

Supplementary Information

for

Diastereoselective synthesis of fuopyranopyridine in ionic-liquid/water without additional catalyst

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Experimental

All chemicals used were of reagent grade and used as received without further purification. Melting points were determined in an open glass capillary method and are uncorrected. ¹H-NMR spectra were recorded at 400 MHz and ¹³C-NMR Spectra at 100 MHz on a Bruker Avance DPX FT spectrometer in CDCl₃ using TMS as an internal reference. Mass spectra were determined on a JEOL SX-102 (FAB) mass spectrometer at 70eV. Elemental analysis was carried out using a Coleman automatic C, H and N analyser. The progress of the reaction was monitored by TLC (Merck silica gel).

General procedure for the synthesis of furopyranopyridine

A mixture of *N*-Methylpiperidin-4-one (10 mmol), aldehyde (10 mmol), and 2,3-dihydrofuran (20 mmol) in [bmim]BF₄ (1 mL)/H₂O (1 mL) was stirred at room temperature for an 25-30 min (**Table 3**). After completion of the reaction, as indicated by TLC, the reaction mixture was washed with diethyl ether (3x10 mL). The combined ether extracts were concentrated in vacuum and the resulting product was directly charged on silica gel column and eluted with a mixture of ethyl acetate/n-hexane (2:7) to afford pure product **4(a-j)**. The remaining ionic liquid was rinsed with ether (2 ml), dried under vacuum at 90°C for 2 h to eliminate any water trapped and reused for subsequent runs.

SPECTRAL DATA

4a. 8-Benzylidene-6-methyl-4-phenyl-2,3,3a,5,6,7,8,9a-octa-hydro-4H-1,9-dioxa-6-aza-cyclopenta[b]naphthalene

m.p. 146-148°C

¹H-NMR (400 MHz): δ 1.81 (m, 2H, 3-CH₂), 2.27 (s, 3H, NCH₃), 2.56 (m, *J* = 3.9 Hz, 1H, 3a-CH), 3.03 (s, 4H, 5,7-CH₂), 3.17 (d, *J* = 4.0 Hz, 1H, 4-CH), 3.75 (t, 2H, 2-CH₂), 5.74 (s, *J* = 4.0 Hz, 1H, 9a-CH), 6.57 (s, 1H, =CH), 7.08-7.30 (m, 10H, Ar)

¹³CNMR (100 MHz): δ 22.7, 29.8, 39.9, 43.6, 53.8, 54.1, 60.5, 104.3, 104.8, 120.4, 125.7, 126.2, 127.6, 128.1, 128.2, 128.4, 134.9, 136.8, 139.4, 147.5

MS m/z: 359 (M⁺),

Anal. calcd. for C₂₄H₂₅NO₂: C, 80.19; H, 7.01; N, 3.90 %; Found C, 80.25; H, 7.06; N, 3.96%

4b. 6-Methyl-8-(4-nitrobenzylidene)-4-(4-nitrophenyl)-2,3,3a,5,6,7,8,9a-octahydro-4H-1,9-dioxa-6-aza-cyclopenta[b]naphthalene

m.p. 174-175°C

¹H-NMR (400 MHz): δ 1.81 (m, 2H, 3-CH₂), 2.27 (s, 3H, NCH₃), 2.56 (m, *J* = 3.9 Hz, 1H, 3a-CH), 3.03 (s, 4H, 5,7-CH₂), 3.17 (d, *J* = 3.9 Hz, 1H, 4-CH), 3.75 (t, 2H, 2-CH₂), 5.74 (s, *J* = 4.0 Hz, 1H, 9a-CH), 6.71 (s, 1H, =CH), 7.38-8.14 (m, 8H, Ar)

¹³CNMR (100 MHz): δ 22.7, 29.8, 39.9, 43.6, 53.8, 54.1, 60.5, 104.3, 104.8, 120.4, 123.4, 123.5, 127.1, 129.2, 136.8, 141.0, 145.5, 145.6, 147.5, 147.6

MS m/z: 449 (M⁺)

Anal. calcd. for $C_{24}H_{23}N_3O_6$: C, 64.13; H, 5.16; N, 9.35 %; Found: C, 64.21; H, 5.11; N, 9.39 %.

4c. 8-(4-Chlorobenzylidene)-4-(4-chlorophenyl)-6-methyl-2,3,3a,5,6,7,8,9a-octahydro-4H-1,9-dioxa-6-aza-cyclopenta[b] naphthalene

m.p. 158-160°C

1H -NMR (400 MHz): δ 1.81 (m, 2H, 3-CH₂), 2.27 (s, 3H, NCH₃), 2.56 (m, J = 3.9 Hz, 1H, 3a-CH), 3.03 (s, 4H, 5,7-CH₂), 3.17 (d, J = 4.0 Hz, 1H, 4-CH), 3.75 (t, 2H, 2-CH₂), 5.74 (s, J = 3.9 Hz, 1H, 9a-CH), 6.57 (s, 1H, =CH), 7.06-7.24 (m, 8H, Ar)

^{13}C NMR (100 MHz): 822.7, 29.8, 39.9, 43.6, 53.8, 54.1, 60.5, 104.3, 104.8, 120.4, 127.6, 128.7, 128.8, 129.7, 131.0, 133.0, 133.0, 137.5, 136.8, 147.5

MS m/z: 427 (M⁺)

Anal. calcd. for $C_{24}H_{23}Cl_2NO_2$: C, 67.29; H, 5.41; N, 3.27 %; Found: C, 67.36; H, 5.47; N, 3.33%.

4d. 6-Methyl-8-(4-methylbenzylidene)-4-p-tolyl-2,3,3a,5,6,7,8,9a-octahydro-4H-1,9-dioxa-6-aza-cyclopenta[b] naphthalene

m.p. 111-113°C

1H -NMR (400 MHz): δ 1.81 (m, 2H, 3-CH₂), 2.27 (s, 3H, NCH₃), 2.35 (s, 6H, CH₃), 2.56 (m, J = 4.0 Hz, 1H, 3a-CH), 3.03 (s, 4H, 5,7-CH₂), 3.17 (d, J = 3.9 Hz, 1H, 4-CH), 3.75 (t, 2H, 2-CH₂), 5.74 (s, J = 3.9 Hz, 1H, 9a-CH), 6.57 (s, 1H, =CH), 7.00-7.18 (m, 8H, Ar)

^{13}C NMR (100 MHz): δ 20.8, 22.7, 29.8, 39.9, 43.6, 53.8, 54.1, 60.5, 104.3, 104.8, 120.4, 126.1, 128.2, 129.0, 129.1, 131.9, 134.9, 136.4, 136.8, 136.9, 147.5

MS m/z: 387 (M⁺)

Anal. calcd. for $C_{26}H_{29}NO_2$: C, 80.59; H, 7.54; N, 3.61 %; Found: C, 80.65; H, 7.58; N, 3.68%.

4e. 8-(4-Methoxybenzylidene)-4-(4-methoxyphenyl)-6-methyl-2,3,3a,5,6,7,8,9a-octahydro-4H-1,9-dioxa-6-aza-cyclopenta[b]naphthaene

m.p.: 102-103°C

1H -NMR (400 MHz): δ 1.81 (m, 2H, 3-CH₂), 2.27 (s, 3H, NCH₃), 2.56 (m, J = 3.9 Hz, 1H, 3a-CH), 3.03 (s, 4H, 5,7-CH₂), 3.17 (d, J = 4.0 Hz, 1H, 4-CH), 3.73 (s, 6H, OCH₃), 3.75 (t, 2H, 2-CH₂), 5.74 (s, J = 4.0 Hz, 1H, 9a-CH), 6.57 (s, 1H, =CH), 6.72-7.19 (m, 8H, Ar)

^{13}C NMR (100 MHz): δ 22.7, 29.8, 39.9, 43.6, 53.8, 54.1, 56.1, 60.5, 104.3, 104.8, 113.9, 114.0, 120.4, 127.2, 127.3, 129.3, 131.7, 136.8, 147.5, 159.2, 161.2

MS m/z: 419 (M⁺)

Anal. calcd. for $C_{26}H_{29}NO_4$: C, 74.44; H, 6.97; N, 3.34 %; Found: C, 74.51; H, 7.01; N, 3.38%.

4f. 8-(4-Hydroxybenzylidene)-4-(4-hydroxyphenyl)-6-methyl-2,3,3a,5,6,7,8,9a-octa-hydro-4H-1,9-dioxa-6-aza-cyclopenta[b]naphthalene

m.p. 189-191°C

¹H-NMR (400 MHz): δ 1.81 (m, 2H, 3-CH₂), 2.27 (s, 3H, NCH₃), 2.56 (m, *J* = 3.9 Hz, 1H, 3a-CH), 3.03 (s, 4H, 5,7-CH₂), 3.17 (d, *J* = 4.0 Hz, 1H, 4-CH), 3.75 (t, 2H, 2-CH₂), 5.0 (s, 2H, OH, exchangeable with D₂O), 5.74 (s, *J* = 3.9 Hz, 1H, 9a-CH), 6.57 (s, 1H, =CH), 6.68-7.13 (m, 8H, Ar)

¹³CNMR (100 MHz): δ 22.7, 29.8, 39.9, 43.6, 53.8, 54.1, 60.5, 104.3, 104.8, 115.5, 115.6, 120.4, 127.5, 127.6, 129.7, 132.0, 136.8, 147.5, 154.5, 156.5

MS m/z: 391 (M⁺)

Anal. calcd. for C₂₄H₂₅NO₄: C, 73.64; H, 6.44; N, 3.58 %; Found C, 73.70; H, 6.49; N, 3.63%.

4g. 6-Methyl-8-(3-nitrobenzylidene)-4-(3-nitrophenyl)-2,3,3a,5,6,7,8,9a-octahydro-4H-1,9-dioxa-6-aza-cyclo-penta[b]naphthalene

m.p. 201-203°C

¹H-NMR (400 MHz): δ 1.81 (m, 2H, 3-CH₂), 2.27 (s, 3H, NCH₃), 2.56 (m, *J* = 4.0 Hz, 1H, 3a-CH), 3.03 (s, 4H, 5,7-CH₂), 3.17 (d, *J* = 4.0 Hz, 1H, 4-CH), 3.75 (t, 2H, 2-CH₂), 5.74 (s, *J* = 3.9 Hz, 1H, 9a-CH), 6.68 (s, 1H, =CH), 7.47-8.23 (m, 8H, Ar)

¹³CNMR (100 MHz): δ 22.7, 28.8, 39.9, 43.6, 53.8, 54.1, 60.5, 104.3, 104.8, 120.4, 120.8, 121.3, 122.8, 123.4, 129.2, 129.3, 132.3, 134.4, 135.8, 136.8, 140.3, 147.5, 148.2, 148.3

MS m/z: 449 (M⁺)

Anal. calcd. for C₂₄H₂₃N₃O₆: C, 64.13; H, 5.16; N, 9.35 %; Found C, 64.19; H, 5.20; N, 9.39%

4h. 8-(3,4-Dimethoxybenzylidene)-4-(3,4-dimethoxyphenyl)-6-methyl-2,3,3a,5,6,7,8,9a-octahydro-4H-1,9-dioxa-6-aza-cyclo-penta[b]naphthalene

m.p. 178-180°C

¹H-NMR (400 MHz): δ 1.81 (m, 2H, 3-CH₂), 2.27 (s, 3H, NCH₃), 2.56 (m, *J* = 4.0 Hz, 1H, 3a-CH), 3.03 (s, 4H, 5,7-CH₂), 3.17 (d, *J* = 3.9 Hz, 1H, 4-CH), 3.73 (s, 12H, OCH₃), 3.75 (t, 2H, 2-CH₂), 5.74 (s, *J* = 3.9 Hz, 1H, 9a-CH), 6.57 (s, 1H, =CH), 6.52-6.75 (m, 6H, Ar)

¹³CNMR (100 MHz): δ 22.7, 30.1, 39.9, 43.6, 53.8, 54.1, 56.2, 60.5, 104.3, 104.8, 112.8, 114.8, 114.9, 115.0, 119.5, 120.4, 121.6, 128.2, 132.7, 136.8, 144.8, 146.8, 147.4, 147.5, 147.5

MS m/z: 479 (M⁺)

Anal. calcd. for C₂₈H₃₃NO₆: C, 70.13; H, 6.94; N, 2.92 %; Found C, 70.18; H, 6.98; N, 2.97%.

4i. 8-(3-Chlorobenzylidene)-4-(3-chlorophenyl)-6-methyl-2,3,3a,5,6,7,8,9a-octahydro-4H-1,9-dioxa-6-aza-cyclo-penta[b]naphthalene

m.p. 167-168°C

¹H-NMR (400 MHz): δ 1.81 (m, 2H, 3-CH₂), 2.27 (s, 3H, NCH₃), 2.56 (m, *J* = 4.0 Hz, 1H, 3a-CH), 3.03 (s, 4H, 5,7-CH₂), 3.17 (d, *J* = 3.9 Hz, 1H, 4-CH), 3.75 (t, 2H, 2-CH₂), 5.74 (s, *J* = 4.0 Hz, 1H, 9a-CH), 6.57 (s, 1H, =CH), 7.00-7.31 (m, 8H, Ar)

¹³CNMR (100 MHz): δ 22.7, 29.3, 39.9, 43.6, 53.8, 54.1, 60.5, 104.3, 104.8, 120.4, 124.3, 126.1, 126.4, 126.6, 128.1, 128.7, 129.7, 129.8, 133.6, 133.7, 136.3, 136.8, 140.8, 147.5

MS m/z: 427 (M⁺)

Anal. calcd. for C₂₄H₂₃Cl₂NO₂: C, 66.77; H, 5.41; N, 3.27 %; Found C, 66.82; H, 5.46; N, 3.31%.

4j. 8-(2-Chlorobenzylidene)-4-(2-chlorophenyl)-6-methyl-2,3,3a,5,6,7,8,9a-octa-hydro-4H-1,9-dioxa-6-aza-cyclo-penta[b] naphthalene

m.p. 213-214°C

¹H-NMR (400 MHz): δ 1.81 (m, 2H, 3-CH₂), 2.27 (s, 3H, NCH₃), 2.56 (m, 1H, J = 4.0 Hz, 3a-CH), 3.03 (s, 4H, 5,7-CH₂), 3.17 (d, J = 3.9 Hz, 1H, 4-CH), 3.75 (t, 2H, 2-CH₂), 5.74 (s, J = 3.9 Hz, 1H, 9a-CH), 6.57 (s, 1H, =CH), 7.02-7.24 (m, 8H, Ar)

¹³CNMR (100 MHz): δ 20.7, 22.7, 39.9, 43.3, 53.8, 54.1, 60.5, 104.3, 104.8, 120.4, 126.4, 126.5, 127.1, 127.6, 128.6, 128.7, 129.1, 129.7, 131.5, 133.6, 135.3, 136.8, 139.8, 147.5

MS m/z: 427 (M⁺)

Anal. calcd. for C₂₄H₂₃Cl₂NO₂: C, 67.29; H, 5.41; N, 3.27 %; Found C, 67.32; H, 5.47; N, 3.33 %.