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Palladium-Catalyzed Synthesis of Pyrayaquinones, Murrayaquinones, and Murrayafoline-B

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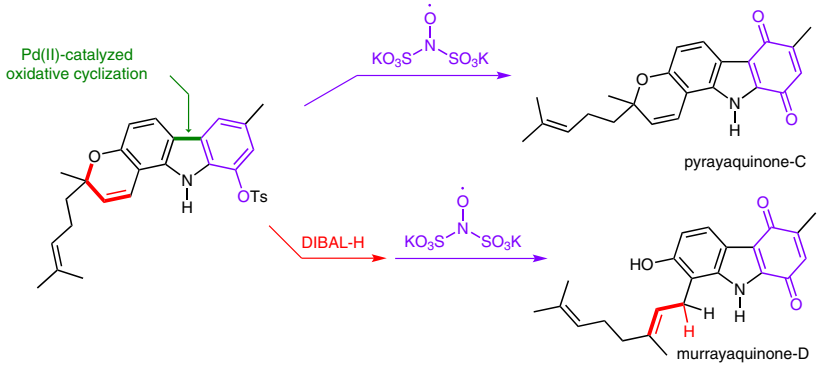
Dedicated to Professor Dieter Enders on the occasion of his 70th birthday.



Received: 08.08.2016
Accepted after revision: 06.09.2016
Published online: 11.10.2016
DOI: 10.1055/s-0036-1588322; Art ID: ss-2016-m0558-op

Abstract We describe the total synthesis of murrayafoline-B and seven carbazole-1,4-quinone alkaloids. A palladium(II)-catalyzed oxidative cyclization is used to construct the carbazole skeleton. Pyran annulation and oxidation provide pyrayaquinone-A, -B, and -C. DIBAL-H-promoted reductive ring opening of pyrano[3,2-*a*]carbazole precursors leads to the prenylated and geranylated carbazole-1,4-quinone alkaloids murrayaquinone-B, -C, -D, and -E and to murrayafoline-B.

Key words carbazole, alkaloids, quinones, natural products, total synthesis, palladium, Frémy's salt, ring opening

Carbazole alkaloids have been the topic of scientific interest due to their unique chemical and medicinal properties.[1] Various methods have been developed for construction of the carbazole skeleton, with many relying on transition-metal-mediated and -catalyzed reactions.[2] We previously developed iron-mediated[3] and palladium-catalyzed approaches to carbazole alkaloids.[4] The latter relies on a palladium(II)-catalyzed oxidative cyclization of diarylamines by double C–H bond activation.[5] The feasibility of this reaction had been first demonstrated on a carbazole-1,4-quinone.[4a] Several quinoid carbazoles have been isolated from natural sources and their promising pharmacological potential, e.g., anti-TB activity, has induced scientific interest.[1f,6] The carbazole-1,4-quinones **1**–**8** have been obtained from *Murraya euchrestifolia* (Rutaceae), one of the main natural sources of carbazole alkaloids (Figure 1). Pyrayaquinone-A (**1**) and -B (**2**) were isolated first in 1985 by Furukawa and co-workers from the acetone extract of the root bark of *Murraya euchrestifolia* Hayata collected in Taiwan.[7] The structures were assigned based on spectroscopic data and confirmed by total synthesis.[7,8] In 1986, Ramesh and Kapil outlined the first synthesis of pyrayaquinone-B (**2**)[9] and in 1987, the same authors reported an alternative route to **2** and a synthetic access to pyrayaquinone-A (**1**).[10] Pyrayaquinone-C (**3**) was isolated by Furukawa and co-workers in 1988 from the same natural source as compounds **1** and **2**.[11] The first isolation of murrayaquinone-B (**5**) was communicated by Furukawa and co-workers in 1983.[12] Full details of the extraction and purification were reported in 1985 together with the isolation and structural elucidation of murrayaquinone-A (**4**), -C (**7**), and -D (**8**).[13] Murrayaquinone-E (**6**) was first described by the same group six years later.[14] In contrast to compounds **1**–**5**, **7**, and **8**, compound **6** was not obtained from the root bark, but from the stem bark of *M. euchrestifolia*.

Various approaches to murrayaquinone-A (**4**) have been developed,[1b,1f,15] the first one being reported by Kapil in 1987.[10] We described an iron-mediated and a palladium-catalyzed synthesis of murrayaquinone-A (**4**) in 1993 and 2003, respectively.[16] The groups of Moody and Kapil described synthetic routes to murrayaquinone-B (**5**) in 1985 and 1986.[17] Only recently, Norcott and McErlean reported the total synthesis of the carbazolequinones **2**, **3**, and **5**–**8**.[18] Herein, we describe our route to the carbazole-1,4-quinone alkaloids pyrayaquinone-A–C (**1**–**3**) and murrayaquinone-B–E (**5**–**8**) utilizing a common precursor.

Our projected route relies on late-stage oxidation of a 1-hydroxycarbazole to the corresponding quinoid natural products **5**–**8** (Scheme 1). The prenylated or geranylated carbazoles **9** would be generated by our recently developed DIBAL-H-mediated reductive pyran ring opening of pyranocarbazoles **10**.[19] The latter also represent the precursors to the pyrayaquinones **2** and **3** and are available by pyran ring annulation at the hydroxycarbazole **13**, which in turn is synthesized by palladium(II)-catalyzed oxidative cyclization of the corresponding diarylamine. Pyrayaquinone-A (**1**) would be available by regioselective pyran ring annulation

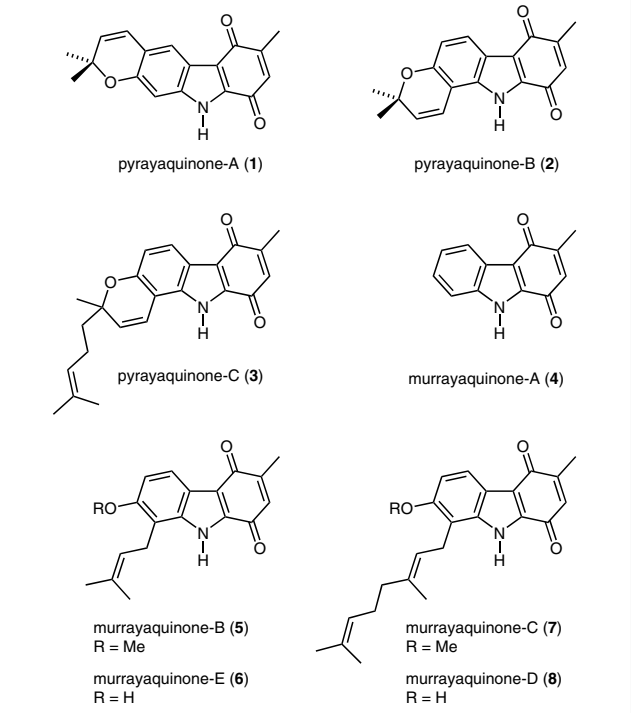
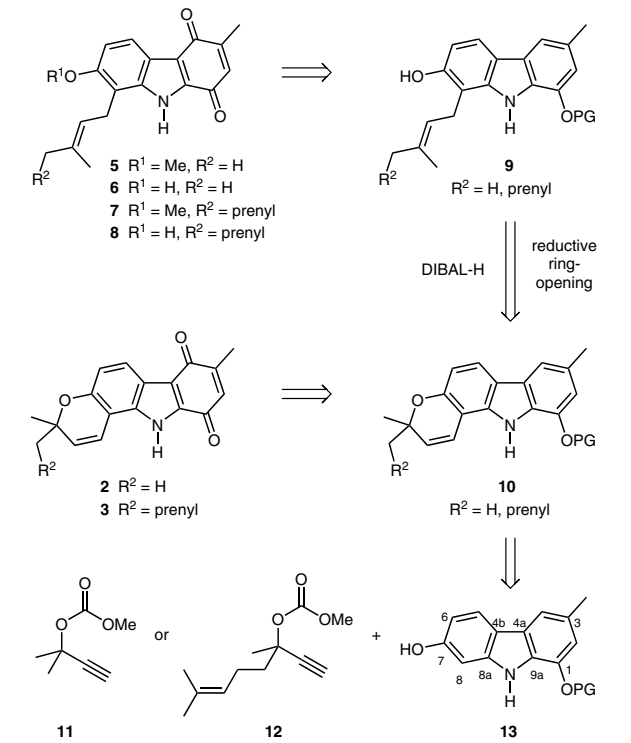


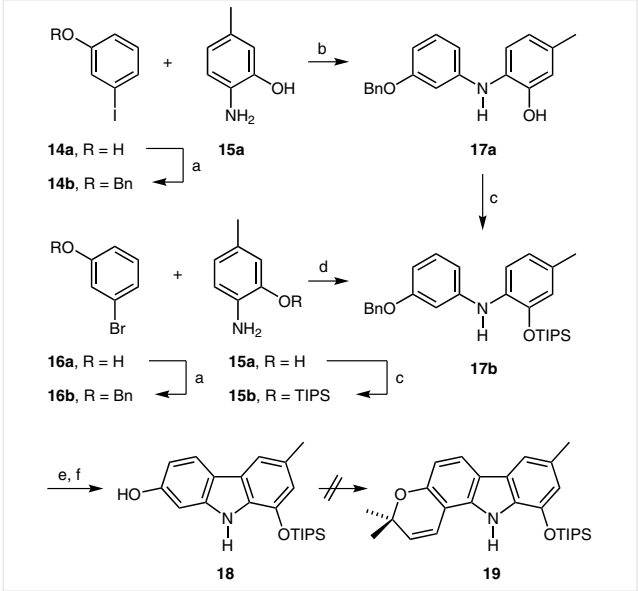
Figure 1 Naturally occurring carbazole-1,4-quinone alkaloids



Scheme 1 Retrosynthetic analysis of the carbazole-1,4-quinones **2**, **3**, and **5–8**

at the C-6–C-7 linkage of the hydroxycarbazole **13** and subsequent oxidation (not shown). Analogously to our previous syntheses of other oxygenated pyrano[3,2-*a*]carbazoles, we initially used the triisopropylsilyloxycarbazole **18** for pyran annulation (Scheme 2).[4d,4f,19a] Copper(I)-catalyzed Ullmann-type coupling[20] of 3-(benzyloxy)iodobenzene (**14b**) and the hydroxyaniline **15a** was followed by O-silylation to provide the diarylamine **17b** in high yield. This sequence proved to be superior to the Buchwald–Hartwig amination of the bromoarene **16b** and the triisopropylsilyl-protected aniline **15b**, which provided the desired diarylamine **17b** only in very low yield (probably due to steric hindrance). Palladium(II)-catalyzed oxidative cyclization and hydrogenolytic benzyl ether cleavage afforded the desired carbazole **18** in good yield (71%). However, attempts at pyran annulation with hydroxycarbazole **18** using either Casiraghi's [Ti(O*i*-Pr)$_4$/prenal][21a] or Dufresne's method [PhB(OH)$_2$/propionic acid/prenal][21b] provided mixtures of compounds, while Godfrey's protocol [CuCl$_2$/DBU/1,1-dimethylpropargyl methyl carbonate (**11**)][22] induced migration of the silyl group.[4f,21] The latter reaction parallels the DBU-induced cleavage of phenolic silyl ethers that was reported by Kim and co-workers in 2007.[23]

Due to the difficulties associated with the silyl group of the hydroxycarbazole **18**, we decided to replace both protecting groups and used instead the 7-methoxycarbazol-1-

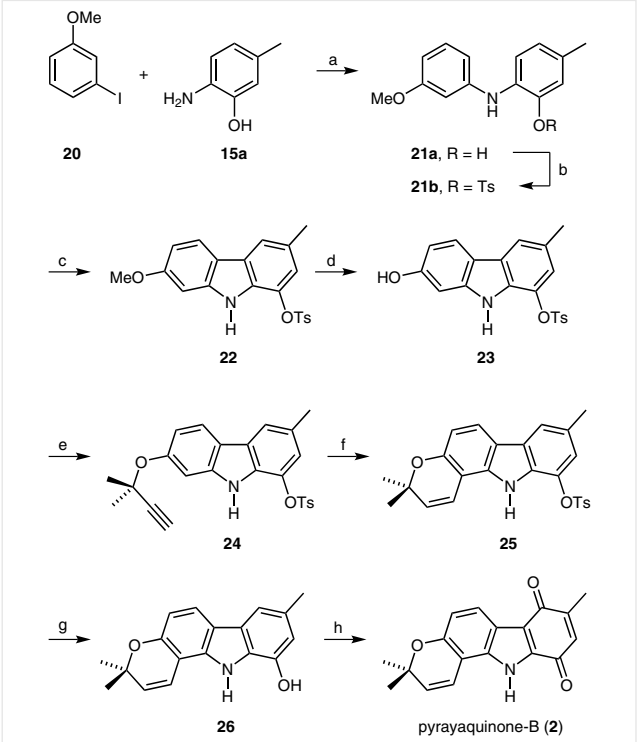


Scheme 2 Synthesis of the 7-hydroxy-1-(silyloxy)carbazole **18**. *Reagents and conditions*: (a) BnBr (1.5 equiv), K$_2$CO$_3$ (1.5 equiv), acetone, r.t., 6 h (**14b**: 99%; **16b**: 73%); (b) **14b** (1.0 equiv), **15a** (2.0 equiv), CuI (20 mol%), K$_3$PO$_4$ (2.0 equiv), DMF, 80 °C, 18 h (85%); (c) TIPSCl (1.2 equiv), ImH (1.2 equiv), DMF, 50 °C, 24 h (**15b**: 84%; **17b**: 96%); (d) **16b** (1.0 equiv), **15b** (1.3 equiv), Pd(OAc)$_2$ (6 mol%), XPhos (12 mol%), toluene, reflux, 25 h (9%); (e) Pd(OAc)$_2$ (15 mol%), Cu(OAc)$_2$ (2.5 equiv), AcOH, 130 °C, microwave (300 W), 30 min; (f) H$_2$ (1 atm), Pd/C (2 wt%), EtOAc, r.t., 3 d (71%, 2 steps).

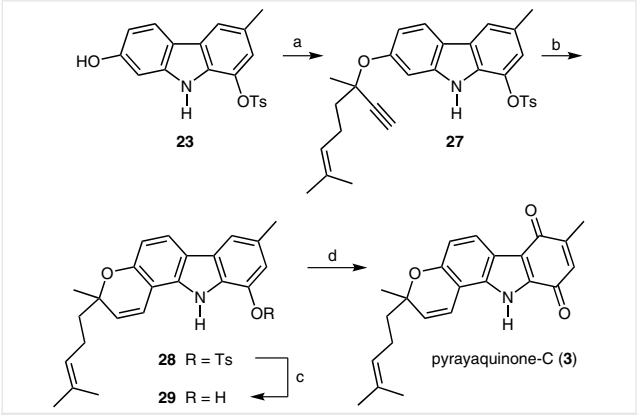
yl tosylate **22** for our synthesis (Scheme 3). Copper(I)-catalyzed Ullmann-type coupling of *m*-iodoanisole (**20**) and the aminocresol **15a** provided the diarylamine **21a** in high yield. O-Tosylation and treatment of the resulting tosyl-protected diarylamine **21b** with catalytic amounts of palladium(II) acetate and potassium carbonate in pivalic acid at 100 °C led to the desired 7-methoxycarbazole **22**. The methyl ether was cleaved by heating of **22** in a mixture of acetic acid and hydrobromic acid to provide the 7-hydroxycarbazole **23** in good yield. The pyran ring was then annulated using Godfrey's method.[22] Treatment of compound **23** with 1,1-dimethylpropargyl methyl carbonate (**11**) in the presence of catalytic amounts of copper(II) chloride and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) gave the propargyloxycarbazole **24**, thermally-induced rearrangement of which finally provided the pyrano[3,2-*a*]carbazole **25**. Lithium aluminum hydride induced cleavage of the tosyl group afforded the hydroxycarbazole **26**, which already had been an intermediate in Kapil's synthesis of pyrayaquinone-B (**2**).[9] Oxidation using Frémy's salt[24] provided compound **2** in 46% yield, which is superior to the oxidation with PCC (30% yield)[9] as reported by Kapil. Our route led to natural product **2** in eight steps and 27% overall yield.

Pyrayaquinone-C (**3**) was synthesized following the same route using a C_{10}-unit for the pyran annulation (Scheme 4). Copper(II)-catalyzed treatment of the 2-hydroxycarbazole **23** with 3,7-dimethyloct-6-en-1-yn-3-yl methyl carbonate (**12**) and DBU followed by thermally induced rearrangement afforded the homoprenyl-substituted pyranocarbazole **28**. Base-induced cleavage of the sulfonic ester and oxidation led to pyrayaquinone-C (**3**) in eight steps and 30% overall yield. Unfortunately, compound **23** could not be transformed into the pyrano[2,3-*b*]carbazole, pyrayaquinone-A (**1**). Various conditions for pyran annulation using **23** following either Godfrey's,[22] Casiraghi's,[21a] or Dufresne's methods[21b] provided mainly the [3,2-*a*] annulated product **25**, and at best trace amounts of **30**, the potential precursor to compound **1**.[4f,21] Substitution at the nitrogen atom with bulky protecting groups did not significantly change the regioselectivity.[4d,25] Alternative methods, e.g., lithiation/prenal addition, Friedel–Crafts acylation or esterification/Fries rearrangement failed as well.[26] Finally, we decided to use a prenylation/cyclization approach (Scheme 5).

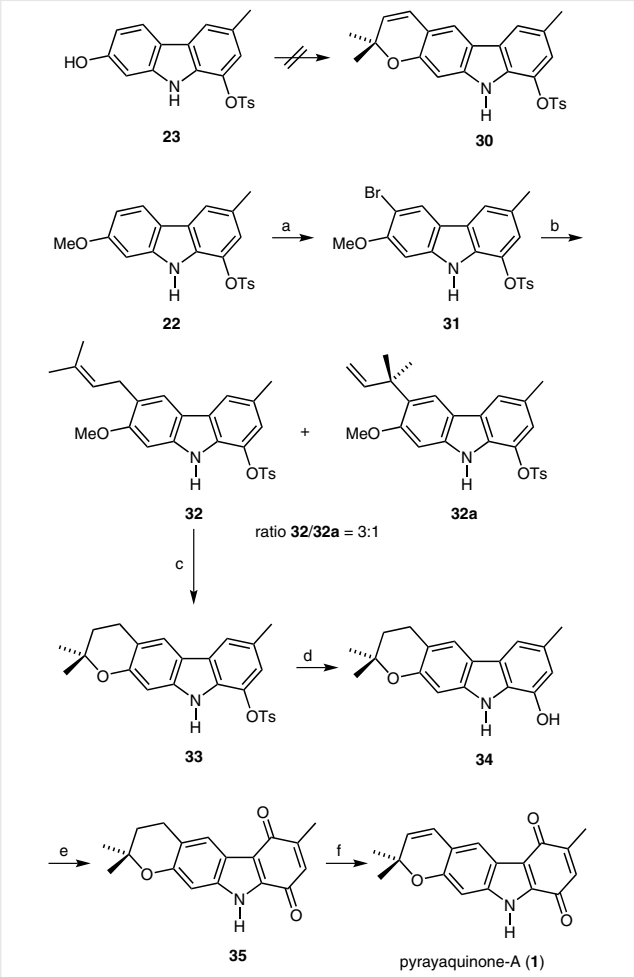
Regioselective bromination at C-6 of the tosyl-protected 7-methoxycarbazole **22** and prenylation of the resulting 6-bromocarbazole **31** by Suzuki–Miyaura coupling with prenylboronic acid pinacol ester provided the 6-prenylcarbazole **32**.[27] In agreement with Choshi and Hibino,[27b] but in contrast to Ma,[27a] we observed, isolated, and characterized the *tert*-prenylated isomer **32a** as a side product (ratio of **32**/**32a** = 3:1). Treatment of **32** with pyridinium chloride induced cleavage of the methyl ether and subsequent pyran ring closure, probably by intramolecular electrophilic addition at the prenyl double bond, to afford the tetrahydropy-



Scheme 3 Synthesis of pyrayaquinone-B (**2**). *Reagents and conditions*: (a) **20** (1.0 equiv), **15a** (2.1 equiv), CuI (26 mol%), K_3PO_4 (2.0 equiv), DMF, 80 °C, 8.5 h (90%); (b) TsCl (1.1 equiv), Na_2CO_3 (20 mol%), $Bu_4N^+Cl^-$ (2 mol%), NaOH (4.1 equiv), $PhCl–H_2O$ (3:4), r.t., 3 h (100%); (c) $Pd(OAc)_2$ (20 mol%), K_2CO_3 (19 mol%), PivOH, 100 °C, 22 h (85%); (d) HBr (aqueous, 48%), AcOH, reflux, 2 h (90%); (e) $CuCl_2·2H_2O$ (0.85 mol%), DBU (2.0 equiv), 1,1-dimethylpropargyl methyl carbonate (**11**) (2.0 equiv), MeCN, r.t., 28 h; (f) toluene, reflux, 19 h (85%, 2 steps); (g) $LiAlH_4$ (6.6 equiv), THF, reflux, 2 h; (h) $(KSO_3)_2NO$ (3.0 equiv), acetone–H_2O (1:1), r.t., 2.5 h (46%, 2 steps).



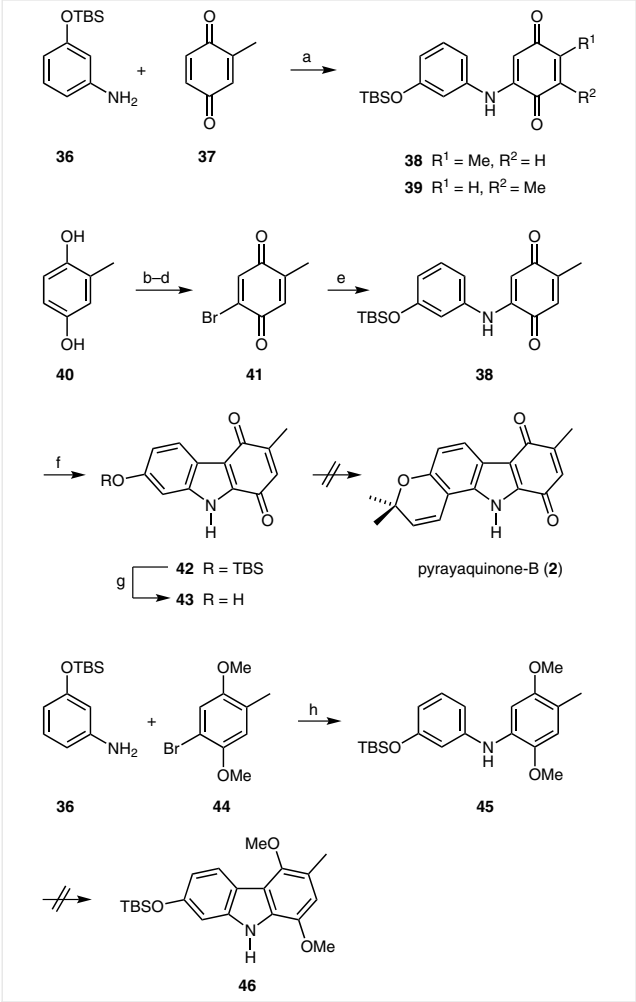
Scheme 4 Synthesis of pyrayaquinone-C (**3**). *Reagents and conditions*: (a) $CuCl_2·2H_2O$ (2.7 mol%), DBU (2.2 equiv), 3,7-dimethyloct-6-en-1-yn-3-yl methyl carbonate (**12**) (2.2 equiv), MeCN, r.t., 45 h (69%); (b) toluene, reflux, 22 h (100%); (c) NaOH (57 equiv), EtOH–H_2O (5:1), reflux, 2.5 h; (d) $(KSO_3)_2NO$ (3.7 equiv), acetone–H_2O (1:1), r.t., 18 h (64%, 2 steps).



Scheme 5 Synthesis of pyrayaquinone-A (**1**). *Reagents and conditions*: (a) *N*-bromosuccinimide (NBS) (1.0 equiv), CH_2Cl_2, r.t., 3 d (94%); (b) 3-methyl-2-butenylboronic acid pinacol ester [$Me_2C{=}CHCH_2B(pin)$] (1.9 equiv), $(Ph_3P)_4Pd$ (10 mol%), NaOH (40 equiv), toluene–H_2O (1:1), r.t., 21 h (**32**: 74%; **32a**: 25%); (c) Py·HCl (39 equiv), neat, 170 °C, 5 h (80%); (d) $LiAlH_4$ (10.6 equiv), THF, reflux, 14 h; (e) $(KSO_3)_2NO$ (6.9 equiv), acetone–H_2O (1:1), r.t., 40 min (60%, 2 steps); (f) DDQ (2.2 equiv), toluene, 100 °C, 3.5 h (86%).

rano[2,3-*b*]carbazole **33**. Cleavage of the sulfonic ester followed by oxidation with Frémy's salt and dehydrogenation finally provided pyrayaquinone-A (**1**) in nine steps and 22% overall yield.

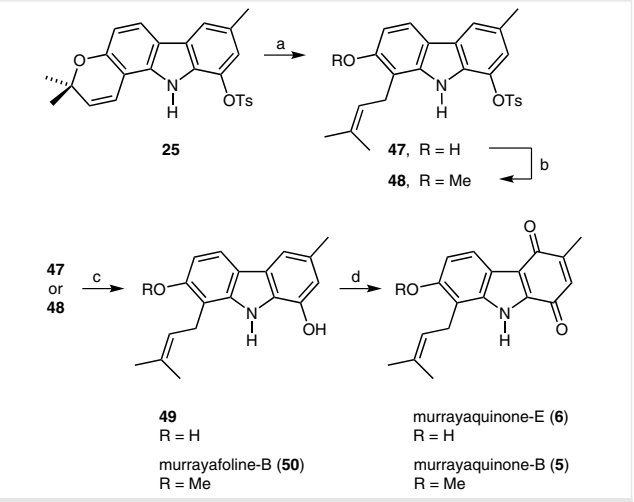
We also explored alternative routes to the pyranocarbazoles **1**–**3**. In an early approach, we thought to apply a pyran ring annulation to the hydroxycarbazole-1,4-quinone **43** (Scheme 6). Our first route to the latter compound started with reaction of the aniline **36** and two equivalents of 2-methyl-1,4-benzoquinone (**37**). The silyloxyaniline **36** was synthesized from *m*-nitrophenol by O-silylation and subsequent iron/acetic acid mediated reduction of the nitro group. The addition/oxidation reaction of **36** and **37** provided an almost inseparable mixture of the desired (phenylamino)quinone **38** and the regioisomer **39**.[8,16b] The quinone **38** was selectively synthesized by Buchwald–Hartwig amination of the bromoquinone **41**, available in three steps from the hydroquinone **40**, and the silyloxyaniline **36**. Palladium(II)-catalyzed oxidative cyclization of **38** in acetic acid at reflux using copper(II) acetate as the oxidant, our original conditions for the palladium(II)-catalyzed oxidative cyclization,[4a,16b] provided the silyloxy-substituted carbazole-1,4-quinone **42** in good yield. TBAF-induced cleavage of the silyl ether finally led to the desired hydroxycarbazolequinone



Scheme 6 An attempted alternative approach to the pyrayaquinones-A–C (**1**–**3**). *Reagents and conditions*: (a) **36** (1.0 equiv), **37** (2.0 equiv), H_2O–MeOH–AcOH (15:5:1), –4 °C, 48 h (compound mixture, purification of which provided **38** in 29% yield); (b) Me_2SO_4 (3.0 equiv), K_2CO_3 (5.0 equiv), acetone, r.t., 3 h; (c) bromine (1.1 equiv), NaOAc (2.0 equiv), AcOH, r.t., 85 min; (d) cerium ammonium nitrate (CAN) (2.5 equiv), MeCN–H_2O (7:2), r.t., 1 h (97%, 3 steps); (e) **36** (1.2 equiv), $Pd(OAc)_2$ (12 mol%), XPhos (25 mol%), Cs_2CO_3 (1.5 equiv), toluene, 100 °C, 2 h (62%); (f) $Pd(OAc)_2$ (33 mol%), $Cu(OAc)_2$ (2.5 equiv), AcOH, 100 °C, 5 h (74%); (g) TBAF (1.3 equiv), THF, 0 °C, 10 min (90%); (h) **44** (1.0 equiv), **36** (1.3 equiv), $Pd(OAc)_2$ (6 mol%), XPhos (12 mol%), Cs_2CO_3 (1.2 equiv), toluene, reflux, 20 h (97%).

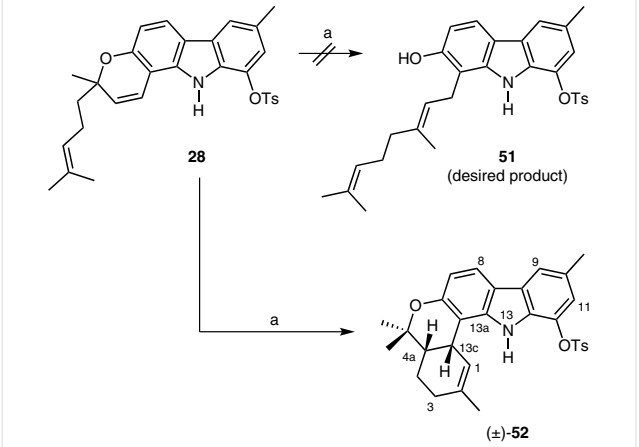
43. Unfortunately, all attempts to annulate a pyran ring at **43** failed. We suspect that the electron-poor quinoid ring system was responsible for this failure. Finally, we envisaged the synthesis of the 1,4-dimethoxycarbazole **46** (Scheme 6). Buchwald–Hartwig amination of the aniline **36** and bromoarene **44**, the precursor of the quinone **41**, provided diarylamine **45**. Since our attempts to achieve an oxidative cyclization of the electron-rich diarylamine **45** led only to decomposition, this route was abandoned.

We then turned our attention to the prenyl- and geranyl-substituted carbazole-1,4-quinones **5**–**8** (Schemes 7–9). DIBAL-H-mediated reductive pyran ring opening[19] of compound **25** by treatment with an excess of silicon tetrachloride and DIBAL-H in toluene at –78 °C followed by warming to room temperature provided the 7-hydroxy-8-prenylcarbazole **47** in 77% yield (Scheme 7). Removal of the tosyl group and oxidation using Frémy's salt led to murrayaquinone-E (**6**) in 75% yield (9 steps, 34% overall yield). The corresponding 7-*O*-methyl derivative, murrayaquinone-B (**5**), was obtained following the same route. O-Methylation of the carbazole **47** and subsequent detosylation led to murrayafoline-B (**50**), a natural product that like the carbazolequinones **1**–**8** has been isolated from *M. euchrestifolia*.[13] Our approach constitutes only the second synthesis of murrayafoline-B (**50**) and led to the natural product in nine steps and 40% overall yield. The only other route known so far, published by Kapil in 1986, provided this natural product in less than 1% overall yield.[17c] Treatment of murrayafoline-B (**50**) with Frémy's salt afforded murrayaquinone-B (**5**) in 68% yield (10 steps, 27% overall yield).



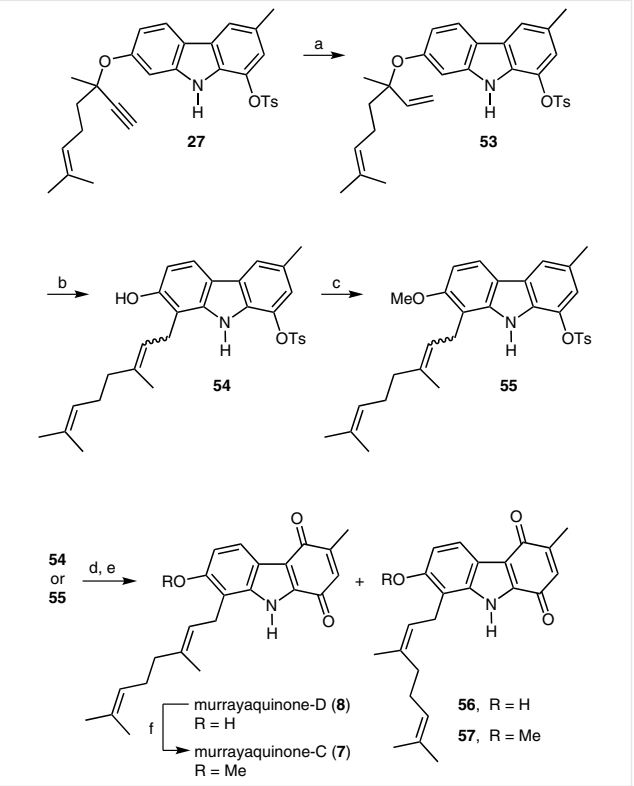
Scheme 7 Synthesis of murrayafoline-B (**50**), murrayaquinone-B (**5**), and murrayaquinone-E (**6**). *Reagents and conditions*: (a) DIBAL-H (6.6 equiv), $SiCl_4$ (6.6 equiv), toluene, –78 °C to r.t., 22 h (77%); (b) Me_2SO_4 (5.0 equiv), K_2CO_3 (4.7 equiv), acetone, r.t. to 40 °C, 16 h (94%); (c) $LiAlH_4$ (6.8 equiv), THF, reflux, (16 h, **49**; 18 h, **50**: 94%) (d) $(KSO_3)_2NO$ (5.6 equiv), acetone–H_2O (1:1), r.t., (68 h, **6**: 75%, 2 steps; 3 d, **5**: 68%).

Application of the reaction conditions for our DIBAL-H-mediated pyran ring-opening reaction to the homoprenyl-substituted pyrano[3,2-*a*]carbazole **28** surprisingly did not provide the desired geranylcarbazole **51**, but instead the isochromeno[4,3-*a*]carbazole **52** in up to 60% yield (Scheme 8). The *cis*-relationship of C4a-H and C13c-H was assigned based on comparison of the ^1H NMR data with those of related structures.[28] The geranylated carbazole-1,4-quinones **7** and **8** were finally synthesized using a Claisen rearrangement as the key step (Scheme 9). Partial hydrogenation of the propargyloxycarbazole **27**, the direct precursor to pyranocarbazole **28**, followed by thermally induced Claisen rearrangement provided compound **54** as a mixture of double bond isomers (ratio *E*/*Z* = 1.3:1). Removal of the tosyl group, oxidation with Frémy's salt, and separation of the isomers led to murrayaquinone-D (**8**) and the corresponding *Z*-isomer **56**. Murrayaquinone-C (**7**) was synthesized from intermediate **54** by initial O-methylation to give **55** followed by detosylation and oxidation. The two stereoisomers **7** and **57** (ratio = 3:1) could not be separated in this case. However, a pure sample of the *E*-isomer, murrayaquinone-C (**7**), was prepared by O-methylation of murrayaquinone-D (**8**) following Norcott and MacErlean's procedure,[18] who described the sequential treatment of 3.5 mg of **8** with an equimolar amount of butyllithium and an excess of iodomethane at –78 °C to provide 2.5 mg of murrayaquinone-C (**7**) (70% yield). In our hands this transformation proved to be difficult and provided murrayaquinone-C (**7**) in 59% yield (10 mg scale).



Scheme 8 DIBAL-H-promoted reaction of the pyrano[3,2-*a*]carbazole **28**. *Reagents and conditions*: (a) DIBAL-H (4.0 equiv), $SiCl_4$ (4.0 equiv), CH_2Cl_2, –78 °C to r.t., 20 h (60%).

The pyranocarbazolequinones pyrayaquinone-A (**1**), -B (**2**), and -C (**3**), the prenylated or geranylated carbazolequinones murrayaquinone-B (**5**), -C (**7**), -D (**8**), and -E (**6**), and murrayafoline-B (**50**) were synthesized from 7-methoxy-3-



Scheme 9 Synthesis of murrayaquinone-C (**7**), and murrayaquinone-D (**8**). *Reagents and conditions*: (a) H_2 (1 atm), Lindlar catalyst (10 wt%), EtOAc, r.t., 22 h; (b) DMF, 180 °C, microwave (300 W), 1 h (79%, 2 steps; ratio of *E*/*Z* = 1.3:1); (c) Me_2SO_4 (5.2 equiv), K_2CO_3 (4.7 equiv), acetone, r.t. to 50 °C, 17.5 h (92%); (d) $LiAlH_4$ (10 equiv), THF, reflux, 22 h; (e) $(KSO_3)_2NO$ (14 equiv), acetone–H_2O (1:1), r.t. (22 h, **8**: 37%, 2 steps; **56**: 19%, 2 steps; 64 h, **7** and **57**: 62%, 2 steps, ratio of **7**/**57** = 3:1); (f) BuLi (1.0 equiv), MeI (50 equiv), THF, –78 °C to r.t., 22 h (59%).

methyl-1-tosyloxycarbazole (**22**) as a common precursor, which was obtained in three steps and 77% overall yield based on commercially available compounds. Pyran annulation and oxidation provided pyrayaquinone-A (**1**) in nine steps and 22% overall yield, pyrayaquinone-B (**2**) in eight steps and 27% overall yield, and pyrayaquinone-C (**3**) in eight steps and 30% overall yield. DIBAL-H-mediated ring opening of an intermediate pyrano[3,2-*a*]carbazole led to murrayaquinone-E (**6**) in nine steps and 34% overall yield and to murrayaquinone-B (**5**) in 10 steps and 27% overall yield. Murrayafoline-B (**50**) (9 steps, 40% yield) was obtained en route to murrayaquinone-B (**5**). Claisen rearrangement of a pyrayaquinone-C (**3**) precursor provided murrayaquinone-C (**7**) in 10 steps and 8% overall yield and murrayaquinone-D (**8**) in nine steps and 14% overall yield. Our route provided the latter compounds, **7** and **8**, for the first time as pure diastereoisomers. Moreover, the superiority of our palladium-catalyzed approach is emphasized by a comparison of the overall yields for our syntheses of the pyrayaquinones-A–C (**1**–**3**), the murrayaquinones-B–E (**5**–**8**), and murrayafoline-B (**50**) with those of the alternative routes described in the literature (Table 1).

All reactions were carried out in oven-dried glassware using anhydrous solvents under an argon atmosphere, unless stated otherwise. CH_2Cl_2, MeCN, THF, and toluene were dried using a solvent purification system (MBraun-SPS). Petroleum ether (PE) refers to the hydrocarbon mixture with a boiling range of 40–65 °C. $Pd(OAc)_2$ was recrystallized from glacial AcOH. All other chemicals were used as received from commercial sources. Flash chromatography was performed using silica gel from Acros Organics (0.035–0.070 mm), occasionally on a Büchi Sepacore system equipped with a UV monitor. TLC was performed with TLC plates from Merck (60 F254) using UV light for visualization. A CEM Discover microwave reactor was utilized for reactions taking place under microwave irradiation. Melting

Table 1 Comparison of the Different Synthetic Routes to the Pyrayaquinones **1**–**3**, the Murrayaquinones **5**–**8**, and Murrayafoline-B (**50**)

Carbazole alkaloid	No. of steps	Overall yield (%)	Previous total syntheses	
			No. of steps	Overall yield (%)
pyrayaquinone-A (**1**)	9	22	2[10] 5[8]	2.9[a] 0.5
pyrayaquinone-B (**2**)	8	27	6[18] 2[10] 5[8]	7 2.9[a] 0.7
pyrayaquinone-C (**3**)	8	30	6[18]	12
murrayaquinone-B (**5**)	10	27	6[18] 8[17a,17b] 7[17c]	10 0.9[a] 0.2[a]
murrayaquinone-C (**7**)	10	8	6[18]	9
murrayaquinone-D (**8**)	9	14	5[18]	12
murrayaquinone-E (**6**)	9	34	5[18]	10
murrayafoline-B (**50**)	9	40	6[17c]	0.8[a]

[a] Based on non-commercial starting material.

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 DRX 500 and Avance III 600 spectrometers. ACD/NMR Processor Academic Edition and Bruker TopSpin V2.1 were used for processing. 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 a EuroVector EuroEA3000 elemental analyzer.

1-(Benzyloxy)-3-iodobenzene (14b)

K_2CO_3 (4.71 g, 34.1 mmol) and benzyl bromide (4.05 mL, 5.83 g, 34.0 mmol) were added to a solution of 3-iodophenol (**14a**) (5.00 g, 22.7 mmol) in acetone (30 mL) at r.t. under an argon atmosphere and the mixture was stirred at r.t. for 6 h. Methanol (75 mL) and aqueous NH_4OH (25%, 75 mL) were added and stirring was continued for another 5 h. The mixture was extracted with Et_2O, the combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. Column chromatography (silica gel, isohexane–EtOAc, 3:1 to 1:1) provided compound **14b** (6.98 g, 22.5 mmol, 99%) as a colorless solid.

Mp 50.8–51.8 °C.

UV (MeOH): 210, 226 (sh), 277, 284 nm.

IR (ATR): 2934, 1582, 1562, 1520, 1475, 1460, 1415, 1398, 1381, 1323, 1302, 1273, 1235, 1158, 1059, 1008, 988, 918, 867, 842, 824, 773, 750, 698, 678 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 5.03 (s, 2 H), 6.94 (ddd, *J* = 8.5, 2.5, 0.9 Hz, 1 H), 7.00 (t, *J* = 8.2 Hz, 1 H), 7.30 (dt, *J* = 7.6, 1.3 Hz, 1 H), 7.32–7.37 (m, 2 H), 7.37–7.44 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 70.28 (CH_2), 94.49 (C), 114.62 (CH), 124.18 (CH), 127.65 (2 CH), 128.29 (CH), 128.79 (2 CH), 130.25 (CH), 130.94 (CH), 136.53 (C), 159.45 (C).

MS (EI): *m*/*z* (%) = 310 (15) [M^+], 92 (13), 91 (100), 65 (13), 64 (7), 63 (10).

Anal. Calcd for $C_{13}H_{11}IO$: C, 50.35; H, 3.58. Found: C, 50.92; H, 3.58.

2-{[3-(Benzyloxy)phenyl]amino}-5-methylphenol (17a)

A 25 mL round-bottom flask was charged with iodoarene **14b** (3.00 g, 9.67 mmol), 2-amino-5-methylphenol (**15a**) (2.38 g, 19.3 mmol), K_3PO_4 (4.11 g, 19.4 mmol), CuI (368 mg, 1.93 mmol), and DMF (14 mL) under an argon atmosphere. The reaction mixture was stirred for 18 h at 80 °C, diluted with EtOAc and washed with 2 M hydrochloric acid. The aqueous layer was extracted with EtOAc, the combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. Purification by column chromatography (silica gel, isohexane–EtOAc, 8:1) provided diarylamine **17a** (2.51 g, 8.22 mmol, 85%) as a brown oil.

UV (MeOH): 211, 277, 296 (sh) nm.

IR (ATR): 3504, 3462, 3379, 3034, 2919, 1593, 1493, 1451, 1391, 1319, 1290, 1257, 1221, 1178, 1149, 1112, 1082, 1013, 972, 945, 911, 850, 821, 772, 745, 693, 624 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.32 (s, 3 H), 4.98 (s, 2 H), 5.96 (br s, 1 H), 6.34–6.40 (m, 2 H), 6.49 (ddd, *J* = 8.2, 2.4, 0.8 Hz, 1 H), 6.69 (ddd, *J* = 7.9, 1.9, 0.6 Hz, 1 H), 6.82 (d, *J* = 1.3 Hz, 1 H), 7.04 (d, *J* = 7.9 Hz, 1 H), 7.11 (t, *J* = 8.0 Hz, 1 H), 7.28–7.41 (m, 5 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.37 (CH_3), 70.05 (CH_2), 102.54 (CH), 106.50 (CH), 108.69 (CH), 116.17 (CH), 121.75 (CH), 125.36 (C), 126.31 (CH), 127.71 (2 CH), 128.08 (CH), 128.69 (2 CH), 130.34 (CH), 137.05 (C), 137.75 (C), 147.41 (C), 151.94 (C), 160.16 (C).

MS (EI): *m*/*z* (%) = 306 (15), 305 (68) [M^+], 214 (8), 186 (17), 184 (8), 171 (5), 170 (5), 92 (8), 91 (100), 77 (8), 65 (17), 39 (5).

Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.84; H, 6.32; N, 4.64.

N-[3-(Benzyloxy)phenyl]-4-methyl-2-[(triisopropylsilyl)oxy]aniline (17b)

A mixture of diarylamine **17a** (2.67 g, 8.74 mmol), TIPSCl (2.03 g, 10.5 mmol), imidazole (714 mg, 10.5 mmol), and DMF (20 mL) was stirred under air at 50 °C for 24 h. A saturated aqueous solution of NH_4Cl was added and the mixture was extracted with Et_2O. The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. Purification by column chromatography (silica gel, isohexane–EtOAc, 10:1 to 3:1) provided diarylamine **17b** (3.86 g, 8.36 mmol, 96%) as a highly viscous orange oil.

UV (MeOH): 278, 309 (sh) nm.

IR (ATR): 3424, 3032, 2943, 2865, 1595, 1558, 1520, 1494, 1457, 1406, 1265, 1213, 1177, 1155, 1123, 1027, 997, 969, 881, 806, 734, 681 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.11 (d, *J* = 7.6 Hz, 18 H), 1.25–1.36 (m, 3 H), 2.26 (s, 3 H), 5.04 (s, 2 H), 6.53 (dd, *J* = 8.2, 2.5 Hz, 1 H), 6.64–6.70 (m, 3 H), 6.75 (t, *J* = 2.2 Hz, 1 H), 7.15 (t, *J* = 8.2 Hz, 1 H), 7.21 (d, *J* = 8.5 Hz, 1 H), 7.29–7.45 (m, 5 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.99 (3 CH), 18.17 (6 CH_3), 21.14 (CH_3), 70.07 (CH_2), 103.81 (CH), 106.78 (CH), 110.30 (CH), 117.30 (CH), 119.25 (CH), 121.76 (CH), 127.66 (2 CH), 128.05 (CH), 128.71 (2 CH), 130.15 (CH), 130.76 (C), 130.92 (C), 137.24 (C), 144.75 (C), 145.34 (C), 159.98 (C).

ESI-MS (+25 V): *m*/*z* = 462.4 [M + H]$^+$.

ESI-MS (–25 V): *m*/*z* = 460.0 [M – H]$^-$.

7-Hydroxy-3-methyl-1-[(triisopropylsilyl)oxy]carbazole (18)

A 10 mL microwave tube was charged with diarylamine **17b** (100 mg, 0.217 mmol), $Pd(OAc)_2$ (7.3 mg, 33 µmol), $Cu(OAc)_2$ (99.0 mg, 0.543 mmol), and glacial acetic acid (1 mL). The mixture was irradiated in a microwave reactor (300 W, 130 °C) for 30 min. An aqueous solution of K_2CO_3 was added and the mixture was extracted with EtOAc. The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated.

The residue was dissolved in EtOAc (5 mL) and Pd/C (10%, 20 mg) was added. The mixture was vigorously stirred for 3 d at r.t. under a hydrogen atmosphere. The solvent was evaporated and the residue was purified by column chromatography (silica gel, isohexane–EtOAc, 4:1 to 1:1) to provide hydroxycarbazole **18** (56.5 mg, 0.153 mmol, 71%) as a highly viscous brown oil.

UV (MeOH): 241, 302 nm.

Fluorescence (MeOH, exc. 250 nm): 364 nm.

IR (ATR): 3477, 3388, 2942, 2865, 2053, 2030, 1997, 1630, 1584, 1499, 1453, 1392, 1341, 1314, 1283, 1211, 1159, 1132, 1102, 1070, 1007, 957, 921, 881, 831, 785, 684, 644 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.16 (d, *J* = 7.6 Hz, 18 H), 1.39 (sept, *J* = 7.6 Hz, 3 H), 2.45 (s, 3 H), 6.65 (d, *J* = 0.9 Hz, 1 H), 6.70 (dd, *J* = 8.2, 2.2 Hz, 1 H), 6.88 (d, *J* = 2.2 Hz, 1 H), 7.34–7.37 (m, 1 H), 7.81 (br s, 1 H), 7.81 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.08 (3 CH), 18.23 (6 CH_3), 21.88 (CH_3), 97.09 (CH), 108.47 (CH), 112.39 (CH), 114.71 (CH), 118.25 (C), 121.40 (CH), 125.07 (C), 129.76 (C), 130.06 (C), 140.86 (C), 141.03 (C), 154.60 (C).

ESI-MS (+25 V): *m*/*z* = 370.3 $[M + H]^+$.

ESI-MS (–25 V): *m*/*z* = 368.1 $[M - H]^-$, 737.2 $[2M - H]^-$.

2-[(3-Methoxyphenyl)amino]-5-methylphenol (21a)

A 100 mL round-bottom flask was charged with 3-iodoanisole (**20**) (5.03 g, 21.5 mmol), 2-amino-5-methylphenol (**15a**) (5.58 g, 45.3 mmol), K_3PO_4 (9.12 g, 42.9 mmol), CuI (995 mg, 5.52 mmol), and DMF (30 mL) under an argon atmosphere. The reaction mixture was stirred for 8.5 h at 80 °C, then diluted with EtOAc and washed with 2 M hydrochloric acid. The aqueous layer was extracted with EtOAc, the combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. Purification by column chromatography (silica gel, isohexane–EtOAc, 8:1) provided diarylamine **21a** (4.43 g, 19.3 mmol, 90%) as a colorless solid.

Mp 77.5–78.0 °C.

UV (MeOH): 206 (sh), 212, 276, 299 (sh) nm.

IR (ATR): 3413, 3344, 3008, 2980, 2913, 1598, 1501, 1458, 1331, 1315, 1295, 1262, 1239, 1207, 1152, 1084, 1029, 956, 936, 868, 829, 770, 683, 631 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.32 (s, 3 H), 3.74 (s, 3 H), 5.88 (br s, 1 H), 6.27 (t, *J* = 2.2 Hz, 1 H), 6.34 (dd, *J* = 8.2, 2.0 Hz, 1 H), 6.42 (dd, *J* = 8.2, 2.2 Hz, 1 H), 6.70 (dd, *J* = 8.4, 1.7 Hz, 1 H), 6.83 (d, *J* = 1.6 Hz, 1 H), 7.06 (d, *J* = 7.9 Hz, 1 H), 7.11 (t, *J* = 8.0 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.37 (CH_3), 55.31 (CH_3), 101.49 (CH), 105.37 (CH), 108.18 (CH), 116.07 (CH), 121.75 (CH), 125.52 (C), 126.38 (CH), 130.33 (CH), 137.66 (C), 147.69 (C), 152.05 (C), 160.96 (C).

MS (EI): *m*/*z* (%) = 229 (100) $[M^+]$, 212 (13), 198 (16), 197 (16), 186 (9), 184 (9), 77 (16), 65 (11), 63 (9).

2-[(3-Methoxyphenyl)amino]-5-methylphenyl 4-Methylbenzenesulfonate (21b)

Tosyl chloride (730 mg, 3.83 mmol) was added to a mixture of diarylamine **21a** (806 mg, 3.52 mmol), Na_2CO_3 (74.0 mg, 698 μmol), $Bu_4N^+Cl^-$ (23.0 mg, 82.8 μmol), NaOH (573 mg, 14.3 mmol), H_2O (20 mL) and chlorobenzene (15 mL) under air. The reaction mixture was stirred for 3 h at r.t. and then diluted with CH_2Cl_2 and 2 M HCl. After separation, the aqueous layer was extracted with EtOAc. The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. Purification by column chromatography (silica gel, isohexane–EtOAc, 5:1 to 2:1) provided diarylamine **21b** (1.37 g, 3.57 mmol, 100%) as a colorless solid.

Mp 85.0–85.5 °C.

UV (MeOH): 222 (sh), 281, 294 (sh) nm.

IR (ATR): 3404, 2970, 1601, 1515, 1493, 1375, 1307, 1182, 1153, 1084, 1042, 948, 931, 883, 815, 778, 739, 695, 661 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.26 (s, 3 H), 2.31 (s, 3 H), 3.75 (s, 3 H), 5.65 (br s, 1 H), 6.26 (t, *J* = 2.2 Hz, 1 H), 6.33 (dd, *J* = 7.7, 1.7 Hz, 1 H), 6.42 (dd, *J* = 8.2, 2.2 Hz, 1 H), 6.94 (ddd, *J* = 8.2, 1.9, 0.6 Hz, 1 H), 7.00 (d, *J* = 1.6 Hz, 1 H), 7.07 (t, *J* = 8.0 Hz, 1 H), 7.13–7.17 (m, 3 H), 7.65–7.68 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.75 (CH_3), 21.75 (CH_3), 55.28 (CH_3), 103.02 (CH), 106.16 (CH), 110.04 (CH), 119.49 (CH), 124.41 (CH), 128.34 (CH), 128.45 (2 CH), 129.80 (2 CH), 129.97 (CH), 131.44 (C), 132.26 (C), 133.04 (C), 139.44 (C), 143.89 (C), 145.72 (C), 160.57 (C).

ESI-MS (+25 V): *m*/*z* = 384.3 $[M + H]^+$.

ESI-MS (–25 V): *m*/*z* = 382.0 $[M - H]^-$.

Anal. Calcd for $C_{21}H_{21}NO_4S$: C, 65.78; H, 5.52; N, 3.65; S, 8.36. Found: C, 66.41; H, 5.95; N, 3.68; S 8.19.

7-Methoxy-3-methyl-9*H*-carbazol-1-yl 4-Methylbenzenesulfonate (22)

A 100 mL round-bottom flask was charged with diarylamine **21b** (500 mg, 1.30 mmol), $Pd(OAc)_2$ (59.0 mg, 0.263 mmol), K_2CO_3 (35.0 mg, 0.253 mmol), and pivalic acid (5.00 g) under air. The reaction mixture was stirred for 22 h at 100 °C, then diluted with EtOAc and washed with 2 M aqueous NaOH solution. After separation, the aqueous layer was extracted with EtOAc. The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. Purification by column chromatography (silica gel, isohexane–EtOAc, 5:1) provided the 7-methoxycarbazole **22** (420 mg, 1.10 mmol, 85%) as a colorless solid.

Mp 167.5–168.0 °C.

UV (MeOH): 221 (sh), 237, 251 (sh), 303, 317 (sh) nm.

Fluorescence (MeOH, exc. 237 nm): 374 nm.

IR (ATR): 3389, 2922, 1624, 1492, 1450, 1365, 1344, 1306, 1276, 1190, 1170, 1076, 1029, 974, 880, 852, 803, 780, 879, 663 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.35 (s, 3 H), 2.44 (s, 3 H), 3.90 (s, 3 H), 6.55 (s, 1 H), 6.84 (dd, *J* = 8.5, 2.2 Hz, 1 H), 6.89 (d, *J* = 1.9 Hz, 1 H), 7.31 (d, *J* = 7.9 Hz, 2 H), 7.61 (s, 1 H), 7.73–7.78 (m, 2 H), 7.84 (d, *J* = 8.5 Hz, 1 H), 8.29 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.31 (CH_3), 21.88 (CH_3), 55.76 (CH_3), 95.01 (CH), 109.04 (CH), 116.83 (C), 118.50 (CH), 118.89 (CH), 121.24 (CH), 126.97 (C), 128.79 (2 CH), 129.52 (C), 129.93 (2 CH), 130.60 (C), 131.95 (C), 133.83 (C), 141.57 (C), 145.84 (C), 159.67 (C).

ESI-MS (+25 V): *m*/*z* = 382.3 $[M + H]^+$, 404.3 $[M + Na]^+$, 785.4 $[2M + Na]^+$.

ESI-MS (–25 V): *m*/*z* = 380.1 $[M - H]^-$.

Anal. Calcd for $C_{21}H_{19}NO_4S$: C, 66.12; H, 5.02; N, 3.67; S, 8.40. Found: C, 66.58; H, 5.27; N, 3.68; S, 8.29.

7-Hydroxy-3-methyl-1-(tosyloxy)carbazole (23)

A mixture of the carbazole **22** (2.32 g, 6.08 mmol), acetic acid (70 mL), and 48% aqueous hydrobromic acid (35 mL) was refluxed for 2 h under air. After diluting with H_2O and EtOAc, the layers were separated and the aqueous layer was extracted with EtOAc. The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. Purification by column chromatography (silica gel, isohexane–EtOAc, 3:1) provided the 7-hydroxycarbazole **23** (2.02 g, 5.50 mmol, 90%) as a colorless solid.

Mp 184.5–185.5 °C.

UV (MeOH): 221 (sh), 238, 252 (sh), 304 nm.

Fluorescence (MeOH, exc. 237 nm): 358 nm.

IR (ATR): 3350, 2922, 1732, 1698, 1626, 1582, 1493, 1452, 1348, 1318, 1237, 1204, 1163, 1073, 976, 884, 849, 812, 773, 732, 666 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.35 (s, 3 H), 2.44 (s, 3 H), 6.56 (d, *J* = 0.9 Hz, 1 H), 6.74 (dd, *J* = 8.5, 2.2 Hz, 1 H), 6.81 (d, *J* = 1.9 Hz, 1 H), 7.28–7.33 (m, 2 H), 7.60 (s, 1 H), 7.74–7.78 (m, 2 H), 7.81 (s, 1 H), 8.26 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.30 (CH_3), 21.87 (CH_3), 97.31 (CH), 109.22 (CH), 117.12 (C), 118.48 (CH), 118.96 (CH), 121.42 (CH), 126.92 (C), 128.77 (2 CH), 129.55 (C), 129.94 (2 CH), 130.65 (C), 131.92 (C), 133.82 (C), 141.59 (C), 145.91 (C), 155.38 (C).

ESI-MS (+10 V): *m*/*z* = 368.2 $[M + H]^+$.

ESI-MS (–25 V): *m*/*z* = 366.0 $[M - H]^-$, 732.6 $[2M - H]^-$.

Anal. Calcd for $C_{20}H_{17}NO_4S$: C, 65.38; H, 4.66; N, 3.81; S, 8.73. Found: C, 65.84; H, 4.85; N, 3.89; S, 8.18.

3-Methyl-7-[(2-methylbut-3-yn-2-yl)oxy]-1-(tosyloxy)carbazole (24)

DBU (22.0 µL, 22.4 mg, 0.147 mmol) and $CuCl_2·2H_2O$ (1.0 mg, 5.9 µmol) were added to a stirring solution of the 7-hydroxycarbazole **23** (41.0 mg, 0.112 mmol) in MeCN (3 mL) at 0 °C under an argon atmosphere. Subsequently, 1,1-dimethylpropargyl methyl carbonate (**11**) (20.6 mg, 0.145 mmol) in MeCN (1 mL) was added. The mixture was stirred at 0 °C for 3 h, then it was allowed to warm to r.t. After 20 h, an additional portion of 1,1-dimethylpropargyl methyl carbonate (**11**) (20.6 mg, 0.145 mmol) was added and the mixture was stirred for 3 d at the same temperature. Evaporation of the solvent and subsequent column chromatography (silica gel, isohexane–EtOAc, 4:1) provided propargyloxycarbazole **24** (37.8 mg, 87.3 µmol, 78%) as a colorless solid.

Mp 116.5–118.0 °C.

UV (MeOH): 238, 248 (sh), 258 (sh), 299 nm.

Fluorescence (MeOH, exc. 238 nm): 361 nm.

IR (ATR): 3392, 3280, 2986, 2920, 2111, 1622, 1583, 1486, 1451, 1398, 1360, 1336, 1304, 1272, 1260, 1217, 1190, 1173, 1133, 1077, 1000, 972, 866, 850, 825, 806, 779, 690, 663 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.70 (s, 6 H), 2.36 (s, 3 H), 2.44 (s, 3 H), 2.62 (d, *J* = 0.9 Hz, 1 H), 6.57 (s, 1 H), 7.06 (ddd, *J* = 8.5, 2.0, 0.8 Hz, 1 H), 7.31 (d, *J* = 8.5 Hz, 2 H), 7.34 (d, *J* = 2.2 Hz, 1 H), 7.63 (s, 1 H), 7.76 (d, *J* = 8.2 Hz, 2 H), 7.84 (d, *J* = 8.5 Hz, 1 H), 8.32 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.31 (CH_3), 21.88 (CH_3), 29.82 (2 CH_3), 73.04 (C), 74.09 (CH), 86.49 (C), 103.94 (CH), 115.26 (CH), 118.79 (CH), 119.34 (CH), 120.50 (CH), 124.86 (C), 126.81 (C), 128.80 (2 CH), 129.45 (C), 129.93 (2 CH), 130.92 (C), 131.94 (C), 133.89 (C), 140.81 (C), 145.86 (C), 155.13 (C).

ESI-MS (+10 V): *m*/*z* = 434.3 $[M + H]^+$.

Anal. Calcd for $C_{25}H_{23}NO_4S$: C, 69.26; H, 5.35; N, 3.23; S, 7.40. Found: C, 69.92; H, 5.47; N, 3.39; S, 7.00.

3,3,8-Trimethyl-10-(tosyloxy)-3,11-dihydropyrano[3,2-*a*]carbazole (25)

Method A (from 24)

A solution of propargyloxycarbazole **24** (37.0 mg, 85.5 µmol) in toluene (3 mL) was refluxed for 16 h under air. Evaporation of the solvent and subsequent column chromatography (silica gel, isohexane–EtOAc, 20:1) provided pyranocarbazole **25** (36.9 mg, 85.3 µmol, 100%) as a colorless solid.

Method B (from 23)

DBU (1.04 g, 6.83 mmol) and $CuCl_2·2H_2O$ (5.0 mg, 29 µmol) were added to a stirred solution of the 7-hydroxycarbazole **23** (1.25 g, 3.40 mmol) in MeCN (15 mL) under air at r.t. Subsequently, 1,1-dimethylpropargyl methyl carbonate (**11**) (967 mg, 6.80 mmol) in MeCN (5 mL) was added. The mixture was stirred at r.t. for 28 h, then the solvent was evaporated and the mixture was filtered over a short pad of silica gel (isohexane–EtOAc, 3:1).

The solvent was evaporated, the crude mixture was dissolved in toluene (25 mL) and refluxed for 19 h under air. Evaporation of the solvent and subsequent column chromatography (silica gel, isohexane–EtOAc, 4:1 to 1:1) provided pyranocarbazole **25** (1.26 g, 2.91 mmol, 85%) as a colorless solid.

Mp 199.0–201.0 °C.

UV (MeOH): 230, 236, 278 (sh), 287, 326, 352 nm.

Fluorescence (MeOH, exc. 287 nm): 405 nm.

IR (ATR): 3425, 3386, 2955, 2915, 2030, 1976, 1639, 1597, 1580, 1484, 1451, 1402, 1366, 1341, 1302, 1282, 1255, 1213, 1189, 1175, 1151, 1115, 1090, 1051, 1010, 984, 967, 898, 852, 803, 779, 754, 721, 690, 661 cm^{-1}.

^1H NMR (600 MHz, DMSO-d_6): δ = 1.41 (s, 6 H), 2.32 (s, 3 H), 2.34 (s, 3 H), 5.79 (d, *J* = 9.8 Hz, 1 H), 6.59 (d, *J* = 8.3 Hz, 1 H), 6.74–6.77 (m, 1 H), 7.07 (d, *J* = 10.2 Hz, 1 H), 7.34–7.39 (m, 2 H), 7.68 (s, 1 H), 7.74 (d, *J* = 8.3 Hz, 1 H), 7.78–7.83 (m, 2 H), 11.09 (s, 1 H).

^{13}C NMR (150 MHz, DMSO-d_6): δ = 20.87 (CH_3), 21.10 (CH_3), 27.44 (2 CH_3), 75.84 (C), 104.89 (C), 109.26 (CH), 116.32 (C), 117.65 (CH), 117.71 (CH), 118.14 (CH), 120.52 (CH), 126.15 (C), 128.14 (C), 128.66 (2 CH), 129.13 (CH), 129.82 (2 CH), 130.07 (C), 131.48 (C), 133.69 (C), 136.97 (C), 145.73 (C), 151.38 (C).

ESI-MS (+25 V): *m*/*z* = 434.3 $[M + H]^+$.

ESI-MS (–25 V): *m*/*z* = 432.1 $[M - H]^-$.

Anal. Calcd for $C_{25}H_{23}NO_4S$: C, 69.26; H, 5.35; N, 3.23; S, 7.40. Found: C, 69.24; H, 5.43; N, 3.25; S, 6.90.

Pyrayaquinone-B (2)

$LiAlH_4$ (2.4 M in THF, 0.20 mL, 0.48 mmol) was added to a solution of pyranocarbazole **25** (31.3 mg, 72.2 µmol) in THF (7 mL) under an argon atmosphere at r.t. The solution was refluxed for 2 h and subsequently quenched with H_2O at 0 °C. After extraction with EtOAc, the combined organic layers were dried ($MgSO_4$), the solvent was evaporated and the residue was filtered over a short pad of silica gel (isohexane–EtOAc, 4:1) to yield crude 10-hydroxy-3,3,8-trimethyl-3,11-dihydropyrano[3,2-*a*]carbazole (**26**) (13.3 mg, 47.6 µmol).

The crude hydroxycarbazole **26** (12.4 mg, 44.4 µmol) was dissolved in acetone (7 mL) under air. Subsequently, potassium nitrosodisulfonate (Frémy's salt) (35.7 mg, 0.133 mmol) in H_2O (7 mL) was added and the mixture was stirred vigorously at r.t. for 2.5 h. The mixture was diluted with EtOAc. After extraction with EtOAc, the combined organic layers were dried ($MgSO_4$). Evaporation of the solvent and subsequent column chromatography (silica gel, isohexane–EtOAc, 4:1) provided pyrayaquinone-B (**2**) (9.1 mg, 31 µmol, 46%) as a dark purple solid.

Mp 225–230 °C (sublimed) [Lit.[7] 244 °C (dec.)].

UV (MeOH): 247, 268 (sh), 317, 409 nm.

Fluorescence (MeOH, exc. 247 nm): 361 nm.

IR (ATR): 3275, 3084, 2975, 2921, 2056, 2030, 2009, 1975, 1734, 1717, 1699, 1629, 1605, 1578, 1539, 1498, 1466, 1420, 1399, 1376, 1356, 1323, 1265, 1211, 1156, 1135, 1117, 1053, 1021, 993, 942, 898, 848, 825, 767, 725, 694 cm^{-1}.

^{1}H NMR (500 MHz, pyridine-d_5): δ = 1.48 (s, 6 H), 2.07 (d, *J* = 1.6 Hz, 3 H), 5.69 (d, *J* = 9.8 Hz, 1 H), 6.49 (q, *J* = 1.6 Hz, 1 H), 7.12 (dd, *J* = 8.5, 0.6 Hz, 1 H), 7.15 (dd, *J* = 9.8, 0.6 Hz, 1 H), 8.31 (d, *J* = 8.5 Hz, 1 H), 13.72 (br s, 1 H).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.47 (s, 6 H), 2.14 (d, *J* = 1.5 Hz, 3 H), 5.71 (d, *J* = 9.8 Hz, 1 H), 6.45 (q, *J* = 1.6 Hz, 1 H), 6.58 (d, *J* = 9.8 Hz, 1 H), 6.86 (d, *J* = 8.7 Hz, 1 H), 7.94 (d, *J* = 8.7 Hz, 1 H), 9.22 (br s, 1 H).

^{13}C NMR (125 MHz, pyridine-d_5): δ = 15.80 (CH_3), 27.65 (2 CH_3), 76.69 (C), 106.96 (C), 115.73 (CH), 117.58 (CH), 117.70 (C), 119.70 (C), 123.14 (CH), 130.24 (CH), 132.26 (CH), 136.67 (C), 147.49 (C), 152.35 (C), 180.03 (C=O), 183.99 (C=O); 1 C not visible due to signal overlap with solvent peaks.

^{13}C NMR (150 MHz, $CDCl_3$): δ = 16.28 (CH_3), 27.80 (2 CH_3), 76.87 (C), 105.69 (C), 116.00 (CH), 116.21 (CH), 117.85 (C), 119.05 (C), 123.28 (CH), 130.64 (CH), 131.73 (CH), 134.24 (C), 134.78 (C), 148.35 (C), 152.64 (C), 179.98 (C=O), 183.93 (C=O).

ESI-MS (+10 V): *m*/*z* = 294.2 $[M + H]^+$, 609.1 $[2M + Na]^+$.

ESI-MS (–10 V): *m*/*z* = 291.9 $[M - H]^-$.

Anal. Calcd for $C_{18}H_{15}NO_3$: C, 73.71; H, 5.15; N, 4.78. Found: C, 73.26; H, 5.40; N, 4.68.

7-[(3,7-Dimethyloct-6-en-1-yn-3-yl)oxy]-3-methylcarbazol-1-yl 4-Methylbenzenesulfonate (27)

DBU (160 µL, 163 mg, 1.07 mmol) and $CuCl_2 \cdot 2H_2O$ (2.5 mg, 15 µmol) were added to a stirring solution of the 7-hydroxycarbazole **23** (201 mg, 0.548 mmol) in MeCN (4 mL) at 0 °C under an argon atmosphere. Subsequently, 3,7-dimethyloct-6-en-1-yn-3-yl methyl carbonate (**12**) (230 mg, 1.09 mmol) in MeCN (2 mL) was added. The mixture was allowed to warm to r.t. After 21 h, additional portions of 3,7-dimethyloct-6-en-1-yn-3-yl methyl carbonate (**12**) (20.0 mg, 95.1 µmol) and DBU (20 µL, 0.13 mmol) were added and the mixture was stirred for 24 h at the same temperature. EtOAc and 2 M hydrochloric acid were added, the layers were separated and the aqueous layer was extracted with EtOAc. The combined organic layers were dried ($MgSO_4$). Evaporation of the solvent and subsequent column chromatography (silica gel, isohexane–EtOAc, 15:1) provided propargyloxycarbazole **27** (190 mg, 0.379 mmol, 69%) as a yellow solid.

Mp 130.0–131.0 °C.

UV (MeOH): 222 (sh), 238, 249 (sh), 299, 323, 337 (sh) nm.

Fluorescence (MeOH, exc. 237 nm): 365 nm.

IR (ATR): 3393, 3304, 2972, 2917, 2853, 1733, 1621, 1584, 1492, 1450, 1397, 1370, 1337, 1304, 1267, 1214, 1176, 1151, 1078, 972, 906, 876, 848, 803, 772, 664 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.63 (s, 3 H), 1.65 (s, 3 H), 1.71 (d, *J* = 0.9 Hz, 3 H), 1.89 (ddd, *J* = 13.6, 11.7, 5.4 Hz, 1 H), 1.99 (ddd, *J* = 13.6, 11.7, 5.0 Hz, 1 H), 2.23–2.41 (m, 2 H), 2.36 (s, 3 H), 2.44 (s, 3 H), 2.64 (s, 1 H), 5.17 (tsept, *J* = 7.2, 1.4 Hz, 1 H), 6.55–6.57 (m, 1 H), 7.05 (dd, *J* = 8.5, 2.2 Hz, 1 H), 7.29–7.32 (m, 2 H), 7.33 (d, *J* = 1.9 Hz, 1 H), 7.63 (s, 1 H), 7.74–7.78 (m, 2 H), 7.84 (d, *J* = 8.5 Hz, 1 H), 8.31 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.84 (CH_3), 21.31 (CH_3), 21.88 (CH_3), 23.35 (CH_2), 25.85 (CH_3), 27.10 (CH_3), 42.69 (CH_2), 75.35 (C), 76.08 (C), 85.50 (CH), 103.92 (CH), 115.30 (CH), 118.64 (C), 118.78 (CH), 119.30 (CH), 120.47 (CH), 123.66 (CH), 126.83 (C), 128.80 (2 CH), 129.43 (C), 129.93 (2 CH), 130.90 (C), 131.95 (C), 132.33 (C), 133.88 (C), 140.81 (C), 145.86 (C), 155.16 (C).

ESI-MS (+25 V): *m*/*z* = 502.5 $[M + H]^+$, 524.5 $[M + Na]^+$.

ESI-MS (–25 V): *m*/*z* = 500.1 $[M - H]^-$.

Anal. Calcd for $C_{30}H_{31}NO_4S$: C, 71.83; H, 6.23; N, 2.79; S, 6.39. Found: C, 71.97; H, 6.53; N, 2.70; S, 5.93.

3,8-Dimethyl-3-(4-methylpent-3-enyl)-10-(tosyloxy)-3,11-dihydropyrano[3,2-*a*]carbazole (28)

A solution of propargyloxycarbazole **27** (74.0 mg, 0.148 mmol) in toluene (4 mL) was refluxed for 22 h under air. Evaporation of the solvent and subsequent column chromatography (silica gel, isohexane–EtOAc, 15:1) provided pyranocarbazole **28** (74.0 mg, 0.148 mmol, 100%) as a yellow solid.

Mp 149.0–151.0 °C.

UV (MeOH): 226 (sh), 233, 238, 279 (sh), 288, 326, 336 (sh), 352 nm.

Fluorescence (MeOH, exc. 237 nm): 365 nm.

IR (ATR): 3383, 2971, 2923, 2846, 2030, 1640, 1581, 1485, 1474, 1448, 1371, 1340, 1304, 1275, 1213, 1187, 1175, 1122, 1087, 1051, 1008, 982, 969, 911, 887, 850, 805, 784, 757, 719, 666 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.45 (s, 3 H), 1.62 (s, 3 H), 1.66 (d, *J* = 1.3 Hz, 3 H), 1.72 (ddd, *J* = 13.9, 11.0, 6.0 Hz, 1 H), 1.80 (ddd, *J* = 13.9, 10.4, 6.6 Hz, 1 H), 2.11–2.20 (m, 2 H), 2.36 (s, 3 H), 2.43 (s, 3 H), 5.11 (tsept, *J* = 7.3, 1.3 Hz, 1 H), 5.68 (d, *J* = 9.8 Hz, 1 H), 6.56–6.60 (m, 2 H), 6.71 (dd, *J* = 8.5, 0.6 Hz, 1 H), 7.28–7.33 (m, 2 H), 7.57 (d, *J* = 0.6 Hz, 1 H), 7.67 (d, *J* = 8.5 Hz, 1 H), 7.73–7.78 (m, 2 H), 8.05 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.79 (CH_3), 21.32 (CH_3), 21.88 (CH_3), 22.88 (CH_2), 25.82 (CH_3), 26.18 (CH_3), 41.01 (CH_2), 78.71 (C), 104.95 (C), 110.23 (CH), 117.09 (C), 117.21 (CH), 118.47 (CH), 119.04 (CH), 120.63 (CH), 124.18 (CH), 127.36 (C), 128.78 (2 CH), 128.98 (CH), 129.78 (C), 129.99 (2 CH), 130.53 (C), 131.93 (C), 132.09 (C), 133.99 (C), 136.97 (C), 145.94 (C), 152.45 (C).

ESI-MS (+10 V): *m*/*z* = 502.5 $[M + H]^+$, 524.6 $[M + Na]^+$.

ESI-MS (–25 V): *m*/*z* = 500.1 $[M - H]^-$.

Anal. Calcd for $C_{30}H_{31}NO_4S$: C, 71.83; H, 6.23; N, 2.79; S, 6.39. Found: C, 72.02; H, 6.38; N, 2.75; S, 6.08.

Pyrayaquinone-C (3)

A mixture of pyrano[3,2-*a*]carbazole **28** (74.0 mg, 0.148 mmol), NaOH (340 mg, 8.5 mmol), ethanol (4.7 mL), and H_2O (1.0 mL) was refluxed for 2.5 h. EtOAc was added, the layers were separated and the aqueous layer was extracted with EtOAc. The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. The residue was subjected to filtration over a short pad of silica gel (isohexane–EtOAc, 15:1) to provide crude hydroxycarbazole **29** (44.4 mg, 0.130 mmol).

The crude hydroxycarbazole **29** (35.3 mg, 0.102 mmol) was dissolved in acetone (4 mL) under air. Subsequently, potassium nitrosodisulfonate (Frémy's salt) (101.7 mg, 0.379 mmol) in H_2O (4 mL) was added and the mixture was stirred vigorously at r.t. for 18 h. The mixture was diluted with EtOAc. After extraction with EtOAc, the combined organic layers were dried ($MgSO_4$). Evaporation of the solvent and subsequent column chromatography (silica gel, isohexane–EtOAc, 2:1) provided pyrayaquinone-C (**3**) (26.7 mg, 74.0 µmol, 64%) as a dark purple solid.

Mp 218.0–220.0 °C (dec.) [Lit.[11] 223 °C (dec.)].

UV (MeOH): 248, 270 (sh), 320, 410 nm.

Fluorescence (MeOH, exc. 247 nm): 375 nm.

IR (ATR): 3257, 3085, 2966, 2914, 2846, 2438, 2055, 2030, 2009, 1978, 1661, 1630, 1606, 1580, 1541, 1501, 1468, 1421, 1405, 1370, 1305, 1261, 1208, 1169, 1134, 1082, 1056, 1022, 991, 942, 909, 865, 847, 823, 781, 731, 703 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.44 (s, 3 H), 1.57 (s, 3 H), 1.65 (d, *J* = 0.9 Hz, 3 H), 1.71 (ddd, *J* = 13.9, 11.0, 6.0 Hz, 1 H), 1.78 (ddd, *J* = 13.9, 10.1, 6.6 Hz, 1 H), 2.07–2.21 (m, 2 H), 2.15 (d, *J* = 1.9 Hz, 3 H), 5.09 (tsept, *J* = 7.3, 1.3 Hz, 1 H), 5.68 (d, *J* = 10.1 Hz, 1 H), 6.45 (d, *J* = 1.6 Hz, 1 H), 6.61 (d, *J* = 9.8 Hz, 1 H), 6.86 (d, *J* = 8.5 Hz, 1 H), 7.94 (d, *J* = 8.5 Hz, 1 H), 9.28 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.28 (CH_3), 17.78 (CH_3), 22.84 (CH_2), 25.81 (CH_3), 26.30 (CH_3), 41.08 (CH_2), 79.26 (C), 105.48 (C), 116.12 (CH), 116.40 (CH), 117.85 (C), 118.93 (C), 123.23 (CH), 123.97 (CH), 129.70 (CH), 131.74 (CH), 132.10 (C), 134.29 (C), 134.73 (C), 148.32 (C), 152.89 (C), 180.00 (C), 183.95 (C).

ESI-MS (+25 V): *m*/*z* = 362.4 $[M + H]^+$, 745.4 $[2M + Na]^+$.

ESI-MS (–25 V): *m*/*z* = 360.1 $[M - H]^-$, 743.3 $[2M + Na - 2 H]^-$.

HRMS: *m*/*z* $[M]^+$ calcd for $C_{23}H_{23}NO_3$: 361.1678; found: 361.1662.

6-Bromo-7-methoxy-3-methyl-1-(tosyloxy)carbazole (31)

N-Bromosuccinimide (234 mg, 1.31 mmol) was added to a solution of the carbazole **22** (500 mg, 1.31 mmol) in CH_2Cl_2 (30 mL) under an argon atmosphere. The reaction mixture was stirred for 3 d at r.t., then the solvent was evaporated. Purification by column chromatography (silica gel, isohexane–EtOAc, 8:1 to 6:1) provided bromocarbazole **31** (566 mg, 1.23 mmol, 94%) as a colorless solid.

Mp 200.0–201.0 °C.

UV (MeOH): 238, 263 (sh), 306, 324 (sh), 337 (sh) nm.

Fluorescence (MeOH, exc. 306 nm): 384 nm.

IR (ATR): 3424, 2972, 2945, 2919, 2853, 1621, 1491, 1454, 1397, 1364, 1333, 1289, 1215, 1198, 1171, 1079, 1036, 973, 873, 845, 813, 803, 779, 753, 703, 661 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 2.45 (s, 3 H), 3.97 (s, 3 H), 6.51–6.59 (m, 1 H), 6.92 (s, 1 H), 7.32 (d, *J* = 8.7 Hz, 2 H), 7.57 (d, *J* = 0.8 Hz, 1 H), 7.71–7.83 (m, 2 H), 8.10 (s, 1 H), 8.43 (br s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.30 (CH_3), 21.89 (CH_3), 56.61 (CH_3), 94.66 (CH), 104.10 (C), 117.66 (C), 118.68 (CH), 119.48 (CH), 124.77 (CH), 126.04 (C), 128.80 (2 CH), 129.98 (2 CH), 130.20 (C), 130.76 (C), 131.83 (C), 133.88 (C), 140.45 (C), 145.96 (C), 155.18 (C).

ESI-MS (+25 V): *m*/*z* = 460.2/462.2 $[M + H]^+$.

ESI-MS (–50 V): *m*/*z* = 457.8/459.8 $[M - H]^-$.

Anal. Calcd for $C_{21}H_{18}BrNO_4S$: C, 54.79; H, 3.94; N, 3.04; S, 6.96. Found: C, 55.17; H, 3.87; N, 3.09; S, 7.23.

7-Methoxy-3-methyl-6-(3-methylbut-2-enyl)-1-(tosyloxy)carbazole (32) and 6-(1,1-Dimethylprop-2-enyl)-7-methoxy-3-methyl-1-(tosyloxy)carbazole (32a)

A mixture of bromocarbazole **31** (50.0 mg, 0.109 mmol), 3-methyl-2-butenylboronic acid pinacol ester (40.0 mg, 0.204 mmol), $(PPh_3)_4Pd$ (13.0 mg, 11.2 µmol), NaOH (175 mg, 4.38 mmol), toluene (2 mL), and H_2O (2 mL) was vigorously stirred at r.t. under an argon atmosphere. After 21 h, H_2O was added and the mixture was extracted with EtOAc. Evaporation of the solvent and subsequent column chromatography (silica gel, isohexane–EtOAc, 8:1) provided prenylcarbazole **32** (36.2 mg, 80.5 µmol, 74%), and *tert*-prenylcarbazole **32a** (12.1 mg, 26.9 µmol, 25%) both as colorless solids.

Prenylcarbazole 32

Mp 141.0–141.5 °C.

UV (MeOH): 239, 251 (sh), 263 (sh), 305, 323 (sh), 335 (sh) nm.

Fluorescence (MeOH, exc. 239 nm): 373 nm.

IR (ATR): 3415, 3028, 2969, 2923, 2840, 1734, 1717, 1698, 1684, 1623, 1595, 1579, 1485, 1456, 1376, 1334, 1294, 1230, 1216, 1190, 1175, 1162, 1118, 1093, 1063, 1017, 961, 876, 842, 816, 786, 764, 705 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.76 (d, *J* = 0.8 Hz, 3 H), 1.78 (d, *J* = 1.1 Hz, 3 H), 2.35 (s, 3 H), 2.44 (s, 3 H), 3.43 (d, *J* = 6.8 Hz, 2 H), 3.92 (s, 3 H), 5.39 (tsept, *J* = 7.2, 1.5 Hz, 1 H), 6.49–6.55 (m, 1 H), 6.86 (s, 1 H), 7.30 (s, 2 H), 7.60 (dd, *J* = 1.5, 0.8 Hz, 1 H), 7.68 (s, 1 H), 7.72–7.78 (m, 2 H), 8.25 (br s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$,): δ = 17.94 (CH_3), 21.29 (CH_3), 21.86 (CH_3), 26.04 (CH_3), 28.94 (CH_2), 55.77 (CH_3), 93.16 (CH), 116.04 (C), 118.42 (CH), 118.49 (CH), 120.49 (CH), 123.29 (CH), 123.59 (C), 127.18 (2 CH), 128.79 (2 CH), 129.22 (C), 129.90 (C), 130.41 (C), 132.06 (C), 132.37 (C), 133.90 (C), 140.00 (C), 145.75 (C), 157.68 (C).

ESI-MS (+10 V): *m*/*z* = 450.4 $[M + H]^+$.

ESI-MS (–10 V): *m*/*z* = 448.2 $[M - H]^-$.

Anal. Calcd for $C_{26}H_{27}NO_4S$: C, 69.46; H, 6.05; N, 3.12; S, 7.13. Found: C, 69.45; H, 6.25; N, 3.06; S, 6.87.

tert-Prenylcarbazole 32a

Mp 193.0–194.5 °C.

IR (ATR): 3397, 2998, 2969, 2949, 2917, 2866, 1628, 1597, 1580, 1496, 1454, 1366, 1292, 1254, 1195, 1169, 1087, 1062, 1014, 976, 904, 884, 855, 809, 782, 714, 657, 633 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.54 (s, 6 H), 2.34 (s, 3 H), 2.44 (s, 3 H), 3.88 (s, 3 H), 4.96 (dd, *J* = 17.3, 1.4 Hz, 1 H), 4.97 (dd, *J* = 10.7, 1.4 Hz, 1 H), 6.27 (dd, *J* = 17.3, 10.7 Hz, 1 H), 6.50 (s, 1 H), 6.89 (s, 1 H), 7.30 (d, *J* = 7.9 Hz, 2 H), 7.62 (s, 1 H), 7.74 (d, *J* = 8.5 Hz, 2 H), 7.85 (s, 1 H), 8.29 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.31 (CH_3), 21.88 (CH_3), 27.95 (2 CH_3), 40.87 (C), 55.51 (CH_3), 94.59 (CH), 109.79 (CH_2), 115.72 (C), 118.31 (CH), 118.54 (CH), 118.58 (CH), 127.47 (C), 128.80 (2 CH), 129.32 (C), 129.90 (2 CH), 130.22 (C), 130.52 (C), 131.93 (C), 133.90 (C), 140.12 (C), 145.77 (C), 148.81 (CH), 158.77 (C).

ESI-MS (+25 V): *m*/*z* = 450.3 $[M + H]^+$.

Anal. Calcd for $C_{26}H_{27}NO_4S$: C, 69.46; H, 6.05; N, 3.12; S, 7.13. Found: C, 68.62; H, 5.99; N, 3.07; S, 6.82.

2,2,7-Trimethyl-9-(tosyloxy)-2,3,4,10-tetrahydropyrano[2,3-*b*]carbazole (33)

A 1.5 mL GC-vial was charged with prenylcarbazole **32** (30.0 mg, 66.7 µmol) and pyridinium chloride (300 mg, 2.60 mmol). The mixture was stirred at 170 °C for 5 h, then H_2O was added and the mixture was extracted with EtOAc. Evaporation of the solvent and subsequent column chromatography (silica gel, isohexane–EtOAc, 8:1) provided the tetrahydropyrano[2,3-*b*]carbazole **33** (23.3 mg, 53.5 µmol, 80%) as a colorless solid.

Mp 167.5–168.5 °C.

UV (MeOH): 220, 236 (sh), 242, 254 (sh), 310, 326 (sh), 340 (sh) nm.

Fluorescence (MeOH, exc. 242 nm): 375 nm.

IR (ATR): 3415, 2969, 2922, 2846, 2054, 2030, 2010, 1640, 1580, 1494, 1455, 1436, 1368, 1336, 1291, 1255, 1217, 1175, 1153, 1118, 1094, 1065, 973, 940, 848, 812, 770 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 (s, 6 H), 1.87 (t, *J* = 6.8 Hz, 2 H), 2.35 (s, 3 H), 2.43 (s, 3 H), 2.95 (t, *J* = 6.6 Hz, 2 H), 6.58 (s, 1 H), 6.75 (s, 1 H), 7.27–7.32 (m, 2 H), 7.55 (s, 1 H), 7.63 (s, 1 H), 7.75 (s, 2 H), 8.02 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.31 (CH_3), 21.86 (CH_3), 22.94 (CH_2), 27.09 (2 CH_3), 33.25 (CH_2), 74.70 (C), 98.46 (CH), 114.48 (C), 116.77 (C), 118.31 (CH), 118.85 (CH), 120.52 (CH), 126.98 (C), 128.73 (2 CH), 129.11 (C), 129.89 (2 CH), 130.79 (C), 132.13 (C), 133.78 (C), 140.41 (C), 145.77 (C), 154.06 (C).

ESI-MS (+10 V): *m*/*z* = 436.4 $[M + H]^+$.

ESI-MS (–25 V): *m*/*z* = 434.1 $[M - H]^-$.

Anal. Calcd for $C_{25}H_{25}NO_4S$: C, 68.94; H, 5.79; N, 3.22; S, 7.36. Found: C, 68.98; H, 5.89; N, 3.25; S, 7.41.

2,2,7-Trimethyl-2,3,4,10-tetrahydropyrano[2,3-*b*]carbazole-6,9-dione (35)

Lithium aluminum hydride (2.4 M in THF, 0.50 mL, 1.2 mmol) was added to a solution of compound **33** (49.0 mg, 0.113 mmol) in THF (8 mL) under an argon atmosphere at r.t. The solution was refluxed for 14 h and subsequently quenched with H_2O at 0 °C, then a saturated aqueous solution of sodium potassium tartrate was added. After extraction with EtOAc, the combined organic layers were dried ($MgSO_4$), the solvent was evaporated and the residue was filtered over a short pad of silica gel (isohexane–EtOAc, 1:1). The solvent was evaporated and the residue was dissolved in acetone (7 mL).

This solution was added to a stirred solution of potassium nitrosodisulfonate (Frémy's salt) (210 mg, 0.783 mmol) in H_2O (7 mL) at r.t. under air. The mixture was stirred vigorously at the same temperature for 40 min. The mixture was diluted with EtOAc. After extraction with EtOAc, the combined organic layers were dried ($MgSO_4$). Evaporation of the solvent and subsequent column chromatography (silica gel, isohexane–EtOAc, 7:1) provided the tetrahydropyrano[2,3-*b*]carbazole-dione **35** (20.0 mg, 67.7 mmol, 60%) as a dark purple solid.

Mp 225–230 °C (sublimed).

UV (MeOH): 232, 265, 293 (sh), 425 nm.

Fluorescence (MeOH, exc. 232 nm): 343 nm.

IR (ATR): 3244, 3183, 2969, 2925, 1658, 1626, 1604, 1574, 1559, 1532, 1498, 1458, 1439, 1398, 1378, 1338, 1295, 1268, 1243, 1216, 1154, 1120, 1092, 1005, 976, 927, 898, 879, 857, 841, 750, 720, 680, 664, 606 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (s, 6 H), 1.86 (t, *J* = 6.9 Hz, 2 H), 2.14 (d, *J* = 1.6 Hz, 3 H), 2.96 (t, *J* = 6.9 Hz, 2 H), 6.43 (q, *J* = 1.6 Hz, 1 H), 6.82 (s, 1 H), 7.90 (s, 1 H), 9.12 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.25 (CH_3), 23.11 (CH_2), 27.15 (2 CH_3), 32.99 (CH_2), 75.24 (C), 99.05 (CH), 116.94 (C), 118.51 (C), 121.02 (C), 122.81 (CH), 131.76 (CH), 134.89 (C), 137.54 (C), 148.20 (C), 154.84 (C), 179.98 (C=O), 184.01 (C=O).

ESI-MS (+25 V): *m*/*z* = 296.3 $[M + H]^+$, 613.2 $[2M + Na]^+$.

ESI-MS (–50 V): *m*/*z* = 293.9 $[M - H]^-$.

Pyrayaquinone-A (1)

A mixture of compound **35** (20.0 mg, 67.7 µmol), DDQ (33.8 mg, 0.149 mmol) and toluene (3 mL) was stirred at 100 °C under air. After 3.5 h, the solvent was removed and the residue was subjected to column chromatography (silica gel, isohexane–EtOAc, 1:1) to provide pyrayaquinone-A (**1**) (17.0 mg, 58.0 µmol, 86%) as a dark purple solid.

Mp 225–230 °C (dec.) [Lit.[7] 222 °C (dec.)].

UV (MeOH): 214, 250, 459 nm.

Fluorescence (MeOH, exc. 250 nm): 360 nm.

IR (ATR): 3177, 3133, 2976, 2928, 2140, 2048, 2030, 2009, 1975, 1716, 1659, 1630, 1604, 1573, 1534, 1490, 1471, 1457, 1442, 1376, 1360, 1320, 1295, 1272, 1216, 1188, 1154, 1116, 1085, 1039, 1007, 979, 905, 888, 867, 849, 768, 741, 694 cm^{-1}.

^{1}H NMR (600 MHz, DMSO-d_6): δ = 1.39 (s, 6 H), 2.02 (d, *J* = 1.9 Hz, 3 H), 5.84 (d, *J* = 9.8 Hz, 1 H), 6.52 (q, *J* = 1.5 Hz, 1 H), 6.60 (d, *J* = 9.8 Hz, 1 H), 6.77 (s, 1 H), 7.68 (s, 1 H), 12.54 (s, 1 H).

^{13}C NMR (150 MHz, DMSO-d_6): δ = 15.46 (CH_3), 27.64 (2 CH_3), 76.42 (C), 99.23 (CH), 116.00 (C), 118.34 (C), 118.73 (CH), 119.97 (C), 122.45 (CH), 131.51 (CH), 131.61 (CH), 135.09 (C), 138.48 (C), 147.12 (C), 152.26 (C), 179.17 (C=O), 183.07 (C=O).

MS (EI): *m*/*z* (%) = 293 (13) $[M^+]$, 278 (100), 250 (4), 222 (4).

Anal. Calcd for $C_{18}H_{15}NO_3$: C, 73.71; H, 5.15; N, 4.78. Found: C, 73.88; H, 5.63; N, 4.55.

3-[(*tert*-Butyldimethylsilyl)oxy]aniline (36)

A solution of 3-nitrophenol (500 mg, 3.59 mmol), TBSCl (2.00 g, 15.9 mmol), and imidazole (1.50 g, 22.0 mmol) in DMF (10 mL) was stirred under an argon atmosphere for 24 h at r.t. The mixture was diluted with EtOAc and H_2O and the layers were separated. The aqueous layer was extracted with EtOAc, and the combined organic layers were washed with brine and dried (Na_2SO_4). The solvent was evaporated and the residue was purified by column chromatography (silica gel, PE–EtOAc, 6:1) to provide *tert*-butyldimethyl-(3-nitrophenoxy)silane (825 mg, 3.26 mmol, 92%).

A mixture of *tert*-butyldimethyl-(3-nitrophenoxy)silane (400 mg, 1.58 mmol), EtOH (20 mL), and Pd/C (10%, 80 mg) was vigorously shaken in a Parr hydrogenation apparatus under a hydrogen atmosphere (4 bar) for 8 h. Filtration over a short pad of Celite (EtOAc) and evaporation of the solvent provided the aniline **36** (348 mg, 1.56 mmol, 99%) as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.19 (s, 6 H), 0.98 (s, 9 H), 3.56–3.60 (br s, 2 H), 6.19 (td, *J* = 2.3, 0.4 Hz, 1 H), 6.25 (ddd, *J* = 8.0, 2.3, 0.8 Hz, 1 H), 6.29 (ddd, *J* = 8.0, 2.3, 0.8 Hz, 1 H), 6.99 (td, *J* = 2.3, 0.4 Hz, 1 H).

For further spectroscopic data, see ref. 29.

2-Bromo-5-methylcyclohexa-2,5-diene-1,4-dione (41)

K_2CO_3 (27.6 g, 200 mmol) and Me_2SO_4 (11.5 mL, 15.2 g, 121 mmol) were added to solution of toluhydroquinone (**40**) (5.00 g, 40.3 mmol) in acetone (30 mL) at r.t. under an argon atmosphere. The mixture was stirred at the same temperature for 3 h. H_2O and Et_2O were added, the layers were separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated.

The residue and NaOAc (6.62 g, 80.7 mmol) were dissolved in glacial acetic acid (40 mL) and bromine (2.28 mL, 7.10 g, 44.4 mmol) was added over a period of 25 min under air at r.t. The mixture was stirred for another 60 min. A saturated aqueous solution of $NaHCO_3$ was added slowly and the mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried ($MgSO_4$), and the solvent was evaporated.

The residue was dissolved in MeCN (70 mL). Ceric ammonium nitrate (54.8 g, 100 mmol) and H_2O (20 mL) were added at r.t. under air and the mixture was stirred vigorously for 1 h. Et_2O and H_2O were added, the layers were separated and the aqueous layer was extracted with Et_2O. The combined organic layers were dried ($MgSO_4$), the solvent was evaporated and the residue was purified by column chromatography (silica gel, isohexane–EtOAc, 15:1) to provide the quinone **41** (7.85 g, 39.1 mmol, 97%) as a yellow solid.

Mp 97.0–98.5 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.08 (d, *J* = 1.6 Hz, 3 H), 6.80 (q, *J* = 1.6 Hz, 1 H), 7.28 (s, 1 H).

For additional spectroscopic data, see ref. 30.

2-({3-[(*tert*-Butyldimethylsilyl)oxy]phenyl}amino)-5-methylcyclohexa-2,5-diene-1,4-dione (38)

A solution of quinone **41** (75 mg, 0.37 mmol) in toluene (3 mL) was added using a syringe pump to a stirred mixture of the aniline **36** (100 mg, 0.448 mmol), Cs_2CO_3 (176 mg, 0.540 mmol), $Pd(OAc)_2$ (10 mg, 44 µmol), and XPhos (45 mg, 94 µmol) in toluene (20 mL) at 100 °C under an argon atmosphere within 1 h. The mixture was stirred at the same temperature for another 1 h. The solvent was evaporated and the residue was purified by column chromatography (silica gel, isohexane–EtOAc, 20:1 to 15:1) to provide compound **38** (79 mg, 0.23 mmol, 62%) as a dark red solid.

Mp 108.5–109.5 °C.

UV (MeOH): 215, 263, 500 nm.

IR (ATR): 3248, 3055, 2952, 2928, 2857, 2056, 1643, 1575, 1525, 1483, 1422, 1358, 1256, 1190, 1122, 983, 863, 834, 775, 681 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.21 (s, 6 H), 0.98 (s, 9 H), 2.09 (d, *J* = 1.6 Hz, 3 H), 6.17 (s, 1 H), 6.56 (q, *J* = 1.6 Hz, 1 H), 6.63–6.69 (m, 2 H), 6.81 (dd, *J* = 8.1, 1.6 Hz, 1 H), 7.20 (br s, 1 H), 7.22 (t, *J* = 8.1 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –4.23 (2 CH_3), 16.62 (CH_3), 18.35 (C), 25.78 (3 CH_3), 101.40 (CH), 114.02 (CH), 115.09 (CH), 117.24 (CH), 129.40 (CH), 130.44 (CH), 138.74 (C), 142.97 (C), 149.81 (C), 156.90 (C), 183.96 (C=O), 186.85 (C=O).

MS (EI): *m*/*z* (%) = 343 (87) [M$^+$], 286 (41), 271 (26), 258 (100), 243 (11), 242 (11), 212 (22), 75 (19), 73 (10).

Anal. Calcd for $C_{19}H_{25}NO_3Si$: C, 66.44; H, 7.34; N, 4.08. Found: C, 66.72; H, 7.56; N, 3.80.

7-[(*tert*-Butyldimethylsilyl)oxy]-3-methyl-1*H*-carbazole-1,4(9*H*)-dione (42)

A mixture of compound **38** (70.0 mg, 0.204 mmol), $Pd(OAc)_2$ (15 mg, 67 µmol), $Cu(OAc)_2$ (91 mg, 0.50 mmol), and glacial acetic acid (1.5 mL) was stirred at 100 °C under air for 5 h. An aqueous solution of K_2CO_3 was added and the mixture was extracted with EtOAc. The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. Column chromatography (silica gel, isohexane–EtOAc, 15:1 to 5:1) provided the carbazolequinone **42** (51.6 mg, 0.151 mmol, 74%) as a dark purple solid.

Mp >300 °C (dec.).

UV (MeOH): 214, 264, 500 nm.

Fluorescence (MeOH, exc. 264 nm): 298 nm.

IR (ATR): 3180, 2953, 2927, 2855, 2056, 2030, 1627, 1603, 1569, 1537, 1432, 1241, 1161, 1101, 965, 869, 832, 777, 664, 639 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 0.22 (s, 6 H), 0.97 (s, 9 H), 2.05 (d, *J* = 1.6 Hz, 3 H), 6.58 (q, *J* = 1.6 Hz, 1 H), 6.82–6.99 (m, 2 H), 7.91 (d, *J* = 9.1 Hz, 1 H), 12.55 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = –4.48 (2 CH_3), 15.55 (CH_3), 18.00 (C), 25.57 (3 CH_3), 102.96 (CH), 115.76 (C), 118.57 (CH), 118.79 (C), 122.56 (CH), 131.60 (CH), 135.51 (C), 138.71 (C), 147.38 (C), 154.21 (C), 179.63 (C=O), 183.24 (C=O).

MS (EI): *m*/*z* (%) = 341 (33) [M$^+$], 285 (36), 284 (100).

Anal. Calcd for $C_{19}H_{23}NO_3Si$: C, 66.83; H, 6.79; N, 4.10. Found: C, 66.63; H, 7.04; N, 4.01.

7-Hydroxy-3-methyl-1*H*-carbazole-1,4(9*H*)-dione (43)

TBAF (1 M in THF, 255 µL, 0.255 mmol) was added to a solution of the carbazolequinone **42** (67.0 mg, 0.196 mmol) in THF (5 mL) at 0 °C under an argon atmosphere, and the mixture was stirred for 10 min. H_2O was added and the mixture was extracted with EtOAc. The combined organic layers were dried ($MgSO_4$), the solvent was evaporated and the residue was purified by column chromatography (silica gel, isohexane–EtOAc, 3:1 to 1:1) to provide hydroxycarbazolequinone **43** (40.0 mg, 0.176 mmol, 90%) as a dark purple solid.

Mp >300 °C.

UV (MeOH): 228, 262, 288 (sh), 403 nm.

Fluorescence (MeOH, exc. 262 nm): 364 nm.

IR (ATR): 3514, 3201, 1659, 1621, 1601, 1533, 1517, 1473, 1419, 1380, 1256, 1213, 1181, 1155, 1139, 1100, 1010, 974, 953, 879, 843, 816, 783, 744, 694 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.03 (d, *J* = 1.6 Hz, 3 H), 6.52 (q, *J* = 1.6 Hz, 1 H), 6.80–6.85 (m, 2 H), 7.81 (d, *J* = 9.5 Hz, 1 H), 9.75 (br s, 1 H), 12.39 (br s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 15.51 (CH_3), 97.44 (CH), 115.40 (CH), 116.04 (C), 116.97 (C), 122.45 (CH), 131.56 (CH), 134.67 (C), 139.25 (C), 147.06 (C), 156.91 (C), 179.45 (C), 183.37 (C).

MS (EI): *m*/*z* (%) = 227 (100) [M$^+$], 199 (47), 170 (37), 159 (22), 130 (14), 103 (14), 76 (16), 39 (11).

For additional spectroscopic data, see ref. 18.

***N*-{3-[(*tert*-Butyldimethylsilyl)oxy]phenyl}-2,5-dimethoxy-4-methylaniline (45)**

A solution of compound **44** (1.17 g, 5.05 mmol) in toluene (10 mL) was added using a syringe pump to a stirred mixture of the aniline **36** (1.48 g, 6.62 mmol), Cs_2CO_3 (1.96 g, 6.00 mmol), $Pd(OAc)_2$ (67.0 mg, 298 µmol), and XPhos (286 mg, 600 µmol) in toluene (50 mL) at reflux under an argon atmosphere within 2 h. The mixture was stirred at the same temperature for another 18 h. The reaction mixture was allowed to cool to r.t. and filtered over Celite (EtOAc). Removal of the solvent and purification of the residue by column chromatography (silica gel, isohexane–EtOAc, 99:1 to 85:15) afforded compound **45** (1.83 g, 4.90 mmol, 97%) as a colorless oil.

IR (ATR): 3417, 2949, 2930, 2856, 1594, 1492, 1465, 1393, 1254, 1204, 1176, 1155, 1044, 983, 837, 778, 690 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.20 (s, 6 H), 0.98 (s, 9 H), 2.19 (s, 3 H), 3.74 (s, 3 H), 3.82 (s, 3 H), 5.98 (br s, 1 H), 6.40 (dd, *J* = 8.0, 1.9 Hz, 1 H), 6.63 (t, *J* = 2.2 Hz, 1 H), 6.69–6.70 (m, 1 H), 6.70 (s, 1 H), 6.90 (s, 1 H), 7.10 (t, *J* = 8.1 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = –4.11 (2 CH_3), 16.03 (CH_3), 18.41 (C), 25.91 (3 CH_3), 56.41 (CH_3), 56.66 (CH_3), 101.07 (CH), 109.58 (CH), 111.21 (CH), 112.68 (CH), 114.36 (CH), 117.99 (C), 130.13 (CH), 130.89 (C), 142.79 (C), 144.75 (C), 151.86 (C), 156.90 (C).

MS (EI): *m*/*z* (%) = 373 (92) [M$^+$], 358 (100), 269 (8), 75 (9), 73 (10).

Anal. Calcd for $C_{21}H_{31}NO_3Si$: C, 67.52; H, 8.36; N, 3.75. Found: C, 67.80; H, 8.42; N, 3.81.

7-Hydroxy-3-methyl-8-(3-methylbut-2-en-1-yl)-1-(tosyloxy)carbazole (47)

Silicon tetrachloride (432 mg, 2.54 mmol) and DIBAL-H (1 M in *n*-hexane, 2.50 mL, 2.50 mmol) were added slowly to a solution of pyranocarbazole **25** (165 mg, 0.381 mmol) in toluene (50 mL) under an argon atmosphere at –78 °C. The mixture was allowed to warm to r.t. and was stirred for 22 h. After quenching slowly with H_2O at 0 °C,

EtOAc and saturated aqueous sodium potassium tartrate solution were added. The aqueous layer was extracted with EtOAc and the combined organic layers were dried ($MgSO_4$). Evaporation of the solvent and subsequent column chromatography (silica gel, isohexane–EtOAc, 10:1 to 5:1) provided prenylcarbazole **47** (128 mg, 0.294 mmol, 77%) as a colorless solid.

Mp 127.0–127.5 °C.

UV (MeOH): 226, 243, 253 (sh), 304, 319 (sh) nm.

Fluorescence (MeOH, exc. 243 nm): 364 nm.

IR (ATR): 3507, 3402, 2954, 2917, 1622, 1492, 1451, 1420, 1398, 1352, 1282, 1227, 1204, 1187, 1171, 1091, 1020, 972, 853, 803, 778, 737, 663 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.83 (d, *J* = 1.3 Hz, 3 H), 1.94 (s, 3 H), 2.36 (s, 3 H), 2.44 (s, 3 H), 3.57 (d, *J* = 7.3 Hz, 2 H), 5.16 (br s, 1 H), 5.36 (tsept, *J* = 7.1, 1.4 Hz, 1 H), 6.54 (s, 1 H), 6.73 (d, *J* = 8.5 Hz, 1 H), 7.30 (d, *J* = 7.9 Hz, 2 H), 7.58 (s, 1 H), 7.68 (d, *J* = 8.2 Hz, 1 H), 7.74 (d, *J* = 8.2 Hz, 2 H), 8.23 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.21 (CH_3), 21.32 (CH_3), 21.88 (CH_3), 24.47 (CH_2), 25.95 (CH_3), 108.89 (C), 109.81 (CH), 117.15 (C), 118.51 (CH), 118.90 (CH), 118.91 (CH), 121.10 (CH), 127.44 (C), 128.77 (2 CH), 129.48 (C), 129.91 (2 CH), 130.73 (C), 132.06 (C), 133.97 (C), 135.63 (C), 140.91 (C), 145.76 (C), 152.94 (C).

ESI-MS (+25 V): *m*/*z* = 436.6 $[M + H]^+$, 458.4 $[M + Na]^+$.

ESI-MS (–25 V): *m*/*z* = 434.1 $[M - H]^-$.

Anal. Calcd for $C_{25}H_{25}NO_4S$: C, 68.94; H, 5.79; N, 3.22; S, 7.36. Found: C, 68.59; H, 6.39; N, 3.21; S, 6.84.

7-Methoxy-3-methyl-8-(3-methylbut-2-en-1-yl)-1-(tosyloxy)carbazole (48)

K_2CO_3 (310 mg, 2.24 mmol) and Me_2SO_4 (225 µL, 299 mg, 2.37 mmol) were added to a solution of the hydroxycarbazole **47** (206 mg, 0.473 mmol) in acetone (10 mL) under an argon atmosphere at r.t. The mixture was stirred at the same temperature for 14 h, then it was stirred at 40 °C for another 2 h. H_2O was added and the mixture was extracted with EtOAc. The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. Subsequent column chromatography (silica gel, isohexane–EtOAc, 4:1) provided the carbazole **48** (199 mg, 0.443 mmol, 94%) as a colorless solid.

Mp 133.0–134.5 °C.

UV (MeOH): 223, 244, 254 (sh), 303, 321 (sh), 333 (sh) nm.

Fluorescence (MeOH, exc. 223 nm): 368 nm.

IR (ATR): 3445, 3405, 3379, 2955, 2916, 2860, 2830, 1729, 1617, 1484, 1455, 1435, 1358, 1293, 1268, 1216, 1188, 1172, 1083, 1019, 970, 848, 802, 762, 738, 673 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.79 (d, *J* = 0.9 Hz, 3 H), 1.94 (s, 3 H), 2.35 (s, 3 H), 2.43 (s, 3 H), 3.59 (d, *J* = 7.3 Hz, 2 H), 3.92 (s, 3 H), 5.30 (tsept, *J* = 7.3, 1.3 Hz, 1 H), 6.53–6.57 (m, 1 H), 6.86 (d, *J* = 8.5 Hz, 1 H), 7.27–7.31 (m, 2 H), 7.59–7.60 (m, 1 H), 7.74 (d, *J* = 8.2 Hz, 2 H), 7.76 (d, *J* = 8.5 Hz, 1 H), 8.25 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.13 (CH_3), 21.31 (CH_3), 21.87 (CH_3), 23.99 (CH_2), 25.93 (CH_3), 56.79 (CH_3), 105.20 (CH), 111.75 (C), 117.53 (C), 118.42 (CH), 118.60 (CH), 119.02 (CH), 121.94 (CH), 127.29 (C), 128.75 (2 CH), 129.28 (C), 129.88 (2 CH), 131.07 (C), 132.11 (C), 133.60 (C), 133.95 (C), 141.11 (C), 145.70 (C), 156.15 (C).

ESI-MS (+10 V): *m*/*z* = 450.4 $[M + H]^+$.

ESI-MS (–25 V): *m*/*z* = 448.2 $[M - H]^-$.

Murrayafoline-B (50)

Lithium aluminum hydride (2.4 M in THF, 1.95 mL, 4.68 mmol) was added to a solution of the carbazole **48** (300 mg, 0.667 mmol) in THF (30 mL) under an argon atmosphere at r.t. The solution was refluxed for 18 h and subsequently quenched with H_2O at 0 °C, then a saturated aqueous solution of sodium potassium tartrate was added. After extraction with EtOAc, the combined organic layers were dried ($MgSO_4$), the solvent was evaporated and the residue was subjected to column chromatography (silica gel, isohexane–EtOAc, 15:1) which provided murrayafoline-B (**50**) (186 mg, 0.630 mmol, 94%) as a brown solid.

Mp 121.0–123.0 °C (Lit.[13] syrup; Lit.[17c] 212–214 °C).

UV (MeOH): 232 (sh), 245, 253 (sh), 283, 300, 322, 335 nm.

Fluorescence (MeOH, exc. 245 nm): 366 nm.

IR (ATR): 3432, 3298, 2960, 2910, 2835, 2050, 2030, 2010, 1973, 1620, 1589, 1535, 1512, 1490, 1455, 1417, 1373, 1351, 1313, 1291, 1253, 1220, 1172, 1082, 1031, 995, 974, 953, 875, 833, 809, 788, 694 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.74 (d, *J* = 1.3 Hz, 3 H), 1.89 (s, 3 H), 2.45 (s, 3 H), 3.63 (d, *J* = 6.9 Hz, 2 H), 3.93 (s, 3 H), 5.02 (br s, 1 H), 5.32 (tsept, *J* = 6.9, 1.3 Hz, 1 H), 6.58 (s, 1 H), 6.86 (d, *J* = 8.5 Hz, 1 H), 7.37 (s, 1 H), 7.78 (d, *J* = 8.5 Hz, 1 H), 7.97 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.13 (CH_3), 21.61 (CH_3), 24.06 (CH_2), 25.84 (CH_3), 56.82 (CH_3), 104.89 (CH), 111.52 (CH), 111.57 (C), 112.63 (CH), 118.16 (C), 118.49 (CH), 122.43 (CH), 126.05 (C), 127.40 (C), 129.60 (C), 132.97 (C), 140.56 (C), 140.64 (C), 155.66 (C).

MS (EI): *m*/*z* (%) = 295 (100) $[M^+]$, 280 (49), 264 (17), 249 (10), 240 (65), 210 (28).

Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 76.98; H, 7.26; N, 4.61.

Murrayaquinone-E (6)

Lithium aluminum hydride (2.4 M in THF, 0.80 mL, 1.9 mmol) was added to a solution of prenylcarbazole **47** (122 mg, 0.280 mmol) in THF (35 mL) under an argon atmosphere at r.t. The solution was refluxed for 16 h and subsequently quenched with H_2O at 0 °C, then a saturated aqueous solution of sodium potassium tartrate was added. After extraction with EtOAc, the combined organic layers were dried ($MgSO_4$), the solvent was evaporated and the residue was filtered over a short pad of silica gel (isohexane–EtOAc, 10:1 to 5:1). The solvent was evaporated to provide the crude, very air-sensitive dihydroxycarbazole **49**.

A solution of compound **49** in acetone (3 mL) was added to a stirred solution of potassium nitrosodisulfonate (Frémy's salt) (420 mg, 1.57 mmol) in H_2O (35 mL) at r.t. under air. Subsequently, acetone (32 mL) was added and the mixture was stirred vigorously at the same temperature for 68 h. The mixture was diluted with EtOAc. After extraction with EtOAc, the combined organic layers were dried ($MgSO_4$). Evaporation of the solvent and subsequent column chromatography (silica gel, isohexane–EtOAc, 5:1) provided murrayaquinone-E (**6**) (61.9 mg, 0.210 mmol, 75%) as a dark purple solid.

Mp 201.0 °C (dec.) (Lit.[14] brown oil; Lit.[18] 88–89 °C).

UV (MeOH): 231, 263, 283, 412 nm.

Fluorescence (MeOH, exc. 230 nm): 360 nm.

IR (ATR): 3371, 3273, 2976, 2914, 2851, 1602, 1527, 1466, 1419, 1374, 1289, 1246, 1168, 1139, 1031, 1013, 991, 949, 873, 853, 813, 794, 772, 699, 658 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.79 (d, *J* = 1.3 Hz, 3 H), 1.87 (s, 3 H), 2.14 (d, *J* = 1.6 Hz, 3 H), 3.57 (d, *J* = 6.9 Hz, 2 H), 5.20–5.45 (m, 1 H), 6.45 (q, *J* = 1.6 Hz, 1 H), 6.88 (d, *J* = 8.5 Hz, 1 H), 7.94 (d, *J* = 8.5 Hz, 1 H), 8.92 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.29 (CH_3), 18.26 (CH_3), 24.26 (CH_2), 25.88 (CH_3), 109.54 (C), 115.77 (CH), 117.70 (C), 119.01 (C), 120.68 (CH), 121.67 (CH), 131.70 (CH), 134.80 (C), 136.22 (C), 138.01 (C), 148.32 (C), 153.13 (C), 179.92 (C=O), 183.97 (C=O).

MS (EI): *m*/*z* (%) = 295 (66) [M$^+$], 280 (12), 265 (10), 252 (6), 240 (100), 211 (6), 183 (6), 154 (7).

Murrayaquinone-B (5)

A solution of potassium nitrosodisulfonate (Frémy's salt) (187 mg, 0.698 mmol) in H_2O (7 mL) was added to a solution of murrayafoline-B (**50**) (29.4 mg, 99.7 µmol) in acetone (7 mL) and the mixture was stirred vigorously at r.t. under air for 3 d. The mixture was diluted with EtOAc. The aqueous layer was separated, extracted with EtOAc, and the combined organic layers were dried ($MgSO_4$). Evaporation of the solvent and subsequent column chromatography (silica gel, isohexane–EtOAc, 10:1) provided murrayaquinone-B (**5**) (20.8 mg, 67.3 µmol, 68%) as a dark purple solid.

Mp 220.5–221.0 °C (Lit.[12] 221–223 °C).

UV (MeOH): 231, 263, 404 nm.

Fluorescence (MeOH, exc. 230 nm): 368 nm.

IR (ATR): 3284, 2960, 2916, 2853, 2134, 2048, 2030, 2009, 1977, 1641, 1608, 1558, 1536, 1513, 1469, 1439, 1416, 1372, 1331, 1289, 1257, 1170, 1141, 1083, 1033, 993, 951, 875, 842, 805, 787, 705, 678 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.75 (d, *J* = 0.9 Hz, 3 H), 1.85 (s, 3 H), 2.14 (d, *J* = 1.9 Hz, 3 H), 3.57 (d, *J* = 6.9 Hz, 2 H), 3.91 (s, 3 H), 5.25 (tsept, *J* = 6.7, 1.6 Hz, 1 H), 6.44 (q, *J* = 1.6 Hz, 1 H), 7.03 (d, *J* = 8.8 Hz, 1 H), 8.01 (d, *J* = 8.8 Hz, 1 H), 8.96 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.28 (CH_3), 18.17 (CH_3), 23.82 (CH_2), 25.83 (CH_3), 56.81 (CH_3), 110.87 (CH), 112.66 (C), 117.34 (C), 119.12 (C), 121.26 (CH), 121.68 (CH), 131.63 (CH), 134.15 (C), 135.22 (C), 138.07 (C), 148.33 (C), 156.12 (C), 179.99 (C=O), 183.90 (C=O).

MS (EI): *m*/*z* (%) = 309 (100) [M$^+$], 294 (41), 279 (39), 266 (13), 264 (14), 254 (59), 241 (14), 224 (18).

2,5,5,10-Tetramethyl-12-(tosyloxy)-3,4,4a,5,13,13c-hexahydroisochromeno[4,3-*a*]carbazole (52)

$SiCl_4$ (136 mg, 800 µmol) and then DIBAL-H (1 M in hexane, 0.80 mL, 0.80 mmol) were added slowly at –78 °C to a solution of the pyrano[3,2-*a*]carbazole **28** (100 mg, 0.199 mmol) in CH_2Cl_2 (17 mL). The cooling was removed and the mixture was stirred for 20 h. The mixture was cooled to 0 °C, quenched by the addition of H_2O and EtOAc, and the layers were separated. The organic layer was washed with a saturated aqueous solution of sodium potassium tartrate. The aqueous layer was extracted with EtOAc. The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. Purification of the residue by column chromatography (silica gel, isohexane–EtOAc, 15:1) provided the isochromeno[4,3-*a*]carbazole **52** (60.0 mg, 0.120 mmol, 60%) as a highly viscous colorless oil.

UV (MeOH): 229, 238, 278 (sh), 288, 309 (sh), 353 (sh) nm.

Fluorescence (MeOH, exc. 238 nm): 368 nm.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.34 (s, 3 H), 1.48 (s, 3 H), 1.49–1.66 (m, 2 H), 1.78 (s, 3 H), 1.82 (ddd, *J* = 11.9, 5.6, 3.0 Hz, 1 H), 1.94–2.12 (m, 2 H), 2.33 (s, 3 H), 2.43 (s, 3 H), 3.72–3.88 (m, 1 H), 6.18 (d, *J* = 4.4 Hz, 1 H), 6.49 (s, 1 H), 6.72 (d, *J* = 8.5 Hz, 1 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 7.55 (s, 1 H), 7.69 (d, *J* = 8.2 Hz, 1 H), 7.75 (d, *J* = 8.5 Hz, 2 H), 8.62 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.36 (CH_2), 21.31 (CH_3), 21.87 (CH_3), 23.73 (CH_3), 25.65 (CH_3), 26.29 (CH_3), 30.18 (CH_2), 32.23 (CH), 39.98 (CH), 76.43 (C), 107.69 (C), 111.59 (CH), 116.94 (C), 118.17 (CH), 118.48 (CH), 119.16 (CH), 120.11 (CH), 127.47 (C), 128.81 (2 CH), 129.43 (C), 129.88 (2 CH), 130.30 (C), 131.79 (C), 133.89 (C), 138.08 (C), 140.46 (C), 145.71 (C), 152.07 (C).

ESI-MS (+50 V): *m*/*z* = 502.4 [M + H]$^+$, 524.4 [M + Na]$^+$, 1025.4 [2M + Na]$^+$.

ESI-MS (–25 V): *m*/*z* = 500.3 [M – H]$^-$.

8-(3,7-Dimethylocta-2,6-dienyl)-7-hydroxy-3-methyl-1-(tosyloxy)carbazole (54)

A mixture of propargyloxycarbazole **27** (198 mg, 0.395 mmol), Lindlar catalyst (10%, 20 mg), and EtOAc (10 mL) was vigorously stirred at r.t. under a hydrogen atmosphere for 22 h. After filtration (EtOAc) and removal of the solvent, the residue was dissolved in DMF (3 mL) in a 10 mL microwave tube and irradiated in a microwave reactor (300 W, 180 °C) for 60 min. After cooling to r.t., H_2O was added and the mixture was extracted with EtOAc. The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. Subsequent column chromatography (silica gel, isohexane–EtOAc, 5:1) provided the hydroxycarbazole **54** as a mixture of diastereoisomers [ratio *E*/*Z* = 1.3:1 (determined by ^{1}H NMR)] (157 mg, 0.312 mmol, 79%) as a yellow solid. Further column chromatography (48 mg) using a Büchi Sepacore apparatus [silica gel, isohexane–EtOAc, 100:0 (20 min) to isohexane–EtOAc, 85:15 (80 min)] afforded 3 fractions in which one or the other diastereoisomer was enriched (*E*/*Z* as determined by ^{1}H NMR given in parentheses): 11.0 mg (1:10); 10.7 mg (1:1.3); 25.7 mg (3:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.59 (*E*, s) and 1.67 (*Z*, s, 3 H), 1.66 (*E*, s) and 1.73 (*Z*, s, 3 H), 1.83 (*Z*, d, *J* = 1.3 Hz) and 1.93 (*E*, s, 3 H), 2.08–2.19 (*E*, m, 4 H) and 2.20–2.27 (*Z*, m, 2 H) and 2.32–2.40 (*Z*, m, 2 H), 2.35 (s, 3 H), 2.44 (s, 3 H), 3.57 (d, *J* = 6.9 Hz, 2 H), 5.00–5.15 (*E*, m) and 5.17–5.27 (*Z*, m, 1 H), 5.33–5.41 (m, 1 H), 6.55 (s, 1 H), 6.73 (*Z*, d, *J* = 8.5 Hz) and 6.74 (*E*, d, *J* = 8.5 Hz, 1 H), 7.26–7.33 (m, 2 H), 7.58 (s, 1 H), 7.685 (*Z*, d, *J* = 8.5 Hz) and 7.687 (*E*, d, *J* = 8.5 Hz, 1 H), 7.74 (d, *J* = 8.2 Hz, 2 H), 8.20 (*E*, s) and 8.23 (*Z*, s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.59 (*E*) and 23.63 (*Z*, CH_3), 17.86 (*E*) and 17.91 (*Z*, CH_3), 21.33 (CH_3), 21.88 (CH_3), 24.21 (*Z*) and 24.46 (*E*, CH_2), 25.82 (*E*) and 25.93 (*Z*, CH_3), 26.55 (*Z*) and 26.58 (*E*, CH_2), 32.36 (*Z*) and 39.82 (*E*, CH_2), 108.84 (*E*) and 108.88 (*Z*, C), 109.85 (*Z*) and 109.97 (*E*, CH), 117.08 (*E*) and 117.11 (*Z*, C), 118.49 (CH), 118.89 (CH), 118.94 (CH), 120.82 (*E*) and 121.69 (*Z*, CH), 123.91 (*Z*) and 123.97 (*E*, CH), 127.44 (*Z*) and 127.48 (*E*, C), 128.77 (2 CH), 129.48 (*Z*) and 129.50 (*E*, C), 129.91 (2 CH), 130.67 (*E*) and 130.69 (*Z*, C), 132.08 (C), 132.13 (*E*) and 132.60 (*Z*, C), 133.97 (C), 139.46 (*E*) and 139.62 (*Z*, C), 140.82 (*Z*) and 140.84 (*E*, C), 145.75 (C), 153.06 (*Z*) and 153.22 (*E*, C).

ESI-MS (+25 V): *m*/*z* = 504.3 [M + H]$^+$, 526.3 [M + Na]$^+$.

Anal. Calcd for $C_{30}H_{33}NO_4S$: C, 71.54; H, 6.60; N, 2.78; S, 6.37. Found: C, 71.38; H, 7.21; N, 2.77; S, 5.74.

8-(3,7-Dimethylocta-2,6-dien-1-yl)-7-methoxy-3-methyl-1-(tosyloxy)carbazole (55)

K_2CO_3 (130 mg, 0.940 mmol) and Me_2SO_4 (90 µL, 0.13 g, 0.99 mmol) were added to a solution of the hydroxycarbazole **54** (ratio *E*/*Z* = 1.3:1) (100 mg, 0.199 mmol) in acetone (5 mL) under an argon atmosphere at r.t. The mixture was stirred at the same temperature for 15

h, then Me_2SO_4 (36 µL, 50 mg, 0.40 mmol) was added and the mixture was stirred at 50 °C for a further 2.5 h. H_2O was added and the mixture was extracted with EtOAc. The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. Subsequent column chromatography (silica gel, isohexane–EtOAc, 4:1) provided the carbazole **55** [ratio *E*/*Z* = 1.3:1 (determined by ^{1}H NMR)] (94.9 mg, 0.183 mmol, 92%) as a colorless solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.57 (*E*, s) and 1.68 (*Z*, s, 3 H), 1.62 (*E*, d, *J* = 0.6 Hz) and 1.73 (*Z*, d, *J* = 0.9 Hz, 3 H), 1.81 (*Z*, d, *J* = 1.3 Hz) and 1.95 (*E*, d, *J* = 0.6 Hz, 3 H), 2.06–2.16 (*E*, m, 4 H) and 2.20–2.27 (*Z*, m, 2 H) and 2.37–2.41 (*Z*, m, 2 H), 2.36 (s, 3 H), 2.43 (s, 3 H), 3.61 (d, *J* = 6.9 Hz, 2 H), 3.92 (*Z*, s) and 3.93 (*E*, s, 3 H), 5.05–5.12 (*E*, m) and 5.23–5.28 (*Z*, m, 1 H), 5.28–5.37 (m, 1 H), 6.53–6.61 (m, 1 H), 6.86 (*Z*, d, *J* = 8.5 Hz) and 6.87 (*E*, d, *J* = 8.5 Hz, 1 H), 7.27–7.31 (m, 2 H), 7.58–7.62 (*E*, m) and 7.60 (*Z*, d, *J* = 0.6 Hz, 1 H), 7.71–7.81 (m, 3 H), 8.23 (*E*, br s) and 8.27 (*Z*, br s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 16.53 (*E*) and 23.64 (*Z*, CH_3), 17.81 (*E*) and 17.88 (*Z*, CH_3), 21.31 (CH_3), 21.85 (CH_3), 23.70 (*Z*) and 23.86 (*E*, CH_2), 25.78 (*E*) and 25.90 (*Z*, CH_3), 26.73 (*Z*) and 26.78 (*E*, CH_2), 32.36 (*Z*) and 39.83 (*E*, CH_2), 56.70 (*Z*) and 56.78 (*E*, CH_3), 105.12 (*Z*) and 105.21 (*E*, CH), 111.72 (*Z*) and 111.81 (*E*, C), 117.48 (*E*) and 117.52 (*Z*, C), 118.40 (CH), 118.57 (CH), 119.02 (*E*) and 119.05 (*Z*, CH), 121.67 (*E*) and 122.48 (*Z*, CH), 124.36 (*Z*) and 124.38 (*E*, CH), 127.25 (*Z*) and 127.27 (*E*, C), 128.72 (2 CH), 129.28 (C), 129.87 (2 CH), 131.02 (C), 131.57 (C), 132.04 (*Z*) and 132.14 (*E*, C), 133.93 (C), 137.09 (*E*) and 137.59 (*Z*, C), 141.08 (C), 145.67 (C), 156.11 (*Z*) and 156.16 (*E*, C).

ESI-MS (+10 V): *m*/*z* = 518.4 $[M + H]^+$.

ESI-MS (–10 V): *m*/*z* = 516.1 $[M - H]^-$.

Murrayaquinone-D (8) and 8-[(*Z*)-3,7-Dimethylocta-2,6-dien-1-yl]-7-hydroxy-3-methyl-1*H*-carbazole-1,4(9*H*)-dione (56)

$LiAlH_4$ (2.4 M in THF, 1.44 mL, 3.46 mmol) was added to a solution of carbazole **54** (ratio *E*/*Z* = 1.3:1) (174.5 mg, 0.347 mmol) in THF (22 mL) under an argon atmosphere at r.t. The solution was heated at reflux for 22 h and quenched with H_2O at 0 °C. A saturated aqueous solution of sodium potassium tartrate was added and the mixture was extracted with EtOAc. The organic layers were combined and the solvent was evaporated.

The residue was dissolved in acetone (19 mL), a solution of potassium nitrosodisulfonate (Frémy's salt) (804 mg, 3.00 mmol) in H_2O (19 mL) was added at r.t. under air and the mixture was stirred vigorously for 3.5 h. An additional portion of Frémy's salt (500 mg, 1.86 mmol) was added and the mixture was stirred for another 18.5 h. The mixture was extracted with EtOAc and the combined organic layers were dried ($MgSO_4$). Evaporation of the solvent and subsequent multiple column chromatography (silica gel, isohexane–EtOAc, 8:1) provided murrayaquinone-D (**8**) (47.4 mg, 0.130 mmol, 37%) as the more polar fraction and the corresponding *Z*-isomer **56** (23.9 mg, 65.8 µmol, 19%) as the less polar fraction. Murrayaquinone-D (**8**) and the *Z*-isomer **56** were obtained as dark purple solids.

Murrayaquinone-D (8)

Mp 175.0–177.0 °C (Lit.[13] 164–168 °C).

UV (MeOH): 231, 263, 412 nm.

Fluorescence (MeOH, exc. 263 nm): 363 nm.

IR (ATR): 3261, 2962, 2919, 2030, 2010, 1980, 1716, 1658, 1604, 1529, 1469, 1419, 1377, 1311, 1287, 1246, 1140, 1014, 992, 951, 874, 816, 699, 669 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.58 (s, 3 H), 1.65 (d, *J* = 1.1 Hz, 3 H), 1.87 (d, *J* = 1.1 Hz, 3 H), 2.07–2.13 (m, 4 H), 2.14 (d, *J* = 1.9 Hz, 3 H), 3.58 (d, *J* = 6.8 Hz, 2 H), 5.05 (tsept, *J* = 6.8, 1.5 Hz, 1 H), 5.29–5.41 (m, 2 H), 6.45 (q, *J* = 1.5 Hz, 1 H), 6.89 (d, *J* = 8.7 Hz, 1 H), 7.94 (d, *J* = 8.7 Hz, 1 H), 8.96 (br s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 16.27 (CH_3), 16.62 (CH_3), 17.86 (CH_3), 24.29 (CH_2), 25.80 (CH_3), 26.53 (CH_2), 39.75 (CH_2), 109.50 (C), 115.89 (CH), 117.70 (C), 119.01 (C), 120.49 (CH), 121.68 (CH), 123.72 (CH), 131.69 (CH), 132.34 (C), 134.80 (C), 138.02 (C), 140.01 (C), 148.32 (C), 153.32 (C), 179.86 (C=O), 183.96 (C=O).

ESI-MS (+25 V): *m*/*z* = 364.3 $[M + H]^+$, 386.4 $[M + Na]^+$, 749.5 $[2M + Na]^+$.

ESI-MS (–50 V): *m*/*z* = 362.1 $[M - H]^-$, 747.2 $[2M + Na - 2 H]^-$.

Anal. Calcd for $C_{23}H_{25}NO_3$: C, 76.01; H, 6.93; N, 3.85. Found: C, 75.91; H, 7.18; N, 3.76.

8-[(*Z*)-3,7-Dimethylocta-2,6-dien-1-yl]-7-hydroxy-3-methyl-1*H*-carbazole-1,4(9*H*)-dione (56)

Mp 163.0–165.0 °C.

UV (MeOH): 231, 263, 412 nm.

Fluorescence (MeOH, exc. 263 nm): 363 nm.

IR (ATR): 3409, 3273, 3159, 2963, 2920, 2854, 2056, 2030, 2009, 1716, 1699, 1639, 1593, 1526, 1469, 1376, 1281, 1250, 1159, 1138, 1041, 952, 896, 875, 811, 719, 690 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.64 (s, 3 H), 1.69 (d, *J* = 1.1 Hz, 3 H), 1.80 (q, *J* = 1.4 Hz, 3 H), 2.14 (d, *J* = 1.9 Hz, 3 H), 2.16–2.23 (m, 2 H), 2.27–2.33 (m, 2 H), 3.58 (dd, *J* = 7.0, 0.9 Hz, 2 H), 5.17 (tsept, *J* = 7.2, 1.5 Hz, 1 H), 5.30–5.38 (m, 2 H), 6.45 (q, *J* = 1.5 Hz, 1 H), 6.88 (d, *J* = 8.7 Hz, 1 H), 7.94 (d, *J* = 8.7 Hz, 1 H), 9.00 (br s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 16.26 (CH_3), 17.87 (CH_3), 23.52 (CH_3), 24.01 (CH_2), 25.87 (CH_3), 26.38 (CH_2), 32.33 (CH_2), 109.59 (C), 115.81 (CH), 117.70 (C), 119.03 (C), 121.30 (CH), 121.68 (CH), 123.65 (CH), 131.71 (CH), 132.86 (C), 134.80 (C), 138.02 (C), 140.09 (C), 148.31 (C), 153.21 (C), 179.89 (C=O), 183.96 (C=O).

ESI-MS (+25 V): *m*/*z* = 364.3 $[M + H]^+$, 749.5 $[2M + Na]^+$.

ESI-MS (–50 V): *m*/*z* = 362.1 $[M - H]^-$, 747.2 $[2M + Na - 2 H]^-$.

Murrayaquinone-C (7) and 8-[(*Z*)-3,7-Dimethylocta-2,6-dienyl]-7-methoxy-3-methyl-1*H*-carbazole-1,4(9*H*)-dione (57)

Method A: Synthesis of 7 from Carbazole 55

Lithium aluminum hydride (2.4 M in THF, 0.60 mL, 1.4 mmol) was added to a solution of carbazole **55** (ratio *E*/*Z* = 3:1) (83.9 mg, 0.162 mmol) in THF (10 mL) under an argon atmosphere at r.t. The solution was refluxed for 18 h and subsequently quenched with H_2O at 0 °C, then a saturated aqueous solution of sodium potassium tartrate was added. After extraction with EtOAc, the organic layers were combined and the solvent was evaporated. Filtration of the residue (silica gel, isohexane–EtOAc, 15:1) afforded a crude material (58.8 mg, 0.162 mmol), which was partly (40.0 mg, 0.108 mmol) dissolved in acetone (7 mL).

A solution of potassium nitrosodisulfonate (Frémy's salt) (207 mg, 0.772 mmol) in H_2O (7 mL) was added at r.t. under air. After stirring vigorously for 64 h, the mixture was extracted with EtOAc and the combined organic layers were dried ($MgSO_4$). Evaporation of the solvent and subsequent column chromatography (silica gel, isohexane–EtOAc, 10:1) provided the compounds **7** and **57** in a ratio of 3:1 (25.4 mg, 67.4 µmol, 62%) as a dark purple solid.

Method B: Synthesis of 7 from Murrayaquinone-D (8)

A solution of butyllithium (2.5 M in hexane, 11.6 µL, 29.0 µmol) was added to a solution of murrayaquinone-D (**8**) (10.5 mg, 28.9 µmol) in THF (2 mL) at –78 °C under an argon atmosphere. Subsequently, methyl iodide (90 µL, 1.4 mmol) was added and the mixture was allowed to warm to r.t. After 22 h, H_2O was added and the mixture was extracted with EtOAc. The combined organic layers were dried ($MgSO_4$). Evaporation of the solvent and subsequent column chromatography (silica gel, isohexane–EtOAc, 4:1) provided murrayaquinone-C (**7**) (6.3 mg, 17 µmol, 59%) as a dark purple solid and reisolated murrayaquinone-D (**8**) (3.0 mg, 8.3 µmol, 29%).

Mp 156.0–158.0 °C (Lit.[13] 158–159 °C).

UV (MeOH): 202, 231, 263, 405, 516 (sh) nm.

Fluorescence (MeOH, exc. 231 nm): 367 nm.

IR (ATR): 3283, 2967, 2918, 2852, 2055, 2031, 2008, 1641, 1606, 1538, 1512, 1461, 1442, 1417, 1373, 1331, 1287, 1256, 1171, 1141, 1086, 1035, 995, 951, 876, 808, 790, 709, 629 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.57 (s, 3 H), 1.62 (s, 3 H), 1.86 (s, 3 H), 2.02–2.13 (m, 4 H), 2.14 (d, *J* = 1.6 Hz, 3 H), 3.60 (d, *J* = 6.9 Hz, 2 H), 3.92 (s, 3 H), 4.98–5.13 (m, 1 H), 5.27 (dt, *J* = 1.3, 6.9 Hz, 1 H), 6.44 (q, *J* = 1.6 Hz, 1 H), 7.04 (d, *J* = 8.8 Hz, 1 H), 8.02 (d, *J* = 8.8 Hz, 1 H), 8.94 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.29 (CH_3), 16.56 (CH_3), 17.83 (CH_3), 23.80 (CH_2), 25.78 (CH_3), 26.69 (CH_2), 39.75 (CH_2), 56.85 (CH_3), 110.91 (CH), 112.69 (C), 117.30 (C), 119.15 (C), 121.26 (CH), 121.54 (CH), 124.02 (CH), 131.63 (CH), 131.91 (C), 135.24 (C), 137.86 (C), 138.12 (C), 148.34 (C), 156.14 (C), 179.93 (C=O), 183.93 (C=O).

ESI-MS (+25 V): *m*/*z* = 378.3 $[M + H]^+$.

ESI-MS (–25 V): *m*/*z* = 376.3 $[M - H]^-$.

8-[(*Z*)-3,7-Dimethylocta-2,6-dienyl]-7-methoxy-3-methyl-1*H*-carbazole-1,4(9*H*)-dione (57)

^1H NMR (500 MHz, $CDCl_3$): δ = 1.64 (s, 3 H), 1.68 (s, 3 H), 1.76 (d, *J* = 1.3 Hz, 3 H), 2.14 (d, *J* = 1.3 Hz, 3 H), 2.16–2.21 (m, 2 H), 2.26–2.32 (m, 2 H), 3.54–3.63 (m, 2 H), 3.91 (s, 3 H), 5.14–5.23 (m, 1 H), 5.23–5.31 (m, 1 H), 6.44 (d, *J* = 1.6 Hz, 1 H), 7.03 (d, *J* = 8.8 Hz, 1 H), 8.02 (d, *J* = 8.8 Hz, 1 H), 8.99 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.27 (CH_3), 17.85 (CH_3), 23.50 (CH_3), 23.56 (CH_2), 25.84 (CH_3), 26.51 (CH_2), 32.30 (CH_2), 56.77 (CH_3), 110.83 (CH), 112.68 (C), 117.30 (C), 119.14 (C), 121.26 (CH), 122.26 (CH), 124.02 (CH), 131.64 (CH), 132.39 (C), 135.23 (C), 137.80 (C), 138.09 (C), 148.32 (C), 156.09 (C), 179.93 (C=O), 183.91 (C=O).

Acknowledgment

We would like to thank Max Kaulfuß, Adrian Kishonti, Vicky Langer, Alexander Purtsas, and Patrick Zimdars for experimental support.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1588322.

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