

## Supporting Information

### Experimental Section

Reactions were generally performed under an inert atmosphere (argon) in flame-dried flasks. Solvents and reagents were added by syringes (polypropylene or Hamilton-microliter syringes) through a septum or a three-way valve under positive argon pressure. Solids were added as a solution or as powder or chunks under positive argon pressure.

Solvents: dry tetrahydrofuran, dichloromethane, toluene, and acetonitrile were taken from the Braun Solvent Purification System 800. Triethylamine and diisopropylamine were distilled before used ( $\text{CaH}_2$ ) and stored with activated 4 Å molecular sieves or KOH. Methanol and dimethylformamide (DMF) were purchased in p. A. quality and stored under argon with activated 4 Å molecular sieves. Hexane (mixture of isomers) was distilled from  $\text{CaH}_2$ . Ethyl acetate was distilled from  $\text{K}_2\text{CO}_3$  and  $\text{CaCl}_2$ .

Preparative column chromatography was performed on silica gel (230-400 mesh, Merck or Fluka) or on neutral alumina (100-250 mesh, Fluka; deactivation to obtain activity grade III by addition of 6 % water).

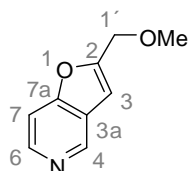
NMR spectra were recorded using either the Bruker (AC 500, AV 700) or JOEL (ECX 400, Eclipse 500) instruments at 300 K.  $^{13}\text{C}$ -NMR spectra are proton-decoupled. Multiplicity is indicated as follows: s (singlet),  $s_{br}$  (broad singlet), d (doublet), t (triplet), q (quartet), quint (quintet), dd (doublet of doublet), dt (doublet of triplet), td (triplet of doublet), sex (sextet), m (multiplet),  $m_c$  (centered multiplet). For detailed peak assignments 2D-spectra were measured (COSY, HMQC, HMBC and NOESY). For  $^1\text{H}$ -NMR spectroscopy, the singlets of chloroform ( $\delta = 7.26$  ppm) were used as internal standards and for  $^{13}\text{C}$ -NMR spectroscopy the triplet of deuteriochloroform ( $\delta = 77.0$  ppm) was used. IR-spectra were recorded using the JASCO FT/IR-4100 type A instrument with TGS-detector. UV-VIS spectra were measured in a quartz cuvette in a Scinco S-3150 PDA photospectrometer. Mass spectra were recorded using an Agilent 6210 ESI-TOF instrument. Elemental analyses were performed using the Perkin-Elmer CHN-Analyzer 2400, Vario EL or Vario ELIII instruments. Melting points were measured with a Reichert apparatus Thermovar and are uncorrected.

**4-Hydroxy-3-iodopyridine (2) and 4-Hydroxy-3,5-diiodopyridine (3):** According to ref. 1, a three-necked bottom flask was charged with acetonitrile (30 mL), 4-hydroxypyridine (1) (380 mg, 4.00 mmol) and  $\text{NaHCO}_3$  (504 mg, 6.00 mmol). To this mixture,  $\text{Me}_4\text{NCl}_2\text{I}$  (544 mg, 2.00 mmol, dissolved in 30 mL of acetonitrile), was slowly added with a syringe pump within 2 h. The mixture was further stirred for 3 h at room temperature and then neutralized with 10% aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution (40 mL). After extraction with dichloromethane (3 x 40 mL) the combined organic extracts were dried ( $\text{Na}_2\text{SO}_4$ ), filtrated and concentrated under reduced pressure. Column chromatography (silica gel, acetone/methanol, 10:1) provided 389 mg of a yellowish solid consisting of **2** (81%) and **3** (5%).

Data of **2**: (m. p. >230 °C; lit.: m. p. 303 °C)  $^1\text{H}$  NMR  $[(\text{CD}_3)_2\text{CO}, 400 \text{ MHz}]$ :  $\delta = 6.16$  (d,  $J = 7.1 \text{ Hz}$ , 1 H, 5-H), 7.69 (dd,  $J = 7.1, 1.6 \text{ Hz}$ , 1 H, 6-H), 8.26 (d,  $J = 1.6 \text{ Hz}$ , 1 H, 2-H), 11.47 (s<sub>br</sub>, 1 H, OH) ppm;  $^{13}\text{C}$  NMR  $[(\text{CD}_3)_2\text{CO}]$ , 101 MHz):  $\delta = 92.2$  (s, C-3), 113.1 (d, C-2), 138.0 (d, C-6), 143.8 (d, C-5), 173.6 (s, C-4) ppm. These data agree with those of ref. 1.

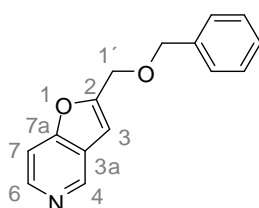
Data of **3**:  $^1\text{H}$  NMR  $[(\text{CD}_3)_2\text{CO}, 500 \text{ MHz}]$ :  $\delta = 8.27$  (s, 2 H, 2-H, 6-H), 11.95 (s<sub>br</sub>, OH) ppm;  $^{13}\text{C}$  NMR  $[(\text{CD}_3)_2\text{CO}, 126 \text{ MHz}]$ :  $\delta = 86.5$  (s, C-3, C-5), 143.0 (s, C-2, C-6), 170.5 (s, C-4) ppm.

**2-Methoxymethylfuro[3,2-c]pyridine (7)**: 4-Hydroxy-3-iodopyridine (**2**) (1.23 g, 5.58 mmol), Pd(OAc)<sub>2</sub> (95 mg, 0.42 mmol), PPh<sub>3</sub> (440 mg, 1.67 mmol) and CuI (60 mg, 0.32 mmol) were added to a two-necked bottom flask, dissolved in DMF (25 mL) and *i*Pr<sub>2</sub>NH (12.9 mL). After addition of methyl propargyl ether (**4**) (62% in toluene, 782 mg, 11.2 mmol) the mixture was stirred at 70 °C for 25 h. After cooling to room temperature the mixture was concentrated under reduced pressure. Column chromatography (silica gel, hexanes/ethyl acetate, 1:1) provided 689 mg (76%) of **7** as yellowish oil. The product is not very stable at room temperature and discolored to brownish after a few days.



$^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 3.45$  (s, 3 H, OMe), 4.57 (s, 2 H, OCH<sub>2</sub>), 6.75 (s, 1 H, 3-H), 7.41 (d,  $J = 5.7 \text{ Hz}$ , 1 H, 7-H), 8.47 (d,  $J = 5.7 \text{ Hz}$ , 1 H, 6-H), 8.88 (s, 1 H, 4-H) ppm;  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 101 MHz):  $\delta = 58.6$  (q, OMe), 66.7 (t, C-1'), 103.7 (d, C-3), 107.2 (d, C-7), 125.5 (s, C-3a), 144.2 (d, C-4), 144.7 (d, C-6), 155.3 (s, C-2), 159.6 (s, C-7a) ppm; IR (ATR):  $\nu = 3110\text{--}3040$  (=C-H), 2990–2825 (C-H), 1610–1575 (C=C, C=N), 1265 (C-O) cm<sup>-1</sup>; HRMS (ESI-TOF):  $m/z$  [M + H]<sup>+</sup> calcd. for C<sub>9</sub>H<sub>10</sub>NO<sub>2</sub>: 164.0711, found: 164.0707;  $m/z$  [M + Na]<sup>+</sup> calcd. for C<sub>9</sub>H<sub>9</sub>NNaO<sub>2</sub>: 186.0531, found: 186.0525.

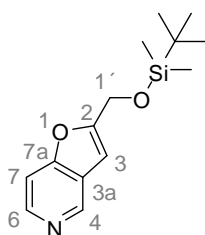
**2-Benzyloxymethylfuro[3,2-c]pyridine (8)**: 4-Hydroxy-3-iodopyridine (**2**) (730 mg, 3.30 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (289 mg, 0.25 mmol), and CuI (36 mg, 0.19 mmol) were added to a two-necked bottom flask, dissolved in DMF (23 mL) and *i*Pr<sub>2</sub>NH (7.6 mL). After addition of benzyl propargyl ether (**5**) (578 mg, 3.96 mmol) the mixture was stirred at 70 °C for 23 h. After cooling to room temperature the mixture was concentrated under reduced pressure. The obtained residue was dissolved in ethyl acetate and filtrated through alumina. Column chromatography (silica gel, hexanes/ethyl acetate, 1:1) provided 488 mg (75%) of **8** as yellowish oil. The product is not very stable at room temperature and discolored to brownish after a few weeks.



$^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 4.61$  (s, 2 H, OCH<sub>2</sub>), 4.63 (s, 2 H, OCH<sub>2</sub>), 6.74 (s, 1 H, 3-H), 7.20–7.38 (m, 5 H, Ph), 7.40–7.48 (m, 1 H, 7-H), 8.42–8.47 (m, 1 H, 6-H), 8.86 (s, 1 H, 4-H) ppm;  $^{13}\text{C}$ g NMR (CDCl<sub>3</sub>,

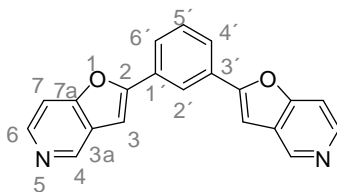
101 MHz):  $\delta$  = 64.2 (t, C-1'), 72.7 (t, CH<sub>2</sub>Ph), 103.8 (d, C-3), 107.2 (d, C-7), 125.5 (s, C-3a), 128.1, 128.2, 128.6, 137.4 (3 d, s, Ph), 144.1 (d, C-4), 144.7 (d, C-6), 155.3 (s, C-2), 159.6 (s, C-7a) ppm; IR (ATR):  $\nu$  = 3085–3010 (=C–H), 2985–2805 (C–H), 1605–1585 (C=C, C=N), 1270–1235 (C–O) cm<sup>-1</sup>; UV-VIS (CHCl<sub>3</sub>, lg  $\epsilon$ ):  $\lambda$  = 252 (3.90) nm; HRMS (ESI-TOF):  $m/z$  [M + H]<sup>+</sup> calcd. for C<sub>15</sub>H<sub>14</sub>NO<sub>2</sub>: 240.1024, found 240.1022;  $m/z$  [M + Na]<sup>+</sup> calcd. for C<sub>15</sub>H<sub>13</sub>NNaO<sub>2</sub>: 262.0844, found: 262.0839;  $m/z$  [2M + Na]<sup>+</sup> calcd. for C<sub>30</sub>H<sub>26</sub>NNaO<sub>2</sub>: 501.1785, found: 501.1796; C<sub>15</sub>H<sub>13</sub>NO<sub>2</sub> (239.3): calcd. C 75.30, H 5.48, N 5.85; found: C 75.43, H 5.67, N 5.70.

**2-[(*tert*-Butyldimethylsiloxy)methyl]furo[3,2-*c*]pyridine (9):** 4-Hydroxy-3-iodopyridine (**2**) (1.23 g, 5.58 mmol), Pd(OAc)<sub>2</sub> (95 mg, 0.42 mmol), PPh<sub>3</sub> (440 mg, 1.67 mmol) and CuI (60 mg, 0.32 mmol) were added to a two-necked bottom flask, dissolved in DMF (25 mL) and *i*Pr<sub>2</sub>NH (12.9 mL). After addition of *tert*-butyldimethylsiloxy propargyl ether (**6**) (62% in dichloromethane, 3.06 g, 11.2 mmol) the mixture was stirred at 70 °C for 24 h. After cooling to room temperature it was concentrated under reduced pressure, the residue was dissolved in ethyl acetate and filtrated through Celite. The filtrate was concentrated and purified by column chromatography (silica gel, hexanes/ethyl acetate, 4:1) to give 1.11 g (75%) of **9** as yellowish oil. The product is not very stable at room temperature and discolored to brownish after a few weeks.



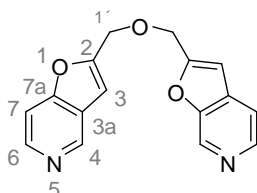
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 0.13, 0.93 (2 s, 6 H, 9 H, SiMe<sub>2</sub>*t*Bu), 4.80 (d,  $J$  = 1.0 Hz, 2 H, 1'-H), 6.67 (q,  $J$  = 1.0 Hz, 1 H, 3-H), 7.38 (dt,  $J$  = 5.7, 1.0 Hz, 1 H, 7-H), 8.44 (d,  $J$  = 5.7 Hz, 1 H, 6-H), 8.85 (d,  $J$  = 1.0 Hz, 1 H, 4-H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz):  $\delta$  = 5.2, 18.5, 25.9 (q, s, q, SiMe<sub>2</sub>*t*Bu), 58.7 (t, C-1'), 101.6 (d, C-3), 107.1 (d, C-7), 125.8 (s, C-3a), 144.0 (d, C-4), 144.4 (d, C-6), 158.5 (s, C-2), 159.5 (s, C-7a) ppm; IR (ATR):  $\nu$  = 3055–3035 (=C–H), 2955–2855 (C–H), 1600–1460 (C=C, C=N), 1135–1080 (C–O) cm<sup>-1</sup>; UV-VIS (MeCN, lg  $\epsilon$ ):  $\lambda$  = 242 (4.05) nm ; HRMS (ESI-TOF):  $m/z$  [M + H]<sup>+</sup> calcd. for C<sub>14</sub>H<sub>22</sub>NO<sub>2</sub>Si: 264.1420, found: 264.1385.

**1',3'-Di(furo[3,2-*c*]pyridin-2-yl)benzene (15):** 4-Hydroxy-3-iodopyridine (**2**) (603 mg, 2.73 mmol), Pd(OAc)<sub>2</sub> (45 mg, 0.20 mmol), PPh<sub>3</sub> (214 mg, 0.81 mmol) and CuI (29 mg, 0.15 mmol) were added to a two-necked bottom flask and dissolved in DMF (14 mL) and *i*Pr<sub>2</sub>NH (8.2 mL). After addition of 1,3-diethynylbenzene (**11**) (160 mg, 1.22 mmol) the mixture was stirred at 70 °C for 20 h. After cooling to room temperature the mixture was concentrated under reduced pressure. The residue was purified by multiple column chromatography (silica gel, dichloromethane/7N NH<sub>3</sub> in methanol, 15:1, 10:1) to furnish 255 mg (67%) of **15** as pale yellow solid.



M. p. 244–248 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 700 MHz): δ = 7.21 (s, 2 H, 3-H), 7.53 (d, *J* = 5.7 Hz, 2 H, 7-H), 7.60 (t, *J* = 7.7 Hz, 1 H, 5'-H), 7.90 (dd, *J* = 7.7, 1.7 Hz, 2 H, 4'-H, 6'-H), 8.39 (t, *J* = 1.7 Hz, 1 H, 2'-H), 8.54 (d, *J* = 5.7 Hz, 2 H, 6-H), 8.98 (s, 2 H, 4-H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz): δ = 100.1 (d, C-3), 107.2 (d, C-7), 122.0 (d, C-2'), 126.1 (d, C-4', C-6'), 126.6 (s, C-3a), 129.8 (d, C-5'), 130.5 (s, C-1', C-3'), 144.3 (d, C-4), 145.0 (d, C-6), 156.2 (s, C-2), 159.4 (s, C-7a) ppm; IR (ATR): ν = 3080–3005 (=C–H), 2960–2850 (C–H), 1605–1555 (C=C, C=N), 1260 (C–O) cm<sup>-1</sup>; UV-VIS (MeCN, lg ε): λ = 298 (4.80) nm ; UV-VIS (CHCl<sub>3</sub>, lg ε): λ = 300 (4.78) nm ; HRMS (ESI-TOF) *m/z* [M + H]<sup>+</sup> calcd. for C<sub>20</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub>: 313.0977, found: 313.0979; C<sub>20</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub> (312.3): calcd. C 76.91, H 3.87, N 8.97; found: C 76.91, H 3.85, N 8.76.

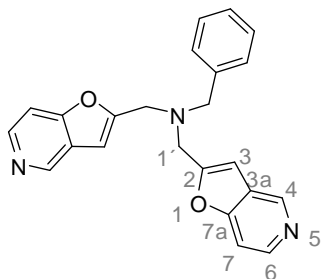
**2-[(Furo[3,2-c]pyridin-2-ylmethoxy)methyl]furo[3,2-c]pyridine (16):** 4-Hydroxy-3-iodopyridine (**2**) (442 mg, 2.00 mmol), Pd(OAc)<sub>2</sub> (34 mg, 0.15 mmol), PPh<sub>3</sub> (157 mg, 0.60 mmol) and CuI (21 mg, 0.11 mmol) were added to a two-necked bottom flask and dissolved in DMF (17.8 mL) and *i*Pr<sub>2</sub>NH (9.2 mL). After addition of dipropargyl ether **12** (94 mg, 1.00 mmol) the mixture was stirred at 70 °C for 24 h. After cooling to room temperature the mixture was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate/methanol, 20:1) to afford 72 mg (62%) of **16** as yellowish solid. The product is not very stable at room temperature and discolored to brownish after a few weeks.



Melting range: 118–138 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ = 4.76 (s, 4 H, 1-H'), 6.82 (s, 2 H, 3-H), 7.42 (d, *J* = 5.7 Hz, 2 H, 7-H), 8.50 (d, *J* = 5.7 Hz, 2 H, 6-H), 8.90 (s, 2 H, 4-H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz): δ = 64.7 (t, C-1'), 104.6 (d, C-3), 107.3 (d, C-7), 125.4 (s, C-3a), 144.4 (d, C-4), 145.1 (d, C-6), 154.6 (s, C-2), 159.8 (s, C-7a) ppm; IR (ATR): ν = 3115–3005 (=C–H), 2965–2855 (C–H), 1610–1435 (C=C, C=N), 1135 (C–O) cm<sup>-1</sup>; UV-VIS (CHCl<sub>3</sub>, lg ε): λ = 247 (4.40) nm ; UV-VIS (MeCN, lg ε): λ = 243 (4.40) nm ; HRMS (ESI-TOF): *m/z* [M + H]<sup>+</sup> calcd. for C<sub>16</sub>H<sub>13</sub>N<sub>2</sub>O<sub>3</sub>: 281.0926, found: 281.0933; *m/z* [M + Na]<sup>+</sup> calcd. for C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>NaO<sub>3</sub>: 303.0740, found: 303.0751; *m/z* [M + K]<sup>+</sup> calcd. for C<sub>16</sub>H<sub>12</sub>KN<sub>2</sub>O<sub>3</sub>: 319.0480, found: 319.0491; *m/z* [2M + H]<sup>+</sup> calcd. for C<sub>32</sub>H<sub>25</sub>N<sub>4</sub>O<sub>6</sub>: 561.1769, found 561.1776; C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub> (280.3): calcd. C 68.56, H 4.32, N 9.99 ; found : C 68.35, H 4.48, N 9.86.

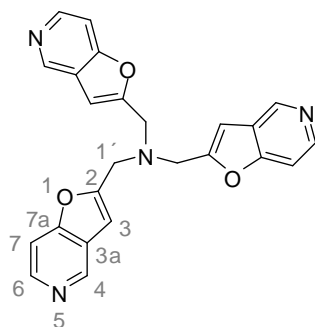
**N-Benzyl-di(furo[3,2-c]pyridin-2-ylmethyl)amine (17) :** 4-Hydroxy-3-iodopyridine (**2**) (460 mg, 2.08 mmol), Pd(OAc)<sub>2</sub> (47 mg, 0.21 mmol), PPh<sub>3</sub> (218 mg, 0.82 mmol) and CuI (40 mg, 0.21 mmol) were added to a two-necked bottom flask and dissolved in DMF (19 mL) and *i*Pr<sub>2</sub>NH (9.6 mL). After addition of dialkyne **13** (156 mg, 0.90 mmol) the mixture was stirred at 70 °C for 24 h. After cooling to room

temperature the mixture was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, ethyl acetate/methanol 20:1) to afford 135 mg (41%) of **17** as yellow-brownish oil. The product is not very stable at room temperature and discolored to dark brown after a few weeks.



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 700 MHz):  $\delta$  = 3.81 (s, 2 H,  $\text{NCH}_2$ ), 3.94 (s, 4 H,  $\text{NCH}_2$ ), 6.73 (s, 2 H, 3'-H, 3''-H), 7.27–7.31, 7.33–7.38, 7.40–7.42 (3 m, 1 H, 2 H, 2 H, Ph), 7.43 (mc, 2 H, 7'-H, 7''-H), 8.48 (d,  $J$  = 5.7 Hz, 2 H, 6-H', 6''-H), 8.88 (d,  $J$  = 0.7 Hz, 2 H, 4'-H, 4''-H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 176 MHz):  $\delta$  = 50.3 (t,  $\text{NCH}_2$ ), 58.1 (t,  $\text{NCH}_2$ ), 103.8 (d, C-3', C-3''), 107.2 (d, C-7', C-7''), 125.8 (s, C-3'a, C-3''a), 127.7, 128.7, 128.9, 138.1 (3 d, s, Ph), 143.7 (d, C-4), 144.3 (d, C-6), 156.6 (s, C-2', C-2''), 159.6 (s, C-7'a, C-7''a) ppm; HRMS (ESI-TOF):  $m/z$  [ $\text{M} + \text{H}$ ] $^+$  calcd. for  $\text{C}_{23}\text{H}_{20}\text{N}_3\text{O}_2$ : 370.1550, found 370.1540.

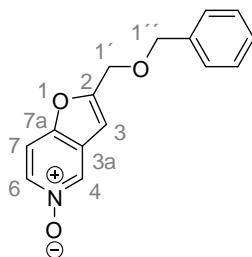
**Tri(furo[3,2-c]pyridin-2-ylmethyl)amine (18)**: 4-Hydroxy-3-iodopyridine (**2**) (884 mg, 4.00 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (94 mg, 0.081 mmol), and  $\text{CuI}$  (11 mg, 0.056 mmol) were added to a two-necked bottom flask and dissolved in DMF (28 mL) and  $i\text{Pr}_2\text{NH}$  (9.2 mL). After addition of triyne **14** (156 mg, 0.90 mmol) the mixture was stirred at 70 °C for 16 h. After cooling to room temperature the mixture was concentrated under reduced pressure. The residue was purified by multiple column chromatography (silica gel, ethyl acetate/methanol, 20:1) to afford 385 mg (94%) of **18** as light brownish oil. The product is not stable at room temperature and discolored to dark brown after a few days.



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 4.05 (s, 6 H, 1'-H), 6.78 (s, 3 H, 3-H), 7.42 (d,  $J$  = 5.7 Hz, 3 H, 7-H), 8.48 (d,  $J$  = 5.7 Hz, 3 H, 6-H), 8.88 (s, 3 H, 4-H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 176 MHz):  $\delta$  = 50.2 (t,  $\text{NCH}_2$ ), 104.1 (d, C-3), 107.0 (d, C-7), 125.3 (s, C-3a), 143.7 (d, C-4), 144.4 (d, C-6), 155.3 (s, C-2), 159.4 (s, C-7a) ppm; HRMS (ESI-TOF):  $m/z$  [ $\text{M} + \text{H}$ ] $^+$  calcd. for  $\text{C}_{24}\text{H}_{19}\text{N}_4\text{O}_3$ : 411.1457, found 411.1453.

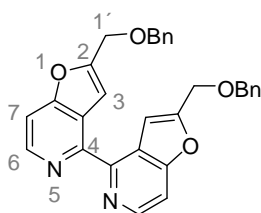
**2-(Benzyloxymethyl)furo[3,2-c]pyridine 5-Oxide (19)**: To a solution of compound **8** (110 mg, 0.459 mmol) in dichloromethane (3 mL) was added *m*-chloroperoxybenzoic acid (70%, 158 mg, 0.918 mmol) and the mixture was stirred at room temperature for 3 d. Saturated aqueous  $\text{NaHCO}_3$  solution was

added and the mixture was extracted with dichloromethane (3 x 5 mL). The combined organic phases were dried (Na<sub>2</sub>SO<sub>4</sub>), filtrated and concentrated under reduced pressure. Column chromatography (silica gel, ethyl acetate/methanol, 15:1) provided 117 mg (quantitative) of **19** as colorless solid.



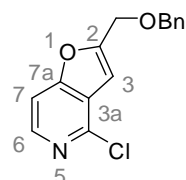
M. p. 121–125 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 700 MHz): δ = 4.61 (s, 2 H, OCH<sub>2</sub>), 4.63 (s, 2 H, OCH<sub>2</sub>), 6.65 (s, 1 H, 3-H), 7.21–7.35 (m, 6 H, Ph, 7-H), 8.14 (dd, *J* = 7.1, 1.0 Hz, 1 H, 6-H), 8.51 (s, 1 H, 4-H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 176 MHz): δ = 64.1 (t, OCH<sub>2</sub>), 73.2 (t, OCH<sub>2</sub>), 103.1 (d, C-3), 109.0 (d, C-7), 127.4 (s, C-3a), 128.0, 128.2, 128.7 (3 d, Ph), 132.7 (d, C-4), 136.4 (d, C-6), 137.1 (s, Ph), 151.8 (s, C-2), 159.6 (s, C-7a) ppm; IR (ATR): ν = 3110–3020 (=C–H), 2960–2845 (C–H), 1470–1435 (C=C, C=N), 1200 (C–O), 815 (N–O) cm<sup>-1</sup>; UV-VIS (MeCN, lg ε): λ = 241 (4.42) nm ; HRMS (ESI-TOF): *m/z* [M + H]<sup>+</sup> calcd. for C<sub>15</sub>H<sub>14</sub>NO<sub>3</sub>: 256.0974, found: 265.0977; C<sub>15</sub>H<sub>13</sub>NO<sub>3</sub> (255.3): C 70.58; H 5.13, N 5.49; found: C 70.68, H 5.40, N 5.59.

**2,2-Di(benzyloxymethyl)-4,4-bifuro[3,2-c]pyridine (20)**: According to ref. 3, in a Schlenk flask, compound **19** (110 mg, 0.431 mmol) was dissolved in acetonitrile (6 mL) and 3Å molecular sieves (1.00 g) was added. After stirring at room temperature for 30 min, triethylamine (0.24 mL, 1.72 mmol) and bromotrimethylsilane (0.16 mL, 1.22 mmol) were added and the mixture was heated under reflux for 19 h. All volatile components were removed under reduced pressure and the residue was extracted with dichloromethane (3 x 20 mL). The combined organic phases were dried (Na<sub>2</sub>SO<sub>4</sub>), filtrated and concentrated under reduced pressure. Column chromatography (silica gel, hexanes/ethyl acetate, 3:1) furnished 14 mg (14%) of **20** as pale yellow solid (melting range: 156–162 °C) and 56 mg (54%) of **8** (54%) as yellowish oil.



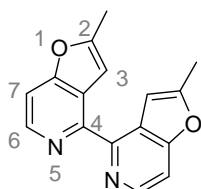
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 700 MHz): δ = 4.66 (s, 4 H, OCH<sub>2</sub>), 4.72 (s, 4 H, OCH<sub>2</sub>), 7.29–7.41 (m, 10 H, Ph), 7.47 (dd, *J* = 5.6, 0.8 Hz, 2 H, 7-H), 7.80 (s, 2 H, 3-H), 8.63 (d, *J* = 5.6 Hz, 2 H, 6-H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 126 MHz): δ = 64.4 (t, OCH<sub>2</sub>), 72.7 (t, OCH<sub>2</sub>), 107.2 (d, C-7), 107.5 (d, C-3), 124.4 (s, C-3a), 128.1, 128.1, 128.7, 137.7 (3 d, s, Ph), 144.0 (d, C-6), 151.4 (s, C-2), 155.8 (s, C-4), 161.2 (s, C-7a) ppm; IR (ATR): ν = 3140–2990 (=C–H), 2950–2860 (C–H), 1595–1455 (C=C, C=N), 1125 (C–O) cm<sup>-1</sup>; UV-VIS (MeCN, lg ε): λ = 322 (4.52) nm ; UV-VIS (CHCl<sub>3</sub>, lg ε): λ = 324 (4.37) nm ; HRMS (ESI-TOF): *m/z* [M + H]<sup>+</sup> calcd. for C<sub>30</sub>H<sub>25</sub>N<sub>2</sub>O<sub>4</sub>: 477.1814, found: 477.1819; C<sub>30</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub> (476.5): C 75.61, H 5.08, N 5.88; C 74.66, H 5.47, N 6.28.

**2-(Benzyloxymethyl)-4-chlorofuro[3,2-c]pyridine (21):** Compound **19** (320 mg, 1.25 mmol) was dissolved in  $\text{CDCl}_3$  (0.8 mL) and  $\text{POCl}_3$  (0.92 mL, 10.2 mmol) was added. The mixture was stirred under reflux for 1 d, then diluted with water (5 mL) and extracted with chloroform (3 x 20 mL). The combined organic phases were washed with water (40 mL), dried ( $\text{Na}_2\text{SO}_4$ ) and filtrated. After removal of the solvent under reduced pressure the crude product (449 mg) was purified by column chromatography (silica gel, hexanes/ethyl acetate, 5:1) to furnish 213 mg (62%) of **21** as colorless oil. The product is slightly instable at room temperature and discolored yellowish and partially solidified.



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 4.65 (s, 2 H,  $\text{OCH}_2$ ), 4.66 (s, 2 H,  $\text{OCH}_2$ ), 6.80 (s, 1 H, 3-H), 7.29–7.35 (m, 1 H, Ph), 7.60–7.38 (m, 5 H, Ph, 7-H), 8.26 (d,  $J$  = 5.7 Hz, 1 H, 6-H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  = 64.1 (t,  $\text{OCH}_2$ ), 72.9 (t,  $\text{OCH}_2$ ), 103.7 (d, C-3), 106.9 (d, C-7), 124.8 (s, C-3a), 128.0, 128.2, 128.7, 137.3 (3 d, s, Ph), 144.06 (d, C-6), 144.1 (s, C-4), 156.2 (s, C-2), 160.5 (s, C-7a) ppm; IR (ATR):  $\nu$  = 3115–3005 (=C–H), 2940–2855 (C–H), 1600–1430 (C=C, C=N), 1070 (C–O)  $\text{cm}^{-1}$ ; HRMS (ESI-TOF):  $m/z$  [ $\text{M} + \text{H}$ ] $^+$  calcd. for  $\text{C}_{15}\text{H}_{13}\text{ClNO}_2$ : 274.0635, found 274.0649;  $m/z$  [ $\text{M} + \text{Na}$ ] $^+$  calcd. for  $\text{C}_{15}\text{H}_{12}\text{ClNNaO}_2$ : 296.0454, found: 296.0468;  $m/z$  [ $2\text{M} + \text{Na}$ ] $^+$  calcd. for  $\text{C}_{30}\text{H}_{24}\text{Cl}_2\text{N}_2\text{NaO}_4$ : 569.1011; found: 69.1039;  $\text{C}_{15}\text{H}_{12}\text{ClNO}_2$  (273.1): calcd. C 65.82, H 4.42, N 5.12; found: C 65.02, H 4.18, N 5.10.

**2,2-Dimethyl-4,4-bifuro[3,2-c]pyridine (22):** According to ref. 4, in a Schlenk flask compound **21** (140 mg, 0.511 mmol) was dissolved in 1,4-dioxane (1.0 mL) and  $\text{NiCl}_2(\text{PPh}_3)_2$  (42 mg, 0.051 mmol),  $\text{PPh}_3$  (54 mg, 0.20 mmol), zinc powder (57 mg, 0.87 mmol) and  $(n\text{Bu})_4\text{NI}$  (283 mg, 0.767 mmol) were added. The mixture was heated to 100 °C for 20 h and after cooling to room temperature the formed solid was filtered off and washed with ethyl acetate. The filtrate was concentrated under reduced pressure and the resulting residue was purified by column chromatography (silica gel, hexanes/ethyl acetate, 20:1) to furnish 27 mg (40%) of **22** as colorless solid.



M. p. 121–124 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 700 MHz):  $\delta$  = 2.54 (s, 6 H, Me), 7.39 (d,  $J$  = 5.5 Hz, 2 H, 7-H), 7.41 (s, 2 H, 3-H), 8.58 (d,  $J$  = 5.5 Hz, 2 H, 6-H) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 176 MHz):  $\delta$  = 14.2 (s, Me), 104.0 (d, C-7), 106.5 (d, C-3), 125.5 (s, C-3a), 142.8 (d, C-6), 150.0 (s, C-4), 157.4 (s, C-2), 160.8 (s, C-7a) ppm; IR (ATR):  $\nu$  = 3145–3020 (=C–H), 2990–2855 (C–H), 1600–1555 (C=C, C=N), 1120 (C–O)  $\text{cm}^{-1}$ ; HRMS (ESI-TOF):  $m/z$  [ $\text{M} + \text{H}$ ] $^+$  calcd. for  $\text{C}_{16}\text{H}_{13}\text{N}_2\text{O}_2$ : 265.0977, found: 265.0989.

## References

1. A. R. Hajipour, M. Arbabian, A. E. Ruoho, *J. Org. Chem.* 2002, **67**, 8622.
2. F. W. Broekman, H. J. C. Tendeloo, *Recl. Trav. Chim. Pays-Bas* 1962, **81**, 107.
3. S. Shiotani, K. Taniguchi *J. Heterocyclic Chem.* 1997, **34**, 493.
4. G. Lin, R. Hong, *J. Org. Chem.* 2001, **66**, 2877.