Supporting Information

Rhodium(NHC)-Catalyzed Amination of Aryl Bromides

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General Methods.

All oxygen or moisture sensitive reactions were performed in oven-dried glassware under the positive pressure of nitrogen. Sensitive liquids and solutions were transferred via syringe or cannula. Concentration of solution was carried out by using a rotary evaporator with a water aspirator, and generally followed by removal of residual solvents on a vacuum line held at 0.1–1 torr. Unless otherwise stated, all commercial reagents and solvents were used without additional purification. $Rh(cod)_2BF_4$ was purchased from STREM chemical company, and I*i*Pr·HCl (1,3-diisopropylimidazolium chloride), *t*-BuONa, and Cs_2CO_3 were purchased from ALDRICH chemical company.

Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F_{254} plates. Visualization on TLC was achieved by the use of UV light (254 nm), treatment with acidic anisaldehdye, 10% ninhydrin in ethanol, 5% phosphormolybdic acid in ethanol, or ceric ammonium molybdate stain followed by heating. Flash column chromatography was undertaken on silica gel (400-630 mesh). Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on FT AM 400 (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS. The following abbreviations were used to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Coupling constants, *J*, were reported in Hertz unit (Hz). Carbon 13 nuclear magnetic resonance spectroscopy (^{13}C NMR) was recorded on FT AM 400 (100 MHz) and was fully decoupled by broad band decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d*.

Small ratio of substrates were determined on Agilent 6980 series GC system with Agilent 5974 network mass selective detector. HP-35MS (Crosslinked 35% PH ME siloxane) was used as capillary column on GC-MS. High resolution mass spectra were obtained from the Korea Basic Science Institute (Daegu) by using FAB or EI method. Inductively coupled plasma atomic emission spectroscopy data were obatained from the Energy and Environment Research Center.

A specimen of suitable size and quality was coated with Paratone oil and mounted onto a glass capillary. Reflection data for complex **4** were collected on a Bruker 1K SMART CCD-based diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å) in Inorganic Molecular Materials Laboratory at Korea University. The hemisphere of reflection data were collected as ω scan frames with 0.3^o / frame and an exposure time of 10 s / frame. Cell parameters were determined and refined by SMART program.[1] Data reduction was performed using SAINT software.[2] The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program.[3] The structures of the compounds were solved by direct methods and refined by full matrix least-squares methods using the SHELXTL program package with anisotropic thermal parameters for all non-hydrogen atoms.[4] The detailed crystallographic data and selected bond lengths and angles are given in Appendix II.

Experimental Procedures:

Preparation of Rh(cod)(NHC)Cl. To a N_2 purged round bottom flask was added lithium *tert*-butoxide (235 mg, 2.95 mmol), $[Rh(cod)Cl]_2$ (600 mg, 1.22 mmol), and THF (20 mL). The mixture was vigorously stirred at room temperature for 30 min under nitrogen atmosphere. A solution of NHC ligand (2.44 mmol) in THF (5 mL) was then added to the Rh-containing solution via a cannula. The resulting solution was stirred for additional 5 h at room temperature under nitrogen atmosphere. Solvent was removed *in vacuo*, and the desired product was isolated by a silica gel column chromatography (ethyl acetate/*n*-hexane, 1:4).

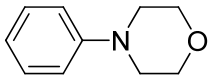
Rh(cod)(I*i*Pr)Cl. 1,3-Diisopropylimidazolium chloride (460 mg, 2.44 mmol) was used for the preparation of the title compound which was isolated by a column chromatography on silica gel (EtOAc/*n*-Hx, 1:1) as a light yellow crystalline solid (720 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (2H, s), 5.71 (2H, m), 4.96 (2H, s), 3.28 (2H, s), 2.37 (4H, m), 1.90 (4H, d, J = 8.6 Hz), 1.45 (12H, d + d, J = 7.0 Hz, 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.0 (Rh-C, d, J = 50.6 Hz), 116.7, 97.9 (Rh-C, d, J = 6.9 Hz), 67.3 (Rh-C, d, J = 14.7), 52.5, 32.9, 28.8, 24.2, 23.2.

Experimental Procedure for the Optimization of Rh-Catalyzed Arylation Reaction (Table 1). To an oven-dried screwed vial were added bromobenzene (31 mg, 0.2 mmol), morpholine (52 mg, 0.6 mmol), sodium *tert*-butoxide (38 mg, 0.4 mmol), metal catalyst (indicated mol %), NHC ligand (indicated equiv if necessary), $AgBF_4$ (indicated equiv if necessary), PCy_3 (indicated equiv if necessary), and 1,2-dimethoxyethane (0.2 mL). The mixture was vigorously stirred at 80 ^{o}C and diluted with ethyl acetate. The crude reaction mixture was filtered through a pad silica gel and organic solvents were removed *in vacuo*. Crude conversion of each reaction was determined by GC-MS using 1,3-benzodioxole as an internal standard.

[**NOTICE! Freshness and purity of the employed rhodium complexes are highly important for the reproducibility of the amination reactions.** Therefore, addition of catalyst and ligand to the reaction vessel was taken place in an argon-charged dry-box. The reaction process itself is not air-sensitive; thus, the addition of substrates and solvent does not require a specific condition. To confirm the reproducibility and certify the reactivity, ***in situ* generation of $Rh(cod)_2BF_4$ from $[Rh(cod)Cl]_2$ with $AgBF_4$** was performed and showed reproducible results.]

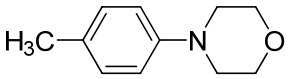
Experimental Procedure for the Amination of Various Aryl Bromides with Amines (Table 2). To an oven-dried screwed vial were added bromoarenes (0.4 mmol), amines (1.2 mmol), sodium *tert*-butoxide (76 mg, 0.8 mmol), $Rh(cod)_2BF_4$ (3.2 mg, 2 mol %), 1,3-diisopropylimidazolium chloride (3.0 mg, 4 mol %), and 1,2-dimethoxyethane (0.4 mL). The mixture was vigorously stirred at 80 ^{o}C for 12 h and diluted with ethyl acetate. The crude

reaction mixture was filtered through a pad of silica gel, and then organic solvents were removed *in vacuo* followed by a silica gel column chromatography (ethyl acetate/*n*-hexane).



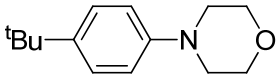
4-Phenylmorpholine (3a, Table 2).[5]

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:10) as a pale brown solid (61 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (2H, m), 6.94-6.89 (3H, m), 3.88-3.86 (4H, m), 3.17-3.15 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 129.0, 119.9, 115.6, 66.8, 49.2.



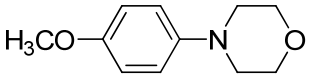
4-(*p*-Tolyl)morpholine (3b, Table 2).[6]

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:10) as a pale yellow solid (68 mg, 98%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (2H, d, J = 8.3 Hz), 6.83 (2H, d, J = 8.3 Hz), 3.87-3.84 (4H, m), 3.11-3.09 (4H, m), 2.28 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 129.7, 129.5, 116.0, 66.9, 49.9, 20.4.



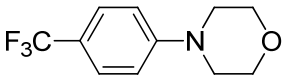
4-(4-*tert*-Butylphenyl)morpholine (3c, Table 2).[7]

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:10) as a beige solid (82 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (2H, d, J = 8.9 Hz), 6.83 (2H, d, J = 8.3 Hz), 3.87-3.84 (4H, m), 3.15-3.12 (4H, m), 1.30 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 142.7, 125.9, 115.4, 67.0, 49.5, 33.9, 31.4.



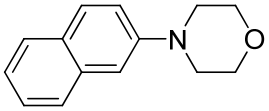
4-(4-Methoxyphenyl)morpholine (3d, Table 2).[6]

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:10) as a white solid (57 mg, 74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88-6.82 (4H, m), 3.85-3.83 (4H, m), 3.75 (3H, s) 3.05-3.02 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 145.6, 117.8, 114.5, 67.0, 55.5, 50.8.



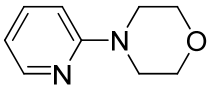
4-[4-(Trifluoromethyl)phenyl]morpholine (3e, Table 2).[8]

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:10) as a white solid (91 mg, 98%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (2H, d, J = 8.7 Hz), 6.89 (2H, d, J = 8.7 Hz), 3.86-3.83 (4H, m), 3.23-3.20 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 128.7 (q, J_{CF} = 269.1 Hz), 126.5 (q, J_{CF} = 3.8 Hz), 126.4, 126.4, 126.4, 126.0, 123.3, 121.5 (q, J_{CF} = 32.4 Hz), 121.1, 120.8, 120.5, 114.3, 66.6, 48.1.



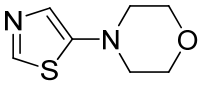
4-(2-Naphthyl)morpholine (3f, Table 2).[9]

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:10) as a pare green solid (79 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.71 (3H, m), 7.43-7.24 (3H, m), 7.12 (1H, d, *J* = 2.4 Hz), 3.92-3.90 (4H, m), 3.27-3.24 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 134.5, 128.8, 128.6, 127.4, 126.7, 126.3, 123.5, 118.8, 110.0, 66.9, 49.7.



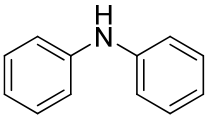
4-(2-Pyridyl)morpholine (3g, Table 2).[10]

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:2) as a yellow oil (59 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.17 (1H, m), 7.49-7.45 (1H, m), 6.65-6.60 (2H, m), 3.81-3.79 (4H, m), 3.48-3.46 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 147.9, 137.5, 113.8, 106.9, 66.7, 45.6.



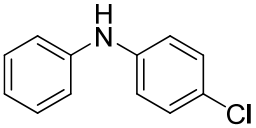
4-(5-Thiazolyl)morpholine (3h, Table 2).

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:1) as a yellow solid (61 mg, 89%); m.p. = 46 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (1H, s), 7.02 (1H, s), 3.80-3.78 (4H, m), 3.08-3.06 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 141.5, 123.1, 66.1, 52.4; HRMS (ESI) m/z calcd. for $C_7H_{10}N_2OS$ $[M]^+$: 170.0514, found: 170.0514.



Diphenylamine (3i, Table 2).[11]

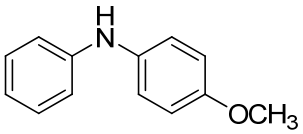
The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:4) as a white solid (52 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (4H, m), 7.11-7.08 (4H, m), 6.98-6.94 (2H, m), 5.69 (1H, s, br); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 129.3, 120.1, 117.8.



4-Chloro-*N*-phenylaniline (3j, Table 2).[12]

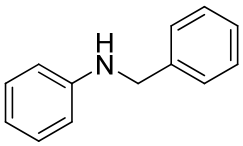
The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:4) as a brown solid (66 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.19 (4H, m), 7.05-6.96

(5H, m), 5.65 (1H, s, br); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 141.8, 129.4, 129.2, 125.5, 121.5, 118.8, 118.1.



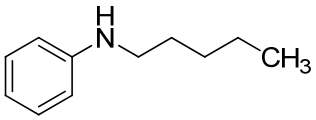
4-Methoxy-*N*-phenylaniline (3k, Table 2).[13]

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:4) as a yellow solid (41 mg, 51%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.21 (2H, m), 7.10-7.07 (2H, m), 6.93-6.85 (5H, m) 5.50 (1H, s, br), 3.81 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 145.1, 135.7, 129.2, 122.1, 119.5, 115.6, 114.6, 55.5.



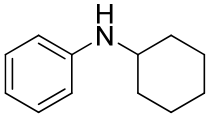
***N*-Benzylaniline (3l, Table 2).**[11]

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:4) as a beige solid (67 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.15 (7H, m), 6.71-6.63 (3H,m), 4.32 (2H, s), 4.02 (1H, s, br); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 139.4, 129.2, 128.6, 127.5, 127.2, 117.5, 112.8, 48.3.



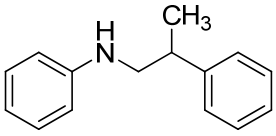
***N*-Pentylaniline (3m, Table 2).**[11]

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:6) as a white solid (58 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.15 (2H, m), 6.70-6.59 (3H,m), 3.58 (1H, s, br), 3.09 (2H, t, J = 7.1 Hz), 1.64-1.60 (2H, m), 1.40-1.35 (4H, m), 0.94-0.90 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 129.2, 117.0, 112.7, 44.0, 29.3, 29.3, 22.5, 14.0.



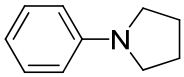
***N*-Cyclohexylaniline (3n, Table 2).**[8]

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:6) as a brown oil (65 mg, 92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.14 (2H, m), 6.69-6.58 (3H,m), 3.50 (1H, s, br), 3.29-3.24 (1H, m), 2.09-2.05 (2H, m), 1.80-1.75 (4H, m), 1.40-1.14 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4, 129.2, 116.8, 113.1, 51.6, 33.5, 25.9, 25.0.



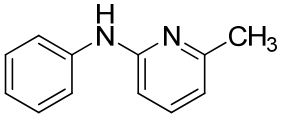
***N*-(2-Phenylpropyl)aniline (3o, Table 2).**[14]

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:4) as a brown oil (79 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.34 (2H, m), 7.29-7.24 (3H, m), 7.24-7.18 (2H, m), 6.75-6.71 (1H, m), 6.62-6.59 (2H, m), 3.60 (1H, s, br), 3.40-3.35 (1H, m), 3.29-3.25 (1H, m), 3.14-3.05 (1H, m), 1.37 (3H, d, J = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 144.5, 129.2, 128.6, 127.2, 126.6, 117.2, 112.9, 50.9, 39.2, 19.7.



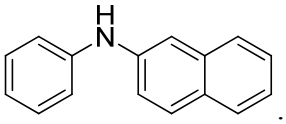
1-Phenylpyrrolidine (3p, Table 2).[8]

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:10) as a yellow oil (56 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.20 (2H, m), 6.67-6.56 (3H,m), 3.29-3.26 (4H, m), 2.01-1.98 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 129.1, 115.3, 111.6, 47.5, 25.4.



6-Methyl-2-(phenylamino)pyridine (3q, Table 2).

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:4) as a yellow oil (66 mg, 90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.29 (5H, m), 7.03-7.00 (1H, m), 6.70 (1H, d, J = 8.3 Hz), 6.63 (1H, s, br), 6.58 (1H, d, J = 7.3 Hz), 2.43 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 155.4, 140.7, 137.9, 129.2, 122.5, 120.2, 114.3, 104.8, 24.2; HRMS (ESI) m/z calcd. for $C_{12}H_{12}N_2$ $[M]^+$: 184.1000, found: 184.1000.

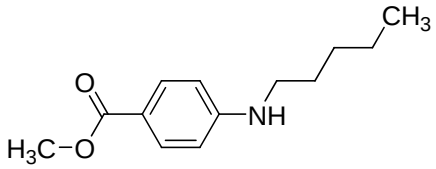


***N*-(2-Naphthyl)aniline (3r, Table 2).**[11]

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:4) as a brown solid (82 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.76 (2H, m), 7.69-7.67 (1H, d, J = 8.2 Hz), 7.46-7.42 (2H, m), 7.37-7.32 (3H, m), 7.25-7.22 (1H, m), 7.20-7.17 (2H, m), 7.04-7.00 (1H, m), 5.84 (1H, s, br); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 140.8, 134.6, 129.4, 129.1, 129.1, 127.6, 126.4, 126.4, 123.4, 121.4, 112.0, 118.2, 111.6.

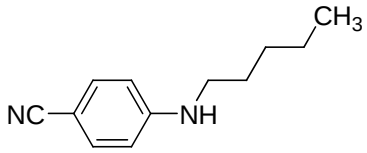
Experimental Procedure for the Amination with Cs_2CO_3 Base (Table 3). To an oven-dried screwed vial were added bromoarene (0.4 mmol), amine (1.2 mmol), cesium carbonate (260 mg, 0.8 mmol), $Rh(cod)_2BF_4$ (3.2 mg, 2 mol %), 1,3-diisopropylimidazolium chloride (3.0 mg, 4 mol %), and 1,2-dimethoxyethane (0.4 mL). The mixture was vigorously stirred at

90 °C for 12 h and diluted with ethyl acetate. The crude reaction mixture was filtered through a pad of silica gel and organic solvents were removed *in vacuo*, and then it was purified by a silica gel column chromatography (ethyl acetate/*n*-hexane).



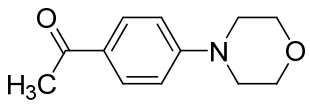
Methyl 4-(pentylamino)benzoate (3s, Table 3).

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:4) as a white solid (84 mg, 95%); m.p. = 71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (2H, d, *J* = 5.0 Hz), 6.51 (2H, d, *J* = 5.0 Hz), 4.10 (1H, s, br), 3.82 (3H, s), 3.14-3.11 (2H, m), 1.62-1.58 (2H, m), 1.37-1.33 (4H, m), 0.91-0.88 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 152.1, 131.5, 117.9, 111.2, 51.4, 43.3, 29.2, 29.0, 22.4, 14.0; HRMS (ESI) m/z calcd. for $C_{13}H_{19}NO_2$ $[M]^+$: 221.1416, found: 221.1416.



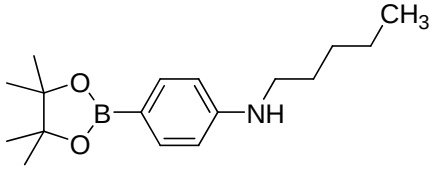
4-(*n*-Pentylamino)benzonitrile (3t, Table 3).

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:4) as a white solid (66 mg, 88%); m.p. = 55 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.36 (2H, m), 6.53-6.50 (2H, m), 4.20 (1H, s, br), 3.13-3.08 (2H, m), 1.62-1.59 (2H, m), 1.37-1.33 (4H, m), 0.91-0.88 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 133.6, 120.5, 112.0, 98.2, 43.1, 29.1, 28.8, 22.3, 13.9; HRMS (ESI) m/z calcd. for $C_{12}H_{16}N_2$ $[M]^+$: 188.1313, found: 188.1313.



4´-Morpholinoacetophenone (3u, Table 3).[11]

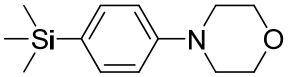
The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:2) as a white solid (70 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (2H, d, *J* = 9.0 Hz), 6.83 (2H, d, *J* = 9.0 Hz), 3.83 (4H, t, *J* = 4.9 Hz), 3.28 (4H, t, *J* = 5.0 Hz), 2.50 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 154.2, 130.3, 128.0, 113.2, 66.5, 47.5, 26.1.



***N*-Pentyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (3v, Table 3).**

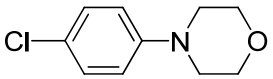
The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:4) as a pale yellow solid (83 mg, 72%); m.p. = 47 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.61 (2H, m), 6.57-6.54 (2H, m), 3.81 (1H, s, br), 3.11 (2H, t, *J* = 7.1 Hz), 1.62-1.58 (2H, m),

1.38-1.33 (4H, m), 1.31 (12H, s) 0.92-0.89 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 136.3, 111.6, 83.1, 43.4, 29.2, 29.1, 24.8, 22.4, 14.0; HRMS (ESI) m/z calcd. for $C_{17}H_{28}BNO_2$ $[M]^+$: 289.2213, found: 289.2216.



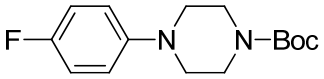
4-[4-(Trimethylsilyl)phenyl]morpholine (3w, Table 3).

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:6) as a yellow solid (92 mg, 98%); m.p. = 42 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (2H, d, J = 8.6 Hz), 6.53 (2H, d, J = 8.6 Hz), 3.87 (4H, t, J = 4.8 Hz), 3.20 (4H, t, J = 4.9 Hz), 0.27 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 134.4, 130.0, 114.8, 66.8, 48.8, -1.0; HRMS (ESI) m/z calcd. for $C_{13}H_{21}NOSi$ $[M]^+$: 235.1392, found: 235.1392.



4-(4-Chlorophenyl)morpholine (3x, Table 3).[8]

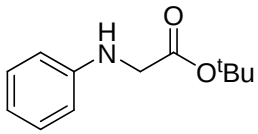
The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:10) as a yellow solid (75 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (2H, d, J = 6.7 Hz), 6.80 (2H, d, J = 9.0 Hz), 3.84-3.82 (4H, m), 3.10-3.08 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 129.0, 124.9, 116.9, 66.7, 49.3.



***tert*-Butyl 4-(4-fluorophenyl)piperazine-1-carboxylate (3y, Table 3).**

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:10) as a white solid (92 mg, 82%); m.p. = 49 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97-6.93 (2H, m), 6.87-6.84 (2H, m), 3.55 (4H, t, J = 5.0 Hz), 3.01 (4H, t, J = 5.2 Hz), 1.46 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7 (d, J_{CF} = 238.2 Hz) 154.7, 148.0 (d, J_{CF} = 2.3 Hz), 118.5 (d, J_{CF} = 7.5 Hz), 115.7 (d, J_{CF} = 21.9 Hz), 80.0, 50.5, 28.4; HRMS (ESI) m/z calcd. for $C_{15}H_{21}FN_2O_2$ $[M]^+$: 280.1587, found: 280.1587.

Experimental Procedure for the Amination of an Amino Acid Ester (Scheme 2). To an oven-dried screwed vial were added bromobenzene (62 mg, 0.4 mmol), glycine *tert*-butyl ester hydrochloride (101 mg, 0.6 mmol), cesium carbonate (391 mg, 1.2 mmol), $Rh(cod)_2BF_4$ (3.2 mg, 2 mol %), 1,3-diisopropylimidazolium chloride (3.0 mg, 4 mol %), and 1,2-dimethoxyethane (1.2 mL). The mixture was vigorously stirred at 90 °C for 12 h and diluted with ethyl acetate. The crude reaction mixture was filtered through a pad of silica gel and organic solvents were removed *in vacuo*, and then it was purified by a silica gel column chromatography (ethyl acetate/*n*-hexane).



***tert*-Butyl 2-(phenylamino)acetate (6, Scheme 2).**[15]

The title compound was purified by a silica gel column chromatography (EtOAc/*n*-Hx, 1:6) as a beige oil (52 mg, 63%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.16 (2H, m), 6.75-6.71 (1H, m), 6.60-6.58 (2H, m), 4.26 (1H, s, br), 3.79 (2H, d, J = 2.8 Hz), 1.48 (9H, 2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 147.2, 129.2, 117.9, 112.9, 81.9, 46.5, 28.0.

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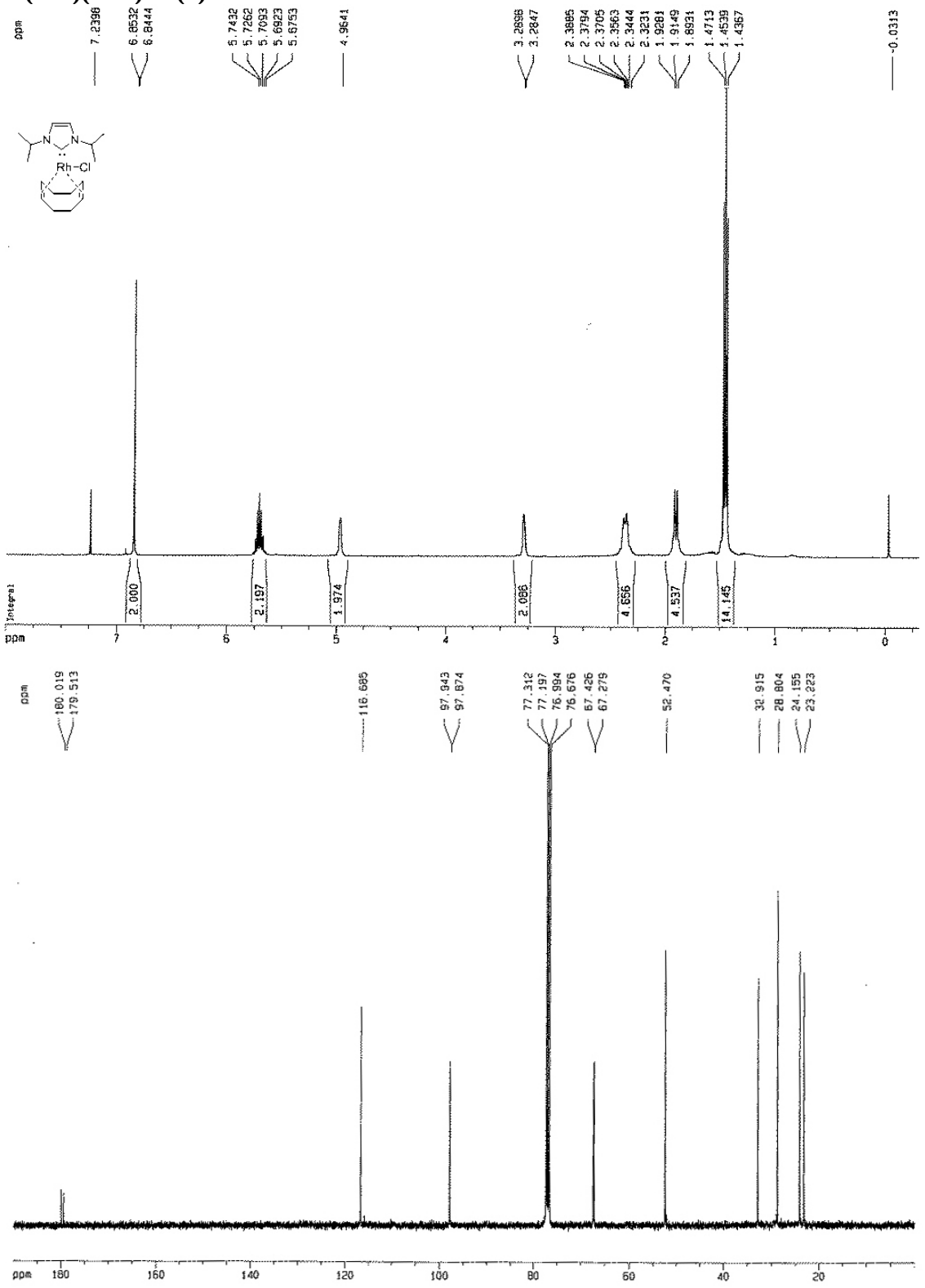
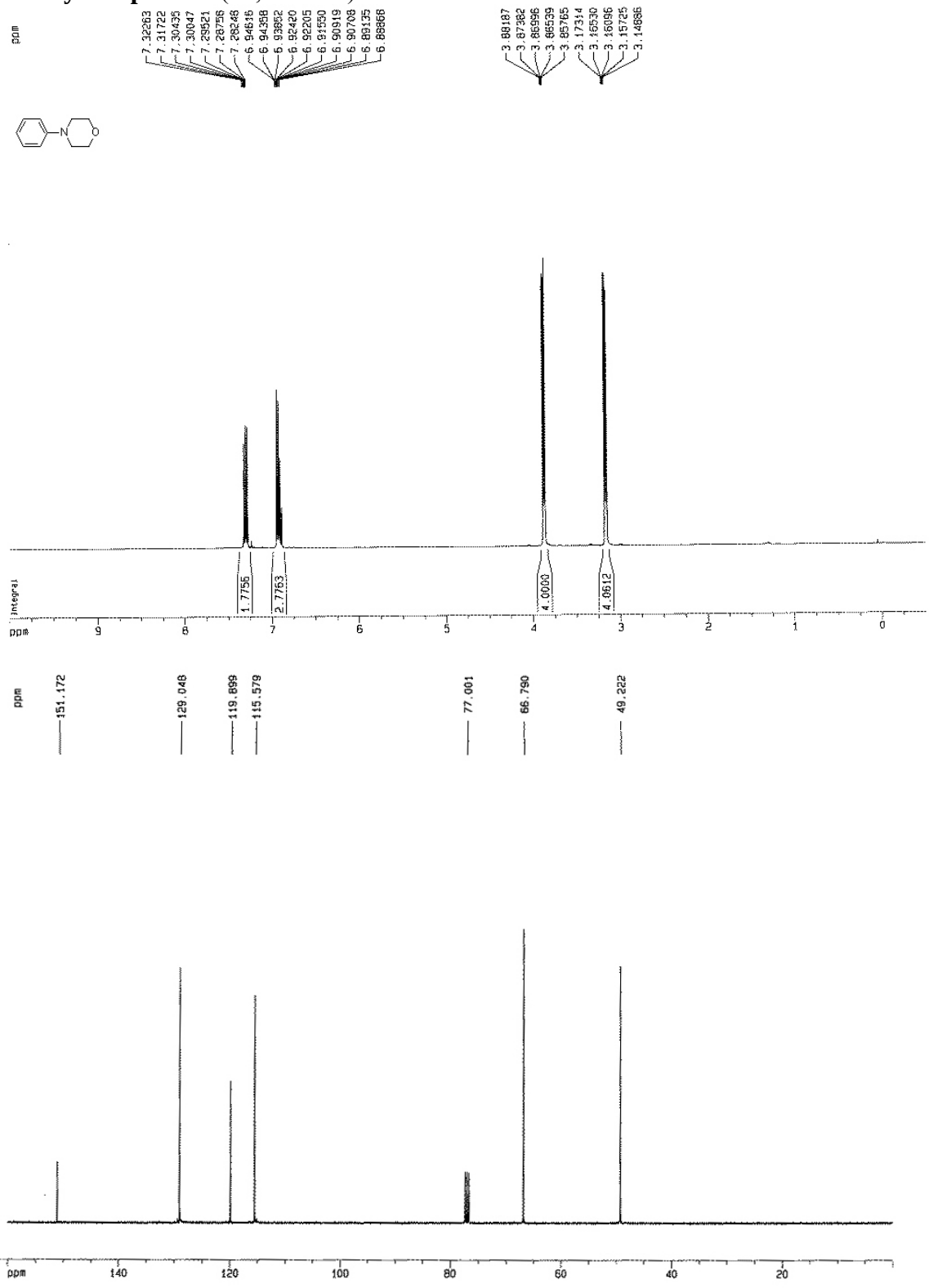
Appendix I

Spectral Copies of ^{1}H and ^{13}C NMR of Compounds Obtained in this Study

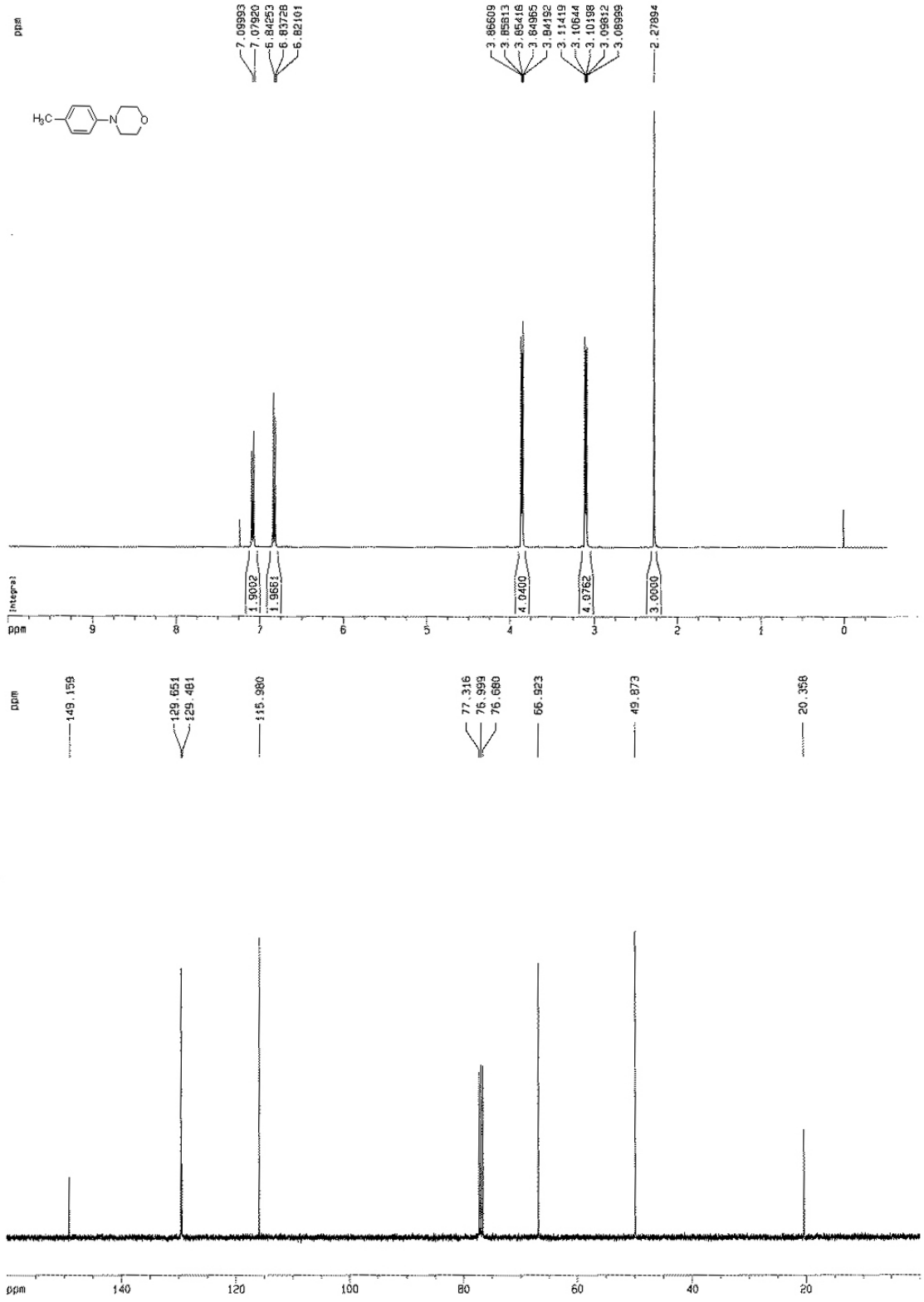
Rh(cod)(I*i*Pr)Cl (4)



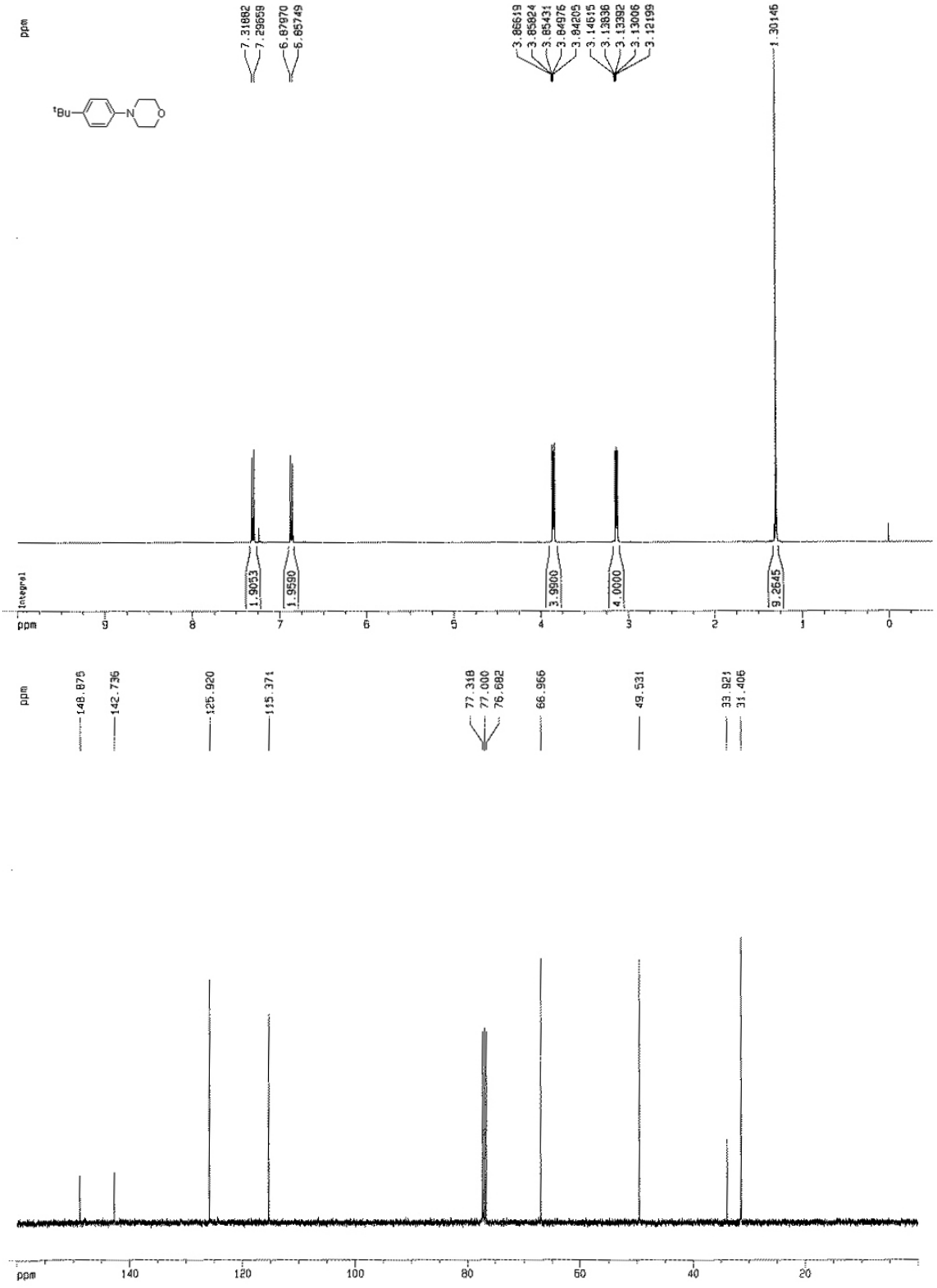
4-Phenylmorpholine (**3a**, Table 2)



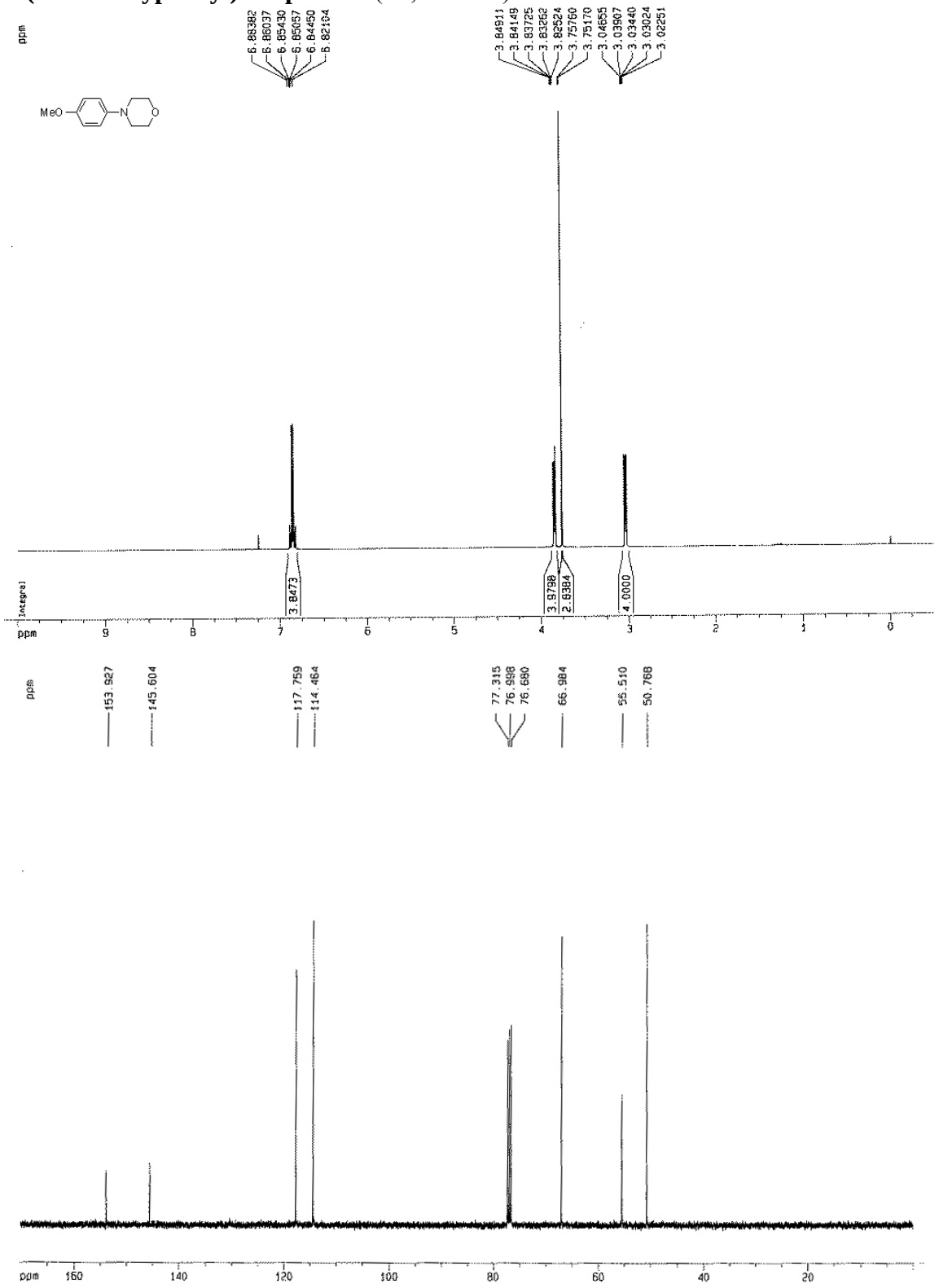
4-(*p*-Tolyl)morpholine (**3b**, Table 2)



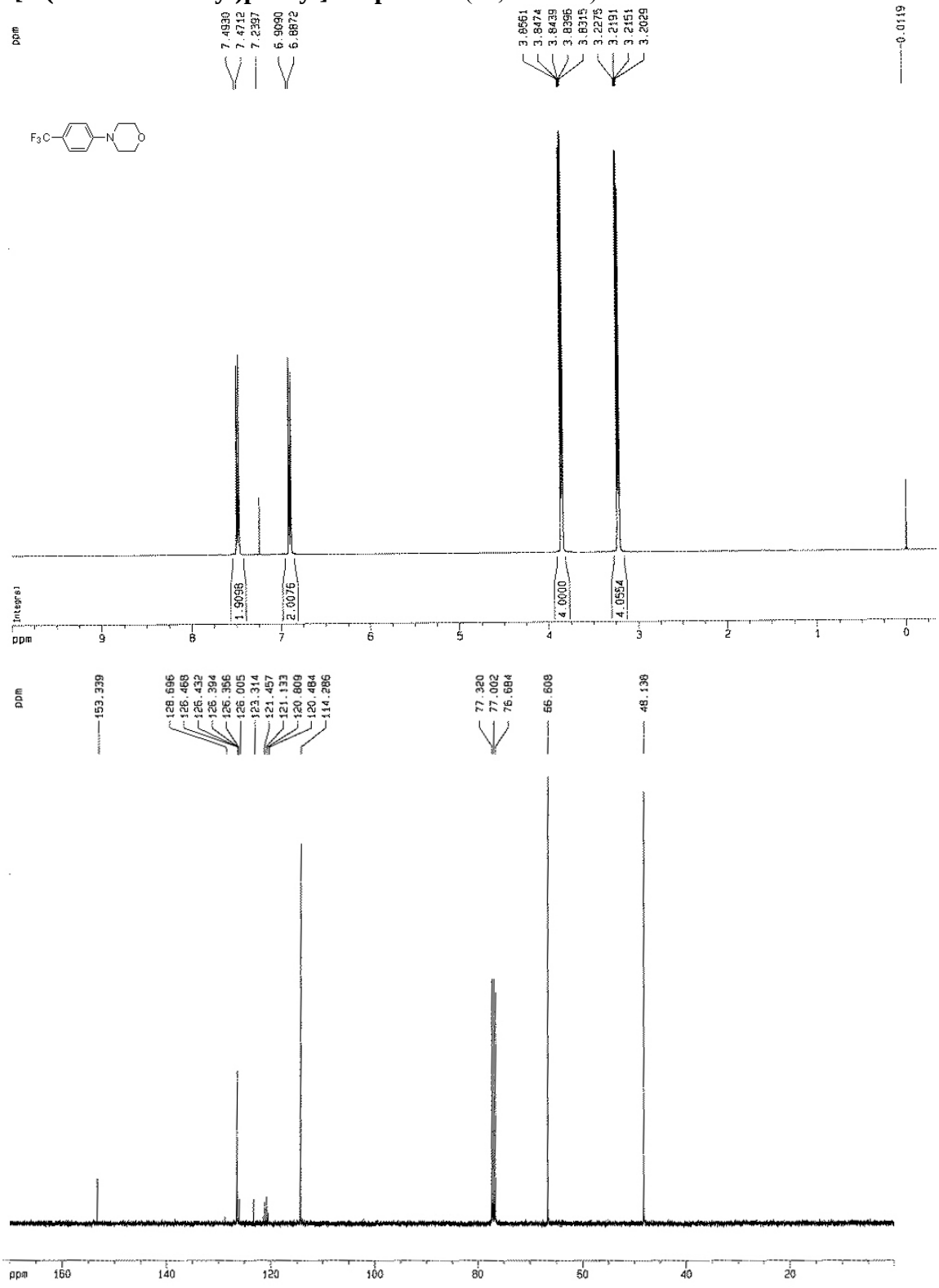
4-(4-*tert*-Butylphenyl)morpholine (**3c**, Table 2)



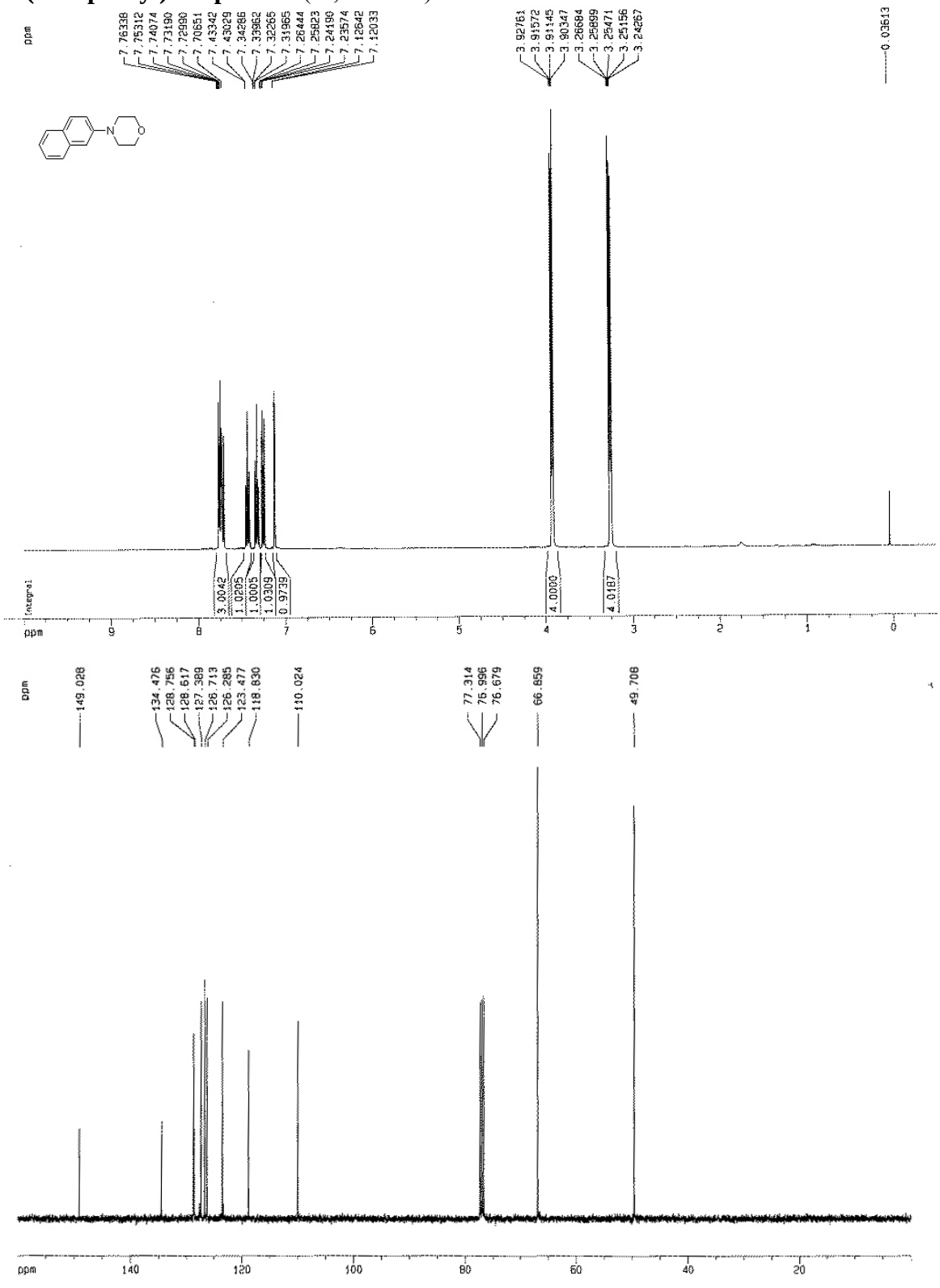
4-(4-Methoxyphenyl)morpholine (**3d**, Table 2)



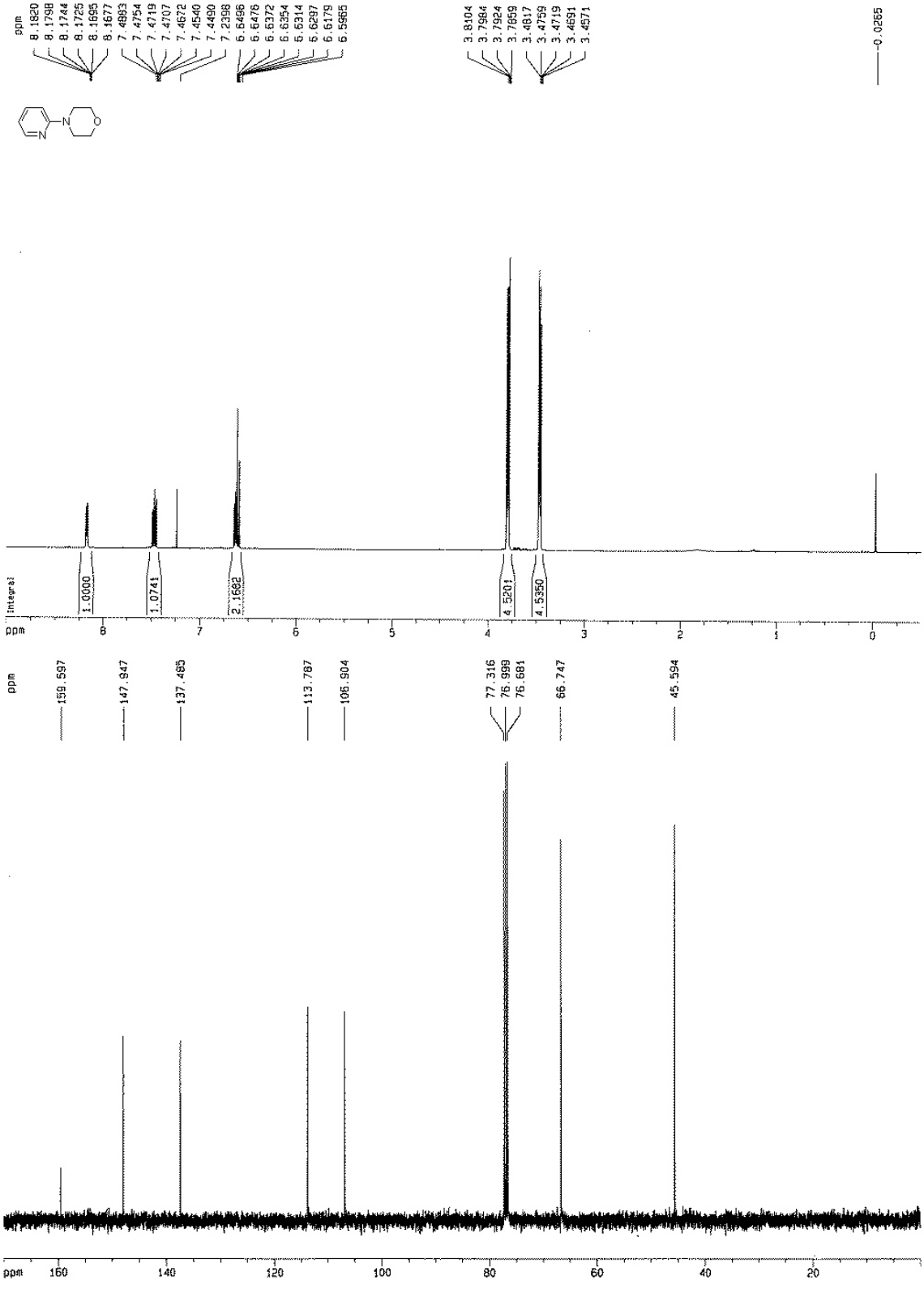
4-[4-(Trifluoromethyl)phenyl]morpholine (**3e**, Table 2)



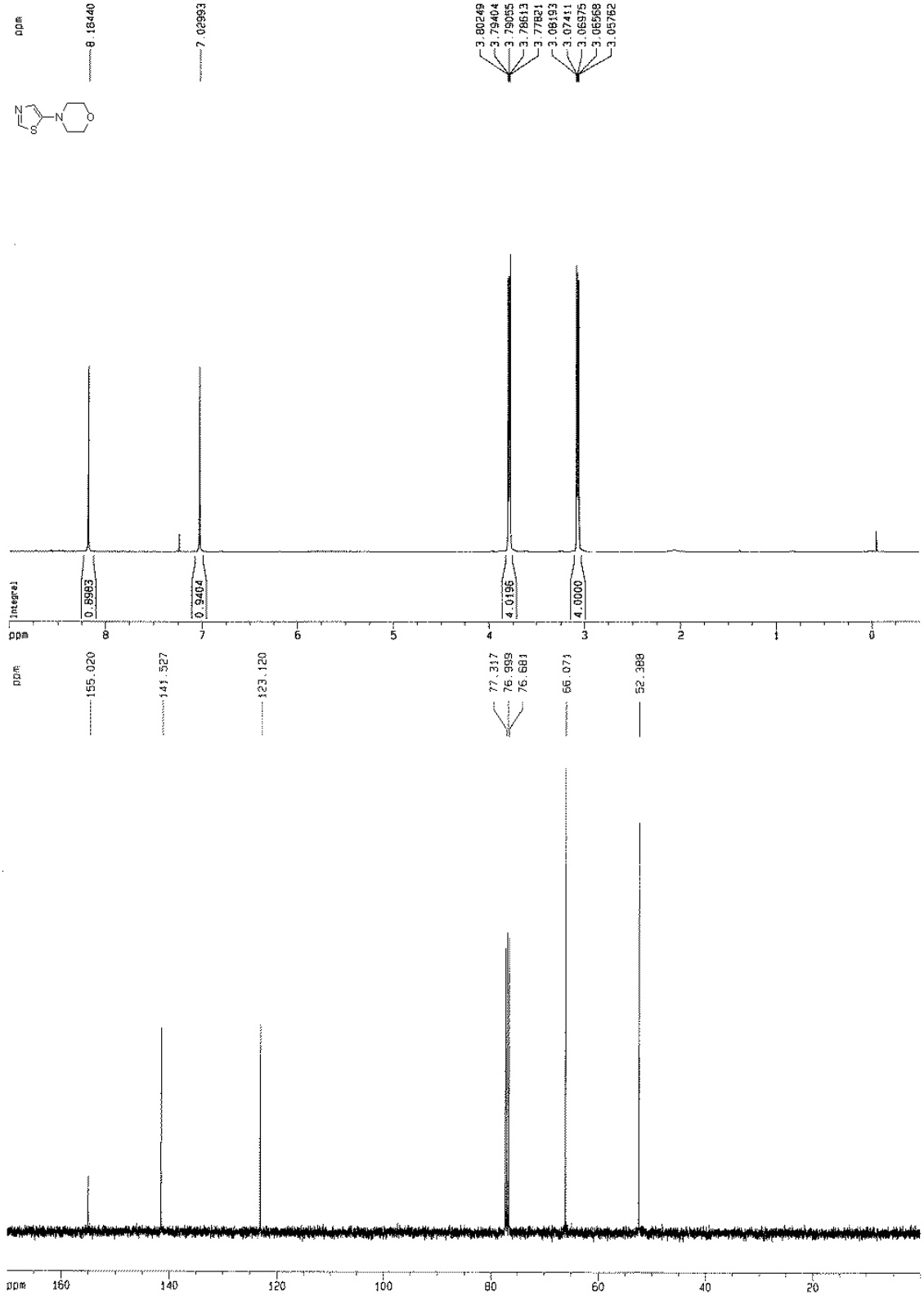
4-(2-Naphthyl)morpholine (**3f**, Table 2)



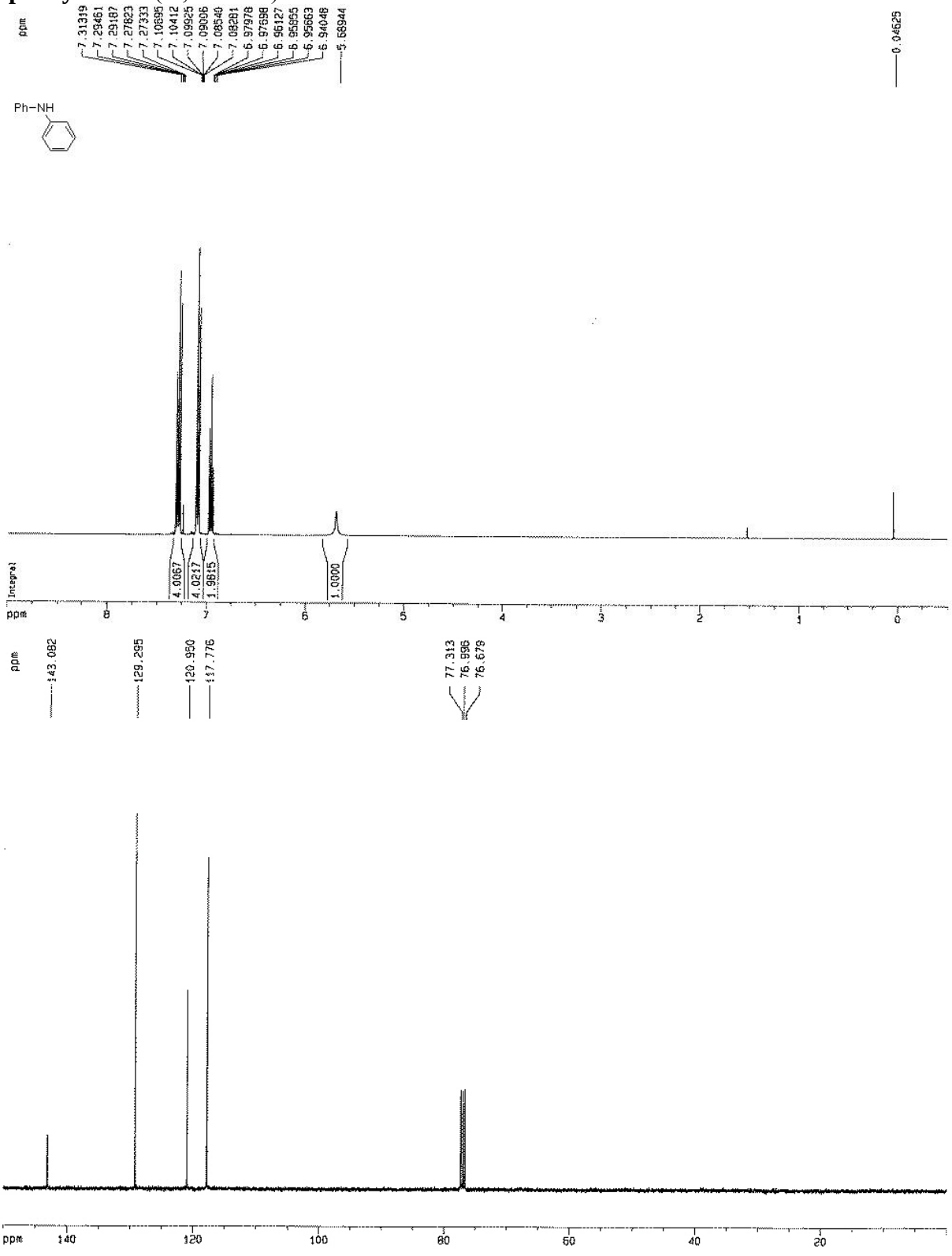
4-(2-Pyridyl)morpholine (**3g**, Table 2)



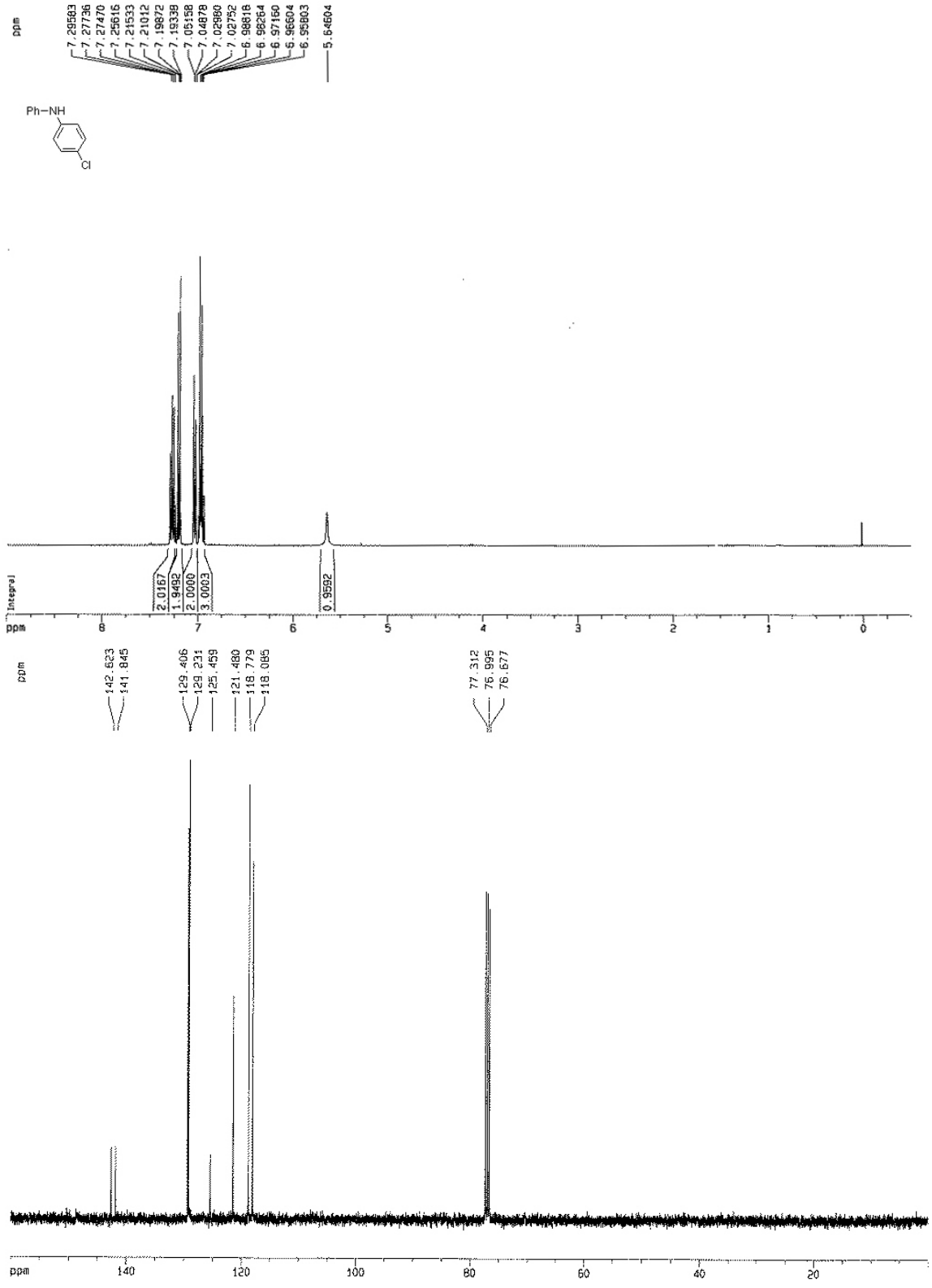
4-(5-Thiazolyl)morpholine (**3h**, Table 2)



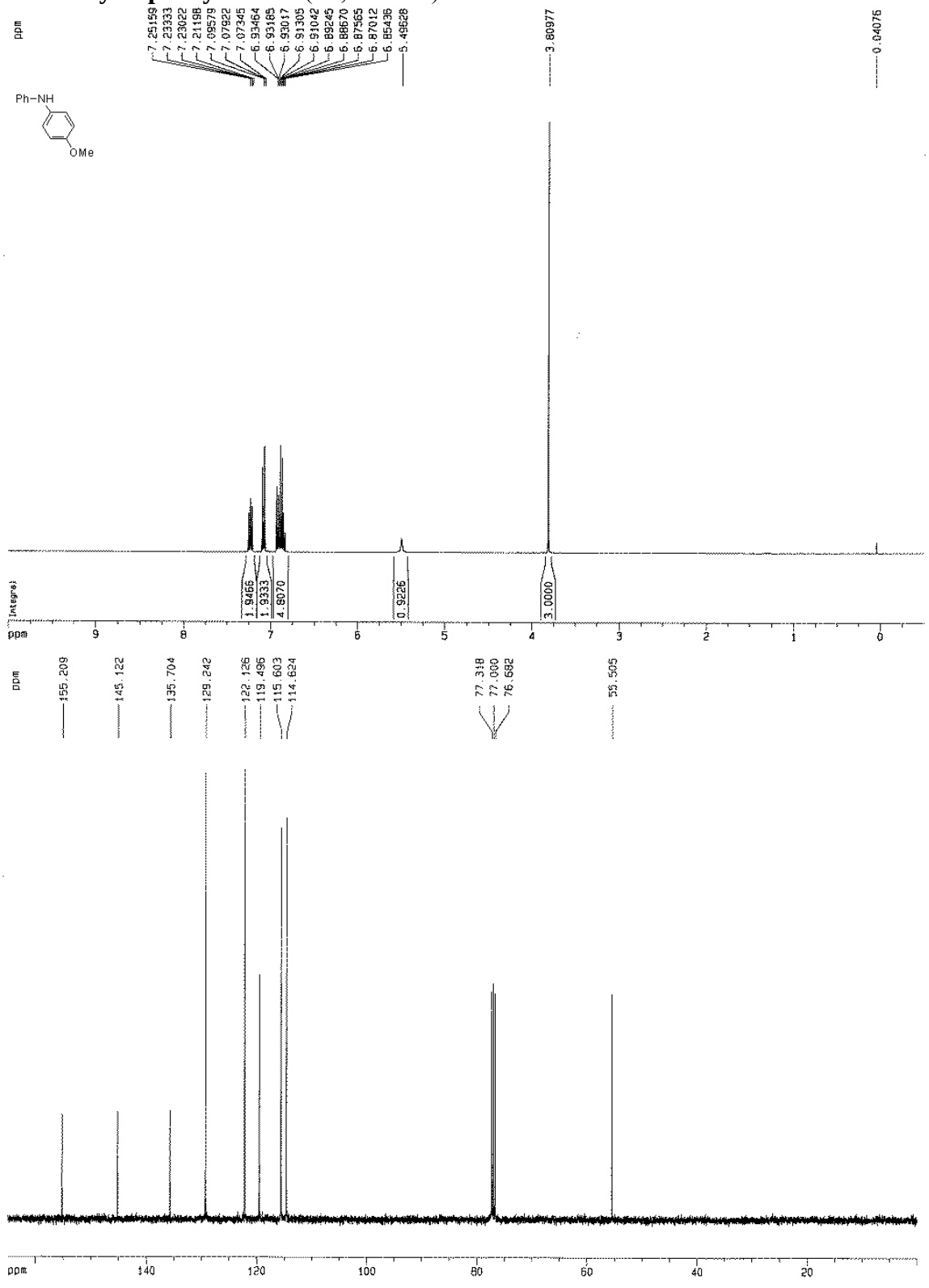
Diphenylamine (**3i**, Table 2)



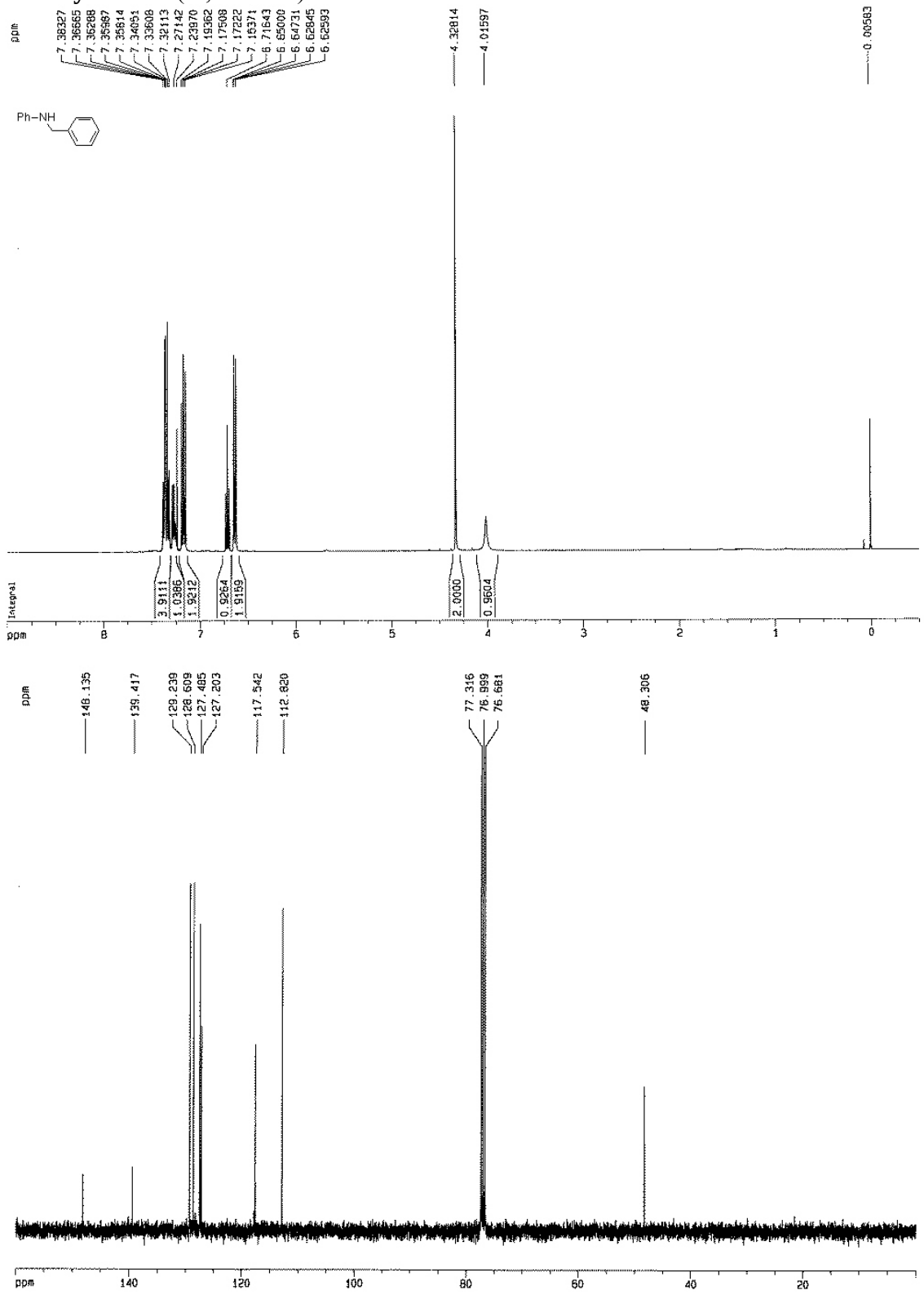
4-Chloro-*N*-phenylaniline (**3j**, Table 2)



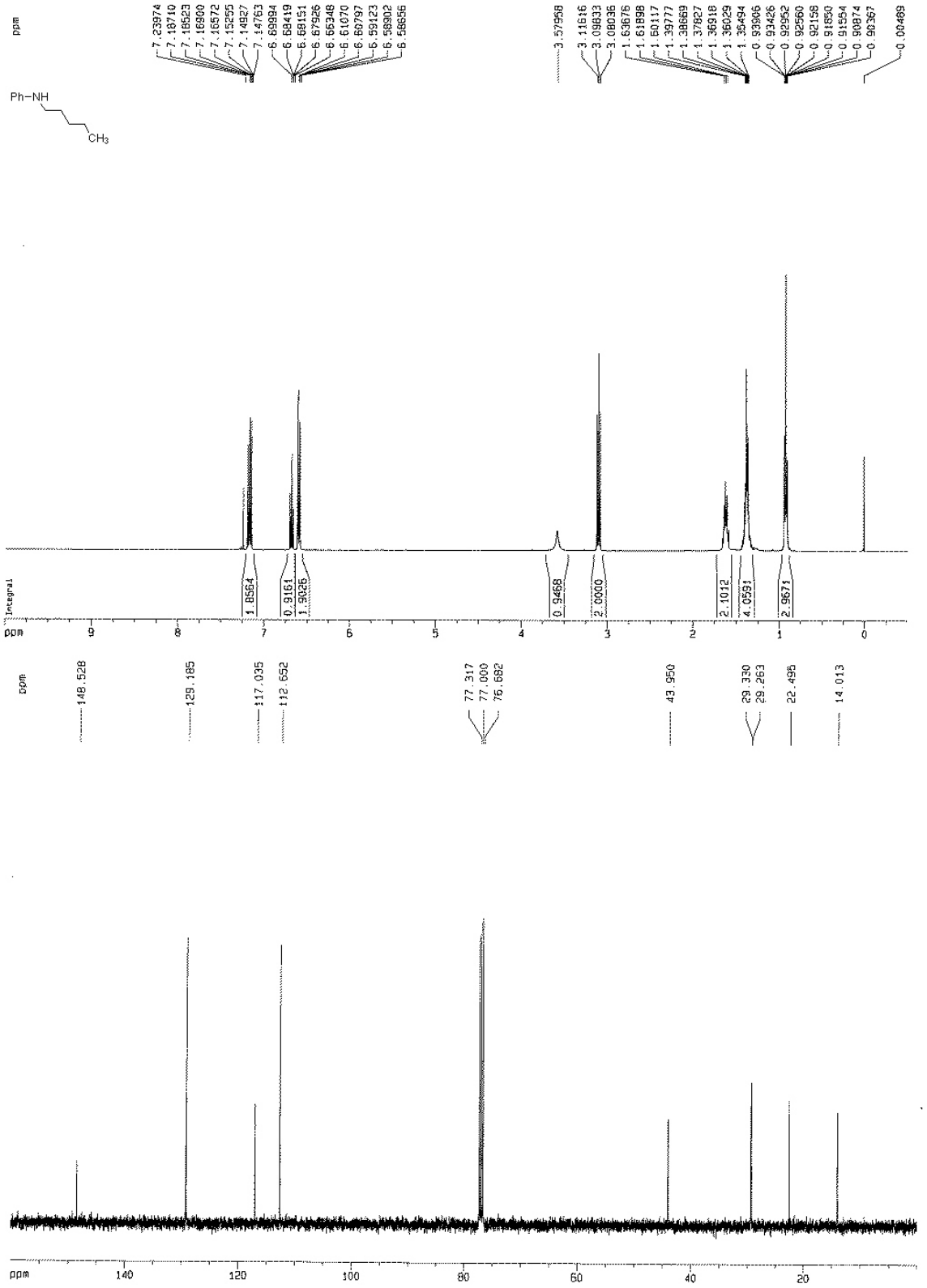
4-Methoxy-*N*-phenylaniline (**3k**, Table 2)



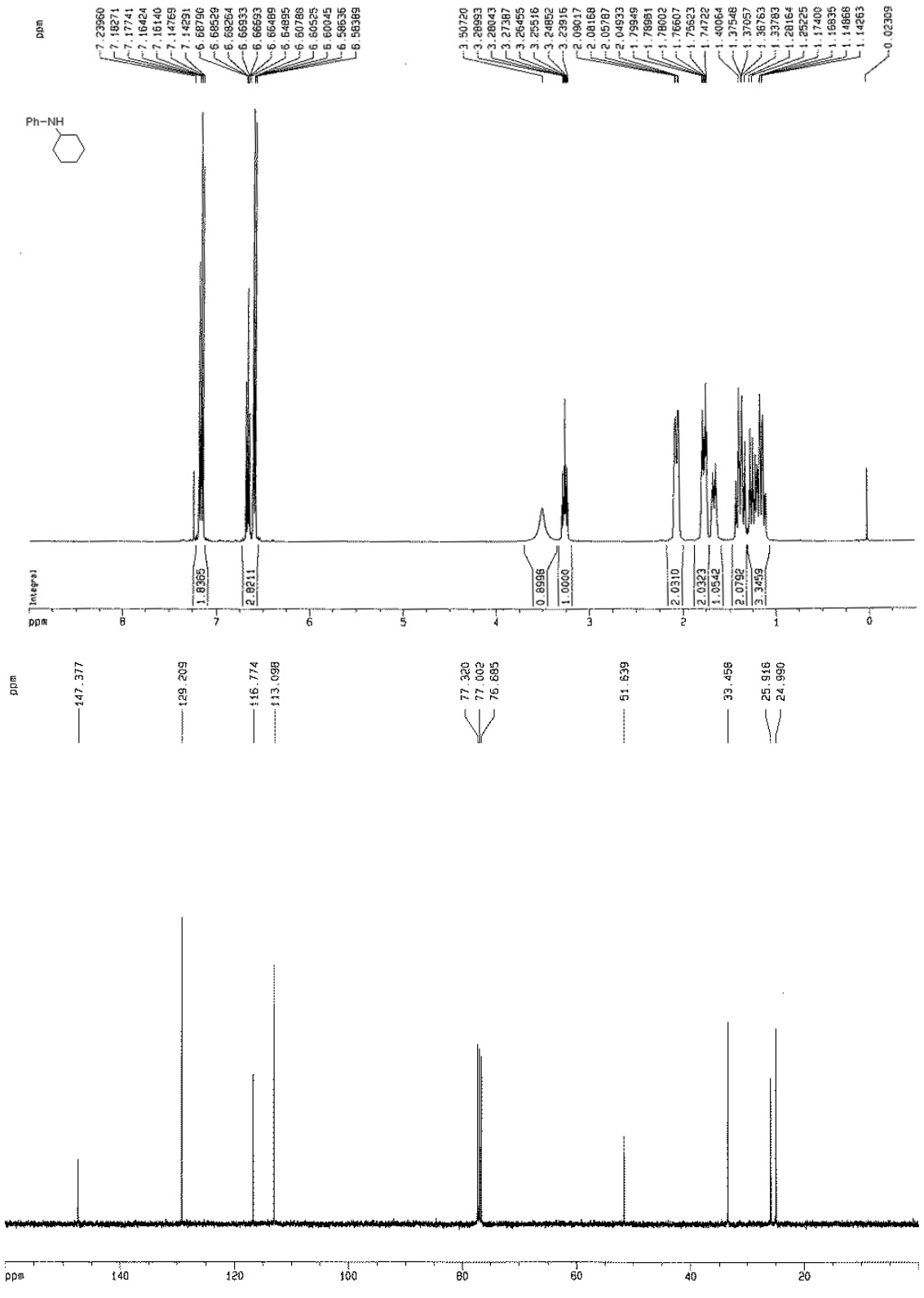
***N*-Benzylaniline** (**3l**, Table 2)



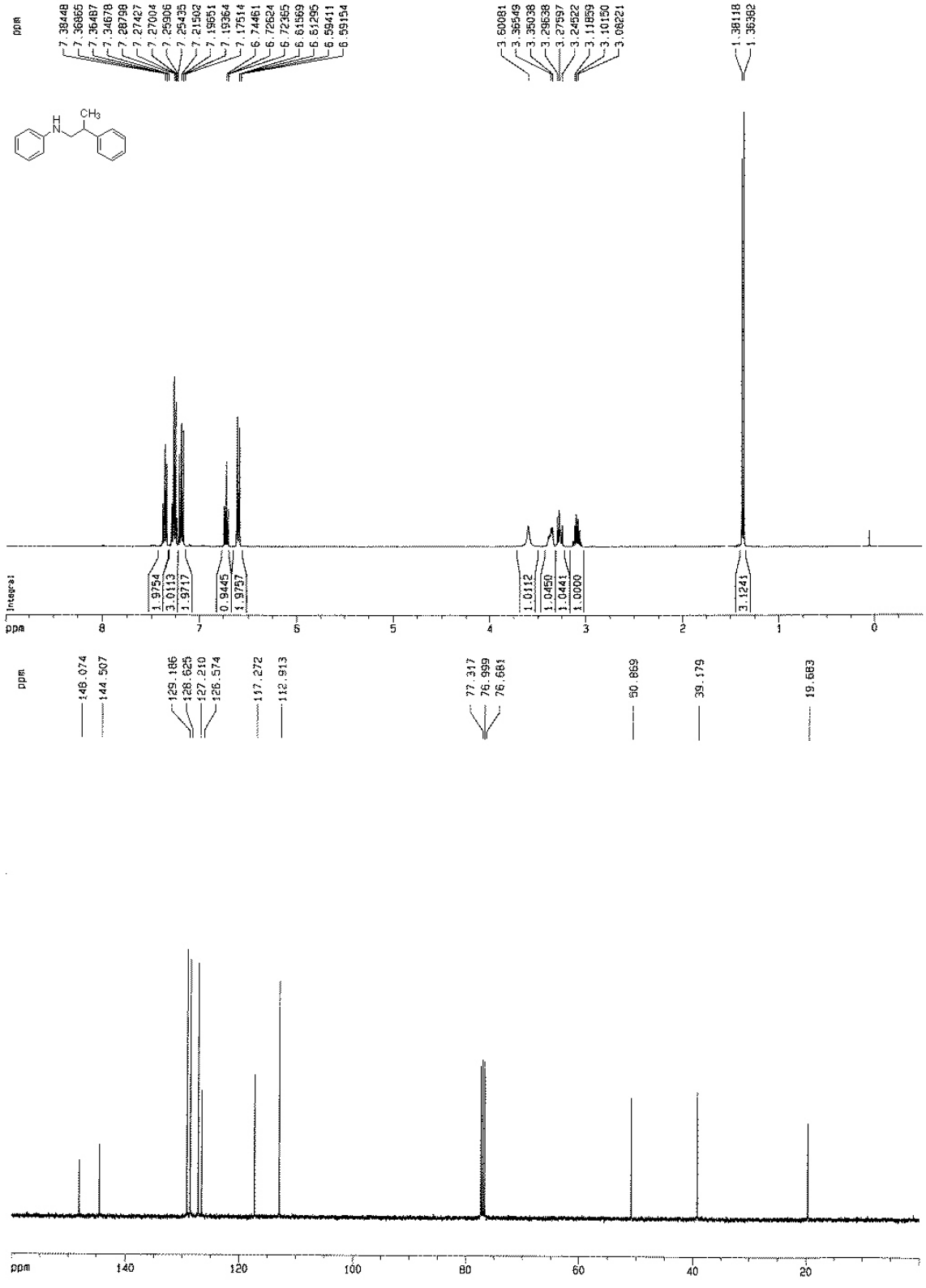
***N*-Pentylaniline** (**3m**, Table 2)



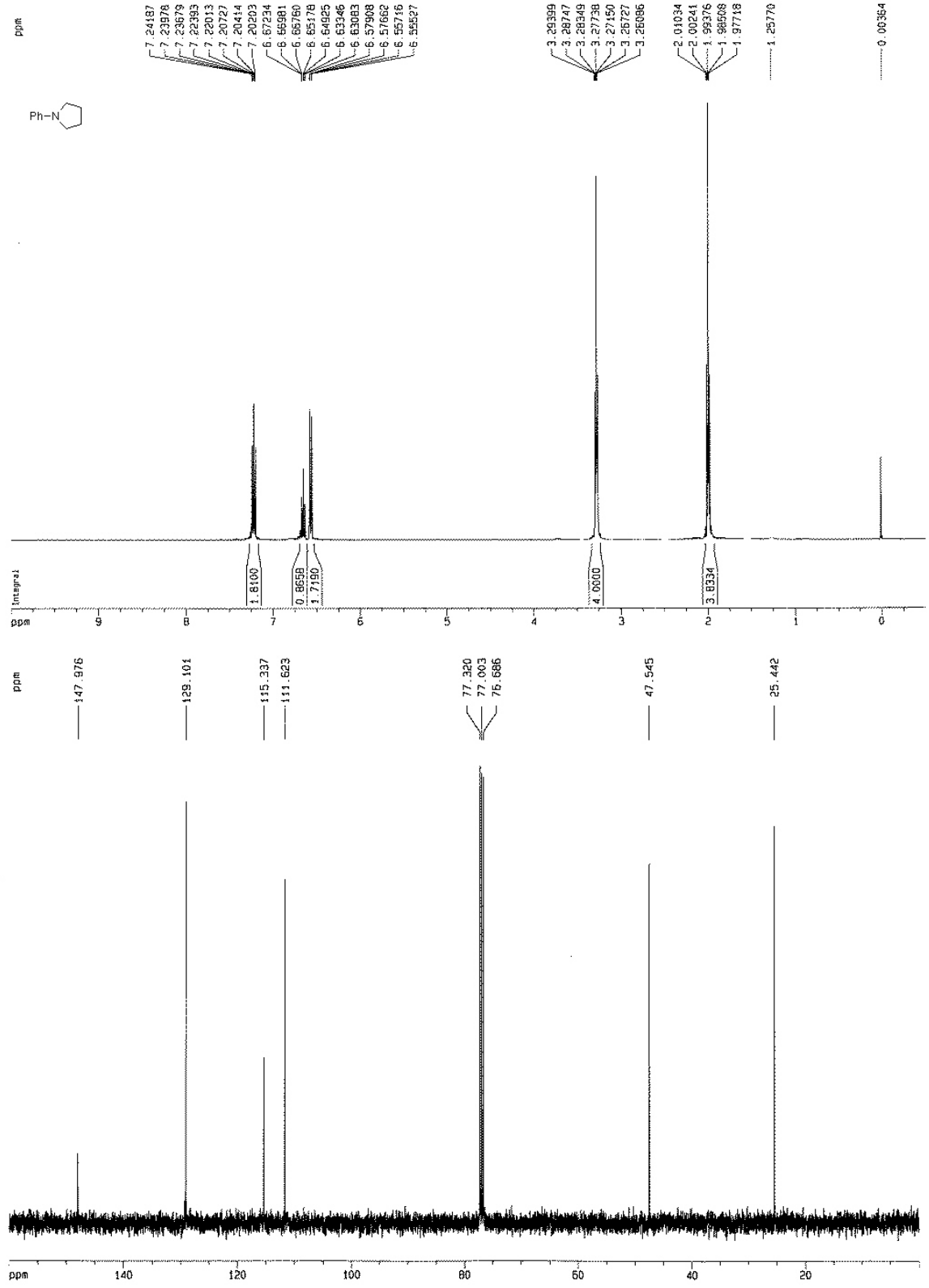
***N*-Cyclohexylaniline** (**3n**, Table 2)



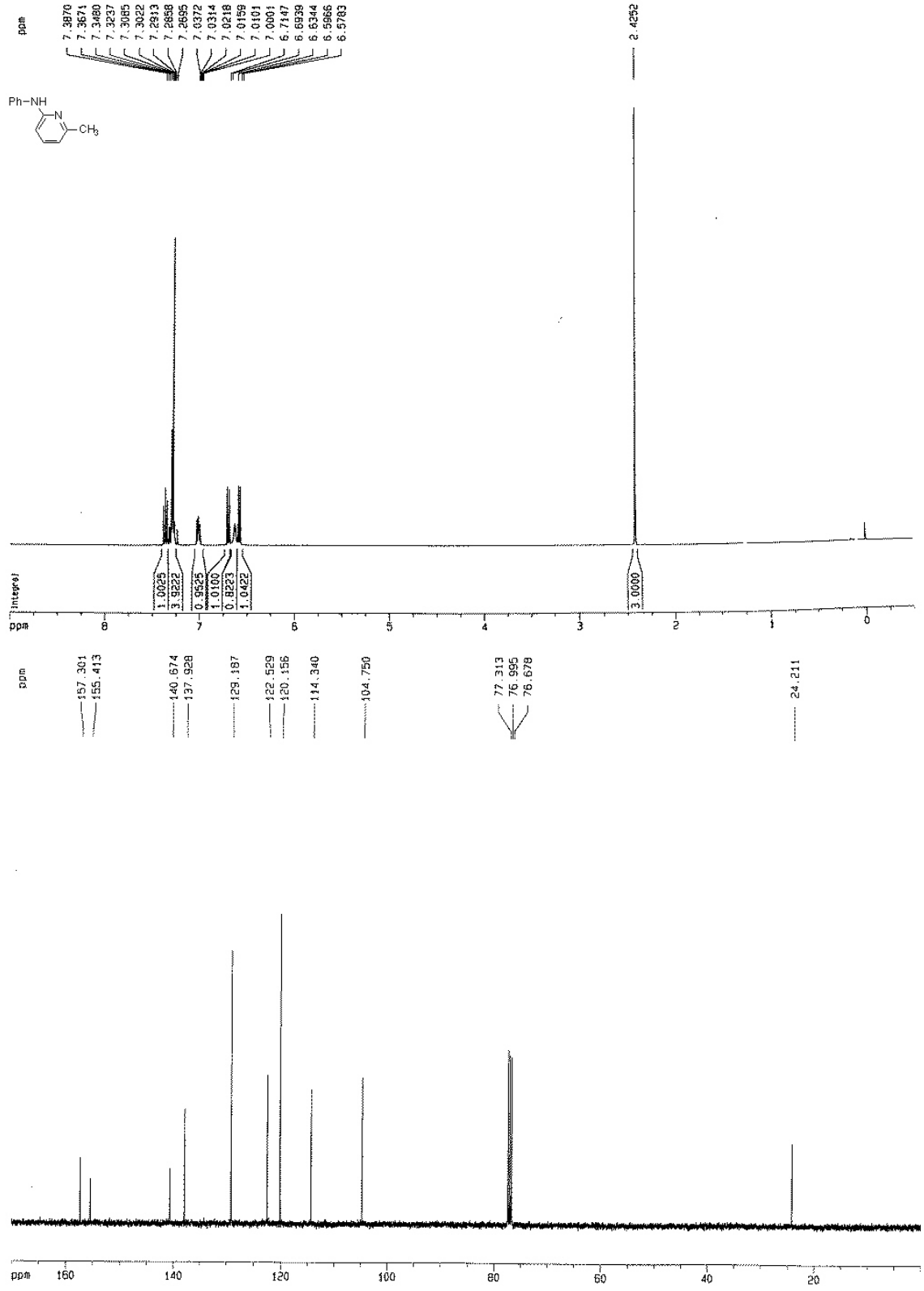
***N*-(2-Phenylpropyl)aniline** (**3o**, Table 2)



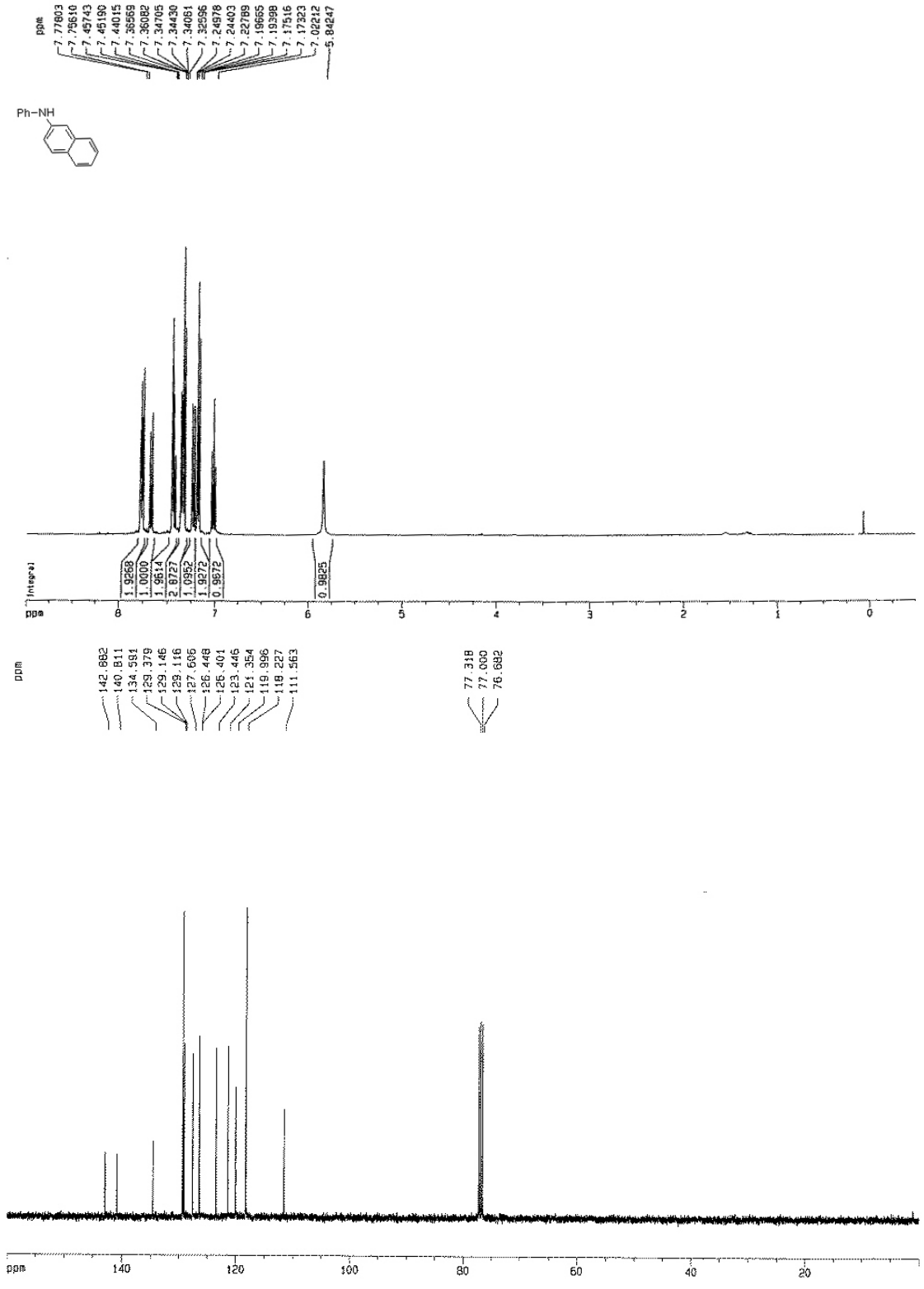
1-Phenylpyrrolidine (**3p**, Table 2)



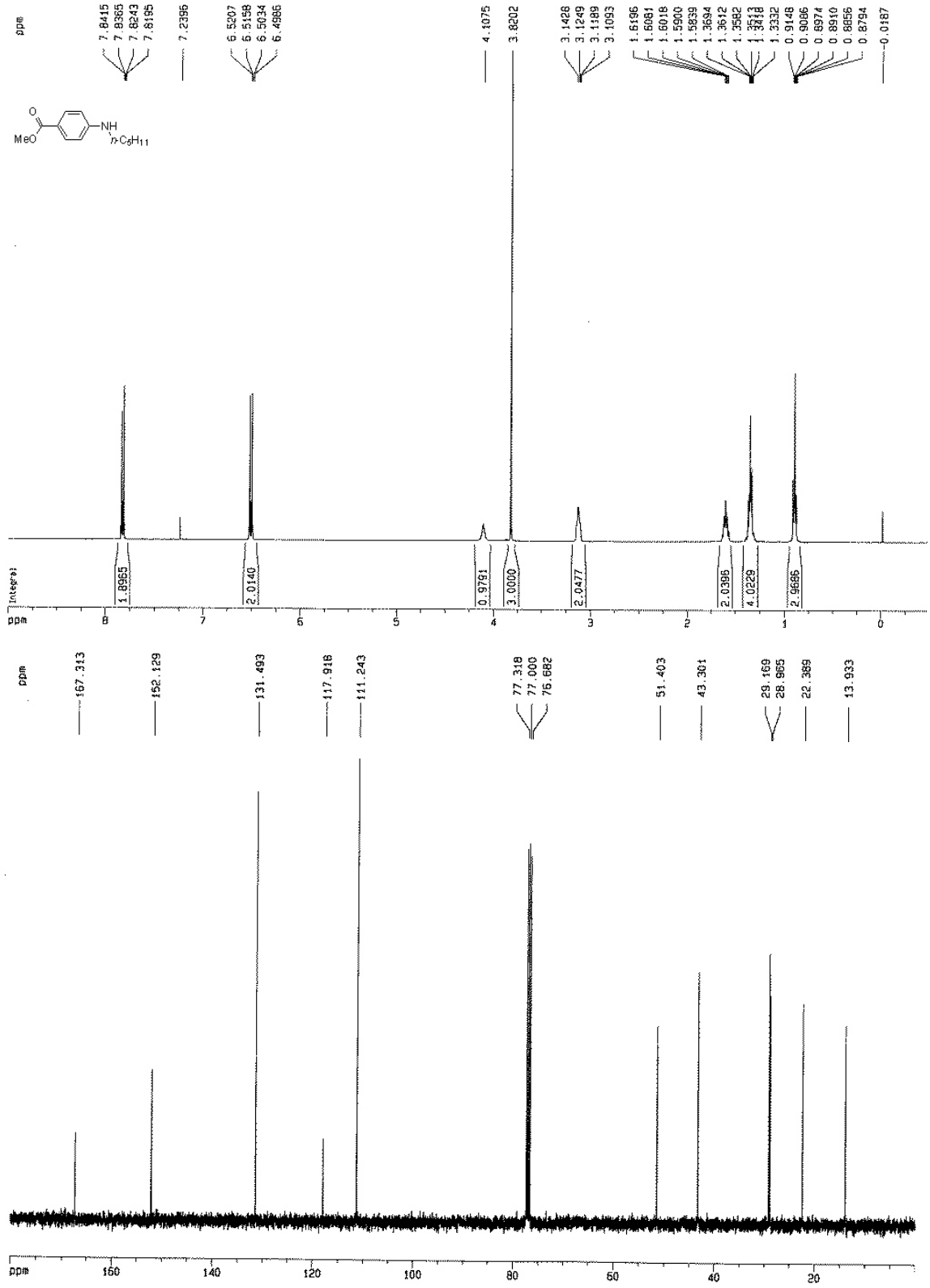
6-Methyl-2-(phenylamino)pyridine (**3q**, Table 2)



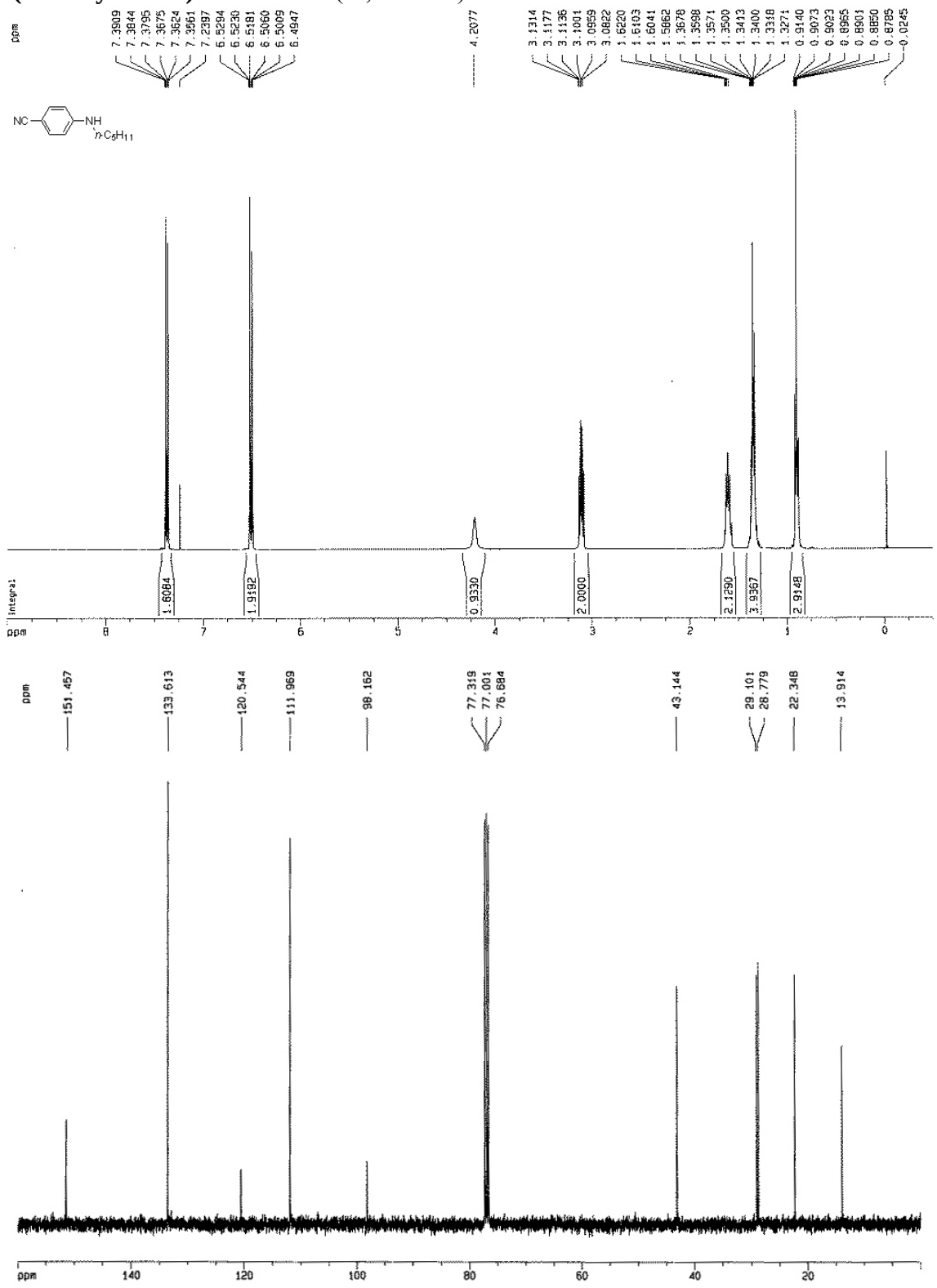
***N*-(2-Naphthyl)aniline** (**3r**, Table 2)



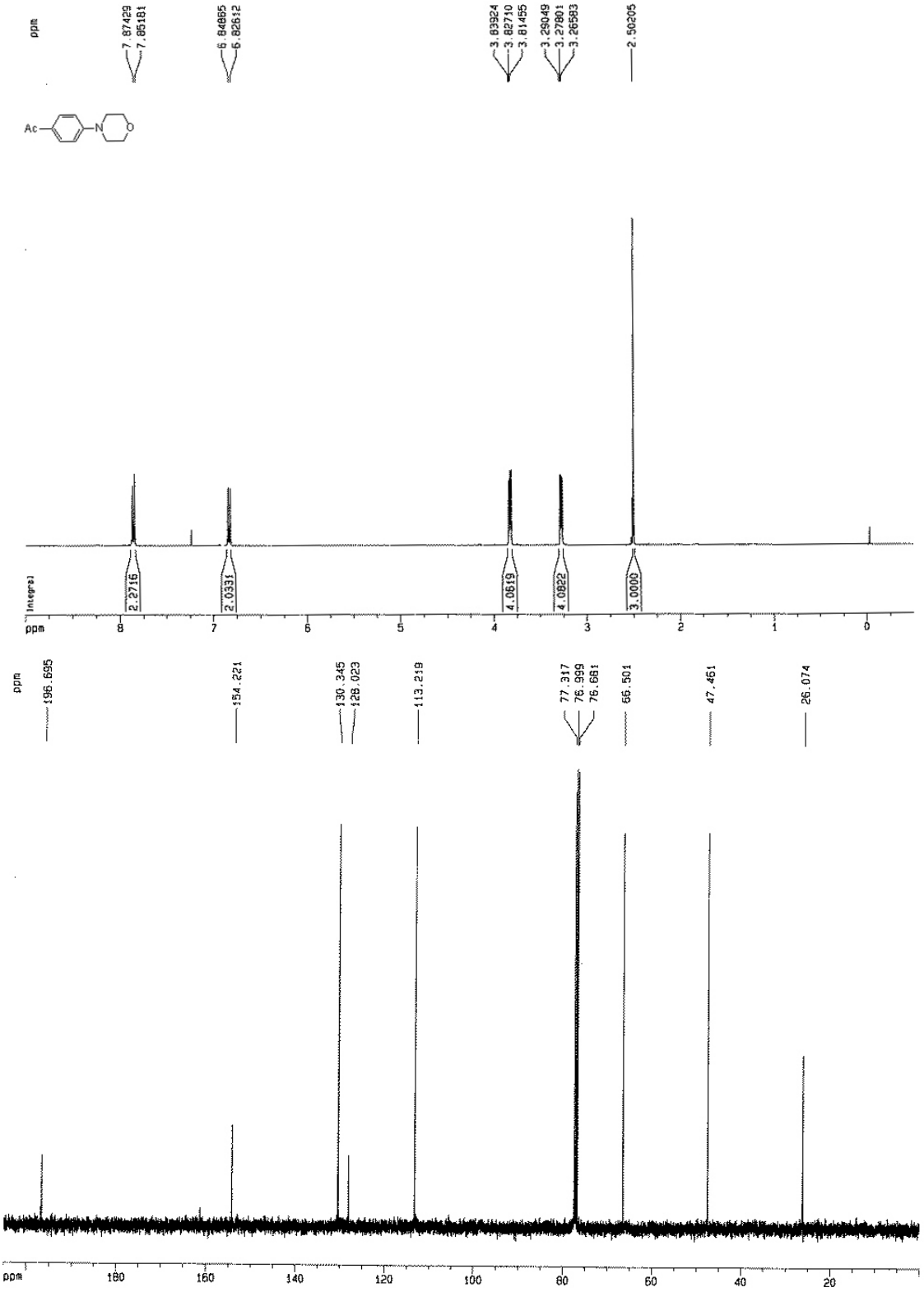
Methyl 4-(pentylamino)benzoate (**3s**, Table 3)



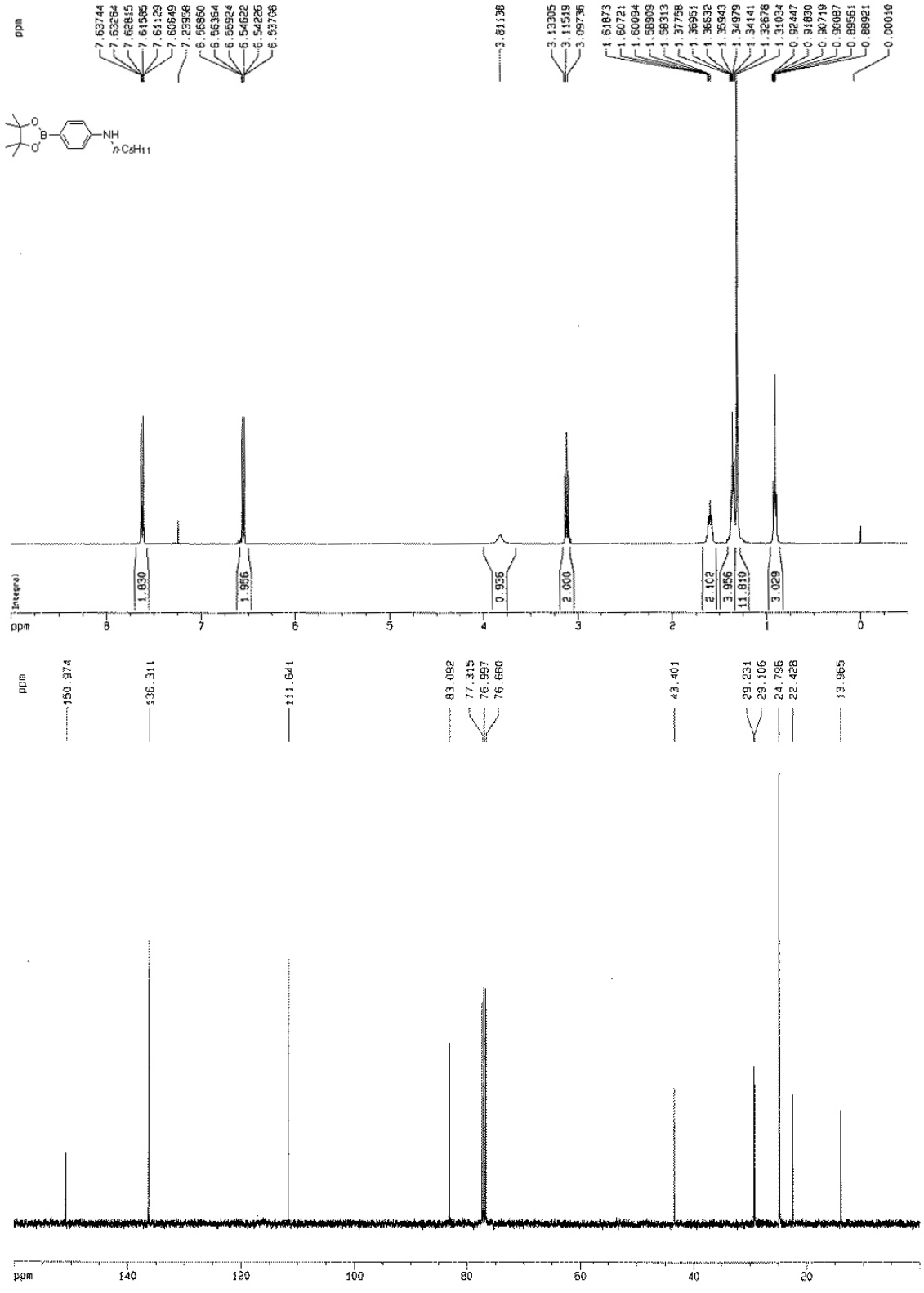
4-(*n*-Pentylamino)benzonitrile (**3t**, Table 3)



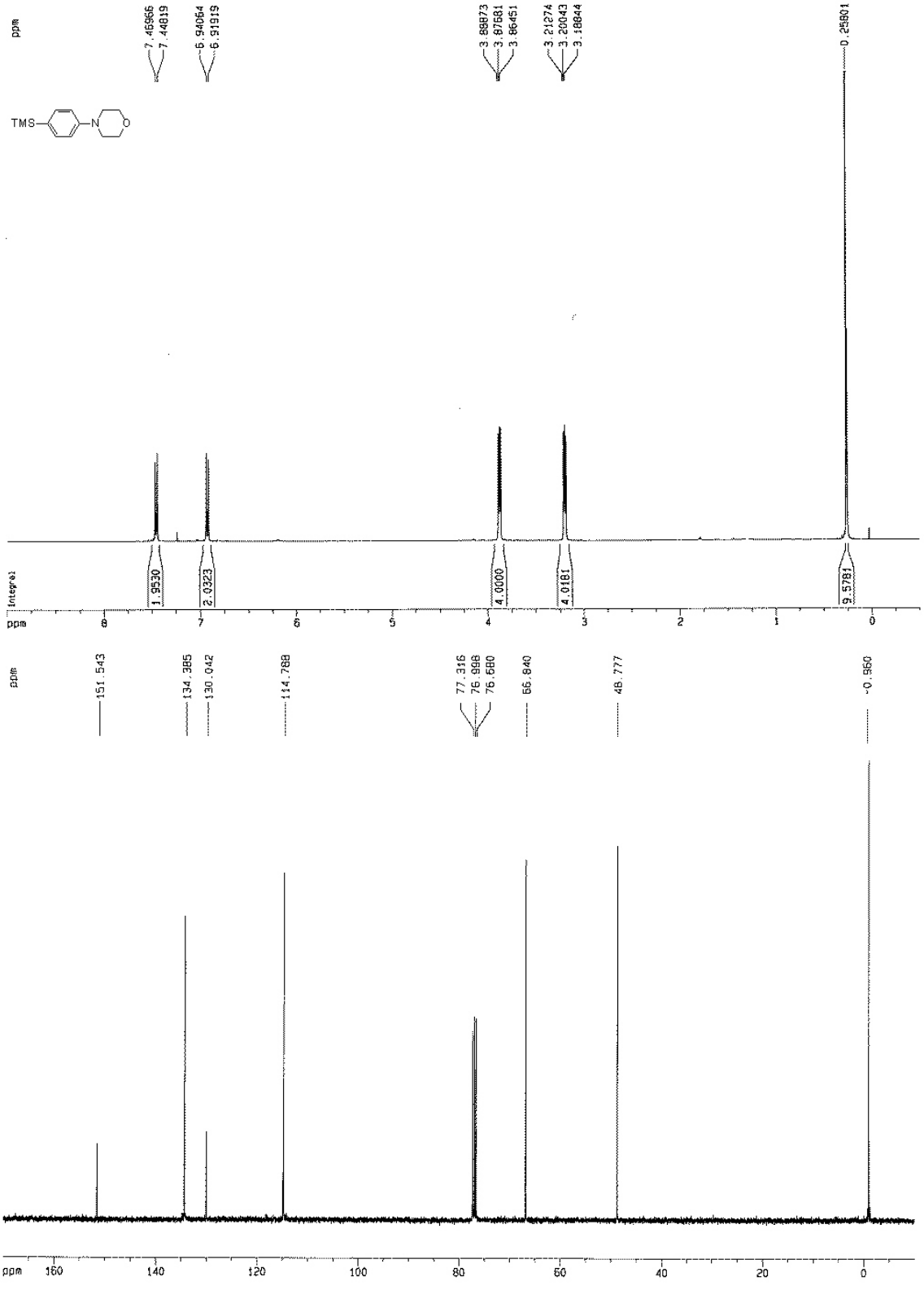
4´-Morpholinoacetophenone (**3u**, Table 3)



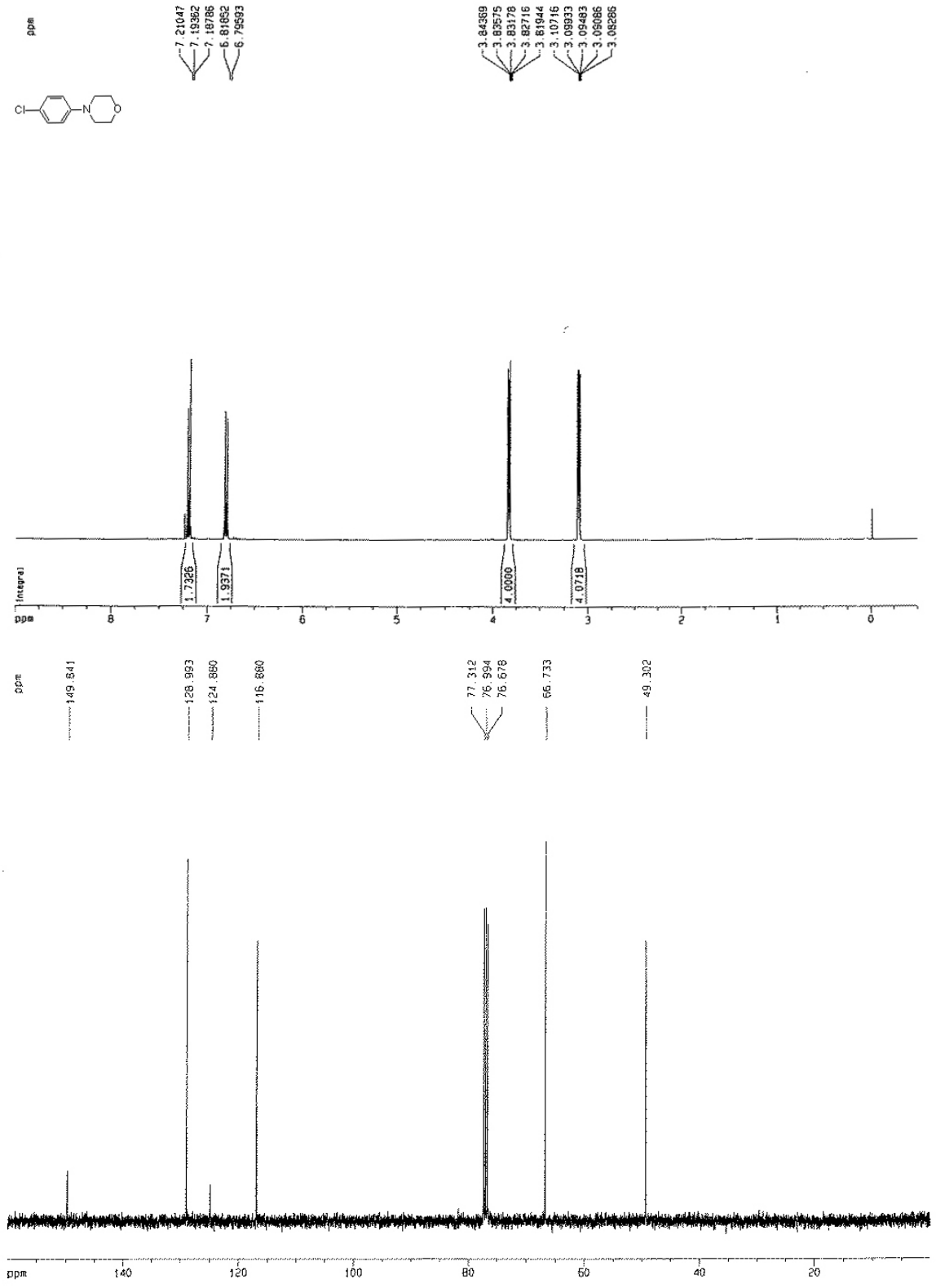
***N*-Pentyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline** (**3v**, Table 3)



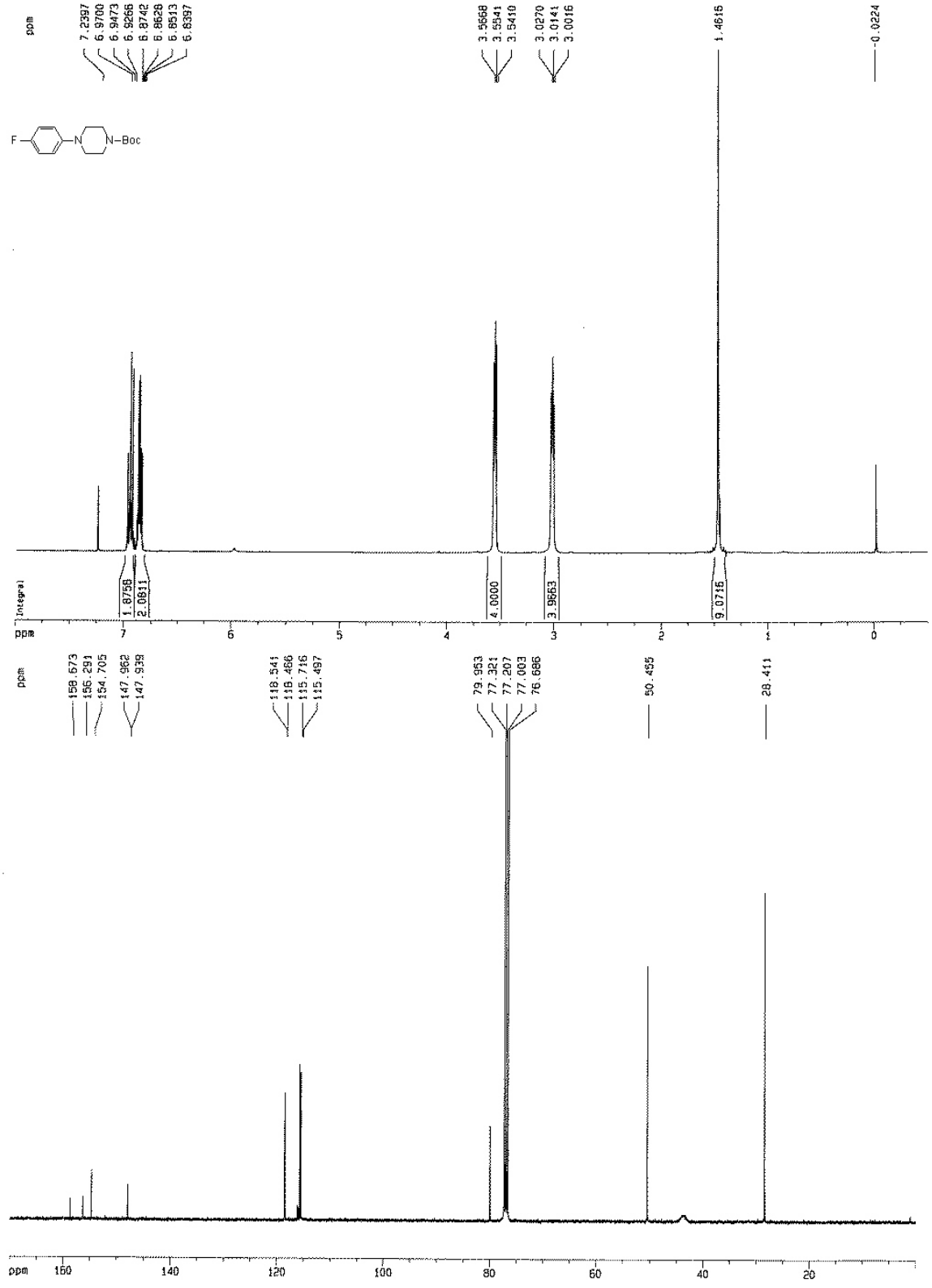
4-[4-(Trimethylsilyl)phenyl]morpholine (**3w**, Table 3)



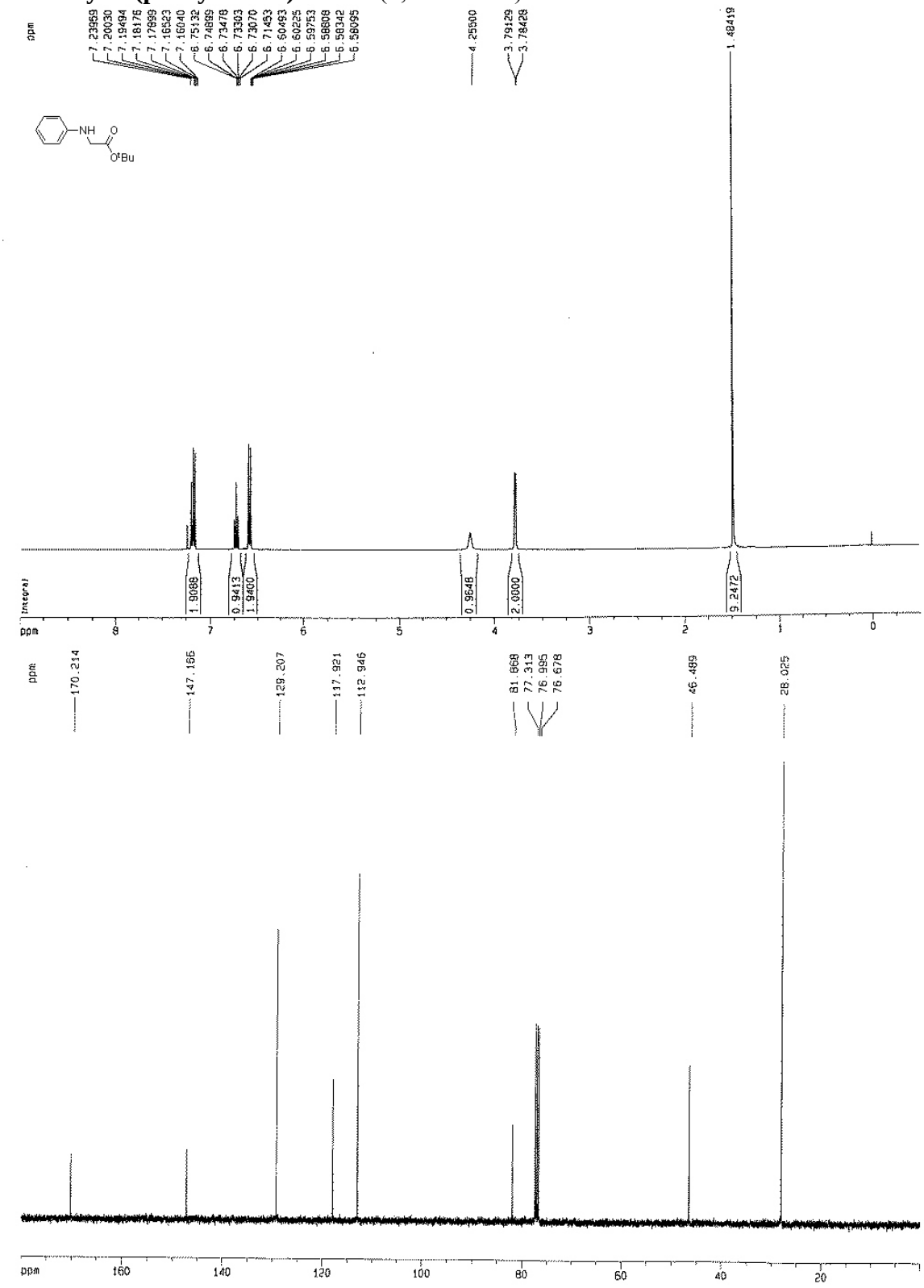
4-(4-Chlorophenyl)morpholine (**3x**, Table 3)



***tert*-Butyl 4-(4-fluorophenyl)piperazine-1-carboxylate** (**3y**, Table 3)



***tert*-Butyl 2-(phenylamino)acetate** (**6**, Scheme 2)



Appendix II

X-Ray Crystallographic Data of a Rh(NHC) Complex 4

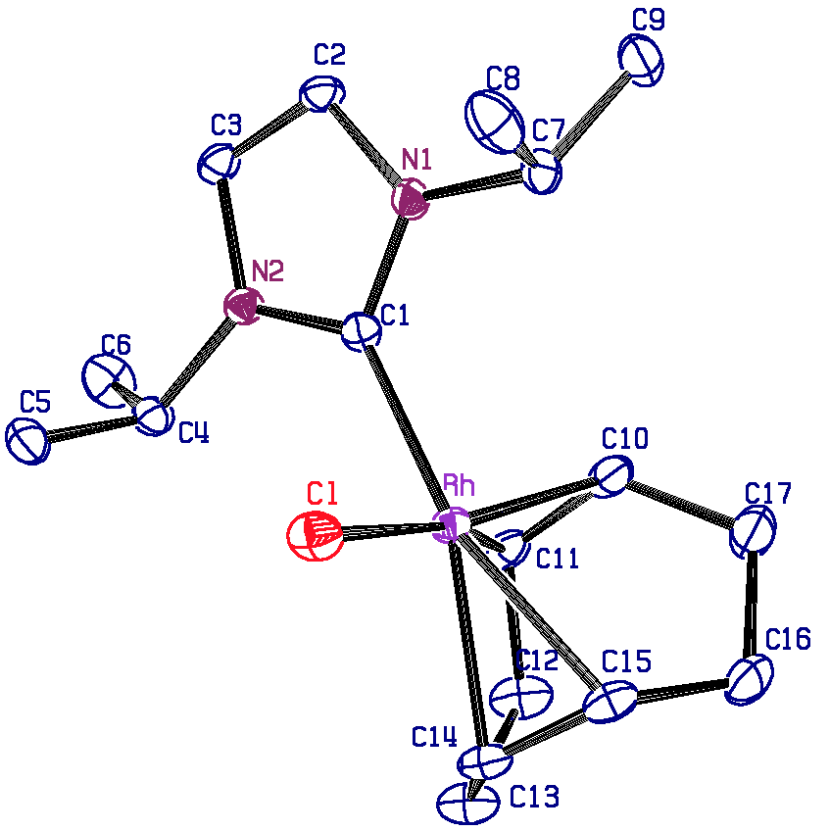


Table S1. Crystal data and structure refinement for Complex **4**.

Identification code	Complex **4**
Empirical formula	$C_{17}H_{28}ClN_2Rh$
Formula weight	398.77
Temerature	296(2) K
Wavelengh	0.71073 A
Unit cell dimensions	a = 10.7478(2) A alpha = 90 deg.
	b = 12.6636(3) A beta = 90 deg.
	c = 26.7573(6) A gamma = 90 deg.
Volume	3641.82(14) A^3
Z, Calculated density	8, 1.455 Mg/m^3
Absorption coefficient	1.081 mm^-1
F(000)	1648
Theta range for data collection	2.43 to 28.81 deg.
Limiting indices	-14<=h<=13, -16<=k<=14, -34<=l<=28
Reflections collected / unique	16292 / 3930 [R(int) = 0.0235]
Completeness to theta = 28.81	82.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	930 / 0 / 194
Goodness-of-fit on F^2	1.091
Final R indices [I>2sigma(I)]	R1 = 0.0287, wR2 = 0.0645
R indices (all data)	R1 = 0.0350, wR2 = 0.0668
Largest diff. peak and hole	0.721 and -0.522 e.A^-3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for Complex **4**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Rh	486(1)	7730(1)	3759(1)	13(1)
Cl	-1133(1)	8470(1)	3260(1)	19(1)
N(1)	557(2)	5898(2)	3030(1)	14(1)
C(14)	446(2)	9107(2)	4258(1)	18(1)
N(2)	-671(2)	5536(2)	3640(1)	14(1)
C(3)	-690(2)	4673(2)	3321(1)	16(1)
C(7)	1363(2)	6501(2)	2686(1)	17(1)
C(5)	-2750(2)	6072(2)	3908(1)	20(1)
C(2)	84(2)	4894(2)	2939(1)	16(1)
C(1)	97(2)	6303(2)	3460(1)	13(1)
C(4)	-1475(2)	5690(2)	4080(1)	16(1)
C(8)	616(2)	6906(2)	2244(1)	25(1)
C(9)	2472(2)	5844(2)	2526(1)	22(1)
C(10)	2280(2)	7194(2)	3947(1)	20(1)
C(6)	-1539(3)	4683(2)	4389(1)	26(1)
C(15)	1359(2)	9286(2)	3910(1)	20(1)
C(11)	1501(2)	7066(2)	4361(1)	19(1)
C(12)	1545(3)	7781(2)	4818(1)	25(1)
C(17)	3230(2)	8059(2)	3872(1)	28(1)
C(13)	643(3)	8714(2)	4782(1)	25(1)
C(16)	2744(2)	9163(2)	4010(1)	26(1)

Table S3. Bond lengths [A] and angles [deg] for Complex **4**.

Rh-C(1)	2.020(2)
Rh-C(10)	2.105(2)
Rh-C(11)	2.119(3)
Rh-C(14)	2.197(3)
Rh-C(15)	2.220(2)
Rh-Cl	2.3850(6)
N(1)-C(1)	1.352(3)
N(1)-C(2)	1.390(3)
N(1)-C(7)	1.478(3)
C(14)-C(15)	1.371(4)
C(14)-C(13)	1.504(4)
N(2)-C(1)	1.362(3)
N(2)-C(3)	1.386(3)
N(2)-C(4)	1.474(3)
C(3)-C(2)	1.348(4)
C(7)-C(9)	1.515(3)
C(7)-C(8)	1.518(4)
C(5)-C(4)	1.525(3)
C(4)-C(6)	1.522(4)
C(10)-C(11)	1.397(4)
C(10)-C(17)	1.511(4)
C(15)-C(16)	1.521(4)
C(11)-C(12)	1.523(4)
C(12)-C(13)	1.531(4)
C(17)-C(16)	1.537(4)
C(1)-Rh-C(10)	89.78(9)
C(1)-Rh-C(11)	93.04(10)
C(10)-Rh-C(11)	38.64(11)
C(1)-Rh-C(14)	161.21(10)
C(10)-Rh-C(14)	97.37(10)
C(11)-Rh-C(14)	82.10(10)
C(1)-Rh-C(15)	162.55(10)
C(10)-Rh-C(15)	81.70(10)
C(11)-Rh-C(15)	89.77(10)
C(14)-Rh-C(15)	36.17(10)
C(1)-Rh-Cl	88.79(7)
C(10)-Rh-Cl	158.27(9)
C(11)-Rh-Cl	163.09(8)
C(14)-Rh-Cl	90.80(7)
C(15)-Rh-Cl	93.52(7)
C(1)-N(1)-C(2)	111.2(2)
C(1)-N(1)-C(7)	123.3(2)
C(2)-N(1)-C(7)	125.2(2)
C(15)-C(14)-C(13)	126.0(2)
C(15)-C(14)-Rh	72.81(16)
C(13)-C(14)-Rh	107.54(17)

C(1)-N(2)-C(3)	110.8(2)
C(1)-N(2)-C(4)	122.9(2)
C(3)-N(2)-C(4)	125.9(2)
C(2)-C(3)-N(2)	107.0(2)
N(1)-C(7)-C(9)	110.7(2)
N(1)-C(7)-C(8)	110.5(2)
C(9)-C(7)-C(8)	112.5(2)
C(3)-C(2)-N(1)	106.4(2)
N(1)-C(1)-N(2)	104.6(2)
N(1)-C(1)-Rh	126.85(17)
N(2)-C(1)-Rh	128.59(19)
N(2)-C(4)-C(6)	110.6(2)
N(2)-C(4)-C(5)	109.2(2)
C(6)-C(4)-C(5)	112.9(2)
C(11)-C(10)-C(17)	126.4(3)
C(11)-C(10)-Rh	71.24(14)
C(17)-C(10)-Rh	110.70(18)
C(14)-C(15)-C(16)	124.3(3)
C(14)-C(15)-Rh	71.02(15)
C(16)-C(15)-Rh	110.76(17)
C(10)-C(11)-C(12)	123.4(2)
C(10)-C(11)-Rh	70.12(15)
C(12)-C(11)-Rh	113.07(17)
C(11)-C(12)-C(13)	112.8(2)
C(10)-C(17)-C(16)	113.5(2)
C(14)-C(13)-C(12)	113.8(2)
C(15)-C(16)-C(17)	112.6(2)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for Complex **4**. The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Rh	15(1)	9(1)	14(1)	0(1)	0(1)	0(1)
Cl	21(1)	16(1)	21(1)	0(1)	-3(1)	5(1)
N(1)	13(1)	12(1)	17(1)	0(1)	2(1)	-1(1)
C(14)	24(1)	13(1)	17(2)	-5(1)	-5(1)	2(1)
N(2)	15(1)	12(1)	14(1)	0(1)	1(1)	0(1)
C(3)	17(1)	11(1)	19(2)	-1(1)	-2(1)	-1(1)
C(7)	18(1)	15(1)	19(2)	0(1)	6(1)	-4(1)
C(5)	17(1)	22(1)	21(2)	-1(1)	5(1)	1(1)
C(2)	17(1)	12(1)	18(2)	-4(1)	-1(1)	2(1)
C(1)	14(1)	11(1)	15(2)	1(1)	0(1)	1(1)
C(4)	18(1)	16(1)	14(2)	-1(1)	3(1)	-2(1)
C(8)	26(1)	24(1)	26(2)	6(1)	8(1)	5(1)
C(9)	16(1)	27(1)	23(2)	-1(1)	4(1)	0(1)
C(10)	18(1)	14(1)	28(2)	-4(1)	-6(1)	0(1)
C(6)	30(1)	26(2)	21(2)	9(1)	6(1)	2(1)
C(15)	27(1)	11(1)	23(2)	-2(1)	-3(1)	-1(1)
C(11)	22(1)	10(1)	24(2)	0(1)	-6(1)	0(1)
C(12)	37(2)	20(1)	20(2)	-1(1)	-7(1)	5(1)
C(17)	19(1)	20(1)	44(2)	-4(1)	-1(1)	-2(1)
C(13)	33(1)	19(1)	22(2)	-4(1)	-4(1)	6(1)
C(16)	25(1)	16(1)	39(2)	-4(1)	1(1)	-6(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for Complex **4**.

	x	y	z	U(eq)
H(13)	-369	9241	4161	22
H(3)	-1151	4057	3363	19
H(7)	1680	7116	2868	21
H(5A)	-2660	6721	3727	30
H(5B)	-3272	6187	4195	30
H(5C)	-3123	5549	3696	30
H(2)	267	4461	2668	19
H(4)	-1103	6243	4288	19
H(8A)	306	6319	2054	38
H(8B)	1139	7335	2036	38
H(8C)	-71	7321	2363	38
H(9A)	2917	5609	2816	33
H(9B)	3013	6264	2321	33
H(9C)	2189	5243	2339	33
H(21)	2206	6697	3693	24
H(15A)	-1970	4147	4204	38
H(15B)	-1977	4822	4695	38
H(15C)	-711	4446	4464	38
H(20)	1115	9497	3592	24
H(22)	926	6517	4357	22
H(17A)	2385	8048	4859	31
H(17B)	1344	7368	5113	31
H(18A)	3489	8062	3525	33
H(18B)	3956	7904	4074	33
H(16A)	-153	8503	4920	30
H(16B)	960	9289	4985	30
H(19A)	2904	9293	4361	32
H(19B)	3196	9688	3818	32