Studies in the Cyclopropparene Series: Cross-Conjugated π-Extended Alkylidenecyclopropparenes

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The first simple and stable cross-conjugated π-extended alkylidenecyclopropparenes **5**, **6** and **15**–**22** have been prepared as coloured crystalline derivatives from use of (*E*,*E*)-1,5-diphenylpenta-2,4-dienone, (*E*,*E*)-1,5-diarylpenta-1,4-dien-3-ones and (*E*,*E*)-2,5-(diarylmethylidene)cyclopentanones with the relevant 1,1-bis(trimethylsilyl)cyclopropa[*b*]naphthalene. The permanent dipole moments of the compounds have been measured, and the conformational preference of the rotamers assessed.

Introduction

The alkylidenecyclopropparenes, for example **3**[1] and **4**,[2] have continued to provide a source of fascination[3,4] since their discovery in 1984,[5] not least because the various derivatives have unexpected polarities,[6−8] fluorescence characteristics[9] and novel properties.[10−12] Recently, we described the preparation of a series of conjugated and cross-conjugated cyclopropparene derivatives containing cyclopentadiene and dithiole subunits. In the main, these compounds are disappointing in that they have limited lifetimes under normal laboratory conditions and are obtained from low-yielding syntheses that has thwarted their possible use in the new organic materials area.[13] Undeterred by these features, we sought to obtain less complex derivatives in the hope that extended conjugation by way of simple substituted π-bonds would provide stable, but more polar derivatives, which can be physically examined. We now describe the 1-pentadienylidene compounds **5** and **6**, and the series of coloured, crystalline 3′-pentadienylidene derivatives **15**−**22** that are stable compounds with enhanced polar character relative to their methylidene homologues and have a conformational preference that matches those of their dienone precursors **7**−**14**.

The recorded polarities of a number of 1*H*-alkylidenecyclopropparenes are unambiguous in that they show that a single exocyclic aryl substituent gives rise to a molecule whose polarity is more than half that of the corresponding diaryl derivative.[6,10,14,15] This stems from the minimal degree of twist of the aryl substituent from the plane containing the cyclopropparene moiety (0−5°) in the monoaryl derivative, which facilitates unimpeded mesomeric π-orbital overlap; the twist in the diaryl derivatives is about 30°.[1,15] This rotation of the double-bond substituents in the exocyclic alkylidenecyclopropparenes is less than that in analogous penta- and heptafulvenes,[16−20] simply because there is a significant volume of free space adjacent to the external three-membered ring σ-bonds − after all, the molecules can be regarded as much as 1,6-didehydroheptafulvenes as cyclopropparenes. Nevertheless, each rotated aryl substituent gives rise to a vector component to the dipole that contributes about 80%. Furthermore, the effect from both aryl substituents is to combine and give a net dipole that is only about 1.6 times higher than that of the monoaryl analogue. In order to provide for an unequivocal enhanced contribution to the polarity in the disubstituted derivatives, essentially the simplest possible conjugating spacer groups have been incorporated from use of the (*E*,*E*)-1,5-diarylpenta-1,4-dien-3-ones **7**−**14**.

Results and Discussion

Commercially available (*E*,*E*)-1,5-diphenylpenta-2,4-dienone (5-phenylpenta-2,4-dienophenone) successfully reacts with the α-silyl anion formed upon reaction of the disilanes **1** and **2** with *t*BuOK[1,5,10] to yield the alkylidenecyclopropparenes **5** and **6** in yields of 50 and 20%, respectively (Scheme 1). By adding the pentadienone to a THF solution of preformed α-silyl anion at −70 °C, the yield of the exocyclic alkene is better than the reaction in which the anion is formed at the same temperature but in the presence of the conjugated dienenone, by a factor of about 3; in all likelihood competing conjugate addition is minimised. The spectral characteristics of **5** and **6** are fully compatible with the unsymmetrical substitution pattern at the exocyclic centre C-8. Thus, the cyclopropparenyl 2-H and 7-H protons

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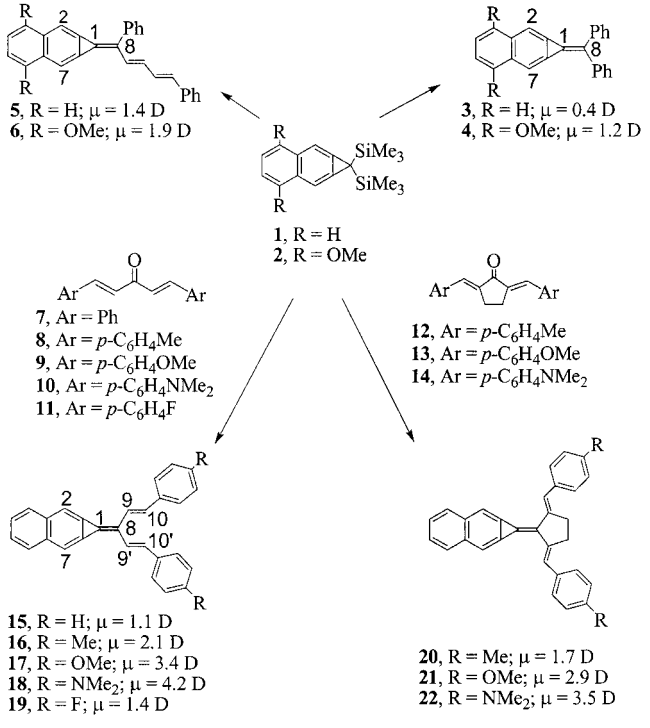
resonate as *para*-coupled doublets ($J \approx 1.7$ Hz), and the (*E*,*E*) stereochemistry of the dienylidene subunit is demonstrated by a characteristic J_{trans} coupling of 16 Hz. The ^{13}C NMR spectra differentiate between the sides of the cycloproparenyl moiety oriented (*E*) and (*Z*) with respect to the exocyclic dienylidene subunit (Exp. Sect.), and C-2/C-7 are markedly more shielded[10] in **6** ($\delta = 101.8$ and 101.9 ppm) than in **5** ($\delta = 106.9$ ppm) due to the spatially proximal OMe functions. As expected,[21] **5** and **6** (1.38 and 1.88 D) are more polar than the diphenyl congeners **3** and **4** (0.44 and 1.19 D), respectively; HF/6-31G** calculations predict that the direction of the dipole lies from the cycloproparene moiety toward the exocyclic substituents. The fact that the diethers **4**[2] and **6** have an *increased* dipole moment relative to their non-ether counterparts **3**[6] and **5**, respectively,[21] provides further experimental verification that the cyclopropa[*b*]naphthalenyl moiety is an electron donor. The degree of twisting of the terminal (C-5′) phenyl groups in **5** and **6** mirrors those in simple (*E*)-stilbenes[22] in that the twist angle is about 18°. Moreover, conformational searching using the SPARTAN molecular mechanics program locates the (*E*,*E*) isomer of **5** in the elongated *s-trans*,*s-trans* form (as drawn) as the energy minimum, while the 18° twist (dihedral) angle of the C-5′ terminal phenyl group is provided from the HF/6-31G** equilibrium geometry; the C-1 phenyl group is essentially nonconjugated as it is rotated almost 90° out of the plane of the cycloproparene.



Scheme 1

In order to provide cycloproparenes with more appropriate π-extended cross-conjugated substituents, the symmetrical pentadienylidene derivatives **15**−**19** have been prepared from the dibenzylideneacetones (ketocyanines) **7**−**11** in yields that range from 32 to 82%; the compounds are stable crystalline solids whose dipole moments have been measured and have the values shown in Scheme 1. The known (*E*,*E*)-ketocyanines **7**−**11** were obtained, in turn, from base-induced double condensation of the appropriate benzaldehyde with acetone [Equation (1)] using the procedure of Olomucki and Le Gall.[23] Aldehydes carrying *p*-CN, *p*-CF_3 and *p*-NO_2 electron-withdrawing functionalities failed to give a product from this reaction that employs sodium hydroxide as the base. The reasons for this are not clear, given that these same aldehydes react in Peterson olefinations with the α-silyl anions derived from **1** and **2** upon treatment with *t*BuOK. In addition, the conformationally locked cycloproparenes **20**−**22** have also been prepared by employing the 2,5-dimethylidenecyclopentanones **12**−**14** as substrates.[24] Each of the cycloproparene derivatives is expected to carry the pendant aryl groups twisted to a comparable extent with that in the precursor ketone.

$$2\mathrm{ArCHO} + \mathrm{MeCOMe} \longrightarrow \mathrm{ArCH}\overset{E}{=}\mathrm{CH\text{-}CO\text{-}CH}\overset{E}{=}\mathrm{CHAr} \quad (1)$$

Spectroscopic analysis of the ketones **7**−**14** and the cycloproparene products **15**−**22** provide data that are fully consistent with the proposed structures (Exp. Sect.). For cycloproparenes **15**−**22**, the singlet nature of 2-H/7-H, the AA′BB′ pattern for 3-H/6-H and the shielding of C-2/C-7 in the ^{13}C spectrum ($\delta = 106-108$ ppm) is as expected,[4,10] while the configuration about the alkenyl spacer groups is confirmed as (*E*,*E*) from the proton-proton spin-spin couplings of about 16 Hz in the alkenyl proton doublets of 9-H/10-H and 9′-H/10′-H (Exp. Sect.).

While the olefin stereochemistries are readily assigned (*E*,*E*), the NMR spectroscopic data do not provide information about the spatial arrangement of the side chains in either the ketocyanines **7**−**14** or the derived alkylidenecycloproparenes **15**−**22**. Quite recently, the solution conformers of *p*,*p*′-(diethylamino)phenylketocyanine **23** have received attention.[25,26] The two degrees of rotational freedom imposed by the two carbon−carbonyl single bonds provide for the three planar rotamers of Figure 1. These were predicated by Marcotte and Fery−Forgues as energy minima with energies (ΔH_f) from AM1 calculations of 170.6 (*s-cis*,*s-cis*), 175.8 (*s-cis*,*s-trans*) and 181.6 (*s-trans*,*s-trans*) kJ·mol^{-1}, respectively.[25] The higher energy *s-trans*,*s-trans* conformer has alkene hydrogen atoms in spatial conflict (Figure 1) and is unlikely to be found in solution, not simply because it is most disfavoured thermodynamically, but because of the 11 kJ·mol^{-1} energy barrier that separates it from the lowest energy form.[25] The fully planar *s-cis*,*s-cis* conformer gains its 6 kJ·mol^{-1} stabilization from hydrogen bonding (Figure 1), but the *s-cis*,*s-trans* rotamer becomes the most stable when one of the terminal aryl groups is twisted by 30° with respect to the plane of the molecule; parent dibenzylideneacetone (**7**) is similar, as has been discussed.[27] For comparative purposes, Marcotte and Fery-

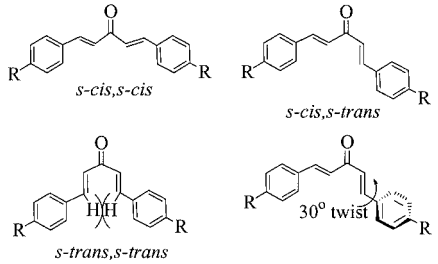
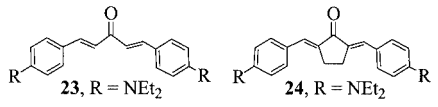


Figure 1. The stable rotamers 1,5-diarylpenta-2,4-dien-3-ones **7**−**11**

Forgues also performed AM1 calculations on the conformationally locked analogue of **23**, namely (*E*,*E*)-2,5-bis(*p*-diethylaminophenyl)methylidenecyclopentanone (**24**), as it has no rotational freedom about the carbonyl−alkene single bonds.[25] The conjugated system of **24** is predicted to be virtually planar and, since such "locked" ketocyanines are readily available from cyclopentanone by the procedure used to prepare **7**−**11**, ketones **12**−**14** have also been prepared by us (Exp. Sect.)[23] and transformed into the cycloproparene derivatives **20**−**22** (Scheme 1).



Infrared studies on dienone **23** in acetonitrile show[25] two C=O bands at approximately 1660 and 1640 cm^{-1} in a ratio of 11:89, while in toluene the bands are at 1664 and 1646 cm^{-1} and have a ratio of 23:77. Distinct carbonyl stretches for the different conformers are to be expected and fit well with results of Venkateshwarlu and Subrahmanyam[28] who have shown that **7** (Ar = Ph) (and many other α,β-unsaturated ketones) has a C=O band of the *s-cis*,*s-cis* conformer as the weaker signal (at higher cm^{-1}) and about 21 cm^{-1} from that of the *s-cis*,*s-trans* rotamer in CCl_4. Thus, the 20 cm^{-1} separation and peak intensities recorded for **23** are fully compatible with the finding that the *s-cis*,*s-trans* rotamer [$\tilde{\nu}$ = 1640 cm^{-1}] strongly dominates in solution. Furthermore, the only IR carbonyl frequency recorded for the *s-cis*,*s-cis*-locked analogue **24** lies close to the weaker band of **23**. The conformational characteristics of the ketocyanines **7**−**11** should be mirrored by the derived alkylidenecyclopropa[*b*]naphthalenes **15**−**22**, but without any stabilizing >C=O···H interactions. As these last compounds have no characteristic intense IR absorption bands (only weak stretches[3] occur in the range 1760−1790 cm^{-1}), conformational information is not easily deduced from IR studies. However, it is possible to obtain estimates of the rotamer distributions in the alkylidenecycloproparenes from use of their measured dipole moments and those of appropriate model compounds.

The *s-cis*,*s-trans* and *s-cis*,*s-cis* rotamers of ketone **23** have dipole moments that have been calculated as 5.3 and 4.2 D, respectively; the nonbonding electron pairs extend the conjugation.[25] By applying the vector model for partial dipole moments (Figure 2), and assuming a twist of about 30° for each aryl substituent as is the case for the cycloproparenes,[1,10,15] the *s-trans*,*s-trans* rotamer should be the most polar isomer with a dipole moment of approximately 6.4 D.[29] The transfer of electron density from "source" to "sink" effectively renders the inductive dipole moment negligible so that the observed dipole will be that caused by mesomeric phenomena.

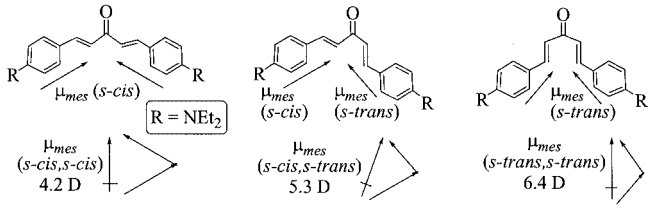
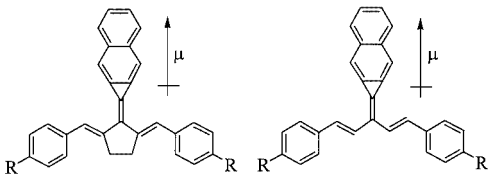


Figure 2. Vector analysis of the partial dipoles of the rotamers of ketocyanine **23**

The conformationally "locked" cycloproparenes **20**−**22** (prepared from cyclopentanones **12**−**14**) comprising *para*-methyl, -methoxy and -dimethylamino substituents have measured dipole moments of 1.73, 2.91 and 3.51 D, respectively (Table 1). Each "locked" molecule carries a nonconjugating ethano bridge and, as such, is an appropriate mimic for the "pure" *s-cis*,*s-cis* rotamer of the corresponding "loose" homologues **16**−**18**. These last compounds are found to be *more polar* [μ = 2.07, 3.38, and 4.23 D, respectively (Table 1)] and therefore, they cannot be present exclusively in the *s-cis*,*s-cis* form; a significant contribution to each dipole must come from the *s-cis*,*s-trans* rotamer. As each dipole moment was measured in benzene solution, the rotamer distribution should agree with the IR measurements in toluene rather than in acetonitrile.[30] Thus, with the use of the AM1-calculated dipoles of the *s-cis*,*s-cis* and *s-cis*,*s-trans* rotamers of (diethylamino)ketocyanine **23** with a ratio of 23:77 in toluene (IR), the solution dipole for the rotameric mixture of **23** is computed as 5.05 D, viz. (0.23 × 4.2) + (0.77 × 5.3) D; this is in good agreement with that measured by us for the bis(dimethylamino) analogue **10** (5.16 D) in benzene. Here, it should be noted that measurement of the dipole moments for equivalent dimethylamino- and diethylamino-substituted alkylidenecyclo-

Table 1. Experimental dipole moments (benzene solution) of cycloproparenes **12**−**14** and **16**−**18**

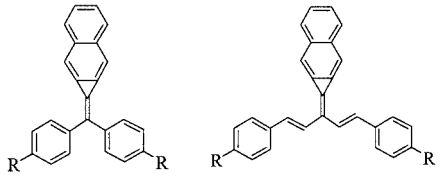


R	"Locked": μ [D]	"Loose": μ [D]
Me	**20**: 1.73	**16**: 2.07
OMe	**21**: 2.91	**17**: 3.38
NMe_2	**22**: 3.51	**18**: 4.23

propanaphthalenes is the same within experimental uncertainty, for example 8,8-diphenylmethylidene: NEt_2 2.9 D, NMe_2 3.0 D[31] and 1,4-dimethoxy-8,8-diphenylmethylidene: NEt_2 2.3 D, NMe_2 2.3 D.[14] On the reasonable assumption that the geometries of the *s-cis,s-cis* and *s-cis,s-trans* rotamers of **15**−**19** are similar to those of **23**, and that the "locked" compounds **20**−**22** are suitable models for the *s-cis,s-cis* rotamers of **16**−**18**, the proportions of *s-cis,s-trans* conformer in benzene solutions of **16**−**18** are estimated to lie in the range 60−80%.[32] Thus, the dipole moment determinations lead to entirely plausible rotamer distributions for **16**−**18** that conform with those of their keto progenitors **8**−**10**.

Each of the pentadienylidene derivatives **15**−**19** has a dipole moment that is greater than its methylidene analogue and in a direction given by 6-31G** calculations (Table 2). This applies whether the cyclopropareneis the electron donor or the electron acceptor. However, the additional conjugation provided by the unencumbered π-bond cannot be presumed to increase polarity in a uniform manner. The 6-31G** calculations show a conformational preference of **15**−**18** for the *s-cis,s-trans* rotamer and provide equilibrium geometries in which the *s-trans* π-bond *and* its terminal aryl ring are held close to the plane of the cyclopropareneforeffective π-overlap, whereas the *s-cis* π-moiety is rotated by about 40° and its attendant aryl group by a further 20°.

Table 2. Experimental dipole moments (benzene solution) of alkylidenecyclopropa[*b*]naphthalenes



R	Methylidene Orientation μ [D]		3′-Pentadienylidene Orientation μ [D]	
H	0.44 [a]	↓	**15**: 1.12	↓
Me	–	↑	**16**: 2.07	↑
OMe	2.40[b]	↑	**17**: 3.38	↑
NMe_2	3.00[c]	↑	**18**: 4.23	↑
F	0.87	↓	**19**: 1.38	↓

[a] This work and ref.[6] [b] Datum taken from ref.[6] [c] Datum taken from refs.[7,15]

The highly coloured compounds **15**−**17** and **19** have UV/Vis absorption bands in the range 470−500 nm as expected from incorporation of the two conjugating spacer units into the lower methylidene homologues. Bis(dimethylamino) compound **18** ($\lambda_{max.}$ = 466 nm) is the exception as it is not fluorescent like is its lower homologue.[9,15] Most likely, the two ethene spacers that extend the conjugation move the aryl rings too far from the cycloproparenemoiety for effective electron transfer and formation of a twisted internal charge transfer (TICT) state.[9] The fine structure evident for **18** (shoulders at 435, 448 and 485 nm; Exp. Sect.) is lost in acetonitrile and, in comparison with the cyclopentano "locked" derivatives **20**−**22** (also nonfluorescent), the "loose" analogues **16**−**18** have longer wavelength absorption maxima. This reflects the dominance of the *s-cis,s-trans* conformer in solution as shown by both experiment and theory. The chemistry and photochemistry of these novel compounds remains to be explored.

Experimental Section

General: Microanalyses were performed by the Analytical Facility of Otago University, Dunedin. Low-resolution electron impact mass spectra were recorded with a Hewlett Packard HP-5995C instrument at 70 eV. APCI mass spectrometry and accurate mass measurements were carried out by Mr. Oleg Zubkov with a PE Biosystem Mariner 5158 TOF mass spectrometer. ^1H and ^{13}C NMR spectra were recorded with a Varian Unity-INOVA 300 spectrometer, operating at 300 and 75 MHz, respectively, for [D]chloroform solutions using the residual solvent peak as internal standard. ^1H NMR multiplicities are defined by the usual notation; coupling constants, *J*, are specified in Hz. The assignments of ^{13}C and ^1H NMR resonances were made with the aid of distortionless enhancement by polarisation transfer (DEPT) and ^1H-^1H and ^{13}C-^1H correlation spectroscopy (COSY) experiments, and confirmed from heteronuclear multiple bond connectivity (HMBC) and heteronuclear single quantum correlation (HSQC) experiments. Assignments are based on the numbering system in Scheme 1 which does not correspond with the nomenclature of the compound names. Infrared spectra were recorded for KBr disks with a Biorad FTS-7 spectrophotometer (±2 cm^{-1}). Ultraviolet/visible (UV/Vis) spectra were acquired with a Hewlett−Packard 8452A diode array spectrophotometer in quartz cells (±1 nm). Melting points were determined with a Reichert hot-stage melting-point apparatus and are uncorrected. Thin layer chromatographic (TLC) analyses were performed using Merck Kieselgel (Alufolien) 60 F_{254} to a thickness of 0.2 mm. Components were detected under UV light (254 or 350 nm), or by spraying with 1:1 $MeOH/H_2SO_4$ (concd.), followed by heating. Radial chromatography was performed with a Chromatotron 9724T instrument (Harrison Research, Palo Alto, California) at 90 rpm. Rotors were coated with gypsum-containing Merck Kieselgel 60 DGF_{254} to thicknesses of 1.0, 2.0, 3.0 or 4.0 mm, and the total mass of solute loaded onto the plate was 0.25, 0.75, 1.15 and 1.5 g, respectively. Solvents were purified before use according to Perrin, Aramarego and Perrin.[33] The light petroleum used was the hexane fraction, b.p. 60−70 °C. Anhydrous tetrahydrofuran (THF) was obtained by distillation immediately prior to use from a dark blue-purple solution of sodium/potassium benzophenone ketyl.

Dipole Moment Measurements: Dipole moments were determined for AnalaR grade benzene solutions (ca. 0.05−0.10 M) by the method of Guggenheim[34] and Smith,[35] using a small (ca. 2 mL) variable capacitance cell with analytically pure (C, H) compounds. Impedance readings were taken with the cell open and closed employing a Hewlett−Packard 913 vector impedance meter operating at 1 MHz. The recordings were taken at ambient temperature. Refractive index measurements were made with an Abbe 60 Refractometer. Benzophenone, diphenyl sulfone, and 2-hydroxynaphthalene were used as reference standards, against which the reproducibility of the cell was verified before and after each series of meas-

urements. Dipole moments were calculated by employing a Microsoft® Excel spreadsheet; values were rounded to 2 decimal points at the end of the algorithm only.

Dipole Moments μ: 3[1,6] (benzene, 21 °C) 0.44 D; **4**[2,14] 1.19 D; **10**[14] (benzene, 21 °C) 5.16 D.

(*E*,*E*)-1,5-Diarylpenta-1,4-dien-3-ones 7−11: The known benzylideneacetones **7**,[23] **8**,[36] **9**,[37] **10**[38] and **11**[39] were prepared from acetone (0.59 g, 0.92 mL, 0.0125 mol) and the relevant benzaldehyde (0.025 mol) in alkaline medium by the procedure of Olomucki and Le Gall.[23] The crude products, rinsed with cold ethanol and purified by flash column chromatography on silica (about 10 g), were used directly.

(*E*,*E*)-2,5-(Diarylmethylidene)cyclopentanones 12−14: The "locked" ketocyanines **12−14** were prepared as described by Kaupp and co-workers,[24] by condensing the relevant benzaldehyde (0.025 mol, 3.72 g) with cyclopentanone (0.0125 mol, 1.05 g, 1.00 mL) in the presence of approximately 40 mol % of benzyltrimethylammonium hydroxide in methanol. The crude products were rinsed with cold ethanol and purified by flash column chromatography on silica (about 10 g).

Alkylidenecycloproparenes 5 and 6: A solution of freshly sublimed potassium *tert*-butoxide (5 equiv.) in THF (about 10 mL) was added dropwise by a syringe needle to a stirred solution of disilane[15] **1** (1 equiv.) in anhydrous tetrahydrofuran (approximately 10 mL) held at −70 °C under nitrogen. The mixture was stirred at −70 °C for 30 min, by which time a deep red colour had developed. To this was added a solution of the carbonyl compound (5 equiv.) in THF (about 10 mL), stirring continued at −70 °C for a further 1 h, and then the cryostat was switched off, and the mixture left to warm to ambient temperature overnight. The mixture was quenched ($NaHCO_3$ satd., 30 mL), the organic products were extracted with dichloromethane (3 × 20 mL), and the organic solution was washed with water (3 × 20 mL), dried ($MgSO_4$, about 2 g), filtered and concentrated under reduced pressure to give a crude product that was purified by radial chromatography.

1-(1,5-Diphenylpenta-2,4-dien-1-ylidene)-1*H*-cyclopropa[*b*]naphthalene (5): Disilane **1**[15] (100 mg, 0.35 mmol) and 5-phenyl-2,4-pentadienophenone (410 mg, 1.75 mmol) gave a bright orange solid and by radial chromatography [light petroleum/dichloromethane (2:1) elution] title compound **5** was obtained. Yield: 62 mg (50%). Dark red microcrystals (light petroleum), m.p. 182.0−183.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.67 (d, $^3J_{trans}$ = 17.0 Hz, 1 H, 12-H), 6.95−7.25 (m, 4 H, 9-H, 16-H, 20-H/24-H), 7.33−7.43 (m, 4 H, 10-H, 21-H/23-H, 22-H), 7.46−7.58 (m, 7 H, 4-H/5-H, 2-H/7-H, 11-H, 15-H/17-H), 7.76 (d, $^3J_{AB}$ = 7.2 Hz, 2 H, 14-H/18-H), 7.84−7.92 (BB′ of AA′BB′, 2 H, 3-H/6-H ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 106.9 (C2/C7), 112.8 (C-1), 119.0 (C-8), 126.4 (C-20/C-24), 126.7 (C-22), 126.8 (C-16), 127.4 (C-21/C-23), 127.5 (C-1a or C-7a), 127.6 (C-4/C-5), 127.9 (C-7a or C-1a), 128.6 (C-15/C-17), 128.7(0) (C-14/C-18), 128.7(5) (C-3/C-6), 130.0 (C-9), 130.9 (C-10), 132.3 (C-11), 132.5 (C-12), 137.6 (C-19), 138.3 (C-13), 138.8 (C-2a or C-6a), 138.9 (C-6a or C-2a) ppm. MS (70 eV): *m*/*z* (%) = 357 (27) $[M + 1]^+$, 356 (100) $[M]^+$, 355 (69), 354 (21), 353 (30), 352 (26), 341 (29), 340 (31), 339 (54), 326 (21), 279 (79), 278 (74), 277 (45), 276 (56), 265 (96), 253 (26), 252 (44), 169 (34). IR (KBr): $\tilde{\nu}$ = 3028, 2926, 2855, 2372, 2345, 1870, 1831, 1774 (w), 1740, 1701, 1685, 1647, 1654 (s), 1636 (s), 1560, 1112, 983, 843 cm^{-1}. UV/Vis (cyclohexane): $\lambda_{max.}$ (log ε) = 328 (4.27), 458 (4.34), 486 nm (4.32). UV/Vis (acetonitrile): $\lambda_{max.}$(log ε) = 328 (4.25), 154 (4.37), 478 nm (4.33). Dipole moment (benzene): μ (22 °C) = 1.38 D. $C_{28}H_{20}$ (356.47): calcd. C 94.34, H 5.66; found C 94.22, H 5.78.

1-(1,5-Diphenylpenta-2,4-dien-1-ylidene)-3,6-dimethoxy-1*H*-cyclopropa[*b*]naphthalene (6): Disilane **2**[2] (100 mg, 0.29 mmol) and 5-phenyl-2,4-pentadienophenone (340 mg, 1.45 mmol) gave an orange solid, and by radial chromatography [light petroleum/dichloromethane (4:1) elution] title compound **6** was obtained. Yield: 28 mg (23%). Orange needles (light petroleum), m.p. 136.0−137.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.96 (s, 6 H, OMe), 6.67 (d, $^3J_{trans}$ = 15.4 Hz, 1 H, 12-H), 6.76 (s, 2 H, 4-H/5-H), 7.08−7.14 (m, 2 H, 10-H and 11-H), 7.22−7.24 (m, 2 H, 21-H/23-H), 7.33−7.38 (m, 3 H, 9-H, 16-H and 22-H), 7.46−7.53 (m, 4 H, 15-H/17-H and 20-H/24-H), 7.78−7.81 (m, 2 H, 14-H/18-H), 7.92 (d, J_{para} = 1.7 Hz, 1 H, 2-H or 7-H) 8.01, d, J_{para} = 1.7 Hz, 1 H, 7-H or 2-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.9 (OMe), 101.8 (C-2 or C-7), 101.9 (C-7 or C-2), 104.5 (C-4/C-5), 113.0 (C-1), 117.5 (C-8), 126.4 (C-20/C-24), 127.3 (C-16), 127.4 (C-21/C-23), 127.6 (C-1a or C-7a), 127.9 (C-7a or C-1a), 128.6 (C-15/C-17), 128.7 (C-14/C-18), 130.1 (C-9), 130.5 (C-10), 131.3 (C-2a or C-6a), 131.4 (C-6a or C-2a), 132.1 (C-11), 132.2 (C-12), 137.7 (C-19), 138.5 (C-13), 150.5 (C-3/C-6) ppm. HRMS (positive APCI): calcd. for $C_{30}H_{25}O_2$ $[M + H]^+$ 417.1254; found 417.1255 (+0.25 mmu). MS (70 eV): *m*/*z* (%) = 417 (11) $[M + 1]^+$, 416 (32) $[M]^+$, 401 (14), 385 (75), 86 (53), 84 (73), 57 (45), 56 (43), 51 (42), 49 (100). IR (KBr): $\tilde{\nu}$ = 2965, 2933, 2830, 2172, 1773 (w), 1613, 1462, 1325, 1260, 1223, 1170, 1103, 1070, 1005, 796, 699 cm^{-1}. UV/Vis (cyclohexane): $\lambda_{max.}$ (log ε) = 228 (4.12), 304 (4.21), 336 (4.30), 456 nm (4.31). UV/Vis (acetonitrile): $\lambda_{max.}$(log ε) = 224 (4.15), 304 (4.24), 334 (4.29), 454 nm (4.27). Dipole moment (benzene): μ (20 °C) = 1.88 D.

Alkylidenecycloproparenes 15−22 and Bis[*p*-(fluorophenyl)methylidene]cyclopropanaphthalene: The method described above for **5** and **6** was employed with the notable exception that *stoichiometric quantities of base* (0.035 mmol) *and carbonyl compound* (0.35 mmol) led to optimum conversion.

(*E*,*E*)-1-(1,5-Diphenylpenta-1,4-dien-3-ylidene)-1*H*-cyclopropa[*b*]naphthalene (15): Light petroleum/dichloromethane (6:1) elution gave title compound **15**. Yield: 40 mg (32%). Yellow flakes (light petroleum), m.p. 106.5−108.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (d, $^3J_{trans}$ = 16.0 Hz, 2 H, 9-H), 7.29 (d, $^3J_{trans}$ = 16.0 Hz, 2 H, 10-H), 7.30−7.35 (m, 6 H, 14-H and 13-H/15-H), 7.47−7.50 (m, 4 H, 4-H/5-H and 2-H/7-H), 7.60 (d, $^3J_{AB}$ = 8.5 Hz, 4 H, 12-H/16-H), 7.87−7.90 (BB′ of AA′BB′, 2 H, 3-H/6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 107.3 (C-2/C-7), 112.7 (C-1), 115.8 (C-8), 124.2 (C-9), 127.1 (C-4/C-5), 127.4 (C-12/C-16), 127.6 (C-1a/C-7a), 128.1 (C-10), 128.6 (C-13/C-15), 128.7 (C-3/C-6), 128.8 (C-14), 137.7 (C-11), 139.2 (C-2a/C-6a) ppm. IR (KBr): $\tilde{\nu}$ = 2971, 2928, 2327, 2174, 1774 (w), 1717, 1654, 1563, 1508, 1176, 1144, 1035, 875 cm^{-1}. UV/Vis (cyclohexane): $\lambda_{max.}$ (log ε) = 306 (3.46), 328 (3.51), 356 (3.66), 476 nm (4.01). UV/Vis (acetonitrile): $\lambda_{max.}$ (log ε) = 306 (3.47), 326 (3.45), 354 (3.62), 472 nm (3.97). Dipole moment (benzene): μ (21 °C) = 1.12 D. $C_{28}H_{20}$ (356.47): calcd. C 94.34, H 5.66; found C 94.42, H 5.58.

(*E*,*E*)-1-[1,5-Bis(*p*-tolyl)penta-1,4-dien-3-ylidene]-1*H*-cyclopropa[*b*]naphthalene (16): Light petroleum/dichloromethane (2:1) elution gave title compound **16**. Yield 74 mg (55%). Red needles (light petroleum), m.p. 122.5−123.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 6 H, Me), 7.21 (d, $^3J_{AB}$ = 8.5 Hz, 4 H, 13-H/15-H), 7.23 (d, $^3J_{trans}$ = 15.5 Hz, 2 H, 9-H), 7.34 (d, $^3J_{trans}$ = 16.0 Hz, 2 H, 10-H), 7.46−7.49 (m, 6 H, 4-H/5-H and 12-H/16-H), 7.51 (s, 2 H, 2-H/7-H), 7.86−7.89 (BB′ of AA′BB′, 2 H, 3-H/6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (Me), 106.6 (C-2/C-7), 111.8 (C-1), 116.3 (C-8), 125.1 (C-9), 126.5 (C-12/C-16), 126.8 (C-4/C-5), 127.9 (C-1a/C-7a), 128.6 (C-3/C-6), 129.0 (C-10), 129.5 (C-13/C-15), 135.0 (C-11), 137.5 (C-14), 139.0 (C-2a/C-6a) ppm. IR (KBr):

$\tilde{\nu}$ = 2971, 2927, 2381, 2326, 2174, 1774 (w), 1719, 1654, 1647, 1636, 1560, 1508, 1458, 1252, 1176, 1144, 1030 cm^{-1}. UV/Vis (cyclohexane): $\lambda_{max.}$ (log ε) = 308 (4.06), 326 (4.15), 340 (4.17), 464 (4.20), 500 nm (4.21). UV/Vis (acetonitrile): $\lambda_{max.}$ (log ε) = 308 (4.09), 324 (4.17), 338 (4.19), 462 (4.22), 496 nm (4.24). Dipole moment (benzene): μ (21 °C) = 2.07 D. $C_{30}H_{24}$ (384.52): calcd. C 93.71, H 6.29; found C 93.65, H 6.35.

(*E*,*E*)-1-[1,5-Bis(*p*-methoxyphenyl)penta-1,4-dien-3-ylidene]-1*H*-cyclopropa[*b*]naphthalene (17): Light petroleum/dichloromethane (4:1) elution gave title compound **17**. Yield: 60 mg, (41%). Red-orange needles (light petroleum), m.p. 165.0−166.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.86 (s, 6 H, OMe), 6.94 (d, J_{AB} = 8.7, 4 H, 13-H/15-H), 7.18 (d, $^3J_{trans}$ = 16.2 Hz, 2 H, 9-H), 7.25 (d, $^3J_{trans}$ = 16.0 Hz, 2 H, 10-H), 7.45−7.48 (AA′ of AA′BB′, 2 H, 4-H/5-H), 7.48 (s, 2 H, 2-H/7-H), 7.55 (d, J_{AB} = 8.7 Hz, 4 H, 12-H/16-H), 7.84−7.88 (BB′ of AA′BB′, 2 H, 3-H/6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.4 (OMe), 106.3 (C-2/C-7), 111.1 (C-1), 114.2 (C-13/C-15), 116.7 (C-8), 124.1 (C-9), 126.7 (C-4/C-5), 127.8 (C-12/C-16), 128.0 (C-1a/C-7a), 128.6 (C-3/C-6), 128.7 (C-10), 130.6 (C-11), 138.9 (C-2a/C-6a), 159.4 (C-14) ppm. IR (KBr): $\tilde{\nu}$ = 2924, 2843, 1774 (w), 1652, 1506, 1498, 1443, 1154, 1096, 756 cm^{-1}. UV/Vis (cyclohexane): (log ε) $\lambda_{max.}$ = 310 (3.44), 336 (3.70), 348 (3.73), 468 (3.93), 504 nm (4.10).UV/Vis (acetonitrile): $\lambda_{max.}$ (log ε) = 310 (3.81), 336 (3.92), 348 (3.95), 464 (4.03), 500 nm (4.02). Dipole moment (benzene): μ (21 °C) = 3.38 D. $C_{30}H_{24}O_2$ (416.52): calcd. C 86.51, H 5.81; found C 86.48, H 5.92.

(*E*,*E*)-1-[1,5-Bis(*p*-dimethylaminophenyl)penta-1,4-dien-3-ylidene]-1*H*-cyclopropa[*b*]naphthalene (18): Light petroleum/dichloromethane (4:1) elution gave title compound **18**. Yield: 126 mg (82%). Orange microcrystals (light petroleum), m.p. 128.5−130.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.03 (s, 12 H, NMe_2), 6.77 (d, $^3J_{AB}$ = 8.7 Hz, 4 H, 13-H/15-H), 7.21 (d, $^3J_{trans}$ = 16.2 Hz, 2 H, 9-H), 7.31 (d, $^3J_{trans}$ = 16.0 Hz, 2 H, 10-H), 7.44 (s, 2 H, 2-H/7-H), 7.45−7.48 (AA′ of AA′BB′, 2 H, 4-H/5-H), 7.52 (d, $^3J_{AB}$ = 8.6 Hz, 4 H, 12-H/16-H), 7.81−7.87 (BB′ of AA′BB′, 2 H, 3-H/6-H ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.1 (NMe_2), 106.3 (C-2/C-7), 109.8 (C-1), 112.6 (C-13/C-15), 117.8 (C-8), 123.6 (C-9), 125.8 (C-11), 126.6 (C-4/C-5), 127.6 (C-1a/C-7a), 127.7 (C-12/C-16), 128.6 (C-3/C-6), 128.7 (C-10), 138.7 (C-2a/C-6a) 149.7 (C-14) ppm. IR (KBr): $\tilde{\nu}$ = 2922, 2856, 2170, 1632, 1604, 1519, 1504, 1384, 1187, 1142, 1053, 875 cm^{-1}. UV/Vis (cyclohexane): $\lambda_{max.}$ (log ε) = 236 (3.84), 260 (3.57), 292 (3.44), 324 (3.35), 435 sh (4.04), 448 sh (4.11), 466 nm (4.19), 485 sh (3.91).UV/Vis (acetonitrile): $\lambda_{max.}$ (log ε) = 236 (3.81), 260 (3.66), 290 (3.59), 322 (3.46), 462 nm (4.10). Dipole moment (benzene): μ (21 °C) = 4.23 D. $C_{32}H_{30}N_2$ (442.61): calcd. C 86.84, H 6.83, N 6.33; found C 86.84, H 6.74, N 6.42.

(*E*,*E*)-1-[1,5-Bis(*p*-fluorophenyl)penta-1,4-dien-3-ylidene]-1*H*-cyclopropa[*b*]naphthalene (19): Light petroleum/dichloromethane (2:1) elution gave title compound **19**. Yield: 93 mg (68%). Orange-red needles (light petroleum), m.p. 147.5−149.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.09 (t, *J* = 8.7 Hz, 4 H, 13-H/15-H), 7.16 (d, $^3J_{trans}$ = 16.2 Hz, 2 H, 9-H), 7.26 (d, $^3J_{trans}$ = 16.2 Hz, 2 H, 10-H), 7.48−7.51 (AA′ of AA′BB′, 2 H, 4-H/5-H), 7.53−7.58 (m, 6 H, 2-H/7-H and 12-H/16-H), 7.87−7.90 (BB′ of AA′BB′, 2 H, 3-H/6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 107.0 (C-2/C-7), 112.5 (C-1), 115.5 (C-8), 115.7 (d, $^2J_{C,F}$ = 22 Hz, C-13/C-15), 125.7 (d, $^6J_{C,F}$ = 2.5 Hz, C-9), 127.0 (C-4/C-5), 127.6 (C-1a/C-7a), 127.7 (C-10), 128.0 (d, $^3J_{C,F}$ = 8 Hz, C-12/C-16), 128.7 (C-3/C-6), 133.8 (d, $^4J_{C,F}$ = 3 Hz, C-11), 139.0 (C-2a/C-6a), 162.3 (d, $^1J_{C,F}$ = 248 Hz, C-14) ppm. IR (KBr): $\tilde{\nu}$ = 2923, 2833, 1773 (w), 1636, 1505, 1423, 1384, 1220, 1144, 1094, 952, 816, 734, 610 cm^{-1}. UV/Vis (cyclohexane):): $\lambda_{max.}$ (log ε) = 306 (3.96), 320 (3.94), 332 (3.91), 462 (4.02), 496 nm (3.99). UV/Vis (acetonitrile)): $\lambda_{max.}$ (log ε) = 304 (4.01), 318 (3.98), 330 (3.96), 458 (4.06), 492 nm (4.05). Dipole moment (benzene): μ (22 °C) = 1.38 D. $C_{28}H_{18}F_2$ (392.45): calcd. C 85.69, H 4.62; found C 85.75, H 4.78.

1-[2,5-Bis(*p*-tolylmethylidene)cyclopent-1-ylidene]-1*H*-cyclopropa[*b*]naphthalene (20): Light petroleum/dichloromethane (6:1) elution gave title compound **20** as the most mobile fraction. Yield: 26 mg (18%). Yellow needles (light petroleum), m.p. 132.5−134.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.02 (s, 4 H, 17-H), 2.41 (s, 6 H, Me), 7.26 (d, $^3J_{AB}$ = 8.1 Hz, 4 H, 13-H/15-H), 7.35 (s, 2 H, 10-H), 7.45−7.49 (m, 6 H, 4-H/5-H and 12-H/16-H), 7.50 (s, 2 H, 2-H/7-H), 7.85−7.90 (BB′ of AA′BB′, 2 H, 3-H/6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4 (Me), 32.2 (C-17), 107.6 (C-2/C-7), 111.9 (C-1), 113.4 (C-8), 125.6 (C-9), 126.9 (C-4/C-5), 127.5 (C-1a/C-7a), 127.7 (C-12/C-16), 129.0 (C-3/C-6), 129.4 (C-10), 129.6 (C-13/C-15), 134.2 (C-11), 136.2 (C-14), 138.9 (C-2a/C-6a) ppm. HRMS (positive APCI): calcd. for $C_{32}H_{27}$ $[M + H]^+$ 411.2112; found 411.2116 (+0.97 mmu). IR (KBr): $\tilde{\nu}$ = 3326, 3265, 2927, 2564, 2348, 2267, 1800, 1774 (w), 1564, 1467, 1326, 1308, 1081, 1003, 936, 772 cm^{-1}. UV/Vis (cyclohexane): $\lambda_{max.}$ (log ε) = 210 (4.01), 256 (3.99), 364 (3.85), 410 nm (4.12). UV/Vis (acetonitrile): $\lambda_{max.}$ (log ε) = 210 (4.01), 256 (3.98), 362 (3.83), 408 nm (4.11). Dipole moment (benzene): μ (22 °C) = 1.73 D.

1-{2,5-Bis[(*p*-methoxyphenyl)methylidene]cyclopent-1-ylidene}-1*H*-cyclopropa[*b*]naphthalene (21): Light petroleum/dichloromethane (4:1) elution gave the title compound **21** as the most mobile fraction. Yield: 40 mg (26%). Yellow needles (light petroleum), m.p. 156.5−158.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.05 (s, 4 H, 17-H), 3.86 (s, 6 H, OMe), 6.91 (d, $^3J_{AB}$ = 8.1 Hz, 4 H, 13-H/15-H), 7.16 (s, 2 H, 10-H), 7.45−7.49 (m, 4 H, 4-H/5-H and 2-H/7-H), 7.50 (d, $^3J_{AB}$ = 8.1 Hz, 4 H, 12-H/16-H), 7.84−7.88 (BB′ of AA′BB′, 2 H, 3-H/6-H ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.3 (C-17), 55.3 (OMe), 107.4 (C-2/C-7), 111.6 (C-1), 114.0 (C-13/C-15), 115.1 (C-8), 125.6 (C-9), 126.7 (C-4/C-5), 127.6 (C-1a/C-7a), 128.8 (C-3/C-6), 129.3 (C-10), 129.6 (C-12/C-16), 130.2 (C-11), 138.7 (C-2a/C-6a), 159.2 (C-14) ppm. HRMS (positive APCI): calcd. for $C_{32}H_{27}O_2$ $[M + H]^+$ 443.2011; found 443.2008 (−0.68 mmu). IR (KBr): $\tilde{\nu}$ = 3025, 2927, 1845, 1774 (w), 1654, 1632, 1478, 1426, 1238, 1168, 1009, 993, 854 cm^{-1}. UV/Vis (cyclohexane): $\lambda_{max.}$ (log ε) = 228 (3.76), 246 (3.85), 326 (3.93), 420 nm (4.03). UV/Vis (acetonitrile): $\lambda_{max.}$ (log ε) = 228 (3.76), 246 (3.87), 324 (3.92), 416 nm (4.00). Dipole moment (benzene): μ (22 °C) = 2.91 D.

1-{2,5-Bis[(*p*-dimethylaminophenyl)methylidene]cyclopent-1-ylidene}-1*H*-cyclopropa[*b*]naphthalene (22): Light petroleum/dichloromethane (4:1) elution gave the title compound **22** as the most mobile fraction. Yield: 69 mg (42%). Orange needles (light petroleum), m.p. 136.5−137.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.05 (s, 4 H, 17-H), 3.01 (s, 12 H, NMe_2), 6.80 (d, $^3J_{AB}$ = 8.1 Hz, 4 H, 13-H/15-H), 7.22 (s, 2 H, 10-H), 7.42 (s, 2 H, 2-H/7-H), 7.46−7.57 (m, 6 H, 4-H/5-H and 12-H/16-H), 7.82−7.86 (BB′ of AA′BB′, 2 H, 3-H/6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.6 (C-17), 40.5 (NMe_2), 106.4 (C-2/C-7), 110.1 (C-1), 112.5 (C-13/C-15), 116.5 (C-8), 123.3 (C-9), 126.5 (C-4/C-5), 127.5 (C-1a/C-7a), 128.5 (C-10), 128.6 (C-3/C-6), 128.8 (C-11), 129.6 (C-12/C-16), 138.7 (C-2a/C-6a), 149.8 (C-14) ppm. HRMS (positive APCI): calcd. for $C_{34}H_{33}N_2$ $[M + H]^+$ 469.2643; found 469.2649 (+1.28 mmu). IR (KBr): $\tilde{\nu}$ = 3204, 3122, 2927, 2900, 2774, 1896, 1774 (w). 1652, 1603, 1548, 1449, 1423, 1208, 1193, 1134, 1008, 1000, 923, 855 cm^{-1}. UV/Vis (cyclohexane): $\lambda_{max.}$ (log ε) = 246 (4.00), 256 (3.93), 288 (3.82), 422 nm (4.18). UV/Vis (acetonitrile): $\lambda_{max.}$ (log ε) = 246 (3.84), 254 (3.91), 286 (3.77), 418 nm (4.10). Dipole moment (benzene): μ (22 °C) = 3.51 D.

1-[Bis(*p*-fluorophenyl)methylidene]-1*H*-cyclopropa[*b*]naphthalene: Light petroleum elution gave the title compound. Yield: 38 mg (32%). Bright yellow needles (light petroleum), m.p. 133.0−135.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.13 (t, $J_{AB} \approx {}^3J_{H,F} \approx$ 8.8 Hz, 4 H, 11-H/13-H), 7.46−7.50 (AA′ of AA′BB′, 2 H, 4-H/5-H), 7.52 (s, 2 H, 2-H/7-H), 7.68 (dd, $^3J_{AB}$ = 9.0, $^4J_{H,F}$ = 5.4 Hz, 4 H, 10-H/14-H), 7.85−7.89 (BB′ of AA′BB′, 2 H, 3-H/6-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 107.2 (C-2/C-7), 111.6 (C-1), 115.5 (d, $^2J_{C,F}$ = 22 Hz, C-11/C-13), 117.7 (C-8), 126.8 (C-4/C-5), 128.8 (C-3/C-6), 129.6 (d, $^3J_{C,F}$ = 8 Hz, C-10/C-14), 135.4 (d, $^4J_{C,F}$ = 4 Hz, C-9), 138.7 (C-2a/C-6a), 162.1 (d, $^1J_{C,F}$ = 247 Hz, C-12) ppm. MS (70 eV): *m/z* (%) = 341 (26) $[M + 1]^+$, 340 (100) $[M]^+$, 339 (37) $[M - H]^+$, 338 (59), 336 (15), 318 (13). IR (KBr): $\tilde{\nu}$ = 3037, 2929, 2853, 1769 (w), 1648, 1601, 1506 (s), 1429, 1230, 1136, 1101, 1007, 839, 752 cm^{-1}. UV/Vis (cyclohexane): $\lambda_{max.}$ (log ε) = 228 (4.35), 248 (4.23), 406 (4.25), 430 nm (4.27). UV/Vis (acetonitrile): $\lambda_{max.}$ (log ε) = 230 (4.33), 286 (3.87), 408 (4.21), 434 nm (4.25). Dipole moment (benzene): μ (22 °C) = 0.87 D. $C_{24}H_{14}F_2$ (340.37): calcd. C 84.69, N 4.15; found C 84.79, N 4.12.

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[32] The ratio of dipole moments of the *s-cis,s-cis* and *s-cis,s-trans* rotamers of **16−18** should approximate to the 0.79 value for **23**. Assuming the experimentally determined dipole moments of the "locked' cyclopentanones **20−23** to represent the *s-cis,s-cis* rotamers of **16−18**, the ratio of *s-cis,s-cis* to *s-cis,s-trans* rotamers (benzene solution) of each of **16−18** is approximated as shown for **16** in Equation (2), where *y* = proportion of *s-cis,s-cis* rotamer.
$[y \times \mu\text{-}\mathbf{20}] + [(1 - y) \times \mu\text{-}s\text{-}cis,s\text{-}trans\text{-}\mathbf{16}] = \mu\text{-}\mathbf{16}_{recorded}$ (2)
For **16**: $[y \times 1.73] + [(1 - y) \times 1.73/0.79] = 2.06$; with y = 0.283 and *s-cis,s-cis*/*s-cis,s-trans* = 28:72.
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