Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

DABCO-Promoted synthesis of pyrazoles from tosylhydrazones and nitroalkenes

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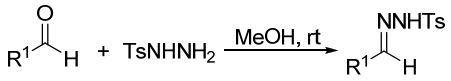
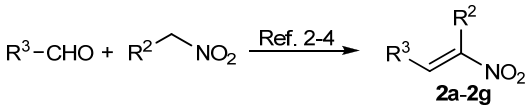
General Information

For product purification by flash column chromatography, silica gel (200-300 mesh) and light petroleum ether (bp. 60-90 ℃) are used. All organic extracts were dried over anhydrous $MgSO_4$. ^1H and ^{13}C NMR spectra were taken on a Varian Mercury-300 or 400 MHz spectrometer. The HRMS data were determined on a Bruker Daltonics APEXII 47e FT-ICR spectrometer.

General Procedure for Preparation of Tosylhydrazones (1a-1e) and Nitroalkenes (2a-2g)

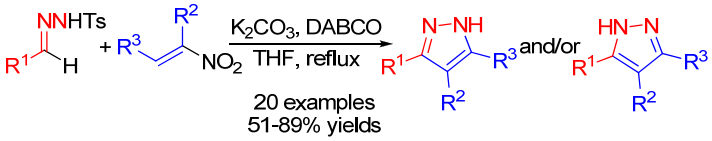


Tosylhydrazones (**1a-1e**) were prepared from $TsNHNH_2$ and corresponding aldehydes by the known procedure.[1] To a rapidly stirred suspension of $TsNHNH_2$ (1.05 equiv) in methanol was added aldehyde (1.0 equiv) dropwise (solid reagents were added portion-wise). A mildly exothermic reaction ensued and the hydrazide dissolved. Within 5-10 min the tosylhydrazone began to precipitate. After approximately 30 min, the mixture was cooled to 0 ℃ and the product was collected by filtration, washed with cooled methanol. All of the obtained solids could be recrystallized from methanol or used without further purification.

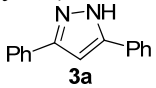


Nitroalkenes (**2a-2g**) were prepared from corresponding aldehydes and nitroalkanes according to references.[2-4]

Procedure for the Synthesis of Pyrazoles 3a-3t and Analytic Data

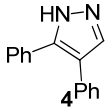


A mixture of tosylhydrazone **1a** (110 mg, 0.4 mmol), nitroalkene **2a** (120 mg, 0.8 mmol), K_2CO_3 (56 mg, 0.4 mmol) and DABCO (27 mg, 0.24 mmol) in THF (4 ml) were stirred under reflux temperature for 8.5 hours. The product was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded **3a** as a white crystalline solid (72 mg, 82% yield) and **4** as a white crystalline solid (14 mg, 16% yield).



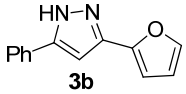
3a

For **3a**: **mp** 181-183 ℃; **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 6.77 (s, 1H), 7.24-7.31 (m, 6H), 7.67 (d, *J* = 6.6 Hz, 4H), 11.70 (brs, 1H) ppm; **^{13}C NMR** (75 MHz, $CDCl_3$) δ = 100.0, 125.6, 128.1, 128.8, 131.1, 148.6 ppm.



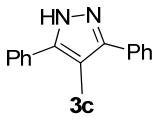
4

For **4**: **mp** 140-142 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.22-7.25 (m, 1H), 7.26-7.34 (m, 7H), 7.46-7.49 (m, 2H), 7.61 (s, 1H), 11.36 (brs, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 119.9, 126.6, 128.2, 128.4, 128.5, 128.6, 131.3, 133.0, 135.0, 143.6 ppm.



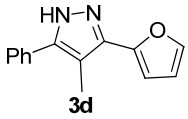
3b

A mixture of tosylhydrazone **1a** (110 mg, 0.4 mmol), nitroalkene **2b** (112 mg, 0.8 mmol), K_2CO_3 (56 mg, 0.4 mmol) and DABCO (27 mg, 0.24 mmol) in THF (4 ml) were stirred under reflux temperature for 12 hours. The product was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded **3b** as a yellow crystalline solid (64 mg, 76% yield). **mp** 106-107 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 6.38 (dd, *J* = 3.2, 1.6 Hz, 1H), 6.57 (d, *J* = 3.2 Hz, 1H), 6.68 (s, 1H), 7.25-7.35 (m, 4H), 7.64-7.66 (m, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 99.2, 106.2, 111.3, 125.6, 128.1, 128.7, 130.7, 141.0, 141.9, 146.9, 147.9 ppm; **HRMS** (ESI): Calcd for $C_{13}H_{11}N_2O$ $[M+H]^+$: 211.0866, found: 211.0863.



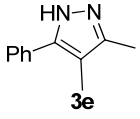
3c

A mixture of tosylhydrazone **1a** (110 mg, 0.4 mmol), nitroalkene **2c** (131 mg, 0.8 mmol), K_2CO_3 (56 mg, 0.4 mmol) and DABCO (27 mg, 0.24 mmol) in THF (4 ml) were stirred under reflux temperature for 4.5 hours. The product was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded **3c** as a white crystalline solid (75 mg, 80% yield). **mp** 171-172 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 2.14 (s, 3H), 7.30-7.33 (m, 2H), 7.37-7.39 (m, 2H), 10.80 (brs, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 10.8, 117.9, 126.4, 127.7, 128.0, 128.3, 130.0, 132.2, 133.6, 141.9, 146.2 ppm; **HRMS** (ESI): Calcd for $C_{16}H_{15}N_2$ $[M+H]^+$: 235.1230, found: 235.1229.



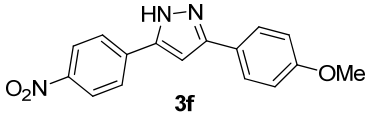
3d

A mixture of tosylhydrazone **1a** (110 mg, 0.4 mmol), nitroalkene **2d** (123 mg, 0.8 mmol), K_2CO_3 (56 mg, 0.4 mmol) and DABCO (27 mg, 0.24 mmol) in THF (4 ml) were stirred under reflux temperature for 7 hours. The product was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded **3d** as a yellow crystalline solid (48 mg, 53% yield). **mp** 103-104 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 2.15 (s, 3H), 6.11 (d, *J* = 3.2 Hz, 1H), 6.37 (s, 1H), 7.24-7.31 (m, 3H), 7.38 (s, 1H), 7.47 (d, *J* = 3.2 Hz, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 11.2, 107.1, 108.6, 110.8, 128.2, 128.3, 132.2, 141.2, 142.4, 147.1, 147.8 ppm; **HRMS** (ESI): Calcd for $C_{14}H_{13}N_2O$ $[M+H]^+$: 225.1022, found: 225.1020.



3e

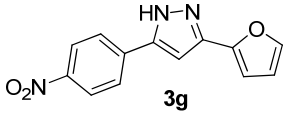
A mixture of tosylhydrazone **1a** (110 mg, 0.4 mmol), nitroalkene **2e** (81 mg, 0.8 mmol), K_2CO_3 (56 mg, 0.4 mmol) and DABCO (27 mg, 0.24 mmol) in THF (4 ml) were stirred under reflux temperature for 3.5 hours. The product was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded **3e** as a white crystalline solid (50 mg, 72% yield). **mp** 78-80 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 2.11 (s, 3H), 2.15 (s, 3H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 7.4 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 2H), 9.78 (brs, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 8.8, 10.5, 110.5, 127.4, 128.5, 132.7, 142.6, 146.0 ppm; **HRMS** (ESI): Calcd for $C_{11}H_{13}N_2$ $[M+H]^+$: 173.1073, found: 173.1071.



3f

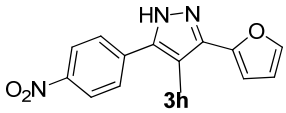
A mixture of tosylhydrazone **1b** (128 mg, 0.4 mmol), nitroalkene **2a** (100 mg, 0.8 mmol), K_2CO_3 (56 mg, 0.4 mmol) and DABCO (27 mg, 0.24 mmol) in THF (4 ml) were stirred under reflux temperature for 4 hours. The product was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded **3f** as a yellow crystalline solid (77 mg, 65% yield). **mp** 190-192 ℃; **^{1}H NMR** (400 MHz, d_6-acetone) δ = 3.86 (s, 3H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.22 (s,

1H), 7.80 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J* = 8.4 Hz, 2H), 8.30 (d, *J* = 8.4 Hz, 2H) ppm; **^{13}C NMR** (100 MHz, d_6-acetone) δ = 55.6, 100.9, 115.2, 123.5, 124.8, 126.7, 127.6, 140.6, 147.9, 160.9 ppm; **HRMS** (ESI): Calcd for $C_{16}H_{14}N_3O_3$ $[M+H]^+$: 296.1030, found: 296.1028.



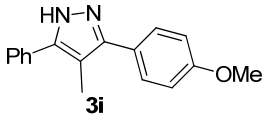
3g

A mixture of tosylhydrazone **1b** (128 mg, 0.4 mmol), nitroalkene **2b** (112 mg, 0.8 mmol), K_2CO_3 (56 mg, 0.4 mmol) and DABCO (27 mg, 0.24 mmol) in THF (4 ml) were stirred under reflux temperature for 10 hours. The product was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded **3g** as a yellow crystalline solid (91 mg, 89% yield). **mp** 261-263 ℃; **^{1}H NMR** (400 MHz, d_6-DMSO) δ = 6.63 (s, 1H), 6.87 (s, 1H), 7.18 (s, 1H), 7.80 (s, 1H), 8.11 (s, 2H), 8.27 (d, *J* = 6.4 Hz, 2H), 13.77 (s, 1H) ppm; **^{13}C NMR** (100 MHz, d_6-DMSO) δ = 100.0, 107.2, 111.8, 124.1, 125.9, 135.7, 139.7, 143.1, 144.2, 146.5, 149.1 ppm; **HRMS** (ESI): Calcd for $C_{13}H_{10}N_3O_3$ $[M+H]^+$: 256.0717, found: 256.0716.



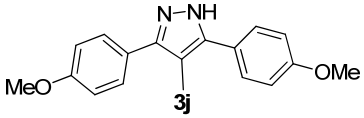
3h

A mixture of tosylhydrazone **1b** (128, 0.4 mmol), nitroalkene **2d** (123 mg, 0.8 mmol), K_2CO_3 (56 mg, 0.4 mmol) and DABCO (27 mg, 0.24 mmol) in THF (4 ml) were stirred under reflux temperature for 10 hours. The product was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded **3h** as a yellow crystalline solid (59 mg, 55% yield). **mp** 138-141 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 2.33 (s, 3H), 6.24 (d, *J* = 3.2 Hz, 1H), 6.46-6.47 (m, 1H), 7.44 (s, 1H), 7.67 (d, *J* = 8.8 Hz, 2H), 8.17 (d, *J* = 8.8 Hz, 2H), 8.86 (brs, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 10.8, 108.5, 109.6, 111.1, 123.6, 128.5, 138.9, 141.4, 142.1, 146.6, 147.4 ppm; **HRMS** (ESI): Calcd for $C_{14}H_{12}N_3O_3$ $[M+H]^+$: 270.0873, found: 270.0868.



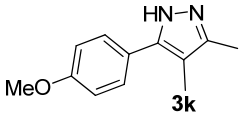
3i

A mixture of tosylhydrazone **1c** (122 mg, 0.4 mmol), nitroalkene **2c** (131 mg, 0.8 mmol), K_2CO_3 (56 mg, 0.4 mmol) and DABCO (27 mg, 0.24 mmol) in THF (4 ml) were stirred under reflux temperature for 10 hours. The product was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded **3i** as a white crystalline solid (65 mg, 61% yield). **mp** 170-172 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 2.19 (s, 3H), 3.75 (s, 3H), 6.74 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 7.2 Hz, 2H), 7.23-7.34 (m, 5H), 10.52 (brs, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 11.1, 55.1, 113.8, 117.4, 124.5, 126.4, 128.3, 129.2, 130.0, 133.8, 142.3, 145.6, 159.2 ppm; **HRMS** (ESI): Calcd for $C_{17}H_{17}N_2O$ $[M+H]^+$: 265.1335, found: 265.1333.



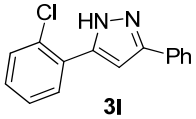
3j

A mixture of tosylhydrazone **1c** (122 mg, 0.4 mmol), nitroalkene **2a** (100 mg, 0.8 mmol), K_2CO_3 (56 mg, 0.4 mmol) and DABCO (27 mg, 0.24 mmol) in THF (4 ml) were stirred under reflux temperature for 12 hours. The product was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded **3j** as a white crystalline solid (80 mg, 68% yield). **mp** 150-151 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 2.15 (s, 3H), 3.75 (s, 3H), 3.81 (s, 3H), 6.73 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 2H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 11.0, 55.07, 55.13, 113.7, 113.8, 116.9, 124.6, 126.0, 129.1, 131.1, 142.2, 145.4, 158.1, 159.1 ppm; **HRMS** (ESI): Calcd for $C_{18}H_{19}N_2O_2$ $[M+H]^+$: 295.1441, found: 295.1442.



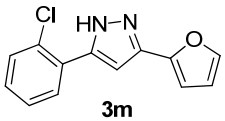
3k

A mixture of tosylhydrazone **1c** (122 mg, 0.4 mmol), nitroalkene **2e** (81 mg, 0.8 mmol), K_2CO_3 (56 mg, 0.4 mmol) and DABCO (27 mg, 0.24 mmol) in THF (4 ml) were stirred under reflux temperature for 10 hours. The product was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded **3k** as a yellow oil (41 mg, 51% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 2.09 (s, 3H), 2.18 (s, 3H), 3.82 (s, 3H), 6.90 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 9.51 (brs, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 8.7, 10.6, 55.2, 110.1, 113.9, 125.0, 128.6, 142.8, 145.3, 159.1 ppm; **HRMS** (ESI): Calcd for $C_{12}H_{15}N_2O$ $[M+H]^+$: 203.1179, found: 203.1179.



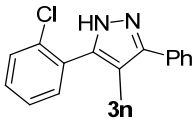
3l

A mixture of tosylhydrazone **1d** (124 mg, 0.4 mmol), nitroalkene **2a** (120 mg, 0.8 mmol), K_2CO_3 (56 mg, 0.4 mmol) and DABCO (27 mg, 0.24 mmol) in THF (4 ml) were stirred under reflux temperature for 10 hours. The product was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded **3l** as a white crystalline solid (80 mg, 78% yield). **mp** 114-115 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 6.97 (s, 1H), 7.18-7.25 (m, 2H), 7.28-7.37 (m, 3H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.61-7.63 (m, 1H), 7.73 (d, *J* = 7.6 Hz, 2H), 10.77 (brs, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 103.6, 125.7, 127.0, 128.1, 128.8, 129.3, 129.8, 130.2, 130.5, 131.5, 131.8, 145.1, 148.6 ppm; **HRMS** (ESI): Calcd for $C_{15}H_{12}N_2Cl$ $[M+H]^+$: 255.0684, found: 255.0684.



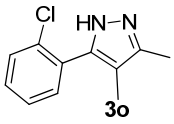
3m

A mixture of tosylhydrazone **1d** (124 mg, 0.4 mmol), nitroalkene **2b** (112 mg, 0.8 mmol), K_2CO_3 (56 mg, 0.4 mmol) and DABCO (27 mg, 0.24 mmol) in THF (4 ml) were stirred under reflux temperature for 10 hours. The product was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded **3m** as a yellow crystalline solid (81 mg, 83% yield). **mp** 114-116 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 6.47 (s, 1H), 6.68 (d, *J* = 3.2 Hz, 1H), 6.91 (s, 1H), 7.26-7.30 (m, 2H), 7.44-7.47 (m, 2H), 7.64-7.66 (m, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 103.0, 106.4, 111.4, 127.0, 129.4, 130.3, 130.5, 131.9, 140.9, 142.0, 144.5, 147.0 ppm; **HRMS** (ESI): Calcd for $C_{13}H_{10}N_2ClO$ $[M+H]^+$: 245.0476, found: 245.0479.



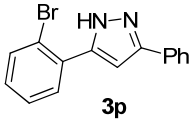
3n

A mixture of tosylhydrazone **1d** (124 mg, 0.4 mmol), nitroalkene **2c** (131 mg, 0.8 mmol), K_2CO_3 (56 mg, 0.4 mmol) and DABCO (27 mg, 0.24 mmol) in THF (4 ml) were stirred under reflux temperature for 4 hours. The product was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded **3n** as a white crystalline solid (56 mg, 52% yield). **mp** 94-95 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 2.13 (s, 3H), 7.07 (d, *J* = 7.2 Hz, 2H), 7.15-7.25 (m, 5H), 7.31-7.35 (m, 2H), 11.00 (brs, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 10.7, 119.3, 126.1, 126.5, 128.2, 129.0, 129.5, 129.8, 132.0, 132.3, 133.4, 134.0, 140.3, 144.7 ppm; **HRMS** (ESI): Calcd for $C_{16}H_{14}N_2Cl$ $[M+H]^+$: 269.0840, found: 269.0842.



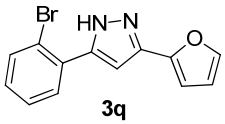
3o

A mixture of tosylhydrazone **1d** (124 mg, 0.4 mmol), nitroalkene **2e** (81 mg, 0.8 mmol), K_2CO_3 (56 mg, 0.4 mmol) and DABCO (27 mg, 0.24 mmol) in THF (4 ml) were stirred under reflux temperature for 4 hours. The product was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded **3o** as a white crystalline solid (51 mg, 61% yield). **mp** 113-115 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.90 (s, 3H), 2.05 (s, 3H), 7.24-7.29 (m, 2H), 7.31-7.35 (m, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 10.85 (brs, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 8.3, 10.1, 112.3, 126.5, 129.4, 129.7, 131.9, 133.8, 141.0, 144.8 ppm; **HRMS** (ESI): Calcd for $C_{11}H_{12}N_2Cl$ $[M+H]^+$: 207.0684, found: 207.0681.



3p

A mixture of tosylhydrazone **1e** (142 mg, 0.4 mmol), nitroalkene **2a** (120 mg, 0.8 mmol), K_2CO_3 (56 mg, 0.4 mmol) and DABCO (27 mg, 0.24 mmol) in THF (4 ml) were stirred under reflux temperature for 4 hours. The product was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded **3p** as a white crystalline solid (97 mg, 81% yield). **mp** 124-126 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 6.94 (s, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.23-7.38 (m, 4H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 7.2 Hz, 2H), 8.94 (brs, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 103.7, 121.7, 125.7, 127.5, 128.1, 128.8, 129.6, 130.9, 131.3, 132.1, 133.7, 146.7, 148.3 ppm; **HRMS** (ESI): Calcd for $C_{15}H_{12}N_2Br$ $[M+H]^+$: 299.0178, found: 299.0174.

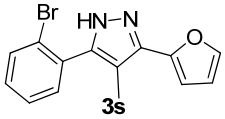


3q

A mixture of tosylhydrazone **1e** (142 mg, 0.4 mmol), nitroalkene **2b** (112 mg, 0.8 mmol), K_2CO_3 (56 mg, 0.4 mmol) and DABCO (27 mg, 0.24 mmol) in THF (4 ml) were stirred under reflux temperature for 8 hours. The product was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded **3q** as a yellow crystalline solid (81 mg, 70% yield). **mp** 113-116 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 6.48 (dd, *J* = 2.8, 1.6 Hz, 1H), 6.71 (d, *J* = 3.2 Hz, 1H), 6.87 (s, 1H), 7.20-7.26 (m, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.45 (s, 1H), 7.59 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 8.31 (brs, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 103.1, 106.4, 111.4, 121.7, 127.5, 129.7, 130.9, 131.7, 133.7, 140.7, 142.0, 146.0, 147.0 ppm; **HRMS** (ESI): Calcd for $C_{13}H_{10}N_2BrO$ $[M+H]^+$: 288.9971, found: 288.9974.

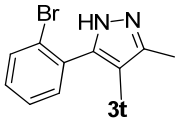
3r

A mixture of tosylhydrazone **1e** (142 mg, 0.4 mmol), nitroalkene **2c** (131 mg, 0.8 mmol), K_2CO_3 (56 mg, 0.4 mmol) and DABCO (27 mg, 0.24 mmol) in THF (4 ml) were stirred under reflux temperature for 4 hours. The product was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded **3r** as a white crystalline solid (75 mg, 60% yield). **mp** 116-119 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 2.13 (s, 3H), 7.07 (d, *J* = 7.2 Hz, 2H), 7.15-7.25 (m, 5H), 7.30-7.32 (m, 1H), 7.55 (d, *J* = 7.6 Hz, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 10.7, 119.1, 124.1, 126.1, 127.1, 128.2, 129.1, 129.7, 132.5, 132.9, 133.3, 134.1, 140.2, 146.3 ppm; **HRMS** (ESI): Calcd for $C_{16}H_{14}N_2Br$ $[M+H]^+$: 313.0335, found: 313.0331.



3s

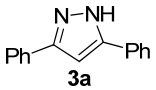
A mixture of tosylhydrazone **1e** (142 mg, 0.4 mmol), nitroalkene **2d** (123 mg, 0.8 mmol), K_2CO_3 (56 mg, 0.4 mmol) and DABCO (27 mg, 0.24 mmol) in THF (4 ml) were stirred under reflux temperature for 5 hours. The product was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded **3s** as a white crystalline solid (75 mg, 62% yield). **mp** 115-117 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 2.13 (s, 3H), 5.75 (d, *J* = 2.8 Hz, 1H), 6.26 (d, *J* = 1.2 Hz, 1H), 7.25-7.28 (m, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 10.9, 105.0, 110.1, 110.7, 124.4, 127.2, 130.0, 132.2, 132.8, 134.6, 139.4, 140.59, 140.61, 148.3 ppm; **HRMS** (ESI): Calcd for $C_{14}H_{12}N_2BrO$ $[M+H]^+$: 303.0128, found: 303.0131.



3t

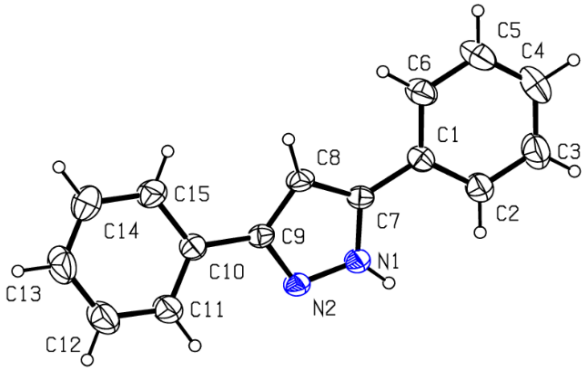
A mixture of tosylhydrazone **1e** (142 mg, 0.4 mmol), nitroalkene **2e** (81 mg, 0.8 mmol), K_2CO_3 (56 mg, 0.4 mmol) and DABCO (27 mg, 0.24 mmol) in THF (4 ml) were stirred under reflux temperature for 5 hours. The product was extracted with CH_2Cl_2 and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by chromatography on silica gel afforded **3t** as a white crystalline solid (65 mg, 64% yield). **mp** 116-118 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 1.90 (s, 3H), 2.09 (s, 3H), 7.20-7.26 (m, 1H), 7.32 (d, *J* = 4.4 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 9.98 (brs, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 8.3, 10.2, 112.2, 123.9, 127.1, 129.6, 132.1, 132.9, 134.1, 141.2, 146.2 ppm; **HRMS** (ESI): Calcd for $C_{11}H_{12}N_2Br$ $[M+H]^+$: 251.0178, found: 251.0180.

X-Ray Ellipsoid Plots of 3a



3a

The structure of **3a** was unambiguously established by NMR and single-crystal X-ray analysis. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 939872



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1. V. K. Aggarwal, E. Alonso, I. Bae, G. Hynd, K. M. Lydon, M. J. Palmer, M. Patel, M. Porcelloni, J. Richardson, R. A. Stenson, J. R. Studley, J.-L. Vasse, C. L. Winn, *J. Am. Chem. Soc.* **2003**, *125*, 10926.

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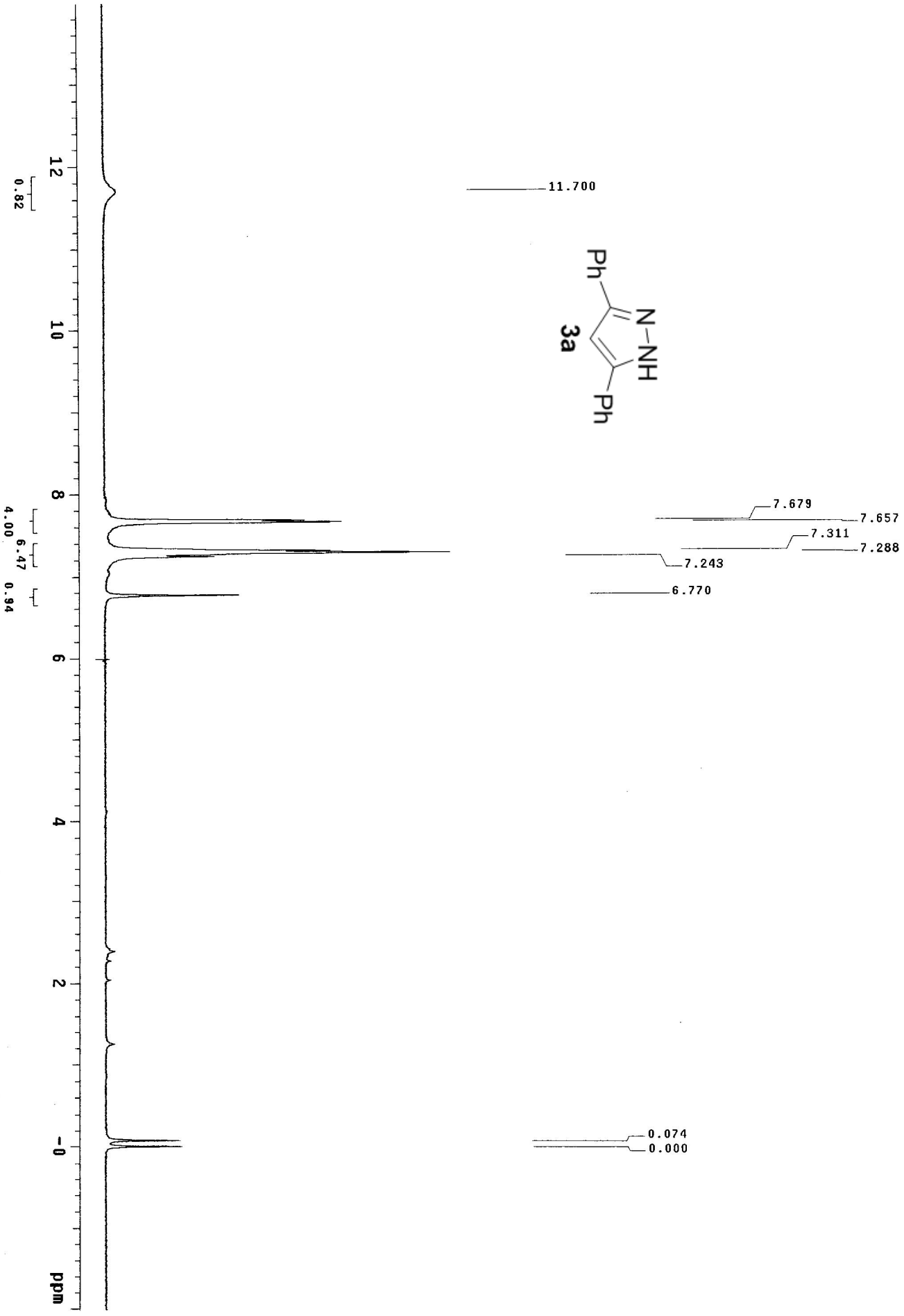
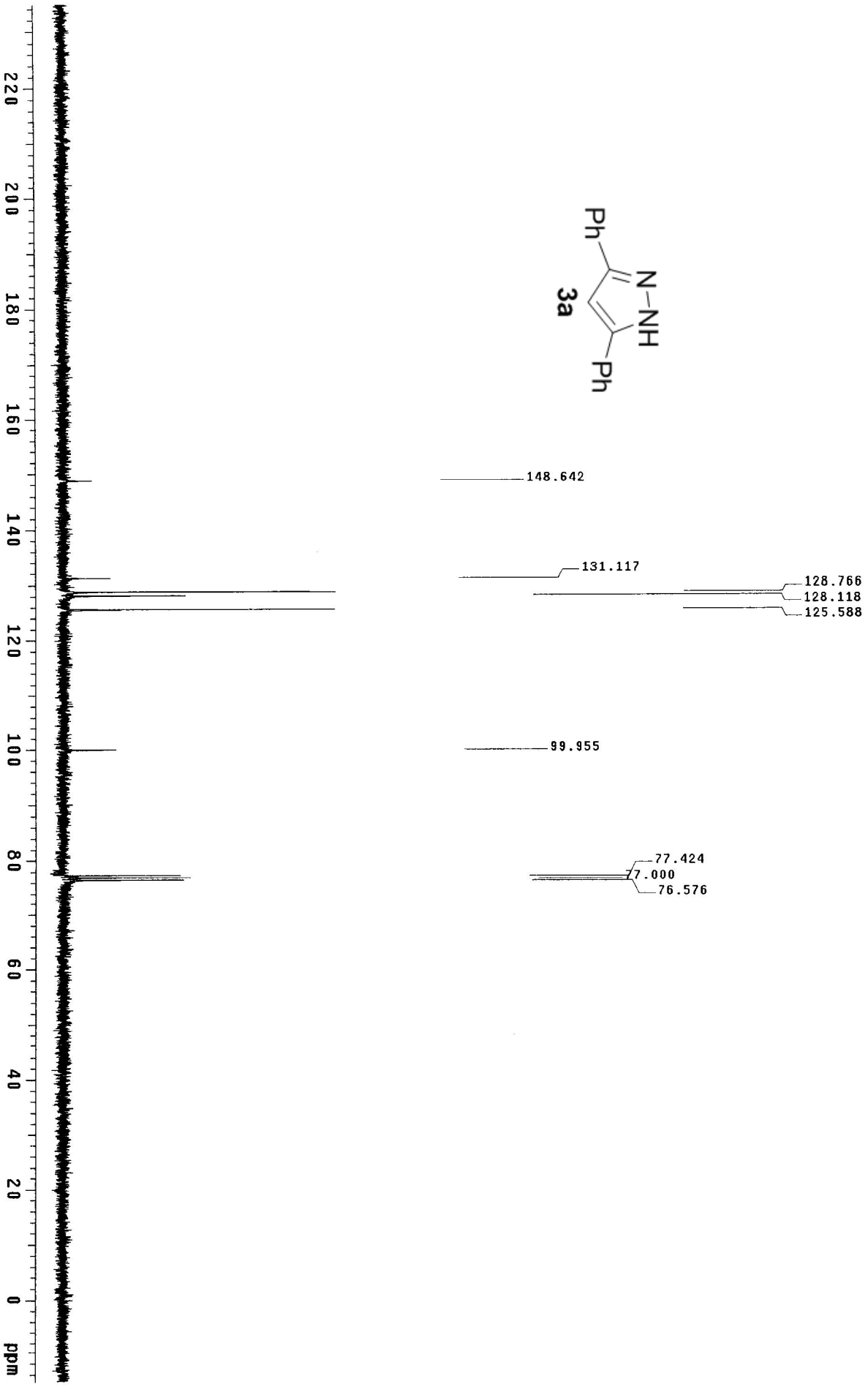
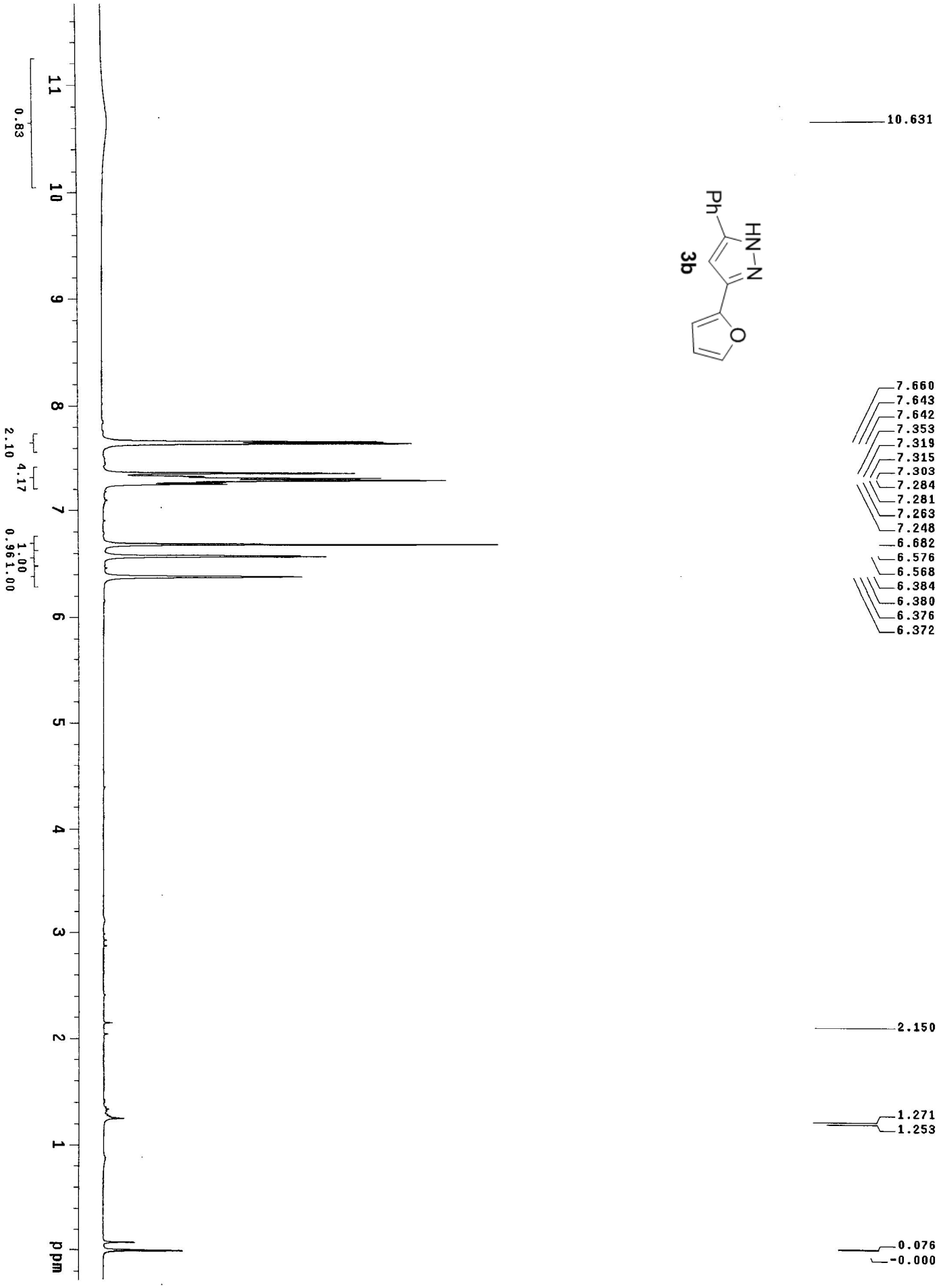
3. G. Vallejos, A. Fierro, M. C. Rezende, S. Sepúlveda-Bozab, M. Reyes-Parada, *Bioorg. Med. Chem.* **2005**, *13*, 4450.

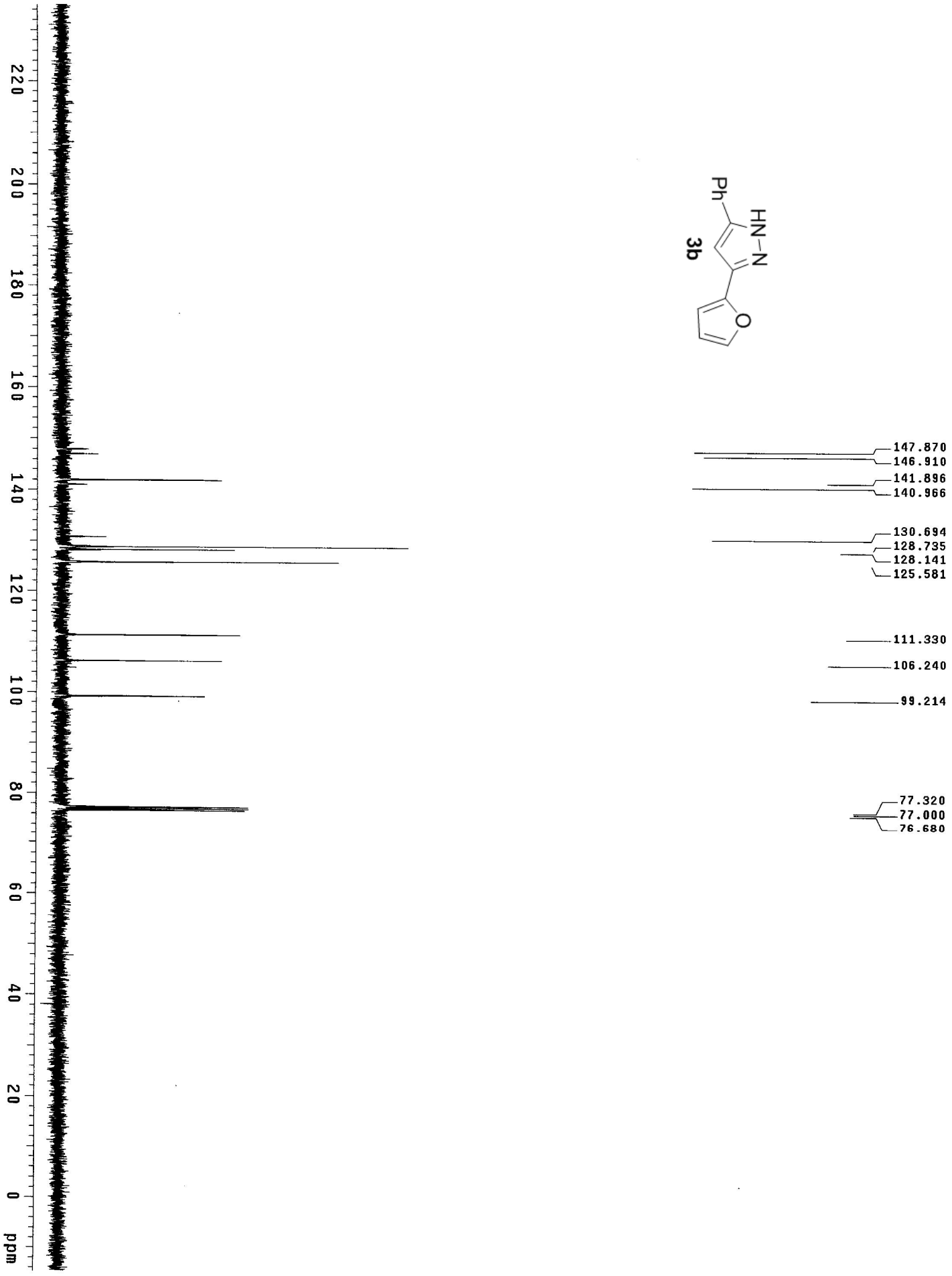
4. E. Dumez, R. Faure, J.-P. Dulcère, *Eur. J. Org. Chem.* **2001**, 2577.

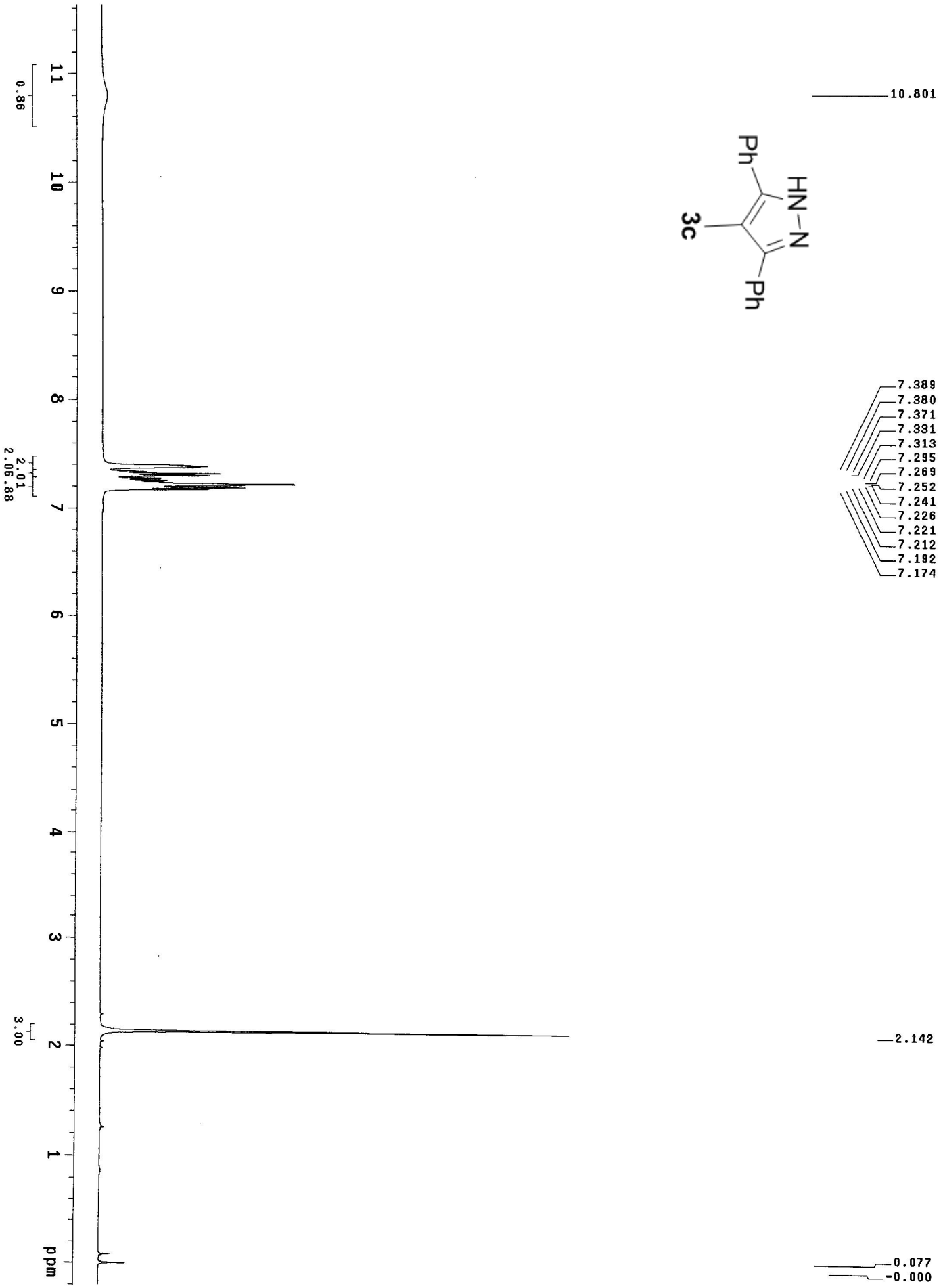
Copies of ^{1}H and ^{13}C Spectra of Products







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7.371
7.331
7.313
7.295
7.269
7.252
7.241
7.226
7.221
7.212
7.192
7.174
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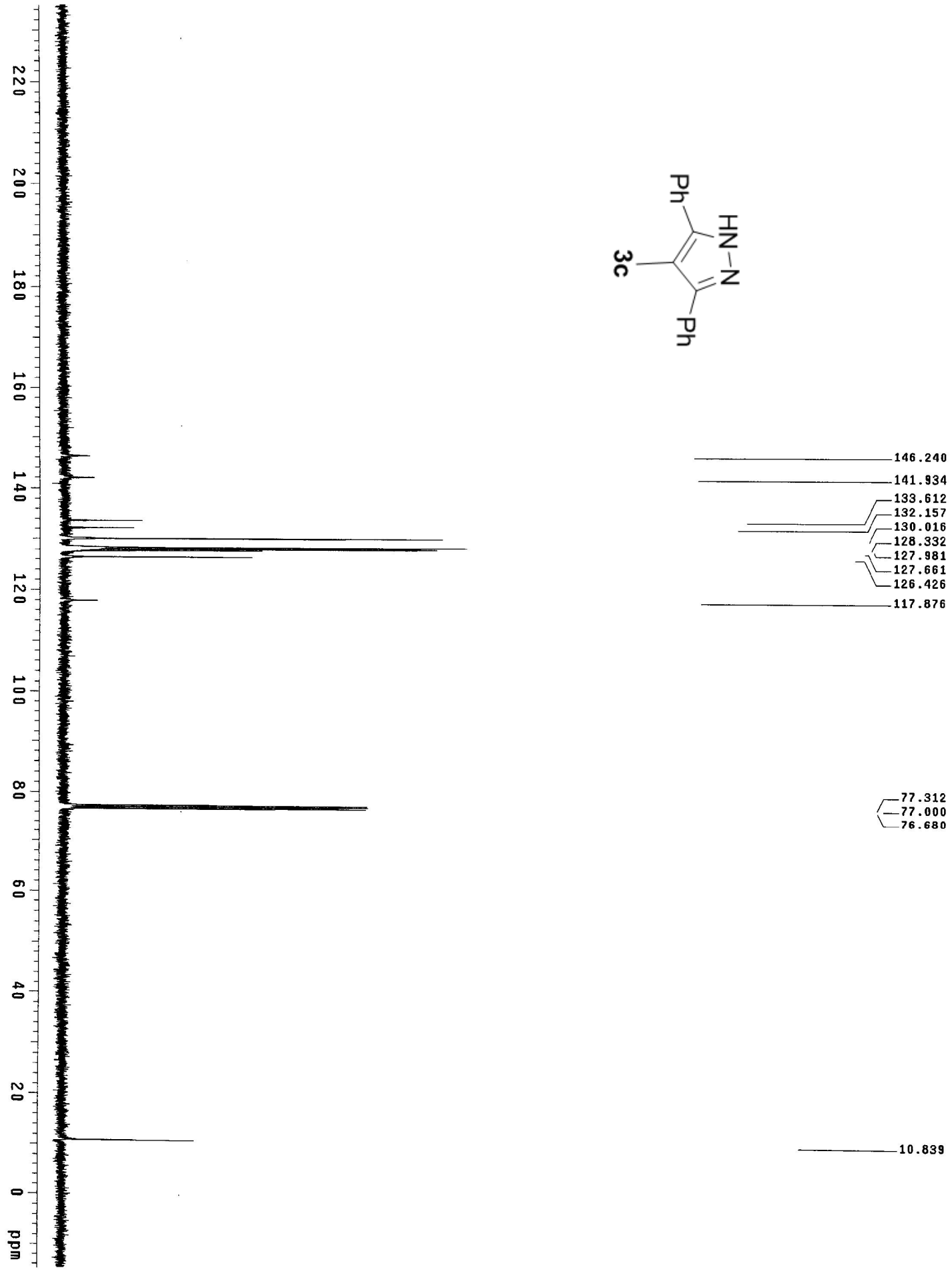
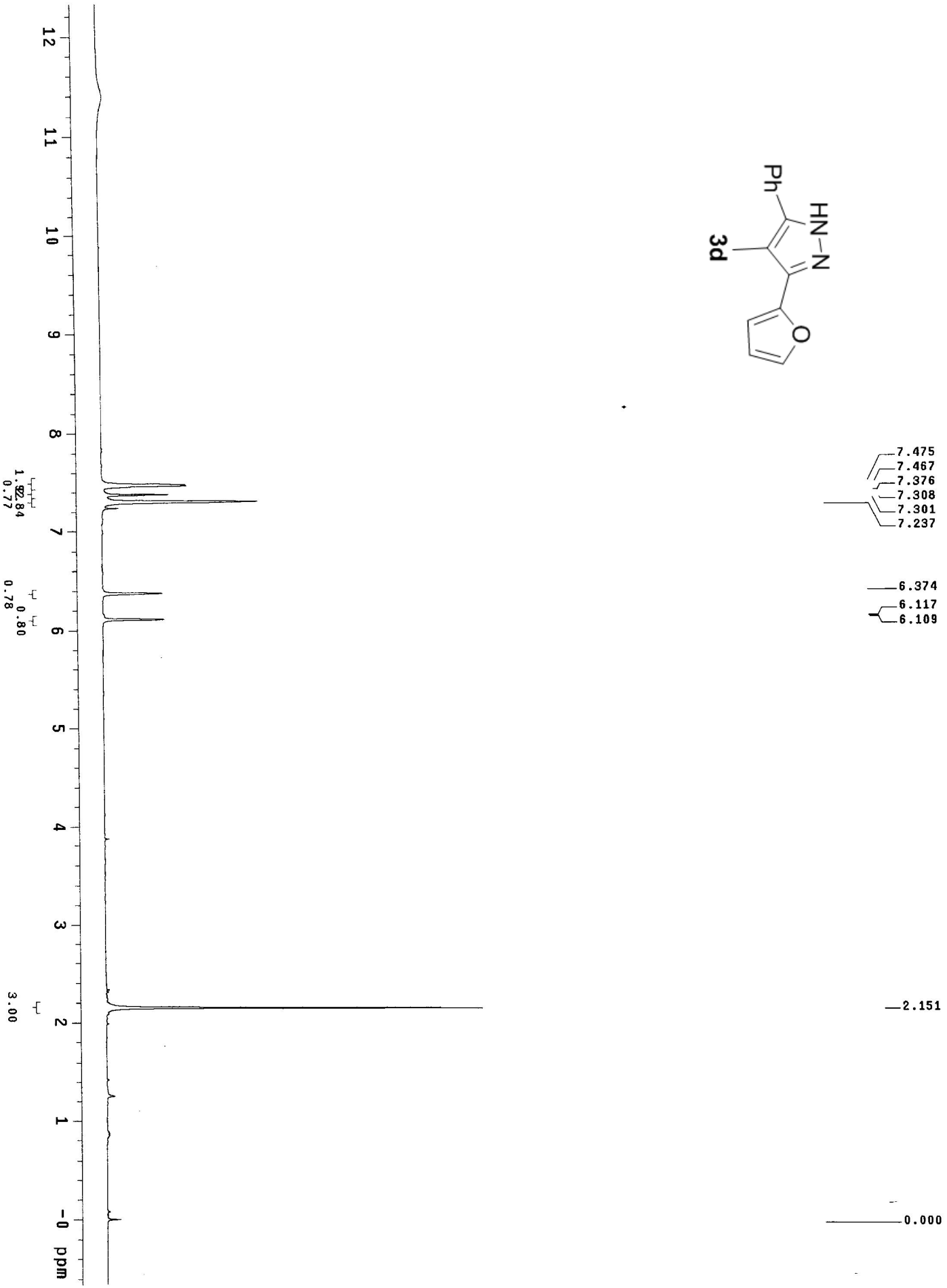
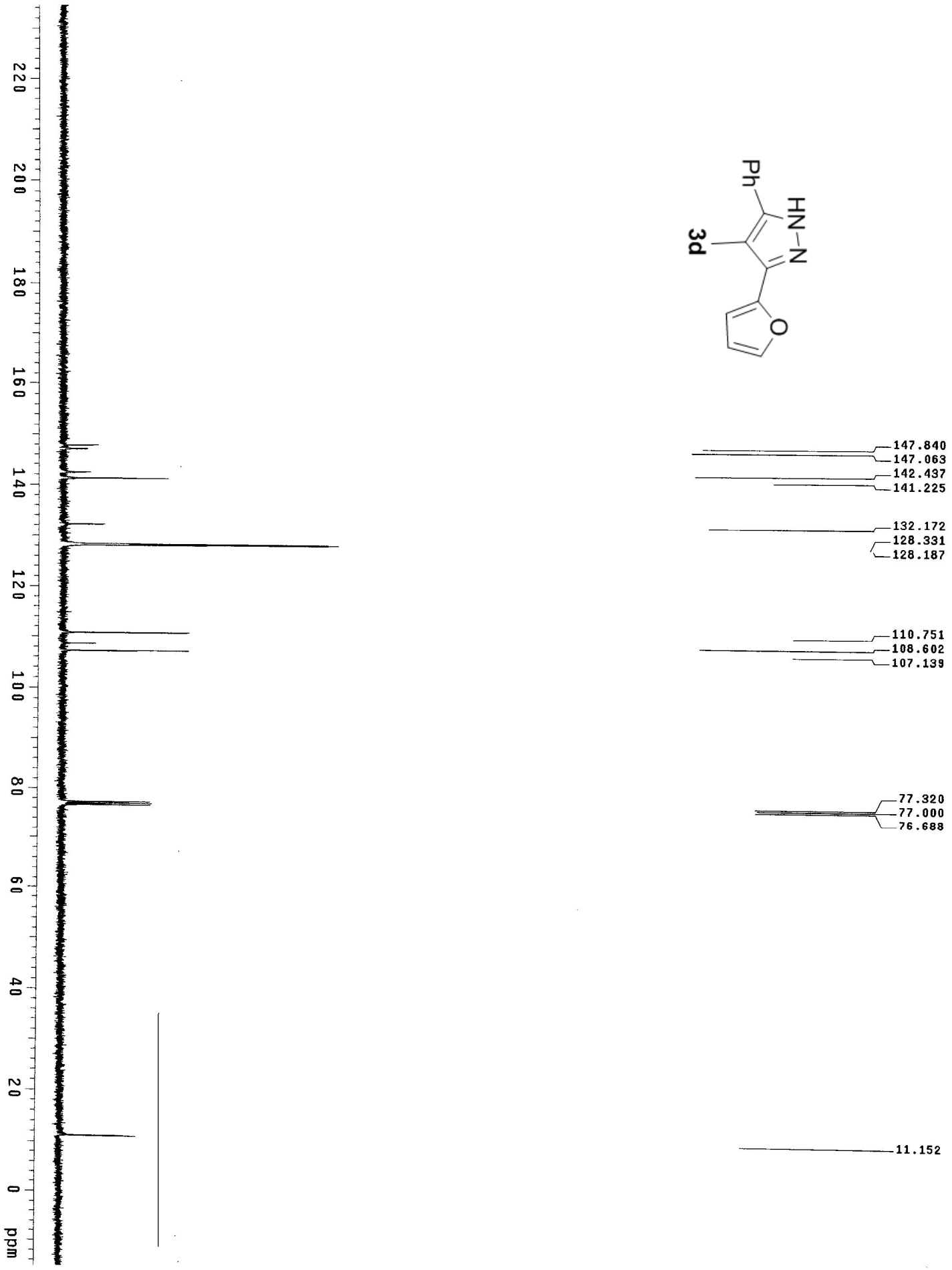
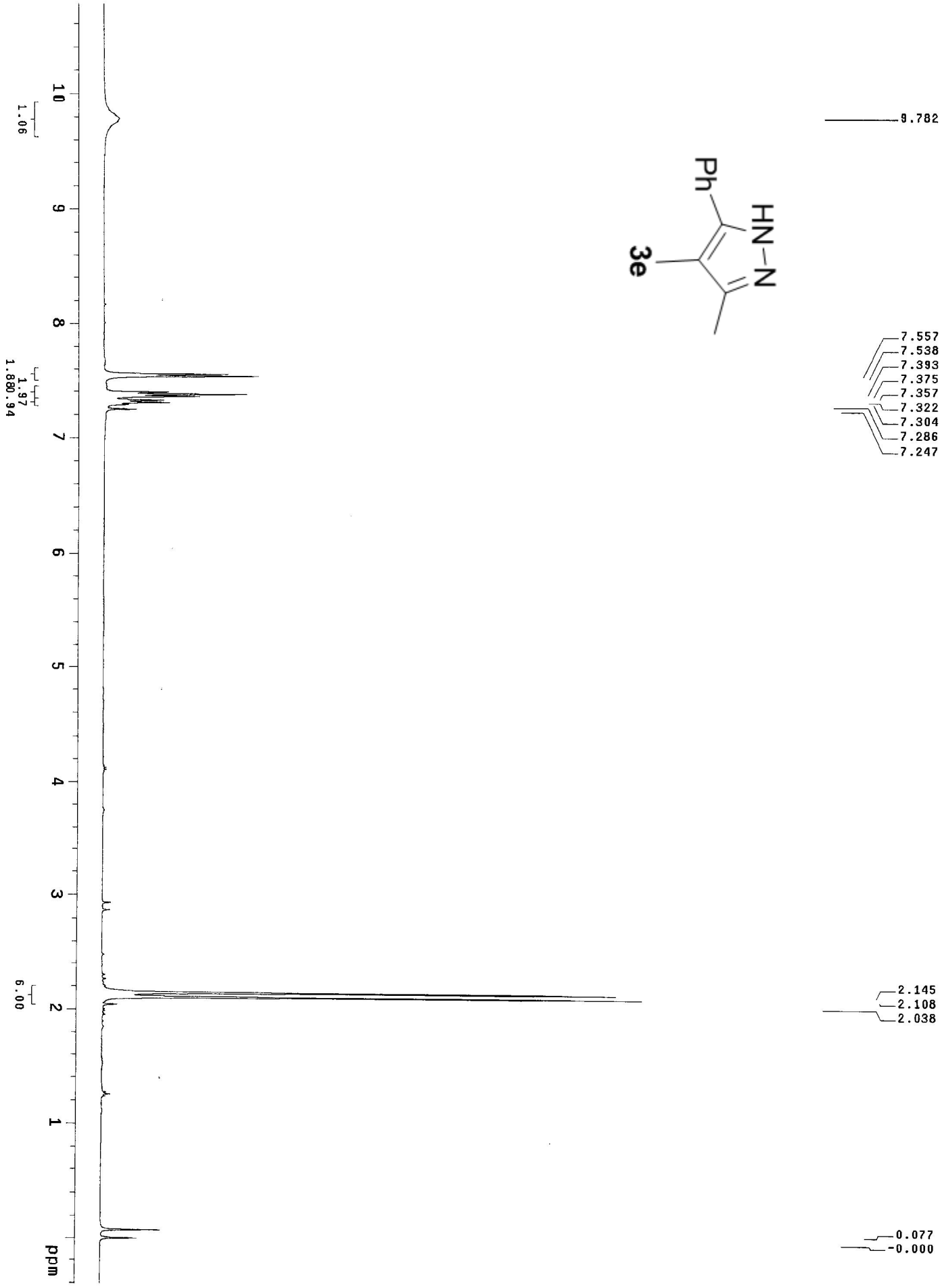
2.01
2.06.88
3.00
ppm
Ph
HN–N
Ph
3c








3e
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7.286
7.247
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2.108
2.038
0.077
-0.000
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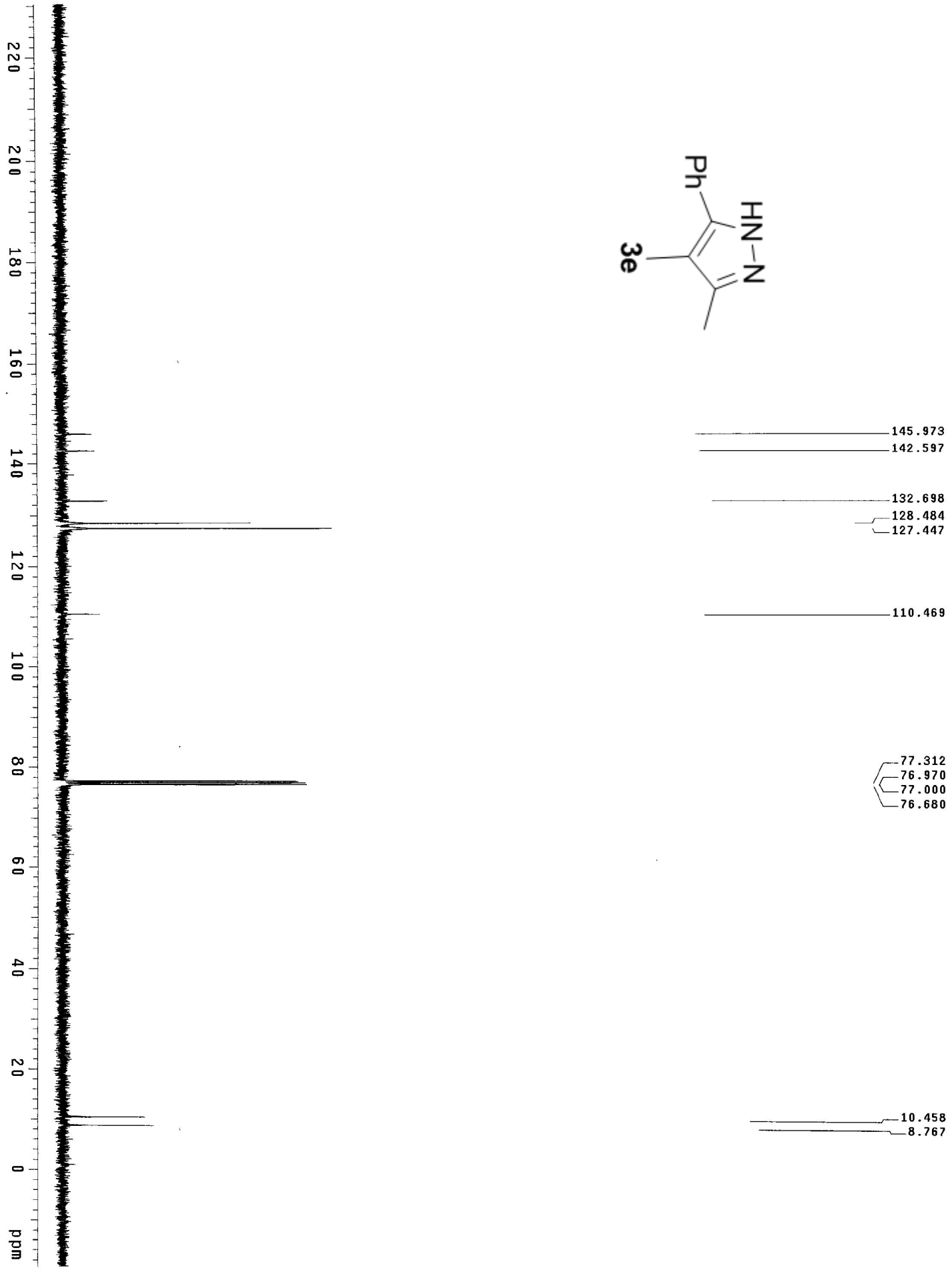
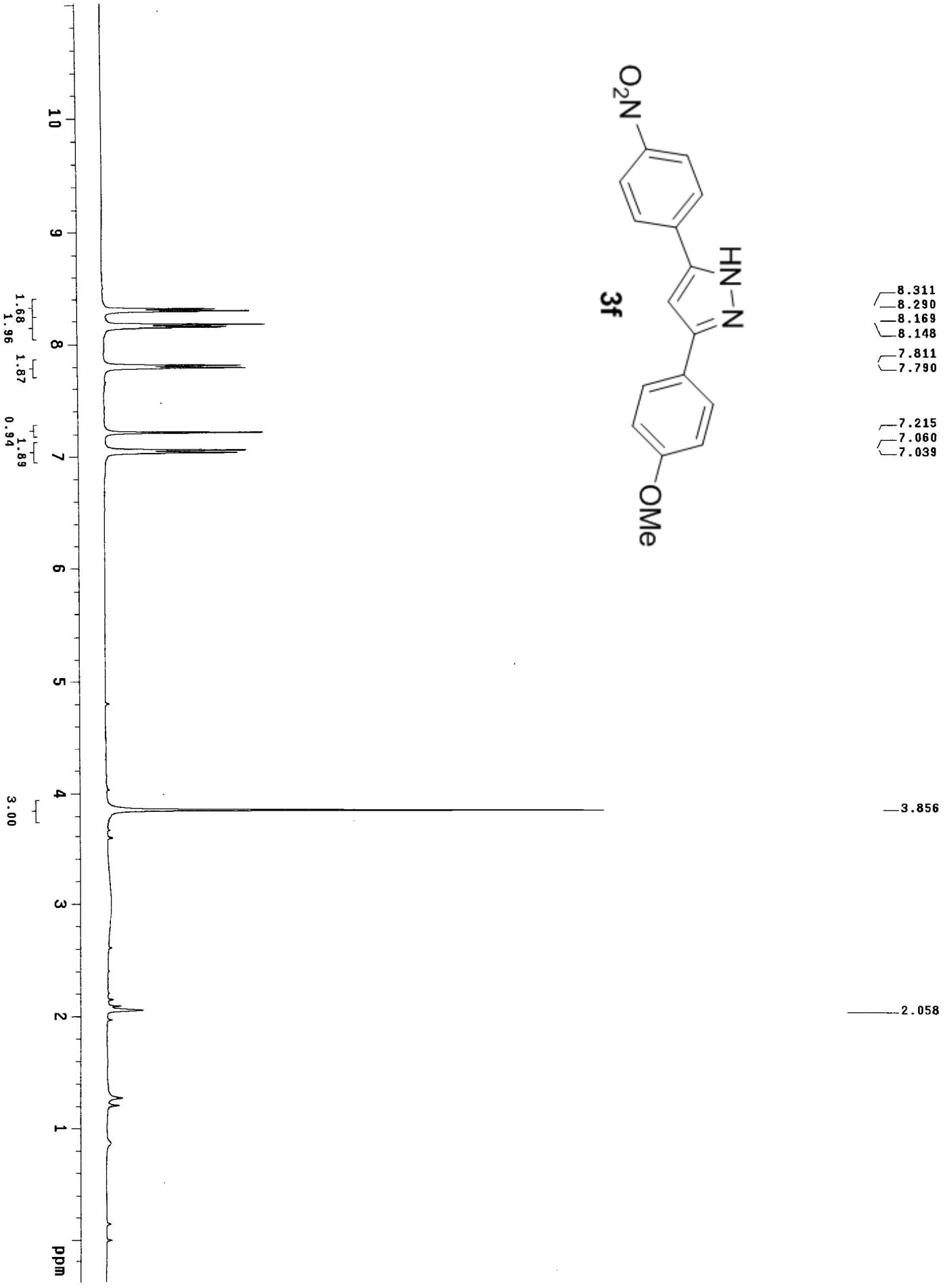
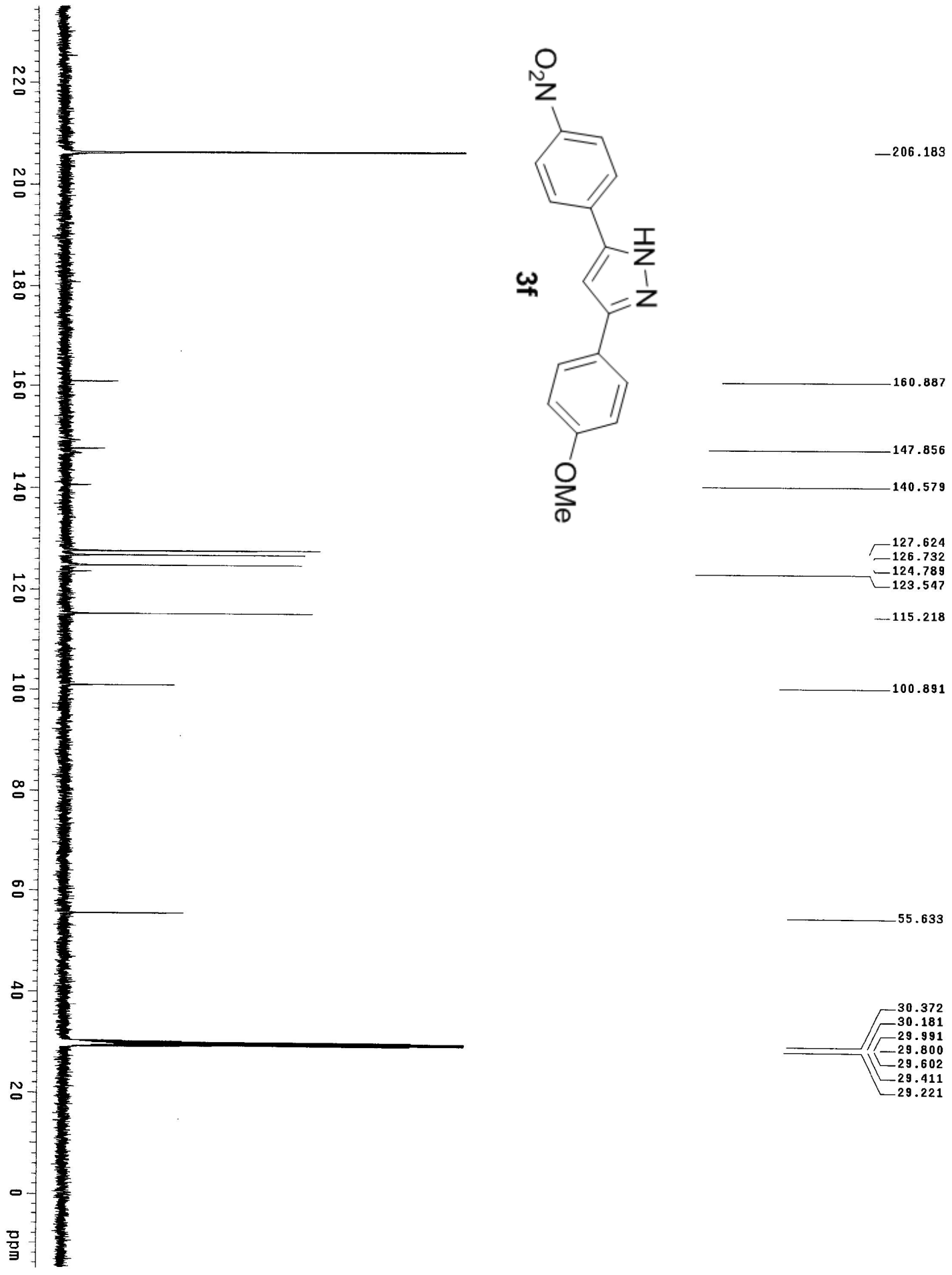
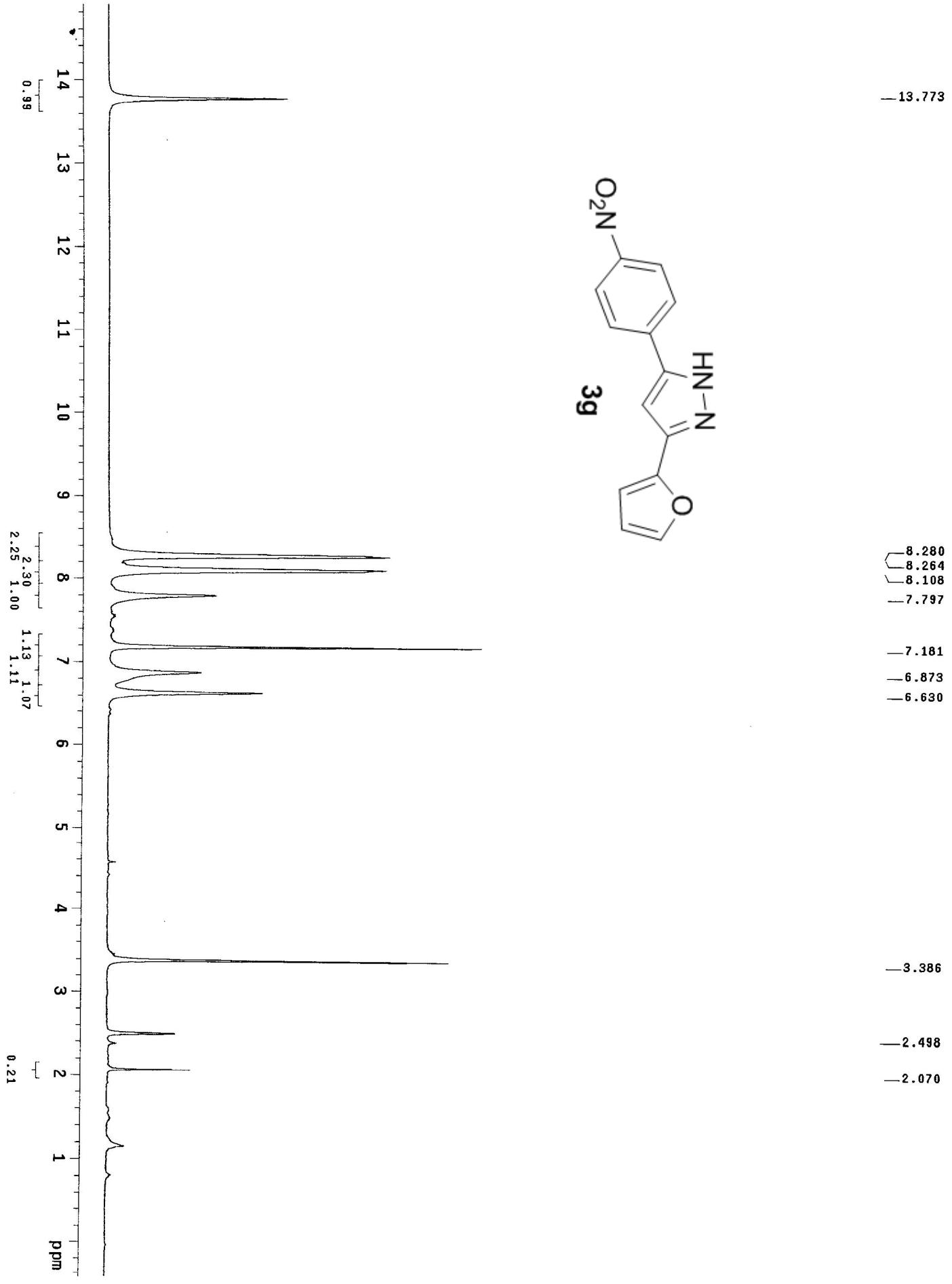
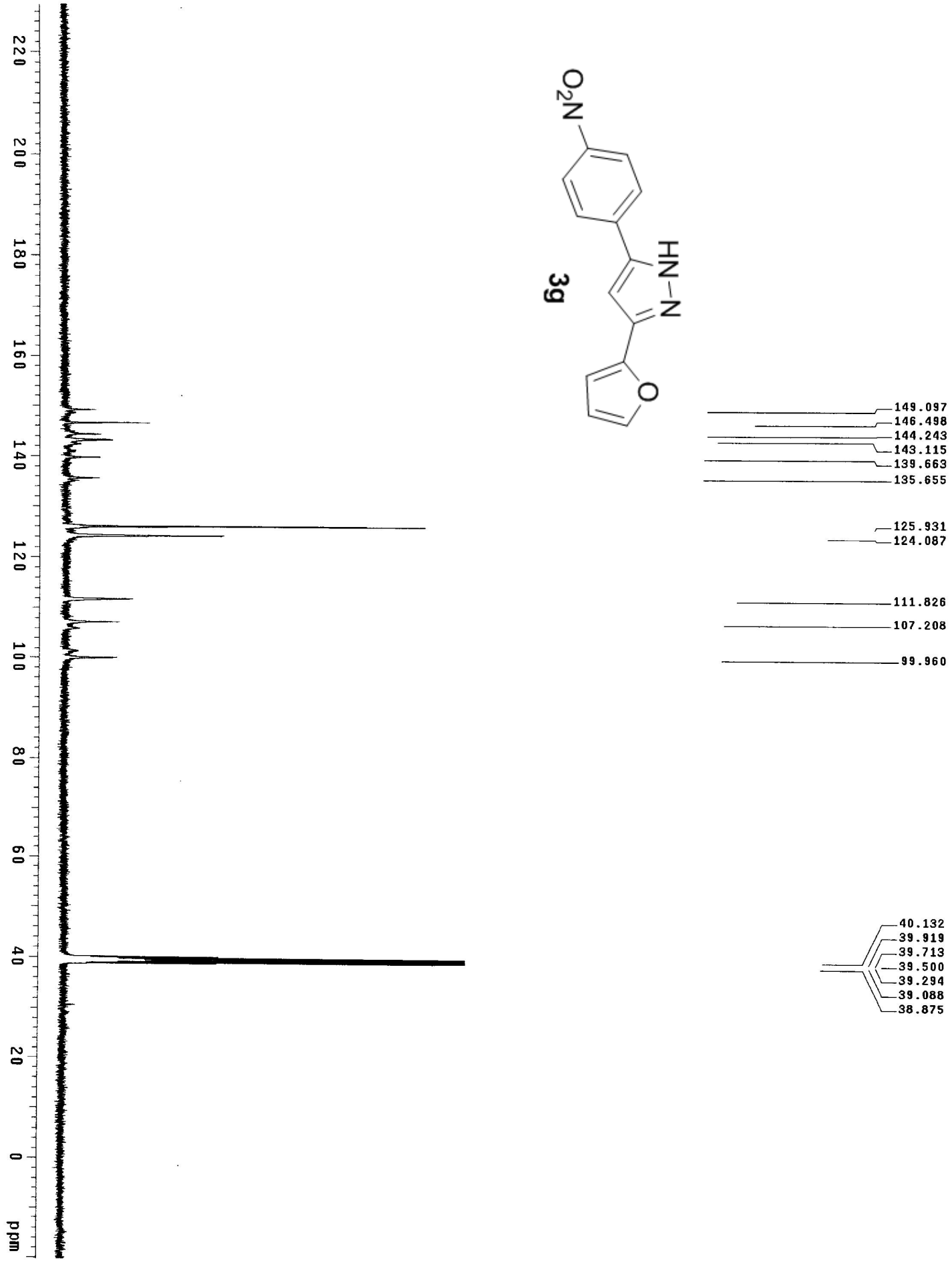
1.97
1.88
0.94
6.00
10
9
8
7
6
5
4
3
2
1
ppm

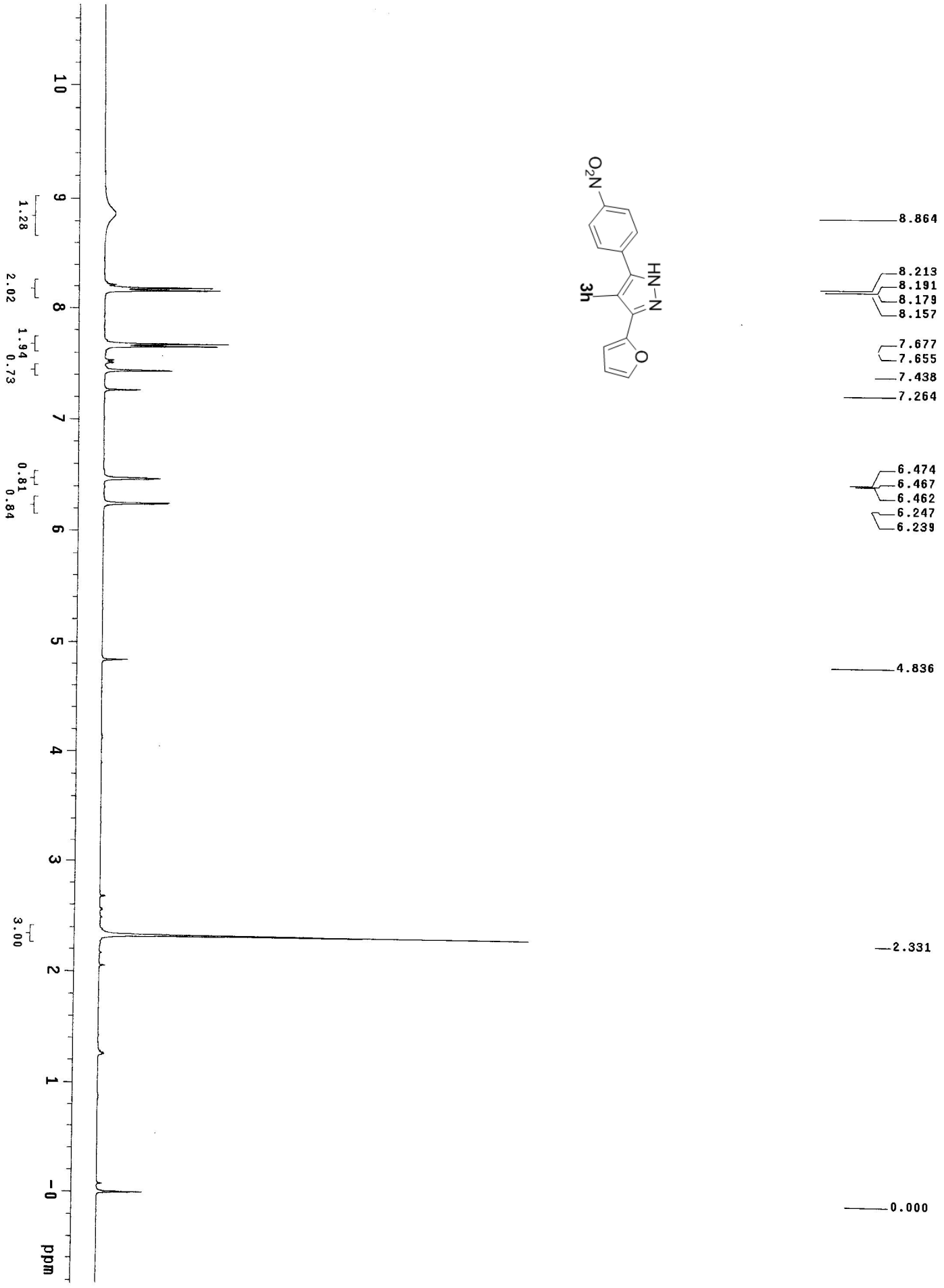


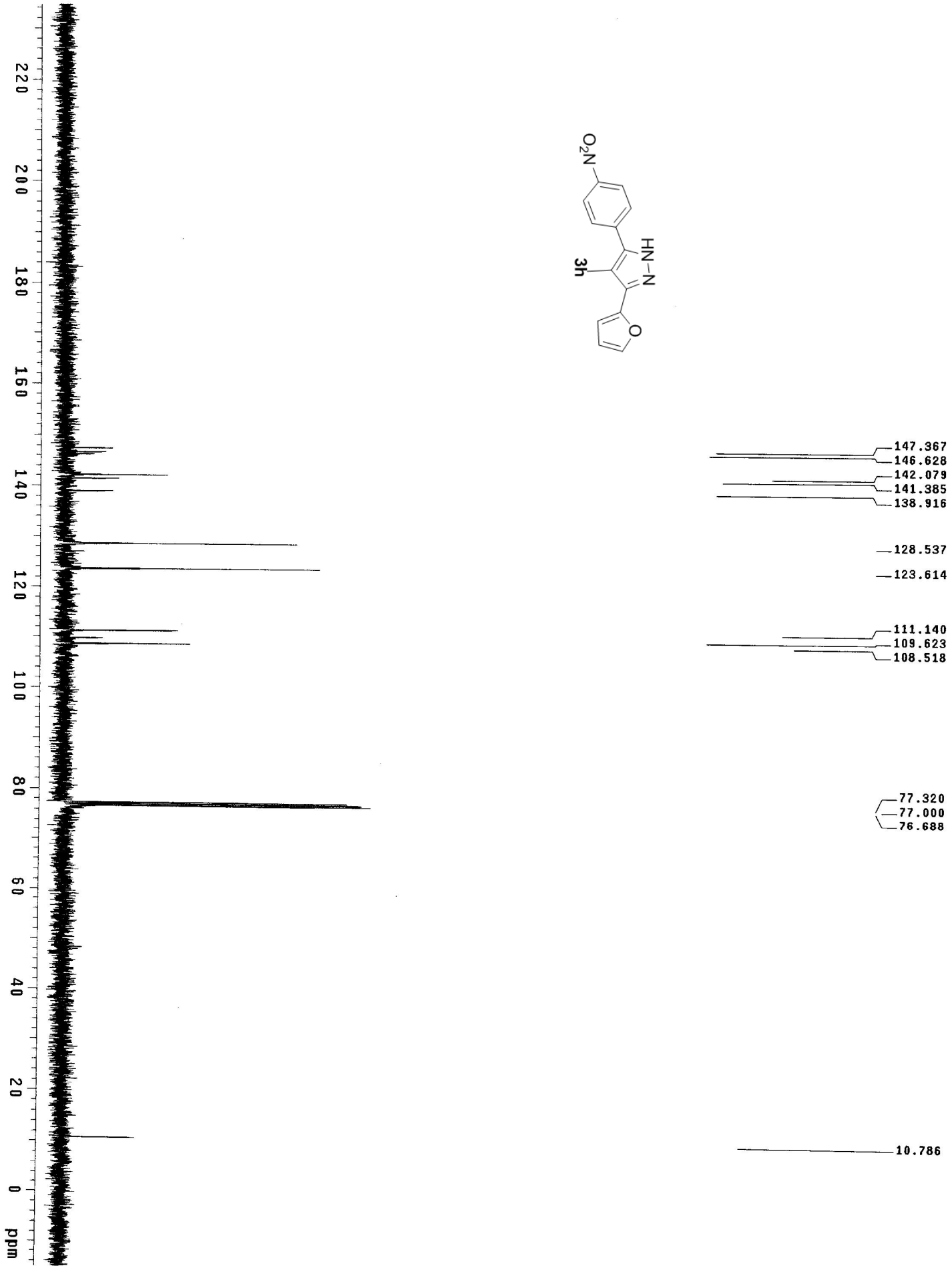


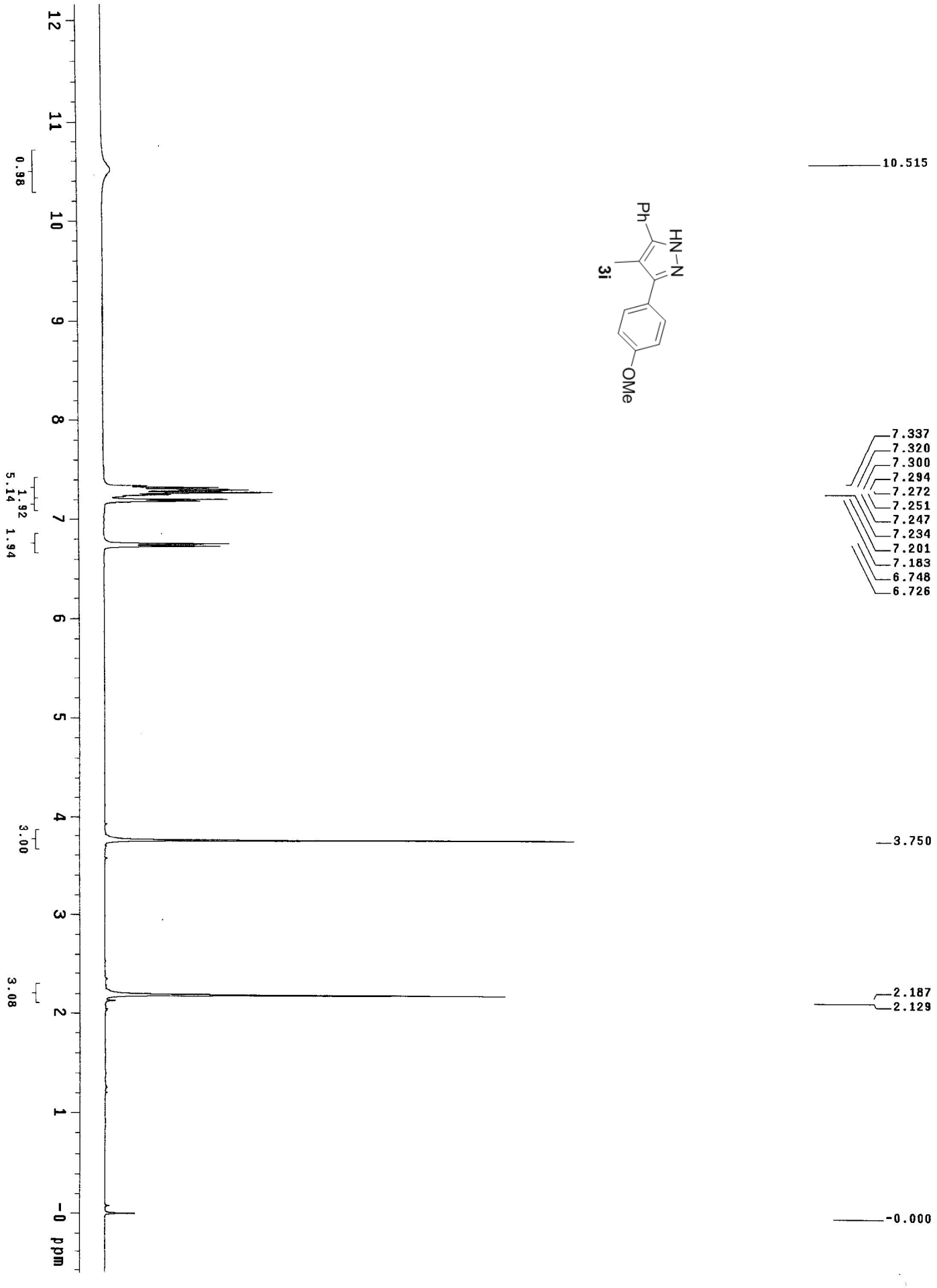


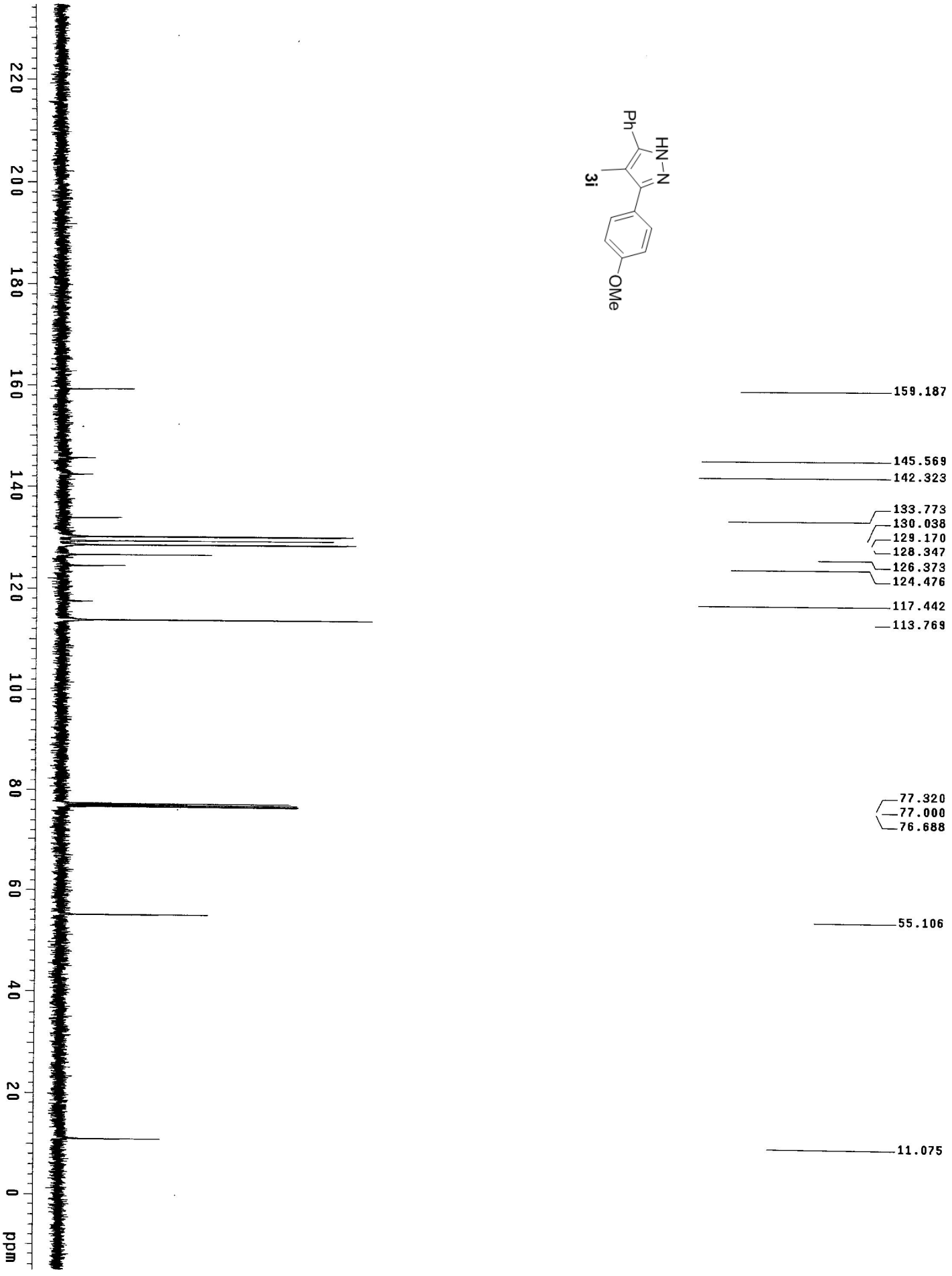


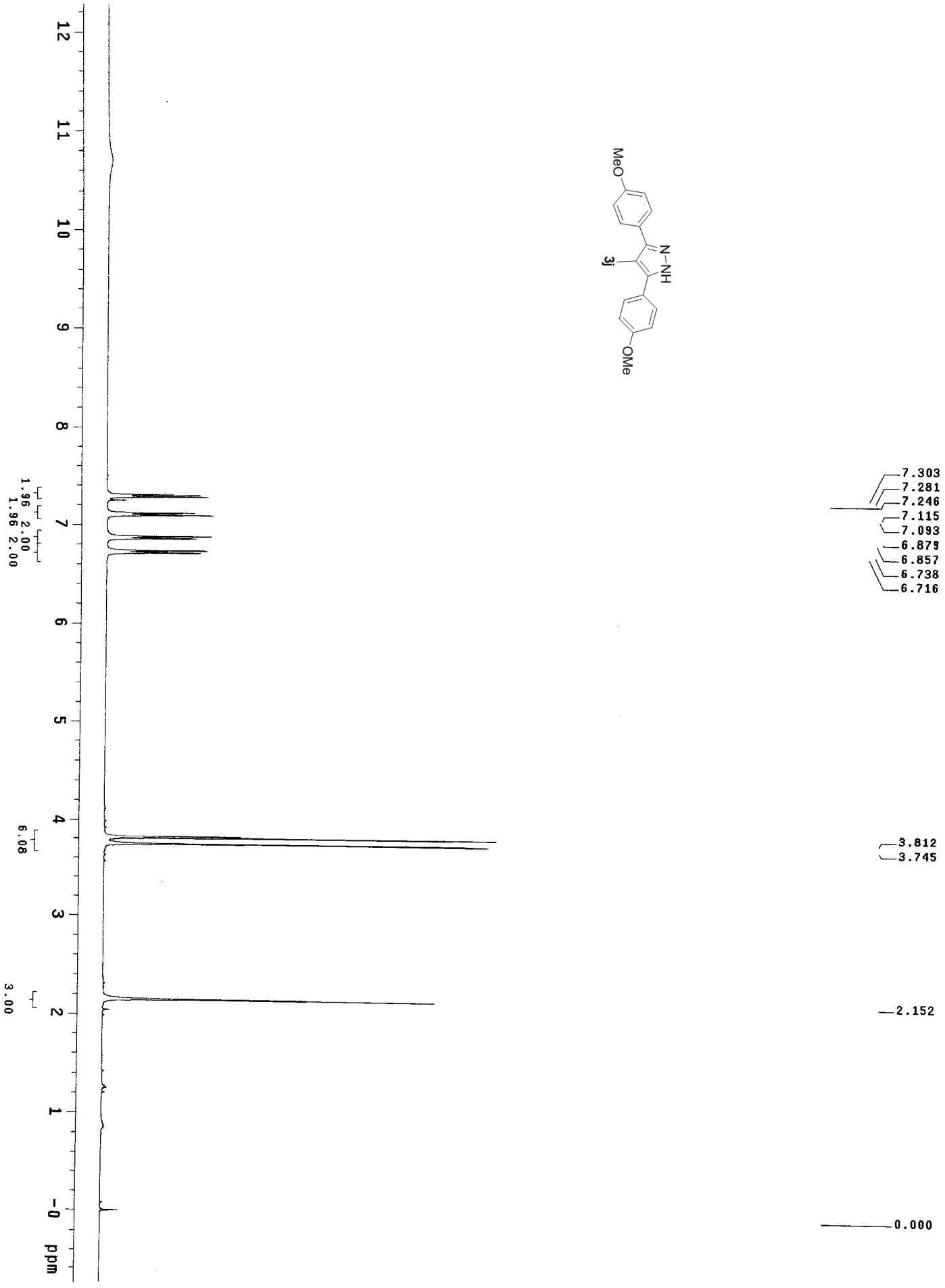


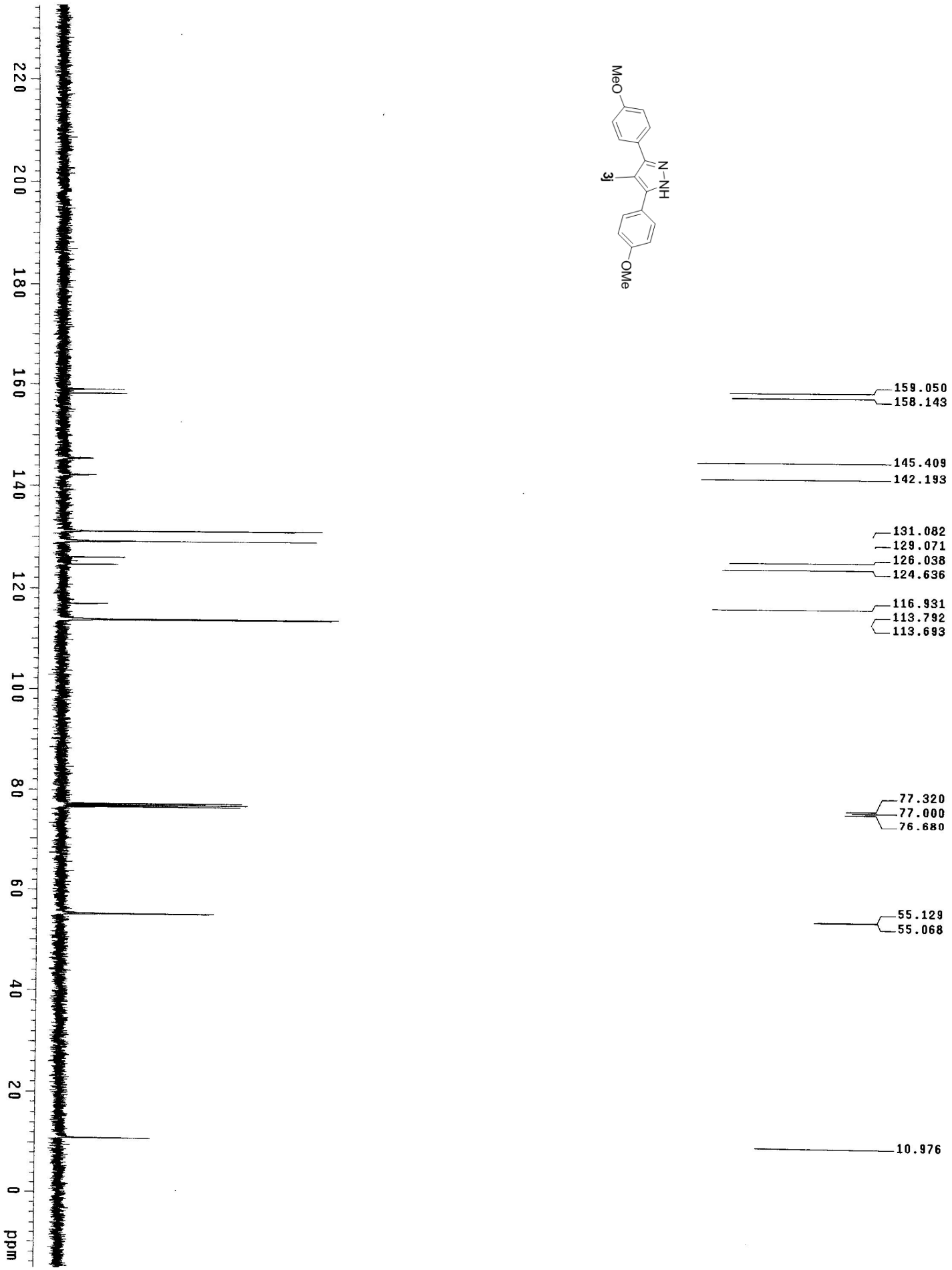


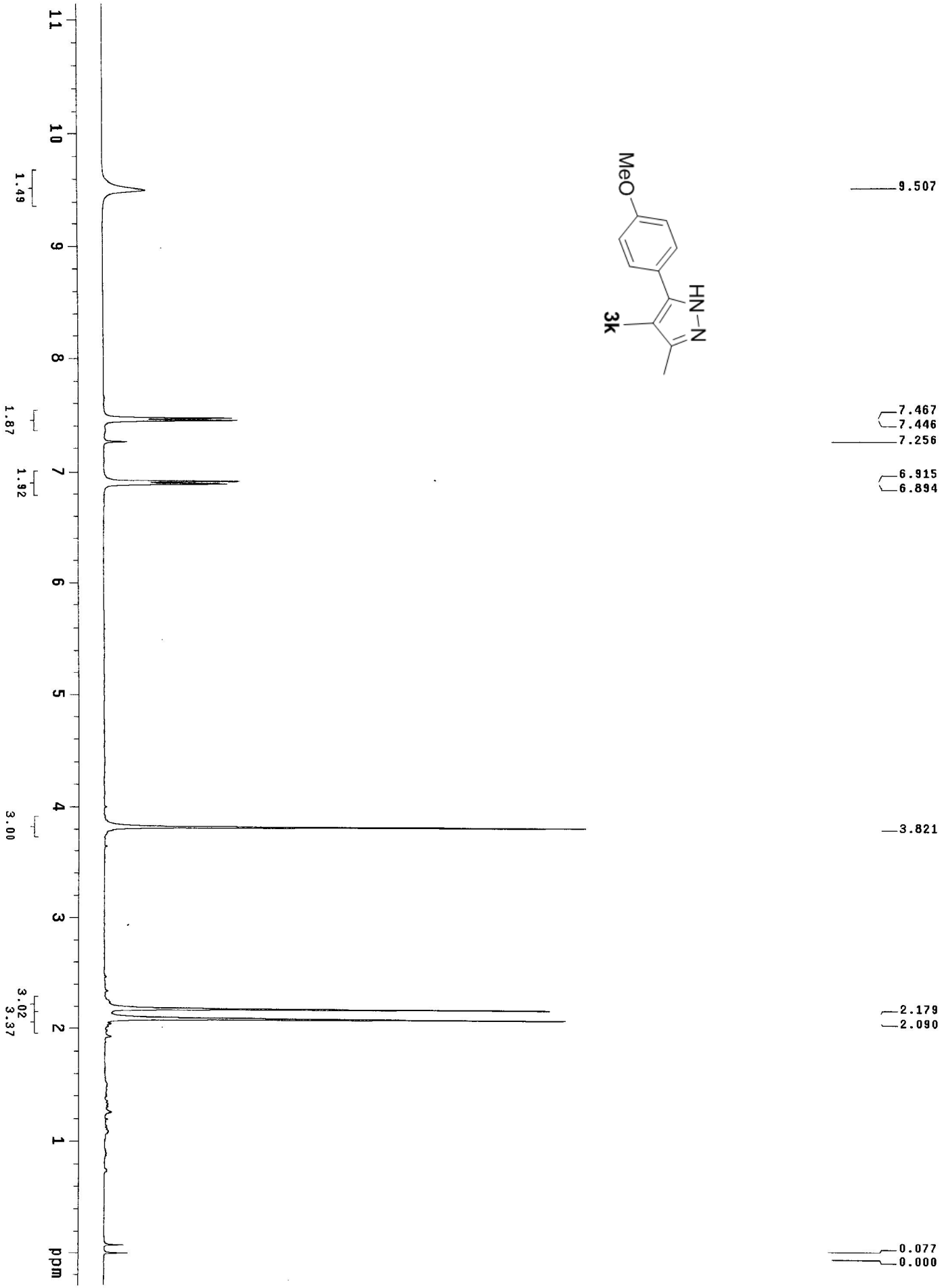


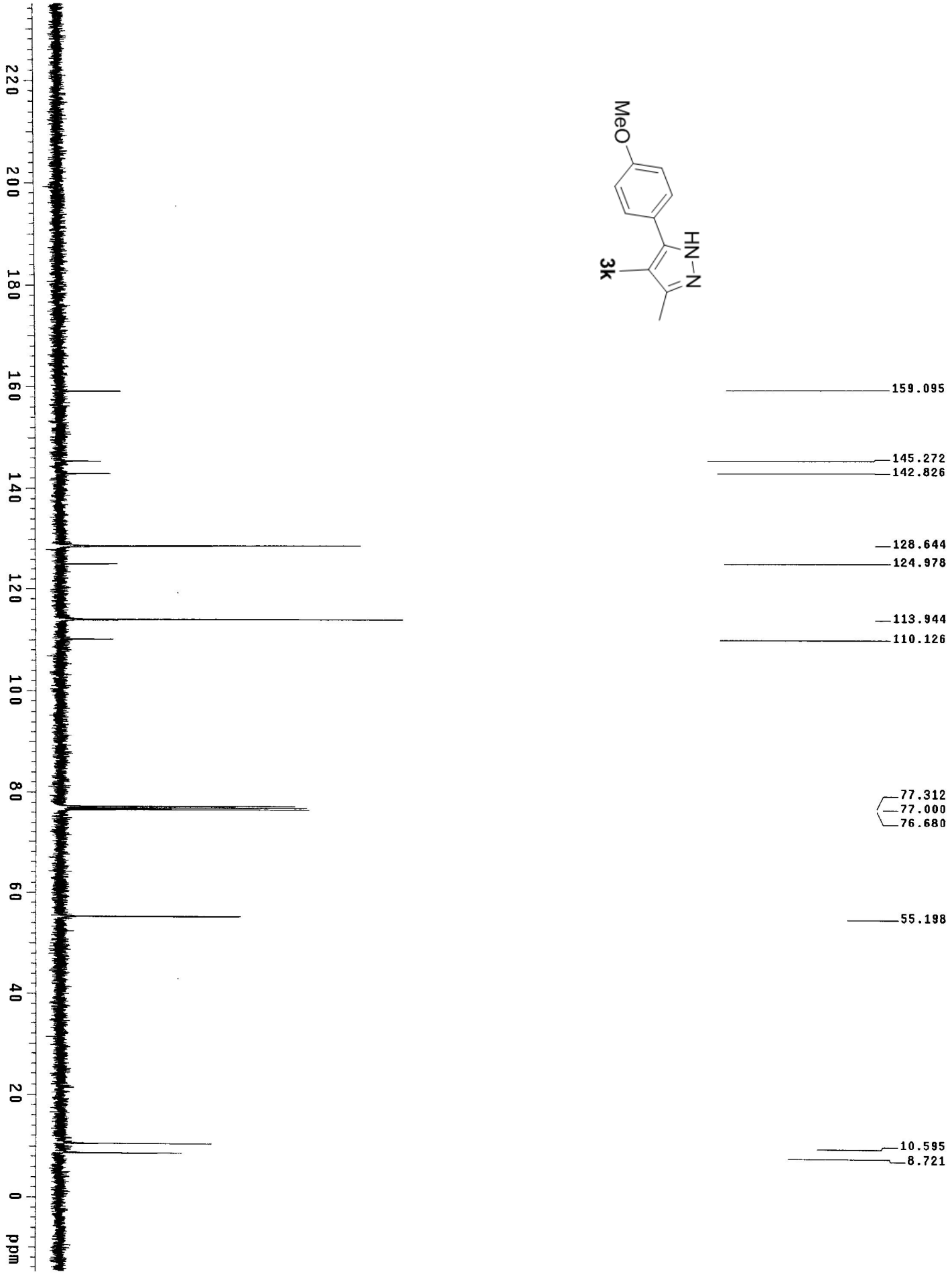


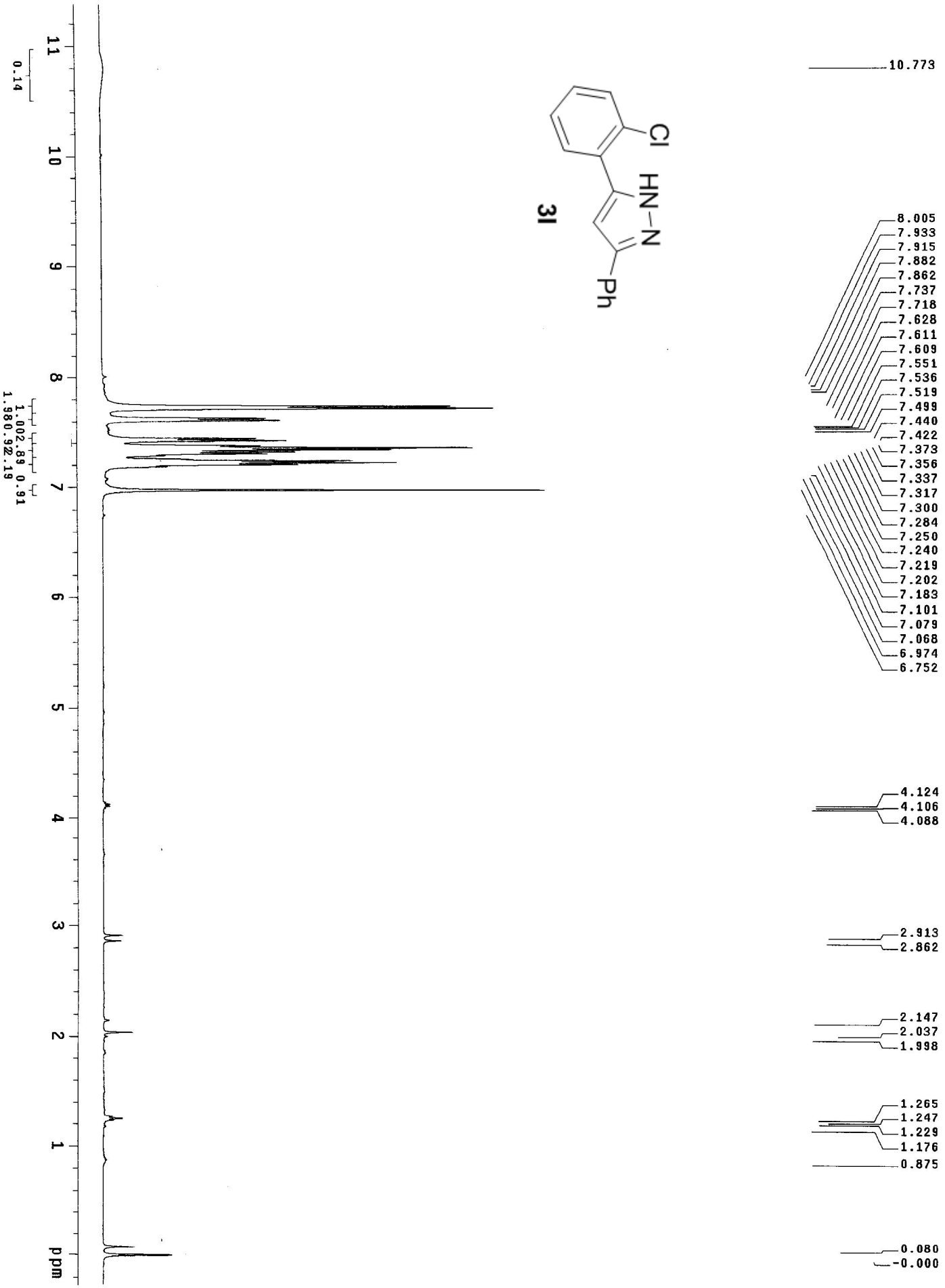


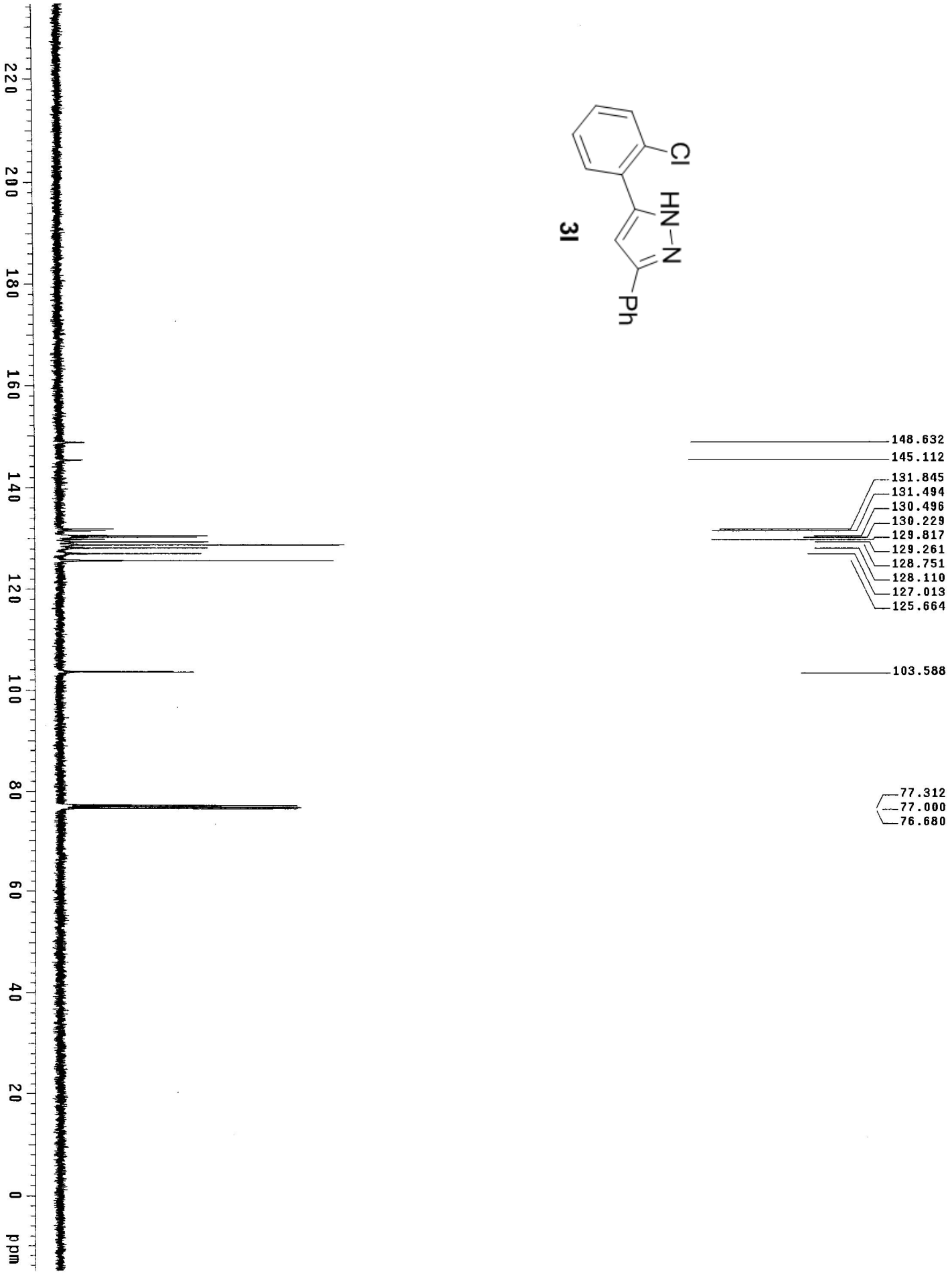


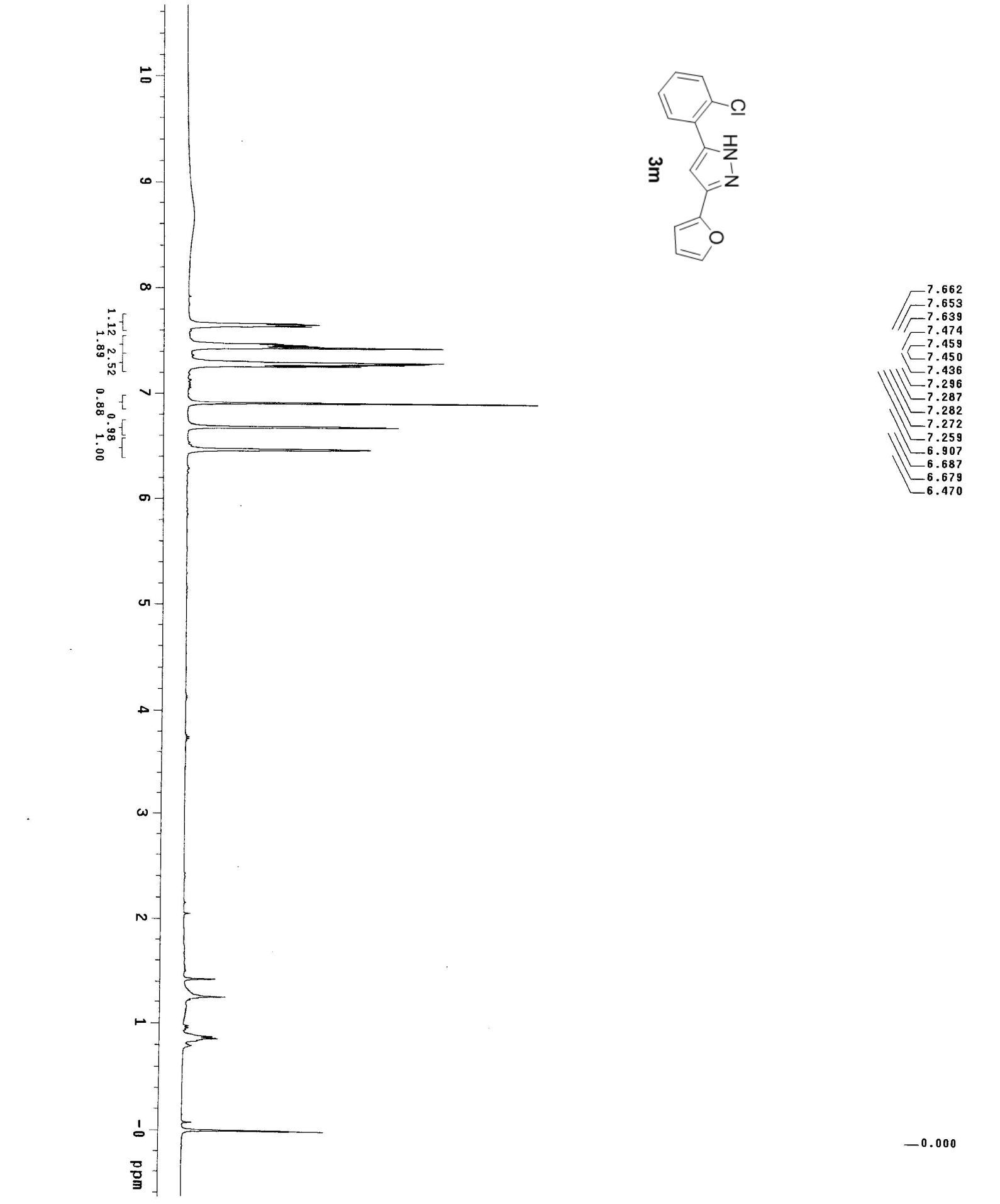


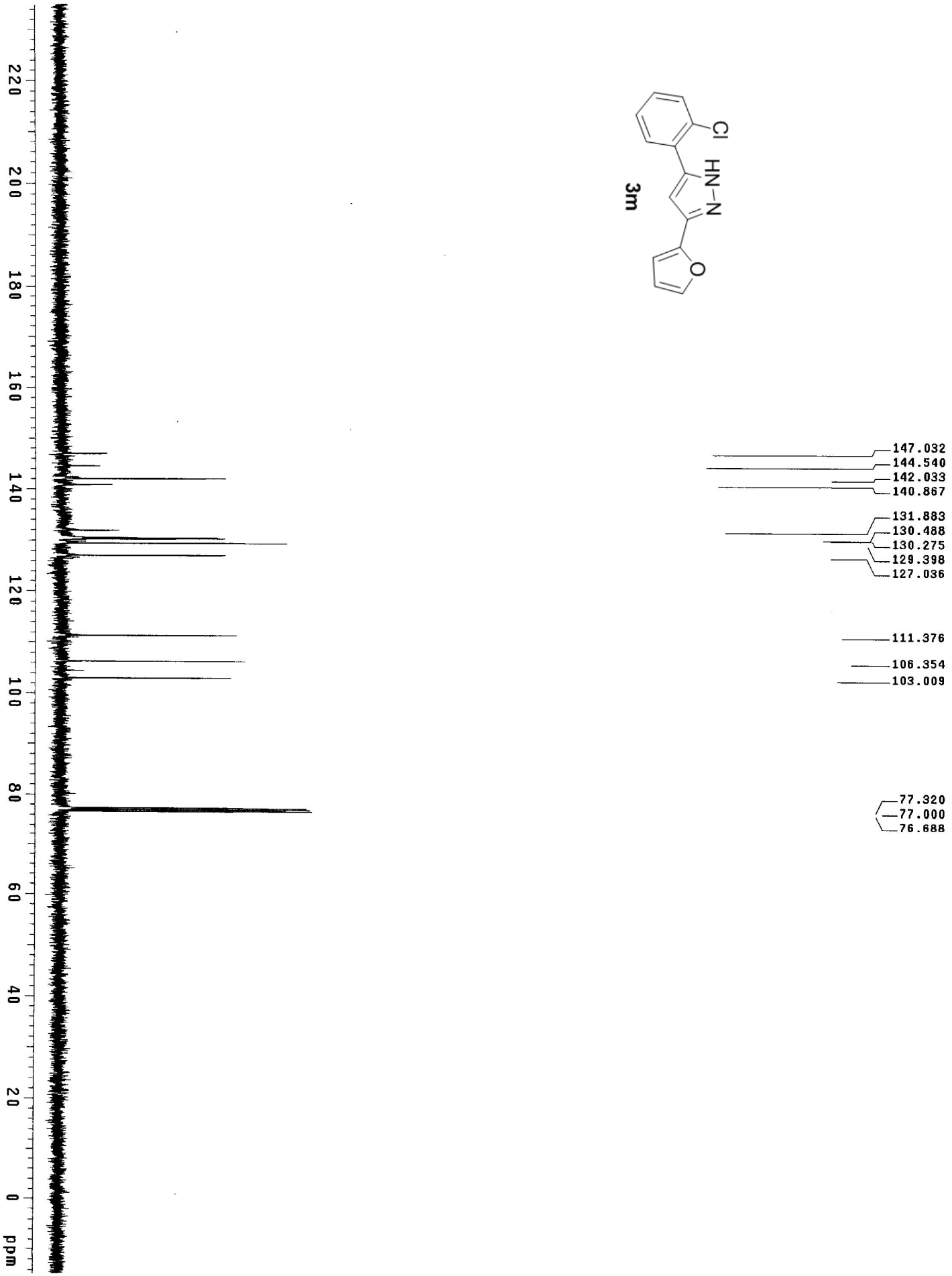


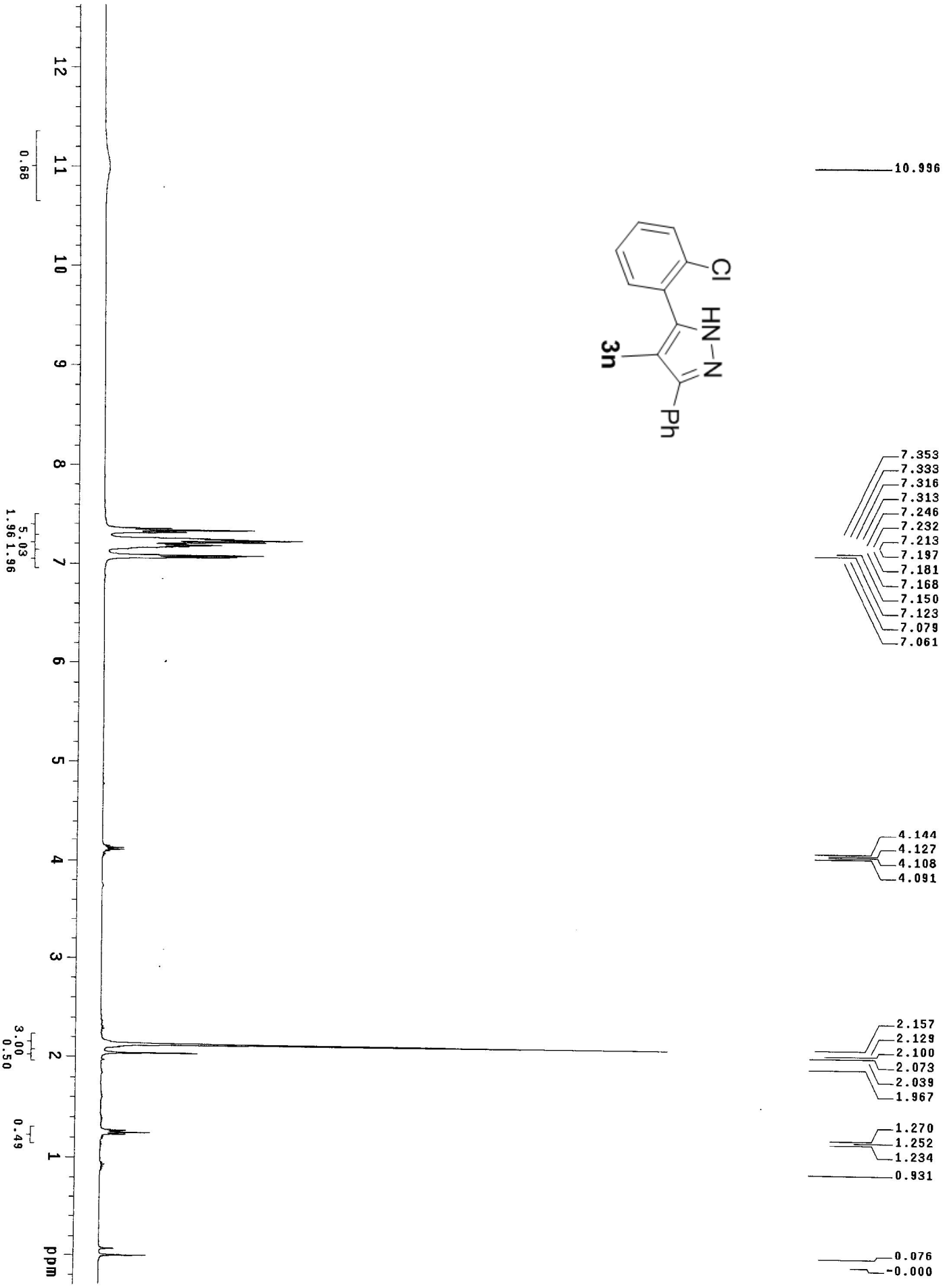








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7.232
7.213
7.197
7.181
7.168
7.150
7.123
7.079
7.061
4.144
4.127
4.108
4.091
2.157
2.129
2.100
2.073
2.039
1.967
1.270
1.252
1.234
0.931
0.076
-0.000
0.68
5.03
1.96 1.96
3.00
0.50
0.49
ppm