

Supporting Information

Selective Synthesis of Nitrogen Bi-heteroarenes by a Hydrogen Transfer-Mediated Direct α , β -Coupling Reaction

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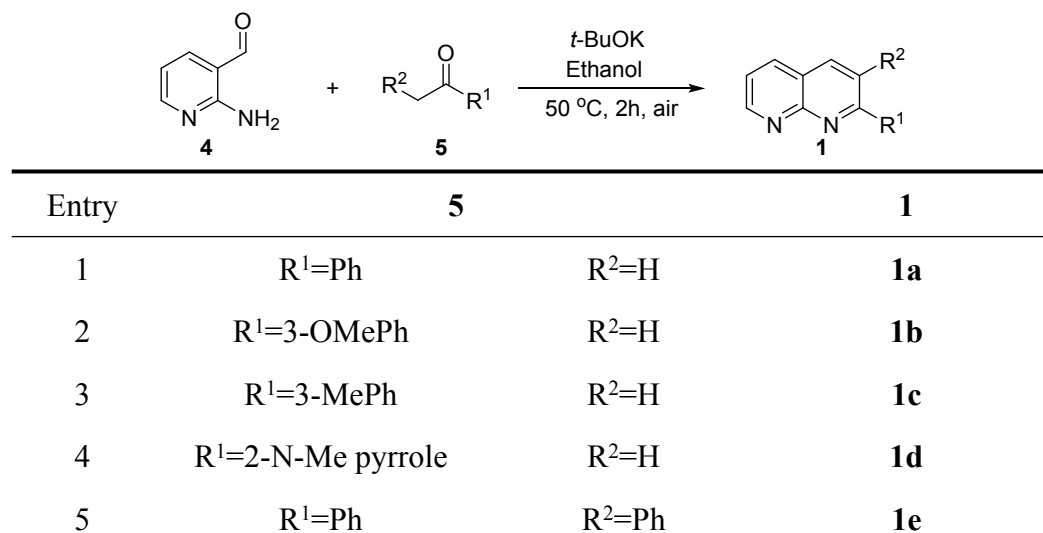
1. General information

All the obtained products were characterized by melting points (m.p.), ¹H-NMR, ¹³C-NMR and infrared spectra (IR). Melting points were measured on an Electrothermal SGW-X4 microscopy digital melting point apparatus and are uncorrected. IR spectra were recorded on a FT/IR-2000 spectrometer. ¹H-NMR and ¹³C-NMR spectra were obtained on Bruker-400 and referenced to 7.27 ppm for chloroform solvent with TMS as internal standard (0 ppm). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m). TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm. Unless otherwise stated, all the reagents were purchased from commercial sources (J&KChem, TCI, Fluka, Acros, SCRC), used without further purification.

2. Substrates preparation

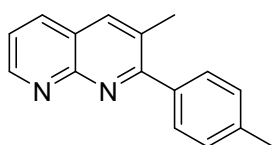
The preparation of 1,8-naphthyridines **1**. **4** (5 mmol), **5** (5 mmol), *t*-BuOK (20 mol %), and ethanol (10 mL) were introduced in a flask (50 mL). Then, it was stirred at 50 °C under atmosphere for 2 hours. After cooling down to room temperature, the reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by column chromatography.

Scheme S1. Synthesis of substrates 1,8-naphthyridines



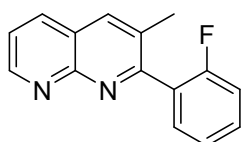
6	R ¹ =4-OMePh	R ² =4-OMePh	1f
7	R ¹ =H	R ² =H	1g
8	R ¹ =CH ₃	R ² =H	1h
9	R ¹ =Ph	R ² =CH ₃	1i
10	R ¹ =Ph	R ² =CH ₃ CH ₂	1j
11	R ¹ =2-FPh	R ² =CH ₃	1k
12	3,4-dihydronaphthalen-1(2 <i>H</i>)-one		1l

3-methyl-2-(p-tolyl)-1,8-naphthyridine



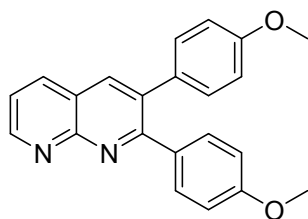
Yellow solid, 89% yield, m.p.: 134-135 °C; ¹H NMR (400 MHz, CDCl₃): δ 9.04 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.99 (s, 1H), 7.62 (d, *J* = 6.9 Hz, 2H), 7.40 (dd, *J* = 7.9, 4.1 Hz, 1H), 7.28 (d, *J* = 7.2 Hz, 2H), 2.52 (s, 3H), 2.42 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 163.36, 154.81, 152.82, 138.46, 137.67, 137.24, 135.92, 130.64, 129.27, 128.74, 121.78, 121.71, 21.35, 20.73. IR (KBr): 3036, 2963, 1601, 1476, 1452, 1305, 1248, 799 cm⁻¹. MS (EI, m/z): 234 [M]⁺.

2-(2-fluorophenyl)-3-methyl-1,8-naphthyridine



White oil, 69% yield; ¹H NMR (400 MHz, CDCl₃): δ 9.07 (s, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 8.03 (s, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.44 (dd, *J* = 12.8, 8.5 Hz, 2H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.16 (t, *J* = 9.2 Hz, 1H), 2.42 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 160.92, 159.43, 158.47, 154.64, 152.96, 136.52 (d, *J* = 342.0 Hz), 132.00, 131.59 (d, *J* = 14.4 Hz), 130.56 (d, *J* = 32 Hz), 128.12 (d, *J* = 84 Hz), 124.34 (d, *J* = 13.6 Hz), 122.20 (d, *J* = 22.4 Hz), 115.53, 115.31, 18.98 (d, *J* = 18.4 Hz). IR (KBr): 3045, 2287, 1598, 1550, 1484, 1446, 1215, 1108, 1010, 798, 783 cm⁻¹. MS (EI, m/z): 238 [M]⁺.

2,3-bis(4-methoxyphenyl)-1,8-naphthyridine



Yellow solid, 76% yield, m.p.: 130-131 °C; ¹H NMR (400 MHz, CDCl₃): δ 9.08(s, 1H), 8.16

(d, $J = 6.8$ Hz, 1H), 8.07(s, 1H), 7.54 (d, $J = 6.8$ Hz, 2H), 7.43 (m, 1H), 7.19 (d, $J = 6.8$ Hz, 2H), 6.86 (d, $J = 6.8$ Hz, 2H), 6.79(d, $J = 6.8$ Hz, 2H), 3.81(s, 3H), 3.79(s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 160.93, 159.96, 159.13, 155.12, 153.37, 138.16, 136.52, 135.16, 132.17, 131.96, 130.73, 121.88, 121.46, 113.96, 113.20, 55.27, 55.20. IR (KBr): 3014, 2285, 1596, 1515, 1250, 1180, 1029, 841 cm^{-1} . MS (EI, m/z): 342 $[\text{M}]^+$.

3. Typical procedure for the synthesis of 2aa'

Condition: under N_2 atmosphere, 2-phenyl-1,8-naphthyridine 1a (0.2 mmol), Isopropanol (0.6 mmol), $\text{Pd}(\text{OAc})_2$ (3 mol %), NaOH (0.2 mmol), and 1,4-dioxane (1.0 mL) were introduced in a Schlenk tube (50 mL) equipped with a gas-releasing meter. Then, the Schlenk tube was closed and the resulting mixture was stirred at 125 $^\circ\text{C}$ for 16 h. After cooling down to room temperature, the reaction mixture was concentrated by removing the solvent under vacuum. Finally, the residue was purified by preparative TLC on silica to give 7,7'-diphenyl-2,3'-bi(1,8-naphthyridine) 2aa'.

Scheme S2. Substrates employed for synthesizing target product

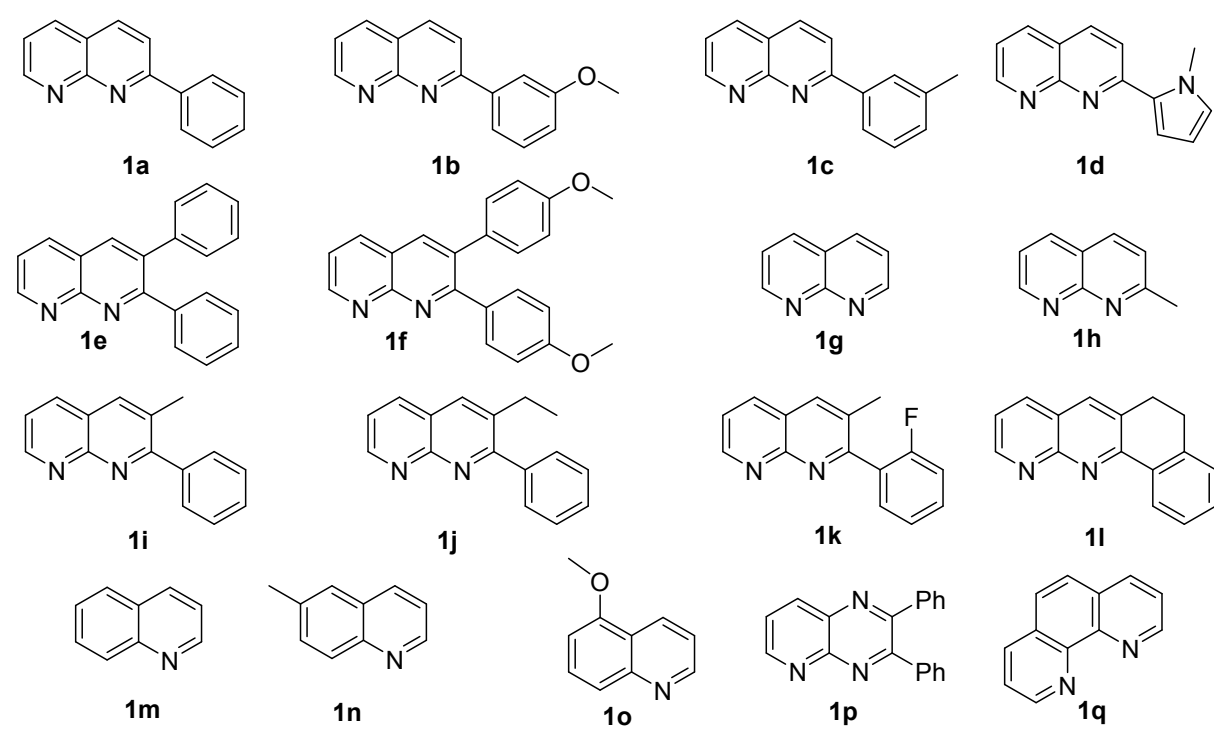


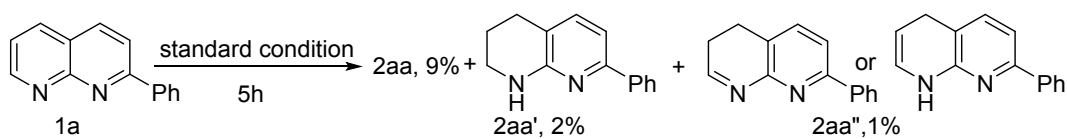
Table S2. Synthesis of substituted product ^a



entry	1	product 2, Yield ^a [%]
1	1a	2aa' , 63%, 16 h
2	1b	2bb' , 42%, 16 h
3	1c	2cc' , 42%, 16 h
4	1d	2dd' , 21%, 16 h
5	1e	2ee' , 74%, 16 h
6	1f	2ff' , 71%, 16 h
7	1g	2gg' , 34%, 16 h
8	1h	2hh' , 31%, 16 h
9	1i	2ii' , 62%, 16 h
10	1j	2jj' , 52%, 16 h
11	1k	2kk' , 42%, 16 h
12	1l	2ll' , 31%, 16 h
13	1m	2mm' , 30%, 16 h
14	1n	2nn' , 41%, 16 h
15	1o	2oo' , 36%, 16 h
16	1p	2pp' , 48%, 16 h
17	1q	2qq' , 32%, 16 h

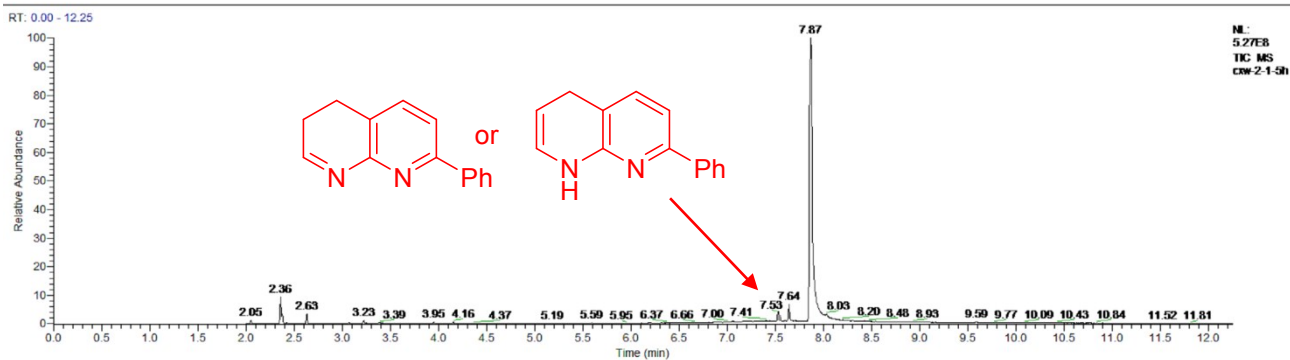
^aYield with respect to condition-A: **1** (0.2 mmol), Pd(OAc)₂ (3 mol%), NaOH (0.2 mmol), *i*-propanol (0.6 mmol), 125 °C.

Scheme S3. Detection of control experiments

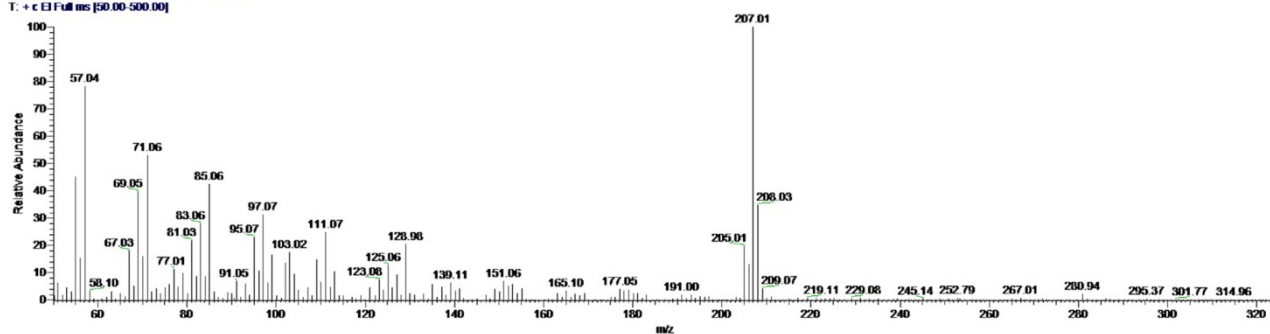


D:\DATA\CXW\cxw-2-1-5h

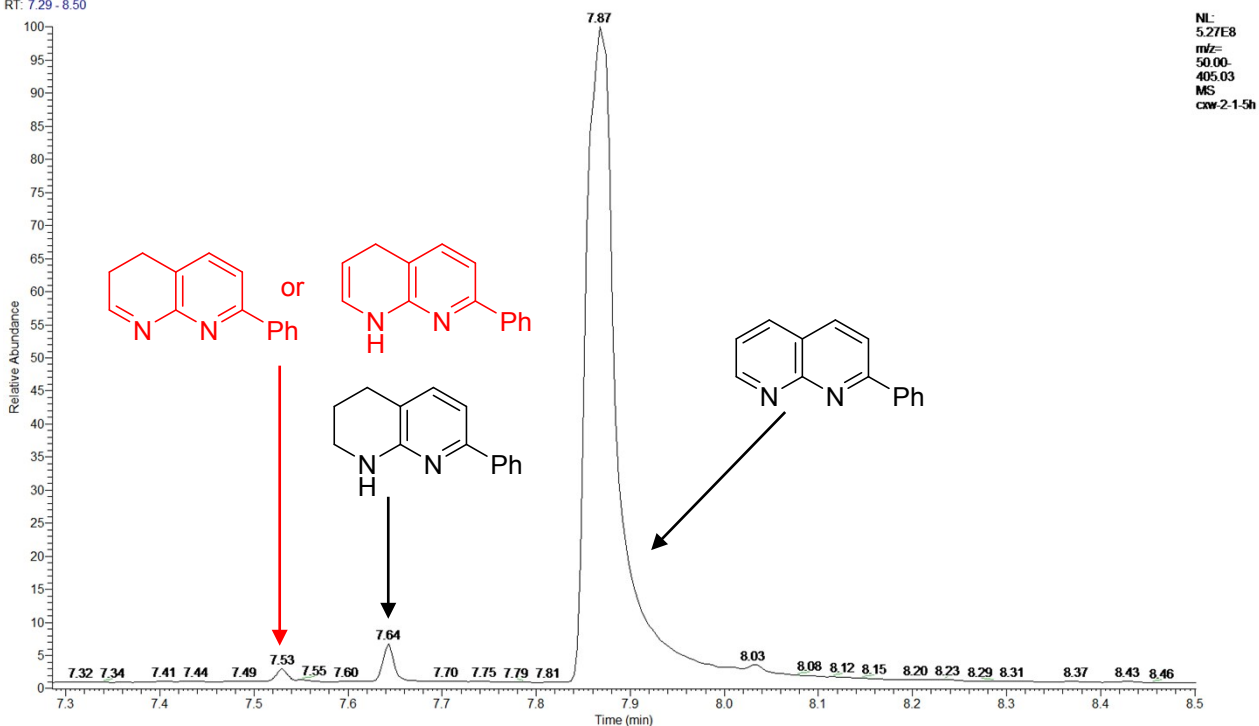
03/08/17 22:21:54



cxw-2-1-5h #1625 RT: 7.52 AV: 1 NL: 8.81E5
T: + e3 Full ms [50.00-500.00]



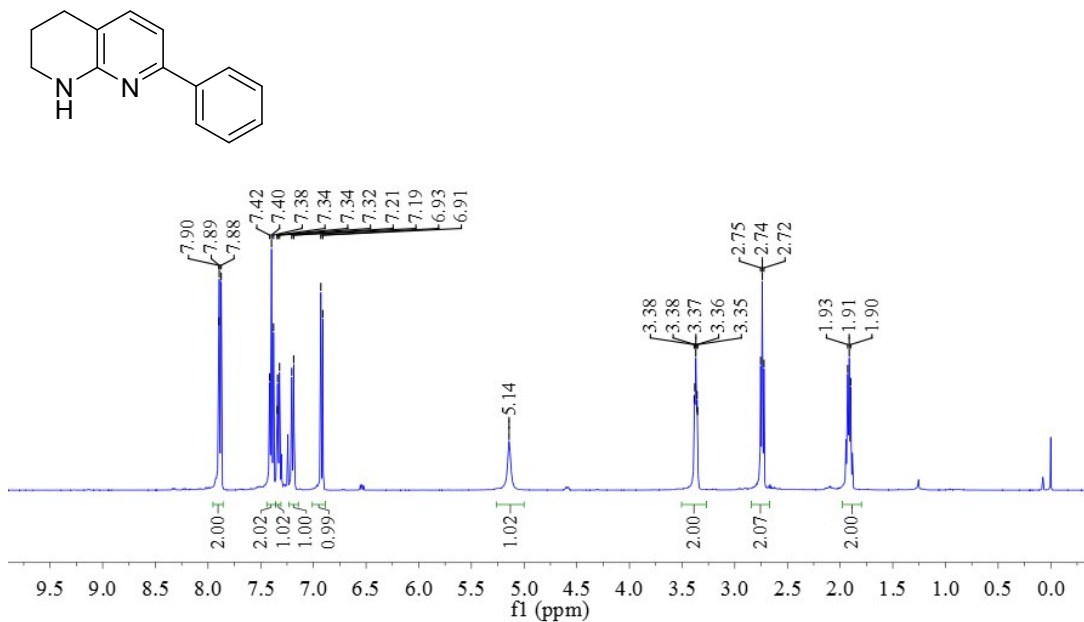
RT: 7.29 - 8.50



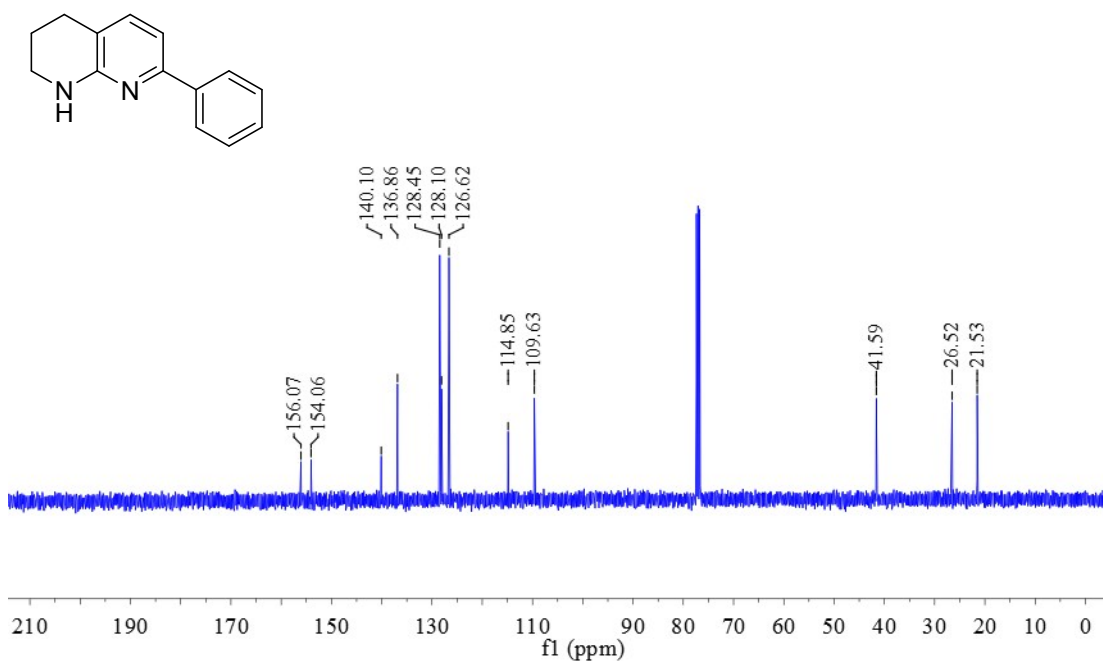
Analytic data of the side product

^1H NMR (400 MHz, CDCl_3): δ 7.97- 7.84 (m, 2H), 7.41 (t, $J = 11.3, 4.2$ Hz, 2H), 7.37 - 7.30 (m, 1H), 7.21 (d, $J = 7.5, 0.8$ Hz, 1H), 6.92 (d, $J = 7.5$ Hz, 1H), 5.14 (s, 1H), 3.42 (t, 2H), 2.75 (t, $J = 6.3$ Hz, 2H), 1.99 - 1.88 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 155.96, 153.89, 139.87, 136.94, 128.46, 128.16, 126.61, 114.95, 109.66, 41.61, 26.48, 21.49.

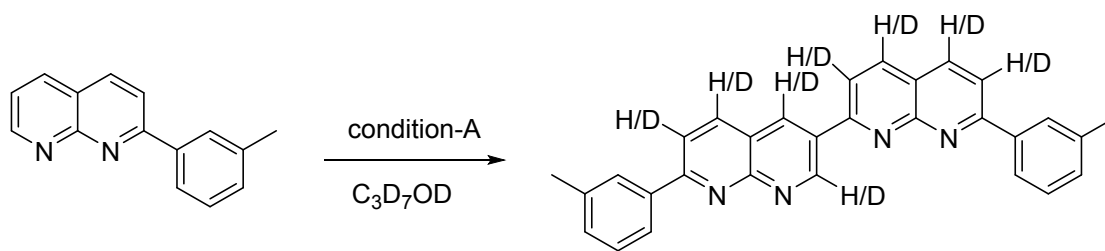
^1H - NMR spectrum of side product



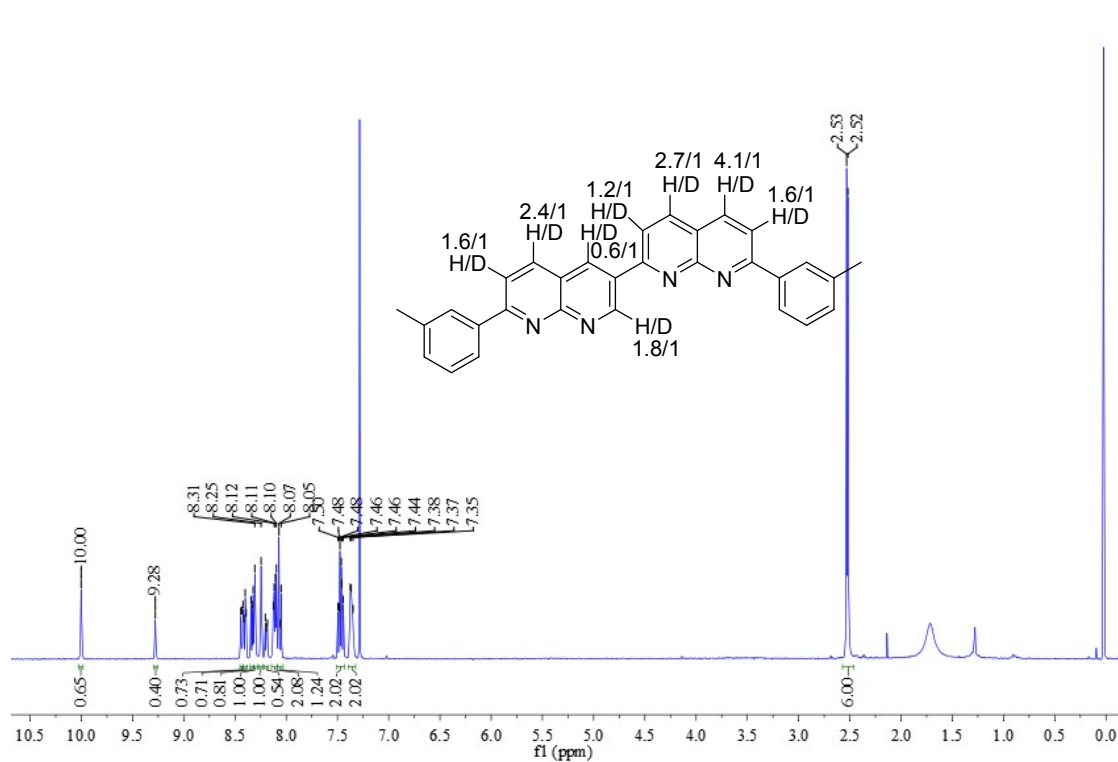
^{13}C - NMR spectrum of side product



4. Deuterium labeling experiment

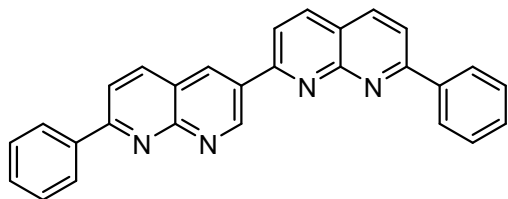


1H - NMR spectrum of deuterated product



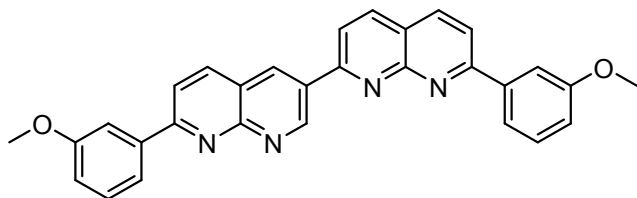
5. Analytical data of the obtained compounds

(1) 7,7'-diphenyl-2,3'-bi(1,8-naphthyridine) (2aa')



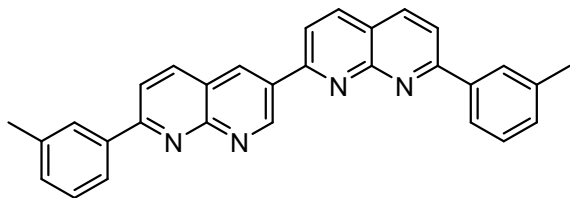
Yellow solid, m.p.: 320.8-322.5 °C; ¹H NMR (400 MHz, CDCl₃): δ 9.98 (s, 1H), 9.21 (s, 1H), 8.66 - 8.21 (m, 7H), 8.14 (s, 1H), 8.06 (s, 1H), 8.01 (d, *J* = 7.3 Hz, 1H), 7.67 – 7.44 (m, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 161.54, 161.06, 157.37, 156.55, 156.22, 152.91, 138.58, 138.54, 138.33, 138.16, 137.60, 136.32, 131.88, 130.35, 130.26, 128.87, 128.12, 128.02, 121.24, 121.04, 120.24, 119.19. IR (KBr): 3055, 2924, 2853, 1596, 1459, 1301, 1267, 1024, 764, 693 cm⁻¹. HRMS (ESI): Calcd. for C₂₈H₁₈N₄ [M+H]⁺: 411.1604; found: 411.1605.

(2) 7,7'-di-*m*-tolyl-2,3'-bi(1,8-naphthyridine) (2bb')



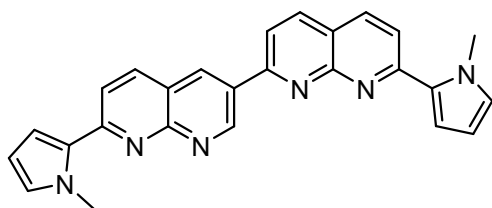
Yellow solid, m.p.: 266-267 °C; ¹H NMR (400 MHz, CDCl₃): δ 9.98 (s, 1H), 9.19 (s, 1H), 8.36 (t, *J* = 9.7 Hz, 2H), 8.29 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 8.07 – 7.97 (m, 3H), 7.93 (s, 1H), 7.83 (t, *J* = 6.7 Hz, 2H), 7.45 (q, *J* = 8.0 Hz, 2H), 7.11 – 7.02 (m, 2H), 3.97 (s, 3H), 3.96 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): 161.43, 160.94, 160.26, 160.21, 157.41, 156.54, 156.17, 152.93, 140.04, 139.87, 138.56, 138.19, 137.58, 136.31, 131.95, 129.82, 129.77, 121.39, 121.16, 120.52, 120.50, 120.45, 120.41, 119.23, 117.04, 116.67, 113.01, 112.62, 55.60. IR (KBr): 2956, 2924, 2853, 1600, 1530, 1477, 1455, 1289, 1245, 1213, 1038, 855, 813, 781 cm⁻¹. HRMS (ESI): Calcd. for C₃₀H₂₂N₄O₂ [M+H]⁺: 471.1816; found: 471.1806.

(3) 7,7'-bis(3-methoxyphenyl)-2,3'-bi(1,8-naphthyridine) (2cc')



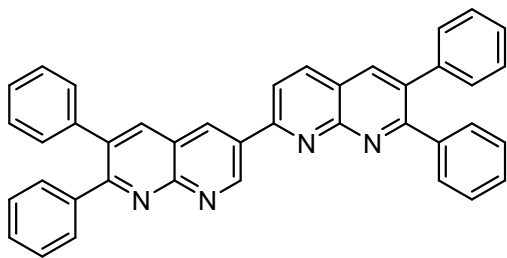
Yellow solid, m.p.: 262-263 °C; ¹H NMR (400 MHz, CDCl₃): δ 9.96 (s, 1H), 9.15 (s, 1H), 8.33 (dd, *J* = 12.5, 8.5 Hz, 2H), 8.28 - 8.23 (m, 2H), 8.20 (s, 1H), 8.13 - 7.96 (m, 5H), 7.43 (q, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 6.5 Hz, 2H), 2.50 (s, 3H), 2.48 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 161.65, 161.13, 157.35, 156.58, 156.21, 152.92, 138.64, 138.46, 138.25, 138.10, 137.48, 136.19, 131.81, 131.15, 131.07, 128.86, 128.78, 128.72, 128.70, 125.14, 125.01, 121.18, 120.99, 120.29, 119.11, 21.53, 21.50. IR (KBr): 3036, 2998, 2918, 2850, 1600, 1545, 1437, 1309, 942, 856, 802, 783 cm⁻¹. HRMS (ESI): Calcd. for C₃₀H₂₂N₄ [M+H]⁺: 439.1917; found: 439.1914.

(4) 7,7'-bis(1-methyl-1H-pyrrol-2-yl)-2,3'-bi(1,8-naphthyridine) (2dd')



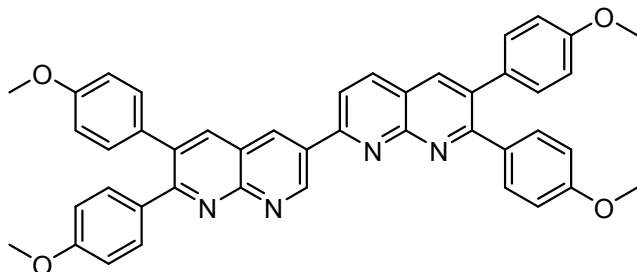
Red-brown solid, m.p.: 123-124 °C; ¹H NMR (400 MHz, CDCl₃): δ 9.79 (s, 1H), 8.99 (s, 1H), 8.16 (dd, *J* = 15.9, 8.4 Hz, 2H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.79 (dd, *J* = 15.2, 8.6 Hz, 2H), 6.93 (d, *J* = 3.1 Hz, 1H), 6.87 (s, 3H), 6.25 (s, 2H), 4.34 (s, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 156.02, 155.30, 155.00, 154.77, 151.27, 136.80, 136.19, 135.32, 134.86, 130.48, 130.36, 130.17, 128.44, 128.03, 120.32, 120.26, 119.05, 118.77, 117.19, 113.51, 113.20, 107.35, 107.32, 37.59, 37.03. IR (KBr): 2952, 2924, 2852, 1593, 1542, 1460, 1420, 1378, 1068, 810, 732 cm⁻¹. HRMS (ESI): Calcd. for C₂₆H₂₀N₆ [M+H]⁺: 417.1822; found: 417.1818.

(5) 6,6',7,7'-tetraphenyl-2,3'-bi(1,8-naphthyridine) (2ee')



Red-brown solid, m.p.: 269-270 °C; ¹H NMR (400 MHz, CDCl₃): δ 10.01 (s, 1H), 9.29 (s, 1H), 8.42 (d, *J* = 8.3 Hz, 1H), 8.31 (s, 1H), 8.28 - 8.16 (m, 2H), 7.57 (t, *J* = 8.6 Hz, 4H), 7.41 - 7.23 (m, 16H). ¹³C NMR (101 MHz, CDCl₃): δ 162.68, 162.23, 157.23, 155.54, 155.24, 152.85, 139.57, 139.42, 139.23, 139.10, 138.29, 138.18, 136.37, 136.28, 136.09, 132.39, 130.53, 130.34, 129.70, 128.73, 128.63, 128.52, 128.45, 127.89, 127.79, 127.72, 121.23, 121.08, 119.71. IR (KBr): 3057, 2948, 2837, 1640, 1597, 1457, 1413, 1267, 1024, 739, 701 cm⁻¹. HRMS (ESI): Calcd. for C₄₀H₂₆N₄ [M+H]⁺: 563.2230; found: 563.2234.

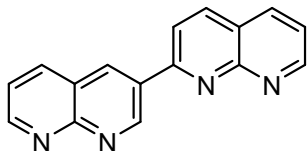
(6) 6,6',7,7'-tetrakis(4-methoxyphenyl)-2,3'-bi(1,8-naphthyridine) (2ff')



Red-brown solid, m.p.: 273-275 °C; ¹H NMR (400 MHz, CDCl₃): δ 9.94 (s, 1H), 9.14 (d, *J* = 3.5 Hz, 1H), 8.31 (dd, *J* = 8.2, 3.3 Hz, 1H), 8.18 (d, *J* = 2.3 Hz, 1H), 8.14 - 8.05 (m, 2H), 7.60 - 7.50 (m, 4H), 7.21 (t, *J* = 6.6 Hz, 4H), 6.88 (t, *J* = 8.2 Hz, 4H), 6.81 (t, *J* = 7.5 Hz, 4H), 3.83 (s, 3H), 3.82 (s, 3H), 3.81 (s, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 161.14, 160.65,

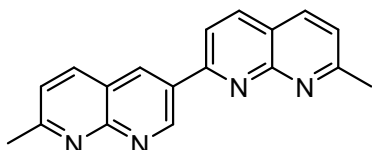
159.13, 159.03, 158.23, 158.21, 155.99, 154.49, 154.14, 151.58, 137.80, 136.86, 134.87, 134.72, 134.48, 131.21, 131.06, 130.93, 130.87, 130.70, 129.77, 129.76, 120.02, 119.88, 118.33, 113.04, 112.97, 112.33, 112.22, 54.28, 54.24, 54.22. IR (KBr): 3041, 2998, 2930, 2835, 1596, 1512, 1459, 1441, 1292, 1249, 1175, 1027, 832, 808, 738 cm^{-1} . HRMS (ESI): Calcd. for $\text{C}_{44}\text{H}_{34}\text{N}_4\text{O}_4$ $[\text{M}+\text{H}]^+$: 683.2653; found: 683.2654.

(7) 2,3'-bi(1,8-naphthyridine) (2gg')



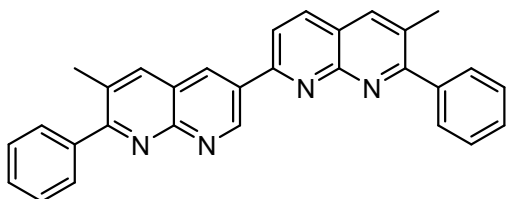
Yellow solid, m.p.: 170-151 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 9.98 (d, $J = 2.4$ Hz, 1H), 9.24 (d, $J = 2.5$ Hz, 1H), 9.22 - 9.15 (m, 2H), 8.39 (d, $J = 8.5$ Hz, 1H), 8.36 (dd, $J = 8.1, 1.9$ Hz, 1H), 8.27 (dd, $J = 8.1, 1.9$ Hz, 1H), 8.21 (d, $J = 8.5$ Hz, 1H), 7.60 - 7.52 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 156.77, 156.57, 156.08, 154.45, 154.45, 152.53, 138.64, 138.04, 136.96, 136.64, 132.10, 122.82, 122.47, 122.45, 122.18, 119.44. IR (KBr): 3054, 2987, 1599, 1563, 1441, 1425, 1265, 850, 813, 741 cm^{-1} . HRMS (ESI): Calcd. for $\text{C}_{16}\text{H}_{10}\text{N}_4$ $[\text{M}+\text{Na}]^+$: 281.0798; found: 281.0796.

(8) 7,7'-dimethyl-2,3'-bi(1,8-naphthyridine) (2hh')



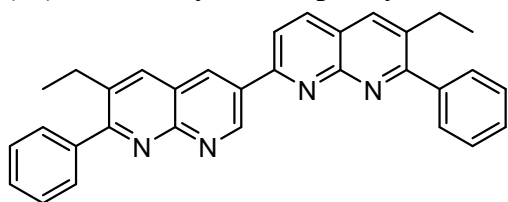
Red-brown oil; ^1H NMR (400 MHz, CDCl_3): δ 9.91 (s, 1H), 9.21 (s, 1H), 8.31 (d, $J = 8.4$ Hz, 1H), 8.21 (d, $J = 8.2$ Hz, 1H), 8.13 (d, $J = 7.9$ Hz, 2H), 7.43 (t, $J = 8.1$ Hz, 2H), 2.87 (s, 3H), 2.85 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 164.09, 164.06, 156.78, 156.37, 155.93, 152.24, 138.09, 137.69, 136.70, 136.21, 131.57, 123.65, 123.27, 120.44, 120.11, 118.54, 25.83, 25.78. IR (KBr): 2975, 2922, 2852, 1601, 1554, 1434, 1264, 1085, 1047, 879, 851, 804, 742 cm^{-1} . HRMS (ESI): Calcd. for $\text{C}_{18}\text{H}_{14}\text{N}_4$ $[\text{M}+\text{Na}]^+$: 309.1111; found: 309.1106.

(9) 6,6'-dimethyl-7,7'-diphenyl-2,3'-bi(1,8-naphthyridine) (2ii')



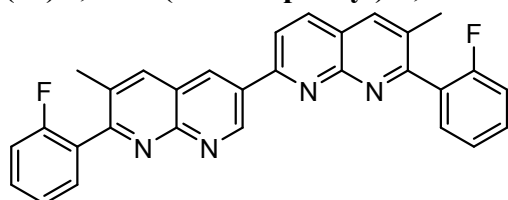
Yellow solid, m.p.: 288-289 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 9.90 (s, 1H), 9.15 (s, 1H), 8.30 (d, $J = 8.4$ Hz, 1H), 8.13 (d, $J = 7.9$ Hz, 2H), 8.07 (s, 1H), 7.73 (d, $J = 7.3$ Hz, 2H), 7.69 (d, $J = 7.3$ Hz, 2H), 7.55 - 7.44 (m, 6H), 2.56 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): 164.64, 164.11, 156.57, 155.18, 154.75, 152.02, 140.07, 139.98, 138.49, 137.47, 137.37, 135.37, 132.11, 131.25, 131.07, 129.33, 129.06, 128.71, 128.65, 128.20, 128.08, 121.40, 121.22, 119.31, 20.75, 20.60. IR (KBr): 2956, 2924, 2852, 1600, 1545, 1489, 1267, 1009, 811, 774, 732 cm^{-1} . HRMS (ESI): Calcd. for $\text{C}_{30}\text{H}_{22}\text{N}_4$ $[\text{M}+\text{H}]^+$: 439.1917; found: 439.1913.

(10) 6,6'-diethyl-7,7'-diphenyl-2,3'-bi(1,8-naphthyridine) (2jj')



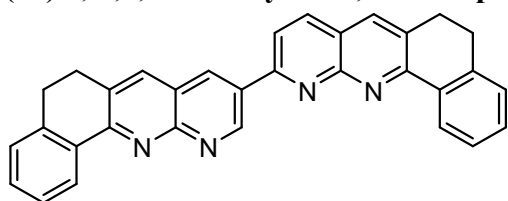
Yellow solid, m.p.: 286-287 °C; ¹H NMR (400 MHz, CDCl₃): δ 9.91 (d, *J* = 2.4 Hz, 1H), 9.25 (d, *J* = 2.4 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 8.24 - 8.17 (m, 2H), 8.14 (s, 1H), 7.72 - 7.61 (m, 4H), 7.52 - 7.44 (m, 6H), 2.97 - 2.85 (m, 4H), 1.29 - 1.22 (m, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 164.84, 164.37, 156.65, 154.90, 154.51, 152.01, 140.12, 140.06, 137.58, 137.33, 137.15, 136.67, 135.71, 135.62, 132.17, 129.11, 128.89, 128.55, 128.50, 128.18, 128.10, 121.61, 121.40, 119.28, 25.99, 14.62, 14.59. IR (KBr): 3057, 2975, 2928, 1600, 1453, 1417, 1267, 1048, 740, 702 cm⁻¹. HRMS (ESI): Calcd. for C₃₂H₂₆N₄ [M+H]⁺: 467.2230; found: 467.2228.

(11) 7,7'-bis(2-fluorophenyl)-6,6'-dimethyl-2,3'-bi(1,8-naphthyridine) (2kk')



Brown solid, m.p.: 272-273 °C; ¹H NMR (400 MHz, CDCl₃): δ 9.93 (d, *J* = 1.9 Hz, 1H), 9.15 (d, *J* = 2.1 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 8.18 - 8.10 (m, 2H), 8.07 (s, 1H), 7.67 - 7.56 (m, 2H), 7.50 - 7.41 (m, 2H), 7.33 - 7.25 (m, 2H), 7.23 - 7.11 (m, 2H), 2.45 (s, 3H), 2.44 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 160.39 (d, *J* = 27.3 Hz), 159.47 (d, *J* = 249.5 Hz), 156.45, 155.06, 154.60, 152.09, 137.66, 137.55, 136.78, 135.40, 132.69, 132.44, 132.26, 131.66 (d, *J* = 3.5 Hz), 131.37 (d, *J* = 3.5 Hz), 130.69 (d, *J* = 8.1 Hz), 128.03 (d, *J* = 16.2 Hz), 124.46 (d, *J* = 3.4 Hz), 124.38 (d, *J* = 3.3 Hz), 121.76, 121.58, 119.58, 115.61 (d, *J* = 6.1 Hz), 115.39 (d, *J* = 6.2 Hz), 19.13 (s), 19.08 (s). IR (KBr): 2976, 2928, 2897, 1638, 1602, 1489, 1452, 1416, 1268, 1088, 1048, 880, 740 cm⁻¹. HRMS (ESI): Calcd. for C₃₀H₂₀F₂N₄ [M+H]⁺: 475.1729; found: 475.1734.

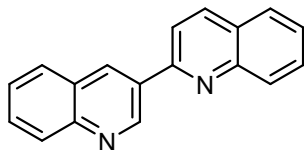
(12) 5,5',6,6'-tetrahydro-9,10'-binaphtho[1,2-b][1,8]naphthyridine (2ll')



Brown solid, m.p.: 295-298 °C; ¹H NMR (400 MHz, CDCl₃): δ 9.86 (s, 1H), 9.17 (s, 1H), 8.79 (s, 2H), 8.27 (d, *J* = 8.0 Hz, 1H), 8.09 (s, 2H), 7.99 (s, 1H), 7.52 - 7.38 (m, 4H), 7.33 - 7.22 (m, 2H), 3.33 - 3.14 (m, 4H), 3.13 - 2.98 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ 157.51, 157.43, 156.53, 155.82, 151.63, 139.73, 139.63, 137.47, 135.85, 135.27, 134.51, 133.98, 133.91, 132.66, 132.35, 131.89, 130.71, 127.94, 127.44, 127.40, 127.34, 121.96, 121.68, 119.05, 28.68, 28.65, 28.15, 28.13. IR (KBr): 2923, 2852, 1595, 1498, 1467, 1411, 1265, 783,

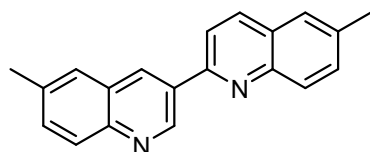
740 cm^{-1} . HRMS (ESI): Calcd. for $\text{C}_{32}\text{H}_{22}\text{N}_4$ $[\text{M}+\text{H}]^+$: 463.1917; found: 463.1917.

(13) 2,3'-biquinoline (2mm')



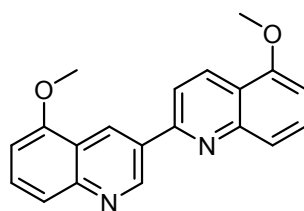
Brown solid, m.p.: 175-176 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 9.78 (d, $J = 2.1$ Hz, 1H), 8.95 (d, $J = 1.6$ Hz, 1H), 8.33 (d, $J = 8.6$ Hz, 1H), 8.24 (dd, $J = 15.0, 8.5$ Hz, 2H), 8.05 (d, $J = 8.6$ Hz, 1H), 8.01 (d, $J = 8.1$ Hz, 1H), 7.90 (d, $J = 8.1$ Hz, 1H), 7.80 (t, $J = 7.6$ Hz, 2H), 7.67 - 7.56 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 154.45, 149.54, 148.46, 147.93, 137.27, 134.88, 132.17, 130.36, 130.11, 129.79, 129.02, 128.63, 127.90, 127.60, 127.40, 127.23, 126.88, 118.65. IR (KBr): 3054, 2923, 2850, 1729, 1682, 1602, 1498, 1427, 1372, 1309, 1265, 1123, 1102, 967, 827, 745 cm^{-1} . MS (EI, m/z): 256.1 $[\text{M}]^+$.

(14) 6,6'-dimethyl-2,3'-biquinoline (2nn')



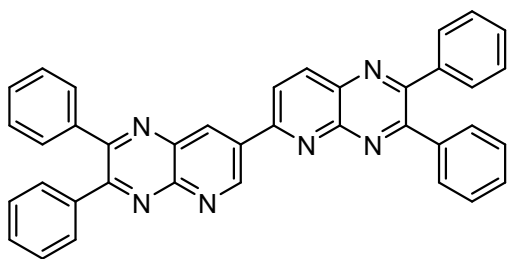
Brown solid, m.p.: 208-209 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 9.68 (d, $J = 2.1$ Hz, 1H), 8.81 (s, 1H), 8.21 (d, $J = 8.6$ Hz, 1H), 8.13 (d, $J = 8.4$ Hz, 1H), 8.10 (d, $J = 8.6$ Hz, 1H), 7.97 (d, $J = 8.6$ Hz, 1H), 7.73 (s, 1H), 7.66 - 7.58 (m, 3H), 2.59 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 153.84, 148.77, 147.06, 146.68, 137.00, 136.75, 136.46, 133.89, 132.47, 132.33, 132.25, 129.44, 128.78, 127.95, 127.37, 126.42, 118.68, 21.64. IR (KBr): 3008, 2921, 2851, 1627, 1503, 1431, 1354, 1301, 1124, 967, 919, 829, 636 cm^{-1} . MS (EI, m/z): 284.13 $[\text{M}]^+$.

(15) 5,5'-dimethoxy-2,3'-biquinoline (2oo')



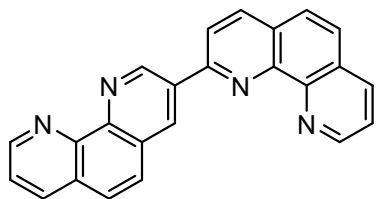
Brown oil; ^1H NMR (400 MHz, CDCl_3): δ 9.79 (d, $J = 2.3$ Hz, 1H), 9.28 (d, $J = 2.0$ Hz, 1H), 8.68 (d, $J = 8.8$ Hz, 1H), 8.01 (d, $J = 8.8$ Hz, 1H), 7.81 (d, $J = 8.5$ Hz, 1H), 7.77 (d, $J = 8.5$ Hz, 1H), 7.69 - 7.63 (m, 2H), 6.91 (d, $J = 7.7$ Hz, 1H), 6.87 (d, $J = 7.7$ Hz, 1H), 4.07 (s, 3H), 4.04 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 9.79 (d, $J = 2.3$ Hz, 1H), 9.28 (d, $J = 2.0$ Hz, 1H), 8.68 (d, $J = 8.8$ Hz, 1H), 8.01 (d, $J = 8.8$ Hz, 1H), 7.81 (d, $J = 8.5$ Hz, 1H), 7.77 (d, $J = 8.5$ Hz, 1H), 7.69 - 7.63 (m, 2H), 6.91 (d, $J = 7.7$ Hz, 1H), 6.87 (d, $J = 7.7$ Hz, 1H), 4.07 (s, 3H), 4.04 (s, 3H). IR (KBr): 3451, 3006, 1643, 1626, 1583, 1467, 1371, 1307, 1255, 1163, 1097, 1025, 991, 918, 805, 749 cm^{-1} . HRMS (ESI): Calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 317.1285; found: 317.1288.

(16) 2,2',3,3'-tetraphenyl-6,7'-bipyrido[2,3-b]pyrazine (2pp')



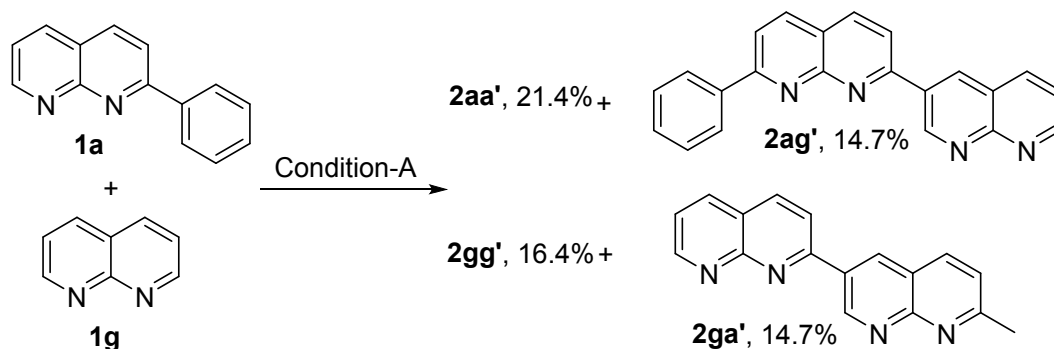
Red oil; ^1H NMR (400 MHz, CDCl_3): 10.25 (s, 1H), 9.25 (d, $J = 2.1$ Hz, 1H), 8.69 (d, $J = 8.6$ Hz, 1H), 8.41 (d, $J = 8.6$ Hz, 1H), 7.71 - 7.65 (m, 4H), 7.63 - 7.57 (m, 4H), 7.44 - 7.39 (m, 7H), 7.38 - 7.32 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3): δ 157.86, 156.92, 155.85, 155.27, 154.35, 153.94, 150.00, 149.72, 145.22, 138.44, 138.34, 138.10, 138.05, 137.30, 136.05, 133.83, 130.28, 130.24, 130.06, 129.90, 129.64, 129.54, 129.50, 129.45, 129.27, 128.44, 128.36, 128.29, 128.22, 126.20. IR (KBr): 3035, 2979, 2923, 1591, 1543, 1458, 1442, 1384, 1328, 1189, 1022, 820, 769 cm^{-1} . HRMS (ESI): Calcd. for $\text{C}_{38}\text{H}_{24}\text{N}_6$ $[\text{M}+\text{H}]^+$: 565.2135; found: 565.2135.

(17) 2,3'-bi(1,10-phenanthroline) (2qq')



Yellow solid, m.p.: 207-208 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): 9.87 (s, 1H), 9.46 (s, 1H), 9.26 (d, $J = 2.9$ Hz, 1H), 9.20 (d, $J = 3.1$ Hz, 1H), 8.39 (d, $J = 8.3$ Hz, 1H), 8.31 (d, $J = 8.4$ Hz, 1H), 8.26 (t, $J = 6.7$ Hz, 2H), 8.02 (d, $J = 8.8$ Hz, 1H), 7.86 - 7.75 (m, 3H), 7.68 - 7.60 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3): δ 154.53, 150.45, 150.33, 148.90, 146.45, 146.27, 146.15, 146.06, 137.32, 136.30, 136.05, 136.04, 135.78, 134.26, 129.20, 129.10, 128.69, 128.06, 127.33, 126.93, 126.36, 123.21, 120.84. IR (KBr): 3051, 2985, 2953, 1511, 1417, 1266, 854, 740 cm^{-1} . HRMS (ESI): Calcd. for $\text{C}_{24}\text{H}_{14}\text{N}_4$ $[\text{M}+\text{H}]^+$: 359.1291; found: 359.1289.

(20) mixture of the cross-coupling reaction



2ag'/2ga', Yellow solid, m.p.: 281-282 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 10.01 (d, $J = 2.5$ Hz, 1H), 9.98 (d, $J = 2.5$ Hz, 1H), 9.29 (d, $J = 2.5$ Hz, 1H), 9.25 (d, $J = 2.5$ Hz, 1H), 9.22 (td, $J = 4.2, 1.9$ Hz, 2H), 8.45 - 8.38 (m, 5H), 8.37 (d, $J = 1.2$ Hz, 1H), 8.36 - 8.32 (m, 3H), 8.29

(dd, $J = 8.1, 2.0$ Hz, 1H), 8.24 (d, $J = 8.5$ Hz, 1H), 8.18 (d, $J = 8.4$ Hz, 1H), 8.10 (d, $J = 8.5$ Hz, 1H), 8.07 (d, $J = 8.5$ Hz, 1H), 7.62 - 7.50 (m, 8H). IR (KBr): 3051, 3031, 2924, 2852, 1599, 1556, 1480, 1440, 1297, 1267, 848, 812, 760 cm^{-1} . HRMS (ESI): Calcd. for $\text{C}_{22}\text{H}_{14}\text{N}_4$ $[\text{M}+\text{H}]^+$: 335.1291; found: 335.1292.

6. The application of the obtained compounds

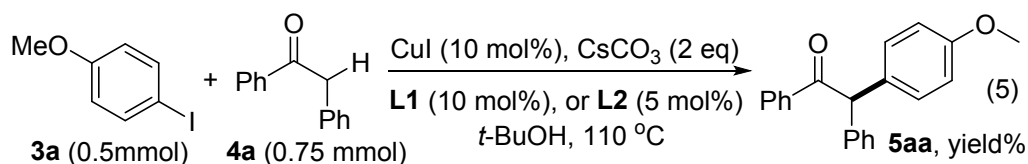
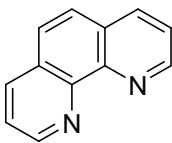
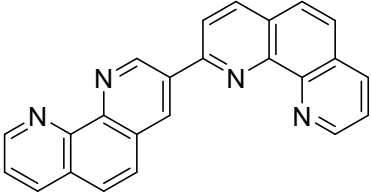


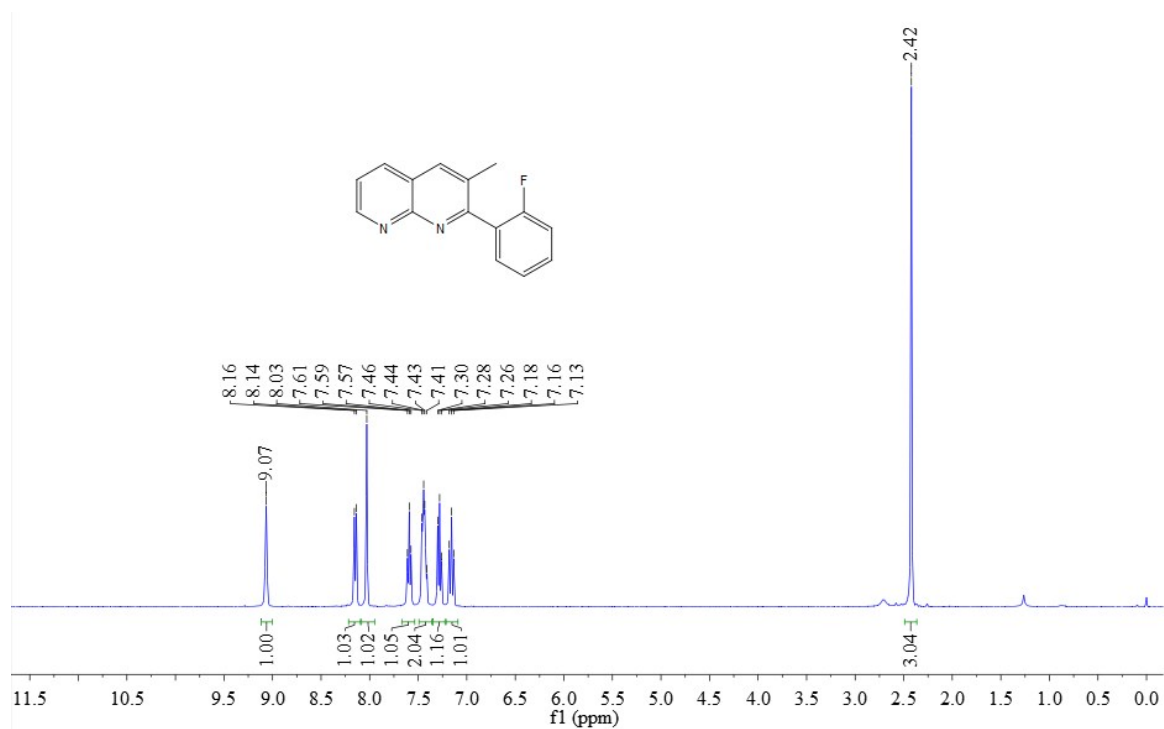
Table S3. Comparison of the performance of Copper-catalyzed α -arylation of deoxybenzoin in $t\text{BuOH}$ using different ligands **L**.^[a]

L	Time(h)	Yield (%) ^[b]
 L1	2	5.4
	4	6.4
	8	10.4
	14	59.8
	20	71.4
	26	70.3
 L2	2	16.4
	4	43.4
	8	71.7
	14	90.5
	20	90.5
	26	90.6

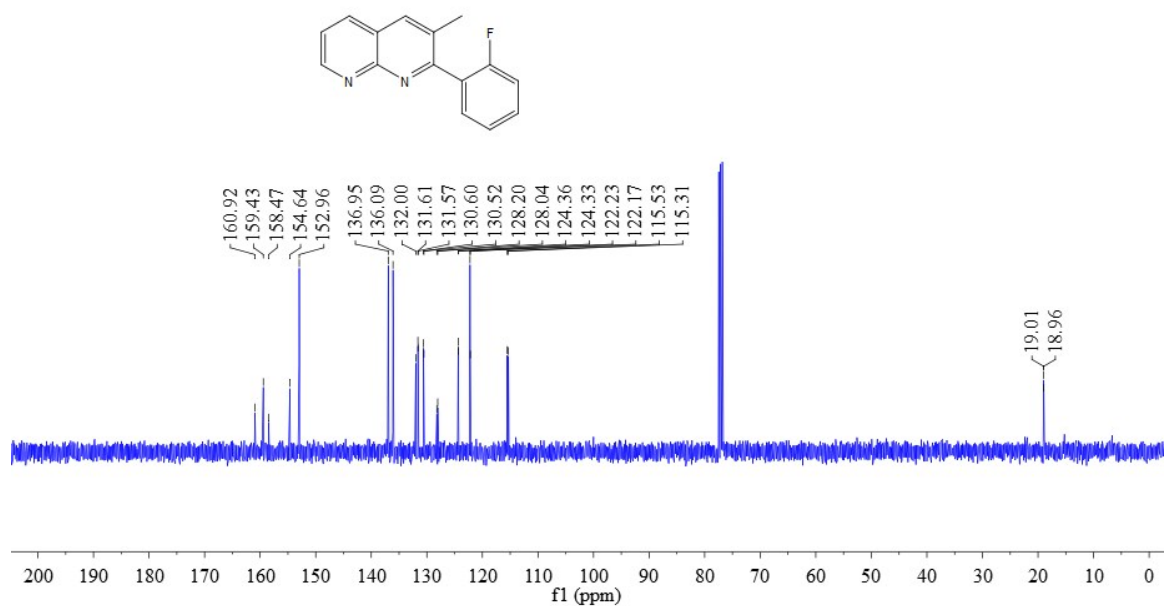
[a] Reactions performed on 0.5 mmol scale (ketone/ ArI =1.5:1). [b] Yields determined by GC/MS.

7. NMR spectra of products

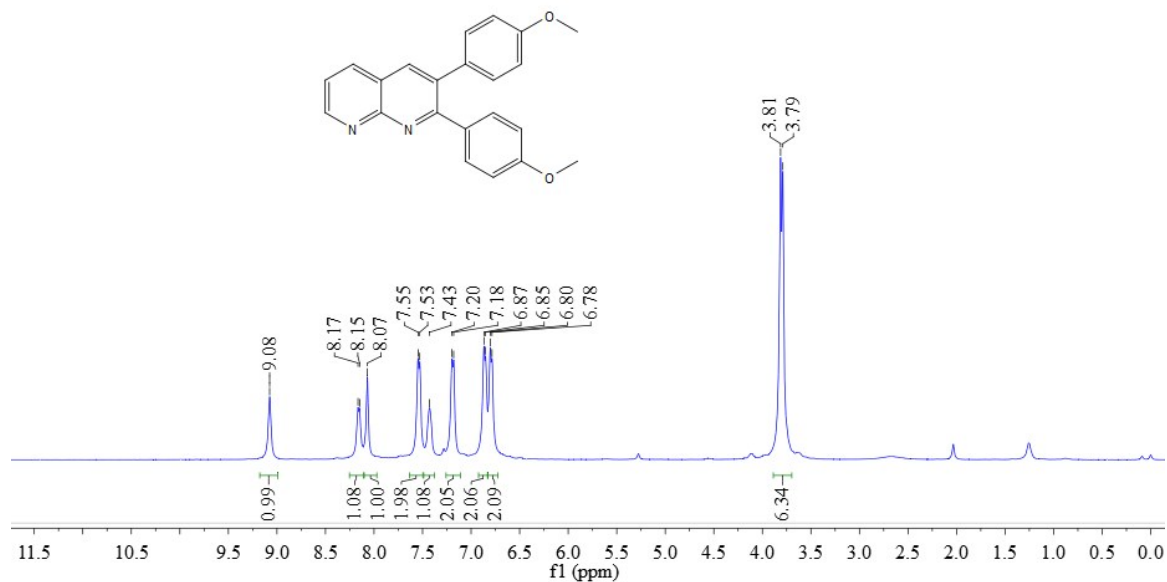
^1H - NMR spectrum of 2-(2-fluorophenyl)-3-methyl-1,8-naphthyridine



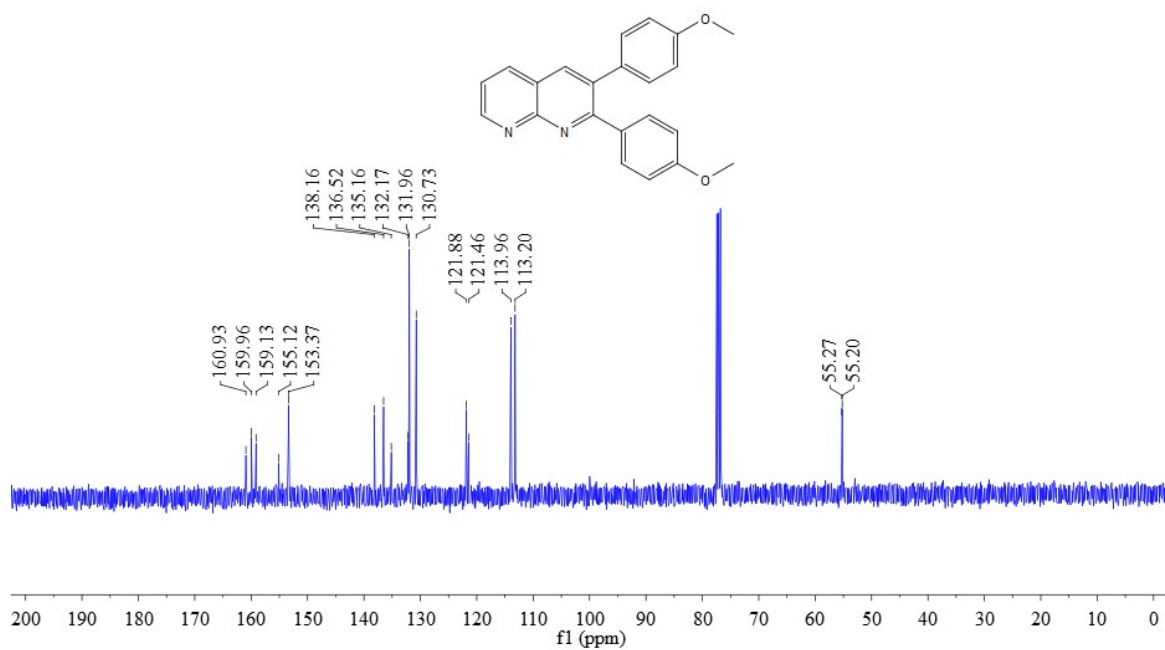
^{13}C -NMR spectrum of 2-(2-fluorophenyl)-3-methyl-1,8-naphthyridine



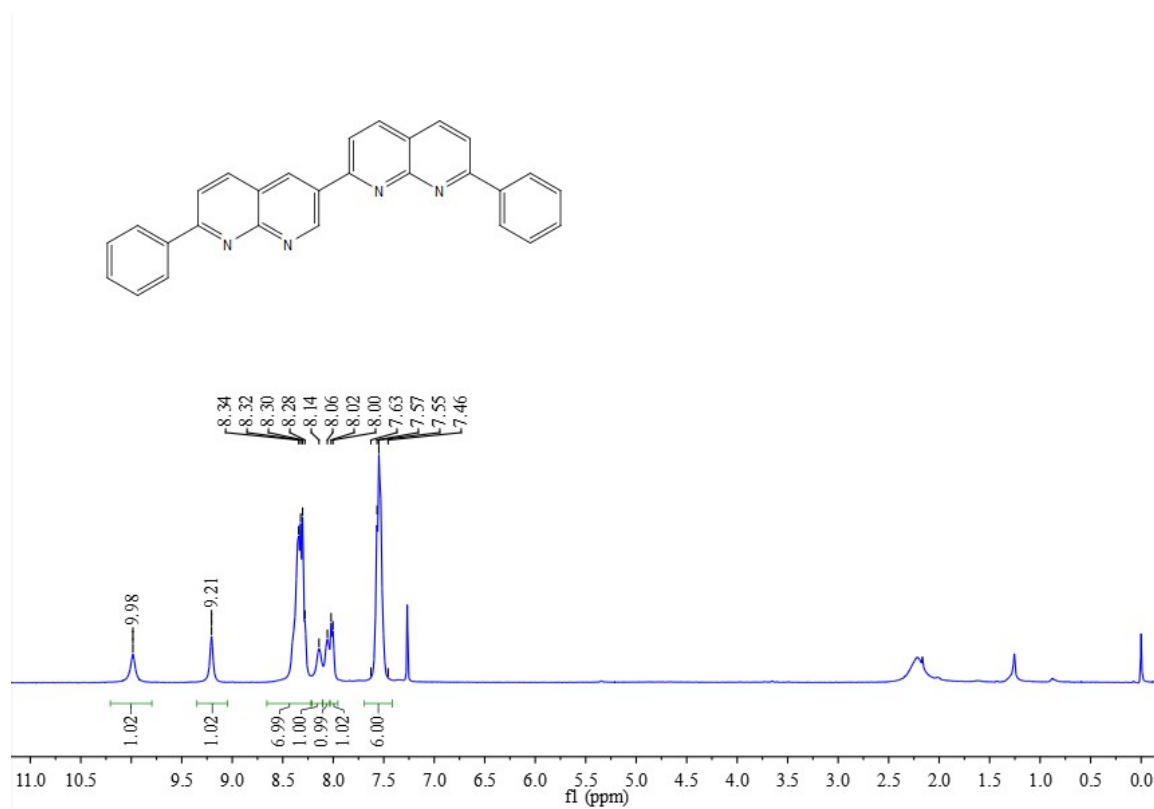
¹H-NMR spectrum of 2,3-bis(4-methoxyphenyl)-1,8-naphthyridine



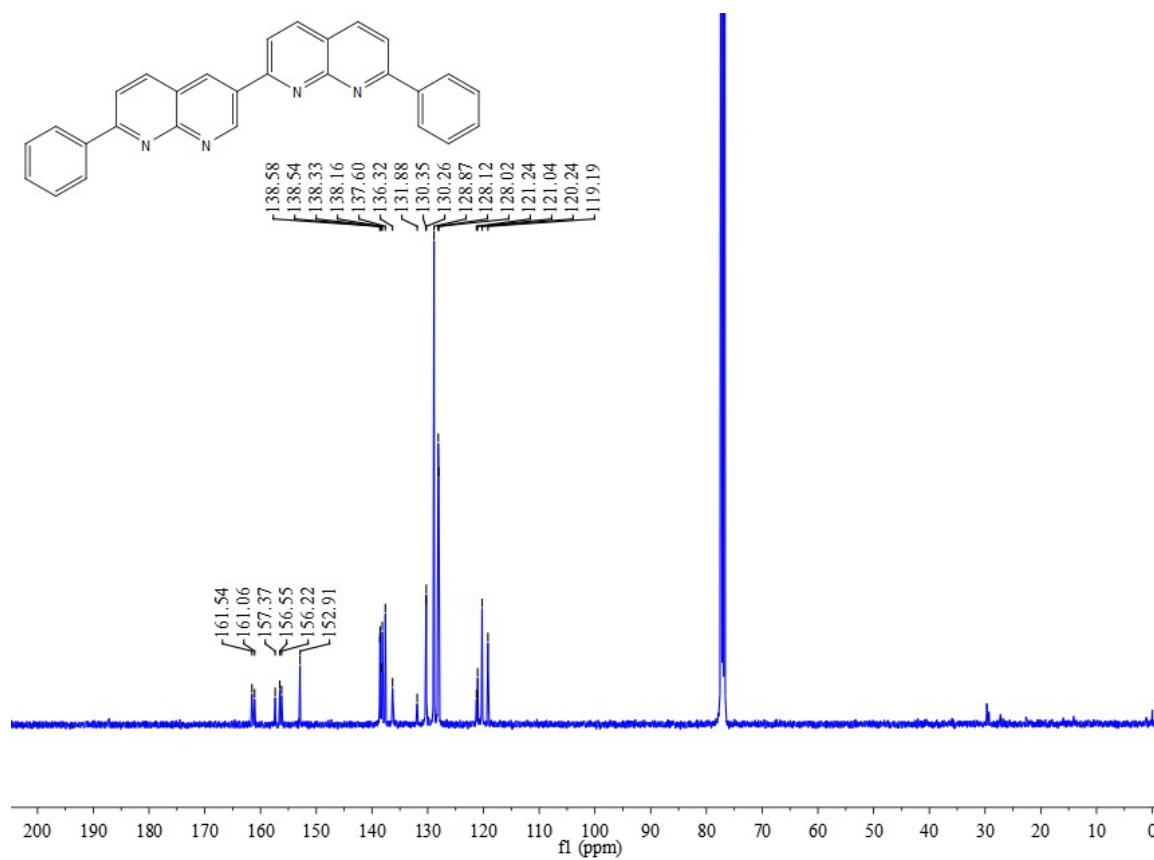
¹³C-NMR spectrum of 2,3-bis(4-methoxyphenyl)-1,8-naphthyridine



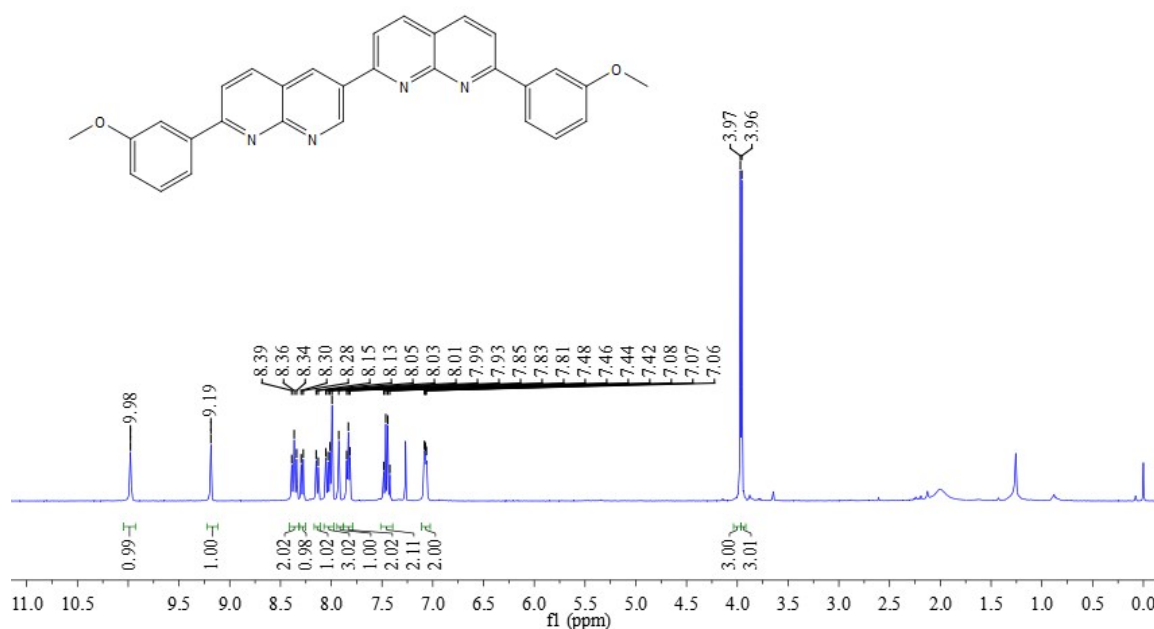
¹H-NMR spectrum of 7,7'-diphenyl-2,3'-bi(1,8-naphthyridine) (2aa')



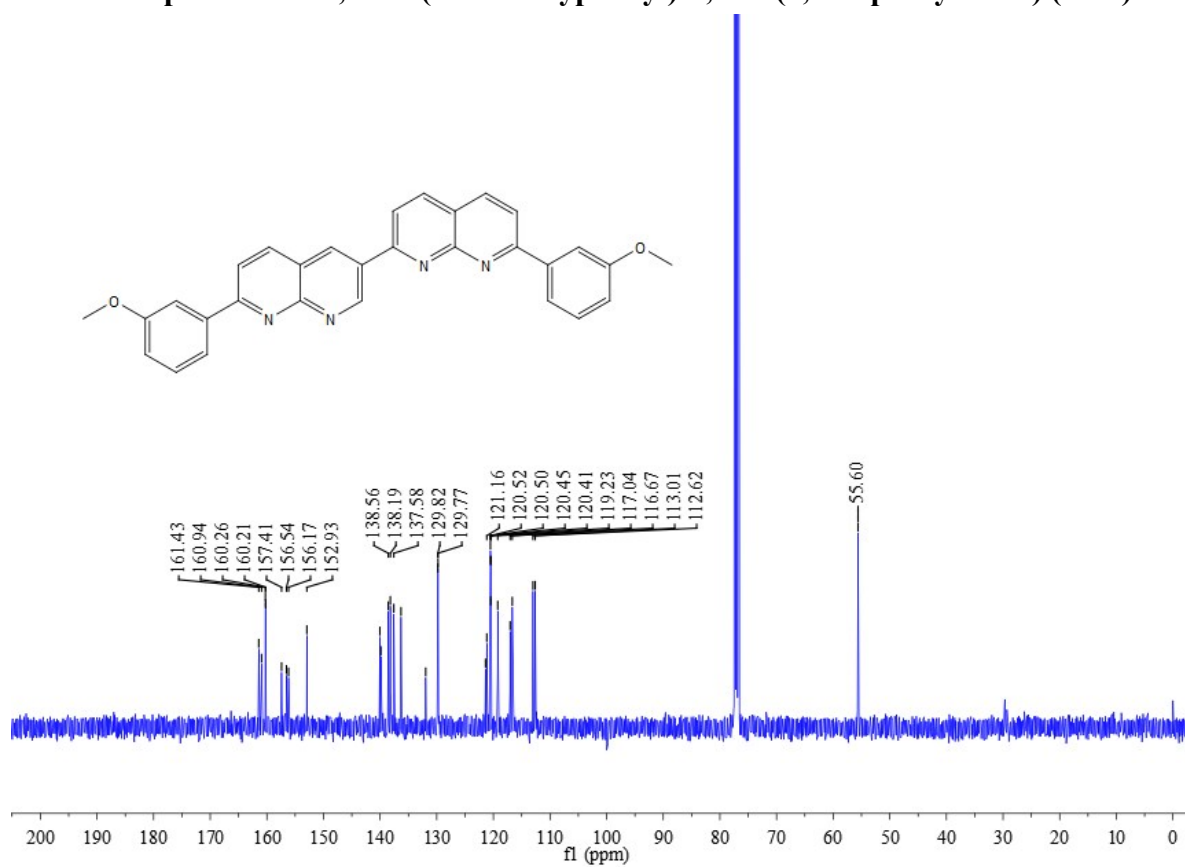
¹³C-NMR spectrum of 7,7'-diphenyl-2,3'-bi(1,8-naphthyridine) (2aa')



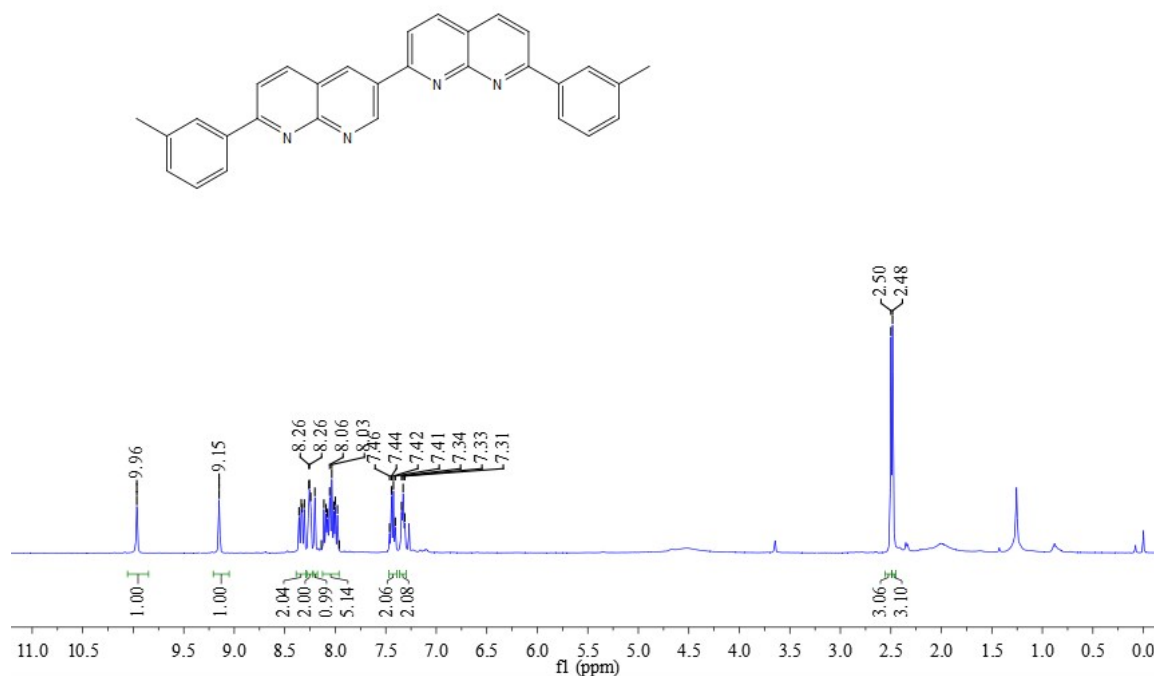
¹H-NMR spectrum of 7,7'-bis(3-methoxyphenyl)-2,3'-bi(1,8-naphthyridine) (2bb')



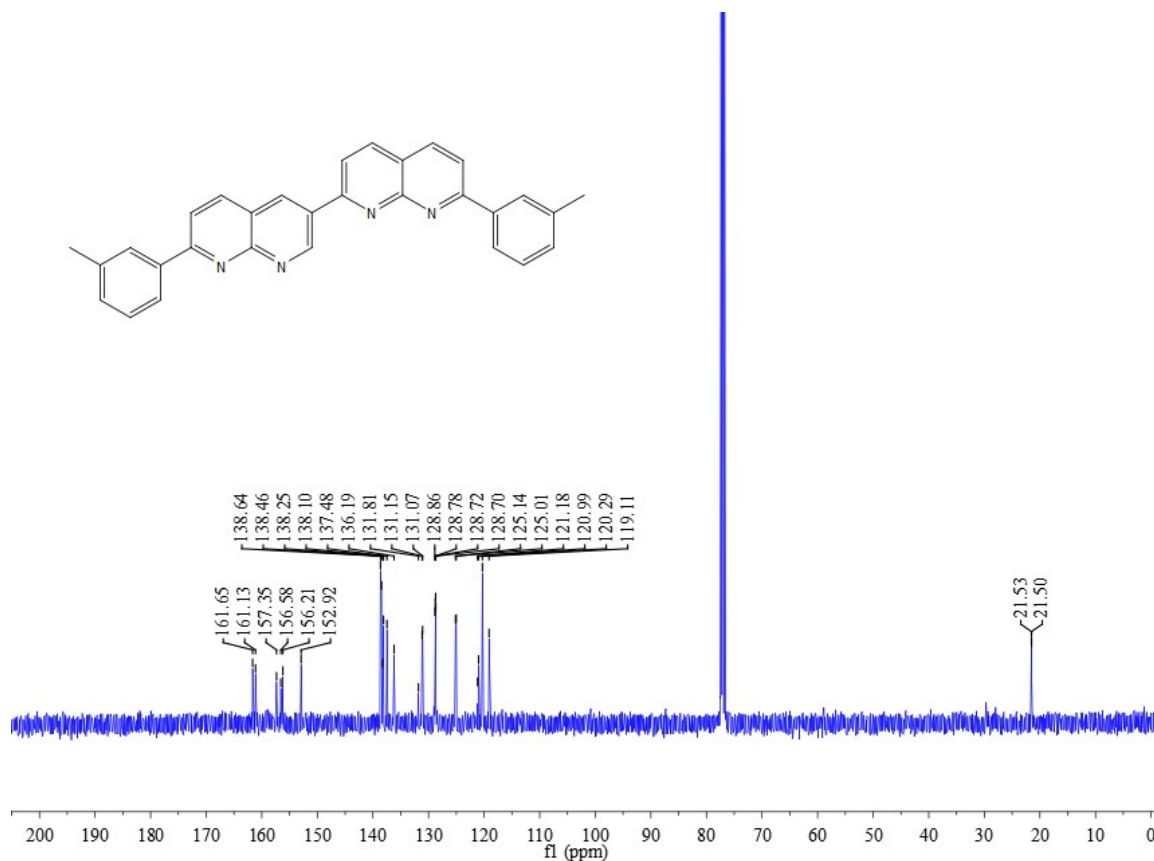
¹³C-NMR spectrum of 7,7'-bis(3-methoxyphenyl)-2,3'-bi(1,8-naphthyridine) (2bb')



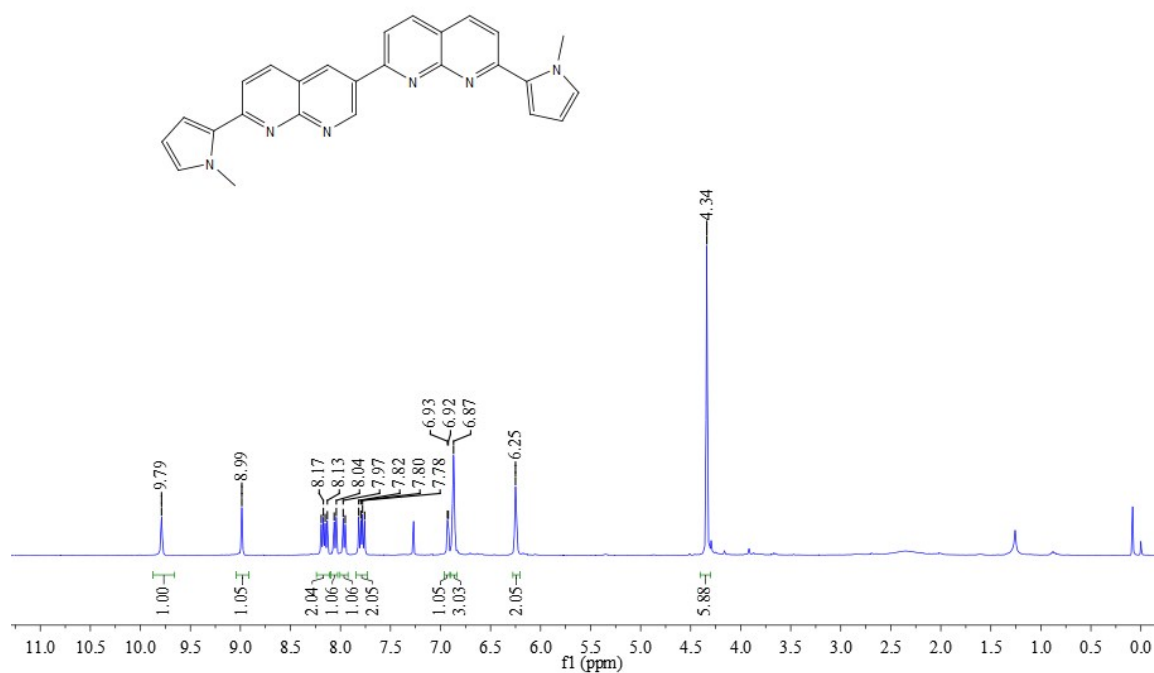
¹H-NMR spectrum of 7,7'-di-m-tolyl-2,3'-bi(1,8-naphthyridine) (2cc')



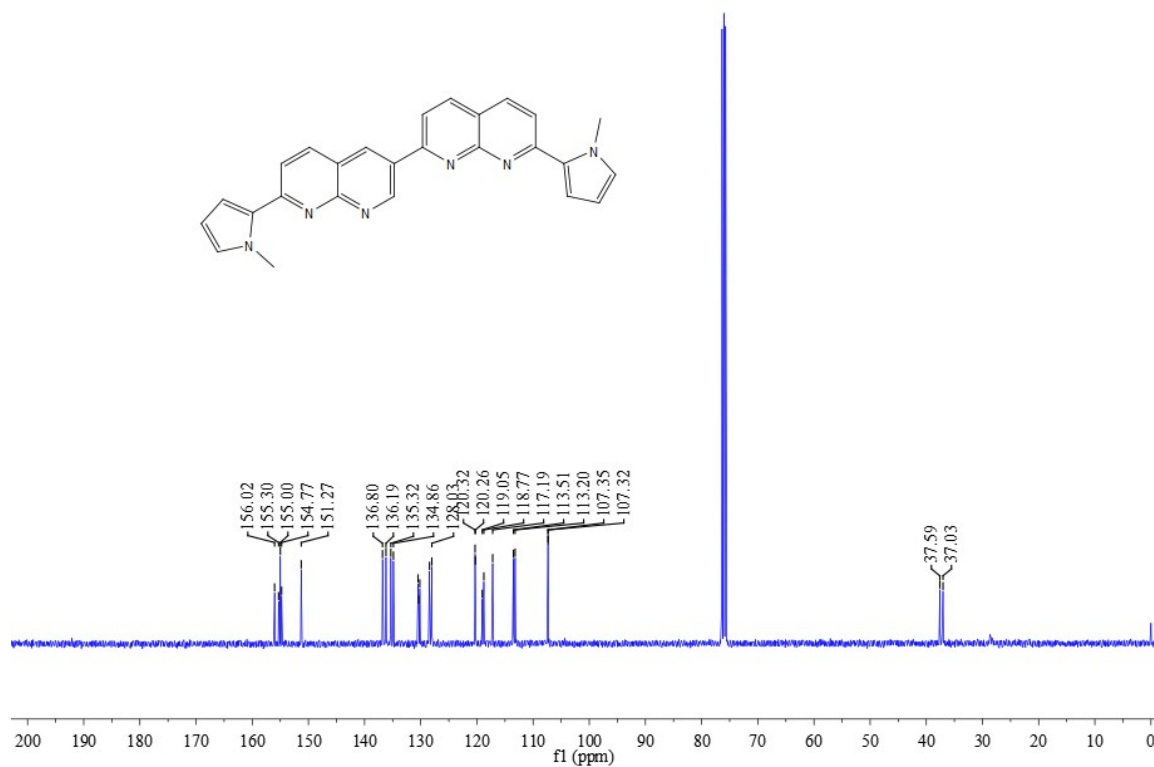
¹³C-NMR spectrum of 7,7'-di-m-tolyl-2,3'-bi(1,8-naphthyridine) (2cc')



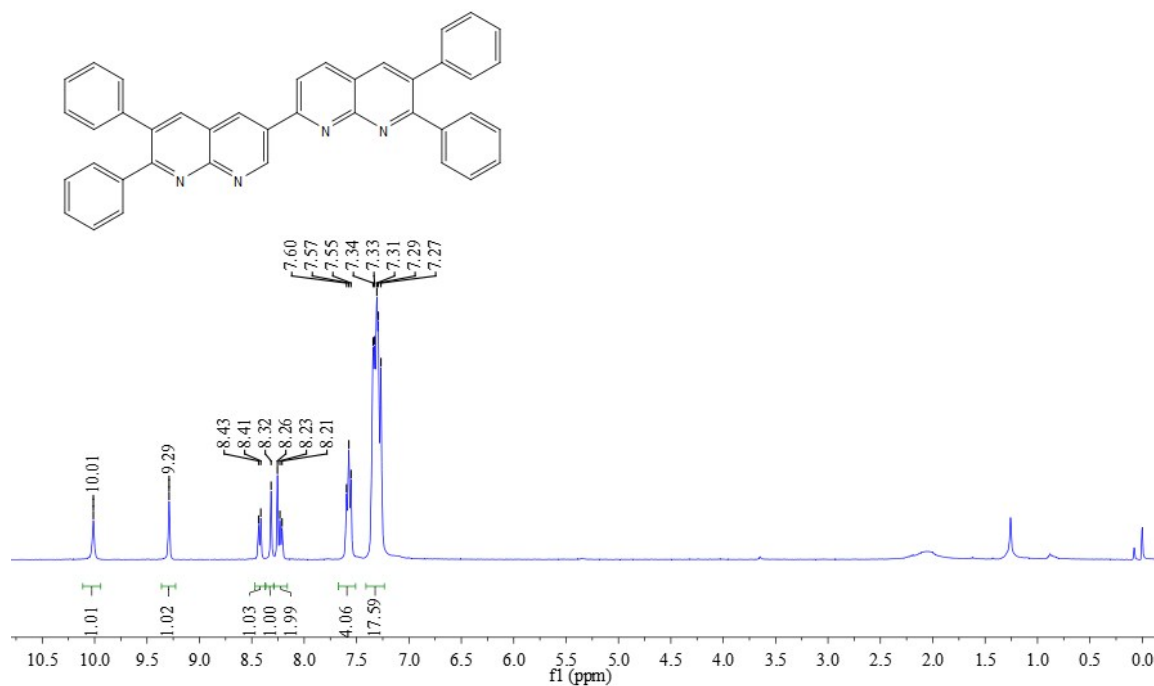
¹H-NMR spectrum of 7,7'-bis(1-methyl-1H-pyrrol-2-yl)-2,3'-bi(1,8-naphthyridine) (2dd')



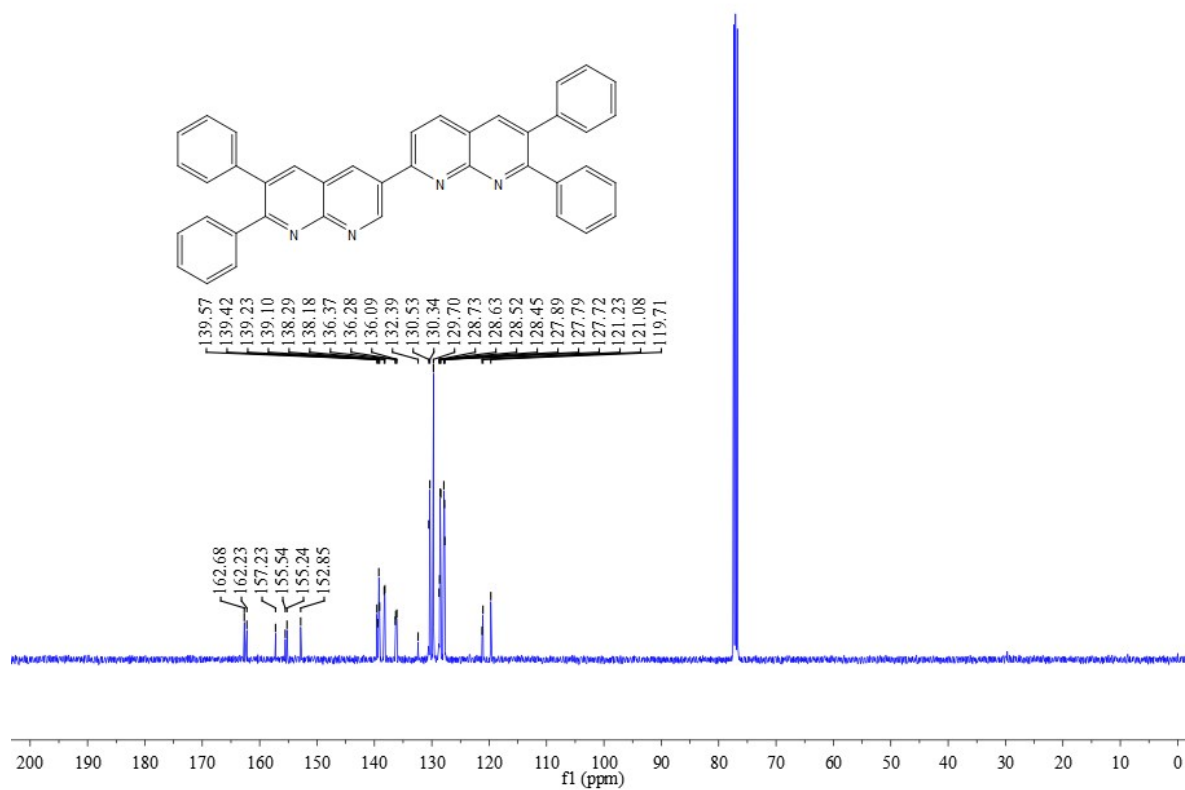
¹³C-NMR spectrum of 7,7'-bis(1-methyl-1H-pyrrol-2-yl)- 2,3'-bi (1,8-naphthyridine) (2dd')



¹H-NMR spectrum of 6,6',7,7'-tetraphenyl-2,3'-bi(1,8-naphthyridine) (2ee')

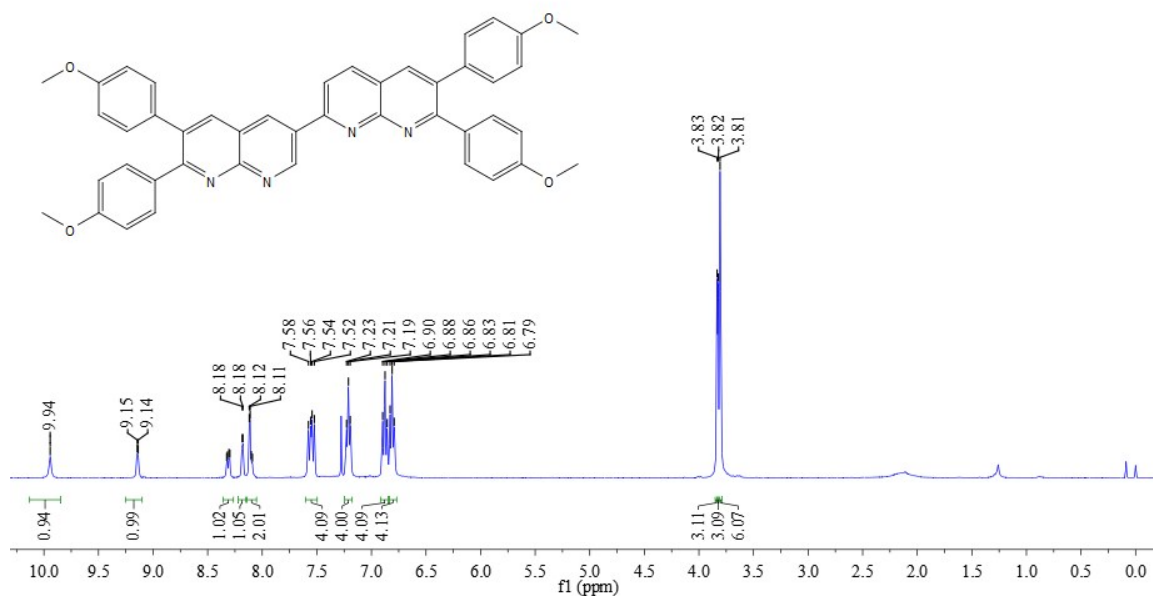


¹³C-NMR spectrum of 6,6',7,7'-tetrakis(4-phenyl)-2,3'-bi(1,8-naphthyridine) (2ee')

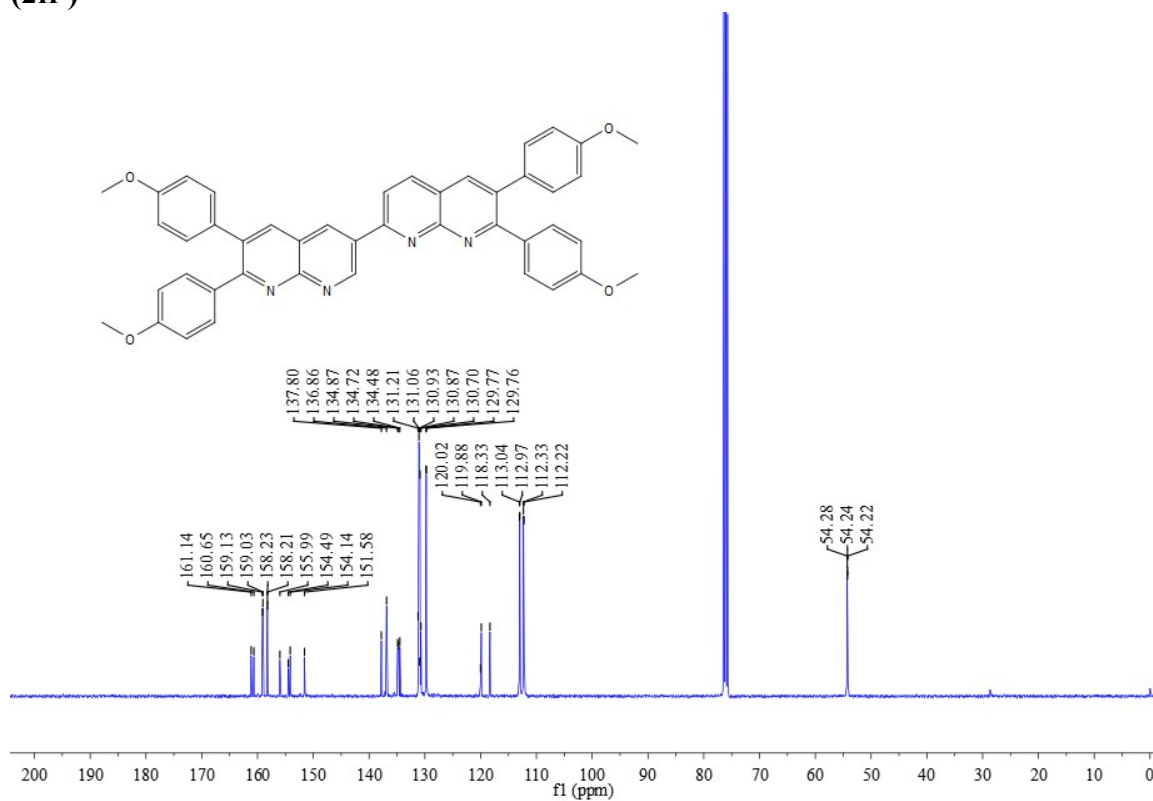


¹H-NMR spectrum of 6,6',7,7'-tetrakis(4-methoxyphenyl)-2,3'-bi(1,8-naphthyridine)

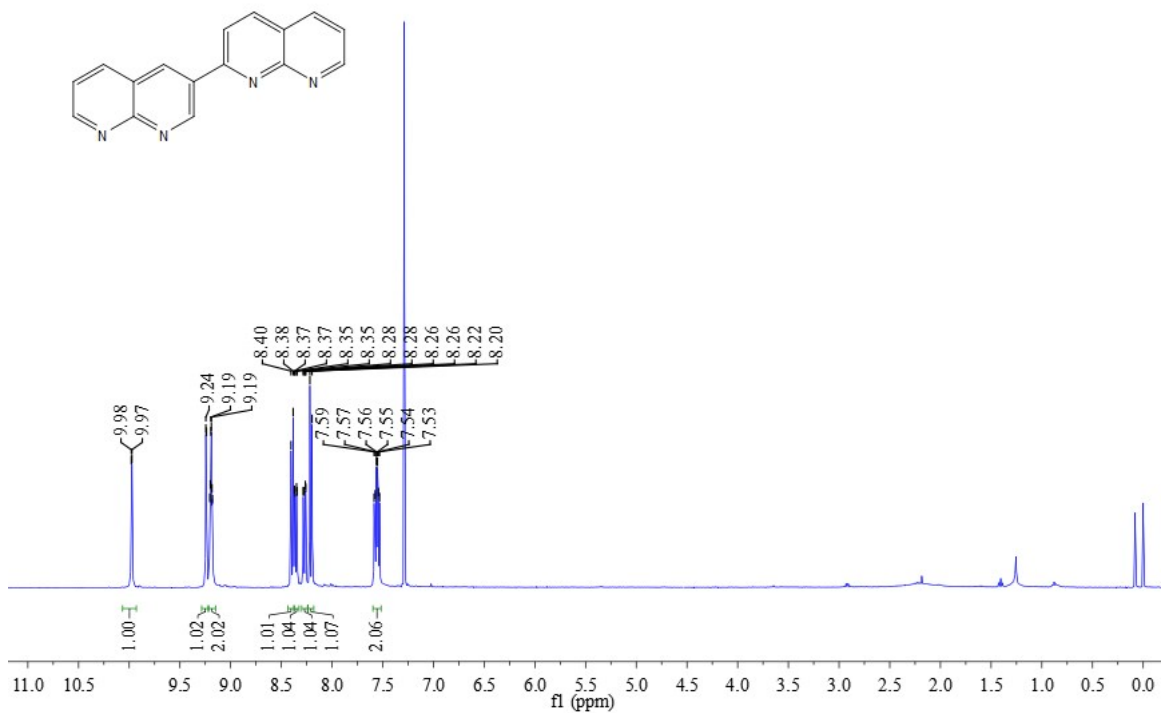
(2ff')



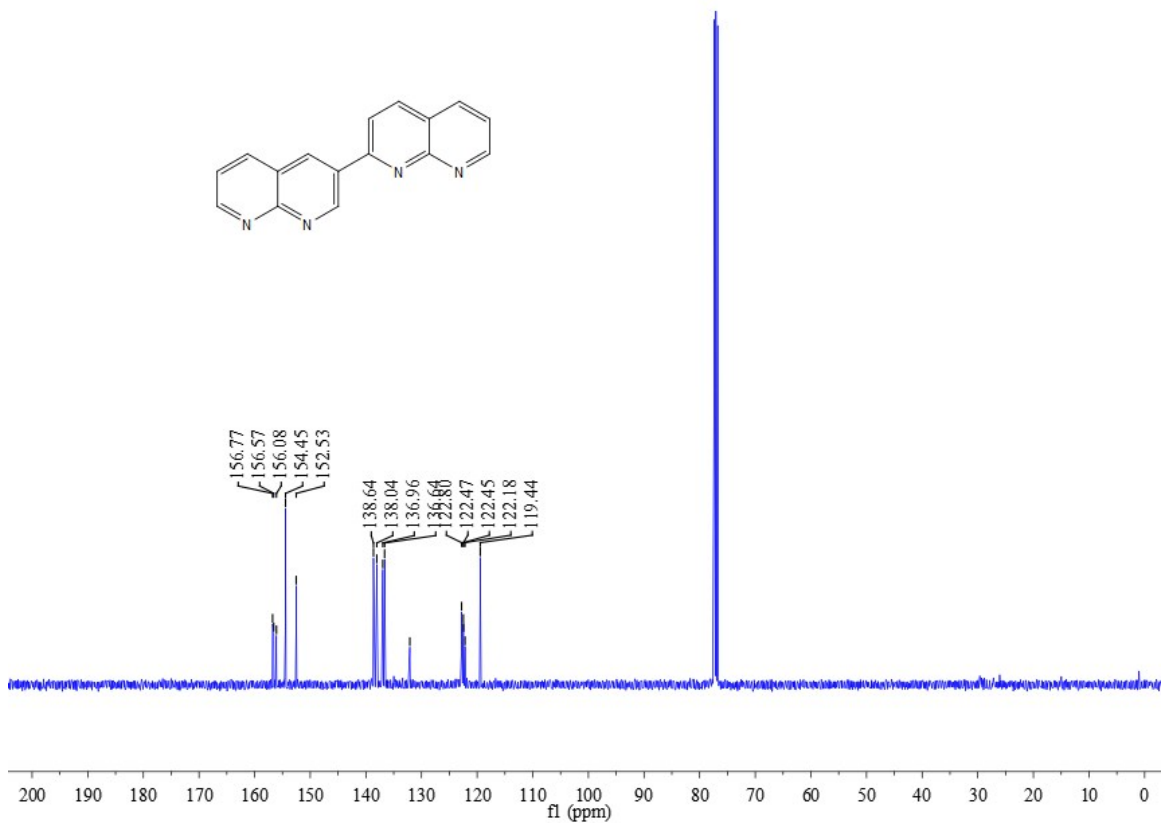
¹³C-NMR spectrum of 6,6',7,7'-tetrakis(4-methoxyphenyl)-2,3'-bi(1,8-naphthyridine) (2ff')



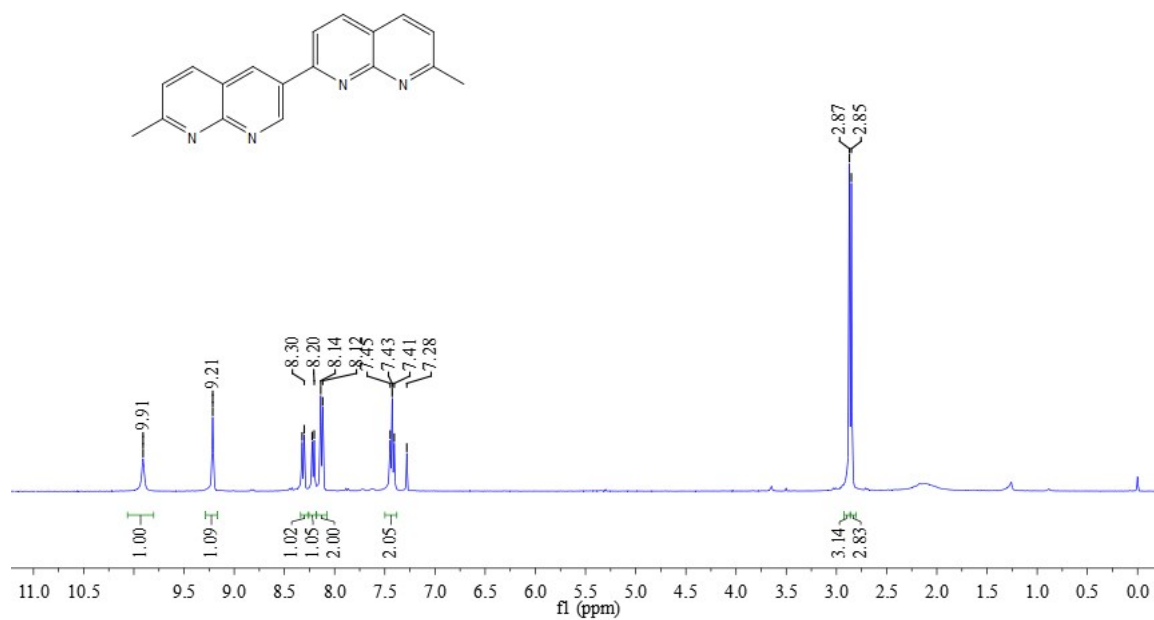
¹H-NMR spectrum of 2,3'-bi(1,8-naphthyridine) (2gg')



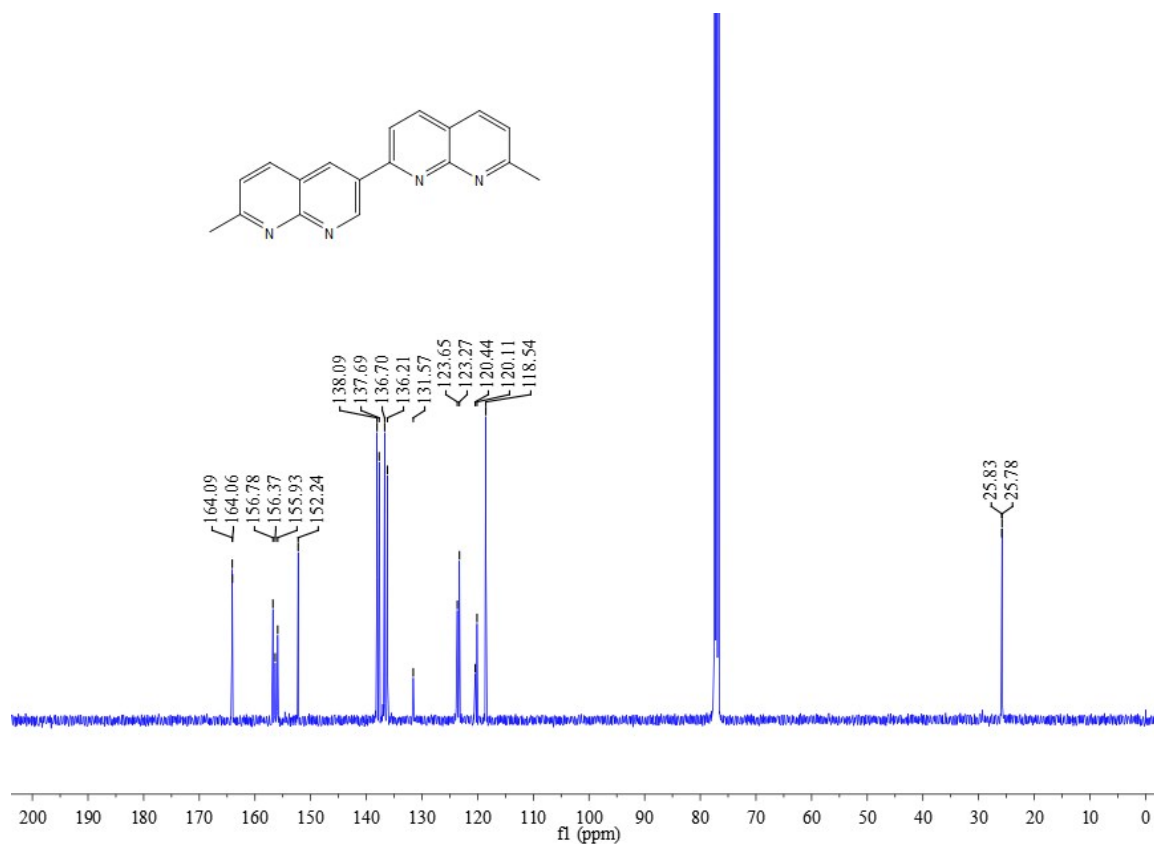
¹³C-NMR spectrum of 2,3'-bi(1,8-naphthyridine) (2gg')



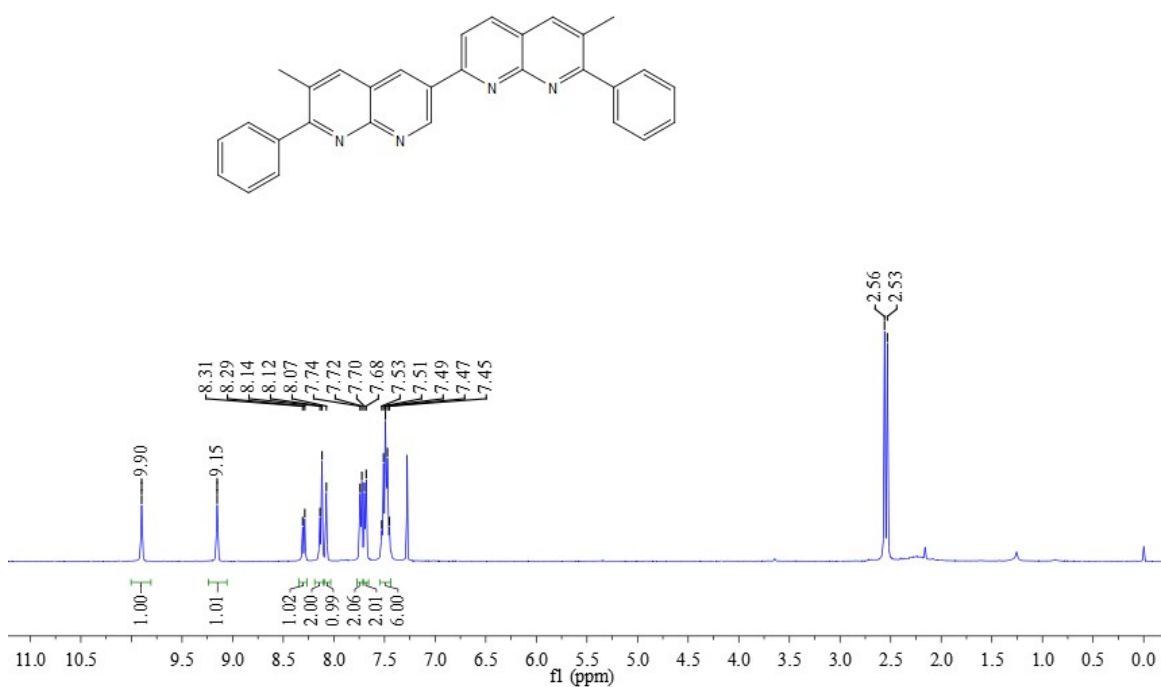
¹H-NMR spectrum of 7,7'-dimethyl-2,3'-bi(1,8-naphthyridine) (2hh')



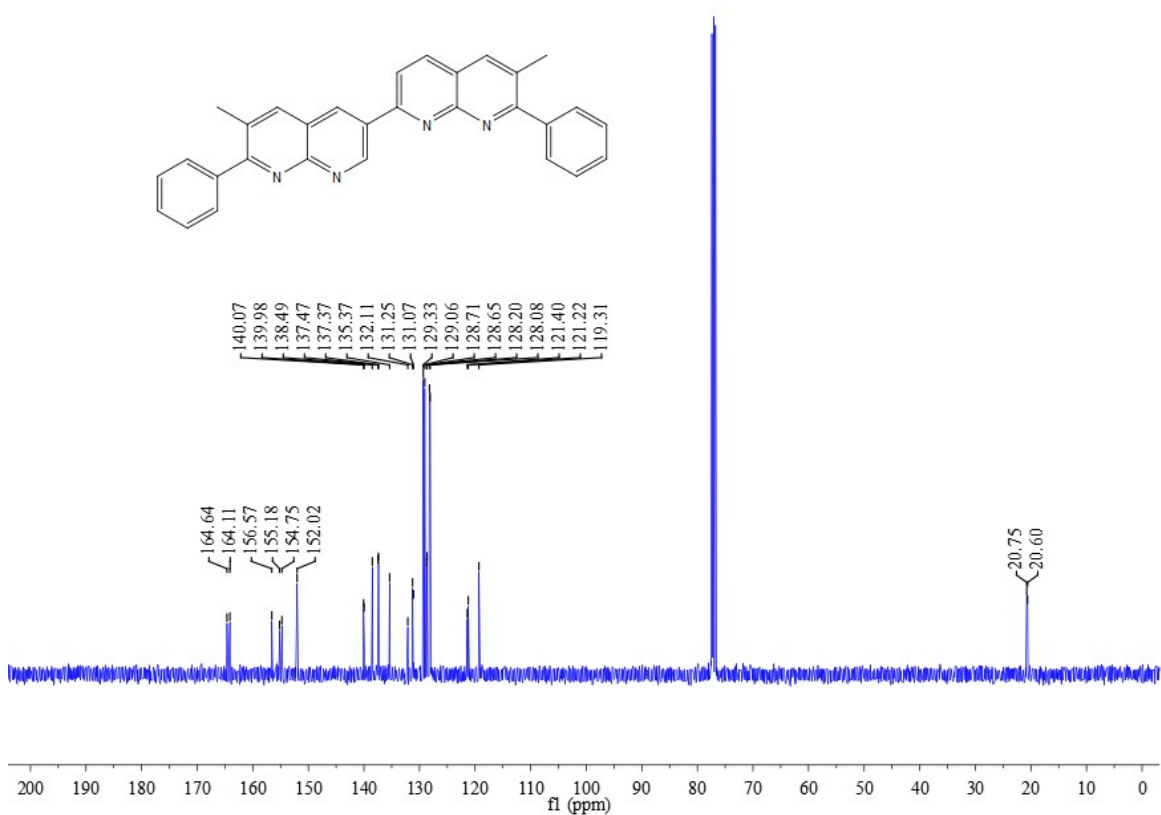
¹³C-NMR spectrum of 7,7'-dimethyl-2,3'-bi(1,8-naphthyridine) (2hh')



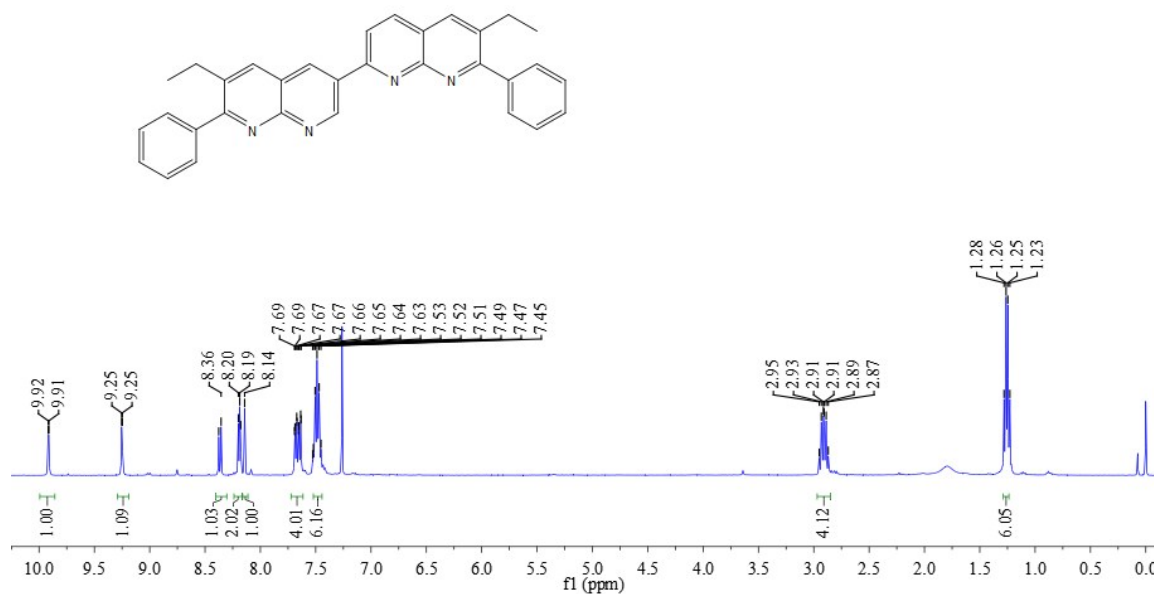
¹H-NMR spectrum of 6,6'-dimethyl-7,7'-diphenyl-2,3'-bi(1,8-naphthyridine) (2ii')



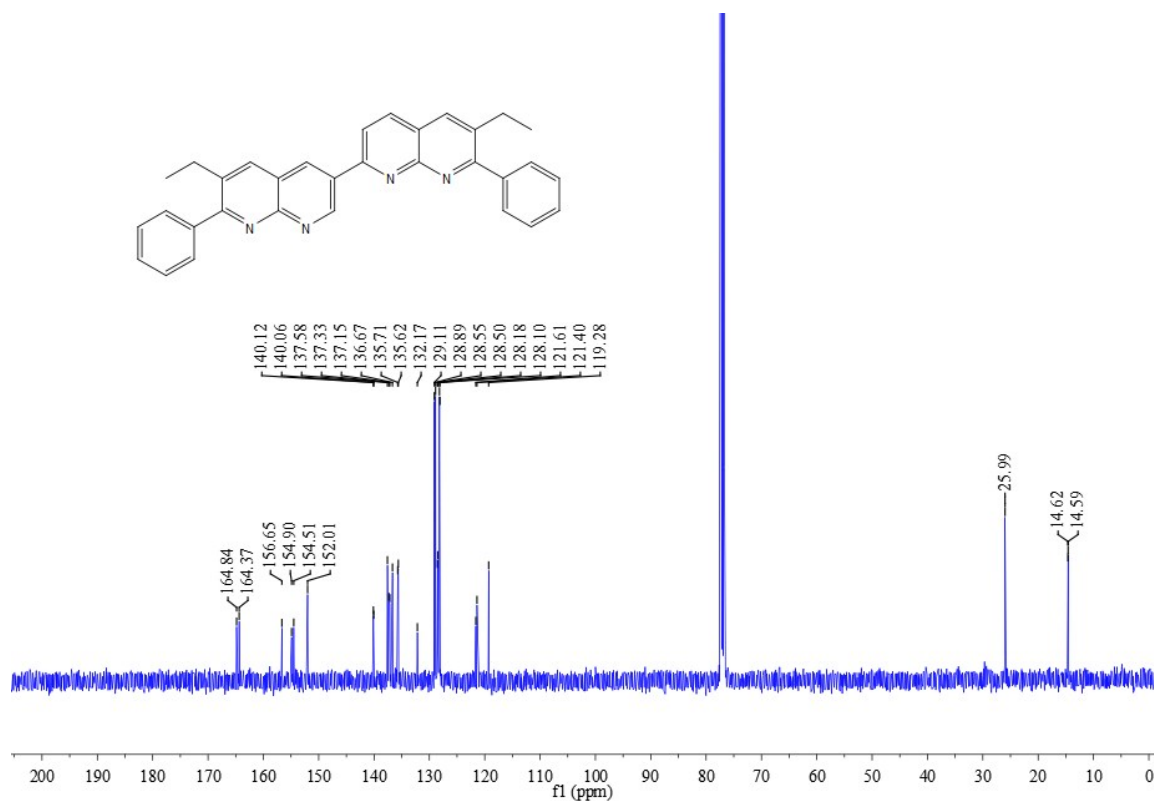
¹³C-NMR spectrum of 6,6'-dimethyl-7,7'-diphenyl-2,3'-bi(1,8-naphthyridine) (2ii')



¹H-NMR spectrum of 6,6'-diethyl-7,7'-diphenyl-2,3'-bi(1,8-naphthyridine) (2jj')

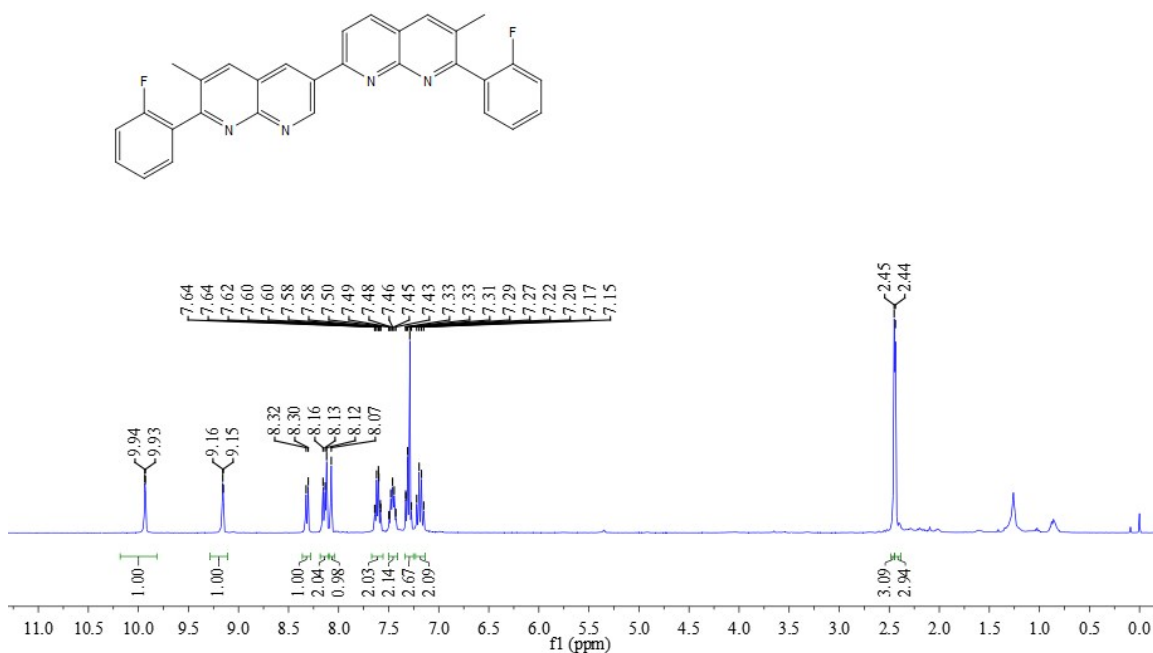


¹³C-NMR spectrum of 6,6'-diethyl-7,7'-diphenyl-2,3'-bi(1,8-naphthyridine) (2jj')

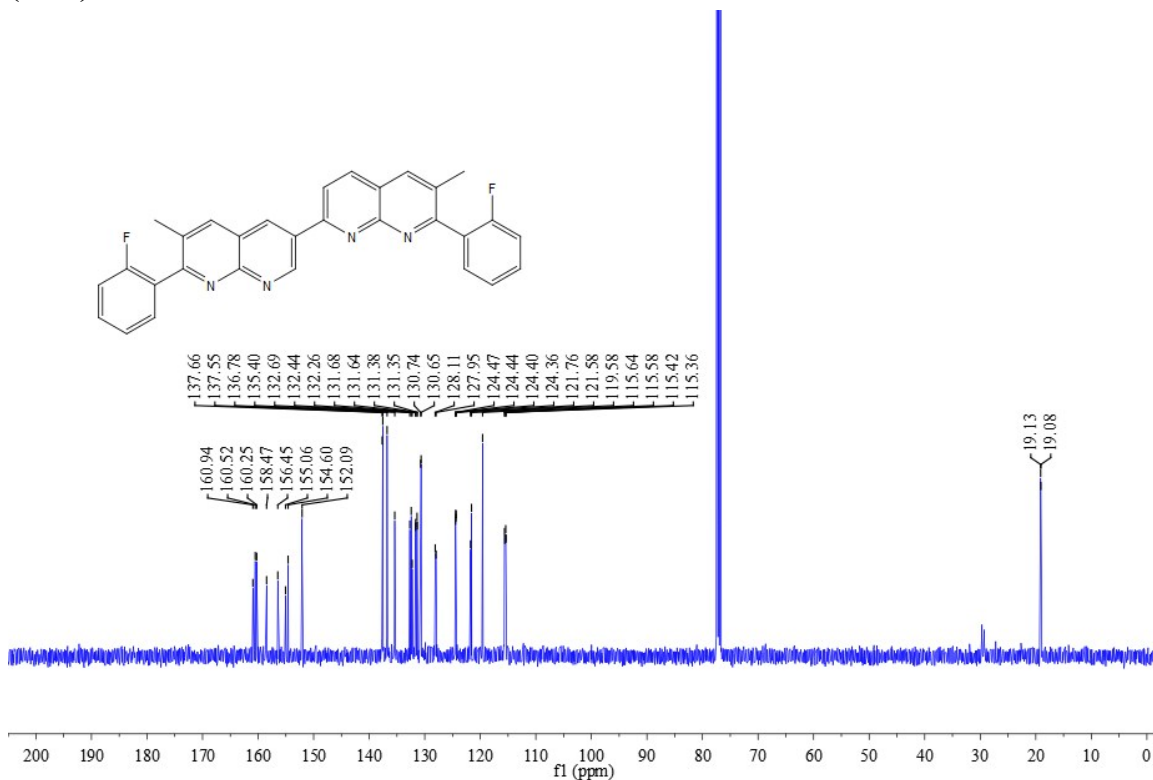


¹H-NMR spectrum of 7,7'-bis(2-fluorophenyl)-6,6'-dimethyl-2,3'-bi (1,8-naphthyridine)

(2kk')

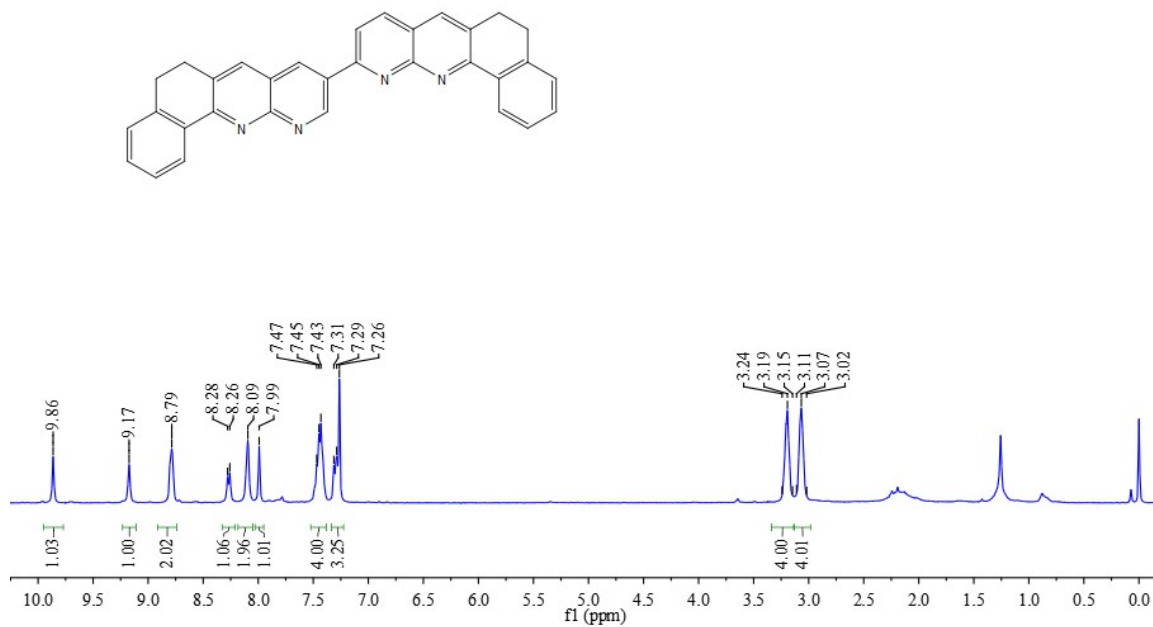


¹³C-NMR spectrum of 7,7'-bis(2-fluorophenyl)-6,6'-dimethyl-2,3'-bi(1,8-naphthyridine) (2kk')



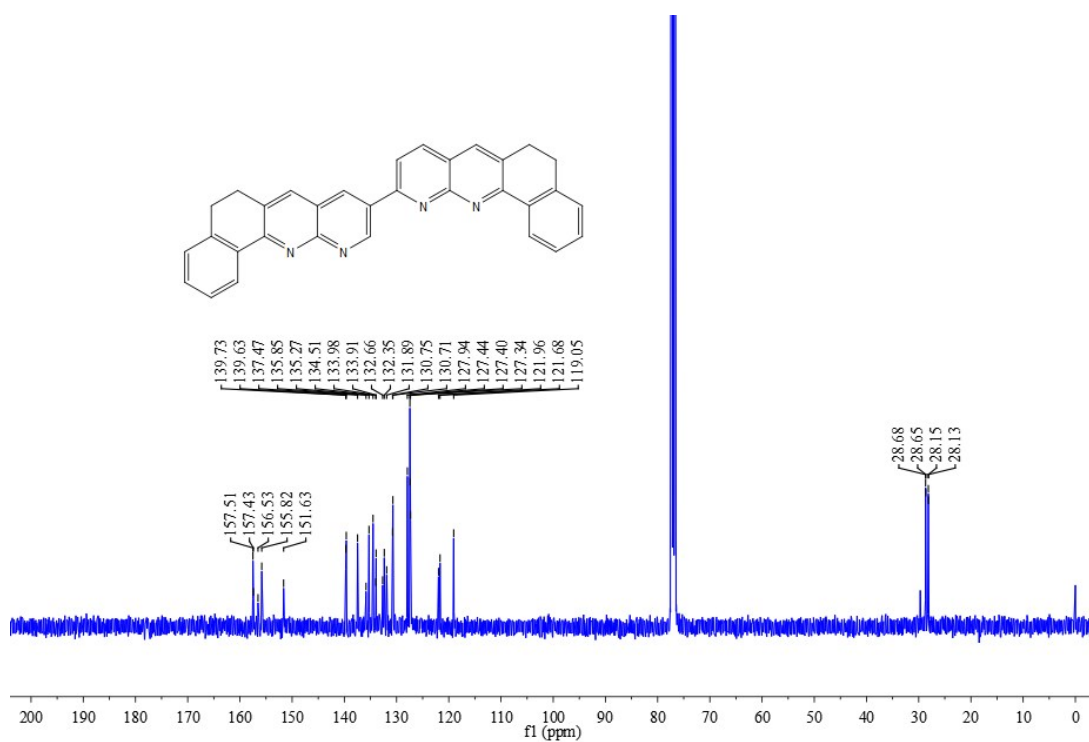
¹H-NMR spectrum of 5,5',6,6'-tetrahydro-9,10'-binaphtho[1,2-b] [1,8] naphthyridine

(2II')

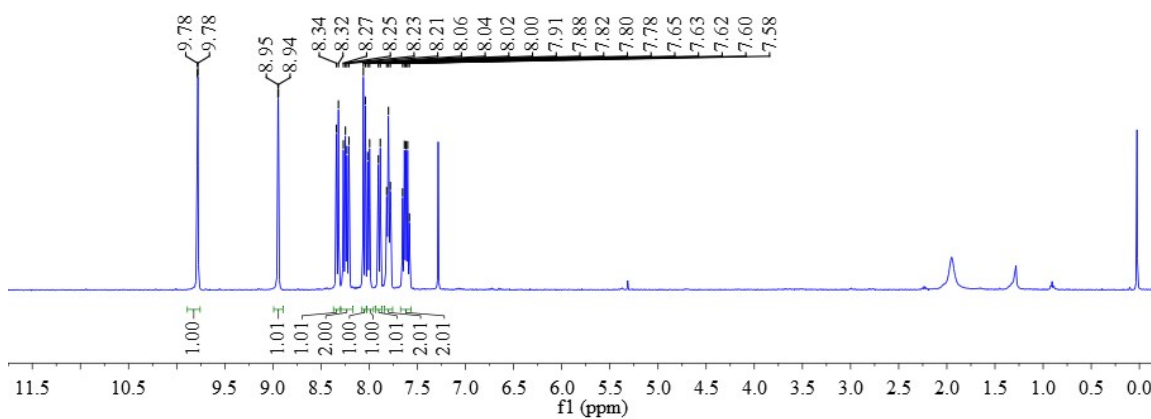
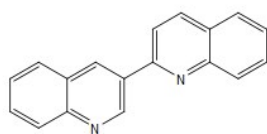


¹³C-NMR spectrum of 5,5',6,6'-tetrahydro-9,10'-binaphtho[1,2-b][1,8]naphthyridine

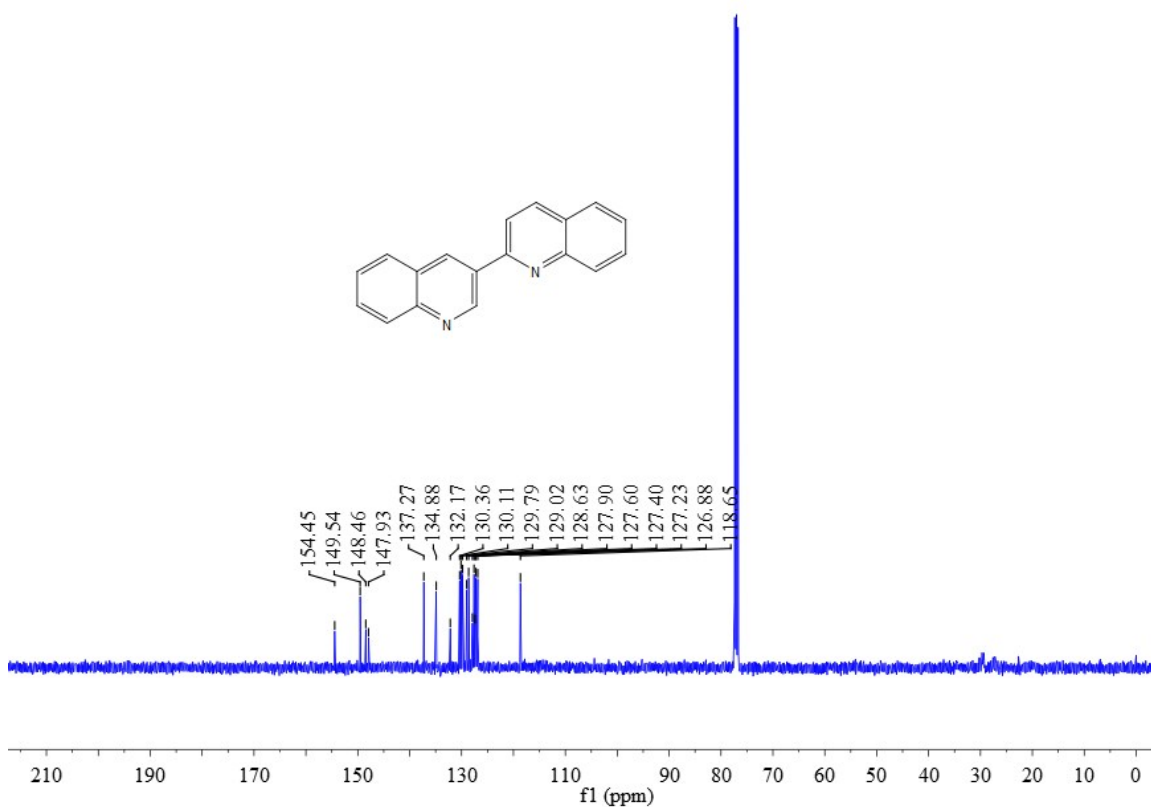
(2II')



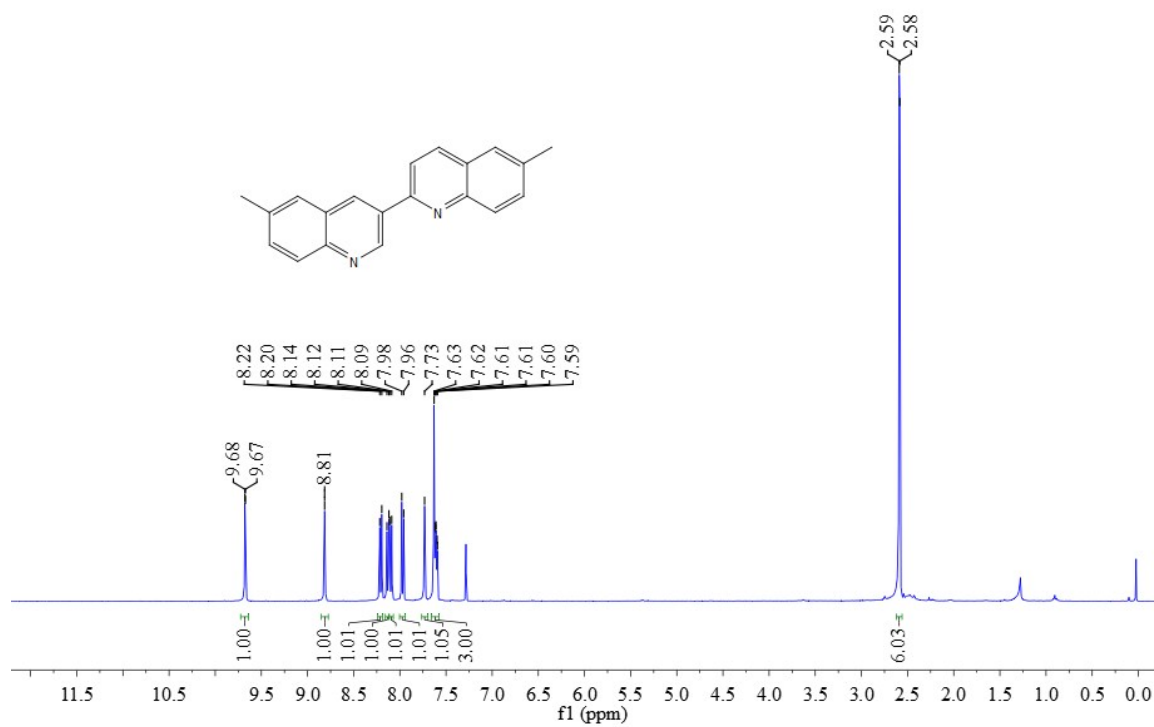
¹H-NMR spectrum of 2,3'-biquinoline (2mm')



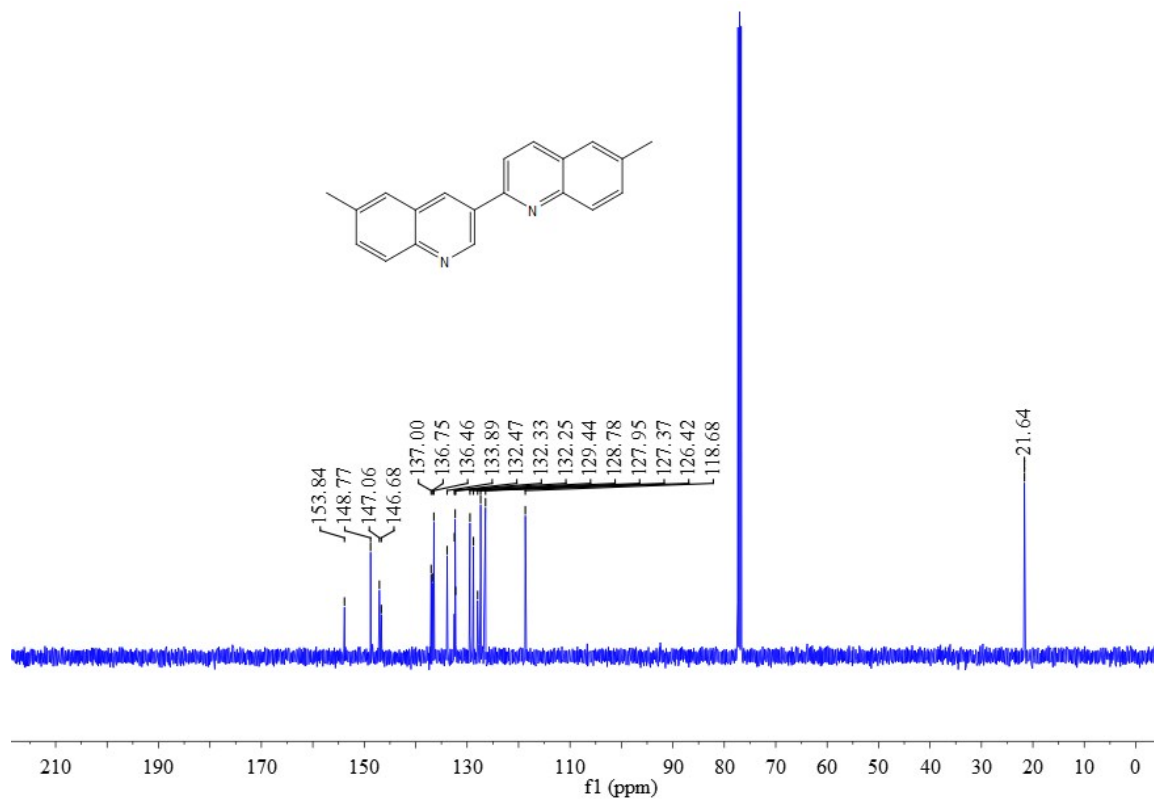
¹³C-NMR spectrum of 2,3'-biquinoline (2mm')



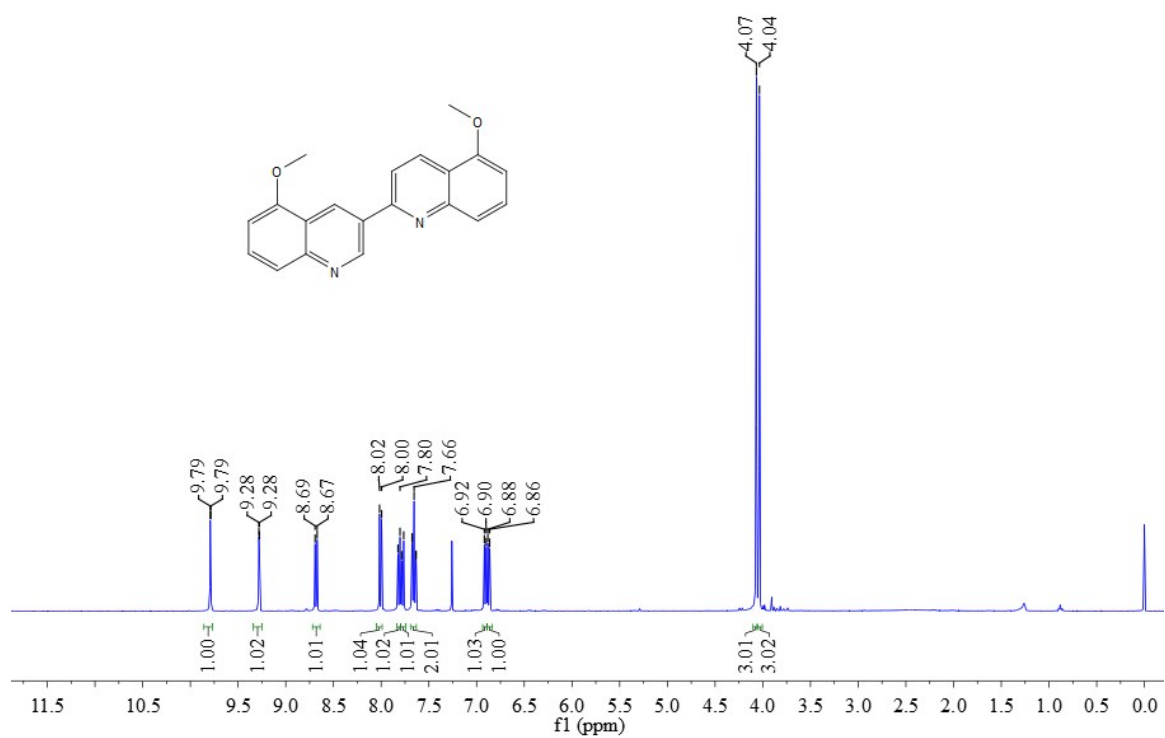
¹H-NMR spectrum of 6,6'-dimethyl-2,3'-biquinoline (2nn')



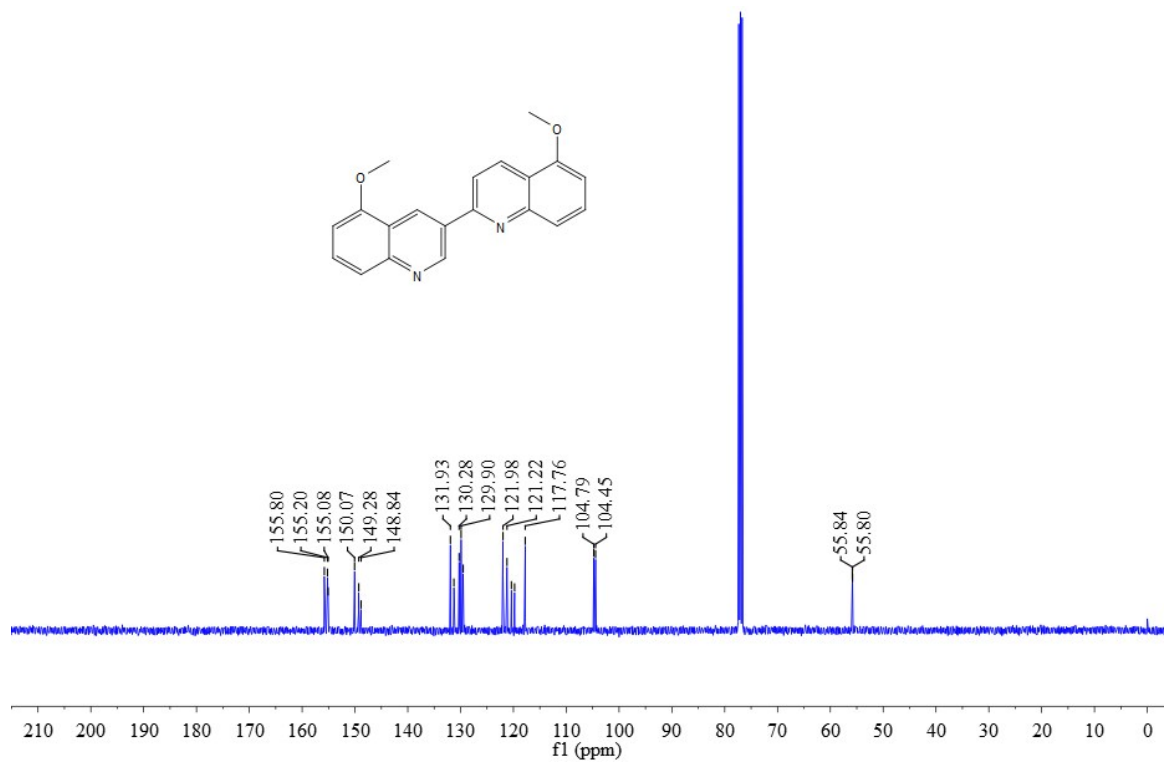
¹³C-NMR spectrum of 6,6'-dimethyl-2,3'-biquinoline (2nn')



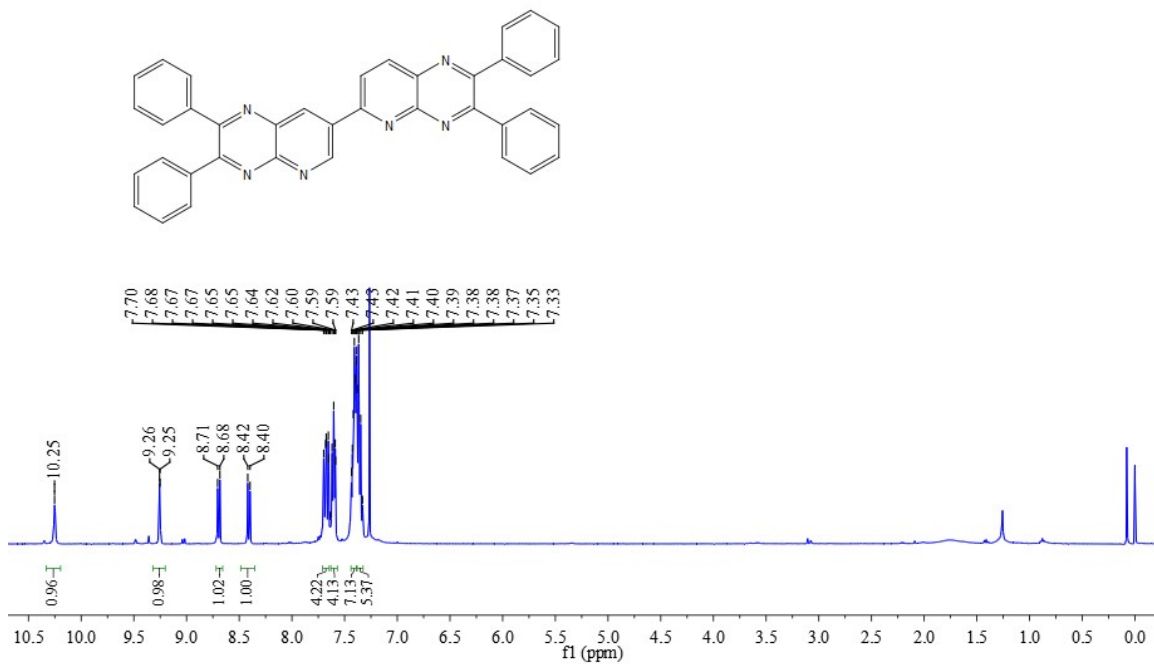
¹H-NMR spectrum of 5,5'-dimethoxy-2,3'-biquinoline (2oo')



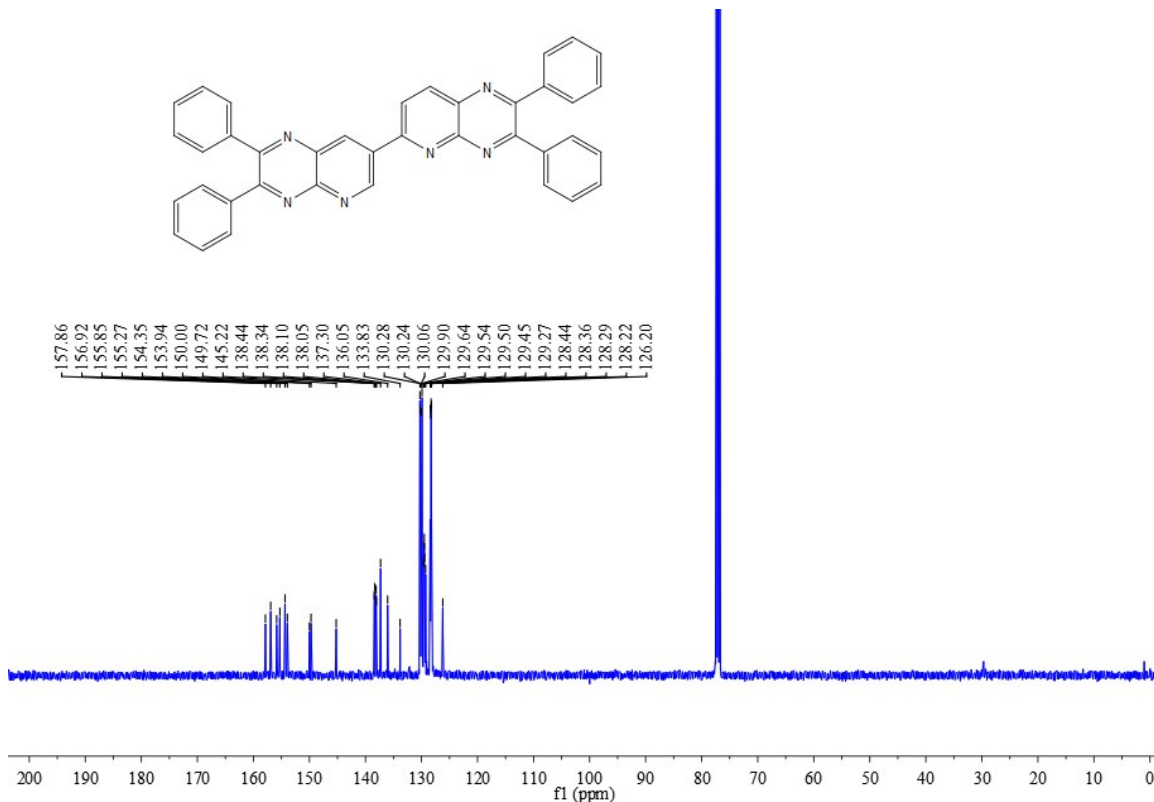
¹³C-NMR spectrum of 5,5'-dimethoxy-2,3'-biquinoline (200')



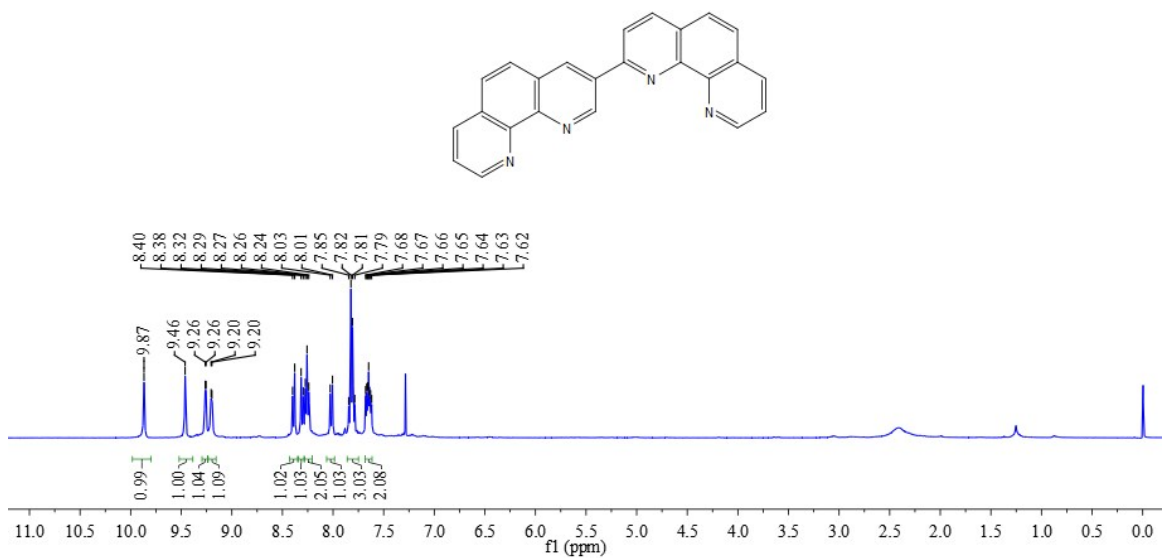
¹H-NMR spectrum of 2,2',3,3'-tetraphenyl-6,7'-bipyrido[2,3-b]pyrazine (2pp')



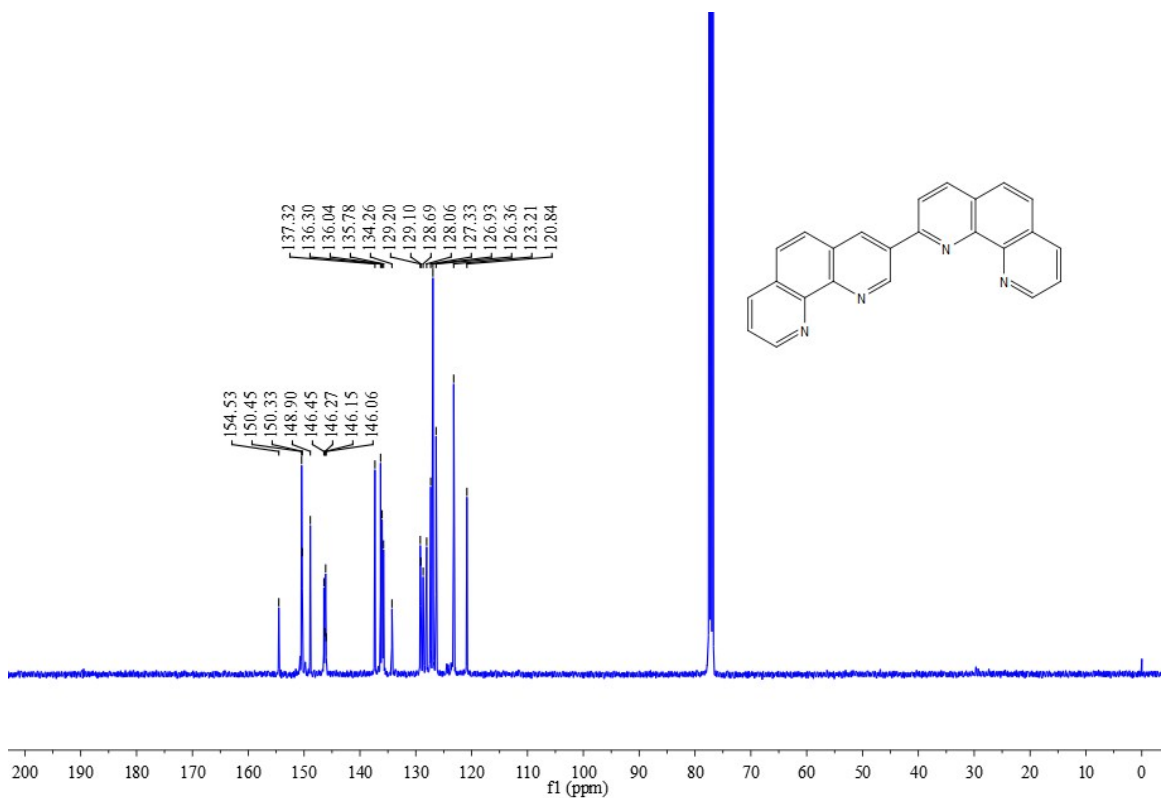
¹³C-NMR spectrum of 2,2',3,3'-tetraphenyl-6,7'-bipyrido[2,3-b]pyrazine (2pp')



¹H-NMR spectrum of 2,3'-bi(1,10-phenanthroline) (2qq')



¹³C-NMR spectrum of 2,3'-bi(1,10-phenanthroline) (2qq')



¹H-NMR spectrum of 2ag' and 2ga'

