

Supporting Information

for

PdCl₂(dppf)-Catalyzed *in situ* Coupling of 2-Hydroxypyridines with Aryl Boronic Acids Mediated by PyBroP and the Application for one-pot Chemo- and Regioselective Construction of two Distinct Aryl-Aryl Bonds

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Table of Contents:

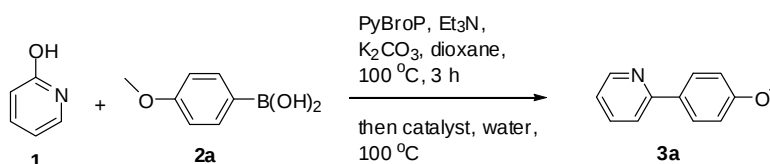
General information and reaction procedure	S2
Reaction condition optimization, Tables, and Figures.....	S3
Product characterization.....	S6
References.....	S17
Spectra of coupling products.....	S18

Experimental Section

General Information

All reactions were carried out under N₂ atmosphere. The solvents were dried over Zeolite. Palladium and nickel catalysts were purchased from J&K Chemical Ltd or Alfa Aesar. Unless noted, the ¹H-NMR spectra were recorded at 400 or 600 MHz in CDCl₃ or DMSO-d₆, and the ¹³C-NMR spectra were recorded at 100 or 125 MHz in CDCl₃ or DMSO-d₆ with TMS as internal standard. All shifts were given in ppm. All coupling constants (*J* values) were reported in Hertz (Hz). High resolution mass was measured by using IonSpec 7.0T MALDI-FTICRMs. Column chromatography was performed on silica gel 100 mesh. UV/VIS spectra were recorded on UV-visible spectrophotometer of Shimadzu with Model UV-2550.

General procedure for the one-pot coupling of 2-OH pyridines and boronic acids (taking the reaction of 2-OH pyridine **1** and 4-methoxyphenylboronic acid **2a** as a representative):



A schlenk tube charged with 2-OH pyridine (0.5 mmol, 1.0 equiv), PyBroP (0.75 mmol, 1.5 equiv), K₂CO₃ (1.5 mmol 3 equiv), and a magnetic bar was evacuated under high vacuum and backfilled with N₂ for three times. Triethylamine (1.5 mmol, 3 equiv) and dried dioxane (6 mL) were injected under N₂ *via* syringe. The reaction mixture was stirred at 100 °C for 3 h. The reaction vessel was then recharged with 4-Methoxyphenylboronic acid (1.0 mol, 2.0 equiv), PdCl₂(dppf) (0.025 mmol, 5 mol %), and H₂O (300 µl). The heterogeneous mixture was stirred at 100 °C until the pyridine phosphonium salt had disappeared as monitored by TLC. The reaction mixture was diluted with CH₂Cl₂ (*ca.* 30 mL) and washed with water (20 mL × 3). The organic layer was dried over anhydrous Na₂SO₄, filtered, concentrated, and purified by chromatography on silica gel (hexane/EtOAc = 10/1, v/v) to give 87.9 mg (95 %) of 2-(4-methoxyphenyl)pyridine as a white solid.

Table S1. One-pot construction of two distinct biaryls from two intermolecular phenolic OHs.^a

Entry	2-OH pyridines vs. common phenol	(HO) ₂ B-Ar ₁ vs. (HO) ₂ B-Ar ₂	Products	Yield ^b
1				96%
				90% ^c
2				96%
				77%
3				82% ^d
				70%
4				72%
				74%

[a] Reaction conditions: 2-OH quinoline **3** or 2-OH pyridine **1** (0.5 mmol), phenol **6** (0.5 mmol), PyBroP (1.5 mmol), Et₃N (3.0 mmol), K₃PO₄ (4.0 mmol) in dioxane (6 mL) at 100 °C for 3 h; then PdCl₂(dppf) (10 mol % relative to **4** or **1**), boronic acid (HO)₂B-Ar₁ (0.75 mmol) at 100 °C for 4 h; then NiCl₂(dppp) (20 mol % relative to phenol **6**), boronic acid (HO)₂B-Ar₂ (1.0 mmol) at 100 °C for 20 h. [b] Isolated yield. [c] Yield was determined by ¹H-NMR due to the contamination of a small amount of inseparable by-product derived from the homocoupling of boronic acid **2f**. [d] The molar amount of boronic acid **2a** was reduced from 0.75 mmol to 0.6 mmol.

Spectroscopies of UV-vis titration:

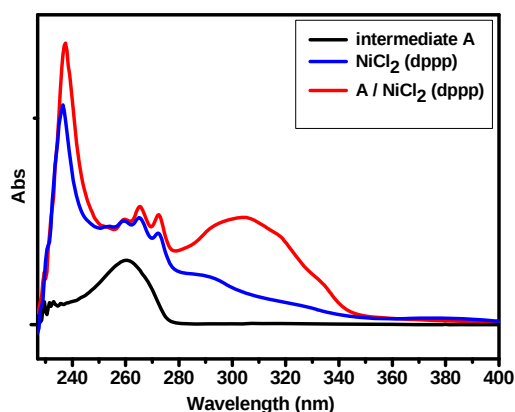


Figure S1. UV-vis spectra of intermediate **A** (black), NiCl₂(dppp) (blue), and the mixture of **A** and NiCl₂(dppp) (red) (*ca.* 10⁻⁶ mol/l in dioxane).

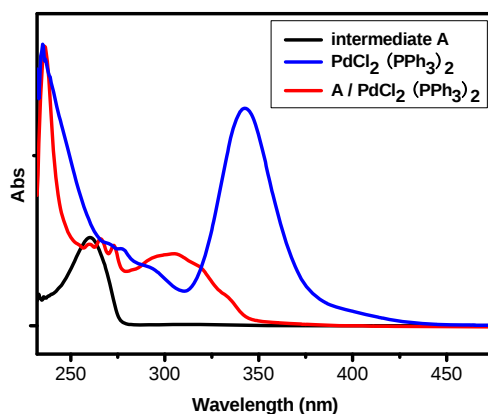


Figure S2. UV-vis spectra of intermediate **A** (black), PdCl₂(PPh₃)₂ (blue), and the mixture of **A** and PdCl₂(PPh₃)₂ after heating in dioxane (*ca.* 10⁻⁶ mol/L in dioxane)

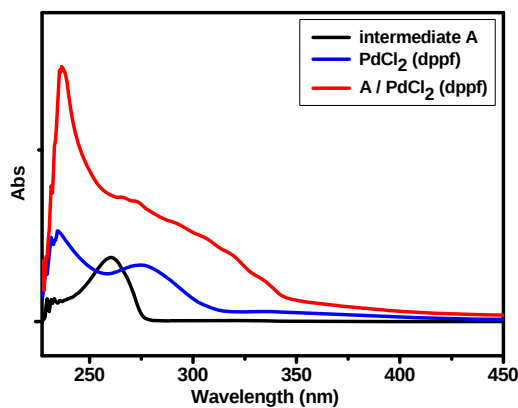


Figure S3. UV-vis spectra of intermediate **A** (black), PdCl₂(dppf) (blue), and the mixture of **A** and PdCl₂(dppf) after heating in dioxane (*ca.* 10⁻⁶ mol/L in dioxane)

To clarify the possible reasons for the low catalytic activity of $\text{PdCl}_2(\text{dppf})$ and $\text{NiCl}_2(\text{dppp})$, the UV-vis titration was carried out. The results showed that for the free $\text{NiCl}_2(\text{dppp})$ catalyst and intermediate **A** (Eq. S1), an absorption band around 260 nm was observed respectively (Figure S1). However, when a mixture of catalyst and **A** was heated in dioxane at 100 °C for 2-4 h, the absorption behavior of the resulting mixture was changed profoundly with a new band appeared at *ca.* 310 nm. Such a remarkable change implies that there is a strong interaction between the metal ions and intermediate **A**, forming most possibly a relatively stable six-membered chelates **B**, although the new band is attributed to the ligand centered $\pi\text{-}\pi^*$ transition (LCT) or the metal-to-ligand charge transfer (MLCT) deserves a detailed clarification. Similarly, a strong coordination between $\text{PdCl}_2(\text{PPh}_3)_2$ and **A** was also observed (Figure S2). As a result, the strong interaction between the phosphonium salt **A** and metal ions is assumed to suppress the reduction of M(II) to M(0), and ultimately, preventing the followed oxidative addition of pyridyl C–O bond to M(0) center, the key step to drive the catalytic cycle.

However, UV-vis titration showed that only negligible coordination between $\text{PdCl}_2(\text{dppf})$ and the phosphonium salt **A** was observed (Figure S3). These results further confirmed that the coordination strength between the metal ions of the catalysts and the intermediate **A** influences profoundly the coupling efficiency of 2-OH pyridine and boronic acids.

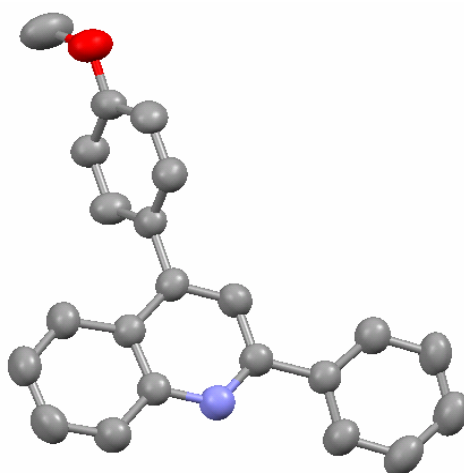
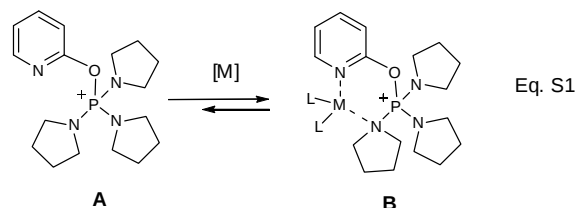
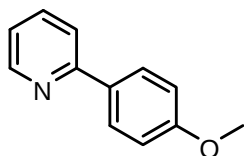


Figure S4. Single X-ray structure of compound **9a**.

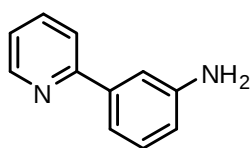
Product characterization

2-(4-methoxyphenyl)pyridine (3a)



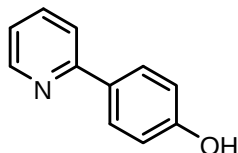
$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 3.87 (s, 3H), 7.01 (d, J = 8.8 Hz, 2H), 7.18 (t, J = 5.9 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.73 (t, J = 7.0 Hz, 1H), 7.97 (d, J = 8.8 Hz, 2H), 8.66 (d, J = 4.3 Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 55.3, 114.1, 119.7, 121.3, 128.1, 131.9, 136.6, 149.4, 157.0, 160.4. Spectral data match those previously reported.¹⁻²

3-(pyridin-2-yl)benzenamine (3b)



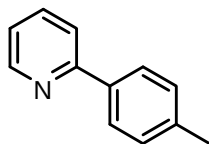
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 3.65 (s, 3H), 6.74 (d, J = 7.6 Hz, 1H), 7.19-7.23 (m, 1H), 7.26 (t, J = 3.9 Hz, 1H), 7.33 (d, J = 7.7 Hz, 1H), 7.38 (s, 1H), 7.68-7.74 (m, 2H), 8.67 (d, J = 4.7 Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 113.5, 115.7, 117.1, 120.5, 122.0, 129.5, 136.5, 140.3, 146.8, 149.4, 157.4. Spectral data match those previously reported.¹

4-(pyridin-2-yl)phenol (3c)



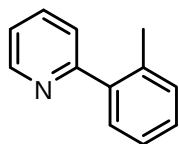
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 6.87 (d, J = 8.4 Hz, 2H), 7.20 (t, J = 6.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.72-7.76 (m, 1H), 7.84 (d, J = 8.4 Hz, 2H), 8.64 (d, J = 4.8 Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 29.7, 115.9, 116.2, 120.6, 121.5, 128.6, 130.7, 137.3, 148.9, 157.6, 157.8. Spectral data match those previously reported.¹

2-p-tolylpyridine (3d)



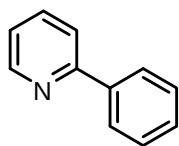
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 2.40 (s, 3H), 7.17-7.21 (m, 1H), 7.27 (t, J = 7.1 Hz, 2H), 7.69-7.74 (m, 2H), 7.90 (d, J = 8.2 Hz, 2H), 8.68 (d, J = 4.8 Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 120.2, 121.7, 126.7, 129.4, 136.6, 138.9, 149.5, 157.4. Spectral data match those previously reported.²

2-o-tolylpyridine (3e)



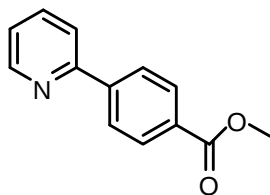
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 2.36 (s, 3H), 7.22-7.30 (m, 4H), 7.41 (d, J = 7.8 Hz, 2H), 7.72-7.76 (m, 1H), 8.70 (d, J = 4.8 Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 121.5, 123.9, 125.7, 128.1, 129.5, 130.6, 135.6, 135.9, 140.3, 149.1, 159.9. Spectral data match those previously reported.²

2-phenylpyridine (3f)



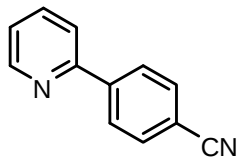
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 8.70 (d, J = 4.4 Hz, 1H), 7.99 (d, J = 7.2 Hz, 2H), 7.75 (m, 2H), 7.49-7.39 (m, 3H), 7.25-7.21 (m, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 120.5, 122.0, 126.9, 128.7, 128.9, 136.7, 139.3, 149.6, 157.4. Spectral data match those previously reported.²

methyl 4-(pyridin-2-yl)benzoate (3g)



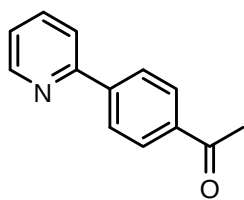
$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 3.95 (s, 3H), 7.28-7.31 (m, 1H), 7.79-7.80 (m, 1H), 8.09 (d, J = 8.5 Hz, 2H), 8.16 (d, J = 8.6 Hz, 2H), 8.74 (d, J = 4.8 Hz, 1 H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 52.1, 121.0, 122.8, 126.8, 130.0, 130.3, 136.9, 143.4, 149.8, 156.1, 166.8. Spectral data match those previously reported.³

4-(pyridin-2-yl)benzonitrile (3h)



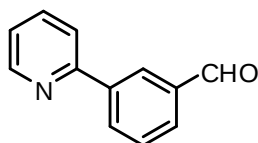
$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 7.32-7.34 (m, 1H), 7.76-7.78 (m, 3H), 7.81-7.84 (m, 1H), 8.13 (d, J = 8.4 Hz, 2H), 8.74 (d, J = 4.6 Hz, 1 H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 112.4, 118.8, 121.0, 123.3, 127.4, 132.5, 137.1, 143.4, 150.0, 155.2. Spectral data match those previously reported.¹

1-(4-(pyridin-2-yl)phenyl)ethanone (3i)



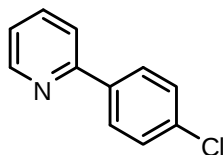
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 2.65 (s, 3H), 7.29-7.32 (m, 1H), 7.80-7.81 (m, 1H), 8.06-8.12 (m, 4H), 8.75 (d, $J = 4.7$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 26.7, 121.0, 122.9, 127.0, 128.8, 136.9, 137.2, 143.5, 149.9, 156.1, 197.8. Spectral data match those previously reported.³

3-(pyridin-2-yl)benzaldehyde (3j)



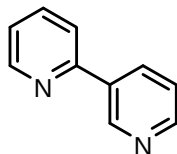
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.26-7.32 (m, 1H), 7.64 (t, $J = 7.7$ Hz, 1H), 7.81 (d, $J = 3.9$ Hz, 2H), 7.94 (d, $J = 3.9$ Hz, 1H), 8.30 (d, $J = 7.6$ Hz, 1 H), 8.51 (s, 1H), 8.73 (d, $J = 4.8$ Hz, 1H), 10.11 (s, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 120.5, 122.7, 128.3, 129.4, 129.6, 132.6, 136.7, 136.9, 140.1, 149.7, 155.7, 192.1. Spectral data match those previously reported.⁴

2-(4-chlorophenyl)pyridine (3k)



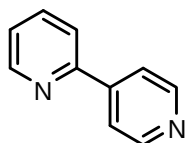
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.25 (t, $J = 6.0$ Hz, 1H), 7.45 (d, $J = 8.5$ Hz, 2H), 7.71 (d, $J = 7.9$ Hz, 1H), 7.74-7.78 (m, 1H), 7.95 (d, $J = 8.5$ Hz, 2H), 8.69 (d, $J = 4.7$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 120.3, 122.3, 128.1, 128.8, 135.0, 136.8, 137.7, 149.6, 156.1. Spectral data match those previously reported.¹

3-(pyridin-2-yl)pyridine (3l)



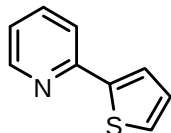
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.28-7.31 (m, 1H), 7.39-7.42 (m, 1H), 7.74-7.82 (m, 2H), 8.31-8.34 (m, 1H), 8.66 (s, 1 H), 8.72 (s, 1H), 9.21 (s, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 120.5, 122.8, 123.6, 134.3, 134.9, 136.9, 148.2, 149.8, 150.0, 154.8. Spectral data match those previously reported.¹

4-(pyridin-2-yl)pyridine (3m)



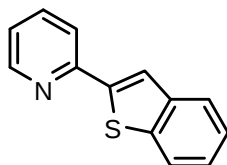
¹H-NMR (CDCl₃, 600 MHz) δ: 7.34-7.36 (m, 1H), 7.81-7.84 (m, 2H), 7.92 (d, *J* = 4.6 Hz, 2H), 8.75 (t, *J* = 7.0 Hz, 3H); ¹³C-NMR (CDCl₃, 125 MHz) δ: 120.9, 121.1, 123.8, 137.1, 146.6, 150.2, 150.2, 154.6. Spectral data match those previously reported.⁵

2-(thiophen-2-yl)pyridine (3n)



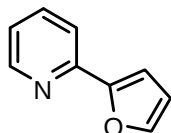
¹H-NMR (CDCl₃, 400 MHz) δ: 7.10-7.16 (m, 2H), 7.40 (d, *J* = 5.1 Hz, 1H), 7.59 (d, *J* = 3.6 Hz, 1H), 7.64-7.70 (m, 2H), 8.58 (d, *J* = 4.8 Hz, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ: 118.7, 121.8, 124.4, 127.5, 127.9, 136.5, 144.8, 149.4, 152.5. Spectral data match those previously reported.¹

2-(benzo[b]thiophen-2-yl)pyridine (3o)



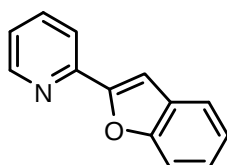
¹H-NMR (CDCl₃, 600 MHz) δ: 7.22 (t, *J* = 6.0 Hz, 1H), 7.34-7.37 (m, 2H), 7.75 (t, *J* = 7.3 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.87 (d, *J* = 8.9 Hz, 2H), 8.65 (t, *J* = 4.7 Hz, 1H); ¹³C-NMR (CDCl₃, 125 MHz) δ: 119.6, 121.1, 122.6, 124.1, 125.0, 136.6, 140.4, 144.8, 149.7, 152.5. Spectral data match those previously reported.⁶

2-(furan-2-yl)pyridine (3p)



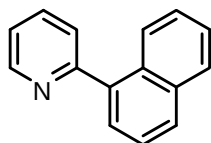
¹H-NMR (CDCl₃, 600 MHz) δ: 6.52-6.53 (dd, *J* = 6.5 Hz, 1H), 7.06 (d, *J* = 3.3 Hz, 1H), 7.12-7.14 (m, 1H), 7.52 (s, 1H), 7.67-7.71 (m, 2H), 8.59 (d, *J* = 4.7 Hz, 1H); ¹³C-NMR (CDCl₃, 125 MHz) δ: 108.5, 112.0, 118.5, 121.8, 136.6, 143.2, 149.3, 149.5, 153.5. Spectral data match those previously reported.⁷

2-(benzofuran-2-yl)pyridine (3q)



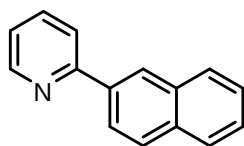
¹H-NMR (CDCl₃, 600 MHz) δ: 7.24-7.27 (m, 2H), 7.32-7.35 (m, 1H), 7.44 (s, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.77-7.80 (m, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 8.69 (d, *J* = 4.6 Hz, 1H); ¹³C-NMR (CDCl₃, 125 MHz) δ: 104.8, 111.5, 119.8, 121.7, 125.2, 128.8, 136.7, 149.2, 149.9, 155.0, 155.3. Spectral data match those previously reported.⁷

2-(naphthalen-1-yl)pyridine (3r)



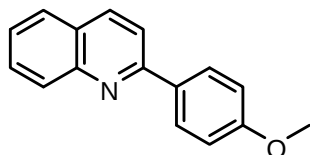
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.33-7.36 (m, 1H), 7.45-7.52 (m, 2H), 7.55 (d, $J = 7.2$ Hz, 1H), 7.57-7.61 (m, 2H), 7.81-7.86 (m, 1H), 7.90-7.92 (m, 2H), 8.09 (d, $J = 9.1$ Hz, 1H), 8.81 (d, $J = 4.8$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 122.0, 125.0, 125.2, 125.6, 125.8, 126.4, 127.4, 128.3, 131.1, 133.9, 136.3, 138.5, 149.5, 159.2. Spectral data match those previously reported.⁸⁻⁹

2-(naphthalen-2-yl)pyridine (3s)



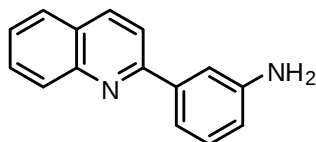
$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 7.27-7.28 (m, 1H), 7.50-7.52 (m, 2H), 7.79-7.82 (m, 1H), 7.87-7.90 (m, 2H), 7.95-7.96 (m, 2H), 8.14-8.15 (m, 1H), 8.49 (s, 1H), 8.76 (d, $J = 4.6$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 120.8, 122.1, 124.5, 126.3, 126.3, 126.5, 128.7, 133.5, 136.6, 136.8, 149.7, 157.3. Spectral data match those previously reported.⁹

2-(4-methoxyphenyl)quinoline (5a)



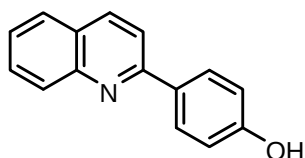
$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 3.89 (s, 3H), 7.06 (d, $J = 8.7$ Hz, 2H), 7.50 (t, $J = 7.4$ Hz, 1H), 7.71 (t, $J = 7.6$ Hz, 1H), 7.81 (d, $J = 8.0$ Hz, 1H), 7.85 (d, $J = 8.6$ Hz, 1H), 8.15 (d, $J = 8.6$ Hz, 3H), 8.19 (d, $J = 8.6$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 114.1, 114.3, 118.5, 125.9, 126.9, 127.4, 128.9, 129.5, 132.2, 136.6, 148.3, 156.9, 160.8. Spectral data match those previously reported.¹⁰

3-(quinolin-2-yl)benzenamine (5b)



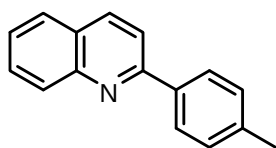
$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 3.74 (s, 2H), 6.72-6.78 (dd, $J = 6.8$ Hz, 1H), 7.29 (t, $J = 7.8$ Hz, 1H), 7.46-7.51 (m, 2H), 7.56 (s, 1H), 7.71 (t, $J = 7.7$ Hz, 1H), 7.79-7.83 (dd, $J = 7.8$ Hz, 2H), 8.16-8.18 (dd, $J = 8.7$ Hz, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 112.4, 118.8, 120.9, 123.3, 127.4, 132.5, 137.1, 143.4, 150.0, 155.2. Spectral data match those previously reported.¹¹

4-(quinolin-2-yl)phenol (5c)



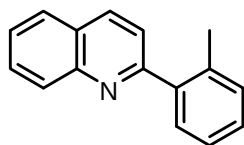
$^1\text{H-NMR}$ (DMSO- d_6 , 600 MHz) δ : 6.93 (d, J = 8.6 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.74 (t, J = 7.6 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 8.7 Hz, 1H), 8.15 (d, J = 8.6 Hz, 2H), 8.37 (d, J = 8.6 Hz, 1H), 9.84 (s, 1 H); $^{13}\text{C-NMR}$ (CDCl_3 , 125MHz) δ : 115.6, 118.1, 125.7, 126.5, 127.7, 128.7, 129.5, 129.6, 136.8, 147.5, 156.0, 159.0.

2-p-tolylquinoline (5d)



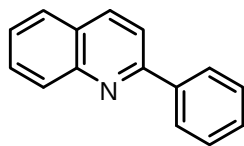
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 2.44 (s, 3H), 7.34 (d, J = 7.9 Hz, 2H), 7.51 (t, J = 7.5 Hz, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 8.6 Hz, 1H), 8.09 (d, J = 8.0 Hz, 2H), 8.19 (t, J = 8.2 Hz, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 21.3, 118.8, 126.1, 127.1, 127.4, 127.4, 129.5, 136.7, 139.4, 148.2, 157.3. Spectral data match those previously reported.¹²

2-o-tolylquinoline (5e)



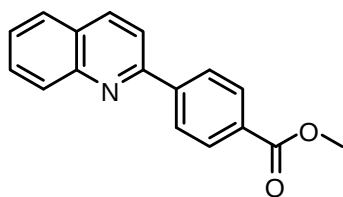
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 2.42 (s, 3H), 7.29-7.36 (m, 3H), 7.49-7.51 (m, 1H), 7.53-7.58 (m, 2 H), 7.72-7.76 (m, 1H), 7.87 (d, J = 8.2 Hz, 1H), 8.18 (d, J = 8.5 Hz, 1H), 8.22 (d, J = 8.4 Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 20.3, 122.3, 126.0, 126.4, 126.7, 127.5, 128.5, 129.6, 130.8, 136.0, 140.7, 147.9, 160.3. Spectral data match those previously reported.⁸

2-phenylquinoline (5f)



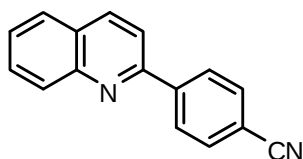
$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 7.48 (t, J = 7.0 Hz, 1H), 7.54 (t, J = 7.3 Hz, 3H), 7.75 (s, 1 H), 7.85 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.5 Hz, 1H), 8.19 (d, J = 7.5 Hz, 3H), 8.25 (s, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 119.0, 126.3, 127.2, 128.8, 129.3, 129.6, 129.7, 136.8, 139.6, 148.2, 157.3. Spectral data match those previously reported.¹²

methyl 4-(quinolin-2-yl)benzoate (5g)



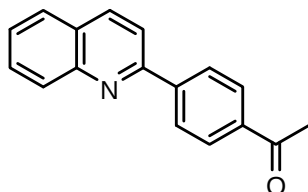
$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 3.97 (s, 3H), 7.57 (t, J = 7.4 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.93 (d, J = 8.6 Hz, 1H), 8.21 (d, J = 8.3 Hz, 3H), 8.27 (t, J = 8.6 Hz, 3H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 52.2, 76.7, 77.0, 77.3, 118.9, 126.8, 127.5, 130.1, 137.0, 143.7, 148.3, 156.0, 166.9. Spectral data match those previously reported.¹³

4-(quinolin-2-yl)benzonitrile (5h)



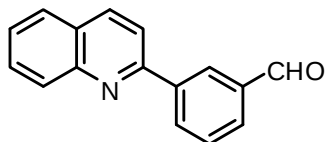
$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 7.59 (t, J = 7.5 Hz, 1H), 7.77 (t, J = 7.7 Hz, 1H), 7.81 (d, J = 8.3 Hz, 2H), 7.87 (d, J = 8.2 Hz, 2H), 8.19 (d, J = 8.5 Hz, 1H), 8.30 (t, J = 8.4 Hz, 3H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 112.7, 118.5, 118.8, 127.1, 127.5, 128.0, 132.5, 137.2, 143.6, 148.2, 154.8. Spectral data match those previously reported.¹⁴

1-(4-(quinolin-2-yl)phenyl)ethanone (5i)



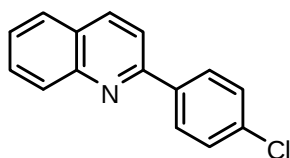
$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 2.68 (s, 3H), 7.58 (t, J = 7.4 Hz, 1H), 7.78 (t, J = 7.5 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.5 Hz, 1H), 8.13 (d, J = 8.4 Hz, 2H), 8.30 (d, J = 8.3 Hz, 4H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 26.8, 118.9, 126.8, 127.4, 127.5, 128.8, 129.8, 129.9, 137.0, 137.4, 143.7, 148.2, 155.8, 197.8. Spectral data match those previously reported.¹³

3-(quinolin-2-yl)benzaldehyde (5j)



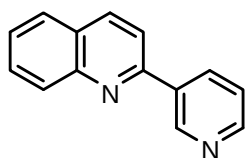
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.58 (t, J = 7.5 Hz, 1H), 7.71 (t, J = 7.7 Hz, 1H), 7.77 (t, J = 7.7 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.96 (d, J = 8.6 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 8.24 (d, J = 8.2 Hz, 1H), 8.31 (d, J = 8.6 Hz, 1H), 8.51 (d, J = 5.9 Hz, 1H), 8.70 (s, 1H), 10.17 (s, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 118.5, 126.7, 127.5, 128.9, 129.5, 129.7, 129.9, 130.1, 133.3, 136.9, 137.1, 140.4, 148.1, 155.6, 192.2.

2-(4-chlorophenyl)quinoline (5k)



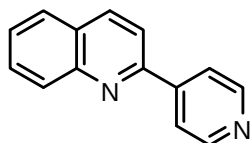
$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 7.50(d, $J=8.4$, 2 H), 7.55 (t, $J=7.4$ Hz, 1H), 7.74 (t, $J=7.5$ Hz, 1H), 7.85 (t, $J=8.4$ Hz, 2H), 8.14 (d, $J=8.4$ Hz, 2H), 8.17 (s, 1H), 8.25 (d, $J=8.4$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 118.5, 126.5, 127.2, 127.5, 128.8, 129.0, 135.6, 137.0, 137.9, 148.1, 155.9. Spectral data match those previously reported.¹⁵

2-(pyridin-3-yl)quinoline (5l)



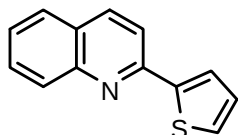
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.45-7.48 (m, 1H), 7.57 (t, $J=7.4$ Hz, 1H), 7.76 (t, $J=7.2$ Hz, 1H), 7.87 (d, $J=8.2$ Hz, 1H), 7.90 (d, $J=8.6$ Hz, 1H), 8.19 (d, $J=8.5$ Hz, 1H), 8.29 (d, $J=8.2$ Hz, 1H), 8.53 (d, $J=8.0$ Hz, 1H), 8.71 (d, $J=3.7$ Hz, 1H), 9.76 (s, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 118.4, 123.6, 126.7, 127.3, 127.5, 129.7, 129.9, 134.8, 135.0, 137.1, 148.3, 148.8, 150.2, 154.6. Spectral data match those previously reported.¹⁶

2-(pyridin-4-yl)quinoline (5m)



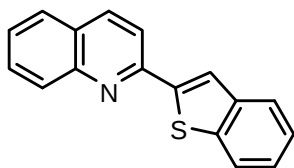
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 7.61 (t, $J=7.5$ Hz, 1H), 7.76-7.80 (m, 1H), 7.88 (d, $J=8.0$ Hz, 1H), 7.93 (d, $J=8.6$ Hz, 1H), 8.09 (d, $J=6.0$ Hz, 2H), 8.21 (d, $J=8.5$ Hz, 1H), 8.31 (d, $J=8.6$ Hz, 1H), 8.80 (d, $J=5.7$ Hz, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 118.2, 121.4, 127.0, 127.4, 127.6, 129.8, 129.9, 137.0, 146.3, 148.1, 150.3, 154.1. Spectral data match those previously reported.¹⁷

2-(thiophen-2-yl)quinoline (5n)



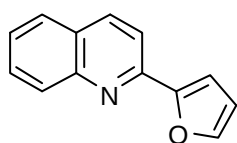
$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 7.17 (t, $J=4.3$ Hz, 1H), 7.47-7.50 (m, 2H), 7.70 (t, $J=7.6$ Hz, 1H), 7.75-7.81 (m, 3H), 8.14 (t, $J=8.1$ Hz, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 117.6, 125.8, 126.0, 127.1, 127.4, 128.0, 128.5, 129.2, 129.8, 136.6, 145.4, 148.1, 152.3. Spectral data match those previously reported.¹²

2-(benzo[b]thiophen-2-yl)quinoline (5o)



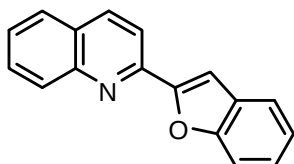
$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 7.37-7.38 (m, 2H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.73 (t, $J = 8.4$ Hz, 1H), 7.80 (d, $J = 6.1$ Hz, 1H), 7.83-7.86 (m, 1H), 7.89-7.92 (m, 1H), 7.95 (d, $J = 8.6$ Hz, 1H), 7.98 (s, 1H), 8.15 (d, $J = 8.5$ Hz, 1H), 8.20 (d, $J = 8.6$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 117.8, 122.4, 122.6, 124.3, 124.5, 125.3, 127.5, 136.6, 140.4, 145.5, 148.1, 152.2. Spectral data match those previously reported.¹⁸

2-(furan-2-yl)quinoline (5p)



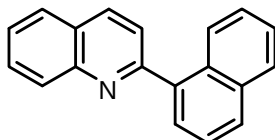
$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 6.60 (s, 1H), 7.22 (s, 1H), 7.50 (t, $J = 7.4$ Hz, 1H), 7.70 (s, 1H), 7.71 (t, $J = 7.6$ Hz, 1H), 7.79 (d, $J = 8.1$ Hz, 1H), 7.84 (d, $J = 8.6$ Hz, 1H), 8.17 (t, $J = 8.2$ Hz, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 29.6, 76.7, 77.0, 77.3, 110.0, 112.1, 117.3, 126.1, 127.0, 127.4, 129.2, 129.7, 136.5, 144.0, 148.0, 148.9, 153.6. Spectral data match those previously reported.¹²

2-(benzofuran-2-yl)quinoline (5q)



$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 7.29 (t, $J = 7.4$ Hz, 1H), 7.38 (t, $J = 7.7$ Hz, 1H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.64 (t, $J = 8.6$ Hz, 2H), 7.70 (d, $J = 7.7$ Hz, 1H), 7.75 (t, $J = 7.6$ Hz, 1H), 7.84 (d, $J = 8.1$ Hz, 1H), 8.04 (d, $J = 8.5$ Hz, 1H), 8.21 (d, $J = 8.0$ Hz, 1H), 8.25 (d, $J = 8.5$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 106.2, 111.8, 108.1, 121.7, 123.3, 125.5, 126.7, 127.6, 136.7, 148.2, 149.0, 155.2, 155.6. Spectral data match those previously reported.¹²

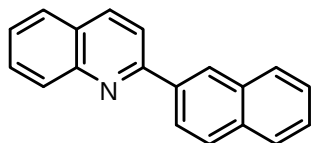
2-(naphthalen-1-yl)quinoline (5r)



$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 7.47 (t, $J = 7.6$ Hz, 1H), 7.52 (t, $J = 6.9$ Hz, 1H), 7.60 (t, $J = 7.6$ Hz, 2H), 7.72 (t, $J = 6.8$ Hz, 2H), 7.78 (t, $J = 7.1$ Hz, 1H), 7.91-7.96 (m, 3H), 8.14 (d, $J = 8.4$ Hz, 1H), 8.23 (d, $J = 8.3$ Hz, 1H), 8.30 (d, $J = 8.4$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 123.2, 125.3, 125.9, 126.5, 127.0, 127.5, 127.7, 128.4, 129.1, 129.7, 131.3. Spectral data match those

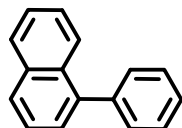
previously reported.¹⁹

2-(naphthalen-2-yl)quinoline (5s)



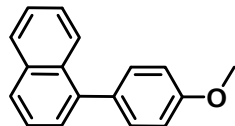
¹H-NMR (CDCl₃, 600 MHz) δ: 7.52-7.55 (m, 3H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.89 (t, *J* = 4.7 Hz, 1H), 8.00 (d, *J* = 8.7 Hz, 2H), 8.04 (d, *J* = 8.5 Hz, 2H), 8.24 (t, *J* = 9.4 Hz, 2H), 8.38 (d, *J* = 8.5, 1H), 8.62 (s, 1H); ¹³C-NMR (CDCl₃, 100 MHz) δ: 119.1, 125.0, 126.3, 126.7, 127.1, 127.5, 127.7, 128.5, 128.8, 129.7, 133.5, 133.9, 136.8, 148.3, 157.1. Spectral data match those previously reported.¹⁰

1-phenylnaphthalene (7a)



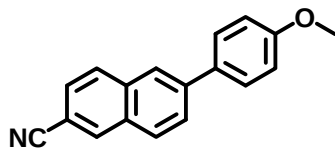
¹H-NMR (CDCl₃, 600 MHz) δ: 7.41-7.53 (m, 9H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.7 Hz, 2H). Spectral data match those previously reported.²⁰

1-(4-methoxyphenyl) naphthalene (7b)



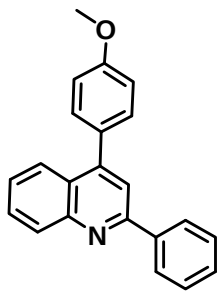
¹H-NMR (CDCl₃, 600 MHz), δ: 3.89 (s, 3H), 7.04 (d, *J* = 8.5 Hz, 2H), 7.40-7.43 (m, 4H), 7.47-7.52 (m, 2H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.89-7.93(m, 2H). Spectral data match those previously reported.²⁰

6-(4-methoxyphenyl) naphthalene-2-carbonitrile (7d)



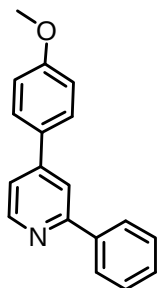
¹H-NMR (CDCl₃, 400 MHz) δ: 3.88 (s, 3H), 7.05 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 2H), 8.00 (s, 1H), 8.21 (s, 1H). Spectral data match those previously reported.²⁰

4-(4-methoxyphenyl)-2-phenylquinoline (9a)



$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 3.92 (s, 3 H), 7.09 (d, $J = 8.2$ Hz, 2H), 7.45-7.49 (m, 2H), 7.51-7.54 (m, 4 H), 7.43 (t, $J = 7.4$ Hz, 1H), 7.80 (s, 1H), 7.96 (d, $J = 8.3$ Hz, 1H), 8.20 (d, $J = 7.6$ Hz, 2H), 8.24 (d, $J = 8.3$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 55.4, 114.1, 119.3, 125.6, 125.9, 126.2, 127.6, 128.8, 129.2, 129.4, 130.8, 139.7, 148.8, 156.9, 159.8.

4-(4-methoxyphenyl)-2-phenylpyridine (9b)



$^1\text{H-NMR}$ (CDCl_3 , 600 MHz) δ : 3.89 (s, 3 H), 7.05 (d, $J = 8.6$ Hz, 2H), 7.43-7.47 (m, 2H), 7.52 (t, $J = 7.5$ Hz, 2H), 7.68 (d, $J = 8.6$ Hz, 2H), 7.92 (s, 1 H), 8.07 (d, $J = 7.6$ Hz, 2H), 8.73 (d, $J = 5.2$ Hz, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz) δ : 55.2, 114.4, 118.0, 119.6, 126.9, 128.1, 128.6, 128.9, 130.5, 139.4, 148.6, 149.8, 157.8, 160.4.

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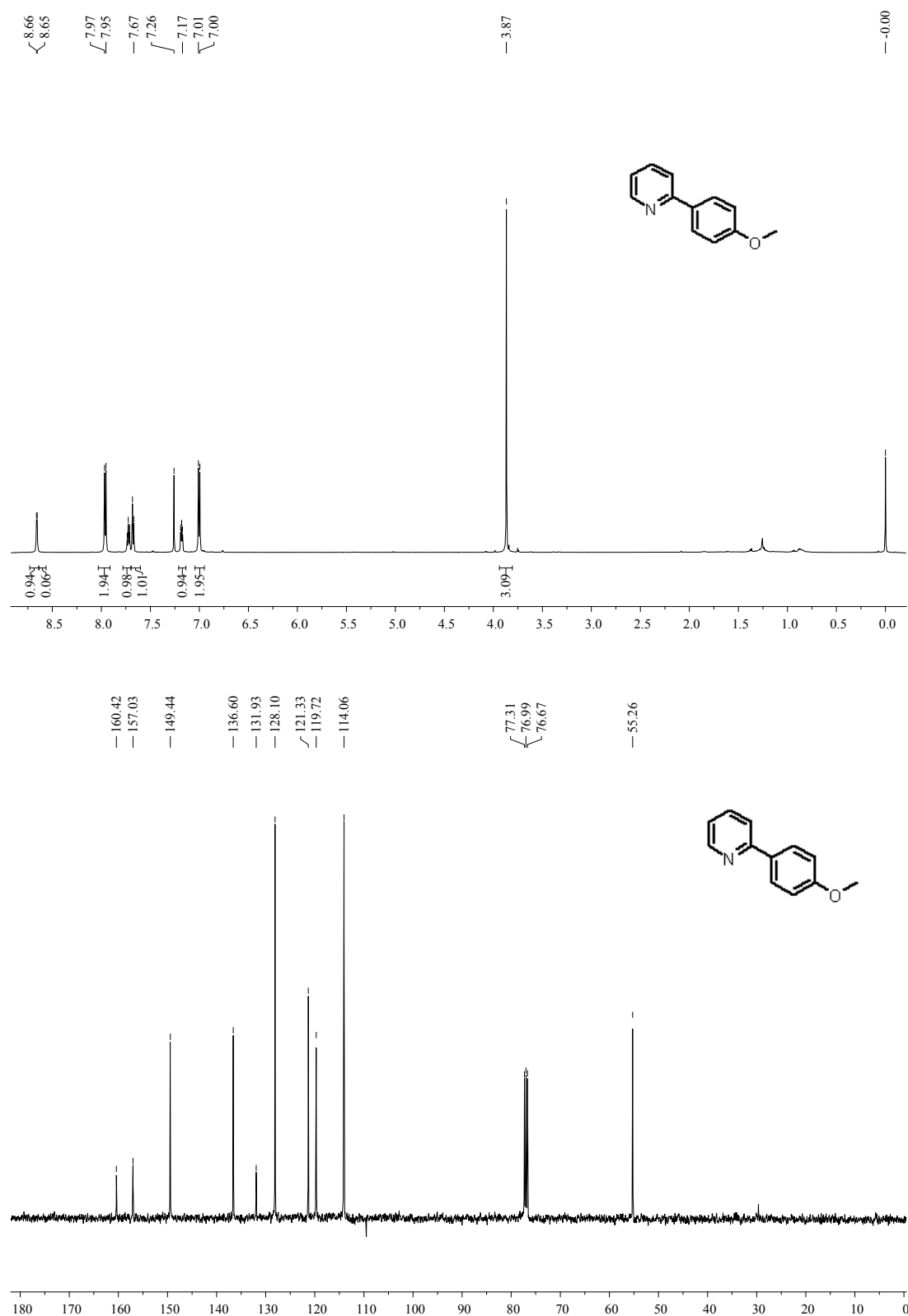


Figure S5. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-(4-methoxyphenyl)pyridine (**3a**)

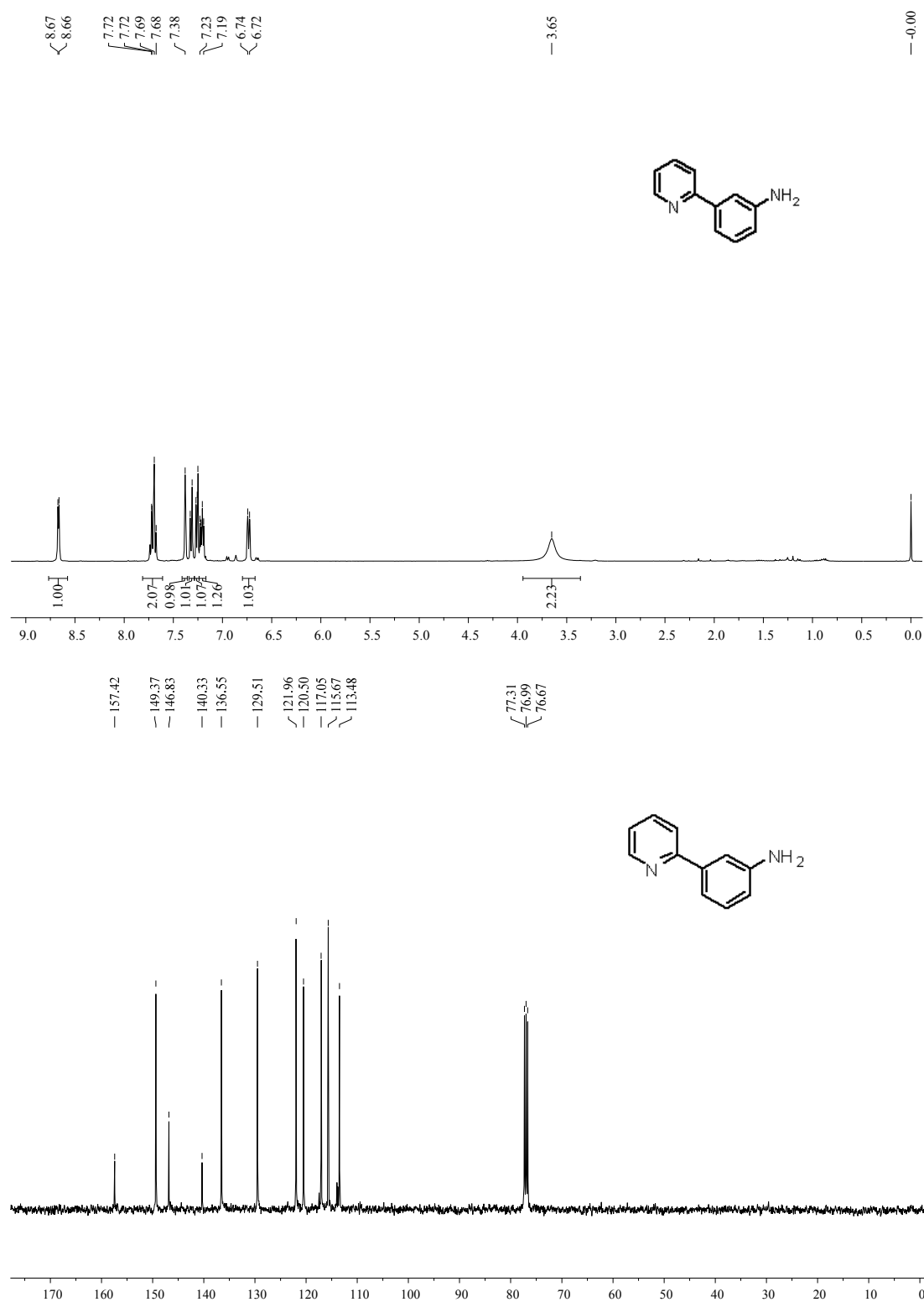
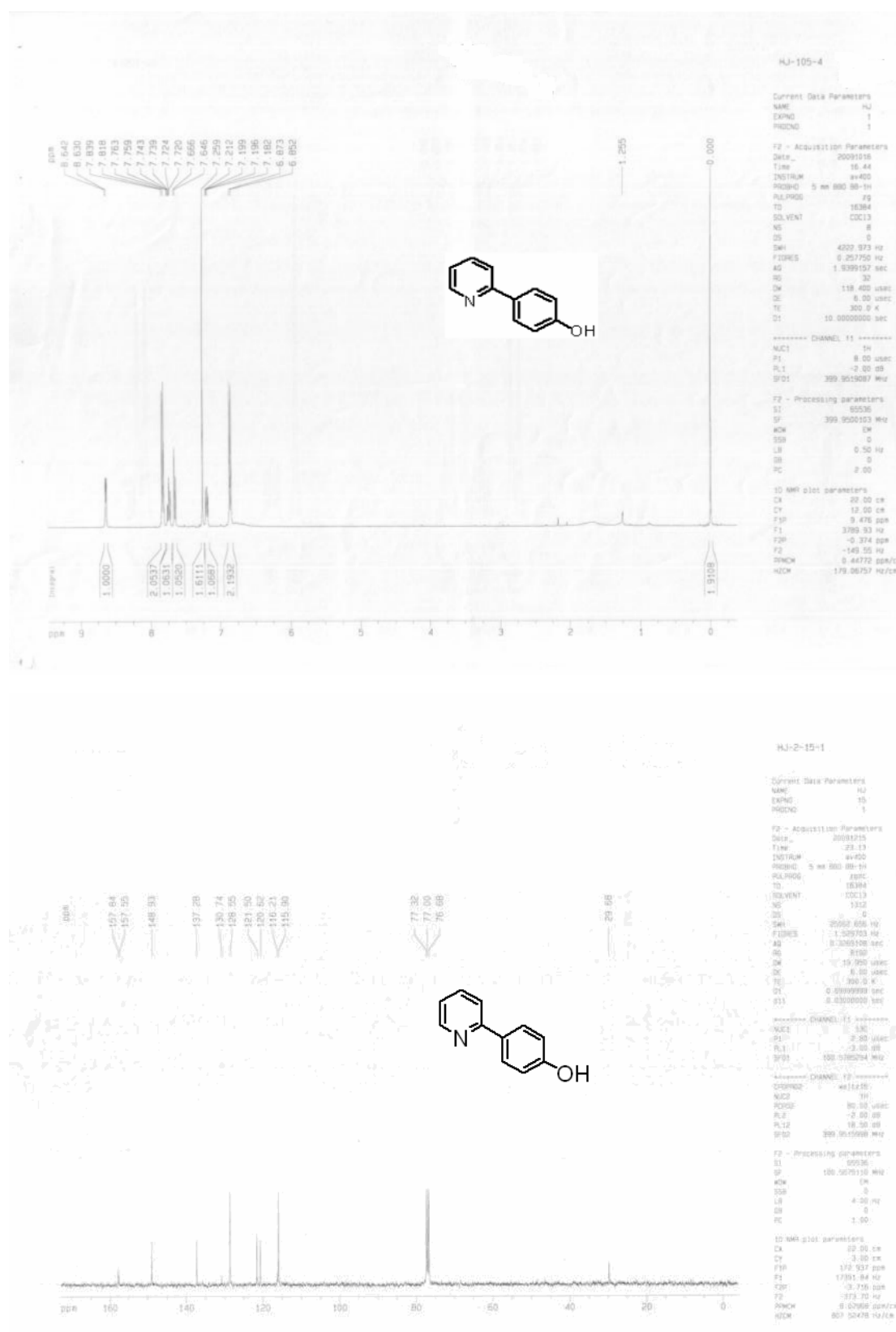


Figure S6. ¹H- (upper) and ¹³C-NMR (lower) spectra of 3-(pyridin-2-yl)benzenamine (**3b**)



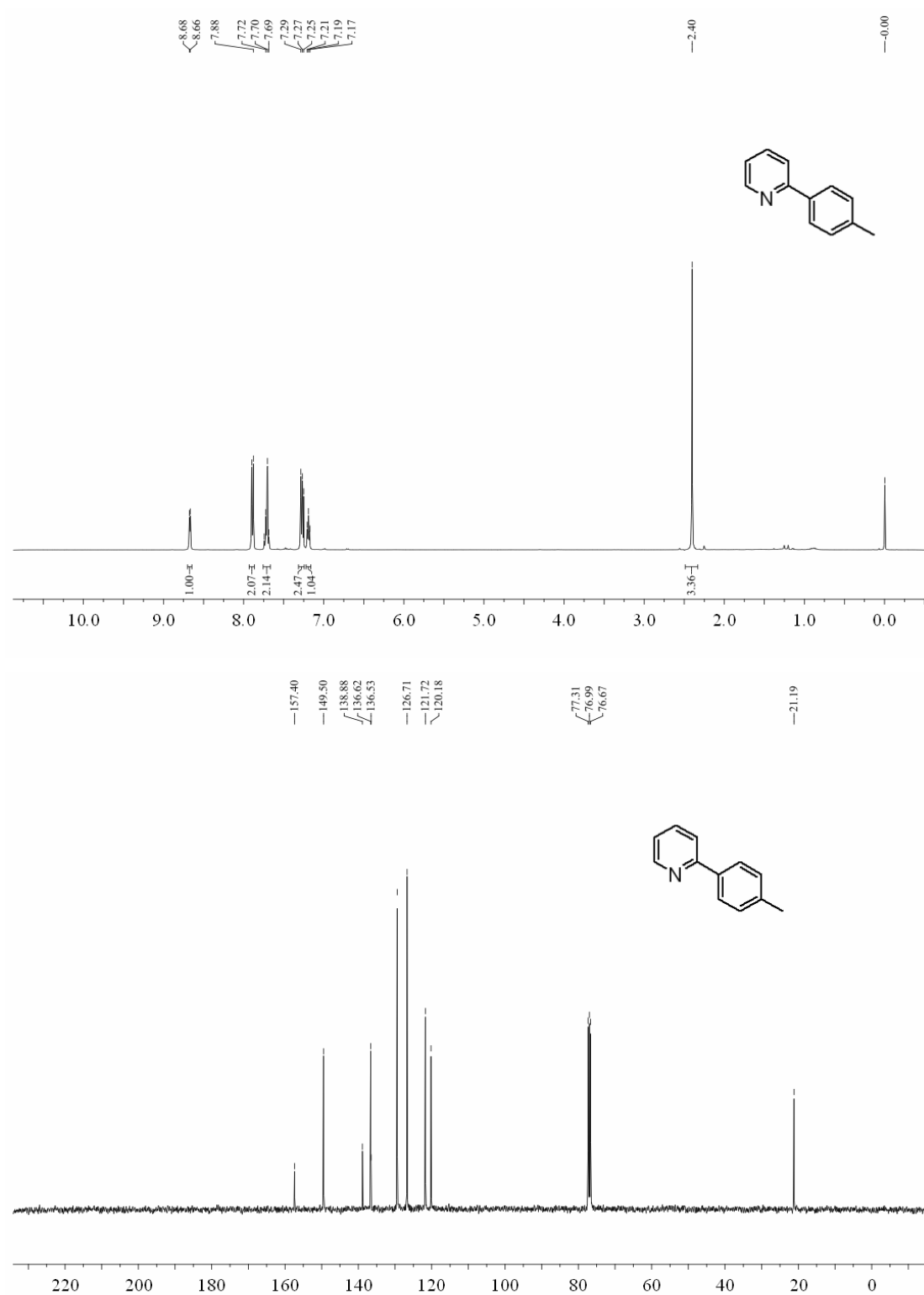


Figure S8. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-p-tolylpyridine (**3d**)

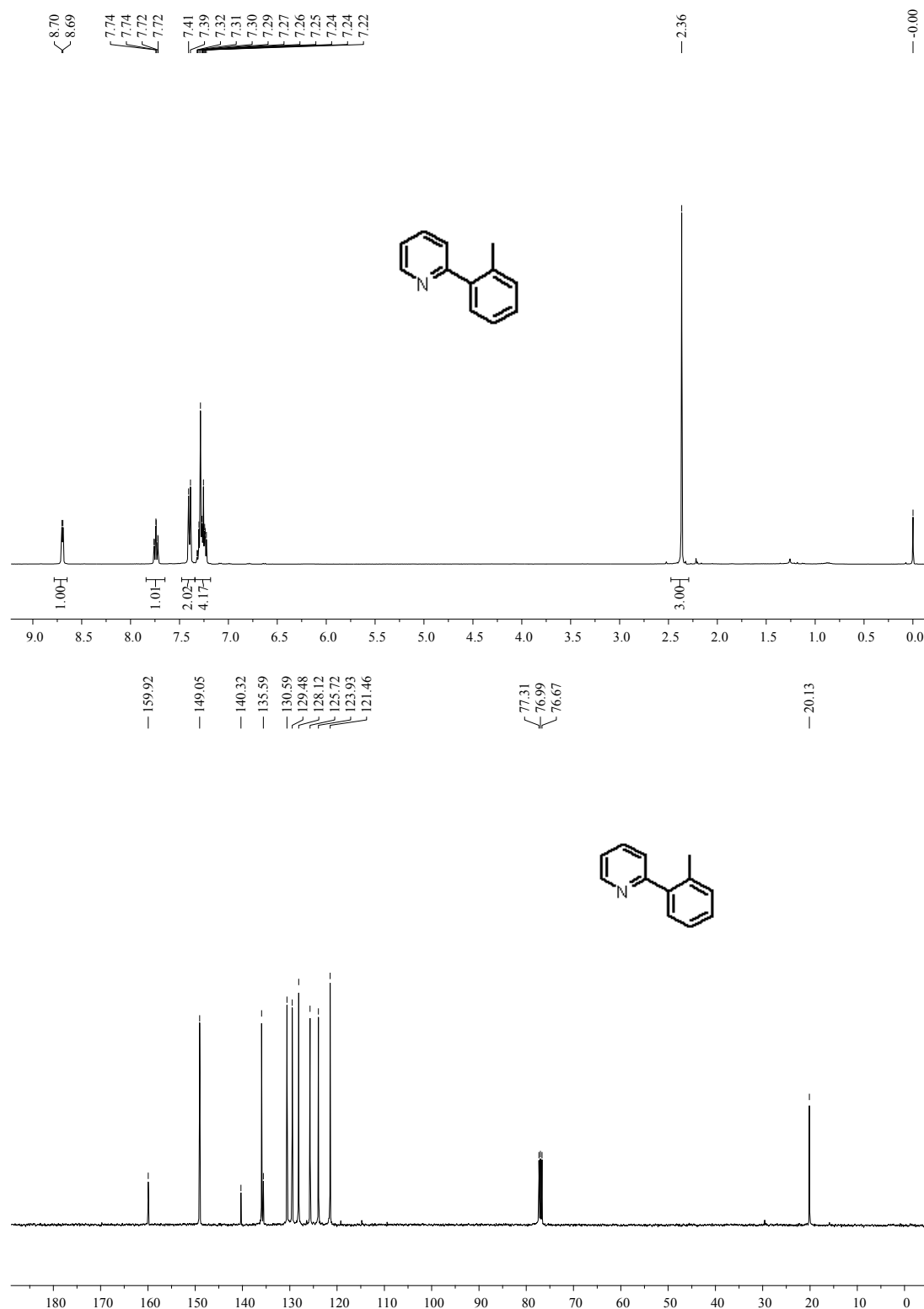


Figure S9. ^1H - (upper) and ^{13}C -NMR (lower) spectra of 2-o-tolylpyridine (3e)

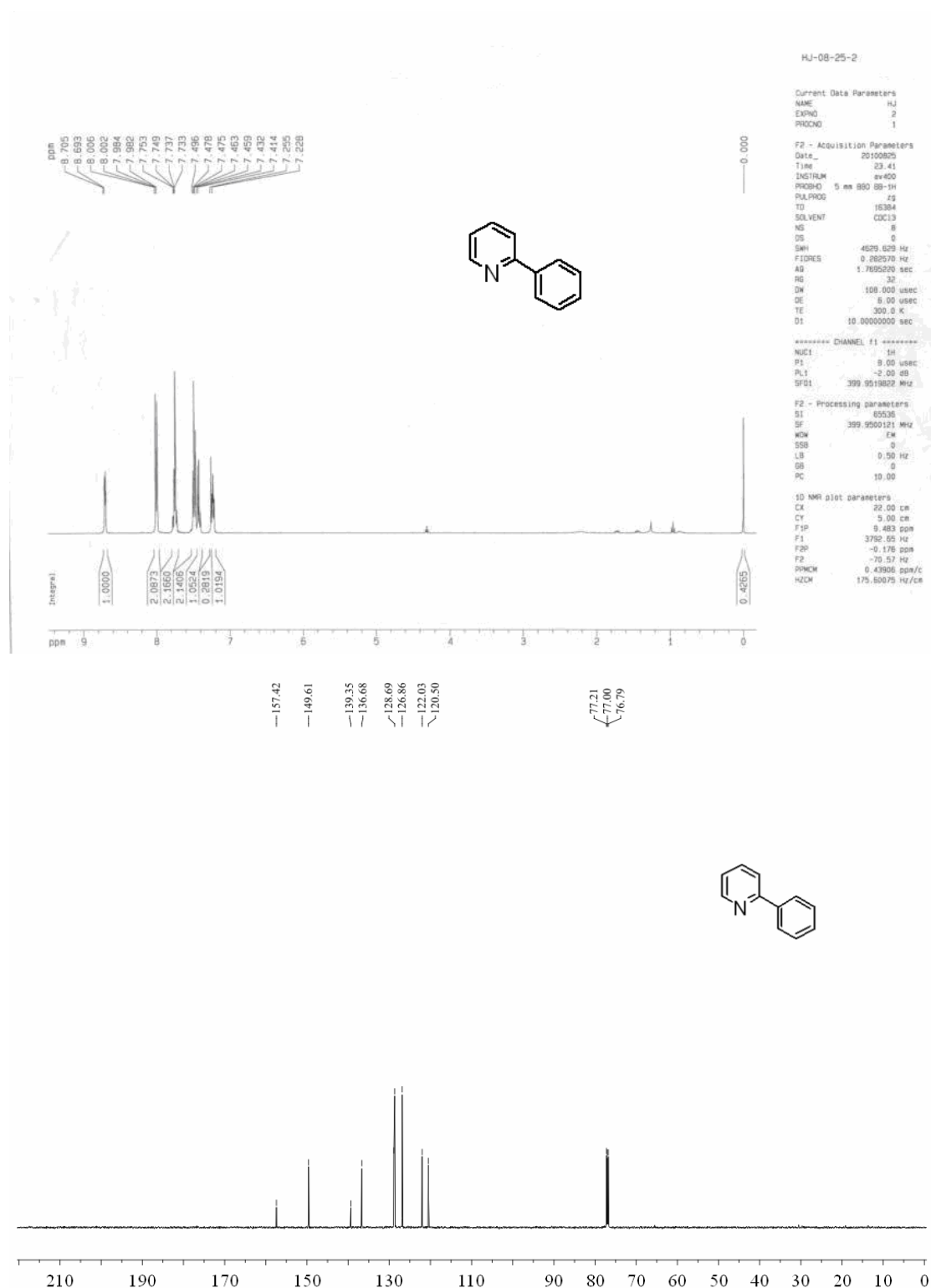


Figure S10. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-phenylpyridine (**3f**)

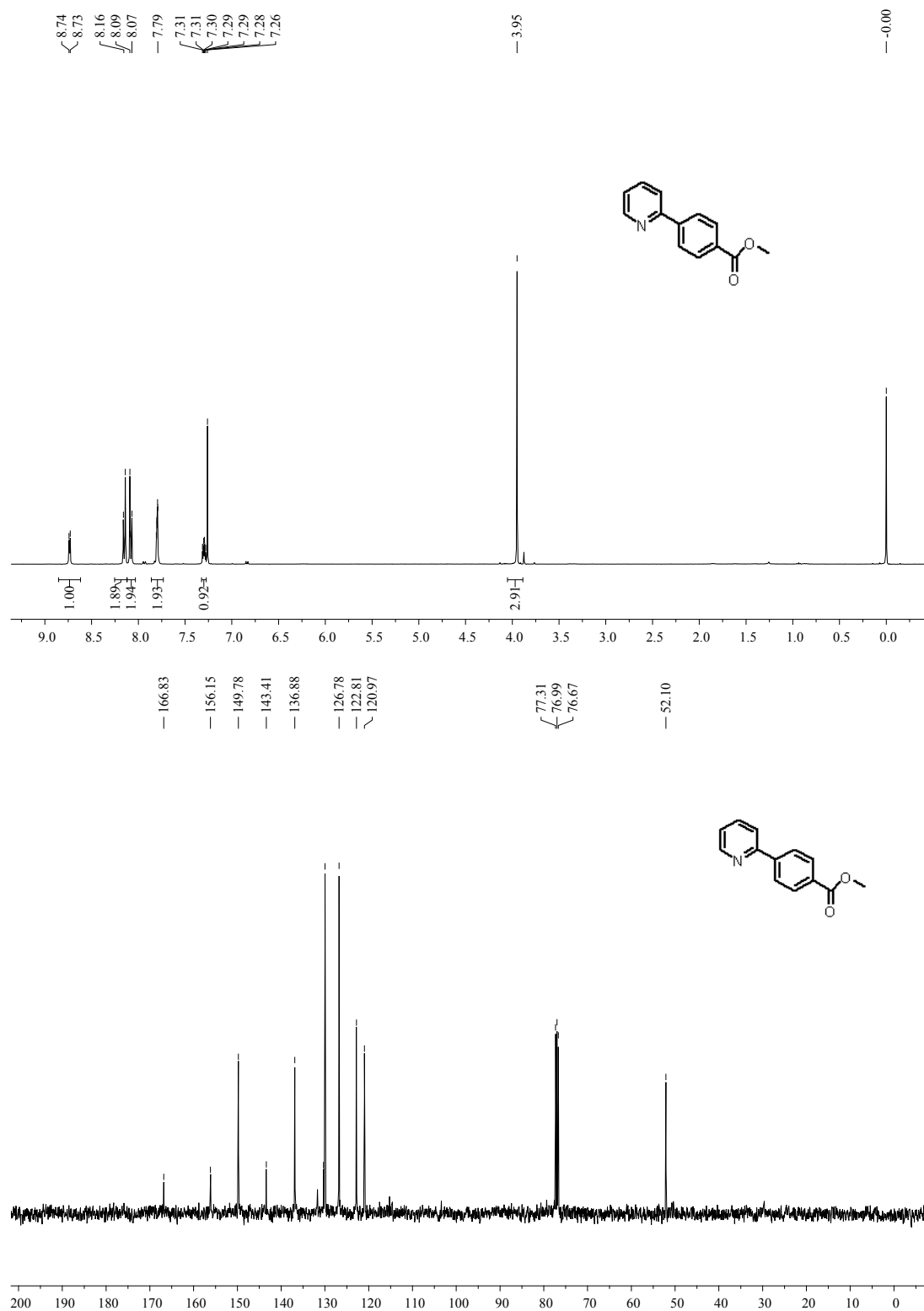


Figure S11. ¹H- (upper) and ¹³C-NMR (lower) spectra of methyl 4-(pyridin-2-yl)benzoate (**3g**)

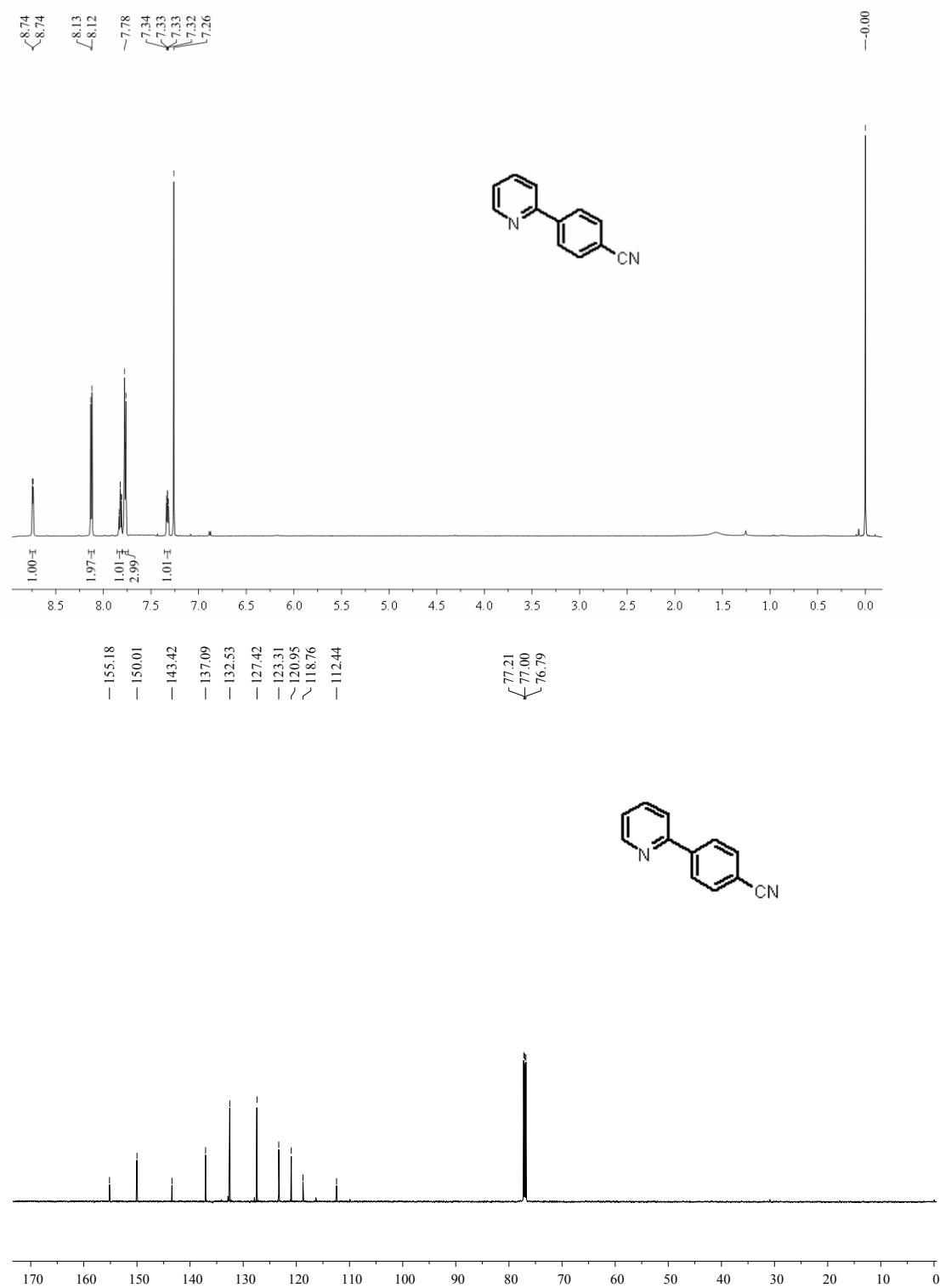


Figure S12. ¹H- (upper) and ¹³C-NMR (lower) spectra of 4-(pyridin-2-yl)benzonitrile (**3h**)

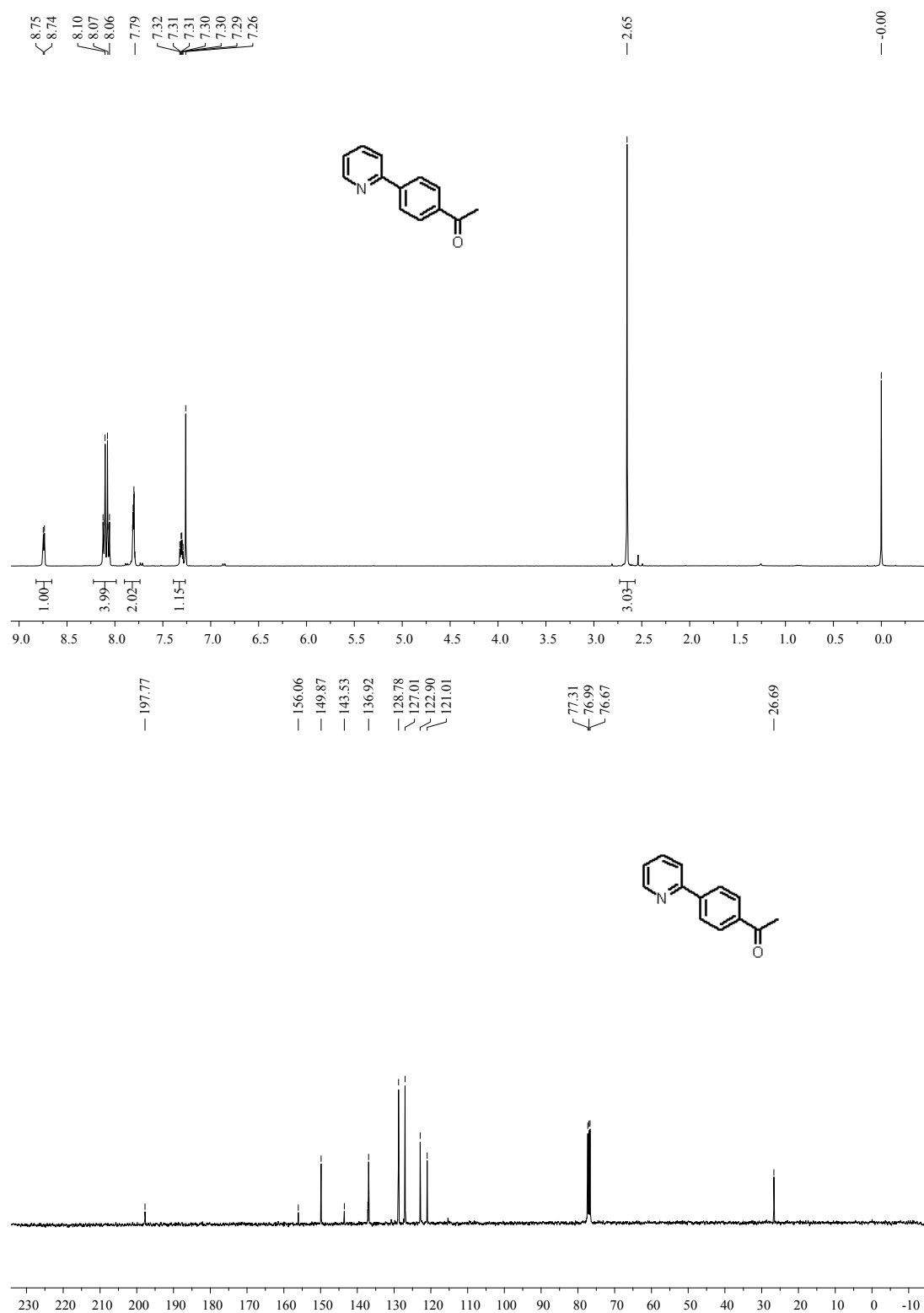


Figure S13. ¹H- (upper) and ¹³C-NMR (lower) spectra of 1-(4-(pyridin-2-yl)phenyl)ethanone (**3i**)

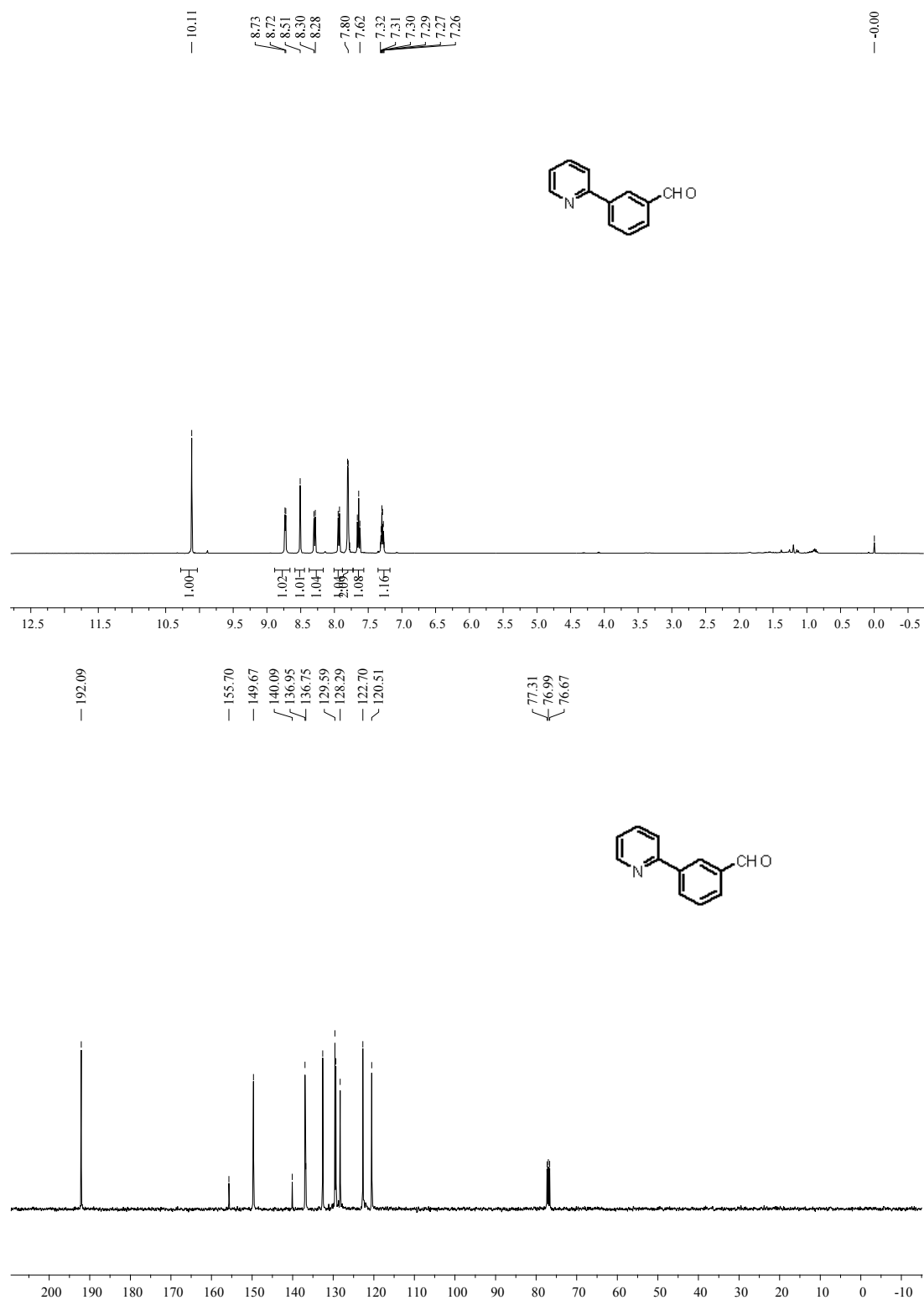


Figure S14. ¹H- (upper) and ¹³C-NMR (lower) spectra of 3-(pyridin-2-yl)benzaldehyde (**3j**)

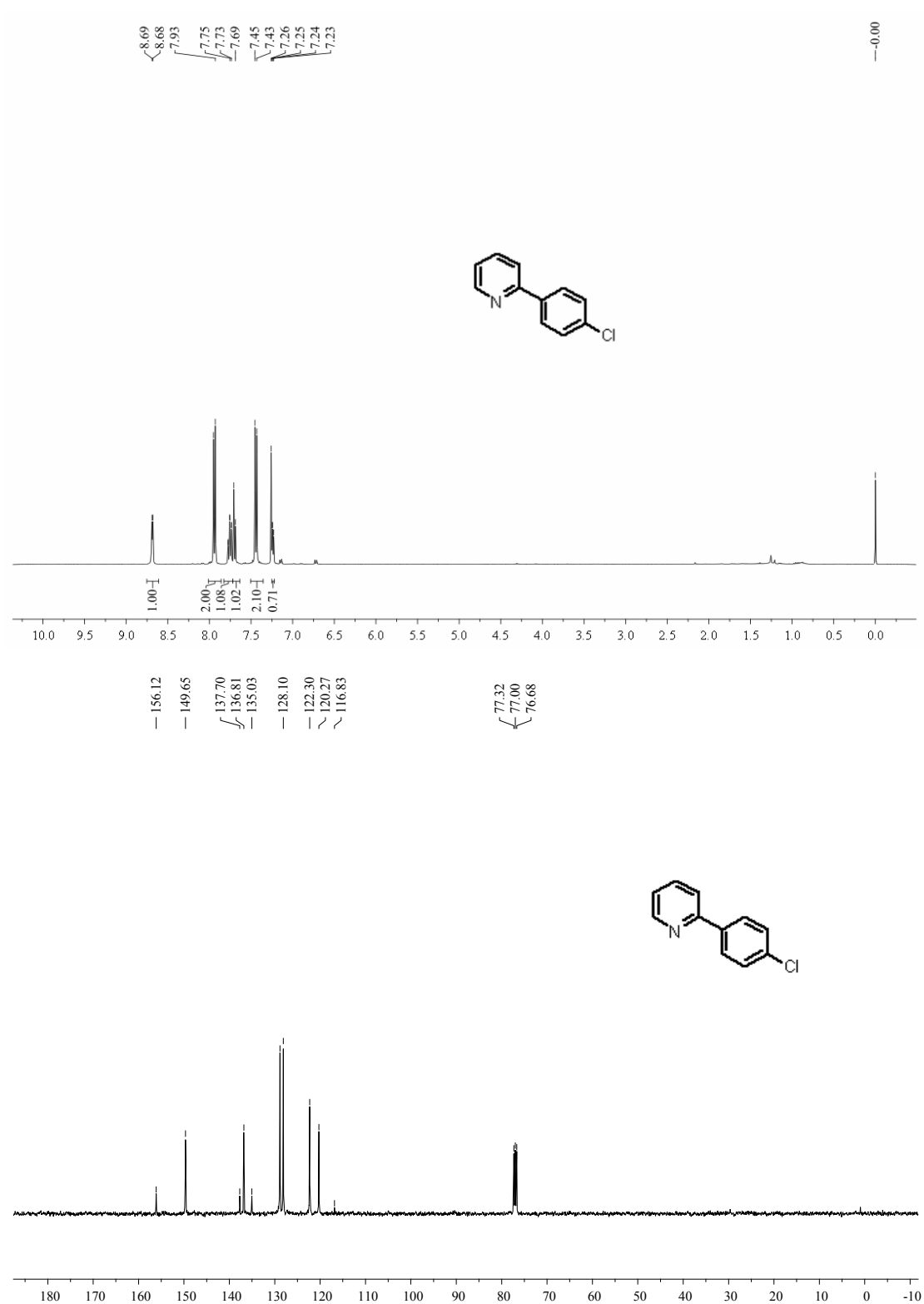


Figure S15. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-(4-chlorophenyl)pyridine (**3k**)

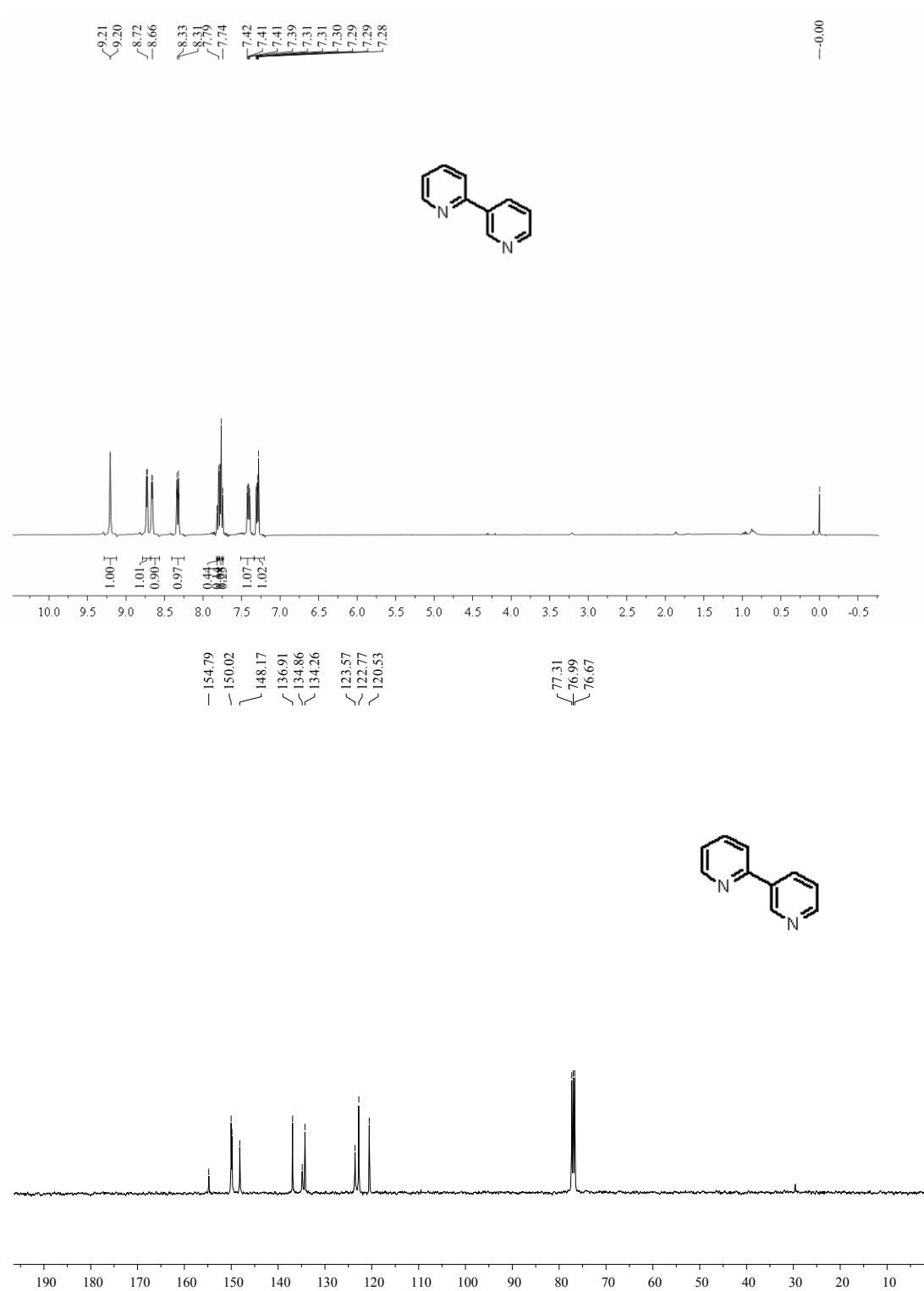


Figure S16. ¹H- (upper) and ¹³C-NMR (lower) spectra of 3-(pyridin-2-yl)pyridine (**3I**)

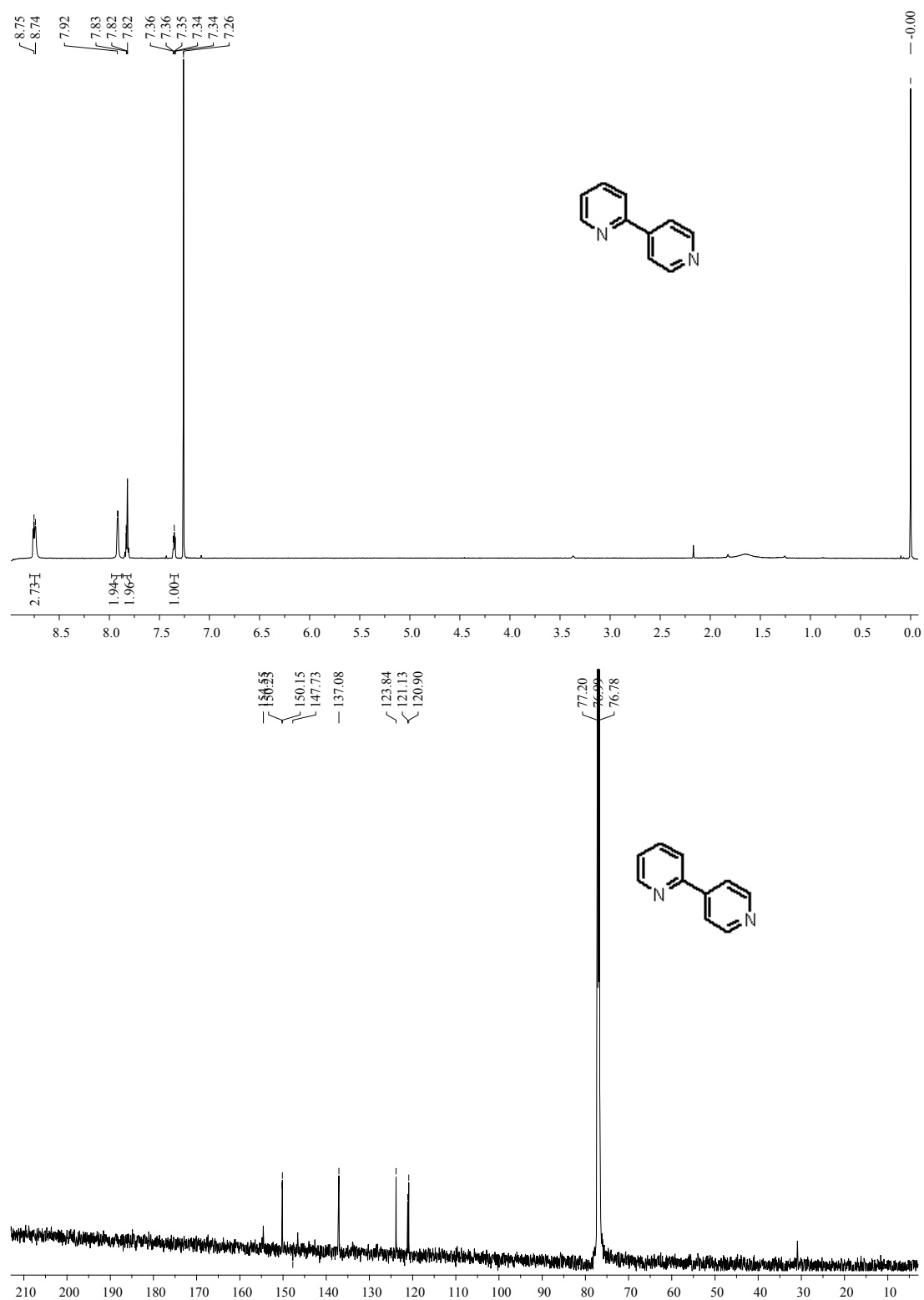


Figure S17. ¹H- (upper) and ¹³C-NMR (lower) spectra of 4-(pyridin-2-yl)pyridine (**3m**)

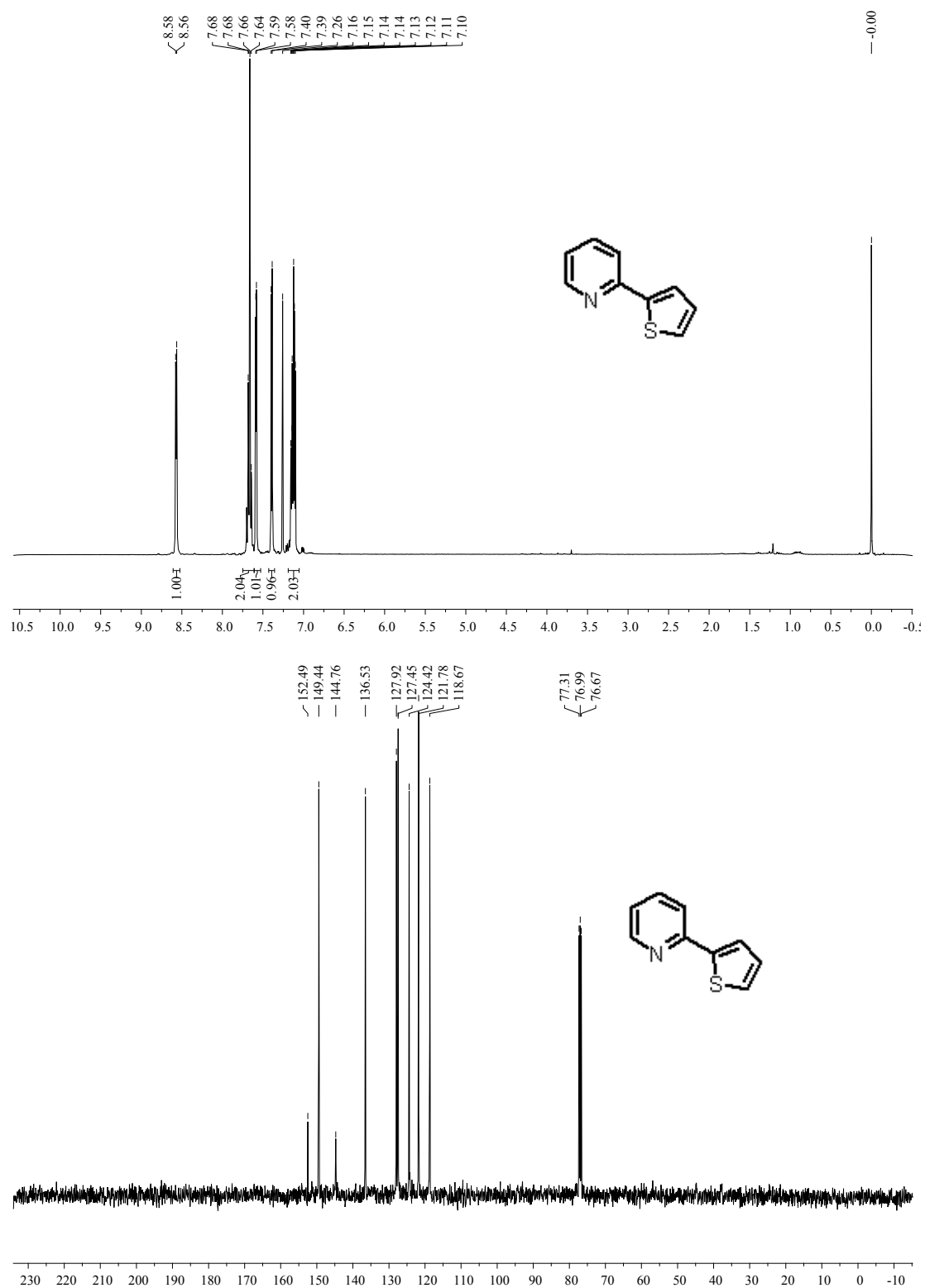


Figure S18. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-(thiophen-2-yl)pyridine (**3n**)

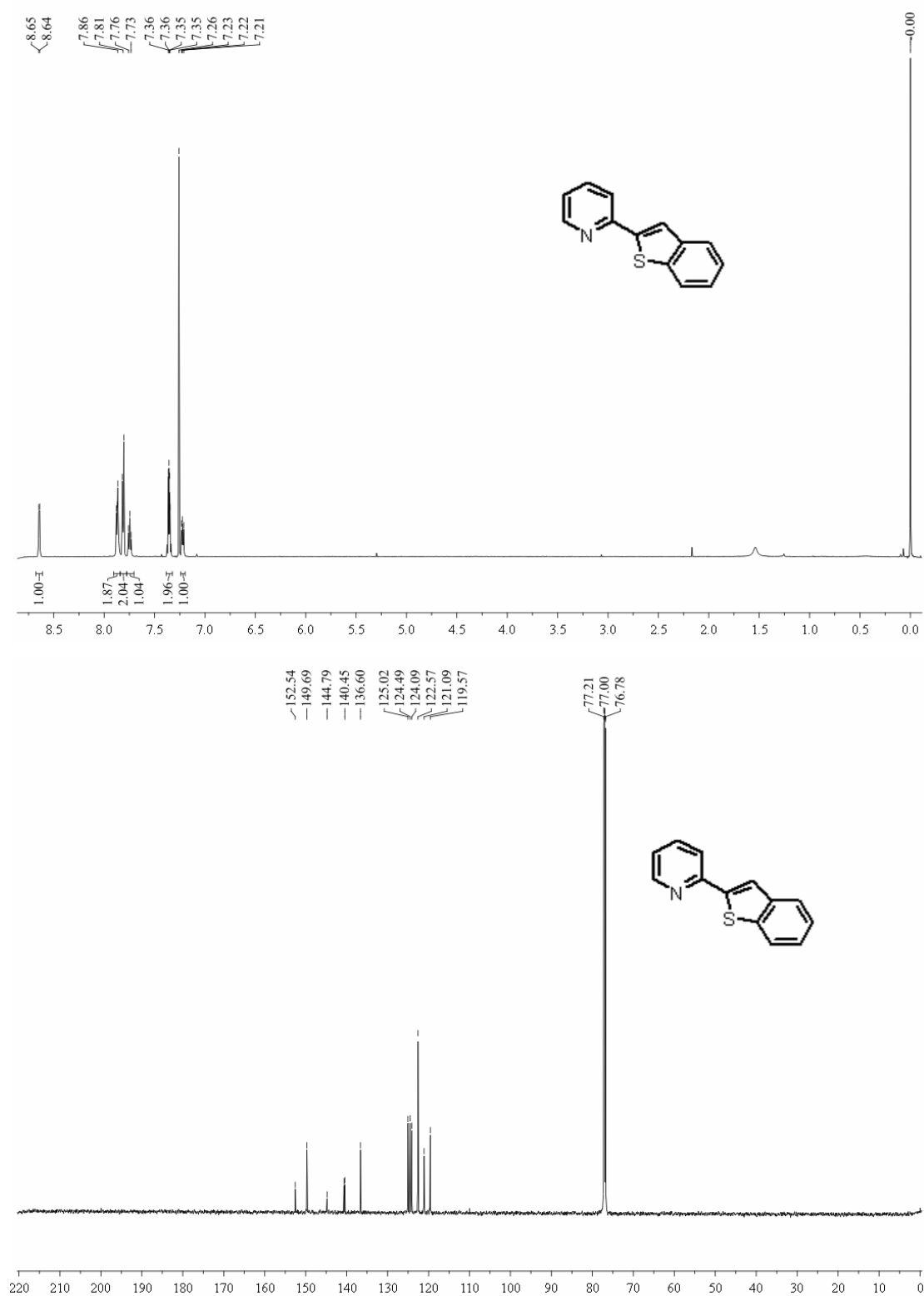


Figure S19. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-(benzo[b]thiophen-2-yl)pyridine (**30**)

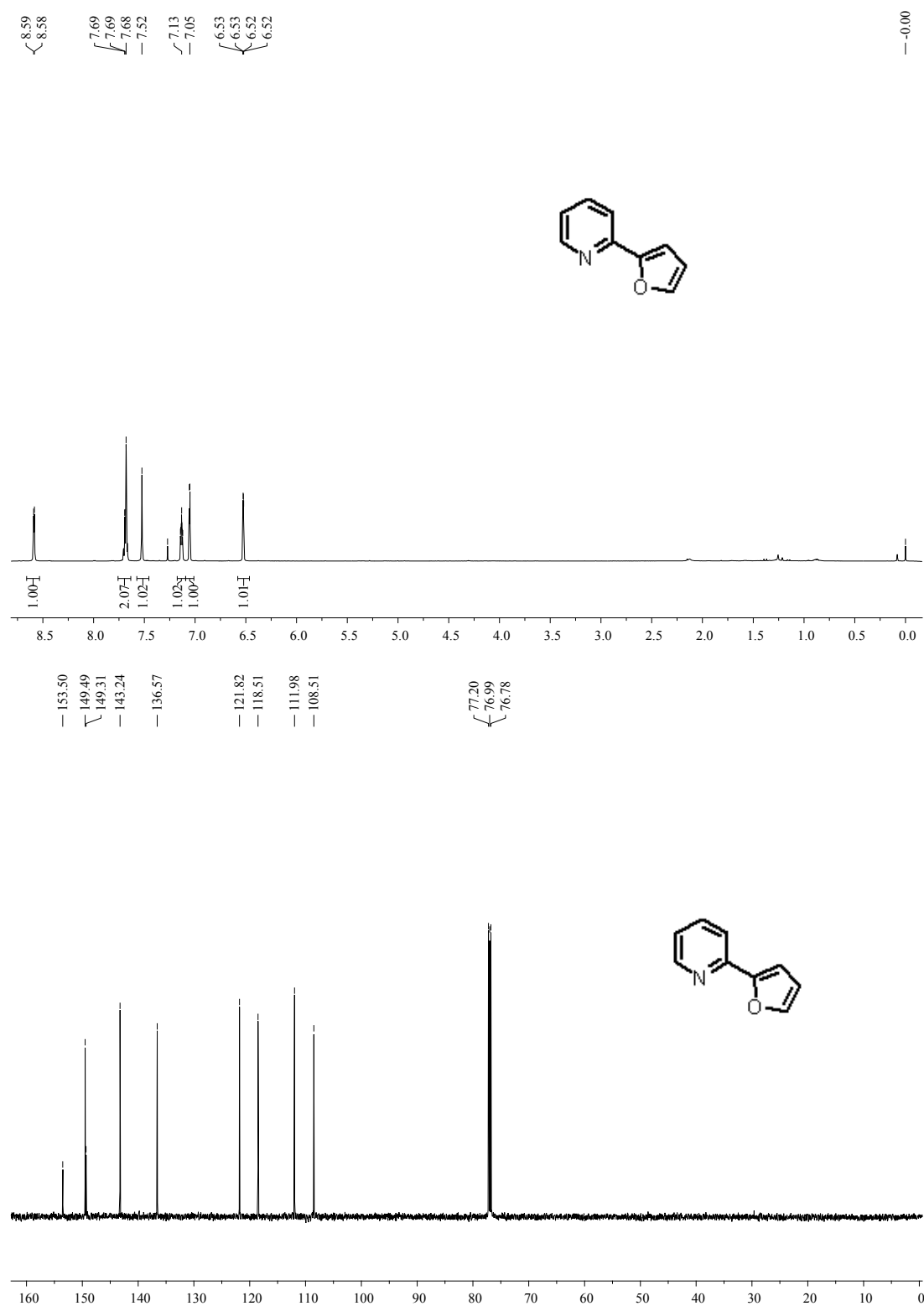


Figure S20. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-(furan-2-yl)pyridine (**3p**)

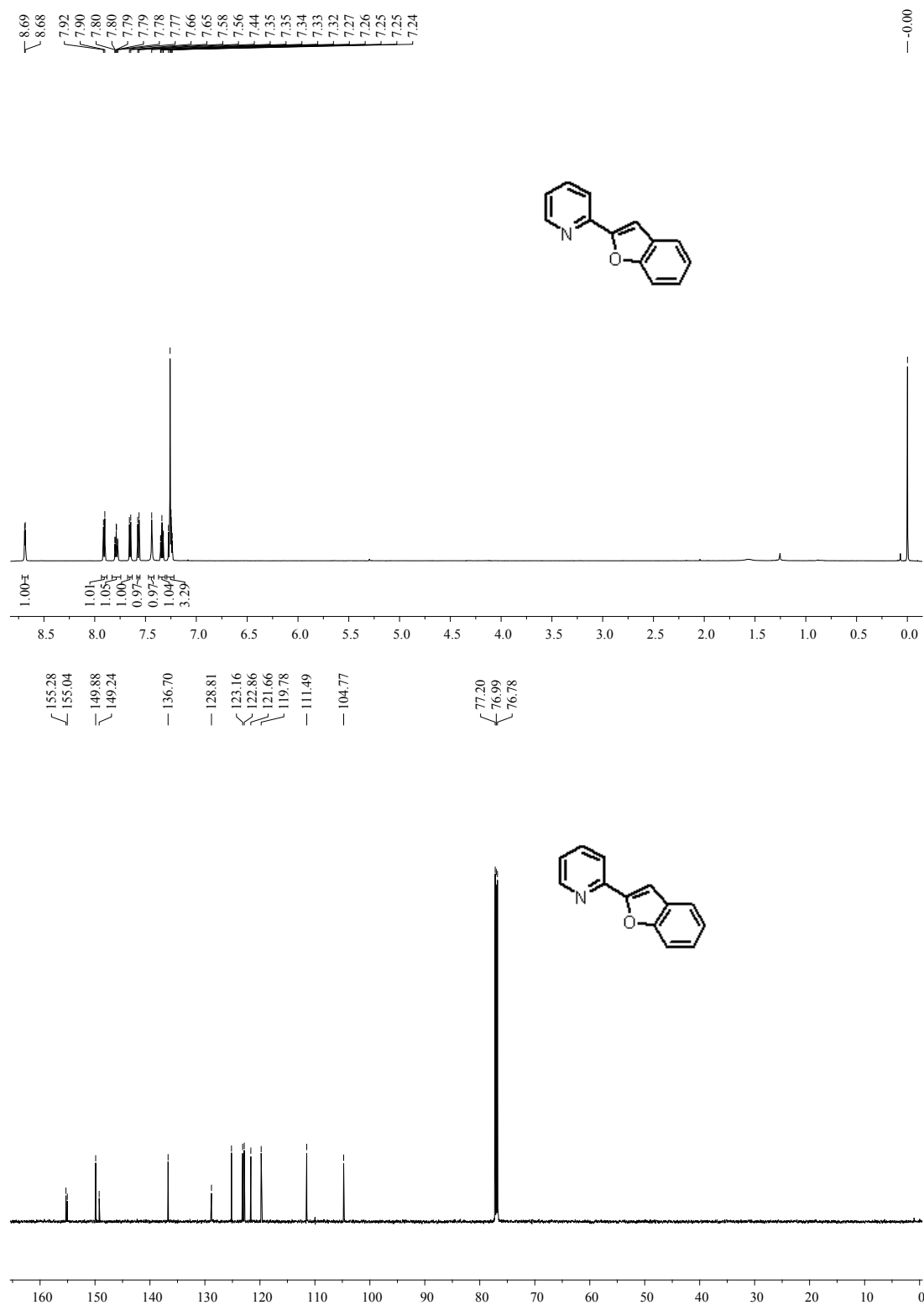


Figure S21. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-(benzofuran-2-yl)pyridine (**3q**)

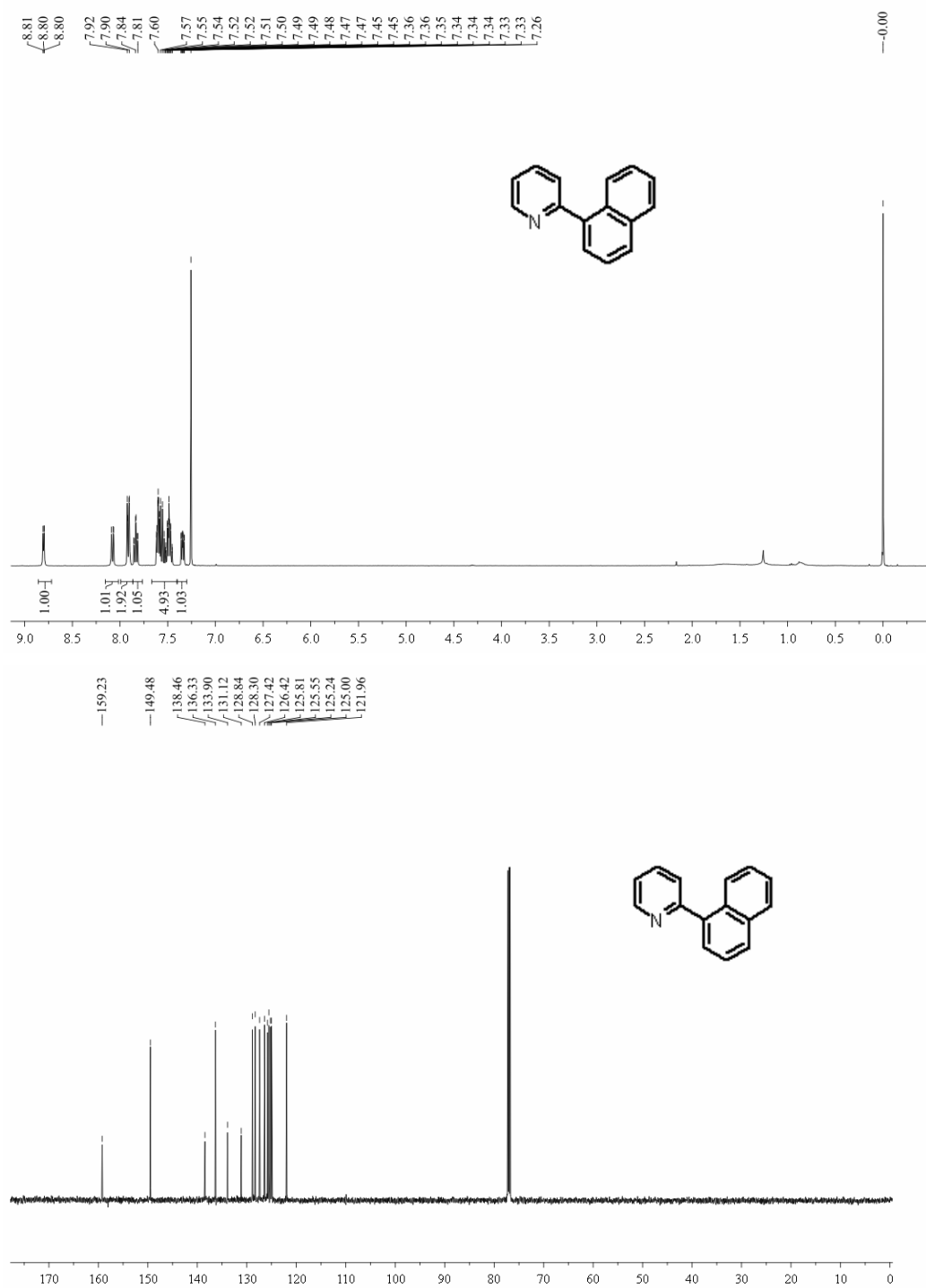


Figure S22. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-(naphthalen-1-yl)pyridine (**3r**)

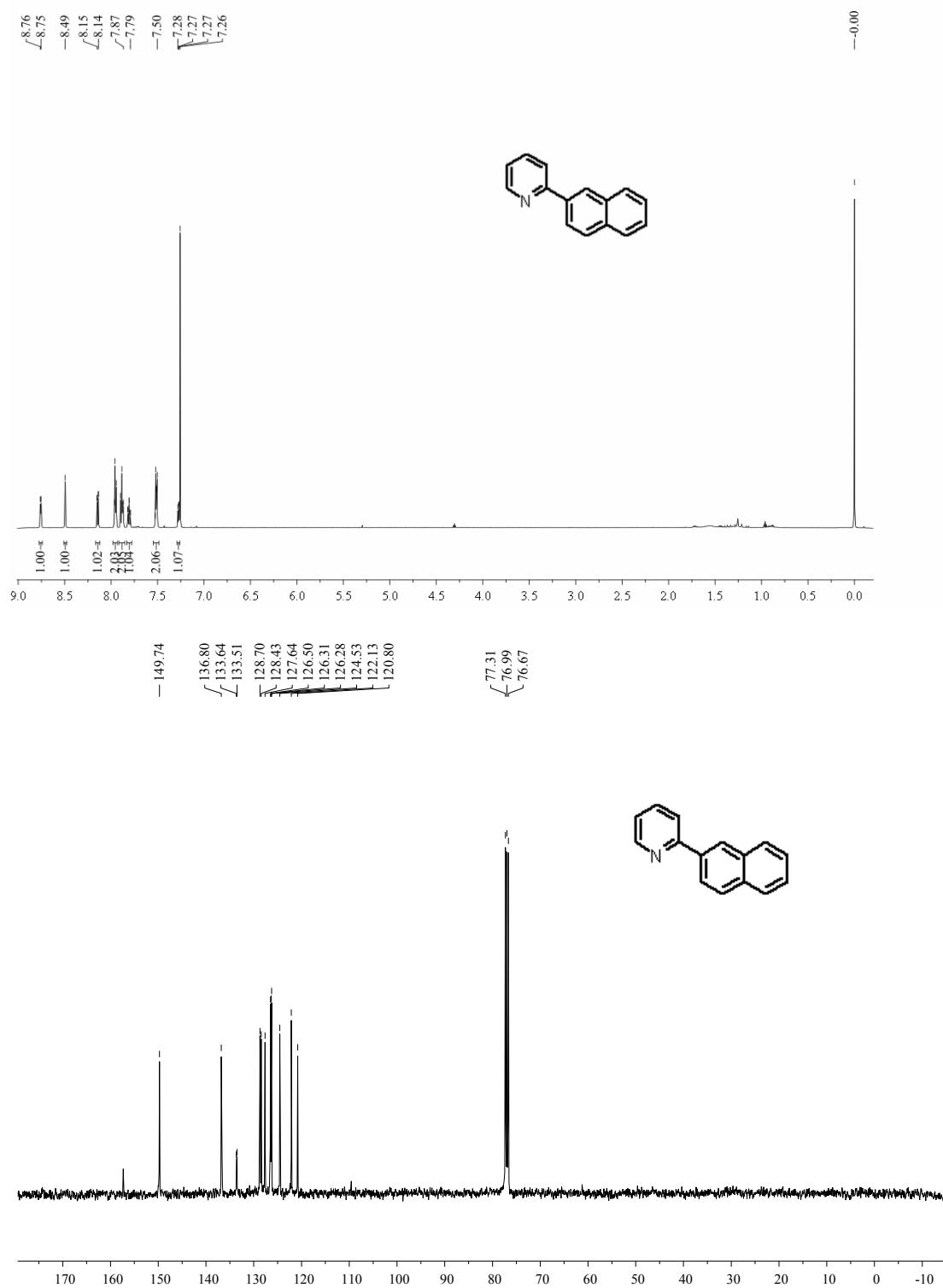


Figure S23. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-(naphthalen-2-yl)pyridine (**3s**)

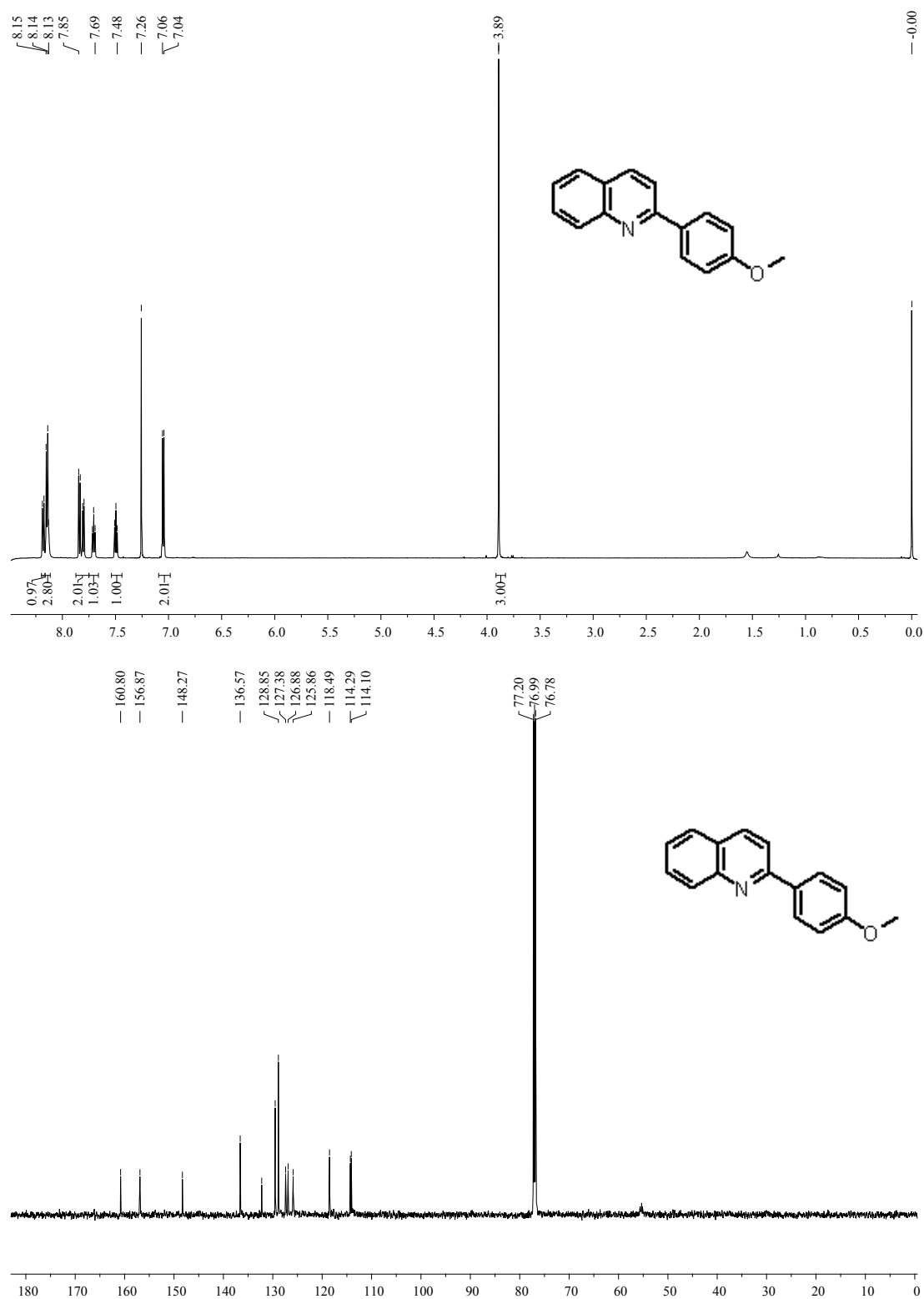


Figure S24. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-(4-methoxyphenyl)quinoline (**5a**)



Figure S25. ¹H- (upper) and ¹³C-NMR (lower) spectra of 3-(quinolin-2-yl)benzenamine (**5b**)

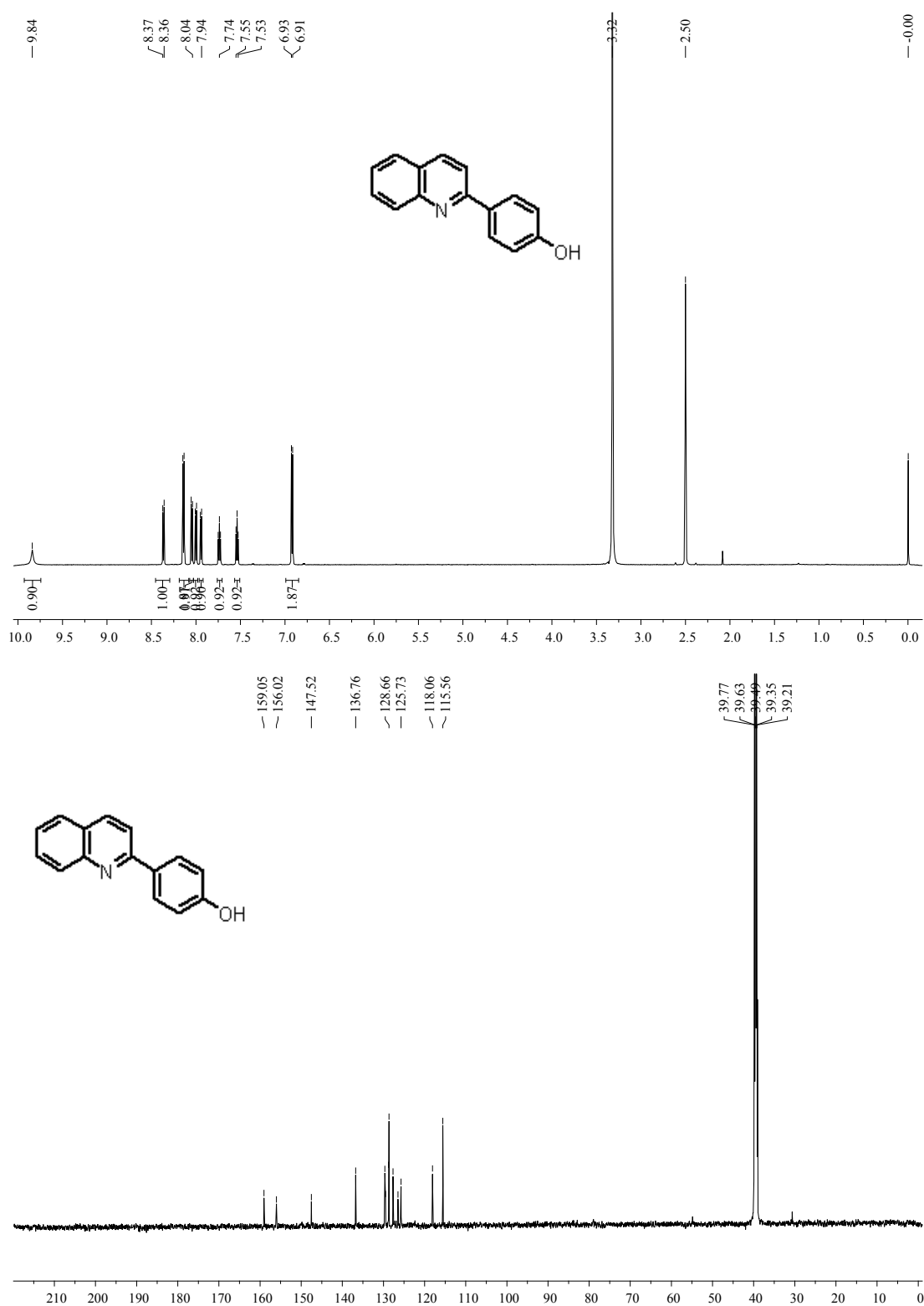


Figure S26. ¹H- (upper) and ¹³C-NMR (lower) spectra of 4-(quinolin-2-yl)phenol (5c)

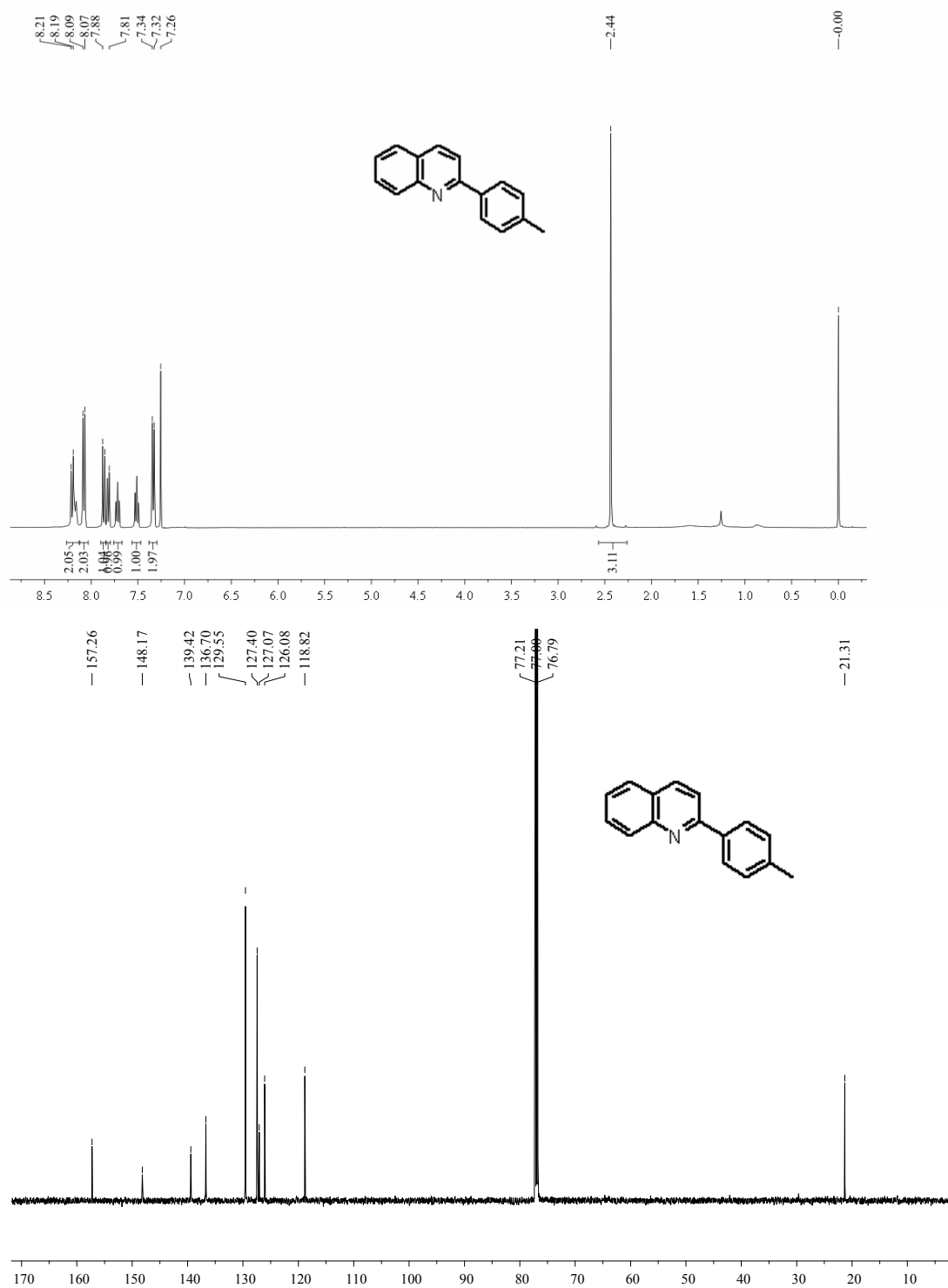


Figure S27. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-p-tolylquinoline (**5d**)

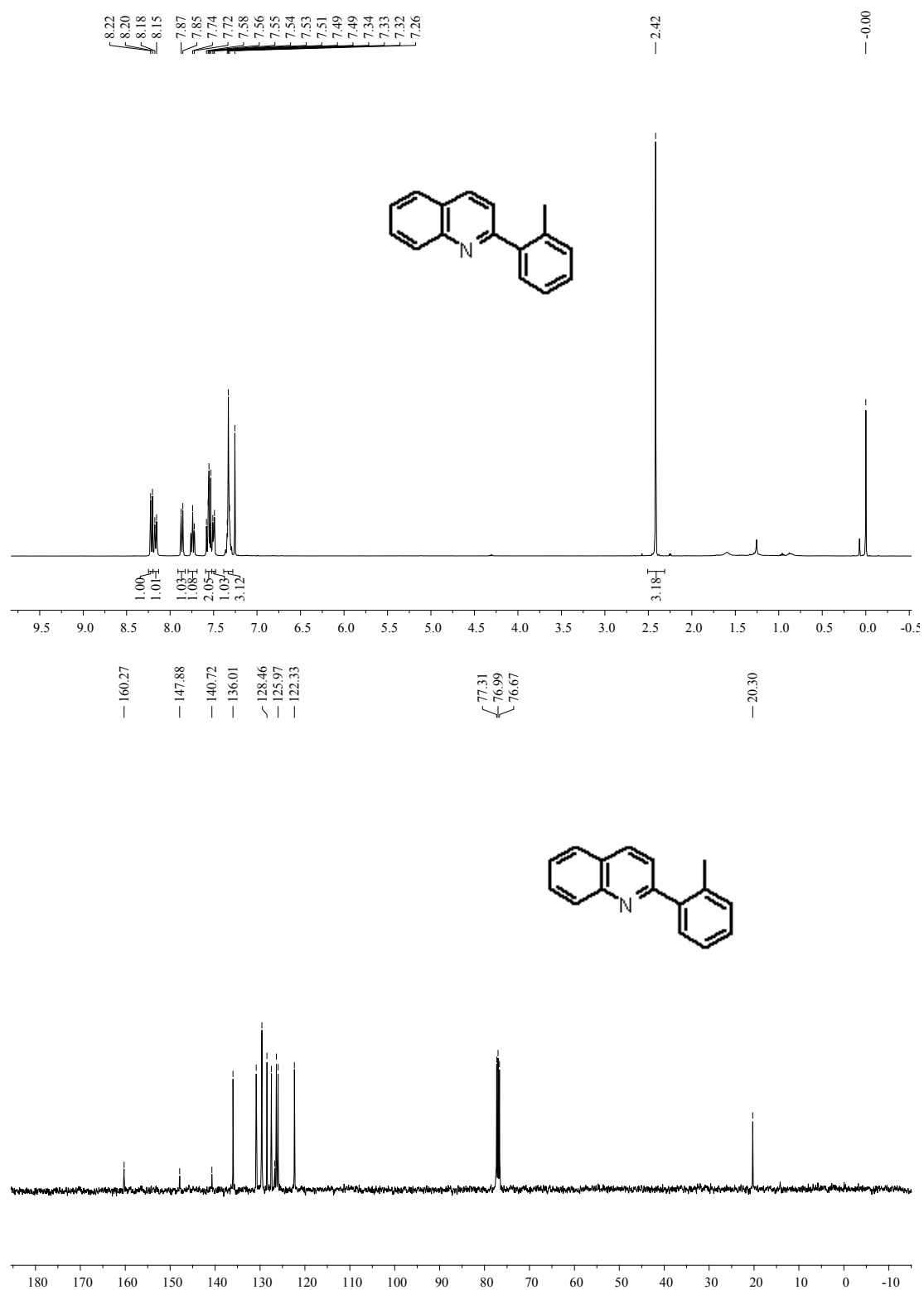


Figure S28. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-o-tolylquinoline (**5e**)

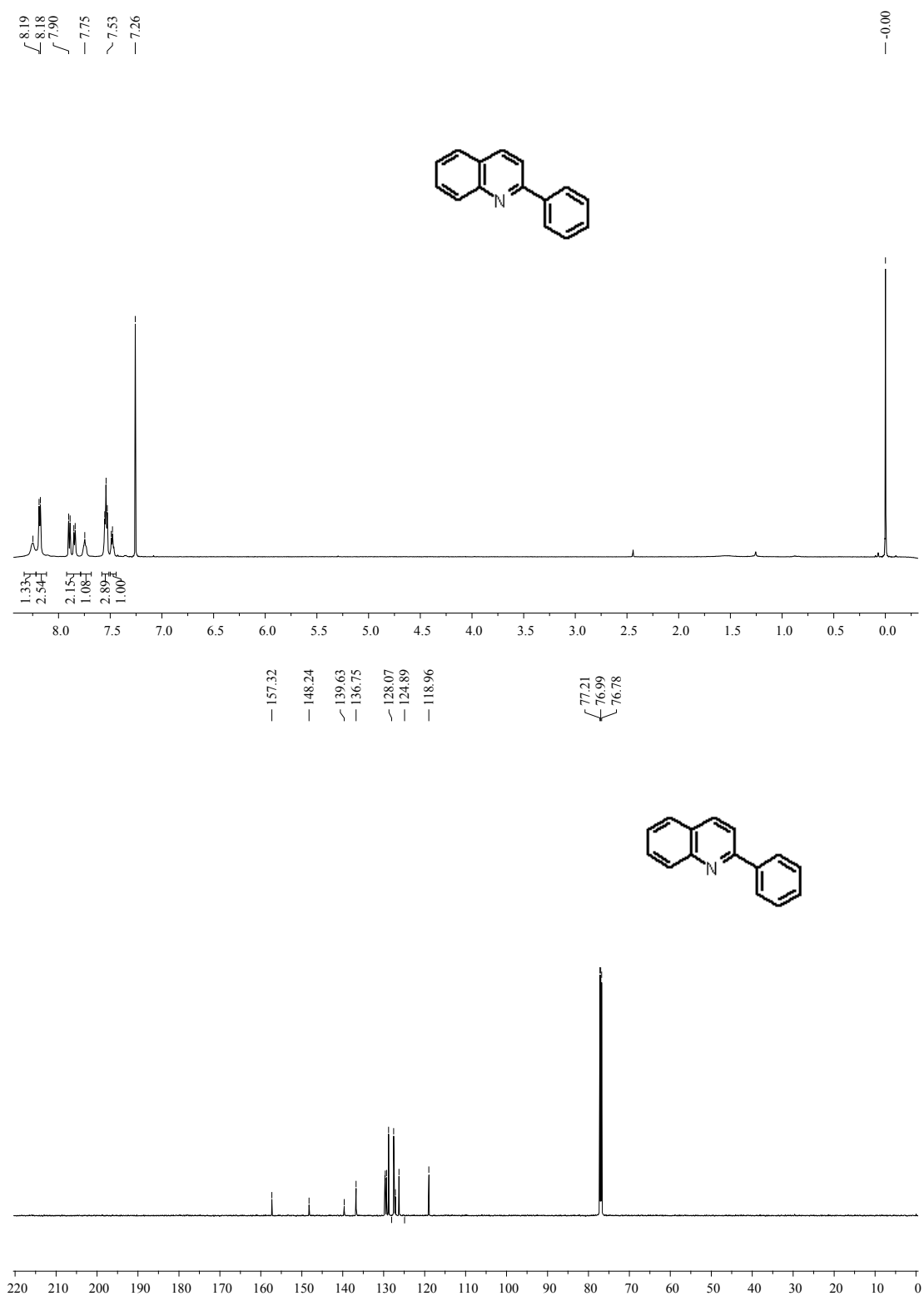


Figure S29. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-phenylquinoline (**5f**)

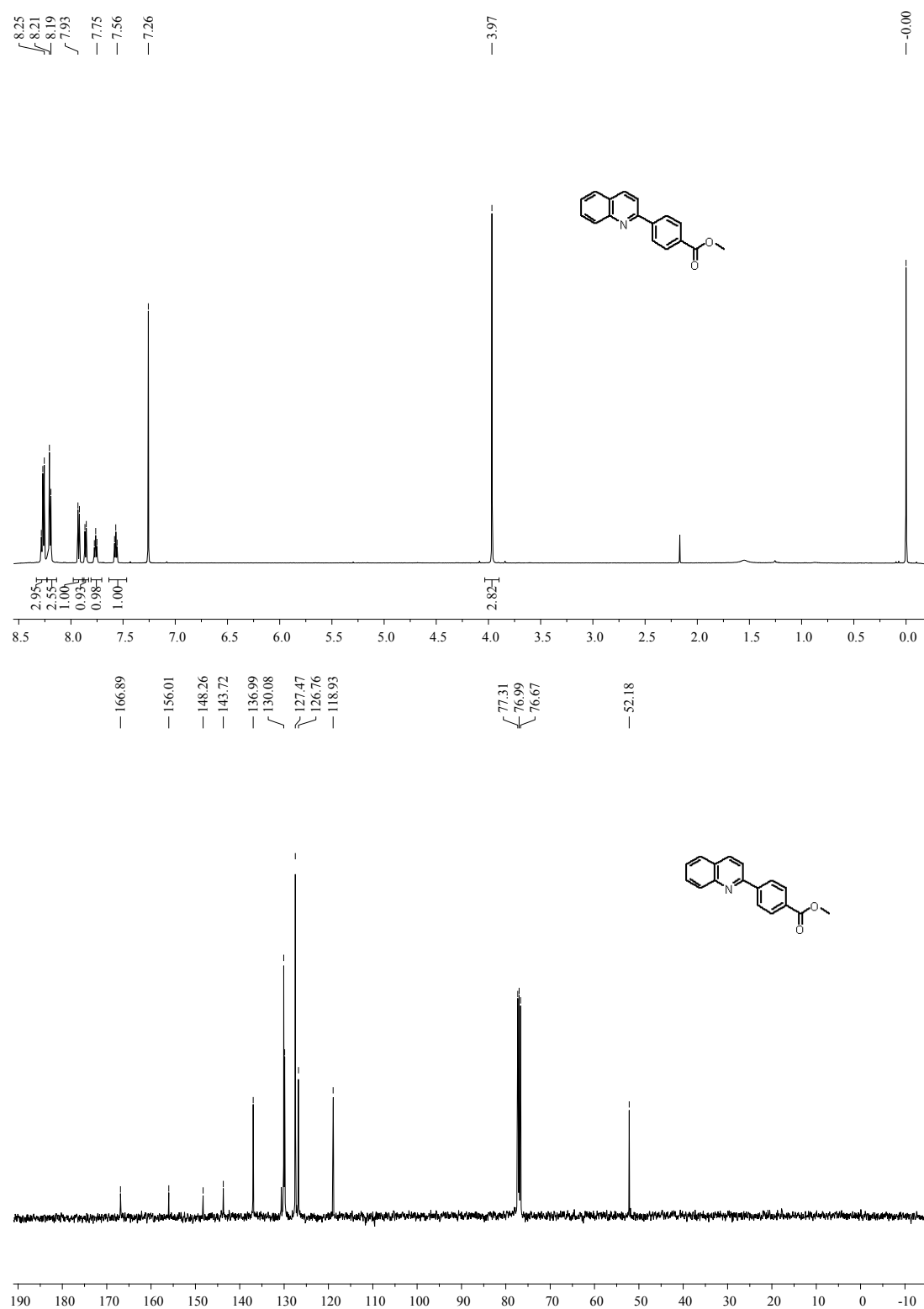


Figure S30. ¹H- (upper) and ¹³C-NMR (lower) spectra of methyl 4-(quinolin-2-yl)benzoate (**5g**)

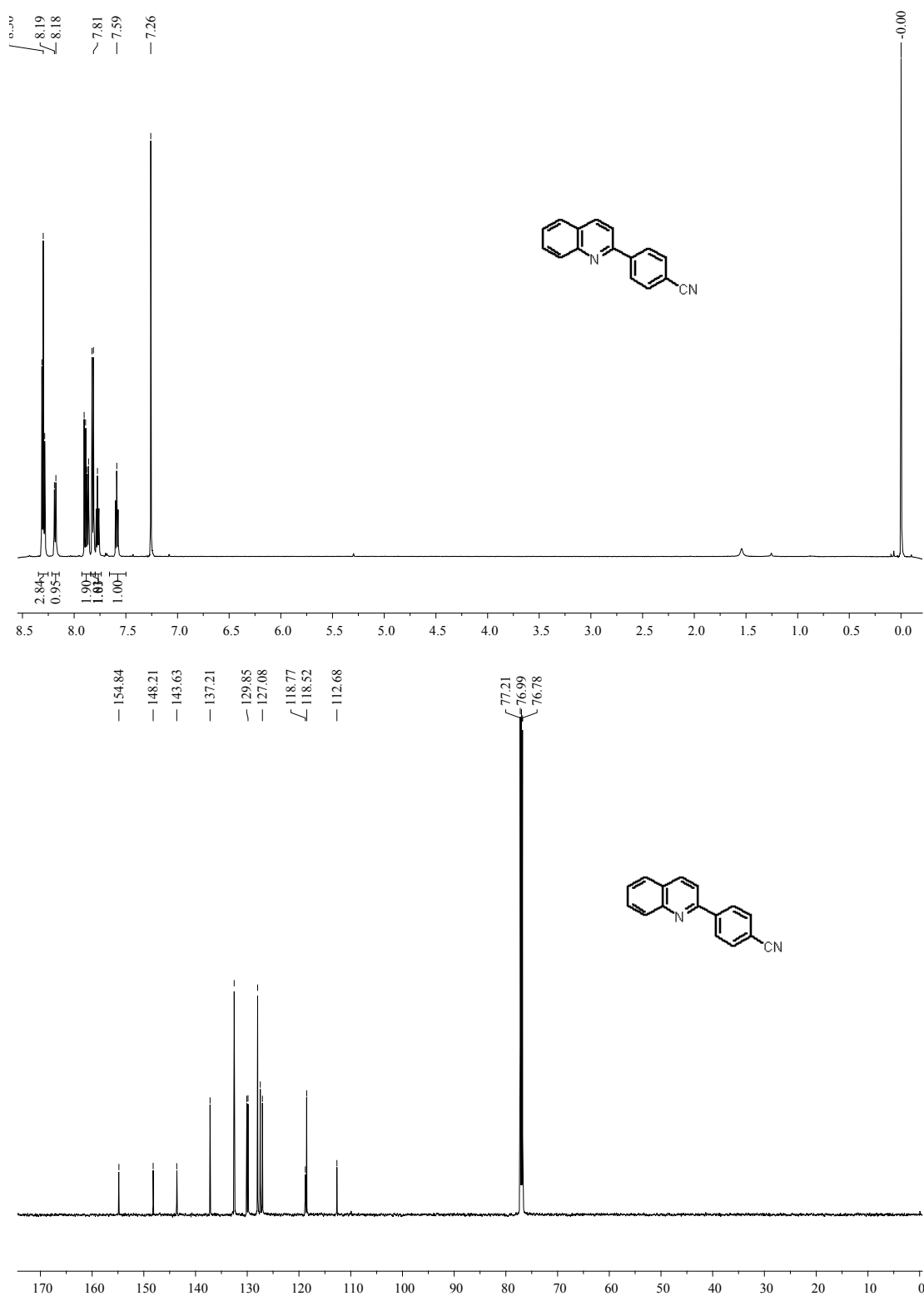


Figure S31. ¹H- (upper) and ¹³C-NMR (lower) spectra of 4-(quinolin-2-yl)benzonitrile (**5h**)

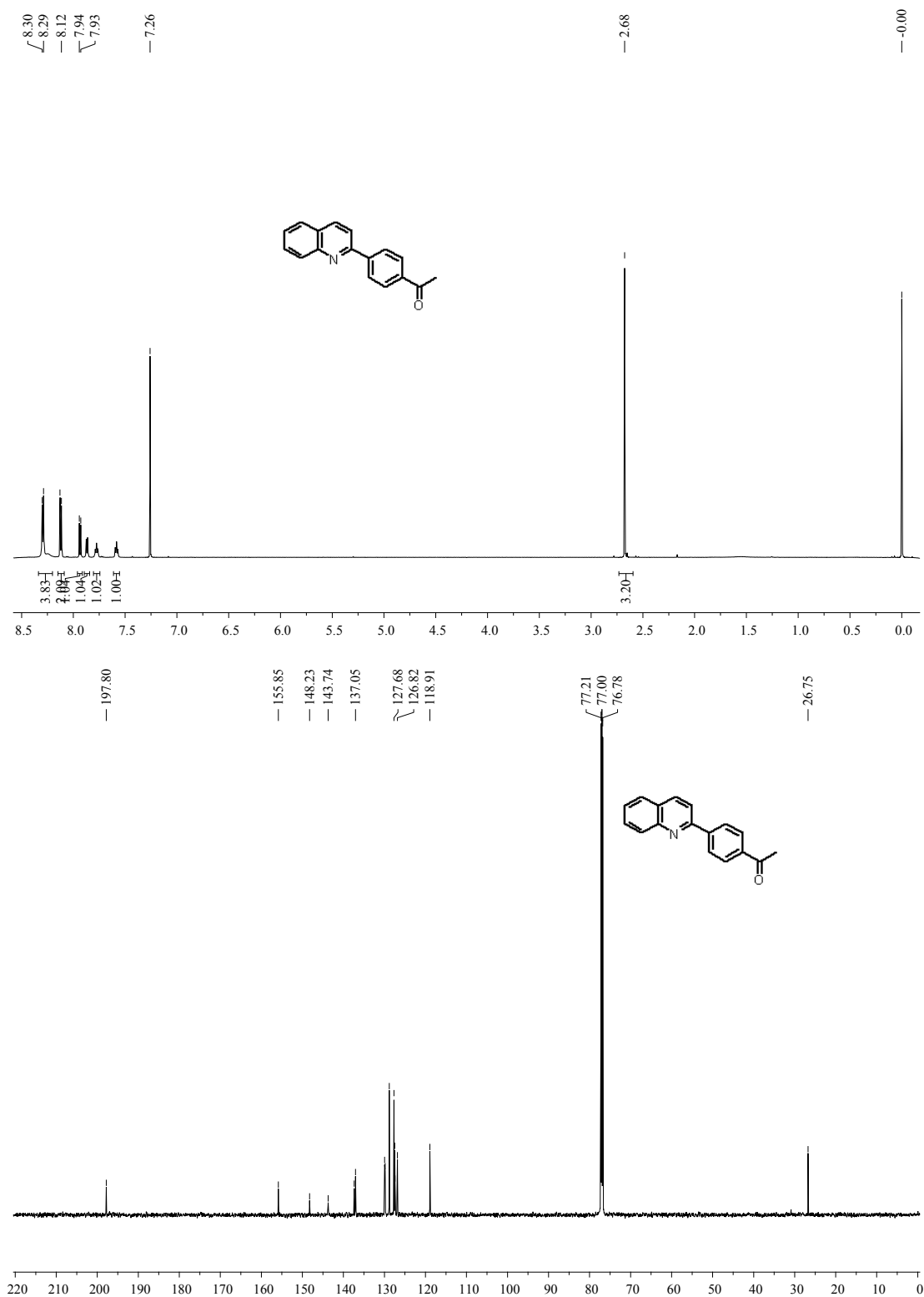


Figure S32. ¹H- (upper) and ¹³C-NMR (lower) spectra of 1-(4-(quinolin-2-yl)phenyl)ethanone (5i)

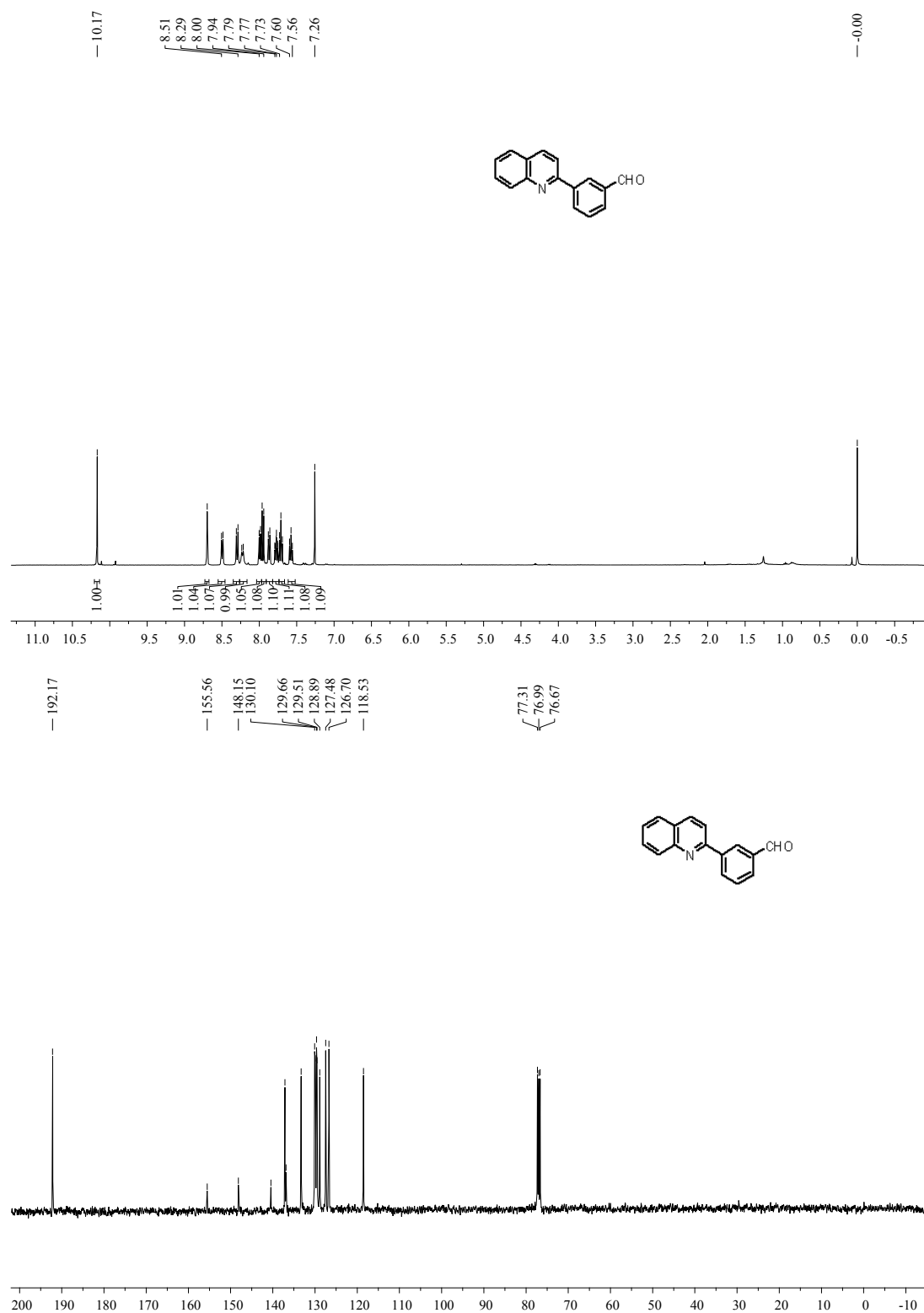


Figure S33. ¹H- (upper) and ¹³C-NMR (lower) spectra of 3-(quinolin-2-yl)benzaldehyde (**5j**)

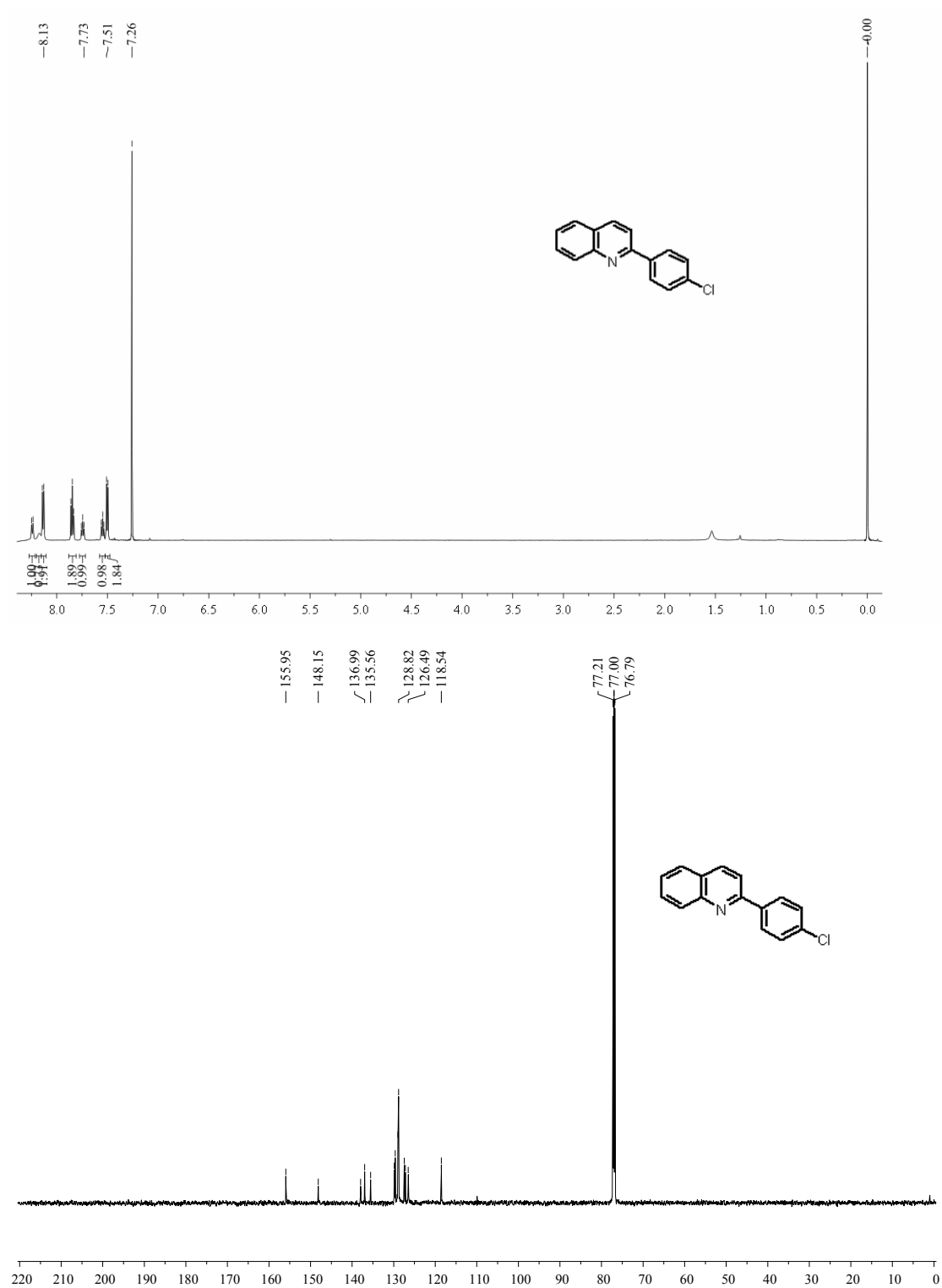


Figure S34. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-(4-chlorophenyl)quinoline (**5k**)

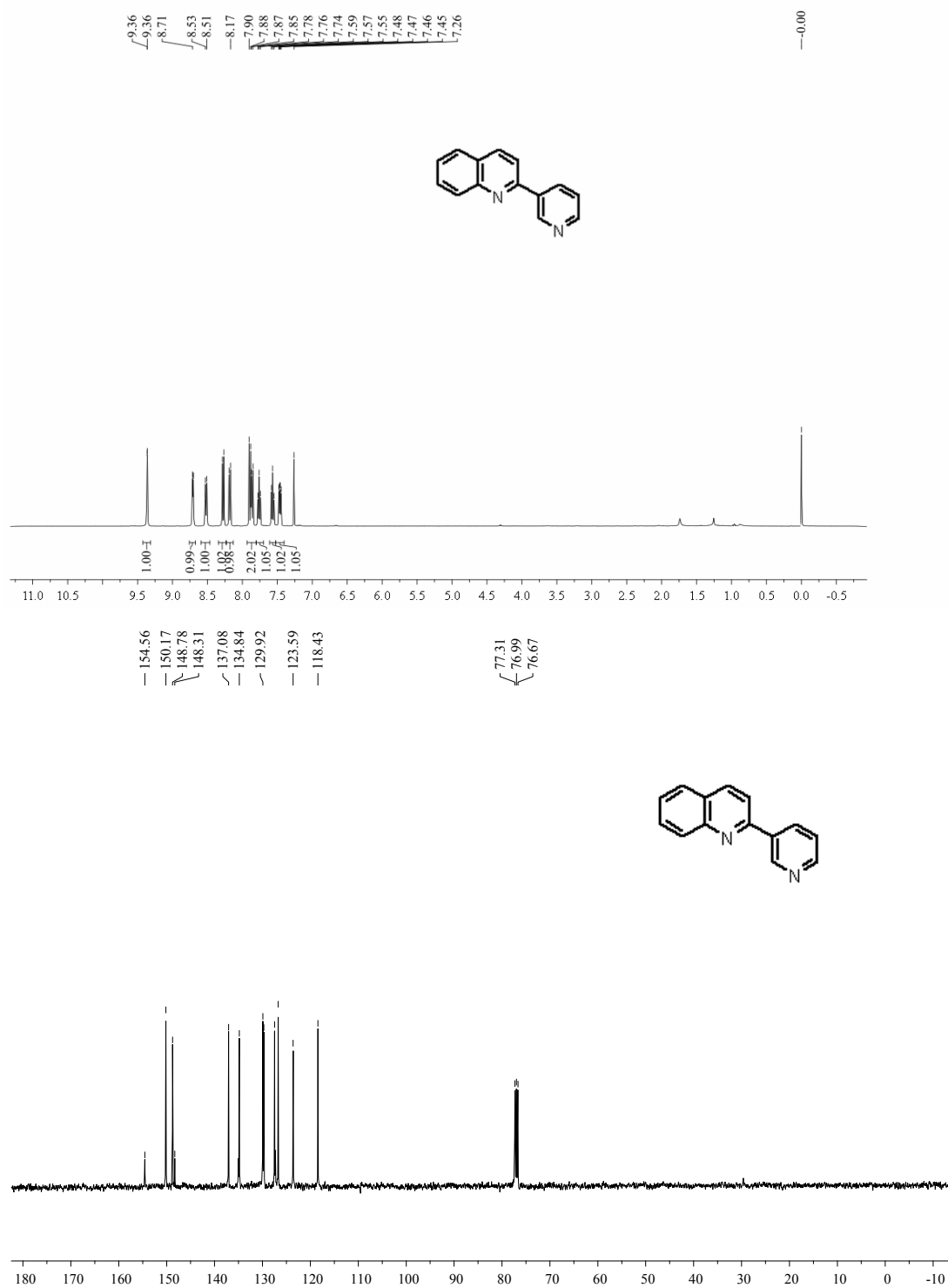


Figure S35. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-(pyridin-3-yl)quinoline (**51**)

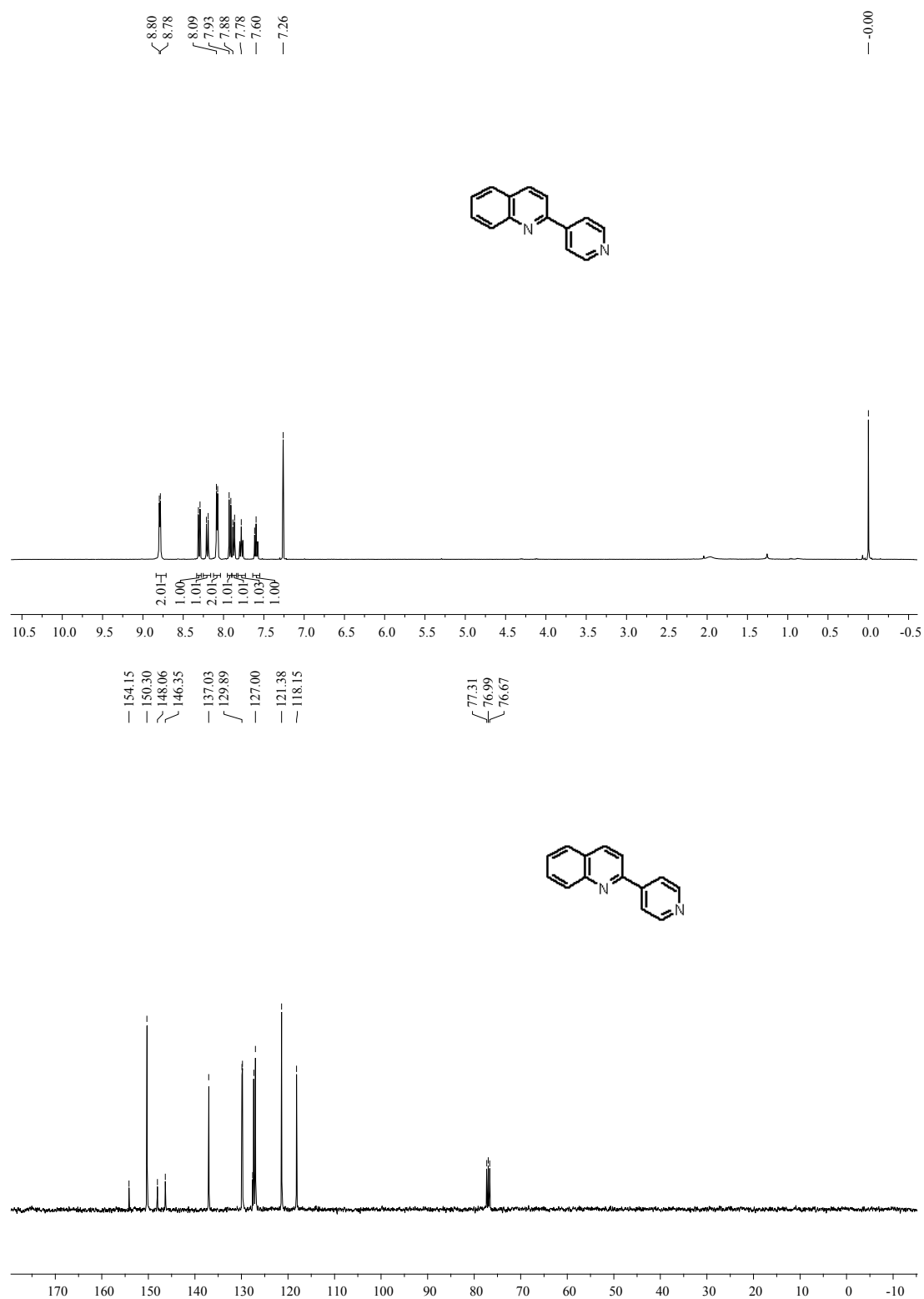


Figure S36. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-(pyridin-4-yl)quinoline (**5m**)

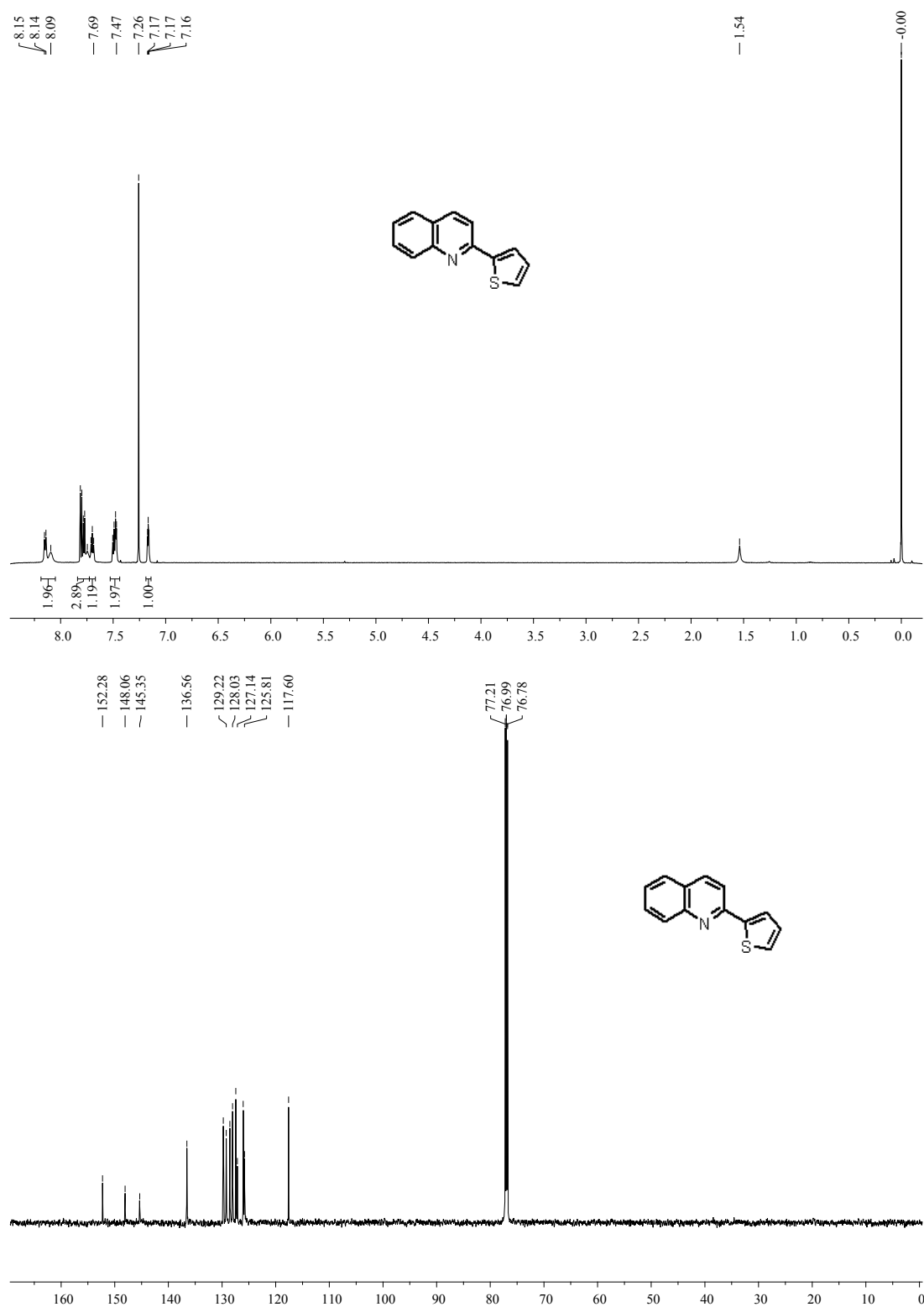


Figure S37. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-(thiophen-2-yl)quinoline (**5n**)

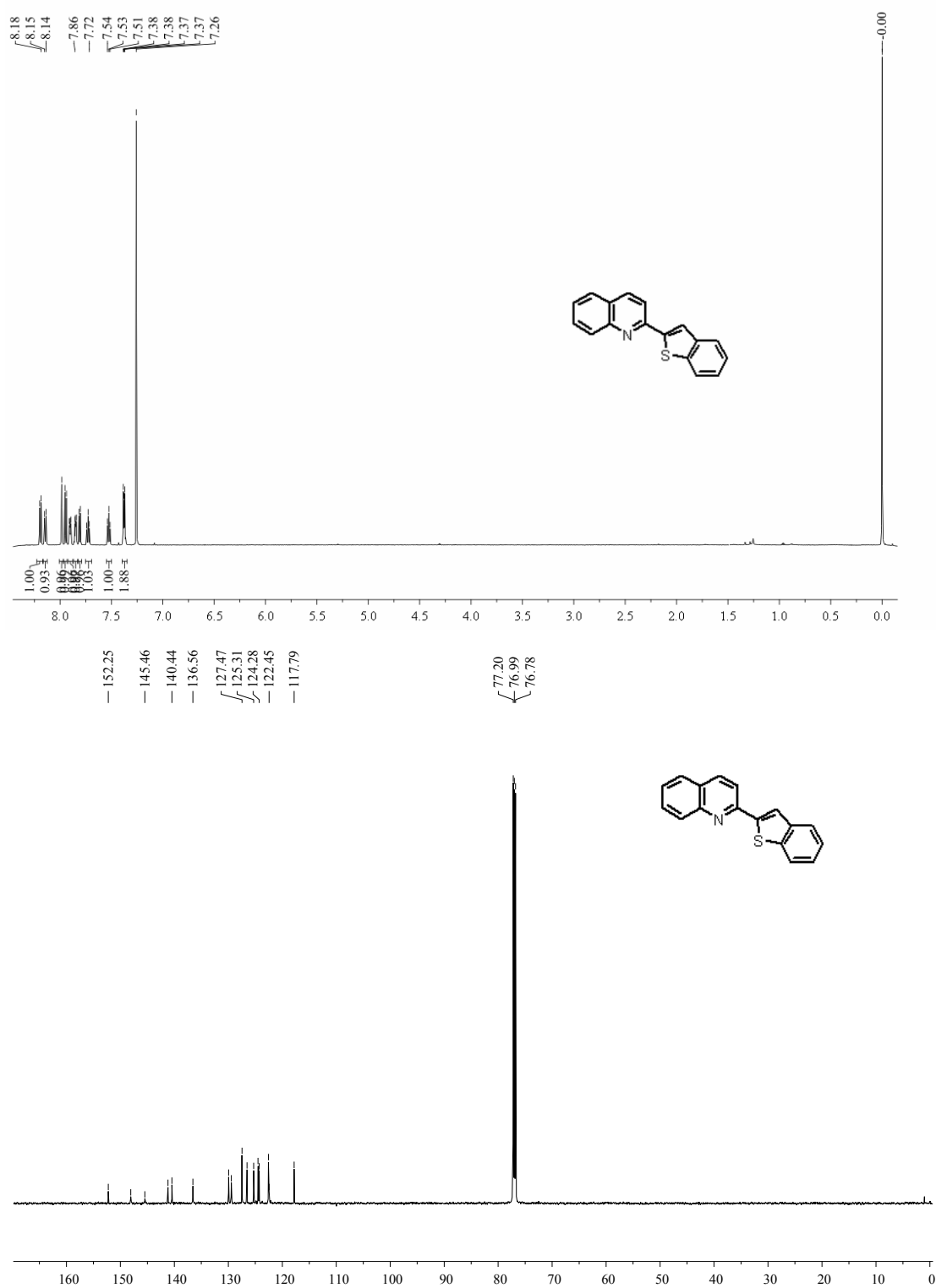


Figure S38. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-(benzo[b]thiophen-2-yl)quinoline (**50**)

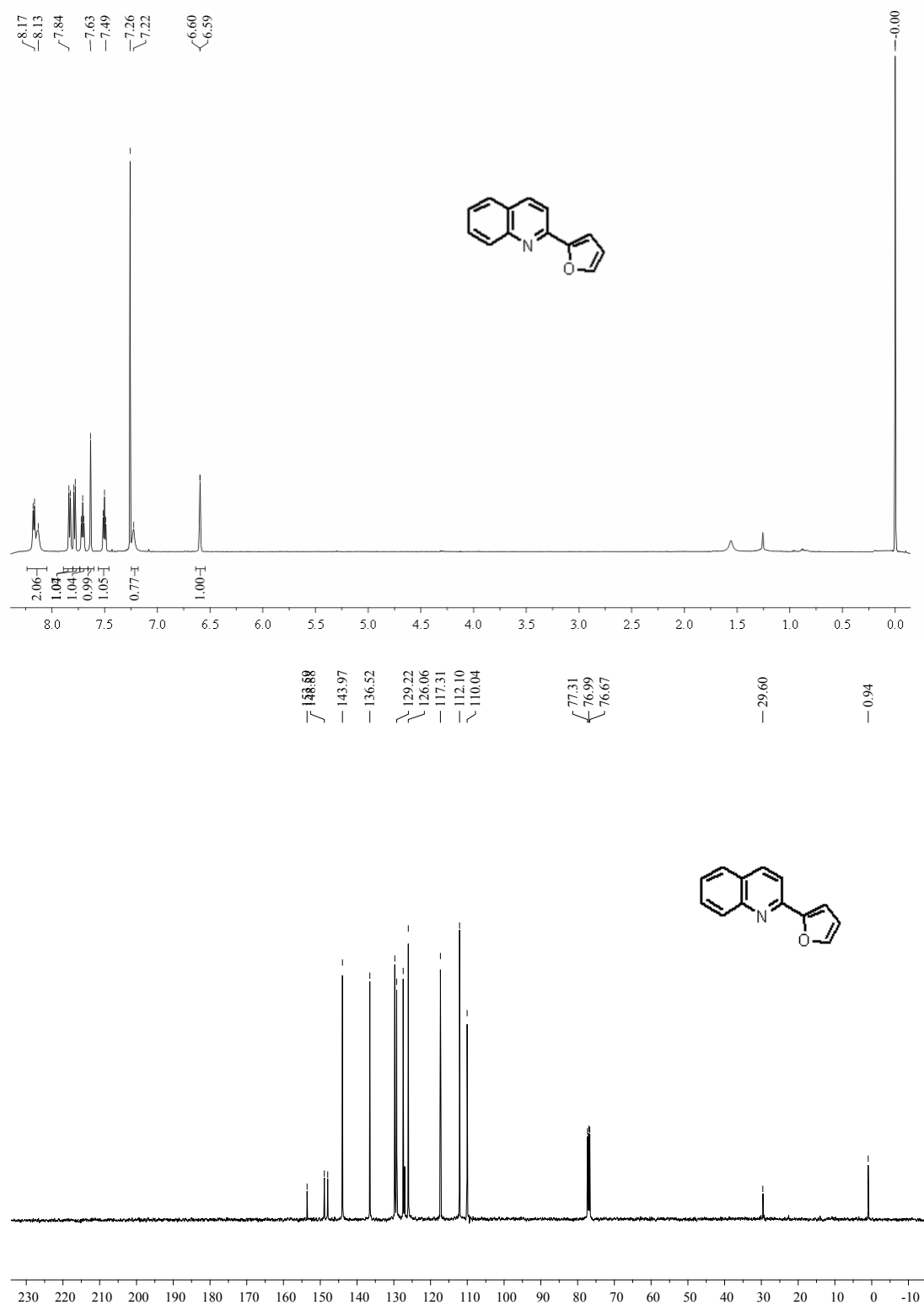


Figure S39. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-(furan-2-yl)quinoline (**5p**)

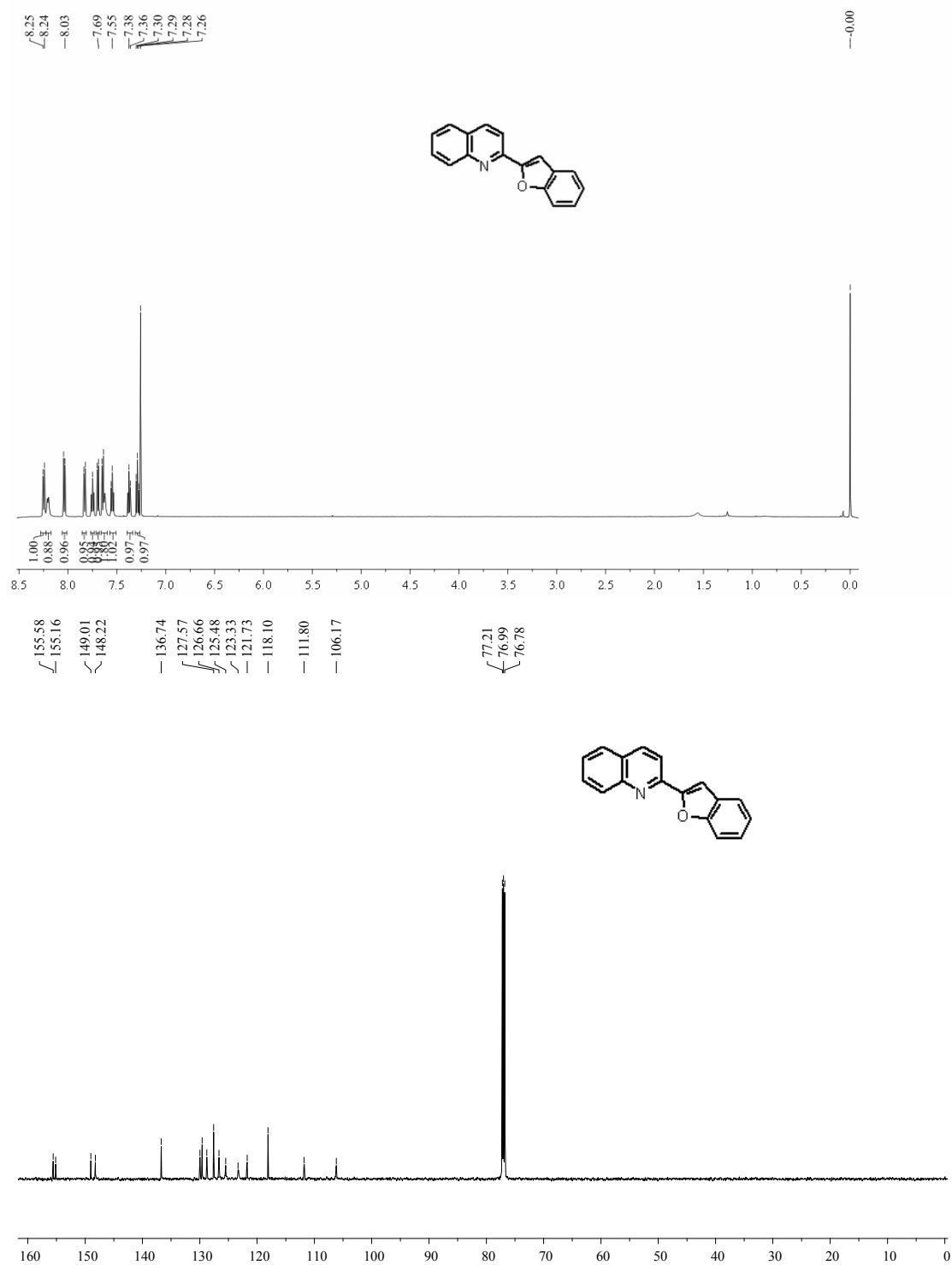


Figure S40. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-(benzofuran-2-yl)quinoline (**5q**)

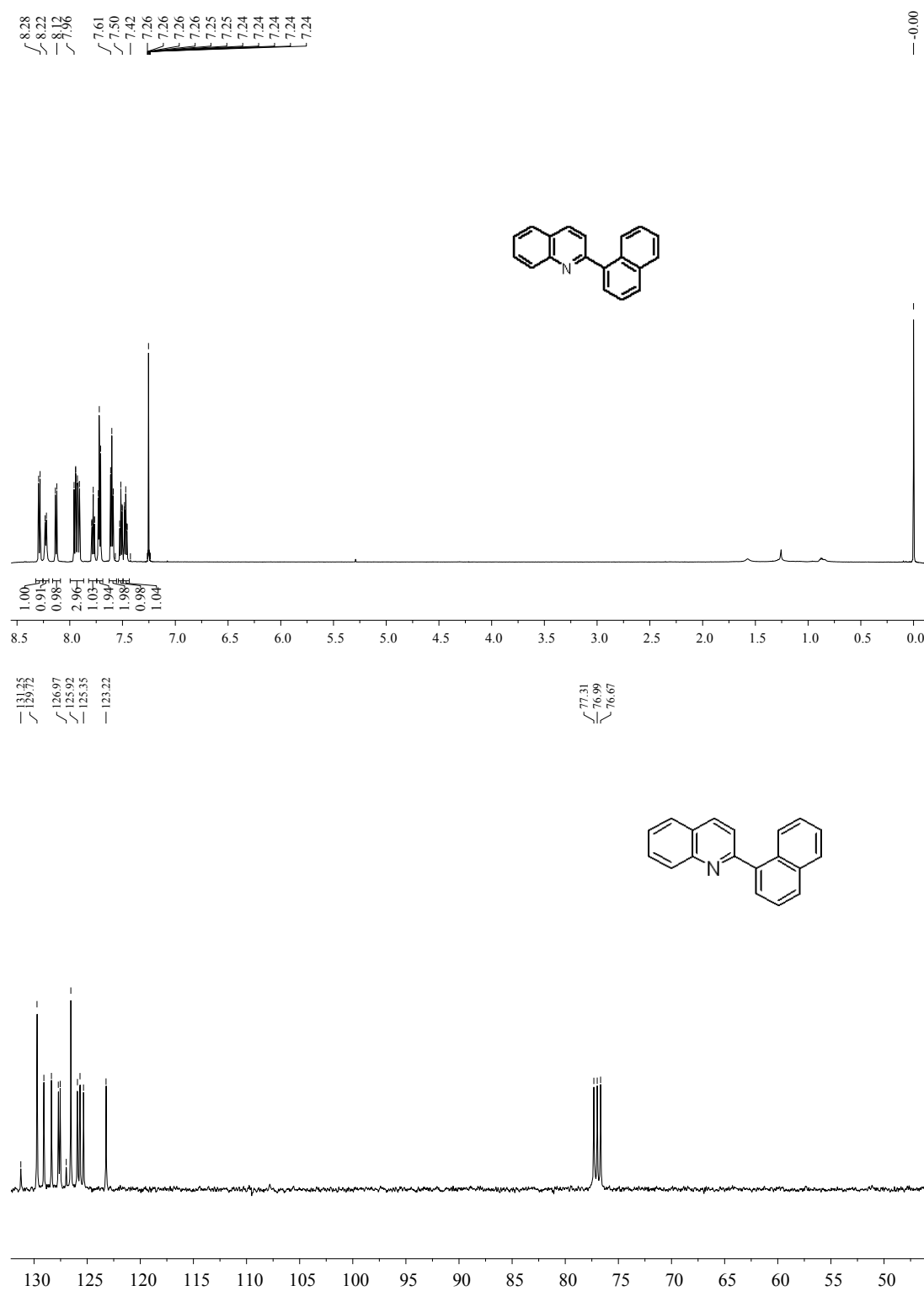


Figure S41. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-(naphthalen-1-yl)quinoline (**5r**)

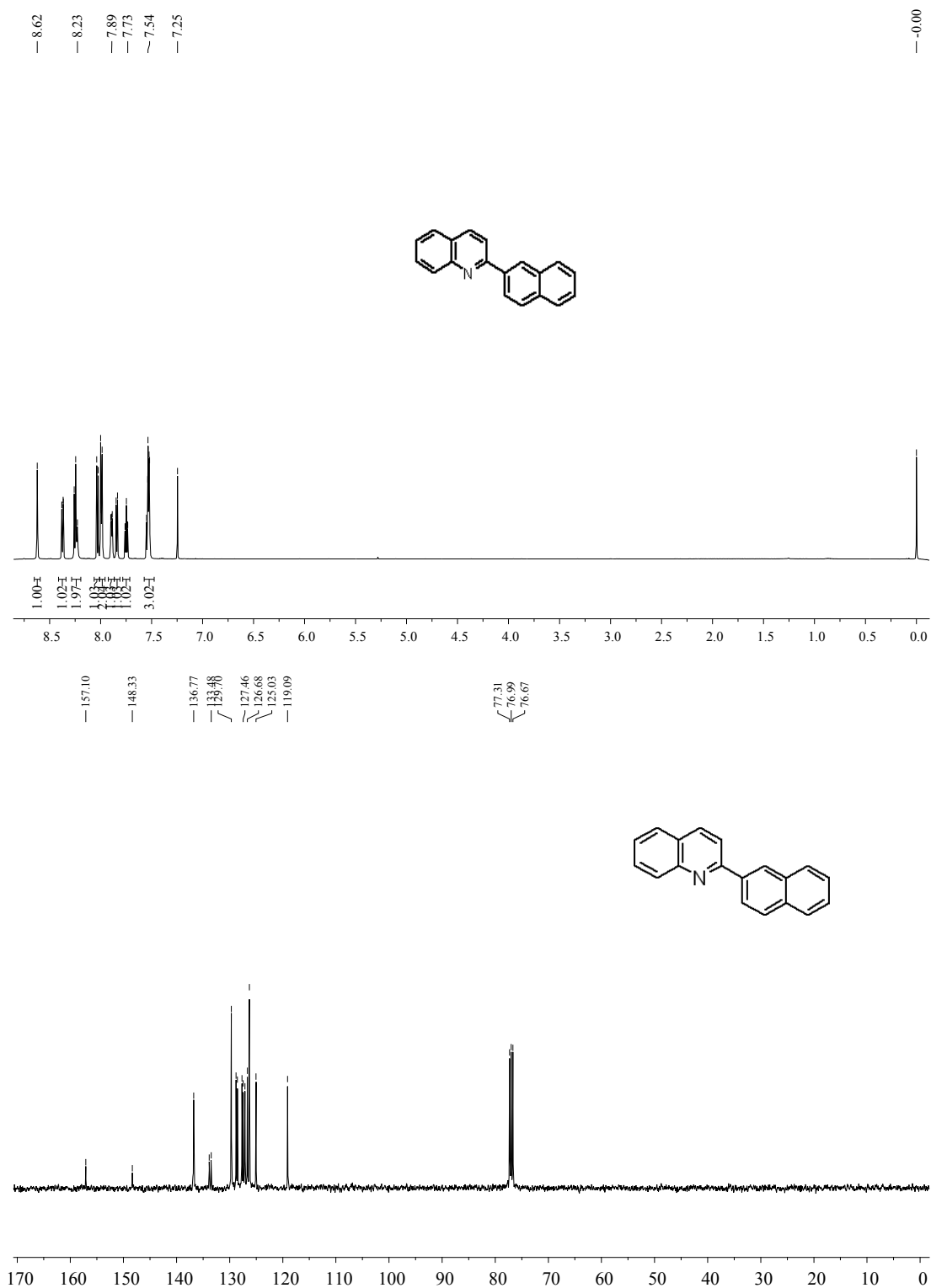


Figure S42. ¹H- (upper) and ¹³C-NMR (lower) spectra of 2-(naphthalen-2-yl)quinoline (5s)

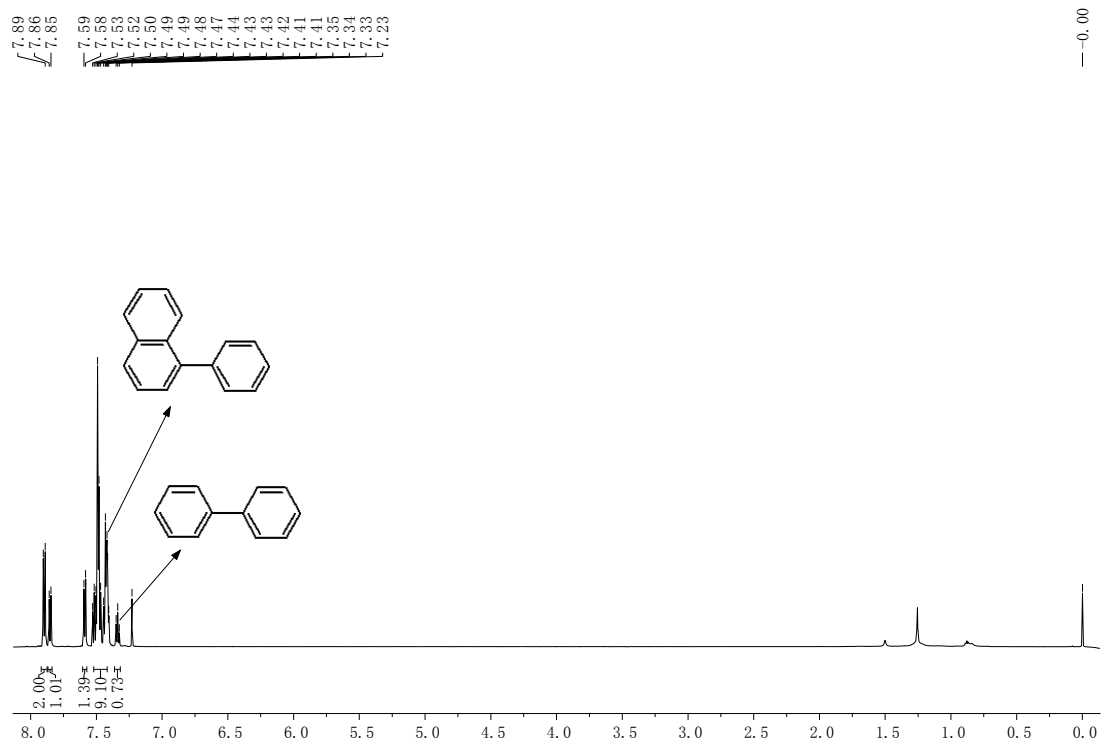


Figure S43. ¹H spectra of 1-phenylnaphthalene (7a)

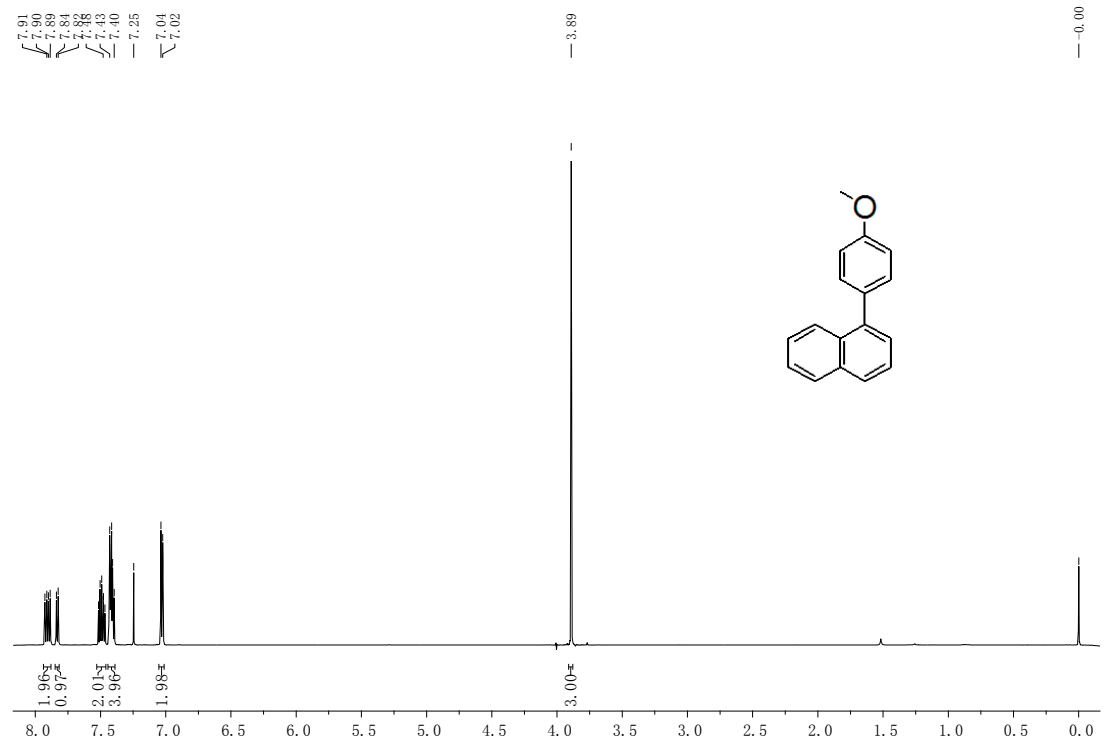


Figure S44. ¹H spectra of 1-(4-methoxyphenyl) naphthalene (7b)

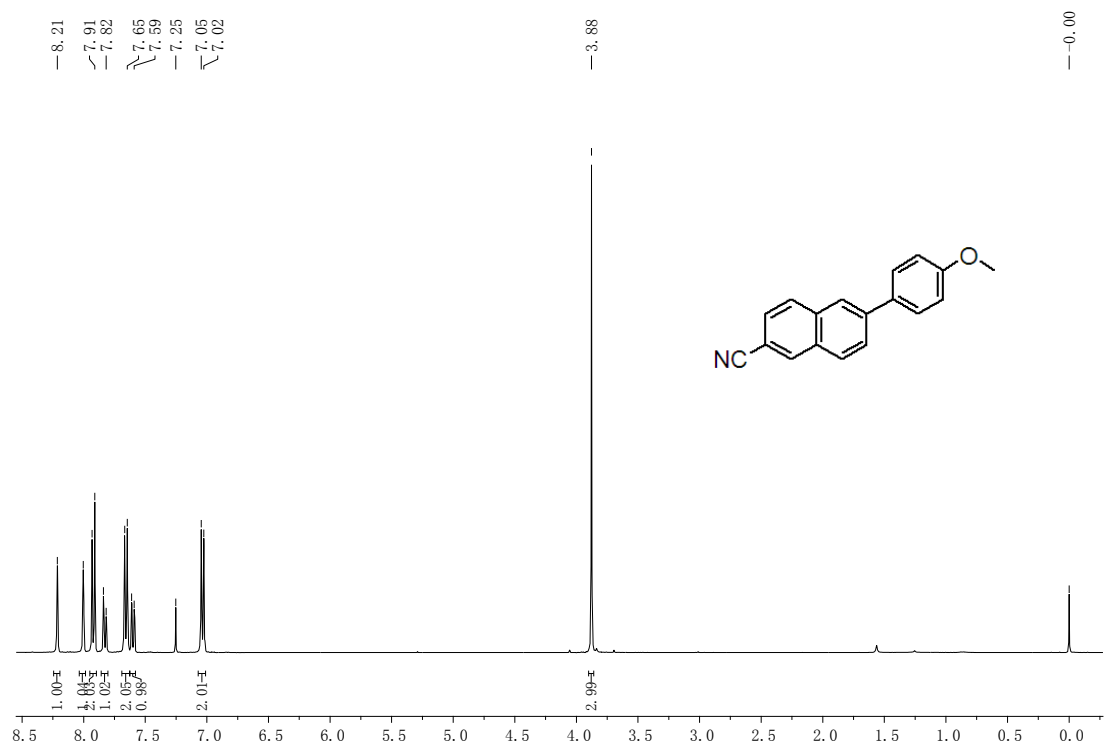


Figure S45. ¹H spectra of 6-(4-methoxyphenyl) naphthalene-2-carbonitrile (**7d**)

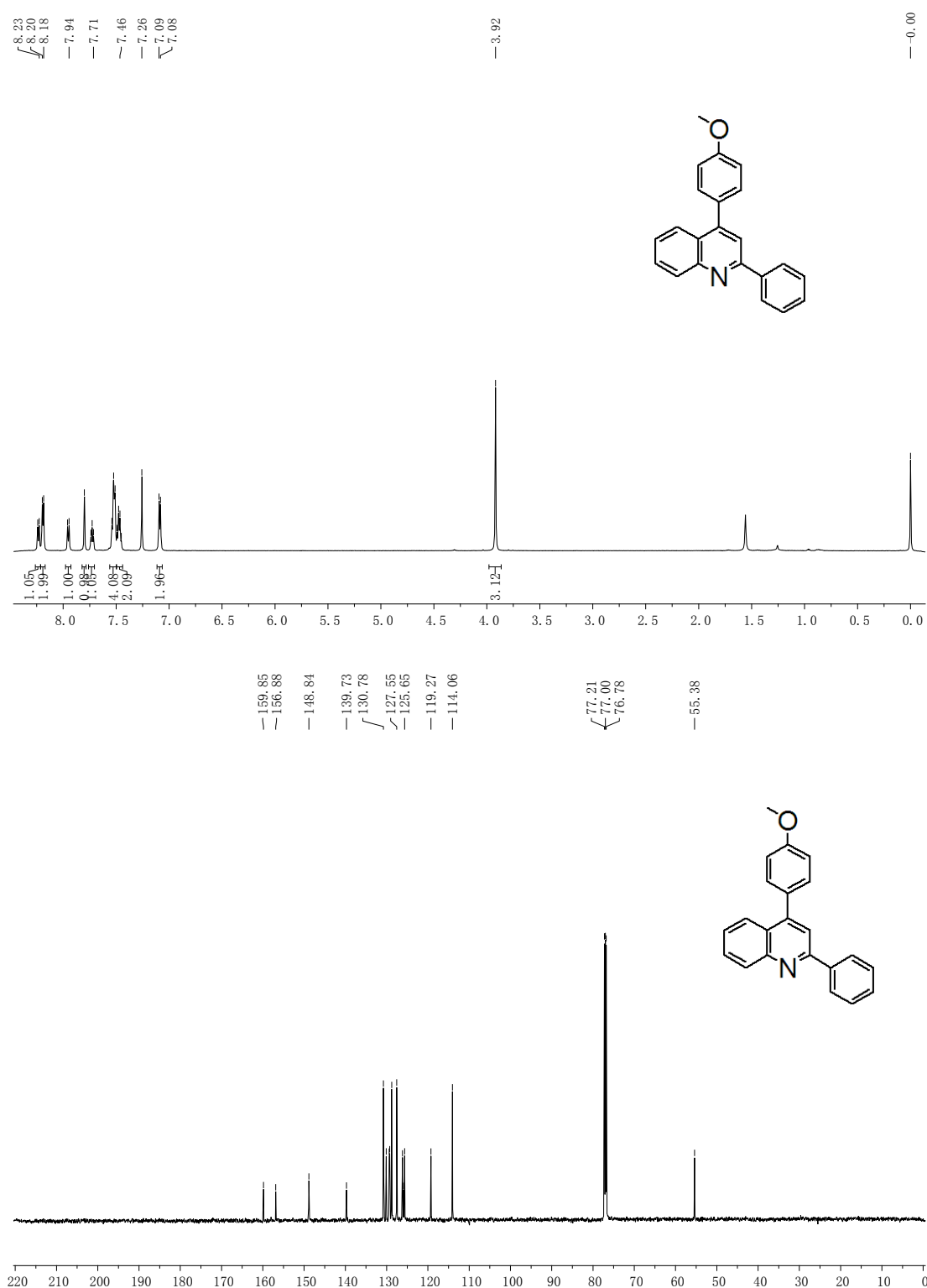


Figure S46. ¹H- (upper) and ¹³C-NMR (lower) spectra of 4-(4-methoxyphenyl)-2-phenylquinoline (**9a**)

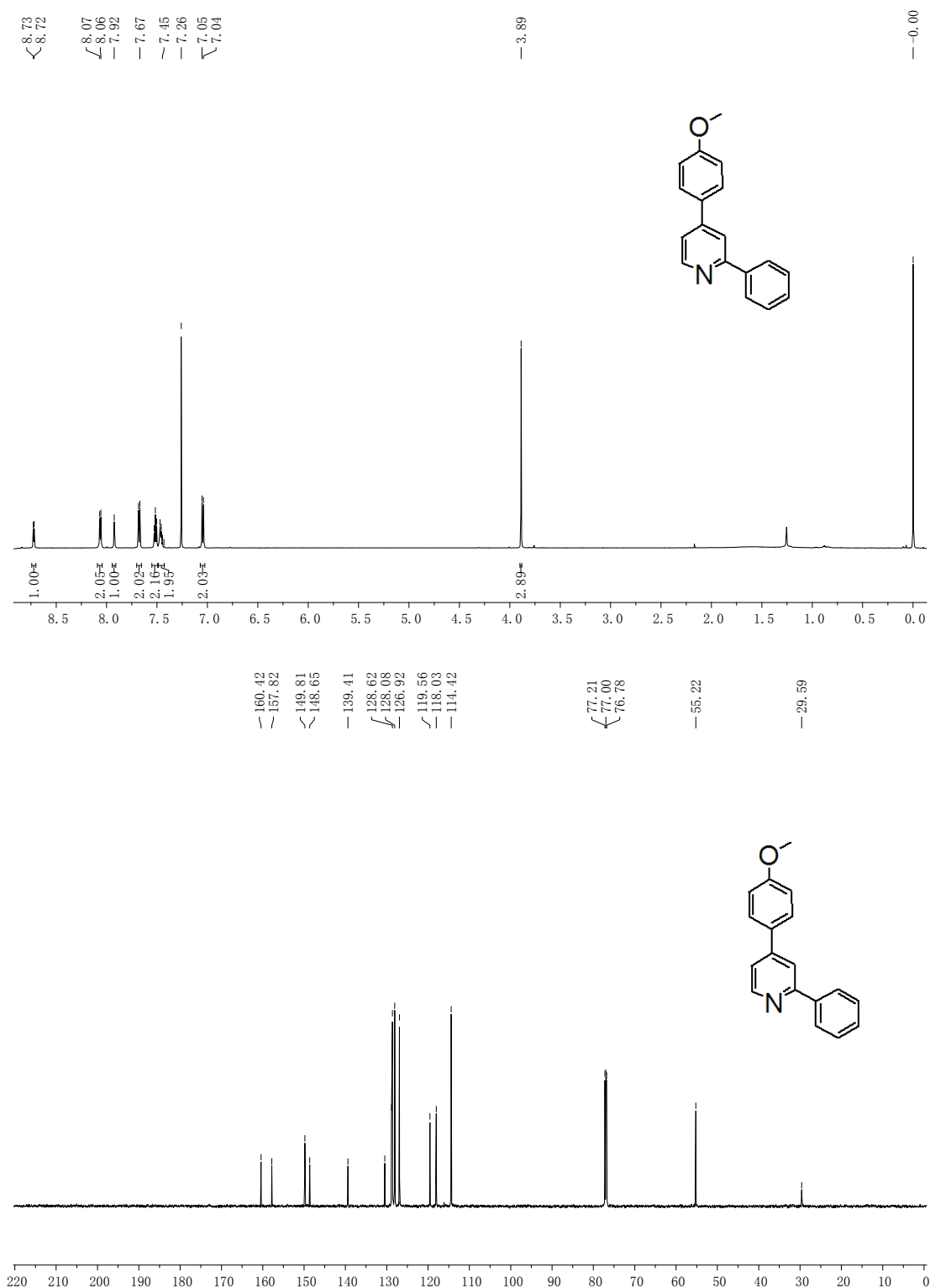


Figure S47. ¹H- (upper) and ¹³C-NMR (lower) spectra of 4-(4-methoxyphenyl)-2-phenylpyridine (**9b**)