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Tetralones as precursors for the synthesis of 2,2′-disubstituted 1,1′-binaphthyls and related compounds

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ABSTRACT

Using tetralones as starting materials, the synthesis of biaryl compounds is described in this paper. The tetralones were initially converted into 1-bromo-3,4-dihydro-2-naphthalenecarbaldehydes before effecting aromatization into the corresponding naphthalenes. These products were then subjected to Suzuki–Miyaura cross-coupling reactions, with a variety of aromatic boronic acids containing substituents in the *ortho* position, to afford biaryl compounds. The biaryl compounds possess heteroatom containing substituents *ortho* to the newly formed biaryl axis.

1. Introduction

The synthesis of aromatic compounds containing biaryl axes is important as a result of the biological activities associated with biaryl natural products,[1] as well as their use as ligands in transition metal catalyzed reactions.[2] Amongst this class of compounds are biaryl compounds that possess two-heteroatom containing methylene substituents *ortho* to the biaryl axis.

For example, the axially chiral secondary amine catalyst **1**, which finds application in the asymmetric hydroxyamination reaction, has two methylene substituents attached to a shared nitrogen atom (Fig. 1).[3] In addition, the equivalent naphthyl basic skeleton, 1,1′-bis(hydroxymethyl)-2,2′-binaphthyl **2**, is found as a motif in Crams host–guest complexation work.[4] The naturally occurring compound tellimagrandin II **3** contains two carbonyl functions flanking the biaryl axis that could be derived from the corresponding biaryl methyl alcohols.[5]

Another class of related biaryl compounds of interest to chemists is the binaphthyl diol **4**.[6] These compounds have been investigated as potential chiral photochromic optical triggers for liquid crystals.[7]

General methods for the synthesis of biaryl compounds include the use of oxidative coupling methods.[8] Otherwise, traditional methods for the assembly of the biaryl axis such as the Suzuki–Miyaura, Stille and related reactions are generally used.[9–11]

For example, as shown in Figure 2 the synthesis of **5** proceeds by means of a nickel-catalyzed coupling between arylbromide **6** and Grignard **7**. When this is mediated in the presence of a chiral ferrocene as shown in Figure 2, products with good enantiomeric excess are obtained.[12] Biaryl **5** can then be transformed into **8** in a number of steps.

Recently, we have published the synthesis of aryl naphthalenes using a different approach, where one of the rings of the naphthalene was derived from commercially available α-tetralones **9**.[13] The tetralones are easily converted into halovinylaldehydes **10** before being coupled with a variety of aromatic boronic acids **11** to provide the aryldihydronaphthalenes **12**. These were then converted into 1,2-disubstituted aryl naphthalenes such as **13** (Scheme 1).[14]

On completion of this work, we realized that if the aryl boronic acid partner in this reaction contained a suitable substituent *ortho* to the boronic acid moiety we would be able to assemble racemic biarylnaphthalenes, such as **2**, in a novel manner by using a commercial tetralone as the starting material. Work toward this goal, as well as related chemistry, is described in this paper.

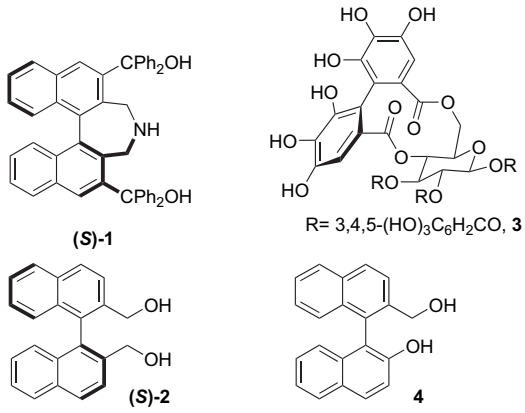

Figure 1.

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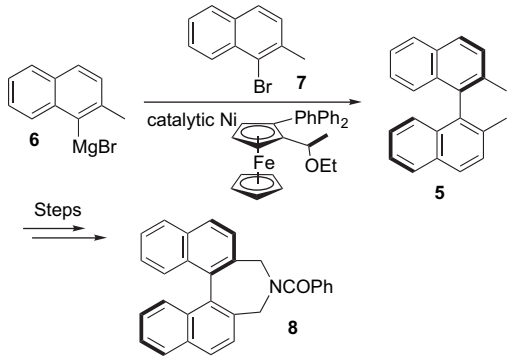
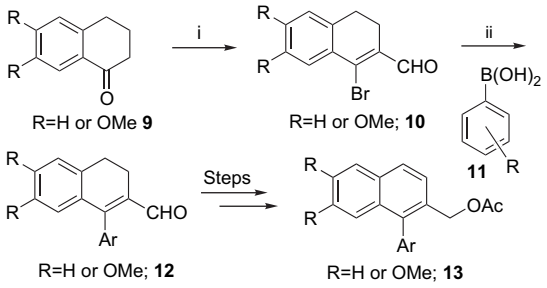
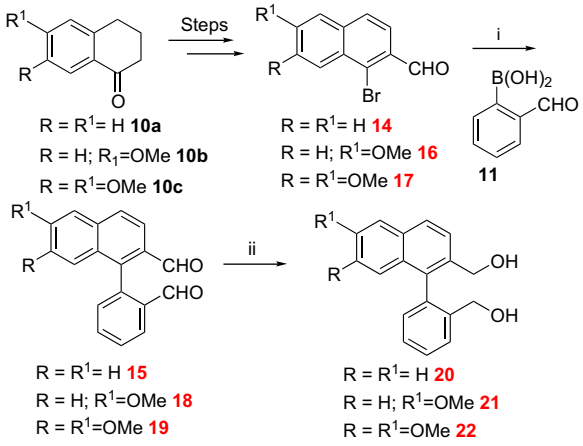


Figure 2.



Scheme 1. Reagents and conditions: (i) DMF, PBr_3, CH_2Cl_2, reflux; (ii) cat. $Pd(PPh_3)_4$, aq Na_2CO_3, boronic acid **11**, DME/EtOH, reflux.



Scheme 2. Reagents and conditions: (i) cat. $Pd(PPh_3)_4$, aq Na_2CO_3, boronic acid **11**, DME/EtOH, reflux; (ii) $NaBH_4$, EtOH reflux.

2. Results and discussion

Starting from **14** (prepared from α-tetralone **10a** as previously described[13]) using the well-developed Suzuki–Miyaura reaction conditions, in the presence of commercially available formylboronic acid **11**, resulted in the formation of the desired product **15** in excellent yields. Treatment of naphthylaldehydes **16** and **17**, prepared from tetralones **10b** and **10c** under the same reaction conditions (details described in Section 3) also afforded the desired compounds **18** and **19** in excellent yield. All three naphthylaldehydes were then reduced with sodium borohydride to afford the desired products **20**, **21**, and **22** each containing two methyl alcohol substituents *ortho* to the newly formed biaryl axis (Table 1).

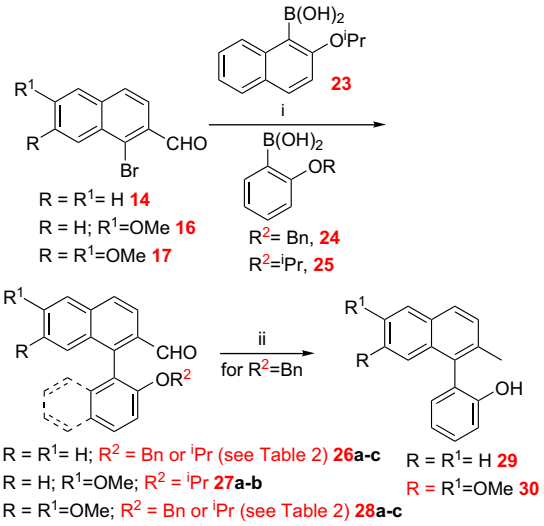
Alternatively, the three naphthalene derivatives **14**, **16**, and **17** were subjected to the same Suzuki–Miyaura reaction conditions in the presence of 2-isopropoxynaphthylboronic acid **23**, 2-benzyl oxyphenyl boronic acid **24**, and isopropoxyphenylboronic acid **25**

Table 1
Yields for Scheme 2

Entry	%	Entry	%
14→15	76	**15→20**	98
16→18	70	**18→21**	77
17→19	80	**19→22**	94

as shown in Scheme 3 and Table 2 afforded biarylnaphthalenes **26a–c**, **27a–b**, and **28a–c** in good yields.

The next step entailed the removal of the isopropyl or benzyl protecting group of either the phenol or naphthol and this proved to



Scheme 3. Reagents and conditions: (i) cat. $Pd(PPh_3)_4$, aq Na_2CO_3, boronic acid, DME/EtOH, reflux; (ii) H_2, Pd/C, EtOAc.

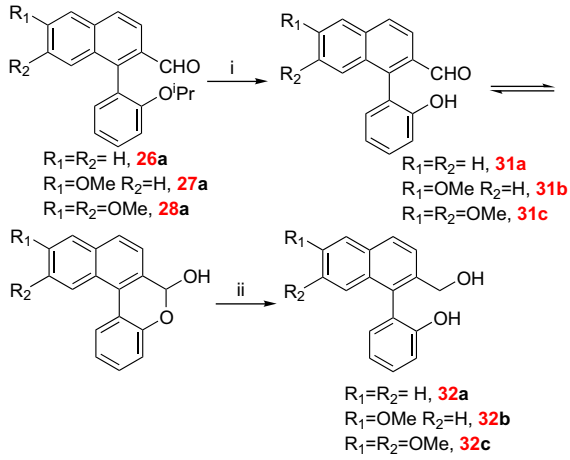
be problematic. For both **26c** and **28c** the protecting group was a benzyl and we wished to remove it using standard hydrogenation conditions with catalytic Pd/C. However, on performing the reaction this not only resulted in the removal of the benzyl substituent but also in the reduction of the aldehyde to the corresponding methyl substituent to afford **29** and **30**, respectively (Scheme 3 and Table 2).

As a next step the removal of the isopropyl protecting group of **26a**, **27a**, and **28a** was attempted. Exposure of both substrates to $AlCl_3$ in dichloromethane resulted in a mixture of products **31a–c**, presumably as a mixture of both the hydroxyaldehydes and lactol as shown in Scheme 4.[15] However, the uncharacterized mixture of each product was reduced with lithium aluminum hydride to afford **32a–c**, unfortunately only in mediocre yield over two steps (Table 3).

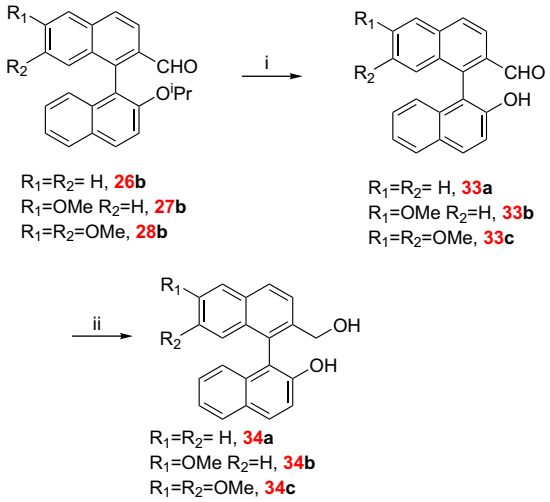
Removal of the isopropyl protecting groups of the related naphthyl equivalents **26b–b** did not meet with the same complications and **33a–c** were isolated in good yields (Scheme 5). Presumably this is as a result of more steric hindrance in the naphthyl series and, therefore, cyclization is not taking place. All three of these products were reduced separately into the desired alcohols **34a–c** in good yields.

Table 2
Yields for Scheme 3

Entry	$ArOR^2$	%	Entry	%
14→26a	Phenyl, R^2=^{i}Pr	97		
14→26b	Naphthyl, R^2=^{i}Pr	79		
14→26c	Phenyl, R^2=Bn	94	**26c→29**	68
16→27a	Phenyl, R^2=^{i}Pr	74		
16→27b	Naphthyl, R^2=^{i}Pr	87		
17→28a	Phenyl, R^2=^{i}Pr	80		
17→28b	Naphthyl, R^2=^{i}Pr	60		
17→28c	Phenyl, R^2=Bn	97	**28c→30**	73



Scheme 4. Reagents and conditions: (i) $AlCl_3$, CH_2Cl_2; (ii) $NaBH_4$, EtOH.



Scheme 5. Reagents and conditions: (i) $AlCl_3$, CH_2Cl_2; (ii) $NaBH_4$, EtOH.

In summary, by using tetralones as starting materials, biaryl compounds containing substituents *ortho* to the biaryl axes can easily be synthesized. These *ortho* disubstituted products can potentially be utilized as ligands in metal catalyzed reactions.

3. Experimental

3.1. General

All reagents used were analytical grade reagents from Fluka and Aldrich. *n*-BuLi was obtained from Aldrich and used as supplied. THF was dried by distillation from sodium wire/benzophenone, DMF by distillation from CaH_2. All other solvents were BDH/HP high purity grade and distilled before use. Thin layer chromatography was carried out on Macherey-Nagel Alugram Sil G/UV_{254} Plates, pre-coated with 0.25 mm silica gel 60. Detection was done under ultra violet light at 254 nm. For column chromatography, Macherey-Nagel silica gel (32–63 microns) was used, with gel mass 30 times that of sample, eluting with the stated solvent mixtures. Melting points were determined on a Reichert hot-stage microscope. Infrared spectra were run on the Bruker Vector 22 Fourier Transform spectrometer. Absorption maxima are reported in wavenumbers (cm^{-1}), with s=strong, m=medium, and w=weak. NMR spectroscopic analysis was done on an Ultrashield 300 MHz/54 Bohr magnet. The frequency at which ^1H NMR spectra were reported was 300.131 MHz (rounded to 300 MHz) using tetramethylsilane at 0.000 ppm as a standard. These spectra are reported as parts per million (ppm), with s=singlet, d=doublet, dd=doublet of a doublet, t=triplet, m=multiplet. The ^{13}C NMR spectra were reported at a frequency of 75.475 MHz (rounded to 75 MHz) using $CDCl_3$ at 77.00 ppm as a standard.

3.2. 1-Bromo-2-naphthaldehyde 14

1-Bromo-3,4-dihydro-2-naphthaldehyde (0.45 g, 1.89 mmol), selenium powder (0.30 g, 5.69 mmol) and dimethyl sulfoxide (0.5 ml) were slowly heated to 180 °C. The reaction mixture was heated at the same temperature for 5 min. The mixture was then allowed to cool to room temperature before being filtered and washed with excess dichloromethane. The excess solvent was removed on a rotary evaporator to obtain a black oil that was purified by column chromatography using 5% ethyl acetate/hexane as eluent to give the desired product **14** as a bright yellow solid (0.31 g, 69% yield). Mp=106–108 °C;[13] ^1H NMR δ/ppm 10.67 (1H, s, CHO), 8.53–8.50 (1H, m, ArH), 7.95–7.84 (3H, m, 3×ArH), 7.72–7.67 (2H, m, 2×ArH).

Table 3
Comparison of yields over two steps for Schemes 4 and 5

Entry	%	Entry	%
26a→32a	45	**26b→34a**	97
27a→32b	41	**27b→34b**	75
28a→32c	52	**28b→34c**	84

3.3. 1-Bromo-6-methoxy-2-naphthaldehyde 16

Using the same procedure as described above, 6-methoxy-1-bromo-3,4-dihydro-2-naphthaldehyde (3.98 g, 14.9 mmol) was converted to 6-methoxy-1-bromo-2-naphthaldehyde **16** in the presence of selenium powder (2.30 g, 29.8 mmol) and dimethyl sulfoxide (2 ml). The product was obtained as a light brown solid (2.85 g, 72% yield). Mp=123–126 °C;[13] ^1H NMR δ/ppm 10.58 (1H, s, CHO), 8.36 (1H, d, *J*=9.4 Hz, ArH), 7.87 (1H, d, *J*=8.6 Hz, ArH), 7.68 (1H, d, *J*=8.8 Hz, ArH), 7.28 (1H, dd, *J*=2.5, 9.4 Hz, ArH), 7.11 (1H, d, *J*=2.5 Hz, ArH), 3.96 (3H, s, OMe).

3.4. 1-Bromo-6,7-dimethoxy-2-naphthaldehyde 17

Using the same procedure as described above, 6,7-dimethoxy-1-bromo-3,4-dihydro-2-naphthaldehyde (2.56 g, 8.65 mmol) was converted to 6,7-dimethoxy-1-bromo-2-naphthaldehyde in the presence of selenium powder (1.37 g, 17.3 mmol) and dimethyl sulfoxide (2 ml). Product **17** was obtained as a light brown oil (1.62 g, 64% yield). IR ν_{max} (cm^{-1}) 1684 (s, C=O stretch), 1610 (s, C=C stretch); ^1H NMR δ/ppm 10.56 (1H, s, CHO), 7.77 (1H, d, *J*=8.4 Hz, 4-H), 7.76 (1H, s, 8-H), 7.61 (1H, d, *J*=8.4 Hz, 3-H), 7.07 (1H, s, 5-H), 4.06 (3H, s, OMe), 4.03 (3H, s, OMe); ^{13}C NMR δ/ppm 191.8 (CHO), 151.2 (C), 150.1 (C), 132.6, 128.8 (C), 127.9 (C), 126.7 (C), 125.3 (CH), 121.8 (CH), 105.6 (2×CH), 55.4 (2×OMe); MS (EI) *m*/*z* (%) 296 (M^{+81}Br, 100), 295 (56), 294 (98), 293 (43), 206 (31), 178 (13), 150 (23), 144 (19), 116 (19), 115 (15); HRMS calculated for $C_{13}H_{11}O_3{}^{79}Br$ M^+ 293.9892, found 293.9907.

3.5. 1-(2-Formylphenyl)-2-naphthaldehyde 15

To $[Pd(PPh_3)_4]$ (0.52 g, 0.440 mmol) was added deoxygenated solutions of 1-bromo-2-naphthaldehyde **14** (1.00 g, 4.42 mmol) in DME (15 ml) and 2-formylphenylboronic acid (1.00 g, 6.64 mmol) in ethanol (10 ml). This was followed by a deoxygenated solution of aqueous sodium carbonate (4.06 g, 37.6 mmol in 19 ml water). The

resultant mixture was heated at reflux under nitrogen for 46 h over which time it turned deep red. After allowing to cool to room temperature, the mixture was quenched with water (50 ml) and the organic material extracted with dichloromethane (3×100 ml). The resultant organic extracts were combined, dried ($MgSO_4$), filtered through a Celite plug and the excess solvent removed using a rotary evaporator. The resultant oil was purified by column chromatography using 30% ethyl acetate/hexane as eluent to afford dial **15** as a thick light brown oil (0.87 g, 76%).[16] IR ν_{max} (cm^{-1}) 1694 (vs, C=O), 1595 (m, C=C stretch); ^{1}H NMR δ/ppm 9.84 (1H, s, CHO), 9.56 (1H, s, CHO), 8.17 (1H, dd, J=1.5, 7.6 Hz, ArH), 8.10 (1H, d, J=8.6 Hz, ArH), 8.00 (1H, d, J=8.6 Hz, ArH), 7.95 (1H, d, J=8.1 Hz, ArH), 7.78–7.60 (3H, m, 3×ArH), 7.48–7.36 (3H, m, 3×ArH); ^{13}C NMR δ/ppm 191.2 (CHO), 190.5 (CHO), 141.9 (C), 138.6 (C), 135.7 (C), 135.6 (C), 133.7 (CH), 132.8 (C), 132.2 (CH), 131.9 (C), 129.1 (CH), 129.1 (CH), 129.1 (CH), 128.4 (CH), 128.3 (CH), 127.5 (CH), 127.1 (CH), 122.2 (CH); MS (EI) m/z (%) 260 (M^+, 25), 232 (28), 231 (100), 200 (11), 101 (9), 43 (3); HRMS calculated for $C_{18}H_{12}O_2$ M^+ 260.0837, found 260.0844.

3.6. 1-(2-Formylphenyl)-6-methoxy-2-naphthaldehyde 18

In a similar way as described above 1-bromo-6-methoxy-2-naphthaldehyde **16** (2.06 g, 7.77 mmol) in DME (20 ml) was stirred together with 2-formylphenylboronic (1.75 g, 11.6 mmol), ethanol (10 ml) and [$Pd(PPh_3)_4$] (0.90 g, 0.777 mmol) to give naphthaldehyde **18** as a brown oil (1.58 g, 70%). IR ν_{max} (cm^{-1}) 1693, 1677 (s, C=O stretch), 1617 and 1595 (s, C=C stretch); ^{1}H NMR δ/ppm 9.76 (1H, s, CHO), 9.56 (1H, s, CHO), 8.15 (1H, d, J=7.5 Hz, ArH), 8.07 (1H, d, J=8.7 Hz, ArH), 7.88 (1H, d, J=8.7 Hz, ArH), 7.75–7.68 (2H, m, 2×ArH), 7.42 (1H, d, J=6.9 Hz, ArH), 7.26–7.24 (2H, m, 2×ArH), 7.09 (1H, dd, J=2.6, 9.2 Hz, ArH), 3.95 (3H, s, OCH_3); ^{13}C NMR δ/ppm 190.9 (CHO), 190.5 (CHO), 160.1 (C-6), 141.8 (C), 138.9 (C), 137.7 (C), 135.6 (C), 133.6 (CH), 132.1 (CH), 130.4 (C), 129.2 (CH), 128.7 (CH), 128.1 (CH), 128.0 (C), 127.9 (CH), 123.0 (CH), 120.2 (CH), 106.6 (CH), 55.5 (OCH_3); MS (EI) m/z (%) 290 (M^+, 45), 262 (22), 261 (100), 218 (19), 189 (25), 85 (15), 82 (22), 71 (20), 57 (43), 43 (38); HRMS calculated for $C_{19}H_{14}O_3$ M^+ 290.0943, found 290.0940.

3.7. 6,7-Dimethoxy-1-(2-formylphenyl)-2-naphthaldehyde 19

Using a similar method as described above, 1-bromo-6,7-dimethoxy-2-naphthaldehyde **17** (1.00 g, 3.39 mmol) in DME (10 ml) was mixed with 2-formylphenylboronic acid (0.76 g, 5.08 mmol) in ethanol (5 ml) using [$Pd(PPh_3)_4$] as the catalyst (0.39 g, 0.339 mmol) gave dial **19** as a thick brown oil (0.86 g, 80% yield). IR ν_{max} (cm^{-1}) 1682 (s, C=O), 1619, 1595 (s, C=C stretch); ^{1}H NMR δ/ppm 9.77 (1H, s, CHO), 9.57 (1H, s, CHO), 8.18 (1H, d, J=7.6 Hz, ArH), 7.99 (1H, d, J=8.6 Hz, ArH), 7.86 (1H, d, J=8.6 Hz, ArH), 7.81–7.68 (2H, m, 2×ArH), 7.45 (1H, d, J=7.4 Hz, ArH), 7.24 (1H, s, 5-H), 6.56 (1H, s, 8-H), 4.05 (3H, s, OCH_3), 3.67 (3H, s, OCH_3); ^{13}C NMR δ/ppm 191.2 (CHO), 190.8 (CHO), 151.9 (C), 150.6 (C), 139.8 (C), 139.4 (C), 135.5 (C), 133.8 (CH), 132.5 (C), 132.1 (CH), 130.9 (C), 129.2 (CH), 128.4 (C), 127.9 (CH), 127.4 (CH), 121.3 (CH), 106.7 (CH), 105.3 (CH), 56.1 (OCH_3), 55.6 (OCH_3); MS (EI) m/z (%) 320 (M^+, 33), 291 (54), 216 (53), 206 (30), 178 (10), 150 (19), 86 (10), 84 (65), 82 (100); HRMS calculated for $C_{20}H_{16}O_4$ M^+ 320.1049, found 320.1043.

3.8. 1-(2-Hydroxymethyl-phenyl)-2-naphthyl]-methanol 20

To a solution of dial **15** (0.83 g, 3.19 mmol) in ethanol (5 ml) was added sodium borohydride (0.30 g, 7.97 mmol) portion-wise. The reaction mixture warmed up and stirring was continued at room temperature for 5 min before being poured into a separating funnel containing water (50 ml). The organic material was extracted with dichloromethane (3×100 ml) and the organic extracts combined and dried ($MgSO_4$) before being filtered through a Celite plug. The excess dichloromethane was removed using a rotary evaporator. The resultant oil purified by column chromatography using 30–50% ethyl acetate/hexane as an eluent to obtain diol **20** as a thick yellowish oil (0.82 g, 98%). IR ν_{max} (cm^{-1}) 3406 (br s, O–H stretch), 1605, 1567 (s, C=C stretch); ^{1}H NMR δ/ppm 7.89 (1H, d, J=8.4 Hz, ArH), 7.87 (1H, d, J=7.8 Hz, ArH), 7.63 (1H, d, J=8.4 Hz, ArH), 7.56 (1H, dd, J=1.5, 7.2 Hz, ArH), 7.50–7.39 (3H, m, 3×ArH), 7.36–7.30 (1H, m, ArH), 7.18 (2H, br d, J=8.4 Hz, 2×ArH), 4.46 (1H, d, J=11.7 Hz, ArCH_aH_bOH), 4.42 (1H, d, J=11.7 Hz, ArCH_aH_bOH), 4.26 (1H, d, J=11.6 Hz, PhCH_cH_dOH), 4.04 (1H, d, J=11.6 Hz, PhCH_cH_dOH), 2.96 (2H, br s, 2×OH); ^{13}C NMR δ/ppm 139.5 (C), 137.6 (C), 136.6 (C), 136.2 (C), 132.9 (C), 132.6 (C), 130.6 (CH), 129.9 (CH), 128.4 (CH), 128.4 (CH), 128.2 (CH), 127.9 (CH), 127.3 (CH), 126.3 (CH), 126.2 (CH), 125.9 (CH), 63.1 (CH_2OH), 63.0 (CH_2OH); MS (EI) m/z (%) 264 (M^+, 26), 246 (100), 231 (58), 215 (76), 202 (55); HRMS calculated for $C_{18}H_{16}O_2$ M^+ 264.1150, found 264.1132.

3.9. [1-(2-Hydroxymethyl-phenyl)-6-methoxynaphthalen-2-yl]-methanol 21

Using the same methodology as outlined above, dial **18** (1.35 g, 4.65 mmol) in ethanol (10 ml) was converted into the diol **21** using sodium borohydride (0.44 g, 11.6 mmol). The product was obtained as sticky white flakes, which were further crystallized from dichloromethane and hexane to give a white crystalline solid (1.06 g, 77% yield). Mp=147–148 °C; IR ν_{max} (cm^{-1}) 3385 (br s, O–H stretch), 1625, 1605 (s, C=C stretch); ^{1}H NMR δ/ppm 7.76 (1H, d, J=8.4 Hz, ArH), 7.56–7.51 (2H, m, 2×ArH), 7.47–7.37 (2H, m, 2×ArH), 7.16–7.12 (2H, m, 2×ArH), 7.07 (1H, d, J=9.2 Hz, ArH), 6.98 (1H, dd, J=2.5, 9.2 Hz, ArH), 4.39 (1H, d, J=11.6 Hz, ArCH_aH_bOH), 4.35 (1H, d, J=11.6 Hz, ArCH_aH_bOH), 4.22 (1H, d, J=11.6 Hz, PhCH_cH_dOH), 4.02 (1H, d, J=11.6 Hz, PhCH_cH_dOH), 3.91 (3H, s, OCH_3), 3.23 (2H, br s, 2×OH); ^{13}C NMR δ/ppm 157.6 (6-C), 139.5 (C), 137.7 (C), 136.7 (C), 134.2 (C), 133.9 (C), 130.5 (CH), 129.9 (CH), 129.3 (C), 128.3 (CH), 128.0 (2×CH), 127.9 (CH), 127.1 (CH), 118.8 (CH), 105.9 (CH), 62.9 (CH_2OH), 62.8 (CH_2OH), 55.3 (OCH_3); MS (EI) m/z (%) 294 (M^+, 28), 276 (27), 264 (23), 188 (100), 171 (28), 159 (27), 144 (19), 128 (15), 115 (24), 91 (14); HRMS calculated for $C_{19}H_{18}O_3$ M^+ 294.1256, found 294.1256.

3.10. [1-(2-Hydroxymethyl-phenyl)-6,7-dimethoxy-naphthalen-2-yl]-methanol 22

Binaphthaldehyde **19** (0.80 g, 2.49 mmol) in ethanol (6 ml) was similarly converted to diol **22** (0.75 g, 94% yield) using sodium borohydride (0.24 g, 6.24 mmol). The product was obtained as a thick yellow oil. IR ν_{max} (cm^{-1}) 3337 (br s, O–H stretch), 1508 (s, C=C stretch); ^{1}H NMR δ/ppm 7.72 (1H, d, J=8.3 Hz, ArH), 7.57–7.54 (1H, m, ArH), 7.48–7.39 (3H, m, 3×ArH), 7.17 (1H, d, J=8.7 Hz, ArH), 7.15 (1H, s, 5-H), 6.40 (1H, s, 8-H), 4.41 (1H, d, J=11.5 Hz, ArCH_aH_bOH), 4.36 (1H, d, J=11.4 Hz, ArCH_aH_bOH), 4.25 (1H, d, J=11.6 Hz, PhCH_cH_dOH), 4.06 (1H, d, J=11.6 Hz, PhCH_cH_dOH), 4.00 (3H, s, OCH_3), 3.63 (3H, s, OCH_3), 3.04 (2H, br s, 2×OH); ^{13}C NMR δ/ppm 149.6 (C), 149.5 (C), 139.5 (C), 137.8 (C), 135.4 (C), 134.5 (C), 130.4 (CH), 129.9 (CH), 128.8 (C), 128.3 (CH), 128.2 (C), 128.1 (CH), 126.6 (CH), 125.7 (CH), 106.4 (CH), 105.0 (CH), 63.1 (CH_2OH), 62.7 (CH_2OH), 55.8 (OCH_3), 55.5 (OCH_3); MS (EI) m/z (%) 325 (M+1, 16), 324 (M^+, 81), 306 (100), 291 (20), 278 (17), 275 (23), 261 (19), 245 (17), 215 (15), 203 (16), 189 (17); HRMS calculated for $C_{20}H_{20}O_4$ M^+ 324.1362, found 324.1364.

3.11. 1-(2-Isopropoxyphenyl)-2-naphthaldehyde 26a

Bromonaphthaldehyde **14** (1.00 g, 4.25 mmol) in DME (10 ml) was stirred together with 2-isopropoxyphenylboronic acid **25**

(1.15 g, 6.38 mmol) in ethanol (8 ml) using [Pd(PPh$_3$)$_4$] (0.49 g, 0.425 mmol) in a similar way as described above to give product **26a** as a thick light brown oil (1.21 g, 97% yield). IR ν_{max} (cm^{-1}) 1676 (s, C=O), 1618 (s, C=C stretch); ^{1}H NMR δ/ppm 9.88 (1H, s, CHO), 8.06 (1H, d, J=8.6 Hz, ArH), 7.90 (2H, d, J=8.9 Hz, 2×ArH), 7.64–7.56 (2H, m, 2×ArH), 7.44–7.38 (1H, m, ArH), 7.26–7.23 (2H, m, 2×ArH), 7.11–7.05 (2H, m, 2×ArH), 4.46–4.38 (1H, m, OC*H*(CH$_3$)$_2$), 1.06 (3H, d, J=6.0 Hz, OCH(C*H*$_3$)$_2$), 0.97 (3H, d, J=6.0 Hz, OCH(C*H*$_3$)$_2$); ^{13}C NMR δ/ppm 193.2 (CHO), 156.0 (C), 143.6 (C), 136.2 (C), 132.8 (CH), 132.5 (C), 132.0 (C), 131.2 (C), 129.9 (CH), 128.4 (CH), 128.1 (CH), 128.0 (CH), 127.5 (CH), 126.4 (CH), 124.9 (C), 121.9 (CH), 120.2 (CH), 113.7 (CH), 70.4 (O*C*H(CH$_3$)$_2$), 21.8 (OCH(*C*H$_3$)$_2$), 21.7 (OCH(*C*H$_3$)$_2$); MS (EI) m/z (%) 292 (M+2, 18), 291 (M+1, 15), 290 (M$^+$, 63), 249 (40), 248 (72), 247 (50), 231 (100), 219 (31), 202 (28), 189 (28); HRMS calculated for $C_{20}H_{18}O_2$ M$^+$ 290.1307, found 290.1295.

3.12. 1-(2-Isopropoxynaphthyl)-2-naphthaldehyde 26b

Similarly, 1-bromo-2-naphthaldehyde **14** (1.00 g, 4.25 mmol) in DME (15 ml) was stirred together with 2-isopropoxynaphthylboronic acid **23** (1.28 g, 6.38 mmol) in ethanol (7 ml) using catalytic [Pd(PPh$_3$)$_4$] (0.48 g, 0.425 mmol) and sodium carbonate (3.71 g, 36.2 mmol in 16 ml of water) to give naphthaldehyde **26b** as a thick light brown oil (1.52 g, 79%). IR ν_{max} (cm^{-1}) 1687 (s, C=O), 1623, 1594 (s, C=C stretch); ^{1}H NMR δ/ppm 9.69 (1H, s, CHO), 8.15 (1H, d, J=8.6 Hz, ArH), 8.01–7.86 (4H, m, 4×ArH), 7.59–7.54 (1H, m, ArH), 7.42 (1H, d, J=9.0 Hz, ArH), 7.35–7.23 (4H, m, 4×ArH), 6.96 (1H, d, J=8.3 Hz, ArH), 4.61–4.49 (1H, m, OC*H*(CH$_3$)$_2$), 1.06 (3H, d, J=5.9 Hz, OCH(C*H*$_3$)$_2$), 0.94 (3H, d, J=5.9 Hz, OCH(C*H*$_3$)$_2$); ^{13}C NMR δ/ppm 192.8 (CHO), 153.7 (C), 142.0 (C), 136.2 (C), 134.6 (C), 132.7 (C), 132.1 (C), 130.3 (CH), 128.6 (C), 128.5 (CH), 128.2 (CH), 128.1 (CH), 127.9 (CH), 127.2 (CH), 126.9 (CH), 126.5 (CH), 125.0 (CH), 123.8 (CH), 121.9 (CH), 118.6 (C), 115.6 (CH), 71.0 (O*C*H(CH$_3$)$_2$), 21.9 (OCH(*C*H$_3$)$_2$); MS (EI) m/z (%) 342 (M+2, 16), 341 (M+1, 16), 340 (M$^+$, 62), 298 (88), 281 (28), 269 (32), 252 (34), 239 (69), 155 (13), 144 (100), 127 (17); HRMS calculated for $C_{24}H_{20}O_2$ M$^+$ 340.1463, found 340.1463.

3.13. 1-(2-Benzyloxyphenyl)-2-naphthaldehyde 26c

Using the same experimental procedure as described above bromonaphthaldehyde **14** (1.50 g, 6.81 mmol) in DME (15 ml) was stirred together with 2-benzyloxyphenyl boronic acid **24** (2.17 g, 9.57 mmol) in ethanol (10 ml) using [Pd(PPh$_3$)$_4$] (0.74 g, 0.681 mmol) as catalyst to obtain the desired naphthaldehyde **26c** as a thick light brown oil (2.04 g, 94% yield). IR ν_{max} (cm^{-1}) 1675 (s, C=O), 1618 (s, C=C stretch); ^{1}H NMR δ/ppm 9.90 (1H, s, CHO), 8.07 (1H, d, J=8.6 Hz, ArH), 7.93–7.89 (2H, m, 2×ArH), 7.63–7.56 (2H, m, 2×ArH), 7.47–7.39 (2H, m, 2×ArH), 7.28–7.25 (1H, m, 1×ArH), 7.15–7.08 (5H, m, 5×ArH), 6.95–6.93 (2H, m, 2×ArH), 5.04 (1H, d, J=18.1 Hz, one of OCH$_2$), 4.92 (1H, d, J=18.1 Hz, one of OCH$_2$); ^{13}C NMR δ/ppm 192.9 (CHO), 156.5 (C), 144.3 (C), 136.6 (C), 136.2 (C), 132.6 (CH), 132.5 (C), 131.3 (C), 130.0 (CH), 128.5 (CH), 128.2 (2×CH), 128.1 (CH), 127.6 (CH), 127.6 (CH), 126.6 (2×CH), 124.5 (C), 121.9 (CH), 120.8 (CH), 112.8 (CH), 70.0 (OCH$_2$), two CH carbons not observed; MS (EI) m/z (%) 338 (M$^+$, 5), 276 (3), 231 (8), 200 (4), 184 (4), 91 (100), 65 (12); HRMS calculated for $C_{24}H_{18}O_2$ M$^+$ 338.1307, found 338.1298.

3.14. 1-(2-Isopropoxyphenyl)-6-methoxy-2-naphthaldehyde 27a

Bromomethoxynaphthaldehyde **16** (1.35 g, 5.09 mmol) in DME (10 ml) was mixed with 2-isopropoxyphenylboronic acid **25** (1.74 g, 7.64 mmol) in ethanol (7 ml) and using [Pd(PPh$_3$)$_4$] (0.59 g, 0.509 mmol) as catalyst to give product **27a** as a light brown oil (1.42 g, 74% yield). IR ν_{max} (cm^{-1}) 1677 (vs, C=O), 1618, 1596 (s, C=C stretch); ^{1}H NMR δ/ppm 9.81 (1H, s, CHO), 8.03 (1H, d, J=8.6 Hz, ArH), 7.78 (1H, d, J=8.6 Hz, ArH), 7.52 (1H, d, J=9.2 Hz, ArH), 7.47–7.42 (1H, m, ArH), 7.24–7.18 (2H, m, 2×ArH), 7.09–7.04 (3H, m, 3×ArH), 4.45–4.37 (1H, m, OC*H*(CH$_3$)$_2$), 3.97 (3H, s, OCH$_3$), 1.06 (3H, d, J=6.0 Hz, [OCH(C*H*$_3$)$_2$]), 0.99 (3H, d, J=6.0 Hz, [OCH(C*H*$_3$)$_2$]); ^{13}C NMR δ/ppm 193.4 (CHO), 160.1 (C), 156.4 (C), 144.1 (C), 138.5 (C), 133.2 (CH), 130.3 (CH), 130.0 (C), 129.3 (CH), 128.1 (C), 127.2 (CH), 125.5 (C), 123.2 (CH), 120.6 (CH), 119.4 (CH), 114.2 (CH), 106.7 (CH), 70.8 (O*C*H(CH$_3$)$_2$), 55.8 (OCH$_3$), 22.3 (OCH(*C*H$_3$)$_2$); MS (EI) m/z (%) 320 (M$^+$, 2), 263 (21), 218 (100), 131 (31), 100 (9), 69 (62); HRMS calculated for $C_{21}H_{20}O_3$ M$^+$ 320.1412, found 320.1399.

3.15. (2-Isopropoxynaphthyl)-6-methoxy-2-naphthaldehyde 27b

Suzuki coupling of bromomethoxynaphthaldehyde **16** (1.00 g, 3.77 mmol) in DME (10 ml) with 2-isopropoxynaphthylboronic acid **23** (1.30 g, 5.66 mmol) in ethanol (7 ml) using catalytic [Pd(PPh$_3$)$_4$] (0.59 g, 0.377 mmol) gave naphthaldehyde **27b** (1.22 g, 87% yield) as a thick light brown oil. IR ν_{max} (cm^{-1}) 1694 (vs, C=O), 1595 (s, C=C stretch); ^{1}H NMR δ/ppm 9.62 (1H, s, CHO), 8.12 (1H, d, J=8.6 Hz, ArH), 7.99 (1H, d, J=9.0 Hz, ArH), 7.87 (2H, d, J=9.0 Hz, 2×ArH), 7.40 (1H, d, J=9.0 Hz, ArH), 7.35–7.30 (1H, m, ArH), 7.25–7.21 (3H, m, 3×ArH), 6.98–6.92 (2H, m, 2×ArH), 4.55 (1H, septet, J=6.0 Hz, OC*H*(CH$_3$)$_2$), 3.93 (3H, s, OCH$_3$), 1.06 (3H, d, J=6.0 Hz, OCH(C*H*$_3$)$_2$), 0.96 (3H, d, J=6.0 Hz, OCH(C*H*$_3$)$_2$); ^{13}C NMR δ/ppm 192.8 (CHO), 159.8 (C), 153.8 (C), 142.2 (C), 138.1 (C), 134.7 (C), 130.5 (C), 130.3 (CH), 129.1 (CH), 128.7 (C), 128.0 (C), 127.9 (CH), 127.0 (CH), 126.9 (CH), 125.2 (CH), 123.9 (CH), 122.9 (CH), 119.2 (CH), 118.9 (C), 115.8 (CH), 106.3 (CH), 71.3 (O*C*H(CH$_3$)$_2$), 55.4 (OCH$_3$), 22.1 (OCH(*C*H$_3$)$_2$), 21.9 (OCH(*C*H$_3$)$_2$); MS (EI) m/z (%) 371 (M+1, 17), 370 (M$^+$, 64), 328 (100), 311 (32), 268 (17), 255 (29), 239 (39), 226 (48), 185 (10); HRMS calculated for $C_{25}H_{22}O_3$ M$^+$ 370.1569, found 370.1574.

3.16. 6,7-Dimethoxy-1-(2-isopropoxyphenyl)-2-naphthaldehyde 28a

Similarly, bromodimethoxynaphthaldehyde **17** (0.50 g, 1.69 mmol) in DME (10 ml) was reacted with 2-isopropoxyphenylboronic acid **25** (0.46 g, 2.54 mmol) in ethanol (7 ml) using catalytic [Pd(PPh$_3$)$_4$] (0.20 g, 0.169 mmol) to give product **28a** as a thick light brown oil (0.47 g, 80% yield). IR ν_{max} (cm^{-1}) 1678 (s, C=O), 1598 (s, C=C stretch); ^{1}H NMR δ/ppm 9.81 (1H, s, CHO), 7.94 (1H, d, J=8.5 Hz, ArH), 7.75 (1H, d, J=8.5 Hz, ArH), 7.48–7.42 (1H, m, ArH), 7.26–7.24 (1H, m, ArH), 7.18 (1H, s, ArH), 7.11–7.06 (2H, m, 2×ArH), 6.87 (1H, s, ArH), 4.46–4.38 (1H, m, OC*H*(CH$_3$)$_2$), 4.04 (3H, s, OCH$_3$), 3.74 (3H, s, OCH$_3$), 1.07 (3H, d, J=6.0 Hz, OCH(C*H*$_3$)$_2$), 1.01 (3H, d, J=6.0 Hz, OCH(C*H*$_3$)$_2$); ^{13}C NMR δ/ppm 193.2 (CHO), 155.9 (C), 151.4 (C), 149.6 (C), 142.0 (C), 132.8 (C), 132.6 (CH), 130.0 (C), 129.8 (CH), 128.0 (C), 126.2 (CH), 125.3 (C), 120.8 (CH), 120.3 (CH), 113.8 (CH), 106.5 (CH), 106.0 (CH), 69.9 (O*C*H(CH$_3$)$_2$), 55.9 (OCH$_3$), 55.6 (OCH$_3$), 21.8 (OCH(*C*H$_3$)$_2$); MS (EI) m/z (%) 351 (M+1, 25), 350 (M$^+$, 100), 307 (90), 306 (41), 290 (95), 280 (29), 205 (12), 120 (18), 83 (10); HRMS calculated for $C_{22}H_{22}O_4$ M$^+$ 350.1518, found 350.1507.

3.17. 6,7-Dimethoxy-1-(2-isopropoxynaphthyl)-2-naphthaldehyde 28b

Suzuki coupling of bromodimethoxynaphthaldehyde **17** (1.00 g, 3.65 mmol) in DME (10 ml) with 2-isopropoxynaphthylboronic acid **23** (1.07 g, 5.05 mmol) in ethanol (7 ml) using catalytic [Pd(PPh$_3$)$_4$] (0.36 g, 0.365 mmol) gave naphthaldehyde **28b** as

yellow flakes (0.81 g, 60% yield). Mp=64–67 °C; IR ν_{max} (cm^{-1}) 1679 (vs, C=O), 1621, 1594 (s, C=C stretch); ^{1}H NMR δ/ppm 9.61 (1H, s, CHO), 8.04 (1H, d, J=8.5 Hz, ArH), 7.99 (1H, d, J=9.1 Hz, ArH), 7.85 (1H, d, J=7.9 Hz, ArH), 7.82 (1H, d, J=7.9 Hz, ArH), 7.42 (1H, d, J=9.1 Hz, ArH), 7.36–7.30 (1H, m, ArH), 7.24–7.20 (2H, m, 2×ArH), 7.00 (1H, d, J=8.4 Hz, ArH), 6.58 (1H, s, ArH), 4.56–4.49 (1H, m, OC*H*(CH_3)$_2$), 4.04 (3H, s, OCH_3), 3.47 (3H, s, OCH_3), 1.07 (3H, d, J=6.0 Hz, [OCH(CH_3)$_2$]), 0.99 (3H, d, J=6.0 Hz, [OCH(CH_3)$_2$]); ^{13}C NMR δ/ppm 192.3 (CHO), 153.7 (C), 151.5 (C), 149.7 (C), 140.0 (C), 134.5 (CH), 132.8 (CH), 130.9 (CH), 130.3 (C), 130.2 (C), 128.7 (CH), 128.3 (CH), 127.9 (C), 127.8 (C), 126.9 (CH), 125.2 (CH), 123.9 (C), 121.0 (CH), 119.2 (CH), 115.8 (C), 106.6 (CH), 105.9 (CH), 55.9 (OCH(CH_3)$_2$), 55.5 (OCH_3), 55.4 (OCH_3), 22.3 (OCH(CH_3)$_2$), 22.2 (OCH(CH_3)$_2$); MS (EI) m/z (%) 401 (M+1, 18), 400 (M^+, 62), 359 (25), 358 (100), 298 (14), 293 (22), 271 (13), 239 (16), 226 (22), 213 (20); HRMS calculated for $C_{26}H_{24}O_4$ M^+ 400.1675, found 400.1681.

3.18. 6,7-Dimethoxy-1-(2-benzyloxyphenyl)-2-naphthaldehyde 28c

In a similar manner as described above bromodimethoxynaphthaldehyde **17** (1.00 g, 3.37 mmol) in DME (15 ml) was stirred with to 2-benzyloxyphenyl boronic acid **24** (1.16 g, 5.05 mmol) in ethanol (7 ml) using catalytic [Pd(PPh_3)$_4$] (0.39 g, 0.337 mmol) to afford naphthaldehyde **28c** as a thick light yellow oil (1.30 g, 97% yield). IR ν_{max} (cm^{-1}) 1677 (s, C=O), 1620, 1595 (s, C=C stretch); ^{1}H NMR δ/ppm 9.84 (1H, s, CHO), 7.97 (1H, d, J=8.5 Hz, ArH), 7.77 (1H, d, J=8.5 Hz, ArH), 7.46–7.41 (1H, m, ArH), 7.28 (1H, dd, J=1.6, 7.3 Hz, ArH), 7.19 (1H, s, ArH), 7.18–7.09 (5H, m, 5×ArH), 6.99–6.97 (2H, m, 2×ArH), 6.81 (1H, s, ArH), 4.99 (2H, s, OCH_2), 4.04 (3H, s, OCH_3), 3.68 (3H, s, OCH_3), one CH not apparent; ^{13}C NMR δ/ppm 192.9 (CHO), 156.4 (C), 151.5 (C), 149.7 (C), 141.6 (C), 136.7 (C), 132.8 (C), 132.4 (CH), 130.2 (C), 129.9 (CH), 128.3 (2×CH), 128.0 (C), 127.6 (CH), 126.6 (2×CH), 126.5 (CH), 124.9 (C), 120.9 (CH), 112.9 (CH), 106.6 (CH), 105.9 (CH), 69.9 (OCH_2), 56.0 (OCH_3), 55.6 (OCH_3); MS (EI) m/z (%) 399 (M^++1, 19), 398 (M^+, 64), 307 (21), 291 (100), 279 (11), 248 (11), 91 (85); HRMS calculated for $C_{26}H_{22}O_4$ M^+ 398.1518, found 398.1526.

3.19. 2-(2-Methyl-naphthalen-1yl)-phenol 29

Naphthaldehyde **26c** (1.00 g, 3.13 mmol) together with ethyl acetate (15 ml) and 10% Pd/C (35 mg, 0.313 mmol) was stirred under an atmosphere of hydrogen gas for 8 h. After filtering off the Pd/C the excess solvent was removed on a rotary evaporator. After column chromatography of the residue product **29** (0.47 g, 68% yield) was produced as a yellowish oil. IR ν_{max} (cm^{-1}) 3411 (br s, O–H stretch), 1581 (s, C=C stretch); ^{1}H NMR δ/ppm 7.83–7.78 (2H, m, 2×ArH), 7.42–7.31 (5H, m, 5×ArH), 7.10–6.99 (3H, m, 3×ArH), 2.22 (3H, s, CH_3);[16] ^{13}C NMR δ/ppm 153.2 (C), 135.5 (C), 132.9 (C), 132.2 (C), 131.4 (C), 130.9 (CH), 129.2 (CH), 128.6 (CH), 128.3 (CH), 127.8 (CH), 126.4 (CH), 125.4 (CH), 125.2 (CH), 125.0 (C), 120.5 (CH), 115.5 (CH), 20.6 (CH_3).

3.20. 2-(6,7-Dimethoxy-2-methyl-naphthalen-1yl)-phenol 30

To a solution of naphthaldehyde **28c** (1.50 g, 3.76 mmol) in ethyl acetate (20 ml) was added 10% Pd/C (0.04 g, 0.376 mmol) in one portion. After evacuating the system, hydrogen gas was allowed to diffuse slowly from a balloon into the stirred reaction vessel. The reaction was then stirred for a period of 8 h. An aliquot of the reaction was taken and characterized by NMR spectroscopy and the results showed that the *O*-benzyl group was still intact but the aromatic aldehyde had been reduced to an alcohol. Therefore, extra Pd/C was added to the reaction and the reaction mixture stirred under a hydrogen atmosphere over a period of another 8 h. The mixture was filtered and ethyl acetate removed on a rotary evaporator to give a white solid that was crystallized from dichloromethane and hexane. The resultant crystalline solid proved to be product **30** (0.81 g, 73% yield). Mp=61–62 °C; IR ν_{max} (cm^{-1}) 3538 (vs, br, O–H stretch), 1575 (s, C=C stretch); ^{1}H NMR δ/ppm 7.65 (1H, d, J=8.3 Hz, ArH), 7.39–7.32 (1H, m, ArH), 7.29 (1H, d, J=8.3 Hz, ArH), 7.15–7.03 (4H, m, 4×ArH), 6.68 (1H, s, ArH), 3.99 (3H, s, OCH_3), 3.71 (3H, s, OCH_3), 2.21 (3H, s, CH_3); ^{13}C NMR δ/ppm 152.9 (C), 149.7 (C), 148.9 (C), 133.5 (C), 130.2 (CH), 129.9 (C), 129.2 (CH), 128.6 (C), 127.8 (C), 126.8 (CH), 126.7 (CH), 125.2 (C), 120.6 (CH), 115.4 (CH), 106.4 (CH), 104.1 (CH), 55.7 (OCH_3), 55.4 (OCH_3), 20.1 (CH_3); MS (EI) m/z (%) 295 (M+1, 21), 294 (M^+, 100), 264 (4), 221 (3), 189 (3), 94 (2); HRMS calculated for $C_{19}H_{18}O_3$ M^+ 294.1256, found 294.1252.

3.21. 2-(2-Hydroxymethyl-naphthalen-1-yl)-phenol 32a

Naphthaldehyde **26a** (1.00 g, 3.44 mmol) was treated with aluminum trichloride (0.92 g, 6.89 mmol) in dichloromethane (20 ml) at room temperature for 1 h. Water was added to the mixture and the organic material extracted into dichloromethane (2×40 ml). After separation of the organic layer it was dried ($MgSO_4$) and the solvent evaporated. The resultant phenol/lactol was exposed to sodium borohydride (16 mg, 4.30 mmol) in ethanol (10 ml) for 30 min. Water was added to the reaction mixture before diethyl ether was used to extract the organic material. Separation of the organic layer and drying ($MgSO_4$) followed by evaporation of the organic layer afford diol **32a** as a white solid (0.39 g, 45% yield). Mp=165–167 °C (lit. 117–118 °C or 167–168 °C);[17] ^{1}H NMR δ/ppm 7.82 (1H, d, J=8.0 Hz, ArH), 7.80 (1H, d, J=8.4 Hz, ArH), 7.54 (1H, d, J=8.5 Hz, ArH), 7.47–7.26 (4H, m, 4×ArH), 7.06–6.95 (3H, m, 3×ArH), 4.44 (1H, d, J=12.6 Hz, CH_aH$_b$OH), 4.39 (1H, d, J=12.5 Hz, CH$_a$$H_b$OH).

3.22. 2-(2-Hydroxymethyl-6-methoxynaphthalen-1-yl)-phenol 32b

Using the same procedure as described above, isopropyl ether **27a** (1.00 g, 3.57 mmol) was deprotected using aluminum trichloride (0.95 g, 7.14 mmol) in dichloromethane (20 ml) and then reduced to the diol **32b** (0.36 g, 41% yield) using sodium borohydride (0.17 g, 4.46 mmol) in ethanol (10 ml). The product was obtained as a white crystalline solid. Mp=66–68 °C; IR ν_{max} (cm^{-1}) 3316 (br s, O–H stretch), 1624 (s, C=C stretch); ^{1}H NMR δ/ppm 7.69 (1H, d, J=8.5 Hz, ArH), 7.49 (1H, d, J=8.4 Hz, ArH), 7.31–7.26 (2H, m, 2×ArH), 7.10–6.95 (5H, m, 5×ArH), 4.42 (1H, d, J=12.4 Hz, CH_aH$_b$OH), 4.32 (1H, d, J=13.3 Hz, CH$_a$$H_b$OH), 3.88 (3H, s, OCH_3); ^{13}C NMR δ/ppm 157.6, 153.5, 134.6, 134.4, 132.7, 131.4, 129.4, 128.1, 127.8, 127.5, 127.1, 124.6, 120.5, 118.9, 116.3, 105.9, 63.6 (CH_2OH), 55.2 (OCH_3); MS (EI) m/z (%) 281 (M+1, 5), 280 (M^+, 28), 262 (86), 261 (100), 220 (16), 189 (16), 188 (17), 85 (49), 84 (76), 47 (17), 43 (14); HRMS calculated for $C_{18}H_{16}O_3$ M^+ 280.1099, found 280.1085.

3.23. 2-(2-Hydroxymethyl-6,7-dimethoxynaphthalen-1-yl)-phenol 32c

In the same manner as outlined above, naphthaldehyde **28a** (1.05 g, 3.38 mmol) was treated with aluminum trichloride (0.90 g, 6.77 mmol) in dichloromethane (25 ml) and then with sodium borohydride (0.16 g, 4.22 mmol) in ethanol (10 ml) to give the diol **32c** as white flakes (0.46 g, 52% yield). Mp=66–68 °C; IR ν_{max} (cm^{-1}) 3460 (br s, O–H stretch), 1577 (s, C=C stretch); ^{1}H NMR δ/ppm 7.71 (1H, d, J=8.4 Hz, ArH), 7.47 (1H, d, J=8.3 Hz, ArH), 7.38–7.32 (1H, m, ArH), 7.13 (1H, s, ArH), 7.12 (1H, d, J=6.8 Hz, ArH), 7.05 (2H, d, J=7.7 Hz, 2×ArH), 6.66 (1H, s, ArH), 4.42 (2H, s, CH_2OH), 3.99 (3H, s, OCH_3), 3.69 (3H, s, OCH_3); ^{13}C NMR δ/ppm 153.5 (C), 149.9 (C), 149.7 (C), 135.3 (C), 131.2 (CH), 130.9 (C), 129.7 (CH), 129.3 (C),

128.6 (C), 127.3 (CH), 124.9 (CH), 124.8 (C), 120.8 (CH), 116.4 (CH), 106.4 (CH), 104.7 (CH), 63.9 (CH_2OH), 55.8 (OCH_3), 55.5 (OCH_3); MS (EI) *m*/*z* (%) 310 (M^+, 15), 292 (35), 291 (29), 263 (18), 218 (100), 214 (10), 149 (11), 130 (27), 68 (77), 41 (11); HRMS calculated for $C_{19}H_{18}O_4$ M^+ 310.1205, found 310.1201.

3.24. 1-(2′-Hydroxynaphthalen-2-yl)-2-naphthaldehyde 33a

To a solution of naphthaldehyde **26b** (0.96 g, 2.69 mmol) in dichloromethane (10 ml) was added aluminum trichloride (0.75 g, 5.39 mmol) in one portion. The reaction mixture immediately turned deep red whilst warming up in the process. The mixture was stirred at room temperature for 15 min after which time water was added dropwise until the effervescence had stopped. The mixture was then extracted with dichloromethane (3×100 ml) and the organic extracts combined before being dried ($MgSO_4$), filtered through a Celite plug and then the excess solvent was removed using a rotary evaporator. The resultant brown oil was purified using column chromatography with 10% ethyl acetate/hexane as an eluent to obtain naphthaldehyde **33a** as white flakes (0.78 g, 98% yield). Mp=97–98 °C (lit. 70–71 °C);[18] ^{1}H NMR δ/ppm 9.67 (1H, s, CHO), 8.16 (1H, d, *J*=8.6 Hz, ArH), 8.04 (1H, d, *J*=8.6 Hz, ArH), 7.96 (2H, d, *J*=8.7 Hz, 2×ArH), 7.89–7.87 (1H, m, ArH), 7.65–7.59 (1H, m, ArH), 7.45 (1H, d, *J*=8.2 Hz, ArH), 7.39–7.22 (4H, m, 4×ArH), 6.93 (1H, d, *J*=8.4 Hz, ArH).

3.25. 1-(2′-Hydroxynaphthalen-2-yl)-6-methoxy-2-naphthaldehyde 33b

In a similar manner as described above, methoxynaphthaldehyde **27b** (1.10 g, 2.97 mmol) in dichloromethane (15 ml) was converted to naphthaldehyde **33b** (0.79 g, 81% yield), using aluminum trichloride (0.79 g, 5.94 mmol) to afford the product as a brown solid. Mp=187–190 °C; IR ν_{max} (cm^{-1}) 3372 (br s, O–H stretch), 1683 (s, C=O), 1618 (s, C=C stretch); ^{1}H NMR δ/ppm 9.63 (1H, s, CHO), 8.17 (1H, d, *J*=8.7 Hz, ArH), 7.96 (2H, d, *J*=8.8 Hz, 2×ArH), 7.88 (1H, d, *J*=7.7 Hz, ArH), 7.37–7.23 (5H, m, 5×ArH), 7.03 (1H, dd, *J*=2.5, 9.2 Hz, ArH), 6.96 (1H, d, *J*=8.4 Hz, ArH), 3.96 (3H, s, OCH_3); ^{13}C NMR δ/ppm 191.9 (CHO), 160.5 (C), 151.6 (C), 138.7 (C), 134.4 (C), 131.5 (C), 130.9 (CH), 128.8 (C), 128.6 (CH), 128.4 (CH), 128.2 (CH), 127.8 (C), 127.4 (CH), 124.6 (CH), 123.9 (CH), 123.5 (CH), 120.3 (CH), 117.4 (CH), 113.8 (C), 106.7 (CH), 55.5 (OCH_3); MS (EI) *m*/*z* (%) 329 (M+1, 25), 328 (M^+, 100), 311 (26), 220 (29), 186 (51), 185 (36), 144 (24), 68 (36); HRMS calculated for $C_{22}H_{16}O_3$ M^+ 328.1099, found 328.1110.

3.26. 1-(2′-Hydroxynaphthalen-2-yl)-6,7-dimethoxy-2-naphthaldehyde 33c

Naphthaldehyde **28b** (0.70 g, 1.75 mmol) in dichloromethane (10 ml) was converted to the desired product **33c** (0.54 g, 86% yield), as white flakes, using aluminum trichloride (0.47 g, 3.49 mmol) in the same manner as described above to yield the product as white crystals. Mp=195–197 °C; IR ν_{max} (cm^{-1}) 3376 (br s, O–H stretch), 1681 (s, C=O), 1601 (s, C=C stretch); ^{1}H NMR δ/ppm 9.60 (1H, s, CHO), 8.08 (1H, d, *J*=8.5 Hz, ArH), 7.97 (1H, d, *J*=8.9 Hz, ArH), 7.93 (1H, d, *J*=8.6 Hz, ArH), 7.89 (1H, d, *J*=8.2 Hz, ArH), 7.38–7.26 (4H, m, 4×ArH), 6.99 (1H, d, *J*=8.4 Hz, ArH), 6.66 (1H, s, ArH), 4.05 (3H, s, OCH_3), 3.96 (3H, s, OCH_3); ^{13}C NMR δ/ppm 192.1 (CHO), 160.3 (C), 151.6 (C), 138.9 (C), 134.7 (C), 132.1 (C), 130.9 (CH), 128.8 (C), 128.3 (C), 128.2 (CH), 127.9 (CH), 127.3 (CH), 124.6 (CH), 123.8 (CH), 121.6 (CH), 117.4 (CH), 106.9 (CH), 106.4 (C), 104.9 (CH), 55.5 (OCH_3), two carbons not visible; MS (EI) *m*/*z* (%) 359 (M+1, 27), 358 (M^+, 100), 341 (17), 215 (10), 113 (7); HRMS calculated for $C_{23}H_{18}O_4$ M^+ 358.1205, found 358.1202.

3.27. 2′-Hydroxymethyl-[1,1′]binaphthalenyl-2-ol 34a

To a solution of naphthaldehyde **33a** (0.77 g, 2.58 mmol) in ethanol (5 ml) was added sodium borohydride (0.12 g, 3.23 mmol) portion-wise. The reaction mixture warmed up and was stirred at room temperature for 5 min before being poured into a separating funnel containing water (50 ml). The organic material was extracted with dichloromethane (3×100 ml) and the organic extracts combined, dried ($MgSO_4$) before being filtered through a Celite plug. The excess dichloromethane was removed on a rotary evaporator and the resultant oil purified by column chromatography using 30–50% ethyl acetate/hexane as an eluent to obtain the diol **34a** as cream-white flakes (0.76 g, 99% yield). Mp=162–164 °C (lit. Mp=172–173 °C);[18] IR ν_{max} (cm^{-1}) 3321 (br s, O–H stretch), 1579 (s, C=C stretch); ^{1}H NMR δ/ppm 7.90–7.82 (4H, m, 4×ArH), 7.67 (1H, d, *J*=8.5 Hz, ArH), 7.45–7.41 (1H, m, ArH), 7.31–7.13 (5H, m, 5×ArH), 6.87 (1H, d, *J*=8.4 Hz, ArH), 4.31 (2H, s, CH_2OH); ^{13}C NMR δ/ppm 151.1 (C), 138.3 (C), 133.7 (C), 133.3 (CH), 132.9 (C), 129.9 (CH), 129.8 (C), 129.2 (CH), 128.9 (C), 128.1 (2×CH), 127.4 (C), 126.7 (CH), 126.3 (CH), 126.1 (CH), 125.9 (CH), 124.4 (CH), 123.5 (CH), 117.9 (CH), 116.8 (C), 63.4 (CH_2OH); MS (EI) *m*/*z* (%) 300 (M^+, 27), 284 (22), 283 (28), 281 (100), 252 (30), 239 (19), 126 (12), 113 (6), 43 (8); HRMS calculated for $C_{21}H_{16}O_2$ M^+ 300.1150, found 300.1164.

3.28. 2′-Hydroxymethyl-6′-methoxy-[1,1′]binaphthalenyl-2-ol 34b

In a similar manner as outlined above, naphthaldehyde **33b** (0.60 g, 1.83 mmol) in ethanol (5 ml) was reduced to yield the diol **34b** (0.55 g, 92% yield) as white flakes, using sodium borohydride (0.09 g, 2.28 mmol) as the reductant. Mp=89–92 °C; IR ν_{max} (cm^{-1}) 3372 (br s, O–H stretch), 1617 (s, C=C stretch); ^{1}H NMR δ/ppm 7.86–7.79 (3H, m, 3×ArH), 7.63 (1H, d, *J*=8.5 Hz, ArH), 7.32–7.16 (4H, m, 4×ArH), 7.08 (1H, d, *J*=9.2 Hz, ArH), 6.93–6.87 (2H, m, 2×ArH), 4.35 (2H, br s, CH_2OH), 3.90 (3H, s, OCH_3); ^{13}C NMR δ/ppm 157.9 (C), 151.2 (C), 136.2 (C), 134.8 (C), 133.7 (C), 130.0 (CH), 129.7 (C), 129.0 (C), 128.4 (C), 128.2 (CH), 128.1 (CH), 127.6 (CH), 127.3 (CH), 126.8 (CH), 124.4 (CH), 123.5 (CH), 119.4 (CH), 117.9 (CH), 117.0 (C), 106.2 (CH), 63.6 (CH_2OH), 55.3 (OCH_3); MS (EI) *m*/*z* (%) 330 (M^+, 18), 312 (100), 311 (70), 239 (15), 113 (5); HRMS calculated for $C_{22}H_{18}O_3$ M^+ 330.1256, found 330.1254.

3.29. 2′-Hydroxymethyl-6′,7′-dimethoxy-[1,1′]binaphthalenyl-2-ol 34c

Using the same experimental procedure as described above, aldehyde **33c** (0.65 g, 1.81 mmol) in ethanol (5 ml) was reduced to afford the diol **34c** (0.64 g, 98% yield) as brownish flakes using sodium borohydride (0.09 g, 2.27 mmol) as the reducing agent. Mp=88–90 °C; IR ν_{max} (cm^{-1}) 3319 (br s, O–H stretch), 3026 (s, C–H stretch), 1581 (s, C=C stretch), 1040 (s, C–H stretch); ^{1}H NMR δ/ppm 7.89–7.82 (2H, m, ArH), 7.76 (1H, d, *J*=8.3 Hz, ArH), 7.56 (1H, d, *J*=8.4 Hz, ArH), 7.32–7.15 (4H, m, 4×ArH), 6.93 (1H, d, *J*=8.4 Hz, ArH), 6.41 (1H, s, ArH), 5.67 (1H, br s, OH), 4.31 (2H, br s, CH_2OH), 3.94 (3H, s, OCH_3), 3.44 (3H, s, OCH_3); ^{13}C NMR δ/ppm 151.1 (C), 150.1 (C), 149.7 (C), 136.7 (C), 133.5 (C), 129.9 (CH), 129.4 (C), 128.9 (C), 128.8 (C), 128.1 (C), 128.0 (CH), 127.6 (CH), 126.7 (CH), 124.9 (CH), 124.3 (CH), 123.5 (CH), 117.9 (CH), 117.1 (C), 106.5 (CH), 104.6 (CH), 63.7 (CH_2OH), 55.8 (OCH_3), 55.4 (OCH_3); MS (EI) *m*/*z* (%) 361 (M+1, 5), 360 (M^+, 18), 343 (21), 342 (100), 311 (21), 309 (11), 283 (6), 226 (6), 113 (6); HRMS calculated for $C_{23}H_{20}O_4$ M^+ 360.1362, found 360.1362.

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