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Diene-yne cyclisation reactions of 1-ethynyl-2-vinyl-3,4-dihydronaphthalenes and 1-ethynyl-2-vinylnaphthalenes

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The reaction of 1-ethynyl-2-vinyl-3,4-dihydronaphthalenes and 1-ethynyl-2-vinylnaphthalenes over $RuCl_2$(*p*-cymene) PPh_3 leads to 9,10-dihydrophenanthrenes and phenanthrenes in those cases where the ethynyl group in the substrates carries a terminal proton. When 1-phenylethynyl-2-vinyl-3,4-dihydronaphthalenes or 1-phenylethynyl-2-vinylnaphthalenes are reacted over $Pt(PPh_3)_4$, 1-methylene-1*H*-benz[*e*]-4,5-dihydroindenes and 1-methylene-1*H*-benz[*e*]indenes are formed.

Keywords: diene-ynes, cyclisation, ruthenium, platinum, catalysis, fulvenes

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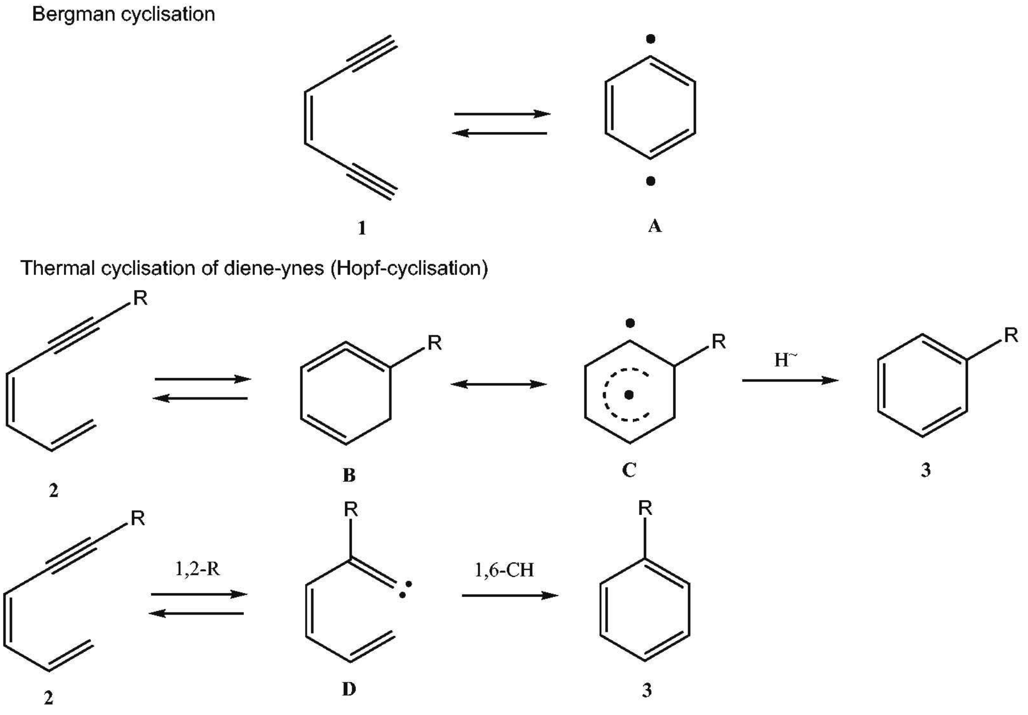
While ene-diyne cyclisations (Bergman reaction) have been subject to extensive investigations,[1-4] diene-yne cyclisations have been studied much less frequently (Scheme 1). In contrast to ene-diynes, the geometry of diene-ynes is far from optimal for intramolecular cyclisation reactions. Thus, cyclisations of this type can only be accomplished when the geometry of the transition state is greatly changed from that of the educts. Nevertheless, it is possible to submit diene-ynes thermally to intramolecular cyclisation reactions. Thus, the parent compound, hexa-1,3-dien-5-yne (**2**, R = H) can be transformed to benzene at 274°C (Hopf cyclisation, Scheme 1)[5] and at 500 °C, the reaction gives benzene in 50% yield.[5] Further diene-ynes have been subjected to similar conditions to furnish cyclisation products.[6-11] In certain cases, one or both olefinic moieties of the diene component can be part of an aromatic system. In these cases the Hopf cyclisation has been used for the construction of bowl-shaped polycyclic aromatic hydrocarbons (PAHs)[6,7,8] as sub-units of fullerenes. Efforts have been devoted to the elucidation of the mechanism of the thermal cyclisation of diene-ynes[12-16] and it has been found that different mechanisms compete, depending on the reaction temperature. At lower temperatures, up to 550 °C, the cyclisations are thought to occur through a two-step mechanism via cyclohexa-1,2,4-trienes **B** with a strong biradical character. At higher temperatures, it has been found that an isomerisation of the alkynes to vinylidenecarbenes **D** occurs, which then react by a 1,6-CH insertion (Scheme 1). Competing 1,5-CH insertion can yield indenes and acenaphthenes as side-products,[17] depending on the substrates. A fulvene structure has also been isolated as side product,[15] most likely arising via a biradical intermediate. As the thermal diene-yne cyclisations, mentioned above, all necessitate high temperatures, most functional groups are not compatible with the reaction conditions. Thus, milder reaction conditions are preferable with lower reaction temperatures as found in the cyclisation reactions of yne-ene allenes **4** to benzenes **5** (Myers–Saito-cyclisation, Scheme 2)[18,19] and to fulvenes **6** (Schmittel cyclisation, Scheme 2).[20] In the case of terminal acetylenes such as **7**, the cyclisation of diene-ynes can proceed via transformation of a metal vinylidene species, *e.g.* via **G** (*vide infra*) (Scheme 3). Here, the use of ruthenium[21,22] (Scheme 3) and tungsten,[23-25] and with less favourable results,



Scheme 1

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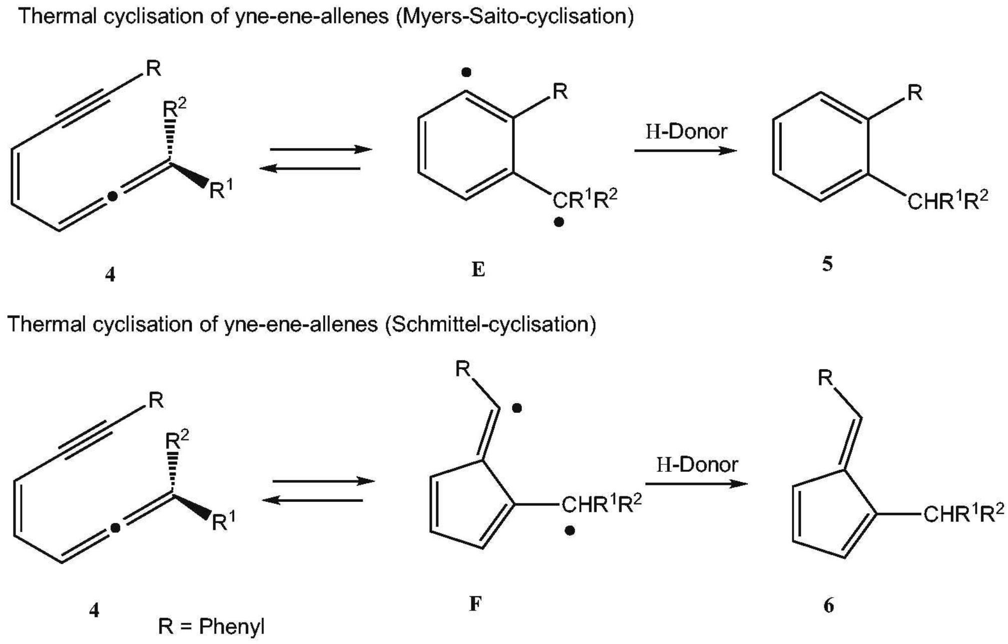
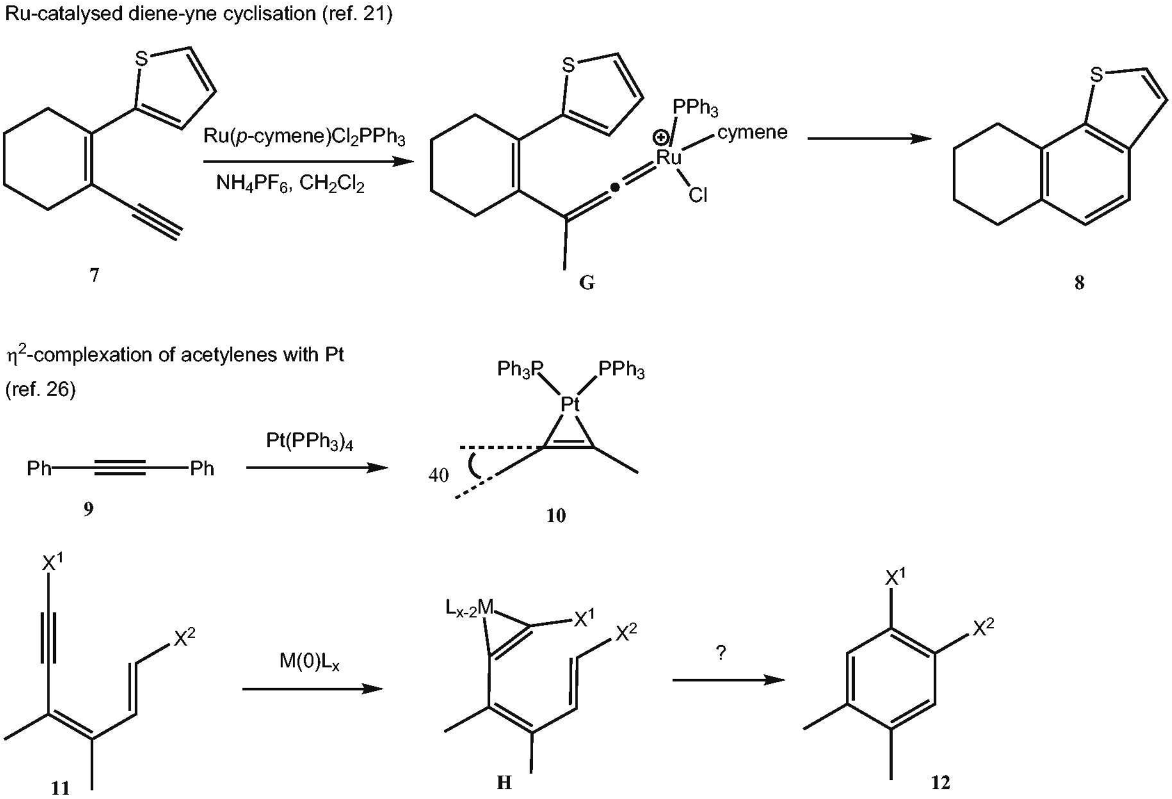


Scheme 2

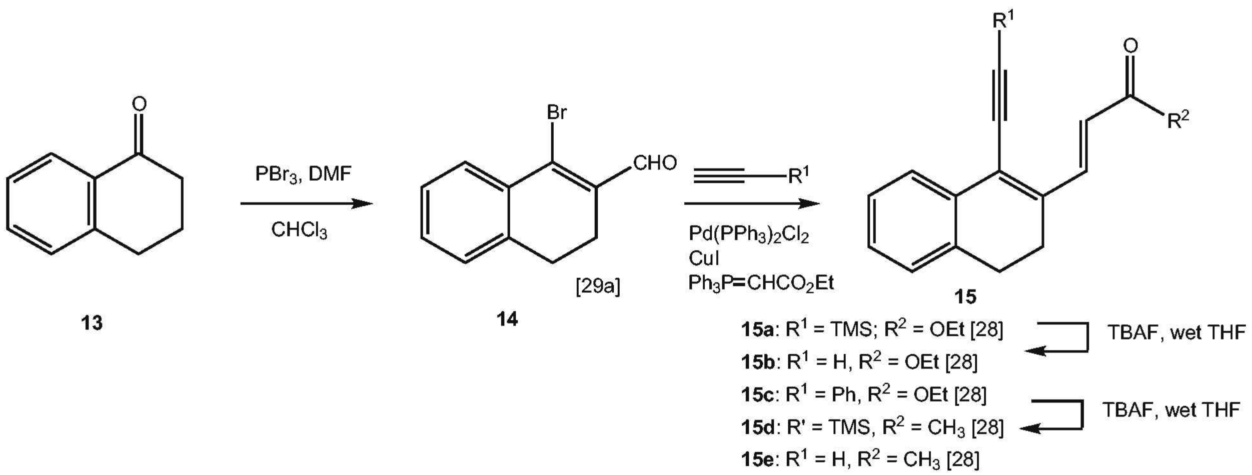
of chromium and molybdenum catalysts has been reported. In the case of diene-ynes with internal acetylene moieties, the complexation of a metal to the alkyne moiety in η^2-fashion[26,27] as in **10** can be envisaged (Scheme 3). This would give a unit possessing more of the character and geometry of an alkene allowing subsequent cyclisation of the complexed diene-yne. We have recently developed a one-pot synthesis of 1-ethynyl-2-vinyl-3,4-dihydronaphthalenes **15** from 1-bromo-2-formyl-3,4-dihydronaphthalenes **14**,[28] and we became interested in their metal catalysed yne-diene cyclisation reactions, utilising both of the latter approaches.

Tetralones such as **13** can easily be transformed into the corresponding bromo-enaldehydes, such as **14**, by the Arnold–Vilsmeier reaction (Scheme 4).[29] The bromo-enaldehydes **14** can then react in a one-pot Sonogashira-coupling–Wittig reaction to furnish 1-ethynyl-2-vinyl-3,4-dihydronaphthalenes **15a, c, d**[28] and, after desilyation with tetra-*n*-butylammonium fluoride (TBAF) in wet THF, to give **15b** and **15e**. 1-Ethynyl-2-vinylnaphthalene (**15f**) was synthesised from **15a**, either by desilylation to **15b** (TBAF, wet THF) and subsequent dehydration with 2,3-dicyano-4,5-dichloroparabenzoquinone (DDQ) in refluxing benzene, or by dehydration of **15a** to **15g**



Scheme 3

Access to diene-ynes via Arnold-Vilsmeier and subsequent one-pot Sonogashira–Wittig olefination protocol (Refs. 28, 29)



Scheme 4

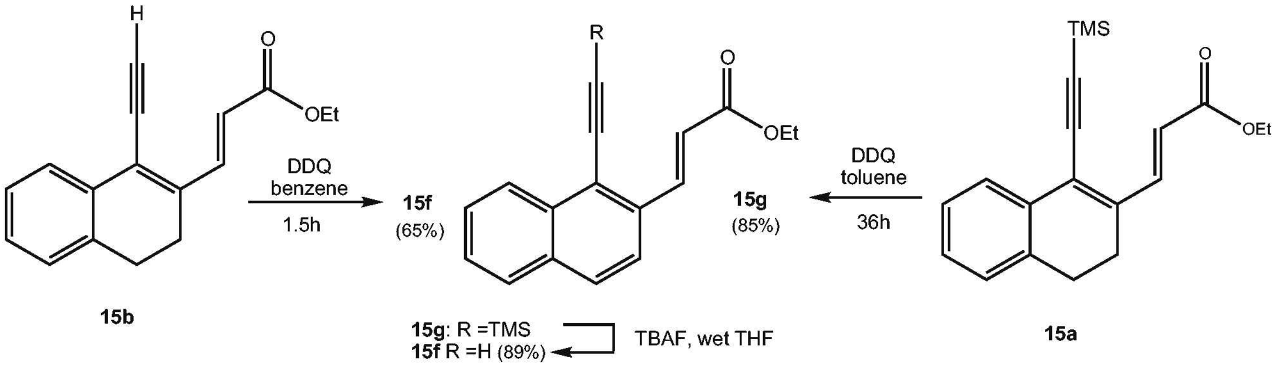
with DDQ in refluxing toluene and subsequent desilylation using TBAF in wet THF (Scheme 5). Compound **15i** was prepared from **15e** by Luche reduction ($NaBH_4$, $CeCl_3$) followed by acetylation (Ac_2O, Py) (Scheme 6). It is necessary to protect the hydroxy group in **15h** for the subsequent diene-yne cyclisation.

The resultant 1-ethynyl-2-vinyldihydronaphthalenes **15b**, **15e**, and **15i** and 1-ethynyl-2-vinylnaphthalene **15f** were subjected to metal-catalysed diene-yne cyclisation reactions. While Iwasawa and Maeyama[23,24] have shown that diene-ynes, possessing a terminal proton, can be cyclised in presence of $W(CO)_5(THF)$, in the present case, Ru(*p*-cymene) Cl_2PPh_3[30] was used as the catalyst, as described by Merlic and Pauly.[21] In this manner, diene-ynes **15b**, **15e**, **15f**, and **15i** were cyclised in fair yield to give a ready access to areno-annelated compounds **16a–d** (Scheme 6). The reaction is thought to proceed via a ruthenium vinylidene intermediate (see Scheme 3).[21]

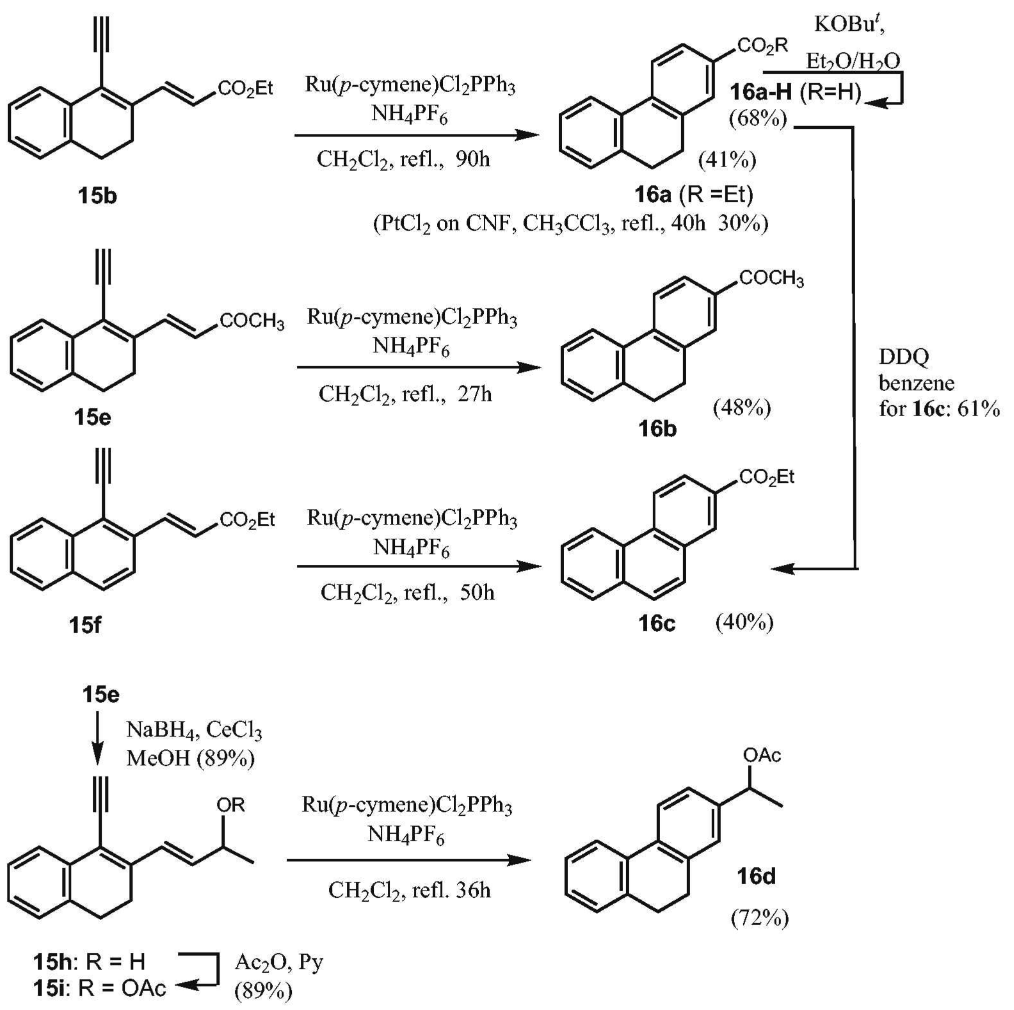
Recently, Fuerstner and Mamane[31] described the Pt-catalysed cyclisation of 2-ethynylbiphenyls to phenanthrenes, which incorporates aspects of the diene-yne cyclisation. Initial experiments on the cyclisation of dihydronaphthalene based diene-ynes of type **15** with $Pt(PPh_3)_4$ as catalyst, however, gave the corresponding phenanthrenes as the cyclised product in very poor yield (typically: $Pt(PPh_3)_4$, mesitylene, 135 °C, 45 h, 2% yield). It must be noted, however, that the cyclisation of **15b** to **16a** also proceeds in the presence of platinum dichloride. Here, platinum dichloride was immobilised on a solid support (carbon nanofibres, CNFs).[32] Higher reaction temperatures were needed (74 °C *vs* 40 °C) than in the ruthenium catalysed transformation of **15b** to **16a**, when 1,1,1-trichloroethane was used as solvent (Scheme 6). While initially a η^2-complexation of the platinum species to the alkyne moiety was taken into consideration when planning the reaction sequence (*vide supra*), it may well be that a metal vinylidene intermediate is also active in this catalytic reaction. Such end-on complexations have been discussed in the absorption of acetylene itself on Pt-surfaces, where the upright bridge bonded μ-vinylidene of the form $Pt_2 =C=CH_2$ has been characterised by vibrational spectroscopy.[33] Laser ablated Pt atoms have also been found to react with acetylene to form platinum vinylidene ($Pt =C=CH_2$).[34] It has been known that noble metals on solid supports can go into solution and redeposit on the support, so that even for solid supported catalysts of this type a homogeneous reaction can be considered.[35]

Compound **16a** can be derivatised[36] to two potent inhibitors of human steroid 5α-reductase.[37,38] Thus, **16a** can be hydrolysed to inhibitor **16a–H** with $KOBu^t/H_2O$ in ether according to a general procedure by Gassman (Scheme 6).[39] It can also be dehydrogenated to **16c**, the direct precursor of potent steroid 5α-reductase inhibitor phenanthrene-2-carboxylate. Alternatively, **16c** can be prepared by diene-yne cyclisation from **15f**.

Next, we turned our attention to diene-ynes with an internal alkyne unit, in which 1-arylethynyl-2-vinyl-3,4-dihydronaphthalenes **15** were used as substrates. Again, the compounds can be prepared by a one-pot or by a stepwise Sonogashira–Wittig olefination (Schemes 4 and 7).

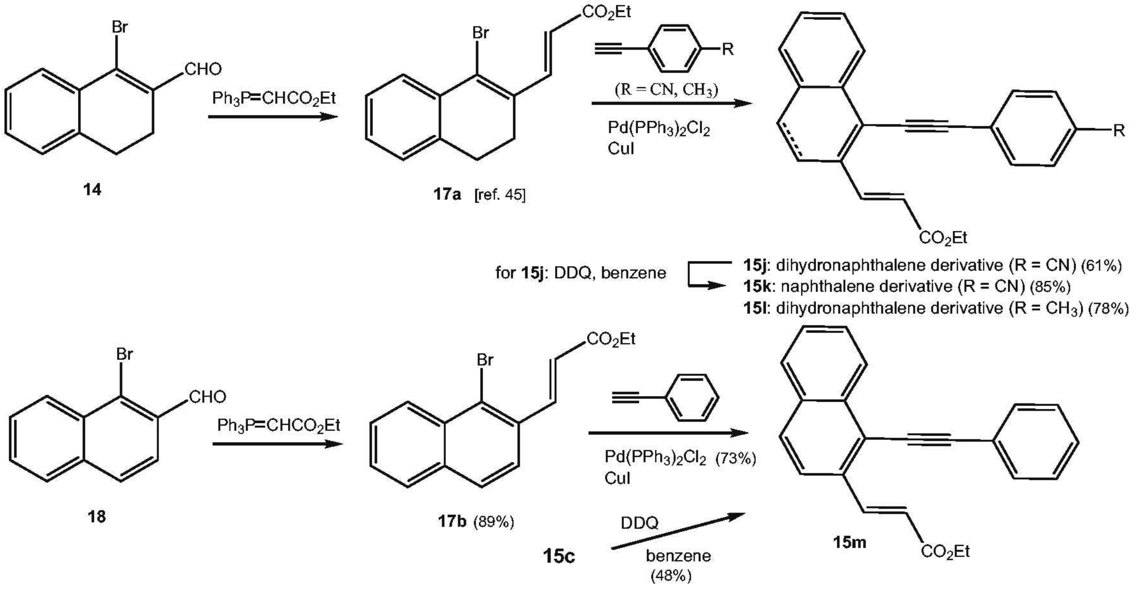


Scheme 5

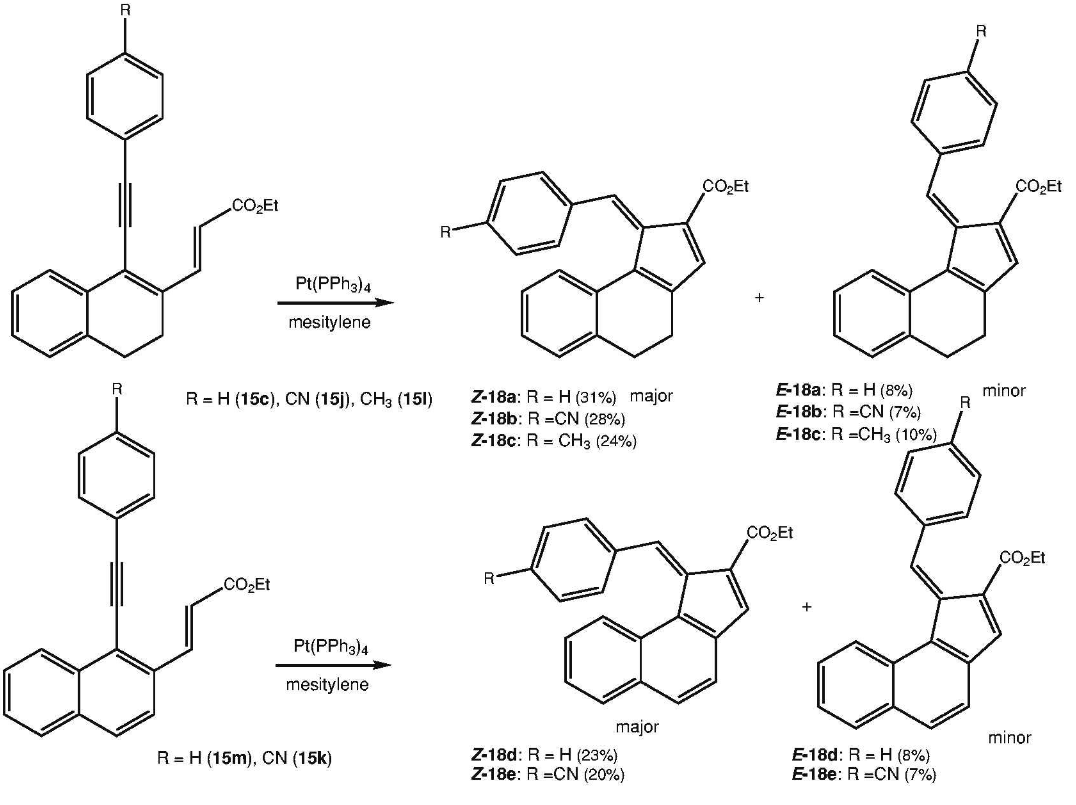


Scheme 6

A number of platinum complexes and platinum salts were used in the initial attempts at diene-yne cylisation of these substrates. When tetrakis(triphenylphosphine)platinum(0) [$Pt(PPh_3)_4$] was added to **15c** in CD_2Cl_2, a platinum complex was formed, which could be characterised by ^1H and ^{13}C NMR spectroscopy, but which could not be identified unequivocally. This platinum complex did not react further and give cyclised products under the conditions tried (DMF, rt; DMF, 80 °C; DMF, reflux; dry thermolysis on quartz [350 °C; $p < 10$ Torr]). However, the reaction of **15c** in mesitylene at 135 °C in the



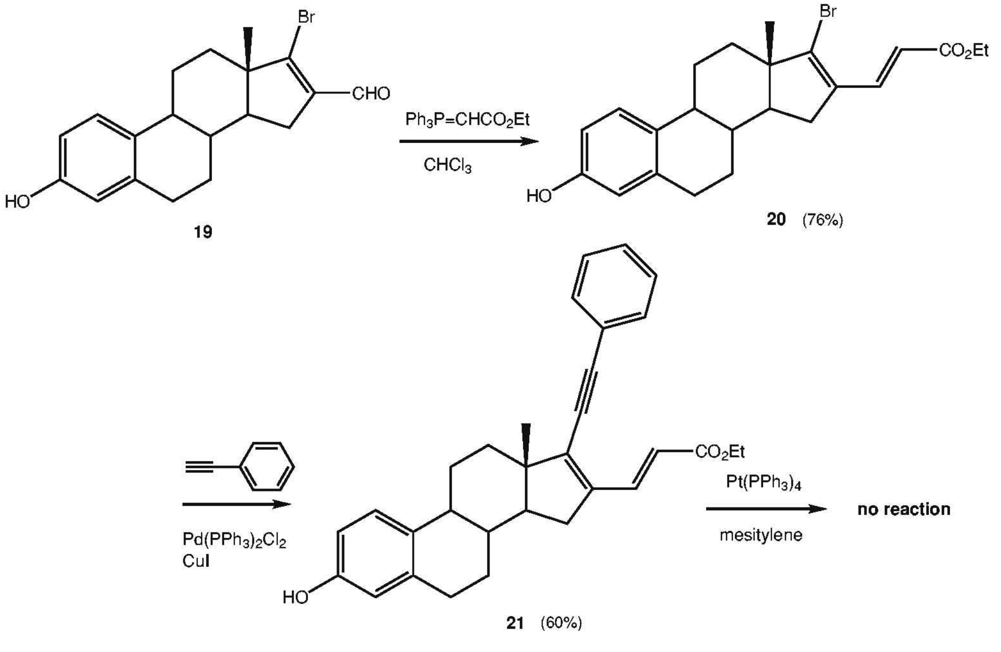
Scheme 7



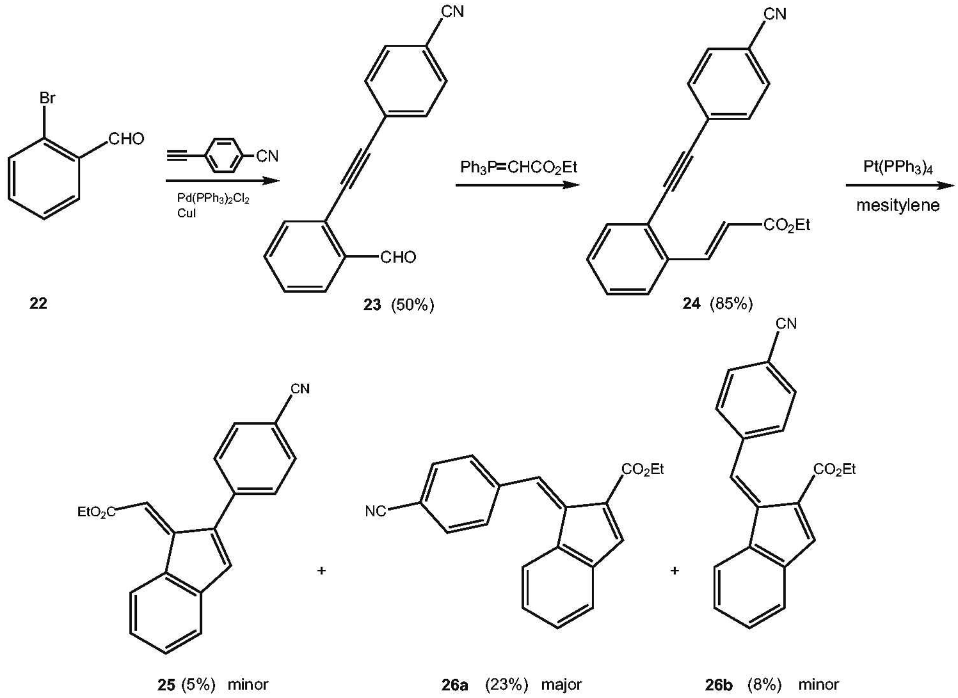
Scheme 8

presence of Pt(PPh$_3$)$_4$ led to a reddening of the solution and 1-methylene-1*H*-benz[*e*]-4,5-dihydroindenes **18a** was isolated in moderate yield (Scheme 8).

The fulvenes form as a mixture of *E*- and Z-isomers, where the *Z*-isomer is the predominant isomer. In the *Z*-isomers, the protons of the benzo- as well as the phenyl group are shifted to high-field due to the proximity of the two aromatic ring systems. The stereostructure of the *E*-isomer was confirmed by NOE experiments. Over prolonged periods of time, the pure *Z*-isomer equilibrates in solution to give a mixture of *E*- and *Z*-isomer. Neat *Z*-isomers, *e.g.* **18b**, have been found to undergo slow decomposition. It must be noted that under the strict exclusion of oxygen (air), the reaction does not take place. In the presence of oxygen, a small amount of the solvent mesitylene is oxidised to 3,5-dimethylbenzaldehyde which, in certain cases, complicates the work-up as residual 3,5-dimethylbenzaldehyde has to be removed *in vacuo* after column chromatographic separation of the compounds. This indicates that under the reaction conditions the Pt(0) species is partially oxidised, most probably to Pt(II). Instead



Scheme 9



Scheme 10

of mesitylene, 4-*tert*-butylbenzene can be used as a solvent. The reaction does not proceed with $PtCl_2$ as catalyst under otherwise identical conditions. As part of our on-going study[41-43] on E-ring annelated estranes as novel ligands for the estrogen receptor, a solution of the estrane based diene-yne **20** in mesitylene was heated in the presence of $Pt(PPh_3)_4$, but in this case unfortunately no reaction could be observed (Scheme 9).

2-Arylethynylcinnamate **24** was also heated in mesitylene in the presence of $Pt(PPh_3)_4$ at 135 °C. The substrate **24** was prepared from 2-bromobenzaldehyde (**22**) by a sequential Sonogashira coupling–Wittig olefination (Scheme 10). Reversal of the transformation sequence, *i.e.* Wittig olefination followed by Sonogashira coupling, gave the product in much lower yield as the Sonogashira coupling proceeds only with difficulty (10% yield). Again, a solution of 2-arylethynylcinnamate **24** in mesitylene undergoes cyclisation, when reacted over $Pt(PPh_3)_4$ and gives fulvene **26** as *E*- and *Z*-isomers. Single crystals of ***Z*-26** could be obtained and an X-ray crystal structure of ***Z*-26** has been carried out confirming the structure of **26**.[44] Interestingly, in this reaction, fulvene **25** is formed as a side-product. The structure of **25** was also verified by X-ray crystal structure analysis.[44]

In conclusion, 1-ethynyl-2-vinyl-3,4-dihydronaphthalenes **15b**, **15e** and **15i** as well as 1-ethynyl-2-vinylnaphthalenes **15f** have been found to undergo diene-yne cyclisation reactions to dihydrophenanthrenes and phenanthrenes, respectively, catalysed by Ru(*p*-cymene)Cl_2PPh_3. In an exploratory reaction, it was found that the reaction proceeds also with $PtCl_2$ immobilised on a carbon nanofibre material [CN28-580 °C, HCl treated]. Diene-ynes **15** and **24**, which possess an internal alkyne moiety, could be cyclised to fulvenes **18**, **25** and **26**, catalysed by $Pt(PPh_3)_4$. Studies on the scope of the latter reaction concerning the range of possible substrates and catalysts as well as mechanistic studies are underway.

Experimental

General

Melting points were measured on a Yanaco microscopic hot-stage and are uncorrected. IR spectra were measured with JASCO IR-700 and Nippon Denshi JIR-AQ2OM machines. ^1H and ^{13}C NMR spectra were recorded with a JEOL EX-270 spectrometer. The chemical shifts are relative to TMS (solvent $CDCl_3$, unless otherwise noted). Partially, assignments of ^{13}C signals were aided by DEPT (= Distortionless Enhancement by Polarisation Transfer) measurements. Mass spectra were measured with a JMS-01-SG-2 spectrometer (EI, 70 eV). Column chromatography was carried out on Wakogel 300.

Diisopropylamine (DIPA) was stored over KOH and distilled from KOH and DME was distilled from calcium hydride before use. Tetrakis(triphenylphosphine)platinum(0) [$Pt(PPh_3)_4$] and bis(triphenylphosphine)palladium(II) dichloride [$(PPh_3)_2PdCl_2$] were obtained commercially. Ru(*p*-cymene)Cl_2PPh_3 was prepared according to the literature.[32] 4-Cyanophenylacetylene was synthesised from 4-bromobenzonitrile and trimethylsilylacetylene with subsequent desilylation (i. 4-bromobenzonitrile, trimethylsilylacetylene, N,N-diisopropylamine, $Pd(PPh_3)_2Cl_2$, CuI, DME; ii. tetrabutylammonium fluoride, THF). Compounds **14**[29a], **15a–e**[28] and **17a**[45] were prepared according to the literature. The conjugated phosphoranes ethoxycarbonylmethylidenetriphenylphosphorane, benzoylmethylidenetriphenylphosphorane, and acetylmethylidenetriphenylphosphorane were synthesised following the literature methods (i) ethyl bromoacetate, bromoacetophenone or bromoacetone, triphenylphosphine, chloroform; (ii) aq. Na_2CO_3, CH_2Cl_2).[46-48]

In general, the diene-yne cyclisation reactions of terminal alkyenes with Ru(*p*-cymene)Cl_2PPh_3 were carried out under an inert atmosphere (argon), while diene-yne cyclisations of internal alkynes were run under a normal atmosphere (air). Deaerated solvents were used for the Sonogashira coupling reactions.

Ethyl 1-ethynylnapthalen-2-ylacrylate (**15f**). *Method A:* A solution of **15b** (350 mg, 1.4 mmol) and DDQ (567 mg, 2.5 mmol) in benzene (20 ml) was heated at 80 °C for 90 min. The mixture was then concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (hexane/ether 6:1) to give **15f** (225 mg, 65%) as a colourless solid; m.p. 108 °C. (Found: 250.0989. $C_{17}H_{14}O_2$ requires: M^+, 250.0994); ν_{max} (KBr/cm^{-1}) 3240, 2980, 1700, 1631, 1306, 1257, 1181, 1034, 989, 816, 755; δ_H (270 MHz, $CDCl_3$) 1.36 (3H, t, $^3J = 7.0$ Hz), 3.88 (1H, s), 4.30 (2H, q, $^3J = 7.0$ Hz), 6.59 (1H, d, $^3J = 15.9$ Hz), 7.52–7.83 (5H, m), 8.42 (1H, d, $^3J = 8.4$ Hz), 8.47 (1H, d, $^3J = 15.9$ Hz); δ_C (67.8 MHz, $CDCl_3$) 14.4, 60.6, 79.0, 89.2, 120.6, 121.3, 122.3, 127.1, 127.6, 128.1, 129.2, 133.5, 133.8, 135.1, 142.5, 166.9; MS (EI, 70 eV) *m/z* (%) 250 (M^+) (9.9), 176 (16), 58 (100). (Found: C, 81.75; H, 5.70. $C_{17}H_{14}O_2$ requires, C, 81.58; H, 5.64%).

Method B: A mixture of **15a** (973 mg, 3.0 mmol) and DDQ (1.36 g, 6.0 mmol) in toluene (30 ml) was held at reflux for 36 h. Thereafter, the cooled solution was concentrated *in vacuo*, and the residue was subjected to column chromatography on silica gel (hexane/ether 10:1) to give ethyl 1-trimethylsilylethynylnapthalen-2-ylacrylate (**15g**)

(830 mg, 85%) as a colourless oil; (Found: 323.1468. $C_{20}H_{23}O_2Si$ requires: MH^+, 323.1467 [FAB]); ν_{max} (neat/cm^{-1}) 3058, 2150, 1713, 1632, 1294, 1260, 1175, 1041, 846; δ_H (270 MHz, $CDCl_3$) 0.40 (9H, s, $SiMe_3$), 1.39 (3H, t, $^3J = 7.3$ Hz), 4.32 (2H, q, $^3J = 7.3$ Hz), 6.61 (1H, d, $^3J = 16.2$ Hz), 7.55–7.84 (3H, m), 8.40 (1H, m), 8.50 (1H, d, $^3J = 16.2$ Hz); δ_C (67.8 MHz, $CDCl_3$) 0.0, 14.3, 60.5, 100.3, 107.7, 120.2, 122.3, 122.4, 127.2, 127.4 (2C), 127.5, 128.1, 128.8, 133.5, 134.7, 142.8, 166.9; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 323 (MH^+) (100), 277 (32), 205 (29). A solution of **15g** (447 mg, 1.39 mmol) and TBAF (2.0 mmol) in THF (7 ml) was stirred for 2 h at RT. Water (30 ml) was then added and the mixture was extracted with chloroform (3 × 15 ml). The combined organic phase was dried over anhydrous $MgSO_4$, concentrated in vacuo, and the residue was subjected to column chromatography on silica gel (hexane/ether 5 : 1) to give **15f** (310 mg, 89%).

4-(1-Ethynyl-3,4-dihydronaphthalen-2-yl)-but-3-en-2-ol (**15h**): To a mixture of **15e** (112 mg, 0.5 mmol) and $CeCl_3$ (292 mg, 1.2 mmol) in MeOH (7 ml) was added $NaBH_4$ (38 mg, 1.0 mmol) at 0 °C. The resulting mixture was stirred at rt for 5 min. The solution was diluted carefully with water. The mixture was then extracted with $CHCl_3$ (3 × 10 ml). The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Column chromatography of the residue on silica gel (hexane/ether/$CHCl_3$ 1 : 1 : 1) gave **15h** (94 mg, 89%) as a colourless oil; (Found: 224.1202. $C_{16}H_{16}O$ requires: M^+, 224.1201); ν_{max} (neat)/cm^{-1} 3286, 3016, 2968, 2884, 2090, 1487, 1452, 1367, 1294, 1244, 1216, 1144, 1123, 1060, 968, 944, 762; δ_H (270 MHz, $CDCl_3$) 1.37 (3H, d, $^3J = 6.7$ Hz, CH_3), 1.56 (1H, bs, OH), 2.54 (2H, dd, $^3J = 8.6$ Hz, $^3J = 7.6$ Hz), 2.83 (2H, dd, $^3J = 8.6$ Hz, $^3J = 7.6$ Hz), 3.52 (1H, s), 4.53 (1H, dt, $^3J = 6.7$ Hz, $^3J = 6.7$ Hz), 6.07 (1H, dd, $^3J = 15.9$ Hz, $^3J = 6.7$ Hz), 7.13–7.25 (4H, m), 7.67 (1H, d, $^3J = 7.3$ Hz); δ_C (67.8 MHz, $CDCl_3$) 23.41, 23.73, 27.15, 69.16, 79.84, 85.37, 118.65, 125.80, 126.65, 127.02, 127.59, 129.18, 133.21, 135.00, 136.26, 142.61; MS (EI, 70 eV) *m/z* (%) 224 (M^+, 31), 179 (53), 165 (100).

4-(1-Ethynyl-3,4-dihydronaphthalen-2-yl)-2-acetylbut-3-en-2-ol (**15i**): To **15h** (85 mg, 0.38 mmol) in dry CH_2Cl_2 (3 ml) was added pyridine (68 mg, 0.90 mmol) and acetic anhydride (77 mg, 0.76 mmol). The solution was stirred for 5 h at rt. Water (10 ml) was then added, and the mixture was extracted with chloroform (2 × 10 ml) The organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Column chromatography on silica gel (hexane/ether/$CHCl_3$ 2.5 : 1 : 1) gave **15i** (90 mg, 89%) as a slowly crystallising, colourless oil; (Found: 266.1304. $C_{18}H_{18}O_2$ requires: M^+, 266.1307); ν_{max} (neat/cm^{-1}) 3284 (sharp peak), 3024, 2980, 2934, 2090 (weak), 1733, 1452, 1371, 1240, 1156, 1041, 970, 766; δ_H (270 MHz, $CDCl_3$) 1.41 (3H, d, $^3J = 6.5$ Hz, $C(OAc)C\underline{H}_3$), 3.53 (1H, s), 2.08 (3H, s, $OCOC\underline{H}_3$); 2.53 (2H, dd, $^3J = 8.1$ Hz, $^3J = 7.6$ Hz), 2.83 (2H, dd, $^3J = 8.1$ Hz, $^3J = 7.6$ Hz), 5.56 (1H, dt, $^3J = 6.8$ Hz, $^3J = 6.5$ Hz), 5.99 (1H, dd, $^3J = 15.9$ Hz, $^3J = 6.8$ Hz), 7.11–7.24 (4H, m), 7.68 (1H, d, $^3J = 7.6$ Hz); δ_C (67.8 MHz, $CDCl_3$) 20.41, 21.38, 23.59, 27.09, 71.12, 79.68, 85.52, 119.21, 125.90, 126.67, 127.00, 127.69, 130.85, 131.33, 133.17, 135.04, 142.20, 170.32; MS (EI, 70 eV) *m/z* (%) 266 (M^+, 41), 224, 206 (89), 191 (100), 178 (59), 165 (71).

Ethyl 9,10-dihydrophenanthrene-2-carboxylate (**16a**): A mixture of **15b** (252 mg, 1.0 mmol), Ru(*p*-cymene)Cl_2PPh_3 (28.4 mg, 5 mol%) and NH_4PF_6 (10 mol%, 16.3 mg) in CH_2Cl_2 (13 ml) was stirred at 45 °C for 90 h under inert atmosphere. The crude reaction mixture was then concentrated and the residue was subjected to column chromatography on silica gel (hexane/ether 8 : 1) to yield **16a** (104 mg, 41%) as an oil. ν_{max} (neat/cm^{-1}) 2960, 1720, 1600; δ_H (270 MHz, $CDCl_3$) 1.41 (3H, t, $^3J = 7.1$ Hz), 2.88–2.95 (4H, m), 4.39 (2H, q, $^3J = 7.1$ Hz), 7.25–7.35 (3H, m), 7.79 (2H, d, $^3J = 7.9$ Hz), 7.91 (1H, s), 7.97 (1H, dd, $^3J = 7.9$ Hz, $^4J = 1.9$ Hz); δ_C (99.45 MHz, $CDCl_3$) 14.37, 28.81 (2C), 60.86, 123.57, 124.31, 128.23 (2C), 128.37, 129.02, 129.22 (2C), 133.57, 137.28, 137.94, 138.83, 166.61 (CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 253 (MH^+) (7.5).

2-Acetyl-9,10-dihydrophenanthrene (**16b**): **15e** (33 mg, 0.15 mmol) was added to a solution of Ru(*p*-cymene)Cl_2PPh_3 (8.6 mg, 15 µmol) and ammonium hexafluorophosphate [NH_4PF_6] (5.0 mg, 30 µmol) in CH_2Cl_2 (3 ml). The solution was stirred for 27 h under reflux. The crude material was then subjected to column chromatography on silica gel (hexane/ether/$CHCl_3$ 4 : 1 : 1) to give **16b** (16 mg, 48%) as a colourless solid; (Found: MH^+, 223.1122. $C_{16}H_{15}O$ requires: MH^+, 223.1123); ν_{max} (KBr)/cm^{-1} 2932, 1679, 1604, 1555, 1483, 1417, 1357, 1273, 1253, 1181, 960, 833, 771, 734, 671; δ_H (270 MHz, $CDCl_3$) 2.61 (3H, s, $COCH_3$), 2.86–2.98 (4H, m), 7.21–7.31 (3H, m), 7.78–7.91 (4H, m); δ_C (67.8 MHz, $CDCl_3$) 26.6, 28.8, 28,9, 123.8, 124.4, 127.2, 128.1, 128.4, 128.6, 133.5, 135.8, 137.5, 138.0, 139.2, 197.8; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 223 (47) [MH^+], 222 (28) [M^+].

Ethyl phenanthrene-2-carboxylate (**16c**): *Method A*: **15f** (75 mg, 0.3 mmol) was added to a solution of Ru(*p*-cymene)Cl_2PPh_3 (8.5 mg, 15 µmol) and NH_4PF_6 (4.9 mg, 30 µmol) in CH_2Cl_2 (4 ml). The solution was stirred for 50 h at reflux. The crude mixture was subjected to column chromatography on silica gel (hexane/ether 4 : 1) to give **16c** (30 mg, 40%) as a colourless solid; (Found: M^+, 250.0990. $C_{17}H_{14}O_2$ requires: M^+, 250.0994); ν_{max} (KBr)/cm^{-1}2980, 2924, 1714, 1627, 1601, 1529, 1494, 1386, 1367, 1308, 1191, 1110, 1092, 1027, 812, 746; δ_H (270 MHz, $CDCl_3$) 1.47 (3H, t, $^3J = 7.0$ Hz), 4.49 (2H, q, $OC\underline{H}_2$, $^3J = 7.0$ Hz), 7.62–7.73 (2H, m), 7.79 (1H, d, $^3J = 9.2$ Hz), 7.83 (1H, d, $^3J = 9.2$ Hz), 7.93 (1H, m), 8.27 (1H, dd, $^3J = 8.4$ Hz, $^4J = 1.9$ Hz), 8.62 (1H, d, $^4J = 1.9$ Hz), 8.70–8.75 (2H, m); δ_C (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135) 14.42 (+ , CH_3), 61.13 (–), 122.86 (+ , CH), 123.28 (+ , CH), 126.47 (+ , CH), 126.94 (+ , CH), 127.24 (+ , CH), 127.64 (+ , CH), 127.74 (+ , CH), 128.34 (C_{quat}), 128.70 (+ , CH), 129.76 (C_{quat}), 130.78 (+ , CH), 131.43 (C_{quat}), 132.92 (C_{quat}), 133.30 (C_{quat}), 166.70 (C_{quat}, C=O); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 251 (6.7) [MH^+], 250 (6.9) [M^+]. *Method B*: A mixture of **16a** (104 mg, 0.41 mmol) and DDQ (227 mg, 1.0 mmol) in benzene (10 ml) was kept at reflux for 10 h. The reaction mixture was concentrated *in vacuo* and the residue was subjected to column chromatography on silica gel (hexane/ether 2:1) to give **16c** (71 mg, 61%).

9,10-Dihydrophenanthrene-2-carboxylic acid (**16a–H**): To a mixture of **16a** (70 mg, 0.28 mmol), tert-KOBu (400 mg, 3.6 mmol) in ether (10 ml) was added water (0.1 ml) and the resulting mixture was stirred for 12 h at RT. Water (15 ml) was then added and the solution was acidified with conc. aq. HCl. Then, the mixture was extracted with chloroform (3 × 15 ml), the organic phase dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Column chromatography of the residue on silica gel (ether) gave **16a–H** (43 mg, 68%) as a colourless solid, m.p. 213 °C (lit. 214–215 °C); (Found: M^+, 224.0834. $C_{15}H_{12}O_2$ requires: M^+, 224.0837); ν_{max} (KBr)/cm^{-1} 2924, 1685, 1611, 1427, 1295, 1255, 1190, 934, 748; δ_H (270 MHz, $CDCl_3$) 2.87–2.94 (4H, m), 7.28–7.38 (3H, m), 7.61–7.67 (2H, m), 7.99 (1H, d, $^4J = 2.4$ Hz), 8.06 (1H, dd, $^3J = 8.3$ Hz, $^4J = 2.4$ Hz); δ_C (67.8 MHz, $CDCl_3$) 28.77, 28.82, 123.75, 124.46, 127.18, 127.68, 128.35, 128.68, 128.97, 129.91, 133.44, 137.48, 138.09, 139.86, 171.44; MS (70 eV) *m/z* (%): 224 (78) [M^+], 179 (100).

2-(1-Acetoxyethyl)-9,10-dihydro-phenanthrene (**16d**): **15i** (90 mg, 0.3[4] mmol) was added to a solution of Ru(*p*-cymene)Cl_2PPh_3 (8.5 mg, 15 µmol) and NH_4PF_6 (4.9 mg, 30 µmol) in CH_2Cl_2 (5 ml). The solution was stirred for 36 h at reflux. The crude mixture was subjected to column chromatography on silica gel (hexane/ether 4 : 1) to give **16c** (65 mg, 72%); oil; (Found: 266.1305. Calcd for $C_{18}H_{18}O_2$: 266.1307); ν_{max} (neat/cm^{-1}) 2930, 1735, 1369, 1240, 1063, 1024, 945, 830, 770, 735; δ_H (270 MHz, $CDCl_3$) 1.57 (3H, d, $^3J = 6.7$ Hz), 2.11 (3H, s, CH_3), 2.88 (4H, bs), 5.89 (1H, q, $^3J = 6.7$ Hz); 7.22–7.33 (5H, m), 7.72 (2H, m); δ_C (67.8 MHz, $CDCl_3$) 21.41, 22.06, 28.94, 29.09, 72.19, 123.68, 123.82, 124.71, 125.95, 126.93, 127.44, 128.10, 134.12, 134.22, 137.32, 137.94, 140.62, 170.39; MS (EI, 70 eV) *m/z* (%) 266 (M^+, 100), 224 (22), 207 (75), 178 (39).

1-(4-Cyanophenylethynyl)-2-ethoxycarbonylethenyl-3,4-dihydronaphthalene (**15j**): A solution of **17a** (280 mg, 0.92 mmol), 4-cyanophenylacetylene (234 mg, 1.84 mmol), $Pd(PPh_3)_2Cl_2$ (20 mg, 2.8×10^{-5} mol), CuI (10 mg, 5.2×10^{-5} mol) and dry diisopropylamine (DIPA, 0.8 ml) in anhydrous DME (8 ml) was kept at 80 °C for 19 h. The reaction mixture was cooled, water (20 ml) was added, and the mixture was extracted with chloroform (3 × 15 ml). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Column chromatography of the residue on silica gel (hexane/ether/$CHCl_3$ 2 : 1 : 1) gave **15j** (199 mg, 61%) as a colourless solid; m.p. 116 °C; (Found: M^+, 353.1415. $C_{24}H_{19}O_2N$ requires M, 353.1416); ν_{max} (KBr/cm^{-1}) 3060, 3020, 2950, 2198, 756; δ_H (270 MHz, $CDCl_3$) 1.35 (3H, t, $^3J = 7.0$ Hz), 2.63 (2H, m), 2.91 (2H, m), 4.28 (2H, q, $^3J = 7.0$ Hz), 6.18 (1H, d, $^3J = 15.7$ Hz), 7.20 (1H, m), 7.26–7.30 (2H, m), 7.66 (2H, d, $^3J = 8.6$ Hz), 7.71 (2H, d, $^3J = 8.6$ Hz), 7.74 (1H, m), 8.28 (1H, d, $^3J = 15.7$ Hz); δ_C (67.8 MHz, $CDCl_3$) 14.3 (CH_3), 22.6 (CH_2), 26.9 (CH_2), 60.6 (OCH_2), 89.3 (C_{quat}), 97.9 (C_{quat}), 111.9 (C_{quat}), 118.4 (C_{quat}), 119.8 (CH), 125.2 (C_{quat}), 126.6 (CH), 126.9 (CH), 127.5 (CH), 127.7 (C_{quat}), 129.1 (CH), 132.1 (2C, CH), 132.2 (2C, CH), 132.4 (C_{quat}), 135.8 (C_{quat}), 140.7 (C_{quat}), 142.9 (CH), 167.1 (C_{quat}, CO); MS (EI, 70 eV) *m/z* = 353 (M^+) (100), 325 (69), 280 (83), 277 (82).

1-(4-Cyanophenylethynyl)-2-ethoxycarbonylethenyl-naphthalene (**15k**): A mixture of **15j** (144 mg, 0.41 mmol) and DDQ (167 mg, 0.72 mmol) in benzene (6 ml) was kept at 80 °C for 12 h. Direct column chromatography of the cooled mixture on silica gel (hexane/ether/$CHCl_3$ 1 : 1 : 1) yielded **15k** (122 mg, 85%) as pale yellow needles; m.p. 167 °C; (Found: M^+, 351.1263. $C_{24}H_{17}O_2N$ requires M, 351.1259); ν_{max} (KBr/cm^{-1}) 3060, 2978, 2924, 2200, 814, 756; δ_H (270 MHz, $CDCl_3$) 1.38 (3H, t, ^3J = 7.0 Hz), 4.32 (2H, q, ^3J = 7.0 Hz), 6.63 (1H, d, ^3J = 16.2 Hz), 7.56–7.87 (9H, m), 8.42 (1H, d, ^3J = 8.4 Hz), 8.53 (1H, d, ^3J = 16.2 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.4 (CH_3), 60.7 (OCH_2), 89.3 (C_{quat}), 99.4 (C_{quat}), 112.0 (C_{quat}), 118.4 (C_{quat}), 120.5 (CH), 121.3 (C_{quat}), 122.5 (CH), 126.8 (CH), 127.7 (CH), 127.8 (CH), 128.3 (CH), 129.6 (CH), 132.1 (2C, CH), 132.2 (2C, CH), 133.3 (C_{quat}), 133.6 (C_{quat}), 134.9 (C_{quat}), 142.4 (CH), 166.8 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) = 351 (M^+) (78), 277 (100), 249 (30), 130 (52) (Found: C, 82.21; H, 4.81, N, 4.06. $C_{24}H_{17}O_2N$ requires, C, 82.03; H, 4.88; N, 3.99%).

1-(4-Methylphenylethynyl)-2-ethoxycarbonylethenyl-3,4-dihydronaphthalene (**15l**): A solution of **17a** (504 mg, 1.63 mmol), 4-methylphenylacetylene (359 mg, 3.10 mmol), $Pd(PPh_3)_2Cl_2$ (20 mg, 2.8 × 10^{-5} mol), CuI (4 mg, 2.1 × 10^{-5} mol) and dry diisopropylamine (DIPA, 0.44 ml) in anhydrous DME (10 ml) was kept at 70 °C for 77 h. The reaction mixture was cooled, water (40 ml) was added, and the mixture was extracted with chloroform (3 × 30 ml). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Column chromatography of the residue on silica gel (hexane/ether/$CHCl_3$ 8:1:1) gave **15l** (437 mg, 78%) as a slowly crystallising oil; (Found: MH^+, 343.1697. $C_{24}H_{23}O_2$ requires MH, 351.1698 [FAB]); ν_{max} (neat/cm^{-1}) 3063, 2956, 2198, 1710, 1610, 981, 756; δ_H (270 MHz, $CDCl_3$) 1.35 (3H, t, ^3J = 7.0 Hz, CH_3), 2.39 (3H, s, CH_3), 2.60 (2H, m), 2.86 (2H, m), 4.27 (2H, q, ^3J = 7.0 Hz, OCH_2), 6.12 (1H, d, ^3J = 15.7 Hz), 7.16–7.29 (3H, m), 7.18 (2H, d, ^3J = 8.1 Hz), 7.52 (2H, d, ^3J = 8.1 Hz), 7.83 (1H, m), 8.36 (1H, d, ^3J = 15.7 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.3 (CH_3), 21.6 (CH_3), 23.5 (CH_2), 27.1 (CH_2), 60.4 (OCH_2), 84.7 (C_{quat}, ethynyl), 100.5 (C_{quat}, ethynyl), 118.8 (CH), 119.9 (C_{quat}), 126.3 (C_{quat}), 126.8 (CH), 126.9 (CH), 127.3 (CH), 128.7 (CH), 129.2 (2C, CH), 131.6 (2C, CH), 133.1 (C_{quat}), 136.0 (C_{quat}), 143.5 (CH), 138.7 (C_{quat}), 139.0 (C_{quat}), 143.6 (CH), 167.3 (C_{quat}, CO); MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) 343 (MH^+) (1.2).

1-Phenylethynyl-2-ethoxycarbonylethenylnaphthalene (**15m**): Method A. A solution of **15c** (231 mg, 0.70 mmol) and dichlorodicyanobenzoquinone (DDQ, 286 mg, 1.26 mmol) in benzene (9 ml) was kept at reflux for 12 h. The cooled solution was subjected directly to column chromatography on silica gel (hexane/ether/$CHCl_3$ 6 : 1 : 1) to furnish **15m** (109 mg, 48%) as a slowly crystallising, colourless oil; (Found: M^+, 326.1307. $C_{23}H_{18}O_2$ requires M, 326.1307); ν_{max} (KBr/cm^{-1}) 3056, 2978, 2924, 2202, 1712, 1598, 1303, 1259, 1176, 1038, 814, 753; δ_H (270 MHz, $CDCl_3$) 1.38 (3H, t, ^3J = 7.0 Hz), 4.32 (2H, q, ^3J = 7.0 Hz), 6.63 (1H, d, ^3J = 15.9 Hz), 7.41–7.85 (10H, m), 8.51 (1H, d, ^3J = 7.8 Hz), 8.61 (1H, d, ^3J = 15.9 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.3 (CH_3), 60.6 (CH_2), 85.3 (C_{quat}), 101.6 (C_{quat}), 120.0 (CH), 122.5 (CH), 122.6 (C_{quat}), 123.0 (C_{quat}), 127.2 (CH), 127.5 (CH), 127.6 (CH), 128.2 (CH), 128.5 (2C, CH), 128.7 (CH), 128.8 (CH), 131.7 (2C, CH), 133.4 (C_{quat}), 133.6 (C_{quat}), 134.1 (C_{quat}), 142.9 (CH), 167.1 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) = 326 (51) (M^+), 298 (51), 252 (100), 105 (48). *Method B*: A mixture of **23a** (260 mg, 0.85 mmol), phenylacetylene (156 mg, 1.53 mmol), CuI (15 mg, 7.8 × 10^{-5} mol), $Pd(PPh_3)_2Cl_2$ (30 mg, 4.3 × 10^{-5} mol), and dry DIPA (0.9 ml) in dry DME (9 ml) was kept at 70 °C for 19 h. To the cooled solution was given water (15 ml) and the mixture was extracted with chloroform (2 × 20 ml). The combined organic phase was dried over anhydrous $MgSO_4$, concentrated *in vacuo* and separated over column chromatography on silica gel (hexane/ether/$CHCl_3$ 5 : 1 : 1) to give **15m** (202 mg, 73%).

Ethyl (E)-3-(1-bromonaphthalen-2-yl)-acrylate (**17b**): A mixture of 1-bromo-2-formylnaphthalene (**18**, 765 mg, 3.24 mmol) and ethoxycarbonylmethylidenetriphenylphophorane (2.81 g, 8.09 mmol) in chloroform (3 ml) was placed into a beaker closed with Saran Wrap® and was heated in an oven at 100 °C for 2 h. Direct column chromatography of the cooled reaction mixture on silica gel (hexane/$CHCl_3$/ether 5:1:1) gave **17b** (876 mg, 89%) as a colourless solid; m.p. 124 °C; (Found: M^+, 304.0095. $C_{15}H_{13}O_2{}^{79}Br$ requires M, 304.0099); ν_{max} (KBr/cm^{-1}) 3057, 1700, 1596, 810, 770, 751; δ_H (270 MHz, $CDCl_3$) 1.37 (3H, t, ^3J = 7.0 Hz, CH_3), 4.31 (2H, q, ^3J = 7.0 Hz, OCH_2), 6.48 (1H, d, ^3J = 15.9 Hz), 7.54–7.82 (5H, m), 8.37 (1H, m), 8.38 (1H, d, ^3J = 15.9 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.3 (CH_3), 60.6 (OCH_2), 121.6 (CH), 123.9 (CH), 126.8 (C_{quat}), 127.7 (CH), 127.9 (CH), 128.0 (CH), 128.1 (CH), 128.2 (CH), 132.1 (C_{quat}), 132.6 (C_{quat}), 134.9 (C_{quat}), 143.9 (CH), 166.5 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 306 ([^{81}Br]M^+), 304 ([^{79}Br]M^+), 225 (45), 197 (100).

1-(E/Z)-Phenylmethylene-2-ethoxycarbonyl-1H-benz[e]-4,5-dihydroindene (***E*/*Z*-18a**): A solution of **15c** (132 mg, 0.40 mmol) and $Pt(PPh_3)_4$ (35 mg, 2.8 × 10^{-5} mol) in mesitylene (3 ml) was kept at 135 °C for 12 h. The cooled reaction mixture was separated over silica gel (eluant, initially hexane, then hexane/$CHCl_3$/ether 10 : 1 : 1) to give ***Z*-18a** as a deep-red oil (41 mg, 31%); (Found: M^+, 328.1458. $C_{23}H_{20}O_2$ requires M, 328.1463); ν_{max} (neat/cm^{-1}) 2950, 1720, 749; δ_C (67.8 MHz, $CDCl_3$) 14.4 (CH_3), 23.7 (CH_2), 29.5 (CH_2), 59.8 (OCH_2), 125.4 (CH), 125.7 (CH), 127.0 (CH), 127.1 (C_{quat}), 127.2 (CH), 127.5 (C_{quat}), 128.1 (2C, CH), 129.2 (CH), 131.7 (C_{quat}), 132.3 (2C, CH), 135.4 (C_{quat}), 135.9 (C_{quat}), 136.4 (C_{quat}), 146.1 (C_{quat}), 164.1 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) = 328 (M^+) (100), 255 (42), 253 (33), 181 (12), 165 (13), 149 (18), 77 (27); and ***E*-18a** as a red oil (10 mg, 8%); (Found: M^+, 328.1462. $C_{23}H_{20}O_2$ requires M, 328.1463); ν_{max} (neat/cm^{-1}) 2956, 1710, 758; δ_H (270 MHz, $CDCl_3$) 0.78 (3H, t, ^3J = 7.0 Hz, CH_3), 2.56 (2H, m), 2.85 (2H, m), 3.67 (2H, q, ^3J = 7.0 Hz, OCH_2), 7.17 (1H, m), 7.25–7.44 (8H, m), 7.55 (1H, d, ^3J = 7.3 Hz), 8.00 (1H, s); δ_C (150.9 MHz, $CDCl_3$) 13.6 (CH_3), 23.1 (CH_2), 29.7 (CH_2), 60.4 (OCH_2), 125.0 (CH), 126.6 (CH), 126.9 (CH), 127.8 (C_{quat}), 128.3 (CH, 2C), 128.5 (CH), 129.1 (CH), 131.1 (CH, 2C), 131.9 (C_{quat}), 135.0 (C_{quat}), 137.6 (C_{quat}), 137.9 (C_{quat}), 139.3 (C_{quat}), 140.8 (C_{quat}), 141.7 (CH), 143.3 (CH), 166.0 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) = 328 (M^+) (100), 252 (46), 181 (29), 77 (52).

1-(E/Z)-4-Cyanophenylmethylene-2-ethoxycarbonyl-1H-benz[e]-4,5-dihydroindene (***E*/*Z*-18b**): A mixture of **15j** (180 mg, 0.5 mmol) and $Pt(PPh_3)_4$ (33 mg, 2.6 × 10^{-5} mol) in mesitylene (4 ml) was kept at 135 °C for 12 h. Direct column chromatography of the cooled reaction mixture on silica gel (initially hexane/$CHCl_3$/ether 5 : 1 : 1 to elute mesitylene, then hexane/$CHCl_3$/ether 3 : 1 : 1) afforded ***Z*-18b** (50 mg, 28%) as a dark red solid; (Found: M^+, 353.1420. $C_{24}H_{19}O_2N$ requires M, 353.1416); ν_{max} (KBr/cm^{-1}) 2958, 2200, 1723; δ_H (270 MHz, $CDCl_3$) 1.37 (3H, t, ^3J = 7.3 Hz), 2.52 (2H, m), 2.86 (2H, m), 4.31 (q, 2H, ^3J = 7.3 Hz), 6.33 (1H, d, ^3J = 7.0 Hz), 6.61 (1H, m), 6.94 (1H, m), 7.13 (1H, d, ^3J = 6.7 Hz), 7.31 (1H, s), 7.44 (4H, vs), 8.62 (1H, s); δ_C (67.8 MHz, $CDCl_3$) 14.4 (CH_3), 23.6 (CH_2), 29.3 (CH_2), 60.0 (OCH_2), 112.1 (C_{quat}), 118.6 (C_{quat}), 125.5 (CH), 126.3 (CH), 126.8 (CH), 127.2 (C_{quat}), 127.6 (CH), 129.2 (C_{quat}), 131.0 (C_{quat}), 131.7 (2C, CH), 132.4 (2C, CH), 135.0 (C_{quat}), 136.0 (C_{quat}), 139.6 (CH), 140.9 (C_{quat}), 141.6 (CH), 163.8 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) = 353 (M^+) (100), 280 (38), 278 (31); and ***E*-18b** (12 mg, 7%) as a red oil; (Found: M^+, 353.1416. $C_{24}H_{19}O_2N$ requires M, 353.1416); ν_{max} (neat/cm^{-1}) 2965, 2205, 1715; δ_H (270 MHz, $CDCl_3$) 0.94 (3H, t, ^3J = 7.3 Hz), 2.58 (2H, m), 2.87 (2H, m), 7.11–7.72 (5H, m), 7.68 (4H, vs), 7.90 (1H, s); MS (EI, 70 eV) *m/z* (%) = 353 (M^+) (11), 280 (15), 141 (34).

1-(E/Z)-p-Tolylmethylene-2-ethoxycarbonyl-1H-benz[e]-4,5-dihydroindene (***E*/*Z*-18c**): A mixture of **15l** (290 mg, 0.85 mmol) and $Pt(PPh_3)_4$ (56 mg, 4.5.10^{-5} mol) in mesitylene (6 ml) was kept at 135 °C for 48 h. Column chromatography of the residue on silica gel (hexane/ether/$CHCl_3$ 20 : 1 : 1) gave **Z-18c** (69 mg, 24%) as a red oil; (Found: M^+, 342.1628. $C_{24}H_{22}O_2$ requires: M^+, 342.1620); ν_{max} (neat/cm^{-1}) 2954, 1722, 1250, 1220, 752; δ_H (270 MHz, $CDCl_3$) 1.37 (3H, t, ^3J = 7.0 Hz), 2.29 (3H, s, CH_3), 2.52 (2H, m), 2.86 (2H, m), 4.30 (2H, q, ^3J = 7.0 Hz), 6.54 – 6.65 (2H, m), 6.91 (1H, m), 6.97 (2H, d, ^3J = 7.8 Hz), 7.11 (1H, d, ^3J = 7.8 Hz), 7.27 (1H, s), 7.28 (2H, d, ^3J = 7.8 Hz), 8.66 (1H, s); δ_C (67.8 MHz, $CDCl_3$) 14.4 (CH_3), 21.4 (CH_3), 23.8 (CH_2), 29.6 (CH_2), 59.8 (OCH_2), 125.4 (CH), 125.6 (CH), 127.0 (CH), 127.2 (CH), 128.8 (2C, CH), 129.2 (C_{quat}), 131.3 (C_{quat}), 132.0 (C_{quat}), 132.6 (2C, CH), 133.6 (C_{quat}), 135.9 (C_{quat}), 137.8 (C_{quat}), 139.7 (C_{quat}), 139.8 (CH), 143.6 (CH), 145.9 (C_{quat}), 164.2 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) = 342 (66) (M^+), 297 (15), 269 (25), 253 (24), 149 (40), 58 (100) and ***E*-18c** (29 mg, 10%) as a slowly solidifying red oil; (Found: M^+, 342.1628. $C_{24}H_{22}O_2$ requires: M^+, 342.1620); ν_{max} (neat/cm^{-1}) 2960, 1715, 1245, 750; δ_H (270 MHz, $CDCl_3$) 0.83 (3H, t, ^3J = 7.3 Hz, CH_3), 2.39 (3H, s, CH_3), 2.57 (2H, m), 2.83 (2H, m), 3.74 (2H, q, ^3J = 7.3 Hz, OCH_2), 7.17–7.30 (5H, m), 7.20 (2H, d, ^3J = 8.1 Hz), 7.33 (2H, d, ^3J = 8.1 Hz), 7.55 (1H, d, ^3J = 7.3 Hz), 7.99 (1H, s); δ_C (67.8 MHz, $CDCl_3$) 13.7 (CH_3), 21.6 (CH_3), 22.9 (CH_2), 29.6 (CH_2), 60.2 (OCH_2), 125.0 (CH), 126.4 (CH), 126.8 (CH), 127.6 (C_{quat}), 128.3 (CH), 128.5 (C_{quat}), 128.9 (2C, CH), 131.3 (2C, CH), 131.9 (C_{quat}), 134.9 (C_{quat}), 135.0 (C_{quat}), 137.6 (C_{quat}), 139.4 (C_{quat}), 140.3 (C_{quat}), 141.9 (CH), 142.8 (CH), 167.5 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) = 342 (100) (M^+), 269 (50).

1-(E/Z)-Phenylmethylene-2-ethoxycarbonyl-1H-benz[e]indene (***E*/*Z*-18d**): A solution of **15k** (109 mg, 0.46 mmol) and $Pt(PPh_3)_4$ (30 mg, 2.5·10^{-5} mol) in mesitylene (3 ml) was kept at 135 °C for 12 h. Direct chromatography of the cooled reaction mixture on silica gel (hexane/$CHCl_3$/ether 5:1:1) gave ***Z*-18d** (25 mg, 23%) as a red-orange solid; m.p. 121 °C; (Found: M^+, 326.1310. $C_{23}H_{18}O_2$ requires M, 326.1307); ν_{max} (KBr/cm^{-1}) 2952, 1718, 1225, 752; δ_H (270 MHz, $CDCl_3$) 1.42 (3H, t, ^3J = 7.3 Hz), 4.36 (2H, q, ^3J = 7.3 Hz), 6.87 (1H, m), 7.18–7.33 (5H, m), 7.42–7.44 (2H, m), 7.53 (1H, d,

^3J = 8.1 Hz), 7.70–7.77 (3H, m), 8.71 (1H,s); δ_C (67.8 MHz, $CDCl_3$) 14.4 (CH_3), 60.3 (OCH_2), 121.4 (CH), 125.1 (CH), 125.4 (CH), 127.5 (CH), 128.4 (C_{quat}), 128.6 (2C, CH), 128.7 (CH), 128.8 (CH), 130.1 (CH), 131.2 (2C, CH), 131.8 (C_{quat}), 133.2 (C_{quat}), 133.8 (C_{quat}), 137.5 (C_{quat}), 138.7 (C_{quat}), 138.8 (CH), 140.1 (CH), 140.4 (C_{quat}), 164.5 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) = 326 (100) (M^+), 281 (23), 252 (73) and ***E*-18d** (9 mg, 8%) as a red-orange oil; (Found: M^+, 326.1306. $C_{23}H_{18}O_2$ requires M, 326.1307); ν_{max} (neat/cm^{-1}) 2953, 1717, 1220, 749; δ_H (270 MHz, $CDCl_3$) 0.87 (3H, t, ^3J = 7.3 Hz), 3.67 (2H, q, ^3J = 7.3 Hz), 7.38–7.61 (9H, m), 7.76 (1H, d, ^3J = 8.1 Hz), 7.87 (1H, d, ^3J = 7.8 Hz), 8.54 (1H, s), 8.56 (1H, d, ^3J = 8.9 Hz); δ_C (67.8 MHz, $CDCl_3$) 13.6 (CH_3), 60.6 (OCH_2), 121.2 (CH), 123.5 (CH), 125.0 (CH), 127.5 (CH), 128.3 (2C, CH), 128.5 (CH), 129.3 (CH), 130.0 (CH), 130.7 (2C, CH), 132.3 (C_{quat}), 132.6 (C_{quat}), 133.9 (C_{quat}), 134.3 (C_{quat}), 138.4 (C_{quat}), 138.5 (C_{quat}), 139.3 (CH), 139.9 (C_{quat}), 140.8 (CH), 166.4 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) = 326 (M^+) (52), 252 (33), 149 (42).

1-(E/Z)-4-Cyanophenylmethylene-2-ethoxycarbonyl-1H-benz[e] indene (***E*/*Z*-18e**): A mixture of **15k** (144 mg, 0.40 mmol) and $Pt(PPh_3)_4$ (28 mg, 2.3 × 10^{-5} mol) in mesitylene (3 ml) was kept at 135 °C for 48 h. Column chromatography of the cooled mixture on silica gel (hexane/ether/$CHCl_3$) gave ***Z*-18e** (29 mg, 20%) as a red-orange solid; m.p. 190 °C; (Found: M^+, 351.1257. $C_{24}H_{17}O_2N$ requires M, 351.1259); ν_{max} (KBr/cm^{-1}) 2954, 2205, 1725, 1225, 748; δ_H (270 MHz, $CDCl_3$) 1.41 (3H, t, ^3J = 7.0 Hz), 4.37 (2H, q, ^3J = 7.0 Hz), 6.91 (1H, m), 7.10 (1H, d, ^3J = 8.9 Hz), 7.25–7.28 (1H, m), 7.48–7.55 (5H, m), 7.74–7.81 (3H, m), 8.63 (1H, s); δ_C (67.8 MHz, $CDCl_3$) 14.4 (CH_3), 60.4 (OCH_2), 111.8 (C_{quat}), 118.7 (C_{quat}), 121.5 (CH), 125.5 (CH), 125.9 (CH), 127.0 (CH), 128.1 (C_{quat}), 129.1 (CH), 130.9 (CH), 131.6 (2C, CH), 131.7 (C_{quat}), 132.2 (2C, CH), 132.4 (C_{quat}), 134.0 (C_{quat}), 136.5 (CH), 140.2 (CH), 140.8 (C_{quat}), 141.1 (C_{quat}), 142.1 (C_{quat}), 164.2 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) = 351 (M^+) (100), 323 (16), 306 (24), 277 (56); and ***E*-18e** as a red-orange oil (10 mg, 7%); (Found: M^+, 351.1255. $C_{24}H_{17}O_2N$ requires M, 351.1259); ν_{max} (neat/cm^{-1}) 2952, 2203, 1715, 753; δ_H (270 MHz, $CDCl_3$) 0.99 (3H, t, ^3J = 7.0 Hz), 3.76 (2H, q, ^3J = 7.0 Hz), 7.43–7.71 (8H, m), 7.80 (1H, d, ^3J = 8.4 Hz), 7.89 (1H, d, ^3J = 8.1 Hz), 8.41 (1H, s), 8.48 (1H, d, ^3J = 8.9 Hz); δ_C (67.8 MHz, $CDCl_3$) 13.8 (CH_3), 60.7 (OCH_2), 111.6 (C_{quat}), 118.6 (C_{quat}), 121.3 (CH), 123.3 (CH), 125.4 (CH), 127.9 (CH), 129.1 (C_{quat}), 129.2 (C_{quat}), 130.1 (2C, CH), 131.0 (2C, CH), 131.8 (2C, CH), 131.9 (C_{quat}), 132.3 (C_{quat}), 134.5 (C_{quat}), 138.7 (C_{quat}), 136.0 (CH), 142.1 (C_{quat}), 142.9 (CH), 165.3 (C_{quat}, CO); MS (Ei, 70 eV) *m/z* (%) = 351 (M^+) (5.9), 249 (9.9).

17-Bromo-16-ethoxycarbonylethenylestra-1,3,5(10),16-tetraen-3-ol (**20**): A mixture of **19** (145 mg, 0.40 mmol) and ethoxycarbonylmethylidenetriphenylphosphorane (224 mg, 0.64 mmol) in chloroform (1.5 ml) was placed into a beaker closed with Saran Wrap® and was heated in an oven at 100 °C for 1 h 40 min. Direct column chromatography of the cooled reaction mixture on silica gel (hexane/$CHCl_3$/ether 3:2:2) gave **20** (131 mg, 76%); (Found: MH^+, 431.1216. $C_{23}H_{28}O_3{}^{79}Br$ requires MH, 431.1222 [FAB]); ν_{max} (KBr/cm^{-1}) 3400–2960 (bs, OH), 1715, 712; δ_H (270 MHz, $CDCl_3$) 0.90 (3H, s, CH_3), 1.32 (3H, t, ^3J = 7.0 Hz), 1.45–2.40 (10H, m), 2.45 (1H, dd, ^2J = 14.6 Hz, ^3J = 6.5 Hz), 2.86 (2H, m), 4.23 (2H, q, ^3J = 7.0 Hz), 4.58 (1H, s, OH), 5.91 (1H, d, ^3J = 15.7 Hz), 6.58 (1H, d, ^4J = 2.7 Hz), 6.63 (1H, dd, ^3J = 8.4 Hz, ^4J = 2.7 Hz), 7.14 (1H, d, ^3J = 8.4 Hz), 7.58 (1H, d, ^3J = 15.7 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.3, 15.5, 26.1, 27.1, 29.4, 31.0, 34.7, 37.4, 44.2, 50.9, 53.3, 60.5, 112.7, 115.3, 120.4, 126.2, 132.3, 135.9, 138.0, 138.5, 143.8, 153.4, 167.1; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 433 ([^{81}Br]MH^+) (0.9), 431 ([^{79}Br]MH^+) (1.2).

17-Phenylethynyl-16-ethoxycarbonylethenylestra-1,3,5(10),16-tetraen-3-ol (**21**): A mixture of **20** (128 mg, 0.30 mmol), phenylacetylene (0.15 ml, 141 mg, 1.38 mmol), $Pd(PPh_3)_2Cl_2$ (5 mg, 7·10^{-6} mol), CuI (1 mg, 5.2·10^{-6} mol) and dry diisopropylamine (DIPA, 0.15 ml) in anhydrous DME (3 ml) was kept at 70 °C for 19 h. Column chromatography of the residue on silica gel (hexane/ether/$CHCl_3$ 1.5 : 1 : 1) gave **21** (80 mg, 60%) as a colourless solid; m.p. 234 °C; (Found: MH^+, 453.2435. $C_{31}H_{33}O_3$ requires MH, 453.2430 [FAB]); ν_{max} (KBr/cm^{-1}) 3400 – 2960 (bs, OH), 1710, 755, 732; δ_H (270 MHz, $CDCl_3$) 0.97 (3H, s, CH_3), 1.32 (3H, t, ^3J = 7.3 Hz), 1.45–2.43 (10H, m), 2.55 (1H, dd, ^2J = 15.1 Hz, ^3J = 6.5 Hz), 2.86 (2H, m), 4.25 (2H, q, ^3J = 7.3 Hz), 4.62 (1H, s, OH), 5.91 (1H, d, ^3J = 15.7 Hz), 6.58 (1H, d, ^4J = 2.7 Hz), 6.64 (1H, dd, ^3J = 8.6 Hz, ^4J = 2.7 Hz), 7.16 (1H, d, ^3J = 8.6 Hz), 7.33–7.36 (3H, m), 7.50–7.54 (2H, m), 7.84 (1H, d, ^3J = 15.7 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.3, 16.5, 26.4, 27.6, 29.4, 31.1, 34.5, 37.5, 44.2, 50.0, 54.2, 60.4, 83.6, 101.4, 112.7, 115.3, 119.2, 123.1, 126.2, 128.4 (2C), 128.6, 131.8 (2C), 132.6, 138.1, 139.3, 142.8, 143.7, 153.4, 167.3; MS (FAB, 3-nitrobenzyl alcohol) *m/z* (%) = 453 (MH^+) (0.9).

4′-Cyano-2-formyldiphenylacetylene (**23**): A mixture of 2-bromobenzaldehyde (**22**, 810 mg, 4.40 mmol), 4-cyanophenylacetylene (720 ml, 5.67 mmol), $Pd(PPh_3)_2Cl_2$ (40 mg, 5.6·10^{-5} mol), CuI (15 mg, 7.9·10^{-5} mol) and dry diisopropylamine (DIPA, 1.4 ml) in anhydrous DME (14 ml) was kept at 75 °C for 18 h. Water (30ml) was added to the cooled solution and the mixture was extracted with chloroform (3 × 20 ml). The combined organic phase was dried over anhydrous $MgSO_4$, concentrated *in vacuo*, and the residue was separated over column chromatography on silica gel (hexane/ether/$CHCl_3$ 3 : 1 : 1) to give **23** (510 mg, 50%) as a solid; m.p. 110 °C; (Found: M^+, 231.0687. $C_{16}H_9NO$ requires M, 231.0684); δ_H (270 MHz, $CDCl_3$) 7.50–7.71 (3H, m), 7.65 ((2H, d, ^3J = 9.2 Hz), 7.69 (2H, d, ^3J = 9.2 Hz), 7.96 (1H, m), 10.59 (1H, s, CHO); MS (EI, 70 eV) *m/z* (%) 231 (M^+) (4.7).

Ethoxy 3-(4′-cyano-diphenylacetylen-2-yl)acrylate (**24**): A mixture of **23** (176 mg, 0.76 mmol) and ethoxycarbonylmethylidenetriphenylphosphorane (424 mg, 1.22 mmol) in $CHCl_3$ (1.5 ml) was placed into a beaker closed with Saran Wrap® and was heated in an oven at 100 °C for 30 min. Direct column chromatography of the mixture on silica gel (hexane/ether/$CHCl_3$ 5 : 1 : 1) gave **24** (89%) as a solid; m.p. 118 °C; (Found: M^+, 301.1106. $C_{20}H_{15}NO_2$ requires M, 301.1103); δ_H (270 MHz, $CDCl_3$) 1.36 (3H, t, ^3J = 7.0 Hz, CH_3), 4.29 (2H, q, ^3J = 7.0 Hz, OCH_2), 6.56 (1H, d, ^3J = 15.9 Hz), 7.36–7.70 (8H, m), 8.25 (1H, d, ^3J = 15.9 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.3, 91.2, 93.5, 111.8, 118.4, 120.2, 122.9, 126.3, 127.7, 129.4, 129.8, 132.0 (2C), 132.1 (2C), 133.0, 136.1, 142.0, 166.7; MS (EI, 70 eV) *m/z* (%) 301 (M^+) (59), 273 (41), 227 (87), 130 (100).

*Cyclisation of **24** in presence of $Pt(PPh_3)_4$*: A mixture of **24** (133 mg, 0.44 mmol) and $Pt(PPh_3)_4$ (31 mg, 2.5·10^{-5} mol) in mesitylene (3 ml) was heated at 135 °C for 16 h. The resulting mixture was subjected directly to column chromatography (hexane/ether/$CHCl_3$ 7 : 1 : 1) to give 1-(*Z*)-Ethoxycarbonylmethylene-2-(4-cyanophenyl)-1*H*-indene (**25**) (7 mg, 5%) as an orange-red slowly crystallising solid; (Found: M^+, 301.1104. $C_{20}H_{15}NO_2$ requires M, 301.1103); ν_{max} (KBr/cm^{-1}) 3018, 2965, 2208, 1715, δ_H (270 MHz, $CDCl_3$) 1.34 (3H, t, ^3J = 7.0 Hz), 4.31 (2H, q, ^3J = 7.0 Hz, OCH_2), 6.25 (1H, s), 6.97 (1H, s), 7.26–7.36 (3H, m), 7.49 (2H, d, ^3J = 8.6 Hz), 7.73 (2H, d, ^3J = 8.6 Hz), 8.60 (1H, d, ^3J = 7.8 Hz); MS (EI, 70 eV) *m/z* (%) 301 (M^+) (10), 227 (15), 153 (39); 1-(*Z*)-(4-cyanophenyl)methylene-2-ethoxycarbonyl-1*H*-indene (**26a**) (31 mg, 23%) as a yellow-orange solid; m.p. 152 °C; (Found: M^+, 301.1105. $C_{20}H_{15}NO_2$ requires M, 301.1103); ν_{max} (KBr/cm^{-1}) 2960, 2210, 1720; δ_H (270 MHz, $CDCl_3$) 1.41 (3H, t, ^3J = 7.0 Hz, CH_3), 4.35 (2H, q, ^3J = 7.0 Hz, OCH_2), 7.06–7.30 (3H, m), 7.42 (1H, d, ^3J = 7.6 Hz), 7.64 (2H, d, ^3J = 8.4 Hz), 7.74 (2H, d, ^3J = 8.4 Hz), 7.75 (1H, s), 8.42 (1H, s); δ_C (67.8 MHz, $CDCl_3$) 14.4, 60.4, 111.8, 118.7, 123.6, 128.0, 128.8, 129.8 (2C), 130.0, 132.3 (2C), 134.8, 134.9, 135.8, 140.6, 141.5, 141.7, 141.9, 164.5; MS (EI, 70 eV) *m/z* (%) 301 (M^+) (100), 256 (61), 246 (38), 228 (77), 202 (41); (Found: C, 79.82; H, 5.00; N, 4.77%. $C_{20}H_{15}NO_2$ requires, C, 79.72; H, 5.02; N, 4.65%); and 1-(*E*)-(4-cyanophenyl)methylene-2-ethoxycarbonyl-1*H*-indene (**26b**) (10 mg, 8%) as a slowly crystallising yellow-orange oil; (Found: M^+, 301.1107. $C_{20}H_{15}NO_2$ requires M, 301.1103); ν_{max} (neat/cm^{-1}) 2960, 2203, 1710; δ_H (270 MHz, $CDCl_3$) 0.94 (3H, t, ^3J = 7.3 Hz, CH_3), 3.82 (2H, q, ^3J = 7.3 Hz, OCH_2), 7.34–7.71 (10H, m); MS (EI, 70 eV) *m/z* (%) 301 (M^+) (92), 273 (16), 256 (48), 228 (64), 84 (100).

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