>-1</sup>): 3477.2, 2925.9, 2854.7, 2224.9, 1595.2, 1495.6, 1255.8, 749.8. HRMS (ESI): calcd for C<sub>13</sub>H<sub>10</sub>FN<sub>2</sub> ([M +H]<sup>+</sup>): 213.0823, found: 213.0819.

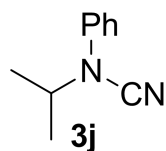


Following the general procedure **A-1**, the title compound was obtained as colorless oil [26 mg (62%) in toluene, 17 mg (41%) in H<sub>2</sub>O]. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) 7.32-7.39 (m, 7H), 7.13

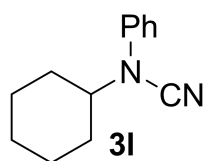
(dd,  $J=8.7, 0.7$  Hz, 2H), 7.09 (t,  $J=7.4$  Hz), 4.81 (s, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  139.72, 134.22, 129.61, 129.04, 128.48, 127.29, 123.65, 115.95, 113.89, 53.67. IR ( $\text{cm}^{-1}$ ): 3448.1, 3034.2, 2927.0, 2218.0, 1597.3, 1497.4, 1227.9, 1177.6, 751.0, 692.5. HRMS (ESI): calcd for  $\text{C}_{14}\text{H}_{13}\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ): 209.1070, found: 209.1073.



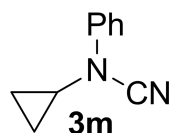
Following the general procedure **A-1**, the title compound was obtained as colorless oil [26 mg (76%) in toluene, 16 mg (46%) in  $\text{H}_2\text{O}$ ].  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.38 (m, 2H), 7.08-7.12 (m, 3H), 3.58 (t,  $J=7.4$  Hz, 2H), 1.81 (qu,  $J=7.5$  Hz, 2H), 1.48 (sept,  $J=7.2$  Hz, 2H), 0.98 (t,  $J=7.4$  Hz, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  139.98, 129.60, 123.40, 115.78, 113.63, 49.10, 29.40, 19.73, 13.60. IR ( $\text{cm}^{-1}$ ): 3449.3, 2961.0, 2930.5, 2218.1, 1633.0, 1599.1, 1498.6, 1383.1, 751.4. HRMS (ESI): calcd for  $\text{C}_{13}\text{H}_{15}\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ): 175.1230, found: 175.1299.



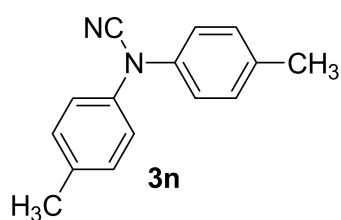
Following the general procedure **A-1**, the title compound was obtained as colorless oil (14 mg (44%) in toluene, 12 mg (38%) in  $\text{H}_2\text{O}$ ). Colorless oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.38 (m, 2H), 7.14-7.16 (m, 2H), 7.10 (tt,  $J=7.4, 1.0$  Hz), 4.01 (sept,  $J=6.5$  Hz, 1), 1.44 (s, 3H), 1.42 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  139.96, 129.66, 123.73, 116.97, 112.02, 50.41, 20.63. IR ( $\text{cm}^{-1}$ ): 3444.5, 2925.8, 2853.6, 2212.7, 1597.4, 1495.6, 1271.3, 1187.8, 750.7. HRMS (ESI): calcd for  $\text{C}_{10}\text{H}_{13}\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ): 160.1073, found: 160.1069.



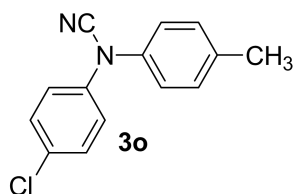
Following the general procedure **A-1**, the title compound was obtained as colorless oil [28 mg (70%) in toluene, 24 mg (60%) in  $\text{H}_2\text{O}$ ].  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (td,  $J=8.0, 7.4$  Hz, 2H), 7.15 (d,  $J=8.0$  Hz, 2H), 7.09 (t,  $J=7.4$  Hz, 1H), 3.56 (tt,  $J=11.6, 3.8$  Hz, 1H), 2.08 (d,  $J=11.4$  Hz, 2H), 1.91 (d,  $J=13.6$  Hz, 2H), 1.60-1.67 (m, 2H), 1.32-1.43 (m, 2H), 1.16-1.29 (m, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  139.91, 129.60, 123.69, 117.02, 112.47, 57.52, 30.99, 25.25, 25.01. IR ( $\text{cm}^{-1}$ ): 3448.8, 2935.4, 2858.4, 2214.0, 1597.0, 1495.7, 1280.1, 1238.2, 1175.2, 751.2. HRMS (ESI): calcd for  $\text{C}_{13}\text{H}_{17}\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ): 201.1386, found: 201.1383.



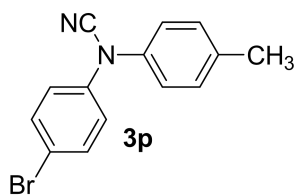
Following the general procedure **A-1**, the title compound was obtained as colorless oil [14 mg (37% yield eliminating ethyl acetate) in toluene, <2 mg (%) in H<sub>2</sub>O]. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.37 (t, *J* = 7.9 Hz), 7.25 (d, *J* = 8.9 Hz, 3H), 7.11 (t, *J* = 7.4 Hz, 1H), 2.97 (tt, *J* = 6.8, 3.5 Hz, 1H), 1.12 – 1.06 (m, 2H), 1.02 – 0.95 (m, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 140.20, 129.44, 123.48, 115.52, 29.96, 8.65. IR (cm<sup>-1</sup>): 3348.4, 2923.3, 2952.6, 2220.8, 1632.4, 1595.7, 1494.0, 1280.2, 750.5. HRMS (ESI): calcd for C<sub>10</sub>H<sub>11</sub>N<sub>2</sub> ([M + H]<sup>+</sup>): 159.0917, found: 159.0917.



Following the general procedure **A-1**, the title compound was obtained as white solid (40 mg, 90%), **MP**: 88-90 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.20 (d, *J* = 8.3 Hz, 4H), 7.14 – 7.10 (m, 4H), 2.36 (s, 6H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 136.75, 136.00, 130.29, 121.15, 112.99, 20.79. IR (cm<sup>-1</sup>): 3450.2, 2924.3, 2854.8, 2222.5, 1636.2, 1506.3, 1267.0, 815.1. HRMS (ESI): calcd for C<sub>15</sub>H<sub>15</sub>N<sub>2</sub> ([M + H]<sup>+</sup>): 223.1230, found: 222.1230.

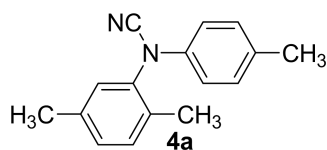


Following the general procedure **A-1**, the title compound was obtained as white solid (47 mg, 97%), **MP**: 75-77 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.52-7.56 (m, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.10-7.13 (m, 2H), 2.38 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 138.43, 137.35, 135.62, 130.79, 130.61, 129.71, 122.66, 120.94, 112.27, 20.88. IR (cm<sup>-1</sup>): 3474.7, 3036.8, 2924.3, 2224.3, 1593.9, 1509.7, 1488.3, 1268.3, 1090.7, 1012.9, 817.9. HRMS (ESI): calcd for C<sub>14</sub>H<sub>12</sub>ClN<sub>2</sub> ([M + H]<sup>+</sup>): 243.0684, found: 243.0677.

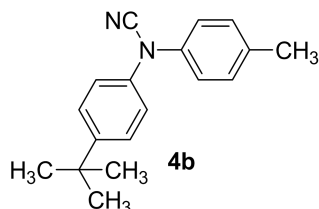


Following the general procedure **A-1**, the title compound was obtained as white solid (45 mg, 78%), **MP**: 85-87 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.48 (d, *J* = 8.9 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.9 Hz, 2H), 2.38 (s, 3H); <sup>13</sup>C NMR (126

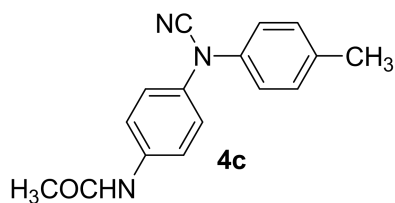
MHz, CDCl<sub>3</sub>)  $\delta$  139.09, 137.55, 135.52, 132.69, 130.69, 122.94, 121.12, 118.33, 112.25, 20.95. IR (cm<sup>-1</sup>): 3474.9, 3035.1, 2923.4, 2221.0, 1632.2, 1587.1, 1483.8, 1259.2, 1071.0, 811.6, 709.3. HRMS (ESI): calcd for C<sub>14</sub>H<sub>12</sub>BrN<sub>2</sub> ([M +H]<sup>+</sup>): 287.1078, found: 287.1077.



Following the general procedure **A-1**, the title compound was obtained as colorless oil (42 mg, 89%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.23 (d, *J* = 7.7 Hz, 1H), 7.12-7.17 (m, 4H), 6.85 (d, *J* = 8.6 Hz, 2H), 2.35 (s, 3H), 2.32 (s, 3H), 2.21 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  138.23, 137.85, 135.41, 133.34, 132.88, 131.68, 130.18, 130.02, 128.27, 115.90, 112.53, 20.70, 20.54, 16.99. IR (cm<sup>-1</sup>): 3476.3, 2923.4, 2864.0, 2215.9, 1612.5, 1508.0, 1266.6, 1144.3, 811.4. HRMS (ESI): calcd for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub> ([M +H]<sup>+</sup>): 237.1386, found: 237.1378.

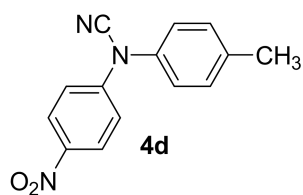


Following the general procedure **A-1**, the title compound was obtained as colorless oil (45 mg, 88%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.41 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.17 – 7.13 (m, 4H), 2.37 (s, 3H), 1.33 (s, 9H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  149.10, 136.73, 136.57, 136.19, 130.33, 126.63, 121.52, 120.49, 112.99, 34.47, 31.25, 20.84. IR (cm<sup>-1</sup>): 3449.2, 2962.5, 2222.7, 1609.9, 1510.3, 1267.0, 816.9. HRMS (ESI): calcd for C<sub>18</sub>H<sub>21</sub>N<sub>2</sub> ([M +H]<sup>+</sup>): 265.1699, found: 265.1701.



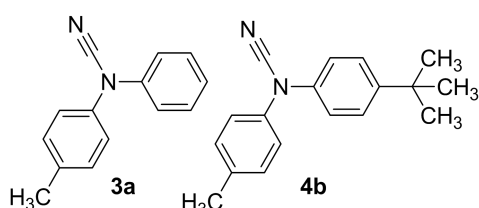
Following the general procedure **A-1**, the title compound was obtained as slight yellow oil (6 mg, 11%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.61 (s, 1H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 2.35 (s, 3H), 2.18 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  168.51, 136.53, 136.34, 136.10, 135.13, 130.43, 121.87, 121.17, 121.21, 112.93, 24.45, 20.84. IR (cm<sup>-1</sup>): 3446.2, 2222.5, 1633.3, 1508.6, 1381.9, 1257.2, 814.8. HRMS (ESI): calcd for C<sub>15</sub>H<sub>16</sub>N<sub>3</sub>O ([M +H]<sup>+</sup>): 266.1288, found: 266.1286.



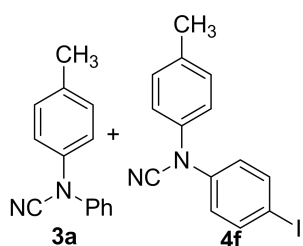


Following the general procedure **A-1**, the title compound was obtained as slight yellow solid (49 mg, 97%), **MP**: 128-130 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 (d,  $J = 9.2$  Hz, 2H), 7.34 (d,  $J = 8.3$  Hz, 2H), 7.28 (d,  $J = 8.4$  Hz, 2H), 7.19 (d,  $J = 9.2$  Hz, 2H), 2.43 (s, 3H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  146.10, 143.80, 139.83, 133.73, 131.26, 125.49, 119.21, 116.88, 110.95, 21.12. IR ( $\text{cm}^{-1}$ ): 3451.6, 2925.8, 2231.8, 1593.1, 1510.9, 1343.3, 1288.3, 1111.8, 819.8, 745.9. HRMS (ESI): calcd for  $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_2$  ( $[\text{M}]^+$ ): 253.0851, found: 253.0854.

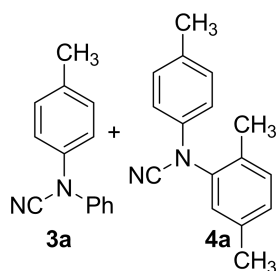
### Spectroscopic data of disubstituted cyanamides mixtures 3a/4b, 3a/4f, 3a/4a and 3d/4g



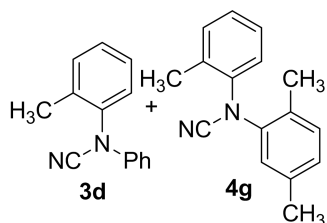
Following the general procedure **A-1**, the title compound was obtained as colorless oil (43 mg, 3a/4b=2.4/1, 96%).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44–7.36 (m, 7.2H), 7.25–7.12 (m, 23.6H), 2.38 (s, 7.4H), 2.37 (s, 3H), 1.33 (s, 9H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  149.08, 139.65, 136.83, 136.70, 136.54, 136.17, 136.06, 130.46, 130.31, 129.67, 126.61, 125.52, 122.42, 121.49, 120.47, 120.00, 112.97, 112.75, 34.45, 31.23, 20.88, 20.83. IR ( $\text{cm}^{-1}$ ): 3449.2, 2962.0, 2925.8, 2223.2, 1595.5, 1509.8, 1265.1, 816.3, 753.9. HRMS (ESI): calcd for  $\text{C}_{18}\text{H}_{21}\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ): 265.1699, found: 265.1703; calcd for  $\text{C}_{14}\text{H}_{13}\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ): 209.1070, found: 209.1075.



Following the general procedure **A-1**, the title compound was obtained as colorless oil (50 mg, 3a/4f=1.5/1, 97%).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (dd,  $J = 6.8$ , 2.0 Hz, 2H), 7.38 (t,  $J = 7.9$  Hz, 1.62H), 7.17–7.26 (m, 9.82H), 6.93 (dd,  $J = 6.8$ , 2.0 Hz, 2H), 2.38 (s, 5.52H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  139.88, 139.65, 138.56, 137.64, 136.82, 136.06, 135.30, 130.68, 130.46, 129.67, 125.52, 123.12, 122.42, 121.15, 120.00, 112.75, 112.12, 88.76, , 20.94, 20.88. IR ( $\text{cm}^{-1}$ ): 3469.4, 2923.4, 2220.5, 1633.9, 1508.1, 1256.6, 8111.2. HRMS (ESI): calcd for  $\text{C}_{14}\text{H}_{12}\text{IN}_2$  ( $[\text{M} + \text{H}]^+$ ): 335.0040; found 335.0040; calcd for  $\text{C}_{14}\text{H}_{13}\text{N}_2$  ( $[\text{M} + \text{H}]^+$ ): 209.1070, found: 209.1070.

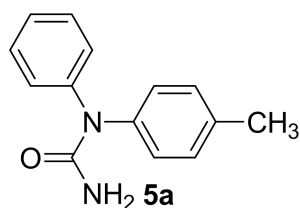


Following the general procedure **A-1**, the title compound was obtained as colorless oil (39 mg, 3a/4a=1.2/1, 89%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.37 – 7.46 (m, 2.4H), 7.08-7.28 (m, 13.5H), 6.85 (d, *J* = 8.6 Hz, 2H), 2.38 (s, .6H), 2.34 (s, 3H), 2.31 (s, 3H), 2.21 (s, 3H). IR (cm<sup>-1</sup>): 3474.7, 2923.7, 2219.0, 1594.4, 1507.6, 1263.5, 812.0. HRMS (ESI): calcd for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub> ([M +H]<sup>+</sup>): 237.1386, found: 237.1388; calcd for C<sub>14</sub>H<sub>13</sub>N<sub>2</sub> ([M +H]<sup>+</sup>): 209.1070, found: 209.1067.

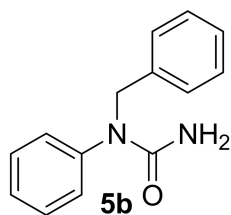


Following the general procedure **A-1**, the title compound was obtained as colorless oil (38 mg, 3d/4g=1/1.5, 85%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.41 – 7.30 (m, 4H), 7.26 (m, 1.5H), 7.22 – 7.17 (m, 2H), 7.14 – 7.07 (m, 3H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.98 – 6.94 (m, 2H), 2.32 (s, 3H), 2.29 (s, 3H), 2.28 (s, 3H), 2.20 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 140.57, 139.18, 138.81, 137.27, 136.39, 135.41, 132.47, 132.04, 132.01, 131.86, 129.62, 129.56, 129.36, 128.11, 128.09, 127.90, 127.22, 127.13, 124.51, 123.81, 123.74, 115.77, 113.56, 112.03, 20.77, 18.07, 17.53, 17.43. IR (cm<sup>-1</sup>): 3468.4, 2954.6, 2924.3, 2216.4, 1597.7, 1491.9, 1259.2, 1122.3, 1039.5, 815.3, 758.3. HRMS (ESI): calcd for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub> ([M +H]<sup>+</sup>): 237.1386, found: 237.1389; calcd for C<sub>14</sub>H<sub>13</sub>N<sub>2</sub> ([M +H]<sup>+</sup>): 209.1070, found: 209.1073.

#### Spectroscopic data of N,N-disubstituted ureas **5a** and **5b**



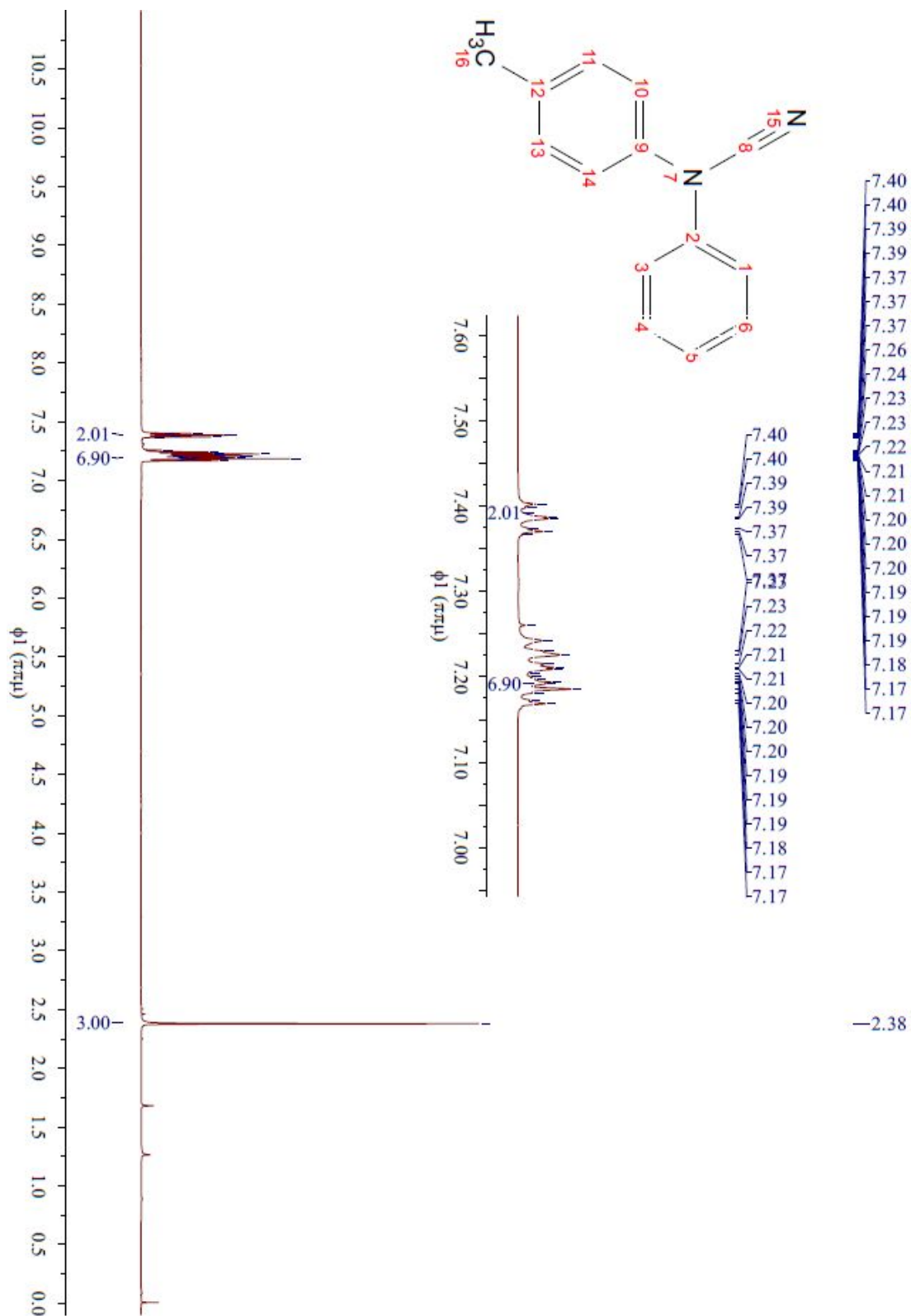
Following the general procedure **B** or **C**, the title compound was obtained as white solid (**B**: 32 mg, 71%, **C**: 32 mg, 73%). **MP**: 158-160 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.27 -7.37(m, 4H), 7.14-7.22 (m, 5H), 5.05 (br, 2H), 2.33 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 157.24, 142.84, 140.03, 136.65, 130.10, 129.19, 127.48, 126.98, 126.08, 20.95. IR (cm<sup>-1</sup>): 3474.9, 3334.7, 2924.2, 2853.3, 2677.2, 1649.6, 1567.5, 1419.1, 1071.7, 816.4. HRMS (ESI): calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>O ([M +H]<sup>+</sup>): 227.1179, found: 227.1175.

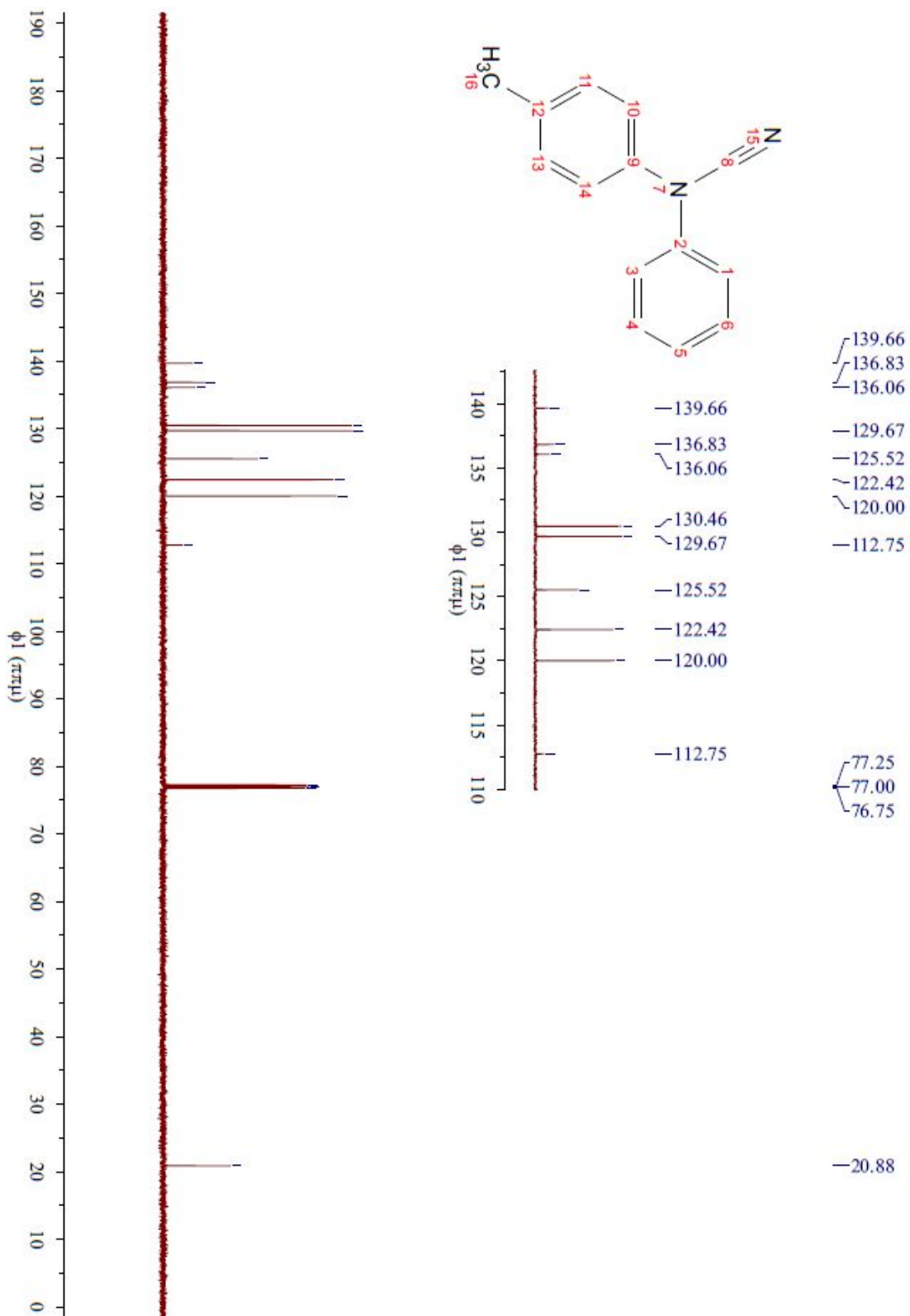


Following the general procedure **B**, the title compound was obtained as white solid (20 mg, 45%). **MP**: 105=107°C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.31-7.37 (m, 2H), 7.21-7.29 (m, 5H), 7.12 (dd, *J* = 5.3, 3.3 Hz, 2H), 4.86 (s, 2H), 4.58 (s, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 157.83, 141.80, 138.20, 129.81, 128.30, 128.28, 128.26, 127.85, 127.15, 52.98. IR (cm<sup>-1</sup>): 3477.78, 1256.6, 1586.9, 1387.5, 695.6. HRMS (ESI): calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>O ([M +H]<sup>+</sup>): 227.1179, found: 227.1178.

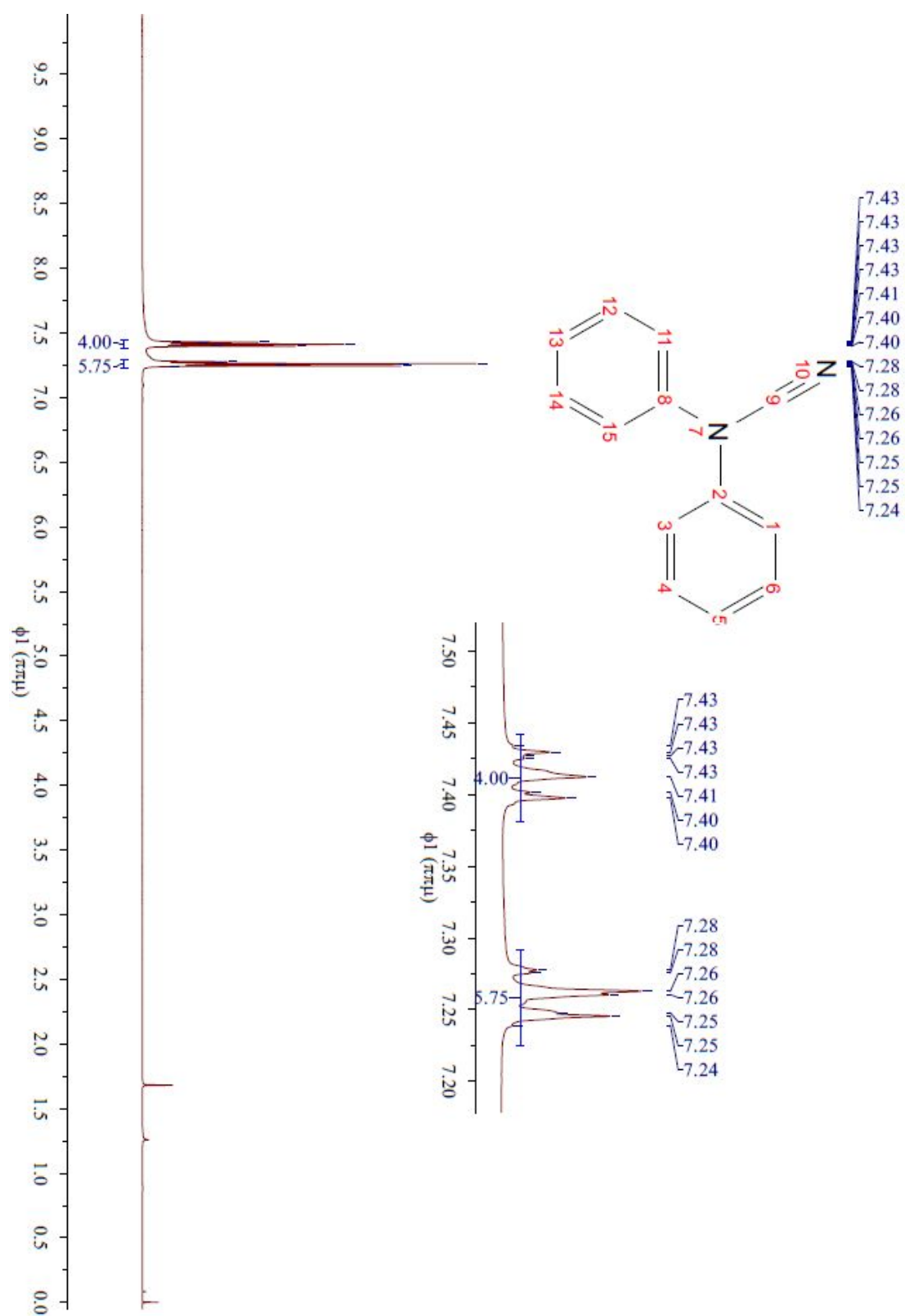
<sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds 3a-3j and 3l-3u

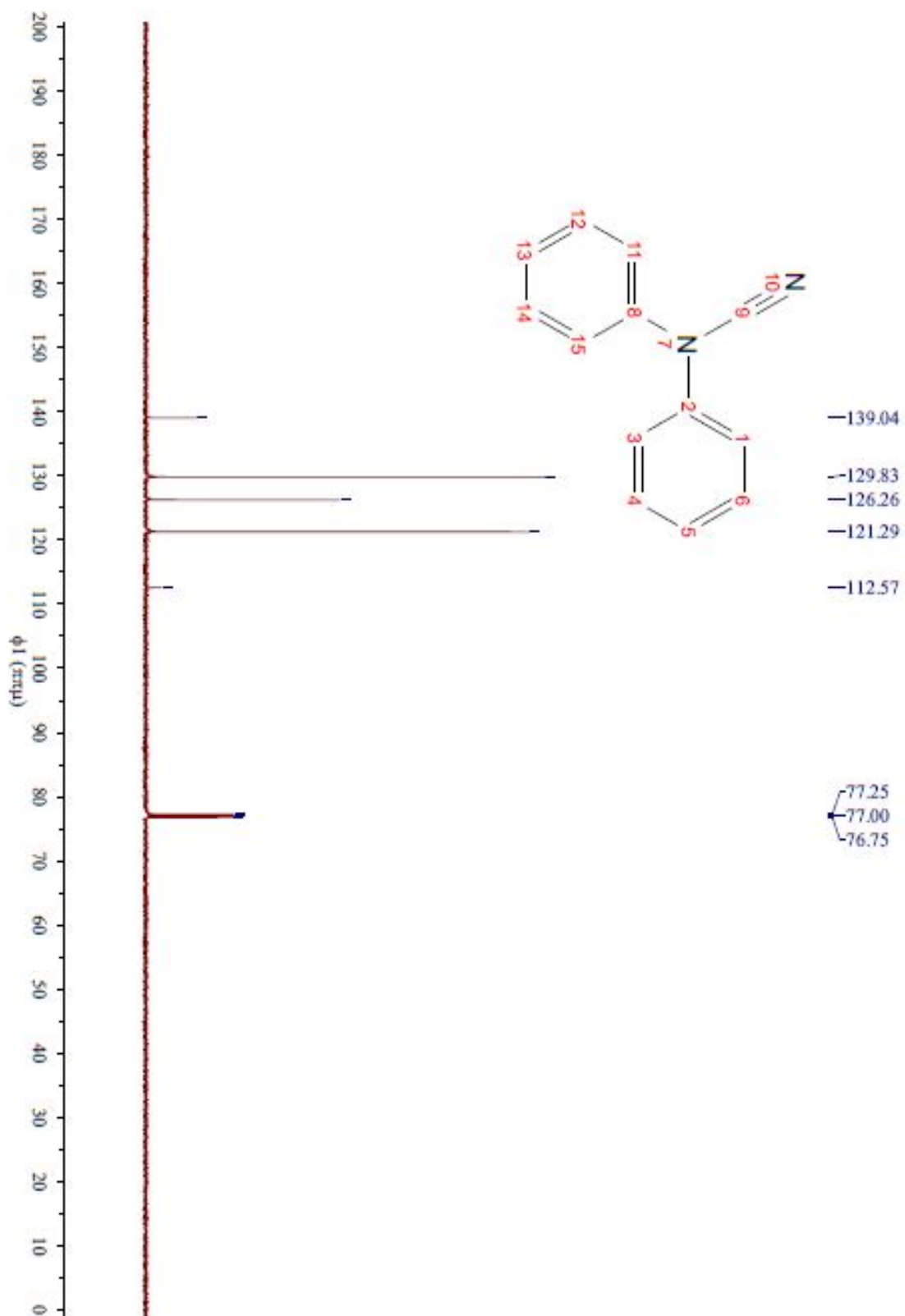
3a:



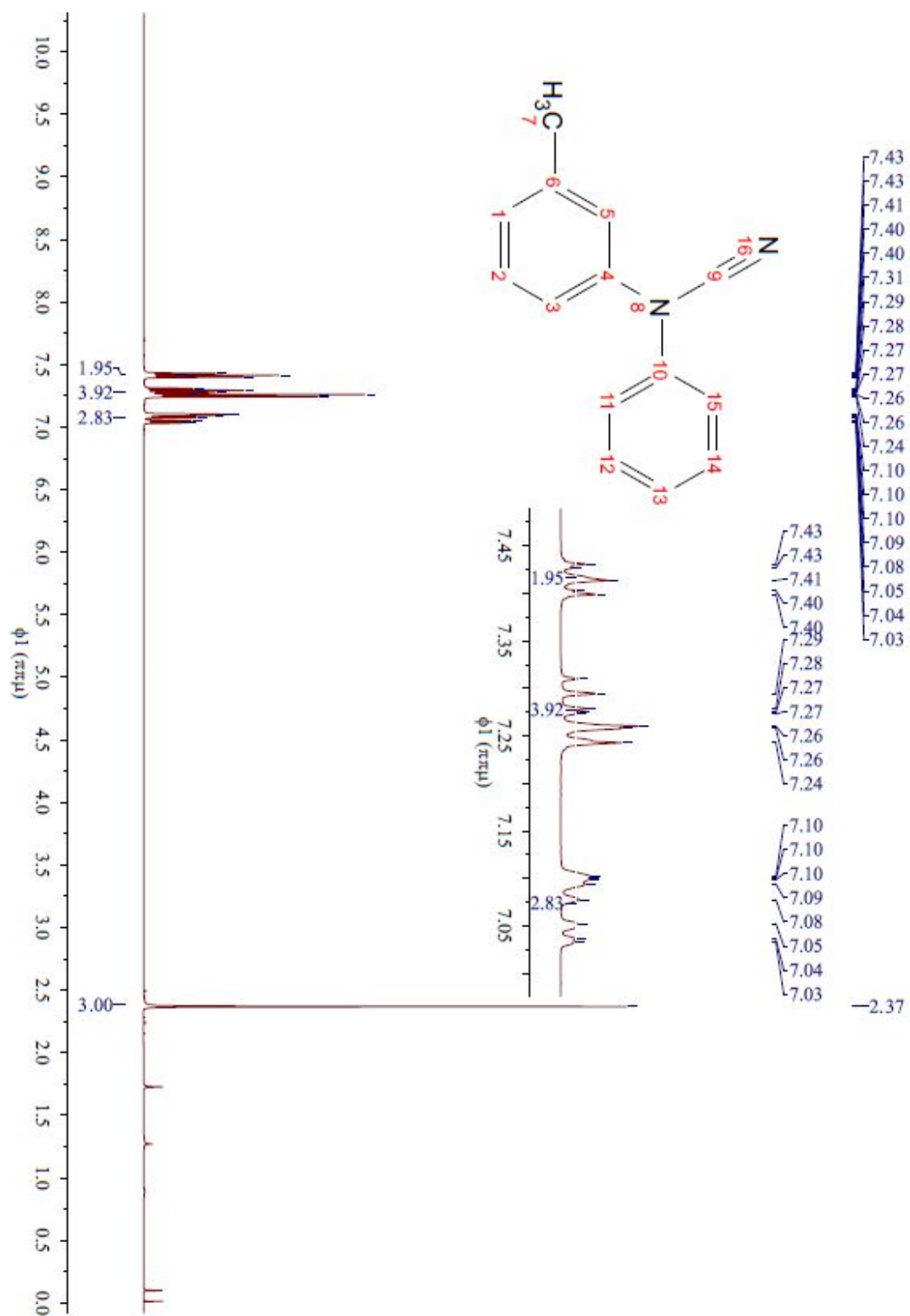


3b:

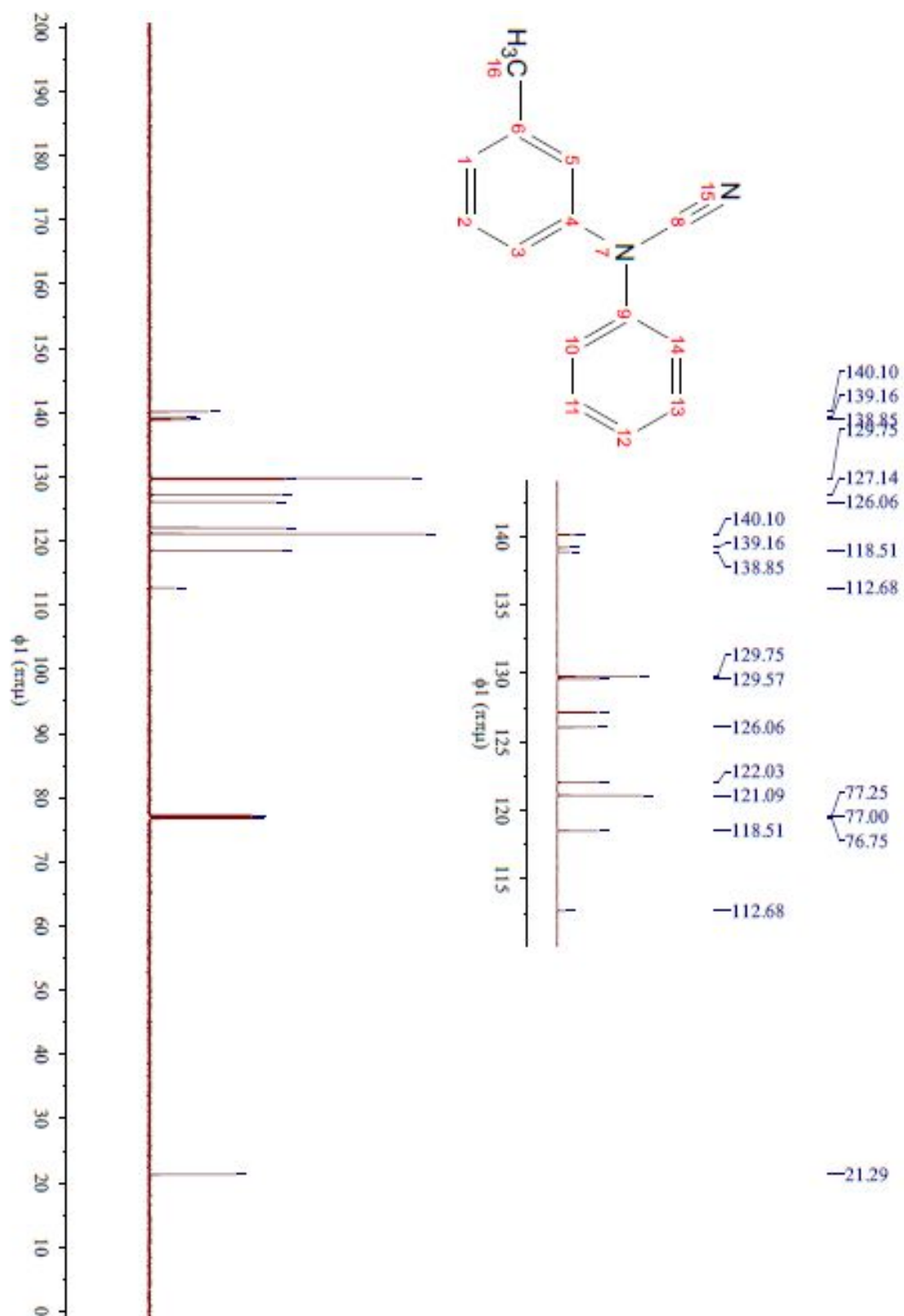




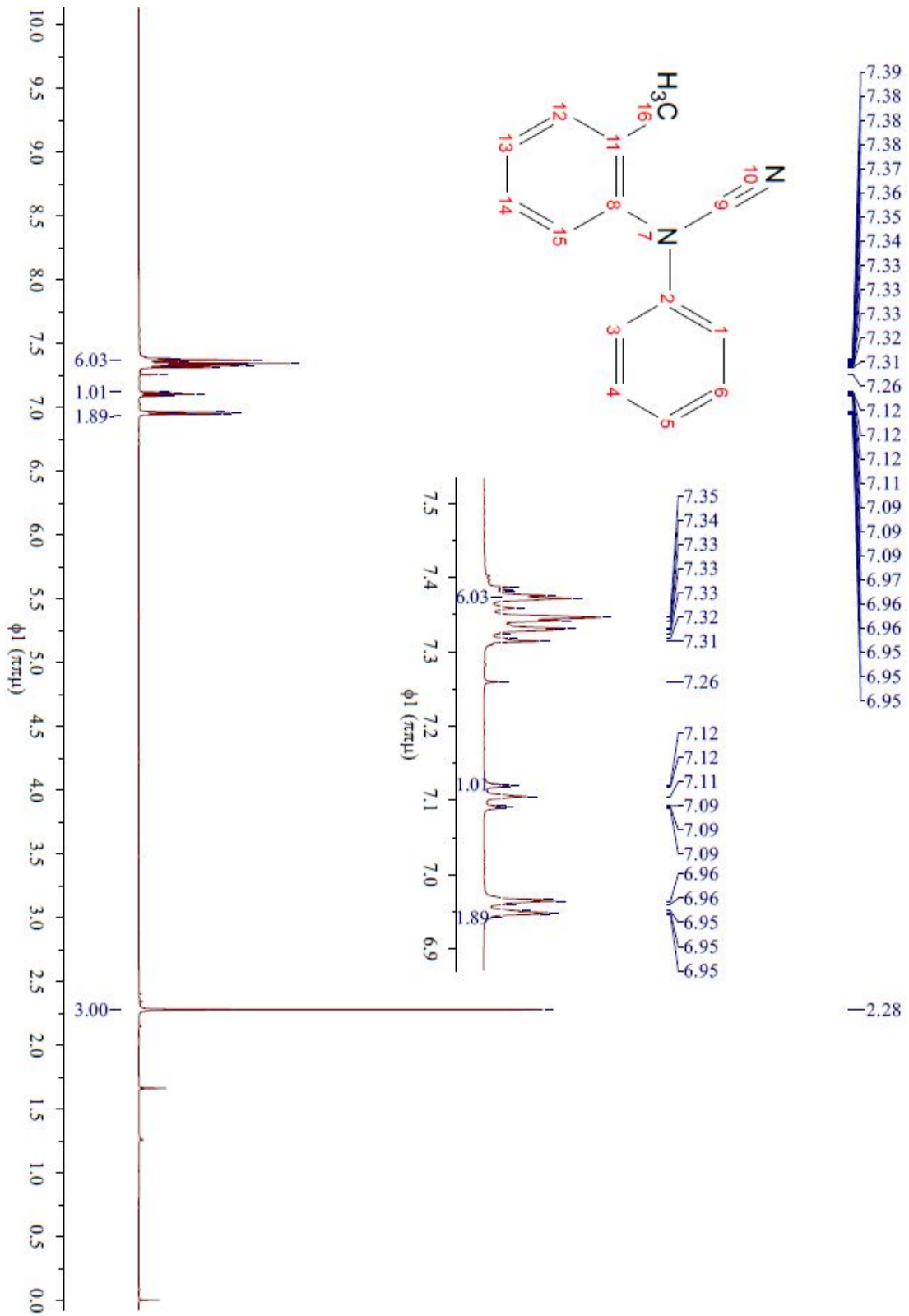
3c:

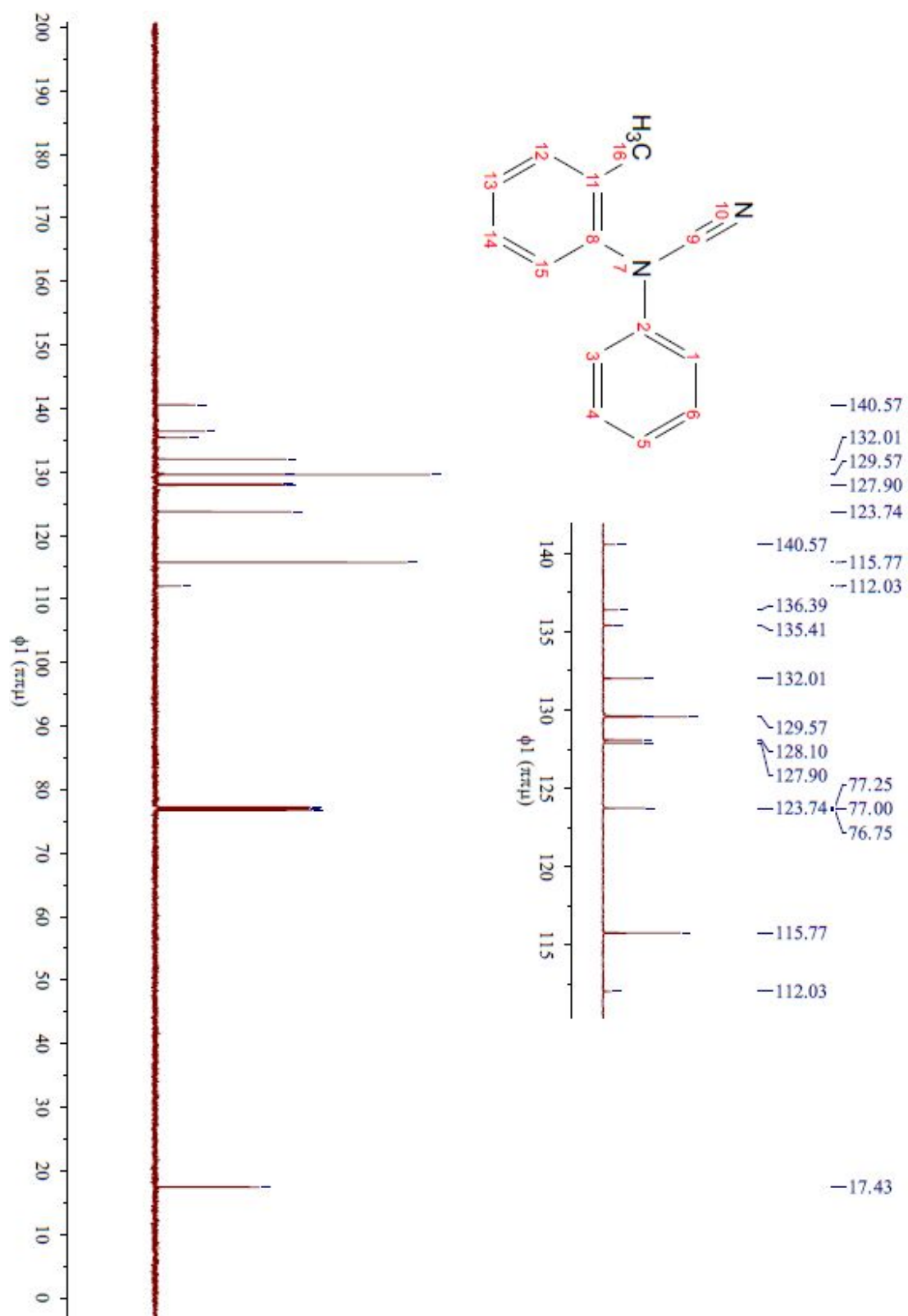




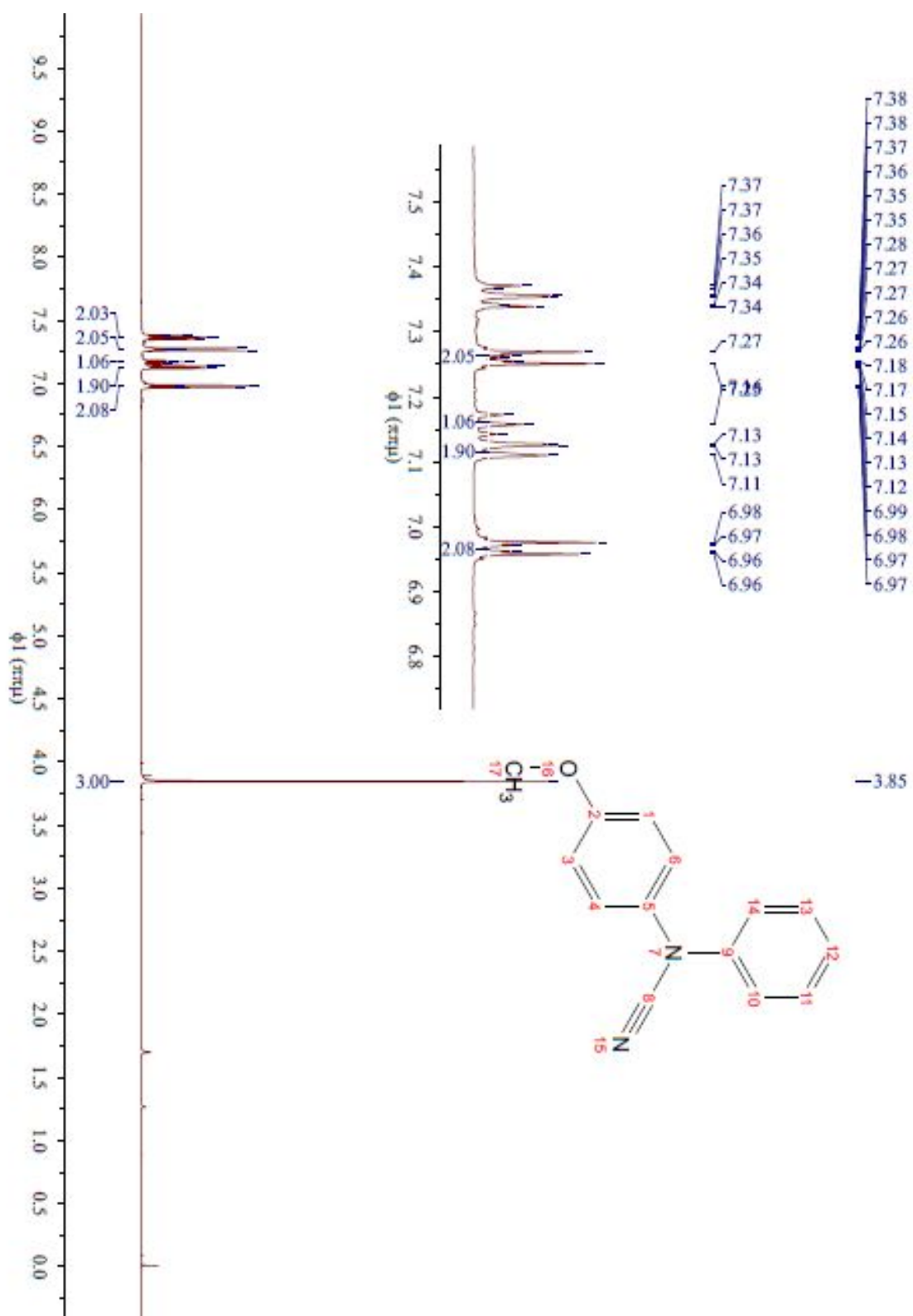


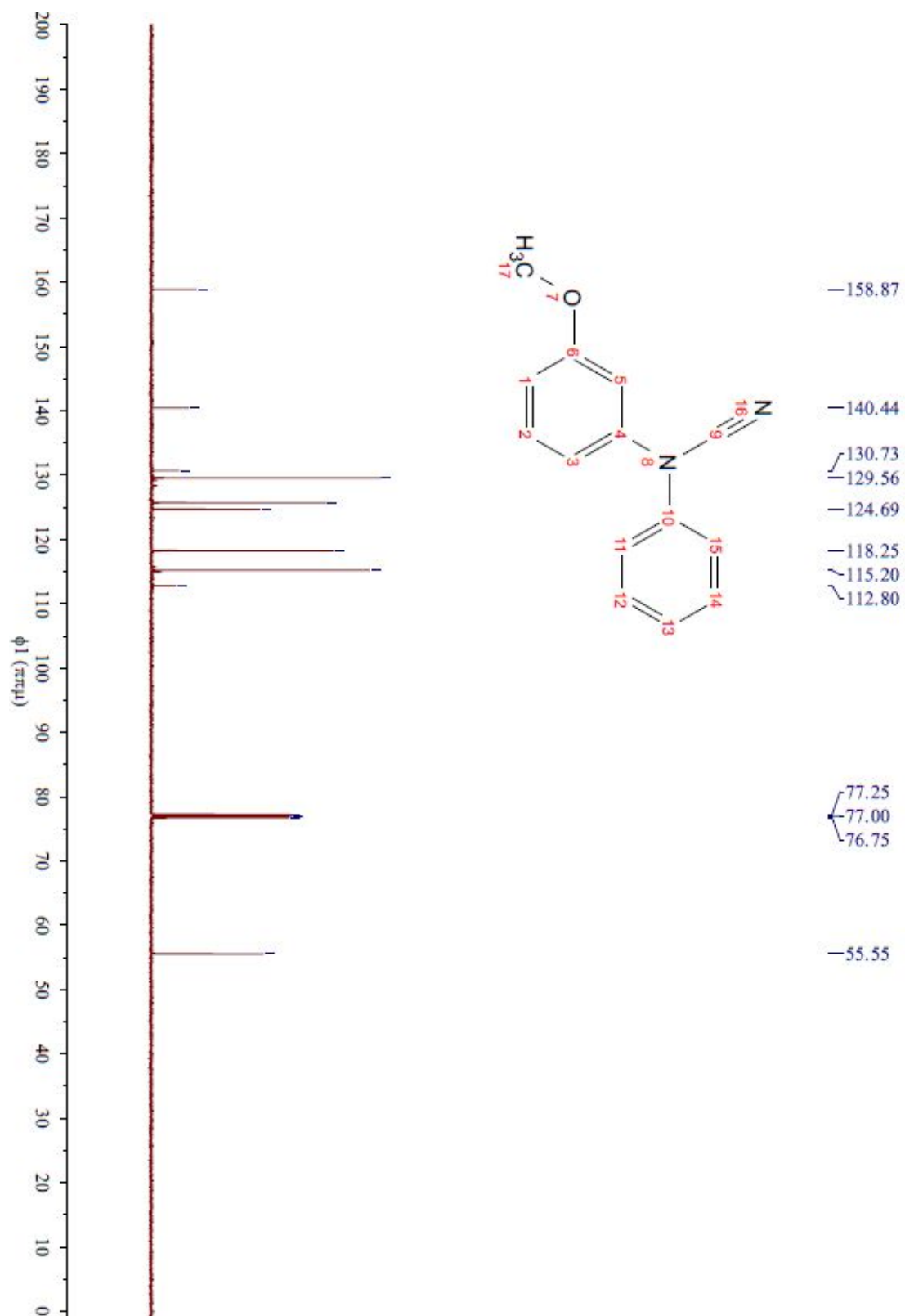
**3d:**



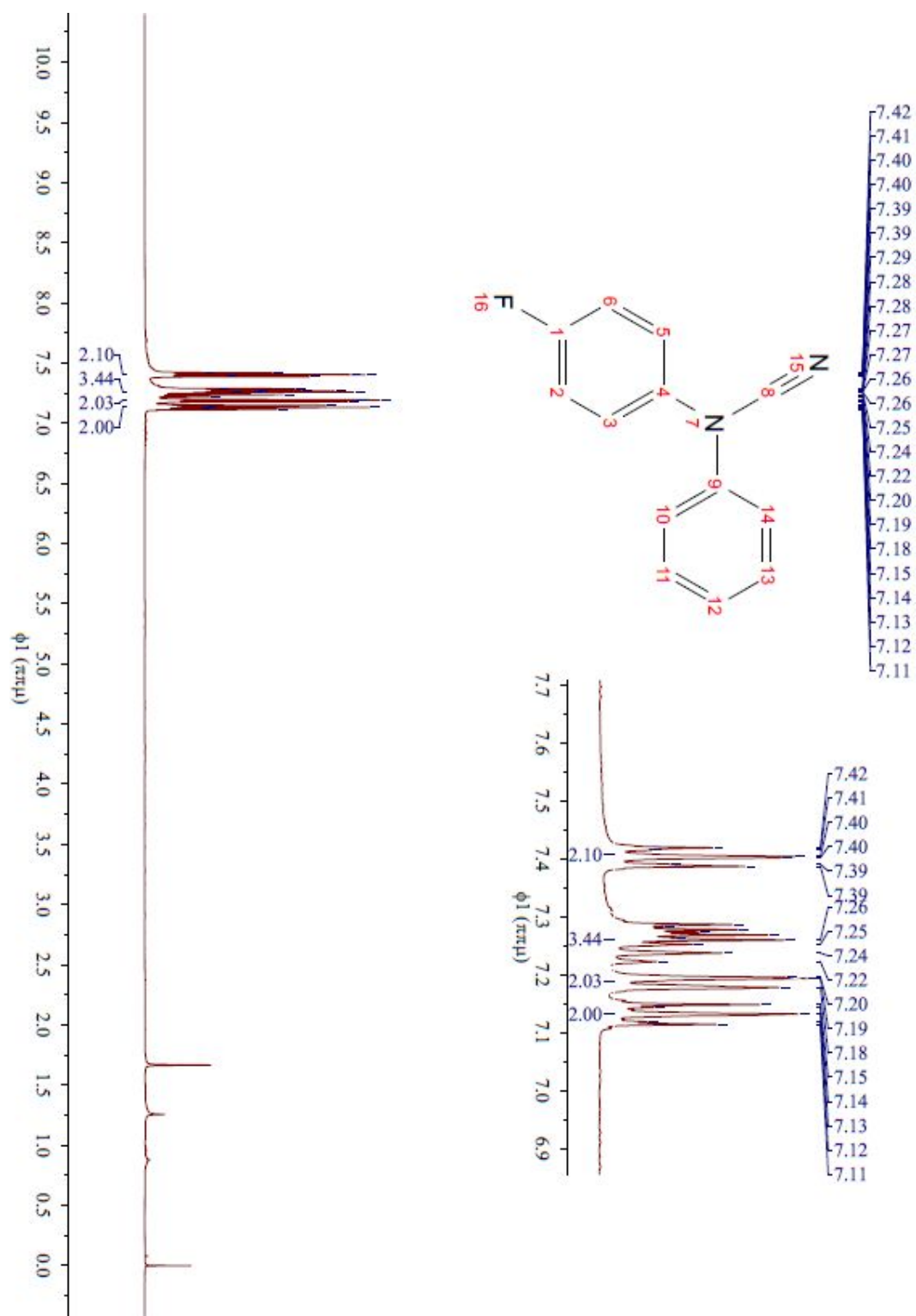


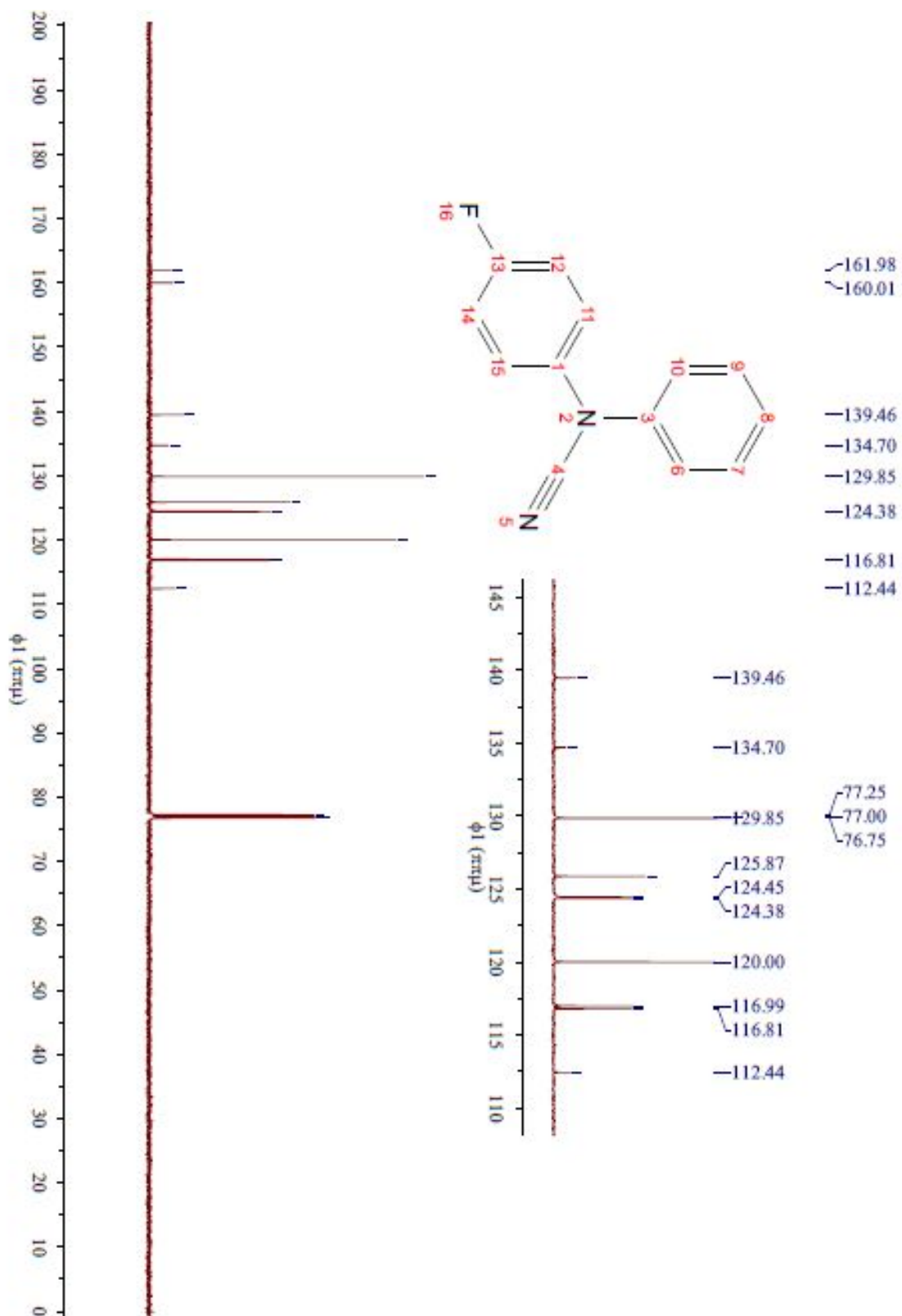
3e:



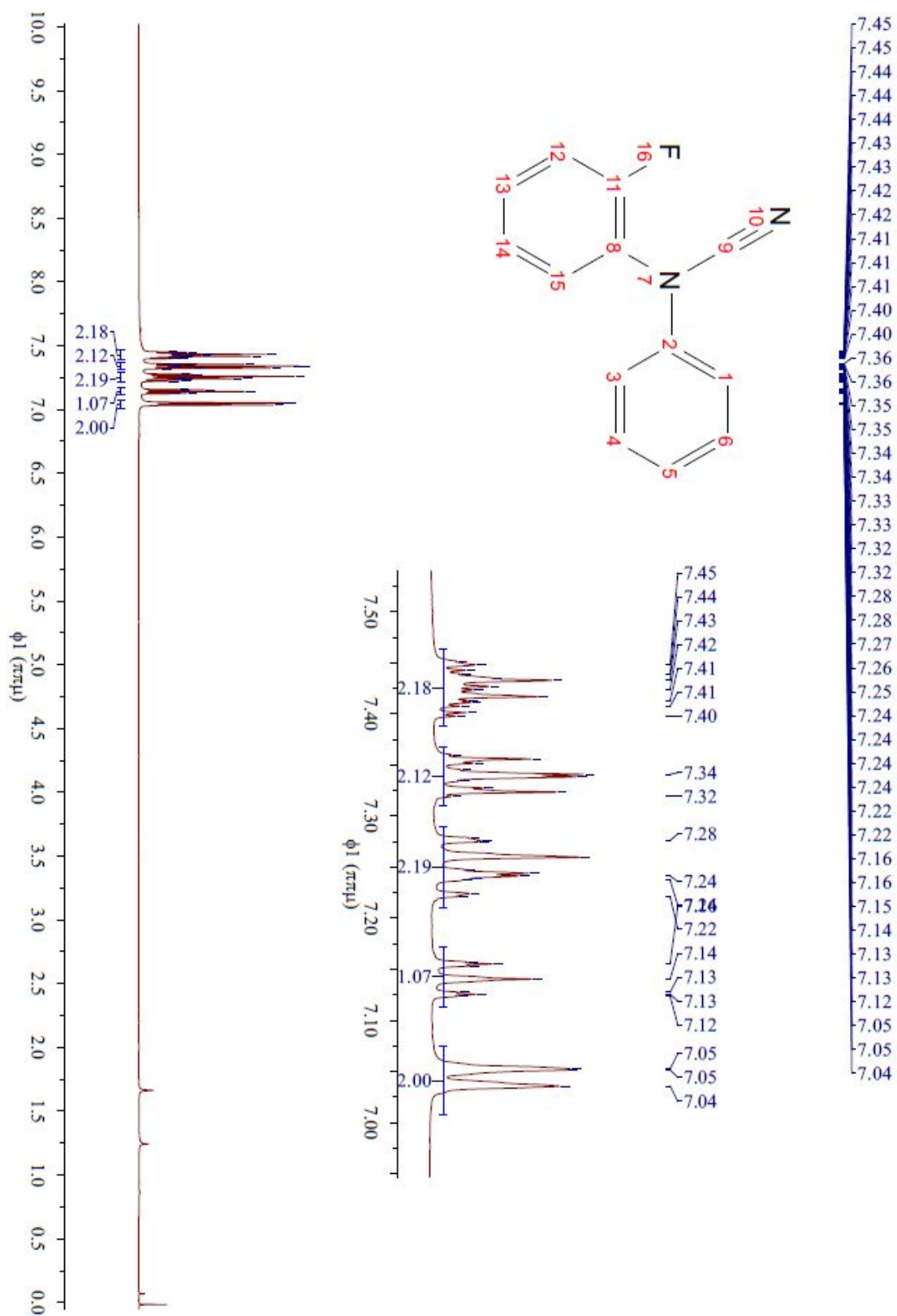


3f.

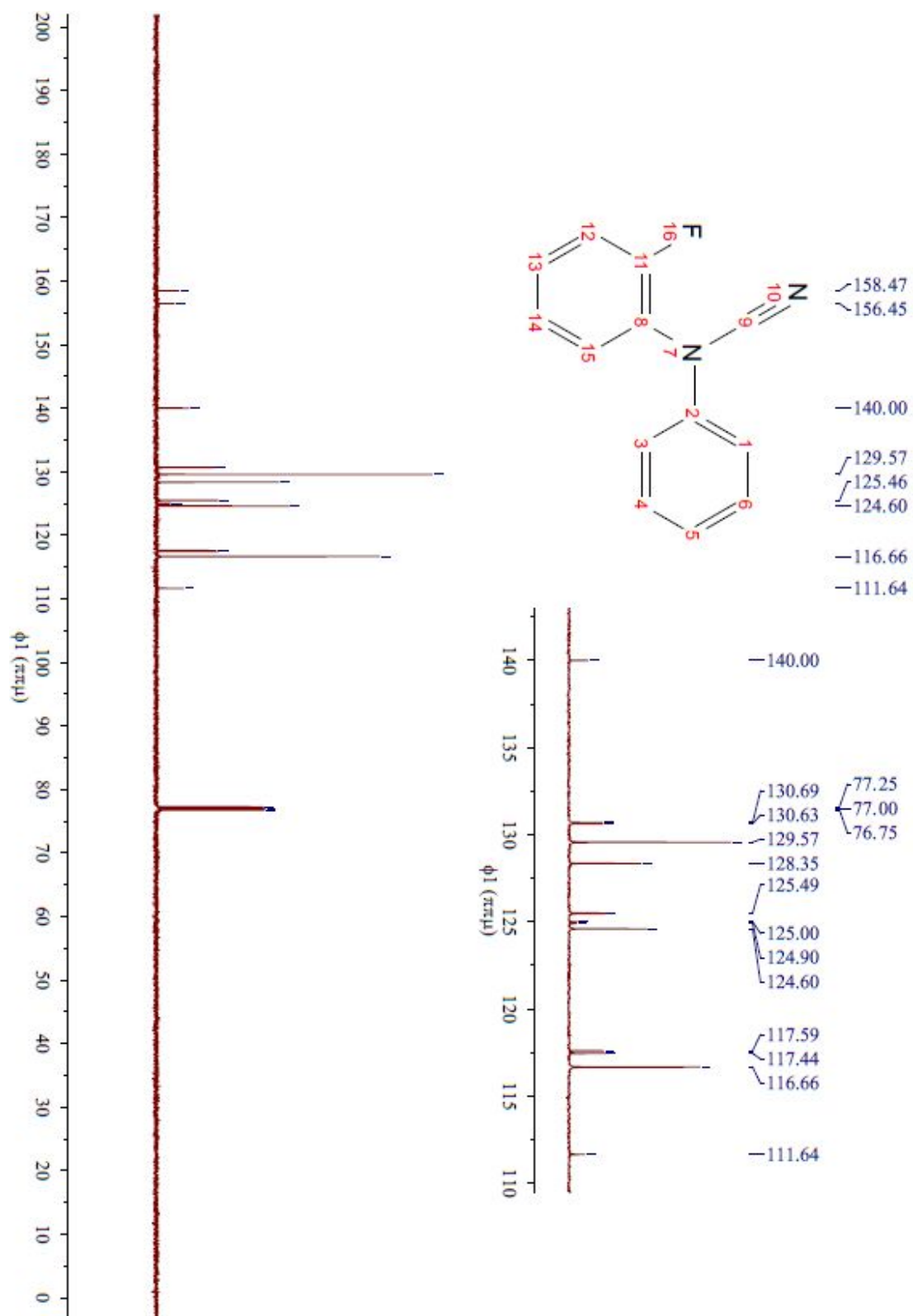




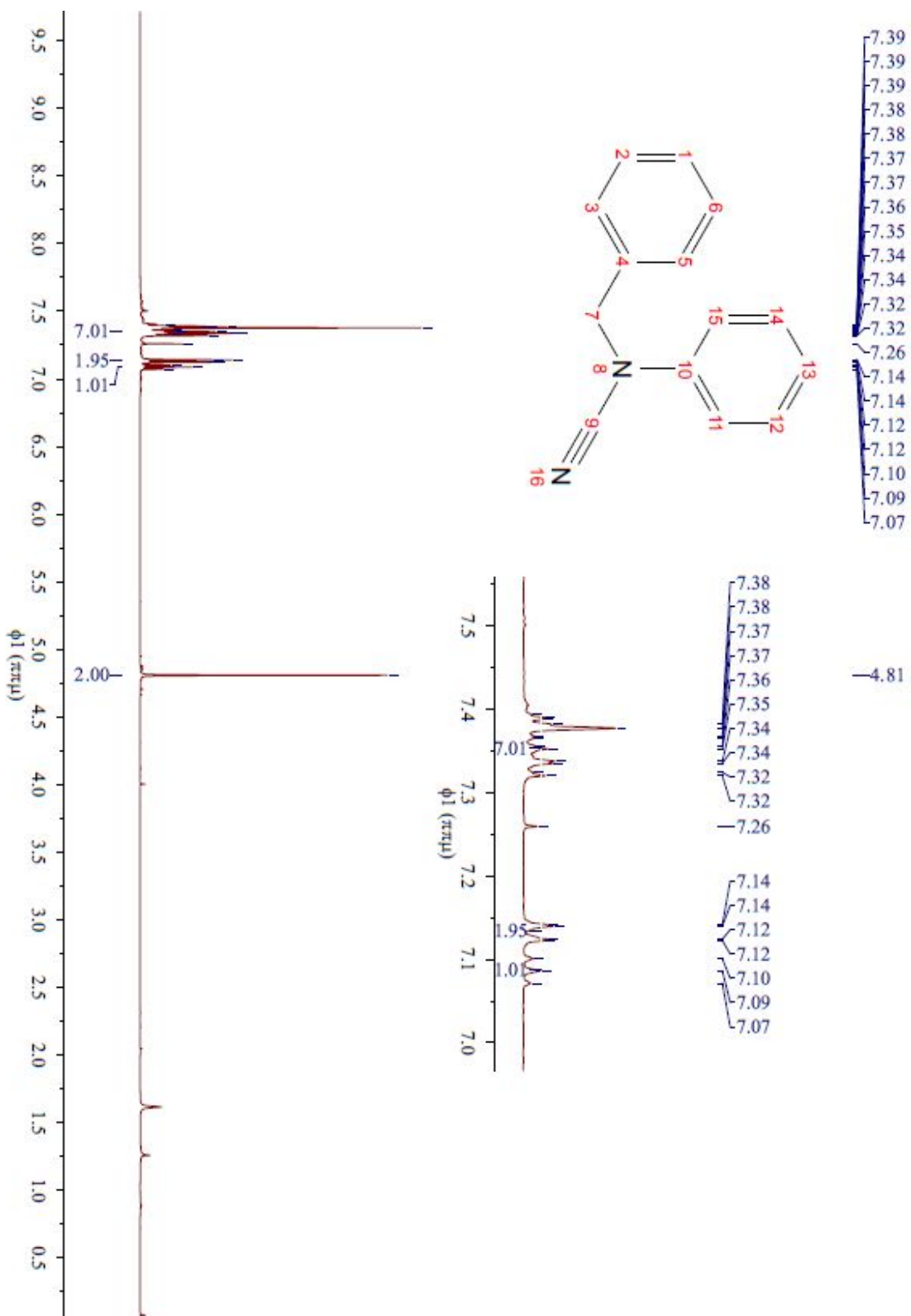
3g:

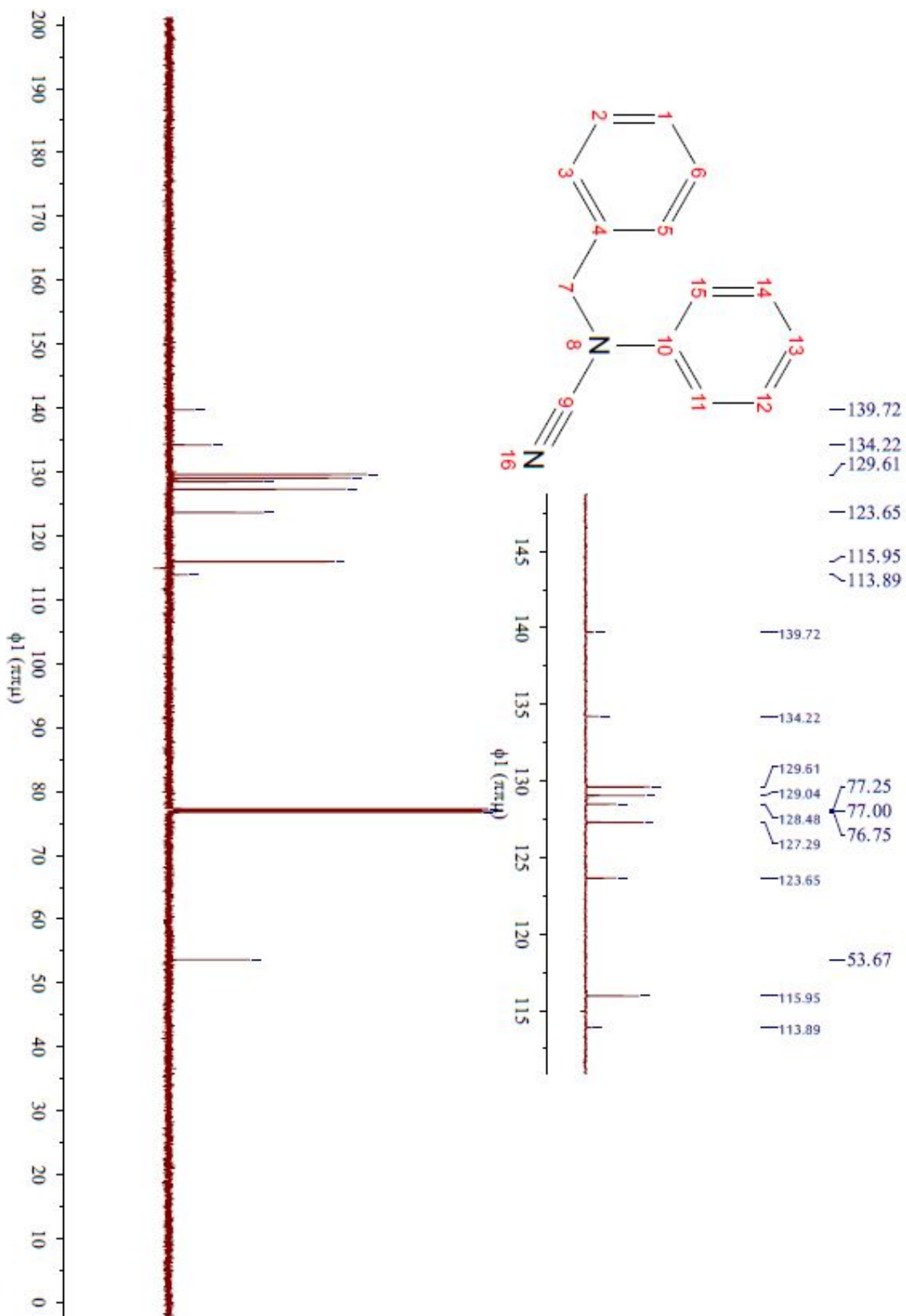




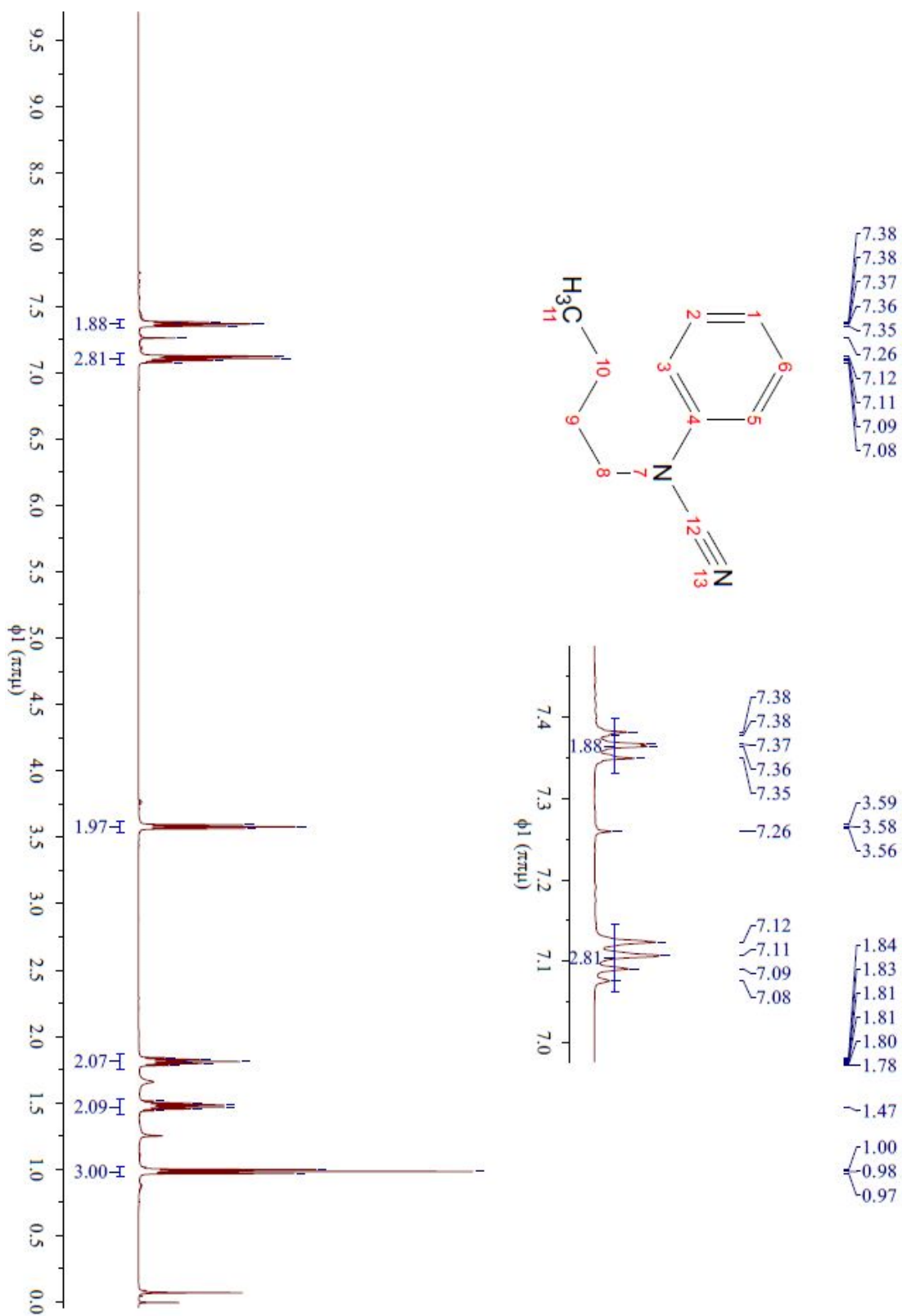


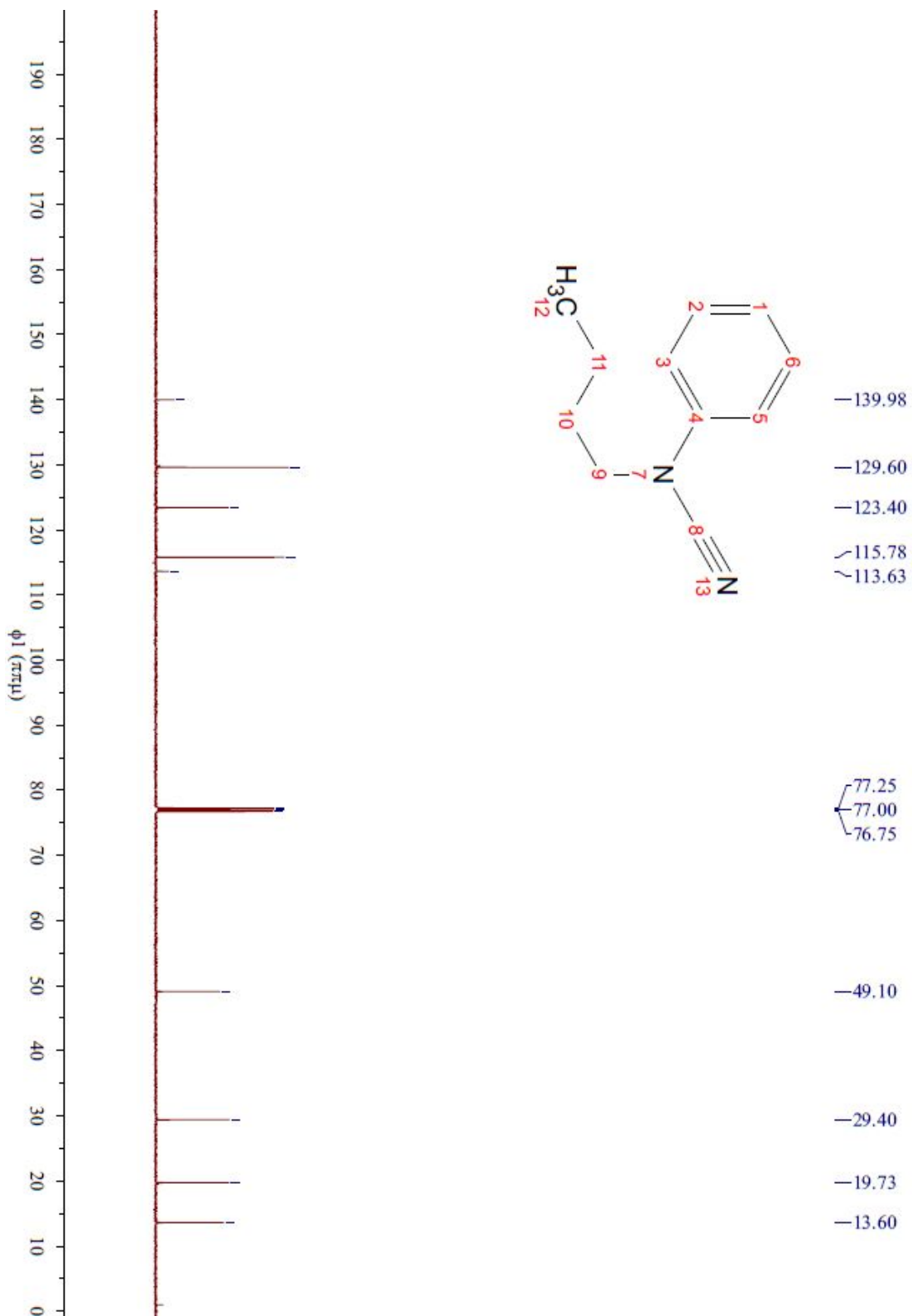
3h:



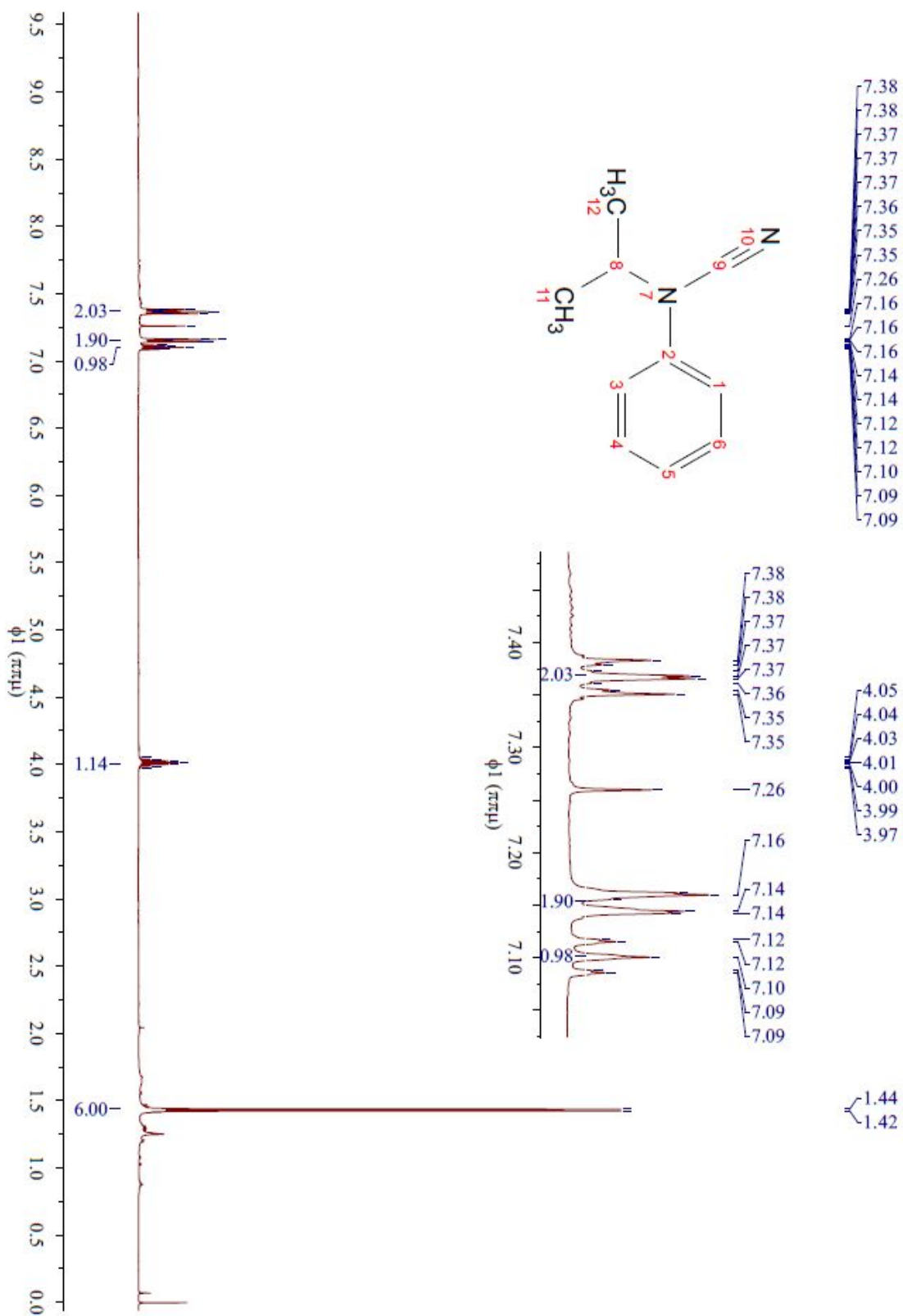


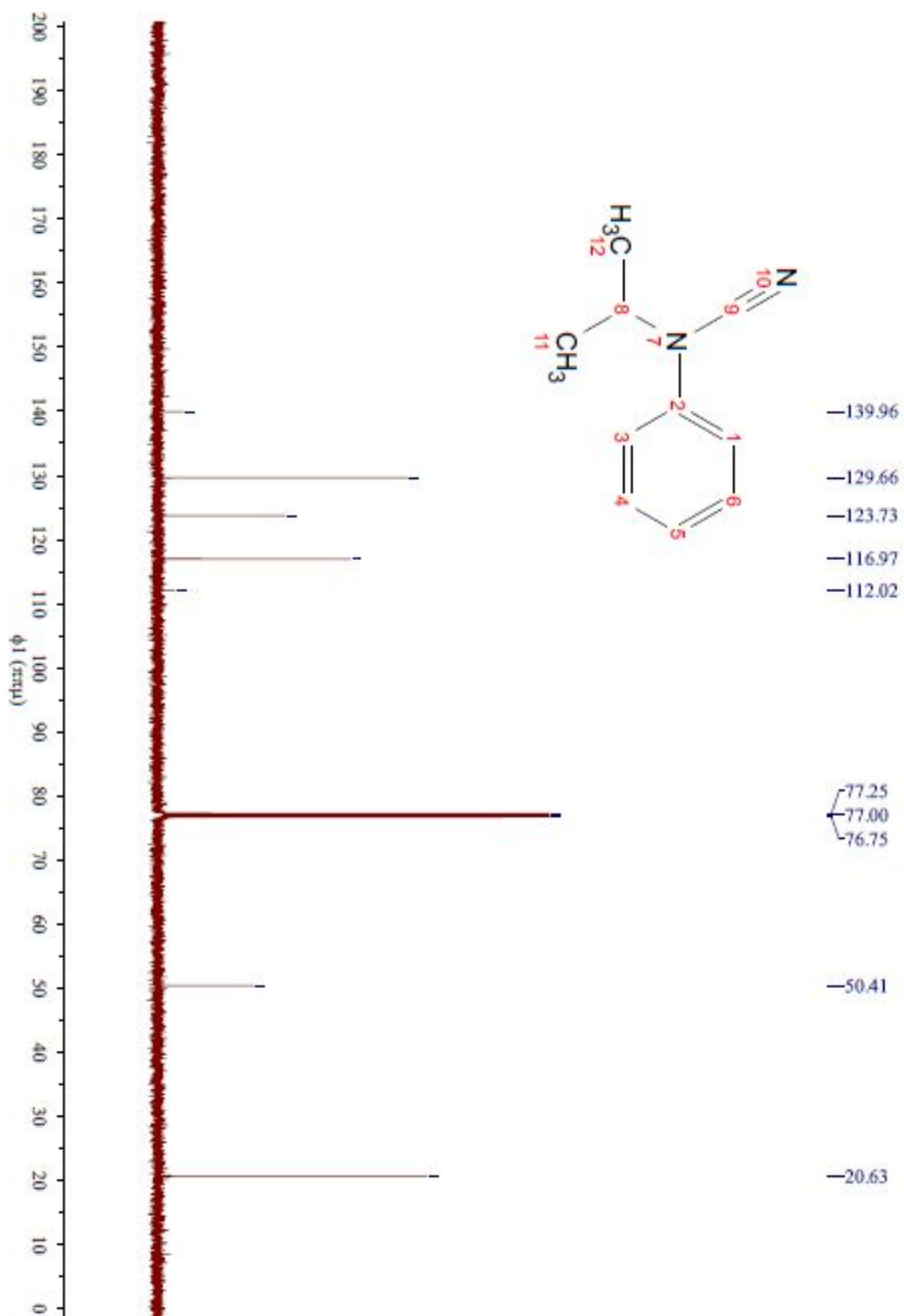
3i:



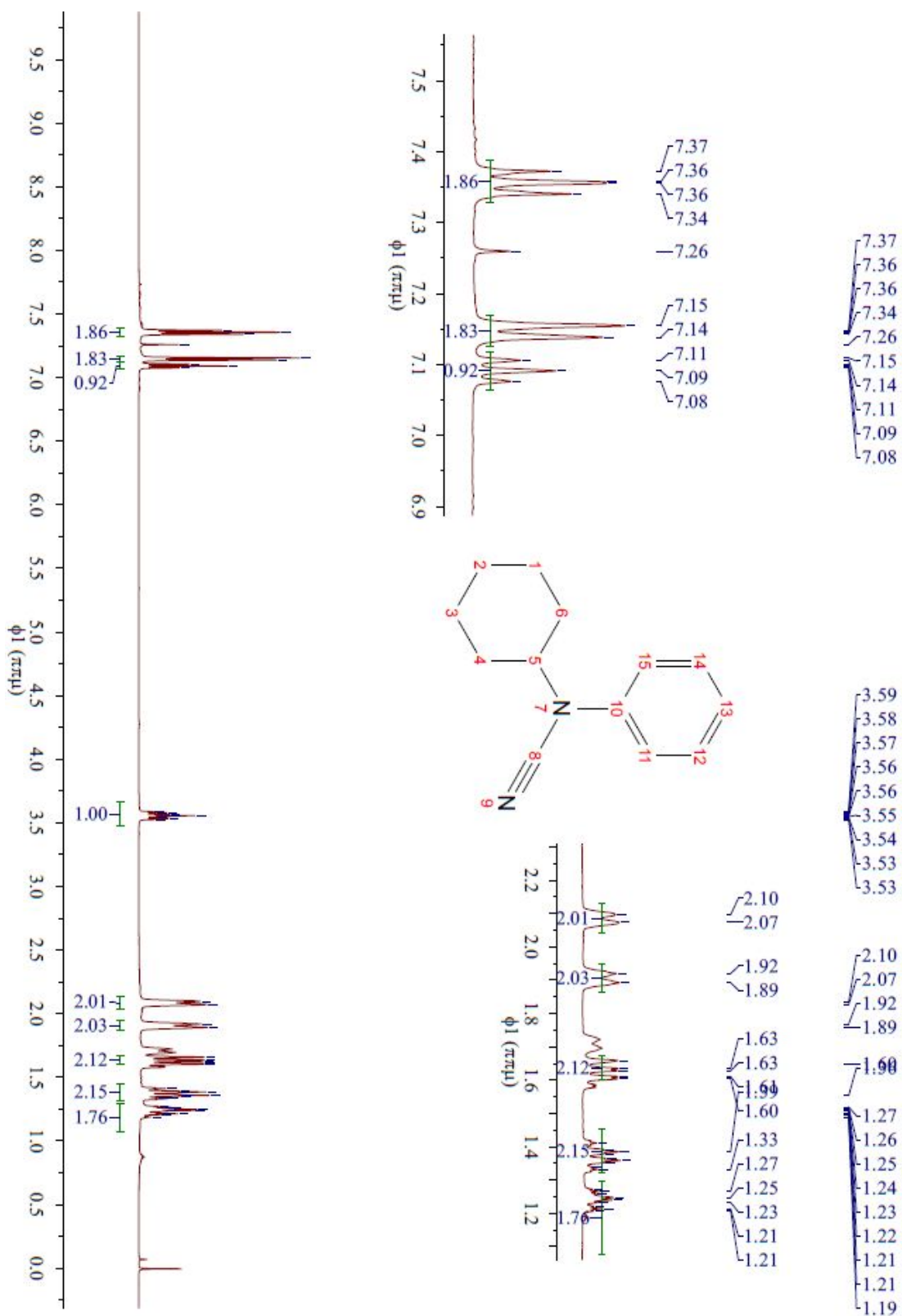


3j:

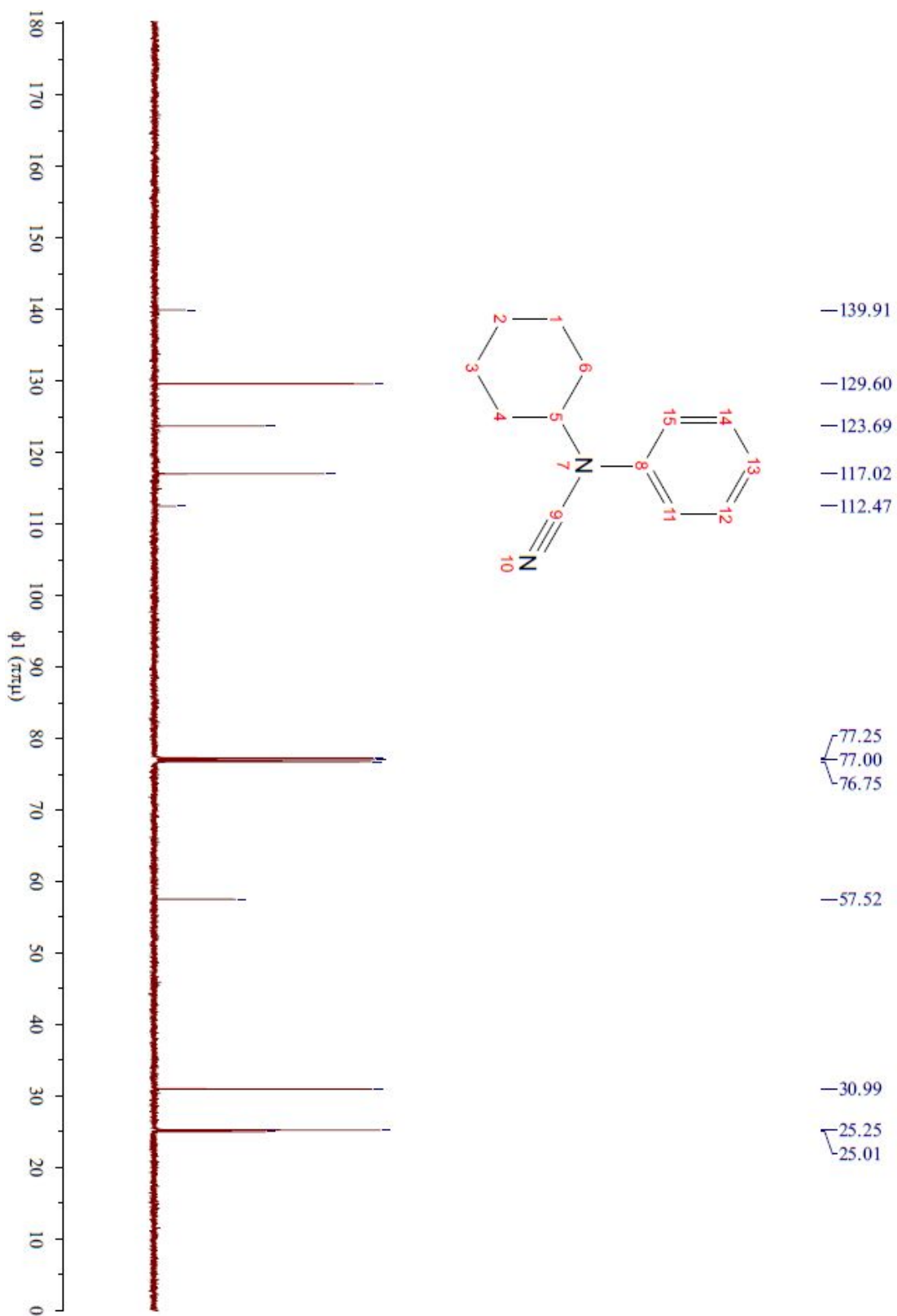




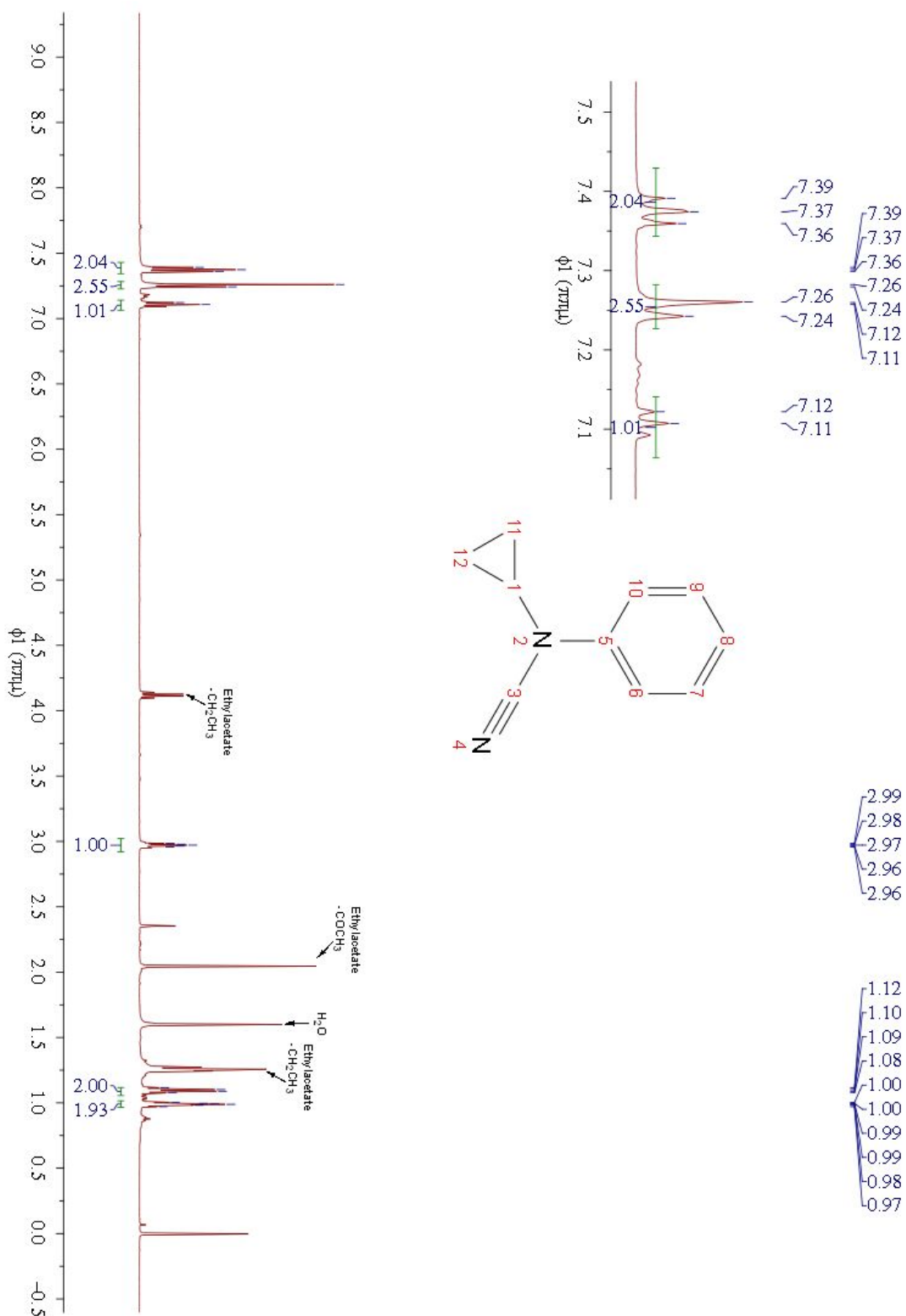
31:

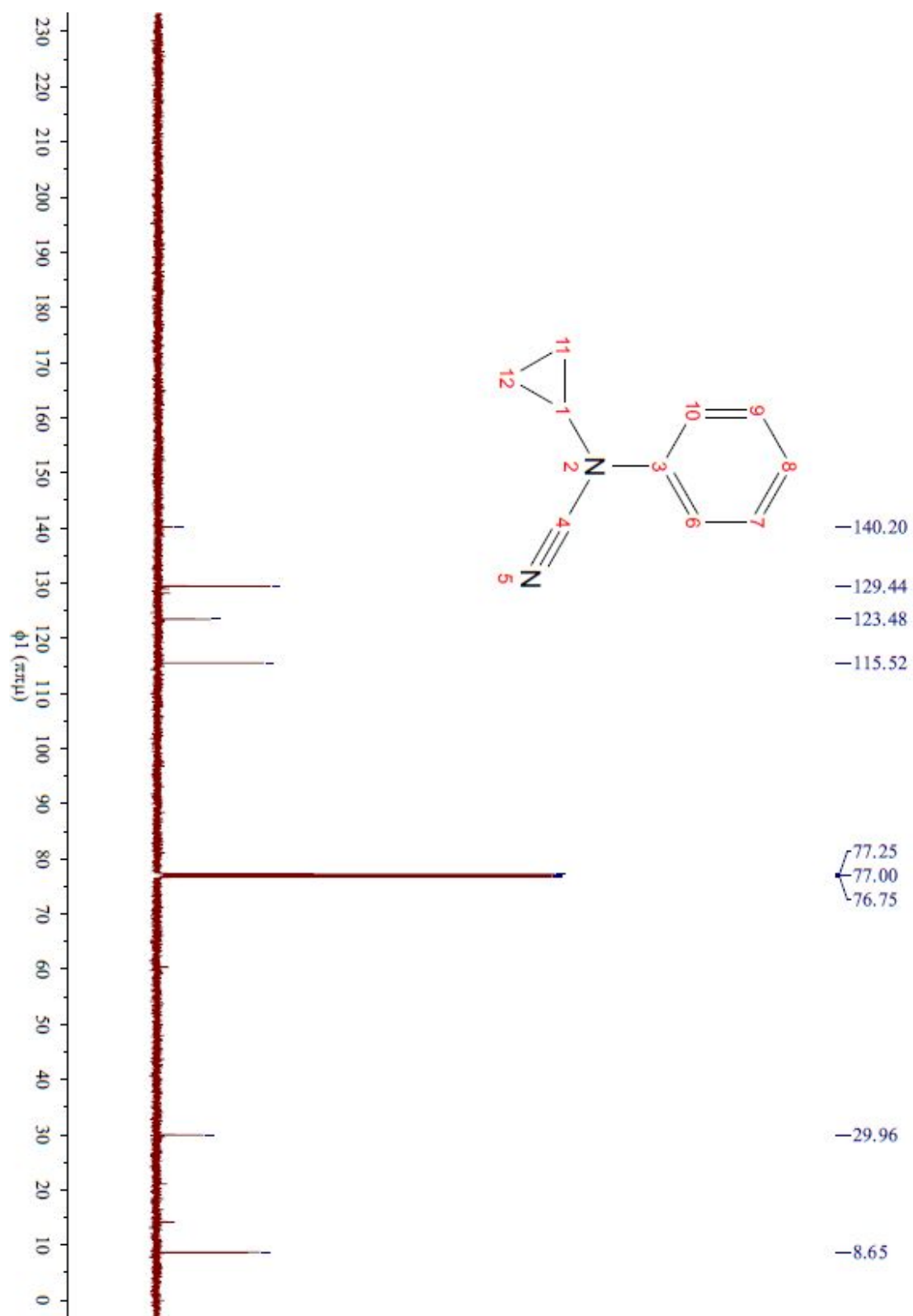




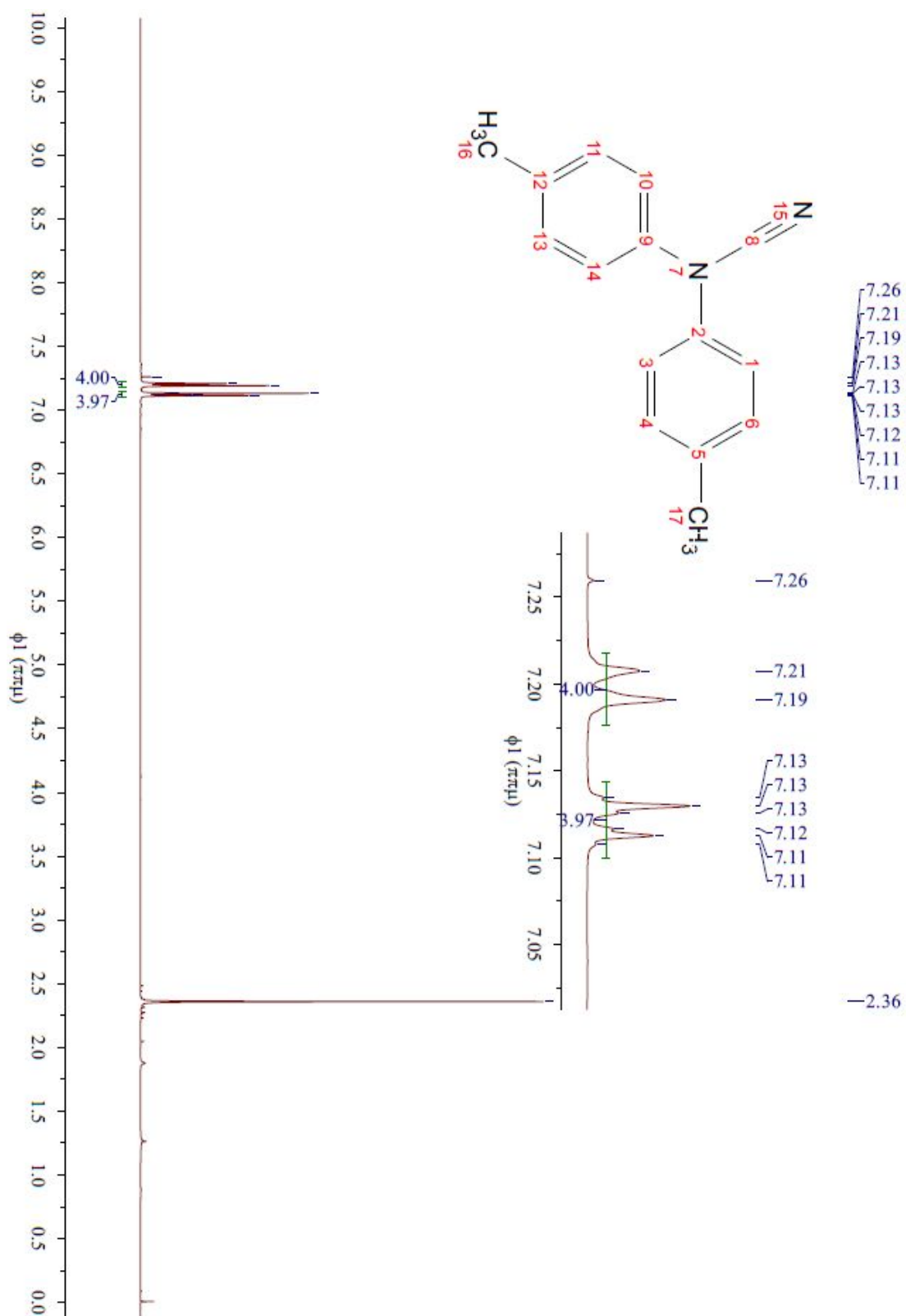


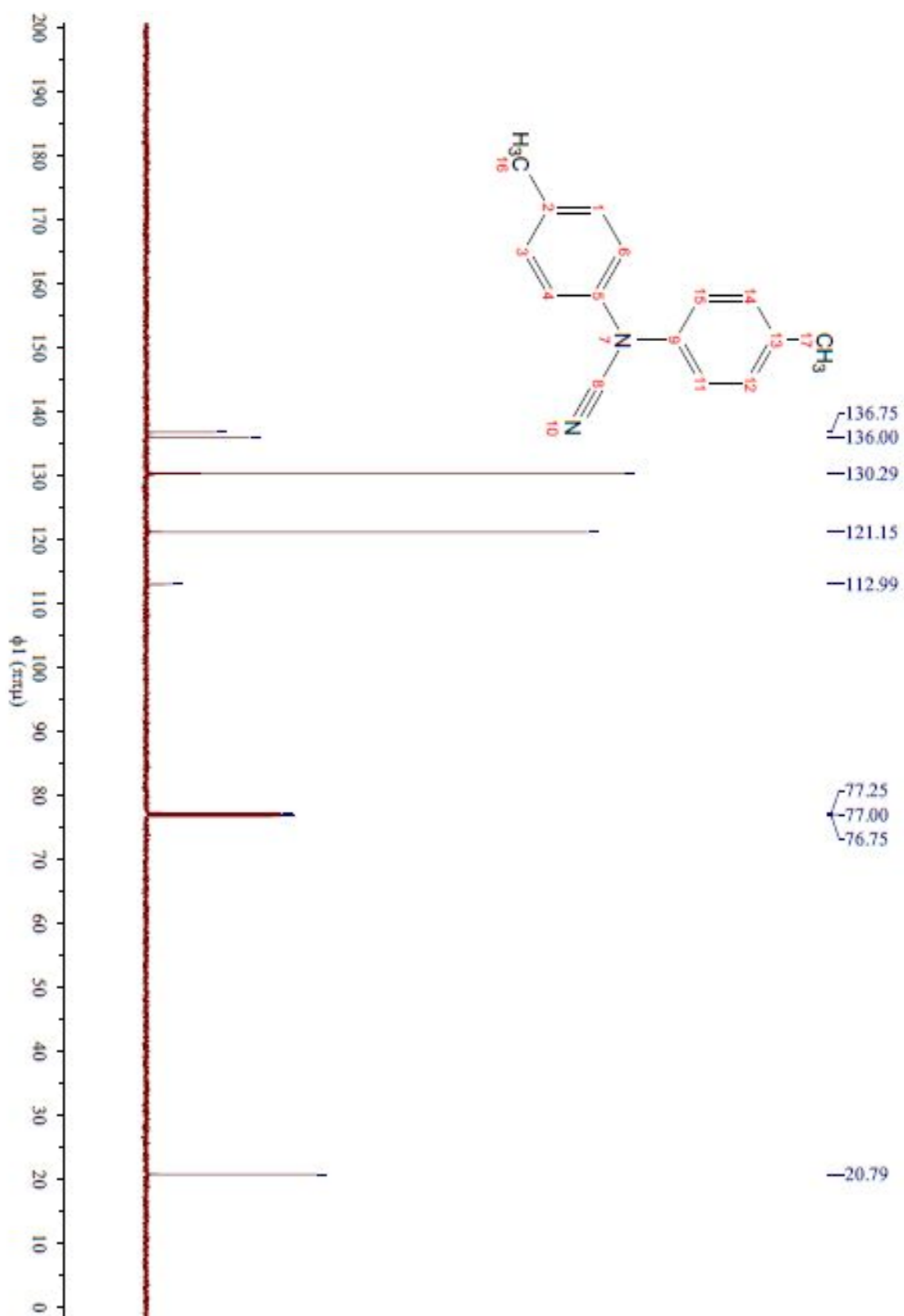
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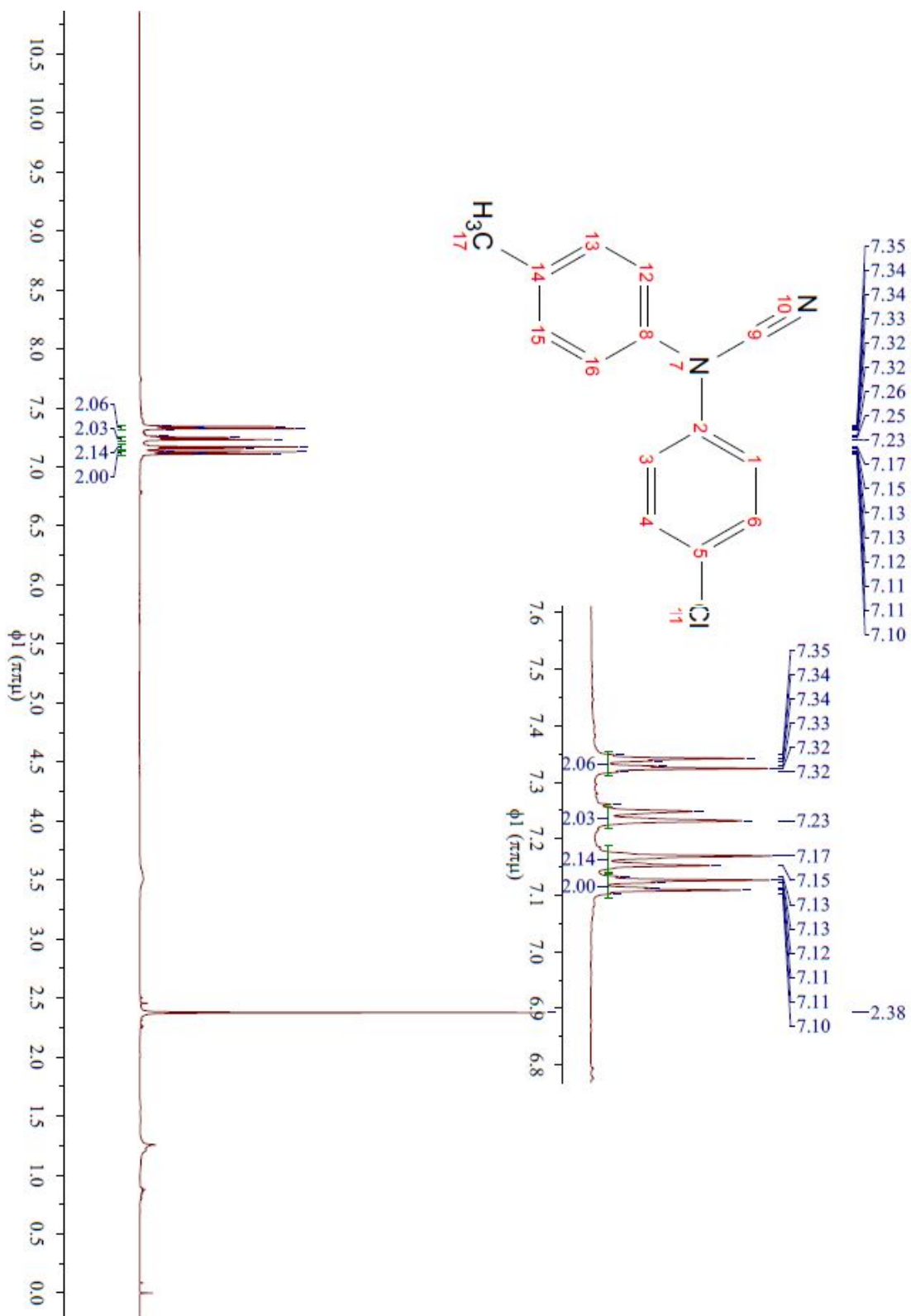


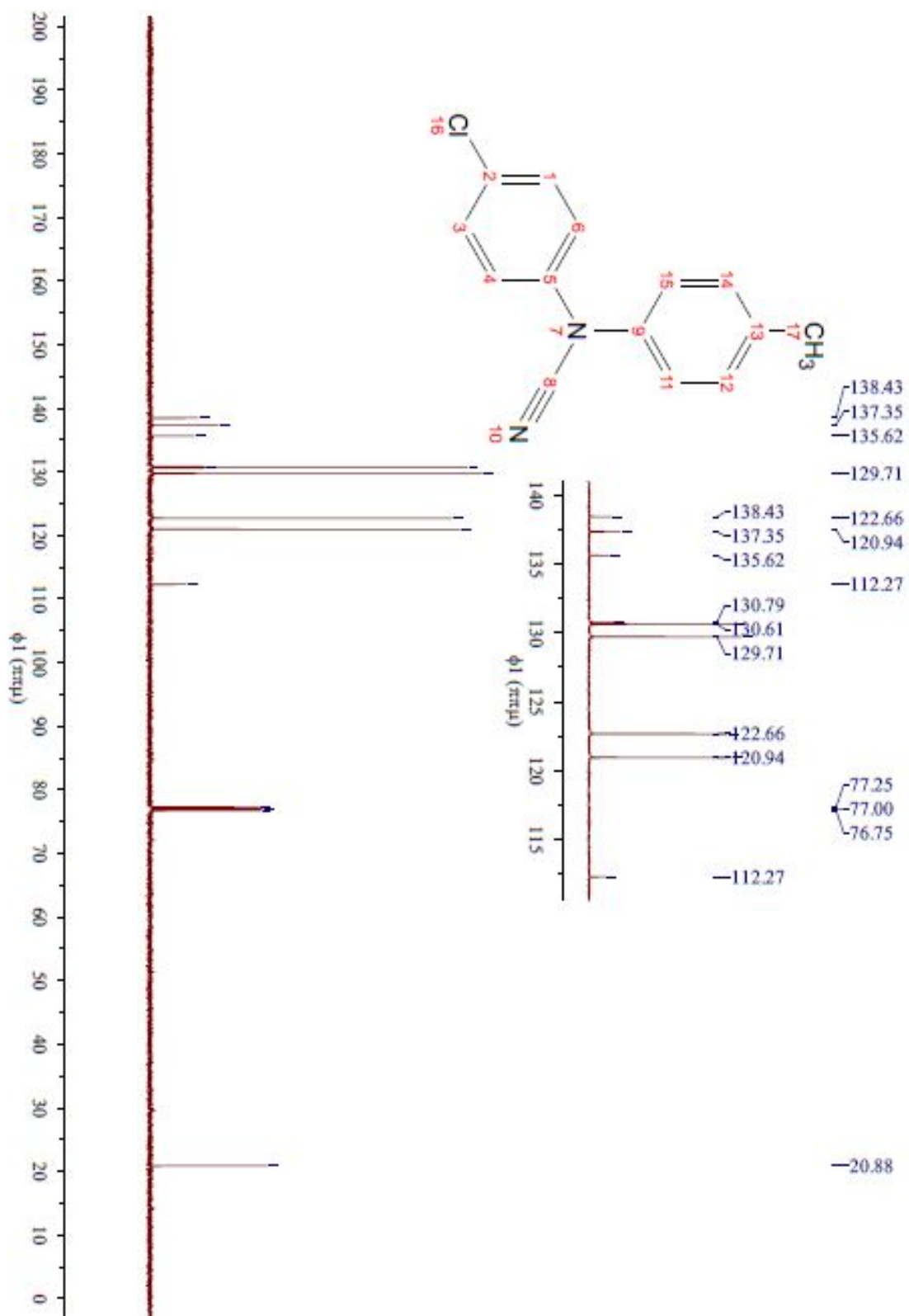
3n:



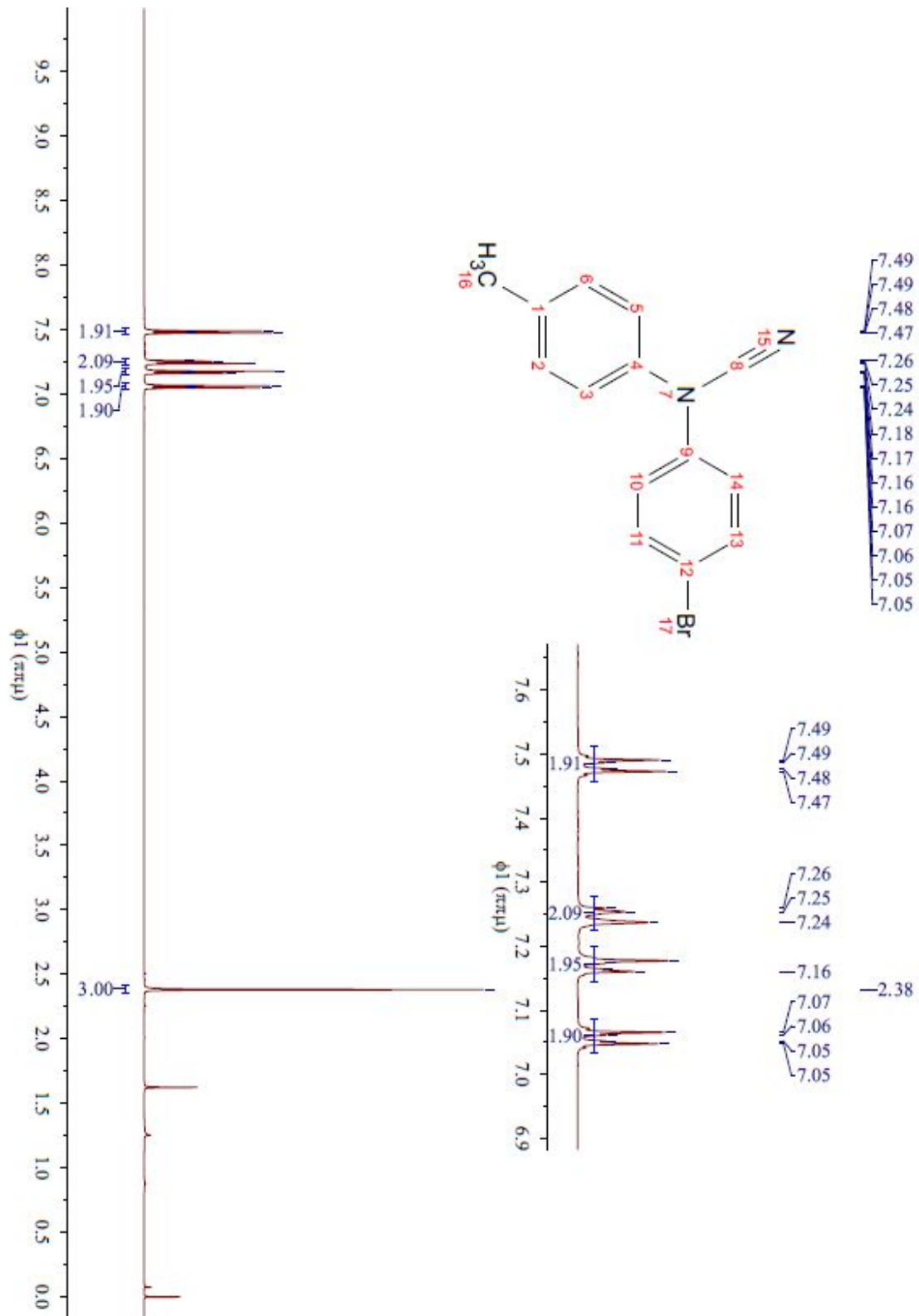


30:

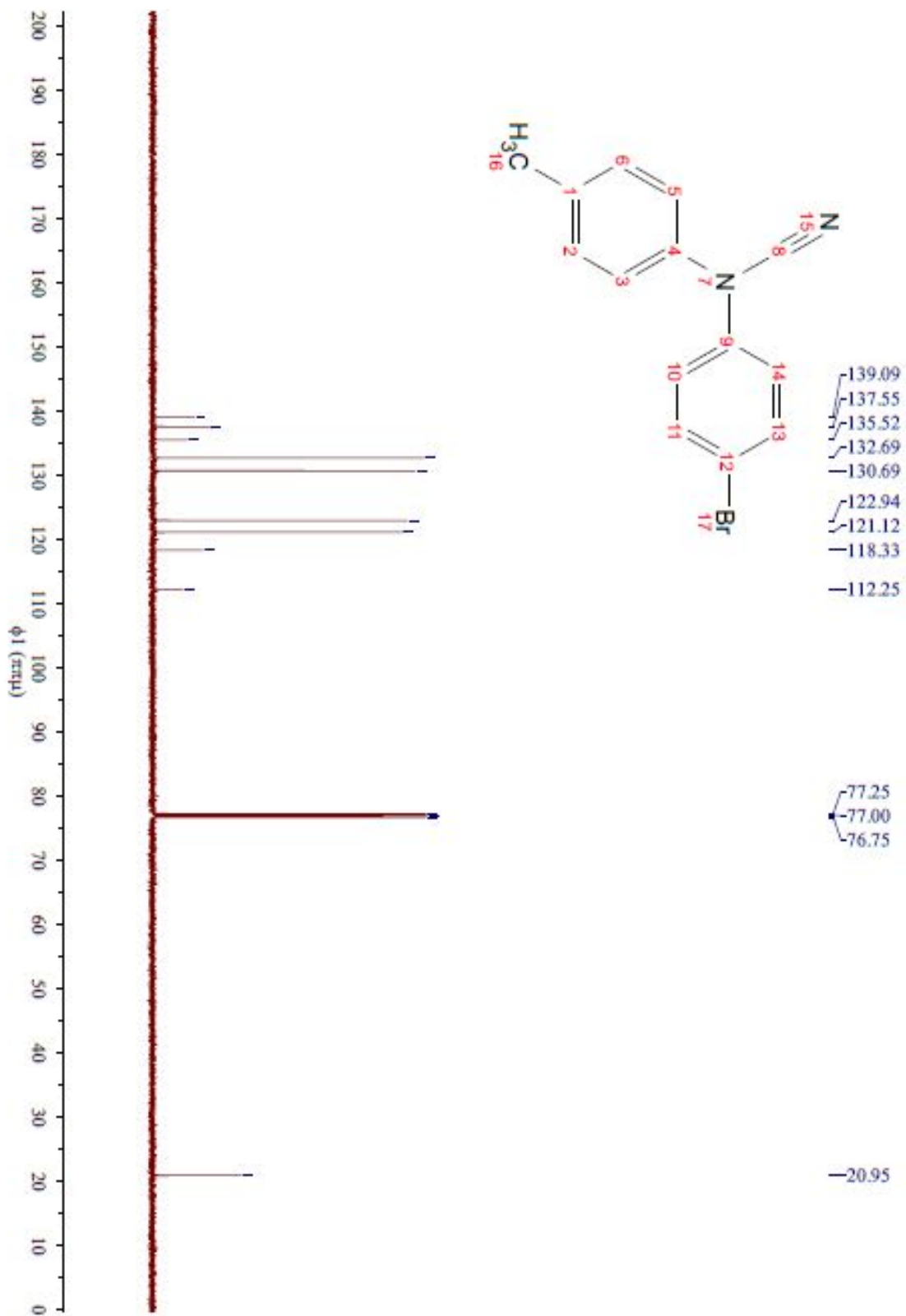




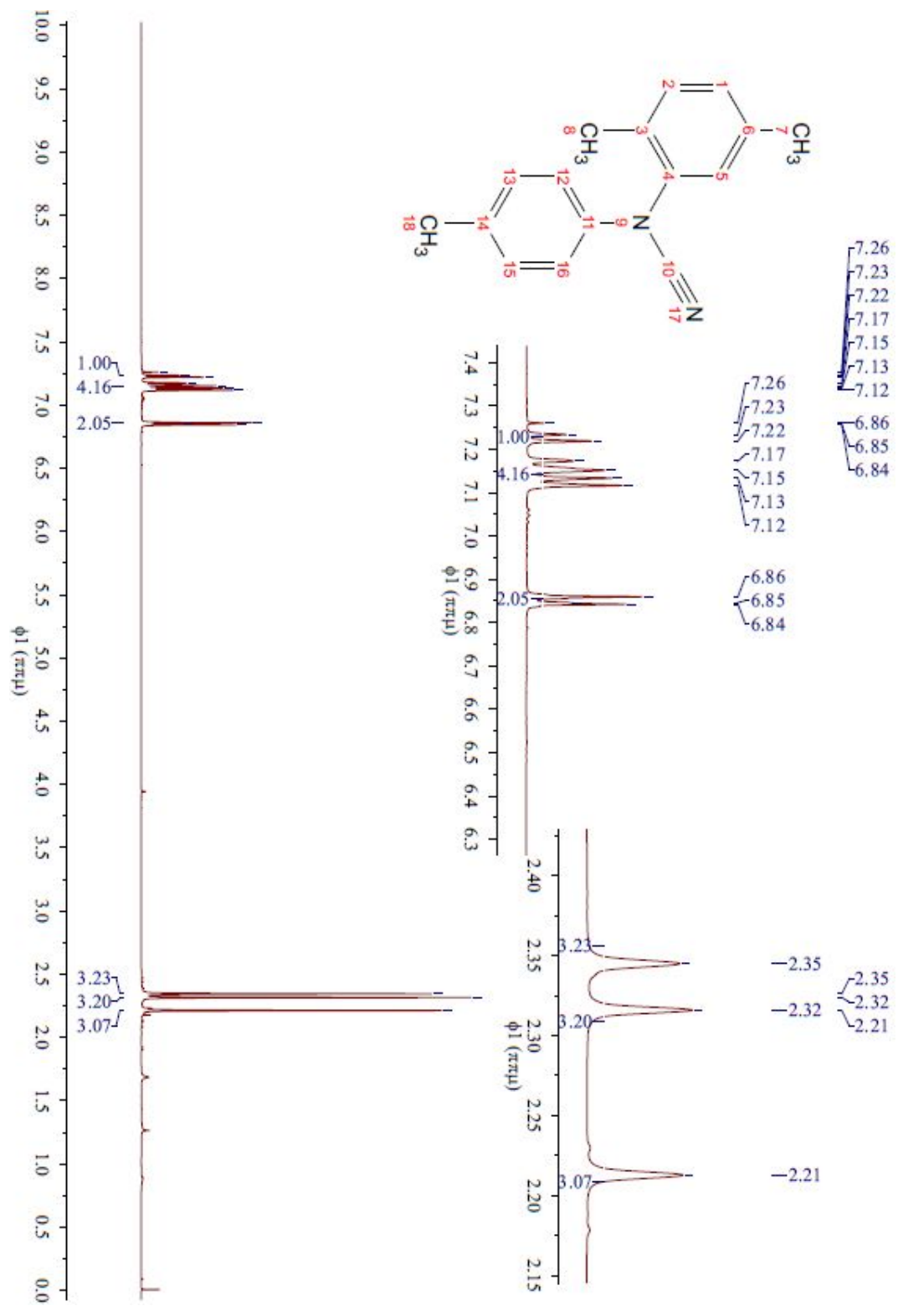
3P

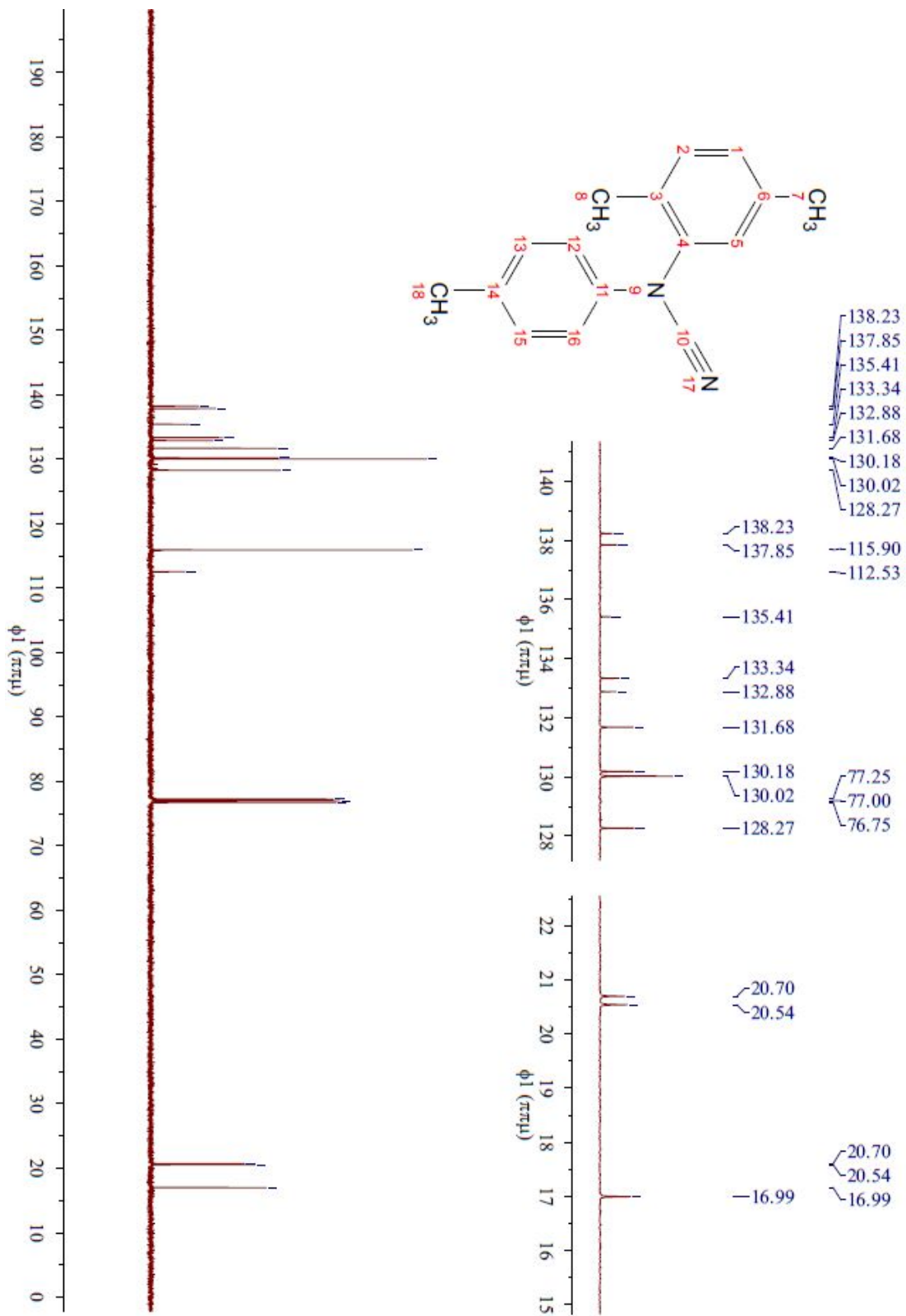




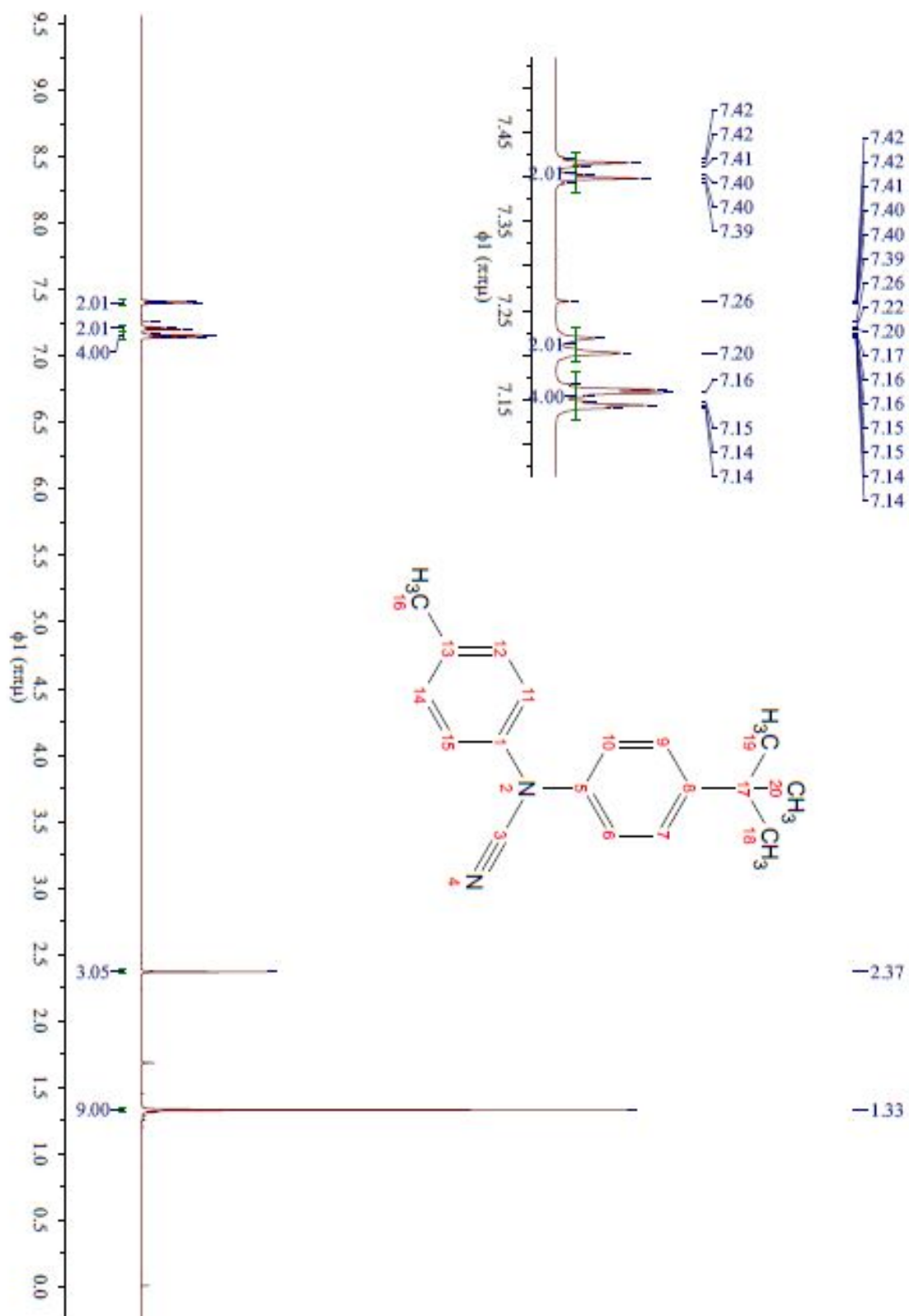


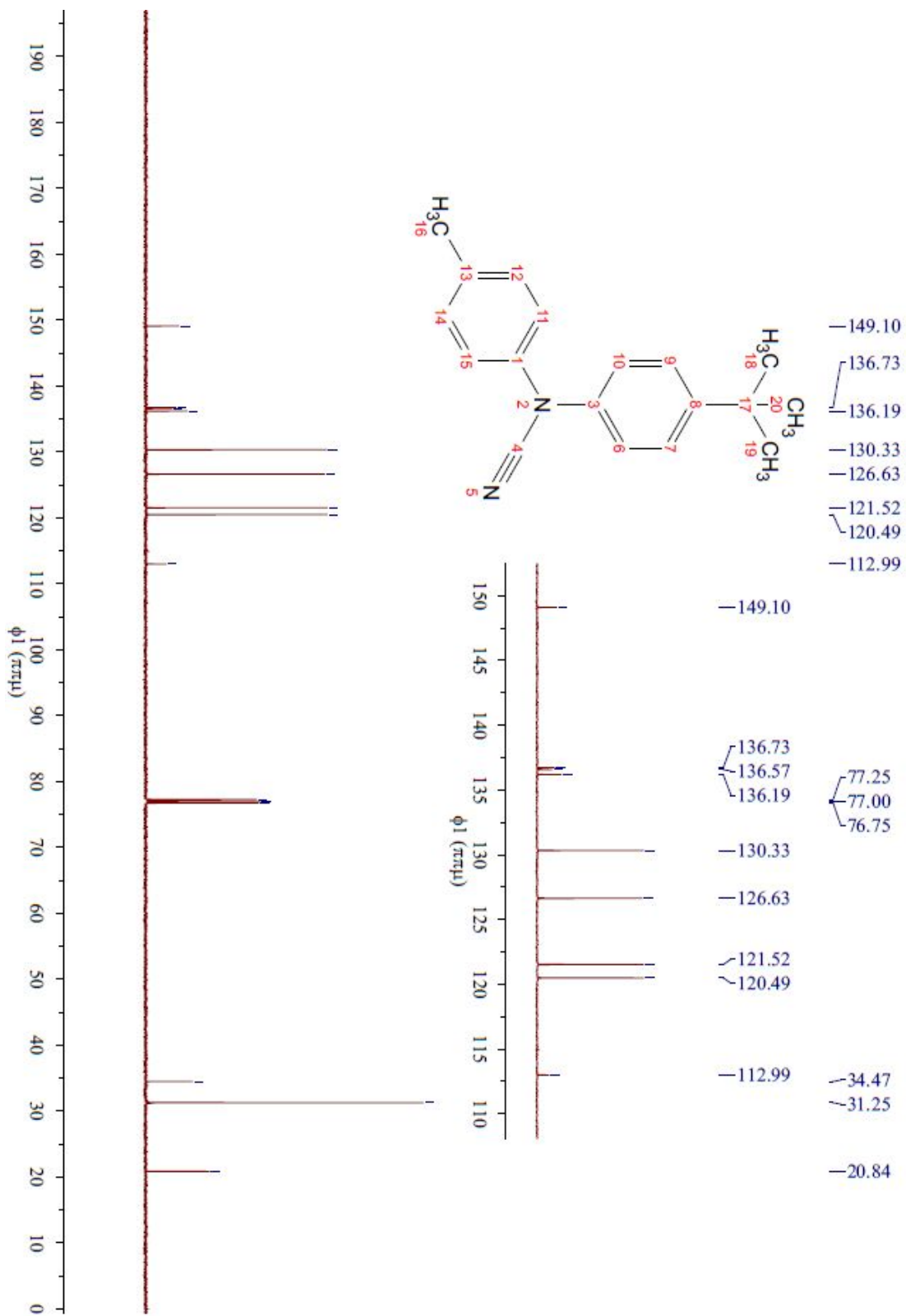
4a:



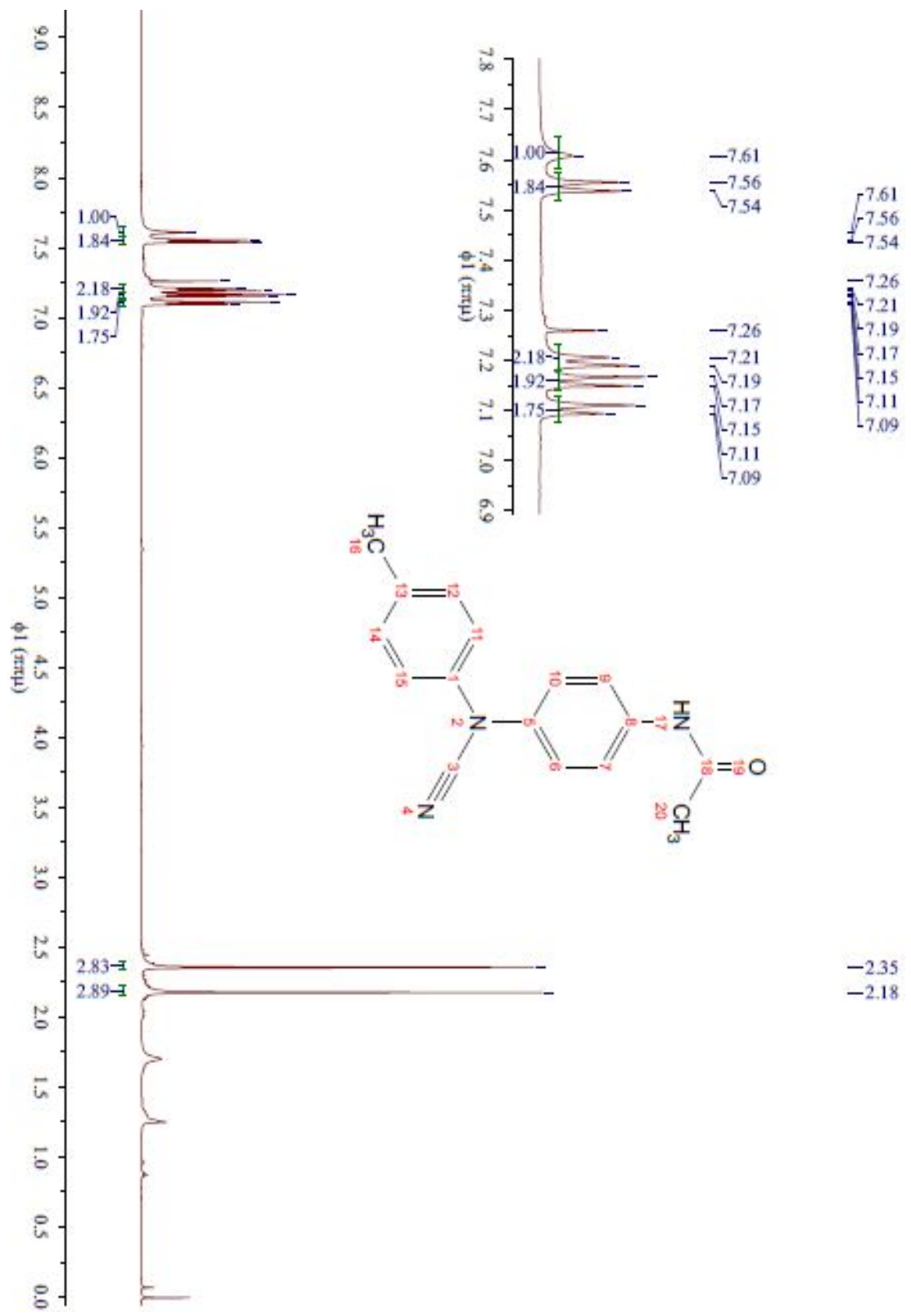


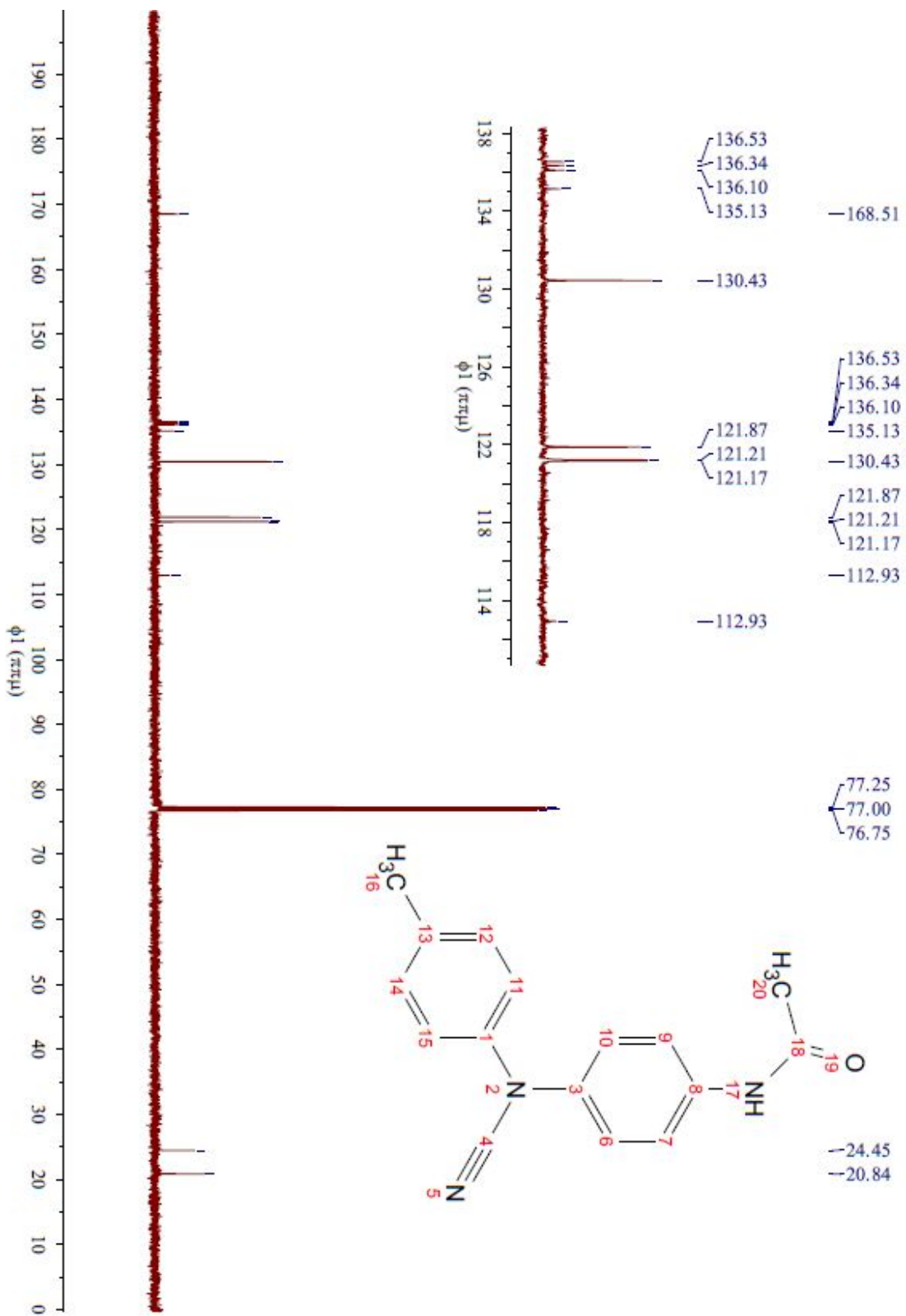
4b:



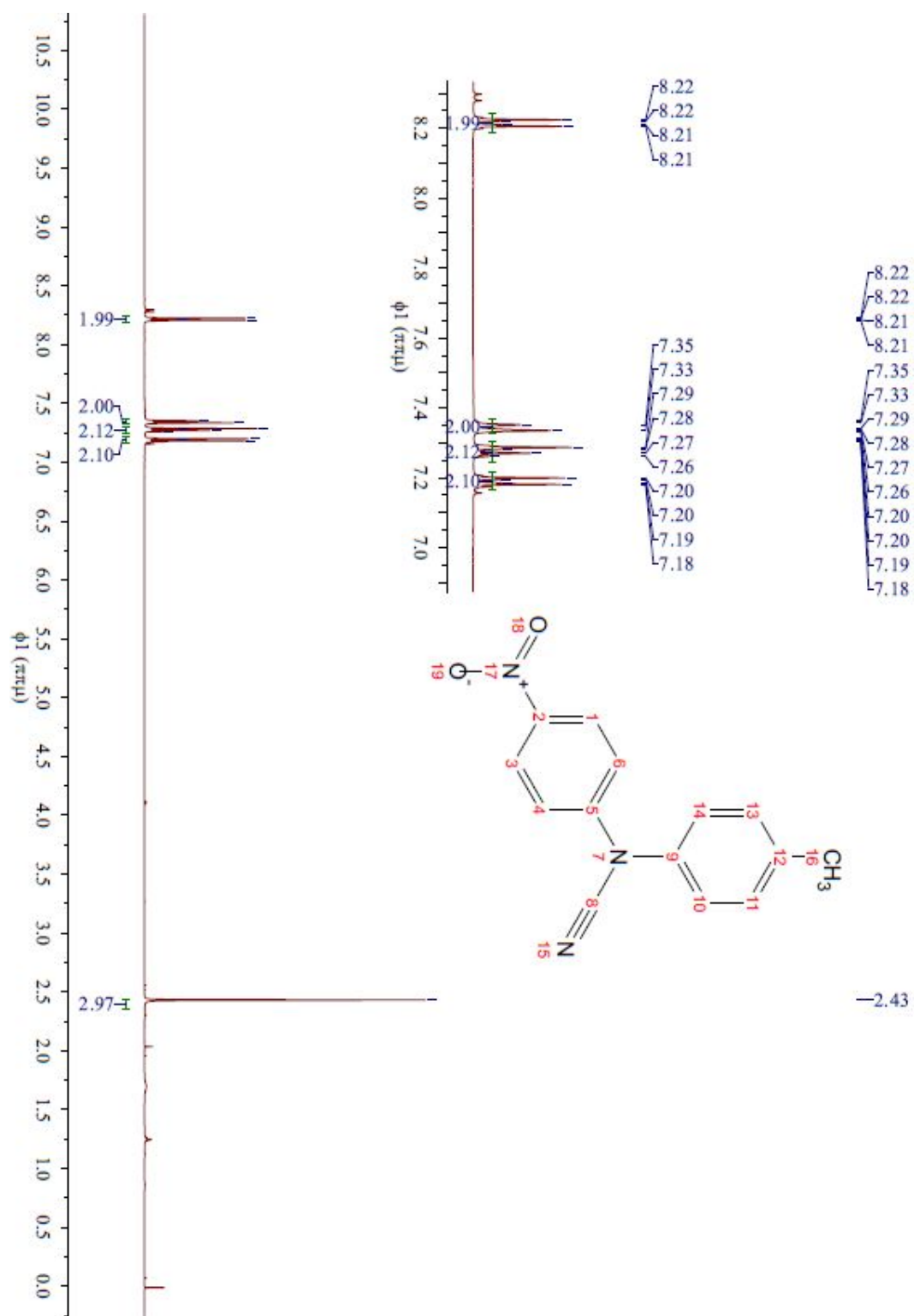


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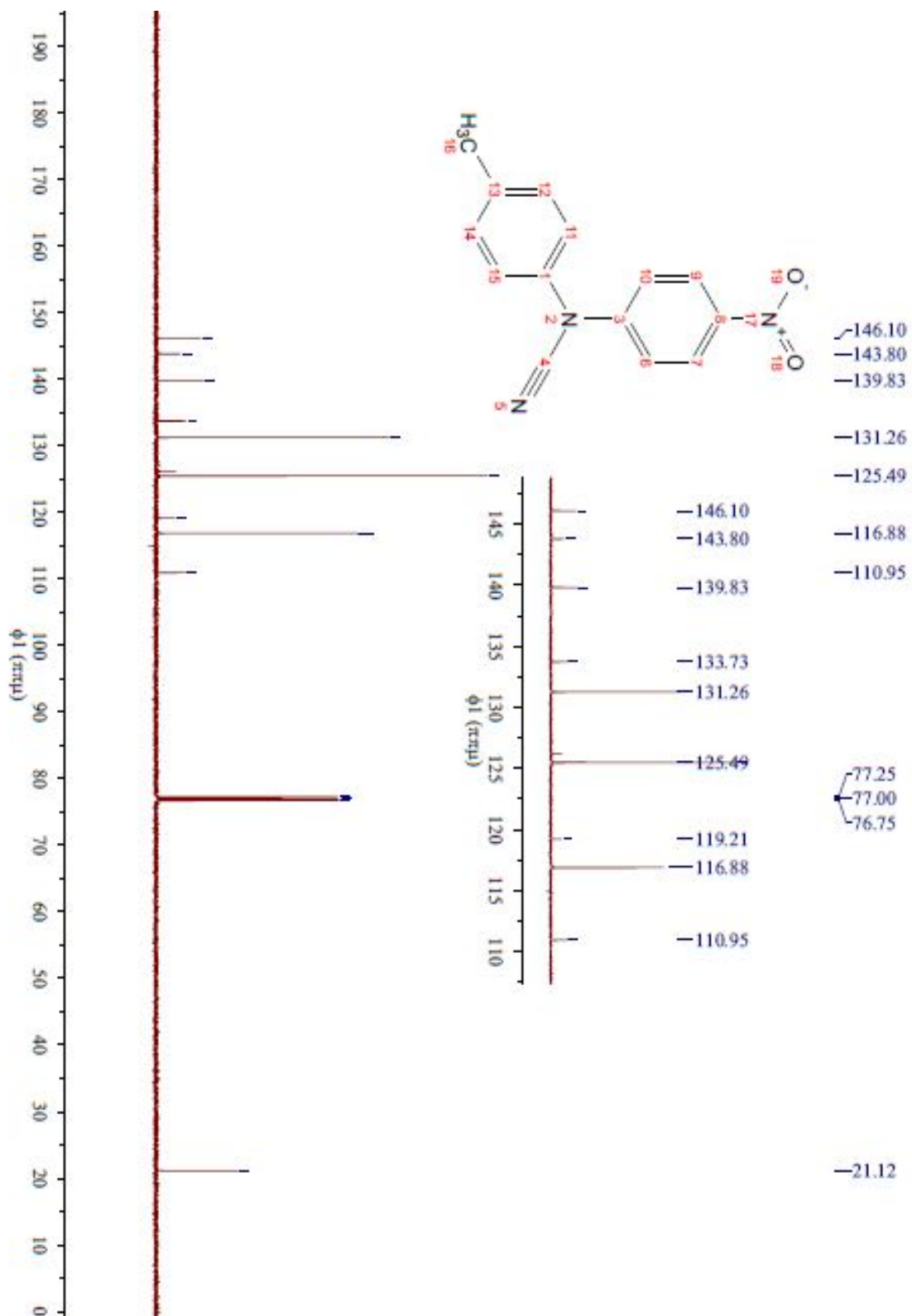




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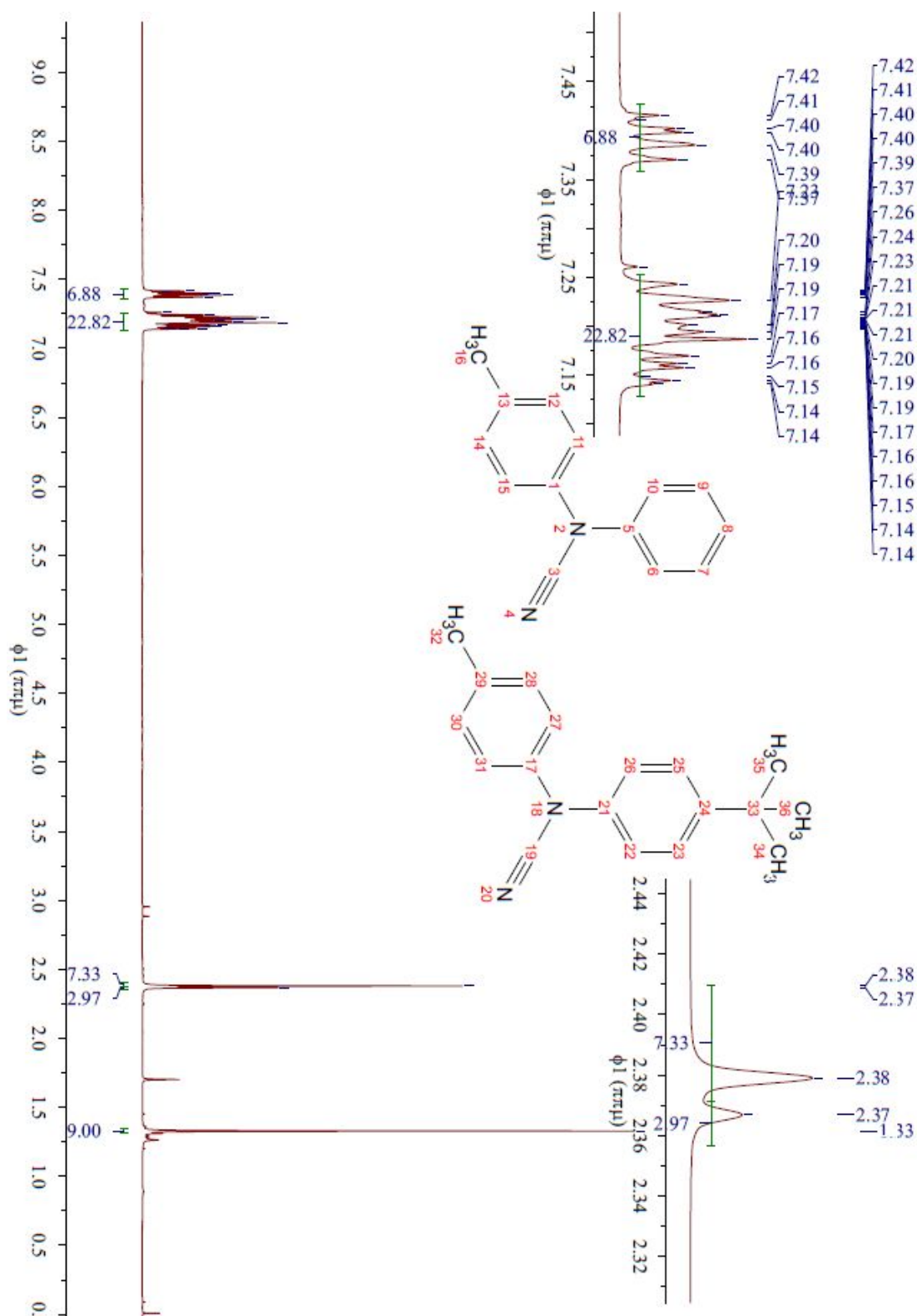


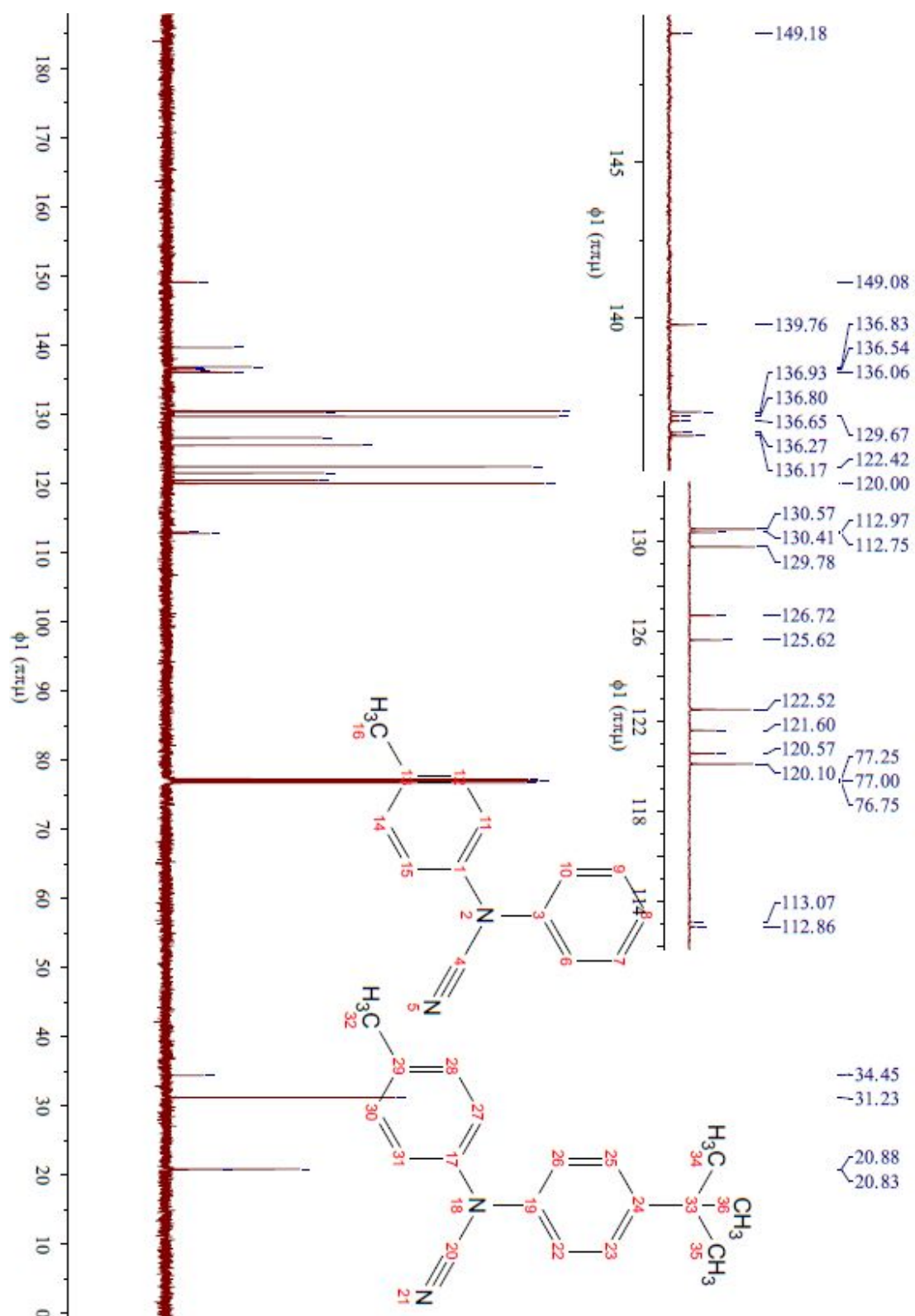




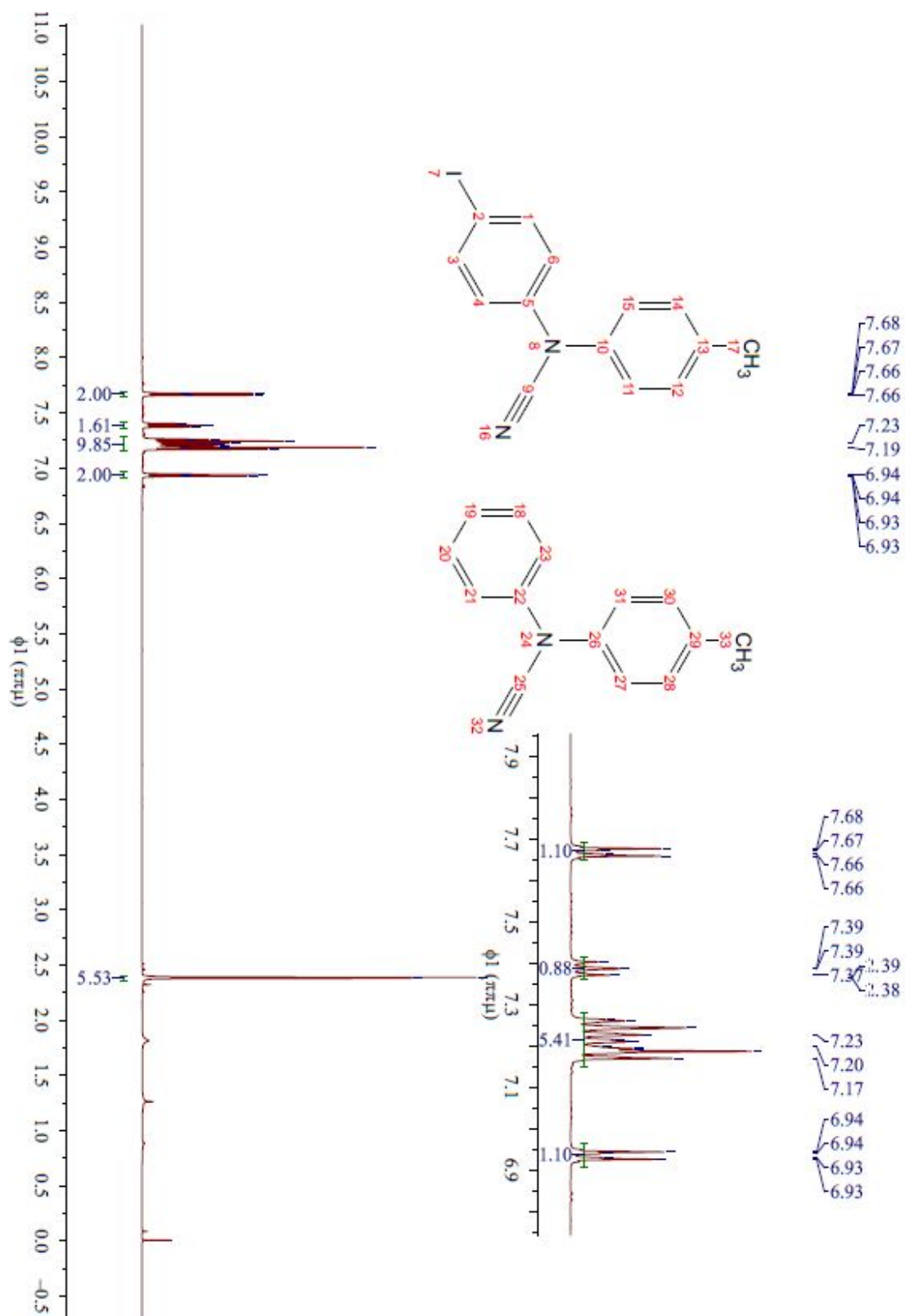
<sup>1</sup>H and <sup>13</sup>C NMR spectra of disubstituted cyanamides mixtures 3a/4b, 3a/4f, 3a/4a and 3d/4g

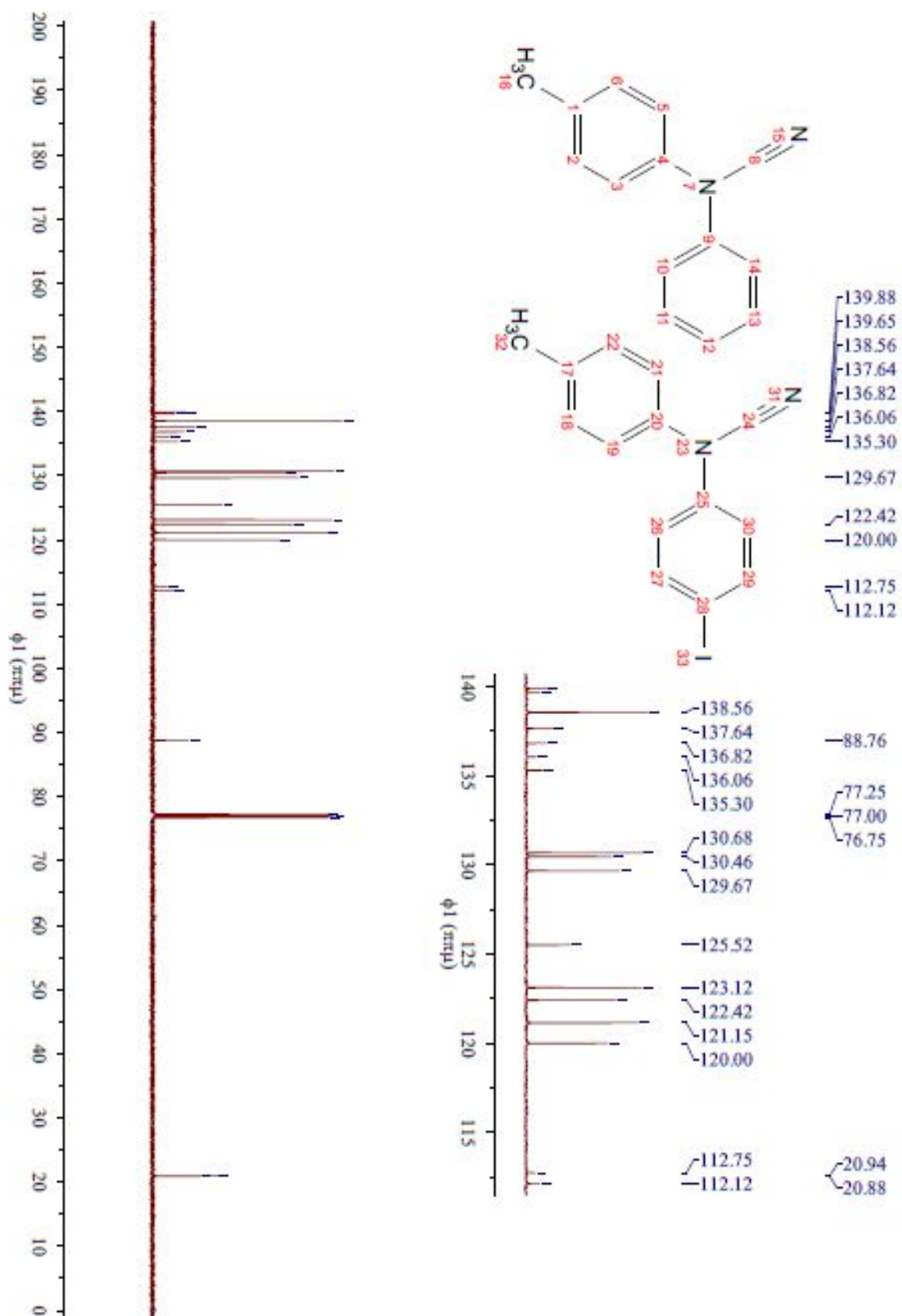
3a/4b:



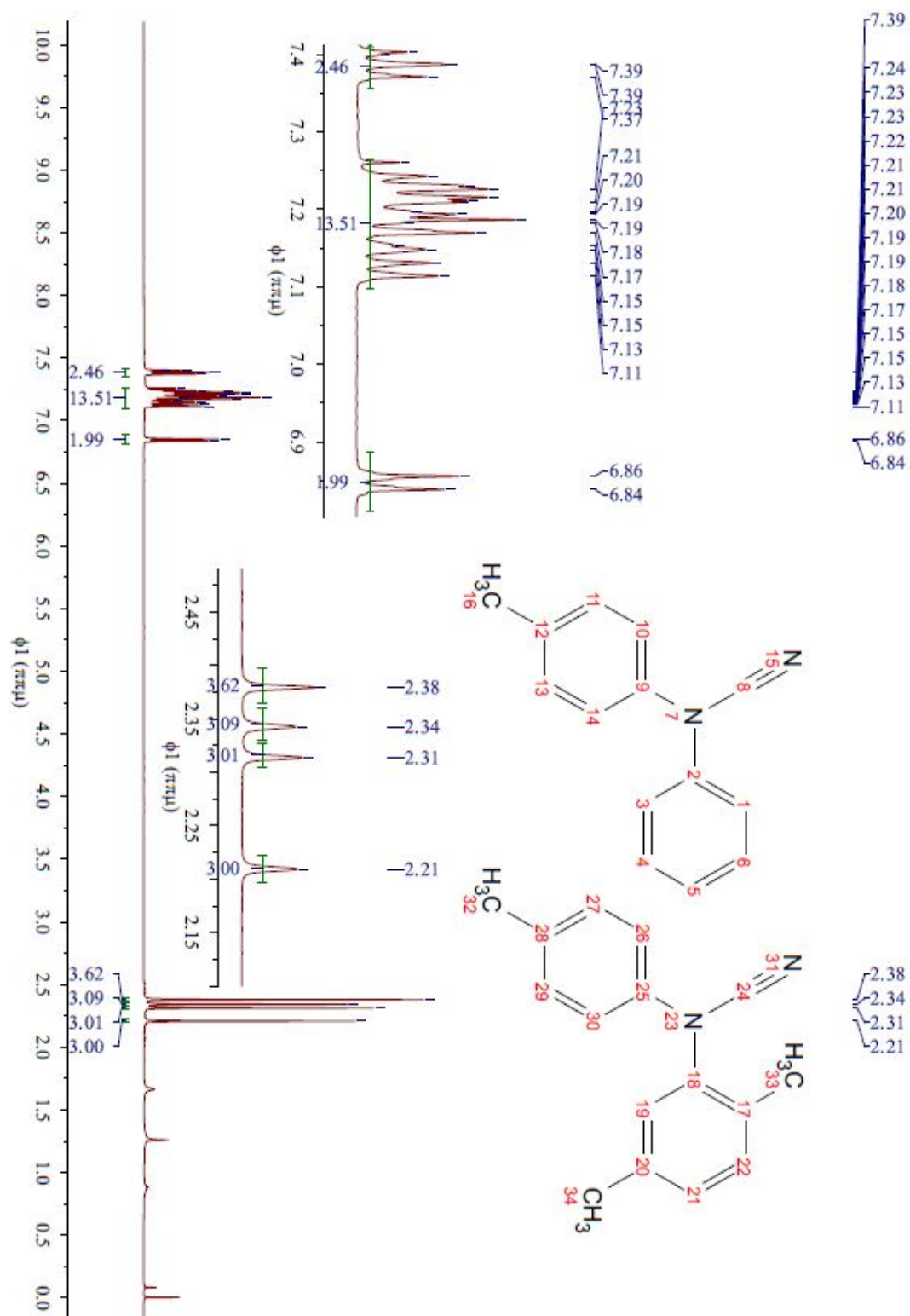


3a/4f:

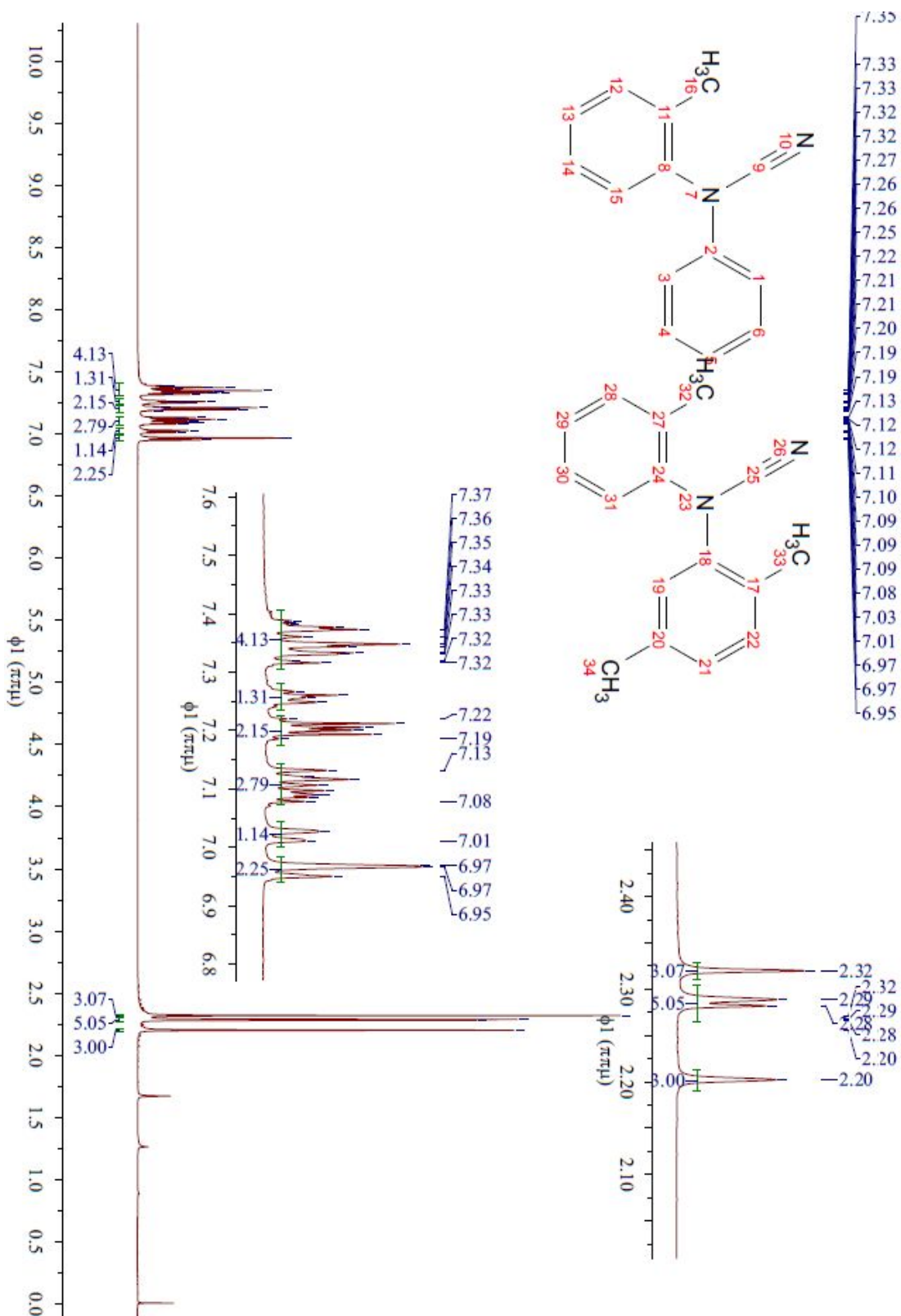


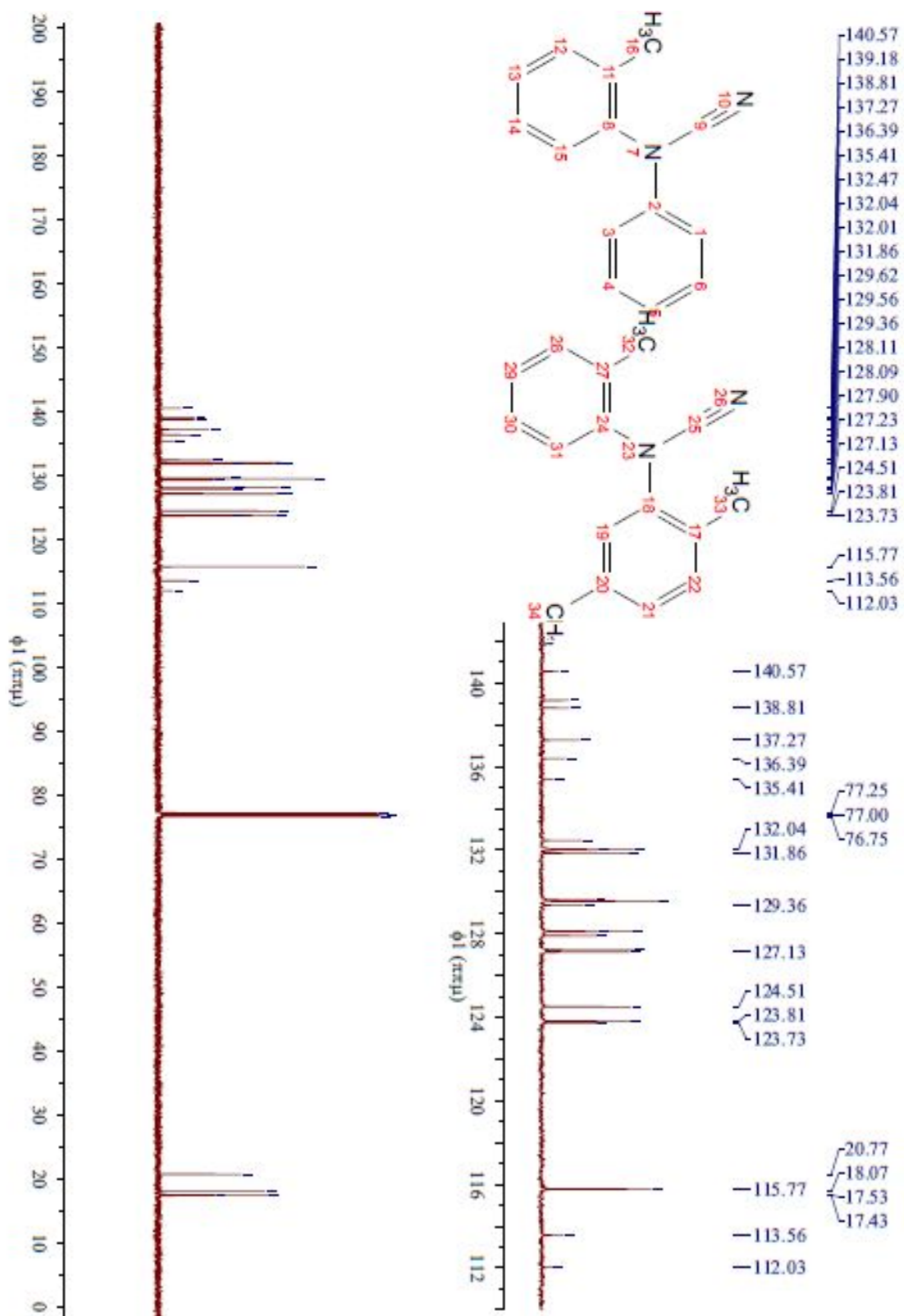


3a/4a:



3d/4g:

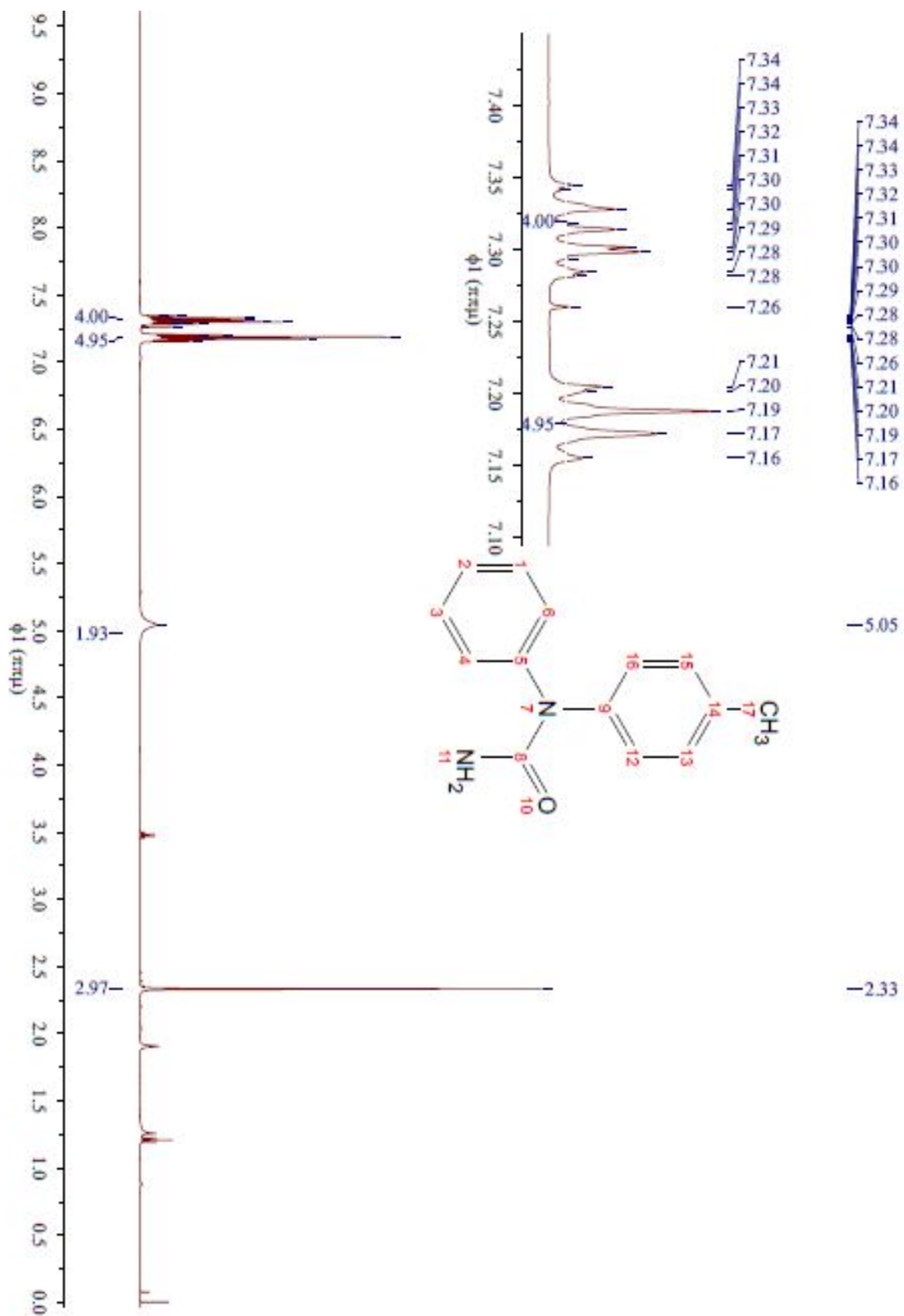


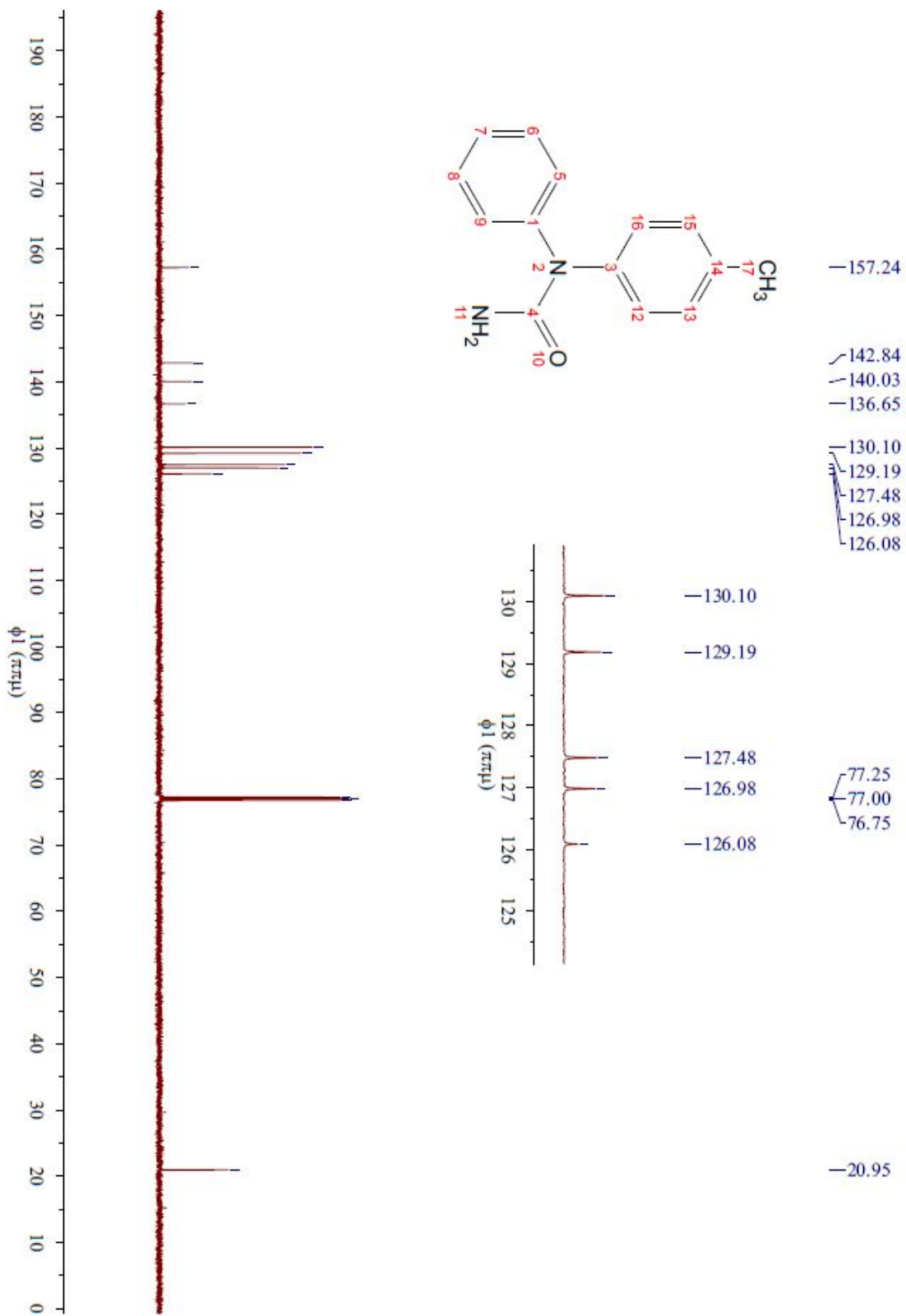




<sup>1</sup>H and <sup>13</sup>C NMR spectra of disubstituted ureas 5a and 5b.

5a:





5b:

