DTBB-Catalyzed lithiation of 2,6-bis(chloromethyl)pyridine

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Dedicated to Professors José Elguero and Pedro Molina
on the occasion of their 70th and 60th birthdays, respectively

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Abstract

The DTBB-catalyzed lithiation of 2,6-bis(chloromethyl)pyridine **1** in the presence of various different carbonyl compounds [i-BuCHO, t-BuCHO, Me_2CO, Et_2CO, n-Pr_2CO $(CH_2)_4CO$, $(CH_2)_5CO$, and norbornan-2-one] in THF at –90°C gives, after hydrolysis with water at temperatures ranging between –90°C and room temperature, the corresponding dihydroxypyridines **2**. Despite the moderate yields obtained, the reaction can be of synthetic interest owing to the easy isolation and purification of the products **2**, whose preparation is difficult by other methodologies.

Keywords: 2,6-Bis(lithiomethyl)pyridine, TBB-catalyzed lithiation, ridentate ligands, electrophilic substitution

Introduction

2,6-Disubstituted pyridines of type **I** containing two coordinating heteroatoms — one in each arm — are interesting structures for the preparation of organometallic complexes **II** used in catalytic processes.[1] Thus, examples of compounds **II** containing osmium,[2] zirconium,[3] tungsten,[3] molybdenum,[1,4] titanium,[1,5] zinc,[6] cobalt,[6] silicon[7] and ruthenium[8] have been reported. In the case of the oxygenated derivatives (Y = O), the corresponding substituted parent compounds have been prepared by successive double deprotonation of 2,6-dimethylpyridine (2,6-lutidine) using n-butyllithium and then further reaction with a carbonyl compound. This method has the problem that after the introduction of the first electrophilic fragment (to give intermediate **III**), the second α-deprotonation (to give intermediate **IV**) competes with the α'-one (to give intermediate **V**), so variable amounts of the corresponding by-product **VI** are produced after hydrolysis, together with the desired product **VII**.[6b,9] In order to avoid separation problems, we thought that an alternative route for generating the di-anionic intermediate **VIII** would be a halogen–lithium exchange, starting from the corresponding 2,6-bis(halomethyl)pyridine (Chart 1). Namely, starting from commercially available 2,6-bis(chloromethyl)pyridine (**1**), it would be possible to perform the corresponding lithiation and reaction with a carbonyl compound. However, one problem associated with the benzylic chlorine–lithium exchange is the Wurtz-type coupling of the organolithium intermediate, which is generally the main process.[10] One way to avoid the problem could be to perform the lithiation at low temperature and in the presence of the electrophile (Barbier-type conditions).[11] Some years ago, we found that the use of a catalytic amount of an arene makes possible the lithiation of a variety of substrates under very mild reaction conditions.[12–14] In this paper we describe the application of this methodology to the lithiation of 2,6-bis(chloromethyl)pyridine in the presence of various carbonyl compounds in order to prepare compounds of type **I** with Y = O.

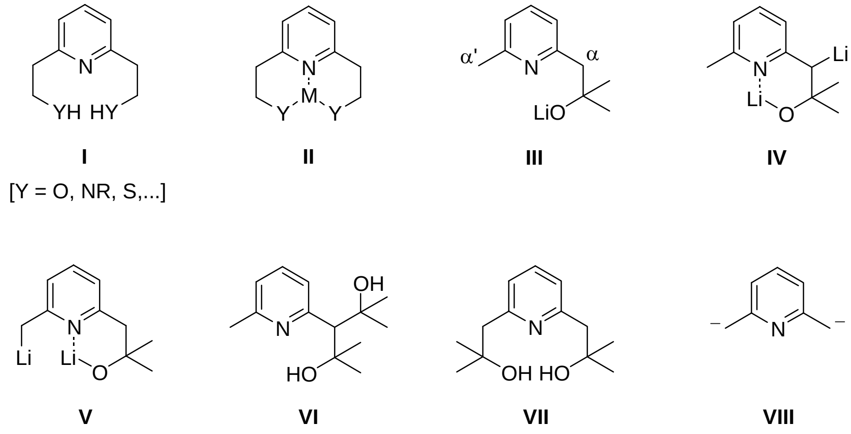
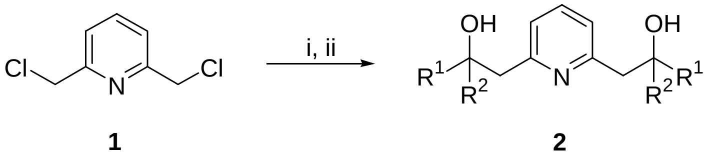


Chart 1. Structures **I** to **VIII**.

Results and Discussion

The reaction of commercially available 2,6-bis(chloromethyl)pyridine (**1**) with an excess of lithium powder (1:7 molar ratio; theoretical ratio 1:4) and a catalytic amount of 4,4'-di-*tert*-butylbiphenyl (DTBB; 1:0.05 molar ratio; 1.25 mol %) in the presence of a carbonyl compound (1:3 molar ratio) in THF at –90°C led, after hydrolysis with water at temperatures between –90°C and room temperature, to the expected diols **2** in moderate yields (Scheme 1 and Table 1). In all cases, the reaction is very clean, compound **2** being contaminated only with the corresponding product of monolithiation **2'** from which chromatographic separation was very simple.



Scheme 1. Reagents and conditions: (i) Li powder, DTBB (1.25 mol %), R^1R^2CO = *i*-BuCHO, *t*-BuCHO, Me_2CO, Et_2CO, n-Pr_2CO $(CH_2)_4CO$, $(CH_2)_5CO$ or norbonan-2-one, THF –90°C, 2h; (ii) H_2O, –90°C to rt.

Table 1. Preparation of compounds **2**

Entry	Electrophile	Product[a] No.	R^1	R^2	Yield (%)
1	^{i}BuCHO	**2a**	H	^{i}Bu	26[b]
2	^{t}BuCHO	**2b**	H	^{t}Bu	53[b]
3	Me_2CO	**2c**	Me	Me	47
4	Et_2CO	**2d**	Et	Et	40
5	$^nPr_2CO$	**2e**	^{n}Pr	^{n}Pr	25
6	$(CH_2)_4CO$	**2f**	$(CH_2)_4$		32
7	$(CH_2)_5CO$	**2g**	$(CH_2)_5$		37
8	Norbonan-2-one	**2h**	-[c]		24

[a] All products **2** were >95% pure (GLC and/or 300 MHz ^{1}H-NMR). [b] A *ca.* 1:1 mixture of diastereomers was obtained (300 MHz ^{13}C NMR). [c] For the structure of compound **2h** see Chart 2.

The process shown in Scheme 1 had to be performed in the presence of the electrophile because, when the same reaction was carried out step-by-step (lithiation followed by addition of the electrophile: Grignard conditions), even at very low temperature, only compound **3** was isolated (95% isolated yield).[15] When fluorenone was used as electrophile, the only compound isolated (apart from the corresponding 'reduced' compound of type **2'**) was the 'dimer' **4**, in poor yield (*ca*. 15%) (Chart 2).

Concerning a possible mechanism to explain the formation of the products **2**–**4**, we think that the initially monolithiated intermediate **IX** reacts with the electrophile present in the reaction medium to give the alkoxide **X**, which then suffers a second lithiation to give the new organolithium intermediate **XI** that condenses with a second molecule of the same carbonyl compound to afford the dialkoxide **XII**, the precursor of the final diols **2**. In the absence of the electrophile, the very reactive intermediate **IX** self-condenses to give the corresponding dimer **3**. Finally, with a bulky ketone such as fluorenone, intermediate **X** prefers to react with the species **IX** (which reacts more slowly with the electrophile) giving the intermediate **XIII**, which by successive lithiation and condensation with a second molecule of the electrophile gives the corresponding dialkoxide precursor of the compound **4** (Chart 3).

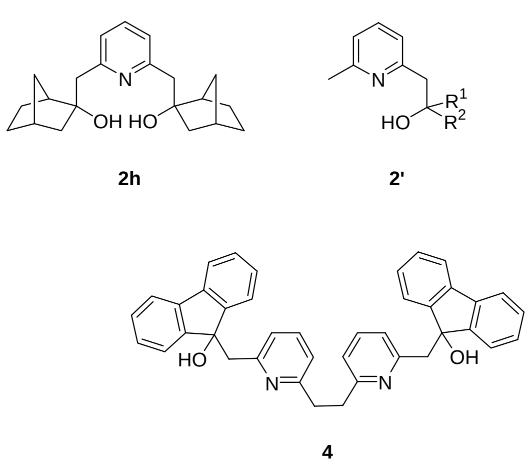


Chart 2. Structures **2–4**.

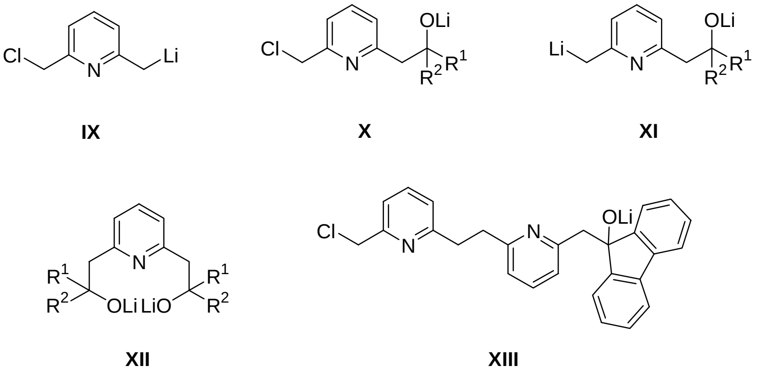
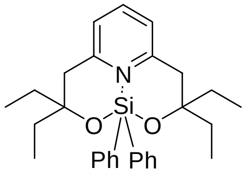


Chart 3. Structures **IX–XIII**.

Finally, we studied the ability of compounds of type **2** to give cyclic compounds. Thus, reaction of the diol **2** with dichlorodiphenylsilane in the presence of triethylamine and using dichloromethane and the solvent, gave compound **5**[16] in 67% isolated yield (81% conversion).



5

Conclusions

From the results described in this Paper we can conclude that the DTBB-catalyzed lithiation of 2,6-bis(chloromethyl)pyridine (**1**) in the presence of carbonyl compounds is an adequate procedure for preparing diols **2**. The isolated yields in pure form are moderate, but the reaction is very clean and the corresponding purification by column chromatography is very easy.

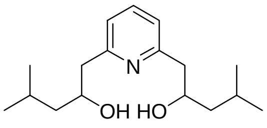
Experimental Section

General Procedures. All reactions were carried out under an atmosphere of argon in oven-dried glassware. All reagents were commercially available (Acros, Aldrich) and were used without further purification. Commercially available anhydrous THF (99.9%, water content $\leq 0.006\%$, Acros) was used as solvent in all the lithiation reactions. Lithium powder was prepared as we have reported previously.[17] Melting points were obtained with a Reichert Thermovar apparatus. Thin layer chromatography was carried out on TLC aluminum sheets with aluminum oxide 60 F_{254} neutral (Merck). IR spectra were measured (film) with a Nicolet Impact 400 D-FT Spectrometer. NMR spectra were recorded with a Bruker AC-300 or a Bruker ADVANCE DRX-500 using $CDCl_3$ as the solvent. LRMS and HRMS were measured with Shimadzu GC/HS QP-5000 and Finnigan MAT95 S spectrometers, respectively.

Preparation of compounds 2 and 4

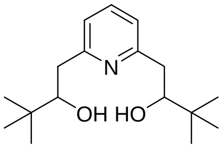
To a cooled green suspension of lithium (49 mg, 7 mmol) and DTBB (13 mg, 0.05 mmol) in THF (3 mL) at -90°C was slowly added (*ca*. 15 min) a solution of the corresponding electrophile (3 mmol) and 2,6-bis(chloromethyl)pyridine (178 mg, 1 mmol) in THF (2 mL). The resulting mixture was stirred for 2 h at the same temperature and was then hydrolyzed with water (5 mL) allowing the temperature to rise to 20°C. The resulting mixture was extracted with ethyl acetate (3×10 mL). The organic layer was dried over anhydrous $MgSO_4$ and evaporated (15 Torr). The resulting residue was then purified by flash chromatography (neutral silica gel, hexane/ethyl acetate). The yield is given in Table 1 (for compounds **2**) and in the text (for compound **4**). Physical, analytical and spectroscopic data follow.

2,6-Bis(2-hydroxy-4-methylpentyl)pyridine (2a). Diastereomeric mixture (1:1 approx., ^{13}C-NMR). Yellow oil; R_f 0.29 (hexane/EtOAc 7:3); ν (film) 3383, 2962, 2874, 1602, 1574 cm^{-1}; δ_H 0.92, 0.93 (24H, 2d, *J* = 6.5, 6.4 Hz, 8×CH_3), 1.22–1.31, 1.46–1.57 (4H, 4H, 2m, 4×C*H*$_2$CHMe$_2$), 1.77–1.90 (4H, m, 4×C*H*Me$_2$), 2.76–2.94 (8H, m, 4×C*H*$_2$Py), 4.08–4.16 (4H, m, 4×CHOH), 7.03 [4H, d, *J* = 7.7, 2×(Py- 3,5-H)], 7.56 (2H, t, *J* = 7.7, 2×Py- 4-H); δ_C 22.1, 22.2, 23.3, 23.4, 24.5 [*C*H(*C*H$_3$)$_2$], 44.5, 44.6, 46.3, 46.4 (CH_2), 69.2 (COH), 121.5 (Py- 3-C), 137.2 (Py- 4-C), 159.1 (Py- 2-C); *m/z* 279 (M^+, 1%), 236 (24), 275 (21), 223 (10), 222 (58), 218 (26), 204 (33), 194 (13), 193 (100), 175 (12), 160 (14), 132 (10), 107 (33), 106 (16); HRMS Calcd. for $C_{17}H_{27}NO$ (M^+-H_2O) 261.2093. Found 261.2081.



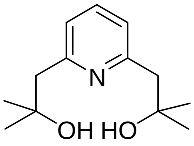
2a

2,6-Bis(2-hydroxy-3,3-dimethyl-butyl)pyridine (2b). Diastereomeric mixture (approx. 1:1, ^{13}C-NMR). Yellow oil; R_f 0.34 (hexane/EtOAc 7:3); ν (film) 3404, 2951, 2852, 1602, 1574 cm^{-1}; δ_H 0.99 (36H, s, $12\times CH_3$), 2.66–2.76, 2.91–2.96 (4H, 4H, 2m, $4\times CH_2$), 3.59–3.68 (4H, m, 4×CHOH), 7.05 [4H, d, *J* = 7.6, 2×(Py- 3,5-H)], 7.56 (2H, t, *J* = 7.6, 2×Py- 4-H); δ_C 25.7, 25.8 (CH_3), 34.7, 34.8 (*C*Me_3), 38.9 (CH_2), 78.8 (COH), 121.4, 121.5 (Py- 3-C), 137.3, 137.5 (Py- 4-C), 160.0 (Py- 2-C); *m/z* 279 (M^+, 1%), 264 (15), 246 (24), 223 (16), 222 (100), 205 (14), 204 (93), 193 (26), 180 (28), 162 (16), 160 (45), 148 (20), 136 (13), 135 (26), 119 (12), 107 (38), 106 (33), 57 (33); HRMS Calcd. for $C_{17}H_{27}NO$ (M^+-H_2O) 261.2093. Found 261.2091.



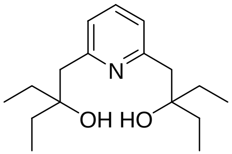
2b

2,6-Bis(2-methyl-2-hydroxypropyl)pyridine (2c).[6b] Colorless crystals; R_f 0.38 (hexane/EtOAc 7:3); mp 78°C (hexane/EtOAc); ν (film) 3384, 2971, 2927, 1594, 1576 cm^{-1}; δ_H 1.23 (12H, s, $4\times CH_3$), 2.91 (4H, s, $2\times CH_2$), 7.06 (2H, d, *J* = 7.8, Py- 3,5-H), 7.58 (1H, t, *J* = 7.8, Py- 4-H); δ_C 29.4 (CH_3), 49.7 (CH_2), 70.7 (COH), 122.3 (Py- 3-C), 137.0 (Py- 4-C), 158.4 (Py- 2-C); *m/z* 223 (M^+, 1%), 190 (39), 165 (58), 148 (13), 147 (100), 146 (29), 132 (20), 107 (25), 106 (17), 59 (21); HRMS Calcd. for $C_{13}H_{19}NO$ (M^+-H_2O) 205.1467. Found 205.1460.



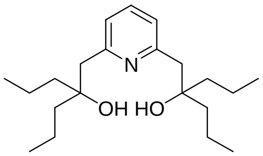
2c

2,6-Bis(2-ethyl-2-hydroxybutyl)pyridine (2d). Yellow oil; R_f 0.76 (hexane/EtOAc 7:3); ν (film) 3386, 2965, 2879, 1593, 1575 cm^{-1}; δ_H 0.89 (12H, t, *J* = 7.5, $4\times CH_3$), 1.44, 1.45 (8H, 2q, *J* = 7.5, *J* = 7.5, 4×C*H*$_2$CH$_3$), 2.87 (4H, s, 2×C*H*$_2$Py), 7.06 (2H, d, *J* = 7.7, Py- 3,5-H), 7.56 (1H, t, *J* = 7.7, Py- 4-H); δ_C 8.0 (CH_3), 30.9 (*C*H$_2$CH$_3$), 45.1 (*C*H$_2$Py), 74.9 (COH), 122.4 (Py- 3-C), 136.9 (Py- 4-C), 158.4 (Py- 2-C); *m/z* 279 (M^+, 1%), 250 (28), 233 (17), 232 (100), 193 (52), 176 (11), 175 (59), 164 (10), 163 (14), 160 (23), 146 (20), 108 (11), 107 (52), 106 (20), 57 (19); HRMS Calcd. for $C_{17}H_{27}NO$ (M^+-H_2O) 261.2093. Found 261.2049.



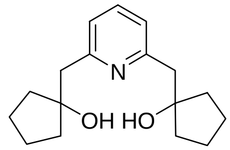
2d

2,6-Bis(2-propyl-2-hydroxypentyl)pyridine (2e). Yellow oil; R_f 0.76 (hexane/EtOAc 7:3); ν (film) 3394, 2957, 2869, 1601, 1580 cm^{-1}; δ_H 0.87 (12H, t, *J* = 2.8, 4×CH$_3$), 1.36 (16H, m, 4×C*H*$_2$C*H*$_2$CH$_3$), 2.88 (4H, s, 2×C*H*$_2$Py), 7.05 (2H, d, *J* = 7.7, Py- 3,5-H), 7.57 (1H, t, *J* = 7.7, Py- 4-H); δ_C 14.6, 14.7 (CH$_3$), 17.0, 17.1 (*C*H$_2$CH$_3$), 41.7, 41.8 (*C*H$_2$CH$_2$CH$_3$), 46.1 (*C*H$_2$Py), 74.5, 74.6 (COH), 122.4 (Py- 3-C), 137.0 (Py- 4-C), 158.5 (Py- 2-C); *m/z* 317 (M$^+$-H$_2$O, 2%), 292 (33), 275 (21), 274 (100), 221 (41), 203 (27), 178 (28), 177 (10), 174 (21), 115 (11), 108 (17), 107 (84), 106 (19), 71 (18), 55 (18); HRMS Calcd. for $C_{21}H_{35}NO$ (M$^+$-H$_2$O) 317.2719. Found 317.2715.



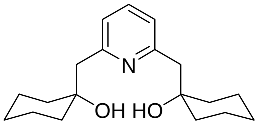
2e

2,6-Bis[(1-hydroxycyclopentyl)methyl]pyridine (2f). Yellow oil; R_f 0.38 (hexane/EtOAc 7:3); ν (film) 3377, 2957, 2869, 1602, 1574 cm^{-1}; δ_H 1.47–1.83 (16H, m, 8× ring CH$_2$), 3.02 (4H, s, 2×C*H*$_2$Py), 7.07 (2H, d, *J* = 7.6, Py- 3,5-H), 7.58 (1H, t, *J* = 7.6, Py- 4-H); δ_C 23.7, 39.8 (ring CH$_2$), 47.5 (*C*H$_2$Py), 81.7 (COH), 122.1 (Py- 3-C), 137.1 (Py- 4-C), 158.8 (Py- 2-C); *m/z* 275 (M$^+$, 3%), 233 (22), 228 (18), 200 (16), 192 (10), 191 (76), 174 (14), 173 (100), 172 (29), 158 (10), 144 (16), 107 (58), 106 (35), 77 (11), 67 (17), 55 (13); HRMS Calcd. for $C_{17}H_{23}NO$ (M$^+$-H$_2$O) 257.1780. Found 257.1774.



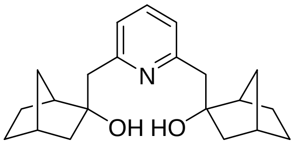
2f

2,6-Bis[(1-hydroxycyclohexyl)methyl]pyridine (2g). Yellow oil; R_f 0.45 (hexane/EtOAc 7:3); ν (film) 3383, 2940, 2860, 1596, 1569 cm^{-1}; δ_H 1.31–1.66 (20H, m, 10× ring CH$_2$), 2.90 (4H, s, 2×C*H*$_2$Py), 7.04 (2H, d, *J* = 7.7, Py- 3,5-H), 7.56 (1H, t, *J* = 7.7, Py- 4-H); δ_C 22.2, 25.7, 37.8 (ring CH$_2$), 48.1 (*C*H$_2$Py), 71.6 (COH), 122.4 (Py- 3-C), 136.9 (Py- 4-C), 158.1 (Py- 2-C); *m/z* 303 (M$^+$, 5%), 260 (14), 247 (12), 242 (37), 206 (15), 205 (100), 188 (14), 187 (87), 186 (16), 172 (12), 158 (15), 144 (16), 132 (10), 108 (12), 107 (85), 106 (43), 81 (24), 79 (12), 77 (11), 55 (20); HRMS Calcd. for $C_{19}H_{27}NO$ (M$^+$-H$_2$O) 285.2093. Found 285.2076.



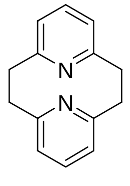
2g

2,6-Bis(2-hydroxybicyclo[2.2.1]hept-2-ylmethyl)pyridine (2h). Diastereomeric mixture (approx. 1:1, ^{13}C-NMR). Yellow oil; R_f 0.59 (hexane/EtOAc 7:3); ν (film) 3410, 2957, 2864, 1596, 1574 cm^{-1}; δ_H 1.07–1.31, 1.50–1.67 (18H, 14H, 2m, 16× ring CH_2), 2.04, 2.19 (8H, 2br s, 8× ring CH), 2.97 (8H, s, 4× C*H*$_2$Py), 4.32 (4H, br s, OH), 7.05 [4H, d, *J* = 7.8, 2×(Py- 3,5-H)], 7.56 (2H, t, *J* = 7.8, 2×Py- 4-H); δ_C 21.7, 21.8, 28.3, 28.4 (ring CH_2), 37.1, 37.1 (ring CH), 38.3, 38.3, 45.4, 45.7 (ring CH_2), 46.0, 46.4 (ring CH), 48.0 (*C*H$_2$Py), 79.0 (COH), 122.3, 122.4 (Py-3-C), 136.9 (Py- 4-C), 158.2, 158.3 (Py- 2-C); *m/z* 327 (M$^+$, 12%), 309 (13), 281 (15), 268 (15), 259 (39), 244 (10), 241 (16), 226 (36), 218 (19), 217 (100), 207 (16), 200 (14), 199 (70), 198 (16), 184 (19), 172 (11), 171 (19), 170 (37), 149 (21), 134 (11), 108 (12), 107 (69), 106 (30), 93 (18), 91 (12), 79 (11), 77 (16), 67 (28), 66 (15), 55 (10); HRMS Calcd. for $C_{21}H_{29}NO_2$ 327.2198. Found 327.2194.



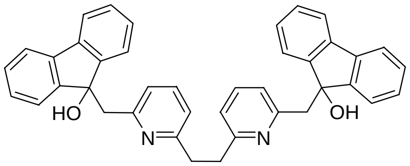
2h

Preparation of [2.2](2,6)pyridinophane (3).[18] To a cooled green suspension of lithium (49 mg, 7 mmol) and DTBB (13 mg, 0.05 mmol) in THF (3 mL) at -90°C was added a solution of 2,6-bis(chloromethyl)pyridine (178 mg, 1 mmol) in THF (2 mL). The resulting mixture was stirred for 2 h at the same temperature and then hydrolyzed with water (5 mL), allowing the temperature to rise to 20°C. The resulting mixture was diluted with ethyl acetate (10mL) and extracted with 2N HCl (3×10 mL). The combined aqueous layers were naturalized with 3M NaOH and extracted with ethyl acetate (3×10 mL) The new combined organic layers were dried ($MgSO_4$) and evaporated (15 Torr). The residue was then purified by recrystallization. The yield is given in the text, and other data follow: White crystals; mp 256°C (hexane/ dichloromethane); ν (film) 2957, 2922, 1592, 1573 cm^{-1}; δ_H 3.22 (8H, s, 4×CH_2), 6.91 (2H, d, *J* = 7.7, Py- 3,5-H), 7.41 (1H, t, *J* = 7.7, Py- 4-H); δ_C 38.2 (CH_2), 120.2 (Py- 3-C), 136.4 (Py- 4-C), 160.6 (Py- 2-C); *m/z* 210 (M$^+$, 9%), 193 (14), 192 (100), 143 (24), 141 (75), 123 (19), 107 (43), 106 (32), 105 (28), 104 (11), 100 (16), 97 (12), 85 (13), 83 (12), 77 (13), 71 (17), 69 (13), 57 (25), 56 (13), 15 (55), 11 (45), 19 (43), 41 (12); HRMS Calcd. for $C_{14}H_{14}N_2$ (M$^+$) 210.1157. Found 210.1158.



3

9-(6-2-[6-(9-Hydroxy-9*H*-9-fluorenylmethyl)-2-pyridyl]ethyl-2-pyridylmethyl)-9*H*-9-fluorenol (4). Colorless crystals; R$_f$ 0.19 (hexane/EtOAc 7:3); mp 186°C (hexane/EtOAc); ν (film) 3240, 3065, 3038, 2940, 2910, 1598, 1574 cm^{-1}; δ$_H$ 3.25 (4H, s, CH_2CH_2), 3.52 (4H, s, 2×C*H*$_2$COH), 6.77 (2H, d, *J* = 7.5, 2×Py- 5-H), 6.91 (4H, d, *J* = 7.3, 2×fluorenyl-1,8-H), 7.1 (4H, dt, *J* = 7.5, *J* = 0.8, 2×fluorenyl-2,7-H), 7.24 (2H, d, *J* = 7.5, Py- 3-H), 7.31 (4H, dt, *J* = 7.5, *J* = 0.8, 2×fluorenyl-3,6-H), 7.49 (2H, t, *J* = 7.5, 2×Py- 4-H), 7.63 (4H, d, *J* = 7.5, 2×fluorenyl-4,5-H); δ$_C$ 36.5 (CH_2CH_2), 45.5 (*C*H$_2$COH), 82.1 (COH), 119.8, 122.3, 122.5, 123.8, 127.5, 128.6, 137.7, 139.1, 149.0, 158.9, 159.3 (ArC); *m/z* 391 (M$^+$-181, 5%), 213 (26), 121 (100), 211 (19), 181 (33), 180 (91), 153 (13), 152 (50), 151 (20), 150 (10), 120 (29); HRMS Calcd. for $C_{27}H_{23}N_2O$ (M$^+$-181) 391.1810. Found 391.1784.



4

Preparation of 3,3,7,7-Tetraethyl-5,5-diphenyl-4,6-dioxa-13-aza-5-silabicyclo[7.3.1]trideca-1(12), 9(13),10-triene (5). To a solution of the corresponding diol **2d** (71mg, 0.25 mmol) and dry Et$_3$N (53mg, 0.52 mmol) in dry dichloromethane (10 mL), dichlorodiphenylsilane (57 μL, 0.34 mmol) was added dropwise. The resulting mixture was heated at reflux for 48h. The solvent was removed under vacuum and the residue washed with water to remove Et$_3$NHCl, and extracted with chloroform (3×10 mL). The organic layer was dried over anhydrous MgSO$_4$ and evaporated (15 Torr). The resulting residue was purified by flash chromatography (neutral alumina gel, hexane/ethyl acetate). The yield is given in the text and other data follow. Colorless crystals; R$_f$ 0.80 (hexane/EtOAc 8:2); mp 95°C (hexane/EtOAc); ν (film) 3071, 2924, 2854, 1595, 1460 cm^{-1}; δ$_H$ 0.86 (12H, t, *J* = 7.4, 4×CH$_3$), 1.41–1.59 (8H, m, 4×C*H*$_2$CH$_3$), 2.93 (4H, s, 2×C*H*$_2$Py), 6.87 (2H, d, *J* = 7.7, Py- 3,5-H), 7.18-7.21 (6H, m, PhH), 7.46 (1H, t, *J* = 7.7, Py- 4-H), 7.67–7.70 (4H, m, PhH); δ$_C$ 8.3 (CH$_3$), 31.6 (*C*H$_2$CH$_3$), 42.9 (*C*H$_2$Py), 80.5 (COH), 121.3 (Py- 3-C), 126.8, 127.5, 134.5, 136.3, 143.5 (ArC), 157.7 (Py- 2-C); *m/z* 459 (M$^+$, 1%), 430 (5), 383 (30), 382 (100); HRMS Calcd. for $C_{27}H_{32}NSiO_2$ (M$^+$-Et) 430.2202. Found 430.2207.

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