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Original Scientific Article

Heck-oxyarylation of 2-phenyl-2*H*-chromenes and 1,2-dihydronaphthalenes

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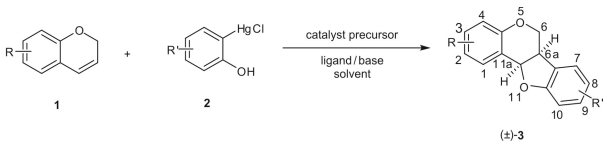
Abstract. The Heck-oxyarylation of racemic 2-phenyl-2*H*-chromene [(±)-**4b**] and 1,2-dihydronaphthalenes (**14a,b**) has been studied with 2-chloromercuriphenols (**5a–d**) in the presence of $Li_2[PdCl_4]$ catalyst. The reactions resulted in the diastereoselective formation of racemic 6-phenylpterocarpans of (6*R*, 6a*R*,11a*R*) relative configuration [(±)-**8a–d**] and their dibenzo[1,3]dioxocine analogues [(±)-**12a–d**] as main products, respectively. The ratio of products and the lack of regioisomeric products (**13a–d**) corroborated the cationic mechanism of the oxyarylation of 2*H*-chromenes, which has been also supported by the transformation of **14a,b** under similar conditions.(doi: 10.5562/cca2103)

Keywords: Pterocarpans; Dibenzo[d,g][1,3]dioxocines; Palladium(0); Oxidative coupling; Reaction mechanism; Catalysis

INTRODUCTION

Pterocarpans are naturally occurring plant products containing a *cis*-fused benzofurano-benzopyran skeleton. Many of them are phytoalexins produced in plants during infections by fungi, viruses or bacteria and subsequently act as protective agents for plants.[1] Moreover, some representatives of this type of natural products have significant oestrogenic activity[2] and others have been reported to inhibit HIV-1 reverse transcriptase in cell cultures[3] and to possess high activity against snake or spider venoms.[4]

Among the wide variety of synthetic routes to racemic pterocarpans [(±)-**3**],[5–16] one of the most commonly used approach[17–22] is based on the Heck-oxyarylation of 2*H*-chromenes (**1**) with 2-chloromercuriphenols (**2**) using equimolar amount of $Li_2[PdCl_4]$ as catalyst (Scheme 1).[7]



Scheme 1. Heck-oxyarylation of 2*H*-chromenes.

In contrast to the reports of Breytenbach[17] we have found that the oxyarylation of 7-benzyloxy-2*H*-chromene (**4a**) with 2-chloromercuri-3,4-methylenedioxyphenol (**5a**) under the conditions published by Horino and Inoue[7] did not take place with complete regioselectivity (**4a**+**5a**→**6a**→**7a**→**8a**), but additional coupled products **12a** and **13a** were also obtained (Scheme 2), probably *via* **10a**→**11a** and **10a** carbocation intermediates, respectively.[23]

In order to study the factors that determine the nature and ration of the three possible products, we studied the effect of an additional C-2 phenyl group on the 2*H*-chromene ring and replacement of its oxygen by a methylene group as well as different substitution pattern of the 2-chloromercuriphenol. Thus Heck-oxyarylations of racemic 2-phenyl-2*H*-chromene [(±)-**4b**] and 1,2-dihydronaphthalenes (**14a,b**) were carried out with three 2-chloromercuriphenols (**5a–c**) in the presence of $Li_2[PdCl_4]$ at room temperature.

RESULTS AND DISCUSSION

The racemic 2-phenyl-2*H*-chromene [(±)-**4b**] was obtained from *rac*-flavanone in two steps according to literature.[24] 2-Chloromercuriphenols (**5a–d**) were prepared from commercially available sesamol (3,4-

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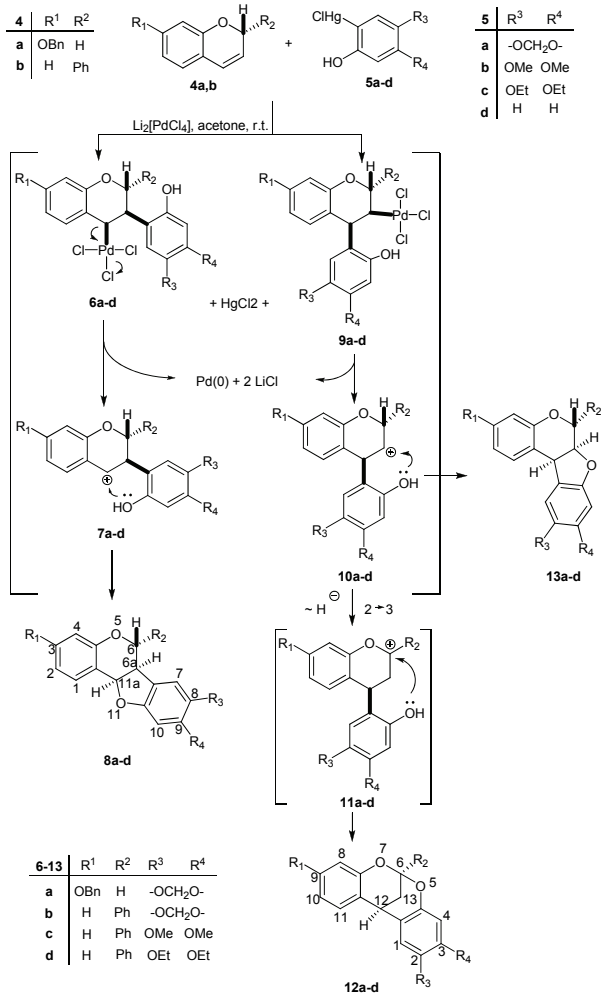


Scheme 2. Proposed sequence of Pd(0)-catalyzed oxyarylation of **4a,b** with **5a-c**.

methylendioxyphenol), 3,4-dimethoxyphenol and 3,4-diethoxyphenol and phenol by mercury (II) acetate, respectively, under the conditions used earlier by two of us.[23] The TLC monitoring of oxyarylation of (±)-**4b** with **5a** has clearly shown that the conversion of the starting material [(±)-**4b**] reached about 50 % in three hours and then changed very slowly with longer reaction time.

Besides the starting material (±)-**4b**, two main products could be isolated by column chromatography whose structures were elucidated by spectroscopic methods. On the basis of ^{1}H, ^{13}C NMR and MS data, the major product could be identified as racemic 6-phenyl-8,9-methylenedioxypterocarpan [(±)-**8b**]. The large coupling constant between of H-6 and H-6a (J = 10.8 Hz) has clearly indicated the *trans* diaxial orientation of H-6, H-6a and thus the *trans* relative configuration of the C-6 phenyl and C-6a aryl groups. The addition of the organopalladium intermediate formed from

Table 1. Compounds formed by oxyarylation of olefin **4a,b**

Entry	Olefin + ArHgCl	Product (Yield / %)[(a)]	Ratio of product
1	**4a** + **5a**	**8a**(53); **13a**(3); **12a**(7.5)	**8a**:**12a** = 7:1
2	**4b** + **5a**	**8b**(8); **13b**(n.d.); **12b**(2)	**8b**:**12b** = 4:1
3	**4b** + **5b**	**8c**(13); **13c**(n.d.); **12c**(5)	**8c**:**12c** = 2.4:1
4	**4b** + **5c**	**8d**(20); **13d**(n.d.); **12d**(23)	**8d**:**12d** = 1:1.1

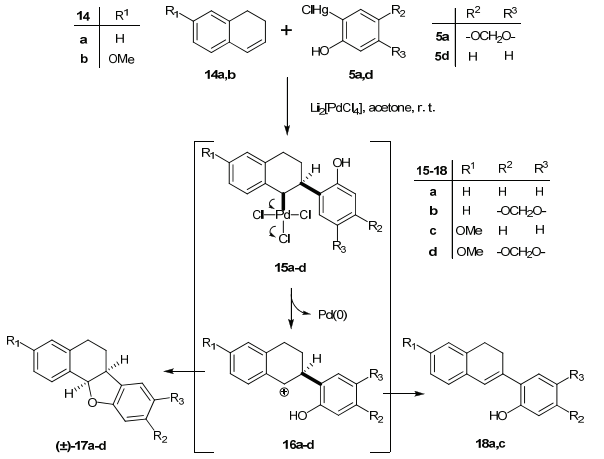
[(a)] isolated yields; n.d. – not detected.

5a by $Li_2[PdCl_4]$ took place at C-3 of (±)-**4b** diastereoselectively, from the opposite side to the C-2 phenyl group to give racemic 6-phenylpterocarpan [(±)-**8b**] with (6*S*, 6a*R*, 11a*R*) relative configuration. The other product was identified as (±)-6-phenyl-6,11-methano-2,3-methylendioxy-6*H*-dibenzo[d,g][1,3]dioxocine [(±)-**12b**] by comparing its NMR and MS data with those of [(±)-**12a**].[23] Due to its bridged structure, the C-6 phenyl and H-12 adopt necessarily *cis* equatorial orientations implying a (6*R*, 12*R*) relative configuration. It is to be noted that neither the diastereomer of (±)-**8b** with (6*R*, 6a*R*, 11a*R*) relative configuration, nor the regioisomeric (±)-**13b** bearing the 3,4-methylenedioxyphenyl group at C-4 of the flavane skeleton could be isolated.

Comparison of the recent findings with our previous observations[23] allowed following conclusions: (i) the Heck-type oxyarylation of (±)-**4b** did not take place with complete regioselectivity leading to the formation of both palladium intermediates **6b** and **9b**, (ii) the ring-closure of the latter *via* the corresponding carbocationic intermediates **10b** and **11b** resulted in the bridged product (±)-**12b**. Since the formation of the (±)-**13b** regioisomer of (±)-**8b** could not be observed, one may assume that the life time of the cationic intermediate **10b** must be very short due to its rapid transformation by a 1,2 hydride-shift to **11b**. The formation of the tertiary carbocation **11b** is clearly enhanced by the presence of the C-2 phenyl group. Accordingly, the ratio of the products (**8b**:**12b**) (Table 1. entry 2) is significantly smaller than that of (**8a**:**12a**) (entry 1) obtained in the reaction of 7-benzyloxy-2*H*-chromene (**4a**) with **5a**.[23]

The formation of the bridged product was also facilitated further by using the **5b** or **5c** dialkoxy chloromercuriphenols possessing an increased nucleophilicty of their hydroxy group (entry 3 and 4). Thus the proposed cationic mechanism of the Heck-oxyarylation of 2*H*-chromenes (**1**) with 2-chloromercuriphenols (**2**) in the presence of of $Li_2[PdCl_4]$ catalyst is justified.

The role of the chromene oxygen in the Heck-oxyarylation was studied in the reaction of 1,2-dihydronaphthalenes (**14a,b**) with 2-chloromercuriphenols (**5a,d**) under the conditions discussed above (Scheme 3).



Scheme 3. Proposed sequence of Pd(0)-catalyzed oxyarylation of **14a,b** with **2** and **5a**.

In the reaction of 1,2-dihydronaphthalene (**14a**) and 2-chloromercuriphenol (**5d**), the formation of 5-carbapterocarpan [(±)-**17a**] and traces of 3-(2-hydroxyphenyl)-1,2-dihydronaphthalene (**18a**) were observed. When an electron rich 2-chloromercuriphenol derivative, such as **5a** was used instead of **5d**, the yield of the heteroannulation product (±)-**17b** improved and the corresponding side-product **18b** could not be detected. The transformation of the electron rich dihydronaphthalene (**14b**) with **5a** took place in a similar manner to result in **17d**. On the other hand, its oxyarylation with **5d** resulted in (±)-**17c** as the minor product and the so called Heck-type product (**18c**) was isolated in 48 % yield. Thus the *syn*-arylpalladation of the double bond of dihydro-naphthalenes **14a,b** gave the corresponding intermediates **15a–d** and subsequent formation of the benzylic carbocations **16a–d** occurred, the latter of which reacted further by ring closure or *β*-elimination resulting in (±)-**17a-d** or **18a,c** respectively, depending on the substitution pattern of the aryl moieties. The formation of the carba analogue of (±)-**13a** (O-5 = CH_2) or **12a** could not be observed. These results also clearly supported the above mentioned cationic mechanism of the Heck-oxyarylation process.

EXPERIMENTAL SECTION

General Procedures

All reagents and organic compounds used were purchased from Sigma-Aldrich. ^{1}H and ^{13}C NMR spectra were recorded at 360 MHz and 90 MHz, respectively with a Brucker AM-360 instrument in $CDCl_3$ with TMS as internal standard. The chemicals shifts are given in *δ* (ppm). Precoated silica gel plates (Kieselgel 60 F 254, 0.25 mm Merck) were applied for analytical and preparative TLC. The ESI-TOF MS measurements were performed on a MicroTOF-Q instrument (Bruker Daltonik GmbH, Bremen, Germany). The yield of (±)-**8b–d** and (±)-**12b–d** belongs to an about 50 % conversion of (±)-**4a**.

General Procedure for the Heck-oxyarylation Reaction

Palladium-chloride (177 mg, 1 mmol) and lithium chloride (84 mg, 2 mmol) were magnetically stirred in dry acetone (10 mL) at room temperature. After 15 min. the 2*H*-chromene derivative (1 mmol) in dry acetone (10 mL) was added and the reaction mixture stirred again for 15 min., followed by the addition of the 2-chloromercuriphenol derivative (1 mmol) suspended in dry acetone (10 mL). Stirring was continued for 3 h. Then brine was added to the reaction mixture and it was filtered off on Celite pad to remove the Pd(0). The products were extracted with ethyl acetate, washed with water and dried over magnesium sulfate. The solvent was removed under reduced pressure to give a viscous oil, whose components were separated by preparative TLC using hexane: ethyl acetate 4:1 as eluent.

(±)-(6S,6aR*,11aR*)-8,9-Methylenedioxy-6-phenylpterocarpan* (**8b**)

Colorless crystals, 76 mg (8 %), m.p. = 192–194 ºC; R_f = 0.8 (hexane:ethyl acetate = 9:1); ^{1}H NMR: 3.48 (1H, dd, *J* = 6.8 Hz, *J* = 10.4 Hz, H-6a), 4.46 (1H, d, *J* = 10.8 Hz, H-6), 5.59 (1H, d, *J* = 6.4 Hz, H-11a), 5.73 (1H, s, H-10), 5.85 (2H, 2s, OCH_2O), 6.47 (1H, s, H-7), 7.02 (1H, d, *J* = 8.2 Hz, H-4), 7.09 (1H, t, *J* = 7.3 Hz, H-2), 7.29-7.33 ($3H_{arom}$, m, H-2′,3,6′), 7.41-7.43 ($3H_{arom}$, s, H-3′,4′,5′), 7.6 (1H, d, *J* = 7.5 Hz, H-1); ^{13}C NMR : 46.8 (C-6a), 79,3 (C-11a), 79.6 (6), 93.4 (10), 101,1 (OCH_2O), 106,2 (7), 117.7 (4), 119,6, 121.8 (1), 128.1, 128.7, 128.9, 130.2 (3), 130.5 (2), 137.9, 141.0 (8), 147.9 (9), 154.1, 155.6; HRMS (*m*/*z*) calcd. for $C_{22}H_{16}NaO_4$ 367.094, found $[M+Na]^+$ 367.092.

(±)-(6S,6aR*,11aR*)-8,9-Dimethoxy-6-phenylpterocarpan* (**8c**)

Colorless crystals, 57 mg (13 %), m.p. = 160–162 ºC; R_f = 0.3 (hexane:ethyl acetate = 4:1); ^{1}H NMR: 3.50 (1H, dd, *J* = 6.8 Hz, *J* = 10.8 Hz, H-6a), 3.5 (3H, s, OCH_3), 3.84 (3H, s, OCH_3), 4.44 (1H, d, *J* = 10.8 Hz, H-6), 5.60 (1H, d, *J* = 6.8 Hz, H-11a), 5.78 (1H, s, H-10), 6.54 (1H, s, H-7), 7.04 (1H, d, *J* = 8.2 Hz, H-4), 7.09 (1H, t, *J* = 7.5 Hz, H-2), 7.30-7.33 ($3H_{arom}$, m, H-2′,3,6′), 7.40-7.42 ($3H_{arom}$, s, H-3′,4′,5′), 7.63 (1H, dd, *J* = 7.5 Hz, *J* = 1.4 Hz, H-1); ^{13}C NMR : 47.4 (C-6a), 55.9 (CH_3), 56.2 (CH_3), 79.2 (C-11a), 79.5 (6), 94.9 (10), 110.1 (7), 116.3, 117.6 (4), 119.7, 121.8 (1), 128.1, 128.6, 130.0 (3), 130.7 (2), 137.9, 142.9 (8), 150.0 (9), 153.5, 155.3; HRMS (*m*/*z*) calcd. for $C_{23}H_{20}NaO_4$ 383.125, found $[M+Na]^+$ 383.124.

(±)-(6S,6aR*,11aR*)-8,9-Diethoxy-6-phenylpterocarpan* (**8d**)
Colorless crystals, 75 g (20 %), m.p. = 153.5–154.8 ºC; R_f = 0.5 (hexane:ethyl acetate = 9:1); ^{1}H NMR: 1.25 (3H, t, J = 6.8 Hz, CH_3), 1.43 (3H, t, J = 6.8 Hz, CH_3), 3.48 (1H, dd, J = 6.8 Hz, J = 11.1 Hz, H-6a), 3.71 (2H, m, OCH_2), 4.03 (2H, m, OCH_2), 4.44 (1H, d, J = 11.1 Hz, H-6), 5.58 (1H, d, J = 6.8 Hz, H-11a), 5.82 (1H, s, H-10), 6.52 (1H, s, H-7), 7.03 (1H, d, J = 7.9 Hz, H-4), 7.10 (1H, t, J = 7.5 Hz, H-2), 7.29-7.33 ($3H_{arom}$, m, H-2′,3,6′), 7.39-7.41 ($3H_{arom}$, s, H-3′,4′,5′), 7.62 (1H, d, J = 7.5 Hz, H-1); ^{13}C NMR : 14.7 (CH_3), 47.4 (C-6a), 64.9 (CH_2), 79.2 (C-11a), 79.5 (6), 94.9 (10), 110.1 (7), 116.3, 117.6 (4), 119.7, 121.8 (1), 128.1, 128.6, 130.0 (3), 130.7 (2), 137.9, 142.9 (8), 150.0 (9), 153.5, 155.3; HRMS (*m*/*z*) calcd. for $C_{25}H_{24}NaO_4$ 411.157, found $[M+Na]^+$ 411.156.

(±)-(6R,12R*)-6,11-Methano-2,3-methylenedioxy-6-phenyl-6H,11H-dibenzo[d,g][1,3]dioxocine* (**12b**)
Colorless crystals, 21 mg (2 %), m.p. = 196–198 ºC; R_f = 0.7 (hexane:ethyl acetate = 9:1); ^{1}H NMR: 2.58 (2H, d, J = 2.8 Hz, H-13), 3.95 (1H, s, H-12), 5.85 (2H, 2s, OCH_2O), 6.56 (1H, s, H-4), 6.69 (1H, s, H-1), 6.91 (1H, t, J = 7.2 Hz, H-10), 7.02 (1H, d, J = 7.9 Hz, H-8), 7.14 (1H, t, J = 7.7 Hz, H-9), 7.21 (1H, d, J = 7.2 Hz, H-11), 7.40-7.47 ($3H_{arom}$, m, H-3′,4′,5′), 7.72 (2H, d, J = 6.8 Hz, H-2′,6′); ^{13}C NMR: 33.5 (13), 33.8 (12), 98.5 (6), 101.1 (4), 103.1 (OCH_2O), 110.2 (1), 116.6 (8), 116.7, 121.3 (11), 126.7, 126.8, 126.9, 127.9 (9), 128.3, 128.7 (10), 141.4, 143.7 (2), 145.6 (3), 148.8, 151.9; HRMS (*m*/*z*) calcd. for $C_{22}H_{16}NaO_4$ 367.094, found $[M+Na]^+$ 367.092.

(±)-(6R,12R*)-2,3-Dimethoxy-6,11-methano-6-phenyl-6H,11H-dibenzo[d,g][1,3]dioxocine* (**12c**)
Colorless crystals, 23 mg (5 %), m.p. = 167–169 ºC; R_f = 0.2 (hexane:ethyl acetate = 4:1); ^{1}H NMR: 2.34 (1H, dd, J_{Hax},H-12 = 3.2 Hz, $J_{Hax,Heq}$ = 13.3 Hz, H-13_{ax}), 2.41 (1H, dd, J_{Heq},H-12 = 2.8 Hz, $J_{Heq,Hax}$ = 13.3 Hz, H-13_{eq}), 3.81 and 3.85 (6H, 2s, 2 OCH_3), 3.98 (1H, t, J = 2.8 Hz, H-12), 6.61 (1H, s, H-4), 6.72 (1H, s, H-1), 6.90 (1H, t, J = 7.5 Hz, H-10), 6.94 (1H, d, J = 7.5 Hz, H-8), 7.15 (1H, t, J = 8.6 Hz, H-9), 7.24 (1H, d, J = 7.5 Hz, H-11), 7.41-7.46 ($3H_{arom}$, m, H 3′,4′,5′), 7.76 (2H, d, J = 8.2 Hz, H-2′,6′); ^{13}C NMR: 33.5 (13), 33.8 (12), 55.9 (CH_3), 56.6 (CH_3), 98.5 (6), 101.1 (4), 110.2 (1), 116.6 (8), 116.7, 121.3 (11), 126.7, 126.8, 126.9, 127.9 (9), 128.3, 128.7 (10), 141.4, 143.7 (2), 145.6 (3), 148.8, 151.9; HRMS (*m*/*z*) calcd. for $C_{23}H_{20}NaO_4$ 383.125, found $[M+Na]^+$ 383.124.

(±)-(6R,12R*)-2,3-Diethoxy-6,11-methano-6-phenyl-6H,11H-dibenzo[d,g][1,3]dioxocine* (**12d**)
Colorless crystals, 85 mg (23 %), m.p. = 115–118 ºC; R_f = 0.4 (hexane:ethyl acetate = 9:1); ^{1}H NMR: 1.40 (6H, t, J = 6.8 Hz, 2 CH_3), 2.32 (1H, dd, J_{Heq},H-12 = 2.8 Hz, $J_{Heq,Hax}$ = 13.3 Hz, H-13_{eq}), 2.40 (1H, dd, J_{Hax},H-12 = 3.2 Hz, $J_{Hax,Heq}$ = 13.3 Hz, H-13_{ax}), 3.96 (1H, t, J = 2.8 Hz, H-12), 4.02 (4H, m, 2 OCH_2), 6.60 (1H, s, H-4), 6.76 (1H, s, H-1), 6.91 (1H, t, J = 7.2 Hz, H-10), 7.02 (1H, d, J = 7.9 Hz, H-8), 7.14 (1H, t, J = 7.9 Hz, H-9), 7.23 (1H, d, J = 7.5 Hz, H-11), 7.40-7.47 ($3H_{arom}$, m, H 3′,4′,5′), 7.75 (2H, d, J = 7.9 Hz, H-2′,6′); ^{13}C NMR: 14.7 (CH_3), 33.5 (13), 33.8 (12), 64.9 (CH_2), 98.5 (6), 101.1 (4), 110.2 (1), 116.6 (8), 116.7, 121.3 (11), 126.7, 126.8, 126.9, 127.9 (9), 128.3, 128.7 (10), 141.4, 143.7 (2), 145.6 (3), 148.8, 151.9; HRMS (*m*/*z*) calcd. for $C_{25}H_{24}NaO_4$ 411.157, found $[M+Na]^+$ 411.156.

(±)-(6aR,11aS*)-5,6,6a,11a-Tetrahydrobenzo[d]naphtho[1,2-b]furan* (**17a**)
White crystals, 59 mg (14 %), m.p. = 39–40 ºC (Ref. 18, 40 ºC); R_f = 0.7 (hexane:ethyl acetate = 9:1); ^{1}H NMR: 1.86 (2H, m, H-6), 2.59 (2H, m, H-5), 3,60 (1H, m, H-6a), 5.58 (1H, d, J = 8.4 Hz, H-11a), 6.70 (1H, d, J = 8Hz, H-10), 6.81 (1H, dt, J = 7.4 Hz, J = 1.48 Hz, H-8), 7.05 ($2H_{arom}$, m, H-2, 4), 7.18 ($3H_{arom}$, m, H-3, 7, 9), 7.46 (1H, dd, J = 7.2 Hz, J = 1.6 Hz, H-1); HRMS (*m*/*z*) calcd. for $C_{16}H_{14}NaO$ 245.094, found: $[M+Na]^+$ 245.090.

(±)-(6aR,11aS*)-8,9-Methylenedioxy-5,6,6a,11a-tetrahydrobenzo[d]naphtho[1,2-b]furan* (**17b**)
White crystals, 152 mg (29 %), m.p. = 84–86 ºC; R_f = 0.6 (hexane:ethyl acetate = 9:1); ^{1}H NMR: 1.87 (2H, m, H-6), 2.67 (2H, m, H-5), 3.57 (1H, m, H-6a), 5.65 (1H, d, J = 8.6 Hz, H-11a), 5.88 (2H, d, J = 5.4 Hz, OCH_2O), 6.37 (1H, s, H-10), 6.70 (1H, s, H-7), 7.14 (1H, d, J = 6.8 Hz, H-4), 7.26 (2H, m, H-2, 3), 7.5 (1H, d, J = 6.5 Hz, H-1); HRMS (*m*/*z*) calcd. for $C_{17}H_{14}NaO_3$ 289.084, found: $[M+Na]^+$ 289.080.

(±)-(6aR,11aS*)-3-Methoxy-5,6,6a,11a-tetrahydrobenzo[d]naphtho[1,2-b]furan* (**17c**)
Yellow oil, 30 mg (3 %); R_f = 0.6 (hexane:ethyl acetate = 7:3); ^{1}H NMR: 1,93 (2H, m, H-6), 2.62 (2H, m, H-5), 3.64 (1H, m, H-6a), 3.77 (3H, d, J = 5.8 Hz, OMe), 5.63 (1H, d, J = 8.6 Hz, H-11a), 7.05 ($7H_{arom}$, m, H-1, 2, 4, 7, 8, 9, 10); HRMS (*m*/*z*) calcd. for $C_{16}H_{14}NaO$ 275.104, found: $[M+Na]^+$ 275.100.

(±)-(6aR,11aS*)-3-Methoxy-8,9-methylenedioxy-5,6,6a,11a-tetrahydrobenzo[d]naphtho[1,2-b]furan* (**17d**)
Yellow oil, 311 mg (30 %); R_f = 0.6 (hexane:ethyl acetate = 7:3); ^{1}H NMR: 1.86 (2H, m, H-6), 2.66 (2H, m, H-5), 3.55 (1H, m, H-6a), 3.80 (3H, s, OMe), 5.63 (1H, d, J = 8.3 Hz, H-11a), 5.88 (2H, d, J = 4.7 Hz, OCH_2O), 6.36 (1H, s, H-10), 6.69 (1H, d, J = 2.1 Hz, H-4), 6.70 (1H, s, H-7), 6.84 (1H, dd, J = 8.3 Hz, J = 2.2 Hz, H-2), 7.42 (1H, d, J = 8.3 Hz, H-1); HRMS (*m*/*z*) calcd. for $C_{18}H_{16}NaO_4$ 319.094, found: $[M+Na]^+$ 319.093.

2-(3,4-Dihydronaphthalen-2-yl)phenol (**18a**)
Brown oil, 32 mg (3 %); R_f = 0.3 (hexane:ethyl acetate = 9:1); ^{1}H NMR: 2.69 (2H, t, J = 8.2 Hz, H-4), 2.99 (2H, t, J = 8 Hz, H-3), 5.56 (1H, s, OH), 6.73 (1H, s, H-1), 6.96 (2H, d, J = 7.6 Hz, H-5, H-8), 7.09-7.24 ($6H_{arom}$, m, H-6,7, H_{phenol}-3, 4, 5, 6); HRMS (*m*/*z*) calcd. for $C_{16}H_{14}NaO$ 245.094, found: $[M+Na]^+$ 245.091.

2-(6-Methoxy-3,4-dihydronaphthalen-2-yl)phenol (**18c**)
Brown oil, 361 mg (48 %); R_f = 0.3 (hexane:ethyl acetate = 7:3); ^{1}H NMR: 2.64 (2H, t, J = 7.9 Hz, H-4), 2.93 (2H, t, J = 7.9, H-3), 3.81 (3H, s, OMe), 5.63 (1H, s, OH), 6.66 (1H, s, H-1), 6.71-7.19 ($7H_{arom}$, m, H-5, 7, 8, H_{phenol}-3, 4, 5, 6); HRMS (*m*/*z*) calcd. for $C_{17}H_{16}NaO_2$ 275.104, found: $[M+Na]^+$ 275.102.

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