Synthesis and their spectroscopic distinction of benzonaphthonaphthyridines and its isomer

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Preparation of Compound (8) & (9), general procedure;

2-Methyl-*N*-(1-naphthyl)quinolin-4-amine (**3**, 2 mmol) and thiophen-2carboxylic acid/furan-2-carboxylic acid (2.5 mmol) were added to polyphosphoric acid (6 g of P₂O₅ in 3 mL of H₃PO₄) and heated at 110 °C for 1 hour. The reaction was monitored by using TLC. After the completion of the reaction, it was poured into ice water, neutralized with saturated sodium bicarbonate solution to remove excess of pyridine-3-carboxylic acid/thiophen-2carboxylic acid/furan-2-carboxylic acid, extracted with ethyl acetate, purified by column chromatography using silica gel and product eluted with petroleum ether : ethyl acetate (97 : 3) mixture to get **8**, **9** which was recrystallised using methanol.

Compound 8

Colourless prisms; mp: 258-260 °C; Yield: (49 %); IR (KBr, cm⁻¹) $\nu_{\max}$: 1637 (C=N), 1599; ¹H NMR (500 MHz, CDCl₃) (ppm) δ_{H} : 2.35 (s, 3H, C₄-CH₃), 2.91 (s, 3H, C₆-CH₃), 6.59 (t, 1H, C₄'-H, *J* = 3.50 Hz, *J* = 1.5 Hz), 7.24 (dd, 1H, C₃-H, *J* = 9.50 Hz, *J* = 1.50 Hz), 7.36 (dd, 1H, C₃'-H, *J* = 3.50 Hz, *J* = 1.00 Hz), 7.45 (t, 1H, C₂-H, *J* = 8.50 Hz), 7.61 (d, 1H, C₉-H, *J* = 8.00 Hz), 7.67 (dd, 1H, C₅'-H, *J* = 4.50 Hz, *J* = 1.50 Hz), 7.79-8.00 (m, 3H, C₈, C₁₁, C₁₂-H), 8.30 (d, 1H, C₁₀-H, *J* = 7.50 Hz), 9.27 (d, 1H, C₁-H, *J* = 9.00 Hz), 9.69 (d, 1H, C₁₃-H, *J* = 8.00 Hz); ¹³C NMR (125 MHz, CDCl₃) (ppm) δ_{C} : 17.79 (C₆-CH₃), 28.90 (C₄-CH₃), 112.27 (C₄'), 118.50 (C_{6a}), 120.09(C₃'), 123.41 (C₁), 124.38 (C₉), 124.82 (C₂), 125.22 (C₈),

125.37 (C_{7a}), 126.14 (C₁₃), 126.42 (C_{14b}), 127.15 (C₁₂), 127.86 (C₁₀), 128.31 (C₃), 129.98 (C₁₁), 132.52 (C_{9a}), 134.00 (C_{13a}), 135.75 (C₄), 139.23 (C₇), 142.44 (C_{5'}), 146.21 (C_{13b}), 147.10 (C_{14a}), 147.40 (C_{2'}), 148.94 (C_{4a}), 157.86 (C₆); MS (EI) m/z (%) 374 (M⁺, 100); Anal. Calcd. for C₂₆H₁₈N₂O (374): C, 83.40; H, 4.85; N, 7.48; Found: C, 83.45; H, 4.88; N, 7.42%.

Compound 9

Colourless prisms; mp: 233-236 °C; Yield: (30 %); IR (KBr, cm⁻¹) v_{max}: 1637 (C=N), 1536; ¹H NMR (500 MHz, CDCl₃) (ppm) δ_H: 2.39 (s, 3H, C₄-CH₃), 2.70 (s, 3H, C₆-CH₃), 7.01 (d, 1H, C₃-H, *J* = 8.50 Hz), 7.16 (t, 1H, C_{4'}-H, *J* = 4.50 Hz), 7.41 (t, 1H, C₂-H *J* = 9.00 Hz), 7.61 (d, 1H, C₉-H, *J* = 8.00 Hz), 7.66 (dd, 1H, C_{5'}-H, *J* = 4.50 Hz, *J* = 1.00 Hz), 7.75-7.82 (m, 3H, C₈, C₁₁, C₁₂-H), 7.91 (dd, 1H, C_{3'}-H *J* = 3.50 Hz, *J* = 1.00 Hz), 8.11 (d, 1H, C₁₀-H, *J* = 8.00 Hz), 9.15 (d, 1H, C₁-H *J* = 8.00 Hz), 9.47 (d, 1H, C₁₃-H *J* = 8.50 Hz); ¹³C NMR (125 MHz, CDCl₃) (ppm) δ_C: 21.88 (C₆-CH₃), 27.79 (C₄-CH₃), 117.90 (C_{6a}), 122.11 (C₁), 124.29 (C₉), 124.73 (C₂), 125.12 (C₈), 125.33 (C_{7a}), 126.03 (C₁₃), 126.39 (C_{14b}), 127.01 (C₁₂), 127.55 (C₁₀), 128.02 (C_{3'}), 128.57 (C₃), 129.78 (C₁₁), 132.27 (C_{9a}), 133.76 (C_{4'}), 134.55 (C_{13a}), 134.80 (C_{5'}), 136.65 (C₄), 137.63 (C_{2'}), 138.59 (C₇), 146.05 (C_{13b}), 147.10 (C_{14a}), 149.09 (C_{4a}), 159.36 (C₆); MS (EI) m/z (%) 390 (M⁺, 100); Anal. Calcd. for C₂₆H₁₈N₂S (390): C, 79.97; H, 4.65; N, 7.17; S, 8.21; Found: C, 80.01; H, 4.61; N, 7.21; S, 8.17%.

Preparation of compound (17) & (18), general procedure;

2-methyl-*N*-phenylbenzo[*h*]quinolin-4-amine (**15**) (2 mmol) and acetic acid/1-naphthoic acid (2.5 mmol) were added to polyphosphoric acid (6 g of P₂O₅ in 3 mL of H₃PO₄) and heated at 160 °C for 3 hours. The reaction was monitored by using TLC. After the completion of the reaction, it was poured into ice water, neutralized with saturated sodium bicarbonate solution to remove excess of benzoic acid/acetic acid/1-naphthoic acid, extracted with ethyl acetate, purified by column chromatography using silica gel and product eluted

with petroleum ether: ethyl acetate (99 : 1) mixture to get **17**, **18** which was recrystallised using methanol.

Compound 17

Pale yellow prisms; mp: 176-178 °C; Yield : (55 %); IR (KBr, cm^{-1}) ν_{max} : 1634 (C=N), 1566, 1521; ^1H NMR (400 MHz, CDCl_3) (ppm) δ_{H} : 2.50 (s, 3H, $\text{C}_6\text{-CH}_3$), 3.22 (s, 3H, $\text{C}_9\text{-CH}_3$), 3.30 (s, 3H, $\text{C}_7\text{-CH}_3$), 7.68-8.11 (m, 6H, C_{14} , C_2 , C_3 , C_8 , C_9 , $\text{C}_{10}\text{-H}$), 8.25 (d, 1H, $\text{C}_{14}\text{-H}$, $J = 8.80$ Hz), 9.35 (d, 1H, $\text{C}_4\text{-H}$, $J_o = 8.00$ Hz, $J_m = 2.00$ Hz), 9.42 (d, 1H, $\text{C}_{13}\text{-H}$, $J = 9.20$ Hz); ^{13}C NMR (100 MHz, CDCl_3) (ppm) δ_{C} : 18.4 ($\text{C}_{11}\text{-CH}_3$), 23.98 ($\text{C}_7\text{-CH}_3$), 29.72 ($\text{C}_6\text{-CH}_3$), 120.99 (C_{6a}), 122.65 (C_{13}), 123.21 (C_{7a}), 124.84 (C_4), 125.93 (C_{12b}), 126.47 (C_3), 126.89 (C_9), 127.03 (C_{14}), 127.33 (C_8), 127.69 (C_2), 128.01 (C_1), 130.11 (C_{4a}), 130.89 (C_{14a}), 131.99 (C_{10}), 135.68 (C_{11}), 137.78 (C_7) 138.54 (C_{11a}), 147.90 (C_{4b}), 149.44 (C_{12a}), 158.92 (C_6); MS (EI) m/z (%) 322 (M^+ , 100); Anal. Calcd. for $\text{C}_{23}\text{H}_{18}\text{N}_2$ (322): C, 85.68; H, 5.63; N, 8.69; Found: C, 85.70; H, 5.671; N, 8.72.

Compound 18

Pale yellow prisms; mp: 242-244 °C; Yield : (59 %); IR (KBr, cm^{-1}) ν_{max} : 1634 1586(C=N) and 1423; ^1H NMR (500 MHz, CDCl_3) (ppm) δ_{H} : 2.43 (s, 3H, $\text{C}_6\text{-CH}_3$), 3.09 (s, 3H, $\text{C}_{11}\text{-CH}_3$), 7.34 (t, 1H, $\text{C}_9\text{-H}$, $J = 7.50$ Hz), 7.40-7.92 (m, 11H, C_2 , C_3 , C_8 , C_{10} , C_4' , C_2' , C_3' , C_5' , C_6' , C_7' , $\text{C}_8'\text{-H}$), 8.04 (d, 1H, $\text{C}_1\text{-H}$, $J = 7.50$ Hz), 8.17 (d, 1H, $\text{C}_{14}\text{-H}$, $J = 7.50$ Hz), 9.29 (d, 1H, $\text{C}_4\text{-H}$, $J_o = 8.50$ Hz, $J_m = 1.50$ Hz), 9.43 (d, 1H, $\text{C}_{13}\text{-H}$, $J = 8.00$ Hz); ^{13}C NMR (125 MHz, CDCl_3) (ppm) δ_{C} : 19.10 ($\text{C}_{11}\text{-CH}_3$), 29.65 ($\text{C}_6\text{-CH}_3$), 119.54 (C_2'), 120.51 (C_{6a}), 122.76 (C_{13}), 123.09 (C_{7a}), 124.66 (C_4), 125.85 (C_{12b}), 126.51 (C_3), 126.78 (C_9), 127.04 (C_{14}), 127.15 (C_8), 127.36 (C_2), 127.59 (C_1), 127.70 (C_8'), 127.86 (C_3') 128.18 (C_4'), 128.36 (C_5'), 128.63 (C_6'), 128.83 (C_7'), 129.63 (C_{4a}), 130.66 (C_{14a}), 131.54 (C_{10}), 132.72 (C_{8a}'), 133.99 (C_{4a}'), 134.37 (C_{11}), 136.29 (C_1'), 137.38 (C_7), 139.86 (C_{11a}), 148.39 (C_{4b}), 149.44 (C_{12a}),

158.98 (C₆); MS (EI) m/z (%) 384 (M⁺, 100), 383 (35), 369 (20), 354 (8), 65 (6), 51 (5) Anal. Calcd. for C₃₂H₂₂N₂ (384) C, 88.45; H, 5.10; N, 6.45; Found : C, 88.47, H 5.15, N 6.48 %.

Preparation of heterosubstituted benzo[b]naphtho[1,2-h][1,6]naphthyridine (19, 20, 21), general procedure;

2-methyl-N-phenylbenzo[h]quinolin-4-amine (**15**) (2 mmol) and pyridine-3-carboxylic acid /thiophen-2carboxylic acid/furan-2-carboxylic acid (2.5 mmol) were added to polyphosphoric acid (6 g of P₂O₅ in 3 mL of H₃PO₄) and heated at 160 °C for 3 hours. The reaction was monitored by using TLC. After the completion of the reaction, it was poured into ice water, neutralized with saturated sodium bicarbonate solution to remove excess of pyridine-3-carboxylic acid/thiophen-2carboxylic acid/furan-2-carboxylic acid, extracted with ethyl acetate, purified by column chromatography using silica gel and product eluted with petroleum ether: ethyl acetate (99 : 3) mixture to get **19, 20, 21** which was recrystallised using methanol.

Compound 19

Pale yellow solid; mp: 245-247 °C; Yield : (51 %); IR (KBr, cm⁻¹) ν_{max} : 1626, 1595, 1568(C=N); ¹H NMR (500 MHz CDCl₃) δ_H: 2.41 (s, 3H, C₆-CH₃), 3.07 (s, 3H, C₁₁-CH₃), 7.22 (t, 1H, C₅'-H *J* = 8.00 Hz, *J* = 4.50 Hz), 7.34 (t, 1H, C₉-H, *J* = 8.00 Hz), 7.59-7.71 (m, 4H, C₂ C₃, C₈, C₁₀-H), 7.79 (dd, 1H, C₆'-H *J* = 2.00 Hz, *J* = 5.50 Hz), 7.84 (dd, 1H, C₄'-H *J* = 2.00 Hz, *J* = 5.00 Hz), 7.97 (s, 1H, C₂'-H), 8.02 (d, 1H, C₁-H, *J* = 9.50 Hz), 8.010 (d, 1H, C₁₄-H, *J* = 7.50 Hz), 9.39 (d, 1H, C₄-H, *J*_o = 8.00 Hz, *J*_m = 1.50 Hz), 9.52 (d, 1H, C₁₃-H, *J* = 9.00 Hz); ¹³C NMR (125 MHz CDCl₃) δ_C: 18.4 (C₁₁-CH₃), 29.7 (C₆-CH₃), 121.12 (C_{6a}), 122.08 (C₁₃), 122.28 (C_{7a}), 124.74 (C₄), 125.98 (C_{12b}), 126.51 (C₃), 126.91 (C₉), 127.06 (C₁₄), 127.06 (C₈), 127.42 (C₂), 127.78 (C₁), 128.34 (C₃', C₅'), 128.52 (C₄'), 129.97 (C_{4a}), 130.74 (C_{14a}), 131.14 (C₁₀), 134.64 (C₁₁), 135.15 (C₂'), 137.48 (C₇) 139.40 (C_{11a}), 147.2 (C₆') 148.35

(C_{4b}), 149.01 (C_{12a}), 159.40 (C₆); MS (385) m/z (%) 385 (M⁺, 100), Anal. Calcd. for C₂₇H₁₉N₃ (385) C, 84.13; H, 4.97; N, 10.90; Found : C, 84.16, H 4.95, N 10.88 %.

Compound 20

Pale yellow prisms; mp: 239-241 °C; Yield : (50 %); IR (KBr, cm⁻¹) $\nu_{\max}$: 1633 (C=N), 1560, 1529; ¹H NMR (500 MHz, CDCl₃) (ppm) δ_{H} : 2.51 (s, 3H, C₆-CH₃), 3.12 (s, 3H, C₉-CH₃), 6.75 (t, 1H, C₄'-H, J = 5.50 Hz), 7.37 (d, 1H, C₃'-H, J = 5.00 Hz), 7.48-8.09 (m, 7H, C₁, C₂, C₃, C₈, C₉, C₁₀, C₅'-H), 8.41 (d, 1H, C₁₄-H, J = 8.80 Hz), 9.36 (d, 1H, C₄-H, J_o = 8.00 Hz, J_m = 2.00 Hz), 9.64 (d, 1H, C₁₃-H, J = 9.20 Hz); MS (374) m/z (%) 374 (M⁺, 100); Anal. Calcd. for C₂₆H₁₈N₂O (374): C, 83.40; H, 4.85; N, 7.48; Found : C, 83.37, H 4.78, N 7.43 %

Compound 21

Colorless solid; mp: 252-254 °C; Yield : (36 %); IR (KBr, cm⁻¹) $\nu_{\max}$: 1629 (C=N), 1577, 1519; ¹H NMR (500 MHz, CDCl₃) δ_{H} : 2.59 (s, 3H, C₆-CH₃), 2.96 (s, 3H, C₉-CH₃), 7.09 (d, 1H, C₁₀-H, J = 8.00 Hz) 7.20 (t, 1H, C₄'-H, J = 5.50 Hz), 7.45-8.16 (m, 7H, C₁, C₂, C₃, C₈, C₉, C₃', C₅'-H), 8.51 (d, 1H, C₁₄-H, J = 8.80 Hz), 9.22 (d, 1H, C₄-H, J_o = 8.00 Hz), 9.61 (d, 1H, C₁₃-H, J = 9.00 Hz); MS (390) m/z (%) 390 (M⁺, 100); Anal. Calcd. for C₂₆H₁₈N₂S (390): C, 79.97; H, 4.65; N, 7.17; S, 8.21; Found : C, 78.01, H 7.15, N 7.15; 8.25 %.

Mass fragmentation of 4,6-dimethyl-7-phenylbenzo[*h*]naphtho[1,2-*b*][1,6] naphthyridine (**5**)

Mass fragmentation of 6,11-dimethylbenzo[*b*]naphtho[1,2-*h*][1,6]naphthyridine (**16**).

4BQOBA...Renuka

^1H - ^1H NMR Spectrum of 6,11-Dimethyl-7-phenylbenzo[b]naphtho[1,2-h][1,6]naphthyridine (16)

4BQOBA...Renuka

HMBC NMR Spectrum of 6,11-Dimethyl-7-phenylbenzo[b]naphtho[1,2-h][1,6]naphthyridine (16)

4BQOT.....Prabha, CBE

Current Data Parameters
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 PROCNO 1

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F2 - Processing parameters
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 GB 0
 PC 1.00

¹H NMR Spectrum of 2-Methyl-N-o-tolylbenzo[h]quinolin-4-amine (15)