Syntheses, X-ray crystal structures and reactivity of fluorenylidene- and dibenzosuberenylidene-allenes: convenient precursors to dispirotetracenes, di-indenotetracenes and 2-phenyl-11b*H*-dibenz[*cd*,*h*]azulene†

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3,3-(Biphenyl-2,2′-diyl)-1-α,α,α-trifluoro-*p*-tolyl-allene, **9**, sequentially forms head-to-tail, **12**, *cis*-tail-to-tail, **13**, and *trans* tail-to-tail, **14**, 1,2-dialkylidene-cyclobutane dimers, each of which has been characterised by X-ray crystallography. Thermolysis at 180 °C yields the dispirotetracene, **15**, and di-indenotetracene, **16**; the latter compound forms an air-stable Diels–Alder adduct, **17**, with *N*-methylmaleimide. In contrast, the dibenzo[*a*,*d*]cycloheptenylidene-allenes, $(C_{14}H_{10})C{=}C{=}C(Br)Ph$, **20a**, and $(C_{14}H_{10})C{=}C{=}C(H)Ph$, **21a**, do not dimerise under relatively mild conditions. However, protonation of the bromo-allene, **20a**, and subsequent addition of hydride, provide a facile entry to the difficultly accessible bowl-shaped dibenz[*cd*,*h*]azulene framework, as in **30**, that had not previously been structurally characterised. Among others, the X-ray crystal structures of **12**, **13**, **14**, **17**, **20a**, **21a** and **30** are reported.

Introduction

In continuation of our ongoing studies of the intermediates involved in the dimerisation of fluorenylidene-allenes, **1**, to yield, ultimately, electroluminescent tetracenes, we recently reported the syntheses, structures and rearrangements of a series of 1,2-bis(alkylidene)cyclobutanes.[1] As shown in Scheme 1, two molecules of the allene yield initially a head-to-tail dimer, **2**, that isomerises sequentially to form a series of diastereomeric tail-to-tail structures **3**, **4** and **5**; finally, at 180 °C, the dispiro-tetracene, **6**, and a di-indenotetracene, **7**, are formed. The latter molecules undergo facile aerial oxidation to the corresponding peroxides, **8**.[2]

The first step of this dimerisation process is thought to involve the linking of the two central allene carbons which approach in a mutually orthogonal fashion to form a bis-allyl diradical;[3] this intermediate then undergoes ring-closure to the head-to-tail isomer, **2**, as in Scheme 2. However, one can readily envisage some degree of charge separation whereby the fluorenide anion stabilises the negative charge and the positive charge is delocalised onto the aryl ring. Experimentally, the ease of allene dimerisation in these systems is very sensitive to the nature of the substituents. Thus, when R is a group that can stabilise a cation, *e.g.* phenyl, *p*-tolyl or *p*-anisyl, head-to-tail dimer formation occurs readily, even below 0 °C.[2] Incorporation of an electron-withdrawing group, as in *p*-CF_3–C_6H_4–C(H)=C=$C_{13}H_8$, **9**, requires 24 h at room temperature for complete dimerisation. Moreover, when R is trimethylsilyl, formation of the head-to-tail dimer occurs only when the system is held at 65 °C for several hours.[4] It is, of course, well-established that a trimethylsilyl group stabilises an anion in the α-position, but a cation only in a β-position.[5]

It is particularly tempting to invoke this situation with the dimerisation of 3,3-(biphenyl-2,2′-diyl)-1-chloro-1-ferrocenyl-allene where the charge deficiency could be very readily alleviated by donation of electron density from the iron atom, as depicted in Scheme 3. Interestingly, however, the dimer produced in this case is the head-to-head isomer that is very severely distorted towards a pseudo-C_2 symmetric butterfly-type geometry in which the link between the two spiro-bonded fluorenyl centres is unusually long (C(3)–C(4) = 1.65 Å).[6]

The *trans*-3,4-diaryl-1,2-bis(fluorenylidene)cyclobutane tail-to-tail dimers, **3** and **5**, adopt C_2-symmetric structures because of the severe steric strain engendered by the overlapping fluorenylidene moieties. With the aim of increasing the steric interactions between the 1,2-bis(alkylidene) fragments, it was decided to attempt the syntheses of the corresponding dibenzosuberenylidene systems with their even larger wingspans. We here report the preparation, X-ray crystallographic characterisation and reactivity of several such allenes.

Results and Discussion

Fluorenone-derived allenes

As noted above, *p*-CF_3–C_6H_4–C(H)=C=$C_{13}H_8$, **9**, undergoes initial head-to-tail dimerisation. As shown in Scheme 4, it is conveniently prepared from *p*-CF_3–C_6H_4–C≡CLi and fluorenone to form the corresponding alkynol, **10**; subsequent reaction with BF_3/Et_3SiH furnishes the alkyne, **11**, that is readily isomerised to the desired allene, **9**. The head-to-tail dimer, **12**, and also the *cis*- and *trans*-3,4-bis(α,α,α-trifluoro-p-tolyl)-1,2-bis(fluorenylidene)-cyclobutanes, **13** and **14**, respectively, have been characterised

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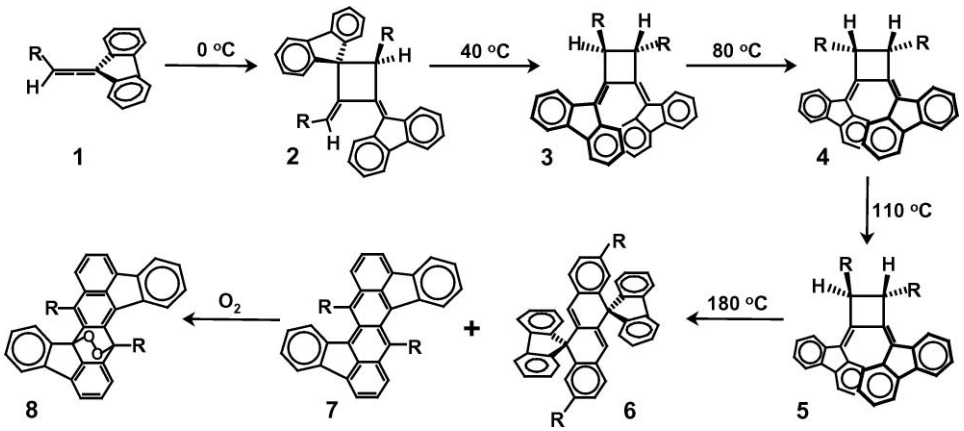
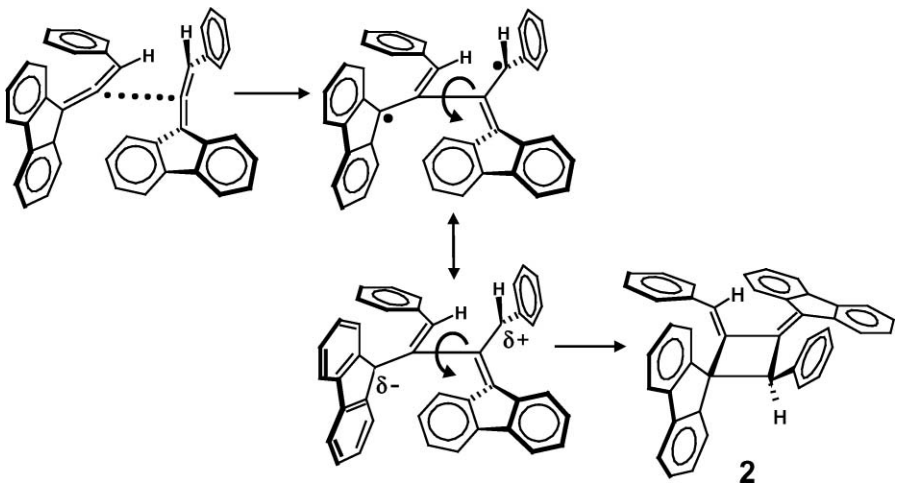
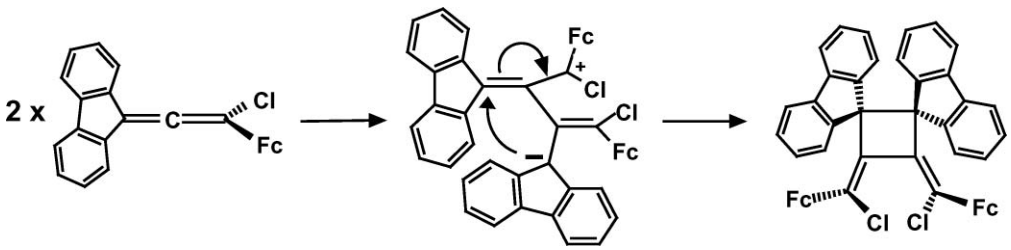
† Electronic supplementary information (ESI) available: Synthetic details and NMR data for molecules **20b**, **20c**, **21a**, **21b**, **23c** and **24a**. CCDC reference numbers 769734 (**12**), 769736 (**13**), 769735 (**14**), 769744 (**17**), 769738 (**20a**), 769745 (**20b**), 769739 (**21a**), 769742 (**23c**), 769737 (**24a**), 769743 (**30**), 769740 (**34**) and 769741 (**38**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c004868b.



Scheme 1 Sequential formation of allene dimers leading ultimately to tetracenes.



Scheme 2 Head-to tail dimerisation of orthogonally oriented allenes.

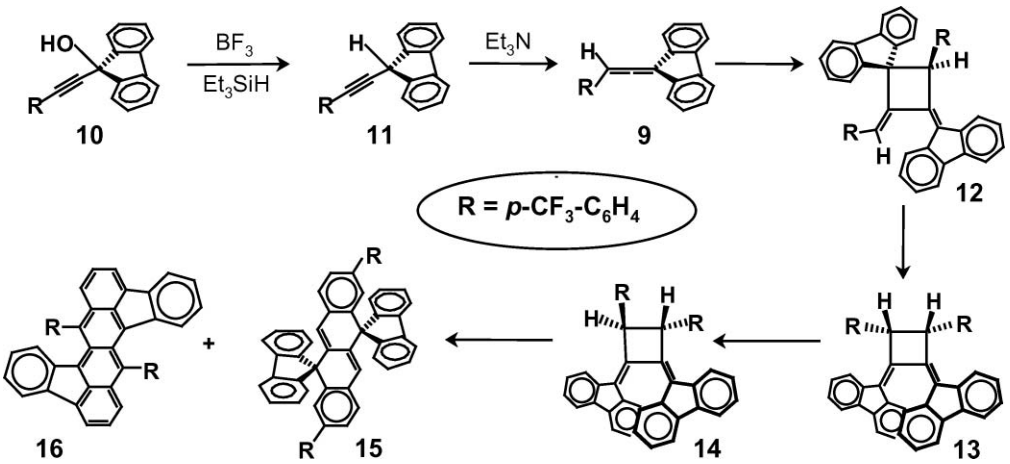


Scheme 3 Head-to-head dimerisation of a ferrocenyl-allene.

X-ray crystallographically and their structures (including space-fill views) appear in Fig. 1, 2 and 3 respectively. The *cis* and *trans* isomers, **13** and **14**, were also readily distinguishable by NMR; in **13**, the overlapping fluorenylidenes break the potential mirror symmetry and make the protons at C(3) and C(4) inequivalent, thus giving rise to a pair of 8.5 Hz doublets. In contrast, the C_2 symmetry of the *trans* isomer rendered them equivalent, thus appearing as a singlet. Thermolysis at 180 °C yields the corresponding α,α,α-trifluoro-*p*-tolyl-substituted dispirotetracene, **15**, as the major product (41%); di-indenotetracene, **16**, is also formed in minor quantities.[7]

The structures reveal that the length of the C(3)–C(4) linkage is a sensitive measure of the strain in these sterically crowded molecules: 1.611 Å in the head-to-tail dimer, **12**, 1.589 and 1.595 Å in the two independent molecules in the unit cell of the *cis* dimer, **13**, but only 1.452 Å in the *trans* dimer, **14**.

In an attempt to protect the di-indenotetracene, **16**, from aerial oxidation, it was dissolved in toluene and heated at reflux in the presence of *N*-methylmaleimide for 24 h; the original blue-green colour was discharged and, after chromatographic separation, the Diels–Alder adduct, **17**, was isolated as a colourless, air-stable solid (Scheme 5). The structure is shown in Fig. 4 and reveals that the *N*-methylmaleimide bridges the C(7b) and (C16) positions analogous to the structure of the di-indenotetracene peroxide, **8**. The *N*-methylmaleimide adduct adopts the *endo* orientation, and one can clearly see a folding and twisting of the tetracene



Scheme 4 Synthesis of α,α,α-trifluoro-*p*-tolyl-substituted tetracenes, **15** and **16**.

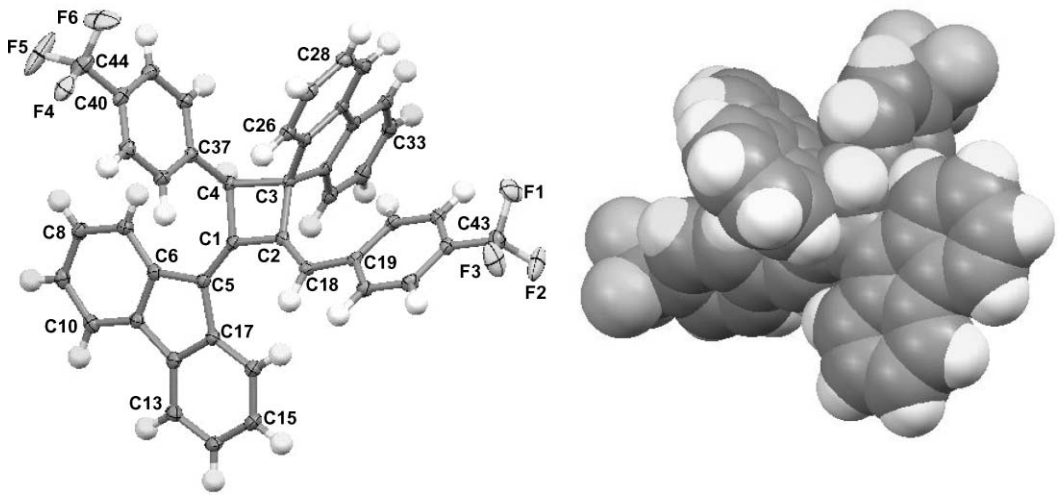


Fig. 1 Bird's eye, and spacefill, view of the structure of 1-(9-fluorenylidene)-4-(α,α,α-trifluoro-*p*-tolyl)-2-[(α,α,α-trifluoro-*p*-tolyl)methylene]-spiro[cyclobutane-3,9′-[9*H*]-fluorene], **12**; thermal ellipsoids are drawn at the 50% probability level.

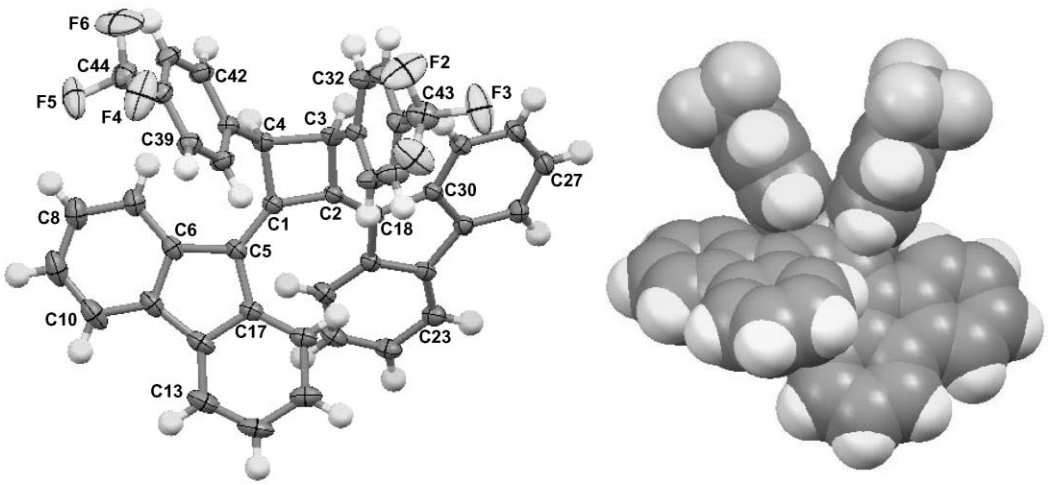


Fig. 2 Bird's eye, and spacefill, view of *cis*-1,2-di(fluorenylidene)-3,4-di(α,α,α-trifluoro-*p*-tolyl)cyclobutane, **13**; thermal ellipsoids are at the 50% probability level.

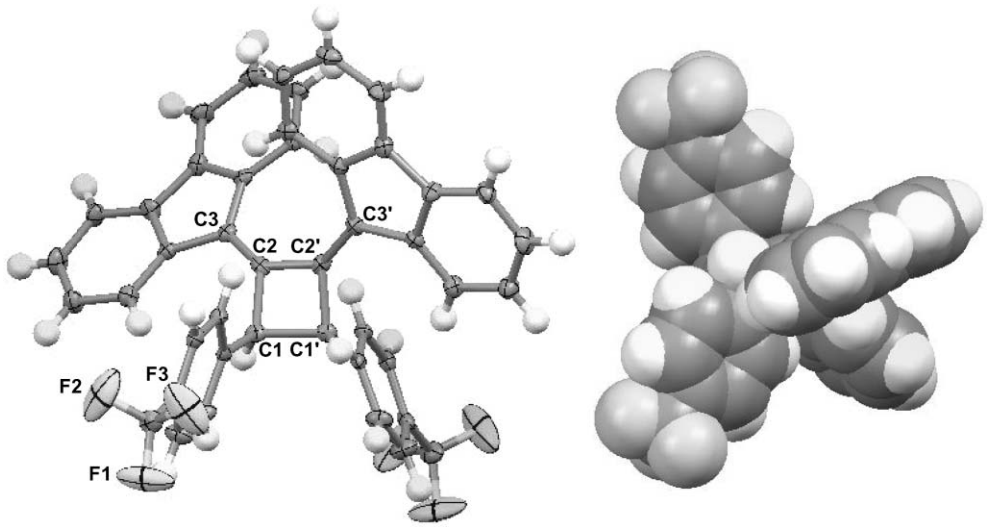


Fig. 3 Bird's eye, and spacefill, view of *trans*-1,2-di(fluorenylidene)-3,4-di(α,α,α-trifluoro-*p*-tolyl)cyclobutane, **14**; thermal ellipsoids are at the 50% probability level.

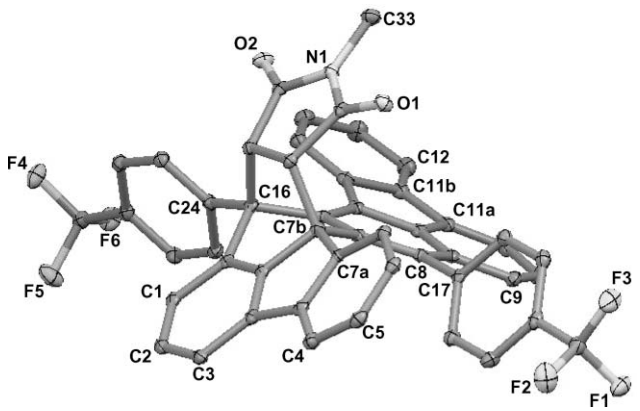


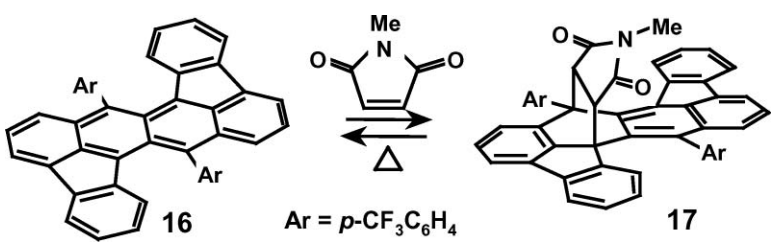
Fig. 4 X-ray crystal structure of **17**, the *endo* Diels–Alder adduct of *N*-methylmaleimide and the di-indenotetracene, **16**; thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been removed for clarity.

framework such that the dihedral angle between the terminal rings is now 124°, *versus* 116° in the case of the peroxide product.[2] In the analogous pentacene-maleimide adduct this dihedral angle is 126.5°.[8] In addition, the α,α,α-trifluoro-*p*-tolyl substituent attached at C(8) is aligned parallel to the six-membered ring of the adjacent fluorenyl group; this is particularly noticeable in the ^{1}H NMR spectrum whereby the fluorenyl-proton signals are markedly shielded. Gratifyingly, upon heating in the solid state, **17** undergoes a retro-Diels–Alder to regenerate the tetracene, thus providing a convenient method of storage.

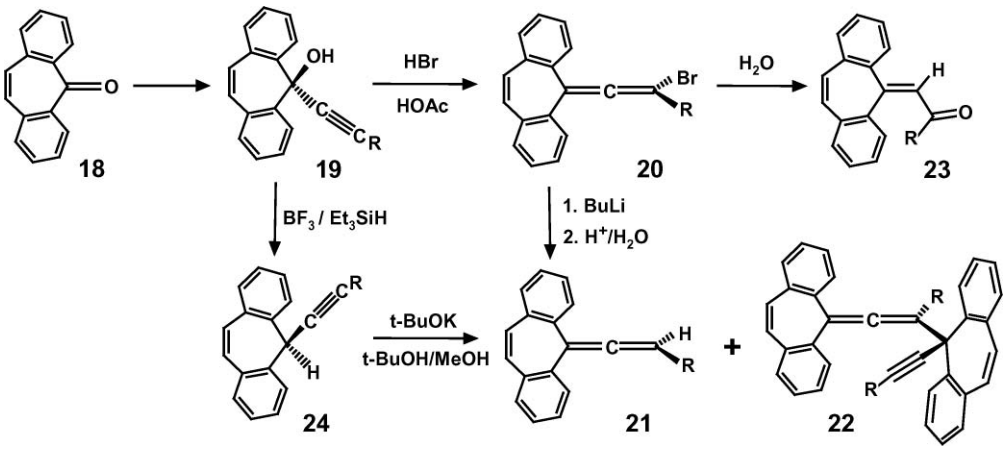
Dibenzosuberenone-derived allenes

As noted above, the *trans* tail-to-tail dimers **3**, **5** and **14** adopt pseudo-C_2 symmetrical conformations caused by the overlap of the fluorenylidene rings with their large wingspans (approximately 8.8 Å). Moreover, the dihedral angle between the fluorenylidene rings in these tail-to-tail dimers is highly dependent on the identity of the substituents at C(3) and C(4). These interplanar angles range from 41° in **3** (R = C_6H_5), to 44° in **14** (R = *p*-CF_3–C_6H_4), 58° in **5** (R = H), and 64° in **5** (R = *p*-CH_3–C_6H_4). With the aim of preparing analogous C_2-symmetric dimers containing dibenzosuberenylidene moieties, dibenzosuberenone, **18**, was treated with a number of alkynyl-lithium reagents and yielded the corresponding alkynols, **19a–c**.

As with the fluorenyl systems discussed above,[4] the alkynols **19a** (R = C_6H_5), **19b** (R = $(CH_3)_3Si$), and **19c** (R = *p*-CF_3–C_6H_4) reacted with HBr in acetic acid[9] to form the corresponding bromoallenes, **20a–c**, in good yields (see Scheme 6). Subsequent lithiation and hydrolysis with water furnished the allenes, **21a,b**, but in very poor yields. Instead, the major products are the propargyl-allenes, **22a,b**, presumably arising by attack of the lithiated allene on unreacted bromoallene; such behaviour has also been observed in the corresponding fluorenylidene systems.[4,10,11] Moreover, the bromoallenes **20a–c** were very sensitive to hydrolysis



Scheme 5 The Diels–Alder adduct, **17**, of *N*-methylmaleimide and the di-indenotetracene, **16**.



Scheme 6 Routes to allenes derived from dibenzosuberenone.

at room temperature, and any trace of moisture and/or acid brought about formation of the conjugated ketones, **23a–c**.

Structures exemplifying the allenes **20** and **21** are shown in Fig. 5 and in the ESI (Figures SI-1 and SI-2) which illustrate clearly the non-planar character of the central cycloheptatriene ring in each case. The conformation of the seven-membered boat is defined by C(4a)–C(5a)–C(9a)–C(11a) [plane 1], C(4a)–C(5)–C(5a) [plane 2] and C(9a)–C(10)–C(11)–C(11a) [plane 3]. In **20a** (and **20b**) the interplanar angles [plane 1]/[plane 2] and [plane 1]/[plane 3] are 34.5° (and 39.0°) and 13.3° (and 21.9°), respectively; the interplanar angles between the two benzo rings are 152.7° (and 140.3°). The allene double bonds are, of course, orthogonal and the C(5)=C(12) bonds, 1.321(3) (and 1.318(4)) Å, are significantly longer than C(12)=C(13)–Br, 1.301(3) (and 1.303(4) Å), as was previously observed for 3,3-(biphenyl-2,2′-diyl)-1-bromo-1-phenyl-allene.[4] In the parent allene, **21a**, the interplanar angles [plane 1]/[plane 2] and [plane 1]/[plane 3] are 41.9° and 18.1°, respectively, and the angle between the two benzo rings is now 149.6°. However, in contrast to its bromoallene precursor, the bond lengths C(5)=C(12) and C(12)=C(13) are now equal (1.309(2) and 1.310(2) Å). These dibenzo[*a*,*d*]cycloheptenylidene-allene boats in which C(5) is trigonal planar are considerably shallower than those previously seen in 5-alkynyl-dibenzosuberen-5-ols where the [plane 1]/[plane 2] and [plane 1]/[plane 3] angles are approximately 55–60° and 25–30°, respectively, and the angle between the wingtip benzo rings is in the range 120–130°.[12,13]

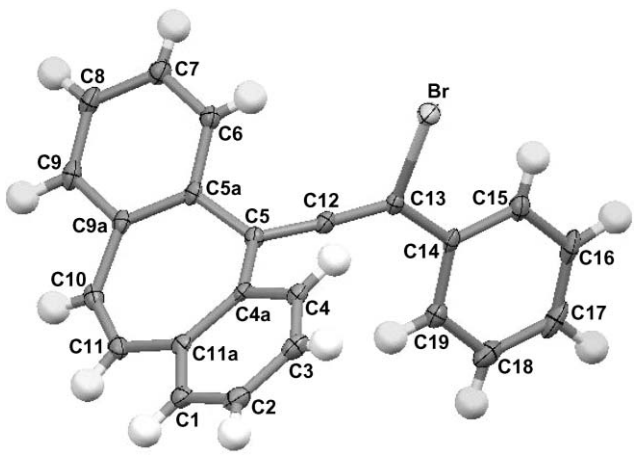
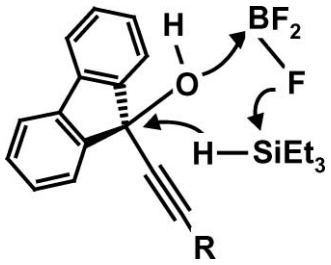


Fig. 5 X-ray crystal structure of bromoallene **20a**; thermal ellipsoids are drawn at the 50% probability level.

The structure of a conjugated ketone, **23c**, (R = *p*-CF_3–C_6H_4) is shown in ESI (Figure SI-3). As expected, the central ring adopts a boat conformation, and the interplanar angles [plane 1]/[plane 2] and [plane 1]/[plane 3] are 49.2° and 25.5°, respectively; the angle between the two benzo rings is now 133.5°. Moreover, the ketonic moiety is twisted 38.4° out of planarity with the adjacent double bond; this parallels the 36° out-of-plane bending of the carbonyl substituent in the conjugated enones derived from the Meyer–Schuster rearrangement of alkynyl-fluorenols.[6]

Nevertheless, the poor yields of allenes **21a,b** mandated that a more efficient synthesis be developed. To this end, 5-phenylethynyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol, **19a**, was treated with boron trifluoride and triethylsilane so as to furnish the corresponding alkyne, **24a**, (shown in ESI as Figure SI-4). The central cycloheptatriene adopts a boat conformation such that the interplanar angles [plane 1]/[plane 2] and [plane 1]/[plane 3] are 58.5° and 30.7°, respectively, and the two peripheral benzo groups form a dihedral angle of 120.9°. However, the phenylethynyl group is now in a pseudo-equatorial position, unlike that of the alkynol precursor, **19a**, or of 5-ethynyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol,[12,13] in both of which the alkyne occupies a pseudo-axial site. One possibility might be that, after addition of the hydride and formation of the alkyne, the dibenzocycloheptatriene boat undergoes a ring flip,[14] thus placing the alkyne in the pseudo-equatorial position. However, one must also consider that, unlike the 9-alkynyl-9*H*-fluoren-9-ol situation for which an intramolecular cyclic six-membered transition state can be envisaged (as in Scheme 7), the dibenzosuberenylidene system can readily exist as a 14π aromatic cation and so the incoming hydride can attack on either face.

Not surprisingly, isomerisation of the alkyne **24a** to the allene **21a** is much more difficult than is the case for the corresponding fluorenyl systems (**11** → **9** in Scheme 4) since the tricyclic framework in **24a** favours formation of a 14π aromatic cation rather than a 16π antiaromatic anion. Thus, treatment with triethylamine fails to bring about this alkyne-to-allene rearrangement; however, this transformation can be accomplished by use of a stronger base.



Scheme 7 Proposed mechanism for the conversion of a 9-alkynyl-9*H*-fluoren-9-ol to the corresponding alkyne using BF_3 and Et_3SiH.

When the alkyne was dissolved in a methanol-*tert*-butanol 1 : 1 mixture, and stirred in the presence of potassium *tert*-butoxide[15] for 24 h at room temperature, the allene **21a** was isolated in 89% yield.

Initial attempts to dimerise the allene **21a** have so far been unsuccessful, possibly because the system requires some degree of charge separation, as indicated in Scheme 2. Since the dibenzosuberenylidene moiety favours cation formation, it may be necessary to incorporate strongly anion-stabilising substituents (*e.g.* nitro or cyano) at the other terminus of the allene, and experiments to explore this concept are continuing.

Synthesis of 2-phenyl-11b*H*-dibenz[*cd*,*h*]azulene

The availability of the bromoallene **20a** raised the possibility of developing a simple route to the benz[*cd*]azulene skeleton, a hitherto relatively inaccessible ring system. The parent molecule, **25a**, was prepared by Boekelheide and Smith in 1966 by means of a difficult multistep route based on the carbene-mediated expansion of the acenaphthene framework (see Scheme 8).[16] Unfortunately, the product is obtainable only in very low overall yield, is very susceptible to polymerisation, and can only be handled at low temperatures in dilute solution. Previously, in 1963, Hafner and Schaum had reported the synthesis of 3,4,7,9-tetramethyl-2*H*-benz[*cd*]azulene, **25b**, but once again, the yields are low and the product readily decomposes.[17] More recently, in 2004, we reported the synthesis and X-ray crystal structure of **26**, the η^6-tricarbonylchromium complex of 8-isopropyl-1-methyl-4-*tert*-butylbenz[*cd*]azulene, **25c**, starting from readily available guaiazulene. In this latter case, the presence of the bulky substituents renders the molecule reasonably stable but, upon prolonged exposure to air, oxidative dehydrogenation leads to the formation of **27**.[18]

In 1966, Galantay reported the formation of 2*H*-dibenz[*cd*,*h*]azulen-2-one, **28**, *via* the Friedel–Crafts cyclisation of the acid chloride, **29** (see Scheme 9). Moreover, it was suggested that the favoured resonance structure would be zwitterionic whereby the ring system behaved as a dibenz[*cd*,*h*]azulenium cation.[19] More recently, a series of 7*H*-naphth[3,2,1-*cd*]azulene-7-ones have been prepared.[20]

In the light of these observations, it was thought that the reaction of bromo-allene **20a** with an acid followed by hydride addition, would bring about formation of a phenyl-substituted dibenz[*cd*,*h*]azulene. Indeed, when a THF solution of **20a** and HBF_4 was held at 0° C for 1 h, heated at reflux for 24 h, treated with triethylsilane at low temperature, and then hydrolysed, 2-phenyl-11b*H*-dibenz[*cd*,*h*]azulene, **30**, was isolated in 10% yield (Scheme 10). The product was fully characterised by NMR spectroscopy and X-ray crystallography. In contrast to the planar polycyclic skeleton of 8-isopropyl-1-methyl-4-*tert*-butylbenz[*cd*]azulene, **25c**, whereby the only sp^3-type carbon is a CH_2 unit at position C(2) in the 5-membered ring,[18] the presence of the proton in a pseudo-axial position at C(11b), a ring junction site, renders the dibenz[*cd*,*h*]benzazulene, **30**, non-planar. The structure is depicted in Fig. 6 and reveals that the 7-membered ring adopts a boat conformation such that the angles [plane 1]/[plane 2] and [plane 1]/[plane 3] are 48.6° and 25.3°, with a dihedral angle of 131.7° between the benzo rings. The indene fragment deviates only 5.8° from planarity, and the 2-phenyl substituent is rotated through 40.8° relative to the five-membered ring. The space-filling representation shown in Fig. 7 emphasises the bowl-shaped character of the molecule.

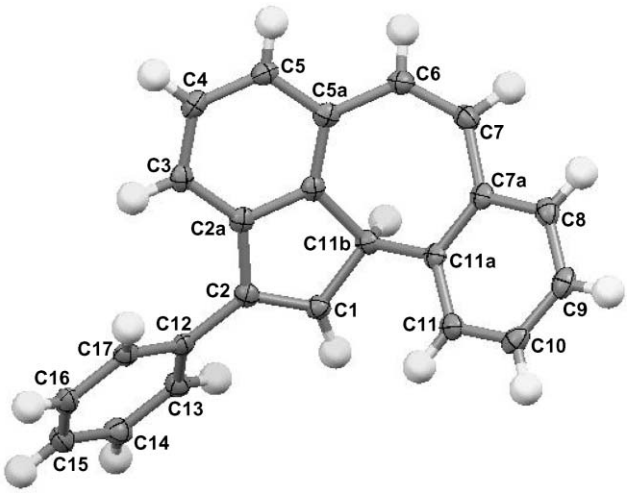


Fig. 6 Bird's eye view of the X-ray crystal structure of 2-phenyl-11b*H*-dibenz[*cd*,*h*]azulene, **30**; thermal ellipsoids are drawn at the 50% probability level.

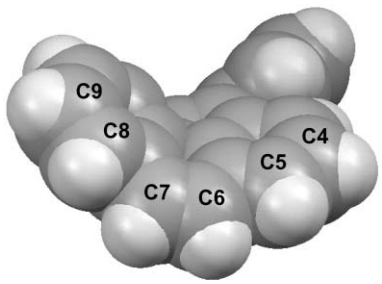
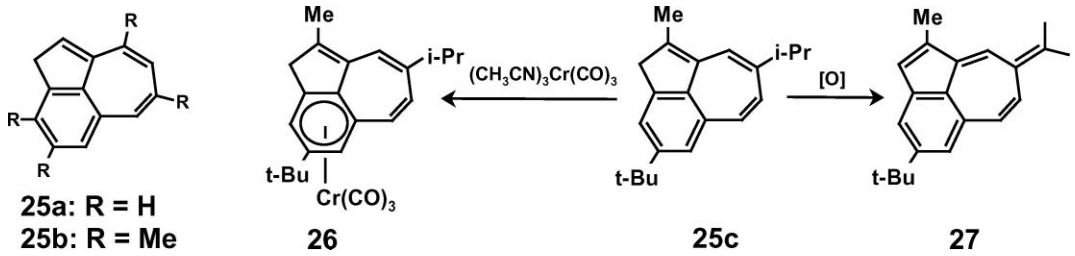
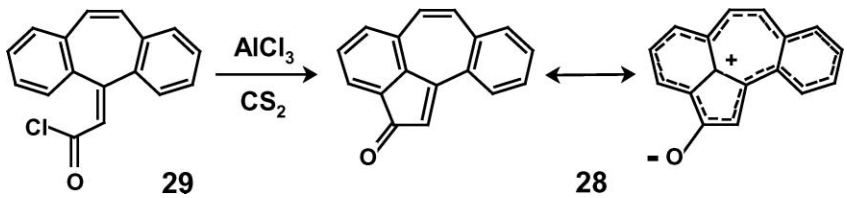


Fig. 7 Space-filling representation of the X-ray crystal structure of 2-phenyl-11b*H*-dibenz[*cd*,*h*]azulene, **30**, emphasizing the bowl-shaped character of the molecule.

One can speculate that the observed molecule with the additional hydrogen attached to C(11b) is favoured over the 2*H*-isomer so as to maintain the aromatic character of the two benzo rings. Interestingly, methyl substitution at the central carbon C(9b) of the benz[*cd*]azulene system, as in **31**, was reported by Hafner in 1986,[21] but no X-ray crystallographic data are available. In that case, the peripheral 12π framework renders the system antiaromatic, as indicated by the NMR shielding of the exterior protons. To the

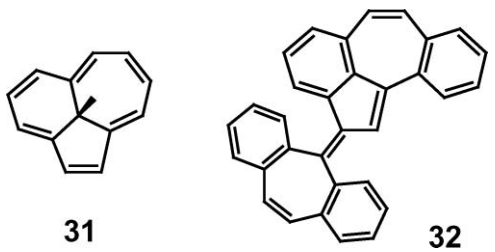


Scheme 8 Structures and reactions of known benz[*cd*]azulenes.



Scheme 9 Formation of 2*H*-dibenz[*cd*,*h*]azulen-2-one, **28**.

best of our knowledge, the most closely analogous molecule to **30** that has been structurally characterised is the palladium-coupled bis-dibenzosuberene system, **32**, which contains an almost flat dibenz[*cd*,*h*]azulene subunit: the angles between [plane 1]/[plane 2] and [plane 1]/[plane 3] are 13.1° and 9.7°, with an angle of 162.9° between the benzo rings. In contrast, the boat conformation of the dibenzosuberenylidene fragment in **32** is normal with angles of 53.2°, 27.6° and 126.7°, respectively.[22]



In terms of a proposed mechanism for the synthesis of **30**, one can visualise initial protonation by HBF_4 at the central allene carbon to form the allyl cation, **33**, Nazarov cyclisation to form the 5-membered ring, elimination of HBr to furnish the tropylium-type cation, **34**, and finally triethylsilane-mediated addition of hydride.

It is particularly informative to note that, when protonation of the bromoallene **20a** was carried out at room temperature in diethyl ether for only a short period of time, and then treated with triethylsilane, two other species were isolated and fully characterised: *Z*-5-(2-bromo-2-phenylethenyl)-5*H*-dibenzo[*a*,*d*]cycloheptene, **35**, and 1-phenyl-3-(dibenzo[*a*,*d*]cycloheptenylidene)-ethanone, **23a**. The structure of **35** was determined by X-ray crystallography and is shown in Fig. 8. Once again, the central cycloheptatriene adopts a boat conformation, whereby the interplanar angles [plane 1]/[plane 2] and [plane 1]/[plane 3] are 50.4° and 28.1°, and the angle between the two benzo rings is now 126.1°. We note that the proton at C(5) is now pseudo-equatorial and the 2-bromo-2-phenylethenyl substituent is in a pseudo-axial position. As shown in Scheme 10, addition of HBF_4 to bromoallene **20a** brings about formation of

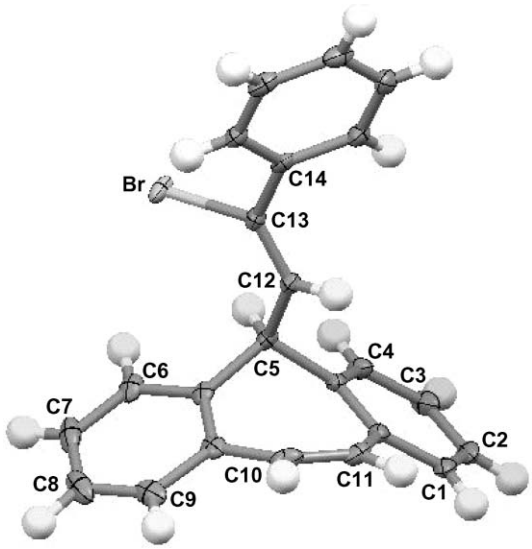
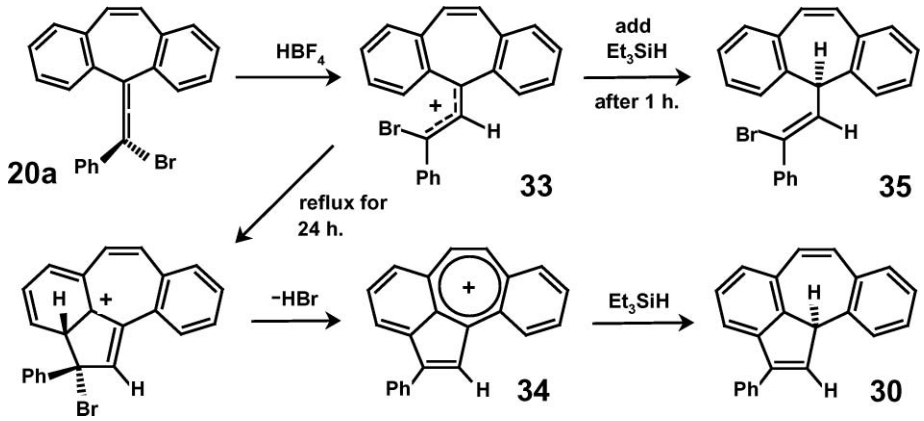


Fig. 8 X-ray crystal structure of *Z*-5-(2-bromo-2-phenylethenyl)-5*H*-dibenzo[*a*,*d*]cycloheptene, **35**; thermal ellipsoids are drawn at the 50% probability level.

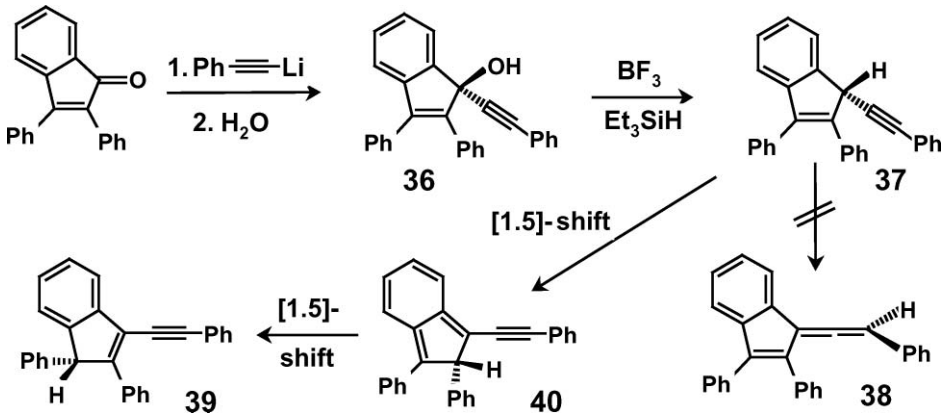
the allyl cation **33**: attack by the hydride at C(5) prior to cyclisation yields the styrene derivative **35**, and hydrolysis of the bromoallene generates the "Meyer–Schuster type" conjugated ketone, **23a**, discussed above.

Attempt to prepare an indenyl-allene

The reaction of 2,3-diphenylindenone with phenylethynyllithium yields, after hydrolysis, 2,3-diphenyl-1-(phenylethynyl)-inden-1-ol, **36**. Subsequent treatment with boron trifluoride and triethylsilane was expected to form 2,3-diphenyl-1-(phenylethynyl)-indene, **37**, that could be isomerised to the required allene, **38**, as in Scheme 11. However, X-ray crystallography revealed that the product was actually 1,2-diphenyl-3-(phenylethynyl)-1*H*-indene, **39**, presumably arising through consecutive symmetry-allowed [1,5]-suprafacial sigmatropic hydrogen shifts *via* the iso-indene, **40**.[23] The structure



Scheme 10 Formation of dibenz[*cd*,*h*]azulene, **30**, from bromoallene **20a**.



Scheme 11 Formation of 1,2-diphenyl-3-(phenylethynyl)-1*H*-indene, **39**.

of the ene-yne, **39**, appears in Fig. 9, and reveals that, as expected for a conjugated system, the (phenylethynyl)indenyl fragment is almost flat.

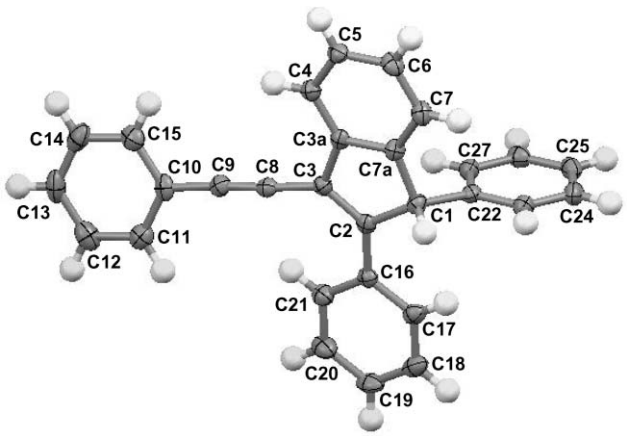
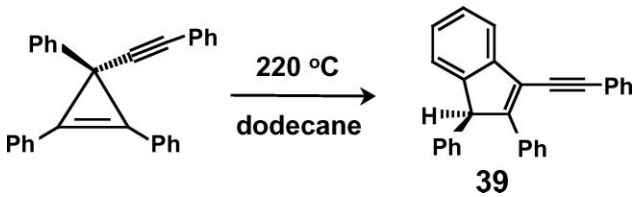


Fig. 9 Molecular structure of 1,2-diphenyl-3-(phenylethynyl)-1*H*-indene, **39**; thermal ellipsoids are drawn at the 50% probability level.

Interestingly, it has been reported[24] that 1,2-diphenyl-3-(phenylethynyl)-1*H*-indene, **39**, was the preferentially formed isomer during the thermolysis of 3-(phenylethynyl)-1,2,3-triphenylcyclopropene (Scheme 12), and the energetics of hydrogen migrations in substituted indenes have been extensively studied.[25]



Scheme 12 Ring opening of 3-(phenylethynyl)-1,2,3-triphenylcyclopropene.

Conclusions

The relative ease of dimerisation of fluorenylidene-allenes is markedly dependent on the identity of the substituent at the other terminus. 3,3-(Biphenyl-2,2′-diyl)-1-(α,α,α-trifluoro-*p*-tolyl)-allene, **9**, sequentially forms head-to-tail, **12**, *cis*-tail-to-tail, **13**, and *trans* tail-to-tail, **14**, dimers, each of which has been characterised by X-ray crystallography. Finally, thermolysis at 180 °C yields the dispirotetracene, **15**, and di-indenotetracene, **16**; the latter compound forms an air-stable Diels–Alder adduct, **17**, with *N*-methylmaleimide. In contrast, the analogous dibenzosuberenylidene-allenes, **20a** and **21a**, do not dimerise under relatively mild conditions, and this may be a consequence of the inability of the substituents at opposite allene termini to stabilise partial positive and negative charges.

However, protonation of the bromo-allene **20a**, and subsequent addition of hydride provide a facile entry to the difficultly accessible dibenz[*cd*,*h*]azulene framework that had not previously been structurally characterised. The maximum width of the planar fluorenyl fragment is ~8.8 Å, whereas the corresponding "wingspan" of the dibenzo[*a*,*d*]cycloheptenyl moiety can vary from 9.0 Å to 9.5 Å depending on the degree of folding of the central seven-membered boat, which in turn controls the interplanar angle between the benzo rings. An attempt to prepare an allene containing a 1,2-diphenylindenyl moiety led instead to 1,2-diphenyl-3-(phenylethynyl)-1*H*-indene, **39**.

Experimental Section

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Varian 300, 400, 500 or 600 MHz spectrometers. Assignments were based on standard 2-dimensional NMR techniques (^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC and HMBC, NOESY). Infrared spectra were recorded on a Perkin–Elmer Paragon 1000 FT-IR spectrometer and were calibrated with polystyrene. Merck silica gel 60 (230–400 mesh) was used for flash chromatography. Melting points were determined on an Electrothermal ENG instrument and are uncorrected. Elemental analyses were carried out by the Microanalytical Laboratory at University College Dublin. 5-Phenyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (**19a**) and 5-(4-trimethylsilyl)phenyl-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (**19b**) were prepared as previously described.[12,13]

9-(α,α,α-Trifluoro-*p*-tolyl)-9*H*-fluoren-9-ol (10)

As previously described for a series of such molecules,[4] nBuLi (3.12 mL of a 1.6 M hexane solution, 5 mmol) was added dropwise to a solution of the alkyne (5 mmol) in tetrahydrofuran (50 mL) at 0 °C, and the solution was allowed to warm to room temperature. After 15 min stirring, the solution was cooled to 0 °C and fluorenone (0.90 g, 5 mmol) was added portion by portion. The solution was stirred at room temperature for 30 min, quenched with water (2 mL) and the solvent was removed on a rotary evaporator. Purification of the crude product by chromatography on alumina using pentane/diethyl ether as eluent gave 9-(α,α,α-trifluoro-*p*-tolyl)-9*H*-fluoren-9-ol, **10**, (85%) m.p. 136-139 °C (Found: C, 75.46; H, 3.78. $C_{22}H_{13}F_3O$ requires C, 75.42 H, 3.74); δ_H (500 MHz, $CDCl_3$): 7.75 (dd, *J* 7.5 and 1.5, 2H, H-1, H-8), 7.62 (d, *J* 7.5, 2H, H-4, H-5), 7.50 (m, 4H, phenyl *m*-H, *o*-H), 7.41 (td, *J* 7.5 and 1.0, 2H, H-3, H-6), 7.35 (td, *J* 7.5 and 1.5, 2H, H-2, H-7), 2.67 (s, 1H, OH); δ_C (125 MHz, $CDCl_3$): 146.9 (C-8a, C-9a), 139.1 (C-4a, C-4b), 132.2 (phenyl *o*-C), 130.3 (q, $^{2}J_{CF}$ 32.8, phenyl *p*-C), 129.9 (C-3, C-6), 128.7 (C-2, C-7), 126.3 (phenyl *ipso*-C), 125.2 (q, $^{3}J_{CF}$ 3.5, phenyl *m*-C), 123.9 (q, $^{1}J_{CF}$ 270, CF_3), 124.4 (C-1, C-8), 120.3 (C-4, C-5), 91.5 (C-10), 81.7 (C-11), 75.2 (C–OH); IR (CH_2Cl_2): 3563 cm^{-1} (OH), 2230 cm^{-1} (C≡C).

9-(α,α,α-Trifluoro-*p*-tolyl)ethynyl-9*H*-fluorene (11)

To 9-[(α,α,α-trifluoro-*p*-tolyl)ethynyl]-9*H*-fluoren-9-ol, **10**, (4.0 g, 11.4 mmol) in dry dichloromethane (120 mL), and cooled to 0 °C, triethylsilane (2.73 mL, 17.1 mmol) was added slowly. Boron trifluoride-etherate (2.1 mL, 17.1 mmol) was added dropwise, and the solution became dark blue. After stirring for 1 h at 0 °C, the reaction was quenched with distilled water, and the mixture extracted with dichloromethane multiple times. The organic layers were combined, washed successively with water and with brine, dried over $MgSO_4$, filtered and concentrated to give a brown oil that was chromatographed on silica gel using dichloromethane/pentane (1 : 9) as eluent to give 9-[(α,α,α-trifluoro-*p*-tolyl)ethynyl]-9*H*-fluorene, **11**, as a pale yellow solid (2.45 g, 7.3 mmol; 64%) m.p. 167–170 °C (Found: C, 78.81; H, 4.13. $C_{22}H_{13}F_3$ requires C, 79.03; H, 3.92); δ_H (500 MHz, $CDCl_3$): 7.78 (d, *J* 7.5, 2H, H-4, H-5), 7.74 (d, *J* 7.5, 2H, H-1, H-8), 7.53 (m, 4H, phenyl *m*-H, *o*-H), 7.44 (t, *J* 7.5, 2H, H-3, H-6), 7.40 (td, *J* 7.5 and 1.0, 2H, H-2, H-7), 5.04 (s, 1H, H-9); δ_C (125 MHz, $CDCl_3$): 143.6 (C-8a, C-9a), 140.6 (C-4a, C-4b), 132.2 (phenyl *o*-C), 129.9 (q, $^{2}J_{CF}$ 32.6, phenyl *p*-C), 128.3 (phenyl *ipso*-C), 128.2 (C-3, C-6), 127.8 (C-2, C-7), 126.3 (q, $^{1}J_{CF}$ 267, CF_3), 125.2 (q, $^{3}J_{CF}$ 3.6, phenyl *m*-C), 125.2 (C-4, C-5), 120.3 (C-1, C-8), 90.2 (C-10), 80.9 (C-11), 39.9 (C-9).

1-(9-Fluorenylidene)-4-(α,α,α-trifluoro-*p*-tolyl)-2-(α,α,α-trifluoro-*p*-tolylmethylene)-spiro[cyclobutane-3,9′-[9*H*]-fluorene] (12)

To 9-[(α,α,α-trifluoro-*p*-tolyl)ethynyl]-9*H*-fluorene, **11**, (2.45 g, 7.3 mmol) suspended in pentane (35 mL) and cooled to 0 °C, was added triethylamine (25 µL, 0.18 mmol), and the suspension was stirred overnight in a cold water bath. The precipitate was filtered, washed with cold pentane and dried to give 1-(9*H*-fluorenylidene)-4-(α,α,α-trifluoro-*p*-tolyl)-2-(α,α,α-trifluoro-*p*-tolylmethylene)-spiro[cyclobutane-3,9′-[9*H*]fluorene], **12**, (2.26 g, 3.38 mmol; 93%) as a yellow powder, m.p. 148–150 °C (Found: C, 79.11; H, 4.39. $C_{44}H_{26}F_6$ requires C, 79.03; H, 3.92); a sample suitable for an X-ray crystal structure determination was obtained by recrystallisation from dichloromethane/hexane; δ_H (500 MHz, $CDCl_3$): 8.58 (d, *J* 8.0, 1H), 7.85 (d, *J* 7.5, 1H), 7.82 (d, *J* 8.0, 1H), 7.78 (d, *J* 8.0, 1H), 7.71 (d, *J* 8.0, 1H), 7.69 (s, 1H), 7.68 (d, *J* 7.5, 1H), 7.65 (br s, 1H), 7.49 (br s, 1H), 7.46 (t, *J* 7.5, 1H), 7.43 (t, *J* 7.5, 1H), 7.35 (t, *J* 7.5, 1H), 7.30 (t, *J*7.5, 1H), 7.29 (brd s, 1H), 7.28 (t, *J* 7.5, 1H), 7.11 (t, *J* 7.5, 1H), 7.09 (d, *J* 8.0, 1H), 7.02 (d, *J* 8.5, 2H), 7.00 (t, *J* 8.0, 1H), 6.61 (d, *J*8.0, 2H), 6.55 (brd s, 1H), 6.52 (t, *J* 7.5, 1H), 5.97 (d, *J* 7.0, 1H), 5.22 (s, 1H); δ_C (125 MHz, $CDCl_3$): 149.3, 146.6, 141.7, 141.5, 141.5, 141.0, 140.9, 140.4, 139.7, 138.1, 138.0, 137.5, 131.1, 129.5 (q, $^{2}J_{CF}$ 32.1), 129.2 (q, $^{2}J_{CF}$ 36.0), 129.0, 128.7, 128.5, 128.3, 128.0, 127.7, 127.4, 126.5, 126.5, 126.1, 125.5 (brd s), 125.1, 124.3 (q, $^{3}J_{CF}$ 3.8), 124.3 (q, $^{1}J_{CF}$ 271), 124.2, 124.0 (q, $^{1}J_{CF}$ 268), 122.8, 120.3, 120.2, 120.0, 119.8, 65.7, 60.9; δ_F (282 MHz, $CDCl_3$): –60.89, –61.22.

Cis-3,4-bis-(α,α,α-trifluoro-*p*-tolyl)-1,2-bis(fluorenylidene)cyclobutane (13)

The head-to-tail dimer, 1-(9-fluorenylidene)-4-(α,α,α-trifluoro-*p*-tolyl)-2-(α,α,α-trifluoro-*p*-tolylmethylene)-spiro[cyclobutane-3,9′-[9*H*]-fluorene], **12**, (450 mg, 0.67 mmol) suspended in toluene (15 mL) was heated at 95 °C for 8 h. After removing the solvent, the crude product was chromatographed on silica gel using toluene/pentane (2 : 8) as eluent, and *cis*-3,4-di-(α,α,α-trifluoro-*p*-tolyl)-1,2-bis(fluorenylidene)cyclobutane, **13**, (87.4 mg, 0.13 mmol; 20%) was isolated as an orange solid, m.p. 202–205 °C (Found: C, 77.27; H, 4.19. $C_{44}H_{26}F_6{\cdot}(C_2H_5)_2O$ requires C, 77.62; H, 4.88); a sample of **13** suitable for an X-ray crystal structure determination was obtained by recrystallisation from

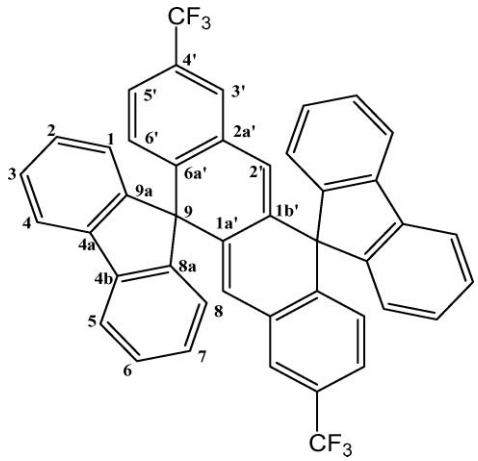
pentane/diethyl ether; δ_H (500 MHz, $CDCl_3$): 7.76 (d, *J* 7.5, 2H), 7.34 (d, *J* 7.0, 1H), 7.34 (d, *J* 7.0, 1H), 7.65 (d, *J* 7.5, 1H), 7.60 (d, *J* 8.0, 2H), 7.53 (brd s, 1H), 7.48 (brd s, 2H), 7.35 (t, *J* 7.5, 1H), 7.33 (td, *J* 7.0 and 1.0, 1H), 7.30 (d, *J* 7.5 Hz, 1H), 7.29 (td, *J* 7.5 and 1.0, 1H), 7.24 (d, *J* 7.5, 1H), 7.16 (td, *J* 7.5 and 1.0, 1H), 7.07 (td, *J* 7.5 and0.5, 2H), 6.90 (td, *J* 7.5 and 1.0, 1H), 6.84 (td, *J* 8.0 and 1.0, 1H), 6.79 (td, *J* 7.5 and 1.0, 1H), 6.70 (brd s, 2H), 6.25 (brd s, 1H), 5.54 (d, *J* 8.5, 1H), 5.37 (d, *J* 8.5, 1H); δ_C (125 MHz, $CDCl_3$): 143.0, 142.2, 142.2, 140.9, 140.8, 140.6, 140.4, 140.4, 139.10, 138.4, 137.0, 137.0, 135.8, 135.6, 129.4 (q, $^2J_{CF}$ 32.8), 129.2, 129.2 (q, $^2J_{CF}$ 32.3), 129.1, 128.8, 128.5, 127.7, 127.6, 127.4, 126.6, 126.5, 126.4, 125.6, 124.5 (brd s), 124.9, 124.25 (brd s), 124.1 (q, $^1J_{CF}$ 270), 124.1 (q, $^1J_{CF}$ 270), 120.3, 119.8, 119.8, 119.6, 57.8, 55.8; δ_F (282 MHz, $CDCl_3$): –61.07, –61.15.

Trans-3,4-bis-(α,α,α-trifluoro-*p*-tolyl)-1,2-bis(fluorenylidene)cyclobutane (14)

Analogously, when the head-to-tail dimer, **12**, (250 mg, 0.37 mmol) suspended in toluene (5 mL) was heated at reflux for 3 days, the orange solid isolated, after removing the solvent and purification by chromatography on silica gel using cyclohexane/toluene (9 : 1) as eluent, was identified as *trans*-3,4-bis-(α,α,α-*p*-trifluorotolyl)-1,2-bis-(fluorenylidene)cyclo-butane, **14**, (165.3 mg, 0.25 mmol; 67%), m.p. 201–204 °C (Found: C, 77.25; H, 4.78. $C_{42}H_{26}F_6{\cdot}(C_2H_5)_2O$ requires C, 77.61; H, 4.85); a sample of **14** suitable for an X-ray crystal structure determination was obtained by recrystallisation from diethyl ether/hexane. δ_H (300 MHz, $CDCl_3$): 7.79 (d, *J* 7.2, 2H), 7.78 (d, *J* 7.5, 2H), 7.63 (brd s, 8H), 7.52 (d, *J* 7.5, 2H), 7.38 (t, *J* 7.5, 2H), 7.32 (t, *J* 7.5, 2H), 7.18 (d, *J* 7.8, 2H), 7.11 (t, *J* 7.8, 2H), 7.08 (t, *J* 7.5, 2H), 4.84 (s, 2H); δ_C (75 MHz, $CDCl_3$): 145.5, 140.8, 140.7, 140.4, 138.1, 136.4, 135.4, 129.8 (q, $^2J_{CF}$ 29.0, phenyl *p*-C), 129.5, 128.9, 127.7, (fluorenyl–CH), 127.6 (phenyl *o*-C), 127.5, 126.6 (q, $^3J_{CF}$ 3.8, phenyl *m*-C), 126.2, 124.4, (fluorenyl–CH), 124.1 (q, $^1J_{CF}$ 276, CF_3), 120.4, 119.9, (fluorenyl–CH), 62.0 (C-3, C-4); δ_F (282 MHz, $CDCl_3$): –60.95.

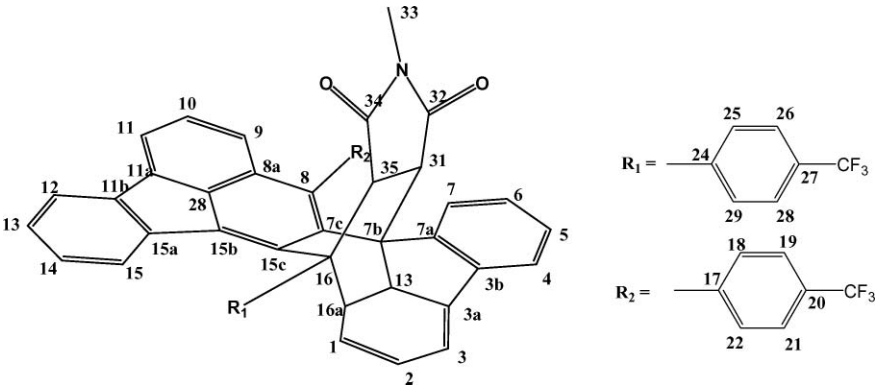
5,9-Dispirofluorenyl-2,8-bis(α,α,α-trifluoro-*p*-tolyl)-5*H*,9*H*-dihydro-tetracene (15)

The head-to-tail dimer, 1-(9-fluorenylidene)-4-(α,α,α-trifluoro-*p*-tolyl)-2-(α,α,α-trifluoro-*p*-tolylmethylene)-spiro[cyclobutane-3,9′-[9*H*]-fluorene], **12**, (1.25 g, 1.87 mmol) dissolved in dimethyl sulfoxide (25 mL) was heated at reflux for 24 h. The mixture was cooled, water was added, and the mixture was extracted with diethyl ether and dichloromethane. The organic phases were combined, cooled to 0 °C for 1 h and filtered to give **15** (343.3 mg, 0.51 mmol; 28%) as a pale yellow solid m.p. 227–229 °C (Found: C, 76.79; H, 3.62. $C_{44}H_{24}F_6{\cdot}0.3CH_2Cl_2$ requires C, 76.88; H, 3.58); chromatographic separation of the filtrate using pentane/toluene yielded additional **15** (162 mg, 0.24 mmol; 13%); δ_H (500 MHz, $CDCl_3$): 7.87 (d, *J* 7.5, H-4, H-5, 4H), 7.45 (td, *J* 7.5, *J* 1.0, 4H, H-3, H-6), 7.23 (dd, *J* 8.0 and 0.5, 2H, H-5′), 7.19 (td, *J* 7.5 and 1.0, 4H, H-2, H-7), 7.11 (dd, *J* 8.0 and 0.5, 4H, H-1, H-8), 6.98 (d, *J* 7.5, 2H, H-6′), 6.55 (s, 2H, H-3′), 6.01 (s, 2H, H-2′); δ_C (125 MHz, $CDCl_3$): 151.5 (C-8a, C-9a), 140.1 (C-4a, C-4b), 139.8 (C-1a', C-1b'), 139.6 (C-2a'), 136.2 (C-6a'), 129.5 (q, $^2J_{CF}$ 32.3, C-4′), 128.5 (C-3, C-6), 128.5 (C-2, C-7), 128.0 (C-6′), 125.5 (C-1, C-8), 124.2 (q, $^3J_{CF}$ 3.8, C-5′), 124.2 (C-2′), 124.0 (q, $^1J_{CF}$ 271, CF_3), 123.1 (q, $^3J_{CF}$ 3.9, C-3′), 120.7 (C-4, C-5), 60.4 (C-9).



Reaction of 8,16-bis(α,α,α-trifluoro-*p*-tolyl)diindeno[1,2,3-*de*:1′,2′,3′-*mn*]tetracene (16) with *N*-methylmaleimide

Under vacuum, the head-to-tail yellow dimer, **12**, (435mg, 0.65 mmol) was heated in the solid state at 200 °C with a heat gun for 30 min. After cooling to room temperature, the blue residue was dissolved in degassed toluene (10 mL), and heated at reflux under nitrogen for 2 h, in the presence of *N*-methylmaleimide (289 mg, 2.6 mmol). When the solution became colourless, the solvent was removed on a rotatory evaporator, and the crude material was chromatographed on a silica gel column using pentane/dichloromethane as eluent to give the Diels–Alder adduct **17**, (45.5 mg, 0.057mmol; 9%) as a white solid, dissociates > 200 °C (Found: C, 76.01; H, 3.70; N, 1.67. $C_{49}H_{27}F_6NO_2$ requires C, 75.87; H, 3.51; N, 1.81); a sample of **17** suitable for an X-ray crystal structure determination was obtained by recrystallisation from pentane/dichloromethane. δ_H (500 MHz, $CDCl_3$): 8.66 (d, *J* 8.5, 1H, H-25), 8.09 (d, *J* 8.5, 1H, H-26), 7.82 (d, *J* 7.0, 1H, H-11), 7.75 (d, *J* 7.0, 1H, H-12), 7.70 (d, *J* 7.5, 1H, H-7), 7.69 (d, *J* 7.0, 2H, H-4, H-21), 7.59 (d, *J* 7.5, 1H, H-3), 7.51 (d, *J* 8.0, 1H, H-22), 7.45–7.41 (m, 3H, H-10, H-28, H-29), 7.24 (t, *J* 8.0, 1H, H-5), 7.18 (t, *J* 7.5, 2H, H-2, H-13), 6.99 (d, *J* 7.5 Hz, 1H, H-9), 6.90 (d, *J* 8.0, 1H, H-19), 6.78 (td, *J* 1.0 and 8.0, 1H, H-14), 6.76 (t, *J* 8.0 Hz, 1H, H-6), 6.32 (d, *J* 8.0, 1H, H-18), 6.29 (d, *J* 8.0, 1H, H-15), 6.15 (d, *J* 8.0, 1H, H-1), 4.26 (d, *J* 9.0 Hz, 1H, H-35), 3.11 (d, *J* 8.5 Hz, 1H, H-31), 2.57 (s, 3 H, H-33); δ_C (125 MHz, $CDCl_3$): 175.9, 175.3 (C-32, C-34), 146.5 (C-16b), 145.9 (C-7a), 142.9 (C-16a), 142.1 (C-16), 141.5 (C-17), 140.8 (C-3b), 140.0 (C-11b), 138.4 (C-7c), 137.9 (C-15a), 137.1 (C-15c), 136.9 (C-11a), 135.5 (C-15b), 135.3 (C-3a), 134.2 (C-8), 133.2 (C-29), 132.4 (C-8b), 131.7 (C-7), 131.6 (C-22), 131.3 (C-18), 130.3 (q, $^2J_{CF}$ 32.5, C-27), 129.7 (q, $^2J_{CF}$ 32.0, C-20), 129.3 (C-8a), 129.1 (C-25), 128.9 (C-15), 128.6 (C-10), 128.5 (C-2), 127.7 (C-13), 127.5 (C-6), 127.4 (C-5), 126.7 (C-14), 125.8 (C-9), 125.7 (q, $^3J_{CF}$ 3.8, C-26), 125.2 (q, $^3J_{CF}$ 3.6, C-28), 124.5 (q, $^1J_{CF}$ 271, CF_3), 124.5 (q, $^1J_{CF}$ 271, CF_3), 123.9-123.7 (m, C-1, C-21, C-19), 120.5 (C-4), 120.3 (C-12), 119.4 (C-3), 119.2 (C-11), 57.3 (C-16), 55.8 (C-7b), 50.8 (C-31), 50.0 (C-35), 25.2 (CH_3).



5-(α,α,α-Trifluoro-*p*-tolyl)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol (19c)

To a solution of 1-ethynyl-4-trifluoromethyl-toluene (3.45 mL, 30 mmol) in dry THF (250 mL), nBuLi (17.15 mL, 27.5 mmol) was added dropwise at −78 °C. After stirring for 1 h at −78 °C, a solution of dibenzosuberenone (5.15 g, 25 mmol) in dry THF (20 mL) was added dropwise. The reaction was stirred for 1 h, quenched with distilled water (150 mL), and extracted with diethyl ether several times. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and the solvent removed to give a yellow oil. The crude product was purified by chromatography on an alumina column using pentane/dichloromethane as eluent to give **19c** (4.36 g, 11.6 mmol; 45%) as a yellow solid, m. p. 79–82 °C (Found: C, 76.23; H, 4.03. $C_{24}H_{15}OF_3$ requires C, 76.59; H, 4.02; δ_H (500 MHz, $CDCl_3$): 8.10 (d, *J* 8.0, 2H, H-4, H-6), 7.56 (d, *J* 8.0, 2H, phenyl *m*-H), 7.51 (d, *J* 8.0, 2H, phenyl *o*-H), 7.47 (td, *J* 7.0 and 1.5, 2H, H-3, H-7), 7.44 (d, *J* 8.0, 2H, H-1, H-9), 7.35 (td, *J* 7.0 and 1.5 Hz, 2H, H-2, H-8), 7.22 (s, 2H, H-10, H-11), 3.23 (s, 1H, OH); δ_C (125 MHz, $CDCl_3$): 140.2 (C-4a, C-5a), 132.9 (C-9a, C-11a), 132.1 (phenyl *o*-C), 131.7 (C-10, C-11), 130.4 (q, $^2J_{CF}$ 32.9, phenyl *p*-C), 129.4 (C-1, C-9), 128.7 (C-3, C-7), 127.4 (C-2, C-8), 126.5 (phenyl *ipso*-C), 125.3 (q, $^3J_{CF}$ 3.9, phenyl *m*-C), 124.0 (q, $^1J_{CF}$ 271, CF_3), 123.5 (C-4, C-6), 93.3 (C-12), 83.5 (C-13), 72.5 (C–OH).

1-Bromo-1-phenyl-2-dibenzo[*a*,*d*]cycloheptenylidene-ethene (20a)

To a cooled solution of 5-phenylethynyl-5*H*-dibenzo-[*a*,*d*]cyclohepten-5-ol, **19a**, (300 mg, 0.97 mmol) in acetic acid (5 mL) was added dropwise a solution of hydrobromic acid (47%, 0.67 g, 3.90 mmol) in water (2.0 mL). Upon stirring for 1 h with cooling, the precipitate was filtered, washed with water and dried. The product was dissolved in THF (5 mL), dried over $MgSO_4$, filtered and concentrated to give **20a** (0.236 g, 0.64 mmol; 66%), as a yellow solid, m.p. 88–92 °C (Found: C, 74.25; H, 4.31. $C_{23}H_{15}Br$ requires C, 74.41; H, 4.07); a sample suitable for an X-ray diffraction structural determination was obtained by recrystallisation from diethyl ether/pentane; δ_H (500 MHz, $CDCl_3$): 7.58 (d, *J* 7.0, 2H, H-4, H-6), 7.56 (dd, *J* 7.0 and 1.5, 2H, phenyl *o*-H), 7.39 (td, *J* 6.8 and 2.5, 2H, H-3, H-7), 7.35 (td, *J* 7.5 and 1.5, 2H, H-2, H-8), 7.34–7.33 (m, 2H, H-1, H-9), 7.31 (t, *J* 8.0, 2H, phenyl *m*-H), 7.25 (td, *J* 7.5 and 1.5, 1H, phenyl *p*-H), 6.85 (s, 2H, H-10, H-11); δ_C (125 MHz, $CDCl_3$): 206.1 (C-12), 135.0 (C-9a, C-11a), 134.5 (C-4a, C-5a), 134.0 (phenyl *ipso*-C), 131.4 (C-10, C-11), 130.0 (C-1, C-9), 129.4 (C-4, C-6), 129.3 (C-3, C-7), 128.5 (C-2, C-8), 128.5 (phenyl *m*-C) 128.5 (phenyl *p*-C), 127.6 (phenyl *o*-C), 117.6 (C-5), 95.5 (C-13); IR ($CDCl_3$): 1926 cm^{-1} (C=C=C).

***Z*-5-(2-Bromo-2-phenylethenyl)-5*H*-dibenzo[*a*,*d*]cycloheptene (35) and 1-phenyl-3-(dibenzo[*a*,*d*]cycloheptenylidene)ethanone (23a)**

To a solution of the bromo-allene **20a** (1.10 g, 2.96 mmol) in diethyl ether (30 mL) was added dropwise at 0 °C a solution of boron trifluoride-etherate (488 μL, 3.56 mmol). Upon stirring 1 h at 0 °C, and 10 h at room temperature, triethylsilane (615 μL, 3.85 mmol) was added dropwise. After stirring for 1 h, the mixture was quenched with water and extracted with diethyl ether several times. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude product was purified by chromatography on silica using dichloromethane/pentane as eluent to give *Z*-5-(2-bromo-2-phenylethenyl)-5*H*-dibenzo[*a*,*d*]-cycloheptene, **35**, (391 mg, 1.05 mmol, 35%) as a white solid (Found: C, 73.65; H, 4.19; Br, 21.23. $C_{23}H_{17}Br$ requires C, 74.00; H, 4.59; Br. 21.41) m.p. 191–193 °C and 1-phenyl-3-(dibenzo[*a*,*d*]cycloheptenylidene)-ethanone, **23a**, (525 mg, 1.70 mmol, 58%) as a yellow solid m.p. 114–116 °C (Found: C, 89.88; H, 5.36. $C_{23}H_{16}O$ requires C, 89.58; H, 5.23); a sample of **35** suitable for an X-ray diffraction structural determination was obtained by recrystallisation from diethyl ether/pentane.

Data for 35. δ_H (500 MHz, $CDCl_3$): 7.55 (dd, *J* 7.5 and 1.5, 2H, H-4, H-6), 7.47–7.35 (m, 6H, H-1, H-9, phenyl *o*-H, *m*-H), 7.33–7.24 (m, 5H, H-2, H-3, H-7, H-8, phenyl *p*-H), 7.07 (s, 2H, H-10, H-11), 6.86 (d, 1H, H-12), 5.27 (d, 1H, H-13); δ_C (125 MHz, $CDCl_3$): 140.0 (C-13), 139.4 (C-4a, C-5a), 134.4 (C-9a, C-11a), 131.6 (C-10, C-11), 129.7 (C-1, C-9), 129.7 (phenyl *ipso*-C, C-12), 129.4 (brd s, C-4, C-6), 129.1 (phenyl *m*-C), 128.5 (phenyl *p*-C), 128.2 (C-3, C-7), 127.9 (phenyl *o*-C), 126.8 (C-2, C-8), 56.0 (C-5).

Data for 23a. δ_H (500 MHz, $CDCl_3$): 7.74 (dd, *J* 7.0 and 1.4, 2H, phenyl *o*-H), 7.58 (d, *J* 7.7, 1H, H-6), 7.44 (td, *J* 6.9 and 1.8, 1H, H-7), 7.39–7.35 (m, 3H, H-8, H-9, phenyl *p*-H), 7.24 (td, *J* 8.4 and 1.2, 2H, phenyl *m*-H), 7.20 (dd, *J* 8.4 and 1.2, 1H, H-1), 7.18 (dd, *J* 7.2 and 1.2, 1H, H-4), 7.13 (td, *J* 7.2 and 1.2, 1H, H-2), 7.09 (td, *J* 7.2 and 1.2 Hz, 1H, H-3), 6.97 (d, *J* 12 Hz, 1H, H-10), 6.94 (d, *J* 12.0, 1H, H-11), 6.55 (s, 1H, H-12); δ_C (125 MHz, $CDCl_3$): 194.8 (C-13), 152.9 (C-5), 140.0 (C-5a), 137.9 (phenyl *ipso*-C), 136.6 (C-4a), 133.9 (C-9a), 133.9 (C-11a), 132.6 (phenyl *p*-C), 131.4 (C-11), 131.2 (C-10), 129.5 (C-12), 129.2 (C-4), 129.2 (C-7), 128.6 (C-9),

Table 1 Crystallographic data for **12**, **13**, **14** and **17**

	12	**13**	**14**	**17**
Formula	$(C_{44}H_{26}F_6)_2{\cdot}C_6H_{14}$	$(C_{44}H_{26}F_6)_4{\cdot}CH_2Cl_2$	$C_{44}H_{26}F_6{\cdot}C_6H_{14}$ [b]	$C_{49}H_{27}NO_2F_6$
M	1423.47	2759.52	668.65	775.72
Crystal system	triclinic	triclinic	orthorhombic	triclinic
Space group	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	*I*ba2 (#45)	$P\bar{1}$ (#2)
a [Å]	9.0486(15)	10.118(3)	10.154(3)	9.4052(11)
b [Å]	11.2654(19)	16.177(4)	16.592(4)	14.5518(17)
c [Å]	18.715(3)	22.818(6)	23.131(6)	14.8501(17)
α [°]	91.991(3)	110.541(4)	90	110.752(2)
β [°]	101.326(3)	97.597(5)	90	107.181(2)
γ [°]	109.783(3)	94.218(5)	90	99.085(2)
V [Å^3]	1749.6(5)	3437.7(16)	3897.0(17)	1735.6(3)
Z	1	1	4	2
ρ_{calcd} [g.cm^{-}3]	1.351	1.333	1.140	1.484
T [K]	100(2)	293(2)	100(2)	100(2)
μ mm^{-}1	0.099	0.137	0.085	0.112
F(000)	738	1418	1376	796
θ Range [°]	1.93 to 26.00	1.91 to 24.00	1.76 to 26.00	1.57 to 24.19
Index ranges	$-11 \le h \le 11$	$-11 \le h \le 11$	$-12 \le h \le 9$	$-10 \le h \le 10$
	$-13 \le k \le 13$	$-18 \le k \le 18$	$-20 \le k \le 20$	$-16 \le k \le 16$
	$-23 \le l \le 23$	$-26 \le l \le 26$	$-26 \le l \le 28$	$-17 \le l \le 17$
Reflections measured	27144	45731	9426	12790
Reflections used	6863	10807	1976	5529
R_{int}	0.0285	0.0274	0.0581	0.0254
Data/restraints/parameters	6863/0/583	10807/2/1031[a]	1976/1/244	5529/0/524
Final *R* values [$I>2\sigma$ (*I*)]:				
*R*1	0.0449	0.0443	0.0526	0.0486
w*R*2	0.1150	0.1086	0.1311	0.1290
R values (all data):				
*R*1	0.0516	0.0622	0.0633	0.0616
*wR*2	0.1203	0.1205	0.1361	0.1363
GOF on *F*2	1.026	1.008	1.031	1.056
Largest diffraction peak and hole (e Å^{-3})	0.708 and –0.456	0.471 and –0.255	0.792 and –0.513	0.440 and –0.280

[a] Both C–Cl distances were restrained to be around 1.75 Å. [b] The solvent could not be located. SQUEEZE was used to compensate for the spread electron density.

128.6 (C-1), 128.4 (C-3), 128.2 (C-2), 128.1 (phenyl *m*-C, C-8), 127.2 (C-6); IR ($CDCl_3$): 1648 cm^{-1} (C=O).

2-Phenyl-11b*H*-dibenz[*cd*,*h*]azulene (30)

To a solution of 1-bromo-2-dibenzo[a,d]cyclo-heptenylidene-1-phenyl-ethene, **20a**, (1.0 g, 2.69 mmol) in THF (30 mL) was added dropwise at 0 °C a solution 1 M of HBF_4 in diethyl ether (740 μL, 5.4 mmol). Upon stirring 1 h at 0 °C and 12 h at reflux, the mixture was cooled to room temperature and triethylsilane (1.3 mL, 8.07 mmol) was added. After stirring 12 h at reflux, the solvent was removed and the crude product was purified by chromatography on silica using dichloromethane/pentane as eluent to give 2-phenyl-11b*H*-dibenz[*cd*,*h*]azulene, **30**, (96.1 mg, 0.33 mmol; 12%) as a white solid, m.p. 134–136 °C (Found: C. 94.66; H, 5.37. $C_{23}H_{16}$ requires C, 94.48; H, 5.52); a sample suitable for an X-ray diffraction structural determination was obtained by recrystallisation from diethyl ether/dichloromethane/hexane; δ_H (500 MHz, $CDCl_3$): 7.71 (d, *J* 7.0, 2H, phenyl *o*-H), 7.55 (d, *J* 7.5, 1H, H-3), 7.50 (t, *J* 7.5, 2H, phenyl *m*-H), 7.42 (t, *J* 7.5, 1H, phenyl *p*-H), 7.38 (d, *J* 7.5 Hz, 1H, H-11), 7.33 (dd, *J* 7.5, and 1.0, 1H, H-8), 7.32 (t, *J* 7.5, 1H, H-4), 7.28 (td, *J* 7.5 and 1.5, 1H, H-10), 7.23 (t, *J* 7.0, 1H, H-9), 7.21 (d, *J* 7.5, 1H, H-5), 7.10 (d, *J* 2.5, 1H, H-1), 7.05 (d, *J* 12.0, 1H, H-7), 7.02 (d, *J* 12.0, 1H, H-6), 4.48 (d, *J* 2.5, 1H, H-11b); δ_C (125 MHz, $CDCl_3$): 146.4 (C-2), 145.1 (C-11c), 141.7 (C-2a), 136.1, 136.0, (C-7a, C-11a), 136.0 (phenyl *ipso*-C), 132.8 (C-1), 132.5 (C-7), 132.2 (C-5a), 130.3 (C-6), 129.7 (C-8), 128.9 (C-10), 128.8 (phenyl *m*-C), 128.1 (phenyl *p*-C), 128.0 (phenyl *o*-C), 127.1 (C-4), 126.5 (C-9), 126.3 (C-11), 125.0 (C-5), 120.5 (C-3), 51.6 (C-11b).

2,3-Diphenyl-1-(phenylethynyl)-inden-1-ol (36)

nBuLi (7.5 mL of a 1.6 M hexane solution, 12 mmol) was added dropwise to a solution of phenylacetylene (1.10 mL, 10 mmol) in THF (50 mL) at 0 °C. After stirring for 15 min at room temperature, the solution was cooled to 0 °C and a solution of 2,3-diphenyl-1*H*-inden-1-one (2.82 g, 10 mmol) in THF (20 mL) was added slowly. The solution was stirred at room temperature for 30 min, quenched with a few drops of water and the solvent evaporated. The crude product was chromatographed on alumina gel using cyclohexane/dichloromethane as eluent to give 1-(phenylethynyl)-2,3-diphenylinden-1-ol, **36**, (3.64 g, 9.46 mmol, 94%) as a white solid, m.p. 134–137 °C (Found: C, 90.18; H, 5.08. $C_{29}H_{20}O$ requires C, 90.60; H, 5.24); δ_H (500 MHz, $CDCl_3$): 7.84–7.80 (m, 1H), 7.71–7.68 (m, 2H), 7.48–.28 (m, 16H), 2.67 (s, 1H, OH); δ_C (125 MHz, $CDCl_3$): 146.8, 144.3, 142.8, 140.3, 134.4, 133.8, 132.1, 129.9, 129.3, 129.3, 128.8, 128.7, 128.4, 128.3, 128.1, 127.9, 127.5, 123.2, 122.6, 121.4, 89.0, 84.2, 78.6; IR (CH_2Cl_2): 3561 cm^{-1} (OH), 2223 cm^{-1} (C≡C).

Table 2 Crystallographic data for **20a**, **30**, **34** and **38**

	20a	**30**	**34**	**38**
Formula	$C_{23}H_{15}Br$	$C_{23}H_{16}$	$C_{23}H_{17}Br$	$C_{29}H_{20}$
M	371.26	292.36	373.28	368.45
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$ (#19)	*Pccn* (#56)	$P2_1/n$ (#14)	*C*2/c (#15)
a [Å]	6.1828(8)	19.553(3)	10.3403(12)	24.337(3)
b [Å]	9.6681(12)	28.605(5)	15.2026(18)	5.7025(7)
c [Å]	27.580(4)	5.3564(9)	11.2081(13)	28.668(3)
α [°]	90	90	90	90
β [°]	90	90	106.127(2)	99.404(2)
γ [°]	90	90	90	90
V [Å^3]	1648.6(4)	2995.9(9)	1692.6(3)	3925.2(8)
Z	4	8	4	8
ρ_{calcd} [g.cm$^-$3]	1.496	1.296	1.465	1.247
T [K]	100(2)	100(2)	100(2)	100(2)
μ mm$^-$1	2.493	0.073	2.428	0.071
F(000)	752	1232	760	1552
θ Range [°]	2.23 to 30.00	1.42 to 23.29	2.32 to 27.00	1.44 to 26.00
Index ranges	$-8 \le h \le 8$ $-13 \le k \le 13$ $-38 \le l \le 38$	$-21 \le h \le 21$ $-31 \le k \le 31$ $-5 \le l \le 5$	$-13 \le h \le 13$ $-19 \le k \le 19$ $-14 \le l \le 14$	$-30 \le h \le 30$ $-7 \le k \le 7$ $-35 \le l \le 35$
Reflections measured	34485	16917	14572	15216
Reflections used	4803	2135	3684	3836
R_{int}	0.0474	0.0431	0.0388	0.0300
Data/restraints/parameters	4803/0/217	2135/0/208	3684/0/285	3836/53/343
Final *R* values [$I>2\sigma$ (*I*)]:				
*R*1	0.0362	0.0418	0.0303	0.0381
w*R*2	0.0897	0.0956	0.0748	0.0865
R values (all data):				
*R*1	0.0386	0.0505	0.0383	
*wR*2	0.0914	0.0991	0.0801	0.0479 0.0922
GOF on *F*2	1.110	1.128	1.030	1.041
Largest diffraction peak and hole (e Å^{-3})	1.905 and –0.365	0.200 and –0.135	0.519 and –0.356	0.219 and –0.155

1,2-diphenyl-3-(phenylethynyl)-1H-indene (39)

To 1-(phenylethynyl)-2,3-diphenylinden-1-ol, **36**, (3.0 g, 7.8 mmol) in dry dichloromethane (80 mL), and cooled to 0 °C, triethylsilane (1.5 mL, 9.36 mmol) was added slowly. Boron trifluoride-etherate (1.2 mL, 9.36 mmol) was added dropwise and the solution became green-black. After stirring for 30 min at 0 °C, the reaction was quenched with distilled water (100 mL), and the mixture was extracted with dichloromethane several times. The organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated to give a brown oil that was chromatographed on silica gel using dichloromethane/pentane as eluent to give 1,2-diphenyl-3-(phenylethynyl)-1*H*-indene, **39**, as a white solid (1.0 g, 2.71 mmol; 35%), m.p. 148–149 °C (lit.[24] 149 °C); a sample suitable for an X-ray crystal structure determination was obtained by recrystallisation from dichloromethane/pentane; δ_H (500 MHz, $CDCl_3$): 7.96 (dd, *J* 7.5 and 1.2 Hz, 2H), 7.70–7.60 (m, 3H), 7.43–7.10 (m, 14H), 5.16 (s, 1H).

Crystal data

Crystal data for **12**, **13**, **14**, **17**, **20a**, **21a**, **23c**, **24a**, **30**, **35** and **39** were collected using using Mo–K_α radiation on a Bruker SMART APEX CCD area detector diffractometer. Data for **12**, **13**, **14**, **17**, **20a**, **30**, **35** and **39** are listed in Tables 1 and 2. Data for **20b**, **21a**, **23c** and **24a** are listed in ESI. A full sphere of the reciprocal space was scanned by phi-omega scans. A semi-empirical absorption correction based on redundant reflections was performed by the program SADABS.[26] Crystal data of **20b** were collected using an Oxford Diffraction SuperNova A diffractometer fitted with an Atlas detector. A twice redundant dataset was collected, assuming that the Friedel pairs are not equivalent. An analytical absorption correction based on the shape of the crystal was performed.[27] The structures were solved by direct methods using SHELXS-97[28] and refined by full matrix least-squares on F^2 for all data using SHELXL-97.[28] Hydrogen atom treatment varied from compound to compound, depending on the crystal quality. All hydrogen atoms in **34**, the ones of the main molecule in **12** and the ordered ones in **24a** were located in the difference fourier map and allowed to refine freely. All other hydrogen atoms were added at calculated positions and refined using a riding model. Their isotropic thermal displacement parameters were fixed to 1.2 times (1.5 times for methyl groups) the equivalent one of the parent atom. Anisotropic thermal displacement parameters were used for all non-hydrogen atoms.

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