

Supporting Information

**Pd/Mannose promoted tandem cross coupling-nitro reduction: Expedient synthesis of aminobiphenyls and aminostilbenes**

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### Characterization data of the synthesized compounds.

**Biphenyl-3-ylamine (3a):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.64-7.59 (m, 2H), 7.50-7.43 (m, 2H), 7.39-7.24 (m, 2H), 7.04 (d,  $J = 7.8$  Hz, 1H), 6.94 (s, 1H), 6.72 (d,  $J = 7.8$  Hz, 1H), 3.73 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.75, 142.48, 141.41, 129.72, 128.68, 127.26, 127.15, 117.72, 114.13, 113.94; MS (ESI)  $m/z$  170  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{12}\text{H}_{12}\text{N}$  170.0964; Found: 170.0970  $[\text{M} + \text{H}]^+$ .

**4-Ethyl-biphenyl-3-ylamine (3b):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.48 (d,  $J = 8.1$  Hz, 2H), 7.26-7.18 (m, 3H), 6.98 (d,  $J = 7.5$  Hz, 1H), 6.89 (s, 1H), 6.66 (d,  $J = 7.8$  Hz, 1H), 3.73 (s, 2H), 2.69 (q,  $J = 7.5$  Hz, 2H), 1.27 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.64, 143.34, 142.42, 138.75, 129.63, 128.16, 127.02, 117.60, 113.59, 113.80, 28.52, 15.89; MS (ESI)  $m/z$  198  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{14}\text{H}_{16}\text{N}^+$  198.1277; Found: 198.1285  $[\text{M} + \text{H}]^+$ .

**3-Naphthalen-1-yl-phenylamine (3c):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.06-7.92 (m, 4H), 7.93 (d,  $J = 7.8$  Hz, 1H), 7.54 (s, 2H), 7.31 (t,  $J = 7.8$  Hz, 1H), 7.17 (d,  $J = 6.6$  Hz, 1H), 7.08 (s, 1H), 6.75 (d,  $J = 7.2$  Hz, 1H), 3.82 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.86, 142.36, 138.77, 133.67, 132.68, 129.81, 128.29, 128.22, 127.66, 126.25, 125.87, 125.73, 125.68, 117.98, 114.25, 114.16; MS (ESI)  $m/z$  219  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{16}\text{H}_{13}\text{N}^+$  220.1121; Found: 220.1132  $[\text{M} + \text{H}]^+$ .

**4'-Methoxy-biphenyl-3-ylamine (3d):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.28-7.22 (m, 2H), 7.18-7.13 (m, 1H), 6.86-6.76 (m, 4H), 6.69 (d,  $J = 8.1$  Hz, 1H), 3.81 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.77, 143.49, 140.62, 130.22, 129.76, 128.36, 127.83, 119.32, 118.52, 115.71, 115.52, 113.93; MS (ESI)  $m/z$  184  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{12}\text{H}_{12}\text{N}_2^+$  185.1073; Found: 185.1075  $[\text{M} + \text{H}]^+$ .

**[1,1'-Biphenyl]-2-amine (3e):**  $^1\text{H}$  NMR (300 MHz, DMSO):  $\delta$  7.51-7.42 (m, 4H), 7.41-7.37 (m, 1H), 7.24-7.17 (m, 2H), 6.91-6.81 (m, 2H), 3.70 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.36, 139.53, 130.49, 129.13, 128.84, 128.53, 127.78, 127.21, 118.80, 115.73; MS (ESI)  $m/z$  170  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{12}\text{H}_{11}\text{N}$  170.0964; Found: 170.0970  $[\text{M} + \text{H}]^+$ .

**4'-Ethyl-biphenyl-4-ylamine (3f):**  $^1\text{H}$  NMR (300MHz,  $\text{CDCl}_3$ ):  $\delta$  7.51 (d,  $J = 7.8$  Hz, 2H), 7.45 (d,  $J = 8.1$ Hz, 2H), 7.28 (d,  $J = 7.8$  Hz, 2H), 6.79 (d,  $J = 8.4$  Hz, 2H), 3.74 (s, 2H), 2.72 (q,  $J = 7.5$  Hz, 2H), 1.32 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  145.60, 142.34, 138.60, 131.65, 128.22, 127.88, 126.37, 115.43, 28.50, 15.68; MS (ESI)  $m/z$  198 $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{14}\text{H}_{16}\text{N}^+$  198.1277; Found: 198.1285  $[\text{M} + \text{H}]^+$ .

**2-Methoxy-biphenyl-3-ylamine (3g):**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.36-7.30 (m, 1H), 7.28-7.25 (m, 1H), 7.12 (t,  $J = 7.5$  Hz, 1H), 7.10-6.99 (m, 2H), 6.75 (d,  $J = 7.2$  Hz, 2H), 6.63-6.60 (m, 1H), 4.15 (s, 2H), 3.79 (s, 3H),  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.47, 145.99, 139.64, 130.90, 128.88, 128.48, 120.72, 120.14, 116.50, 113.93, 111.21, 55.59, MS (ESI)  $m/z$  199  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{13}\text{H}_{14}\text{NO}$  200.1069; Found: 200.1072  $[\text{M} + \text{H}]^+$ .

**2,5-Dimethoxy-biphenyl-3-ylamine (3h):**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.01 (t,  $J = 7.2$  Hz, 1H), 6.88 (d,  $J = 9$  Hz, 1H), 6.87 (d,  $J = 3$  Hz, 1H), 6.75 (s, 1H), 6.67-6.64 (m, 2H), 6.53-6.49 (m, 1H), 4.04 (s, 2H), 3.66 (s, 3H), 3.61 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.68, 150.80, 146.06, 139.50, 131.92, 128.94, 119.99, 116.56, 116.37, 114.07, 113.11, 112.77, 56.42, 55.80; MS (ESI)  $m/z$  230  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{14}\text{H}_{15}\text{NO}_2$  230.1175; Found: 230.1183  $[\text{M} + \text{H}]^+$ .

**4-Naphthyl amine (3i):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.06 (s, 1H), 7.94-7.89 (m, 3H), 7.76 (d,  $J = 8.7$  Hz, 1H), 7.54-7.52 (m, 2H), 7.32 (t,  $J = 7.5$  Hz, 1H), 7.17 (d,  $J = 7.8$  Hz, 1H), 7.07 (s, 1H), 6.75 (d,  $J = 7.2$  Hz, 1H), 3.81 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.85, 142.35, 133.65, 132.67, 129.82, 128.22, 127.66, 126.25, 125.87, 125.73, 125.68, 117.98, 114.25; MS (ESI)  $m/z$  219  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{16}\text{H}_{13}\text{N}^+$  220.1121; Found: 220.1132  $[\text{M} + \text{H}]^+$ .

**2,5-Dimethoxy-biphenyl-4-ylamine (3j):**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.16 (d,  $J = 8.1$  Hz, 2H), 6.85 (d,  $J = 8.4$  Hz, 1H), 6.75-6.69 (m, 2H), 6.57 (d,  $J = 8.1$  Hz, 2H), 4.11 (s, 2H), 3.66 (s, 3H), 3.62 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.73, 149.79, 144.52, 130.75, 129.34, 127.53, 115.35, 113.73, 111.63, 111.18, 55.31, 54.74; MS (ESI)  $m/z$  230  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{14}\text{H}_{15}\text{NO}_2$  230.1175; Found: 230.1181  $[\text{M} + \text{H}]^+$ .

**4'-Ethoxy-[1,1'-biphenyl]-3-amine (3k):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.51 (d,  $J = 8.1$  Hz, 2H), 7.29-7.26 (m, 2H), 7.22 (d,  $J = 7.8$  Hz, 1H), 7.01 (d,  $J = 7.8$  Hz, 1H), 6.92 (s, 1H), 6.69 (d,  $J = 7.8$  Hz, 1H), 3.76 (s, 2H), 2.71 (q,  $J = 7.5$  Hz, 2H), 1.30 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.66, 143.35, 142.42, 138.75, 129.63, 128.17, 127.02, 117.60, 113.86, 113.80, 28.52, 15.59. MS (ESI)  $m/z$  213  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{14}\text{H}_{16}\text{NO}^+$  214.1226; Found: 214.1225  $[\text{M} + \text{H}]^+$ .

**2'-Methyl-biphenyl-3-ylamine (3l):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.29-7.27 (m, 2H), 7.25-7.22 (m, 3H), 6.78 (d,  $J = 7.2$  Hz, 1H), 6.70 (d,  $J = 11.2$  Hz, 2H), 3.72 (s, 2H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.13, 143.17, 142.17, 135.37, 130.24, 129.62, 128.98, 127.16, 125.66, 119.75, 116.05, 113.61, 20.49; MS (ESI)  $m/z$  184  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{13}\text{H}_{14}\text{N}^+$  184.1120; Found: 184.1127  $[\text{M} + \text{H}]^+$ .

**Biphenyl-4,3-diamine (3m):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.41-7.21 (m, 3H), 6.97-6.64 (m, 5H), 3.61 (s, 4H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.64, 145.81, 142.38, 131.73, 129.59, 127.96, 127.31, 117.05, 115.31, 113.26; MS (ESI)  $m/z$  185  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{12}\text{H}_{13}\text{N}_2^+$  185.1073; Found: 185.1076  $[\text{M} + \text{H}]^+$ .

**[1,1'-Biphenyl]-3,3'-diamine (3n):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.20 (t,  $J = 7.8\text{ Hz}$ , 2H), 6.96 (d,  $J = 7.2\text{ Hz}$ , 2H), 6.88 (s, 2H), 6.68-6.65 (m, 2H), 3.71 (s, 4H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.60, 142.63, 129.56, 117.69, 114.10, 113.93; MS (ESI)  $m/z$  184  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{12}\text{H}_{12}\text{N}_2^+$  185.1073; Found: 185.1076  $[\text{M} + \text{H}]^+$ .

**4'-Fluoro-biphenyl-2-ylamine (3o):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.32-7.27 (m, 2H), 7.06-6.96 (m, 4H), 6.71 (t,  $J = 7.5\text{ Hz}$ , 1H), 6.64 (d,  $J = 8.1\text{ Hz}$ , 1H), 3.62 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  163.70, 160.44, 143.55, 135.45 (d,  $J = 3.15\text{ Hz}$ ), 130.81 (d,  $J = 7.95\text{ Hz}$ ), 130.52, 128.71, 126.65, 118.78, 115.89-115.61 (m); MS (ESI)  $m/z$  188  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{12}\text{H}_{11}\text{FN}^+$  188.0870; Found: 188.0874  $[\text{M} + \text{H}]^+$ .

**4-Fluorobiphenyl-3-ylamine (3p):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.42-7.38 (m, 2H), 7.16-7.08 (m, 1H), 6.99 (t,  $J = 8.7\text{ Hz}$ , 2H), 6.82 (d,  $J = 7.2\text{ Hz}$ , 1H), 6.73 (s, 1H), 6.57-6.55 (m, 1H), 3.54 (s, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  164.02, 160.76, 146.88, 141.38, 137.48, 129.78, 128.62 (d,  $J = 7.88\text{ Hz}$ ), 117.39, 115.48 (d,  $J = 24.23\text{ Hz}$ ), 113.71 (d,  $J = 30\text{ Hz}$ ); MS (ESI)  $m/z$  188  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{12}\text{H}_{11}\text{FN}^+$  188.0870; Found: 188.0875  $[\text{M} + \text{H}]^+$ .

**N-(3'-Amino-biphenyl-4-yl)-acetanilide (3q):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.55-7.46 (m, 5H), 7.20 (t,  $J = 7.8\text{ Hz}$ , 1H), 6.95 (d,  $J = 7.8\text{ Hz}$ , 1H), 6.86 (s, 1H), 6.65 (d,  $J = 7.8\text{ Hz}$ , 1H), 3.70 (s, 2H), 2.19 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.71, 146.75,

141.83, 137.44, 137.10, 129.72, 127.55, 120.14, 117.37, 114.00, 113.58, 24.60; MS (ESI)  $m/z$  227  $[M+H]^+$ ; HRMS Calculated for  $C_{14}H_{14}N_2O^+$  227.1184; Found: 227.1184  $[M+H]^+$ .

**3'-Amino-3-methyl-biphenyl-4-carbonitrile (3r):**  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.55 (d,  $J = 7.8$ , 1H), 7.37 (t,  $J = 10.5$ , 2H), 7.19-7.14 (m, 1H), 6.88 (d,  $J = 7.5$  Hz, 1H), 6.80 (s, 1H), 6.66 (d,  $J = 7.2$  Hz, 1H), 3.51 (s, 2H), 2.51 (s, 3H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  146.89, 147.77, 142.23, 140.56, 132.84, 129.99, 128.84, 124.96, 118.40, 117.64, 115.27, 113.75, 111.18, 20.67; MS (ESI)  $m/z$  209  $[M+H]^+$ ; HRMS Calculated for  $C_{14}H_{13}N_2^+$  209.1073; Found: 209.1075  $[M+H]^+$ .

**3'-Amino-[1,1'-biphenyl]-4-carbonitrile (3s):**  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.70-7.61 (m, 4H), 7.27-7.22 (m, 1H), 6.95 (d, 7.5 Hz, 1H), 6.87 (s, 1H), 6.73 (d,  $J = 7.8$  Hz, 1H), 3.81 (s, 2H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  148.47, 147.35, 141.78, 133.88, 131.46, 129.09, 120.41, 118.95, 116.73, 115.06, 112.19; MS (ESI)  $m/z$  194  $(M + H)^+$ ; HRMS Calculated for  $C_{13}H_{11}N_2^+$  195.0917; Found: 195.0921  $[M+H]^+$ .

**3-(1H-Indol-5-yl)-phenylamine (3t):**  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  8.18 (s, 1H), 7.83 (s, 1H), 7.41-7.38 (m, 2H), 7.25-7.20 (m, 2H), 7.06 (d,  $J = 7.8$  Hz, 1H), 6.97 (d,  $J = 1.5$  Hz, 1H), 6.66-6.59 (m, 2H), 3.76 (s, 2H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  146.60, 143.79, 135.33, 129.56, 128.29, 124.80, 121.90, 119.17, 118.08, 114.32, 113.32, 111.12, 102.99; MS (ESI)  $m/z$  208  $[M+H]^+$ ; HRMS Calculated for  $C_{14}H_{13}N_2^+$  209.1073; Found: 209.1071  $[M+H]^+$ .

**3-Styrylaniline (6a):**  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.50 (d,  $J = 7.2$  Hz, 2H), 7.35 (t,  $J = 7.2$  Hz, 1H), 7.23-7.10 (m, 2H), 7.05 (d,  $J = 3$  Hz, 2H), 6.99-6.92 (m, 1H), 6.86 (s, 1H), 6.58 (d,  $J = 15.3$  Hz, 1H), 3.71 (s, 2H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ): 146.75, 138.53, 137.53,

129.70, 128.98, 128.78, 128.66, 127.66, 126.61, 117.46, 114.82, 113.02; MS (ESI)  $m/z$  196  $[M+H]^+$ ; HRMS Calculated for  $C_{14}H_{14}N^+$  196.1121 Found: 196.1126  $[M+H]^+$ .

**3-(2-Naphthalen-2-yl-vinyl)-phenylamine (6b):**  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.84-7.71 (m, 6H), 7.47-7.41 (m, 2H), 7.21-7.12 (m, 2H), 6.98 (d,  $J = 7.5$  Hz, 1H), 6.89 (s, 1H), 6.64–6.61 (d,  $J = 7.5$  Hz, 1H), 3.71 (s, 2H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  146.69, 138.45, 134.92, 133.73, 133.02, 129.64, 129.23, 128.64, 128.29, 127.99, 127.70, 126.56, 126.32, 125.86, 123.56, 117.39, 114.77, 112.94; MS (ESI)  $m/z$  246  $[M+H]^+$ ; HRMS Calculated for  $C_{18}H_{16}N^+$  246.1277; Found: 246.1282  $[M+H]^+$ .

**2-(2-Naphthalen-2-yl-vinyl)-phenylamine (6c):**  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.88 (d,  $J = 8.4$  Hz, 4H), 7.79 (d,  $J = 8.4$  Hz, 1H), 7.53-7.51 (m, 3H), 7.35 (d,  $J = 15.9$  Hz, 1H), 7.29-7.16 (m, 2H), 6.90 (t,  $J = 7.2$  Hz, 1H), 6.78 (d,  $J = 8.1$  Hz, 1H), 3.76 (s, 2H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  144.10, 135.17, 133.78, 133.05, 130.35, 128.80, 128.37, 128.05, 127.76, 127.26, 126.48, 126.42, 125.94, 124.59, 123.94, 123.58, 119.28, 116.41; MS (ESI)  $m/z$  246  $[M+H]^+$ ; HRMS Calculated for  $C_{18}H_{16}N^+$  246.1277; Found: 246.1286  $[M+H]^+$ .

**4-Styryl-phenylamine (6d):**  $^1H$  NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.51 (d,  $J = 7.8$  Hz, 2H), 7.39-7.34 (m, 4H), 7.28-7.22 (m, 1H), 7.06 (d,  $J = 16.2$  Hz, 1H), 6.95 (d,  $J = 16.2$  Hz, 1H), 6.71 (d,  $J = 7.2$  Hz, 2H), 3.77 (s, 2H);  $^{13}C$  NMR (75 MHz,  $CDCl_3$ ):  $\delta$  146.17, 137.97, 128.70, 128.62, 128.05, 127.77, 126.91, 126.12, 125.13, 115.22; MS (ESI)  $m/z$  196  $[M+H]^+$ ; HRMS Calculated for  $C_{14}H_{14}N^+$  196.1121 Found: 196.1128  $[M+H]^+$ .

**3-[2-(4-Tert-Butyl-phenyl)-vinyl]-phenylamine (6e):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.45 (d,  $J$  = 8.4 Hz, 2H),  $\delta$  7.37 (d,  $J$  = 8.7 Hz, 2H), 7.17-7.08 (m, 1H), 7.02 (d,  $J$  = 7.8 Hz, 2H), 6.95-6.91 (m, 1H), 6.84 (s, 1H), 6.61-6.58 (m, 1H), 3.68 (s, 2H), 1.29 (s, 9H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.70, 146.62, 138.64, 134.65, 129.54, 128.35, 128.11, 126.23, 125.59, 117.26, 114.50, 112.83, 34.62, 31.30; MS (ESI)  $m/z$  252  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{18}\text{H}_{21}\text{N}^+$  252.1747; Found: 252.1758  $[\text{M}+\text{H}]^+$ .

**3-[2-(2,5-Dimethyl-phenyl)-vinyl]-phenylamine (6f):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.42 (s, 1H), 7.28 (t,  $J$  = 8.7 Hz, 1H), 7.18 (t,  $J$  = 7.8 Hz, 1H), 7.09 (d,  $J$  = 7.5 Hz, 1H), 7.01 (d,  $J$  = 6.9 Hz, 1H), 6.96 (d,  $J$  = 4.8 Hz, 1H), 6.89 (d,  $J$  = 5.7 Hz, 2H), 6.63 (d,  $J$  = 7.8 Hz, 1H), 3.78 (s, 2H), 2.19 (s, 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.65, 138.85, 136.18, 125.51, 132.76, 130.30, 129.84, 129.58, 128.29, 126.47, 125.94, 117.38, 114.60, 112.88, 21.08, 19.45; MS (ESI)  $m/z$  224  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{16}\text{H}_{18}\text{N}^+$  224.1445; Found: 224.1453  $[\text{M}+\text{H}]^+$ .

**2-[2-(2,5-Dimethyl-phenyl)-vinyl]-phenylamine (6g):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.44-7.39 (m, 1H), 7.38 (s, 1H), 7.28 (s, 1H), 7.18-7.16 (m, 1H), 7.14-7.12 (m, 1H), 7.08 (d,  $J$  = 4.5 Hz, 1H), 7.03 (d,  $J$  = 6.00 Hz, 1H), 6.84 (t,  $J$  = 7.5 Hz, 1H), 6.77-6.71 (m, 1H), 3.82 (s, 2H), 2.26 (s, 6H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.98, 136.44, 135.58, 132.73, 130.33, 128.61, 128.47, 128.34, 127.34, 125.99, 125.28, 124.32, 119.13, 116.18, 21.07, 19.44; MS (ESI)  $m/z$  224  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{16}\text{H}_{18}\text{N}^+$  224.1445; Found: 224.1453  $[\text{M}+\text{H}]^+$ .

**3-[2-(4-Methoxy-phenyl)-vinyl]-phenylamine (6h):**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.51 (d,  $J$  = 8.7 Hz, 2H), 7.11 (d,  $J$  = 5.7 Hz, 1H), 7.07 (d,  $J$  = 3 Hz, 1H), 6.99 (s, 1H), 6.96 (s, 1H), 6.93 (s, 1H), 6.85 (d,  $J$  = 7.5 Hz, 2H), 6.58-6.55 (m, 1H), 4.18 (s, 3H), 3.82 (s, 1H);

$^{13}\text{C}$ NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.05, 147.96, 138.22, 129.91, 129.06, 127.33, 127.12, 126.58, 115.27, 113.81, 113.43, 111.66, 54.65; MS (ESI)  $m/z$  225  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{15}\text{H}_{16}\text{NO}^+$  226.1226; Found: 226.1234  $[\text{M}+\text{H}]^+$ .

**2-[2-(4-Methoxy-phenyl)-vinyl]-phenylamine (6i):**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.58-7.53 (m, 2H), 7.46-7.41 (m, 1H), 7.18-7.11 (m, 1H), 7.07-7.02 (m, 2H), 6.99-6.94 (m, 2H), 6.75-6.71 (m, 2H), 4.34 (s, 2H), 3.83 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  158.94, 144.93, 130.34, 127.94, 127.33, 125.80, 122.58, 121.79, 117.52, 117.00, 115.42, 113.75, 54.64; MS (ESI)  $m/z$  225  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{15}\text{H}_{16}\text{NO}^+$  226.1226; Found: 226.1234  $[\text{M}+\text{H}]^+$ .

**1-{4-[2-(3-Amino-phenyl)-vinyl]-phenyl}-ethanone (6j):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.53 (d,  $J = 8.7$  Hz, 2H), 7.42 (d,  $J = 7.2$  Hz, 1H), 7.17-7.10 (m, 4H), 7.01 (s, 1H), 6.84 (t,  $J = 7.5$  Hz, 1H), 6.77-6.73 (m, 1H), 3.84 (s, 2H), 2.34 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  169.60, 150.02, 143.97, 135.49, 130.76, 129.29, 128.78, 128.05, 127.23, 124.56, 123.76, 121.84, 119.25, 116.36, 115.44, 21.17; MS (ESI)  $m/z$  254  $[\text{M}+\text{H}]^+$ ; HRMS Calculated for  $\text{C}_{16}\text{H}_{16}\text{NO}_2^+$  254.1175; Found: 254.1183  $[\text{M}+\text{H}]^+$ .

**2-(4-nitrophenyl)-2,3-dihydrofuran (6'):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.22 (d,  $J = 8.4$  Hz, 2H), 7.51 (d,  $J = 8.4$  Hz, 2H), 6.48 (d,  $J = 2.1$  Hz, 1H), 5.61 (t,  $J = 10.2$  Hz, 1H), 4.99 (d,  $J = 2.4$  Hz, 1H), 3.17 (t,  $J = 14.7$  Hz, 1H), 2.55 (q,  $J = 6.00$  Hz, 1H),  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.49, 145.13, 126.20, 123.86, 99.05, 81.00, 71.54, 38.01, 29.69.

**2-Nitro-1,1'-biphenyl (7a) :**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (d,  $J = 8.1$  Hz, 1H), 7.65 (t,  $J = 7.5$  Hz, 1H), 7.53-7.44 (m, 5H), 7.39-7.34 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.31, 137.40, 136.35, 132.31, 131.98, 128.71, 128.25, 128.19, 127.91, 124.09.

**3-Nitro-1,1'-biphenyl (7b) :**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.47 (d,  $J = 1.8$  Hz, 1H), 8.23-8.21 (m, 1H), 7.95-7.92 (m, 1H), 7.66-7.60 (m, 3H), 7.55-7.44 (m, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.73, 142.87, 138.66, 133.06, 129.74, 129.19, 128.57, 127.17, 122.04, 121.95.

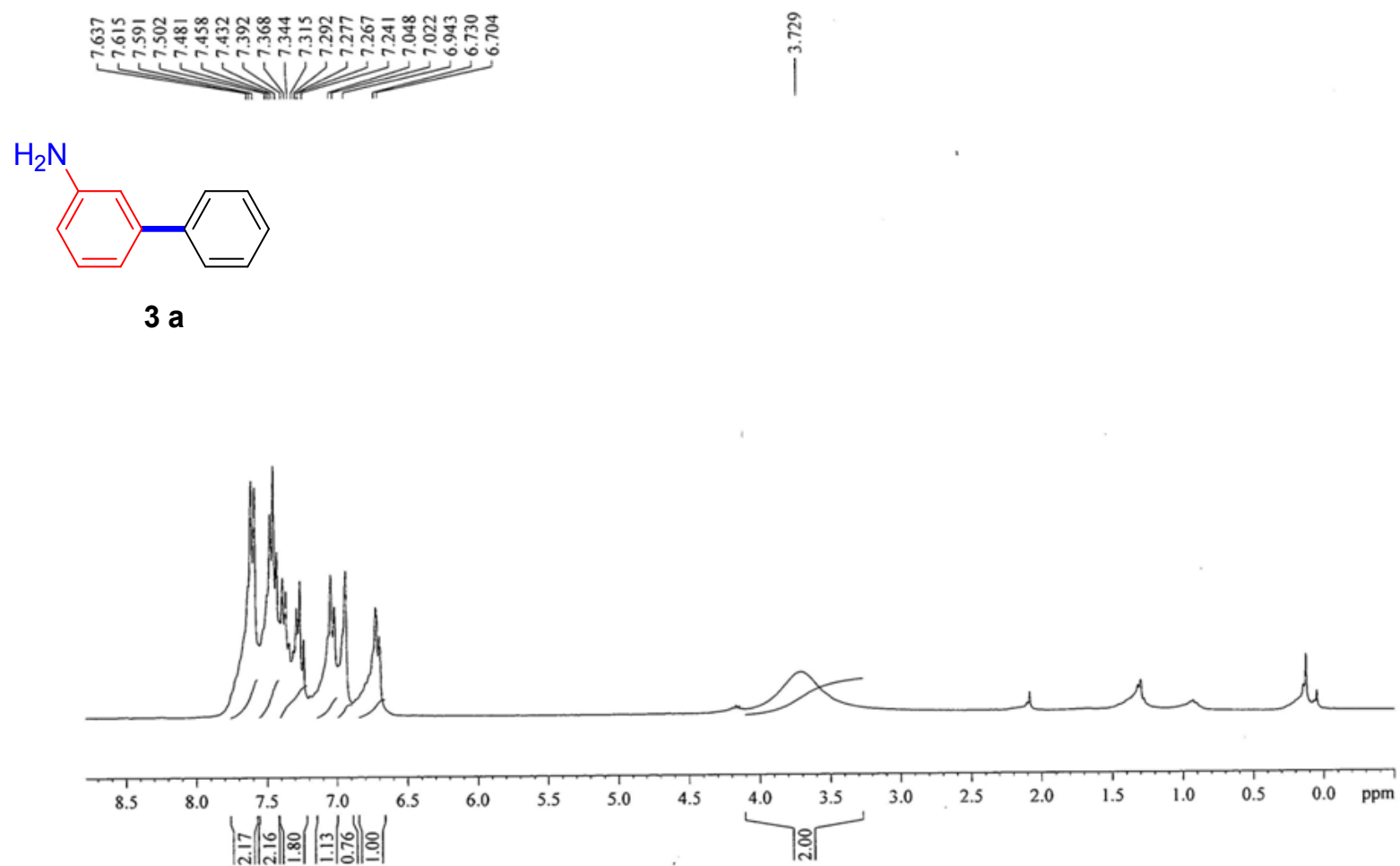
**4-Nitro-1,1'-biphenyl (7c) :**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.32 (d,  $J = 8.7$  Hz, 2H), 7.76 (d,  $J = 8.7$  Hz, 2H), 7.67-7.64 (m, 2H), 7.56-7.47 (m, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  147.64, 147.08, 138.77, 129.18, 128.94, 127.81, 127.40, 124.12.

**3-Methyl-3'-nitro-1,1'-biphenyl (7d):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.45 (t,  $J = 1.8$  Hz, 1H), 8.21-8.18 (m, 1H), 7.94-7.91 (m, 1H), 7.61 (t,  $J = 8.4$  Hz, 1H), 7.45-7.40 (m, 3H), 7.28 (t,  $J = 6$  Hz, 1H), 2.48 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.68, 142.98, 138.91, 138.61, 133.07, 129.67, 129.32, 129.09, 127.90, 124.26, 121.94, 121.91, 21.53.

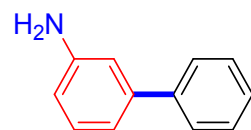
**1-(3'-Nitro-[1,1'-biphenyl]-4-yl)ethanone (7e):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.02 (d,  $J = 8.4$  Hz, 2H), 7.93 (d,  $J = 8.1$  Hz, 1H), 7.67 (t,  $J = 6.9$  Hz, 1H), 7.57-7.40 (m, 4H), 2.63 (s, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.53, 148.88, 142.36, 136.58, 135.43, 132.72, 131.76, 128.97, 128.67, 128.24, 124.42, 26.70.

**3'-Nitro-[1,1'-biphenyl]-4-carbonitrile (7f):**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.51-8.48 (m, 1H), 8.30 (d,  $J = 7.5$  Hz, 1H), 8.01-7.94 (m, 1H), 7.83-7.68 (m, 5H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.85, 143.53, 143.01, 140.83, 133.10, 132.90, 130.24, 127.96, 127.91, 123.35, 122.15, 118.42, 112.40.

## 1. Copies of $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra



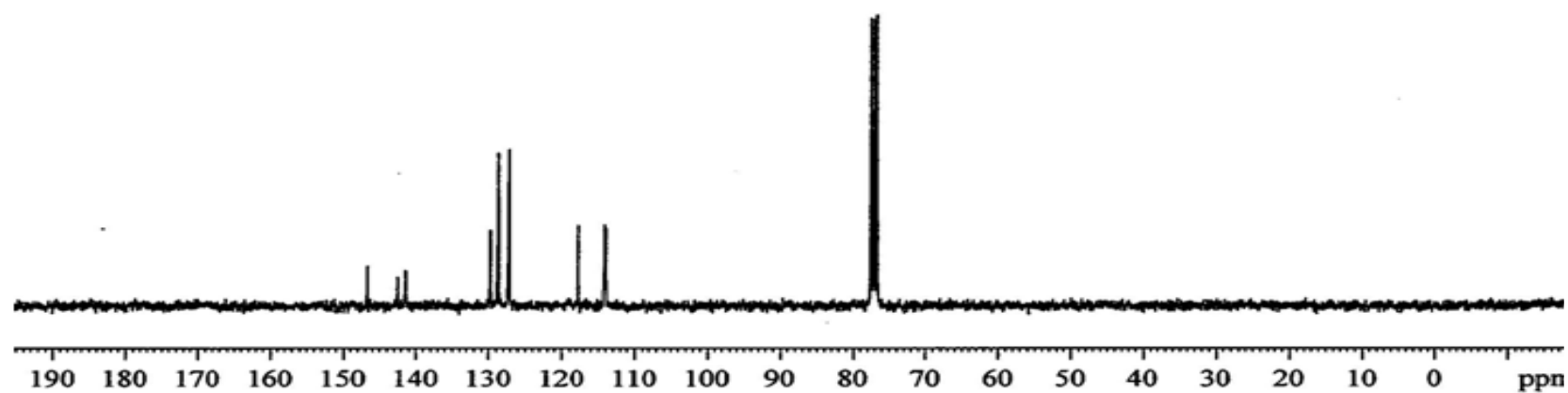
**Spectrum1.** 300 MHz  $^1\text{H}$  NMR of compound **3a**



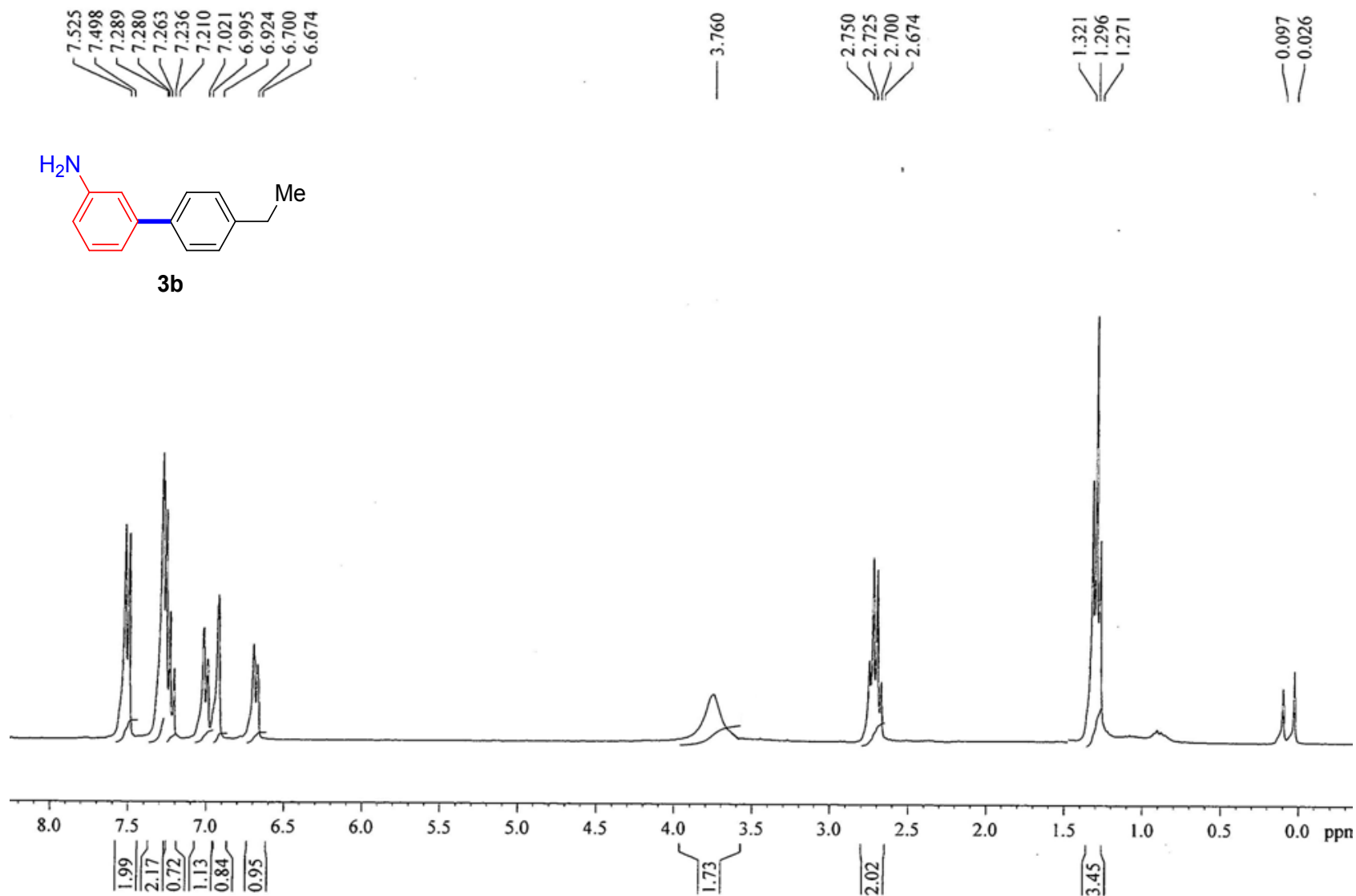
**3 a**

146.748  
142.475  
141.414  
129.721  
128.679  
127.257  
127.147  
117.719  
114.132  
113.938

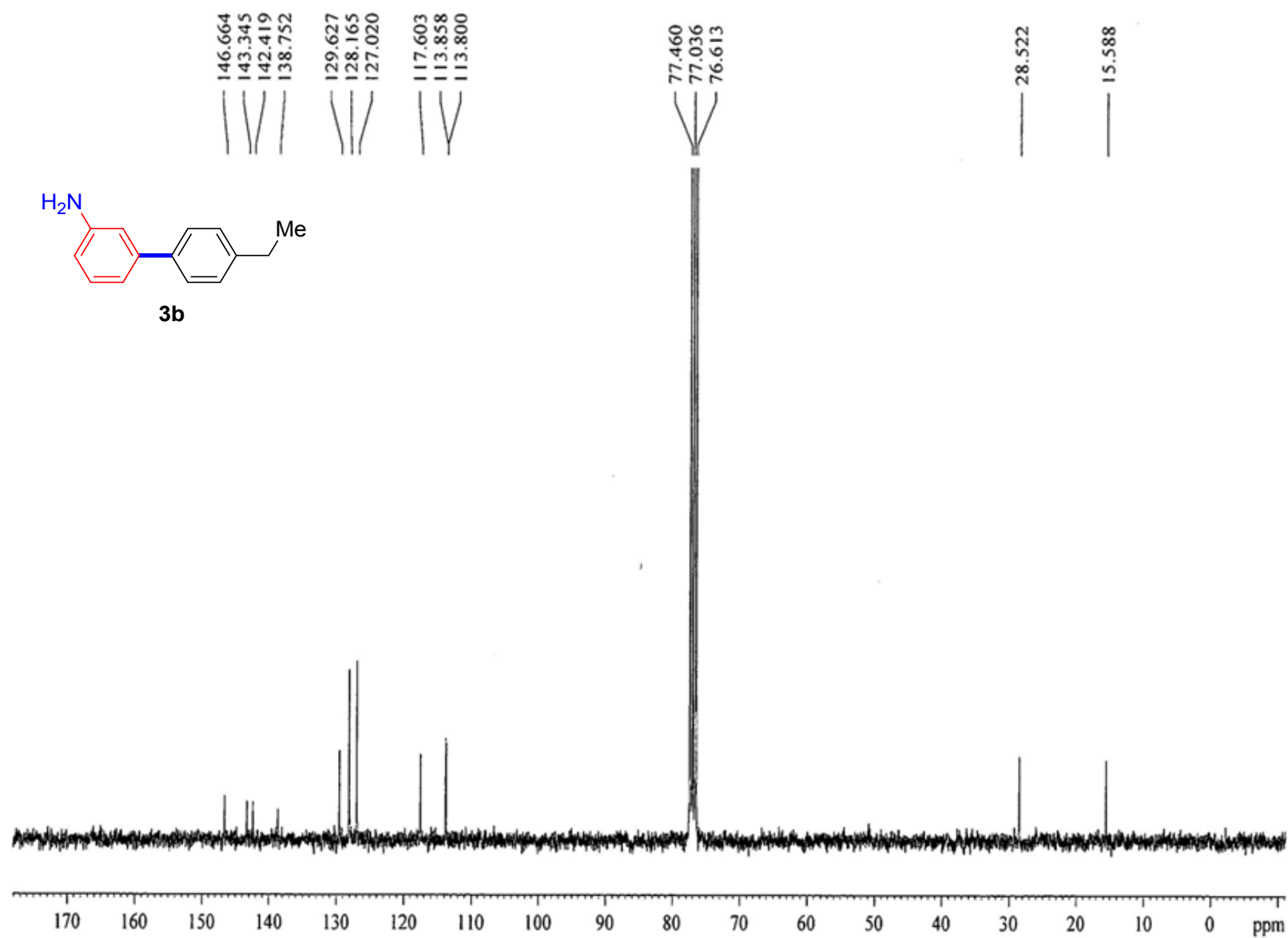
77.511  
77.087  
76.664



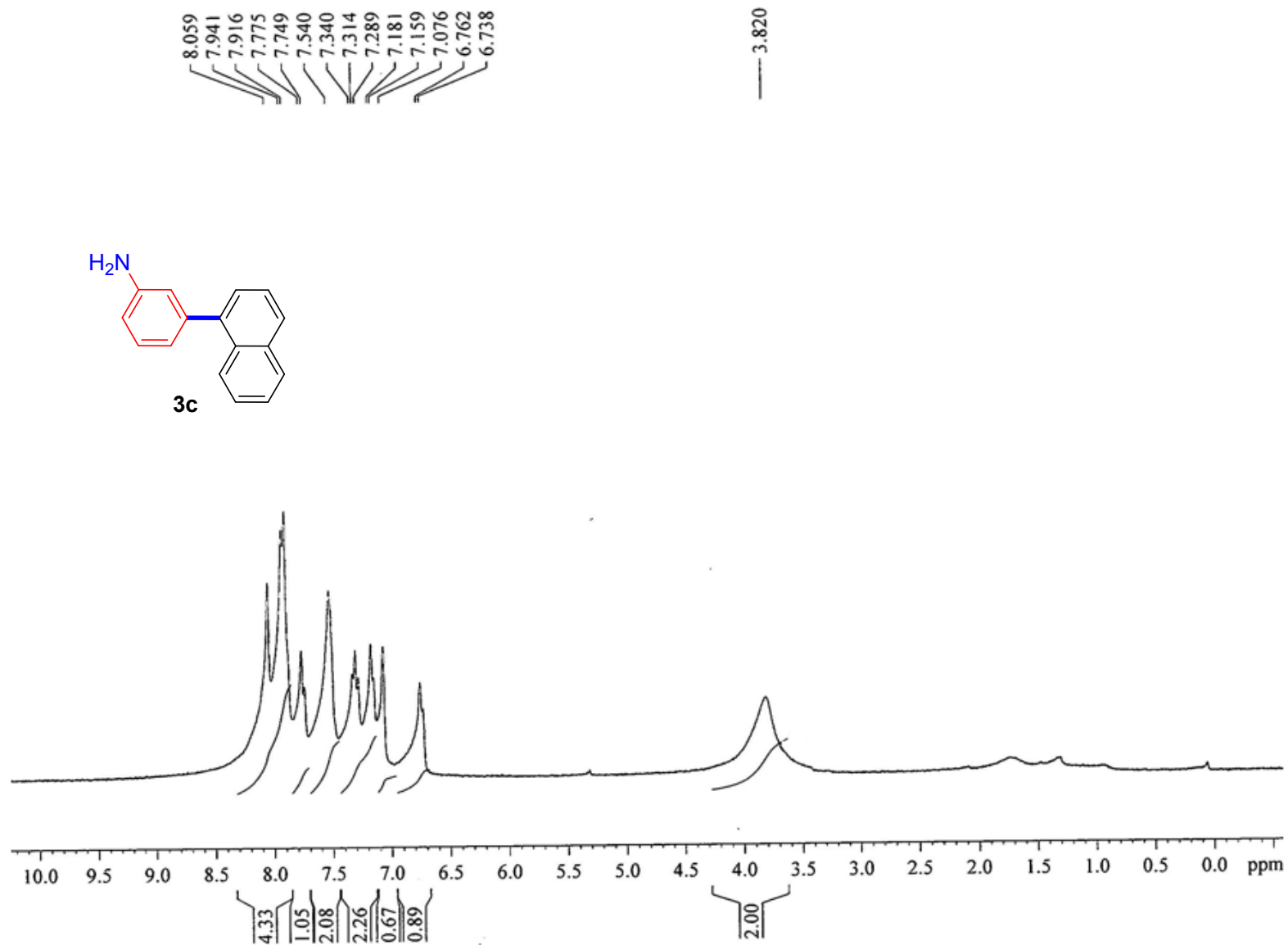
**Spectrum 2.** 75 MHz  $^{13}\text{C}$  NMR of compound **3a**



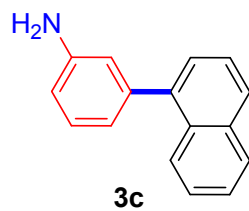
**Spectrum3.** 300 MHz <sup>1</sup>H NMR of compound **3b**



Spectrum4. 75 MHz <sup>13</sup>C NMR of compound **3b**

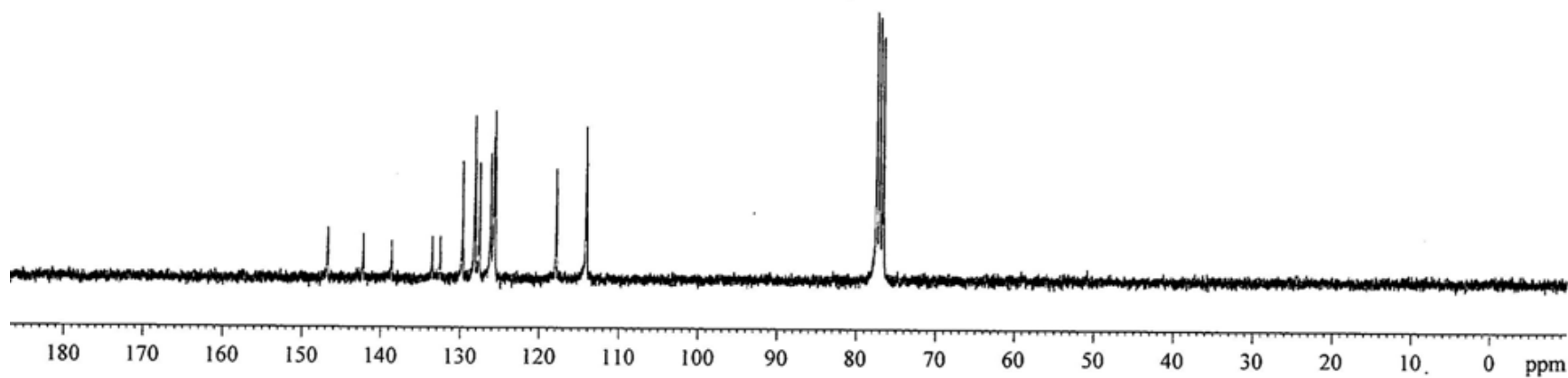


**Spectrum5.** 300 MHz  $^1\text{H}$  NMR of compound **3c**

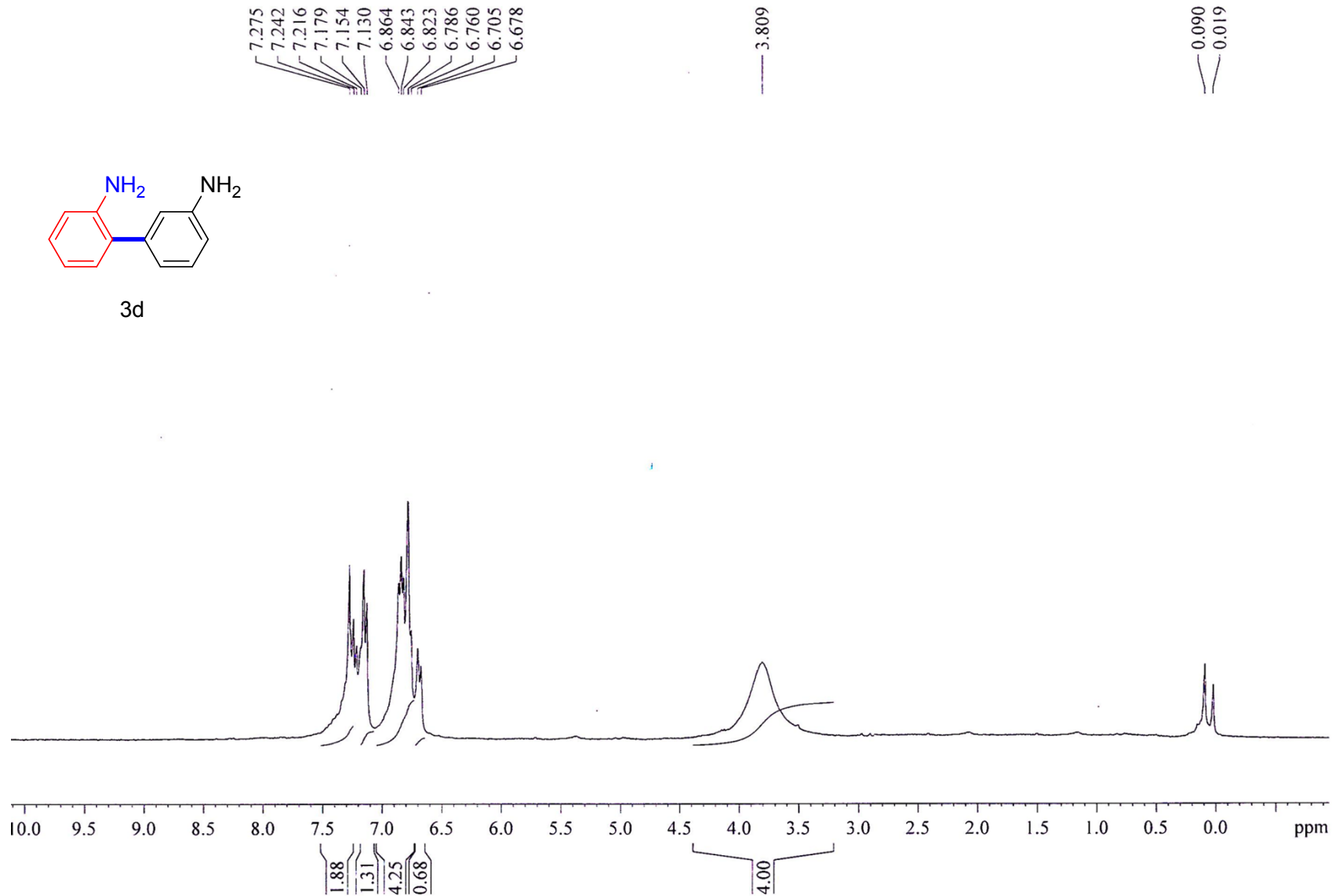


146.858  
 142.359  
 138.768  
 133.668  
 132.683  
 129.813  
 128.287  
 128.220  
 127.661  
 126.245  
 125.874  
 125.725  
 125.675  
 117.981  
 114.248  
 114.162

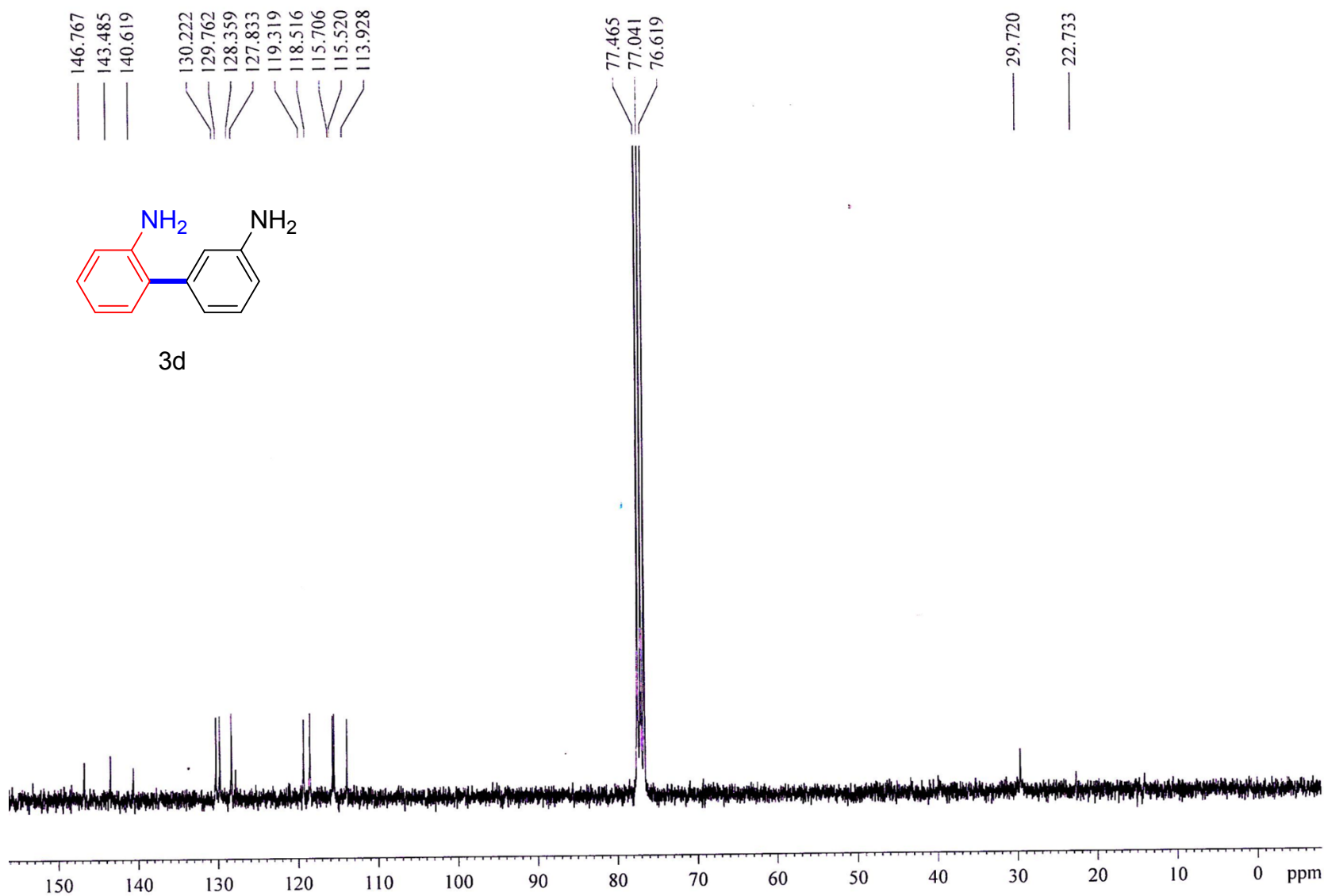
77.507  
 77.083  
 76.659



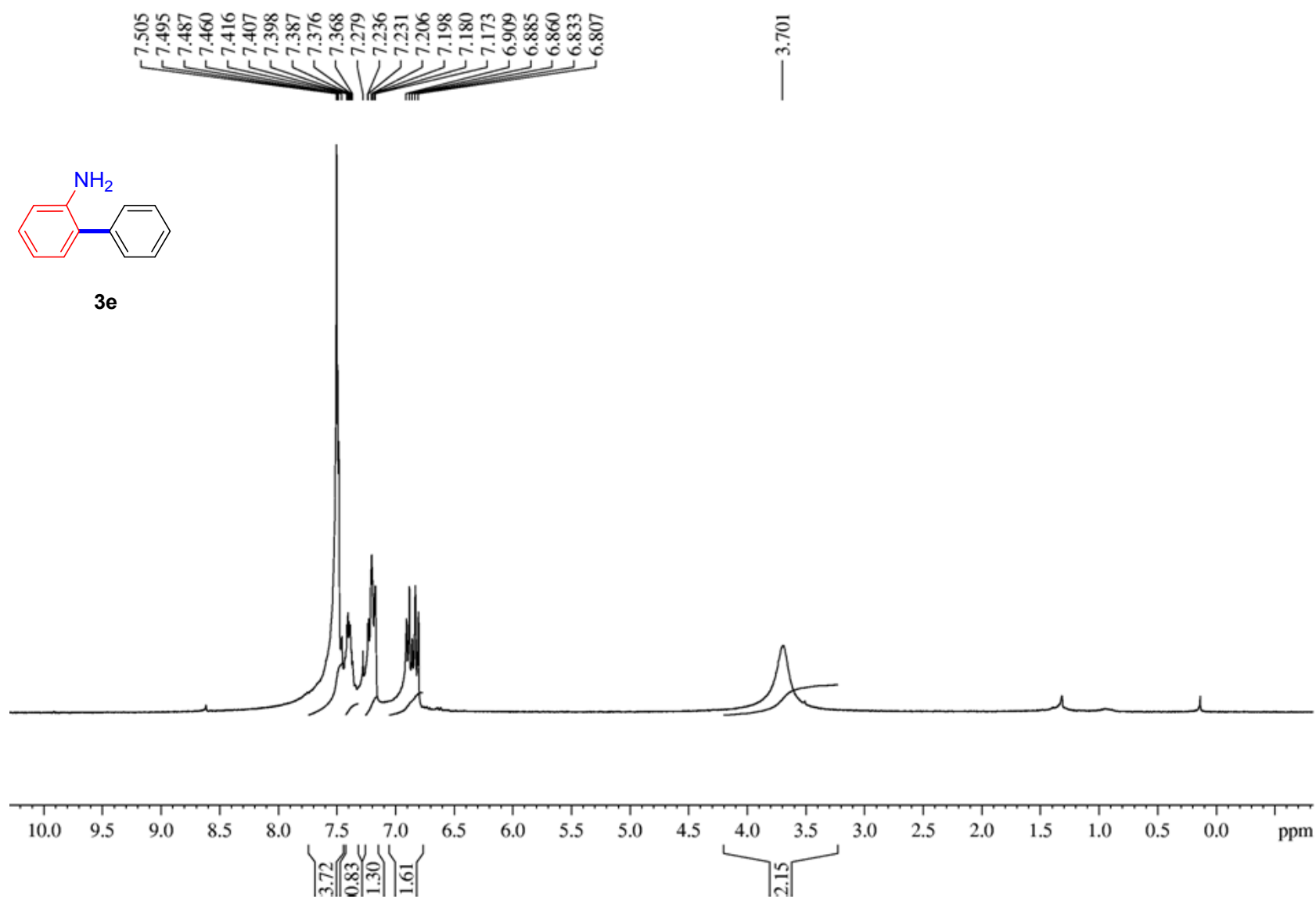
**Spectrum6.** 75 MHz  $^{13}\text{C}$  NMR of compound **3c**



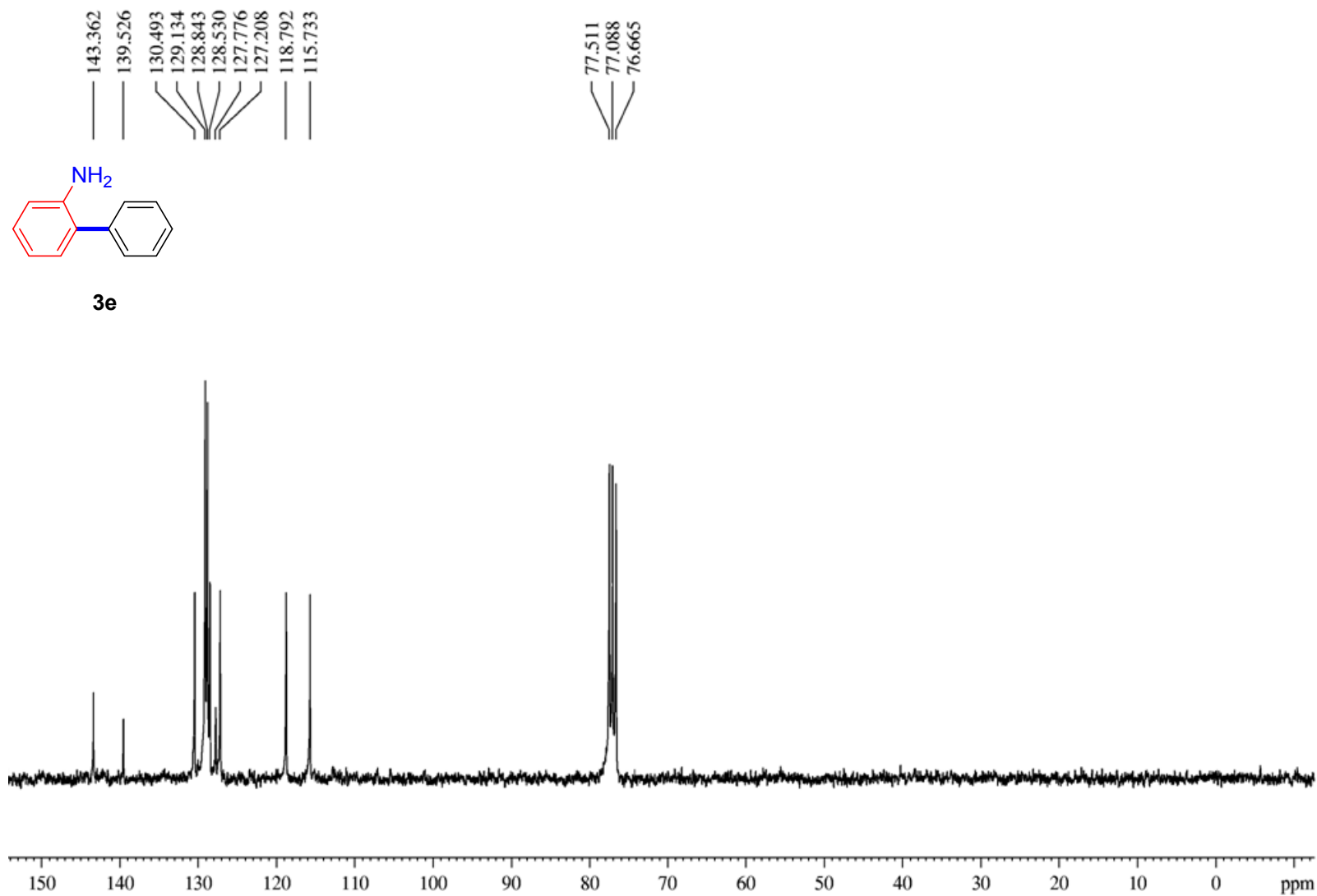
**Spectrum7.** 300 MHz <sup>1</sup>H NMR of compound **3d**



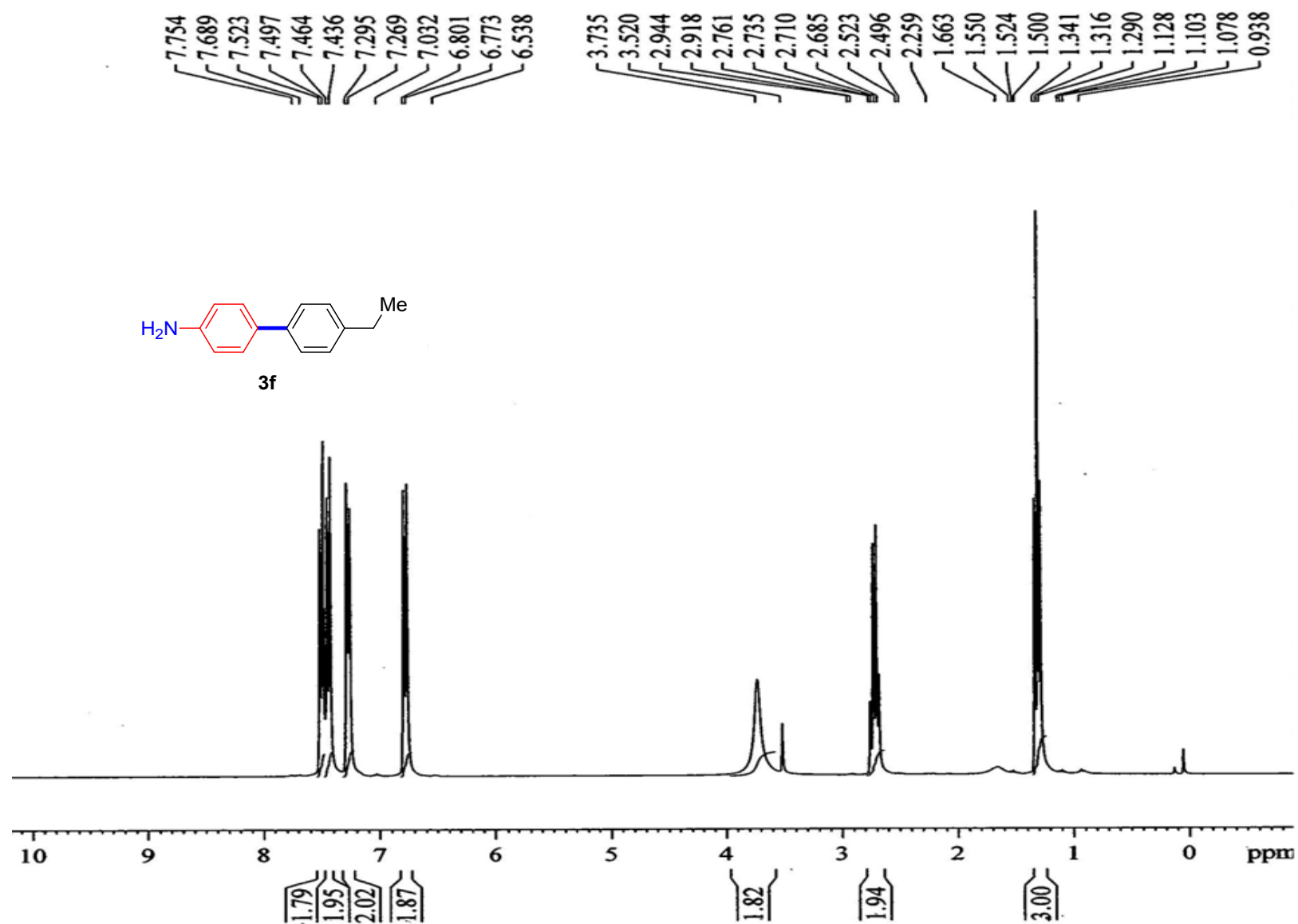
**Spectrum8.** 75 MHz  $^{13}\text{C}$ NMR of compound **3d**



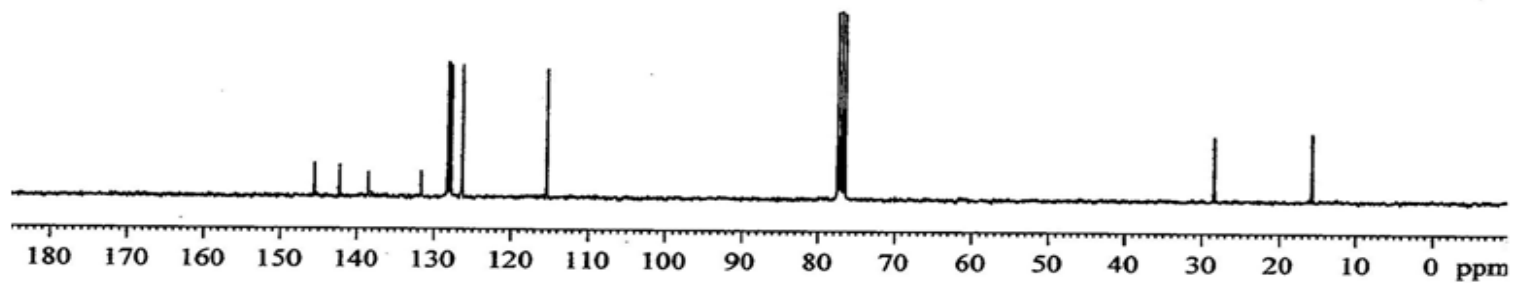
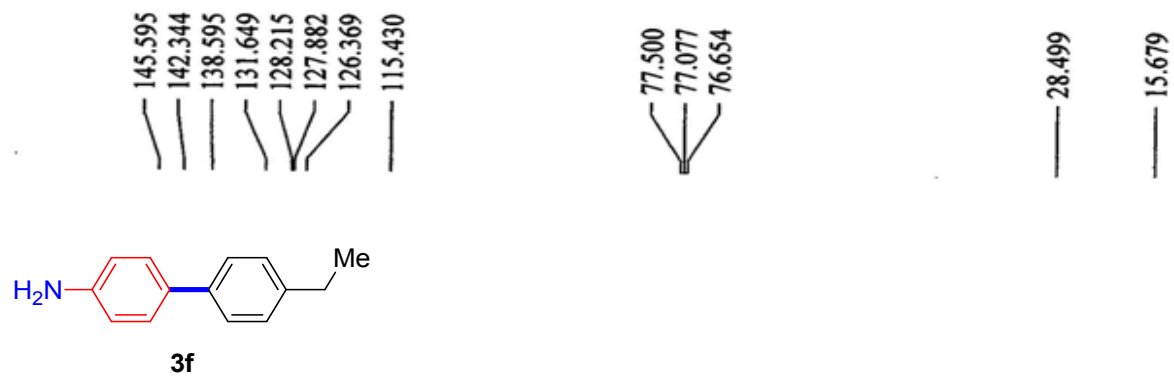
**Spectrum9.** 300 MHz  $^1\text{H}$  NMR of compound **3e**



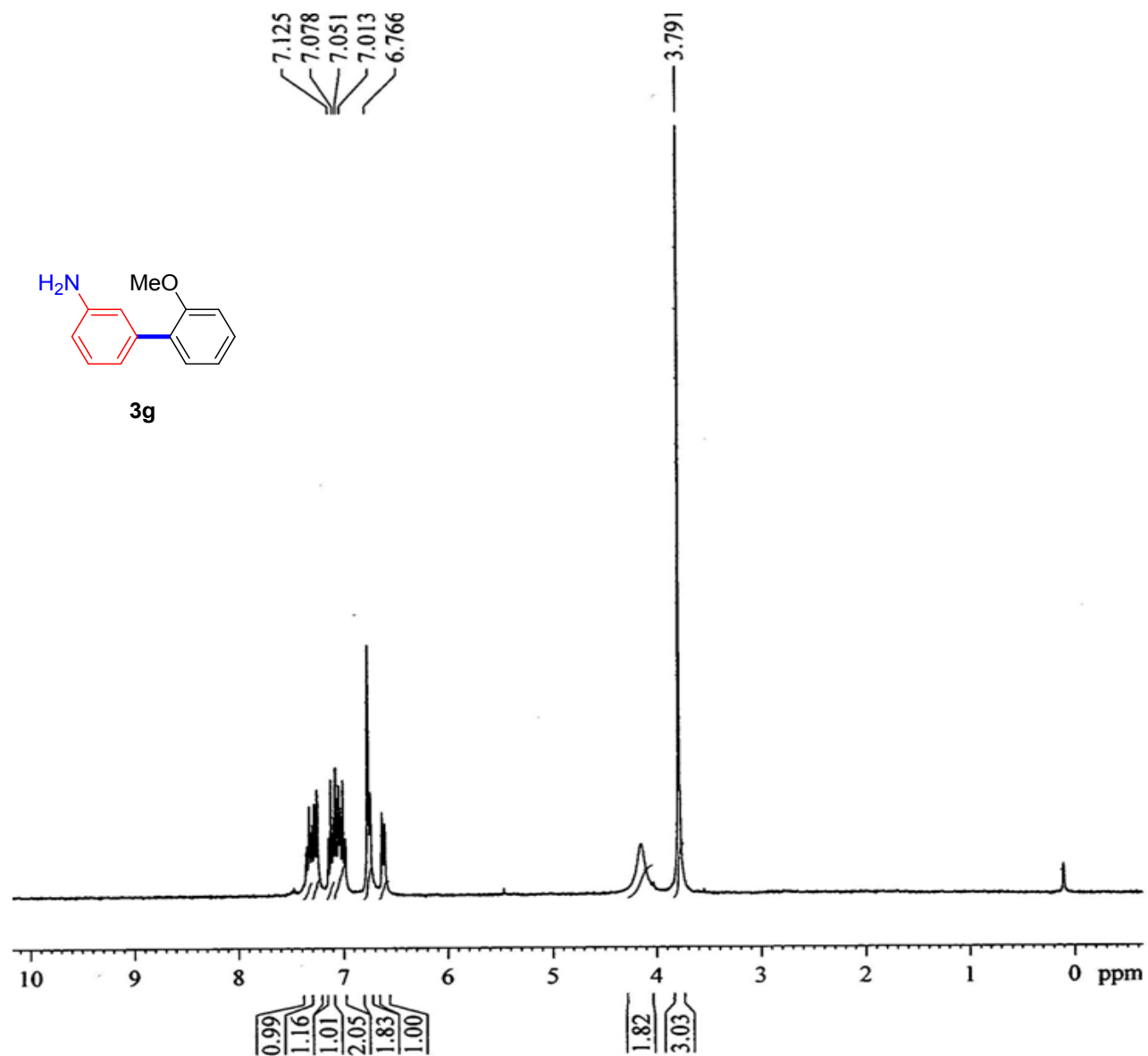
Spectrum 10.75 MHz  $^{13}\text{C}$  NMR of compound **3e**



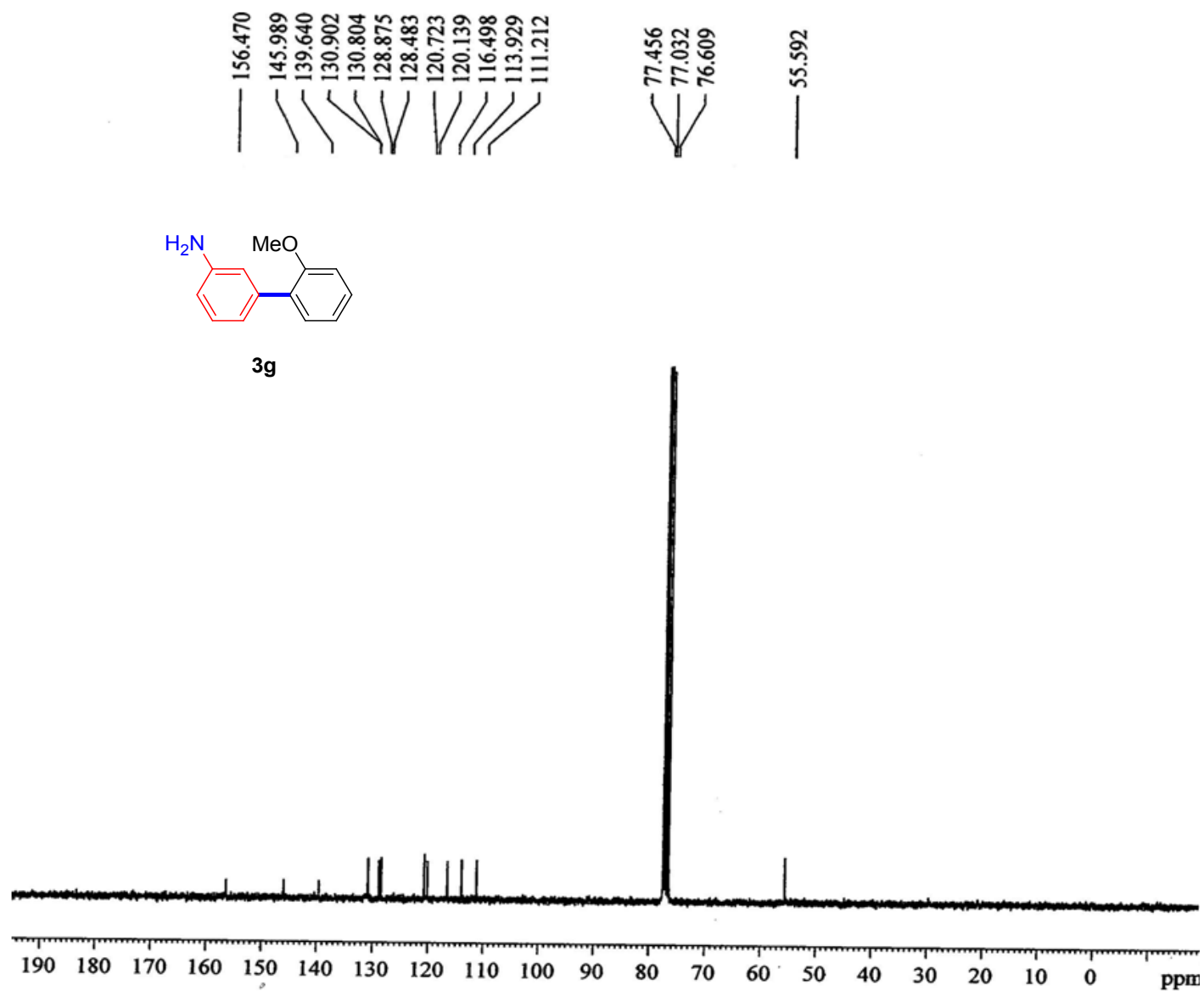
**Spectrum11.** 300 MHz <sup>1</sup>H NMR of compound **3f**



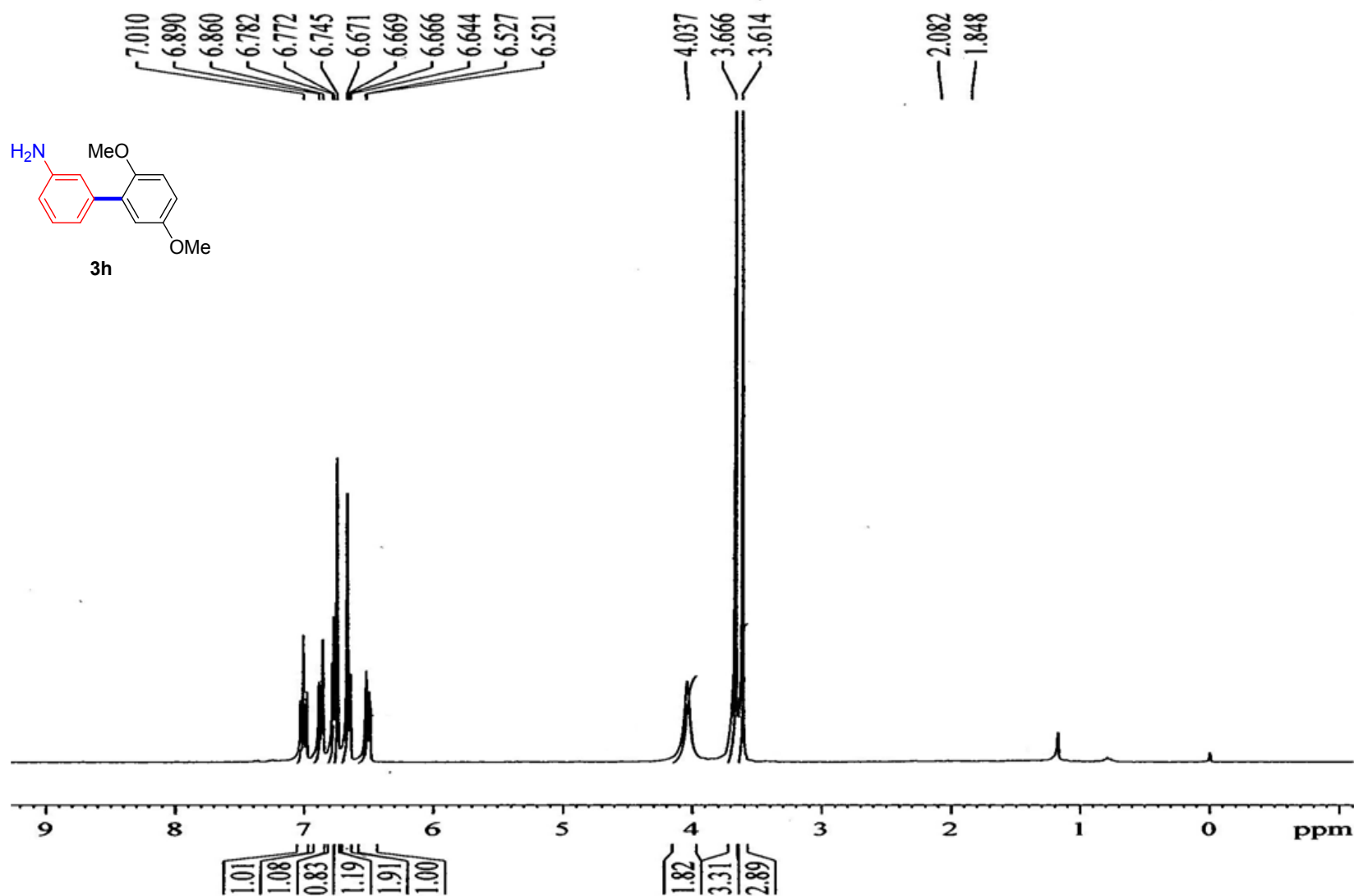
**Spectrum12.** 75 MHz <sup>13</sup>C NMR of compound **3f**



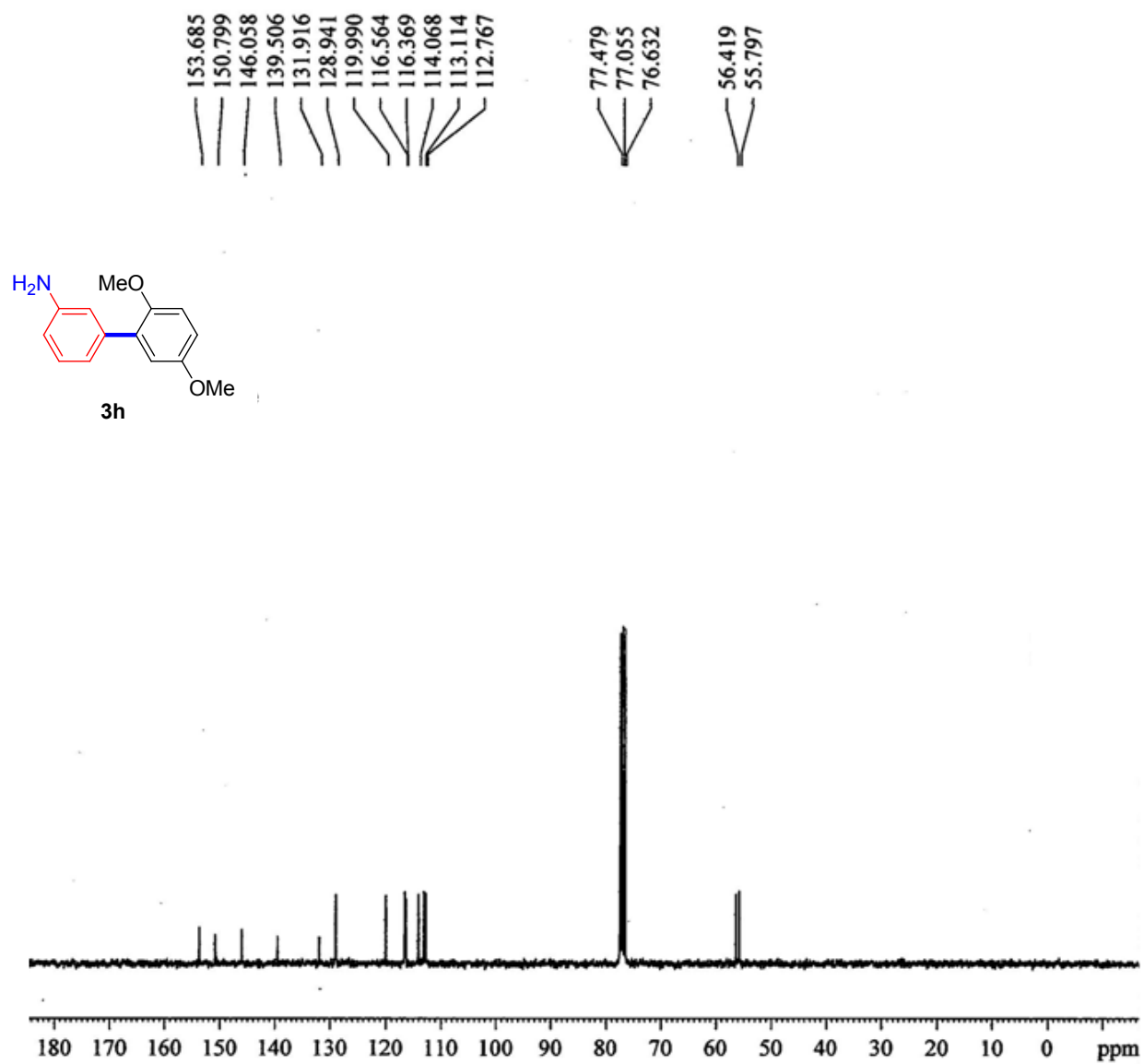
Spectrum13. 300 MHz  $^1\text{H}$  NMR of compound **3g**



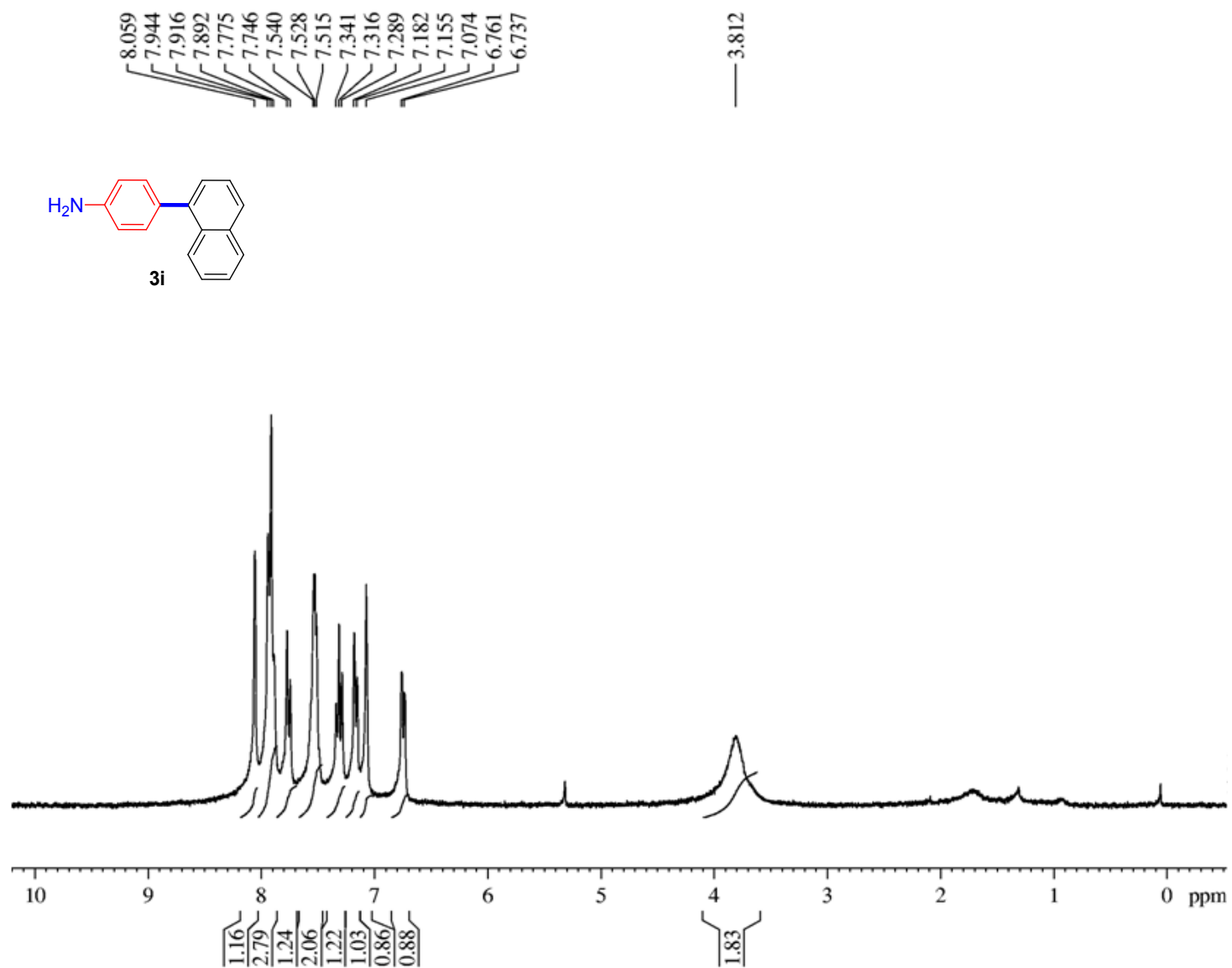
Spectrum14. 75 MHz <sup>13</sup>C NMR of compound **3g**



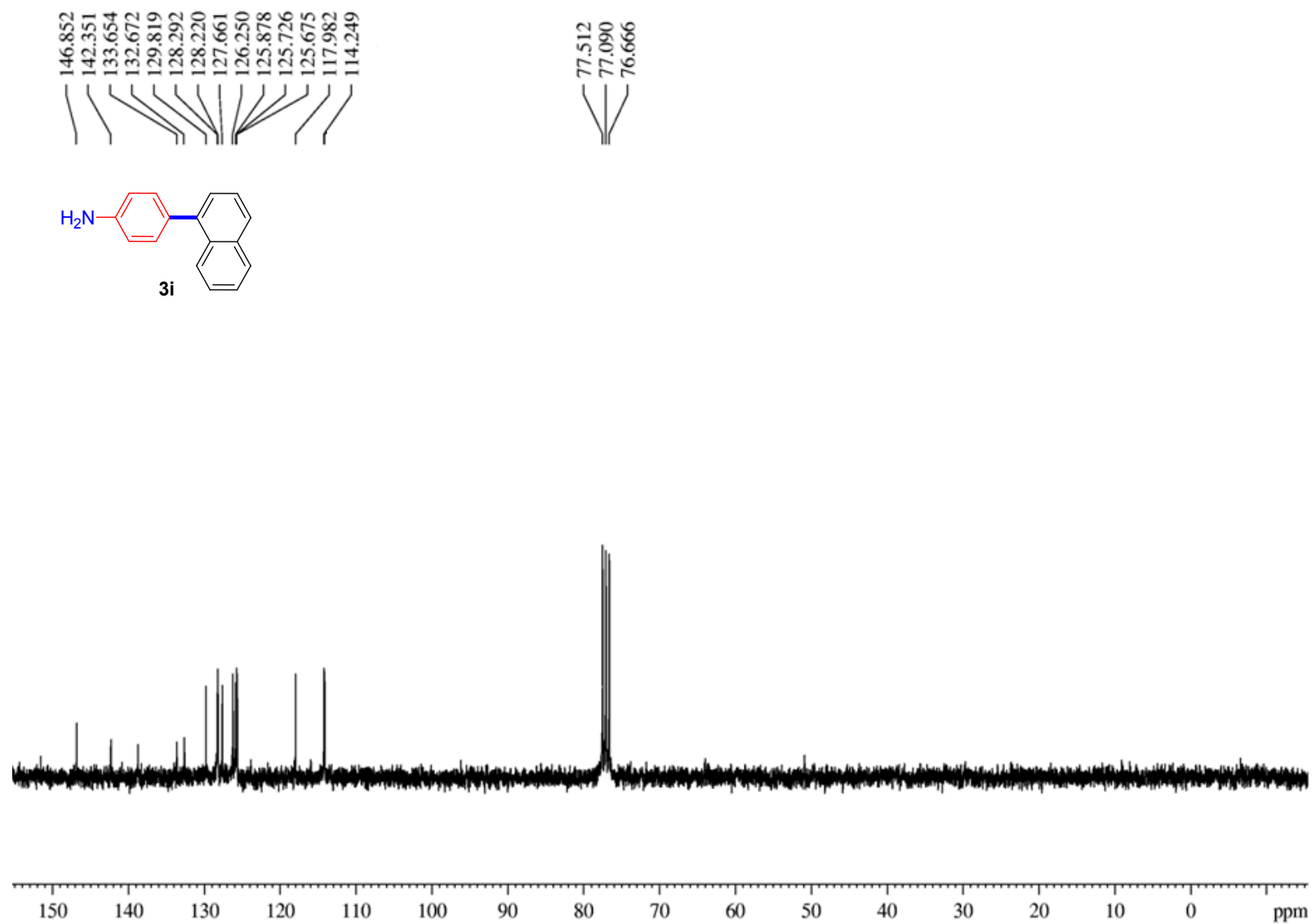
**Spectrum15.** 300 MHz <sup>1</sup>H NMR of compound **3h**



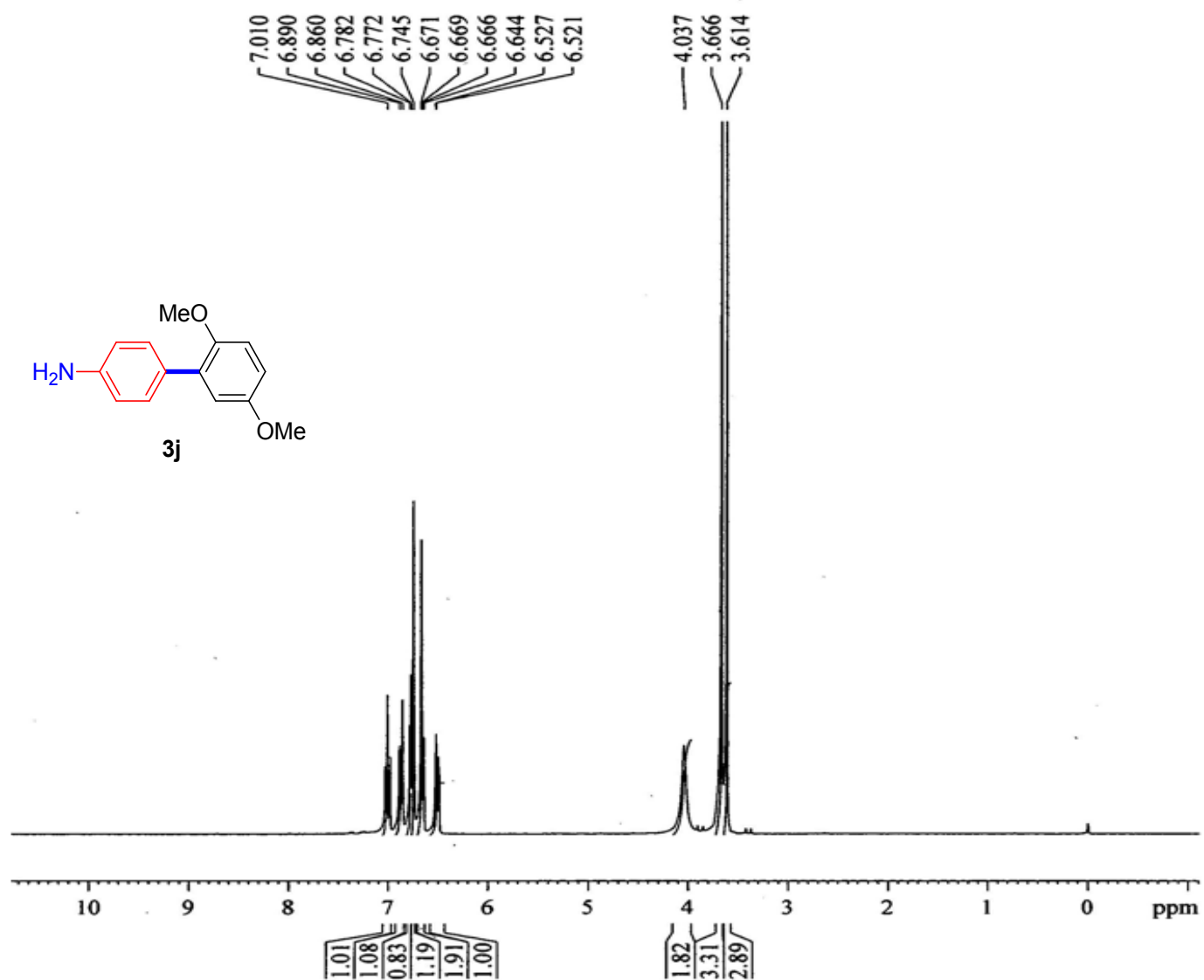
Spectrum16. 75 MHz <sup>13</sup>C NMR of compound **3h**



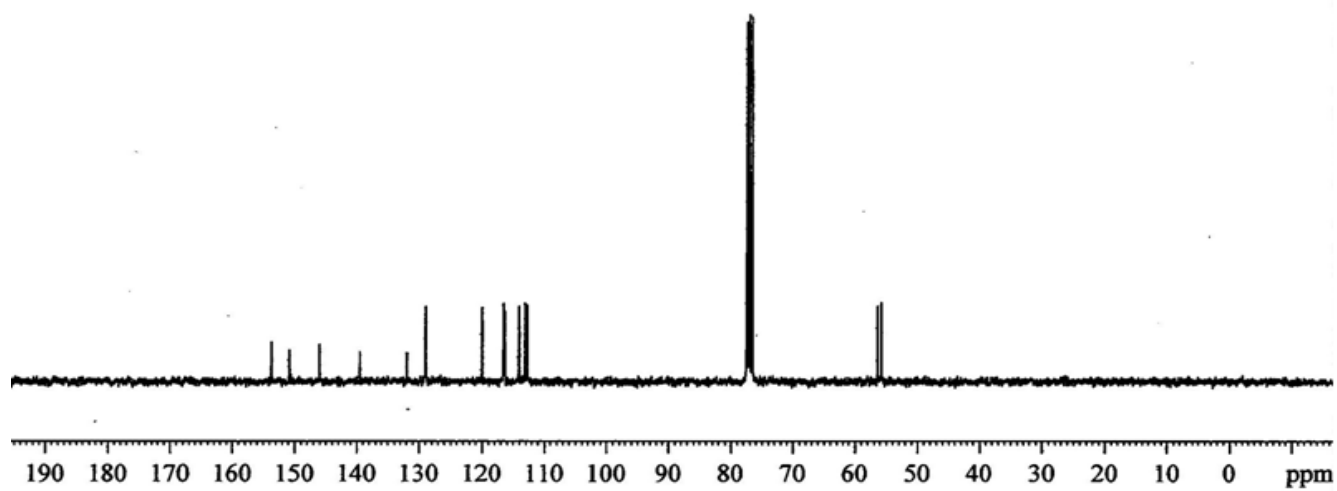
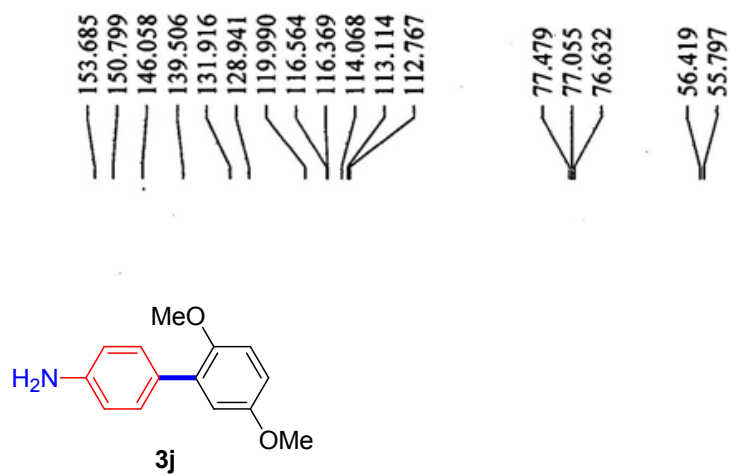
**Spectrum17.** 300 MHz <sup>1</sup>H NMR of compound **3i**



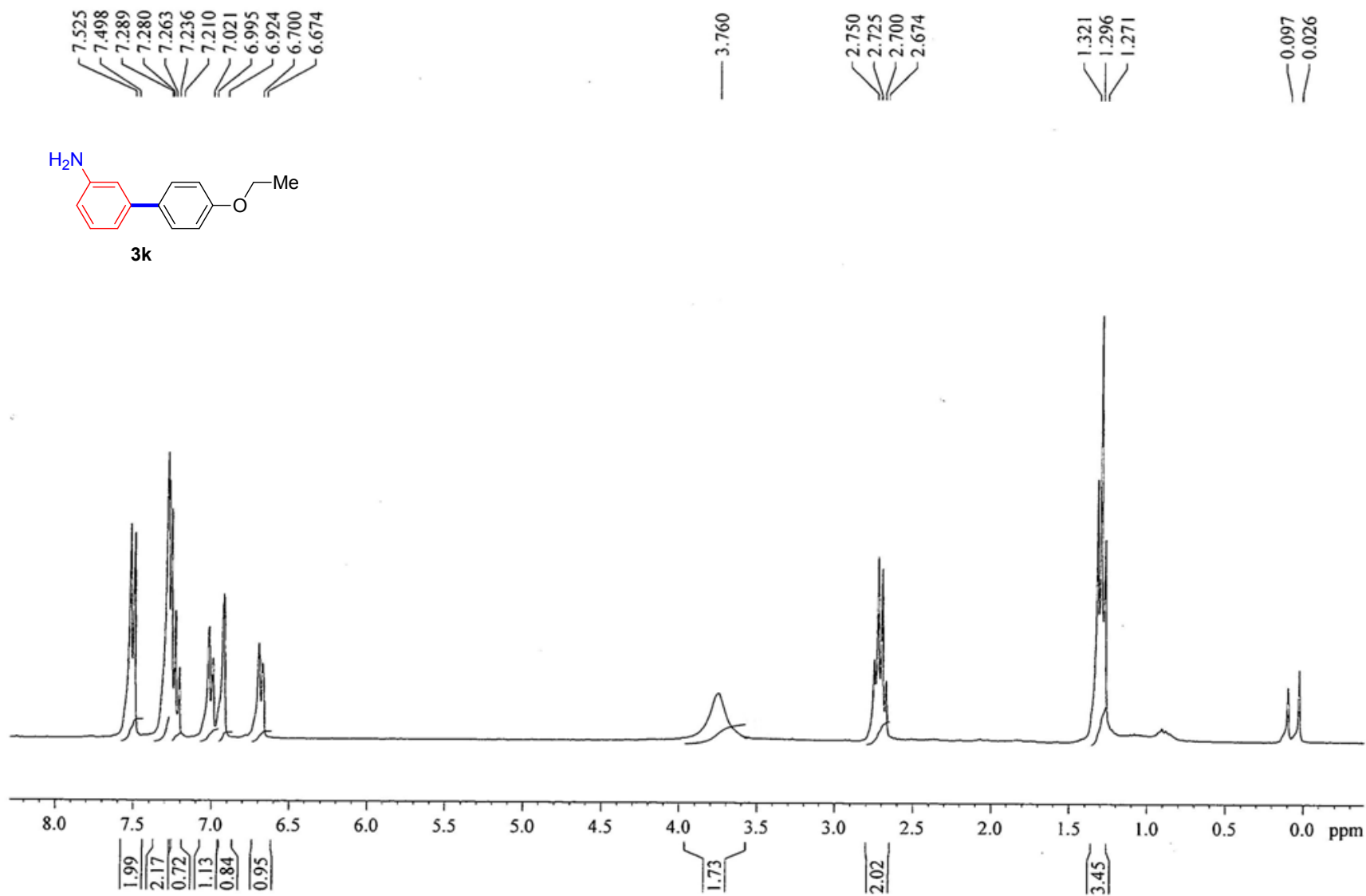
**Spectrum18.** 75 MHz <sup>13</sup>C NMR of compound **3i**



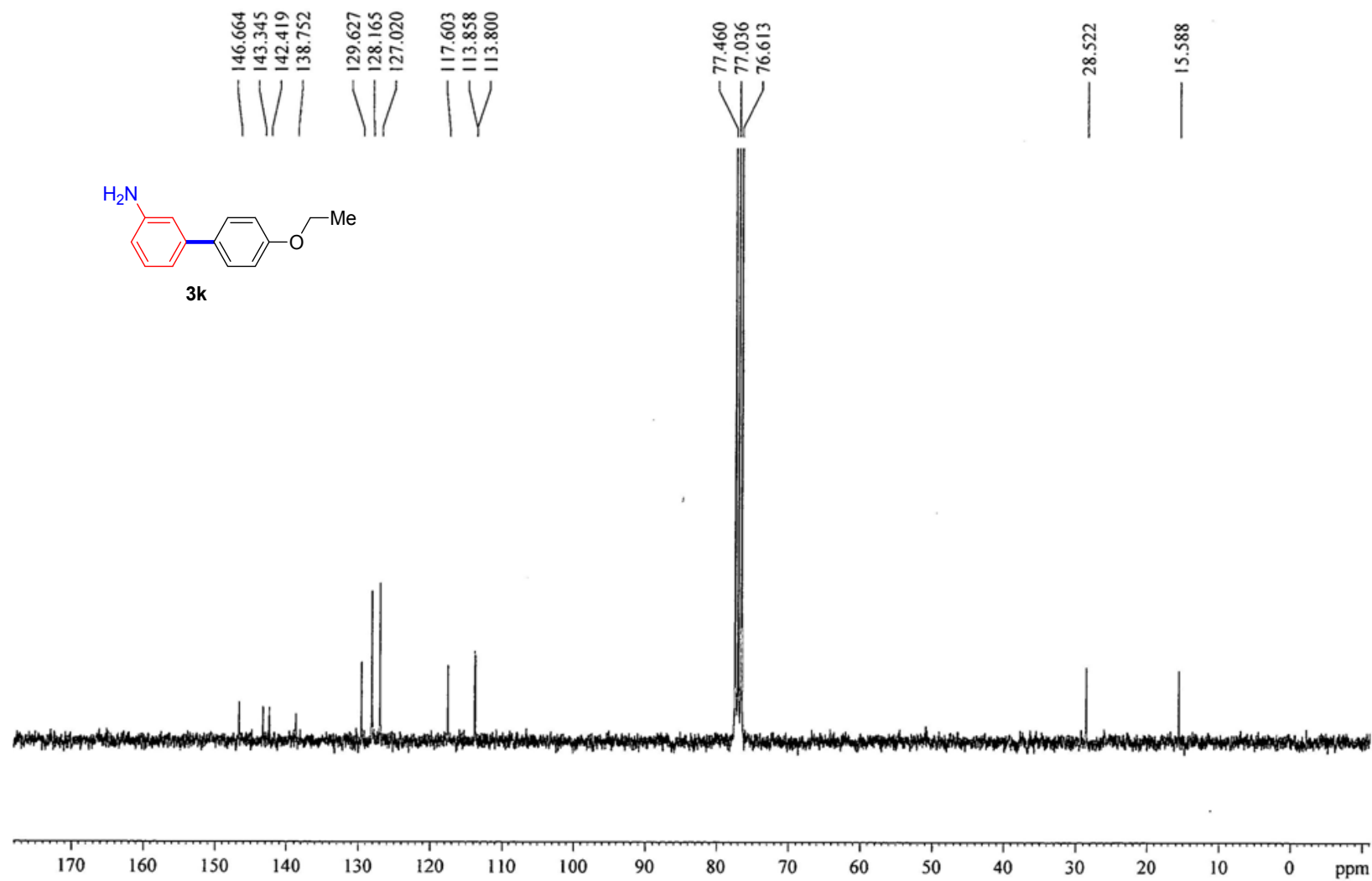
Spectrum19. 300 MHz <sup>1</sup>H NMR of compound **3j**



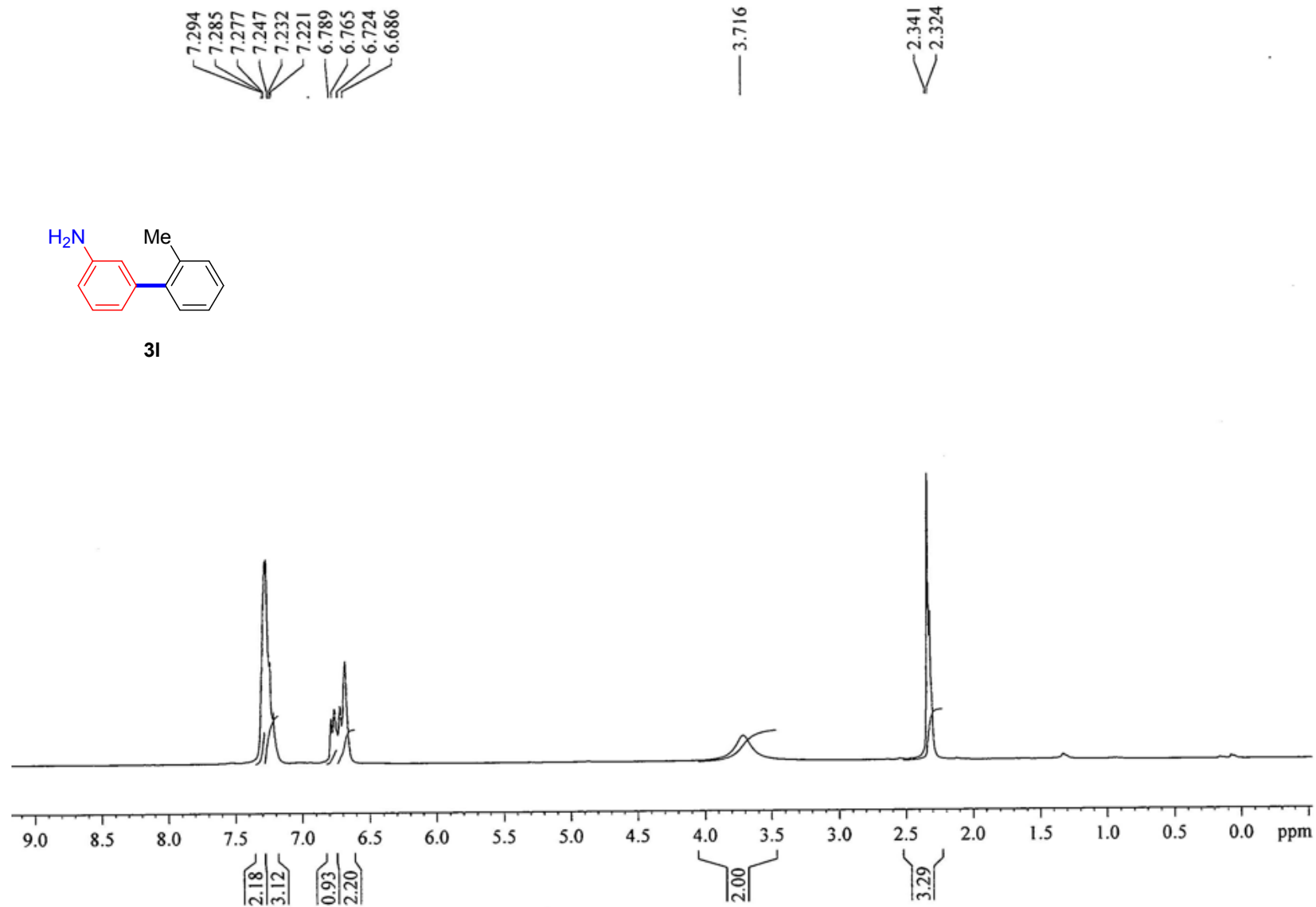
**Spectrum20.** 75 MHz  $^{13}\text{C}$  NMR of compound **3j**



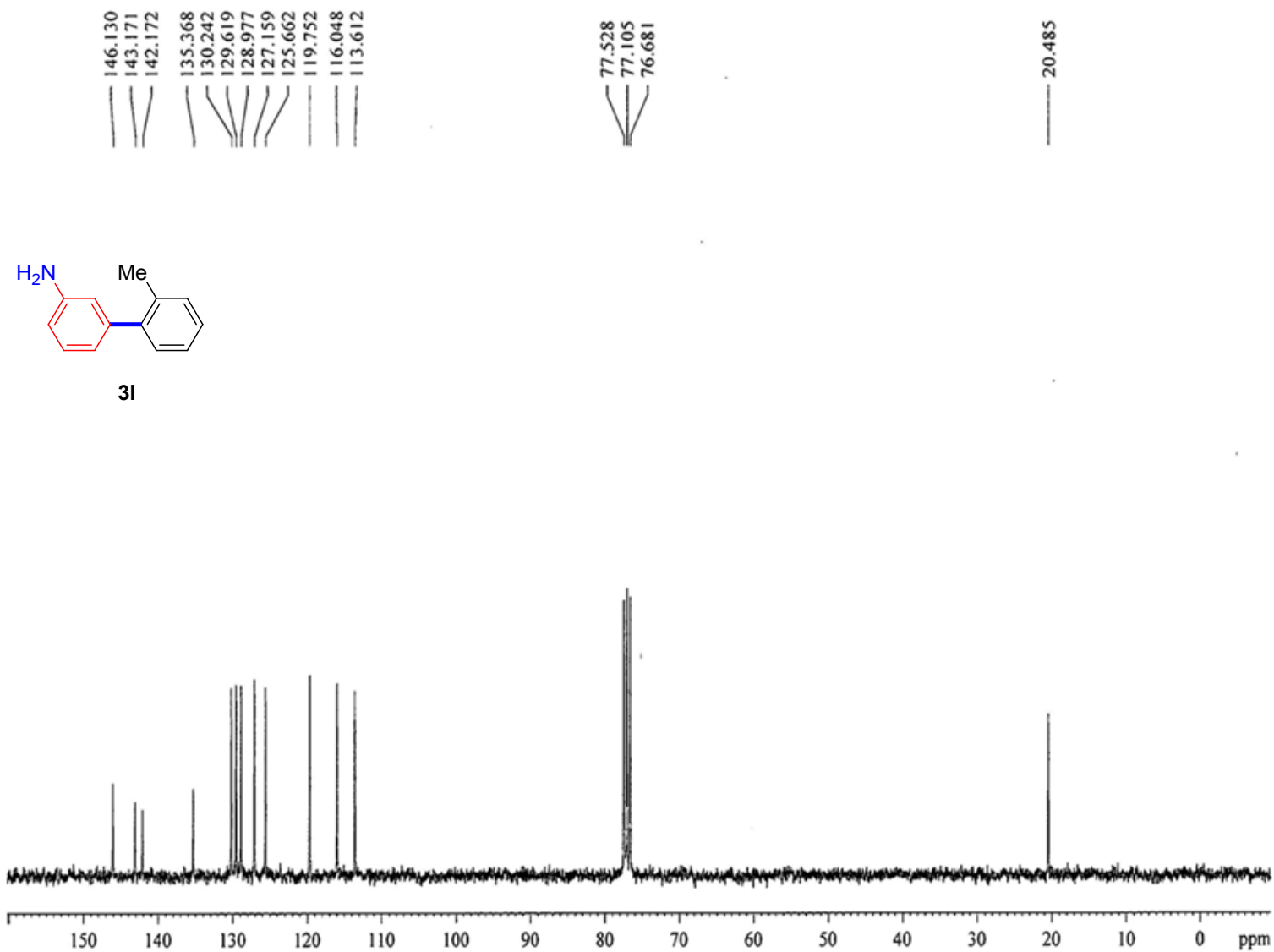
**Spectrum21.** 300 MHz <sup>1</sup>H NMR of compound **3k**

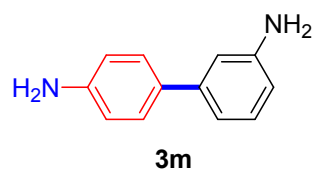


**Spectrum22.** 75 MHz  $^{13}\text{C}$  NMR of compound **3k**



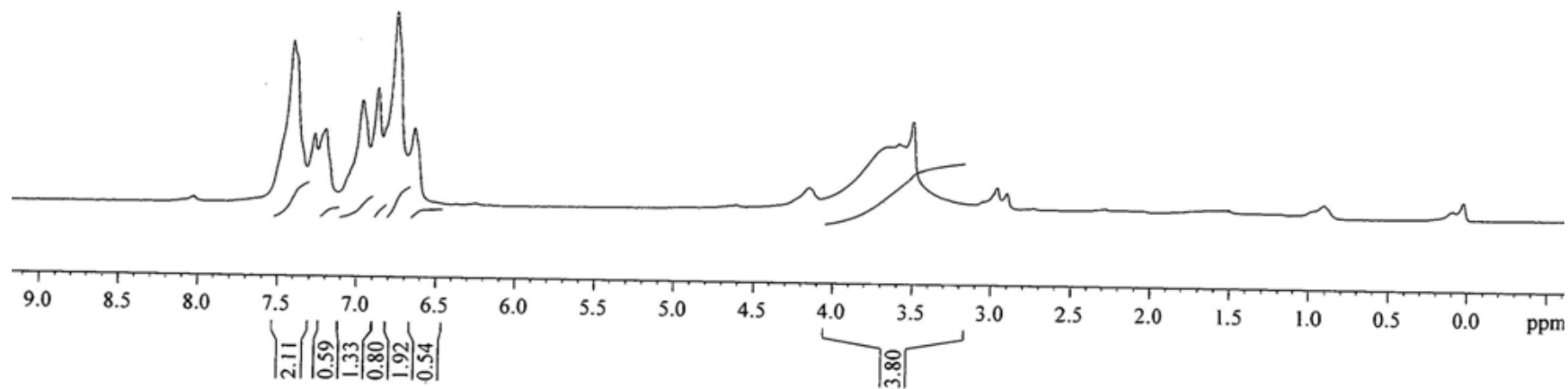
**Spectrum23.** 300 MHz <sup>1</sup>H NMR of compound **3I**



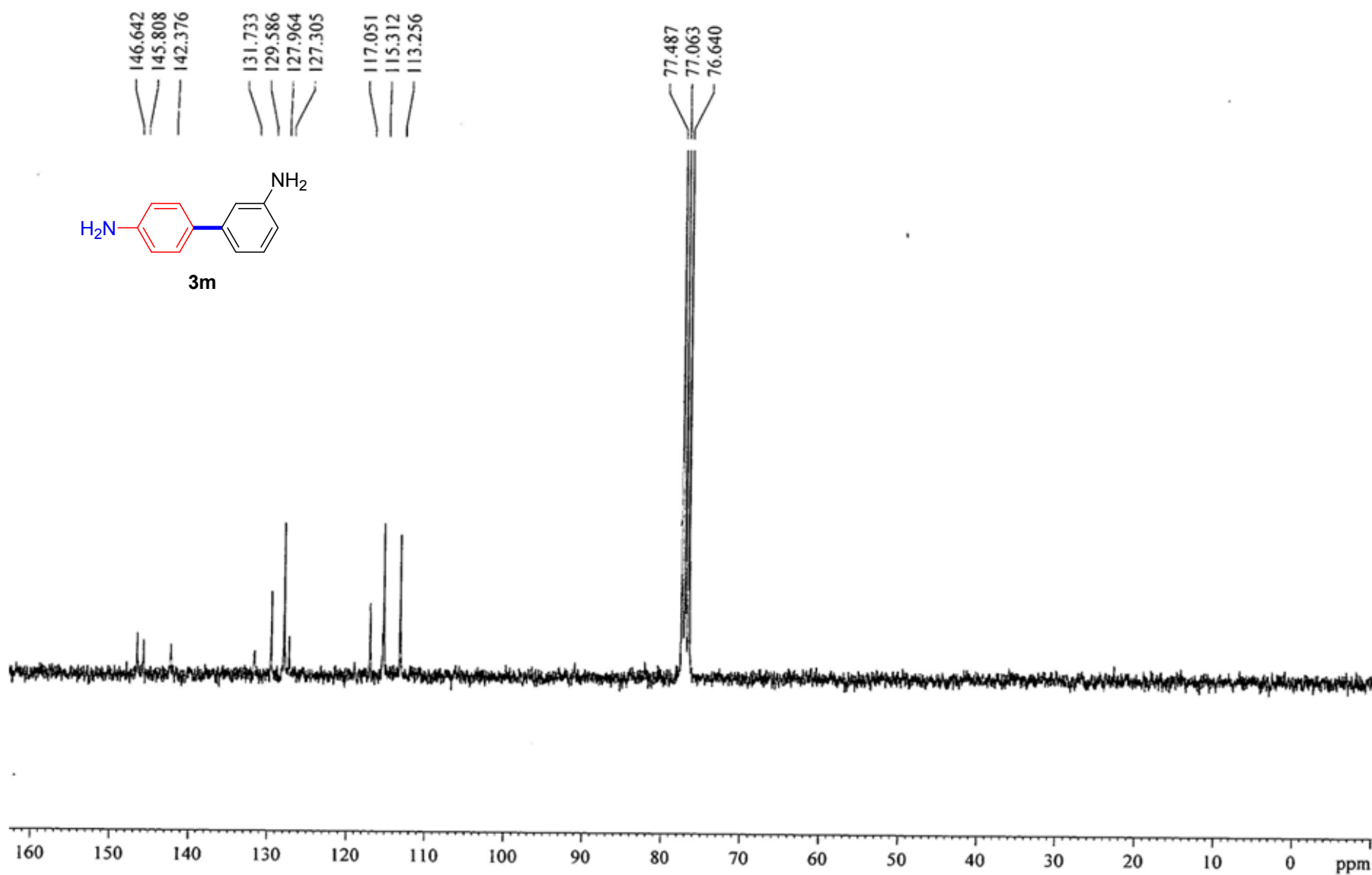


7.413  
 7.273  
 7.205  
 6.971  
 6.877  
 6.761  
 6.643

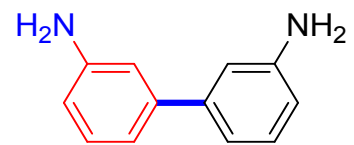
4.151  
 3.994



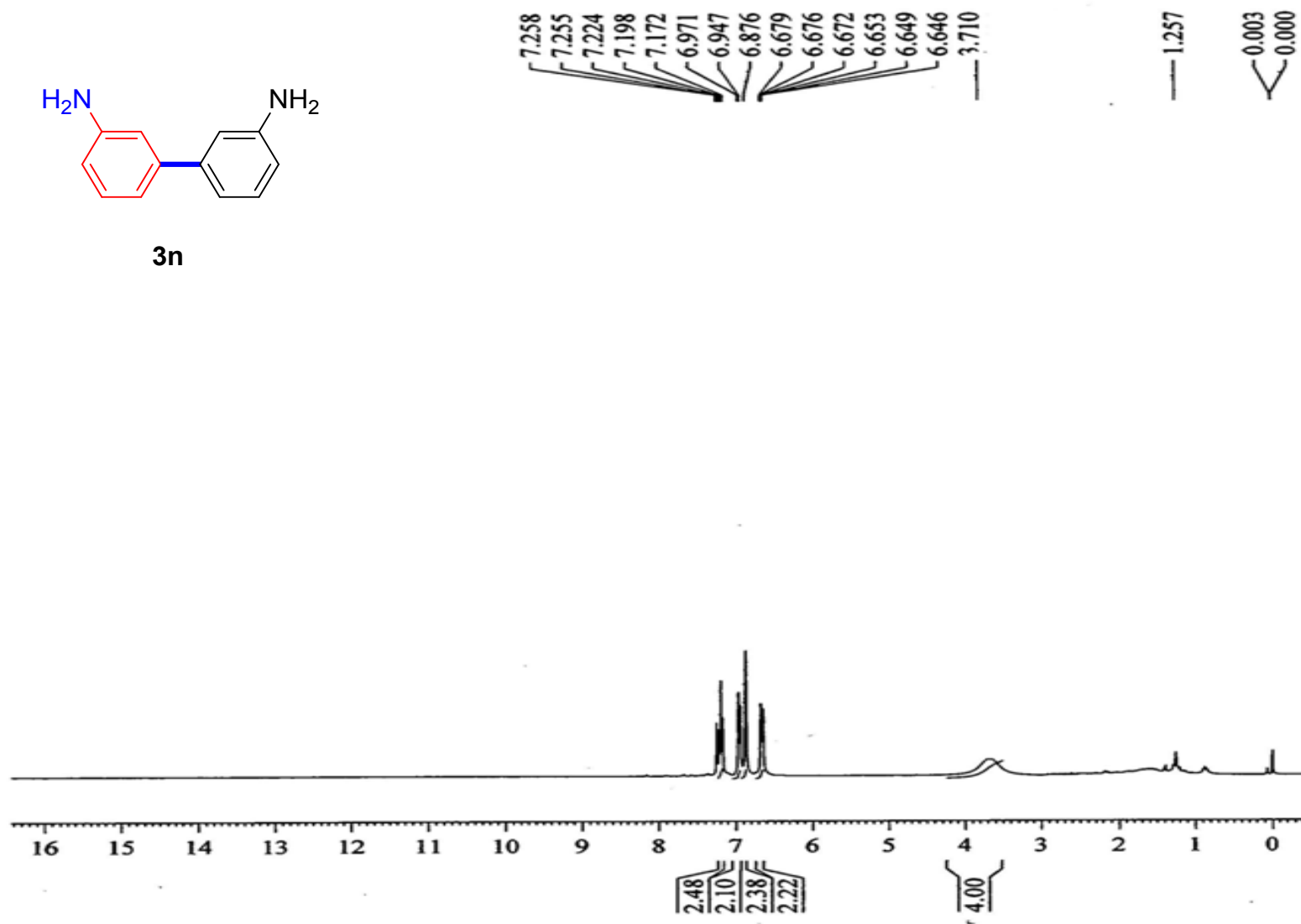
**Spectrum25.** 300 MHz  $^1\text{H}$  NMR of compound **3m**



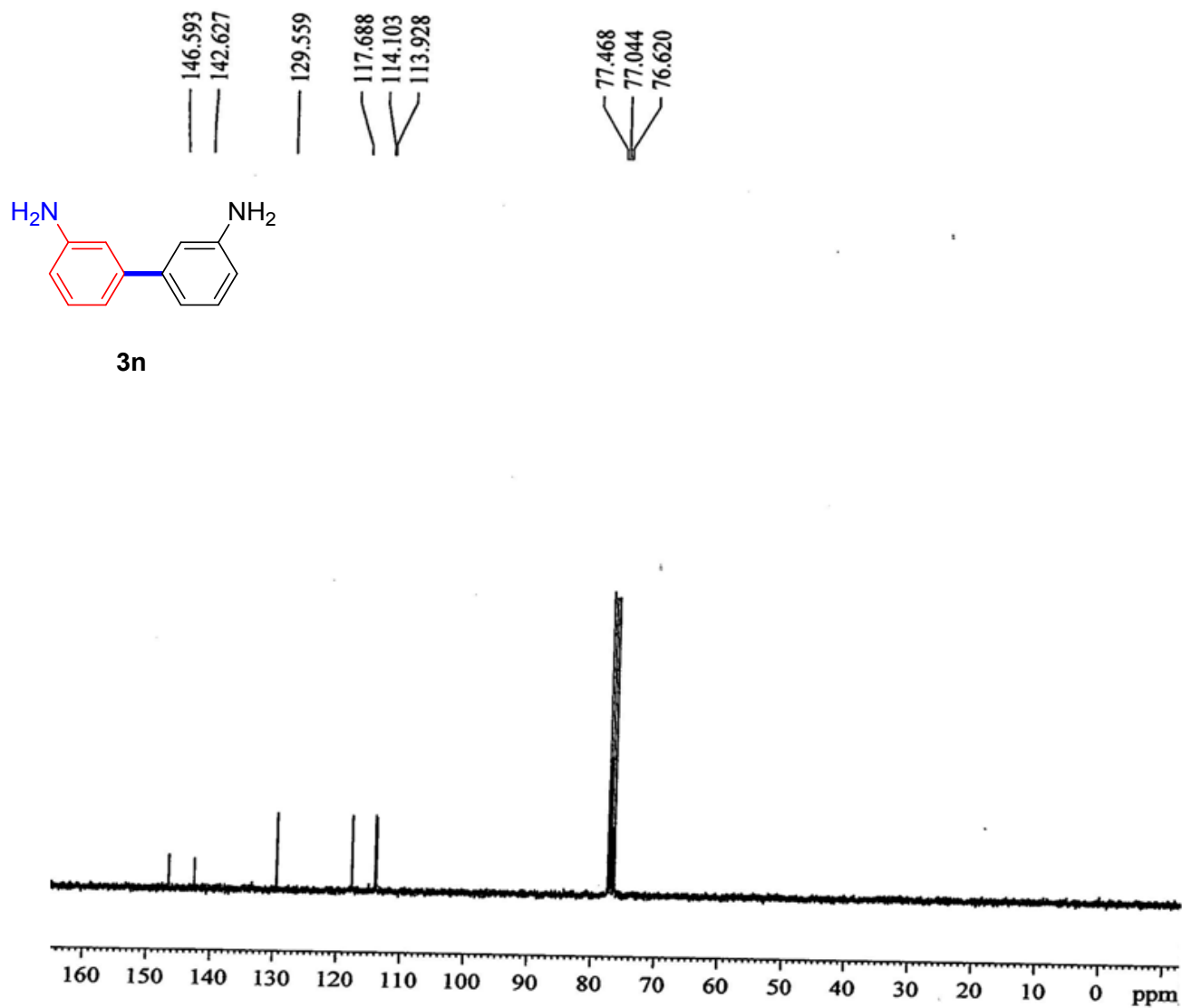
**Spectrum26.** 75 MHz  $^{13}\text{C}$  NMR of compound **3m**



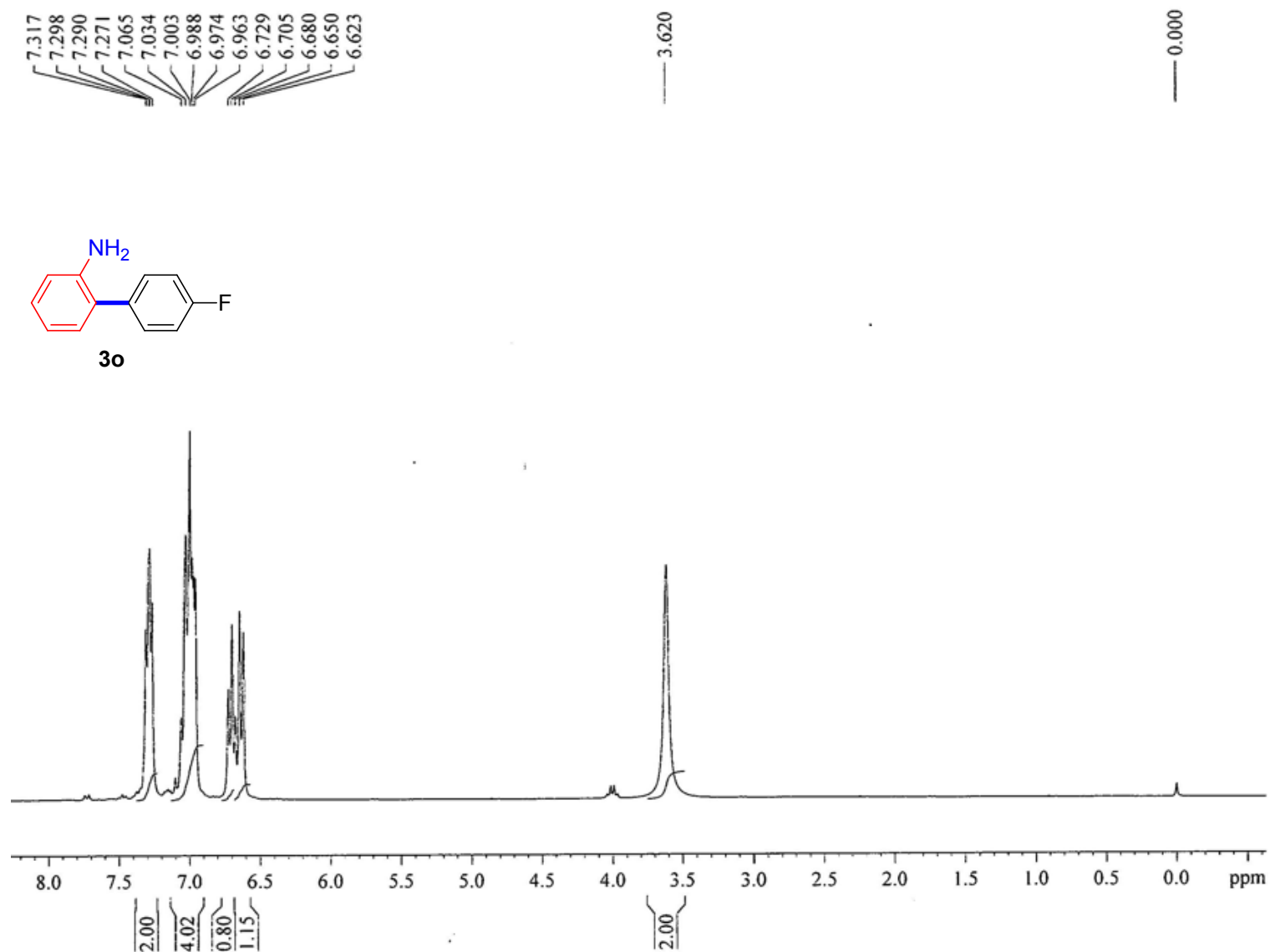
**3n**



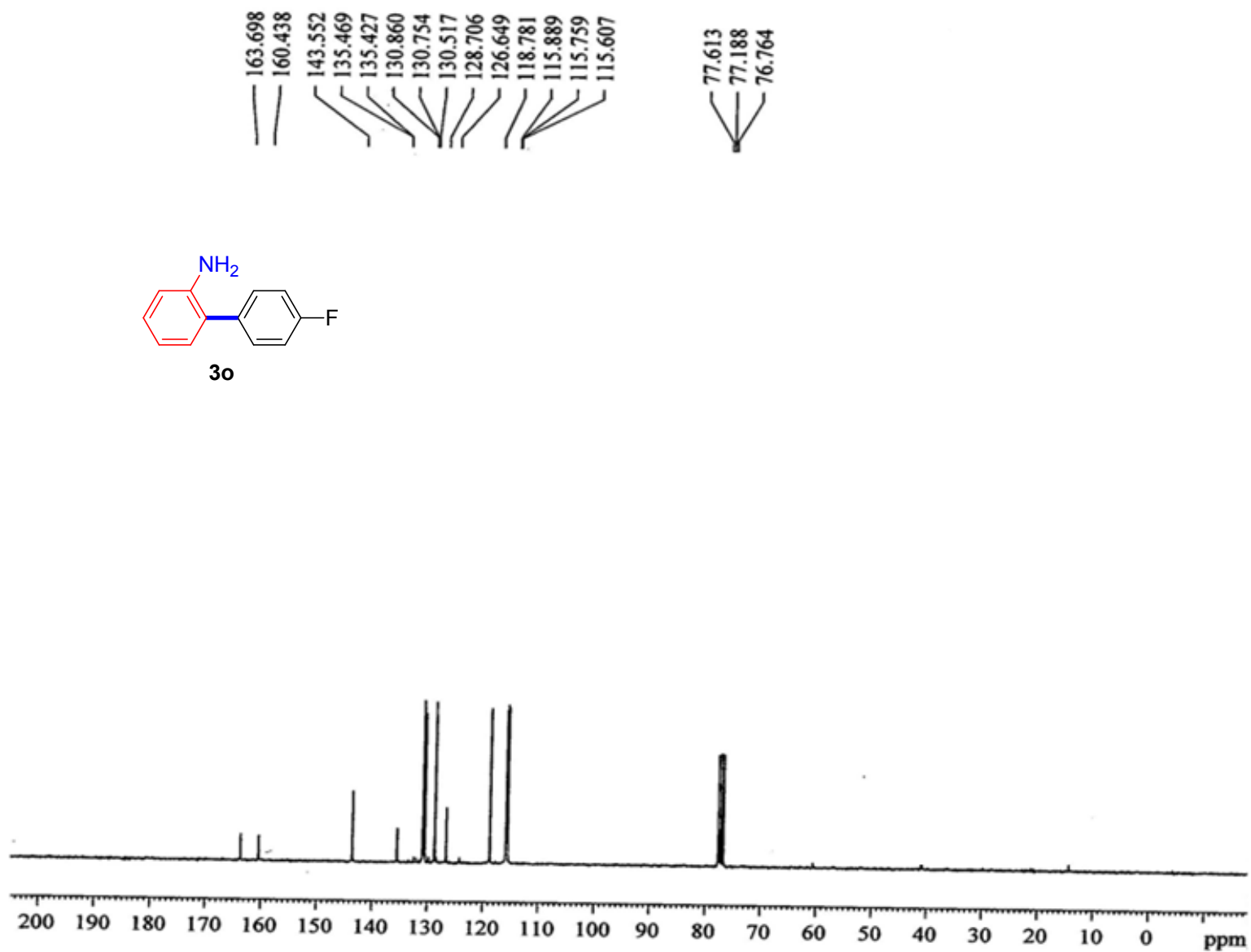
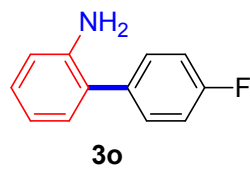
**Spectrum27.** 300 MHz  $^1\text{H}$  NMR of compound **3n**



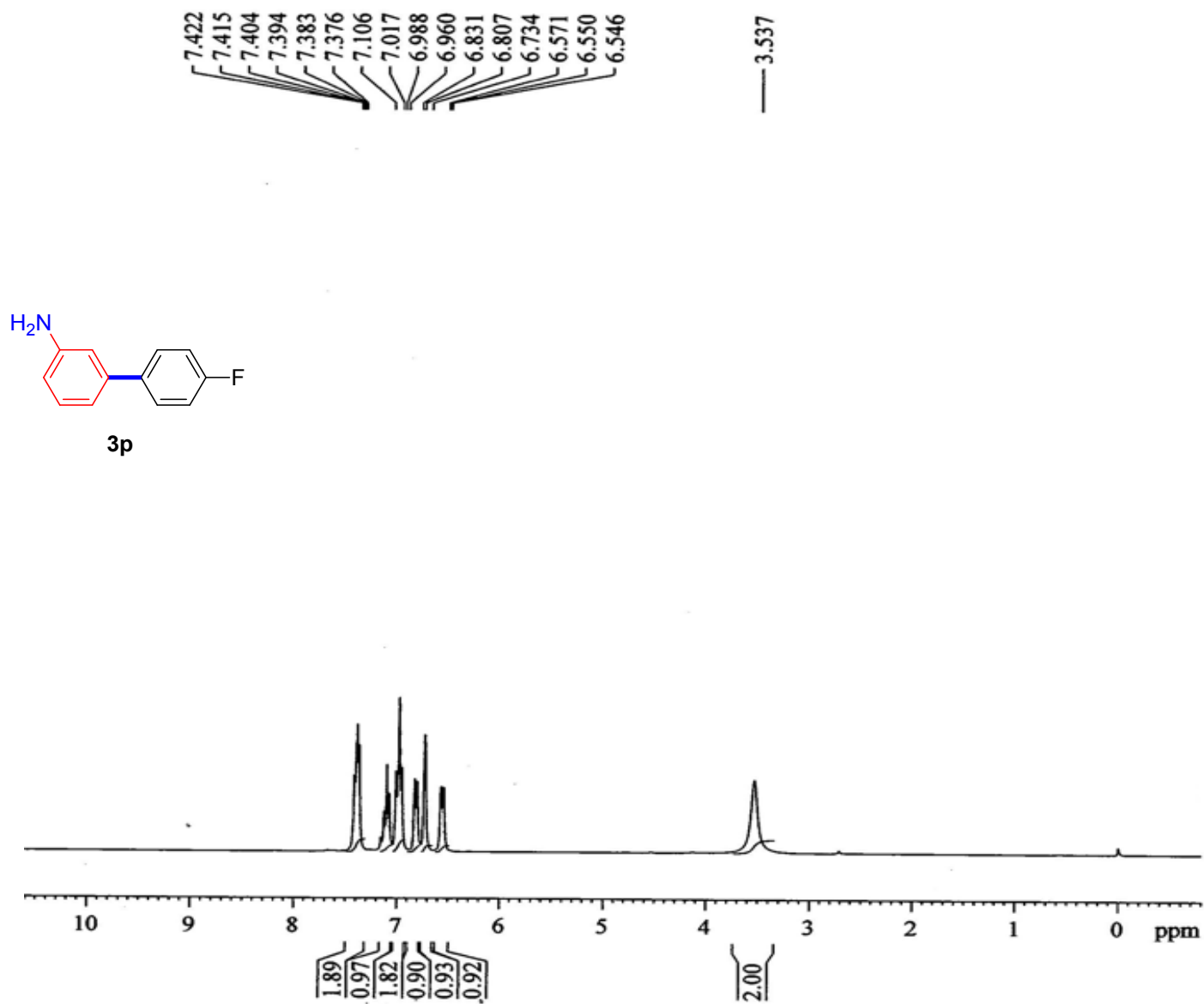
Spectrum28. 75 MHz  $^{13}\text{C}$  NMR of compound **3n**



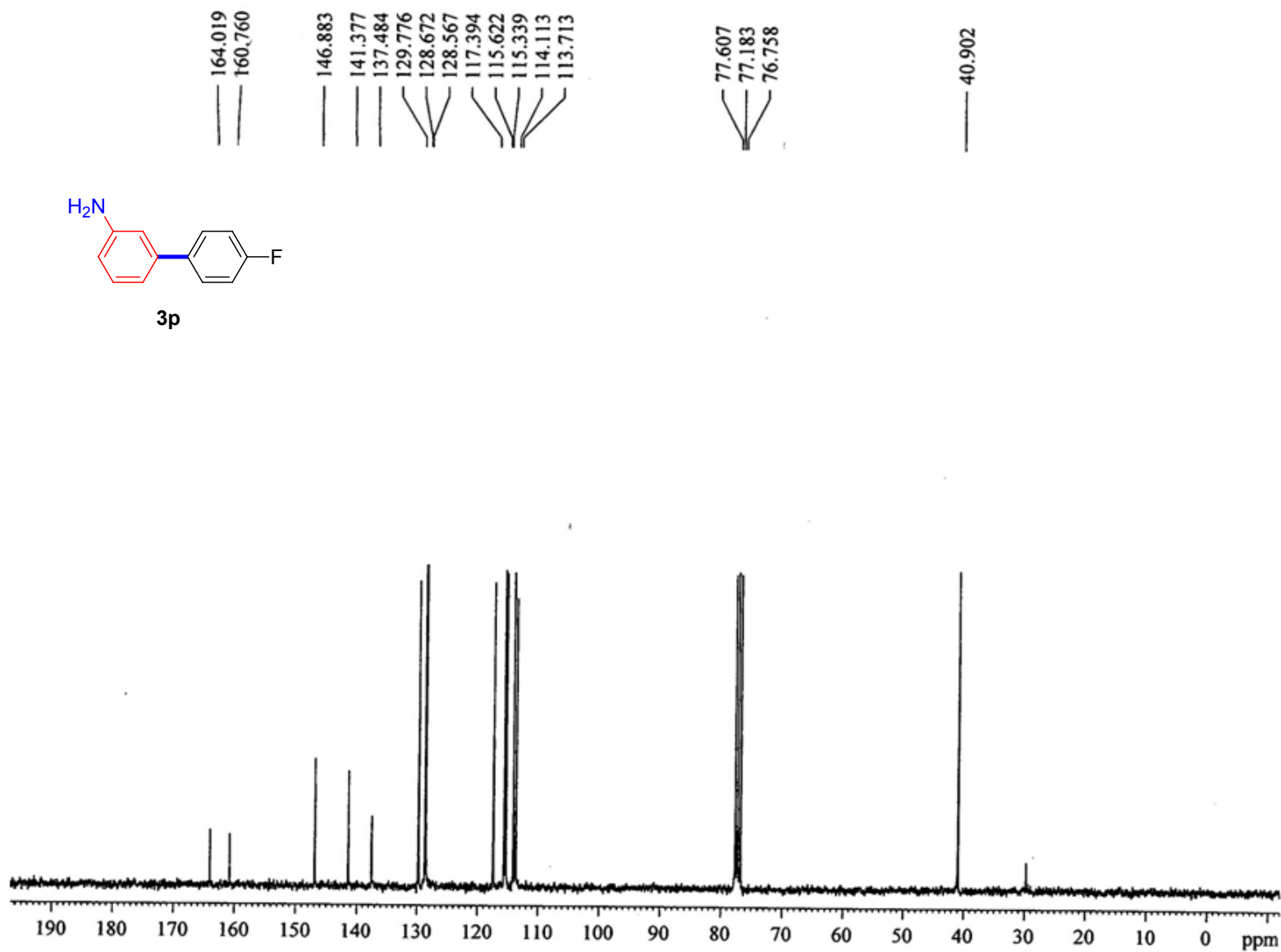
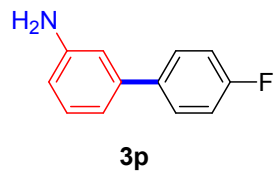
**Spectrum29.** 300 MHz  $^1\text{H}$  NMR of compound **3o**



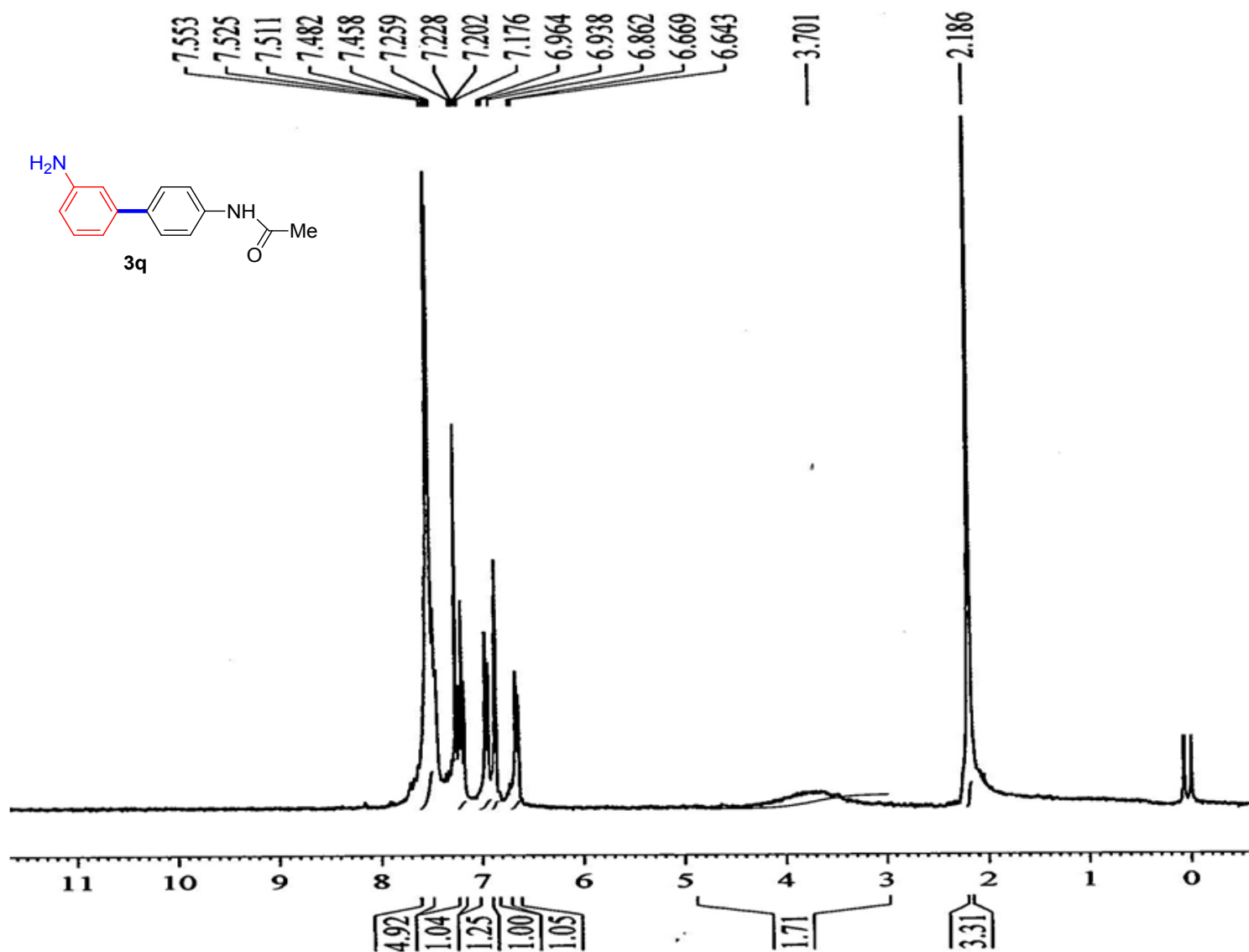
Spectrum30. 75MHz  $^{13}\text{C}$  NMR of compound **3o**



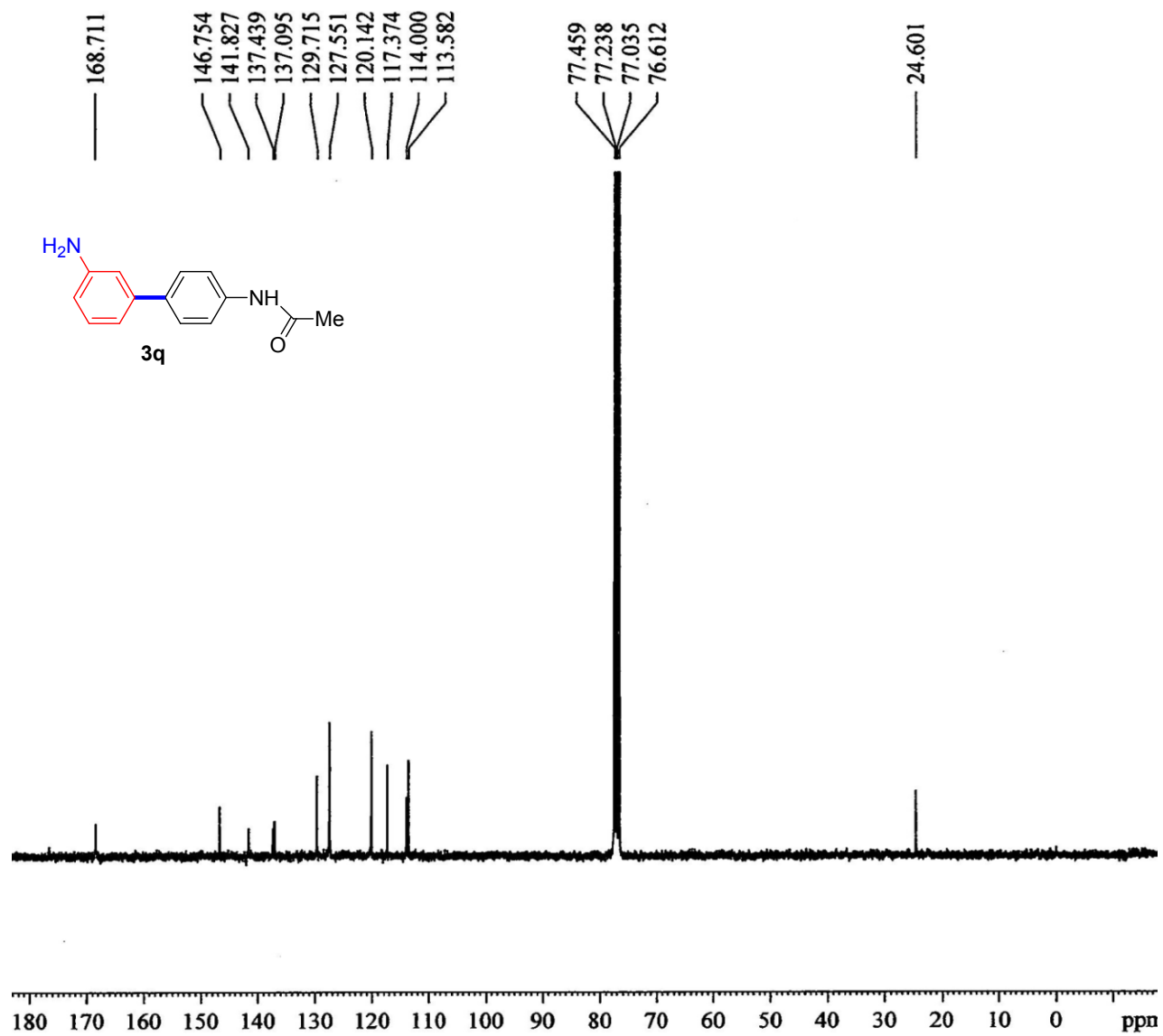
Spectrum31. 300 MHz <sup>1</sup>H NMR of compound **3p**



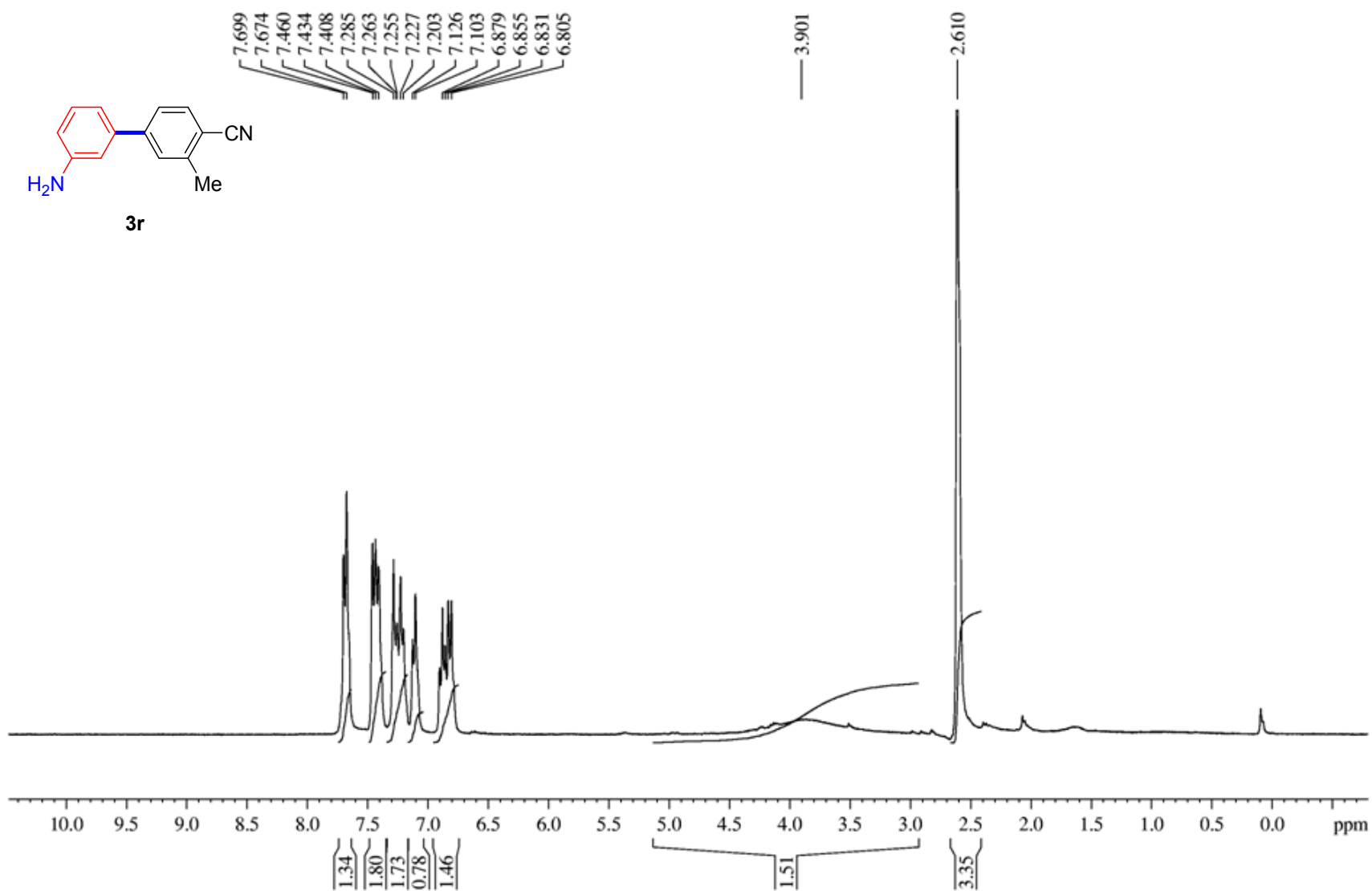
Spectrum32. 75 MHz  $^{13}\text{C}$  NMR of compound **3p**



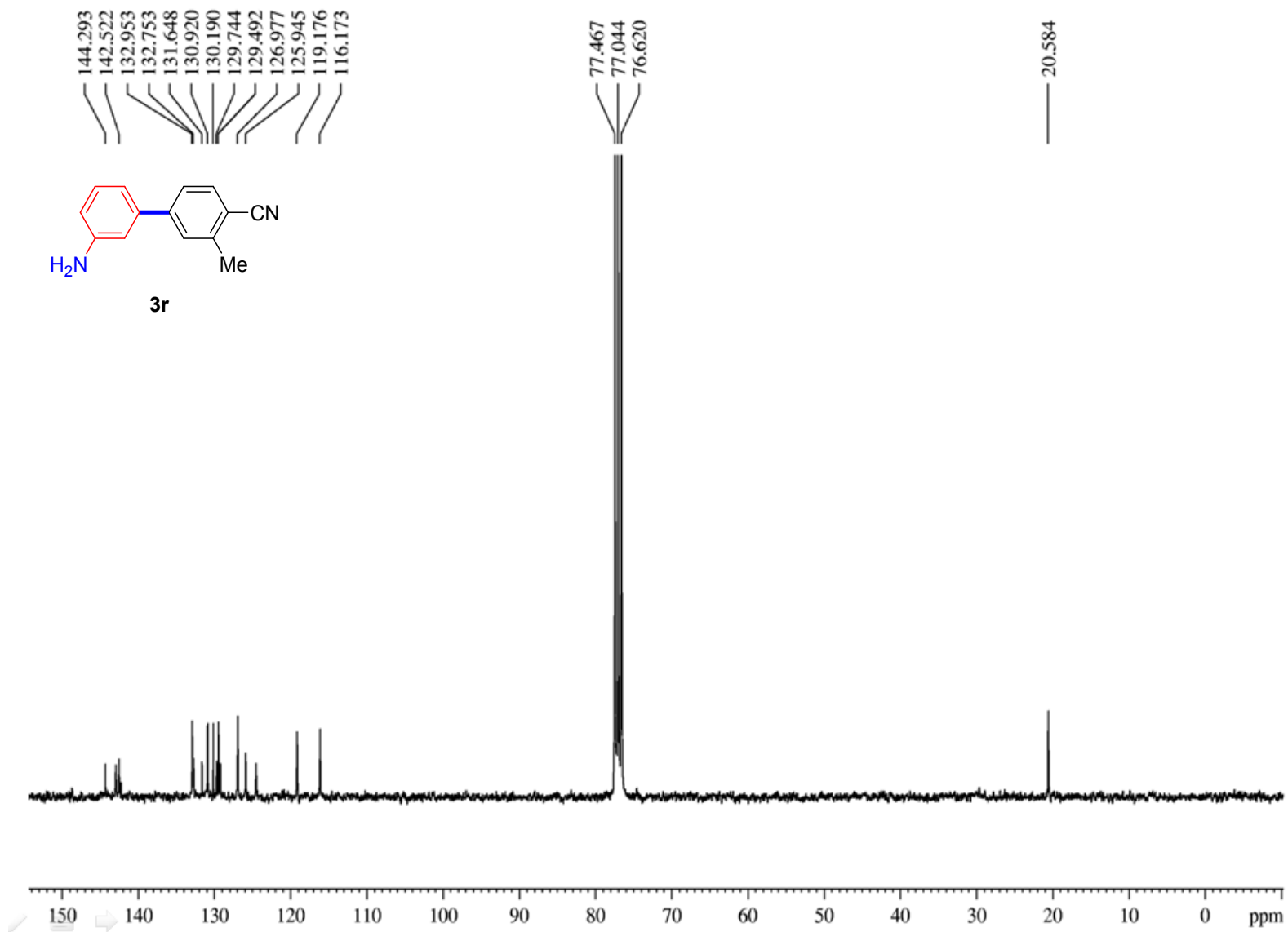
Spectrum33. 300 MHz <sup>1</sup>H NMR of compound **3q**



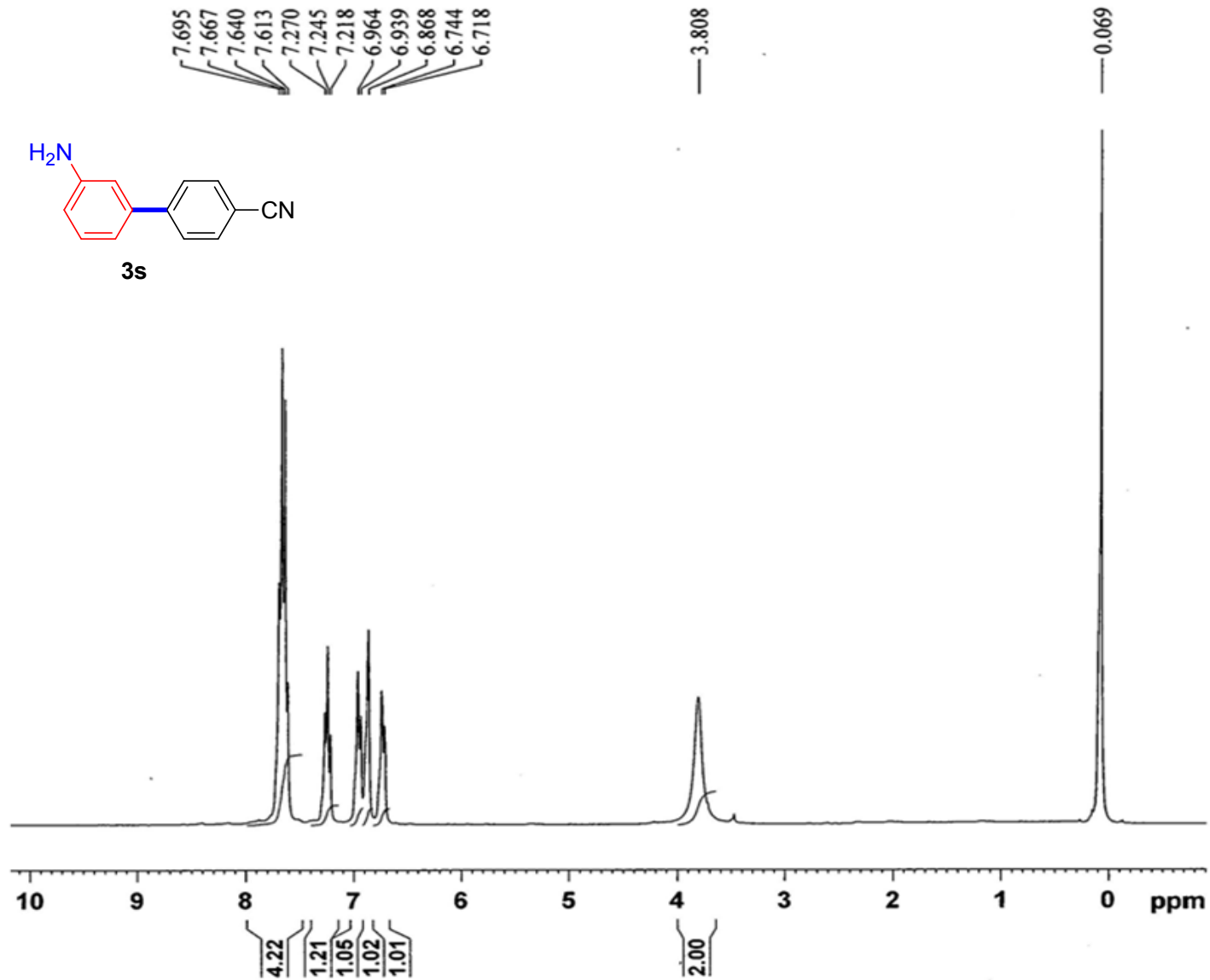
Spectrum34. 75 MHz <sup>13</sup>C NMR of compound **3q**



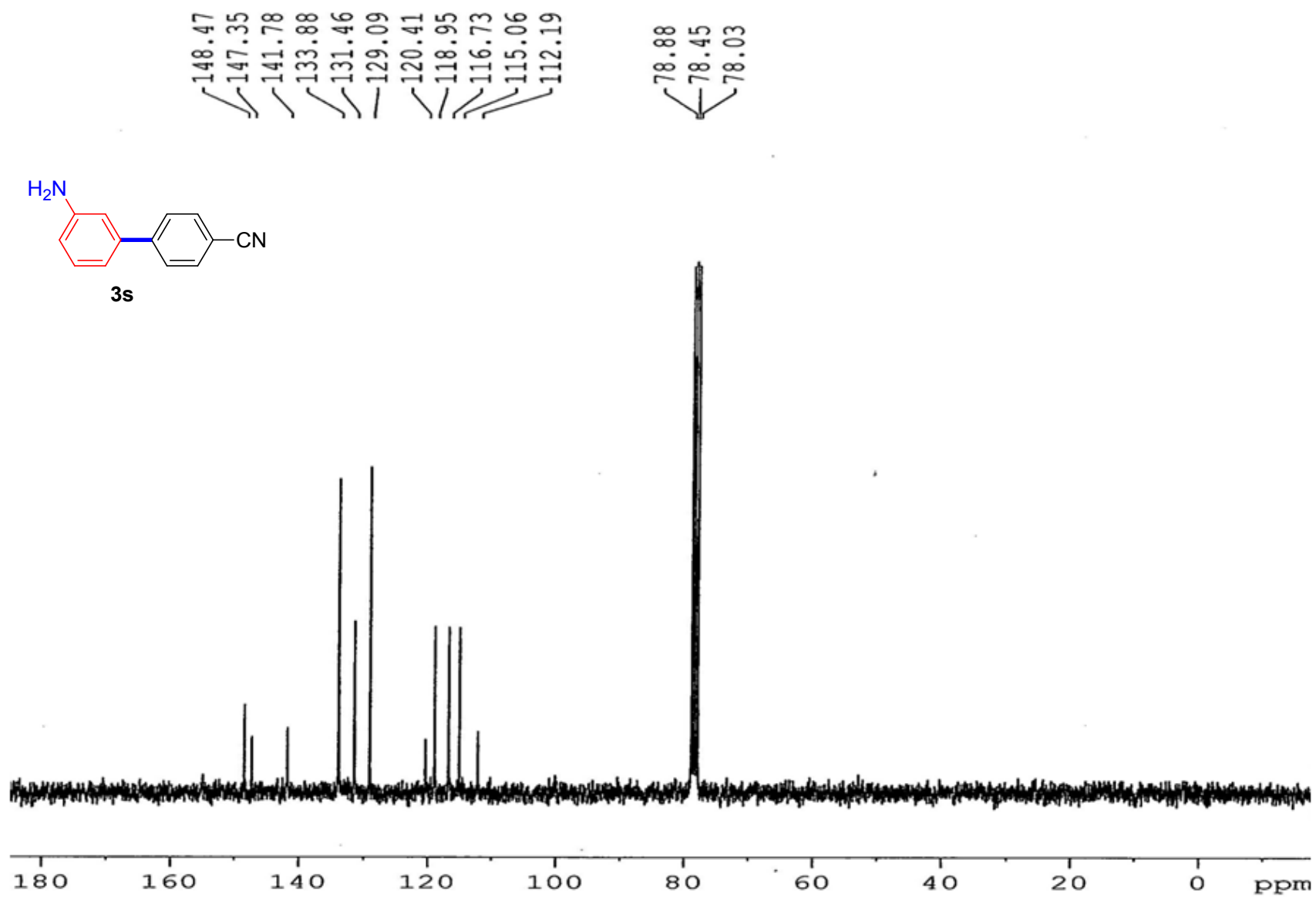
**Spectrum35.** 300 MHz <sup>1</sup>H NMR of compound **3r**



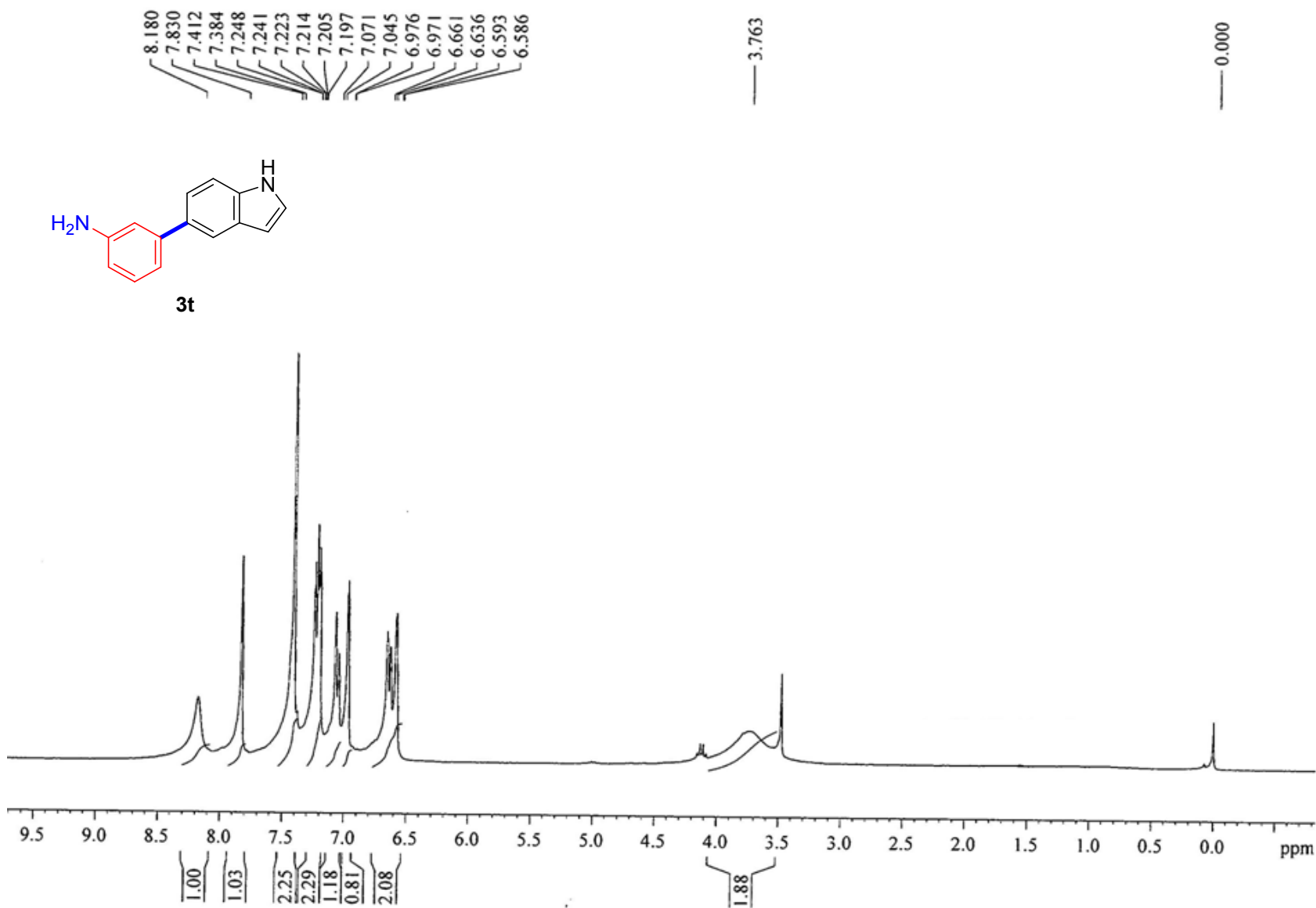
Spectrum36. 75 MHz <sup>13</sup>C NMR of compound **3r**



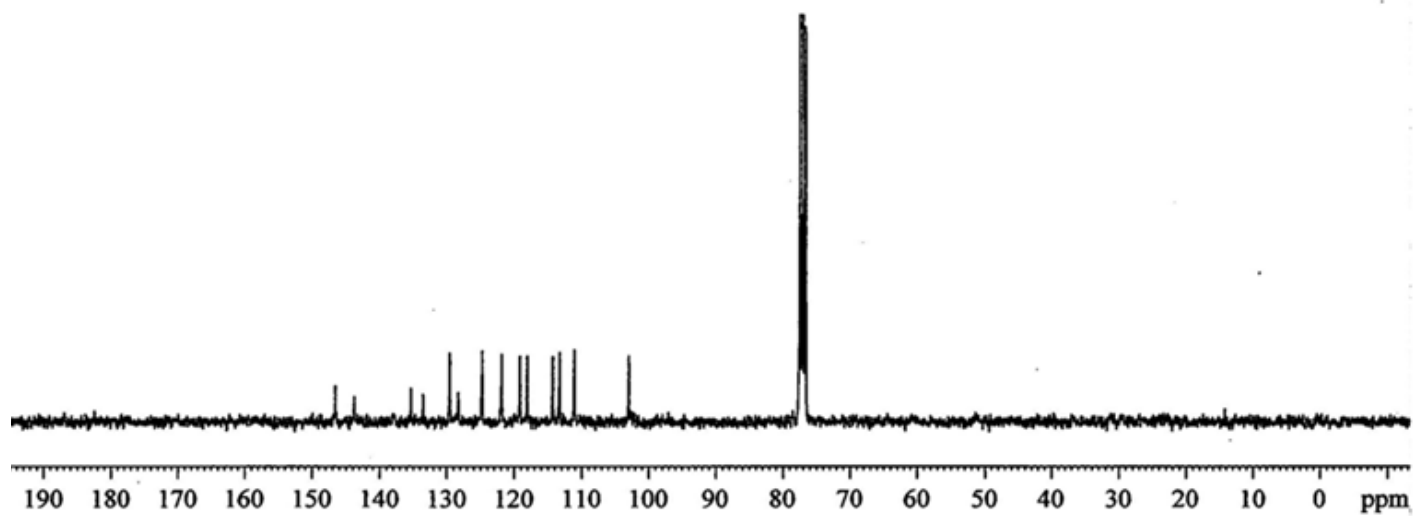
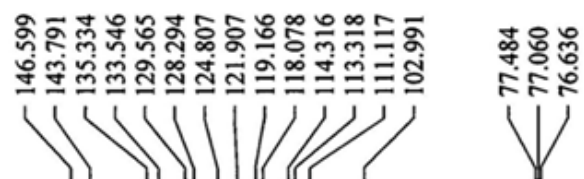
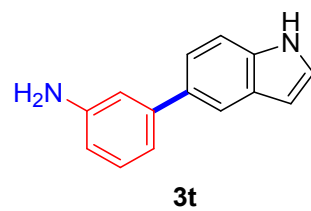
Spectrum37. 300 MHz  $^1\text{H}$  NMR of compound **3s**



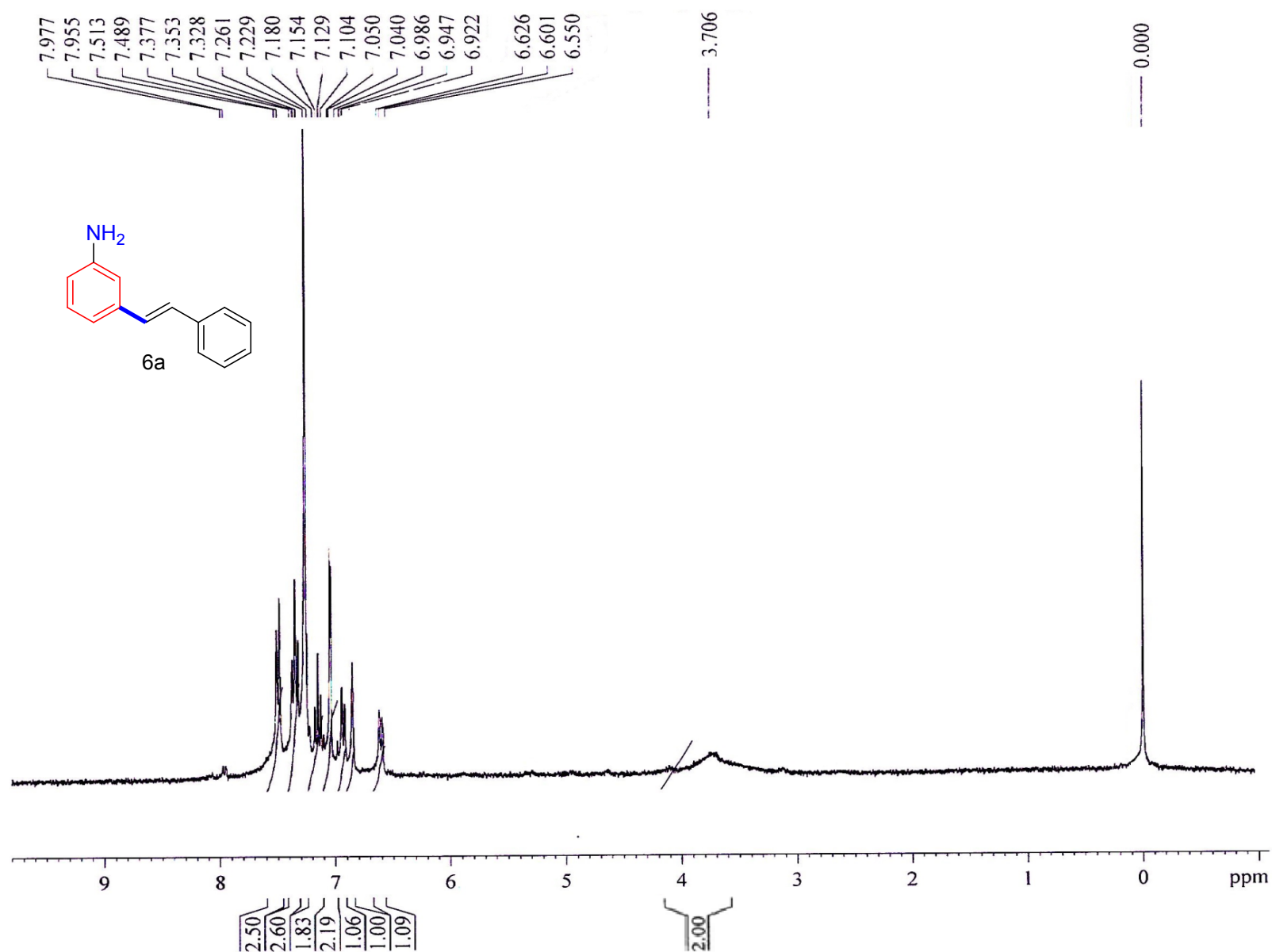
Spectrum38. 75 MHz <sup>13</sup>C NMR of compound **3s**



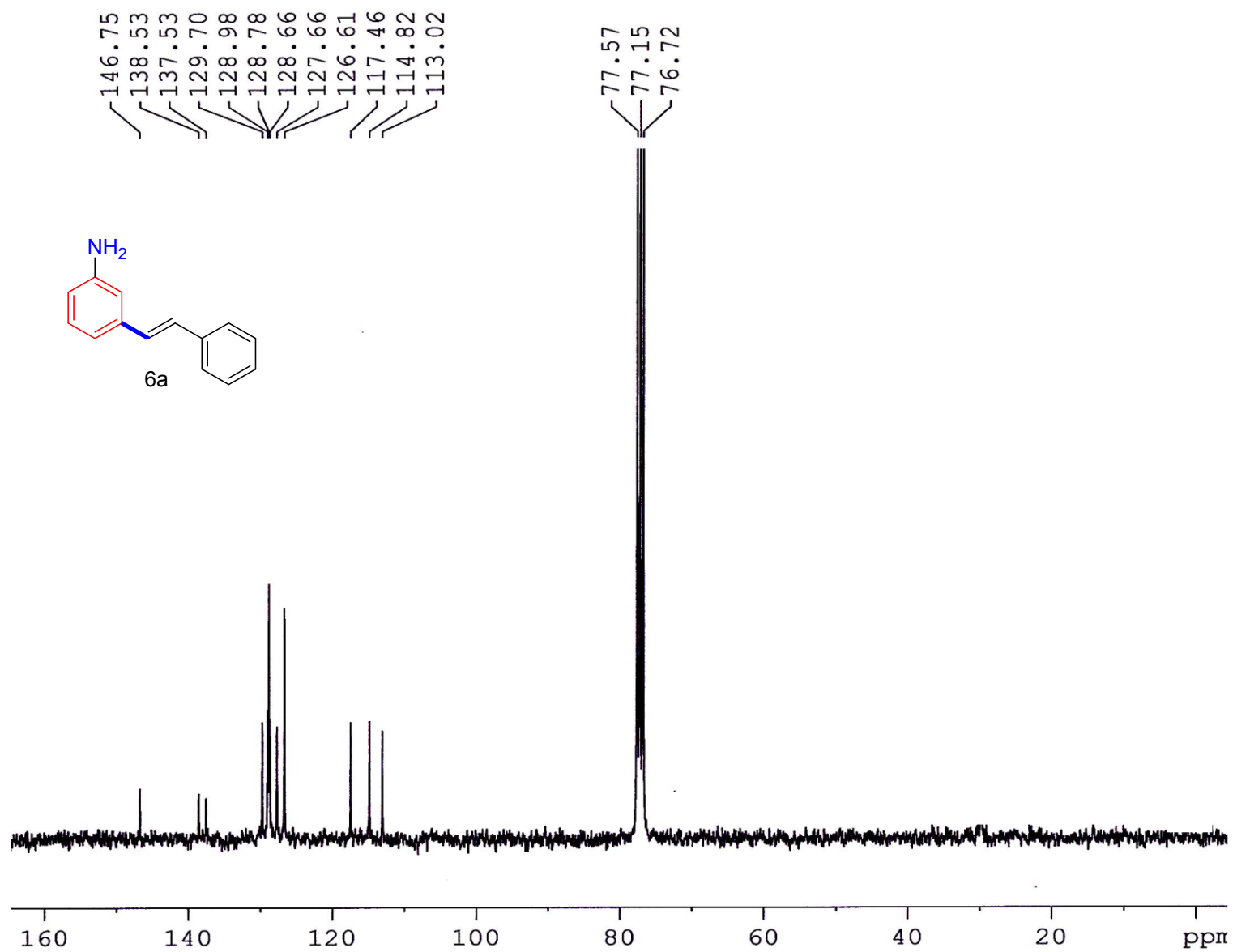
**Spectrum39.** 300 MHz <sup>1</sup>H NMR of compound **3t**



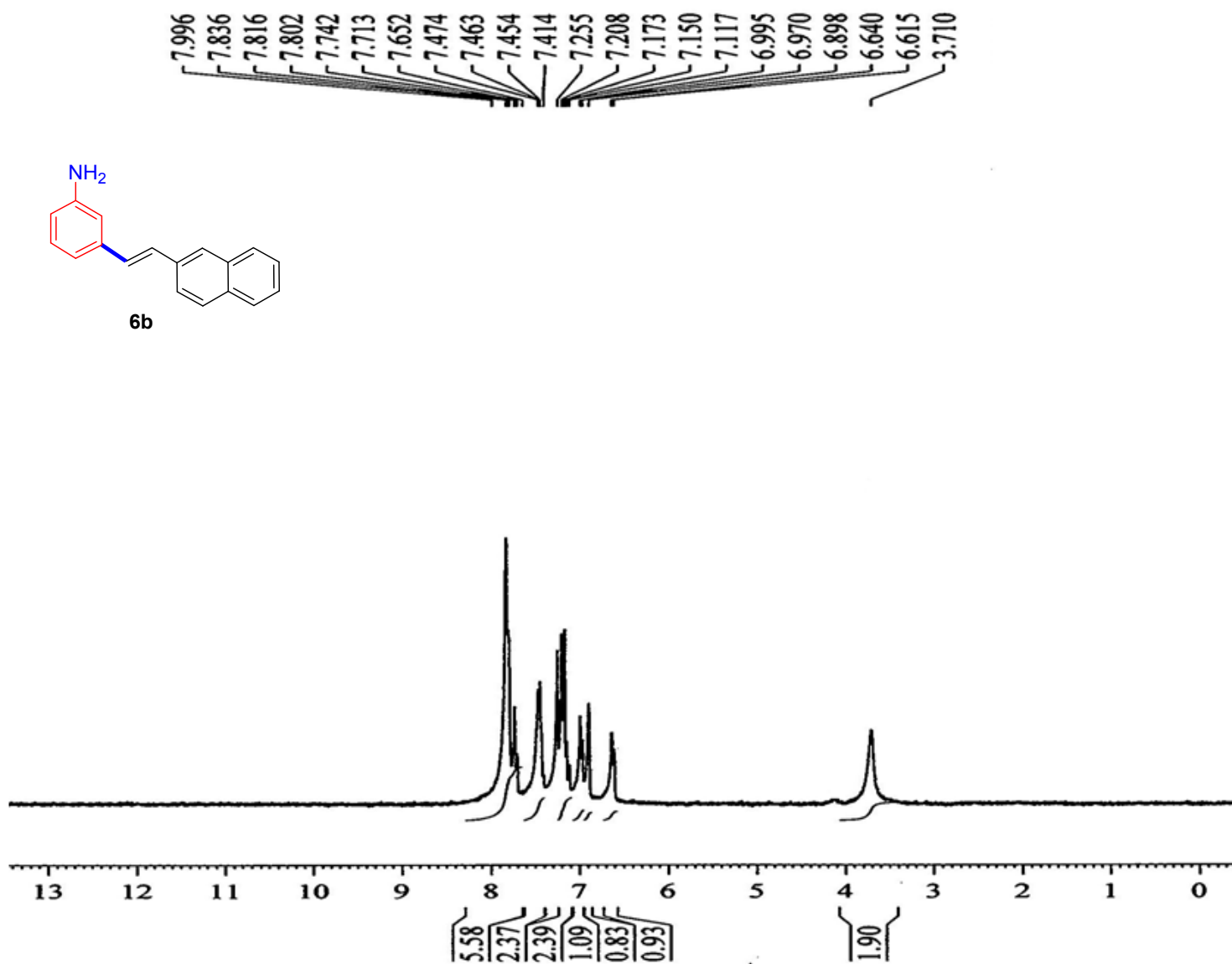
Spectrum40. 75 MHz  $^{13}\text{C}$  NMR of compound 3t



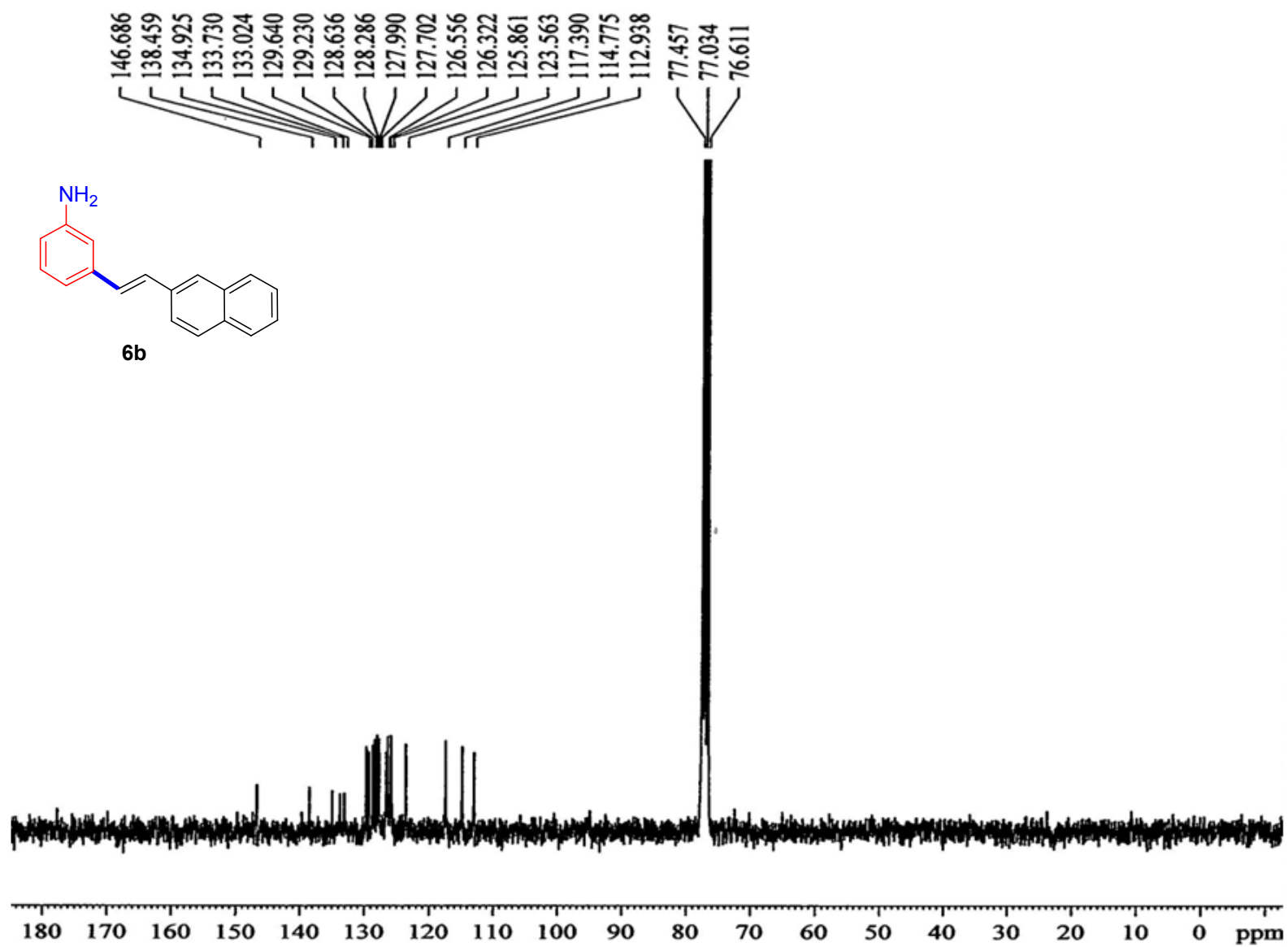
**Spectrum41.** 300 MHz <sup>1</sup>H NMR of compound 6a



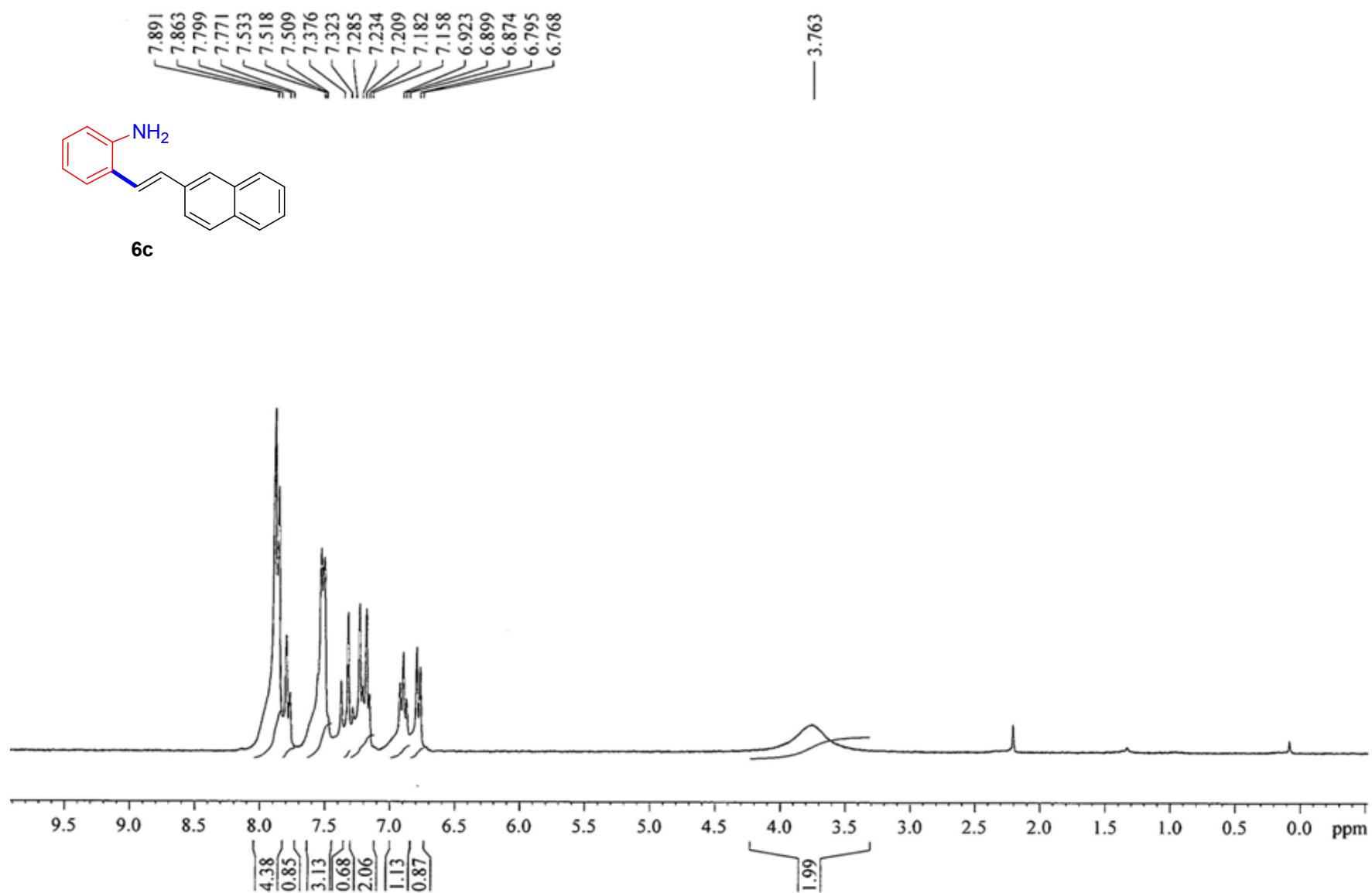
Spectrum42. 75 MHz <sup>13</sup>C NMR of compound 6a



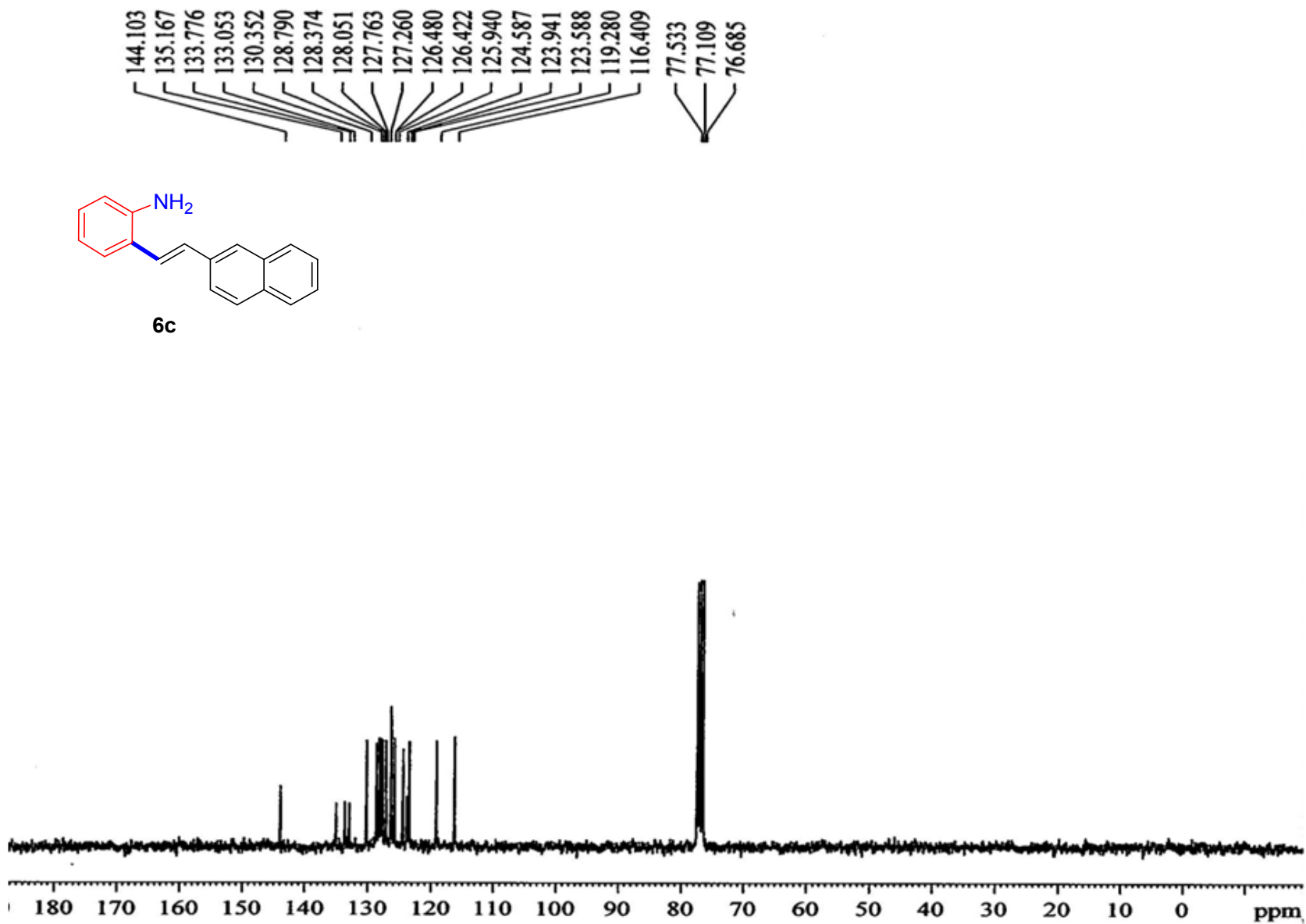
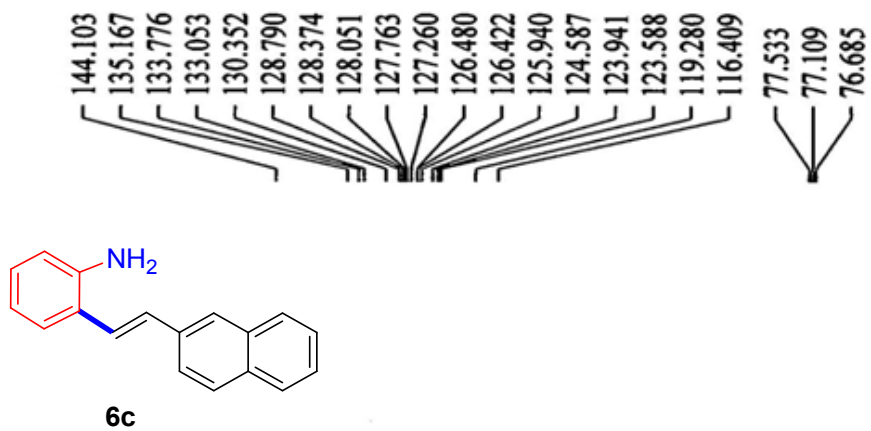
Spectrum 43. 300 MHz <sup>1</sup>H NMR of compound 6a



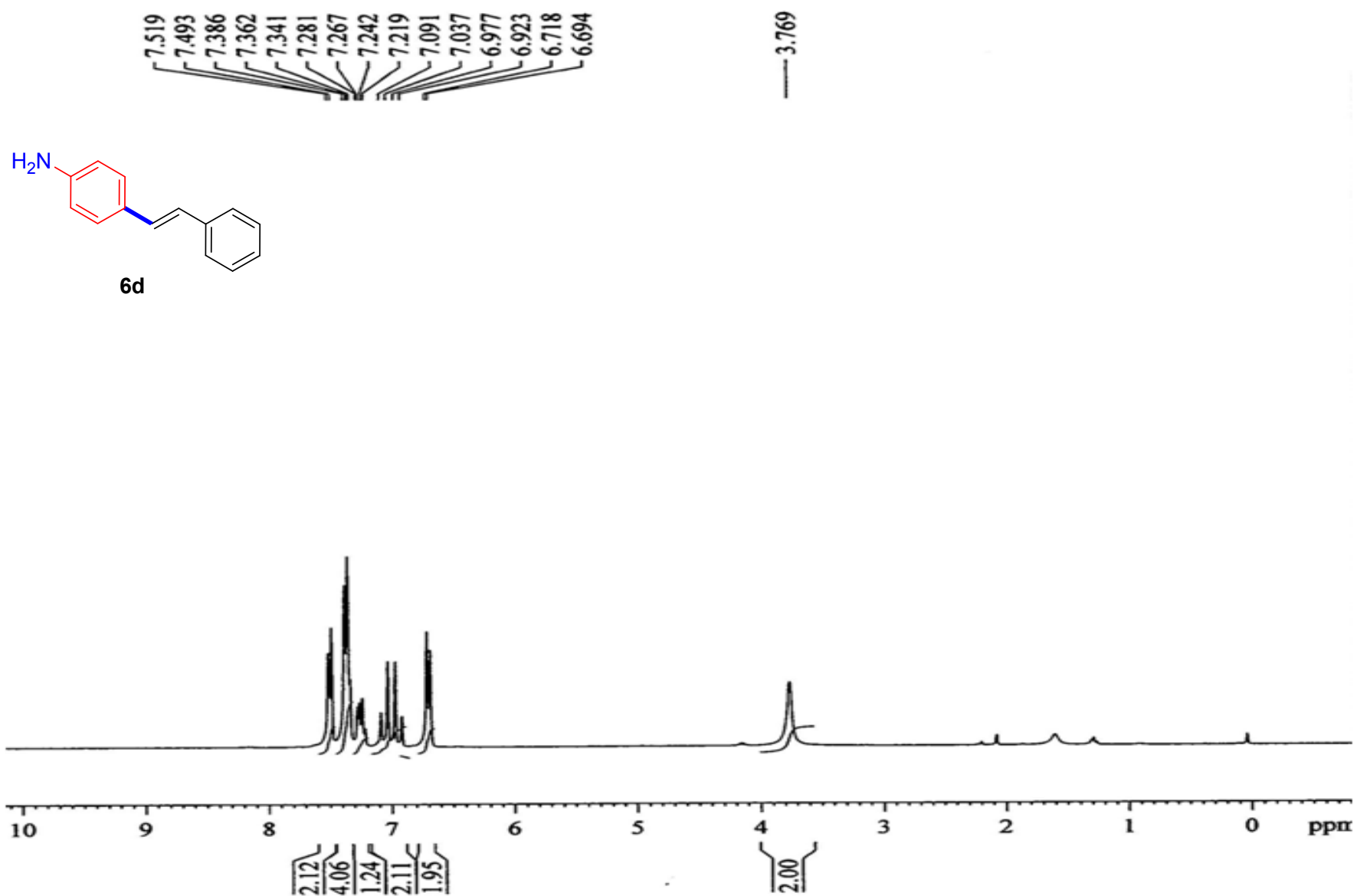
Spectrum44. 75 MHz <sup>13</sup>C NMR of compound **6b**



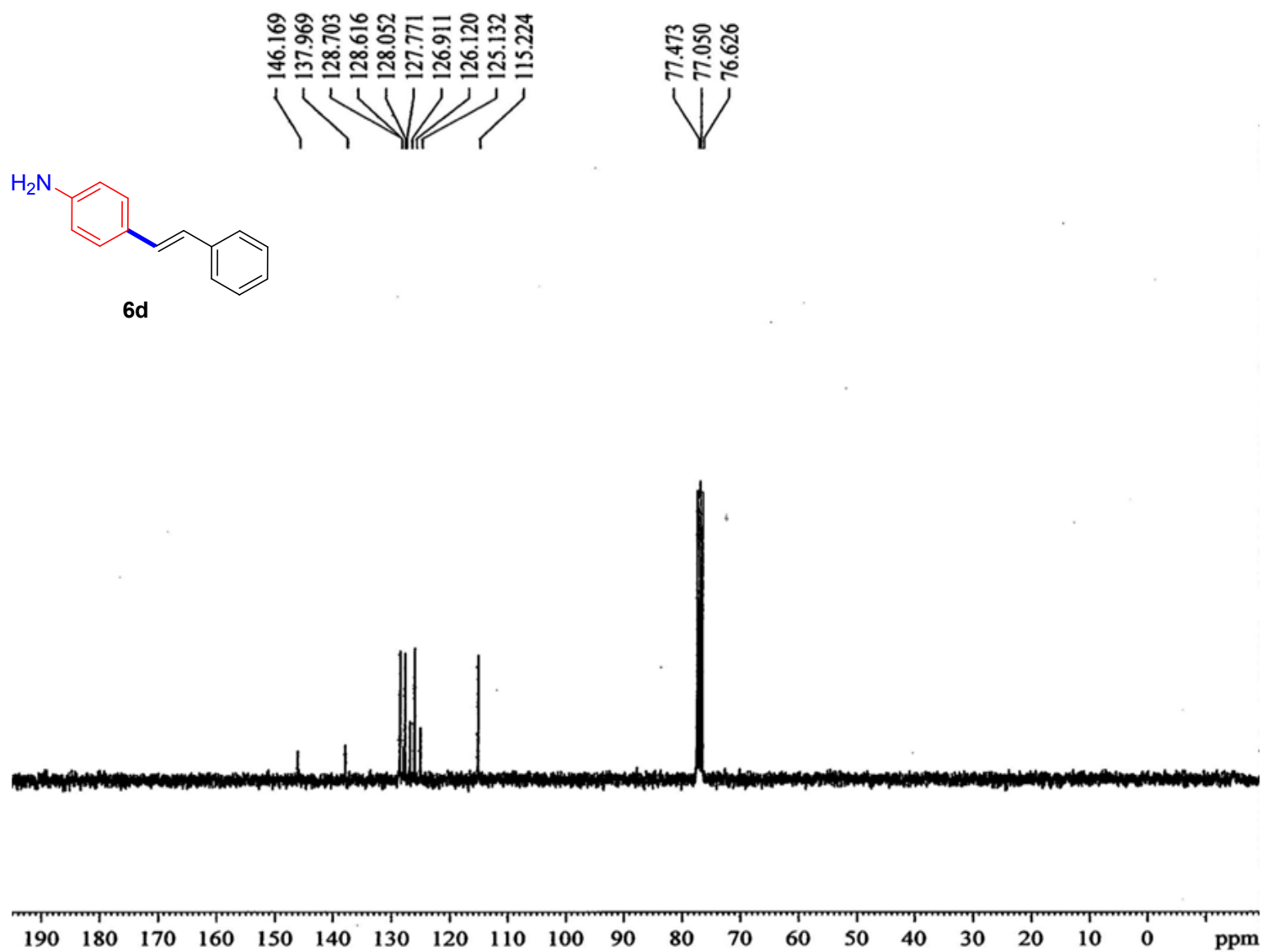
**Spectrum45.** 300 MHz <sup>1</sup>H NMR of compound **6c**



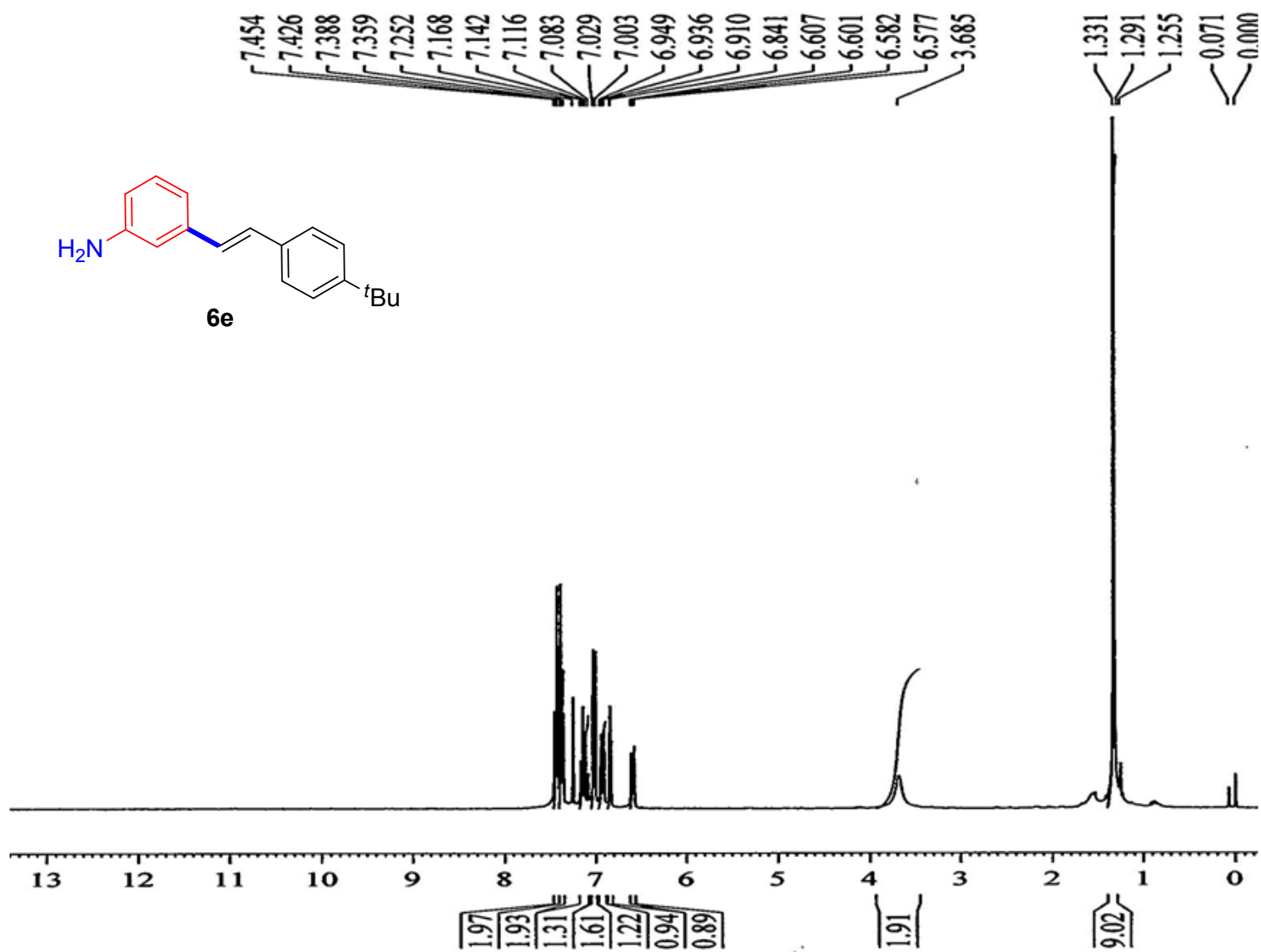
Spectrum46. 75 MHz  $^{13}\text{C}$  NMR of compound 6c



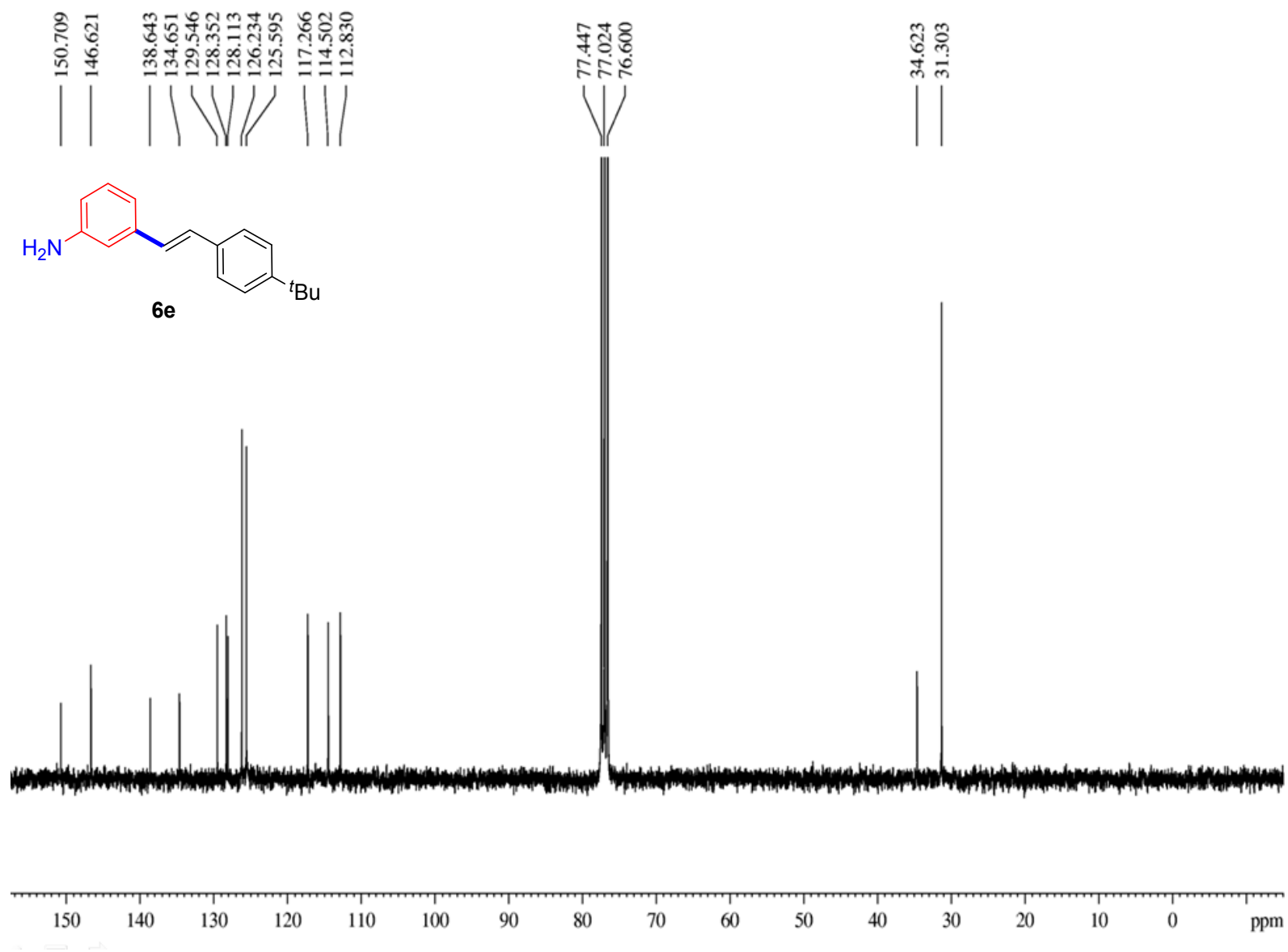
Spectrum 47. 300 MHz <sup>1</sup>H NMR of compound **6d**



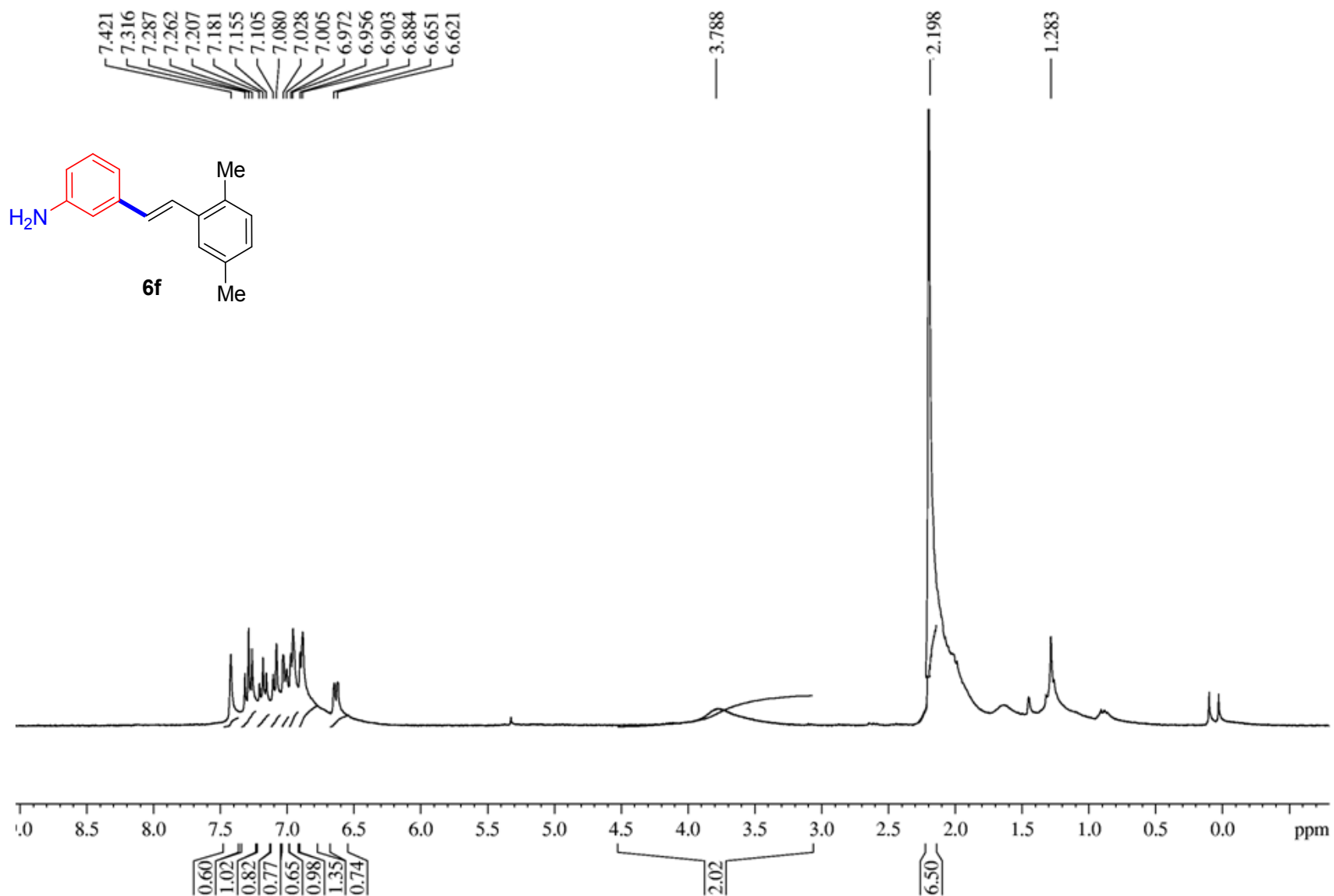
**Spectrum48.** 75 MHz  $^{13}\text{C}$  NMR of compound **6d**



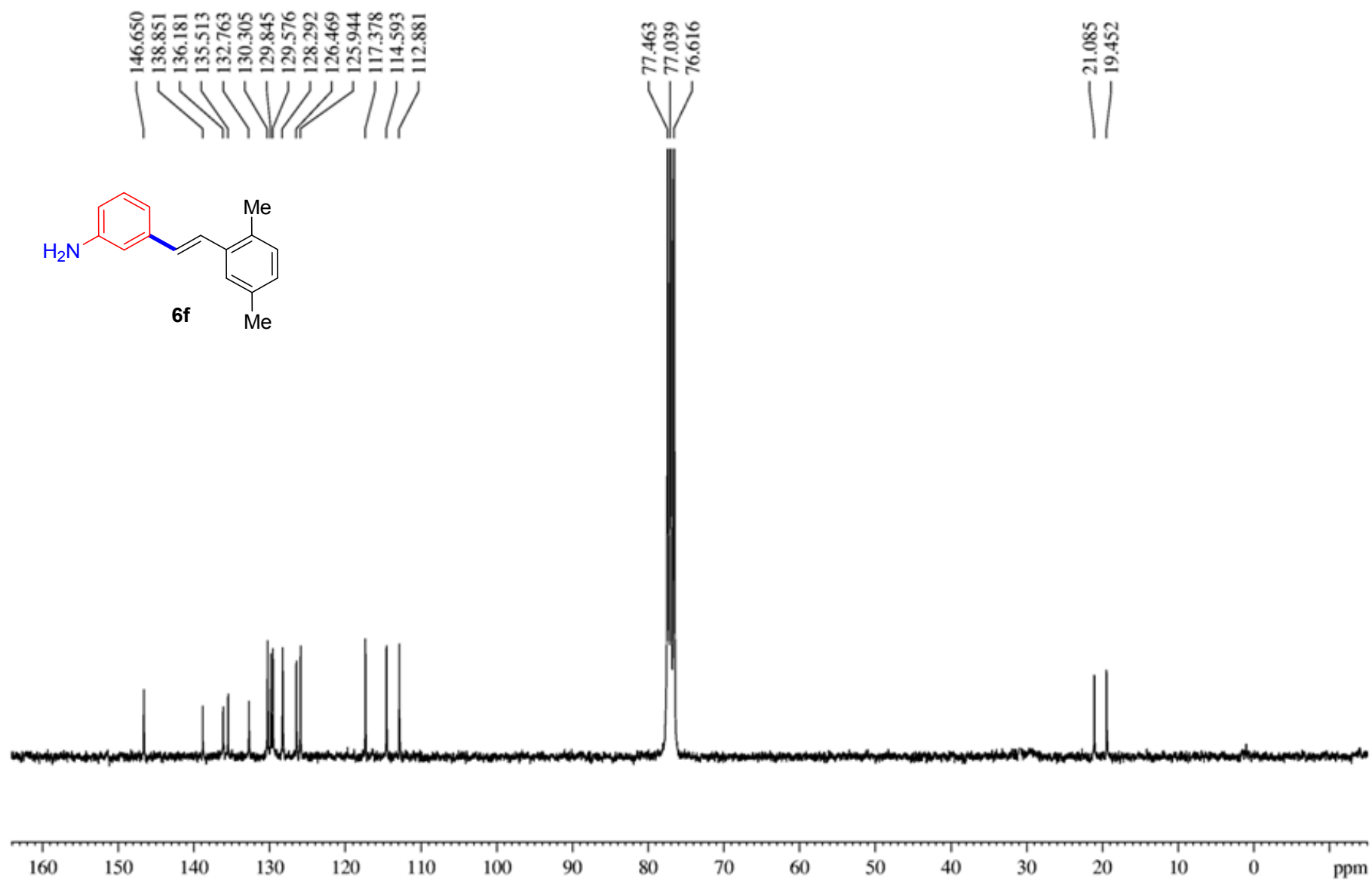
Spectrum49. 300 MHz  $^1\text{H}$  NMR of compound **6e**



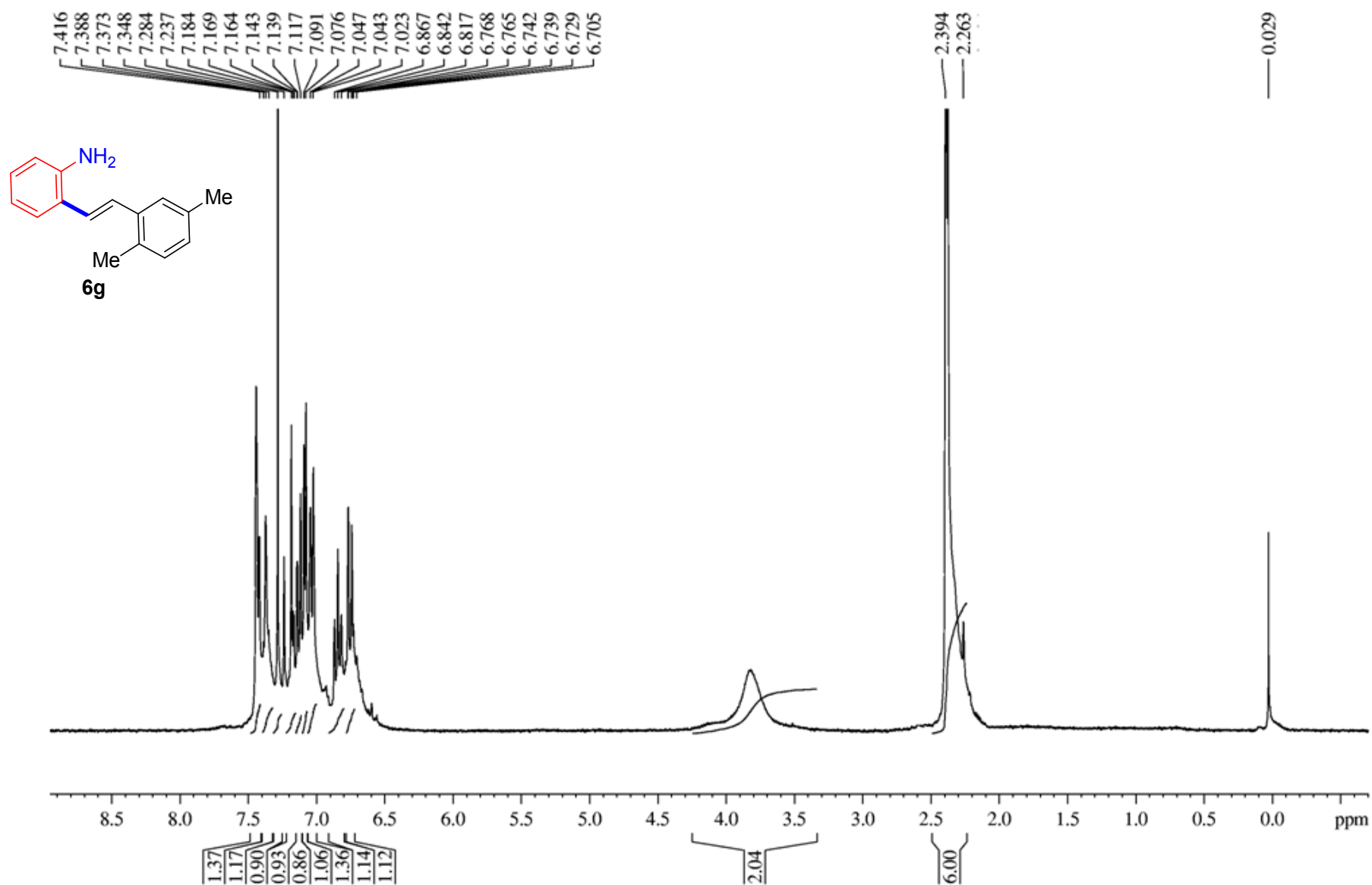
Spectrum50. 75 MHz <sup>13</sup>C NMR of compound **6e**



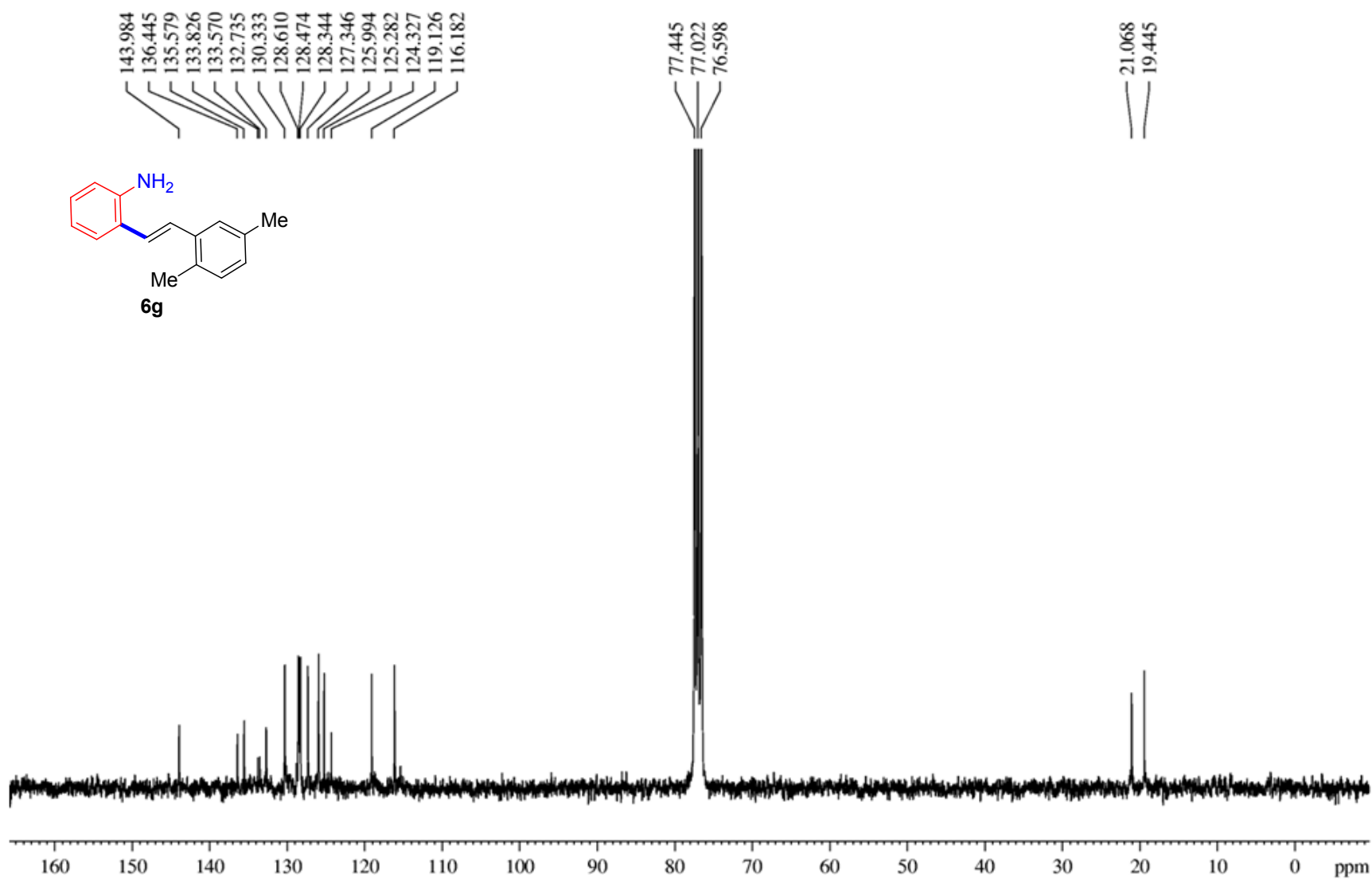
**Spectrum51.** 300 MHz <sup>1</sup>H NMR of compound **6f**



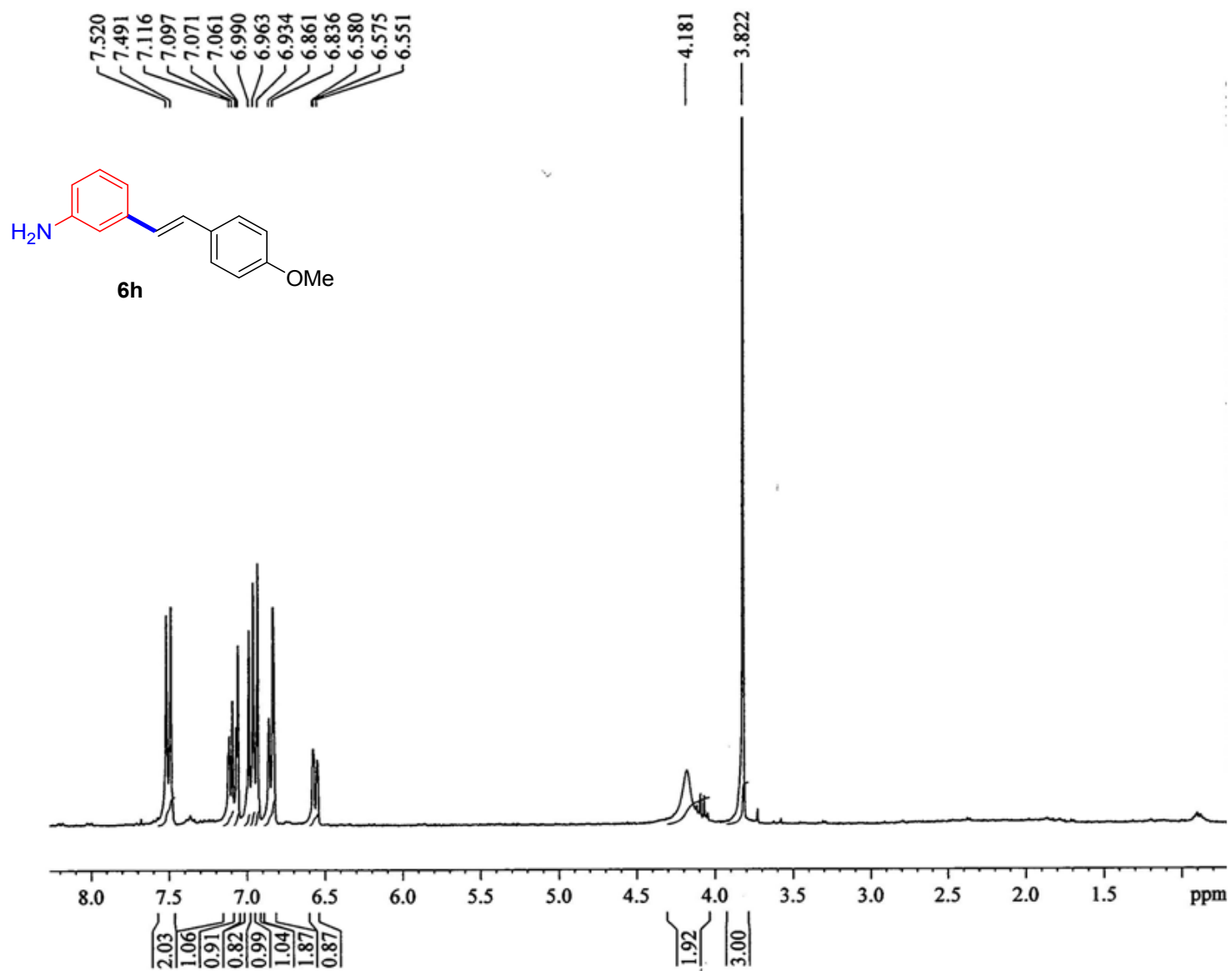
Spectrum52. 75 MHz <sup>13</sup>C NMR of compound **6f**



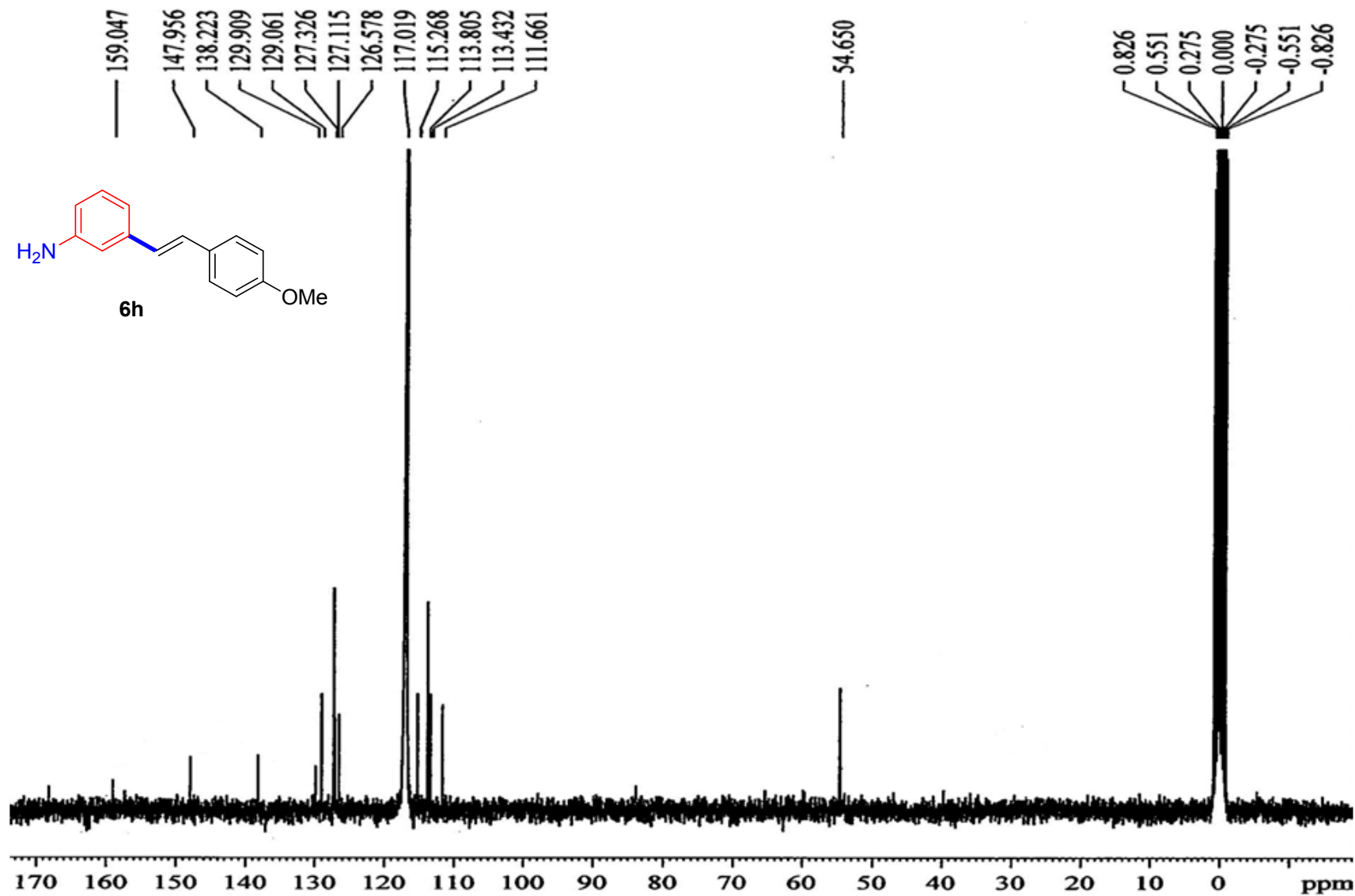
**Spectrum53.** 300 MHz <sup>1</sup>H NMR of compound **6g**



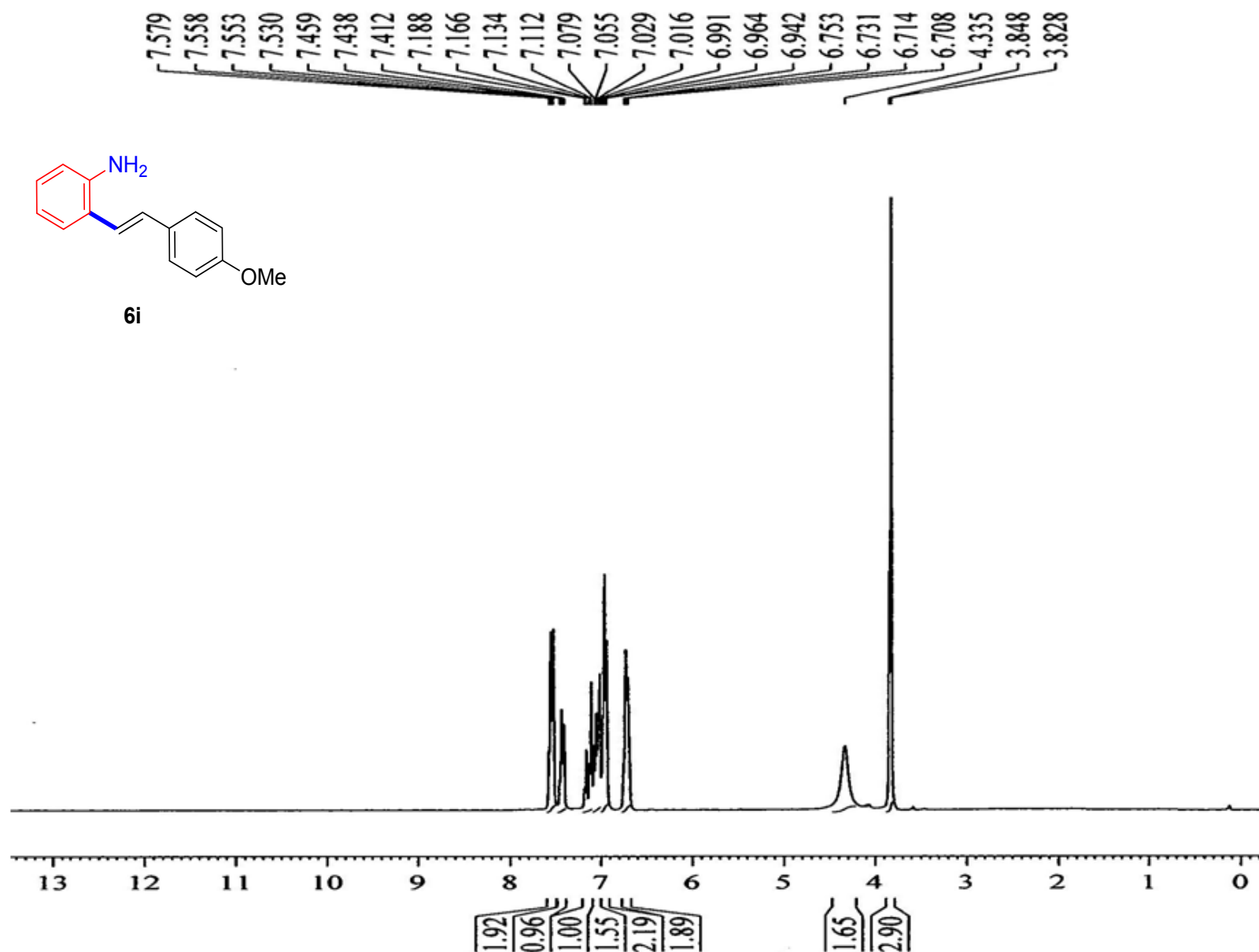
Spectrum54. 75 MHz <sup>13</sup>C NMR of compound **6g**



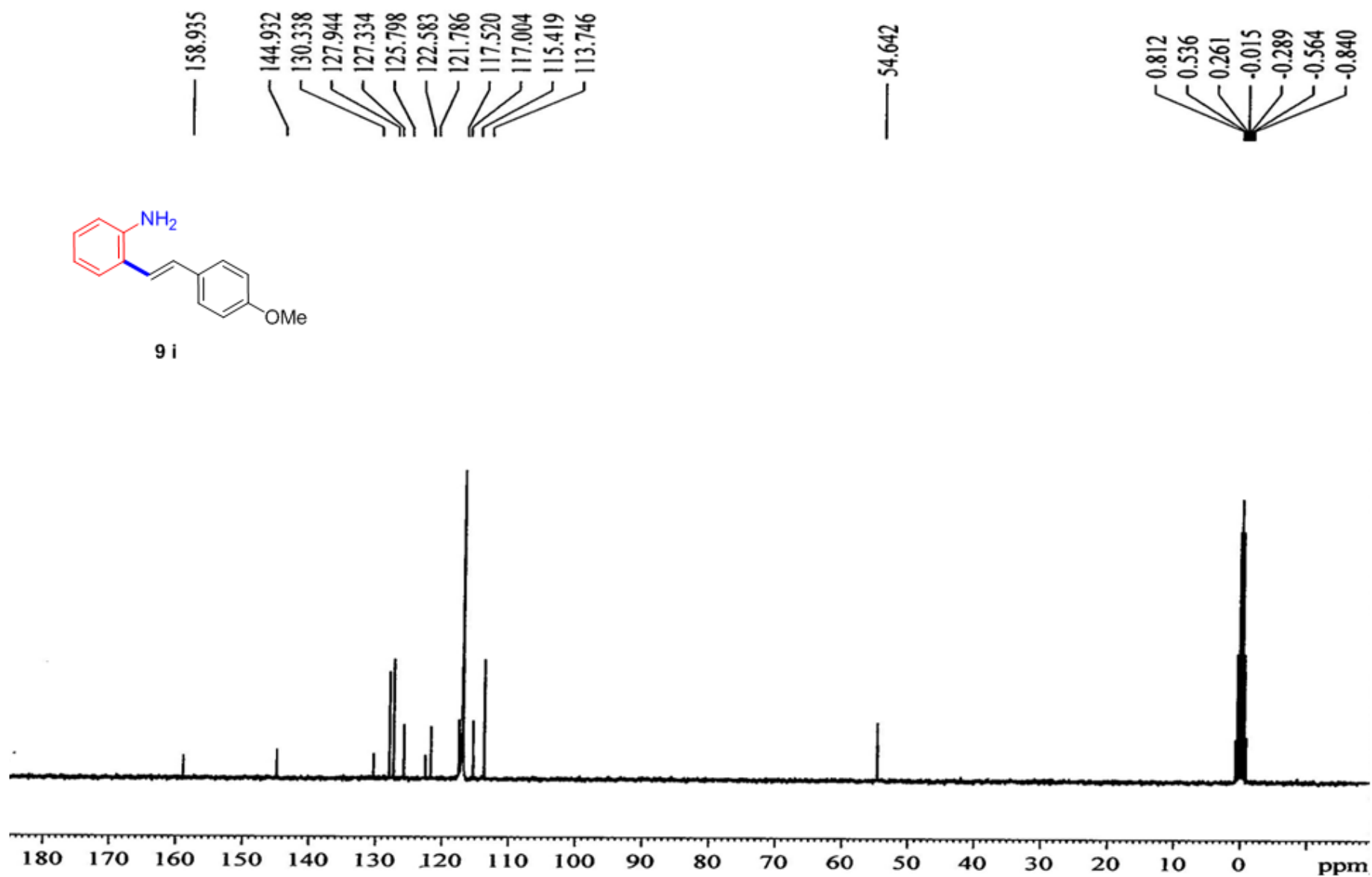
**Spectrum55.** 300 MHz <sup>1</sup>H NMR of compound **6h**



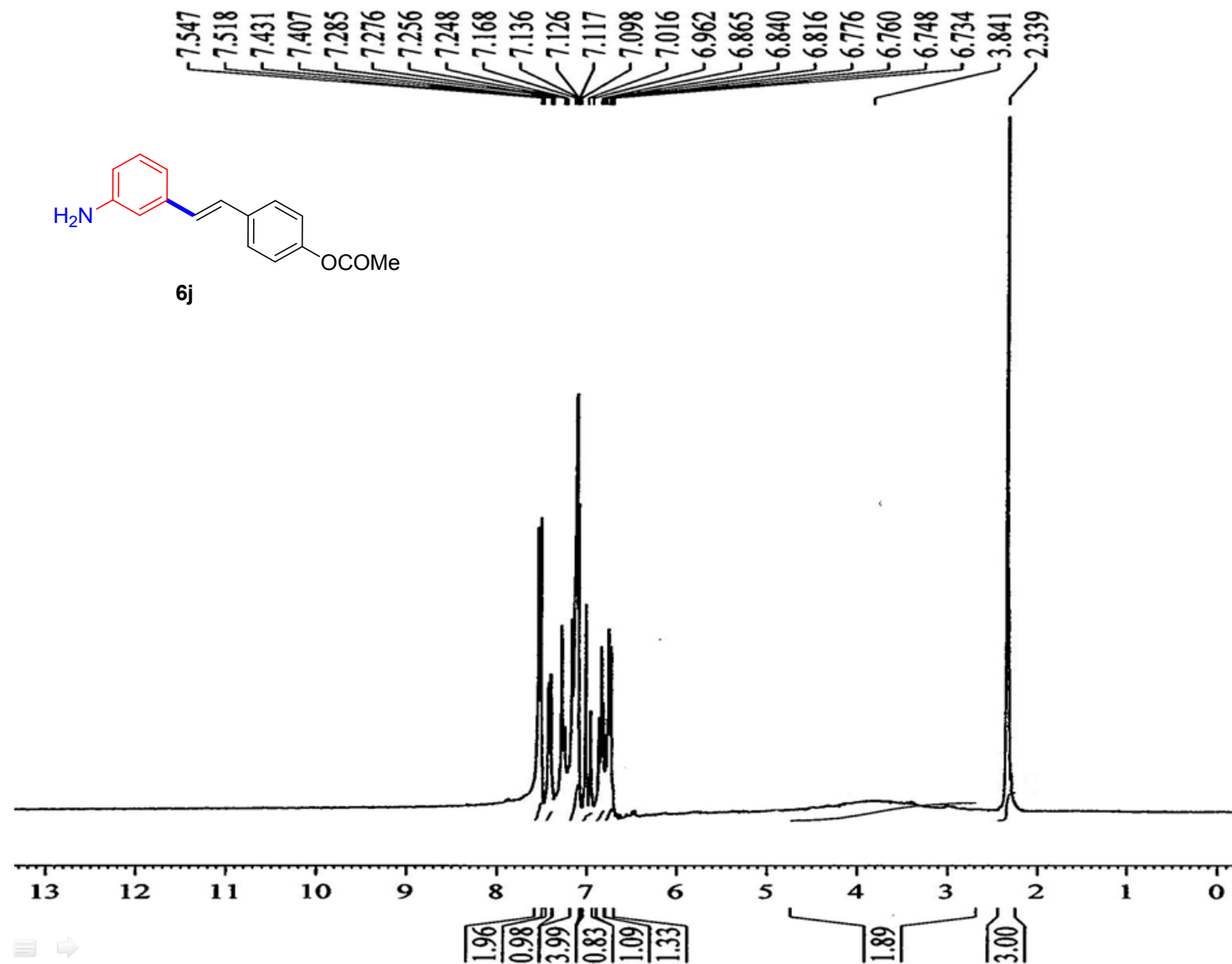
Spectrum56. 75 MHz <sup>13</sup>C NMR of compound **6h**



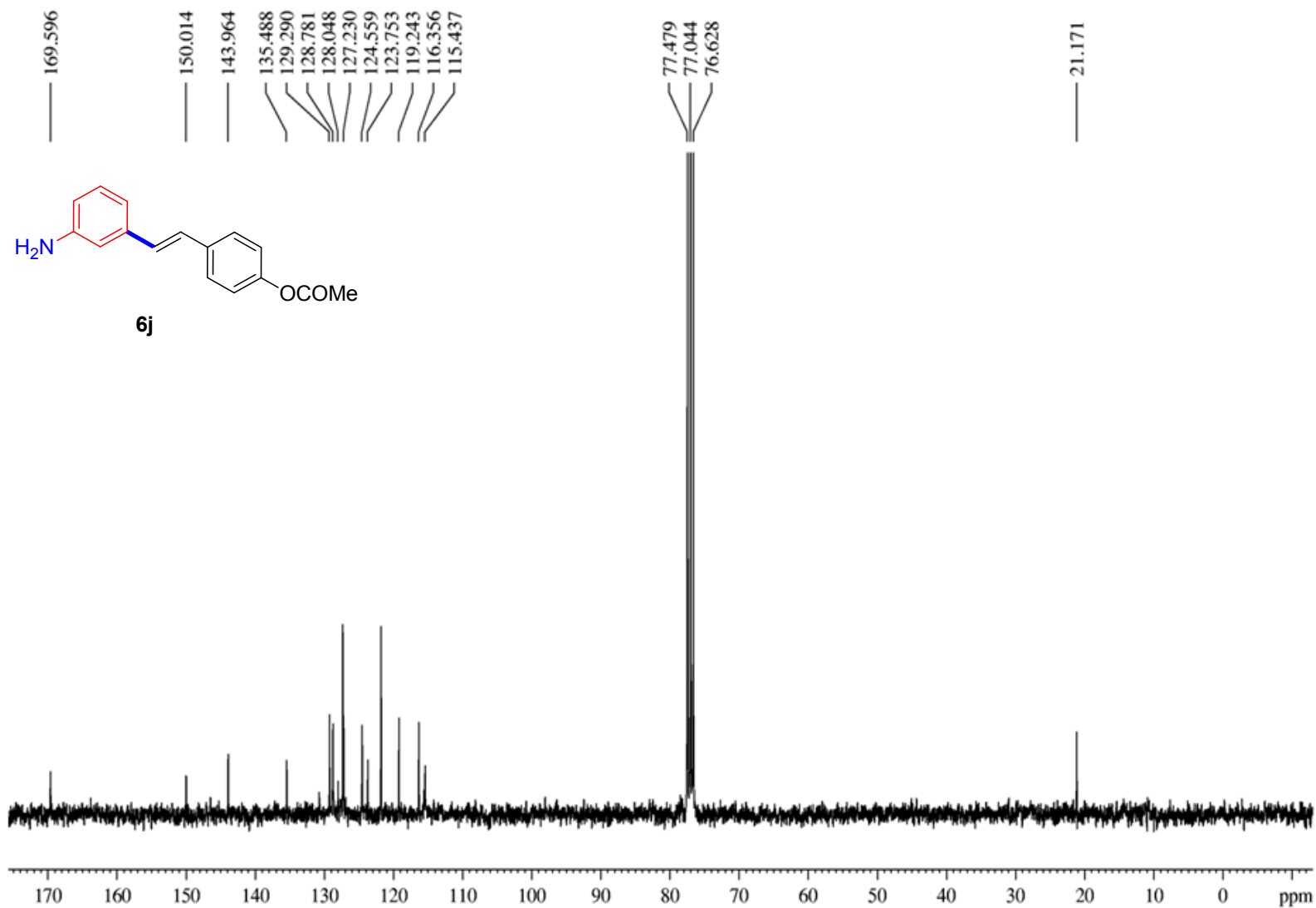
Spectrum 57. 300 MHz <sup>1</sup>H NMR of compound **6i**



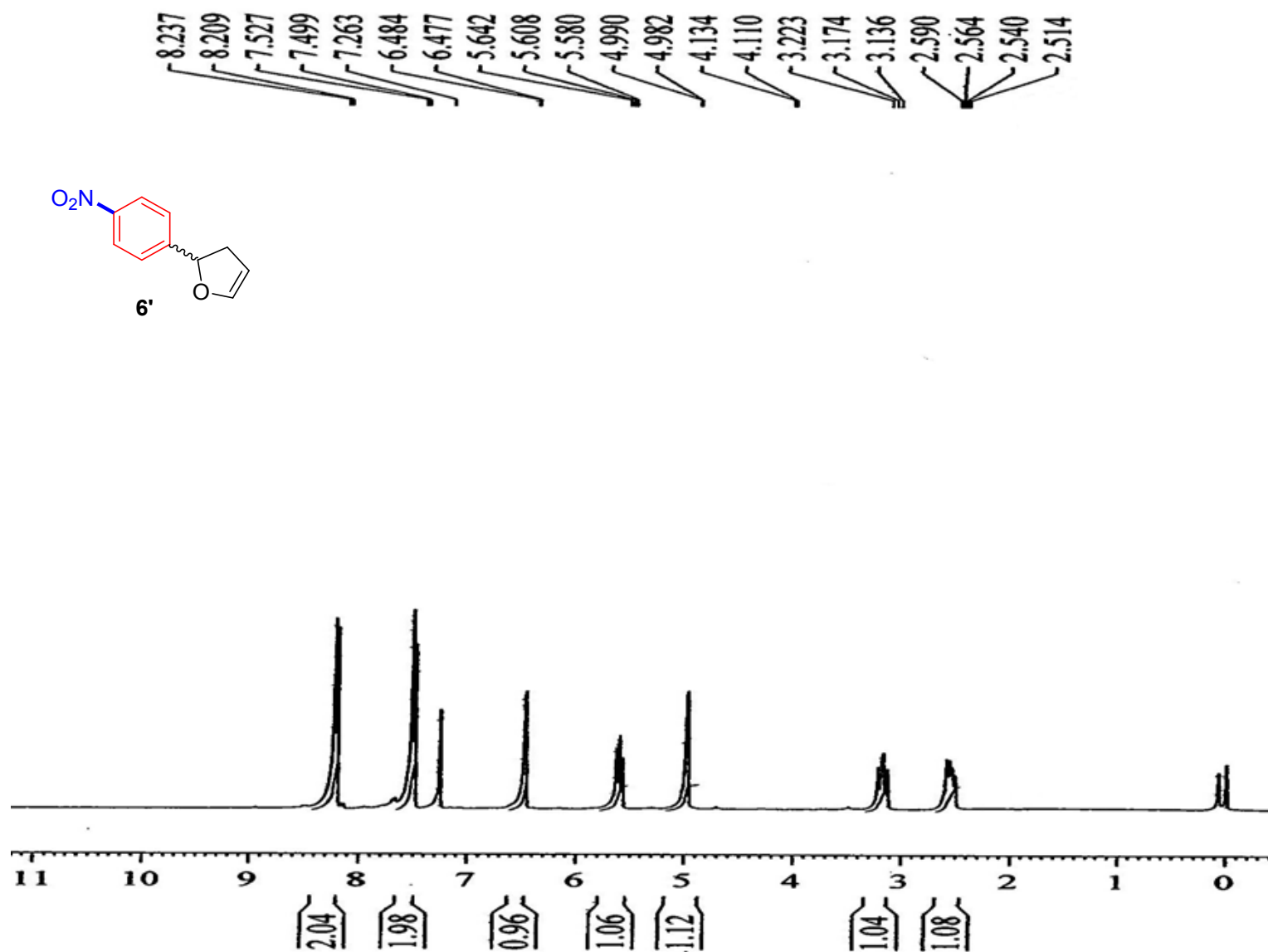
Spectrum58. 75 MHz <sup>13</sup>C NMR of compound **6i**



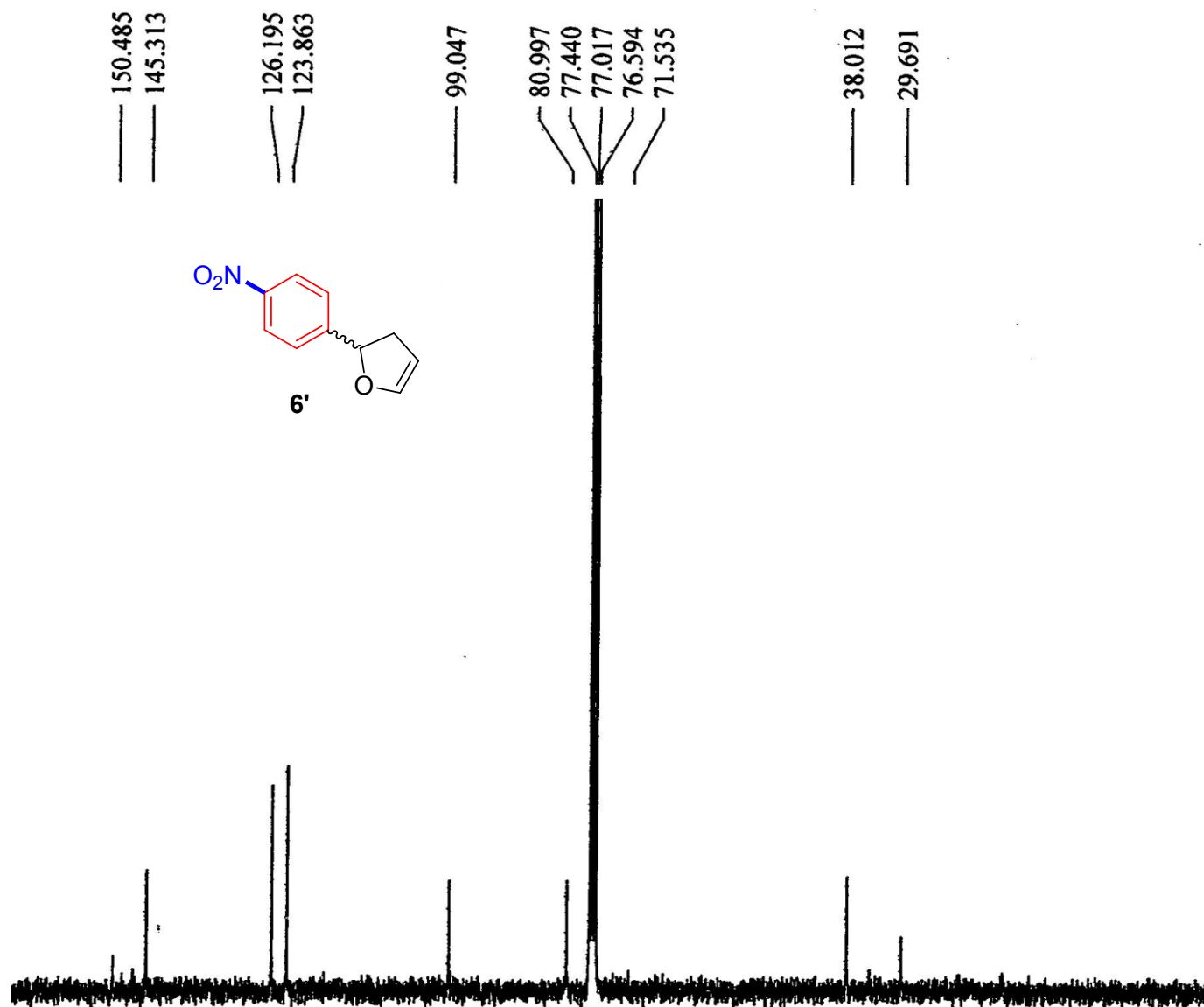
Spectrum59. 300 MHz <sup>1</sup>H NMR of compound **6j**



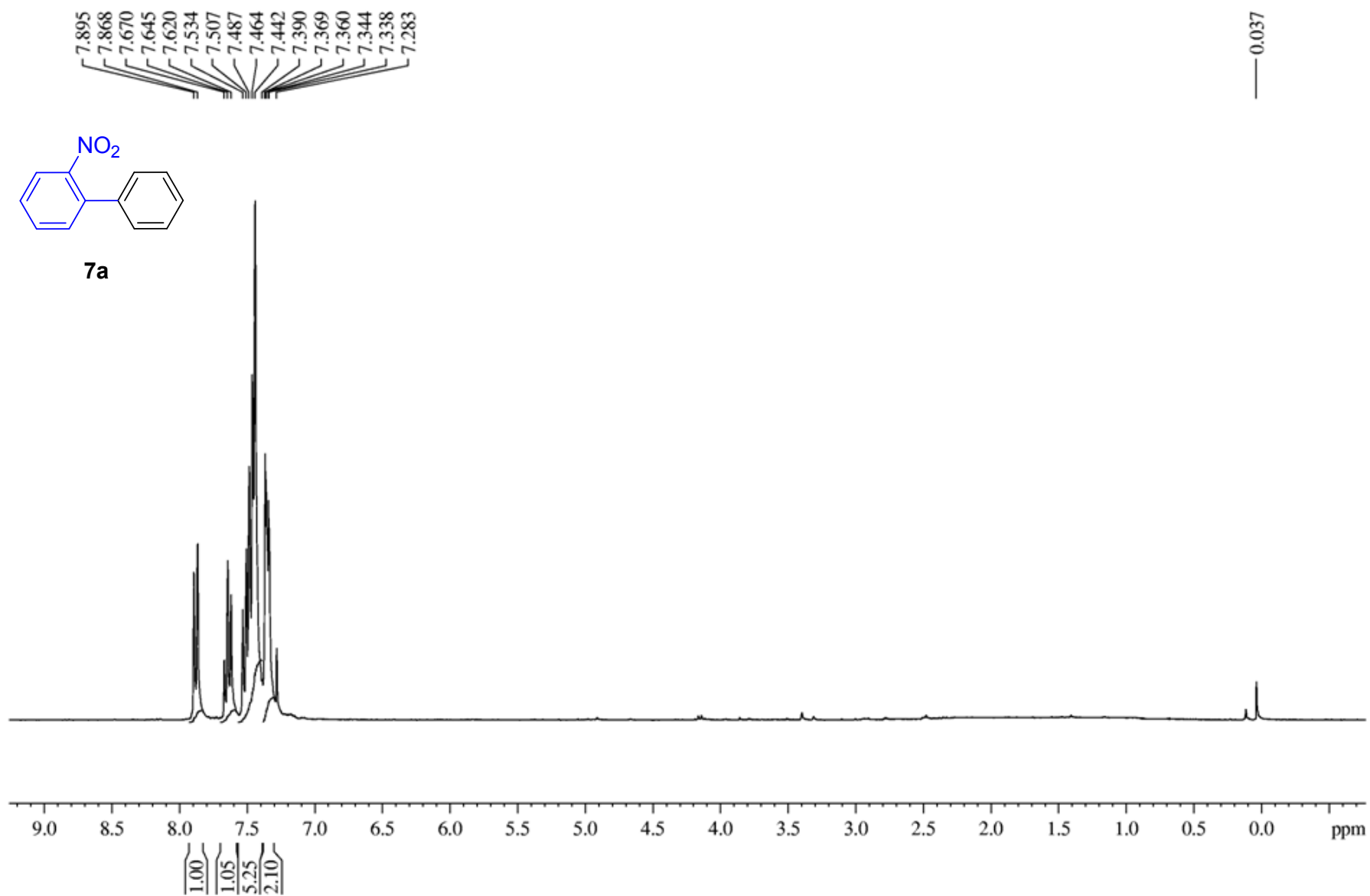
Spectrum60. 75 MHz  $^{13}\text{C}$  NMR of compound **6j**



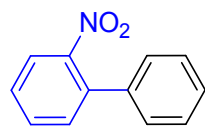
Spectrum**61**. 300 MHz <sup>1</sup>H NMR of compound **6'**



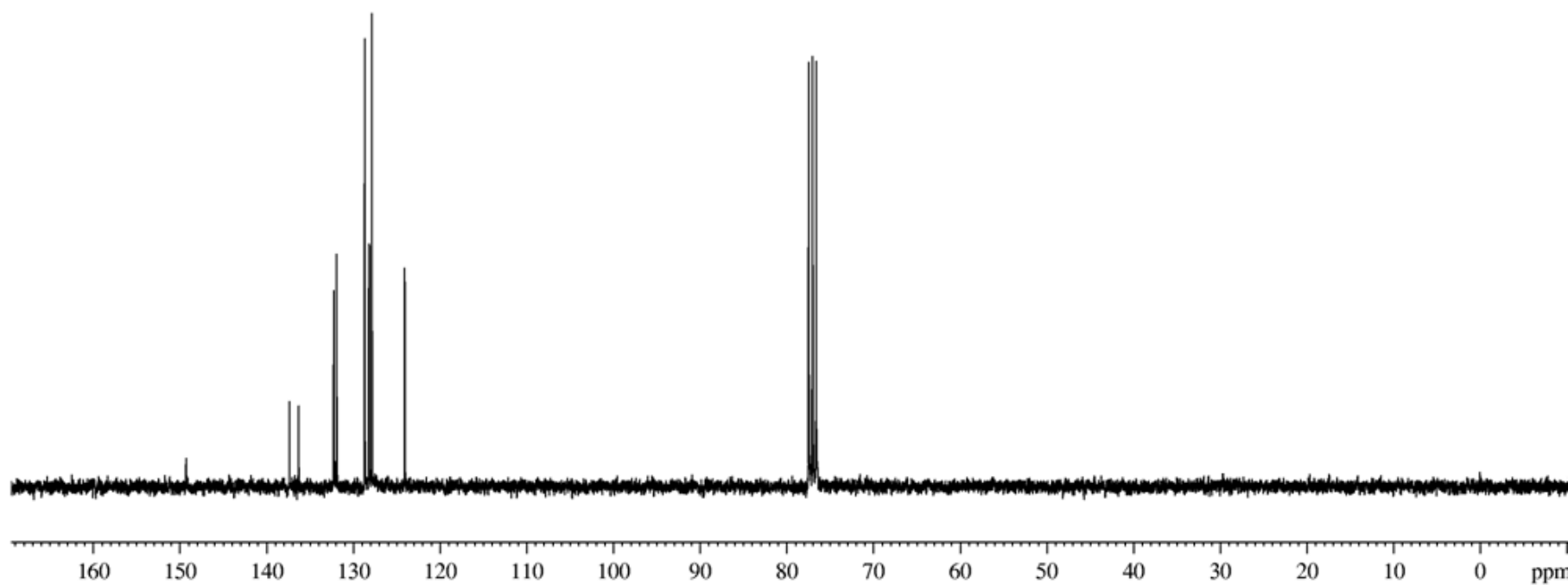
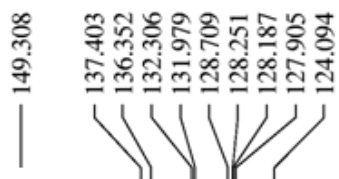
Spectrum62. 75 MHz  $^{13}\text{C}$  NMR of compound **6'**



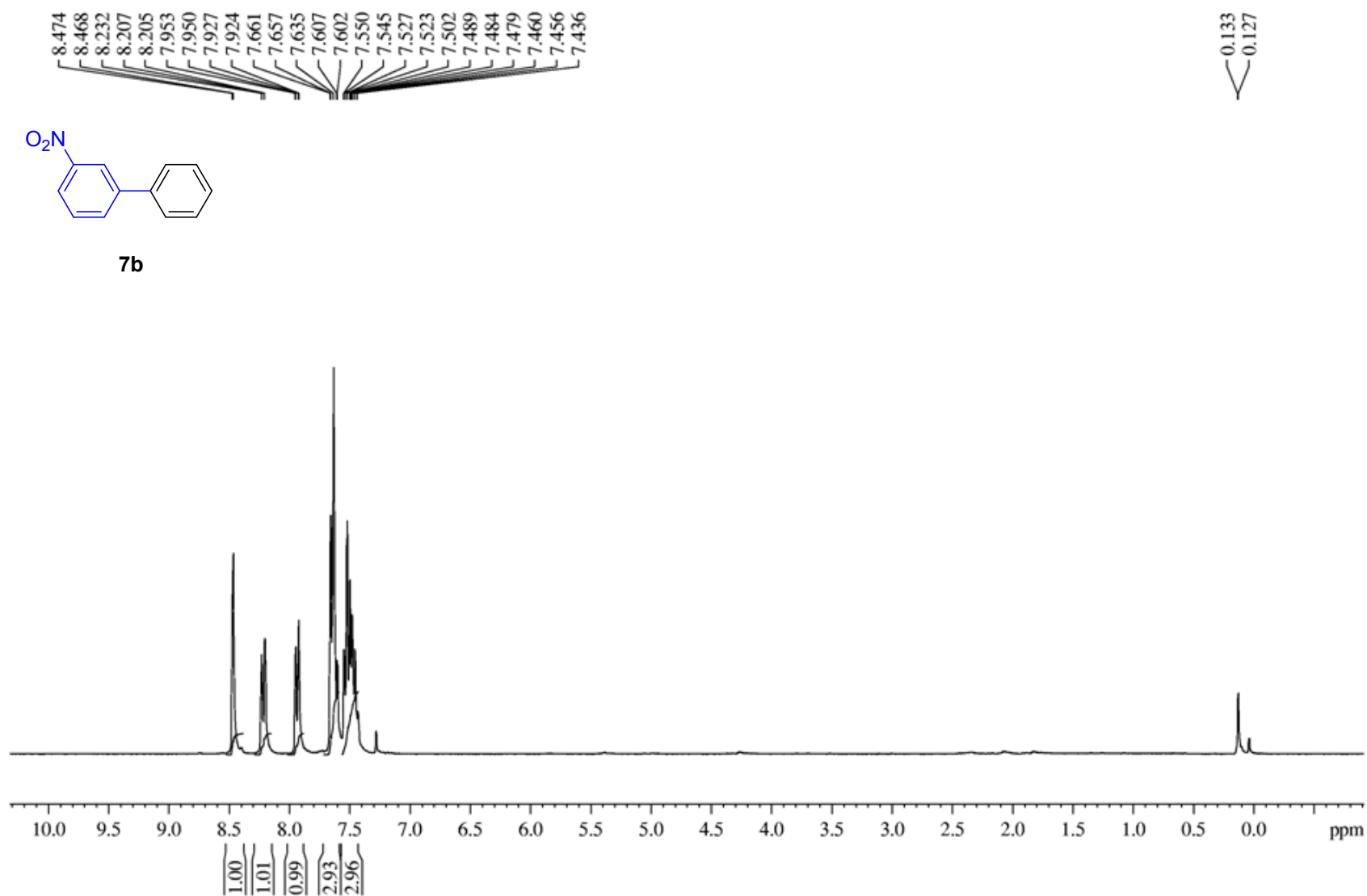
**Spectrum63.** 300 MHz  $^1\text{H}$  NMR of compound **7a**



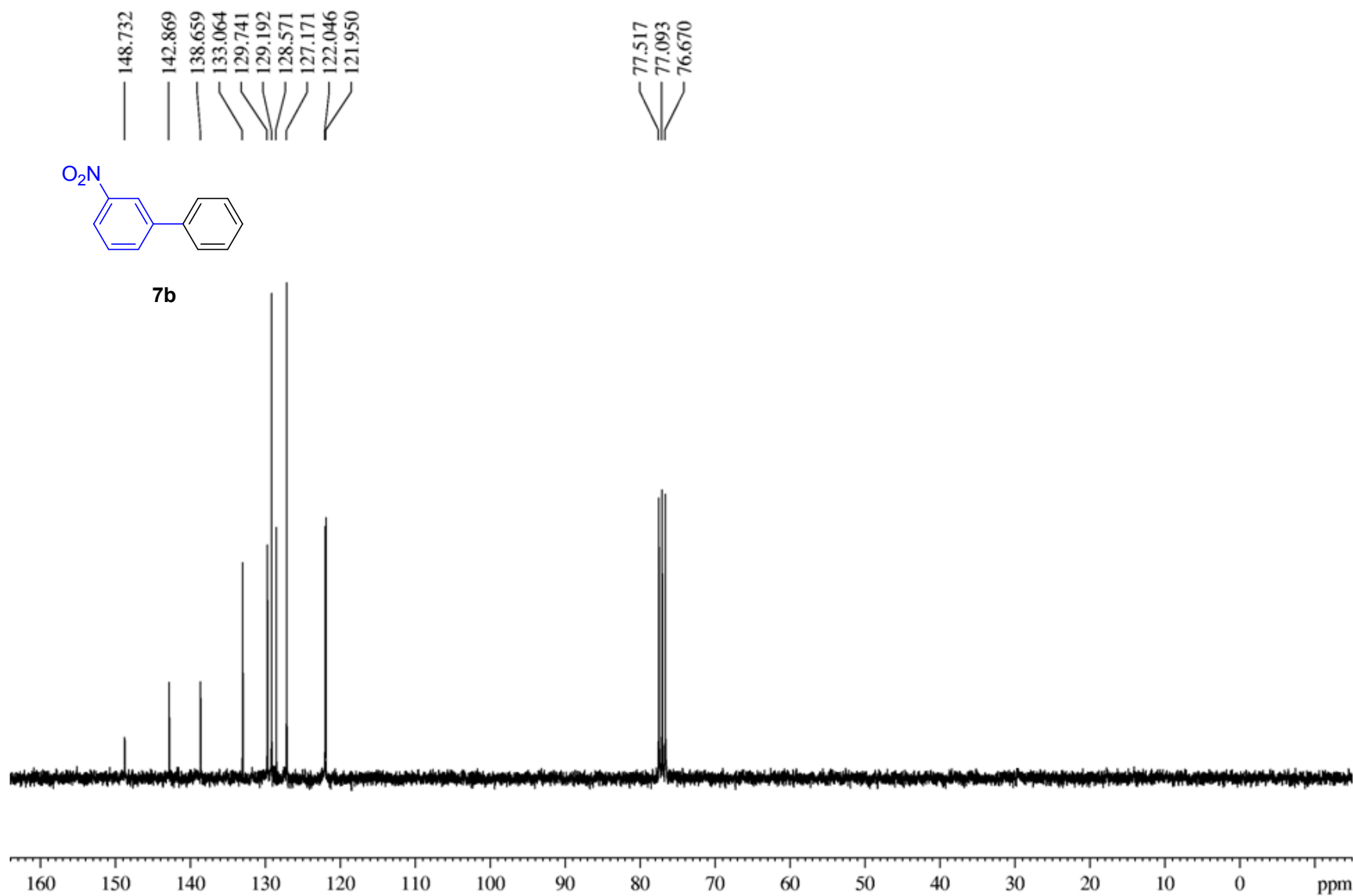
**7a**



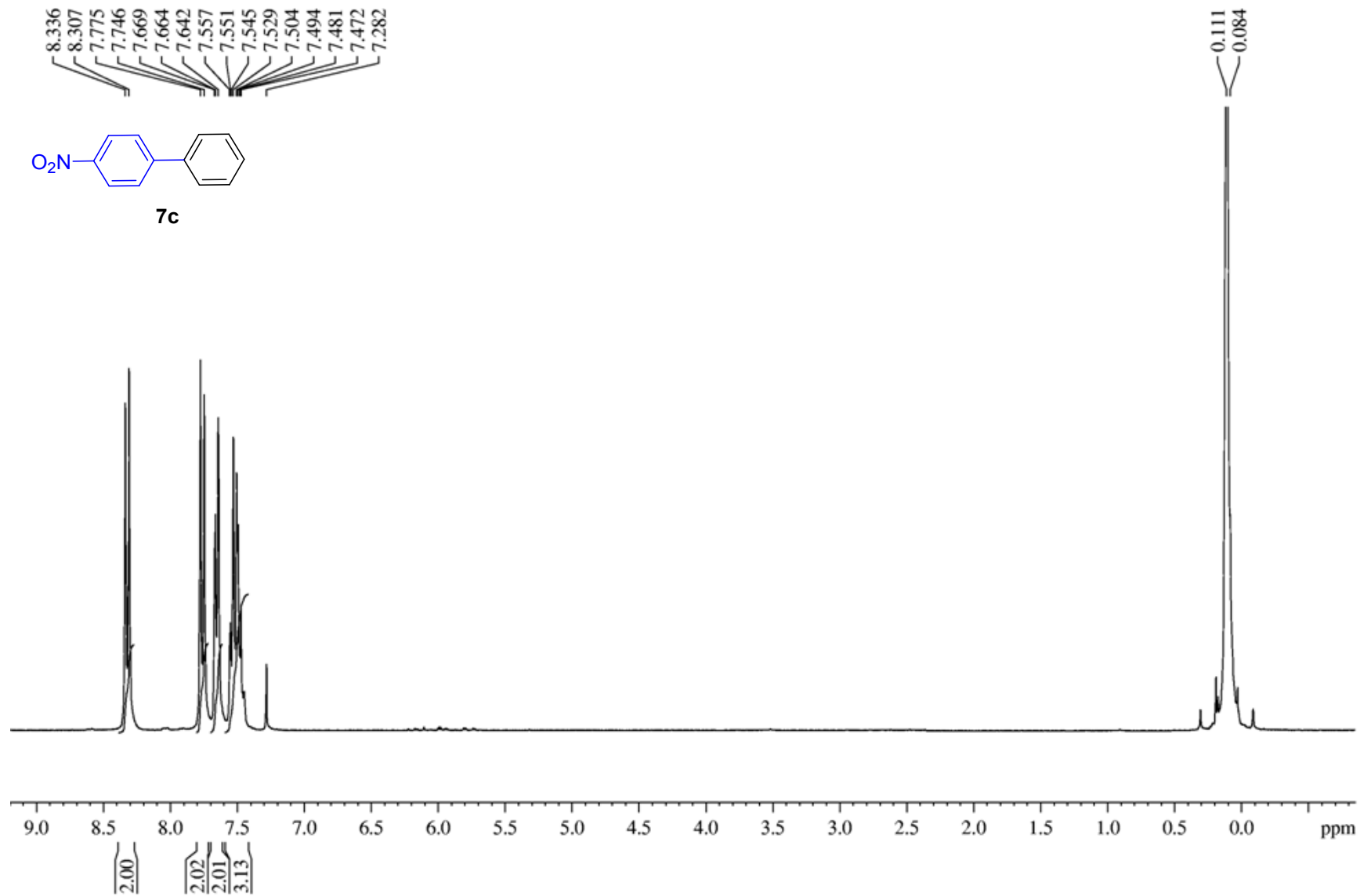
**Spectrum64.** 75 MHz  $^{13}\text{C}$  NMR of compound **7a**



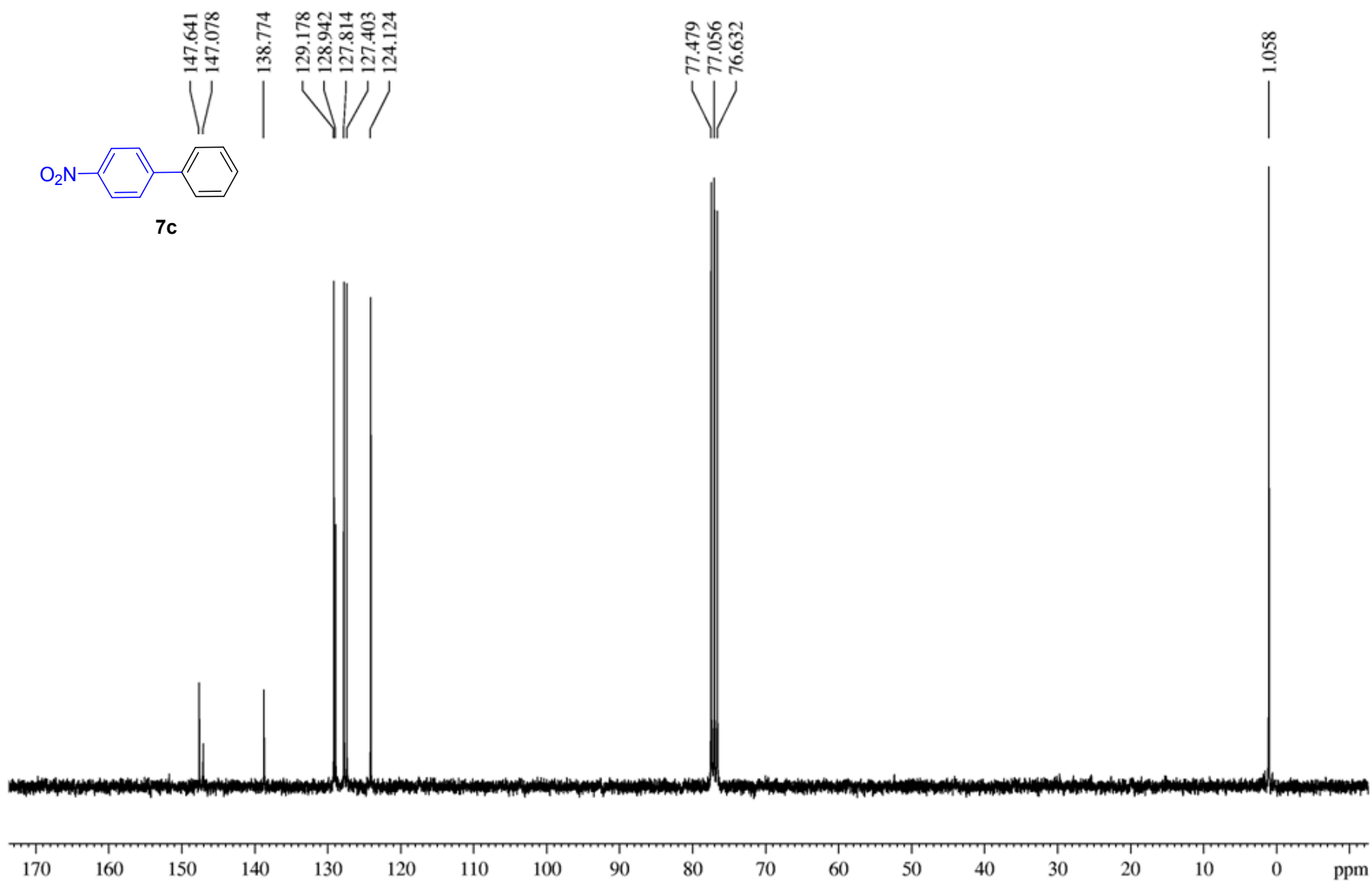
**Spectrum65.** 300 MHz  $^1\text{H}$  NMR of compound **7b**



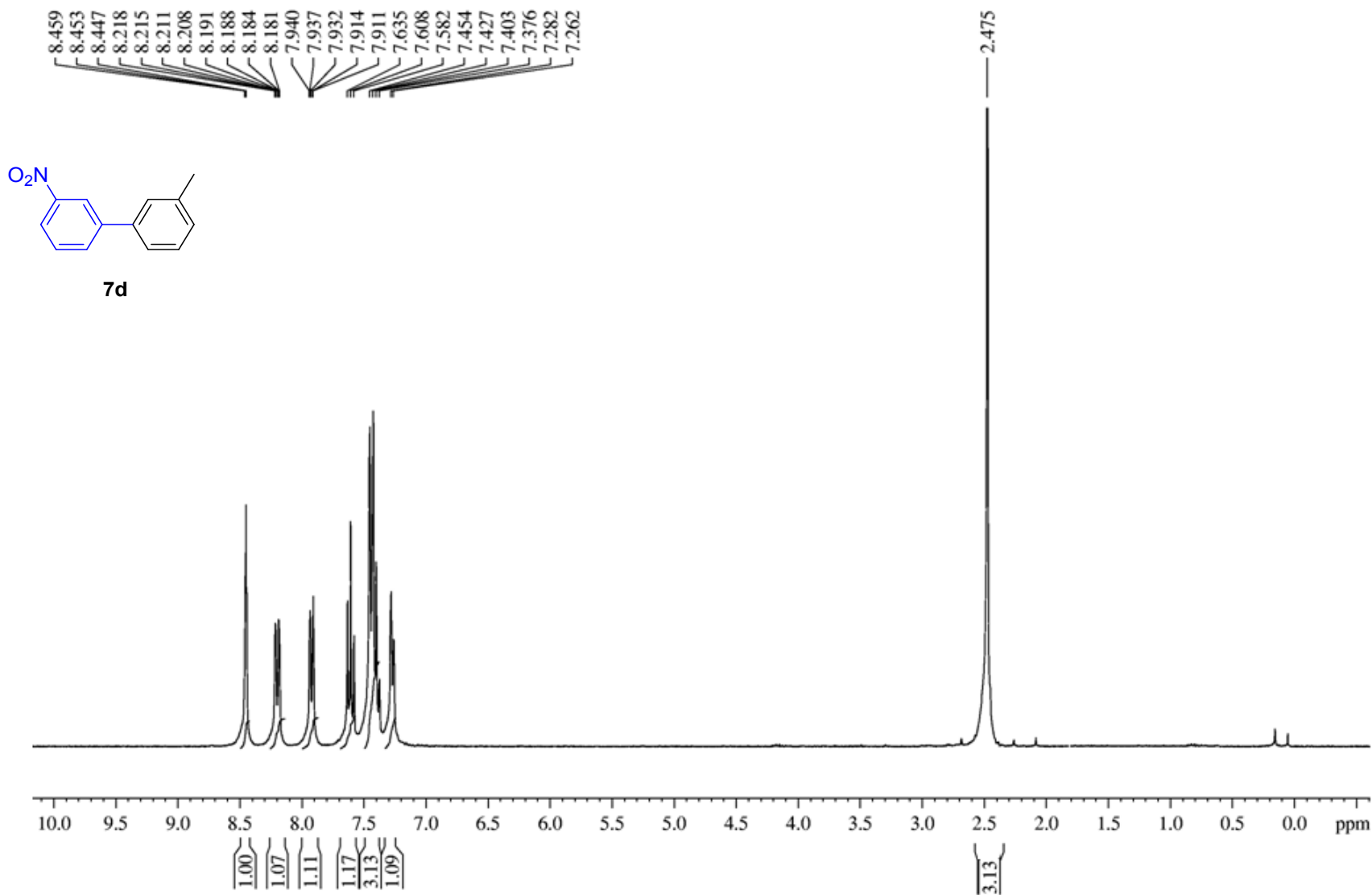
**Spectrum66.** 75 MHz  $^{13}\text{C}$  NMR of compound **7b**



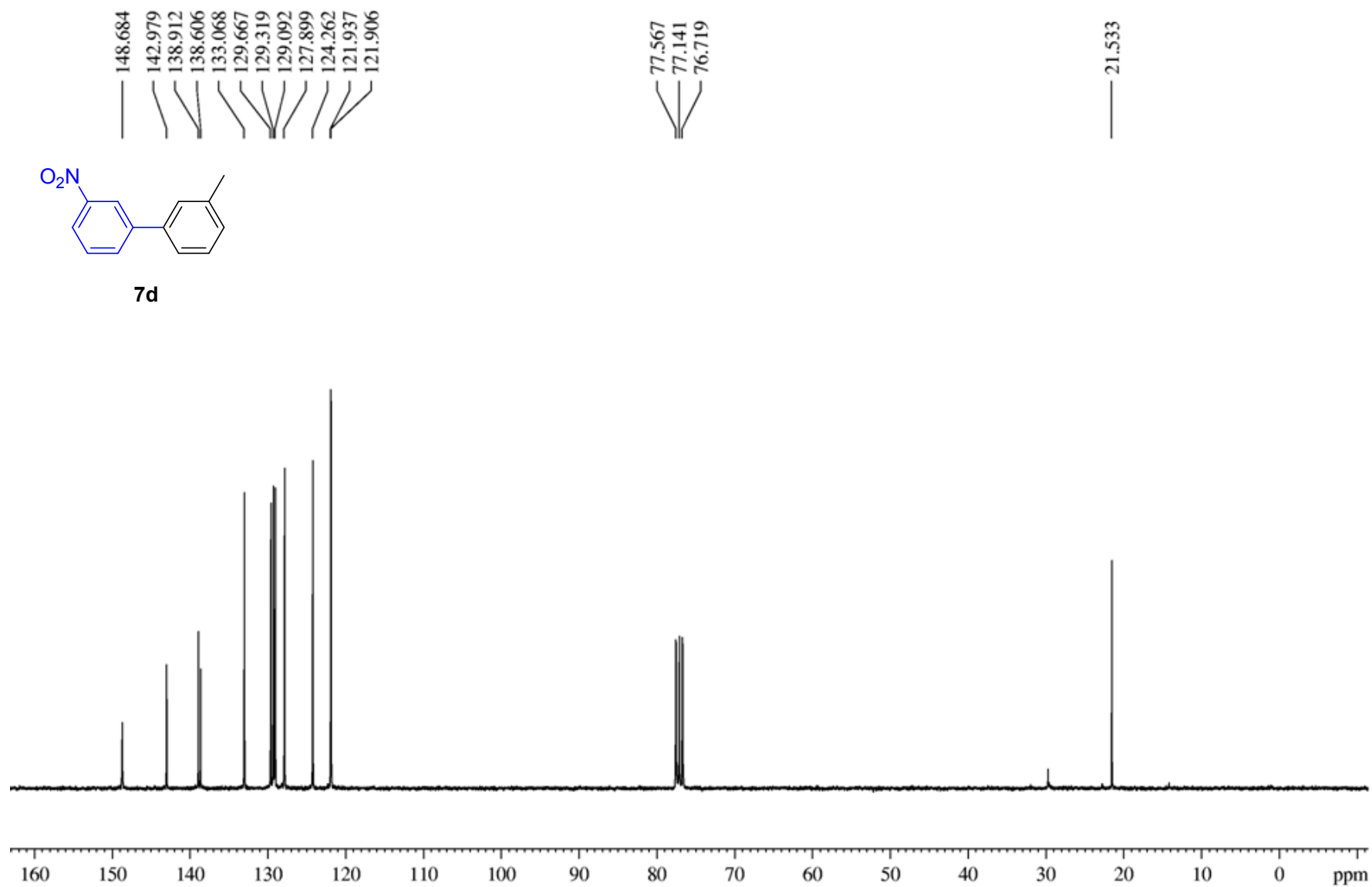
**Spectrum67.** 300 MHz <sup>1</sup>H NMR of compound **7c**



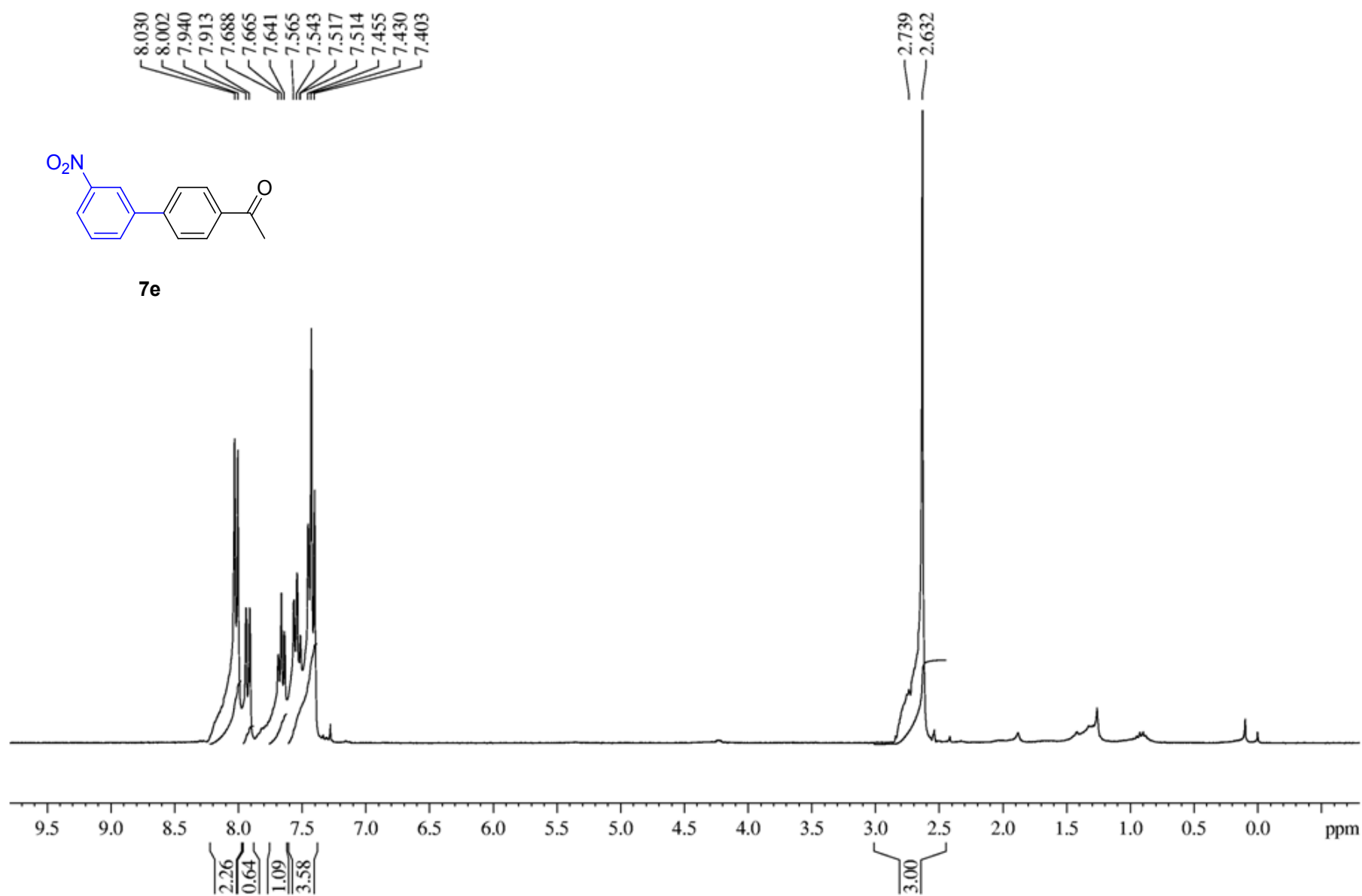
Spectrum68. 75 MHz  $^{13}\text{C}$  NMR of compound **7c**



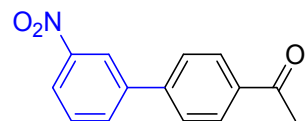
**Spectrum69.** 300 MHz <sup>1</sup>H NMR of compound **7d**



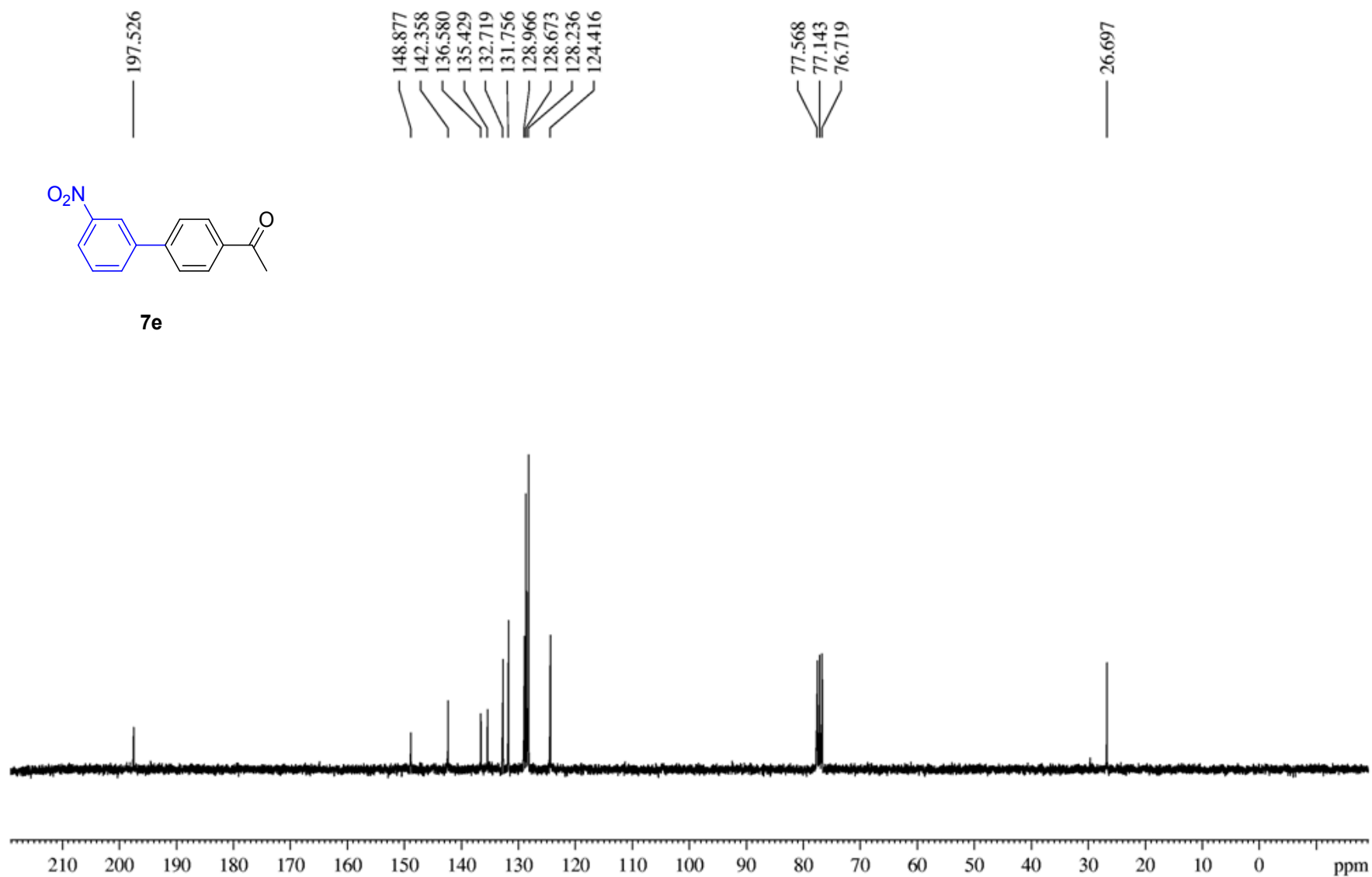
**Spectrum70.** 75 MHz <sup>13</sup>C NMR of compound **7d**



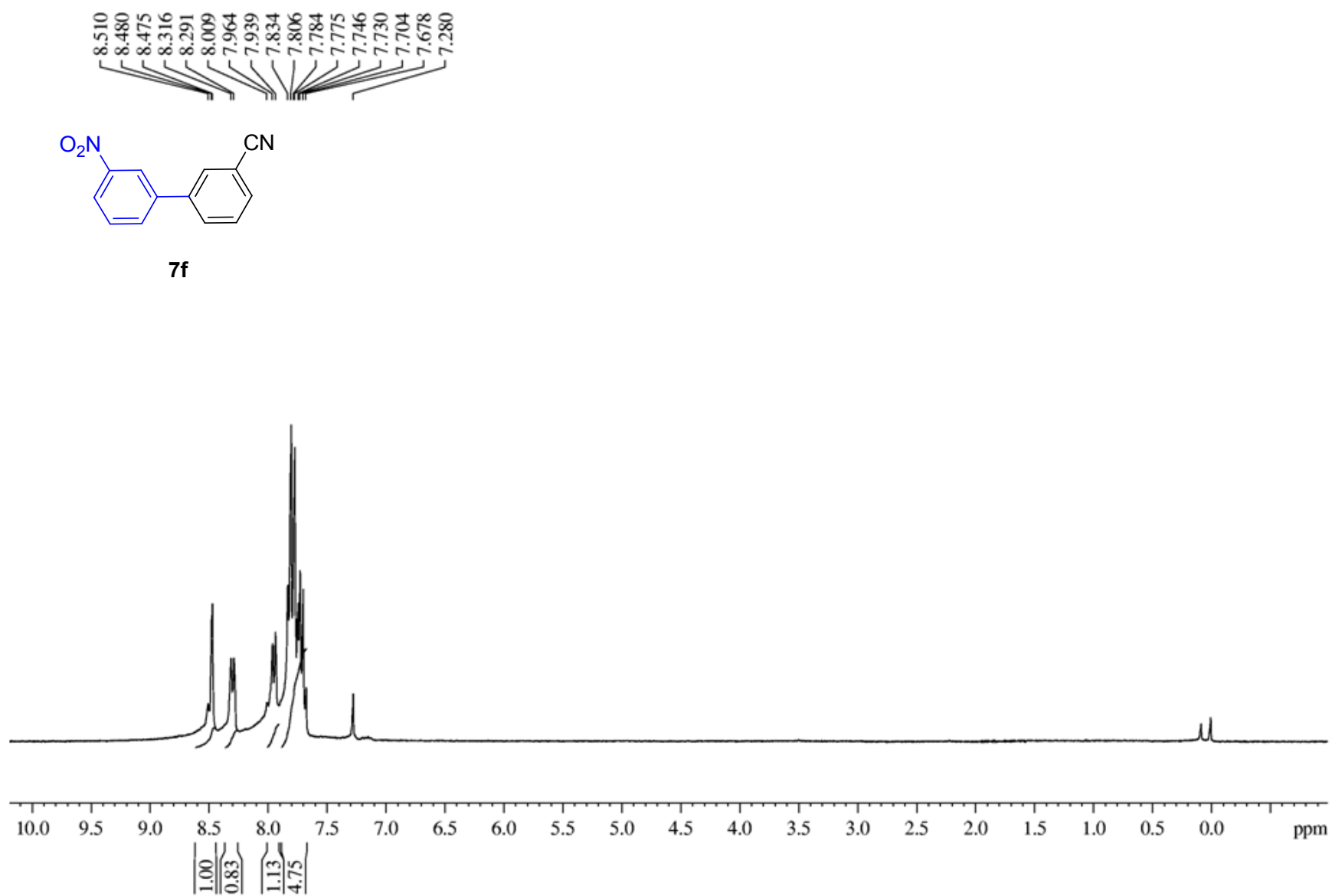
**Spectrum71.** 300 MHz <sup>1</sup>H NMR of compound **7e**



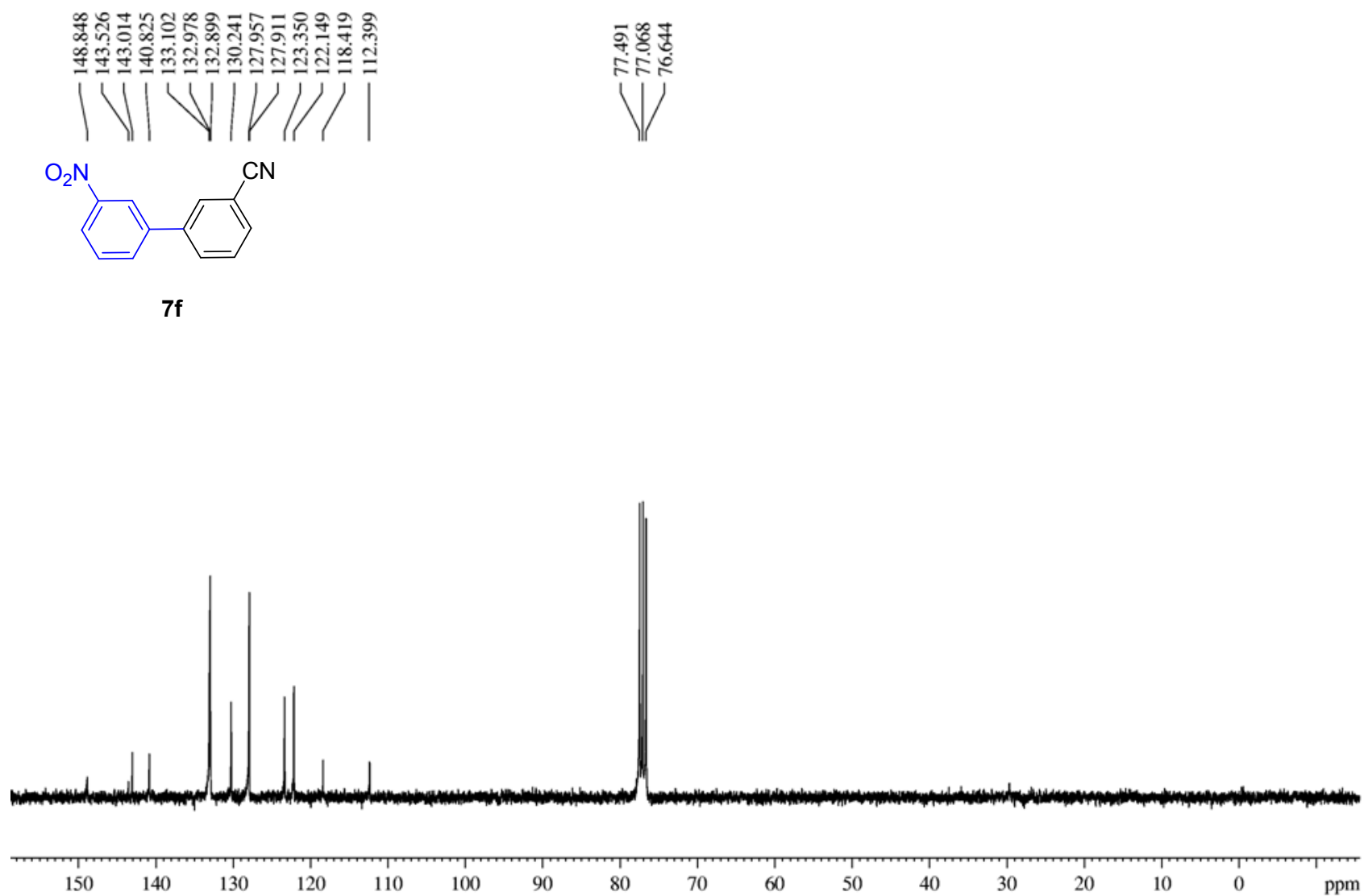
**7e**



**Spectrum 72.** 75 MHz  $^{13}\text{C}$  NMR of compound 7e

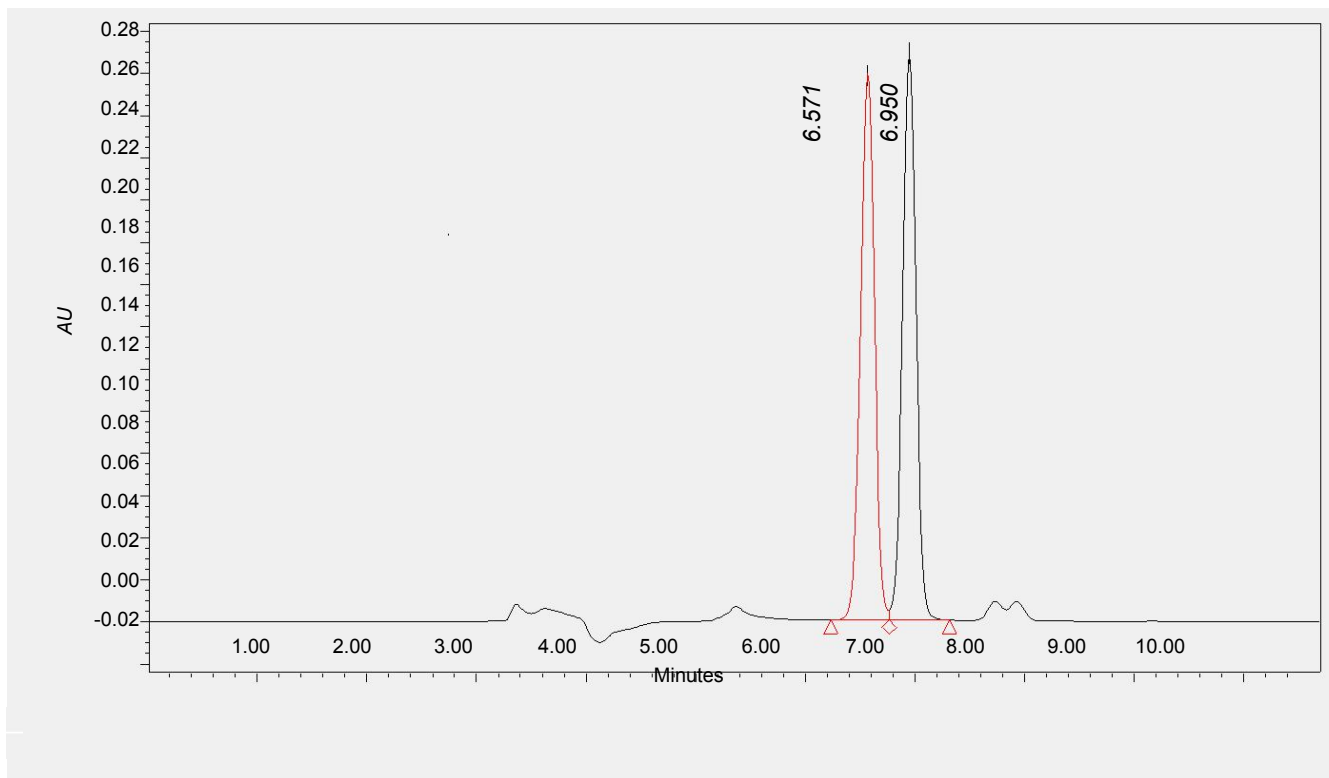


**Spectrum73.** 300 MHz  $^1\text{H}$  NMR of compound **7f**



**Spectrum74.** 75 MHz  $^{13}\text{C}$  NMR of compound **7f**

## 2. HPLC data

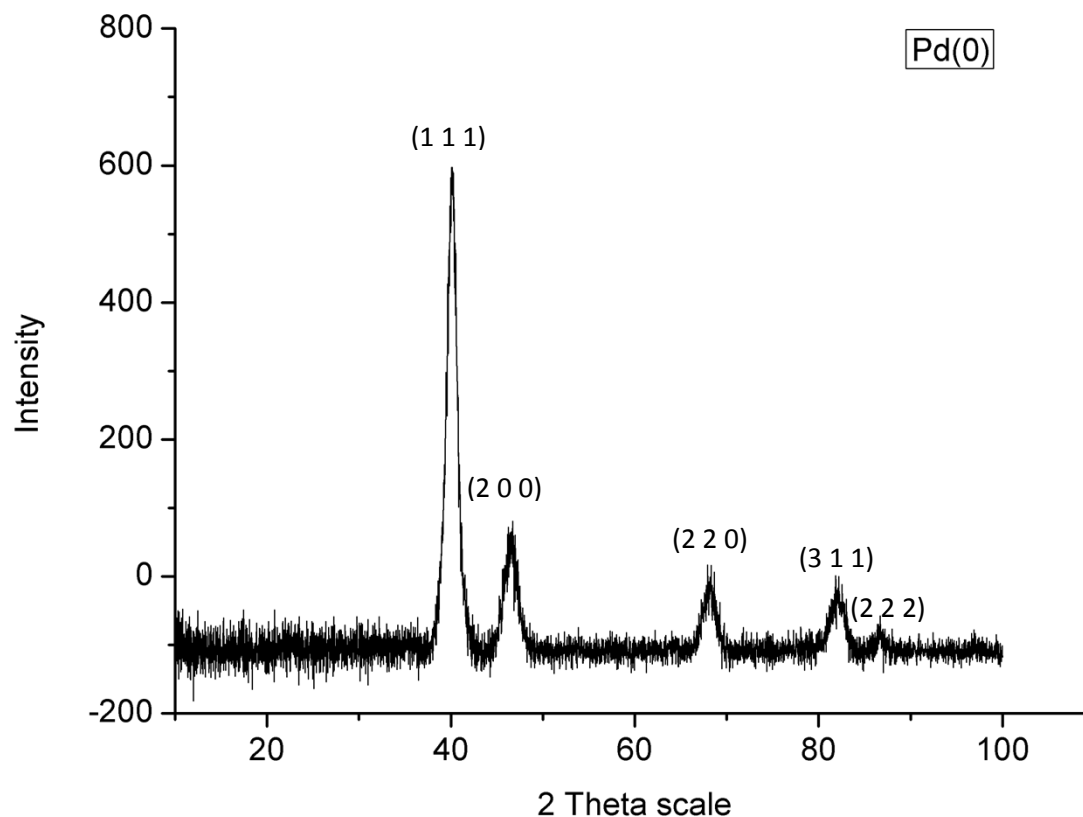


**Figure 1:** HPLC chromatogram of compound 6'

|   | Retention Time | % Area |
|---|----------------|--------|
| 1 | 6.571          | 49.89  |
| 2 | 6.950          | 50.11  |

### 3. Powder XRD Images:

Powder XRD data of palladium (0) oxides is shown below obtained under different conditions. The XRD pattern showed five peaks, which could be readily indexed to Pd(0) both in the peak position and relative intensity (Fig.2) in agreement with the reported data on JCPDS, 782076.



**Figure2 :** Powder XRD Pattern of Palladium(0)