Supporting Information:

tert-Butyl nitrite promoted transamidation of secondary amides under metal and catalyst free conditions

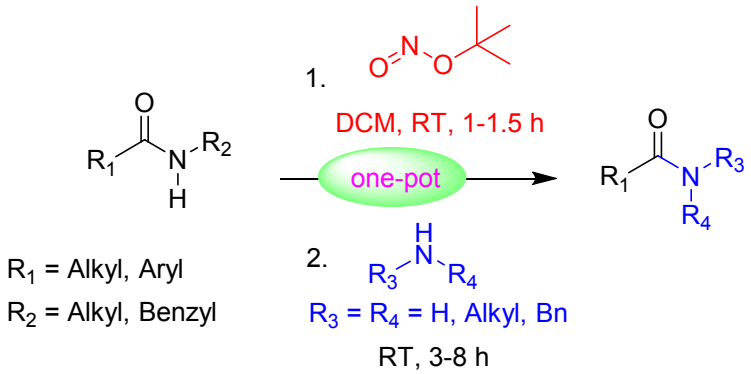
Popuri Sureshbabu,[a#] Sadaf Azeez,[a#] Priyanka Chaudhary,[a] and Jeyakumar Kandasamy [a]*

[a]Department of Chemistry, Indian Institute of Technology (BHU), Varanasi, Uttar Pradesh-221005;
Email: jeyakumar.chy@iitbhu.ac.in

1. General information:

All reactions were performed in round bottom flask under open air condition at room temperature (~25-27 °C). Solvents and chemicals were purchased from commercial sources and used without further purification. The reagent *tert*-butyl nitrite was purchased from Alfa Aesar (Thermo Fisher Scientific). Thin layer chromatography (TLC) was performed using pre-coated plates contained from E. Merck (TLC silica gel 60 F254). TLC plates were visualized by exposure to ultraviolet light (UV) with 254 nm wavelength lamp, then, further analyzed in iodine (I_2) chamber. The column chromatography was performed on silica gel (100-200 mesh) using a mixture of ethyl acetate and hexane as an eluent. The NMR spectra were recorded on Bruker Avance 500 MHz NMR spectrometer using $CDCl_3$. High resolution Mass spectra (ESI-QTOF-MS) was measured on water's Quattro Micro V 4.1. The IR, ^1H NMR and ^{13}C NMR of the products were compared with literature reports. The starting materials (amides) were prepared using the literature procedure.[1]

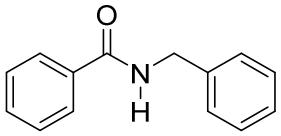
2. Procedure for the transamidation of amides



Amide (1 mmol) was stirred in dichloromethane (5 mL) approximately for 2 min at room temperature to which *tert*-butyl nitrite (1.5 mmol) was added using syringe and allowed to stir for 1-1.5 h at room temperature. The external amines (nucleophiles, 2.2 mmol) was added to the reaction mixture and allowed to stir at room temperature for an appropriate time. The progress of the reaction was monitored by TLC. After completion, dichloromethane was evaporated and subjected for silica gel (100-200 mesh) column chromatography purification (SiO_2: ethyl acetate/hexane) to obtain the corresponding transamidation products.

3. Analytical Data of the Products:

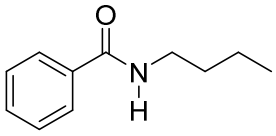
3.1 *N*-Benzylbenzamide (3a)[2]



3a

The title compound was obtained as a white solid. M.p. 99 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.55; Yield 91% (192 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.79 (d, J = 7.3 Hz, 2H), 7.49 (t, J = 7.2 Hz, 1H), 7.40 (t, J = 7.3 Hz, 2H), 7.33 (s, 4H), 7.29 (s, 1H), 6.69 (s, 1H), 4.62 (d, J = 5.2 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.3, 138.1, 134.3, 131.4, 128.6, 128.4, 127.8, 127.4, 126.9, 44.0.

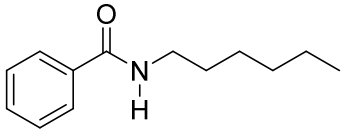
3.2 *N*-Butylbenzamide (3b)[2]



3b

The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.54; Yield 85% (150 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.75 (dd, J = 8.2, 1.1 Hz, 2H), 7.41–7.39 (m, 1H), 7.35–7.31 (m, 2H), 6.75 (s, 1H), 3.39–3.35 (m, 2H), 1.57–1.51 (m, 2H), 1.36–1.31 (m, 2H), 0.89 (dd, J = 8.8, 6.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.5, 134.7, 131.0, 128.2, 126.8, 39.6, 31.5, 20.0, 13.6.

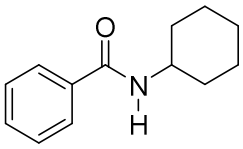
3.3 *N*-Hexylbenzamide (3c)[3]



3c

The title compound was obtained as a pale yellow liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.56; Yield 80% (164 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.76 (d, J = 7.5 Hz, 2H), 7.42 (t, J = 7.2 Hz, 1H), 7.34 (t, J = 7.4 Hz, 2H), 6.78 (s, 1H), 3.37 (q, J = 6.5 Hz, 2H), 1.58–1.52 (m, 2H), 1.32–1.26 (m, 6H), 0.85 (t, J = 6.0 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.5, 134.7, 131.0, 128.2, 126.8, 40.0, 31.3, 29.4, 26.5, 22.4, 13.8.

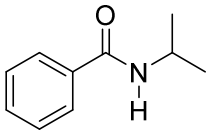
3.4 *N*-Cyclohexylbenzamide (3d)[3]



3d

The title compound was obtained as a white solid. M.p. 154-156 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.60; Yield 90% (182 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ= 7.74 (d, J = 7.7 Hz, 2H), 7.46 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 7.4 Hz, 2H), 6.11 (s, 1H), 3.99–3.93 (m, 1H), 2.01 (d, J = 11.3 Hz, 2H), 1.74 (d, J = 13.4 Hz, 2H), 1.64 (d, J = 12.9 Hz, 1H), 1.44–1.36 (m, 2H), 1.27–1.14 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 166.5, 135.0, 131.1, 128.4, 126.7, 48.6, 33.1, 25.50, 24.8.

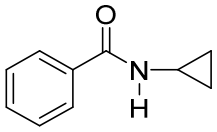
3.5 *N-Iso*propylbenzamide (3e)[2]



3e

The title compound was obtained as a white solid. M.p. 84 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.60; Yield 95% (155 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.74 (d, J = 7.6 Hz, 2H), 7.45 (t, J = 7.0 Hz, 1H), 7.38 (t, J = 7.3 Hz, 2H), 6.15 (s, 1H), 4.29–4.23 (m, 1H), 1.24 (d, J = 6.5 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ= 166.6, 134.9, 131.1, 128.3, 126.7, 41.7, 22.7.

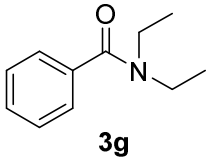
3.6 *N*-Cyclopropylbenzamide (3f)[4]



3f

The title compound was obtained as a white solid. M.p. 54-56 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.66; Yield 73% (117 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.73 (d, J = 7.6 Hz, 2H), 7.43 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.6 Hz, 2H), 6.73 (s, 1H), 2.88–2.83 (m, 1H), 0.81–0.77 (m, 2H), 0.62–0.58 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 168.9, 134.3, 131.2, 128.3, 126.8, 23.0, 6.5.

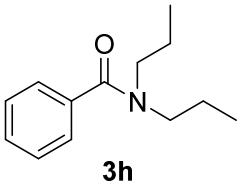
3.7 *N,N*-Diethylbenzamide (3g)[2]



3g

The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.62; Yield 72% (127 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.40–7.33 (m, 5H), 3.52 (s, 2H), 3.22 (s, 2H), 1.23 (s, 3H), 1.08 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 171.2, 137.1, 129.0, 128.2, 126.1, 43.2, 39.1, 14.0, 12.7.

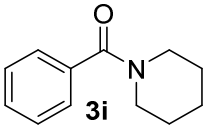
3.8 *N,N*-Dipropylbenzamide (3h)[5]



3h

The title compound was obtained as a pale yellow liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.60; Yield 70% (143 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.32 (d, J = 6.8 Hz, 5H), 3.41 (s, 2H), 3.11 (s, 2H), 1.64 (s, 2H), 1.48 (s, 2H), 0.93 (s, 3H), 0.69 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 171.5, 137.2, 128.7, 128.1, 126.2, 50.4, 46.0, 21.7, 20.5, 11.2, 10.8.

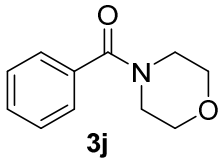
3.9 Phenyl(piperidin-1-yl)methanone (3i)[2]



3i

The title compound was obtained as a white solid. M.p. 48 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.45; Yield 69% (130 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.37 (s, 5H), 3.69 (s, 2H), 3.32 (s, 2H), 1.66 (s, 4H), 1.49 (s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 170.2, 136.4, 129.2, 128.3, 126.6, 48.6, 43.0, 26.4, 25.5, 24.5.

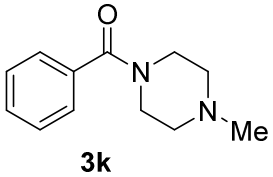
3.10 Morpholino(phenyl)methanone (3j)[2]



3j

The title compound was obtained as a white solid. M.p. 72-74 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.46; Yield 75% (143 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.39 (s, 5H), 3.76 (s, 4H), 3.61 (s, 2H), 3.43 (s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 170.3, 135.2, 129.8, 128.4, 127.0, 66.8. 48.1, 42.5.

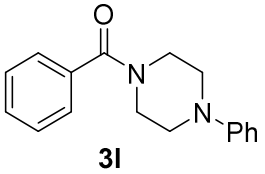
3.11 (4-Methylpiperazin-1-yl)(phenyl)methanone (3k)[6]



3k

The title compound was obtained as oil. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (70:30), R_f = 0.36; Yield 66% (135 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.54–7.35 (m, 5H), 3.76 (s, 2H), 3.40 (s, 2H), 2.44 (s, 3H), 2.27 (s, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 170.1, 135.6, 129.5, 128.3, 126.8, 55.1, 54.5, 47.4, 45.8, 41.8.

3.12 Phenyl(4-phenylpiperazin-1-yl)methanone (3l)[7]

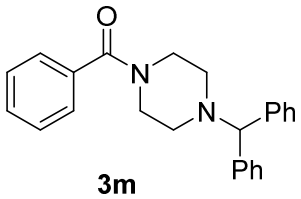


3l

The title compound was obtained as a brown solid. M.p. 94 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (70:30), R_f = 0.66; Yield 72% (191 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.45–7.41 (m, 5H), 7.29 (dd, J = 8.7,

7.3 Hz, 2H), 6.92 (dd, *J* = 15.3, 7.7 Hz, 3H), 3.94 (s, 2H), 3.60 (s, 2H), 3.19 (d, *J* = 61.2 Hz, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 170.3, 150.8, 135.5, 129.7, 129.2, 128.4, 127.0, 120.6, 120.5, 116.7, 116.6, 49.7, 42.0.

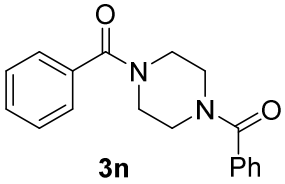
3.13 (4-benzhydrylpiperazin-1-yl)(phenyl)methanone (3m)[8]



3m

The title compound was obtained as a white solid. M.p. 145-146 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (70:30), R_f = 0.60; Yield 67% (238 mg). **^{1}H NMR** (500 MHz, DMSO-d_6) δ= 7.43–7.39 (m, 7H), 7.36–7.34 (m, 2H), 7.29 (t, *J* = 7.6 Hz, 4H), 7.19 (t, *J* = 7.3 Hz, 2H), 4.34 (s, 1H), 3.40 (s, 8H).**^{13}C NMR** (125 MHz, DMSO-d_6) δ = 168.8, 142.4, 135.7, 129.4, 128.5, 128.3, 127.6, 126.9, 126.9, 74.7, 51.6, 51.2, 47.1, 41.5.

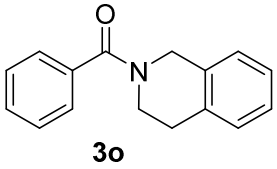
3.14 Piperazine-1,4-diylbis(phenylmethanone) (3n)[9]



3n

The title compound was obtained as a white solid. M.p. 193-195 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (70:30), R_f = 0.55; Yield 65% (191 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.40 (s, 10H), 3.62 (d, *J* = 111.1 Hz, 8H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 170.5, 135.0, 130.0, 128.5, 126.9, 47.6, 42.1.

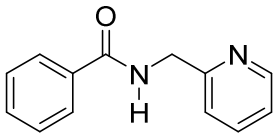
3.15 (3,4-Dihydro*iso*quinolin-2(1H)-yl)(phenyl)methanone (3o)[10]



3o

The title compound was obtained as a light yellow solid. M.p. 127-129 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (70:30), R_f = 0.70; Yield 72% (170 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ= 7.44 (d, *J* = 4.2 Hz, 5H), 7.26-6.91(m, 4H), 4.90 (s, 1H), 4.59 (s, 1H), 4.00 (s, 1H), 3.64 (s, 1H), 2.93 (d, *J* = 56.5 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 170.9, 136.0, 133.7, 132.8, 130.3, 129.7, 128.4, 126.7, 126.5, 125.8, 49.7, 45.2, 44.7, 40.4, 29.5, 28.1.

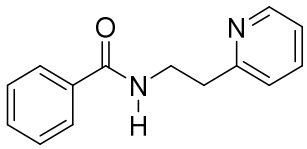
3.16 *N*-(Pyridine-2-ylmethyl)benzamide (3p)[11]



3p

The title compound was obtained as a yellow solid. M.p. 68 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.60; Yield 85% (180 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.52 (d, *J* = 4.7 Hz, 1H), 7.87–7.83 (m, 2H), 7.68 (td, *J* = 7.7, 1.7 Hz, 1H), 7.49-7.46 (m, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.20 (dd, *J* = 7.1, 5.2 Hz, 1H), 4.74 (d, *J* = 5.0 Hz, 2H). 3.45 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.3, 156.1, 148.5, 137.1, 134.1, 131.4, 128.8, 127.0, 122.4, 122.3, 44.5.

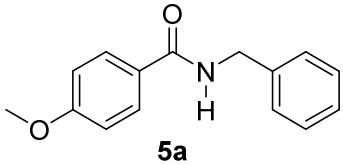
3.17 *N*-(2-(Pyridin-2-yl)ethyl)benzamide(3q)[12]



3q

The title compound was obtained as a pale yellow solid. M.p. 68-70 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (85:15), R_f = 0.60; Yield 78% (176 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.56 (d, *J* = 4.7 Hz, 1H), 7.79–7.77 (m, 2H), 7.74 (td, *J* = 7.7, 1.5 Hz, 1H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.26–7.24 (m, 1H), 3.88 (dd, *J* = 12.2, 5.8 Hz, 2H), 3.66 (s, 1H), 3.18 (t, *J* = 6.3 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.3, 159.1, 147.6, 138.2, 134.4, 131.2, 128.4, 126.9, 124.4, 122.1, 39.0, 36.0.

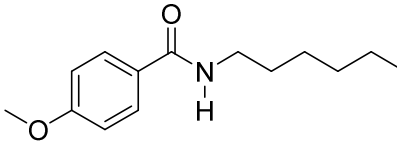
3.18 *N*-Benzyl-4-methoxybenzamide(5a)[13]



5a

The title compound was obtained as a white solid. M.p. 122 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.66; Yield 98% (236 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ= 7.79 (d, *J* = 7.9 Hz, 2H), 7.34–7.29 (m, 4H), 6.90 (d, *J* = 7.9 Hz, 2H), 6.67 (s, 1H), 4.61 (d, *J* = 3.8 Hz, 2H), 3.84 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 166.8, 162.1, 138.4, 128.7, 128.8, 127.7, 127.3, 126.5, 113.6, 55.3, 43.9.

3.19 *N*-Hexyl-4-methoxybenzamide(5b)[13]

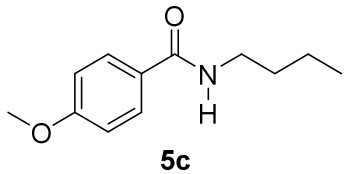


5b

The title compound was obtained as a white solid. M.p. 92 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.64; Yield 95% (223 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.73 (d, *J* = 8.3 Hz, 2H), 6.88 (d, *J* =

8.5 Hz, 2H), 6.28 (s, 1H), 3.82 (s, 3H), 3.40 (dd, *J* = 13.3, 6.7 Hz, 2H), 1.60–1.54 (m, 2H), 1.36–1.24 (m, 6H), 0.87 (t, *J* = 6.2 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ= 166.9, 161.9, 128.5, 127.1, 113.5, 55.2, 40.0, 31.4, 29.6, 26.6, 22.5, 13.95.

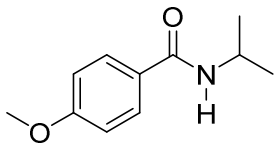
3.20 *N*-Butyl-4-methoxybenzamide(5c)[13]



5c

The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.62; Yield 95% (196 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.44 (s, 1H), 3.79 (s, 3H), 3.38 (dd, *J* = 13.1, 7.1 Hz, 2H), 1.57–1.51 (m, 2H), 1.35 (dd, *J* = 15.1, 7.5 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.0, 161.8, 128.5, 127.0, 113.5, 55.2, 39.6, 31.6, 20.0, 13.6.

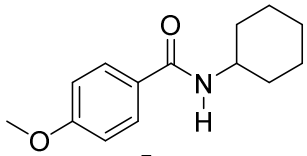
3.21 *N*-*Iso*propyl-4-methoxybenzamide (5d)[14]



5d

The title compound was obtained as a white solid. M.p. 120 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.60; Yield 88% (170 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.03 (s, 1H), 4.26–4.21 (m, 1H), 3.81 (s, 3H), 1.22 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ= 166.1, 161.8, 128.5, 127.1, 113.5, 55.2, 41.6, 22.7.

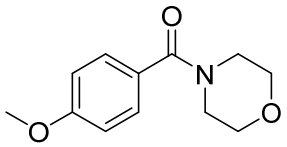
3.22 *N*-Cyclohexyl-4-methoxybenzamide (5e)[15]



5e

The title compound was obtained as a white solid. M.p. 154 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.60; Yield 86% (200 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ= 7.71 (d, *J* = 7.7 Hz, 2H), 6.87 (d, *J* = 8.1 Hz, 2H), 6.04 (s, 1H), 3.93 (d, *J* = 7.6 Hz, 1H), 3.81 (s, 3H), 1.99 (d, *J* = 10.5 Hz, 2H), 1.72 (d, *J* = 12.7 Hz, 2H), 1.62 (d, *J* = 12.2 Hz, 1H), 1.40–1.35 (m, 2H), 1.24–1.15 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ= 166.0, 161.8, 128.5, 127.2, 113.5, 55.3, 48.5, 33.2, 25.5, 24.8.

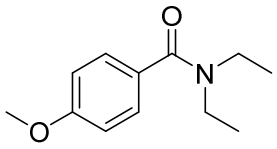
3.23 (4-Methoxyphenyl)(morpholino)methanone(5f)[16]



5f

The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.45; Yield 68% (150 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.36 (d, J = 7.9 Hz, 2H), 6.89 (d, J = 7.9 Hz, 2H), 3.80 (s, 3H), 3.66 (s, 8H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ= 170.2, 160.7, 129.0, 127.2, 113.6, 66.7, 55.2.

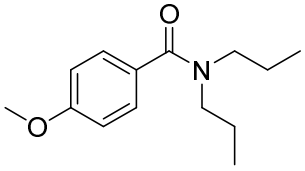
3.24 *N,N*-Diethyl-4-methoxybenzamide (5g)[17]



5g

The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.60; Yield 82% (169 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.31 (d, J = 7.9 Hz, 2H), 6.86 (d, J = 8.0 Hz, 2H), 3.78 (s, 3H), 3.37 (d, J = 74.8 Hz, 4H), 1.14 (b, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 171.1, 160.1, 129.3, 128.0, 113.4, 55.1, 43.1, 39.2, 22.5, 13.9.

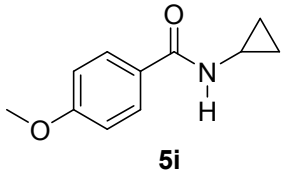
3.25 4-Methoxy-*N,N*-dipropylbenzamide (5h)[18]



5h

The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.60; Yield 67% (157 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ= 7.30 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 8.0 Hz, 2H), 3.79 (s, 3H), 3.30 (d, J = 102.4 Hz, 4H), 1.58 (d, J = 42.9 Hz, 4H), 0.93–0.75 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 171.5, 160.0, 129.4, 128.1, 113.4, 55.1, 50.7, 46.3, 21.7, 20.6, 11.0.

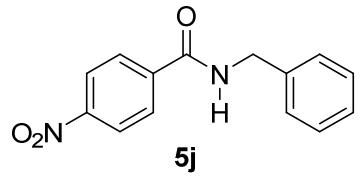
3.26 *N*-Cyclopropyl-4-methoxybenzamide (5i)[19]



5i

The title compound was obtained as viscous liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.70; Yield 66% (126 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ= 7.70 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.32 (s, 1H), 3.82 (s, 3H), 2.87 (dt, J = 10.4, 3.3 Hz, 1H), 0.83 (q, J = 6.7 Hz, 2H), 0.61–0.57 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ= 168.4, 162.1, 128.5, 126.6, 113.6, 55.4 55.2, 23.1, 22.9, 6.7.

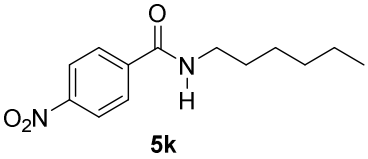
3.27 *N*-Benzyl-4-nitrobenzamide (5j)[20]



5j

The title compound was obtained as a white solid. M.p. 113 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.50; Yield 78% (199 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.22 (d, J = 7.8 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.2 Hz, 5H), 6.85 (s, 1H), 4.62 (d, J = 5.1 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 165.3, 149.5, 139.8, 137.4, 128.8, 128.8, 128.1, 127.8, 123.7, 44.35.

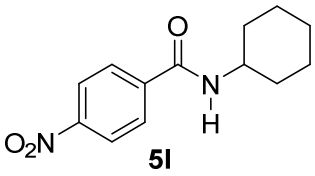
3.28 *N*-Hexyl-4-nitrobenzamide (5k)[21]



5k

The title compound was obtained as a white solid. M.p. 83 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.66; Yield 77% (192 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.19 (d, J = 8.1 Hz, 2H), 7.91 (d, J = 8.1 Hz, 2H), 6.89 (s, 1H), 3.40 (dd, J = 12.8, 6.3 Hz, 2H), 1.60–1.55 (m, 2H), 1.32–1.25 (m, 6H), 0.83 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 165.5, 149.2, 140.3, 128.0, 123.5, 40.3, 31.3, 29.3, 26.5, 22.4, 13.8.

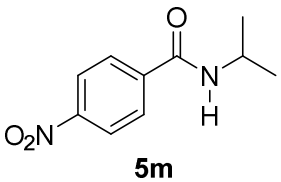
3.29 *N*-Cyclohexyl-4-nitrobenzamide(5l)[15]



5l

The title compound was obtained as a white solid. M.p. 178-179 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.50; Yield 62% (154 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.25 (d, J = 7.7 Hz, 2H), 7.90 (d, J = 7.7 Hz, 2H), 6.16 (d, J = 5.3 Hz, 1H), 4.00–3.94 (m, 1H), 2.03 (d, J = 11.2 Hz, 2H), 1.76 (d, J = 12.1 Hz, 2H), 1.66 (d, J = 12.9 Hz, 1H), 1.41 (q, J = 12.3 Hz, 2H), 1.29–1.18 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 164.5, 149.3, 140.6, 128.0, 123.7, 49.2, 33.0, 25.4, 24.8.

3.30 *N*-*Iso*propyl-4-nitrobenzamide (5m)[14]

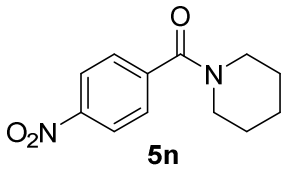


5m

The title compound was obtained as a white solid. M.p. 88 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.50; Yield 64% (133 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.21 (d, J = 8.1 Hz, 2H), 7.90 (d, J = 8.0 Hz, 2H), 6.36 (s, 1H), 4.25 (dq, J = 13.1, 6.5 Hz, 1H), 1.25 (d, J = 6.5 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 164.6, 149.3,

140.5, 128.0, 123.6, 42.3, 22.5.

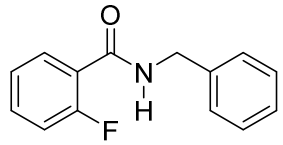
3.31 (4-Nitrophenyl)(piperidin-1-yl)methanone (5n)[22]



5n

The title compound was obtained as a white solid. M.p. 118 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.40; Yield 69% (162 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.25 (d, J = 7.8 Hz, 2H), 7.54 (d, J = 7.8 Hz, 2H), 3.70 (s, 2H), 3.26 (s, 2H), 1.68 (s, 4H), 1.51 (s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 167.8, 148.0, 142.6, 127.7, 123.7, 48.5, 43.1, 26.4, 25.4, 24.3.

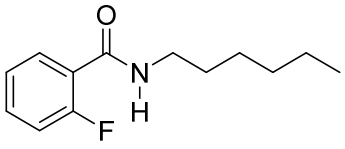
3.32 *N*-Benzyl-2-fluorobenzamide (5o)[23]



5o

The title compound was obtained as a white solid. M.p. 42 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.66; Yield 74% (170 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.16 (t, J = 7.7 Hz, 1H), 7.49 (td, J = 7.3, 1.7 Hz, 1H), 7.39–7.36 (m, 4H), 7.33–7.28 (m, 2H), 7.13 (dd, J = 11.8, 8.5 Hz, 2H), 4.71 (d, J = 5.6 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 163.2 (d, J = 3.7 Hz), 160.5 (d, J = 245 Hz), 137.9, 133.2, 132.0 (d, J = 15.0 Hz), 128.7, 127.6, 127.5, 124.7 (d, J = 3.7 Hz), 120.9 (d, J = 11.2 Hz), 115.9 (d, J = 23.7 Hz), 44.0.

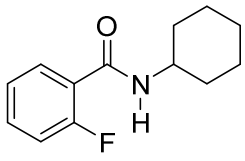
3.33 2-Fluoro-*N*-hexylbenzamide (5p)



5p

The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.60; Yield 66% (147 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.04–8.01 (m, 1H), 7.40–7.39 (m, 1H), 7.19 (dd, J = 10.8, 4.1 Hz, 1H), 7.05 (dd, J = 15.6, 4.6 Hz, 1H), 6.76 (s, 1H), 3.42 (d, J = 6.8 Hz, 2H), 1.57 (d, J = 7.2 Hz, 2H), 1.34–1.27 (m, 6H), 0.85 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 163.1 (d, J = 3.7 Hz), 160.4 (d, J = 245 Hz), 132.9 (d, J = 8.7 Hz), 131.9 (d, J = 2.5 Hz), 124.6 (d, J = 3.7 Hz), 121.2 (d, J = 12.5 Hz), 115.8 (d, J = 23.7 Hz), 40.0, 31.3, 29.3, 26.5, 22.4, 13.9. **HRMS**: Calc. for $C_{13}H_{19}FNO$ $[M+H]^+$: 224.1451, Obser.: 224.1436.

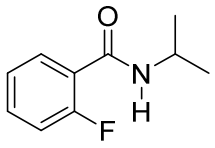
3.34 *N*-Cyclohexyl-2-fluorobenzamide (5q)[24]



5q

The title compound was obtained as a white solid. M.p. 132-134 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.60; Yield 68% (150 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.07 (td, J = 7.9, 1.5 Hz, 1H), 7.43 (td, J = 7.3, 1.7 Hz, 1H), 7.23 (t, J = 7.3 Hz, 1H), 7.08 (dd, J = 11.8, 8.5 Hz, 1H), 6.61 (s, 1H), 4.04–3.98 (m, 1H), 2.01 (dd, J = 12.3, 3.1 Hz, 2H), 1.75–1.71 (m, 2H), 1.65–1.61 (m, 1H), 1.47–1.38 (m, 2H), 1.31–1.21 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 162.1 (d, J = 2.5 Hz), 160.4 (d, J = 245 Hz), 132.8 (d, J = 10.0 Hz), 131.9, 124.6 (d, J = 2.5 Hz), 121.4 (d, J = 11.2 Hz), 115.8 (d, J = 25.0 Hz), 48.5, 32.8, 25.4, 24.6.

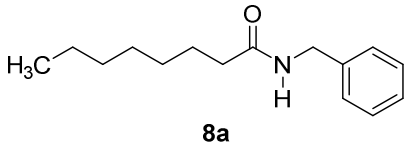
3.35 2-Fluoro-*N*-*iso*propylbenzamide (5r)[25]



5r

The title compound was obtained as a colourless liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.62; Yield 60% (108 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.09–8.06 (m, 1H), 7.46–7.41 (m, 1H), 7.26–7.22 (m, 1H), 7.11–7.07 (m, 1H), 6.54 (s, 1H), 4.34–4.27 (m, 1H), 1.26 (d, J = 6.6 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 162.3 (d, J = 3.7 Hz), 160.5 (d, J = 245 Hz), 132.9 (d, J = 10.0 Hz), 131.9 (d, J = 2.5 Hz), 124.7 (d, J = 2.5 Hz), 121.3 (d, J = 11.2 Hz), 115.8 (d, J = 25.0 Hz), 41.9, 22.7.

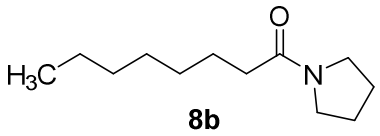
3.36 *N*-Benzyloctanamide (8a)[26]



8a

The title compound was obtained as a white solid. M.p. 64 °C. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.32; Yield 76% (177 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.35–7.29 (m, 2H), 7.26 (dd, J = 6.9, 4.7 Hz, 3H), 5.93 (s, 1H), 4.42 (d, J = 5.7 Hz, 2H), 2.19 (t, J = 7.6 Hz, 2H), 1.65–1.63 (m, 2H), 1.30–1.27 (m, 8H), 0.87 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 173.0, 138.4, 128.6, 127.7, 127.3, 43.4, 36.7, 31.6, 29.2, 28.9, 25.7, 22.5, 14.0.

3.37 1-(pyrrolidin-1-yl)octan-1-one (8b)[27]



8b

The title compound was obtained as a yellow liquid. The residue was purified by column chromatography in silica gel eluting with hexane: EtOAc (80:20), R_f = 0.30; Yield 71% (140 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 3.46 (t, J = 6.9 Hz, 2H), 3.42 (t, J = 6.8 Hz, 2H), 2.27–2.24 (m, 2H), 1.95 (p, J = 6.7 Hz, 2H), 1.85 (p, J = 6.8 Hz, 2H), 1.68–1.62 (m, 2H), 1.35–1.28 (m, 8H), 0.88 (t, J = 6.9 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 171.7, 46.4, 45.4, 34.7, 31.5, 29.3, 28.9, 26.0, 24.8, 24.2, 22.4, 13.9.

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5. ^{1}H and ^{13}C NMR Spectra of the compounds:-

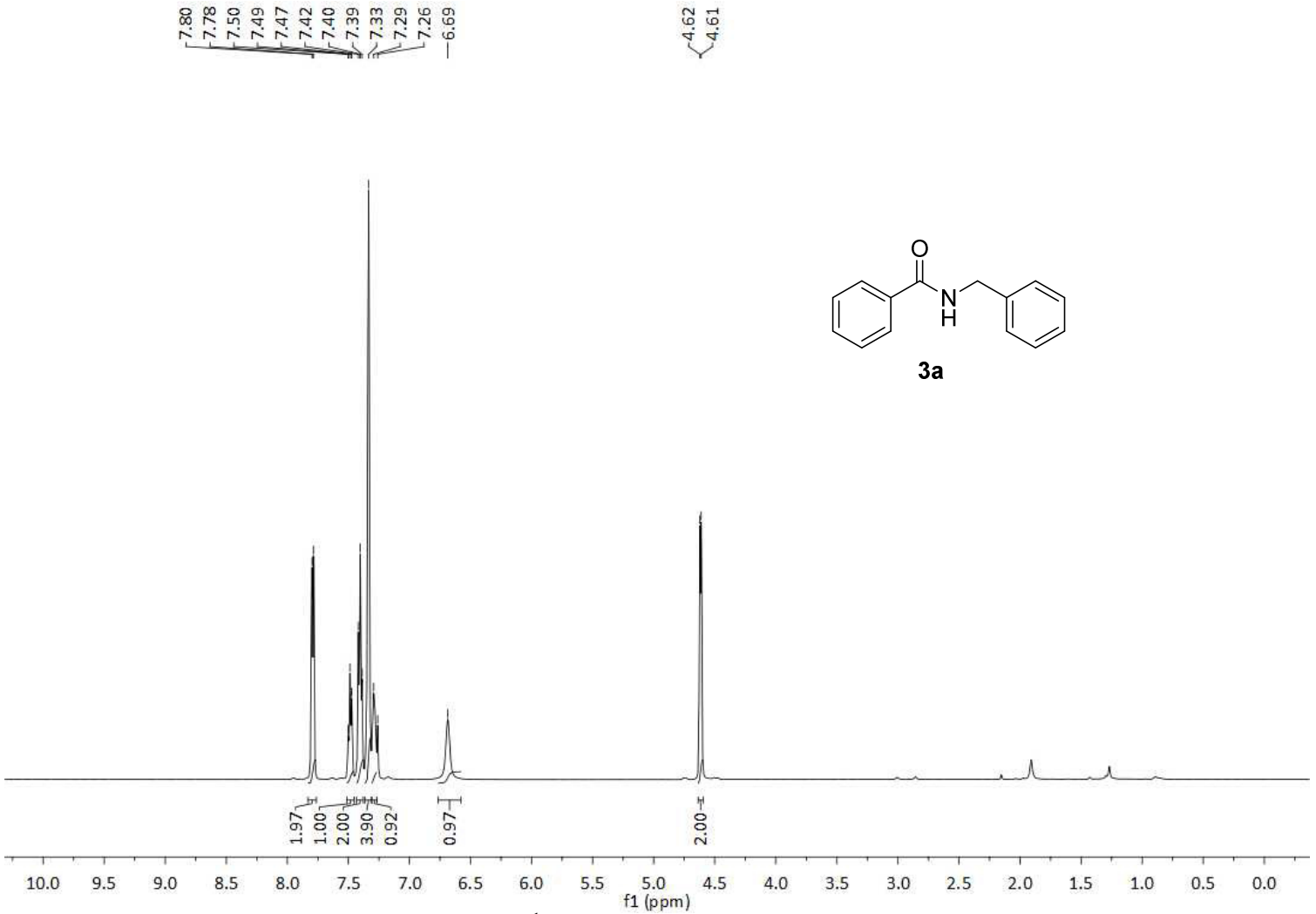


Figure 5.1 ^{1}H NMR of product **3a** in **$CDCl_3$**.

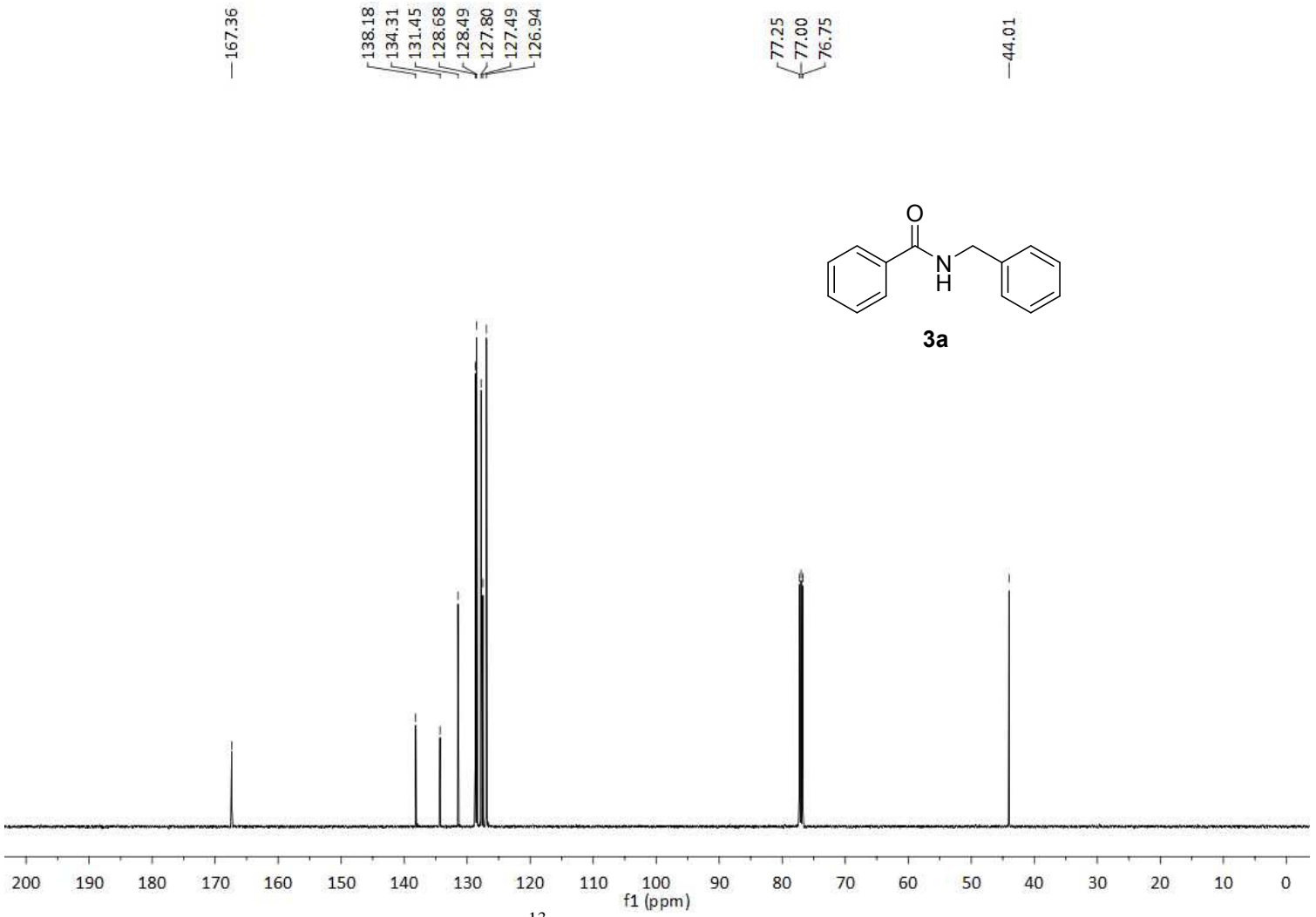


Figure 5.2 ^{13}C NMR of product **3a** in **$CDCl_3$**.

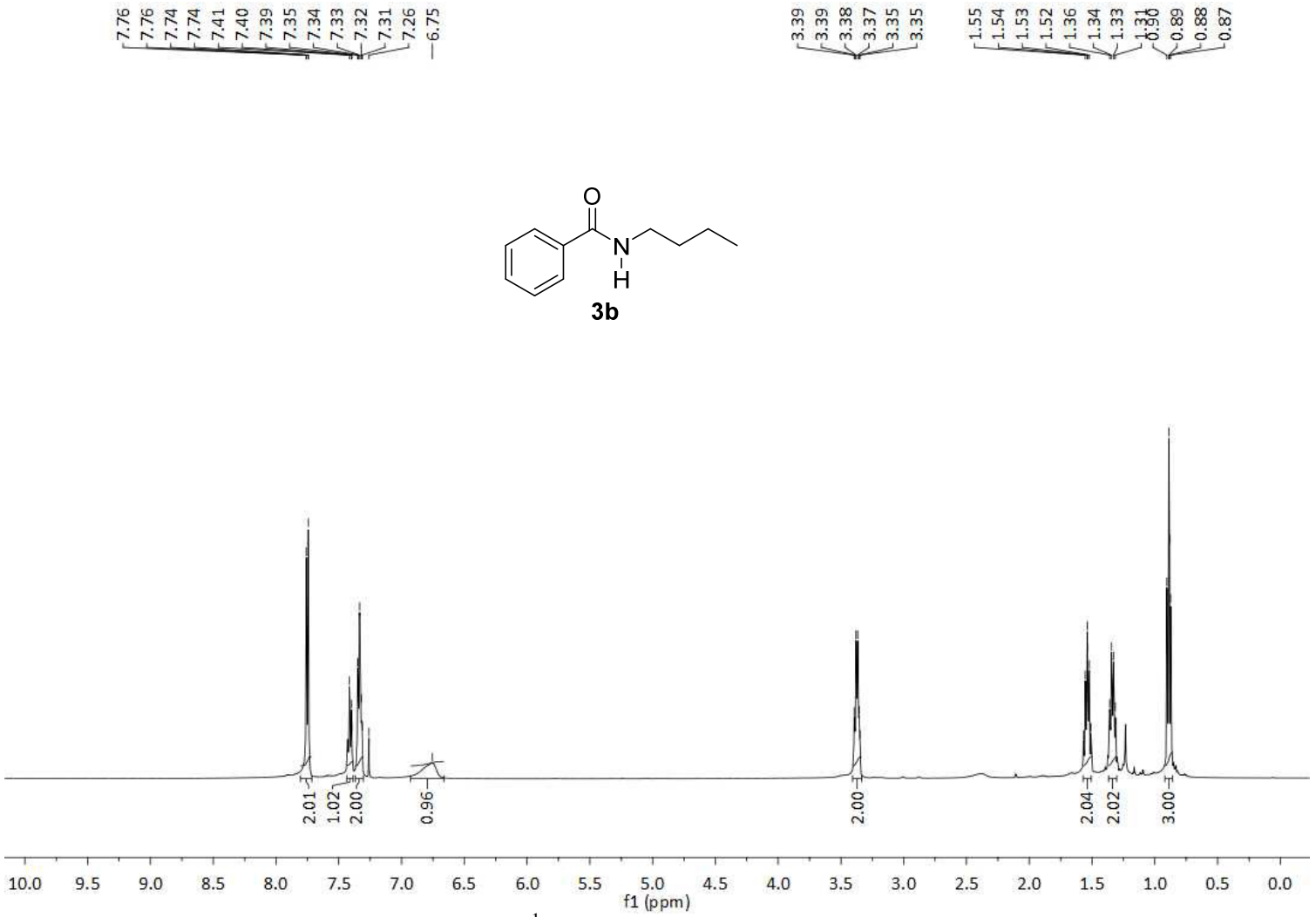


Figure 5.3 ^{1}H NMR of product **3b** in **$CDCl_3$**.

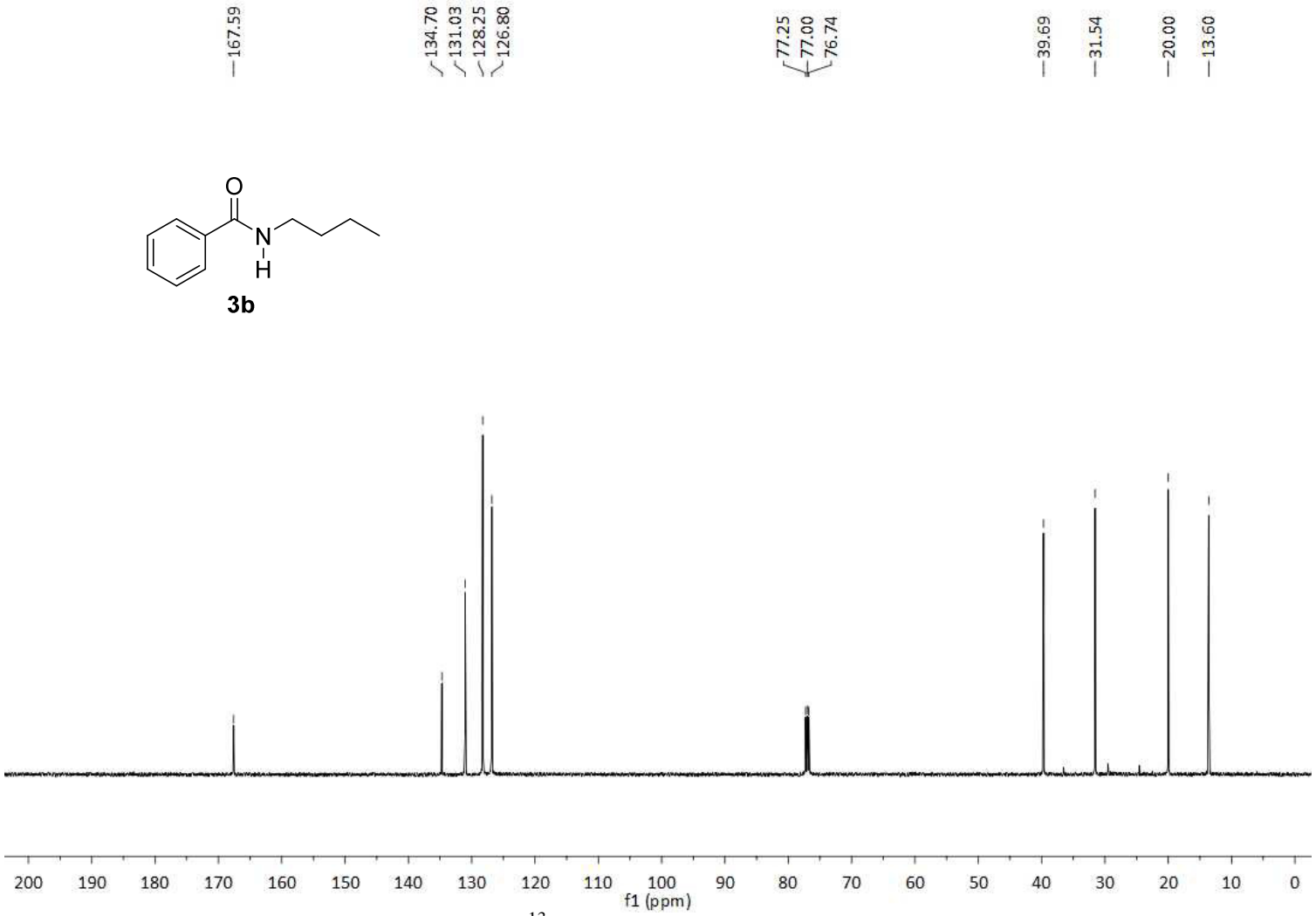


Figure 5.4 ^{13}C NMR of product **3b** in **$CDCl_3$**.

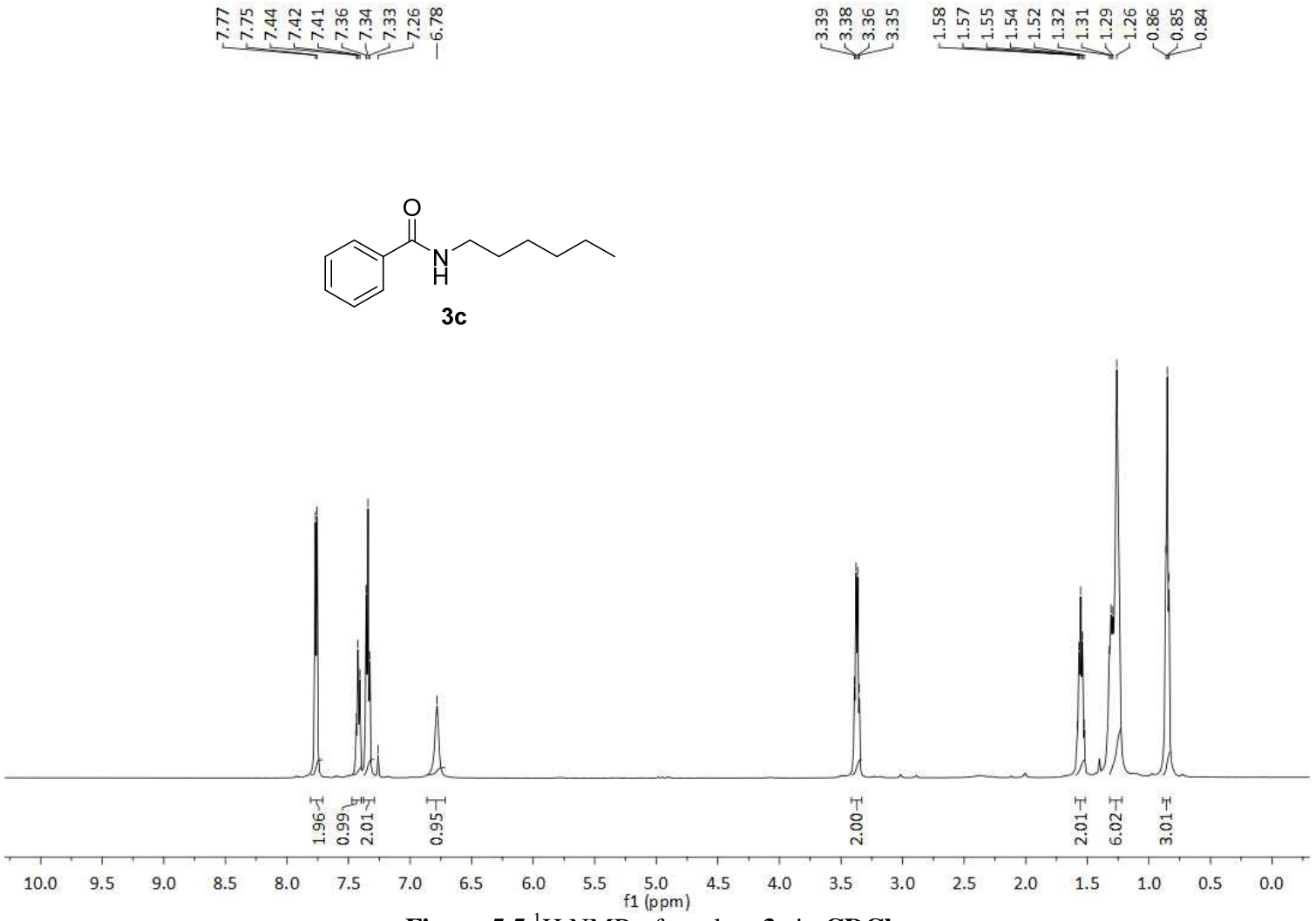


Figure 5.5 ^{1}H NMR of product **3c** in **$CDCl_3$**.

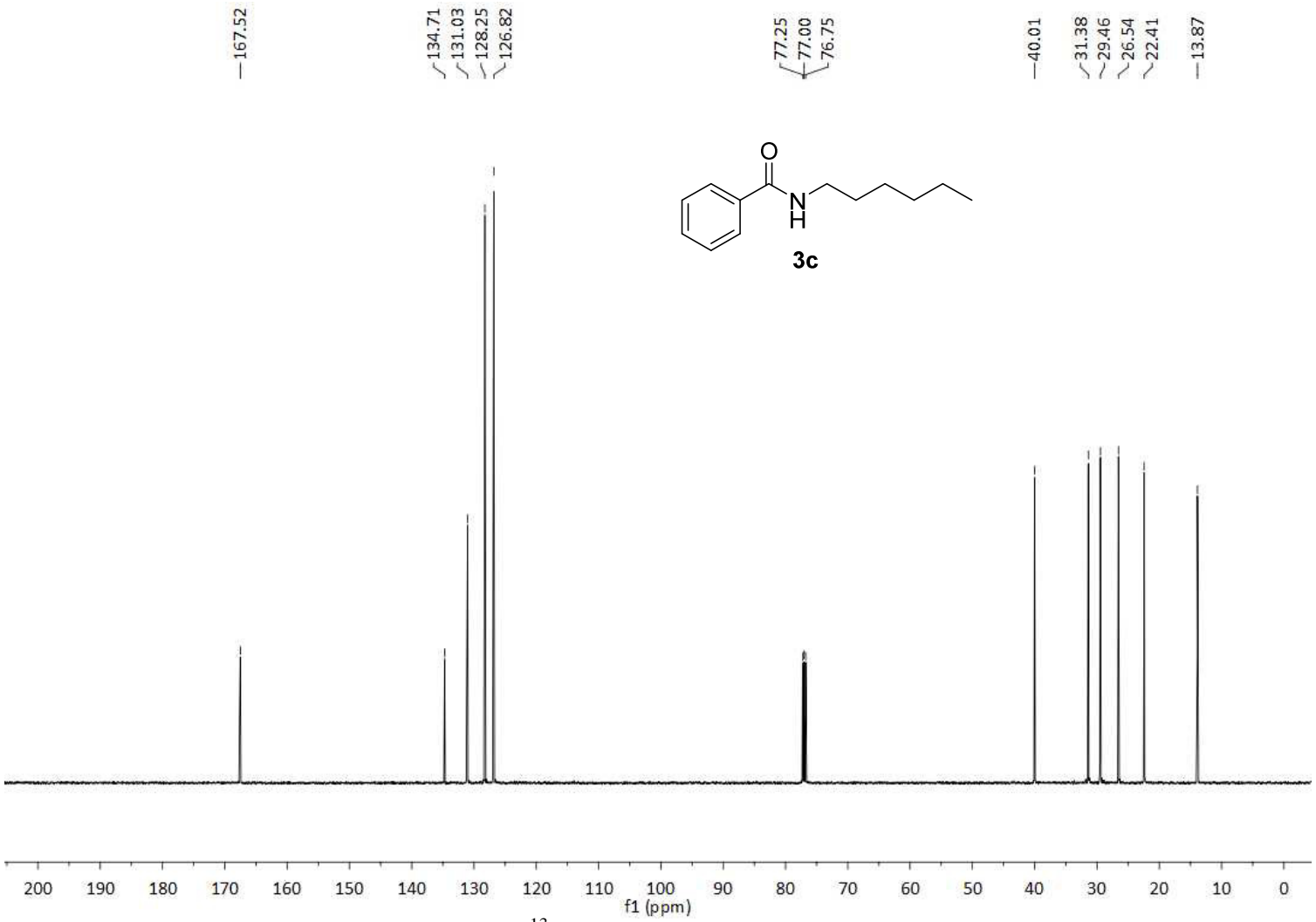


Figure 5.6 ^{13}C NMR of product **3c** in **$CDCl_3$**.

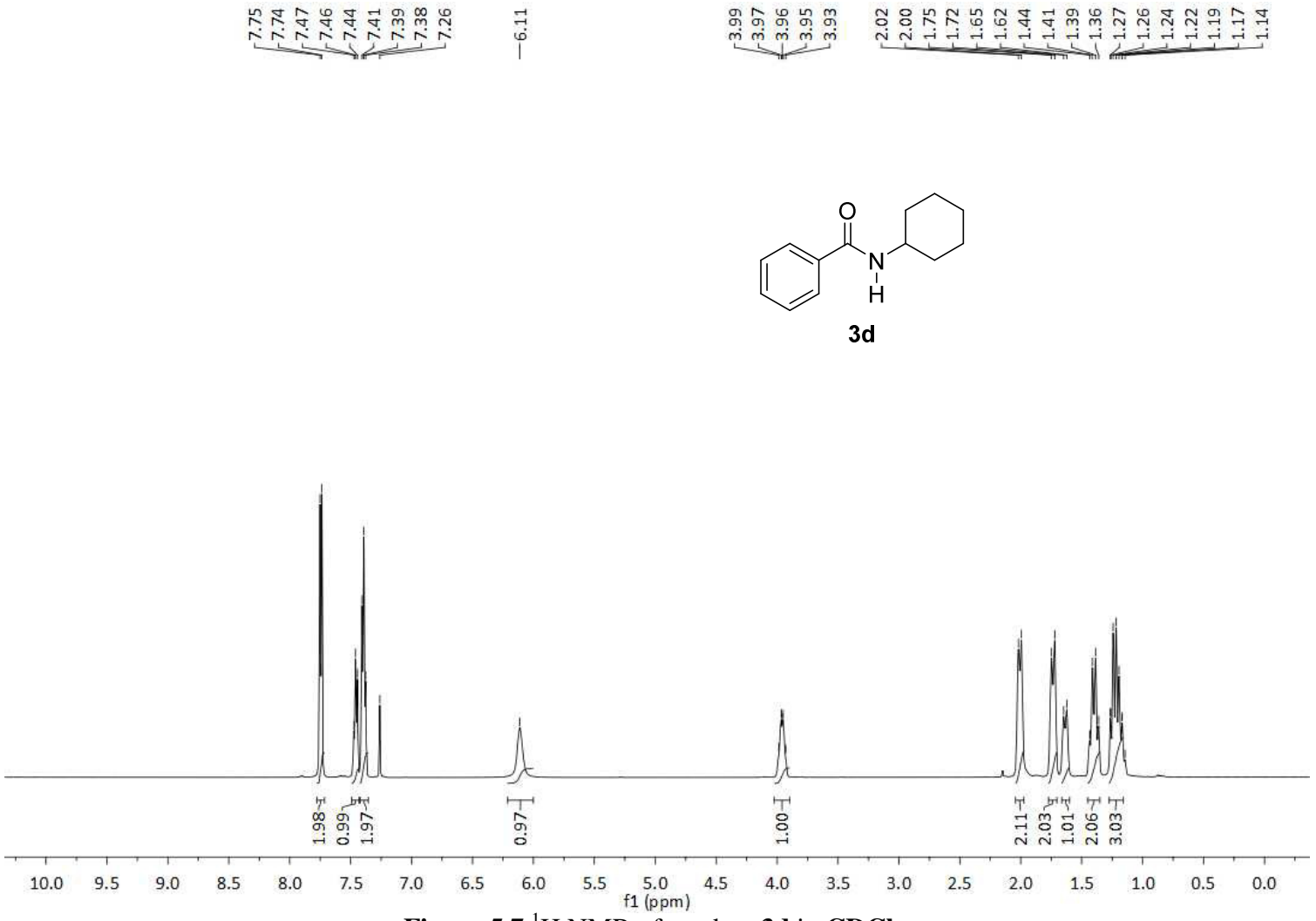


Figure 5.7 ^{1}H NMR of product **3d** in **$CDCl_3$**.

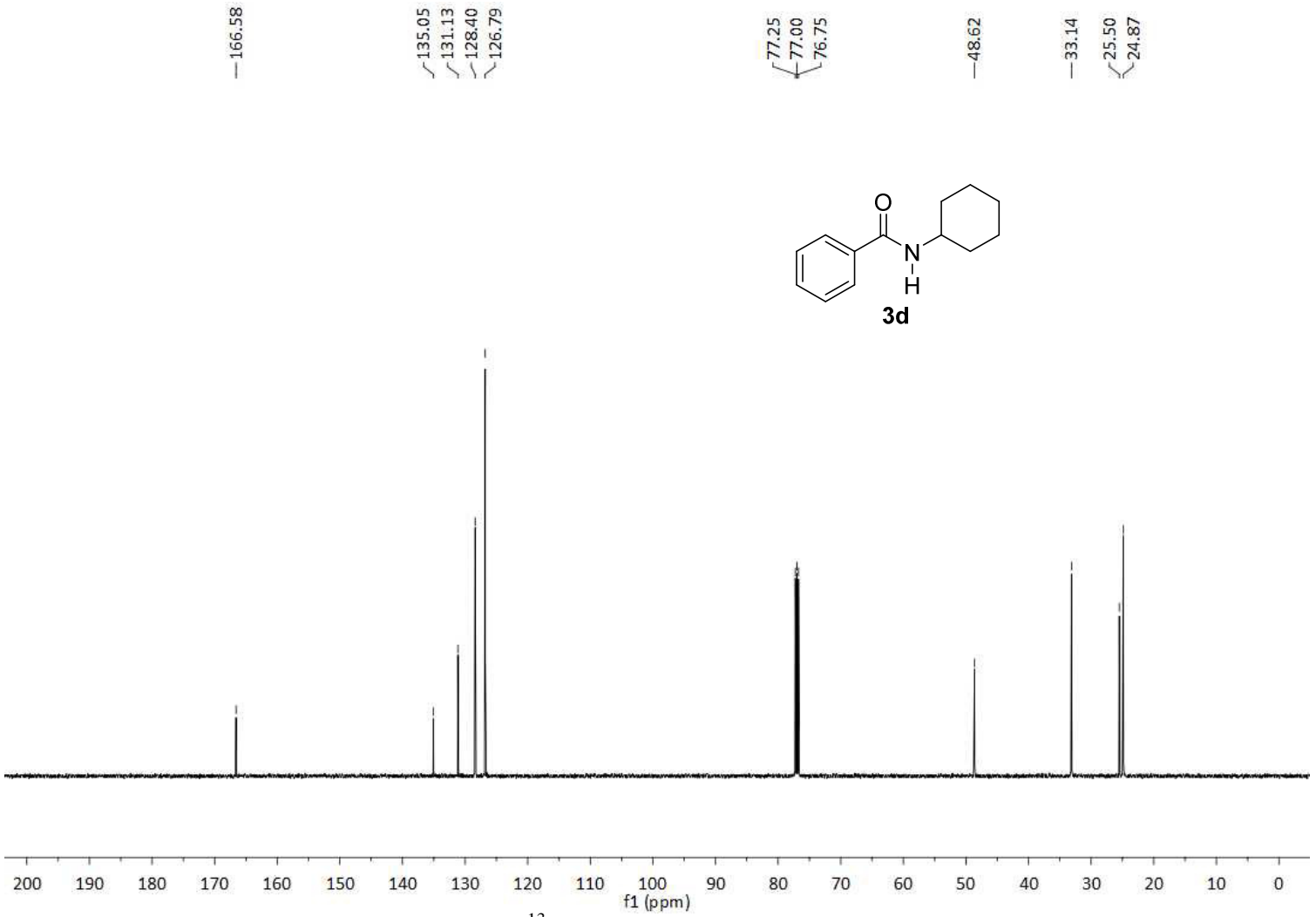


Figure 5.8 ^{13}C NMR of product **3d** in **$CDCl_3$**.

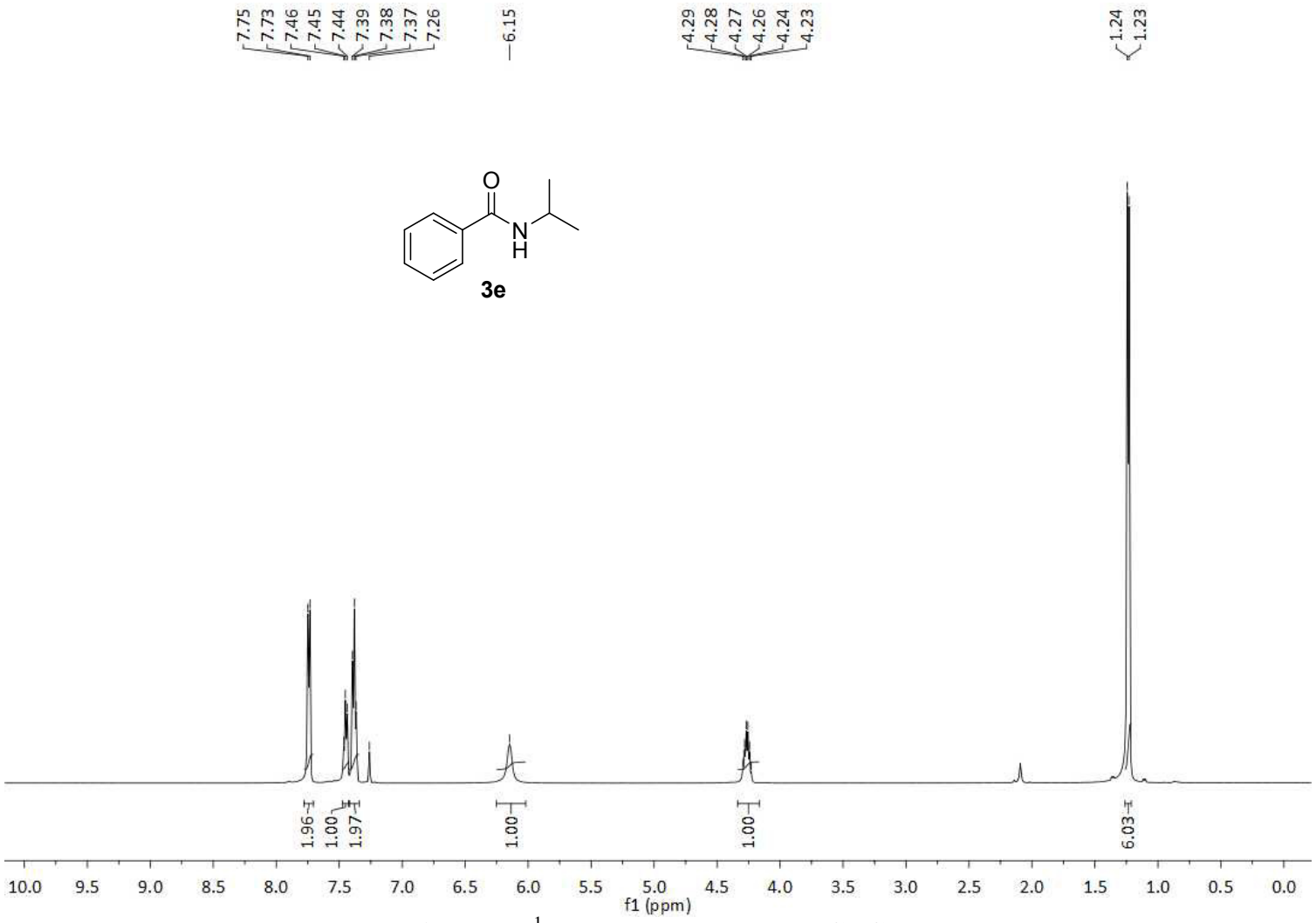


Figure 5.9 ^{1}H NMR of product **3e** in **$CDCl_3$**.

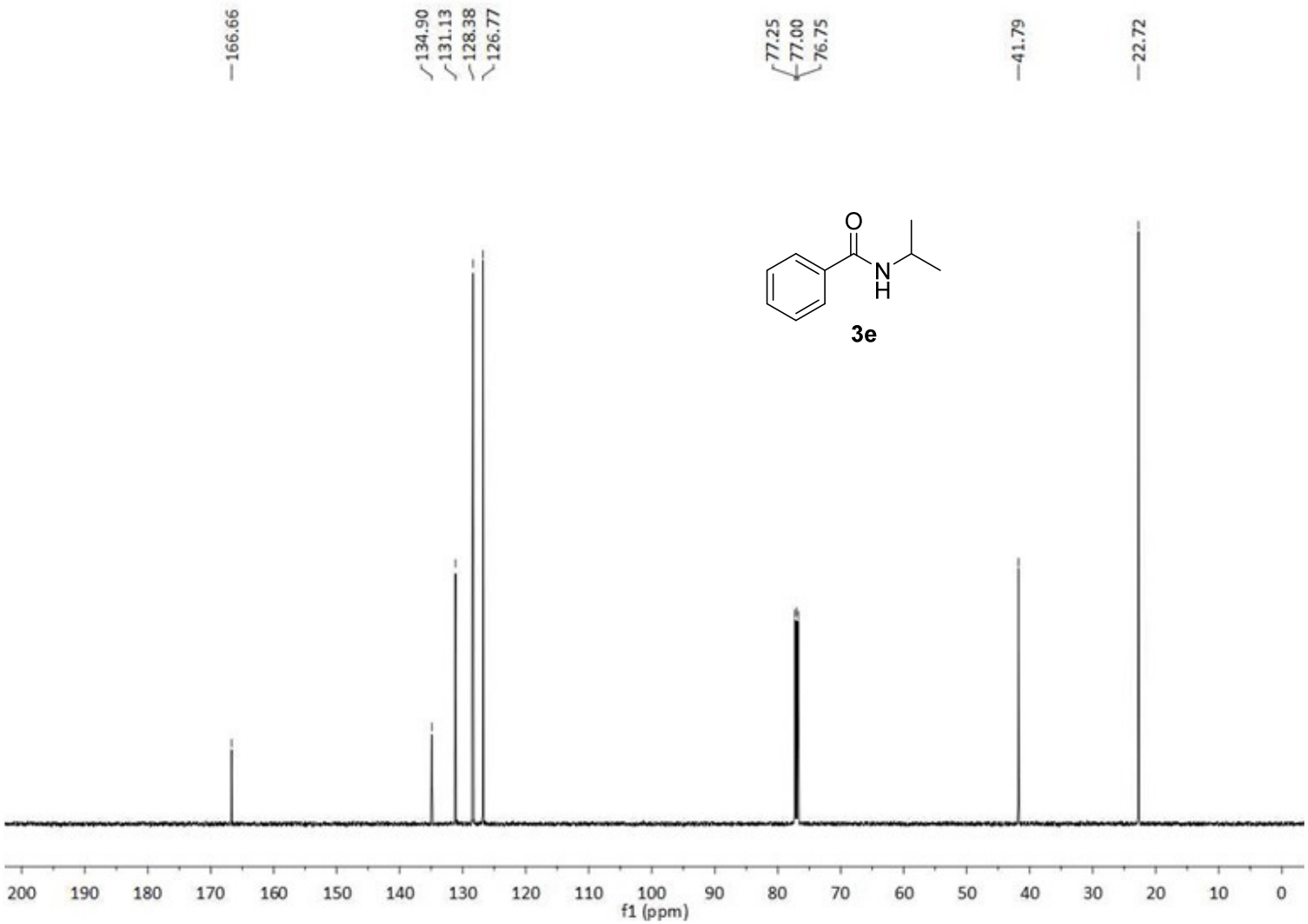


Figure 5.10 ^{13}C NMR of product **3e** in **$CDCl_3$**.

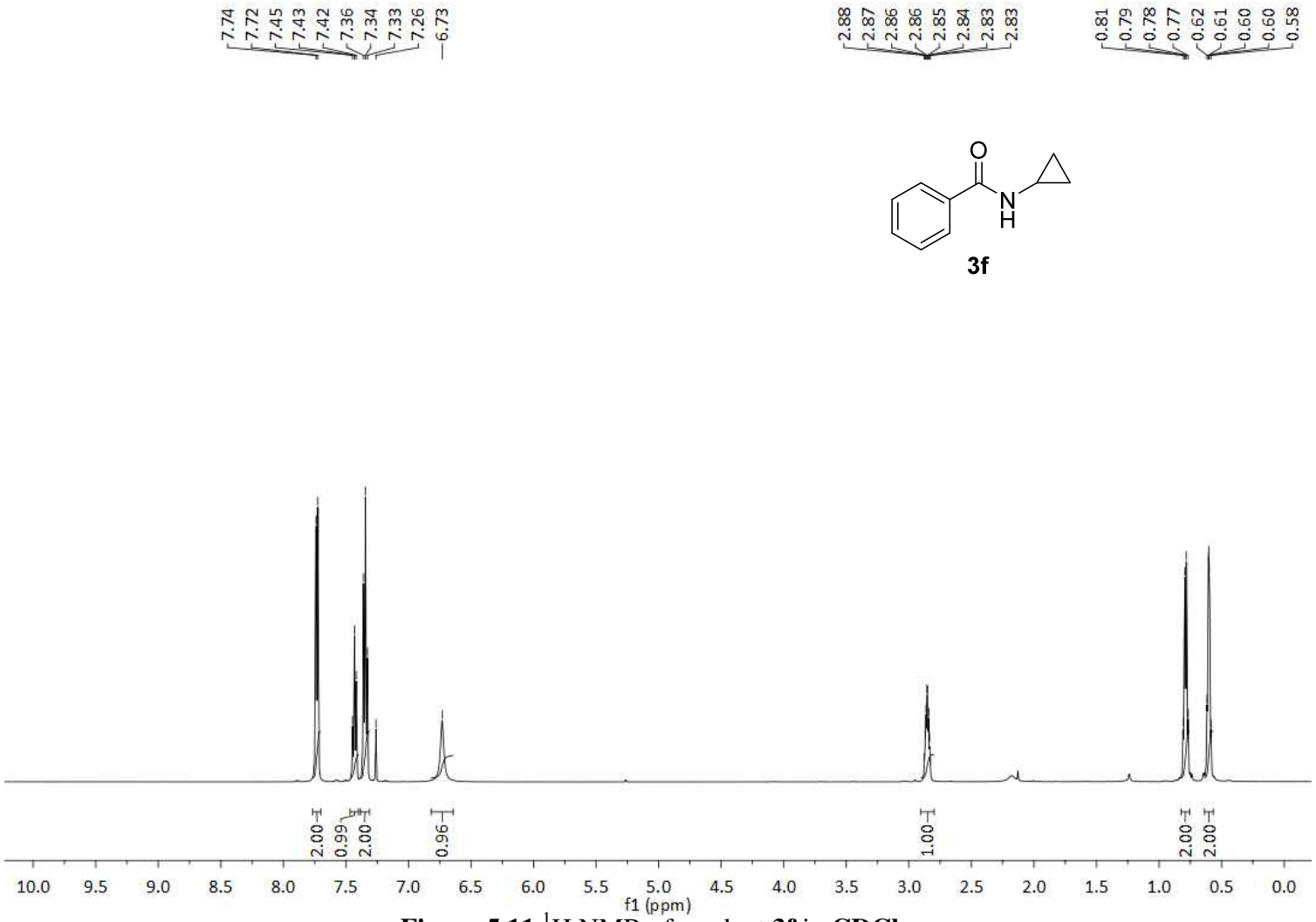


Figure 5.11 ^{1}H NMR of product **3f** in **$CDCl_3$**.

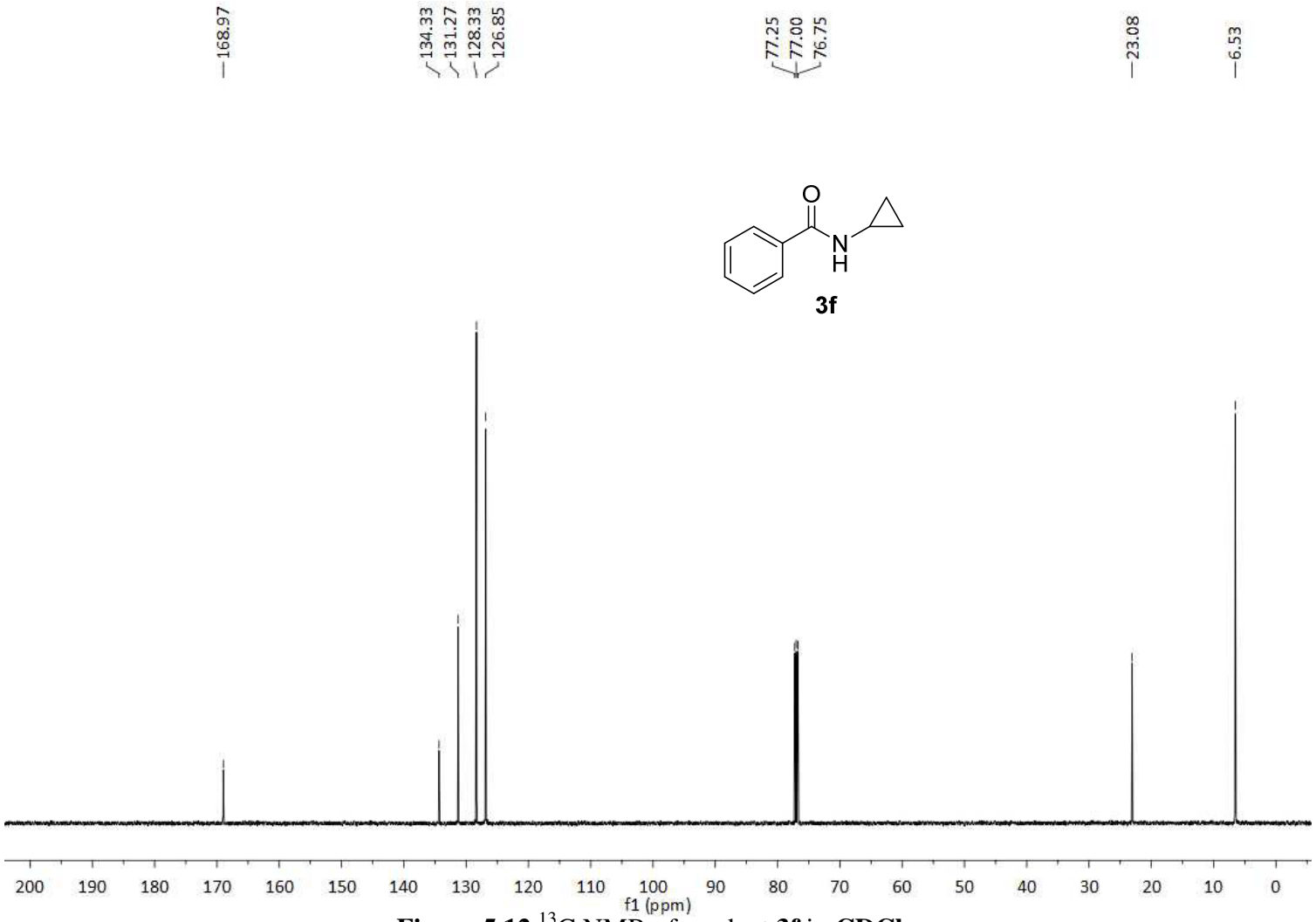


Figure 5.12 ^{13}C NMR of product **3f** in **$CDCl_3$**.

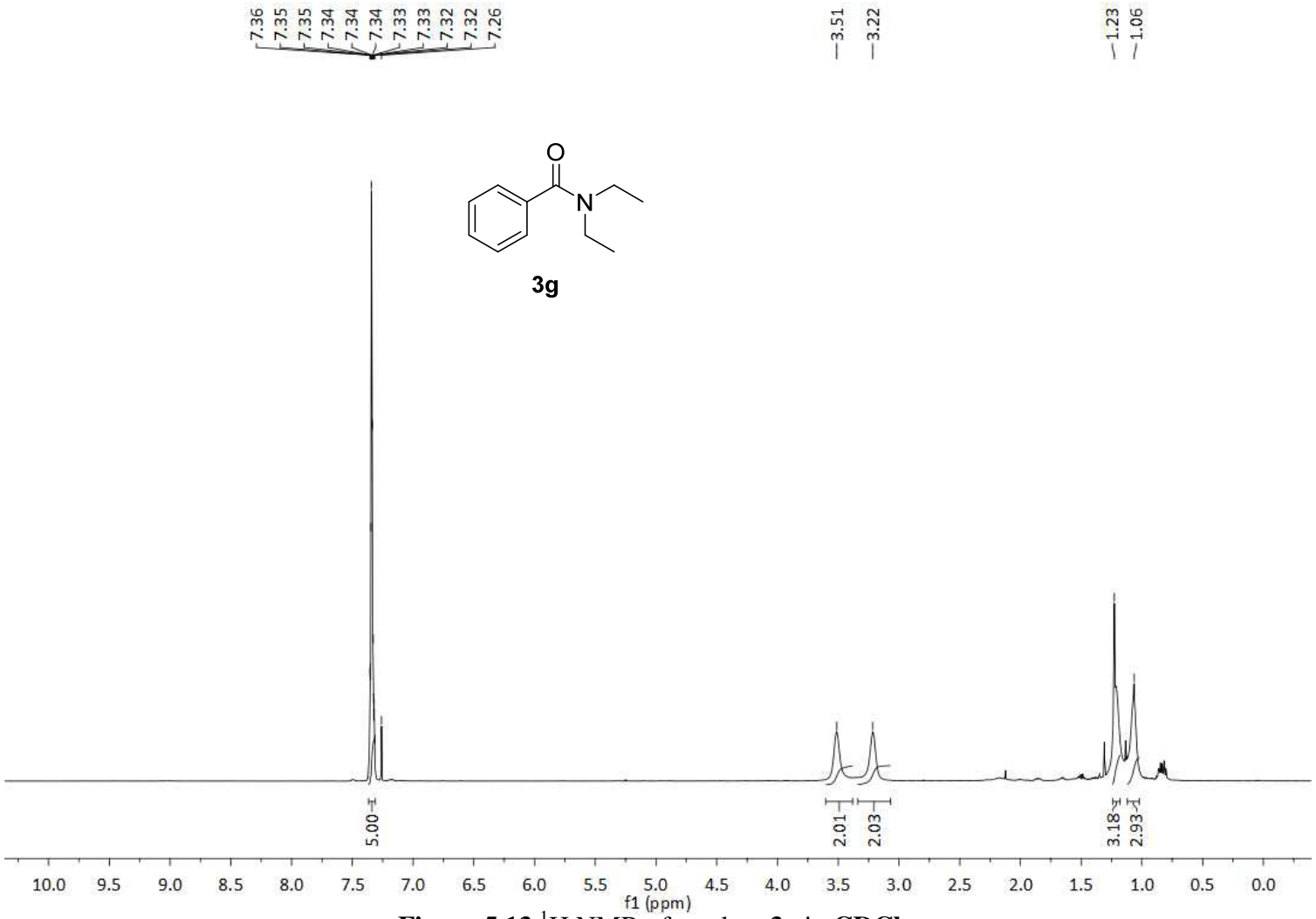


Figure 5.13 ^{1}H NMR of product **3g** in **$CDCl_3$**.

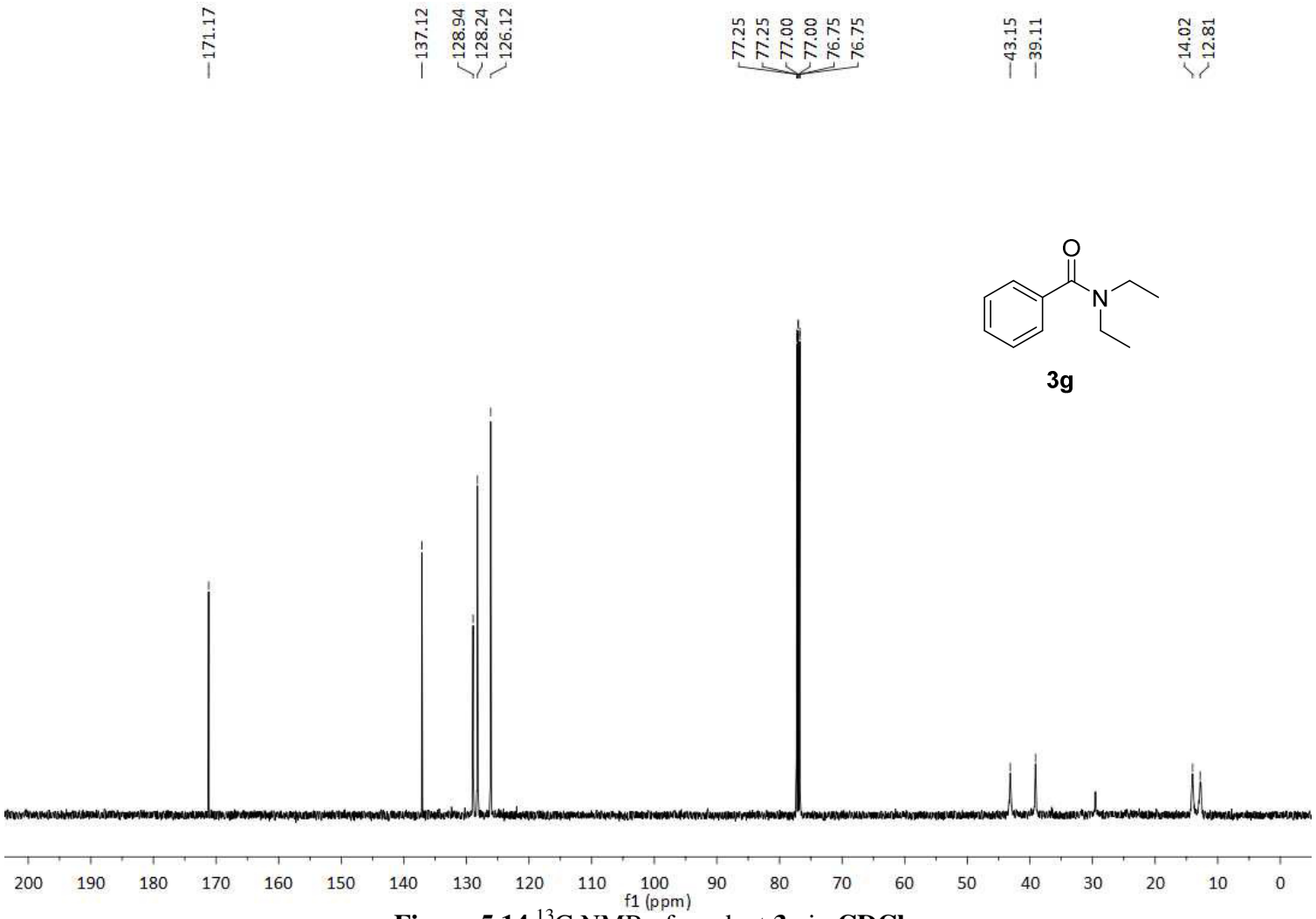


Figure 5.14 ^{13}C NMR of product **3g** in **$CDCl_3$**.

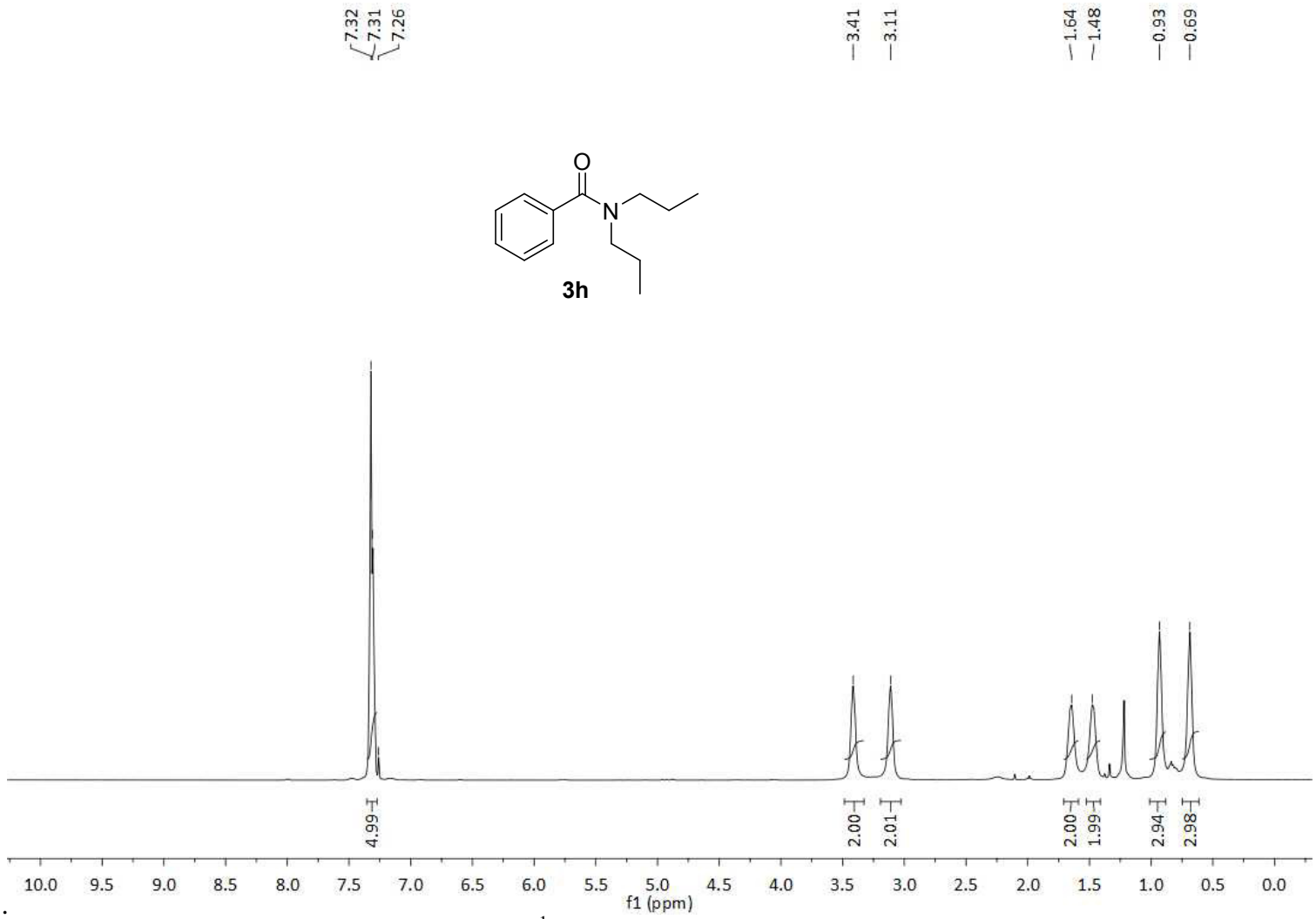


Figure 5.15 ^{1}H NMR of product **3h** in **$CDCl_3$**.

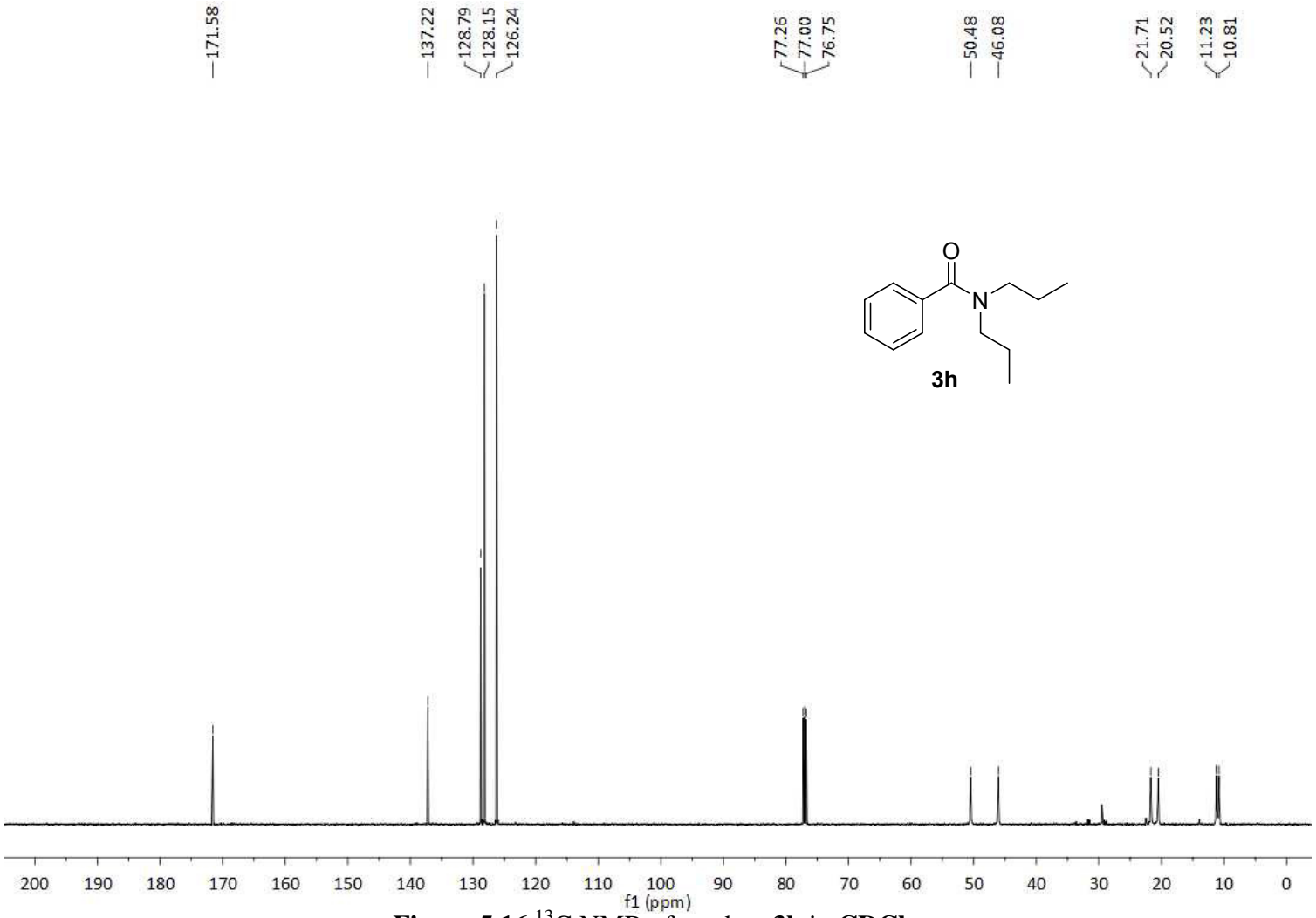


Figure 5.16 ^{13}C NMR of product **3h** in **$CDCl_3$**.

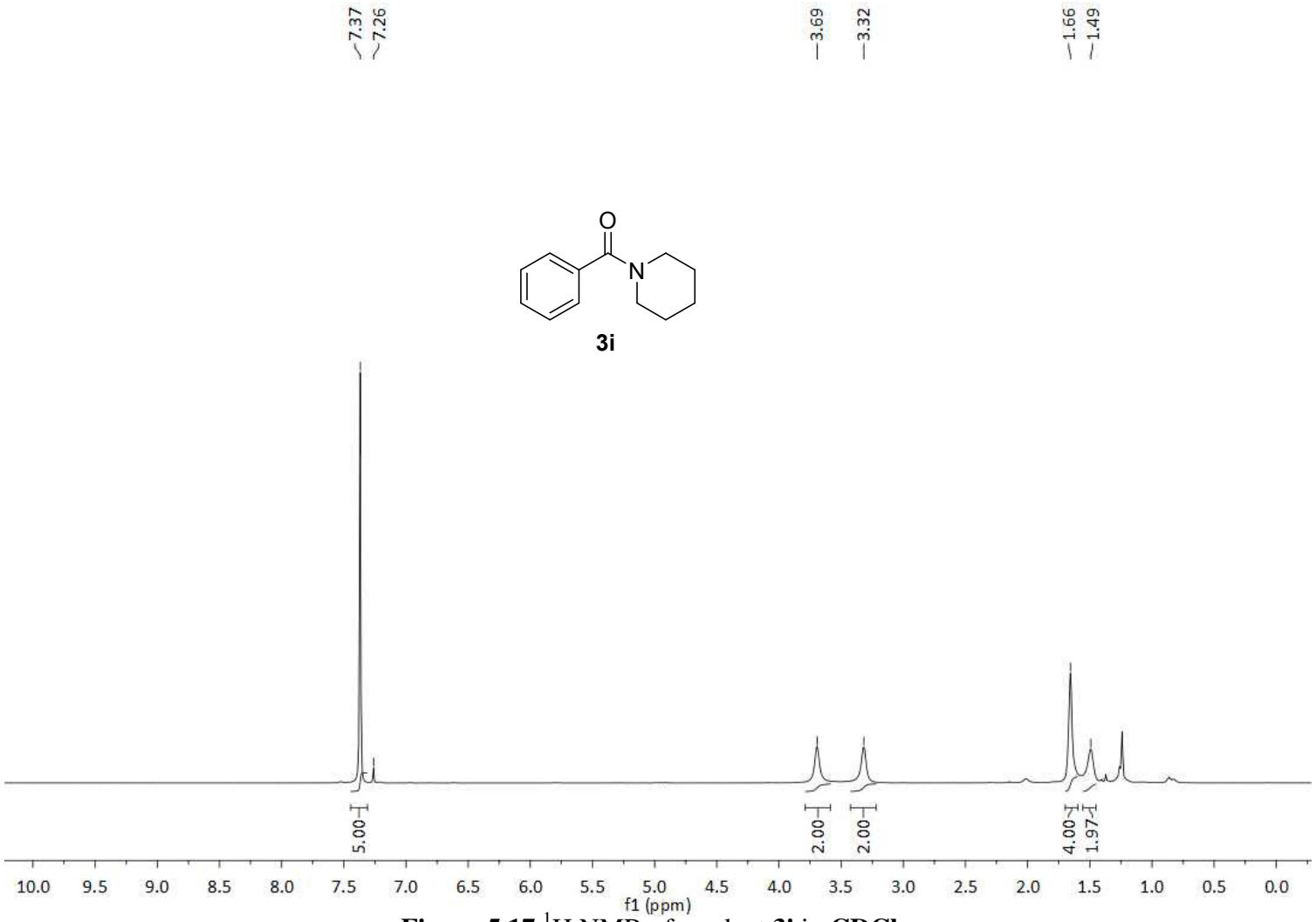


Figure 5.17 ^{1}H NMR of product **3i** in **$CDCl_3$**.

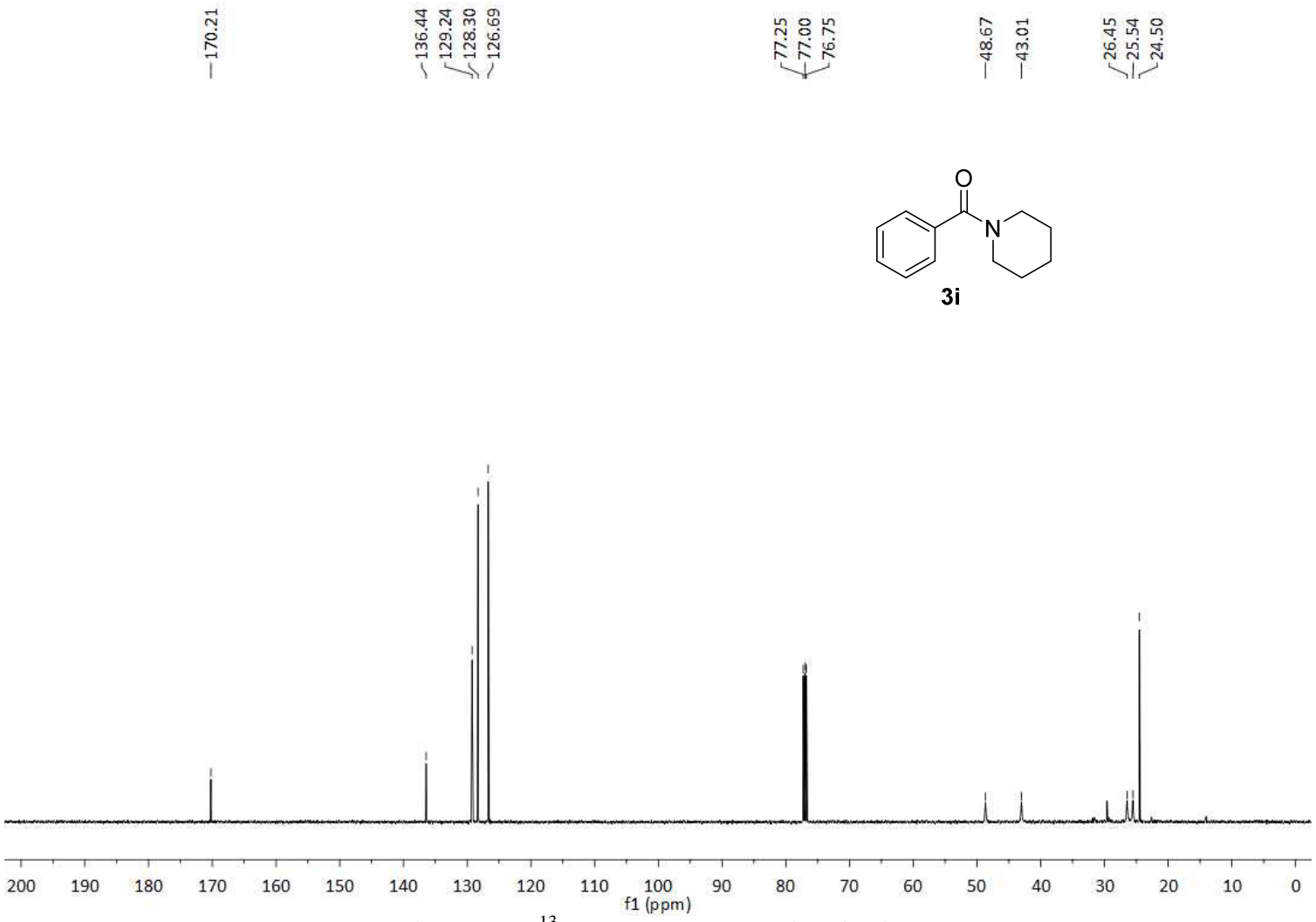


Figure 5.18 ^{13}C NMR of product **3i** in **$CDCl_3$**.

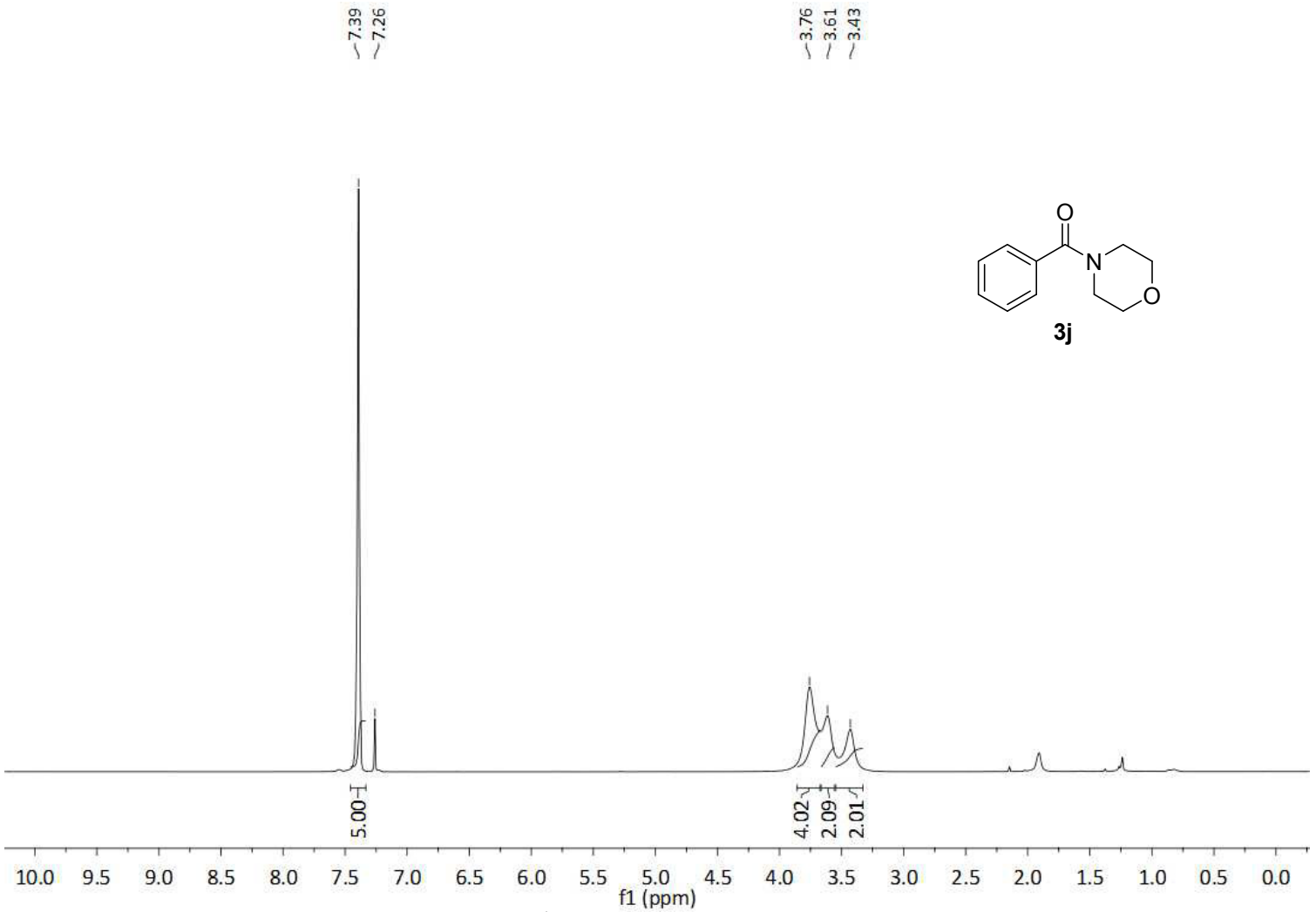
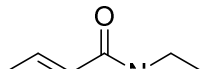


Figure 5.19 ^{1}H NMR of product **3j** in **$CDCl_3$**.



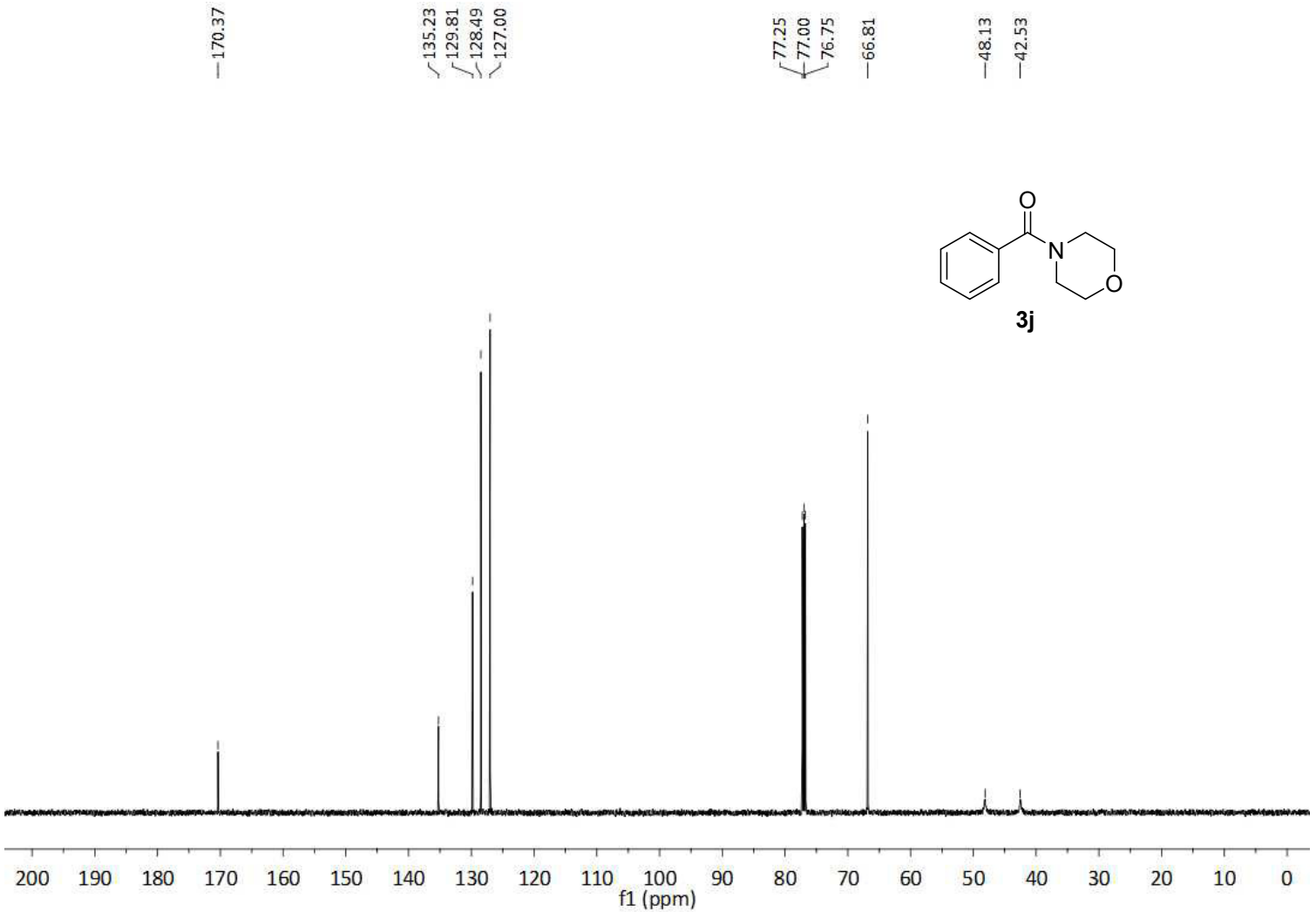


Figure 5.20 ^{13}C NMR of product **3j** in **$CDCl_3$**.

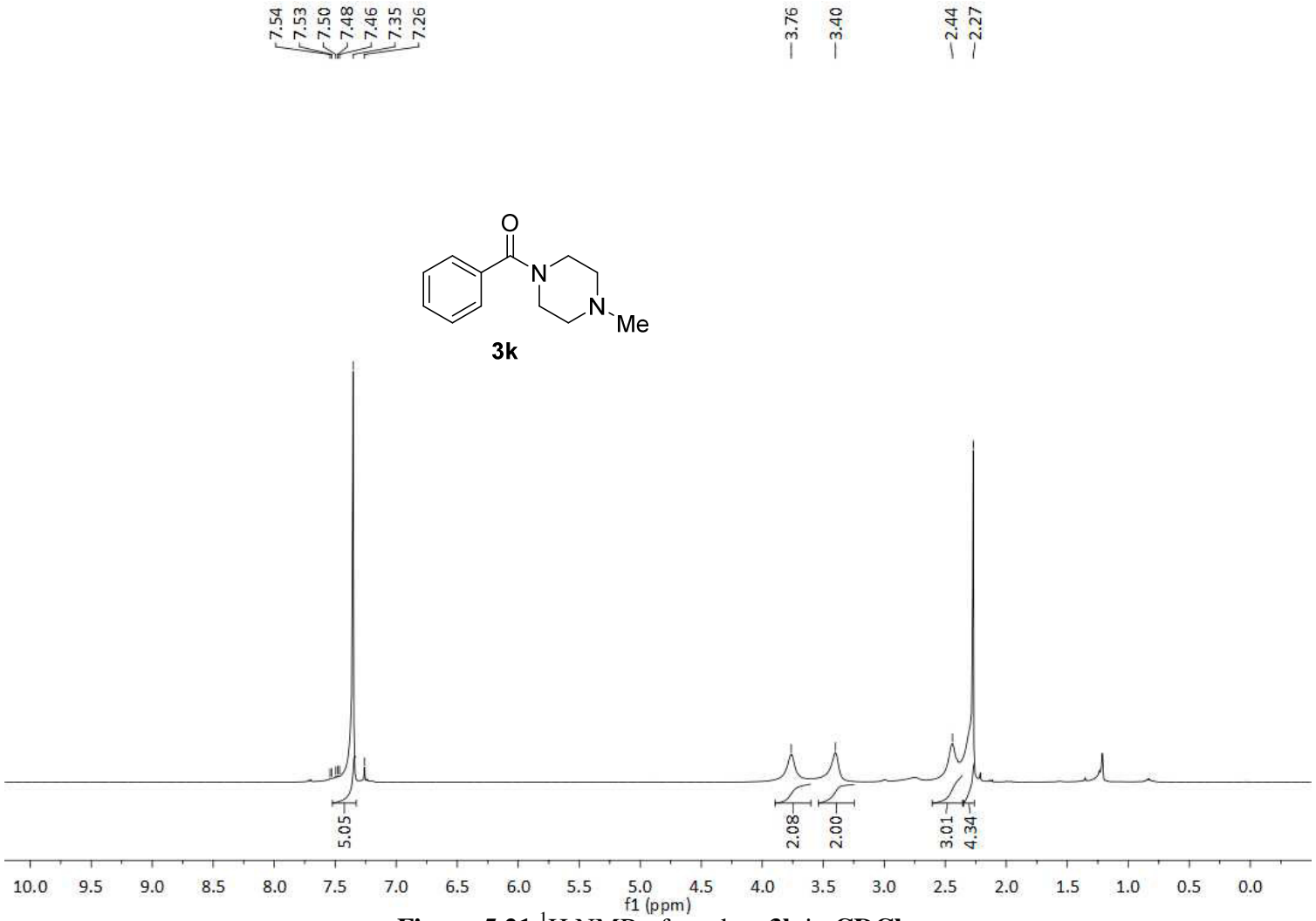


Figure 5.21 ^{1}H NMR of product **3k** in **$CDCl_3$**.

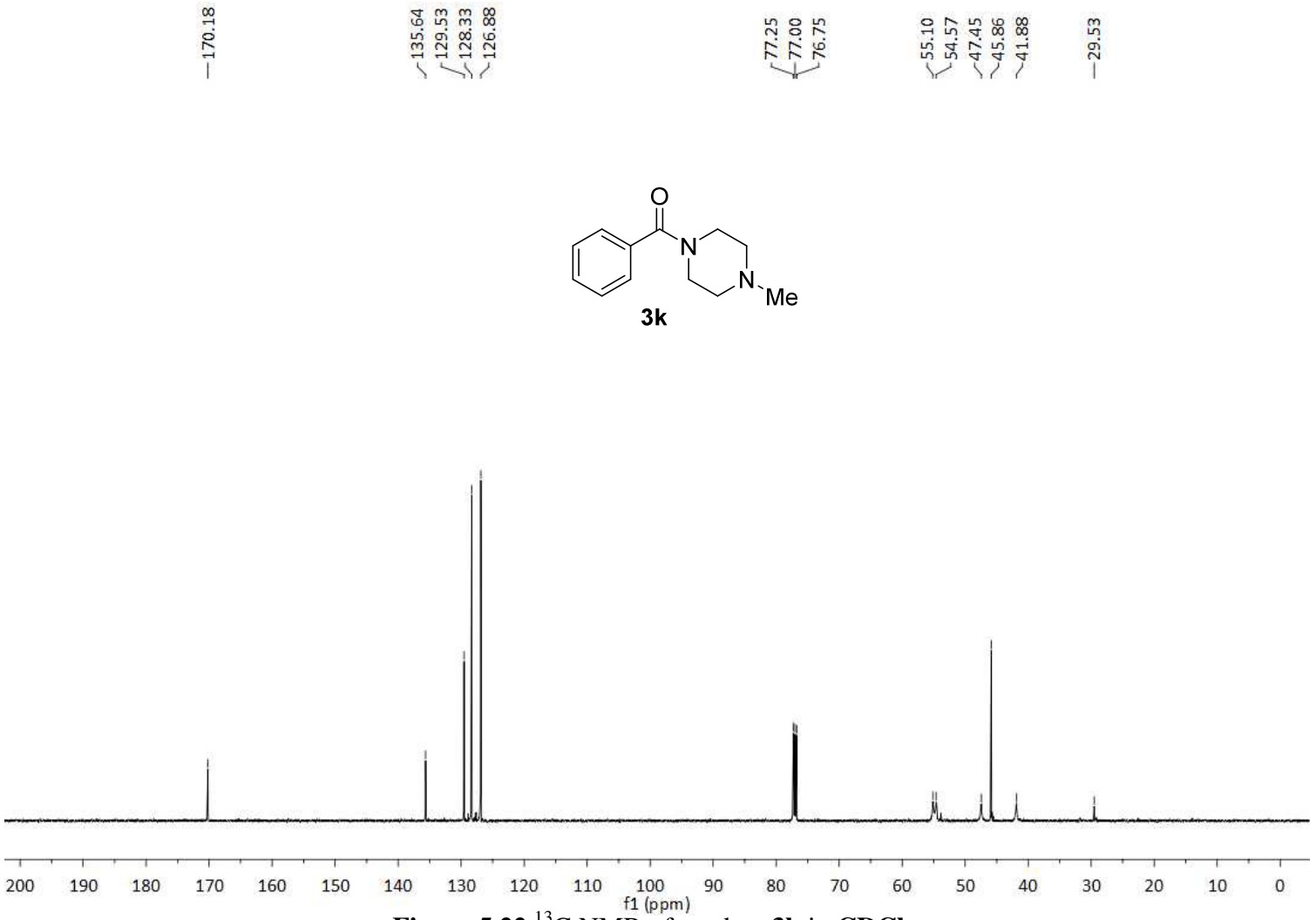


Figure 5.22 ^{13}C NMR of product **3k** in **$CDCl_3$**.

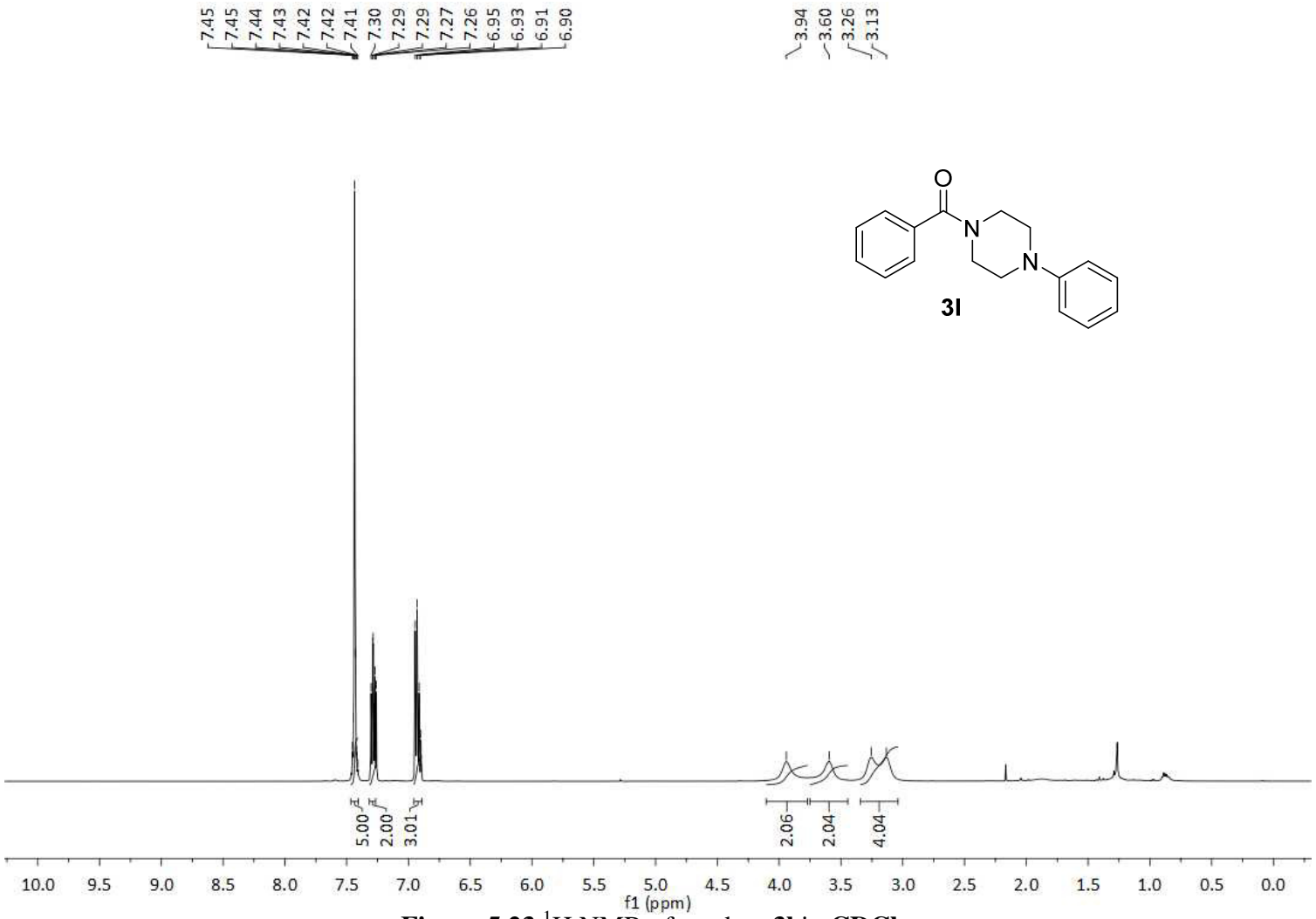


Figure 5.23 ^{1}H NMR of product **3l** in **$CDCl_3$**.

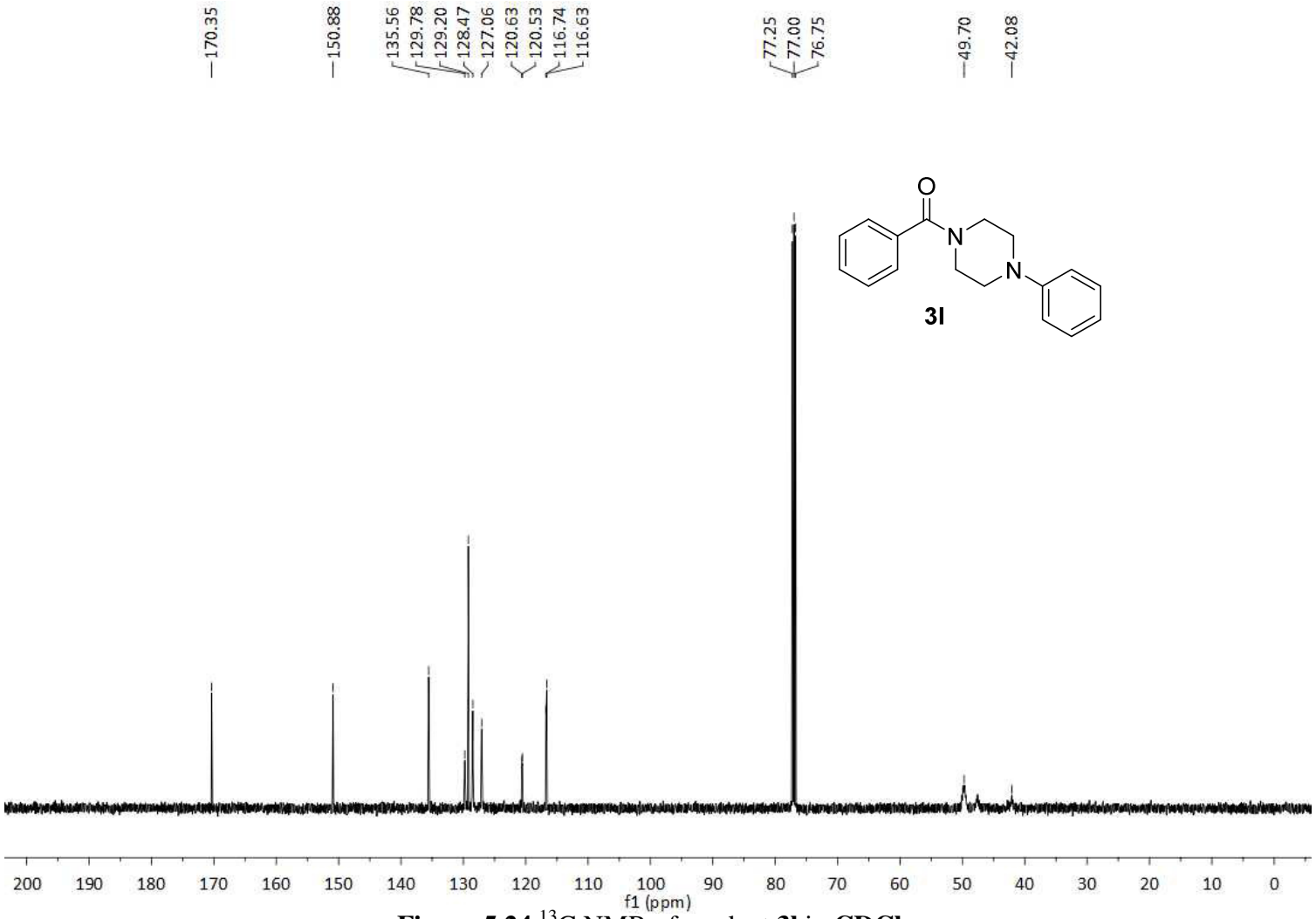


Figure 5.24 ^{13}C NMR of product **3l** in **$CDCl_3$**.

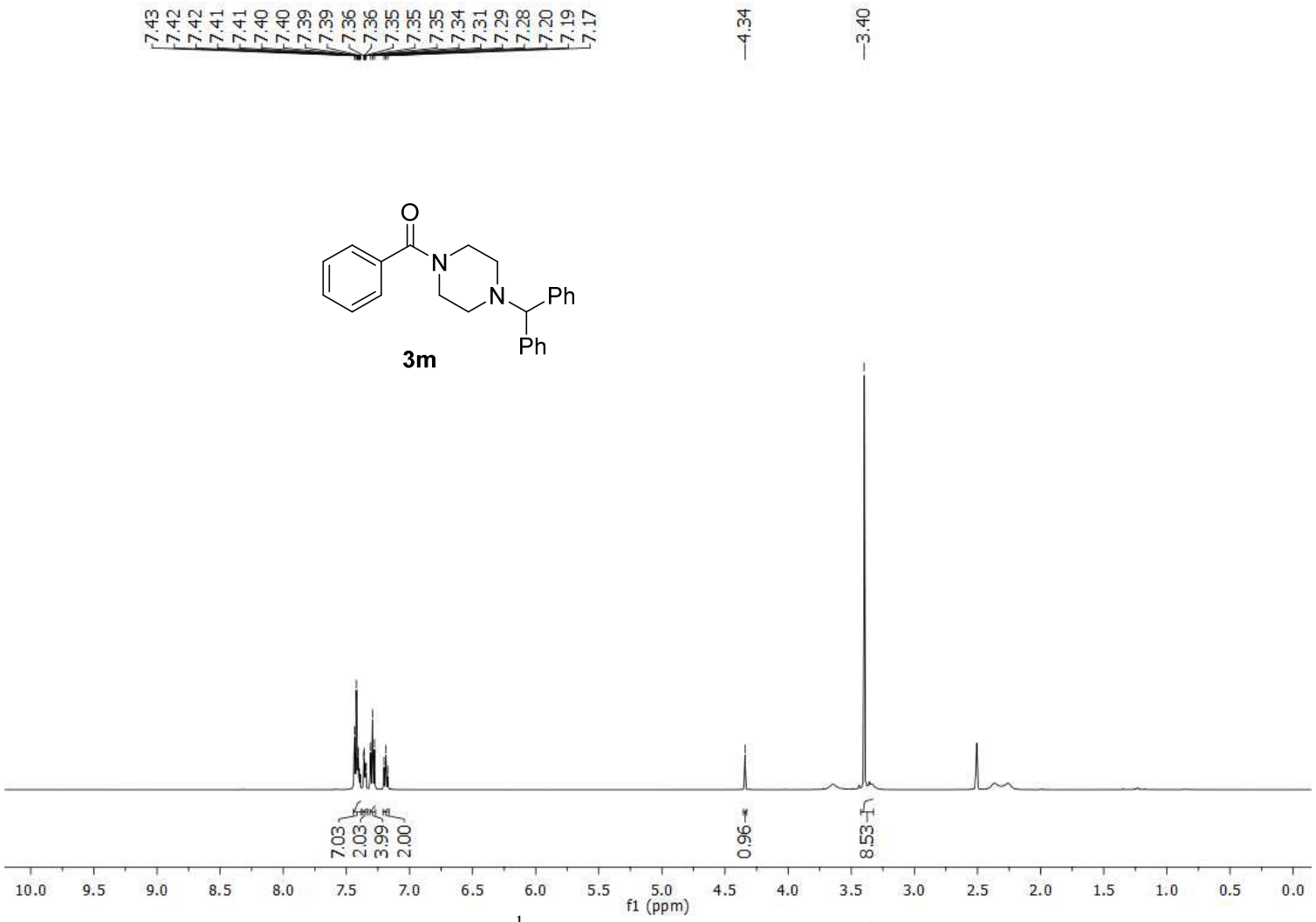


Figure 5.25 ^{1}H NMR of product **3m** in **DMSO-d$_6$**.

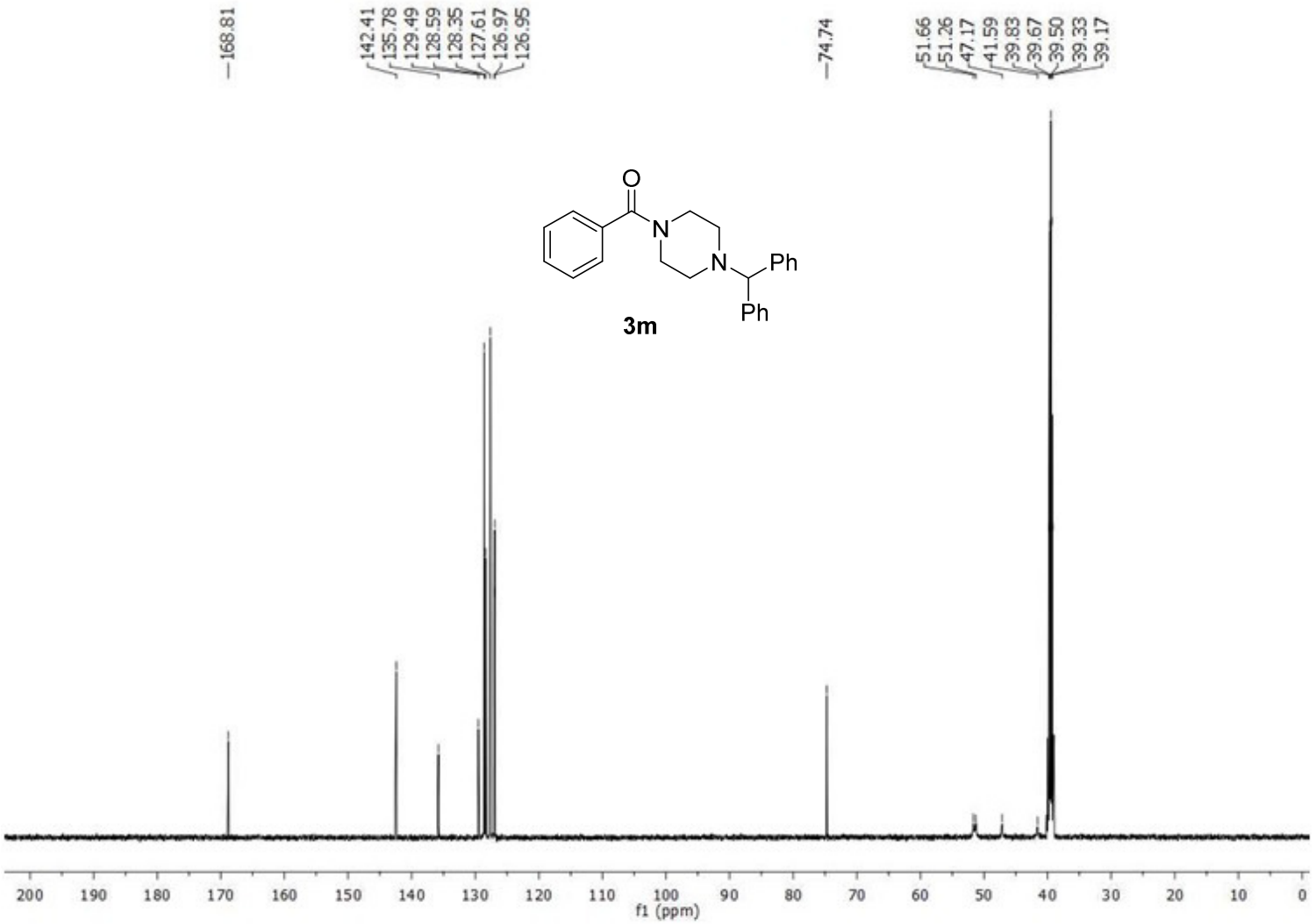


Figure 5.26 ^{13}C NMR of product **3m** in **DMSO-d$_6$**.

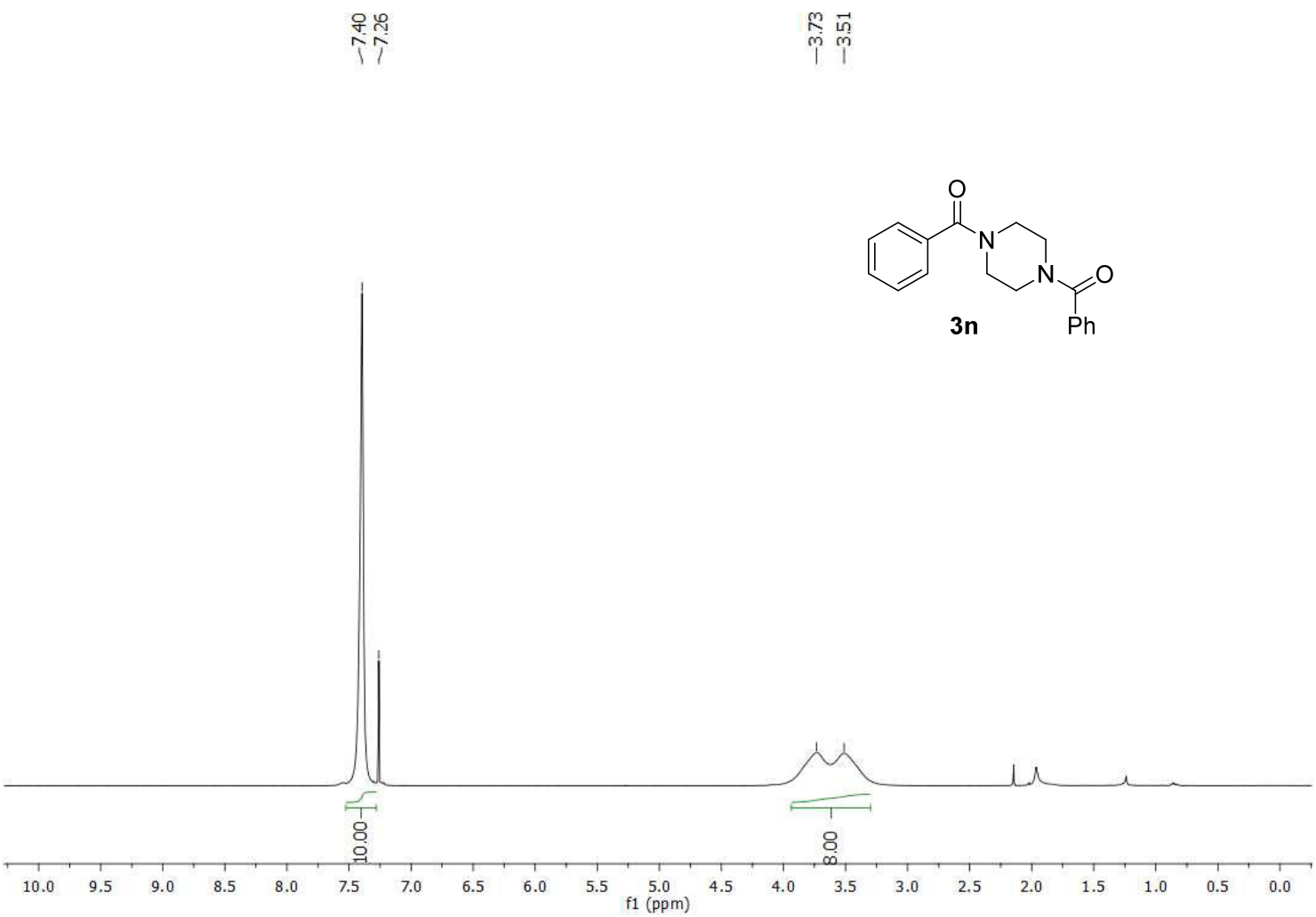


Figure 5.27 ^{1}H NMR of product **3n** in **$CDCl_3$**.

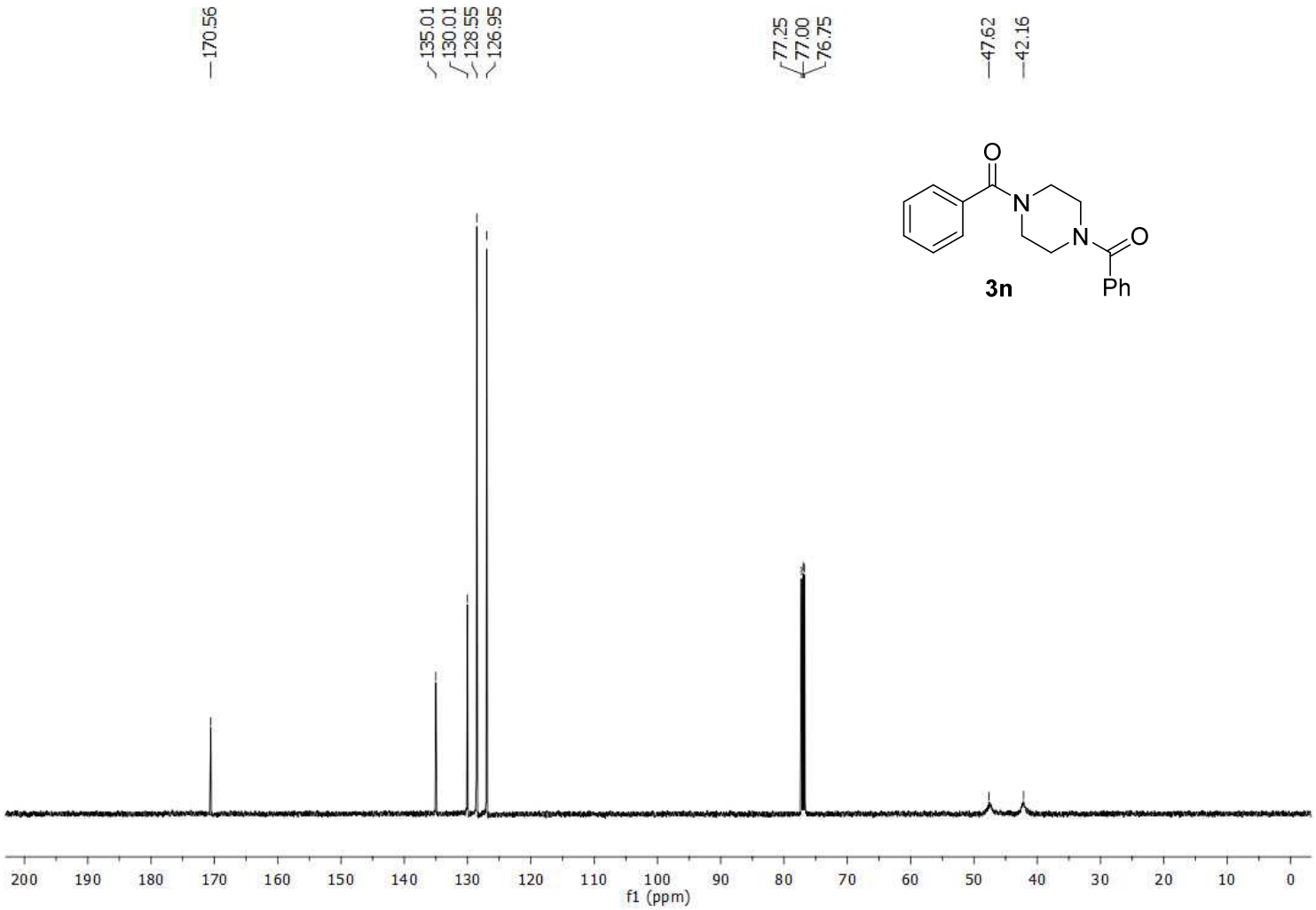


Figure 5.28 ^{13}C NMR of product **3n** in **$CDCl_3$**.

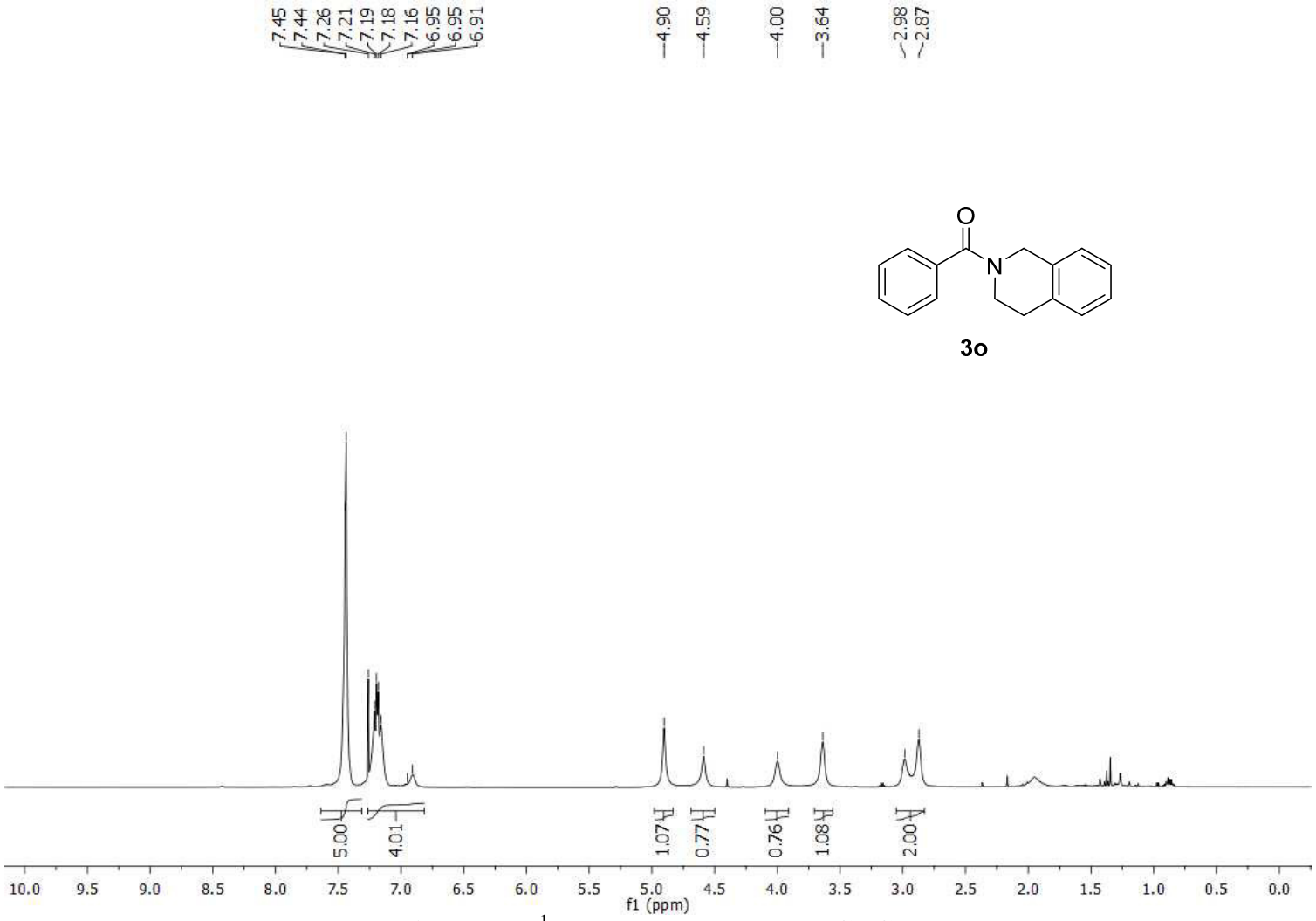


Figure 5.29 ^{1}H NMR of product **3o** in **$CDCl_3$**.

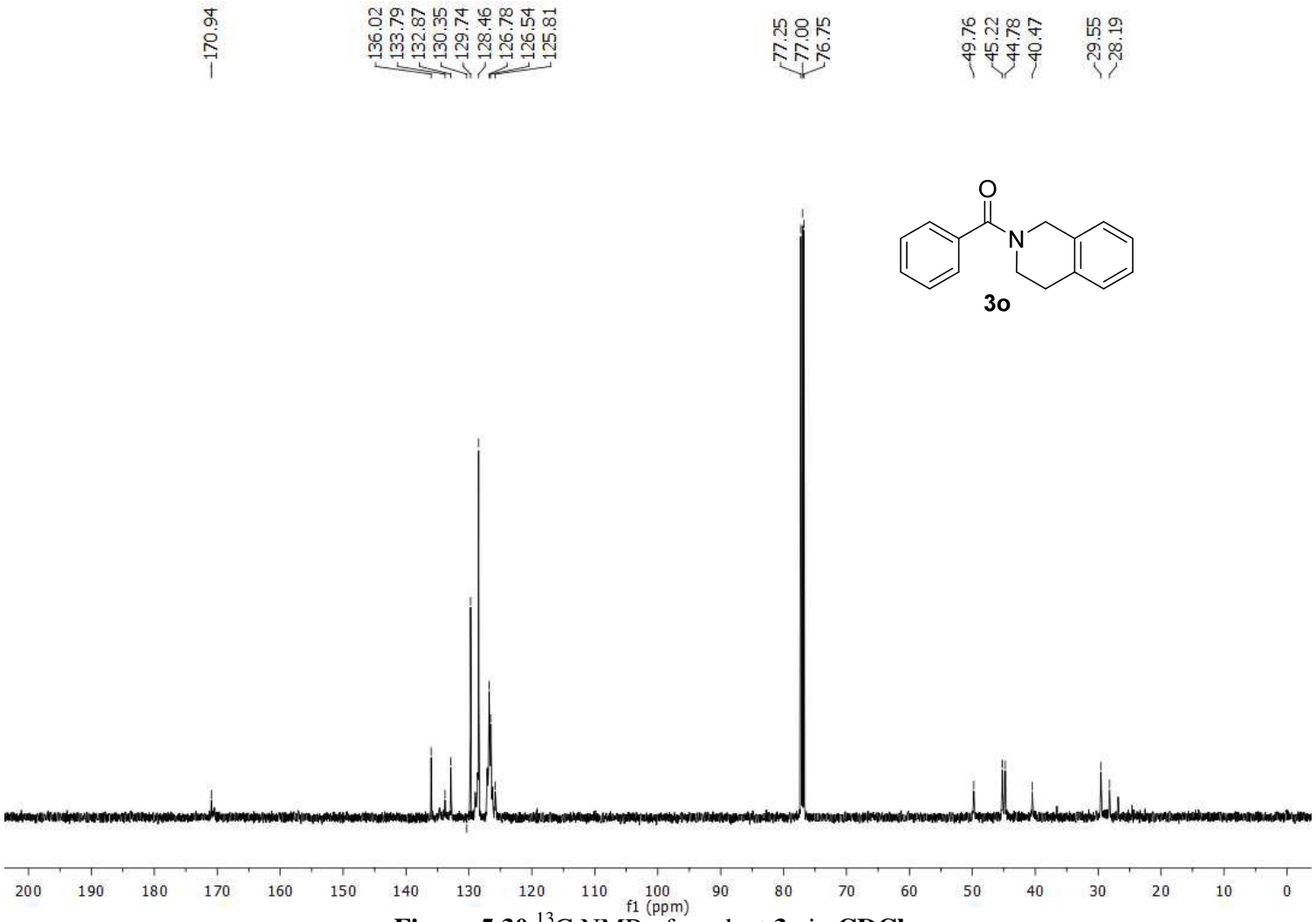


Figure 5.30 ^{13}C NMR of product **3o** in **$CDCl_3$**.

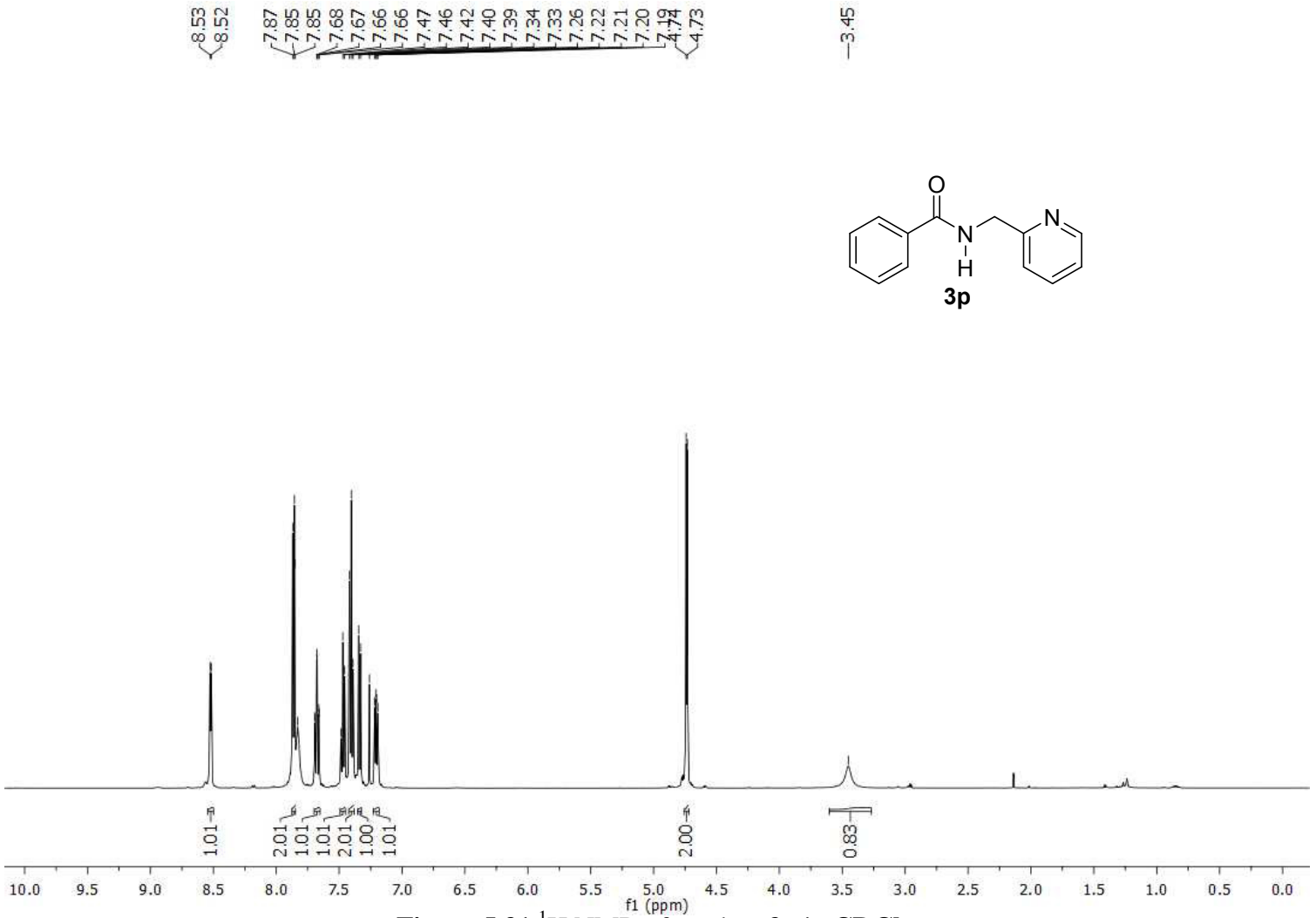


Figure 5.31 ^{1}H NMR of product **3p** in **$CDCl_3$**.

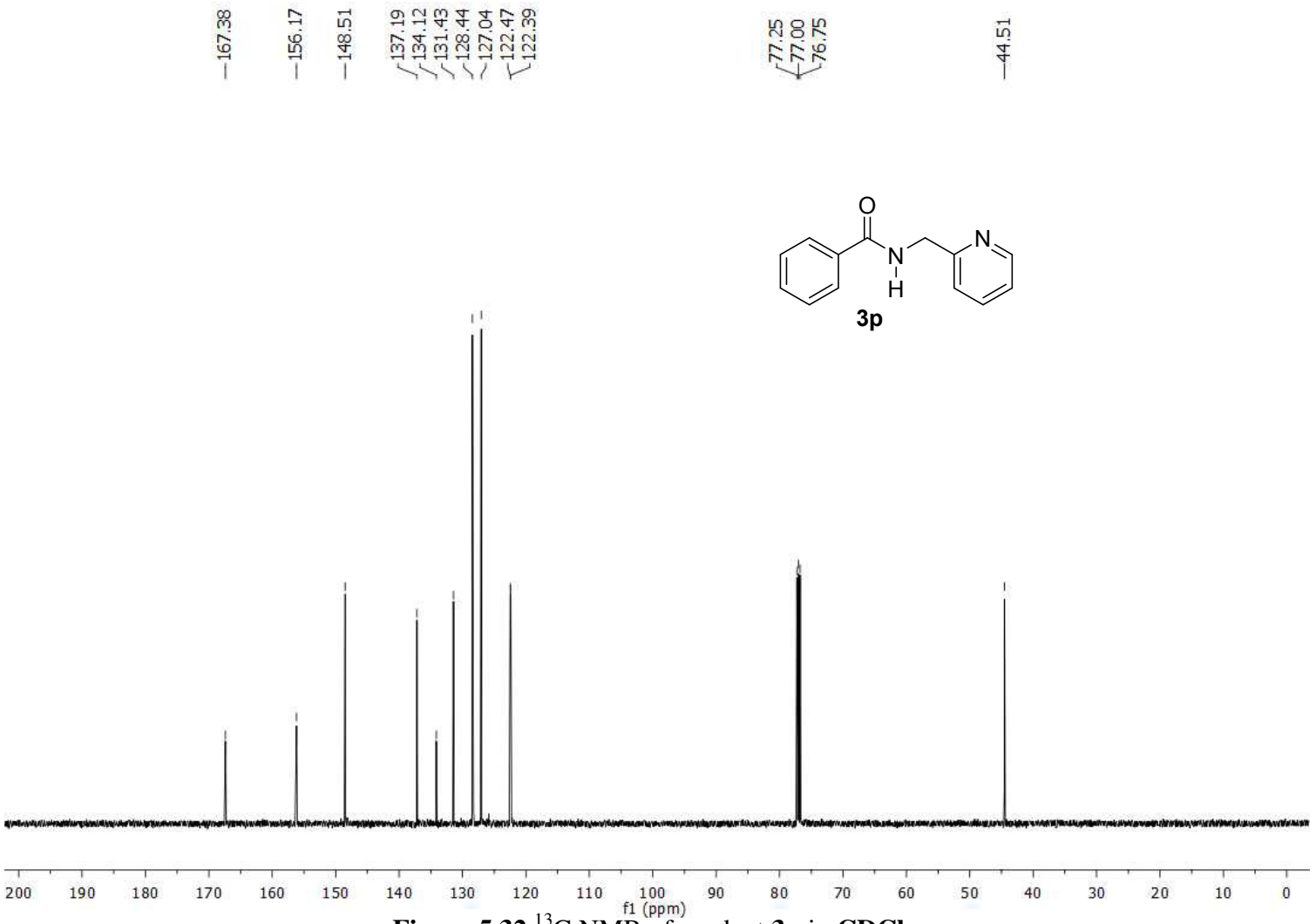


Figure 5.32 ^{13}C NMR of product **3p** in **$CDCl_3$**.

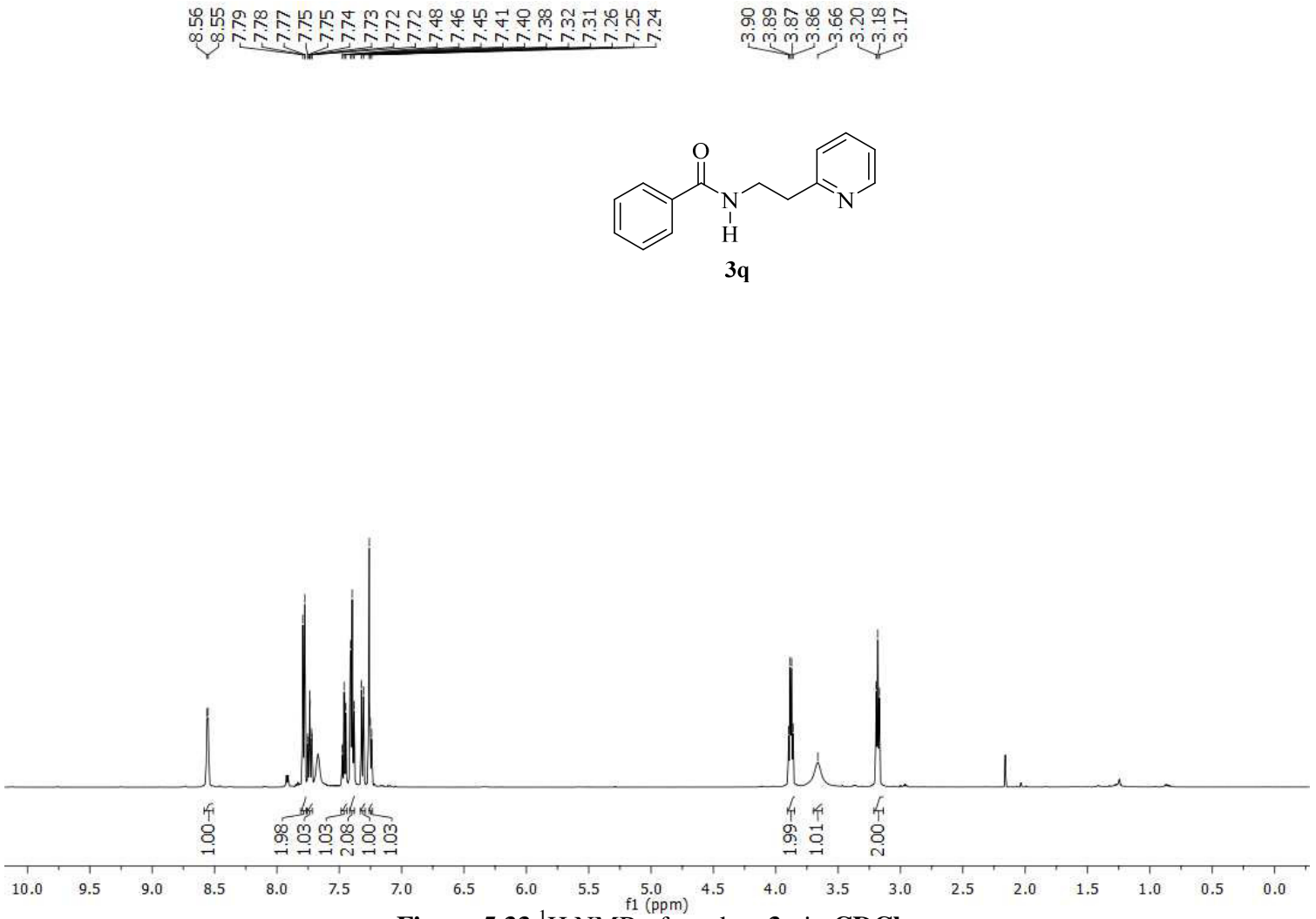


Figure 5.33 ^{1}H NMR of product **3q** in **$CDCl_3$**.

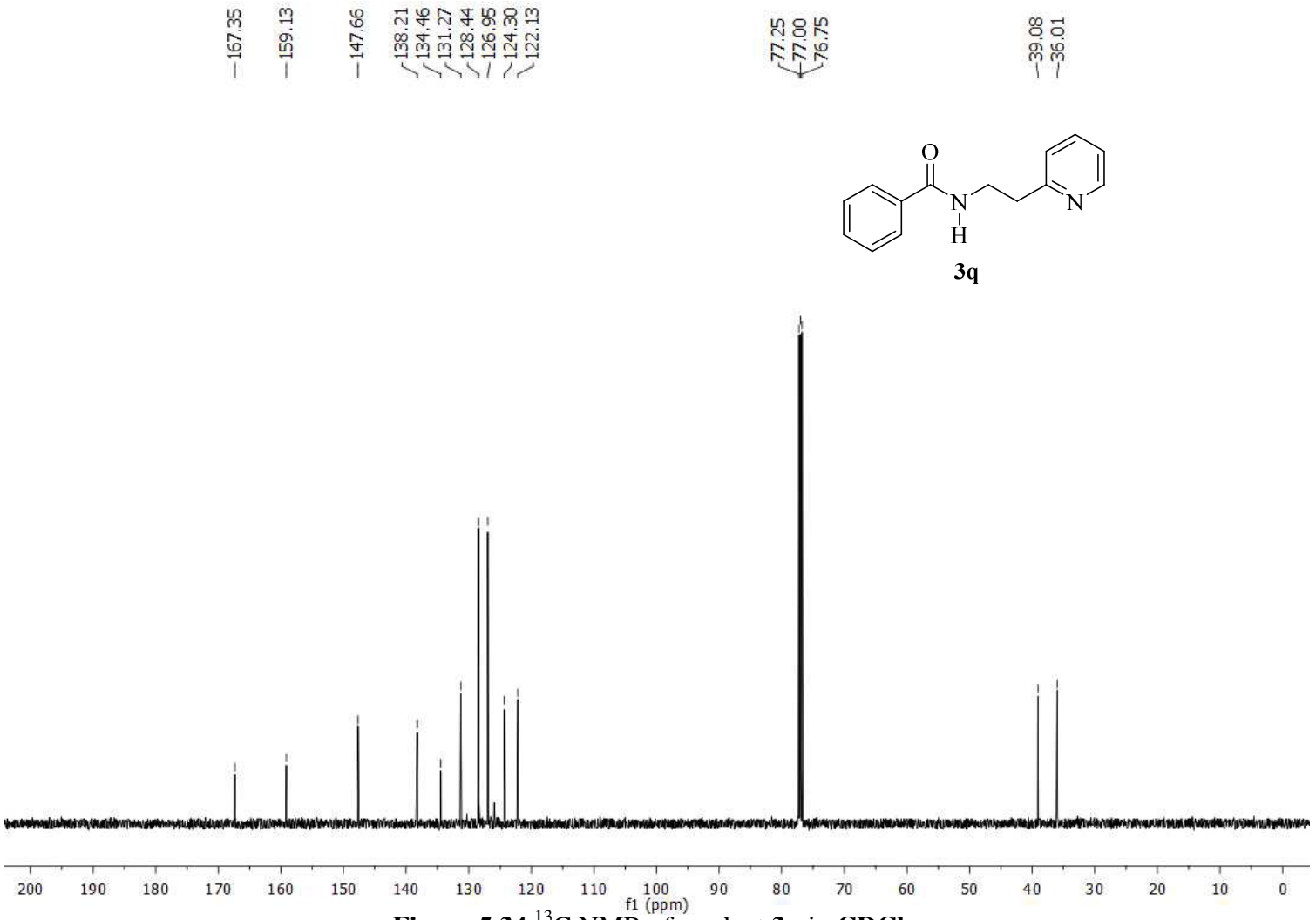


Figure 5.34 ^{13}C NMR of product **3q** in **$CDCl_3$**.

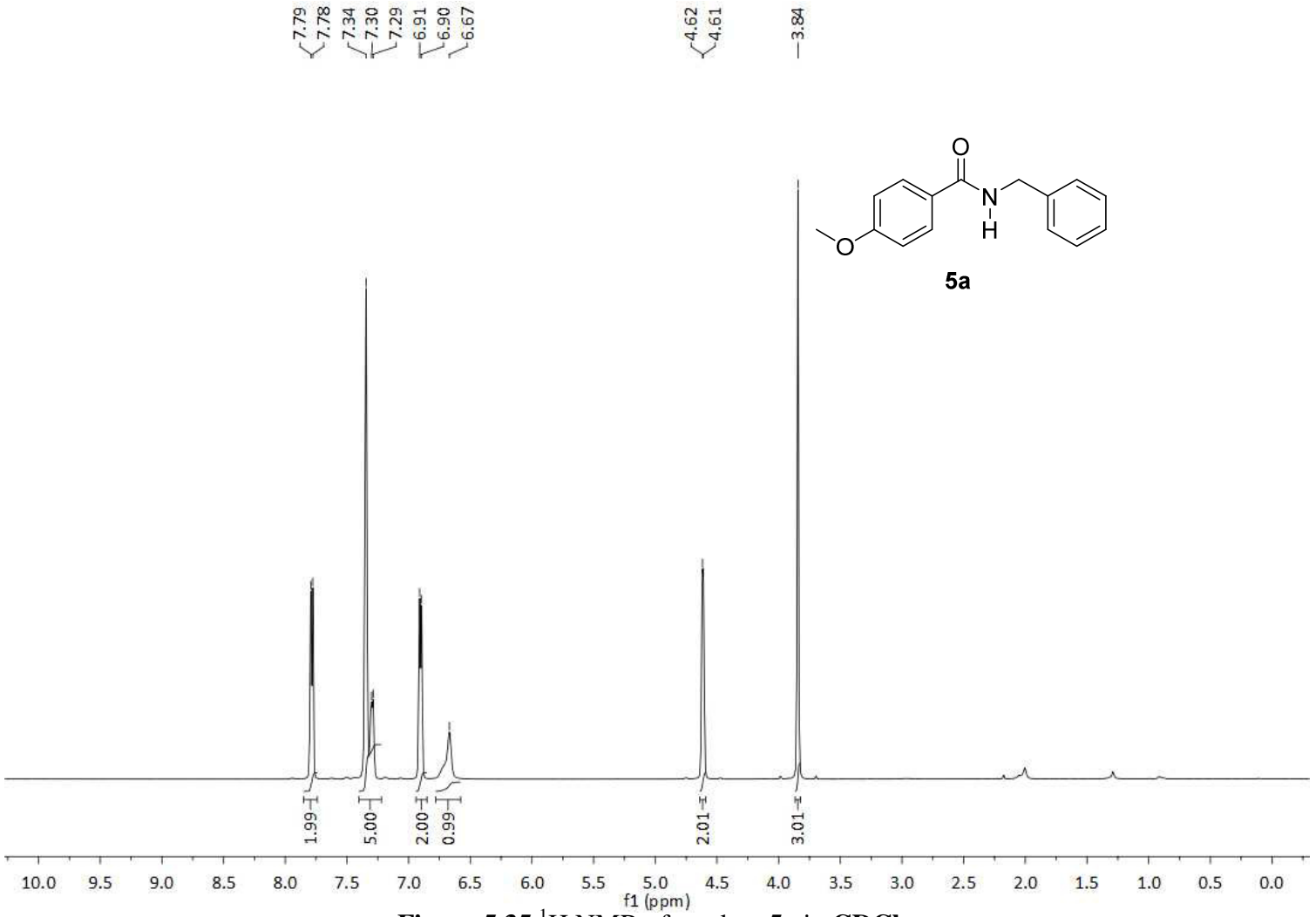


Figure 5.35 ^{1}H NMR of product **5a** in **$CDCl_3$**.

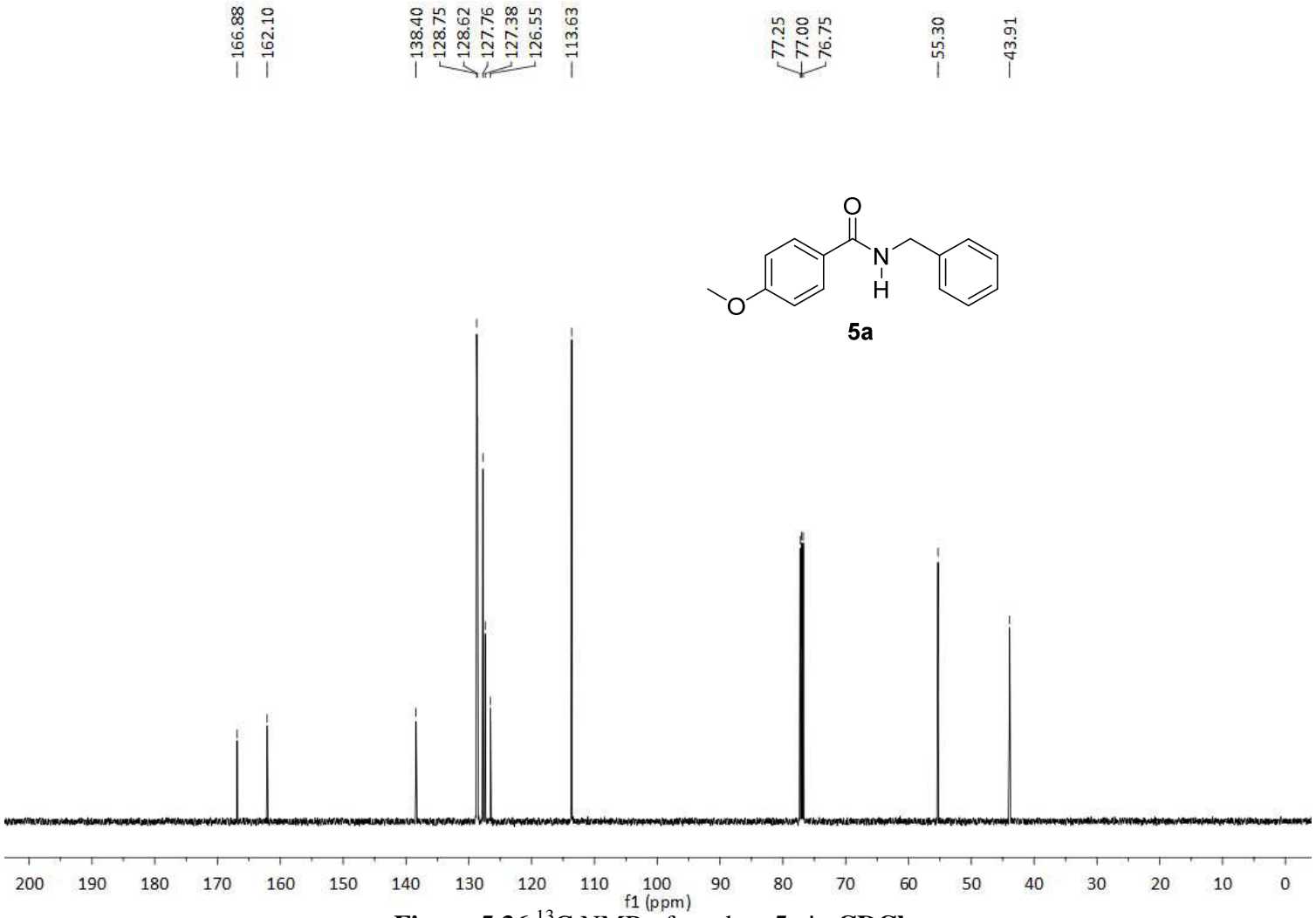


Figure 5.36 ^{13}C NMR of product **5a** in **$CDCl_3$**.

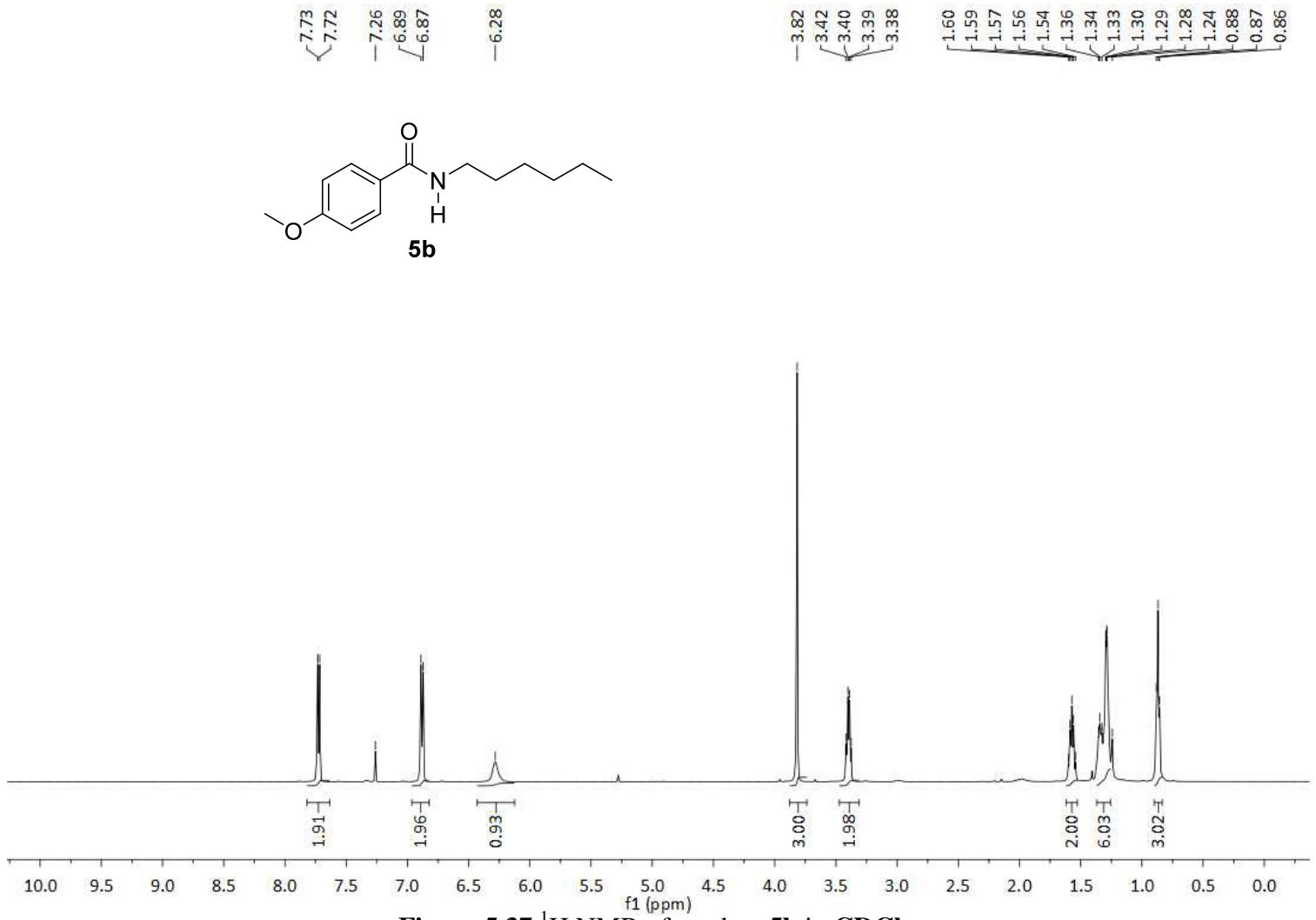


Figure 5.37 ^{1}H NMR of product **5b** in **$CDCl_3$**.

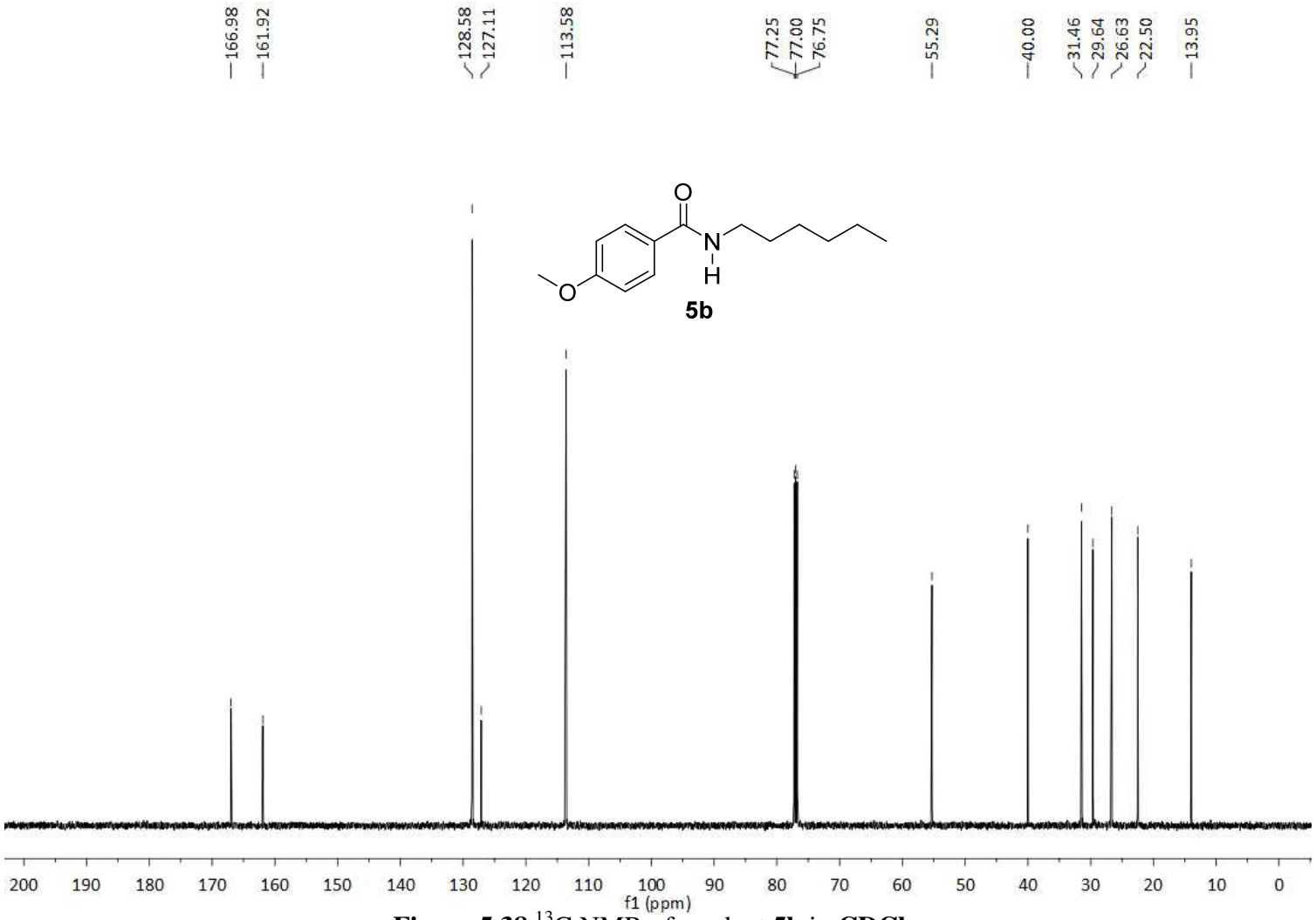


Figure 5.38 ^{13}C NMR of product **5b** in **$CDCl_3$**.

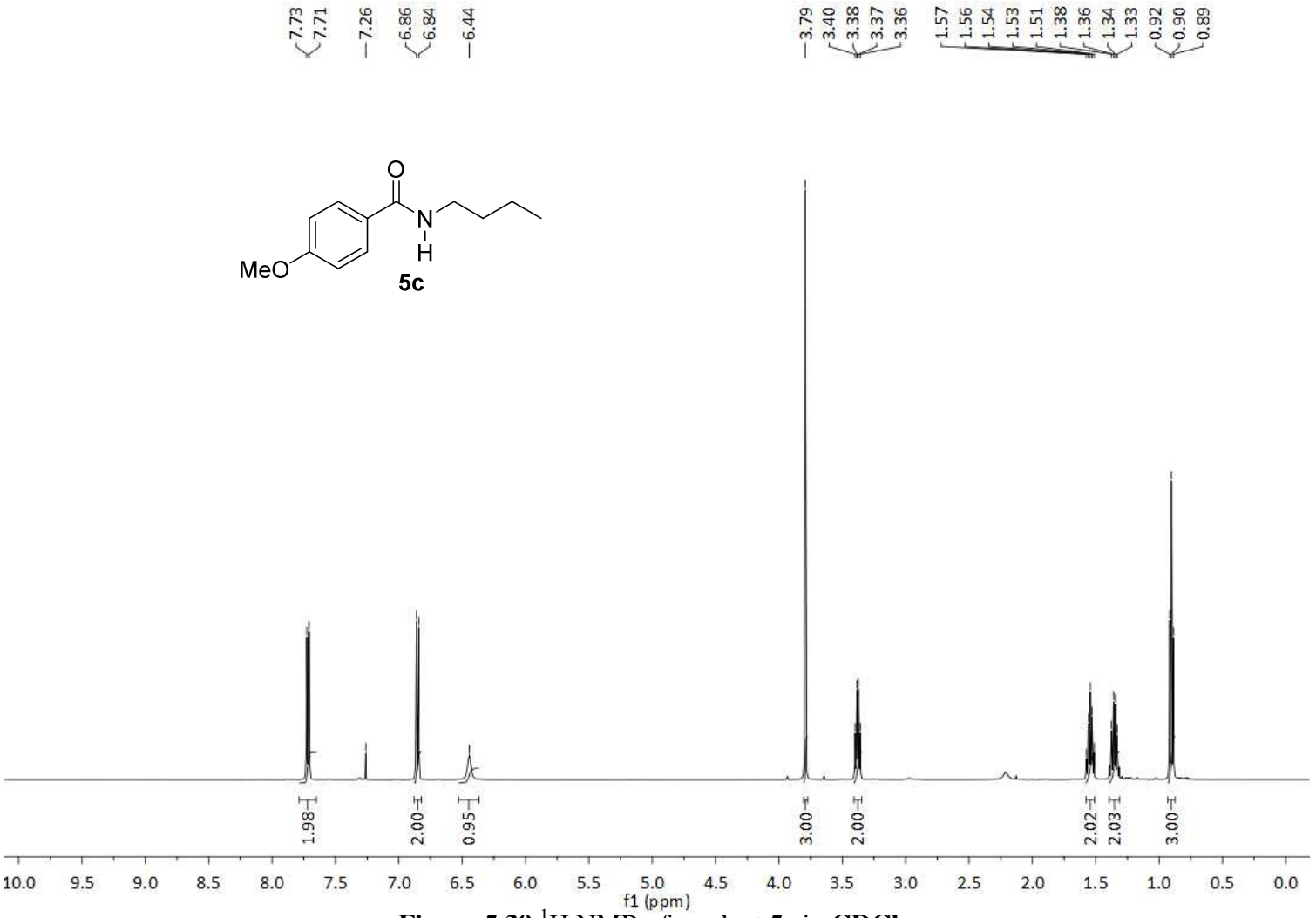


Figure 5.39 ^{1}H NMR of product **5c** in **$CDCl_3$**.

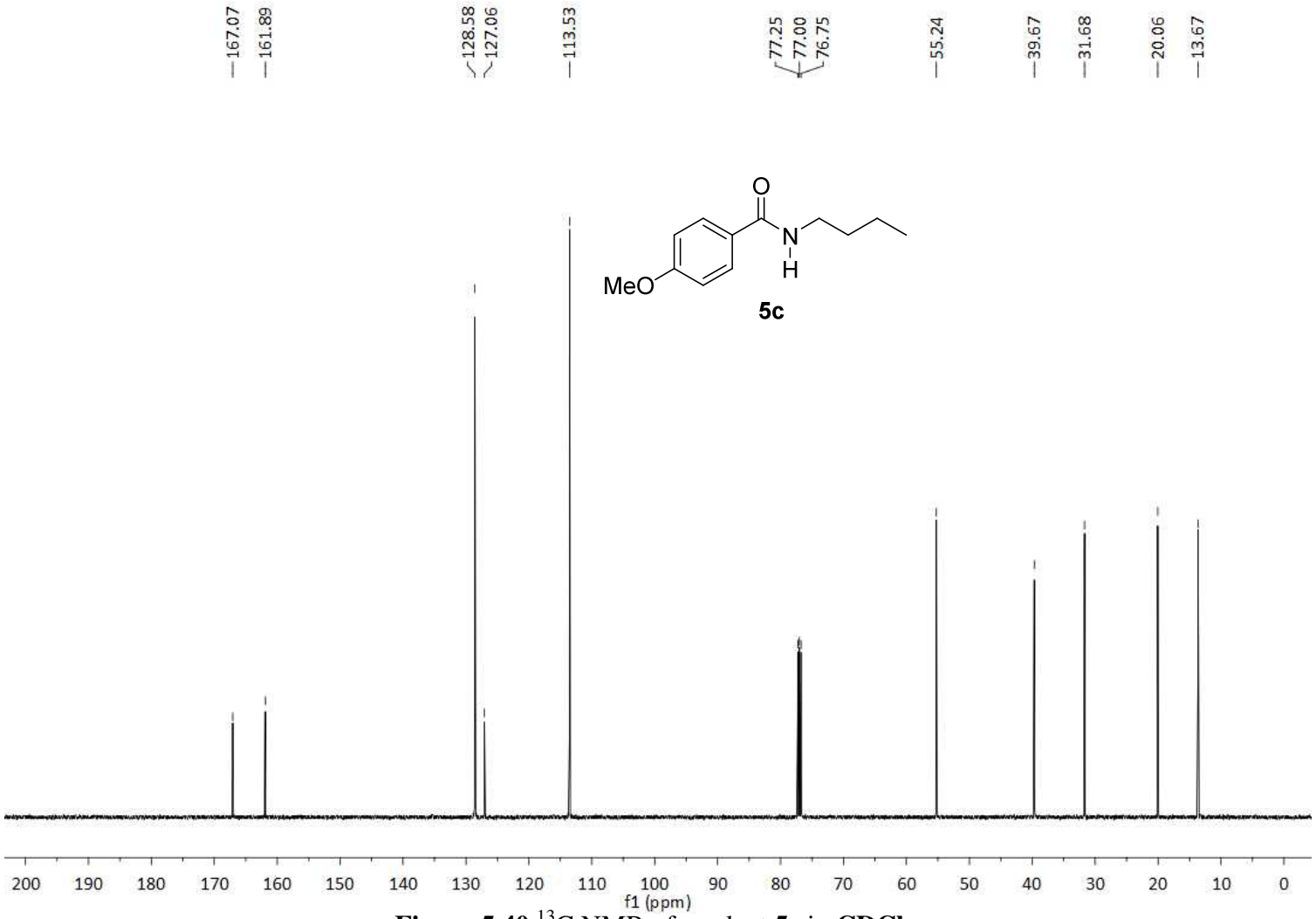


Figure 5.40 ^{13}C NMR of product **5c** in **$CDCl_3$**.

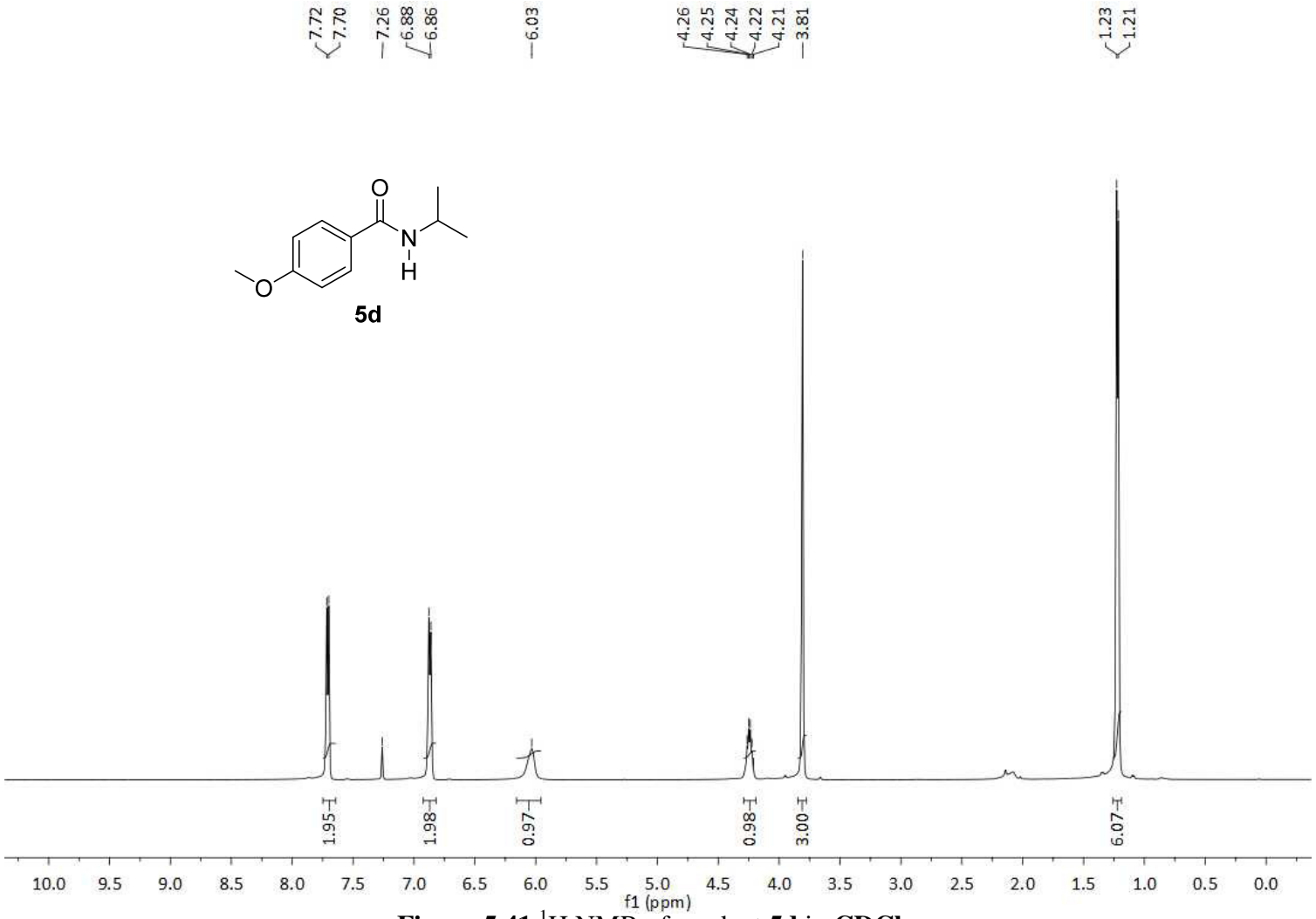


Figure 5.41 ^{1}H NMR of product **5d** in **$CDCl_3$**.

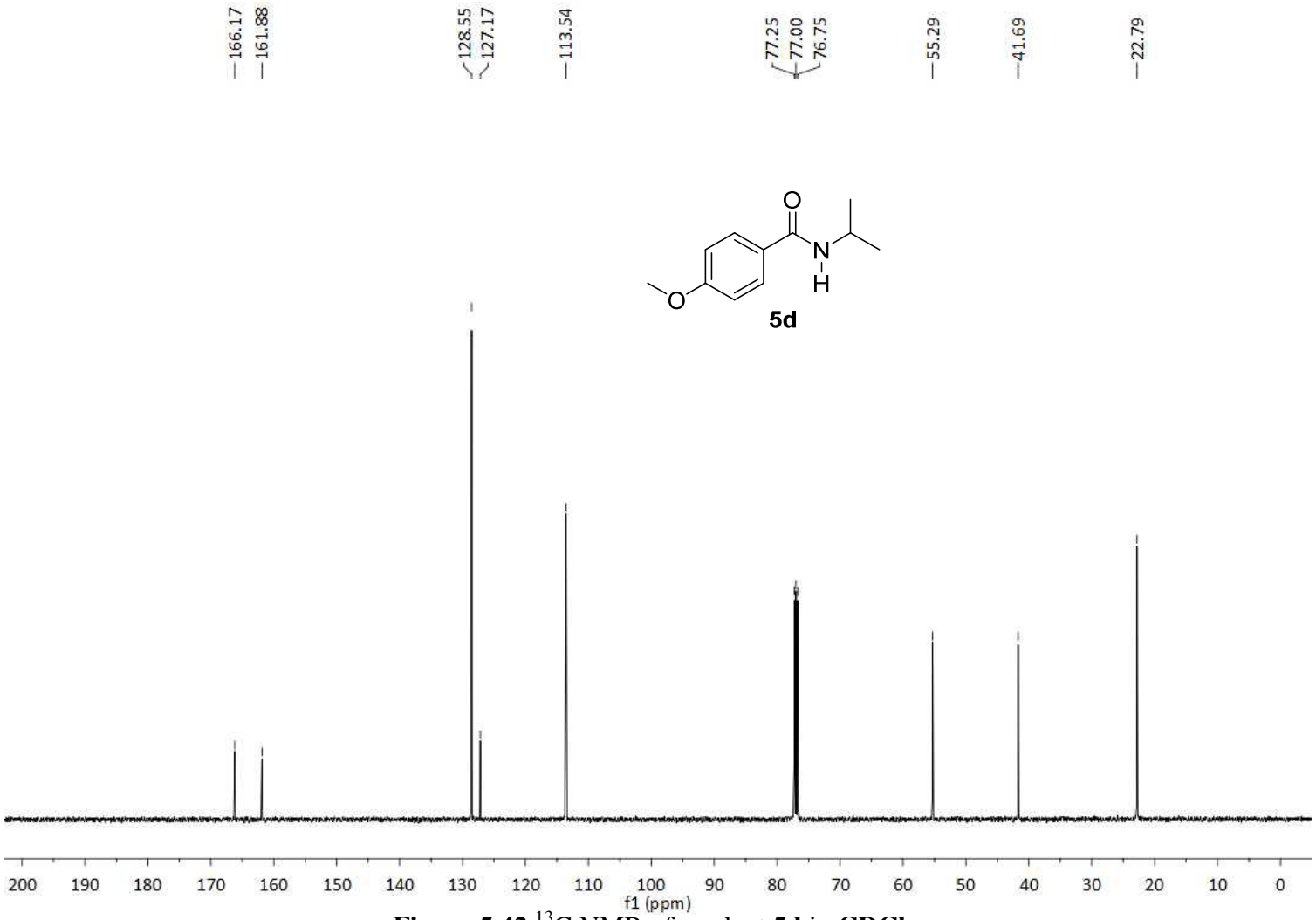


Figure 5.42 ^{13}C NMR of product **5d** in **$CDCl_3$**.

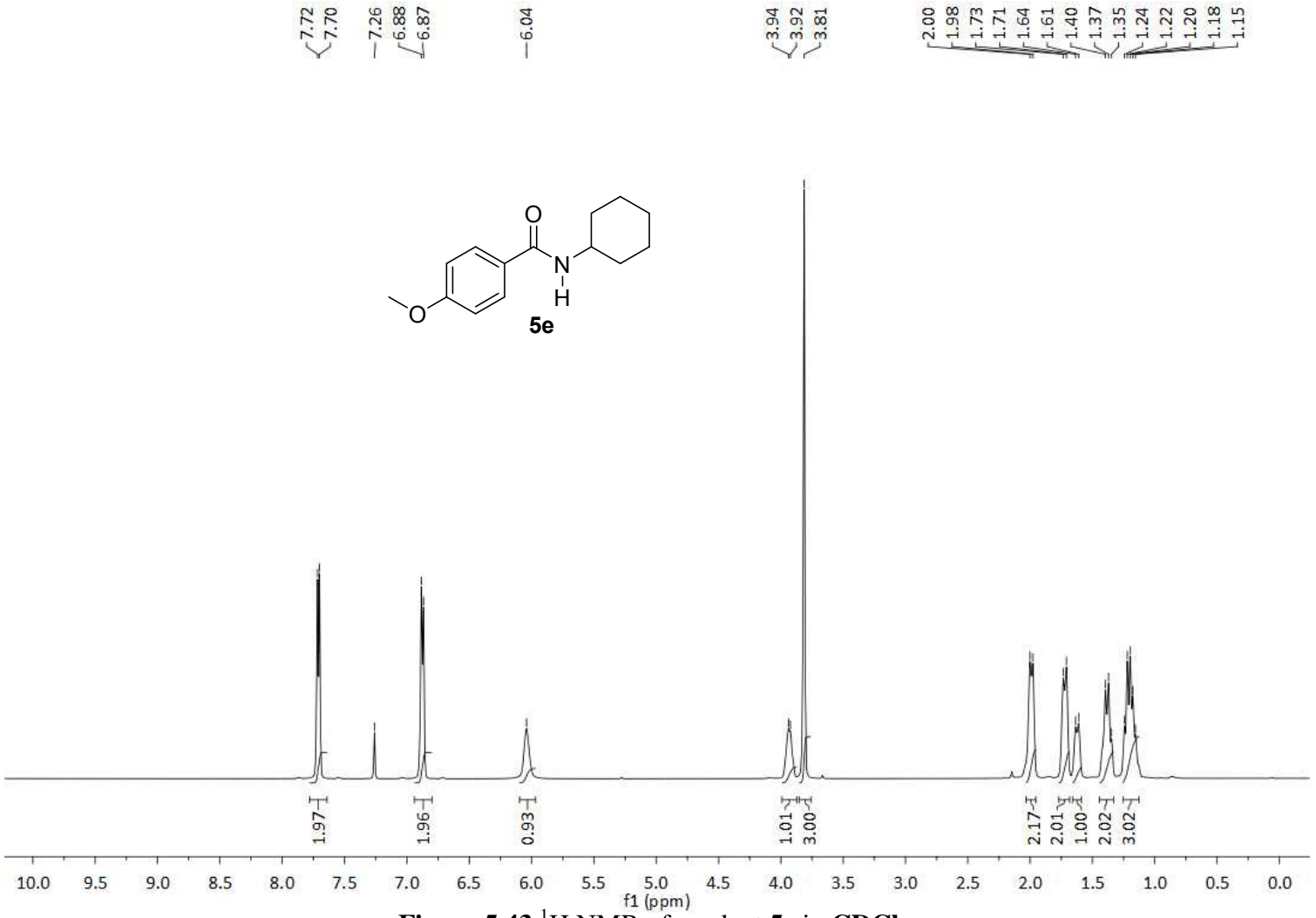


Figure 5.43 ^{1}H NMR of product **5e** in **$CDCl_3$**.

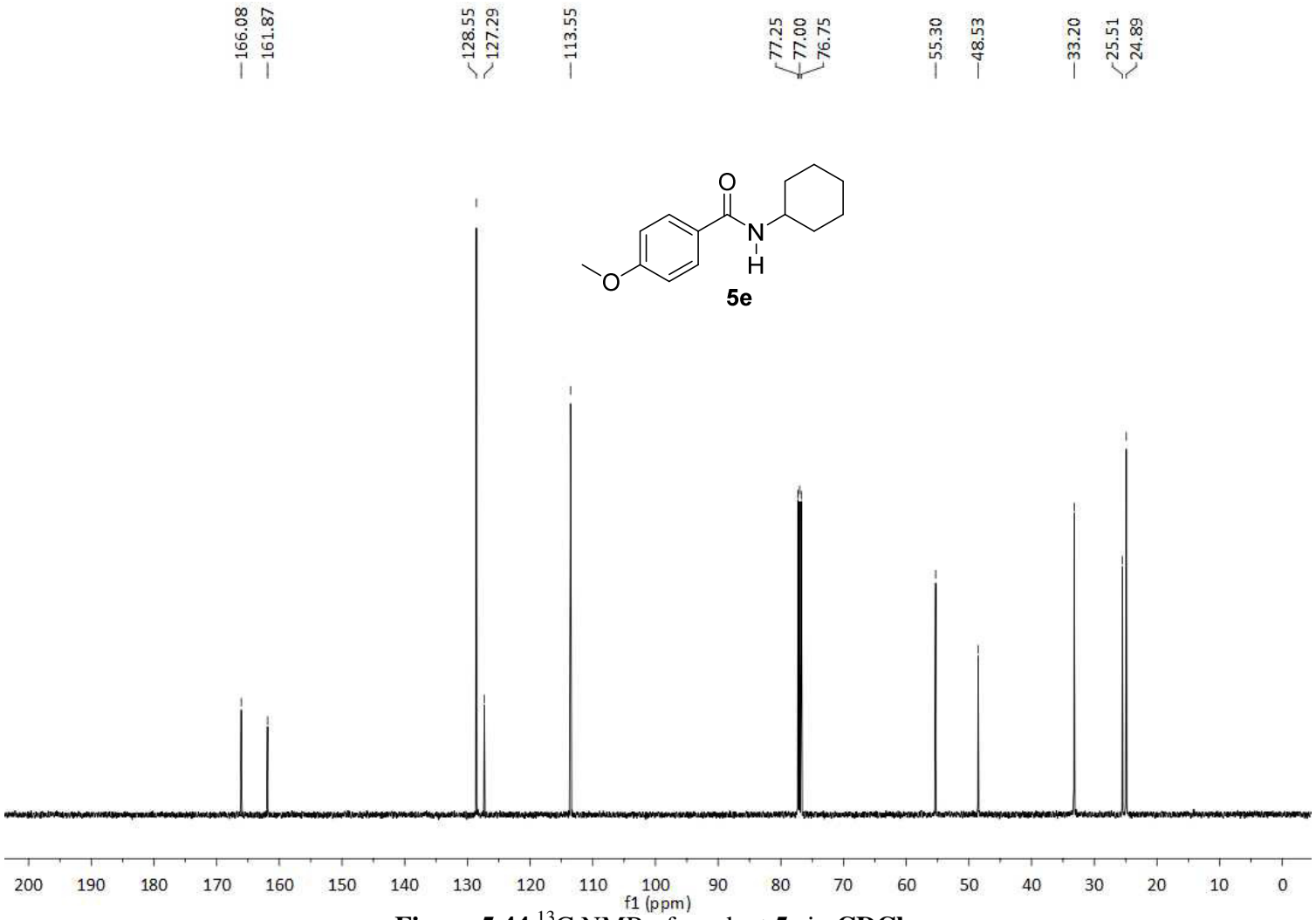


Figure 5.44 ^{13}C NMR of product **5e** in **$CDCl_3$**.

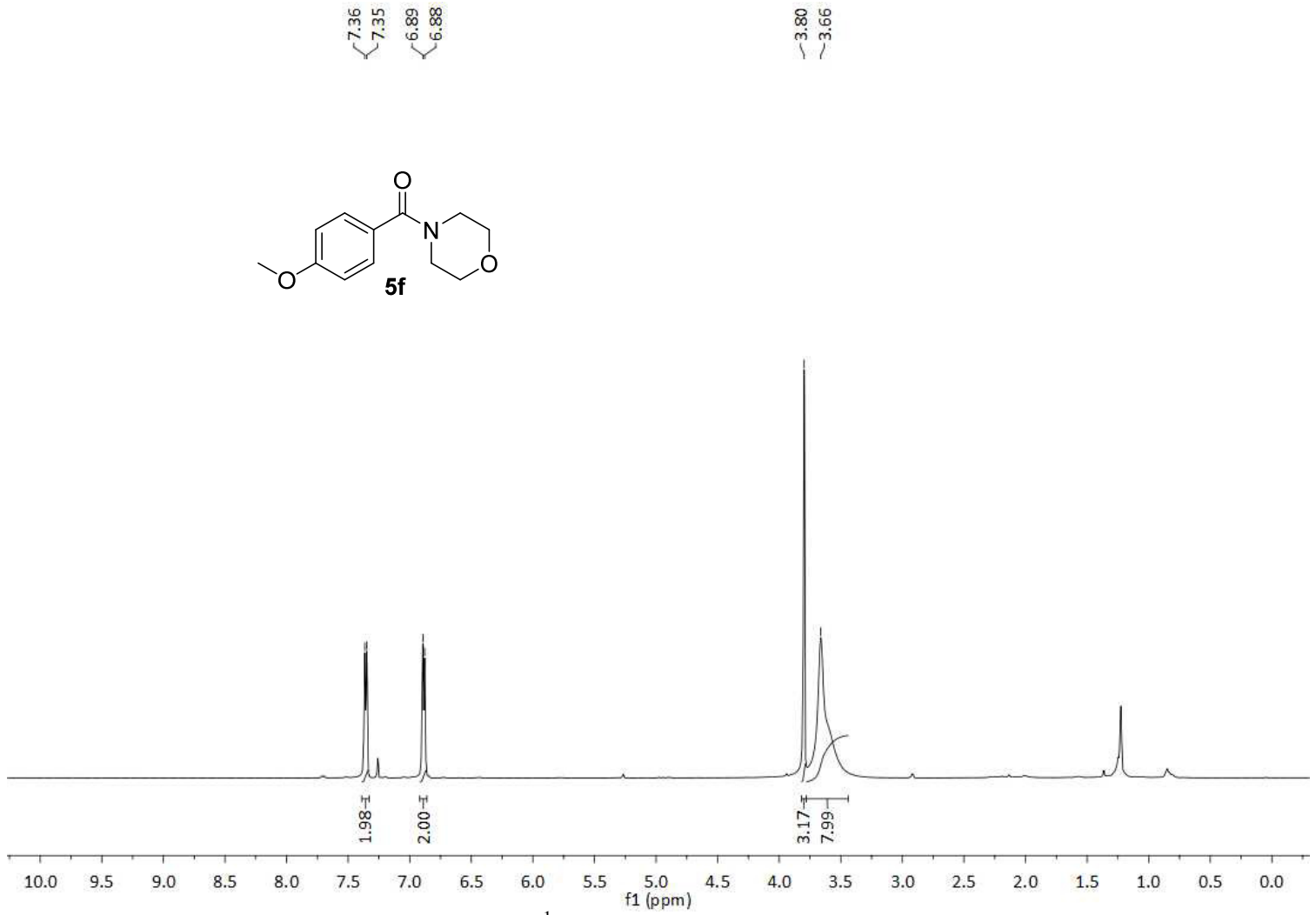


Figure 5.45 ^{1}H NMR of product **5f** in **$CDCl_3$**.

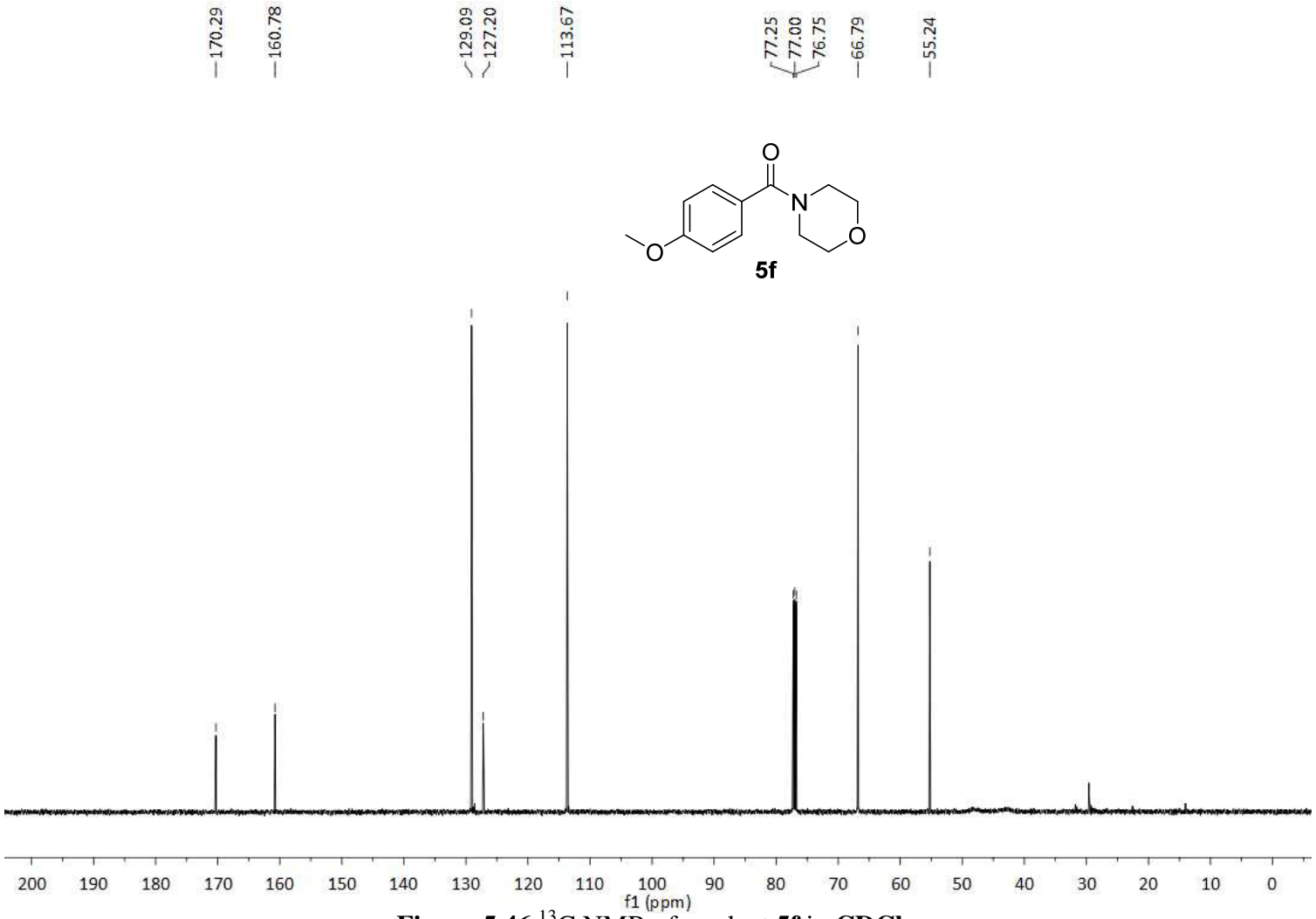


Figure 5.46 ^{13}C NMR of product **5f** in **$CDCl_3$**.

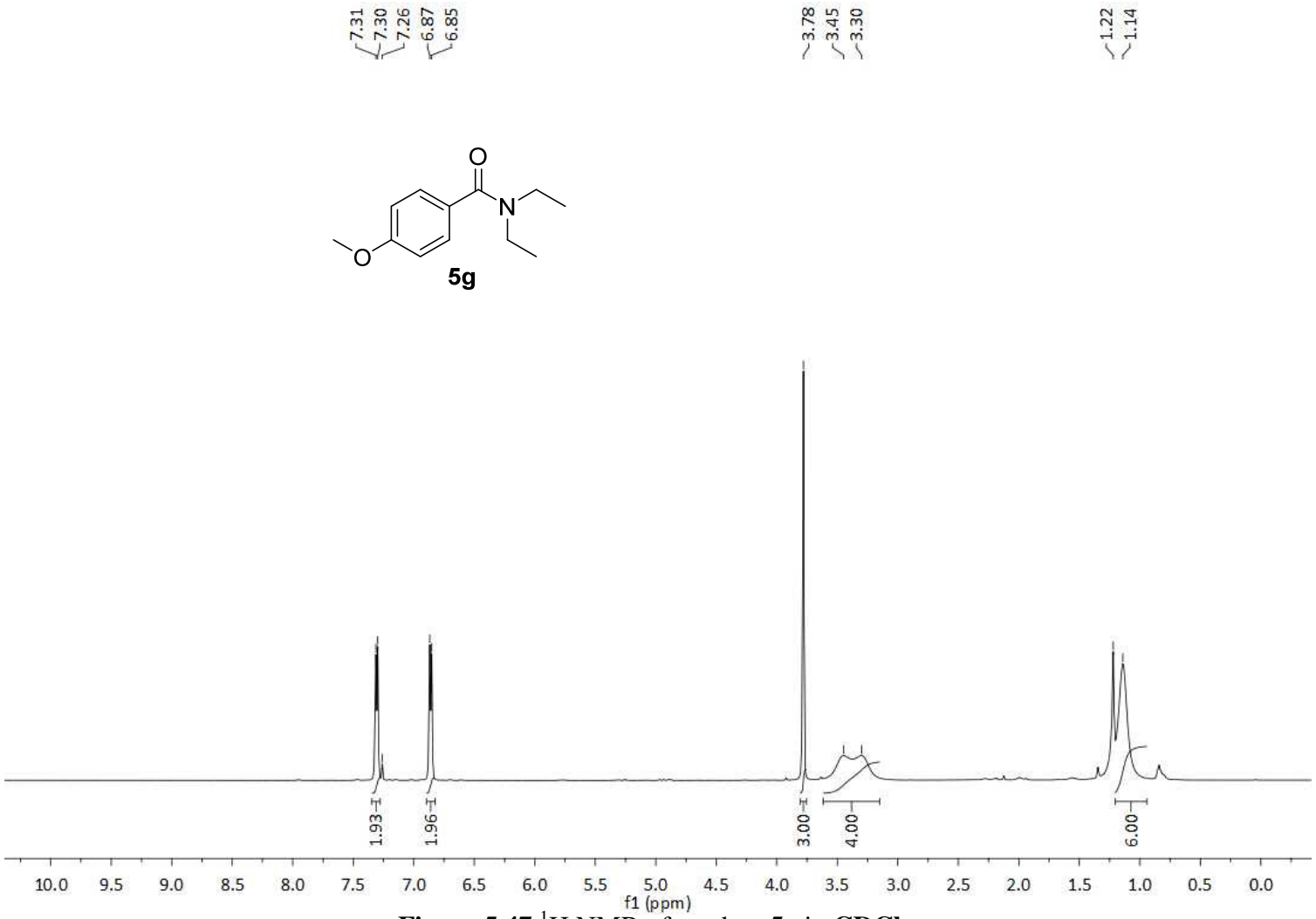


Figure 5.47 ^{1}H NMR of product **5g** in **$CDCl_3$**.

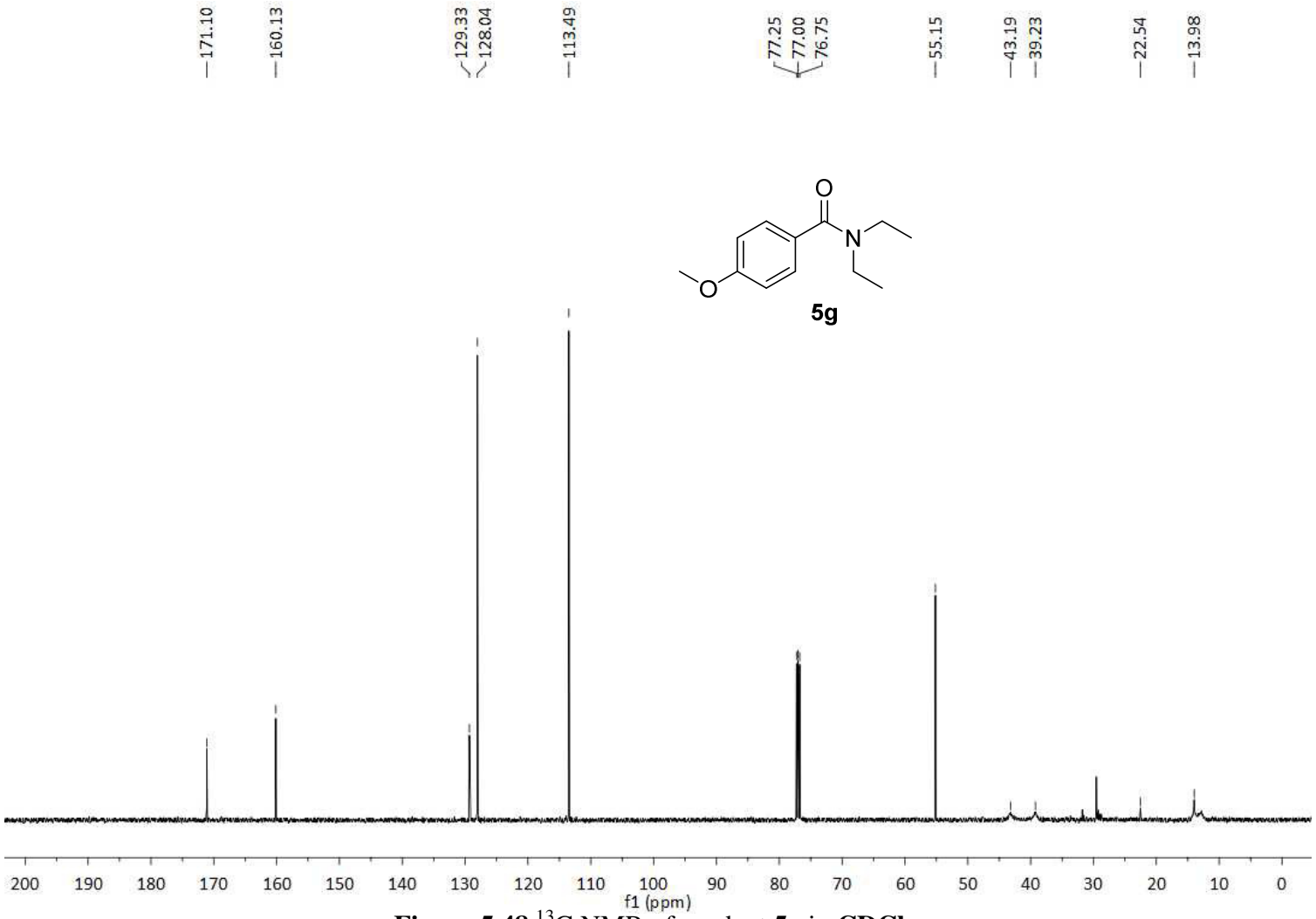


Figure 5.48 ^{13}C NMR of product **5g** in **$CDCl_3$**.

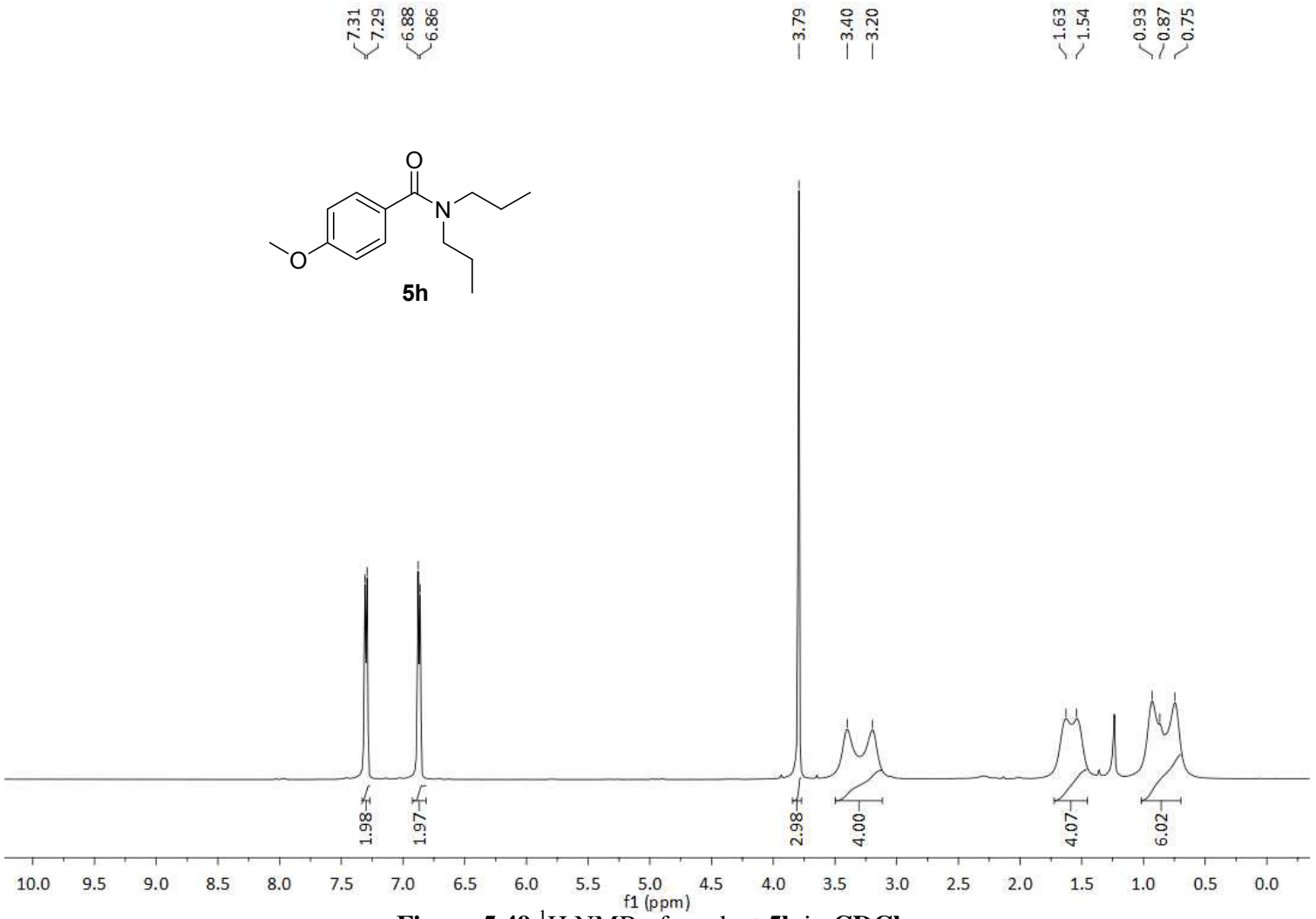


Figure 5.49 ^{1}H NMR of product **5h** in **$CDCl_3$**.

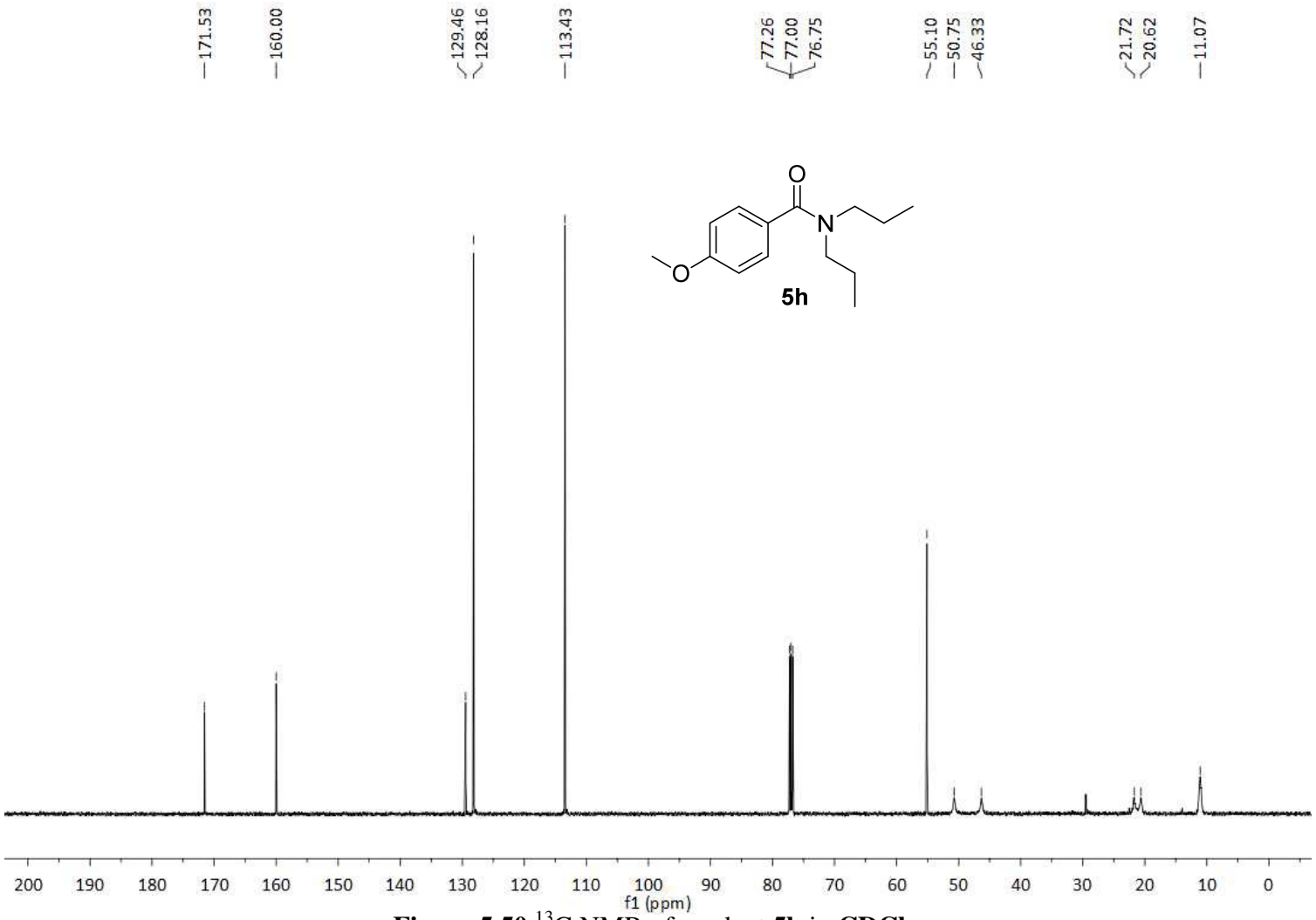


Figure 5.50 ^{13}C NMR of product **5h** in **$CDCl_3$**.

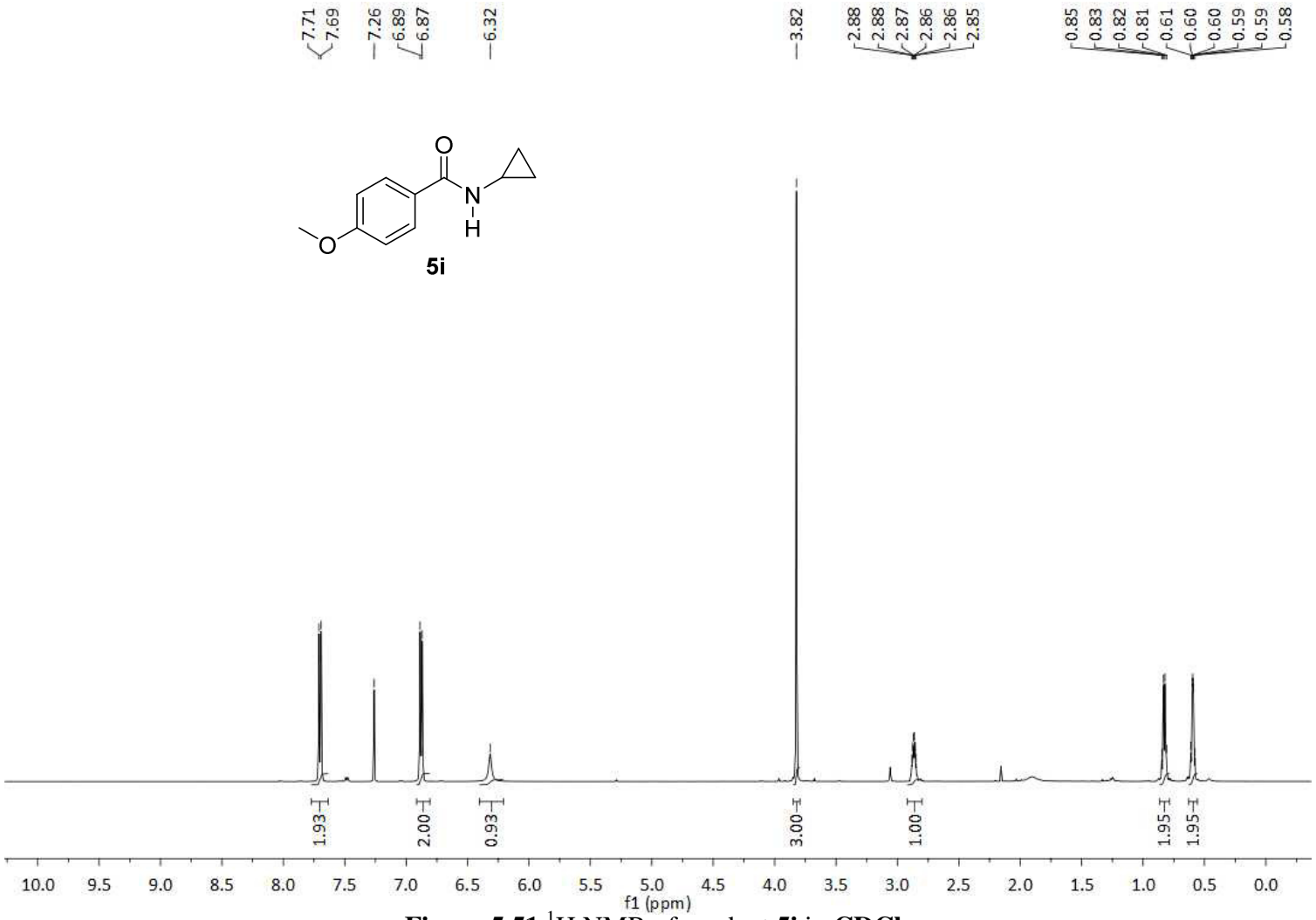


Figure 5.51 ^{1}H NMR of product **5i** in **$CDCl_3$**

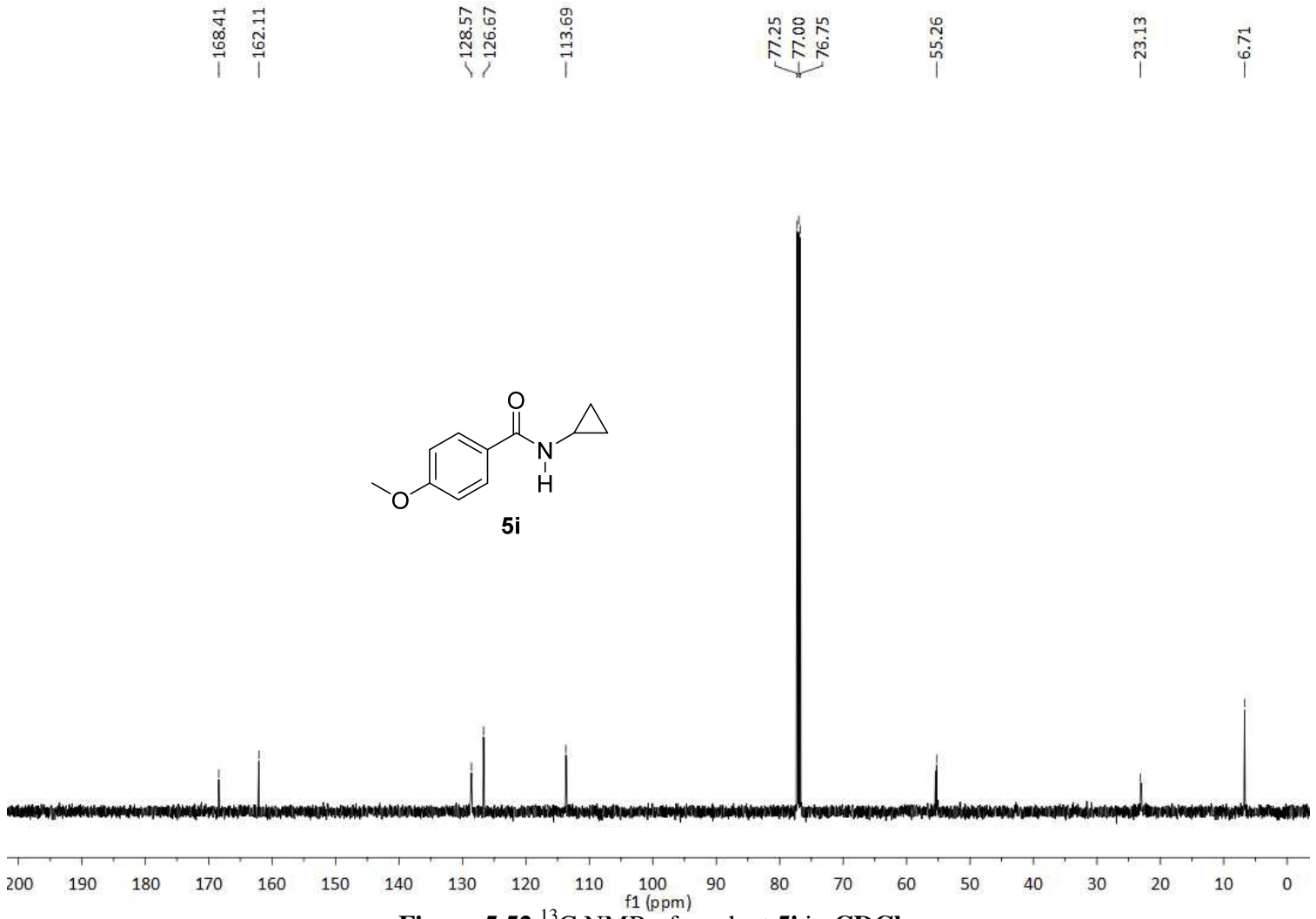


Figure 5.52 ^{13}C NMR of product **5i** in **$CDCl_3$**.

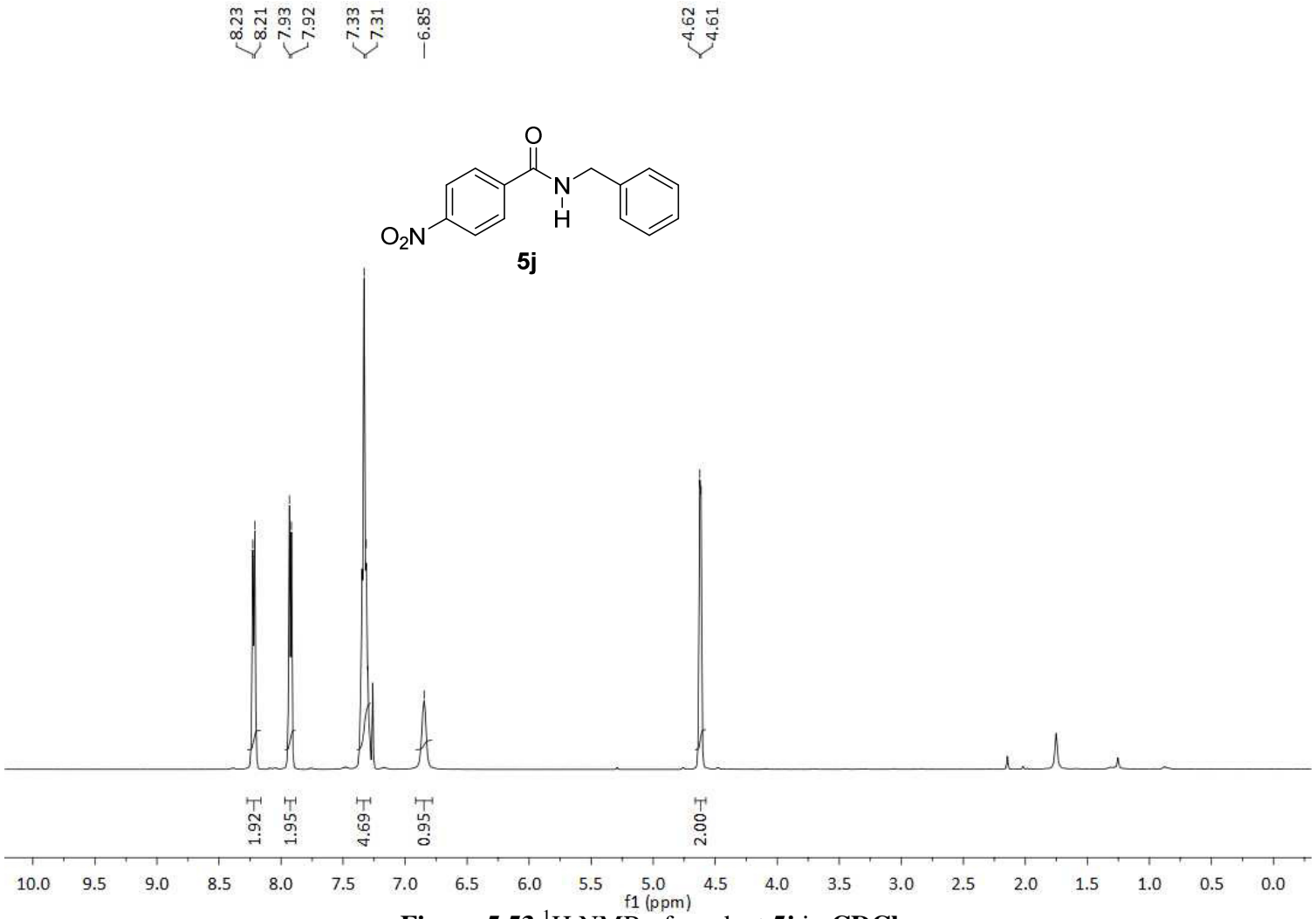


Figure 5.53 ^{1}H NMR of product **5j** in **$CDCl_3$**.

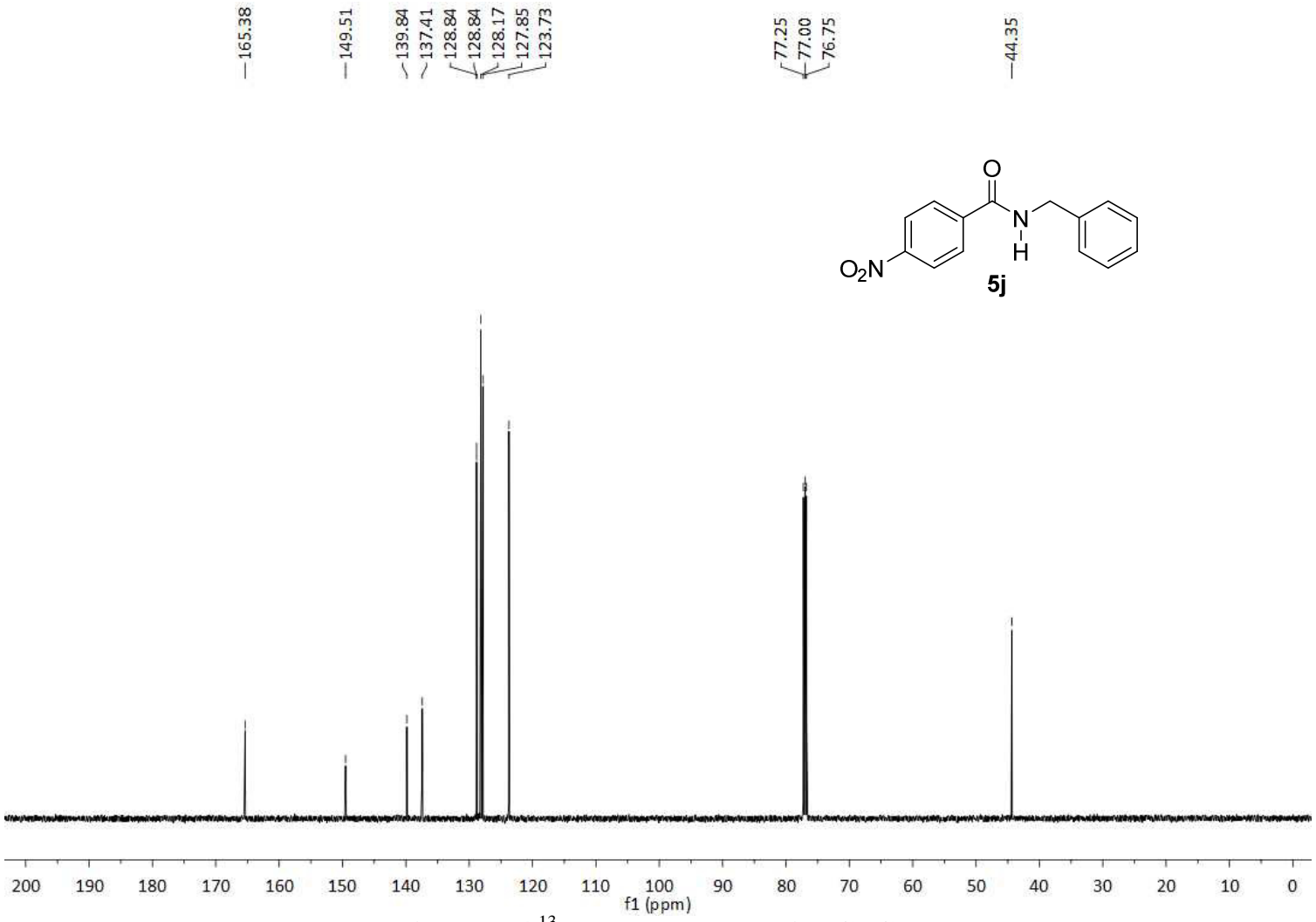


Figure 5.54 ^{13}C NMR of product **5j** in **$CDCl_3$**.

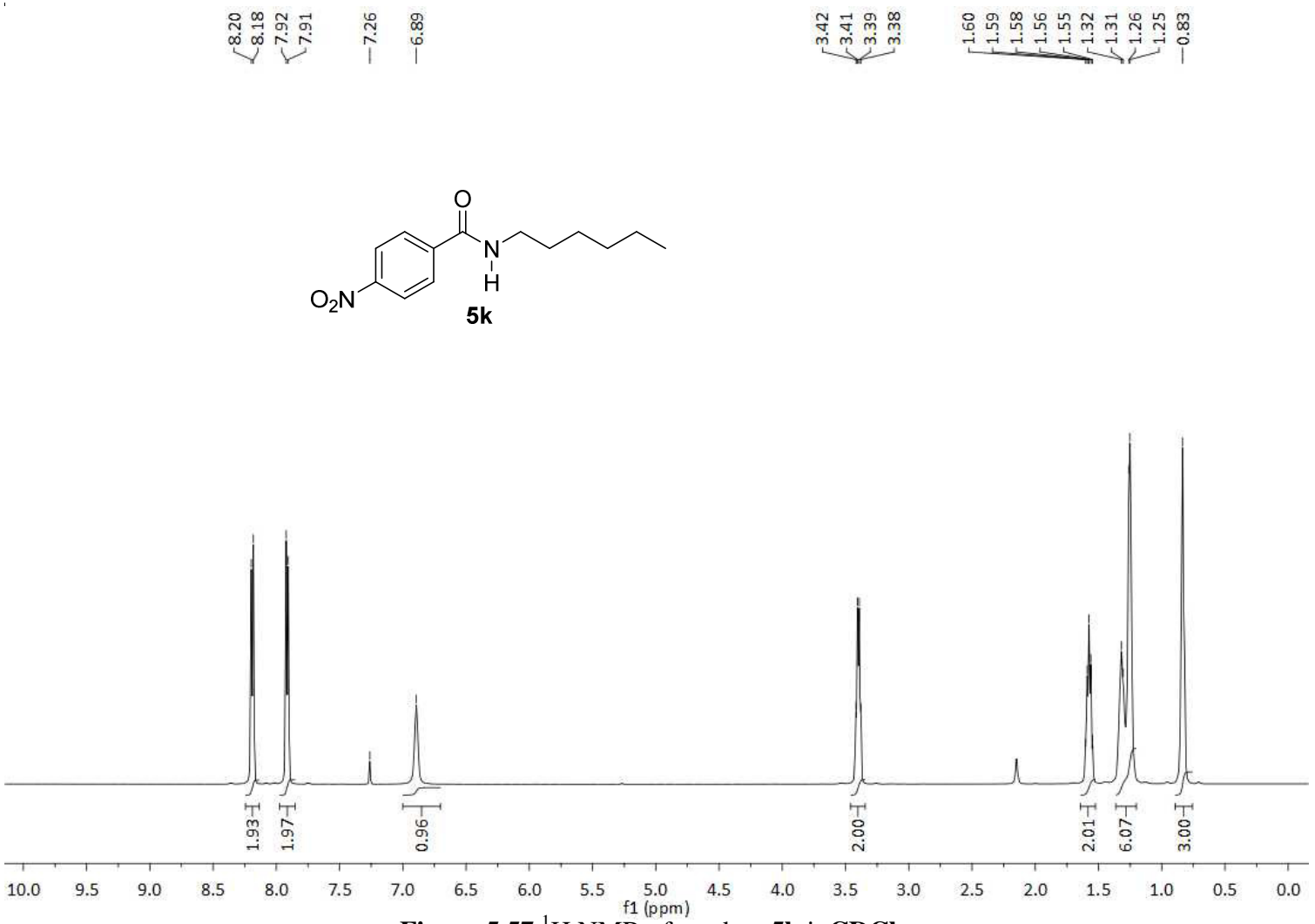


Figure 5.57 ^{1}H NMR of product **5k** in**$CDCl_3$**.

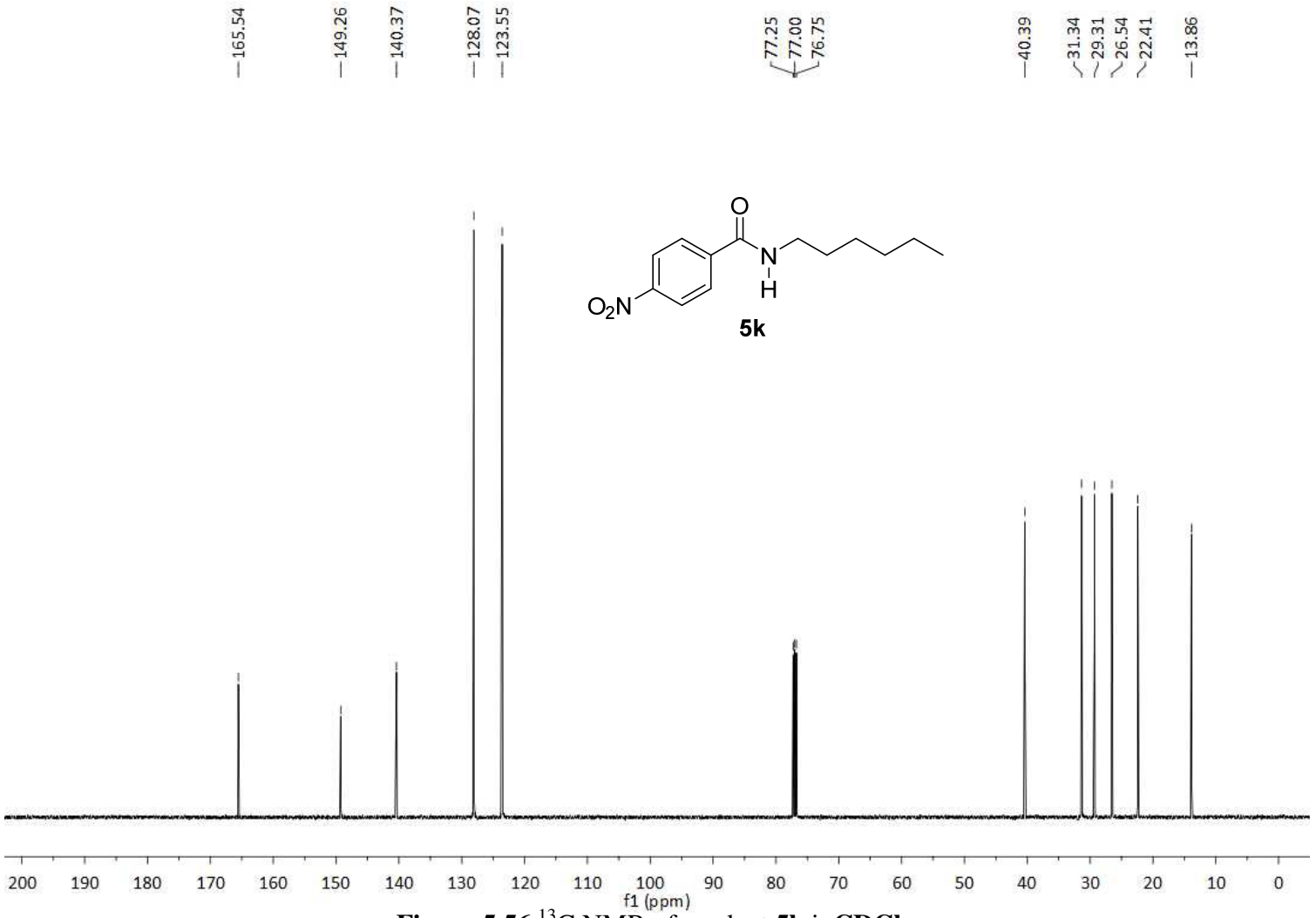


Figure 5.56 ^{13}C NMR of product **5k** in**$CDCl_3$**.

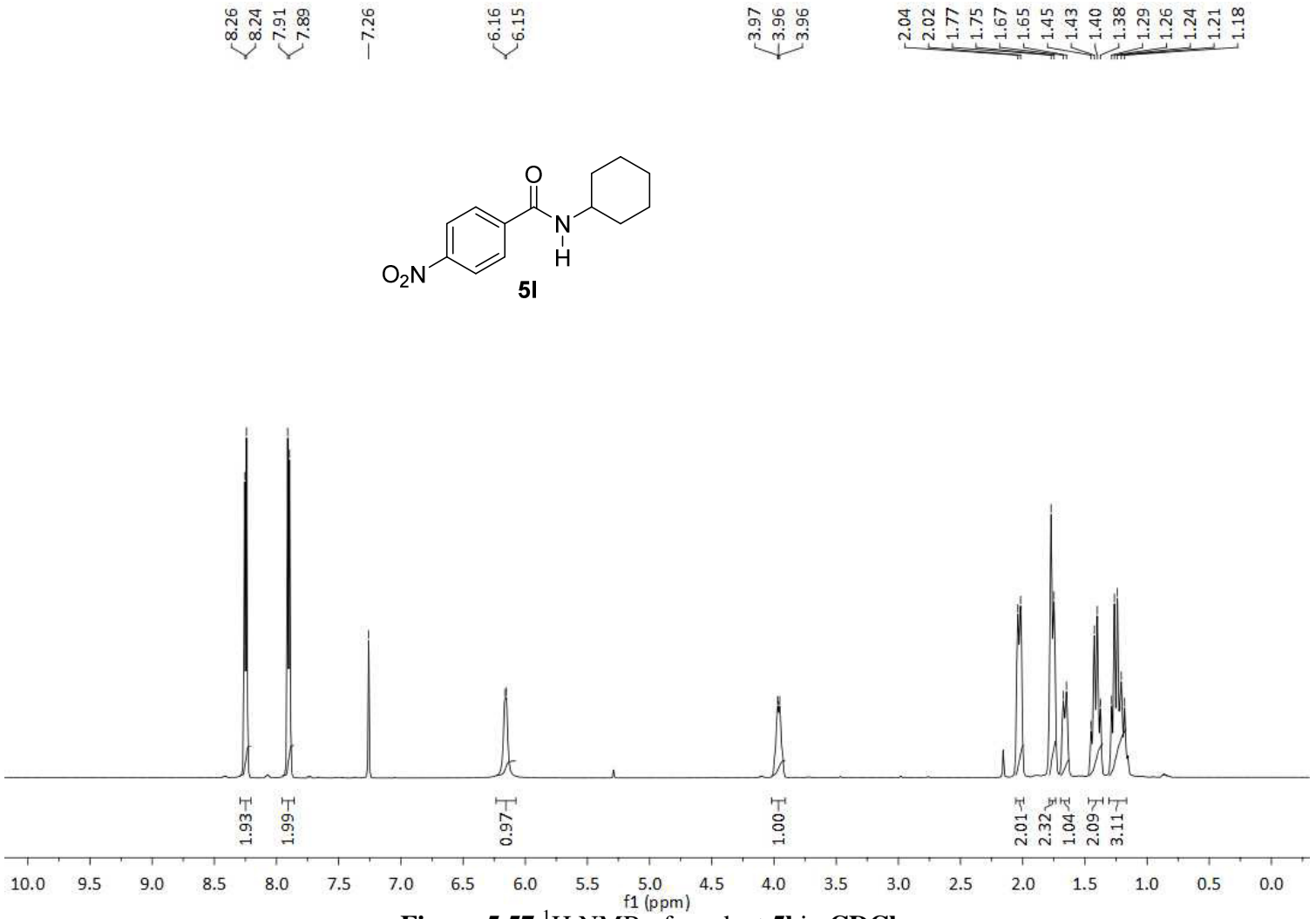


Figure 5.57 ^{1}H NMR of product **5l** in **$CDCl_3$**.

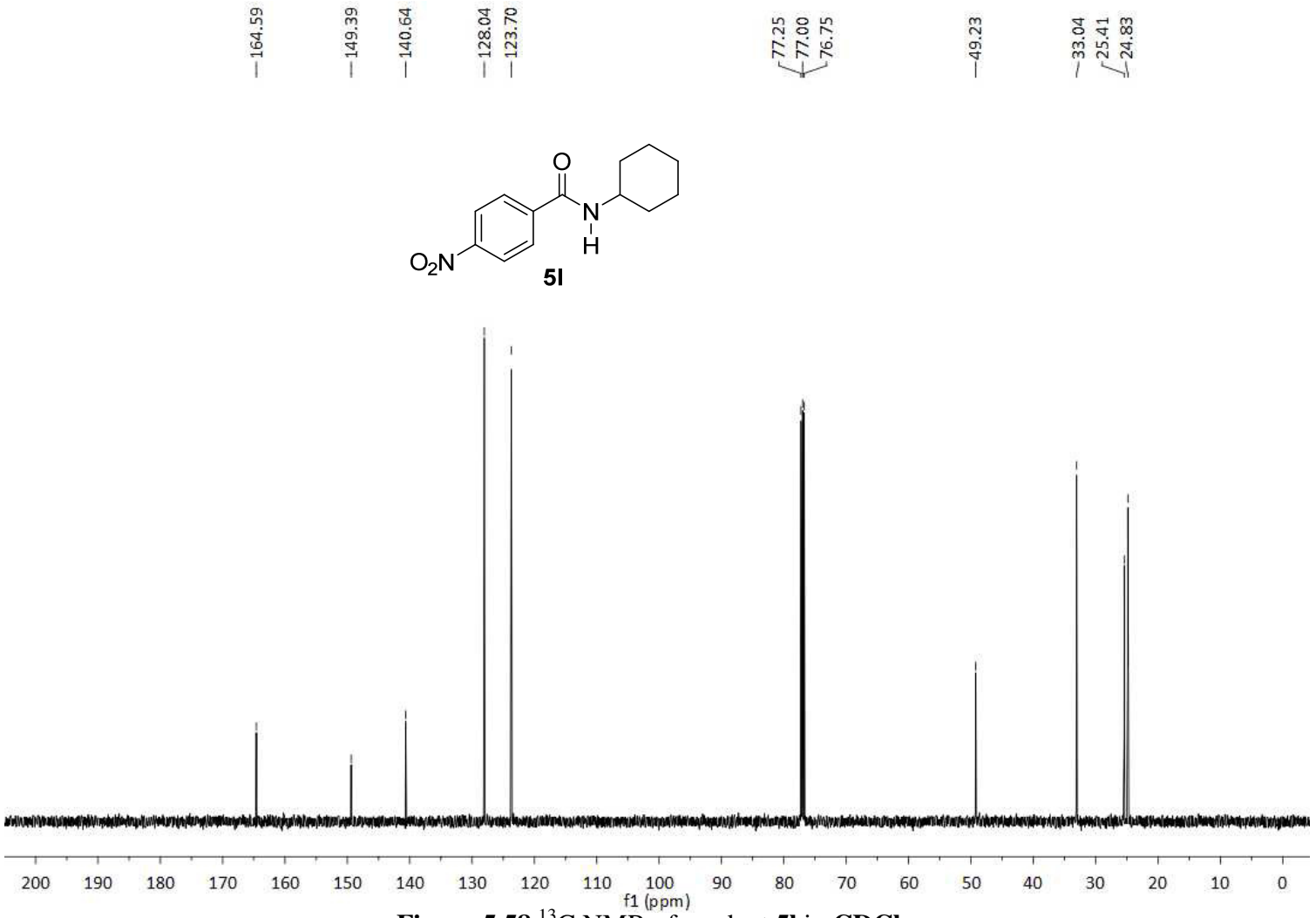


Figure 5.58 ^{13}C NMR of product **5l** in **$CDCl_3$**.

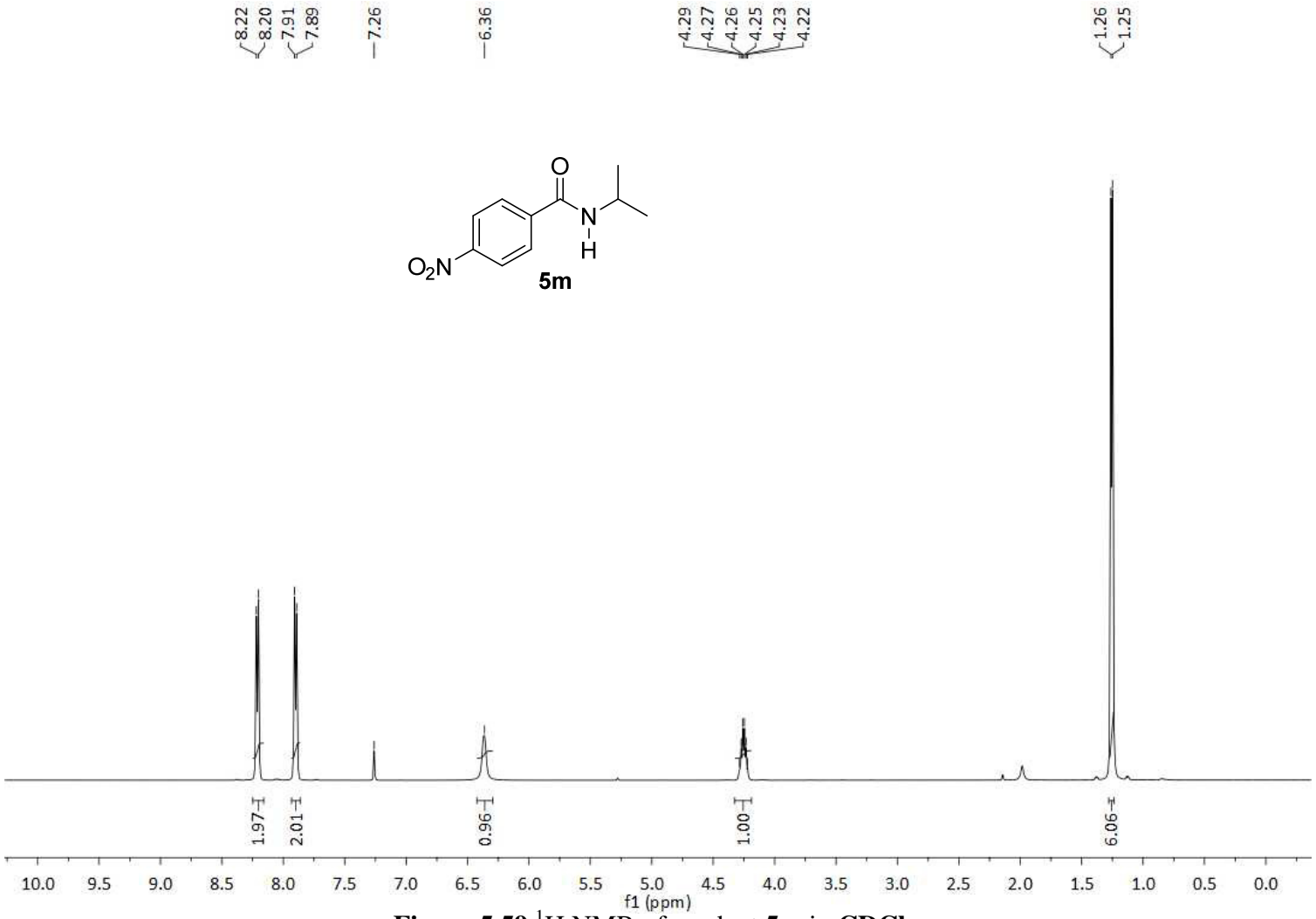


Figure 5.59 ^{1}H NMR of product **5m** in **$CDCl_3$**.

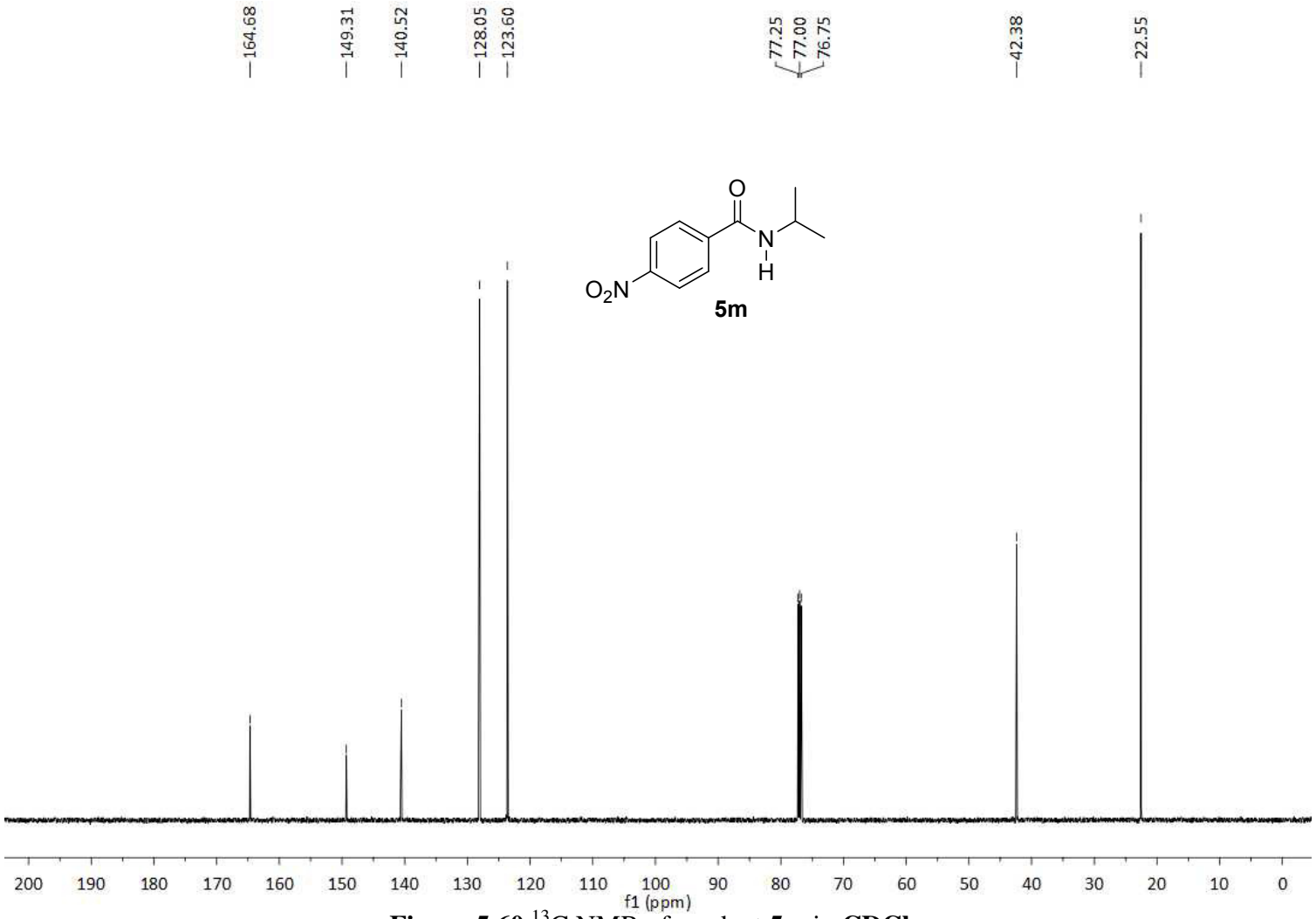


Figure 5.60 ^{13}C NMR of product **5m** in **$CDCl_3$**.

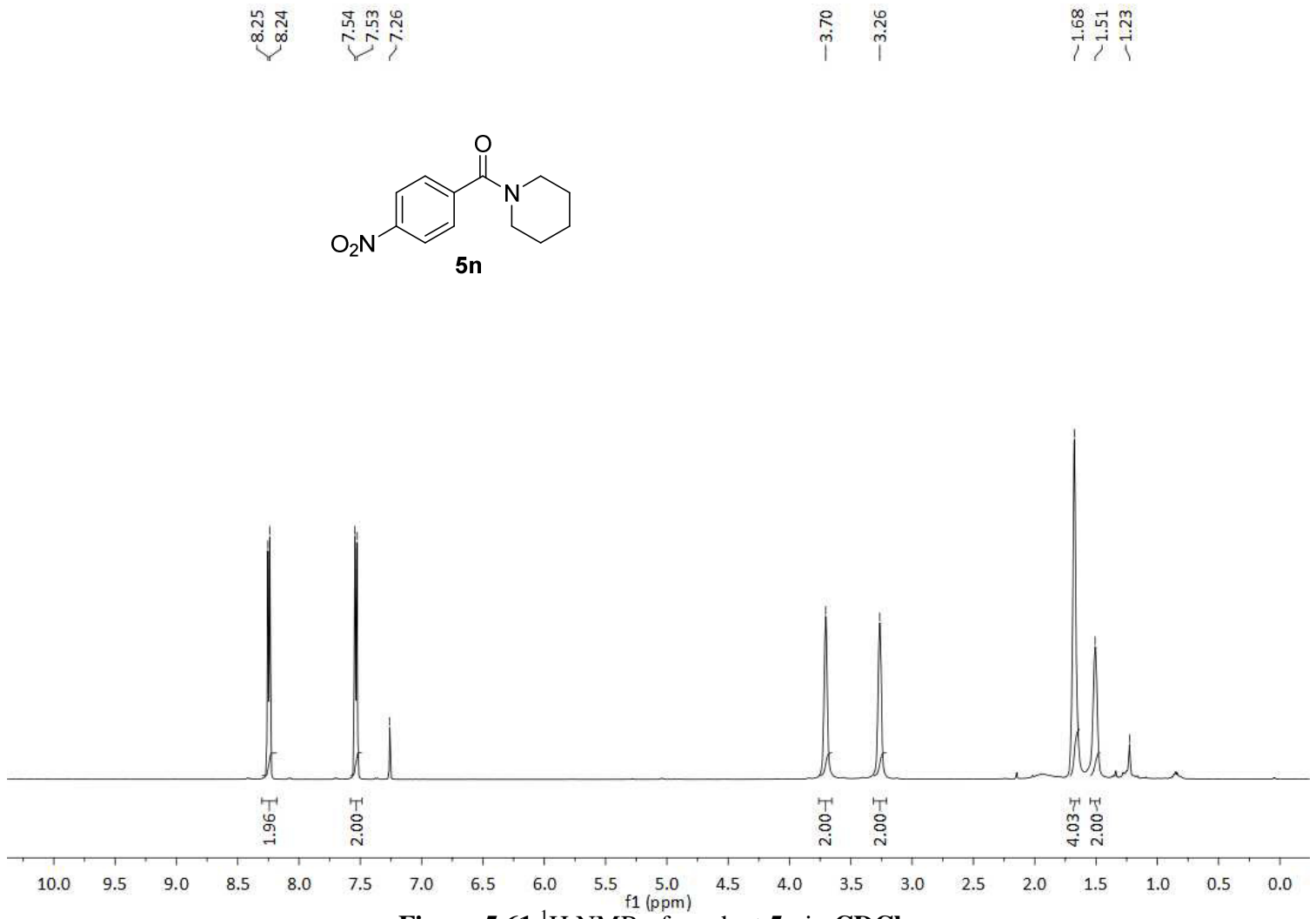


Figure 5.61 ^{1}H NMR of product **5n** in **$CDCl_3$**.

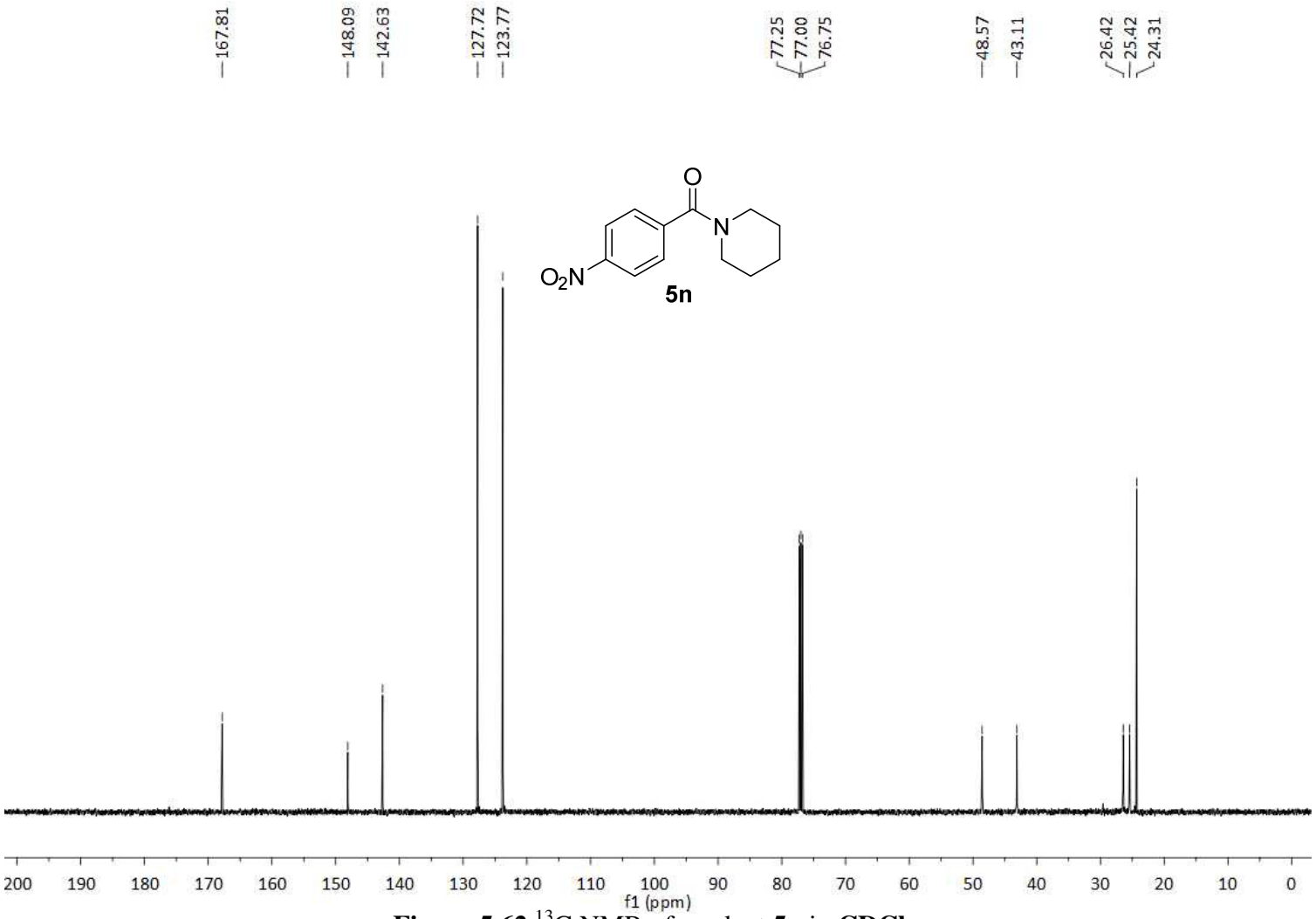


Figure 5.62 ^{13}C NMR of product **5n** in **$CDCl_3$**.

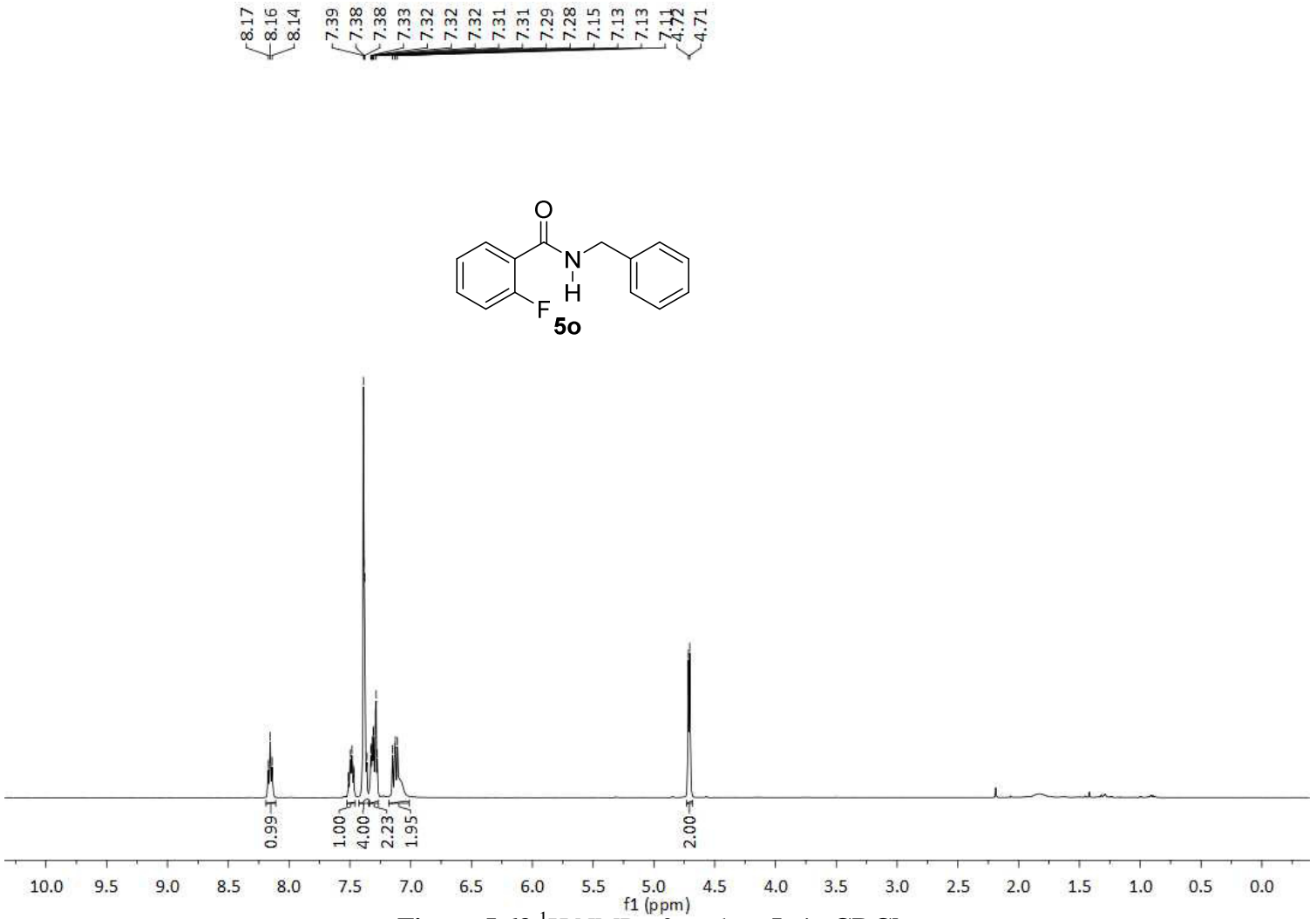


Figure 5.63 ^{1}H NMR of product **5o** in **$CDCl_3$**.

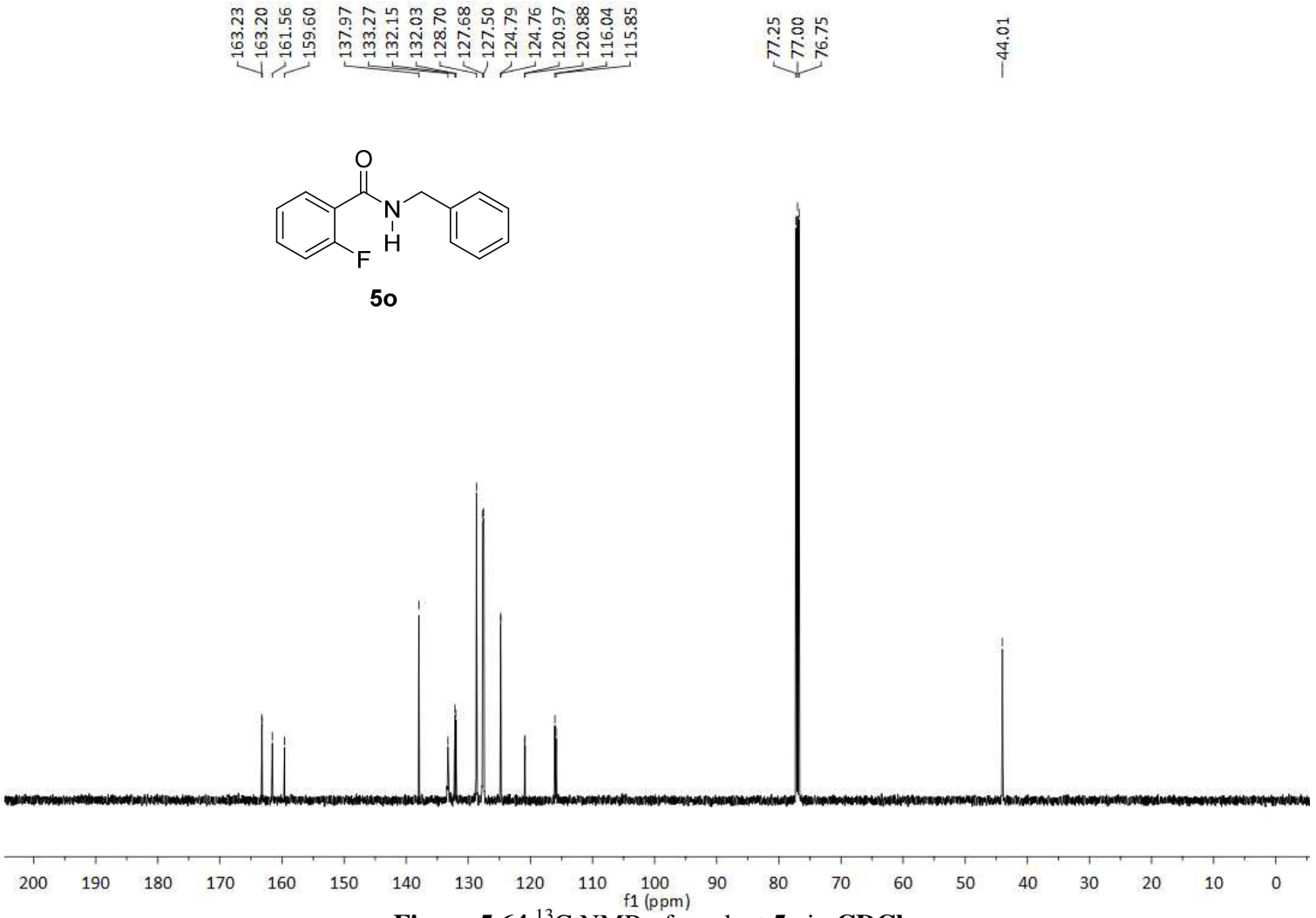


Figure 5.64 ^{13}C NMR of product **5o** in **$CDCl_3$**.

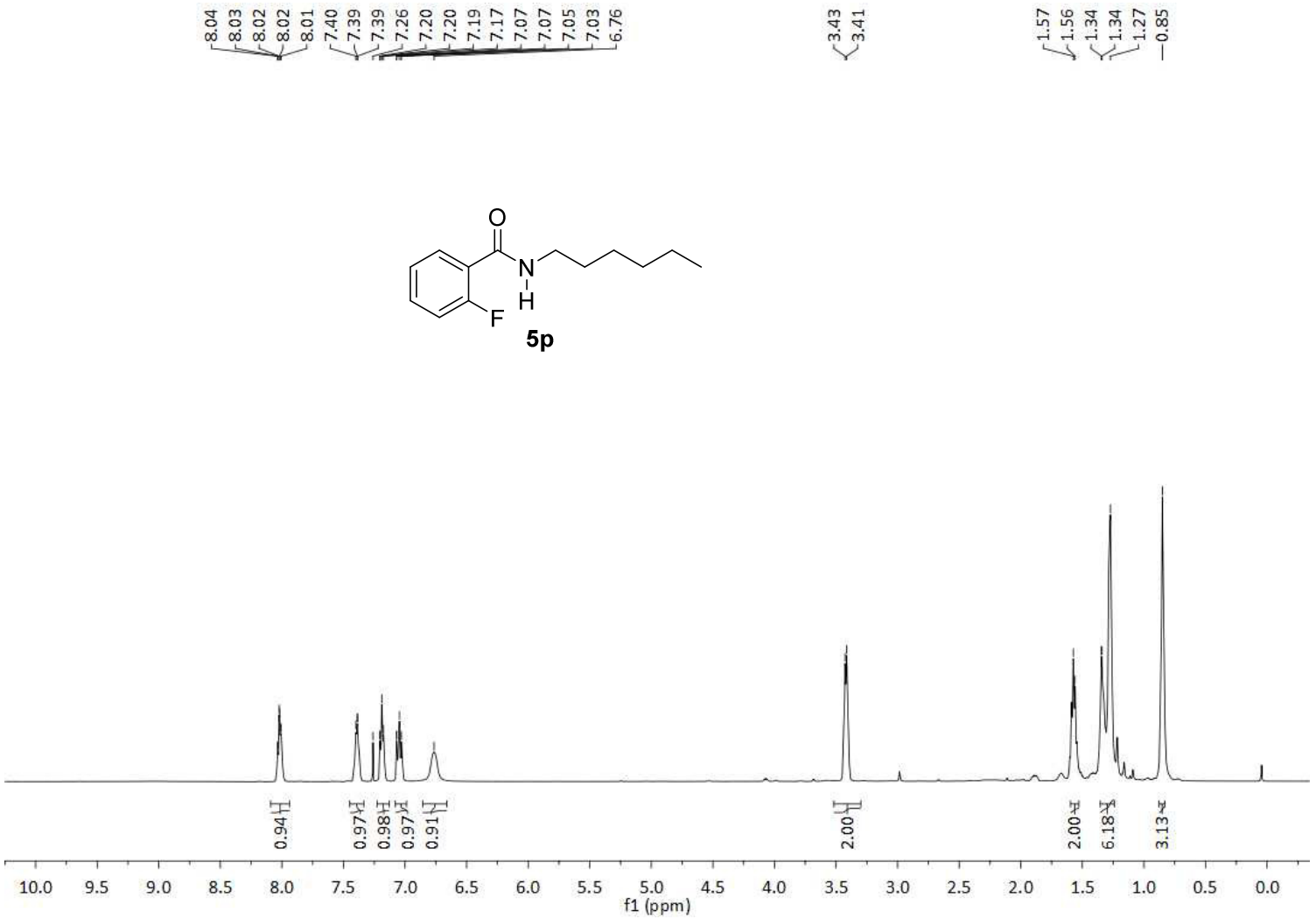


Figure 5.65 ^{1}H NMR of product **5p** in **$CDCl_3$**.

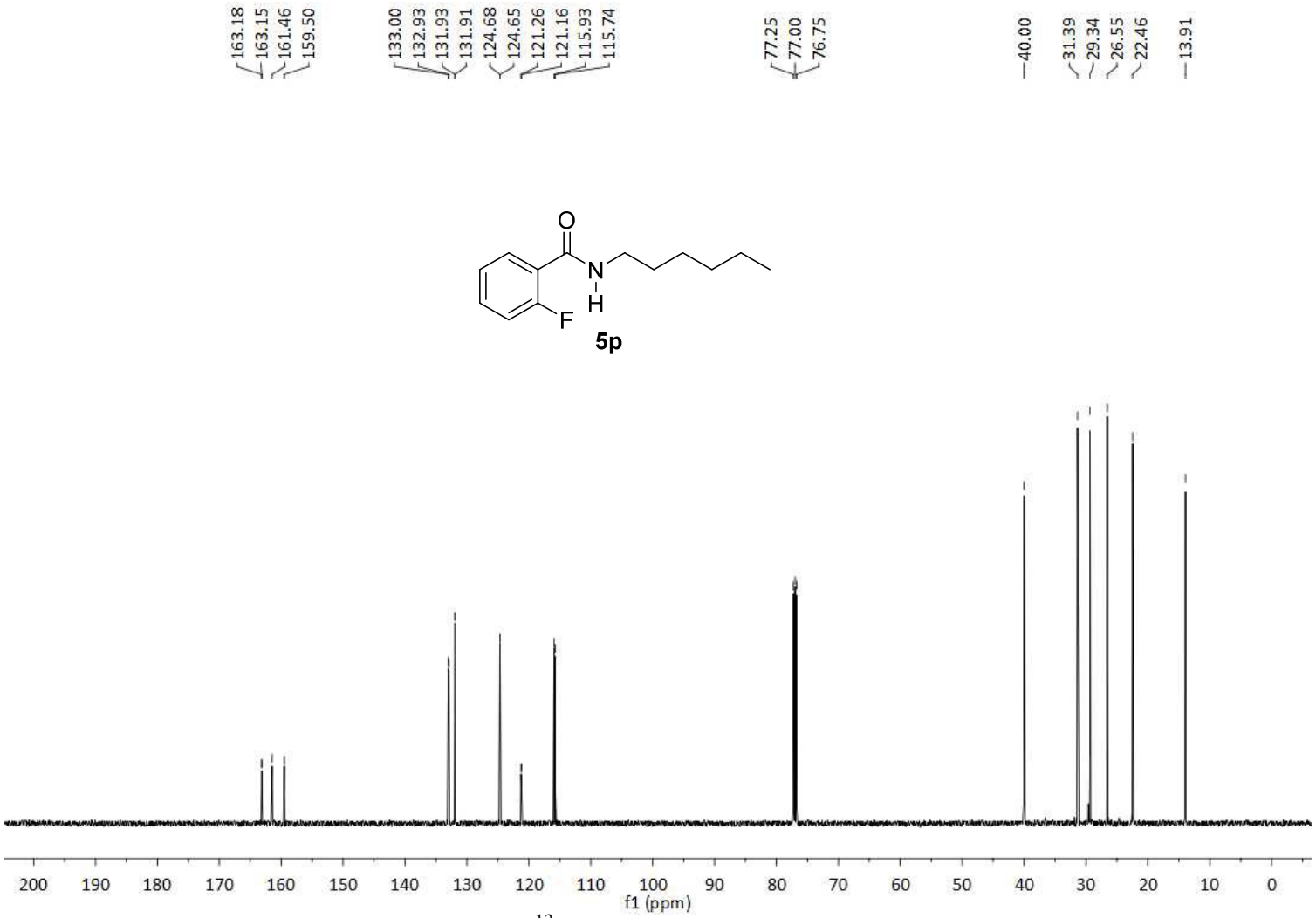


Figure 5.66 ^{13}C NMR of product **5p** in **$CDCl_3$**.

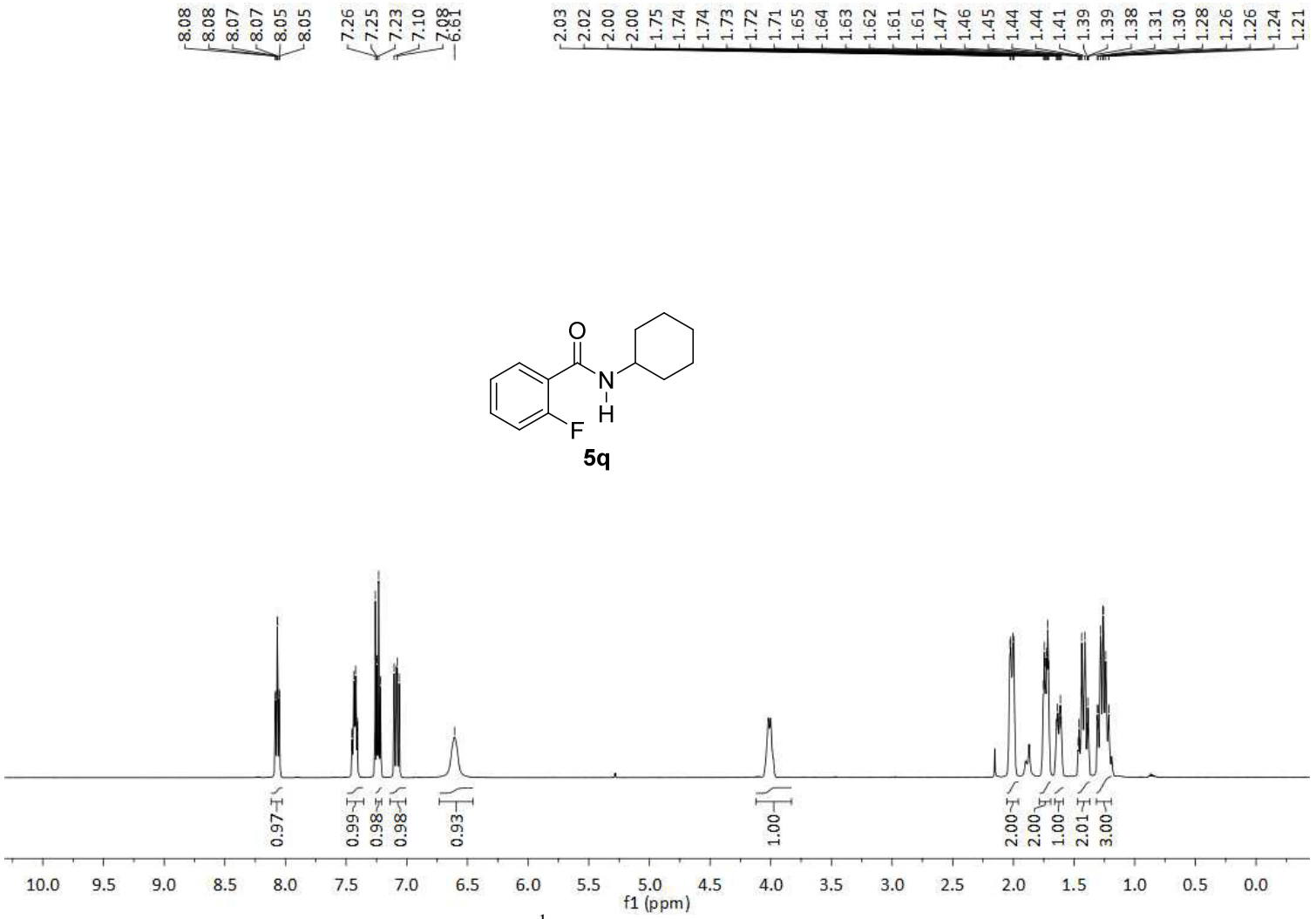


Figure 5.67 ^{1}H NMR of product **5q** in **$CDCl_3$**.

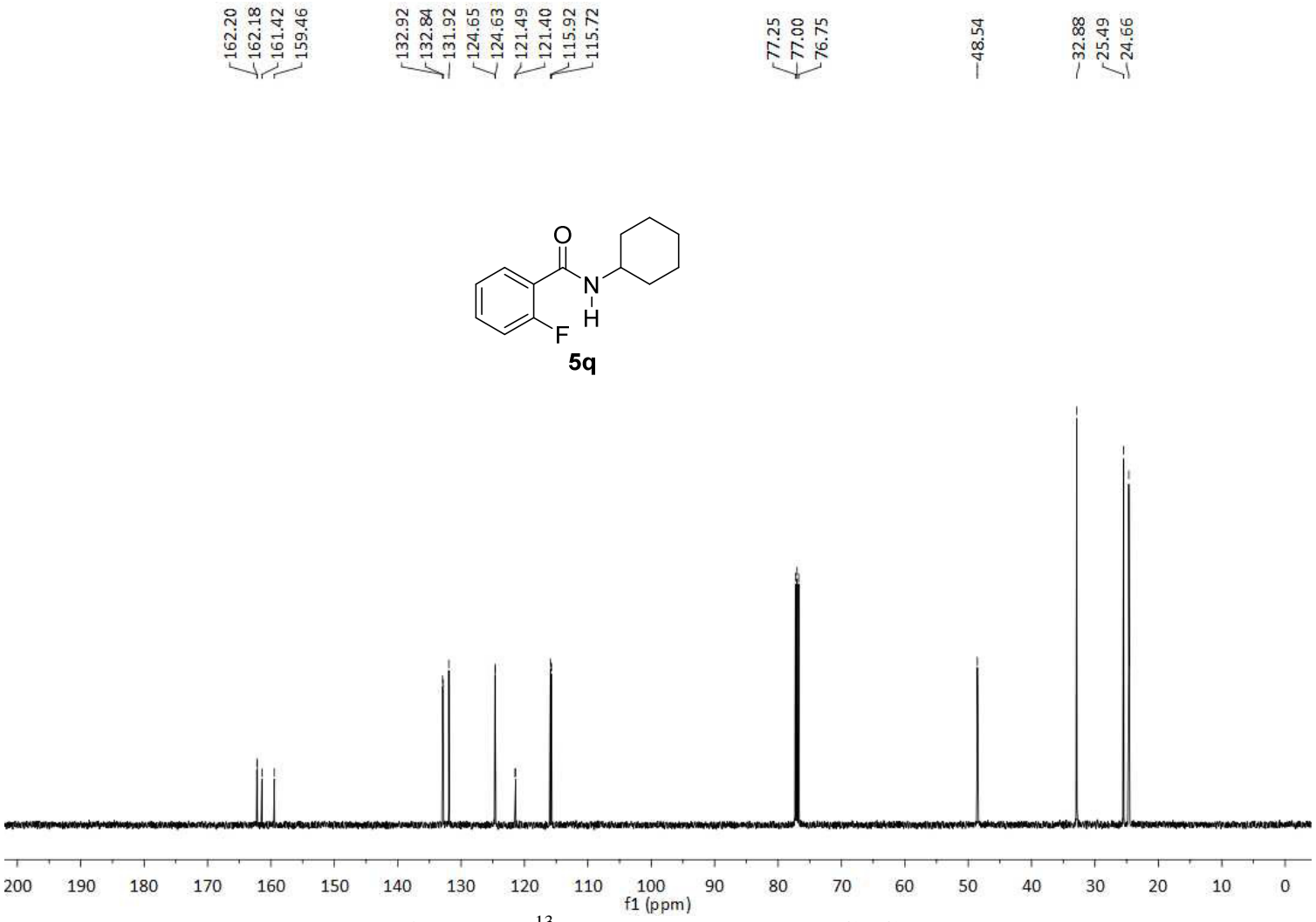


Figure 5.68 ^{13}C NMR of product **5q** in **$CDCl_3$**.

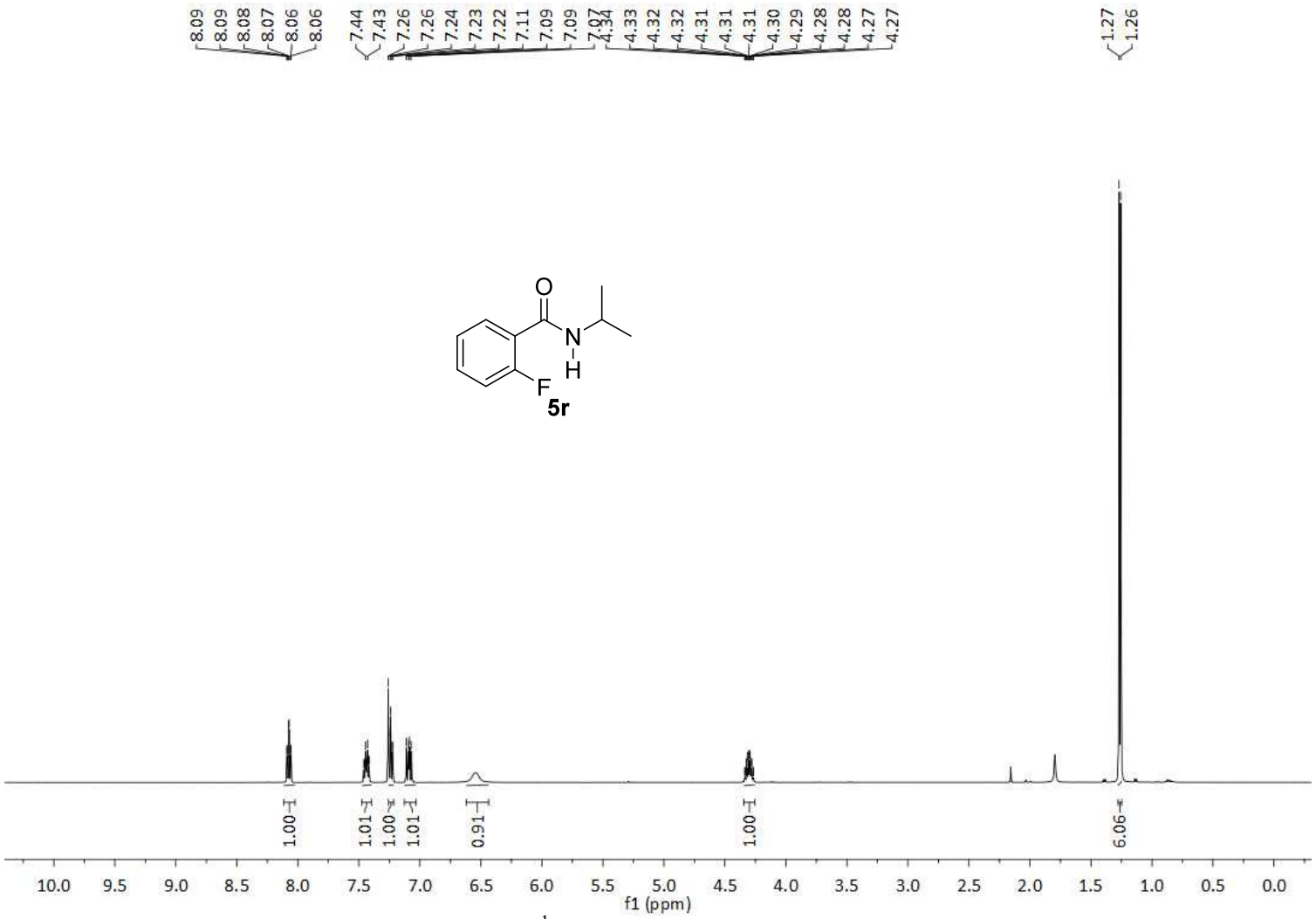


Figure 5.69 ^{1}H NMR of product **5r** in **$CDCl_3$**.

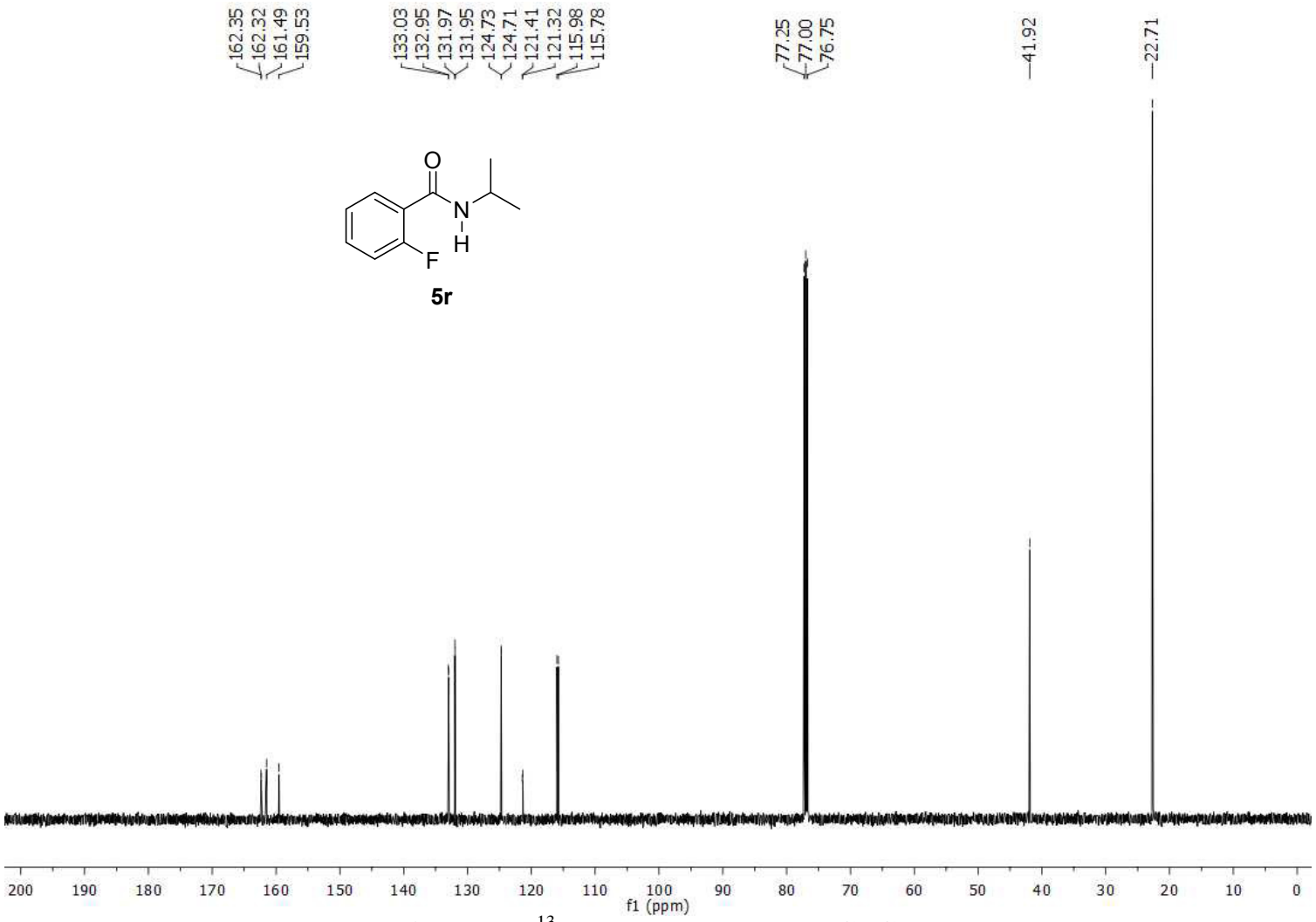


Figure 5.70 ^{13}C NMR of product **5r** in **$CDCl_3$**.

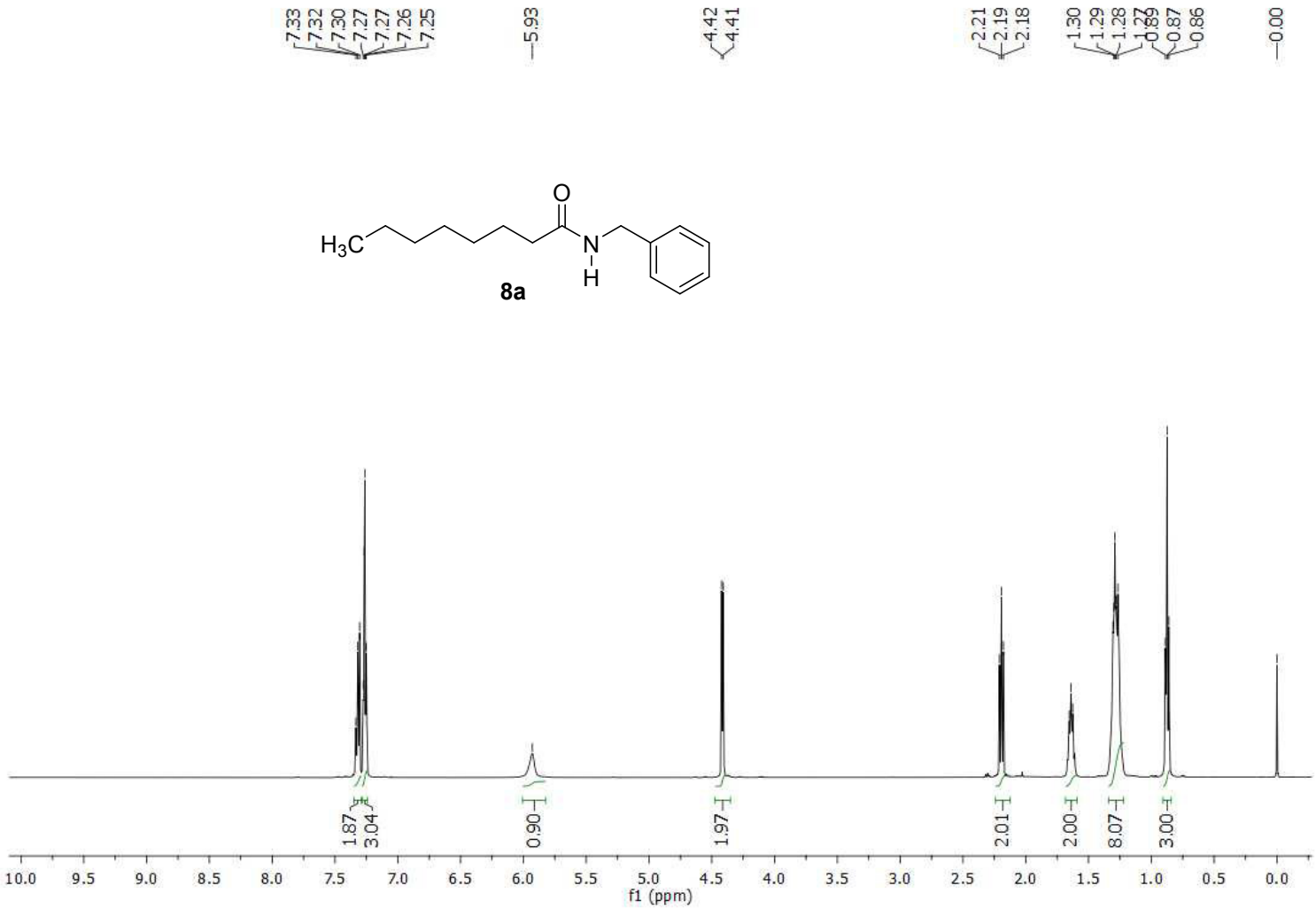


Figure 5.71 ^{1}H NMR of product **8a** in **$CDCl_3$**.

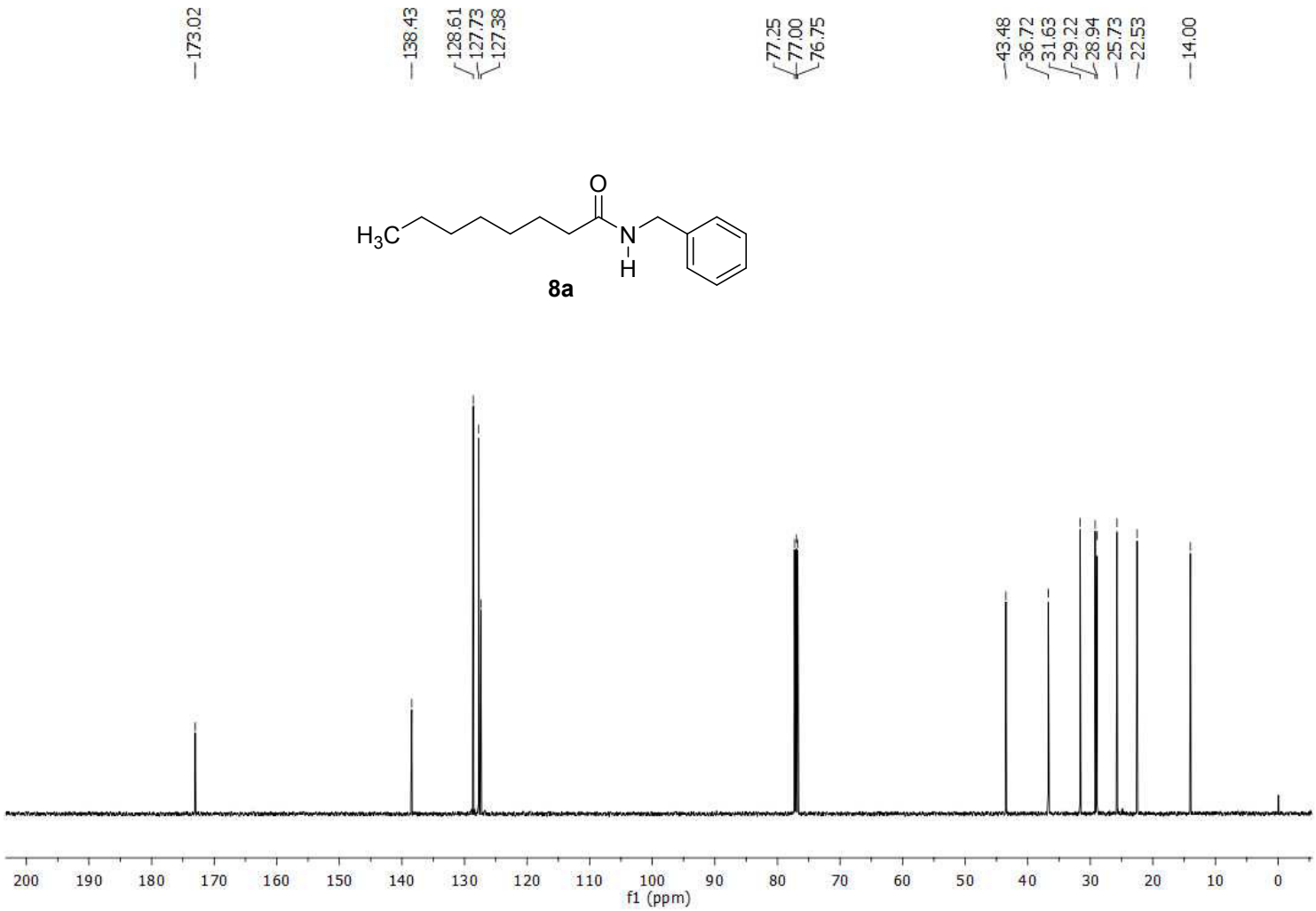


Figure 5.72 ^{13}C NMR of product **8a** in **$CDCl_3$**.

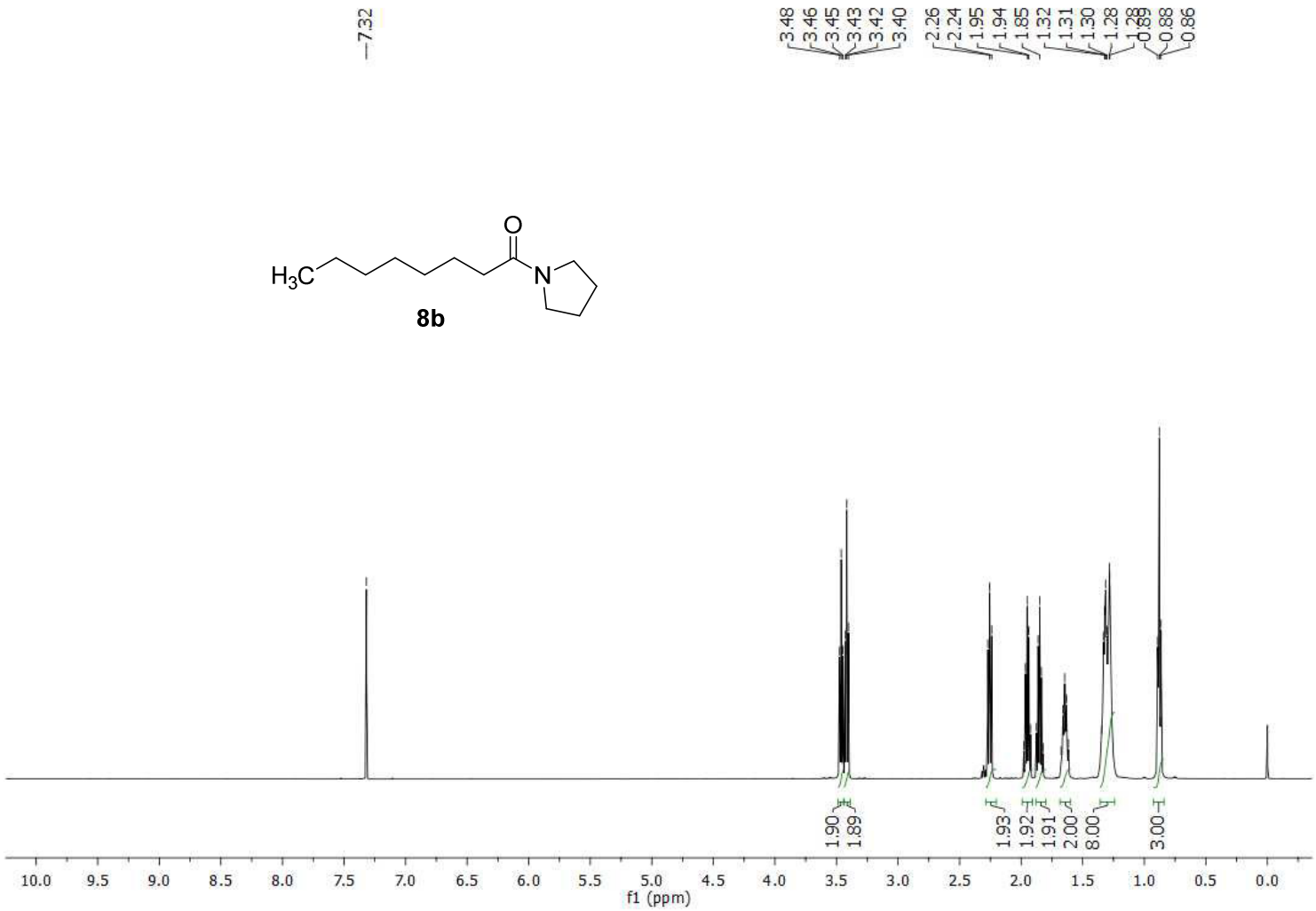


Figure 5.73 ^{1}H NMR of product **8b** in **$CDCl_3$**.

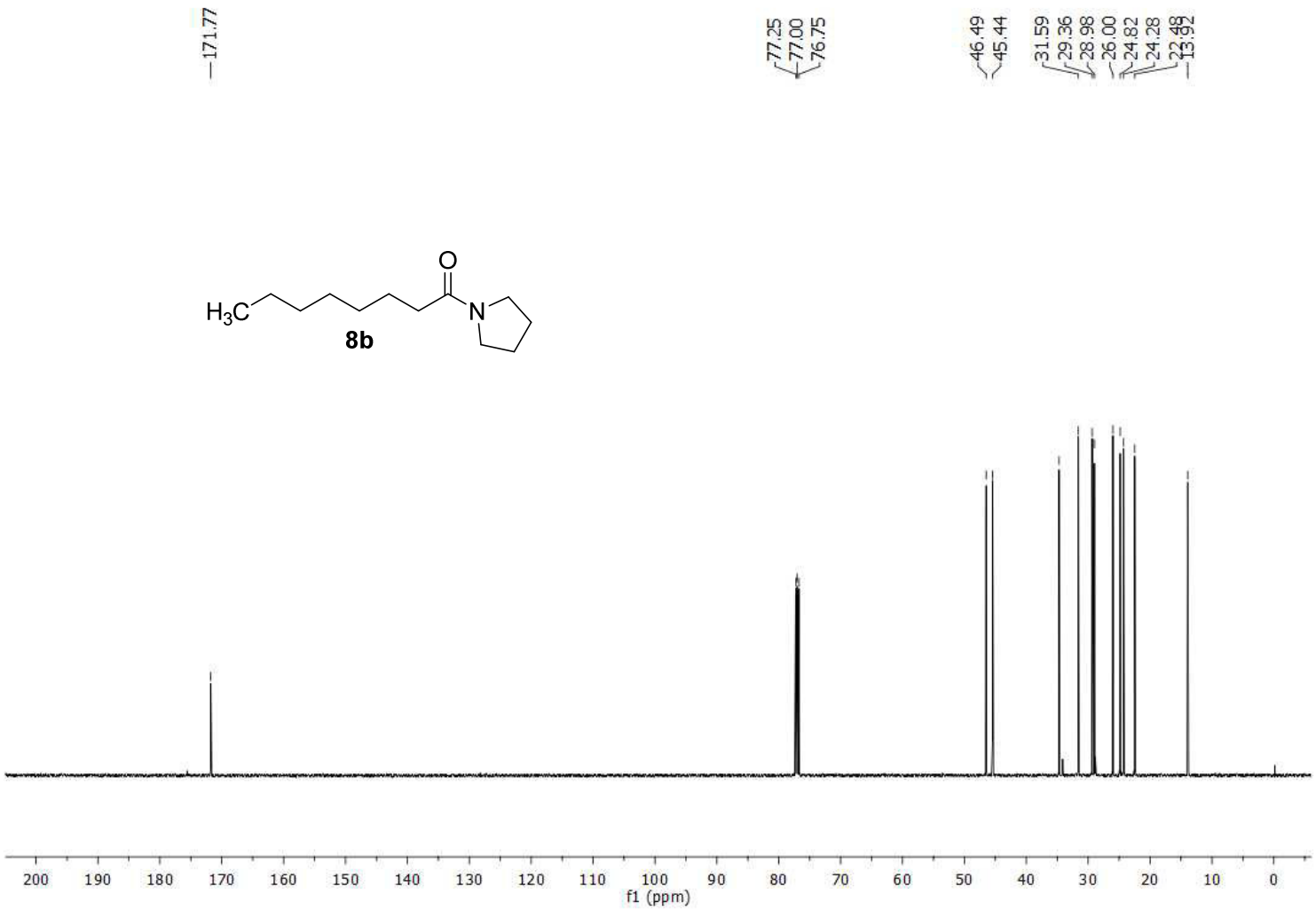


Figure 5.74 ^{13}C NMR of product **8b** in **$CDCl_3$**.