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Synthetic protocols, molecular polarity, and ^{13}C NMR correlations for 1-aryl- and 1-diarylmethylidene-1*H*-cyclopropa[*b*]naphthalenes†

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The Peterson olefination for alkylidenecycloproparene synthesis from a 1,1-disilylcycloproparene has been refined into *five* distinct protocols that have provided 43 new aryl- (**5** and **6**) and diaryl- (**7** and **8**), and aryl(phenyl)- (**9** and **10**) methylidene derivatives. The permanent dipole moments of these and other previously reported compounds have been measured and the direction of the dipole, to or from the cyclopropareny moiety, established for each compound. The ^{13}C NMR spectra are fully assigned and linear correlations of carbon chemical shift with the Hammett σ_p^+ constants for each atom within the cycloproparene moiety are provided for the 8–11 compounds that comprise each substitution pattern present in **5**–**10**.

Introduction

The alkylidenecycloproparenes, *e.g.* **7a**[1] and **8a**,[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.[3,10,11] Recently, we described the preparation of a series of conjugated and cross-conjugated cycloproparene derivatives containing cyclopentadiene and dithiole sub-units,[12] and others with simple π bonds to enhance polarity through extended conjugation.[13] Despite these various advances and the numerous publications involved, the selection of an appropriate synthetic procedure involving α silyl anion **3** (or **4**) and a carbonyl compound to prepare a given alkylidenecycloproparene from Peterson olefination (Scheme 1) has not previously been subjected to detailed examination. We provide here a set of five tested protocols that lead to the formation of a wide range of alkylidenecyclopropa[*b*]naphthalene derivatives; only when none of these work do we regard the compound as unavailable. In establishing these procedures we have provided an extensive range of *p*-aryl-substituted alkylidenecycloproparenes **5**–**10**, the polarities of which have been measured using the procedures of Guggenheim[14] and Smith.[15] Preliminary studies that showed[16,17] correlations of the Hammett σ_p^+ constants for C8 *p*-aryl derivatives with ^{13}C NMR chemical shifts of the cycloproparene moiety are greatly extended.

Results and discussion

Synthetic methods

As a result of our experience in the cycloproparene area,[3] the vagaries of Peterson olefination of carbonyl-containing compounds with α silyl anions **3** and **4** (Scheme 1) have resulted in the development of five protocols for the synthesis of the alkylidenecycloproparenes; four use potassium *tert*-butoxide as desilylating agent and the last employs KF/Bu_4NF (Table 1). Selection of the most appropriate method for a given target molecule depends upon several factors. In the simplest possible case the reaction of stoichiometric quantities of α silyl anion and aldehyde or ketone requires addition of a THF suspension of *tert*-butoxide to a THF solution containing both disilane and carbonyl compound and leads directly to the desired exocyclic alkene in good yield; this is exemplified by the formation of **7a** almost quantitatively; the procedure is termed *Method I* (Table 1). Since carbanion formation from the desilylation of **1** (or **2**) is brought about by use of *tert*-butoxide, the basic environment often precludes subsequent reaction with a carbonyl compound carrying an acidic α proton due to competitive enolate anion formation.[3,4] This is appropriately illustrated by reaction of **1** with acetophenone to give **11** in 39% yield only while reaction with acetone completely fails.[1,18] *Methods II* and *III* allow for initial formation of anion and subsequent exposure of it to the desired carbonyl group either stoichiometrically or in excess; the use of *Method III* has been found particularly effective with α,β-unsaturated ketones.[13] When none of these methods succeeds then the more forcing conditions of *Method IV* may be applied. It is regarded as a 'last resort' module in which both *tert*-butoxide and the carbonyl are used in large excess. In cases where the carbonyl compound carries a base-sensitive substituent, notably a nitro[19] or cyano function, *tert*-butoxide is too strong a base and mild desilylation with fluoride ion is necessary; in these circumstances *Method V* is employed.

Use of these various procedures has provided the range of 3,6-unsubstituted **5**, **7**, and **9** and 3,6-dimethoxycyclopropanaphthalenes **6**, **8** and **10** listed in Tables 2–5. The compounds prepared reflect the commercial availability of the precursor benzaldehydes and benzophenones. The absence of a given functionality, *e.g.* **5c/6c** (NEt_2), **7e/8e** (SMe), and **9k/10k** (CN), does not reflect an inability to prepare the compound rather than the fact that the requisite carbonyl compound was not easily available to us. However, the absence of **6a** does reflect our inability to prepare the compound despite many attempts, while compound **6j** was not formed since, under the reaction conditions, *p*-trifluoromethylbenzaldehyde undergoes Tishchenko-like oxidation and reduction in the presence of anion **4** as we have reported.[20]

The dipole moments of **5**, **7** and **9**, and electron rich 3,6-dimethoxy-containing **6**, **8** and **10** now allow for comparisons that establish unequivocally that the cycloproparene moiety is an electron donor in agreement with molecular orbital calculations.[6,13,21–23] Moreover, the selection of *m*-substituted derivatives (Table 5) further substantiate the conclusions that pertain to inductive and mesomeric donation within the ranges of compounds. For comparison purposes, the range of *p*-aryl-substituted alkylidenecyclopropa[*b*]naphthalenes has been grouped according to the substitution pattern about the exocyclic centre C8. Thus, compounds **5** and **6** (Tables 2 and 5) are derived from substituted benzaldehydes that incorporate a

† Electronic supplementary information (ESI) available: methods applicable to the various experimental procedures, substrate and solvent purification, and instrumentation and spectroscopic analyses. See http://www.rsc.org/suppdata/ob/b4/b411714j/

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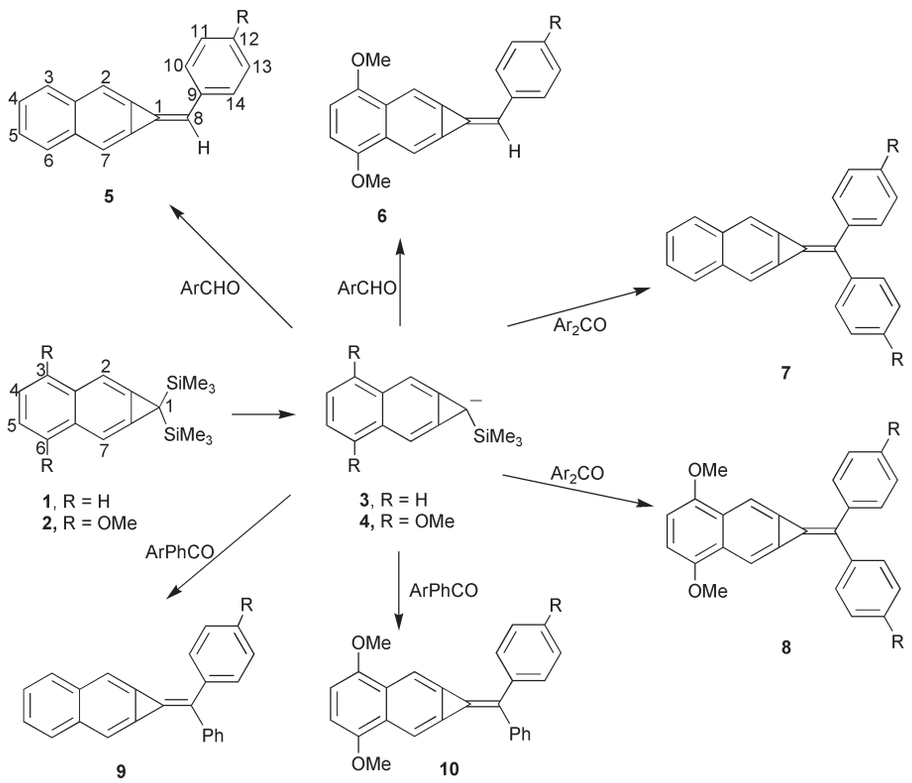
Table 1 Protocols for synthesis of an alkylidene-1*H*-cyclopropa[*b*]naphthalene

Method	Disilane	Second reactant	Induction[a]	Third reactant	When applied
I	**3** or **4**	Carbonyl (1 eq)	—	*t*-BuOK (1 eq)	Method of convenience
II	**3** or **4**	*t*-BuOK (1 eq)	30 min	Carbonyl (1 eq)	Acidic proton(s) present
III	**3** or **4**	*t*-BuOK (5 eq)	30 min	Carbonyl (5 eq)	To negate enolate chemistry
IV	**3** or **4**	Carbonyl (5 eq)	—	*t*-BuOK (5 eq)	To force reaction
V	**3** or **4**	KF/Bu_4NF	—	Carbonyl (5 eq)	In the presence of base-sensitive substituents

[a] The period for anion formation prior to addition of the carbonyl compound.



	a	b	c	d	e	f	g	h	i	j	k	l
R	H	NMe_2	NEt_2	OMe	SMe	Me	F	Cl	Br	CF_3	CN	NO_2

Scheme 1

vinylic proton at C8, olefins **7** and **8** stem from *p*,*p*′- or *m*,*m*′-disubstituted benzophenones (Tables 3 and 5), and **9** and **10** result from use of mono-substituted benzophenones (Tables 4 and 5). The numbering system provides easy comparison between the subclasses but it should be noted that **9a** and **10a** are synonymous with **7a** and **8a**, respectively, since R^2 = H.

The cycloproparenyl moiety is established[8] as an ambiphile capable of accepting or donating electron density aided by the doubly benzylic nature of C1. The present study manipulates both the magnitude and direction of the permanent dipole moment by altering the substitution pattern in the derivatives **5**–**10**. Thus *p*-dimethylaminophenyl and *p*-methoxyphenyl electron donation is compared with *p*-nitrophenyl and *p*-cyanophenyl electron withdrawal.

Given earlier difficulties[19] with the syntheses of the nitro compounds **5l** and **7l**, we presumed that the remaining members of the series would require use of *Method V*. However, *p*-nitrobenzophenone and anions **3** and **4** gave the *p*-nitro derivatives **9l** and **10l** in modest yields of 18 and 19%, respectively (Table 4) using *Method II* (Table 1). In contrast with expectation, *Method V* gave **9l** and **10l** in *lower yields* of 10 and 15%. The syntheses of **6l** and **8l** could only be effected using the milder *Method V* (3,6-dimethoxy-1*H*-cyclopropa[*b*]naphthalene was regenerated almost quantitatively by *Method II*[11,24]) but in only 12 and 25% yield, respectively (Tables 2 and 3).

Nitro-substituted carbonyl compounds are not the only substrates to which the Bu_4NF/KF methodology of *Method V* is applicable. Reactions of **3** and **4** with *p*-cyanobenzaldehyde give exocyclic olefins **5k**[25] and **6k** in 17 and 22%, respectively, employing *Methods I* or *II*, but both reactions were problematic and required several attempts before the desired products were obtained. On using *Method V*, the nitriles were obtained at the first attempt in improved yields of 45 and 67%, respectively (Table 2).

Carbonyl compounds incorporating acidic α protons frequently fail to react in the basic medium required for Peterson olefination due to competitive enolate ion formation (see above). However, use of *Method III* minimises enolate formation and by careful manipulation of the reaction conditions the yield of **11** is increased from 39%[1] to an excellent 85%. In similar vein, 5-phenylpenta-2,4-dienophenone and various

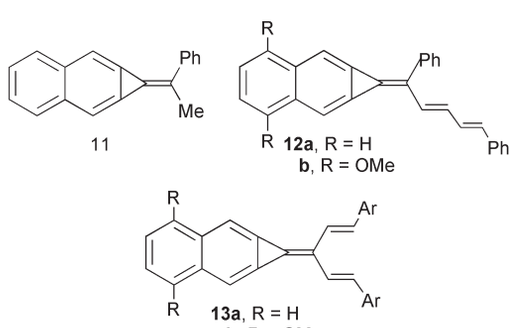
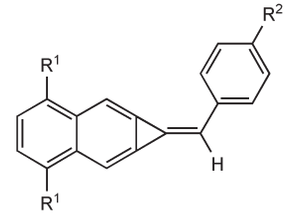


Table 2 1-(Arylmethylidene)-1*H*-cyclopropa[*b*]naphthalenes **5** and **6**



Cmpd.	R^1	R^2	Meth.[a]	%	mp/°C	μ/D	Dir.[b]	Ref.	Cmpd.	R^1	R^2	Meth.[a]	%	mp/°C	μ/D	Dir.[b]	Ref.
5a	H	H	I	59	114–117	1.29[c]	→	1	**6a**	OMe	H	I, II or III	0	—	—	—	[c]
5b	H	NMe_2	I	94	141–142	1.8	←	18	**6b**	OMe	NMe_2	I	63	164–165	1.37[c]	←	2
5d	H	OMe	I	52	115–118	1.4	←	7	**6d**	OMe	OMe	II	83	149–150	0.92	←	[c]
5e	H	SMe	I	61	137–138	1.30[c]	←	53	**6e**	OMe	SMe	I	25	156–157	0.83	←	[c]
5f	H	Me	II	63	144–145	1.14	←	[c]	**6f**	OMe	Me	I	35	147–148	0.64	←	[c]
5g	H	F	II	71	187–188	1.31	→	[c]	**6g**	OMe	F	II	62	122–123	1.55	→	[c]
5h	H	Cl	I	48	155–157	1.41[c]	→	7	**6h**	OMe	Cl	II	78	116–118	1.72	→	[c]
5i	H	Br	I	55	147–148	1.42	→	[c]	**6i**	OMe	Br	I	33	118–120	1.80	→	[c]
5j	H	CF_3	II	62	163–164	3.02	→	[c]	**6j**	OMe	CF_3	—	—	—	—	—	[d]
5k	H	CN	II	17	187–191	2.53[c]	→	25	**6k**	OMe	CN	II	22	136–138	2.86	→	[c]
			V	45								V	67				
5l	H	NO_2	V	8	193–194	Insol.	—	19	**6l**	OMe	NO_2	V	12	147–149	Insol.	—	[c]

[a] For methods, see text. [b] Dipole direction is to (←) or from (→) the cyclopropparene. [c] This work. [d] Only Tishchenko products from the aldehyde are obtained; see ref. 20.

Table 3 1-(Diarylmethylidene)-1*H*-cyclopropa[*b*]naphthalenes **7** and **8**

Cmpd.	R^1	R^2	Meth.[a]	%	mp/°C	μ/D	Dir.[b]	Ref.	Cmpd.	R^1	R^2	Meth.[a]	%	mp/°C	μ/D	Dir.[b]	Ref.
7a	H	H	I	95	110–111	0.41[c]	→	1, 7	**8a**	OMe	H	I	57	188–189	1.19[c]	→	2
7b	H	NMe_2	I	55	179–180	3.0	↓	8, 18	**8b**	OMe	NMe_2	I	21	183–185	2.32	↓	[c]
7c	H	NEt_2	II	21	188–190	2.89	↓	[c]	**8c**	OMe	NEt_2	II	10	159–160	2.34	↓	[c]
7d	H	OMe	I	64	134–136	2.4	↓	7	**8d**	OMe	OMe	I	25	156–157	1.65[c]	↓	2
7g	H	F	II	32	133–135	0.87	↑	[c]	**8g**	OMe	F	II	50	168–169	1.12	↑	[c]
7h	H	Cl	II	55	146–148	1.45	↑	[c]	**8h**	OMe	Cl	II	62	167–169	1.80	↑	[c]
7i	H	Br	I	94	193–194	1.53[c]	↑	12	**8i**	OMe	Br	II	72	153–155	1.81	↑	[c]
7l	H	NO_2	V	84	228–229	4.33[c]	↑	19	**8l**	OMe	NO_2	II	0	177–178	4.65	↑	[c]
												V	25				

[a]For methods, see text. [b]Dipole direction is to (←) or from (→) the cycloproparene. [c]This work.

1,5-diarylpenta-1,4-diene-3-ones react markedly more successfully under the conditions of *Method III* than *Methods I* or *II* to provide the recently reported[13] π extended adducts **12** and **13**.

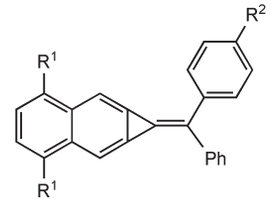
Polarity

The permanent dipole moment of a molecule, μ, can be determined absolutely by direct physical measurement but the direction has to be deduced from electronegativity differences or by *ab initio* calculation. In this work, experimental measurement of the permanent dipoles followed the classical procedure of Guggenheim[14] and Smith[15] that requires both dielectric constant and refractive index measurements. Our small, variable capacitance cell (Fig. 1) was hand-built from a small trimmed capacitor and quantised such that dielectric measurements could be made for a small volume (~2 mL) of the analyte in benzene solution. This system has allowed measurements on compounds obtained from low yielding, small scale reactions, where only $\sim 10^{-5}$ mol of product was obtained. The viability and reproducibility of the cell was confirmed by use of 2-hydroxynaphthalene **14** [μ lit.[26] 1.42 D (22 °C)], phenyl benzoate **15** [μ lit.[26] 1.79 D (20 °C)] or diphenylsulfone **16** [μ lit.[26] 4.98 D (20 °C)] as reference compounds *before and after* the measurement of each cycloproparene. Repeated determination of the standards routinely yielded data within *ca.* ±2% of the published values thereby lending credence to the reliability of the cell. We now report the permanent dipole moments of some forty aryl- and diaryl-alkylidenecyclopropa[*b*]naphthalenes.

Fig. 1 Capacitance cell containing 2 mL of analytical solution, connected to the HP913 probe.

The simplest fulvene, methylidenecyclopropene **17**, has a dipole moment of 1.9 D (determined by a novel microwave method as it is only stable below *ca.* 100 K) predicted to lie towards the exocyclic $=CH_2$ site.[27] The polarity is also evident from the shielding and deshielding of the resonances of the protonated exocyclic (δ 59.6) and endocyclic (δ 132.9) sp^2-carbons,[27–30] and involves a substantial contribution to the structure from the delocalised 2π 3C cationic form **17b**. The unknown cycloproparene homologue **18** is likewise predicted[6] to be an electron donor with its dipole of 1.8 D directed away from the ring system. Chemical shift differences are observed in the isolable cyclopropanaphthalene homologues **5**–**10** such that the exocyclic double bond carbons vary depending upon

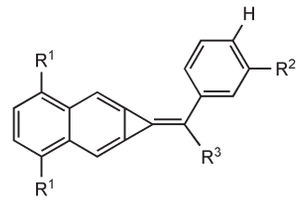
Table 4 1-[Aryl(phenyl)methylidene]-1*H*-cyclopropa[*b*]naphthalenes **9** and **10**



Cmpd.	R^1	R^2	Meth.[a]	%	mp/°C	μ/D	Dir.[b]	Ref.	Cmpd.	R^1	R^2	Meth.[a]	%	mp/°C	μ/D	Dir.[b]	Ref.
7a	H	H	I	95	110–111	0.41[c]	→	1, 7	**8a**	OMe	H	I	57	188–189	1.19[c]	→	2
9b	H	NMe_2	II	20	169–170	1.48	←	[c]	**10b**	OMe	NMe_2	II	56	173–174	1.11	←	[c]
9d	H	OMe	II	65	118–119	1.22	←	[c]	**10d**	OMe	OMe	II	74	131–132	0.80	←	[c]
9g	H	F	I	51	105–106	0.92[c]	→	42	**10g**	OMe	F	II	45	169–171	1.23	→	[c]
9h	H	Cl	II	44	161–163	1.15	→	[c]	**10h**	OMe	Cl	I	50	133–135	1.25	→	[c]
9i	H	Br	I	90	100–101	1.22[c]	→	12	**10i**	OMe	Br	I	74	181–183	1.32	→	[c]
9j	H	CF_3	II	66	146–147	2.89	→	[c]	**10j**	OMe	CF_3	II	81	137–138	3.19	→	[c]
9l	H	NO_2	II	18	176–178	3.10	→	[c]	**10l**	OMe	NO_2	II	19	142–144	3.52	→	[c]
			V	10								V	15				

[a] For methods, see text. [b] Dipole direction is to (←) or from (→) the cycloproparene. [c] This work.

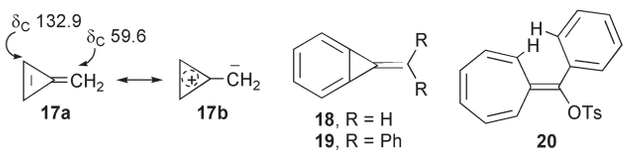
Table 5 *m*-Substituted 1-(arylmethylidene)-1*H*-cyclopropa[*b*]naphthalenes



Cmpd.	R^1	R^2	R^3	Meth.[a]	%	mp/°C	μ/D	Dir.[b]	Ref.	Cmpd.	R^1	R^2	R^3	Meth.[a]	%	mp/°C	μ/D	Dir.[b]	Ref.
5m	H	OMe	H	II	74	150–152	1.06	→	[c]	**6m**	OMe	OMe	H	II	35	122–124	1.48	→	[c]
7o	H	CF_3	*m*-CF_3-C_6H_4	I	82	109–111	3.34[c]	→	40	**8o**	OMe	CF_3	*m*-CF_3-C_6H_4	II	83	185–187	3.91	→	[c]
9n	H	Cl	Ph	II	55	162–164	1.56	→	[c]	**10n**	OMe	Cl	Ph	I	75	155–157	1.90	→	[c]
9o	H	CF_3	Ph	II	66	178–179	2.72	→	[c]	**10o**	OMe	CF_3	Ph	II	55	155–157	3.10	→	[c]

[a] For methods, see text. [b] Dipole direction is to (←) or from (→) the cycloproparene. [c] This work.

the *p*-phenyl substituent(s) present, *e.g.* **5j**, C1/C8: δ 114.0/104.9. Most notable is the fact that as the *para* substituent changes from strong donor (NMe_2) to strong acceptor (NO_2) the exocyclic C8 centre becomes progressively more shielded (see below).



The structure of every cycloproparene subjected to X-ray analysis shows the three-membered ring to be essentially coplanar with the aromatic moiety as the tilt angle between the planes containing the rings is a mere 1–3°.[3,23] In the fulvenes **5** and **6** the conjugating substituent at the exocyclic centre is held essentially planar as the exocyclic C8 proton occupies too small a volume of space to impact. Thus dimethylaminophenyl **5b** (and its 2′-thienylmethylidene analogue) has the attached 6π 6C (and 6π 4CS) ring twisted less than 5° out of the plane containing the cycloproparene;[18] the remainder of **5** and **6** are presumed similar. With diphenyl[1] **19** and bis(dimethylaminophenyl)[18] **7b** the twist angle (ϕ) of substituent rings is between 27° and 35°; all of **7**–**10** are assumed similar. Here one must note that in hepta- and penta-fulvene analogues[31–34] the pendant aromatic rings are twisted out of the plane of the seven- (or five)-membered ring by 37–45°. For example, the steric interference between the proximal hydrogens of enol tosylate **20** forces a twist of 44.8° in the solid state.[35] Importantly, the smaller twist angles in the diarylmethylidenecyclopropanes are more akin to those of various (*E*)-stilbenes[36,37] and nicely consistent with the added spatial freedom available to the exocyclic substituents compared with their heptafulvene analogues, after all fulvenes **5**–**10** can justifiably be viewed as stable derivatives of 2,7-didehydrocycloheptatriene. The smaller twist angles in an alkylidenecyclopropparene, coupled with the doubly benzylic nature of C1, favour mesomerism with no need for the polarisation that is clearly necessary in the heptafulvene congeners.[31,38]

The rotation of the C8 substituents in **7** and **8** results in a dipole moment that is not double that of equivalent planar adduct **5** or **6**. To a first approximation the reduced interaction is proportional to $\cos^2 \phi$,[39] and, with $\phi \sim 30°$, a contribution of ~80% from each aryl substituent is likely. For **5b** and **7b**, $\phi = 5°$ and 28°, respectively,[18] and $\mu_{\mathbf{7b}} \sim 1.6\mu_{\mathbf{5b}}$; experimentally determined values are 1.8 and 3.0 D (1 : 1.67) in remarkably good agreement. Comparisons of **9** with **5**, and **10** with **6** lead to the expectation of $\mu_{\mathbf{9}\,(\text{or }\mathbf{10})} \sim 0.8\mu_{\mathbf{5}\,(\text{or }\mathbf{6})}$ and again the measured dipoles generally give good agreement. However, when inductive effects become important the correlations no longer hold as is evident for the halogen-substituted compounds.

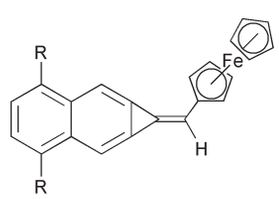
The dipole moments of **6**, **8**, and **10** that carry electron donating methoxyl groups at the 3- and 6-positions of the cyclopropanaphthalene allow for conclusions to be drawn with regard to the direction of polarisation from comparisons with the appropriate non-ethers **5**, **7**, and **9** (Tables 2–5). The dipole of diphenyl-substituted **7a** was reported[7] as 0.4 D and predicted (6-31G**) to be directed away from the cycloproparene nucleus in accord with parent **18**. This surprisingly low value is now confirmed as 0.41 D from duplicate measurements that contrast with benzo homologue **19** (μ 1.0 D).[7] The electron rich 3,6-diether **8a** is notably more polar (1.19 D) and this confirms the direction of polarisation towards the exocyclic site C8.

The available range of **5**–**10** provides a satisfying illustration of mesomeric influence on the polarity present. Thus in **5b** (μ 1.8 D[18]) the *p*-dimethylaminophenyl exerts a polarisation of ~3 D towards the cycloproparene that is lowered by the opposing 1.3 D of the cycloproparene moiety (**5a**) and the dimethoxy-substituted homologue **6b** (1.37 D) (Table 2) provides even more opposition. The lower influence of the twisted C8 substituents in **7**–**10** is illustrated by the dipole moments of **7a/7b** and **8a/8b**. These show the two *p*-Me_2N groups to offer an effective polarisation ~3.4 D towards the cycloproparene that is reduced by the polarity opposing the electron rich nucleus. A similar analysis of the mono-substituted diaryl **9a/b** and **10a/b** shows the impact of the single donor is almost halved compared to the bis(dimethylamino) analogues ($\mu_{\mathbf{7b}}/\mu_{\mathbf{9b}}$: 3.0/1.48; $\mu_{\mathbf{8b}}/\mu_{\mathbf{10b}}$: 2.32/1.11).

Consideration of the *p*-methoxy derivatives **5d**–**10d** leads to a similar set of conclusions though tetra- and tri-methoxy **10d** and **8d** justify comment. In the absence of vector considerations, mesomerism from the C3 and C6 methoxyl groups could well negate the effect of the two *p*-methoxyl substituents in **8d**. Clearly this is not the case, the ether/non-ether archetype established above for the "push–push" systems applies, and electron donation of the *p*-methoxyl groups in **8d** is reduced by the opposing polarisation of the C3- and C6-methoxyl groups to the same extent as **8b** compared to **7b**, *viz.* 0.7 D ($\mu_{\mathbf{7d}}/\mu_{\mathbf{8d}}$: 2.4/1.65); the dipole lies *towards* the cycloproparene moiety. In similar vein, mono-methoxy **10d** has its dipole reduced by 0.4 D compared to **9d**. These results indicate that the diametrically opposed 3- and 6-methoxy groups in **6**, **8**, and **10** enhance the electron donating nature of the cyclopropa[*b*]naphthalenyl moiety by about 0.5 D.

We have commented previously on the ambiphilicity of the cycloproparene nucleus[8,19] and this is further illustrated here. The electron donating aryl substituents of **5b**–**e** contrast with their electron withdrawing counterparts **5j**–**k**. Moreover, interplay between the R^1 and R^2 groups in "push–push" **6**, **8** and **10** (where the 3- and 6-methoxy groups enhance the cycloproparene electron source) is illustrated by a reduced dipole (~0.4–0.5 D) compared to the non-ether counterpart **5**, **7** and **9**, *e.g.* **6b/5b**: 1.37/1.8 D; **6f/5f**: 0.64/1.14 D (Table 3). This contrasts nicely with increased polarity (by ~0.35 D) in the donor–acceptor pairings in the "push–pull" analogues, *e.g.* **6k/5k**: 2.86/2.53 D, and serves to confirm the direction of the dipole. Thus, the electron donating or withdrawing ability of the exocyclic C8 substituent(s) clearly influences both the magnitude and the direction of μ as expected. Moreover, the presence of a strong mesomeric donor far outweighs any opposing inductive withdrawal and renders the latter insignificant.

The incorporation of a d-metal nucleus into a cycloproparene was achieved with **21**[18] and diether **22** is now available. The C8-ferrocenyl moiety donates electron density to the cycloproparene as evidenced by dipole moments of 3.37 and 2.92 D for **21** and **22**, again showing the 0.5 D reduction in the presence of the 3,6-OMe groups.



21, R = H; μ 3.37 D
22, R = OMe; μ 2.92 D

Nitro-containing **5l** and **7l** had been prepared using *Method V* but dipole moment measurements were never performed due to their reported insolubility in benzene.[19] We have now found that sonication of **7l** effects solution and a dipole moment of 4.33 D has been recorded. Even under these conditions **5l** remained insufficiently soluble and its dipole moment remains unknown. The corresponding nitro-containing diethers **6l** and **8l** are now available and have solubilities that mirror those of their respective non-ether homologues. The polarity of diether **8l** (μ 4.65 D) is greater than of **7l** by 0.32 D as expected for a "push–pull" derivative. Of the mono-nitro derivatives **9l** and **10l** (available by both *Methods II* and *V*), sonication was needed to dissolve **10l** and the permanent dipoles of 3.10 and 3.52 D (Table 4) show diether-induced enhancement of ~0.4 D, in good agreement

with that recorded for the cyano-containing derivatives **5k** and **6k** (μ 2.53 and 2.86 D).

For those compounds where inductive effects assume significance, the exocyclic interbond angle (θ) at C8 between the two substituents is important since $\mu_{ind} \propto \cos \theta$. The structures of **7b**[18] and **19**[1] give θ as 125° and 122°, and calculation[6,21] gives θ as 118° for **18**. A comprehensive study on the structural effects of exocyclic C6 substitution in pentafulvenes **23** shows little variation in θ with changes in the substituent(s),[34] and we assume that this is true also for **5**–**10**. Thus data comparisons with the inductively polarised alkylidenecycloproparenes, *e.g.* CF_3, are meaningful since the variations in θ account for <0.75% variation in μ_{ind}, a value within the experimental uncertainty of measurement.

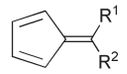
The CF_3-substituted alkylidenecycloproparenes **9j/10j**, **7o/8o**, and **9o/10o** (Tables 4 and 5) are significantly polar. While *p*-trifluoromethyl **5j** (μ 1.42 D) was easily prepared its diether analogue **6j** eluded synthesis as discussed above.[20] The (*p*-trifluorophenyl)phenyl pair **9j/10j** provide dipole moments of μ 2.89 and 3.19 D and, as with the mesomeric *para* electron-withdrawing functions there is a 0.3 D polarity enhancement in the diether. That CF_3 is a weaker electron-withdrawer than NO_2 is shown by its by the smaller dipole moments. The known[40] bis(*m*-trifluorophenyl) **7o** and its diether analogue **8o** have dipoles of 3.34 and 3.91 D, respectively. Here the diether enhancement (~0.6 D) is greater than in the mono-trifluoromethyl derivatives **9o/10o** (0.38 D; **9o**: 2.72 D; **10o**: 3.10 D), the *m*,*m*′-dichloro derivatives **9n/10n** (0.34 D; 1.56/1.90 D), or those compounds bearing *para* electron-withdrawing groups. The weakly inductively withdrawing *m*-methoxy compounds **5m** and **6m** are similar (Table 5).

Finally, the inductive withdrawal/mesomeric release in the halogen-substituted aryl derivatives justifies brief comment. It will be recalled that the small Hammett σ_p^+ values[41] for fluoro-, chloro- and bromo-substituents accord weak donor character to –F, and weak acceptor natures to –Cl and –Br. In each of the *p*-halogen-containing pairs the polarity of the 3,6-diether is the greatest indicating that polarisation is *towards* the halogen-containing exocyclic function, *e.g.***7h/8h**: μ 1.45/1.80 D; **9g**[42]/**10g**: μ 0.92/1.23 D. However, there appears to be no simple correlation that allows for easy separation of the inductive and mesomeric components in these derivatives, but the fluoride is always the least polar with the bromide and chloride comparable to each other (Tables 2–4).

^{13}C NMR correlations

The assignment of ^{13}C NMR resonances has been achieved by application of 2D NMR and, where appropriate, NOE experiments; full data for each compound are provided (Experimental section). In earlier studies, the assignment of the two faces of unsymmetrical derivatives such as **5** were assigned *E* or *Z* with respect to the pendant aryl group on the *assumption* that C2, C2a, C3 and C4 would be the more deshielded of the respective pairs C2/C7 *etc.*, by virtue of the proximal aryl ring (for numbering see Scheme 1).[17] This is now confirmed from NOE studies on **5** and **6** that provide H7···H8 and H2···H10 enhancements and subsequent use of HMBC to correlate to the remaining centres.

The presence of a mesomeric contribution to the molecular polarity from each of the *para* substituents is clear from the "push–push" and "push–pull" dipole moments. However, the influence of the *para* substituent is best illustrated by its systematic influence on the chemical shifts of the cyclopropparenyl carbon atoms of the molecules. The Hammett σ_p^+ substituent constant best represents resonance contributions[43] and correlations with ^{13}C chemical shifts in the fulvene series have been appropriately illustrated by Neuenschwander and his group,[44] for the five-membered ring carbons of aryl-substituted **23**. The use of σ_p^+ substituent correlations with ^{13}C NMR shifts continues to attract attention[45–47] and now extends to heteroatoms.[48,49]



23

In the case at hand, excellent linear correlations of σ_p^+ with the chemical shifts of the cyclopropanaphthalene ring carbons C1–C7a and the exocyclic centre C8 are shown for the compounds pairs **5/6** and **7/8** in Figs. 2 and 3; comparable correlations are found for **9** and **10**. Most notable is the fact that as electron donation from the remote substituent *decreases*, mesomeric donation to C1, C2/C7, and to a lesser extent at C3/C6 (or C4/C5) decreases with the result that the chemical shift increases. The impact at C8, C1a/C7a, and to a lesser extent at C2a/C6a, is the precise opposite and the line slopes reflect this. The fact that a measurable, though small, substituent influence is detected at every carbon centre of the cycloproparene skeleton supports the presence of mesomerism. The twist angle of the aryl substituent in **5** and **6** is negligible (0–5°) and small in **7**–**10** (28–35°; see above). That the influence of the remote substituent(s) remains about the same in the diaryl derivatives (the line slopes are similar) is more in agreement with mesomerism than with π polarisation that is necessary in the more highly twisted 6-aryl-6-methylfulvene **23** (R^1 = aryl; R^2 = Me).[50]

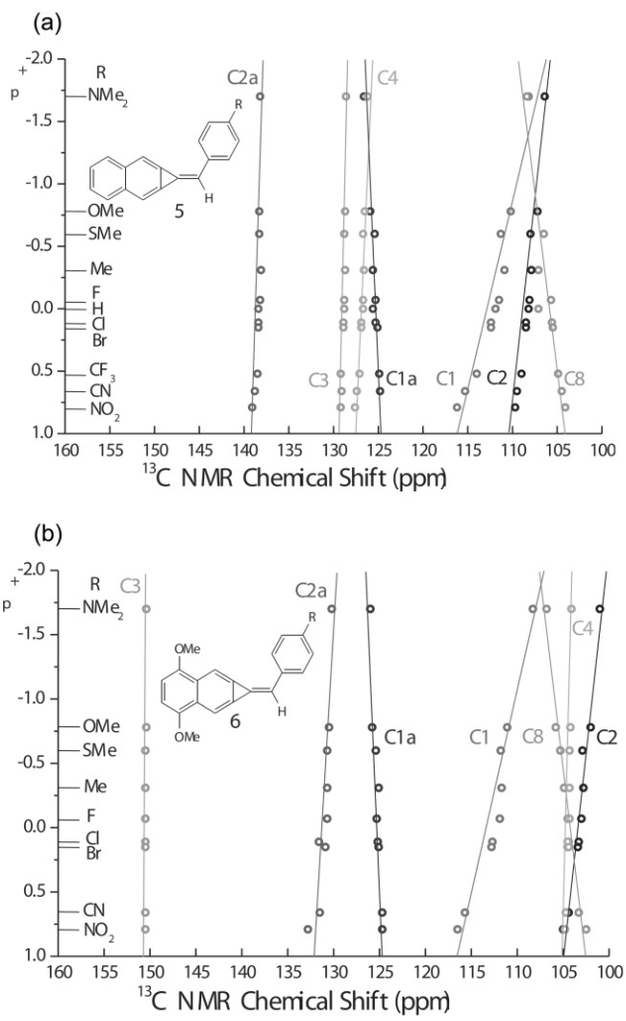


Fig. 2 Plots of Hammett substituents σ_p^+ against ^{13}C NMR chemical shifts for 1-(arylmethylidene)-1*H*-cyclopropa[*b*]naphthalenes (a) **5** and (b) **6**.

Finally, it should be noted that the π-extended pentadienylidene derivatives **13** (Ar = *p*-dimethylaminophenyl, *p*-methoxyphenyl, *p*-fluorophenyl, *p*-tolyl, and phenyl)[13] also provide excellent ^{13}C–σ_p^+ correlations.[51] This shows that the electronic effects continue to be felt well beyond a simple C1 aryl function.

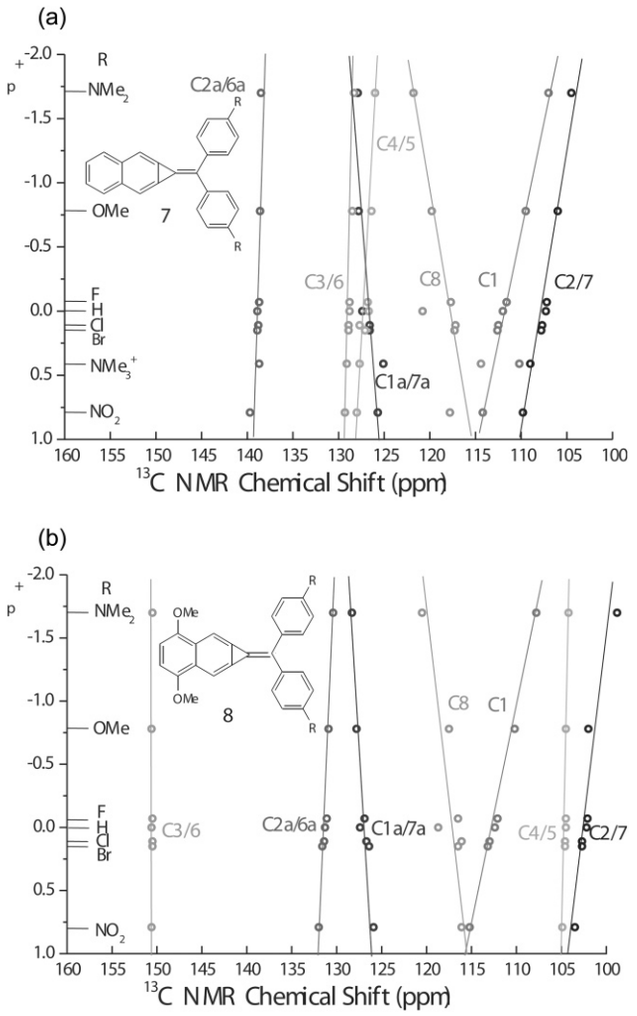


Fig. 3 Plots of Hammett substituents σ_p^+ against ^{13}C NMR chemical shifts for 1-(diarylmethylidene)-1*H*-cyclopropa[*b*]naphthalenes (a) **7** and (b) **8**.

Experimental

General

The methods applicable to the various experimental procedures, substrate and solvent[52] purification, and instrumentation and spectroscopic analyses are provided in the Electronic Supplementary Information.† Nonetheless, it should be note that the assignment of ^{13}C and ^{1}H NMR resonances for new compounds was made with the aid of distortionless enhancement by polarisation transfer (DEPT) and ^{1}H–^{1}H and ^{13}C–^{1}H correlation spectroscopy (COSY) experiments and confirmed by heteronuclear multiple bond connectivity (HMBC) and heteronuclear single quantum correlation (HSQC) experiments. Assignments of δ_H and δ_C for the respective sides C2 and C7 of the cycloproparenes **5**–**10** were made by analogy with the recorded NOE correlations for **5h**, **5i** and **6h**.

Dipole moment measurements

Dipole moments were determined for AnalaR grade benzene solutions (~0.05–0.10 M) by the method of Guggenheim[14] and Smith[15] using a small ~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 on an Abbe 60 Refractometer. 2-Hydroxynaphthalene **14** [μ lit.[26] 1.42 D (22 °C)], benzophenone **15** [μ lit.[26] 1.79 D (20 °C)], and diphenylsulfone **16** [μ lit.[26] 4.98 D (20 °C)] were used as reference standards, against which the reproducibility of the cell was verified. Repeated determinations with these standards routinely yielded data within *ca.* ±2% of the published values. This verifies the accuracy of the cell employed and allows the dipole moment data to be cited to two decimal places since alkylidenecycloproparenes typically have dipole moments ~1.5 D; an uncertainty of ±2% gives 1.5 ± 0.03 D. The dipole moments were calculated using a Microsoft® Excel spreadsheet and rounded to 2 decimal places only at the end of the algorithm.

General synthetic methods for alkylidene-1*H*-cyclopropa[*b*]naphthalenes

Method I. To a stirred solution of disilane **1**[18] (100 mg, 0.35 mmol) or **2**[2] (100 mg, 0.29 mmol) and the carbonyl compound (1 equiv.) in anhydrous THF (*ca.* 10 mL) at −70 °C, under nitrogen, was added dropwise *via* syringe needle a solution of freshly sublimed potassium *tert*-butoxide (1 equiv.) in the same solvent (*ca.* 10 mL). The mixture was stirred at −70 °C for 1 h, whereupon the cryostat was turned off and the mixture warmed to ambient temperature overnight. The mixture was quenched ($NaHCO_3$, sat; 30 mL) and the organics extracted with dichloromethane (3 × 20 mL). The organic layers were combined, washed with water (3 × 20 mL), dried ($MgSO_4$, *ca.* 2 g), filtered, and concentrated under reduced pressure. The crude product was purified by radial chromatography.

Method II. To a stirred solution of disilane **1**[18] (100 mg, 0.35 mmol) or **2**[2] (100 mg, 0.29 mmol) in anhydrous THF (*ca.* 10 mL) at −70 °C, under nitrogen, was added dropwise *via* syringe needle a solution of freshly sublimed potassium *tert*-butoxide (1 equiv.) in the same solvent (*ca.* 10 mL). The mixture was stirred at −70 °C for 30 min, whereupon cycloproparenyl anion formation was assumed from the deep red colour of the reaction mixture. To this was added a THF (*ca.* 10 mL) solution of the carbonyl compound (1 equiv.). The mixture was stirred for a further 1 h at −70 °C whereupon the cryostat was turned off and the mixture warmed to ambient temperature overnight. Work up and purification was as described in *Method I* above.

Method III. To a stirred solution of disilane **1**[18] (100 mg, 0.35 mmol) or **2**[2] (100 mg, 0.29 mmol) in anhydrous THF (*ca.* 10 mL) at −70 °C, under nitrogen, was added dropwise *via* syringe needle a solution of freshly sublimed potassium *tert*-butoxide (5 equiv.) in the same anhydrous solvent (*ca.* 10 mL). The mixture was stirred at −70 °C for 30 min, whereupon a deep red colour was noted. To this was added a THF (*ca.* 10 mL) solution of the carbonyl compound (5 equiv.). The mixture was stirred for a further 1 h at −70 °C whereupon the cryostat was turned off and the mixture warmed to ambient temperature overnight. Work up and purification was as described in *Method I* above.

Method IV. To a stirred solution of disilane **1**[18] (100 mg, 0.35 mmol) or **2**[2] (100 mg, 0.29 mmol) and the carbonyl compound (5 equiv.) in anhydrous THF (*ca.* 10 mL) at −70 °C, under nitrogen, was added dropwise *via* syringe needle a solution of freshly sublimed potassium *tert*-butoxide (5 equiv.) in the same solvent (*ca.* 10 mL). The mixture was stirred at −70 °C for 1 h, whereupon the cryostat was turned off and the mixture warmed to ambient temperature overnight. Work up and purification was as described in *Method I* above.

Method V. To a stirred suspension of disilane **1**[18] (100 mg, 0.35 mmol) or **2**[2] (100 mg, 0.29 mmol), the carbonyl compound (1.5 equiv.), potassium fluoride (10 equiv.) and anhydrous acetonitrile (*ca.* 20 mL), cooled to 0 °C, under argon, was added dropwise, over 4 h *via* syringe pump a solution of tetrabutylammonium fluoride (0.45 equiv.) in anhydrous THF (*ca.* 10 mL). The mixture was stirred at 0 °C for 1 h, and then warmed to ambient temperature overnight. Work up and purification was as described in *Method I* above.

1-(Arylmethylidene)-1*H*-cyclopropa[*b*]naphthalenes 5

The compounds were prepared from 1,1-bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene **1**[18] and the relevant aldehyde according to the specified method described above. *p*-Thiomethylphenyl **5e** and *p*-fluorophenyl **5g** serve as representative examples:

1-(*p*-Thiomethylphenylmethylidene)-1*H*-cyclopropa[*b*]-naphthalene 5e. ***Method I.*** The most mobile fraction from radial chromatography (light petroleum elution) of the dirty yellow solid gave the title compound **5e** as pale yellow needles (light petroleum) (63 mg, 59%), mp 137.5–139.0 °C (lit.[53] 61%, 137–138 °C). Spectroscopic data were in accord with those previously reported.[17,53] μ (23 °C) 1.30 D.

1-(*p*-Fluorophenylmethylidene)-1*H*-cyclopropa[*b*]naphthalene 5g. ***Method II.*** The most mobile fraction from radial chromatography (light petroleum–dichloromethane (4 : 1) elution) of the bright yellow solid gave the title compound **5g** as bright yellow needles (light petroleum) (61 mg, 71%), mp 186.5–187.5 °C (Found: C, 87.66; H, 4.39. $C_{18}H_{11}F$ requires C, 87.78; H, 4.50%). IR ν_{max}/cm^{-1} 2963, 2924, 2854, 2170, 1774 (w), 1629, 1597, 1499, 1384, 1262, 1097 (s), 1049, 849, 803. UV λ_{max} (cyclohexane)/nm 230 (4.28), 282 (4.09), 394 (4.28), 416 (log ε 4.21); λ_{max} (acetonitrile)/nm 228 (4.32), 280 (4.13), 388 (4.34), 412 (log ε 4.28). δ_H (300 MHz; $CDCl_3$) 6.54 (s, 1H, H8), 7.13 (t, *J* 8.4, 2H, H11/13), 7.49–7.51 (AA′ of AA′BB′, 2H, H4/5), 7.56 (d, J_{para} 1.7, 1H, H7), 7.70 (d, J_{para} 1.7, 1H, H2), 7.71–7.76 (m, 2H, H10/14), 7.90–7.95 (BB′ of AA′BB′, 2H, H3/6). δ_C (75 MHz; $CDCl_3$) 105.7 (C8), 108.1 (C7), 108.3 (C2), 111.5 (C1), 115.7 (d, $^2J_{CF}$ 22, C11/13), 125.3 (C7a), 126.7 (C5), 126.8 (C4), 127.2 (C1a), 127.7 (d, $^3J_{CF}$ 8, C10/14), 128.8 (C6), 128.9 (C3), 133.9 (d, $^4J_{CF}$ 3, C9), 138.2 (C6a), 138.9 (C2a), 161.7 (d, $^1J_{CF}$ 247, C12). *m*/*z* (70 eV) 244 (20, M + 1), 243 (100, M), 224 (M − F, 10), 198 (12), 166 (14), 165 (18), 137 (11%). μ (21 °C) 1.31 D.

1-(Arylmethylidene)-3,6-dimethoxy-1*H*-cyclopropa[*b*]-naphthalenes 6

The compounds were prepared from disilane **2**[2] and the relevant aldehyde according to the specified method described above. 1-(*p*-Dimethylaminophenylmethylidene)-3,6-dimethoxy **6b** and 1-(*p*-cyanophenylmethylidene)-3,6-dimethoxy **6k** serve as representative examples:

1-(*p*-Dimethylaminophenyl)methylidene)-3,6-dimethoxy-1*H*-cyclopropa[*b*]naphthalene 6b. ***Method I.*** The most mobile fraction from radial chromatography (light petroleum–dichloromethane (2 : 1) elution) of the dirty orange solid gave the title compound **6b** as orange microcrystals (light petroleum) (53 mg, 55%), mp 164.0–166.0 °C (lit.[2] 63%, 164–165 °C). μ (21 °C) 1.37 D.

1-(*p*-Cyanophenylmethylidene)-3,6-dimethoxy-1*H*-cyclopropa[*b*]naphthalene 6k. ***Method II.*** The most mobile fraction from radial chromatography (light petroleum–dichloromethane (2 : 1) elution) of the dirty yellow solid gave the title compound **6k** as dull yellow microcrystals (light petroleum) (20 mg, 22%), mp 136.0–138.0 °C (Found: C, 80.21; H, 4.76; N, 4.41%. $C_{21}H_{15}NO_2$ requires C, 80.49; H, 4.84; N, 4.47%). IR ν_{max}/cm^{-1} 2925, 2859, 2220, 1777, 1664, 1604, 1466, 1450, 1330, 1261, 1217, 1110, 1034, 1017, 747, 689. UV λ_{max} (cyclohexane)/nm 218 (3.83), 258 (3.81), 322 (4.01), 402 (4.09), 430 (log ε 4.12); λ_{max} (acetonitrile)/nm 216 (3.89), 258 (3.72), 322 (3.96), 402 (4.06), 428 (log ε 4.08). δ_H (300 MHz; $CDCl_3$) 3.99 (s, 3H, OMe), 4.00 (s, 3H, OMe), 6.51 (s, 1H, H8), 6.79 (s, 2H, H4/5), 7.73 (d, $^3J_{AB}$ 8.3, 2H, H11/13), 7.81 (d, $^3J_{AB}$ 8.3, 2H, H10/14), 8.11 (d, J_{para} 1.9, 1H, H7), 8.25 (d, J_{para} 1.9, 1H, H2). δ_C (75 MHz; $CDCl_3$) 55.9 (OMe), 103.3 (C8), 104.4 (C7), 104.6 (C2), 104.7 (C4/5), 108.7 (C12), 115.7 (C1), 119.6 (CN), 124.7 (C7a), 126.2 (C10/14), 126.9 (C1a), 131.5 (C6a), 132.2 (C2a), 132.5 (C11/13), 142.9 (C9), 150.5 (C6), 150.6 (C3). *m*/*z* (70 eV) 314 (23, M + 1), 313 (100, M), 299 (19), 298 (83, M − Me), 284 (14), 283 (65, M − 2Me), 255 (25), 227 (24), 201 (19), 149 (13), 44 (15), 28 (34%). μ (22 °C) 2.86 D.

Method V. Disilane **2** and *p*-cyanobenzaldehyde gave **6k** as dull yellow microcrystals (light petroleum) (60 mg, 67%), identical to the sample above.

1-(Diarylmethylidene)-1*H*-cyclopropa[*b*]naphthalenes 7

The compounds were prepared from disilane **1**[18] and the relevant ketone according to the specified method described above. 1-[Bis(*p*-diethylaminophenyl)methylidene] **7c** serves as a representative example:

1-[Bis(*p*-diethylaminophenyl)methylidene]-1*H*-cyclopropa[*b*]-naphthalene 7c. ***Method II.*** The most mobile fraction from radial chromatography (light petroleum–dichloromethane (4 : 1) elution) of the yellow–brown solid gave the title compound **7c** as dark orange microcrystals (light petroleum) (10 mg, 21%), mp 187.5–188.5 °C (Found: C, 86.00; H, 7.50; N, 6.50. $[M + H]^+$ 447.2793; $C_{32}H_{34}N_2$ requires C, 86.05; H, 7.67; N, 6.28%; 447.2800). IR ν_{max}/cm^{-1} 3053, 2986, 2685, 2410, 2305, 1774 (w), 1421, 1265 (s), 1154, 895. UV λ_{max} (cyclohexane)/nm 274 (3.63), 288 (3.51), 388 (3.39), 452 (3.62), 486 (log ε 3.88); λ_{max} (acetonitrile)/nm 274 (3.83), 306 (3.43), 396 (3.26), 446 (3.58), 490 (log ε 3.59). δ_H (300 MHz; $CDCl_3$) 1.22 (t, *J* 7.1, 12H, 4 × Me), 3.42 (q, *J* 7.1, 8H, 4 × CH_2), 6.85 (d, $^3J_{AB}$ 9.0, 4H, H11/13), 7.37 (s, 2H, H2/7), 7.45–7.48 (AA′ of AA′BB′, 2H, H4/5), 7.80 (d, $^3J_{AB}$ 9.0, 4H, H10/14), 7.84–7.87 (BB′ of AA′BB′, 2H, H3/6). δ_C (75 MHz; $CDCl_3$) 12.8 (Me), 44.4 (CH_2), 103.9 (C2/7), 109.9 (C1), 111.1 (C11/13), 122.0 (C8), 125.4 (C4/5), 128.0 (C1a/7a), 128.1 (C9), 128.3 (C3/6), 129.6 (C10/14), 138.3 (C2a/6a), 147.0 (C12). μ (22 °C) 2.89 D.

1-(Diarylmethylidene)-3,6-dimethoxy-1*H*-cyclopropa[*b*]-naphtha-lenes 8

The compounds were prepared from disilane **2**[2] and the relevant ketone according to the specified method described above. 1-[Bis(*p*-dimethylaminophenyl)methylidene]-3,6-dimethoxy **8b** serves as a representative example:

1-[Bis(*p*-dimethylaminophenyl)methylidene]-3,6-dimethoxy-1*H*-cyclopropa[*b*]naphthalene 8b. ***Method I.*** The most mobile fraction from radial chromatography (light petroleum–dichloromethane (2 : 1) elution) of the orange solid gave the title compound **8b** as orange needles (light petroleum) (27 mg, 21%), mp 183.0–185.0 °C (Found: C, 79.71; H, 6.55; N, 6.30. $[M + H]^+$ 451.2380; $C_{30}H_{30}N_2O_2$ requires C, 79.97; H, 6.71; N, 6.22%; 451.2385). IR ν_{max}/cm^{-1} 3488, 3451, 3322, 3255, 2927, 2924, 1774(w), 1651, 1633, 1499, 1400, 1322, 1103, 989, 799. UV λ_{max} (cyclohexane)/nm 306 (3.64), 336 (3.55), 410 (3.55), 432 (log ε 3.76); λ_{max} (acetonitrile)/nm 306 (3.41), 336 (3.50), 412 (3.66), 430 (log ε 3.70). δ_H (300 MHz; $CDCl_3$) 3.01 (s, 12H, 2 × NMe_2), 3.95 (s, 6H, C3/6–OMe), 6.70 (s, 2H, H4/5), 6.90 (d, $^3J_{AB}$ 8.3, 4H, H11/13), 7.62 (d, $^3J_{AB}$ 8.3, 4H, H10/14), 7.69 (s, 2H, H2/7). δ_C (75 MHz; $CDCl_3$) 40.4 (NMe_2), 55.9 (OMe), 98.8 (C2/7), 104.2 (C4/5), 107.8 (C1), 112.8 (C11/13), 120.5 (C8), 128.1 (C9), 128.3 (C1a/7a), 130.4 (C2a/6a), 139.2 (C10/14), 149.9 (C12), 150.5 (C3/6). μ (21 °C) 2.32 D.

1-[Aryl(phenyl)methylidene]-1*H*-cyclopropa[*b*]naphthalenes 9

The compounds were prepared from disilane **1**[18] and the relevant ketone according to the specified method described above. 1-[(*p*-Nitrophenyl)phenylmethylidene] **9l** serves as a representative example:

1-[(*p*-Nitrophenyl)phenylmethylidene]-1*H*-cyclopropa[*b*]-naphthalene 9l. ***Method II.*** The most mobile fraction from

radial chromatography (light petroleum–dichloromethane (1 : 1) elution) of the orange solid gave the title compound **9l** as dark orange needles (light petroleum) (22 mg, 18%), mp 176.0–177.5 °C (Found: C, 82.20; H, 4.13; N, 4.09. $C_{24}H_{15}NO_2$ requires C, 82.50; H, 4.32; N, 4.01%). IR ν_{max}/cm^{-1} 2927, 2857, 1773 (w), 1731 (w), 1635, 1586, 1449, 1341, 1115, 1032, 963, 857, 698. UV λ_{max} (cyclohexane)/nm 208 (4.21), 228 (4.19), 432 (log ε 3.07); λ_{max} (acetonitrile)/nm 210 (4.16), 238 (4.22), 436 (log ε 3.23). δ_H (300 MHz; $CDCl_3$) 7.41 (tt, $^3J_{AB}$ 7.3, $^4J_{AC}$ 1.6, 1H, H18), 7.48–7.56 (m, 4H, H4/5 and H17/19), 7.69–7.73 (m, 4H, H2/7 and H16/20), 7.91–7.98 (m, 4H, H3/6 and H10/14), 8.31 (d, $^3J_{AB}$ 8.3, 2H, H11/13). δ_C (75 MHz; $CDCl_3$) 108.5 (C2 or C7), 108.8 (C7 or C2), 115.0 (C1), 117.2 (C8), 123.9 (C11/13), 126.4 (C1a or C7a), 126.6 (C7a or C1a), 127.5 (C18), 128.0 (C17/19), 128.1 (C4/5), 128.2 (C16/20), 128.8 (C3/6), 129.0 (C10/14), 138.3 (C15), 139.2 (C2a or C6a), 139.3 (C6a or C2a), 146.3 (C9), 146.5 (C12). *m*/*z* (70 eV) 350 (29, M + 1), 349 (100, M), 303 (45, M–NO_2), 302 (88), 301 (25), 300 (49), 151 (12), 150 (14%). μ (22 °C) 3.10 D.

Method V. Disilane **1** and *p*-nitrobenzophenone gave an orange solid. Radial chromatography (light petroleum–dichloromethane (1 : 1) elution) gave from the most mobile fraction title compound **9l** as dark orange needles (light petroleum) (12 mg, 10%), identical to that obtained above.

1-[Aryl(phenyl)methylidene]-3,6-dimethoxy-1*H*-cyclopropa[*b*]-naphthalenes 10

The compounds were prepared from disilane **2**[2] and the relevant ketone according to the specified method described above. 1-[(*p*-Trifluoromethylphenyl)phenylmethylidene]-3,6-dimethoxy **10j** serves as a representative example:

1-[(*p*-Trifluoromethylphenyl)phenylmethylidene]-3,6-dimethoxy-1*H*-cyclopropa[*b*]naphthalene 10j. ***Method II.*** The most mobile fraction from radial chromatography (light petroleum–dichloromethane (2 : 1) elution) of the yellow solid gave the title compound **10j** as yellow needles (light petroleum) (101 mg, 81%), mp 137.0–138.0 °C (Found: C, 74.83; H, 4.29; F, 13.33. $[M + H]^+$ 433.1412; $C_{27}H_{19}F_3O_2$ requires C, 74.99; H, 4.43; F, 13.18%; 433.1415). IR ν_{max}/cm^{-1} 2930, 2837, 2169, 1782, 1774(w), 1611, 1465, 1438, 1407, 1384, 1341, 1322, 1266, 1225, 1171, 1109, 1066, 1013, 861, 795, 764, 703. UV λ_{max} (cyclohexane)/nm 258 (4.05), 308 (4.02), 320 (4.06), 410 (4.15), 434 (log ε 4.09); λ_{max} (acetonitrile)/nm 252 (3.70), 322 (3.99), 410 (4.12), 432 (log ε 4.09). δ_H (300 MHz; $CDCl_3$) 3.98 (s, 3H, C3– or C6–OMe), 3.99 (s, 3H, C6– or C3–OMe), 6.76 (s, 2H, H4/5), 7.38 (tt, $^3J_{AB}$ 7.4, $^4J_{AC}$ 1.6, 1H, H18), 7.45–7.50 (m, 2H, H17/19), 7.69–7.73 (m, 2H, H11/13), 7.76–7.80 (m, 2H, H16/20), 7.88 (d, $^3J_{AB}$ 8.3, 2H, H10/14), 8.05 (d, J_{para} 1.7, 1H, H2 or H7), 8.07 (d, J_{para} 1.7, 1H, H7 or H2). δ_C (75 MHz; $CDCl_3$) 55.9 (OMe), 102.8 (C2 or C7), 103.0 (C7 or C2), 104.6 (C4/5), 113.9 (C1), 116.8 (C8), 124.4 (q, $^1J_{CF}$ 272, CF_3), 125.3 (q, $^3J_{CF}$ 3, C11/13), 126.7 (C1a or C7a), 126.7(5) (C7a or C1a), 127.4 (C18), 127.9 (C10/14), 128.1 (C16/20), 128.6 (C17/19), 128.6 (q, $^2J_{CF}$ 33, C12), 131.4 (C2a or C6a), 131.5 (C6a or C2a), 138.9 (C15), 143.2 (C9), 150.5 (C3/6). μ (21 °C) 3.19 D.

1-(1-Phenylethylidene)-1*H*-cyclopropa[b]naphthalene 11.

Method III. Disilane 1 and acetophenone gave a yellow solid. Radial chromatography (light petroleum elution) gave from the most mobile fraction title compound 11 as yellow needles (light petroleum) (72 mg, 85%), mp 94–95 °C (lit.[1] 39%, 94–95 °C).

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