CROWDED AROMATIC COMPOUNDS WITH UNUSUAL SHAPES AND STRUCTURES

AN ABSTRACT

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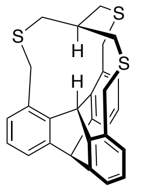
Abstract

Condensation of 1,8,13-tris(mercaptomethyl)triptycene and tris(bromomethyl)methane yields the *in,in*-cyclophane **30** in 8% yield with two inwardly directed methine groups. The X-ray analysis clearly shows that it is the *in,in*-isomer. The proton NMR spectrum displays an obvious coupling between the two methine hydrogens, which was proved by selectively irradiation one of the apical methine proton. The coupling constant is 2.0 Hz, which is the largest through-space coupling observed so far. Based on DFT and MP2 calculations, the hydrogen-hydrogen non-bonded contact distance is estimated to be 1.50-1.53 Å.



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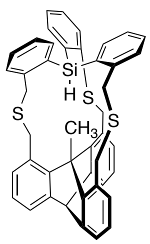

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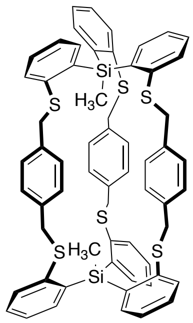

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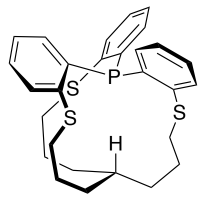
Two *in,in*-cyclophanes **31** and **56**, containing one or two methyl groups in their central cavities, have been synthesized, crystallized and fully characterized by ^{1}H and ^{13}C NMR spectroscopy, MALDI-TOF mass spectrometry, IR spectroscopy, and X-ray crystallography. Cyclophane **31** is the first example of an *in,in*-cyclophane with a methyl group inside the cavity. The IR spectrum clearly shows that the Si-H stretch is blue-shifted from 2177 cm^{-1} in an acyclic model to 2269 cm^{-1}. Based on computational studies, cyclophane **31** has a very short non-bonded H---CH_3 distance of about 2.30 Å. Cyclophane **56** does not have short non-bonded contact distance, but it is the first example of a

macrobicyclic compound that contains two inwardly directed methyl groups.

Three cyclophanes with the formula $(C_{28}H_{31}PS_3)_n$, where n = 1 or 2, were isolated from the base-promoted macrocyclization of tris(2-mercaptophenyl)phosphine and tris(3-bromopropyl)methane. Spectroscopic and X-ray analysis showed them to be the *in,in*-isomer **32**, the *in,out*-isomer **60**, and a dimeric *in,out,in,out*-isomer **61**. Compounds **32** and **61** display approximately C_3-symmetric and C_i-symmetric structures, respectively, in the crystal, but compound **60** adopts two distinct low-symmetry conformations in the solid state. In each case, the observed structures correspond to the lowest energy conformations of their respective isomers as calculated at the B3PW91/6-31G(d) level of theory. The *in,in*-isomer **32** displays a close contact between the phosphine *in*-lone pair and the *in*-methine group, with through-space spin-spin coupling constants of J_{PH} = 9 Hz and J_{PC} = 24 Hz, the latter of which appears to be the largest reported phosphorus-carbon through-space coupling constant.



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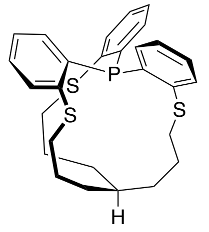

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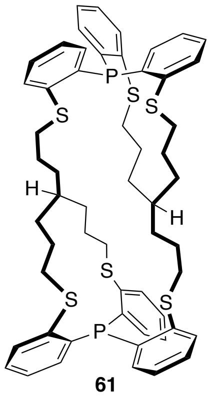
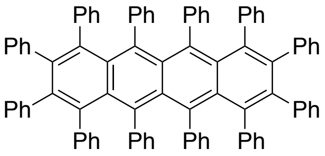


61

Dodecaphenyltetracene (**75**), the largest perphenylacene yet prepared, was synthesized from known tetraphenylfuran, hexaphenylisobenzofuran, and 1,2,4,5-tetrabromo-3,6-diphenylbenzene in three steps. The X-ray structure of the deep red, highly luminescent **75** shows it to be a D_2-symmetric molecule with an end-to-end twist of 97°. The central acene is encapsulated by the peripheral phenyl substituents, and as a result, the molecule is relatively unreactive and even displays reversible electrochemical oxidation and reduction.

Decaphenylphenanthrene (**77**), the first nonlinear perphenyl polycyclic aromatic hydrocarbon to be prepared so far, has been made from tetraphenylfuran and 1,2,3,4-tetrabromo-5,6-diphenylbenzene in two steps. The X-ray structure contains two independent molecules of **77**, and each of them ppssesses approximate C_2 symmetry in the crystal.



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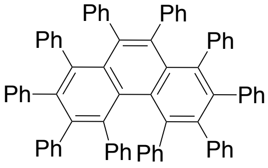

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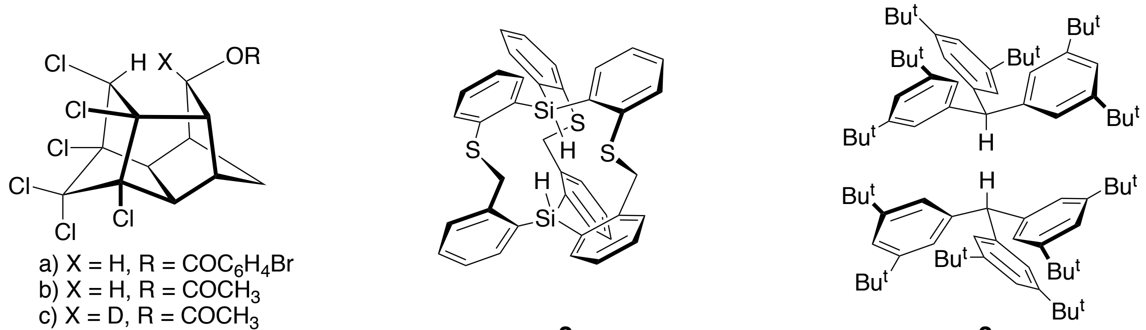
1.1. Short non-bonded contacts

Non-covalent interactions and non-bonded contacts differ from covalent bonds in that they do not involve the sharing of electrons, but rather electrostatic interactions or dispersion forces between molecules or within a molecule. The chemical energy released in the formation of non-covalent interactions is typically on the order of 1-7 kcal/mol. There are various non-covalent interactions, such as electrostatic interactions, van der Waals forces, and hydrophobic effects.

It is common to find non-bonded contacts in molecules, but to make very short non-bonded contacts is challenging. The pentacyclic half-cage compound **1** (Figure 1.1) was first prepared in 1960,[1] but in 1985 Ermer showed that it possessed two hydrogen atoms separated by only 1.617(3) Å, as measured by low-temperature neutron diffraction (Figure 1).[2] At that time, it was the shortest experimentally determined non-bonded hydrogen-hydrogen contact distance. Later, in 2013, Pascal reported an exceptional steric congestion in the *in,in*-bis(hydrosilane) **2**.[3] A combination of crystallographic and computational data indicated that in compound **2**, the central hydrogen-hydrogen non-bonded contact distance was the shortest for any crystallographically characterized compound: approximately 1.56 Å. A later neutron diffraction analysis of compound **2** showed the distance between the central hydrogen atoms to be 1.531(8) Å.[4] In 2018, Schreiner reported the neutron structure of tris(3,5-*tert*-butylphenyl)methane (**3**) at 20 K, which revealed an intermolecular C-H···H-C distance of only 1.566(5) Å.[5] This compound is unique because it crystallizes as a C_3-symmetric dimer in an unusual head-to-head fashion. Quantum chemical computations of the solid state structure at the HSE-3c level of theory reproduce the structure and the close contact well (1.555 Å at 0 K) and emphasize the significance of packing effects.



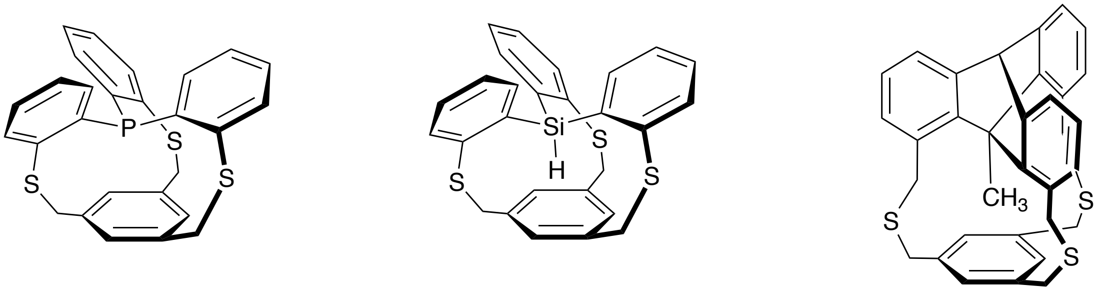
a) X = H, R = COC_6H_4Br
b) X = H, R = $COCH_3$
c) X = D, R = $COCH_3$

1 **2** **3**

Figure 1.1. Examples of molecules having short non-bonded hydrogen-hydrogen contacts

In 1990, Pascal *et al*. reported the synthesis and crystallographic characterization of cyclophane **4** (Figure 1.2).[6] The X-ray structure of compound **4** showed that the phosphine is strongly pyramidalized toward the basal aromatic ring. The average C-P-C bond angle observed in the triarylphosphine is 103°, and the distance from the phosphorus to the ring center is 2.90 Å. Later they reported silicon-containing cyclophane **5**.[7] In the X-ray structure of compound **5**, the distance from the apical silicon to the center of the basal aromatic ring is 3.34 Å, which is the shortest non-bonded silicon-benzene distance. The ^1H NMR spectrum of **5** is characterized by a high-field Si-H resonances (δ 1.04, 5 ppm upfield from the corresponding resonance in an acyclic model), and the IR spectrum shows a high-frequency Si-H stretching band (2457 cm^{-1}, 280 cm^{-1}

above the acyclic model). In 2005, Song *et al*. reported the *in*-methylcyclophane **6** in which the methyl group is forced into the center of the basal aromatic ring, an interesting structural feature. The X-ray structure showed the C_{methyl}-ring centroid distance in molecule **6** to be 2.896(5) Å which was the new "world record" (Figure 2).[8]



4 **5** **6**

Figure 1.2. Other examples of molecules with short non-bonded contacts

1.2 Bridged bicyclic systems

Bridged bicyclic molecules with small rings always have structures in which the bridgehead substituents point outward, as in, for instance, camphor and bicyclo[1.1.1]pentane. Yet for compounds containing medium and large rings, *in/out* isomerism is often observed. It was Simmons and Park who first synthesized a series of macrobicyclic diammonium ions in 1968 (Figure 1.3), and it was they who introduced the term *in/out* stereoisomerism.[9,10,11] They noted that three stereoisomers of the ammonium ions can exist when the number of methylene groups in each linking arm, a, b and c, is greater than six. The different isomers were labeled "*out,out*", "*out,in*", or "*in,in*", depending on the positions of the ammonium hydrogens. Those isomers can interconvert either by protonation/deprotonation (Figure 1.3) or homeomorphic isomerism, as in the case of methine bridgeheads (Figure 1.4).[12]

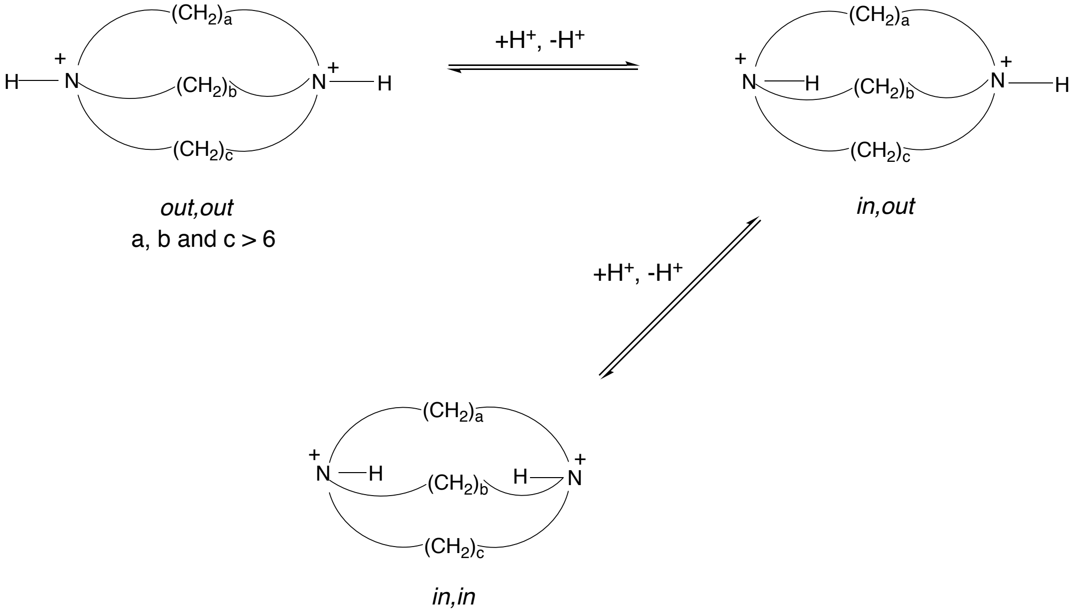


Figure 1.3. *In,out* isomerization of macrocyclic diamines prepared by Simmons and Park

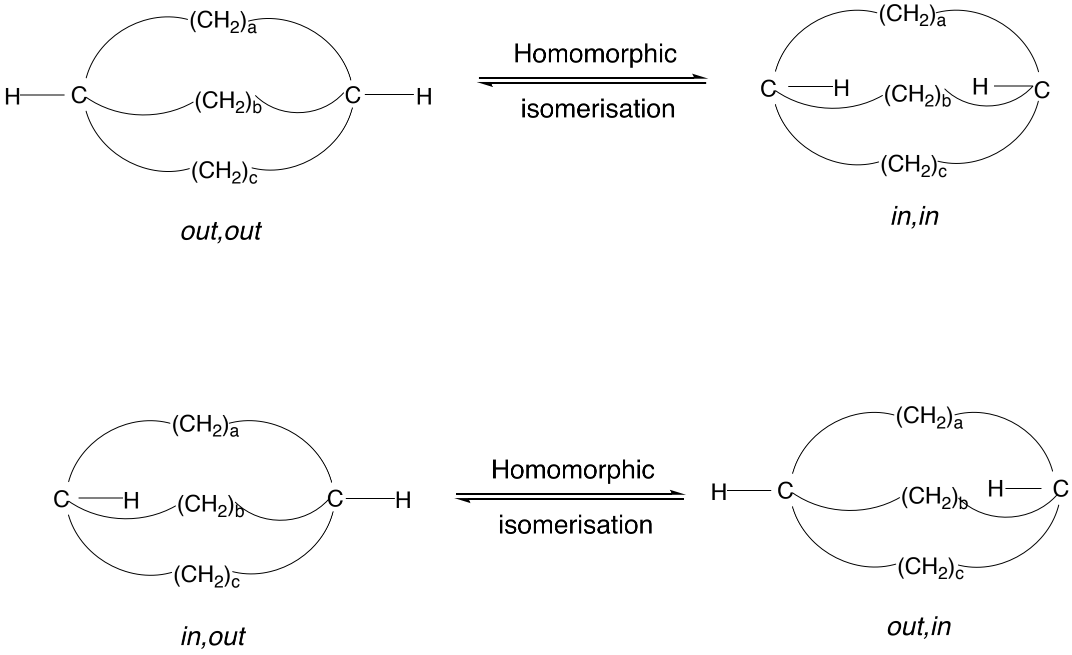
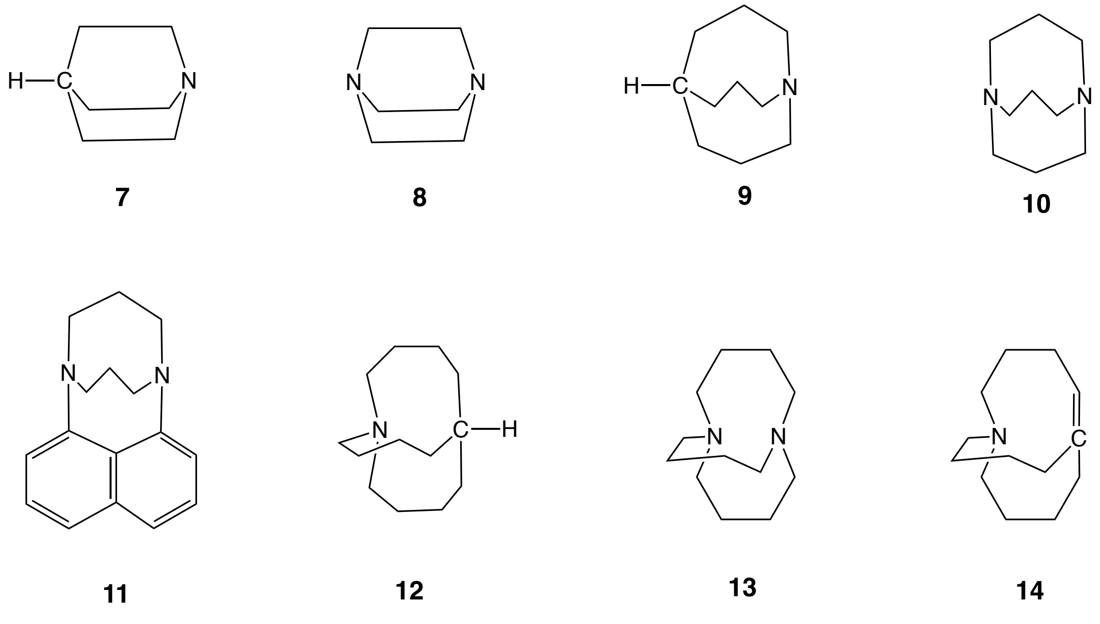


Figure 1.4. Homeomorphic isomerization of *out,out*- to *in in*- and *in,out*- to *out,in*-isomers

Depending on the size of the bridged bicyclic amine or diamine, the nitrogen may be pyramidal *out*, essentially flat, or pyramidal *in*. 1-Azabicyclo[2.2.2]octane (quinuclidine, **7**), and 1,4-diazabicyclo[2.2.2]-octane (DABCO, **8**) are small ring systems, and the bridgehead atoms point out. 1-Azabicyclo[3.3.3]undecane (manxine, **9**) and its corresponding diamine analog, 1,5-diazabicyclo[3.3.3]undecane (**10**), have nearly flat nitrogen atoms[13,14] and the X-ray structure of naphtho-1,5-diazabicyclo[3.3.3]undecane[15] (**11**) shows that the bridgehead amines are practically flat, with C-N-C angles of 118.6°. Even larger ring systems, such as *out*-6H-1-azabicyclo[4.4.4]tetradecane (**12**) and 1,6-diazabicyclo[4.4.4]tetradecane (**13**), in which each linking bridge has been expanded by one methylene from **9** and **10** respectively, possess pyramidal *in* nitrogens. 1-Azabicyclo[4.4.4]tetradec-5-ene (**14**), with its nitrogen lone pair inside, has a strong lone-pair/π-bond interaction and readily reacts with acid to form a propellane.[16]



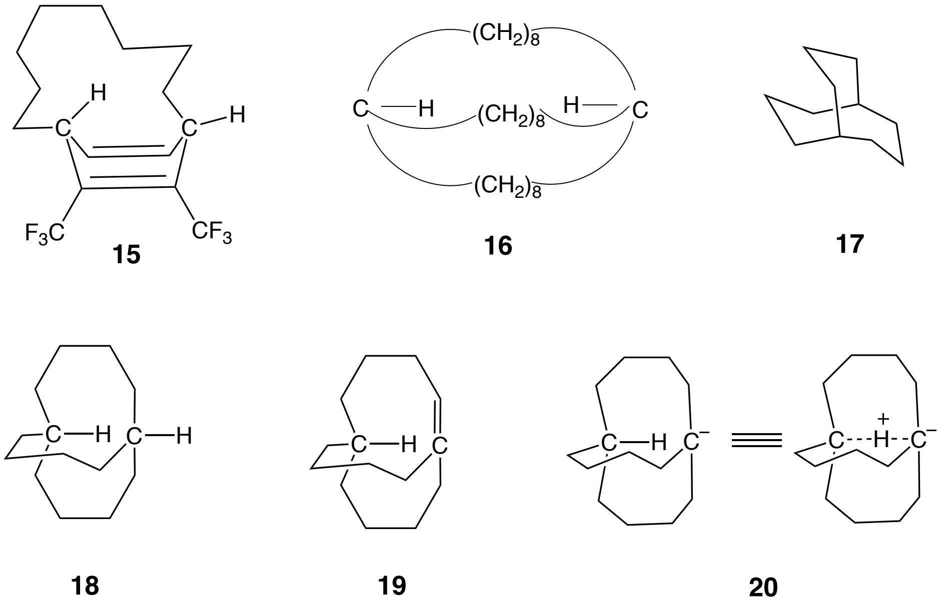
7 **8** **9** **10**

11 **12** **13** **14**

Figure 1.5. Examples of bicyclic compounds with nitrogen bridgeheads

The first bicyclic structures with *in*-CH bridgeheads were compound **15** and *in,in*-bicyclo[8.8.8]hexacosane (**16**), synthesized and reported by Gassman and Thummel,[17,18] and by Park and Simmons, respectively.[19] But how can one predict whether or not any particular bicyclic systems will adopt an *out,out*, *out,in* or *in,in* comformation? *Out,out*-isomers are strongly preferred for small (3- and 4-membered) and common (5- and 6-membered) rings. The borderlines for the existence of *out,in*- or *in,in*-isomers are not so obvious. In an early application of stochastic search procedures,[20,21] Saunders performed molecular mechanics calculations for bicyclic hydrocarbons, ranging from bicyclo[3.2.2]nonane to bicyclo[6.6.6]eicosane.[22] According to these calculations, the most stable geometry goes from *out,out* to *out,in* and finally *in,in* as the rings get larger. Unfortunately, little experimental data exist to verify these predictions. In many respects, symmetrical [3.3.3], [4.4.4] and [5.5.5] bicyclic systems are the most interesting cases. Bicyclo[3.3.3]undecane (**17**) adopts an *out,out* structure,[23] and all known derivatives are *out,out* as well, which is in agreement with Saunders' calculations. However, there is only limited experimental evidence concerning derivatives of bicyclo[4.4.4]tetradecane (**18**), and bicyclo[5.5.5]heptadecane is unknown. According to Saunders' calculations, the *in,out*- and *in,in*-isomers are the most stable conformations for [4.4.4] and [5.5.5] bicyclic alkanes, respectively. McMurry and Hodge[23] prepared *in*-bicyclo[4.4.4]-1-tetradecene (**19**) which they were able to hydrogenate to the most stable *in,out*-bicyclo[4.4.4]tetradecane (**18**). They also found that interesting chemistry resulted because of the strain and proximity of the bridgehead atoms in these ring structures. When **19** was treated with acid, protonation occurred to generate the *in*-bicyclo[4.4.4]-1-

tetradecyl cation (**20**), a stable substance with a symmetrical three center, two electron (μ-hydrido) C-H-C bond. The chemical shift of the hydrido hydrogen is δ -3.5, suggesting a $C^+H^-C^+$ polarization. This type of intrabridgehead interaction is often entropically favorable and driven by strain relief.



15 **16** **17**

18 **19** **20**

Figure 1.6. Examples of macrobicyces with carbon bridgeheads

Although the literature on *in,out*-isomers of methine and amine bridgehead compounds is vast, a very limited number of interactions involving other elements have been studied. A series of bicyclic ring systems with phosphorus as bridgeheads has been described. Compounds **21** and **22** have both nitrogen and phosphorus bridgeheads and [3.3.3] bicyclic skeletons.[24,25] The P-N distance in **22**[26,27] varies from 1.9-2.3 Å depending on substituent Y on phosphorus. The geometry of nitrogen atoms varies from pyramidal inward to essentially flat, and the phosphorus bridgehead progresses from trigonal bipyramidal to tetrahedral outward. Compounds with Y = H are very weak acids, showing that the free PN bases are extremely strong.

In addition, a series of dicationic bicyclic ring structures where both bridgeheads are phosphorus has been synthesized (compounds **24** and **25**).[24,25] Monocation **23**[28,29] is a nucleophilic adduct to compound **24**. The larger dication **24** forms at a faster rate than the smaller dication **25**, and the former is also more stable than the latter because the long P-P bond causes more strain in smaller ring systems (**25**) than in larger ones (**24**). Compound **24** is stable in aqueous solution below pH = 2, while compound **25** decomposes with exposure to even a small amount of water.

Pascal's group published a few aromatic macrobicyclic compounds (**26**-**29**).[30,31] In the ^{1}H NMR spectrum of compound **26**, the central proton resonance is a doublet (δ 9.31, J_{PH} = 25 Hz) due to coupling with the phosphorus, but in addition there exist easily visible ^{29}Si side bands that yield J_{SiH} = 248 Hz. Most interesting is the proton-decoupled ^{29}Si NMR spectrum of **26**, consisting of a lone doublet with strong coupling to phosphorus (J_{SiP} = 76 Hz). For compound **28**, the ^{31}P NMR spectrum shows a pair of doublets with J_{PP} = 175 Hz. The X-ray structure of compound **28** shows P-P contact distances of 3.72 and 3.51 Å in the two independent molecules, both somewhat shorter than the calculated distance of 3.79 Å at the B3PW91/6-31G(d) level. When HCl gas was bubbled into chloroform solutions of compound **28**, protonation occurred as a first-order process to give compound **29**. The new proton resonance (δ 14.08) was a doublet of doublets with J_{PH}'s of 584 and 13 Hz. This new proton is bound to the more basic, sulfur-substituted triaryl phosphine (d_{PH} = 1.29 Å) with the second phosphine at a reasonable hydrogen bonded distance (2.59 Å). It seems that protonation is slow because the *in*-phosphine lone pair only rarely tips away from the center of the molecule to permit a reaction with an acid.

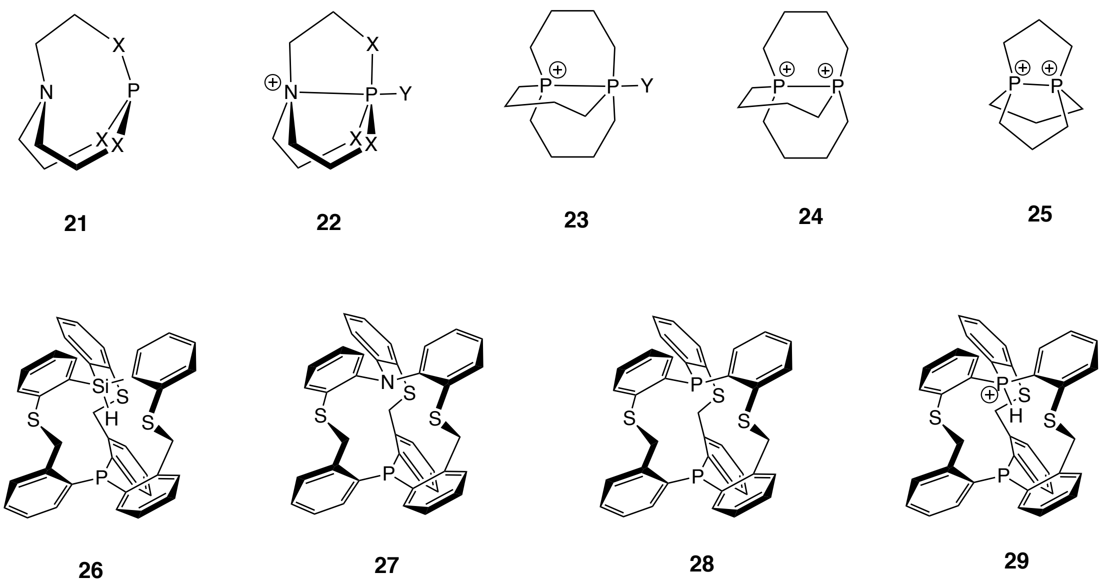
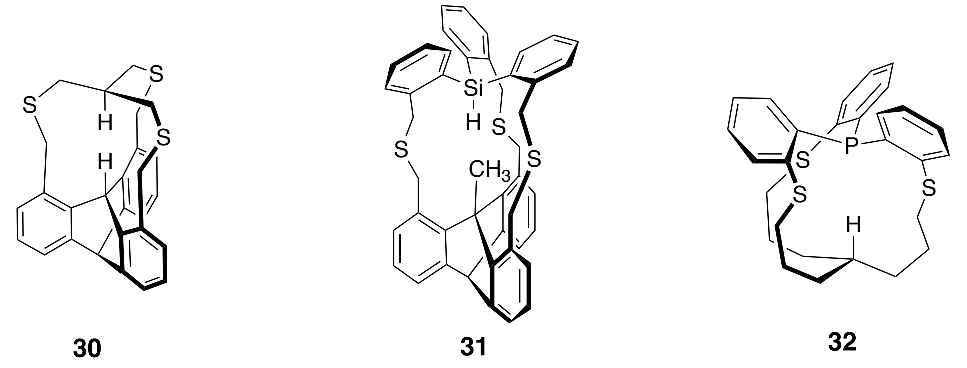


Figure 1.7. Examples of cyclophanes with phosphorus bridgeheads

Can we use modern computational methods to design aromatic bicyclic molecules which have extremely short non-bonded contacts (Figure 1.8)?



$d_{H\text{-}H}$ = 1.497 Å
$d_{C\text{-}C}$ = 3.675 Å
out,in isomer +3.4 kcal/mol

$d_{Si\text{-}H}$ = 1.475 Å
$d_{CH3\text{-}H}$ = 2.419 Å
$d_{CH3\text{-}C}$ = 1.503 Å
out,in isomer +8.6 kcal/mol

$d_{P\text{-}H}$ = 2.796 Å
$d_{H\text{-}C}$ = 1,095 Å
out,in isomer +21.5 kcal/mol
in,out isomer +16.4 kcal/mol

Figure 1.8. Target cyclophanes with their DFT-calculated (B3PW91/cc-pVTZ) non-bonded contacts

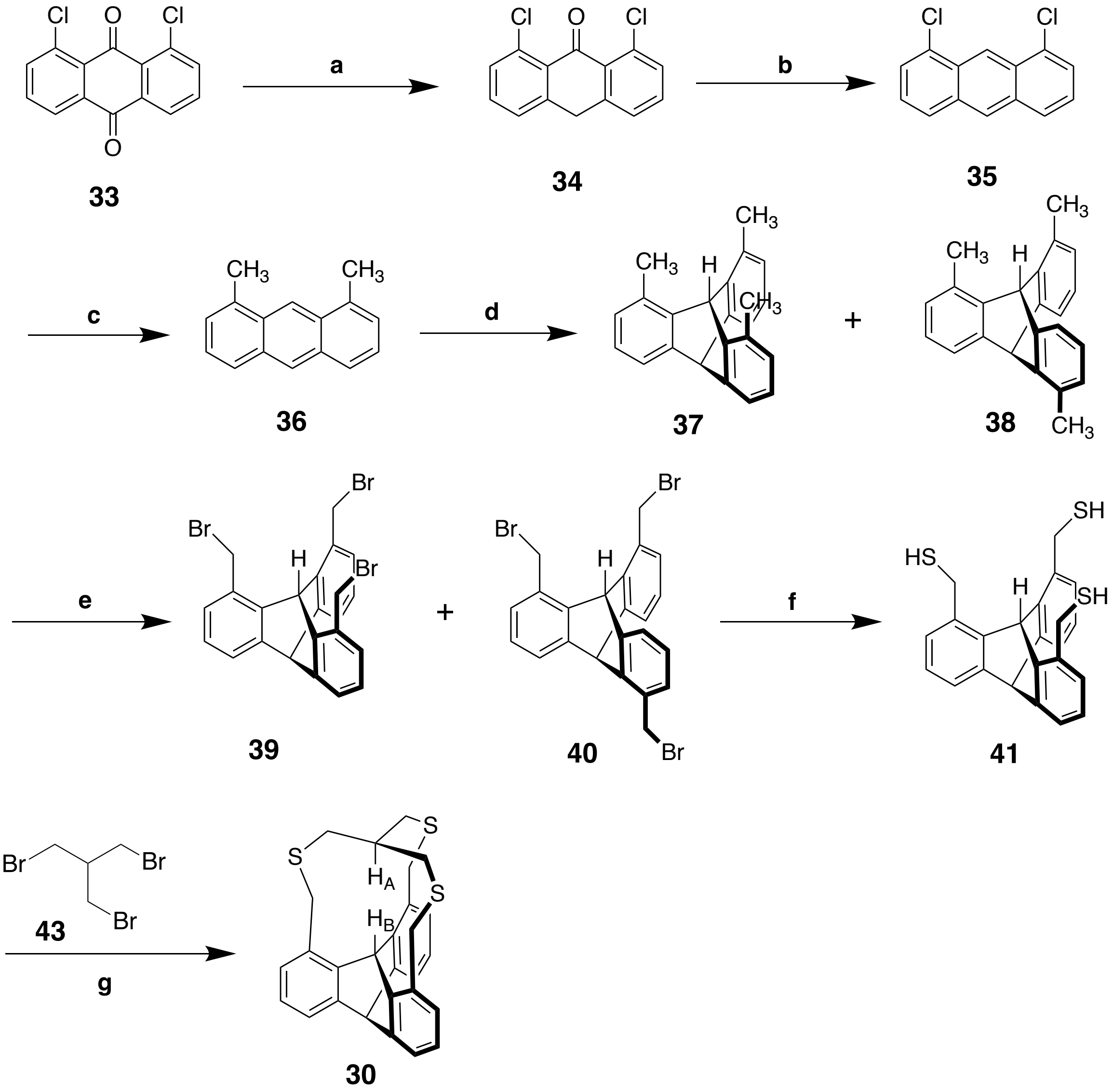
1.3. Synthesis and characterization of an *in,in*-cyclophane with a very short H--H non-bonded contact distance

1.3.1. Synthesis of *in,in*-cyclophane 30

Cyclophane **30** might be made by the base-promoted condensation of the tribromide **43** and trithiol **41**. Tribromide **43** is known[32] and the trithiol **41** can be formed from the known tribromide **39**.[33]

1,8-Dichloroanthraquinone (**33**) was reduced by treatment with Al powder and concentrated sulfuric acid, followed by concentrated HCl and isopropanol, to give 1,8-dichloroanthracene (**35**). Methylation of this aryl chloride with $AlMe_3$ and $Ni(dppp)Cl_2$ was then carried out. Twelve equivalents of trimethylaluminum and 25% Ni catalyst were required to convert all of the starting material into 1,8-dimethylanthracene (**36**). The crude product of the methylation can serve as starting material for the subsequent benzyne addition without further purification. When 1,8-dimethylanthracene (**36**) was treated with 2-amino-6-methylbenzoic acid and isoamyl nitrite in dichloroethane, both the syn and anti trimethyltriptycenes **37** and **38** were obtained in 65% overall yield. Based on NMR analysis, the ratio of the two isomers is 2:1 syn:anti. Bromination of the triptycenes **37** and **38** with NBS and light converted them into the corresponding benzylic bromides. Fortunately, the two product isomers could be separated by recrystallization from $CHCl_3$ and hexanes. The syn tribromide **39** is more soluble in this solvent combination than the anti-isomer, so the mother liquor was collected and concentrated to give pure

39 as a pale yellow solid. Treatment of tribromide **39** with thiourea followed by alkaline hydrolysis gave the trithiol **41**.



Scheme 1.1. Synthesis of *in,in*-cyclophane **30**: (a) Al powder, conc. H_2SO_4; (b) isopropanol, conc. HCl; (c) $AlMe_3$, Ni(dppp)Cl_2, DME, reflux; (d) 2-amino-6-methylbenzoic acid, isoamyl nitrite, 1,2-dichloroethane, reflux; (e) NBS, benzene, light, reflux; (f) thiourea, NaOH; (g) tris(bromomethyl)methane (**43**), KOH, 2:1 benzene-EtOH, reflux

Trithiol **41** and tris(bromomethyl)methane **43** were treated with ethanolic KOH at high dilution in benzene-EtOH (2:1) to give the desired *in,in*-cyclophane **30** as a white solid in 8% yield. Since the majority of the byproducts in the crude reaction mixture were polymeric, the desired product was easily isolated due to its comparatively low polarity.

1.3.2. Proton NMR spectra of *in,in*-cyclophane 30

The ^1H NMR spectrum of **30** shows the expected steric deshielding[34] of the *in*-proton resonances. H_A and H_B are observed at δ 3.94 and δ 7.15, respectively, but the corresponding protons in the precursors **43** and **41** are found at δ 2.42 and δ 6.54, respectively. However, a most unexpected observation is that H_B is a doublet with J_{AB} = 2.0 Hz. Selective irradiation of H_A collapsed the doublet to a singlet; thus this is a rare case of an easily observed, through-space coupling (TSC) of two hydrogen atoms via a direct, non-bonded contact. This is surprising because the TSC observed for the axial hydrogen atoms in compound **2** is no greater than 0.2 Hz.

Indeed, we have been unable to find any other example of so large a TSC via the direct, non-bonded contact of two hydrogen atoms. In Mallory's 1996 review of TSC,[35] he distinguishes between hydrogen-hydrogen TSC mediated by carbon atoms in non-bonded contact (H-C···C-H), which may be large, and the direct TSC of two hydrogen atoms via direct non-bonded contact (C-H···H-C), which were said to be very small in magnitude. However, he provides no examples of the latter type. More surprisingly, in Hierso's 2014 review of TSC,[36] there is no mention of hydrogen-hydrogen TSCs at all. The largest experimentally determined through-space J_{HH} that we have been able to locate is

0.60 Hz for a pair of protons in 2-methoxy[2.2]paracyclophane reported by Dracinsky et al.[37] They observed several other coupling constants ranging from 0.33 Hz to 0.56 Hz, but noted that because of their small magnitude, the TSCs do not result in line splitting, but only in broadening of the NMR resonances. However, at least some of these TSCs may be transmitted in part via C···C non-bonded contacts. From the line widths in the published ^{1}H NMR spectrum[38] of a 1:1 mixture of compounds **1b** and **1c**, the hydrogen–hydrogen TSC constant has also been estimated to be 0.6 Hz, but these hydrogen atoms are separated by only five ordinary bonds; thus some through-bond coupling cannot be excluded. From a computational perspective, GIAO calculations at the B3LYP/6-311++G(2df,2pd) level recommended by Dracinsky et al. give a reasonable J_{AB} = 3.1 Hz for compound **30**.

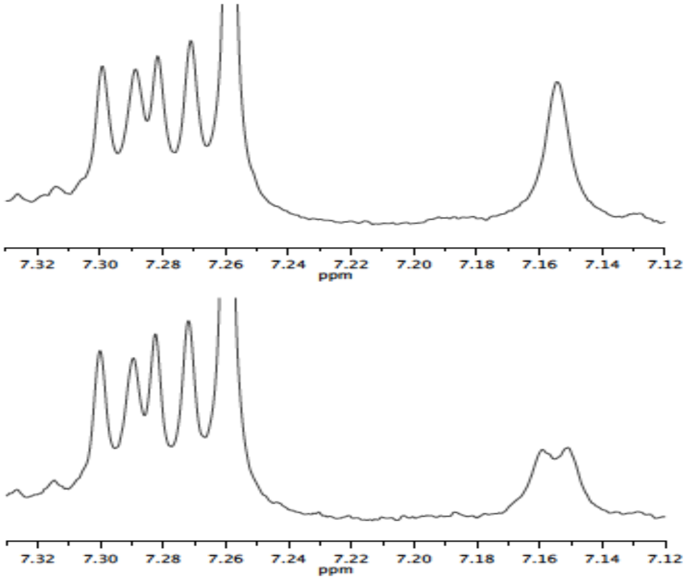


Figure 1.9. Bottom: Downfield region of the ^{1}H NMR spectrum of **30**, including the H_B doublet (δ 7.15). Top: Same region with irradiation of H_A (δ 3.94)

1.3.3. Molecular structure of *in,in*-cyclophane 30

It proved unusually difficult to grow X-ray quality crystals of **30**, but eventually a small crystal (0.17 mm X 0.06 mm X 0.02 mm) was obtained from ethyl acetate solution. Subsequent data collection at 150 K, structure solution, and refinement were non-problematic. Compound **30** crystallizes in the space group $P2_12_12_1$ with Z = 8; thus there are two crystallographically independent molecules in the asymmetric unit, both possessing approximate C_3 symmetry. The molecular structure of **30** is illustrated in Figure 10, unambiguously confirming the *in,in*-geometry. Most significantly, the distances between the apical carbon atoms (d_{CC}) in the two independent molecules were found to be 3.667(8) Å and 3.683(9) Å (see Table 1), which are 0.1 Å shorter than the d_{CC} of 3.780(7) Å observed in the 100 K X-ray structure of dimer **3**.

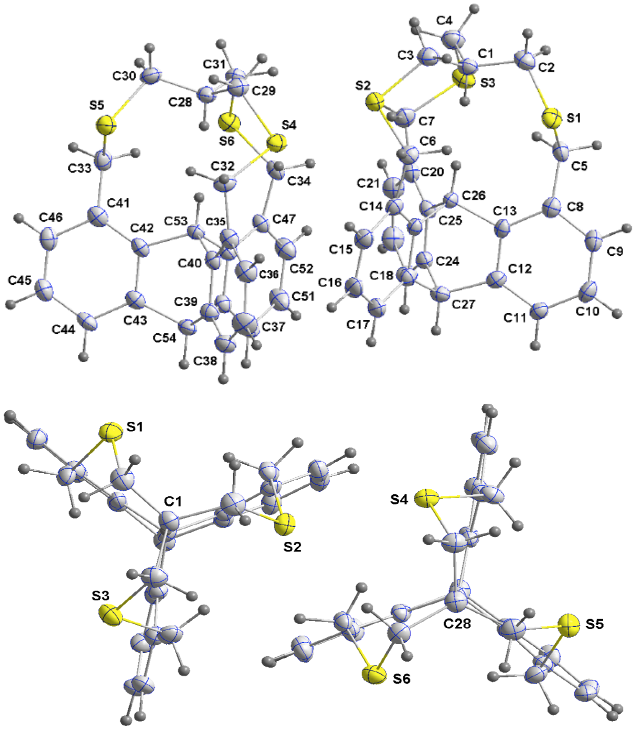


Figure 1.10. Molecular structure of cyclophane **30**. Ellipsoids are set at 50% probability

1.3.4. Computational studies of *in,in*-cyclophane 30

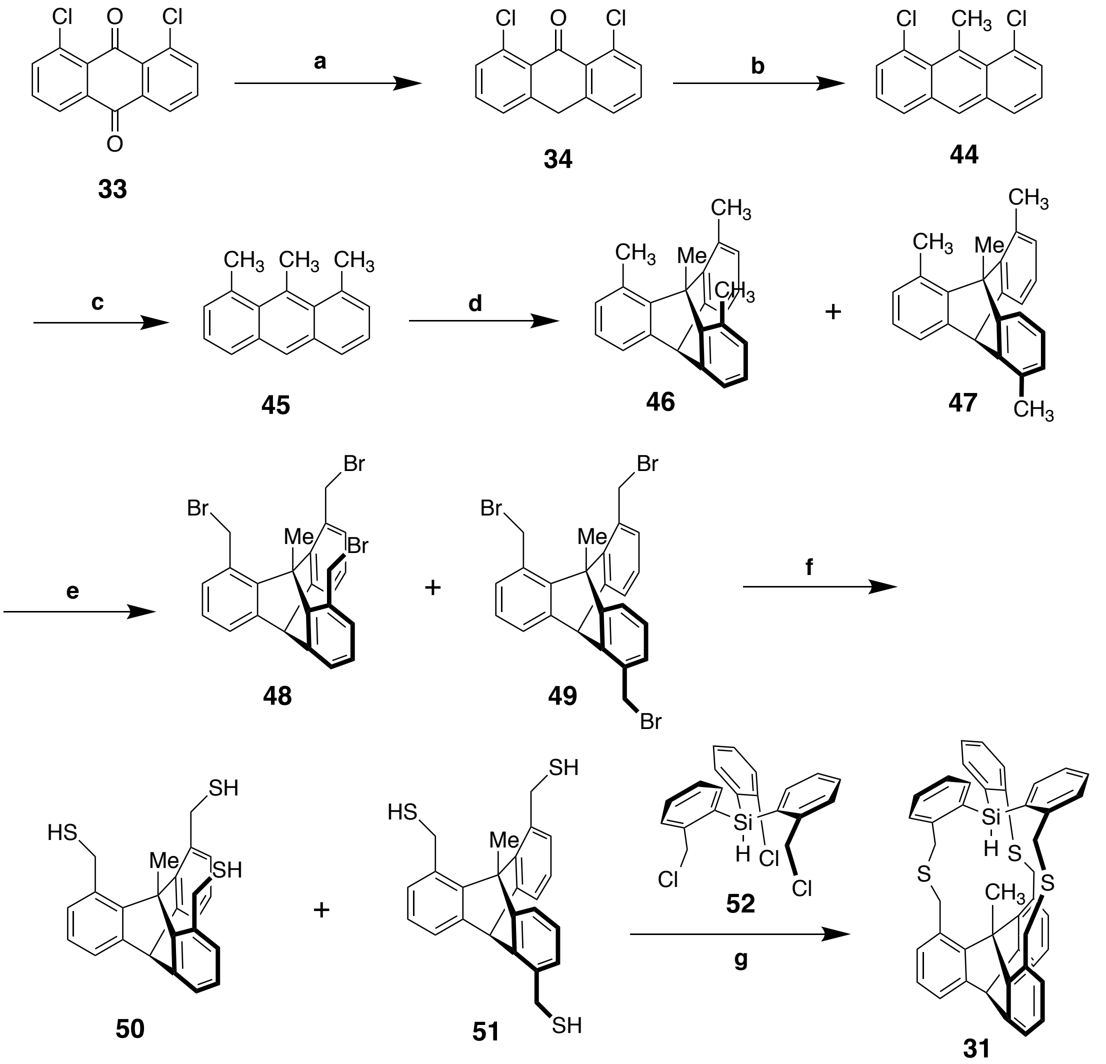
The *in*-hydrogen positions were refined in the X-ray structure, but foreshortening of the C-H distances[39] makes the observed hydrogen-hydrogen distances far too long. For this reason, we must rely on computational methods to estimate d_{HH}. The table below lists the salient interatomic distances calculated by a variety of methods. Among conventional DFT methods, we have observed that the B3PW91 functional[40,52] gives the best contact distances in sterically congested cyclophanes.[41] Geometries obtained with both the modest 6-31G(d) and much larger cc-pVTZ basis sets[42,43] yield very similar structures with d_{CC} = 3.69 Å (slightly longer than the average crystallographic d_{CC} of 3.675 Å) and d_{HH} = 1.53 Å. When dispersion corrections[44] are included, either by adding versions of Grimme's D3 correction[45,46] or by using the M062X functional,[47] the calculated contact distances shorten slightly to d_{CC} = 3.67-3.68 Å and d_{HH} = 1.52 Å. MP2 calculations give d_{CC} similar to the experimental values, but significantly shorter d_{HH} than the DFT methods, owing to less compression of the C-H bonds. Thus for the B3PW91-D3/ccpVTZ and MP2/cc-pVDZ calculations, both of which yield d_{CC} = 3.675 Å, the former gives axial C-H bond distances of 1.079 Å and 1.075 Å, but the latter gives 1.091 Å and 1.087 Å. Interestingly, the neutron structure of **30** yields a C-H bond distance of 1.093 Å for the compressed methines at 20 K and 100 K, and thus it is possible that the MP2 calculations give more nearly accurate estimates of d_{HH}.

Table 1.1. Experimental and calculated interatomic distances for the axial atoms of cyclophane **30**

Method	d_{CC} **[Å]**	d_{HH} **[Å]**
X-ray diffraction (molecule 1)	3.667(8)	1.76(8)
X-ray diffraction (molecule 2)	3.683(9)	1.91(8)
B3PW91/6-31G(d)	3.695	1.532
B3PW91/cc-pVTZ	3.689	1.535
B3PW91-D3/6-31G(d)	3.681	1.519
B3PW91-D3/cc-pVTZ	3.675	1.522
B3PW91-D3(BJ)/6-31G(d)	3.675	1.513
B3PW91-D3(BJ)/cc-pVTZ	3.667	1.515
M062X/6-31G(d)	3.683	1.525
M062X/cc-pVTZ	3.673	1.527
M062X-D3/6-31G(d)	3.684	1.526
M062X-D3/cc-pVTZ	3.675	1.529
MP2/6-31G(d)	3.663	1.505
MP2/cc-pVTZ	3.675	1.497

1.4. Synthesis and characterization of an *in,in*-cyclophane with a very short H--CH_3 non-bonded contact distance

1.4.1. Synthesis of *in,in*-cyclophane 31



Scheme 1.2. Synthesis of *in,in*-cyclophane **31**: (a) Al powder, conc. H_2SO_4; (b) MeMgBr, benzene; (c) $AlMe_3$, Ni(dppp)Cl_2, DME, reflux; (d) 2-amino-6-methylbenzoic acid, isoamyl nitrite, 1,2-dichloroethane, reflux; (e) NBS, benzene, light, reflux; (f) thiourea, NaOH; (g) tris[2-(chloromethyl)phenyl]silane (**52**), KOH, 2:1 benzene-EtOH, reflux

Cyclophane **31** might be made by the base-promoted condensation of the trichloride **52** and trithiol **50**. Trichloride **52** is known[3] and trithiol **50** can be formed from the known tribromide **48**.[8,48]

1,8-Dichloroanthraquinone (**33**) was reduced in the presence of Al powder and concentrated sulfuric acid to give two isomers. Fortunately these two isomers can be separated by recrystallization from $CHCl_3$-hexanes, and anthrone **34** was obtained in pure form in 79% yield. When anthrone **34** was treated with MeMgBr, 1,8-dichloro-9-methylanthracene (**44**) was afforded in 80% yield. Taking the same reaction conditions as used for the sythesis of 1,8-dimethylanthracene (**36**), 1,8,9-trimethylanthracene (**45**) was obtained in 100% yield from 1,8-dichloro-9-methylanthracene (**44**). The methylbenzyne addition to trimethylanthracene **45** produced the two tetramethyltriptycenes **46** and **47** in 64% yield. These two isomers could not be separated by silica gel column chromatography, and, from the ^{1}H NMR spectrum of the mixture, the ratio of the syn isomer **46** to the anti-isomer **47** is 1:2. This is drastically decreased from the 2:1 ratio observed for the syn and anti trimethyltriptycenes in Scheme 2. The bulky 9-methyl group of trimethylanthracene **45** seems to block the syn addition of the benzyne. The mixture was brominated with NBS and light, and two tribromides were obtained. As before, the two tribromides were purified by recrystallization. Unfortunately, even though the syn tribromide **48** is more soluble in $CHCl_3$ and hexanes, no pure **48** was obtained, but the proportion of the syn tribromide **48** was increased in the mixture to a ratio of 2:3. Treatment of tribromide **48** by thiourea followed by alkaline hydrolysis gave the trithiol product **50**. Reaction of the trithiol mixture with trichloride **52** worked well, and, after purification, *in,in*-cyclophane **31** was obtained as a white solid in 30% yield based on the amount of trithiol **50** in the starting mixture.

1.4.2. Proton NMR spectrum of *in,in*-cyclophane 31

The ^1H NMR spectrum of cyclophane **31** shows it to be conformationally rigid. The protons on the bridging methylene groups are diastereotopic, indicating that the enantiomerization of the molecule is slow on the NMR time scale.

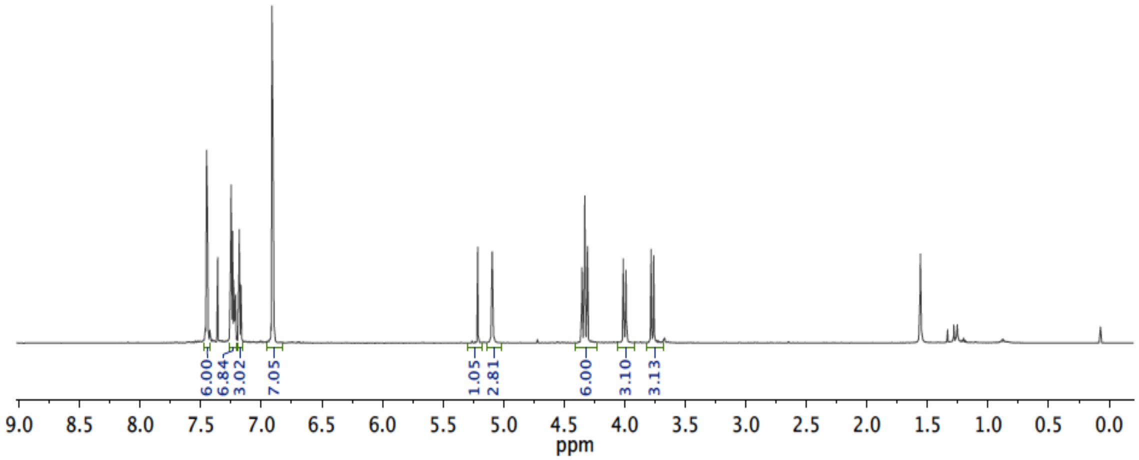


Figure 1.11. Proton NMR spectrum of cyclophane **31**

Manifestations of the close contact are less obvious in the NMR spectra. There is no evidence of through-space spin-spin coupling of the silane and methyl protons in the ordinary ^1H NMR (Figure 1.11) and COSY (Figure 1.12) spectra of compound **31** because no crossing peaks are founded in the COSY spectrum, nor is there evidence of coupling of the silane proton and methyl carbon in the fully proton-coupled ^{13}C NMR spectrum of **31**. The methyl resonance for compound **50** is observed at δ 3.74, while that of compound **31** is found at δ 5.09, an apparent example of steric deshielding, but this conclusion is undermined by the absence of such deshielding for the silane proton, which is observed at δ 6.16 in precursor **52**, but only δ 5.21 in cyclophane **31**.

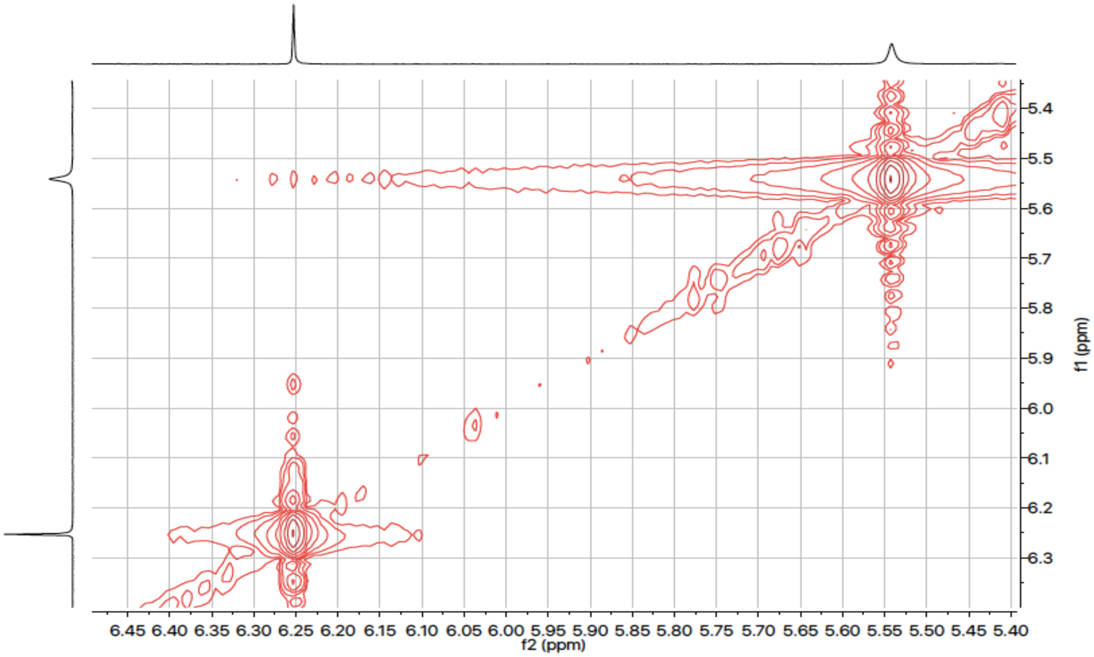


Figure 1.12. COSY spectrum of cyclophane **31**

1.4.3. Molecular structure of the *in,in*-cyclophane 31

Most of the C_3-symmetric cyclophanes that we have prepared in the past gave single crystals large enough for X-ray analysis quite easily, but compound **31** proved more difficult. A wide variety of solvents was examined for compound **31**. The usual result was crystals that were twinned. The structures could be solved, and the *in,in*-geometry could be confirmed, but the refinement was poor. Eventually, the slow crystallization of **31** from THF gave a very good crystal of its bis(THF) solvate. The structure was solved in the common space group $P2_1/c$, and it refined to an excellent $R(F)$ = 3.96%. The molecular structure of compound **31** is illustrated in Figure 1.13.

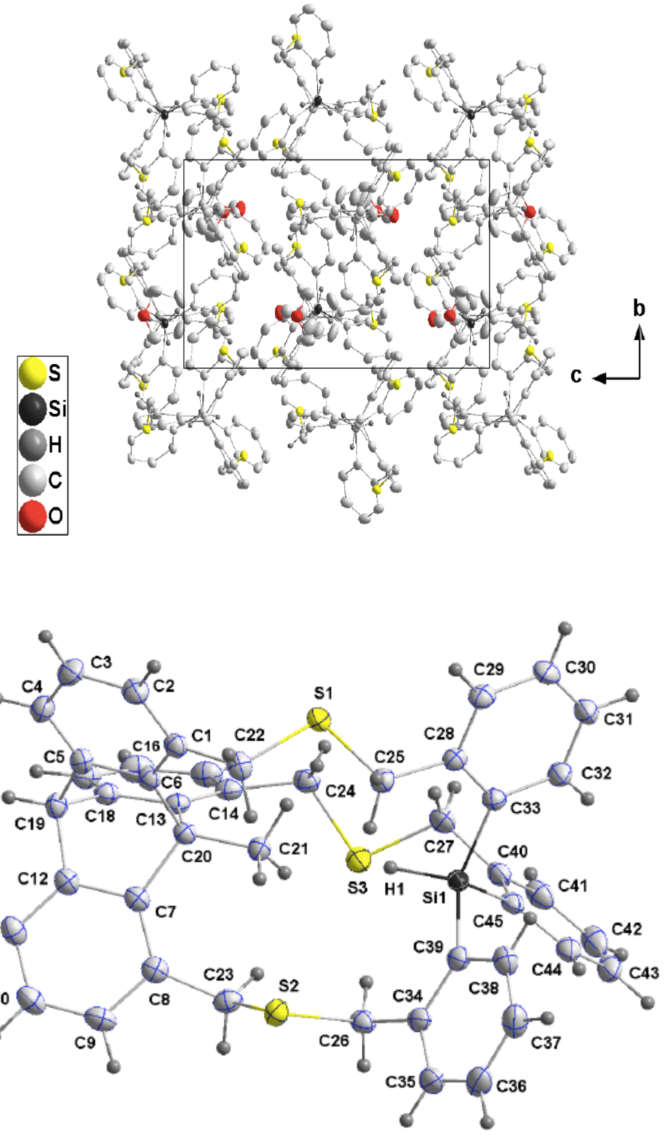


Figure 1.13. X-ray structure of cyclophane **31**

The structure of cyclophane **31** is extremely unusual: it is a rare case of a hydrogen atom pressed close to the "top" of a methyl group. The observed contact distance ($d_{\text{H1-C21}}$ using the crystallographic numbering scheme) is 2.55(2) Å, but of course, the actual distance must be shorter due to foreshortening of the Si-H bond[39] in the X-ray structure. If a standard Si-H bond distance of 1.48 Å is assumed, then the true $d_{\text{H1-C21}}$ contact distance is 2.44 Å.[49] Evidence of steric compression is found in the IR spectrum of compound **31**, where the Si-H stretching frequency of 2269 cm^{-1} is 92 cm^{-1} higher than the same band in an acyclic model (2177 cm^{-1}). This is, however, 188 cm^{-1} less than the Si-H stretch (2457 cm^{-1}) in another very congested *in*-silaphane.[7]

The C-CH_3 bond distance ($d_{C20-C21}$) in cyclophane **31** is also compressed. The average C-CH_3 bond distance for unconstrained, well-determined structures ($R \leq 0.05$) of 9-methyltriptycenes in the Cambridge Structural Database[50,51] is 1.519 ± 0.004 Å (n = 23), which is slightly longer than the experimental bond distance of 1.510(2) Å in **31**. Computational studies of cyclophane **31** using a variety of methods invariably yield even shorter C-CH_3 bond distances, ranging from 1.497 to 1.508 Å.

1.4.4. Computational studies of *in,in*-cyclophane 31

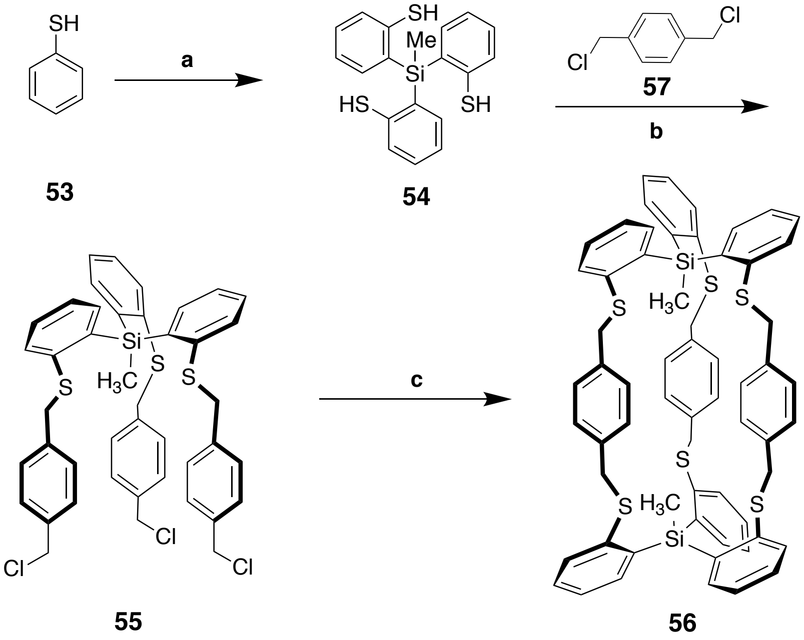
Overall, the conventional B3PW91 functional[40,52] gives structures in the best agreement with the experiment, with both the smaller 6-31G(d) basis set[42] and the much larger cc-pVTZ basis set giving very similar results. When dispersion corrections are included, either with variations of Grimme' s D3 correction[45,46] or by employing the M062X functional,[47] the agreement is poorer. This is most apparent in the silicon-methyl carbon distance ($d_{Si1-C21}$), which is well determined in the X-ray structure at 3.902(2) Å. The B3PW91 functional gives values within 0.01 Å of the experiment, but the dispersion-corrected calculated structures yield values that are too short by 0.08-0.15 Å.

Table 1.2. Experimental and calculated interatomic distances for the axial atoms of cyclophane **31**

Method	$d_{\text{H-C}}$ [Å]	$d_{\text{Si-C}}$ [Å]	$d_{\text{C-C}}$[Å]
X-ray diffraction	2.55(2)	3.902(2)	1.510(2)
B3PW91/6-31G(d)	2.420	3.895	1.508
B3PW91/cc-pVTZ	2.418	3.894	1.503
B3PW91-D3/6-31G(d)	2.311	3.780	1.503
B3PW91-D3/cc-pVTZ	2.320	3.789	1.498
B3PW91-D3(BJ)/6-31G(d)	2.280	3.748	1.502
B3PW91-D3(BJ)/cc-pVTZ	2.287	3.756	1.497
M062X/6-31G(d)	2.337	3.808	1.506
M062X/cc-pVTZ	2.350	3.818	1.502
M062X-D3/6-31G(d)	2.331	3.801	1.506
M062X-D3/cc-pVTZ	2.345	3.812	1.502
MP2/6-31G(d)	2.309	3.777	1.501

1.5. Synthesis and characterization of an *in,in*-cyclophane with two methyl groups inside the cavity

1.5.1. Synthesis of *in,in*-cyclophane 56



Scheme 1.3. Synthesis of *in,in*-cyclophane **56**: (a) *n*-BuLi, trichloromethylsilane, dry THF; (b) 1,4-bis(chloromethyl)benzene (**57**), TEA; (c) compound **54**, KOH, 2:1 benzene-EtOH, reflux

Cyclophane **56** might be made by the base-promoted condensation of the trichloride **55** and trithiol **54**. The tricholoride **55** can be formed from the trithiol **54** in a benzylic substitution reaction; trithiol **54** is known and easily prepared from thiophenol in one step.[53]

Cyclophane **56** is formed in very low yield by the reaction of tris(2-mercaptophenyl)methylsilane (**54**) and commercial 1,4-bis(chloromethyl)benzene (**57**), but the two-step procedure illustrated in Scheme 3 is far superior, if not high-yielding. Compound **54** was first treated with an excess of **57** to give the triple adduct **55** in 60%

yield after purification, and then condensation of **55** with another molecule of **54** at high dilution gave the dimethyl cyclophane **56** in 5% yield.

1.5.2. Proton NMR spectrum of *in,in*-cyclophane 56

The ^{1}H NMR spectrum of *in,in*-cyclophane **56** clearly shows that it is a C_3 symmetric compound. The *in*-methyl groups on the Si atoms appear as one sharp singlet, which falls at δ 0.57, 0.4 ppm upfield from the methylsilane in precursor compound **55** (δ 1.01). The methylene groups appear as sharp singlets, and the lack of diastereotopic methylene resonances is indicative of a relatively high degree of conformational mobility.

1.5.3. Molecular structure of *in,in*-cyclophane 56

In the case of cyclophane **56**, which is highly soluble only in chlorinated solvents, it was very difficult to obtain good crystals. Finally, the evaporation of a relatively dilute solution in nitrobenzene over a period of four months gave single crystals of **56** as its bis(nitrobenzene) solvate. The structure was solved in the space group *P*-1. and it refined to *R*(*F*) = 5.69%. There are two similar but crystallographically independent molecules of compound **56** in the structure, and the molecular structure of one of them is illustrated in Figure 14.

Cyclophane **56** does not possess especially close nonbonded contacts (the methyl groups are approximately 5 Å apart), but the presence of two *in*-methyl groups is, as far as we can tell, unique. Whether a more highly congested *in,in*-dimethyl cyclophane can be prepared is an open question, but if the two methyls could be brought close enough to enmesh the hydrogen atoms, then it might be possible to observe correlated rotation of suitably labeled methyl groups.

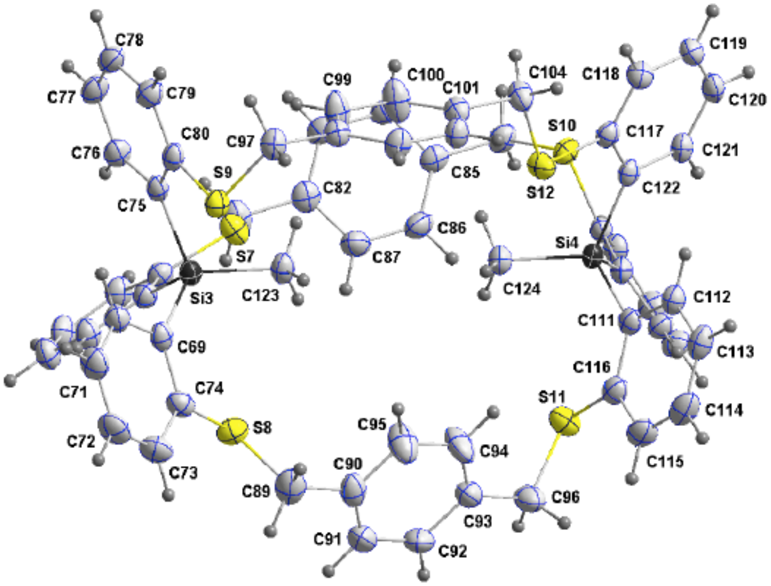


Figure 1.14. X-ray structure of cyclophane **56**

1.6. Synthesis and characterization of multiple isomers of a small, strained phosphaphane

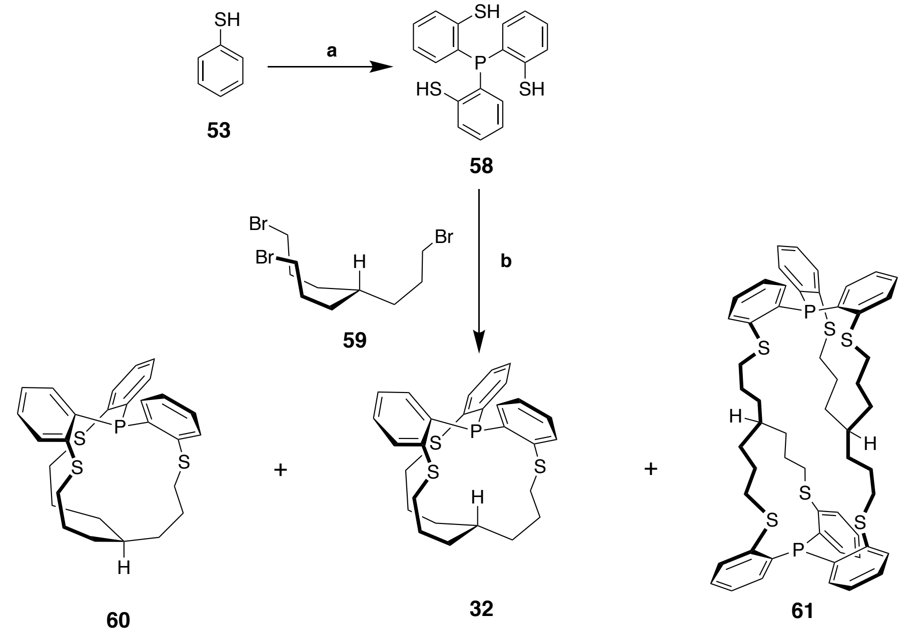
1.6.1. Synthesis of cyclophanes

Cyclophane **32** might be made by the base-promoted condensation of the tribromide **59** and trithiol **58**, which are both known compounds.[31,53]

Treatment of thiophenol with two equivalents of *n*-BuLi followed by phosphorus trichloride gives to form tris(2-mercaptophenyl)phosphine (**58**) in 70% yield. Condensation of trithiol **58** with tris(3-bromopropyl)methane (**59**) at high dilution gave the cyclophane **32**[54] in 10% yield. Additionally, *in,out*-isomer **60** and the dimeric *in,out,in,out*-cyclophane **61** were also isolated in 5% and 10% yield,respectively (Scheme 1.4).

Although compounds **60** and **61** have no close non-bonded contacts, their isolation is noteworthy because in no case has Pascal's group isolated two isomers of the same cyclophane from a single macrocyclization. We do not contend that other isomers have never been formed, but they have eluded isolation and proper characterization. This is due in part to a strong preference to form the more stable isomer, but also to the fact that, in most of these syntheses, our approach has been to carry out the macrocyclization and then to isolate the most prominent, low-polarity component of the mixture. This is generally the desired monomeric *in*- or *in,in*-isomer, because the oligomers and polymers formed in these reactions are decidedly more polar. However, in the few cases where we have diligently searched for other isomers, they have not been found. We note, however, that when others have reported the syntheses of very large macrobicycles where *in* and *out* isomers do not differ greatly in the degree of ring strain, formation of more than one *in/out* stereoisomer is sometimes observed.[55,56]

In this case, the results are very unusual. In the synthesis of the small *in,in*-cyclophane **32** (Scheme 1.4), that would necessarily have a close contact between the *in*-phosphine and the *in*-hydrogen atom, not only was the desired compound **32** isolated, but also its *in,out*-isomer **60** in 5% yield and the dimeric *in,out,in,out*-cyclophane **61** in 10% yield.



Scheme 1.4. Synthesis of three isomers: (a) *n*-BuLi, phosphorus trichloride, dry THF; (b) tris(3-bromopropyl)methane (**59**), KOH, 2:1 benzene-EtOH, reflux

1.6.2. NMR spectrum of *in,in*-cyclophane 32

In the ^{1}H NMR spectrum of **32**, the *in*-methine resonance is a complex multiplet at δ 3.71 ppm. The through-space coupling of the phosphorus and *in*-hydrogen atom was measured by selective irradiation of methylene protons surrounding the apical methine (see the experimental section). In this case, J_{PH} = 9 Hz, a large value, but not nearly so large as the J_{PH} = 25 Hz observed in an *in,in*-cyclophane that contained an interacting phosphine and hydrosilane.[31] HDFT calculations at the B3LYP/6-311++G(2df,2pd) level of theory[40,42,57] recommended by Dracinsky et al.[37] yield reasonable estimates of these through-space coupling constants. The calculated J_{PC} is 21.6 Hz and the calculated J_{PH} is 6.8 Hz, both a bit smaller than the observed values.

The ^{13}C NMR spectrum of compound **32** proved to be particularly interesting. The δ 27.0 resonance corresponds to the *in*-methine carbon atom, and it is a doublet with J_{PC} = 24 Hz. This is much larger than any of the other observed J_{PC}'s involving aliphatic carbons in cyclophanes **32** and **60** (5-8 Hz). Given that six bonds separate the two atoms, this is clearly an example of through-space spin-spin coupling of the phosphorus and the methine carbon atoms. It is admittedly difficult to search the literature for through-space coupling constants, but a through-space J_{PC} of 24 Hz is much larger than any value cited in the reviews of through-space coupling by the Mallorys[35] and Hierso[33] (largest J_{PC} ≈ 8 Hz). Possibly the coupling is enhanced in compound **32** by transmission via the *in*-hydrogen atom.

1.6.3. Molecular structures of cyclophanes 32, 60, 61

Compound **32** crystallized in the common space group $P2_1/c$ (No. 14), and the molecule lies on a general position. It proved to be the *in,in*-isomer, and, as expected, it adopts a very nearly C_3-symmetric conformation, as is invariably the case for the *in,in*-cyclophanes that we have been previously characterized. The structure is illustrated in Figure 1.15. Compound **60** crystallized in the chiral space group $P2_1$ (No. 4) and there are two crystallographically independent molecules in the asymmetric unit. Both of these molecules are *in,out*-isomers, but they are distinctly asymmetric, and one of them is illustrated in Figure 1.15. The simplicity of the NMR spectra of compound **60** is thus the result of rapid dynamic exchange of its various conformations at room temperature.

The dimeric cyclophane **61** crystallized in the space group *P*-1 (No. 2), but it resides on a special position and possesses crystallographic C_i symmetry. There is some disorder in the structure, but the crystal appears to consist entirely of molecules possessing an *in,out,in,out*-conformation (that is, two *in*-P's and two *out*-H's). The structure is illustrated in Figure 1.15. This dimeric C_i-symmetric cyclophane is calculated to have an energy about 3 kcal/mol lower than the monomeric compound **32** (the comparison is based on half the energy of compound **61**; see Table 1.3) as well as the corresponding *in,in,in,in*-conformation, and thus it is not surprising that it is the most abundant cyclophane in the reaction mixture. Indeed, when one considers the relative energies of the three observed isomers, the chief surprise is that *in,out*-isomer **60** is formed at all. Of course, these reactions are not under thermodynamic control, and once two carbon-sulfur bonds have been formed, the stereochemical options are limited in the absence of phosphine inversion, which is slow at the temperature of the macrocyclization.

In,in-cyclophane **32** was the primary target of this study, chiefly for the interaction of the inwardly-directed methine and phosphine. The X-ray structure of compound **32** is quite well determined with an *R*(*F*) of 0.042 at 150 K. The observed distance between the phosphorus and the *in*-hydrogen atoms ($d_{\text{P-H28}}$) is 2.87(3) Å and that between the phosphorus and *in*-carbon atoms ($d_{\text{P-C28}}$) is 3.877(2) Å. Of course, the C-H bond lengths in

X-ray structures are systematically underestimated, but if the crystallographic bond length is "improved" to a standard value of 1.099 Å for methines, then $d_{\text{P-H28}}$ is reduced to 2.78 Å. The sum of the van der Waals radii of phosphorus and hydrogen is 3.05 Å,[58] 0.27 Å greater than $d_{\text{P-H28}}$. Thus this contact is short, but not exceptionally so: non-bonded contact distances between hydrogen atoms and other elements that are as much as 0.9 Å less than the sum of their respective van der Waals radii have been observed in other *in*-cyclophanes.[59]

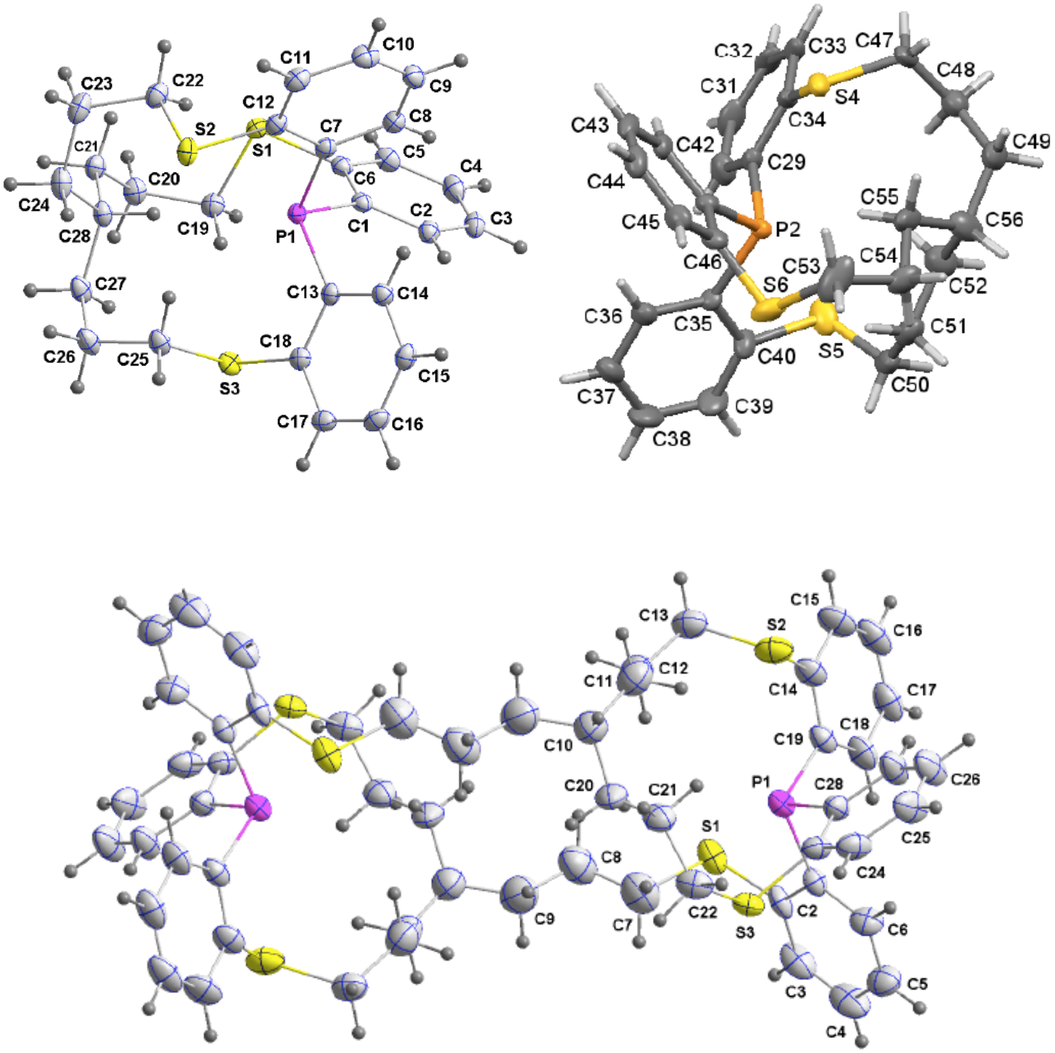


Figure 1.15. X-ray structure of compounds **32** (up left), **60** (up right), **61** (bottom)

1.6.5. DFT calculations for all three isomers

Computational studies at the B3PW91/6-31G(d) level of theory[40,42,52] shed some light on the conformational preferences of cyclophanes **32** and **60** (Table 1.3). The C_3-symmetric *in,in*-isomer **32** appears to be the lowest energy isomer of the monomeric cyclophanes considered here. There exists a C_3-symmetric conformation of compound **60**, but the two C_1-symmetric conformations observed in the crystal structure, which represent distinct potential minima with nearly the same energy, are at least 8 kcal/mol lower in energy than the C_3 conformation, but still 7-8 kcal/mol higher in energy than **32**. There also exists a C_3-symmetric *out,in*-isomer (that is, *out*-P and *in*-H), and a C_3-symmetric *out,out*-isomer, but both are much higher in energy (22 and 35 kcal/mol, respectively) than the *in,in*-isomer **32**. We have not located any C_1-symmetric *out,in*- or *out,out*-confomations that have lower energies than these C_3 conformations, but such structures may exist.

Table 1.3. DFT calculations of cyclophanes **32**, **60**, **61**

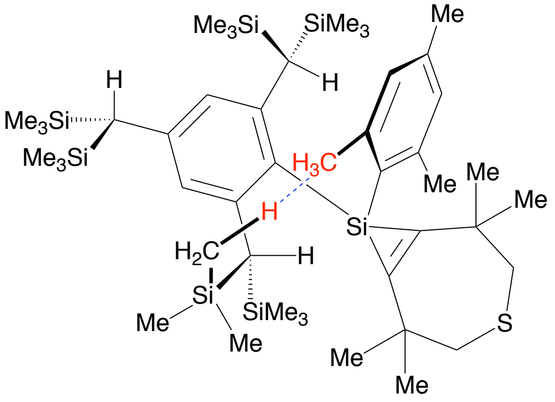
Conformation	ΔE [kcal/mol]	ΔE(E+ZPE)[kcal/mol]	n[a]
C_3 *in,in* (**32**) [b]	0.0	0.0	0
C_3 *out*-P,*in*-H	+22.7	+21.5	0
C_3 *in*-P,*out*-H (**60**)	+17.1	+16.4	0
C_1 *in*-P,*out*-H #1 (**60-1**) [b]	+9.0	+8.1	0
C_1 *in*-P,*out*-H #2 (**60-2**) [b]	+7.7	+7.1	0
C_3 *out,out*	+35.7	+34.9	0
C_i *in,in,in,in* dimer	+1.3	+0.8	0
C_i *in,out,in,out* dimer (**61**) [b]	-2.4	-2.6	0

[a] Number of imaginary frequencies. [b] Conformations observed in X-ray structures.

1.7. Attempted syntheses of other sterically congested *in,in*-cyclophanes

The successful syntheses of the congested *in,in*-cyclophanes above suggest that the use of different known precursors of these cyclophanes (9-substituted triptycenes for example) as building blocks will permit the preparation of a variety of cyclophanes with exceptionally close contacts between functional groups that have so far escaped such “high-pressure” situations. On the following pages the attempted syntheses of cyclophanes with even shorter non-bonded contacts are briefly described.

As described before, we have successfully made the *in*-H*,in*-Me cyclophane **31** with a very short non-bonded contact. Unfortunately, the distance between the hydrogen and methyl group is not the shortest ever observed. The shortest H-methyl distance (2.26 Å) known is found in compound **62** (Figure 1.16).



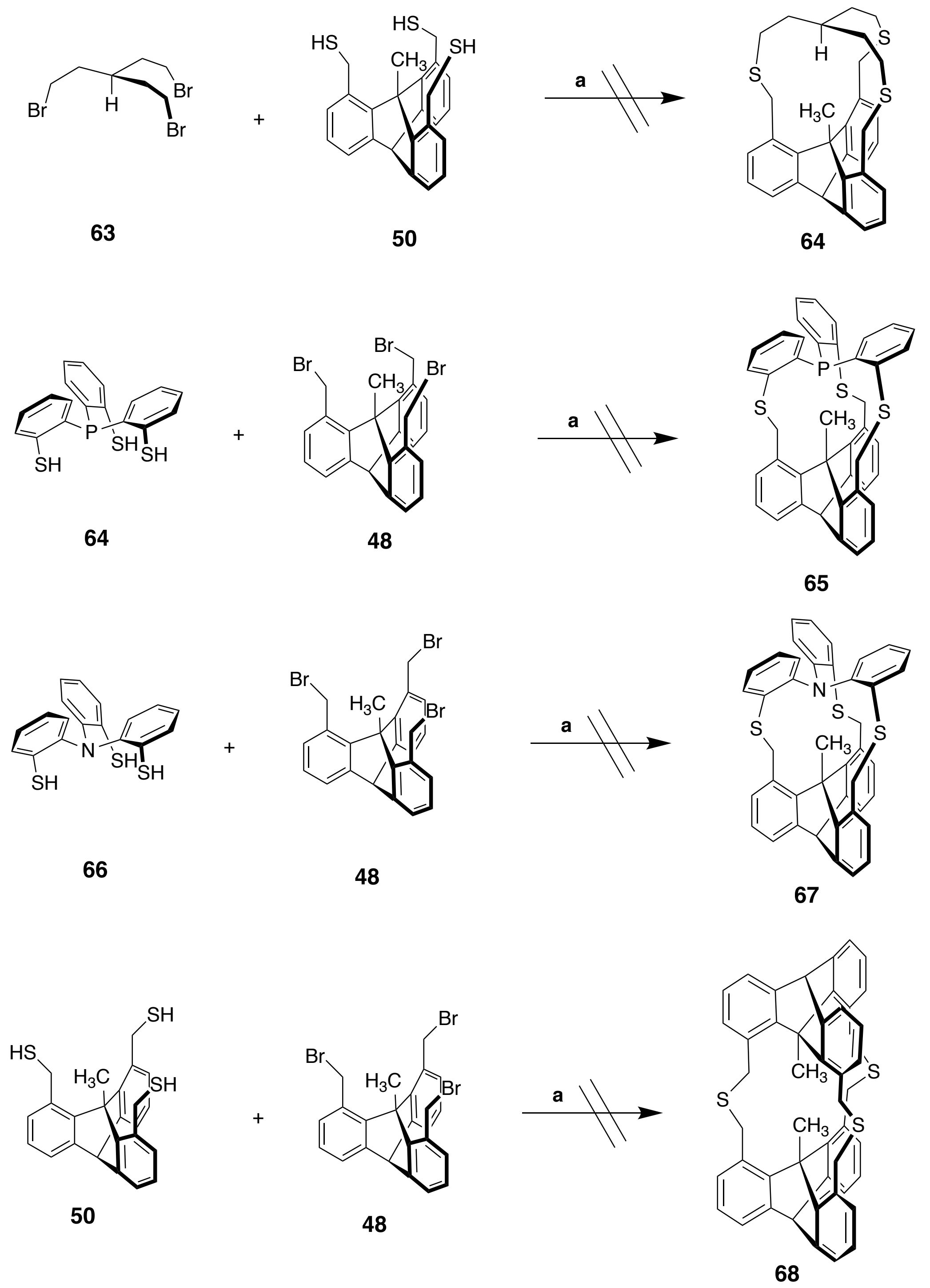
$d_{H\text{-}CH3}$ = 2.26 Å

Figure 1.16. Compound **62** with the shortest known H---Me non-bonded contact

However, if we decrease the numbers of atoms in the cyclophane chains, then we should get a shorter distance between the hydrogen atom and the methyl group. For example, in cyclophane **32**, there are nine atoms in the chains. If we can make a molecule with eight atoms or even seven atoms in the chains, we should get much shorter non-bonded contact distances. Based on that idea, we designed molecule **64**, in which the number of the atoms in the chain is eight. Both compounds **63** and **50** are known. After preparing both precursors, we attempted to make the desired cyclophane by the condensation of **63** with trithiol **50** at high dilution. Unfortunately, none of the desired compounds were found, nor were the *in,out*-isomers observed. Only a few very polar compounds were formed in the reaction.

We also tried to make the cyclophanes **65** and **67** which have short non-bonded P-methyl and N-methyl contact distances, respectively, from the tribromide **48** and trithiols **64** and **66**. Still, no desired compounds were found. For cyclophane **67**, the bridgehead nitrogen atom should be flat and the strain energy is not high. We still do not understand why this synthesis did not succeed.

Cyclophane **68**, which might be made from trithiol **50** and its precursor tribromide **48**, was especially desirable since only the *in,in*-isomer is possible and also because DFT calculations predict a very short d_{CC} of 2.747 Å. After condensation under the usual benzene-EtOH-KOH high dilution conditions, none of the desired product was found.



Scheme 1.5. Attempted syntheses of cyclophanes **64**-**68**: (a) KOH, 2:1 benzene-EtOH, reflux

1.8. Conclusion

Condensation of 1,8,13-tris(mercaptomethyl)triptycene and tris(bromomethyl)methane yields the *in,in*-cyclophane **30** in 8% yield with two inwardly directed methine groups. Compound **30** has been fully characterized by ^1H NMR and ^{13}C NMR spectroscopy, MALDI-TOF mass spectrometry, IR spectroscopy, and X-ray crystallography. The X-ray analysis clearly shows that it is the *in,in*-isomer. The proton NMR spectrum displays an obvious coupling between the two methine hydrogens, which was proved by selective irradiation of one of the apical methine protons. The coupling constant is 2.0 Hz, which is the largest H---H through-space coupling observed so far. Based on DFT and MP2 calculations, the hydrogen-hydrogen non-bonded contact distance is estimated to be 1.50-1.53 Å.

Two *in,in*-cyclophanes **31** and **56**, containing one or two methyl groups in their central cavities, have been synthesized, crystallized and fully characterized by ^1H and ^{13}C NMR spectroscopy, MALDI-TOF mass spectrometry, IR spectroscopy, and X-ray crystallography. Cyclophane **31** is the first example of an *in,in*-cyclophane with a methyl group inside the cavity. The IR spectrum clearly shows that the Si-H stretch is blue-shifted from 2177 cm^{-1} in an acyclic model to 2269 cm^{-1}. Based on computational studies, cyclophane **31** has a very short non-bonded H---CH_3 distance of about 2.30 Å. Cyclophane **56** does not have short non-bonded contact distance, but it is the first example of a macrobicyclic compound that contains two inwardly directed methyl groups.

Three cyclophanes with the formula $(C_{28}H_{31}PS_3)_n$, where n = 1 or 2, were isolated from the base-promoted macrocyclization of tris(2-mercaptophenyl)phosphine (**58**) and tris(3-bromopropyl)methane (**59**). Spectroscopic and X-ray analysis showed them to be the *in,in*-isomer **32**, the *in,out*-isomer **60**, and a dimeric *in,out,in,out*-isomer **61**. Compounds **32** and **61** display approximately C_3-symmetric and C_i-symmetric structures, respectively, in the crystal, but compound **60** adopts two distinct low-symmetry conformations in the solid state. In each case, the observed structures correspond to the lowest energy conformations of their respective isomers as calculated at the B3PW91/6-31G(d) level of theory. The *in,in*-isomer **32** displays a close contact between the phosphine *in*-lone pair and the *in*-methine group, with through-space spin-spin coupling constants of J_{PH} = 9 Hz and J_{PC} = 24 Hz, the latter of which appears to be the largest reported phosphorus-carbon through-space coupling constant.

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Chapter 2. Synthesis and Characterization of Dodecaphenyltetracene and Decaphenylphenanthrene

2.1. Introduction

Polycyclic aromatic hydrocarbons have dramatically changed the landscape of carbon-based materials in the past few decades.[1,2] These materials have opened doors to new technologies such as organic semiconductors, with potential applications in many areas of materials science, including catalysis, organic electronics, energy storage, and spintronics.[3] Obtaining access to nanocarbons of defined size and shape allows chemists to tailor their electronic, magnetic, and optical properties.

An important subclass of polycyclic aromatic hydrocarbons are acenes (Figure 2.1), being linearly fused benzenes, which can be considered one-dimensional nanographenes.[4] In contrast to their angularly fused analogs, namely, the helicenes, the parent (unsubstituted) acenes are planar. However, upon substitution, acenes readily twist out of planarity. The definition of "twisted" is the torsion angles ABCD and BADC.

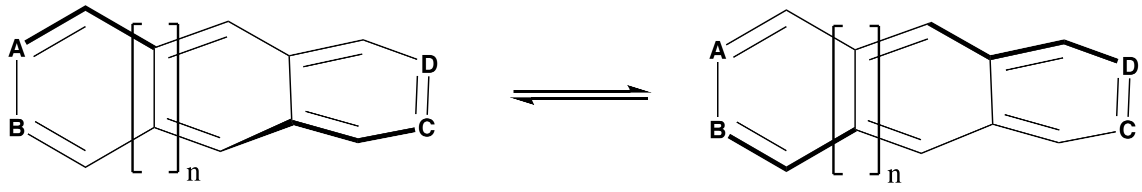
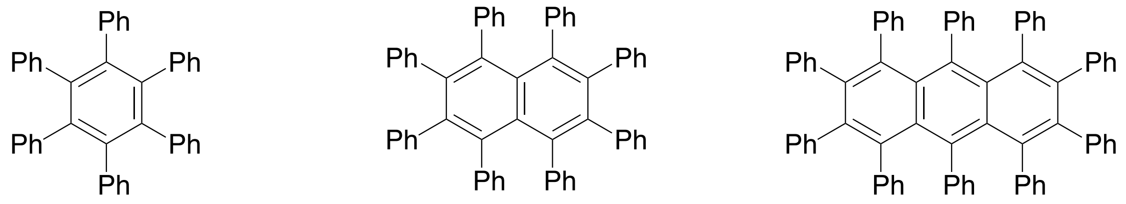


Figure 2.1. Twisted acenes

2.2. Twisted acenes

The conceptually simplest way to deform an acene is to attach several bulky substituents to its periphery by single bonds. In 1933, hexaphenylbenzene (**69**) was first prepared by the cycloaddition of tetraphenylcyclopentadienone and diphenylacetylene.[5] A natural extension of this work might have been the synthesis of other perphenyl aromatic compounds, but this did not occur for many years. In 1996, Pascal et al. reported the synthesis and characterization of octaphenylnaphthalene and decaphenylanthracene.[6] Octaphenylnaphthalene (**70**) was synthesized by the addition of tetraphenylbenzyne to tetraphenylcyclopentadienone, and decaphenylanthracene (**71**) was synthesized by the addition of the same aryne to hexaphenylisobenzofuran followed by deoxygenation of the adduct.



69 **70** **71**

Figure 2.2. Examples of perphenylacenes

X-ray analysis of compound **70** shows a small (3°) twist of the naphthalene, but all other octaarylnaphthalenes are more highly twisted, with end-to-end twists of up to 35°.[7] However, in compound **71**, the anthracene core adopts a longitudinally twisted conformation with a large overall end-to-end twist of 62.8°; the three rings contribute 18.8°, 25.2°, and 18.8°, respectively.

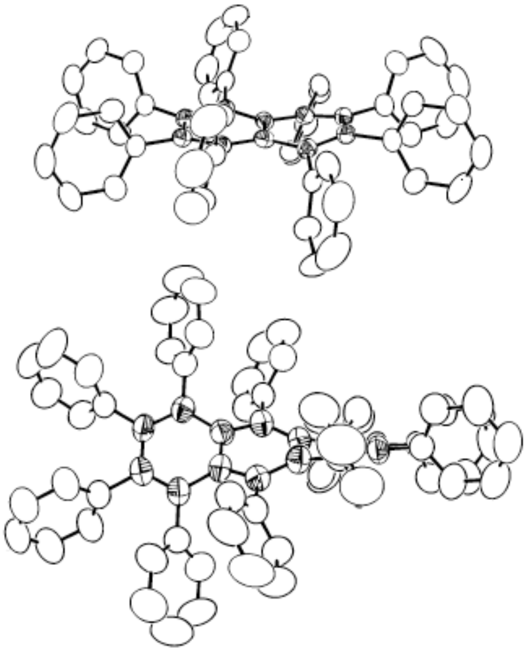
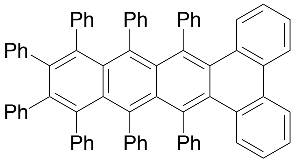


Figure 2.3. X-ray structures of octaphenylnaphthalene (above) and decaphenylanthracene (below)

In 1997, Qiao *et al*. reported a more twisted acene: 9,10,11,12,13,14,15,16-octaphenyldibenzo[*a,c*]naphthacene (**72**).[8] The X-ray structure shows that compound **72** possesses an extraordinary end-to-end twist of 105° (Figure 2.4). The main reason for the greater twist in this compound is the inclusion of two sterically demanding benzo groups in place of phenyls at one end (Figure 2.5).



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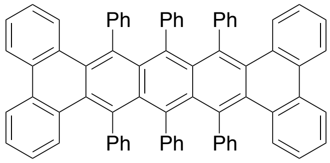

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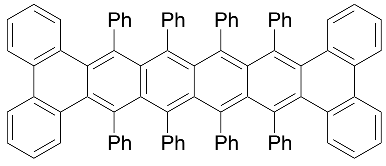


74

Figure 2.4. Examples of highly twisted acenes

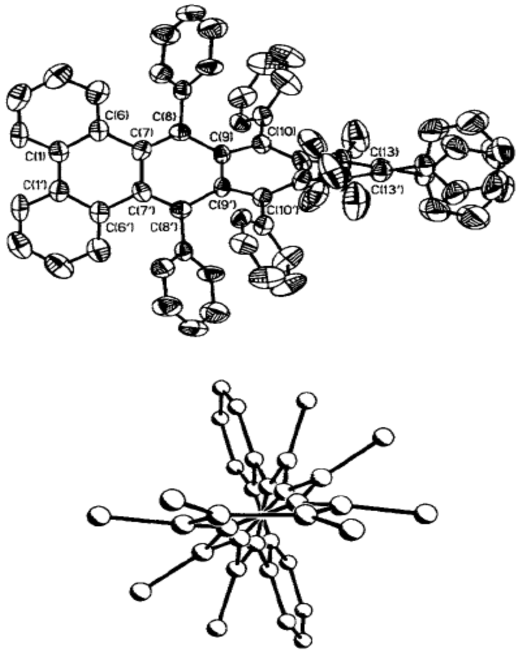


Figure 2.5. Molecular structure of compound **72**

In 2004, Lu *et al*. reported the much more twisted acene **73**[9] (Figure 2.4): 9,10,11,20,21,22 hexaphenyltetrabenzo[*a,c,l,n*]pentacene (**73**) which was prepared by the reaction of 1,3-diphenylphenanthro[9,10-*c*]furan with bisaryne equivalents generated from 1,2,4,5-tetrabromo-3,6-diphenylbenzene in the presence of *n*-butyllithium, followed by deoxygenation of the double adduct with low-valent titanium. The X-ray structure shows the end-to-end twist of the pentacene nucleus in compound **73** is 143.6°. This compound was the most twisted acene yet prepared. As in compound **72**, the four benzo groups force the large twist in compound **73** (Figure 2.6).

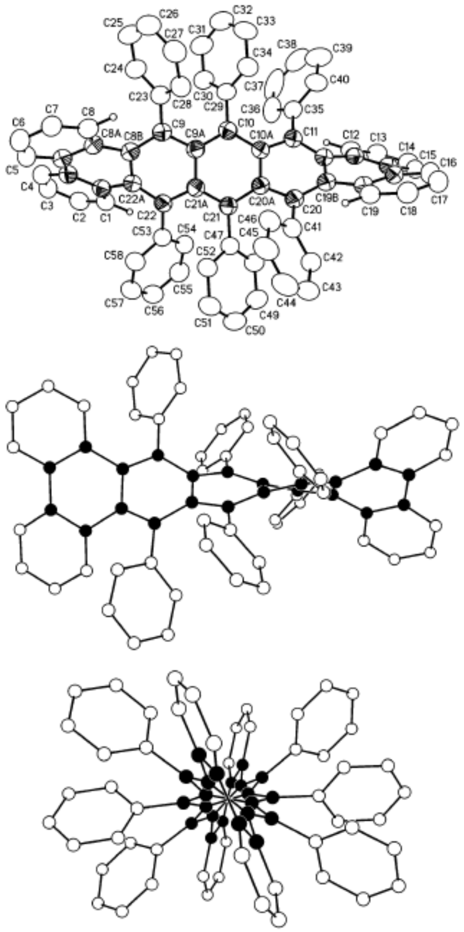


Figure 2.6. Three views of the molecular structure of **73**

Most recently, Clevenger *et al*. reported a longitudinally twisted hexacene: 9,10,11,12,21,22,23,24-octaphenyltetrabenzo[*a,c,n,p*]hexacene (**74**).[10] Most remarkably, hexacene **74** has C4A-C4B-C16A-C16B torsion angle of 183.5°, and it is the most twisted acene prepared so far (Figure 2.7).

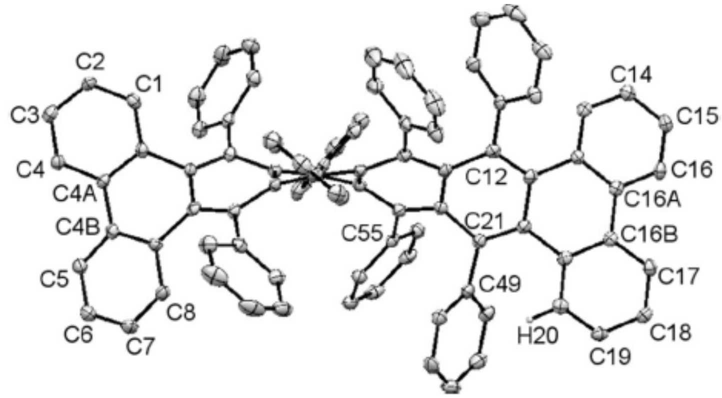


Figure 2.7. X-ray crystal structure of compound **74**

Can we prepare other acenes and related polycycles which are fully phenyl substituted so that the polycycles are highly twisted (Figure 2.8)?

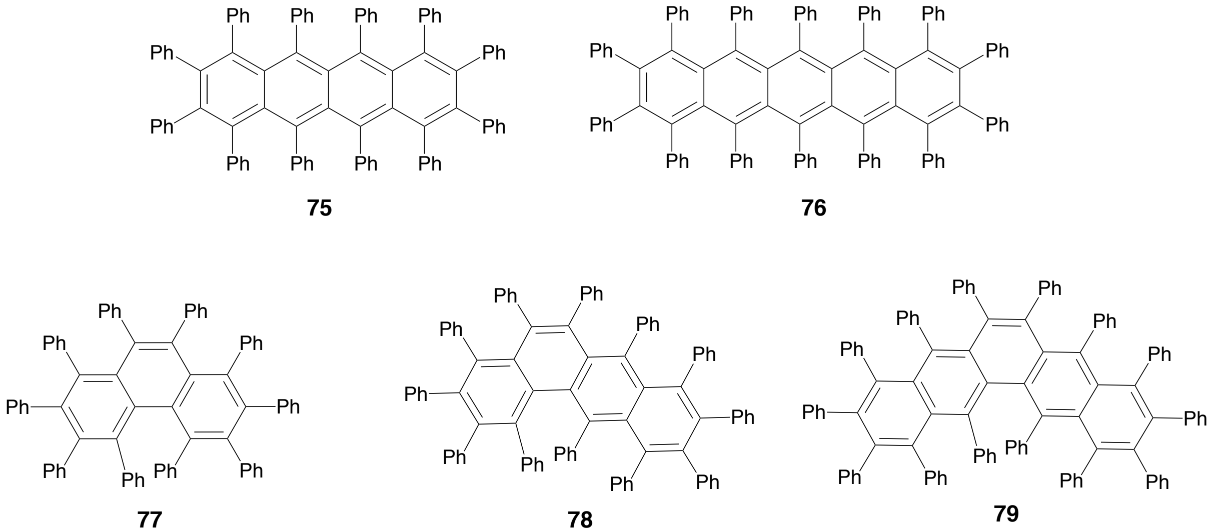
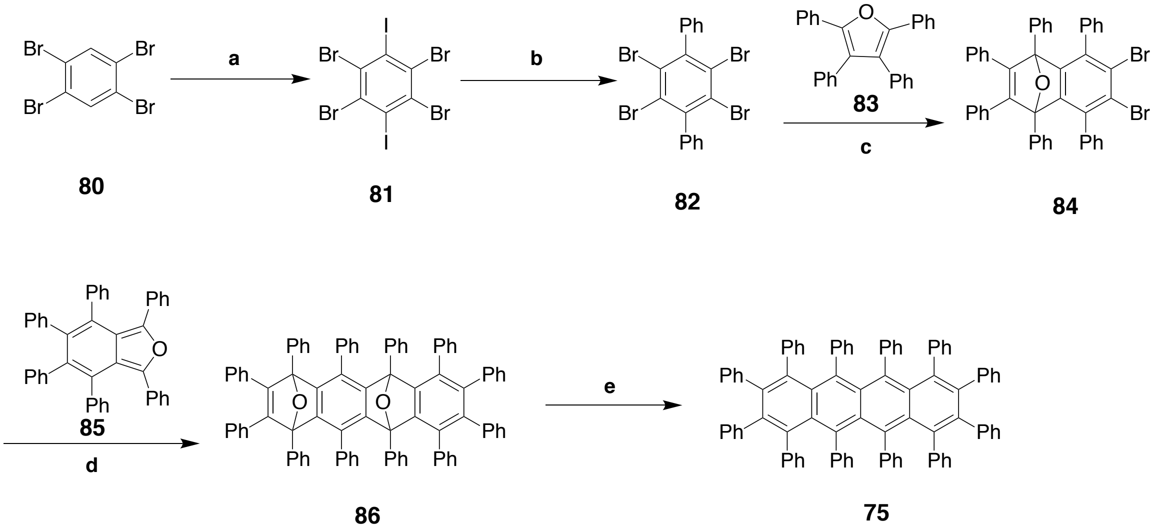


Figure 2.8. Perphenylacene targets

2.3. Synthesis of perphenyltetracene

2.3.1. Synthesis of perphenyltetracene

Based on the structure of the target molecule **75**, a retrosynthetic strategy was proposed in which it can be made by the deoxygenation of compound **86**. Compound **86** may be made by Diels-Alder reaction of compound **84** and isobenzofuran **85** through a benzyne intermediate. Similarly, compound **84** may be formed by the reaction of compounds **82** and **83**. Compound **82** may be easily made by selectively Suzuki coupling of benzeneboronic acid and compound **81,** which in turn can be formed through the iodination of commercially available 1,2,4,5-tetrabromobenzene (**80**).



Scheme 2.1. Synthesis of perphenyltetracene **75**: (a) I_2, $NaIO_3$, conc. H_2SO_4; (b) benzeneboronic acid, $Pd(OAc)_2$, Ph_3P, Na_2CO_3, acetone, argon, reflux; (c) tetraphenylfuran, *n*-BuLi, dry toluene, argon, -78 ^{o}C to RT; (d) hexaphenylisobenzofuran, *n*-BuLi, dry toluene, argon, -78 ^{o}C to RT; (e) $AlCl_3$-$TiCl_3$, *n*-BuLi, ether, argon, -78 ^{o}C to RT

Commercially available 1,2,4,5-tetrabromobenzene (**80**) was treated with iodine and sodium iodate in concentrated sulfuric acid to make 1,4-diiodo-2,3,5,6-tetrabromobenzene (**81**) in 98% yield.[9] We attempted to synthesize 1,4-diphenyl-

2,3,5,6-tetrabromobenzene (**82**) from compound **81** by Ullmann coupling with iodobenzene, but the yield was very low. We then tried a Suzuki coupling reaction to make the target compound **82**. After examing different Pd catalysts, we found that $Pd(OAc)_2$ plus Ph_3P is the best catalyst with which to make compound **82.** It is formed in 80% yield.[11] To make the key intermediate **84**, we attempted to react compound **82** with tetraphenylfuran (**83**) by Diels-Alder reaction via generation of an aryne from **82**. The amount of *n*-BuLi used is critical. With a 1:1 ratio of *n*-BuLi and **82**, some compound **82** remained. When the ratio was increased to 1.3:1, almost all compound **82** was consumed without formation of debromination side products. We successfully made compound **86** by a second Diels-Alder reaction of compound **84** and hexaphenylisobenzofuran (**85**) under similar conditions in a fair yield of 31%. In the second reaction, the amount of *n*-BuLi was increased to a 4:1 ratio to ensure that all **84** was reacted. After obtaining compound **86**, the oxygen atoms were successfully removed by using $TiCl_3$-$AlCl_3$ to make target compound **75** as a bright red solid in 32% yield.

2.3.2. UV spectrum of perphenyltetracene

Solutions of dodecaphenyltetracene **75** are magenta with a longest-wavelength absorption at 566 nm, a red shift of about 100 nm with respect to that of tetracene itself.[12] Compound **75** is also strongly luminescent, with a maximum emission at 613 nm and $\Phi = 0.12$ (Figure 2.9).

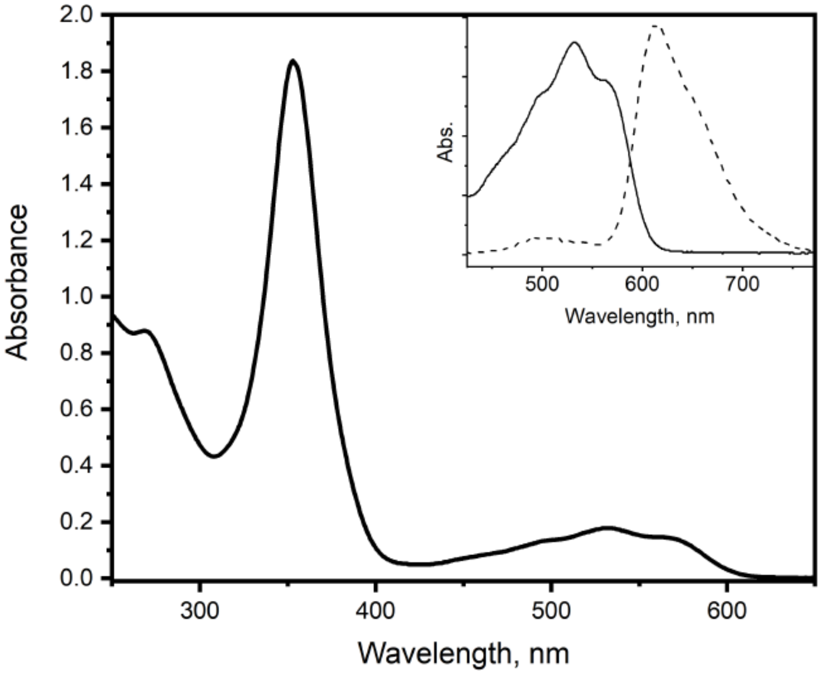


Figure 2.9. UV spectrum (CH_2Cl_2) of a 3.2 x 10^{-5} M solution of compound **75**. Inset: luminescence of **75** (CH_2Cl_2) with excitation at 410 nm. The solid trace is the absorbance (an expansion of part of the full spectrum), and the dotted trace is the luminescence. The intensities of both are in arbitrary units so that the peaks are of roughly the same height

2.3.3. X-ray structure of the perphenyltetracene

Single crystals of compound **75** suitable for X-ray analysis were obtained upon evaporation of a solution in $CHCl_3$/EtOAc. Compound **75** crystallized in the space group *C*2 (No. 5) with *Z* = 4, and the asymmetric unit contains two independent half molecules of **75**. Therefore, the structure contains two crystallographically independent tetracenes, each of which possesses exact C_2 symmetry and approximate D_2 symmetry in the crystal. The molecular structure of one of these molecules is illustrated in Figure 2.10. The tetracene core of compound **75** is smoothly twisted, with overall end-to-end twists of 98(1)° and 96(1)° for the two independent molecules, and it is obviously the most twisted perphenylacene so far prepared (Figure 2.10).

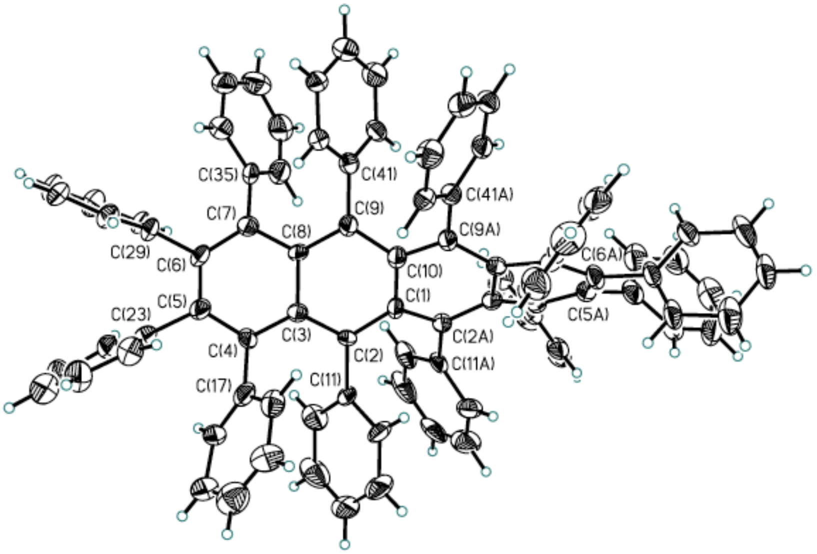


Figure 2.10. Molecular structure of dodecaphenyltetracene (**75**). Thermal ellipsoids are set at 50% probability

2.3.4. Electrochemistry of perphenyltetracene

Compound **75** has a "picket fence" of phenyl substituents, roughly perpendicular to, and out of conjugation with the tetracene, which essentially encapsulates the acene in an inert hydrocarbon sheath. For this reason, compound **75**, like decaphenylanthracene,[13] displays fully reversible electrochemistry with oxidation and reduction observed at +0.69 V and -1.50 V, respectively, versus Ag/AgCl (Figure 2.11). Nevertheless, compound **75** is not completely unreactive, and solutions allowed to stand in the presence of air and light undergo slow decomposition to colorless oxidation products, as we have observed previously for other deeply-colored twisted acenes.[14]

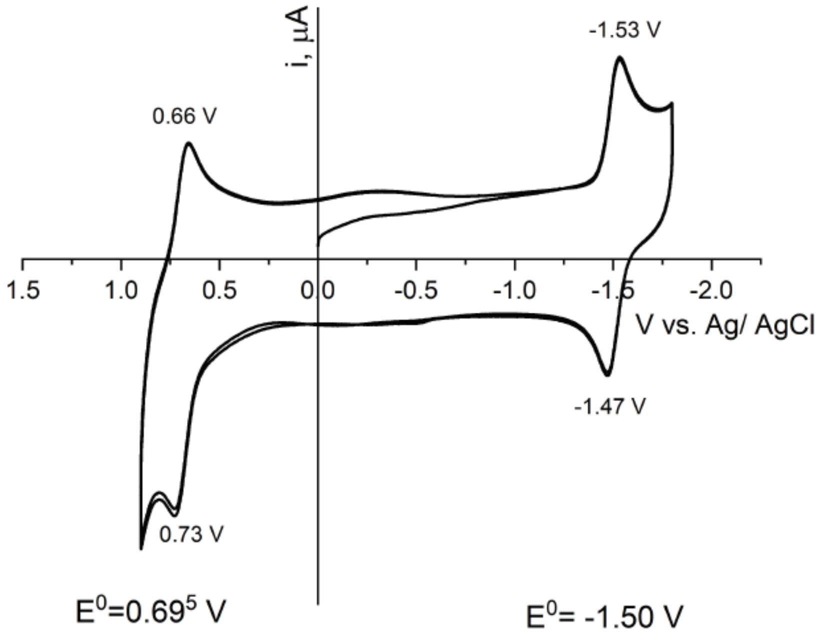


Figure 2.11. Electrochemistry of dodecaphenyltetracene (**75**)

2.3.5. The chirality of perphenyltetracene

The conformation of compound **75** is chiral, but it is unlikely to be configurationally stable under ordinary conditions. As with other twisted acenes, racemization is a multistep process with relatively modest barriers,[15] in contrast to the helicenes, where racemization occurs via a single, difficult step.[16] At the AM1 level of theory,[17] a four-step racemization pathway was identified in which the highest barrier ($\Delta G^{\neq}_{\mathrm{rac}}$) is only 17.3 kcal mol^{-1} (Figure 2.12). If correct, this corresponds to a half-life of less than a second at room temperature.

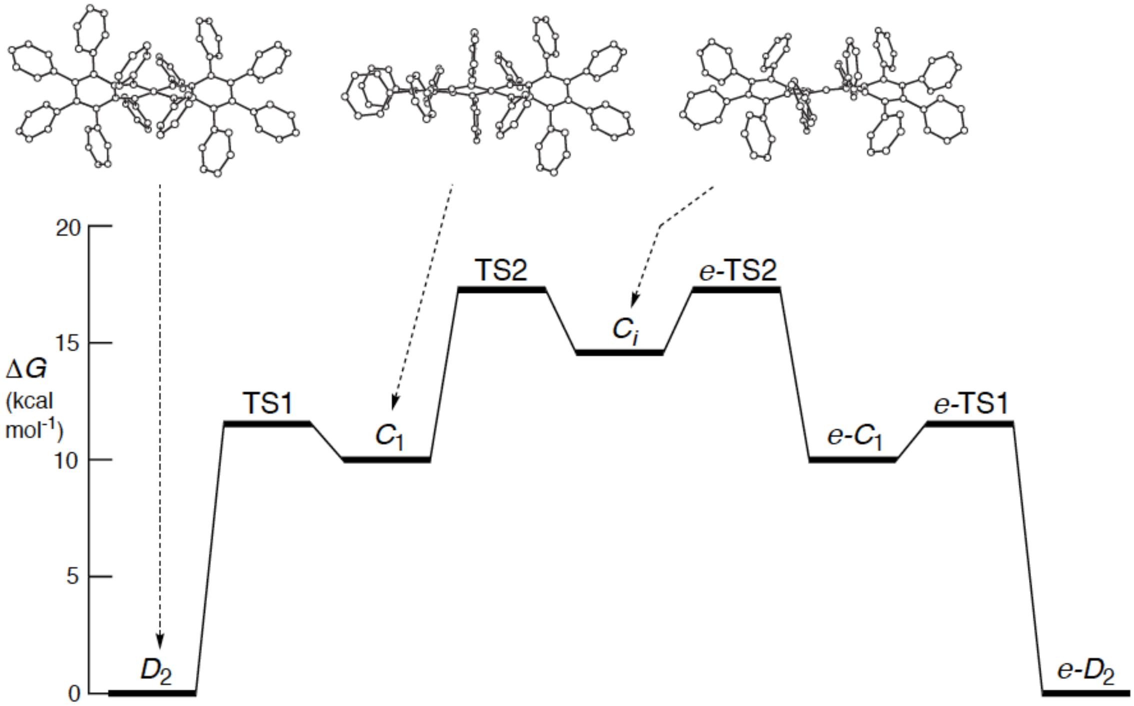
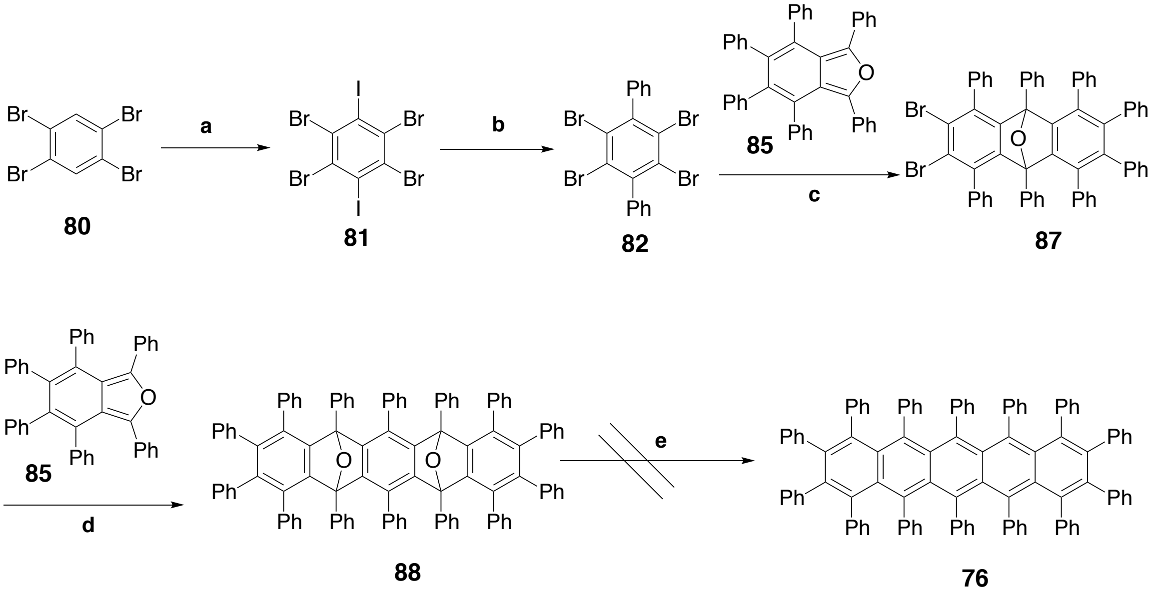


Figure 2.12. The racemization of **75** is a four-step process. The pathway includes a pair of enantiomeric C_1-symmetric intermediates (ΔG_{C1} = +10.0 kcal/mol), a C_i-symmetric intermediate (ΔG_{Ci} = +14.7 kcal/mol), and two pairs of enantiomeric transition state structures (ΔG_{TS1} = +11.8 kcal/mol and ΔG_{TS2} = +17.3 kcal/mol)

2.4. Attempted synthesis of perphenylpentacene

2.4.1. Synthesis of perphenylpentacene

Based on the structure of the target molecule **76**, a retrosynthetic strategy was proposed: pentacene **76** might be made by the deoxygenation of the compound **88**. Compound **88** may be made by Diels-Alder reaction of compound **87** and hexaphenylisobenzofuran (**85)** through a benzyne intermediate. Similarly, Compound **87** may be formed by the reaction of compounds **85** and **82**. Compound **82** may be easily made by selectively Suzuki coupling of benzeneboronic acid and compound **81**, which in turn can be formed through the iodation of commercially available 1,2,4,5-tetrabromobenzene (**80**).



Scheme 2.2. Synthesis of perphenylpentacene **76**: (a)I_2, $NaIO_3$, Conc. H_2SO_4; (b) benzeneboronic acid, $Pd(OAc)_2$, $P(Ph)_3$, $NaCO_3$, acetone, Argon, reflux; (c) tetraphenylfuran, *n*-BuLi, dry toluene, argon, -78 ^{o}C to RT; (d) hexaphenylbenzofuran, *n*-BuLi, dry toluene, argon, -78 ^{o}C to RT; (e) (1), $AlCl_3$-$TiCl_3$, *n*-BuLi, ether, argon, -78 ^{o}C to RT; (2) Zn, acetic acid, reflux; (3), $SnCl_2$

The synthetic pathway is similar to that for perphenyltetracene **76** and the first two steps are the same. commercially available 1,2,4,5-tetrabromobenzene (**80**) was treated with iodine and sodium iodate in concentrated sulfuric acid to make 1,4-diiodo-2,3,5,6-tetrabromobenzene (**81**) in 98% yield, and 1,4-diphenyl-2,3,5,6-tetrabromobenzene (**82**) was formed in 80% yield by the treatment of **81** with benzeneboronic acid, $Pd(OAc)_2$ and Ph_3P. To make the key intermediate **87**, we attempted to react compound **82** with hexaphenylisobenzenefuran（**85**）by Diels-Alder reaction by generation an aryne from **82**. The amount of *n*-BuLi used is critical. With a 1:1 ratio of *n*-BuLi and **82**, some compound **82** remained. When the ratio was increased to 1.3:1, almost all compound **82** was consumed without debromination side products. We successfully made compound **88** by a second Diels-Alder reaction of compound **87** and hexaphenylisobenzofuran under similar conditions in a fair yield of 5%. In the second reaction, the amount of *n*-BuLi was increased to a 4:1 ratio to ensure that all **87** was reacted. After obtaining compound **88**, we first tried to remove the oxygen atoms to make target compound **76** by using $TiCl_3$-$AlCl_3$ reagent in the presence of *n*-BuLi according to the former procedure. Unfortunately, the reaction failed, leaving almost all the starting material unreacted. We then tried to use Zn powder in acetic acid under reflux as a reducing agent to remove the oxygens, but this failed again. Finally, we tried $SnCl_2$ as the reducing agent, but the reaction failed yet again. We presume that this may be because the oxygen atoms are surrounded phenyl rings in a highly congested environment, which blocks the reducing agent from approaching the oxygen atoms.

In order to eliminate any doubt about the identity of what we believed to be compound **88**, a single crystal was grown. An X-ray analysis of the crystal conformed the structure of compound **88** which is shown in Figure 13. Thus, the failures to synthesize perphenylpentacene were due to the use of inadequate reducing agents.

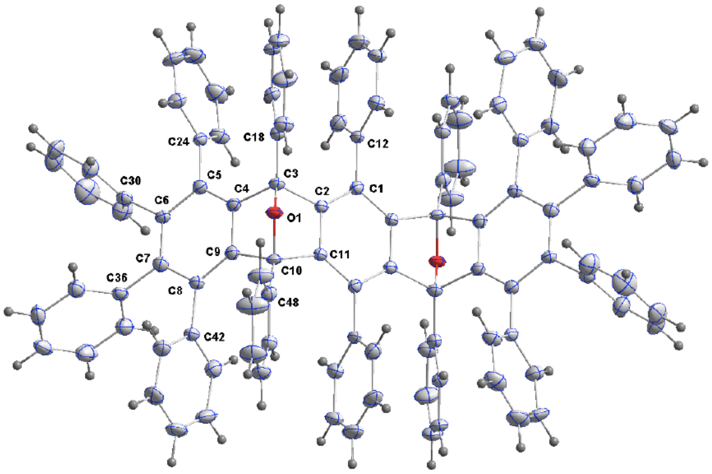
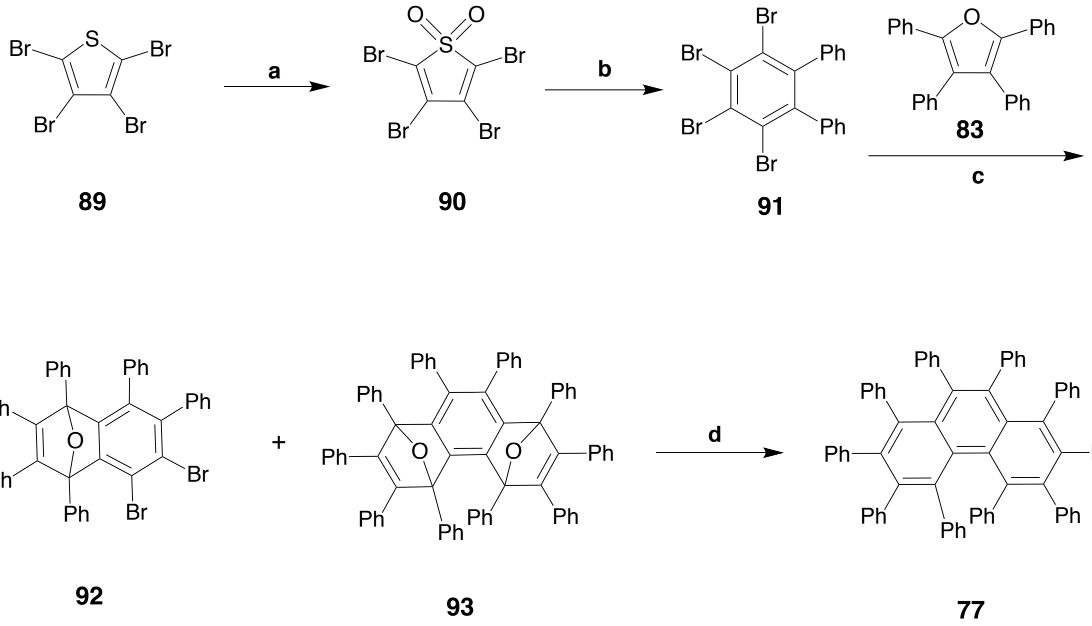


Figure 2.13. Molecular structure of compound **88**

2.5. Synthesis of perphenylphenanthrene

2.5.1. Synthesis of perphenylphenanthrene

Based on the structure of the target molecule **77**, a retrosynthetic strategy was proposed: phenanthrene **77** may be made by the deoxygenation of the compound **93**. Compound **93** may be made by Diels-Alder reaction of compound **92** and tetraphenylfuran (**83**) through a benzyne intermediate. Similarly, compound **92** may be formed by the reaction of compound **91** and tetraphenylfuran (**83**). At high temperature, compound **91** may be made by the reaction of diphenylacetylene and compound **90**, which in turn can be formed through the oxidation of commercially available tetrabromothiophene (**89**).



Scheme 2.3. Synthesis of perphenylphenanthrene **77**: (a) MCPBA, 1,2-dichloroethne, reflux; (b) diphenylacetylene, dichlorobenzene, reflux; (c) tetraphenylfuran, *n*-BuLi, dry toluene, argon, -78 ^{o}C to RT; (d) trimethylsilane chloride, NaI, acetonitrile : dichloromethane = 9:1, argon, RT

Commercially available 2,3,4,5-tetrabromothiophene (**89**) was treated with MCPBA in 1,2-dichloroethane under reflux for 3 days to give sulfone **90** in 60% yield. Sulfone **90** was then reacted with diphenylacetylene in dichlorobenzene under reflux to give 1,2-diphenyl-3,4,5,6-tetrabromobenzene (**91**) in 80% yield. To make the key intermediate **92**, we attempted to react compound **91** with tetraphenylfuran (**83**) by generation of an aryne from **91**. The amount of *n*-BuLi used is critical. With a 1:1 ratio of *n*-BuLi and **91**, some compound **91** remained. After the ratio was increased to 2.4:1, almost all compound **91** was consumed without the formation of debromonation side products. To our surprise, compound **92** was not the only product. We also isolated compound **93** in 35% yield. After obtaining compound **93**, we first tried to remove the oxygen atoms to make target compound **77** by using $TiCl_3$-$AlCl_3$/*n*-BuLi as before for the preparation of compound **75**. Unfortunately, the reaction failed, leaving almost all the starting material unreacted. We then tried to use Zn powder in acetic acid under reflux as a reducing agent to remove the oxygens, but this failed again. Finally, we tried $SnCl_2$ as the reducing agent, but the reaction failed yet again.However, in 2014, Bunz *et al*. reported a similar reaction which employed trimethylsilane chloride as a reducing agent.[18] This method proved to be successful, deoxygenating compound **93** to give the target compound **77** in 54% yield as a light yellow solid.

2.5.2. X-ray structure of perphenylphenanthrene

Single crystals of compound **77** suitable for X-ray analysis were obtained upon evaporation of a solution in benzene and 2-propanol. Each asymmetric unit contains two independent molecules of **77** (Figure 2.14) and each of them processes approximate C_2 symmetry in the crystal.

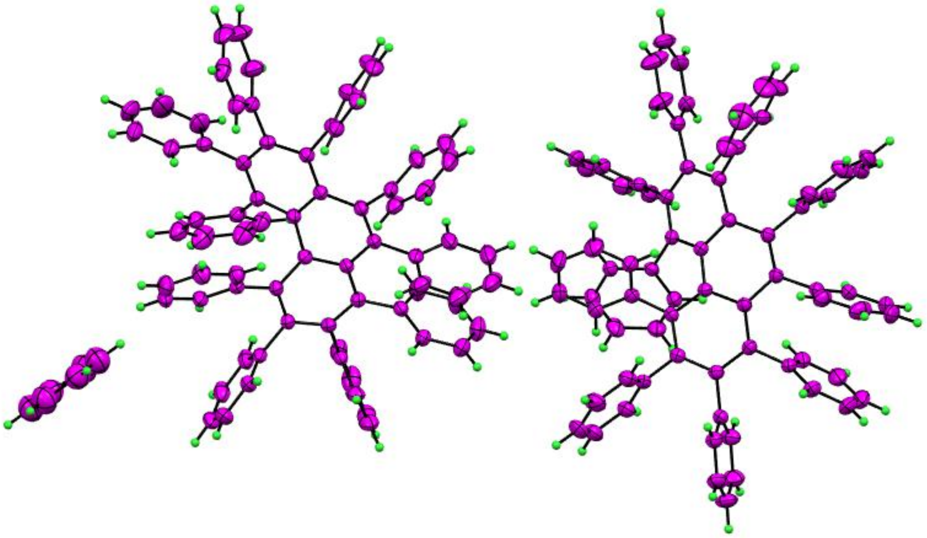


Figure 2.14. Molecular structure of compound **77**

2.6. Conclusions

Dodecaphenyltetracene (**75**) is the largest perphenylacene yet prepared. It has been synthesized, crystallized, and characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, MALDI-TOF mass spectrometry, UV-vis absorption and emission spectroscopy, cyclic voltammetry, and X-ray crystallography. The X-ray analysis shows compound **75** has an end-to-end twist of 97° making it the most twisted perphenylacene yet prepared. It also displays a fully reversible electrochemistry with oxidation and reduction. Compound **75** is magenta with a longest-wavelength absorption at 566 nm, a red shift of about 100 nm with respect to that of tetracene itself. It is also strongly luminescent, with a maximum emission at 613 nm and $\Phi = 0.12$.

Decaphenylphenanthrene (**77**) has been made and characterized by NMR and X-ray analysis. It is, so far, the only nonlinear perphenyl polycyclic aromatic hydrocarbon.

2.7. References

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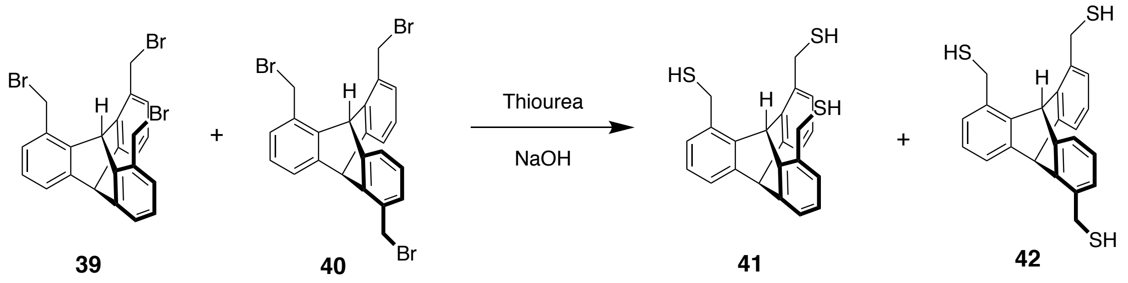
Chapter 3. Experimental Procedures and Selected Spectra

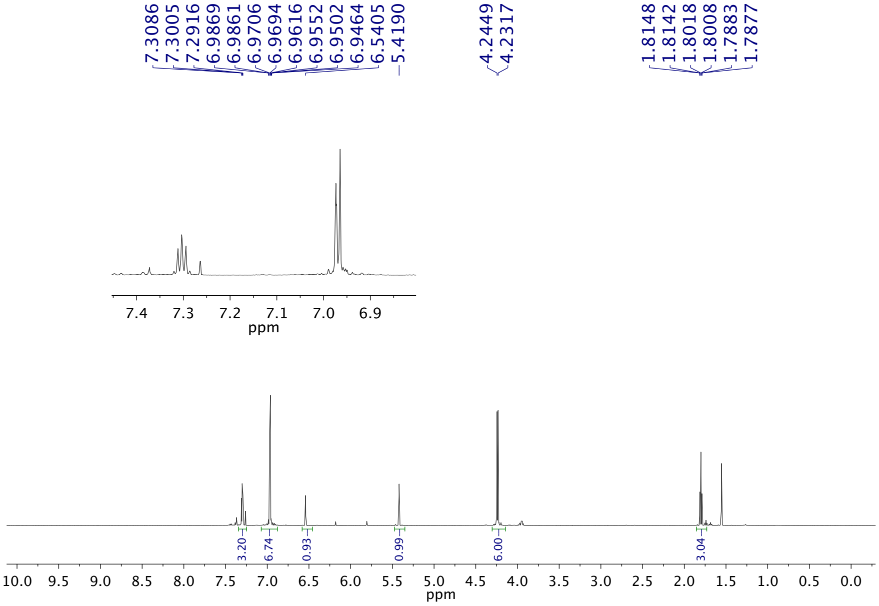
Synthesis of Compound 41



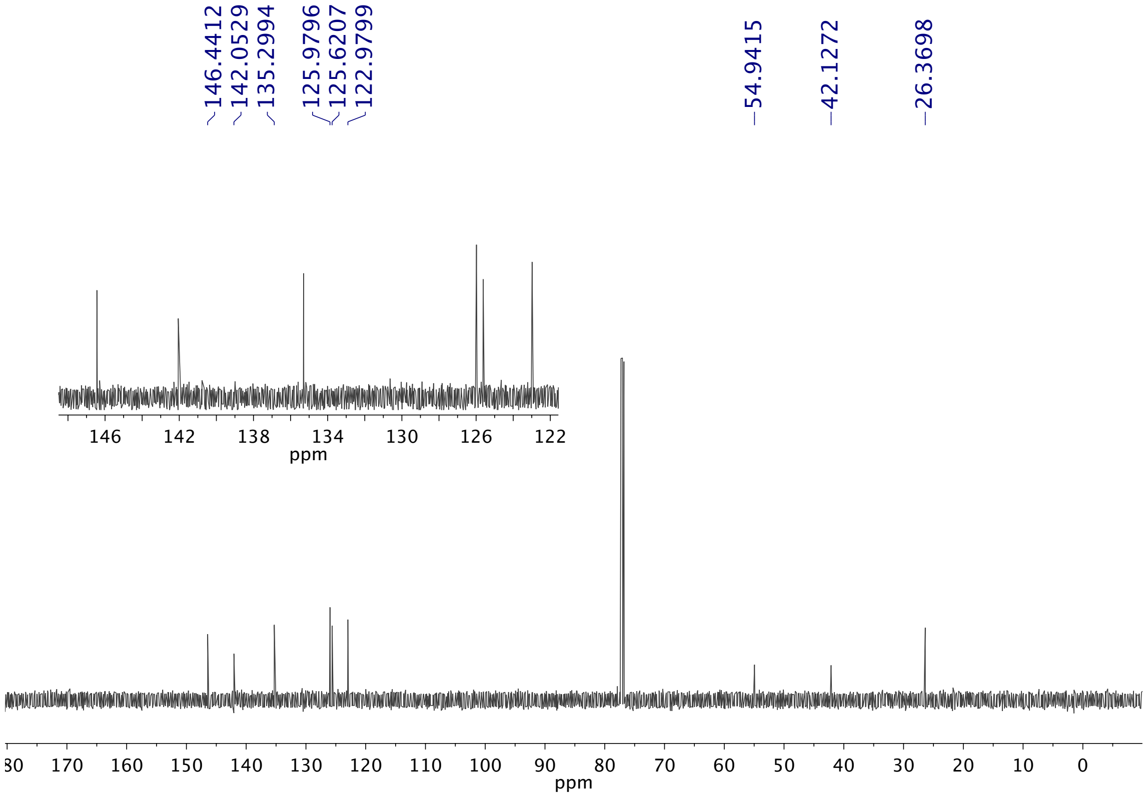
Following the procedure of Song,[1] a 1:1 mixture of 1,8,13-trimethyltriptycene and 1,8,16-trimethyltriptycene (1.05 g, 3.55 mmol) was dissolved in dry benzene (75 mL) under argon. NBS (2.1 g, 11.8 mmol) was added, and the solution was heated to reflux and illuminated with a tungsten lamp for 2 h. After cooling, the orange solution was concentrated to dryness, and the residue was dissolved in CH_2Cl_2 (30 mL). This solution was washed five times with water to remove succinimide, dried over Na_2SO_4, and concentrated. The residual solid was recrystallized from $CHCl_3$-hexanes to give 1,8,16-tris(bromomethyl)triptycene (the undesired anti isomer) as a white solid. The mother liquor was concentrated and subjected to silica gel column chromatography (solvent, 1:1 hexanes-CH_2Cl_2) to give the 1,8,13-tris(bromomethyl)triptycene (**39**) as a light yellow solid (870 mg, 1.63 mmol, 46% yield; but 92% yield based on the amount of 1,8,13-trimethyltriptycene in the starting mixture). This material was contaminated with significant amounts of tetrabrominated product, but it was largely free of the anti-isomer, and therefore used without further purification. ^1H NMR (300 MHz, $CDCl_3$) δ 5.04 (s, 6 H), 5.46 (s, 1 H), 6.53 (s, 1 H), 7.03 (m, 6 H), 7.36 (dd, J = 6.5 Hz, 1.5 Hz, 3 H).

A mixture of tribromide **39** (800 mg, 1.50 mmol) and thiourea (500 mg, 6.58 mmol) in ethanol (40 mL) and THF (40 mL) was heated at reflux with stirring overnight. After cooling, the solution was concentrated to dryness. The residue was dissolved in aqueous NaOH (1.21 g, 29.8 mmol, in 50 mL water), and the solution was heated at reflux under argon for 10 h. The solution was cooled in an ice-water bath, and then 6 *M* HCl (30 mL) was added. The solution was extracted three times with $CHCl_3$, and the combined organics were dried over Na_2SO_4. Concentration gave a sticky brown product that was purified by silica gel column chromatography (solvent, 1:1 hexanes-benzene, then 1:2 hexanes-benzene) to give white solid **41** (170 mg, 0.434 mmol, 29%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.80 (t, *J* = 6.5 Hz, 3 H), 4.24 (d, *J* = 6.5 Hz, 6 H), 5.42 (s, 1 H), 6.54 (s, 1 H), 6.97 (m, 6 H), 7.30 (m, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 26.4, 42.1, 54.9, 123.0, 125.6, 126.0, 135.3, 142.1, 146.4 (9 of 9 expected resonances); HRMS (ESI) *m/z* 415.0593 (M + Na), calcd for $C_{23}H_{20}NaS_3$, 415.0619.

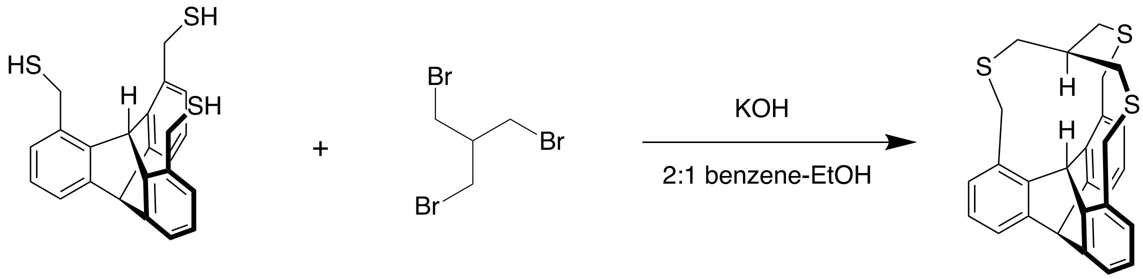
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of Compound **41**



^{13}C NMR Spectrum (126 MHz, $CDCl_3$) of Compound **41**



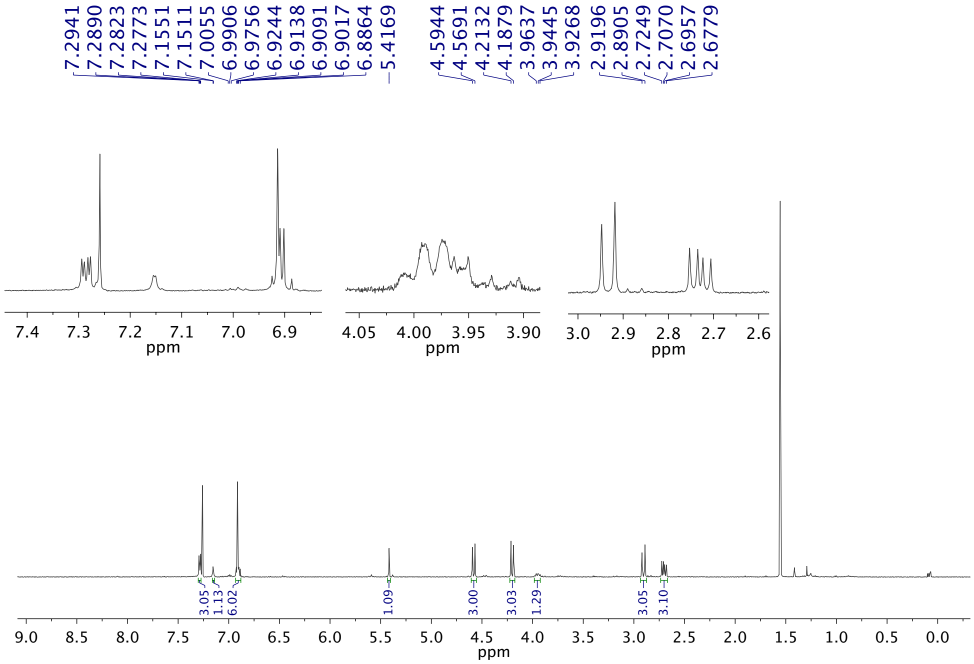
Synthesis of Cyclophane 30



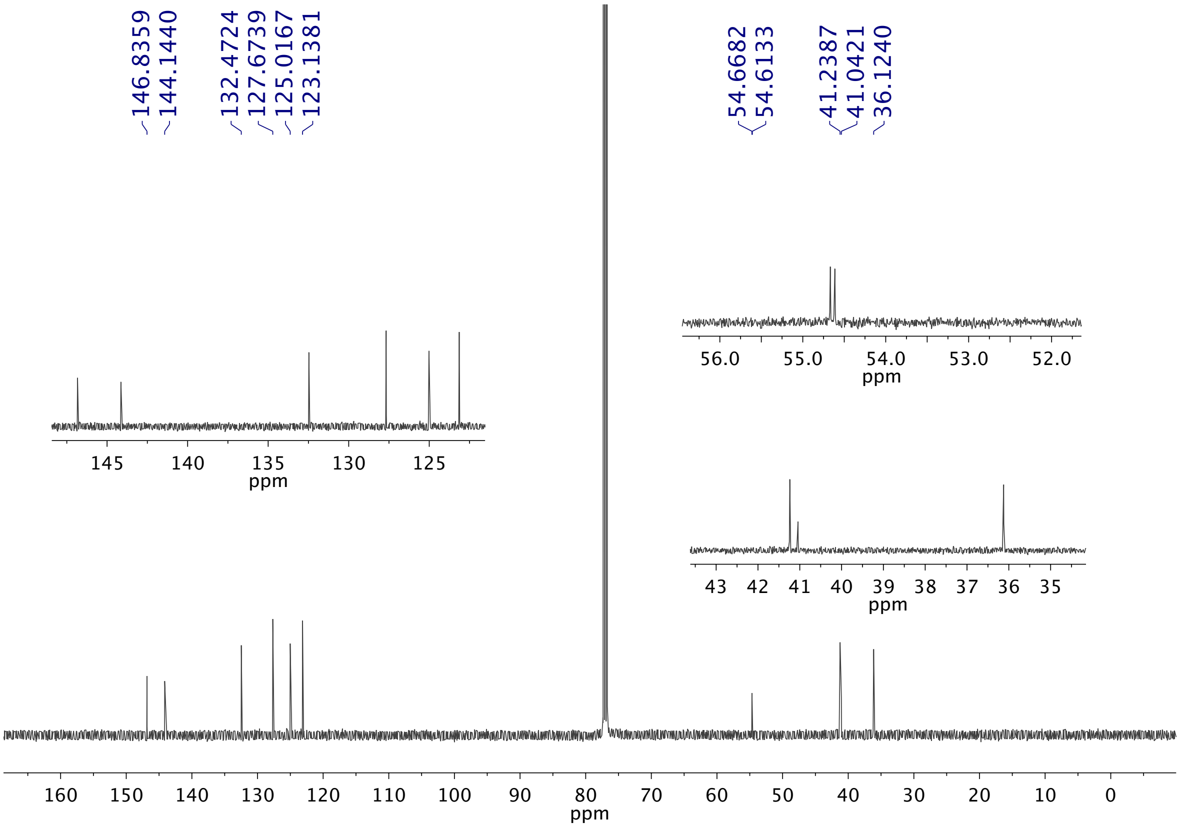
41 **43** **30**

Trithiol **41** (170 mg, 0.434 mmol) and tris(bromomethyl)methane[2] (**43**, 128 mg, 0.434 mmol) were dissolved in 2:1 benzene-EtOH (600 mL). The solution was purged with argon, and then it was heated to reflux. A solution of KOH (97 mg, 1.7 mmol) in EtOH (50 mL) was added dropwise over 1 h, and heating was continued overnight. After cooling, the solution was concentrated to dryness, and the residue was purified by silica gel column chromatography (solvent, 1:1 hexanes-CH_2Cl_2) to give crude cyclophane **30**. Further purification by preparative TLC (silica gel, 1:1 hexanes-benzene) gave pure cyclophane **30** as a white solid (16 mg, 0.036 mmol, 8%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.70 (dd, *J* = 14.5 Hz, 9 Hz, 3 H), 2.90 (d, *J* = 14.5 Hz, 3 H); 3.94 (m, 1 H), 4.20 (d, *J* = 12.5 Hz, 3 H), 4.58 (d, *J* = 12.5 Hz, 3 H), 5.42 (s, 1 H), 6.91 (m, 6 H), 7.15 (d, *J* = 2 Hz, 1 H), 7.28 (m, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 36.1, 41.0, 41.2, 54.6, 54.7, 123.1, 125.0, 127.7, 132.5, 144.1, 146.8 (11 of 11 expected resonances); HRMS (ESI) *m/z* 445.1099 (M + H), calcd for $C_{27}H_{25}S_3$, 445.1113. Single crystals suitable for X-ray analysis were obtained from ethyl acetate solution.

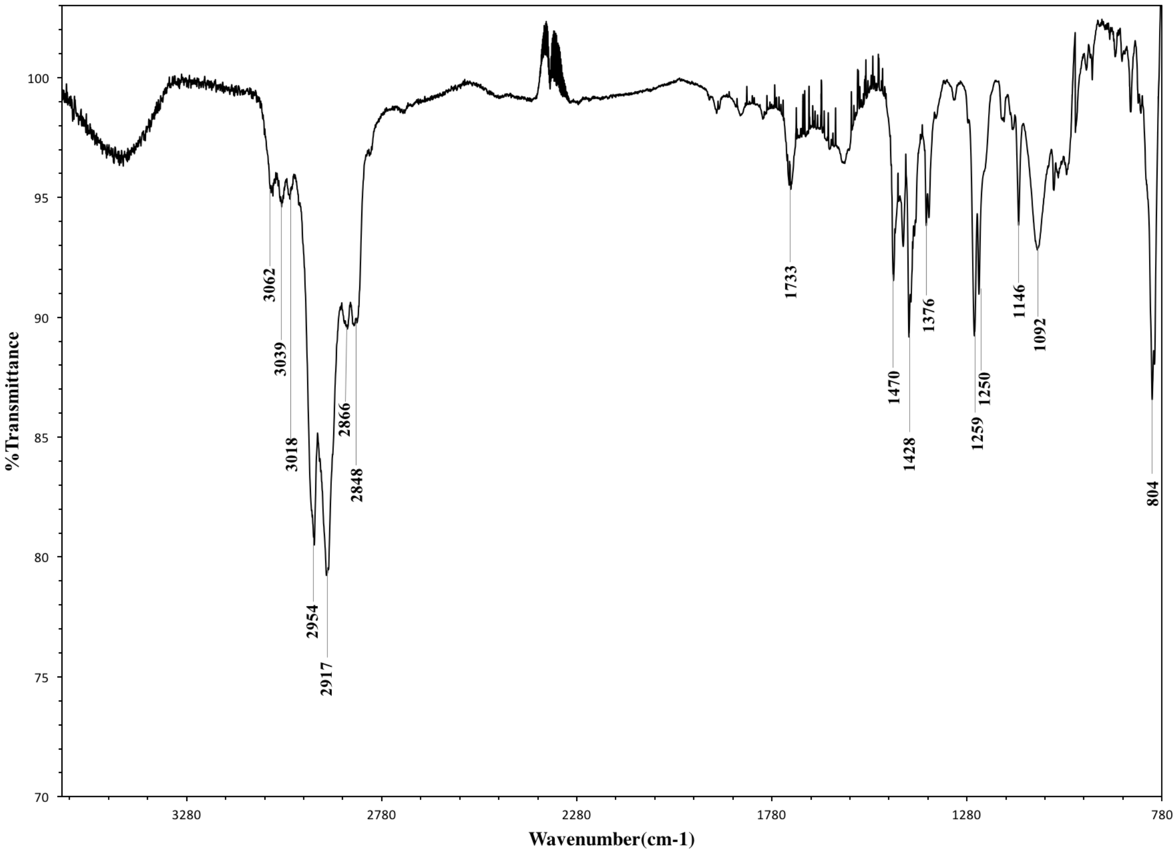
^{1}H NMR Spectrum (500 MHz, CDCl$_3$) of Cyclophane **30**



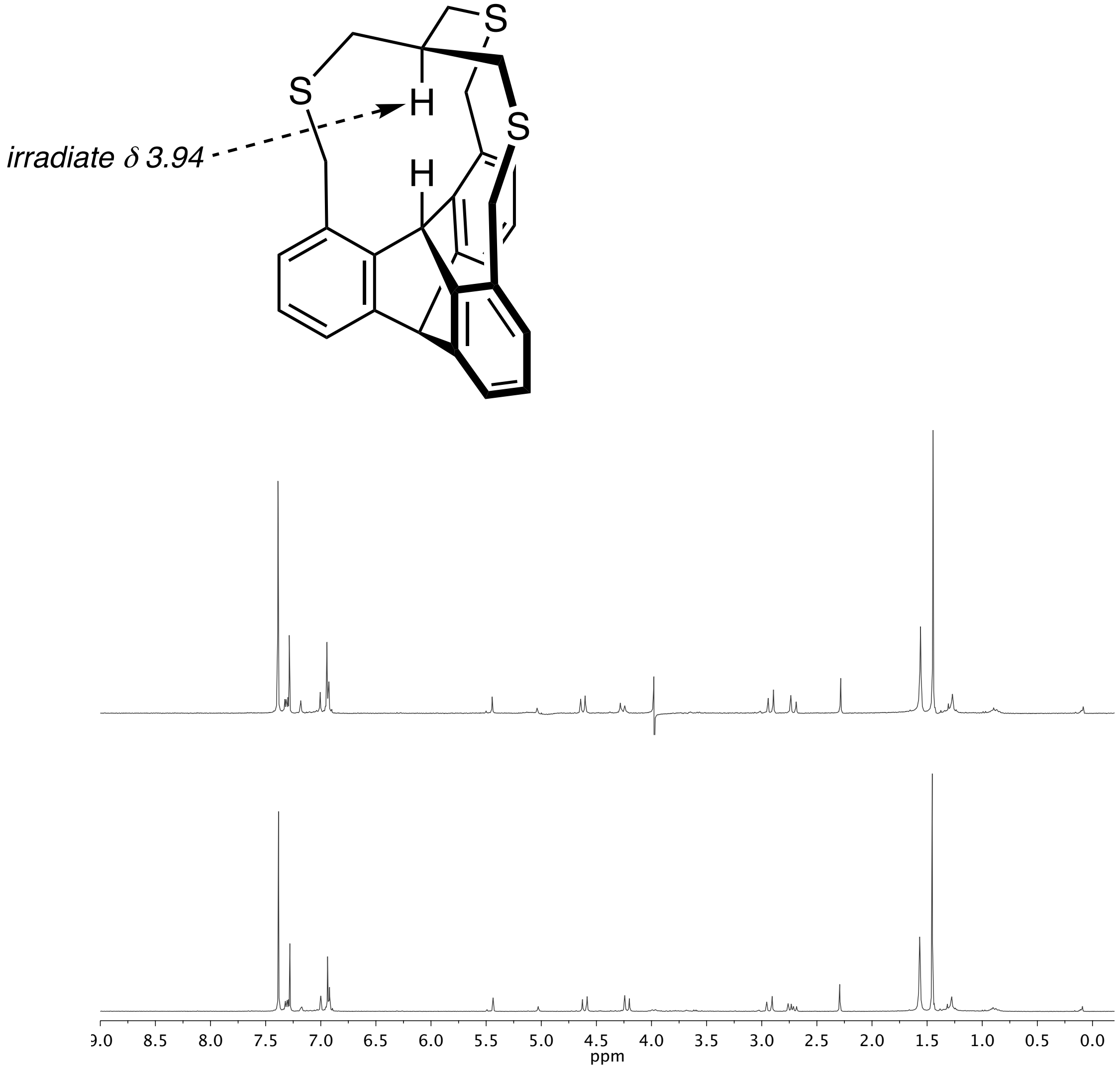
^{13}C NMR Spectrum (126 MHz, $CDCl_3$) of Cyclophane **30**



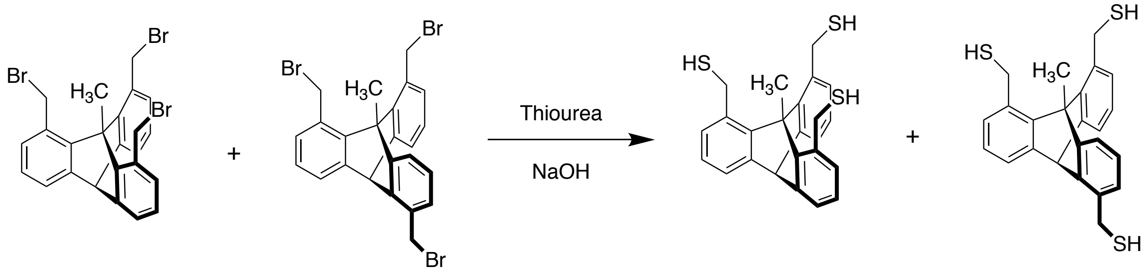
IR Spectrum (KBr) of Cyclophane **30**



Irradiation of the δ 3.94 Resonance of Cyclophane **30** (Full Spectrum). *Top:* Irradiation at δ 3.94; *Bottom:* No Irradiation.



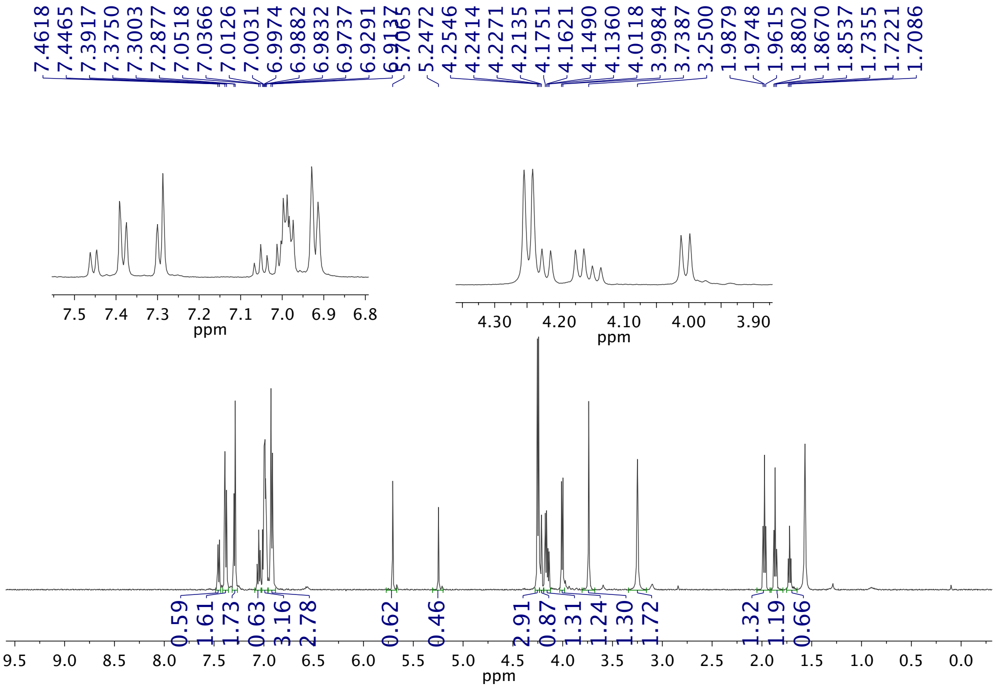
Synthesis of Compound 50



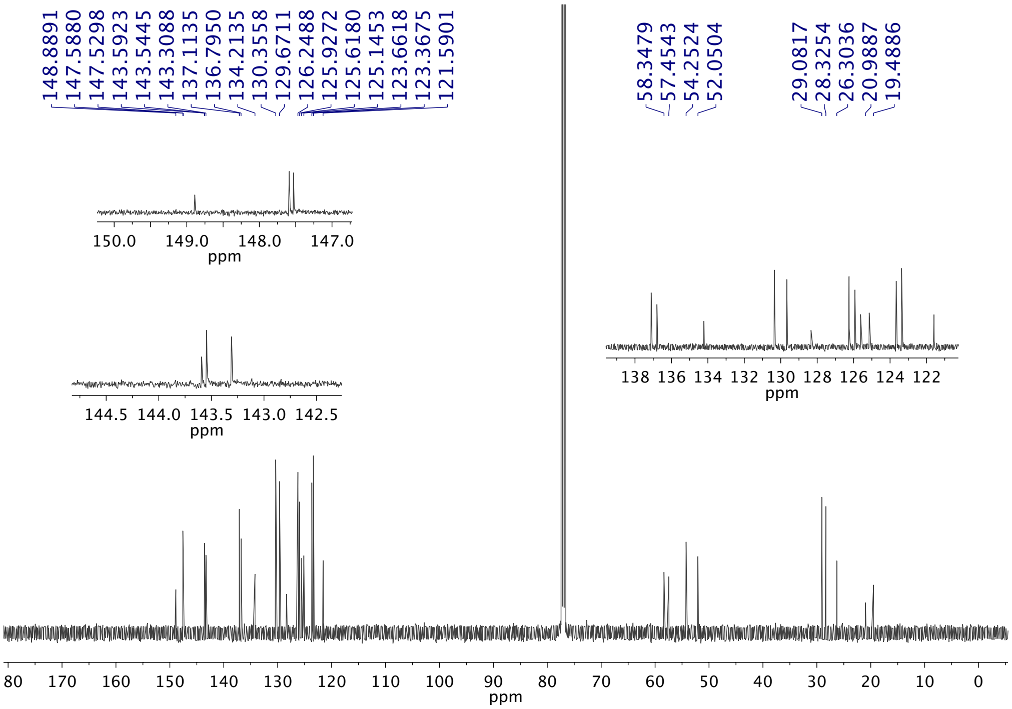
48 **49** **50** **51**

A mixture of tribromides **48** and **49**[3] (800 mg, 1.46 mmol) and thiourea (503 mg, 6.62 mmol) in ethanol (40 mL) and THF (40 mL) was heated at reflux with stirring overnight. After cooling, the solution was concentrated to dryness. The residue was dissolved in aqueous NaOH (1.21 g, 30.2 mmol, in 50 mL water), and the solution was heated at reflux for 10 h under argon. The reaction mixture was cooled in an ice bath, and then 6 M HCl (30 mL) was added. This solution was extracted three times with $CHCl_3$, and the combined organics were dried over Na_2SO_4. Concentration gave a sticky, brown, crude product. This was purified by silica gel column chromatography (solvent, 1:1 hexanes-benzene) to give a roughly 2:3 mixture of compounds **50** and **51** as a white solid (338 mg, 0.831 mmol, 57%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.72 (t, *J* = 6.5 Hz, 0.6 H, 5a), 1.87 (t, *J* = 6.5 Hz, 1.2 H, 5a), 1.97 (t, *J* = 6.5 Hz, 1.2 H, 5), 3.25 (s, 1.8 H, 5a), 3.74 (s, 1.2 H, 4), 4.00 (d, *J* = 6.5 Hz, 1.2 H, 5a), 4.16 (dd, *J* = 13 Hz, 6.5 Hz, 1.2 H, 5), 4.23 (dd, *J* = 13 Hz, 6.5 Hz, 1.2 H, 5), 4.25 (d, *J* = 6.5 Hz, 2.4 H, 5a), 5.25 (s, 0.4 H, 5), 5.71 (s, 0.6 H, 5a), 6.92 (m, 2.5 H), 6.99 (m, 2.5 H), 7.05 (t, J = 7.5 Hz, 0.5 H), 7.29 (m, 1.5 H), 7.38 (m, 1.5 H), 7.45 (d, J = 7.5 Hz, 0.5 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.5, 21.0, 26.3, 28.3, 29.1, 52.0, 54.3, 57.5, 58.3, 121.6, 123.4, 123.7, 125.1, 125.6, 125.9, 126.2, 129.7, 130.4, 134.2, 136.8, 137.1, 143.3, 143.5, 143.6, 147.5, 147.6, 148.9 (27 of 27 resonances expected for the two isomers); MS (MALDI-TOF; matrix, graphite-CF_3CO_2Na) *m/z* 429 (M + Na$^+$, 100).

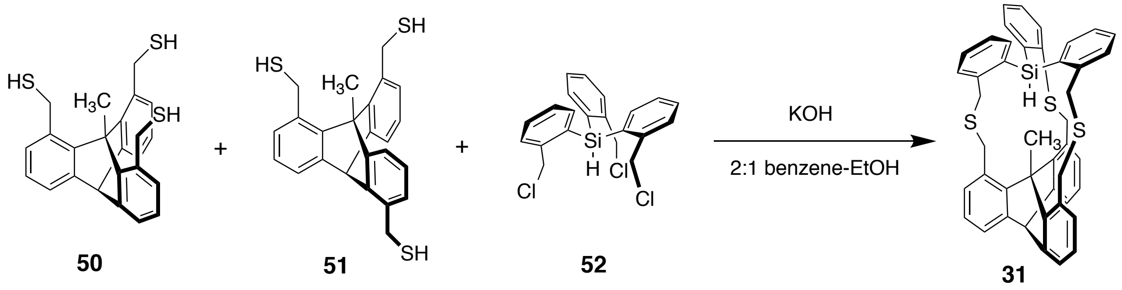
^{1}H NMR Spectrum (500 MHz, CDCl$_3$) of Compound **50/51**



^{13}C NMR Spectrum (126 MHz, CDCl$_3$) of Compound **50/51**

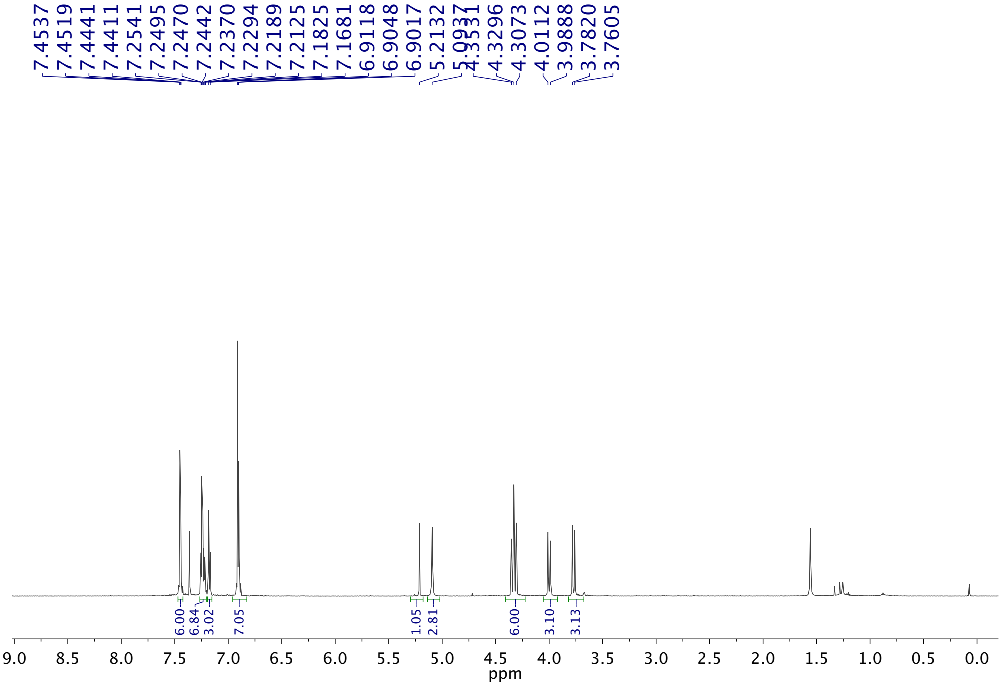


Synthesis of Cyclophane 31

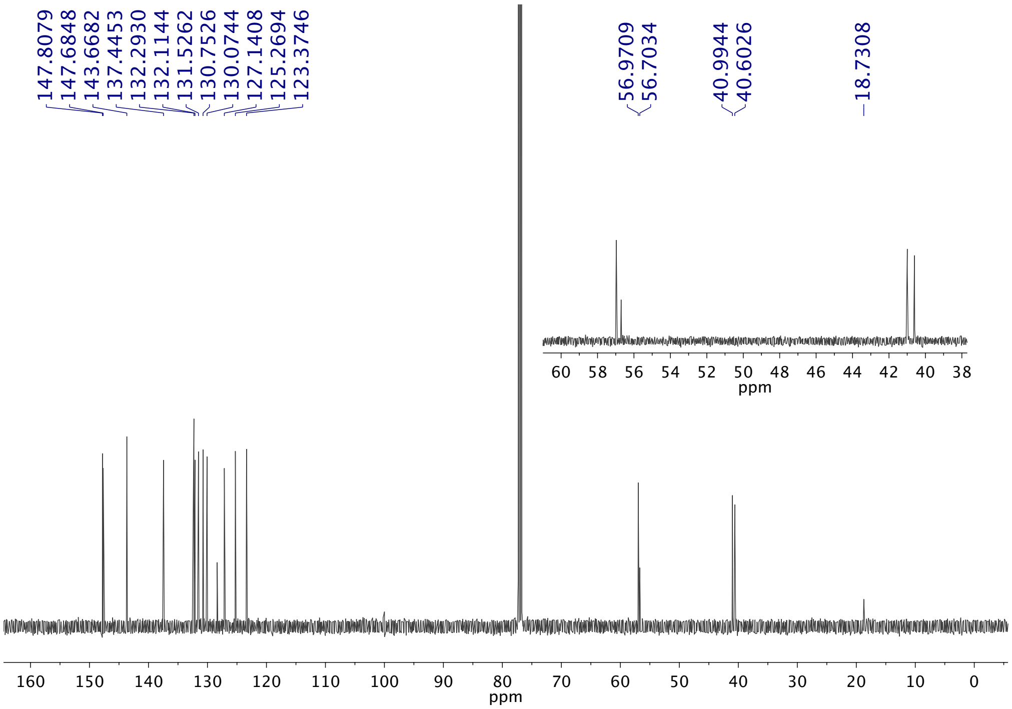


A 5:7 mixture of trithiols **50** and **51** (340 mg, 0.836 mmol) and tris[2-(chloromethyl)phenyl]silane[4] (**52**, 338 mg, 0.833 mmol) were dissolved in 2:1 benzene-ethanol (150 mL). The solution was purged with argon, and then it was heated to reflux. A solution of KOH (187 mg, 3.35 mmol) in 1:3 benzene-ethanol (50 mL) was added dropwise over 1 h, and heating was continued overnight. After cooling, the solution was concentrated to dryness, and the residue was fractionated first by silica gel column chromatography (solvent, 1:1 hexanes-CH_2Cl_2), and then by preparative TLC (silica gel; solvent, 1:3 hexanes-benzene) to give pure cyclophane **31** as a white solid (48 mg, 0.068 mmol, 8% yield, but 20% based on the amount of compound **50** in the starting material). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.77 (d, *J* = 11 Hz, 3 H), 4.00 (d, *J* = 11 Hz, 3 H), 4.32 (d, *J* = 11 Hz, 3 H), 4.34 (d, *J* = 11 Hz, 3 H), 5.09 (s, 3 H), 5.21 (s, 1 H), 6.91 (m, 7 H), 7.17 (d, *J* = 7 Hz, 3 H), 7.24 (m, 6 H), 7.44 (m, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 18.7, 40.6, 41.0, 56.7, 57.0, 123.4, 125.3, 127.1, 130.1, 130.8, 131.5, 132.1, 132.3, 137.4, 143.7, 147.7, 147.8 (17 of 17 expected resonances); HRMS (ESI-TOF) *m/z* 703.1972 (M + H^+), calcd for $C_{45}H_{39}S_3Si^+$, 703.1983.

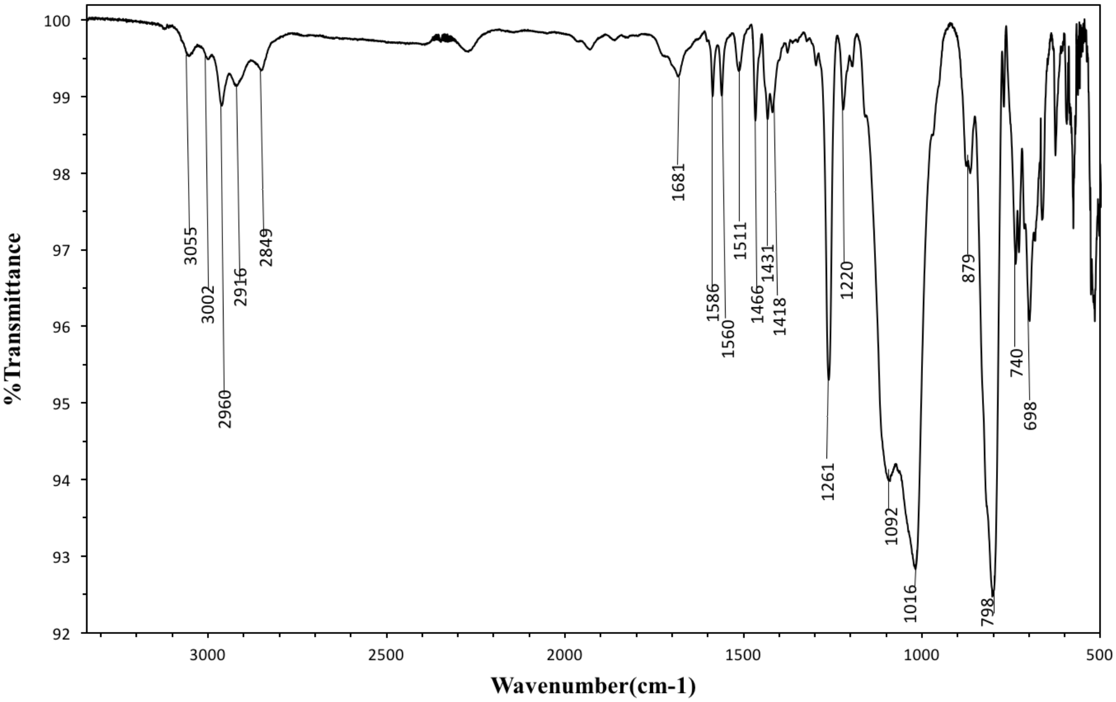
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of Cyclophane **31**



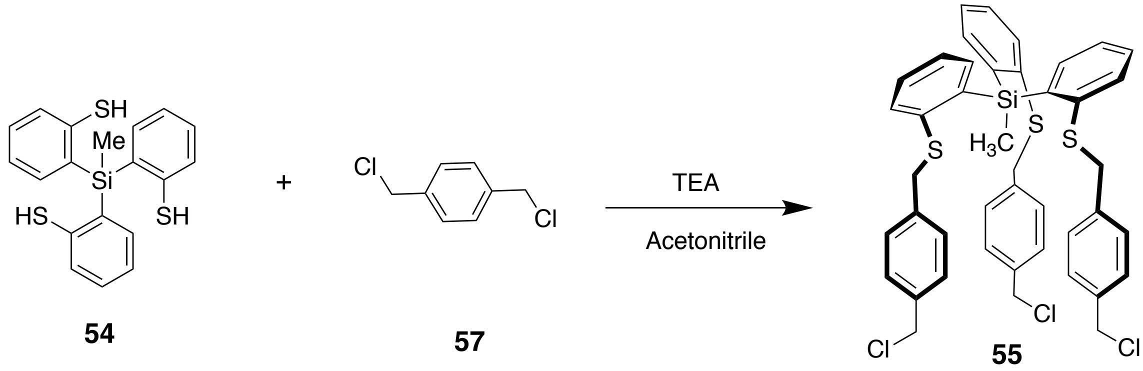
^{13}C NMR Spectrum (126 MHz, CDCl$_3$) of Cyclophane **31**



IR Spectrum of Cyclophane **31**

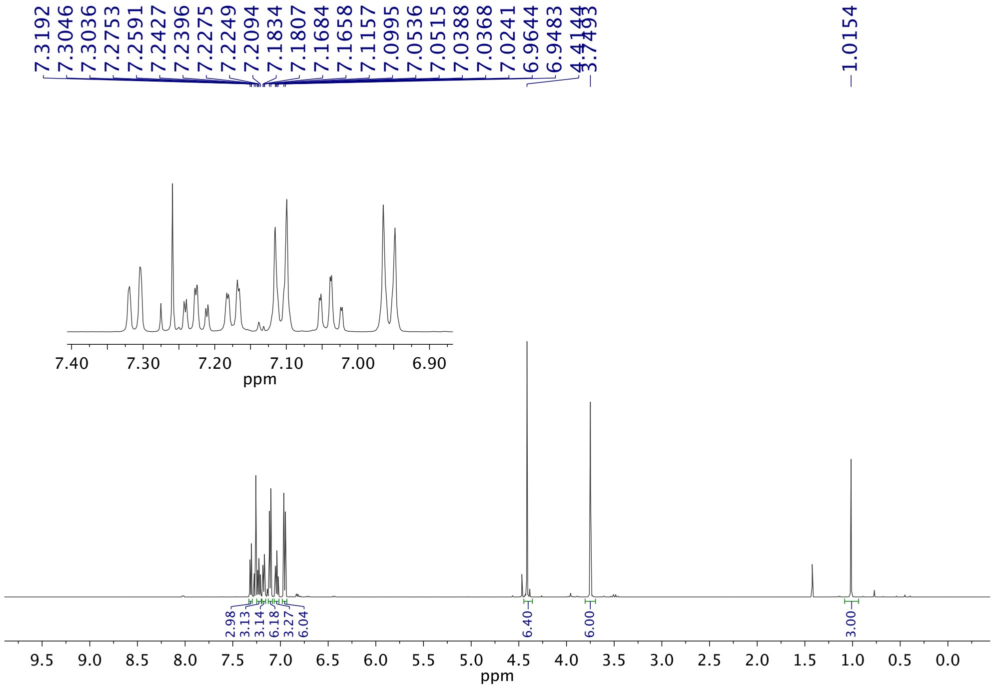


Synthesis of Compound 55

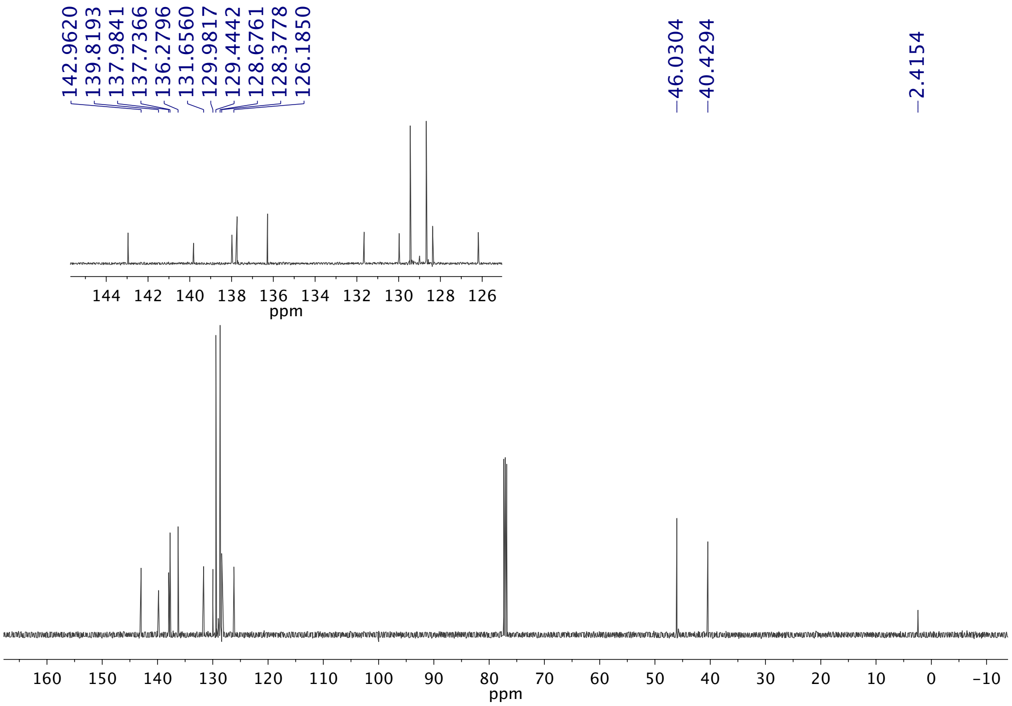


1,4-Bis(chloromethyl)benzene (**57**, 940 mg, 5.37 mmol) and tris(2-mercaptophenyl)methylsilane[5] (**54**, 200 mg, 0.540 mmol) were mixed in acetonitrile (20 mL), and the solution was purged with argon. Triethylamine (0.225 mL, 1.6 mmol) was added with vigorous stirring, and the solution was stirred at room temperature for 3 h. Solid salts were filtered away, and these solids were washed with acetonitrile (20 mL). The combined organics were dried over Na_2SO_4 and concentrated to give a sticky, brown, crude product. This material was purified by silica gel column chromatography (solvent, 1:1 hexanes-benzene) to give compound **55** as a colorless oil (254 mg, 0.323 mmol, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02 (s, 3 H), 3.75 (s, 6 H), 4.41 (s, 6 H), 6.96 and 7.11 (AA'BB' system, 12 H), 7.04 (td, *J* = 7.5 Hz, 1 Hz, 3 H), 7.17 (dd, *J* = 7.5 Hz, 1.5 Hz, 3 H), 7.23 (td, *J* = 7.5 Hz, 1.5 Hz, 3 H), 7.31 (d, *J* = 7.5 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 2.4, 40.4, 46.0, 126.2, 128.4, 128.7, 129.4, 130.0, 131.7, 136.3, 137.7, 138.0, 139.8, 143.0 (14 of 14 expected resonances); MS (MALDI-TOF; matrix, DCTB-CF_3CO_2Na) *m/z* 809 (M + Na^+ [$^{35}Cl_2{}^{37}Cl$], 100).

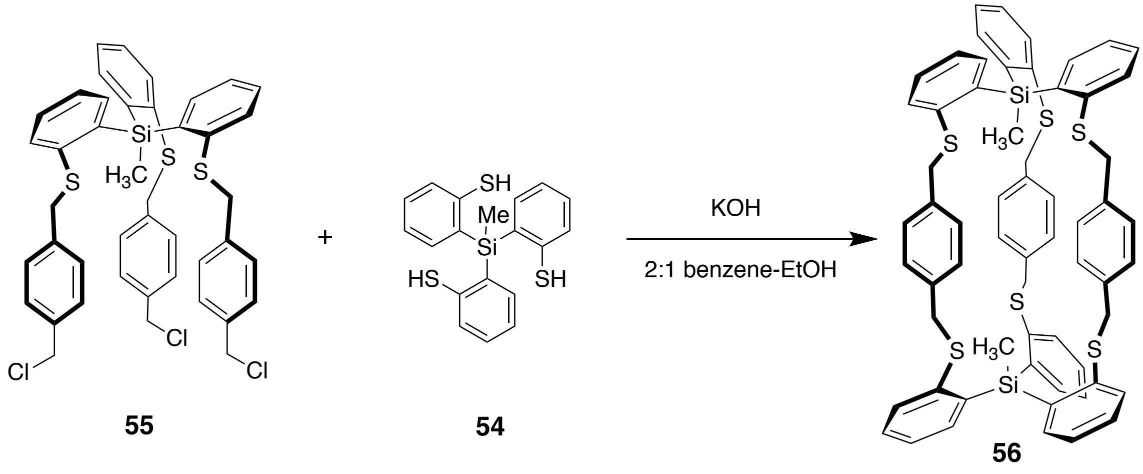
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of Compound **55**



^{13}C NMR Spectrum (126 MHz, $CDCl_3$) of Compound **55**

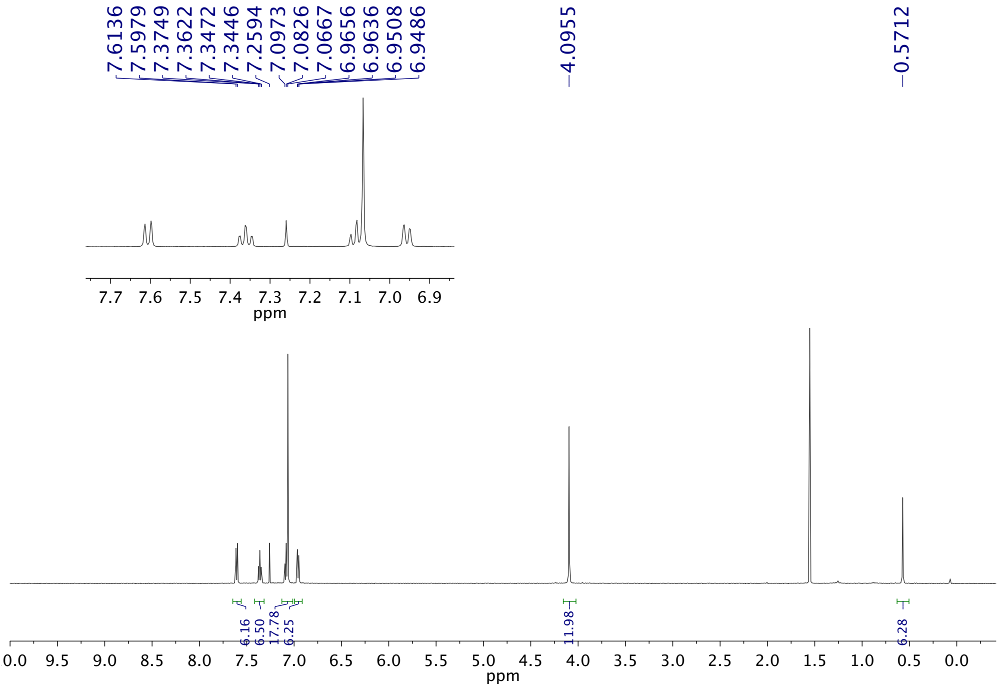


Synthesis of Cyclophane 56

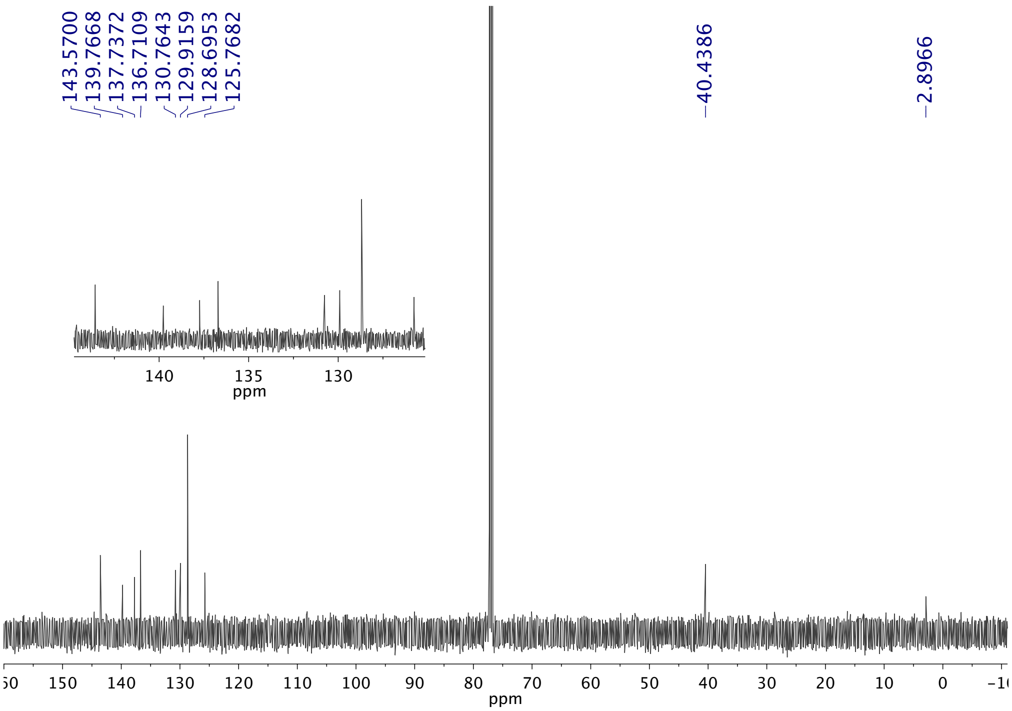


Compound **55** (254 mg, 0.323 mmol) and compound **54** (120 mg, 0.324 mmol) were dissolved in acetonitrile (600 mL). The solution was purged with argon, and then a solution of triethylamine (0.163 mL, 1.2 mmol) in acetonitrile (50 mL) was added dropwise over 1 h, and the solution was stirred overnight at room temperature. The solution was concentrated to dryness, and the residue was fractionated by silica gel column chromatography (solvent, 1:1 hexanes-CH_2Cl_2), and then by preparative TLC (silica gel; solvent, 1:4 hexanes-benzene) to give pure cyclophane **56** as a white solid (16 mg, 0.015 mmol, 4.6%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.57 (s, 6 H), 4.10 (s, 12 H), 6.96 (d, *J* = 7.5 Hz, 6 H), 7.07 (s, 12 H), 7.09 (t, *J* = 7.5 Hz, 6 H), 7.36 (t, *J* = 7.5 Hz, 6 H), 7.61 (d, *J* = 7.5 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 2.9, 40.4, 125.8, 128.7, 129.9, 130.8, 136.7, 137.7, 139.8, 143.6 (10 of 10 expected resonances); MS (MALDI-TOF; matrix, graphite-CF_3CO_2Na) *m/z* 1069 (M + Na^+, 100).

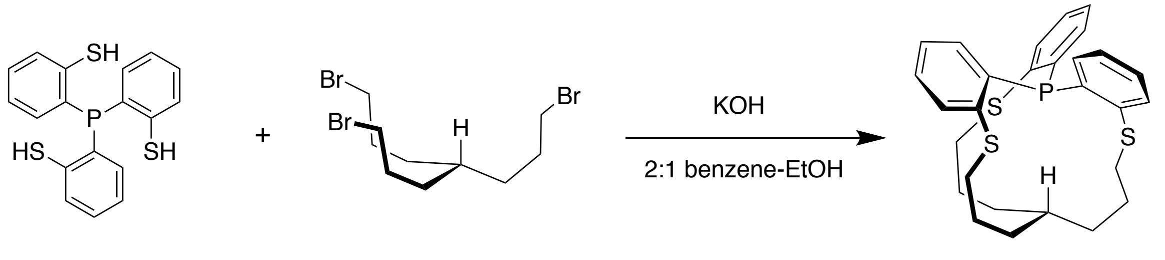
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of Cyclophane **56**



^{13}C NMR Spectrum (126 MHz, CDCl$_3$) of Cyclophane **56**



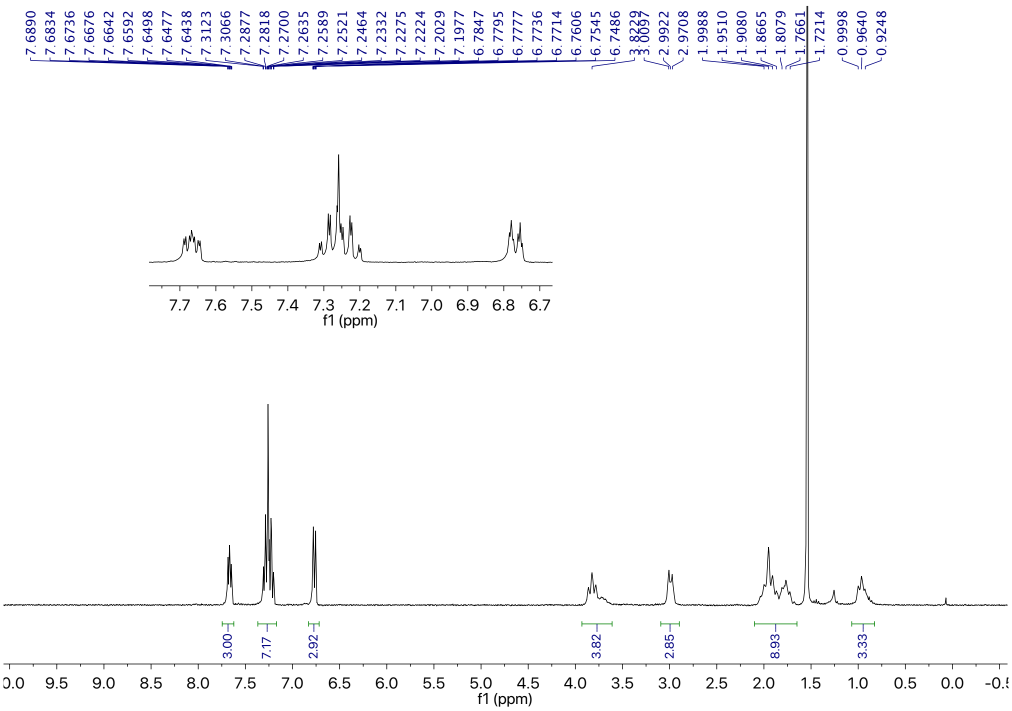
Synthesis of Cyclophane 32



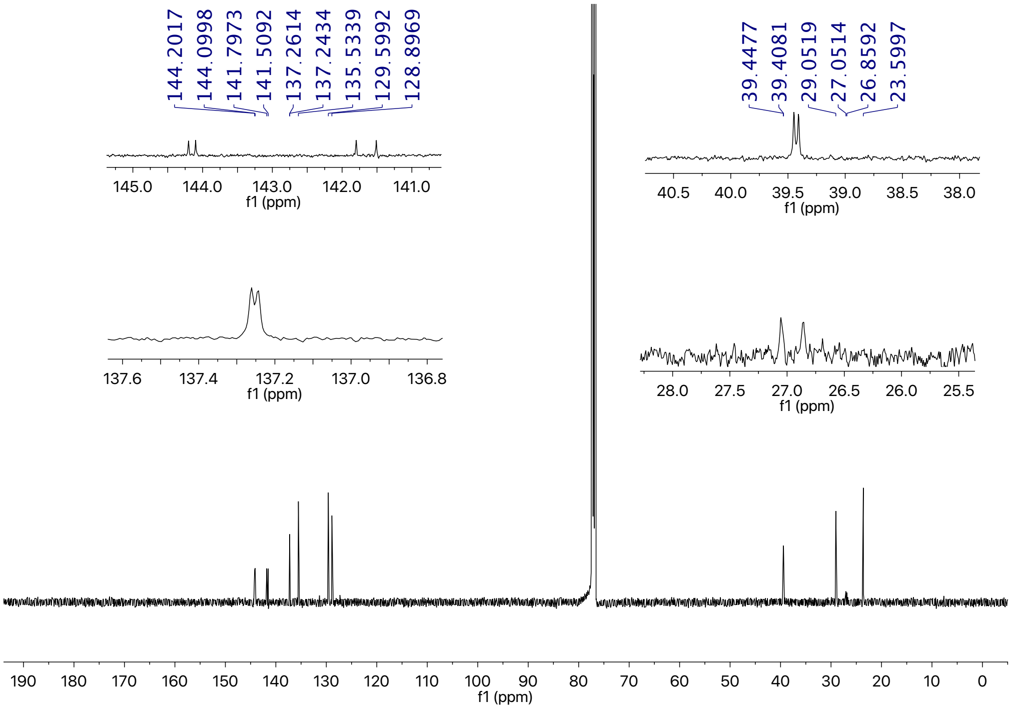
58 **59** **32**

Tris(2-mercaptophenyl)phosphine[6] (**58**, 200 mg, 0.558 mmol) and tris(3-bromopropyl)methane[7] (**59**, 211.5 mg, 0.558 mmol) were dissolved in 2:1 benzene/EtOH (600 mL). The solution was purged with argon and then heated to reflux. A solution of KOH (110 mg, 1.96 mmol) in EtOH (50 mL) was added dropwise over 1 h, and heating was continued overnight. After cooling, the solution was concentrated to dryness, and the residue was fractionated by preparative TLC (solvent, 1:1 hexanes/CH_2Cl_2). Three relatively non-polar components were observed with R_f of 0.80, 0.76, and 0.58. The R_f 0.80 component proved to be the target compound **32** (18.3 mg, 0.0370 mmol, 6.6%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (m, 3 H), 1.77 (m, 3 H), 1.95 (m, 6 H), 2.99 (m, 3 H), 3.71 (qd with fine structure, J_{HH} = 10.5, J_{PH} = 9 Hz, 1 H), 3.82 (t, J = 12 Hz, 3 H), 6.77 (dt, J = 7, 2 Hz, 3 H), 7.26 (m, 6 H), 7.66 (ddd, J = 7, 5 Hz, 2 Hz); ^{13}C NMR (126 MHz, $CDCl_3$): δ 23.6, 27.0 (d, J_{PC} = 24 Hz), 29.1, 39.4 (d, J_{PC} = 5 Hz), 128.9, 129.6, 135.5, 137.3 (d, J_{PC} = 2 Hz), 141.7 (d, J_{PC} = 36 Hz), 144.2 (d, JPC = 13 Hz); HRMS (ESI-TOF) *m/z* 494.1320 ([M]$^+$), calcd. for $C_{28}H_{31}PS_3^+$ = 494.1320.

^1H NMR spectrum (300 MHz, $CDCl_3$) of Cyclophane **32**

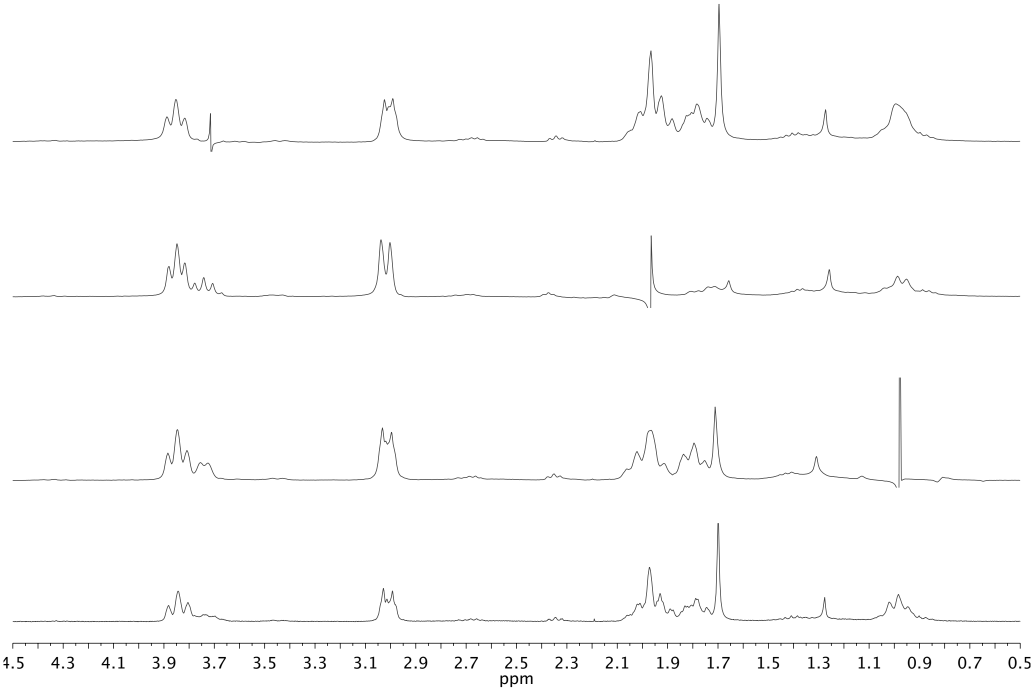


^{13}C NMR spectrum (126 MHz, $CDCl_3$) of Cyclophane **32**

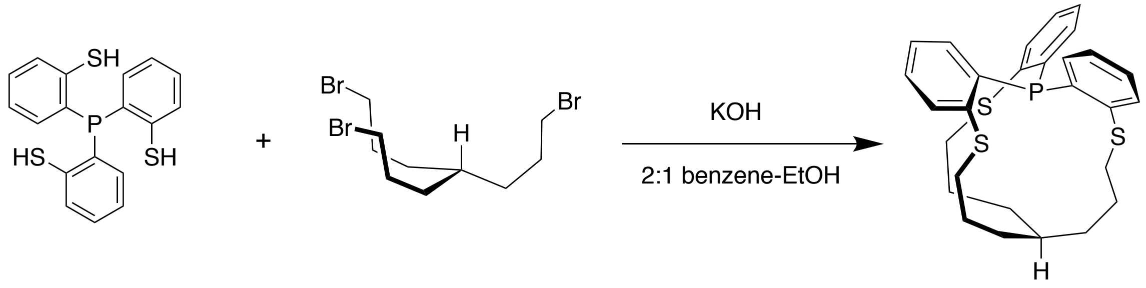


^{1}H spin decoupling experiments (300 MHz, $CDCl_3$) with Cyclophane **32**

Top to bottom: irradiation at δ 3.71, irradiation at δ 1.95, irradiation at δ 0.96, no irradiation.



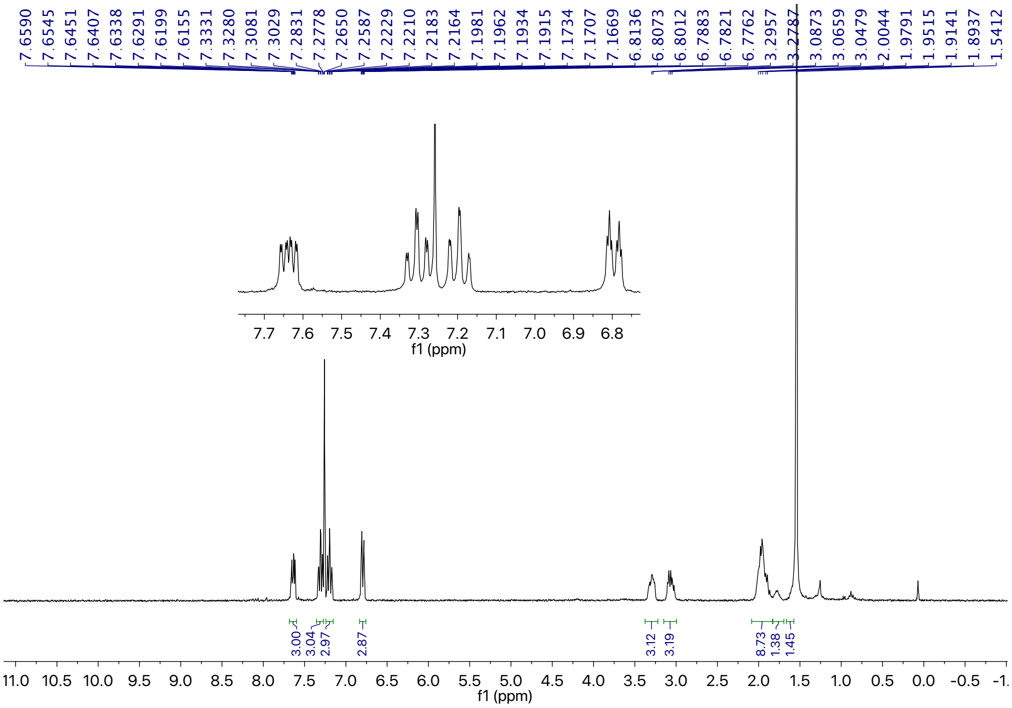
Synthesis of Cyclophane 60



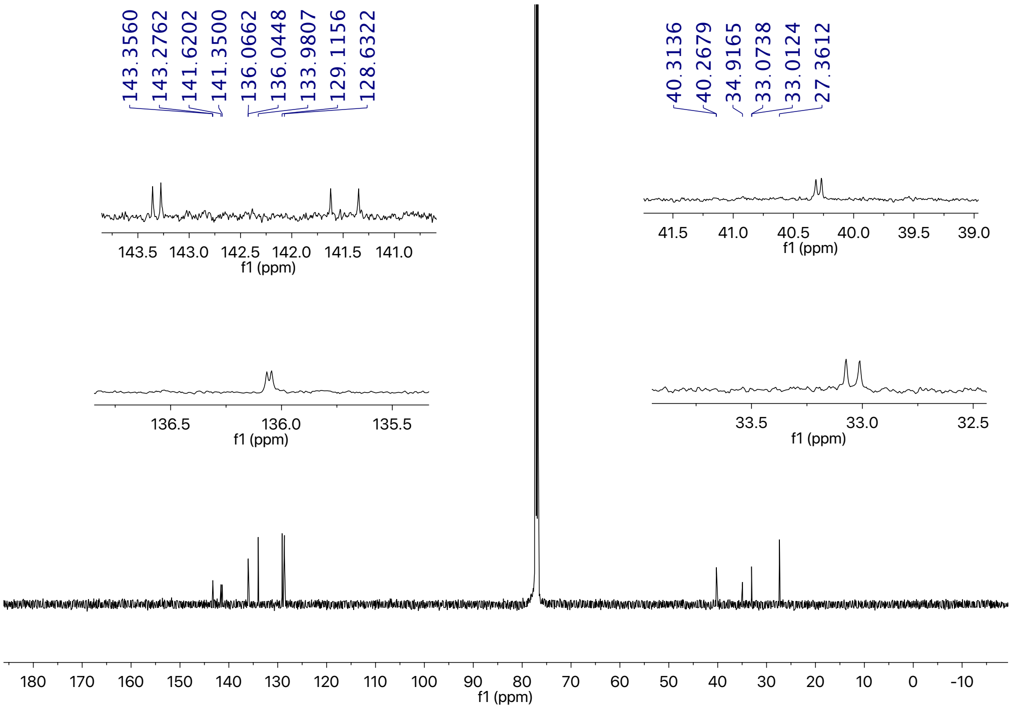
58 **59** **60**

In the same reaction that produced cyclophane **32**, the R_f 0.58 component was proved to be the cyclophane **60** (26.3 mg, 0.0266 mmol, 9.5%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55 (m, 3 H [under the H_2O peak]), 1.78 (m, 1 H), 1.95 (m, 9 H), 3.07 (m, 3 H), 3.29 (m, 3 H), 6.79 (dt, *J* = 7.5, 1.5 Hz, 3 H), 7.20 (td, *J* = 7.5, 1.5 Hz, 3 H), 7.31 (td, *J* = 7.5, 1.5 Hz, 3 H), 7.64 (ddd, *J* = 7.5, 4 Hz, 1.5 Hz); ^{13}C NMR (126 MHz, $CDCl_3$): δ 27.4, 33.0 (d, J_{PC} = 8 Hz), 34.9, 40.3 (d, J_{PC} = 6 Hz), 128.6, 129.1, 134.0, 136.1 (d, J_{PC} = 3 Hz), 141.5 (d, J_{PC} = 34 Hz), 143.3 (d, J_{PC} = 10 Hz); HRMS (ESI-TOF) *m/z* 494.1300 ($[M]^+$), calcd. for $C_{28}H_{31}PS_3^+$ = 494.1320.

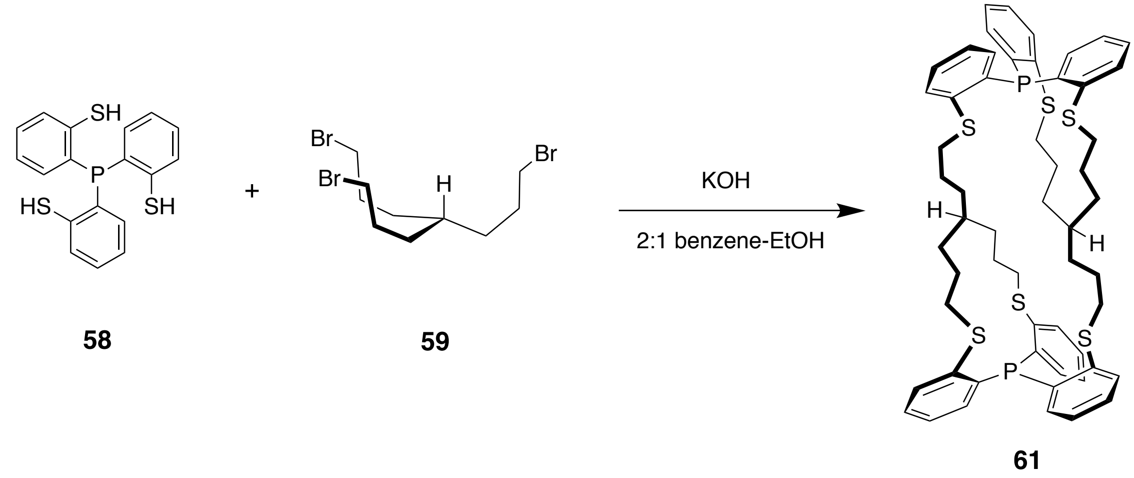
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of Cyclophane **60**



^{13}C NMR spectrum (126 MHz, CDCl$_3$) of Cyclophane **60**

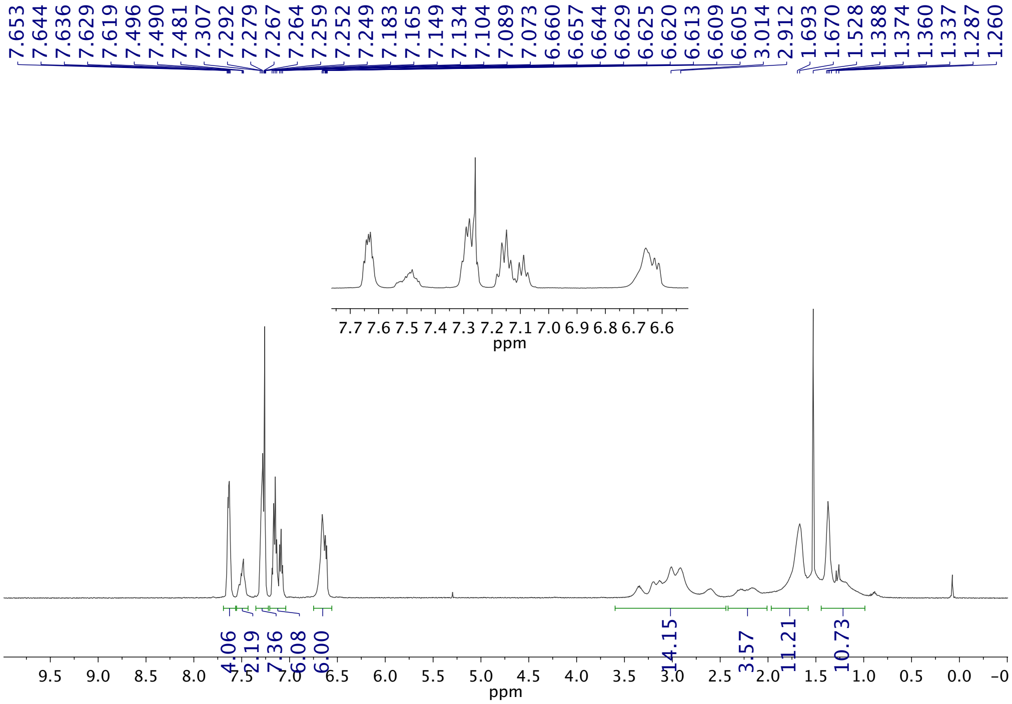


Synthesis of Cyclophane 61

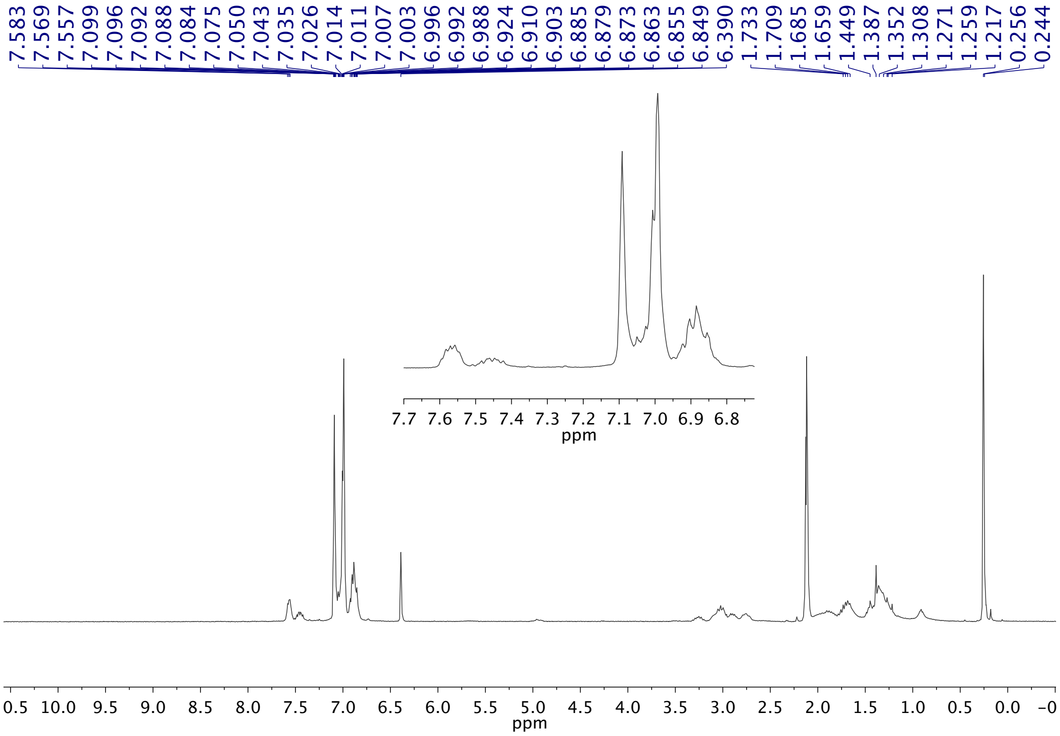


In the same reaction that produced cyclophane **32**, the R_f 0.77 component was the cyclophane **61** (14.5 mg, 0.0294 mmol, 5.0%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.0-3.5 (overlapping broad resonances, 38 H), 6.65 (m, 6 H), 7.13 (m, 6 H), 7.28 (m, 6 H), 7.49 (m, 2 H), 7.64 (m, 4 H) ppm. ^{1}H NMR (300 MHz, 100 °C, [$^2H_8$]toluene) δ 0.91 (m, 3 H), 1.35 (m, 15 H), 1.69 (m, 6 H), 1.88 (m, 6 H), 2.76 (m, 2 H), 2.90 (2 H), 3.02 (m, 3 H), 3.24 (m, 1 H), 6.39 (s, 2 H), 6.88 (m, 8 H), 7.02 (m, ≈ 8 H [under a toluene resonance]), 7.45 (m, 2 H), 7.58 (m, 4 H); ^{13}C NMR spectra of **61** at both room temperature and 100 °C showed both moderately sharp and highly broadened resonances, and were not easily interpretable. HRMS (ESI-TOF) *m/z* 989.2726 ($[M + H]^+$), calcd. for $C_{56}H_{63}P_2S_6^+$ = 989.2724.

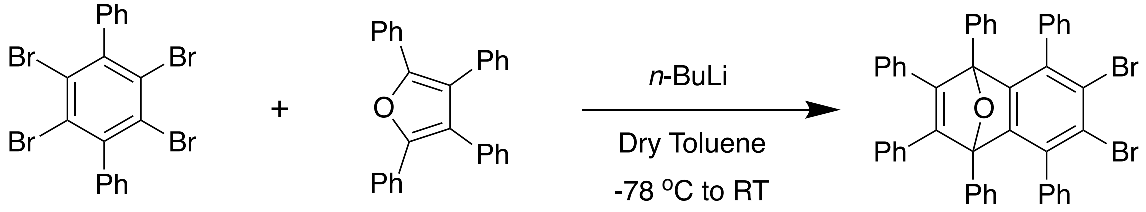
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Cyclophane **61**



^{1}H NMR spectrum (300 MHz, 100 °C, [$^2H_8$]toluene) of Cyclophane **61**



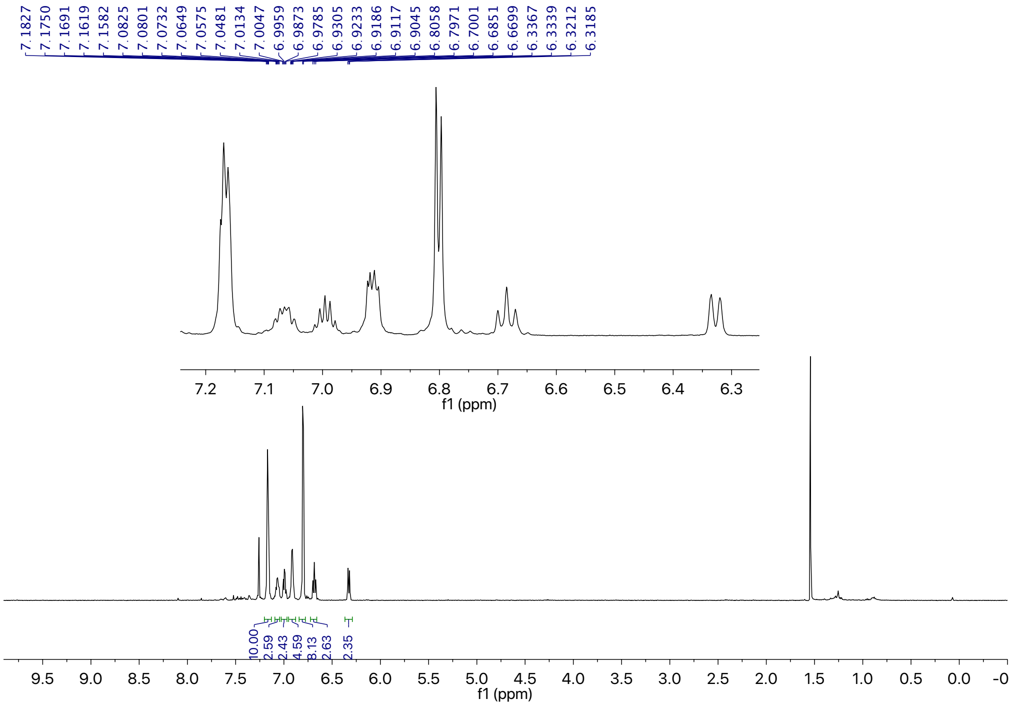
Synthesis of Compound 84



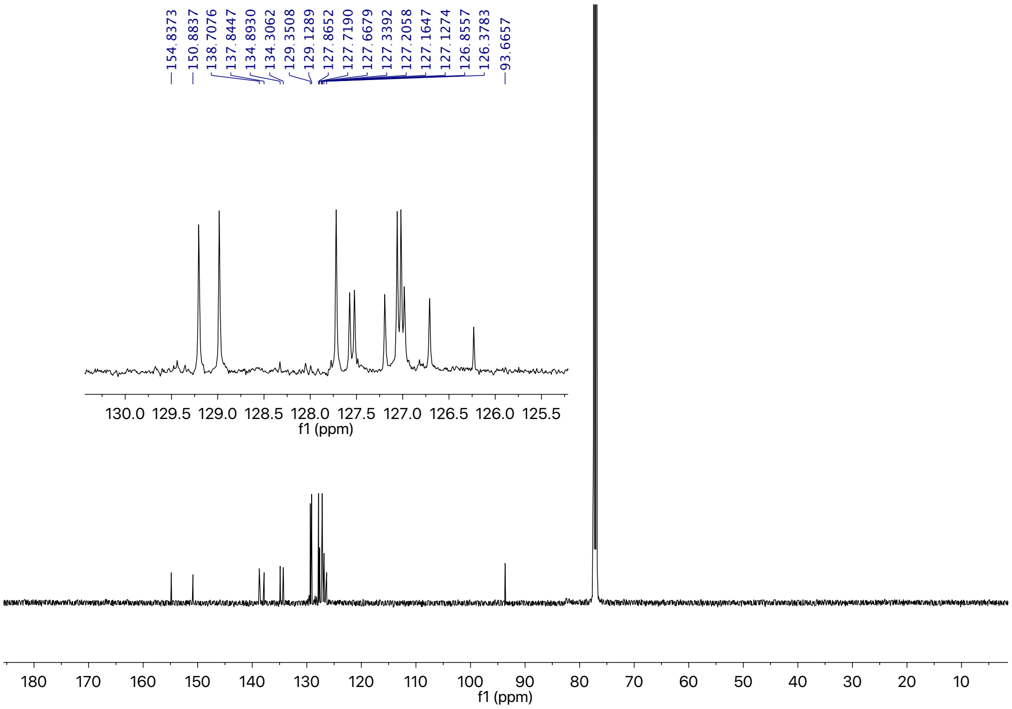
82 **83** **84**

Tetraphenylfuran[8,9] (**83**, 0.82 g, 2.2 mmol) and 1,2,4,5-tetrabromo-3,6-diphenylbenzene[10] (**82**, 1.09 g, 2.00 mmol) were dissolved in dry toluene (50 mL) and cooled to -78 °C with stirring under argon. *n*-Butyllithium (2.5 *M* in hexanes, 1.04 mL, 2.6 mmol) was diluted in dry hexanes (20 mL), and the resulting solution was added dropwise to the cold reaction mixture. The contents were allowed to warm to room temperature with stirring overnight. The reaction was quenched with methanol (50 mL), and ether (200 mL) was added. The resulting suspension was washed twice with saturated NaCl and once with water. The remaining organics were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (solvent, 2:1 hexanes-CH_2Cl_2) to give compound **84** as a white solid (0.674 g, 0.889 mmol, 44%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.33 (d, *J* = 8 Hz, 1 Hz, 2 H), 6.69 (t, *J* = 8 Hz, 2 H), 6.80 (m, 8 H), 6.92 (m, 4 H), 6.99 (m, 2 H), 7.06 (m, 2 H), 7.17 (m, 10 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 93.7, 126.4, 126.9, 127.13, 127.16, 127.21, 127.34, 127.67, 127.72, 127.9, 129.1, 129.4, 134.3, 134.9, 137.8, 138.7, 150.9, 154.8 (18 resonances observed, 17 are expected for fast phenyl rotation, 23 for slow); HRMS (ESI-TOF) *m/z* 757.0716 ($M + H^+$), calcd for $C_{46}H_{31}{}^{79}Br_2O^+$ 757.0737.

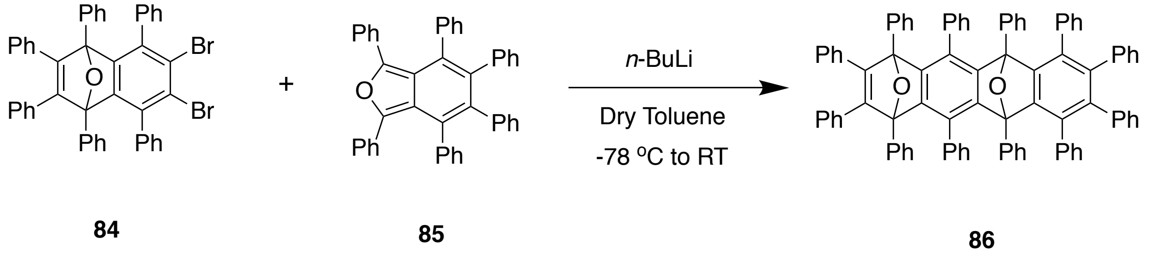
^{1}H NMR Spectrum (500 MHz, CDCl$_3$) of Compound **84**



^{13}C NMR Spectrum (126 MHz, $CDCl_3$) of Compound **84**

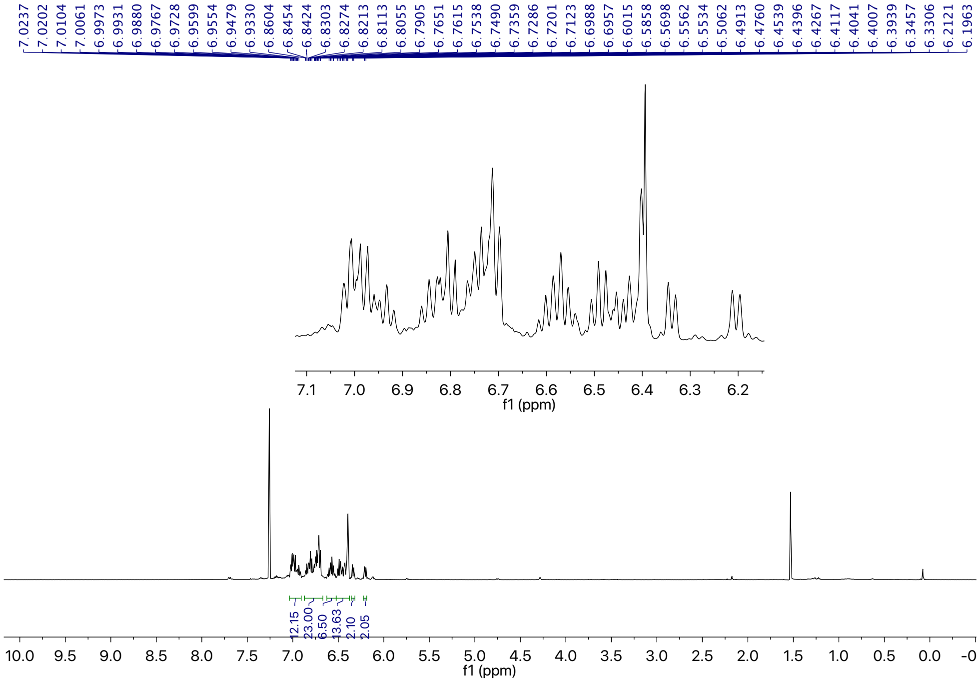


Synthesis of Compound 86

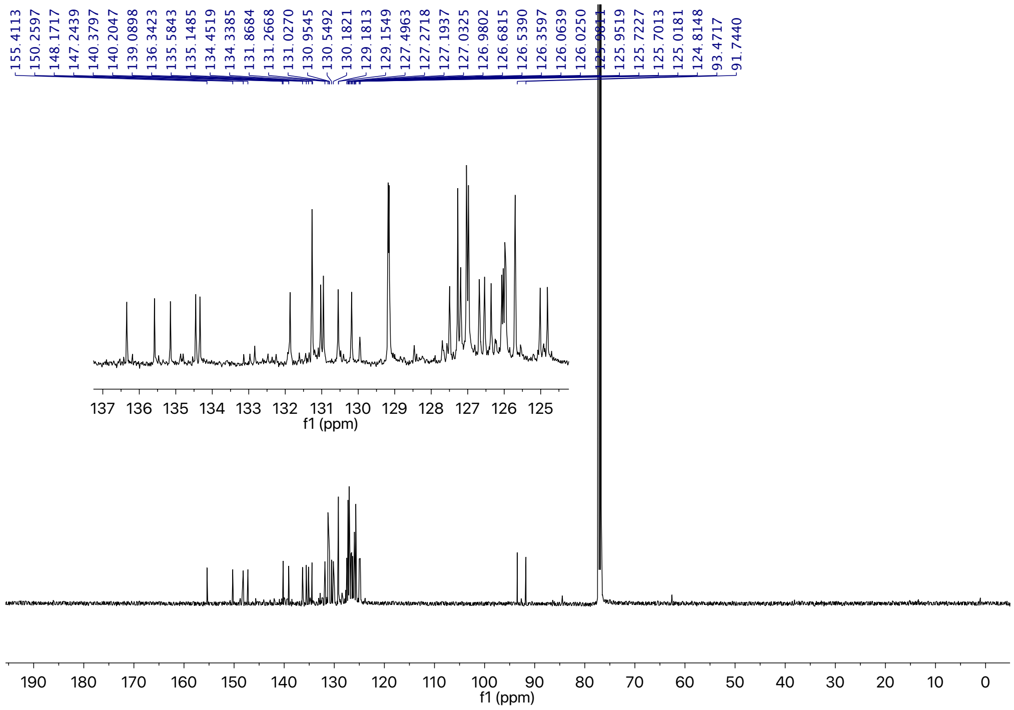


Compound **84** (1.30 g, 1.71 mmol) and hexaphenylisobenzofuran[11] (**85**, 1.08 g, 1.88 mmol) were dissolved in dry toluene (50 mL) and cooled to -78 °C with stirring under argon. *n*-Butyllithium (2.5 *M* in hexanes, 2.74 mL, 6.85 mmol) was diluted in dry hexanes (25 mL), and the resulting solution was added dropwise to the cold reaction mixture. The contents were allowed to warm to room temperature with stirring overnight. The reaction was quenched with methanol (50 mL), and ether (200 mL) was added. The resulting suspension was washed twice with saturated NaCl and once with water. The remaining organics were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (solvent, 1:1 hexanes-CH_2Cl_2) to give compound **86** as a white solid (0.193 g, 0.164 mmol, 9.6%). The isolated sample of **86** appears to be a single stereoisomer, probably the *trans* diepoxide. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.20 (d, *J* = 8 Hz, 2 H), 6.34 (d, *J* = 8 Hz, 2 H), 6.39-6.51 (m, 14 H), 6.55-6.61 (m, 7 H), 6.69-6.86 (m, 23 H), 6.92-7.02 (m, 12 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 91.7, 93.5, 124.8, 125.0, 125.7, 125.95, 125.98, 126.02, 126.06, 126.4, 126.5, 126.7, 126.98, 127.03, 127.2, 127.3, 127.5, 129.15, 129.18, 130.2, 130.6, 130.9, 131.0, 131.3, 131.9, 134.3, 134.5, 135.1, 135.6, 136.3, 139.1, 140.2, 140.4, 147.2, 148.2, 150.3, 155.4 (37 resonances observed; 33 are expected for fast phenyl rotation, 45 for slow); HRMS (ESI-TOF) *m/z* 1173.4678 (M + H$^+$), calcd for $C_{90}H_{61}O_2^+$ 1173.4667.

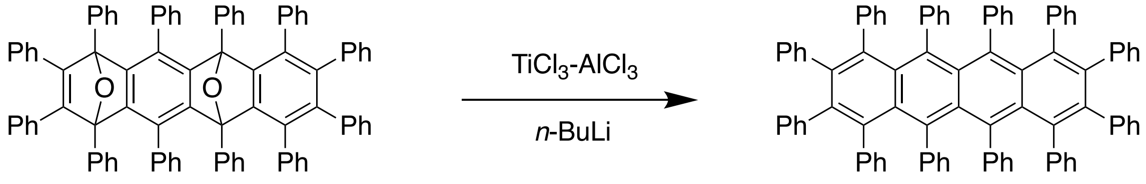
^{1}H NMR Spectrum (500 MHz, CDCl$_3$) of Compound **86**



^{13}C NMR Spectrum (126 MHz, $CDCl_3$) of Compound **86**



Synthesis of Compound 75

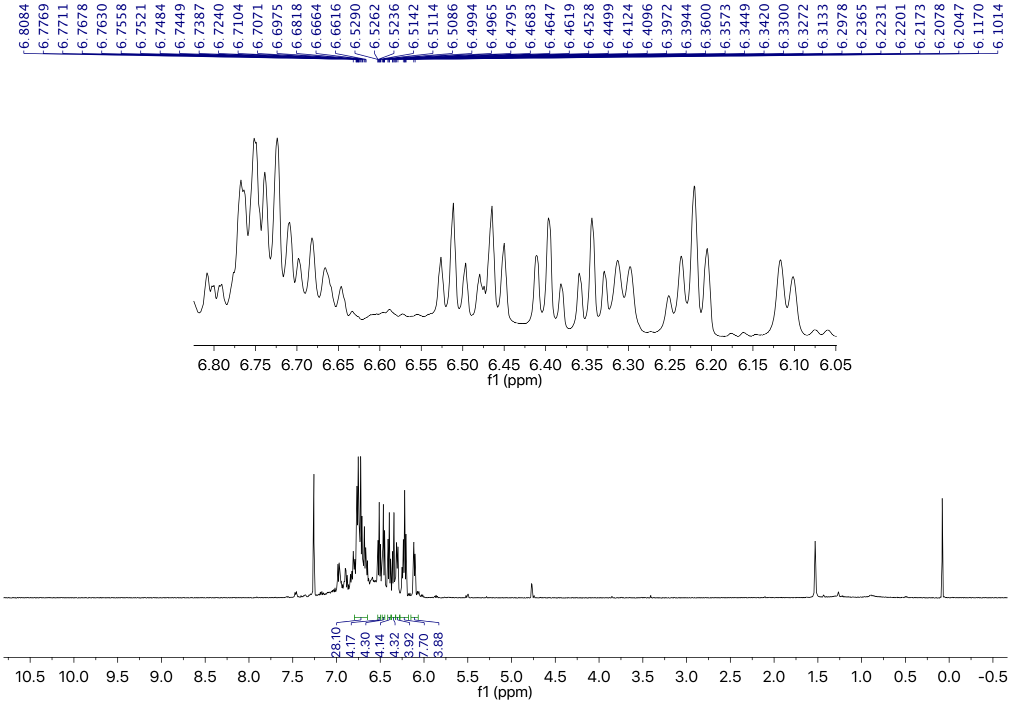


86

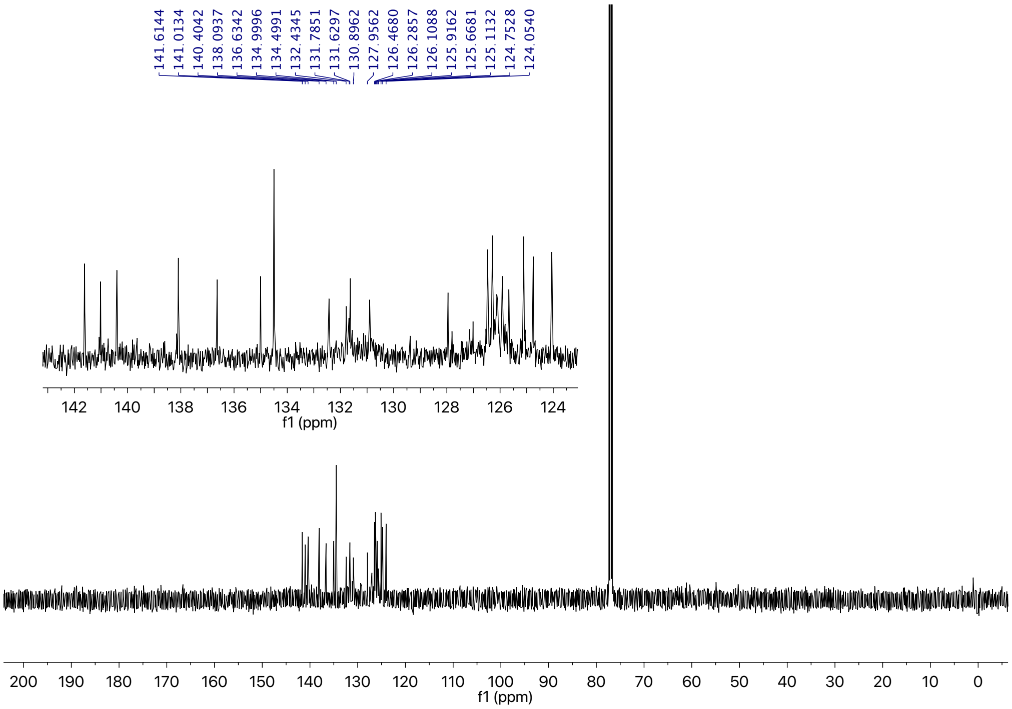
75

$TiCl_3$-$AlCl_3$ (4.2 g, 21 mmol) was mixed with ether (50 mL) and cooled to -78 °C with stirring under argon. A solution of *n*-butyllithium (2.5 M in hexanes, 25 mL, 62.5 mmol) was added dropwise. The mixture was stirred at -78 °C for 1.5 h, and then it was allowed to warm to room temperature over 0.5 h, yielding a dark green solution. A suspension of compound **86** (150 mg, 0.128 mmol) in ether (30 mL) was added dropwise. After stirring overnight, the reaction mixture was washed twice with saturated NaCl, and the red ethereal solution was dried over Na_2SO_4 and concentrated. The crude product was purified by silica gel column chromatography (solvent, 2:1 hexanes-CH_2Cl_2) to give compound **75** as a red solid (46.3 mg, 0.041 mmol, 32%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.11 (d, *J* = 8 Hz, 4 H), 6.22 (m, 8 H), 6.31 (d, *J* = 8 Hz, 4 H), 6.34 (t, *J* = 8 Hz, 4 H), 6.40 (t, *J* = 8 Hz, 4 H), 6.46 (t, *J* = 8 Hz, 4 H), 6.51 (t, *J* = 8 Hz, 4 H), 6.64-6.78 (m, 28 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 124.1, 124.8, 125.1, 125.7, 125.9, 126.1, 126.3, 126.5, 128.0, 130.9, 131.6, 131.8, 132.4, 134.5, 135.0, 136.6, 138.1, 140.4, 141.0, 141.6 (20 resonances observed; 17 are expected for fast phenyl rotation, 23 for slow); MS (MALDI-TOF, DCTB matrix + CF_3CO_2Ag) *m/z* 1249 (M + $^{109}Ag^+$, 3), 1249 (M + $^{107}Ag^+$, 2), 1141 (M^+ [$^{13}C_1$], 100), 1140 (M^+ [$^{13}C_0$], 98). Single crystals, suitable for X-ray analysis, were obtained upon evaporation of a solution in $CHCl_3$-ethyl acetate.

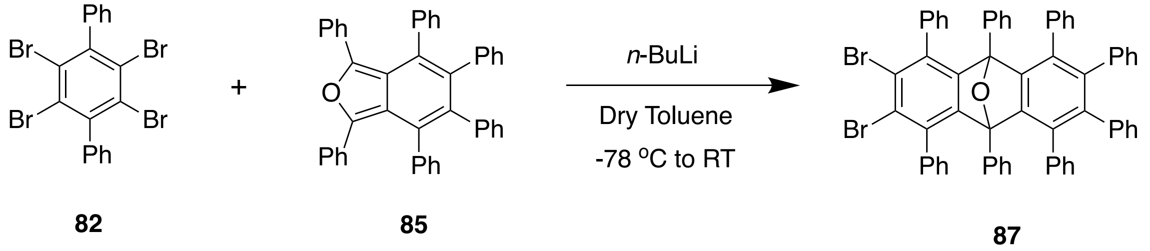
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of Compound **75**



^{13}C NMR Spectrum (126 MHz, CDCl$_3$) of Compound **75**

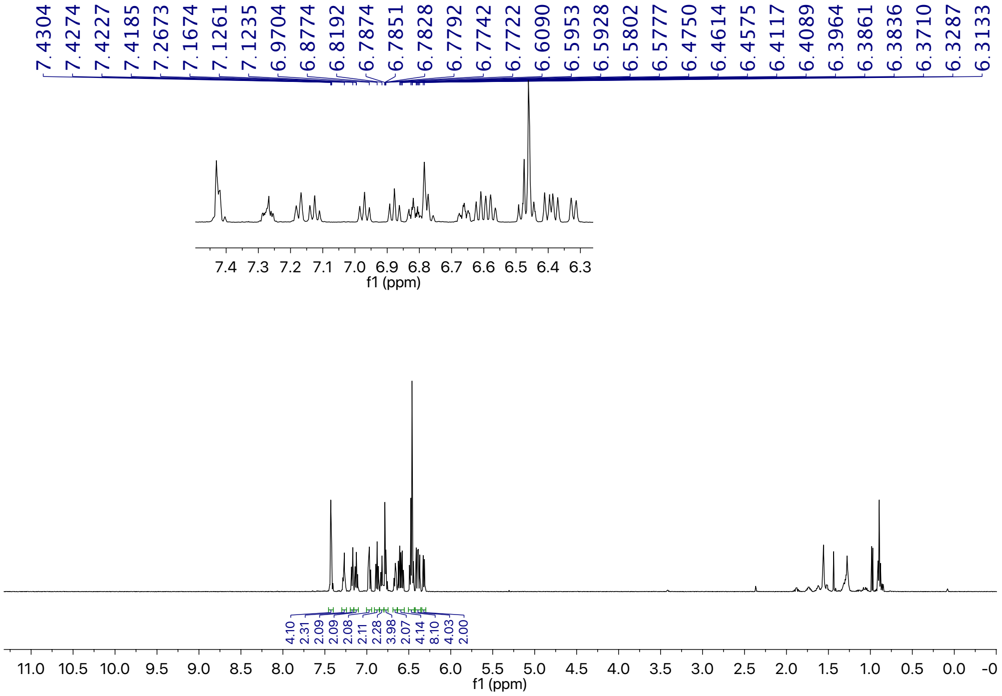


Synthesis of Compound 87

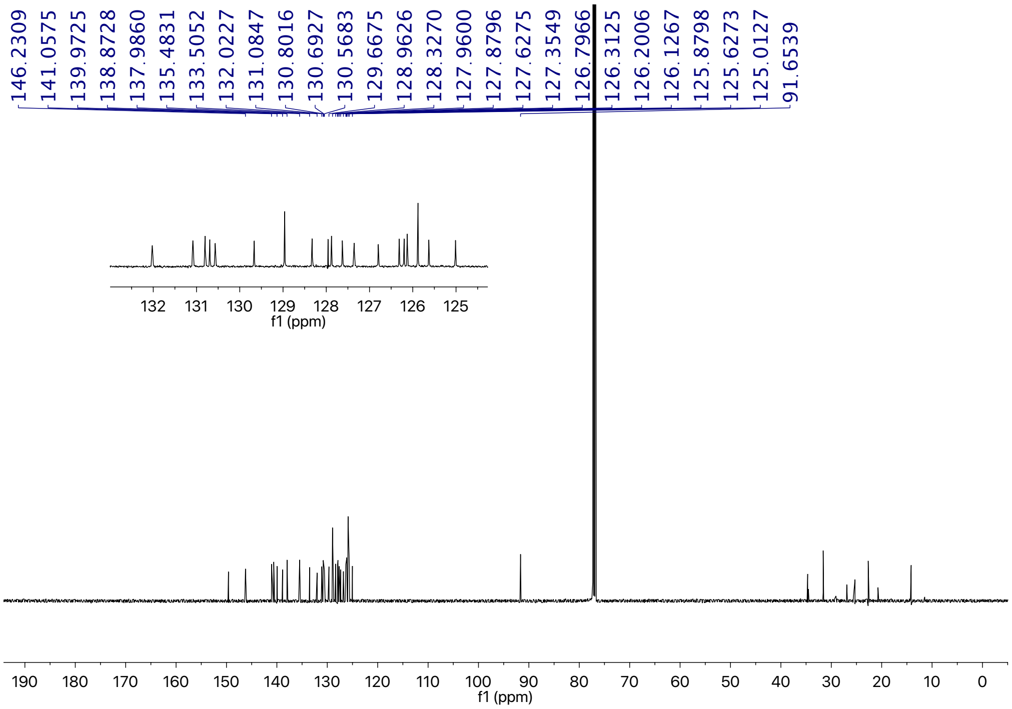


Hexaphenylisobenzofuran (**85**, 1.26 g, 2.19 mmol) and 1,2,4,5-tetrabromo-3,6-diphenylbenzene (**82**, 1.09 g, 2.00 mmol) were dissolved in dry toluene (50 mL) and cooled to -78 °C with stirring under argon. *n*-Butyllithium (2.5 M in hexanes, 1.04 mL, 2.6 mmol) was diluted in dry hexanes (20 mL), and the resulting solution was added dropwise to the cold reaction mixture. The contents were allowed to warm to room temperature with stirring overnight. The reaction was quenched with methanol (50 mL), and ether (200 mL) was added. The resulting suspension was washed twice with saturated NaCl and once with water. The remaining organics were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (solvent, 2:1 hexanes-CH_2Cl_2) to give 2,3-dibromo-9,10-epoxy-9,10-dihydro-1,4,5,6,7,8,9,10-octaphenylanthracene as a white solid (0.73 g, 0.76 mmol, 38%). ^1H NMR (500 MHz, $CDCl_3$) δ 6.31 (d, J = 7.5 Hz, 2 H), 6.37 (dd, J = 7.5 Hz, 1.5 Hz, 2 H), 6.39 (dd, J = 7.5 Hz, 1.5 Hz, 2 H), 6.45 (m, 8 H), 6.59 (m, 4 H), 6.65 (m, 2 H), 6.77 (m, 4 H), 6.81 (m, 2 H), 6.87 (t, J = 7.5 Hz, 2 H), 6.96 (t, J = 7.5 Hz, 2 H), 7.12 (t, J = 7.5 Hz, 2 H), 7.16 (d, J = 7.5 Hz, 2 H), 7.26 (m, 2 H), 7.42 (m, 4 H); MS (MALDI-TOF, DCTB matrix + CF_3CO_2Na) *m/z* 983 (M + Na^+ [$^{79}Br^{81}Br$]).

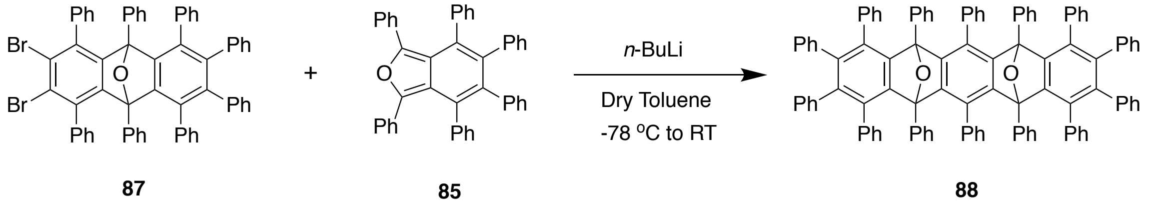
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of Compound **87**



^{13}C NMR Spectrum (126 MHz, CDCl$_3$) of Compound **87**

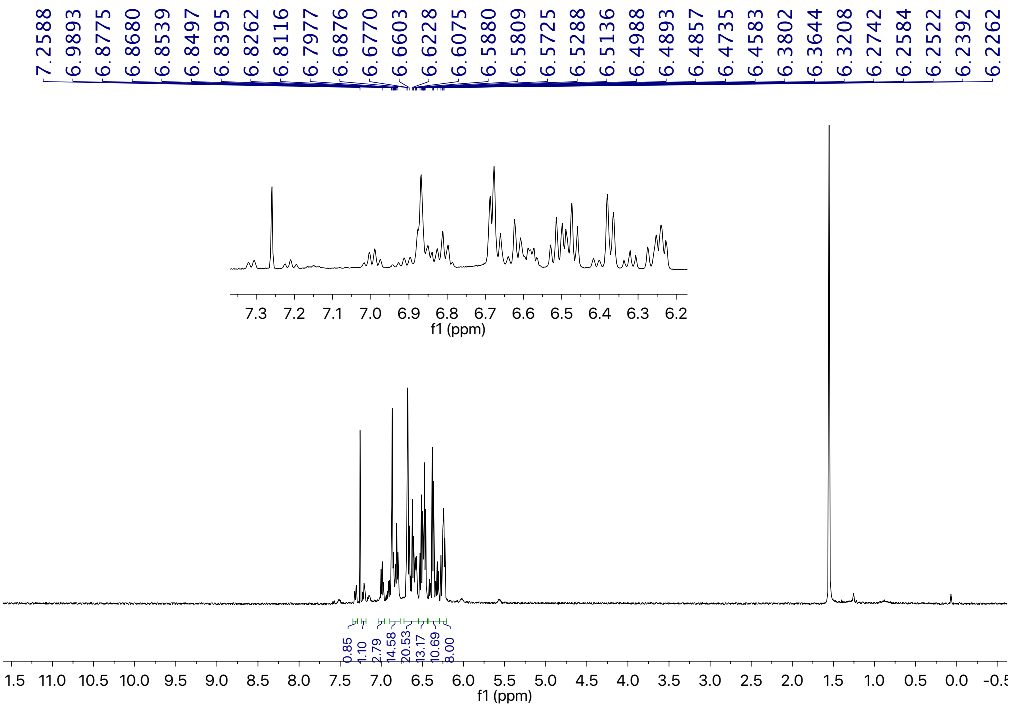


Synthesis of Compound 88

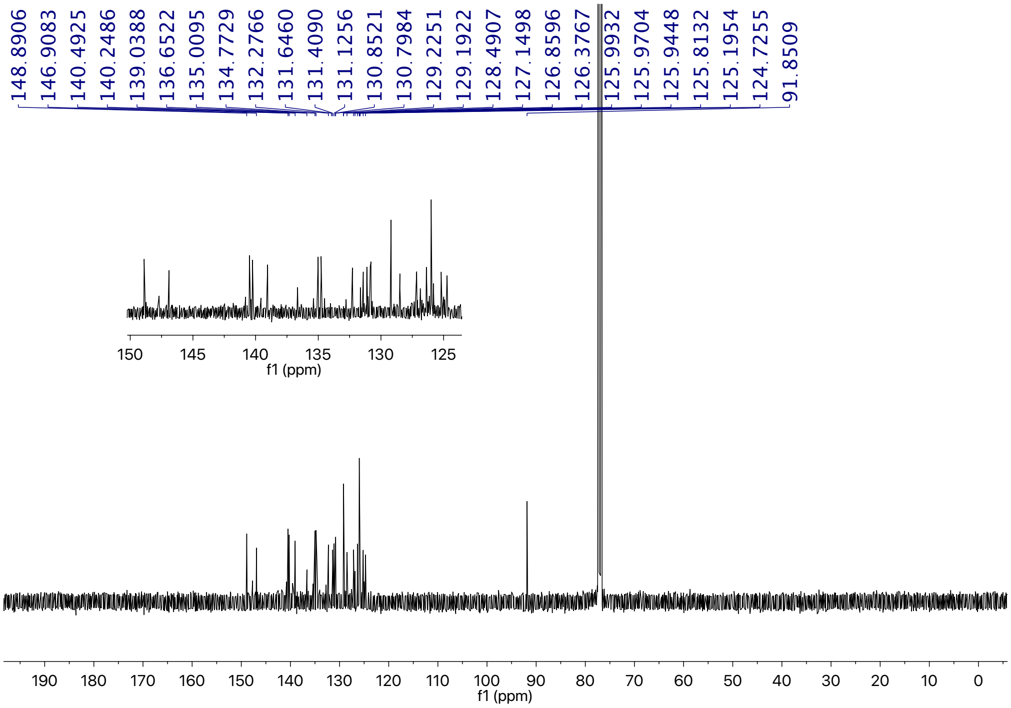


Compound **87** (0.72 g, 0.75 mmol) and hexaphenyl-isobenzofuran (**85**, 0.48 g, 0.84 mmol) were dissolved in dry toluene (50 mL) and cooled to -78 °C with stirring under argon. *n*-Butyllithium (2.5 M in hexanes, 1.2 mL, 3.00 mmol) was diluted in dry hexanes (25 mL), and the resulting solution was added dropwise to the cold reaction mixture. The contents were allowed to warm to room temperature with stirring overnight. The reaction was quenched with methanol (50 mL), and ether (200 mL) was added. The resulting suspension was washed twice with saturated NaCl and once with water. The remaining organics were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (solvent, 3:2 hexanes-CH_2Cl_2) to give crude compound **88**. Further purification by silica gel preparative TLC (solvent, 3:1 hexanes-CH_2Cl_2) gave pure compound **88** as a white solid (0.015 g, 0.011 mmol, 1.5%; 0.6% overall from **82**). NMR analysis (most obviously, the 91.85 and 91.87 resonances in the ^{13}C NMR spectrum) indicates that this material is a 3:1 mixture of the *trans* and *cis* diepoxides. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.25 (m, 8 H), 6.32 (d, *J* = 7.5 Hz, 2 H), 6.37 (m, 7 H), 6.41 (d, *J* = 7.5 Hz, 1 H), 6.49 (m, 13 H), 6.56-6.69 (m, 21 H), 6.79-6.93 (m, 15 H), 6.99 (m, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 91.85 (*trans* C-O), 91.87 (*cis* C-O), 124.7, 125.2, 125.8, 125.94, 125.97, 125.99, 126.0, 126.4, 126.9, 127.1, 128.5, 129.19, 129.22, 130.8, 130.9, 131.1, 131.4, 131.6, 132.3, 134.8, 135.0, 136.7, 139.0, 140.2, 140.5, 146.9, 148.9; MS (MALDI-TOF, DCTB matrix + CF_3CO_2Na) *m/z* 1397 (M + Na^+).

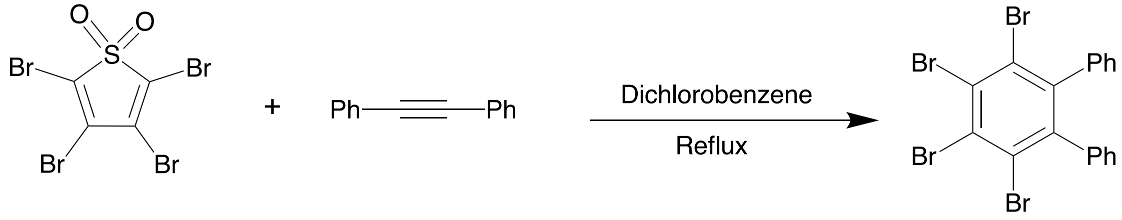
^{1}H NMR Spectrum (500 MHz, CDCl$_3$) of Compound **88**



^{13}C NMR Spectrum (126 MHz, CDCl$_3$) of Compound **88**



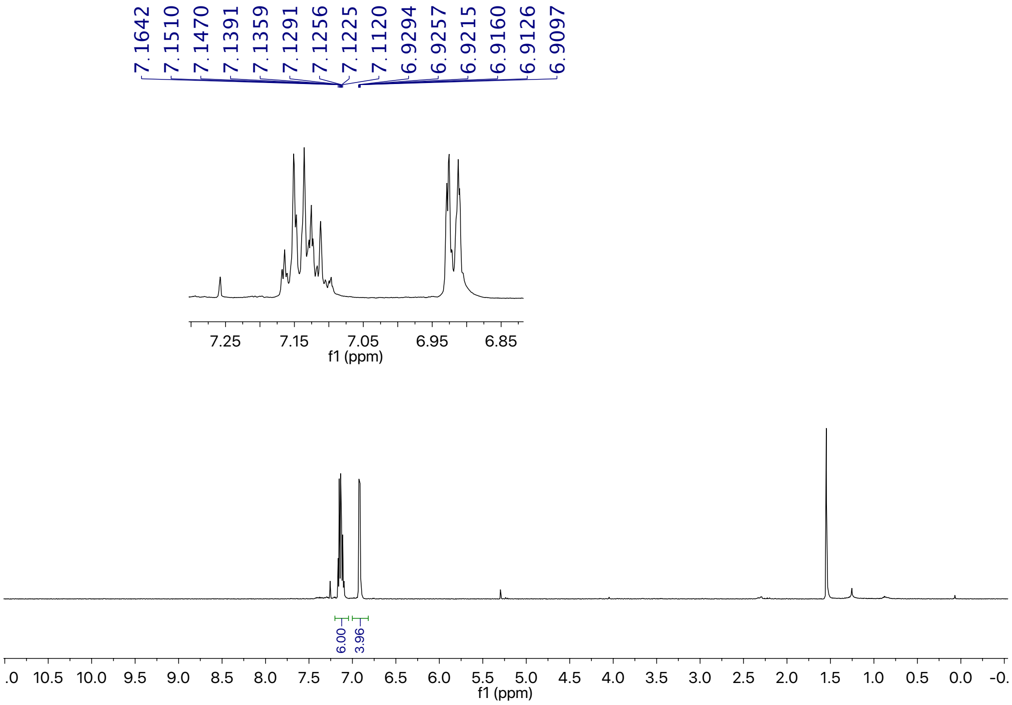
Synthesis of Compound 91



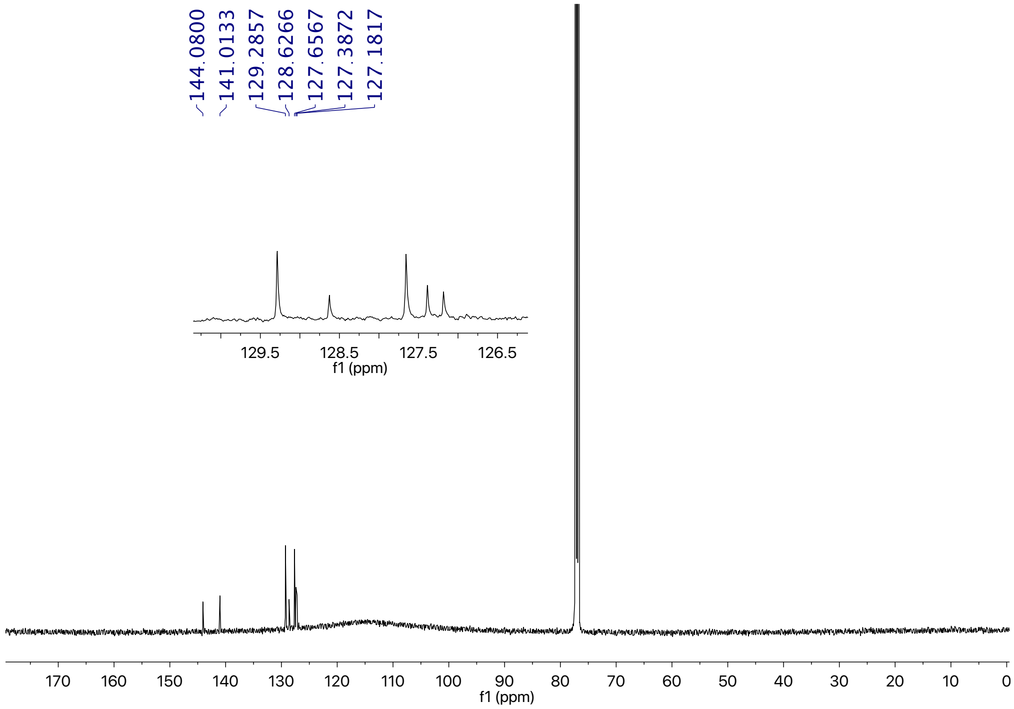
90 **94** **91**

Sulfone[12] (**90**, 3.00 g, 6.95 mmol) and diphenylacetylene (**94**, 1.36 g, 7.65 mmol) were dissolved in to xylenes (5 mL). Then the mixture was heated to 150 °C overnight. The product mixture was purified by silica gel column chromatography (solvent, hexanes) to give compound **91** as a white solid (1.32 g, 2.42 mmol, 35%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (m, 4H), 7.12 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 127.2, 127.4, 127.6, 128.7, 129.3, 141.0, 144.1.

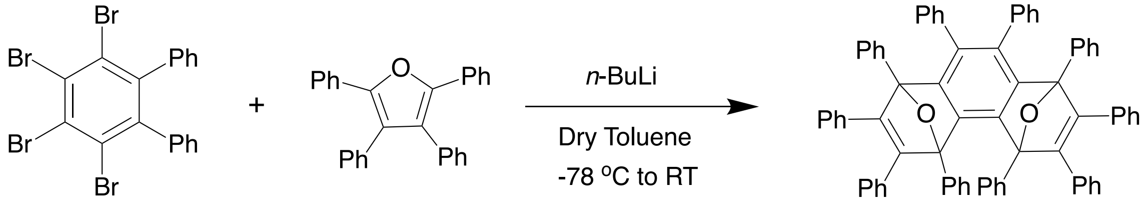
^{1}H NMR Spectrum (500 MHz, CDCl$_3$) of Compound **91**



^{13}C NMR Spectrum (126 MHz, CDCl$_3$) of Compound **91**



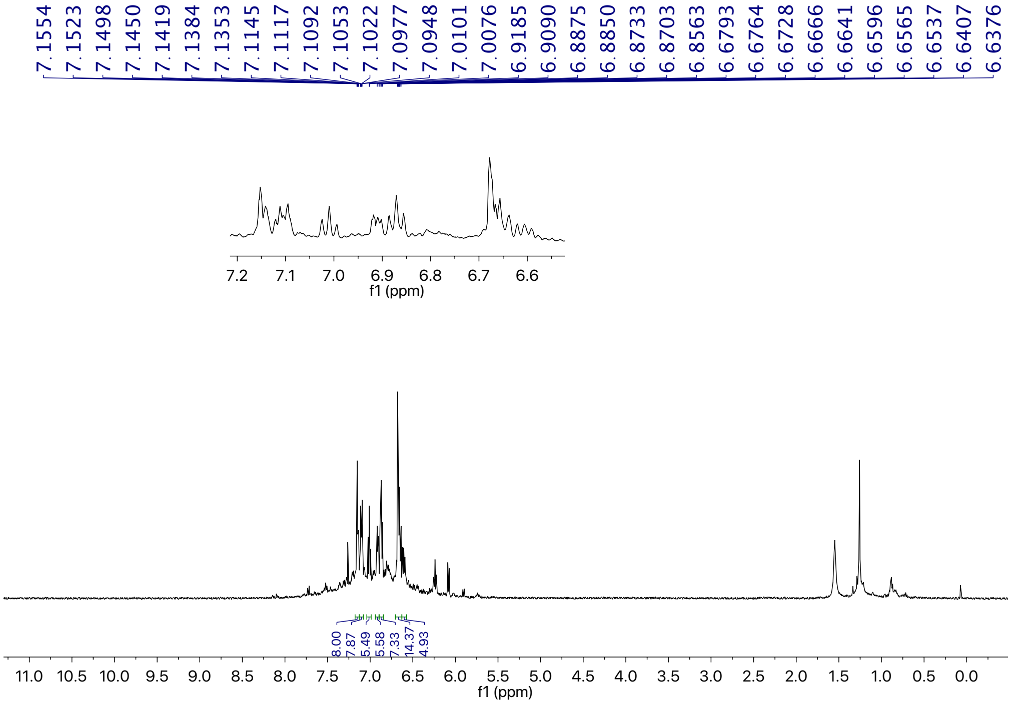
Synthesis of Compound 93



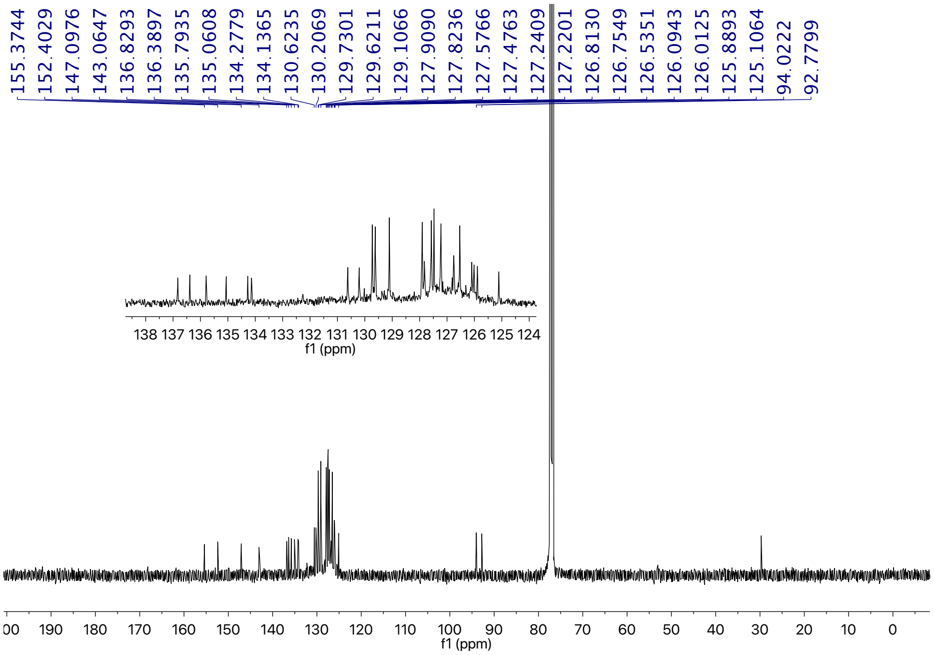
91 **83** **93**

Tetraphenylfuran (**83**, 0.90 g, 2.42 mmol) and 1,2,3,4-tetrabromo-5,6-diphenylbenzene (**91**, 1.32 g, 2.42 mmol) were dissolved in dry toluene (70 mL) and cooled to -78 °C with stirring under argon. *n*-Butyllithium (2.5 *M* in hexanes, 1.94 mL, 4.84 mmol) was diluted in dry hexanes (30 mL), and the resulting solution was added dropwise to the cold reaction mixture. The contents were allowed to warm to room temperature with stirring overnight. The reaction was quenched with methanol (50 mL), and ether (200 mL) was added. The resulting suspension was washed twice with saturated NaCl and once with water. The remaining organics were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (solvent, 2:1 hexanes-CH_2Cl_2) to give compound **93** as a white solid (0.24 g, 0.274 mmol, 11%). ^1H NMR (500 MHz, $CDCl_3$) δ 6.65 (m, 17H), 6.87 (t, *J* = 7.6, 7H), 6.91 (m, 5H), 7.02 (t, *J* = 7.6, 5H), 7.10 (m, 8H), 7.15 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 92.8, 94.0,125.1, 125.9, 126.0, 126.1, 126.5, 126.7, 126.8, 127.2, 127.3, 127.5, 127.6, 127.8, 127.9, 129.1, 129.6, 129.7, 130.0, 130.2, 130.6, 134.1, 134.3, 135.1, 135.8, 136.4, 136.8, 143.1, 147.1, 152.4, 155.4 (31 resonances observed, 27 are expected for fast phenyl rotation, 37 for slow).

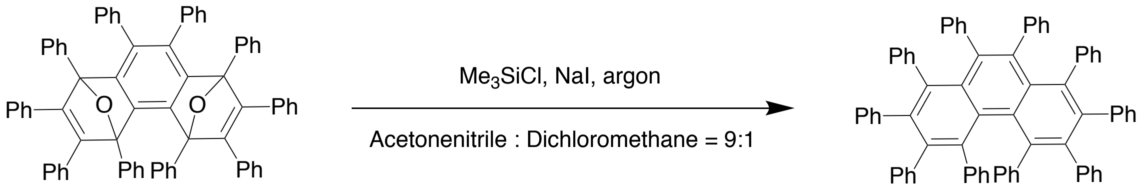
^{1}H NMR Spectrum (500 MHz, CDCl$_3$) of Compound **93**



^{13}C NMR Spectrum (126 MHz, $CDCl_3$) of Compound **93**



Synthesis of Compound 77

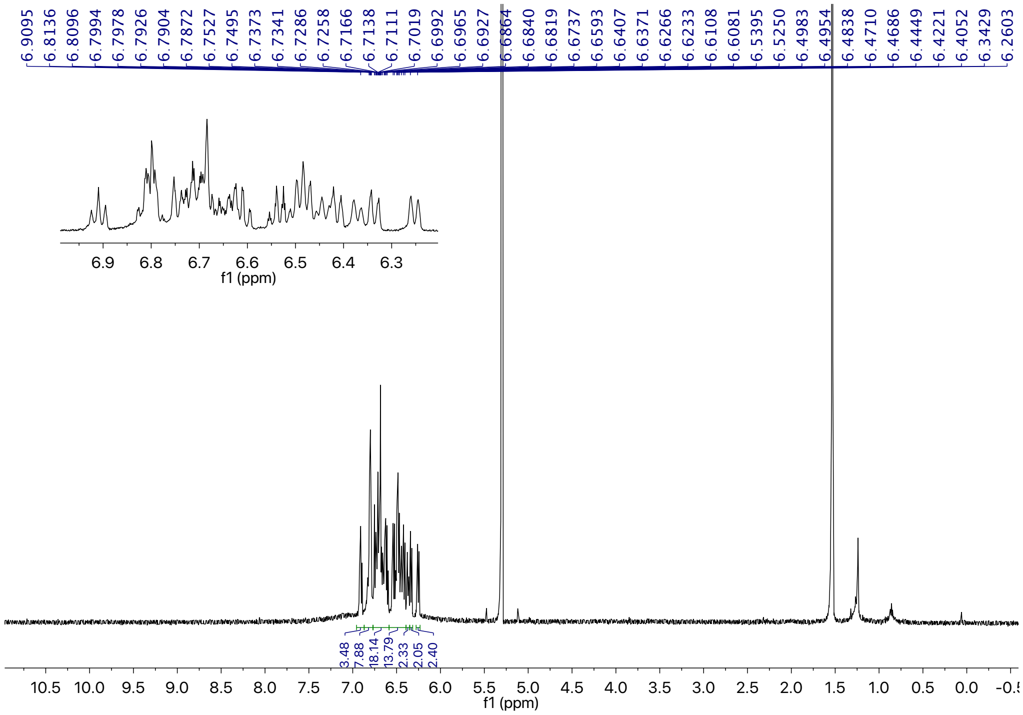


93

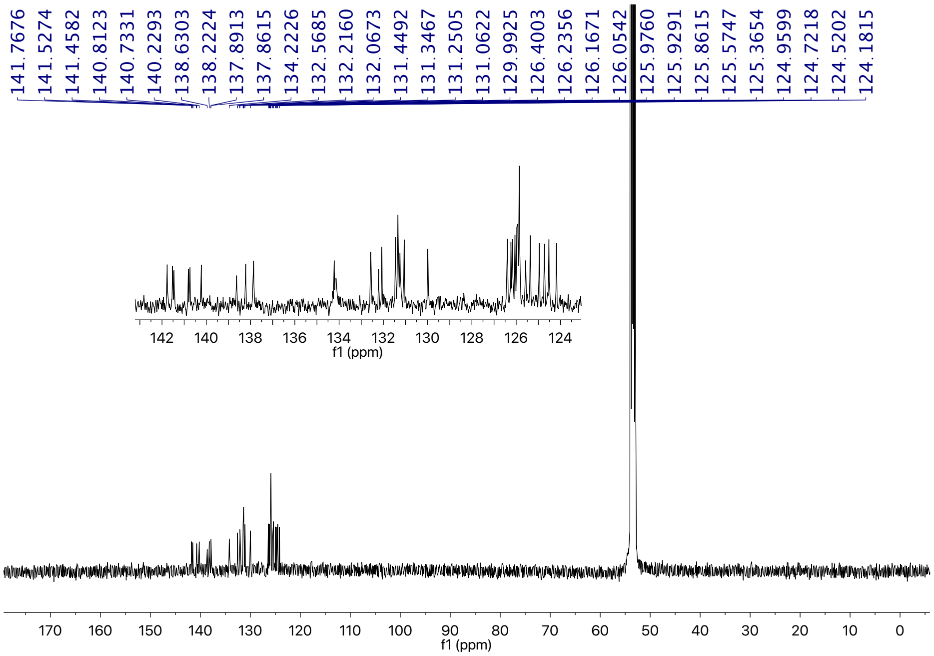
77

Under an inert atmosphere compound **93** (0.24 g, 0.274 mmol) and sodium iodide (0.246 g, 1.64 mmol) were suspended in acetonitrile (9 mL) and dichloromethane (1 mL) at room temperature. Upon addition of trimethylsilyl chloride (0.208 mL, 0.178 g, 1.64 mmol) the mixture changed color to red. TLC monitoring showed full consumption of **93** after 0.5 h. The reaction was diluted with water an extracted with dichloromethane. The combined organic layer was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure.The crude product was purified by silica gel column chromatography (solvent, 2:1 hexanes-CH_2Cl_2) to give compound **77** as a light yellow solid (50.4 mg, 0.054 mmol, 20%). ^1H NMR (500 MHz, CD_2Cl_2) δ 6.26 (d, *J* = 7.6, 2H), 6.34 (d, *J* = 7.6, 2H), 6.37 (d, *J* = 7.6, 2H), 6.48 (m, 14H), 6.69 (m, 18H), 6.81 (m, 8H), 6.91 (t, *J* = 7.6, 4H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 124.2, 124.5, 124.7, 125.0, 125.4, 125.6, 125.8, 125.9, 126.0, 126.1, 126.2, 126.3, 126.4, 130.0, 131.1, 131.3, 131.4, 131.5, 132.1, 132.2, 132.6, 134.2, 137.8, 137.9, 138.2, 138.6, 140.2, 140.7, 140.8, 141.5, 141.5, 141.8 (32 resonances observed; 27 are expected for fast phenyl rotation, 37 for slow); MS (MALDI-TOF, graphite matrix + CF_3CO_2Na) *m/z* 961.9 (M + Na^+). Single crystals, suitable for X-ray analysis, were obtained upon evaporation of a solution in $CHCl_3$-ethyl acetate.

^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of Compound **77**



^{13}C NMR Spectrum (126 MHz, CDCl$_3$) of Compound **77**



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Chapter 4. X-ray Analysis for Selected Compounds

X-ray data for compound 31

Table 4.1. Sample and crystal data for compound **31**

Identification code	RAP128c	
Chemical formula	$C_{53}H_{54}O_2S_3Si$	
Formula weight	847.23 g/mol	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal size	0.079 x 0.100 x 0.283 mm	
Crystal habit	colorless column	
Crystal system	monoclinic	
Space group	*P* 1 21/*c* 1	
Unit cell dimensions	*a* = 25.0223(8) Å	*α* = 90°
	b = 10.0404(3) Å	*β* = 90.0290(10)°
	c = 17.1056(5) Å	*γ* = 90°
Volume	4297.5(2) $Å^3$	
Z	4	
Density (calculated)	1.309 g/cm^3	
Absorption coefficient	2.168 mm^{-1}	
***F*(000)**	1800	

Table 4.2. Data collection and structure refinement for compound **31**

Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Radiation source	INCOATEC IμS microfocus source, Cu-Kα
Theta range for data collection	3.53 to 72.46°
Reflections collected	15504
Independent reflections	8443 [*R*(int) = 0.0331]
Coverage of independent reflections	99.1%
Absorption correction	multi-scan
Max. and min. transmission	0.8470 and 0.5790

Refinement method	Full-matrix least-squares on F^2
Refinement program	*SHELXL* (Sheldrick)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	8443 / 0 / 684
Goodness-of-fit on F^2	1.041
Δ/σ_{max}	0.001
Final R indices	7498 data; $I>2\sigma(I)$ $R1 = 0.0396$, $wR2 = 0.0985$
	all data $R1 = 0.0454$, $wR2 = 0.1015$
Weighting scheme	$w=1/[\sigma^2(F_o^2) + (0.0464P)^2+2.3368P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.543 and -0.347 $e\text{Å}^{-3}$
R.M.S. deviation from mean	0.052 $e\text{Å}^{-3}$

Table 4.3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound **31**

	x/a	y/b	z/c	U(eq)
S1	0.25365(2)	0.20800(4)	0.37887(2)	0.02504(10)
S2	0.25500(2)	0.58323(4)	0.63139(3)	0.02565(10)
S3	0.27299(2)	0.07843(5)	0.69637(2)	0.02595(11)
Si1	0.36997(2)	0.28298(5)	0.56059(3)	0.02103(11)
C1	0.14815(7)	0.28535(17)	0.41191(10)	0.0229(3)
C2	0.11464(7)	0.26279(19)	0.34702(10)	0.0276(4)
C3	0.06103(7)	0.2320(2)	0.35500(11)	0.0306(4)
C4	0.03834(7)	0.22771(19)	0.42904(11)	0.0279(4)
C5	0.07088(7)	0.24648(17)	0.49360(10)	0.0234(3)
C6	0.12603(6)	0.26899(17)	0.48724(10)	0.0209(3)
C7	0.12705(7)	0.38338(17)	0.61730(9)	0.0215(3)
C8	0.15033(7)	0.48247(17)	0.66434(10)	0.0232(3)
C9	0.11609(8)	0.57667(19)	0.69890(11)	0.0294(4)
C10	0.06125(8)	0.5714(2)	0.69120(12)	0.0327(4)
C11	0.03789(7)	0.46620(19)	0.65073(11)	0.0292(4)

	x/a	**y/b**	**z/c**	**U(eq)**
C12	0.07096(7)	0.37358(18)	0.61549(10)	0.0234(3)
C13	0.13616(6)	0.14106(17)	0.61116(9)	0.0208(3)
C14	0.16719(7)	0.03817(17)	0.64344(10)	0.0236(3)
C15	0.14108(8)	0.94277(19)	0.68976(11)	0.0296(4)
C16	0.08635(8)	0.9429(2)	0.70110(11)	0.0315(4)
C17	0.05530(7)	0.03749(19)	0.66332(11)	0.0280(4)
C18	0.08018(7)	0.13478(18)	0.61921(10)	0.0228(3)
C19	0.05103(6)	0.24672(18)	0.57742(10)	0.0236(3)
C20	0.15416(6)	0.27093(17)	0.56867(9)	0.0204(3)
C21	0.21404(6)	0.28638(18)	0.56294(10)	0.0225(3)
C22	0.20321(7)	0.33806(19)	0.39160(10)	0.0248(3)
C23	0.20794(7)	0.48812(19)	0.69215(10)	0.0266(4)
C24	0.22549(7)	0.00883(19)	0.62579(10)	0.0261(4)
C25	0.31320(7)	0.31072(18)	0.39256(10)	0.0234(3)
C26	0.31619(7)	0.51022(19)	0.67213(10)	0.0258(4)
C27	0.33299(7)	0.01544(19)	0.64845(12)	0.0296(4)
C28	0.36162(6)	0.22171(17)	0.39662(9)	0.0212(3)
C29	0.37665(7)	0.15352(19)	0.32926(10)	0.0254(4)
C30	0.41949(7)	0.0664(2)	0.32931(11)	0.0284(4)
C31	0.44879(7)	0.0476(2)	0.39721(11)	0.0292(4)
C32	0.43439(7)	0.1162(2)	0.46450(11)	0.0274(4)
C33	0.39084(6)	0.20355(17)	0.46619(10)	0.0219(3)
C34	0.36405(7)	0.54993(18)	0.62408(10)	0.0248(4)
C35	0.38550(8)	0.6765(2)	0.63668(12)	0.0320(4)
C36	0.42717(8)	0.7234(2)	0.59102(14)	0.0371(5)
C37	0.44794(8)	0.6450(2)	0.53202(13)	0.0365(5)
C38	0.42846(7)	0.5162(2)	0.52123(12)	0.0305(4)
C39	0.38690(7)	0.46527(18)	0.56722(10)	0.0242(3)
C40	0.38350(7)	0.07952(18)	0.67867(10)	0.0261(4)
C41	0.41022(8)	0.0214(2)	0.74169(11)	0.0320(4)
C42	0.45798(8)	0.0742(2)	0.76903(11)	0.0356(5)
C43	0.47993(7)	0.1851(2)	0.73371(11)	0.0322(4)
C44	0.45317(7)	0.2451(2)	0.67167(10)	0.0273(4)
C45	0.40458(7)	0.19497(18)	0.64347(9)	0.0234(3)
O1	0.08642(7)	0.75156(17)	0.36963(10)	0.0500(4)

	x/a	**y/b**	**z/c**	**U(eq)**
C46	0.10566(13)	0.8685(3)	0.40645(17)	0.0614(7)
C47	0.12105(12)	0.8299(3)	0.48776(15)	0.0646(8)
C48	0.12167(15)	0.6801(4)	0.48587(17)	0.0766(9)
C49	0.11618(12)	0.6452(3)	0.40341(17)	0.0596(7)
O2	0.32821(7)	0.73459(19)	0.31401(9)	0.0502(4)
C50	0.27352(9)	0.7273(3)	0.33533(14)	0.0470(5)
C51	0.26793(12)	0.8042(4)	0.4106(2)	0.0740(9)
C52	0.32392(12)	0.8204(3)	0.44042(16)	0.0631(7)
C53	0.35740(11)	0.7374(3)	0.38476(15)	0.0531(6)

X-ray data for compound 30

Table 4.4. Sample and crystal data for compound **30**

Identification code	RAP131	
Chemical formula	$C_{27}H_{24}S_3$	
Formula weight	444.64 g/mol	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal size	0.020 x 0.055 x 0.170 mm	
Crystal habit	colorless plate	
Crystal system	orthorhombic	
Space group	*P* 21 21 21	
Unit cell dimensions	a = 8.4186(2) Å	α = 90°
	b = 19.9288(6) Å	β = 90°
	c = 25.3664(7) Å	γ = 90°
Volume	4255.8(2) $Å^3$	
Z	8	
Density (calculated)	1.388 g/cm^3	
Absorption coefficient	3.262 mm^{-1}	
***F*(000)**	1872	

Table 4.5. Data collection and structure refinement for compound **30**

Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Radiation source	INCOATEC IμS microfocus source, Cu-Kα
Theta range for data collection	2.82 to 68.38°
Index ranges	-10<=h<=10, -22<=k<=24, -30<=l<=29
Reflections collected	30524
Independent reflections	7766 [*R*(int) = 0.0992]
Coverage of independent reflections	99.8%
Absorption correction	multi-scan
Max. and min. transmission	0.9380 and 0.6070
Refinement method	Full-matrix least-squares on F^2
Refinement program	*SHELXL* (Sheldrick)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	7766 / 0 / 557

Goodness-of-fit on F^2	1.057	
Final R indices	6482 data; $I>2\sigma(I)$	$R1 = 0.0545$, $wR2 = 0.1127$
	all data	$R1 = 0.0684$, $wR2 = 0.1192$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0440P)^2+2.4551P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.080(14)	
Largest diff. peak and hole	0.288 and -0.275 eÅ^{-3}	
R.M.S. deviation from mean	0.067 eÅ^{-3}	

Table 4.6. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound **30**

	x/a	**y/b**	**z/c**	**U(eq)**
S1	0.29669(18)	0.66402(8)	0.48401(6)	0.0303(3)
S2	0.51497(19)	0.56444(7)	0.33978(6)	0.0285(3)
S3	0.83782(19)	0.66605(8)	0.45918(7)	0.0321(4)
C1	0.5405(7)	0.6706(3)	0.4107(2)	0.0254(13)
C2	0.4313(8)	0.7145(3)	0.4442(3)	0.0319(15)
C3	0.4701(8)	0.6513(3)	0.3565(2)	0.0320(14)
C4	0.7106(8)	0.6969(3)	0.4064(3)	0.0336(15)
C5	0.4399(7)	0.6386(3)	0.5344(2)	0.0274(13)
C6	0.3649(7)	0.5234(3)	0.3809(2)	0.0261(13)
C7	0.8785(8)	0.5817(3)	0.4333(3)	0.0309(14)
C8	0.4216(7)	0.5686(3)	0.5569(2)	0.0248(13)
C9	0.3408(7)	0.5583(3)	0.6044(2)	0.0278(13)
C10	0.3467(7)	0.4974(3)	0.6307(2)	0.0291(14)
C11	0.4330(6)	0.4445(3)	0.6094(2)	0.0234(12)
C12	0.5076(7)	0.4518(3)	0.5613(2)	0.0233(12)
C13	0.4983(7)	0.5130(3)	0.5345(2)	0.0207(12)
C14	0.4118(7)	0.4568(3)	0.4060(2)	0.0245(13)
C15	0.3480(8)	0.3968(3)	0.3868(3)	0.0298(14)
C16	0.3733(8)	0.3364(3)	0.4107(2)	0.0325(15)
C17	0.4591(8)	0.3331(3)	0.4577(2)	0.0300(14)
C18	0.5221(7)	0.3917(3)	0.4781(2)	0.0231(12)

	x/a	y/b	z/c	U(eq)
C19	0.5032(7)	0.4527(3)	0.4516(2)	0.0202(11)
C20	0.8876(7)	0.5256(3)	0.4734(2)	0.0264(13)
C21	0.0368(7)	0.5008(3)	0.4896(3)	0.0297(14)
C22	0.0483(7)	0.4442(3)	0.5213(3)	0.0320(14)
C23	0.9144(7)	0.4087(3)	0.5359(2)	0.0290(14)
C24	0.7656(7)	0.4320(3)	0.5207(2)	0.0235(12)
C25	0.7540(7)	0.4911(3)	0.4916(2)	0.0222(12)
C26	0.5804(7)	0.5107(3)	0.4811(2)	0.0204(12)
C27	0.6052(7)	0.3993(3)	0.5318(2)	0.0247(13)
S4	0.39393(17)	0.44348(7)	0.25292(6)	0.0275(3)
S5	0.72647(19)	0.35408(8)	0.13162(6)	0.0310(4)
S6	0.93296(17)	0.45295(8)	0.27821(7)	0.0298(3)
C28	0.6901(7)	0.4586(3)	0.2029(2)	0.0260(13)
C29	0.5162(7)	0.4829(3)	0.2017(2)	0.0294(14)
C30	0.7547(8)	0.4424(3)	0.1484(2)	0.0300(14)
C31	0.8013(7)	0.5036(3)	0.2365(2)	0.0276(13)
C32	0.3632(7)	0.3600(3)	0.2237(2)	0.0267(13)
C33	0.8822(7)	0.3188(3)	0.1738(3)	0.0302(14)
C34	0.7870(7)	0.4270(3)	0.3285(2)	0.0250(13)
C35	0.3625(7)	0.3014(3)	0.2613(2)	0.0256(13)
C36	0.2187(8)	0.2712(3)	0.2753(3)	0.0317(14)
C37	0.2128(8)	0.2117(3)	0.3042(3)	0.0364(16)
C38	0.3525(8)	0.1807(3)	0.3196(3)	0.0304(15)
C39	0.4960(7)	0.2100(3)	0.3076(2)	0.0248(13)
C40	0.5019(7)	0.2709(3)	0.2803(2)	0.0218(12)
C41	0.8504(7)	0.2503(3)	0.1977(3)	0.0255(13)
C42	0.7617(6)	0.2428(3)	0.2431(2)	0.0209(12)
C43	0.7525(7)	0.1804(3)	0.2689(2)	0.0235(13)
C44	0.8273(7)	0.1247(3)	0.2476(3)	0.0273(13)
C45	0.9123(7)	0.1322(3)	0.2007(3)	0.0301(14)
C46	0.9242(7)	0.1935(3)	0.1761(3)	0.0284(14)
C47	0.8089(7)	0.3578(3)	0.3505(2)	0.0231(12)
C48	0.7457(7)	0.3006(3)	0.3270(2)	0.0211(12)
C49	0.7444(7)	0.2385(3)	0.3531(2)	0.0222(12)
C50	0.8113(8)	0.2323(3)	0.4026(2)	0.0302(14)

	x/a	**y/b**	**z/c**	**U(eq)**
C51	0.8828(9)	0.2886(3)	0.4252(3)	0.0345(15)
C52	0.8811(8)	0.3497(3)	0.4002(3)	0.0318(14)
C53	0.6700(7)	0.2967(3)	0.2725(2)	0.0198(12)
C54	0.6617(7)	0.1838(3)	0.3209(2)	0.0252(13)

X-ray data for compound 56

Table 4.7. Sample and crystal data for compound **56**

Identification code	RAP134	
Chemical formula	$C_{74}H_{64}N_2O_4S_6Si_2$	
Formula weight	1293.81 g/mol	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal size	0.082 x 0.234 x 0.254 mm	
Crystal habit	colorless plate	
Crystal system	triclinic	
Space group	*P* -1	
Unit cell dimensions	a = 14.9584(5) Å	α = 89.066(2)°
	b = 19.7861(7) Å	β = 73.3120(10)°
	c = 23.8710(8) Å	γ = 75.193(2)°
Volume	6530.3(4) $Å^3$	
Z	4	
Density (calculated)	1.316 g/cm^3	
Absorption coefficient	2.696 mm^{-1}	
***F*(000)**	2712	

Table 4.8. Data collection and structure refinement for compound **56**

Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Radiation source	INCOATEC IµS microfocus source, Cu-Kα
Theta range for data collection	2.31 to 73.35°
Index ranges	-18<=h<=18, -24<=k<=22, -29<=l<=28
Reflections collected	49465
Independent reflections	24345 [*R*(int) = 0.0422]
Coverage of independent reflections	92.7%
Absorption correction	multi-scan
Max. and min. transmission	0.8090 and 0.5480
Refinement method	Full-matrix least-squares on F^2
Refinement program	*SHELXL* (Sheldrick)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	24345 / 304 / 1597

Goodness-of-fit on F^2	1.054	
Δ/σ_{max}	0.001	
Final R indices	18895 data; I>2σ(I)	$R1 = 0.0569$, $wR2 = 0.1272$
	all data	$R1 = 0.0751$, $wR2 = 0.1402$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0448P)^2+8.2475P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.653 and -0.773 eÅ^{-3}	
R.M.S. deviation from mean	0.064 eÅ^{-3}	

Table 4.9. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound **56**

	x/a	y/b	z/c	U(eq)
S1	0.24897(5)	0.24761(4)	0.23993(3)	0.02961(16)
S2	0.39002(6)	0.33096(4)	0.98113(3)	0.03526(18)
S3	0.50584(5)	0.08359(4)	0.04951(4)	0.03364(17)
S4	0.67072(5)	0.38296(4)	0.14924(3)	0.03219(17)
S5	0.77890(5)	0.48027(4)	0.95243(3)	0.02954(16)
S6	0.95094(6)	0.17560(4)	0.95219(3)	0.03452(17)
Si1	0.32246(5)	0.22660(4)	0.09274(3)	0.02266(16)
Si2	0.85026(5)	0.33900(4)	0.01985(3)	0.02377(16)
C1	0.2124(2)	0.29448(14)	0.13753(13)	0.0256(6)
C2	0.1563(2)	0.34017(15)	0.10714(14)	0.0304(6)
C3	0.0832(2)	0.39819(16)	0.13514(15)	0.0350(7)
C4	0.0624(2)	0.41112(16)	0.19462(15)	0.0361(7)
C5	0.1126(2)	0.36602(16)	0.22674(14)	0.0333(7)
C6	0.1882(2)	0.30844(15)	0.19858(13)	0.0275(6)
C7	0.3084(2)	0.22224(15)	0.01610(13)	0.0260(6)
C8	0.2631(2)	0.17164(16)	0.00625(13)	0.0295(6)
C9	0.2396(2)	0.16531(16)	0.95444(14)	0.0328(7)
C10	0.2585(2)	0.21192(17)	0.91195(13)	0.0329(7)
C11	0.3019(2)	0.26361(17)	0.92023(13)	0.0330(7)
C12	0.3284(2)	0.26871(15)	0.97131(13)	0.0280(6)
C13	0.3212(2)	0.13611(15)	0.12052(12)	0.0252(6)
C14	0.2364(2)	0.12719(16)	0.16033(13)	0.0279(6)
C15	0.2295(2)	0.06367(16)	0.18426(14)	0.0323(7)
C16	0.3083(2)	0.00622(16)	0.16770(14)	0.0317(7)

	x/a	y/b	z/c	U(eq)
C17	0.3931(2)	0.01151(15)	0.12709(14)	0.0301(6)
C18	0.4002(2)	0.07570(15)	0.10331(12)	0.0250(6)
C19	0.2634(2)	0.30215(17)	0.29586(13)	0.0326(7)
C20	0.3458(2)	0.33542(16)	0.27337(12)	0.0286(6)
C21	0.4360(2)	0.30408(17)	0.27968(14)	0.0335(7)
C22	0.5116(2)	0.33500(17)	0.26046(15)	0.0363(7)
C23	0.4999(2)	0.39789(16)	0.23309(13)	0.0298(6)
C24	0.4098(2)	0.42910(16)	0.22566(14)	0.0340(7)
C25	0.3340(2)	0.39844(17)	0.24562(14)	0.0344(7)
C26	0.5817(2)	0.43249(18)	0.21349(14)	0.0356(7)
C27	0.4075(3)	0.37557(19)	0.91329(16)	0.0414(8)
C28	0.4855(2)	0.41240(17)	0.90927(13)	0.0332(7)
C29	0.4639(2)	0.48270(17)	0.92652(14)	0.0346(7)
C30	0.5369(2)	0.51508(16)	0.92323(14)	0.0322(7)
C31	0.6336(2)	0.47795(15)	0.90257(13)	0.0282(6)
C32	0.6547(2)	0.40752(17)	0.88559(16)	0.0382(7)
C33	0.5820(3)	0.37519(17)	0.88892(16)	0.0401(8)
C34	0.7129(2)	0.51261(16)	0.89959(15)	0.0342(7)
C35	0.6000(2)	0.00857(16)	0.05822(16)	0.0356(7)
C36	0.6954(2)	0.02453(15)	0.03021(14)	0.0310(6)
C37	0.7399(2)	0.05369(19)	0.06325(15)	0.0416(8)
C38	0.8256(2)	0.07193(19)	0.03730(15)	0.0413(8)
C39	0.8682(2)	0.06199(15)	0.97690(13)	0.0291(6)
C40	0.8242(2)	0.03109(16)	0.94440(14)	0.0315(6)
C41	0.7390(2)	0.01262(16)	0.97039(14)	0.0328(7)
C42	0.9596(2)	0.08216(16)	0.94719(14)	0.0332(7)
C43	0.7527(2)	0.43583(15)	0.12641(13)	0.0275(6)
C44	0.7453(2)	0.49533(16)	0.15992(14)	0.0325(7)
C45	0.8098(2)	0.53570(17)	0.14177(14)	0.0340(7)
C46	0.8828(2)	0.51832(16)	0.08953(13)	0.0310(6)
C47	0.8904(2)	0.45952(16)	0.05577(13)	0.0298(6)
C48	0.8264(2)	0.41671(15)	0.07242(13)	0.0255(6)
C49	0.8835(2)	0.41502(15)	0.91376(13)	0.0256(6)
C50	0.9342(2)	0.42143(16)	0.85532(13)	0.0295(6)
C51	0.0239(2)	0.37648(17)	0.82953(13)	0.0333(7)

	x/a	y/b	z/c	U(eq)
C52	0.0667(2)	0.32670(16)	0.86157(14)	0.0327(7)
C53	0.0166(2)	0.31903(15)	0.91905(13)	0.0277(6)
C54	0.9228(2)	0.36063(14)	0.94568(12)	0.0243(6)
C55	0.9652(2)	0.19273(15)	0.02177(13)	0.0278(6)
C56	0.0179(2)	0.14027(16)	0.04853(15)	0.0327(7)
C57	0.0320(2)	0.15458(17)	0.10148(14)	0.0335(7)
C58	0.9955(2)	0.22149(17)	0.12798(14)	0.0338(7)
C59	0.9450(2)	0.27375(16)	0.10089(13)	0.0302(6)
C60	0.9269(2)	0.26197(15)	0.04786(13)	0.0262(6)
C61	0.4296(2)	0.25529(16)	0.09870(14)	0.0294(6)
C62	0.7397(2)	0.31707(17)	0.01175(14)	0.0323(7)
S7	0.37304(6)	0.83294(4)	0.49493(3)	0.03429(17)
S8	0.45118(6)	0.58490(4)	0.56369(3)	0.03605(18)
S9	0.23350(5)	0.76676(4)	0.75582(3)	0.02917(16)
S10	0.77606(5)	0.98373(4)	0.45092(3)	0.02920(15)
S11	0.91241(6)	0.67888(4)	0.46682(4)	0.03953(19)
S12	0.66979(5)	0.89090(4)	0.65837(3)	0.03231(17)
Si3	0.29332(5)	0.73766(4)	0.61095(3)	0.02506(16)
Si4	0.83659(5)	0.84564(4)	0.52561(3)	0.02376(16)
C63	0.2771(2)	0.73233(15)	0.53522(13)	0.0280(6)
C64	0.2276(2)	0.68391(17)	0.52666(14)	0.0339(7)
C65	0.2066(2)	0.67532(18)	0.47470(15)	0.0381(7)
C66	0.2335(2)	0.71710(18)	0.42952(14)	0.0378(7)
C67	0.2809(2)	0.76690(17)	0.43624(14)	0.0341(7)
C68	0.3044(2)	0.77415(15)	0.48809(13)	0.0294(6)
C69	0.2777(2)	0.65135(16)	0.64262(13)	0.0283(6)
C70	0.1933(2)	0.64941(17)	0.68641(14)	0.0330(7)
C71	0.1783(2)	0.58783(18)	0.71121(16)	0.0405(8)
C72	0.2467(3)	0.52531(18)	0.69051(16)	0.0427(8)
C73	0.3293(3)	0.52438(17)	0.64608(15)	0.0400(8)
C74	0.3462(2)	0.58661(16)	0.62248(14)	0.0316(6)
C75	0.1886(2)	0.81044(15)	0.65474(13)	0.0258(6)
C76	0.1291(2)	0.85441(16)	0.62571(14)	0.0321(7)
C77	0.0551(2)	0.91128(17)	0.65400(15)	0.0368(7)
C78	0.0368(2)	0.92581(17)	0.71332(15)	0.0355(7)

	x/a	y/b	z/c	U(eq)
C79	0.0924(2)	0.88276(16)	0.74409(14)	0.0337(7)
C80	0.1676(2)	0.82611(15)	0.71573(13)	0.0272(6)
C81	0.3985(3)	0.87103(19)	0.42381(15)	0.0396(8)
C82	0.4776(2)	0.90652(17)	0.41894(13)	0.0326(7)
C83	0.4573(2)	0.97810(17)	0.43083(14)	0.0331(7)
C84	0.5315(2)	0.01013(16)	0.42507(13)	0.0316(6)
C85	0.6278(2)	0.97193(15)	0.40601(12)	0.0285(6)
C86	0.6479(2)	0.89983(17)	0.39469(15)	0.0383(7)
C87	0.5738(2)	0.86779(17)	0.40109(16)	0.0394(8)
C88	0.7083(2)	0.00724(17)	0.39769(14)	0.0324(7)
C89	0.5456(3)	0.5240(2)	0.58698(18)	0.0477(9)
C90	0.6407(2)	0.53977(18)	0.55689(16)	0.0392(8)
C91	0.6991(3)	0.50614(18)	0.50401(18)	0.0443(8)
C92	0.7846(2)	0.52201(17)	0.47570(16)	0.0404(8)
C93	0.8149(2)	0.57226(17)	0.49948(14)	0.0345(7)
C94	0.7557(3)	0.6070(2)	0.55240(17)	0.0525(10)
C95	0.6702(3)	0.5908(2)	0.58066(16)	0.0541(10)
C96	0.9085(3)	0.58792(18)	0.46634(17)	0.0434(8)
C97	0.2536(2)	0.82220(17)	0.80860(13)	0.0309(6)
C98	0.3391(2)	0.85210(16)	0.78471(12)	0.0280(6)
C99	0.3469(3)	0.8931(2)	0.73662(15)	0.0441(9)
C100	0.4254(3)	0.9211(2)	0.71600(15)	0.0453(9)
C101	0.4980(2)	0.90970(16)	0.74270(13)	0.0302(6)
C102	0.4912(2)	0.86837(17)	0.79031(14)	0.0348(7)
C103	0.4128(2)	0.83996(17)	0.81076(14)	0.0334(7)
C104	0.5809(2)	0.94269(18)	0.72109(14)	0.0357(7)
C105	0.8774(2)	0.91395(15)	0.41569(13)	0.0255(6)
C106	0.9296(2)	0.91641(16)	0.35690(13)	0.0303(6)
C107	0.0161(2)	0.86722(17)	0.33226(13)	0.0338(7)
C108	0.0018(2)	0.81372(15)	0.42370(13)	0.0295(6)
C109	0.0538(2)	0.81663(17)	0.36590(14)	0.0344(7)
C110	0.91146(19)	0.86041(15)	0.44975(12)	0.0255(6)
C111	0.9075(2)	0.76742(15)	0.55589(13)	0.0270(6)
C112	0.9323(2)	0.78008(17)	0.60645(13)	0.0305(6)
C113	0.9787(2)	0.72650(19)	0.63488(15)	0.0378(7)

	x/a	y/b	z/c	U(eq)
C114	0.0018(2)	0.65849(18)	0.61331(16)	0.0400(8)
C115	0.9800(2)	0.64339(17)	0.56314(16)	0.0389(8)
C116	0.9338(2)	0.69653(16)	0.53412(14)	0.0313(6)
C117	0.7497(2)	0.94431(15)	0.63117(13)	0.0262(6)
C118	0.7465(2)	0.00371(16)	0.66341(13)	0.0314(6)
C119	0.8093(2)	0.04485(16)	0.64176(14)	0.0318(6)
C120	0.8775(2)	0.02714(16)	0.58768(14)	0.0322(7)
C121	0.8820(2)	0.96759(16)	0.55577(13)	0.0284(6)
C122	0.81915(19)	0.92486(15)	0.57555(12)	0.0248(6)
C123	0.4096(2)	0.75563(17)	0.61253(14)	0.0326(7)
C124	0.7213(2)	0.82885(16)	0.52065(13)	0.0298(6)
O1	0.4632(3)	0.8207(2)	0.25754(19)	0.1031(14)
O2	0.3295(3)	0.79202(19)	0.29395(14)	0.0966(13)
N1	0.3895(3)	0.80828(19)	0.25367(15)	0.0638(10)
C125	0.4446(3)	0.81792(18)	0.14718(17)	0.0480(9)
C126	0.4270(4)	0.8227(2)	0.09375(19)	0.0608(11)
C127	0.3388(4)	0.8229(2)	0.0897(2)	0.0685(13)
C128	0.2646(4)	0.8187(2)	0.1383(2)	0.0670(12)
C129	0.2802(3)	0.81360(19)	0.1936(2)	0.0536(10)
C130	0.3712(3)	0.81339(17)	0.19576(15)	0.0404(8)
O3	0.6578(3)	0.67874(19)	0.22056(14)	0.0854(11)
O4	0.5206(3)	0.6550(2)	0.25309(19)	0.0988(13)
N2	0.5927(3)	0.66661(19)	0.26010(17)	0.0626(10)
C131	0.6023(3)	0.66665(18)	0.32013(16)	0.0444(8)
C132	0.6910(3)	0.6658(2)	0.32657(19)	0.0540(10)
C133	0.6984(4)	0.6652(2)	0.3835(2)	0.0687(13)
C134	0.6189(4)	0.6659(2)	0.4306(2)	0.0728(14)
C135	0.5325(4)	0.6672(2)	0.4224(2)	0.0665(13)
C136	0.5228(3)	0.6678(2)	0.36667(18)	0.0547(10)
O5	0.9390(5)	0.5136(3)	0.6512(3)	0.121(2)
O6	0.0233(4)	0.4312(4)	0.6901(3)	0.1100(18)
N3	0.9505(4)	0.4610(3)	0.6781(3)	0.0909(18)
O5A	0.0443(10)	0.3772(7)	0.6825(7)	0.121(2)
O6A	0.9973(11)	0.2900(8)	0.7246(7)	0.1100(18)
N3A	0.9835(5)	0.3454(7)	0.7018(7)	0.0909(18)

	x/a	**y/b**	**z/c**	**U(eq)**
C137	0.8725(3)	0.4240(2)	0.68323(18)	0.105(2)
C138	0.7917(4)	0.44847(17)	0.66359(15)	0.1001(19)
C139	0.7132(3)	0.4198(2)	0.68278(19)	0.105(2)
C140	0.7155(3)	0.3668(2)	0.72161(19)	0.104(2)
C141	0.7962(3)	0.34230(17)	0.74126(15)	0.0861(16)
C142	0.8747(3)	0.3709(2)	0.72207(18)	0.0879(16)
O7	0.0072(5)	0.8856(3)	0.1935(3)	0.0899(18)
O8	0.0030(5)	0.7831(3)	0.2214(3)	0.0953(17)
N4	0.9634(4)	0.8412(3)	0.2100(3)	0.0780(16)
O7A	0.9711(6)	0.9332(5)	0.2025(4)	0.0899(18)
O8A	0.8682(7)	0.0057(4)	0.1669(4)	0.0953(17)
N4A	0.8940(5)	0.9547(4)	0.1926(4)	0.0780(16)
C143	0.8579(2)	0.8555(2)	0.22359(19)	0.0985(19)
C144	0.8214(3)	0.9164(2)	0.19858(18)	0.0965(18)
C145	0.7246(3)	0.93545(16)	0.19998(16)	0.0806(15)
C146	0.6644(2)	0.8937(2)	0.22639(16)	0.0822(15)
C147	0.7008(3)	0.83279(18)	0.25140(15)	0.0920(17)
C148	0.7976(3)	0.81372(17)	0.25000(16)	0.0987(19)

X-ray data for compound 61

Table 4.10. Sample and crystal data for compound **61**

Identification code	RAP138	
Chemical formula	$C_{56}H_{62}P_2S_6$	
Formula weight	989.35 g/mol	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal size	0.106 x 0.162 x 0.238 mm	
Crystal habit	colorless block	
Crystal system	triclinic	
Space group	*P* -1	
Unit cell dimensions	*a* = 9.6080(3) Å	*α* = 107.307(2)°
	b = 10.0386(3) Å	*β* = 93.210(2)°
	c = 16.0644(6) Å	*γ* = 107.3880(10)°
Volume	1393.71(8) $Å^3$	
Z	1	
Density (calculated)	1.179 g/cm^3	
Absorption coefficient	3.061 mm^{-1}	
***F*(000)**	524	

Table 4.11. Data collection and structure refinement for compound **61**

Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Radiation source	'INCOATEC IμS microfocus source', Cu
Theta range for data collection	2.92 to 72.16°
Index ranges	-10<=h<=11, -12<=k<=11, -19<=l<=17
Reflections collected	10676
Independent reflections	5190 [*R*(int) = 0.0284]
Coverage of independent reflections	94.3%
Absorption correction	multi-scan
Max. and min. transmission	0.7370 and 0.5300
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/1 (Sheldrick)

Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5190 / 136 / 316	
Goodness-of-fit on F^2	1.055	
Δ/σ_{max}	0.001	
Final R indices	4363 data; I>2σ(I)	$R1$ = 0.0888, w$R2$ = 0.2306
	all data	$R1$ = 0.1004, w$R2$ = 0.2413
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1062P)^2+3.1027P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.085 and -1.001 eÅ^{-3}	
R.M.S. deviation from mean	0.078 eÅ^{-3}	

Table 4.12. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound **61**

	x/a	**y/b**	**z/c**	**U(eq)**
S1	0.6215(4)	0.0940(4)	0.2627(3)	0.0624(8)
S2	0.651(3)	0.5741(9)	0.160(2)	0.0744(17)
S1A	0.5612(4)	0.1160(4)	0.2631(3)	0.0624(8)
S2A	0.623(3)	0.5604(9)	0.165(2)	0.0744(17)
S3	0.02954(13)	0.58358(12)	0.41679(7)	0.0518(3)
P1	0.80464(12)	0.39347(11)	0.24130(7)	0.0464(3)
C1	0.9013(7)	0.2594(6)	0.2450(6)	0.0453(17)
C2	0.8113(6)	0.1303(7)	0.2555(6)	0.053(2)
C3	0.8708(8)	0.0238(6)	0.2639(6)	0.076(3)
C4	0.0203(9)	0.0463(8)	0.2618(7)	0.091(4)
C5	0.1103(6)	0.1754(9)	0.2513(7)	0.076(3)
C6	0.0509(6)	0.2820(6)	0.2429(6)	0.061(2)
C1A	0.8538(7)	0.2333(6)	0.2525(6)	0.0453(17)
C2A	0.7452(6)	0.1149(7)	0.2631(6)	0.053(2)
C3A	0.7809(8)	0.9955(6)	0.2731(6)	0.076(3)
C4A	0.9252(10)	0.9947(7)	0.2724(7)	0.091(4)
C5A	0.0338(7)	0.1131(9)	0.2617(7)	0.076(3)
C6A	0.9981(6)	0.2324(7)	0.2517(6)	0.061(2)
C7	0.623(2)	0.171(3)	0.3806(7)	0.113(4)
C8	0.4816(16)	0.157(3)	0.4047(10)	0.106(4)
C9	0.4844(18)	0.222(2)	0.5012(11)	0.112(4)
C10	0.6319(12)	0.7756(15)	0.4470(6)	0.084(3)

	x/a	y/b	z/c	U(eq)
C11	0.5938(17)	0.7381(14)	0.3534(7)	0.087(3)
C12	0.4962(17)	0.5795(14)	0.3005(7)	0.089(3)
C13	0.4747(17)	0.5473(14)	0.2012(7)	0.075(3)
C7A	0.6337(19)	0.211(3)	0.3798(7)	0.113(4)
C8A	0.5015(16)	0.201(3)	0.4151(10)	0.106(4)
C9A	0.5260(17)	0.291(2)	0.5101(11)	0.112(4)
C10A	0.6080(12)	0.7049(15)	0.4562(7)	0.084(3)
C11A	0.5539(17)	0.6766(14)	0.3655(7)	0.087(3)
C12A	0.4783(18)	0.5155(14)	0.3068(8)	0.089(3)
C13A	0.4535(17)	0.4942(14)	0.2088(7)	0.075(3)
C14	0.6334(6)	0.3919(6)	0.0957(3)	0.0609(12)
C15	0.5548(7)	0.3320(7)	0.0093(4)	0.0804(17)
C16	0.5574(7)	0.2010(7)	0.9533(4)	0.0788(17)
C17	0.6411(7)	0.1300(7)	0.9801(4)	0.0775(17)
C18	0.7199(7)	0.1877(6)	0.0653(3)	0.0695(14)
C19	0.7168(5)	0.3190(5)	0.1249(3)	0.0523(10)
C20	0.7423(19)	0.723(2)	0.477(2)	0.079(4)
C21	0.878(2)	0.783(3)	0.472(2)	0.069(3)
C20A	0.7386(19)	0.671(2)	0.475(2)	0.079(4)
C21A	0.897(2)	0.804(3)	0.466(2)	0.069(3)
C22	0.0168(6)	0.7510(5)	0.4939(4)	0.0653(13)
C23	0.0618(5)	0.6310(5)	0.3201(3)	0.0513(10)
C24	0.1814(5)	0.7530(6)	0.3220(4)	0.0660(13)
C25	0.2134(6)	0.7807(7)	0.2454(4)	0.0831(19)
C26	0.1273(6)	0.6920(9)	0.1667(5)	0.093(2)
C27	0.0081(6)	0.5705(8)	0.1634(4)	0.0770(17)
C28	0.9726(5)	0.5393(5)	0.2399(3)	0.0523(10)

X-ray data for compound 32

Table 4.13. Sample and crystal data for compound **32**

Identification code	RAP145	
Chemical formula	$C_{28}H_{31}PS_3$	
Formula weight	494.68 g/mol	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal size	0.064 x 0.167 x 0.232 mm	
Crystal habit	colorless plate	
Crystal system	monoclinic	
Space group	*P* 1 21/*c* 1	
Unit cell dimensions	*a* = 10.3116(5) Å	*α* = 90°
	b = 16.6310(8) Å	*β* = 108.753(2)°
	c = 14.8890(7) Å	*γ* = 90°
Volume	2417.8(2) $Å^3$	
Z	4	
Density (calculated)	1.359 g/cm^3	
Absorption coefficient	3.528 mm^{-1}	
***F*(000)**	1048	

Table 4.14. Data collection and structure refinement for compound **32**

Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Radiation source	INCOATEC IµS microfocus source, Cu-Kα
Theta range for data collection	4.11 to 77.22°
Index ranges	-11<=h<=12, -20<=k<=20, -17<=l<=18
Reflections collected	36208
Independent reflections	36208 [*R*(int) = 0.0000]
Coverage of independent reflections	95.7%
Absorption correction	multi-scan
Max. and min. transmission	0.8060 and 0.4950
Refinement method	Full-matrix least-squares on F^2
Refinement program	*SHELXL-2018/1* (Sheldrick)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	36208 / 0 / 414

Goodness-of-fit on F^2	1.023	
Δ/σ_{max}	0.001	
Final R indices	29544 data; $I>2\sigma(I)$	$R1 = 0.0418$, $wR2 = 0.0989$
	all data	$R1 = 0.0538$, $wR2 = 0.1066$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0473P)^2+0.3479P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.376 and -0.400 eÅ^{-3}	
R.M.S. deviation from mean	0.065 eÅ^{-3}	

Table 4.15. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound **32**

	x/a	**y/b**	**z/c**	**U(eq)**
S1	0.57833(6)	0.93008(3)	0.15015(4)	0.01886(14)
S2	0.71697(6)	0.80999(3)	0.47686(4)	0.02113(14)
S3	0.60797(6)	0.63551(3)	0.18663(4)	0.02044(14)
P1	0.77768(5)	0.79440(3)	0.27817(4)	0.01478(14)
C1	0.8150(2)	0.83891(12)	0.17536(15)	0.0164(4)
C2	0.9239(2)	0.81475(13)	0.14476(17)	0.0195(5)
C3	0.9431(2)	0.84707(14)	0.06389(17)	0.0226(5)
C4	0.8524(2)	0.90409(14)	0.01052(17)	0.0238(5)
C5	0.7426(2)	0.92852(13)	0.03897(17)	0.0215(5)
C6	0.7237(2)	0.89652(12)	0.12032(16)	0.0173(4)
C7	0.9002(2)	0.84744(12)	0.37926(16)	0.0168(4)
C8	0.0223(2)	0.88255(13)	0.37619(17)	0.0195(5)
C9	0.1158(2)	0.91594(13)	0.45676(18)	0.0234(5)
C10	0.0890(2)	0.91520(14)	0.54188(18)	0.0245(5)
C11	0.9672(2)	0.88270(14)	0.54630(17)	0.0222(5)
C12	0.8721(2)	0.84974(12)	0.46561(16)	0.0183(4)
C13	0.8665(2)	0.69634(12)	0.28744(16)	0.0165(4)
C14	0.0059(2)	0.68477(13)	0.33614(17)	0.0196(5)
C15	0.0671(2)	0.60976(13)	0.34074(17)	0.0219(5)
C16	0.9898(2)	0.54409(13)	0.29725(17)	0.0230(5)
C17	0.8510(2)	0.55370(13)	0.24981(17)	0.0208(5)
C18	0.7882(2)	0.62892(12)	0.24509(15)	0.0173(4)
C19	0.4583(2)	0.85275(14)	0.08581(17)	0.0211(5)

	x/a	**y/b**	**z/c**	**U(eq)**
C20	0.3184(2)	0.86203(14)	0.09961(17)	0.0222(5)
C21	0.3219(2)	0.86140(14)	0.20289(17)	0.0209(5)
C22	0.6010(2)	0.89171(14)	0.42037(18)	0.0231(5)
C23	0.4547(2)	0.87315(16)	0.41825(18)	0.0261(5)
C24	0.3924(3)	0.79632(15)	0.36468(18)	0.0252(5)
C25	0.5556(2)	0.62888(14)	0.29258(17)	0.0216(5)
C26	0.4004(2)	0.63325(14)	0.2686(2)	0.0255(5)
C27	0.3327(2)	0.70972(13)	0.21669(18)	0.0230(5)
C28	0.3952(2)	0.78942(13)	0.26265(16)	0.0193(5)

X-ray data for compound 75

Table 4.16. Sample and crystal data for compound **75**

Identification code	RAP146	
Chemical formula	$C_{91}H_{61}Cl_3$	
Formula weight	1260.74 g/mol	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal size	0.078 x 0.102 x 0.119 mm	
Crystal system	monoclinic	
Space group	*C* 1 2 1	
Unit cell dimensions	*a* = 23.1292(11) Å	*α* = 90°
	b = 17.7226(9) Å	*β* = 121.517(2)°
	c = 21.4625(11) Å	*γ* = 90°
Volume	7499.9(7) $Å^3$	
Z	4	
Density (calculated)	1.117 g/cm^3	
Absorption coefficient	1.437 mm^{-1}	
***F*(000)**	2632	

Table 4.17. Data collection and structure refinement for compound **75**

Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Radiation source	INCOATEC IμS microfocus source, Cu-Kα
Theta range for data collection	3.35 to 73.14°
Index ranges	-26<=h<=28, -18<=k<=21, -24<=l<=26
Reflections collected	27758
Independent reflections	11421 [*R*(int) = 0.0548]
Absorption correction	multi-scan
Max. and min. transmission	0.8960 and 0.8480
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/1 (Sheldrick)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	11421 / 725 / 831

Goodness-of-fit on F^2	1.034	
Final R indices	8685 data; I>2σ(I)	$R1 = 0.1108$, $wR2 = 0.2881$
	all data	$R1 = 0.1352$, $wR2 = 0.3082$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1211P)^2+51.2895P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.53(6)	
Extinction coefficient	0.0007(1)	
Largest diff. peak and hole	0.665 and -0.510 eÅ^{-3}	
R.M.S. deviation from mean	0.086 eÅ^{-3}	

Table 4.18. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound **75**

	x/a	**y/b**	**z/c**	**U(eq)**
C1	0.0	0.3370(7)	0.0	0.028(2)
C2	0.0637(4)	0.3727(4)	0.0453(5)	0.0261(17)
C3	0.1251(4)	0.3343(5)	0.0686(5)	0.0311(19)
C4	0.1908(4)	0.3577(5)	0.1231(5)	0.0274(17)
C5	0.2460(4)	0.3244(5)	0.1265(5)	0.0325(19)
C6	0.2391(4)	0.2713(5)	0.0743(5)	0.0344(19)
C7	0.1768(4)	0.2360(5)	0.0286(5)	0.0321(19)
C8	0.1189(4)	0.2602(4)	0.0329(5)	0.0287(18)
C9	0.0571(4)	0.2192(5)	0.0051(5)	0.0310(18)
C10	0.0	0.2572(7)	0.0	0.031(3)
C11	0.0669(4)	0.4521(4)	0.0678(5)	0.0307(18)
C12	0.0360(4)	0.4737(6)	0.1065(5)	0.040(2)
C13	0.0404(5)	0.5460(7)	0.1324(6)	0.060(3)
C14	0.0758(5)	0.6016(6)	0.1192(6)	0.049(3)
C15	0.1055(6)	0.5834(6)	0.0797(7)	0.062(3)
C16	0.1017(5)	0.5083(5)	0.0532(5)	0.042(2)
C17	0.2030(4)	0.4082(5)	0.1839(6)	0.037(2)
C18	0.1769(4)	0.3846(6)	0.2275(5)	0.039(2)
C19	0.1928(6)	0.4274(8)	0.2904(7)	0.059(3)
C20	0.2338(6)	0.4865(8)	0.3126(7)	0.061(3)
C21	0.2605(5)	0.5148(7)	0.2675(7)	0.053(3)
C22	0.2406(4)	0.4700(5)	0.2037(5)	0.037(2)
C23	0.3172(4)	0.3457(5)	0.1885(6)	0.039(2)

	x/a	y/b	z/c	U(eq)
C24	0.3402(5)	0.3277(7)	0.2615(6)	0.050(3)
C25	0.4040(5)	0.3473(7)	0.3154(7)	0.059(3)
C26	0.4440(6)	0.3870(8)	0.3026(8)	0.067(3)
C27	0.4250(5)	0.4076(7)	0.2341(8)	0.060(3)
C28	0.3614(4)	0.3841(5)	0.1749(6)	0.041(2)
C29	0.2977(4)	0.2486(5)	0.0680(5)	0.037(2)
C30	0.3515(4)	0.2074(5)	0.1275(6)	0.041(2)
C31	0.4094(5)	0.1886(6)	0.1251(6)	0.052(3)
C32	0.4145(4)	0.2129(7)	0.0665(6)	0.051(3)
C33	0.3620(5)	0.2567(7)	0.0080(7)	0.058(3)
C34	0.3047(4)	0.2719(5)	0.0112(6)	0.040(2)
C35	0.1647(4)	0.1859(5)	0.9668(5)	0.0317(19)
C36	0.2008(5)	0.1178(6)	0.9787(6)	0.044(2)
C37	0.1882(5)	0.0777(6)	0.9152(6)	0.045(2)
C38	0.1409(6)	0.1022(7)	0.8446(6)	0.052(3)
C39	0.1100(5)	0.1690(7)	0.8370(6)	0.052(3)
C40	0.1197(4)	0.2119(6)	0.8940(5)	0.040(2)
C41	0.0529(5)	0.1374(3)	0.9804(5)	0.025(2)
C42	0.0962(5)	0.0850(4)	0.0319(5)	0.031(3)
C43	0.0955(5)	0.0104(4)	0.0115(6)	0.031(3)
C44	0.0513(5)	0.9882(3)	0.9396(6)	0.041(3)
C45	0.0079(5)	0.0406(5)	0.8881(5)	0.043(3)
C46	0.0087(5)	0.1152(4)	0.9085(5)	0.030(3)
C41A	0.0629(10)	0.1335(3)	0.0015(10)	0.025(2)
C42A	0.1105(9)	0.0894(7)	0.0592(9)	0.031(3)
C43A	0.1190(9)	0.0141(7)	0.0476(10)	0.031(3)
C44A	0.0799(10)	0.9829(5)	0.9783(12)	0.041(3)
C45A	0.0322(10)	0.0270(8)	0.9205(9)	0.043(3)
C46A	0.0238(9)	0.1023(7)	0.9321(9)	0.030(3)
C47	0.0	0.3795(10)	0.5	0.049(4)
C48	0.0644(5)	0.3392(7)	0.5431(7)	0.054(3)
C49	0.1218(4)	0.3846(6)	0.5638(6)	0.041(2)
C50	0.1920(5)	0.3601(7)	0.6218(6)	0.049(3)
C51	0.2481(5)	0.3935(7)	0.6249(6)	0.050(3)
C52	0.2366(5)	0.4472(7)	0.5682(7)	0.057(3)

	x/a	y/b	z/c	U(eq)
C53	0.1728(5)	0.4757(7)	0.5221(7)	0.054(3)
C54	0.1164(5)	0.4526(7)	0.5294(6)	0.051(3)
C55	0.0591(5)	0.4992(8)	0.5094(7)	0.058(3)
C56	0.0	0.4621(11)	0.5	0.056(4)
C57	0.0671(13)	0.2616(5)	0.5708(14)	0.046(3)
C58	0.0342(11)	0.2453(8)	0.6079(12)	0.054(4)
C59	0.0344(10)	0.1721(10)	0.6313(10)	0.051(4)
C60	0.0676(11)	0.1152(6)	0.6175(11)	0.070(5)
C61	0.1005(9)	0.1314(7)	0.5804(11)	0.050(4)
C62	0.1003(10)	0.2047(9)	0.5570(12)	0.050(4)
C57A	0.0680(16)	0.2575(6)	0.5608(17)	0.046(3)
C58A	0.0410(14)	0.2312(10)	0.6014(15)	0.054(4)
C59A	0.0498(12)	0.1562(11)	0.6235(12)	0.051(4)
C60A	0.0857(13)	0.1075(6)	0.6050(13)	0.070(5)
C61A	0.1126(11)	0.1338(9)	0.5645(13)	0.050(4)
C62A	0.1038(13)	0.2088(11)	0.5423(15)	0.050(4)
C63	0.2016(5)	0.3122(6)	0.6840(6)	0.039(2)
C64	0.1795(5)	0.3355(6)	0.7290(6)	0.046(2)
C65	0.1954(5)	0.3000(7)	0.7905(6)	0.051(3)
C66	0.2365(5)	0.2330(7)	0.8089(6)	0.055(3)
C67	0.2581(5)	0.2110(6)	0.7681(6)	0.044(2)
C68	0.2438(4)	0.2450(6)	0.7055(6)	0.046(2)
C69	0.3166(5)	0.3750(7)	0.6854(7)	0.050(3)
C70	0.3378(5)	0.3990(6)	0.7539(7)	0.053(3)
C71	0.4018(6)	0.3787(8)	0.8169(8)	0.069(4)
C72	0.4461(5)	0.3345(8)	0.8003(8)	0.066(3)
C73	0.4261(5)	0.3115(7)	0.7324(7)	0.057(3)
C74	0.3601(5)	0.3297(7)	0.6726(7)	0.053(3)
C75	0.3497(6)	0.4217(10)	0.4871(7)	0.057(4)
C76	0.2949(5)	0.4134(9)	0.4964(7)	0.051(4)
C77	0.2939(5)	0.4519(9)	0.5522(8)	0.047(4)
C78	0.3476(7)	0.4987(9)	0.5988(8)	0.050(4)
C79	0.4025(6)	0.5069(9)	0.5895(8)	0.056(4)
C80	0.4035(6)	0.4684(10)	0.5337(8)	0.062(4)
C75A	0.3602(7)	0.4728(11)	0.5096(8)	0.057(4)

	x/a	y/b	z/c	U(eq)
C76A	0.3043(6)	0.4546(9)	0.5146(7)	0.051(4)
C77A	0.3021(5)	0.4768(10)	0.5754(8)	0.047(4)
C78A	0.3557(6)	0.5173(10)	0.6312(7)	0.050(4)
C79A	0.4115(5)	0.5355(10)	0.6261(8)	0.056(4)
C80A	0.4138(6)	0.5133(11)	0.5653(9)	0.062(4)
C81	0.1619(5)	0.5274(6)	0.4608(6)	0.046(2)
C82	0.1152(5)	0.5114(7)	0.3903(6)	0.051(3)
C83	0.1057(6)	0.5555(8)	0.3333(7)	0.060(3)
C84	0.1466(6)	0.6223(8)	0.3502(7)	0.062(3)
C85	0.1904(6)	0.6387(8)	0.4190(7)	0.066(3)
C86	0.1998(5)	0.5957(7)	0.4746(7)	0.055(3)
C87	0.0607(7)	0.5836(5)	0.4941(7)	0.046(4)
C88	0.1049(6)	0.6323(7)	0.5495(6)	0.066(5)
C89	0.1076(8)	0.7080(7)	0.5342(8)	0.089(6)
C90	0.0660(9)	0.7350(6)	0.4635(10)	0.103(8)
C91	0.0218(8)	0.6864(8)	0.4080(7)	0.069(5)
C92	0.0192(7)	0.6107(7)	0.4233(6)	0.072(5)
C87A	0.0371(10)	0.5653(8)	0.4560(9)	0.046(4)
C88A	0.0768(9)	0.6281(12)	0.4917(9)	0.066(5)
C89A	0.0596(12)	0.6981(9)	0.4576(13)	0.089(6)
C90A	0.0027(13)	0.7054(8)	0.3877(14)	0.103(8)
C91A	0.9630(10)	0.6426(12)	0.3520(9)	0.069(5)
C92A	0.9802(9)	0.5726(9)	0.3862(9)	0.072(5)
C93	0.6420(8)	0.9892(9)	0.8691(8)	0.084(4)
Cl1	0.6697(3)	0.9262(3)	0.9353(3)	0.1275(19)
Cl2	0.7016(3)	0.0090(3)	0.8430(4)	0.135(2)
Cl3	0.5678(2)	0.9631(4)	0.7924(3)	0.146(2)

X-ray data for compound 88

Table 4.19. Sample and crystal data for compound **88**

Identification code	RAP148	
Chemical formula	$C_{110}H_{74}Cl_{12}O_2$	
Formula weight	1853.09 g/mol	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal size	0.029 x 0.095 x 0.118 mm	
Crystal habit	colorless plate	
Crystal system	triclinic	
Space group	*P* -1	
Unit cell dimensions	a = 12.3323(4) Å	α = 112.286(2)°
	b = 13.8630(6) Å	β = 91.465(2)°
	c = 16.4991(6) Å	γ = 116.268(2)°
Volume	2276.03(16) Å^3	
Z	1	
Density (calculated)	1.352 g/cm^3	
Absorption coefficient	3.753 mm^{-1}	
***F*(000)**	954	

Table 4.20. Data collection and structure refinement for compound **88**

Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Radiation source	INCOATEC IμS micro--focus source, Cu-Kα
Theta range for data collection	2.98 to 64.89°
Index ranges	-14<=h<=14, -15<=k<=16, -19<=l<=19
Reflections collected	14903
Independent reflections	7447 [*R*(int) = 0.0537]
Coverage of independent reflections	96.3%
Absorption correction	multi-scan
Max. and min. transmission	0.8990 and 0.6660
Refinement method	Full-matrix least-squares on F^2
Refinement program	*SHELXL-2018/1* (Sheldrick)
Function minimized	Σ w(F_o^2 - F_c^2)^2
Data / restraints / parameters	7447 / 6 / 559

Goodness-of-fit on F^2	1.042	
Final R indices	5507 data; I>2σ(I)	$R1 = 0.0756$, w$R2 = 0.1892$
	all data	$R1 = 0.1002$, w$R2 = 0.2088$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1103P)^2+2.9079P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.931 and -0.730 eÅ^{-3}	
R.M.S. deviation from mean	0.090 eÅ^{-3}	

Table 4.21. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound **88**

	x/a	y/b	z/c	U(eq)
O1	0.6256(2)	0.5910(2)	0.71308(16)	0.0202(5)
C1	0.5406(3)	0.6222(3)	0.5175(2)	0.0186(7)
C2	0.5428(3)	0.5882(3)	0.5870(2)	0.0177(7)
C3	0.5811(3)	0.6607(3)	0.6912(2)	0.0191(7)
C4	0.4587(3)	0.6210(3)	0.7250(2)	0.0177(7)
C5	0.3885(3)	0.6753(3)	0.7631(2)	0.0191(7)
C6	0.2854(3)	0.6117(3)	0.7923(2)	0.0195(8)
C7	0.2499(3)	0.4947(3)	0.7792(2)	0.0226(8)
C8	0.3155(3)	0.4369(3)	0.7347(2)	0.0188(7)
C9	0.4197(3)	0.5016(3)	0.7095(2)	0.0186(7)
C10	0.5191(3)	0.4730(3)	0.6668(2)	0.0189(7)
C11	0.5032(3)	0.4691(3)	0.5707(2)	0.0188(7)
C12	0.5837(4)	0.7496(3)	0.5369(2)	0.0209(8)
C13	0.7094(4)	0.8295(3)	0.5526(3)	0.0275(9)
C14	0.7489(4)	0.9476(4)	0.5694(3)	0.0354(10)
C15	0.6619(5)	0.9855(4)	0.5710(3)	0.0424(12)
C16	0.5379(5)	0.9081(4)	0.5571(3)	0.0366(10)
C17	0.4977(4)	0.7893(4)	0.5390(3)	0.0284(9)
C18	0.6876(4)	0.7883(3)	0.7367(2)	0.0227(8)
C19	0.8034(4)	0.8103(4)	0.7724(3)	0.0287(9)
C20	0.9045(4)	0.9250(4)	0.8143(3)	0.0388(11)
C21	0.8907(4)	0.0218(4)	0.8212(3)	0.0354(10)
C22	0.7763(4)	0.0013(3)	0.7867(3)	0.0282(9)
C23	0.6753(4)	0.8869(3)	0.7440(2)	0.0234(8)

	x/a	**y/b**	**z/c**	**U(eq)**
C24	0.4069(3)	0.7937(3)	0.7722(2)	0.0204(8)
C25	0.3367(4)	0.7944(4)	0.7058(3)	0.0273(9)
C26	0.3406(4)	0.9013(4)	0.7161(3)	0.0375(10)
C27	0.4124(4)	0.0046(4)	0.7929(3)	0.0405(11)
C28	0.4807(4)	0.0038(4)	0.8592(3)	0.0396(11)
C29	0.4781(4)	0.8988(4)	0.8499(3)	0.0301(9)
C30	0.2121(4)	0.6693(3)	0.8380(3)	0.0240(8)
C31	0.2607(4)	0.7562(4)	0.9269(3)	0.0332(10)
C32	0.1972(5)	0.8143(4)	0.9697(3)	0.0425(12)
C33	0.0834(5)	0.7850(5)	0.9252(4)	0.0446(12)
C34	0.0317(5)	0.6955(5)	0.8379(4)	0.0482(13)
C35	0.0978(4)	0.6392(4)	0.7947(3)	0.0369(10)
C36	0.1417(3)	0.4329(3)	0.8133(3)	0.0224(8)
C37	0.1538(4)	0.4600(4)	0.9044(3)	0.0288(9)
C38	0.0534(4)	0.4054(4)	0.9368(3)	0.0360(10)
C39	0.9384(4)	0.3218(4)	0.8777(3)	0.0383(11)
C40	0.9257(4)	0.2928(4)	0.7876(3)	0.0389(11)
C41	0.0254(4)	0.3472(4)	0.7548(3)	0.0312(9)
C42	0.2655(3)	0.3106(3)	0.7215(3)	0.0221(8)
C43	0.2945(4)	0.2868(4)	0.7912(3)	0.0295(9)
C44	0.2395(5)	0.1703(4)	0.7813(3)	0.0398(11)
C45	0.1581(5)	0.0760(4)	0.7019(4)	0.0432(12)
C46	0.1287(4)	0.0989(4)	0.6323(3)	0.0374(10)
C47	0.1816(4)	0.2153(4)	0.6422(3)	0.0296(9)
C48	0.5507(3)	0.3900(3)	0.6886(2)	0.0219(8)
C49	0.4719(4)	0.2662(3)	0.6533(3)	0.0241(8)
C50	0.5033(4)	0.1966(4)	0.6802(3)	0.0287(9)
C51	0.6122(4)	0.2473(4)	0.7421(3)	0.0404(11)
C52	0.6904(5)	0.3693(4)	0.7777(4)	0.0485(13)
C53	0.6598(4)	0.4397(4)	0.7507(3)	0.0361(10)
Cl1	0.52358(14)	0.65980(19)	0.97892(13)	0.0829(6)
Cl2	0.77111(14)	0.69381(14)	0.97921(9)	0.0603(4)
Cl3	0.72060(17)	0.88381(15)	0.99768(10)	0.0696(5)
C54	0.6599(5)	0.7270(5)	0.9474(3)	0.0510(13)
Cl4	0.19132(16)	0.44252(15)	0.54615(10)	0.0726(5)

	x/a	**y/b**	**z/c**	**U(eq)**
Cl5	0.14956(19)	0.53133(18)	0.42505(15)	0.1031(8)
Cl6	0.00013(15)	0.28350(14)	0.38219(11)	0.0741(5)
C55	0.1473(5)	0.4096(6)	0.4340(4)	0.0590(15)

X-ray data for compound 60

Table 4.22. Sample and crystal data for compound **60**

Identification code	RAP144	
Chemical formula	$C_{28}H_{31}PS_3$	
Formula weight	494.68 g/mol	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal size	0.058 x 0.145 x 0.239 mm	
Crystal system	monoclinic	
Space group	*P* 1 21 1	
Unit cell dimensions	a = 14.8564(5) Å	α = 90°
	b = 11.8098(4) Å	β = 110.5300(10)°
	c = 15.1095(5) Å	γ = 90°
Volume	2482.61(15) Å^3	
Z	4	
Density (calculated)	1.323 g/cm^3	
Absorption coefficient	3.436 mm^{-1}	
***F*(000)**	1048	

Table 4.23. Data collection and structure refinement for compound **60**

Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Radiation source	INCOATEC IµS microfocus source, Cu-Kα
Theta range for data collection	3.12 to 74.46°
Index ranges	-17<=h<=18, -14<=k<=13, -18<=l<=17
Reflections collected	19426
Independent reflections	8198 [*R*(int) = 0.0345]
Absorption correction	multi-scan
Max. and min. transmission	0.8260 and 0.4940
Refinement method	Full-matrix least-squares on F^2
Refinement program	*SHELXL* (Sheldrick)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	8198 / 1 / 578

Goodness-of-fit on F^2	1.051	
Final R indices	7560 data; I>2σ(I)	$R1 = 0.0693$, $wR2 = 0.1757$
	all data	$R1 = 0.0756$, $wR2 = 0.1829$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0829P)^2+8.5178P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.47(4)	
Largest diff. peak and hole	2.017 and -1.230 eÅ^{-3}	
R.M.S. deviation from mean	0.106 eÅ^{-3}	

Table 4.24. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound **60**

	x/a	**y/b**	**z/c**	**U(eq)**
S1	0.70762(13)	0.3719(2)	0.41468(12)	0.0328(5)
S2	0.45680(17)	0.66422(18)	0.24597(14)	0.0354(5)
S3	0.4811(2)	0.3600(3)	0.01510(19)	0.0561(8)
P1	0.51355(12)	0.40497(15)	0.24075(12)	0.0177(4)
C1	0.5608(5)	0.2632(7)	0.2752(6)	0.0231(16)
C2	0.5198(6)	0.1662(7)	0.2254(7)	0.0317(18)
C3	0.5669(7)	0.0653(8)	0.2380(7)	0.041(2)
C4	0.6581(8)	0.0537(8)	0.3055(9)	0.047(3)
C5	0.6988(6)	0.1446(8)	0.3573(7)	0.034(2)
C6	0.6535(5)	0.2542(7)	0.3459(6)	0.0258(17)
C7	0.4803(5)	0.4565(7)	0.3399(5)	0.0202(15)
C8	0.4804(5)	0.3915(7)	0.4160(5)	0.0229(16)
C9	0.4569(5)	0.4361(8)	0.4900(5)	0.0291(19)
C10	0.4320(5)	0.5492(8)	0.4876(5)	0.0295(19)
C11	0.4307(5)	0.6178(8)	0.4140(5)	0.0289(17)
C12	0.4578(5)	0.5722(7)	0.3409(5)	0.0220(15)
C13	0.3842(6)	0.3734(8)	0.0557(5)	0.0290(18)
C14	0.2907(7)	0.3668(10)	0.9875(6)	0.046(3)
C15	0.2104(6)	0.3623(10)	0.0127(6)	0.040(2)
C16	0.2219(5)	0.3667(9)	0.1056(6)	0.034(2)
C17	0.3114(5)	0.3766(7)	0.1743(5)	0.0201(15)
C18	0.3954(5)	0.3806(7)	0.1522(5)	0.0207(15)
C19	0.8232(6)	0.3822(10)	0.3974(8)	0.048(3)

	x/a	**y/b**	**z/c**	**U(eq)**
C20	0.8292(6)	0.4781(11)	0.3338(7)	0.054(3)
C21	0.7584(7)	0.4819(9)	0.2345(7)	0.046(2)
C22	0.5695(8)	0.7416(8)	0.3012(7)	0.045(3)
C23	0.6651(8)	0.6699(13)	0.3002(8)	0.071(4)
C24	0.6702(7)	0.6752(9)	0.2049(7)	0.049(2)
C25	0.5372(6)	0.4999(9)	0.0330(7)	0.042(2)
C26	0.6386(6)	0.4858(9)	0.0308(7)	0.043(2)
C27	0.7122(7)	0.5772(10)	0.0753(7)	0.049(2)
C28	0.7408(7)	0.5941(8)	0.1898(9)	0.053(3)
S4	0.20236(13)	0.1220(2)	0.41766(12)	0.0297(5)
S5	0.00484(16)	0.1821(2)	0.04086(16)	0.0401(6)
S6	0.94407(17)	0.8542(2)	0.24038(14)	0.0368(5)
P2	0.01135(12)	0.10894(16)	0.24381(12)	0.0174(4)
C29	0.0649(5)	0.2478(7)	0.2857(5)	0.0209(15)
C30	0.0263(6)	0.3498(8)	0.2395(6)	0.0341(19)
C31	0.0819(7)	0.4491(7)	0.2628(7)	0.038(2)
C32	0.1730(7)	0.4450(8)	0.3289(7)	0.040(2)
C33	0.2110(6)	0.3473(8)	0.3773(6)	0.0302(18)
C34	0.1574(5)	0.2499(7)	0.3543(5)	0.0257(17)
C35	0.8949(5)	0.1424(7)	0.1518(5)	0.0196(15)
C36	0.8079(6)	0.1431(8)	0.1692(6)	0.0301(18)
C37	0.7215(6)	0.1571(8)	0.0984(6)	0.035(2)
C38	0.7208(7)	0.1722(10)	0.0027(6)	0.049(3)
C39	0.8070(7)	0.1702(10)	0.9861(5)	0.043(2)
C40	0.8927(6)	0.1573(8)	0.0589(5)	0.0305(18)
C41	0.9736(5)	0.0547(7)	0.3390(5)	0.0211(15)
C42	0.9756(5)	0.1219(8)	0.4178(5)	0.0248(16)
C43	0.9544(6)	0.0718(9)	0.4915(5)	0.033(2)
C44	0.9298(6)	0.9580(9)	0.4892(6)	0.034(2)
C45	0.9257(6)	0.8949(8)	0.4109(5)	0.0305(18)
C46	0.9482(5)	0.9400(8)	0.3371(5)	0.0259(17)
C47	0.3238(6)	0.1108(9)	0.4153(6)	0.038(2)
C48	0.3357(6)	0.0962(8)	0.3235(6)	0.0355(19)
C49	0.3317(6)	0.9766(8)	0.2796(6)	0.0389(19)
C50	0.0325(6)	0.0488(9)	0.0000(6)	0.039(2)

	x/a	**y/b**	**z/c**	**U(eq)**
C51	0.0823(6)	0.9629(8)	0.0738(6)	0.039(2)
C52	0.1798(6)	0.0036(8)	0.1407(6)	0.0384(19)
C53	0.0441(10)	0.7595(9)	0.2915(8)	0.057(3)
C54	0.1193(7)	0.7739(7)	0.2451(6)	0.0378(19)
C55	0.1769(6)	0.8766(9)	0.2828(6)	0.047(3)
C56	0.2362(7)	0.9216(9)	0.2169(7)	0.045(2)

X-ray data for compound 77

Table 4.25. Sample and crystal data for compound **77**

Identification code	RAP167	
Chemical formula	$C_{302}H_{206}$	
Formula weight	3834.66 g/mol	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Crystal size	0.080 x 0.086 x 0.254 mm	
Crystal habit	pale yellow column	
Crystal system	triclinic	
Space group	*P* -1	
Unit cell dimensions	a = 13.0169(7) Å	α = 107.131(3)°
	b = 18.2147(10) Å	β = 95.433(3)°
	c = 26.7284(15) Å	γ = 90.816(3)°
Volume	6023.0(6) $Å^3$	
Z	1	
Density (calculated)	1.057 g/cm^3	
Absorption coefficient	0.453 mm^{-1}	
***F*(000)**	2018	

Table 4.26. Data collection and structure refinement for compound **77**

Diffractometer	'Bruker D8 VENTURE PHOTON 100 CMOS' Bruker D8 VENTURE PHOTON 100 CMOS
Radiation source	'INCOATEC IμS microfocus source' (Cu, λ = 1.54178 Å)
Theta range for data collection	2.54 to 66.77°
Index ranges	-15<=h<=15, -21<=k<=20, -31<=l<=31
Reflections collected	43881
Independent reflections	20672 [*R*(int) = 0.0459]
Coverage of independent reflections	96.7%
Absorption correction	multi-scan
Max. and min. transmission	0.9650 and 0.8940
Structure solution technique	direct methods

Structure solution program	*SHELXT* (Sheldrick)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	*SHELXL 2018/1* (Sheldrick)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	20672 / 0 / 1360	
Goodness-of-fit on F^2	1.033	
Δ/σ_{max}	0.001	
Final R indices	14920 data; I>2σ(I)	$R1$ = 0.0554, w$R2$ = 0.1274
	all data	$R1$ = 0.0788, w$R2$ = 0.1409
Weighting scheme	w=1/[$\sigma^2(F_o^2)+(0.0591P)^2+1.6586P$] where P=($F_o^2+2F_c^2$)/3	
Largest diff. peak and hole	0.332 and -0.237 eÅ^{-3}	
R.M.S. deviation from mean	0.040 eÅ^{-3}	

Table 4.27. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for compound **77**

	x/a	**y/b**	**z/c**	**U(eq)**
C1	0.97844(15)	0.85136(11)	0.69809(8)	0.0295(4)
C2	0.06077(14)	0.82247(11)	0.66678(8)	0.0294(4)
C3	0.05815(15)	0.74470(11)	0.63879(8)	0.0296(4)
C4	0.97055(15)	0.69687(11)	0.63926(7)	0.0296(4)
C5	0.88082(15)	0.72923(11)	0.65904(8)	0.0300(4)
C6	0.88223(15)	0.80902(11)	0.68660(8)	0.0299(4)
C7	0.79091(15)	0.85268(12)	0.70096(8)	0.0314(4)
C8	0.79828(15)	0.92865(12)	0.72966(8)	0.0321(4)
C9	0.89863(15)	0.96627(11)	0.75390(8)	0.0298(4)
C10	0.91119(15)	0.04126(11)	0.79069(8)	0.0308(4)
C11	0.01038(16)	0.07081(11)	0.81278(8)	0.0318(4)
C12	0.09629(16)	0.02350(12)	0.80561(8)	0.0327(4)
C13	0.08453(15)	0.94847(11)	0.77192(8)	0.0309(4)
C14	0.98806(15)	0.92357(11)	0.74074(8)	0.0293(4)
C15	0.13856(15)	0.87837(11)	0.65884(8)	0.0304(4)
C16	0.24392(16)	0.86471(12)	0.65610(8)	0.0362(5)

	x/a	y/b	z/c	U(eq)
C17	0.31062(17)	0.91779(13)	0.64637(9)	0.0435(6)
C18	0.27455(19)	0.98521(14)	0.63939(10)	0.0501(6)
C19	0.17084(19)	0.99981(14)	0.64181(10)	0.0471(6)
C20	0.10377(17)	0.94643(12)	0.65098(9)	0.0381(5)
C21	0.14217(15)	0.70738(11)	0.60640(8)	0.0326(5)
C22	0.20869(16)	0.65951(12)	0.62425(10)	0.0410(5)
C23	0.28300(17)	0.62081(13)	0.59324(11)	0.0488(6)
C24	0.29171(18)	0.63086(14)	0.54452(11)	0.0508(7)
C25	0.22756(18)	0.67950(15)	0.52709(10)	0.0493(6)
C26	0.15268(16)	0.71788(13)	0.55764(8)	0.0393(5)
C27	0.97190(15)	0.61163(11)	0.61632(8)	0.0323(4)
C28	0.00790(18)	0.56728(13)	0.64752(10)	0.0448(6)
C29	0.0058(2)	0.48732(14)	0.62722(13)	0.0573(7)
C30	0.9658(2)	0.45190(14)	0.57638(12)	0.0554(7)
C31	0.9293(2)	0.49499(14)	0.54530(11)	0.0531(7)
C32	0.93322(18)	0.57463(12)	0.56462(9)	0.0416(5)
C33	0.78847(15)	0.67498(11)	0.65250(8)	0.0321(4)
C34	0.72469(16)	0.65096(12)	0.60564(8)	0.0358(5)
C35	0.64356(18)	0.59737(13)	0.59878(9)	0.0429(5)
C36	0.62785(19)	0.56566(15)	0.63823(11)	0.0517(6)
C37	0.69107(19)	0.58802(17)	0.68459(11)	0.0556(7)
C38	0.77176(17)	0.64264(15)	0.69191(10)	0.0471(6)
C39	0.68569(16)	0.81906(12)	0.67619(9)	0.0369(5)
C40	0.65293(19)	0.82190(13)	0.62552(10)	0.0477(6)
C41	0.5545(2)	0.79623(15)	0.60194(12)	0.0620(8)
C42	0.4887(2)	0.76644(16)	0.62859(13)	0.0687(9)
C43	0.5175(2)	0.76198(16)	0.67814(13)	0.0667(9)
C44	0.61753(18)	0.78919(14)	0.70276(11)	0.0518(7)
C45	0.69910(15)	0.96994(12)	0.73401(9)	0.0358(5)
C46	0.63926(17)	0.97357(13)	0.77513(10)	0.0458(6)
C47	0.5447(2)	0.00739(14)	0.77691(12)	0.0573(7)
C48	0.50758(19)	0.03541(15)	0.73698(13)	0.0623(8)
C49	0.5643(2)	0.03201(14)	0.69546(12)	0.0565(7)
C50	0.66107(17)	0.99924(12)	0.69402(10)	0.0435(6)
C51	0.82439(16)	0.09183(11)	0.81097(8)	0.0327(5)

	x/a	y/b	z/c	U(eq)
C52	0.79366(18)	0.09598(14)	0.86016(9)	0.0448(6)
C53	0.7185(2)	0.14581(16)	0.88112(10)	0.0545(7)
C54	0.67450(19)	0.19281(14)	0.85360(11)	0.0535(7)
C55	0.70595(17)	0.18996(13)	0.80532(10)	0.0454(6)
C56	0.78115(16)	0.14007(12)	0.78414(9)	0.0370(5)
C57	0.02519(16)	0.15195(12)	0.84841(8)	0.0361(5)
C58	0.0333(2)	0.16780(15)	0.90234(10)	0.0566(7)
C59	0.0438(3)	0.24327(17)	0.93507(12)	0.0725(9)
C60	0.0486(2)	0.30295(15)	0.91360(13)	0.0653(8)
C61	0.04303(18)	0.28768(14)	0.86021(12)	0.0547(7)
C62	0.03060(17)	0.21251(13)	0.82730(10)	0.0426(5)
C63	0.19749(16)	0.05636(12)	0.83660(8)	0.0379(5)
C64	0.2328(2)	0.03767(18)	0.88152(10)	0.0600(7)
C65	0.3269(2)	0.0685(2)	0.90913(12)	0.0811(10)
C66	0.3859(2)	0.1180(2)	0.89207(12)	0.0729(10)
C67	0.35089(19)	0.13734(15)	0.84773(12)	0.0595(8)
C68	0.25692(17)	0.10678(13)	0.81971(10)	0.0432(5)
C69	0.16597(16)	0.89232(12)	0.77500(8)	0.0359(5)
C70	0.13706(19)	0.82331(13)	0.78356(10)	0.0464(6)
C71	0.2106(2)	0.77284(15)	0.79153(12)	0.0617(7)
C72	0.3146(2)	0.79000(16)	0.79041(12)	0.0658(8)
C73	0.34434(19)	0.85741(15)	0.78150(11)	0.0572(7)
C74	0.27103(16)	0.90765(13)	0.77359(9)	0.0424(5)
C75	0.12674(15)	0.36925(11)	0.71104(7)	0.0279(4)
C76	0.20577(14)	0.37385(11)	0.67827(7)	0.0285(4)
C77	0.19439(15)	0.32855(11)	0.62575(8)	0.0305(4)
C78	0.10937(15)	0.27492(11)	0.60684(7)	0.0296(4)
C79	0.02745(15)	0.27710(12)	0.63719(7)	0.0299(4)
C80	0.03031(15)	0.33258(11)	0.68779(7)	0.0280(4)
C81	0.94024(15)	0.35825(12)	0.71606(7)	0.0289(4)
C82	0.95112(14)	0.41384(11)	0.76420(7)	0.0285(4)
C83	0.05366(15)	0.43877(11)	0.79234(7)	0.0284(4)
C84	0.07249(15)	0.49084(11)	0.84400(8)	0.0295(4)
C85	0.16697(15)	0.49087(11)	0.87359(8)	0.0299(4)
C86	0.24240(15)	0.43850(11)	0.85260(7)	0.0287(4)

	x/a	**y/b**	**z/c**	**U(eq)**
C87	0.23108(14)	0.39742(11)	0.79919(7)	0.0278(4)
C88	0.13907(14)	0.40380(11)	0.76769(7)	0.0278(4)
C89	0.29055(15)	0.43465(12)	0.69811(7)	0.0306(4)
C90	0.26525(17)	0.51030(12)	0.72089(9)	0.0385(5)
C91	0.3411(2)	0.56843(14)	0.73667(11)	0.0551(7)
C92	0.44386(19)	0.55207(15)	0.73103(11)	0.0554(7)
C93	0.47013(17)	0.47753(14)	0.70896(9)	0.0446(6)
C94	0.39429(16)	0.41948(13)	0.69221(8)	0.0352(5)
C95	0.27324(16)	0.33590(12)	0.58980(7)	0.0332(5)
C96	0.34205(17)	0.27823(13)	0.57309(8)	0.0394(5)
C97	0.41641(18)	0.28593(16)	0.54085(9)	0.0474(6)
C98	0.4217(2)	0.35098(16)	0.52463(10)	0.0536(7)
C99	0.3528(2)	0.40829(15)	0.54049(9)	0.0534(7)
C100	0.27838(18)	0.40050(13)	0.57295(8)	0.0422(5)
C101	0.10889(15)	0.21695(12)	0.55398(8)	0.0324(4)
C102	0.10116(16)	0.23892(13)	0.50807(8)	0.0362(5)
C103	0.10388(18)	0.18495(14)	0.45955(8)	0.0448(6)
C104	0.1138(2)	0.10855(15)	0.45562(9)	0.0514(6)
C105	0.1212(2)	0.08532(14)	0.50059(10)	0.0526(6)
C106	0.11826(19)	0.13952(13)	0.54932(9)	0.0430(5)
C107	0.94458(16)	0.21417(12)	0.61976(8)	0.0344(5)
C108	0.87314(17)	0.20481(14)	0.57617(9)	0.0446(6)
C109	0.80036(19)	0.14344(16)	0.56157(10)	0.0570(7)
C110	0.7996(2)	0.09087(15)	0.58994(11)	0.0579(7)
C111	0.87174(19)	0.09899(14)	0.63228(10)	0.0507(6)
C112	0.94384(17)	0.16018(12)	0.64735(9)	0.0395(5)
C113	0.83371(15)	0.33418(12)	0.68916(8)	0.0323(5)
C114	0.78862(17)	0.37309(14)	0.65606(9)	0.0423(5)
C115	0.6884(2)	0.35194(17)	0.63175(10)	0.0577(7)
C116	0.63453(18)	0.29135(18)	0.64056(11)	0.0602(8)
C117	0.67880(18)	0.25335(16)	0.67359(10)	0.0507(7)
C118	0.77721(16)	0.27491(13)	0.69840(8)	0.0383(5)
C119	0.85447(15)	0.43861(12)	0.79003(7)	0.0323(5)
C120	0.81383(16)	0.39552(13)	0.81945(8)	0.0362(5)
C121	0.72135(17)	0.41496(15)	0.84132(8)	0.0439(6)

	x/a	y/b	z/c	U(eq)
C122	0.67107(17)	0.47805(16)	0.83498(9)	0.0503(7)
C123	0.71068(18)	0.52115(16)	0.80609(9)	0.0509(6)
C124	0.80164(17)	0.50089(14)	0.78309(8)	0.0408(5)
C125	0.99892(16)	0.55186(12)	0.86538(8)	0.0365(5)
C126	0.94421(17)	0.55246(14)	0.90759(9)	0.0442(6)
C127	0.8814(2)	0.61274(18)	0.92780(11)	0.0626(8)
C128	0.8756(2)	0.67335(19)	0.90711(14)	0.0787(10)
C129	0.9303(2)	0.67396(17)	0.86552(15)	0.0762(9)
C130	0.9915(2)	0.61289(14)	0.84429(11)	0.0519(6)
C131	0.18514(15)	0.54346(12)	0.92881(8)	0.0352(5)
C132	0.18859(17)	0.51405(15)	0.97131(8)	0.0422(5)
C133	0.19969(18)	0.56245(17)	0.02257(9)	0.0525(7)
C134	0.2069(2)	0.64053(17)	0.03191(10)	0.0614(8)
C135	0.2062(2)	0.67076(16)	0.99038(12)	0.0699(9)
C136	0.1959(2)	0.62216(14)	0.93884(10)	0.0545(7)
C137	0.33350(15)	0.42560(12)	0.88723(7)	0.0324(5)
C138	0.41340(16)	0.48131(13)	0.90741(8)	0.0385(5)
C139	0.50045(17)	0.46614(15)	0.93564(8)	0.0457(6)
C140	0.50840(18)	0.39603(17)	0.94526(9)	0.0522(7)
C141	0.42915(19)	0.34094(15)	0.92660(9)	0.0488(6)
C142	0.34154(17)	0.35538(13)	0.89753(8)	0.0393(5)
C143	0.30705(15)	0.33917(11)	0.77651(7)	0.0287(4)
C144	0.41358(15)	0.35663(12)	0.78363(8)	0.0329(5)
C145	0.48221(16)	0.30096(13)	0.76334(9)	0.0392(5)
C146	0.44652(18)	0.22743(14)	0.73605(10)	0.0474(6)
C147	0.34100(18)	0.20866(13)	0.72855(9)	0.0450(6)
C148	0.27244(16)	0.26449(12)	0.74912(8)	0.0343(5)
C149	0.4090(3)	0.0161(2)	0.52272(15)	0.0856(10)
C150	0.4746(3)	0.9632(2)	0.53564(15)	0.0865(10)
C151	0.5662(3)	0.9472(2)	0.51290(14)	0.0809(9)