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First Total Synthesis of the Cytotoxic Carbazole Alkaloid Excavatine-A and Regioselective Annulation to Pyrano[2,3-*a*]carbazoles and [1,4]Oxazepino[2,3,4-*jk*]carbazoles**

Christian Brütting,[a] Olga Kataeva,[b] Arndt W. Schmidt,[a] and Hans-Joachim Knölker*[a]

Abstract: We describe the first total synthesis of the cytotoxic carbazole alkaloid excavatine-A (**1**). The carbazole framework was constructed via double C–H bond activation of a diarylamine using our palladium(II)-catalyzed oxidative cyclization. Treatment of the intermediate 8-hydroxycarbazoles **8** with prenal (**7**) and different additives led either to the pyrano[2,3-*a*]carbazoles **6** or the [1,4]oxazepino[2,3,4-*jk*]carbazoles **15**. The pyran annulation was investigated to determine the influence of substitution pattern, additives, and reaction time on the selectivity.

Introduction

The main natural sources for carbazole alkaloids are microorganisms and Rutaceae plants. The latter have found applications in traditional Asian folk medicine for the treatment of various diseases.[1] It is assumed that carbazole alkaloids play a major role for the bioactivity of the plant extracts and many carbazole alkaloids display promising antimicrobial, antiviral, anticancerogenic and other pharmacologically useful activities.[2] Excavatine-A (**1**) was isolated in 2013 by Tan and co-workers from the stems and leaves of *Clausena excavata* (Figure 1).[3] Along with the isolation and spectroscopic characterization the authors also reported a cytotoxic activity of compound **1** against A549 and HeLa cell lines. In the course of our ongoing research on biologically active carbazole alkaloids,[4] we reported the total syntheses of the natural products clauszoline-B (**2**),[5] clauszoline-M (**3**),[6] clausine-A (**4**),[6a,7] and clauszoline-H (**5**),[5a,6b] which all have the framework of a 2,8-dioxygenated carbazole in common. Herein, we describe our synthetic approach to excavatine-A (**1**) and the synthesis of pyrano[2,3-*a*]carbazoles **6** and [1,4]oxazepino[2,3,4-*jk*]carbazoles **15** by regioselective annulation of a pyran or oxazepine ring at an 8-hydroxycarbazole **8**.

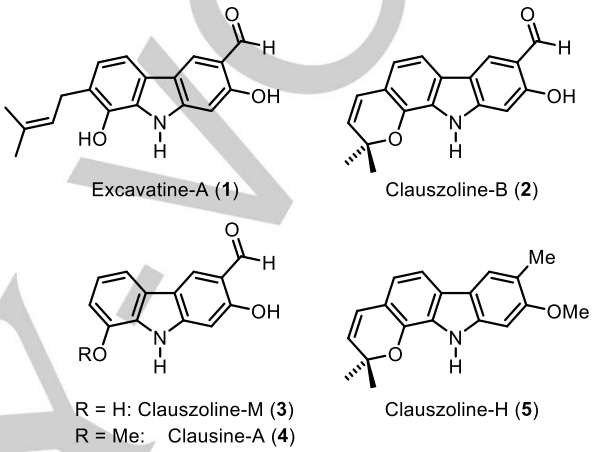
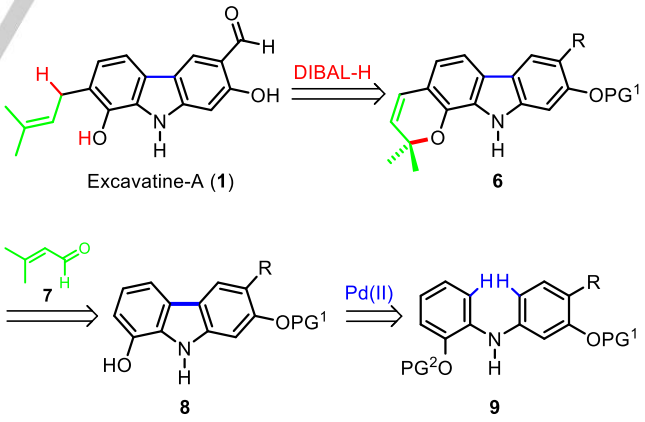


Figure 1. Excavatine-A (**1**) and structurally related carbazole alkaloids.

Results and Discussion



a: R = Me; **b**: R = CN; **c**: R = COOMe; PG^1, PG^2: protecting groups

Scheme 1. Retrosynthetic analysis of excavatine-A (**1**).

Our initial approach to excavatine-A (**1**) was based on introduction of the prenyl substituent by the DIBAL-H-promoted pyran ring opening of pyrano[2,3-*a*]carbazoles **6** developed in our laboratories (Scheme 1).[8] The nitrile or methoxycarbonyl group of **6** would also be reduced under these conditions and thus simultaneously furnish the formyl substituent at C-3 of

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[**] Transition Metals in Organic Synthesis, Part 133. For Part 132, see ref. [23].

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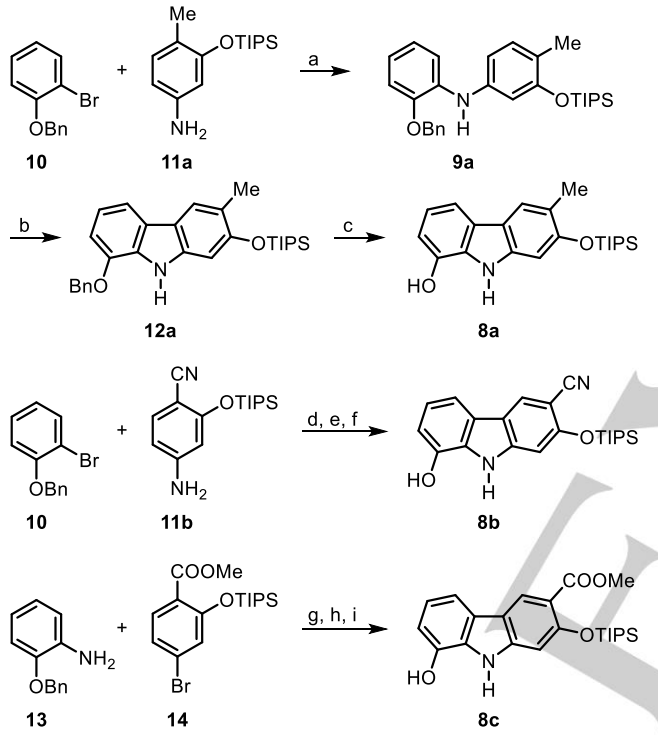
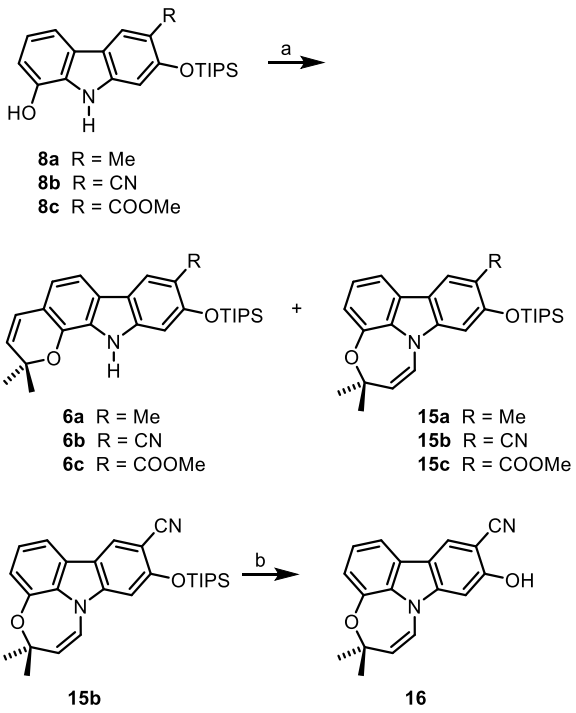
excavatine-A (**1**). Alternatively, the formyl group could be introduced by oxidation of the corresponding 3-methylcarbazole. The required pyrano[2,3-*a*]carbazoles **6** are accessible by pyran-ring annulation at the 8-hydroxycarbazoles **8** using either Godfrey's conditions[9] or by treatment of **8** with prenal (**7**) and Lewis or Brønsted acids as described by Dufresne or Casiraghi.[10] Our group successfully applied all three procedures to the synthesis of various pyranocarbazole alkaloids.[5a,11] The carbazole framework is most conveniently constructed by the palladium(II)-catalyzed oxidative cyclization of diarylamines **9**,[11,12] which are readily available by Buchwald–Hartwig amination.[13]



Scheme 2. Synthesis of 8-hydroxycarbazoles **8a–c**. *Reagents and conditions*: (a) $Pd(OAc)_2$ (6 mol%), SPhos (12 mol%), Cs_2CO_3 (1.2 equiv), toluene, reflux, 4 h (95%); (b) $Pd(OAc)_2$ (15 mol%), $Cu(OAc)_2$ (2.5 equiv), AcOH, air, microwave (300 W), 130 °C, 75 min (82%); (c) H_2 (1 atm), 10% Pd/C, $MeOH/CH_2Cl_2$ (1:1), RT, 23.5 h (91%); (d) $Pd(OAc)_2$ (6 mol%), SPhos (12 mol%), Cs_2CO_3 (1.2 equiv), toluene, reflux, 4 h (93%); (e) $Pd(OAc)_2$ (30 mol%), K_2CO_3 (30 mol%), PivOH, air, 130 °C, 2 h (75%); (f) H_2 (1 atm), 10% Pd/C, $MeOH/CH_2Cl_2$ (1:1), RT, 24 h (93%); (g) $Pd(OAc)_2$ (6 mol%), XPhos (12 mol%), Cs_2CO_3 (1.2 equiv), toluene, reflux, 4 h (98%); (h) $Pd(OAc)_2$ (30 mol%), K_2CO_3 (30 mol%), PivOH, air, 130 °C, 2.5 h (58%); (i) H_2 (1 atm), 10% Pd/C, $MeOH/CH_2Cl_2$ (1:1), RT, 1.5 h (92%). SPhos = 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl; XPhos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl.

First, the precursors for the envisaged pyran ring annulation, the 8-hydroxycarbazoles **8a–c**, have been synthesized (Scheme 2). The 3-methyl-substituted carbazole **8a** was available from the protected bromophenol **10** and the arylamine **11a**. O-Benzylation of *ortho*-bromophenol provided compound **10** which already served as starting material in our syntheses of clauszoline-B (**2**) and clauszoline-H (**5**).[5a] Compound **11a** is prepared from 2-methyl-5-nitrophenol and has been frequently applied to the synthesis of diarylamines.[5a,11e,12a,14] Palladium(0)-catalyzed coupling of **10** and **11a** using SPhos as ligand and cesium carbonate as base provided the diarylamine **9a** in excellent yield. Microwave heating of a mixture of **9a**, pivalic acid, copper(II) acetate, and catalytic amounts of palladium(II) acetate led to the 2,8-dioxygenated carbazole **12a** in 82% yield. Finally, hydrogenolytic cleavage of the benzyl ether provided the 3-methyl-8-hydroxycarbazole **8a** in 3 steps and 71% overall yield on a multigram scale. Thus, the present route to compound **8a** is superior to our previous approach (3 steps and 55% overall yield on a 0.2 g scale) which was reported in the course of our total synthesis of clauszoline-B (**2**) and clauszoline-H (**5**).[5a] The analogous cyano derivative **8b** was synthesized following the same sequence of steps. The required arylamine **11b** was obtained in a two-step sequence from 2-hydroxy-4-nitrobenzonitrile. Buchwald–Hartwig coupling of compound **11b** with **10**, oxidative cyclization of the resulting diarylamine, and debenzylation provided the 8-hydroxycarbazole-3-carbonitrile **8b** in 3 steps and 65% overall yield. The oxidative cyclization to **8b** was achieved by heating a mixture of the intermediate diarylamine, pivalic acid, and potassium carbonate with catalytic amounts of palladium(II) acetate at 130 °C in the presence of air. This experimental procedure provided a much better turnover to carbazole **8b** as compared to the microwave-promoted reaction described above. For synthesis of the carbazole-3-carboxylate **8c**, 2-nitrophenol was transformed into 2-benzyloxyaniline **13**. Subsequent Buchwald–Hartwig coupling with the bromobenzoate **14** followed by oxidative cyclization under the same conditions as described for the synthesis of **8b** and removal of the benzyl group provided 8-hydroxycarbazole-3-carboxylate **8c** in 3 steps and 52% overall yield.

With the 8-hydroxycarbazoles **8a–c** in hand, we investigated different procedures for pyran ring annulation. The formation of an aryl propargyl ether followed by a thermally induced rearrangement (Godfrey's method)[9] could not be applied because the reaction of **8a** with 1,1-dimethylpropargyl methyl carbonate in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) and catalytic amounts of copper(II) chloride did not afford the corresponding product. Application of our protocol, treatment of **8a**, prenal (**7**), propionic acid, and catalytic amounts of phenylboronic acid in toluene at reflux,[5a] but with a reduced reaction time of only 6 h provided a mixture of the desired pyrano[2,3-*a*]carbazole **6a** (41% yield) and the [1,4]oxazepino[2,3,4-*jk*]carbazole **15a** (33% yield) (Scheme 3, Table 1). The side product **15a** could be separated by preparative HPLC but decomposed rapidly on evaporation of the solvent. By increasing the reaction time to 22 h, **15a** was no longer detectable and the desired pyrano[2,3-*a*]carbazole **6a** was obtained in 77% yield. In the total synthesis of clauszoline-B (**2**) and clauszoline-H (**5**), we achieved the conversion of the 8-hydroxycarbazole **8a** into the pyrano[2,3-*a*]carbazole **6a** with 1.5 equiv prenal (**7**), 20 mol% $PhB(OH)_2$, and 110 equiv EtCOOH by heating in toluene at reflux for 3 d (78% yield).[5a] Thus, the formation of the [1,4]oxazepino[2,3,4-*jk*]carbazole **15a** was not observed under those conditions.



Scheme 3. Pyran and [1,4]-oxazepine ring annulation at the 8-hydroxycarbazoles **8a**–**c**. *Reagents and conditions*: (a) see Tables 1 and 2; (b) TBAF (1.2 equiv), THF, 0 °C, 20 min (82%).

Table 1. Pyran and [1,4]-oxazepine ring annulation at the 8-hydroxycarbazole **8a**.

Reagents and conditions	Product(s)
8a, 1,1-dimethylpropargyl methyl carbonate (2.0 equiv), DBU (1.2 equiv), $CuCl_2 \cdot H_2O$ (1 mol%), MeCN, RT, 2 h	decomposition
8a, prenal (**7**) (2.0 equiv), $PhB(OH)_2$ (20 mol%), $EtCO_2H$ (110 equiv), toluene, reflux, 6 h	**6a** (41%) **15a** (33%)
8a, prenal (**7**) (2.0 equiv), $PhB(OH)_2$ (20 mol%), $EtCO_2H$ (110 equiv), toluene, reflux, 22 h	**6a** (77%)

For a better understanding of the mechanism of this annulation process, the reaction was monitored by GC/MS using anthracene as internal standard (Figure 2). The reaction of **8a** with prenal (**7**) in the presence of propionic acid and catalytic amounts of phenylboronic acid at 110 °C led immediately to the formation of the [1,4]oxazepino[2,3,4-*jk*]carbazole **15a**. During the course of this reaction, the concentration of **15a** was increasing rapidly up to a maximum after 1 h and then started to decrease drastically. In contrast, the concentration of the pyrano[2,3-*a*]carbazole **6a** increased more slowly, reached a maximum after 7 h, and subsequently showed an only minor decrease. Apparently, the [1,4]oxazepino[2,3,4-*jk*]carbazole **15a** is formed faster than the pyrano[2,3-*a*]carbazole **6a**. Moreover, the generation of **15a** appears to be a reversible process which ultimately transforms all of compound **15a** into the thermodynamically more stable **6a**. Prolonged exposure of **6a** to the reaction conditions leads to decomposition which explains the minor decrease after 7 h. Mechanistically, the formation of the [1,4]oxazepino[2,3,4-*jk*]carbazole **15** can be explained by initial generation of the iminium salt **17** followed by an intramolecular oxa-Michael addition (Scheme 4, path a).[15] Alternatively, oxa-Michael addition of **8** at the activated prenal (**7**) to give intermediate **18**, tautomerization to oxonium ion **18′**, subsequent intramolecular attack of the carbazole nitrogen atom to give **19**, and elimination of water would finally also lead to **15** (path b). The isomerization of **15** to **6** can be rationalized by reversal of the latter process. Hydrolysis of the enamine moiety of **15** to **18′**, subsequent attack of C-7 at the activated carbonyl group, and elimination of water from **20** provides the pyrano[2,3-*a*]carbazole **6**. The latter could also be formed directly by initial C–C-bond formation via the intermediates **21** and **22** and final electrocyclic ring closure (path c).

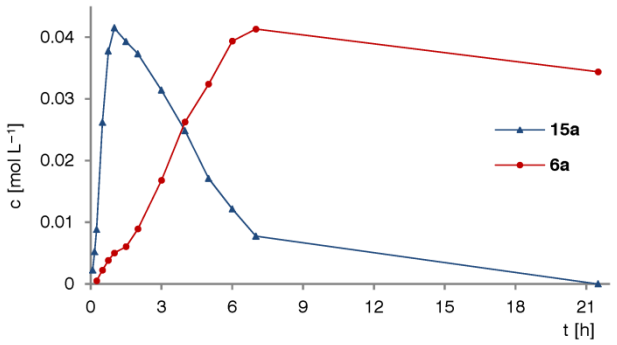


Figure 2. GC/MS monitoring of the transformation of **8a** into **15a** and **6a**. *Reagents and conditions*: **8a** (1.0 equiv), prenal (**7**) (4.0 equiv), anthracene (1.0 equiv), $PhB(OH)_2$ (20 mol%), $EtCO_2H$ (110 equiv), toluene, 110 °C, 21.5 h

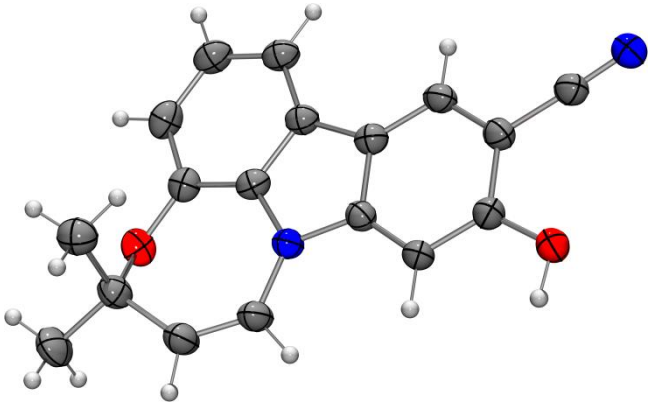
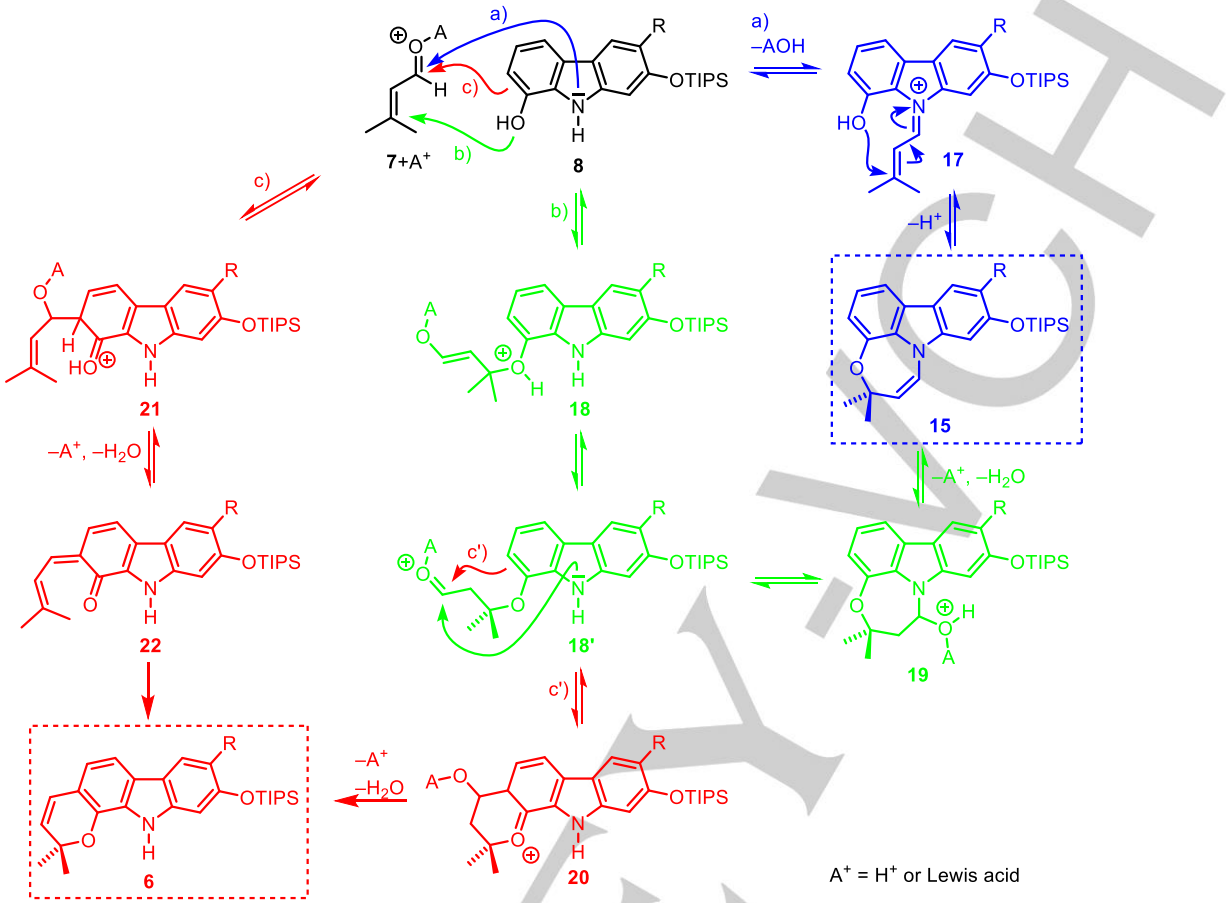


Figure 3. Molecular structure of the [1,4]oxazepino[2,3,4-*jk*]carbazole **16** in the crystal. ORTEP plot showing thermal ellipsoids at the 50% probability level.



Scheme 4. Proposed mechanism for the formation the pyrano[2,3-*a*]carbazole **6** and the [1,4]oxazepino[2,3,4-*jk*]carbazole **15**.

The phenylboronic acid-catalyzed pyran annulation protocol was then applied to the carbazole-3-carbonitrile **8b** (Scheme 3, Table 2). Reaction of **8b** and prenal (**7**) in the presence of phenylboronic acid and propionic acid provided the pyrano[2,3-*a*]carbazole **6b** in 62% yield and the [1,4]oxazepino[2,3,4-*jk*]carbazole **15b** in 18% yield.

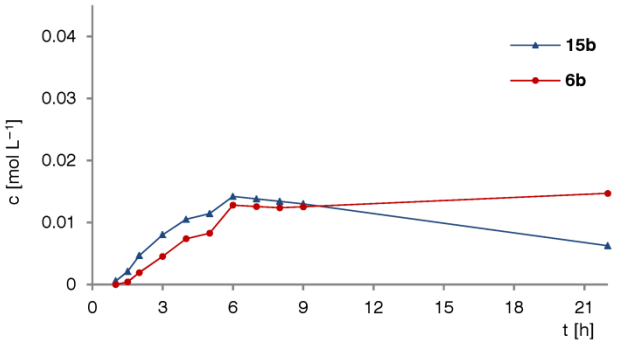


Figure 4. GC/MS monitoring of the transformation of **8b** into **15b** and **6b**. Reagents and conditions: **8b** (1.0 equiv), prenal (**7**) (4.0 equiv), anthracene (1.0 equiv), $PhB(OH)_2$ (20 mol%), $EtCO_2H$ (110 equiv), toluene, 110 °C, 22 h.

In contrast to annulation at the methylcarbazole **8a**, four equivalents of prenal (**7**) were required to provide the pyrano[2,3-*a*]carbazolecarbonitrile **6b** in reasonable yields. Moreover, the side product **15b** could be separated by simple column chromatography and was fully characterized. The structure of **15b** was confirmed by cleavage of the silyl ether and single crystal X-ray analysis of the resulting hydroxy[1,4]oxazepino[2,3,4-*jk*]carbazole **16** (Figure 3).

Monitoring the transformation by GC/MS using anthracene as internal standard revealed a different behavior of the carbazolecarbonitrile **8b** in comparison to the methylcarbazole **8a** (Figure 4). The [1,4]oxazepino[2,3,4-*jk*]carbazole **15b** is formed much more slowly than the [1,4]oxazepino[2,3,4-*jk*]carbazole **15a**, most likely due to the electron-withdrawing substituent *para* to the nitrogen atom which reduces the nucleophilicity of that position. After 6 h the concentration of **15b** is at its maximum and then starts to decrease. Apparently, the formation as well as the rearrangement of compound **15b** both occur more slowly as compared to its methyl analog **15a**. The pyrano[2,3-*a*]carbazole **6b** is generated almost as fast as the [1,4]oxazepino[2,3,4-*jk*]carbazole **15b** and after 6 h the concentration of the pyrano[2,3-*a*]carbazole **6b** remains almost constant. Thus, a short reaction time does not provide

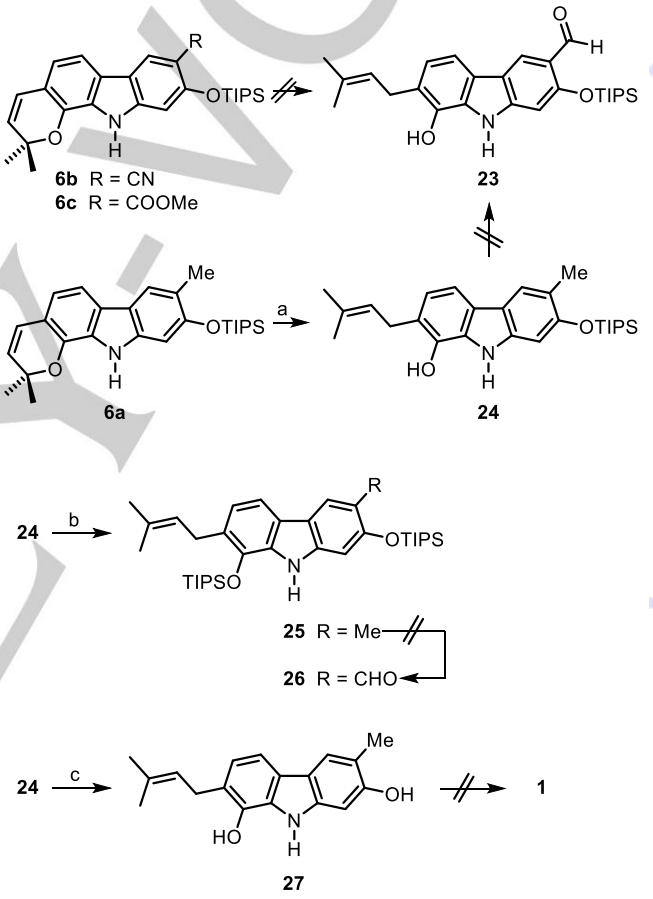
selectively [1,4]oxazepino[2,3,4-*jk*]carbazole **15b** and rearrangement into **6b** occurs only after very long reaction times.

Table 2. Pyran and oxazepine ring annulation at the 8-hydroxycarbazoles **8b** and **8c**.

Compd.	Reagents and conditions	Major product(s)
8b	prenal (**7**) (4.0 equiv), $PhB(OH)_2$ (20 mol%), $EtCO_2H$ (110 equiv), toluene, reflux, 21 h	**6b** (62%) **15b** (18%)
8b	prenal (**7**) (4.0 equiv), $PhB(OH)_2$ (20 mol%), toluene, reflux, 25 h	**6b** (40%) **15b** (35%)
8b	prenal (**7**) (4.0 equiv), $EtCO_2H$ (110 equiv), 4 Å MS, toluene, reflux, 6 h	**15b** (4%)
8b	prenal (**7**) (2.0 equiv), CSA (20 mol%), toluene, reflux, 1 h	**15b** (62%)[a]
8b	prenal (**7**) (2.0 equiv), $PhB(OH)_2$ (20 mol%), CSA (20 mol%), toluene, reflux, 22 h	decomposition
8b	prenal (**7**) (2.0 equiv), EDDA (20 mol%), xylenes, reflux, 22 h[16]	**6b** (9%)
8b	prenal (**7**) (2.0 equiv), $Ti(OiPr)_4$ (4.0 equiv), toluene, RT, 3 d	**6b** (11%)
15b	$PhB(OH)_2$ (20 mol%), $EtCO_2H$ (110 equiv), water (14 equiv), toluene, reflux, 23.5 h	**6b** (32%) **15b** (20%)
8c	prenal (**7**) (4.0 equiv), $PhB(OH)_2$ (20 mol%), $EtCO_2H$ (110 equiv), toluene, reflux, 23 h	**6c** (50%) **15c** (<5%)[b]
8c	prenal (**7**) (2.0 equiv), CSA (20 mol%), toluene, reflux, 1 h	**15c** (52%)[a]

[a] Small amounts of the corresponding pyrano[2,3-*a*]carbazoles **6b** and **6c**, respectively, were detected by TLC and removed by column chromatography. [b] In this case, the [1,4]oxazepino[2,3,4-*jk*]carbazole **15c** could not be purified sufficiently. CSA = camphorsulfonic acid; EDDA = ethylenediamine diacetate.

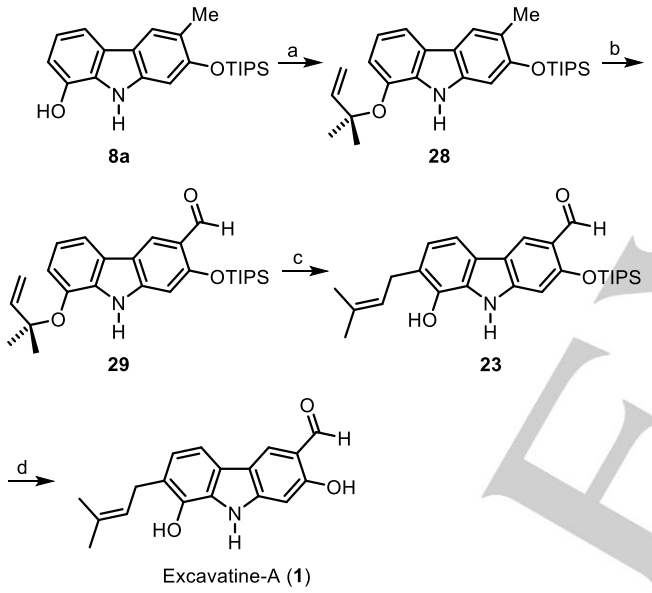
If the reaction was performed in the absence of propionic acid, an almost equimolar mixture of **6b** and **15b** was obtained (Table 2). Much more interesting was the observation that leaving out the Lewis acidic phenylboronic acid led to selective formation of the [1,4]oxazepino[2,3,4-*jk*]carbazole **15b**. The yield of **15b** could be improved by using camphorsulfonic acid (CSA) instead of propionic acid and the [1,4]oxazepino[2,3,4-*jk*]carbazolecarbonitrile **15b** was obtained in 62% yield after a reaction time of only 1 h. A combination of CSA and phenylboronic acid led only to decomposition. Using ethylenediamine diacetate (EDDA)[16] or titanium tetraisopropoxide as activating agents for prenal (**7**) provided selectively **6b** in low yields without any detectable formation of **15b**. Finally, the [1,4]oxazepino[2,3,4-*jk*]carbazole **15b** was treated with catalytic amounts of phenylboronic acid and an excess of propionic acid in order to induce the rearrangement into **6b**. Water was added to compensate for the water which would be generated by the initial condensation of **8b** and **7** (compare the proposed mechanism, Scheme 4, path a). From this reaction, the pyrano[2,3-*a*]carbazole **6b** was isolated in 32% yield along with 20% of starting material. This result demonstrates that the [1,4]oxazepino[2,3,4-*jk*]carbazoles **15** are formed in a reversible process and that rearrangement into the pyrano[2,3-*a*]carbazoles **6** takes place. The reactivity of the methyl carbazole-3-carboxylate **8c** is almost equivalent to the carbazole-3-carbonitrile **8b**. Reaction of **8c** with prenal (**7**) in the presence of phenylboronic acid and propionic acid provided after 23 h the pyrano[2,3-*a*]carbazole **6c** as main product, whereas the reaction of **8c** and **7** in the presence of CSA afforded selectively the [1,4]oxazepino[2,3,4-*jk*]carbazole **15c**.



Scheme 5. DIBAL-H-promoted reductive pyran ring opening of the pyrano[2,3-*a*]carbazoles **6a–c**. *Reagents and conditions*: (a) DIBAL-H (4.0 equiv), $SiCl_4$ (4.0 equiv), toluene, −78 °C to RT, 110 min (72%); (b) TIPSCl (1.3 equiv), DBU (2.4 equiv), CH_2Cl_2, RT, 1 h (94%); (c) TBAF (1.5 equiv), THF, 0 °C, 10 min (89%).

The pyrano[2,3-*a*]carbazoles **6a–c** were then subjected to our DIBAL-H-promoted pyran ring opening (Scheme 5). First, we have treated the cyanopyrano[2,3-*a*]carbazole **6b** and the 3-methoxycarbonylpyrano[2,3-*a*]carbazole **6c** with DIBAL-H since we expected a simultaneous reduction of the cyano and the methoxycarbonyl group at C-3 to the required formyl group. However, this reaction led to inseparable mixtures of compounds from which pure **23** could not be isolated. On the

other hand, treatment of the methylpyrano[2,3-*a*]carbazole **6a** with 4 equivalents of DIBAL-H and silicon tetrachloride in toluene at low temperatures provided the desired prenylcarbazole **24** in 72% yield. Treatment of **24** with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) under a variety of conditions led to either decomposition or no conversion. Thus, the formylcarbazole **23** was inaccessible by this approach. An initial silyl protection of the free hydroxy group at C-8 of compound **24** and subsequent oxidation of the fully protected carbazole **25** did also not afford the corresponding formylcarbazole **26**. In the course of our synthesis of 7-methoxymukonal, we already observed that oxidation of a methyl to a formyl group in *ortho* position to a bulky protecting group is difficult.[14b] Therefore, the silyl ether of compound **24** was cleaved to provide the 1,7-dihydroxycarbazole **27**. However, oxidation of **27** to afford excavatine-A (**1**) was not possible.



Scheme 6. Total synthesis of excavatine-A (**1**) *via* Tsuji-Trost type prenylation. *Reagents and conditions*: a) 1,1-dimethylallyl methyl carbonate (3.0 equiv), $Pd(PPh_3)_4$ (1 mol%), THF, RT, 1 h; (b) DDQ (3.1 equiv), MeOH/THF/water (16:6:1), RT, 1 h; (c) toluene, reflux, 2.5 h (57%, 3 steps); (d) TBAF (1.3 equiv), THF, 0 °C, 5 min (94%).

Since the pyrano[2,3-*a*]carbazoles **6a–c** could not be converted into excavatine-A (**1**), we devised an alternative approach by introduction of the prenyl side chain at the 8-hydroxycarbazole **8a** via O-allylation and subsequent Claisen rearrangement (Scheme 6).[17] Palladium(0)-catalyzed coupling of **8a** and 1,1-dimethylallyl methyl carbonate provided the required *tert*-prenyl ether **28**. The methyl group at C-3 was then oxidized to the corresponding carbaldehyde **29**, thus avoiding treatment of an electron-rich hydroxycarbazole with an oxidant. The carbazole-3-carbaldehyde **29** was then heated in toluene at reflux which induced the Claisen rearrangement to the silyl-protected excavatine-A **23**. Finally, the silyl group was removed by treatment with TBAF to provide excavatine-A (**1**) in 7 steps and 38% overall yield. The spectroscopic data of our synthetic compound **1** are in excellent agreement with those reported for the natural product.

Conclusions

The 8-hydroxycarbazoles **8a–c** with either a methyl, a cyano, or a methoxycarbonyl substituent at C-3 have been synthesized via palladium(II)-catalyzed oxidative cyclization of the corresponding diarylamines. Reaction of the 8-hydroxycarbazoles **8a–c** and prenal (**7**) in the presence of propionic acid and catalytic amounts of phenylboronic acid provided the pyrano[2,3-*a*]carbazoles **6a–c**. The course of the pyran annulation was investigated and the [1,4]oxazepino[2,3,4-*jk*]carbazoles **15a–c** were identified as kinetic intermediates of this process. Ultimatively, rearrangement of **15a–c** leads to the pyrano[2,3-*a*]carbazoles **6a–c** as the thermodynamically more stable products. In the presence of camphorsulfonic acid, the annulation with prenal (**7**) afforded the [1,4]oxazepino[2,3,4-*jk*]carbazoles **15b** and **15c** as major products. Finally, the first total synthesis of the carbazole alkaloid excavatine-A (**1**) was achieved via a Claisen rearrangement of the *tert*-prenylcarbazole **29**. Our synthetic route provided excavatine-A (**1**) in 7 steps and 38% yield.

Experimental Section

All reactions were carried out in oven-dried glassware using anhydrous solvents under an argon atmosphere, unless stated otherwise. CH_2Cl_2, THF, and toluene were dried using a solvent purification system (MBraun-SPS). $Pd(OAc)_2$ was recrystallized from glacial AcOH. All other chemicals were used as received from commercial sources. A CEM Discover microwave reactor was utilized for reactions taking place under microwave irradiation. Flash chromatography was performed using silica gel from Acros Organics (0.035–0.070 mm). TLC was performed with TLC plates from Merck (60 F254) using UV light for visualization. Melting points were measured on a Gallenkamp MPD 350 melting point apparatus. Ultraviolet spectra were recorded on a PerkinElmer 25 UV/Vis spectrometer. Fluorescence spectra were obtained using a Varian Cary Eclipse spectrometer. IR spectra were recorded on a Thermo Nicolet Avatar 360 FT-IR spectrometer using the ATR method (Attenuated Total Reflectance). NMR spectra were recorded on Bruker AC 300, DRX 500 and Avance III 600 spectrometers. Chemical shifts δ are reported in parts per million with the solvent signal as internal standard. Standard abbreviations were used to denote the multiplicities of the signals. Mass spectra were recorded on a Finnigan MAT-95 spectrometer (electron impact, 70 eV) or by GC/MS-coupling using an Agilent Technologies 6890 N GC System equipped with a 5973 Mass Selective Detector (electron impact, 70 eV). ESI-MS spectra were recorded on an Esquire LC with an ion trap detector from Bruker. Positive and negative ions were detected. Elemental analyses were measured on an EuroVector EuroEA3000 elemental analyzer. X-ray crystal structure analyses were performed with a Bruker-Nonius Kappa CCD that was equipped with a 700 series Cryostream low temperature device from Oxford Cryosystems. SHELXS-97,[18] SADABS version 2.10,[19] SHELXL-97,[20] POV-Ray for Windows version 3.7.0.msvc10.win64, and ORTEP-3 for Windows[21] were used as software.

***N*-(2-Benzyloxyphenyl)-4-methyl-3-(triisopropylsilyloxy)aniline (9a):** A solution of bromobenzene **10**[5a] (4.36 g, 16.6 mmol) in toluene (20 mL) was added dropwise over a period of 1 h to a solution of cesium carbonate (6.48 g, 19.9 mmol), aniline **11a**[11e] (5.56 g, 19.9 mmol), SPhos (816 mg, 1.99 mmol), and palladium(II) acetate (223 mg, 0.993 mmol) in toluene (80 mL) at reflux. The reaction mixture was heated at reflux for additional 3 h (total reaction time: 4 h). After cooling to room temperature, the mixture was filtered over a short pad of Celite® (ethyl acetate) and the solvent was evaporated. Purification of the residue by column chromatography (silica gel, isohexane/ethyl acetate, 30:1) gave diarylamine **9a** (7.31 g, 15.8 mmol, 95%) as red oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.10 (d, J = 7.4 Hz, 18 H), 1.22–1.32 (m, 3 H), 2.19 (s, 3 H), 5.13 (s, 2 H), 6.65 (dd, J = 8.0, 2.1 Hz, 1 H), 6.68 (d, J = 2.1 Hz, 1 H), 6.81 (dt, J = 1.6, 7.7 Hz, 1 H), 6.87 (dt, J = 1.5, 7.7 Hz, 1 H), 6.94 (dd, J = 7.9, 1.4 Hz, 1 H), 7.02 (d, J = 8.0 Hz, 1 H), 7.26–7.27 (m, 1 H), 7.32–7.36 (m, 1 H), 7.38–7.41 (m, 2 H), 7.44–7.46 ppm (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.98 (3 CH), 16.44 (CH_3), 18.04 (6 CH_3), 70.76 (CH_2), 110.03 (CH), 112.24 (CH), 112.67 (CH), 114.54 (CH), 119.53 (CH), 121.24 (CH), 122.39 (C), 127.58 (2 CH), 128.09 (CH), 128.62 (2 CH), 131.10 (CH), 133.88 (C), 136.90 (C), 140.73 (C), 147.17 (C), 154.74 ppm (C); IR (ATR): ν = 3424, 3061, 3028, 2943, 2865, 1596, 1558, 1502, 1456, 1408, 1339, 1265, 1242, 1207, 1174, 1125, 1003, 918, 879, 834, 807, 736, 680 cm^{-1}; UV (MeOH): λ = 278, 309 (sh) nm; MS (EI): *m/z* (%) = 461 (100) $[M]^+$, 418 (40), 142 (11), 91 (14); elemental analysis calcd for $C_{29}H_{39}NO_2Si$: C 75.44, H 8.51, N 3.03; found: C 75.05, H 8.70, N 3.22.

1-Benzyloxy-6-methyl-7-(triisopropylsilyloxy)carbazole (12a): A 80 mL microwave tube was charged with diarylamine **9a** (1.00 g, 2.17 mmol), palladium(II) acetate (73 mg, 0.325 mmol), copper(II) acetate (984 mg, 5.41 mmol), and acetic acid (10 mL) under air. The tube was irradiated in the microwave reactor at 130 °C and 300 W for 75 min. The mixture was cooled to room temperature, diluted with diethyl ether, and washed with saturated aqueous potassium carbonate. The aqueous layer was extracted with diethyl ether, the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated. Purification of the residue by column chromatography (silica gel, isohexane/ethyl acetate, 30:1) provided the benzyloxycarbazole **12a** (812 mg, 1.77 mmol, 82%) as light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.14 (d, J = 7.5 Hz, 18 H), 1.30–1.40 (m, 3 H), 2.39 (s, 3 H), 5.23 (s, 2 H), 6.86 (s, 1 H), 6.89 (d, J = 7.7 Hz, 1 H), 7.09 (t, J = 7.8 Hz, 1 H), 7.35–7.39 (m, 1 H), 7.40–7.44 (m, 2 H), 7.50–7.52 (m, 2 H), 7.57 (d, J = 7.8 Hz, 1 H), 7.76 (s, 1 H), 8.07 ppm (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.08 (3 CH), 17.61 (CH_3), 18.10 (6 CH_3), 70.33 (CH_2), 99.90 (CH), 105.94 (CH), 112.37 (CH), 117.39 (C), 119.46 (CH), 121.37 (C), 121.65 (CH), 124.67 (C), 127.85 (2 CH), 128.11 (CH), 128.59 (2 CH), 129.72 (C), 137.08 (C), 138.74 (C), 144.66 (C), 153.57 ppm (C); IR (ATR): ν = 3425, 3061, 3031, 2943, 2865, 1724, 1631, 1580, 1506, 1467, 1435, 1377, 1344, 1323, 1300, 1265, 1227, 1173, 1153, 1078, 1013, 989, 911, 880, 847, 804, 778, 725, 685, 628 cm^{-1}; UV (MeOH): λ = 212, 241, 253, 261 (sh), 300, 321, 334 nm; fluorescence (MeOH): λ_{ex} = 300 nm, λ_{em} = 346, 359 nm. MS (ESI, +10 V): *m/z* = 460.5 $[M+H]^+$; MS (ESI, −75 V): *m/z* = 458.0 $[M-H]^-$; elemental analysis calcd for $C_{29}H_{37}NO_2Si$: C 75.77, H 8.11, N 3.05; found: C 75.65, H 8.39, N 2.80.

1-Hydroxy-6-methyl-7-(triisopropylsilyloxy)carbazole (8a): A mixture of the benzyloxycarbazole **12a** (1.93 g, 4.20 mmol) and 10% Pd/C (386 mg) in methanol (15 mL) and dichloromethane (15 mL) was stirred at room temperature for 23.5 h under a hydrogen atmosphere. The mixture was filtered over Celite® (ethyl acetate) and the solvent was evaporated. Purification by column chromatography (silica gel, isohexane/ethyl acetate, 9:1) provided the 8-hydroxycarbazole **8a** (1.41 g, 3.82 mmol, 91%) as colorless solid. M.p. 77–80 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.15 (d, J = 7.5 Hz, 18 H), 1.32–1.41 (m, 3 H), 2.39 (s, 3 H), 4.93 (br s, 1 H), 6.73 (d, J = 7.6 Hz, 1 H), 6.87 (s, 1 H), 7.01 (t, J = 7.7 Hz, 1 H), 7.54 (d, J = 7.8 Hz, 1 H), 7.76 (s, 1 H), 8.00 ppm (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.09 (3 CH), 17.60 (CH_3), 18.09 (6 CH_3), 99.94 (CH), 109.38 (CH), 112.36 (CH), 117.34 (C), 119.48 (CH), 121.47 (C), 121.70 (CH), 125.54 (C), 128.71 (C), 139.00 (C), 140.80 (C), 153.73 ppm (C); IR (ATR): ν = 3417, 3063, 2943, 2891, 2866, 2031, 1630, 1582, 1554, 1505, 1469, 1438, 1388, 1341, 1268, 1230, 1172, 1153, 1062, 998, 933, 881, 846, 782, 736, 687, 658, 630 cm^{-1}; UV (MeOH): λ = 235, 242, 253 (sh), 300, 323, 335 nm; fluorescence (MeOH): λ_{ex} = 300 nm, λ_{em} = 366 nm; MS (EI): *m/z* (%): 369 (99) $[M]^+$, 326 (100), 298 (29), 284 (19), 270 (15), 256 (14), 254 (16), 224 (24), 212 (21), 211 (14), 196 (19), 183 (12), 167 (15), 59 (19); elemental analysis calcd for $C_{22}H_{31}NO_2Si$: C 71.50, H 8.46, N 3.79; found: C 71.46, H 8.70, N 3.56.

4-Amino-2-(triisopropylsilyloxy)benzonitrile (11b): TIPSCl (3.7 mL, 17 mmol) was added to a solution of 2-hydroxy-4-nitrobenzonitrile (2.20 g, 13.4 mmol) and imidazole (2.74 g, 40.2 mmol) in 1,2-dichloroethane (50 mL) and the reaction mixture was stirred for 3 h at room temperature. The mixture was transferred to a separation funnel (dichloromethane) and washed with water. The aqueous layer was extracted with dichloromethane and the combined organic layers were dried ($MgSO_4$). The solvent was evaporated and the crude intermediate was dissolved in acetic acid (150 mL). Iron powder (7.49 g, 134 mmol) was added and the suspension was heated at 40 °C and 600 mbar for 1 h in the rotary evaporator. The suspension was filtered over Celite® (ethyl acetate), the solvent was evaporated and the residue was taken up in ethyl acetate. The organic solution was washed with saturated aqueous potassium carbonate. The aqueous layer was extracted with ethyl acetate. The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. Purification of the residue by column chromatography (silica gel, isohexane/ethyl acetate, 5:1) provided the cyanoaniline **11b** (3.47 g, 11.9 mmol, 89%) as bright yellow solid. M.p. 61 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.14 (d, J = 7.5 Hz, 18 H), 1.27–1.37 (m, 3 H), 4.04 (br s, 2 H), 6.11 (d, J = 2.1 Hz, 1 H), 6.23 (dd, J = 8.4, 2.1 Hz, 1 H), 7.26 ppm (d, J = 8.4 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.86 (3 CH), 17.88 (6 CH_3), 93.88 (C), 104.42 (CH), 108.01 (CH), 118.21 (C), 134.65 (CH), 151.72 (C), 159.93 ppm (C); IR (ATR): ν = 3474, 3365, 3235, 2945, 2867 2210, 1603, 1565, 1505, 1454, 1420, 1395, 1348, 1262, 1215, 1126, 1070, 986, 920, 881, 832, 683, 646, 606 cm^{-1}; MS (EI): *m/z* (%) = 247 (100) $[M-C_3H_7]^+$, 219 (20), 191 (35), 177 (14), 161 (20), 150 (17); elemental analysis calcd for $C_{16}H_{26}N_2OSi$: C 66.16, H 9.02, N 9.64; found: C 65.99, H 9.01, N 9.51.

4-(2-Benzyloxyphenyl)amino-2-(triisopropylsilyloxy)benzonitrile: A solution of bromobenzene **10**[5a] (800 mg, 3.04 mmol) in toluene (10 mL) was added dropwise over a period of 1 h to a solution of cesium carbonate (1.19 g, 3.65 mmol), cyanoaniline **11b** (1.06 g, 3.65 mmol), SPhos (150 mg, 0.365 mmol), and palladium(II) acetate (41.0 mg, 0.183 mmol) in toluene (22 mL) at reflux and the reaction mixture was heated at reflux for additional 3 h (total reaction time: 4 h). After cooling to room temperature, the mixture was filtered over a short pad of Celite® (ethyl acetate) and the solvent was evaporated. Purification of the residue by column chromatography (silica gel, isohexane/ethyl acetate, 10:1) gave 4-(2-benzyloxyphenyl)amino-2-(triisopropylsilyloxy)benzonitrile (1.34 g, 2.83 mmol, 93%) as colorless solid. M.p. 57–59 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.12 (d, J = 7.4 Hz, 18 H), 1.24–1.34 (m, 3 H), 5.11 (s, 2 H), 6.27 (br s, 1 H), 6.55–6.57 (m, 2 H), 6.93–6.96 (m, 1 H), 6.98–7.02 (m, 2 H), 7.32–7.39 ppm (m, 7 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.78 (3 CH), 17.86 (6 CH_3), 70.89 (CH_2), 95.10 (C), 105.13 (CH), 109.61 (CH), 113.00 (CH), 118.03 (C), 119.09 (CH), 121.09 (CH), 123.10 (CH), 127.49 (2 CH), 128.27 (CH), 128.69 (2 CH), 130.22 (C), 134.35 (CH), 136.45 (C), 148.89 (C), 149.23 (C), 159.82 ppm (C); IR (ATR): ν = 3402, 3335, 2944, 2866, 2214, 1612, 1589, 1499, 1455, 1421, 1346, 1298, 1248, 1213, 1118, 994, 919, 879, 831, 808, 742, 685, 616 cm^{-1}; UV (MeOH): λ = 236 (sh), 291 (sh), 309 nm; MS (ESI, +25 V): *m/z* = 473.5 $[M+H]^+$; elemental

analysis calcd for $C_{29}H_{36}N_2O_2Si$: C 73.69, H 7.68, N 5.93; found: C 73.37, H 7.66, N 5.68.

8-Benzyloxy-2-(triisopropylsilyloxy)carbazole-3-carbonitrile: A mixture of 4-(2-benzyloxyphenyl)amino-2-(triisopropylsilyloxy)benzonitrile (500 mg, 1.06 mmol), palladium(II) acetate (71.2 mg, 0.317 mmol), potassium carbonate (43.8 mg, 0.317 mmol), and pivalic acid (4.5 g) was heated for 2 h at 130 °C under air. The mixture was allowed to cool to room temperature, diluted with diethyl ether, and washed with saturated aqueous potassium carbonate. The aqueous layer was extracted with diethyl ether, the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated. Purification of the residue by column chromatography (silica gel, isohexane/ethyl acetate, 20:1) provided the title carbazolecarbonitrile (372 mg, 0.790 mmol, 75%) as colorless solid. M.p. 84 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.16 (d, J = 7.5 Hz, 18 H), 1.34–1.41 (m, 3 H), 5.23 (s, 2 H), 6.90 (s, 1 H), 6.98 (d, J = 7.9 Hz, 1 H), 7.18 (t, J = 7.9 Hz, 1 H), 7.37–7.44 (m, 3 H), 7.48 (m, 2 H), 7.58 (d, J = 7.8 Hz, 1 H), 8.19 (s, 1 H), 8.38 ppm (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.90 (3 CH), 17.93 (6 CH_3), 70.55 (CH_2), 97.40 (C), 100.64 (CH), 107.60 (CH), 112.64 (CH), 118.11 (C), 118.43 (C), 121.17 (CH), 123.67 (C), 126.38 (CH), 127.95 (2 CH), 128.36 (CH), 128.69 (2 CH), 130.28 (C), 136.57 (C), 142.59 (C), 144.73 (C), 156.66 ppm (C); IR (ATR): ν = 3313, 2944, 2866, 2218, 2030, 2009, 1977, 1633, 1612, 1582, 1509, 1484, 1461, 1390, 1358, 1307, 1274, 1230, 1179, 1155, 1074, 997, 922, 882, 831, 781, 732, 685, 643, 616 cm^{-1}; UV (MeOH): λ = 233, 266, 277 (sh), 327 nm; fluorescence (MeOH): λ_{ex} = 266 nm; λ_{em} = 403 nm; MS (ESI, +25 V): m/z = 471.4 $[M+H]^+$, 958.8 $[2M+NH_4]^+$; elemental analysis calcd for $C_{29}H_{34}N_2O_2Si$: C, 74.00, H 7.28, N 5.95; found: C 74.33, H 7.37, N 5.98.

8-Hydroxy-2-(triisopropylsilyloxy)carbazole-3-carbonitrile (8b): A suspension of 8-benzyloxy-2-(triisopropylsilyloxy)carbazole-3-carbonitrile (203 mg, 0.431 mmol) and 10% Pd/C (20.3 mg) in methanol (15 mL) and dichloromethane (15 mL) was stirred for 24 h at room temperature under a hydrogen atmosphere. The mixture was filtered over Celite® (ethyl acetate) and the solvent was evaporated. Purification of the residue by column chromatography (silica gel, isohexane/ethyl acetate, 5:1) provided the 8-hydroxycarbazole **8b** (152 mg, 0.399 mmol, 93%) as colorless solid. M.p. 209 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.17 (d, J = 7.5 Hz, 18 H), 1.35–1.43 (m, 3 H), 5.46 (s, 1 H), 6.85 (dd, J = 7.6, 0.4 Hz, 1 H), 6.91 (s, 1 H), 7.10 (t, J = 7.8 Hz, 1 H), 7.55 (d, J = 7.9 Hz, 1 H), 8.18 (s, 1 H), 8.39 ppm (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.91 (3 CH), 17.94 (6 CH_3), 97.22 (C), 100.66 (CH), 111.15 (CH), 112.57 (CH), 118.12 (C), 118.49 (C), 121.17 (CH), 124.41 (C), 126.40 (CH), 129.30 (C), 141.17 (C), 142.90 (C), 156.81 ppm (C); IR (ATR): ν = 3316, 2944, 2866, 2223, 1620, 1585, 1507, 1486, 1463, 1392, 1356, 1314, 1283, 1232, 1180, 1152, 1058, 1014, 995, 937, 881, 831, 784, 732, 686, 636 cm^{-1}; UV (MeOH): λ = 234, 267, 279 (sh), 333 nm; fluorescence (MeOH): λ_{ex} = 267 nm; λ_{em} = 413 nm; MS (ESI, +25 V): m/z = 381.3 $[M+H]^+$, 778.6 $[2M+NH_4]^+$; elemental analysis calcd for $C_{22}H_{28}N_2O_2Si$: C 69.43, H 7.42, N: 7.36; found: C 69.56, H 7.58, N 7.24.

1-Benzyloxy-2-nitrobenzene: Benzyl bromide (6.4 mL, 54 mmol) was added over a period of 20 min to a refluxing solution of 2-nitrophenol (5.00 g, 35.9 mmol) and potassium carbonate (7.45 g, 53.9 mmol) in acetone (100 mL) and the mixture was heated at reflux for 40 min (total reaction time: 1 h). The mixture was cooled to room temperature, transferred to a separation funnel (dichloromethane), and washed with water. The aqueous layer was extracted with dichloromethane, the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated. Purification of the residue by column chromatography (silica gel, isohexane/ethyl acetate, 15:1) afforded 1-benzyloxy-2-nitrobenzene (7.82 g, 34.1 mmol, 95%) as bright yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.24 (s, 2 H), 7.04 (ddd, J = 8.2, 7.4, 0.8 Hz, 1 H), 7.12 (dd, J = 8.3, 0.8 Hz, 1 H), 7.32–7.35 (m, 1 H), 7.38–7.41 (m, 2 H), 7.46 (m, 2 H), 7.50 (ddd, J = 8.3, 7.4, 1.7 Hz, 1 H), 7.86 ppm (dd, J = 8.2, 1.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 71.07 (CH_2), 115.06 (CH), 120.60 (CH), 125.66 (CH), 126.92 (2 CH), 128.19 (CH), 128.68 (2 CH), 134.00 (CH), 135.53 (C), 140.21 (C), 151.86 ppm (C); IR (ATR): ν = 3064, 3034, 2873, 1606, 1579, 1559, 1520, 1453, 1347, 1276, 1253, 1164, 1089, 996, 913, 858, 771, 739, 695, 671, 660, 619 cm^{-1}; MS (ESI, +10 V): m/z = 247.1 $[M+NH_4]^+$, 252.0 $[M+Na]^+$, 480.7 $[2M+Na]^+$; elemental analysis calcd for $C_{13}H_{11}NO_3$: C 68.11, H 4.84, N 6.11; found: C 68.46, H 5.04, N: 6.33.

2-Benzyloxyaniline (13): Iron powder (19.0 g, 340 mmol) was added to a solution of 1-benzyloxy-2-nitrobenzene (7.82 g, 34.1 mmol) in acetic acid (200 mL) and the suspension was heated for 3 h 30 min at 40 °C and 600 mbar using a rotary evaporator. The mixture was filtered (Celite® ethyl acetate) and the solvent was evaporated. The residue was taken up in diethyl ether and the solution was washed with saturated aqueous potassium carbonate. The aqueous layer was extracted with diethyl ether the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated. Purification of the residue by column chromatography (silica gel, isohexane/ethyl acetate, 4:1) provided the arylamine **13** (6.19 g, 31.1 mmol, 91%) as pale pink solid. M.p. 37–38 °C (lit.: 39–40 °C)[22]; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.08 (br s, 2 H), 5.10 (s, 2 H), 6.72–6.76 (m, 1 H), 6.78–6.85 (m, 2 H), 6.88 (dd, J = 8.0, 1.0 Hz, 1 H), 7.32–7.35 (m, 1 H), 7.38–7.41 (m, 2 H), 7.45 ppm (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 70.35 (CH_2), 112.03 (CH), 115.19 (CH), 118.38 (CH), 121.45 (CH), 127.54 (2 CH), 127.95 (CH), 128.53 (2 CH), 136.43 (C), 137.16 (C), 146.43 ppm (C); IR (ATR): ν = 3468, 3378, 3058, 3032, 2880, 1609, 1559, 1542, 1501, 1475, 1454, 1388, 1340, 1277, 1210, 1140, 1080, 1035, 1011, 912, 856, 776, 743, 724, 694, 653, 619 cm^{-1}; MS (EI): m/z (%) = 199 (64) $[M]^+$, 108 (83), 91 (100), 80 (34), 65 (15); MS (ESI, +25 V): m/z = 200.1 $[M+H]^+$.

Methyl 4-bromo-2-hydroxybenzoate: Boron tribromide (1 M in CH_2Cl_2, 18.3 mL, 18.3 mmol) was added at −78 °C to a solution of methyl 4-bromo-2-methoxybenzoate (2.05 g, 8.36 mmol) in dichloromethane (100 mL) and the solution was stirred at −78 °C for 5 min and at 0 °C for 10 min. The reaction was quenched with iced water and the layers were separated. The organic layer was washed with water and the combined aqueous layers were extracted with dichloromethane. The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated to provide methyl 4-bromo-2-hydroxybenzoate (1.95 g, 8.44 mmol, 100%) as colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.95 (s, 3 H), 7.02 (dd, J = 8.5, 1.8 Hz, 1 H), 7.18 (d, J = 1.8 Hz, 1 H), 7.68 (d, J = 8.5 Hz, 1 H), 10.83 ppm (s, 1 H).

Methyl 4-bromo-2-(triisopropylsilyloxy)benzoate (14): DBU (0.19 mL, 1.3 mmol) and TIPSCl (0.14 mL, 0.65 mmol) were added sequentially to a solution of methyl 4-bromo-2-hydroxybenzoate (100 mg, 0.433 mmol) in dichloromethane (4 mL) and the mixture was stirred at room temperature for 1 h. The mixture was transferred to a separation funnel (dichloromethane) and washed with a saturated aqueous solution of ammonium chloride. The aqueous layer was extracted with dichloromethane, the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated. Purification of the residue by column chromatography (silica gel, isohexane/ethyl acetate, 30:1) afforded the silyl ether **14** (162 mg, 0.418 mmol, 97%) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.11 (d, J = 7.4 Hz, 18 H), 1.27–1.36 (m, 3 H), 3.85 (s, 3 H), 7.02 (d, J = 1.8 Hz, 1 H), 7.09 (dd, J = 8.4, 1.8 Hz, 1 H), 7.62 ppm (d, J = 8.4 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.00 (3 CH), 17.84 (6 CH_3), 51.93 (CH_3), 121.41 (C), 123.53 (CH), 123.76 (CH), 126.58 (C), 132.74 (CH), 156.25 (C), 166.68 ppm (C=O); IR (ATR): ν = 2946, 2892, 2867, 1735, 1713, 1585, 1554, 1516, 1476, 1435, 1402, 1281, 1226, 1189, 1132, 1088, 1015, 997, 932, 883, 857, 820, 771, 756, 686, 666 cm^{-1}; MS (EI): m/z (%) = 343/345 (100/100) $[M-C_3H_7]^+$, 259/257 (20/14),

245/243 (11/11), 89 (21), 75 (16), 59 (18); elemental analysis calcd for $C_{17}H_{27}BrO_3Si$: C 52.71, H 7.03; found: C 52.91, H 7.23.

Methyl 4-((2-benzyloxyphenyl)amino)-2-(triisopropylsilyloxy)benzoate: A solution of bromoarene **14** (250 mg, 0.645 mmol) in toluene (5 mL) was added dropwise over a period of 1 h to a refluxing solution of cesium carbonate (252 mg, 0.773 mmol), benzyloxyaniline **13** (154 mg, 0.773 mmol), XPhos (36.9 mg, 77.4 µmol), and palladium(II) acetate (8.7 mg, 38.8 µmol) in toluene (5 mL) and the mixture was heated at reflux for 3 h (total reaction time: 4 h). After cooling to room temperature, the mixture was filtered over a short pad of Celite® (ethyl acetate) and the solvent was evaporated. Purification of the residue by column chromatography (silica gel, isohexane/ethyl acetate, 10:1) gave methyl 4-((2-benzyloxyphenyl)amino)-2-(triisopropylsilyloxy)benzoate (320 mg, 0.633 mmol, 98%) as bright red oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.10 (d, J = 7.5 Hz, 18 H), 1.23–1.31 (m, 3 H), 3.82 (s, 3 H), 5.12 (s, 2 H), 6.57–6.60 (m, 2 H), 6.93–6.96 (m, 2 H), 6.98–7.00 (m, 1 H), 7.34–7.41 (m, 6 H), 7.75 ppm (d, J = 9.2 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.10 (3 CH), 17.92 (6 CH_3), 51.36 (CH_3), 70.86 (CH_2), 106.82 (CH), 109.47 (CH), 112.79 (CH), 113.39 (C), 117.98 (CH), 121.10 (CH), 122.00 (CH), 127.50 (2 CH), 128.19 (CH), 128.67 (2 CH), 131.16 (C), 133.63 (CH), 136.62 (C), 148.06 (C), 148.65 (C), 157.71 (C), 166.92 ppm (C=O); IR (ATR): ν = 3412, 3342, 2945, 2889, 2866, 1720, 1697, 1653, 1613, 1590, 1512, 1500, 1455, 1433, 1415, 1347, 1277, 1252, 1211, 1140, 1115, 1086, 1001, 967, 919, 879, 826, 772, 742, 693 cm^{-1}; UV (MeOH): λ = 244 (sh), 290 (sh), 316 nm. MS (ESI, +10 V): m/z = 506.6 [M+H]$^+$, 1032.8 [2M+Na]$^+$; elemental analysis calcd for $C_{30}H_{39}NO_4Si$: C 71.25, H 7.77, N 2.77; found: C 70.98, H 7.73, N: 2.99.

8-Benzyloxy-3-methoxycarbonyl-2-(triisopropylsilyloxy)carbazole: A mixture of methyl 4-((2-benzyloxyphenyl)amino)-2-(triisopropylsilyloxy)benzoate (1.48 g, 2.93 mmol), palladium(II) acetate (197 mg, 0.877 mmol), potassium carbonate (121 mg, 0,876 mmol), and pivalic acid (18.8 g) was heated at 130 °C under air for 2.5 h. The mixture was allowed to cool to room temperature, diluted with diethyl ether, and washed with a saturated aqueous solution of potassium carbonate. The aqueous layer was extracted with diethyl ether, the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated. Purification of the residue by column chromatography (silica gel, isohexane/ethyl acetate, 15:1) provided 8-benzyloxy-3-methoxycarbonyl-2-(triisopropylsilyloxy)carbazole (851 mg, 1.69 mmol, 58%) as bright yellow solid. M.p. 55–58 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.13 (d, J = 7.5 Hz, 18 H), 1.31–1.40 (m, 3 H), 3.91 (s, 3 H), 5.23 (s, 2 H), 6.86 (s, 1 H), 6.95 (d, J = 7.9 Hz, 1 H), 7.15 (t, J = 7.9 Hz, 1 H), 7.36–7.45 (m, 3 H), 7.51 (m, 2 H), 7.61 (d, J = 7.9 Hz, 1 H), 8.26 (br s, 1 H), 8.52 ppm (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.17 (3 CH), 17.97 (6 CH_3), 51.71 (CH_3), 70.46 (CH_2), 101.37 (CH), 107.08 (CH), 112.76 (CH), 115.36 (C), 117.62 (C), 120.61 (CH), 124.68 (C), 124.88 (CH), 127.91 (2 CH), 128.25 (CH), 128.64 (2 CH), 130.24 (C), 136.76 (C), 142.52 (C), 144.69 (C), 154.96 (C), 167.91 ppm (C); IR (ATR): ν = 3349, 2944, 2889, 2865, 2056, 2030, 2007, 1705, 1677, 1633, 1581, 1476, 1458, 1433, 1387, 1355, 1312, 1221, 1180, 1106, 1066, 999, 972, 907, 881, 843, 778, 755, 737, 687, 648 cm^{-1}; UV (MeOH): λ = 236, 247 (sh), 268, 280 (sh), 323, 336 (sh) nm; fluorescence (MeOH): λ_{ex} = 268 nm, λ_{em} = 429 nm; MS (ESI, +10 V): m/z = 504.6 [M+H]$^+$; elemental analysis calcd for $C_{30}H_{37}NO_4Si$: C 71.53, H 7.40, N 2.78; found: C 71.24, H 7.47, N 2.71.

Methyl 8-hydroxy-2-(triisopropylsilyloxy)carbazole-3-carboxylate (8c): A mixture of 8-benzyloxy-3-methoxycarbonyl-2-(triisopropylsilyloxy)carbazole (850 mg, 1.69 mmol) and 10% Pd/C (85 mg) in methanol (25 mL) and dichloromethane (25 mL) was stirred at room temperature under a hydrogen atmosphere for 1.5 h. The mixture was filtered over Celite® (ethyl acetate) and the solvent was evaporated. Purification of the crude product by column chromatography (silica gel, isohexane/ethyl acetate, 5:1) provided the 8-hydroxycarbazole **8c** (644 mg, 1.56 mmol, 92%) as colorless solid. M.p. 180–181 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.13 (d, J = 7.5 Hz, 18 H), 1.32–1.38 (m, 3 H), 3.93 (s, 3 H), 5.57 (br s, 1 H), 6.81 (d, J = 7.4 Hz, 1 H), 6.86 (s, 1 H), 7.05 (t, J = 7.8 Hz, 1 H), 7.56 (d, J = 7.8 Hz, 1 H), 8.33 (br s, 1 H), 8.52 ppm (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.16 (3 CH), 17.95 (6 CH_3), 51.87 (CH_3), 101.37 (CH), 110.70 (CH), 112.63 (CH), 115.10 (C), 117.65 (C), 120.65 (CH), 124.92 (CH), 125.38 (C), 129.27 (C), 141.07 (C), 142.84 (C), 155.10 (C), 168.39 ppm (C); IR (ATR): ν = 3360, 3326, 2942, 2889, 2866, 1699, 1659, 1625, 1588, 1509, 1487, 1458, 1431, 1404, 1353, 1314, 1272, 1233, 1190, 1112, 1050, 976, 931, 881, 844, 825, 778, 756, 736, 683, 660, 644 cm^{-1}; UV (MeOH): λ = 236, 247 (sh), 269, 282 (sh), 325 nm; fluorescence (MeOH): λ_{ex} = 269 nm, λ_{em} = 451 nm; MS (EI): m/z (%) = 370 (100) [M−C_3H_7]$^+$; MS (ESI, +25 V): m/z = 414.4 [M+H]$^+$, 849.5 [2M+Na]$^+$; elemental analysis calcd for $C_{23}H_{31}NO_4Si$: C 66.79, H 7.56, N 3.39; found: C 66.90, H 7.70, N 3.34.

2,2,8-Trimethyl-9-triisopropylsilyloxy-2,11-dihydropyrano[2,3-*a*]carbazole (6a) and 5,5,11-Trimethyl-10-triisopropylsilyloxy-5*H*-[1,4]oxazepino[2,3,4-*jk*]carbazole (15a): Prenal (**7**) (0.42 mL, 4.3 mmol) was added to a solution of the 8-hydroxycarbazole **8a** (800 mg, 2.16 mmol), phenylboronic acid (53 mg, 0.43 mmol), and propionic acid (17.8 mL, 238 mmol) in toluene (40 mL) and the mixture was heated at reflux for 22 h. The solvent was evaporated, the residue was taken up in diethyl ether and washed with saturated aqueous potassium carbonate. The aqueous layer was extracted with diethyl ether, the combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. Purification of the crude product by column chromatography (silica gel, isohexane/ethyl acetate, 40:1) afforded the pyrano[2,3-*a*]carbazole **6a** (730 mg, 1.68 mmol, 77%) as yellow solid. M.p. 139 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.14 (d, J = 7.5 Hz, 18 H), 1.34 (m, 3 H), 1.49 (s, 6 H), 2.37 (s, 3 H), 5.56 (d, J = 9.8 Hz, 1 H), 6.47 (d, J = 9.8 Hz, 1 H), 6.83 (d, J = 7.9 Hz, 1 H), 6.84 (s, 1 H), 7.41 (d, J = 7.9 Hz, 1 H), 7.70 (s, 1 H), 7.95 ppm (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.09 (3 CH), 17.58 (CH_3), 18.10 (6 CH_3), 28.12 (2 CH_3), 76.60 (C), 99.89 (CH), 111.32 (CH), 116.18 (C), 117.54 (C), 117.96 (CH), 121.36 (C), 121.51 (CH), 123.19 (CH), 125.33 (C), 128.10 (CH), 128.73 (C), 137.91 (C), 139.45 (C), 153.64 ppm (C); IR (ATR): ν = 3474, 3425, 3355, 3035, 2942, 2865, 1733, 1697, 1626, 1574, 1557, 1468, 1425, 1397, 1363, 1296, 1262, 1242, 1212, 1171, 1145, 1122, 1073, 1030, 997, 953, 920, 883, 847, 830 802, 760, 721, 682, 641 cm^{-1}; UV (MeOH): λ = 231, 257, 289, 312, 325, 350, 365 nm; fluorescence (MeOH): λ_{ex} = 325 nm; λ_{em} = 365 nm; MS (EI): m/z (%) = 435 (60) [M]$^+$, 420 (100), 392 (13), 278 (11); elemental analysis calcd for $C_{27}H_{37}NO_2Si$: C 74.43, H 8.56, N: 3.21; found: C 74.78, H 8.59, N 3.05.

The [1,4]oxazepino[2,3,4-*jk*]carbazole **15a** could not be isolated in pure form. The ^{1}H NMR and ^{13}C NMR signals were assigned from the mixture of **6a** and **15a**. The mass spectrum was obtained by separation of **6a** and **15a** in a GC/MS apparatus: ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.17 (d, J = 7.5 Hz, 18 H), 1.33–1.41 (m, 3 H), 1.51 (s, 6 H), 2.40 (s, 3 H), 5.44 (d, J = 9.2 Hz, 1 H), 6.87 (s, 1 H), 6.95 (d, J = 9.3 Hz, 1 H), 6.99 (dd, J = 7.9, 0.7 Hz, 1 H), 7.15 (t, J = 7.7 Hz, 1 H), 7.60 (dd, J = 7.6, 0.8 Hz, 1 H), 7.76 ppm (s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.09 (3 CH), 17.48 (CH_3), 18.11 (6 CH_3), 29.46 (2 CH_3), 79.82 (C), 98.44 (CH), 113.13 (CH), 116.62 (CH), 116.89 (CH), 117.24 (C), 121.59 (CH), 121.79 (CH), 122.31 (CH), 122.96 (C), 126.31 (C), 130.45 (C), 138.22 (C), 143.32 (C), 153.99 ppm (C); MS (EI): m/z (%) = 435 (100) [M]$^+$, 420 (12), 392 (36).

8-Cyano-2,2-dimethyl-9-triisopropylsilyloxy-2,11-dihydropyrano[2,3-*a*]carbazole (6b): Prenal (**7**) (150 µL, 1.57 mmol) was added to a solution of the 8-hydroxycarbazole **8b** (300 mg, 0.788 mmol), phenylboronic acid (19 mg, 0.16 mmol), and propionic acid (6.5 mL, 87 mmol) in toluene (9.3 mL) and the mixture was heated at reflux for 4 h.

An additional portion of prenal (**7**) (150 µL, 1.57 mmol) was added and the mixture was heated at reflux for further 17 h. The mixture was transferred to a separatory funnel (ethyl acetate) and washed with saturated aqueous potassium carbonate. The aqueous layer was extracted with ethyl acetate, the combined organic layers were dried (Na_2SO_4), and the solvent was evaporated. Purification of the crude product by column chromatography (silica gel, isohexane/ethyl acetate, 20:1) afforded the less polar oxazepino[2,3,4-*jk*]carbazole **15b** (63 mg, 0.14 mmol, 18%) and as the more polar fraction pyrano[2,3-*a*]carbazolecarbonitrile **6b** (213 mg, 0.487 mmol, 62%) as orange solid. M.p. >210 °C (dec.); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.17 (d, J = 7.5 Hz, 18 H), 1.34–1.42 (m, 3 H), 1.50 (s, 6 H), 5.62 (d, J = 9.8 Hz, 1 H), 6.48 (d, J = 9.8 Hz, 1 H), 6.88 (s, 1 H), 6.91 (d, J = 7.9 Hz, 1 H), 7.43 (d, J = 7.9 Hz, 1 H), 8.12 (s, 1 H), 8.32 ppm (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.90 (3 CH), 17.93 (6 CH_3), 28.13 (2 CH_3), 77.06 (C), 97.26 (C), 100.56 (CH), 111.77 (CH), 117.81 (C), 118.25 (C), 118.45 (C), 119.38 (CH), 122.78 (CH), 124.12 (C), 126.05 (CH), 129.16 (CH), 129.19 (C), 138.00 (C), 143.27 (C), 156.71 ppm (C); IR (ATR): v = 3300, 3035, 2947, 2866, 2219, 1620, 1564, 1467, 1433, 1399, 1309, 1264, 1229, 1178, 1145, 1122, 1075, 1014, 961, 886, 840, 828, 803, 757, 685, 626 cm^{-1}; UV (MeOH): λ = 243, 268, 288, 328, 353, 368 nm; fluorescence (MeOH): λ_{ex} = 328 nm; λ_{em} = 402 nm; MS (EI): m/z (%) = 446 (26) $[M]^+$, 431 (27), 403 (100), 347 (12), 166 (18); elemental analysis calcd for $C_{27}H_{34}N_2O_2Si$: C 72.60, H 7.67, N 6.27; found: C 72.48, H 7.96, N 5.91.

5,5-Dimethyl-10-(triisopropylsilyloxy)-5*H*-[1,4]oxazepino[2,3,4-*jk*]carbazole-11-carbonitrile (15b): Prenal (**7**) (25 µL, 0.26 mmol) was added to a solution of the 8-hydroxycarbazole **8b** (50.0 mg, 0.131 mmol) and camphorsulfonic acid (6.1 mg, 26 µmol) in toluene (3 mL) and the mixture was heated at reflux for 1 h. The cooled reaction mixture was diluted with ethyl acetate and washed with saturated aqueous potassium carbonate. The aqueous layer was extracted twice with ethyl acetate, the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated. Purification of the residue by column chromatography (silica gel, isohexane/ethyl acetate, 20:1) provided the oxazepino[2,3,4-*jk*]carbazolecarbonitrile **15b** (36.1 mg, 80.8 µmol, 62%) as bright yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.19 (d, J = 7.5 Hz, 18 H), 1.39–1.45 (m, 3 H), 1.52 (s, 6 H), 5.58 (d, J = 9.4 Hz, 1 H), 6.902 (d, J = 9.4 Hz, 1 H), 6.903 (s, 1 H), 7.07 (dd, J = 7.9, 0.9 Hz, 1 H), 7.23 (t, J = 7.8 Hz, 1 H), 7.63 (dd, J = 7.8, 0.9 Hz, 1 H), 8.17 ppm (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.91 (3 CH), 17.95 (6 CH_3), 29.36 (2 CH_3), 79.90 (C), 98.71 (C), 99.35 (CH), 113.64 (CH), 117.95 (C), 118.04 (C), 118.39 (CH), 119.61 (CH), 121.47 (CH), 122.99 (CH), 125.02 (C), 126.06 (CH), 131.12 (C), 141.85 (C), 143.39 (C), 157.23 ppm (C); IR (ATR): v = 2944, 2889, 2866, 2222, 1736, 1658, 1623, 1498, 1459, 1431, 1397, 1366, 1299, 1221, 1165, 1150, 1066, 997, 960, 942, 907, 881, 811, 783, 737, 716, 685, 651 cm^{-1}; UV (MeOH): λ = 255, 266, 293, 349 (sh) nm; fluorescence (MeOH): λ_{ex} = 293 nm, λ_{em} = 396 nm; MS (EI): m/z (%) = 446 (25) $[M]^+$, 404 (48), 403 (100), 375 (14), 347 (14); elemental analysis calcd for $C_{27}H_{34}N_2O_2Si$: C 72.60, H 7.67, N 6.27; found: C 72.30, H 7.92, N 5.87.

10-Hydroxy-5,5-dimethyl-5*H*-[1,4]oxazepino[2,3,4-*jk*]carbazole-11-carbonitrile (16): TBAF (1 M in THF, 0.36 mL, 0.36 mmol) was added at 0 °C to a solution of silyloxycarbazole **15b** (132 mg, 0.296 mmol) in THF (6 mL) and the mixture was stirred at 0 °C for 20 min. Water and diethyl ether were added, the layers were separated, and the organic layer was washed with water. The aqueous layer was extracted twice with diethyl ether, the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated. Purification of the residue by column chromatography (silica gel, isohexane/ethyl acetate, 2:1) provided the hydroxy-5*H*-[1,4]oxazepino[2,3,4-*jk*]carbazole **16** (70.6 mg, 0.243 mmol, 82%) as bright yellow solid. M.p. >230 °C (dec.); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.43 (s, 6 H), 5.62 (d, J = 9.3 Hz, 1 H), 6.98 (dd, J = 7.7, 0.6 Hz, 1 H), 7.19 (s, 1 H), 7.21 (t, J = 7.7 Hz, 1 H), 7.28 (d, J = 9.4 Hz, 1 H), 7.80 (dd, J = 7.7, 0.6 Hz, 1 H), 8.51 (s, 1 H), 11.28 ppm (br s, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.95 (2 CH_3), 79.70 (C), 93.72 (C), 96.26 (CH), 113.93 (CH), 116.17 (C), 117.57 (CH), 117.85 (C), 119.02 (CH), 122.28 (CH), 122.73 (CH), 124.99 (C), 126.40 (CH), 130.27 (C), 141.95 (C), 142.77 (C), 159.18 ppm (C); IR (ATR): v = 3206, 3060, 2978, 2926, 2232, 1666, 1628, 1606, 1578, 1554, 1520, 1501, 1473, 1430, 1368, 1340, 1296, 1272, 1222, 1196, 1164, 1138, 1109, 1069, 1041, 959, 883, 828, 806, 774, 736, 717, 687, 642 cm^{-1}; UV (MeOH): λ = 221, 254, 266 (sh), 295, 330 nm; fluorescence (MeOH): λ_{ex} = 295 nm, λ_{em} = 397 nm; MS (ESI, +25 V): m/z = 291.1 $[M+H]^+$, 598.1 $[M+NH_4]^+$; elemental analysis calcd for $C_{18}H_{14}N_2O_2$: C 74.47, H 4.86, N 9.65; found: C 74.32, H 4.85, N 9.45.

Crystallographic data: $C_{18}H_{14}N_2O_2$, M = 290.31 g mol^{-1}. crystal size: 0.491 x 0.105 x 0.069 mm^3, orthorhombic, space group: $Pna2_1$, a = 9.3354(2) Å, b = 11.1168(2) Å, c = 27.9603(5) Å, V = 2901.71(10) Å^3, Z = 8, ρ_{calcd} = 1.329 g cm^{-3}, μ = 0.712 mm^{-1}, λ = 1.54178 Å, T = 198(2) K, θ range = 3.161–68.524°, reflections collected: 17329, independent reflections: 4593 (R_{ant} = 0.0224), 409 parameters. The structure was solved by direct methods and refined by full-matrix least squares on F^2; final R indices ($I>2\sigma(I)$]: R_1 = 0.0291, wR_2 = 0.0780; max. residual electron density: 0.099 e Å^{-3}. CCDC-1532574 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Methyl 2,2-dimethyl-9-(triisopropylsilyloxy)-2,11-dihydropyrano-[2,3-*a*]carbazole-8-carboxylate (6c): Prenal (**7**) (47 µL, 0.49 mmol) was added at room temperature to a solution of the 8-hydroxycarbazole **8c** (100 mg, 242 µmol), phenylboronic acid (5.9 mg, 48 µmol), and propionic acid (2.0 mL, 27 mmol) in toluene (1.5 mL). The mixture was heated at reflux for 4 h. An additional portion of prenal (**7**) (47 µL, 0.49 mmol) was added and the mixture was heated at reflux for further 19 h (total reaction time: 23 h). The solvent was evaporated, the residue taken up in diethyl ether, and the solution was washed with saturated aqueous potassium carbonate. The aqueous layer was extracted with diethyl ether, the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated. The crude product was purified by column chromatography (silica gel, isohexane/ethyl acetate, 25:1) to afford 10.3 mg of a less polar fraction containing **15c** and the more polar pyrano[2,3-*a*]carbazole **6c** (57.4 mg, 120 µmol, 50%) as yellow solid. M.p. 79–80 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.14 (d, J = 7.5 Hz, 18 H), 1.31–1.39 (m, 3 H), 1.50 (s, 6 H), 3.90 (s, 3 H), 5.59 (d, J = 9.8 Hz, 1 H), 6.47 (d, J = 9.8 Hz, 1 H), 6.85 (s, 1 H), 6.88 (d, J = 7.9 Hz, 1 H), 7.46 (d, J = 7.9 Hz, 1 H), 8.19 (br s, 1 H), 8.46 ppm (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.18 (3 CH), 17.98 (6 CH_3), 28.15 (2 CH_3), 51.68 (CH_3), 76.87 (C), 101.31 (CH), 111.83 (CH), 115.27 (C), 117.27 (C), 117.76 (C), 118.92 (CH), 122.93 (CH), 124.65 (CH), 125.22 (C), 128.74 (CH), 129.17 (C), 137.95 (C), 143.20 (C), 155.06 (C), 167.84 ppm (C); IR (ATR): v = 3334, 3035, 2944, 2865, 1699, 1652, 1622, 1564, 1458, 1433, 1398, 1373, 1315, 1242, 1218, 1180, 1157, 1122, 1100, 1065, 1030, 1015, 957, 920, 885, 846, 830, 806, 785, 750, 728, 684, 639 cm^{-1}; UV (MeOH): λ = 244, 258, 270 (sh), 287, 324, 350, 365 nm; fluorescence (MeOH): λ_{ex} = 287 nm, λ_{em} = 375 nm; MS (EI): m/z (%) = 479 (2) $[M]^+$, 436 (100) $[M-C_3H_7]^+$, 406 (12), 211 (14); elemental analysis calcd for $C_{28}H_{37}NO_4Si$: C 70.11, H 7.77, N 2.92; found: C 70.06, H 7.97, N 2.79.

Methyl 5,5-dimethyl-10-(triisopropylsilyloxy)-5*H*-[1,4]oxazepino-[2,3,4-*jk*]carbazole-11-carboxylate (15c): Prenal (**7**) (93 µL, 0.97 mmol) was added to a solution of the 8-hydroxycarbazole **8c** (200 mg, 0.484 mmol) and camphorsulfonic acid (22.5 mg, 96.9 µmol) in toluene (12 mL) and the mixture was heated at reflux for 1 h. The cooled reaction mixture was diluted with diethyl ether, the layers were separated, and the organic

layer was washed with saturated aqueous potassium carbonate. The aqueous layer was extracted twice with diethyl ether, the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated. Purification of the crude product by column chromatography (silica gel, isohexane/ethyl acetate, 25:1) provided the [1,4]oxazepino[2,3,4-*jk*]carbazole **15c** (122 mg, 0.254 mmol, 52%) as bright yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.16 (d, *J* = 7.5 Hz, 18 H), 1.34–1.41 (m, 3 H), 1.52 (s, 6 H), 3.92 (s, 3 H), 5.52 (d, *J* = 9.3 Hz, 1 H), 6.87 (s, 1 H), 6.92 (d, *J* = 9.4 Hz, 1 H), 7.03 (dd, *J* = 7.8, 0.8 Hz, 1 H), 7.20 (t, *J* = 7.8 Hz, 1 H), 7.66 (dd, *J* = 7.7, 0.8 Hz, 1 H), 8.49 ppm (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.18 (3 CH), 18.01 (6 CH_3), 29.45 (2 CH_3), 51.82 (CH_3), 79.87 (C), 100.07 (CH), 113.66 (CH), 116.62 (C), 117.44 (C), 117.76 (CH), 118.65 (CH), 121.83 (CH), 122.54 (CH), 124.67 (CH), 126.09 (C), 131.06 (C), 141.78 (C), 143.36 (C), 155.43 (C), 167.49 ppm (C); IR (ATR): ν = 2944, 2892, 2866, 1726, 1700, 1655, 1625, 1589, 1565, 1498, 1470, 1459, 1426, 1396, 1362, 1238, 1211, 1138, 1114, 1090, 1065, 908, 881, 831, 776, 736, 715, 682, 652 cm^{-1}; UV (MeOH): λ = 220, 257, 269 (sh), 296 nm; fluorescence (MeOH): λ_{ex} = 296 nm, λ_{ex} = 426 nm; MS (ESI, +50 V): *m/z* = 480.4 $[M+H]^+$, 448.5 $[M-OCH_3]^+$; elemental analysis calcd for $C_{28}H_{37}NO_4Si$: C 70.11, H 7.77, N 2.92; found: C 70.33, H 8.08, N 3.05.

1-Hydroxy-6-methyl-2-(3-methylbut-2-en-1-yl)-7-(triisopropylsilyloxy)carbazole (24): Silicon tetrachloride (0.76 mL, 6.6 mmol) and then diisobutylaluminum hydride (1 M in toluene, 6.6 mL, 6.6 mmol) were added slowly at −78 °C to a solution of pyrano[2,3-*a*]carbazole **6a** (720 mg, 1.65 mmol) in toluene (35 mL). The mixture was stirred for 5 min at −78 °C, the external cooling was removed, and the mixture was stirred for further 105 min. The reaction mixture was diluted with diethyl ether. The organic layer was separated and washed with saturated aqueous sodium bicarbonate. The aqueous layer was extracted with diethyl ether and the combined organic layers were dried ($MgSO_4$). Evaporation of the solvent and purification of the crude material by column chromatography (silica gel, isohexane/ethyl acetate, 15:1) provided the prenylcarbazole **24** (522 mg, 1.19 mmol, 72%) as brown oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.14 (d, *J* = 7.5 Hz, 18 H), 1.31–1.40 (m, 3 H), 1.81 (d, *J* = 1.0 Hz, 3 H), 1.86 (s, 3 H), 2.37 (s, 3 H), 3.52 (d, *J* = 7.2 Hz, 2 H), 5.40–5.43 (m, 1 H), 6.85 (s, 1 H), 6.89 (d, *J* = 7.9 Hz, 1 H), 7.43 (d, *J* = 7.9 Hz, 1 H), 7.71 (s, 1 H), 7.89 ppm (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.09 (3 CH), 17.58 (CH_3), 17.97 (CH_3), 18.09 (6 CH_3), 25.79 (CH_3), 30.56 (CH_2), 99.99 (CH), 111.64 (CH), 117.51 (C), 120.59 (C), 121.12 (CH), 121.15 (C), 121.46 (CH), 122.49 (CH), 124.00 (C), 129.57 (C), 135.23 (C), 139.09 (C), 139.93 (C), 153.35 ppm (C); IR (ATR): ν = 3416, 2942, 2865, 1697, 1628, 1573, 1504, 1471, 1434, 1374, 1331, 1299, 1227, 1170, 1145, 1100, 1067, 999, 923, 879, 852, 800, 715, 683, 613 cm^{-1}; UV (MeOH): λ = 238, 254, 302, 321, 334 nm; fluorescence (MeOH): λ_{ex} = 302 nm, λ_{em} = 361 nm; MS (EI): *m/z* (%) = 437 (100) $[M]^+$, 394 (23), 382 (17), 338 (24), 326 (25), 325 (17), 310 (15), 280 (14), 224 (15), 180 (11), 59 (17), 43 (14); elemental analysis calcd for $C_{27}H_{39}NO_2Si$: C 74.09, H 8.98, N 3.20; found: C 73.77, H 9.02, N 3.33.

6-Methyl-2-(3-methylbut-2-en-1-yl)-1,7-bis(triisopropylsilyloxy)carbazole (25): DBU (0.20 mL, 1.3 mmol) and TIPSCl (0.15 mL, 0.70 mmol) were added sequentially to a solution of the 1-hydroxycarbazole **24** (238 mg, 0.544 mmol) in dichloromethane (8 mL) and the mixture was stirred at room temperature for 1 h. Diethyl ether was added and the solution was washed with a saturated aqueous solution of ammonium chloride. The aqueous layer was extracted with diethyl ether and the combined organic layers were dried ($MgSO_4$). Evaporation of the solvent and purification of the residue by column chromatography (silica gel, isohexane/ethyl acetate, 40:1) provided the bis(silyloxy)carbazole **25** (305 mg, 0.513 mmol, 94%) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.15 (d, *J* = 7.5 Hz, 18 H), 1.16 (d, *J* = 7.5 Hz, 18 H), 1.33–1.43 (m, 6 H), 1.74 (s, 3 H), 1.77 (d, *J* = 0.7 Hz, 3 H), 2.37 (s, 3 H), 3.49 (d, *J* = 7.1 Hz, 2 H), 5.35–5.38 (m, 1 H), 6.78 (s, 1 H), 6.92 (d, *J* = 7.9 Hz, 1 H), 7.47 (d, *J* = 7.9 Hz, 1 H), 7.61 (br s, 1 H), 7.70 ppm (s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.14 (3 CH), 14.05 (3 CH), 17.60 (CH_3), 17.88 (CH_3), 18.06 (6 CH_3), 18.12 (6 CH_3), 25.77 (CH_3), 28.41 (CH_2), 99.92 (CH), 112.53 (CH), 117.93 (C), 121.04 (CH), 121.26 (C), 121.38 (CH), 123.42 (CH), 123.59 (C), 126.77 (C), 132.25 (C), 132.28 (C), 138.78 (C), 138.85 (C), 153.18 ppm (C); IR (ATR): ν = 3482, 2943, 2889, 2866, 2053, 2030, 2007, 1967, 1630, 1570, 1500, 1471, 1419, 1394, 1364, 1347, 1291, 1226, 1170, 1147, 1070, 1001, 948, 919, 879, 865, 823, 795, 768, 733, 714, 680 cm^{-1}; UV (MeOH): λ = 216, 242, 254, 303, 320, 332 nm; fluorescence (MeOH): λ_{ex} = 303 nm, λ_{em} = 345, 358 nm; MS (EI): *m/z* (%) = 593 (100) $[M]^+$, 550 (8), 494 (6), 438 (5), 436 (4), 392 (4); elemental analysis calcd for $C_{36}H_{59}NO_2Si_2$: C 72.79, H 10.01, N 2.36; found: C 72.92, H 10.18, N 2.47.

1,7-Dihydroxy-6-methyl-2-(3-methylbut-2-en-1-yl)carbazole (27): TBAF (1 M in THF, 0.83 mL, 0.83 mmol) was added at 0 °C to a solution of carbazole **24** (244 mg, 0.557 mmol) in THF (10 mL) and the mixture was stirred at 0 °C for 10 min. Water and ethyl acetate were added, the layers were separated, and the organic layer was washed with water. The aqueous layer was extracted with ethyl acetate, the combined organic layers were dried ($MgSO_4$), and the solvent was evaporated. Purification by column chromatography (silica gel, isohexane/ethyl acetate, 2:1) provided the 1,7-dihydroxycarbazole **27** (139 mg, 0.494 mmol, 89%) as brown solid. M.p. 153–156 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.81 (d, *J* = 1.0 Hz, 3 H), 1.86 (s, 3 H), 2.39 (s, 3 H), 3.53 (d, *J* = 7.0 Hz, 2 H), 5.41–5.44 (m, 1 H), 6.84 (s, 1 H), 6.90 (d, *J* = 7.9 Hz, 1 H), 7.44 (d, *J* = 7.9 Hz, 1 H), 7.71 (s, 1 H), 8.04 ppm (br s, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.18 (CH_3), 18.01 (CH_3), 25.80 (CH_3), 30.33 (CH_2), 96.73 (CH), 111.49 (CH), 116.11 (C), 117.73 (C), 121.08 (C), 121.16 (CH), 121.69 (CH), 122.61 (CH), 123.82 (C), 129.61 (C), 134.86 (C), 139.33 (C), 139.89 (C), 152.86 ppm (C); ^{1}H NMR (500 MHz, acetone-d_6): δ = 1.72 (d, *J* = 0.8 Hz, 3 H), 1.75 (s, 3 H), 2.32 (s, 3 H), 3.49 (d, *J* = 7.3 Hz, 2 H), 5.35–5.39 (m, 1 H), 6.85 (d, *J* = 7.9 Hz, 1 H), 6.97 (s, 1 H), 7.40 (d, *J* = 7.9 Hz, 1 H), 7.68 ppm (s, 1 H); ^{13}C NMR (125 MHz, acetone-d_6): δ = 16.68 (CH_3), 17.83 (CH_3), 25.86 (CH_3), 28.94 (CH_2), 97.18 (CH), 111.77 (CH), 117.33 (C), 117.55 (C), 121.24 (CH), 121.90 (CH), 123.43 (C), 124.32 (C), 124.60 (CH), 131.02 (C), 131.87 (C), 140.07 (C), 140.65 (C), 155.05 ppm (C); ^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.69 (s, 3 H), 1.72 (s, 3 H), 2.22 (s, 3 H), 3.40 (d, *J* = 7.7 Hz, 2 H) 5.31–5.34 (m, 1 H), 6.74 (d, *J* = 7.9 Hz, 1 H), 6.87 (s, 1 H), 7.30 (d, *J* = 7.9 Hz, 1 H), 7.60 (s, 1 H), 8.59 (s, 1 H), 9.24 (s, 1 H), 10.25 ppm (s, 1 H); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 16.52 (CH_3), 17.70 (CH_3), 25.58 (CH_3), 27.91 (CH_2), 96.33 (CH), 110.49 (CH), 115.54 (C), 115.95 (C), 119.92 (CH), 120.84 (CH), 122.35 (C), 122.62 (C), 123.88 (CH), 130.17 (C), 130.47 (C), 139.15 (C), 139.37 (C), 154.12 ppm (C); IR (ATR): ν = 3416, 3375, 3329, 2968, 2912, 2853, 1625, 1581, 1507, 1469, 1445, 1372, 1341, 1294, 1266, 1221, 1159, 1135, 1062, 1000, 908, 878, 846, 802, 788, 737, 673, 662, 621 cm^{-1}; UV (MeOH): λ = 235, 251 (sh), 300, 315, 330 nm; fluorescence (MeOH): λ_{ex} = 300 nm, λ_{em} = 360 nm; MS (EI): *m/z* (%) = 281 (77) $[M]^+$, 264 (10), 251 (11), 225 (100), 196 (21), 183 (11), 168 (12), 167 (11), 55 (20), 39 (19); HRMS (ESI): *m/z* calcd for $C_{18}H_{20}NO_2^+$ $[M+H]^+$: 282.149; found: found: 282.147.

6-Methyl-1-((2-methylbut-3-en-2-yl)oxy)-7-(triisopropylsilyloxy)carbazole (28): A solution of 1,1-dimethylallyl methyl carbonate (585 mg, 4.06 mmol) in THF (7.5 mL) was added to a mixture of the 8-hydroxycarbazole **8a** (500 mg, 1.35 mmol) and tetrakistriphenylphosphinepalladium (15.6 mg, 13.5 µmol) and the mixture was stirred at room temperature for 1 h. The mixture was filtered over a short pad of Celite® (dichloromethane) and the solvent was evaporated. Purification of the residue by column chromatography (silica gel, isohexane/ethyl acetate, 30:1) and drying in high vacuum for 15 min provided the *tert*-prenyl ether **28** (602 mg) as yellow solid which was

used directly for the next transformation. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.15 (d, J = 7.4 Hz, 18 H), 1.33–1.39 (m, 3 H), 1.57 (s, 6 H), 2.38 (s, 3 H), 5.18 (dd, J = 10.9, 0.9 Hz, 1 H), 5.29 (dd, J = 17.6, 0.9 Hz, 1 H), 6.24 (dd, J = 17.6, 10.9 Hz, 1 H), 6.86 (s, 1 H), 6.986 (d, J = 1.7 Hz, 1 H), 6.993 (s, 1 H), 7.56–7.57 (m, 1 H), 7.74 (s, 1 H), 7.96 ppm (br s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 11.42 (3 CH), 17.59 (CH_3), 18.12 (6 CH_3), 27.23 (2 CH_3), 80.28 (C), 99.83 (CH), 113.25 (CH), 113.50 (CH_2), 114.65 (CH), 117.54 (C), 118.96 (CH), 121.26 (C), 121.60 (CH), 124.84 (C), 133.12 (C), 138.68 (C), 141.21 (C), 144.40 (CH), 153.52 ppm (C).

8-((2-Methylbut-3-en-2-yl)oxy)-2-(triisopropylsilyloxy)carbazole-3-carbaldehyde (29): DDQ (937 mg, 4.13 mmol) was added to a solution of the above *tert*-prenyl ether **28** in MeOH (42 mL), THF (15.5 mL), and water (2.6 mL) and the mixture was stirred at room temperature for 1 h. The solution was transferred to a separatory funnel (diethyl ether) and washed with water. The aqueous layer was extracted with diethyl ether, the combined organic layers were dried (Na_2SO_4), and the solvent was evaporated. The crude product was purified by column chromatography (silica gel, isohexane/ethyl acetate, 15:1) to provide the carbazolecarbaldehyde **29** as yellow solid which was used directly for the next transformation. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 1.14 (d, J = 7.5 Hz, 18 H), 1.41 (m, 3 H), 1.53 (s, 6 H), 5.16 (dd, J = 10.9, 0.9 Hz, 1 H), 5.23 (dd, J = 17.6, 0.9 Hz, 1 H), 6.26 (dd, J = 17.6, 10.9 Hz, 1 H), 7.03 (m, 3 H), 7.76 (m, 1 H), 8.42 (s, 1 H), 10.44 (s, 1 H), 11.23 ppm (s, 1 H).^{13}C NMR (150 MHz, DMSO-d_6): δ = 12.45 (3 CH), 17.88 (6 CH_3), 26.63 (2 CH_3), 80.68 (C), 100.27 (CH), 114.06 (CH_2), 114.43 (CH), 117.06 (CH), 118.01 (C), 119.75 (C), 120.02 (CH), 120.95 (CH), 124.50 (C), 134.34 (C), 141.16 (C), 143.94 (CH), 145.07 (C), 157.29 (C), 188.40 ppm (CHO).

8-Hydroxy-7-(3-methylbut-2-en-1-yl)-2-(triisopropylsilyloxy)carbazole-3-carbaldehyde (23): The above carbazolecarbaldehyde **29** was dissolved in toluene (10 mL) and the solution was heated at reflux for 2.5 h. The solvent was evaporated and the residue was purified by column chromatography (silica gel, isohexane/ethyl acetate, 5:1) to provide the silyl-protected excavatine-A **23** (350 mg, 0.775 mmol, 57%). M.p. 226 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 1.12 (d, J = 7.6 Hz, 18 H), 1.40 (m, 3 H), 1.71 (d, J = 0.4 Hz, 3 H), 1.72 (s, 3 H), 3.43 (d, J = 7.3 Hz, 2 H), 5.30–5.33 (m, 1 H), 6.88 (d, J = 7.9 Hz, 1 H), 7.01 (s, 1 H), 7.53 (d, J = 7.9 Hz, 1 H), 8.34 (s, 1 H), 8.92 (s, 1 H), 10.42 (s, 1 H), 11.01 ppm (s, 1 H); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 12.39 (3 CH), 17.75 (CH_3), 17.86 (6 CH_3), 25.59 (CH_3), 27.94 (CH_2), 100.30 (CH), 111.87 (CH), 118.32 (C), 119.47 (C), 120.36 (CH), 121.71 (CH), 122.45 (C), 123.37 (CH), 125.30 (C), 131.12 (C), 131.64 (C), 139.64 (C), 145.10 (C), 157.01 (C), 188.34 ppm (CHO); IR (ATR): ν = 3291, 2965, 2942, 2883, 2865, 2152, 2007, 1975, 1745, 1649, 1632, 1574, 1507, 1470, 1455, 1431, 1393, 1354, 1327, 1246, 1215, 1188, 1098, 1071, 1014, 989, 937, 903, 881, 849, 820, 798, 787, 724, 688, 640 cm^{-1}; UV (MeOH): λ = 218, 244, 279, 295 (sh), 362 nm; fluorescence (MeOH): λ_{ex} = 279 nm, λ_{em} = 311, 403 nm; MS (ESI, +10 V): m/z = 452.3 $[M+H]^+$; MS (ESI, −50 V): m/z = 450.3 $[M-H]^-$, 901.5 $[2M-H]^-$; HRMS (ESI): m/z calcd for $C_{27}H_{38}NO_3Si^+$ $[M+H]^+$: 452.2615; found: 452.2613; elemental analysis calcd for $C_{27}H_{37}NO_3Si$: C 71.80, H 8.26, N 3.10; found: C 72.40, H 8.20, N 3.24.

Excavatine-A (2,8-Dihydroxy-7-(3-methylbut-2-en-1-yl)carbazole-3-carbaldehyde) (1): TBAF (1 M in THF, 0.43 mL, 0.43 mmol) was added at 0 °C to a solution of silyloxycarbazole **23** (150 mg, 0.332 mmol) in THF (6 mL) and the mixture was stirred for 5 min. Water and ethyl acetate were added, the layers were separated, and the organic layer was washed with water. The aqueous layers were extracted with ethyl acetate, the combined organic layers were dried (Na_2SO_4), and the solvent was evaporated. Purification of the residue by flash chromatography (silica gel, isohexane/ethyl acetate, 3:1) provided excavatine-A (**1**) (92.5 mg, 0.313 mmol, 94%) as yellow solid. M.p. 187 °C (lit.: pale-yellow powder, no m.p. given)[3]; ^{1}H NMR (600 MHz, acetone-d_6): δ = 1.73 (d, J = 0.8 Hz, 3 H), 1.76 (s, 3 H), 3.53 (d, J = 7.3 Hz, 2 H), 5.36–5.40 (m, 1 H), 6.92 (s, 1 H), 7.00 (d, J = 7.9 Hz, 1 H), 7.55 (d, J = 7.9 Hz, 1 H), 7.87 (br s, 1 H), 8.35 (s, 1 H), 9.97 (s, 1 H), 10.44 (br s, 1 H), 11.44 ppm (br s, 1 H); ^{13}C NMR (150 MHz, acetone-d_6): δ = 17.86 (CH_3), 25.86 (CH_3), 28.91 (CH_2), 97.48 (CH), 112.61 (CH), 116.11 (C), 119.15 (C), 123.13 (CH), 123.89 (CH), 123.93 (C), 126.16 (C), 128.25 (CH), 132.26 (C), 132.65 (C), 140.53 (C), 146.95 (C), 161.57 (C), 196.54 ppm (CHO); IR (ATR): ν = 3361, 2971, 2909, 2854, 1737, 1647, 1630, 1610, 1590, 1573, 1509, 1470, 1399, 1344, 1321, 1273, 1227, 1199, 1163, 1096, 1069, 1042, 980, 908, 891, 848, 826, 804, 780, 741, 722, 660 cm^{-1}; UV (MeOH): λ = 219, 243, 280, 298 (sh), 356 nm; fluorescence (MeOH): λ_{ex} = 280 nm, λ_{em} = 315 nm; MS (ESI, +10 V): m/z = 296.1 $[M+H]^+$, 613.1 $[2M+Na]^+$; MS (ESI, −25 V): 293.9 $[M-H]^-$, 589.0 $[2M-H]^-$; HRMS (ESI): m/z calcd for $C_{18}H_{18}NO_3^+$ $[M+H]^+$: 296.1281; found: 296.1276.

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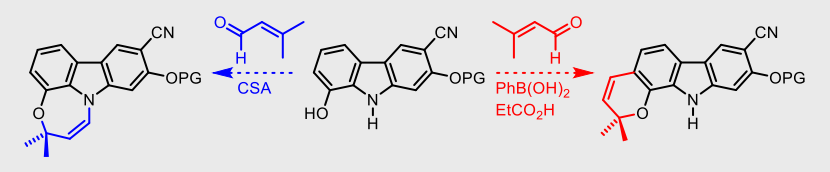
Natural Product Synthesis

FULL PAPER



We describe the first total synthesis of the 2,8-dioxygenated carbazole alkaloid excavatine-A. Reaction of the intermediate 8-hydroxycarbazoles with prenal under Brønsted acid catalysis afforded [1,4]oxazepino[2,3,4-*jk*]carbazoles, whereas a combination of Lewis and Brønsted acid led to pyrano[2,3-*a*]carbazoles.

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First Total Synthesis of the Cytotoxic Carbazole Alkaloid Excavatine-A and Regioselective Annulation to Pyrano[2,3-*a*]carbazoles and [1,4]Oxazepino[2,3,4-*jk*]carbazoles