DOI: 10.1002/ejoc.200600905

# From Allenes to Tetracenes: A Synthetic and Structural Study of Silyl- and Halo-Allenes and Their Dimers

**Emilie V. Banide,[a] Bevin C. Molloy,[a] Yannick Ortin,[a] Helge Müller-Bunz,[a] and Michael J. McGlinchey*[a]**

**Keywords:** Allenes / Dimerizations / Long bonds

9-Alkynylfluoren-9-ols of type $C_{13}H_8$(OH)–C≡C–R, where R is phenyl (**1a**), *p*-tolyl (**1b**), *p*-methoxyphenyl (**1c**), or trimethylsilyl (**1d**), react with HBr to yield the corresponding bromoallenes $C_{12}H_8$C=C=C(Br)R (**13a**–**d**). Lithiation and hydrolysis of **13d** yields 3,3-(biphenyl-2,2′-diyl)-1-(trimethylsilyl)allene (**20**), which forms successively the head-to-tail dimer 1-(9-fluorenylidene)-4-(trimethylsilyl)-2-[(trimethylsilyl)methylene]spiro[cyclobutane-3,9′-[9*H*]fluorene] (**21**) and the tail-to-tail dimer *trans*-3,4-bis(trimethylsilyl)-1,2-di(fluorenylidene)-cyclobutane (**23**) both of which exhibit long (ca. 1.6 Å) C(3)–C(4) bonds. Treatment of **21** and **23** with TBAF brings about desilylation to **22** and **24**, respectively. In the latter case, removal of the bulky trimethylsilyl groups reduces the C(3)–C(4) bond length in 1,2-di(fluorenylidene)cyclobutane (**24**) to a more normal value of 1.547 Å; however, the large wingspan of the severely overlapping fluorenylidene moieties retains the $C_2$ symmetry of the system. Prolonged exposure to sunlight of the disilylated head-to-tail dimer **21** results in homolysis of the long C(3)–C(4) bond, generation of a peroxide, and ultimately formation of the lactol **25**. X-ray crystallographic data are reported for, among others, **1c**, **13a**, **21**, **22**, **23**, **24**, **25**, and also for 3,3-(biphenyl-2,2′-diyl)-1-chloroallene (**12**).



## Introduction

In continuation of our studies on the syntheses and dimerizations of fluorenylidene-derived allenes to form bis-(alkylidene)cyclobutanes, and ultimately tetracenes,[1–3] we wished to incorporate substituents containing other main group elements, in particular silicon and/or halogens. Since many tetracenes are known to be electroluminescent,[4] it was hoped that the introduction of a wider range of functional groups into the precursor allenes would allow greater control of their luminescent and other photophysical or electro-conductive properties. We here report the preparation and crystallographic characterization of a number of silyl- and halo-allenes, as well as the resulting dimerisation products.

## Results and Discussion

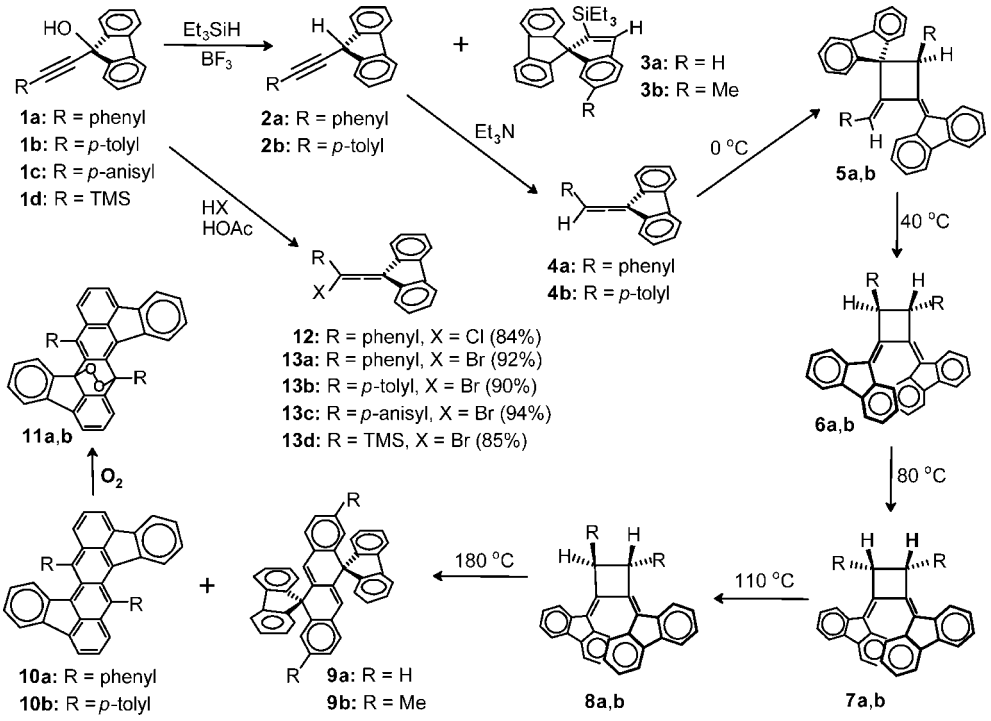
The reaction of fluorenone with lithio-alkynes yields, after hydrolysis, the corresponding 9-alkynyl-fluoren-9-ols, where R = phenyl, **1a**, *p*-tolyl, **1b**, *p*-methoxyphenyl, **1c**, or trimethylsilyl, **1d** (Scheme 1). As a representative example, the X-ray crystal structure of **1c** is shown in Figure 1. In the solid state, the molecules are linked in a linear fashion such that each hydroxy group is hydrogen-bonded to the methoxy substituent in an adjacent molecule.

A general method for the conversion of an alkynol into the corresponding alkyne, **2**, involves treatment with $Et_2O{\cdot}BF_3$ and triethylsilane.[5] Presumably, the reaction proceeds via coordination of the hydroxy group to boron, transfer of fluoride from boron to silicon, and delivery of a hydride from silicon to carbon, possibly in a six-membered transition state. The spiro-bonded indenylfluorenes **3a** and **3b** are also formed in appreciable quantities. Subsequent reaction of the alkynes **2** with triethylamine brings about efficient isomerization to allenes **4**, that dimerize in a head-to-tail fashion giving 1,2-bis(alkylidene)cyclobutanes **5**.[6] As discussed previously,[3] and shown in Scheme 1, the head-to-tail dimers **5**, are sequentially transformed via a series of diastereomeric tail-to-tail dimers, **6**→**7**→**8**, that ultimately, when thermolysed at 180 °C, yield the dispirotetracenes **9**, and the diindeno-tetracenes **10**. Although the blue, electroluminescent tetracenes **10** are stable under a nitrogen atmosphere, when exposed to air they undergo gradual oxidation to the corresponding peroxides **11**.

The complete sequence of molecular transformations from **2a** through **11a**, where R is phenyl, has been unambiguously elucidated by X-ray crystallography,[1–3,7] and Figure 2 depicts the structure of orange *trans*-1,2-di(fluorenylidene)-3,4-di(*p*-tolyl)cyclobutane (**8b**), that arose from the dimerisation of 3,3-(biphenyl-2,2′-diyl)-1-(*p*-tolyl)allene (**4b**), formed in situ from the alkyne **2b** in the presence of

[a] School of Chemistry and Chemical Biology, University College Dublin,
Belfield, Dublin 4, Ireland




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

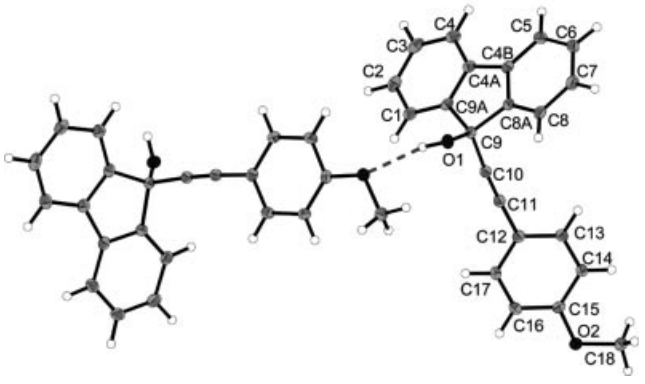



Figure 1. X-ray crystal structure of 9-(*p*-anisylethynyl)fluoren-9-ol (**1c**).

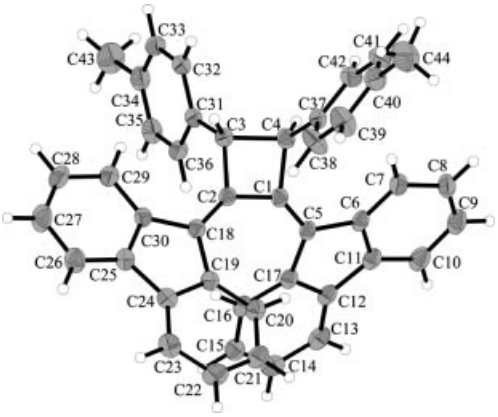



Figure 2. X-ray crystal structure of *trans*-1,2-di(fluorenylidene)-3,4-di(*p*-tolyl)cyclobutane (**8b**).

base. The C(3)–C(4) bond length in **8b** is 1.595(3) Å, and the dihedral angle between the fluorenylidene planes is 64°. Note that in **8b** the helical arrangement of the overlapping exocyclic fluorenylidenes matches that of the *trans*-disposed hydrogens in the four-membered ring. In the precursor **6b** the helicity of the fluorenylidenes is reversed such that they are oriented in the same sense as the *trans*-disposed phenyl groups in the cyclobutane ring. Thermolysis of the ditolyl derivative **8b** yields the dispirotetracene **9b** and the blue diindenotetracene **10b**; the latter species is very susceptible to peroxide formation giving **11b**.

However, the above-mentioned procedure for the conversion of the 9-alkynyl-fluorenols, **1**, to the corresponding alkynes, **2**, fails when the R group possesses a substituent with a lone pair to which the $BF_3$ can coordinate, e.g. the methoxy group in **1c**; likewise, the reaction fails for **1d**, where R is $Me_3Si$ which is susceptible to attack by fluoride. Consequently, we chose to treat the alkynols **1** with HCl and HBr to generate haloallenes **12** and **13**, respectively; conversion to the corresponding Grignard or organolithium reagent and subsequent hydrolysis would be expected to yield the required allenes directly. Although chloroallenes of the type $Ar_2C{=}C{=}CRX$ are generally not isolable because they so readily dimerize,[8,9] in our hands slow addition of dilute aqueous HCl to **1a** at 0 °C yielded 3,3-(biphenyl-2,2′-diyl)-1-chloro-1-phenylallene (**12**). The analogous bromoallenes **13a**–**d** were likewise preparable by reaction with HBr in acetic acid, and the molecular structures of $C_{13}H_8{=}C{=}C(X)Ph$ where X = Cl (for **12**) and X = Br

(for **13a**) appear in parts a,b of Figure 3, respectively. The allene double bonds are, of course, orthogonal and in both cases the C(9)=C(10) bond [1.313(4) Å in **12**; 1.321(3) Å in **13a**] is significantly longer than the C(10)=C(11)–X bond [1.298(4) Å in **12**; 1.292(3) Å in **13a**].

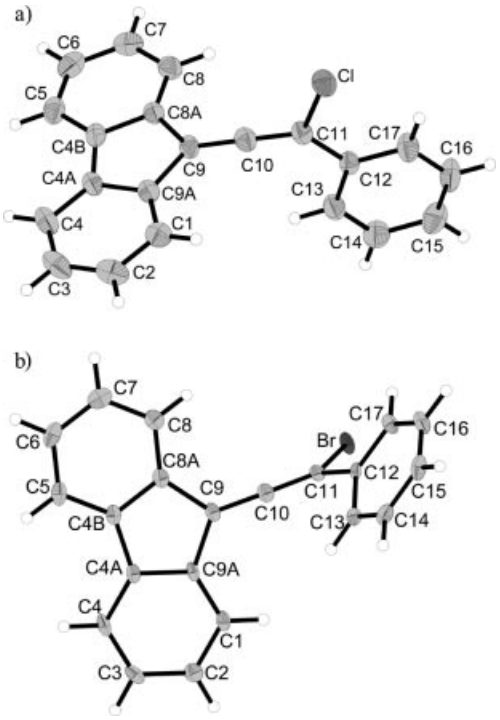



Figure 3. a) X-ray crystal structure of chloroallene **12**. b) X-ray crystal structure of the bromoallene **13a**.

As shown in Scheme 2, successive treatment of ethynyltrimethylsilane with n-butyllithium and fluorenone yielded, after hydrolysis, not only the expected 9-(trimethylsilyl)ethynyl-9*H*-fluoren-9-ol (**1d**), but also the by-product 9,9′-(ethyne-1,2-diyl)bis(fluoren-9-ol) (**14**) whereby two fluoren-9-ol moieties are linked by a triple bond. This observation is in agreement with an earlier report.[10] Treatment of **14** with cold dilute aqueous HBr produced 3,3-(biphenyl-2,2′-diyl)-1-bromo-1-(9-hydroxy-9*H*-fluorenyl)allene (**15**), whose X-ray crystal structure appears as Figure 4. As with **12** and **13a**, the C(9)=C(10) bond connecting the fluorenylidene to the central allene C atom [1.318(3) Å] is significantly longer than the C(10)=C(11)–Br bond [1.286(3) Å].

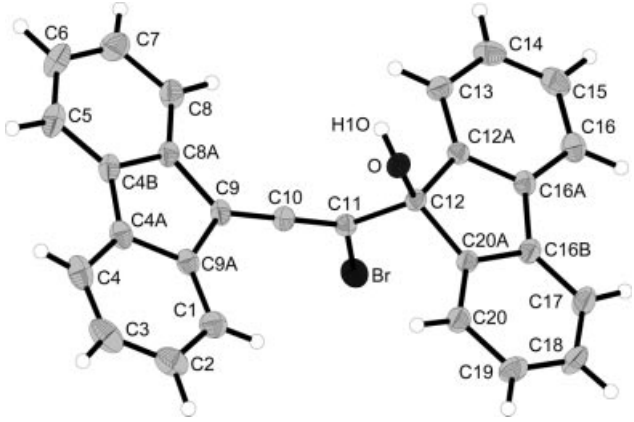
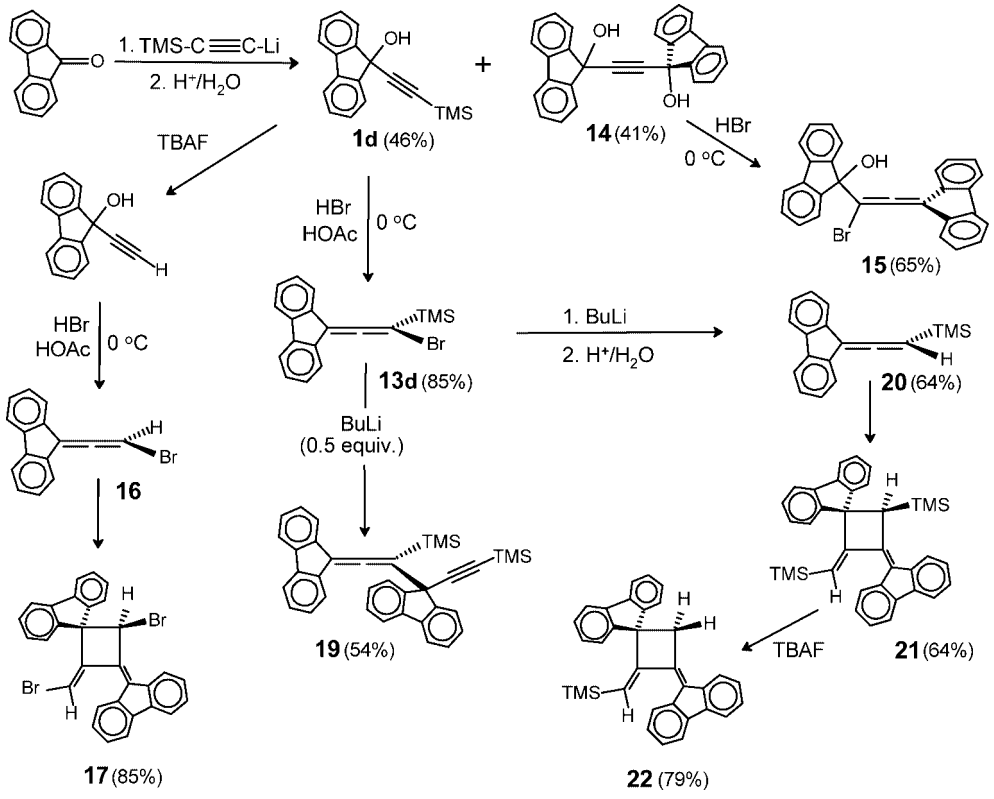



Figure 4. X-ray crystal structure of 3,3-(biphenyl-2,2′-diyl)-1-bromo-1-(9-hydroxy-9*H*-fluorenyl)allene (**15**).




Scheme 2. Bromo- and silyl-allenes and their corresponding dimers.

The reaction of 9-[(trimethylsilyl)ethynyl]-9*H*-fluoren-9-ol (**1d**) with TBAF generated 9-ethynyl-9*H*-fluoren-9-ol;[10] subsequent treatment with dilute aqueous HBr produced 3,3-(biphenyl-2,2′-diyl)-1-bromoallene (**16**) that, when stirred for 5 h at room temperature, yielded the yellow head-to-tail dimer 4-bromo-2-(bromomethylene)-1-(9-fluorenylidene)spiro[cyclobutane-3,9′-[9*H*]fluorene] (**17**). The structure of **17**, established by X-ray crystallography, is shown in Figure 5, and confirms the previous proposal that was based primarily on an analysis of the UV spectroscopic data.[11] The C(3)–C(4) bond length of 1.586 Å in **17** is rather long, but is considerably shorter than the value of 1.605 Å previously reported for the phenyl analogue **5a**.[3,7]

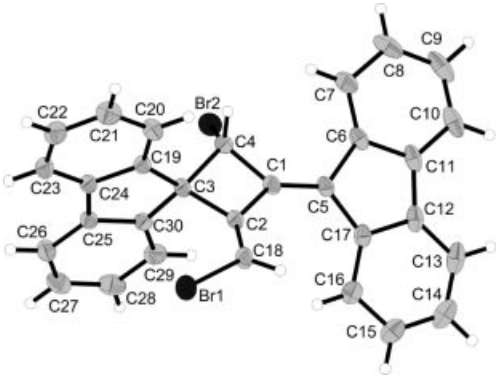



Figure 5. X-ray crystal structure of the head-to-tail bromoallene dimer **17**.

As noted above, treatment of **1d** with cold, dilute HBr furnished 3,3-(biphenyl-2,2′-diyl)-1-bromo-1-(trimethylsilyl)allene (**13d**). We are aware of only a single prior report[12] on the preparation and reactivity of **13d**, whereby treatment with a thiolate anion produced not only the spiro-bonded fluorenylcyclopropene **18**, but also 3,3-(biphenyl-2,2′-diyl)-1-(trimethylsilyl)-1-[9-(trimethylsilylethynyl)-9*H*-fluorenyl]allene (**19**) which may have arisen via coupling of two canonical forms of the 9-alkynyl-fluorenyl radical, as in Scheme 3. Indeed, a series of analogous hexa-1,2-dien-5-ynes have been prepared via the copper-mediated coupling of 1-aroyl-3,3-(biphenyl-2,2′-diyl)-1-chloroallenes;[13] these head-to-tail allenyl dimers exhibit photochromism in the solid state.[14]

Interestingly, the dimer **19** was also formed when a deficit of butyllithium was added dropwise to the bromoallene **13d**, and its structure appears as shown in Figure 6. In contrast, addition of **13d** to butyllithium, and subsequent hydrolysis, yielded the desired 3,3-(biphenyl-2,2′-diyl)-1-(trimethylsilyl)allene (**20**) that was isolated and fully characterized spectroscopically; however, when the allene **20** was stirred in cyclohexane for 24 h, it gradually formed the head-to-tail dimer **21**. The structure of **21** is shown in Figure 7 and reveals a long C(3)–C(4) bond (1.605 Å) between the $sp^3$-C atoms in the cyclobutane ring. This value matches the C(3)–C(4) bond length of 1.605 Å previously observed in the phenyl analogue **5a**. However, the additional steric

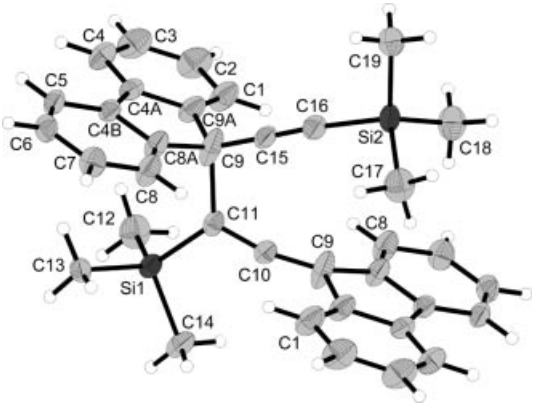



Figure 6. X-ray crystal structure of the bis(trimethylsilyl)hexa-1,2-dien-5-yne **19**.

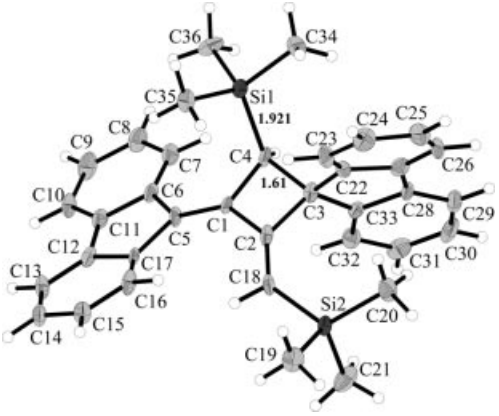
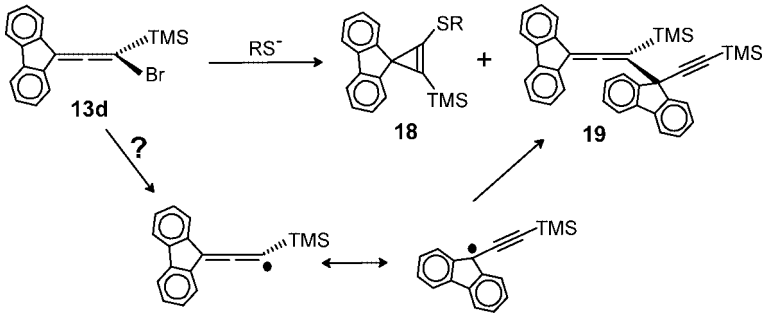



Figure 7. X-ray crystal structure of the head-to-tail silyl-allene dimer **21**.




Scheme 3. Formation of the radical dimer **19**.

strain engendered by replacing the planar phenyl substituent in **5a** by a much more voluminous trimethylsilyl group has to be accommodated. One might have anticipated an even greater lengthening of the C(3)–C(4) bond, but instead the situation is alleviated by a marked increase in the Si(1)–C(4) distance. The system crystallizes with two independent molecules in the unit cell; the Si(1)-methyl bond lengths are normal (average of the six values is 1.866 Å), but the Si–C(ring) distances are now 1.921(6) and 1.931(6) Å in the two independent molecules. Treatment of **21** with TBAF preferentially removes the trimethylsilyl substituent bonded to C(4), the $sp^3$-C atom in the cyclobutane ring, to yield **22** (Scheme 2) in which the C(3)–C(4) bond is now a more normal 1.575(3) Å (Figure 8).

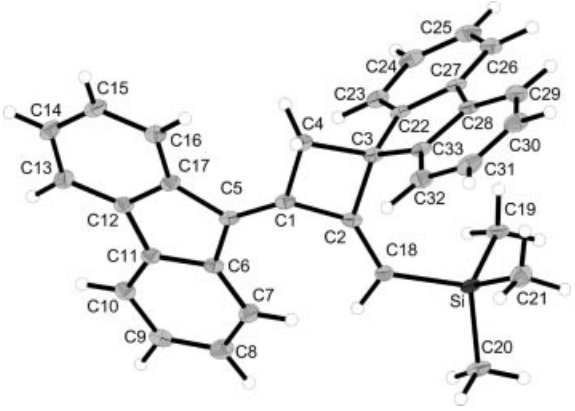



Figure 8. X-ray crystal structure of **22**, obtained by mono-desilylation of **21**.

Thermolysis of the silylallene **20** yields the expected tail-to-tail isomer *trans*-3,4-bis(trimethylsilyl)-1,2-di(fluorenylidene)cyclobutane (**23**) whose structure appears in Figure 9 (see parts a and b). In this case, the quality of the available crystals was not ideal, but sufficient to establish the atom connectivity as being analogous to that exhibited by the ditolyl tail-to-tail dimer **8b**. Once again, the C(3)–C(4) bond in **23** is apparently rather long (ca. 1.6 Å) and the dihedral angle between the fluorenylidene planes is ca. 60°, but we cannot claim high accuracy for these values. However, the $C_2$ character of the molecule is evident whereby the helicity of the two *trans* trimethylsilyl groups is opposite to that of the overlapping fluorenylidene moieties.

As shown in Figure 10, treatment of **23** with TBAF removes both of the trimethylsilyl substituents to yield the "parent" 1,2-di(fluorenylidene)cyclobutane (**24**) in which the C(3)–C(4) bond now exhibits a normal value of 1.547(2) Å in the absence of bulky groups. Nevertheless, there is still considerable overlap of the two fluorenylidene moieties and the dihedral angle between them is now 58°.

Interestingly, when a solution of the disilyl head-to-tail dimer **21** was left in sunlight for several weeks, the crystalline product that eventually formed was characterised as the lactol, **25**, whose structure is shown in part a of Figure 11, and which also exhibits intermolecular hydrogen bonding, as depicted in part b of Figure 11. The lactol appears to

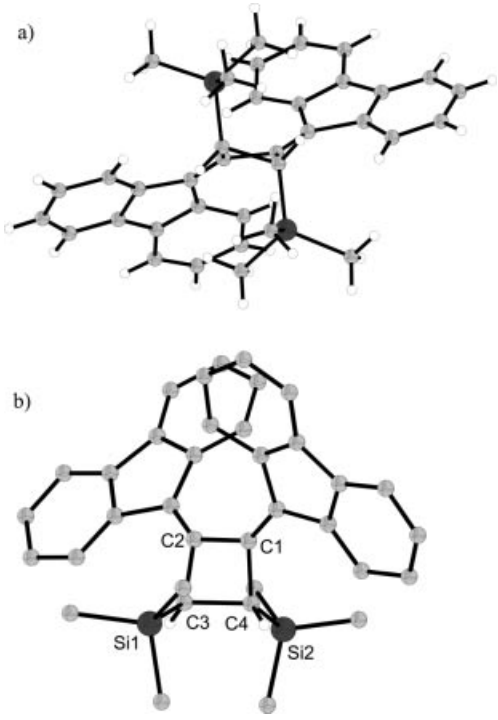



Figure 9. a) X-ray crystal structure of the *trans*-tail-to-tail silyl-allene dimer **23** viewed along the $C_2$ axis. b) Bird's eye view of **23** with fluorenylidene hydrogens removed for clarity.

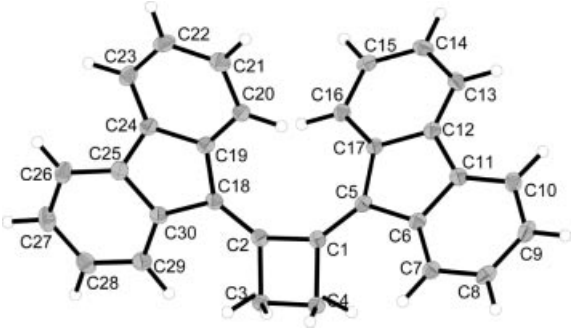



Figure 10. X-ray crystal structure of 1,2-di(fluorenylidene)cyclobutane (**24**).

have arisen from reaction of **21** with dioxygen, and also involves loss of a trimethylsilyl moiety. One might surmise that the long (1.605 Å) C(3)–C(4) bond in **21** is cleaved photolytically to form a diradical that reacts with dioxygen to yield initially a peroxide, **26**. As depicted in Scheme 4, subsequent rupture of the oxygen–oxygen linkage in **26**, migration of silicon from carbon to oxygen through a Brook radical rearrangement, ring closure to form the 3,4-dialkylidene-tetrahydofuran ring, and finally hydrolysis of the Si–O bond would yield the observed product **25**. Related precedents include the formation of lactols upon thermolysis of 1,2-dioxacyclohexanes,[15] and of tetracene peroxides.[16]

It is noteworthy that when 2,7-dinitrofluorenone is used instead of fluorenone, the major product found after thermolysis of 9-(phenylethynyl)-9*H*-2,7-dinitrofluorene at

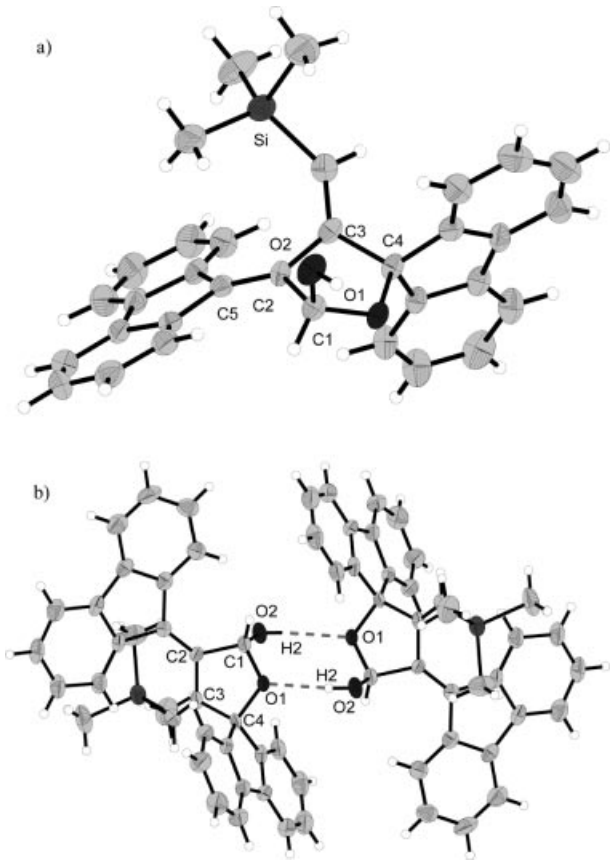
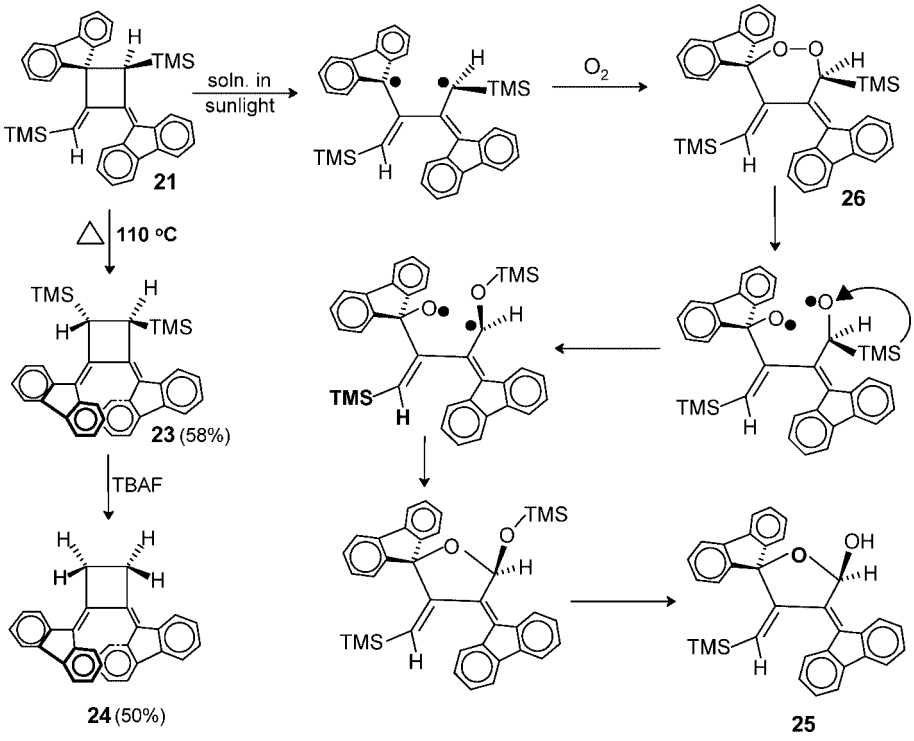



Figure 11. a) X-ray crystal structure of the lactol **25**. b) Intermolecular hydrogen bonding in the lactol **25**.

180 °C is the dinitro-dispirotetracene **27**; only traces of the dinitro-diindenotetracene **28** analogous to **10** are observed. The mechanism of tetracene formation is thought to proceed via a diradical intermediate,[3] and the preferential formation of **27** over **28** is presumably a reflection of the presence of the *meta*-nitro group which is less than ideally situated to stabilize radical character localized on the *ortho*-C of the fluorenyl moiety.[17] As depicted in Scheme 5, this is a requirement for expansion of the cyclobutane to form a six-membered ring, thus initiating the sequence leading to diindenotetracene formation. Hence, the more favoured process is ring expansion onto an *ortho*-C of the adjacent phenyl group, and subsequently leads to the corresponding dispiro-tetracene.

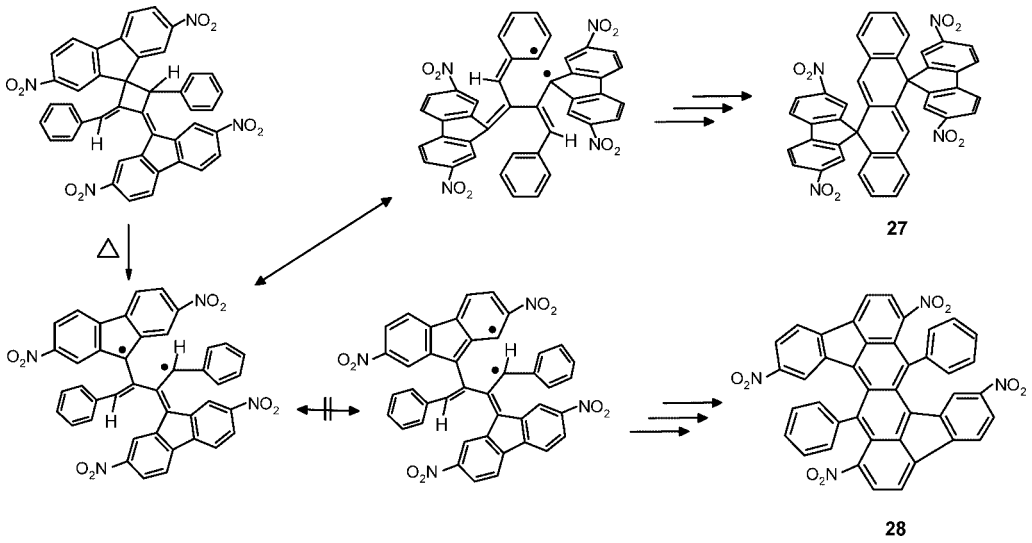
## Conclusions

The bromo- and silyl-allenes **16** and **20** yield 1,2-dialkylidene-cyclobutane, head-to-tail dimers **17** and **21**, respectively; mono-desilylation of **21** occurs at the four-membered ring to furnish **22**. Thermolysis of **20** formed the tail-to-tail dimer *trans*-3,4-bis(trimethylsilyl)-1,2-di(fluorenylidene)-cyclobutane (**23**) which exhibits a long (ca. 1.6 Å) C(3)–C(4) bond. Double desilylation of **23** reduces the C(3)–C(4) bond length in 1,2-di(fluorenylidene)cyclobutane (**24**) to 1.547 Å; however, the large wingspan of the severely overlapping fluorenylidene moieties retains the $C_2$ symmetry of the system. In solution, the long C(3)–C(4) bond of **21** is readily cleaved and reacts with oxygen to yield the lactol **25**.




Scheme 4. Proposed mechanism of formation of lactol **25**.




Scheme 5. Preferential formation of spirotetracenes rather than diindenotetracenes.

## Experimental Section

$^1$H- and $^{13}$C-NMR spectra were recorded on Varian Inova 300 MHz, 400 MHz or 500 MHz spectrometers. Assignments of δ values (ppm) were based on standard 2D NMR techniques ($^1$H-$^1$H COSY, $^1$H-$^{13}$C HSQC and HMBC, NOESY). Electrospray mass spectrometry was performed on a Micromass Quattro micro instrument. 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.

**Syntheses of 9-Alkynylfluoren-9-ols 1a–c:** In a typical procedure, *n*BuLi (3.12 mL of a 1.6 M hexane solution, 5 mmol) was added dropwise to a solution of 4-ethynylanisole (3.12 mL, 5 mmol) in tetrahydrofuran (50 mL) at 0 °C, and the solution was warmed to room temperature. After 15 min stirring, the solution was cooled to 0 °C and fluorenone (901 mg, 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-[(*p*-methoxy)ethynyl]-9*H*-fluoren-9-ol (**1c**) (930 mg, 3.13 mmol; 63%) as a white powder, m.p. 120–122 °C. A sample suitable for an X-ray diffraction structural determination was obtained by recrystallisation from chloroform. Similarly, **1a** and **1b** were prepared and characterized by comparison with literature data.[12,18,19]

**Data for 1b:** $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.73 (dd, 2 H, $J$ = 7.0 Hz, $J$ = 1.0 Hz, 1-H, 8-H), 7.57 (dd, 2 H, $J$ = 7.0 Hz, $J$ = 1.5 Hz, 4-H, 5-H), 7.35 (td, 2 H, $J$ = 7.5 Hz, $J$ = 1.5 Hz, 3-H, 6-H), 7.31 (td, 2 H, $J$ = 7.5 Hz, $J$ = 1.5 Hz, 2-H, 7-H), 7.28 (dd, 2 H, $J$ = 8.0 Hz, $J$ = 1.5 Hz, phenyl *o*-H), 7.02 (d, 2 H, $J$ = 8.5 Hz, phenyl *m*-H), 3.34 (s, 1 H, OH), 2.27 (s, 3 H, $CH_3$). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 147.4 (C-8a, C-9a), 139.1 (C-4a, C-4b), 138.7 (phenyl *p*-C), 131.9 (phenyl *o*-C), 129.6 (C-3, C-6), 129.0 (phenyl *m*-C), 128.6 (C-2, C-7), 124.5 (C-4, C-5), 120.2 (C-1, C-8), 119.4 (phenyl *ipso*-C), 88.4 (C-10), 83.4 (C-11), 75.3 (C–OH), 21.5 ($CH_3$). IR ($CH_2Cl_2$): $\tilde{\nu}$ = 3650 cm$^{-1}$ (alcohol), 2220 cm$^{-1}$ (C≡C). $C_{22}H_{16}O$ (296.37): calcd. C 89.16, H 5.44, O 5.40; found C 88.25, H 5.58.

**Data for 1c:** $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.81 (dd, 2 H, $J$ = 7.5 Hz, $J$ = 0.5 Hz, 1-H, 8-H), 7.66 (dd, 2 H, $J$ = 7.5 Hz, $J$ = 0.5 Hz, 4-H, 5-H), 7.44 (td, 2 H, $J$ = 7.5 Hz, $J$ = 1.5 Hz, 3-H, 6-H), 7.39 (td, 2 H, $J$ = 7.0 Hz, $J$ = 1.5 Hz, 2-H, 7-H), 7.39 (d, 2 H, $J$ = 8.5 Hz, phenyl *o*-H), 6.82 (d, 2 H, $J$ = 9.0 Hz, phenyl *m*-H), 3.79 (s, 3 H, $CH_3$), 2.78 (s, 1 H, OH). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 159.9 (phenyl *p*-C), 147.5 (C-8a, C-9a), 139.2 (C-4a, C-4b), 133.5 (phenyl *o*-C), 129.7 (C-3, C-6), 128.7 (C-2, C-7), 124.4 (C-1, C-8), 120.3 (C-4, C-5), 114.6 (phenyl *ipso*-C), 113.9 (phenyl *m*-C), 87.7 (C-10), 83.3 (C-11), 75.4 (C–OH), 55.3 ($OCH_3$). IR (liquid, $CH_2Cl_2$): $\tilde{\nu}$ = 3560 cm$^{-1}$ (alcohol), 2225 cm$^{-1}$ (C≡C). $C_{22}H_{16}O_2$ (312.37): calcd. C 84.59, H 5.16; found C 84.27, H 5.24.

**9-[(Trimethylsilyl)ethynyl]-9*H*-fluoren-9-ol (1d) and 9,9′-(Ethyne-1,2-diyl)bis(fluoren-9-ol) (14):** Following the procedure described in ref.[10], *n*BuLi (21.5 mL of a 1.6 M hexane solution, 34.4 mmol) was added dropwise to a solution of trimethylsilylacetylene (3.1 mL, 21.6 mmol) in tetrahydrofuran (250 mL) at –78 °C and the solution was warmed to room temperature. After 30 min stirring, the solution was cooled to –78 °C and a solution of fluorenone (5.77 g, 32 mmol) in THF (10 mL) was added dropwise via a cannula. The solution was stirred at –78 °C for 30 min, at room temperature for 28 h, quenched with water, and extracted with diethyl ether several times. The organic layers were combined, washed with brine, dried with $Na_2SO_4$, filtered and concentrated to give a pale yellow oil. A first crystallisation from tetrahydrofuran/pentane gave the side product **14** (1.83 g, 8.87 mmol; 41%) as a white powder, m.p. 218–220 °C (ref.[10] 228 °C). The filtrate was concentrated, and the resulting solid was recrystallised from pentane to give **1d** (2.80 g, 10.06 mmol; 46.5%) as a pale yellow solid.

**Data for 1d:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.70 (dd, 2 H, $J$ = 1.2 Hz, $J$ = 6.6 Hz), 7.61 (dd, 2 H, $J$ = 0.9 Hz, $J$ = 6.9 Hz), 7.38 (td, 2 H, $J$ = 1.2 Hz, $J$ = 7.2 Hz), 7.35 (td, 2 H, $J$ = 1.2 Hz, $J$ = 7.2 Hz), 2.56 (s, 1 H), 0.16 (s, 9 H).

**Data for 14:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.63 (d, 4 H, $J$ = 7.2 Hz), 7.58 (d, 4 H, $J$ = 7.5 Hz), 7.36 (td, 4 H, $J$ = 1.3 Hz, $J$ = 7.5 Hz), 7.30 (td, 4 H, $J$ = 1.2 Hz, $J$ = 7.5 Hz), 3.70 (s, 2 H, OH).

**9-[(*p*-Tolyl)ethynyl]-9*H*-fluorene (2b) and Spiro Compound 3b:** To a solution of 9-(*p*-tolyl)ethynyl-9*H*-fluoren-9-ol (**1b**) (300 mg, 1.01 mmol) in dry dichloromethane (10 mL), cooled to 0 °C, triethylsilane (242 μL, 1.51 mmol) was added slowly. Boron trifluoride-etherate (124 μL, 1.01 mmol) was added dropwise. After stirring for 15 min at 0 °C, the reaction was quenched with distilled water, and the mixture was extracted with diethyl ether several times. The organic layers were combined, washed with brine, dried with $MgSO_4$, filtered and concentrated to give a brown oil that was chromatographed on silica gel using dichloromethane/pentane (1:9) as eluent. Fluorene **2b** was isolated as a pale yellow solid (186 mg, 0.66 mmol; 66%). A second product, identified as **3b**, was also obtained (39 mg, 0.1 mmol; 10%).

**Data for 2b:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.82 (d, 2 H, $J$ = 7.0 Hz, 4-H, 5-H), 7.81 (d, 2 H, $J$ = 7.0 Hz, 1-H, 8-H), 7.48 (t, 2 H, $J$ = 7.5 Hz, 3-H, 6-H), 7.43 (t, 2 H, $J$ = 7.5 Hz, 2-H, 7-H), 7.38 (d, 2 H, $J$ = 8.5 Hz, phenyl *o*-H), 7.14 (d, 2 H, $J$ = 8.0 Hz, phenyl *m*-H), 5.08 (s, 1 H, 9-H), 2.38 (s, 3 H, $CH_3$). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 144.4 (C-8a, C-9a), 140.5 (C-4a, C-4b), 138.1 (phenyl *p*-C), 131.8 (phenyl *o*-C), 129.1 (phenyl *m*-C), 128.0 (C-3, C-6), 127.7 (C-2, C-7), 125.2 (C-1, C-8), 120.5 (phenyl *ipso*-C), 120.1 (C-4, C-5), 86.4 (C-10), 82.3 (C-11), 40.0 (C-9), 21.5 ($CH_3$). IR (liquid, $CH_2Cl_2$): $\tilde{\nu}$ = 2225 cm$^{-1}$ (C≡C).

**Data for 3b:** $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.79 (d, 2 H, $J$ = 7.5 Hz, 4-H, 5-H), 7.35 (td, 2 H, $J$ = 7.5 Hz, $J$ = 1.0 Hz, 3-H, 6-H), 7.32 (s, 1 H, 3′-H), 7.29 (d, 1 H, $J$ = 7.5 Hz, 4′-H), 7.12 (td, 2 H, $J$ = 7.5 Hz, $J$ = 1.0 Hz, 2-H, 7-H), 7.03 (dd, 1 H, $J$ = 7.5 Hz, $J$ = 1.0 Hz, 5′-H), 6.83 (d, 2 H, $J$ = 7.5 Hz, 1-H, 8-H), 6.39 (d, 1 H, $J$ = 0.5 Hz, 7′-H), 2.15 (s, 3 H, phenyl-$CH_3$), 0.65 (t, 9 H, $J$ = 8.0 Hz, $CH_3$), 0.08 (q, 6 H, $J$ = 8.0 Hz, $CH_2$). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 152.3 (C-7a′), 150.5 (C-2′), 146.5 (C-8a, C-9a), 143.9 (C-3′), 142.7 (C-3a′), 142.3 (C-4a, C-4b), 136.0 (C-6a′), 127.9 (C-5′), 127.7 (C-3, C-6), 127.4 (C-2, C-7), 124.2 (C-1, C-8), 123.1 (C-7′), 120.4 (C-4′), 120.1 (C-4, C-5), 72.2 (C-9), 21.5 (phenyl-$CH_3$), 7.2 ($CH_3$), 3.0 ($CH_2$). $C_{27}H_{28}Si$ (380.60): calcd. C 85.21, H 7.41; found C 85.13, H 7.70.

**1-(9*H*-Fluorenylidene)-4-(*p*-tolyl)-2-[(*p*-tolyl)methylene]spiro[cyclobutane-3,9′-[9*H*]fluorene] (5b):** To 9-[(*p*-tolyl)ethynyl]-9*H*-fluorene (**2b**) (1.06 g, 3.79 mmol) suspended in pentane (20 mL) and cooled to 0 °C, was added triethylamine (11 μL, 0.08 mmol). The suspension was stirred overnight in a cold water bath. The precipitate was filtered, washed with cold pentane and dried to give **5b** (981 mg, 1.75 mmol; 92%) as an orange solid.

**Data for 5b:** $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 8.65 (d, 1 H, $J$ = 8.00 Hz), 7.86 (d, 1 H, $J$ = 8.0 Hz), 7.81 (d, 1 H, $J$ = 7.5 Hz), 7.78 (d, 1 H, $J$ = 7.5 Hz), 7.70 (d, 1 H, $J$ = 7.5 Hz), 7.69 (d, 1 H, $J$ = 7.0 Hz), 7.65 (s, 1 H), 7.43 (t, 1 H, $J$ = 7.5 Hz), 7.40 (t, 1 H, $J$ = 7.5 Hz), 7.36 (t, 1 H, $J$ = 7.5 Hz), 7.27 (t, 1 H, $J$ = 8.0 Hz), 7.26 (t, 1 H, $J$ = 7.0 Hz), 7.22 (d, 1 H, $J$ = 8.0 Hz), 7.12 (t, 1 H, $J$ = 7.5 Hz), 7.00 (t, 1 H, $J$ = 7.5 Hz), 6.90–6.80 (s, brd), 6.62 (d, 2 H, $J$ = 8.0 Hz), 6.58 (t, 1 H, $J$ = 7.5 Hz), 6.45 (d, 2 H, $J$ = 8.0 Hz), 6.42–6.30 (s, brd), 6.17 (d, 1 H, $J$ = 7.5 Hz), 5.12 (s, 1 H), 2.24 (s, 3 H), 2.11 (s, 3 H). $^{13}$C NMR (125 MHz, $CDCl_3$): **$\delta$ =** 150.2, 144.7, 143.3, 142.1, 141.4, 140.5, 139.8, 139.8, 138.5, 137.9, 137.6, 136.5, 134.9, 131.9, 131.0, 128.9, 128.2, 128.1, 128.0, 127.7, 127.6, 127.4, 127.2, 127.1, 126.7, 126.1, 125.3, 124.0, 122.9, 120.0, 119.8, 119.7, 119.3, 65.6, 61.6, 21.3, 21.2.

***cis*-1,2-Di(fluorenylidene)-3,4-di(*p*-tolyl)cyclobutane (7b) and *trans*-1,2-Di(fluorenylidene)-3,4-di(*p*-tolyl)cyclobutane (8b):** Spiro compound **5b** (400 mg, 0.71 mmol) was dissolved in toluene (8 mL) and heated at reflux overnight. The solvent was removed and the residue was purified on silica column using cyclohexane/dichloromethane/ethyl acetate (90:9:1) as eluent. The cyclobutane derivative **8b** (297 mg, 0.53 mmol; 74%), m.p. 156–160 °C, was isolated as a major product. A sample suitable for an X-ray diffraction structural determination was obtained by recrystallisation from diethyl ether/pentane. NMR examination of the second fraction (100 mg, 0.18 mmol) indicated a 3:1 ratio of the red dimer **6b** and the orange dimer **7b**. The mixture of **6b** and **7b** was triturated in acetonitrile to give **7b** (20 mg, 0.04 mmol; 5%) as a pure orange solid, m.p. 208–211 °C.

**Data for 7b:** $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.74 (d, 1 H, $J$ = 7.6 Hz), 7.71 (d, 2 H, $J$ = 7.6 Hz), 7.65 (d, 1 H, $J$ = 8.0 Hz), 7.62 (d, 1 H, $J$ = 7.6 Hz), 7.39 (d, 1 H, $J$ = 7.6 Hz), 7.32–7.26 (m, 4 H), 7.24 (td, 2 H, $J$ = 0.8 Hz, $J$ = 7.6 Hz), 7.12 (td, 1 H, $J$ = 0.8 Hz, $J$ = 7.6 Hz), 7.07 (td, 1 H, $J$ = 1.2 Hz, $J$ = 7.6 Hz), 7.05 (s, brd), 7.03 (td, 1 H, $J$ = 1.2 Hz, $J$ = 7.6 Hz), 6.90 (d, 1 H, $J$ = 7.6 Hz), 6.85 (td, 1 H, $J$ = 0.8 Hz, $J$ = 7.6 Hz), 6.85 (s brd), 6.77 (td, 1 H, $J$ = 1.2 Hz, $J$ = 7.6 Hz), 6.27 (s, brd), 6.04 (s, brd), 5.32 (d, 1 H, $J$ = 7.6 Hz), 5.23 (d, 1 H, $J$ = 7.6 Hz), 2.18 (s, 3 H), 2.12 (s, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 145.3, 141.0, 139.5, 139.2, 139.2, 139.1, 137.8, 136.6, 136.5, 135.3, 135.0, 135.0, 134.0, 133.2, 128.6, 128.3, 127.7, 127.6, 127.4, 126.9, 126.6, 126.6, 126.3, 126.1, 125.5, 125.4, 124.8, 124.5, 119.2, 118.7, 118.7, 118.6, 58.2, 56.4, 30.6, 22.1, 22.1, 2.4.

**Data for 8b:** $^1$H NMR (500 MHz, $CDCl_3$) numbering is in agreement with the crystal structure: $\delta$ = 7.76 (d, 2 H, $J$ = 7.0 Hz, 10-H, 26-H), 7.75 (d, 2 H, $J$ = 6.5 Hz, 13-H, 23-H), 7.55 (d, 2 H, $J$ = 8.0 Hz, 7-H, 29-H), 7.39 (d, 4 H, $J$ = 8.0 Hz, phenyl *o*-H), 7.34 (d, 2 H, $J$ = 7.5 Hz, 16-H, 20-H), 7.33 (td, 2 H, $J$ = 7.5 Hz, $J$ = 1.0 Hz, 9-H, 27-H), 7.30 (td, 2 H, $J$ = 8.0 Hz, $J$ = 1.0 Hz, 14-H, 22-H), 7.14 (d, 4 H, $J$ = 7.5 Hz, phenyl *m*-H), 7.09 (td, 2 H, $J$ = 7.5 Hz, $J$ = 0.5 Hz, 15-H, 21-H), 7.04 (td, 2 H, $J$ = 7.5 Hz, $J$ = 1.0 Hz, 8-H, 28-H), 4.77 (s, 2 H, 3-H, 4-H), 2.33 (s, 6 H, $CH_3$). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 143.4 (C-1, C-2), 140.5 (C-12, C-24), 140.2 (C-11, C-25), 138.9 (C-31, C-37), 138.6 (C-17, C-19), 136.7 (C-6, C-30), 136.7 (phenyl *p*-C), 134.5 (C-5, C-18), 130.0 (phenyl *m*-C), 128.6 (C-9, C-27), 128.3 (C-14, C-22), 128.2 (C-8, C-28), 127.5 (C-15, C-21), 127.4 (phenyl *o*-C), 126.2 (C-7, C-29), 124.8 (C-16, C-20), 120.0 (C-13, C-23), 119.5 (C-10, C-26), 62.2 (C-3, C-4), 21.2 ($CH_3$). $C_{42}H_{28}$·0.5$Et_2O$ (569.74): calcd. C 92.76, H 5.84; found C 92.26, H 6.20.

**3,3-(Biphenyl-2,2′-diyl)-1-chloro-1-phenylallene (12):** To a cooled solution of **1a** (300 mg, 1.06 mmol) in acetic acid (10 mL) was added dropwise a 2 N solution of hydrochloric acid (1.0 mL). Upon stirring for 15 min with cooling, the precipitate was filtered and washed with water. To the cooled filtrate was added dropwise a 2 N solution of hydrochloric acid (1.0 mL). After stirring for 10 min, the new precipitate was filtered, washed with water, combined with the first one and dried to give **12** (267 mg, 0.89 mmol; 84%) as a pale yellow powder. A sample suitable for an X-ray diffraction structural determination was obtained by recrystallisation from diethyl ether/pentane.

**Data for 12:** $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.75 (dt, 2 H, $J$ = 7.0 Hz, $J$ = 1.0 Hz, 4-H,5-H), 7.66 (dt, 2 H, $J$ = 7.0 Hz, $J$ = 1.5 Hz, phenyl *o*-H), 7.63 (dt, 2 H, $J$ = 7.5 Hz, $J$ = 1.0 Hz, 1-H, 8-H), 7.42 (td, 2 H, $J$ = 7.5 Hz, $J$ = 1.5 Hz, 3-H, 6-H), 7.40–7.33 (m, 3 H, phenyl *m*-H, *p*-H), 7.31 (td, 2 H, $J$ = 7.5 Hz, $J$ = 1.0 Hz, 2-H, 7-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 200.6 (C-10), 140.2 (C-4a, C-4b), 136.4 (C-8a, C-9a), 133.0 (phenyl *ipso*-C), 129.6 (C-3, C-6), 129.1 (phenyl *p*-C), 128.8 (phenyl *m*-C), 127.7 (C-2, C-7), 126.8 (phenyl *o*-C), 124.3 (C-1, C-8), 120.5 (C-4, C-5), 114.3, 111.7 (C-9, C-11). IR (liquid, $CHCl_3$): $\tilde{\nu}$ = 1936 cm$^{-1}$ (C=C=C).

$C_{21}H_{13}Cl·0.2\,CH_2Cl_2$ (317.77): calcd. C 80.13, H 4.25; found C 80.08, H 4.09.

**3,3-(Biphenyl-2,2′-diyl)-1-bromo-1-phenylallene (13a):** To a cooled solution of **1a** (600 mg, 2.13 mmol) in acetic acid (18 mL) was added dropwise a solution of hydrobromic acid (47%, 1.83 g, 10.65 mmol) in water (5.3 mL). Upon stirring for 1 h with cooling, the precipitate was filtered, washed with water, dried to give **13a** (669 mg, 1.94 mmol; 91%) as a pale yellow powder. A sample suitable for an X-ray diffraction structural determination was obtained by recrystallisation from diethyl ether/pentane.

**Data for 13a:** $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.78 (dd, 2 H, $J$ = 7.0 Hz, $J$ = 1.0 Hz, 4-H, 5-H), 7.72–7.69 (m, 2 H, phenyl *o*-H), 7.68 (d, 2 H, $J$ = 7.0 Hz, 1-H, 8-H), 7.44 (td, 2 H, $J$ = 7.5 Hz, $J$ = 1.5 Hz, 3-H, 6-H), 7.42–7.35 (m, 3 H, phenyl *m*-H, *p*-H), 7.35 (td, 2 H, $J$ = 7.5 Hz, $J$ = 1.0 Hz, 2-H, 7-H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 200.0 (C-10), 140.0 (C-4a, C-4b), 136.3 (C-8a, C-9a), 133.4 (phenyl *ipso*-C), 129.5 (C-3, C-6), 129.2 (phenyl *p*-C), 128.7 (phenyl *m*-C), 127.9, 127.7 (C-2, C-7, phenyl *o*-C), 124.4 (C-1, C-8), 120.6 (C-4, C-5), 112.5 (C-9), 98.4 (C-11). IR (KBr): $\tilde{\nu}$ = 1934 cm$^{-1}$ (C=C=C). $C_{21}H_{13}Br$ (345.24): calcd. C 73.06, H 3.80, Br 23.14; found C 72.80, H 3.76, Br 22.69.

**3,3-(Biphenyl-2,2′-diyl)-1-bromo-1-(*p*-tolyl)allene (13b):** To a cooled solution of **1b** (523 mg, 1.77 mmol) in acetic acid (15 mL) was added dropwise a solution of hydrobromic acid (47%, 1.50 g, 8.7 mmol) in water (5 mL). Upon stirring for 1 h with cooling, the precipitate was filtered, washed with water, dried to give **13b** (570 mg, 1.59 mmol; 90%) as an orange powder.

**Data for 13b:** $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.77 (d, 2 H, $J$ = 8.0 Hz, 4-H, 5-H), 7.67 (d, 2 H, $J$ = 7.5 Hz, 1-H, 8-H), 7.59 (d, 2 H, $J$ = 8.5 Hz, phenyl *o*-H), 7.44 (td, 2 H, $J$ = 7.5 Hz, $J$ = 1.0 Hz, 3-H, 6-H), 7.34 (td, 2 H, $J$ = 7.5 Hz, $J$ = 0.5 Hz, 2-H, 7-H), 7.20 (d, 2 H, $J$ = 8.0 Hz, phenyl *m*-H), 2.41 (s, 3 H, $CH_3$). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 199.8 (C-2′), 140.0 (C-4a, C-4b), 139.4 (phenyl *p*-C), 136.4 (C-8a, C-9a), 133.5 (C-3′a), 129.4, 129.4 (C-3, C-6, phenyl *m*-C), 127.8 (phenyl *o*-C), 127.6 (C-2, C-7), 124.4 (C-1, C-8), 120.5 (C-4, C-5), 112.3 (C-9), 98.5 (C-3′), 21.3 ($CH_3$). IR (KBr): $\tilde{\nu}$ = 1922 cm$^{-1}$ (C=C=C).

**3,3-(Biphenyl-2,2′-diyl)-1-bromo-1-(*p*-methoxyphenyl)allene (13c):** To a cooled solution of **1c** (550 mg, 1.77 mmol) in acetic acid (15 mL) was added dropwise a solution of hydrobromic acid (47%, 1.50 g, 8.7 mmol) in water (5 mL). Upon stirring for 1 h with cooling, the precipitate was filtered, washed with water, dried to give **13c** (620 mg, 1.65 mmol; 94%) as an orange powder.

**Data for 13c:** $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.77 (d, 2 H, $J$ = 8.0 Hz, 4-H, 5-H), 7.67 (d, 2 H, $J$ = 8.0 Hz, 1-H, 8-H), 7.62 (dt, 2 H, $J$ = 9.0 Hz, $J$ = 2.0 Hz, phenyl *o*-H), 7.43 (td, 2 H, $J$ = 7.5 Hz, $J$ = 1.0 Hz, 3-H, 6-H), 7.34 (td, 2 H, $J$ = 7.5 Hz, $J$ = 0.5 Hz, 2-H, 7-H), 6.92 (dt, 2 H, $J$ = 9.0 Hz, $J$ = 2.0 Hz, phenyl *m*-H), 3.85 (s, 3 H, $CH_3$). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 199.5 (C-10), 160.5 (phenyl *p*-C), 140.0 (C-4a, C-4b), 136.5 (C-8a, C-9a), 129.4, 129.3 (C-3, C-6, phenyl *o*-C), 127.6 (C-2, C-7), 125.6 (phenyl *ipso*-C), 124.3 (C-1, C-8), 120.5 (C-4, C-5), 114.1 (phenyl *m*-C), 112.3 (C-9), 98.3 (C-11), 55.6 ($OCH_3$). IR (KBr): $\tilde{\nu}$ = 1921 cm$^{-1}$ (C=C=C).

**3,3-(Biphenyl-2,2′-diyl)-1-bromo-1-(trimethylsilyl)allene (13d):** To a cooled solution of **1d** (200 mg, 0.72 mmol) in acetic acid (4 mL) was added dropwise a solution of hydrobromic acid (47%, 465 mg, 2.71 mmol) in water (1.35 mL). Upon stirring for 3 h at room temperature, the precipitate was filtered, washed with water, dried to give **13d** (208 mg, 0.61 mmol; 85%) as a pale yellow powder.

**Data for 13d:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.73 (d, 2 H, $J$ = 6.9 Hz), 7.59 (d, 2 H, $J$ = 7.2 Hz), 7.39–7.29 (m, 4 H), 0.32 (s, 9 H, $CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 199.6 (C-10), 139.1 (C-4a, C-4b), 137.0 (C-8a, C-9a), 128.8 (C-3, C-6), 127.4 (C-2, C-7), 123.8 (C-1, C-8), 120.5 (C-4, C-5), 108.7 (C-9), 92.2 (C-11), –1.2 ($CH_3$). $C_{18}H_{17}BrSi$ (341.32): calcd. C 63.34, H 5.02, Br 23.41; found C 63.40, H 4.96, Br 23.05.

**3,3-(Biphenyl-2,2′-diyl)-1-bromo-1-(9-hydroxy-9*H*-fluorenyl)allene (15):** To a solution of **14** (446 mg, 1.16 mmol) in acetic acid (10 mL) was added dropwise a solution of hydrobromic acid (47%, 1.86 g, 10.8 mmol) in water (5.4 mL). Upon stirring for 48 h at room temperature, the precipitate was filtered, washed with water, dried to give **15** (340 mg, 1.94 mmol; 65%) as a pale yellow powder, m.p. 192–196 °C. A sample suitable for an X-ray diffraction structural determination was obtained by recrystallisation from dichloromethane.

**Data for 15:** $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.77 (d, 2 H, $J$ = 7.0 Hz), 7.67 (d, 2 H, $J$ = 7.0 Hz), 7.64 (d, 2 H, $J$ = 7.5 Hz), 7.55 (d, 2 H, $J$ = 7.5 Hz), 7.41 (t, 2 H, $J$ = 7.5 Hz), 7.38 (t, 2 H, $J$ = 7.0 Hz), 7.36 (t, 2 H, $J$ = 7.0 Hz), 7.31 (t, 2 H, $J$ = 7.0 Hz), 2.90 (s, 1 H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 195.6, 146.3, 140.0, 139.6, 136.1, 129.2, 128.2, 127.4, 123.8, 120.2, 120.2, 113.4, 101.3, 83.2. IR (liquid, $CHCl_3$): $\tilde{\nu}$ = 3562 cm$^{-1}$ (alcohol), 1951 cm$^{-1}$ (C=C=C). MS(ES+): 369.1 (M – Br). $C_{28}H_{17}BrO·Et_2O$ (523.47): calcd. C 73.42, H 5.20, Br 15.26; found C 73.05, H 4.23, Br 15.39.

**3-(9*H*-Fluorenylidene)-2-bromo-4-(bromomethylene)spiro[cyclobutane-1,9′-[9*H*]fluorene] (17):** To a solution of 9-ethynyl-9*H*-fluoren-9-ol (386 mg, 1.87 mmol) in acetic acid (9 mL) was added dropwise a solution of hydrobromic acid (47%, 1.61 g, 9.36 mmol) in water (4.7 mL). Upon stirring for 5 h at room temperature, the precipitate was filtered, washed with water, vacuum down in presence of toluene, and dried to give **17** (426 mg, 0.79 mmol; 85%) as a yellow powder, m.p. 207–210 °C. A sample suitable for an X-ray diffraction structural determination was obtained by recrystallisation from diethyl ether/pentane.

**Data for 17:** $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 8.07 (d, 1 H, $J$ = 8.0 Hz), 7.95 (d, 1 H, $J$ = 7.5 Hz), 7.79 (d, 2 H, $J$ = 7.5 Hz), 7.75 (d, 2 H, $J$ = 8.0 Hz), 7.73 (d, 1 H, $J$ = 7.5 Hz), 7.49 (t, 1 H, $J$ = 8.0 Hz), 7.43–7.38 (m, 4 H), 7.36 (s, 1 H), 7.32 (td, 2 H, $J$ = 1.5 Hz, $J$ = 7.5 Hz), 7.28 (t, 2 H, $J$ = 8.0 Hz), 5.89 (s, 1 H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 145.9, 145.2, 143.1, 142.0, 141.4, 141.3, 140.8, 138.0, 137.4, 137.1, 135.3, 129.9, 129.3, 128.8, 128.7, 128.1, 128.0, 127.7, 127.6, 127.6, 126.5, 124.1, 122.9, 120.4, 120.1, 120.1, 120.0, 107.4, 64.6, 53.9.

**3,3-(Biphenyl-2,2′-diyl)-1-(trimethylsilyl)-1-{9-[(trimethylsilyl)-ethynyl]-9*H*-fluorenyl}allene (19):** To a solution of *n*BuLi (725 µL, 1.16 mmol) in tetrahydrofuran (10 mL) was added at –78 °C a solution of **13d** (620 mg, 1.82 mmol) in tetrahydrofuran (5 mL). After stirring 15 min at –78 °C, 15 min at room temperature, the mixture was cooled down at 0 °C, and tetrafluoroboric acid (54% in solution in diethyl ether, 160 µL, 1.16 mmol) was added. The mixture was stirred for an extra 20 min at room temperature, quenched with water, and extracted several times with diethyl ether. The organic layers were combined, washed with brine, dried with $MgSO_4$, filtered and concentrated to give a dark red oil. The crude product was purified by silica chromatography using pentane/dichloromethane as eluent to give **19** (256 mg, 0.49 mmol, 54%) as the major product. A sample suitable for an X-ray diffraction structural determination was obtained by recrystallisation from diethyl ether/pentane.

**Data for 19:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.87–7.84 (m, 2 H), 7.82–7.75 (m, 6 H), 7.50–7.46 (m, 4 H), 7.45–7.40 (m, 4 H), –0.4 (s, 18 H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 205.3, 147.5, 140.5,

139.0, 138.1, 128.6, 128.3, 127.2, 127.0, 125.8, 122.4, 120.3, 120.2, 111.7, 105.5, 105.4, 87.6, 54.3, 0, –0.6. IR (liquid, $CHCl_3$): $\tilde{\nu}$ = 2164 $cm^{-1}$ (C≡C), 1919 $cm^{-1}$ (C=C=C). MS(ES+): 523 (M).

**3,3-(Biphenyl-2,2′-diyl)-1-(trimethylsilyl)allene (20):** A cooled (0 °C) solution of **13d** (1.23 g, 3.60 mmol) in tetrahydrofuran (30 mL) was added very slowly, at –78 °C to a solution of *n*BuLi (1.6 M in solution in tetrahydrofuran, 2.7 mL, 4.32 mmol) in tetrahydrofuran (60 mL). After stirring for 15 min at –78 °C, acetic acid (250 μL, 4.32 mmol) was added. The mixture was allowed to warm up to 0 °C and then stirred for 1 h at this temperature. After removing the solvent, the crude was dissolved in diethyl ether, filtered through celite and the filtrate was concentrated to give an orange oil. The oil was purified by silica chromatography using pentane as eluent to give **20** (602.6 mg, 2.30 mmol, 63.7%) as the major product.

**Data for 20:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.88–7.80 (m, 2 H), 7.67–7.60 (m, 2 H) (1-H, 4-H, 5-H, 8-H), 7.46–7.31 (m, 4 H, 2-H, 3-H, 6-H, 7-H), 6.06 (s, 1 H, H11). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 205.3 (C-10), 138.8, 137.5 (C-4a, C-4b, C-8a, C-9a), 126.8 (C-2, C-3, C-6, C-7), 122.3, 120.2 (C-1, C-4, C-5, C-8), 100.4 (C-9), 91.6 (C-11), –0.2 (TMS). IR (liquid, $CH_2Cl_2$): $\tilde{\nu}$ = 1920 $cm^{-1}$ (C=C=C). $C_{18}H_{18}Si$ (262.42): calcd. C 82.38, H 6.91; found C 82.11, H 6.90.

**1-(9*H*-Fluorenylidene)-4-(trimethylsilyl)-2-[(trimethylsilyl)methylene]spiro[cyclobutane-1,9′-[9*H*]fluorene] (21):** 3,3-(Biphenyl-2,2′-diyl)-1-(trimethylsilyl)allene (346 mg, 1.32 mmol) dissolved in cyclohexane was heated at reflux overnight. After removing the solvent, the crude product was purified by chromatography on silica gel with pentane as eluent, and **21** was isolated as a yellow solid (223 mg, 0.42 mmol; 64%). A sample suitable for an X-ray diffraction structural determination was obtained by recrystallisation from diethyl ether/chloroform. A second product, identified as **23** (90 mg, 0.17 mmol; 26%), was also obtained.

**Data for 21:** $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 8.45 (d, 1 H, $J$ = 8.00 Hz), 7.82 (d, 1 H, $J$ = 7.50 Hz), 7.79 (d, 1 H, $J$ = 8.0 Hz), 7.76 (d, 1 H, $J$ = 7.50 Hz), 7.74 (dd, 1 H, $J$ = 1.00 Hz, $J$ = 7.50 Hz), 7.73 (dd, 1 H, $J$ = 1.00 Hz, $J$ = 7.50 Hz), 7.70 (d, 1 H, $J$ = 7.50 Hz), 7.60 (d, 1 H, $J$ = 7.50 Hz), 7.42 (td, 1 H, $J$ = 1.00 Hz, $J$ = 7.50 Hz), 7.37 (td, 1 H, $J$ = 1.00 Hz, $J$ = 7.50 Hz), 7.37 (td, 1 H, $J$ = 1.00 Hz, $J$ = 7.50 Hz), 7.29 (td, 2 H, $J$ = 1.00 Hz, $J$ = 7.50 Hz), 7.25 (td, 1 H, $J$ = 1.00 Hz, $J$ = 7.50 Hz), 6.65 (s, 1 H), 3.99 (s, 1 H), –0.16 (s, 9 H), –0.48 (s, 9 H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 160.0, 152.0, 150.0, 148.4, 141.9, 140.2, 139.8, 139.2, 138.4, 130.3, 128.1, 127.7, 127.5, 127.5, 126.9, 126.9, 126.2, 126.9, 126.2, 125.8, 125.8, 125.2, 124.2, 123.6, 120.2, 119.9, 119.9, 119.6, 64.0, 49.9, 1.2, –0.9. $C_{36}H_{36}Si_2$ (524.85): calcd. C 82.38, H 6.91; found C 82.45, H 7.51.

**1-(9*H*-Fluorenylidene)-2-[(trimethylsilyl)methylene]spiro[cyclobutane-3,9′-[9*H*]fluorene] (22):** At room temperature, to a solution of **21** (680 mg, 1.30 mmol) in tetrahydrofuran (5 mL) and acetic acid (519 μL, 9.07 mmol) was added dropwise tetrabutylammonium fluoride solution (1 M in THF, 5.18 mL, 5.18 mmol). After stirring 3 h at room temperature, the solvent was removed. The crude material was dissolved in diethyl ether, filtered through celite, and the filtrate was concentrated to give a yellow solid. The crude product was purified by chromatography on silica gel using pentane/dichloromethane as eluent, and **22** (466 mg, 1.03 mmol; 79.2%) was isolated as a yellow solid, m.p. 169–172 °C. A sample suitable for an X-ray diffraction structural determination was obtained by recrystallisation from diethyl ether/pentane.

**Data for 22:** $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.81 (d, 1 H, $J$ = 7.50 Hz, 7-H), 8.26 (d, 1 H, $J$ = 7.50 Hz, 10-H), 8.24 (d, 1 H, $J$ = 7.50 Hz, 13-H), 8.20 (d, 2 H, $J$ = 7.50 Hz, 23-H, 32-H), 8.02 (d, 2 H, $J$ = 7.50 Hz, 26-H, 29-H), 7.99 (d, 1 H, $J$ = 8.10 Hz, 16-H), 7.90–7.67 (m, 8 H, 8-H, 9-H, 14-H, 15-H, 25-H, 26-H, 31-H, 32-H), 7.14 (s, 1 H, 18-H), 4.23 (s, 2 H, 4-H), 0.00 (s, 9 H, TMS). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 159.1, 143.8 (C-1, C-5), 150.2 (C-27, C-28), 140.6 (C-22, C-33), 140.5 (C-11), 140.1, 140.0 (C-12, C-17), 137.3 (C-6), 130.8 (C-2), 129.0 (C-18), 128.2 (C-9), 127.9 (C-25, C-30), 127.8 (C-24, C-31), 127.2 (C-8), 124.3 (C-7), 124.0 (C-16), 123.8 (C-26, C-29), 120.0 (C-10), 120.0 (C-23, C-32), 119.9 (C-13), 60.4 (C-3), 41.2 (C-4), –0.9 (TMS). $C_{33}H_{28}Si$ (452.67): calcd. C 87.56, H 6.23; found C 86.88, H 6.25.

***trans*-1,2-Di(fluorenylidene)-3,4-bis(trimethylsilyl)cyclobutane (23):** Allene **20** (310 mg, 1.18 mmol), dissolved in toluene, was heated at reflux overnight. After removing the solvent, the crude material was triturated with diethyl ether to give **23** (180 mg, 0.34 mmol; 58%) as an orange solid. A sample for an X-ray diffraction structural determination was obtained by recrystallisation from diethyl ether/pentane.

**Data for 23:** $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.83 (d, 2 H, $J$ = 7.50 Hz, 10-H, 26-H), 7.79 (d, 2 H, $J$ = 7.50 Hz, 7-H, 29-H), 7.75 (d, 2 H, $J$ = 7.50 Hz, 13-H, 23-H), 7.41 (t, 2 H, $J$ = 7.50 Hz, 9-H, 27-H), 7.36 (td, 2 H, $J$ = 1.00 Hz, $J$ = 7.50 Hz, 8-H, 28-H), 7.36 (d, 2 H, $J$ = 7.50 Hz, 16-H, 20-H), 7.24 (t, 2 H, $J$ = 7.50 Hz, 14-H, 22-H), 6.91 (t, 2 H, $J$ = 7.50 Hz, 15-H, 21-H), 3.37 (s, 2 H, 3-H, 4-H), 0.11 (s, 18 H, TMS). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 148.6 (C-1, C-2), 140.2 (C-11, C-25), 139.0 (C-12, C-24), 138.8 (C-6, C-30), 137.1 (C-17, C-19), 129.1 (C-5, C-18), 127.6, 127.5 (C-9, C-14, C-22, C-27), 127.1 (C-15, C-21), 126.7 (C-8, C-28), 125.7 (C-16, C-20), 123.9 (C-7, C-29), 120.0 (C-10, C-26), 119.2 (C-13, C-23), 40.9 (C-3, C-4), –0.9 (TMS).

**1,2-Di(fluorenylidene)cyclobutane (24):** At room temperature, to a solution of **23** (136 mg, 0.26 mmol) in tetrahydrofuran (3 mL) and acetic acid (104 μL, 1.82 mmol) was added dropwise tetrabutylammonium fluoride solution (1 M in THF, 1.04 mL, 1.04 mmol). After stirring overnight at room temperature, the solvent was removed and the crude material was triturated in diethyl ether and filtered to give an orange solid. The crude product was purified by chromatography on silica gel using pentane/dichloromethane as eluent. Cyclobutane derivative **24** was isolated as an orange solid (47.6 mg, 0.13 mmol; 50%). A sample for an X-ray diffraction structural determination was obtained by recrystallisation from diethyl ether/pentane.

**Data for 24:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.80 (d, 2 H, $J$ = 7.20 Hz), 7.74 (d, 2 H, $J$ = 7.80 Hz), 7.70 (d, 2 H, $J$ = 7.20 Hz), 7.40 (d, 2 H, $J$ = 7.50 Hz), 7.34 (t, 2 H, $J$ = 7.50 Hz), 7.26 (t, 2 H, $J$ = 7.50 Hz), 7.18 (d, 2 H, $J$ = 7.80 Hz), 6.93 (t, 2 H, $J$ = 7.50 Hz), 3.78–3.63 (m, 2 H), 3.54–3.40 (m, 2 H). $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 143.5 (C-1, C-2), 140.4 (C-11, C-25), 139.8 (C-12, C-24), 139.5 (C-6, C-30), 136.6 (C-17, C-19), 132.3 (C-5, C-18), 128.2 (C-14, C-22), 128.1 (C-9, C-27), 127.2 (C-8, C-28), 127.1 (C-15, C-21), 126.4 (C-16, C-20), 124.3 (C-7, C-29), 120.2 (C-10, C-26), 119.5 (C-13, C-23), 33.9 (C-3, C-4).

**Dinitro-dispirotetracene 27:** A mixture of the 2,7-dinitro-9-(phenylethynyl)-9*H*-fluorene dimers (210 mg, 0.3 mmol) suspended in dimethyl sulfoxide (6 mL) was heated at reflux overnight. The mixture was cooled, water was added and the mixture was extracted with diethyl ether and dichloromethane. The organic phases were combined, washed with brine. Chromatographic separation with cyclohexane/dichloromethane gave **27** (23.7 mg, 0.03 mmol; 10%).

**Data for 27:** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.43 (dt, 2 H, $J$ = 0.9 Hz, $J$ = 8.4 Hz, 3-H, 6-H), 8.11 (d, 2 H, $J$ = 8.4 Hz, 4-H, 5-H),

8.00 (t, 2 H, $J$ = 0.6 Hz, 1-H, 8-H), 7.12 (t, 1 H, $J$ = 7.5 Hz), 7.02 (d, 1 H, $J$ = 7.5 Hz), 6.90 (t, 1 H, $J$ = 7.5 Hz), 6.30 (d, 1 H, $J$ = 7.8 Hz), 6.04 (s, 1 H, 2′-H). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ = 153.9 (C-8a, C-9a), 148.9 (C-2, C-7), 143.7 (C-4a, C-4b), 135.6, 135.0, 132.2, 129.3, 128.7, 125.7, 125.5, 124.8, 122.6, 120.7, 60.9 (C-9);

**X-ray Measurements for 1c, 8b, 12, 13a, 15, 17, 19, 21, 22, 24, 25:** Crystal data were collected using a Bruker SMART APEX CCD area detector diffractometer, and are listed in Table 1 and Table 2. A full sphere of the reciprocal space was scanned by phi-omega scans. Pseudo-empirical absorption correction based on redundant

Table 1. Crystallographic data for **1c**, **8b**, **12**, **13a**, **15** and **17**.

| | **1c** | **8b** | **12** | **13a** | **15** | **17** |
|---|---|---|---|---|---|---|
| Formula | $C_{22}H_{16}O_2$ | $C_{44}H_{32}$ | $C_{21}H_{13}Cl$ | $C_{21}H_{13}Br$ | $C_{28}H_{17}BrO$ | $C_{30}H_{18}Br_2$ |
| $M$ | 312.35 | 560.70 | 300.76 | 345.22 | 449.33 | 538.26 |
| Crystal system | orthorhombic | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | $Pca2_1$ | $P2_1/c$ | $P2_1/c$ | $P2_1$ | $P2_1/n$ | $P2_1/c$ |
| $a$ [Å] | 8.9042(10) | 12.549(2) | 12.788(4) | 6.0699(5) | 8.6252(9) | 8.1664(14) |
| $b$ [Å] | 10.9978(13) | 22.060(4) | 14.541(4) | 9.5752(7) | 15.4599(16) | 23.591(4) |
| $c$ [Å] | 16.0086(19) | 12.661(2) | 8.872(2) | 13.3300(10) | 15.5640(17) | 12.096(2) |
| $\alpha$ [°] | 90 | 90 | 90 | 90 | 90 | 90 |
| $\beta$ [°] | 90 | 116.916(3) | 110.113(4) | 100.0480(10) | 98.113(2) | 95.650(3) |
| $\gamma$ [°] | 90 | 90 | 90 | 90 | 90 | 90 |
| $V$ [Å$^3$] | 1567.7(3) | 3125.3(9) | 1549.0(8) | 762.86(10) | 2054.6(4) | 2319.0(7) |
| $Z$ | 4 | 4 | 4 | 2 | 4 | 4 |
| $\rho_{calcd.}$ [g cm$^{-3}$] | 1.323 | 1.192 | 1.290 | 1.503 | 1.453 | 1.542 |
| $T$ [K] | 100(2) | 113(2) | 293(2) | 100(2) | 293(2) | 293(2) |
| $\mu$ [mm$^{-1}$] | 0.084 | 0.067 | 0.240 | 2.687 | 2.018 | 3.511 |
| $2\theta_{max}$ [°] | 54.00 | 48.00 | 48.00 | 56.54 | 48.00 | 48.00 |
| Reflns. measured | 12219 | 40338 | 7849 | 12816 | 13297 | 28903 |
| Reflns. used | 1775 | 4908 | 2417 | 3547 | 3224 | 3633 |
| $R_{int}$ | 0.0315 | 0.0772 | 0.0245 | 0.0367 | 0.0232 | 0.0646 |
| Parameters | 222 | 401 | 199 | 199 | 343 | 289 |
| Final $R$ values [$I>2\sigma(I)$]: | | | | | | |
| $R_1$ | 0.0295 | 0.0504 | 0.0443 | 0.0284 | 0.0305 | 0.0348 |
| $wR_2$ | 0.0738 | 0.0966 | 0.1064 | 0.0692 | 0.0748 | 0.0882 |
| $R$ values (all data): | | | | | | |
| $R_1$ | 0.0301 | 0.0739 | 0.0597 | 0.0294 | 0.0371 | 0.0467 |
| $wR_2$ | 0.0742 | 0.1048 | 0.1138 | 0.0696 | 0.0783 | 0.0948 |
| GOF on $F^2$ | 1.024 | 1.082 | 1.044 | 1.016 | 1.044 | 1.025 |

Table 2. Crystallographic data for **19**, **21**, **22**, **24** and **25**.

| | **19** | **21** | **22** | **24** | **25** |
|---|---|---|---|---|---|
| Formula | $C_{36}H_{34}Si_2$ | $C_{36}H_{36}Si_2$ | $C_{33}H_{28}Si$ | $C_{30}H_{20}$ | $C_{33}H_{28}O_2Si{\cdot}C_4H_{10}O$ |
| $M$ | 522.81 | 524.83 | 452.64 | 380.46 | 558.76 |
| Crystal system | monoclinic | triclinic | monoclinic | orthorhombic | monoclinic |
| Space group | $P2_1/n$ | $P\bar{1}$ | $P2_1/c$ | $Pbca$ | $P2_1/c$ |
| $a$ [Å] | 8.6151(15) | 9.719(2) | 16.547(5) | 18.877(2) | 13.933(5) |
| $b$ [Å] | 8.9325(15) | 14.877(3) | 14.094(4) | 7.4718(8) | 11.992(4) |
| $c$ [Å] | 19.748(3) | 20.757(5) | 10.880(3) | 26.734(3) | 19.497(6) |
| $\alpha$ [°] | 90 | 87.826(4) | 90 | 90 | 90 |
| $\beta$ [°] | 101.671(3) | 89.834(4) | 105.220(5)° | 90 | 99.043(6) |
| $\gamma$ [°] | 90 | 80.219(4) | 90 | 90 | 90 |
| $V$ [Å$^3$] | 1488.3(4) | 2955.5(12) | 2448.3(12) | 3770.6(7) | 3217.2(18) |
| $Z$ | 2 | 4 | 4 | 8 | 4 |
| $\rho_{calcd.}$ [g cm$^{-3}$] | 1.167 | 1.180 | 1.228 | 1.340 | 1.154 |
| $T$ [K] | 100(2) | 100(2) | 100(2) | 100(2) | 293(2) |
| $\mu$ [mm$^{-1}$] | 0.142 | 0.143 | 0.116 | 0.076 | 0.107 |
| $2\theta_{max}$ [°] | 48.00 | 52.00 | 54.00 | 50.00 | 40.00 |
| Reflns. measured | 9671 | 23136 | 20367 | 26020 | 12192 |
| Reflns. used | 2328 | 11418 | 5309 | 3311 | 3008 |
| $R_{int}$ | 0.0274 | 0.0750 | 0.0543 | 0.0468 | 0.0864 |
| Parameters | 217 | 1022 | 419 | 351 | 374 |
| Final $R$ values [$I>2\sigma(I)$]: | | | | | |
| $R_1$ | 0.0429 | 0.1077 | 0.0610 | 0.0392 | 0.0718 |
| $wR_2$ | 0.0951 | 0.2509 | 0.1549 | 0.0936 | 0.1726 |
| $R$ values (all data): | | | | | |
| $R_1$ | 0.0539 | 0.1347 | 0.0780 | 0.0525 | 0.1195 |
| $wR_2$ | 0.1016 | 0.2679 | 0.1699 | 0.0992 | 0.1989 |
| GOF on $F^2$ | 1.042 | 1.066 | 1.036 | 1.072 | 1.048 |

reflections was performed by the program SADABS.[20] The structures were solved by direct methods using SHELXS-97[21] and refined by full-matrix least-squares on $F^2$ for all data using SHELXL-97.[22] Hydrogen atom treatment varied from compound to compound, depending on the crystal quality. In **15** and **24**, all hydrogen atoms were located in the difference fourier map and allowed to refine freely with isotropic thermal displacement factors. The same applies to the hydrogen atom attached to oxygen in **1c**. All other hydrogen atoms were added at calculated positions and refined using a riding model. Their isotropic temperature factors were fixed to 1.2 times (1.5 times for methyl groups) the equivalent isotropic displacement parameters of the carbon atom the H-atom is attached to. Anisotropic temperature factors were used for all non-hydrogen atoms.

CCDC-622230 (for **1c**), -622232 (for **8b**), -622233 (for **12**), -622231 (for **13a**), -622235 (for **15**), -622234 (for **17**), -622239 (for **19**), -622237 (for **21**), -623871 (for **22**), -622238 (for **24**) and -622236 (for **25**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## Acknowledgments

We thank Science Foundation Ireland and University College Dublin for generous financial support.

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Received: October 17, 2006
Published Online: January 25, 2007

  