Supporting Information

Catalytic Synthesis of Substituted Indoles and Quinolines from the Dehydrative C-H Coupling of Arylamines with 1,2- and 1,3-Diols

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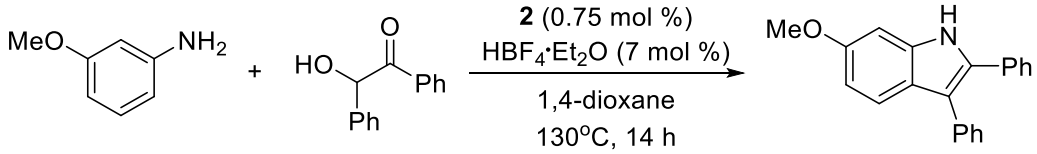
1. General Information

All operations were carried out in a nitrogen-filled glove box or by using standard high vacuum and Schlenk techniques unless otherwise noted. Solvents were freshly distilled over appropriate drying reagents. Chlorobenzene and toluene were distilled from purple solutions of sodium and benzophenone, and hexanes was dried over calcium hydride prior to use. All organic substrates were received from commercial sources and were used without further purification. The ^{1}H, ^{2}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on a Varian 300 or 400 MHz FT-NMR spectrometer, and the data are reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent; coupling constant(s) in Hz; integration. Mass spectra were recorded from Agilent 6850 GC-MS spectrometer with a HP-5 (5% phenylmethylpolysiloxane) column (30 m, 0.32 mm, 0.25 μm). High resolution mass spectra were obtained at the Mass Spectrometry/ICP Lab, Department of Chemistry and Biochemistry, University of Wisconsin-Milwaukee, Milwaukee, WI. Elemental analyses were performed at the Midwest Microlab, Indianapolis, IN.

2. Experimental Procedure

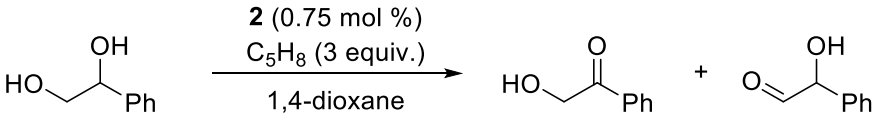
General Procedure for the Catalytic Synthesis of Indole and Quinoline Products. In a glove box, complex **2** (13 mg, 0.75 mol %) and $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %) were dissolved in 1,4-dioxane (1 mL) in a 25 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. The resulting mixture was stirred for 5 to 10 min until the solution turned to a pale green color. In an alternative procedure, the complex **1** (17 mg, 3 mol %) and $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %) were dissolved in 1,4-dioxane (1 mL). An arylamine (1.0 mmol), a diol (1.5 mmol), cyclopentene (204 mg, 3 equiv) and 1,4-dioxane (2 mL) were added to the reaction tube. After the tube was sealed, it was brought out of the glove box, and was stirred in an oil bath set at 110-130 °C (130-150 °C for the quinoline products) for 14 h. The reaction tube was taken out of the oil bath, and was cooled to room temperature. After the tube was open to air, the solution was filtered through a short silica gel column by eluting with CH_2Cl_2 (10 mL), and the filtrate was analyzed by GC-MS. Analytically pure product was isolated by a simple column chromatography on silica gel (280-400 mesh, hexanes/EtOAc).

Catalyst Screening. In a glove box, a catalyst (3 mol % Ru atom) and an additive (7 mol %) were dissolved in a solvent (1 mL) in a 25 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. After stirring for 5 to 10 min, aniline (47 mg, 0.5 mmol), 1-phenyl-1,2-ethanediol (104 mg, 0.75 mmol), and cyclopentene (102 mg, 3 equivalents) in a solvent (2 mL) were added to the reaction tube. The tube was brought out of the glove box, and was stirred in an oil bath set at 110 °C for 14 h. The product yield was determined by ^{1}H NMR using hexamethylbenzene as an internal standard. The results are summarized in Table S1.



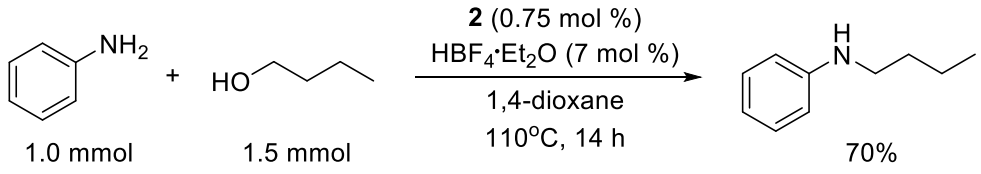
(Eq. S1)

Reaction of Aniline with *α*–Hydroxyketone. In a glove box, complex **2** (13 mg, 0.75 mol %) and $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %) were dissolved in 1,4-dioxane (1 mL) in a 25 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. The resulting mixture was stirred for 5 to 10 min until the solution turned to a pale green color. Then, 3-methoxyaniline (123 mg, 1.0 mmol), benzoin (318 mg, 1.5 mmol) and 1,4-dioxane (2 mL) were added to the reaction tube. After the tube was sealed, it was brought out of the glove box, and was stirred in an oil bath set at 130 °C for 14 h. The reaction tube was taken out of the oil bath, and was cooled to room temperature. Analytically pure product was isolated by a simple column chromatography on silica gel (280-400 mesh, *n*-hexane/EtOAc).



(Eq. S2)

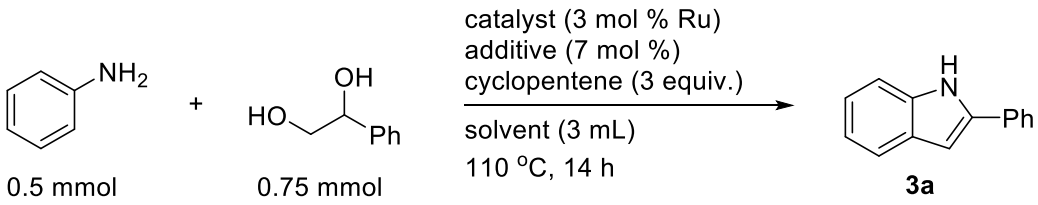
Dehydrogenation of 1-Phenyl-1,2-ethanediol. In a glove box, complex **2** (13 mg, 0.75 mol %), 1-phenyl-1,2-ethanediol (138 mg, 1.0 mmol) and cyclopentene (204 mg, 3 equiv) were dissolved in 1,4-dioxane (3 mL) in a 25 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. The tube was brought out of the glove box, and was stirred in an oil bath set at 110 °C for 3 h. The reaction tube was taken out of the oil bath, and was cooled to room temperature. The crude mixture was analyzed by ^{1}H NMR.



(Eq. S3)

Reaction of Aniline with *n*-Butanol. In a glove box, complex **2** (13 mg, 0.75 mol %) and $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %) were dissolved in 1,4-dioxane (1 mL) in a 25 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. The resulting mixture was stirred for 5 to 10 min until the solution turned to a pale green color. Aniline (93 mg, 1.0 mmol), *n*-butanol (111 mg, 1.5 mmol) and 1,4-dioxane (2 mL) were added to the reaction tube. After the tube was sealed, it was brought out of the glove box, and was stirred in an oil bath set at 110 °C for 14 h. The reaction tube was taken out of the oil bath, and was cooled to room temperature. Analytically pure product was isolated by a simple column chromatography on silica gel (280-400 mesh, *n*-hexane/EtOAc).

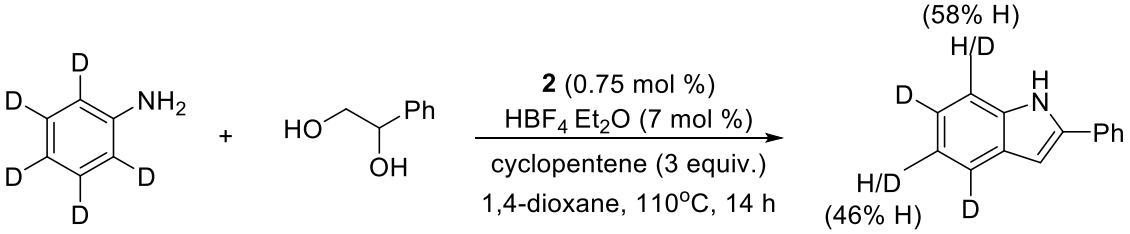
Table S1. Catalyst Screening for the Reaction of Aniline with 1-Phenyl-1,2-ethanediol.[a]



0.5 mmol 0.75 mmol **3a** (Eq. S4)

entry	catalyst	additive	solvent	yield (%)[b]
1	$[RuH(CO)(PCy_3)]_4(O)(OH)_2$	---	1,4-dioxane	0
2	$[RuH(CO)(PCy_3)]_4(O)(OH)_2$	NH_4PF_6	1,4-dioxane	18
3	$[RuH(CO)(PCy_3)]_4(O)(OH)_2$	$HBF_4{\cdot}Et_2O$	1,4-dioxane	96
4	$[RuH(CO)(PCy_3)]_4(O)(OH)_2$	$HBF_4{\cdot}Et_2O$	chlorobenzene	46
5	$[RuH(CO)(PCy_3)]_4(O)(OH)_2$	$HBF_4{\cdot}Et_2O$	toluene	42
6	$[RuH(CO)(PCy_3)]_4(O)(OH)_2$	$HBF_4{\cdot}Et_2O$	dichloroethane	17
7	$[RuH(C_6H_6)(CO)(PCy_3)]^+BF_4^-$	---	1,4-dioxane	19
8	$[RuH(C_6H_6)(CO)(PCy_3)]^+BF_4^-$	$HBF_4{\cdot}Et_2O$	1,4-dioxane	83
9	$[RuH(CO)(CH_3CN)_2(PCy_3)_2]^+BF_4^-$	---	1,4-dioxane	0
10	$RuHCl(CO)(PCy_3)_2$	---	1,4-dioxane	0
11	$RuHCl(CO)(PCy_3)_2$	$HBF_4{\cdot}Et_2O$	1,4-dioxane	23
12	$RuCl_2(PPh_3)_3$	---	1,4-dioxane	< 3
13	$RuCl_2(PPh_3)_3$	$HBF_4{\cdot}Et_2O$	1,4-dioxane	42
14	$RuCl_3{\cdot}3H_2O$	---	1,4-dioxane	0
15	$[Ru(COD)Cl_2]_x$	$HBF_4{\cdot}Et_2O$	1,4-dioxane	< 3
16	$[RuCl_2(p\text{-cymene})]_2$	---	1,4-dioxane	0
17	$[RuCl_2(p\text{-cymene})]_2$	$HBF_4{\cdot}Et_2O$	1,4-dioxane	0
18	$Ru_3(CO)_{12}$	---	1,4-dioxane	0
19	$Ru_3(CO)_{12}$	NH_4PF_6	1,4-dioxane	0
20	$RuH_2(CO)(PPh_3)_3$	---	1,4-dioxane	0
21	PCy_3	$HBF_4{\cdot}Et_2O$	1,4-dioxane	0
22	---	$HBF_4{\cdot}Et_2O$	1,4-dioxane	0

[a] Reaction conditions: catalyst (3 mol % Ru equivalents), additive (7 mol %), aniline (0.5 mmol), 1-phenyl-1,2-ethanediol (0.75 mmol), cyclopentene (1.5 mmol), 1,4-dioxane (2 mL), 110 °C, 14 h. [b] The product yield of **3a** was determined by ^{1}H NMR using hexamethylbenzene as an internal standard.



0.5 mmol 0.75 mmol (Eq. S5)

3. Deuterium Labeling Study. In a glove box, complex **2** (7 mg, 0.75 mol %) and $HBF_4{\cdot}OEt_2$ (6 mg, 7 mol %) were dissolved in 1,4-dioxane (1 mL) in a 25 mL Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar. The resulting mixture was stirred for 5 to 10 minutes until the solution turned to a pale green color. Then, aniline-2,3,4,5,6-d_5 (49 mg, 0.5 mmol), 1-phenyl-1,2-ethanediol (104 mg, 0.75 mmol), and cyclopentene

(102 mg, 3 equiv) in 1,4-dioxane (1 mL) were added to the reaction tube. After the tube was sealed, it was brought out of the glove box, and was stirred in an oil bath set at 110 °C for 14 h. Analytically pure product was isolated by a simple column chromatography on silica gel (280-400 mesh, *n*-hexane/EtOAc). The ^{1}H and ^{2}H NMR spectra of the product **3a**-*d* are shown in Figure S1.

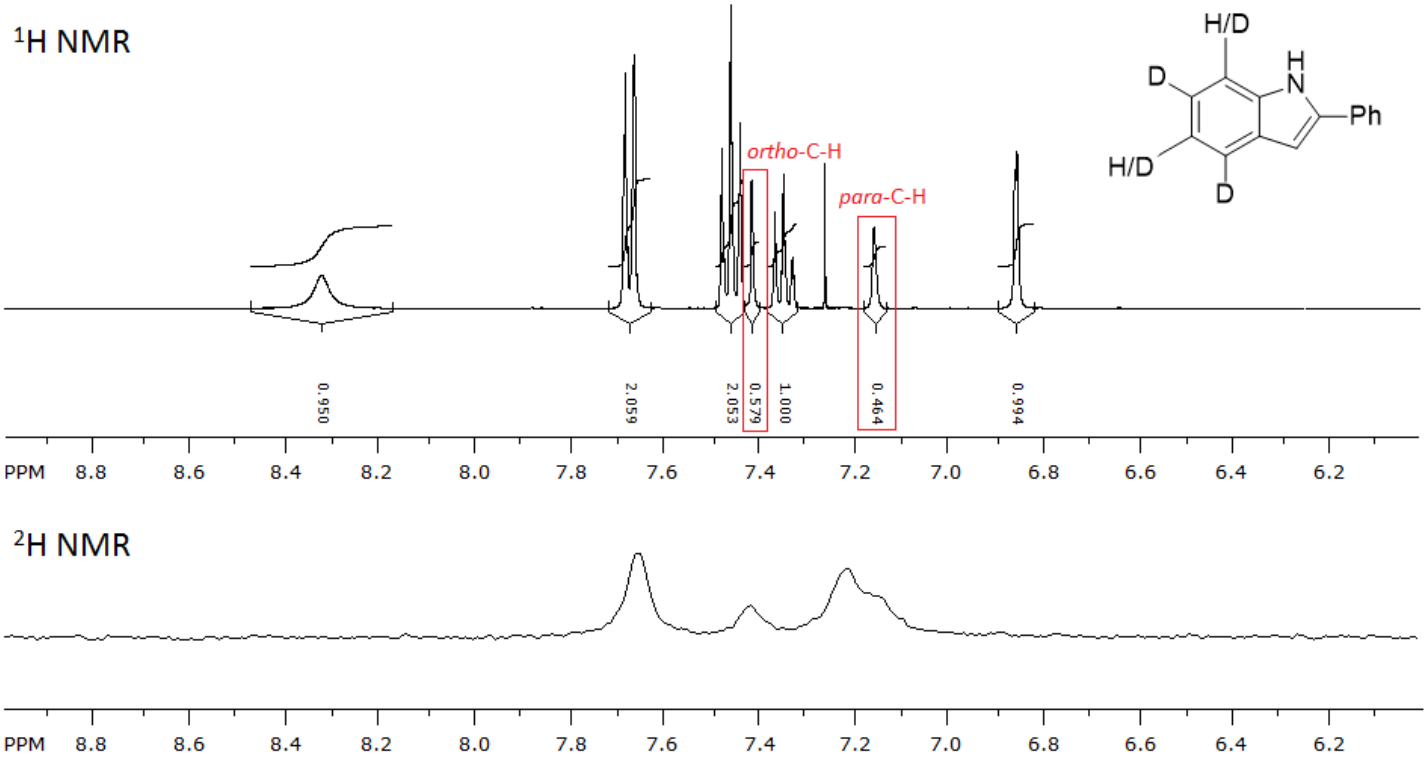
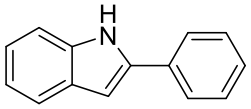


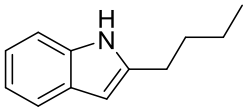
Figure S1. ^{1}H and ^{2}H NMR Spectra of the Product **3a**-*d* Isolated from the Reaction of Aniline-2,3,4,5,6-d_5 with 1-Phentyl-1,2-ethanediol.

4. Characterization Data of the Products



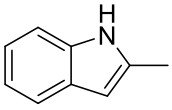
3a

Table 2, compound 3a. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), aniline (93 mg, 1.0 mmol), 1-phenyl-1,2-ethanediol (207 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 110 °C for 14 h. The product **3a** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 181 mg, 94%. Data for **3a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (br s, 1H), 7.69-7.65 (m, 3H), 7.49-7.44 (m, 2H), 7.43-7.40 (m, 1H), 7.38-7.33 (m, 1H), 7.26-7.21 (m, 1H), 7.19-7.14 (m, 1H), 6.87-6.85 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 137.8, 136.8, 132.3, 129.2, 129.0, 127.7, 125.1, 122.3, 120.6, 120.2, 110.9, 99.9 ppm; GC-MS for $C_{14}H_{11}N$, *m/z* = 193 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[S1,S2]



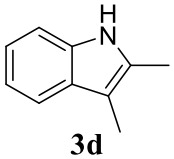
3b

Table 2, compound 3b. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), aniline (93 mg, 1.0 mmol), 1,2-hexanediol (177 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 120 °C for 14 h. The product **3b** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1). Isolated yield: 128 mg, 74%. Data for **3b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (br s, 1H), 7.58-7.55 (m, 1H), 7.32-7.29 (m, 1H), 7.18-7.09 (m, 2H), 6.29-6.26 (m, 1H), 2.80-2.73 (m, 2H), 1.77-1.69 (m, 2H), 1.45 (sextet, *J* = 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.0, 135.7, 128.8, 120.8, 119.7, 119.5, 110.2, 99.4, 31.2, 27.9, 22.4, 13.8 ppm; GC-MS for $C_{12}H_{15}N$, *m/z* = 173 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[S1]



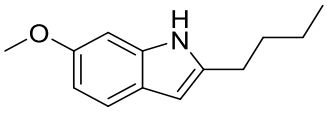
3c

Table 2, compound 3c. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), aniline (93 mg, 1.0 mmol), 1,2-propanediol (114 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 140 °C for 14 h. The product **3c** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 80 mg, 61%. Data for **3c**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (br s, 1H), 7.57-7.53 (m, 1H), 7.30-7.27 (m, 1H), 7.17-7.08 (m, 2H), 6.26-6.24 (m, 1H), 2.44 (d, *J* = 0.9 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 136.0, 135.0, 129.0, 120.9, 119.6(2C), 110.2, 100.3, 13.7 ppm; GC-MS for C_9H_9N, *m/z* = 131 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[S3,S4]



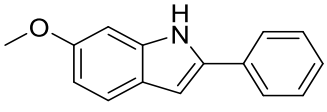
3d

Table 2, compound 3d. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), aniline (93 mg, 1.0 mmol), 2,3-butanediol (135 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equiv) was stirred at 130 °C for 14 h. The product **3d** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 100:1 to 40:1). Isolated yield: 87 mg, 60 %. Data for **3d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (br s, 1H), 7.50-7.47 (m, 1H), 7.27-7.24 (m, 1H), 7.15-7.07 (m, 2H), 2.37 (s, 3H), 2.24 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 135.1, 130.6, 129.4, 120.8, 119.0, 117.9, 110.0, 107.1, 11.5, 8.4 ppm; GC-MS for $C_{10}H_{11}N$, *m/z* = 145 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[S5]



3e

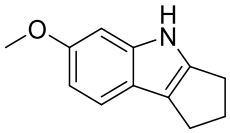
Table 2, compound 3e. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 3-methoxyaniline (123 mg, 1.0 mmol), 1,2-hexanediol (177 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equiv) was stirred at 110 °C for 14 hours. The product **3e** was isolated by a column chromatography on silica gel (hexanes/EtOAc = 100:1 to 40:1). Isolated yield: 162 mg, 80 %. Data for **3e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (br s, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 6.80 (d, *J* = 2.3 Hz, 1H), 6.77 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.18-6.16 (m, 1H), 3.85 (s, 3H), 2.72 (t, *J* = 7.5 Hz, 2H), 1.74-1.64 (m, 2H), 1.48-1.37 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.6, 138.8, 136.4, 123.0, 120.1, 108.9, 99.0, 94.5, 55.7, 31.3, 27.9, 22.4, 13.9 ppm; GC-MS for $C_{13}H_{17}NO$, *m/z* = 203 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[S6]



3f

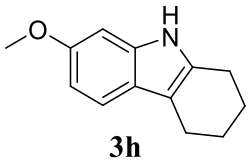
Table 2, compound 3f. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 3-methoxyaniline (123 mg, 1.0 mmol), 1-phenyl-1,2-ethanediol (207 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 130 °C for 14 h. The product **3f** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 203 mg, 91 %. Data for **3f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (br s, 1H), 7.64-7.60 (m, 2H), 7.51 (d, *J* = 8.6 Hz, 1H), 7.45-7.40 (m, 2H), 7.32-7.27 (m, 1H), 6.90 (d, *J* = 2.3 Hz, 1H), 6.81 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.77-6.76 (m, 1H), 3.87 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 156.6, 137.6, 136.8, 132.5, 129.0, 127.2, 124.7, 123.5, 121.3, 110.2, 99.8,

94.4, 55.6 ppm; GC-MS for $C_{15}H_{13}NO$, *m/z* = 223 (M^+). ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[S7]



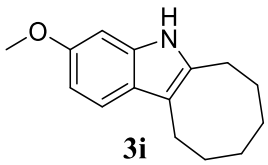
3g

Table 2, compound 3g. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 3-methoxyaniline (123 mg, 1.0 mmol), 1,2-cyclopentanediol (153 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 110 °C for 14 hours. The product **3g** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 116 mg, 62 %. Data for **3g**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (br s, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 6.83 (d, *J* = 2.3 Hz, 1H), 6.75 (dd, *J* = 8.5, 2.3 Hz, 1H), 3.84 (s, 3H), 2.86-2.77 (m, 4H), 2.56-2.48 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.3, 142.2, 141.7, 119.5, 119.3, 118.9, 108.5, 95.8, 55.8, 28.6, 25.9, 24.5 ppm; GC-MS for $C_{12}H_{13}NO$, *m/z* = 187 (M^+). ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[S8]



3h

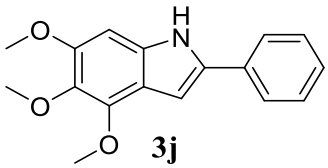
Table 2, compound 3h. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 3-methoxyaniline (123 mg, 1.0 mmol), 1,2-cyclohexanediol (174 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 110 °C for 14 h. The product **3h** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 171 mg, 85 %. Data for **3h**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (br s, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 6.80 (d, *J* = 2.3 Hz, 1H), 6.75 (dd, *J* = 8.5, 2.3 Hz, 1H), 3.84 (s, 3H), 2.72-2.64 (m, 4H), 1.93-1.82 (m, 4H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.7, 136.3, 132.8, 122.3, 118.2, 109.9, 108.2, 94.8, 55.8, 23.3, 23.2, 23.2, 20.9 ppm; GC-MS for $C_{13}H_{15}NO$, *m/z* = 201 (M^+). ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[S9]



3i

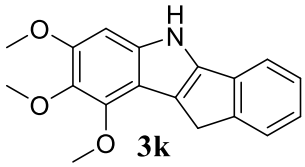
Table 2, compound 3i. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 3-methoxyaniline (123 mg, 1.0 mmol), 1,2-cyclooctanediol (216 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 140 °C for 14 h. The product **3i** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). The isolated product **3i** contained ca. 20% of the side product 2-(3-methoxyanilino)cyclooctanone. ^1H NMR yield of **3i**: 57 %. Data for **3i**: ^1H NMR (400

MHz, DMSO-d_6) δ 10.43 (br s, 1H), 7.24 (d, J = 8.5 Hz, 1H), 6.79 (d, J = 2.2 Hz, 1H), 6.60 (dd, J = 8.5, 2.2 Hz, 1H), 3.74 (s, 3H), 2.81-2.72 (m, 4H), 1.71-1.59 (m, 4H), 1.43-1.31 (m, 4H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 154.7, 135.6, 134.5, 122.6, 117.5, 109.5, 107.6, 94.3, 55.2, 29.7, 29.3, 25.6(2C), 25.1, 21.8 ppm; GC-MS for $C_{15}H_{19}NO$, m/z = 229 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{15}H_{20}NO$ ($[M+H]^+$): 230.1539, Found: 230.1530.



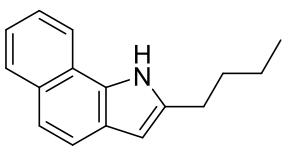
3j

Table 2, compound 3j. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4{\cdot}OEt_2$ (12 mg, 7 mol %), 3,4,5-trimethoxyaniline (183 mg, 1.0 mmol), 1-phenyl-1,2-ethanediol (207 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 135 °C for 14 h. The product **3j** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 20:1). Isolated yield: 266 mg, 94 %. Data for **3j**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.37 (br s, 1H), 7.63-7.60 (m, 2H), 7.44-7.39 (m, 2H), 7.31-7.27 (m, 1H), 6.86 (dd, J = 2.3, 0.6 Hz, 1H), 6.63 (d, J = 0.6 Hz, 1H), 4.14 (s, 3H), 3.90 (s, 3H), 3.86 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.3, 145.7, 136.0, 135.8, 133.9, 132.3, 129.0, 127.2, 124.6, 116.4, 97.5, 89.4, 61.5, 60.8, 56.2 ppm; GC-MS for $C_{17}H_{17}NO_3$, m/z = 283 (M^+); Anal. Calcd for $C_{17}H_{17}NO_3$: C, 72.07; H, 6.05; N, 4.94. Found: C, 72.27; H, 6.28; N, 4.97.



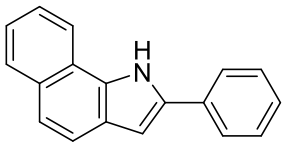
3k

Table 2, compound 3k. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4{\cdot}OEt_2$ (12 mg, 7 mol %), 3,4,5-trimethoxyaniline (183 mg, 1.0 mmol), 1,2-dihydroxyindan (225 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 140 °C for 14 h. The product **3k** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1). Isolated yield: 183 mg, 62 %. Data for **3k**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (br s, 1H), 7.53-7.50 (m, 1H), 7.40-7.37 (m, 1H), 7.31-7.27 (m, 1H), 7.20-7.15 (m, 1H), 6.67 (s, 1H), 4.12 (s, 3H), 3.93 (s, 3H), 3.87 (s, 3H), 3.80 (s, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.7, 147.4, 145.5, 141.6, 137.4, 136.4, 135.0, 126.5, 125.2, 124.1, 120.2, 116.7, 113.0, 91.2, 61.6, 61.4, 56.3, 31.7 ppm; GC-MS for $C_{18}H_{17}NO_3$, m/z = 295 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{18}H_{18}NO_3$ ($[M+H]^+$): 296.1281, Found: 296.1274.



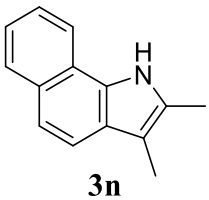
3l

Table 2, compound 3l. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 1-naphthylamine (143 mg, 1.0 mmol), 1,2-hexanediol (177 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 130 °C for 14 h. The product **3l** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 141 mg, 63 %. Data for **3l**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (br s, 1H), 7.97-7.92 (m, 2H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.54-7.49 (m, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.44-7.39 (m, 1H), 6.42-6.41 (m, 1H), 2.86 (t, *J* = 7.6 Hz, 2H), 1.79 (quintet, *J* = 7.6 Hz, 2H), 1.48 (sextet, *J* = 7.5 Hz, 2H), 1.01 (t, *J* = 7.5 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.1, 129.8, 128.9, 125.2, 124.6, 123.2, 121.4, 120.3, 120.3, 119.0, 101.1, 31.6, 28.0, 22.4, 13.9 ppm (one carbon signal obscured or overlapping); GC-MS for $C_{16}H_{17}N$, *m/z* = 223 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[S1]



3m

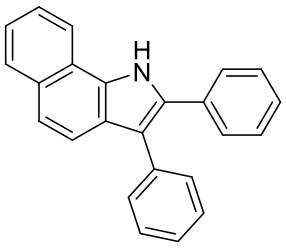
Table 2, compound 3m. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 1-naphthylamine (143 mg, 1.0 mmol), 1-phenyl-1,2-ethanediol (207 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 100 °C for 14 h. The product **3m** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 180 mg, 74 %. Data for **3m**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (br s, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.76-7.71 (m, 3H), 7.59-7.53 (m, 2H), 7.52-7.43 (m, 3H), 7.37-7.33 (m, 1H), 6.98 (d, *J* = 2.3 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.2, 132.5, 131.3, 130.5, 129.1, 129.0, 127.4, 125.6, 125.3, 124.9, 123.9, 121.5, 121.2, 120.6, 119.3, 101.7 ppm; GC-MS for $C_{18}H_{13}N$, *m/z* = 243 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[S1,S2]



3n

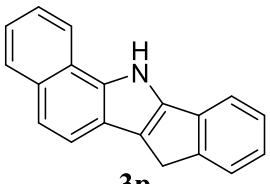
Table 2, compound 3n. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 1-naphthylamine (143 mg, 1.0 mmol), 2,3-butanediol (135 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 130 °C for 14 h. The product **3n** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 141 mg, 72 %. Data for **3n**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (br s, 1H), 7.92 (d, *J* = 8.3, 2H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.52-7.47 (m, 1H), 7.41-7.36 (m, 1H), 2.46 (s, 3H), 2.32 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 129.9, 129.1, 128.9,

128.8, 125.1, 124.9, 123.1, 121.2, 119.7, 119.1, 118.6, 108.9, 11.6, 8.6 ppm; GC-MS for $C_{14}H_{13}N$, *m/z* = 195 (M^+). ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[S10]



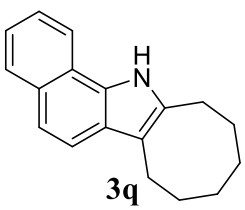
3o

Table 2, compound 3o. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 1-naphthylamine (143 mg, 1.0 mmol), *meso*-hydrobenzoin (321 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 130 °C for 14 h. The product **3o** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 135 mg, 42 %. Data for **3o**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.93 (br s, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.82-7.78 (m, 1H), 7.61-7.43 (m, 9H), 7.42-7.31 (m, 4H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 135.0, 132.7, 132.5, 130.7, 130.5, 130.2, 128.9, 128.7, 128.5, 128.0, 127.4, 126.3, 125.6, 124.5, 124.1, 121.4, 121.2, 119.5, 119.4, 116.8 ppm; GC-MS for $C_{24}H_{17}N$, *m/z* = 319 (M^+). ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[S11]



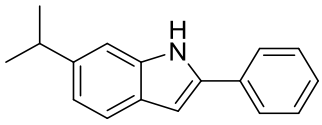
3p

Table 2, compound 3p. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 1-naphthylamine (143 mg, 1.0 mmol), 1,2-dihydroxyindan (225 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 130 °C for 14 h. The product **3p** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 161 mg, 63 %. Data for **3p**: ^1H NMR (400 MHz, acetone-d_6) δ 11.59 (br s, 1H), 8.34-8.31 (m, 1H), 7.95-7.92 (m, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.64-7.61 (m, 1H), 7.57-7.50 (m, 3H), 7.42-7.37 (m, 1H), 7.36-7.31 (m, 1H), 7.21-7.16 (m, 1H), 3.77 (s, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6) δ 148.4, 143.1, 136.4, 136.0, 131.2, 129.6, 127.5, 126.3, 126.3, 125.2, 124.3, 124.0, 123.5, 121.3, 121.3, 121.0, 120.2, 118.2, 30.7 ppm; GC-MS for $C_{19}H_{13}N$, *m/z* = 255 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{19}H_{14}N$ ($[M+H]^+$): 256.1121, Found: 256.1114.



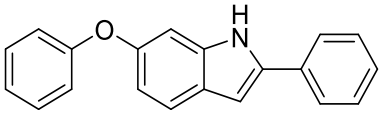
3q

Table 2, compound 3q. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 1-naphthylamine (143 mg, 1.0 mmol), 1,2-cyclooctanediol (216 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 120 °C for 14 h. The product **3q** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 212 mg, 85 %. Data for **3q**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (br s, 1H), 8.00-7.93 (m, 2H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.56-7.51 (m, 1H), 7.46-7.41 (m, 1H), 3.02-2.94 (m, 4H), 1.87-1.78 (m, 4H), 1.58-1.46 (m, 4H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 133.8, 129.8, 128.9, 128.8, 125.1, 124.1, 123.0, 121.4, 119.6, 119.1, 118.5, 113.5, 29.9, 29.8, 26.0, 25.8, 25.8, 22.2 ppm; GC-MS for $C_{18}H_{19}N$, *m/z* = 249 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{18}H_{20}N$ ($[M+H]^+$): 250.1590. Found 250.1582.



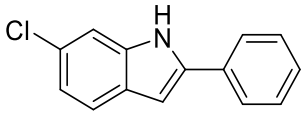
3r

Table 3, compound 3r. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 3-isopropylaniline (135 mg, 1.0 mmol), 1-phenyl-1,2-ethanediol (207 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 110 °C for 14 h. The product **3r** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 200 mg, 85 %. Data for **3r**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (br s, 1H), 7.69-7.65 (m, 2H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.49-7.44 (m, 2H), 7.38-7.33 (m, 1H), 7.29-7.27 (m, 1H), 7.10 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.84 (dd, *J* = 2.1, 0.8 Hz, 1H), 3.08 (septet, *J* = 7.0 Hz, 1H), 1.38 (d, *J* = 7.0 Hz, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.6, 137.4, 137.1, 132.5, 128.9, 127.4, 127.4, 124.9, 120.3, 119.7, 108.1, 99.8, 34.4, 24.4 ppm; GC-MS for $C_{17}H_{17}N$, *m/z* = 235 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[S2]



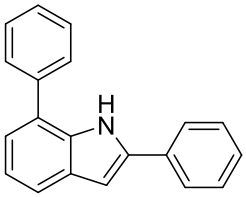
3s

Table 3, compound 3s. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 3-phenoxyaniline (185 mg, 1.0 mmol), 1-phenyl-1,2-ethanediol (207 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 110 °C for 14 h. The product **3s** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 20:1). Isolated yield: 251 mg, 88 %. Data for **3s**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.50 (br s, 1H), 7.82-7.78 (m, 2H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.46-7.40 (m, 2H), 7.38-7.32 (m, 2H), 7.30-7.26 (m, 1H), 7.10-7.05 (m, 1H), 7.01-6.96 (m, 3H), 6.90-6.88 (m, 1H), 6.75 (dd, *J* = 8.5, 2.2 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 158.1, 152.0, 137.9, 137.6, 132.1, 129.9, 129.0, 127.3, 125.3, 124.8, 122.7, 121.2, 117.9, 112.6, 101.5, 98.7 ppm; GC-MS for $C_{20}H_{15}NO$, *m/z* = 285 (M^+); Anal. Calcd for $C_{20}H_{15}NO$: C, 84.19; H, 5.30; N, 4.91. Found: C, 84.34; H, 5.49; N, 4.96.



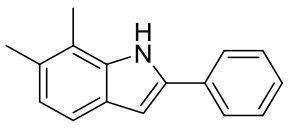
3t

Table 3, compound 3t. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 3-chloroaniline (127 mg, 1.0 mmol), 1-phenyl-1,2-ethanediol (207 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 110 °C for 14 h. The product **3t** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 175 mg, 77 %. Data for **3t**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.71 (br s, 1H), 7.87-7.83 (m, 2H), 7.54 (d, J = 8.4 Hz, 1H), 7.50-7.44 (m, 2H), 7.40 (d, J = 2.0 Hz, 1H), 7.36-7.31 (m, 1H), 7.01 (dd, J = 8.4, 2.0 Hz, 1H), 6.94-6.93 (m, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 138.8, 137.5, 131.7, 129.0, 127.8, 127.4, 126.0, 125.1, 121.4, 119.8, 110.8, 98.8 ppm; GC-MS for $C_{14}H_{10}NCl$, *m/z* = 227 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[S2,S4]



3u

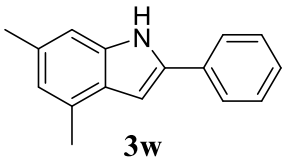
Table 3, compound 3u. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 2-aminobiphenyl (169 mg, 1.0 mmol), 1-phenyl-1,2-ethanediol (207 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 110 °C for 14 h. The product **3u** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 229 mg, 85 %. Data for **3u**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (br s, 1H), 7.80-7.76 (m, 2H), 7.74-7.67 (m, 3H), 7.66-7.60 (m, 2H), 7.54-7.46 (m, 3H), 7.40-7.36 (m, 1H), 7.33-7.29 (m, 2H), 6.98-6.97 (m, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.2, 138.1, 134.6, 132.2, 129.6, 129.2, 128.9, 128.2, 127.7, 127.4, 125.4, 125.2, 122.2, 120.7, 119.9, 100.4 ppm; GC-MS for $C_{20}H_{15}N$, *m/z* = 269 (M^+); Anal. Calcd for $C_{20}H_{15}N$: C, 89.19; H, 5.61; N, 5.20. Found: C, 89.00; H, 5.73; N, 5.27.



3v

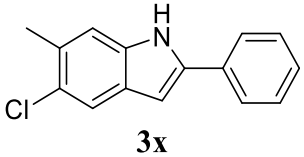
Table 3, compound 3v. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 2,3-dimethylaniline (121 mg, 1.0 mmol), 1-phenyl-1,2-ethanediol (207 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 120 °C for 14 h. The product **3v** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 214 mg, 97 %. Data for **3v**: ^{1}H

NMR (400 MHz, $CDCl_3$) δ 8.14 (br s, 1H), 7.75-7.72 (m, 2H), 7.53-7.45 (m, 3H), 7.40-7.36 (m, 1H), 7.07-7.04 (m, 1H), 6.87-6.86 (m, 1H), 2.49 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 137.1, 137.0, 132.6, 129.8, 128.9, 127.3, 127.1, 124.9, 123.0, 117.8, 117.6, 100.4, 19.4, 13.1 ppm; GC-MS for $C_{16}H_{15}N$, *m/z* = 221 (M^+); Anal. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.99; H, 6.90; N, 6.43.



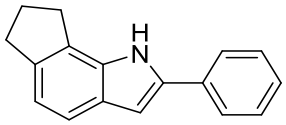
3w

Table 3, compound 3w. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4{\cdot}OEt_2$ (12 mg, 7 mol %), 3,5-dimethylaniline (121 mg, 1.0 mmol), 1-phenyl-1,2-ethanediol (207 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 130 °C for 14 h. The product **3w** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 202 mg, 91 %. Data for **3w**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (br s, 1H), 7.69-7.66 (m, 2H), 7.51-7.46 (m, 2H), 7.40-7.35 (m, 1H), 7.02 (s, 1H), 6.90-6.87 (m, 2H), 2.64 (s, 3H), 2.51 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 136.9, 136.5, 132.5, 132.3, 129.7, 128.9, 127.2, 126.9, 124.8, 122.3, 108.4, 98.3, 21.7, 18.7 ppm; GC-MS for $C_{16}H_{15}N$, *m/z* = 221 (M^+); Anal. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.83; H, 6.84; N, 6.36.



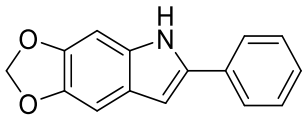
3x

Table 3, compound 3x. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4{\cdot}OEt_2$ (12 mg, 7 mol %), 4-chloro-3-methylaniline (141 mg, 1.0 mmol), 1-phenyl-1,2-ethanediol (207 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 110 °C for 14 h. The product **3x** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). The isolated product **3x** contained ca. 40 % of the byproduct 5-chloro-4-methyl-2-phenylindole. Isolated yield (mixture of two isomers): 196 mg, 81 %. Data for **3x**: ^1H NMR (400 MHz, DMSO-d_6) δ 11.6 (br s, 1H), 7.86-7.81 (m, 2H), 7.56 (s, 1H), 7.47-7.43 (m, 2H), 7.34 (s, 1H), 7.33-7.30 (m, 1H), 6.84-6.83 (m, 1H), 2.41 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 138.6, 136.2, 131.9, 129.0, 128.1, 128.1, 127.7, 125.0, 119.5, 113.0, 98.1, 20.4 ppm (one carbon signal obscured or overlapped); GC-MS for $C_{15}H_{12}NCl$, *m/z* = 241 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{15}H_{13}NCl$ ($[M+H]^+$): 242.0731. Found: 242.0730. Data for **3x**: ^1H NMR (400 MHz, DMSO-d_6) δ 11.7 (br s, 1H), 7.90-7.86 (m, 2H), 7.49-7.45 (m, 2H), 7.35-7.32 (m, 1H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 1H), 7.04-7.02 (m, 1H), 2.52 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 138.4, 135.2, 131.9, 130.0, 129.0, 127.7, 126.0, 125.1, 123.5, 122.2, 110.4, 98.0, 16.0 ppm.



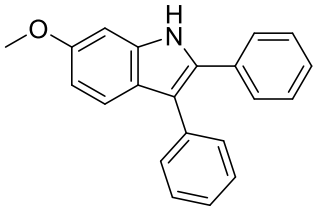
3y

Table 3, compound 3y. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 4-aminoindan (133 mg, 1.0 mmol), 1-phenyl-1,2-ethanediol (207 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 120 °C for 14 h. The product **3y** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 210 mg, 90 %. Data for **3y**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (br s, 1H), 7.73-7.69 (m, 2H), 7.52-7.45 (m, 3H), 7.37-7.33 (m, 1H), 7.12 (d, J = 8.0 Hz, 1H), 6.89 (d, J = 2.1 Hz, 1H), 3.15-3.08 (m, 4H), 2.33-2.24 (m, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.0, 137.0, 133.9, 132.6, 128.9, 127.8, 127.3, 125.2, 124.9, 118.6, 117.2, 100.6, 33.2, 29.9, 25.4 ppm; GC-MS for $C_{17}H_{15}N$, *m/z* = 233 (M^+); Anal. Calcd for $C_{17}H_{15}N$: C, 87.52; H, 6.48; N, 6.00. Found: C, 87.56; H, 6.58; N, 6.06.



3z

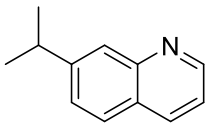
Table 3, compound 3z. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 3,4-(methylenedioxy)aniline (137 mg, 1.0 mmol), 1-phenyl-1,2-ethanediol (207 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 120 °C for 14 h. The product **3z** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 189 mg, 80 %. Data for **3z**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (br s, 1H), 7.61-7.57 (m, 2H), 7.44-7.39 (m, 2H), 7.30-7.25 (m, 1H), 7.00 (s, 1H), 6.86 (s, 1H), 6.72-6.70 (m, 1H), 5.95 (s, 2H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.1, 143.2, 136.6, 132.4, 131.8, 129.0, 127.1, 124.5, 123.1, 100.6, 100.2, 99.1, 91.9 ppm; GC-MS for $C_{15}H_{11}NO_2$, *m/z* = 237 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[S12]



3aa

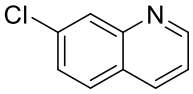
Equation 3, compound 3aa. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 3-methoxyaniline (123 mg, 1.0 mmol) and benzoin (318 mg, 1.5 mmol) was stirred at 130 °C for 14 h. The product **3aa** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 20:1). Isolated yield: 245 mg, 82 %. Data for **3aa**: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.39 (br s, 1H), 7.44-7.31 (m, 9H), 7.30-7.24 (m, 2H), 6.93 (d, J = 2.2 Hz, 1H), 6.71 (dd, J = 8.7, 2.2 Hz, 1H), 3.80 (s, 3H) ppm; ^{13}C{^{1}H}

NMR (100 MHz, DMSO-d_6) δ 156.1, 136.9, 135.4, 132.7, 132.7, 129.7, 128.7, 128.5, 127.9, 127.2, 126.1, 122.4, 119.4, 113.3, 110.0, 94.3, 55.2 ppm; GC-MS for $C_{21}H_{17}NO$, *m/z* = 299 (M^+). ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[S13]



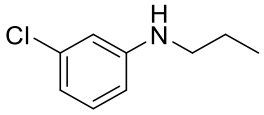
4a

Table 4, compound 4a. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 3-isopropylaniline (135 mg, 1.0 mmol), 1,3-propanediol (114 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 130 °C for 14 h. The product **4a** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1). Isolated yield: 118 mg, 69 %. Data for **4a**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.87 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.93 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.45 (dd, *J* = 8.4, 1,7 Hz, 1H), 7.32 (dd, *J* = 8.2, 4.2 Hz, 1H), 3.12 (septet, *J* = 6.9 Hz, 1H), 1.36 (d, *J* = 6.9 Hz, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.5, 150.2, 148.5, 135.6, 127.5, 126.6, 126.5, 125.5, 120.3, 34.2, 23.7 ppm; GC-MS for $C_{12}H_{13}N$, *m/z* = 171 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{12}H_{14}N$ ($[M+H]^+$): 172.1121, Found: 172.1111 (best result out of two repeated runs).



4b

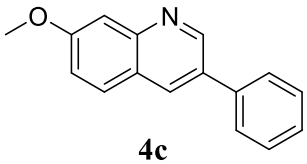
Table 4, compound 4b. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 3-chloroaniline (127 mg, 1.0 mmol), 1,3-propanediol (114 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 130 °C for 14 h. The product **4b** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1). Isolated yield: 33 mg, 20 %. Data for **4b**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.88 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.11-8.07 (m, 2H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.46 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.36 (dd, *J* = 8.2, 4.2 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.2, 148.4, 135.8, 135.2, 128.9, 128.3, 127.5, 126.5, 121.2 ppm; GC-MS for C_9H_6NCl, *m/z* = 163 (M^+). ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[S14]



5b

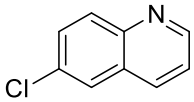
Table 4, compound 5b. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 3-chloroaniline (127 mg, 1.0 mmol), 1,3-propanediol (114 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 130 °C for 14 h. The product **5b** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 114 mg, 67 %. Data for **5b**: ^1H NMR (400 MHz,

$CDCl_3$) δ 7.08 (t, *J* = 8.0 Hz, 1H), 6.68-6.65 (m, 1H), 6.59-6.58 (m, 1H), 6.49-6.45 (m, 1H), 3.73 (br s, 1H), 3.06 (t, *J* = 7.1 Hz, 2H), 1.65 (sextet, *J* = 7.2 Hz, 2H), 1.01 (t, *J* = 7.2 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.5, 134.9, 130.1, 116.7, 112.0, 111.0, 45.5, 22.5, 11.5 ppm; GC-MS for $C_9H_{12}NCl$, *m/z* = 169 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_9H_{13}NCl$ ($[M+H]^+$): 170.0731, Found: 170.0728.



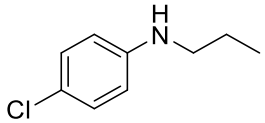
4c

Table 4, compound 4c. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4{\cdot}OEt_2$ (12 mg, 7 mol %), 3-methoxyaniline (127 mg, 1.0 mmol), 2-phenyl-1,3-propanediol (228 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 140 °C for 14 h. The product **4c** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1). Isolated yield: 129 mg, 55 %. Data for **4c**: ^1H NMR (400 MHz, $CDCl_3$) δ 9.10 (d, *J* = 2.3 Hz, 1H), 8.23 (d, *J* = 2.3 Hz, 1H), 7.76 (d, *J* = 8.9 Hz, 1H), 7.71-7.68 (m, 2H), 7.54-7.49 (m, 2H), 7.46 (d, *J* = 2.5 Hz, 1H), 7.44-7.39 (m, 1H), 7.24 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.98 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.7, 149.9, 149.0, 138.0, 133.0, 131.8, 129.1, 129.0, 127.8, 127.2, 123.2, 120.2, 107.1, 55.5 ppm; GC-MS for $C_{16}H_{13}NO$, *m/z* = 235 (M^+). ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[S15]



4d

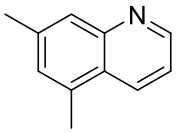
Table 4, compound 4d. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4{\cdot}OEt_2$ (12 mg, 7 mol %), 4-chloroaniline (127 mg, 1.0 mmol), 1,3-propanediol (114 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 130 °C for 14 h. The product **4d** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1). Isolated yield: 54 mg, 33 %. Data for **4d**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.87 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.04-8.00 (m, 1H), 8.01 (d, *J* = 9.0 Hz, 1H), 7.75 (d, *J* = 2.4 Hz, 1H), 7.61 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.38 (dd, *J* = 8.3, 4.2 Hz, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.5, 146.5, 135.0, 132.2, 131.0, 130.3, 128.7, 126.3, 121.8 ppm; GC-MS for C_9H_6NCl, *m/z* = 163 (M^+). ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[S16]



5d

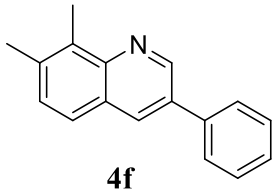
Table 4, compound 5d. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4{\cdot}OEt_2$ (12 mg, 7 mol %), 4-chloroaniline (127 mg, 1.0 mmol), 1,3-propanediol (114 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 130 °C for 14 h. The product **5d** was isolated by a column chromatography on

silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 87 mg, 51 %. Data for **5d**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.09 (m, 2H), 6.54-6.49 (m, 2H), 3.64 (br s, 1H), 3.05 (t, *J* = 7.1 Hz, 2H), 1.68-1.58 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.0, 129.0, 121.5, 113.7, 45.8, 22.6, 11.6 ppm; GC-MS for $C_9H_{12}NCl$, *m/z* = 169 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[S17]



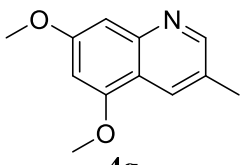
4e

Table 4, compound 4e. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4{\cdot}OEt_2$ (12 mg, 7 mol %), 3,5-dimethylaniline (121 mg, 1.0 mmol), 1,3-propanediol (114 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 130 °C for 14 h. The product **4e** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1). Isolated yield: 91 mg, 58 %. Data for **4e**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.17-8.14 (m, 1H), 7.70 (s, 1H), 7.25 (dd, *J* = 8.4, 4.2 Hz, 1H), 7.13 (s, 1H), 2.56 (s, 3H), 2.46 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.7, 148.6, 139.1, 133.9, 132.0, 129.1, 126.4, 125.5, 119.7, 21.6, 18.2 ppm; GC-MS for $C_{11}H_{11}N$, *m/z* = 157 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[S18]



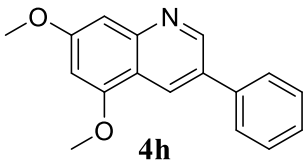
4f

Table 4, compound 4f. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4{\cdot}OEt_2$ (12 mg, 7 mol %), 2,3-dimethylaniline (121 mg, 1.0 mmol), 2-phenyl-1,3-propanediol (228 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 130 °C for 14 h. The product **4f** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1). Isolated yield: 140 mg, 60 %. Data for **4f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, *J* = 2.4 Hz, 1H), 8.23 (d, *J* = 2.4 Hz, 1H), 7.74-7.71 (m, 2H), 7.63 (d, *J* = 8.3 Hz, 1H), 7.55-7.50 (m, 2H), 7.45-7.41 (m, 1H), 7.40, (d, *J* = 8.3 Hz, 1H), 2.81 (s, 3H), 2.54 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.5, 146.4, 138.1, 137.1, 134.1, 133.3, 132.3, 129.9, 129.1, 127.8, 127.2, 126.3, 125.0, 20.7, 13.3 ppm; GC-MS for $C_{17}H_{15}N$, *m/z* = 233 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[S15,19,20]



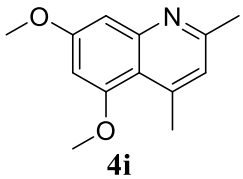
4g

Table 4, compound 4g. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 3,5-dimethoxyaniline (153 mg, 1.0 mmol), 2-methyl-1,3-propanediol (135 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 140 °C for 14 h. The product **4g** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1). Isolated yield: 156 mg, 77 %. Data for **4g**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.14 (s, 1H), 6.95 (s, 1H), 6.43 (s, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 2.41 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.2, 155.3, 152.4, 148.3, 129.5, 127.2, 116.3, 99.3, 97.9, 55.5, 55.3, 18.4 ppm; GC-MS for $C_{12}H_{13}NO_2$, *m/z* = 203 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{12}H_{14}NO_2$ ($[M+H]^+$): 204.1019, Found: 204.1015.



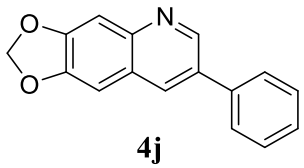
4h

Table 4, compound 4h. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 3,5-dimethoxyaniline (153 mg, 1.0 mmol), 2-phenyl-1,3-propanediol (228 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 150 °C for 14 h. The product **4h** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1). Isolated yield: 222 mg, 84 %. Data for **4h**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, *J* = 2.4 Hz, 1H), 8.61 (d, *J* = 2.4 Hz, 1H), 7.73-7.69 (m, 2H), 7.52-7.47 (m, 2H), 7.42-7.37 (m, 1H), 7.05 (d, *J* = 2.2 Hz, 1H), 6.54 (d, *J* = 2.2 Hz, 1H), 3.98 (s, 3H), 3.96 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.2, 156.1, 150.1, 149.4, 138.3, 130.9, 129.0, 128.1, 127.6, 127.1, 116.5, 99.4, 98.4, 55.8, 55.6 ppm; GC-MS for $C_{17}H_{15}NO_2$, *m/z* = 265 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{17}H_{16}NO_2$ ($[M+H]^+$): 266.1176, Found: 266.1170.



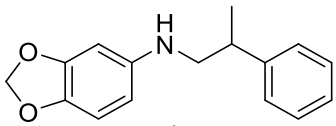
4i

Table 4, compound 4i. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 3,5-dimethoxyaniline (153 mg, 1.0 mmol), 2,4-pentanediol (156 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 150 °C for 14 h. The product **4i** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1). Isolated yield: 88 mg, 41 %. Data for **4i**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, *J* = 2.4 Hz, 1H), 6.83-6.82 (m, 1H), 6.41 (d, *J* = 2.4 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 2.74 (s, 3H), 2.58 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.3, 158.7, 158.5, 151.3, 145.5, 121.9, 114.7, 100.1, 97.6, 55.4, 55.3, 24.6, 24.0 ppm; GC-MS for $C_{13}H_{15}NO_2$, *m/z* = 217 (M^+); HRMS (IT-TOF/ESI) Calcd for $C_{13}H_{16}NO_2$ ($[M+H]^+$): 218.1176, Found: 218.1171.



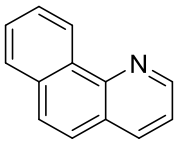
4j

Table 4, compound 4j. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 3,4-(methylenedioxy)aniline (137 mg, 1.0 mmol), 2-phenyl-1,3-propanediol (228 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 140 °C for 14 hours. The product **4j** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1). Isolated yield: 158 mg, 63 %. Data for **4j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 2.3 Hz, 1H), 8.08 (d, J = 2.3 Hz, 1H), 7.68-7.64 (m, 2H), 7.52-7.47 (m, 2H), 7.43-7.38 (m, 2H), 7.08 (s, 1H), 6.10 (s, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.6, 148.1, 147.3, 145.5, 137.9, 132.3, 132.2, 129.0, 127.8, 127.2, 125.0, 105.6, 102.8, 101.7 ppm; GC-MS for $C_{16}H_{11}NO_2$, m/z = 249 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[S15]



5j

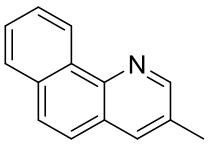
Table 4, compound 5j. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 3,4-(methylenedioxy)aniline (137 mg, 1.0 mmol), 2-phenyl-1,3-propanediol (228 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 140 °C for 14 h. The product **5j** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 40:1). Isolated yield: 56 mg, 22 %. Data for **5j**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.31 (m, 2H), 7.27-7.20 (m, 3H), 6.65 (d, J = 8.3 Hz, 1H), 6.21 (d, J = 2.3 Hz, 1H), 6.01 (dd, J = 8.3, 2.3 Hz, 1H), 5.85 (s, 2H), 3.36 (br s, 1H), 3.28 (dd, J = 12.2, 6.0 Hz, 1H), 3.17 (dd, J = 12.2, 8.4 Hz, 1H), 3.09-3.00 (m, 1H), 1.33 (d, J = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.3, 144.4, 143.8, 139.5, 128.7, 127.2, 126.6, 108.6, 104.6, 100.5, 96.1, 51.9, 39.1, 19.8 ppm; GC-MS for $C_{16}H_{17}NO_2$, m/z = 255 (M^+). HRMS (IT-TOF/ESI) Calcd for $C_{16}H_{18}NO_2$ ($[M+H]^+$): 256.1332, Found: 256.1330.



4k

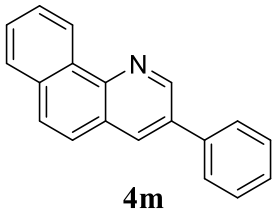
Table 4, compound 4k. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 1-naphthylamine (143 mg, 1.0 mmol), 1,3-propanediol (114 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 130 °C for 14 h. The product **4k** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1). Isolated yield: 122 mg, 68 %. Data for **4k**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34-9.30 (m, 1H), 9.03-9.00 (m, 1H), 8.17-8.14 (m, 1H), 7.91 (d, J = 7.7 Hz, 1H), 7.81 (d, J = 8.8 Hz, 1H), 7.79-7.65 (m, 3H), 7.53-7.49 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.8, 146.5, 135.8, 133.5,

131.4, 128.1, 127.8, 127.7, 127.0, 126.3, 125.3, 124.3, 121.7 ppm; GC-MS for $C_{13}H_9N$, *m/z* = 179 (M^+). ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[S21]



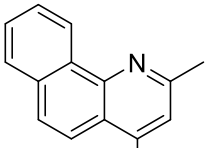
4l

Table 4, compound 4l. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 1-naphthylamine (143 mg, 1.0 mmol), 2-methyl-1,3-propanediol (135 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 140 °C for 14 h. The product **4l** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1). Isolated yield: 111 mg, 58 %. Data for **4l**: ^1H NMR (400 MHz, $CDCl_3$) δ 9.30-9.27 (m, 1H), 8.84 (d, *J* = 2.2 Hz, 1H), 7.90-7.86 (m, 2H), 7.78-7.72 (m, 2H), 7.70-7.65 (m, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 2.52 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 150.2, 144.4, 135.0, 133.1, 131.4, 131.2, 127.7, 127.6, 127.6, 126.9, 126.0, 125.0, 124.0, 18.5 ppm; GC-MS for $C_{14}H_{11}N$, *m/z* = 193 (M^+). ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[S22]



4m

Table 4, compound 4m. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 1-naphthylamine (143 mg, 1.0 mmol), 2-phenyl-1,3-propanediol (135 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 130 °C for 14 h. The product **4m** was isolated by a column chromatography on silica gel (*n*-hexane/EtOAc = 100:1 to 10:1). Isolated yield: 143 mg, 56 %. Data for **4m**: ^1H NMR (400 MHz, $CDCl_3$) δ 9.34-9.31 (m, 1H), 9.28 (d, *J* = 2.3 Hz, 1H), 8.31 (d, *J* = 2.3 Hz, 1H), 7.94-7.90 (m, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.80-7.69 (m, 4H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.57-7.52 (m, 2H), 7.48-7.43 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.8, 145.5, 137.9, 134.5, 133.5, 133.3, 131.3, 129.1, 128.1, 128.1, 128.0, 127.8, 127.3, 127.2, 126.1, 125.4, 124.3 ppm; GC-MS for $C_{19}H_{13}N$, *m/z* = 255 (M^+). ^1H and ^{13}C NMR spectral data are in good agreement with the literature data.[S20]



4n

Table 4, compound 4n. A dioxane (3.0 mL) solution of complex **2** (13 mg, 0.75 mol %), $HBF_4 \cdot OEt_2$ (12 mg, 7 mol %), 1-naphthylamine (143 mg, 1.0 mmol), 2,4-pentanediol (156 mg, 1.5 mmol), and cyclopentene (204 mg, 3 equivalents) was stirred at 130 °C for 14 h. The product **4n** was isolated by a column chromatography on

silica gel (*n*-hexane/EtOAc = 100:1 to 10:1). Isolated yield: 108 mg, 52 %. Data for **4n**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38-9.33 (m, 1H), 7.91-7.88 (m, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.73-7.64 (m, 2H), 7.25 (s, 1H), 2.79 (s, 3H), 2.71 (s, 3H) ppm; $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 157.2, 145.6, 143.9, 133.4, 131.6, 127.7, 127.5, 126.7, 126.2, 124.7, 123.7, 123.3, 121.2, 25.3, 19.0 ppm; GC-MS for $C_{15}H_{13}N$, *m/z* = 207 (M^+). ^{1}H and ^{13}C NMR spectral data are in good agreement with the literature data.[S23]

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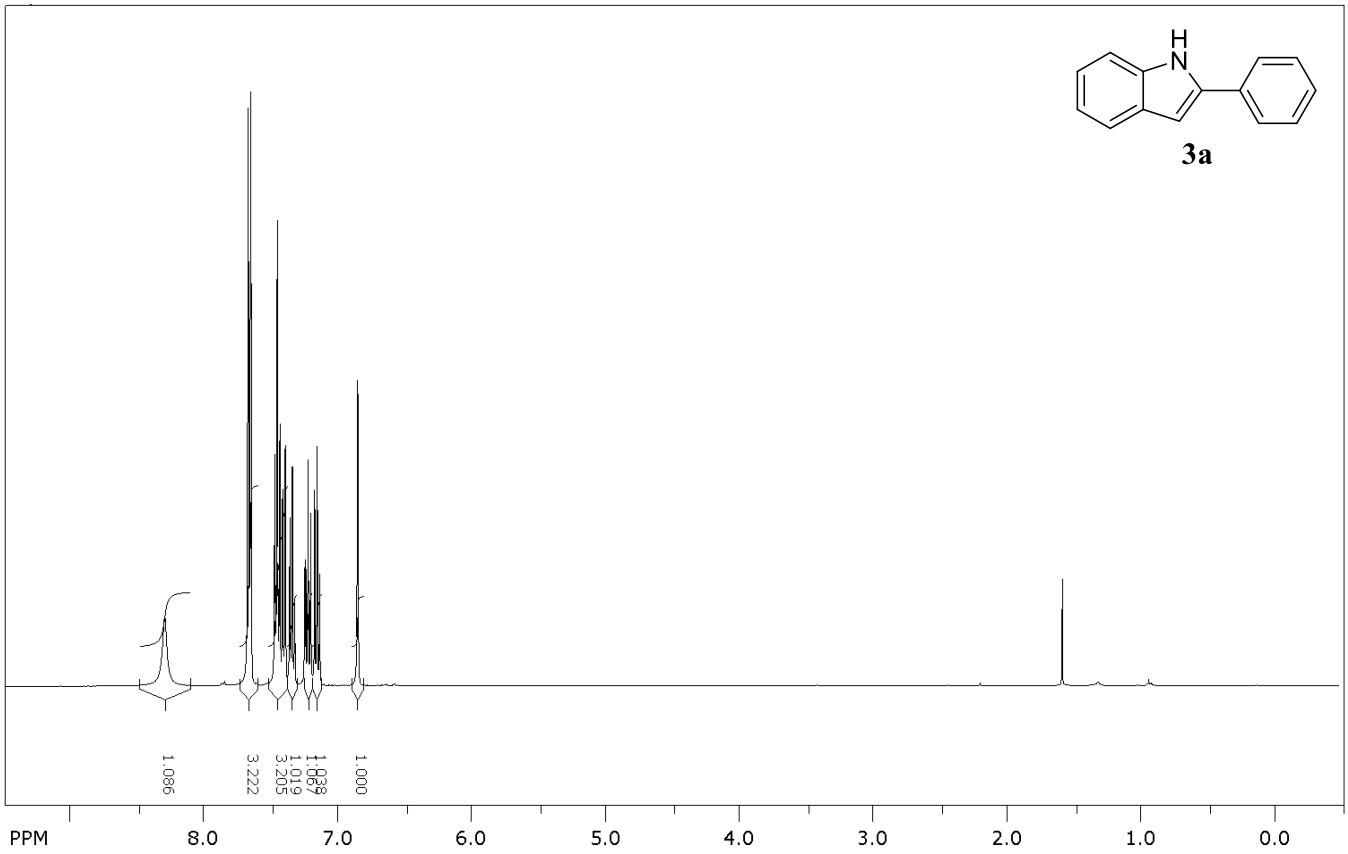
5. ^{1}H and ^{13}C NMR Spectra of the Products



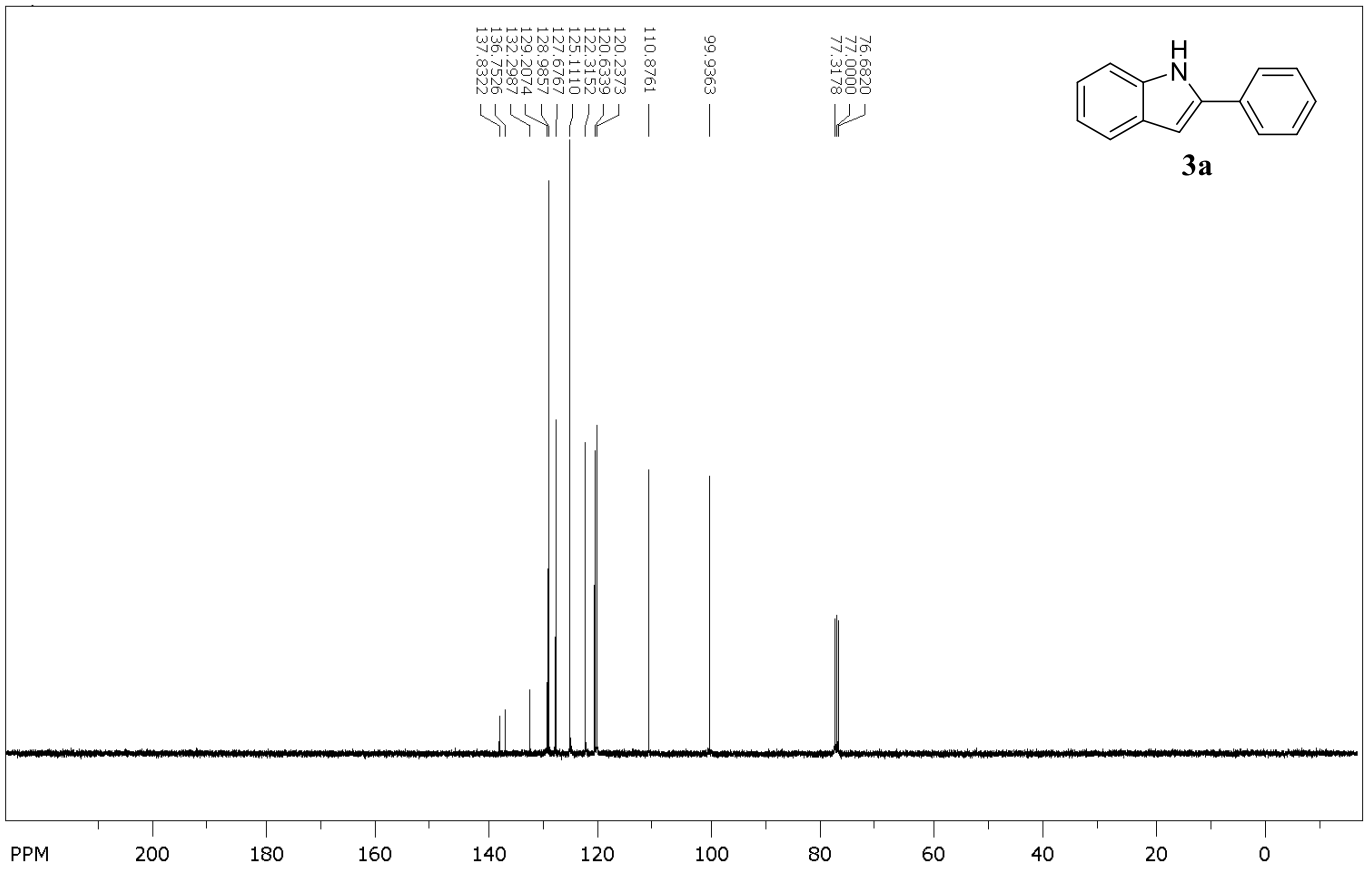


Figure S2. ^{1}H and ^{13}C NMR Spectra of **3a** in $CDCl_3$.

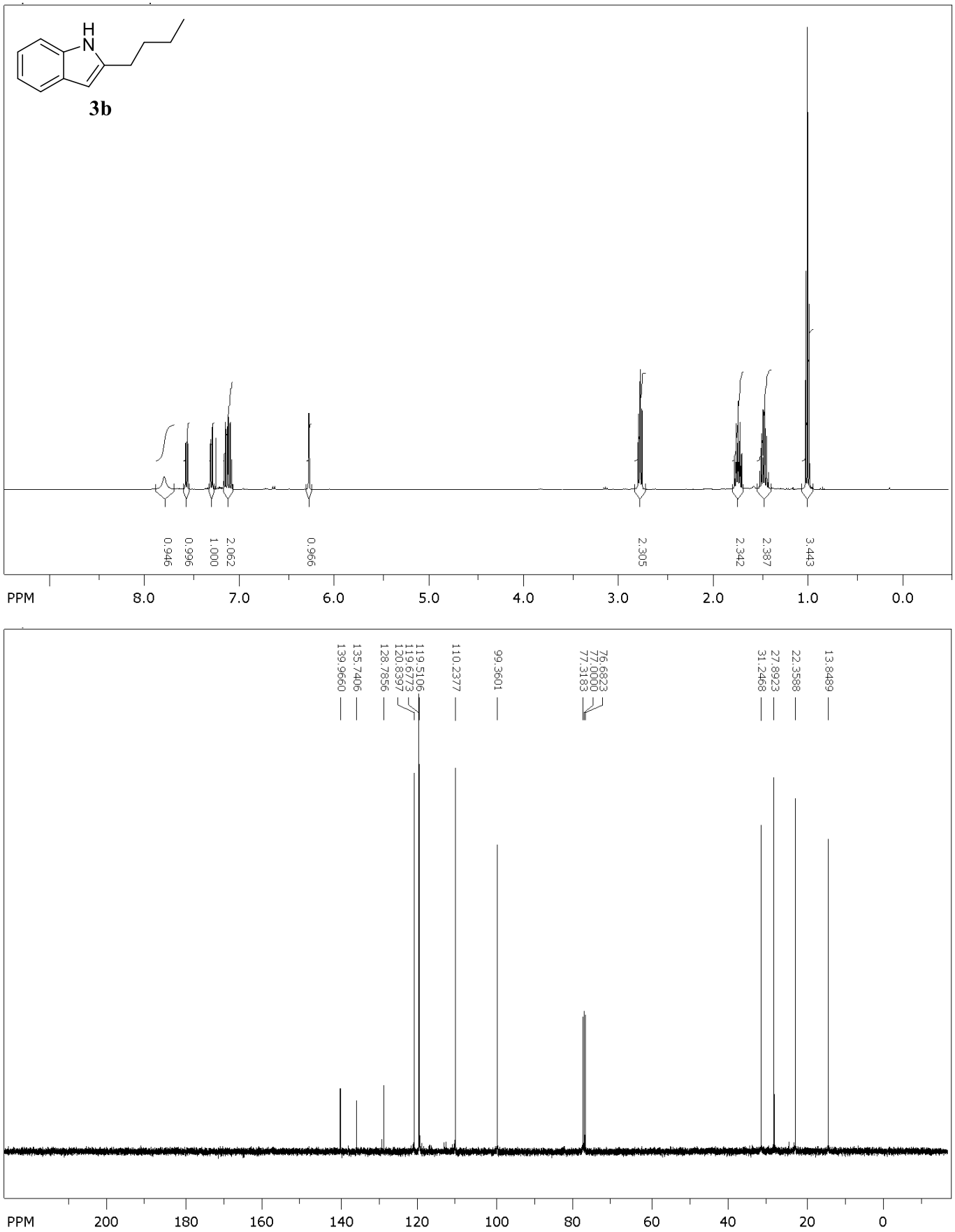
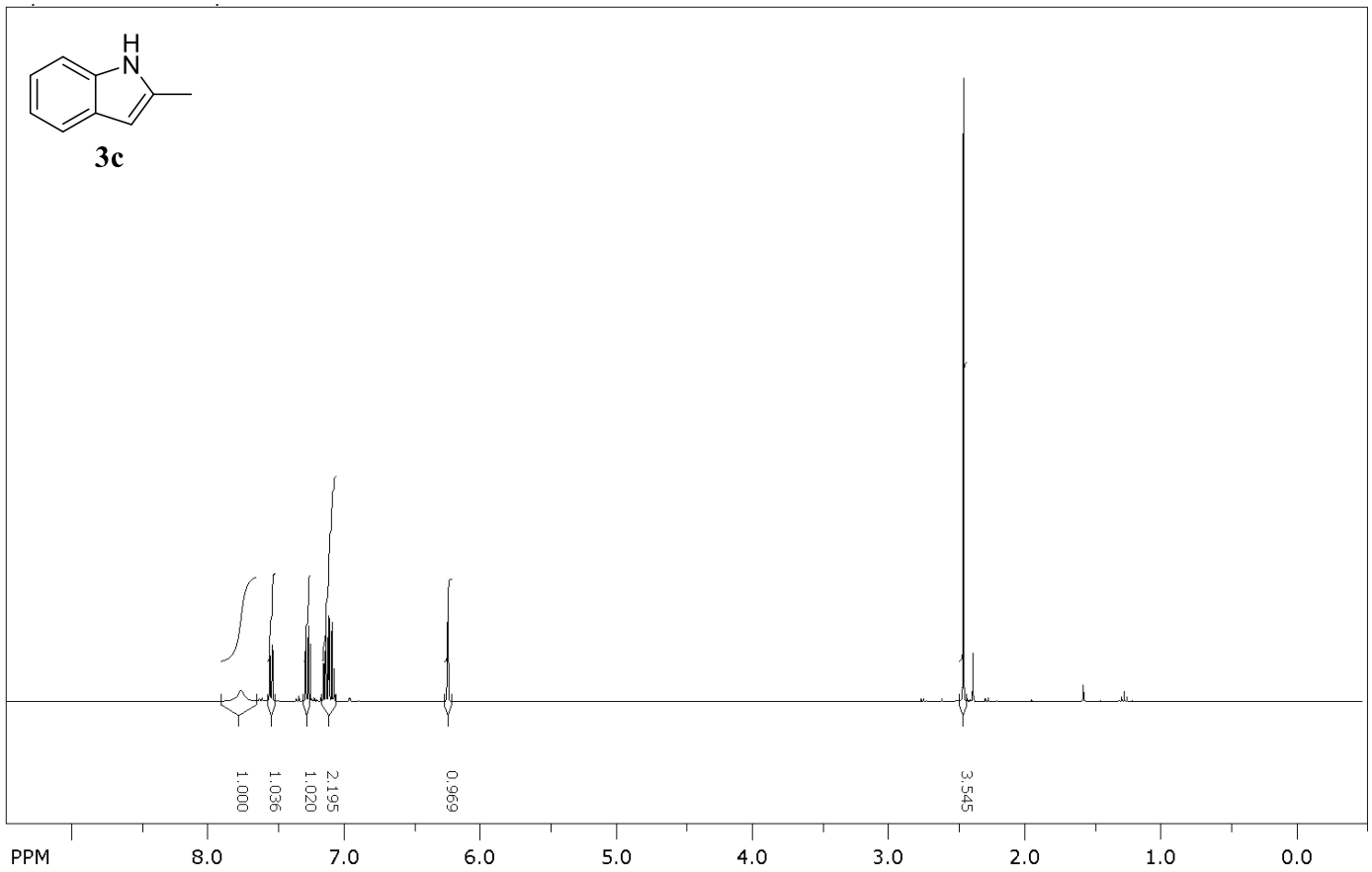


Figure S3. ^{1}H and ^{13}C NMR Spectra of **3b** in $CDCl_3$.



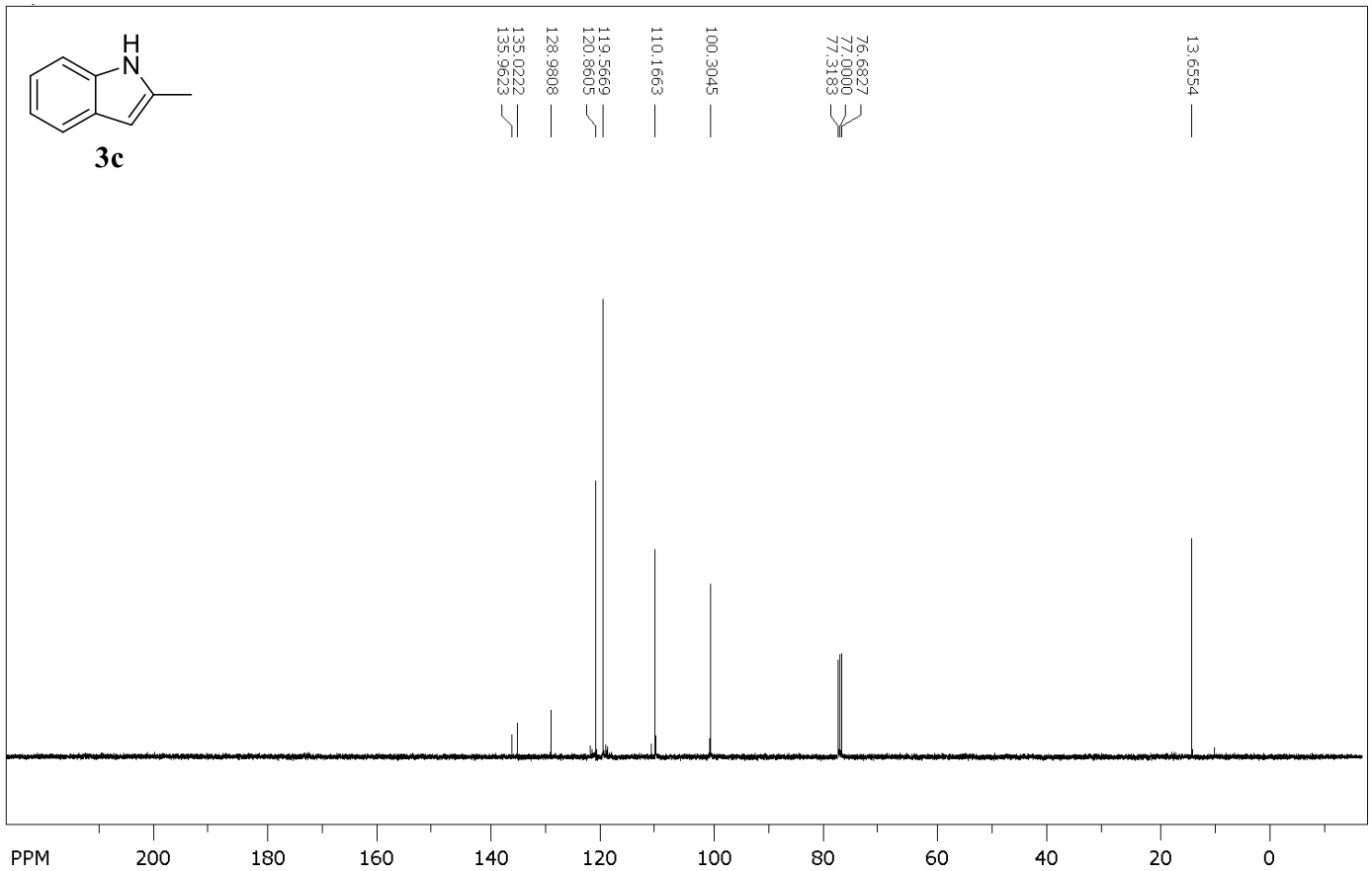


Figure S4. ^{1}H and ^{13}C NMR Spectra of **3c** in $CDCl_3$.

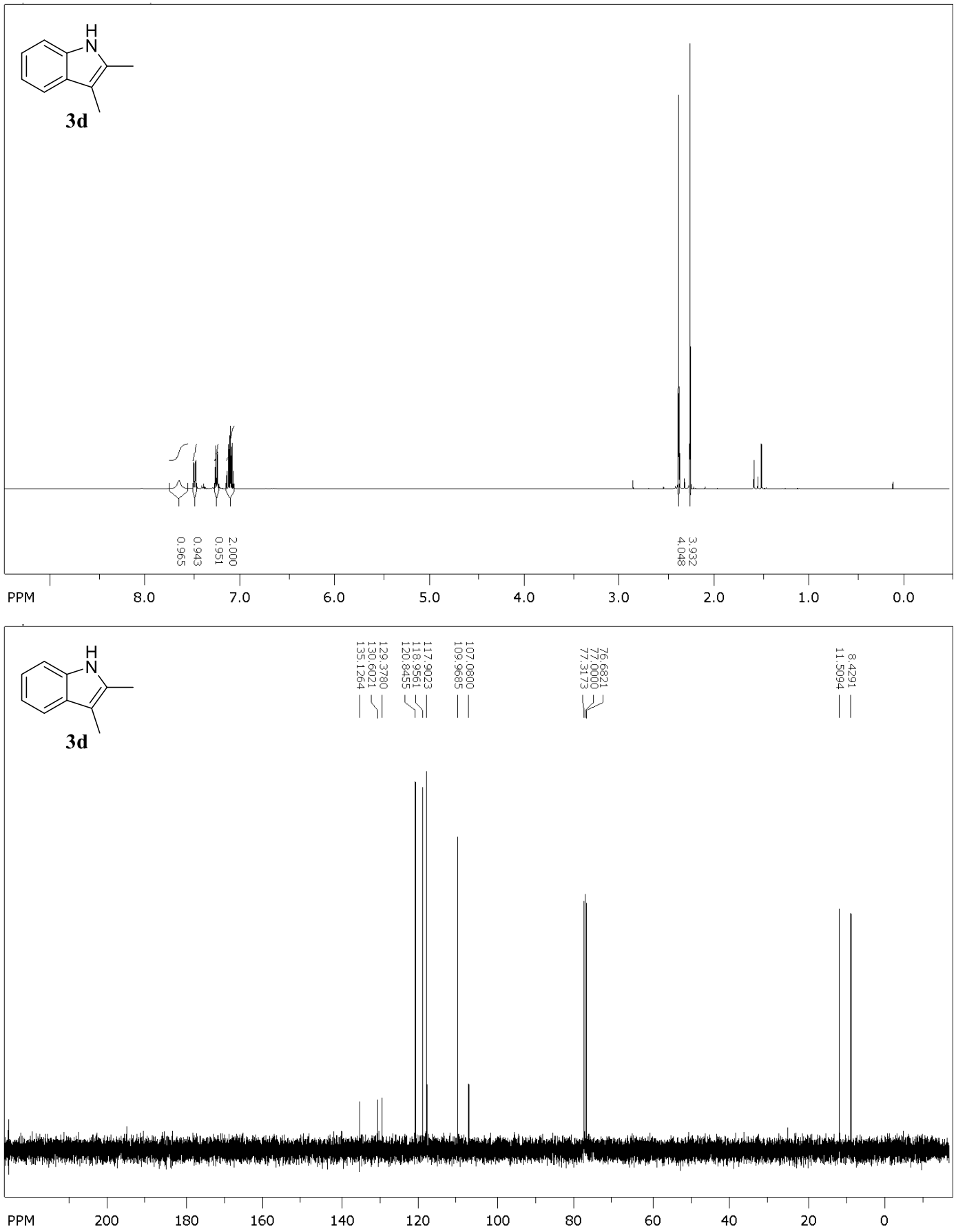


Figure S5. ^{1}H and ^{13}C NMR Spectra of **3d** in $CDCl_3$.

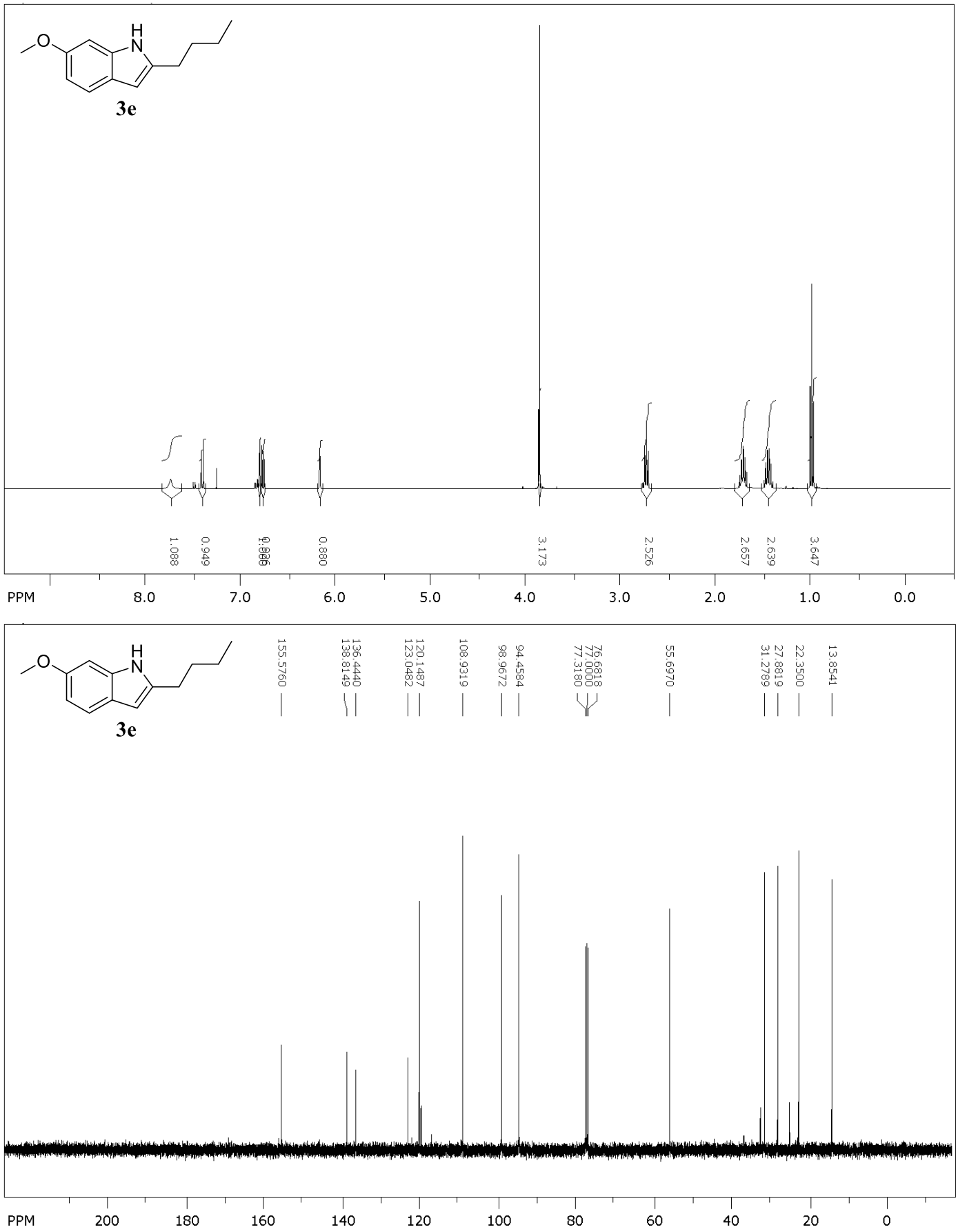


Figure S6. ^{1}H and ^{13}C NMR Spectra of **3e** in $CDCl_3$.

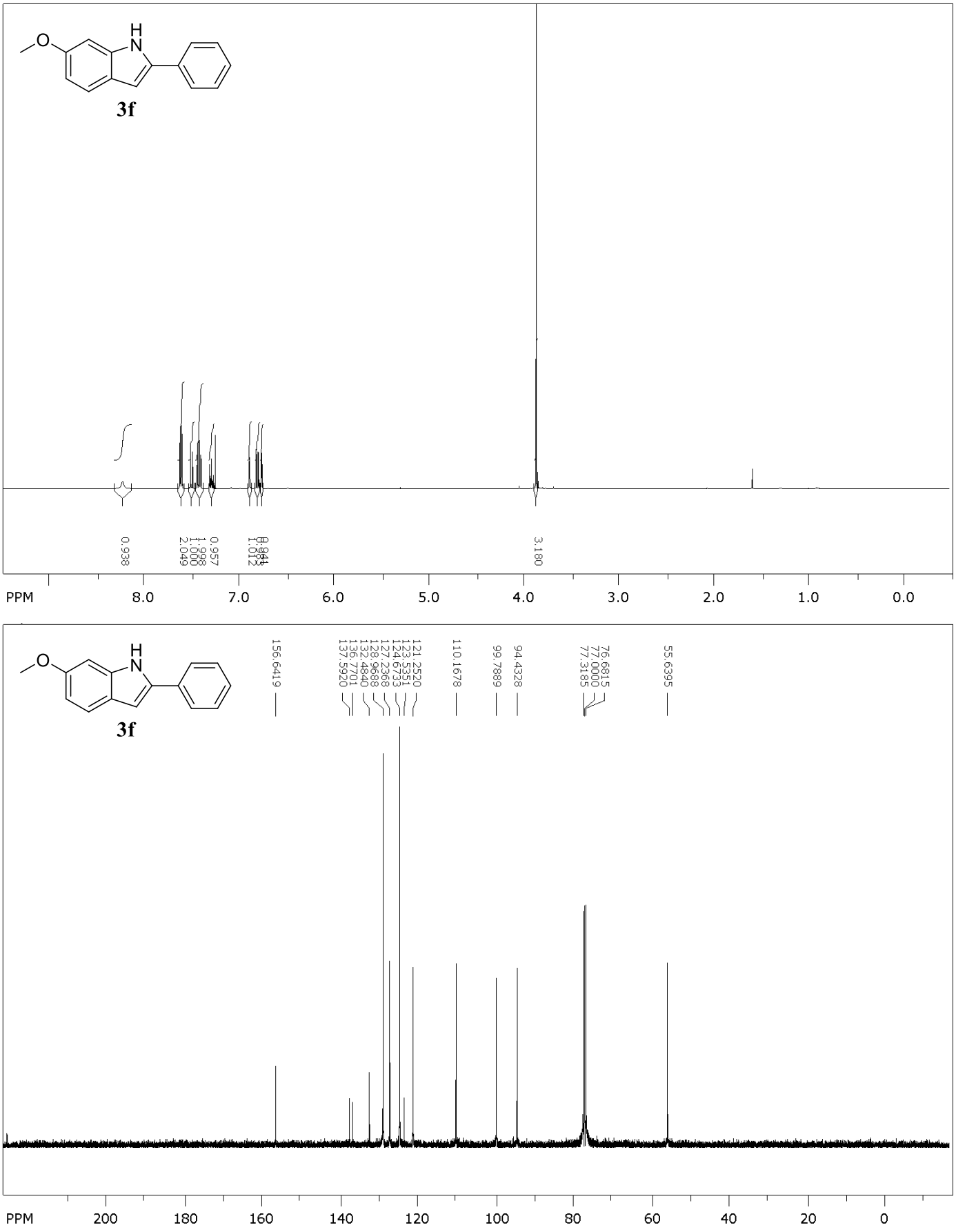


Figure S7. ^{1}H and ^{13}C NMR Spectra of **3f** in $CDCl_3$.

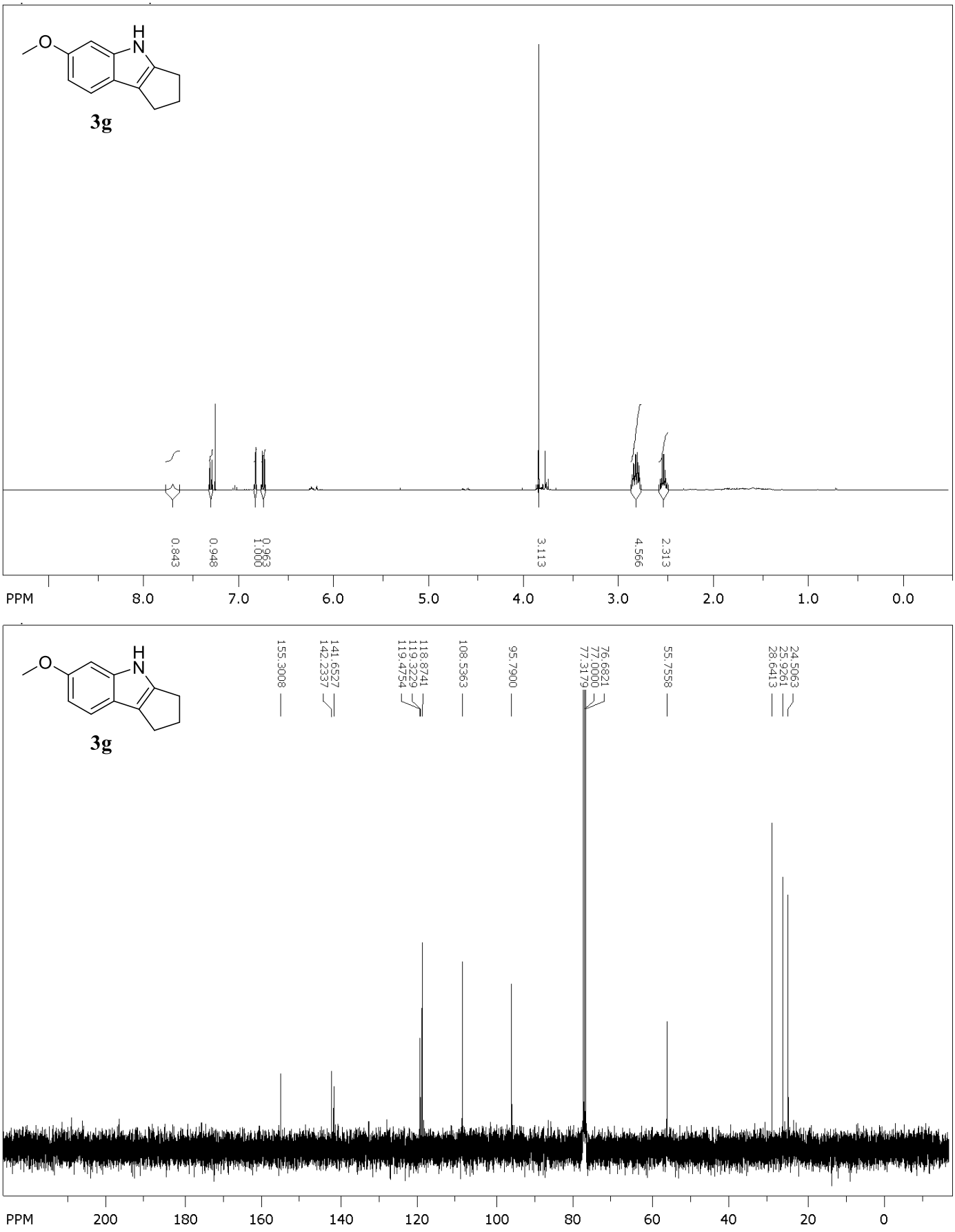


Figure S8. ^{1}H and ^{13}C NMR Spectra of **3g** in $CDCl_3$.

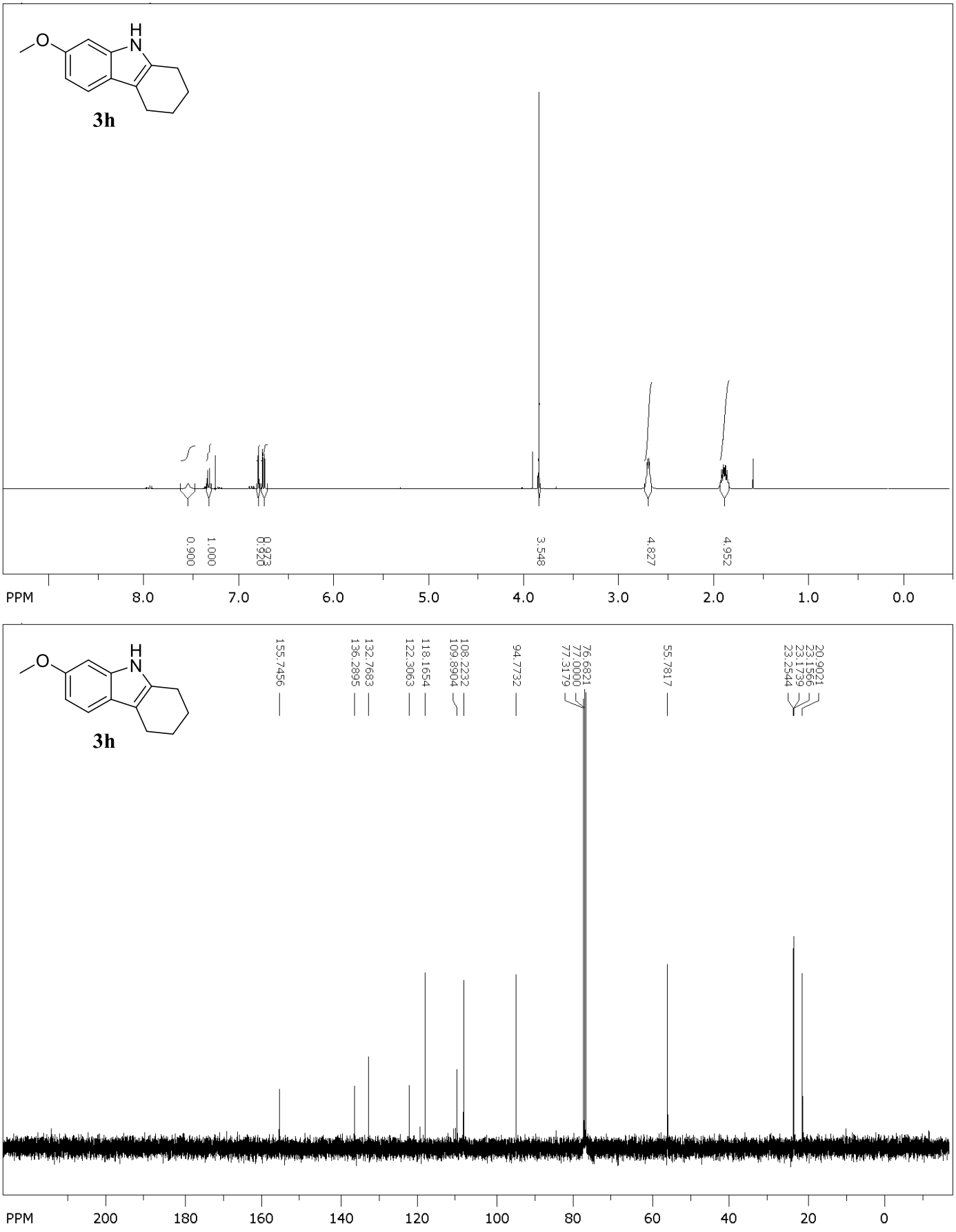


Figure S9. ^{1}H and ^{13}C NMR Spectra of **3h** in $CDCl_3$.

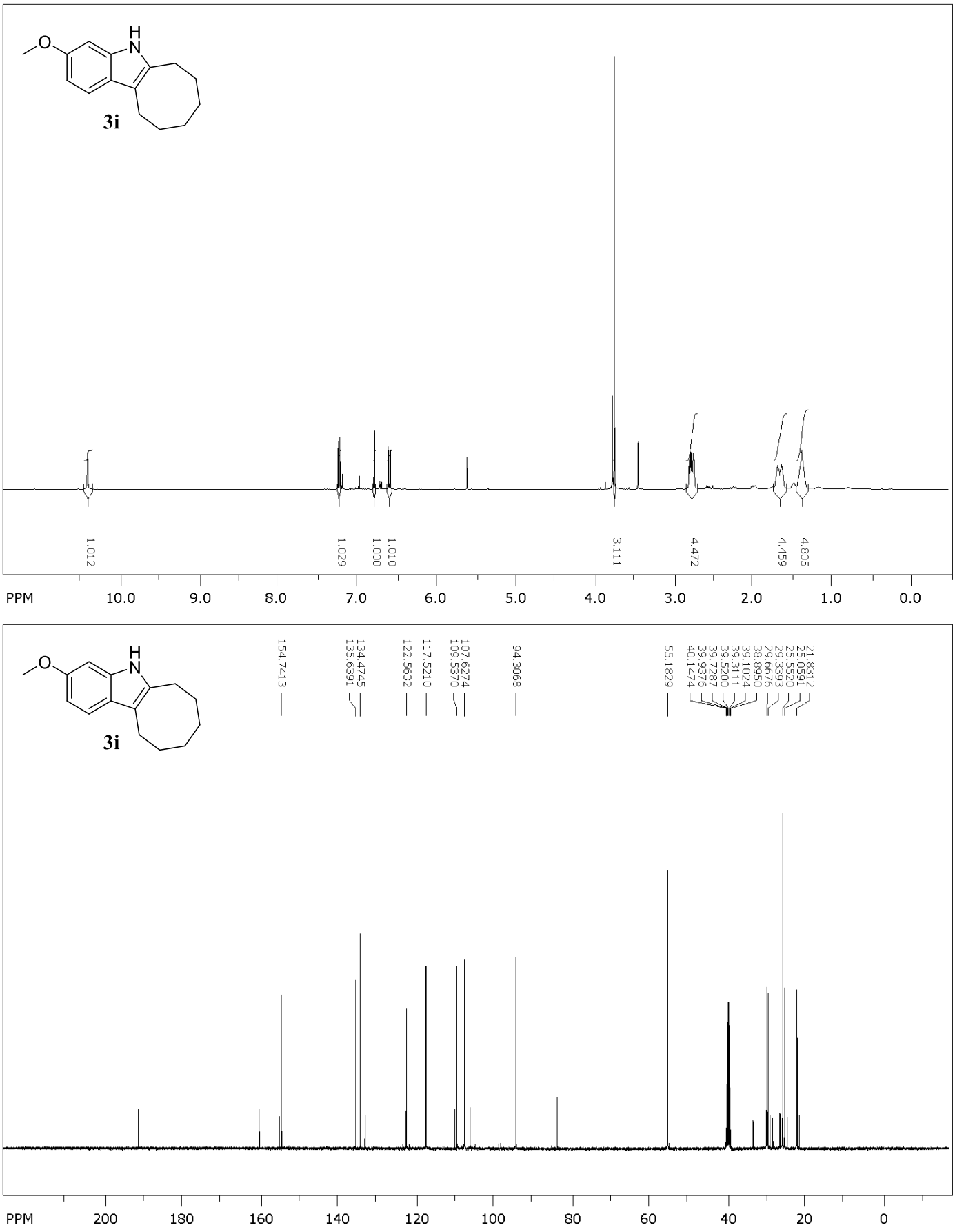


Figure S10. ^{1}H and ^{13}C NMR Spectra of **3i** in DMSO-d_6.

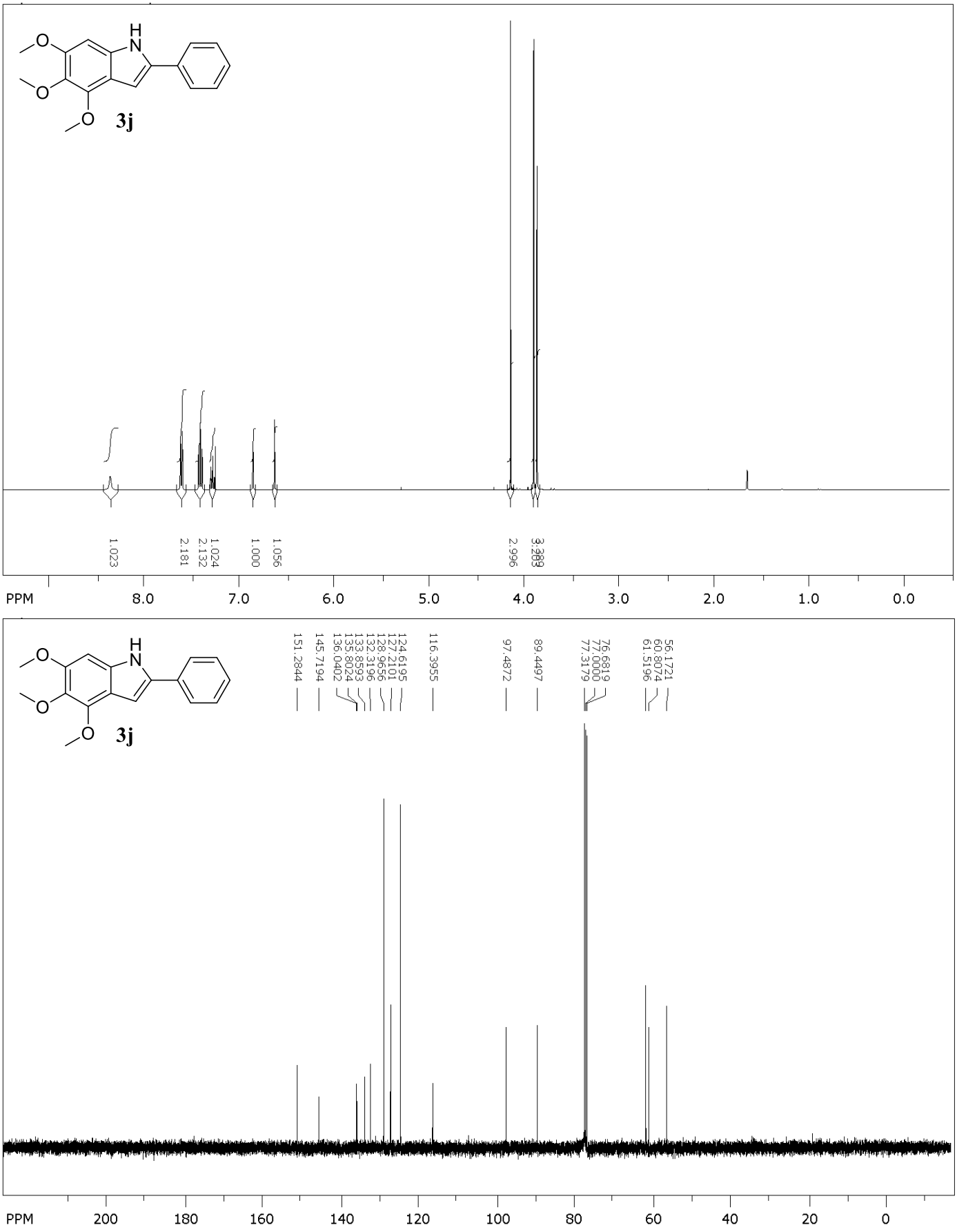


Figure S11. ^{1}H and ^{13}C NMR Spectra of **3j** in $CDCl_3$.

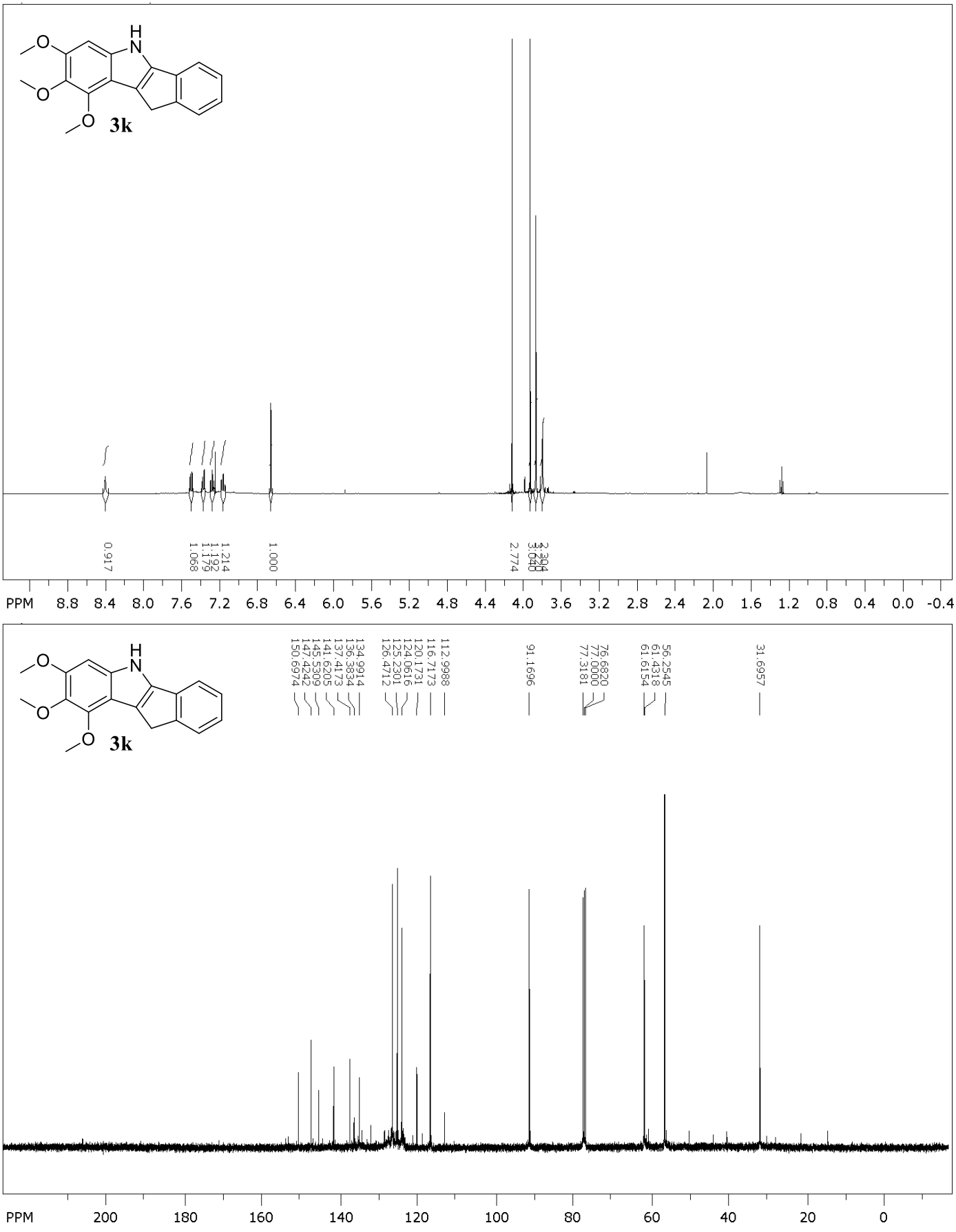


Figure S12. ^{1}H and ^{13}C NMR Spectra of **3k** in $CDCl_3$.

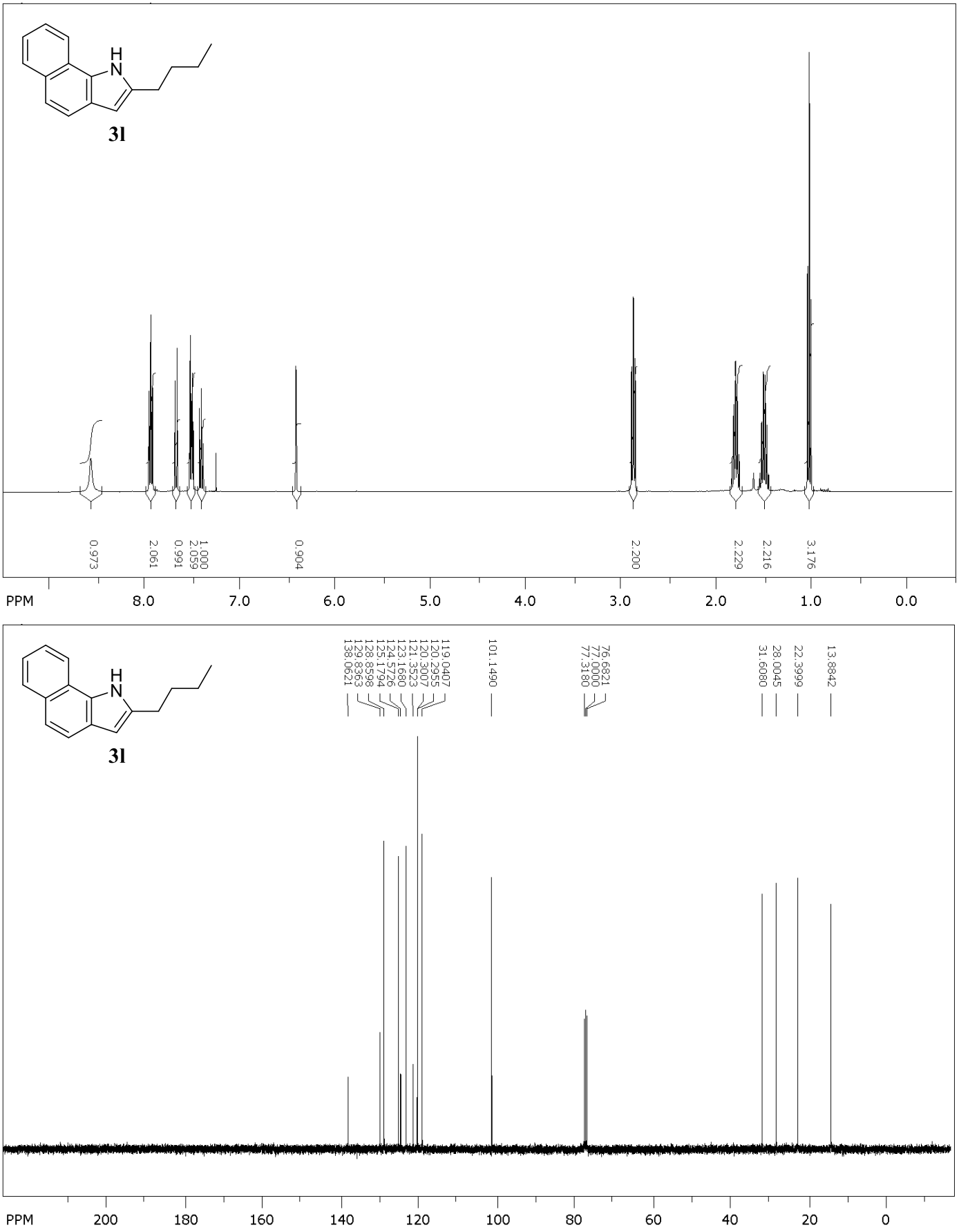


Figure S13. ^{1}H and ^{13}C NMR Spectra of **3l** in $CDCl_3$.

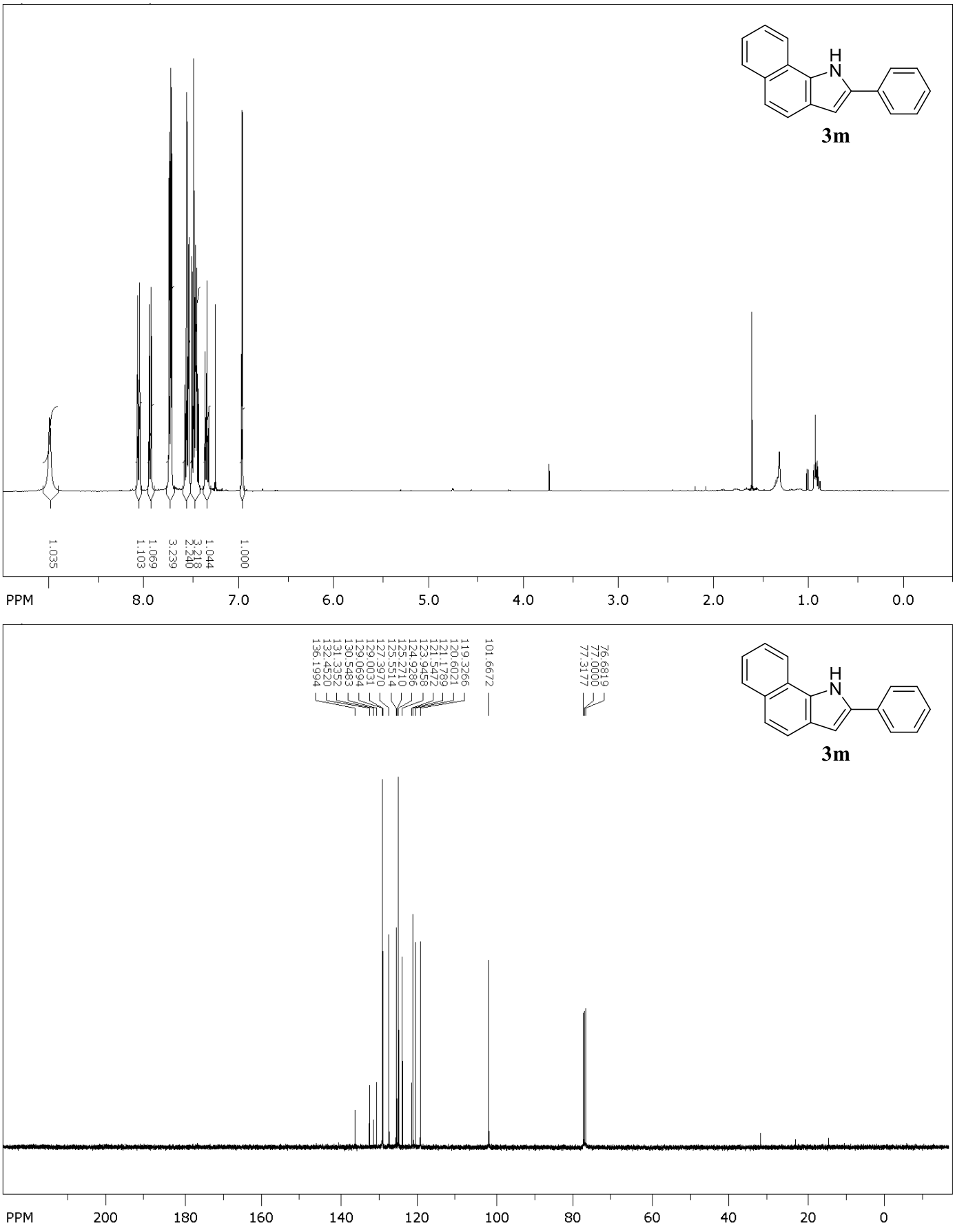


Figure S14. ^{1}H and ^{13}C NMR Spectra of **3m** in $CDCl_3$.

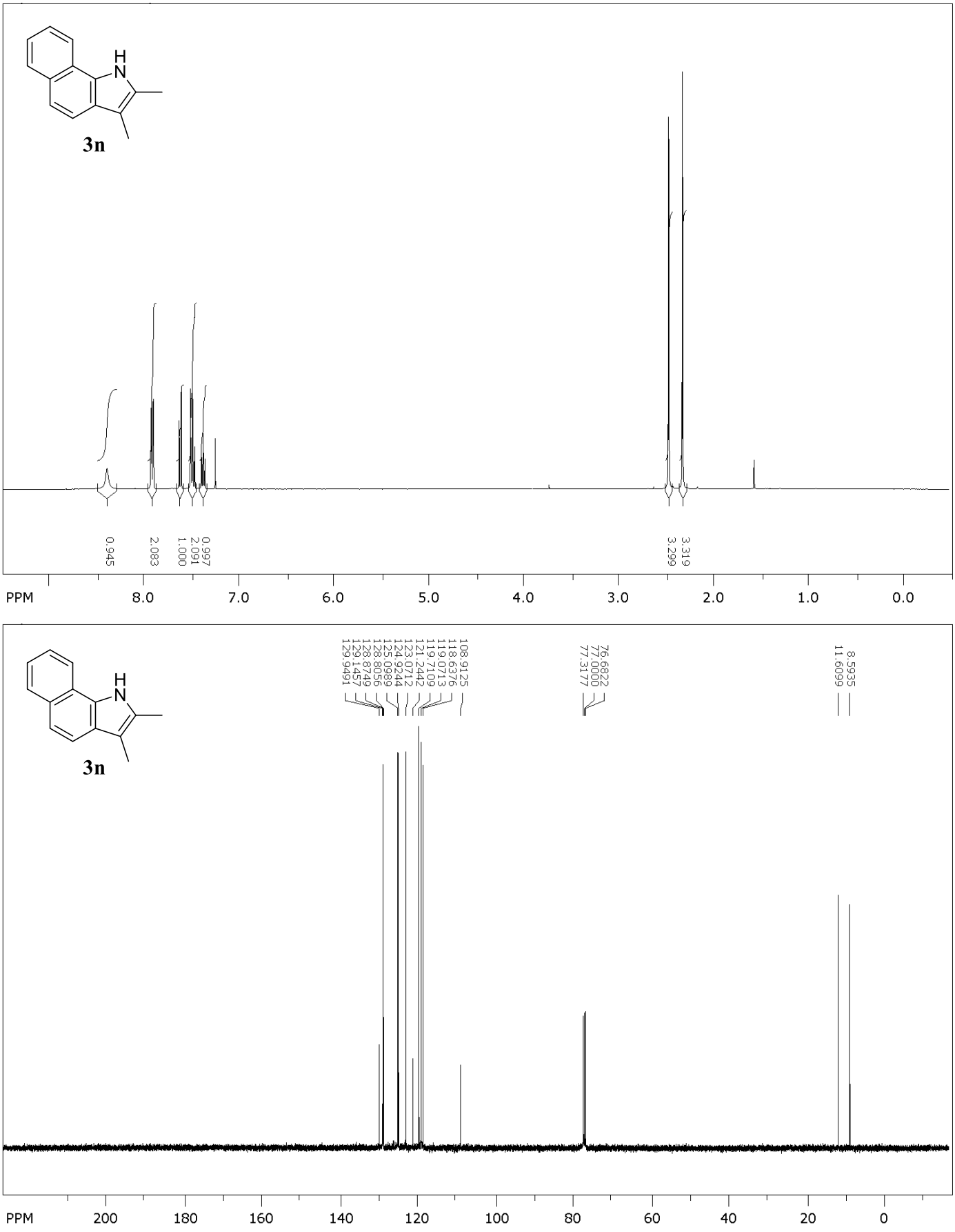


Figure S15. ^{1}H and ^{13}C NMR Spectra of **3n** in $CDCl_3$.

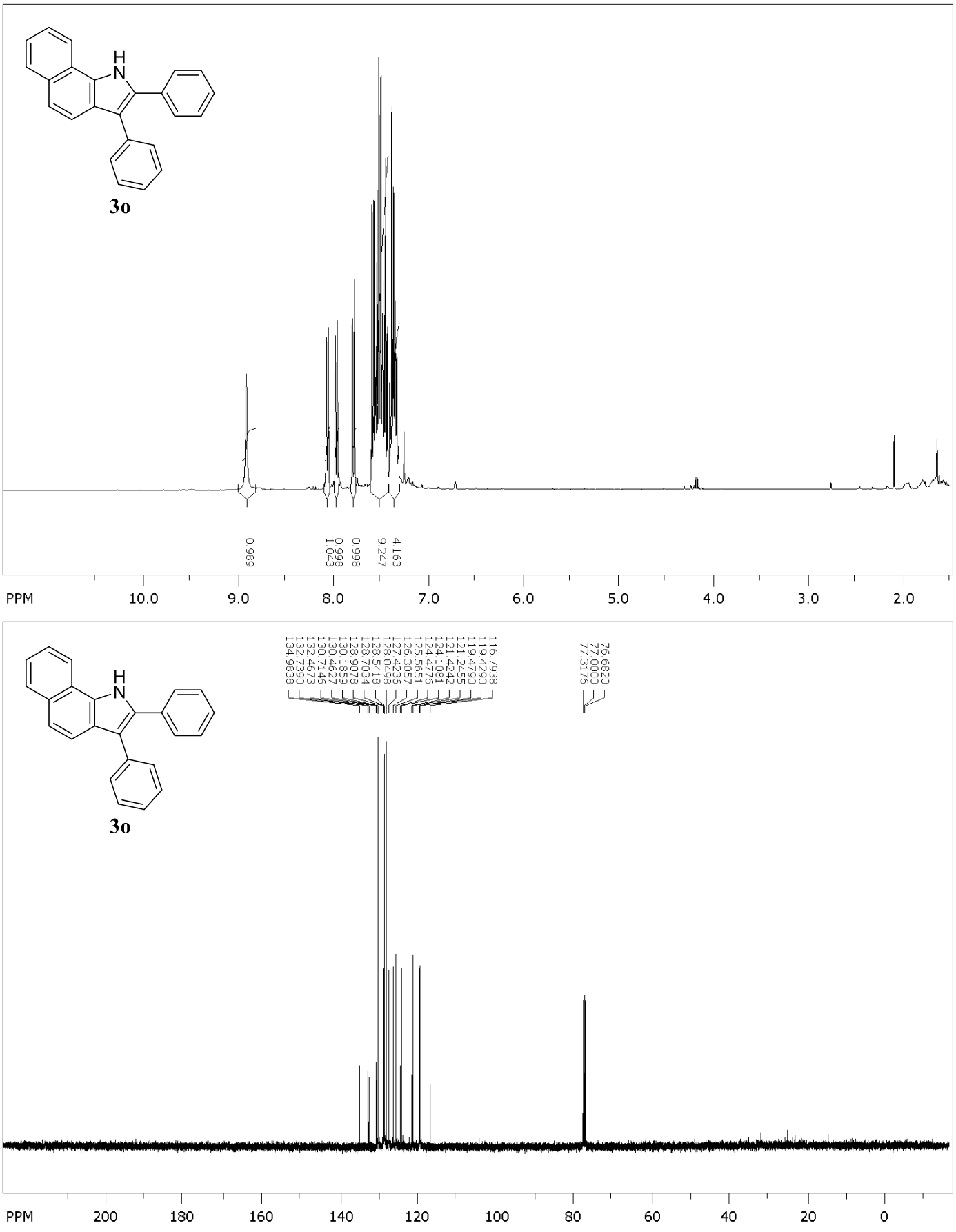


Figure S16. ^{1}H and ^{13}C NMR Spectra of **3o** in $CDCl_3$.

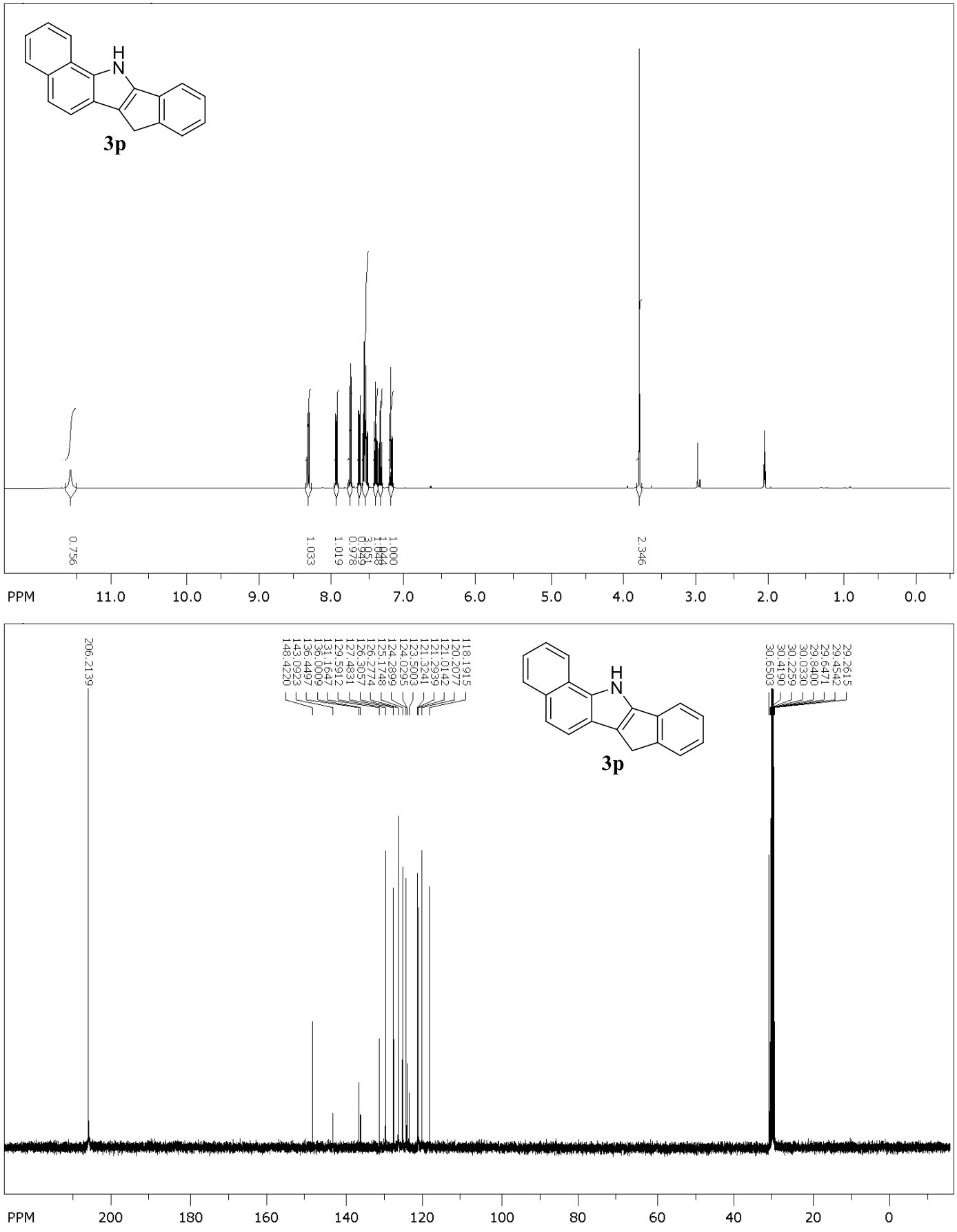


Figure S17. ^{1}H and ^{13}C NMR Spectra of **3p** in acetone-d_6.

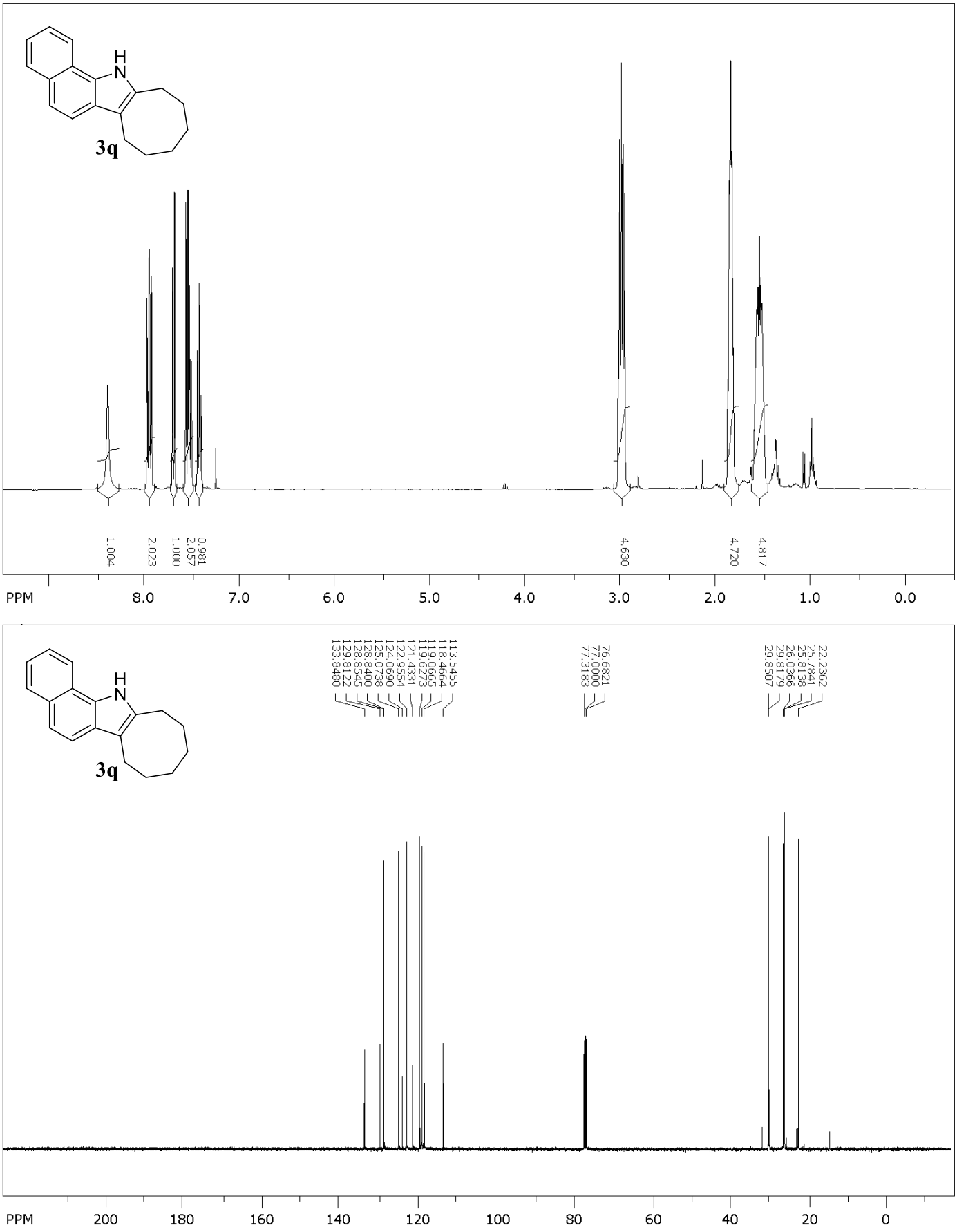


Figure S18. ^{1}H and ^{13}C NMR Spectra of **3q** in $CDCl_3$.

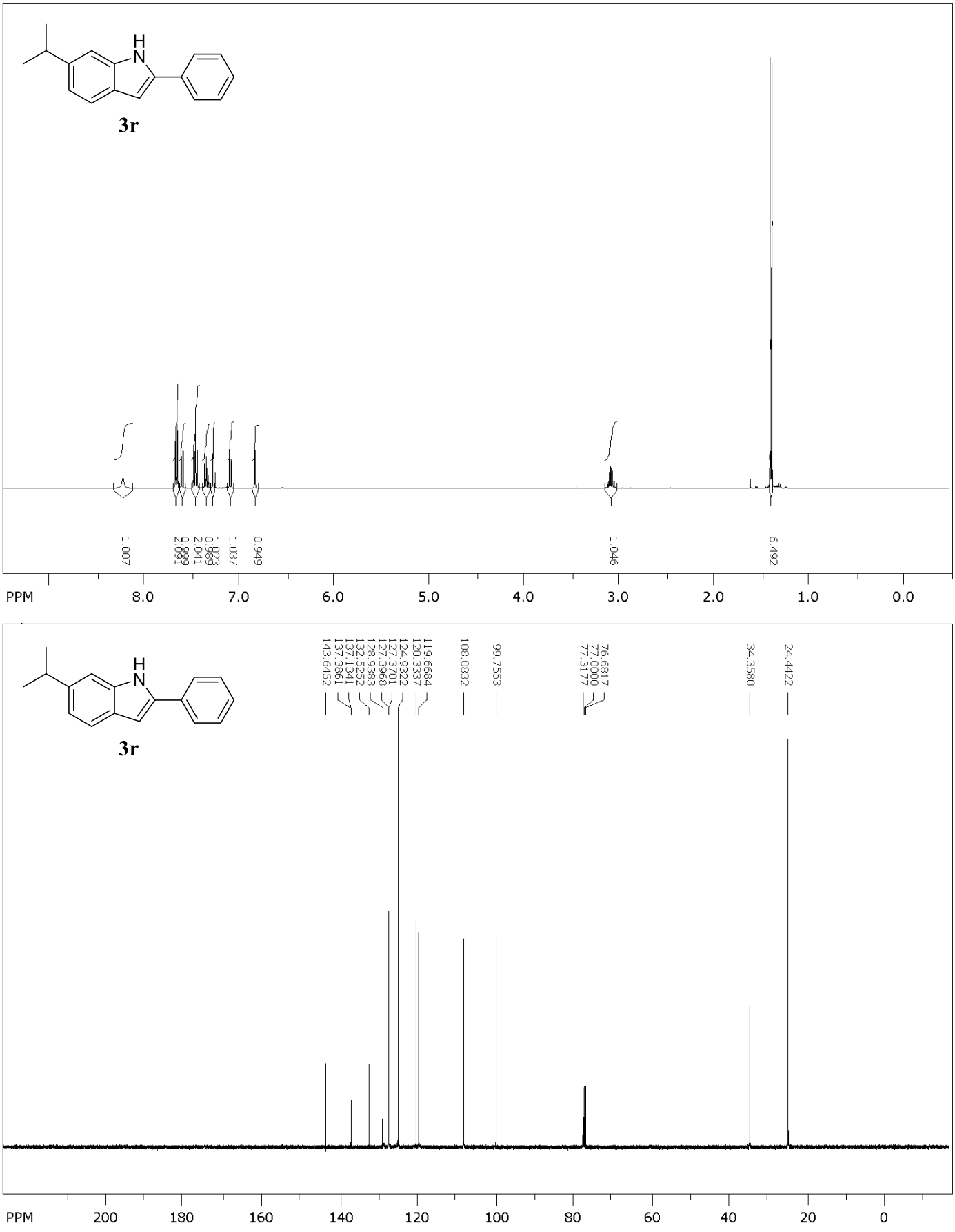


Figure S19. ^{1}H and ^{13}C NMR Spectra of **3r** in $CDCl_3$.

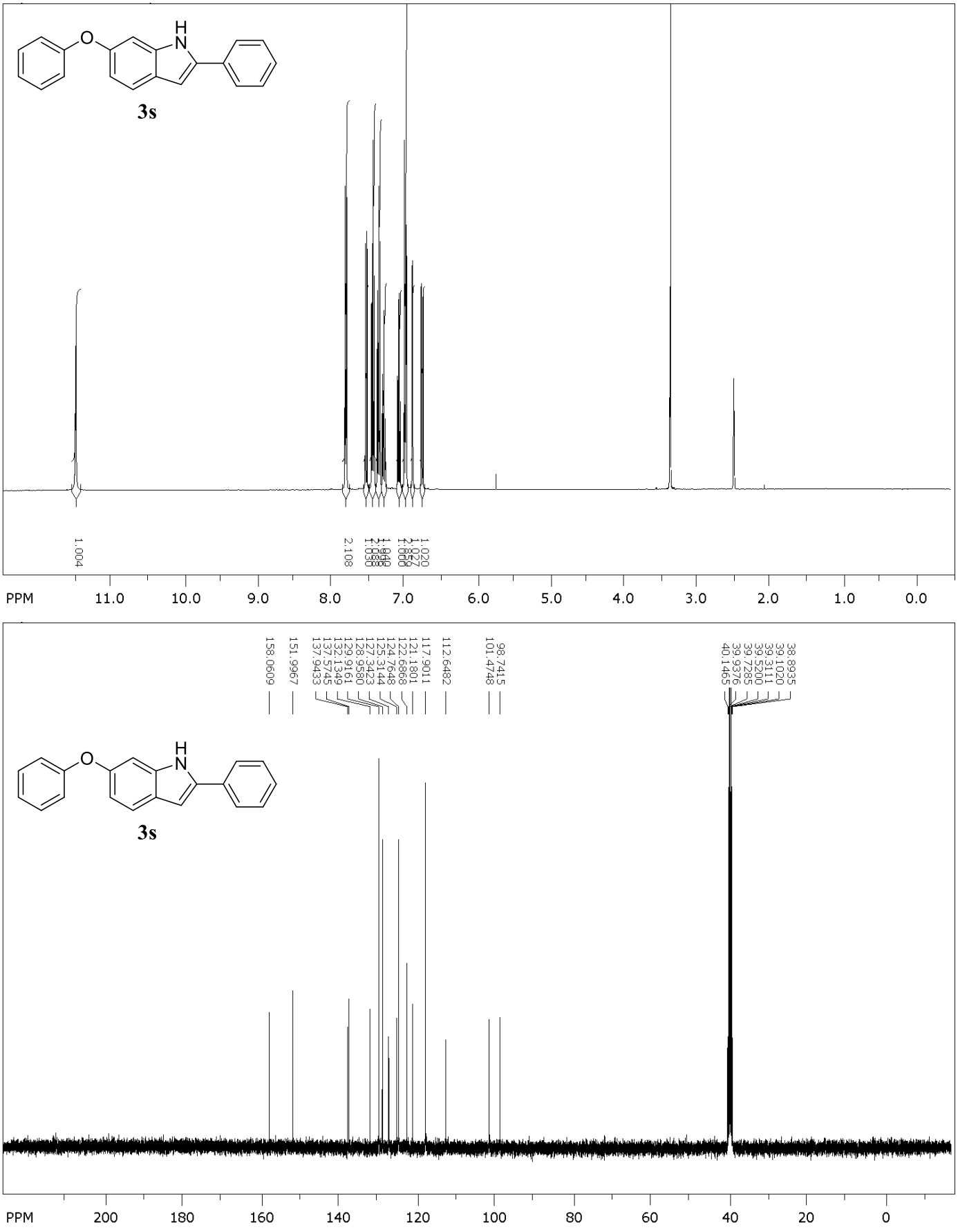


Figure S20. ^{1}H and ^{13}C NMR Spectra of **3s** in DMSO-d_6.

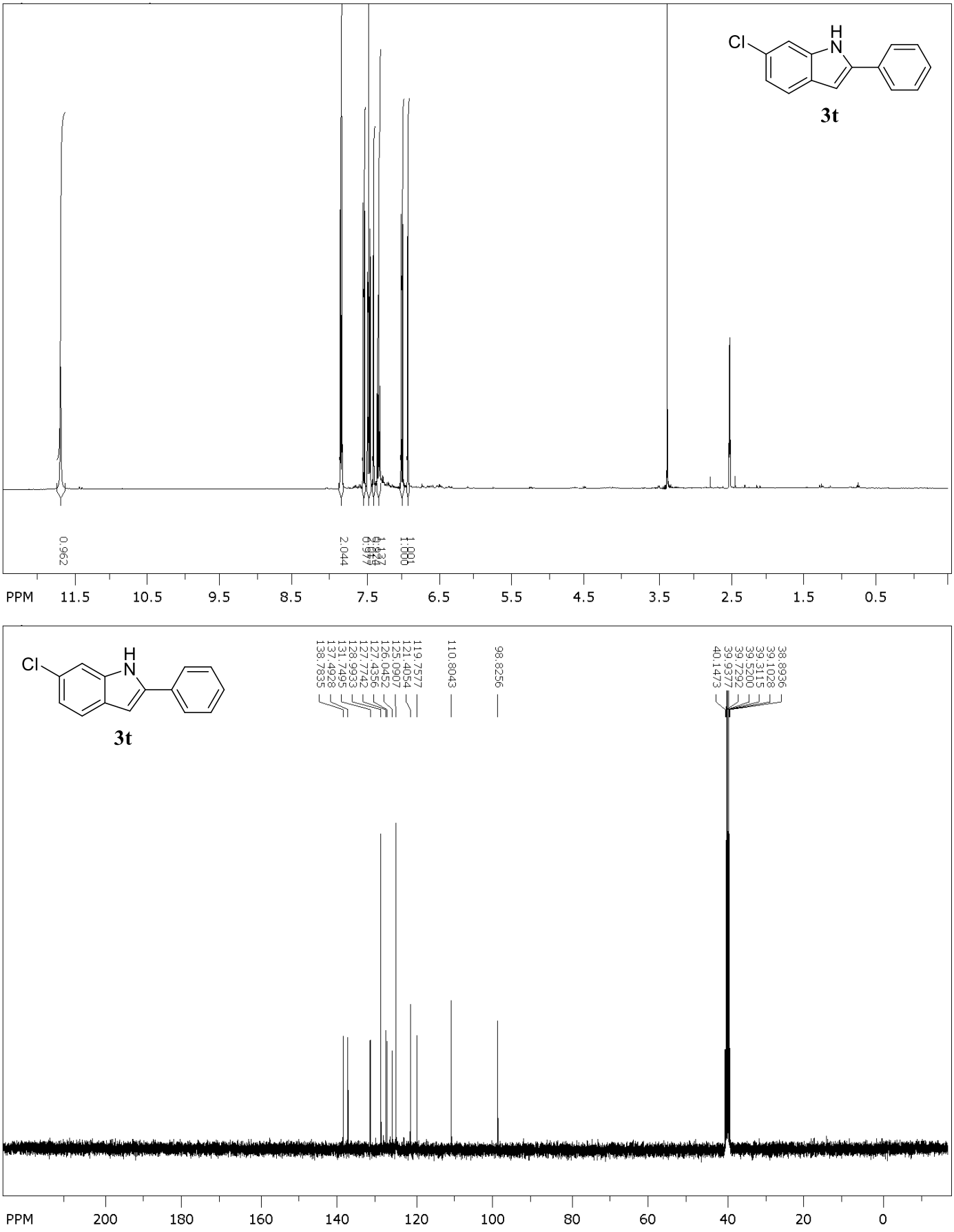
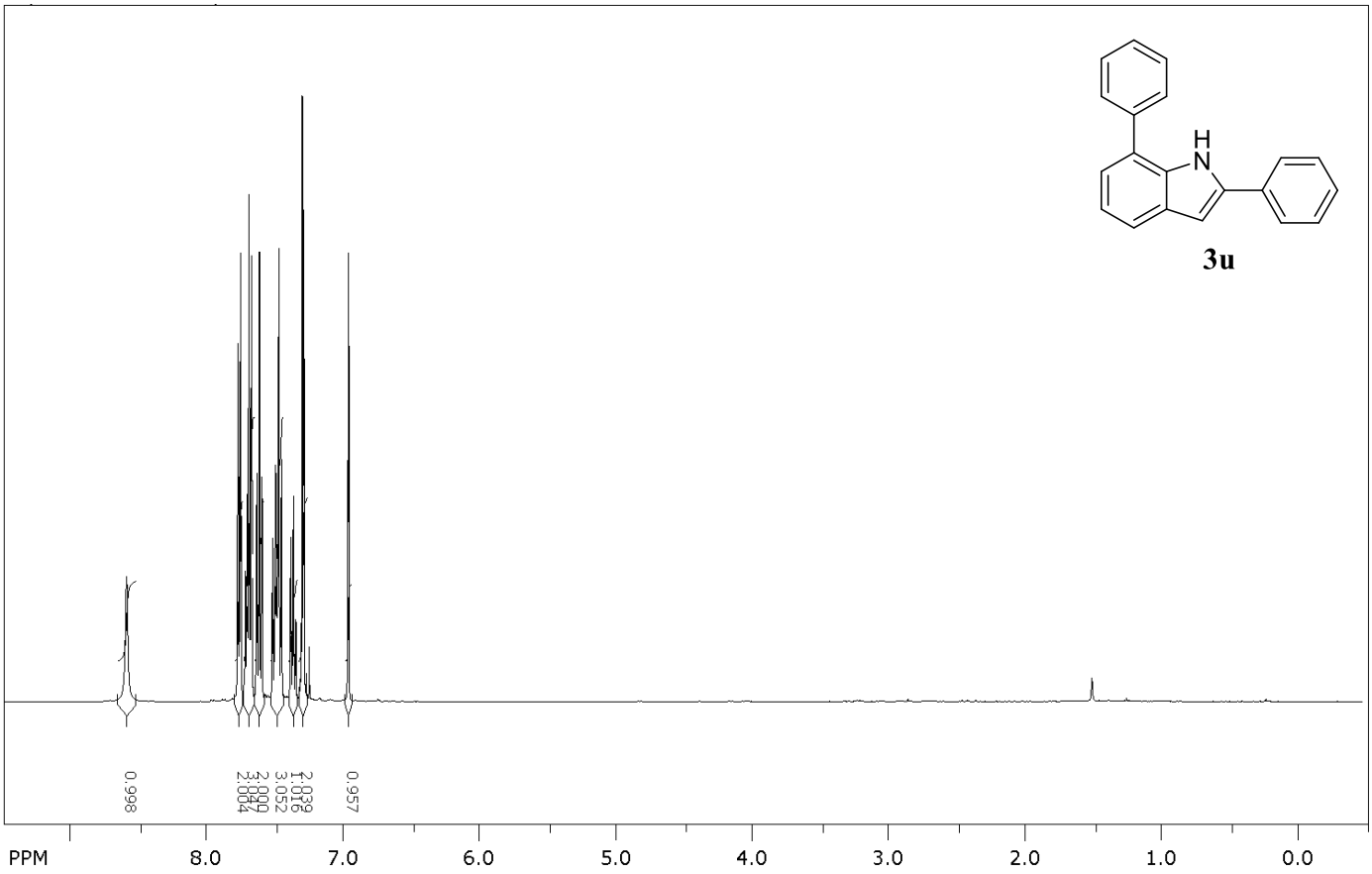


Figure S21. ^{1}H and ^{13}C NMR Spectra of **3t** in DMSO-d_6.



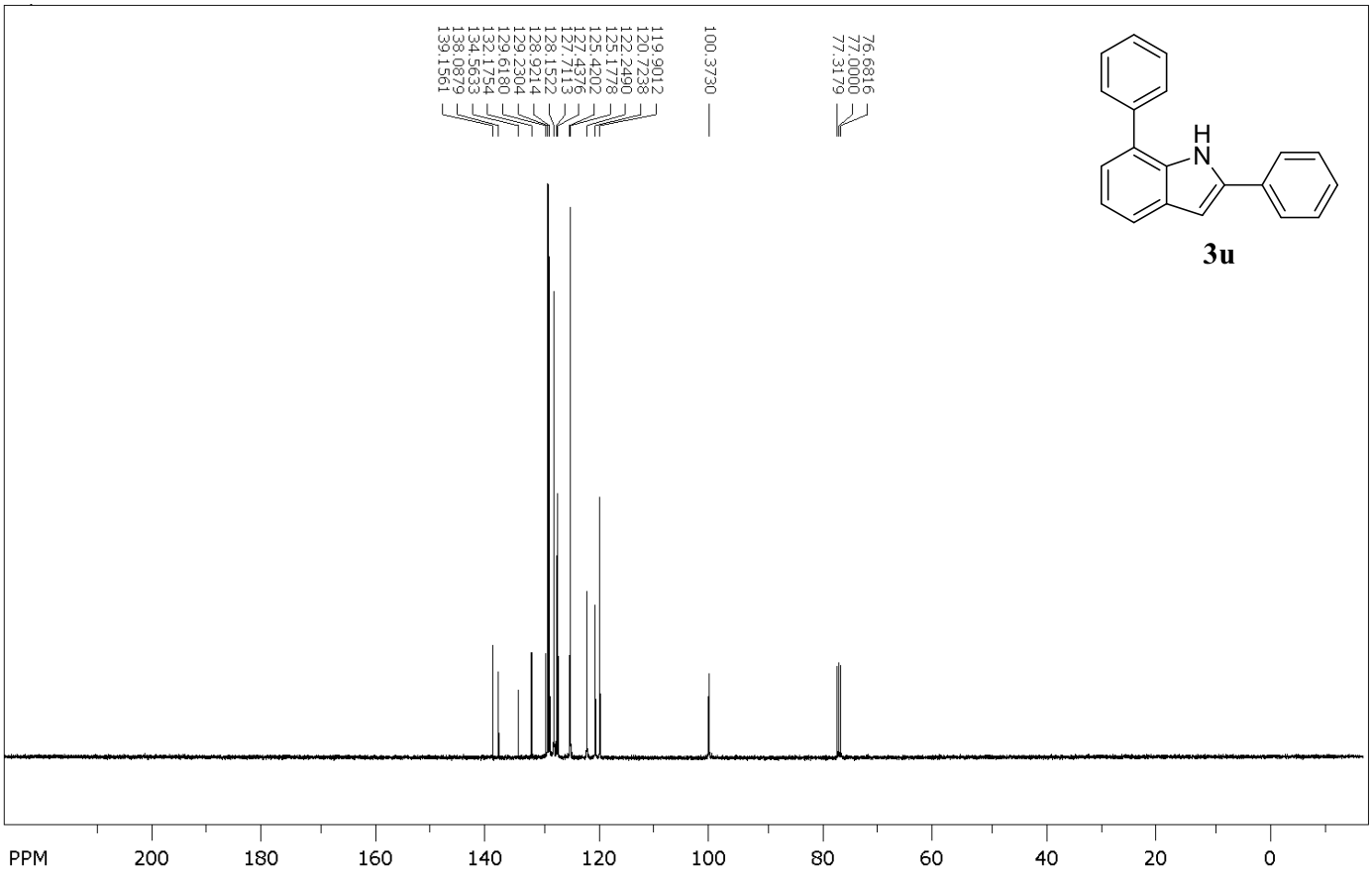


Figure S22. ^{1}H and ^{13}C NMR Spectra of **3u** in $CDCl_3$.

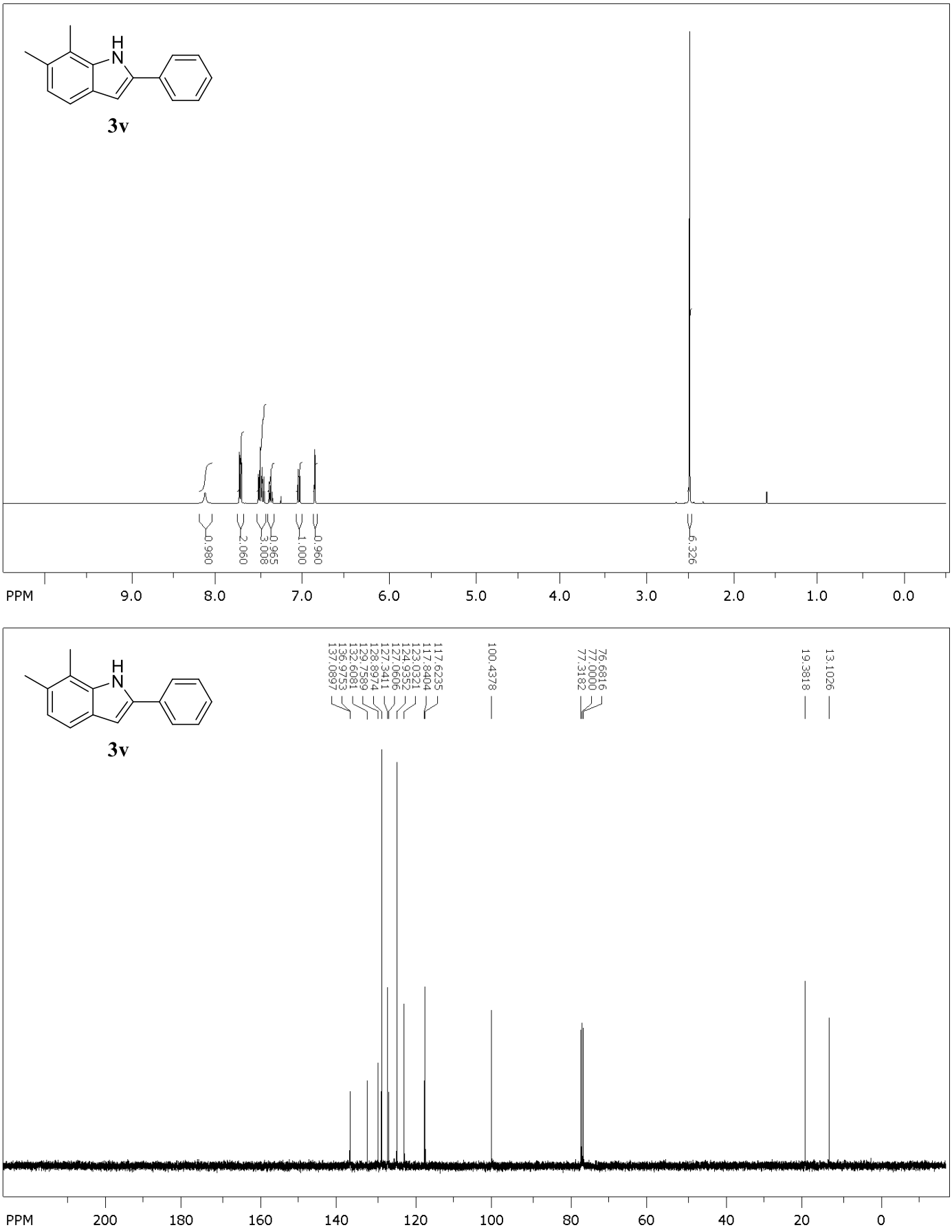


Figure S23. ^{1}H and ^{13}C NMR Spectra of **3v** in $CDCl_3$.

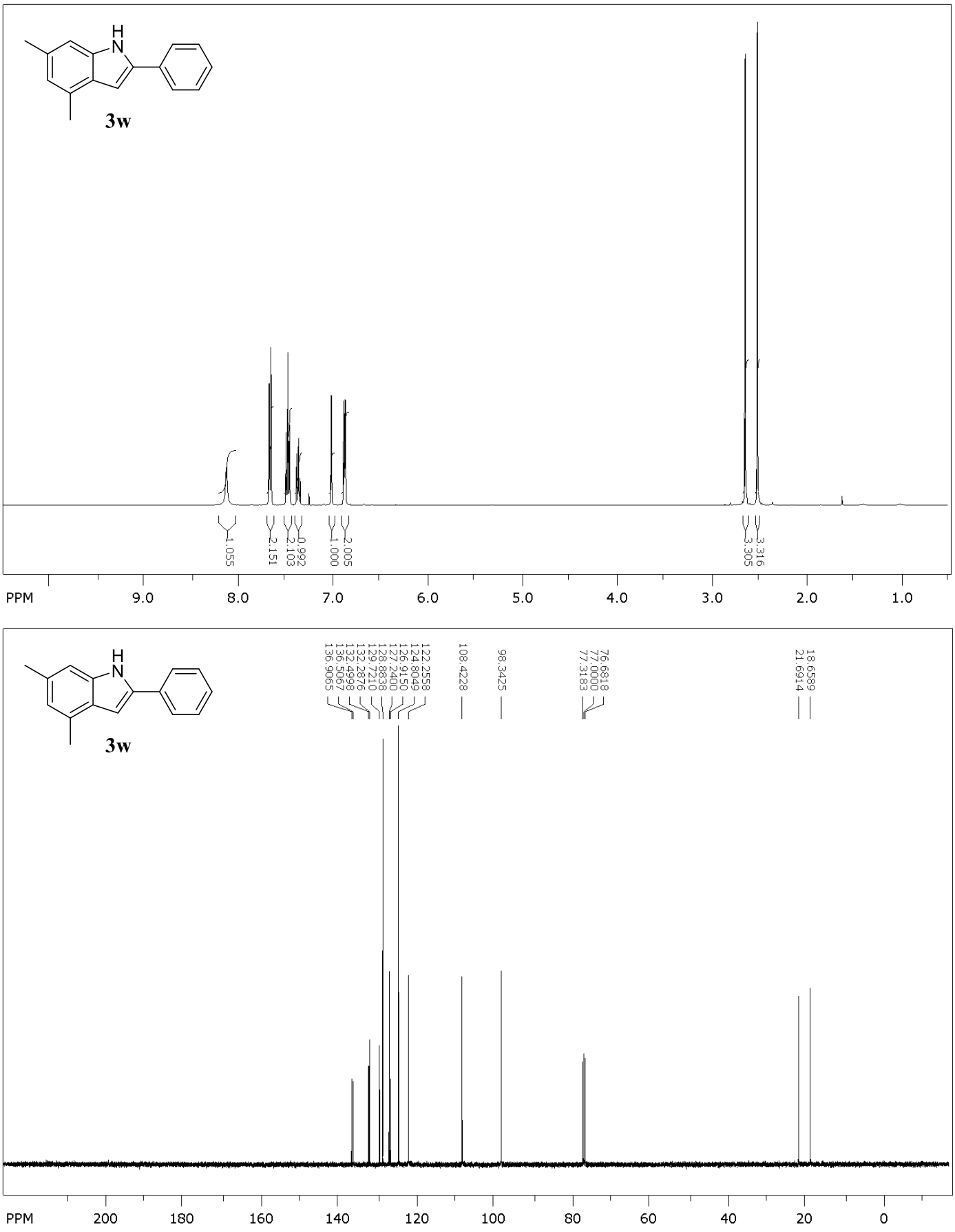


Figure S24. ^{1}H and ^{13}C NMR Spectra of **3w** in $CDCl_3$.

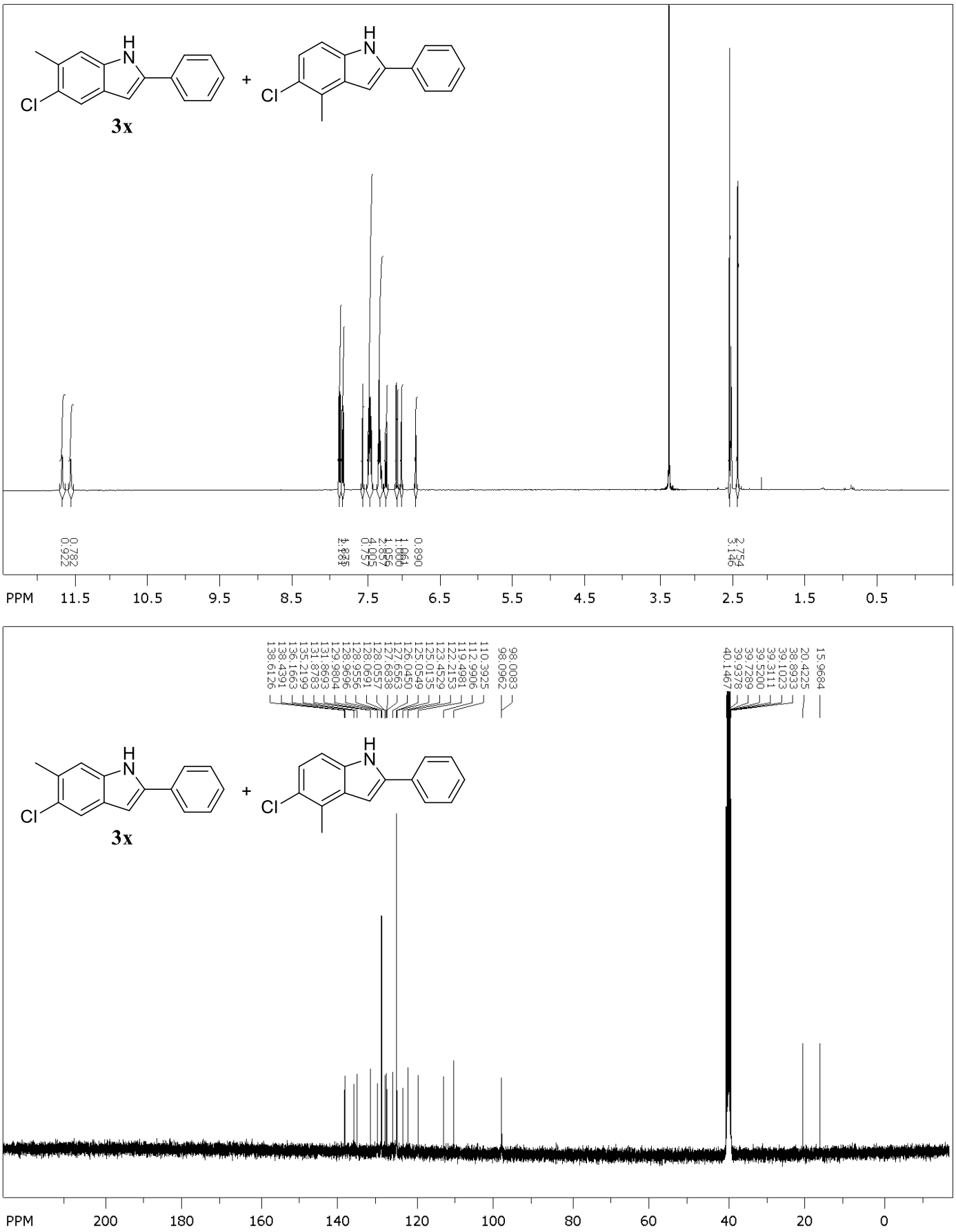


Figure S25. ^{1}H and ^{13}C NMR Spectra of **3x** in DMSO-d_6.

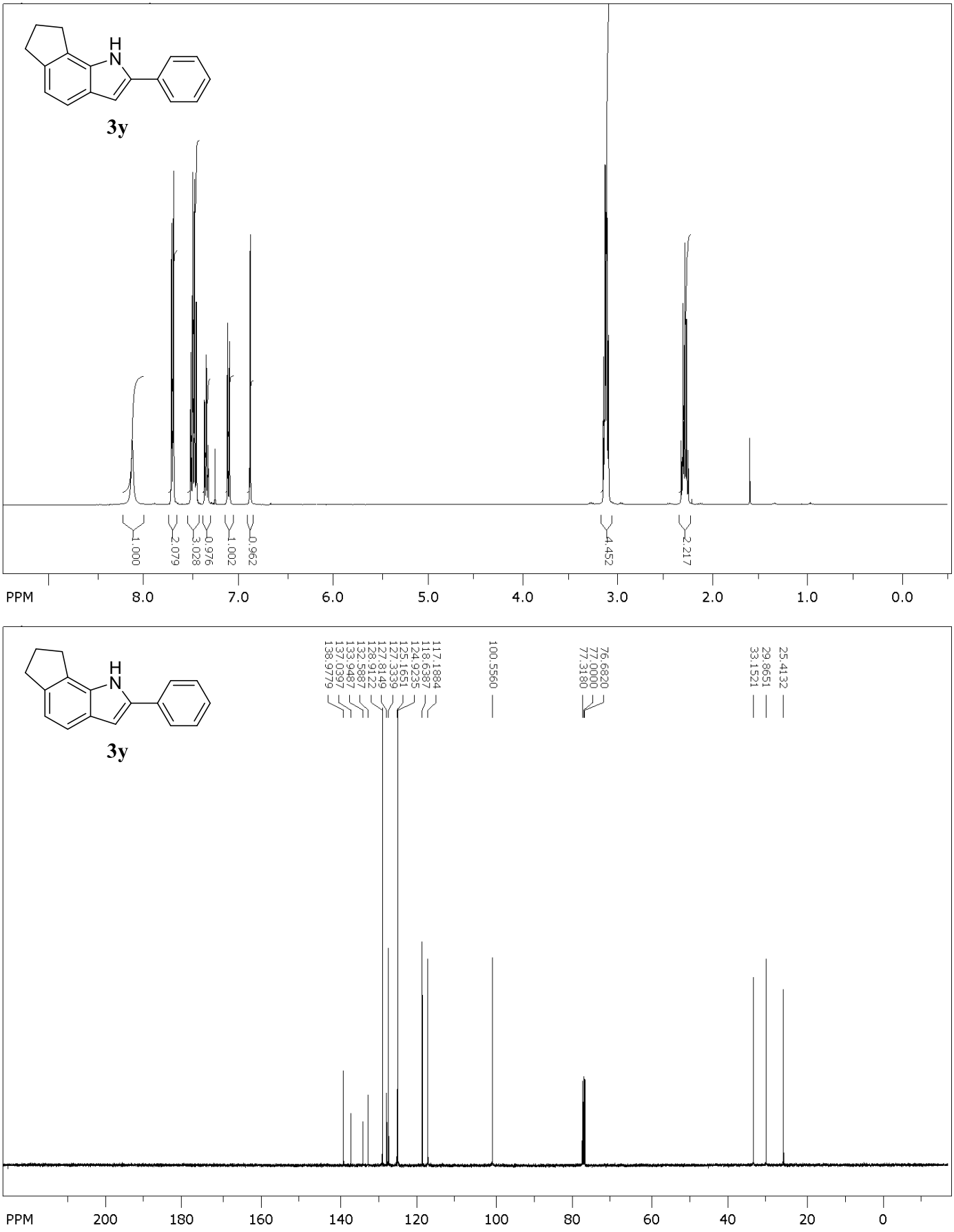


Figure S26. ^{1}H and ^{13}C NMR Spectra of **3y** in $CDCl_3$.

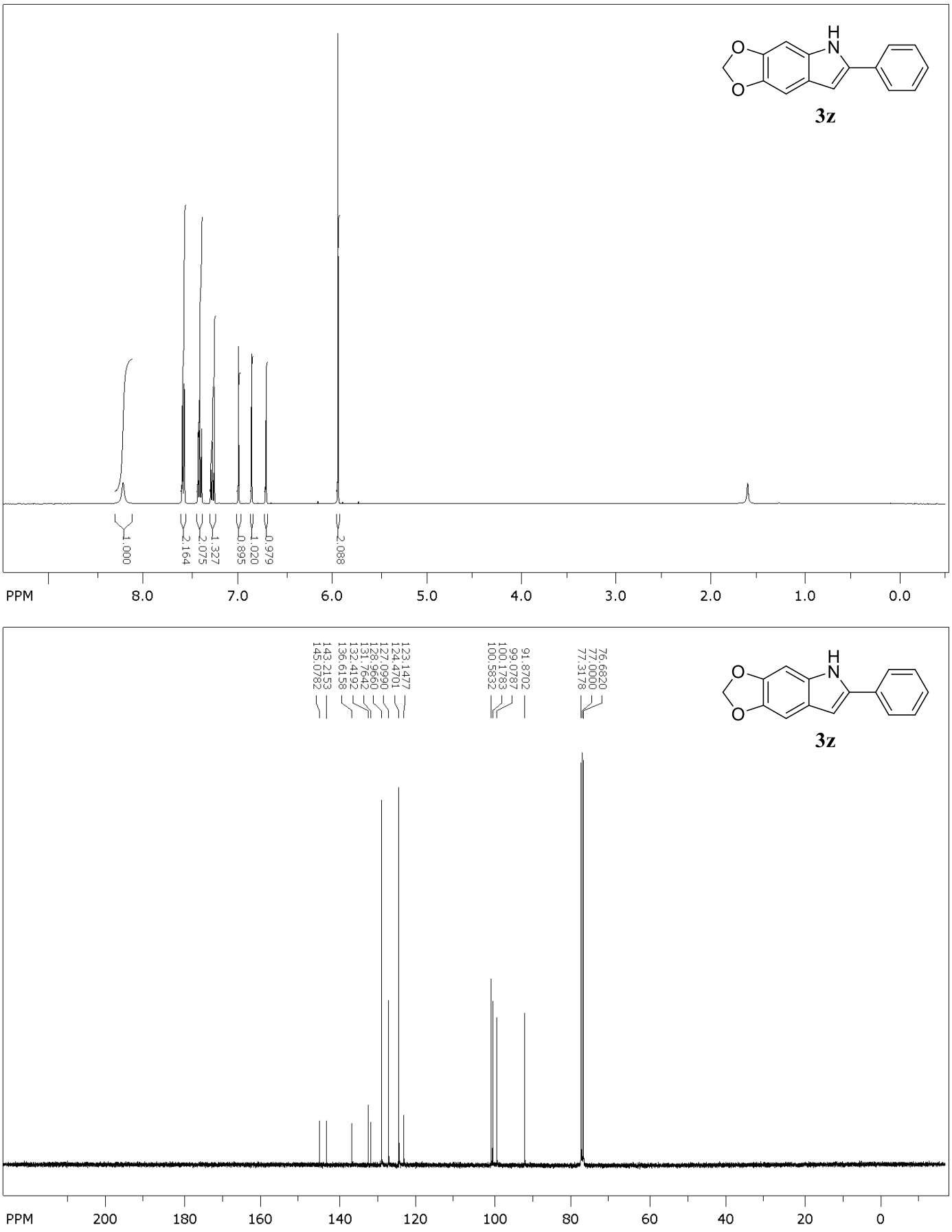


Figure S27. ^{1}H and ^{13}C NMR Spectra of **3z** in $CDCl_3$.

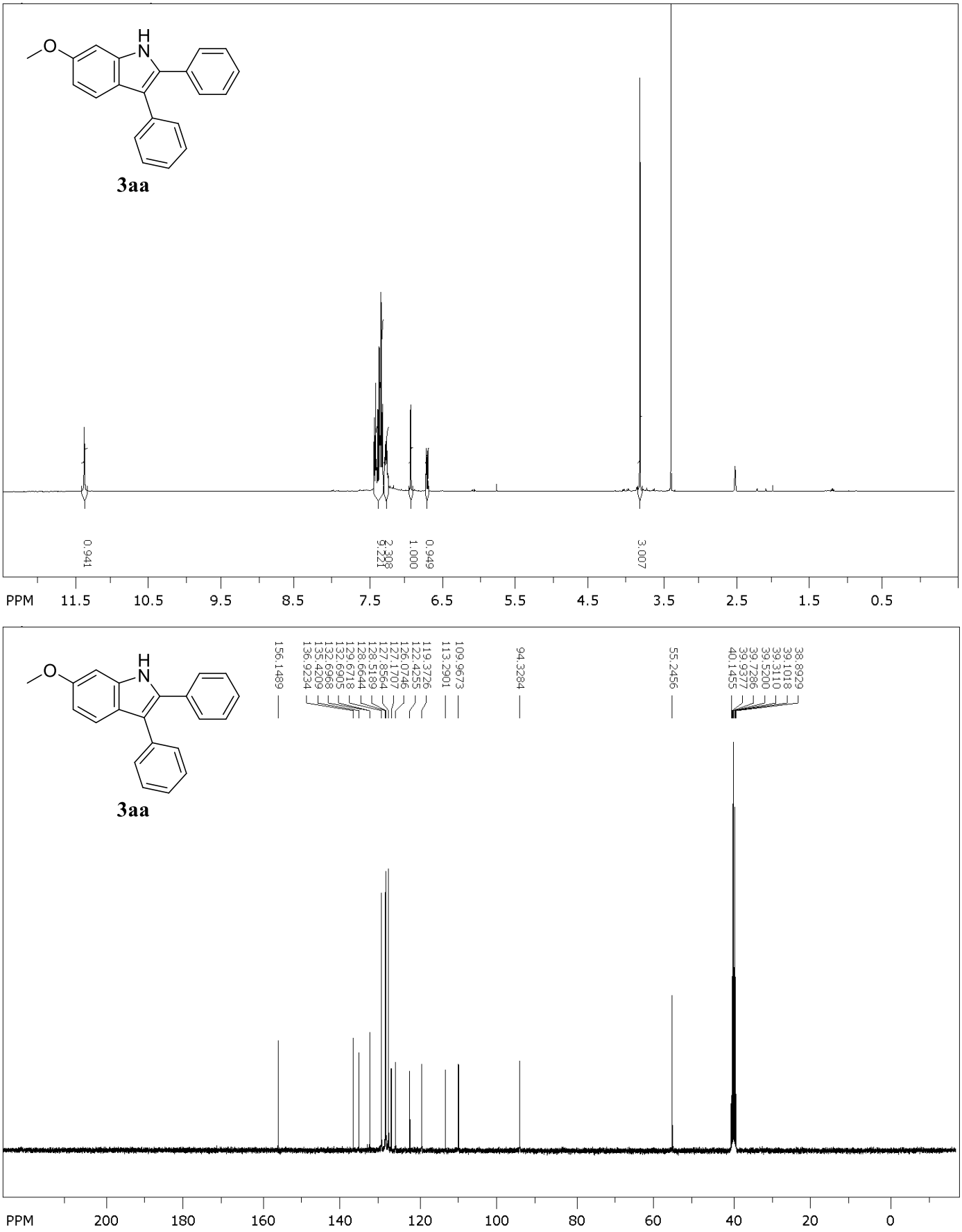


Figure S28. ^{1}H and ^{13}C NMR Spectra of **3aa** in DMSO-d_6.

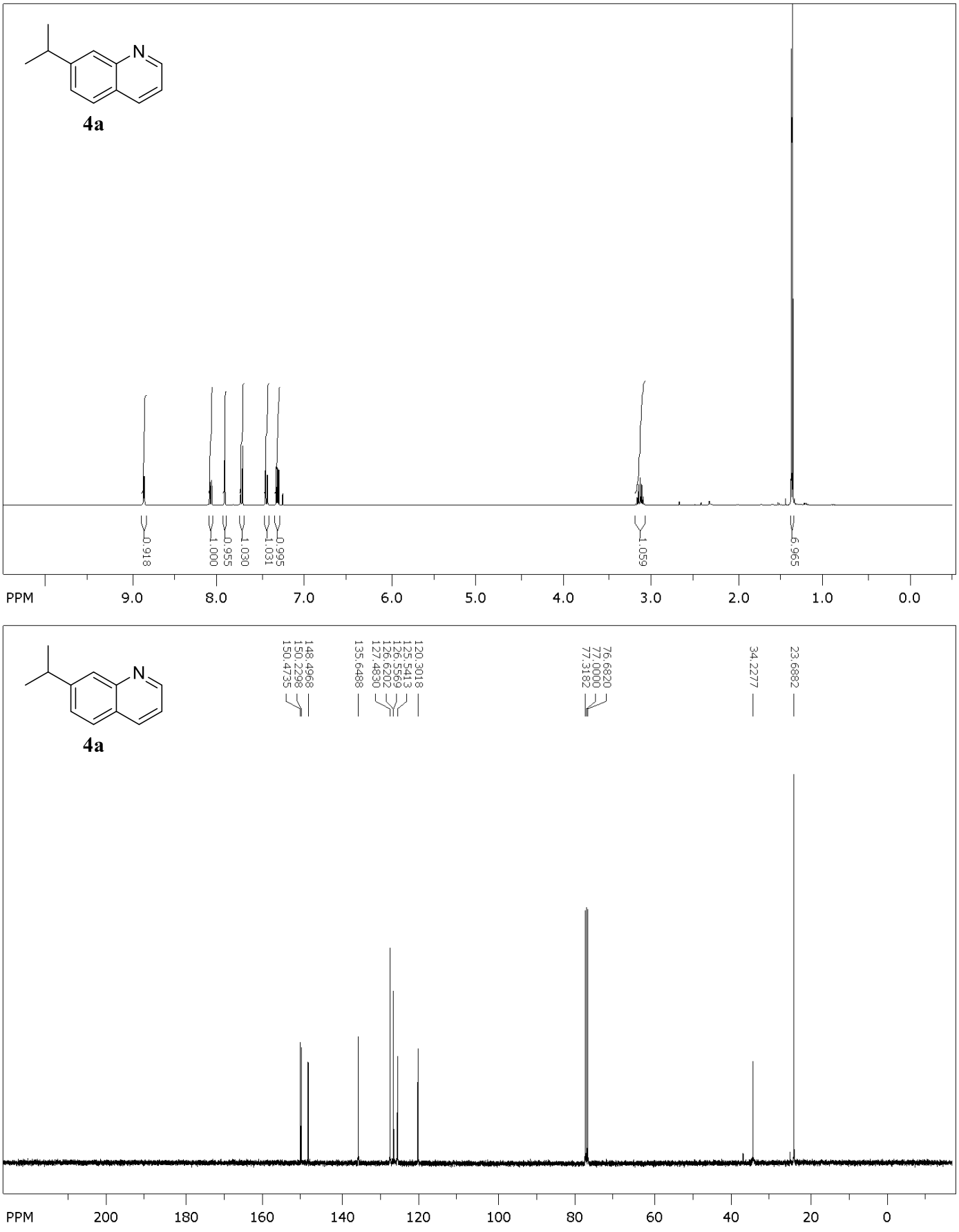


Figure S29. ^{1}H and ^{13}C NMR Spectra of **4a** in $CDCl_3$.

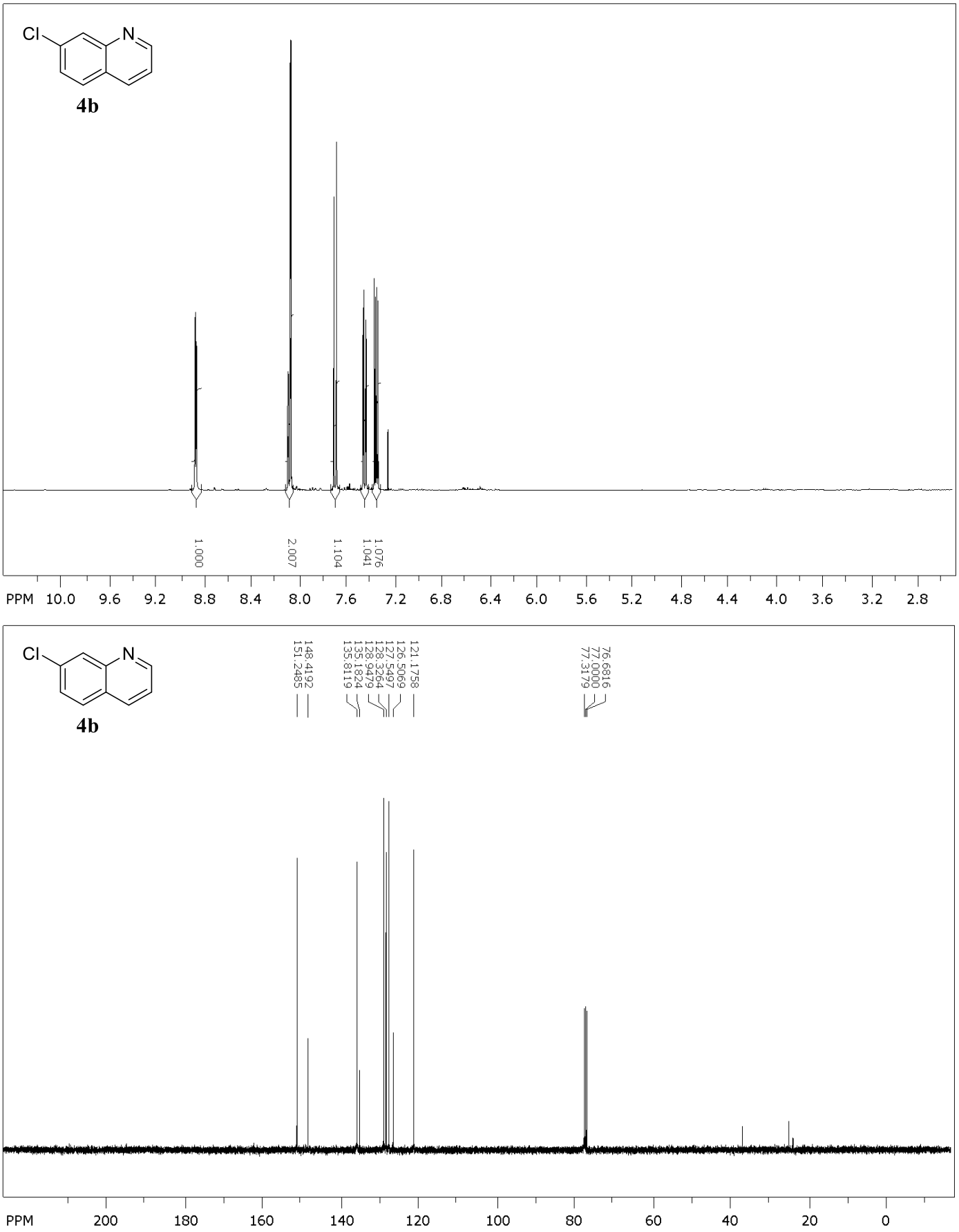
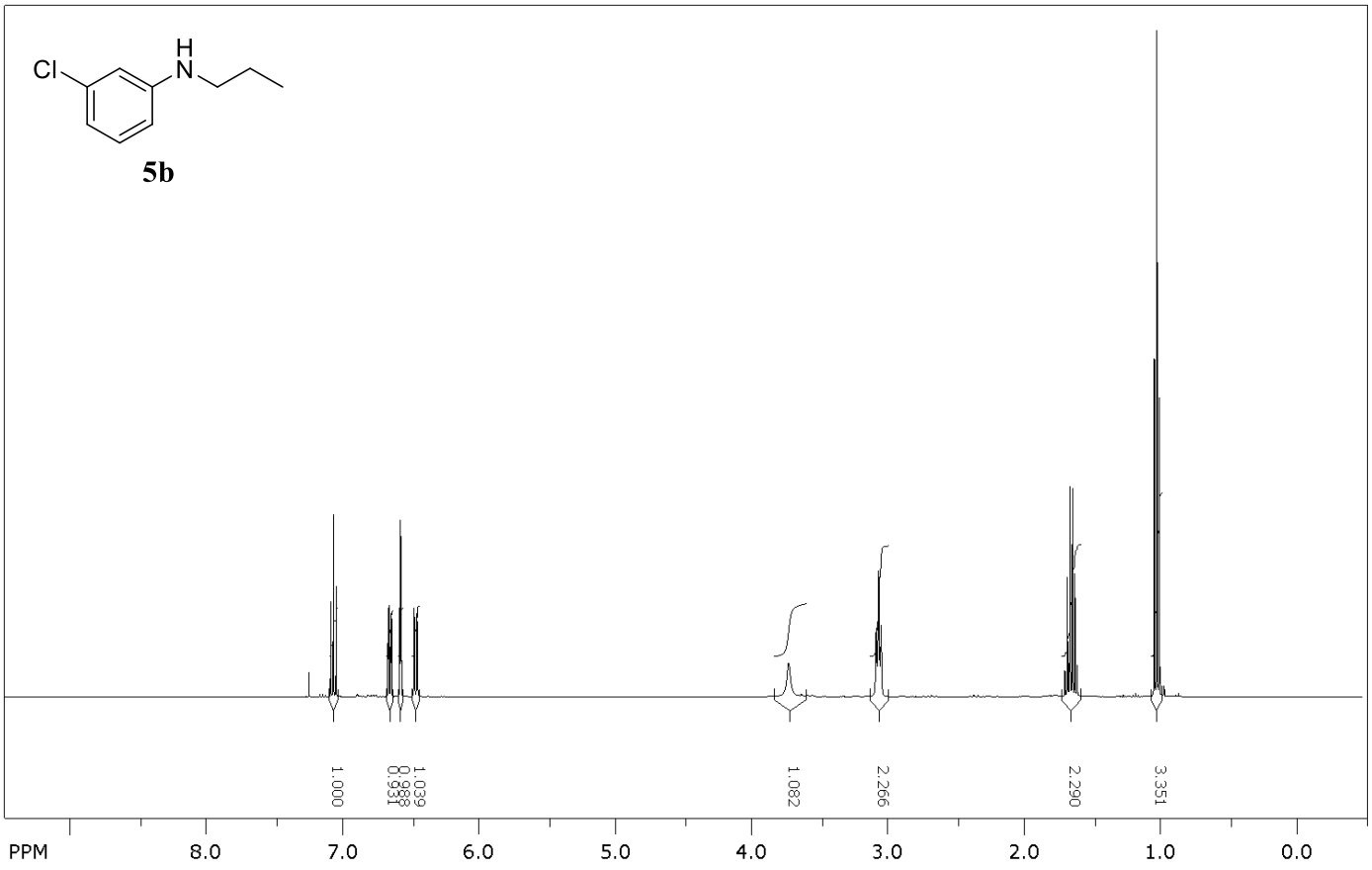


Figure S30. ^{1}H and ^{13}C NMR Spectra of **4b** in $CDCl_3$.



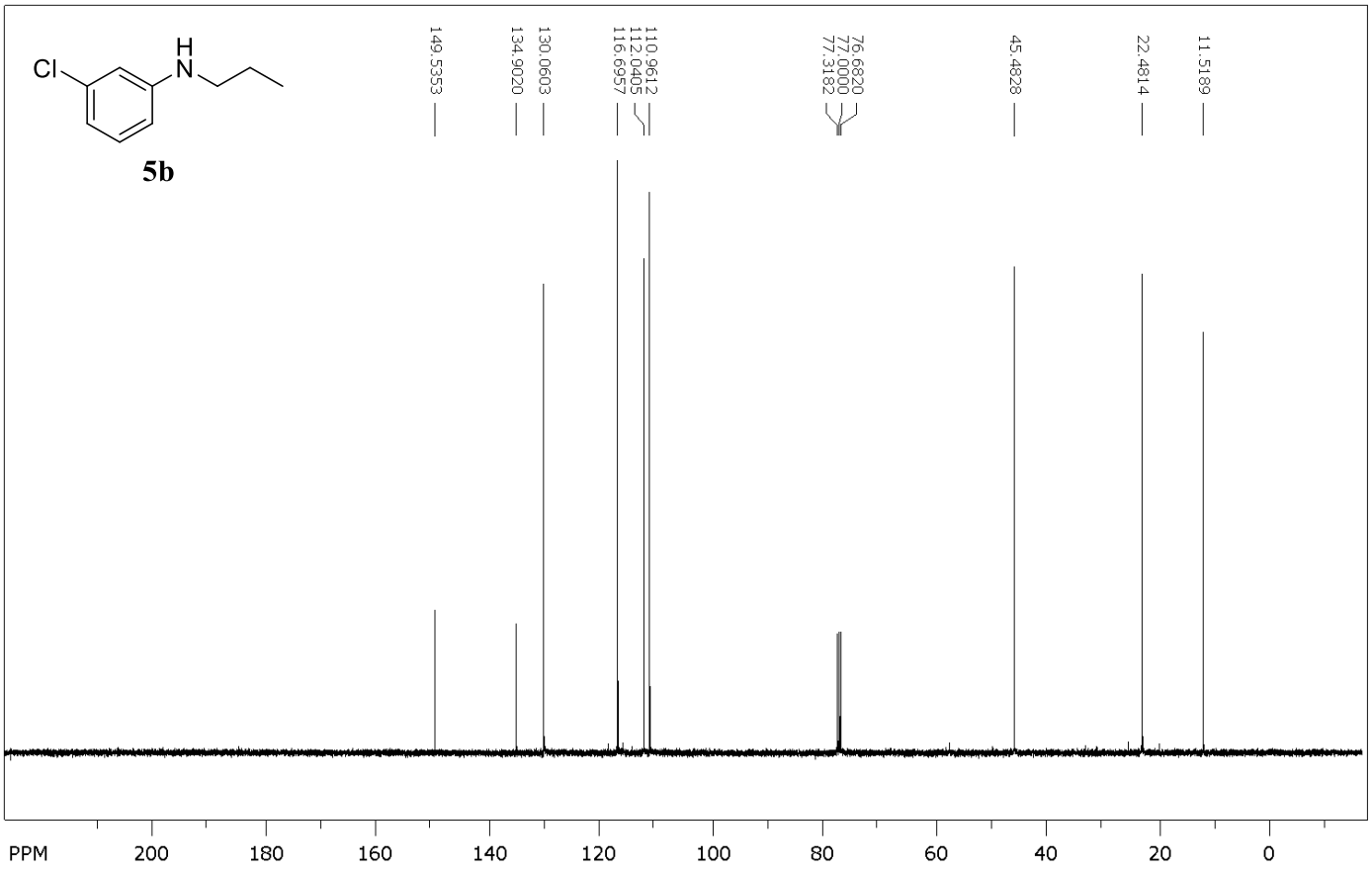


Figure S31. ^{1}H and ^{13}C NMR Spectra of **5b** in $CDCl_3$.

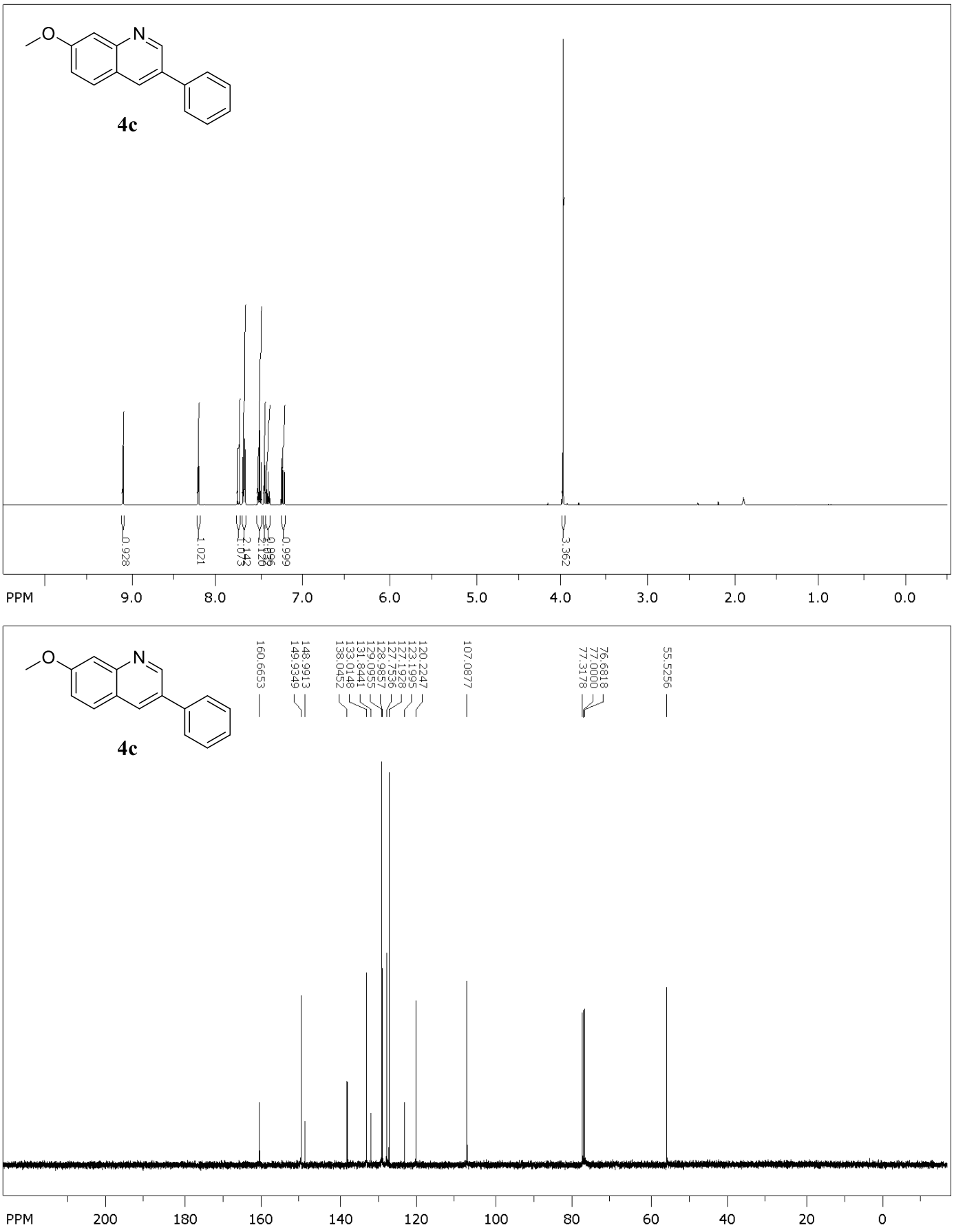


Figure S32. ^{1}H and ^{13}C NMR Spectra of **4c** in $CDCl_3$.

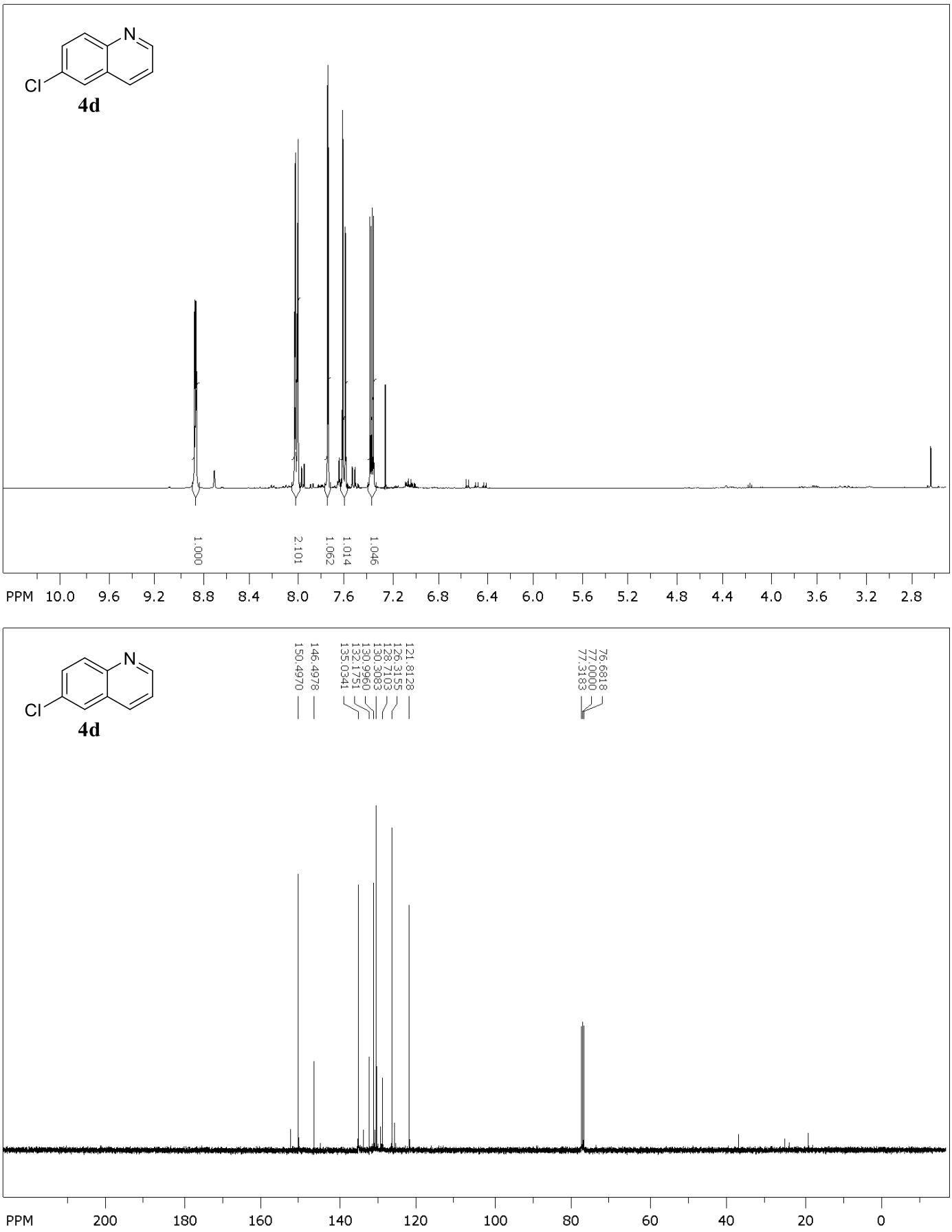


Figure S33. ^{1}H and ^{13}C NMR Spectra of **4d** in $CDCl_3$.

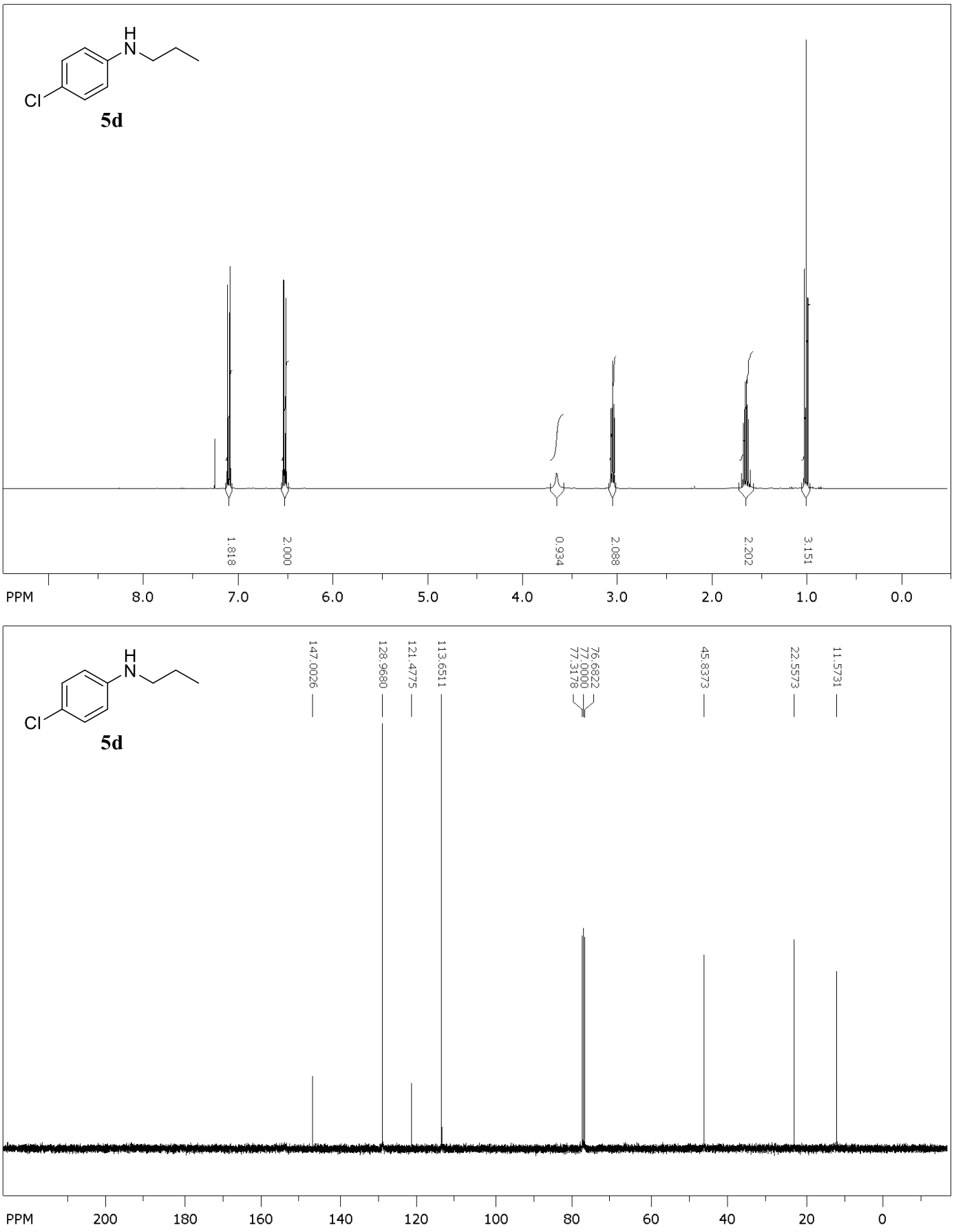


Figure S34. ^{1}H and ^{13}C NMR Spectra of **5d** in $CDCl_3$.

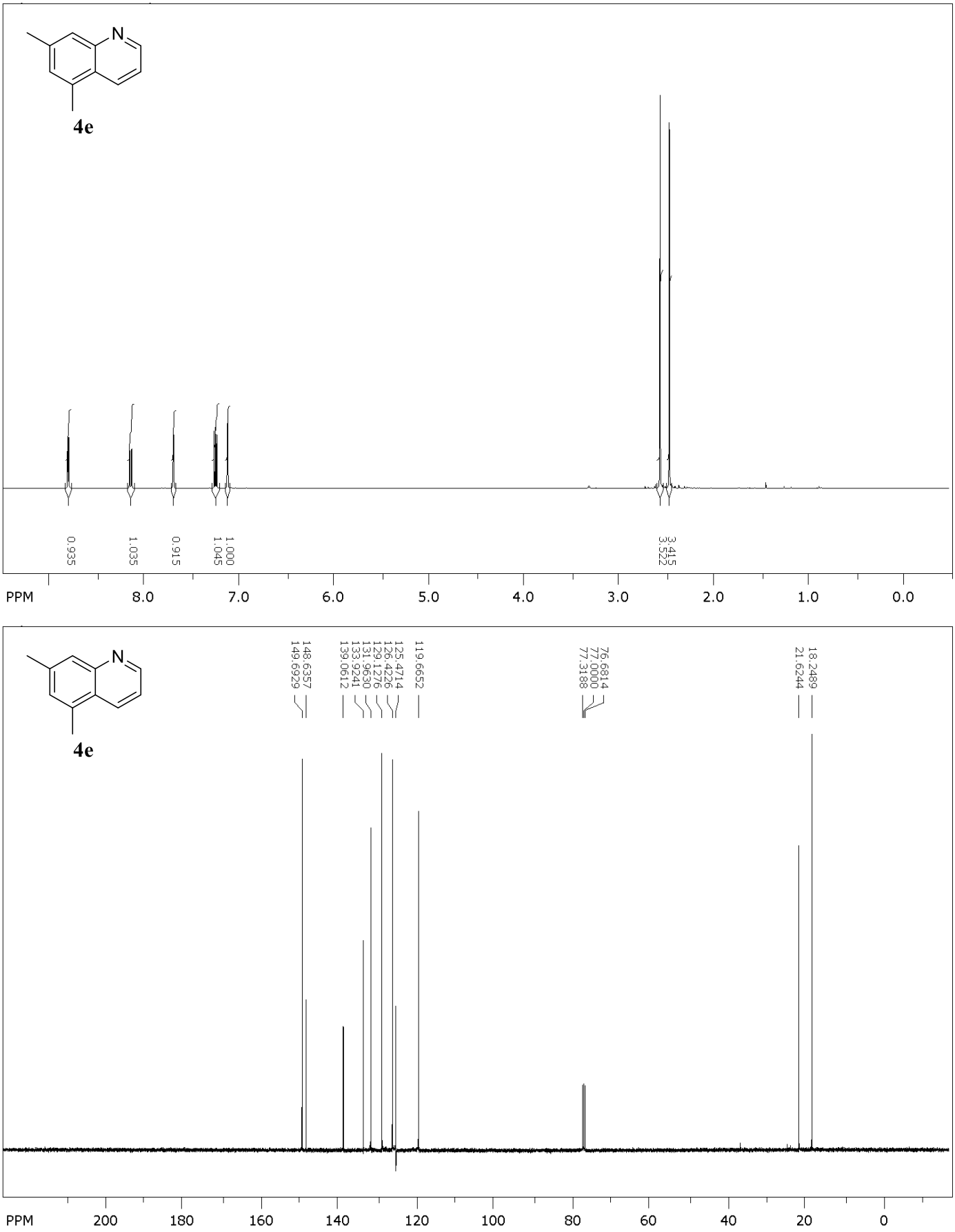


Figure S35. ^{1}H and ^{13}C NMR Spectra of **4e** in $CDCl_3$.

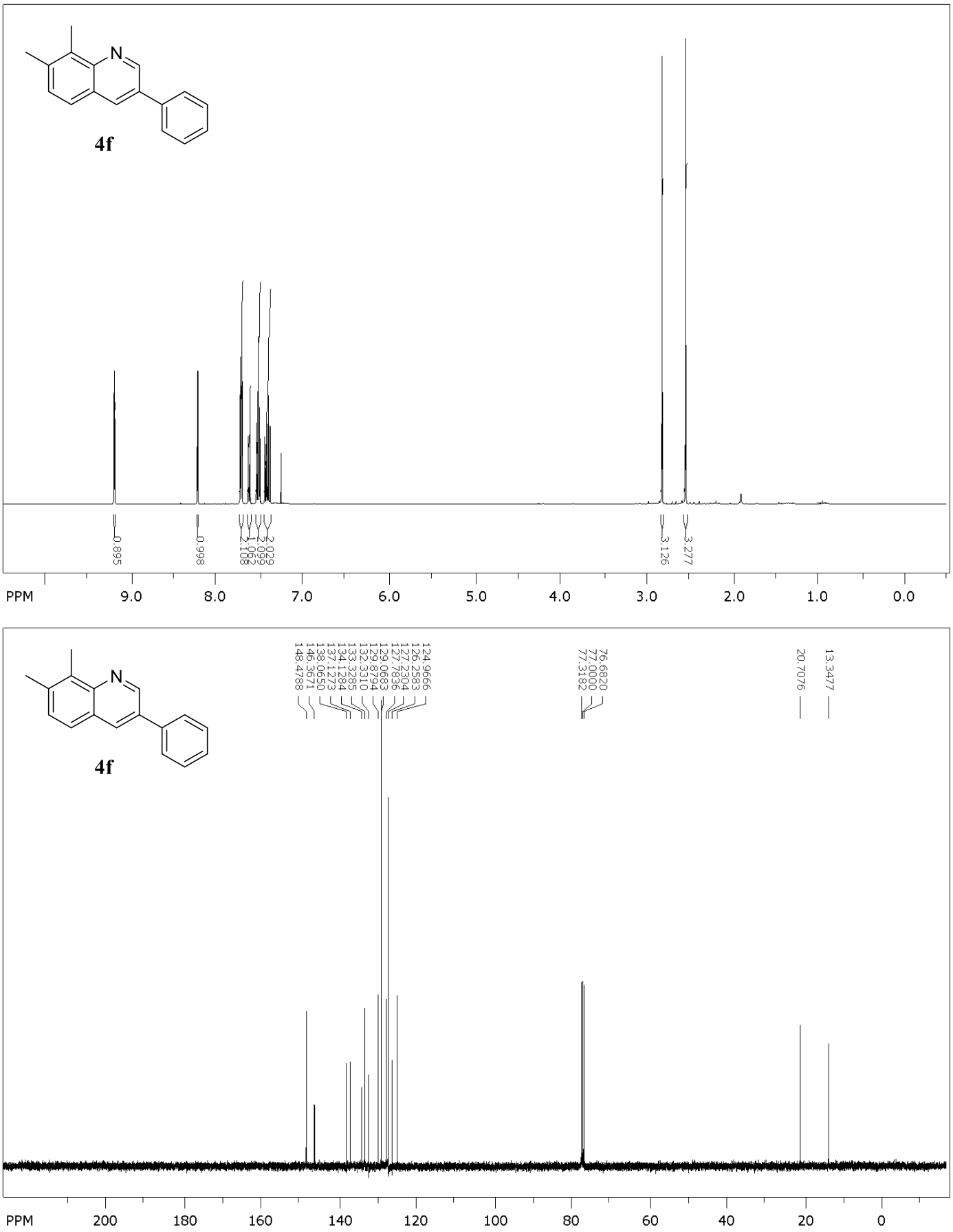


Figure S36. ^{1}H and ^{13}C NMR Spectra of **4f** in $CDCl_3$.

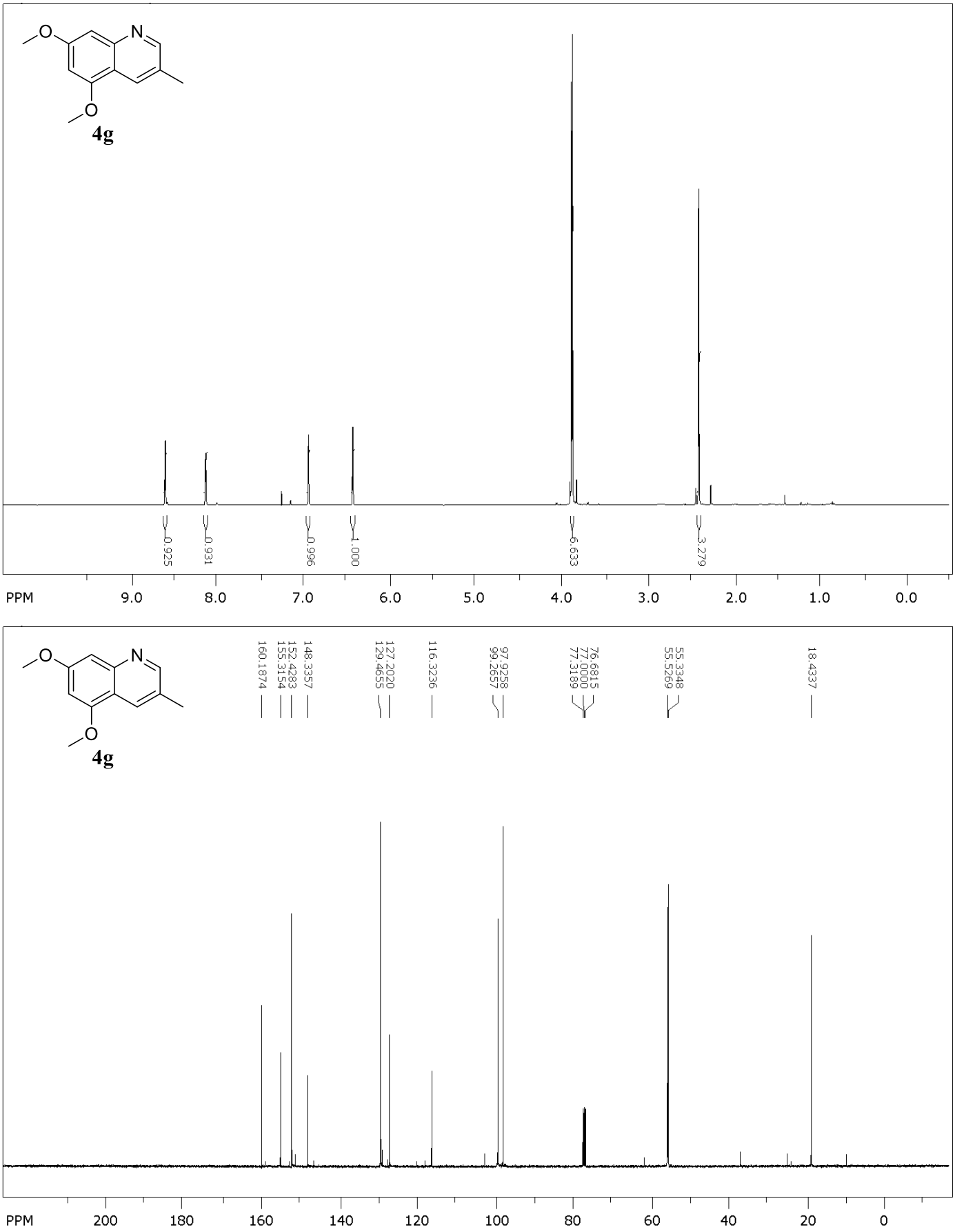


Figure S37. ^{1}H and ^{13}C NMR Spectra of **4g** in $CDCl_3$.

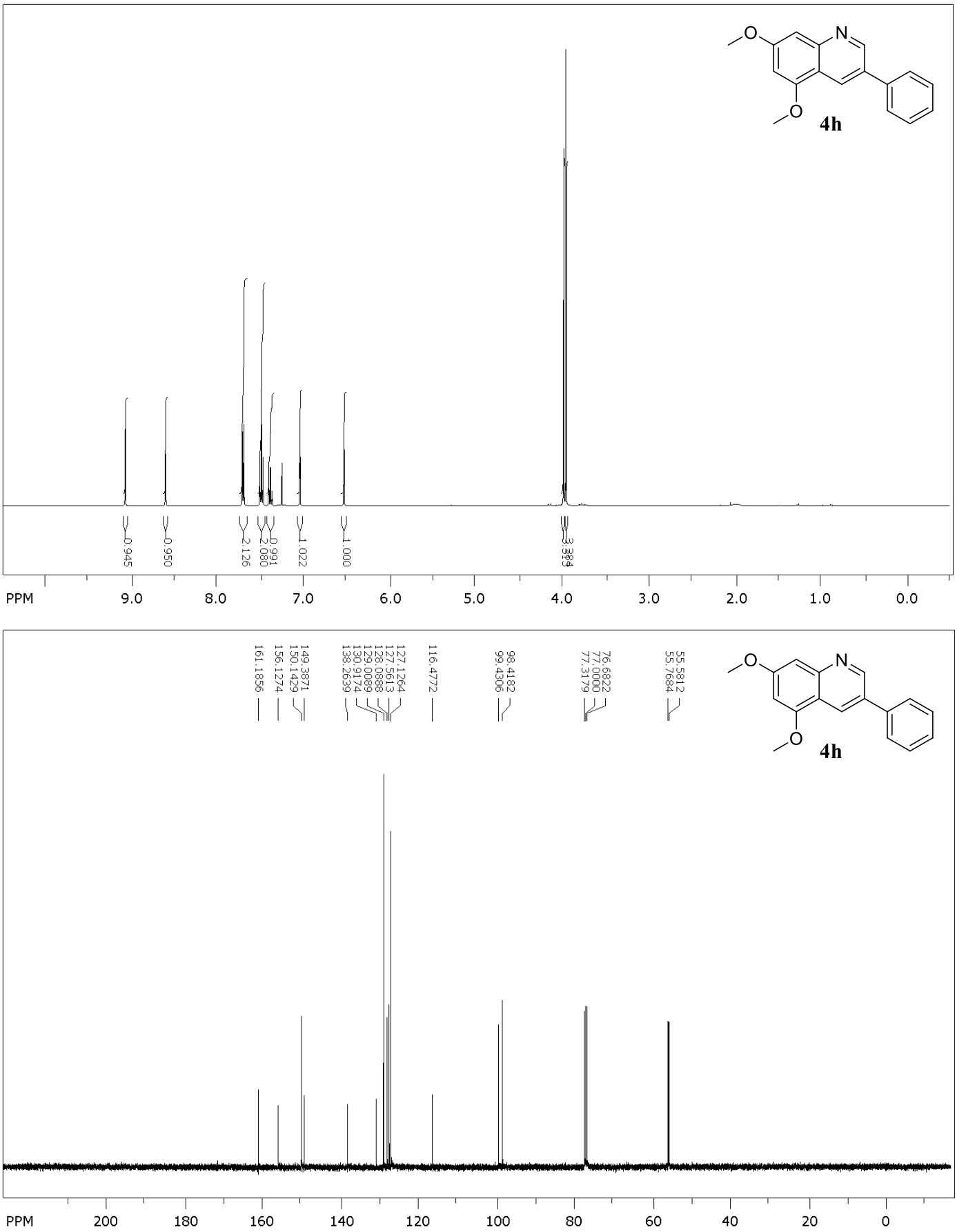
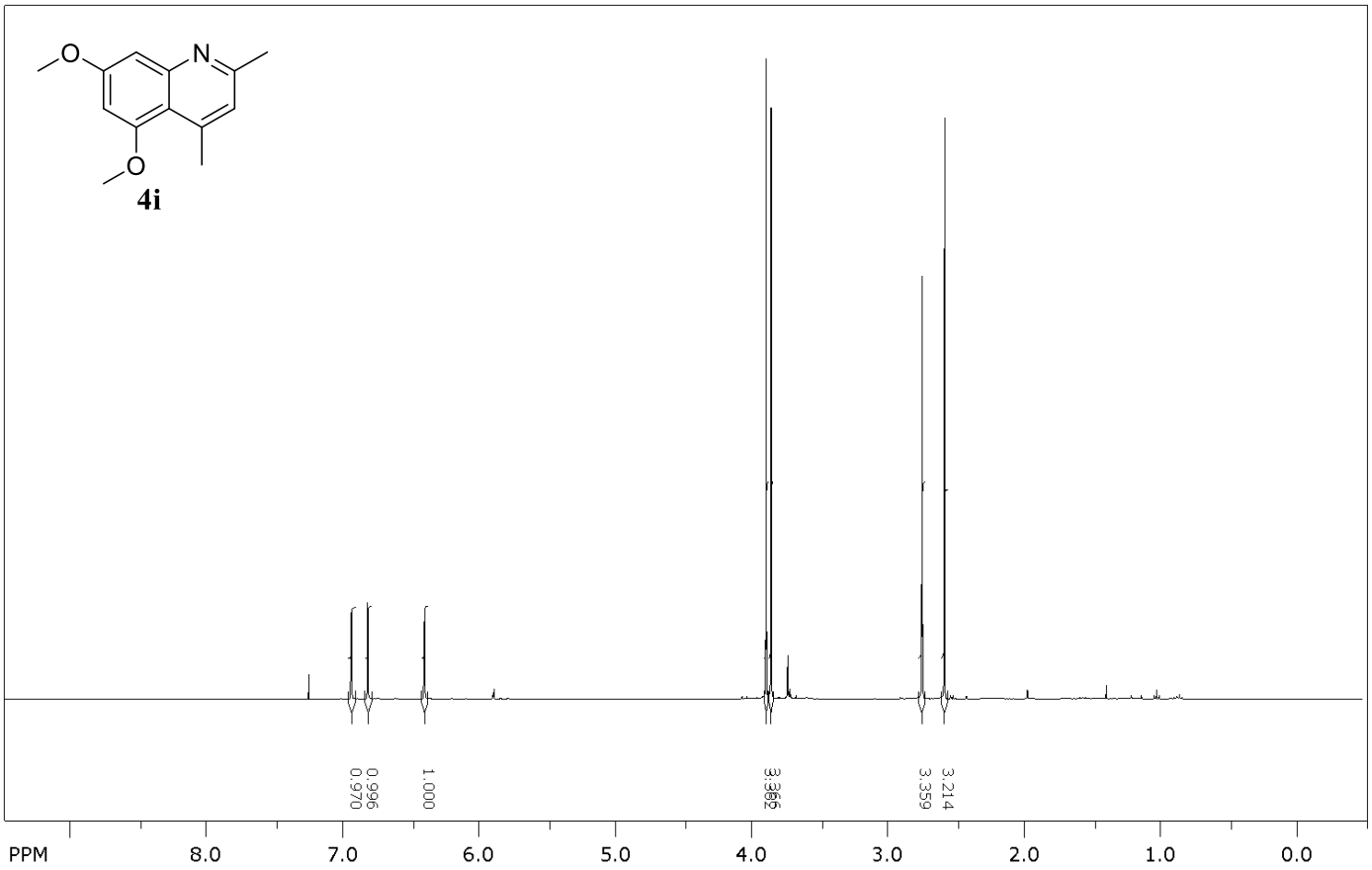


Figure S38. ^{1}H and ^{13}C NMR Spectra of **4h** in $CDCl_3$.



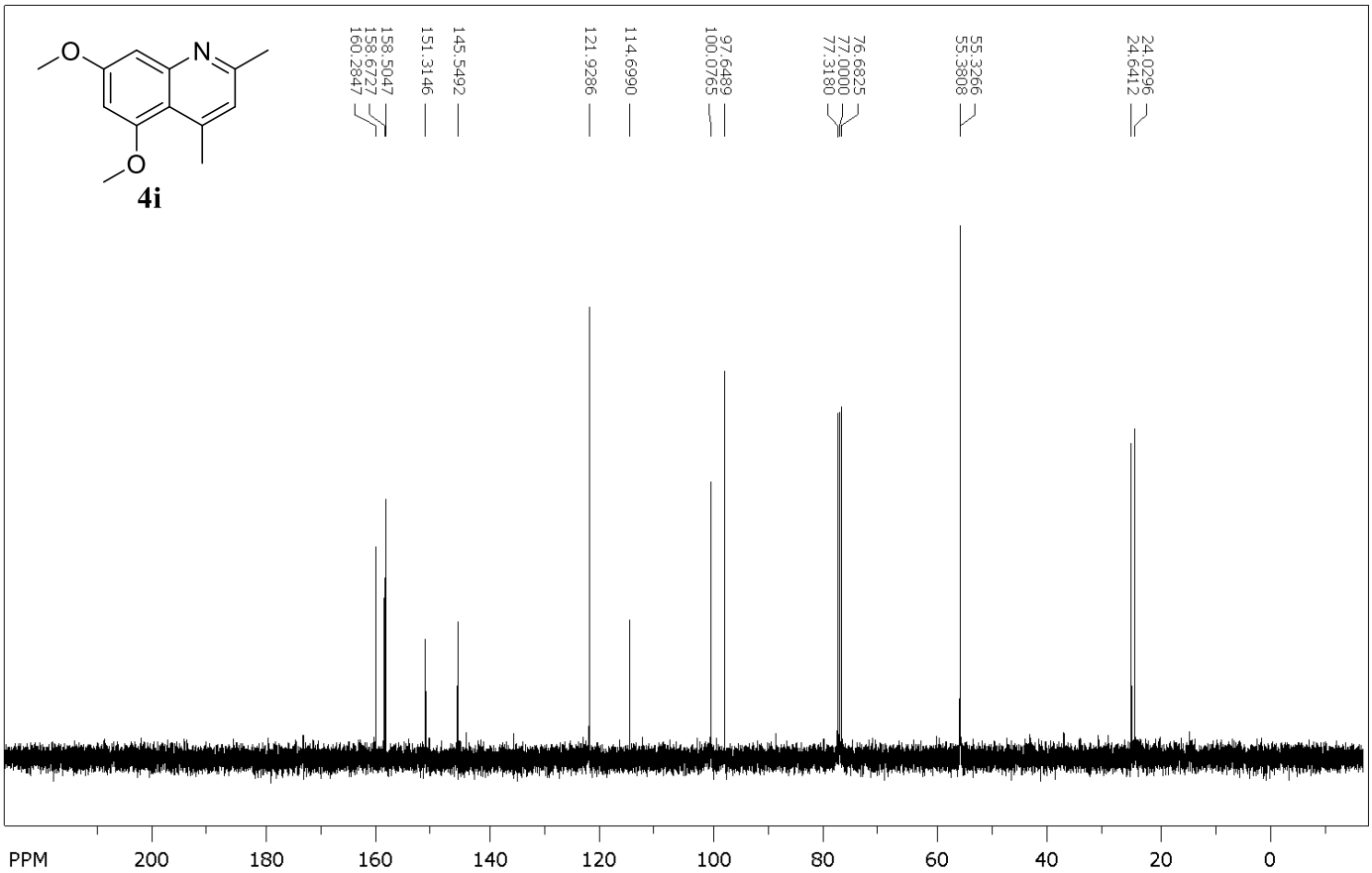


Figure S39. ^{1}H and ^{13}C NMR Spectra of **4i** in $CDCl_3$.

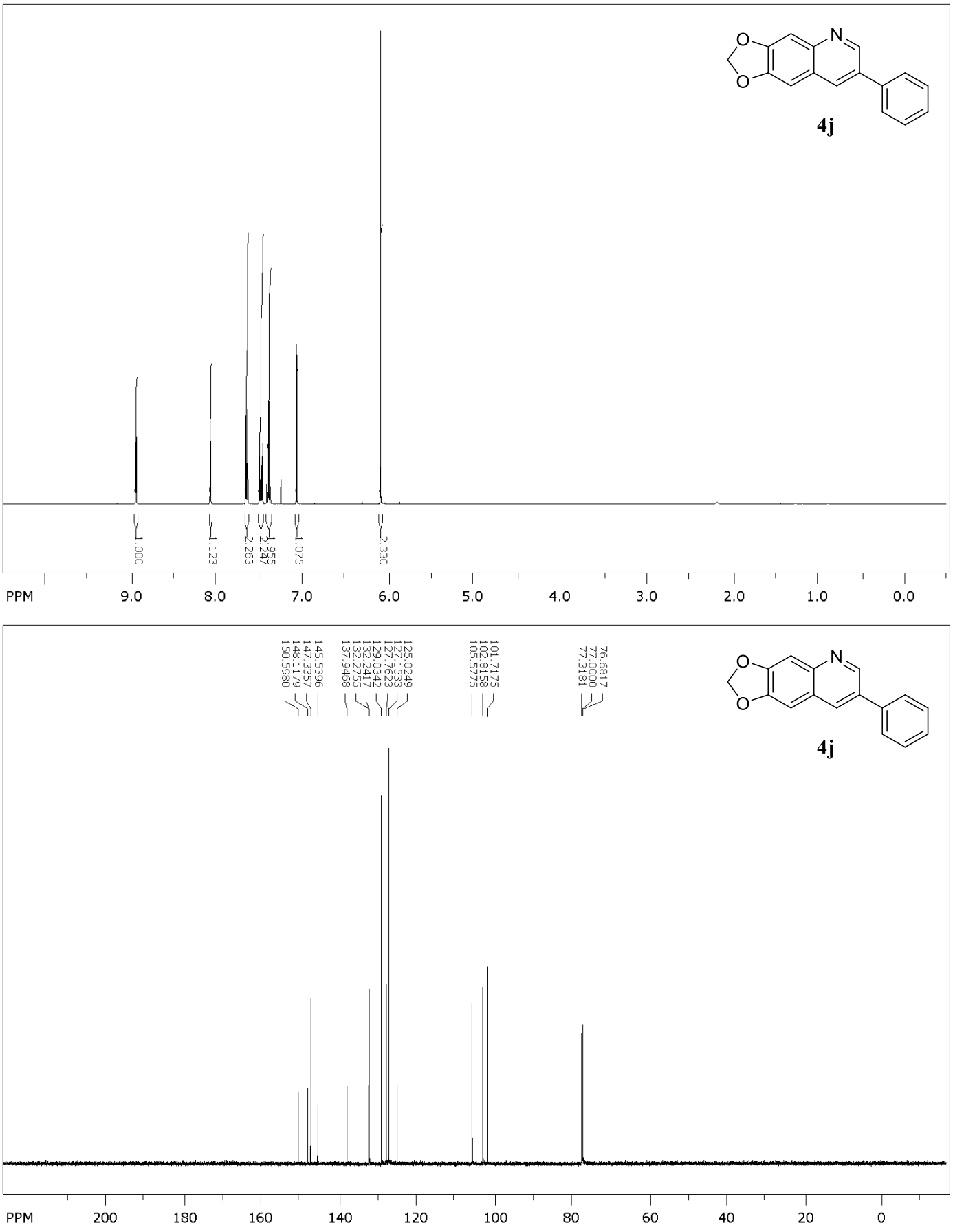


Figure S40. ^{1}H and ^{13}C NMR Spectra of **4j** in $CDCl_3$.

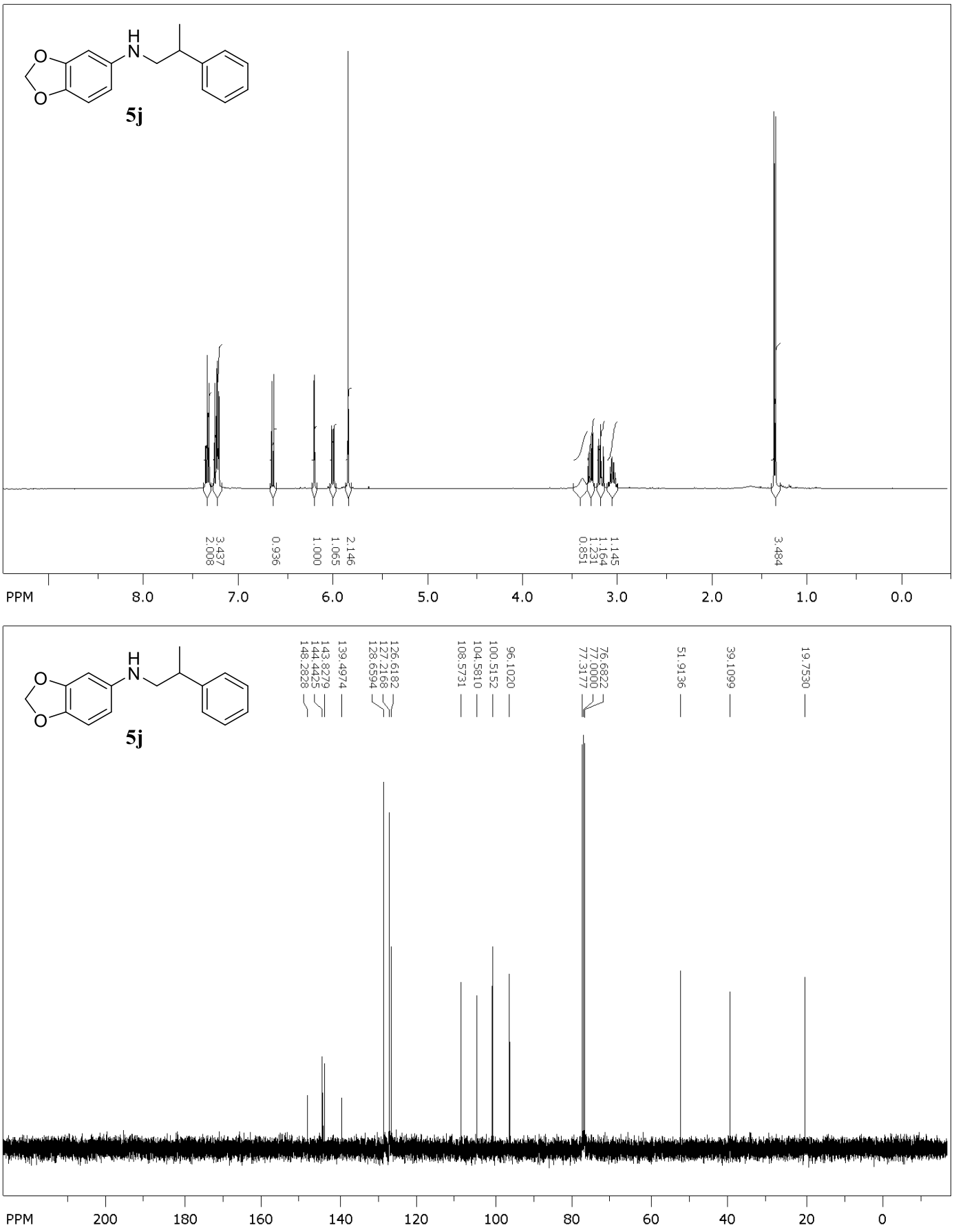


Figure S41. ^{1}H and ^{13}C NMR Spectra of **5j** in $CDCl_3$.

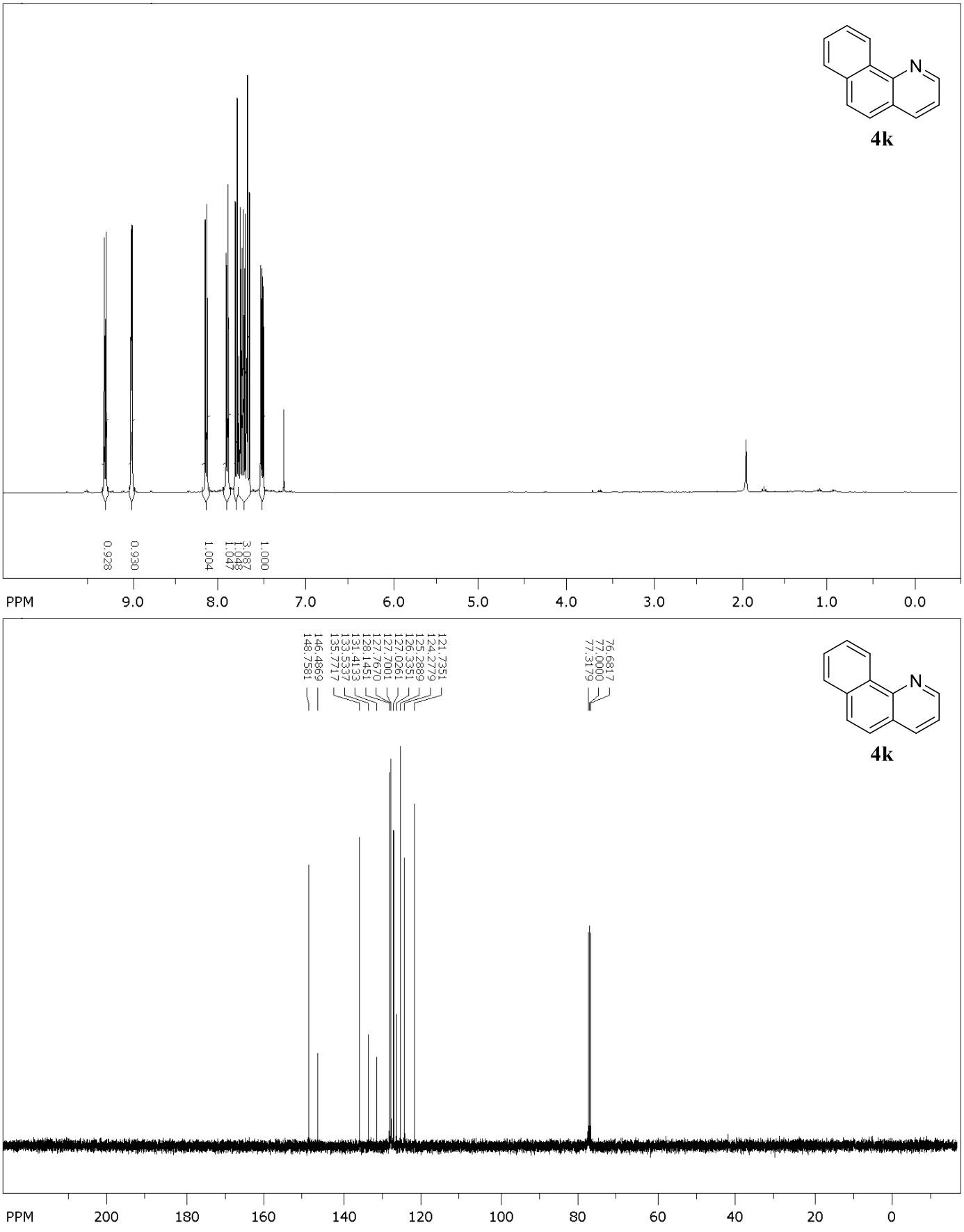


Figure S42. ^{1}H and ^{13}C NMR Spectra of **4k** in $CDCl_3$.

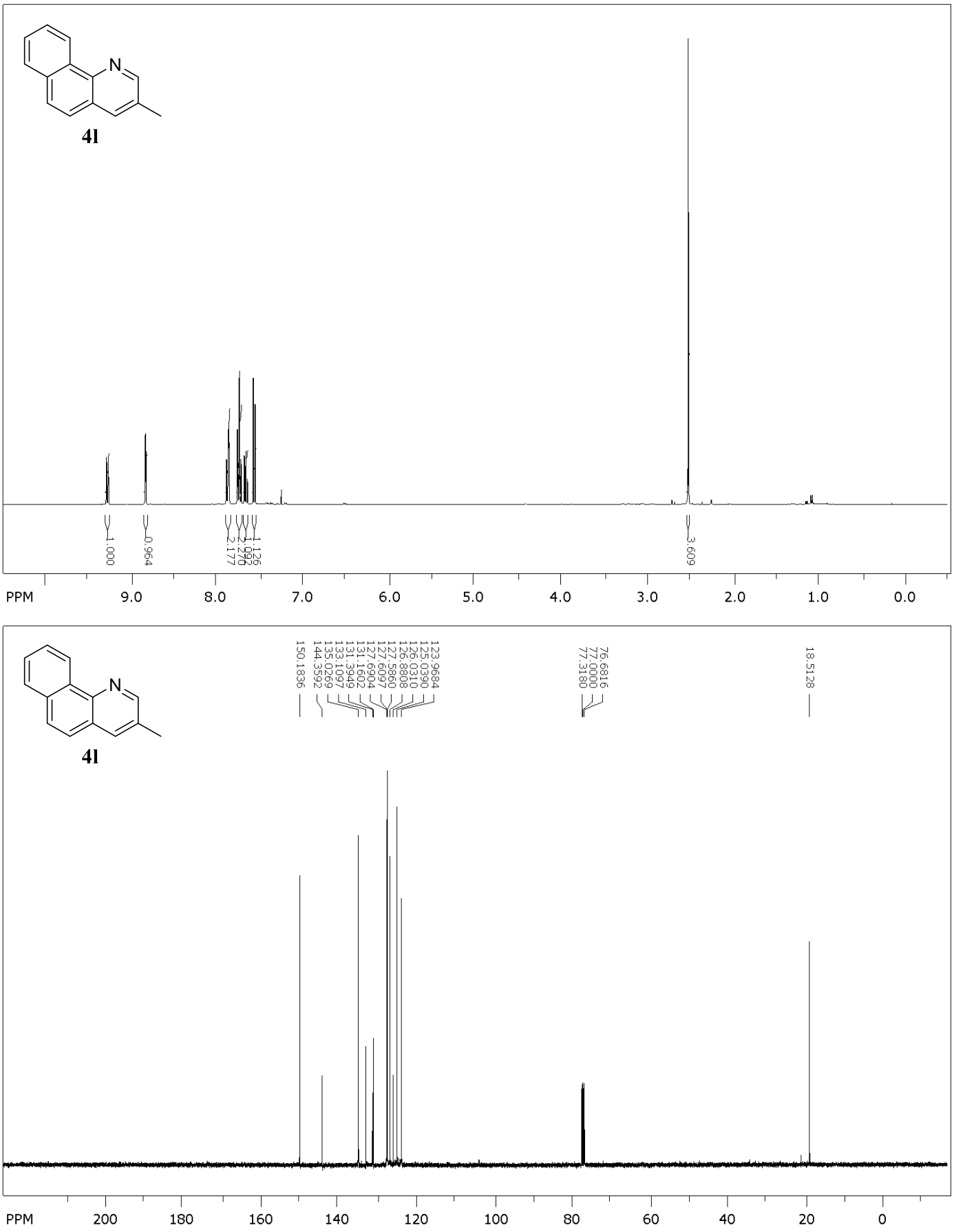
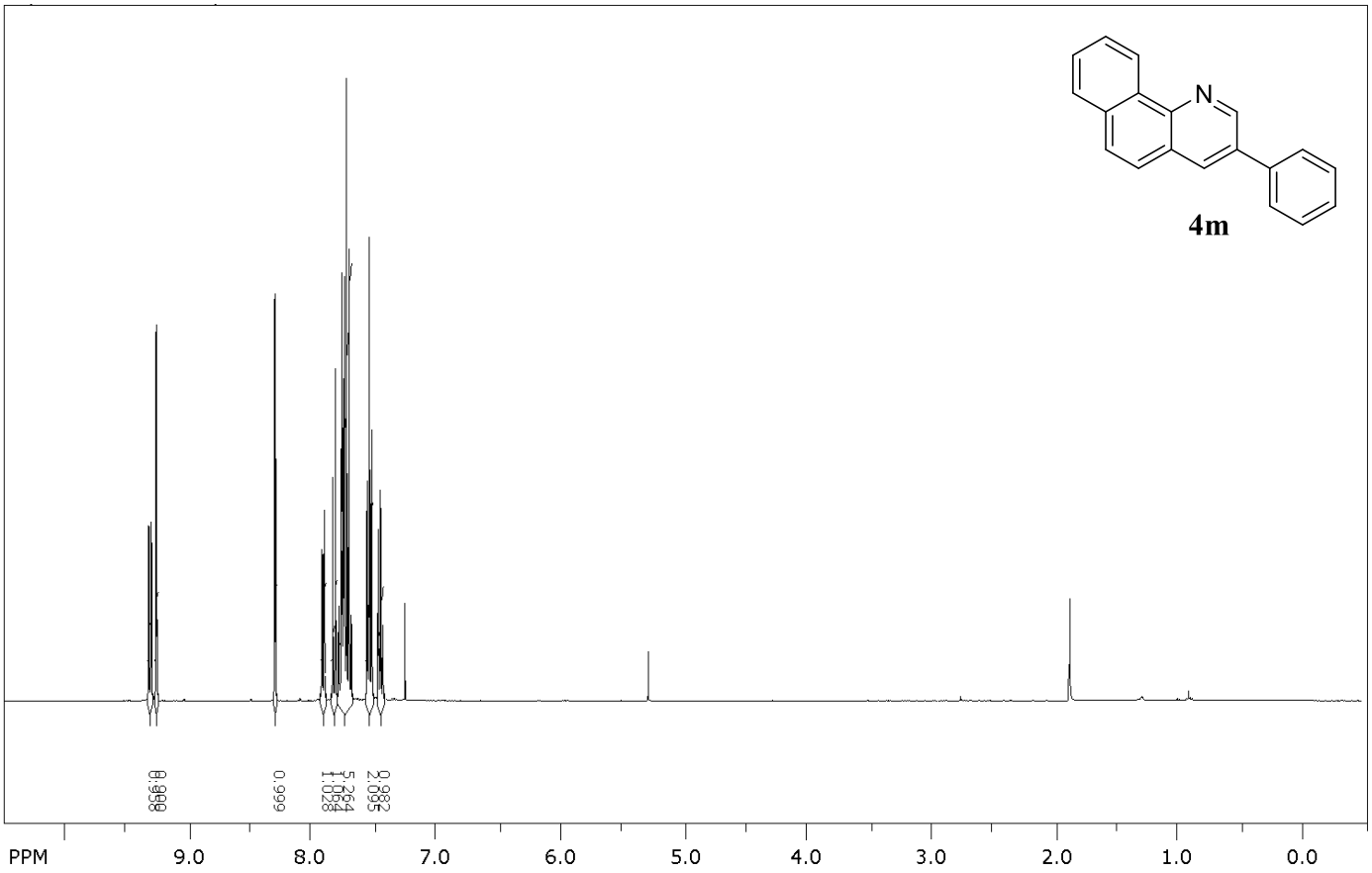


Figure S43. ^{1}H and ^{13}C NMR Spectra of **4l** in $CDCl_3$.



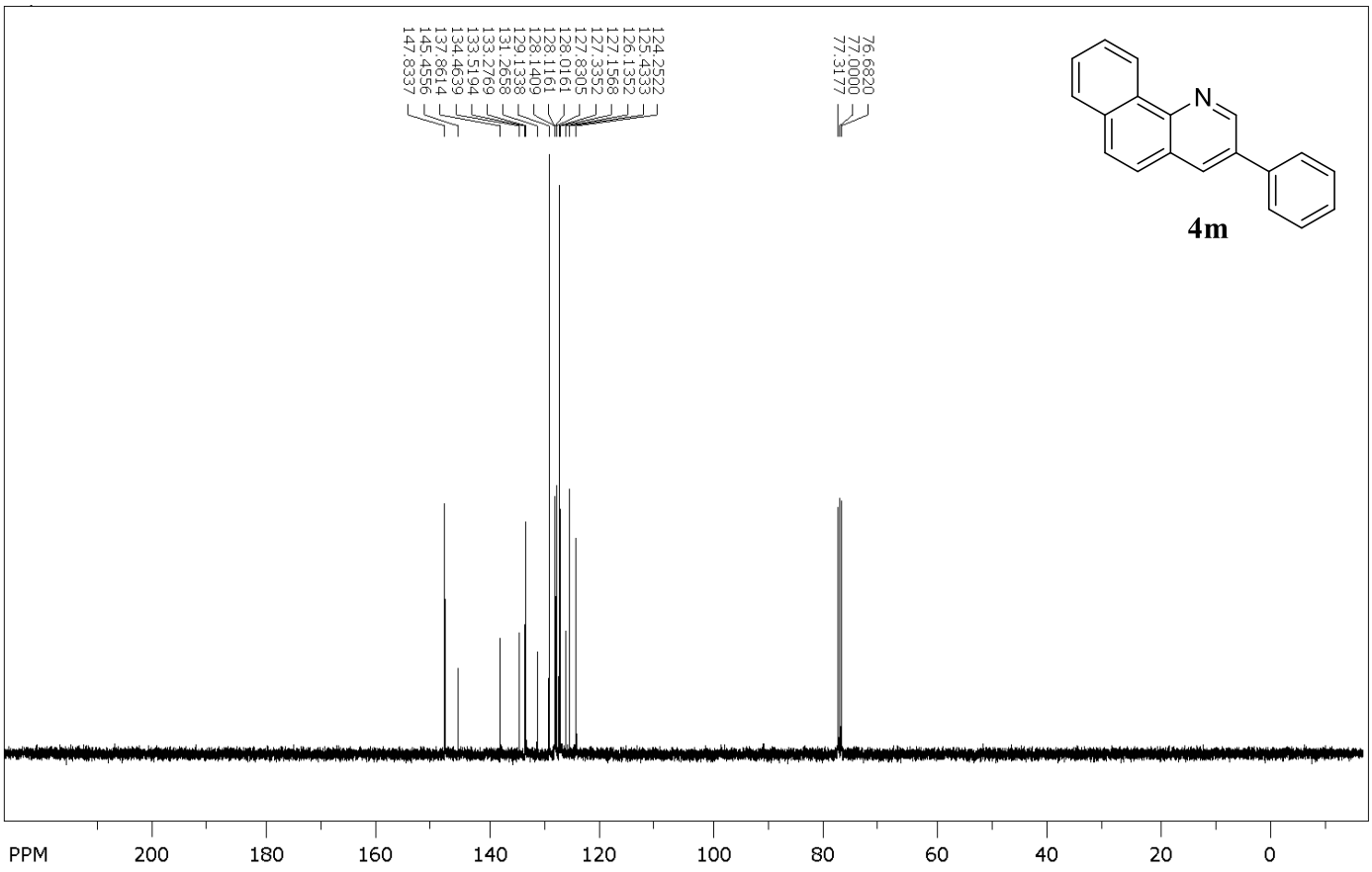


Figure S44. ^{1}H and ^{13}C NMR Spectra of **4m** in $CDCl_3$.

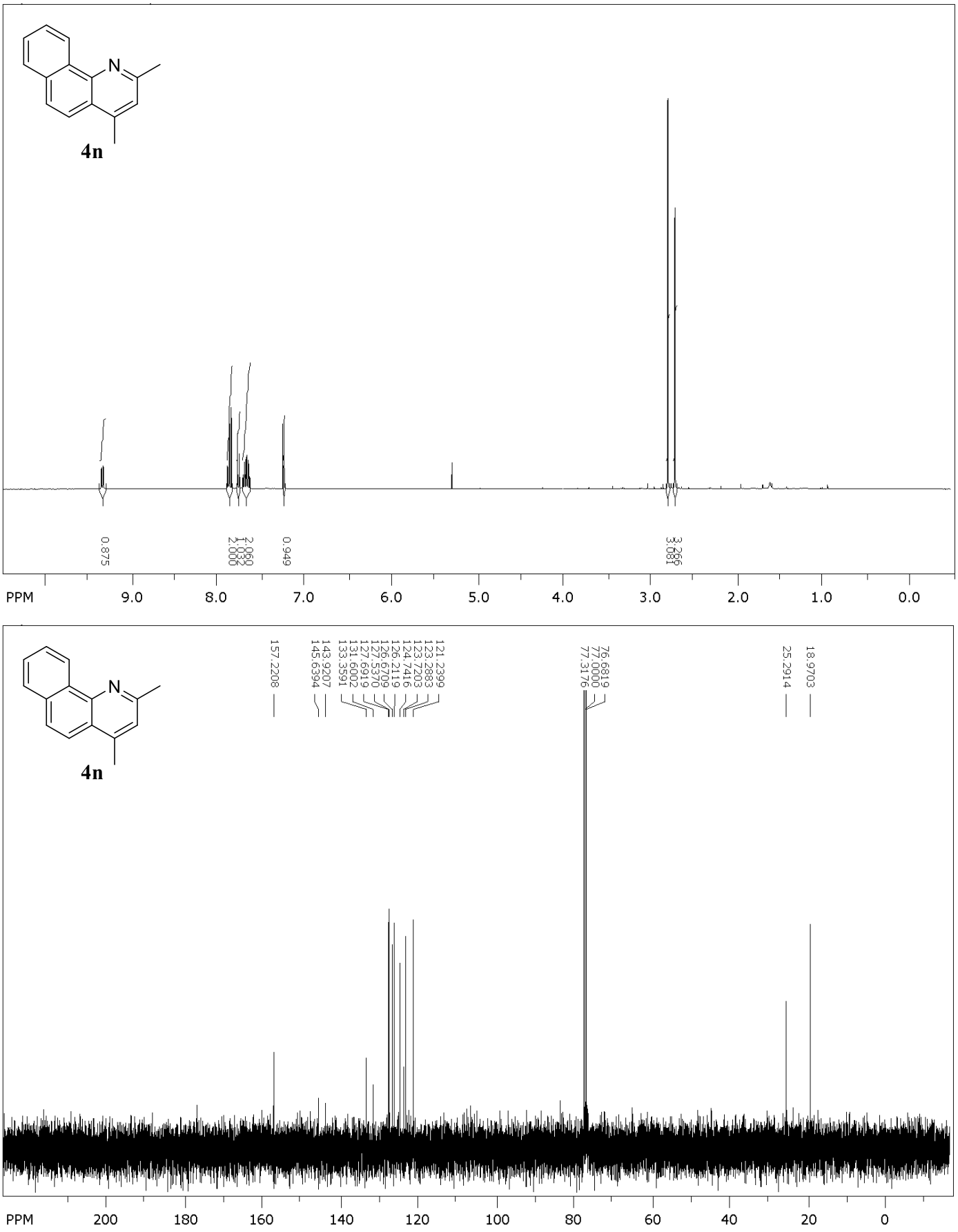


Figure S45. ^{1}H and ^{13}C NMR Spectra of **4n** in $CDCl_3$.