

Acid catalysed reaction of indanones, tetralones and benzosuberone with neopentyl glycol and other alkanediols under forced conditions

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Upon reaction with an excess of 2,2-dimethylpropane-1,3-diol (neopentyl glycol, NPG) under acid catalysis, indanones and tetralones yield indenenes and dihydronaphthalenes, respectively. The reaction can also be carried out with butane-1,3-diol.

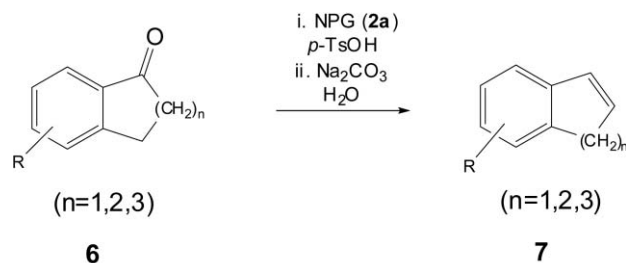
Keywords: indanones, tetralones, indenenes, 1,2-dihydronaphthalenes, alkene synthesis

The protection of the keto function as a cyclic acetal through its reaction with glycerols is widely used.¹ 2,2-Dimethylpropane-1,3-diol (neopentyl glycol, NPG, **2a**) is a typical glycol which is used in such a transformation, and where 5,5-dimethyl-1,3-dioxanes^{2,3} are obtained as the protected compounds. In the preparation of acetals derived from steroidal ketones with neopentyl glycol,^{4–6} under forced, acidic conditions, and when using long reaction times, 17-*O*-[2',2'-dimethyl-2'-(5'',5''-dimethyl-1'',3''-dioxanyl)ethyl] substituted estra-3,17 β -diols are produced,⁷ in which the original 17-keto function has undergone a formal reduction (Scheme 1). Vuligonda *et al.*⁸ have also described an acid catalysed conversion of a number of α -tetralones to dihydronaphthalenes, where pentane-2,4-diol (**2c**) was used as reactant, again under long reaction times. Both reactions were explained by a reductive hydride transfer to the ketone as key mechanistic step.^{7,8} Consequently, we have studied the reaction of benzylic ketones with neopentyl glycol and other alkanediols and have found that α -benzocycloalkenones in general form benzocycloalkadienes, when they are subjected to reactions with neopentyl glycol and with butane-1,3-diol using acid catalysis under forced conditions. The transformation is the subject of this communication.

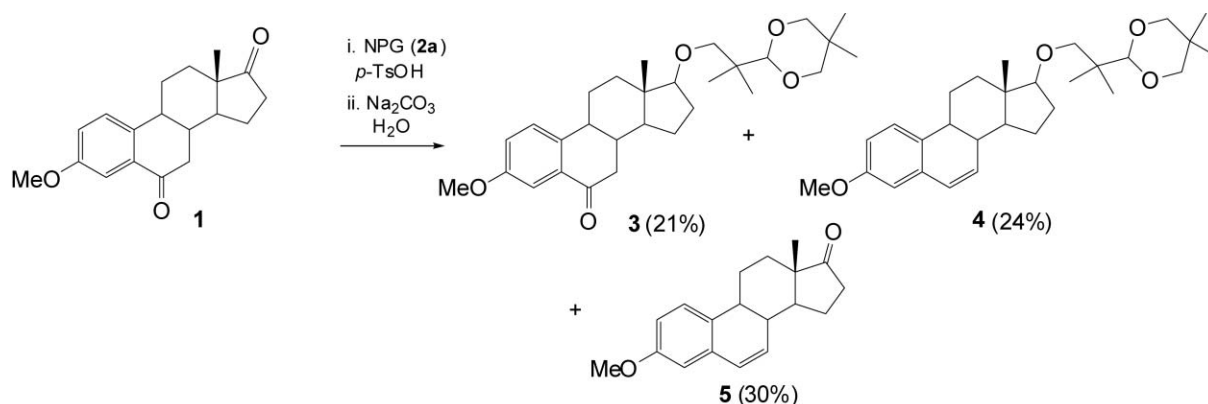
Reaction of estrones with neopentyl glycol (NPG, **2a**) in refluxing benzene with the azeotropic removal of the water which was formed gives the corresponding acetals in good yield within 30 min. However, when 6-keto estrone **1** was heated with an excess amount of neopentyl glycol in refluxing benzene or in toluene using long reaction times, 17-*O*-[2',2'-dimethyl-2'-(5'',5''-dimethyl-1'',3''-dioxanyl)ethyl] steroidal ethers **4** and **5** as well as estra-1,3,5(10),6-tetraene (**6**) were formed (Scheme 1, see also ref. 7). The occurrence of

estra-1,3,5(10),6-tetraenes **5** and **6** indicate that a neopentyl glycol reacts with a benzylic ketone in a similar manner to that which had been reported by Vuligonda *et al.* with pentane-1,3-diol (**2c**).⁸

In general, we have found that replacing the quaternary sp³-hybridised carbon adjacent to the carbonyl group as in the steroidal series with an sp²-hybridised carbon as in the case of α -benzocycloalkenones alters the course of the reaction and leads, under forced conditions, to benzocycloalkadienes instead of to the [2',2'-dimethyl-2'-(5'',5''-dimethyl-1'',3''-dioxanyl)ethyl]-substituted derivatives (*e.g.*, to **3**) (Scheme 2, Table 1). Mechanistically, it is possible, however, that in both cases there is an initial hydride shift from the alcohol component to the keto functionality (see below and Scheme 3). The reaction of 1-tetralones **6f–i** with NPG with *p*-TsOH catalysis has been found to give 1,2-dihydronaphthalenes **7f–i**. Indan-1-ones **6a–e** reacted comparably well to indenenes **7a–e** whilst benzosuberone (**6j**) gave benzocycloheptadiene **7j** (Table 1).

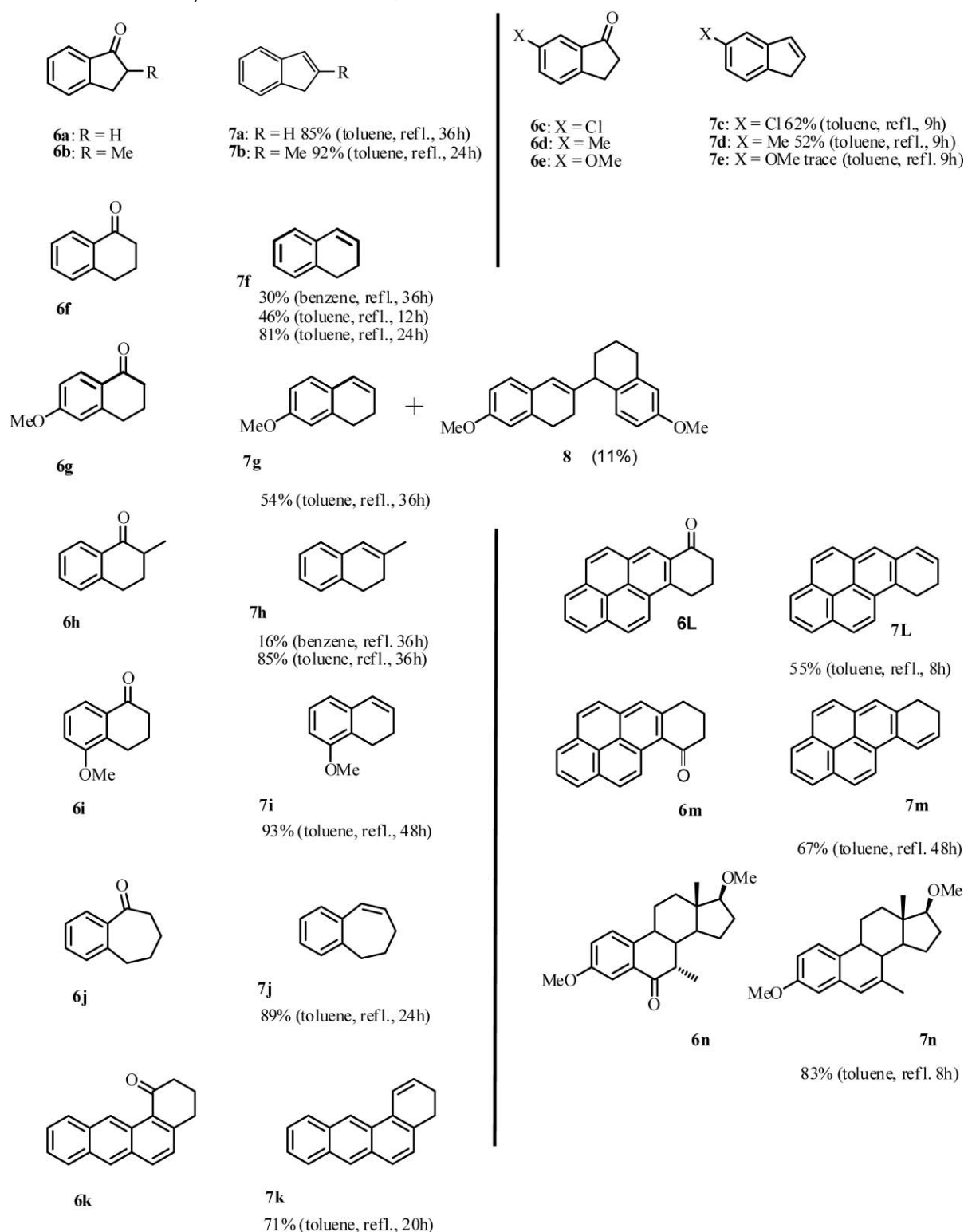


Scheme 2 Reaction of a benzocycloalkenone with neopentyl glycol under forced conditions.



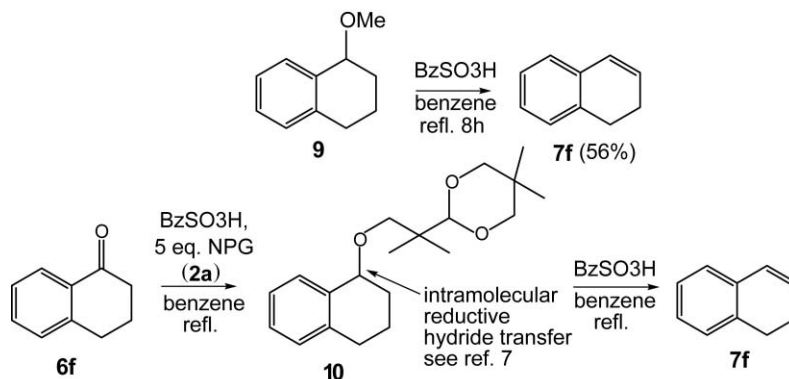
Scheme 1 Reaction of a 6-ketoestrone with neopentyl glycol under forced conditions.⁷

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Table 1 Reaction of benzocycloalkanones with NPG (**2a**) under forced acidic conditions

A possible mechanism for the reaction can be formulated with [2',2'-dimethyl-2'-(5'',5''-dimethyl-1'',3''-dioxanyl)ethyl]tetrahydronaphthols **10** as intermediates, where a subsequent acid catalysed elimination reaction would lead to the products (Scheme 3). It must be stated, however, that 1-[2',2'-dimethyl-2'-(5'',5''-dimethyl-1'',3''-dioxanyl)ethyl]-1,2,3,4-tetrahydronaphthol **10** could not be isolated under the reaction conditions, while the reaction proceeded to give the corresponding olefins in good yield, and thus the potential intermediacy of these compounds could not be confirmed. Only in the case of the 5-methoxyindanone (**6e**), which gave the

corresponding 5-methoxyindene (**7e**) in very poor yield, was the ether-acetal detected by ¹H NMR analysis of the reaction mixture. That a benzyl cation is involved in the final step of the transformation may be noted by the isolation of side products, such as dimer **8**, which may be formed by reaction of the stabilised benzyl cation with dihydronaphthalene (**7g**). That an 1-alkoxy-1,2,3,4-tetrahydronaphthalene is easily converted to a 1,2-dehydronaphthalene under the conditions was shown by the acid catalysed reaction of 1-methoxy-1,2,3,4-tetrahydronaphthalene (**9**) to give 1,2-dihydronaphthalene (**7f**).



Scheme 3 Tentative mechanism for the formation of dihydronaphthalene (**7f**) from 1-tetralone via ether-acetal (**10**).

Not only is the electronic character of the aromatic ring of the α -benzocycloalkenone important for the outcome of the overall reaction, where overt stabilisation of a benzylic cation intermediate by an electron rich benzo group leads to dimeric side-products, but also the nature of the substituent at the β -position is important. Here, an alkyl substituent such as a methyl group has been found to be advantageous. Suitable substrates include the higher-annelated systems **6k–m**. However, the acid-catalysed transformation of benzothiophenone **11** does not give the corresponding acetal. In this case, two alkoxybenzo[*b*]thiophenes, **12a** and **12b**, were isolated from the reaction, signalling the dominant contribution of the hydroxybenzothiophene tautomer (Scheme 4).

The reaction discussed above proceeds equally well with butane-1,3-diol (**2b**) (Table 2), although ethane-1,2-diol cannot be used. With the latter, the ketones are recovered, after water is added to the reaction mixture upon termination of the reaction. Reactions of **6g** with neopentyl glycol (**2a**), butane-1,3-diol (**2b**), and pentane-2,4-diol (**2c**) gave the product **7g** in almost identical yield (Table 2). No product was formed with butane-1,2,4-triol, and only a trace of alkene is formed with butane-1,2-diol.

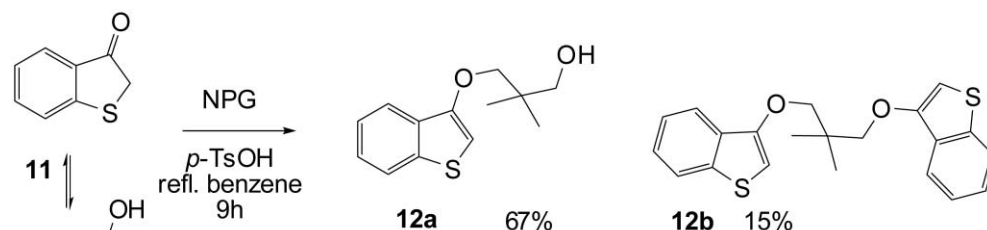
In summary, it has been found that 1-indanones, 1-tetralones, and benzosuberone can be converted to indenenes, 1,2-dihydronaphthalenes, and benzocycloheptadiene when heated with butane-1,3-diol (**2b**) or with neopentyl glycol (**2a**) under acid catalysis. The reaction is a good alternative to the classic reduction, dehydration protocol. This is particularly the case in the preparation of *estra-1,3,5(10),6-tetraenes* from the readily accessible 6-ketoestra-1,3,5(10)-trienes which is usually carried out by reduction–dehydration^{4,6} or by a two step Shapiro reaction.⁷ Lastly, the direct access of 9,10-dihydrobenzo[*a*]pyrene (**7l**) from commercial 9,10-dihydrobenzo[*a*]pyren-7(8*H*)-one (**6l**) and the complementary access of 7,8-dihydrobenzo[*a*]pyrene (**7m**) from 7,8-dihydrobenzo[*a*]pyren-10(9*H*)-one (**6m**), coupled with the easy availability of **6m** by a surprising site-selective oxidation of 7,8,9,10-tetrahydrobenzo[*a*]pyrene, provide important starting materials

for the synthesis of dihydrodiols of polycyclic aromatic hydrocarbons.⁹

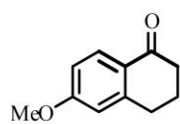
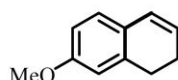
Experimental

Melting points were measured on a Yanaco microscope hotstage and are uncorrected. IR spectra were measured with JASCO IR-700 and Nippon Denshi JIR-AQ20M instruments. ¹H and ¹³C NMR spectra were recorded with a JEOL EX-270 spectrometer (¹H at 270 MHz, ¹³C at 67.8 MHz), a JEOL Lambda 400 FT-NMR spectrometer (¹H at 395.7 MHz, ¹³C at 99.45 MHz), a Varian 200 MHz NMR spectrometer (¹H at 200 MHz), and a Varian 400 MHz NMR spectrometer (¹H at 399.7 MHz, ¹³C at 100.5 MHz). The assignments of the carbon signals were aided by DEPT 90 and DEPT 135 experiments (DEPT = Distortionless Enhancement by Polarisation Transfer). Here, (–) denotes secondary carbons, (+) primary or tertiary carbons and (C_{quat}) quaternary carbons. The chemical shifts are relative to TMS (solvent CDCl₃, unless otherwise noted). Mass spectra were measured with a JMS-01-SG-2 spectrometer and with an Agilent 6310 Ion Trap. Column chromatography was carried out on Wakogel 300. Ketones **6a**, **6c–g**, **6i–l** were acquired commercially. Ketones **6b** and **6h** were prepared by α -methylation of ketones **6a** and **6f**, respectively. **6m** was synthesised by site-selective oxidation of 7,8,9,10-tetrahydrobenzo[*a*]pyrene (KMnO₄, PTC), itself available through hydrogenation of **7l**. 1-Methoxytetrahydronaphthalene (**9**) (KOH, MeI, DMSO)¹⁰ and 5-bromo-6-methoxy-1-tetralone (**6o**) (NBS, H₂O, H₂SO₄)¹¹ were synthesised according to known procedures. **6n** was prepared by oxidation of the benzylic position of di-*O*-methyl-estra-1,3,5(10)-trien-3,17 β -diol (KMnO₄, PTC) and subsequent conjugate addition of methyl iodide to its enolate, in a manner earlier described.^{4,5} 5-(4-Docosanyloxyphenyl)-6-methoxytetral-1-one (**6p**) was prepared by Suzuki-Miyaura reaction of **6o** and the respective 4-docosanyloxyphenylboronic acid [dioxane, (PPh₃)₂PdCl₂, 2 equiv. PPh₃, aq. Na₂CO₃], where the boronic acids was synthesised from the corresponding *p*-docosanyloxybromobenzene (a. *n*-BuLi, B(OR)₃, THF; b. HCl).¹²

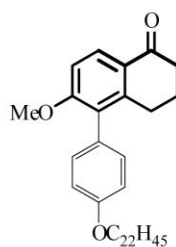
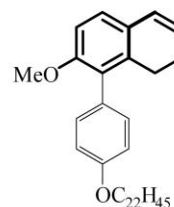
Indene (7a): A solution of 1-indanone (**6a**, 500 mg, 3.8 mmol), neopentyl glycol (**2a**, 1.53 g, 15.6 mmol) and *p*-toluenesulfonic acid (100 mg) in benzene (6 mL) was stirred at 80 °C for 24 h. Thereafter, a saturated aq. Na₂CO₃ solution (5 mL) was added, and the mixture was extracted with ether (3 x 20 mL). The ether was removed carefully, and the residue was subjected to a bulb-to-bulb distillation using a glass tube oven (model GTO-258S SIBATA) to yield indene (**7a**,



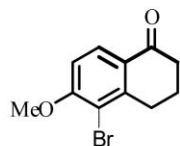
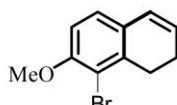
Scheme 4

Table 2 Reaction using different alkanediols**6g****7g**

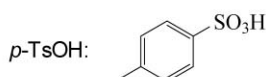
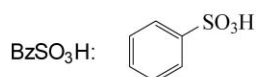
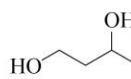
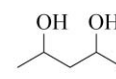
NPG (**2a**), *p*-TsOH: 54% (toluene, refl., 36h)
butane-1,3-diol (**2b**), BzSO₃H: 65% (benzene, refl., 22h)
pentane-2,4-diol (**2c**), BzSO₃H: 67% (benzene, refl., 22h)

**6p****7p**

butane-1,3-diol (**2b**), BzSO₃H: 75% (benzene, refl., 13h)
pentane-2,4-diol (**2c**), BzSO₃H: 73% (benzene, refl., 13h)

**6o****7o**

butane-1,3-diol (**2b**), BzSO₃H: 68% (benzene, refl., 15h)
pentane-2,4-diol (**2c**), BzSO₃H: 68% (benzene, refl., 15h)

**2a****2b****2c**

375 mg, 85%) as a colourless oil; (neat/cm⁻¹) ν_{\max} 3054, 3025, 2890, 1460, 1395, 766, 720, 695; δ_{H} (270 MHz, CDCl₃) 3.39 (2H, bs), 6.55 (1H, d, ³*J* = 5.7 Hz), 6.88 (1H, dm, ³*J* = 5.7 Hz), 7.19 (1H, m), 7.26 (1H, m), 7.40 (1H, d, ³*J* = 7.4 Hz), 7.46 (1H, d, ³*J* = 9.0 Hz); δ_{C} (67.8 MHz, CDCl₃) 39.0, 121.0, 123.7, 124.5, 126.3, 132.1, 134.0, 143.7, 144.8; MS (EI, 70 eV) *m/z* (%) 116 (M⁺, 95).

2-Methylindene (7b): Colourless oil. (Found: M⁺, 130.0784. C₁₀H₁₀ requires M⁺, 130.0783). (neat/cm⁻¹) ν_{\max} 2924, 1459, 1354, 1175, 1107, 826, 749, 715; δ_{H} 2.15 (3H, s, CH₃), 3.28 (2H, s), 6.48 (1H, s), 7.08 (1H, m), 7.17–7.25 (2H, m), 7.35 (1H, d, ³*J* = 7.3 Hz); δ_{C} 16.7 (CH₃), 42.7 (–), 119.7 (CH), 123.3 (CH), 123.5 (CH), 126.2 (CH), 127.2 (CH), 143.3 (C_{quat}), 145.9 (C_{quat}), 146.0 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 130 (100) [M⁺], 115 (70) [M⁺–CH₃].

5-Chloroindene (7c): Colourless oil. (Found: M⁺, 150.0236. C₉H₇³⁵Cl requires M⁺, 150.0236). (neat/cm⁻¹) ν_{\max} 3066, 2892, 1605, 1551, 1460, 1390, 1077, 946, 891, 869, 805, 692, 678; δ_{H} (270 MHz, CDCl₃) 3.37 (2H, s), 6.61 (1H, dt, ³*J* = 5.7 Hz, ³*J* = 1.9 Hz), 6.82 (1H, dm, ³*J* = 5.7 Hz), 7.15 (1H, dd, ³*J* = 8.1 Hz, ⁴*J* = 1.9 Hz), 7.36 (1H, d, ³*J* = 8.1 Hz), 7.37 (1H, d, ⁴*J* = 1.9 Hz); δ_{C} (67.8 MHz, CDCl₃) 38.7 (CH₂), 121.1 (CH), 124.4 (CH), 124.5 (CH), 131.3 (CH), 132.2 (C_{quat}), 136.0 (C_{quat}), 141.8 (CH), 146.6 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 152 ([³⁷Cl]M⁺, 13), 150 ([³⁵Cl]M⁺, 48).

5-Methylindene (7d): Colourless oil. (Found: M⁺, 130.0782. C₁₀H₁₀ requires M⁺, 130.0783). (neat/cm⁻¹) ν_{\max} 3060, 3022, 2918, 1621, 1557, 1495, 1473, 1393, 945, 914, 803, 729, 693; δ_{H} 2.48 (3H, s, CH₃), 3.35 (2H, bs), 6.53 (dt, 1H, ³*J* = 5.7 Hz, ³*J* = 1.9 Hz), 6.82 (1H, dm, ³*J* = 5.7 Hz), 7.00 (1H, d, ³*J* = 7.6 Hz), 7.18 (1H, s), 7.35 (1H, d, ³*J* = 7.6 Hz); δ_{C} 21.1 (CH₃), 38.4 (–), 121.6 (CH), 123.1 (CH), 125.2 (CH), 131.8 (CH), 134.7 (CH), 135.6 (C_{quat}), 140.4 (C_{quat}), 152.9 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 130 (100) [M⁺].

1,2-Dihydronaphthalene (7f): Colourless oil. (neat/cm⁻¹) ν_{\max} 3030, 2932, 2882, 2929, 1486, 1453, 1427, 1277, 1094, 1030, 1026, 1009, 780, 745, 691, 581; δ_{H} (270 MHz, CDCl₃) 2.29–2.35 (2H, m), 2.79 (2H, t, ³*J* = 8.1 Hz), 6.01 (1H, dt, ³*J* = 9.5 Hz, ³*J* = 4.9 Hz), 6.45 (1H, d, ³*J* = 9.5 Hz), 7.00 (1H, m), 7.08–7.14 (3H, m); δ_{C} (67.8 MHz, CDCl₃) 23.2 (CH₂), 27.5 (CH₂), 125.9 (CH), 126.4 (CH), 126.8 (CH), 127.5 (CH), 127.8 (CH), 128.6 (CH), 134.1 (C_{quat}), 135.5 (C_{quat}); MS (EI, 70 eV) *m/z* (%) 130 (97).

7-Methoxy-1,2-dihydronaphthalene (7g): Colourless oil. (Found: M⁺, 160.0890. C₁₁H₁₂O requires M⁺, 160.0888). (neat/cm⁻¹) ν_{\max} 3030,

2934, 2832, 1601, 1574, 1468, 1434, 1344, 1265, 1237, 1096, 1080, 803, 783, 700; δ_{H} (270 MHz, CDCl₃) 2.28–2.33 (2H, m), 2.79 (2H, dd, ³*J* = 8.6 Hz, ³*J* = 8.4 Hz), 3.83 (3H, s, OCH₃), δ_{C} (67.8 MHz, CDCl₃) 19.4 (–), 22.6 (–), 55.5 (+, OCH₃), 109.6 (CH), 118.9 (CH), 123.1 (C_{quat}), 126.6 (CH), 127.6 (CH), 128.8 (CH), 135.1 (C_{quat}), 156.1 (C_{quat}); MS (EI, 70 eV) *m/z* (%) 160 (M⁺, 100).

7-Methoxy-3-(6'-methoxy-1',2',3',4'-tetrahydronaphth-1'-yl)-1,2-dihydronaphthalene (8): Off-white solid; (Found: M⁺, 320.1770. C₂₂H₂₄O₂ requires M⁺, 320.1776). δ_{H} (270 MHz, CDCl₃) 1.73–1.77 (2H, m), 1.89–1.93 (2H, m), 2.10–2.13 (2H, m), 2.70–2.77 (4H, m), 3.58 (1H, s), 3.78 (3H, s, OCH₃), 3.79 (3H, s, OCH₃), 6.14 (1H, s), 6.64–6.68 (4H, m), 6.91 (1H, d, ³*J* = 8.9 Hz), 7.09 (1H, d, ³*J* = 8.1 Hz); δ_{C} (67.8 MHz, CDCl₃, DEPT 90, DEPT 135) 21.4 (–), 24.9 (–), 28.8 (–), 29.1 (–), 30.2 (–), 46.5 (+, CH), 55.2 (+, OCH₃), 55.3 (+, OCH₃), 111.1 (+, CH), 112.0 (+, CH), 113.4 (+, CH), 113.5 (+, CH), 124.2 (+, CH), 126.4 (+, CH), 128.1 (C_{quat}), 128.3 (C_{quat}), 130.3 (+, CH), 136.5 (C_{quat}), 138.9 (C_{quat}), 143.1 (C_{quat}), 157.7 (C_{quat}), 158.2 (C_{quat}); MS (EI, 70 eV) *m/z* (%) 320 (M⁺, 100), 160 (98).

3-Methyl-1,2-dihydronaphthalene (7h): Colourless oil. (Found: M⁺, 144.0935. C₁₁H₁₂ requires M⁺, 144.0939). (neat/cm⁻¹) ν_{\max} 3062, 3016, 2962, 2924, 2880, 1652, 1604, 1486, 1441, 1109, 1019, 974, 875, 842, 752, 729; δ_{H} (270 MHz, CDCl₃) 1.90 (3H, s, CH₃), 2.23 (2H, dd, ³*J* = 8.4 Hz, ³*J* = 8.1 Hz), 2.81 (2H, dd, ³*J* = 8.4 Hz, ³*J* = 8.1 Hz), 6.21 (1H, d, ⁴*J* = 2.1 Hz), 6.94 (1H, d, ³*J* = 7.0 Hz), 7.02–7.25 (3H, m); δ_{C} (67.8 MHz, CDCl₃) 23.5 (CH₃), 28.1 (–), 28.8 (–), 122.7 (CH), 125.1 (CH), 125.9 (CH), 126.3 (CH), 127.1 (CH), 128.2 (C_{quat}), 135.0 (C_{quat}), 138.2 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 144 (50) [M⁺], 129 (100) [M⁺–CH₃].

8-Methoxy-1,2-dihydronaphthalene (7i): Colourless oil. (Found: M⁺, 160.0887. C₁₁H₁₂O requires M⁺, 160.0888). (neat/cm⁻¹) ν_{\max} 3028, 2932, 2830, 1609, 1570, 1501, 1464, 1427, 1394, 1305, 1277, 1250, 1152, 1122, 1108, 1038, 818, 568; δ_{H} (270 MHz, CDCl₃) 2.27–2.30 (2H, m), 2.77 (2H, t, ³*J* = 8.4 Hz), 3.78 (3H, s, OCH₃), 5.88 (dt, 1H, ³*J* = 9.5 Hz, ³*J* = 4.6 Hz), ³*J* = 6.40 (1H, d, ³*J* = 9.5 Hz), 6.67–6.70 (2H, m), 6.93 (1H, d, ³*J* = 8.9 Hz); δ_{C} (67.8 MHz, CDCl₃) 23.0 (–), 28.0 (–), 55.2 (OCH₃), 111.1 (CH), 113.8 (CH), 125.9 (CH), 126.8 (CH), 127.1 (CH), 127.4 (C_{quat}), 137.2 (C_{quat}), 158.6 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 160 (M⁺, 100), 145 (42), 115 (52).

Benzocycloheptadiene (benzosuberene, 7j):¹³ Colourless oil. (Found: M⁺, 144.0936. C₁₁H₁₂ requires M⁺, 144.0939). δ_{H} (270 MHz,

CDCl₃) 1.83–1.65 (2H, m), 2.15–2.30 (2H, m), 2.72–2.84 (2H, m), 5.75 (1H, dt, ³J = 11.9 Hz, ⁴J = 3.9 Hz), 6.33 (1H, dt, ³J = 11.9 Hz, ⁴J = 1.9 Hz), 7.09–7.11 (4, m); MS (EI, 70 eV) *m/z* (%) = 144 (M⁺) (36), 129 (100).

3,4-Dihydrobenzo[*a*]anthracene (7k):¹⁴ (Found: M⁺, 230.1098. C₁₈H₁₄ requires M⁺, 230.1096). *v*_{max} (KBr/cm⁻¹) 1656, 1540, 875, 740, 706, 679; δ_{H} (270 MHz, CDCl₃) 2.42–2.44 (2H, m), 2.97 (2H, t, ³J = 8.7 Hz), 6.31 (1H, dt, ³J = 10.0 Hz, ³J = 4.9 Hz), 7.28 (1H, d, ³J = 8.6 Hz), 7.41–7.45 (3H, m), 7.83 (1H, d, ³J = 8.6 Hz), 7.94–7.99 (2H, m), 8.36 (1H, s), 8.63 (1H, s); δ_{C} (67.8 MHz, CDCl₃) 22.9 (CH₂), 28.5 (CH₂), 120.8 (CH), 123.3 (CH), 125.1 (CH), 125.3 (CH), 126.7 (CH), 127.0 (CH), 127.1 (CH), 127.9 (CH), 128.3 (C_{quat}), 128.4 (C_{quat}), 128.5 (CH), 129.0 (CH), 130.9 (C_{quat}), 131.4 (C_{quat}), 131.8 (C_{quat}), 132.3 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 230 (100) [M⁺], 215 (22).

9,10-Dihydrobenzo[*a*]pyrene (7l):¹⁵ Colourless solid, m.p. 146 °C. (Found: M⁺, 254.1098. C₂₀H₁₄ requires M⁺, 254.1096). (KBr/cm⁻¹) *v*_{max} 3028, 2926, 2874, 2824, 1598, 1438, 1418, 1297, 1180, 882, 840, 823, 705, 682; δ_{H} 2.53–2.61 (2H, m), 3.49 (2H, dd, ³J = 8.2 Hz, ³J = 8.1 Hz), 6.25 (1H, dt, ³J = 9.7 Hz, ³J = 3.9 Hz), 6.84 (1H, d, ³J = 9.7 Hz), 7.84 (1H, s), 7.90–8.12 (6H, m), 8.25 (1H, d, ³J = 9.4 Hz); δ_{C} 23.3 (2C), 123.0, 123.2, 124.6, 124.8, 125.0, 125.6, 126.7, 127.5, 128.0 (2C), 128.3, 128.7, 129.3, 129.6, 129.7, 130.7, 131.3, 131.9; MS (EI, 70 eV) *m/z* (%) = 254 (100) [M⁺], 239 (23).

7,8-Dihydrobenzo[*a*]pyrene (7m):⁹ Colourless solid, mp. 127 °C. (Found: M⁺, 254.1100. C₂₀H₁₄ requires M⁺, 254.1096). (KBr/cm⁻¹) *v*_{max} 1176, 883, 839, 827, 775, 756, 730, 704, 677; δ_{H} 2.47–2.54 (2H, m), 3.23 (2H, dd, ³J = 8.1 Hz, ³J = 7.8 Hz), 6.41 (1H, dt, ³J = 10.0 Hz, ³J = 4.9 Hz), 7.55 (1H, d, ³J = 10.0 Hz), 7.91–8.14 (7H, m), 8.35 (1H, d, ³J = 9.4 Hz); δ_{C} 23.1 (–), 29.1 (–), 122.3 (CH), 123.8 (CH), 124.5 (CH), 124.7 (CH), 125.0 (CH), 125.1 (C_{quat}), 125.5 (CH), 126.0 (C_{quat}), 126.9 (CH), 127.2 (CH), 127.4 (CH), 128.0 (C_{quat}), 129.3 (C_{quat}), 130.1 (C_{quat}), 130.5 (CH), 130.7 (C_{quat}), 131.2 (C_{quat}), 134.1 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 254 (100) [M⁺].

3,17-Di-(*O*-methyl)-7-estra-1,3,5(10),6-tetraen-3,17 β -diol (7n): Colourless solid; m.p. 121 °C; (Found: M⁺, 312.2089. C₂₁H₂₈O₂ requires M⁺, 312.2089). (KBr/cm⁻¹) *v*_{max} 2924, 2848, 1605, 1500, 1459, 1266, 1202, 1105, 1039, 871; δ_{H} (270 MHz, CDCl₃) 0.78 (3H, s, CH₃), 1.30–2.45 (11H, m), 1.96 (3H, s, CH₃), 3.25 (1H, m), 3.38 (3H, s, CH₃), 3.78 (3H, s, CH₃), 6.20 (1H, s), 6.56 (1H, d, ⁴J = 2.7 Hz), 6.68 (1H, dd, ³J 8.4 Hz, ⁴J = 2.7 Hz), 7.16 (1H, d, ³J = 8.4 Hz); δ_{C} (67.8 MHz, CDCl₃) 11.5, 24.5 (2C), 26.9, 27.5, 36.7, 41.8, 42.1, 44.8, 47.3, 55.3, 57.9, 89.7, 110.4, 111.0, 124.34, 125.3, 131.4, 135.9, 143.7, 158.2; MS (EI, 70 eV) *m/z* (%) 312 (M⁺, 23).

5-Bromo-6-methoxy-1,2-dihydronaphthalene (7o): Off-white solid; δ_{H} (200 MHz, CDCl₃) 2.27–2.79 (2H, m), 2.89 (2H, dd, ³J = 8.6, ³J = 8.2 Hz), 3.86 (3H, s, OCH₃), 5.86–5.93 (1H, m), 6.33 (1H, d, ³J = 9.8 Hz), 6.67 (1H, d, ³J = 8.2 Hz), 6.90 (1H, d, ³J = 8.2 Hz); δ_{C} (50.3 MHz, CDCl₃) 22.5 (CH₂), 27.3 (CH₂), 55.8 (OCH₃), 108.6 (CH), 111.2 (C_{quat}), 124.9 (CH), 125.9 (CH), 126.2 (CH), 128.3 (C_{quat}), 136.2 (C_{quat}), 154.6 (C_{quat}); MS: 241.0 (⁸¹BrMH⁺), 239.0 (⁷⁹BrMH⁺)

5-(4-Docosanyloxyphenyl)-6-methoxy-1,2-dihydronaphthalene (7p): Colourless solid; m.p. 88 °C. (KBr/cm⁻¹) 3033, 2920, 2849, 1607, 1571, 1512, 1472, 1239, 1175, 1065, 826, 718, 589; δ_{H} (400 MHz, CDCl₃) 0.88 (3H, t, ³J = 6.8 Hz, CH₃), 1.24–1.27 (36H, m), 1.46 (2H, m), 1.78–1.82 (2H, m), 2.12–2.18 (2H, m), 2.52 (2H, t, ³J = 8.0 Hz), 3.71 (3H, s, OCH₃), 3.99 (2H, t, ³J = 6.8 Hz, OCH₂), 5.90 (dt, 1H, ³J = 9.6 Hz, ³J = 4.4 Hz), 6.47 (dt, 1H, ³J = 9.6 Hz, ⁴J = 1.8 Hz), 6.76 (1H, d, ³J = 8.4 Hz), 6.94 (2H, d, ³J = 8.8 Hz), 7.00 (1H, d,

³J = 8.4 Hz), 7.12 (2H, d, ³J = 8.8 Hz); δ_{C} (100.5 MHz, CDCl₃) 14.1 (CH₃), 22.7 (CH₂), 23.0 (CH₂), 25.4 (CH₂), 26.1 (CH₂), 29.4 (CH₂), 29.6 (CH₂), 29.7 (15C, CH₂), 31.9 (CH₂), 55.7 (OCH₃), 67.9 (OCH₂), 108.2 (CH), 113.9 (2C, CH), 125.8 (CH), 126.1 (CH), 127.5 (C_{quat}), 127.6 (CH), 128.9 (C_{quat}), 129.5 (C_{quat}), 131.2 (2C, CH), 135.5 (C_{quat}), 156.4 (C_{quat}), 158.0 (C_{quat}); MS 561.5 (MH⁺).

3-(3-Hydroxy-2,2-dimethyl-propyloxy)-benzo[*b*]thiophene (12a): Colourless solid; m.p. 93 °C. (Found: M⁺, 236.0871). (KBr/cm⁻¹) *v*_{max} 3850 (bs, OH), 2960, 2870, 1572, 1530, 1466, 1439, 1378, 1352, 1181, 1161, 1138, 1120, 1046, 1013, 866, 760, 732; δ_{H} 1.10 (6H, s, 2 CH₃), 3.61 (2H, bs), 3.94 (2H, s), 6.31 (1H, s), 7.34–7.39 (2H, m), 7.73–7.79 (2H, m); δ_{C} 21.7 (2C, CH₃), 36.6 (C_{quat}), 69.7 (–), 96.2 (CH), 120.8 (CH), 122.9 (CH), 123.7 (CH), 125.2 (CH), 133.2 (C_{quat}), 137.7 (C_{quat}), 150.9 (C_{quat}); MS (EI, 70 eV) *m/z* (%) 236 (17) [M⁺], 150 (100), 121 (20).

1,3-(2,2-Dimethylpropyl bis(benzo[*b*]thien-3-yl) ether (12b): Colourless solid; m.p. 83 °C. (Found: M⁺, 368.0904. C₂₁H₂₀O₂S₂ requires M⁺, 368.0905). (KBr/cm⁻¹) *v*_{max} 3116, 2912, 1572, 1530, 1460, 1433, 1351, 1179, 1161, 1138, 1118, 867, 798, 758, 717; δ_{H} (270 MHz, CDCl₃) 1.29 (6H, s, 2 CH₃), 4.07 (4H, s), 6.31 (2H, s), 7.30–7.37 (4H, m), 7.71–7.82 (4H, m); δ_{C} 22.1 (2C, CH₃), 36.3 (C_{quat}), 75.2 (2C, –), 96.1 (2C, CH), 120.9 (2C, CH), 122.8 (2C, CH), 123.6 (2C, CH), 125.2 (2C, CH), 132.2 (2C, C_{quat}), 137.6 (2C, C_{quat}), 151.0 (2C, C_{quat}); MS (EI, 70 eV) 368 (65) [M⁺], 219 (31), 150 (100), 121 (76).

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