Electronic Supplementary Information for

Direct synthesis of *N*-alkylated amides *via* tandem hydration/*N*-alkylation reaction from nitriles, aldoximes and alcohols

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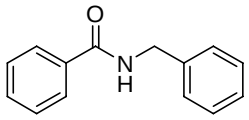
General Experimental Details

High-resolution mass spectra (HRMS) were obtained on a HPLC-Q-Tof MS(Micro) spectrometer and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M+Na]^+$. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 500 MHz using a Bruker Avance 500 spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane or ppm relative to the center of the singlet at 7.26 ppm for $CDCl_3$ and 2.50 ppm for DMSO-d_6. Coupling constants J values are reported in Hertz (Hz), and the splitting patterns were designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 125 MHz using a Bruker Avance 500 spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for $CDCl_3$ and 39.5 ppm for DMSO-d_6. ^{13}C NMR spectra were routinely run with broadband decoupling.

All reactions were run under an atmosphere of nitrogen, unless otherwise indicated. Anhydrous solvents were transferred *via* oven-dried syringe. Reaction tubes were oven-dried and cooled under a stream of nitrogen. Reactions tubes were purchased from Beijing Synthware Glass Inc. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates.

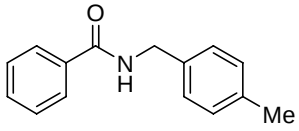
General procedure for iridium-catalyzed tandem synthesis of *N*-alkylated amines from nitriles, aldoxime and alcohols. To an oven-dried, nitrogen purged 25 ml Schlenk tube were added $[Cp^*IrCl_2]_2$ (0.01 mmol, 1 mol%), nitrile (1 mmol), *n*-butylaldoxime (1.1 mmol, 1.1 equiv.) and toluene (1 ml), and the mixture was heated at 100 ^{o}C for 6 h. The reaction mixture was allowed to cool to ambient temperature and alcohol (1.3 mmol) and Cs_2CO_3 (0.2 mmol, 0.2 equiv.) were added. The Schlenk tube was flushed with nitrogen and the mixture was further heated at 130 ^{o}C for 12h. The reaction mixture was cooled to ambient temperature, concentrated in *vacuo* and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding product.

N-benzylbenzamide (5aa)[1]



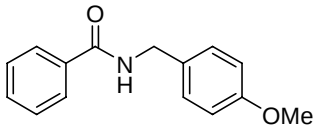
1) **1a** (103 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3a** (140 mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).
5aa, yellow solid, 179 mg, 85% yield.
mp 96-97 ^oC (lit.[1] mp 105 ^oC); ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 7.6 Hz, 2H, ArH), 7.50 (t, J = 7.4 Hz, 1H, ArH), 7.42 (t, J = 7.6 Hz, 2H, ArH), 7.36-7.35 (m, 4H, ArH), 7.32-7.28 (m, 1H, ArH), 6.46 (br s, 1H, NH), 4.65 (d, J = 5.6 Hz, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 138.2, 134.3, 131.5, 128.7, 128.5, 127.9, 127.6, 126.9, 44.1.

N-(4-methylbenzyl)benzamide (5ab)[2]



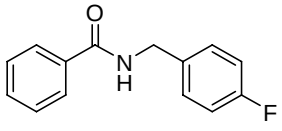
1) **1a** (103 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3b** (159 mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).
5ab, light grey solid, 180 mg, 80% yield.
mp 137-138 ^oC (lit.[2] mp 137 ^oC); ^1H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 7.3 Hz, 2H, ArH), 7.49 (t, J = 7.4 Hz, 1H, ArH), 7.42 (t, J = 7.6 Hz, 2H, ArH), 7.25 (d, J = 7.8 Hz, 2H, ArH), 7.16 (d, J = 7.8 Hz, 2H, ArH), 6.36 (br s, 1H, NH), 4.60 (d, J = 5.6 Hz, 2H, CH_2), 2.35 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 137.2, 135.1, 134.4, 131.4, 129.3, 128.4, 127.8, 126.9, 43.8, 21.0.

N-(4-methoxybenzyl)benzamide (5ac)[3]



1) **1a** (103 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3c** (180 mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).
5ac, pale grey solid, 207 mg, 86% yield.
mp 96-97 ^oC (lit.[3] mp 97-98 ^oC); ^1H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 7.2 Hz, 2H, ArH), 7.50 (t, J = 7.4 Hz, 1H, ArH), 7.42 (t, J = 7.5 Hz, 2H, ArH), 7.29 (d, J = 8.4 Hz, 2H, ArH), 6.89 (d, J = 8.7 Hz, 2H, ArH), 6.32 (br s, 1H, NH), 4.58 (d, J = 5.6 Hz, 2H, CH_2), 3.81 (s, 3H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 159.2, 134.5, 131.5, 130.2, 129.3, 128.6, 126.9, 114.2, 55.3, 43.7.

N-(4-fluorobenzyl)benzamide (5ad)[4]

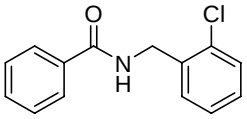


1) **1a** (103 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3d** (164 mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).

5ad, creamy white solid, 195 mg, 85% yield.

mp 107-108 °C (lit.[4] mp 114-116 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 7.3 Hz, 2H, ArH), 7.51 (t, J = 7.4 Hz, 1H, ArH), 7.43 (t, J = 7.6 Hz, 2H, ArH), 7.33 (dd, J = 8.4 Hz and 5.6 Hz, 2H, ArH), 7.03 (t, J = 8.6 Hz, 2H, ArH), 6.44 (br s, 1H, NH), 4.62 (d, J = 5.8 Hz, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 162.2 (d, $J_{C\text{-}F}$ = 244.7 Hz), 134.2, 134.0, 131.6, 129.5 (d, $J_{C\text{-}F}$ = 8.0 Hz), 128.6, 126.9, 115.5 (d, $J_{C\text{-}F}$ = 21.3 Hz), 43.3.

N-(2-Chlorobenzyl)-benzamide (5ae)[5]

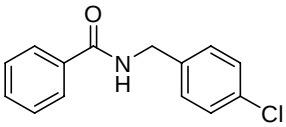


1) **1a** (103 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3e** (185 mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).

5ae, light yellow solid, 204 mg, 83% yield.

mp 107-108 °C (lit.[5] mp 108-109 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 7.5 Hz, 2H, ArH), 7.51-7.38 (m, 5H, ArH), 7.26-7.24 (m, 2H, ArH), 6.62 (br s, 1H, NH), 4.74 (d, J = 5.9 Hz, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 135.5, 134.1, 133.4, 131.5, 129.9, 129.4, 128.8, 128.4, 127.0, 126.9, 41.8.

N-(4-chlorobenzyl)benzamide (5af)[6]

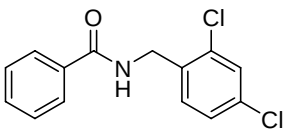


1) **1a** (103 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3f** (185 mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).

5af, creamy white solid, 195 mg, 79% yield.

mp 139-140 °C (lit.[6] mp 141 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 7.4 Hz, 2H, ArH), 7.51 (t, J = 7.3 Hz, 1H, ArH), 7.43 (t, J = 7.6 Hz, 2H, ArH), 7.32-7.27 (m, 4H, ArH), 6.46 (br s, 1H, NH), 4.61 (d, J = 5.7 Hz, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 136.8, 134.1, 133.2, 131.6, 129.0, 128.7, 128.5, 127.0, 43.2.

N-(2,4-dichlorobenzyl)benzamide (5ag)[5]



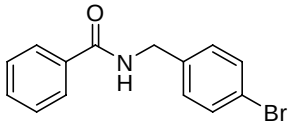
1) **1a** (103 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3g** (230mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).

5ag, grey solid, 233 mg, 83% yield.

mp 93-94 °C (lit.[5] mp 90-91 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 7.5 Hz, 2H, ArH), 7.51 (t, J = 7.4 Hz, 1H, ArH), 7.45-7.40 (m, 4H, ArH), 7.23 (dd, J = 8.3 Hz and 2.0 Hz, 1H, ArH), 6.62 (br s, 1H,

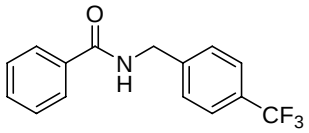
NH), 4.69 (d, J = 6.1 Hz, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 134.2, 134.1, 133.90, 133.87, 131.7, 130.8, 129.2, 128.5, 127.2, 126.9, 41.3.

N-(4-bromobenzyl)benzamide (5ah)[5]



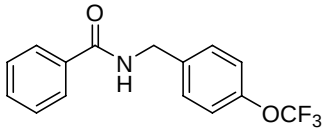
1) **1a** (103 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3h** (243 mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).
5ah, creamy white solid, 232 mg, 80% yield.
mp 134-135 °C (lit.[5] mp 134-135 °C); ^1H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 7.5 Hz, 2H, ArH), 7.53-7.42 (m, 5H, ArH), 7.24 (d, J = 7.9 Hz, 2H, ArH), 6.47 (br s, 1H, NH), 4.60 (d, J = 5.7 Hz, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 137.3, 134.0, 131.7, 131.6, 129.4, 128.5, 126.9, 121.2, 43.3.

N-(4-(trifluoromethyl)benzyl)benzamide (5ai)[7]



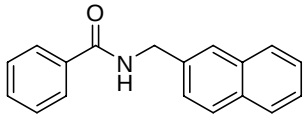
1) **1a** (103 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3i** (229 mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).
5ai, white solid, 229 mg, 82% yield.
mp 140-141 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 6.4 Hz, 2H, ArH), 7.61-7.45 (m, 7H, ArH), 6.57 (br s, 1H, NH), 4.71 (s, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6, 142.4, 134.0, 131.8, 129.8 (q, $J_{C\text{-}F}$ = 32.5 Hz), 128.6, 127.9, 127.0, 125.6 (d, $J_{C\text{-}F}$ = 3.5 Hz), 124.1 (q, $J_{C\text{-}F}$ = 270.5 Hz), 43.5.

N-(4-(trifluoromethoxy)benzyl)benzamide (5aj)[5]



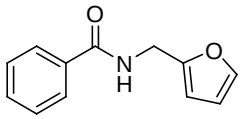
1) **1a** (103 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3j** (250 mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).
5aj, earthy yellow solid, 248 mg, 84% yield.
mp 134-135 °C (lit.[5] mp 129-130 °C); ^1H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 7.3 Hz, 2H, ArH), 7.52 (t, J = 7.4 Hz, 1H, ArH), 7.44 (t, J = 7.5 Hz, 2H, ArH), 7.38 (d, J = 8.4 Hz, 2H, ArH), 7.19 (d, J = 8.2 Hz, 2H, ArH), 6.49 (br s, 1H, NH), 4.65 (d, J = 5.7 Hz, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6, 148.5, 137.1, 134.1, 131.6, 129.1, 128.5, 127.0, 121.1, 120.4 (q, $J_{C\text{-}F}$ = 255.4 Hz), 43.1.

N-(naphthalen-2-ylmethyl)benzamide (5ak)[5]



1) **1a** (103 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3k** (237 mg, 1.5 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).
5ak, white solid, 214 mg, 82% yield.
mp 141-142 °C (lit.[5] mp 142-143 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84-7.79 (m, 6H, ArH), 7.52-7.42 (m, 6H, ArH), 6.51 (br s, 1H, NH), 4.81 (d, *J* = 5.5 Hz, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 135.6, 134.3, 133.3, 132.7, 131.5, 128.5, 127.69, 127.65, 127.0, 126.5, 126.3, 125.9, 44.2.

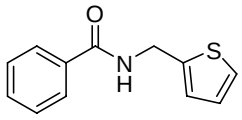
N-(furan-2-ylmethyl)benzamide (5al)[8]



1) **1a** (103 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3l** (128 mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).
5al, light yellow solid, 161 mg, 80% yield.

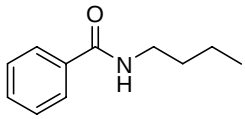
mp 98-99 °C (lit.[8] mp 99-100 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.5 Hz, 2H, ArH), 7.50 (t, *J* = 7.5 Hz, 1H, ArH), 7.43 (t, *J* = 7.5 Hz, 2H, ArH), 7.38 (s, 1H, ArH), 6.48 (br s, 1H, NH), 6.33 (d, *J* = 18.5 Hz, 2H, ArH), 4.64 (d, *J* = 6.0 Hz, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 151.1, 142.2, 134.1, 131.5, 128.5, 127.0, 110.5, 107.6, 36.9.

N-(thiophen-2-ylmethyl)benzamide (5am)[3]



1) **1a** (103 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3m** (148 mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).
5am, brown solid, 185 mg, 85% yield.
mp 117-118 °C (lit.[3] mp 120 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 2H, ArH), 7.50 (t, *J* = 7.3 Hz, 1H, ArH), 7.43 (t, *J* = 7.5 Hz, 2H, ArH), 7.26-7.25 (m, 1H, ArH), 7.05 (d, *J* = 2.95 Hz, 1H, ArH), 6.98 (t, *J* = 4.2 Hz, 1H, ArH), 6.46 (br s, 1H, NH), 4.82 (d, *J* = 5.6 Hz, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 140.8, 134.1, 131.5, 128.5, 127.0, 126.8, 126.1, 125.2, 38.7.

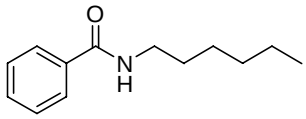
N-butylbenzamide (5an)[9]



1) **1a** (103 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3n** (148 mg, 2 mmol), KO*t*Bu (22 mg, 0.2 equiv.).
5an, white solid, 139 mg, 78% yield.
mp 37-38 °C (lit.[9] mp 39-41 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.5 Hz, 2H, ArH), 7.49 (t, *J* = 7.25 Hz, 1H, ArH), 7.44-7.41 (m, 2H, ArH), 6.10 (br s, 1H, NH), 3.46 (q, *J* = 6.7 Hz, 2H, NCH_2), 1.64-1.57 (m, 2H, CH_2), 1.46-1.39 (m, 2H, CH_2), 0.96 (t, *J* = 7.3 Hz, 3H, CH_3); ^{13}C NMR (125 MHz,

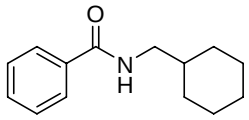
$CDCl_3$) δ 167.5, 134.8, 131.1, 128.4, 126.8, 39.7, 31.6, 20.1, 13.7.

N-hexylbenzamide (5ao)[10]



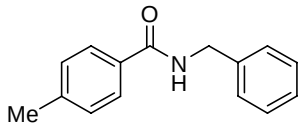
1) **1a** (103 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3o** (204 mg, 2 mmol), KO*t*Bu (22 mg, 0.2 equiv.).
5ao, white solid, 168 mg, 82% yield.
mp 41-42 °C (lit.[10] mp 42-44 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.0 Hz, 2H, ArH), 7.50-7.47 (m, 1H, ArH), 7.42 (t, *J* = 7.5 Hz, 2H, ArH), 6.15 (br s, 1H, NH), 3.45 (q, *J* = 6.8 Hz, 2H, NCH_2), 1.67-1,58 (m, 2H, CH_2), 1.41-1.30 (m, 6H, 3xCH_2), 0.90 (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 134.8, 131.2, 128.4, 126.8, 40.1, 31.4, 29.6, 26.6, 22.5, 14.0.

N-(cyclohexylmethyl)benzamide (5ap)[5]



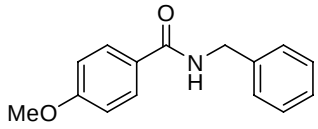
1) **1a** (103 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3p** (228 mg, 2 mmol), KO*t*Bu (22 mg, 0.2 equiv.).
5ap, light grey solid, 185 mg, 85% yield.
mp 103-104 °C (lit.[5] mp 102-103 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.3 Hz, 2H, ArH), 7.49 (t, *J* = 7.3 Hz, 1H, ArH), 7.43 (t, *J* = 7.5 Hz, 2H, ArH), 6.18 (br s, 1H, NH), 3.45 (t, *J* = 6.4 Hz, 2H, NCH_2), 1.80-1.73 (m, 4H, 2xCH_2), 1.69-1.65 (m, 2H, CH_2), 1.63-1.55 (m, 1H, CH), 1.29-1.14 (m, 2H, CH_2), 1.00 (q, *J* = 11.8 Hz, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.6, 134.9, 131.2, 128.4, 126.8, 46.2, 38.0, 30.9, 26.3, 25.8.

N-benzyl-4-methylbenzamide (5ba)[1]



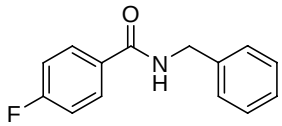
1) **1b** (117 mg, 1 mmol), **2b** (113 mg, 1.3 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3a** (162 mg, 1.5 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).
5ba, light yellow solid, 183 mg, 81% yield.
mp 132-133 °C (lit.[1] mp 133 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H, ArH), 7.36-7.28 (m, 5H, ArH), 7.23 (d, *J* = 8.0 Hz, 2H, ArH), 6.37 (br s, 1H, NH), 4.64 (d, *J* = 5.7 Hz, 2H, CH_2), 2.39 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 141.9, 138.3, 131.5, 129.2, 128.7, 127.9, 127.5, 126.9, 44.0, 21.4.

N-benzyl-4-methoxybenzamide (5ca)[11]



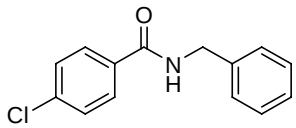
1) **1c** (133 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3a** (140 mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).
5ca, light yellow solid, 183 mg, 76% yield.
mp 121-122 °C (lit.[11] mp 129-130 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.9 Hz, 2H, ArH), 7.35 (d, *J* = 4.35 Hz, 4H, ArH), 7.32-7.28 (m, 1H, ArH), 6.92 (d, *J* = 8.9 Hz, 2H, ArH), 6.34 (br s, 1H, NH), 4.64 (d, *J* = 5.7 Hz, 2H, CH_2), 3.84 (s, 3H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.8, 162.1, 138.4, 128.7, 128.7, 127.8, 127.5, 126.6, 113.7, 55.3, 44.0.

N-benzyl-4-fluorobenzamide (5da)[12]



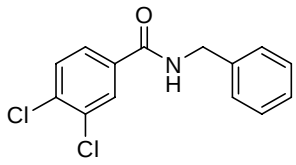
1) **1d** (121 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3a** (140 mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).
5da, grey solid, 190 mg, 83% yield.
mp 141-142 °C (lit.[12] mp 143-144 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (t, *J* = 7.1 Hz, 2H, ArH), 7.37-7.29 (m, 5H, ArH), 7.10 (t, *J* = 8.6 Hz, 2H, ArH), 6.34 (br s, 1H, NH), 4.64 (d, *J* = 5.7 Hz, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 164.7 (d, $J_{C\text{-}F}$ = 250.2 Hz), 138.1, 130.5, 129.3 (d, $J_{C\text{-}F}$ = 8.8 Hz), 128.7, 127.8, 127.6, 115.5 (d, $J_{C\text{-}F}$ = 21.7 Hz), 44.1.

N-benzyl-4-chlorobenzamide (5ea)[13]



1) **1e** (137 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3a** (140 mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).
5ea, maize yellow solid, 199 mg, 81% yield.
mp 162-163 °C (lit.[13] mp 163-166 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.5 Hz, 2H, ArH), 7.40 (d, *J* = 8.5 Hz, 2H, ArH), 7.36-7.34 (m, 4H, ArH), 7.32-7.28 (m, 1H, ArH), 6.38 (br s, 1H, NH), 4.63 (d, *J* = 5.7 Hz, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.4, 137.9, 137.7, 132.7, 128.8, 128.4, 127.8, 127.6, 44.1.

N-benzyl-3,4-dichlorobenzamide (5fa)[5]



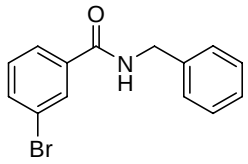
1) **1f** (172 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);

2) **3a** (140 mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).

5fa, light orange solid, 253 mg, 90% yield.

mp 105-106 °C (lit.[5] mp 111-112 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 1.3 Hz, 1H, ArH), 7.60 (d, *J* = 8.5 Hz, 1H, ArH), 7.50 (d, *J* = 8.4 Hz, 1H, ArH), 7.38-7.26 (m, 5H, ArH), 6.36 (br s, 1H, NH), 4.63 (d, *J* = 5.4 Hz, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 137.6, 135.9, 134.1, 133.0, 130.6, 129.2, 128.8, 127.8, 127.7, 126.1, 44.2.

N-benzyl-3-bromobenzamide (5ga)[14]



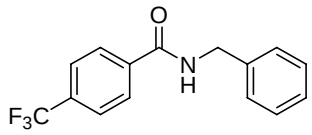
1) **1g** (182 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);

2) **3a** (140 mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).

5ga, yellow solid, 235 mg, 81% yield.

mp 87-88 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H, ArH), 7.71 (d, *J* = 7.0 Hz, 1H, ArH), 7.63 (d, *J* = 8.0 Hz, 1H, ArH), 7.35-7.26 (m, 6H, ArH), 6.43 (br s, 1H, NH), 4.64 (d, *J* = 5.0 Hz, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 137.8, 136.2, 134.3, 130.2, 130.0, 128.7, 127.7, 127.5, 125.6, 122.6, 44.1.

N-benzyl-4-(trifluoromethyl)benzamide (5ha)[15]



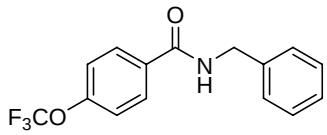
1) **1h** (171 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);

2) **3a** (140 mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).

5ha, brick-red solid, 224 mg, 80% yield.

mp 169-170 °C (lit.[15] mp 149-151 °C); ^{1}H NMR (500 MHz, DMSO-d6) δ 9.28 (t, *J* = 5.6 Hz, 1H, NH), 8.09 (d, *J* = 8.2 Hz, 2H, ArH), 7.87 (d, *J* = 8.2 Hz, 2H, ArH), 7.34-7.23 (m, 5H, ArH), 4.51 (d, *J* = 5.9 Hz, 2H, CH_2); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.1, 139.3, 138.1, 131.2 (q, J_{C-F} = 31.7 Hz), 128.3, 128.2, 127.3, 126.8, 125.3, 123.9 (q, J_{C-F} = 270.9 Hz), 42.8.

N-benzyl-4-(trifluoromethoxy)benzamide (5ia)[5]



1) **1i** (187 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);

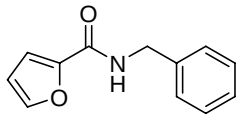
2) **3a** (140 mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).

5ia, field grey solid, 242 mg, 82% yield.

mp 136-137 °C (lit.[5] mp 139-140 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.7 Hz, 2H, ArH), 7.38-7.25 (m, 7H, ArH), 6.40 (br s, 1H, NH), 4.64 (d, *J* = 5.7 Hz, 2H, CH_2); ^{13}C NMR (125 MHz,

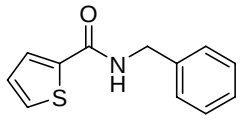
$CDCl_3$) δ 166.1, 151.5, 137.9, 132.8, 128.9, 128.8, 127.8, 127.7, 120.6, 120.3 (q, J_{C-F} = 256.7 Hz), 44.2.

N-benzylfuran-2-carboxamide (5ja)[16]



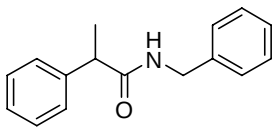
1) **1j** (93 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3a** (140 mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).
5ja, marroon solid, 169 mg, 84% yield.
mp 105-106 °C (lit.[16] 112-113 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (s, 1H, ArH), 7.35-7.26 (m, 5H, ArH), 7.15 (d, *J* = 3.5 Hz, 1H, ArH), 6.66 (br s, 1H, NH), 6.50 (dd, *J* = 3.5 Hz and 1.8 Hz, 1H, ArH), 4.62 (d, *J* = 5.9 Hz, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2, 147.8, 143.8, 138.0, 128.7, 127.8, 127.5, 114.3, 112.1, 43.1.

N-benzylthiophene-2-carboxamide (5ka)[1]



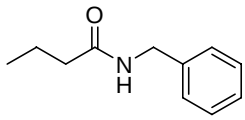
1) **1k** (109 mg, 1 mmol), **2b** (96 mg, 1.1 mmol), $[Cp^*IrCl_2]_2$ (8 mg, 0.01 mol, 1 mol%), toluene (1 ml);
2) **3a** (140 mg, 1.3 mmol), Cs_2CO_3 (65 mg, 0.2 equiv.).
5ka, grey solid, 187 mg, 86% yield.
mp 114-115 °C (lit.[1] mp 119.5-120.5 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 3.7 Hz, 1H, ArH), 7.47 (d, *J* = 5.1 Hz, 1H, ArH), 7.36-7.28 (m, 5H, ArH), 7.07 (t, *J* = 4.4 Hz, 1H, ArH), 6.26 (br s, 1H, NH), 4.63 (d, *J* = 5.8 Hz, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.8, 138.8, 138.0, 130.0, 128.7, 128.1, 127.8, 127.6, 127.5, 43.9.

N-benzyl-2-phenylpropanamide (5la)[2]



1) **1l** (131 mg, 1 mmol), **2b** (113 mg, 1.3 mmol), $[Cp^*IrCl_2]_2$ (16 mg, 0.02 mol, 2 mol%), toluene (1 ml);
2) **3a** (216 mg, 2 mmol), KO*t*Bu (44 mg, 0.4 equiv.).
5la, white solid, 182 mg, 76% yield.
mp 76-77 °C (lit.[2] mp 76 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.24 (m, 8H, ArH), 7.15 (d, *J* = 7.0 Hz, 2H, ArH), 5.64 (br s, 1H, NH), 4.44-4.35 (m, 2H, CH_2), 3.60 (q, *J* = 7.2 Hz, 1H, CH), 1.57 (d, *J* = 7.5 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.0, 141.2, 138.3, 128.8, 128.5, 127.6, 127.4, 127.2, 127.2, 47.0, 43.4.

N-benzylbutyramide (5ma)[17]



1) **1m** (69 mg, 1 mmol), **2a** (77 mg, 1.3 mmol), $[Cp^*IrCl_2]_2$ (16 mg, 0.02 mol, 2 mol%), toluene (1 ml); 2) **3a** (216 mg, 2 mmol), KO*t*Bu (44 mg, 0.4 equiv.).

5ma, white solid, 139 mg, 78% yield.

mp 47-48 ^oC (lit.[17] mp 41-44 ^oC); ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, J = 7.5 Hz, 2H, ArH), 7.28-7.26 (m, 3H, ArH), 5.7 (br s, 1H, NH), 4.44 (d, J = 5.5 Hz, 2H, NCH_2), 2.19 (t, J = 7.5 Hz, 2H, CH_2), 1.73-1.65 (m, 2H, CH_2), 0.96 (t, J = 7.4 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9, 138.3, 128.6, 127.7, 127.4, 43.4, 38.6, 19.1, 13.7.

References

1 X. Cui, Y. Zhang, F. Shi and Y. Deng, *Chem.-Eur. J.* 2011, **17**, 1021-1028.

2 T. Maki, K. Ishihara and H. Yamamoto, *Org. Lett.* 2006, **8**, 1431-1434.

3 G. A. Molander and M. A. Hiebel, *Org. Lett.* 2010, **12**, 4876-4879.

4 A. Khalafi-Nezhad, H. Foroughi, M. M. Doroodmand and F. Panahi, *J. Mater. Chem.* 2011, **21**, 12842-12851.

5 F. Li, P. Qu, J. Ma, X. Zou and C. Sun, *ChemCatChem* 2013, **5**, 2178-2182.

6 R. Pricet and R. R. Lindat, *J. Org. Chem.* 1962, **27**, 1066-1067.

7 M. D. Hill, M. Movassaghi, *Synthesis* 2008, 823-827.

8 J. M. Yeung and E. E. Knaus, *Eur. J. Med. Chem.* 1986, **21**, 181-185.

9 T. Gajda, A. Zweirzak, *Synthesis* 1981, 1005-1008.

10 T. Ohshima, T. Iwasaki, Y. Maegawa, A. Yoshiyama and K. Mashima, *J. Am. Chem. Soc.* 2008, **130**, 2944-2945.

11 B. Roberts, D. Liptrot , L. Alcaraz, T. Luker and M. J. Stocks, *Org. Lett.* 2010, **12**, 4280-4283.

12 C. Mamat, A. Flemming, M. Köckerling, J. Steinbach and F. Wuest, *Synthesis* 2009, **19**, 3311-3321.

13 E. Petricci, C. Mugnaini, M. Radi, F. Corelli and M. Botta, *J. Org. Chem.* 2004, **69**, 7880-7887.

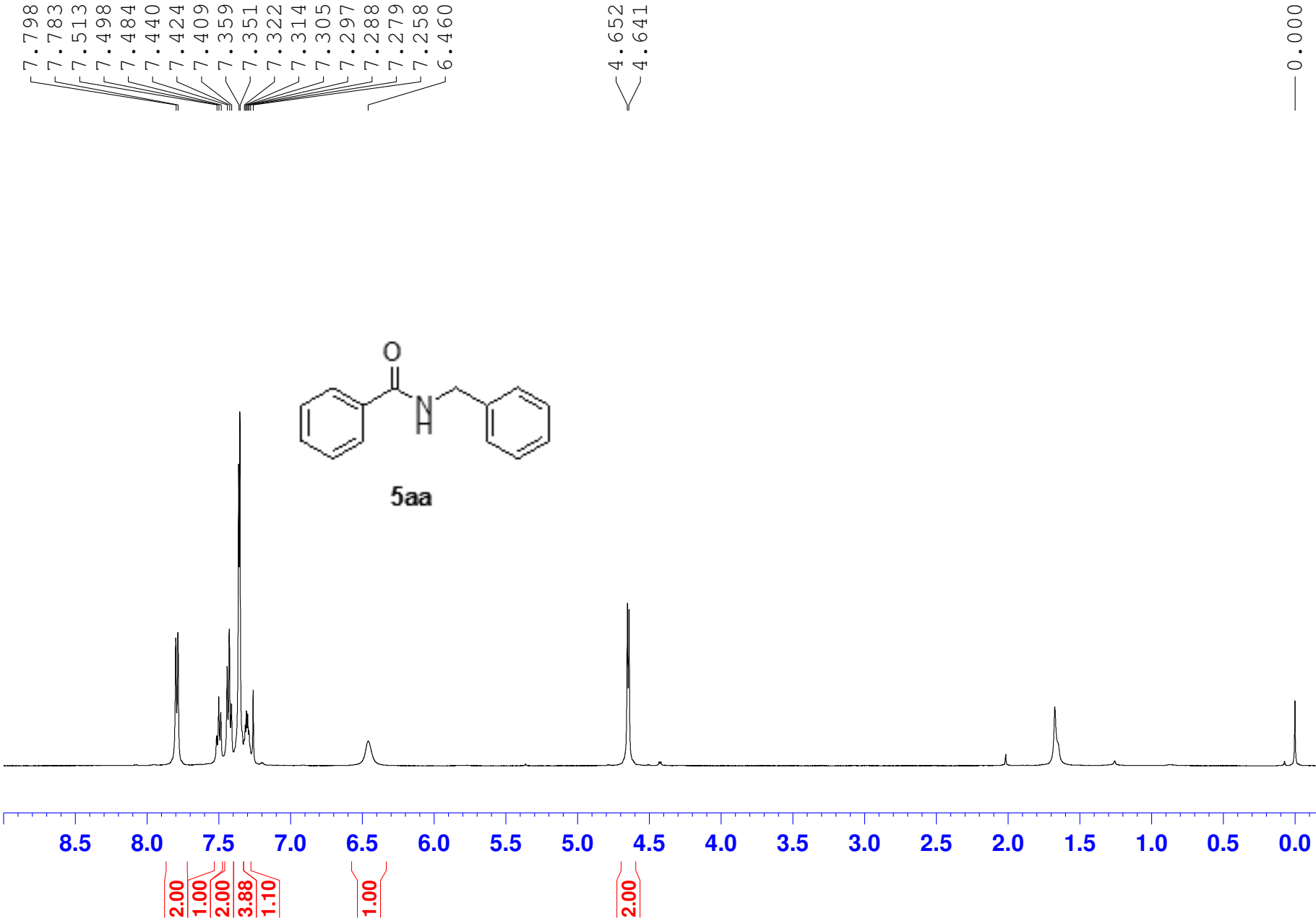
14 T. Suzuki, M. N. A. Khan, H. Sawada, E. Imai, Y. Itoh, K. Yamatsuta, N. Tokuda, J. Takeuchi, T. Seko, H. Nakagawa and N. Miyata, *J. Med. Chem.* 2012, **55**, 5760-5773.

15 A. R. Prosser, J. E. Banning, M. Rubina and M. Rubin, *Org. Lett.* 2010, **12**, 3968-3971.

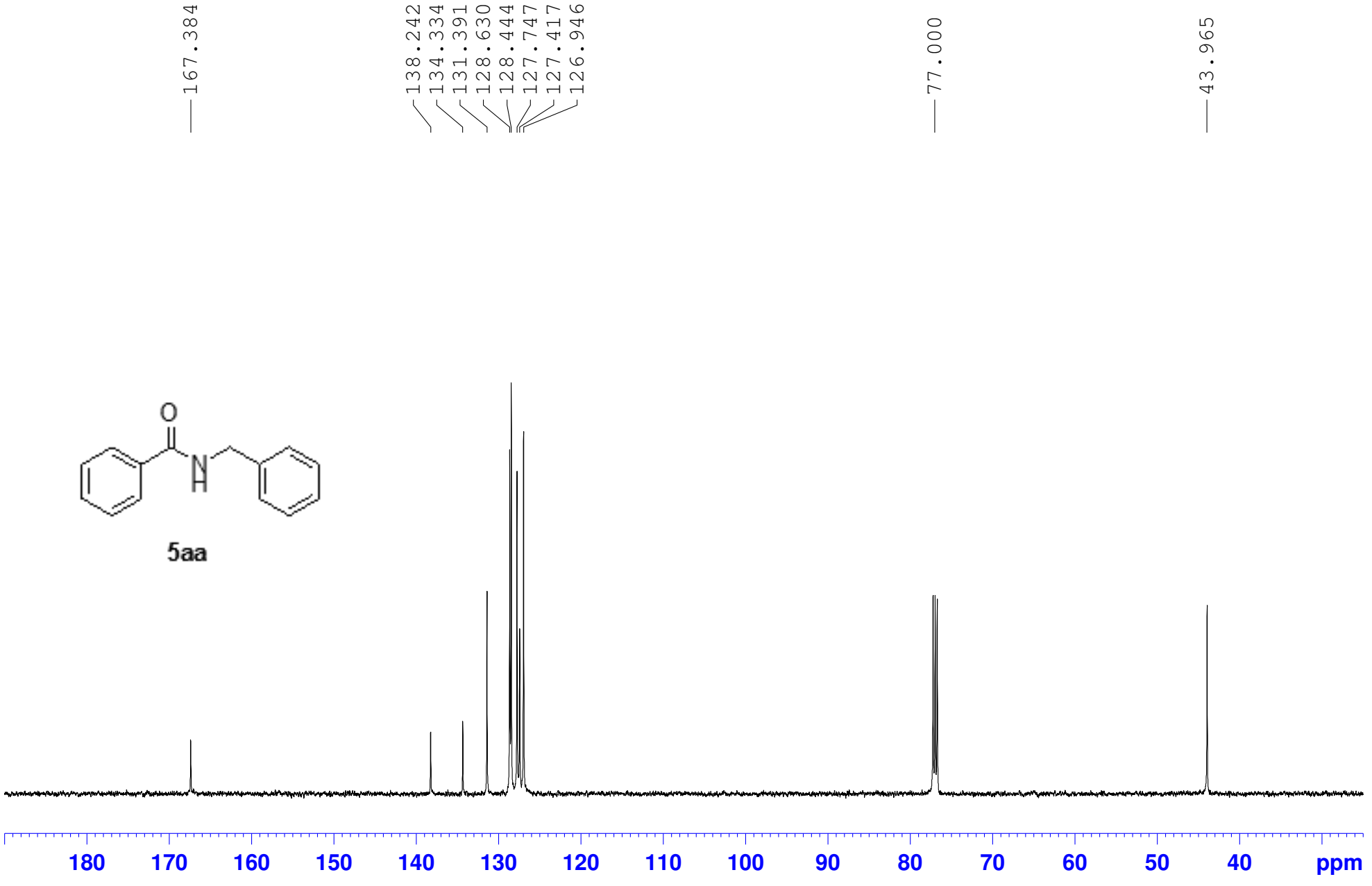
16 C. Chen, Y. Zhang and S. H. Hong, *J. Org. Chem.* 2011, **76**, 10005-10010.

17 S. Kushner, R. I. Cassell, J. Morton II and J. H. Williams, *J. Org. Chem.* 1951, **16**, 1283-1288.

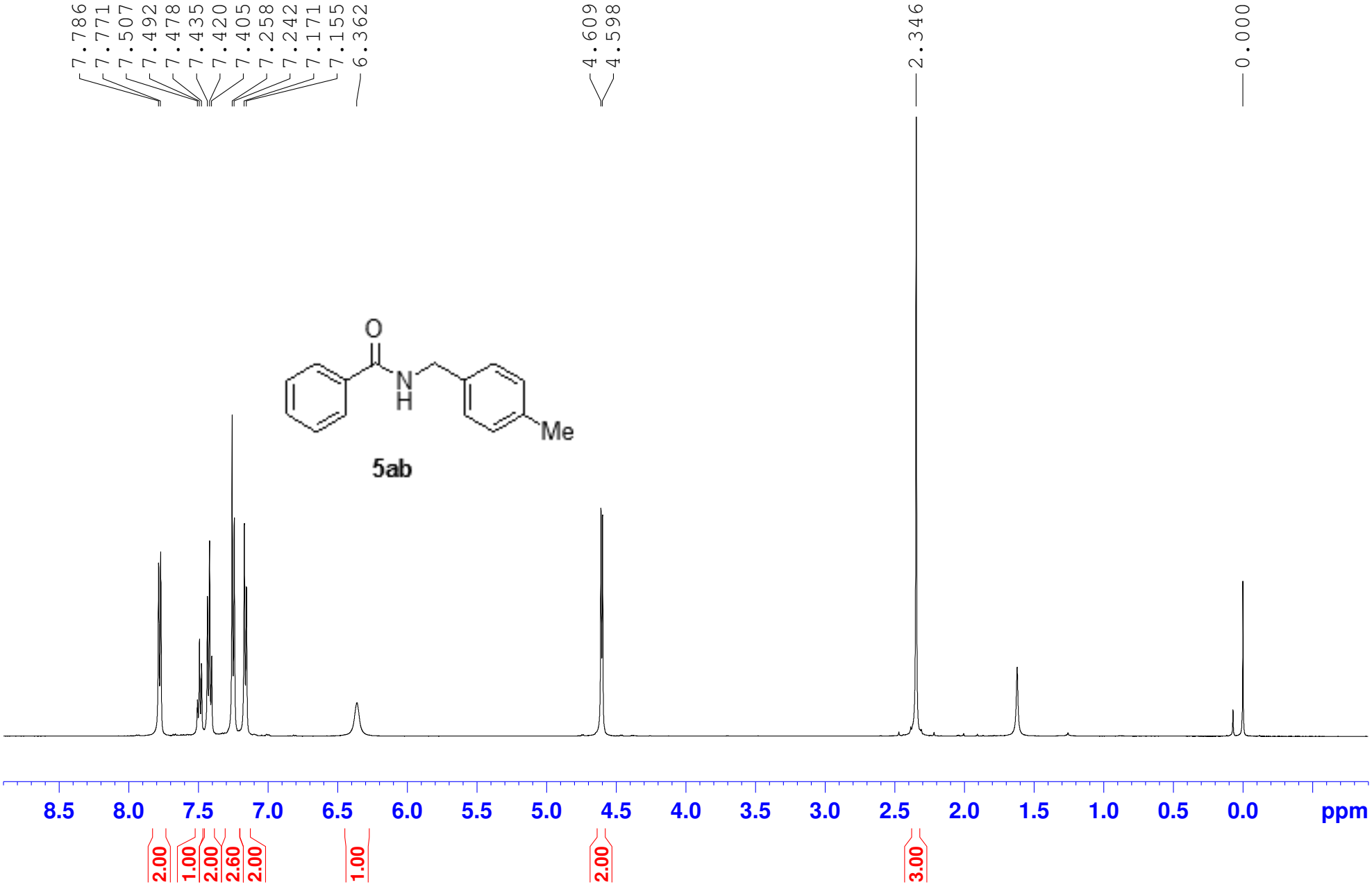
N-benzylbenzamide
Proton CDCl3



N-benzylbenzamide
C13CPD CDCl3



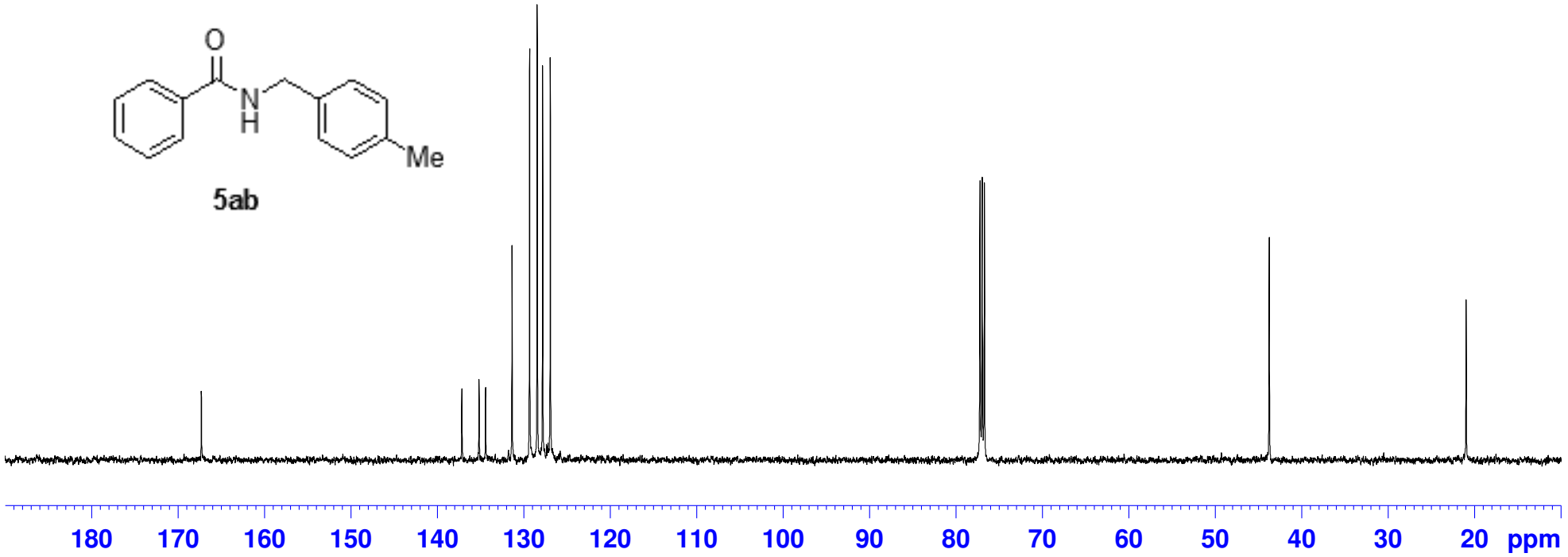
N-(4-methylbenzyl)benzamide
Proton CDCl3



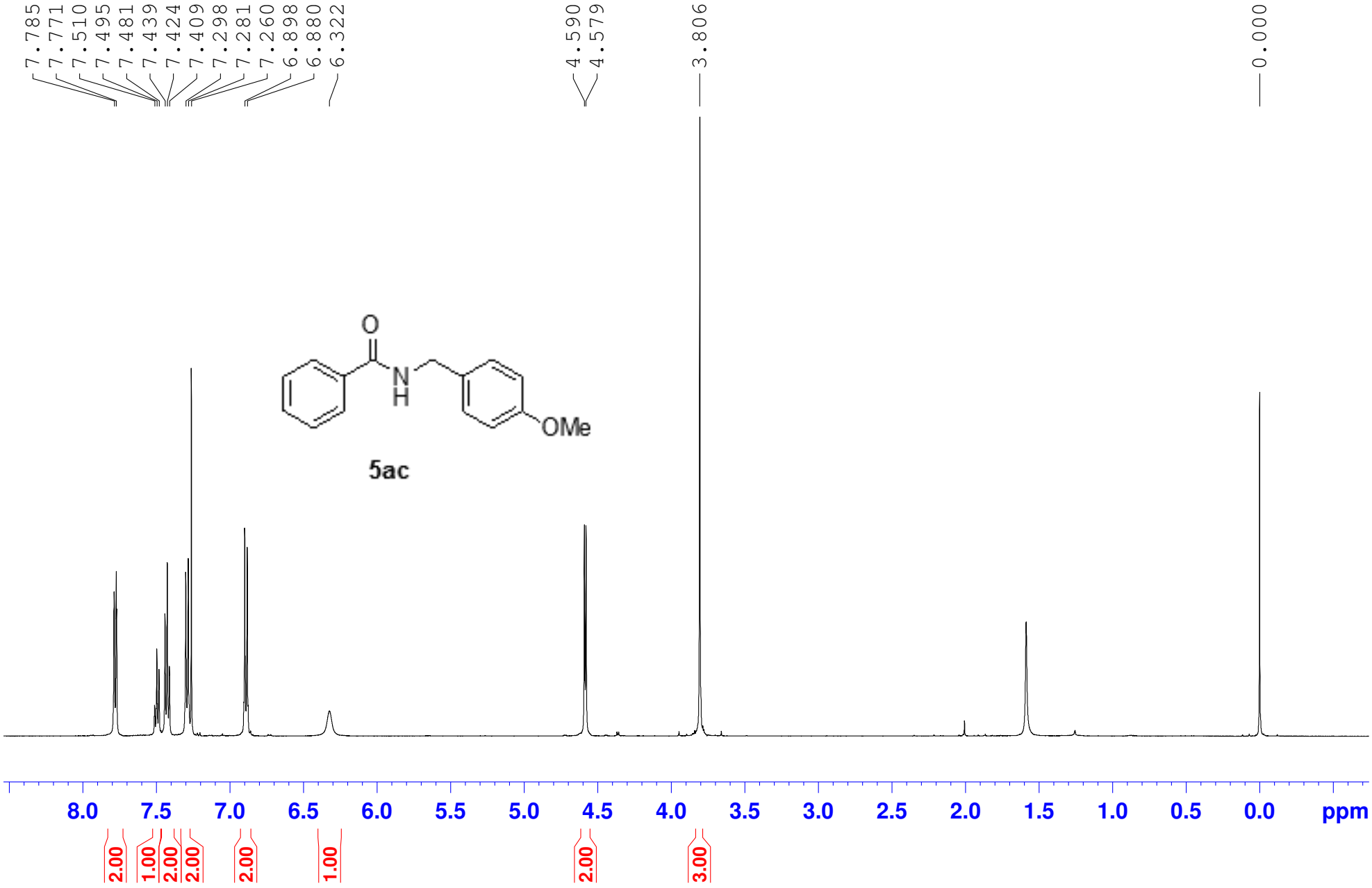
N-(4-methylbenzyl)benzamide
C13CPD CDCl3

167.289
137.149
135.166
134.412
131.352
129.316
128.432
127.806
126.916
77.000
43.782
21.003

5ab



N-(4-methoxybenzyl)benzamide
Proton CDCl3



N-(4-methoxybenzyl)benzamide
C13CPD CDCl3

167.261
159.035
134.429
131.366
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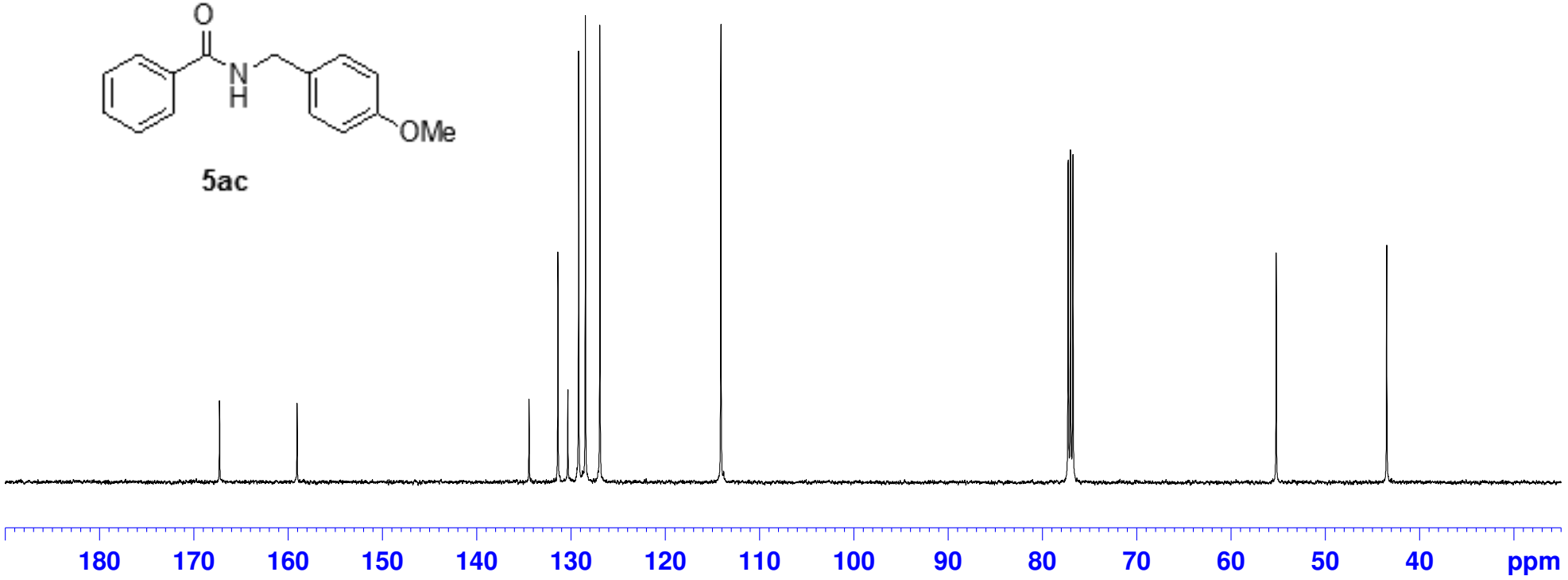
129.171
128.453
126.917
114.087
77.000
55.233
43.511

5ac

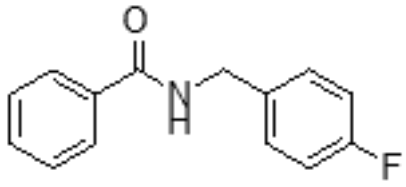


N-(4-fluorobenzyl)benzamide
Proton CDCl3

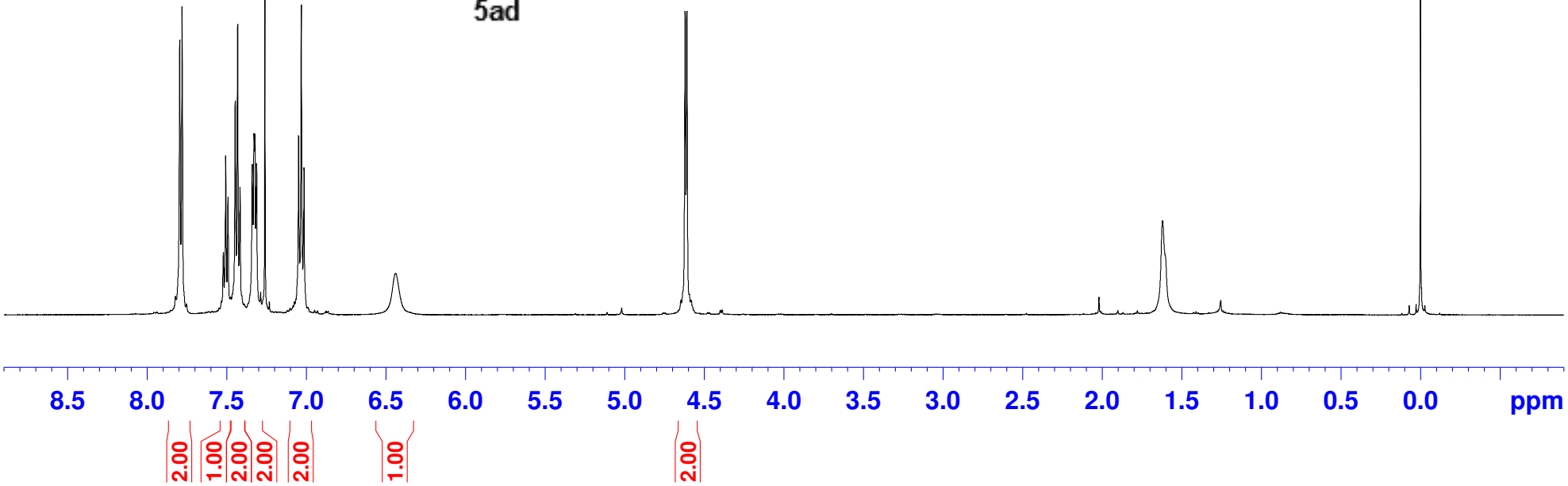
7.793
7.778
7.522
7.507
7.492
7.447
7.431
7.417
7.340
7.329
7.324
7.313
7.260
7.049
7.032
7.014
6.441

4.620
4.609

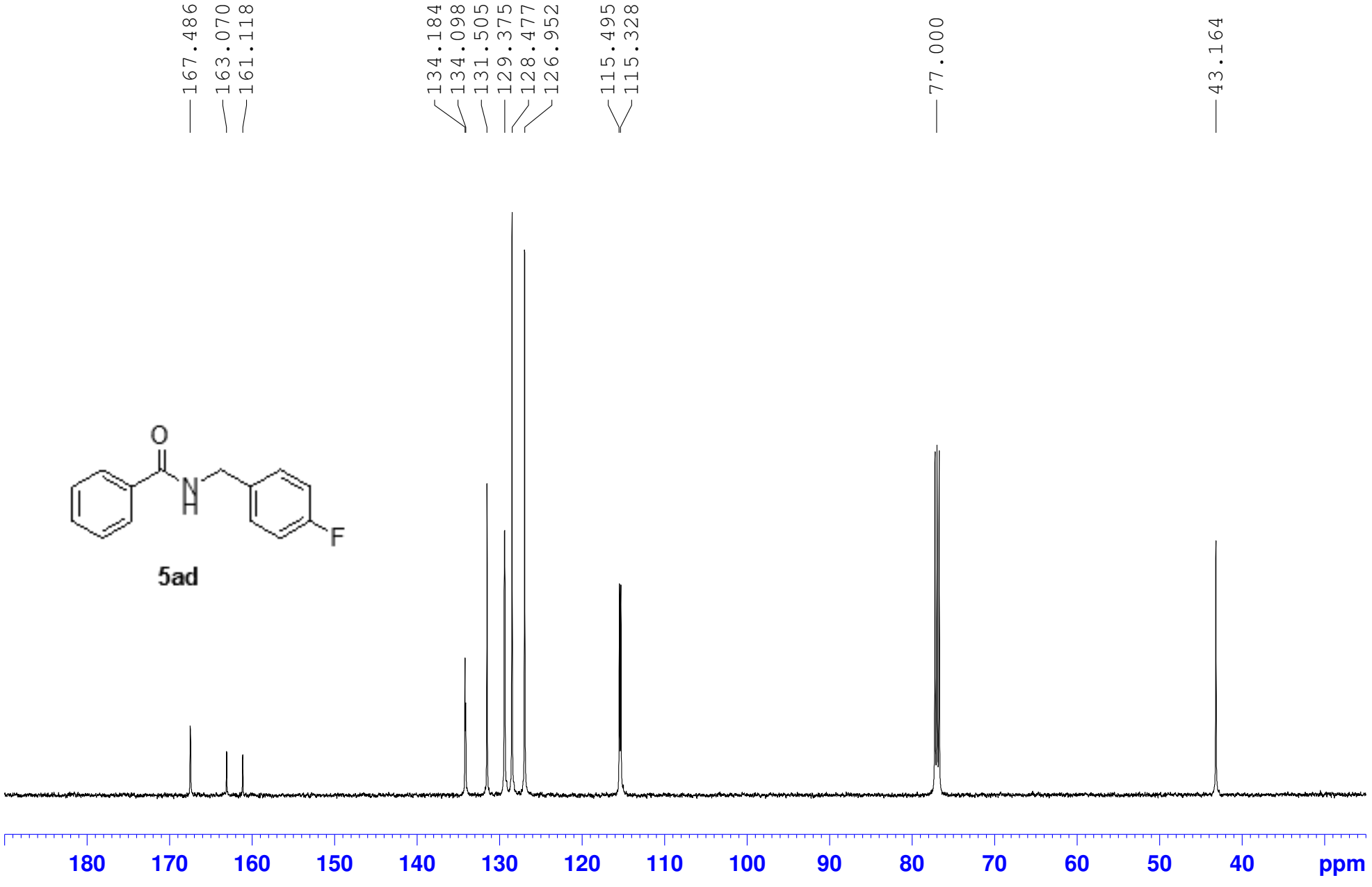
0.000



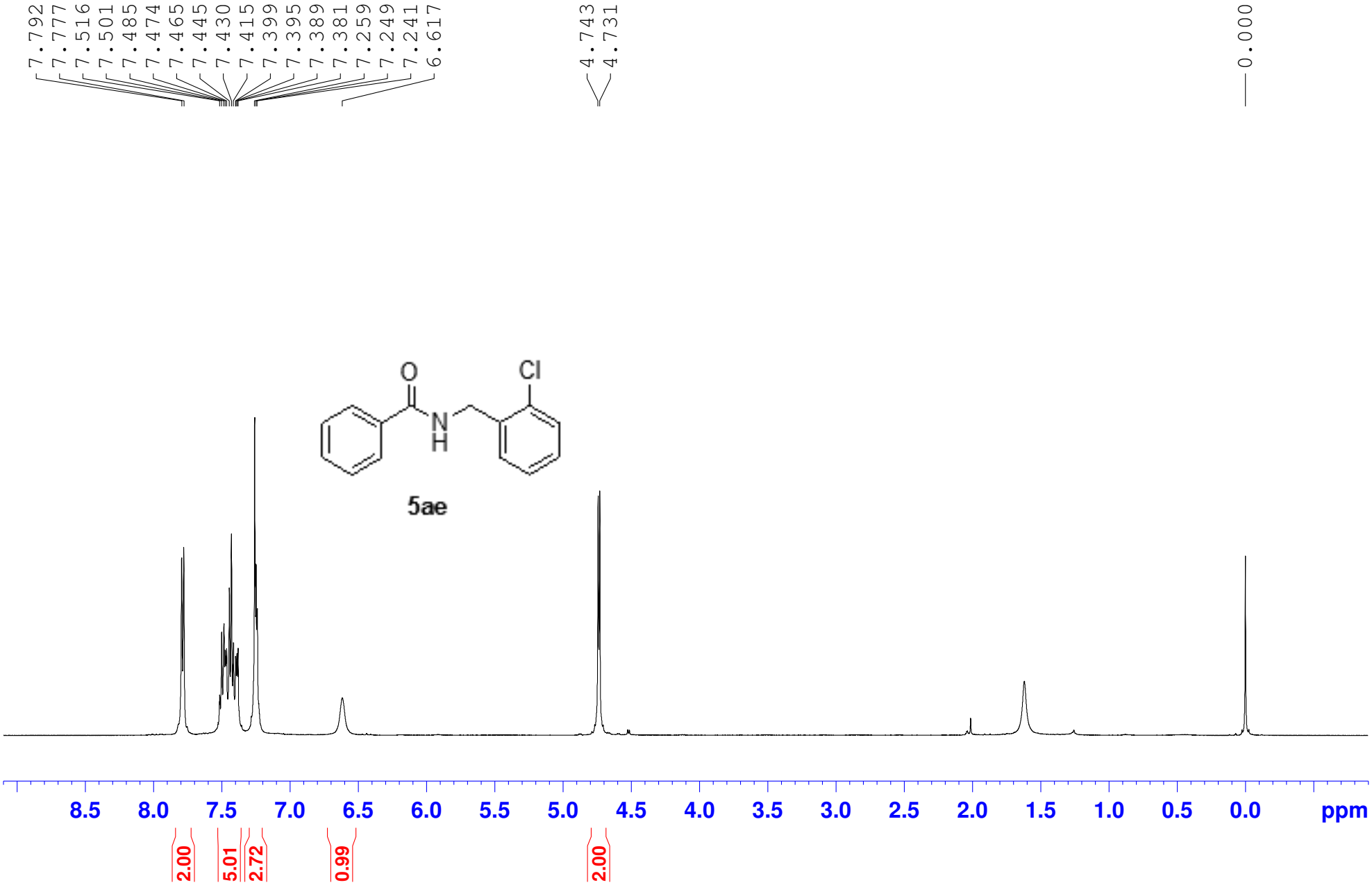
5ad



N-(4-fluorobenzyl)benzamide
C13CPD CDCl3



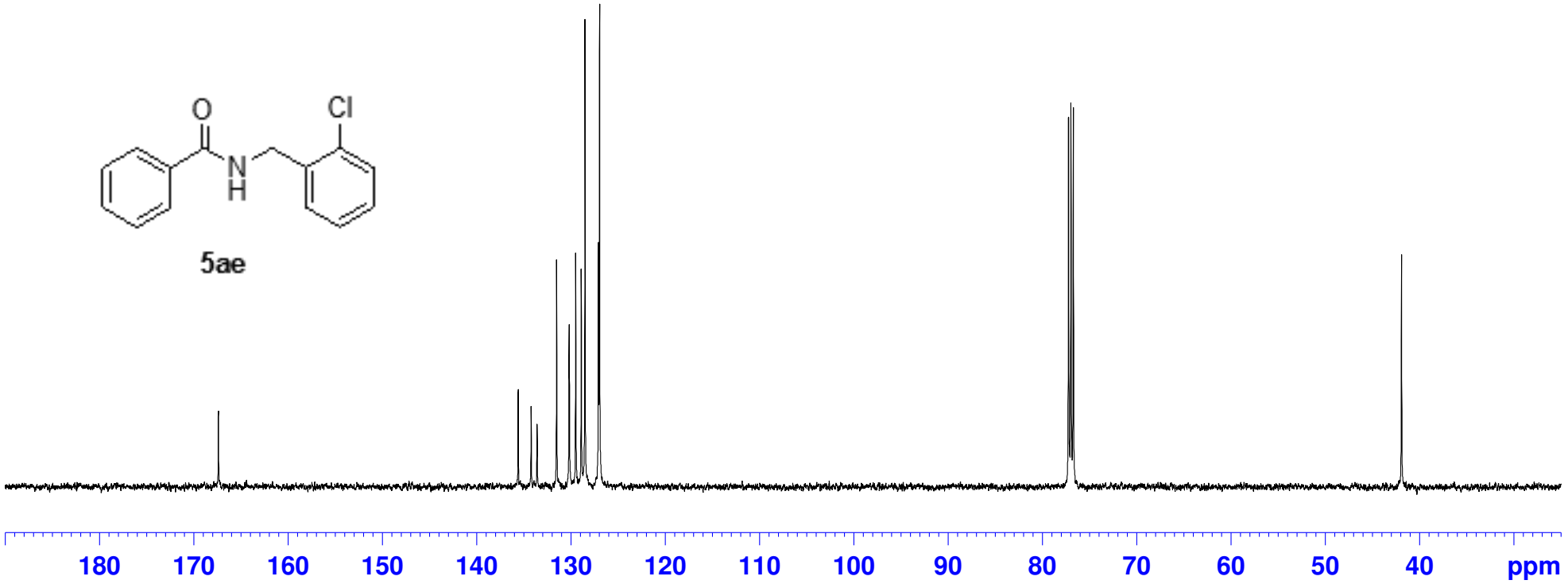
N-(2-chlorobenzyl)benzamide
Proton CDCl3



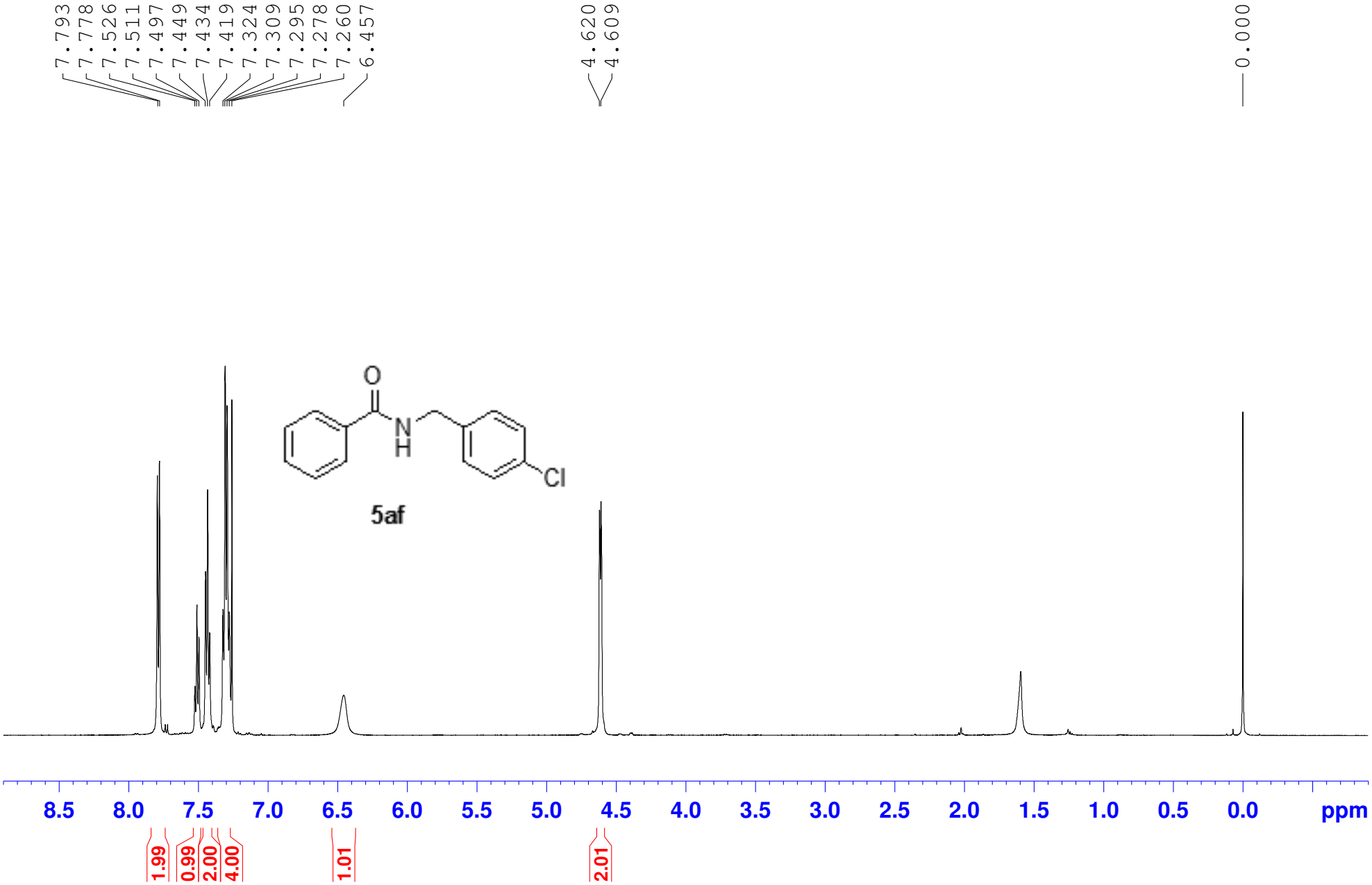
N-(2-chlorobenzyl)benzamide
C13CPD CDCl3

167.376
135.585
134.211
133.583
131.506
130.181
129.481
128.897
128.505
127.068
126.952
77.000
41.939

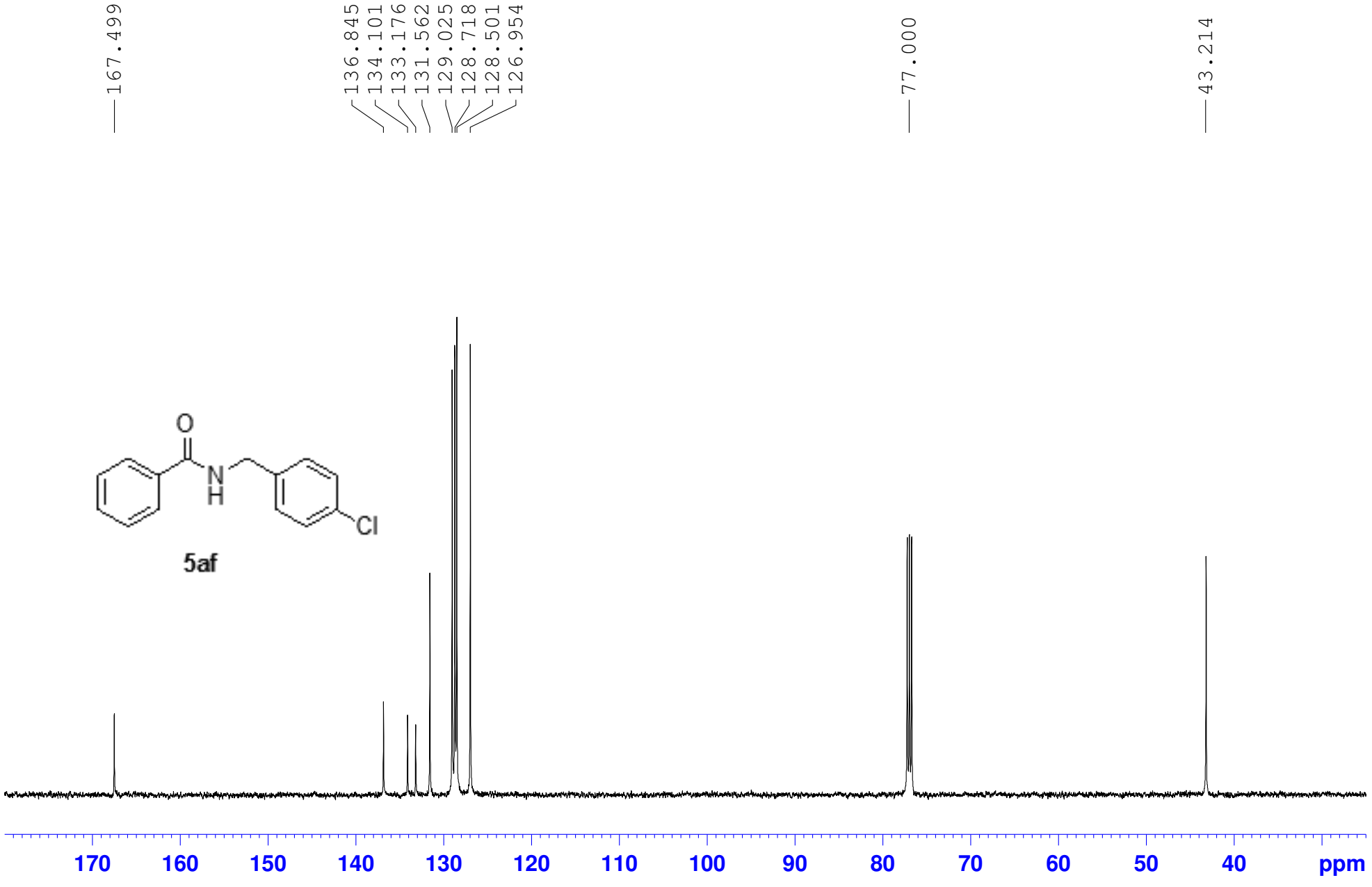
5ae



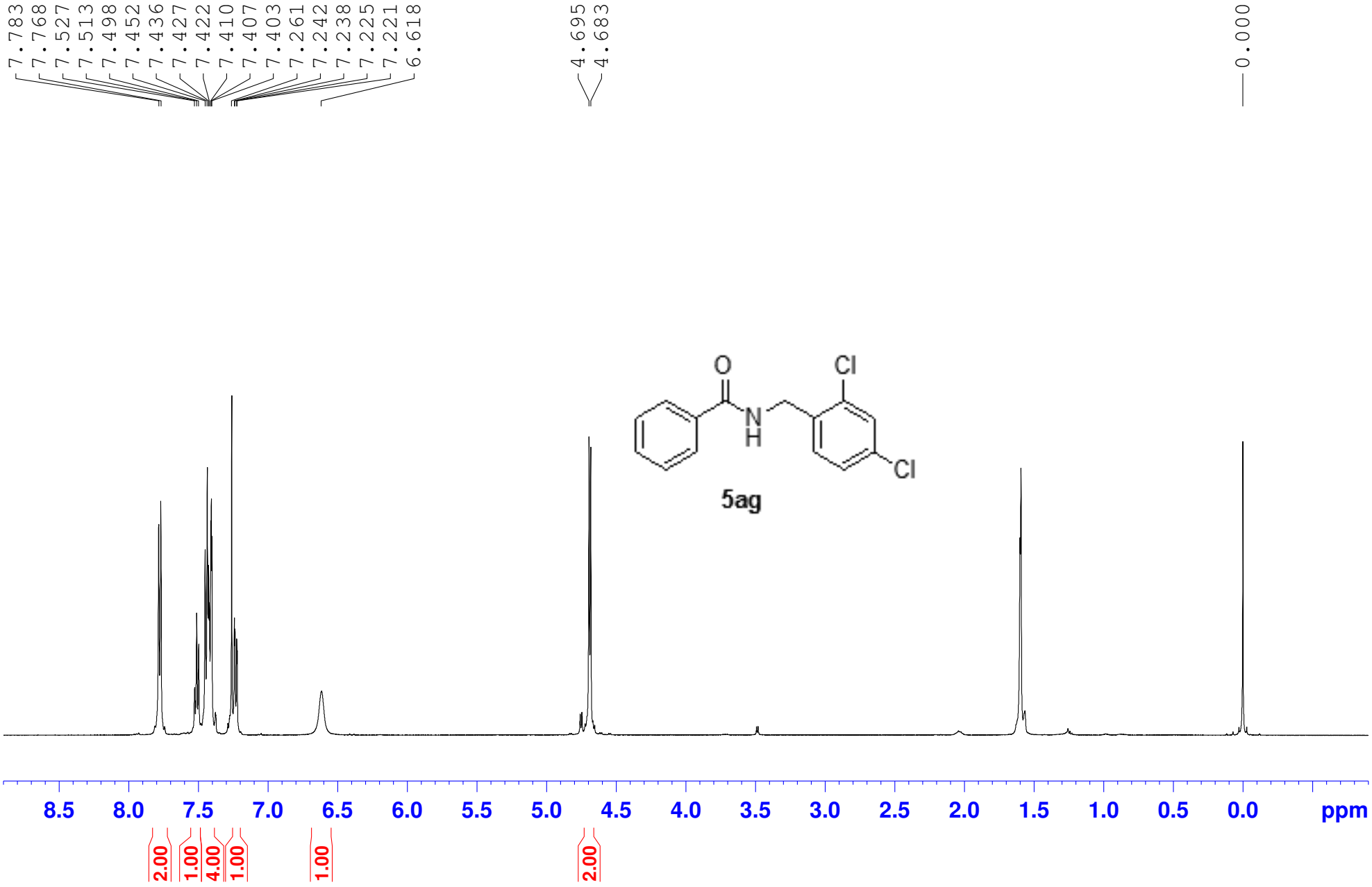
N-(4-chlorobenzyl)benzamide
Proton CDCl3



N-(4-chlorobenzyl)benzamide
C13CPD CDCl3



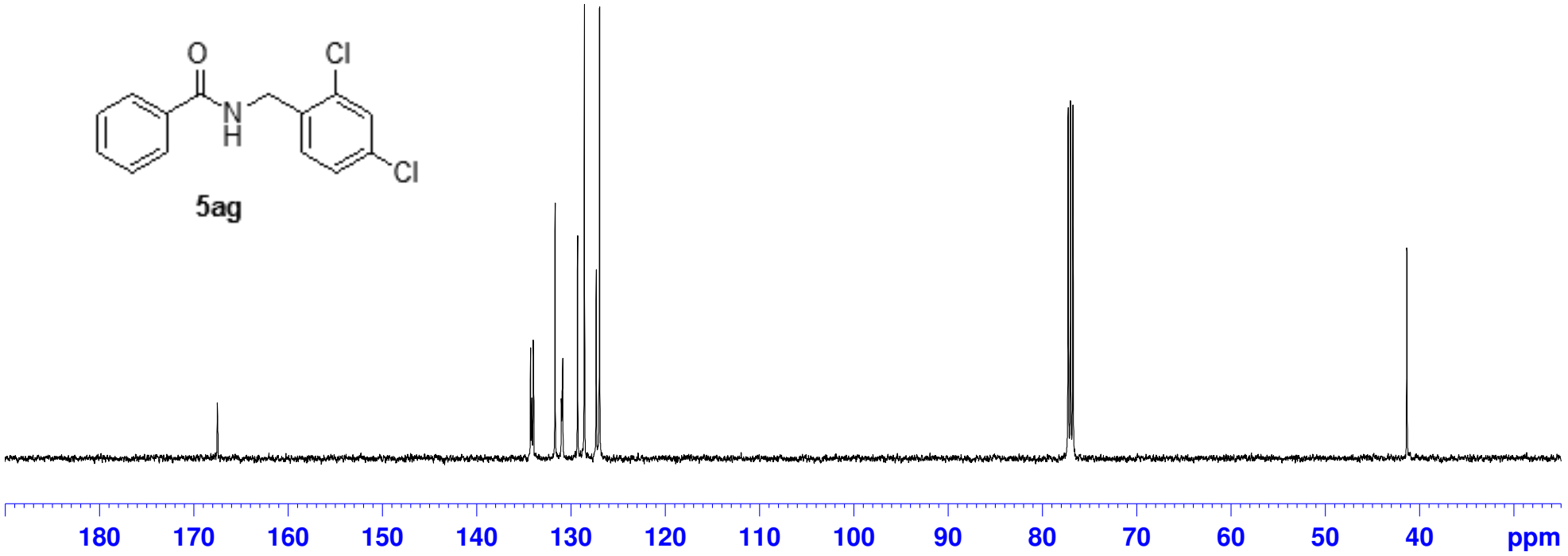
N-[(2,4-dichlorophenyl)methyl]- Benzamide
Proton CDCl3



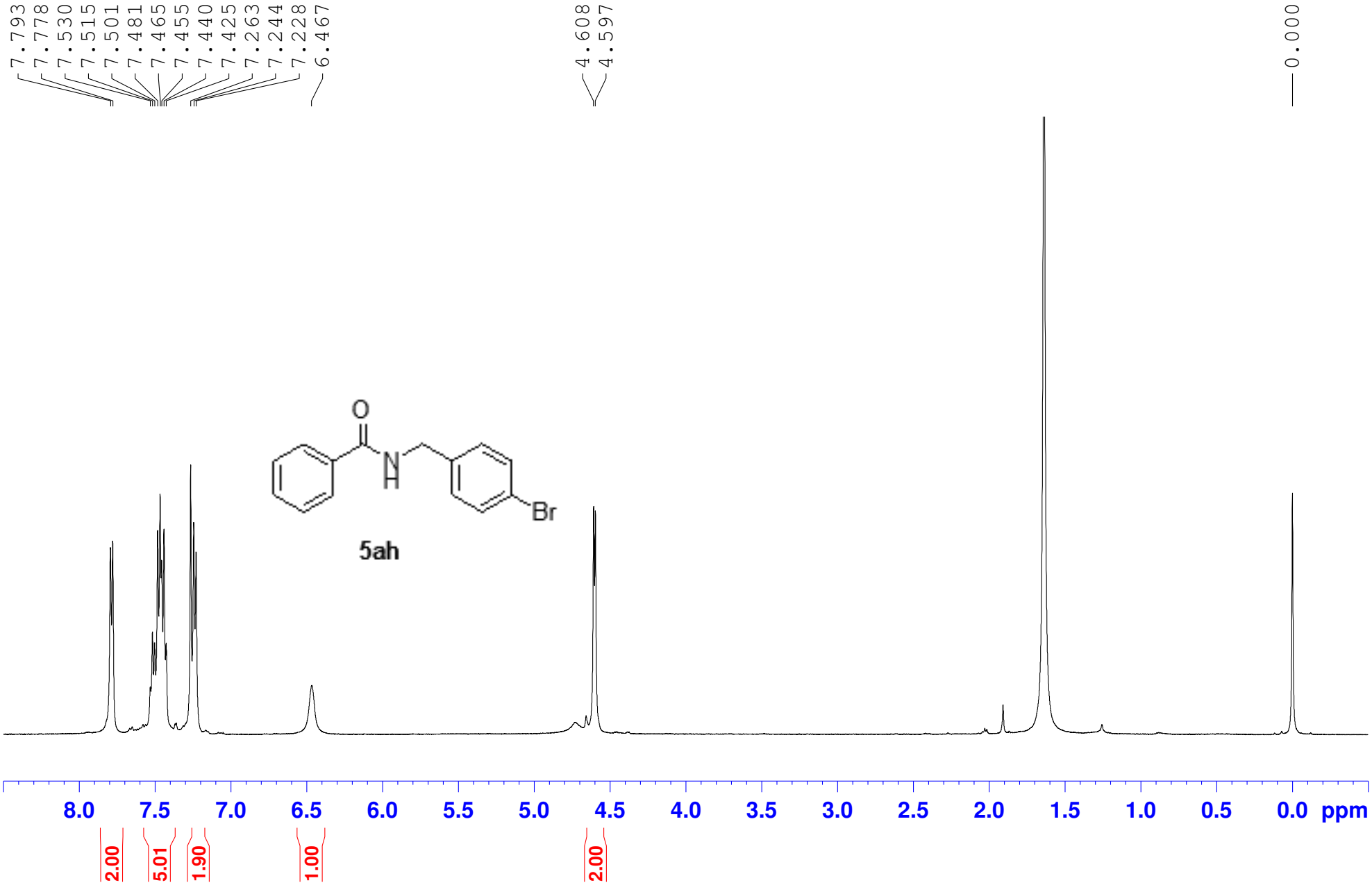
N-[(2,4-dichlorophenyl)methyl]- Benzamide
C13CPD CDCl3

167.498
134.270
134.119
133.979
131.670
131.007
130.852
129.281
128.555
127.293
126.954
77.000
41.368

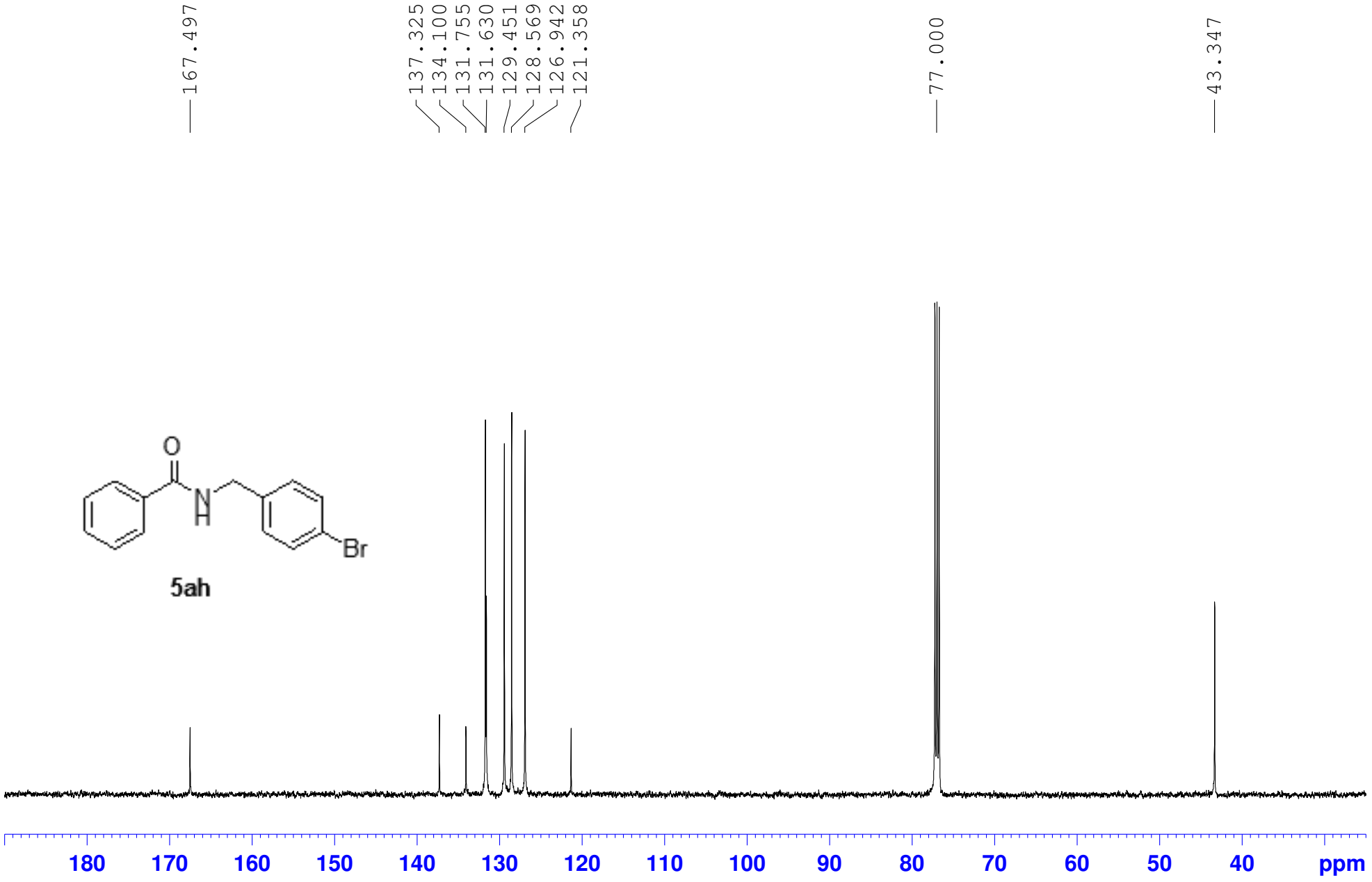
5ag



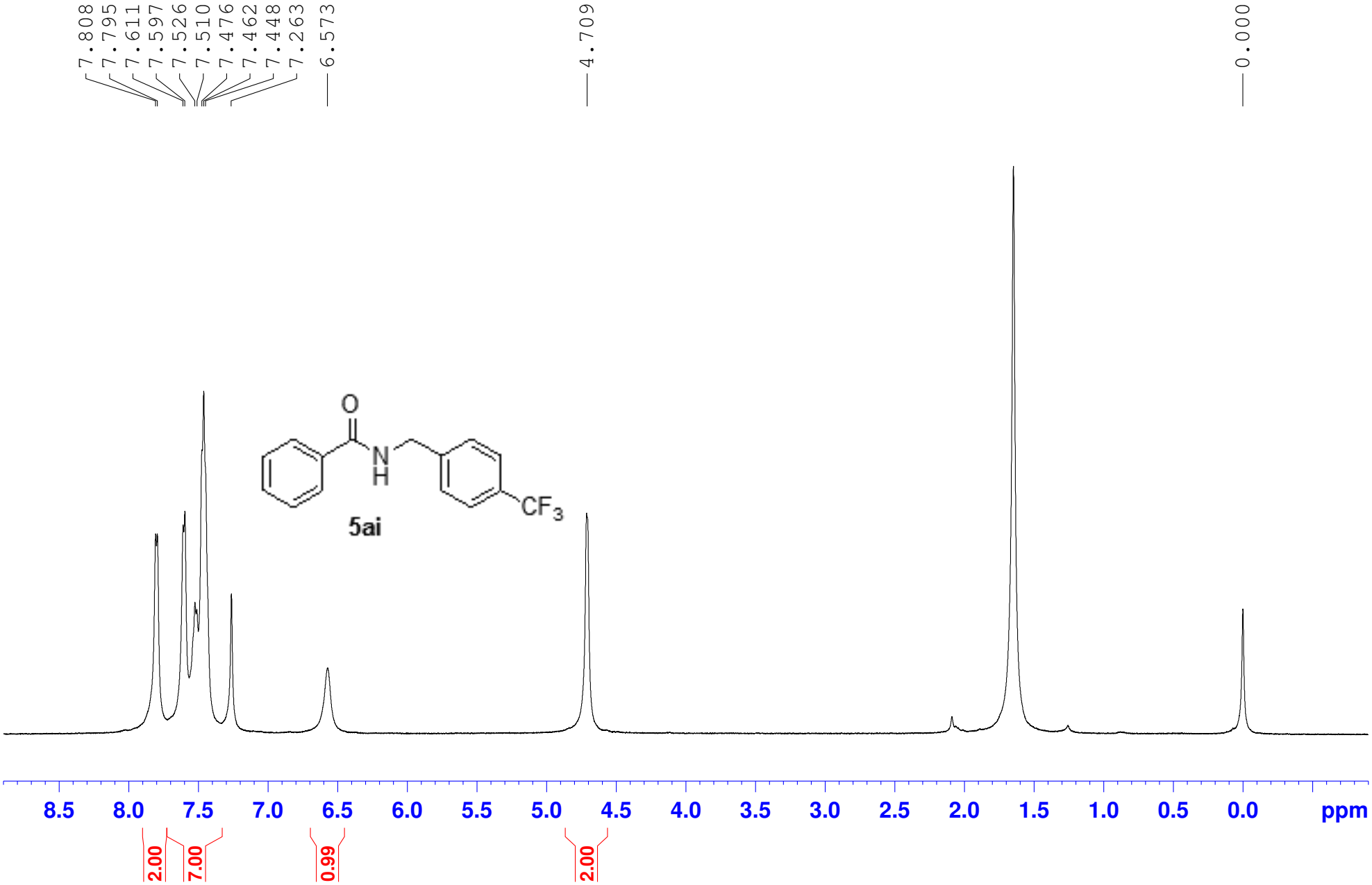
N-(4-bromobenzyl)benzamide
Proton CDCl3



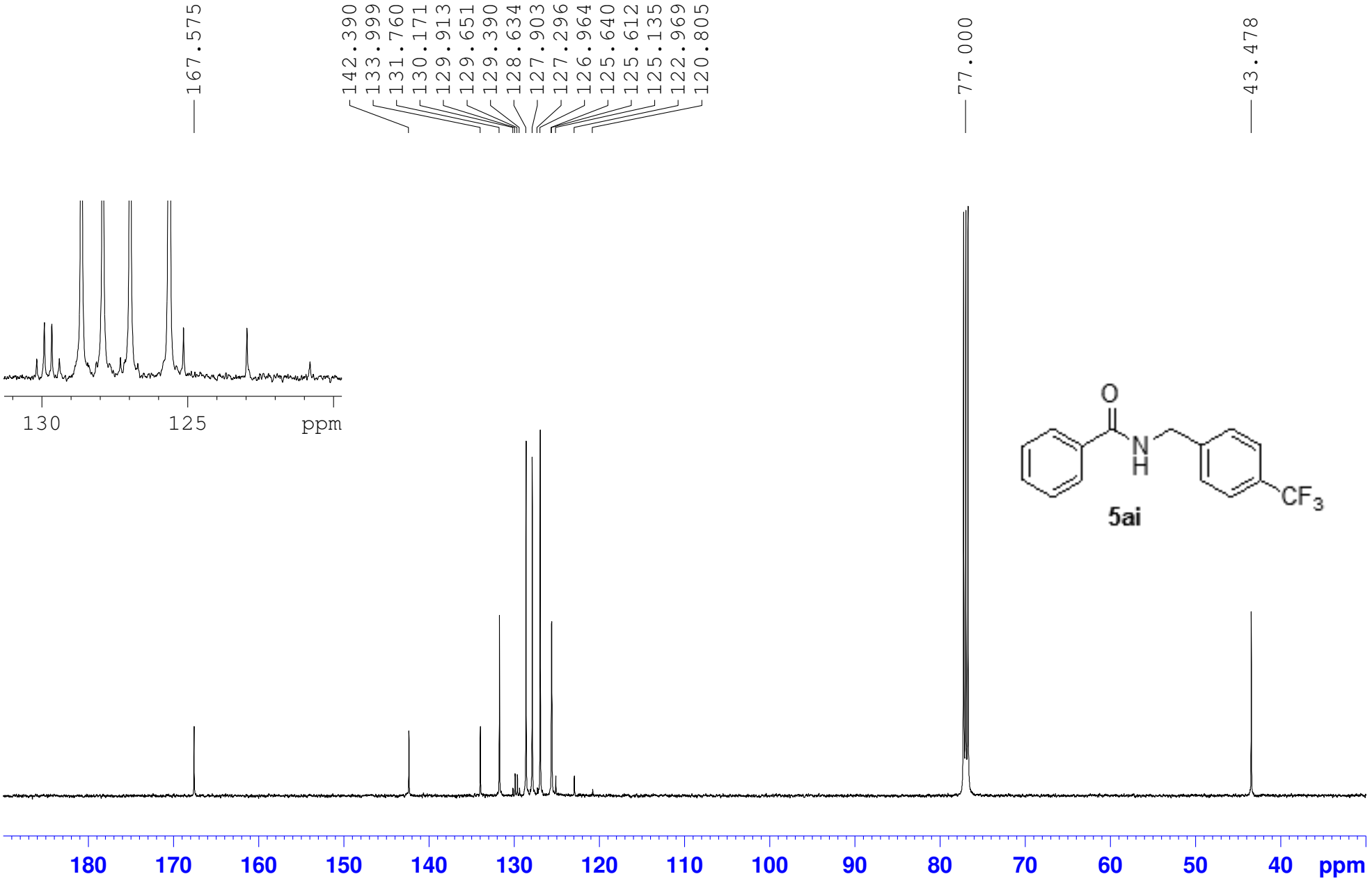
N-(4-bromobenzyl)benzamide
C13CPD CDCl3



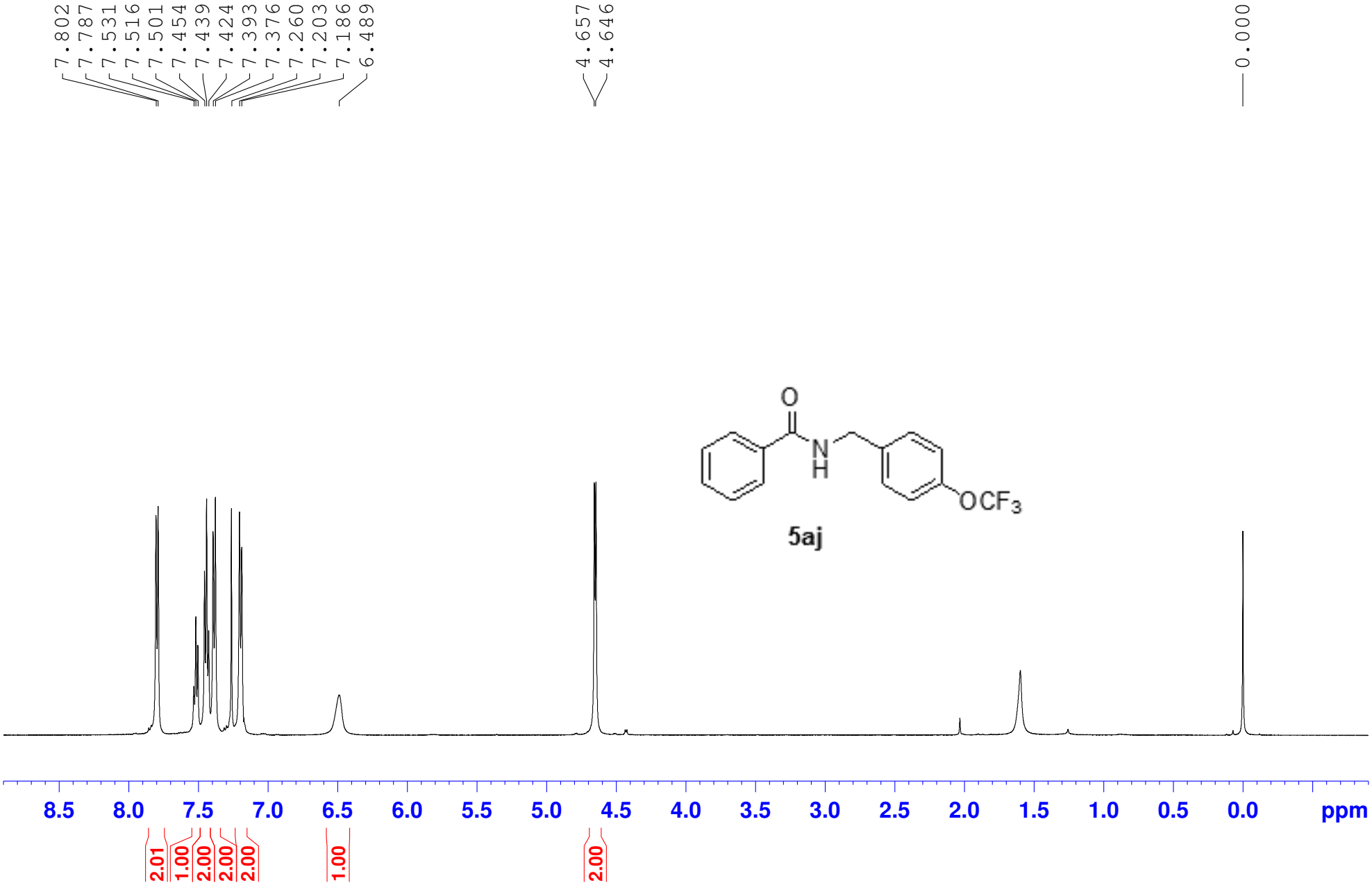
N-(4-(trifluoromethyl)benzyl)benzamide
Proton CDCl3



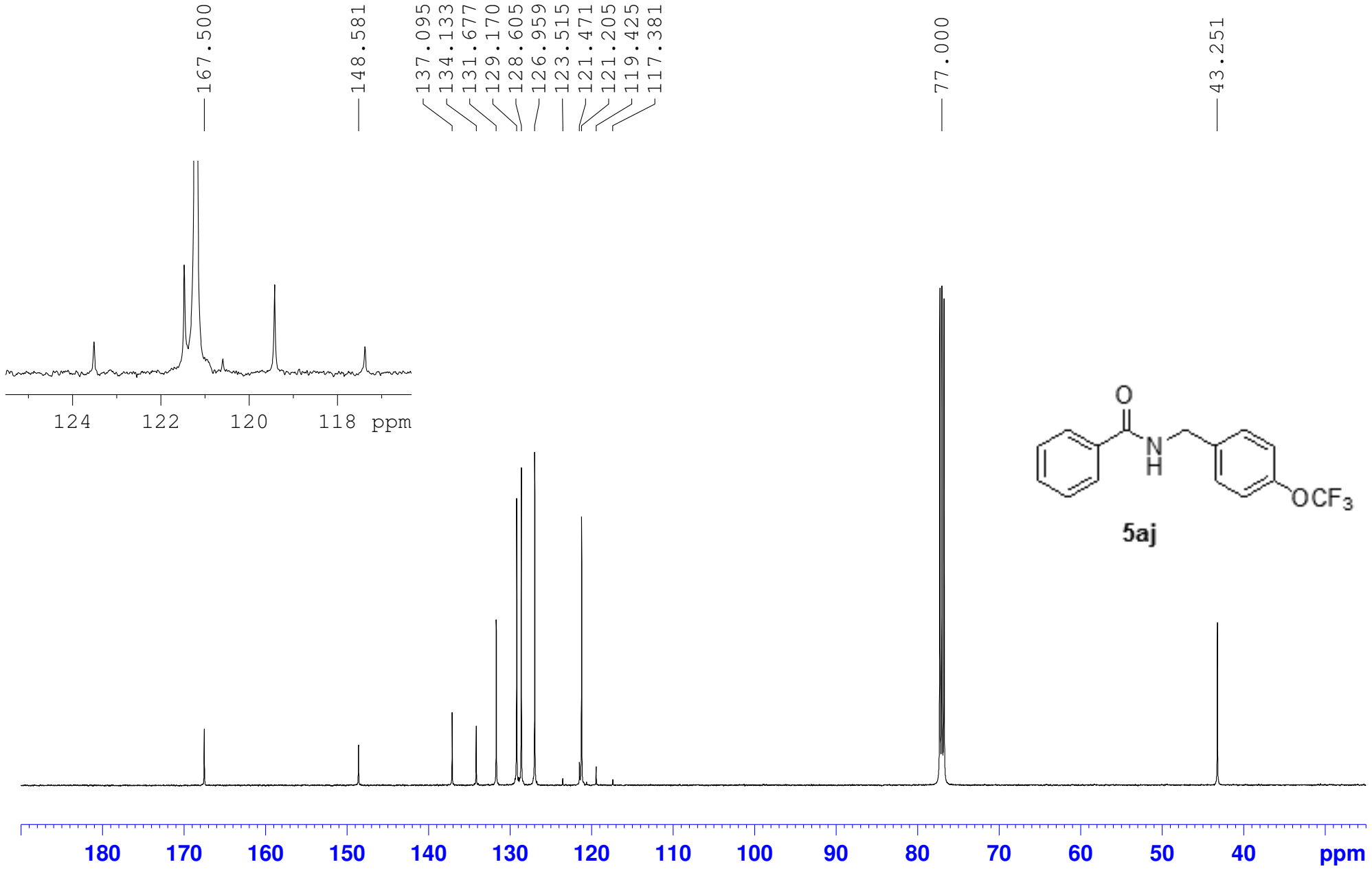
N-(4-(trifluoromethyl)benzyl)benzamide
C13CPD CDCl3



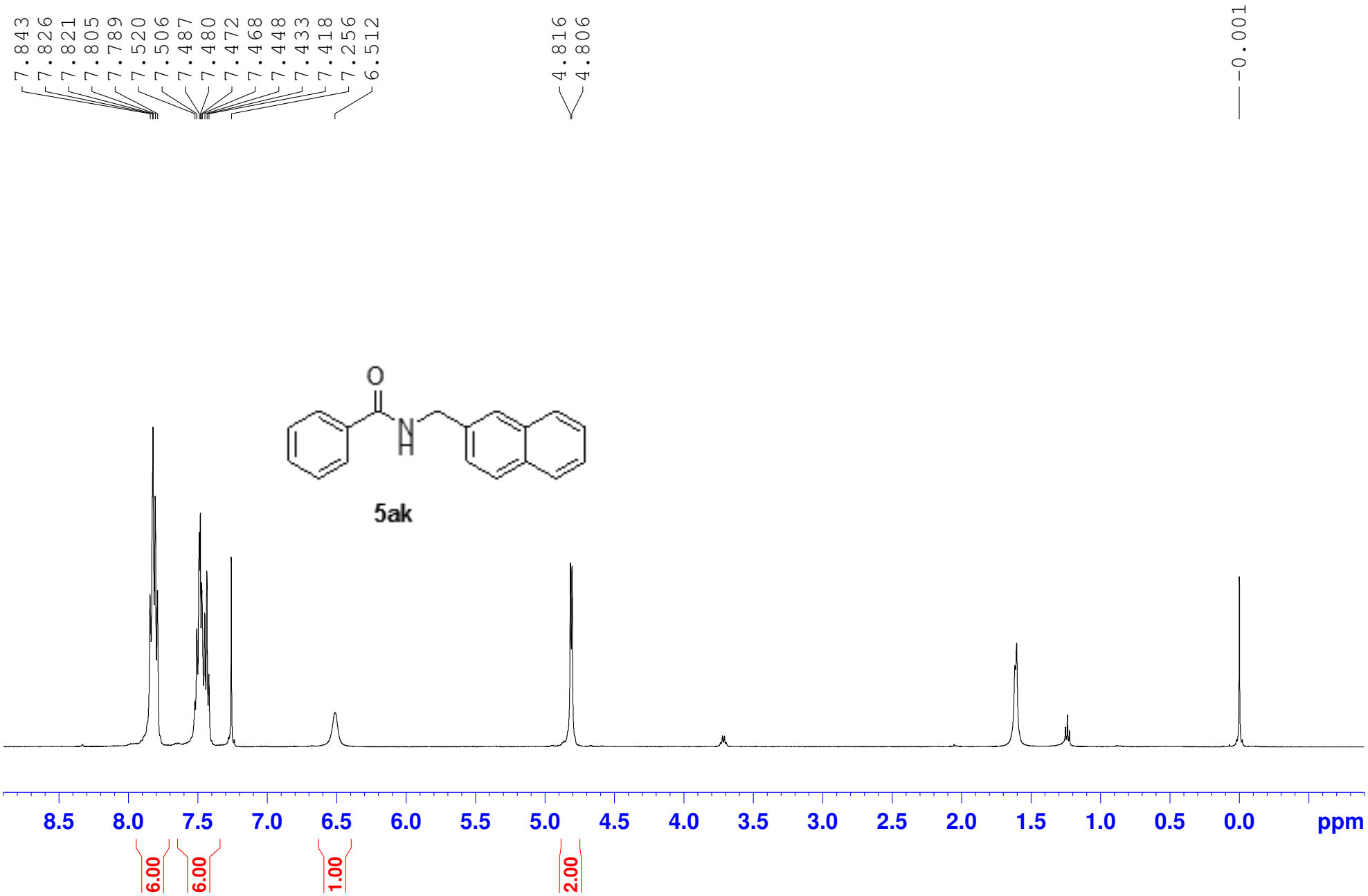
N-(4-(trifluoromethoxy)benzyl)benzamide
Proton CDCl3



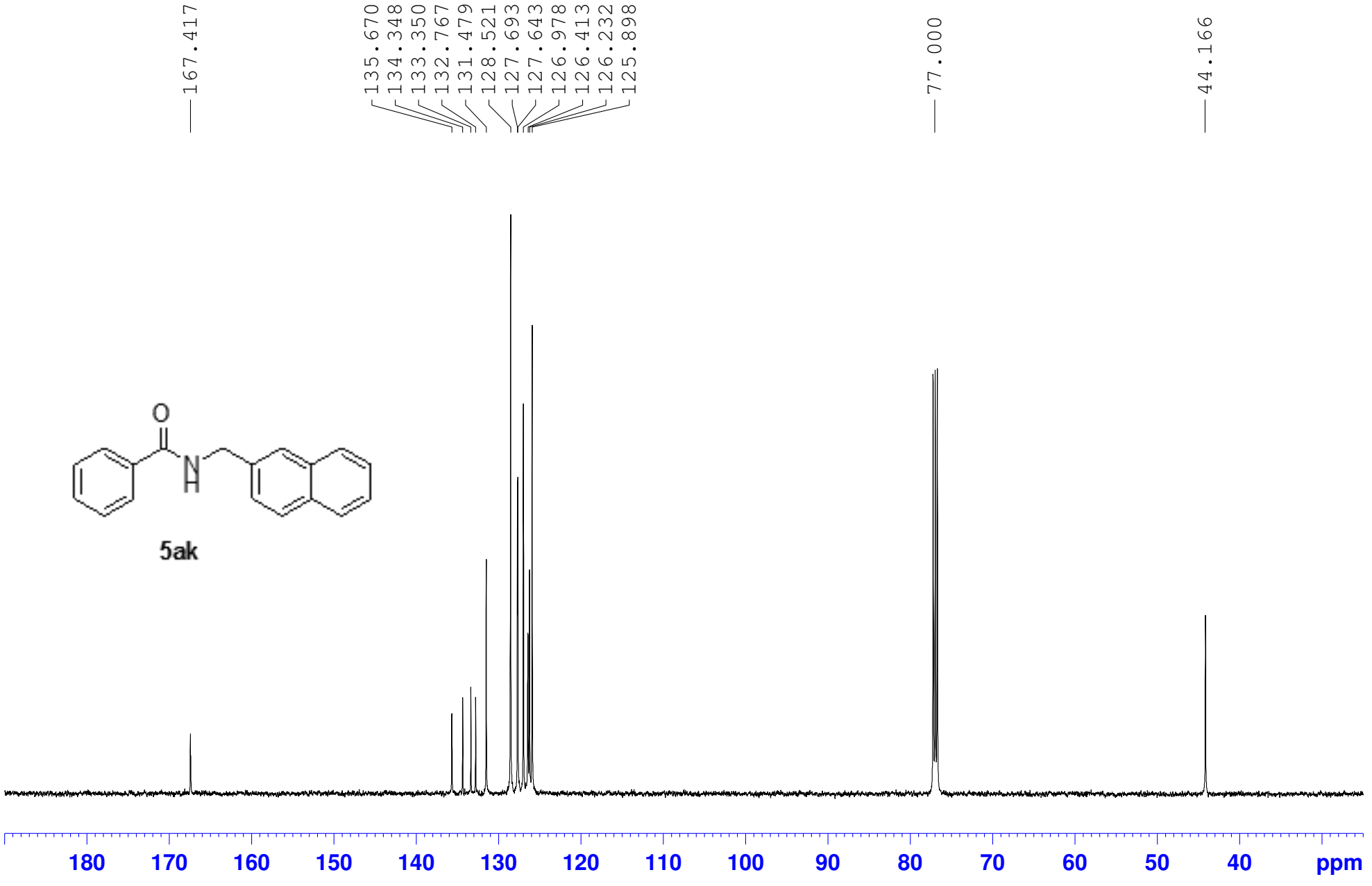
N-(4-(trifluoromethoxy)benzyl)benzamide
C13CPD CDCl3



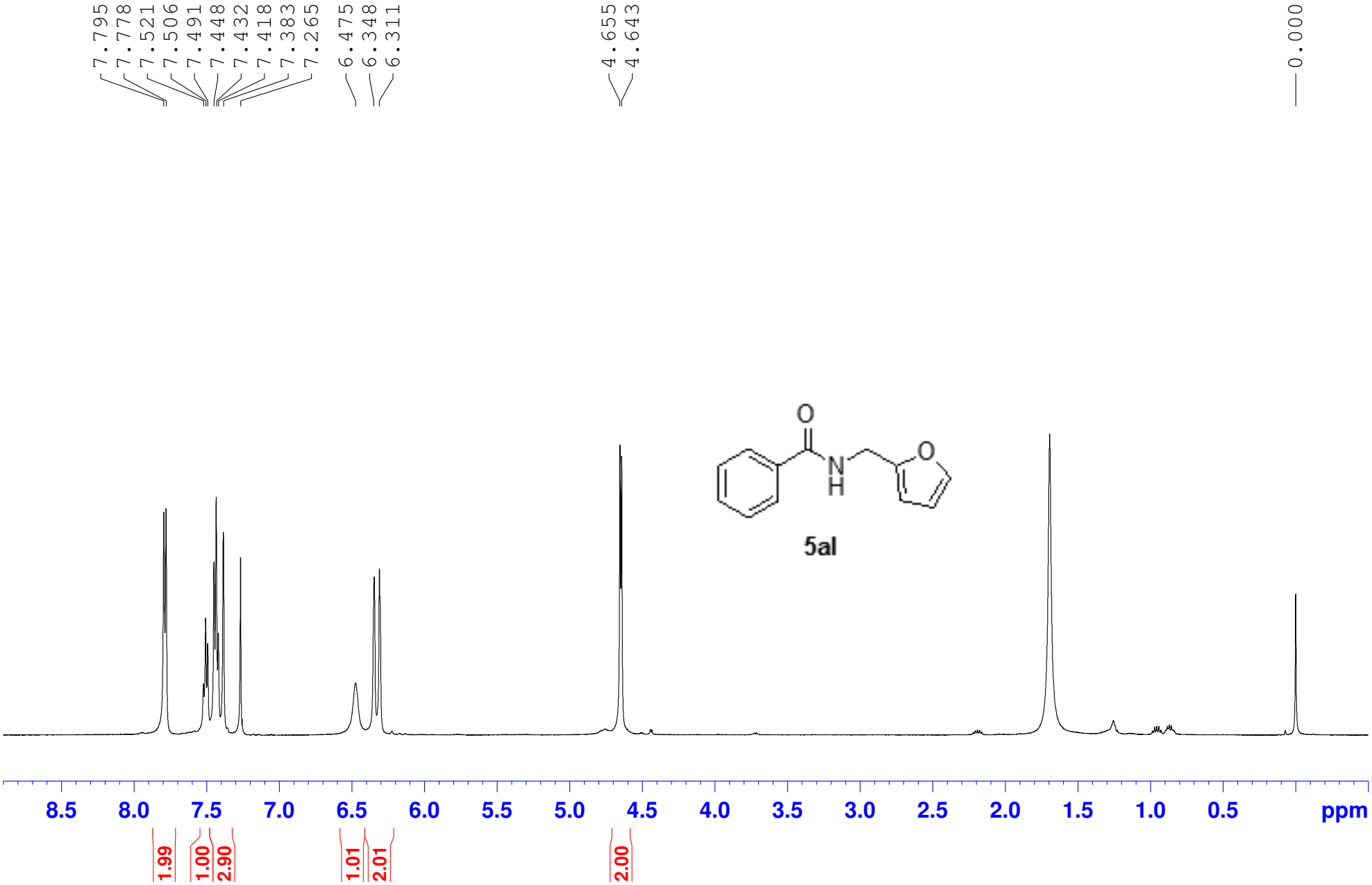
N-(naphthalen-2-ylmethyl)benzamide
Proton CDCl3



N-(naphthalen-2-ylmethyl)benzamide
C13CPD CDCl3



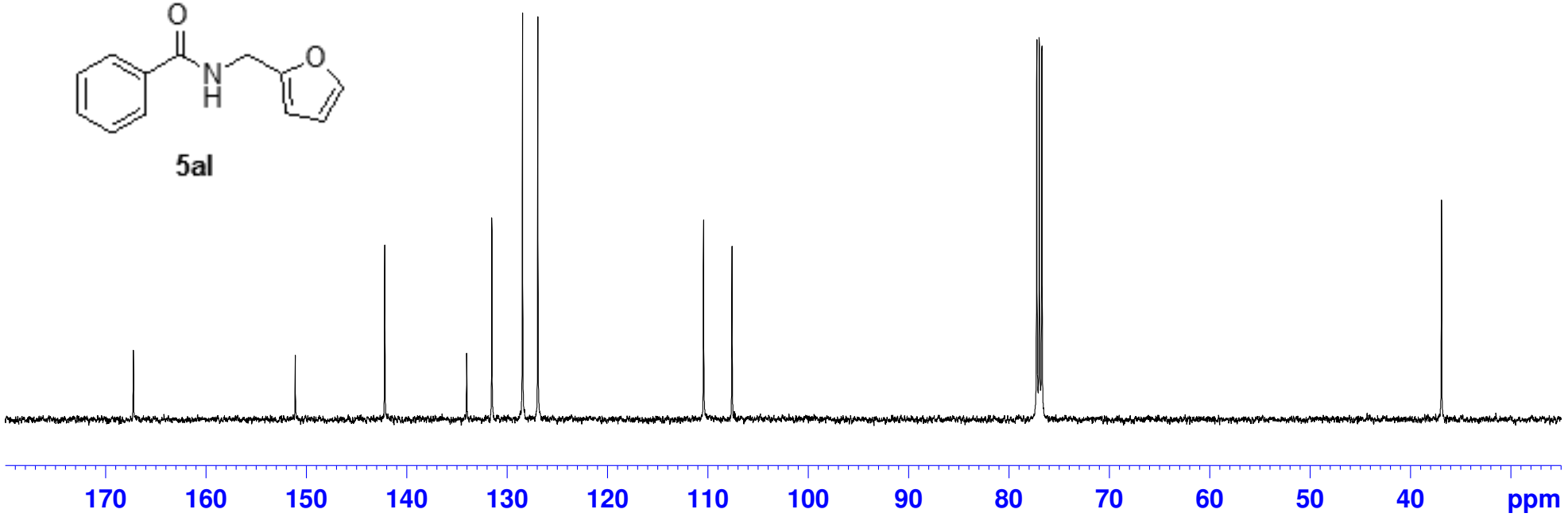
N-(furan-2-ylmethyl)benzamide
Proton CDCl3



N-(furan-2-ylmethyl)benzamide
C13CPD CDCl3

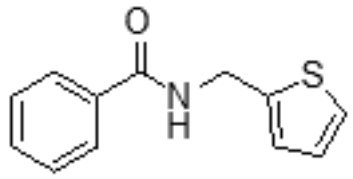
167.261
151.130
142.217
134.053
131.544
128.493
126.958
110.451
107.614
77.000
36.924

5al



N-(thiophen-2-ylmethyl)benzamide
Proton CDCl3

7.791
7.776
7.519
7.504
7.489
7.445
7.429
7.415
7.260
7.246
7.051
7.045
6.984
6.976
6.967
6.463
4.827
4.816
0.000



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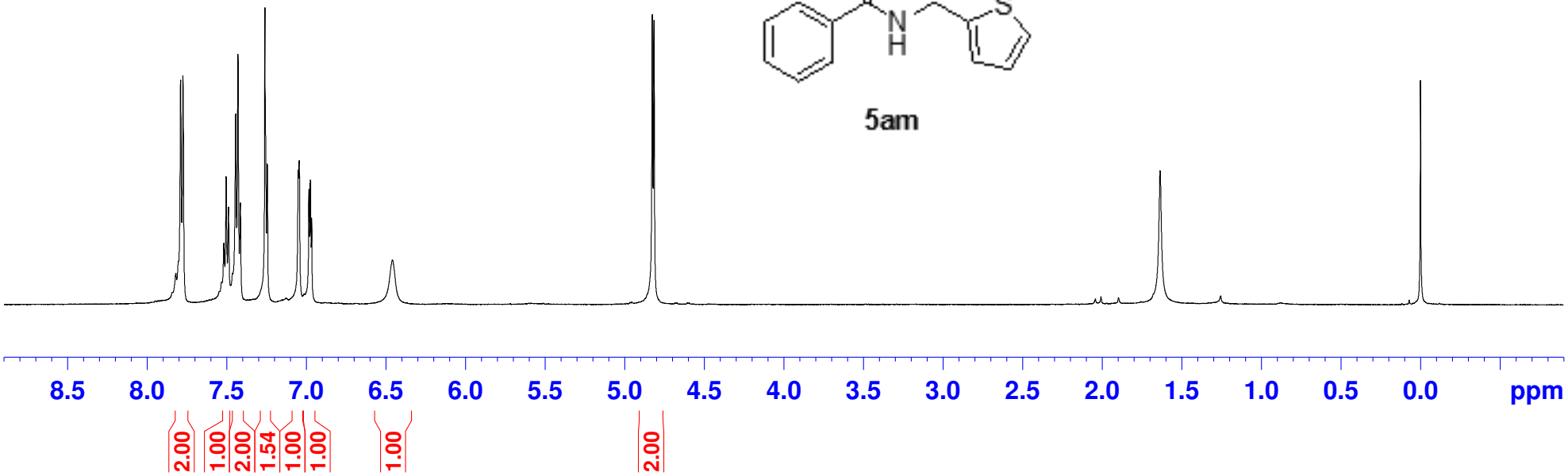
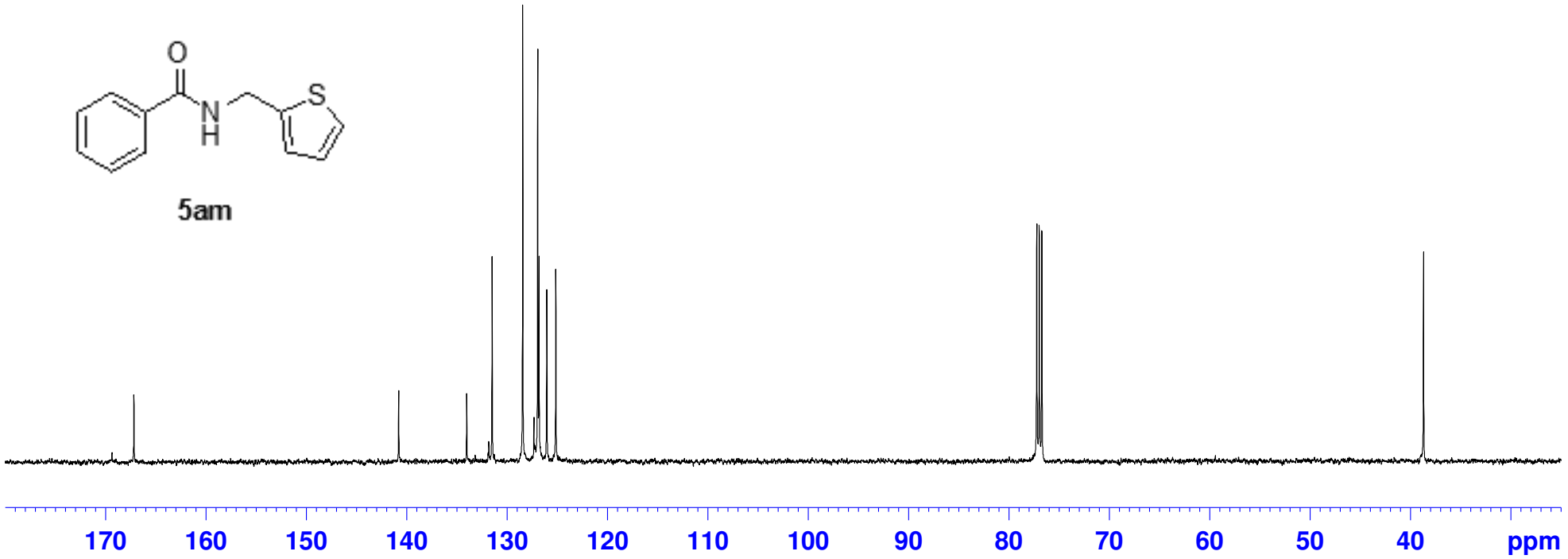


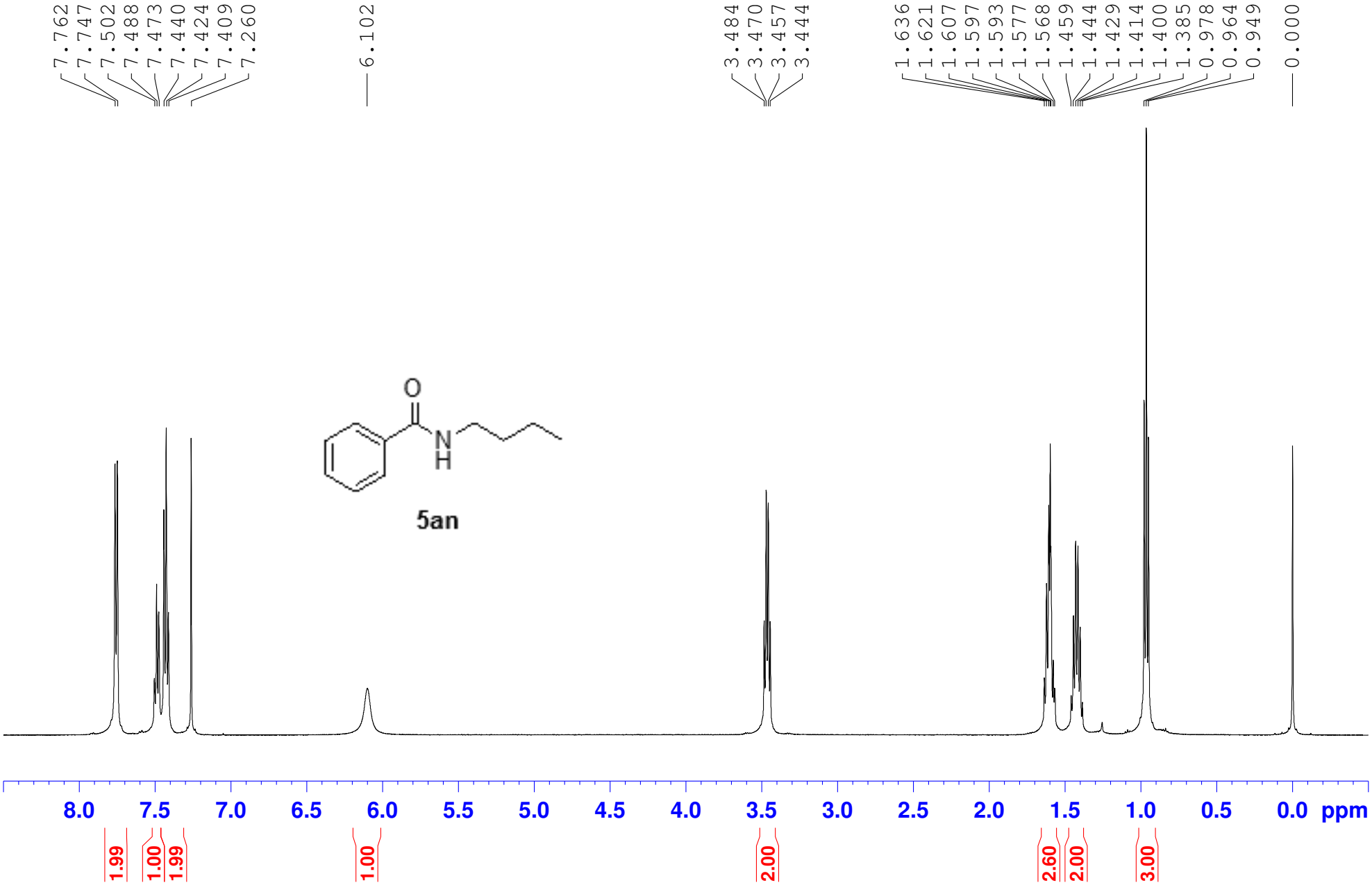
N-(thiophen-2-ylmethyl)benzamide
C13CPD CDCl3

167.203
140.822
134.054
131.518
128.470
126.974
126.842
126.070
125.169
77.000
38.714

5am



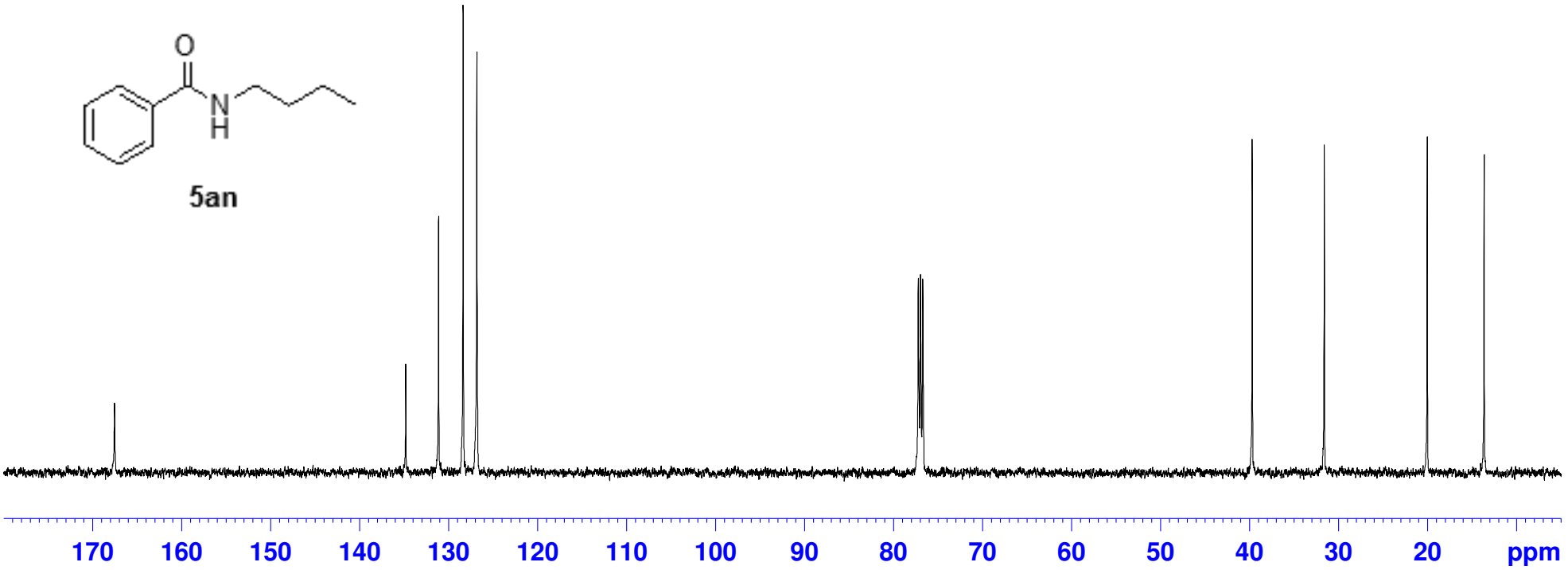
N-butylbenzamide
Proton CDCl3



N-butylbenzamide
C13CPD CDCl3

167.526
134.804
131.109
128.360
126.809
77.001
39.725
31.634
20.061
13.668

5an



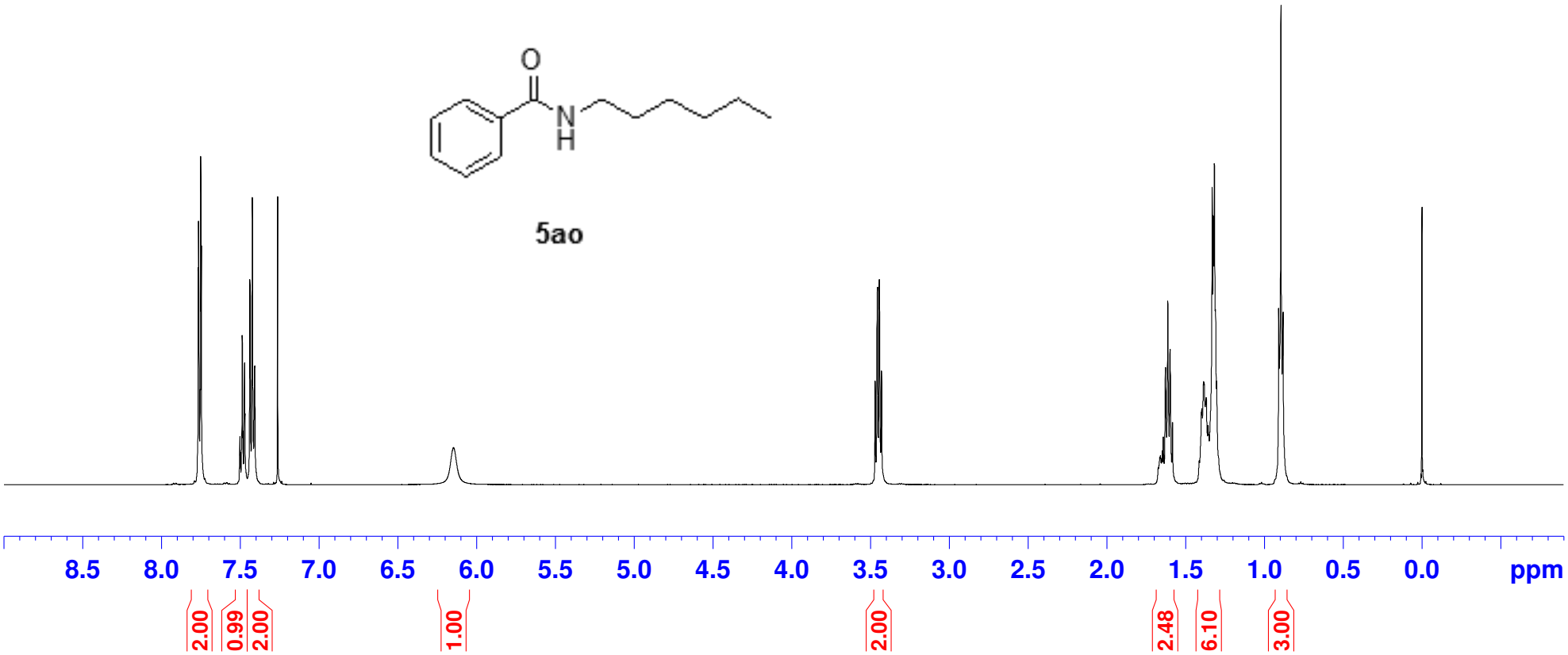
N-hexylbenzamide
Proton CDCl3

7.765
7.751
7.505
7.502
7.500
7.492
7.488
7.483
7.475
7.473
7.470
7.439
7.423
7.409
7.263
6.147

3.471
3.457
3.444
3.430

1.674
1.665
1.649
1.628
1.613
1.599
1.583
1.414
1.399
1.386
1.369
1.358
1.331
1.317
1.303
0.909
0.895
0.881
0.000

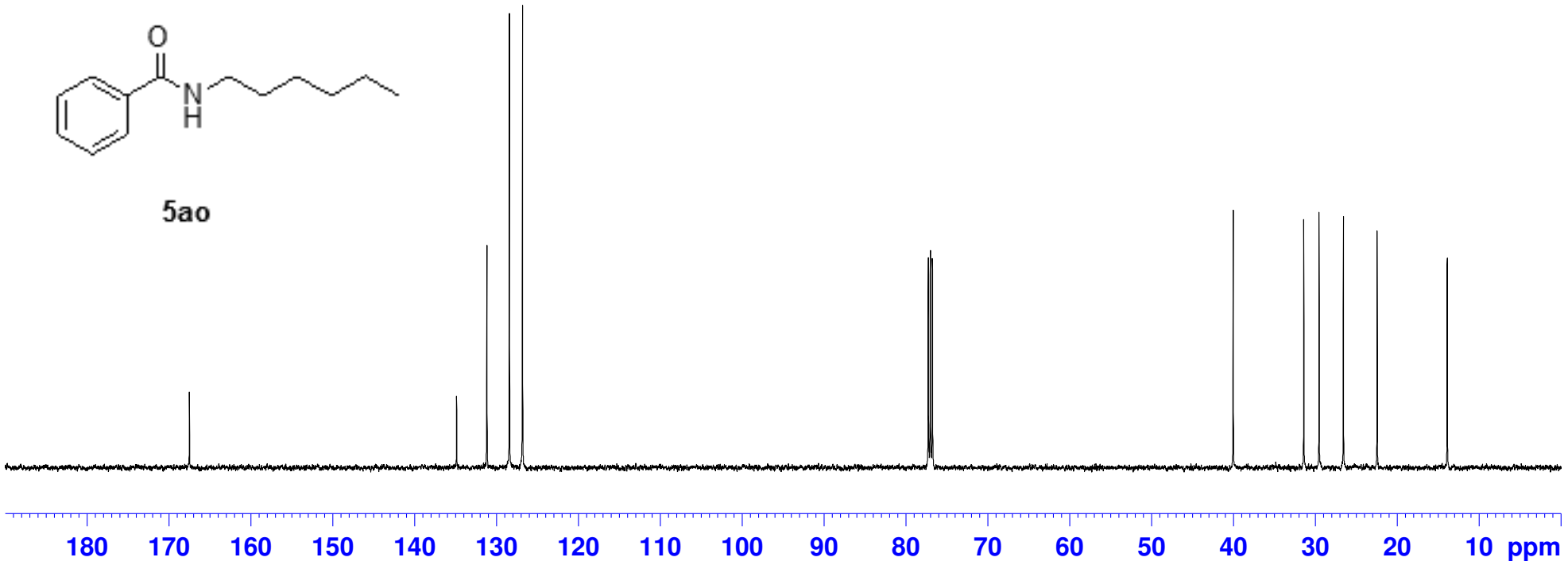
5ao



N-hexylbenzamide
C13CPD CDCl3

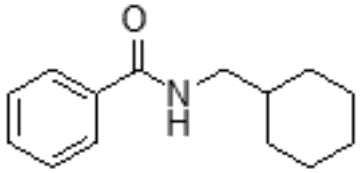
167.492
134.858
131.157
128.405
126.809
77.000
40.066
31.447
29.577
26.609
22.484
13.924

5ao



N-(cyclohexylmethyl)benzamide
Proton CDCl3

7.768
7.754
7.505
7.490
7.476
7.443
7.427
7.413
7.263
6.183
3.320
3.308
3.295
1.802
1.773
1.733
1.693
1.651
1.614
1.599
1.585
1.569
1.555
1.548
1.291
1.267
1.241
1.214
1.188
1.163
1.138
1.040
1.016
0.992
0.969
0.000



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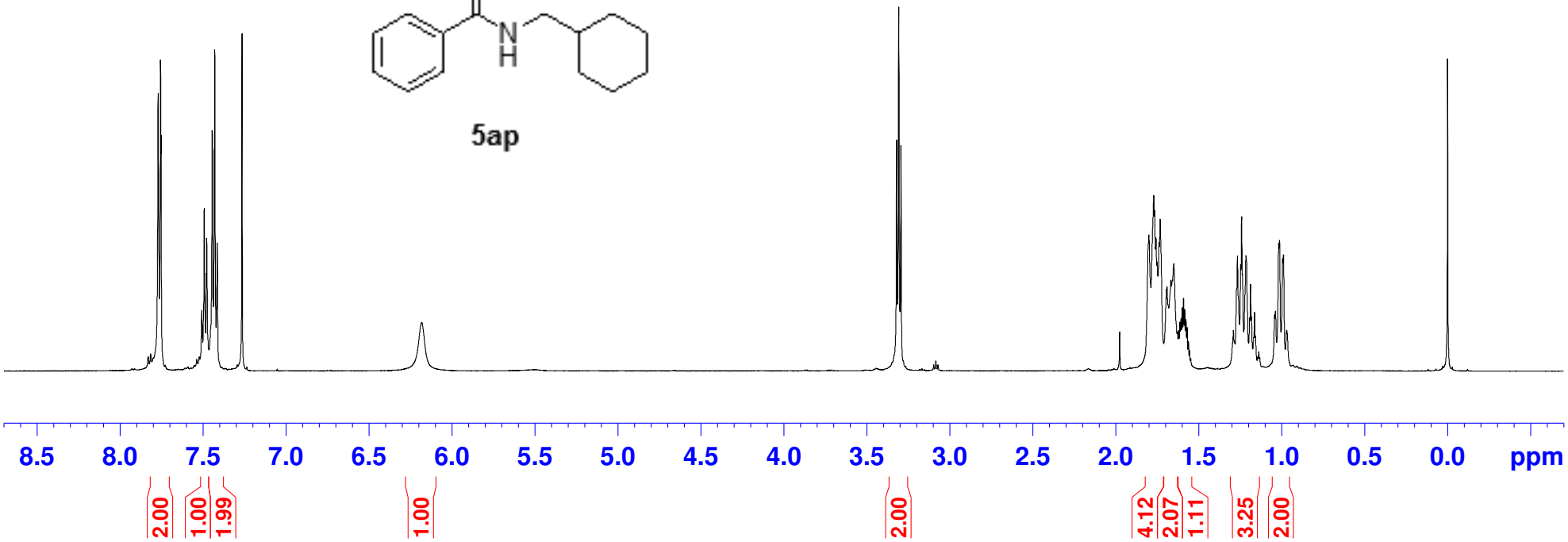
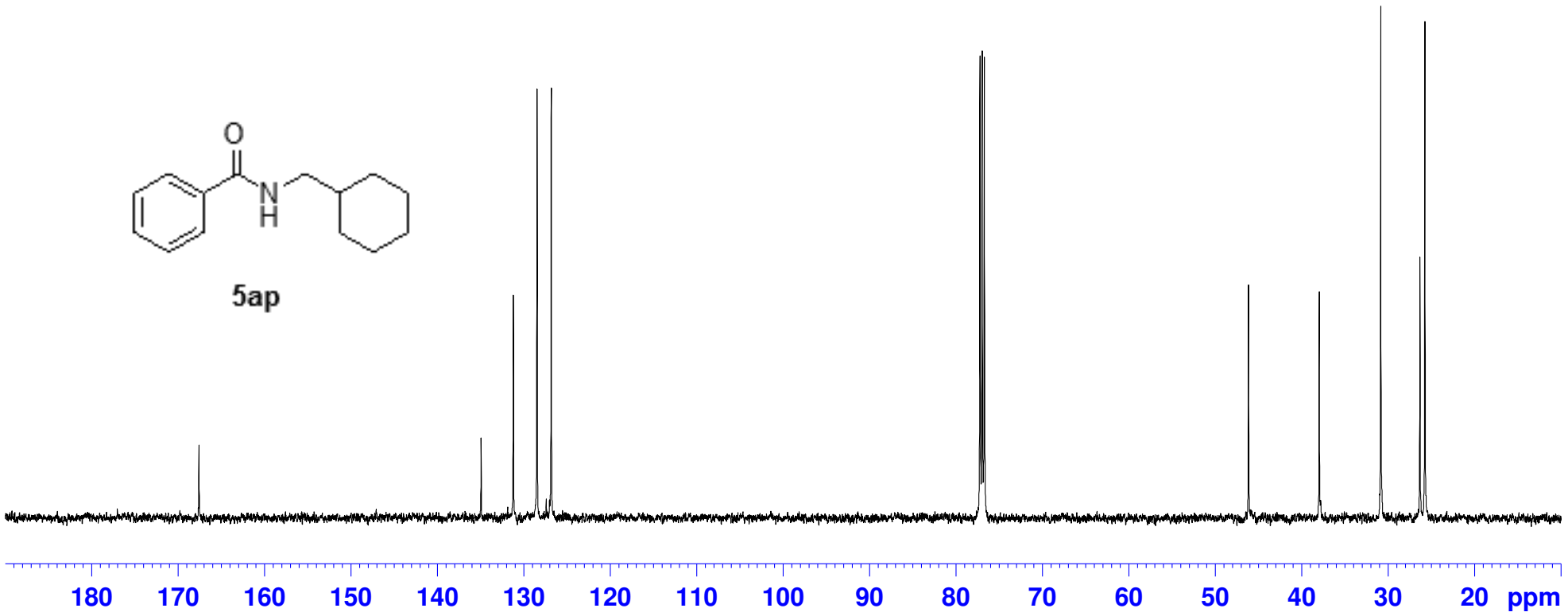


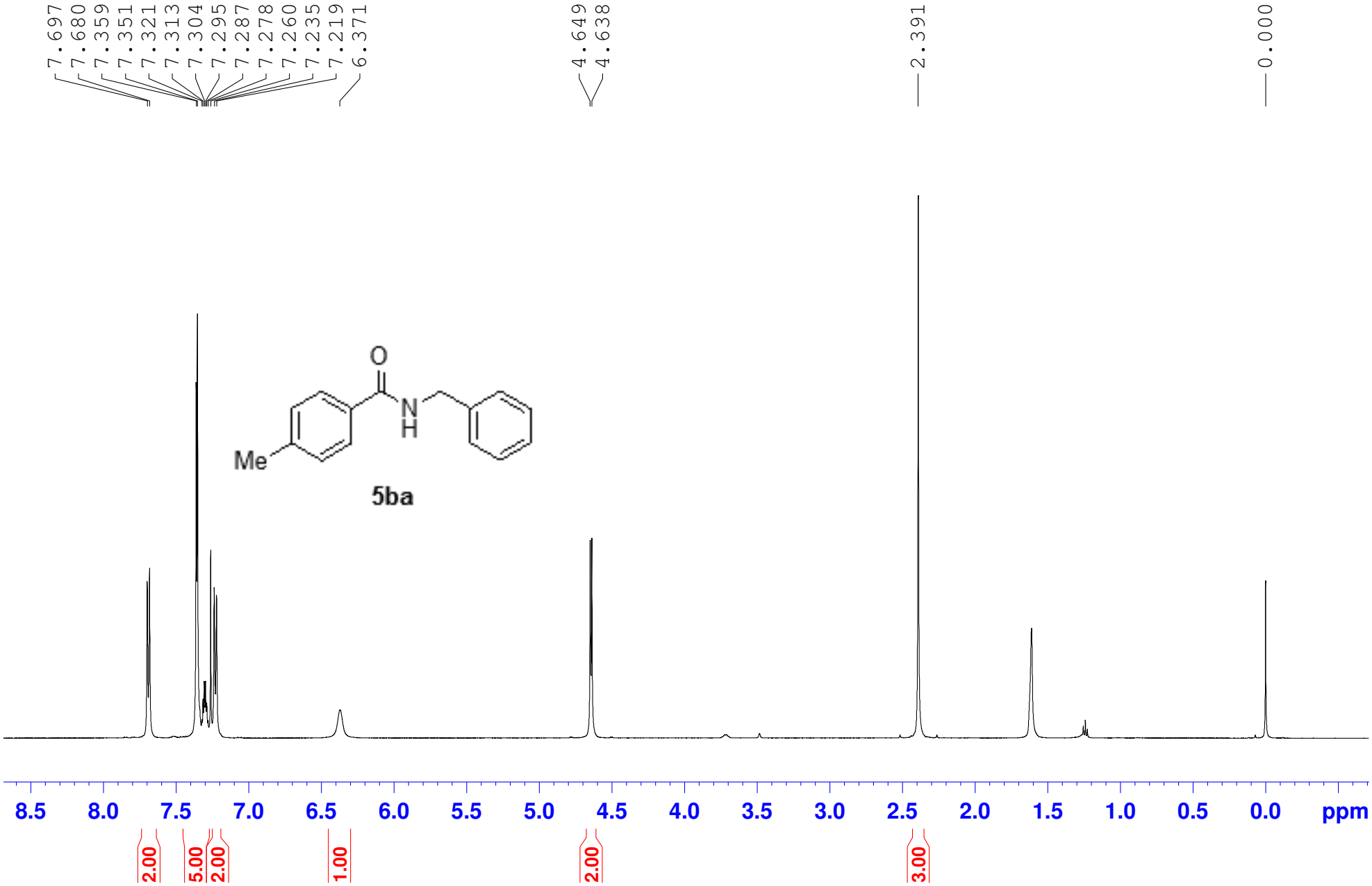
N-(cyclohexylmethyl)benzamide
C13CPD CDCl3

167.562
134.925
131.194
128.449
126.813
77.000
46.179
38.003
30.881
26.355
25.778

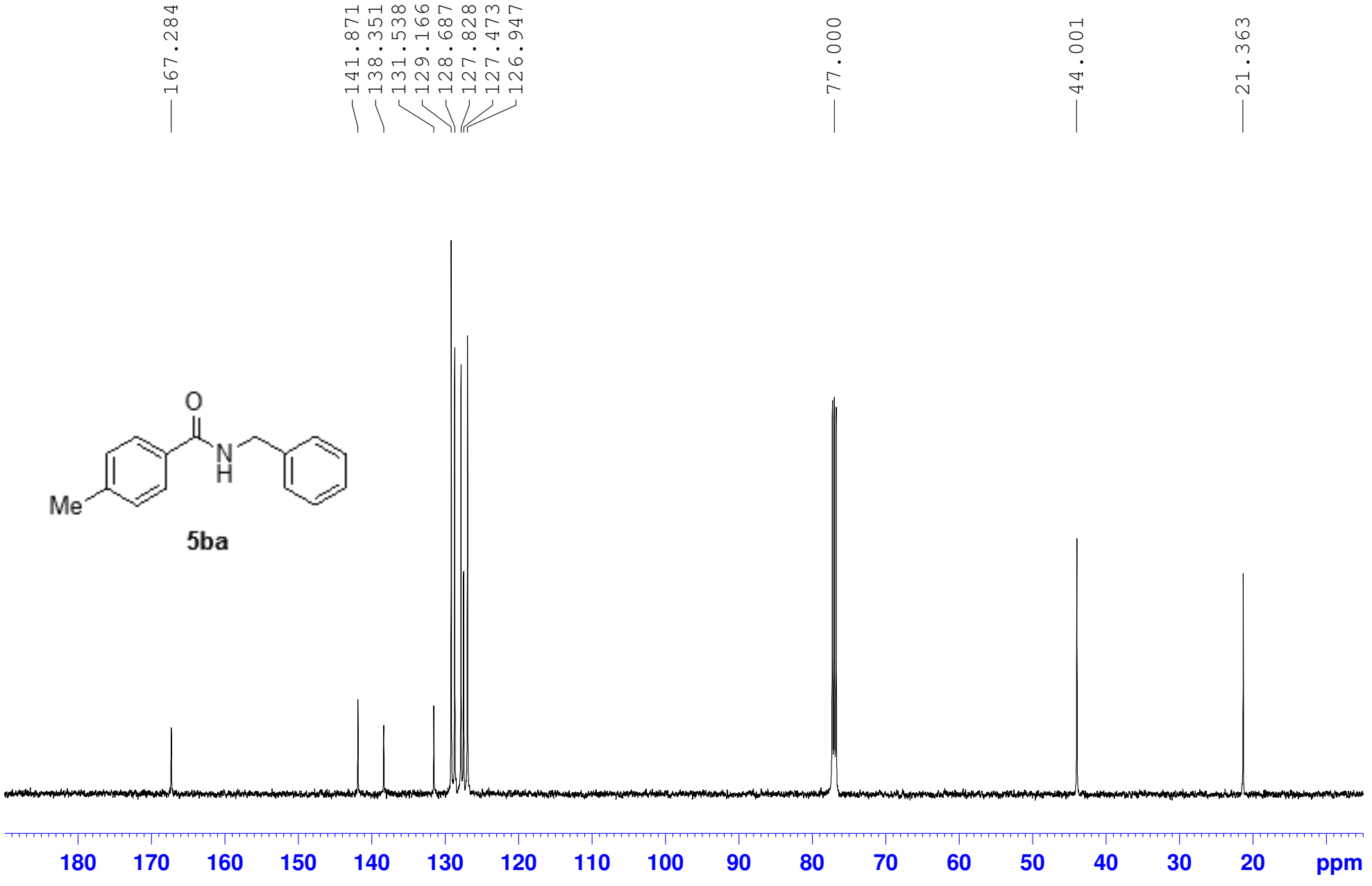
5ap



N-Benzyl-4-methyl-benzamide
Proton CDCl3



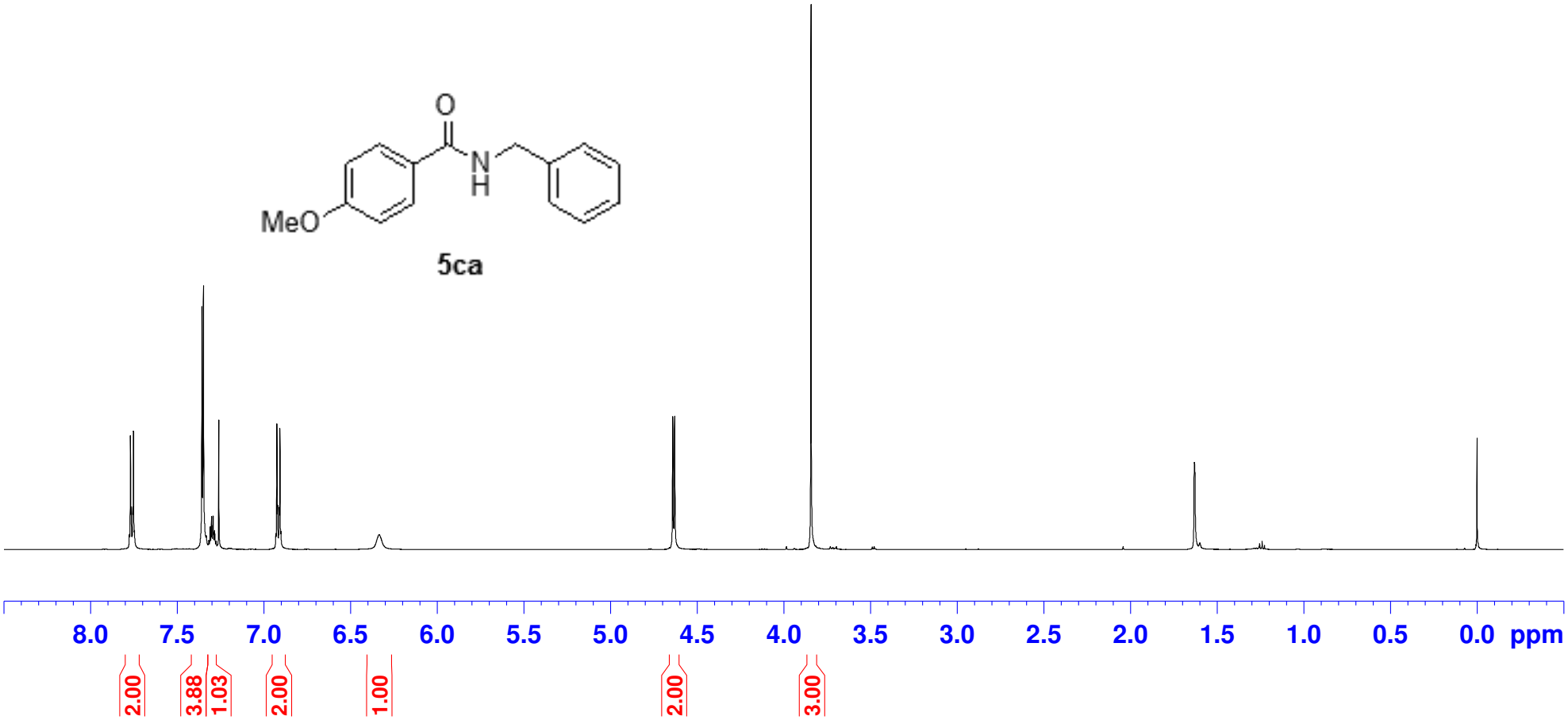
N-Benzyl-4-methyl-benzamide
C13CPD CDCl3



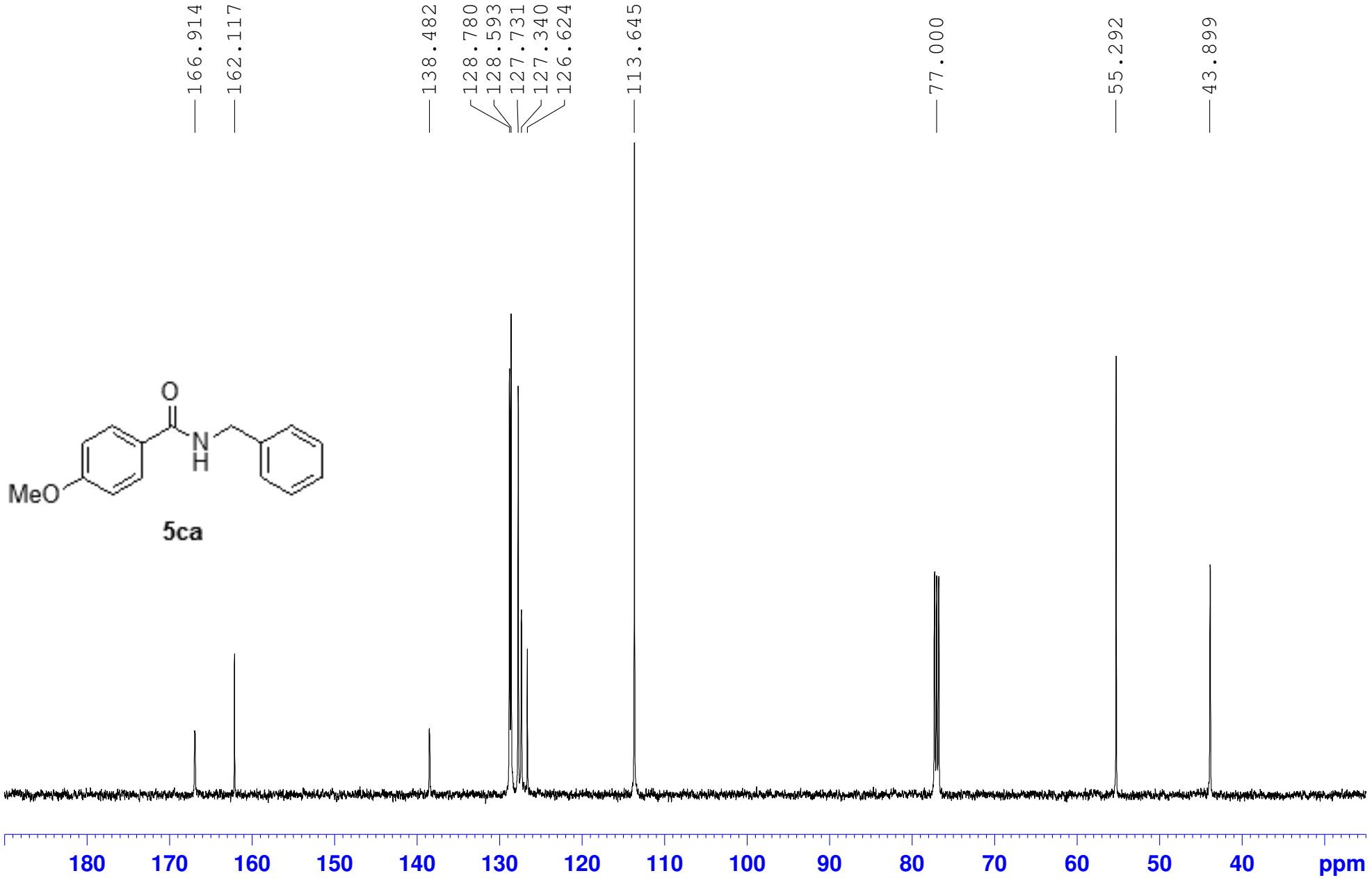
N-benzyl-4-methoxybenzamide
Proton CDCl3

7.768
7.750
7.358
7.349
7.318
7.310
7.302
7.293
7.285
7.276
7.260
6.925
6.908
6.336
4.641
4.630
3.843
0.000

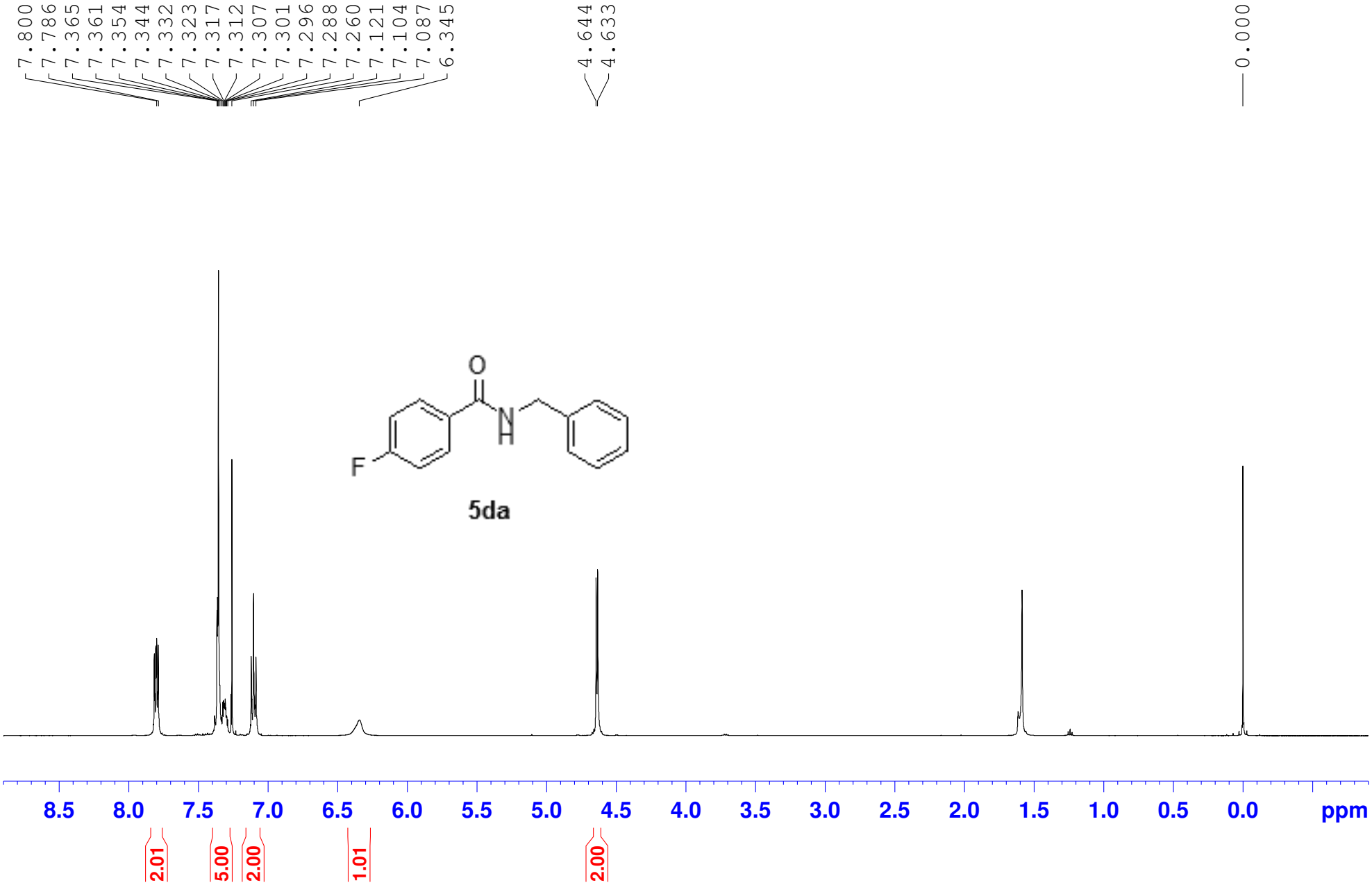
5ca



N-benzyl-4-methoxybenzamide
C13CPD CDCl3



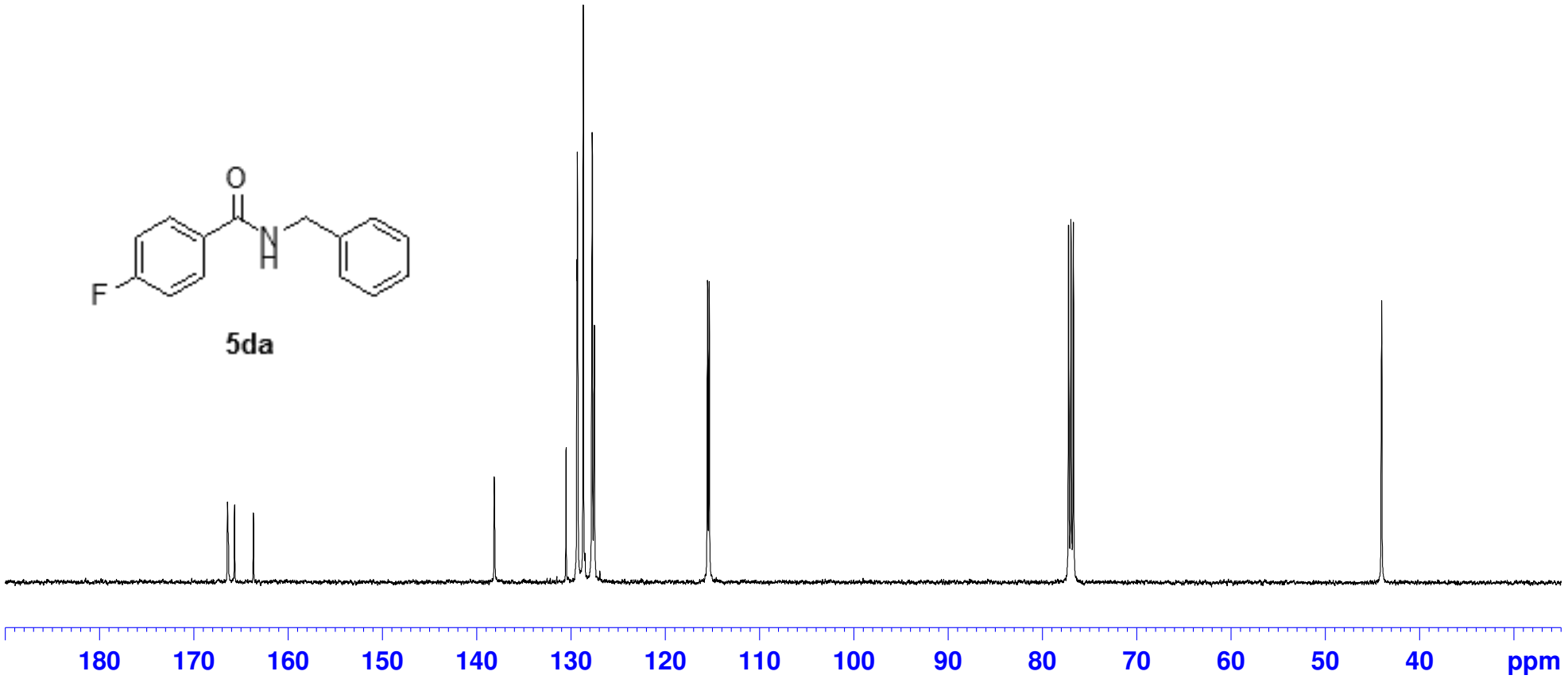
N-Benzyl-4-fluoro-benzamide
Proton CDCl3



N-Benzyl-4-fluoro-benzamide
C13CPD CDCl3

166.425
165.665
163.659
138.132
130.507
129.360
129.296
128.669
127.723
127.490
115.535
115.363
77.000
44.033

5da

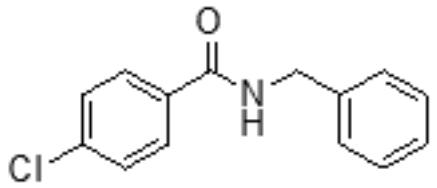


N-benzyl-4-chlorobenzamide
Proton CDCl3

7.735
7.718
7.408
7.391
7.378
7.363
7.350
7.338
7.305
7.298
7.293
7.288
7.281
7.320
7.259
6.375

4.639
4.628

0.000



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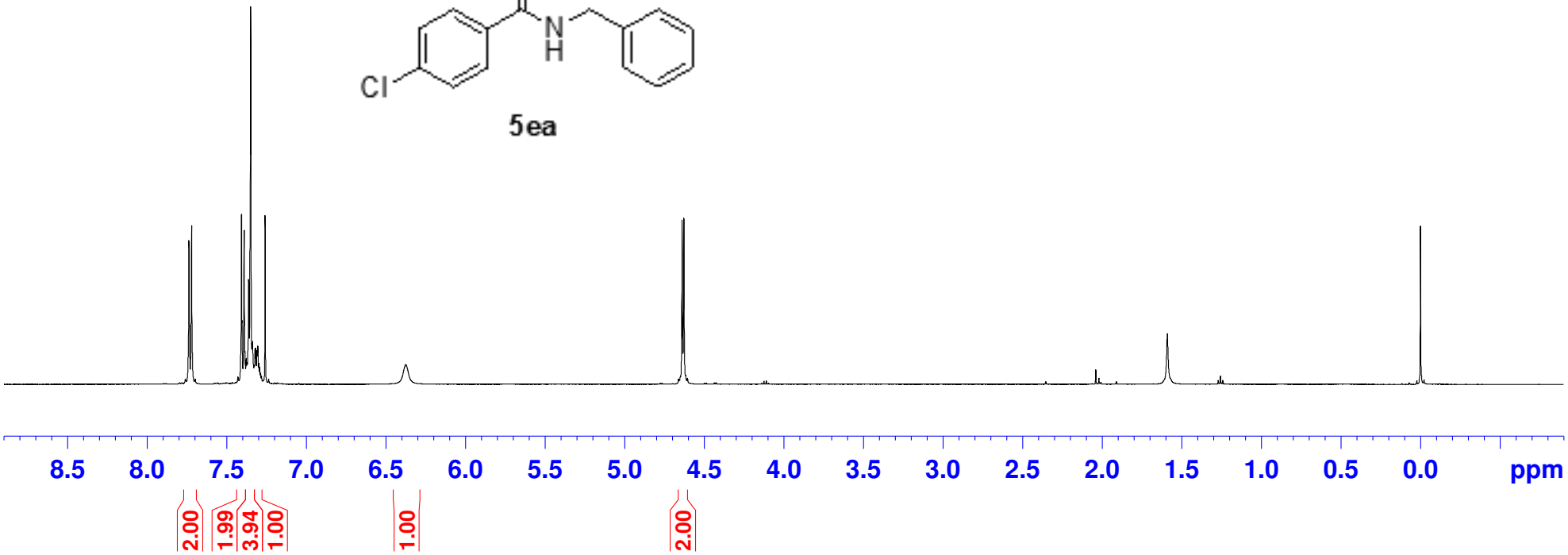
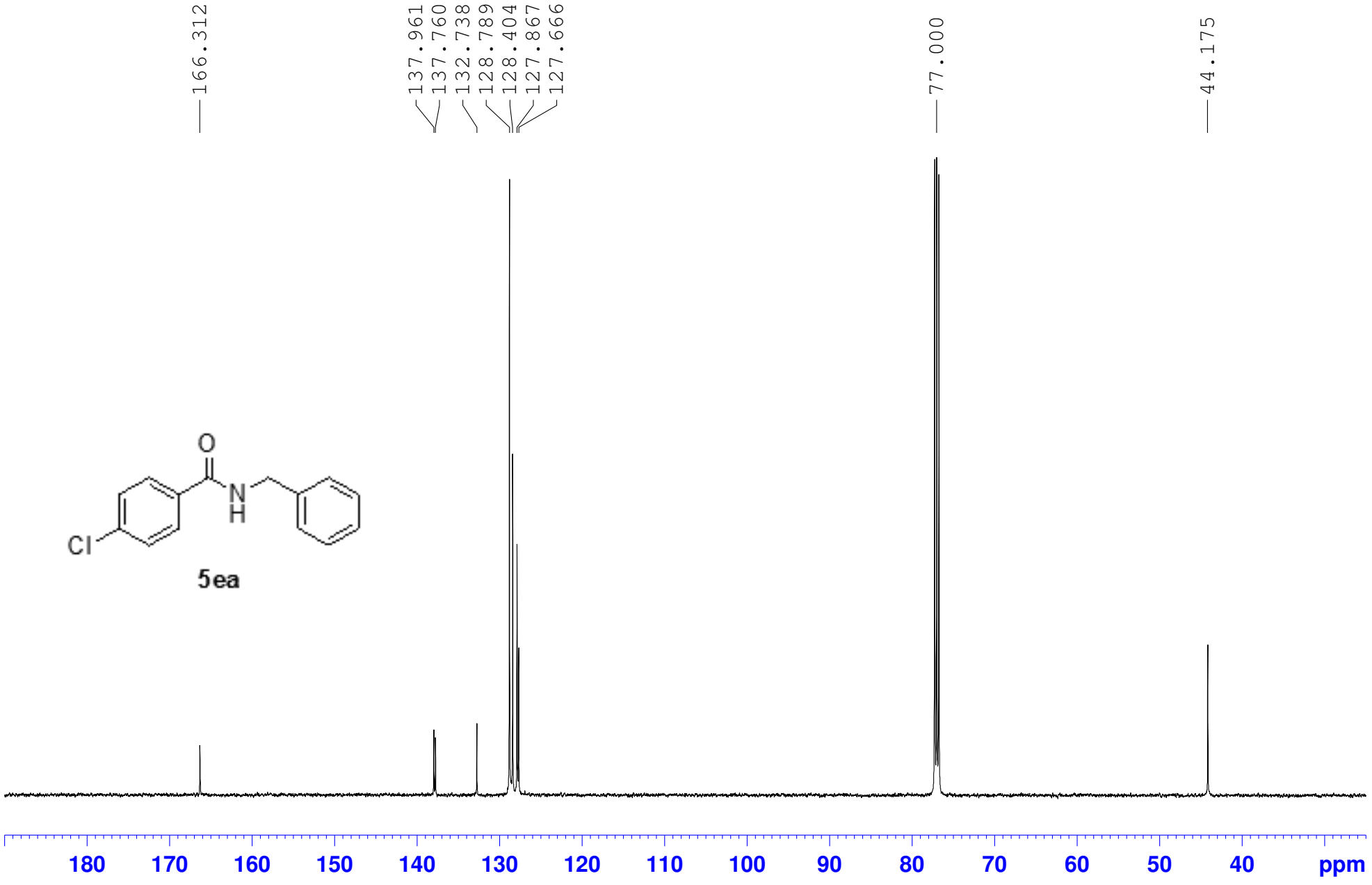
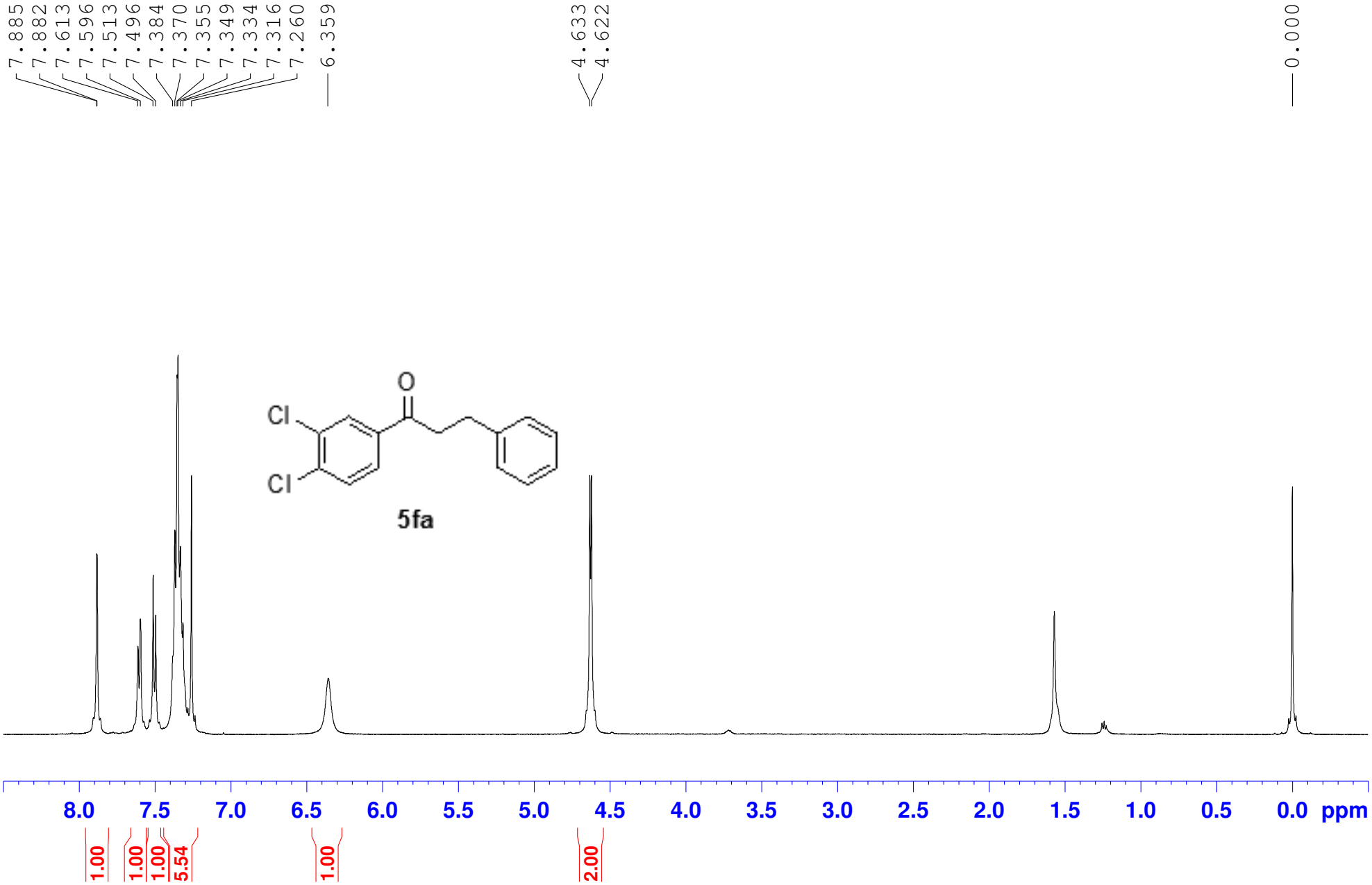


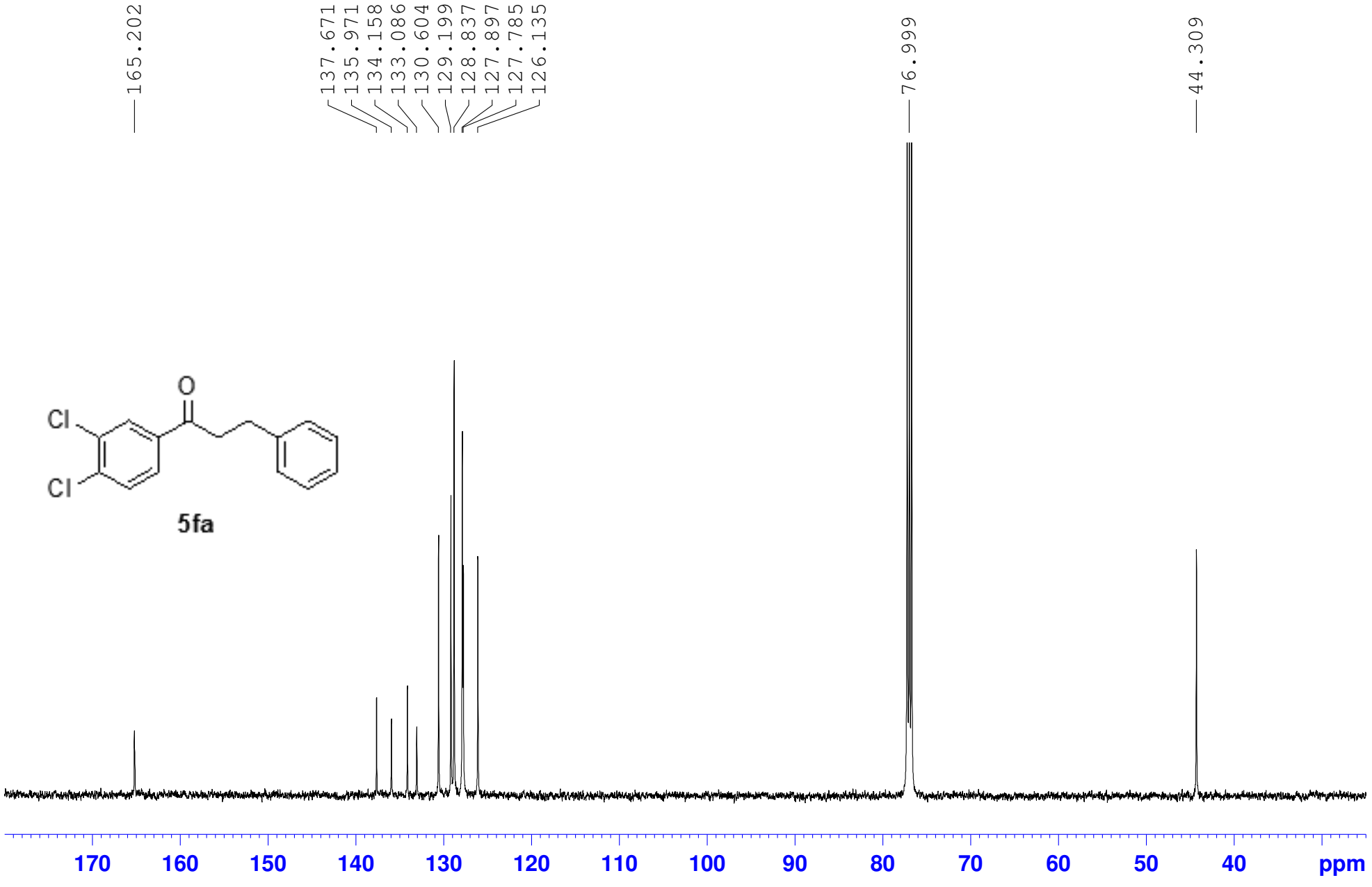
N-benzyl-4-chlorobenzamide
C13CPD CDCl3



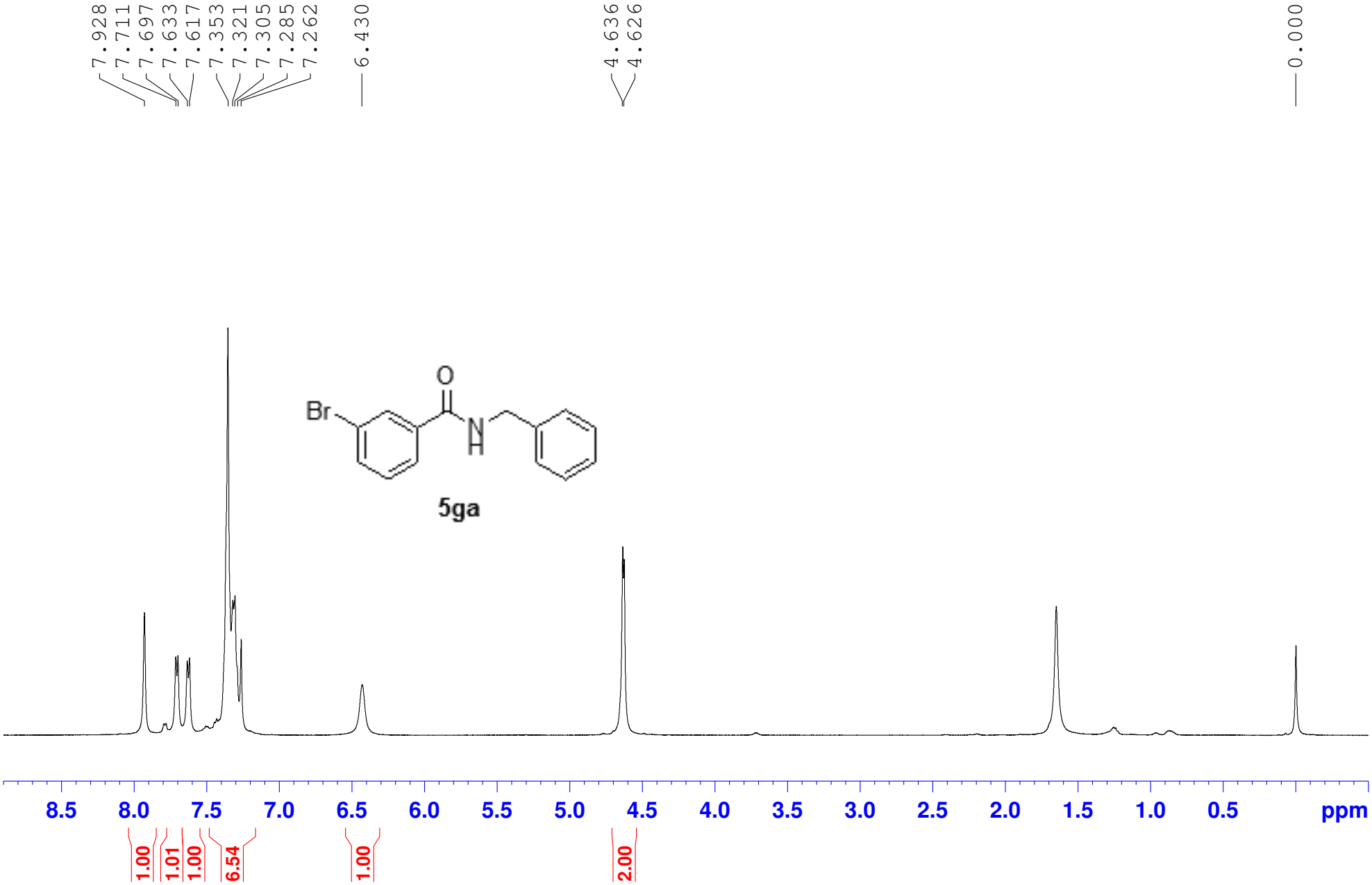
N-benzyl-3,4-dichlorobenzamide
Proton CDCl3



N-benzyl-3,4-dichlorobenzamide
C13CPD CDCl3

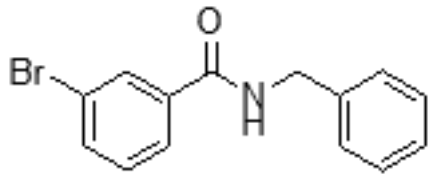


N-benzyl-3-bromobenzamide
Proton CDCl3



N-benzyl-3-bromobenzamide
C13CPD CDCl3

166.052
137.816
136.225
134.345
130.187
130.012
128.658
127.738
127.526
125.566
122.603
77.000
44.064



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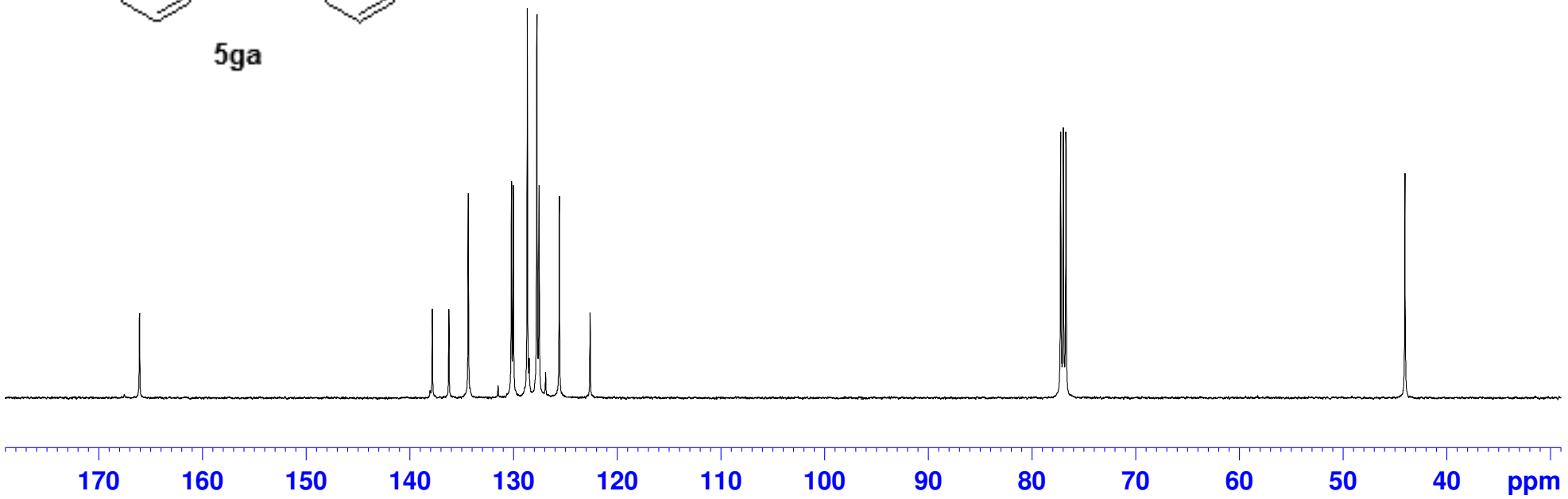
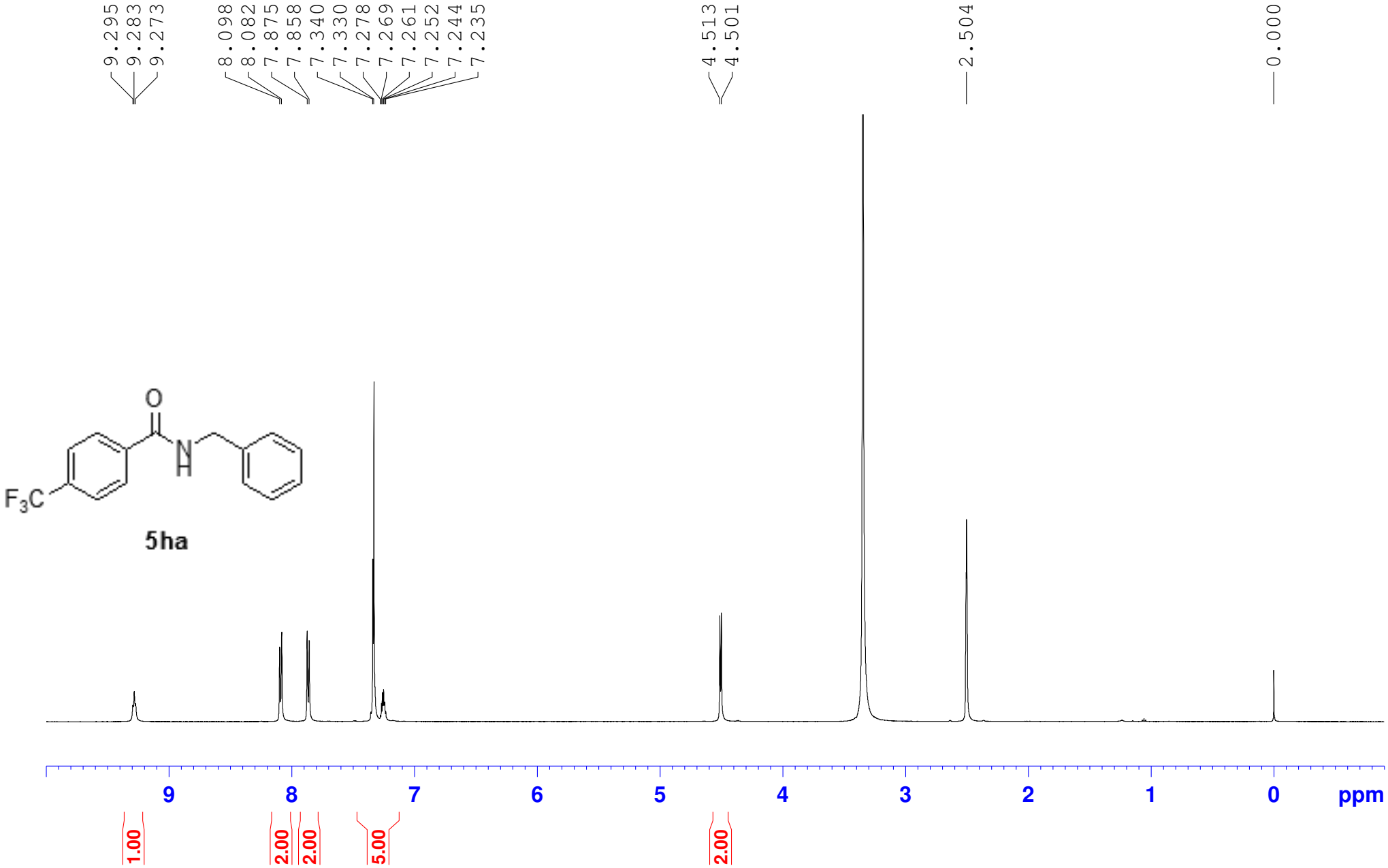
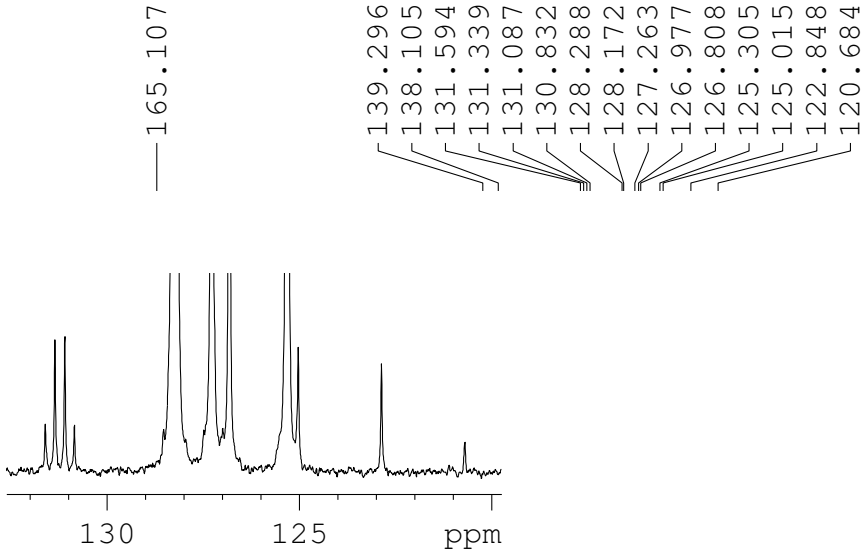


N-benzyl-4-(trifluoromethyl)benzamide
Proton DMSO-d6



N-benzyl-4-(trifluoromethyl)benzamide
C13CPD DMSO-d6



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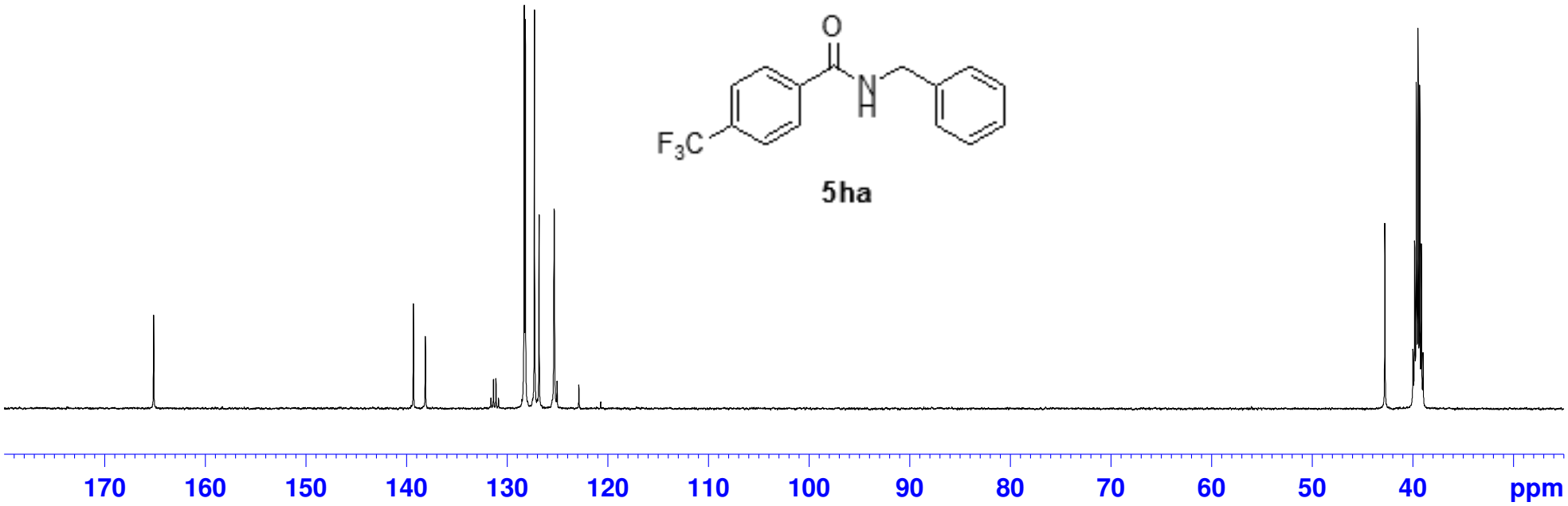
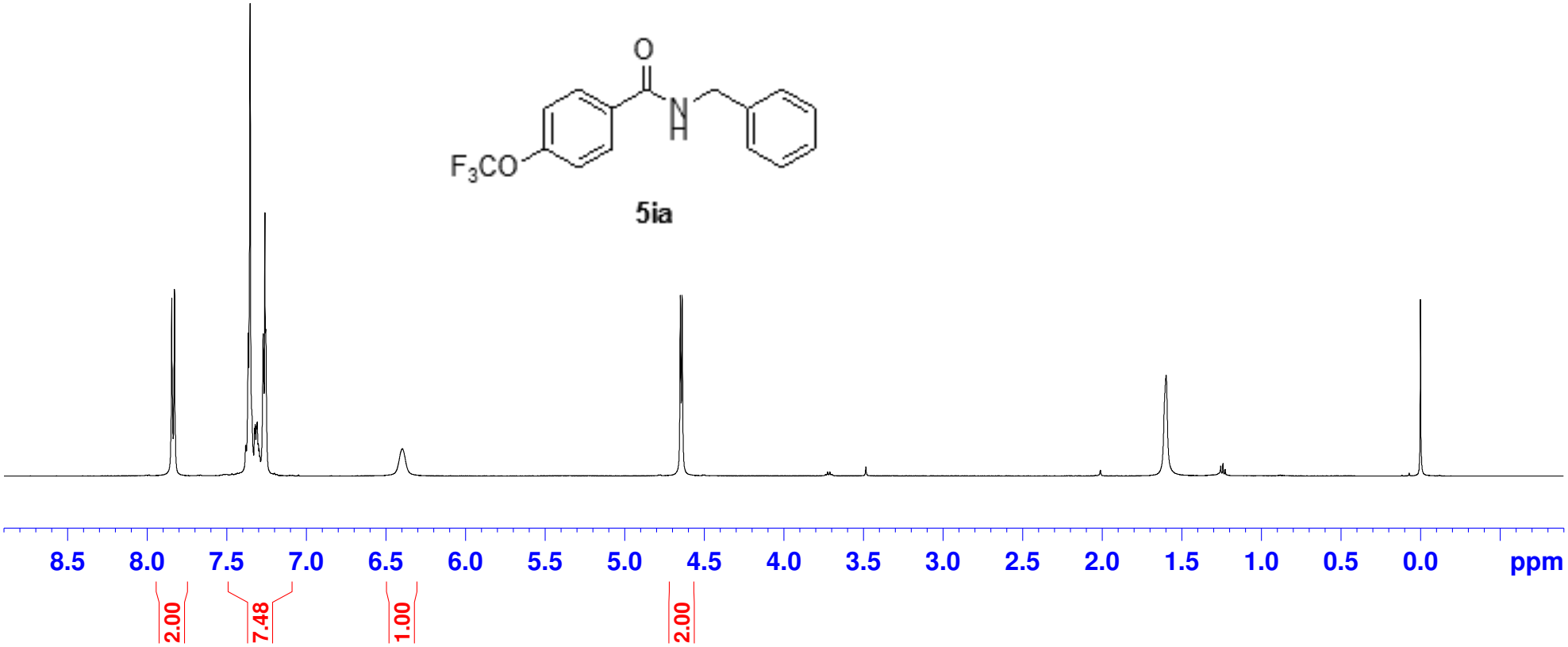


N-benzyl-4-(trifluoromethoxy)benzamide
Proton CDCl3

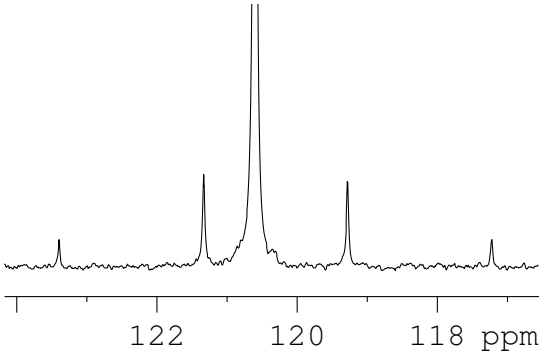
7.843
7.826
7.381
7.365
7.354
7.326
7.322
7.314
7.309
7.302
7.297
7.292
7.271
7.261
7.255
6.397
4.650
4.639
0.000

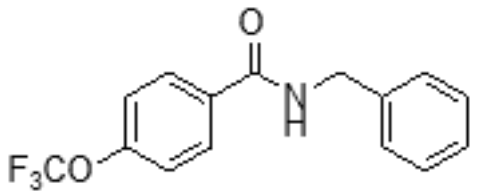
5ia



N-benzyl-4-(trifluoromethoxy)benzamide
C13CPD CDCl3

166.098
151.498
137.927
132.833
128.867
128.795
127.842
127.688
123.384
121.332
120.596
119.277
117.222
77.000
44.204





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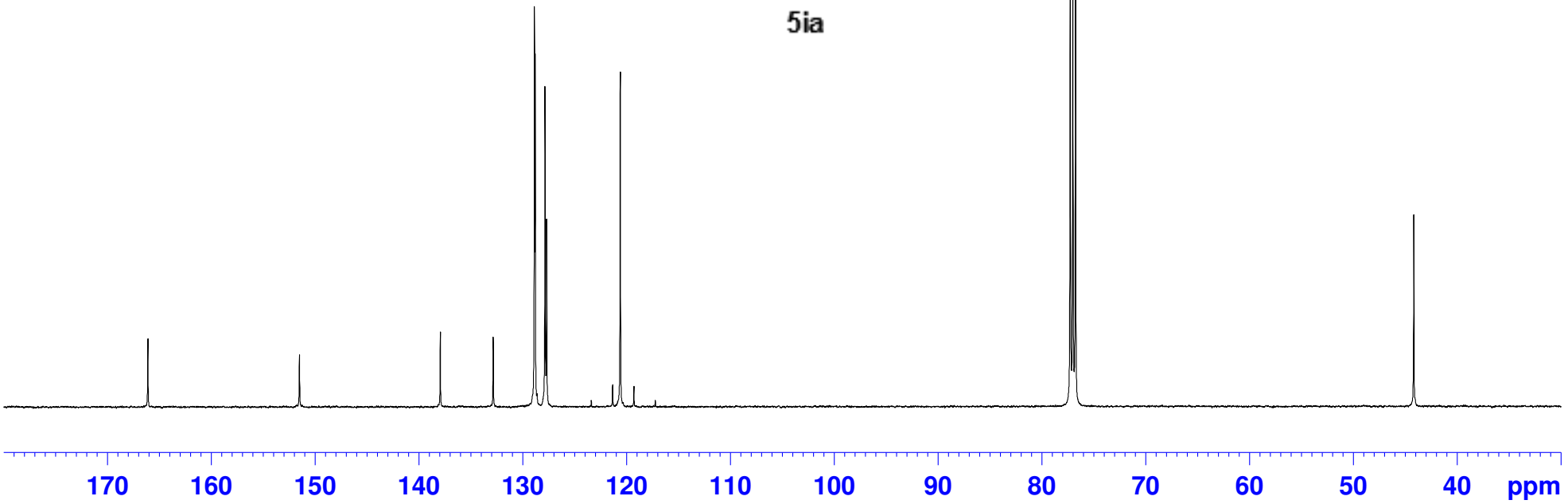
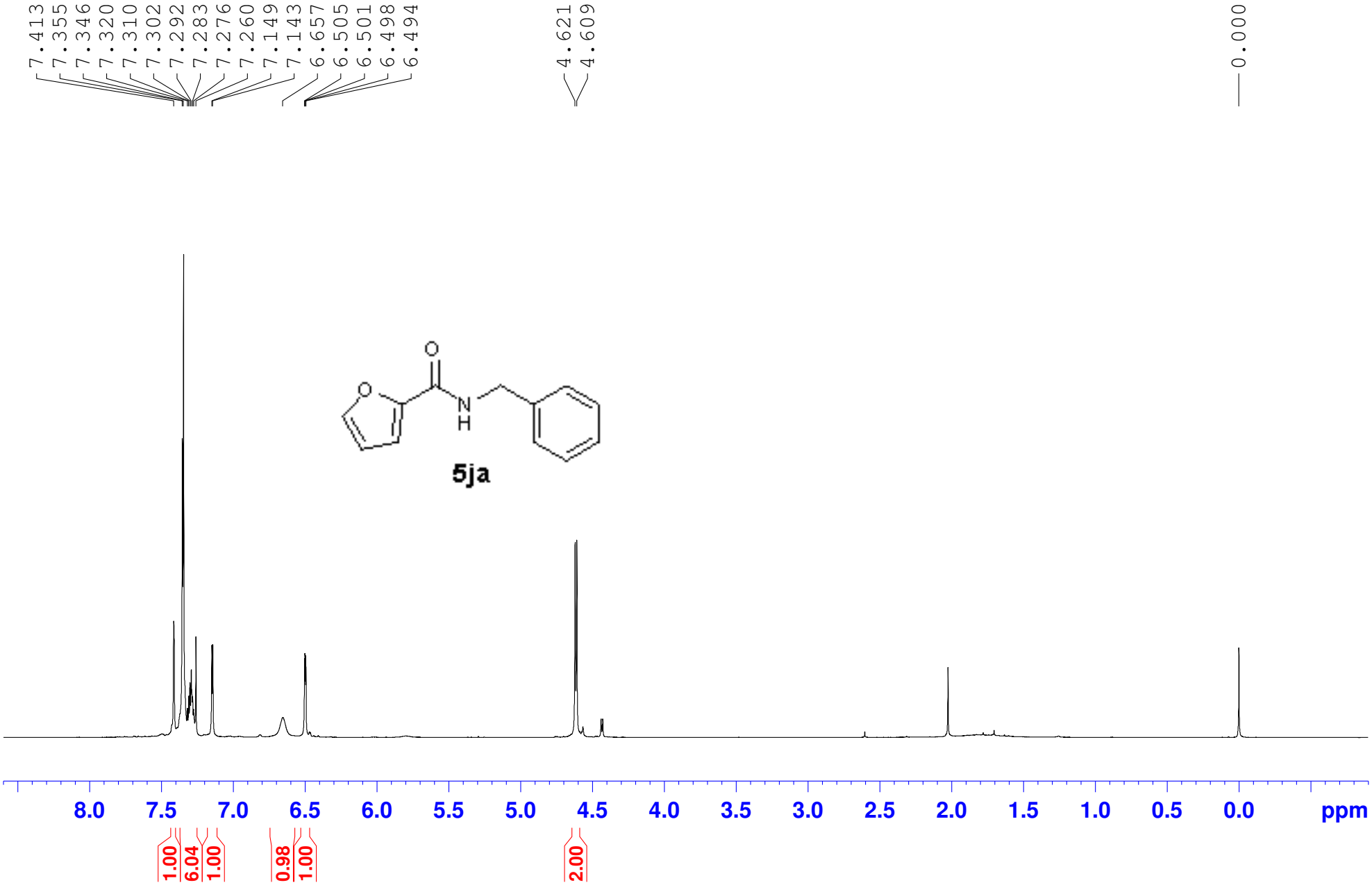
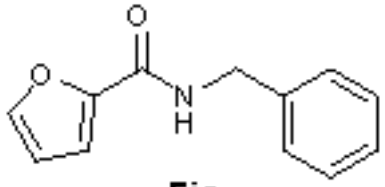


N-benzylfuran-2-carboxamide
Proton CDCl3



N-benzylfuran-2-carboxamide
C13CPD CDCl3

158.276
147.821
143.864
137.956
128.663
127.792
127.520
114.331
112.069
77.000
43.082



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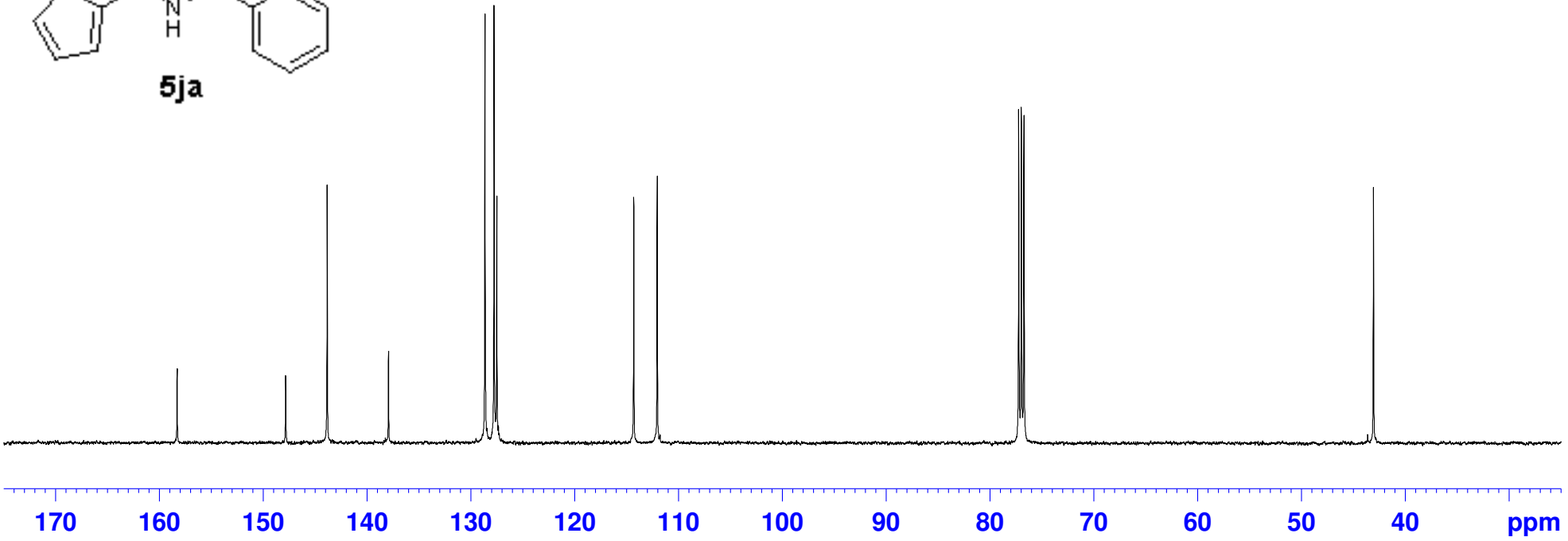
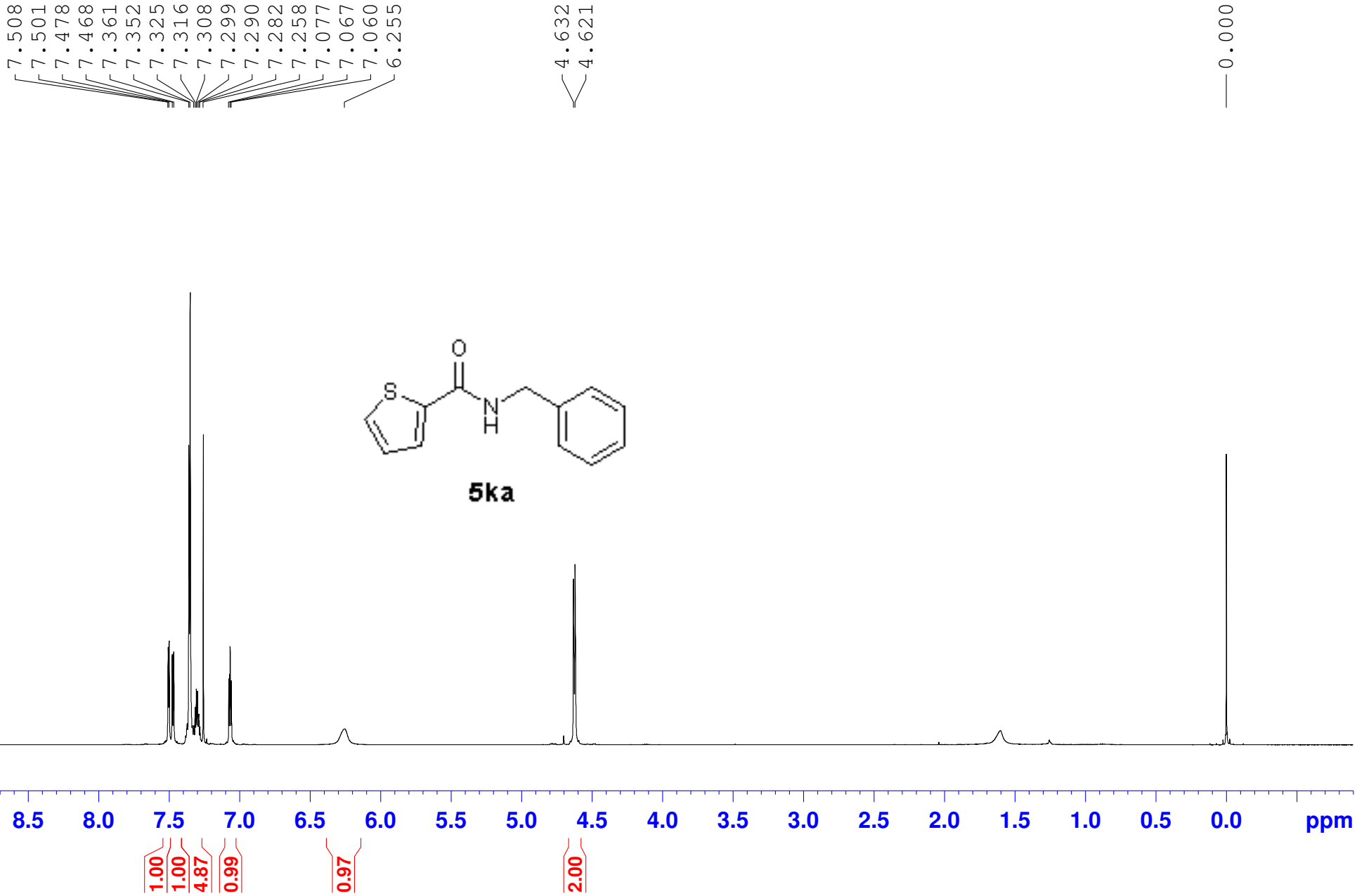
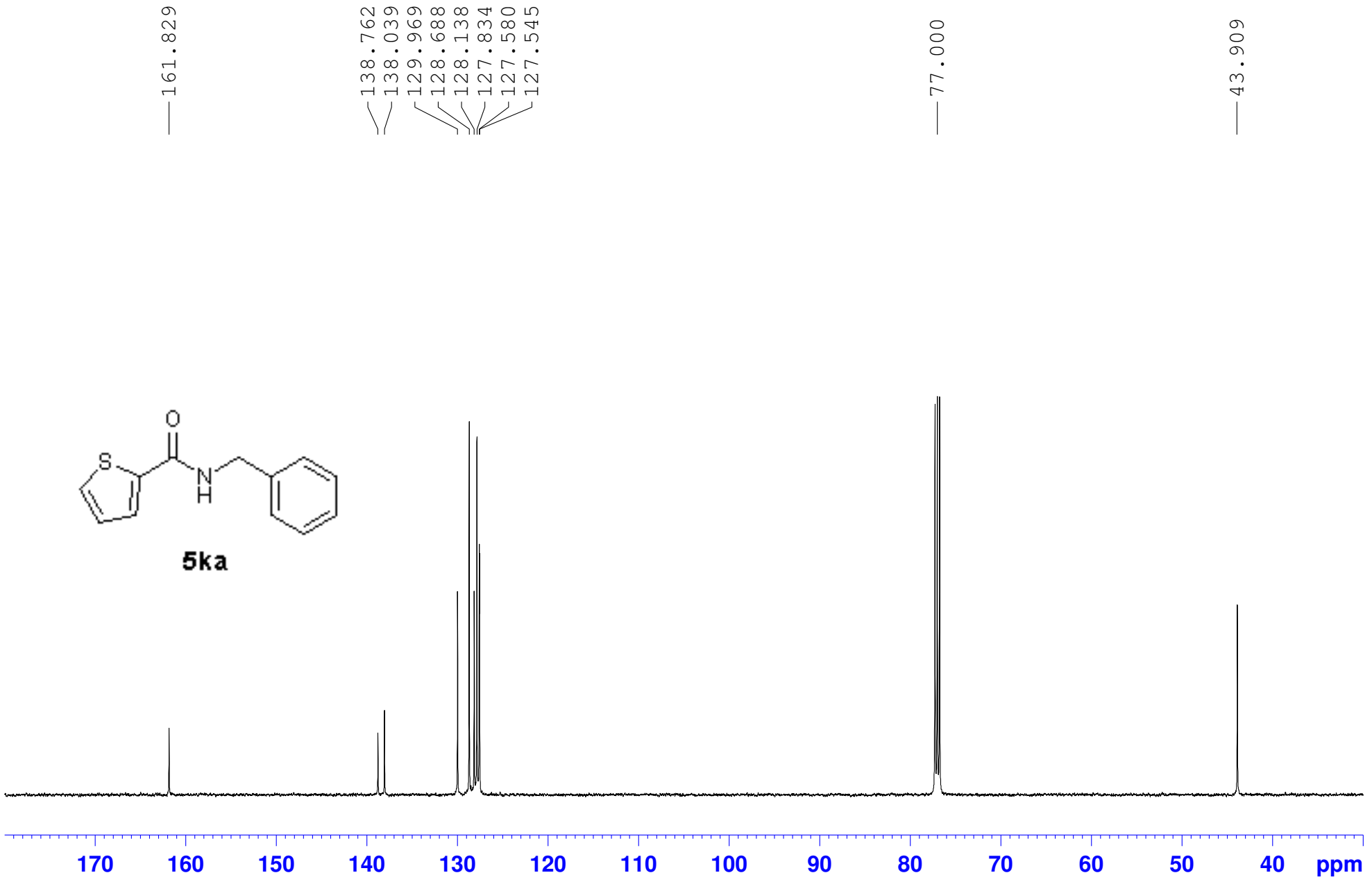


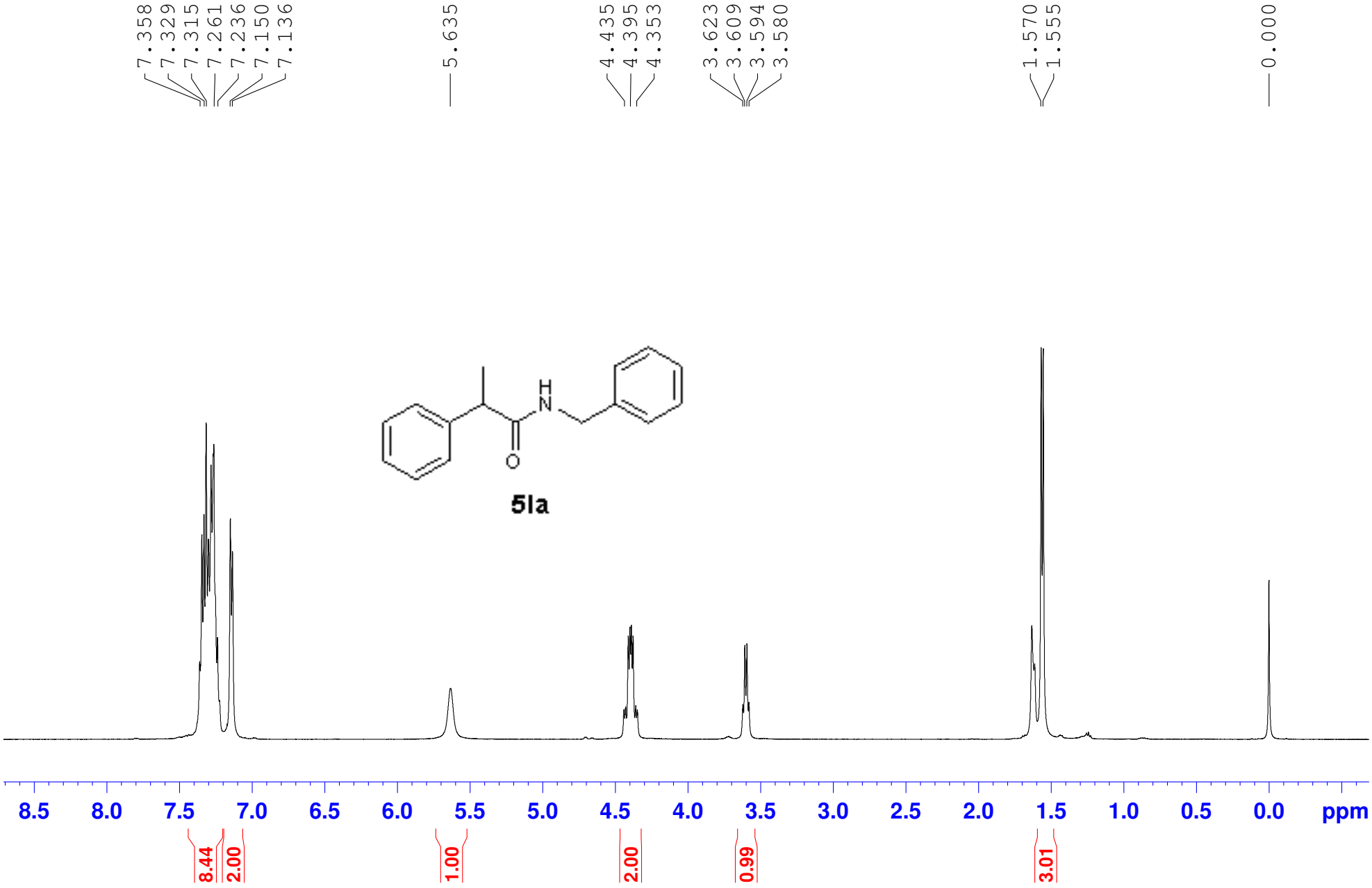
N-benzylthiophene-2-carboxamide
Proton CDCl3



N-benzylthiophene-2-carboxamide
C13CPD CDCl3

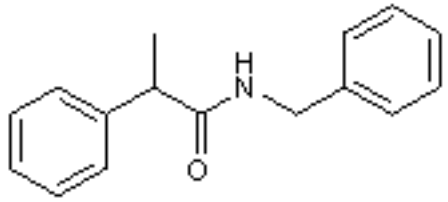


N-benzyl-2-phenylpropanamide
Proton CDCl3



N-benzyl-2-phenylpropanamide
C13CPD CDCl3

174.012
141.242
138.260
128.837
128.516
127.569
127.354
127.243
127.203
77.001
47.024
43.435
18.475



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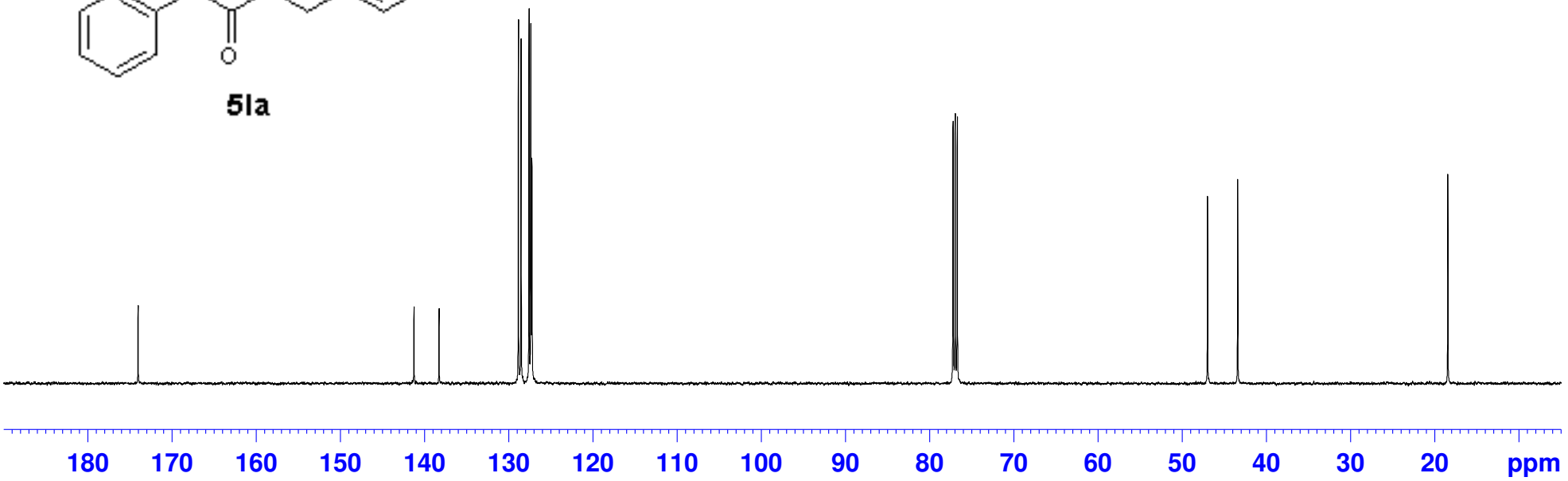
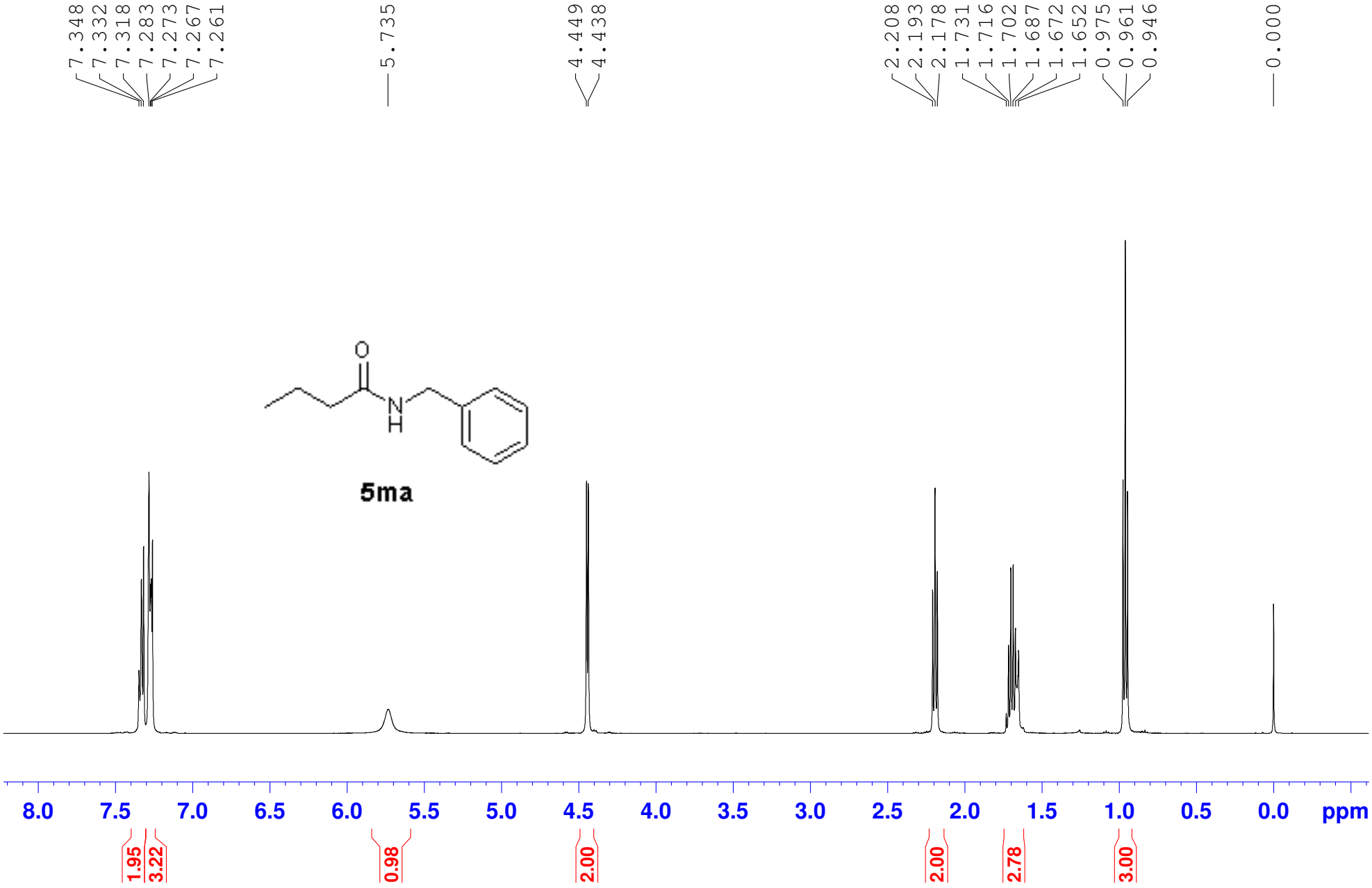


N-benzylbutyramide
Proton CDCl3



N-benzylbutyramide
C13CPD CDCl3