Supporting Information

Regioselective Copper-catalyzed Amination of Bromobenzoic Acids Using Aliphatic and Aromatic Amines

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Contents

1. Synthetic Procedures.

All commercially available reagents and solvents were used without further purification. NMR spectra were obtained at 300 MHz (^{1}H NMR) and 75 MHz (^{13}C NMR). Chemical shifts are reported in ppm relative to TMS. UV absorption and fluorescence spectra were collected under nitrogen using carefully degassed solvents. The excitation (emission) wavelength of **9** in degassed water was 390 (462) nm. The quantum yield of **9** was determined as 0.12 using degassed ethanol under inert atmosphere and a concentration range of 3.5 x 10^{-6} to 2.0 x 10^{-5} M.[1] *N*-(1-Pyrene)anthranilic acid was excited at 335 nm and relative integrated intensities of the emission spectra were compared to pyrene.

General Amination Procedure.

A mixture of aniline (9.3 mmol), 2-bromobenzoic acid (8.8 mmol), K_2CO_3 (8.8 mmol), Cu powder (0.2-0.3 micron, 0.8 mmol), Cu_2O (<5 micron, 0.4 mmol) and 3 ml of 2-ethoxyethanol was refluxed at 130 ^{o}C for 24 hours under nitrogen. The cooled reaction mixture was poured into 30 ml of water to which decolorized charcoal was added. The mixture was filtrated through Celite. The crude product was obtained by precipitation upon acidification of the filtrate with diluted HCl (pH was adjusted to 5 to 6). The solid residue was dissolved in 100 ml of 5% aqueous Na_2CO_3. The solution was filtered through Celite and the final product was obtained by precipitation as described above.

***N*-Phenylanthranilic acid** (**3**).[2] Anthranilic acid **3** was obtained from 2-bromobenzoic acid, **1** and aniline, **2** as a white solid in 86% yield. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 6.75 (dd, *J* = 7.9 Hz, 8.3 Hz, 1H), 7.13 (dd, *J* = 7.3 Hz, 8.6 Hz, 1H), 7.20-7.50 (m, 5H), 8.05

(d, *J* = 7.6 Hz, 1H), 9.33 (bs, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 111.0, 114.7, 117.8, 123.8, 124.7, 130.0, 133.2, 135.8, 140.9, 149.5, 174.3.

***N*-(1-Naphthyl)anthranilic acid** (**7**).[3] Anthranilic acid **7** was obtained from **1** and 1-aminonaphthalene, **4**, as an off-white solid in 97% yield. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 6.73 (dd, *J* = 7.3 Hz, 7.6 Hz, 1H), 6.85(d, *J* = 8.6 Hz, 1H), 7.23-7.29 (m, 1H), 7.46-7.51 (m, 4H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.89-7.92 (m, 1H), 8.08(m, 2H), 9.60 (bs, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ =110.5, 114.2, 117.5, 122.8, 123.5, 126.5, 126.5, 127.1, 129.1, 130.8, 133.1, 135.5, 136.0, 136.9, 151.2, 174.2.

***N*-(2-Naphthyl)anthranilic acid (8)**.[4] Anthranilic acid, **8**, was obtained from 2-bromobenzoic acid, **1**, and 2-naphthylamine, **5**, as a pale violet solid in 90% yield. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 6.85 (ddd, *J* = 2.0 Hz, 7.0 Hz, 9.0 Hz, 1H), 7.35-7.49 (m, 5H), 7.73 (d, *J* = 2.0 Hz, 1H), 7.79-7.90 (m, 3H), 7.98 (dd, *J* = 1.7 Hz, 7.9 Hz, 1H), 9.90 (bs, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ = 113.1, 114.2, 115.9, 117.8, 122.2, 124.3, 126.4, 126.8, 127.5, 129.2, 129.7, 131.9, 134.0, 134.2, 138.3, 146.7, 170.0.

***N*-(1-Pyrenyl)anthranilic acid** (**9**). Amination of 2-bromobenzoic acid, **1**, with 1-aminopyrene, **6**, afforded anthranilic acid **9** as an off-white solid in 55% yield. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 6.94 (dd, *J* = 7.4 Hz, 7.4 Hz, 1H), 7.14 (d, *J* = 8.3 Hz, 1H), 7.43 (dd, *J* = 8.0 Hz, 7.4 Hz, 1H), 8.09-8.41 (m, 10H), 10.7 (bs, 1H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 114.2, 118.1, 122.0, 122.1, 124.8, 124.9, 125.4, 125.7, 125.8, 126.4, 126.7, 127.2, 128.0, 128.2, 131.4, 131.7, 133.6, 134.6, 135.2, 148.8, 172.7. Anal. calcd. for $C_{23}H_{15}NO_2$: C, 81.88; H, 4.48; N, 4.15. Found: C, 81.63; H, 4.74; N, 4.32.

***N*-Phenyl-4-fluoroanthranilic acid (13).**[5] Anthranilic acid, **12**, was obtained from 2-bromo-4-fluorobenzoic acid, **10**, acid and aniline, **2**, as a pale violet solid in 82% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.48 (ddd, J = 2.4 Hz, 6.8 Hz, $J_{H,F}$ = 8.4 Hz, 1H), 6.85 (dd, J = 2.4 Hz, $J_{H,F}$ = 12.2 Hz, 1H), 7.23 (dd, J = 7.3 Hz, 7.3 Hz, 1H), 7.30 (dd, J = 1.2 Hz, 7.3 Hz, 2H), 7.44 (dd, J = 7.3 Hz, 7.3 Hz, 2H), 8.09 (dd, J = 6.8 Hz, $J_{H,F}$ = 9.0 Hz, 1H), 9.49 (bs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 98.7 (d, $J_{C,F}$ = 26.4 Hz), 104.0 (d, $J_{C,F}$ = 22.9 Hz), 122.8, 124.0, 128.6, 134.3 (d, $J_{C,F}$ = 11.8 Hz), 138.4, 150.5 (d, $J_{C,F}$ = 12.6 Hz), 166.6 (d, $J_{C,F}$ = 253.1 Hz), 172.1.

***N*-Phenyl-5-bromoanthranilic acid (14).** Anthranilic acid, **13**, was obtained from 2,5-dibromobenzoic acid, **11**, and aniline, **2**, as a light green solid in 84% yield. ^{1}H NMR (300 MHz, methanol-d_4) δ = 7.29-7.33 (m, 2H), 7.38-7.42 (m, 2H), 7.48-7.60 (m, 3H), 8.23 (d, J = 2.4 Hz, 1H), ^{13}C NMR (75 MHz, DMSO-d_6) δ = 108.3, 116.7, 122.1, 122.6, 124.4, 130.2, 134.3, 137.2, 140.7, 147.0, 169.4. Anal. Calcd for $C_{13}H_{10}BrNO_2$: C, 53.45; H, 3.45; N, 4.79. Found: C, 53.02; H, 3.92; N, 4.47.

***N*-Phenyl-4-chloroanthranilic acid (15)**.[6] Anthranilic acid, **15**, was obtained from 2-bromo-4-chlorobenzoic acid, **12**, and aniline, **2**, as a slightly green solid in 94% yield.^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.70 (dd, J = 2.0 Hz, 8.8 Hz, 1H), 7.13 (d, J = 2.0 Hz, 1H), 7.17-7.28 (m, 3H), 7.39 (dd, J = 8.1 Hz, 8.1 Hz, 2H), 7.96 (d, J = 8.5 Hz, 1H), 9.35 (bs, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ = 107.4, 112.3, 116.4, 122.8, 124.0, 128.7, 132.9, 138.4, 140.8, 148.9, 172.0.

***N*-(3-Chlorophenyl)anthranilic acid** (**23**).[7] Amination of **1** with 3-chloroaniline, **16**, gave anthranilic acid **23**, as an off-white solid in 84% yield. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 6.82 (dd, J = 7.3 Hz, 7.6 Hz, 1H), 7.08 (d, J = 7.8 Hz, 1H), 7.14 (d, J = 7.8 Hz, 1H), 7.26-7.30 (m, 3H), 7.40 (dd, J = 7.6 Hz, 7.8 Hz, 1H), 8.06 (d, J = 7.3 Hz, 1H), 9.32 (bs,

1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 114.2, 114.7, 118.5, 118.8, 119.9, 122.1, 130.9, 132.0, 133.9, 134.0, 142.6, 145.8, 169.9.

***N*-(3-Bromophenyl)anthranilic acid (24).**[8] Anthranilic acid, **24**, was obtained from 2-bromobenzoic acid, **1**, and 3-bromoaniline, **17**, as a brown solid in 81% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.82 (ddd, *J* = 1.0 Hz, 7.6 Hz, 7.6 Hz, 1H), 7.18-7.28 (m, 4H), 7.39 (dd, *J* = 1.7 Hz, 7.7 Hz, 1H), 7.43 (d, *J* = 1.5 Hz, 1H), 8.06 (dd, *J* = 1.5 Hz, 8.1 Hz, 1H), 9.31 (bs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 111.9, 115.1, 118.8, 121.6, 123.7, 125.9, 127.4, 131.4, 133.4, 136.0, 142.7, 148.5, 173.9.

***N*-(4-Methoxyphenyl)anthranilic acid** (**25**).[9] Anthranilic acid **25** was obtained from **1** and 4-methoxyaniline, **18**, as a white powder in 88% yield. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 3.83 (s, 3H), 6.68 (dd, *J* = 7.3 Hz, 7.3 Hz, 1H), 6.93 (dd, *J* = 8.6 Hz, 8.6 Hz 3H), 7.18 (d, *J* = 8.6 Hz, 2H), 7.26-7.32 (m, 1H), 8.0 (d, *J* = 8.6 Hz, 1H)), 9.60 (bs, 1H). ^{13}C-NMR (75 MHz, DMSO-d_6) δ = 55.2, 111.4, 112.8, 114.8, 116.3, 125.1, 131.9, 133.0., 134.2, 148.9, 156.1, 170.2.

***N*-(4-Nitrophenyl)anthranilic acid** (**26**).[9] Anthranilic acid **26** was produced from **1** and 4-nitroaniline, **19**, as a yellow solid in 53% yield. ^{1}H-NMR (300 MHz, CD_3OD) δ = 7.22 (dd, *J* = 7.1 Hz, 7.8 Hz, 1H), 7.50 (m, 2H), 7.68-7.78 (m, 2H), 8.26 (d, *J* = 8.1 Hz, 1H), 8.36-8.36 (m, 2H). ^{13}C-NMR (75 MHz, CD_3OD) δ = 118.1, 118.2, 118.8, 122.2, 127.1, 133.7, 135.3, 142.6, 145.4, 150.0, 171.5.

***N*-(4-Carboxyphenyl)anthranilic acid** (**27**).[10] Anthranilic acid **27** was obtained from 2-bromobenzoic acid, **1**, and 4-aminobenzoic acid, **20**, using two equivalents of K_2CO_3 as a white solid in 80% yield. ^{1}H-NMR (300 MHz, CD_3OD) δ = 7.00-7.06 (m, 1H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.56-7.59 (m, 2H), 7.98 (d, *J* = 8.8 Hz, 2H), 8.04 (d, *J* = 8.3 Hz, 1H), 9.91

(bs, 1H). ^{13}C-NMR (75 MHz, CD_3OD) δ = 115.3, 116.2, 117.9, 119.6, 123.5, 131.2, 132.0, 134.1, 144.6, 145.6, 167.1, 169.7.

***N*-(4-Hydroxyphenyl)anthranilic acid (28).**[11] Anthranilic acid, **28**, was obtained from 2-bromobenzoic acid, **1**, and 4-aminophenol, **21**, as a violet solid in 63% yield. ^{1}H NMR (300 MHz, methanol-d_4) δ = 6.81 (ddd, *J* = 1.0 Hz, 7.6 Hz, 7.6 Hz, 1H), 6.97-7.01 (m, 2H), 7.08 (dd, *J* = 1.2 Hz, 8.8 Hz, 1H), 7.21-7.27 (m, 2H), 7.43 (ddd, *J* = 1.7 Hz, 7.7 Hz, 7.9 Hz, 1H), 8.11 (dd, *J* = 1.7 Hz, 8.1 Hz, 1H). ^{13}C NMR (75 MHz, methanol-d_4) δ = 112.5, 114.4, 117.2, 117.3, 127.4, 133.4, 134.0, 135.4, 151.7, 156.0, 172.4.

***N*-(4-Cyanophenyl)anthranilic acid (29).**[12] Anthranilic acid, **29**, was obtained from 2-bromobenzoic acid, **1**, and 4-aminobenzonitrile, **22**, as a yellow solid in 71% yield. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 7.13 (ddd, *J* = 2.0 Hz, 7.1 Hz, 7.2 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.61-7.68 (m, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 8.22 (d, *J* = 7.3 Hz, 1H), ^{13}C NMR (75 MHz, methanol-d_4) δ = 104.4, 117.9, 119.5, 120.7, 121.5, 133.7, 135.1, 145.8, 147.9, 171.9.

***N*-Phenyl-5-carboxyanthranilic acid (30).** Anthranilic acid, **30**, was obtained from 4-bromoisophthalic acid, **26**, and aniline, **2**, as an off-white solid in 99% yield. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 7.25-7.29 (m, 2H), 7.40 (d, *J* = 7.8 Hz, 2H), 7.51 (dd, *J* = 7.3 Hz, 7.8 Hz, 2H), 7.96 (dd, *J* = 2.2 Hz, 8.8 Hz, 1H), 8.62 (d, *J* = 2.2 Hz, 1H), 10.35 (bs, 1H). ^{13}C NMR (75 MHz, methanol-d_4) δ = 112.4, 113.9, 119.7, 124.9, 126.3, 130.9, 136.4, 136.5, 140.9, 153.3, 169.8, 171.6. Anal. Calcd $C_{14}H_{11}NO_4$: C, 65.37; H, 4.31; N, 5.44. Found: C, 65.07; H, 4.39; N, 5.35.

***N*-(2,6-Dimethylphenyl)anthranilic acid (34).**[13] Amination of **1** with 2,6-dimethylaniline, **31**, afforded acid **34** as a white powder in 68% yield. ^{1}H-NMR (300

MHz, $CDCl_3$) δ = 2.21 (s, 6H), 6.22 (d, *J* = 8.5 Hz, 1H), 6.66 (dd, *J* = 7.1 Hz, 7.1 Hz, 1H), 7.10-7.20 (m, 3H), 7.24 (dd, *J* = 7.6 Hz, 7.8 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 8.88 (bs, 1H). ^{13}C-NMR (75 MHz, CD_3OD) δ = 18.5, 112.0, 115.7, 126.3, 128.3, 132.8, 134.1, 135.6, 135.9, 137.0, 149.9, 173.8.

***N*-(2-*tert*-Butylphenyl)anthranilic acid** (**35**).[14] Anthranilic acid **35** was produced from 2-bromobenzoic acid, **1**, and 2-*tert*-butylaniline, **32**, as white crystals in 53% yield. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.41 (s, 9H), 6.65 (dd, *J* = 7.0 Hz, 7.9 Hz, 1H), 7.15 (d, *J* = 8.6 Hz, 1H), 7.17-7.28 (m, 4H), 7.47-7.50 (m, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 9.21 (bs, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 31.3, 35.7, 110.0, 114.8, 116.7, 126.6, 127.6, 128.1, 129.8, 133.1, 135.9, 139.4, 147.1, 151.4, 173.7.

***N*-(2-*Iso*propylphenyl)anthranilic acid** (**36**).[15] Amination of 2-bromobenzoic acid with 2-isopropylaniline, **333**, gave anthranilic acid **36** as a white powder in 78% yield. ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 1.22 (d, *J* = 6.9 Hz, 6H), 3.21 (sept, *J* = 6.9 Hz, 1H), 4.68 (bs, 1H), 6.68 (dd, *J* = 7.2 Hz, 7.4 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 7.22-7.40 (m, 4H), 8.1 (dd, *J* = 1.7 Hz, 8.2 Hz, 1H), 9.18 (bs, 1H). ^{13}C-NMR (75 MHz, DMSO-d_6) δ = 23.6, 28.4, 112.0, 113.6, 117.0, 125.7, 126.1, 127.1, 127.3, 132.5. 135.0, 137.9, 143.6, 149.8, 171.0.

***N*-Phenyl-3-methylanthranilic acid (38).**[16] Anthranilic acid, **38**, was obtained from 2-bromo-3-methylbenzoic acid, **37**, and aniline, **2**, as an off-white solid in 58% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.07 (s, 3H), 6.75 (dd, *J* = 1.0 Hz, 8.6 Hz, 2H), 6.93 (dd, *J* = 7.3 Hz, 8.1 Hz, 1H), 7.08 (dd, *J* = 7.6 Hz, 7.6 Hz, 1H), 7.22 (ddd, *J* = 1.0 Hz, 7.6 Hz, 8.6 Hz, 2H), 7.39 (dd, *J* = 1.2 Hz, 7.3 Hz, 1H), 8.00 (dd, *J* = 1.2 Hz, 8.1 Hz, 1H). ^{13}C

NMR (75 MHz, $CDCl_3$) δ = 19.5, 118.2, 120.6, 121.4, 122.8, 129.1, 130.2, 133.4, 137.2, 144.2, 144.3, 172.4.

***N*-Benzylanthranilic acid (42).**[17] Anthranilic acid, **42**, was obtained from 2-bromobenzoic acid, **1**, and benzylamine, **39**, as a white solid in 82% yield after chromatographic purification on silica gel using 40% ethyl acetate in hexanes as the mobile phase. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.48 (s, 2H), 6.18 (dd, *J* = 8.3 Hz, 8.3 Hz, 2H), 7.26-7.35 (m, 6H), 7.98 (dd, *J* = 1.2 Hz, 7.8 Hz, 1H), 8.05 (bs, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ = 46.9, 109.0, 111.9, 115.1, 126.9, 127.2, 128.7, 132.6, 135.6, 138.7, 151.6, 173.5.

***N*-Phenylethylanthranilic acid (43).**[18] Anthranilic acid, **43**, was obtained from 2-bromobenzoic acid, **1**, and phenethylamine, **40**, as a yellow solid in 91% yield after chromatographic purification on silica gel using 40% ethyl acetate in hexanes as the mobile phase. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.98 (t, *J* = 7.1, 2H), 3.47 (t, *J* = 7.1 Hz, 2H), 6.60 (ddd, *J* = 1.0 Hz, 7.1 Hz, 9.5 Hz, 1H), 6.71 (d, *J* = 8.6 Hz, 1H), 7.22-7.42 (m, 6H), 8.00 (dd, *J* = 1.7 Hz, 8.1 Hz, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ = 35.9, 44.8, 109.1, 111.7, 115.1, 126.9, 129.0, 129.2, 133.1, 136.0, 139.4, 151.9, 174.7.

***N*-Cyclohexylanthranilic acid (44)**.[19] Anthranilic acid, **44**, was obtained from 2-bromobenzoic acid, **1**, and cyclohexylamine, **41**, as a slightly yellow solid in 65% yield after chromatographic purification on silica gel using 40% ethyl acetate in hexanes as the mobile phase. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.28-1.44 (m, 5H), 1.62-1.65 (m, 1H), 1.76-1.80 (m, 2H), 2.02-2.05 (m, 2H), 3.35-3.43 (m, 1H), 6.56 (ddd, *J* = 1.0 Hz, 8.1 Hz, 8.6 Hz, 1H), 6.71 (d, *J* = 8.6 Hz, 1H), 7.34 (ddd, *J* = 1.7 Hz, 8.1 Hz, 8.6 Hz, 1H), 7.98

(dd, J = 1.7 Hz, 8.1 Hz, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ = 25.0, 26.1, 33.2, 50.9, 108.6, 112.1, 114.4, 133.2, 135.8, 151.3, 174.7.

2. UV, Fluorescence and Single Crystal Analysis Data of Anthranilic Acid 9.

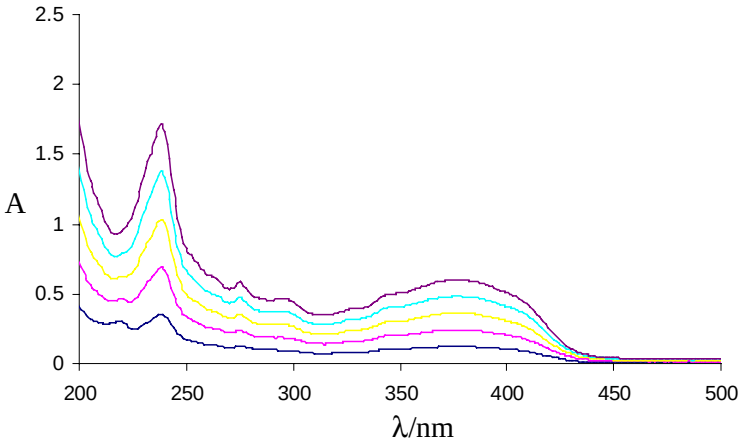
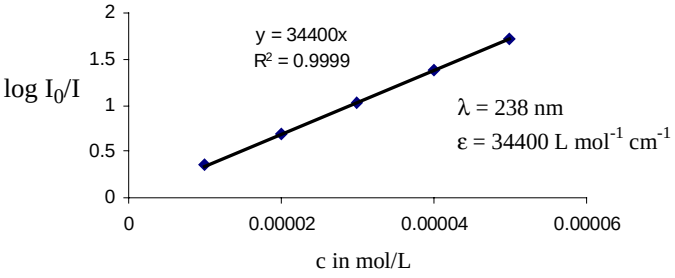


Figure 1. UV spectra of **9** at 10^{-5} M, 2.0 x 10^{-5} M, 3.0 x 10^{-5} M, 4.0 x 10^{-5} M, 5.0 x 10^{-5} M in 3.0 x 10^{-4} K_2CO_3.

The extinction coefficients of **9** at 238 and 378 nm in 3.0 x 10^{-4} K_2CO_3 were determined as 34400 L x mol^{-1} x cm^{-1} and 12009 L x mol^{-1} x cm^{-1}, respectively.



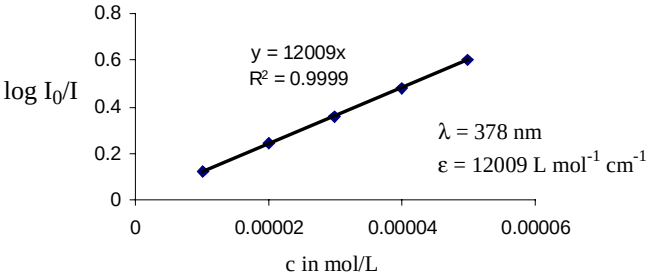


Figure 2. Determination of extinction coefficients of **9**.

Addition of 2.5 10^{-5} to 1.25 10^{-4} M of Hg(II) to a 25 μM solution of **9** in 3 x 10^{-4} M K_3PO_4 (pH = 8.0) showed fluorescence quenching in accordance with the Benesi-Hildebrand equation (1) derived for a 1:1 complex, Figures 3 and 4.[20] Benesi-Hildebrand plotting gave an association constant for Hg(II)-**9** of 1262 M^{-1}

$$\frac{I_0}{I-I_0} = \frac{b}{a-b}\left\{\frac{1}{K[\mathrm{M}]} + 1\right\} \quad (1)$$

where I_0 is the inherent fluorescence intensity of **9**, I is the fluorescence intensity in presence of an analyte, [M] is the analyte concentration, and K is the association constant, a and b are constants.

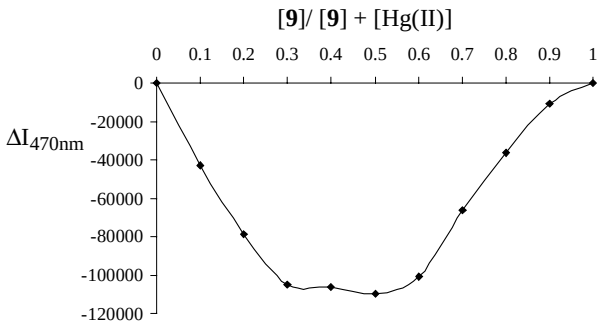


Figure 3. Job plot of $HgCl_2$ and **9** recorded at 470 nm in aqueous 3 x 10^{-4} M K_3PO_4 solution (pH = 8.0). The sum of concentrations was fixed at 80.0 μM.

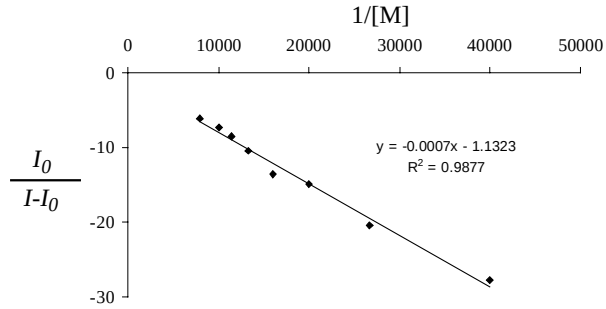


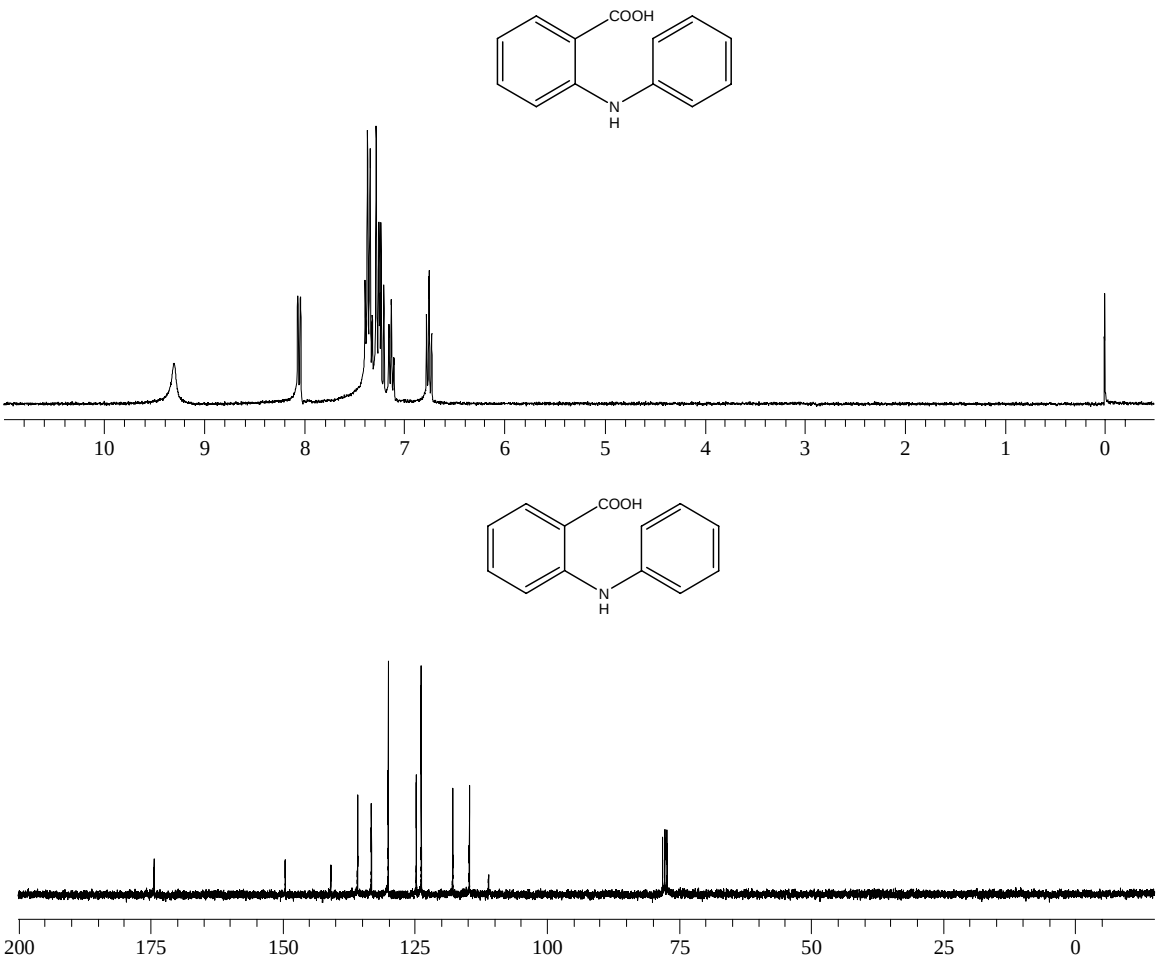
Figure 4. Benesi-Hildebrand plot of **9** in the presence of Hg(II). The concentration of **9** was 25.0 μM. The concentration of Hg(II) was 0.0, 25.0, 37.5, 50.0, 62.5, 75.0, 87.6, 100.0, and 125.0 μM. Excitation (emission) wavelength: 390 nm (460 nm).

X-ray Single-Crystal Structure Analysis.

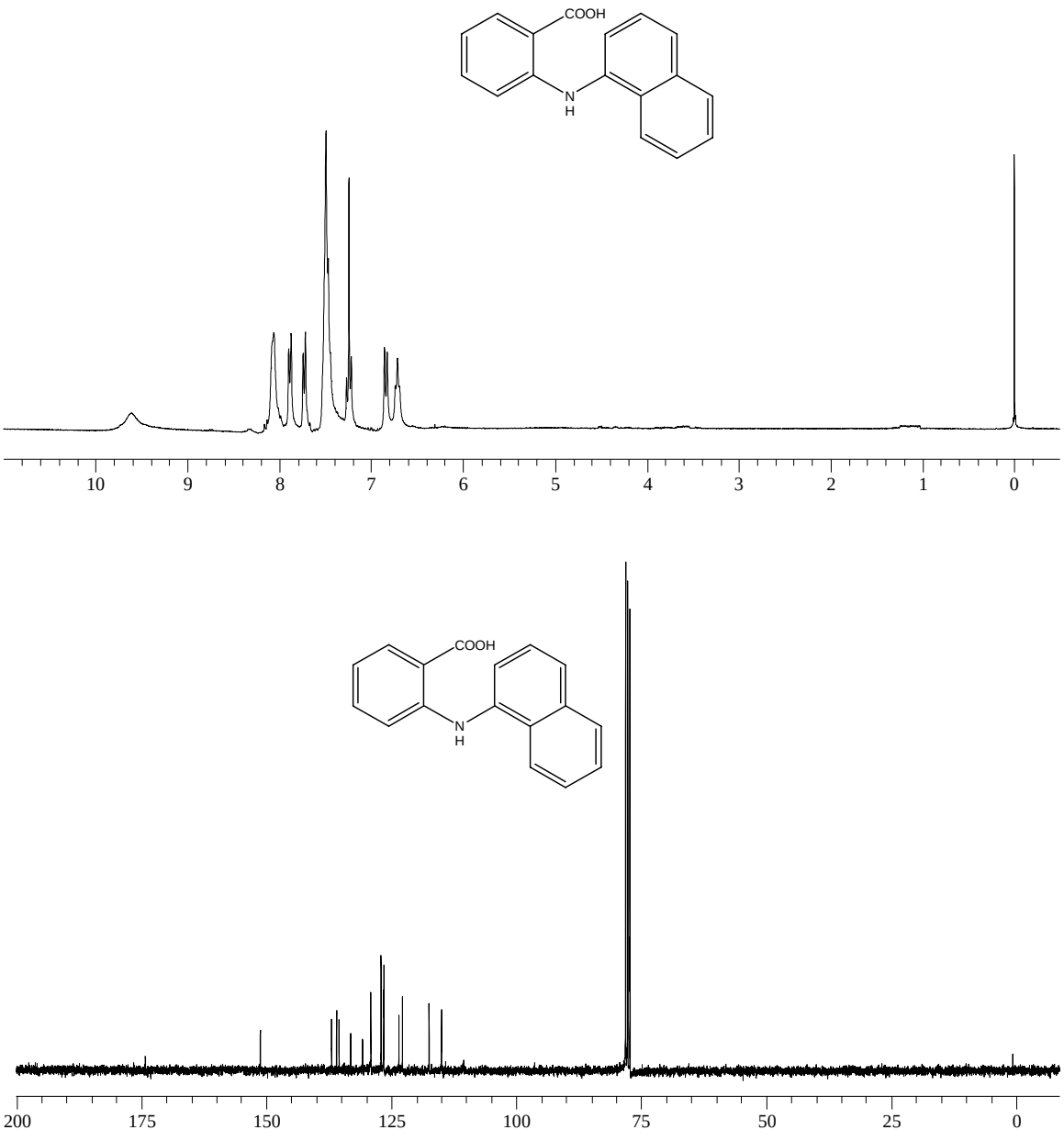
Single crystal X-ray diffractions of **9** were performed at 173 K by using a Siemens platform diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). $2\theta_{max}$ = 54.0°, 4593 independent reflections (R_{int} = 2.68 %), of which 3121 were above 4σ(*F*). R1 = 0.0593, wR2 = 0.1393 with I > 2σ(I), R_{σ} = 0.0372, GooF = 1.091, $\Delta\rho_{max}$ = 0.28 e $Å^{-3}$, $\Delta\rho_{min}$ = -0.24 e $Å^{-3}$. Data were integrated with the Siemens SAINT program and corrected for the affects of absorption using SADABS. The structure was solved by direct methods and refined with full-matrix least-squares analysis using SHELX-97-2 software. Non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms were placed in calculated positions and refined with a riding model. Crystallographic data for **9** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 261130. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, United Kingdom (Fax: 44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

3. NMR spectra of *N*-aryl anthranilic acids

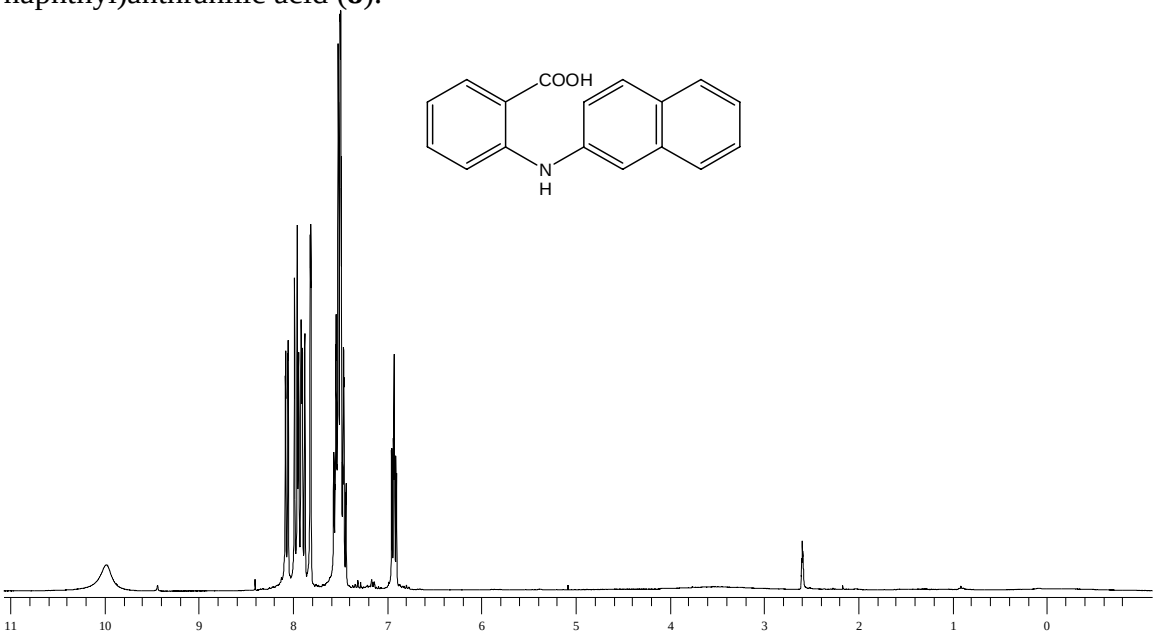
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) of *N*-phenylanthranilic acid (**3**).

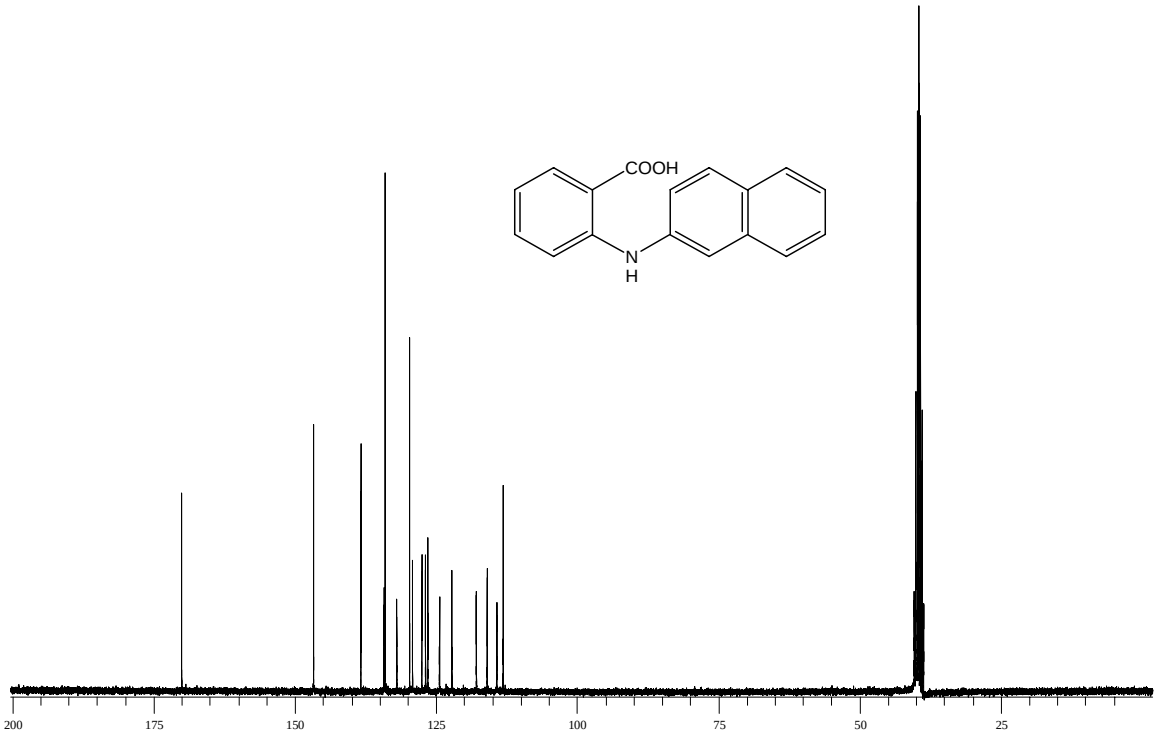


^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) of *N*-(1-naphthyl)anthranilic acid (**7**).

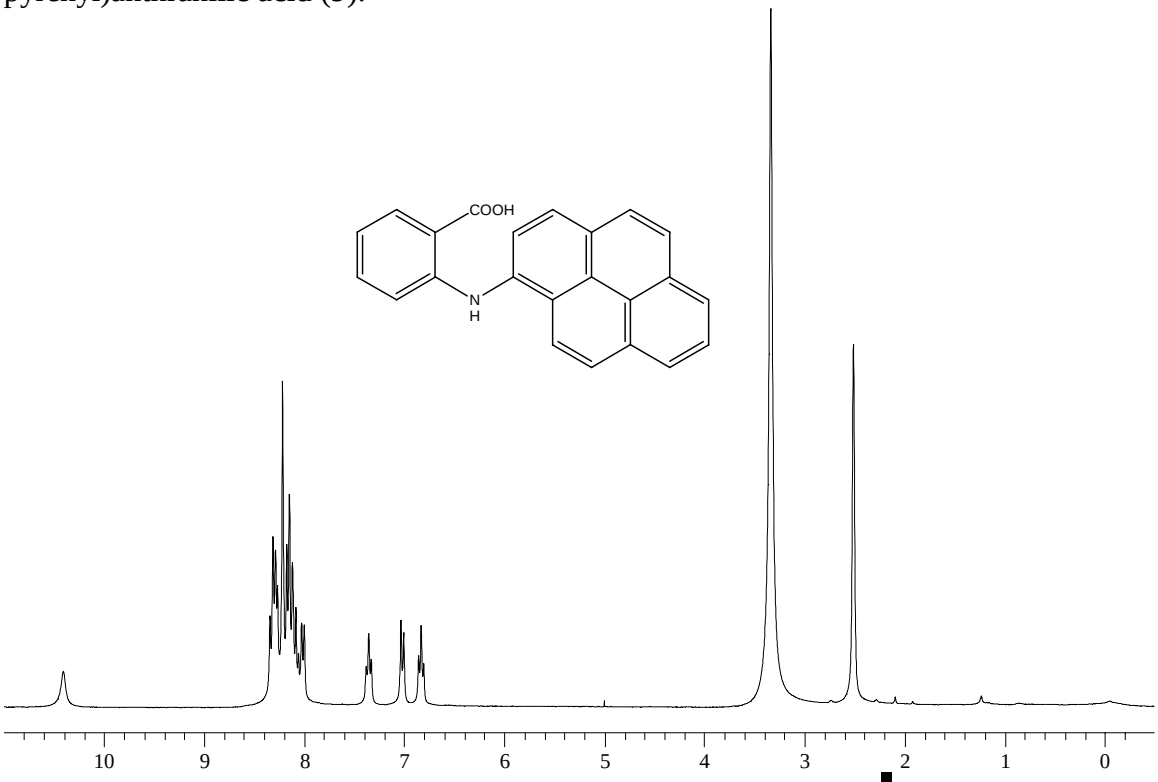


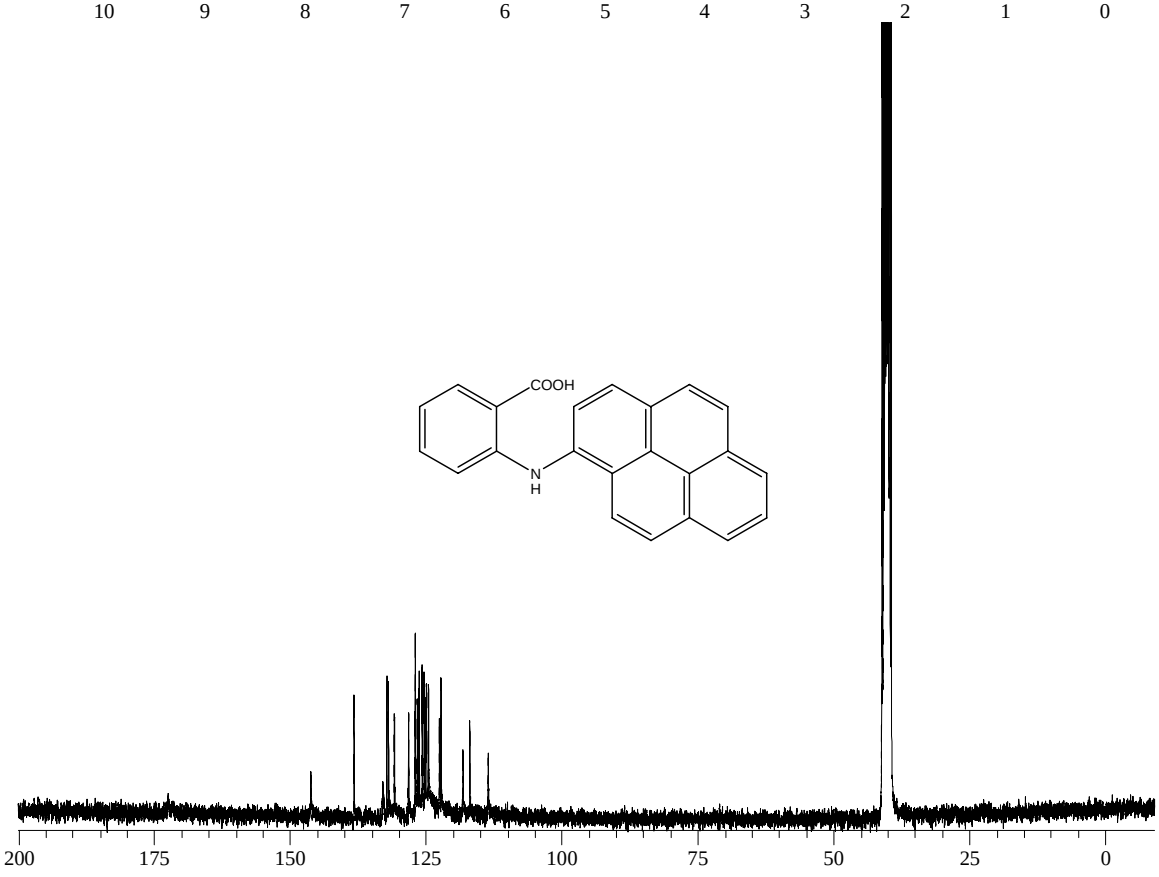
^{1}H-NMR (300 MHz, DMSO-d_6) and ^{13}C-NMR (75 MHz, DMSO-d_6) of *N*-(2-naphthyl)anthranilic acid (**8**).



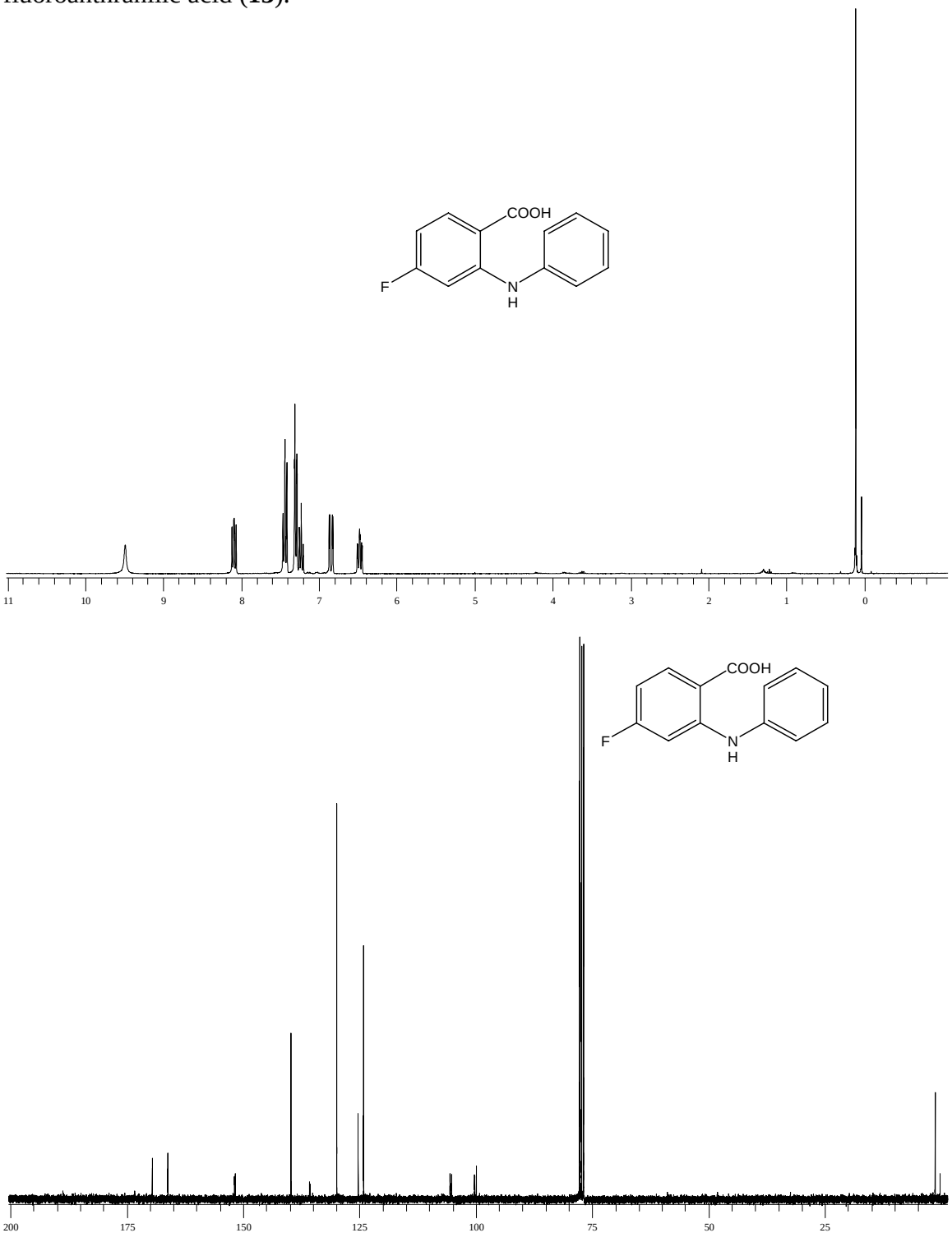


^{1}H-NMR (300 MHz, DMSO-d_6) and ^{13}C-NMR (75 MHz, DMSO-d_6) of *N*-(1-pyrenyl)anthranilic acid (**9**).

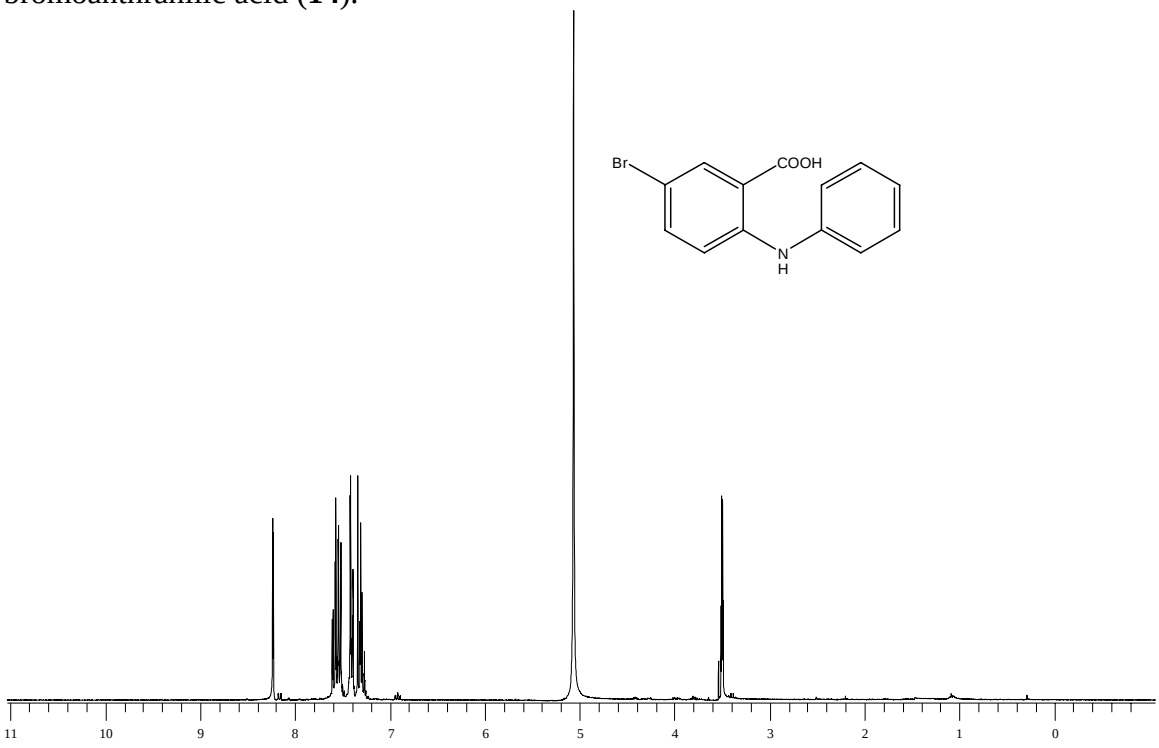


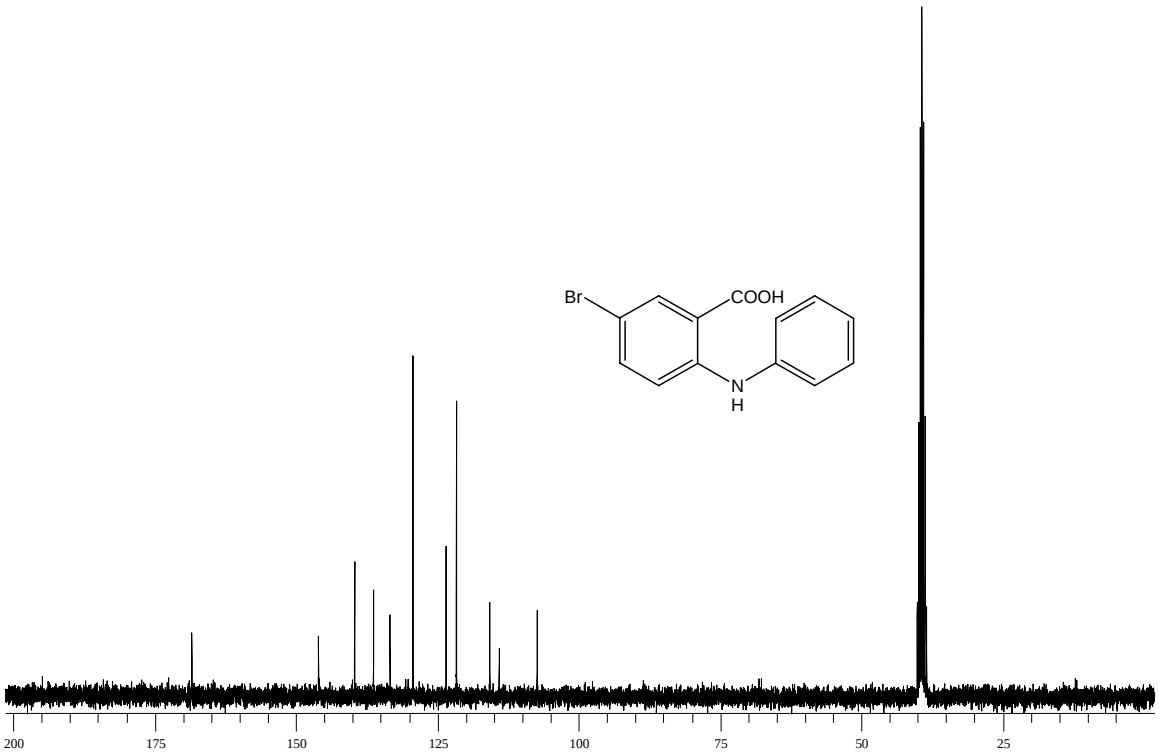


^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) of *N*-phenyl-4-fluoroanthranilic acid (**13**).

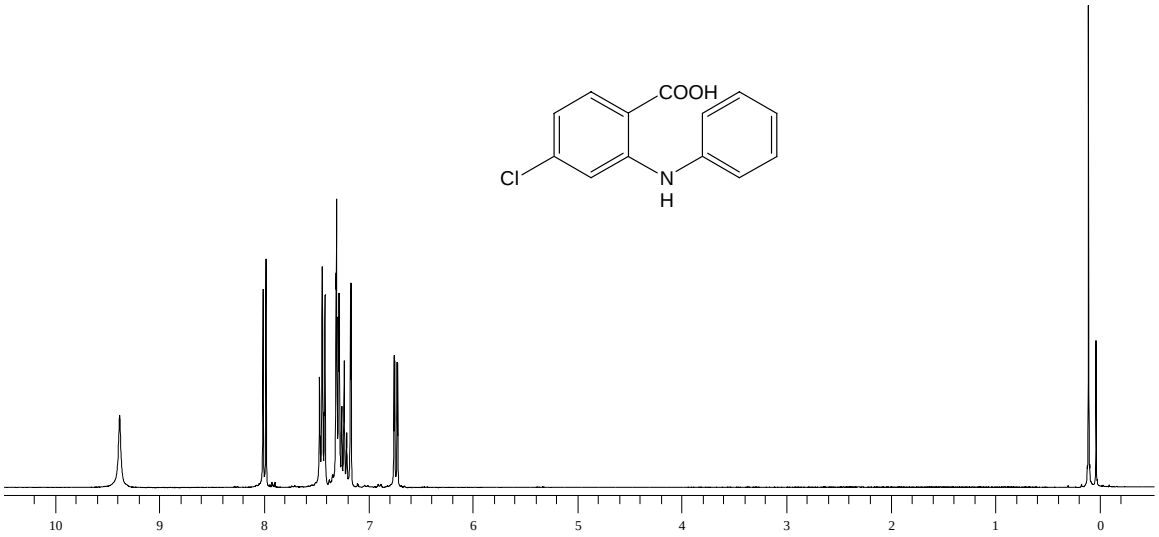


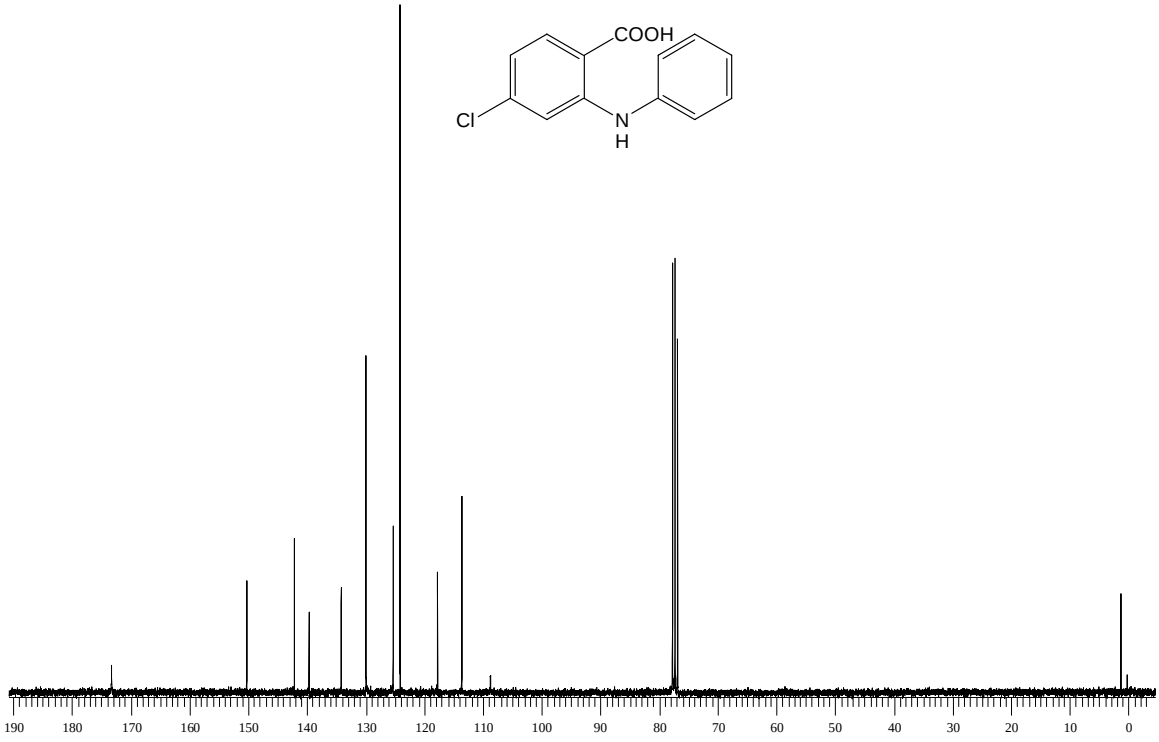
^{1}H-NMR (300 MHz, methanol-d_4) and ^{13}C-NMR (75 MHz, DMSO-d_6) of *N*-phenyl-5-bromoanthranilic acid (**14**).



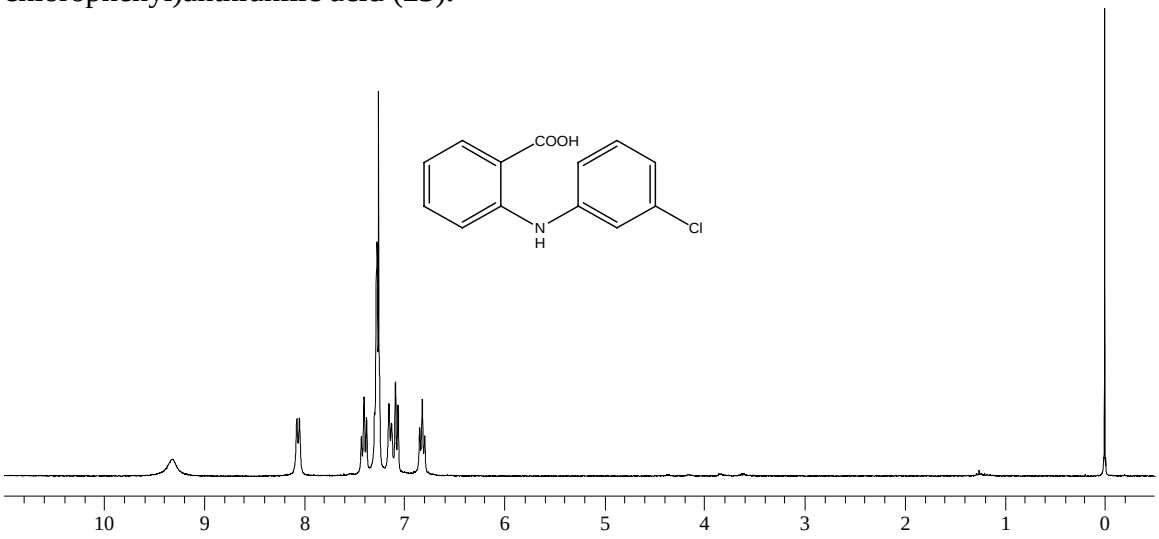


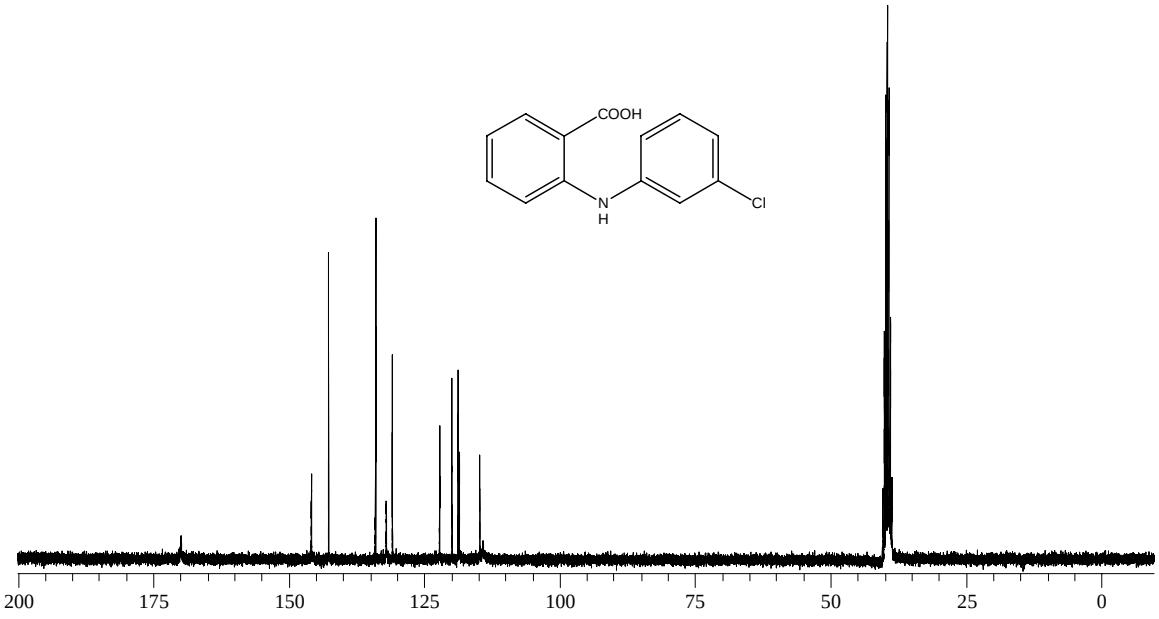
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) of *N*-phenyl-4-chloroanthranilic acid (**15**).



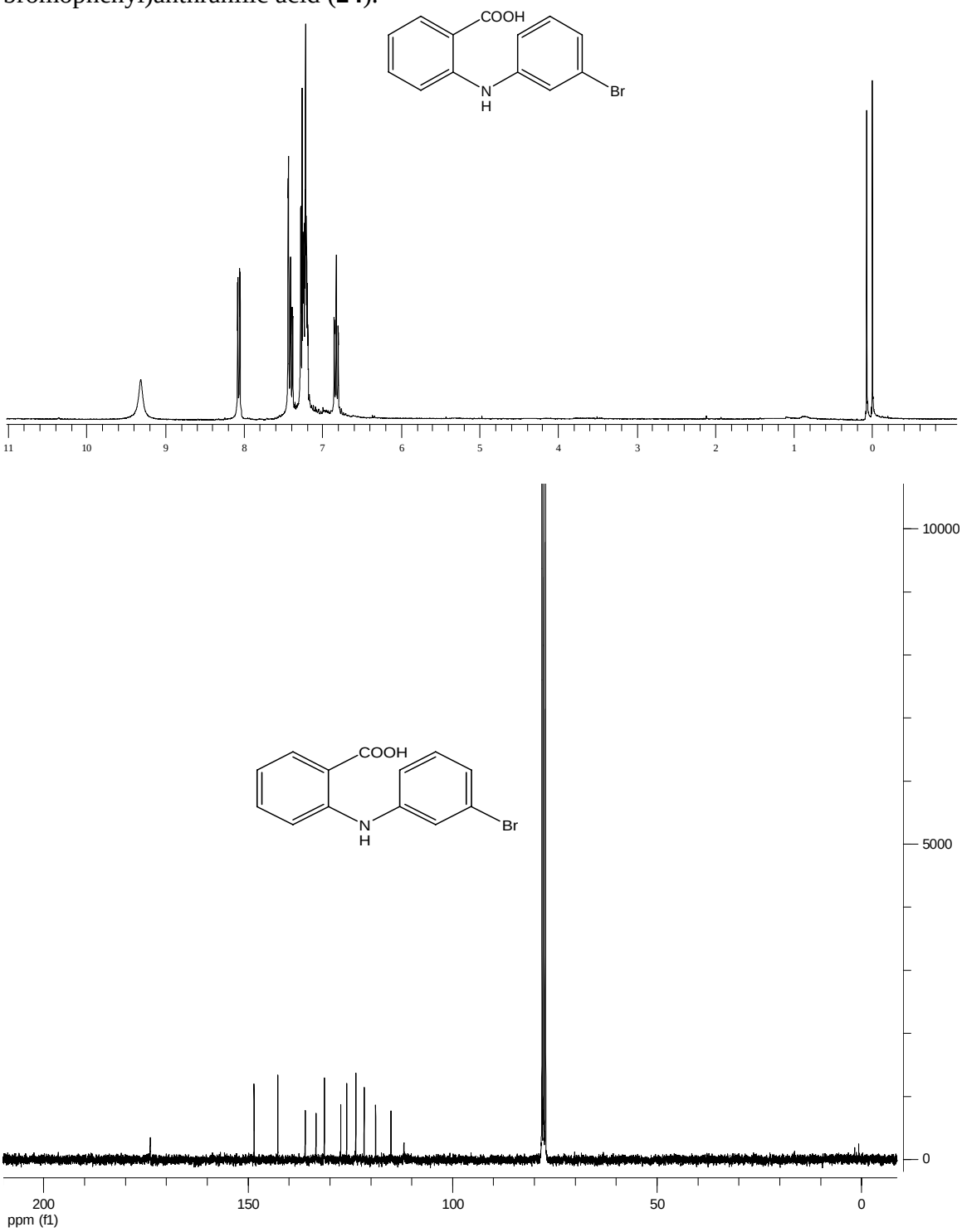


^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) of *N*-(3-chlorophenyl)anthranilic acid (**23**).

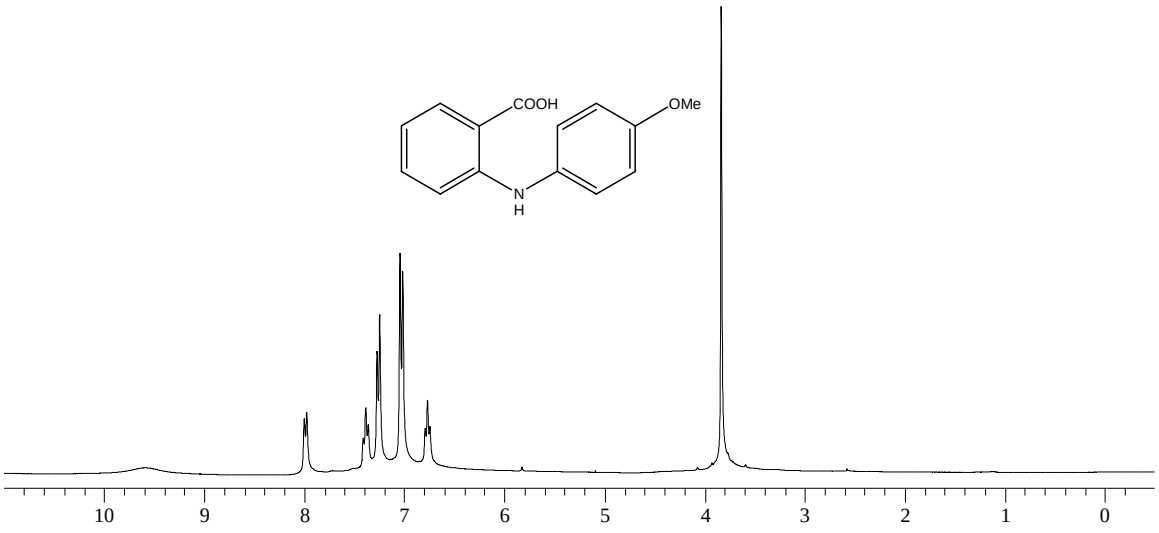


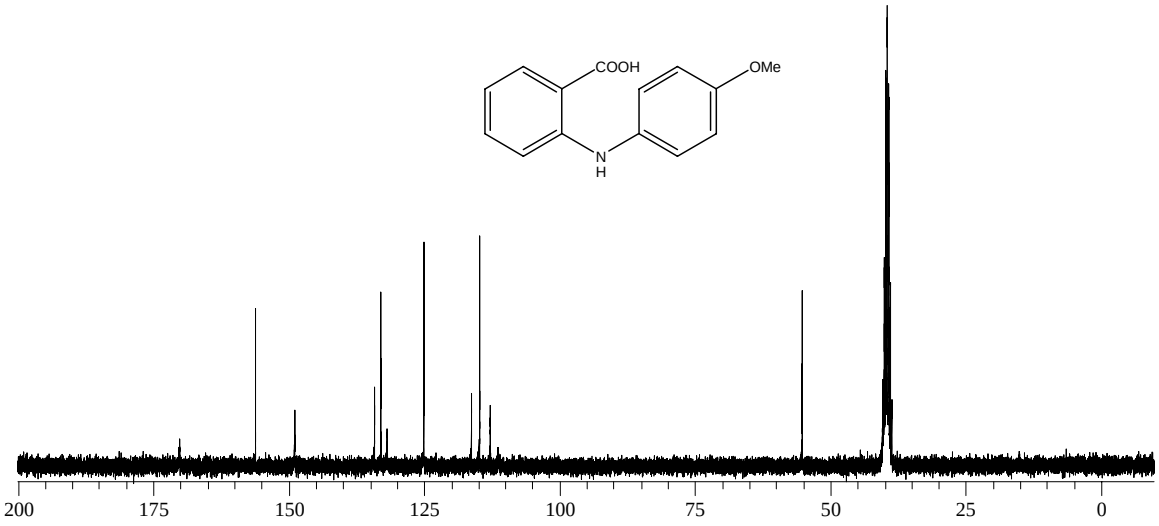


^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) of *N*-(3-bromophenyl)anthranilic acid (**24**).

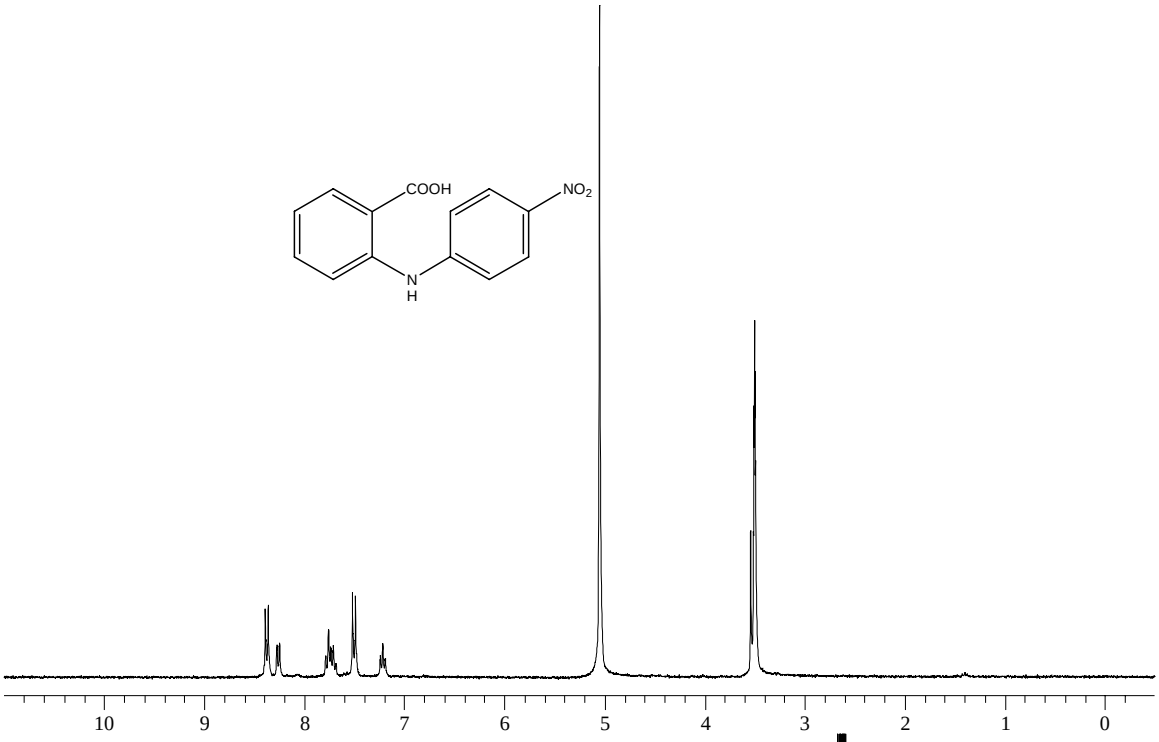


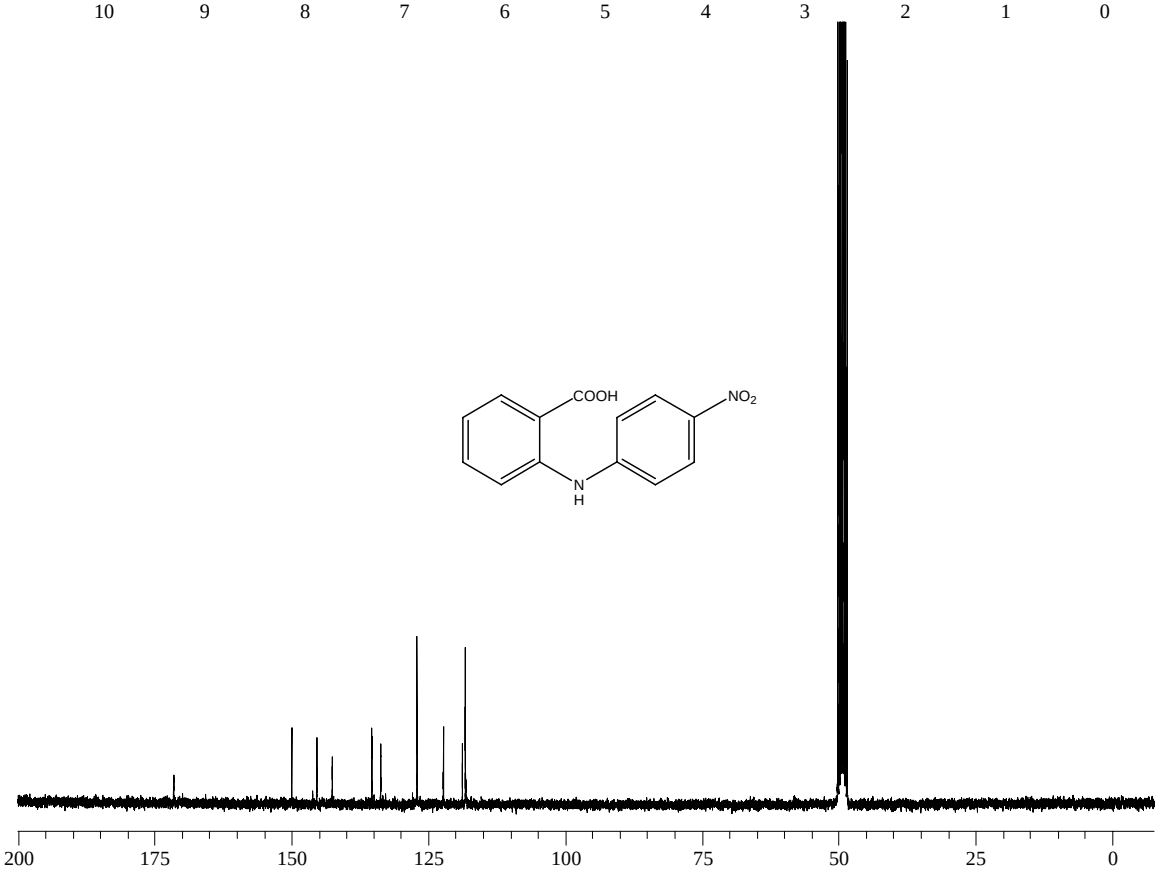
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, DMSO-d_6) of *N*-(4-methoxyphenyl)anthranilic acid (**25**).



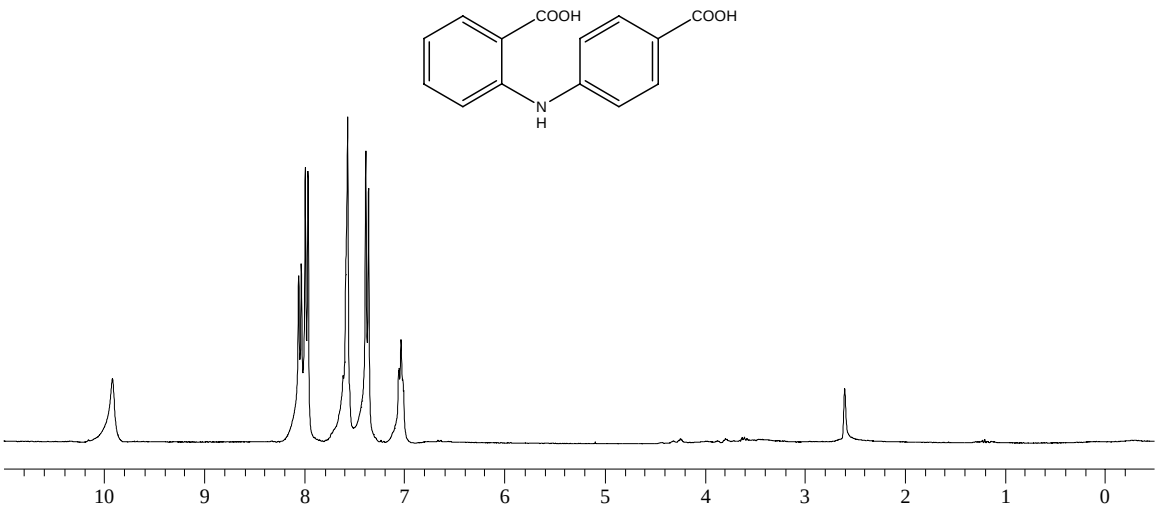


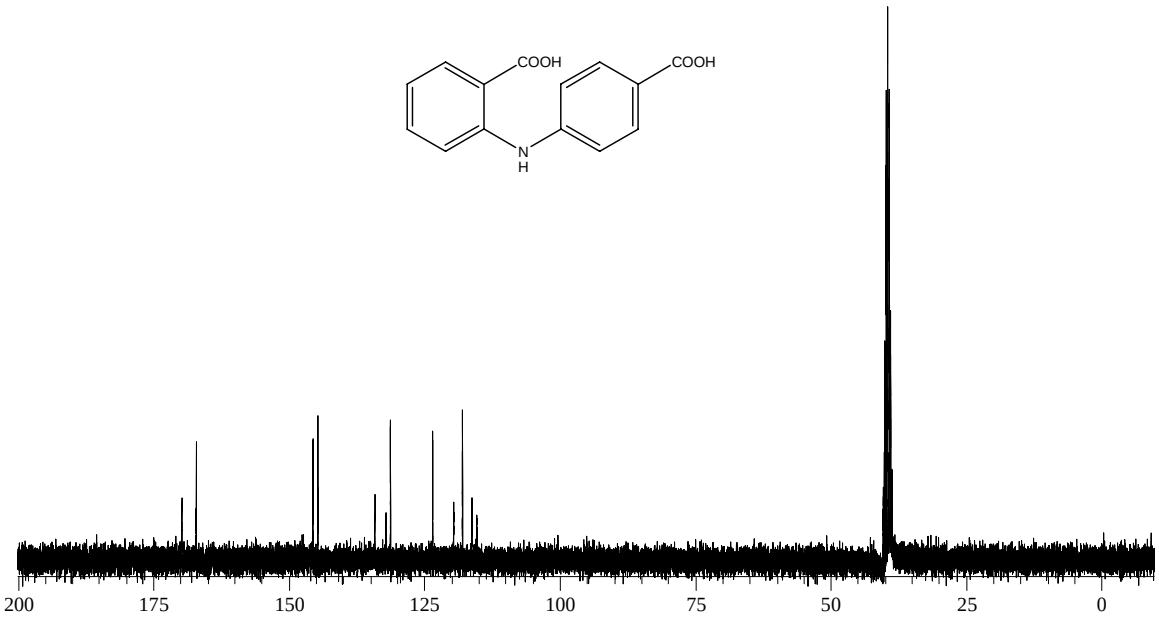
^{1}H-NMR (300 MHz, methanol-d_4) and ^{13}C-NMR (75 MHz, methanol-d_4) of *N*-(4-nitrophenyl)anthranilic acid (**26**).



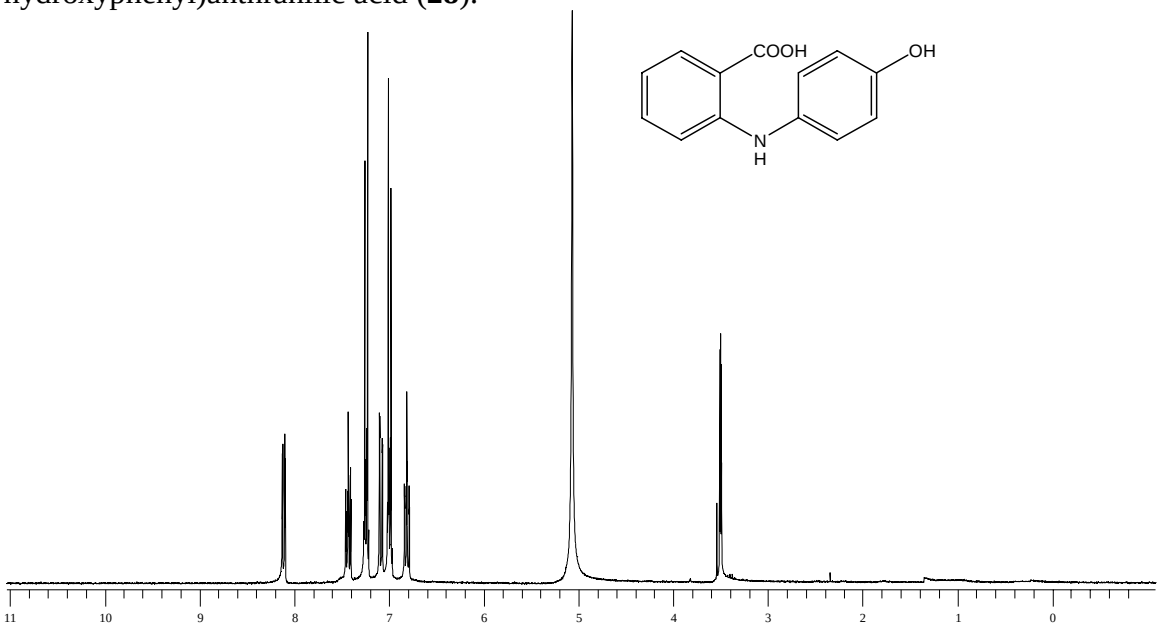


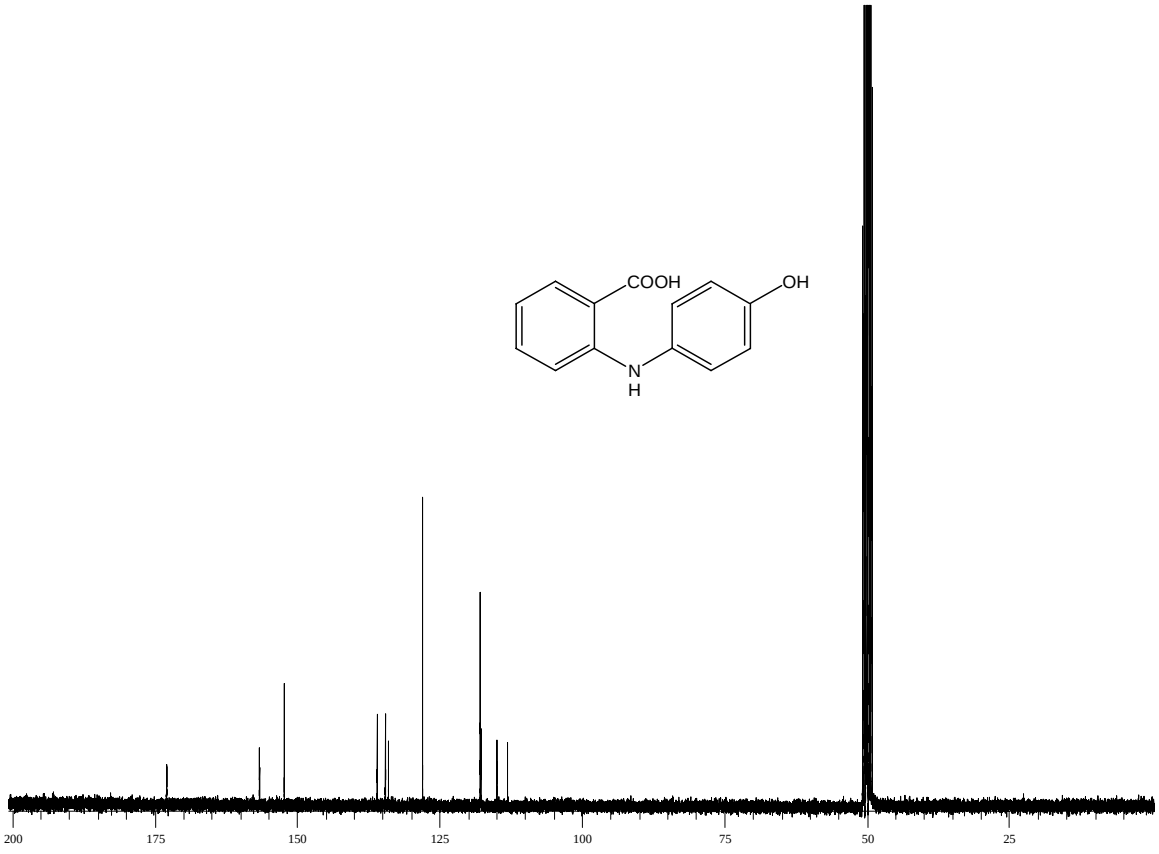
^{1}H-NMR (300 MHz, methanol-d_4) and ^{13}C-NMR (75 MHz, methanol-d_4) of *N*-(4-carboxyphenyl)anthranilic acid (**27**)**.**



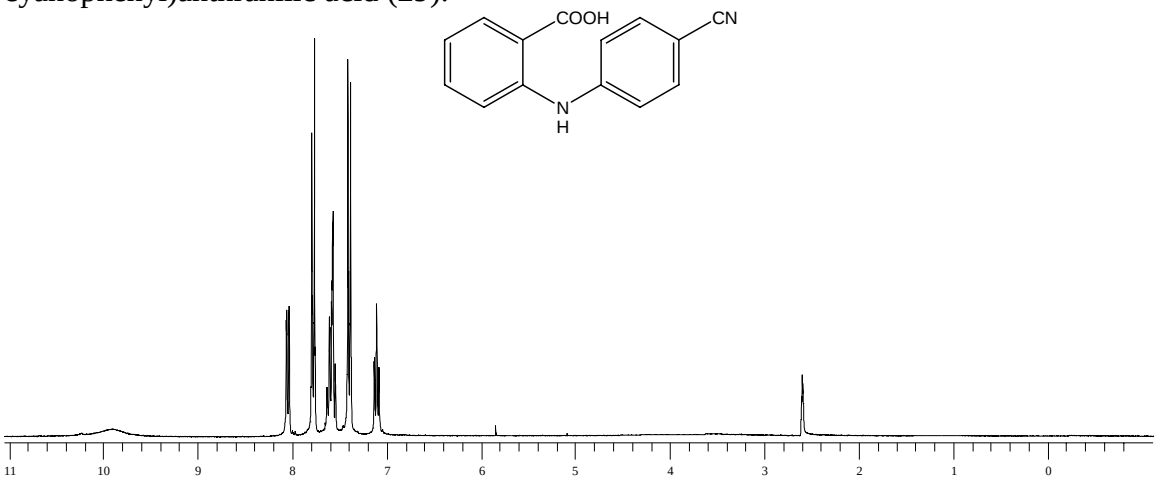


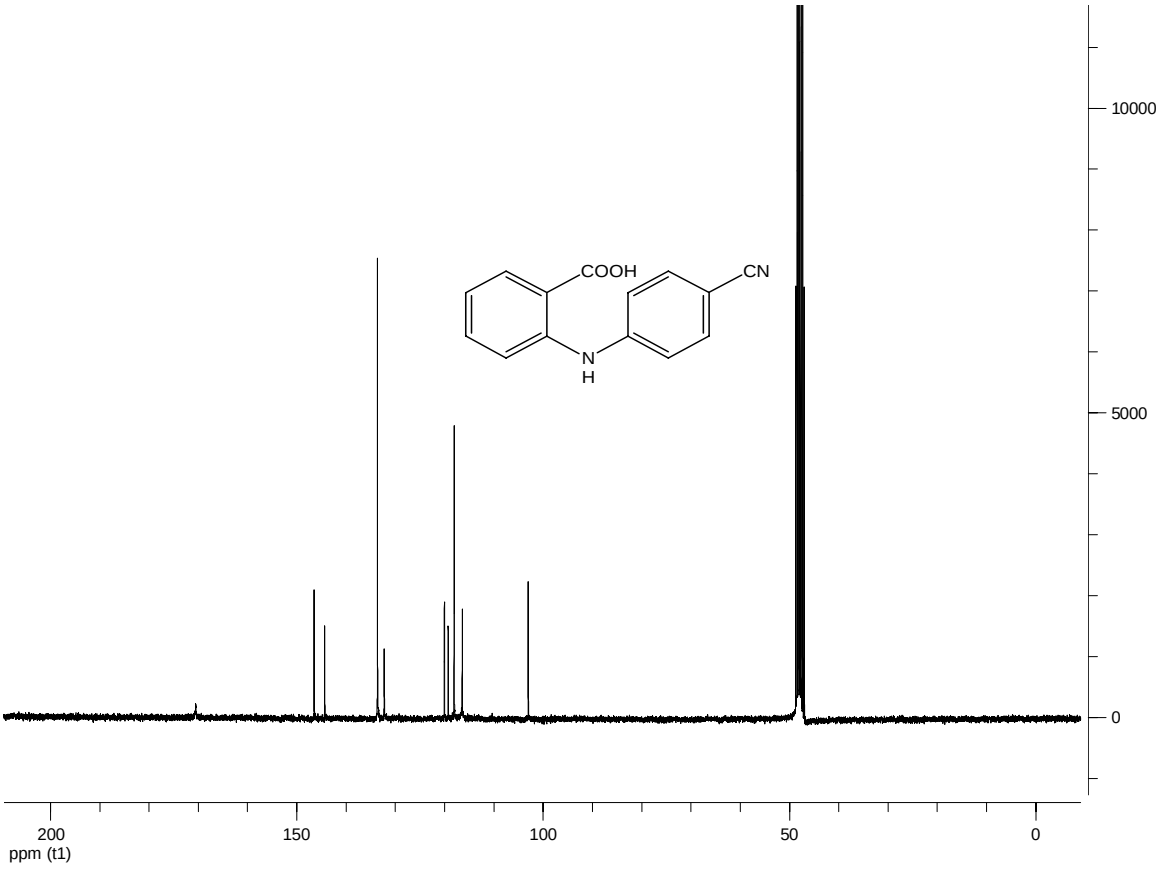
^{1}H-NMR (300 MHz, methanol-d_4) and ^{13}C-NMR (75 MHz, methanol-d_4) of *N*-(4-hydroxyphenyl)anthranilic acid (**28**).



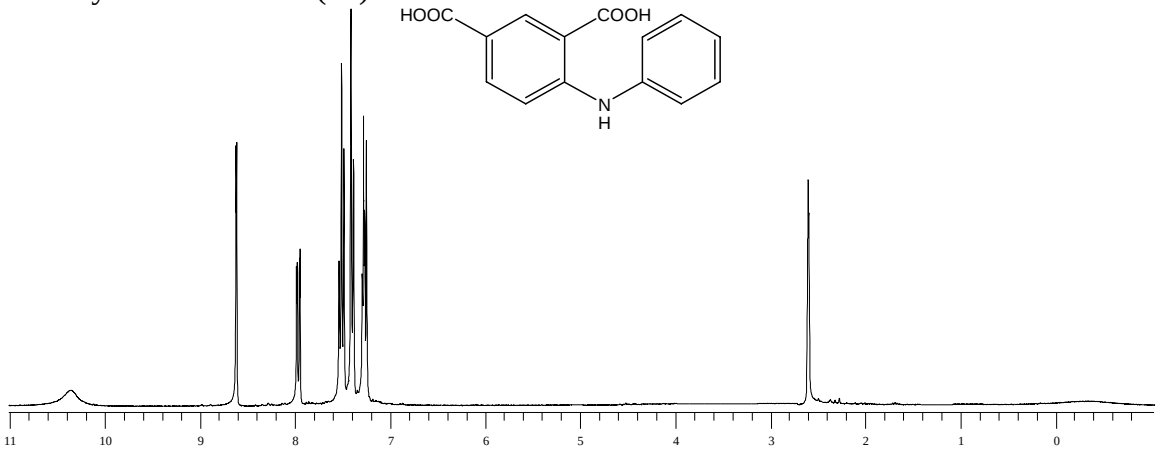


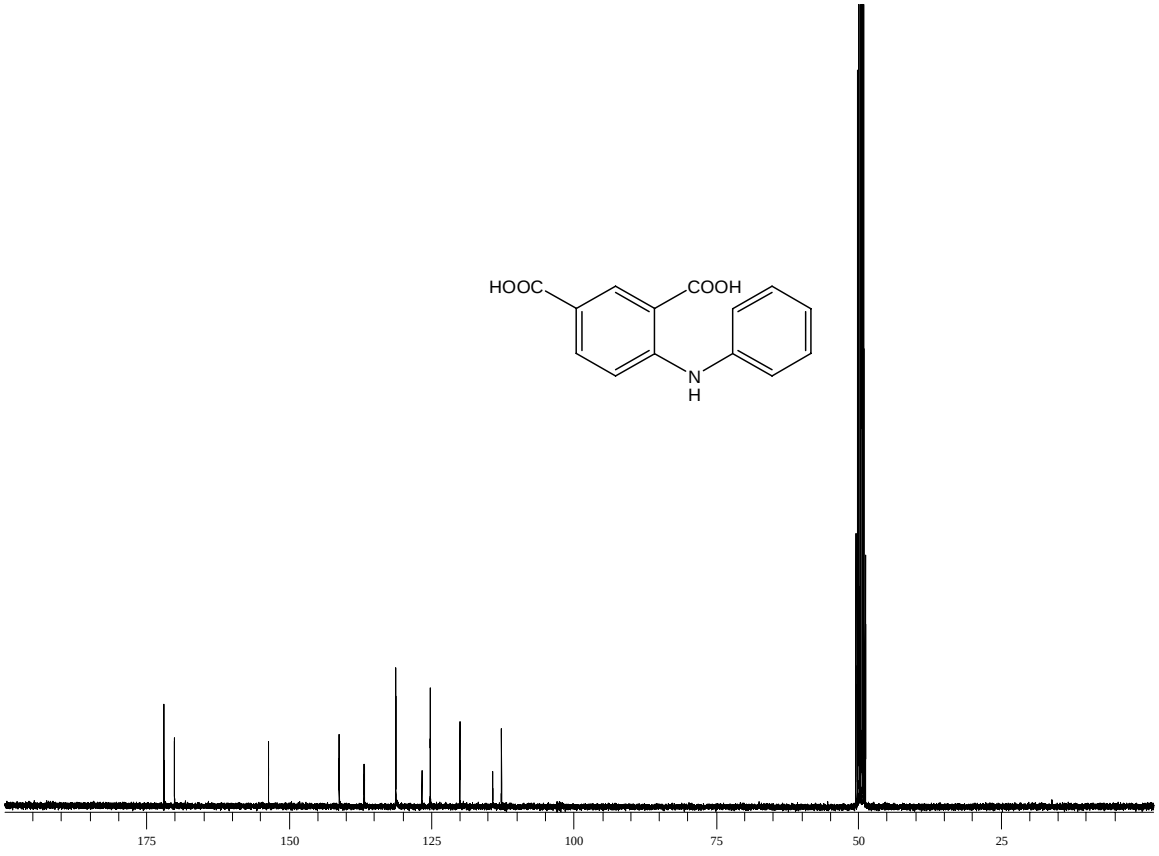
^{1}H-NMR (300 MHz, DMSO-d_6) and ^{13}C-NMR (75 MHz, methanol-d_4) of *N*-(4-cyanophenyl)anthranilic acid (**29**).



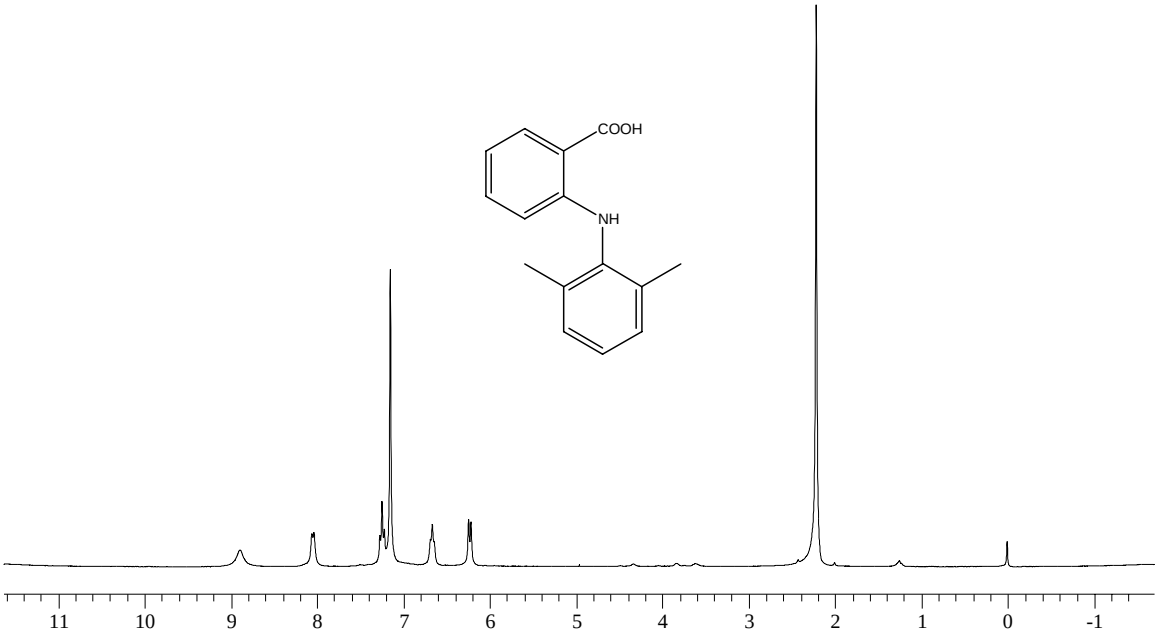


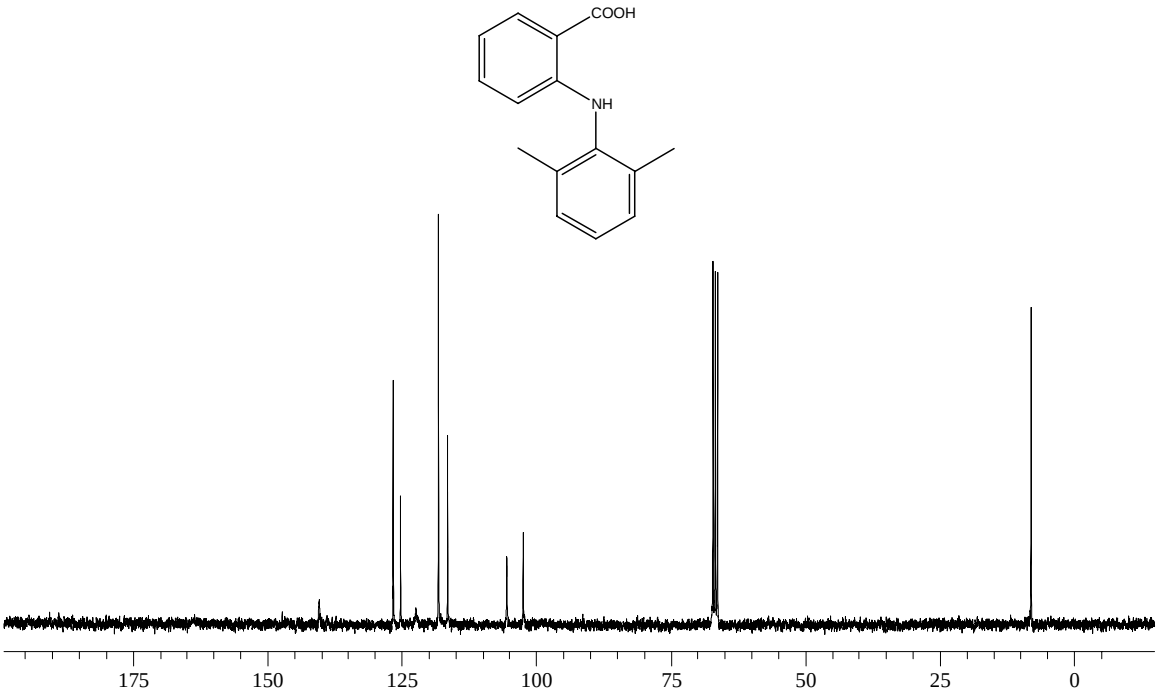
^{1}H-NMR (300 MHz, DMSO-d_6) and ^{13}C-NMR (75 MHz, methanol-d_4) *N*-phenyl-5-carboxyanthranilic acid (**30**).



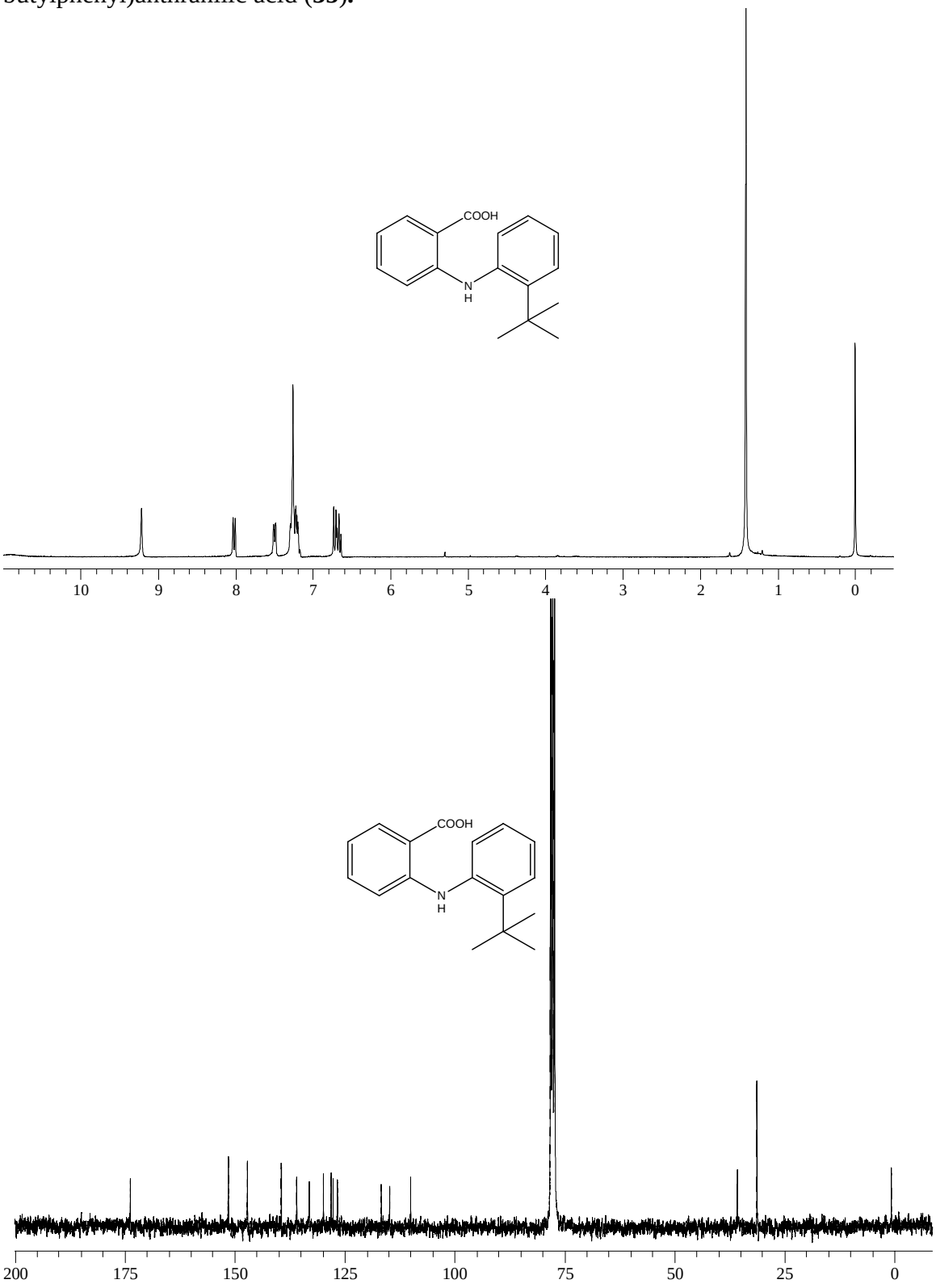


^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, methanol-d_4) of *N*-(2,6-dimethylphenyl)anthranilic acid (**34**).

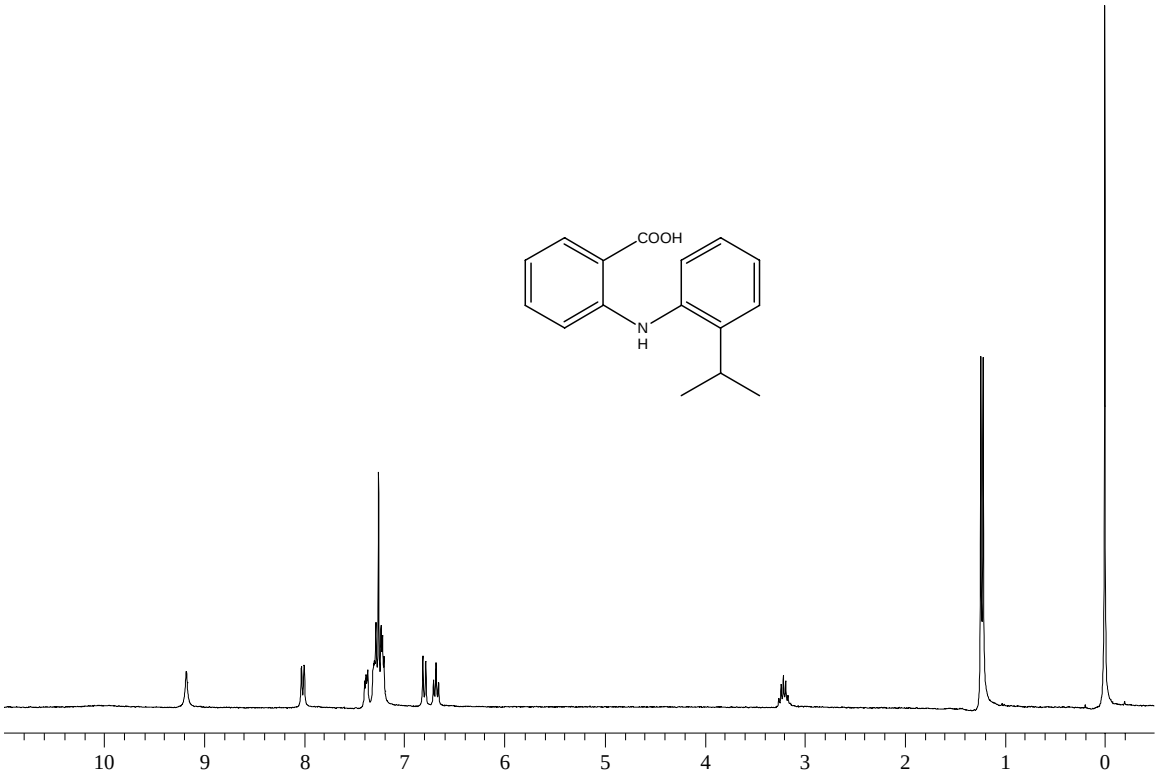


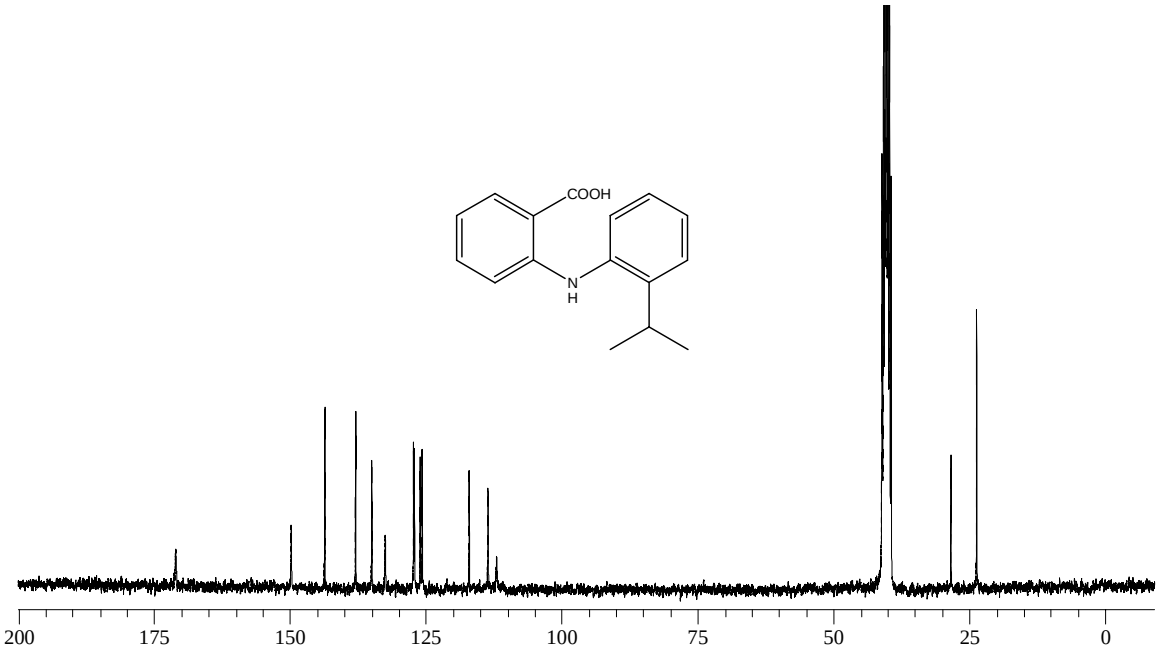


^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) of *N*-(2-*tert*-butylphenyl)anthranilic acid (**35**).

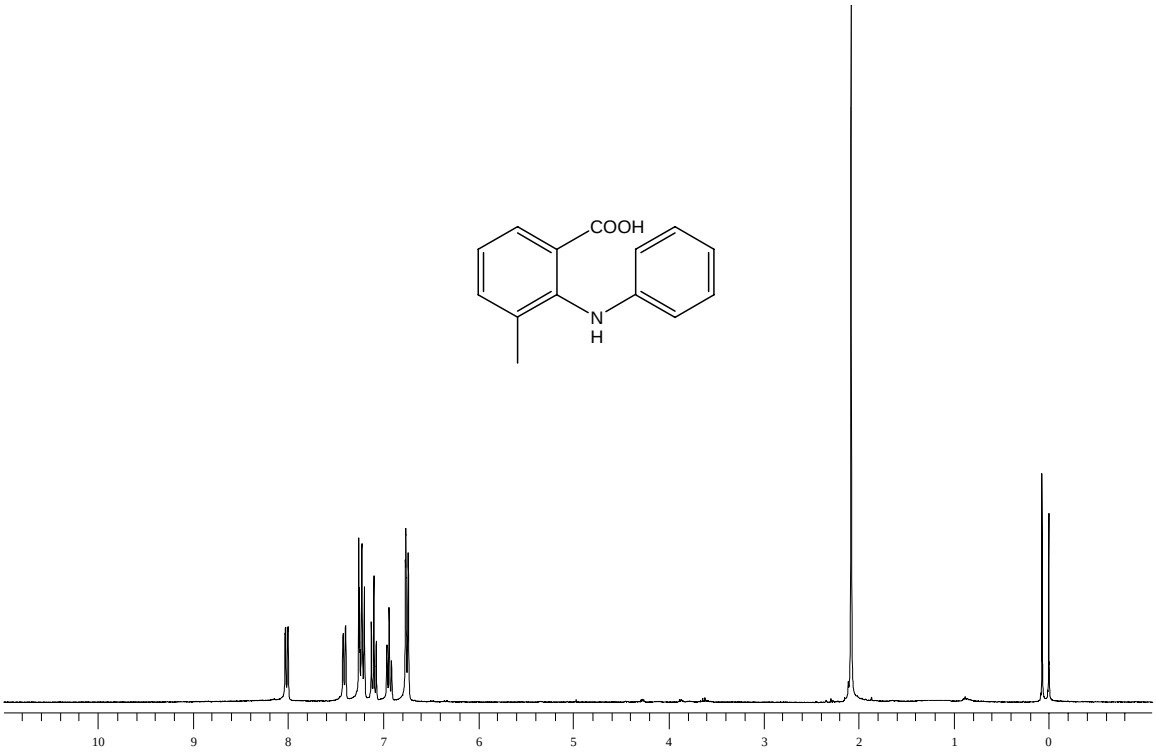


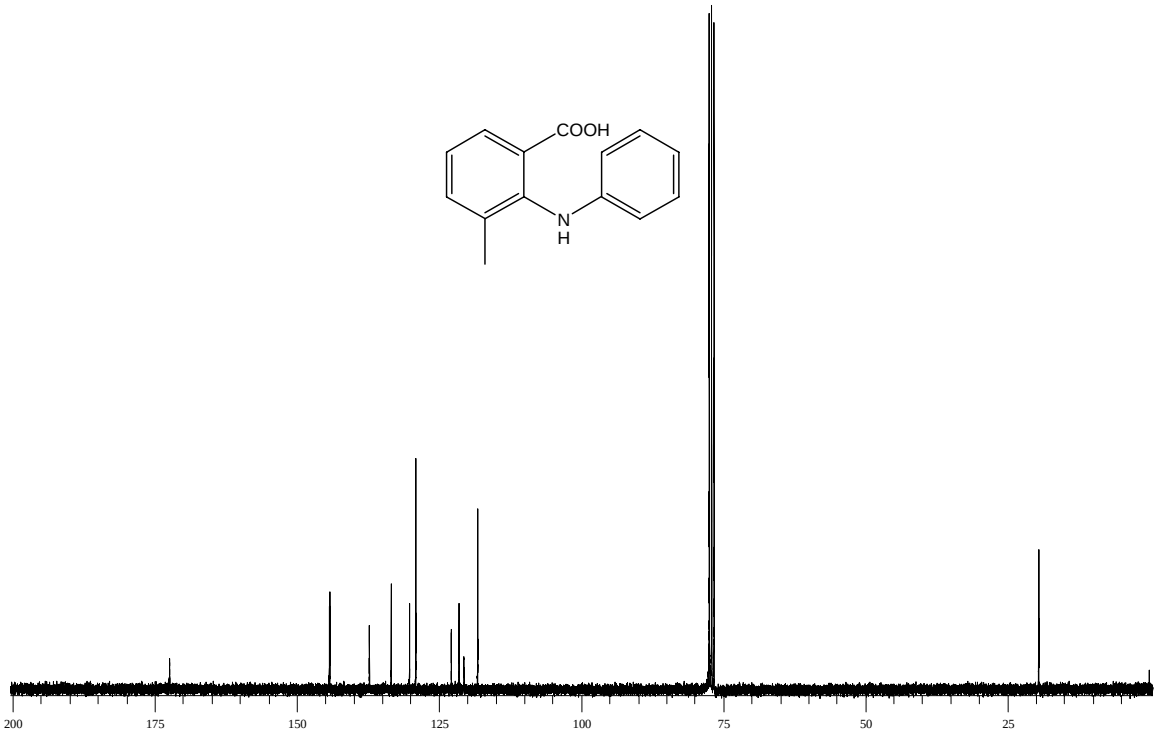
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, DMSO-d_6) of *N*-(2-isopropylphenyl)anthranilic acid (**36**).



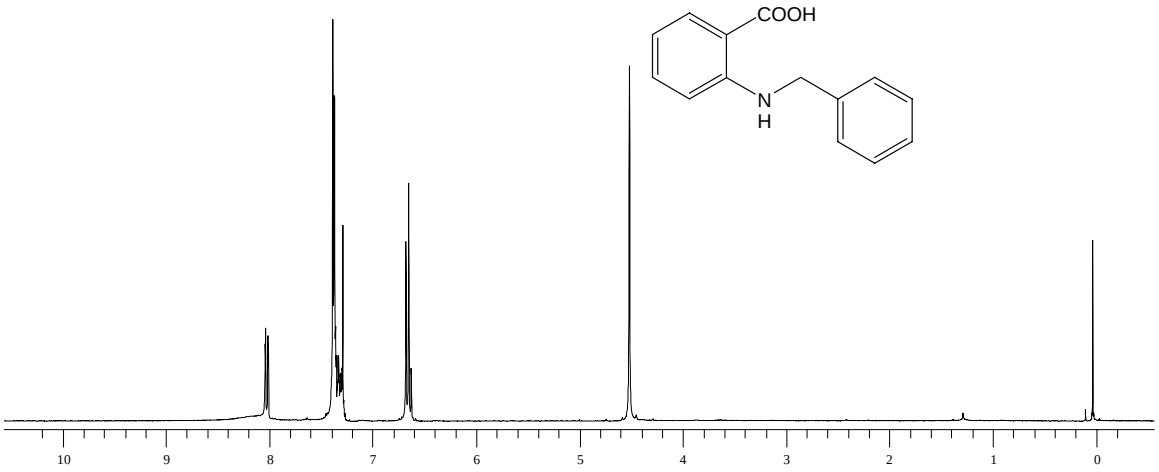


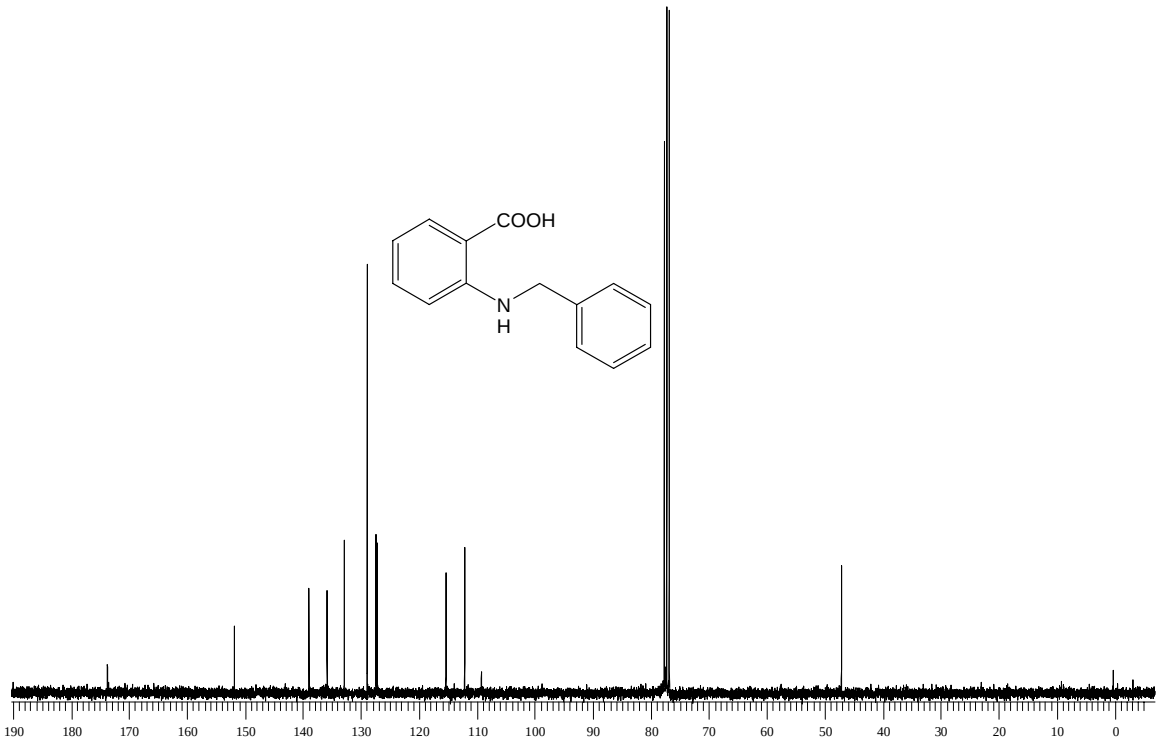
^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) of *N*-phenyl-3-methylanthranilic acid (**38**).



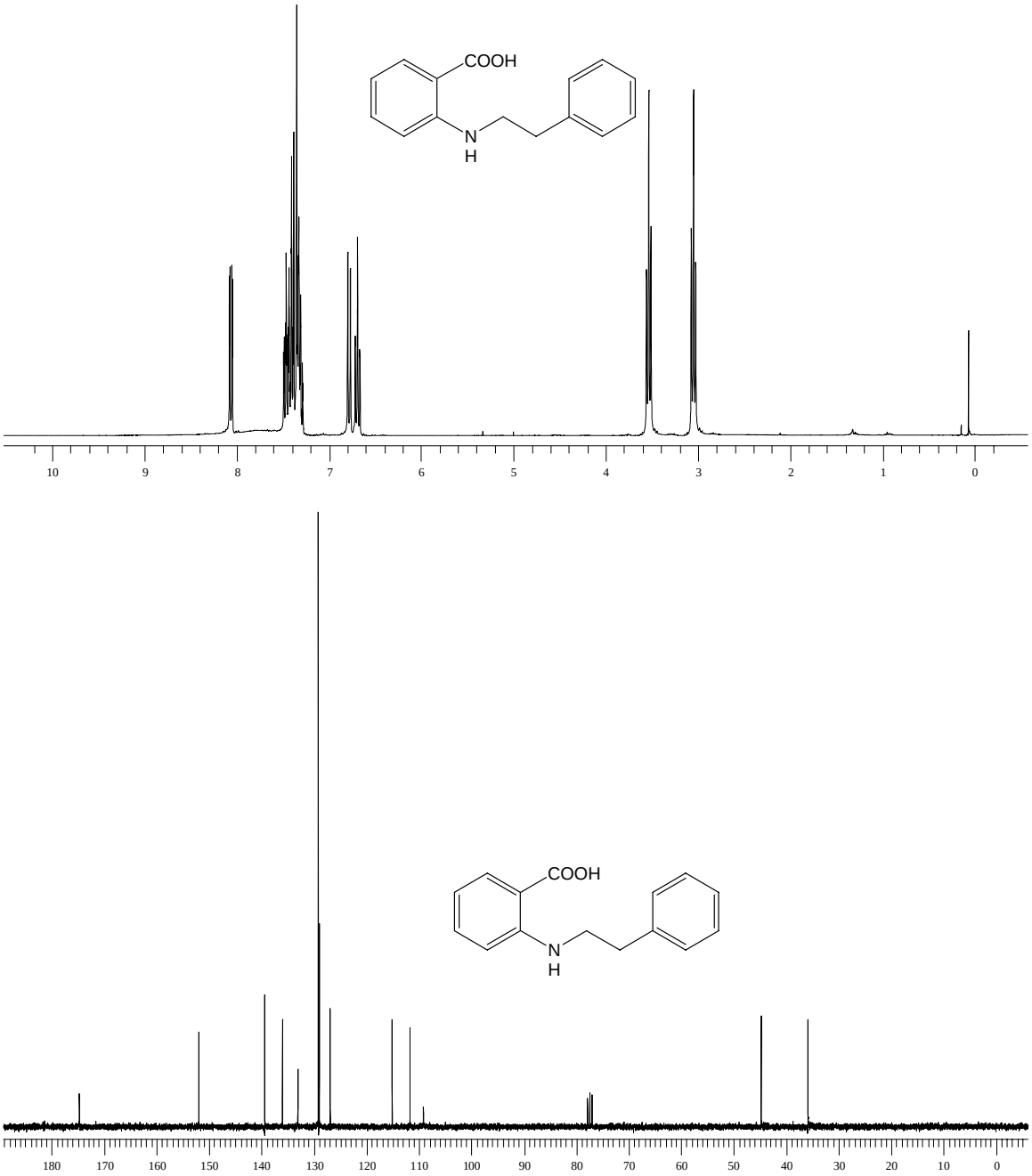


^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) of *N*-benzylanthranilic acid **(42).**

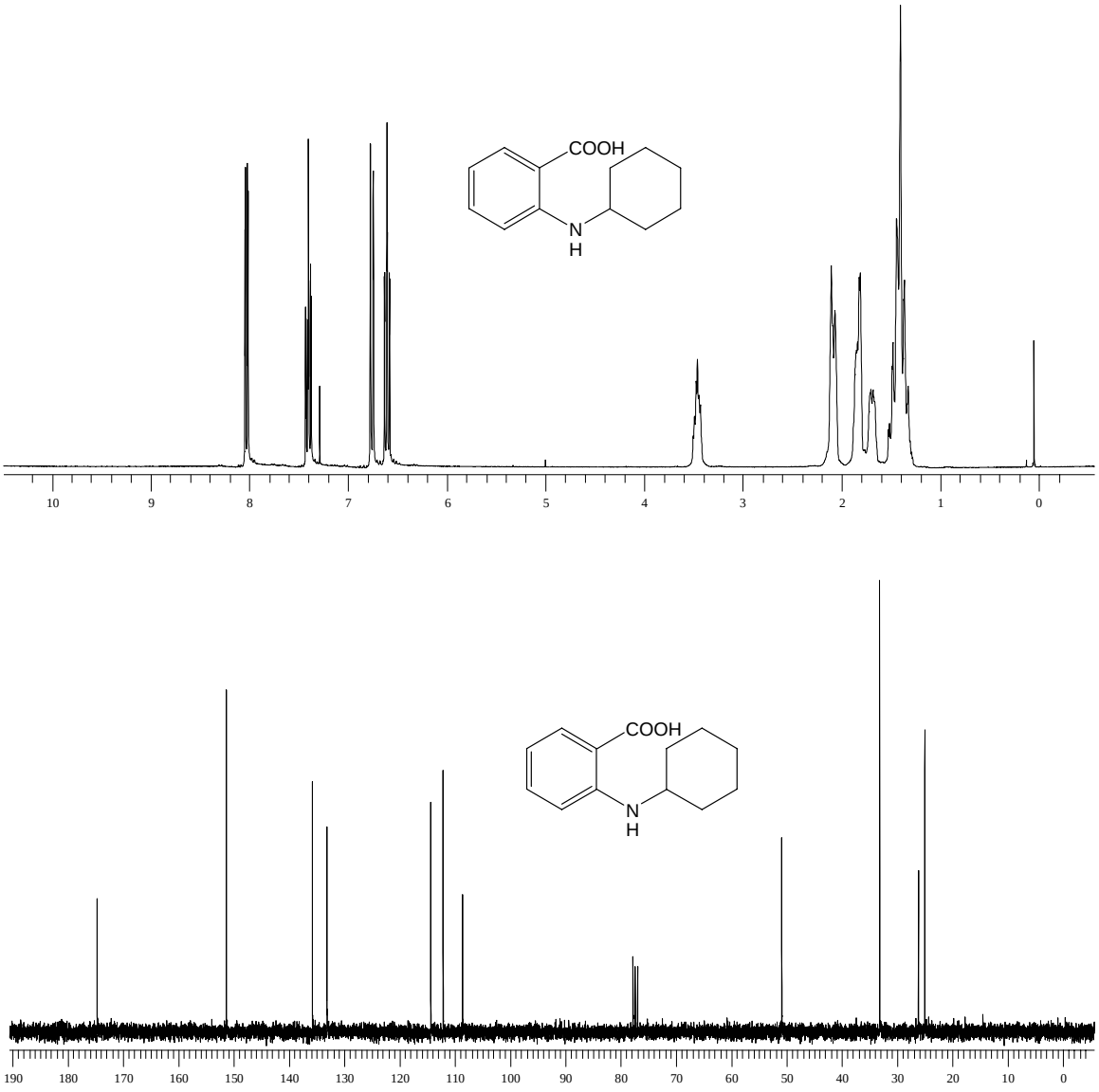




^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) of *N*-phenethylanthranilic acid **(43).**



^{1}H-NMR (300 MHz, $CDCl_3$) and ^{13}C-NMR (75 MHz, $CDCl_3$) of *N*-cyclohexylanthranilic acid **(44).**



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