Studies in the cycloproparene series: cycloaddition reactions of diarylmethylidenecycloproparenes[†1]

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It is a pleasure to dedicate this paper to Professor Don Cameron in recognition of his outstanding contribution to Australasian chemistry

Abstract

Diarylmethylidenecyclopropanaphthalenes **4b-d** add diphenylisobenzofuran (DPIBF) and α-pyrone across the exocyclic double bond to give ring expanded products **11b-d** and **13b-d** that result from subsequent relief of ring strain in the non-isolable spirocyclic intermediates **10** and **12**, respectively. The benzene homologues **3b** and **3c** add DPIBF across the bridge bond to give the norcaradiene adducts **19b** and **19c**.

These observations match expectation based upon the loss of aromaticity in the arene moiety caused by addition to the bridge bond. The cycloadditions have been studied also by ab initio quantum mechanical calculations at the MP2/6-31G(d)//HF/6-31G(d) and MP3 levels of theory. With acetylenic(phenyl)-iodonium triflates **14** formal [2+2] cycloaddition to the exocyclic π bond of **4b-d** leads to the 2,3-disubstituted naphthalenes **18b-d**. The structures of the iodonium salt **18d** and the bridge adduct **19b** are confirmed from structure determination by X-ray crystallographic methods.

Keywords: Ab initio calculations, strained aromatics, acetylenic-iodonium salts, crystal structures, cyclobutanes, Diels-Alder cycloaddition, norcaradienes

Introduction

The class of strained aromatic hydrocarbons known as the cyclopropanarenes,[2] and illustrated by the parent molecule 1*H*-cyclopropabenzene (**1**) and 1*H*-cyclopropa[*b*]naphthalene (**2**), has provided a wealth of fascinating chemistry since the first authenticated derivative was reported in 1964.

1   2   3   4
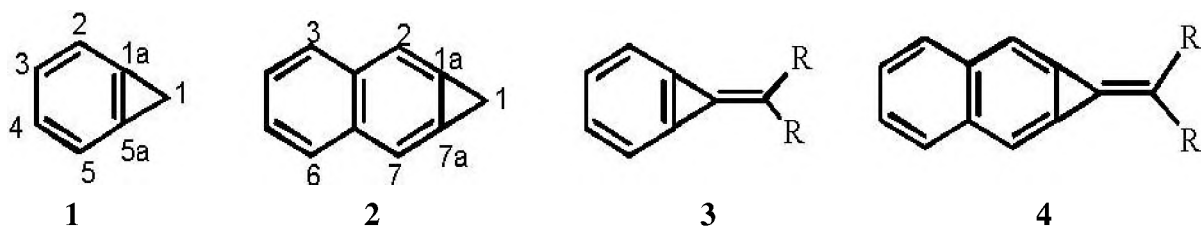
In particular, the pKa of **1** is estimated[3] as *ca.* 36 and the C-1 cyclopropabenzenyl anion and its naphthalenyl analogue can be generated and used in synthesis.[1,4-7] Indeed, it is through use of these C-1 anions, e.g. **5**, that the transformation a cycloproparene C-1 from sp[3] to sp[2] with an attendant exocyclic double bond has been achieved, thereby generating the intriguing class of unusual compounds known as the alkylidenecycloproparenes, e.g. **3** and **4**.[2,4-7] Thus anion **5** is easily converted via **6** into a-silyl anion **7** that undergoes Peterson olefination with a range of non-enolisable aldehydes or ketones to give **4** (Scheme 1).

The alkylidenecycloproparenes **3** and **4** have attracted considerable attention themselves in recent times as unusual, highly strained synthetic molecules whose physical characteristics have been assessed and whose chemical behaviour has been investigated with a variety of reagents.[2-4] Nonetheless, the behaviour of the compounds in cycloadditions has not been addressed previously.[8] We report here an experimental and theoretical study of the [2+4] cycloadditions of the selected methylidenecycloproparenes **3b,c** and **4b-d** with the dienes diphenylisobenzofuran (DPIBF) and α-pyrone, as well as the behaviour of the naphthalene derivatives with the markedly electron deficient acetylenic(phenyl)iodonium triflate **14**.
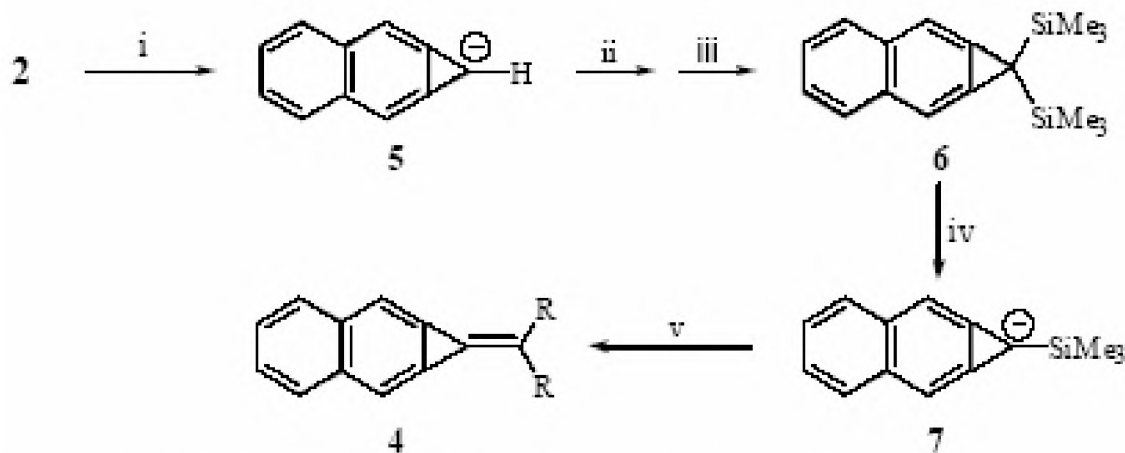

Reagents: i) BuLi; ii) TMSCl; iii) BuLi, TMSCl; iv) KOBu^t; *v)* R$_2$CO

Scheme 1

X-ray crystallographic data that confirm the structures of products **18d** and **19b** are also reported. The theoretical calculations have employed ab initio quantum mechanical calculations methods at the MP2/6-31G(d)// HF/6-31G(d) level for studying the reactions of the unknown[4] parents **3a** and **4a** with furan and the semiempirical method was used for calculating the reactions of the diphenyl compounds **3b** and **4b** with DPIBF as actually examined experimentally.

Results and Discussion

The cycloproparene hydrocarbons **1** and **2** have available two potential sites for cycloaddition, namely the C1a-C5a (or 7a) bridge bond and the three-membered ring σ bond. With the HOMO of **1** located at the bridge and C3—C4 bonds, it is not surprising that the molecule behaves as an electron rich dienophile and adds dienes across the bridge resulting in a range of derivatives that transform into other interesting compounds.[2] However, cycloaddition across the strained three-membered ring σ bond can also occur especially with four-electron electrophilic dipolar reagents.[9] With DPIBF, **1** displays both reaction modes dependent on the specific conditions employed. Addition to the bridge results in both *endo* and *exo* adducts **8** while ring opening gives **9** (Scheme 2).[10]

8, R = H   9, R = H or RR = benzo fusion
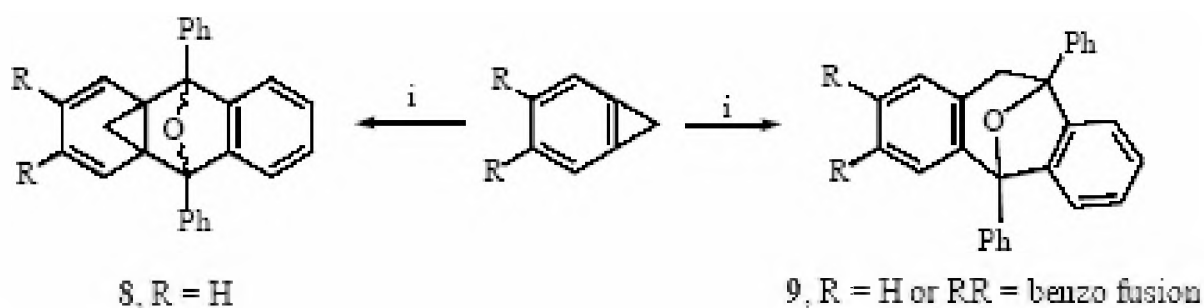
Reagent: i) diphenylisobenzofuran -DPIBF

Scheme 2

In comparison, cyclopropanaphthalene **2** predominantly opens the three-membered ring by addition across the σ bond thereby avoiding the high energy orthoquinodimethane intermediate demanded from loss of aromaticity in both six-membered rings.[9,10]

In comparison to the above, the methylidene derivatives **3** and **4** offer the exocyclic double bond as an additional site for reaction. It is, therefore, more than idle curiosity that demands an answer to the question of regioselectivity in the cycloadditions of these compounds. The outcome must result in novel products that likely transform into other interesting materials irrespective of the site of addition and we now report on these.

Experimental Study

The readily available and representative diarylmethylidenecyclopropanaphthalenes **4b**,[6] **4c**,[11] and **4d**,[12] and the more difficultly obtained benzenoid homologues **3b**[6] and **3c**[11] were selected for examination and prepared according the published procedures.

When heated with DPIBF in dry degassed toluene for several days **4b** provides a pale yellow solid 1:1 addition product the ^{13}C NMR of which does not show the characteristically shielded C2/7 resonances (105-115 ppm) of the cycloproparene precursor.[2] This clearly implies the absence of **4b** and any product in which the cycloproparenyl moiety is retained. Moreover, the proliferation of aromatic carbon resonances (Experimental) demands a lack of symmetry. The product is identified as the cyclobutanaphthalene **11b** (55%). The ^{13}C NMR clearly displays three of the four cyclobutarenyl carbons (δ 76.1, sp^3; 150.3 and 163.1, aromatic sp^2)] and the side-chain carbonyl carbon is at δ 198.2; IR absorptions for the side-chain conjugated carbonyl and the exocyclic olefinic bond are recorded at 1665 and 1738 cm^{-1}, respectively.[13] In like manner, reaction of the dimethoxy **4c** and bis(trifluoromethyl) **4d** lead to the corresponding cyclobutarenes **11c** (32%) and **11d** (42%).

Liotta *et al.* have reported that Diels-Alder cycloadditions show an enhanced rate when conducted in ethylene glycol particularly with hydrophobic diene/dienophile pairs and, additionally, the influence of salt effects on Diels-Alder cycloadditions has been reviewed.[14] In the cases of additions of **4b-d** to DPIBF, ethylene glycol facilitates the reactions as they are essentially complete in 7 h with product yields increased to 42-62%.


a: R = H
b: R = Ph
c: R = *p*-MeOC$_6$H$_4$-
d: R = *m*-CF$_3$C$_6$H$_4$-

Reagent: i) DPIBF
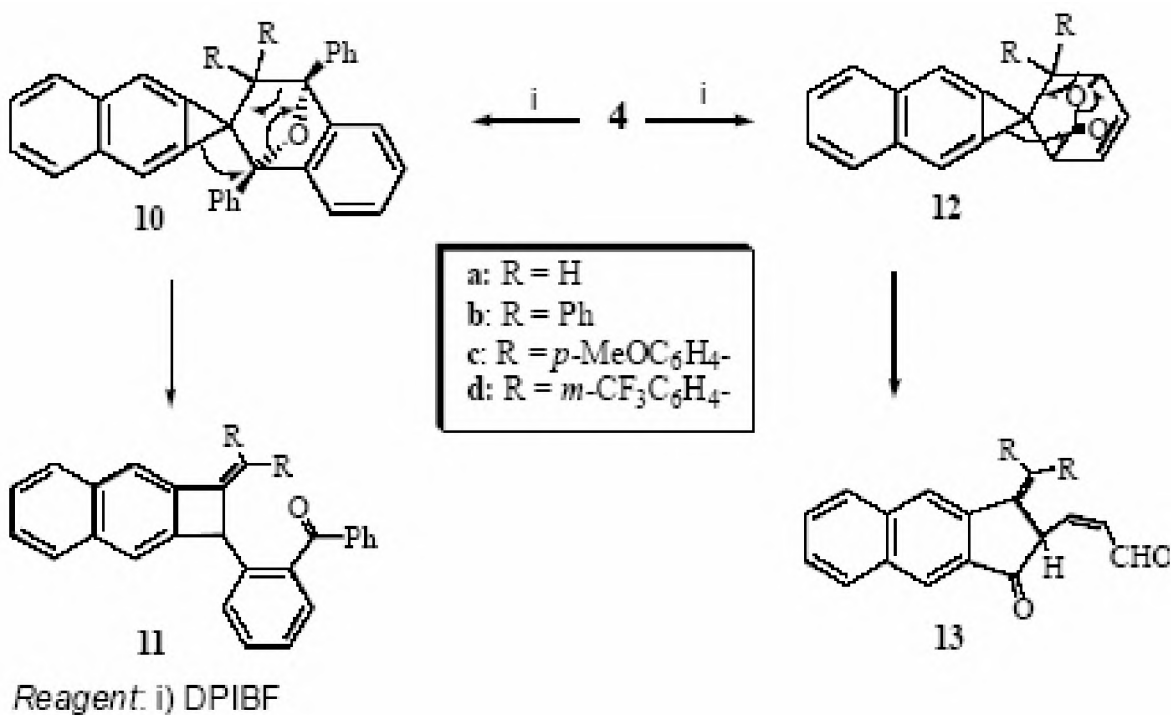
Scheme 3

The formation of the cyclobutarenyl products **11** shows that cycloproparenes **4** resist addition to both the bridge and strained σ bonds and that any addition across the exocyclic double bond must result in subsequent rearrangement of the product. The formation of **11** is best rationalized from initial [2+4] addition across the exocyclic π bond to give the novel spirocycles **10**. These highly strained compounds are able to release strain by way of cycloproparenyl—cyclobutarenyl ring expansion[2,7] with concomitant cleavage of the ether bridge and diaryl ketone formation, as depicted in Scheme 3. Analogous ether bridge cleavage has recently been reported by Kitamura *et al.* for DPIBF adducts of norbornynes.[15] While the Diels-Alder cycloaddition with **4** proceeds to a strained (and transient) cycloadduct, it does so without involving the bridge bond and the (presumably) higher energy orthoquinodimethane, cf. **8** (Scheme 2 and below).

The reactions of **4b-d** with α-pyrone also provide product that is best rationalized from additon to the exocyclic double bond of the substrate. Again the use of ethylene glycol in place of toluene as solvent is notably beneficial, viz. the reaction period for **4b** reduces from days to 7 h and the yield increases from 12 to 50%. The products are identified as the substituted benzindanones **13b-d** (Experimental) that arise from comparable rearrangement of the initially formed spirocycles **12**. In these cases rapid migration of the three-membered ring σ bond to the carbonyl carbon triggers formation of the (*Z*)-enal functionality with ring expansion from three to five-members (Scheme 3). Opening of the lactone moiety in this way is presumed to be facile as diene products resulting from the more traditional decarboxylation[16] were not observed.
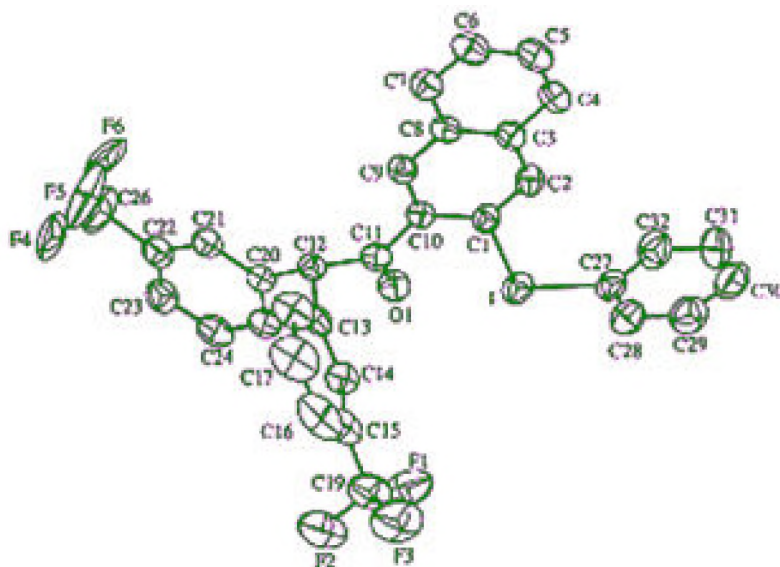
Figure 1. ORTEP diagram of the cation of **18d** with crystallographic numbering.
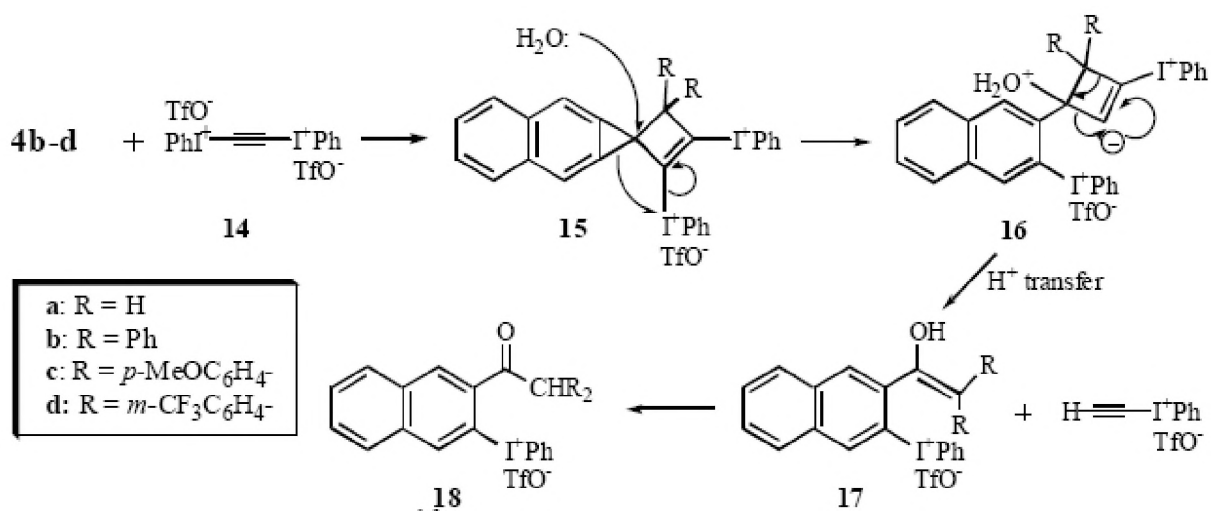
Scheme 4

It was of also interest to see if the methylidene derivatives **4** would behave as electron-rich donors in [2+2] reactions. In this context the strong electron withdrawing capacity of the iodonium moiety seemed ideal[17] particularly in light of the availability of the acetylenic (phenyl)iodonium triflate **14**.[18] Reactions of **4b-d** with bis-iodonium salt **14** proceed at ambient temperature over 7 h to give the naphthyl iodonium triflates **18b-d** in yields of 40-60%. The ^{1}H NMR spectra of **18b-d** each display a single methine proton as the only aliphatic signal (δ 2.35-2.45) while the IR spectra show conjugated ethanone stretching frequency at ca. 1650 cm^{-1}. The structure of the bis(trifluoromethyl) derivative **18d** has been confirmed by single crystal X-ray analysis (see Fig. 1 and below). The route by which **4** is transformed into **18** is less obvious than for the diene additions. Nonetheless, interaction with the exocyclic double to give the spirohexenes **15** is plausible (Scheme 4). Subsequent reaction of these with water during work-up triggers three-membered ring expansion with ejection of iodonium acetylide as shown from **16**. This leads to enol **17** and mono-iodonium triflate after proton transfer. Enol—keto tautomerism in **17** accounts for **18**. The proposal is supported by isolation of the methoxy analogue of enol ether **17b** when the reaction was performed in the presence of methanol.
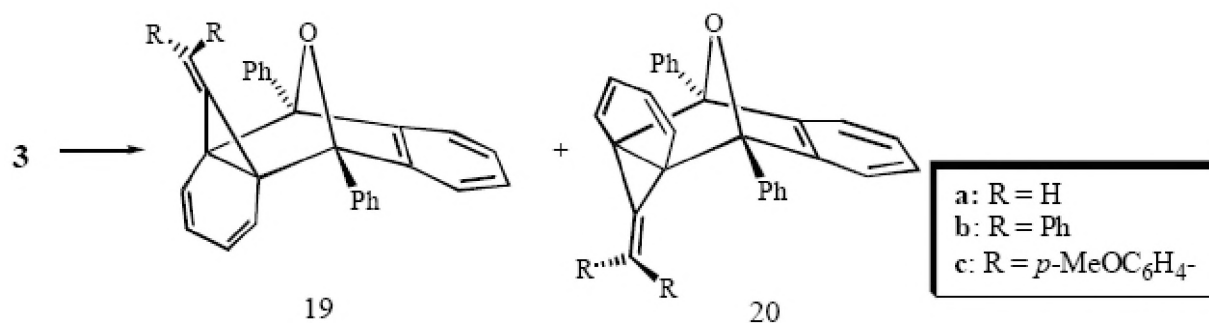

Scheme 5

In contrast to the foregoing, we find that the methylidenecyclopropabenzenes **3** are more reluctant to undergo cycloaddition. While ethylene glycol again facilitates the reactions in comparison to toluene, the cycloadditions of **3b** and **3c** to DPIBF still require 24 h at 120°C rather that the 7 h at 110°C for **4b-d**. These reactions return some unchanged DPIBF but both **3b** and **3c** give a single crystalline 1:1 cycloadduct in a yield of 48 and 27%, respectively. That these compounds are propelladienes **19** or **20** (Scheme 5) is immediately obvious from the ^{1}H NMR spectra as they each exhibit an AA'BB' pattern in the olefinic region (δ 5.65 and 6.11), and they do not show a carbonyl stretching frequency in the IR. However, the orientation of these Diels-Alder adducts as *endo* **19** or *exo* **20** with respect to the fused benzenoid ring of **3** (cf. Scheme 2) is not obvious and there are no in-built structural features that allow for easy differentiation. As noted above, **1** adds DPIBF across the bridge bond to give both *endo* and *exo* [2+4] products as well as the unsymmetrical adduct from addition to the strained σ bond (Scheme 2);[10] it provides no precedent. Determination of the structure of product from **3b** depended upon X-ray crystallographic methods and these show the compound to be *endo* **19b** with the oxygen atom and the three-membered ring *syn* (see Fig. 2 and below); that from **3c** is assigned as **19c** by analogy.

Unlike DPIBF, α-pyrone fails to add to **3**. In either toluene or THF (used as solvent in the reaction with **1**) starting materials are returned unchanged. In comparison, ethylene glycol intercepts substrates **3b** and **3c** to give products whose structures have yet to be resolved.[19]

One must ask why the regioselectivity exhibited by **3** and **4** is so different. Unfortunately FMO analysis[20] cannot rationalize the experimental findings as the HOMO and LUMO of both **3** and **4** are concentrated at the exocyclic bond. To gain some insight into the different regioselectivity, the interaction of furan and DPIBF with the unknown parent methylidene compounds **3a** and **4a** as well the diphenyl derivatives **3b** and **4b** actually employed in the study have been examined using ab initio and semiempirical PM3 methods.
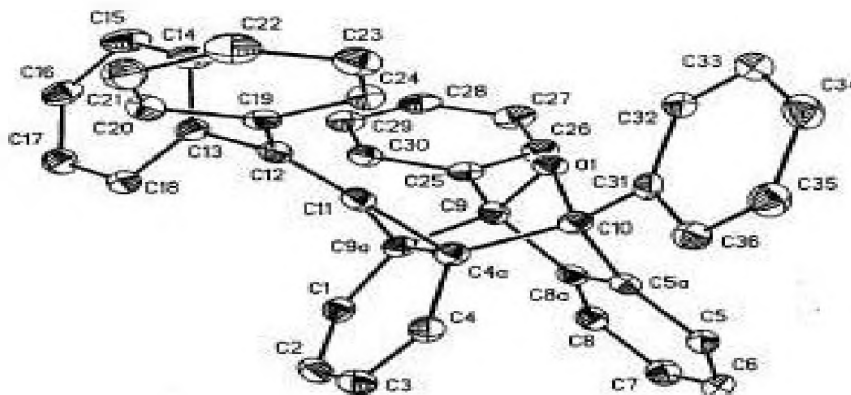
Figure 2. ORTEP diagram of the cation of **19b** with crystallographic numbering.

Theoretical Study

The cycloaddition reactions of the unknown parent cycloproparene olefins **3a** and **4a** with furan have been studied at the ab initio MP2/6-31G(d)// HF/6-31G(d) (i.e. MP2/6-31G(d) single point energy calculations at the HF/6-31G(d) optimised geometries) level of theory using the programs Gausian 92[21] and Spartan 3.1.[22] Vibrational frequencies were computed for all structures at the HF/6-31G(d) level of theory in order to characterise them as minima (no imaginary frequencies) or transition state,TS (one imaginary frequency). Zero-point energies (ZPEs) were also calculated at HF/6-31G(d). All ab initio energies reported in the discussion are calculated (unless stated otherwise) at the MP2/6-31G(d)//HF/6-31G(d) level and include unscaled ZPEs.

Of the possible [4 +2] cycloadditions of **3a** with furan the calculations predict that the transition states for *exo* and *endo* addition to the bridge bond and addition to the exocyclic double bond have essentially the *same* activation energy (+18.7, +18.4 and +18.2 kcal mol^{-1}, respectively). No kinetic preference can be expected and the thermodynamically more stable product will result not from addition to the bridge, but to the exocyclic double bond to give product analogous to **10** (the corresponding reaction energies (ΔHrxn) are: -11.8, -6.2 and -20.4 kcal mol^{-1}, respectively). Of the two modes of addition to the bridge *endo* addition is predicted to give (on the basis of thermodynamics) the furan analogue of **19a** in which the oxygen atom and the exocyclic double bond are *syn* (ΔHrxn: *endo*, -11.8; *exo*, -6.2 kcal mol^{-1}). It is clear that the calculations do not replicate the experimental observations in which **19b,c** are isolated from **3b,c** with DPIBF (Scheme 5). In contrast to this, the cyclopropanaphthalene analogue **4a** shows a clear kinetic regioselectivity for furan addition to the exocyclic double bond [$\Delta\Delta EA$ (the difference in activation energies) is -14.2 and $\Delta\Delta H$rxn -19.6 kcal mol^{-1}, respectively] as is observed for the substituted substrates employed. The calculation also show that *exo/endo* additions to the bridge have the same activation energy (ΔEA +29.4 and +29.0 kcal mol^{-1}) but *endo* addition is again thermodynamically favoured, this time by 5.4 kcal mol^{-1}.

Of course the substrates employed in the experimental study reflect the alkylidenecycloproparenes available and these carry bulky substituents. The size of the molecules involved has restricted further examination to the semiempirical PM3 level. The reactions of **3a** and **4a** with furan at the PM3 level are in qualitative agreement with the ab initio results. Regioselectivity for the exocyclic double bond is found for both cycloproparenes but for **3a** there is only a 2 kcal mol^{-1} energy difference (ΔHrxn *endo/exo*/exocyclic: -12.8/-12.1/-14.8 kcal mol^{-1}); for **4a** there is a clear reaction energy preference ($\Delta\Delta H$rxn -14.8 kcal mol^{-1}; ΔHrxn *endo/exo*/exocyclic: -0.1/-0.3/-15.1 kcal mol^{-1}). Next we assessed the influence of substituents on the methylidenecycloproparene by examining the diphenyl substituted substrates **3b** and **4b** in Diels-Alder reactions with furan; the regioselectivity is now changed from exocyclic to bridge addition (ΔHrxn **3b**: *endo/exo*/exocyclic -12.4/-11.9/+2.8; **4b**: *endo/exo*/exocyclic -0.6/-0.1/+2.5 kcal mol^{-1}). In contrast, reaction of DPIBF with the unsubstituted parents **3a** and **4a** provides data in agreement with the experimental observation. Thus benzenoid **3a** gives regioselective *endo* addition of DPIBF to the bridge according to the calculations with a preference of 1.6 kcal mol^{-1} (ΔHrxn *endo/exo*/exocyclic: -20.6/-17.5/-19.0 kcal mol^{-1}). In contrast, naphthalene **4a** has a clear preference for the exocyclic double bond by some 12.1 kcal mol^{-1} (ΔHrxn *endo/exo*/exocyclic: -8.8/-5.8/-20.9 kcal mol^{-1}).

The dramatic changes calculated with substituent incorporation on one reactant are mirrored when the PM3 method is applied to the actual substrates employed, viz. the diphenyl derivatives **3b** and **4b** with DPIBF. In the case of **3b** marked preference is for bridge addition (ΔHrxn *endo/exo*/exocyclic: -19.8/-18.0/+4.2 kcal mol^{-1}) and the *endo* transition states that are involved. We conclude, therefore, that the observed experimental regioselectivity in these reactions is governed by a combination of steric effects and solvent influences that dictate the precise transition structure involved. This failure of theory is rather unexpected (and disappointing) in view of the general success of ab initio calculations to reproduce reliably the transition state energies (and thus relative reactivity, regioselectivity, etc.) of a wide variety of Diels-Alder and other cycloaddition reactions.[23]

It will be interesting to study if density functional theory (DFT) calculations will provide better agreement with experiment.

X-ray Crystallographic Analyses

In order to provide unambiguous proof of the formation of the naphthyliodonium triflates **18**, the crystal structure of **18d** has been determined. A suitable crystal was obtained by slow crystallization from a saturated MeCN/C_6H_{14} solution and the X-ray determination performed using a CAD4 four circle diffractometer with Mo-Kα radiation. Relevant data pertaining to the analysis are in Table 1, an elipsoid plot for the cationic component of **18d** (crystallographic numbering appended) is shown in Figure 1, and selected bond lengths and angles appear in Table 2.

Table 1. Experimental data for structure analyses of **18d** and **19b**[a]

	18d	19b
Crystal size (mm3)	0.40 x 0.35 x 0.23	0.25 x 0.35 x 0.30
Chemical formula	$C_{33}H_{20}O_4F_9SI$	$C_{40}H_{28}O$
Temperature (K)	ambient	120
Space group	$P2(1)/c$	$P1$
Space group no.	14	2
Z	4	2
a (Å)	12.046(1)	9.557(2)
b (Å)	18.822(2)	10.111(3)
c (Å)	15.416(2)	14.752(4)
α (°)	90.00(0)	84.73(2)
β (°)	112.055(3)	82.55(2)
γ (°)	90.00(0)	88.08(2)
V (Å3)	3239.38	1407.2(6)
$d_{calc.}$ (g cm^{-3})	1.667	1.238
μ (mm^{-1})		0.07
2Θ range (°)	$2 \leq 2\Theta \leq 48$	$3 \leq 2\Theta \leq 45$
<u>Unique reflections</u>		
Observed reflections	5663	4944
$F_o \geq 4\sigma(F)$	3699	3499
R, R_w	0.0492, 0.0515	0.0518, 0.0516

[a] Deposited with the Cambridge Crystallographic Data Centre.as: **18d:** CCDC 160279; **19b** CCDC 160957.

The structure is confirmed as 1-(2'-naphthyl-3'-phenyliodonium)-2,2-bis(3"-trifluoromethylphenyl)ethanone triflate (**18d**). In similar vein, a crystal of **19b** was obtained (acetonitrile/hexane) and the X-ray determination performed using a Nicolet R3m/V diffractometer with Mo-Kα radiation. Relevant data pertaining to this analysis appear in Tables 1 and 3, and the elipsoid plot with numbering scheme is Figure 2. The compound is confirmed as [4aα,9α,9aα,10α]-9,10-diphenyl-11-diphenylmethylidene-4a,9,9a,10-tetrahydro-9,10-epoxy-4a,9a,-methanoanthracene (**19b**).

Table 2. Selected bond lengths (Å) and angles (°) for **18d**[a]

Bond Length		Bond Angle	
C1—C2	1.363(4)	C1—C10—C9	120.3(3)
C1—C10	1.427(4)	C1—I—C27	94.8(1)
C2—C3	1.417(4)	I—C1—C2	118.8(2)
C3—C8	1.412(5)	I—C1—C10	118.4(2)
C8—C9	1.417(4)	C2—C1—C10	122.7(3)
C9—C10	1.383(4)	C1—C2—C3	120.0(3)
C10—C11	1.472(5)	C2—C3—C8	118.7(3)
C11—C12	1.521(5)	C3—C8—C9	119.8(3)
C11—O1	1.232(4)	C8—C9—C10	121.1(3)
C1—I	2.131(3)	C10—C11—C12	119.8(3)
I—C27	2.094(4)	O1—C11—C10	119.0(3)
		O1—C11—C12	121.1(3)

[a] Numbers in parenthesis are the estimated standard deviations in the least significant digit.

Table 3. Selected bond lengths (Å) and angles (°) for **19b**[a]

Bond Length		Bond Angle	
C1—C2	1.344(4)	C9—O1—C10	99.3(2)
C2—C3	1.460(4)	C2—C1—C9a	120.6(2)
C3—C4	1.342(4)	C1—C2—C3	122.1(2)
C4—C4a	1.487(4)	C2—C3—C4	123.3(2)
C4a—C9a	1.584(3)	C3—C4—C4a	120.6(2)
C1—C9a	1.485(3)	C4—C4a—C9a	116.0(2)
C4a—C10	1.576(3)	C1—C9a—C4a	116.9(2)
C4a—C11	1.475(4)	C9a—C4a—C11	57.6(2)
C9a—C11	1.477(3)	C4a—C9a—C11	57.5(2)
C9—C9a	1.553(3)	C4a—C11—C9a	64.9(2)
C11—C12	1.330(4)	C4a—C11—C12	148.6(2)
		C9a—C11—C12	145.4(2)

[a] Numbers in parenthesis are the estimated standard deviations in the least significant digit.

Experimental Section

General Procedures: These have appeared previously.[7] NMR spectra were recorded at 300 (^{1}H) and 75 MHz (^{13}C) in (D)chloroform solutions for **11, 13** and **19**, and in CD3CN for **18b-d**.

Cycloaddition reactions of 3 and 4 with DPIBF

To a solution of **3** or **4** in dry, degassed, ethylene glycol under nitrogen was added diphenylisobenzofuran (DPIBF, 2.0 mol. equiv.). The mixture was heated to 110°C for ca. 7 h for **4**, but 120°C for 24 h for **3**. The mixture was cooled and the solvent removed in vacuum. The crude product was purified by flash column chromatography over silica gel. Hexane/ethyl acetate (9:1) elution gave the cyclobutarenes **11** from **4**. The products from **3** were obtained from light petroleum elution (which displaced unchanged DPIBF) followed by flushing the column with CH_2Cl_2.

A. Cyclobutarene (11b). 4b[6]

(152 mg, 0.5 mmol) and DPIBF (270 mg, 1.0 mmol) gave **11b** (154 mg, 55%) as a pale yellow solid, mp 124-125°C: IR (CCl_4) 805, 937, 1026, 1074, 1153, 1180, 1194, 1278, 1315, 1448, 1490, 1596, 1659, 1665 (C=O), 1738, 3026, 3061 cm^{-1}; ^{1}H NMR δ 7.1-7.8 (complex m); ^{13}C NMR δ 76.1 (cyclobutyl), 120.3, 126.6, 126.9, 128.3, 128.7, 129.4, 130.0, 132.8, 138.2, 140.2, 150.3, 163.1, 198.2 (C=O); MS *m/z* 574 (M$^+$). Anal. Calcd for $C_{44}H_{30}O$: C, 91.95; H, 5.26. Found: C, 92.02; H, 5.24.

B. Cyclobutarene (11c). 4c[11]

(182 mg, 0.5 mmol) and DPIBF (270 mg, 1.0 mmol) gave **11c** (101 mg, 32%) as a pale orange solid, mp 103-104°C: IR (CCl_4) 874, 910, 1023, 1067, 1081, 1153, 1189, 1222, 1271, 1392, 1397, 1460, 1590, 1618, 1670 (C=O), 1742, 2925, 2960, 3028 cm^{-1}; ^{1}H NMR δ 3.62 (s, 2xOMe), 7.2-7.3 (m, 7H), 7.3-7.5 (m, 10H), 7.5-7.8 (m, 11H); ^{13}C NMR δ 53.4 (OMe), 77.2 (cyclobutyl), 123.1, 125.1, 125.3, 125.6, 125.9, 126.3, 128.2, 129.0, 129.3, 130.4, 134.6, 149.1, 161.2, 196.3 (C=O); MS *m/z* 634 (M$^+$). Anal. Calcd for $C_{46}H_{34}O_3$: C, 87.04; H, 5.40. Found: C, 86.97; H, 5.46.

C. Cyclobutarene (11d). 4d[12]

(220 mg, 0.5 mmol) and DPIBF (270 mg, 1.0 mmol) gave **11d** (150 mg, 42%) as an orange solid, mp 98-99°C: IR (CCl_4) 810, 839, 864, 886, 900, 979, 1035, 1076, 1133, 1192, 1247, 1365, 1392, 1434, 1463, 1478, 1661 (C=O), 1737, 2869,

2902, 2935, 2961, 2968, cm^{-1}; ^{1}H NMR δ 7.1-8.0 (complex m); ^{13}C NMR δ 79.3 (cyclobutyl), 126.4, 128.0, 129.8, 130.0, 131.3, 131.9, 133.2, 134.1, 137.4, 137.9, 138.2, 151.3, 159.4, 199.1 (C=O); ^{19}F NMR (CD3CN) δ -81.5; MS m/z 710 (M$^+$). Anal. Calcd for $C_{46}H_{28}OF_6$: C, 77.74; H, 3.97. Found: C, 77.83; H, 4.10.

D. Norcaradiene (19b). 3b[6]

(100 mg, 0.39 mmol) and DPIBF (212 mg, 0.79 mmol) gave firstly unchanged dpibf (58 mg, 27%) then (with CH_2Cl_2) **19b** as a green oil which crystallized (light petroleum) (97 mg, 48%), mp 242-244°C: IR 3048, 3032, 3005, 1956, 1885, 1813, 1601, 1495, 1456, 1444, 1375, 1298, 1155, 1074, 1011, 989; ^{1}H NMR δ 5.67 (dd, J 2.3, 7.5 Hz, 2H); 6.11 (dd, J 2.3, 7.5, 2H); 7.05-7.60 (m, 24H); ^{13}C NMR δ 45.42 C4a(9a); 91.80 C9(10); 120.75, 122.31, 122.34, 126.01, 127.26, 127.80, 128.39, 128.45, 128.51 all CH; 130.87, 134.50, 135.18, 140.08, 149.92 all C; MS m/z 525, 524 (10.0, 23.4%; M); 420, 419 (5.7, 15.5; M-PhCO); 341, 339 (17.3, 16.5), 271, 270 (22.9, 100; dpibf); 254 (16.0, M-dpibf), 252 (21.1, M-dpibf-H2), 165 (30.4), 105 (31.3, PhCO), 77 (32.9). Anal. Calcd for $C_{40}H_{28}O$: C, 91.56; H 5.38. Found: C, 91.48; H 5.53. The product is confirmed as **19b** from X-ray crystal structure analysis.

With toluene as solvent the yield of **19b** was 41% and the recovered DPIBF was 44%.

E. Norcaradiene (19c). 3c[11]

(100 mg, 0.32 mmol) and DPIBF (172 mg, 0.64 mmol) gave unchanged DPIBF (103 mg, 60%) followed by 19c (50 mg, 27%) as pale brown needles (CH_2Cl_2/light petroleum, 1:1), mp 223.5-225°C: IR 3036, 2963, 2932, 2834, 1605, 1508, 1447, 1283, 1246, 1171, 1028, 835, 745, 704, 693, 552; ^{1}H NMR δ 3.80 (s, 2xOCH$_3$); 5.64 (dd, J 2.2, 7.5 Hz, 2H); 6.11 (dd, J 2.2, 7.5 Hz, 2H); 6.69 (d, J 8.6, 4H; 7.05-7.12, m, 8H); 7.29-7.60 (m, 10H); ^{13}C NMR δ 45.5, C4a(9a); 55.3, 2xOCH$_3$, 91.7, C9(10); 113.13, 120.7, 122.1, 122.6, 126.0, 128.4, 128.5, 130.6 all CH; 127.9, 133.06, 133.6, 135.3, 150.0, 159.0 all C; MS m/z 585, 584 (6.0, 13.4%; M); 480, 479 (3.7, 9.9; M-PhCO); 315, 314 (24.8, 100; M-dpibf); 300, 299 (12.7, 46.4; M-dpibf-CH$_3$); 271, 270 (17.9, 68.1; dpibf); 105 (20.1, PhCO), 77 (25.3). Anal. Calcd for $C_{42}H_{32}O_3$: C, 86.26; H, 5.52. Found: C, 86.04; H, 5.44.

With toluene as solvent the yield of **19c** was 18% and the recovered DPIBF was 77%.

Cycloaddition reactions of 3 and 4 with a -pyrone

To a solution of **3** or **4** in dry, degassed, ethylene glycol under nitrogen was added excess of α-pyrone. For **4** the mixture was heated to 110°C for ca. 12 h while 120°C and 24 h were employed for **3**. After cooling, the solvent was removed under reduced pressure and the crude product purified. The indanone product **13** from **4** was obtained from flash column chromatography (silica gel, 9:1 hexane/ethyl acetate elution) while for **3** column chromatography employed ethyl acetate/light petroleum (1:7) elution.

A. Benz[*f*]indanone (13b). 4b[6]

(100mg, 0.33 mmol) and α-pyrone (53 μl, 0.66 mmol) gave **13b** (66 mg, 50%) as a brown solid, mp 92-93°C: IR (CCl$_4$) 880, 925, 1087, 1134, 1175, 1189, 1265, 1343, 1425, 1487, 1597, 1618, 1640 (C=O), 1715 (CHO), 1775, 2850, 2965, 3025, 3088 cm^{-1}; ^{1}H NMR δ 3.10 (d, 1H, cyclopentyl), 5.81 (d, 1H, vinyl), 6.32 (dd, 1H vinyl), 6.9-7.8 (complex m, 14H), 7.85 (bs, 2H), 9.48 (s, CHO); ^{13}C NMR δ 76.6 (cyclopentyl) 122.1, 123.1, 123.2, 123.5, 123.7, 124.2, 124.6, 124.8, 125.3, 127.2, 129.2, 130.0, 131.3, 161.3 (C=O), 193.0 (CHO); MS *m/z* 400 (M$^+$). Anal. Calcd for C$_{29}$H$_{20}$O$_2$: C, 82.16; H, 6.89. Found: C, 82.28; H, 6.80.

B. Benz[*f*]indanone (13c). 4c[11]

(100mg, 0.27 mmol) and α-pyrone (44μl, 0.55 mmol) gave **13c** (31.2 mg, 25%) as a brown solid, mp 100-101°C: IR (CCl$_4$) 801, 834, 1008, 1020, 1031, 1113, 1160, 1178, 1253, 1287, 1461, 1510, 1602, 1626, 1671, 1720, 1773, 2838, 2928, 2962, 3054 cm^{-1}; ^{1}H NMR δ 3.05 (d, 1H, cyclopentyl), 3.51 (s, 2xOMe), 5.89 (d, 1H, vinyl), 5.98 (dd, 1H, vinyl), 6.7-8.0 (m, 14H), 9.53 (s, CHO); ^{13}C NMR δ 51.4 (OMe), 74.6 (cyclopentyl), 120.9, 121.3, 122.3, 122.6, 123.0, 123.7, 124.0, 124.3, 125.3, 125.5, 125.8, 126.2, 127.1, 164.1 (C=O), 189.2 (CHO); MS *m/z* (444, M$^+$). Anal. Calcd for C$_{31}$H$_{24}$O$_4$: C, 80.85; H, 5.25. Found: C, 80.72; H, 5.31.

C. Benz[*f*]indanone (13d). 4d[12]

(100 mg, 0.23 mmol) and α-pyrone (40 μl, 0.50 mmol) gave **13d** (24.0 mg, 16%) as a deep orange solid, mp 87-88°C: IR (CCl$_4$) 799, 829, 897, 1076, 1088, 1121, 1179, 1313, 1324, 1445, 1540, 1612, 1632, 1718, 1777, 2888, 2934, 3055, 3074 cm^{-1}; ^{1}H NMR δ 3.13 (d, 1H, cyclopentyl), 6.17 (d, 1H vinyl), 6.32 (dd, 1H, vinyl), 7.2-7.9 (m, 12H), 8.43 (bs, 2H), 9.71 (s, CHO); ^{13}C NMR δ 78.3 (cyclopentyl), 123.2, 123.5, 123.9, 124.6, 124.7, 124.9, 125.5, 125.8, 126.6, 127.8, 129.5, 132.3, 159.4 (C=O), 197.3 (CHO); ^{19}F NMR (CD$_3$CN) δ -80.9; MS *m/z* 536 (M$^+$). Anal. Calcd for C$_{31}$H$_{18}$O$_2$F$_6$: C, 69.41; H, 3.38. Found: C, 69.15; H, 3.45.

D. 3b[6] (70 mg, 0.28 mmol) and α-pyrone (100 mg, 1.1 mmol) provided a pale green-yellow oil (73.1 mg, 92%) which has eluded identification.

　　　With either refluxing toluene for 48 h or THF at 70°C for 5 days only unchanged starting material were recovered.

E. 3c[11] (100 mg, 0.32 mmol) and α-pyrone (61 mg, 0.64 mmol) provided no product until the column was flushed with methanol. A white amorphous solid (53.1 mg, 44%) that has eluded identification was obtained.

　　　With either refluxing toluene for 24 h or THF at 70°C for 5 days only unchanged starting material were recovered.

Cycloaddition reactions of 4 with acetylenic bis-iodonium triflate (14).

　To a solution of **4** in dry, degassed acetonitrile (10 mL) under nitrogen was added the bis-iodonium salt **14**[18] (1.0 mol. equiv.) and the mixture was stirred at RT for 7 h. The solvent was removed in vacuum and the crude product recrystallized (CH_2Cl_2/C_6H_{14}) to give cycloadduct **18**. All NMR data recorded below are for CD_3CN solutions.

A. Naphthyl iodonium salt (18b). 4b[6]
(100 mg, 0.33 mmol) and **14**[18] (240 mg, 0.33 mmol) gave **18b** (119 mg, 53%) as a white solid, mp 125°C (dec): IR (CCl_4) 946, 1028, 1069, 1083, 1121, 1194, 1245 (OTf), 1260, 1442, 1493, 1542, 1598, 1651 (C=O), 2874, 2935, 2962, 3028, 3054 cm^{-1}; ^1H NMR δ 2.31, (s, >CH-), 6.83 (bs, 2H), 7.0-7.5 (m, 11H), 7.59 (bs, 2H), 8.0-8.15 (m, 4H), 8.25-8.45 (m, 2h); ^{13}C NMR δ 52.4 (CH), 122.3, 123.9, 125.8, 127.1, 128.3, 128.7, 129.8, 130.4, 130.9, 131.7, 133.2, 134.5, 137.2, 195.2 (C=O); ^{19}F NMR δ -78.7; MS (FAB) *m/z* 525 (M$^+$-OTf). Anal. Calcd for $C_{31}H_{22}O_4SF_3I$: C, 55.20; H, 3.29. Found: C, 54.89; H, 3.41.

B. Naphthyl iodonium salt (18c). 4c[11]
(100 mg, 0.27 mmol) and **14**[18] (200 mg, 0.27 mmol) gave **18c** (85 mg, 39%) as a pale brown solid, mp 97-99°C (dec): IR (CCl_4) 828, 1032, 1123, 1177, 1245 (OTf), 1286, 1440, 1463, 1510, 1581, 1607, 1624, 1658 (C=O), 2836, 2908, 2932, 2953, 3000, 3058 cm^{-1}; ^1H NMR δ 2.34, (s, 1H, CH), 3.84 (s, 2xOMe), 7.3-8.5 (complex m, 19H); ^{13}C NMR δ 54.5 (CH) 121.5, 122.5, 122.9, 124.1, 124.8, 126.1, 126.3, 126.8, 128.2, 128.6, 129.4, 130.2, 131.4, 134.1, 135.3, 198.4 (C=O); ^{19}F NMR δ -78.9; MS (FAB) *m/z* 585 (M$^+$-OTf). Anal. Calcd for $C_{33}H_{26}O_6SF_3I$: C, 53.96; H, 3.57. Found: C, 53.45; H, 3.24.

C. Naphthyl iodonium salt (18d). 4d[12]

(100 mg, 0.23 mmol) and **14**[18] (170 mg, 0.23 mmol) gave **18d** (112 mg, 60%) as a white solid, mp 116°C (dec): IR (CCl$_4$) 891, 994, 1028, 1077, 1126, 1165, 1226, 1245 (OTf), 1258, 1281, 1330, 1446, 1578, 1617, 1645 (C=O), 3063, 3069 cm^{-1}; ^{1}H NMR δ 2.45 (s, >CH-), 7.2-7.3 (m, 4H), 7.65-7.75 (m, 4H), 7.9-8.3 (m, 7H), 8.45-8.55 (m, 4H); ^{13}C NMR δ 57.3 (CH), 123.9, 124.3, 124.9, 125.5, 126.0, 126.2, 126.3, 126.8, 127.3, 128.4, 129.1, 131.3, 132.8, 135.6, 139.8, 140.5, 201.0 (C=O); ^{19}F NMR δ -78.5 (OTf), -82.1 (CF$_3$); MS (FAB) *m/z* 661 (M$^+$-OTf). Anal. Calcd for C$_{33}$H$_{20}$O4SF$_9$I: C, 48.90; H, 2.49. Found: C, 48.13; H, 2.35.

Supporting Information.

Supplementary crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic data Centre as supplementary publications: CCDC 160279 (**18d**) and 160957 (**19b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Rd., Cambridge, CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

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19. With ethylene glycol as solvent **3b** provides an amorphous mass from two molecules interacting with one of solvent (*m/z* 570); compound **3c** gives a 1:1 adduct (*m/z* 376) under the same conditions. The structures have not been elucidated.

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