Sulfur-bridged molecular racks: *O,S*-sesquinorbornadienes, *CNS*-[3] and *CNOS*-[4]polynorbornanes

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Dedicated to Professor Charles W. Rees on the occasion of his 75th birthday

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Abstract

Thiophene has been reacted under high-pressure (10 kbar) and temperature (100^0C) with *N*-methylmaleimide and *N*-phenylmaleimide to produce Diels-Alder *exo*- and *endo*-adducts in modest yields (25-36%). Reaction of 7-oxanorbornadiene-2,3-dicarboxylic anhydride **6**, a highly reactive dienophile, with thiophene occurred under high-pressure (10 kbar) at 100^oC to yield stereoisomeric 1:1-adducts by site selective attack at the maleic anhydride type of π-bond. This approach afforded the first examples of *syn*- and *anti*- heterobridged sesquinorbornadiene anhydrides **8** and **9** containing a sulfur bridge. Similar reaction of isobenzothiophene with **6** was even more facile as reaction occurred at room temperature and atmospheric pressure to yield benzo-analogues **12** and **13**. Thermal fragmentation involving loss of furan and sulfur occurred from both classes of adducts under FVP (370 ^{0}C, 0.005 mbar) to produce phthalic anhydride or naphthalene-2,3-dicarboxylic anhydride respectively. The putative 7-thianorbornadiene intermediates **20** and **22**, generated by loss of furan, were not detected. Reaction of *exo*-*N*-methyl 7-thianorbornene-5,6-dicarboxylic imide **4a** with the ester-activated cyclobutenoaziridine **16** provided access to *CNS*-[3]polynorbornane **18**, while similar addition of the *exo,endo*-isomer of *O,S*-benzosesquinorbornadiene **13** to **16** afforded the *CNOS*-[4]polynorbornane **19**. These are the first *S*-bridged [n]polynorbornanes to be reported. Molecular modelling (AM1) has shown that S^n-[n]polynorbornadienes have a curved topology greater than O^n-[n]polynorbornadienes but less than N^n-[n]polynorbornadienes.

Keywords: 7-Thianorbornenes, cycloaddition, AM1, modelling, high-pressure

Introduction

The use of [n]polynorbornanes and related molracs as scaffolds for vectorially positioning functionality has been realized through the syntheses of V- and U-shaped *bis*-porphyrin cavity systems.[1] The value of their metalated derivatives as supramolecular building blocks has been

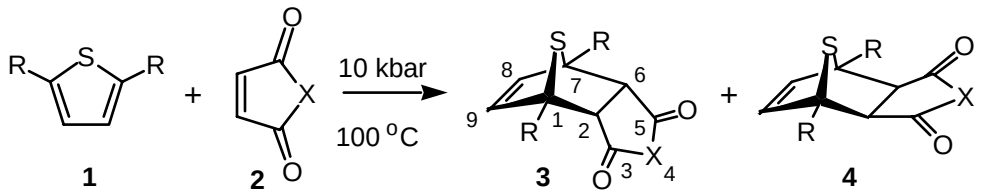
exploited in the co-ordinative assembly of pyridyl components to form universal joints,[2] as non-covalently linked donor/acceptor electron transfer agents[3] and more recently for self-assembly into large container molecules.[4] In other applications, [n]polynorbornanes have served as spacer molecules for separating attached intercalators in order to promote optimal DNA/substate binding.[5]

Results and Discussion

The choice of specific [n] polynorbornanes[6] or related molracs[7] has been predicated on scaffold topology meted by synthetic accessibility. Systems containing polyoxygen or polynitrogen bridges, as well as repeating combinations of *C,O* and *C,N* bridges have been described by our group.[8] This has opened the way to produce a number of novel [n]polynorbornanes, the curvature of which was governed by the various combinations of *C,N,O* bridge components. In a natural extension of this series, we sought to add systems with sulfur bridges to the repertoire, an area that has been little investigated here-to-fore.[9]

In this paper, we explore ways to redress this deficiency and report on the synthesis of *OS*-sequinorbornadienes, a *CNS*-[3]polynorbornane, a *COS*-[3]polynorbornane and a *CNOS*-[4]polynorbornane in which four different atom bridges are incorporated.

High pressure addition of dienophiles to thiophene



Scheme 1

Table 1. Isomer distribution and yields for the reaction of maleimides and maleic anhydride to thiophenes under high pressure

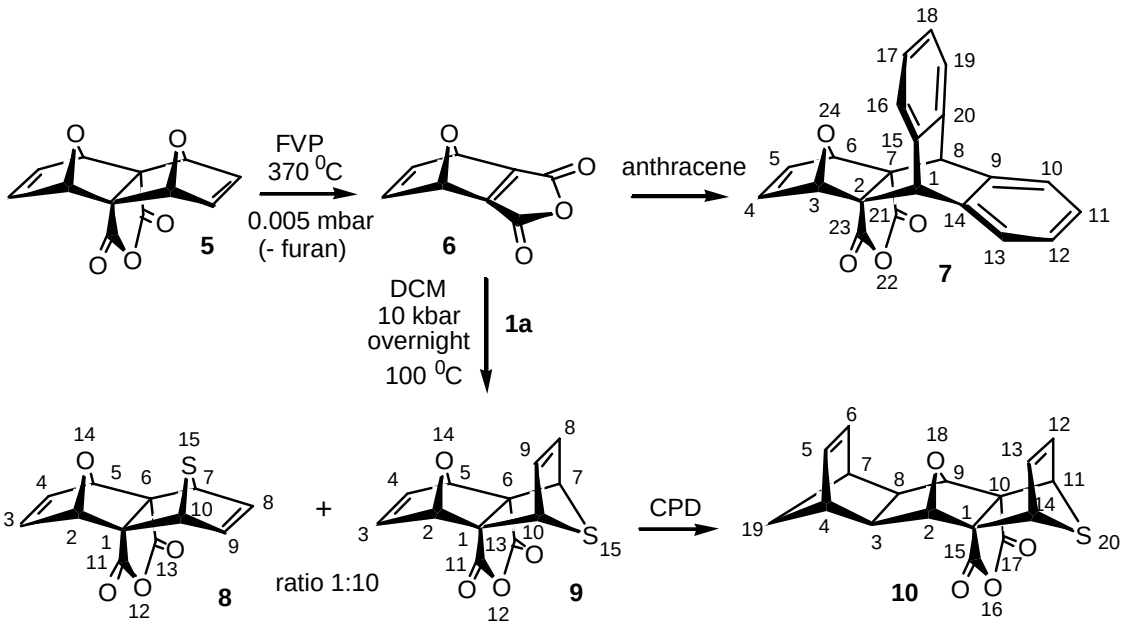
Series	R	X	**3:4** ratio	yield %
a	H	NMe	1.4:1	25
b	H	NPh	1.7:1	36
c	H	O	1:10	35*
d	Me	NMe	1.2:1	29

* Kotsuki *et al. report formation of* ***4c*** *in 37-47% yield (ref 11)*

Our approach commenced with the preparation of the sulfur-bridged norbornenes **3** and **4** and a study of their dienophilicity. In spite of the reluctance of thiophene to participate as a 1,3-diene in Diels-Alder reactions, there was a report on the addition of maleic anhydride to thiophene at high-pressure and temperature.[11] That report also noted that dimethyl maleate, dimethyl fumarate, acrolein and other common dienophiles failed to add under the high-pressure conditions.

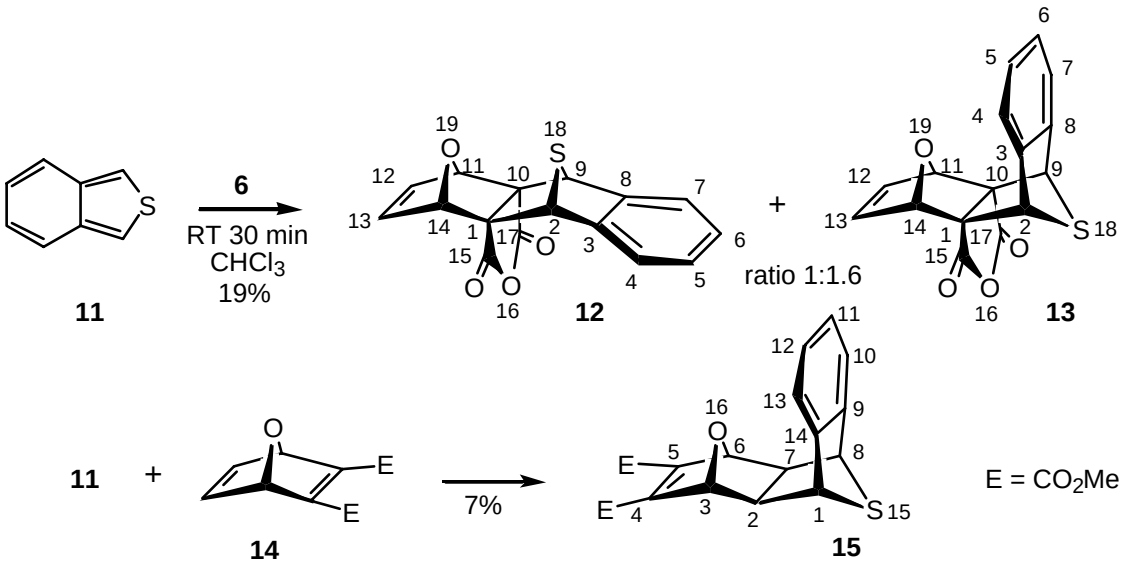
We have now found that *N*-substituted maleimides also add to thiophene at high-pressure and temperature. Reaction of *N*-methyl maleimide **2a** with thiophene **1a** occurred under high-pressure (10 kbar) and temperature (100^{o}C) to give a 1.4:1 mixture of *endo*- and *exo*- [4π+2π] adducts **3a** and **4a** respectively (Scheme 1). This reaction was general and similar mixtures of stereoisomers were formed in the reaction of thiophene **1a** with *N*-phenyl maleimide **2b** and of 2,5-dimethylthiophene **1d** with *N*-methyl maleimide (see Table 1, Scheme 1). In all cases, the *endo*-isomers were the preferred product although significant quantities of the *exo*-isomers were also obtained. In comparison, the high-pressure reaction (100^{o}C, 15 kbar) between thiophene and maleic anhydride, first reported by Kotsuki *et al*.,[11] was reported to produce almost exclusively the *exo*-adduct **4c**. We have repeated this reaction and found that careful evaluation of the reaction mixture by ^{1}H-NMR showed that the *endo*-isomer **3c** was also present, but it could not be isolated, possibly because of cycloreversion to starting materials at atmospheric pressure.[12] Structural assignments to the various cycloadducts were made on the basis of chemical shifts and coupling constants (see Table 2)

We have reported elsewhere that 7-oxanorbornadiene-2,3-dicarboxylic anhydride **6** was especially reactive in Diels-Alder reactions,[13] eg, we find that anthracene added at room temperature and ambient pressure to form adduct **7** (Scheme 2). Reaction between dienophile **6** and thiophene was more difficult but could be achieved at 100 ^{o}C by working under high pressure (10 kbar) to afford adducts **8** and **9** by site selective, *exo*-face addition to the maleic anhydride type of π-bond of **6**. The structures of these adducts were assigned on the basis of NMR data (see Table 3). The *syn O,S*-sesquinorbornadiene **8** and its *anti*-isomer **9** are the first examples of this ring system, although *S*-oxides related to the *anti*-isomer **9** have been reported in the bridgehead methyl series derived from 2,5-dimethylthiophene sulphoxide.[14]



Scheme 2

The reduced Diels-Alder reactivity of 7-thianorbornenes compared with the 7-oxanorbornenes was illustrated by the reaction of **9**, a compound containing both sub-units, with excess cyclopentadiene which yielded adduct **10** by site selective addition at the 7-oxanorbornene π-bond, albeit in very low yield.



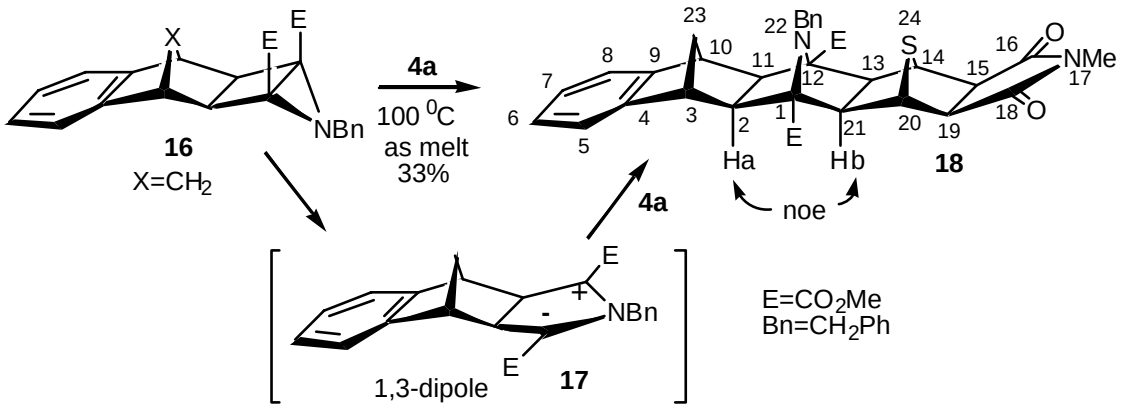
Scheme 3

The activated dienophile **6** reacted with isobenzothiophene (IBT) **11**, generated *in situ*,[15] under even milder conditions (ambient temperature and pressure) to form 1:1-adducts **12** and **13** in a reaction that exhibited the same site selectivity as that observed for thiophene (Scheme 3).

That this reaction occurred at room temperature within 30 minutes whereas the reaction between **6** and thiophene required high pressure and temperature, reinforced the improved Diels-Alder reactivity of isobenzothiophene relative to thiophene. In another example, IBT **11** was reacted (70 ^{o}C, $CHCl_3$,12 hr) with the less dienophilic dimethyl 7-oxanorbornadien-2,3-dicarboxylate **14** to form the 1:1 adduct **15**. In this case, the site-selectivity changed to favor reaction at the unsubstituted π-bond[18] while the stereoselectivity was such that only the *exo, anti*-adduct **15** was observed. Li *et al.* have reported[14] that tetramethylthiophene-*S*-oxide reacted with **14** to yield an adduct with the corresponding site and stereoselectivity.[18]

The olefin π-bonds in adducts **3a-d** and **4a-d** were extremely reluctant to enter into [4π+2π] cycloaddition reactions. No cycloaddition occurred between **4a** and inverse electron-demand heterocycles such as 3,6-di(2-pyridy1)-*s*-tetrazine, 2,5-bis(trifluoromethyl)-1,3,4-oxadiazole or regular electron-demand 1,3-dienes including cyclopentadiene (trace of product detected by NMR), cyclopentadienones or ester-activated cyclobutane epoxides under thermal, high pressure or photochemical conditions. By comparison, all these reactions have been reported to proceed with 7-oxanorbornenes.[19]

Preparation of higher-order sulfur-bridged [n]polynorbornanes

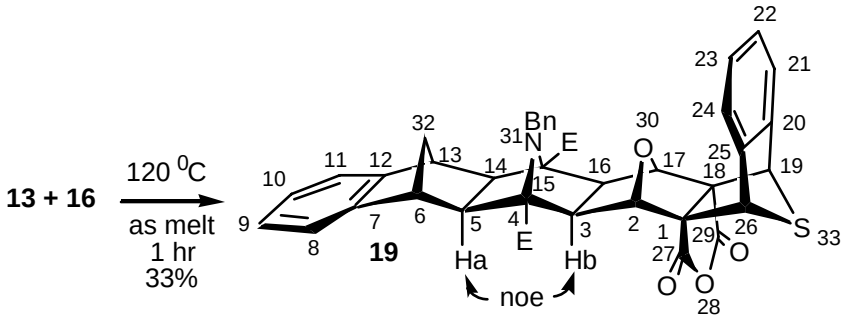


Scheme 4

The exception was reaction of **4a** with the aziridine **16** at 100 ^{0}C in the absence of solvents, where the intermediate 1,3-dipole **17**, formed from the thermal ring opening of the aziridine **16**, was trapped by the π-bond of **4a** to yield the *CNS*-[3]polynorbornane **18** (Scheme 4).

Formation of the first [4]polynorbornane with different atoms in each of the single-atom bridges was obtained by reaction of the major *O,S*-benzosesquinorbornadiene **13** with aziridine **16** (Scheme 5). The reaction was conducted at 120 ^{0}C for 1 hour in the absence of solvent and produced the *CNOS*-[4]polynorbornane **19** in 33% yield. There was ample precedent for the *exo,exo*-coupling of aziridines of type **16** with 7–oxanorbornenes,[22] and this stereochemistry was confirmed by NOESY measurements between Ha and Hb. The reaction of **16** with the sulfur-bridged norbornene **13** was the first of its kind, so the assignment of stereochemistry was

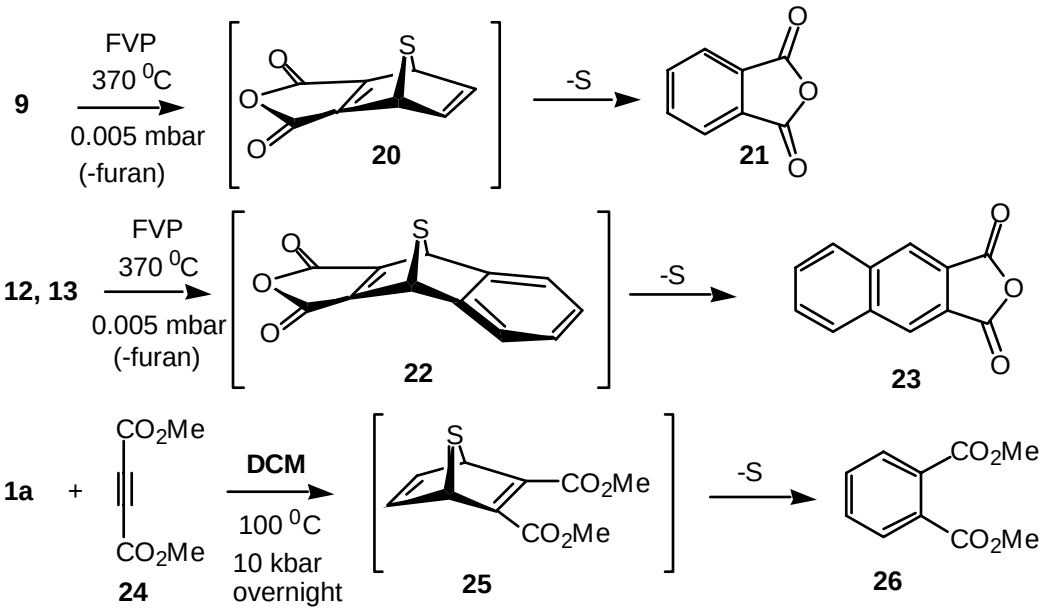
especially important. Again NOESY measurements in **18** between Ha and Hb confirmed that coupling was again *exo,exo*-selective. The ^{1}H NMR data and structural assignments for **18** and **19** are presented in Table 4.



Scheme 5

A positive feature of the above results was the fact that a range of aziridines related to **16** has already been reported[22b] in which the X-bridges (Scheme 4) have been replaced by spirocyclopropyl, isopropylidene, oxygen or substituted nitrogen. As well, the nitrogen substituent of the aziridine has been also varied, eg methyl, methoxymethyl, p-methoxybenzyl or phenyl, further widening the range of *X,N,S*-bridged [3]polynorbornanes available by this protocol. Thus, an opportunity to map the role of sulfur as a flanking 'sentinel' may be established in the future.

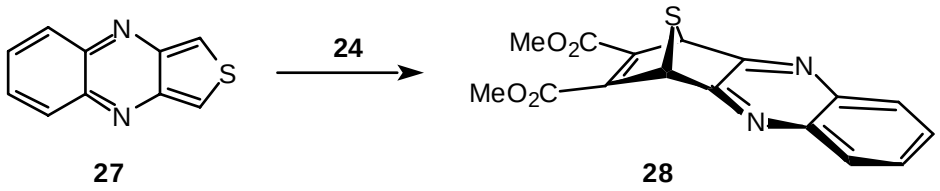
Towards multisulfur-bridged [n]polynorbornanes



Scheme 6

The high reactivity of 7-oxanorbornadiene-2,3-dicarboxylic anhydride **6** in Diels-Alder cycloadditions (*vide supra*) was paralleled by its bridged-nitrogen counterpart.[23] On this basis, the *S*-bridged analogue, 7-thianorbornadiene-2,3-dicarboxylic anhydride **20**, should be activated towards cycloaddition relative to 7-thianorbornenes, thereby offering entry to *S,S*-sesquinorbornadiene anhydrides by reaction with thiophene or isobenzothiophene. Our approach to the preparation of **20** was modeled on the retro-Diels-Alder route used for the preparation of **6** (see, Scheme 2). We reasoned that furan rather than thiophene would be the better dienofuge and FVP of *O,S*-sesquinorbornadiene anhydride **9** should produce 7-thianorbornadiene-2,3-dicarboxylic anhydride **20** by loss of furan. In practice, FVP of **9** at 370^{0}C/0.005 mbar produced phthalic anhydride **21** as the main product. Similar FVP of a mixture of *O,S*-benzosesquinorbornadienes **12** and **13** yielded naphthalene-2,3-dicarboxylic anhydride **23** in 60% yield (Scheme 6). We consider that 7-thianorbornadienes **20** and **22** were produced but ejected sulfur under the reaction conditions to form the aromatic anhydrides **21** and **23**. This proposal for sulfur loss found support in the literature where it has been reported that other attempts to form 7-thianorbornadienes, such as the reaction of benzyne with thiophene, yielded naphthalene rather than the expected 7-thianorbornadiene.[24] In the same vein, we have found that reaction of thiophene with dimethyl acetylenedicarboxylate (DMAD) **24** (100^{0}C, 10 kbar) produced dimethyl phthalate **26**, a result logically explained by loss of sulfur from the first-formed 7-thianorbornadiene **27** (Scheme 6). Interestingly, reaction of DMAD **24** with 4,9-diazaisonaphthothiophene **27** has been reported to give the stable 7-thianorbornadiene **28** in a rare example of this class of sulfur bicycle.[25]

These results thwarted our attempts to form dithiasesquinorbornadienes, although the reported stability of **28** does appear to leave open opportunities to form **20** or **22** using milder methods.

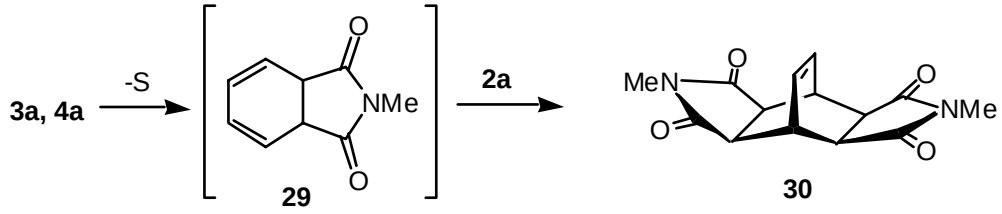


27 **28**

Scheme 7

Extrusion of the sulfur bridge was also implicated in the high-pressure reaction of thiophene with *N*-methyl maleimide at 100^{0}C, which gave a sulfur-free product as well as the 1:1-adducts **3a** and **4a** (*vide supra)*. This by-product was assigned the *bis*(maleimide) structure **30** on the basis of ^{1}H and ^{13}C NMR data and high resolution mass spectrometry (found *m/z* = 274.0954). It was considered to arise by *N*-methyl maleimide addition to the intermediate 1,2-dihydrophthalimide **29**, itself formed by loss of sulfur from 1:1-adducts **3a** and **4a**. Subjecting a mixture of 1:1-adducts **3a** and **4a** to the same thermal and high-pressure conditions, but with no added *N*-methyl maleimide, also yielded *bis*-maleimide **30**. This result indicated that retro-Diels-Alder reaction of adducts **3a** and **4a** must have occurred under the reaction conditions

competitively with loss of the sulfur-bridge to form cyclohexadiene **29**. Reaction of *N*-methyl maleimide with 1,3-diene **27** to form symmetrical adduct **30** has precedent in the reaction of maleic anhydride with 1,2-dihydrophthalic anhydride.[26]



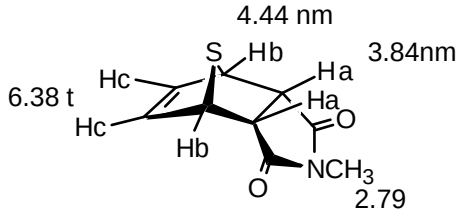
Scheme 8

^{1}H NMR Chemical shift data and stereochemical structural assignments

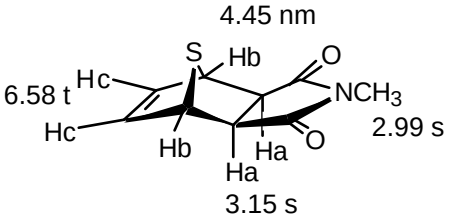
The simple *endo*-stereoisomeric 1:1-adducts **3a-c** can be readily distinguished from their *exo*-isomers **4a-c** on the basis of vicinal H,H-coupling between Ha and Hb, since the former are coupled whereas the latter show no coupling (Table 2). The chemical shifts of the *N*-methyl substituents in **3a** and **4a** also provided a reliable stereo-marker, since the *endo*-stereochemistry placed the *N*-methyl group in the shielding zone of the olefinic π-bond.[27] This caused an upfield shift of about 0.2 ppm relative to the *exo*-isomer. It was this chemical shift feature which allowed stereo-assignment for **3d**, **4d**, in which the bridgehead methyl groups precluded the use of vicinal H,H-coupling data.

In the sesquinorbornadiene anhydrides (Table 3a), the use of vicinal H,H coupling was again precluded by the presence of the anhydride moiety at the stereo-defining positions. Further, the lack of *N*-methyl groups precluded the second method used above. In this case, we have used another NMR argument based on the chemical shift of the bridgehead protons. The basis for this method resulted from the shielding by the newly formed π-bond on the adjacent bridgehead protons in sesquinorbornadienes with *exo,endo*-geometry. The method was typified by model compounds **5** and **31** in the *O,O*-sesquinorbornadiene anhydride system (Table 3a). The C2v-symmetry of the *syn*-facial isomer **5** was defined by two chemical shifts: the bridgehead protons at δ 5.22 and the olefinic protons at δ 6.71. In the *anti*-isomer **31**, there are two sets of bridgehead protons, which display significantly different chemical shifts (Δδ = 0.48 ppm). The upfield shift of Ha relative to Hb, being attributed to shielding of Ha by the through-space related olefinic bond. Such shifts were a reliable method for stereochemical assignments, and the 0.39 ppm upfield shift of bridgehead proton Ha in **9** relative to bridgehead proton Ha in **8** has allowed the *syn*-stereochemistry to be assigned to **8** and the *anti*-stereochemistry to **9**.

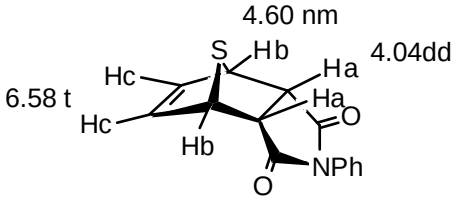
Table 2. [1]H-NMR Chemical shift assignments for adducts formed in the high-pressure reaction of thiophenes **1a, 1d** with *N*-substituted maleimides **2a, 2b** and maleic anhydride **2c**



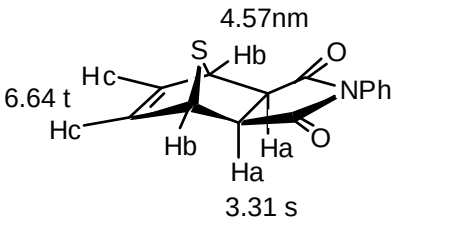
3a



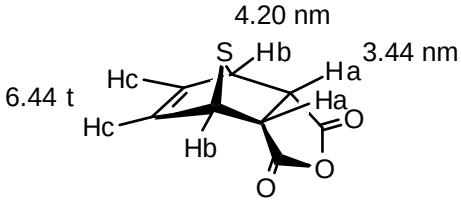
4a



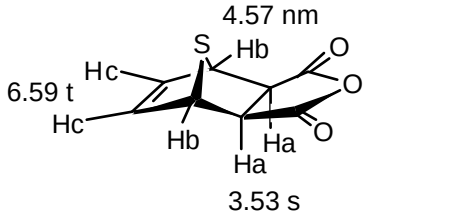
3b



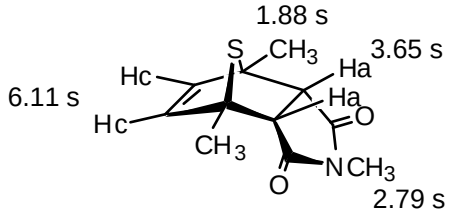
4b



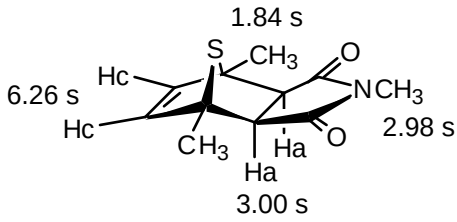
3c



4c

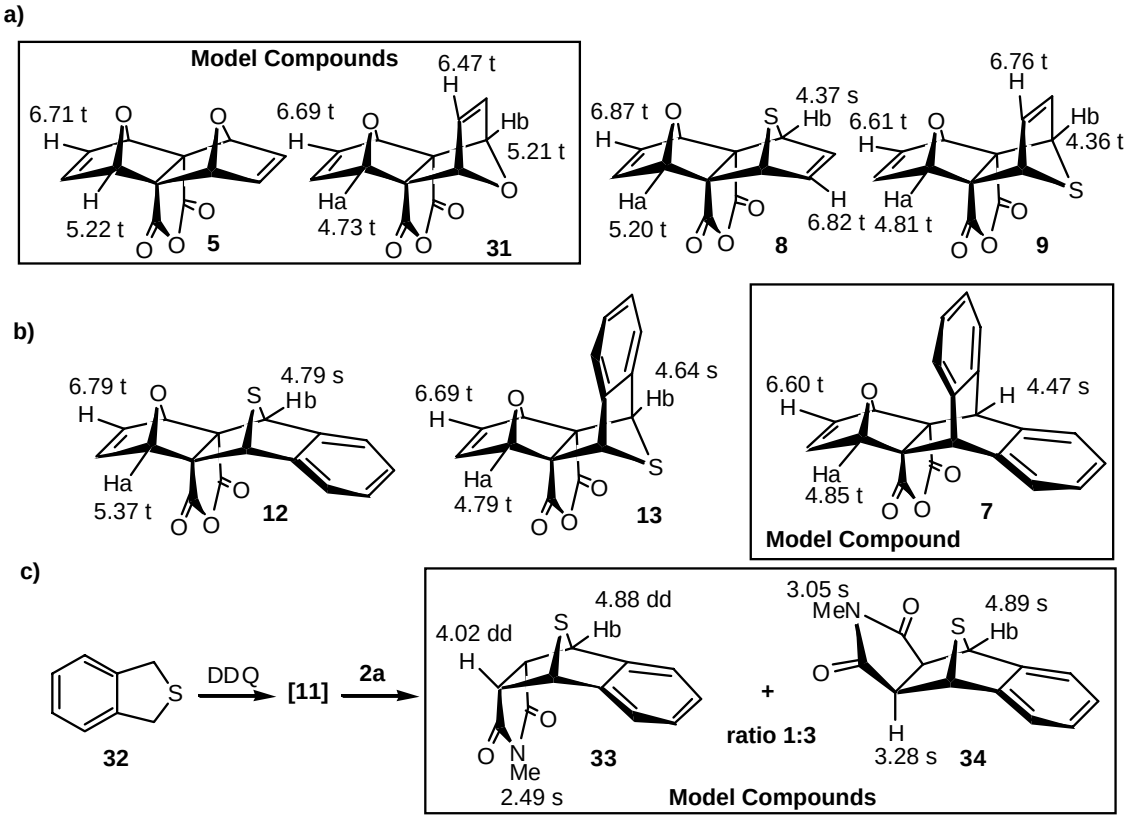


3d



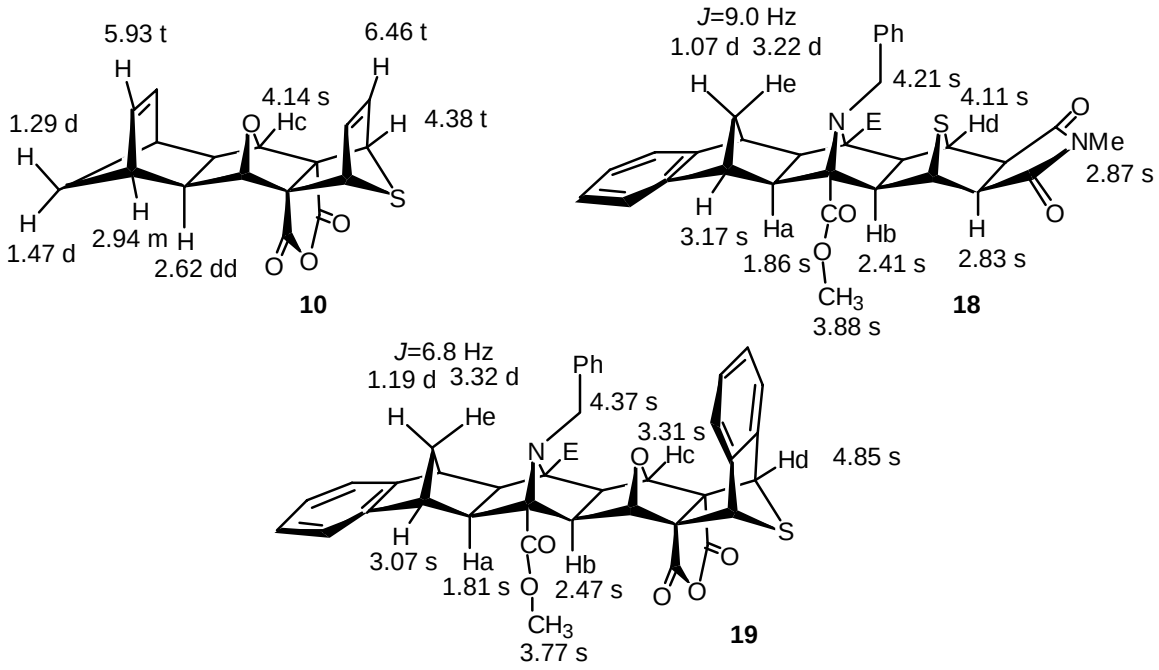
4d

Table 3. [1]H-NMR Chemical shift assignments for *O,S*-sesquinorbornadiene anhydrides **8** and **9**, and their benzoanalogues **12** and **13**, together with model systems **5, 7, 31, 33, 34** (isomers **33** and **34** were formed by reaction of isobenzothiophene **11** with *N*-methylmaleimide **2a**)



With the *O,S*-benzosesquinorbornadienes **12** and **13**, a similar shielding effect on bridgehead protons Ha was apparent (Table 3b) and was attributed to the anisotropy of the benzene ring. The observed effect was even more pronounced in this case with a shift difference between bridgehead protons Ha in **12** and **13** of 0.58 ppm. The similarity between bridgehead protons Ha in model compound **7** (where there must be similar shielding from the benzene ring), with bridgehead protons Ha in **13** was in keeping with the bent-frame stereochemistry assigned to **13**. The second set of model compounds **33** and **34** (Table 3c) confirmed that there was little difference in chemical shift at the bridgehead protons Hb of the sulfur bridge. This observation ruled out a role for the imide ring irrespective of its configuration and confirmed that shift differences in the compounds discussed above, eg **8** v **9** or **12** v **13** were the result of anisotropy from another source, *viz* olefinic π-bond in the former pair or aryl ring in the latter pair. The proton chemical shift of the *N*-methyl group was again diagnostic of stereochemistry with the *endo*-isomer **33** being shifted upfield by 0.56 ppm relative to **34**, owing to the shielding influence of the aryl ring.

Table 4. [1]H-NMR chemical shift assignments for [3]polynorbornanes **10, 18** and the [4]polynorbornane **19**, each containing a single sulfur bridge



Chemical shift assignments for [n]polynorbornanes **18** and **19** have been determined on the basis of coupling data, comparison of chemical shift data with other [n]polynorbornanes derived from aziridine **16** or chemical shift data collected in this paper. Noteworthy features include:
i) the significant downfield shift (steric compression)[28] of the methano-bridge protons (He) adjacent to the nitrogen bridge in compounds **18** and **19**
ii) the large upfield shift of the oxa-bridge bridgehead proton (Hc) in **19** caused by anisotopic shielding of the aryl ring as discussed above.
iii) a similar upfield shift of Hc in **10** of reduced magnitude has been ascribed to olefinic π-bond shielding
iv) the downfield shift (δ 4.85) of the sulfur bridgehead protons Hd in **19** consistent with their benzylic nature and in keeping with model structures **33** and **34**. The related bridgehead protons Hd in **18** lack the fused aromatic ring and occur at δ 4.11.

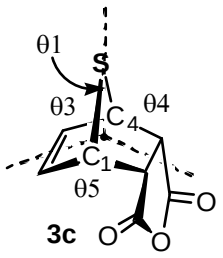
Molecular modeling

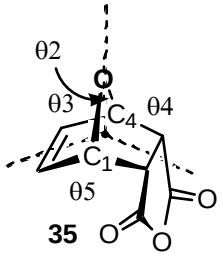
In this section we address several issues pursuant to the shape of *S*-bridged [n]polynorbornanes. In particular, separate sections dealing with i) the 3D geometry of 7-thianorbornenes and *S*-bridged sesquinorbornadienes, ii) the topology of multi-*S*-bridged [n]polynorbornanes and iii) the conformational (invertomer) preferences of *N*-benzyl substituents in XNS-[n]polynorbornanes are presented, in that order.

i) 7-Thianorbornene and *S*-bridged sesquinorbornadienes

Calculations have been conducted at the AM1 level of theory on *endo*-7-thianorbornene anhydride **3c** and its oxygen heterologue **35** and the energy-minimized structures determined. Aside from selected bond angles and bond lengths, inter-planar angles relating the planes defined by the bridgehead carbons and the heteroatom, the etheno bridge or the ethano bridge were determined. Comparisons between the inter-planar angles (θ3 and θ4) indicated the relationship of the hetero-bridge with the boat-shaped cyclohexene ring that constituted the carbocyclic frame. These angular differences revealed that the oxygen bridges were bent away from the etheno-bridge and towards the ethano-bridge to a larger extent than the sulfur bridges. Reference to the inter-planar angles between the carbocyclic bridges showed that the cyclohexene ring component in the oxygen bridged system **35** was more puckered (by ca 6°) than its sulfur counterpart **3c**. The separation of the bridgehead carbons C_1 and C_4 in the two systems (2.418 v 2.205 Å) provided an additional measure of the geometrical change in the cyclohexene ring. In spite of the fact that the C-S bonds in **3c** are significantly longer than the C-O bonds in **35** (1.84 v 1.47 Å), the shape of the carbocylic frames of the two structures remained similar. This becomes apparent in AMI minimised structures of **3c** and **35** and the overlay of the two shown in Figure 1. The inter-planar angles (θ5) between the etheno and the ethano bridges are 117.61° for **3c** and 111.70° for **35** and this largely determines the shape of the fused products, *viz* the increased curvature of sulfur-bridged systems compared to their oxygen analogues (*vide supra*).

Table 5. Calculated parameters (AM1) for heteronorbornene anhydrides **3c** and **35**





Bridge Angle (θ1,θ2)	$C_1SC_4 = 82.15^o$	$C_1OC_4 = 97.47^o$
Inter-planar Angles	θ3 = 124.55° θ4 = 117.84° θ5 = 117.61	θ3 = 128.62° θ4 = 119.68° θ5 = 111.70°
Bridge Bond Lengths	$C_{1(4)}$-S = 1.840Å	$C_{1(4)}$-O = 1.467Å
Bridgehead Separations	C_1 C_4 = 2.418Å	C_1 C_4 = 2.205Å

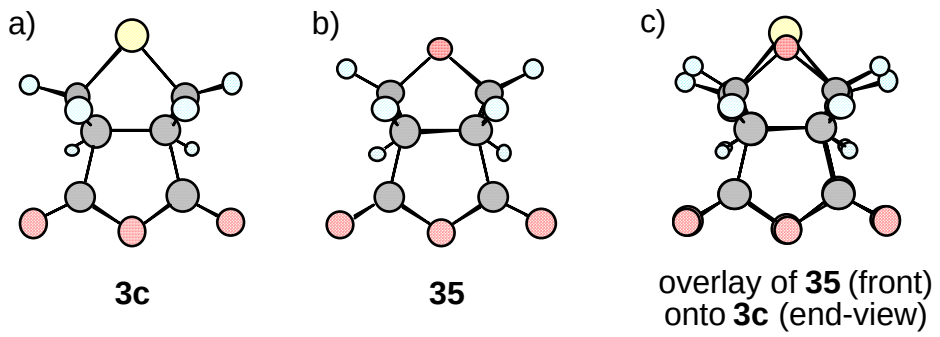
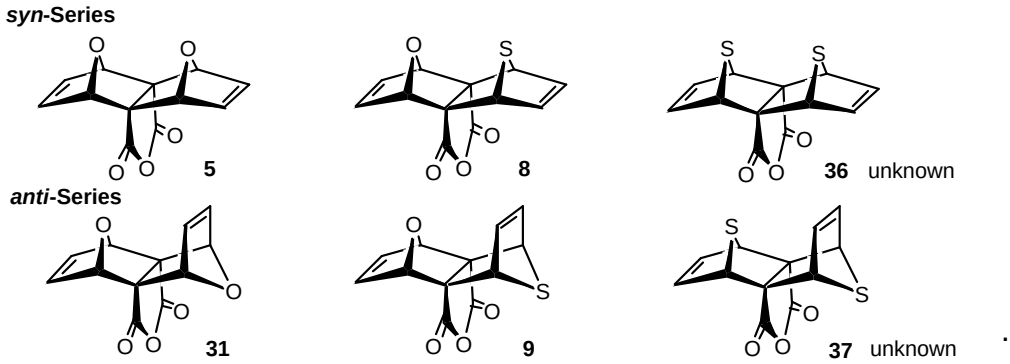


Figure 1. The minimized (AM1) structure for a) 7-thianorbornene-5,6-dicarboxylic anhydride **3c**, b) 7-oxanorbornene-5,6-dicarboxylic anhydride **35**, c) overlay of **3c** and **35** from an end-view perspective.

In the related XY-sesquinorbornadiene anhydride systems, the energy-minimized structures (AM1) for the *syn*-isomers in the *O,O*-, *S,S*- and *O,S*-systems have been computed (Figure 2 a, b, c respectively) and the parameters for these and the corresponding *anti*-isomers tabulated in Table 6. As a generalization, it was clear once again that the geometry of all the systems were similar with only small but significant changes. In the *syn*-series where the two hetero-bridges are juxtaposed, it was possible to determine the role of each heteroatom on the sesquinorbornadiene geometry. *S,O*-interaction in **8** caused an away movement of the *O*-bridge and attendant shift of the ethano-bridge towards the anhydride ring. Reference to overlays of **35** on **8** (Figure 2g) and **3c** on **8** (Figure 2h) demonstrated that both the *S*-bridge and the *O*-bridge had been moved outwards and that both etheno-bridges bent downwards as reflected in the decreased inter-planar angles. That the *S*-bridge was the cause of the second bridge distortion was confirmed by the outward bending of both *S*-bridges in the *S,S*-system **36**. In contrast, the *O,O*-sesquinorbornadiene anhydride **5** showed no *O*-bridge distortion.

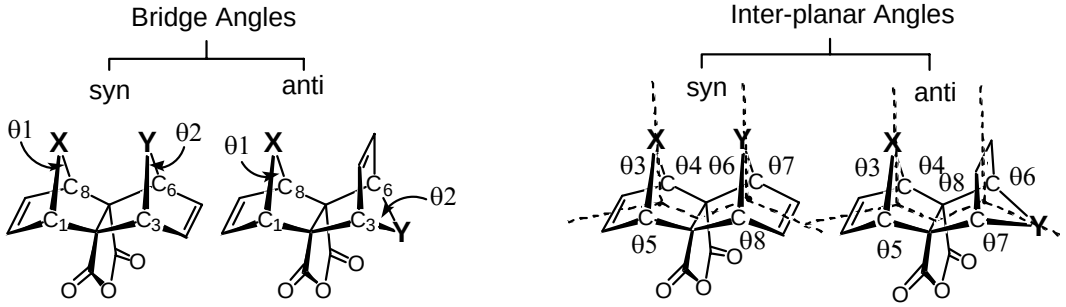
Comparison of the geometries of the *O,O*-system **5** with the *S,S*-system **36** demonstrated that despite the differences in bond length (C-O v C-S), cyclohexene interplanar angles (110.88^{o} for **5** v 116.02^{o} for **36**) as well as the heterobridge interactions (*O,O* v *S,S*), these parameters turn out to be compensatory and the frame projections (especially those of the cyclohexene subunits which constitute the zig zag carbocyclic frame) were surprisingly similar. Indeed, the separations of the terminal sp2 carbons of the separate π-bonds were almost identical (4.93 Å in **5** v 4.87 in **36**). Of course, these small differences are additive and can be expected to still make substantial differences in curvature to the frames of larger [n]polynorbornadienes.

Table 6. Bond lengths and inter-planar angles for the *syn*- and *anti*-isomers of the *O,O, O,S, S,S*-bridged sesquinorbornadiene anhydrides as determined by AM1 calculations



Sesqui-norbornadiene anhydride	Bond Lengths (Å)		Distances (Å)			Bridge Angles C_1XC_8 C_3YC_6		Inter-planar Angles (degrees)*			
	C-X	C-Y	C_1-C_8	C_3-C_6	X-Y	θ1	θ2	θ3	θ4	θ6	θ7
O,O *syn*- **5**	1.466	1.466	2.214	2.214	2.625	98.06	98.06	128.30	120.82	120.82	128.30
O,S *syn*- **8**	1.463	1.837	2.210	2.423	2.859	98.12	82.51	127.41	122.44	123.10	121.68
S,S *syn*- **36**	1.831	1.831	2.417	2.417	2.875	82.60	82.60	121.28	122.70	122.70	121.28
O,O *anti*- **31**	1.467	1.471	2.217	2.218	3.853	98.16	97.88	127.64	121.77	119.46	128.18
O,S *anti*- **9**	1.465	1.847	2.211	2.433	4.226	94.97	82.37	127.79	121.49	119.23	123.18
S,S *anti*- **37**	1.837	1.850	2.421	2.431	4.485	82.46	82.16	121.76	122.89	118.57	122.52

* θ5 = 360-(θ3+θ4); θ8 = 360-(θ6+θ7)



ii)Topology of *S*-bridged [n]polynorbornanes

Revisiting the role of heteroatom-bridges (N and O systems described earlier)[6,8] in governing the shape of [n]polynorbornadienes, we have calculated (AM1) structures for two hypothetical systems, *viz* the S^9-polynorbornadiene **38** and $(CS)^4C$-polynorbornadiene **39** (Diagram 1, Figure 4). A comparison of the radii of curvature of these *S*-bridged systems placed them respectively between the corresponding N^9- and O^9- (same atom-bridge series) and the $(CN)^4C$- and $(CO)^4C$-analogues (alternate atom-bridge series) as shown in the Tables **7a,b**.

38 X = S S^9-[9]polynorbornane

39 X = CH_2 $(CS)^4C$-[9]polynorbornane

Diagram 1

A consequence of replacing alternative sulfur bridges in **38** by methano-bridges to form **39** was that the curvature of the carbocyclic frame in **39** became more curved and the inter-planar relationship (angle ϕ) of the terminal norbornenes changed from being divergent in **38** to convergent in **39**. This structural feature was not apparent in the oxygen or nitrogen hetero-[n]polynorbornanes studied earlier: both series are convergent in the N^9 and $(CN)^4C$-systems and both divergent in the O^9 and $(CO)^4C$-systems.

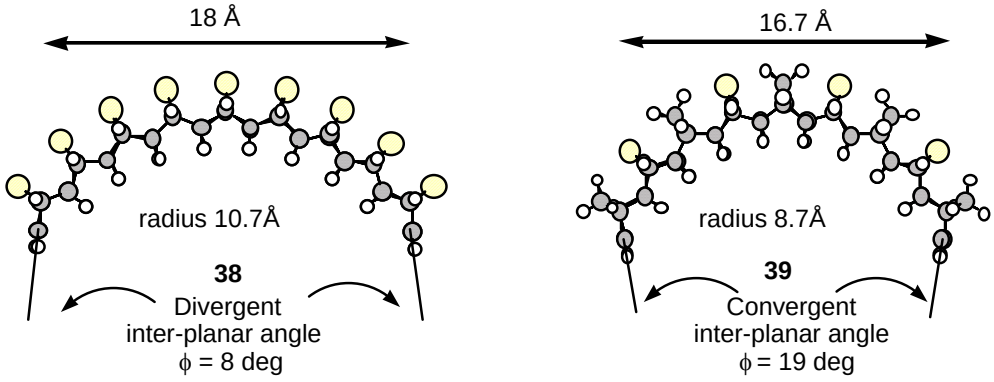


Figure 4. Molecular models (AM1) of *S*^{9}-[9]polynorbornadiene **38** and $(CS)^4C$-[9]polynorbornadiene **39**.

Table 7. Radius of curvature of carbocyclic frame in a) same atom-bridged X^9[9]polynorbornadienes and b) alternate atom-bridged $(CX)^4C$-[9]polynorbornadienes

a) Same atom-bridged series

[9]Polynorbornadiene	Radius Å
C^9	5.9
$(NMe)^9$	7.1
S^9	10.7
O^9	13.7

b) Alternate atom-bridged series

[9]Polynorbornadiene	Radius Å
$(CNMe)^4C$	7.0
$(CS)^4C$	8.7
$(CO)^4C$	11.2

iii) *N*-Benzyl invertomerisation in *XNS*-trident polynorbornanes

Molecular modeling had not been conducted previously for [3]polynorbornadienes containing a sulfur bridge (*XNS*-tridents). The molecular model (AM1) of the *CNS*-

[3]polynorbornane **18**, revealed that the methylene of the *N*-benzyl group was positioned on the sulfur side rather than on the side of the methano-bridge. This was not unexpected since our earlier results on the effects of flanking 'sentinel' groups (Y) in *CN(Bn)Y*- tridents had demonstrated the dominance of the CH_2-sentinel over oxygen and nitrogen sentinels.[22b]

The *ONS*-trident system offered an interesting comparison since this would be the first example of different hetero-bridge sentinels which are not complicated by substituents. It should be appreciated that the *ONO*-tridents are dynamic and do not assume a preferred invertomer geometry in solution. Calculations (AM1) indicated that the *ONS- tridents* exhibited two minimum energies, one for the invertomer adjacent to the *O*-bridge and another adjacent to the *S*-bridge with the former being favored by 3.3 kcal/mol. An experimental study relating to this topic is currently under investigation.

The model (AM1) of the *CNOS*-[4]isopolynorbornane **19** where the *N*-benzyl was positioned between a methano-bridge and an oxygen-bridge, a system with precedent in the *CNO*-trident series, again favored the invertomer directed towards the *O*-bridge (see Figure 1b). The critical bridge *N*-*O* distance was 2.97Å, typical of such tridentane structures.[22]

Another structural feature of **19** was the inter-planar relationship of the terminal benzene rings. As a consequence of the *S*-bridge having an *anti*-relationship to the other bridges of the polynorbornane the terminal benzene rings are pointing in opposite directions and the modeling shows that they are not far removed from being parallel. Such an orientation should be helpful in molecular design for the orientation of functionality on molecular frames.

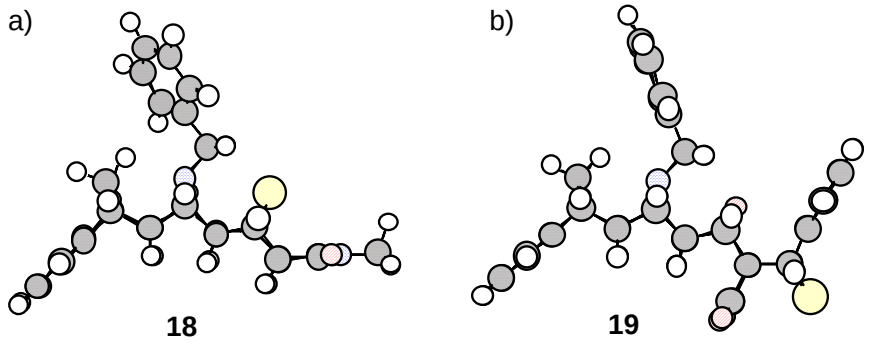


Figure 5. Molecular Models (AM1) of (a) *CNS*-[3]polynorbornane **18** (b) *CNOS*-[4]polynorbornane **19**.

Conclusions

This study has demonstrated that 7-thianorbornenes were extremely poor as dienophiles or dipolarophiles, a property that severely restricted their use for the building of sulfur-bridged [n]polynorbornanes. However, the ability of 7-thianorbornene **4a** to react stereo-selectively at the olefinic π-bond with ester-activated aziridinocyclobutene **16** to yield the cycloadduct **18** has

proved the exception to the rule and has opened the way for preparing other *XNS*-[3]polynorbornanes.

By incorporating the sulfur bridge within an *O,S*-sesquinorbornadiene such as **13** allowed site-selective coupling at the activated 7-oxanorbornene π-bond and accession to the prototype *XNOS*-[4]polynorbornane **19**. This coupling protocol should also be suitable for 7-oxanorbornenes such as **9**, **12** and **13** and has the potential to be extended to the other aziridinocyclobutene reagents mentioned above. As well, cycloaddition with other 4π-reagents should also be possible, since 7-oxanorbornenes are known to participate in Diels-Alder and 1,3-dipolar coupling reactions.

Attempts to produce 7-thianorbornadiene-2,3-dicarboxylic anhydride **20** or its benzo-analogue **22** in order to improve their dienophilicity and dipolarophilicity, via FVP-induced retro-Diels-Alder reactions involving loss of furan from adducts **8**, **9** or **12, 13** were thwarted by additional loss of the sulfur bridge under the thermal condition and led only to aromatic products. Clearly, special methods will need to be devised to form 7-thianorbornadienes **20** or **22**.

S-Bridged alicycles has remained a challenging area of synthesis and this study has exposed some of the deficiencies of cycloaddition chemistry in this area. Nevertheless, the first *S*-bridged [n]polynorbornadiene has been prepared, some light has been shone on the way ahead and interesting challenges delineated for those wishing to follow down this road of research.

Experimental Section

General Procedures. Melting points, which are uncorrected, were obtained on a Reinhart Micro hot stage melting point apparatus Model YOSCO No. 67885. ^{1}H NMR spectra were recorded at 300 or 400 MHz. ^{13}C NMR spectra were recorded by using an inverse gated sequence at 75.4 MHz. Unless otherwise stated all data were acquired using $CDC1_3$ solutions with TMS as an internal standard and are reported on the appropriate δ_H and δ_C scales. Coupling constants are reported in Hz.

The silica gel used for column chromatography was silica gel 60 (230-400 mesh). TLC was performed on Merck aluminium sheets coated with silica gel $50F_{254}$. Centrifugal radial chromatography was carried out with a Chromatotron, Model No. 7924T, using 1mm plates coated with silica gel 60 F_{254}.

Mass spectra were obtained by EI or PCI (photochemical ionisation) on a Hewlett Packard 5988A spectrometer or by EI or ESMS (electrospray mass spectrometry) on a Micromass Platform II single quadripole mass spectrometer.

Reaction of *N*-methylmaleimide with thiophene. A solution of *N*-methylmaleimide (60 mg, 0.54 mmol) and thiophene (excess) in dichloromethane (1 ml) was pressurized at 10 kbar and heated to 100 ^{O}C overnight. After cooling, solvent and excess thiophene were removed *in vacuo* and the residue separated by radial chromatography (petroleum ether - ethyl acetate 10:1, then the solvent polarity was gradually increased to ethyl acetate). Elution order **4a** (12 mg, 11 %,

m.p. 137-139 °C), **3a** (15 mg, 14 %, m.p. 150-152 °C), compound **30** (4 mg, 1 %, m.p. 282-284 °C).

(1α,2α,6α,7α) 4-Methyl-4-aza-10-thiatricyclo[5.2.1.0^{2,6}]deca-8-en-3,5-dione (*endo*- adduct) *3a*. NMR data: δ_H ($CDCl_3$) 2.79 (3H, s), 3.84 (2H, dd, *J*=1.4 Hz, *J*=2.0 Hz), 4.44 (2H, nm), 6.38 (2H, t, *J*=2.0 Hz). δ_C ($CDCl_3$) 24.9, 51.6, 53.0, 137.2, 175.4. HRMS (*m/z*): calcd. for $C_9H_9NO_2S$: 195.0354 found: 195.0348.

(1α,2β,6β,7α) 4-Methyl-4-aza-10-thiatricyclo[5.2.1.0^{2,6}]deca-8-en-3,5-dione (*exo*-adduct) (4a). NMR data: δ_H ($CDCl_3$) 2.99 (3H, s), 3.15 (2H, s), 4.45 (2H, t, *J*=2.2 Hz), 6.58 (2H, t, *J*=2.2 Hz). δ_C ($CDCl_3$) 25.2, 50.6, 53.8, 140.1, 176.5. HRMS (m/z): calcd. for $C_9H_9NO_2S$: 195.0354 found: 195.0357.

(1α,2β,6β,7α,8β,12β) 4,10-Dimethyl-4,10-diazatetracyclo[5.5.2.0^{2,6}.0^{8,12}]tetradec-13-en-3,5,9,11-tetraone (30). NMR data: δ_H($CDCl_3$), 2.78 (6H, s), 2.98 (4H, br s), 3.73 (2H, s), 6.08 (2H, dd, *J*=3.1 Hz, *J*=4.3 Hz). HRMS (*m/z*): calcd. for $C_{14}H_{14}N_2O_4$: 274.0954 found: 274.0954.

Reaction of *N*-phenylmaleimide with thiophene. A solution of *N*-phenyl maleimide (200 mg, 1.156 mmol) and thiophene (excess) in dichlomethane (1 ml) was pressurized at 10 kbar and 100 °C overnight. After cooling, solvent and excess of thiophene was removed *in vacuo* and residue separated by radial chromatography (petroleum ether - ethyl acetate 10:1, then the solvent polarity was gradually increased to ethyl acetate). Elution order **4b** (31 mg, 10 %, m.p. 166-169 °C), **3b** (76 mg, 26 %, m.p. 174-175 °C)

(1α,2α,6α,7α) 4-Phenyl-4-aza-10-thiatricyclo[5.2.1.0^{2,6}]deca-8-en-3,5-dione (*endo*- adduct) (3b). NMR data: δ_H($CDCl_3$) 4.04 (2H, dd, *J*=1.5, *J*=2.2 Hz), 4.60 (2H, nm), 6.58 (2H, t, *J*=2.2 Hz), 7.11-7.14 (2H, m), 7.39-7.44 (3H, m), δ_C ($CDCl_3$) 51.2, 53.0, 126.4, 128.8, 129.1, 131.5, 136.8, 173.9. HRMS (*m/z*): calcd. for $C_{11}H_{11}O_2NS$: 257.0511 found: 257.0506.

(1α,2β,6β,7α) 4-Phenyl-4-aza-10-thiatricyclo[5.2.1.0^{2,6}]deca-8-en-3,5-dione (*exo*- adduct) (4b). NMR data: δ_H($CDCl_3$) 3.31 (2H, s), 4.57 (2H, t, *J*=2.1 Hz), 6.64 (2H, t, *J*=2.1 Hz), 7.25-7.28 (2H, m), 7.39-7.46 (3H, m). δ_C ($CDCl_3$) 50.6, 54.3, 122.8, 129.3, 129.6, 132.3, 140.4, 175.6. HRMS (*m/z*): calcd. for $C_{14}H_{11}NO_2S$: 257.0511 found: 257.0515.

Reaction of maleic anhydride with thiophene. A solution of maleic anhydride (100 mg, 1.161 mmol) and thiophene (excess) in dichloromethane (1 ml) was pressurized at 10 kbar and heated at 100 °C overnight. After cooling, solvent and excess of thiophene was removed *in vacuo* and residue separated by radial chromatography (petroleum ether - ethyl acetate 10:1, then the solvent polarity was gradually increased to ethyl acetate). The known *endo*-adduct **4c** was isolated in pure form, whereas the previously unreported *exo*-isomer **3c** was only observed as a minor component by ^{1}H NMR and could not be isolated.

(1α,2β,6β,7α) 4-Oxa-10-thiatricyclo[5.2.1.0^{2,6}]deca-8-en-3,5-dione (*exo*-isomer) (3c). NMR data: δ_H ($CDCl_3$) 3.53 (2H, s), 4.57 (2H, s), 6.59 (2H, t).

Reaction of *N*-methylmaleimide with 2,5-dimethylthiophene. A solution of *N*-methyl maleimide (100 mg, 0.90 mmol) and 2,5-dimethylthiophene (excess) in dichloromethane (1 ml) was pressurized at 10 kbar and 100 ^{o}C overnight. After cooling, solvent and excess of thiophene was removed *in vacuo* and residue separated by radial chromatography (petroleum ether - ethyl acetate 10:1, then the solvent polarity was gradually increased to ethyl acetate). Elution order **4d** (33 mg, 16 %, m.p. 169-171 ^{o}C), **3d** (27 mg, 13 %, m.p. 160-162 ^{o}C)

(1α,2α,6α,7α) 1,4,7-Trimethyl-4-aza-10-thiatricyclo[5.2.1.0^{2,6}]deca-8-en-3,5-dione (endo-adduct) (3d). NMR data: δ_H ($CDCl_3$) 1.88 (6H, s), 2.79 (3H, s), 3.65 (2H, s), 6.11 (2H, s). δ_C ($CDCl_3$) 18.3, 24.3, 58.1, 65.1, 141.0, 174.7. HRMS (m/z): calcd. for $C_{11}H_{13}NO_2S$: 223.0667 found: 223.0662.

(1α,2β,6β,7α) 1,4,7-Trimethyl-4-aza-10-thiatricyclo[5.2.1.0^{2,6}]deca-8-en-3,5-dione (exo-adduct) (4d). NMR data: δ_H ($CDCl_3$) 1.84 (6H, s), 2.98 (3H, s), 3.00 (2H, s), 6.26 (2H, s). δ_C ($CDCl_3$) 16.9, 24.3, 56.3, 65.1, 145.0, 174.9. HRMS (*m/z*): calcd. for $C_{11}H_{13}NO_2S$: 223.0667 found: 223.0664.

Reaction of anthracene with 7-oxanorbornadiene-2,3-dicarboxylic anhydride (6). The reaction was conducted in chloroform solution at room temperature. The product was isolated by solvent evaporation and purified by recrystallisation from ethyl acetate/light petroleum, mp 158-159 ^{o}C decomp (hot block).

(1α,2β,3α,6α,7β,8α)-22,24-Dioxaheptacyclo[6.6.6.3^{2,7}.1^{3,6}.0^{2,7}.0^{9,14}.0^{15,20}]tetracos-4,9,11,13,15,17,19-heptaen-21,23-dione (7). NMR data δ_H ($DCD1_3$) 4.77 (2H, s), 4.85 (2H, s), 6.60 (2H, s), 7.14 (2H, m), 7.21 (2H, m), 7.31 (2H, m), 7.34 (2H, s). δ_C ($CDCl_3$) 48.0, 68.0, 82.1, 124.7, 125.4, 127.4, 127.7, 127.9, 128.2, 138.7, 170.1. HRMS (m/z): calcd for $C_{22}H_{14}O_4$: 342.0892 found: 342.0893.

Reaction of thiophene with 7-oxanorbornadien-2,3-dicarboxylic anhydride (6). A solution of anhydride **6** (113 mg, mixture with uncracked **5** in 1.4:1 ratio, 0.287 mmol) and thiophene (600 mg, excess) in dichloromethane (1 ml) was pressurized at 10 kbar and heated at 100 ^{o}C overnight. Solvent and excess thiophene were removed in vacuo and the residue subjected to radial chromatography (petroleum ether - ethyl acetate 10:1, then the solvent polarity was gradually increased to ethyl acetate) to afford, in order of elution, **8** (7 mg, 10 %, m.p. 139-141 ^{o}C) and **9** (32 mg, 45 %, m.p. 185-186 ^{o}C).

(1α,2β,5β,6α,7α1α) 12,14-Dioxa-15-thiapentacyclo[4.4.3.1^{2,5}.1^{7,10}.0^{1,6}]pentadeca-3,8-dien-11,13-dione (*syn-O,S*-sesquinorbornadiene anhydride) (8). NMR data: δ_H ($CDCl_3$) 4.37 (2H, t, *J*=1.9 Hz), 5.20 (2H, t, *J*=0.9 Hz), 6.82 (2H, t, J=0.9 Hz), 6.87 (2H, t, *J*=1.9 Hz). δ_C ($CDCl_3$) 53.9, 75.5, 81.7, 140.9, 144.5, 169.1. HRMS (*m/z*): calcd. for $C_{12}H_8O_4S$: 248.0143 found: 248.0154.

ια,2β,5β,6α,7β1β)12,14-Dioxa-15-thiapentacyclo[4.4.3.1^{2,5}.1^{7,10}.0^{1,6}]pentadeca-3,8-dien-11,13-dione (*anti-O,S*-sesquinorbornadiene anhydride) (9). NMR data: δ_H ($CDCl_3$): 4.36 (2H, t, *J*=2.1 Hz), 4.81 (2H, t, *J*=0.9 Hz), 6.61 (2H, t, *J*=2.1 Hz), 6.76 (2H, t, *J*=0.9 Hz). δ_C ($CDCl_3$)

54.9, 75.6, 80.5, 138.3, 140.3, 170.2. HRMS (*m/z*): calcd. for $C_{12}H_8O_4S$: 248.0143 found: 248.0136.

Reaction of cyclopentadiene with *O,S*-sesquinorbornadiene anhydride (9). Product **10** was obtained in low yield (ca 1%) by reaction of **9** with cyclopentadiene (excess) in chloroform overnight in a sealed glass tube at 80 ^oC. Solvent was removed *in vacuo* and cyclopentadiene dimer under high vacuum. Partial purification was achieved by radial chromatography (petroleum ether - ethyl acetate 10:1).
NMR data (determined from crude spectrum): $\delta_H(CDCl_3)$ 1.29 (1H, d, *J*=8.2 Hz), 1.49 (1H, dt, *J*=8.2 Hz, *J*=1.8 Hz), 2.62 (2H, dd, *J*=2.4 Hz, *J*=1.6 Hz), 2.94 (2H, m), 4.14 (2H, s), 4.38 (2H, t, *J*=2.2 Hz), 5.93 (2H, t, *J*=1.8 Hz), 6.47 (2H, t, *J*=2.2 Hz).

General procedure for isobenzothiophene (IBT) preparation and *in situ* trapping with dienophiles[17].
A solution of 2-thiaindane[16] (100 mg, 0.735 mmol) and 2,3-dichloro-5,6-dicyano1,4-benzoquinone (DDQ) (500 mg, 2.202 mmol) in chloroform (1 ml) was stirred at 70-80 ^oC overnight with an excess of dienophile. Solvent was removed *in vacuo* and the residue subjected to radial chromatography (silica, petroleum ether - ethyl acetate 10:1, then the solvent polarity was gradually increased to ethyl acetate).

Reaction of isobenzothiophene (11) with 7-oxanorbornadien-2,3-dicarboxylic anhydride (6). The instability of **6** required that it be produced immediately prior to reaction. The flash vacuum pyrolysis (FVP) process for the elimination of furan from the *syn-O,O*-sesquinorbornadiene **5**[13] was conducted at temperatures in the range 350-390 ^oC (unpacked pyrex tube, 0.001 mbar) since a compromise was required whereby breakdown of **5** was maximized but not so high that product **6** was subjected to further fragmentation to form furan-3,4-dicarboxylic anhydride by loss of acetylene. The sample used for the production of **12** (11 mg, 8%, m.p. 164-166 ^oC) and **13** (16 mg, 11 %, m.p. 183-184 ^oC) was a 2:1 mixture of anhydride **6** with uncracked **5** (120 mg) and yields were calculated on this basis.
(1α,2β,9β̃ια̣11β̣14β̣)-16,19-Dioxa-18-thiahexacyclo[8.4.3.1^{2,9}.1^{11,14}.0^{1,10}.0^{3,8}] nonadeca-3,5,7,12-tetraen-15,17-dione (*exo,exo*-adduct) (12). NMR data: δ_H ($CDCl_3$) 4.79 (2H, s), 5.37 (2H, t, *J*=0.9 Hz), 6.79 (2H, t, *J*=0.9 Hz), 7.07 (2H, dd, *J*=5.5 Hz, *J*=2.9 Hz); 71.6 (2H, dd, *J*=5.5 Hz, *J*=2.9 Hz). δ_C ($CDCl_3$) 58.4, 75.1, 81.6, 122.0, 128.1, 140.3, 146.3. HRMS (*m/z*): calcd. for $C_{16}H_{10}O_4S$: 298.0299 found: 298.0303.
(1α,2β,9β̃ια11β14β̣)-16,19-Dioxa-18-thiahexacyclo[8.4.3.1^{2,9}.1^{11,14}.0^{1,10}.0^{3,8}] nonadeca-3,5,7,12-tetraen-15,17-dione (*exo,endo*-adduct) (13). NMR data: δ_H ($CDCl_3$) 4.64 (2H, s), 4.79 (2H, s), 6.69 (2H, s), 7.14 (2H, dd, *J*=5.1 Hz, *J*=3.3 Hz); 7.22 (2H, dd, *J*=5.1 Hz, *J*=3.3 Hz). δ_C ($CDCl_3$) 57.1, 75.3, 80.7, 122.0, 129.2, 139.9, 143.7, 169.9.
HRMS (*m/z*): calcd. for $C_{16}H_{10}O_4S$: 298.0299 found: 298.0294.

Reaction of isobenzothiophene 11 with dimethyl 7-oxanorbornadien-2,3-dicarboxyate (14). The product **15** (6 mg) was obtained in 7% yield, m.p. 144-147 °C

ıα,2β,3α,6α,7β,8α Dimethyl 16-oxa-15-thiapentacyclo[6.6.1.$1^{3,6}$.$0^{2,7}$.$0^{9,14}$] hexadeca-4,9,11,13-tetraen-4,5-dicarboxylate 15. NMR data: δ_H ($CDCl_3$) 3.80 (6H, s), 4.39 (2H, t, *J*=0.9 Hz), 4.63 (2H, s), 6.56 (2H, t, *J*=0.9 Hz), 7.05-7.10 (4H, m). δ_C ($CDCl_3$) 60.7, 74.8, 82.7, 120.1, 128.3, 139.0, 146.8, 172.1. HRMS (m/z): calcd. for $C_{18}H_{16}O_5S$: 344.0718 found: 344.0731.

Reaction of isobenzothiophene with *N*-methylmaleimide. Following chromatography, the *endo*-adduct **33** was obtained (33 mg, 12%) as an oil, together with the *exo*-adduct **34** (11 mg, 4%) which was also an oil.

(1α,8α,9α13α) 11-Methyl-11-aza-14-thiatetracyclo[6.5.1.$0^{2,7}$.$0^{9,13}$]tetradeca-2,4,6,-trien-10,12-dione (*endo*-adduct) (33).

NMR data: δ_H ($CDCl_3$) 2.49 (3H, s), 4.02 (2H, dd, *J*=1.6 Hz, *J*=2.9 Hz), 4.88 (2H, dd, *J*=1.6 Hz, *J*=2.9 Hz), 7.05 (2H, dd, *J*=3.3 Hz, *J*=5.3 Hz), 7.14 (2H, dd, *J*=3.3 Hz, *J*=5.3 Hz). δ_C ($CDCl_3$) 30.1, 53.4, 55.4, 125.9, 129.8, 142.8, 174.9. HRMS (*m/z*): calcd. for $C_{13}H_{11}O_2NS$: 245.0510 found: 245.0509.

(1α,8α,9β13β)-11-Methyl-11-aza-14-thiatetracyclo[6.5.1.$0^{2,7}$.$0^{9,13}$]tetradeca-2,4,6,-trien-10,12-dione (*exo*-adduct) (34).

NMR data: δ_H ($CDCl_3$) 3.05 (3H, s), 3.28 (2H, s), 4.89 (2H, s), 7.07 (2H, dd, *J*=3.5 Hz, *J*=5.1 Hz), 7.23 (2H, dd, *J*=3.5 Hz, *J*=5.1 Hz), δ_C 29.8, 51.9, 56.0, 120.6, 129.2, 146.6, 176.4. HRMS (*m/z*): calcd. for $C_{13}H_{11}O_2NS$: 245.0510 found: 245.0514.

Flash vacuum pyrolysis (FVP). The mixture of adducts **12** and **13** (20 mg, 0.067 mmol) was subjected to FVP at 370 °C (0.005 mbar) to afford naphthalene 2,3-dicarboxylic anhydride **23**, as a yellow-colored solid (8 mg, 60 %).

(1α,2β,3α1α11β12α13β14α15β19β,20α,21β) Dimethyl 22-benzyl-17-methyl-17,22-diaza-24-thiaheptacyclo[10.9.1.1^{3,10}.$0^{2,11}$.$0^{4,9}$.$0^{13,21}$.$0^{15,19}$]tricos-4,6,8-trien-1,12-dicarboxylate (CNS-[3]polynorbornane) (18). A solution of aziridine **16** (80 mg, 0.0205 mmol) and alkene **4a** (40 mg, 0.205 mmol) in chloroform was evaporated to dryness and melted at 100 °C for 1 hour. The resulting mixture was subjected to radial chromatography (petroleum ether - ethyl acetate 10:1, then the solvent polarity was gradually increased to ethyl acetate) to afford pure *CNS*-[3]polynorbornane **18** as a colourless solid (49 mg, 41 %, m.p. 175-176 °C).

NMR data: δ_H ($CDCl_3$) 1.07 (1H, d, *J*=9.0 Hz), 1.86 (2H, s), 2.41 (2H, s), 2.83 (2H, s), 2.87 (2H, s), 3.17 (2H, s), 3.22 (2H, d, *J*=9.0 Hz), 3.88 (6H, s), 4.11 (2H, s), 4.21 (2H, s), 6.99-7.08 (4H, s), 7.17-7.19 (1H, m), 7.26 (2H, t, *J*=6.0 Hz), 7.44 (2H, d, *J*=7.1 Hz). δ_C 25.3, 43.5, 46.9, 52.0, 52.4, 52.5, 57.4, 57.8, 60.9, 76.3, 121.1, 126.2, 126.5, 128.2, 126.9, 142.8, 149.6, 170.3, 176.4. HRMS (*m/z*): calcd. for $C_{33}H_{32}O_6N_2S$: 584.1981 found: 584.1974.

(1α,2β,3α,4β,5α,6β13β14α15β16α17β18α19α,26α) Dimethyl 31-benzyl-26,29-dioxo-31-aza-28,30-dioxa-33-thia-undecacyclo[16.8.3.1^{2,17}.$1^{4,15}$.$1^{6,13}$.$1^{19,26}$.$0^{1,18}$.$0^{3,16}$. $0^{5,14}$.$0^{7,12}$.$0^{20,25}$]tritriacont-7,9,11,20,22,24-hexaen-4,15-dicarboxylate (*CNOS*-

[4]polynorbornadiene) (19). A mixture of aziridine **16** (100 mg, 0.257 mmol) and alkene **13** (48 mg, 0.161 mmol) was melted at 120 ^{o}C for 1 hour. The resulting mixture was subjected to radial chromatography (petroleum ether - ethyl acetate 10:1, then the solvent polarity was gradually increased to ethyl acetate) to afford **19** as a colourless solid (37 mg, 33 %, m.p. 270-272 ^{o}C). NMR data: δ_H ($CDCl_3$) 1.19 (1H, d, *J*=9.0 Hz), 1.81 (2H, s), 2.47 (2H, s), 3.07 (2H, s), 3.32 (2H, s), 3.33 (1H, d, *J*=9.0 Hz), 3.77 (6H, s), 4.37 (2H, s), 4.85 (2H, s), 7.04-7.05 (6H, m), 7.19-7.31 (7H, m). δ_C 43.8, 46.2, 52.5, 53.4, 56.4, 56.9, 58.9, 75.8, 77.4, 79.4, 121.2, 121.6, 125.4, 126.5, 126.6, 128.0, 128.3, 135.6, 143.4, 149.2, 169.5, 170.2. HRMS (*m/z*): calcd. for $C_{40}H_{33}O_8NS$: 687.1927 found: 687.1927.

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