Synthesis of Pterocarpans by Means of a "Disfavored" 5-*endo-trig* Radical Cyclization Reaction

Kalpathy Chidambareswaran Santhosh,[a] Ariamala Gopalsamy,[a] and Kalputtu Kuppuswamy Balasubramanian*[a]

Dedicated to Professor Jean F. Normant on the occasion of his 65th birthday

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A successful synthesis of pterocarpans **1**, based on a "disfavored" 5-*endo-trig* radical cyclization reaction, has been accomplished. The radical precursor 4-(2′-bromoaryloxy)-2*H*-chromene **8** was synthesized in six steps, starting from aryl propynyl ether **2**. On treatment with tributyltin hydride in refluxing benzene, aryl enol ether **8** underwent radical cyclization to furnish the pterocarpan **1.** A deuterium label study was performed to prove the occurrence of 5-*endo-trig* radical cyclization. This methodology was extended further to synthesize a class of hitherto unknown pterocarpans **13.** A novel and stereoselective route towards the synthesis of aryl ethers of bromohydrins by means of the Mitsunobu reaction is also described.

Introduction

The chemistry of free radicals has witnessed stupendous growth in recent years. Free radical reactions are extensively used for carbon−carbon bond formation in organic synthesis.[1] The tin hydride method[2] has established itself as the most important and versatile method for conducting radical reactions, and has proven to be potentially useful for the construction of carbo-, hetero-, and macrocycles. Pterocarpans are an important class of naturally occurring isoflavanoids,[3] many of which act as phytoalexins. 6a,11a-Dihydro-6*H*-benzo[4,5]furo[3,2-*c*]chromene **1c** is representative of a wide range of pterocarpan phytoalexins produced by "leguminosae" plants when challenged by fungal infections. Pterocarpan analogues cabenegrins A-1 and A-2, which are potent anti-snake venom antidotes, have been isolated and synthesized by Nakanishi.[3e] Pterocarpans are also known to exhibit anti-tumor properties.[3f] Owing to their interesting biological activities, pterocarpans have attracted considerable attention and a few synthetic routes have been developed.[4] The earlier methods for the synthesis of pterocapans commonly employed reduction and cyclization of the corresponding 2-hydroxyisoflavanones.[4b−4d] Other approaches to the synthesis of pterocarpans are Heck arylation,[4e−4h] 1,3-Michael−Claisen annulation reaction,[4i] and Lewis acid catalyzed cycloaddition of 1,4-benzoquinones to chromenes.[4j−4l] Recently, an aldol condensation of phenyl acetates with benzaldehydes to afford pterocarpans has been reported.[4m,4n] The synthesis of pterocarpans by radical cyclization approaches, however, has not so far been attempted. As part of a general study of the synthesis of condensed oxygen heterocycles, we undertook the synthesis of pterocarpans and related systems by means of radical cyclization reactions. This method[5] produces the furan C−C bond of pterocarpan in the key step, which involves an intramolecular radical arylation, making use of the stereospecific and regiospecific nature of the radical cyclization reaction. This route permits a more general and effective synthesis of pterocarpans.

Results and Discussion

From the retrosynthetic perspective, **1** can be disconnected at the C−C bond "*a*" (Figure 1), giving the radical precursor **8**. The syntheses of variously substituted enol ethers **8a−c** involved the use of aryl propynyl ethers **2a−c** as starting materials.[6] Thermal rearrangement[7] of **2a** was carried out in polyethylene glycol 200 (PEG 200), affording the 2*H*-chromene **3a**. The olefin **3a** was converted[8] into bromohydrin **4a** in 80% yield, by use of *N*-bromosuccinimide in wet dimethyl sulfoxide. On treatment with powdered potassium hydroxide,[9] this *trans*-bromohydrin afforded 3,4-epoxychroman **5a** in 85% yield. Treatment of **5a** with 1-bromo-2-naphthol furnished the alcohol **6a** in 94% yield.[10]

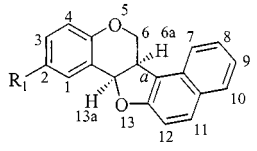

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Figure 1. Structure of **1**

[a] Department of Chemistry, Indian Institute of Technology Chennai 600036, India
Fax: (internat.) + 91-44/235-0509
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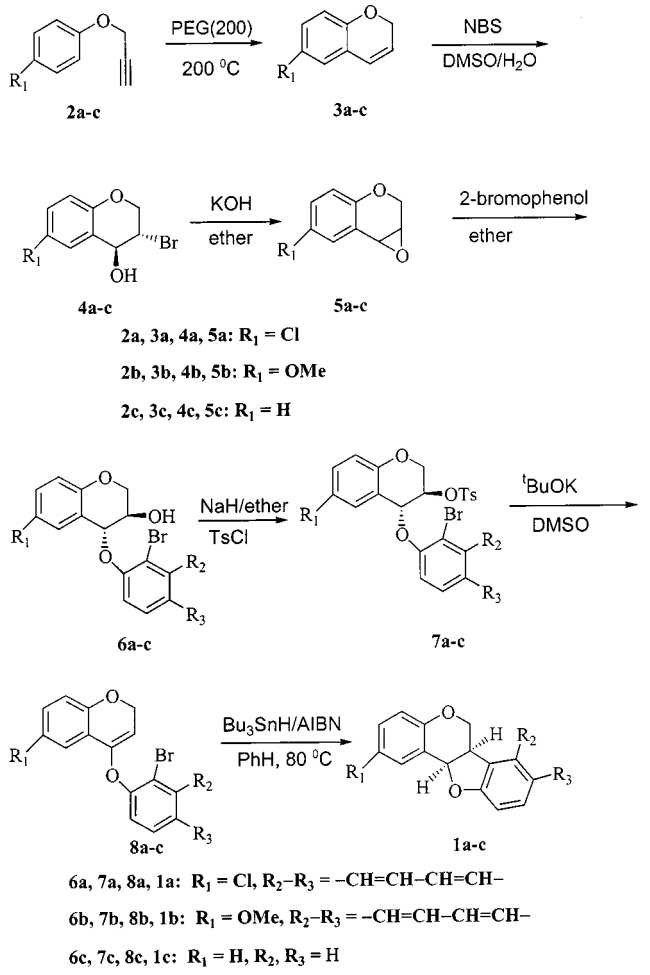
Conversion of alcohol **6a** into the tosylate, followed by elimination using potassium *tert*-butoxide in DMSO, yielded the enol ether **8a**. This synthetic sequence, depicted in Scheme 1, was found to be general when extended to the other substrates, **8b** and **8c**.



Scheme 1

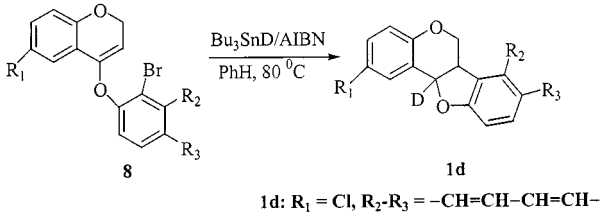
When refluxed in benzene with tributyltin hydride in the presence of AIBN, substrate **8a** afforded the cyclized product **1a** as a white solid (m.p. 205 °C) in 88% yield. The presence of long range coupling (J_{bd} = 1.5 Hz), together with the vicinal coupling (J_{ba} = 11.5 Hz), in the ^{1}H NMR spectrum of **1a** suggests a half-chair conformation for the pyran ring in the molecule. The *cis* ring junction favored by thermodynamic considerations is evident from J_{cd} = 7.5 Hz.

When extended to the other enol ethers **8b** and **8c**, the cyclization furnished cyclized products **1b** and **1c** in good yields. The spectral characteristics and melting point of the pterocarpan **1c** were found to be identical with those reported in the literature.[4a] The crude product was in all cases found to be homogenous, and ^{1}H NMR revealed the absence of the simple reduced product.

Mechanistic Investigation

In radical reactions, the determining factors for regioselectivity and stereoselectivity are the steric and stereoelectronic effects.[1] The rules for ring-closure, though originally formulated for ionic cyclizations, were found to be extendable to radical reactions.[2a] Thus, according to Baldwin's rule,[11] 5-*endo-trig* is a disfavored process. It may be noted that only a few examples of 5-*endo-trig* cyclization processes are known.[12] The facile radical ring closure in this study prompted us to probe the mechanistic aspects more deeply.

Under the radical reaction conditions detailed in Scheme 1, substrate **8** might yield compound **1** either through a disallowed 5-*endo-trig* cyclization, or through an allowed 4-*exo-trig* cyclization followed by an aryl group migration. The 4-*exo-trig* cyclization can easily be ruled out, as the C–C bond breakage is not as facile as that of C–O, since the latter would generate a more conjugated and stable primary radical. In order to establish the occurrence of 5-*endo-trig* radical cyclization unambiguously, a deuterium label study was carried out. Thus, when the cyclization of **8a** was performed using tributyltin deuteride, a smooth reaction was observed, resulting in the isolation of a white solid **1d** in 90% yield (Scheme 2). The ^{1}H NMR spectrum showed the absence of any signal at δ = 5.6 due to the benzylic proton 4-H. The deuterium label study thus provided clear evidence of the 5-*endo-trig* radical cyclization.

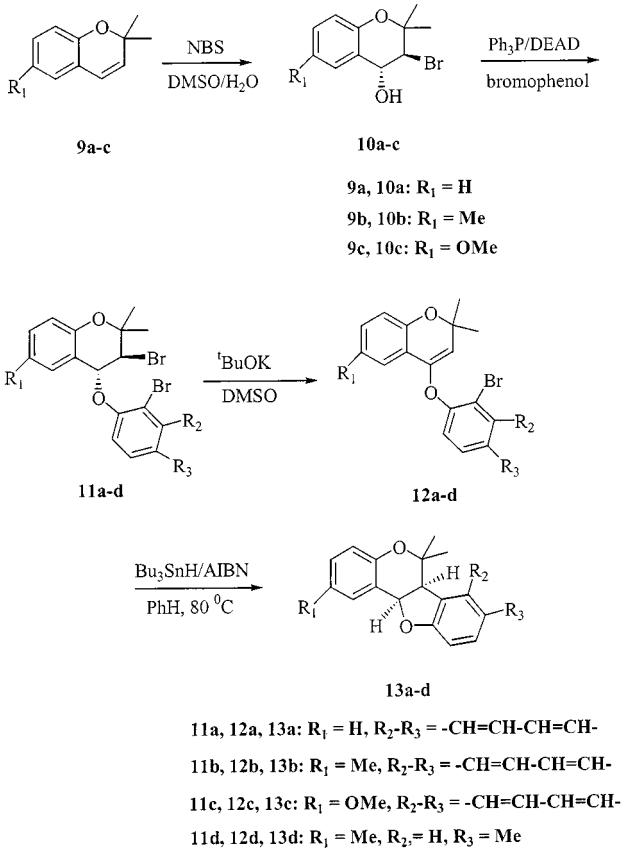


Scheme 2

Encouraged by the success of this unusual cyclization procedure, we extended this methodology to the synthesis of a new class of pterocarpans by a slightly modified route. To this end, the required key substrate **12** was synthesized in five steps. The intermediate aryl 1,1-dimethyl-2-propynyl ethers and 2,2-dimethyl-2*H*-chromenes were prepared by literature procedures.[13] Chromene **9a** was converted into the corresponding *trans*-bromohydrins **10a** in 85% yield by Dalton's method.[8] Conversion of the bromohydrin **10a** to the *trans*-aryl ether **11a** was achieved in a stereoselective manner by means of a Mitsunobu reaction with 1-bromo-2-naphthol in the presence of triphenylphosphane and DEAD.[14] It is worth mentioning here that the synthesis of aryl ethers of bromohydrins under basic or acidic conditions is very difficult.[15] The observed coupling constant between 3-H and 4-H (J = 5.38 Hz) clearly indicated that the relative stereochemistry at C-3 and C-4 was *trans*.

Treatment of **11a** with potassium *tert*-butoxide in dry DMSO at room temperature resulted in a clean conversion into the enol ether **12a**, in 81% yield. The enol ether was found to be extremely unstable and underwent hydrolysis

to form 2,2-dimethylchroman-4-one upon chromatographic purification over silica gel. When **12a** was refluxed with tributyltin hydride and AIBN in benzene for 20 h, a colorless solid (m.p. 118−119 °C) was obtained. The spectroscopic data clearly indicated that the obtained compound was the corresponding pterocarpan **13a** (Scheme 3). The other enol ethers **12b−d** underwent similar cyclization to afford the hitherto unknown pterocarpans **13b−d** in good yields.



Scheme 3

Conclusion

This report describes a novel and general method, based on radical cyclization, for the synthesis of pterocarpans. The deuterium label study provided unambiguous evidence for the occurrence of 5-*endo-trig* radical cyclization. Stereoselective syntheses of variously substituted aryl ethers of bromohydrins were achieved by use of the Mitsunobu reaction. This investigation also resulted in the synthesis of 6,6-dimethylpterocarpans.

Experimental Section

General Remarks: Reported melting points were determined with a Toshniwal melting point apparatus, and are uncorrected. − ^{1}H and ^{13}C NMR spectra were recorded with a Jeol GS × 400 spectrometer at 400 MHz and 100.5 MHz, respectively. Spectra were recorded at ambient temperature, with $CDCl_3$ as solvent. Chemical shifts are reported in ppm relative to tetramethylsilane (unless otherwise specified). − Low-resolution electron impact mass spectra were taken at an ionization potential of 70 eV. − IR spectra were recorded as solutions or neat with a Perkin−Elmer 1310 spectrometer. − The elemental analyses were obtained from RSIC, IIT, Madras. − Compounds **2a−c**, **3a−c**, **4a−c**, **5a−c**, and **9a−c** were prepared according to literature procedures.[8,13,16]

General Procedure for the Synthesis of Chromenols 6: Bromophenol or 1-bromo-2-naphthol (1.1 mmol) was added at room temperature to a solution of epoxide **5** (1 mmol) in ether (10 mL). The reaction mixture was stirred for 1 h. Removal of the solvent, followed by purification by column chromatography on silica gel (ethyl acetate/hexane = 1:9), afforded **6**.

(3*R,4*R**)-4-[(1-Bromo-2-naphthyl)oxy]-6-chloro-3,4-dihydro-2*H*-3-chromenol (6a):** Yield 94%. − M.p. 117−118 ° C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3500, 3020−2850, 1480, 1250−1180, 1010 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 2.3 (br. s, 1 H, 3-H), 4.1−4.5 (m, 3 H, 2-H), 5.0 (m, 1 H, 4-H), 6.5−7.5 (m, 8 H, Ar-H), 7.9 (d, *J* = 0.8 Hz, 1 H, Ar-H). − MS: *m*/*z* (%) = 404 (24) [M$^+$]. − $C_{19}H_{14}BrClO_3$ (403.98): calcd. C 56.25; H 3.48; found C 56.37; H 3.62.

(3*R,4*R**)-4-[(1-Bromo-2-naphthyl)oxy]-6-methoxy-3,4-dihydro-2*H*-3-chromenol (6b):** Yield 96%. − M.p. 142 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3500, 3000−2800, 1480, 1250−1180, 1010 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 2.32 (br. s, 1 H, 3-H) 3.6 (s, 3 H, OCH_3), 4.1−4.5 (m, 2 H, 2-H), 5.0 (m, 1 H, 4-H), 6.4−7.5 (m, 8 H, Ar-H), 7.9 (d, *J* = 0.8 Hz, 1 H Ar-H). − MS: *m*/*z* (%) = 400 (56) [M$^+$]. − $C_{20}H_{17}BrClO_4$ (400.03): calcd. C 59.87, H 4.27; found C 59.98, H 4.42.

(3*R,4*R**)-4-(2-Bromophenoxy)-3,4-dihydro-2*H*-3-chromenol (6c):** Yield 82%. − IR (neat): $\tilde{\nu}$ = 3500−3200, 3050−2820, 1580, 1480, 1200 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ =2.8 (br. s, 1 H, 3-H), 4.2−4.6 (m, 3 H, 2-H), 5.3 (m, 1 H, 4-H), 6.4−7.4 (m, 8 H, Ar-H). − MS: *m*/*z* (%) = 320 (62) [M$^+$].

General Procedure for the Synthesis of Tosylates 7: Alcohol **6** (1 mmol) in ether (10 mL) was added at room temperature to a suspension of sodium hydride (1.2 mmol) in ether (5 mL). The mixture was stirred for 1 h. The reaction mixture was cooled to −22 °C, *p*-toluenesulfonyl chloride (1.1 mmol) was added in one portion, and stirring was continued for 1 h. Inorganic salts were filtered off and the filtrate was washed with water (10 × 2 mL) and dried ($MgSO_4$). Removal of the solvent afforded the tosylate **7**, which was further purified by recrystallization, (hexane/benzene, 8:2).

(3*R,4*R**)-4-[(1-Bromo-2-naphthyl)oxy]-6-chloro-3,4-dihydro-2*H*-3-chromen-3-yl Tosylate (7a):** Yield 91%. − M.p. 165−166 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3010−2900, 1590, 1480, 1200−1180, 1000, 850 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 2.01 (s, 3 H, Ar-CH_3), 3.95−40.1(m, 1 H, 3-H), 4.5 (t, *J* =10 Hz, 2-H^a), 4.6 (m, 1 H, 2-H^b), 5.1 (d, *J* = 3.0 Hz, 1 H, 4-H), 6.4−7.5 (m, 12 H, Ar-H), 7.9 (d, *J* = 0.8 Hz, 1 H, Ar-H). − MS: *m*/*z* (%) = 558 (12) [M$^+$]. − $C_{26}H_{20}BrClO_5S$ (557.99): calcd. C, 55.78, H 3.60; found C 55.62, H 3.90.

(3*R,4*R**)-4-[(1-Bromo-2-naphthyl)oxy]-6-methoxy-3,4-dihydro-2*H*-3-chromen-3-yl Tosylate (7b):** Yield 88%. − M.p. 132 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3010−2800, 1585, 1480, 1200−1180, 1000, 850 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 2.0 (s, 3 H, Ar-CH_3), 3.75 (s, 3 H, OCH_3) 4.10−4.25 (m, 1 H, 3-H), 4.80 (t, *J* =10 Hz, 1 H, 2-H^a), 5.10 (m, 1 H, 2-H^b) 5.60 (d, *J* = 3.0 Hz, 1 H, 4-H), 6.80−8.01 (m, 12 H, Ar-H), 8.1 (d, *J* = 0.8 Hz, 1 H, Ar-H). − MS: *m*/*z* (%) = 554 (10) [M$^+$]. − $C_{27}H_{23}BrClO_6S$ (554.04): calcd. C, 58.38, H 4.17; found C 58.22, H 4.32.

(3*R,4*R**)-4-(2-Bromophenoxy)-3,4-dihydro-2*H*-3-chromen-3-yl Tosylate(7c):** Yield 80%, oil. − IR (neat): $\tilde{\nu}$ = 3050, 2800, 1600, 1480, 1210, 1175, 1000, 850 cm^{-1}. − ^1H NMR ($CDCl_3$) δ = 2.2 (s, 3 H, Ar-CH_3), 3.9−4.05 (m, 1 H, 3-H), 4.7 (t, *J* =10 Hz, 2 H, 2-H), 5.4 (d, *J* = 3 Hz, 1 H, 4-H), 6.8−7.9 (m, 12 H, Ar-H). − MS: *m*/*z* (%) = 474 (22) [M^+].

General Procedure for the Synthesis of Chromenes 8 and 10: The tosylate **7** (1 mmol) in DMSO (3 mL) was added dropwise at room temperature, over a period of 10 min, to a suspension of potassium *tert*-butoxide (2 mmol) in DMSO (10 mL). The resulting mixture was stirred for 1 h. The reaction mixture was quenched with water and extracted with ether (3 × 20 mL). The combined ether extracts were washed with water (2 × 20 mL) and brine (2 × 20 mL), and dried (Na_2SO_4). The organic layer was concentrated under reduced pressure. The crude product was further purified by column chromatography on neutral alumina, using hexane as eluent. A similar procedure was adopted to yield **12** from **11**.

4-(1-Bromonaphthalen-2-yloxy)-6-chloro-2*H*-chromene (8a): Yield 78%. − M.p. 132−133 °C. − IR ($CHCl_3$): 3010−2900, 1580, 1420, 1210−1190, 1000, 850 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 4.6 (t, *J* = 4.0 Hz, 1 H, 3-H), 4.9 (d, *J* = 4.0 Hz, 2 H, 2-H), 6.75−7.0 (m, 8 H, Ar-H), 8.2 (d, *J* = 0.8 Hz, 1 H, Ar-H). − MS: *m*/*z* (%) = 386 (100) [M^+].

4-(1-Bromonaphthalen-2-yloxy)-6-methoxy-2*H*-chromene (8b): Yield 76%. − M.p. 136 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3010−2900, 1580, 1420, 1200−1190, 1000, 850 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 3.8 (s, 3 H, OCH_3), 4.65 (t, *J* = 4.0 Hz, 1 H, 3-H), 4.8 (d, *J* = 4.0 Hz, 2 H, 2-H), 6.75−6.85 (m, 2 H, Ar-H), 7.2−7.9 (m, 6 H, Ar-H), 8.3 (d, *J* = 0.8 Hz, 1 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 55.9 (O*C*H_3), 65.5 (C-2), 98.0 (C-3), 107.5, 114.1, 116.0 116.5, 120.3, 121.0, 125.9, 126.9, 127.8, 128.2, 129.1, 131.9, 133.2, 149.1, 149.4, 149.8, 154.3. − MS: *m*/*z* (%) = 382 (100) [M^+].

4-(2-Bromophenoxy)-2*H*-chromene (8c): Yield 72%, viscous liquid. − IR (neat): $\tilde{\nu}$ = 3050−2850, 1575 1400, 1220−1190 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 4.7 (t, *J* = 4.0 Hz, 1 H, 3-H), 4.9 (d, *J* = 4.0 Hz, 2 H, 2-H), 6.6−7.7 (m, 8 H, Ar-H). − MS: *m*/*z* (%) = 302 (100) [M^+].

General Procedure for the Synthesis of Pterocarpans 1 and 13: Tributyltin hydride (1.1 mmol) and a catalytic amount of AIBN (ca. 20 mg) were added to a solution of enol ether **8** (1 mmol) in benzene (50 mL) and the solution was refluxed for 4 h (20 h for compound **13**). The solvent was removed under reduced pressure and the residue was then dissolved in ether (20 mL). Saturated KF solution (10 mL) was added and the mixture was stirred for 3 h. The ether layer was separated and washed with water (3 × 20 mL), aq. $NaHCO_3$ (2 × 20 mL), and brine (2 × 20 mL). Concentration and chromatography on silica gel, using hexane as eluent, gave the cyclized products. A similar procedure was applied to obtain **13** from compound **12**.

(6a*S,13a*S**)-2-Chloro-6a,13a-dihydro-6*H*-5,13-dioxadibenzo-[*a*,*g*]fluorene (Pterocarpan 1a):** Yield 88%. − M.p. 205 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3010−2800, 1600, 1450, 1210−1180 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 3.6 (t, *J* = 11.5 Hz, 1 H, 3-H), 4.0−4.1(m, 1 H, 2-H^a), 4.62 (ddd, *J* = 11.5, 6, 1.5 Hz, 1 H, 2-H^b), 5.65 (br. d, *J* = 7.5 Hz, 1 H, 4-H), 6.9−7.9 (m, 9 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 39.9 (C-6a), 75.9 (C-6), 76.2 (C-13a), 112.4, 114.2, 117.5, 118.4, 118.9, 120.3, 122.2, 123.2, 127.3, 129.1, 129.7, 130.1, 130.9, 149.7, 154.5, 157.3. − HRMS ($C_{19}H_{13}ClO_2$): calcd. 308.0604; found 308.0596. − $C_{19}H_{13}ClO_2$ (308.06): calcd. C 73.91, H 4.24; found C 73.54, H 4.16.

(6a*S,13a*S**)-2-Methoxy-6a,13a-dihydro-6*H*-5,13-dioxadibenzo-[*a*,*g*]fluorene (Pterocarpan 1b):** Yield 90%. − M.p. 201 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3020−2850, 1600, 1450, 1210−1180, 1000 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 3.6 (t, *J* = 11.5 Hz, 1 H, 6a-H), 3.85 (s, 3 H, OCH_3), 4.0−4.1 (m, 1 H, 6-H^a), 4.55−4.65 (ddd, *J* = 11.5, 6, 1.5 Hz, 1 H, 6-H^b), 5.7 (br. d, *J* = 7.5 Hz, 1 H, 11a-H), 6.9−7.9 (m, 9 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 39.6 (C-6a), 56.7(OCH_3), 77.9 (C-6), 78.0 (C-13a), 112.4, 118.6, 119.0, 121.5, 122.7, 123.4 126.7, 127.4, 129.1, 129.8, 130.2, 130.7, 154.2, 157.2. − MS: *m*/*z* (%) = 304 (100) [M^+]. − $C_{20}H_{16}O_3$ (304.11): calcd. C 78.94, H 5.26. found C 78.80; H 5.28.

(6a*S,11a*S**)-6a,11a-Dihydro-6*H*-benzo[4,5]furo[3,2-*c*]chromene (Pterocarpan 1c):** Yield 82%. − M.p. 125−126 °C (ref.[4a] m.p. 125−126 °C). − IR ($CHCl_3$): $\tilde{\nu}$ = 3000−2900, 1600, 1450, 1240−1180 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 3.6−3.8 (m, 1 H, 6a-H), 4.25−4.37 (m, 2 H, 6-H), 4.55(d, *J* = 6 Hz, 1 H, 11a-H), 6.87−7.57 (m, 8 H, Ar-H). − MS: *m*/*z* (%) = 224 (100) [M^+]. − HRMS ($C_{15}H_{12}O_2$): calcd. 224.0837, found 224.0822.

(6a*S,13a*S**)-2-Chloro-6a-hydro-13a-deuterio-6*H*-5,13-dioxadibenzo[*a*,*g*]fluorene (Pterocarpan 1d):** Yield 90%. − M.p. 205 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3010−2800, 1600, 1450, 1210−1180 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 3.5 (t, *J* = 11.5 Hz, 1 H, 6a-H), 4.0−4.1 (m, 1 H, 6-H^a), 4.6 (dd, *J* = 11.5, 6 Hz, 1 H, 6-H^b), 6.9−7.9 (m, 9 H, Ar-H). − HRMS ($C_{19}H_{12}ClDO_2$): calcd. 309.0657; found 309.0660. − $C_{19}H_{12}ClDO_2$ (309.06): calcd. C 73.67, H 4.55; found C 73.32, H 4.38.

(3*S,4*R**)-3-Bromo-2,2-dimethyl-3,4-dihydro-2*H*-chromen-4-ol (10a):** Yield 85%. − M.p. 105 °C (ref.[16] 106 °C). − IR ($CHCl_3$): $\tilde{\nu}$ = 3600, 2870−3000, 1480, 1420, 1252, 1180 cm^{-1} − ^1H NMR ($CDCl_3$): δ = 1.40 (s, 3 H, CH_3), 1.60 (s, 3 H, CH_3) 2.6 (br. s, 1 H, exchangeable with D_2O, OH) 4.2 (d, *J* = 9.28 Hz, 1 H, 4-H) 4.92 (d, *J* = 9.28 Hz, 1 H, 4-H), 6.8−7.6 (m, 4 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 19.8 (CH_3), 28.8 (CH_3), 63.0 (C-3), 70.3 (C-2), 78.8 (C-4), 116.9, 121.1, 122.3, 127.5, 129.7, 151.9. − MS: *m*/*z* (%) = 256 (28) [M^+].

(3*S,4*R**)-3-Bromo-2,2,6-trimethyl-3,4-dihydro-2*H*-chromen-4-ol (10b):** Yield 85%. − M.p. 123 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3580, 2870−3000, 1480, 1260, 1180, 1060 cm^{-1}. − ^1H NMR ($CDCl_3$): δ =1.39 (s, 3 H, CH_3), 1.59 (s, 3 H, CH_3) 2.29 (s, 3 H, Ar-CH_3) 2.40 (br. s, 1 H exchangeable with D_2O, OH) 3.91−4.11 (d, *J* = 9.9 Hz, 1 H, 3-H) 4.69−4.9 (d, *J* = 9.9 Hz, 1 H, 4-H), 6.81−7.31(m, 3 H, Ar-H). − MS: *m*/*z* (%) = 270 (24) [M^+].

(3*S,4*R**)-3-Bromo-6-methoxy-2,2-dimethyl-3,4-dihydro-2*H*-chromen-4-ol (10c):** Yield 82%. − M.p. 75 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3580, 2870−3000, 1480, 1260, 1175, 1050 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 1.37 (s, 3 H, CH_3), 1.57 (s, 3 H, CH_3) 2.53 (br. s, 1 H exchangeable with D_2O, OH) 3.76 (s, 3 H, OCH_3), 3.95−4.13 (d, *J* = 9.8 Hz, 1 H, 3-H) 4.72−4.87 (d, *J* = 9.8 Hz, 1 H, 4-H), 6.68−7.28 (m, 3 H, Ar-H). − MS: *m*/*z* (%) = 286 (20) [M^+].

General Procedure for the Mitsunobu Coupling Reactions: Triphenylphosphane (1.1 mmol), bromohydrin **12** (1 mmol), bromophenol (1.2 mmol), and dry benzene (10 mL) were placed in a dry, three-necked flask purged with argon. DEAD (1.2 mmol) was injected dropwise through a septum over a period of 10 min. The reaction was strongly exothermic and the color of the DEAD slowly disappeared. The reaction mixture was stirred for 8 h. The precipitated diethyl hydrazodicarboxylate was filtered and the organic layer was washed with 5% sodium hydroxide solution (2 × 20 mL) and then with water (3 × 20 mL). After drying with anhydrous sodium sulfate, the solvent was removed under vacuum and the residue was

purified by flash chromatography on silica gel, using hexane as eluent, to afford the aryl ethers of bromohydrins **11**.

(3*S,4*R**)-3-Bromo-4-(1-bromonaphthalen-2-yloxy)-2,2-dimethylchromane (11a):** Yield 84%. − M.p. 143−144 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 2976, 1621, 1592, 1486, 1458, 1340, 1226, 1118, 1040 cm^{-1} − ^1H NMR ($CDCl_3$): δ = 1.47 (s, 3 H, CH_3), 1.59 (s, 3 H, CH_3) 4.44 (d, *J* = 5.37 Hz, 1 H, 3-H) 5.7 (d, *J* = 5.37 Hz, 1 H, 4-H), 6.82−8.18 (m, 10 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 24.9 (CH_3), 26.4 (CH_3), 56.7 (C-3), 77.3 (C-2), 78.3 (C-4), 110.7, 115.8, 117.6, 119.0, 121.3, 124.9, 126.6, 127.9, 128.1, 129.1, 129.4, 130.3, 130.4, 133.4, 152.5, 152.5. − HRMS ($C_{21}H_{18}Br_2O_2$): calcd. 459.9673; found 459.9696.

(3*S,4*R**)-3-Bromo-4-(1-bromonaphthalen-2-yloxy)-2,2,6-trimethylchromane (11b):** Yield 82%. − M.p. 130−131 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 2976, 1622, 1590, 1491, 1452, 1340 cm^{-1} − ^1H NMR ($CDCl_3$): δ = 1.53 (s, 3 H, CH_3), 1.66 (s, 3 H, CH_3) 2.24 (s, 3 H, Ar-CH_3), 4.50 (d, *J* = 5.37 Hz, 1 H 3-H) 5.76 (d, *J* = 5.37 Hz, 1 H, 4-H), 6.81−8.27 (m, 9 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 20.6 (CH_3), 24.9 (CH_3), 26.3 (Ar-CH_3), 56.9 (C-3), 77.1(C-2), 78.4 (C-4), 110.7, 115.7, 117.4, 118.6, 124.9, 126.6, 127.9, 128.1, 129.2, 129.5, 130.3, 130.6, 131.3, 133.4, 150.3, 152.6. − HRMS ($C_{22}H_{20}Br_2O_2$): calcd. 473.9830; found 473.9862.

(3*S,4*R**)-3-Bromo-4-(1-bromonaphthalen-2-yloxy)-6-methoxy-2,2-dimethylchromane (11c):** Yield 84%. − M.p. 135−136 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 2976, 1619, 1596, 1491, 1459, 1350, 1264, 1155, 1132, 1040 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 1.50 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3) 3.67 (s, 3 H, OCH_3), 4.50 (d, *J* = 5.37 Hz, 1 H, 3-H) 5.78 (s, *J* = 5.37 Hz, 1 H, 4-H), 6.82−8.28 (m, 9 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 24.9 (CH_3), 26.2 (CH_3), 55.7 (OCH_3), 56.8 (C-3), 77.1 (C-2), 78.6 (C-4), 110.8, 112.9, 115.83, 117.4, 118.4, 119.3, 125.0, 126.6, 127.9, 128.1, 129.2, 130.3, 133.4, 146.4, 152.5, 153.9. − HRMS ($C_{22}H_{20}Br_2O_3$): calcd. 489.9779; found 489.9778.

(3*S,4*R**)-3-Bromo-4-(2-bromo-4-methylphenoxy)-2,2,6-trimethylchromane (11d):** Yield 82%. − M.p. 105 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 2960, 1596, 1488, 1411, 1273, 1129, 1049 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 1.44 (s, 3 H, CH_3), 1.54 (s, 3 H, CH_3) 2.19 (s, 3 H, Ar-CH_3) 2.24 (s, 3 H, Ar-CH_3), 4.32 (d, *J* = 4.89 Hz, 1 H, 3-H) 5.48 (s, *J* = 4.89 Hz, 1 H, 4-H), 6.70−7.36 (m, 6 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 20.5 (CH_3), 20.9 (CH_3), 26.0 (Ar-CH_3), 26.1 (Ar-CH_3), 56.6 (C-3), 77.9 (C-4), 113.1, 114.8, 117.6, 118.6, 129.3, 130.1, 130.8, 131.5, 133.0, 134.7, 150.6, 152.7. − HRMS ($C_{19}H_{20}Br_2O_2$): calcd. 437.9830; found 437.9848.

4-(1-Bromonaphthalen-2-yloxy)-2,2-dimethyl-2*H*-chromene (12a): Yield 81%. − M.p. 100−101 °C. − IR $CHCl_3$): $\tilde{\nu}$ = 2972, 1622, 1604, 1596, 1492, 1440, 1352, 1292, 1170, 1139, 1072 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 1.42 (s, 6 H, CH_3) 4.57 (s, 1 H, 3-H), 6.85−8.30 (m, 9 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 28.4 (CH_3), 78.8 (C-2), 106.8 (C-3), 113.4, 116.0, 117.9, 118.0, 120.3, 120.5, 121.9, 125.0, 125.5, 126.5, 127.5, 127.9, 128.7, 129.9, 147.3, 149.7, 153.6. − HRMS ($C_{22}H_{19}BrO_3$): calcd. 380.0412; found 380.0423.

4-(1-Bromonaphthalen-2-yloxy)-2,2,6-trimethyl-2*H*-chromene (12b): Yield 78%. − M.p. 106−107 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 2960, 1625, 1598, 1491, 1442, 1356, 1292, 1168, 1139, 1072 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 1.39 (s, 6 H, CH_3) 2.30 (s, 3 H, Ar-CH_3), 4.52 (s, 1 H, 3-H), 6.75−8.31 (m, 9 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 20.8 (CH_3), 28.5 (Ar-CH_3), 77.4 (C-2), 106.9 (C-3), 113.9, 116.2, 118.0, 121.0, 122.4, 125.9, 126.8, 127.8, 128.2, 129.1, 130.0, 130.7, 131.7, 133.1, 147.9, 150.0, 151.7. − HRMS ($C_{21}H_{17}BrO_2$): calcd. 394.0568; found 394.0588.

4-(1-Bromonaphthalen-2-yloxy)-6-methoxy-2,2-dimethyl-2*H*-chromene (12c): Yield 80%. − M.p. 103−104 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 2962, 1612, 1603, 1459, 1385, 1308, 1227, 1152, 1120, 1030 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 1.42 (s, 6 H, CH_3), 3.82 (s, 3 H, OCH_3), 4.64 (s, 1 H, 3-H) 6.87−8.40 (m, 9 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 28.3 (CH_3), 55.8 (OCH_3), 77.3 (C-2), 107.0 (C-3), 107.7, 113.8, 115.9, 117.1, 118.8, 120.9, 125.9, 126.8, 127.8, 128.2, 129.1, 131.7, 133.1, 147.7, 147.7, 149.9, 153.8. − HRMS ($C_{21}H_{17}BrO_2$): calcd. 410.0575; found 410.0563.

4-(2-Bromo-4-methylphenoxy)-2,2,6-trimethyl-2*H*-chromene (12d): Yield 85%. − M.p. 88−89 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 2960, 1612, 1603, 1458, 1459, 1411, 1353, 1267, 1164, 1065 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 1.39 (s, 6 H, CH_3) 2.28 (s, 3 H, Ar-CH_3), 2.33 (s, 3 H, Ar-CH_3), 4.48 (s, 1 H, 3-H), 6.64−7.40 (m, 6 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 20.5 (CH_3), 20.73 (Ar-CH_3), 28.5 (Ar-CH_3), 77.4 (C-2), 106.4 (C-3), 115.1, 116.1, 116.2, 117.9, 122.4, 126.8, 129.3, 129.8, 130.6, 130.8, 134.0, 135.7, 147.9, 151.8. − HRMS ($C_{19}H_{19}BrO_2$): calcd. 358.0568; found 358.0594.

(6a*R,13a*S**)-6,6-Dimethyl-6a,13a-dihydro-6*H*-5,13-dioxadibenzo[*a*,*g*]fluorene (Pterocarpan 13a):** Yield 82%. − M.p. 118−119 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 2990, 1622, 1582, 1490, 1462, 1360, 1264, 1036, 950 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 0.93 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 3.86 (d, *J* = 7.32 Hz, 1 H, 6a-H), 5.65 (d, *J* = 7.32 Hz, 1 H, 13a-H), 6.96−7.85 (m, 10 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 20.0 (CH_3), 30.6 (CH_3), 48.4 (C-6a), 76.5 (*C*-6), 80.0 (C-13a), 112.3, 118.0, 119.5, 120.3, 121.3, 122.9, 123.9, 126.7, 129.1, 129.8, 130.0, 130.1, 130.3, 130.9, 153.3, 158.6. − HRMS ($C_{21}H_{18}O_2$): calcd. 302.1306; found 302.1316.

(6a*R,13a*S**)-2,6,6-Trimethyl-6a,13a-dihydro-6*H*-5,13-dioxadibenzo[*a*,*g*]fluorene (Pterocarpan 13b):** Yield 85%. − M.p. 123 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 2991, 1628, 1554, 1484, 1462, 1372, 1254, 1120, 950 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 0.80 (s, 3 H, CH_3) 1.58 (s, 3 H, CH_3), 2.3 (s, 3 H, Ar-CH_3), 3.8 (d, *J* = 7.44 Hz, 1 H, 6a-H) 5.55 (d, *J* = 7.44 Hz, 1 H, 13a-H), 6.8−7.82 (m, 9 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 20.0 (CH_3), 20.6 (CH_3), 30.6 (Ar-CH_3), 48.5 (C-6a), 77.4 (C-6), 80.1 (C-13a), 112.2, 117.7, 119.1, 120.40, 122.9, 123.9, 126.7, 129.0, 129.8, 130.1, 130.3, 130.6, 130.9, 131.0, 151.0, 158.5. − HRMS ($C_{22}H_{20}O_2$): calcd. 316.1463; found 316.1482.

(6a*R,13a*S**)-2-Methoxy-6,6-dimethyl-6a,13a-dihydro-6*H*-5,13-dioxadibenzo[*a*,*g*]fluorene (Pterocarpan 13c):** Yield 82%. − M.p. 159−160 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 2992, 1625, 1580, 1491, 1459, 1366, 1264, 1161, 1129, 1056, 950 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 0.90 (s, 3 H, CH_3) 1.65 (s, 3 H, CH_3), 3.82 (d, *J* = 7.32 Hz, 1 H, 6a-H), 3.83 (s, 3 H, OCH_3), 5.60 (d, *J* = 7.32 Hz, 1 H, 13a-H), 6.89−7.84 (m, 9 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 19.8 (CH_3), 30.6 (CH_3), 48.5 (C-6a), 55.8 (OCH_3), 76.7 (C-6), 80.2 (C-13a), 112.2, 113.2, 117.3, 118.8, 119.8, 120.3, 122.9, 123.9, 126.7, 129.0, 129.8, 130.3, 130.9, 147.1, 154.0, 158.4. − HRMS ($C_{22}H_{20}O_3$): calcd. 332.1412; found 332.1432.

(6a*R,11a*S**)-2,6,6,8-Tetramethyl-6a,11a-dihydro-6*H*-benzo[4,5]-furo[3,2-*c*]chromene (Pterocarpan 13d):** Yield 84%. − M.p. 106 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 2992, 1616, 1588, 1490, 1459, 1260, 1129, 1035 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 0.87 (s, 3 H, CH_3) 1.56 (s, 3 H, CH_3), 2.31 (s, 3 H, Ar-CH_3), 2.33 (s, 3 H, Ar-CH_3), 3.37 (d, *J* = 7.55 Hz, 1 H, 6a-H) 5.46 (d, *J* = 7.55 Hz, 1 H, 13a-H), 6.74−7.36 (m, 6 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 20.0 (CH_3), 20.6 (CH_3), 20.9 (Ar-CH_3), 27.6 (Ar-CH_3), 49.6 (C-6a), 76.1 (C-6), 78.4 (C-13a), 109.4, 117.7, 119.9, 125.9, 128.3, 129.4, 130.0, 130.1, 130.6, 130.7, 150.8, 158.0. − HRMS ($C_{19}H_{20}O_2$): calcd. 280.1463; found 280.1488.

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