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Methodology for the synthesis of 1,2-disubstituted arylnaphthalenes from α-tetralones

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Abstract—α-Tetralones were initially converted into 1-bromo-dihydronaphthalene-2-carbaldehydes and 1-bromo-naphthalene-2-carbaldehydes. These precursors were then subjected to Suzuki coupling reactions to afford 1,2-disubstituted aryldihydronaphthalenes and 1,2-disubstituted arylnaphthalenes, respectively. The former products were oxidized with DDQ to give 1,2-disubstituted arylnaphthalenes.

1. Introduction

The synthesis of aromatic compounds containing biaryl axes continues to be important as a result of the biological activities associated with the biaryl natural products[1] as well as their use as ligands in transition metal catalysed reactions.

For example, the naturally occurring compound (*S*)-gossypol **1** (Fig. 1) contains a biaryl axis. Restricted rotation about this axis imparts chirality to the molecule. Pharmacologically it is known to be an oral antifertility agent, and it shows potential for the treatment of HIV infections, diabetic complications and cancer.[2] Recent work has also shown that the phenyl-naphthalene core is effective in thyromimetics[3a] and shows high ceramide-mediated proapoptotic activity on human breast cancer cells.[3b]

Apart from their interesting biological activity, biaryl naphthalene compounds also find application as chiral catalysts. The first and most frequently used chiral phosphine ligand is BINAP **2** (Fig. 1). This is illustrated by the work of Noyori who has shown that the ruthenium complexes of **2** are capable of effecting asymmetric hydrogenations and have even found industrial applications.[4,5]

The atropisomers of (1,1′-binaphthyl)-2,2′-diol **3** and its derivatives (Fig. 1) are widely used in asymmetric synthesis, either as ligands or as chiral auxiliaries. For example, the binaphthol derivative **4** has been used as a chiral ligand in the copper-catalysed Michael addition of dialkylzinc reagents to cyclic α,β-unsaturated ketones.[6] In addition, an important contribution using binaphthols in organic synthesis has come from the group of Shibasaki[7,8] in that it has been shown that a number of characterised heterobimetallic asymmetric binaphthols are capable of catalyzing a variety of reactions.

General methods for the synthesis of biaryl compounds include the use of oxidative coupling methods.[9] Otherwise, traditional methods for the assembly of the biaryl axis such as the Suzuki–Miyaura[10,11] and Stille reactions are used.[12] For the synthesis of suitably substituted biaryl compounds

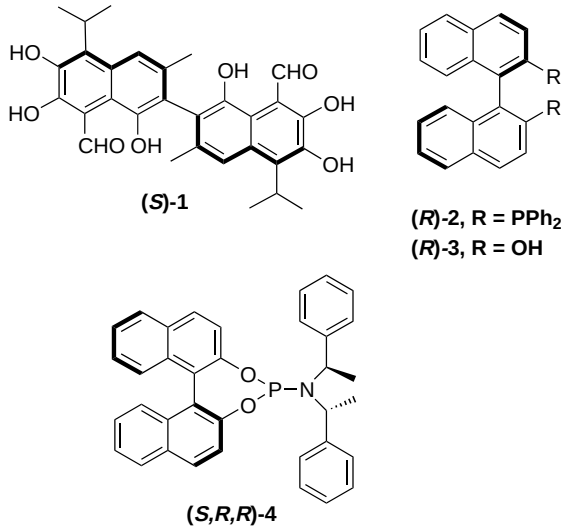

Figure 1.

Keywords: Suzuki-Miyaura coupling reactions; Aromatization; Arylnaphthalenes; α-Tetralone.
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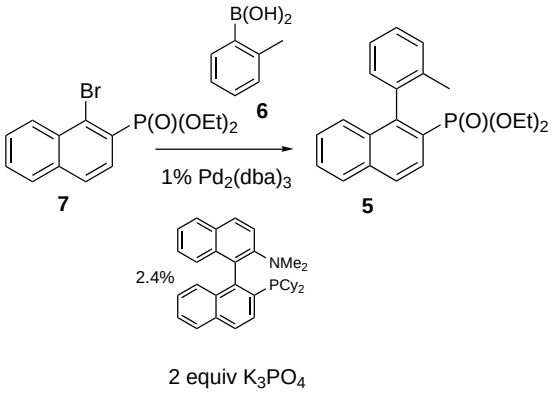
both of these methods depend on the synthesis of suitably substituted aromatic compounds and in the case of arylnaphthalenes the synthesis depends on the availability of suitably substituted naphthalenes.[13] For example, the arylnaphthalene **5** has been made by the coupling of tolylboronic acid **6** and **7** (Scheme 1).[14]



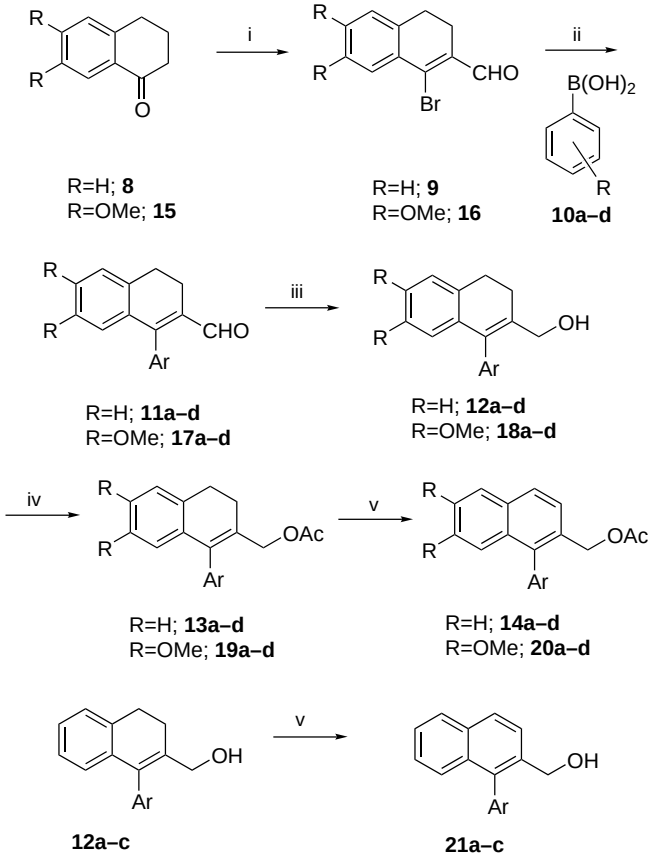
Scheme 1.

Our research group has been involved in the synthesis of biaryl compounds and naphthalenes[15] and in this paper we report on the use of α-tetralones as suitable commercially available substrates for the synthesis of simple arylnaphthalenes. We show that α-tetralones can be used as 'substitutes' for naphthalenes as these are readily converted into the naphthalene portion of the arylnaphthalene. Related results on the use of tetralones for building substituted naphthalenes have been reported by two other research group.[3,16]

2. Results and discussion

Following literature protocol, readily available α-tetralone **8** was converted into the known dihydronaphthalene **9** in good yield as shown in Scheme 2.[17,18] Using our well-developed Suzuki–Miyaura reaction conditions we then attempted to produce a number of aryldihydronaphthalenes. Reaction of **9** with catalytic $Pd(PPh_3)_4$ in the presence of boronic acids **10a–d** and aqueous Na_2CO_3 and DME afforded the desired Suzuki coupling products **11a–d** in good to excellent yields.[19] Subsequently the products were then reduced to alcohols **12a–d** using sodium borohydride in ethanol. The resultant alcohols **12a–d** were protected as their esters using acetic anhydride and pyridine to give **13a–d**. Finally, all that was required was the oxidation of dihydronaphthalenes **13a–d** to afford the desired biaryl naphthalenes. The use of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in CH_2Cl_2 afforded good yields of the desired arylnaphthalenes **14a–d** from **13a–d** demonstrating that tetralones can be used as substitutes for naphthalenes.

Dimethoxybromodihydronaphthalene-2-carbaldehyde **16** was synthesized from a different tetralone substrate, 6,7-dimethoxytetralone **15**, using DMF and potassium tribromide in CH_2Cl_2 in a similar manner to that described for tetralone **8**. As shown in Scheme 2 the exposure of **16** to boronic acids **10a–d** under aqueous Suzuki coupling reaction conditions in the presence of $[Pd(PPh_3)_4]$ gave



Scheme 2. Reagents and Conditions: (i) DMF, PBr_3, CH_2Cl_2, reflux, R = H, 70%; R = OMe, 63%; (ii) cat. $Pd(PPh_3)_4$, aqueous Na_2CO_3, boronic acid **10**, DME/EtOH, reflux; (iii) $NaBH_4$, EtOH, rt; (iv) Ac_2O, pyridine, reflux; (v) DDQ, CH_2Cl_2, reflux; for yields see Table 1.

aryl 6,7-dimethoxycarbaldehydes **17a–d** in good yields. Reduction of the carbaldehydes **17a–d** using sodium borohydride in ethanol gave dimethoxydihydronaphthalene alcohols **18a–d** in very good yields. As in the previous series, the resultant alcohols were then protected as their esters to give **19a–d**. The subsequent dimethoxydihydronaphthalene esters were then dehydrogenated as before to the envisaged substituted biaryl dimethoxynaphthalenes **20a–d** using DDQ in CH_2Cl_2 and the products were obtained in satisfactory yields (Table 1).

It has to be mentioned that an attempt was made to aromatize some of the dihydronaphthalene carbaldehydes **11a–d** using DDQ as reagent in CH_2Cl_2, as was done with the dihydronaphthalene esters. Unfortunately, in all cases only the starting material was obtained or uncharacterizable products were obtained.

In order to try and decrease the number of steps required to obtain the desired biaryl naphthalenes, the aromatization reaction was attempted on the related alcohols **12a–c**. (Scheme 2). Three of the dihydronaphthalene alcohols **12a–c** were aromatized using this methodology to afford **21a–c** in good yields.

As an alternative to produce the same arylnaphthalene alcohols we decided to investigate aromatization of the initial dihydronaphthalenes with alternative reagents. After

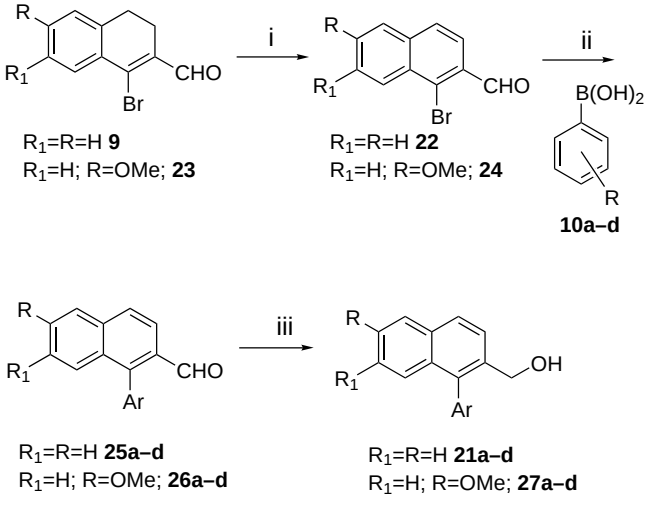
Table 1. Yields for Scheme 2

Entry	Ar	%		%	Entry	%	Entry	%	Entry	%
9→11a	3,4,5-(MeO)C_6H_2	83	**11a→12a**	100	**12a→13a**	98	**13a→14a**	78	**12a→21a**	82
9→11b	Naphthyl	93	**11b→12b**	94	**12b→13b**	94	**13b→14b**	95	**12b→21b**	79
9→11c	Ph	100	**11c→12c**	94	**12c→13c**	82	**13c→14d**	93	**12c→21c**	77
9→11d	2-MePh	78	**11d→12d**	94	**12d→13d**	94	**13d→14d**	100		
16→17a	3,4,5-(MeO)C_6H_2	88	**17a→18a**	87	**18a→19a**	80	**19a→20a**	74		
16→17b	Naphthyl	87	**17b→18b**	100	**18b→19b**	89	**19b→20b**	78		
16→17c	Ph	83	**17c→18c**	100	**18c→19c**	88	**19c→20c**	100		
16→17d	2-MePh	98	**17d→18d**	87	**18d→19d**	88	**19d→20d**	78		

extensive experimentation with **9** it was found that careful treatment of the substrate with selenium powder in a small amount of DMSO for 5 min at 170 °C resulted in acceptable yields of the desired product **22**. The related monomethoxydihydronaphthalene **23** also gave the desired naphthalene **24** in good yield (72%). The remaining steps for the production of a variety of 1-arylnaphthalenes were straightforward. Treatment of both **22** and **24** with the boronic acids **10a–d** gave the desired naphthalenes **25a–d** and **26a–d** with an aldehyde substituent in the 2-position. All the aldehydes were then reduced with $NaBH_4$ to give alcohols **21a–d** as well as the monomethoxynaphthalenes **27a–d** (Table 2, Scheme 3).

Table 2. Yields for Scheme 3

Entry	Ar	%	Entry	%
22→25a	3,4,5-(MeO)C_6H_2	94	**25a→21a**	82
22→25b	Naphthyl	89	**25b→21b**	93
22→25c	Ph	87	**25c→21c**	91
22→25d	2-MePh	94	**25d→21d**	95
24→26a	3,4,5-(MeO)C_6H_2	80	**26a→27a**	89
24→26b	Naphthyl	74	**26b→27b**	95
24→26c	Ph	90	**26c→27c**	100
24→26d	2-MePh	71	**26d→27d**	93

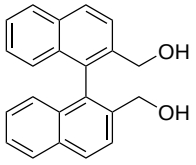


Scheme 3. Reagents and Conditions: (i) Se powder, DMSO, 170 °C, R=H, 69%; R=OMe, 72%; (ii) cat. $Pd(PPh_3)_4$, aqueous Na_2CO_3, boronic acid **10**, DME/EtOH, reflux; (iii) $NaBH_4$, EtOH, rt; for yields see Table 2.

In conclusion, we have developed a new straight-forward method for the synthesis of arylnaphthalenes where the regiochemistry of the product is defined unambiguously from the tetralone. This eliminates the difficulties of preparing 1-bromonaphthalenes by direct bromination of naphthalenes, as these reactions generally afford mixtures of products, particularly if the naphthalene is substituted. For example, bromination of 6,7-dimethoxy-2-naphthaldehyde would not afford **24**.

Specifically, we have been able to develop a two step procedure for the synthesis of aryldihydronaphthalenes **11a–d** and **17a–d** from tetralones **8** and **15**, which can be converted into the corresponding arylnaphthalenes. In addition, a two step procedure for the synthesis of 1-bromo-2-formylnaphthalenes (**22** and **24**) has been developed. These products can be utilized in Suzuki–Miyaura reactions to afford biaryl compounds.

Future work will entail the introduction of an oxygen substituent in the *ortho* position of the boronic acid. This will provide arylnaphthalenes such as **28** with two oxygen containing substituents *ortho* to the biaryl axis. These will be potential ligands for metal catalyzed reactions.



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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 μm) 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, dt=doublet of a 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.

3.1.1. Bromo-3,4-dihydronaphthalene-2-carbaldehyde 9. Dry DMF (8.02 mL, 103.2 mmol) in dry CH_2Cl_2 (50 mL) was cooled to 0 °C and phosphorus tribromide (8.00 mL, 89.5 mmol) was added drop-wise. The mixture was stirred at 0 °C for 1 h during which time a pale yellow suspension was formed. A solution of α-tetralone **8** (4.58 mL, 5.03 g, 34.4 mmol) in dry CH_2Cl_2 (90 mL) was added and the mixture was heated under reflux for 1 h. After cooling to 0 °C, aqueous $NaHCO_3$ was added slowly until the effervescence had subsided. Extraction of the organic material into CH_2Cl_2 (3×100 mL) was followed by drying the organic layer ($MgSO_4$). The solution was filtered through a Celite plug and evaporation of the excess solvent resulted into brown oil. Column chromatography eluting with 30% ethyl acetate/hexane gave the product **9** as a brown solid (5.71 g, 70%) with identical spectroscopic data to that described in the literature.[17,18]

3.1.2. 1-Bromo-6,7-dimethoxy-3,4-dihydronaphthalene-2-carbaldehyde 16. Dry DMF (0.56 mL, 7.27 mmol) in dry CH_2Cl_2 (20 mL) was cooled to 0 °C and phosphorus tribromide (0.60 mL, 6.30 mmol) was added drop-wise. The mixture was stirred at 0 °C for 2 h and a pale yellow suspension was formed. A solution of 6,7-dimethoxy-α-tetralone **15** (0.50 g, 2.42 mmol) in dry CH_2Cl_2 (30 mL) was added and the mixture was stirred at reflux for 12 h. After cooling to 0 °C, aqueous $NaHCO_3$ was added slowly until the effervescence had subsided. Extraction of the organic material into CH_2Cl_2 (3×100 mL) was followed by drying of the organic layer ($MgSO_4$), filtration through a Celite plug and evaporation of the excess solvent, which resulted into a yellow oil. Column chromatography (30% ethyl acetate/hexane) gave **16** as a yellow crystalline solid (0.45 g, 63%). This decomposed on standing and was therefore used immediately. IR ν_{max} (cm^{-1}) 1659 (s, C=O stretch), 1601, 1589, 1549 (s, C=C stretch); ^1H NMR δ/ppm 10.19 (1H, s, CHO), 7.42 (1H, s, Ar-H), 6.71 (1H, s, Ar-H), 3.95 (3H, s, OMe), 3.94 (3H, s, OMe), 2.80–2.75 (2H, m, CH_2), 2.64–2.58 (2H, m, CH_2); ^{13}C NMR δ/ppm 23.0 (CH_2), 27.1 (CH_2), 56.1 (OCH_3), 56.2 (OCH_3), 110.5 (CH), 112.1 (CH), 125.6 (C), 132.4 (C), 133.0 (C), 139.2 (C), 147.7 (C), 151.5 (C), 192.9 (CHO); MS (EI) *m/z* (%): 298 ($M^{+81}Br$, 94), 296 ($M^{+79}Br$, 100), 286 (17), 206 (50), 265 (22), 189 (53), 188 (43), 178 (24), 174 (19), 150 (42), 145 (35), 115 (39), 102 (22), 63 (18); HRMS calculated for $C_{13}H_{13}O_3{}^{79}Br$ M^+ 296.0048, found 296.0019.

3.1.3. 3,4,5-Trimethoxyphenylboronic acid 10a. To a stirred solution of 1-bromo-3,4,5-trimethoxybenzene (0.50 g, 2.02 mmol) in THF (30 mL) at −78 °C under nitrogen was added *n*-BuLi (1.56 mL, 2.22 mmol) drop-wise. The reaction mixture was stirred at −78 °C for 30 min before trimethylborate (0.68 mL, 6.07 mmol) was added and the mixture stirred for another 30 min at −78 °C. The subsequent mixture was then allowed to warm to room temperature before being acidified with aqueous 10% HCl. Extraction of the organic material into CH_2Cl_2 (3×100 mL) was followed by drying the organic layer ($MgSO_4$) before being concentrated under reduced pressure to give a cream white semi-solid **10a** (0.43 g, 100%) that was not purified further.

3.1.4. 1-Naphthylboronic acid 10b. In a similar manner to that described above bromonaphthalene (0.50 g, 2.41 mmol) in THF (40 mL) was converted into boronic acid **10b** (0.26 g, 63%) using *n*-BuLi (1.90 mL, 12.66 mmol) and $B(OMe)_3$ (0.81 mL, 7.24 mmol).

3.1.5. Phenylboronic acid 10c. Boronic acid **10c**, a cream white semi-solid (1.47 g, 89%) was synthesized from bromobenzene (1.43 mL, 13.58 mmol), *n*-BuLi (1.87 mL, 14.9 mmol) and $B(OMe)_3$ (1.96 mL, 4.07 mmol) in a similar way as described above.

3.1.6. *o*-Tolylboronic acid 10d. Using the same procedure as described above 2-bromotoluene (1.40 mL, 11.63 mmol) was converted to boronic acid **10d**, a white solid (1.34 g, 85%).

3.1.7. 1-(3,4,5-Trimethoxyphenyl)-3,4-dihydronaphthalene-2-carbaldehyde 11a. To $[Pd(PPh_3)_4]$ (0.22 g, 0.19 mmol) was added a deoxygenated solution of **9** (0.46 g, 1.940 mmol) in DME (10 mL). This was followed by a deoxygenated solution of boronic acid **10a** (0.62 g, 2.91 mmol) in ethanol (5 mL), and then a deoxygenated solution of aqueous sodium carbonate (1.77 g, 16.5 mmol in 8.2 mL water). The resultant mixture was heated under reflux under nitrogen for 46 h over which time the solution turned deep red. After allowing the mixture to cool to room temperature, it was quenched with water (50 mL) and the organic material was then extracted with CH_2Cl_2 (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 subsequent oil was purified by column chromatography (30% ethyl acetate/hexane) to afford the desired product **11a** as a brown solid (4.80 g, 83%). Mp=112–114 °C; IR ν_{max} (cm^{-1}) 1659 (s, C=O stretch), 1575, 1564 (s, C=C stretch); ^1H NMR δ/ppm 9.65 (1H, s, CHO), 7.26–7.31 (2H, m, 2×ArH), 7.19–7.16 (1H, m, ArH), 6.99–6.96 (1H, m, ArH), 6.51 (2H, s, 2×ArH), 3.93 (3H, s, OCH_3), 3.84 (6H, s, 2×OCH_3), 2.94–2.89 (2H, m, CH_2), 2.71–2.65 (2H, m, CH_2); ^{13}C NMR δ/ppm 20.2 (CH_2), 27.5 (CH_2), 56.2 (2×OCH_3), 60.9 (OCH_3), 107.7 (2×ArCH), 126.7 (CH), 127.8 (CH), 128.3 (CH), 130.2 (CH), 130.7 (C), 134.2 (C), 134.8 (C), 138.0 (C), 138.5 (C), 153.1 (2×C), 154.2 (C), 193.4 (CHO); MS (EI) *m/z* (%): 325 (M+1, 22), 324 (M^+, 100), 293 (22), 281 (52), 265 (18), 168 (31), 153 (25), 51 (11); HRMS calculated for $C_{20}H_{20}O_4$ M^+ 324.1362, found 324.1362.

3.1.8. 1-(1-Naphthyl)-3,4-dihydronaphthalene-2-carbaldehyde 11b. Using the same procedure as outlined above **11b**, a light brown oil (0.55 g, 93%) was obtained from a mixture of $[Pd(PPh_3)_4]$ (0.25 g, 0.21 mmol), dihydronaphthalene **9** (0.50 g, 2.11 mmol), boronic acid **10b** (0.54 g, 3.16 mmol, in ethanol 5 mL) and aqueous sodium carbonate (1.90 g, 17.9 mmol in 8.9 mL of water). IR ν_{max} (cm^{-1}) 1660 (s, C=O stretch), 1607, 1561 (m, C=C stretch); ^1H NMR δ/ppm 9.40 (1H, s, CHO), 7.92 (2H, t,

J=8.8 Hz, 2×ArH), 7.59–7.34 (5H, m, 5×ArH), 7.31–7.24 (2H, m, 2×ArH), 6.95 (1H, t, J=7.7 Hz, ArH), 6.64 (1H, d, J=7.7 Hz, ArH), 3.02–3.08 (2H, m, CH_2), 2.84–2.94 (1H, m, CH), 2.66–2.77 (1H, m, CH); ^{13}C NMR δ/ppm 20.1 (CH_2), 27.7 (CH_2), 125.1 (CH), 125.9 (CH), 126.3 (CH), 126.8 (CH), 126.9 (CH), 127.9 (CH), 128.1 (CH), 128.4 (CH), 128.4 (CH), 128.9 (CH), 130.2 (CH), 132.6 (C), 132.9 (C), 133.5 (C), 135.0 (C), 135.8 (C), 138.1 (C), 153.0 (C), 193.0 (CHO); MS (EI) m/z (%): 285 (M+1, 62), 284 (M^+, 100), 283 (89), 268 (27), 265 (39), 256 (62), 255 (89), 254 (33), 253 (68), 252 (73), 250 (27), 241 (27), 240 (43), 239 (67), 228 (33), 226 (22), 165 (21), 129 (22), 128 (73), 127 (39), 126 (42), 119 (22), 113 (20); HRMS calculated for $C_{21}H_{16}O$ M^+ 284.1201, found 284.1202.

3.1.9. 1-Phenyl-3,4-dihydronaphthalene-2-carbaldehyde 11c. In a similar manner as described above a mixture of [$Pd(PPh_3)_4$] (0.25 g, 0.21 mmol), dihydronaphthalene **9** (0.50 g, 2.11 mmol), boronic acid **10c** (0.39 g, 3.16 mmol, in ethanol 7 mL) and aqueous sodium carbonate (1.90 g, 17.9 mmol in 8.9 mL of water) was used to synthesize **11c** as a light brown crystalline solid (0.49 g, 100%). Mp=68–71 °C; IR ν_{max} (cm^{-1}) 1658 (s, C=O stretch), 1607, 1596 (m, C=C stretch); ^{1}H NMR δ/ppm 9.63 (1H, s, CHO), 7.50–7.47 (3H, m, 3×ArH), 7.35–7.30 (4H, m, 4×ArH), 7.18–7.12 (1H, dt, J=7.8, 1.9 Hz, ArH), 6.90 (1H, d, J=7.7 Hz, ArH), 2.97–2.92 (2H, m, CH_2), 2.76–2.71 (2H, m, CH_2); ^{13}C NMR δ/ppm 20.2 (CH_2), 27.5 (CH_2) 126.6 (CH), 127.8 (CH), 128.2 (2×CH), 128.4 (2×CH), 130.2 (C), 130.4 (2×C), 134.3 (C), 135.0 (C), 135.2 (ArC), 138.6 (C), 154.4 (ArC), 193.4 (CHO); MS (EI) m/z (%): 234 (M^+, 100), 233 (52), 205 (73), 202 (66), 189 (26), 178 (35), 165 (26), 128 (49), 127 (27), 78 (25), 29 (31); HRMS calculated for $C_{17}H_{14}O$ M^+ 234.1045, found 234.1045.[19]

3.1.10. 1-(*o*-Tolyl)-3,4-dihydronaphthalene-2-carbaldehyde 11d. Similarly [$Pd(PPh_3)_4$] (0.24 g, 0.210 mmol), a solution of dihydronaphthalene **9** (0.50 g, 2.11 mmol) in DME (10 mL), a solution of boronic acid **10d** (0.43 g, 3.16 mmol) in ethanol (5 mL), and a solution of aqueous sodium carbonate (1.90 g, 17.9 mmol in 8.9 mL of water) was used to synthesize carbaldehyde **11d** as a yellow crystalline solid (0.41 g, 78%). Mp=59–61 °C; IR ν_{max} (cm^{-1}) 1660 (s, C=O stretch), 1606, 1599 (m, C=C stretch); ^{1}H NMR δ/ppm 9.48 (1H, s, CHO), 7.35–7.25 (5H, m, 5×ArH), 7.16 (1H, d, J=6.9 Hz, ArH), 7.10 (1H, dt, J=7.8, 2.4 Hz, ArH), 6.73 (1H, d, J=7.8 Hz, ArH), 2.94 (2H, t, J=8.0 Hz, CH_2), 2.83–2.73 (1H, m, CH), 2.66–2.55 (1H, CH), 2.08 (3H, s, CH_3); ^{13}C NMR δ/ppm 19.6 (CH_3), 19.8 (CH_2), 27.5 (CH_2), 125.7 (CH), 126.7 (CH), 127.5 (CH), 127.9 (CH), 128.5 (CH), 130.2 (CH), 130.2 (CH), 130.5 (CH), 134.3 (C), 134.4 (C), 134.8 (C), 136.7 (C), 138.4 (C), 154.2 (C), 193.1 (CHO); MS (EI) m/z (%): 249 (M+1, 23), 248 (M^+, 74), 247 (35), 233 (100), 229 (28), 215 (51), 203 (51), 202 (53); HRMS calculated for $C_{18}H_{16}O$ M^+ 248.1201, found 248.1198.

3.1.11. 6,7-Dimethoxy-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalene-2-carbaldehyde 17a. To [$Pd(PPh_3)_4$] (0.19 g, 0.16 mmol) was added a deoxygenated solution of dihydronaphthalene **16** (0.48 g, 1.62 mmol) in DME (10 mL). This was followed by a deoxygenated solution of boronic acid **10a** (0.51 g, 2.42 mmol) in ethanol (5 mL), and then a deoxygenated solution of aqueous sodium carbonate (1.45 g, 13.7 mmol in 6.9 mL water). The resultant mixture was refluxed under nitrogen for 64 h during which time the mixture turned deep red. After allowing it to cool down to room temperature, the mixture was quenched with water (50 mL) and the organic material extracted with CH_2Cl_2 (3×100 mL). The resultant organic extracts were combined, dried ($MgSO_4$), and then filtered through a Celite plug and the excess solvent removed using a rotary evaporator. The subsequent oil was purified by column chromatography using 30% ethyl acetate/hexane as eluent to afford carbaldehyde **17a** as a yellow crystalline solid (0.55 g, 88%). Mp=139–141 °C; IR ν_{max} (cm^{-1}) 1652 (s, C=O stretch), 1603, 1581, 1556 (m, C=C stretch); ^{1}H NMR δ/ppm 9.59 (1H, s, CHO), 6.79 (1H, s, ArH), 6.52 (2H, s, 2×ArH), 6.49 (1H, s, ArH), 3.94 (3H, s, OCH_3), 3.93 (3H, s, OCH_3), 3.85 (6H, s, 2×OCH_3), 3.65 (3H, s, OCH_3), 2.88–2.82 (2H, m, CH_2), 2.70–2.64 (2H, m, CH_2); ^{13}C NMR δ/ppm 20.9 (CH_2), 27.8 (CH_2), 56.3 (OCH_3), 56.4 (OCH_3), 56.6 (2×OCH_3), 61.3 (OCH_3), 108.1 (2×CH), 111.4 (CH), 112.4 (CH), 127.6 (C), 131.3 (C), 132.8 (C), 133.1 (C), 138.4 (C), 147.8 (C), 151.2 (C), 153.4 (2×C), 154.9 (C), 193.5 (CHO); MS (EI) m/z (%): 385 (M+1, 27), 384 (M^+, 100), 372 (52), 371 (31), 370 (45), 369 (31), 368 (93), 366 (24), 353 (30), 343 (39), 337 (32), 195 (20), 181 (20), 28 (70); HRMS calculated for $C_{22}H_{24}O_6$ M^+ 384.1573, found 384.1573.

3.1.12. 6,7-Dimethoxy-1-(1-naphthyl)-3,4-dihydronaphthalene-2-carbaldehyde 17b. Using the same procedure as outlined above, a mixture of [$Pd(PPh_3)_4$] (0.12 g, 0.10 mmol), dihydronaphthalene **16** (0.30 g, 1.01 mmol), boronic acid **10b** (0.26 g, 1.51 mmol, in ethanol 5 mL) and aqueous sodium carbonate (0.91 g, 8.58 mmol in 4.5 mL of water) was used to synthesize carbaldehyde **17b** as a light brown oil (0.28 g, 87%). IR ν_{max} (cm^{-1}) 1652 (s, C=O stretch), 1604, 1557 (s, C=C stretch); ^{1}H NMR δ/ppm 9.44 (1H, s, CHO), 7.84 (2H, t, J=9.0 Hz, 2×ArH), 7.51–7.27 (5H, m, 5×ArH), 6.74 (1H, s, ArH), 6.07 (1H, s, ArH), 3.84 (3H, s, OCH_3), 3.26 (3H, s, OCH_3), 2.94–2.76 (3H, m, CH_2+CH), 2.67–2.56 (1H, m, CH); ^{13}C NMR δ/ppm 20.7 (CH_2), 27.5 (CH_2), 55.8 (OCH_3), 55.9 (OCH_3), 110.9 (CH), 111.6 (CH), 124.9 (CH), 125.9 (CH), 126.3 (CH), 126.7 (CH), 127.6 (C), 128.3 (CH), 128.3 (CH), 128.8 (CH), 132.2 (C), 132.5 (C), 133.0 (C), 133.4 (C), 133.9 (C), 147.4 (C), 150.7 (C), 153.2 (C), 192.7 (CHO); MS (EI) m/z (%): 345 (M+1, 63), 344 (M^+, 100), 315 (49), 313 (22), 262 (50), 239 (27), 232 (24), 226 (21), 205 (31), 189 (23), 128 (79), 119 (29), 115 (24), 85 (35), 83 (52); HRMS calculated for $C_{23}H_{20}O_3$ M^+ 344.1412, found 344.1412.

3.1.13. 6,7-Dimethoxy-1-phenyl-3,4-dihydronaphthalene-2-carbaldehyde 17c. In a similar manner as described above [$Pd(PPh_3)_4$] (0.12 g, 0.10 mmol), dihydronaphthalene **16** (0.30 g, 1.01 mmol), boronic acid **10c** (0.18 g, 1.51 mmol, in ethanol 5 mL) and aqueous sodium carbonate (0.91 g, 8.58 mmol in 4.3 mL of water) afforded **17c** as a yellow solid (0.22 g, 83%). Mp=114–117 °C; IR ν_{max} (cm^{-1}) 1650 (s, C=O stretch), 1605, 1557 (s, C=C stretch); ^{1}H NMR δ/ppm 9.53 (1H, s, CHO), 7.48–7.45 (3H, m, 3×ArH), 7.32–7.29 (2H, m, 2×ArH), 6.81 (1H, s, ArH), 6.39 (1H, s, ArH), 3.95 (3H, s, OCH_3), 3.61 (3H, s, OCH_3), 2.90–2.85 (2H, m, CH_2), 2.72–2.68 (2H, m, CH_2); ^{13}C NMR

δ/ppm 20.4 (CH_2), 27.4 (CH_2), 55.9 (2×OCH_3), 110.9 (CH), 111.9 (CH), 127.1 (C), 128.4 (2×CH), 128.6 (CH), 130.4 (2×CH), 132.4 (C), 132.6 (C), 135.4 (C), 147.2 (C), 150.6 (C), 154.6 (C), 192.9 (CHO); MS (EI) *m/z* (%): 295 (M+1, 26), 294 (M^+, 100), 293 (21), 265 (22), 189 (15), 178 (19); HRMS calculated for $C_{19}H_{18}O_3$ M^+ 294.1256, found 294.1256.

3.1.14. 6,7-Dimethoxy-1-(*o*-tolyl)-3,4-dihydronaphthalene-2-carbaldehyde 17d. Similarly [$Pd(PPh_3)_4$] (0.20 g, 0.11 mmol), dihydronaphthalene **16** (0.50 g, 1.68 mmol) in DME (10 mL), boronic acid **10d** (0.36 g, 2.52 mmol, in ethanol 10 mL) and aqueous sodium carbonate (1.56 g, 14.30 mmol in 7.4 mL of water) afforded carbaldehyde **17d** as a light brown oil (0.51 g, 98%). IR ν_{max} (cm^{-1}) 1656 (s, C=O stretch), 1606 (m, C=C stretch); ^{1}H NMR δ/ppm 9.41 (1H, s, CHO), 7.35–7.25 (3H, m, 3×ArH), 7.16 (1H, d, *J*=7.4 Hz, ArH), 6.79 (1H, s, ArH), 6.24 (1H, s, ArH), 3.93 (3H, s, OCH_3), 3.57 (3H, s, OCH_3), 2.90–2.83 (2H, m, CH_2), 2.78–2.73 (1H, m, CH), 2.64–2.55 (1H, m, CH), 2.08 (3H, s, CH_3); ^{13}C NMR δ/ppm 19.6 (CH_3), 19.9 (CH_2), 27.4 (CH_2), 55.9 (2×OCH_3), 110.9 (CH), 111.0 (CH), 125.7 (CH), 126.9 (C), 128.5 (CH), 130.2 (CH), 130.4 (CH), 132.4 (C), 132.5 (C), 134.9 (C), 136.6 (C), 147.6 (C), 150.7 (C), 154.5 (C), 192.8 (CHO); MS (EI) *m/z* (%): 308 (M^+, 100), 249 (16), 108 (31), 58 (20); HRMS calculated for $C_{20}H_{20}O_3$ M^+ 308.1412, found 308.1396.

3.1.15. [1-(3,4,5-Trimethoxyphenyl)-3,4-dihydronaphthalen-2-yl]methanol 12a. To a solution of carbaldehyde **11a** (0.51 g, 1.57 mmol) in ethanol (30 mL) was added $NaBH_4$ (0.07 g, 1.96 mmol). The reaction mixture was stirred at room temperature for 2 h after which time it turned cream white. The mixture was then extracted with CH_2Cl_2 (3×100 mL). The organic extracts were combined, dried ($MgSO_4$), and then filtered through a Celite plug and concentrated in vacuo. The subsequent colourless oil was purified by column chromatography using 30% ethyl acetate/hexane as eluent to afford **12a** as a white crystalline solid (0.51 g, 100%). Mp=115–116 °C; IR ν_{max} (cm^{-1}) 3421 (m, broad, OH stretch), 1583, 1507 (s, C=C stretch); ^{1}H NMR δ/ppm 7.17–7.02 (3H, m, 3×ArH), 6.72 (1H, dd, *J*=7.3, 1.0 Hz, ArH), 6.39 (2H, s, 2×ArH), 4.12 (2H, s, CH_2OH), 3.89 (3H, s, OCH_3), 3.80 (6H, s, 2×OCH_3), 2.90 (2H, dd, *J*=8.4, 7.6 Hz, CH_2), 2.54 (2H, dd, *J*=8.4, 7.5 Hz, CH_2), 1.85 (1H, s, CH_2OH); ^{13}C NMR δ/ppm 25.1 (CH_2), 28.1 (CH_2), 55.9 (2×OCH_3), 60.8 (OCH_3), 63.5 (CH_2OH), 106.9 (2×CH), 126.1 (CH), 126.2 (CH), 126.8 (CH), 127.1 (CH), 133.9 (C), 135.4 (C), 135.8 (C), 135.9 (C), 136.8 (C), 153.0 (2×C), (one quaternary carbon missing); MS (EI) *m/z* (%): 327 (M+1, 22), 326 (M^+, 100), 297 (25), 295 (27) 181 (10), 168 (24), 165 (14), 129 (21); HRMS calculated for $C_{20}H_{22}O_4$ M^+ 326.1518, found 326.1519.

3.1.16. [1-(1-Naphthyl)-3,4-dihydronaphthalen-2-yl]methanol 12b. Similarly using $NaBH_4$ (0.05 g, 1.32 mmol) in EtOH (10 mL) carbaldehyde **11b** (0.30 g, 1.06 mmol) was reduced to alcohol **12b**, a cream white semi-solid (0.29 g, 94%). IR ν_{max} (cm^{-1}) 3384 (s, broad, OH stretch), 1648, 1588, 1576 (m, C=C stretch); ^{1}H NMR δ/ppm 7.87 (2H, t, *J*=7.3 Hz, 2×ArH), 7.68 (1H, d, *J*=8.5 Hz, ArH), 7.54–7.43 (2H, m, 2×ArH), 7.38–7.29 (2H, m, 2×ArH), 7.24–7.20 (1H, m, ArH), 7.07–7.12 (1H, m, ArH), 6.90 (1H, t, *J*=7.5 Hz, ArH), 6.41 (1H, d, *J*=7.7 Hz, ArH), 3.92 (2H, s, CH_2OH), 3.08–3.02 (2H, m, CH_2), 2.73–2.65 (2H, m, CH_2); ^{13}C NMR δ/ppm 25.2 (CH_2), 28.4 (CH_2), 63.8 (CH_2OH), 125.5 (CH), 125.7 (CH), 125.9 (CH), 126.1 (CH), 126.3 (CH), 126.4 (CH), 126.9 (CH), 127.2 (CH), 127.5 (CH), 127.7 (CH), 128.3 (CH), 132.6 (C), 133.7 (C), 133.9 (C), 135.3 (C), 135.9 (C), 137.7 (C), (one quaternary carbon missing); MS (EI) *m/z* (%): 286 (M^+, 21), 268 (32), 267 (45), 255 (41), 253 (62), 251 (77), 249 (19), 239 (24), 238 (64), 229 (19), 228 (24), 225 (31), 215 (29), 165 (28), 152 (21), 141 (36), 129 (50), 128 (100), 127 (52), 115 (55), 77 (21), 31 (42); HRMS calculated for $C_{21}H_{18}O$ M^+ 286.1358, found 286.1356.

3.1.17. (1-Phenyl-3,4-dihydronaphthalen-2-yl)methanol 12c. Using the same procedure as outlined above, $NaBH_4$ (0.03 g, 0.19 mmol) in EtOH (10 mL) carbaldehyde **11c** (0.17 g, 0.72 mmol) afforded alcohol **12c** as a yellow oil (0.16 g, 94%). IR ν_{max} (cm^{-1}) 3386 (s, broad, OH stretch), 1654, 1598 (m, C=C stretch); ^{1}H NMR δ/ppm 7.37–7.29 (3H, m, 3×ArH), 7.13–7.11 (3H, m, 3×ArH), 7.08–7.06 (1H, dd, *J*=7.3, 1.1 Hz, ArH), 6.99 (1H, t, *J*=7.2 Hz, ArH), 6.60 (1H, d, *J*=7.6 Hz, ArH), 4.02 (2H, s, CH_2OH), 2.86 (2H, dd, *J*=8.4, 7.5 Hz, CH_2), 2.51 (2H, dd, *J*=8.4, 7.5 Hz, CH_2); ^{13}C NMR δ/ppm 25.0 (CH_2), 28.1 (CH_2), 63.3 (CH_2OH), 126.0 (CH), 126.1 (CH), 126.7 (CH), 126.9 (CH), 127.0 (CH), 128.2 (2×CH), 129.8 (2×CH), 135.5 (C), 135.8 (C), 135.9 (C), 136.1 (C), 138.3 (C); MS (EI) *m/z* (%): 237 (M+1, 20), 236 (M^+, 100), 235 (20), 234 (62), 233 (33), 224 (24), 218 (38), 217 (36), 215 (24), 208 (36), 205 (77), 204 (25), 203 (46), 202 (52), 189 (21), 179 (26), 178 (36), 165 (23), 159 (21), 130 (23), 129 (34), 128 (20), 127 (22), 115 (35), 105 (23), 101 (23), 91 (76), 77 (26); HRMS calculated for $C_{17}H_{16}O$ M^+ 236.1201, found 236.1201.

3.1.18. [1-(*o*-Tolyl)-3,4-dihydronaphthalen-2-yl]methanol 12d. Similarly using $NaBH_4$ (0.05 g, 1.41 mmol) in EtOH (10 mL) carbaldehyde **11d** (0.32 g, 1.13 mmol) was reduced to alcohol **12d**, a white semi-solid (0.30 g, 94%). IR ν_{max} (cm^{-1}) 3416 (s, broad, OH stretch), 1629 (m, C=C); ^{1}H NMR δ/ppm 7.26–6.99 (7H, m, 7×ArH), 6.50 (1H, d, *J*=7.6 Hz, ArH), 3.98 (2H, s, CH_2OH), 2.93 (2H, dd, *J*=8.3, 7.7 Hz, CH_2), 2.56 (2H, dd, *J*=8.5, 7.5 Hz, CH_2), 2.06 (3H, s, $ArCH_3$); ^{13}C NMR δ/ppm 19.4 (CH_2), 24.9 (CH_2), 28.3 (CH_3), 63.6 (CH_2OH), 125.5 (CH), 125.8 (CH), 126.4 (CH), 126.8 (CH), 127.2 (CH), 127.4 (CH), 129.9 (CH), 130.1 (CH), 135.1 (C), 135.4 (C), 135.5 (C), 135.7 (C), 136.8 (C), 137.7 (C); MS (EI) *m/z* (%): 251 (M+1, 40), 250 (M^+, 100), 235 (66), 232 (26), 219 (59), 218 (27), 217 (74), 216 (20), 215 (44), 204 (38), 203 (47), 202 (53), 179 (23), 178 (27), 159 (30), 129 (36), 128 (25), 119 (34), 115 (29), 105 (52), 101 (20), 91 (43), 43 (39); HRMS calculated for $C_{18}H_{18}O$ M^+ 250.1358, found 250.1358.

3.1.19. [6,7-Dimethoxy-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalen-2-yl]methanol 18a. In a similar manner as described above, $NaBH_4$ (0.06 g, 1.72 mmol) in EtOH (10 mL) was used to reduce carbaldehyde **17a** (0.53 g, 1.34 mmol) to alcohol **18a**, a white semi-solid (0.46 g, 87%). IR ν_{max} (cm^{-1}) 3517 (s, broad, OH stretch), 1651 (m, C=C stretch); ^{1}H NMR δ/ppm 6.66 (1H, s, ArH), 6.33 (2H, s, 2′ and 6′-H), 6.24 (1H, s, ArH), 4.04 (2H, s, CH_2OH), 3.83 (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 3.75

(6H, s, 2×OCH_3), 3.54 (3H, s, OCH_3), 2.78 (2H, dd, J= 8.4, 7.6 Hz, CH_2), 2.46 (2H, dd, J=8.5, 7.6 Hz, CH_2); ^{13}C NMR δ/ppm 25.5 (CH_2), 27.9 (CH_2), 55.9 (OCH_3), 56.1 (3×OCH_3), 60.9 (OCH_3), 63.8 (CH_2OH), 106.9 (2′ and 6′-C), 110.7 (CH), 110.9 (CH), 128.5 (C), 128.6 (C), 133.6 (C), 133.9 (C), 135.8 (C), 136.9 (C), 146.9 (C), 147.9 (C), 153.4 (2×C); MS (EI) m/z (%): 387 (M+1, 63), 386 (M^+, 100), 357 (22), 355 (44), 189 (21), 164 (18), 152 (16), 31 (12); HRMS calculated for $C_{22}H_{24}O_6$ M^+ 386.1729, found 386.1729.

3.1.20. [6,7-Dimethoxy-1-(1-naphthyl)-3,4-dihydronaphthalen-2-yl]methanol 18b. Similarly $NaBH_4$ (0.03 g, 0.19 mmol) in EtOH (10 mL), reduced carbaldehyde **17b** (0.25 g, 0.73 mmol) to alcohol **18b**, obtained as a light brown oil (0.25 g, 100%). IR ν_{max} (cm^{-1}) 3481 (m, broad, OH stretch), 1604 (m, C=C stretch); ^{1}H NMR δ/ppm 7.76 (2H, t, J=7.3 Hz, 2×ArH), 7.58 (1H, d, J=8.4 Hz, ArH), 7.42–7.31 (2H, m, 2×ArH), 7.27–7.19 (2H, m, 2×ArH), 6.67 (1H, s, ArH), 5.89 (1H, s, ArH), 3.78 (2H, s, CH_2OH), 3.77 (3H, s, OCH_3), 3.23 (3H, s, OCH_3), 2.91–2.84 (2H, m, CH_2), 2.59–2.54 (2H, m, CH_2); ^{13}C NMR δ/ppm 25.3 (CH_2), 28.1 (CH_2), 55.8 (OCH_3), 55.9 (OCH_3), 63.7 (CH_2OH), 110.5 (CH), 110.9 (CH), 125.4 (CH), 125.7 (CH), 125.8 (CH), 126.1 (CH), 127.3 (CH), 127.6 (CH), 128.2 (CH), 128.8 (C), 132.5 (C), 133.4 (C), 133.6 (C), 135.5 (2×C), 135.9 (C), 146.9 (C), 147.9 (C); MS (EI) m/z (%): 347 (M+1, 43), 346 (M^+, 100), 345 (21), 344 (53), 330 (25), 315 (34), 239 (24), 226 (18), 215 (19); HRMS calculated for $C_{23}H_{22}O_3$ M^+ 346.1569, found 346.1569.

3.1.21. (6,7-Dimethoxy-1-phenyl-3,4-dihydronaphthalen-2-yl)methanol 18c. Using the same procedure as described above, $NaBH_4$ (0.03 g, 0.81 mmol) in EtOH (10 mL) reduced aldehyde **17c** (0.17 g, 0.65 mmol) to alcohol **18c** obtained as a light yellow oil (0.20 g, 100%). IR ν_{max} (cm^{-1}) 3449 (m, broad, OH stretch), 1573, (m, C=C stretch); ^{1}H NMR δ/ppm 7.41–7.30 (3H, m, 3×ArH), 7.18–7.15 (2H, m, 2×ArH), 6.72 (1H, s, ArH), 6.19 (1H, s, ArH), 4.06 (2H, s, CH_2OH), 3.88 (3H, s, OCH_3) 3.56 (3H, s, OCH_3), 2.85 (2H, t, J=8.1 Hz, CH_2), 2.54 (2H, t, J= 8.1 Hz, CH_2); ^{13}C NMR δ/ppm 25.5 (CH_2), 28.0 (CH_2), 55.8 (OCH_3), 55.9 (OCH_3), 63.7 (CH_2OH), 110.8 (CH), 110.9 (CH), 127.1 (CH), 128.2 (2×CH), 128.5 (C), 128.8 (C), 129.9 (2×CH), 133.8 (C), 135.8 (C), 138.4 (C), 146.9 (C), 147.9 (C); MS (EI) m/z (%): 296 (M^+, 12), 263 (14), 219 (69), 154 (43), 131 (22), 87 (23), 57 (100), 41 (23); HRMS calculated for $C_{19}H_{20}O_3$ M^+ 296.1412, found 296.1403.

3.1.22. [6,7-Dimethoxy-1-(*o*-tolyl)-3,4-dihydronaphthalen-2-yl]methanol 18d. Similarly $NaBH_4$ (0.05 g, 1.29 mmol) in EtOH (10 mL) was used to reduce aldehyde **17d** (0.32 g, 1.04 mmol) to alcohol **18d** obtained as a yellow semi-solid (0.28 g, 87%). IR ν_{max} (cm^{-1}) 3508 (m, broad, OH stretch), 1605, 1573 (m, C=C stretch); ^{1}H NMR δ/ppm 7.27–7.19 (3H, m, 3×ArH), 7.06 (1H, d, J=6.7 Hz, ArH), 6.74 (1H, s, ArH), 6.06 (1H, s, ArH), 3.97 (2H, s, CH_2OH), 3.87 (3H, s, OCH_3), 3.54 (3H, s, OCH_3), 2.89–2.84 (2H, m, CH_2), 2.57–2.52 (2H, m, CH_2), 2.06 (3H, s, $ArCH_3$); ^{13}C NMR δ/ppm 19.5 (CH_3), 25.2 (CH_2), 28.1 (CH_2), 55.9 (OCH_3), 56.0 (OCH_3), 63.8 (CH_2OH), 110.0 (CH), 111.1 (CH), 125.8 (CH), 127.5 (CH), 128.2 (C), 128.4 (C), 130.0 (2×C), 133.5 (C), 135.0 (C), 136.7 (C), 137.8 (C), 147.2 (C), 147.9 (C); MS (EI) m/z (%): 311 (M+1, 19), 310 (M^+, 80), 309 (23), 308 (75), 294 (33), 293 (35), 279 (56), 191 (26), 189 (26), 166 (40), 148 (100), 83 (30), 57 (38), 43 (27), 41 (22); HRMS calculated for $C_{20}H_{22}O_3$ M^+ 310.1569, found 310.1569.

3.1.23. [1-(3,4,5-Trimethoxyphenyl)-3,4-dihydronaphthalen-2-yl]methyl acetate 13a. A mixture of alcohol **12a** (0.38 g, 1.16 mmol), pyridine (5 mL) and acetic anhydride (5 mL) was refluxed under nitrogen for 16 h during which time the mixture turned black. After cooling to room temperature, excess solvent was removed under reduced pressure and the resultant oil purified by column chromatography using 30% ethyl acetate/hexane as eluent to afford the acetate **13a** as yellow crystalline solid (0.42 g, 98%). Mp=81–83 °C; IR ν_{max} (cm^{-1}) 1734 (s, C=O stretch), 1584 (s, C=C stretch); ^{1}H NMR δ/ppm 7.16–7.07 (3H, m, 3×ArH), 6.74 (1H, d, J=7.3 Hz, ArH), 6.41 (2H, s, 2′ and 6′-H), 4.61 (2H, s, CH_2OAc), 3.90 (3H, s, OCH_3), 3.82 (6H, s, 2×OCH_3), 2.92 (2H, dd, J=8.4, 7.7 Hz, CH_2), 2.46 (2H, dd, J=8.4, 7.7 Hz, CH_2), 2.07 (3H, s, OAc); ^{13}C NMR δ/ppm 20.9 (CH_2), 25.4 (OAc), 27.9 (CH_2), 56.0 (2× OCH_3), 60.8 (OCH_3), 65.6 (CH_2OAc), 106.8 (2′ and 6′-C), 126.3 (CH), 126.3 (CH), 127.1 (CH), 127.2 (CH), 131.0 (C), 133.4 (C), 135.4 (C), 135.6 (C), 137.0 (C), 138.3 (C), 153.1 (2×C), 170.9 ($OCOCH_3$); MS (EI) m/z (%): 369 (M+1, 11), 368 (M^+, 51), 309 (12), 308 (18), 293 (22), 278 (33), 277 (100), 246 (17); HRMS calculated for $C_{22}H_{24}O_5$ M^+ 368.1624, found 368.1620.

3.1.24. [1-(1-Naphthyl)-3,4-dihydronaphthalen-2-yl]methyl acetate 13b. In a similar manner as described above alcohol **12b** (0.25 g, 0.87 mmol) gave **13b** as a yellow oil (0.27 g, 94%). IR ν_{max} (cm^{-1}) 1734 (s, C=O stretch), 1593 (m, C=C stretch); ^{1}H NMR δ/ppm 7.86–7.82 (2H, m, 2×ArH), 7.65 (1H, d, J=8.5 Hz, ArH), 7.52–7.42 (2H, m, 2×ArH), 7.39–7.29 (2H, m, 2×ArH), 7.18 (1H, d, J=7.3 Hz, ArH), 7.08 (1H, t, J=7.4 Hz, ArH), 6.87 (1H, t, J=7.5 Hz, ArH), 6.41 (1H, d, J=7.7 Hz, ArH), 4.42 (2H, s, CH_2OAc), 3.02 (2H, m, CH_2), 2.60–2.54 (2H, m, CH_2), 1.92 (3H, s, OAc); ^{13}C NMR δ/ppm 20.8 (CH_2), 25.5 (OAc), 28.2 (CH_2), 65.6 (CH_2OAc), 125.6 (CH), 125.9 (CH), 126.0 (CH), 126.1 (CH), 126.2 (CH), 126.3 (CH), 127.3 (2×CH), 127.6 (CH), 128.0 (CH), 128.4 (CH), 132.5 (C), 133.0 (C), 133.8 (C), 135.3 (C), 135.6 (C), 135.8 (C), 136.3 (C), 171.0 ($OCOCH_3$); MS (EI) m/z (%): 329 (M+1, 25), 328 (M^+, 77), 270 (29), 269 (100), 268 (53), 267 (56), 266 (58), 265 (74), 263 (21), 255 (41), 254 (52), 253 (99), 252 (97), 249 (22), 241 (25), 240 (31), 239 (67), 228 (25), 226 (23), 165 (23), 141 (60), 133 (20), 129 (32), 128 (29), 127 (25), 126 (51), 117 (26), 115 (28), 91 (30), 43 (63); HRMS calculated for $C_{23}H_{20}O_2$ M^+ 328.1463, found 328.1463.

3.1.25. (1-Phenyl-3,4-dihydronaphthalen-2-yl)methyl acetate 13c. Similarly alcohol **12c** (0.25 g, 1.06 mmol afforded acetate **13c** as a yellow oil (0.24 g, 82%). IR ν_{max} (cm^{-1}) 1735 (s, C=O stretch), 1656, 1598 (m, C=C stretch); ^{1}H NMR δ/ppm 7.39–7.33 (3H, m, 3×ArH), 7.18–7.09 (5H, m, 5×ArH), 7.02 (1H, t, J=7.3 Hz, ArH), 6.63 (1H, d, J=7.6 Hz, ArH), 4.56 (2H, s, CH_2OAc), 2.92 (2H, dd, J=8.3, 7.7 Hz, CH_2), 2.46 (2H, dd, J=8.3, 7.7 Hz, CH_2), 2.04 (3H, s, OAc); ^{13}C NMR δ/ppm) 20.9 (CH_2), 25.7 (OAc), 27.6 (CH_2), 65.5 (CH_2OAc), 126.2 (CH), 126.4

(CH), 127.2 (CH), 127.2 (CH), 127.3 (CH), 128.3 (2×CH), 129.9 (2×CH), 131.1 (C), 135.6 (C), 135.8 (C), 137.9 (C), 138.3 (C), 170.9 ($OCOCH_3$); MS (EI) *m/z* (%): 278 (M^+, 55), 266 (20), 234 (22), 220 (29), 219 (100), 218 (62), 217 (62), 216 (75), 215 (76), 205 (42), 204 (55), 203 (95), 202 (92), 191 (40), 189 (41), 179 (23), 178 (51), 165 (33), 141 (26), 129 (37), 128 (31), 127 (21), 115 (44), 101 (23), 91 (89), 77 (22), 43 (73); HRMS calculated for $C_{19}H_{18}O_2$ M^+ 278.1307, found 278.1307.

3.1.26. [1-(*o*-Tolyl)-3,4-dihydronaphthalen-2-yl]methyl acetate 13d. Similarly alcohol **12d** (0.20 g, 0.80 mmol) gave acetate **13d** as a light brown oil (0.22 g, 94%). IR ν_{max} (cm^{-1}) 1725 (s, C=O stretch), 1605, 1575 (m, C=C stretch); ^1H NMR δ/ppm 7.27–7.01 (7H, m, 7×ArH), 6.52 (1H, d, J=7.6 Hz, ArH), 4.50 (1H, d, J=14.4 Hz, one of CH_2OAc), 4.43 (1H, d, J=14.4 Hz, one of CH_2OAc), 2.93 (2H, dd, J=8.4, 7.7 Hz, CH_2), 2.47 (2H, dd, J=8.4, 7.5 Hz, CH_2), 2.06 (3H, s, $ArCH_3$)[a], 2.03 (3H, s, $OCOCH_3$)[a], assignments with the same superscript may be interchanged; ^{13}C NMR δ/ppm 19.4 ($ArCH_3$), 20.9 (CH_2), 25.1 (OAc), 28.1 (CH_2), 65.4 (CH_2OAc), 125.6 (CH), 125.8 (CH), 126.4 (CH), 127.1 (CH), 127.2 (CH), 127.7 (CH), 130.0 (2×CH), 131.0 (C), 135.0 (C), 135.4 (C), 136.7 (C), 137.2 (C), 137.4 (C), 170.9 ($OCOCH_3$); MS (EI) *m/z* (%): 292 (M^+, 10), 232 (24), 217 (100), 105 (6), 91 (5), 43 (9); HRMS calculated for $C_{20}H_{20}O_2$ M^+ 292.1463, found 292.1425.

3.1.27. [6,7-Dimethoxy-1-(3,4,5-trimethoxyphenyl)-3,4-dihydronaphthalen-2-yl]methyl acetate 19a. Using the same procedure as outlined above alcohol **18a** (0.37 g, 0.96 mmol) afforded acetate **19a** as light yellow oil (0.33 g, 80%). IR ν_{max} (cm^{-1}) 1731 (s, C=O stretch), 1583 (s, C=C stretch); ^1H NMR δ/ppm 6.73 (1H, s, ArH), 6.42 (2H, s, 2′ and 6′-H), 6.32 (1H, s, ArH), 4.60 (2H, s, CH_2OAc), 3.90 (3H, s, OCH_3), 3.89 (3H, s, OCH_3), 3.82 (6H, s, 2×OCH_3), 3.62 (3H, s, OCH_3), 2.85 (2H, dd, J=8.4, 7.6 Hz, CH_2), 2.44 (2H, dd, J=8.4, 7.8 Hz, CH_2), 2.07 (3H, s, OAc); ^{13}C NMR δ/ppm 20.9 (CH_2), 25.8 (OAc), 27.7 (CH_2), 55.8 (OCH_3), 55.9 (OCH_3), 56.1 (2×OCH_3), 60.9 (OCH_3), 65.8 (CH_2OAc), 106.9 (2′ and 6′-C), 110.8 (CH), 110.9 (CH), 128.2 (C), 128.5 (C), 128.7 (C), 133.5 (C), 137.0 (C), 138.1 (C), 147.0 (C), 148.2 (C), 153.1 (2×C), 171.0 ($OCOCH_3$); MS (EI) *m/z* (%): 352 (M^+, 54), 188 (28), 87 (14), 57 (77), 43 (100); HRMS calculated for $C_{22}H_{24}O_4$ M^+ 352.1675, found 352.1743.

3.1.28. [6,7-Dimethoxy-1-(1-naphthyl)-3,4-dihydronaphthalen-2-yl]methyl acetate 19b. Similarly alcohol **18b** (0.17 g, 0.49 mmol) afforded acetate **19b** as yellow semi-solid (0.17 g, 89%). IR ν_{max} (cm^{-1}) 1730 (s, C=O stretch), 1605 (m, C=C stretch); ^1H NMR δ/ppm 7.88–7.84 (2H, m, 2×ArH), 7.65 (1H, d, J=8.4 Hz, ArH), 7.54–7.42 (2H, m, 2×ArH), 7.37–7.31 (2H, m, 2×ArH), 6.77 (1H, s, ArH), 5.99 (1H, s, ArH), 4.43 (1H, d, J=12.2 Hz, one of CH_2OAc), 4.38 (1H, d, J=12.2 Hz, one of CH_2OAc), 3.87 (3H, s, OCH_3), 3.33 (3H, s, OCH_3), 2.97–2.89 (2H, m, CH_2), 2.59–2.53 (2H, m, CH_2), 1.95 (3H, s, OAc); ^{13}C NMR δ/ppm 20.8 (CH_2), 25.7 (OAc), 27.9 (CH_2), 55.8 (OCH_3), 55.9 (OCH_3), 65.6 (CH_2OAc), 110.6 (CH), 110.9 (CH), 125.4 (CH), 125.8 (2×CH), 126.0 (CH), 127.4 (CH), 127.9 (CH), 128.1 (C), 128.2 (CH), 128.5 (C), 130.5 (C), 132.3 (C), 133.6 (C), 135.5 (C), 135.9 (C), 147.0 (C), 148.1 (C), 170.9 ($OCOCH_3$); MS (EI) *m/z* (%): 389 (M+1, 29), 388 (M^+, 100), 329 (32), 328 (71), 327 (23), 298 (25), 297 (54), 239 (24), 141 (19); HRMS calculated for $C_{25}H_{24}O_4$ M^+ 388.1675, found 388.1675.

3.1.29. (6,7-Dimethoxy-1-phenyl-3,4-dihydronaphthalen-2-yl)methyl acetate 19c. Similarly alcohol **18c** (0.15 g, 0.58 mmol) gave acetate **19c** as a yellow solid (0.17 g, 88%). Mp=106 °C; IR ν_{max} (cm^{-1}); 1732 (s, C=O stretch), 1605, 1573 (m, C=C stretch); ^1H NMR δ/ppm 7.43–7.34 (3H, m, 3×ArH), 7.19–7.16 (2H, m, 2×ArH), 6.72 (1H, s, ArH), 6.20 (1H, s, ArH), 4.54 (2H, s, CH_2OAc), 3.89 (3H, s, OCH_3) 3.56 (3H, s, OCH_3), 2.85 (2H, dd, J=8.5, 7.6 Hz, CH_2), 2.44 (2H, dd, J=8.4, 7.7 Hz, CH_2), 2.04 (3H, s, OAc); ^{13}C NMR δ/ppm 20.9 (CH_2), 25.7 (CH_2), 27.7 (CH_3), 55.8 (OCH_3), 55.9 (OCH_3), 65.6 (CH_2OH), 110.8 (CH), 110.9 (CH), 127.3 (CH), 128.2 (2×CH), 128.5 (C), 128.8 (C), 129.8 (2×CH), 137.9 (C), 138.1 (C), 146.9 (C), 148.0 (2×C), 171.1 ($OCOCH_3$), (one quaternary carbon missing); MS (EI) *m/z* (%): 339 (M+1, 31), 338 (M^+, 100), 336 (36), 279 (71), 278 (95), 277 (53), 248 (41), 247 (64), 245 (32), 203 (27), 189 (24), 165 (21), 91 (21), 43 (66); HRMS calculated for $C_{21}H_{22}O_4$ M^+ 338.1518, found 338.1519.

3.1.30. [6,7-Dimethoxy-1-(*o*-tolyl)-3,4-dihydronaphthalen-2-yl]methyl acetate 19d. In a similar manner as described above alcohol **18d** (0.28 g, 0.90 mmol) afforded acetate **19d** as cream white semi-solid (0.28 g, 88%). IR ν_{max} (cm^{-1}); 1731 (s, C=O stretch), 1605, 1510 (s, C=C stretch); ^1H NMR δ/ppm 7.26–7.21 (3H, m, 3×ArH), 7.07 (1H, d, J=6.6 Hz, ArH), 6.73 (1H, s, ArH), 6.08 (1H, s, ArH), 4.48 (1H, d, J=12.1 Hz, one of CH_2OAc), 4.42 (1H, d, J=12.1 Hz, one of CH_2OAc), 3.88 (3H, s, OCH_3), 3.54 (3H, s, OCH_3), 2.90–2.84 (2H, m, CH_2), 2.45 (2H, dd, J=8.7, 7.4 Hz, CH_2), 2.06 (3H, s, OAc)[a], 2.03 (3H, s, $ArCH_3$)[a], assignments with the same superscript may be interchanged; ^{13}C NMR δ/ppm 19.3 ($ArCH_3$), 20.9 (CH_2), 25.4 (OAc), 27.8 (CH_2), 55.9 (2×OCH_3), 65.5 (CH_2OAc), 109.9 (CH), 110.9 (CH), 125.8 (CH), 127.6 (CH), 127.9 (C), 128.4 (C), 128.7 (C), 129.9 (CH), 130.0 (CH), 136.6 (C), 137.1 (C), 137.3 (C), 147.2 (C), 148.1 (C), 171.1 ($OCOCH_3$); ^{13}C NMR δ/ppm 20.1 (CH_2), 27.7 (CH_2), 125.1 (CH), 125.9 (CH), 126.3 (CH), 126.76 (CH), 126.79 (CH), 127.9 (CH), 128.1 (CH), 128.39 (CH), 128.4 (CH), 128.9 (CH), 130.2 (CH), 132.6 (C), 132.9 (C), 133.5 (C), 135.0 (C), 135.8 (C), 138.1 (C), 153.0 (C), 193.0 (CHO); MS (EI) *m/z* (%): 353 (M+1, 24), 352 (M^+, 40), 351 (10), 292 (53), 277 (100), 245 (33), 201 (27), 115 (27), 43 (44); HRMS calculated for $C_{22}H_{24}O_4$ M^+ 352.1675, found 352.1766.

3.1.31. [1-(3,4,5-Trimethoxyphenyl)naphthalen-2-yl]-methyl acetate 14a. To a solution of acetate **13a** (0.50 g, 1.46 mmol) in dry CH_2Cl_2 (30 mL) was added DDQ (0.85 g, 1.98 mmol) and the mixture immediately turned green. The reaction mixture was then refluxed under nitrogen for 16 h over which time it turned pale green. After allowing to cool to room temperature, the mixture was poured into an aqueous solution of 5% $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2 (3×100 mL). The organic extracts were combined, washed with brine (20 mL), dried ($MgSO_4$), filtered through Celite plug and the excess solvent removed in vacuo. The resultant oil was purified by column

chromatography using 30% ethyl acetate as eluent to obtain the substituted naphthalene **14a** as an orange solid (0.39 g, 78%). Mp = 85–87 °C; IR ν_{max} (cm^{-1}) 1734 (s, C=O stretch), 1582 (s, C=C stretch); ^{1}H NMR δ/ppm 7.89–7.85 (2H, m, 2×ArH), 7.60–7.54 (2H, m, 2×ArH), 7.51–7.38 (2H, m, 2×ArH), 6.55 (2H, s, 2′ and 6′-H), 5.07 (2H, s, CH_2OAc), 3.96 (3H, s, OCH_3), 3.82 (6H, s, 2×OCH_3), 2.07 (3H, s, OAc); ^{13}C NMR δ/ppm 20.9 (OAc), 56.0 (2×OCH_3), 60.9 (OCH_3), 64.7 (CH_2OAc), 107.3 (2′ and 6′-C), 126.0 (2×CH), 126.2 (CH), 126.7 (CH), 127.7 (CH), 127.9 (CH), 130.8 (C), 132.6 (C), 133.0 (C), 133.2 (C), 137.3 (C), 139.3 (C), 153.0 (2×C), 170.6 ($OCOCH_3$); MS (EI) *m/z* (%): 367 (M+1, 66), 366 (M^+, 100), 320 (39), 305 (48), 291 (33), 277 (29), 276 (28), 275 (24), 189 (23), 43 (29); HRMS calculated for $C_{22}H_{22}O_5$ M^+ 366.1467, found 366.1468.

3.1.32. [1-(1-Naphthyl)naphthalen-2-yl]methyl acetate 14b. In a similar manner as described above DDQ (0.21 g, 0.91 mmol) was used to convert acetate **13b** (0.20 g, 0.61 mmol) into **14b**, obtained as a light yellow oil (0.19 g, 95%). IR ν_{max} (cm^{-1}) 1738 (s, C=O stretch), 1593, 1587 (m, C=C stretch); ^{1}H NMR δ/ppm 7.98–7.89 (4H, m, 4×ArH), 7.67–7.58 (2H, m, 2×ArH), 7.47–7.39 (3H, m, 3×ArH), 7.24–7.16 (4H, m, 4×ArH), 4.93 (1H, d, J=12.5 Hz, one of CH_2OAc), 4.84 (1H, d, J=12.5 Hz, one of CH_2OAc), 1.84 (3H, s, OAc); ^{13}C NMR δ/ppm 20.6 (OAc), 64.7 (CH_2OAc), 125.4 (CH), 125.9 (CH), 126.1 (2×CH), 126.2 (CH), 126.3 (CH), 126.4 (CH), 126.8 (CH), 127.8 (CH), 127.9 (CH), 128.1 (CH), 128.2 (CH), 128.2 (CH), 132.0 (C), 132.8 (C), 133.1 (C), 133.2 (C), 133.6 (C), 135.4 (C), 137.4 (C), 171.0 ($OCOCH_3$); MS (EI) *m/z* (%): 327 (M+1, 51), 326 (M^+, 97), 284 (21), 268 (20), 267 (60), 266 (85), 265 (100), 263 (27), 262 (43), 253 (40), 251 (64), 249 (21), 238 (23), 43 (19); HRMS calculated for $C_{23}H_{18}O_2$ M^+ 326.1307, found 326.1307.

3.1.33. (1-Phenylnaphthalen-2-yl)methyl acetate 14c. Similarly acetate **13c** (0.14 g, 0.50 mmol) afforded the arylnaphthalene **14c** as light yellow oil (0.13 g, 93%) using DDQ (0.17 g, 0.75 mmol) in CH_2Cl_2 (15 mL). IR ν_{max} (cm^{-1}) 1738 (s, C=O stretch), 1597 (m, C=C stretch); ^{1}H NMR δ/ppm 7.88–7.83 (2H, m, 2×ArH), 7.57 (1H, d, J=8.5 Hz, ArH), 7.47–7.43 (5H, m, 5×ArH), 7.30–7.15 (3H, m, 3×ArH), 5.00 (2H, s, CH_2OAc), 2.02 (3H, s, OAc); ^{13}C NMR δ/ppm) 20.9 (CH_3), 64.7 (CH_2OH), 125.9 (CH), 126.1 (CH), 126.2 (CH), 126.7 (CH), 127.6 (CH), 127.7 (CH), 127.8 (CH), 128.2 (2×CH), 130.2 (2×CH), 130.8 (C), 132.7 (C), 133.1 (C), 137.8 (C), 139.5 (C), 170.6 ($OCOCH_3$); MS (EI) *m/z* (%): 277 (M+1, 24), 276 (M^+, 100), 234 (23), 215 (78), 202 (34); HRMS calculated for $C_{19}H_{16}O_2$ M^+ 276.1150, found 276.1113.

3.1.34. [1-(*o*-Tolyl)naphthalen-2-yl]methyl acetate 14d. Similarly using DDQ (0.46 g, 1.53 mmol) in CH_2Cl_2 (30 mL) acetate **13d** (0.20 g, 0.51 mmol) afforded the substituted naphthalene **14d** as a light brown crystalline solid (0.20 g, 100%). Mp = 86–90 °C; IR ν_{max} (cm^{-1}) 1736 (s, C=O stretch); ^{1}H NMR δ/ppm 7.88–7.83 (2H, m, 2×ArH), 7.58 (1H, d, J=8.5 Hz, ArH), 7.46–7.41 (1H, m, ArH), 7.35–7.27 (5H, m, 5×ArH), 7.13 (1H, d, J=7.5 Hz, ArH), 4.97 (1H, d, J=12.4 Hz, one of CH_2OAc), 4.95 (1H, d, J=12.4 Hz, one of CH_2OAc), 2.00 (3H, s, $ArCH_3$)[a], 1.91 (3H, s, OAc)[a]; ^{13}C NMR δ/ppm 19.9 ($ArCH_3$)[a], 20.7 ($OCOCH_3$)[a], 64.7 (CH_2OAc), 125.8 (CH), 126.0 (CH), 126.1 (CH), 126.1 (CH), 126.3 (CH), 127.7 (CH), 127.8 (CH), 127.9 (CH), 129.9 (CH), 130.0 (CH), 130.7 (C), 132.2 (C), 133.1 (C), 136.9 (C), 137.1 (C), 138.7 (C), 170.9 ($OCOCH_3$), assignments with the same superscript may be interchanged; MS (EI) *m/z* (%): 291 (M+1, 30), 290 (M^+, 85), 231 (80), 229 (89), 216 (75), 215 (100), 202 (50), 189 (22), 149 (31), 43 (71); HRMS calculated for $C_{20}H_{18}O_2$ M^+ 290.1307, found 290.1307.

3.1.35. [6,7-Dimethoxy-1-(3,4,5-trimethoxyphenyl)-naphthalen-2-yl]methyl acetate 20a. Using DDQ (0.48 g, 2.10 mmol) in CH_2Cl_2 (30 mL) according to the same procedure as outlined above acetate **19a** (0.30 g, 0.70 mmol) gave the naphthalene **20a** as yellow crystalline solid (0.22 g, 74%). Mp = 150–152 °C; IR ν_{max} (cm^{-1}) 1736 (s, C=O stretch), 1625, 1583 (s, C=C stretch); ^{1}H NMR δ/ppm 7.64 (1H, d, J=8.4 Hz, ArH), 7.36 (1H, d, J=8.4 Hz, ArH), 7.08 (1H, s, ArH), 6.76 (1H, s, ArH), 6.48 (2H, s, 2′ and 6′-H), 4.94 (2H, s, CH_2OH), 3.93 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 3.76 (6H, s, 2×OCH_3), 3.67 (3H, s, OCH_3), 1.98 (3H, s, OAc); ^{13}C NMR δ/ppm 20.9 (OAc), 55.7 (OCH_3), 55.8 (OCH_3), 56.1 (2×OCH_3), 60.9 (OCH_3), 64.9 (CH_2OAc), 105.4 (CH), 106.2 (CH), 107.2 (2×CH), 124.8 (CH), 126.2 (CH), 128.2 (C), 129.1 (C), 129.2 (C), 133.6 (C), 137.2 (C), 138.1 (C), 149.5 (C), 149.6 (C), 153.1 (2×C), 170.6 ($OCOCH_3$); MS (EI) *m/z* (%): 427 (M+1, 19), 426 (M^+, 70), 81 (18), 69 (41), 57 (29), 55 (23), 43 (27), 41 (21), 31 (23), 28 (100); HRMS calculated for $C_{24}H_{26}O_7$ M^+ 426.1679, found 426.1678.

3.1.36. [6,7-Dimethoxy-1-(1-naphthyl)naphthalen-2-yl]methyl acetate 20b. Similarly acetate **19b** (0.22 g, 0.57 mmol) gave the substituted arylnaphthalene **20b**, as a yellow solid (0.17 g, 78%) using DDQ (0.13 g, 0.57 mmol) in CH_2Cl_2 (15 mL). Mp = 110–114 °C; IR ν_{max} (cm^{-1}) 1736 (s, C=O stretch), 1624 (m, C=C stretch); ^{1}H NMR δ/ppm 7.85 (2H, t, J=7.8 Hz, 2×ArH), 7.72 (1H, d, J=8.4 Hz, ArH), 7.53–7.32 (4H, m, 4×ArH), 7.18–7.14 (2H, m, 2×ArH), 7.11 (1H, s, ArH), 6.35 (1H, s, ArH), 4.82 (1H, d, J=12.3 Hz, one of CH_2OAc), 4.69 (1H, d, J=12.3 Hz, one of CH_2OAc), 3.91 (3H, s, OCH_3), 3.36 (3H, s, OCH_3), 1.72 (3H, s, OAc); ^{13}C NMR δ/ppm 20.6 (OAc), 55.4 (OCH_3), 55.8 (OCH_3), 64.9 (CH_2OAc), 105.5 (CH), 106.2 (CH), 124.9 (CH), 125.4 (CH), 125.9 (CH), 126.0 (2×CH), 126.4 (CH), 127.8 (CH), 128.2 (CH), 128.2 (CH), 128.8 (C), 129.2 (C), 130.3 (C), 132.6 (C), 133.6 (C), 135.7 (C), 136.1 (C), 149.6 (C), 149.7 (C), 170.5 ($OCOCH_3$); MS (EI) *m/z* (%): 387 (M+1, 25), 386 (M^+, 100), 385 (26), 384 (90), 372 (32), 371 (22), 370 (27), 368 (19), 344 (20), 343 (27), 149 (25); HRMS calculated for $C_{25}H_{22}O_4$ M^+ 386.1518, found 386.1519.

3.1.37. (6,7-Dimethoxy-1-phenylnaphthalen-2-yl)methyl acetate 20c. Similarly dihydronaphthalene **19c** (0.17 g, 0.56 mmol) gave the substituted naphthalene **20c** as a yellow crystalline solid (0.17 g, 100%) using DDQ (0.38 g, 1.66 mmol) in CH_2Cl_2 (20 mL). Mp = 75–78 °C; IR ν_{max} (cm^{-1}) 1736 (s, C=O stretch), 1624 (m, C=C stretch); ^{1}H NMR δ/ppm 7.62 (1H, d, J=8.4 Hz, ArH), 7.36–7.33 (4H, m, 4×ArH), 7.23–7.19 (2H, m, 2×ArH), 7.06 (1H, s, ArH), 6.63 (1H, s, ArH), 4.87 (2H, s, CH_2OAc), 3.90 (3H, s,

OCH_3) 3.59 (3H, s, OCH_3), 1.93 (3H, s, OAc); ^{13}C NMR δ/ppm 20.9 (OAc), 55.4 (OCH_3), 55.8 (OCH_3), 64.9 (CH_2OAc), 105.4 (CH), 106.1 (CH), 124.9 (CH), 126.1 (CH), 127.5 (CH), 128.3 (2×CH), 129.1 (C), 129.1 (C), 129.9 (2×CH), 138.1 (C), 138.3 (C), 149.4 (C), 149.5 (C), 170.6 ($OCOCH_3$), (one quaternary carbon missing); MS (EI) *m/z* (%): 337 (M+1, 59), 336 (M^+, 100), 265 (19), 246 (37), 245 (56), 215 (24), 203 (26), 202 (33), 191 (22), 189 (40), 43 (42); HRMS calculated for $C_{21}H_{20}O_4$ M^+ 336.1362, found 336.1362.

3.1.38. [6,7-Dimethoxy-1-(*o*-tolyl)naphthalen-2-yl]-methyl acetate 20d. In a similar manner as described above dihydronaphthalene **19d** (0.31 g, 0.88 mmol) was converted into naphthalene **20d**, which was obtained as a yellow solid (0.24 g, 78%) using DDQ (0.20 g, 0.88 mmol) in CH_2Cl_2 (20 mL). Mp=91–93 °C; IR ν_{max} (cm^{-1}) 1736 (s, C=O stretch), 1624 (m, C=C stretch); ^1H NMR δ/ppm 7.73 (1H, d, J=8.4 Hz, ArH), 7.45 (1H, d, J=8.4 Hz, ArH), 7.36–7.25 (3H, m, 3×ArH), 7.16 (1H, s, ArH), 7.16–7.14 (1H, s, ArH), 6.53 (1H, s, ArH), 4.93 (1H, d, J=12.2 Hz, one of CH_2OAc), 4.87 (1H, d, J=12.2 Hz, one of CH_2OAc), 4.00 (3H, s, OCH_3), 3.67 (3H, s, OCH_3), 2.00 (3H, s, $ArCH_3$), 1.94 (3H, s, $OCOCH_3$); ^{13}C NMR δ/ppm 19.5 ($ArCH_3$), 20.8 ($OCOCH_3$), 55.5 (OCH_3), 55.8 (OCH_3), 64.9 (CH_2OAc), 104.8 (CH), 106.3 (CH), 124.9 (CH), 125.9 (CH), 126.0 (CH), 127.9 (CH), 129.0 (C), 129.1 (C), 129.9 (2×CH), 136.8 (C), 137.5 (C), 137.6 (C), 149.6 (C), 149.7 (C), 170.7 ($OCOCH_3$), (one quaternary carbon missing); MS (EI) *m/z* (%): 351 (M+1, 44), 350 (M^+, 100), 291 (26), 290 (28), 276 (15), 275 (19), 260 (17), 259 (46), 202 (17), 189 (16), 43 (18); HRMS calculated for $C_{22}H_{22}O_4$ M^+ 350.1518, found 350.1517.

3.1.39. [1-(3,4,5-Trimethoxyphenyl)naphthalen-2-yl]-methanol 21a. To a solution of dihydronaphthalenylmethanol **12a** (0.11 g, 0.34 mmol) in CH_2Cl_2 (15 mL) was added DDQ and a green solution resulted. The resultant mixture was refluxed for 16 h after which time it turned dark brown. The mixture was then allowed to cool to room temperature before being neutralized with 5% $NaHCO_3$ (10 mL) and being extracted with CH_2Cl_2 (3×50 mL). The organic extracts were combined, washed with brine and concentrated under reduced pressure to give a brown oil. The oil was purified by column chromatography using 30% ethylacetate/hexane as an eluent to give **21a** as a yellow solid (0.09 g, 82%). Mp=90–91 °C; IR ν_{max} (cm^{-1}) 3488 (s, broad, OH stretch), 1582 (s, C=C stretch); ^1H NMR δ/ppm 7.90 (1H, d, J=8.4 Hz, ArH), 7.87 (1H, d, J=8.5 Hz, ArH), 7.69 (1H, d, J=8.5 Hz, ArH), 7.54 (1H, d, J=8.3 Hz, ArH), 7.49–7.37 (2H, m, 2×ArH), 6.53 (2H, s, 2′ and 6′-H), 4.61 (2H, s, CH_2OH), 3.95 (3H, s, OCH_3), 3.81 (6H, s, 2×OCH_3); ^{13}C NMR δ/ppm 56.1 (2×OCH_3), 60.9 (OCH_3), 63.4 (CH_2OH), 107.2 (2×CH), 125.7 (2×CH), 126.1 (CH), 126.6 (CH), 127.8 (CH), 128.0 (CH), 132.6 (C), 132.8 (C), 133.6 (C), 135.6 (C), 137.1 (C), 137.9 (C), 153.0 (2×C); MS (EI) *m/z* (%): 325 (M+1, 10), 324 (M^+, 100), 219 (9), 165 (7), 18 (7); HRMS calculated for $C_{20}H_{20}O_4$ M^+ 324.1361, found 324.1351.

3.1.40. [1-(1-Naphthylnaphthalen-2-yl]methanol 21b. In a similar manner to that described above DDQ (0.48 g, 2.09 mmol) was used to convert dihydronaphthalene **12b** (0.40 g, 1.39 mmol) into **21b**, a brown crystalline solid (0.31 g, 79%). Mp=116–119 °C; IR ν_{max} (cm^{-1}) 3386 (s, broad, OH stretch), 1592, 1568 (m, C=C stretch); ^1H NMR δ/ppm 7.89–7.79 (4H, m, 4×ArH), 7.67 (1H, d, J=8.5 Hz, ArH), 7.51–7.46 (1H, m, ArH), 7.38–7.28 (3H, m, 3×ArH), 7.17–7.06 (4H, m, 4×ArH), 4.32 (1H, d, J=13.0 Hz, one of CH_2OH), 4.27 (1H, d, J=13.0 Hz, one of CH_2OH); ^{13}C NMR δ/ppm 63.3 (CH_2OH), 125.4 (CH), 125.7 (2×CH), 125.8 (CH), 126.0 (CH), 126.1 (CH), 126.4 (CH), 126.9 (CH), 127.8 (CH), 127.9 (CH), 128.1 (CH), 128.3 (2×CH), 132.7 (C), 132.8 (C), 133.0 (C), 133.6 (C), 135.5 (C), 135.7 (C), 136.7 (C); MS (EI) *m/z* (%): 285 (M+1, 23), 284 (M^+, 100), 265 (32), 128 (18); HRMS calculated for $C_{21}H_{16}O$ M^+ 284.1201, found 284.1202.

3.1.41. (1-Phenylnaphthalen-2-yl)methanol 21c. Similarly dihydronaphthyl alcohol **12c** (0.26 g, 1.10 mmol) afforded naphthalene **21c** as a light yellow oil (0.20 g, 78%) using DDQ (0.25 g, 1.10 mmol) in CH_2Cl_2 (25 mL). IR ν_{max} (cm^{-1}) 3420 (m, broad, OH stretch), 1596 (s, C=C stretch); ^1H NMR δ/ppm 7.89 (1H, d, J=8.4 Hz, ArH), 7.87 (1H, d, J=8.4 Hz, ArH), 7.68 (1H, d, J=8.5 Hz, ArH), 7.49–7.41 (5H, m, 5×ArH), 7.37–7.34 (3H, m, 3×ArH), 4.56 (2H, s, CH_2OH); ^{13}C NMR δ/ppm 63.3 (CH_2OH), 125.6 (CH), 125.7 (CH), 125.9 (CH), 126.5 (CH), 127.4 (CH), 127.7 (CH), 127.9 (CH), 128.3 (2×CH), 130.0 (2×CH), 132.6 (C), 132.8 (C), 135.5 (C), 137.8 (C), 138.1 (C); MS (EI) *m/z* (%): 235 (M+1, 28), 234 (M^+, 100), 215 (50), 205 (46), 202 (35), 157 (14), 129 (22), 108 (16); HRMS calculated for $C_{17}H_{14}O$ M^+ 234.1045, found 234.1046.

3.1.42. 1-Bromonaphthalene-2-carbaldehyde 22. 1-Bromo-3,4-dihydronaphthalene-2-carbaldehyde (0.45 g, 1.898 mmol), selenium powder (0.30 g, 5.694 mmol) and dimethyl sulfoxide (0.5 mL) were slowly heated to 170 °C. The reaction mixture was heated at the same temperature for 5 min where sputtering took place. After sputtering had ceased, the mixture was allowed to cool to room temperature before being filtered and washed with an excess amount of CH_2Cl_2. 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 eluant to give the desired product **22** as a bright yellow solid (0.31 g, 69%). Mp=106–108 °C; IR ν_{max} (cm^{-1}) 1687 (s, C=O stretch), 1619, 1597 (s, C=C stretch); ^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); ^{13}C NMR δ/ppm 124.1 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 128.4 (CH), 128.5 (C), 129.7 (CH), 131.1 (C), 132.1 (C), 137.2 (C), 192.8 (CHO); MS (EI) *m/z* (%): 235 ($M^{+81}Br$, 99), 233 ($M^{+79}Br$, 100), 206 (28), 127 (35), 126 (89), 63 (15); HRMS calculated for $C_{11}H_7O^{79}Br$ M^+ 233.9680, found 233.9708.

3.1.43. 6-Methoxy-1-bromo-3,4-dihydronaphthalene-2-carbaldehyde 23. Dry DMF (8.0 mL, 102.1 mmol) in dry CH_2Cl_2 (60.0 mL) was cooled to 0 °C and phosphorus tribromide (8.4 mL, 88.52 mmol) was added drop-wise. The mixture was stirred at 0 °C for 1 h and a cream white suspension formed. A solution of 6,7-dimethoxy-α-tetralone (6.00 g, 34.05 mmol) in dry CH_2Cl_2 (50 mL) was added and the mixture was heated under reflux for 16 h. After cooling to 0 °C, aqueous $NaHCO_3$ was added slowly until the

effervescence had subsided. Extraction of the organic material into CH_2Cl_2 (3×100 mL) was followed by drying the organic layer ($MgSO_4$). The solution was filtered through a Celite plug and evaporation of the excess solvent resulted into brown oil. Column chromatography eluting with 30% ethyl acetate/hexane gave the product **23** as a yellow solid (7.79 g, 86%). Mp=61–62 °C; IR ν_{max} (cm^{-1}) 1659 (s, C=O stretch), 1606, 1586, 1552 (s, C=C stretch); ^{1}H NMR δ/ppm 10.20 (1H, s, CHO), 7.83 (1H, d, J=8.7 Hz, 8-H), 6.82 (1H, dd, J=8.7, 2.6 Hz, 7-H), 6.72 (1H, d, J=2.5 Hz, 5-H), 3.86 (3H, s, OMe), 2.80 (2H, dd, J=8.4, 7.2 Hz, CH_2), 2.60 (2H, dd, J=8.7, 6.0 Hz, CH_2); ^{13}C NMR δ/ppm 22.7 (CH_2), 27.7 (CH_2), 55.4 (OCH_3), 112.1 (CH), 113.3 (CH), 125.9 (C), 130.7 (CH), 132.1 (C), 139.0 (C), 141.2 (C), 162.0 (C), 192.9 (CHO); MS (EI) m/z (%): 267 (M^{+81}Br, 80), 265 (M^{+79}Br, 83), 236 (28), 187 (46), 159 (97), 158 (100), 144 (59), 128 (41), 115 (81); HRMS calculated for $C_{12}H_{11}O_2^{79}Br$ M^+ 265.9942, found 265.9936.

3.1.44. 6-Methoxy-1-bromonaphthalene-2-carbaldehyde 24. Using the same procedure as described above, 6-methoxy-1-bromo-3,4-dihydronaphthalene-2-carbaldehyde **23** (3.98 g, 14.90 mmol) was converted into 7-methoxy-1-bromonaphthalene-2-carbaldehyde **24** in the presence of selenium powder (2.30 g, 29.80 mmol) and dimethyl sulfoxide (2 mL). The product was obtained as a light brown solid (2.85 g, 72%). Mp=123–126 °C; IR ν_{max} (cm^{-1}) 1682 (s, C=O stretch), 1620 (s, C=C stretch); ^{1}H NMR δ/ppm 10.58 (1H, s, CHO), 8.36 (1H, d, J=9.4 Hz, 8-H), 7.87 (1H, d, J=8.7 Hz, 3- or 4-H), 7.68 (1H, d, J=8.7 Hz, 3- or 4-H), 7.28 (1H, dd, J=9.4, 2.5 Hz, 7-H), 7.11 (1H, d, J=2.5 Hz, 5-H), 3.96 (3H, s, OMe); ^{13}C NMR δ/ppm 55.6 (OCH_3), 106.4 (CH), 120.7 (CH), 124.7 (CH), 126.9 (CH) 127.2 (C), 129.4 (C), 129.8 (CH), 130.4 (C), 139.0 (C), 160.6 (C), 192.5 (CHO); MS (EI) m/z (%): 265 (M^{+81}Br, 47), 263 (M^{+79}Br, 46), 261 (100), 202 (17), 156 (16), 113 (22), 73 (17); HRMS calculated for $C_{12}H_9O_2^{79}Br$ M^+ 263.9786, found 263.9750.

3.1.45. 1-(3,4,5-Trimethoxyphenyl)-naphthalene-2-carbaldehyde 25a. To [$Pd(PPh_3)_4$] (0.14 g, 0.127 mmol) was added deoxygenated solutions of **22** (0.30 g, 1.276 mmol) in DME (10 mL) and 3,4,5-trimethoxy-1-phenylboronic acid **10a** (0.38 g, 1.914 mmol) in ethanol (5 mL). This was followed by a deoxygenated solution of aqueous sodium carbonate (1.06 g, 10.85 mmol in 5.0 mL water). The resultant mixture was refluxed 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 (10 mL) and the organic material extracted with CH_2Cl_2 (3×25 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 subsequent oil was purified by column chromatography using 30% ethyl acetate/hexane as the eluent to afford the desired product **25a** as a yellow solid (0.40 g, 94%). Mp=89–92 °C; IR ν_{max} (cm^{-1}) 1694 (s, C=O stretch), 1626, 1597 (s, C=C stretch); ^{1}H NMR δ/ppm 9.96 (1H, s, CHO), 8.05 (1H, d, J=8.6 Hz, ArH), 7.93 (2H, d, J=8.4 Hz, 2×ArH), 7.76 (1H, d, J=8.2 Hz, ArH), 7.65–7.61 (1H, m, ArH), 7.52–7.48 (1H, m, ArH), 6.63 (2H, s, 2′ and 6′-H), 3.85 (9H, s, 3×OCH_3); ^{13}C NMR δ/ppm 56.2 (2×OCH_3), 60.8 (OCH_3), 108.2 (2×CH), 121.9 (CH), 123.5 (C), 126.9 (CH), 127.6 (CH), 128.1 (CH), 128.3 (CH), 128.7 (CH), 130.6 (C), 131.1 (C), 132.4 (C), 136.0 (C), 146.3 (C), 152.9 (2×C), 192.7 (CHO); MS (EI) m/z (%): 323 (M+1, 22), 322 (M^+, 100), 279 (63), 219 (15), 165 (24); HRMS calculated for $C_{20}H_{18}O_4$ M^+ 322.1205, found 322.1186.

3.1.46. 1-(1-Naphthyl)-naphthalene-2-carbaldehyde 25b. Using the same procedure as described above, **22** (0.30 g, 1.276 mmol) was reacted with 1-naphthylboronic acid **10b** (0.31 g, 1.914 mmol) under Suzuki coupling conditions to give **25b** as a yellow crystalline solid (0.32 g, 89%). Mp=112–114 °C; IR ν_{max} (cm^{-1}) 1687 (s, C=O stretch), 1619 and 1593 (m, C=C stretch); ^{1}H NMR δ/ppm 9.68 (1H, s, CHO), 8.15 (1H, d, J=8.6 Hz, ArH), 8.02–7.92 (4H, m, 4×ArH), 7.62–7.54 (2H, m, 2×ArH), 7.49–7.44 (2H, m, 2×ArH), 7.36 (1H, d, J=8.1 Hz, ArH), 7.31–7.25 (2H, m, 2×ArH), 7.20 (1H, d, J=8.4 Hz, ArH); ^{13}C NMR δ/ppm 122.1 (CH), 125.0 (CH), 126.2 (CH), 126.3 (CH), 126.8 (CH), 126.9 (CH), 127.7 (CH), 128.2 (CH), 128.3 (CH), 128.6 (CH), 128.8 (CH), 128.9 (CH), 129.1 (CH), 132.1 (C), 132.9 (C), 133.0 (C), 133.3 (C), 133.5 (C), 136.1 (C), 144.8 (C), 192.4 (CHO); MS (EI) m/z (%): 283 (M+1, 23), 282 (M^+, 100), 281 (81), 265 (26), 253 (86), 252 (97), 126 (35), 113 (15); HRMS calculated for $C_{21}H_{14}O$ M^+ 282.1045, found 282.1035.

3.1.47. 1-Phenylnaphthalene-2-carbaldehyde 25c. Substituted naphthalene **25c** was obtained as a light yellow oil (0.26 g, 87%) from the Suzuki coupling of bromonaphthalene carbaldehyde **22** (0.30 g, 1.276 mmol) and 1-phenylboronic acid (0.22 g, 1.914 mmol) using the same procedure as outlined above. ^{1}H NMR δ/ppm 9.89 (1H, s, CHO), 8.06 (1H, d, J=8.6 Hz, ArH), 7.92 (2H, d, J=9.7 Hz, 2×ArH) 7.67–7.58 (2H, m, 2×ArH), 7.52–7.51 (3H, m, 3×ArH), 7.47–7.31 (3H, m, 3×ArH); ^{13}C NMR δ/ppm 122.1 (CH), 126.8 (CH), 127.7 (CH), 128.2 (CH), 128.2 (2×CH), 128.3 (CH), 128.4 (CH), 128.7 (CH), 130.9 (2×CH), 131.2 (C), 132.4 (C), 135.2 (C), 136.1 (C), 146.5 (C), 192.6 (CHO); MS (EI) m/z (%): 233 (M+1, 18), 232 (M^+, 100), 202 (64), 101 (18); HRMS calculated for $C_{17}H_{12}O$ M^+ 232.0888, found 232.0865.

3.1.48. 1-(*o*-Tolyl)naphthalene-2-carbaldehyde 25d. Using the same procedure as outlined above, tolylnaphthalene carbaldehyde **25d** was synthesized as a yellow crystalline solid (0.29 g, 94%) from the Suzuki coupling of carbaldehyde **22** (0.30 g, 1.276 mmol) and *o*-tolylboronic acid **10d**. Mp=60–61 °C; IR ν_{max} (cm^{-1}) 1687 (s, C=O stretch), 1626, 1618, 1596 (s, C=C stretch); ^{1}H NMR δ/ppm 9.82 (1H, s, CHO), 8.07 (1H, d, J=8.6 Hz, ArH), 7.93 (2H, d, J=9.1 Hz, 2×ArH), 7.64–7.59 (1H, m, ArH), 7.48–7.31 (5H, m, 5×ArH), 7.24 (1H, d, J=6.6 Hz, ArH), 1.96 (3H, s, $ArCH_3$); ^{13}C NMR δ/ppm 20.0 ($ArCH_3$), 122.0 (CH), 125.7 (CH), 126.9 (CH), 127.2 (CH), 128.3 (CH), 128.4 (CH), 128.6 (CH), 128.8 (CH) 130.1 (CH), 130.9 (CH), 131.0 (C), 132.1 (C), 134.8 (C), 136.2 (C), 137.3 (C), 146.3 (C), 192.6 (CHO); MS (EI) m/z (%): 246 (M^+, 100), 231 (38), 218 (88), 202 (43), 130 (39), 99 (10), 68 (74); HRMS calculated for $C_{18}H_{14}O$ M^+ 246.1045, found 246.1049.

3.1.49. 1-(3,4,5-Trimethoxyphenyl)-6-methoxynaphthalene-2-carbaldehyde 26a. In the same way as outlined above, 7-methoxy-1-bromonaphthalene **24** (0.30 g, 1.132 mmol) and 3,4,5-trimethoxy-1-phenylboronic acid **10a** (0.36 g, 1.697 mmol) were subjected to Suzuki coupling reaction conditions to give the desired product **26a**, as a light yellow crystalline solid (0.32 g, 80%). Mp = 132–134 °C; IR ν_{max} (cm^{-1}) 1690 (s, C=O stretch), 1623, 1599 (s, C=C stretch); ^{1}H NMR δ/ppm 9.89 (1H, s, CHO), 8.02 (1H, d, J=8.6 Hz, 4-H), 7.80 (1H, d, J=8.6 Hz, 3-H), 7.65 (1H, d, J=9.2 Hz, 8-H), 7.21 (1H, d, J=2.5 Hz, 5-H), 7.13 (1H, dd, J=9.2, 2.5 Hz, 7-H), 6.61 (2H, s, 2′ and 6′-H), 3.96 (6H, s, 2×OCH_3), 3.84 (6H, s, 2×OCH_3); ^{13}C NMR δ/ppm 55.4 (OCH_3), 56.2 (2×OCH_3), 61.0 (OCH_3), 106.3 (CH), 108.2 (2×CH), 119.5 (CH), 122.7 (CH), 127.0 (CH), 127.4 (C), 129.3 (CH), 129.5 (C), 130.8 (C), 137.7 (C), 137.9 (C), 146.4 (C), 152.9 (2×C), 159.9 (C), 192.4 (CHO); MS (EI) m/z (%): 352 (M^+, 57), 309 (23), 304 (25), 246 (100), 231 (36), 215 (37), 202 (35), 185 (30), 115 (19); HRMS calculated for $C_{21}H_{20}O_5$ M^+ 352.1311, found 352.1341.

3.1.50. 6-Methoxy-1-(1-naphthyl)naphthalene-2-carbaldehyde 26b. Using the same procedure as described above, bromonaphthalene carbaldehyde **24** (0.30 g, 1.132 mmol) and 1-naphthylboronic acid **10b** (0.29 g, 1.697 mmol) were coupled to give biaryl **26b**, as a yellow solid (0.26 g, 74%). Mp = 181–184 °C; IR ν_{max} (cm^{-1}) 1676 (s, C=O stretch), 1619 (m, C=C stretch); ^{1}H NMR δ/ppm 9.61 (1H, s, CHO), 8.12 (1H, d, J=8.6 Hz, ArH), 8.01 (1H, d, J=8.3 Hz, ArH), 7.96 (1H, d, J=8.3 Hz, ArH), 7.89 (1H, d, J=8.7 Hz, ArH), 7.63–7.58 (1H, m, ArH), 7.50–7.46 (2H, m, 2×ArH), 7.32–7.19 (4H, m, 4×ArH), 6.96 (1H, dd, J=9.2, 2.6 Hz, 7-H), 3.93 (3H, s, OCH_3); ^{13}C NMR δ/ppm 55.4 (OCH_3), 106.3 (CH), 119.5 (CH), 122.8 (CH), 124.9 (CH), 126.1 (CH), 126.2 (CH), 126.7 (CH), 127.3 (CH), 128.1 (C), 128.2 (CH), 128.8 (CH), 129.0 (CH), 129.4 (CH), 130.4 (C), 133.0 (C), 133.2 (C), 133.4 (C), 138.0 (C), 144.9 (C), 159.9 (C), 192.2 (CHO); MS (EI) m/z (%): 313 (M+1, 23), 312 (M^+, 100), 239 (33), 218 (43), 144 (13), 130 (19), 68 (33); HRMS calculated for $C_{22}H_{16}O_2$ M^+ 312.1150, found 312.1174.

3.1.51. 6-Methoxy-1-phenylnaphthalene-2-carbaldehyde 26c. In the same manner as detailed above, carbaldehyde **26c** was synthesized as a thick yellow oil (0.27 g, 90%) from the Suzuki coupling of carbaldehyde **24** (0.30 g, 1.132 mmol) and phenylboronic **10c** (0.20 g, 1.697 mmol). IR ν_{max} (cm^{-1}) 1681 (s, C=O stretch), 1616, 1573 (s, C=C stretch); ^{1}H NMR δ/ppm 9.81 (1H, s, CHO), 8.04 (1H, d, J=8.7 Hz, 4-H), 7.79 (1H, d, J=8.7 Hz, 3-H) 7.51–7.49 (4H, m, 4×ArH), 7.38–7.35 (2H, m, 2×ArH), 7.21–7.19 (1H, m, ArH), 7.08 (1H, dd, J=9.3, 2.6 Hz, 7-H), 6.92–6.83 (1H, m, ArH), 3.93 (3H, s, OCH_3); ^{13}C NMR δ/ppm 55.4 (OCH_3), 106.3 (CH), 119.3 (CH), 120.3 (C), 122.8 (CH), 127.0 (CH), 127.4 (C), 128.1 (2×CH) 129.3 (CH), 129.5 (CH), 130.8 (2×CH), 135.2 (C), 137.9 (C), 146.7 (C), 159.9 (C), 192.5 (CHO); MS (EI) m/z (%): 263 (M+1, 33), 262 (M^+, 40), 218 (100), 130 (61), 99 (11), 68 (82); HRMS calculated for $C_{18}H_{14}O_2$ M^+ 262.0993, found 262.0991.

3.1.52. 6-Methoxy-1-(*o*-tolyl)naphthalene-2-carbaldehyde 26d. 1-Bromo-7-methoxynaphthalene-2-carbaldehyde **24** (0.30 g, 1.132 mmol) and *o*-tolylboronic **10d** (0.22 g, 1.697 mmol) were coupled in the same manner as described above to give the desired product **26d**, as a light yellow oil (0.22 g, 71%). IR ν_{max} (cm^{-1}) 1674 (s, C=O stretch), 1618 (s, C=C stretch); ^{1}H NMR δ/ppm 9.74 (1H, s, CHO), 8.04 (1H, d, J=8.6 Hz, 4-H), 7.80 (1H, d, J=8.6 Hz, 3-H), 7.44–7.29 (4H, m, 4×ArH), 7.25–7.21 (2H, m, 2×ArH), 7.07 (1H, dd, J=9.2, 2.5 Hz, 7-H), 3.95 (3H, s, OCH_3), 1.96 (3H, s, $ArCH_3$); ^{13}C NMR δ/ppm 19.9 ($ArCH_3$), 55.4 (OCH_3), 106.4 (CH), 119.4 (CH), 122.8 (CH), 125.6 (CH), 126.9 (CH), 128.5 (CH), 128.9 (CH) 129.3 (C), 130.0 (CH), 130.7 (CH), 130.9 (C), 134.9 (C), 137.2 (C), 138.0 (C), 146.3 (C), 160.0 (C), 192.3 (CHO); MS (EI) m/z (%): 277 (M+1, 21), 276 (M^+, 100), 261 (32), 245 (16), 215 (22), 202 (24); HRMS calculated for $C_{19}H_{16}O_2$ M^+ 276.1150, found 276.1156.

3.1.53. [1-(3,4,5-Trimethoxyphenyl)naphthalen-2-yl]-methanol 21a. To a solution of carbaldehyde **25a** (0.17 g, 0.527 mmol) in ethanol (5 mL) was added $NaBH_4$ (0.03 g, 0.659 mmol). The reaction mixture was stirred at room temperature for 5 min after which time it turned cream white. The mixture was quenched with water (5 mL) before being extracted with CH_2Cl_2 (3×15 mL). The organic extracts were combined, dried ($MgSO_4$), and then filtered through a Celite plug and concentrated in vacuo. The subsequent colourless oil was purified by column chromatography using 30% ethyl acetate/hexane as eluent to afford **21a** as light yellow crystalline solid (0.14 g, 82%) with identical spectroscopic data to that described previously.

3.1.54. [1-(1-Naphthyl)naphthalen-2-yl]methanol 21b. In the same manner as outlined above, carbaldehyde **25b** (0.30 g, 1.062 mmol) was converted to a biaryl alcohol **21b**, as a brown solid (0.28 g, 93%) using sodium borohydride (0.05 g, 1.328 mmol) with identical spectroscopic data to that described previously.

3.1.55. (1-Phenylnaphthalen-2-yl)methanol 21c. Using sodium borohydride (0.05 g, 1.238 mmol) in the manner as outlined above, phenylnaphthyl carbaldehyde **25c** (0.23 g, 0.990 mmol) was converted into alcohol **21c**, as a yellow sticky oil (0.21 g, 91%) with identical spectroscopic data to that described previously.

3.1.56. [1-(*o*-Tolyl)naphthalen-2-yl]methanol 21d. The desired product **21d**, was synthesized as a thick yellow oil (0.19 g, 95%) from carbaldehyde **25d** (0.20 g, 0.812 mmol) using sodium borohydride (0.04 g, 1.015 mmol) in the same way as described above. IR ν_{max} (cm^{-1}) 3408 (s, broad, OH stretch), 1621, 1596, 1572 (s, C=C stretch); ^{1}H NMR δ/ppm 7.90 (1H, d, J=8.4 Hz, ArH), 7.87 (1H, d, J=7.5 Hz, ArH), 7.70 (1H, d, J=8.4 Hz, ArH), 7.48–7.43 (1H, m, ArH), 7.35–7.24 (5H, m, 5×ArH), 7.14 (1H, d, J=7.3 Hz, ArH), 4.48 (2H, s, CH_2OH), 1.91 (3H, s, $ArCH_3$); ^{13}C NMR δ/ppm 19.7 ($ArCH_3$), 63.4 (CH_2OH), 125.7 (2×CH), 125.9 (CH), 126.0 (CH), 126.1 (CH), 127.9 (2×CH), 128.0 (CH), 130.0 (CH), 130.1 (CH), 132.2 (C), 132.9 (C), 135.4 (C), 136.9 (C), 137.1 (C), 137.6 (C); MS (EI) m/z (%): 248 (M^+, 60), 230 (100), 218 (20), 215 (69), 202 (34), 82 (19);

HRMS calculated for $C_{18}H_{16}O$ M^+ 248.1201, found 248.1248.

3.1.57. [6-Methoxy-1-(3,4,5-trimethoxyphenyl)naphthalen-2-yl]methanol 27a. Using the same procedure as described above, carbaldehyde **26a** (0.18 g, 0.511 mmol) in ethanol (5 mL) was converted into the alcohol **27a** produced as white flakes (0.16 g, 89%) using sodium borohydride (0.02 g, 0.638 mmol). Mp=163–164 °C; IR ν_{max} (cm^{-1}), 1690 (s, C=O stretch), 1623 (s, C=C stretch); ^1H NMR δ/ppm 7.79 (1H, d, J=8.5 Hz, 4-H), 7.63 (1H, d, J=8.5 Hz, 3-H), 7.44 (1H, d, J=9.2 Hz, 8-H), 7.17 (1H, d, J=2.5 Hz, 5-H), 7.06 (1H, dd, J=9.2, 2.6 Hz, 7-H), 6.52 (2H, s, 2′ and 6′-H), 4.58 (2H, s, CH_2OH), 3.95 (3H, s, OCH_3), 3.92 (3H, s, OCH_3), 3.82 (6H, s, 2×OCH_3); ^{13}C NMR δ/ppm 55.3 (OCH_3), 56.1 (2×OCH_3), 60.9 (OCH_3), 63.4 (CH_2OH), 105.7 (CH), 107.1 (2×CH), 118.7 (CH), 126.5 (CH), 126.8 (CH), 128.0 (C), 128.2 (CH), 133.3 (C), 133.7 (C), 134.1 (C), 137.1 (C), 138.0 (C), 153.1 (2×C), 157.5 (C); MS (EI) m/z (%): 354 (M^+, 42), 304 (100), 264 (23), 213 (35), 175 (21), 152 (11); HRMS calculated for $C_{21}H_{22}O5$ M^+ 354.1467, found 354.1448.

3.1.58. [6-Methoxy-1-(1-naphthyl)naphthalen-2-yl]-methanol 27b. Sodium borohydride (0.03 g, 0.880 mmol) was used as explained above to convert carbaldehyde **26b** (0.22 g, 0.704 mmol) in ethanol (8 mL) into the alcohol **27b**, as a light brown solid (0.21 g, 95%). Mp=142–143 °C; IR ν_{max} (cm^{-1}) 3366 (s, broad, OH stretch), 1625, 1598, 1579 (m, C=C stretch); ^1H NMR δ/ppm 7.96–7.92 (2H, m, 2×ArH), 7.87 (1H, d, J=8.5 Hz, ArH), 7.73 (1H, d, J=8.5 Hz, ArH), 7.59 (1H, d, J=7.1 Hz, ArH), 7.57 (1H, d, J=8.2 Hz, ArH), 7.48–7.43 (1H, m, ArH), 7.39 (1H, d, J=7.0 Hz, ArH), 7.28–7.18 (3H, m, 3×ArH), 7.07 (1H, d, J=9.2 Hz, 8-H), 6.90 (1H, dd, J=9.2, 2.5 Hz, 7-H), 4.37 (2H, s, CH_2OH), 3.91 (3H, s, OCH_3); ^{13}C NMR δ/ppm 55.3 (OCH_3), 63.4 (CH_2OH), 105.8 (CH), 118.7 (CH), 125.4 (CH) 125.8 (CH), 126.0 (CH), 126.4 (CH), 126.6 (CH), 127.1 (CH), 127.8 (CH), 128.0 (CH), 128.2 (CH), 128.3 (CH), 128.5 (C), 132.8 (C), 133.6 (C), 134.2 (C), 134.5 (C), 135.8 (C), 135.9 (C), 157.5 (C); MS (EI) m/z (%): 315 (M+1, 24), 314 (M^+, 100), 252 (16), 239 (17), 218 (39), 130 (14), 68 (28); HRMS calculated for $C_{22}H_{18}O_2$ M^+ 314.1307, found 314.1352.

3.1.59. (6-Methoxy-1-phenylnaphthalen-2-yl)methanol 27c. Carbaldehyde **26c** (0.18 g, 0.686 mmol) in ethanol (5 mL) was converted into the alcohol **27c**, as a thick yellow oil (0.18 g, 100%) using sodium borohydride (0.03 g, 0.858 mmol) in the same manner as outlined above. IR ν_{max} (cm^{-1}) 3385 (s, broad, OH stretch), 1625, 1598, 1575 (s, C=C stretch); ^1H NMR δ/ppm 7.70 (1H, d, J=8.4 Hz, 4-H), 7.55 (1H, d, J=8.4 Hz, 3-H), 7.46–7.36 (4H, m, 4×ArH), 7.24–7.09 (4H, m, 4×ArH), 6.94 (1H, dd, J=9.2, 2.5 Hz, 7-H), 4.44 (2H, s, CH_2OH), 3.84 (3H, s, OCH_3); ^{13}C NMR δ/ppm 55.3 (OCH_3), 63.4 (CH_2OH), 105.8 (CH), 118.6 (CH), 126.6 (CH), 126.8 (CH), 127.4 (CH), 128.2 (CH), 128.3 (2×CH), 130.1 (2×CH), 130.9 (C), 133.4 (C), 134.2 (C), 138.1 (C), 138.2 (C), 157.5 (C); MS (EI) m/z (%): 264 (M^+, 100), 235 (26), 202 (24), 159 (12), 94 (32), 82 (85); HRMS calculated for $C_{18}H_{16}O_2$ M^+ 264.1150, found 264.1146.

3.1.60. [6-Methoxy-1-(*o*-tolyl)naphthalen-2-yl]methanol 27d. In the same way as described above, sodium borohydride (0.02 g, 0.678 mmol) was used to convert carbaldehyde **26d** (0.15 g, 0.543 mmol) in ethanol (5 mL) into the alcohol **27d**, produced as a light yellow oil (0.14 g, 93%). IR ν_{max} (cm^{-1}) 3405 (s, broad, OH stretch), 1625, 1598, 1576 (s, C=C stretch); ^1H NMR δ/ppm 7.78 (1H, d, J=8.4 Hz, 4-H), 7.64 (1H, d, J=8.4 Hz, 3-H), 7.36–7.24 (3H, m, 3×ArH), 7.18–7.12 (3H, m, 3×ArH), 7.00 (1H, dd, J=9.2, 2.6 Hz, 7-H), 4.45 (2H, s, CH_2OH), 3.91 (3H, s, OCH_3), 1.91 (3H, s, $ArCH_3$); ^{13}C NMR δ/ppm 19.7 ($ArCH_3$), 55.3 (OCH_3), 63.3 (CH_2OH), 105.9 (CH), 118.7 (CH), 125.8 (CH), 126.5 (CH), 126.7 (CH), 127.7 (CH), 127.8 (CH), 129.9 (CH), 130.0 (CH), 133.2 (C), 134.2 (C), 136.9 (C), 137.2 (C), 137.7 (C), 157.5 (C) (one quaternary carbon missing); MS (EI) m/z (%): 278 (M^+, 19), 260 (14), 129 (15), 108 (43), 84 (63), 82 (100), 46 (20); HRMS calculated for $C_{19}H_{18}O_2$ M^+ 278.1306, found 278.1297.

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