UNUSUAL CROWDED ORGANIC ARCHITECTURES

AN ABSTRACT

SUBMITTED ON THE FIRST DAY OF OCTOBER 2015

TO THE DEPARTMENT OF CHEMISTRY

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OF THE SCHOOL OF SCIENCE AND ENGINEERING

OF TULANE UNIVERSITY

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

BY

JIE ZONG

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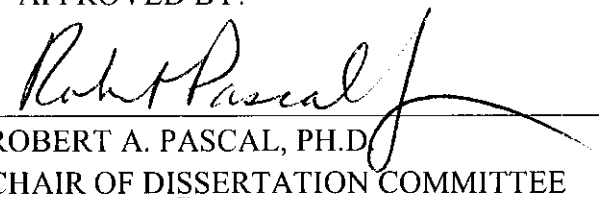

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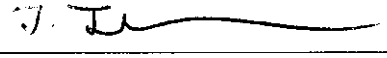

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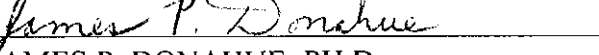

JAMES P. DONAHUE, PH.D.

Abstract

Molecules with unusual steric crowding are always interesting in chemistry. They give the opportunity to explore the limits of stable molecular structures and the synthesis of unnatural products. They also provide points of calibration for modern computational methods. This dissertation describes the design, synthesis and characterization of two types of crowded complex aromatic compounds.

The goal of the first project was to synthesize *in*-keto cyclophanes, that is, molecules with ketone oxygens pressed toward the centers of benzene rings. Several likely precursors were synthesized and fully characterized, but attempts to make the *in*-keto cyclophanes themselves were unsuccessful. The nonbonded interaction between the ketone oxygen and basal benzene ring may be so close in the target structures as to prevent the formation of an *in*-keto cyclophane.

The second project describes the design, synthesis and characterization of several macrobicyclic, bis(triarylelement)-containing cyclophanes with various bridgehead heteroatoms. Computational studies accurately predicted that when the bridgehead substituents are small (lone pairs or protons), an *in,in* bridgehead stereochemistry is strongly favored, but larger bridgehead substituents favor the formation of *in,out* stereoisomers. The NMR spectra of several of these compounds show unusual through-space spin-spin coupling between atoms along the central axis. Most importantly, one of these compounds, an *in,in*-bis(hydrosilane), possesses a

hydrogen-hydrogen nonbonded contact distance of approximately 1.56 Å, a new "world record" for such a contact in any crystallographically characterized compound.

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I owe great thanks to my dissertation committee members. Dr. Janarthanan Jayawickramarajah who taught my first organic course in Tulane, gave me many helpful suggestions, and helped me have a better understanding of physical organic chemistry. Dr. James P. Donahue, has always been very nice and helped me to have a better understanding of organometallic chemistry, which helped in some of my later projects. Dr. Bruce C. Gibb brought many interesting and useful apparatus to Tulane, and it always helped to stop by their lab and to see how they work.

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Lastly, I offer my regards and blessings to all of those who supported me in any way during the completion of my graduate study.

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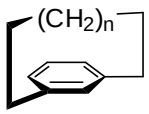
1.1 Introduction

A cyclophane is a molecule consisting of an aromatic unit (often a benzene ring) and a chain of atoms that forms a bridge between two non-adjacent positions of the aromatic ring. Some simple cyclophane types are [*n*]metacyclophanes (**1**), [*n*]paracyclophanes (**2**) and [*n,n'*]paracyclophanes (**3**). The prefixes meta and para correspond to the usual arene substitution patterns and *n* refers to the number of atoms making up the bridge. More complex derivatives with multiple aromatic units and bridges forming cagelike structures are also known.



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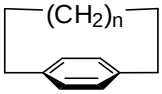

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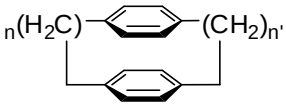

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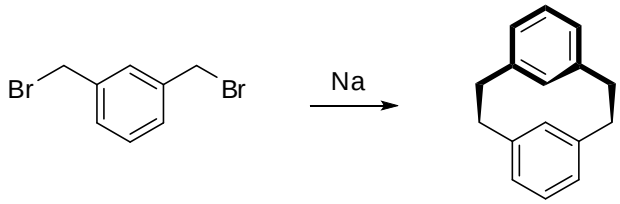
Cyclophanes are well-studied in organic chemistry because they may adopt unusual conformations due to strain. These bridged aromatic compounds often exhibit extraordinary physical and chemical properties that can be attributed to their unusual molecular architecture and the strain present in their cyclic frameworks.

At the end of the 19th century, [*2.2*]metacyclophane (**4**), was synthesized by Pellegrin using the Wurtz–Fittig reaction (Scheme 1).[1] This was the first cyclophane to

Scheme 1. Synthesis of cyclophane **4**



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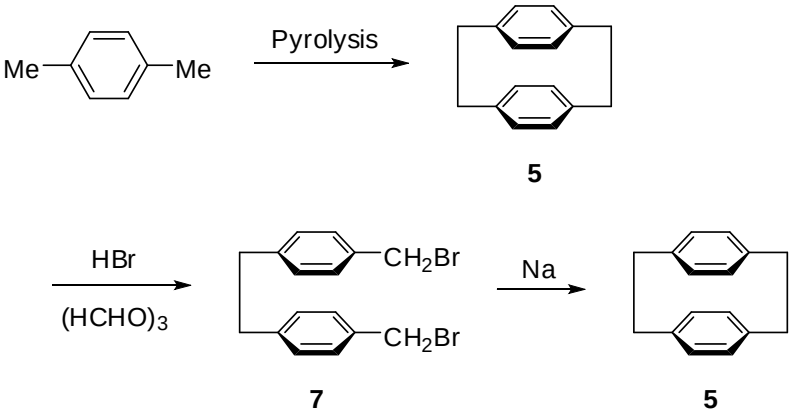
Scheme 2. Synthesis of cyclophane **5** in different approaches



5

6 **7** **5**

be reported.

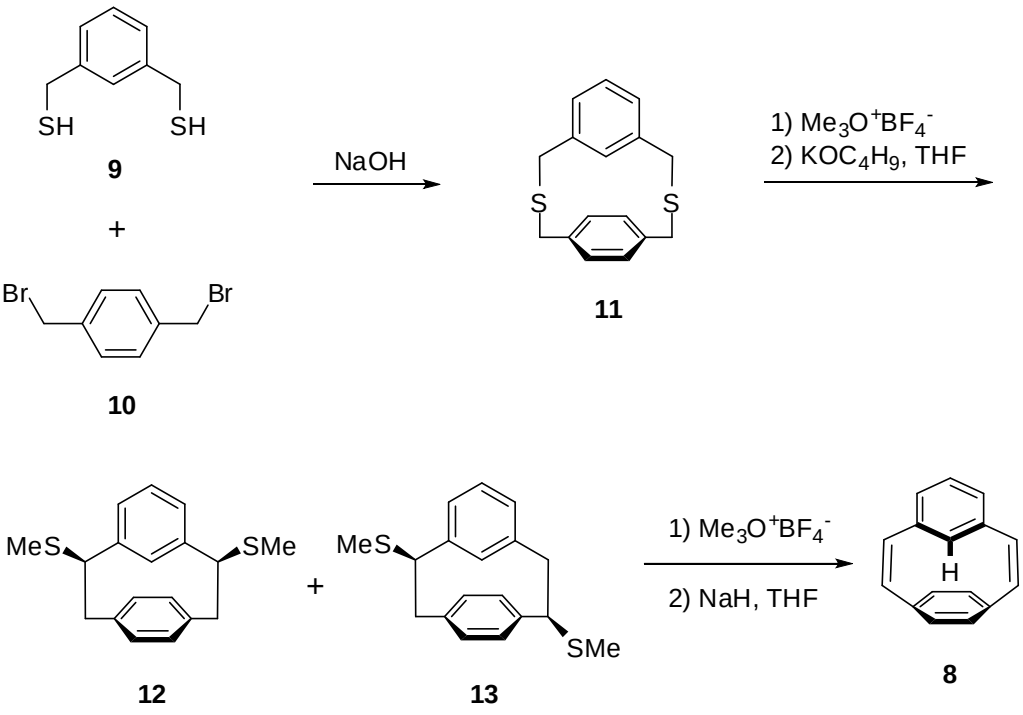
In 1949, Brown and Farthing made [*2.2*]paracyclophane (**5**) by low pressure pyrolysis of *p*-xylene.[2] Two years later, Cram and Steinberg synthesized **5** directly by intramolecular Wurtz reaction of dibromide **7**, and they prepared many derivatives of **5** (Scheme 2).[3]

This latter work laid the basis for entry of a new group of aromatic compounds onto the stage of chemistry, and it helped to evolve them from chemical curiosities to an attractive and intensively studied class of molecules in modern organic chemistry. Since then, a large number of cyclophanes with enormously varied functionalities has been synthesized for both theoretical interest and practical applications.[4][5][6][7][8][9]

One favorite theme in cyclophane chemistry is the enforcement of close contacts between unreactive functional groups and aromatic rings. Specifically, our research group has asked, “How closely can functional group X approach the center of a benzene ring?”

For this discussion, the distance from X to the center of the ring is called the X---Ar contact, and the nonbonded distance from X to a specific carbon atom is designated an X---C contact. Triple hyphens indicate nonbonded contacts between groups (e.g. H---Ar, O---C), and short hyphens are used for covalent bonds (e.g. C-H, C-O).[10]

Scheme 3. Synthesis of metaparacyclophane **8**



The smallest X is hydrogen. What is the “world record” for close hydrogen-arene nonbonded contacts? The X-ray structures of cyclophanes were exhaustively reviewed in

1983, and at that time the shortest H---Ar distance was 2.11 Å in Boekelheide's metaparacyclophane **8**.[11][12] It was made by cyclization of 1,3-bis(mercaptomethyl)-benzene (**9**) and 1,4-bis(bromomethyl)benzene (**10**) to give thioether **11**, followed by Stevens rearrangement and Hofmann elimination (Scheme 3).

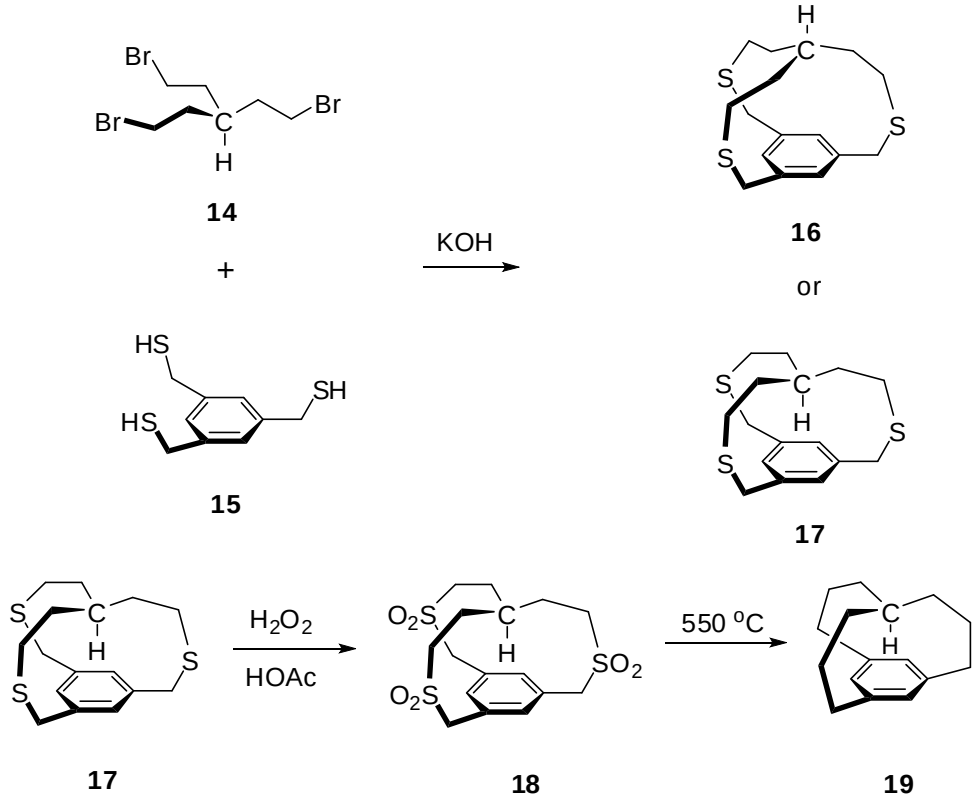
However, as the upper benzene ring is not perpendicular to the lower one, the hydrogen atom is neither directly above nor pointed directly at the center of the basal benzene ring. Could some molecule have the C-H bond point directly at the center of the benzene ring? How could it be made?

The answer could not be more suprising: such a molecule had already been synthesized by Ricci et al. by condensation of tribromide **14** and trithiol **15** in 1976 (Scheme 4),[13] but its unique geometry was not recognized at the time. When Pascal et al. reproduced synthesis of compound **16**, they could not find any peak in its ^{1}H NMR spectrum that corresponded to the apical proton in the region from 0 to 8 ppm. They immediately suspected that it must have been shifted far upfield, but if so, then the cyclophane had to be the *in* isomer **17**, rather than the *out* isomer **16**. They proved that the product was indeed the *in* isomer **17**, as shown by a septet at δ -1.68 in its ^{1}H NMR spectrum, a heavily shielded proton resonance. They then made the trisulfone derivative **18** by boiling **17** in hydrogen peroxide and acetic acid, and X-ray analysis showed an H---Ar distance of 2.13 Å. The distance was close, but brief pyrolysis[14] of **18** at 500-600 ℃ gave the even smaller *in*-cyclophane **19** in 11% yield.[15]

In compound **19**, the chemical shift of the *in*-H is δ -4.03, which is exceptionally

shielded due to the diamagnetic anisotropy of the benzene ring. Additionally, the ^{13}C-^{1}H coupling (J_{CH}) of 120 Hz showed that the apical carbon is flattened, and the IR stretch at 3325 cm^{-1} (frequency enhancement of 400 cm^{-1} from a normal C-H stretch) also indicated that the H---Ar contact must be extremely tight. However, no X-ray structure has been obtained for this waxy solid.

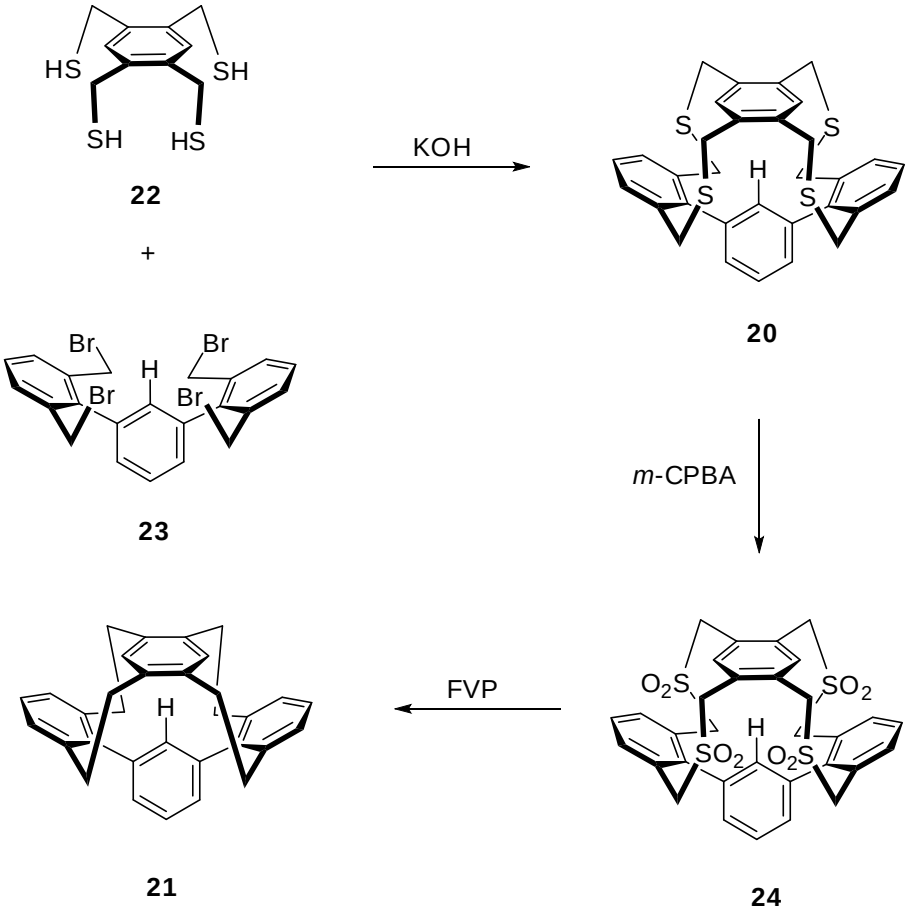
Scheme 4. Synthesis of cyclophanes **17** and **19**



In an entirely different approach, Hart et al. synthesized the equally tight *in*-cyclophanes **20** and **21** (Scheme 5), which are called "cappedophanes".[16][17] Cyclophane **20** was made by condensation of tetrabromide **23** with tetrathiol **22**.

Hydrocarbon **21** was made by oxidation to tetrasulfone **24** followed by flash vacuum pyrolysis (FVP). In the X-ray structure of compound **20**, it was seen that the H---Ar distance is 2.00 Å, which was the shortest observed up to that time, but no crystal structure of the more crowded **21** was achieved.

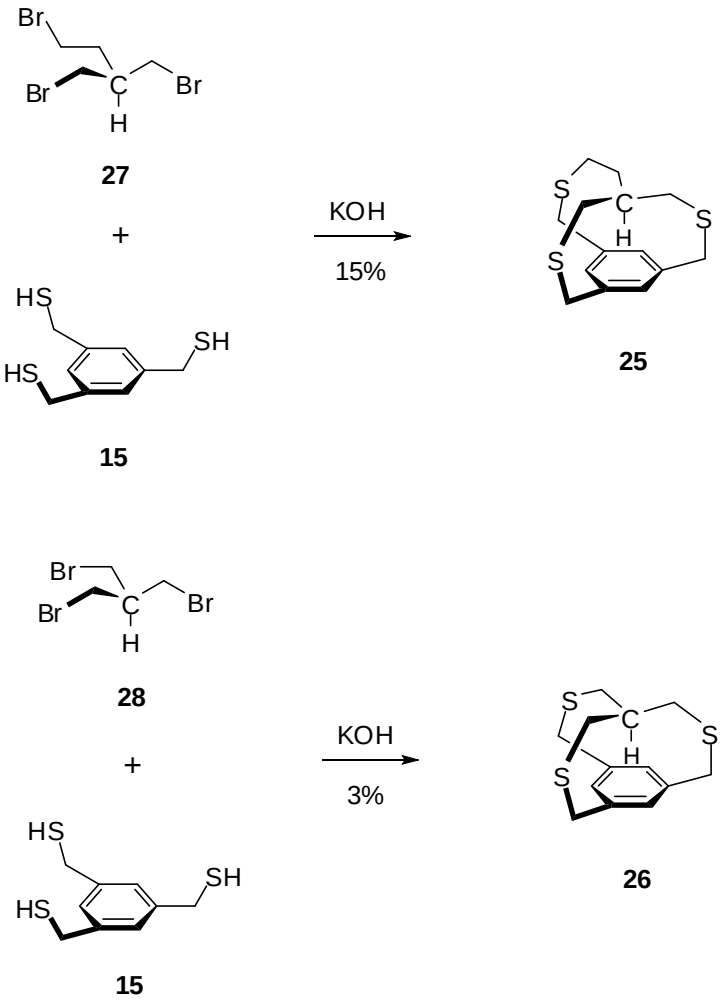
Scheme 5. Synthesis of cappedophanes



Although FVP methods had been used to form the very tight cyclophanes **19** and **21**, molecular mechanics calculations [MM2(85)] clearly indicated that *in*-cyclophanes even

as tight as **19** are more stable than their *out* isomers. In 1989, Pascal et al. made cyclophanes **25** and **26** in 15% and 3% yields, respectively, by direct condensation of smaller tribromides (**27**, **28**) and trithiol **15** (Scheme 6).[18]

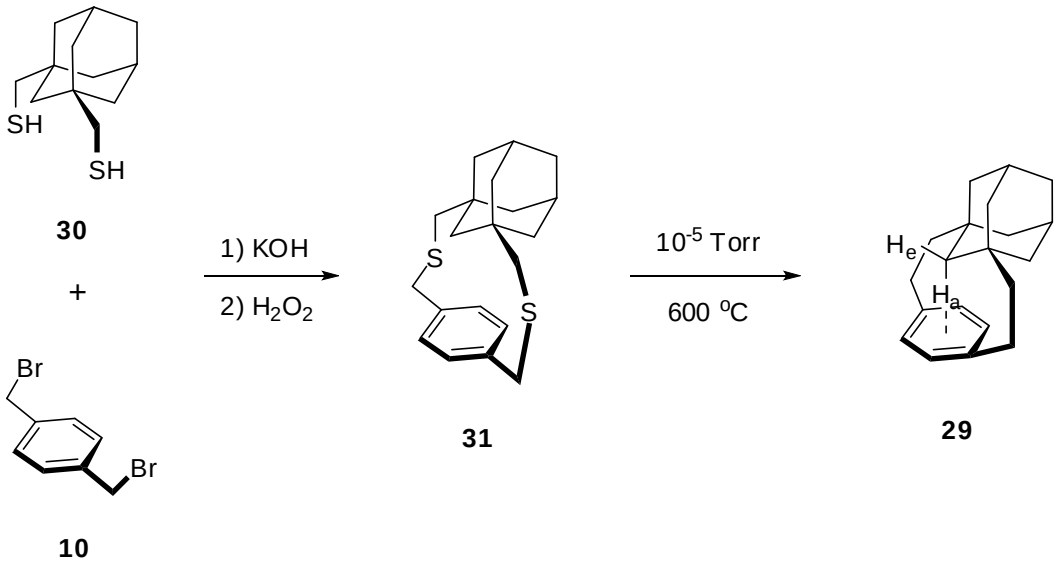
Scheme 6. Synthesis of cyclophanes **25** and **26**



Their X-ray structures placed the *in*-hydrogen atoms much closer to the benzene ring than previously observed, with H---Ar distances of 1.86 Å and 1.68 Å, respectively. In

addition, many of the spectral phenomena displayed by cyclophane **26**, such as $\delta_{in\text{-}H}$ = 2.84 ppm, J_{CH} = 128 Hz, and ν_{CH} = 3260 cm^{-1}, also showed that the H---Ar contact was extremely close.

Scheme 7. Synthesis of adamantanophane **29**

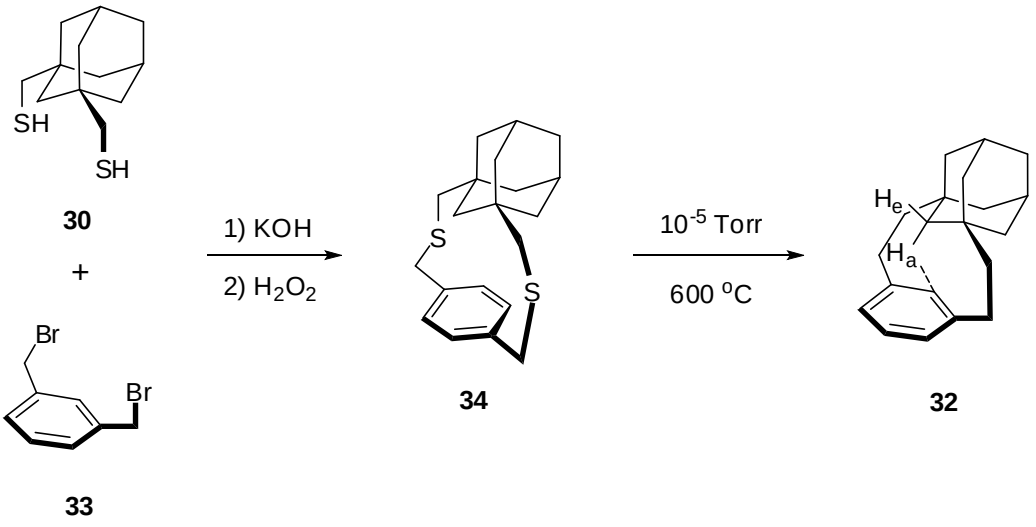


Today's "world record" for an H---Ar nonbonding contact belongs to the so-called "adamantanophane" **29** made by Vögtle and coworkers in 1993 (Scheme 7).[19] The synthesis of **29** involved cyclization of 1,3-bis(mercaptomethyl)adamantane (**30**) and dihalide **10** to give cyclophane **31**, followed by oxidation with H_2O_2 and sulfone pyrolysis. It was found that one of the hydrogens (H_a) displayed an ^1H NMR resonance at δ -4.08 and points directly toward the center of the basal ring, while the equatorial hydrogen (H_e), showing an ^1H NMR resonance at δ -1.01, is less shielded. The X-ray

structure of **29** reveals that its benzene ring is boat shaped, which indicates that the molecule has high strain. The H---Ar distance is only 1.64 Å and it remains the closest such contact observed so far.

Vögtle and coworkers also made adamantanophane **32** by similar methods (Scheme 8).[20] In its X-ray structure, the axial hydrogen (H_a) is moved toward one side of the benzene ring. The H---Ar distance is 2.02 Å, longer than in **29** but the H---C contact is only 1.98 Å, which is the closest H---C contact observed so far.

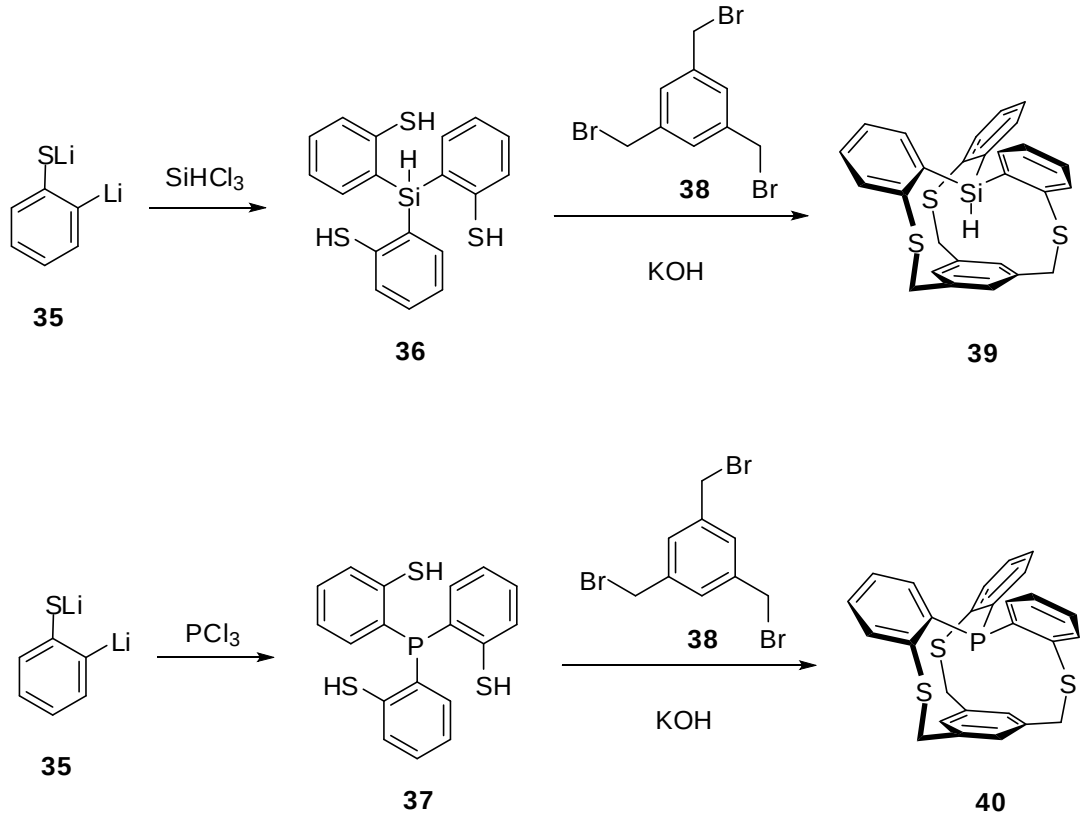
Scheme 8. Synthesis of adamantanophane **32**



Although it seems hard to break the records of these adamantanophanes, Pascal and coworkers found that their C_3 symmetric frameworks permitted them to include functional groups other than alkanes. They used the dilithium derivative of thiophenol (**35**) for the synthesis of the triarylelement trithiols **36** and **37**,[21][22] which were then subjected

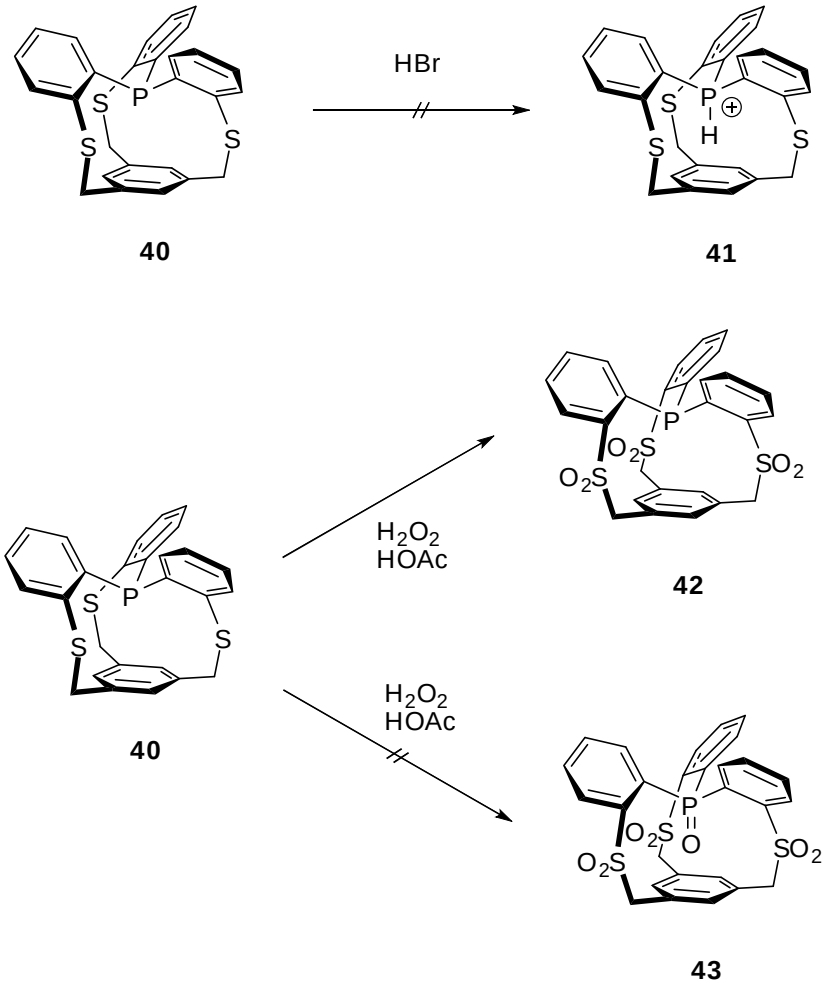
to cyclization reactions with tribromide **38** to give the *in*-silane **39** and the *in*-phosphine **40** (Scheme 9).[23][24]

Scheme 9. Synthesis of *in*-silane **39** and *in*-phosphine **40**



The spectroscopic data for cyclophane **39** show that it has an ultrashort nonbonding contact between the H_{Si} and the basal benzene ring: $\delta_{in\text{-}H}$ = 1.04 ppm (5 ppm upfield from an acyclic model) and ν_{SiH} = 2457 cm^{-1} (280 cm^{-1} higher than an acyclic model). The crystal structure shows that it has an H_{Si}---Ar contact of 1.86 Å and an H_{Si}---C contact of 2.32 Å, which remain the closest such contacts so far observed.

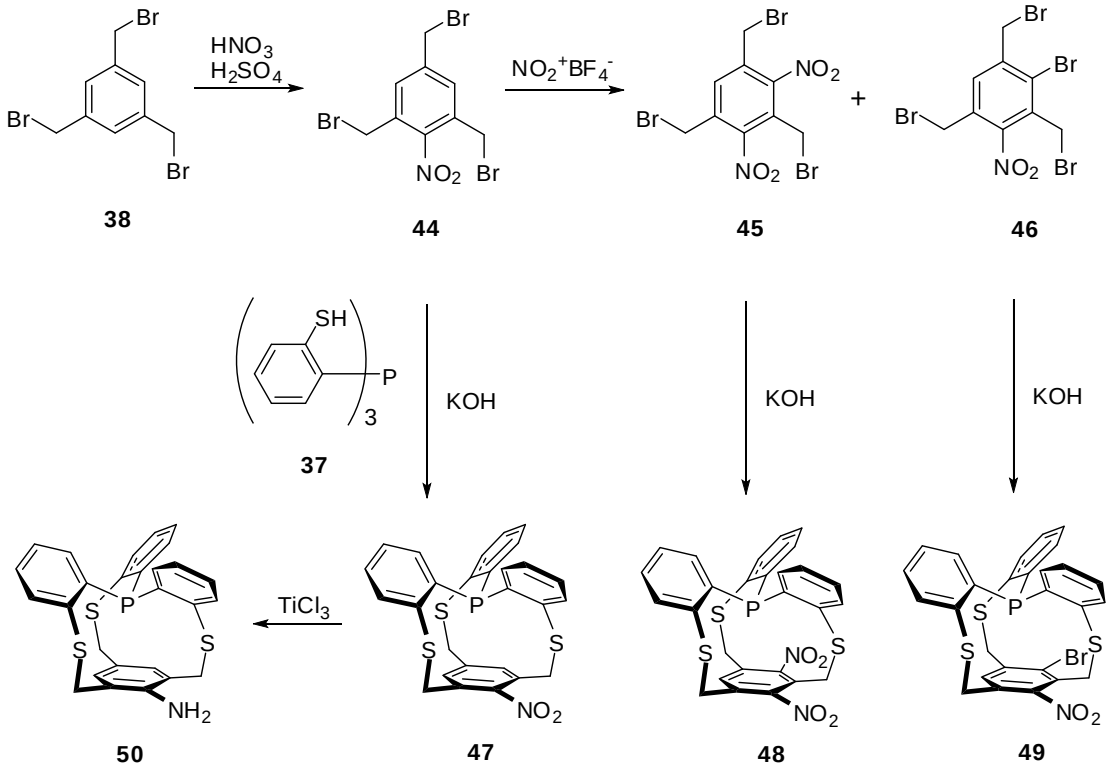
Scheme 10. Reactions of cyclophane **40**



The spectroscopic data for cyclophane **40** show that there is strong spin-spin coupling between the phosphorus atom and the basal aromatic ring [$J_{P,C(methine)}$ = 7.5 Hz and $J_{P,C(quaternary)}$ = 3.5 Hz]. The phosphorus atom of **40** is extremely unreactive. It cannot be protonated by anhydrous HBr to form compound **41**, and even in refluxing hydrogen peroxide and acetic acid, only the corresponding trisulfone **42** formed without formation of phosphine oxide **43** (Scheme 10). All these features indicate that the contact between

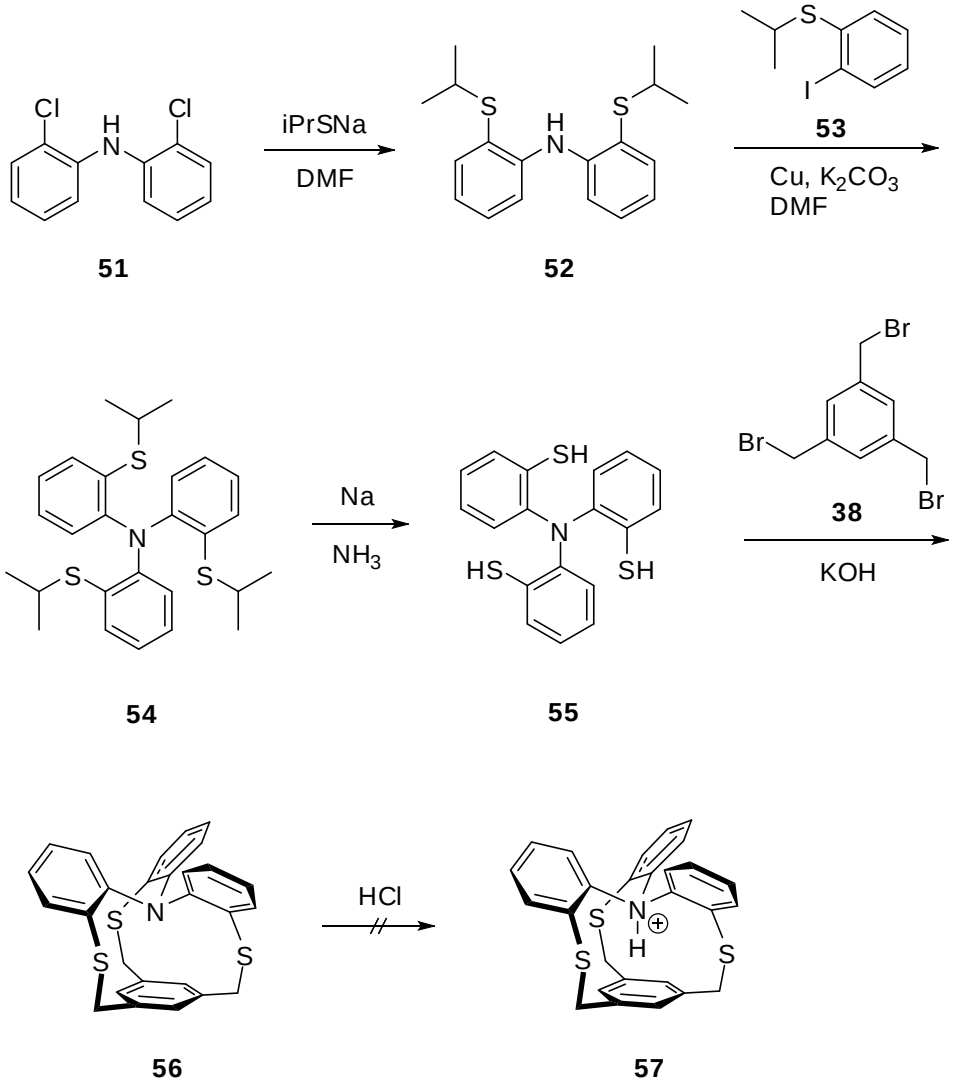
the phosphorus atom and the basal aromatic ring is very close. The crystal structure of **40** shows a P---Ar contact of 2.90 Å and a P---C contact of about 3.2 Å, the former of which is the closest P---Ar contact so far beheld.

Scheme 11. Synthesis of derivatives of **40**



Several derivatives of **40** with basal rings bearing nitro, halogen, and amino substituents (**47**-**50**) have also been prepared and crystallographically characterized (Scheme 11).[25] The mononitro compound **47** and dinitro compound **48** are brightly colored, due to strong charge-transfer absorptions in their UV spectra, and the nitro derivative was resolved into stable enantiomers, which exhibit extremely high ellipticities

Scheme 12. Synthesis of *in*-aminophane **54** and attempted protonation reaction



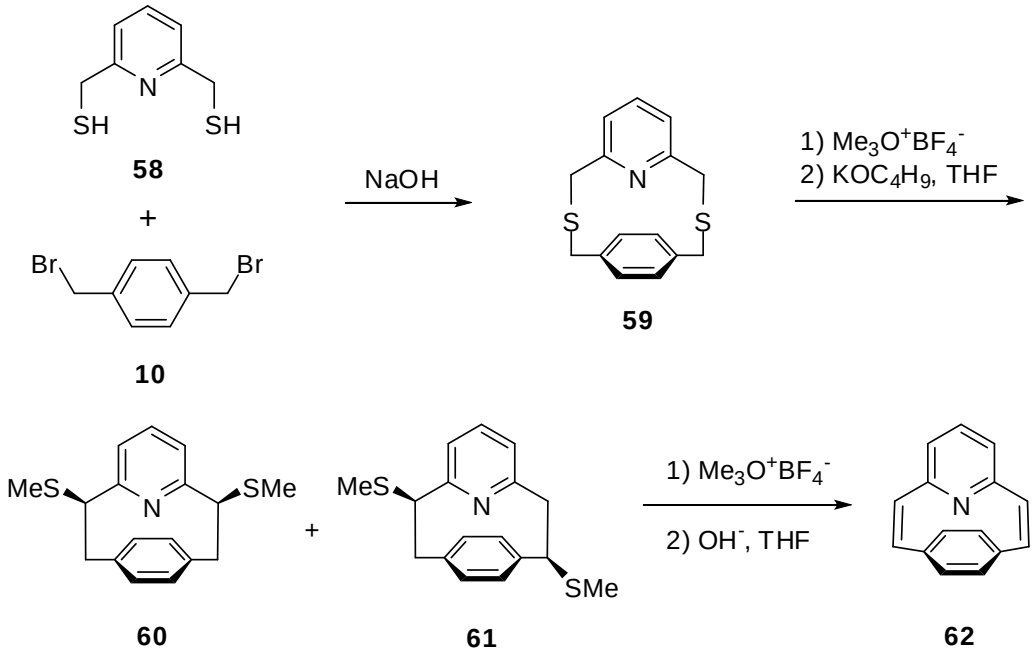
in their circular dichroism spectra.

With the closest P---Ar contact achieved, one may wonder whether the substitution of nitrogen for phosphorus in the triaryl-element-capped cyclophane will result in the closest N---Ar contact. Block's one-step synthesis is not applicable to amines, but Pascal and coworkers were able to make the nitrogen containing trithiol **55** by Ullmann reaction of thioether **52** and **53** to give trithioether **54**, followed by cleavage with Na/NH_3.

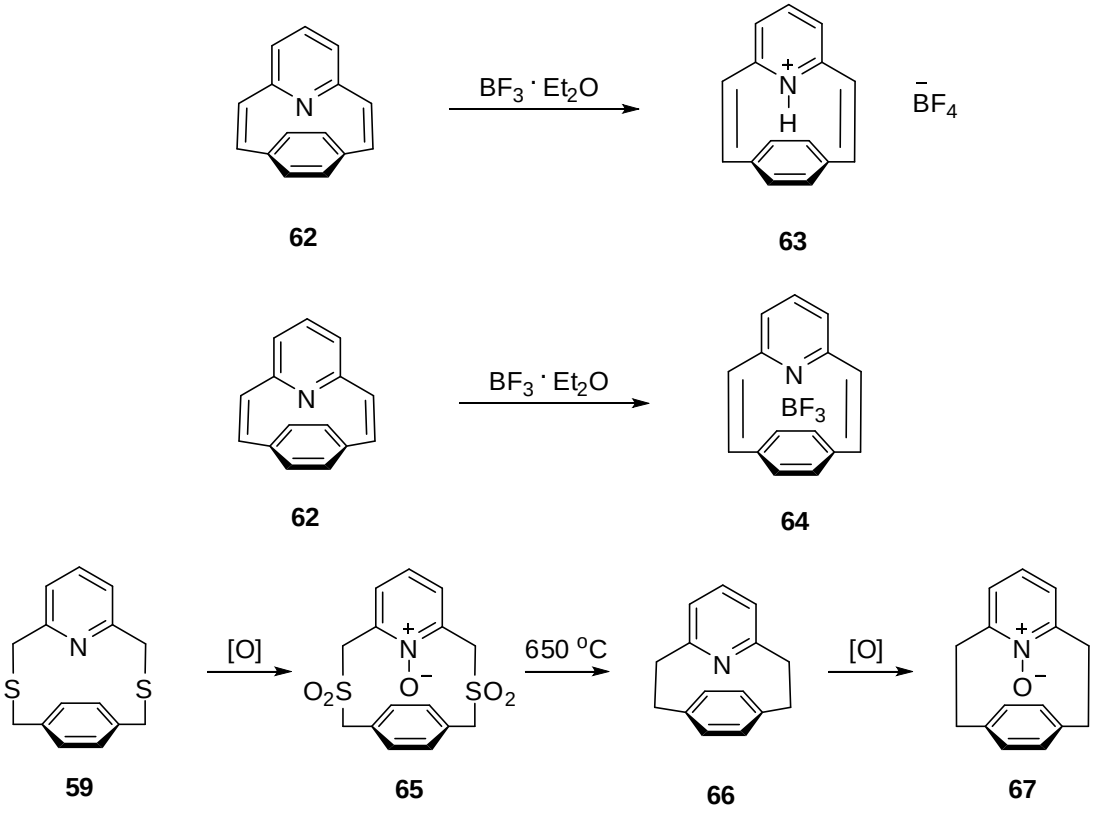
Thioethers **52** and **53** were made by reacting sodium isopropylthiolate with the corresponding halogenated precursors. Condensation of trithiol **55** with 1,3,5-tris(bromomethyl)benzene (**38**) gave cyclophane **56** in an only 0.7% yield, but the product was easily isolated by chromatography (Scheme 12).[26] The crystal structures showed N---Ar contacts of 3.419 Å and 3.398 Å in two independent molecules, which are nearly 0.5 Å greater than the P---Ar contacts (2.90 Å - 2.98 Å). Protonation was attempted with cyclophane **56**, but there was no evidence of a protonated cyclophane **57**. Insufficient material was available for other reactions, such as oxidation.

The tightest N---Ar contact is found in Boekelheide's pyridinophane **62**, which was made by condensation of 2,6-bis(mercaptomethyl)pyridine (**58**) with p-xylylene dibromide (**10**), followed by Stevens rearrangement and Hofmann elimination (Scheme 13).[27][28] The crystal structure showed that the heterocycle is perpendicular to the basal benzene ring. It also indicated an N---Ar contact of only 2.44 Å, and two N---C contacts of only 2.67 Å, almost 0.6 Å less than the sum of the van der Waals radii of nitrogen and carbon. Unlike the "molecular iron maiden" **40** and its relatives, the nitrogen in **62** and its derivatives is still reactive: it forms salts with ordinary acids and a complex with boron trifluoride, and it can be converted into the N-oxide (Scheme 14). This reactivity probably results from the two armed structure of **62** and its derivatives, which retains considerable flexibility.

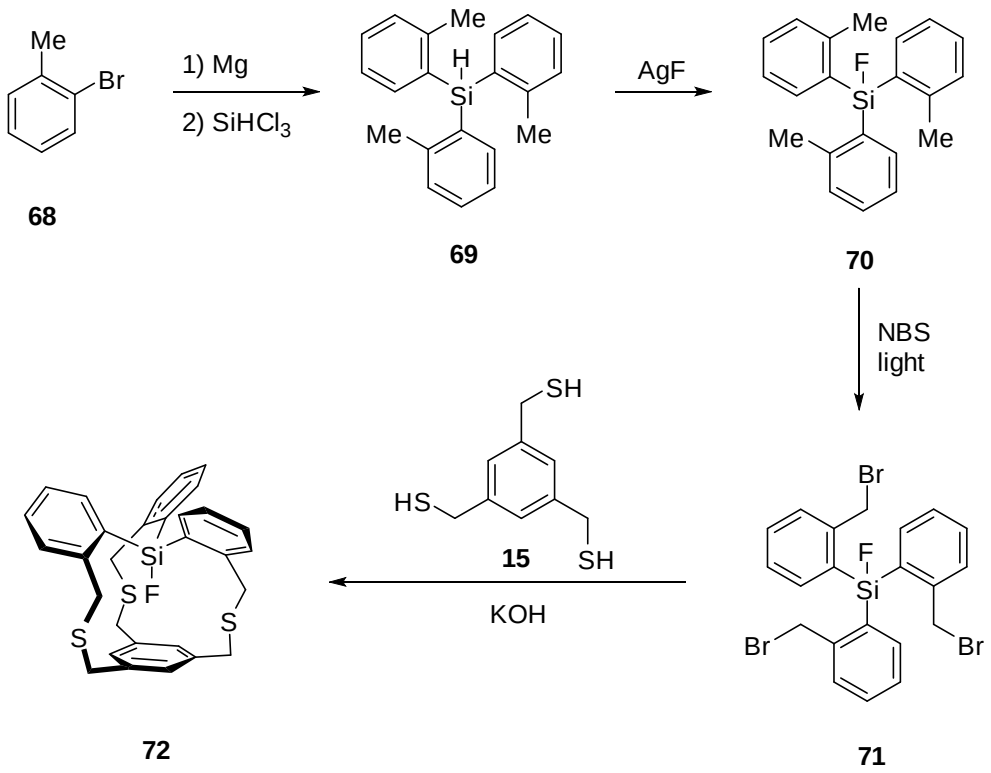
Scheme 13. Synthesis of pyridinophane **62**



Scheme 14. Reactions of cyclophanes **59** and **62**



Scheme 15. Synthesis of *in*-fluorosilaphane **72**

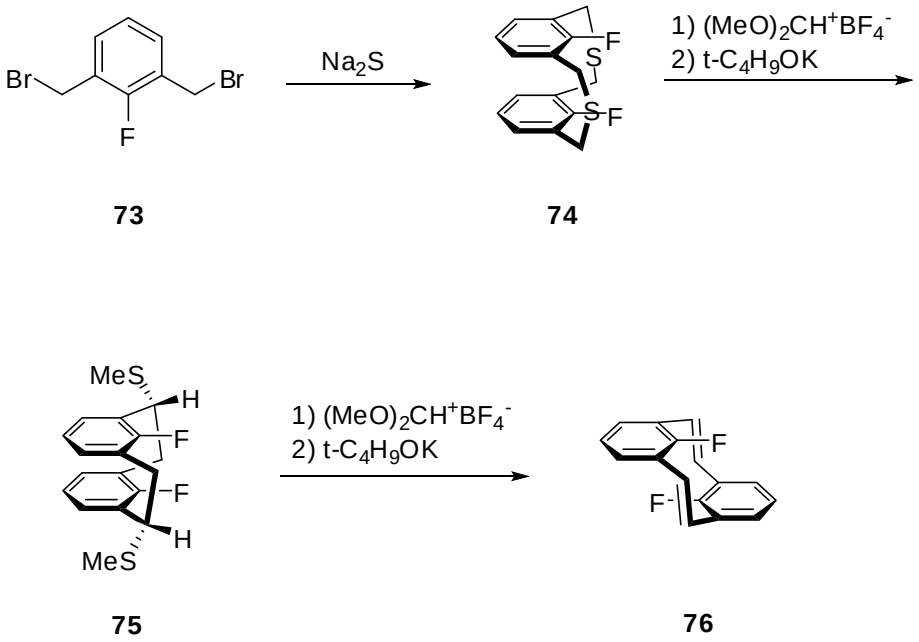


As stated above, cyclophane **39** has the closest H_{Si}---Ar contact and H_{Si}---C contact. It would be interesting to substitute Si-H with Si-F and to see if it gives the closest F---Ar contact or F---C contact. Pascal and coworkers answered this question with *in*-fluorosilaphane **72**, prepared by the condensation of the corresponding trithiol **15** with a tribromide **71** in only 0.4% yield (Scheme 15). The *in*-fluorosilaphane **72** has an F---Ar distance of 2.81 Å, and at the time it was the "molecular iron maiden" with the biggest *in* atom so far. However, the extremely low yield impeded any serious attempt to extrude the sulfur atoms, which might give a closer F---Ar contact.[29][30]

The tightest F---Ar and F---C distances, both 2.70 Å, were found in Boekelheide's

metacyclophane **76**, prepared by condensation of 2,6-bis(bromomethy1)fluorobenzene **73**, followed by Stevens rearrangement and Hofmann elimination (Scheme 16), although the fluorine atom is not pointed directly to the benzene ring.[31][32]

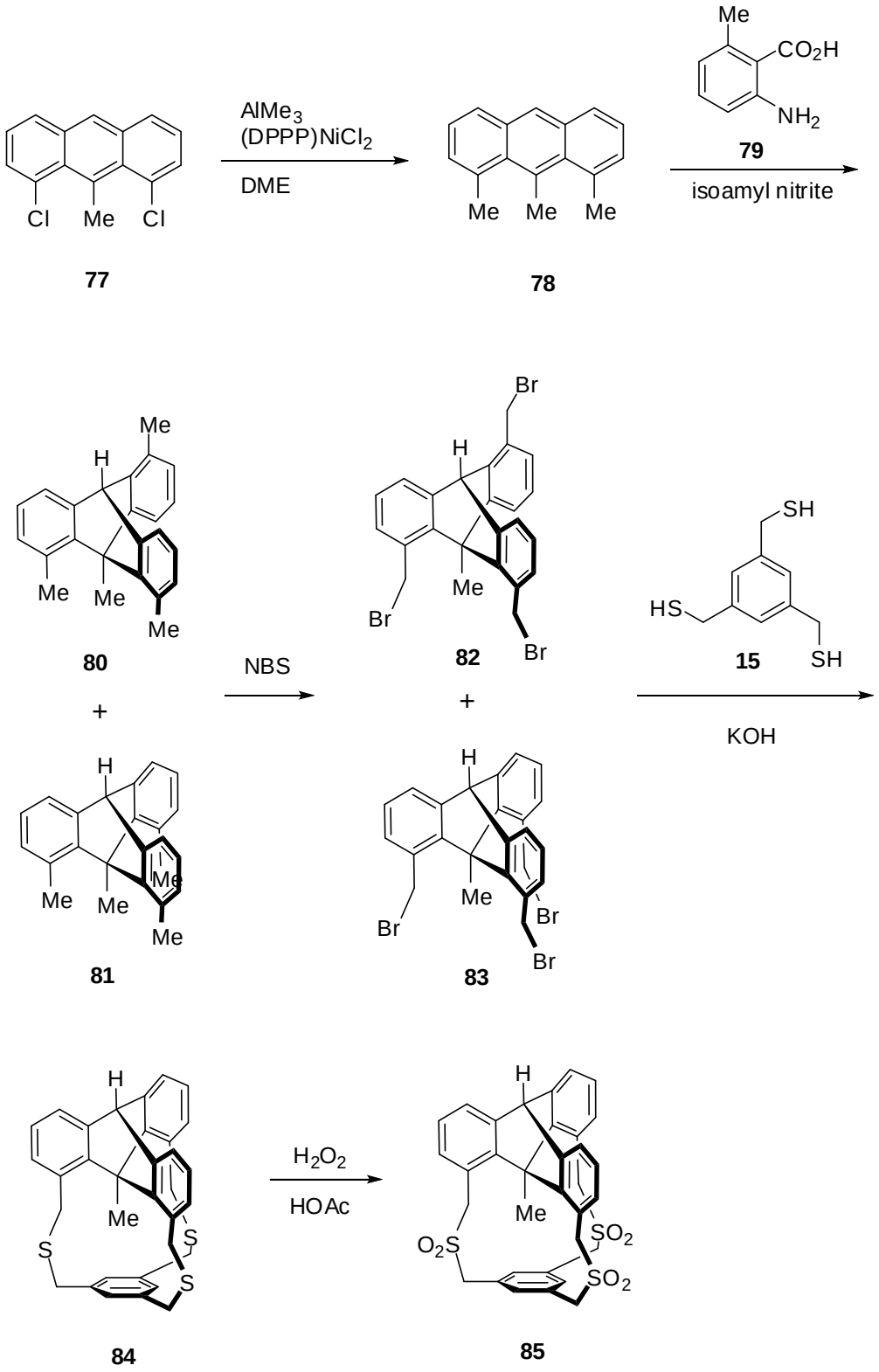
Scheme 16. Synthesis of metacyclophane **76**



73 **74** **75** **76**

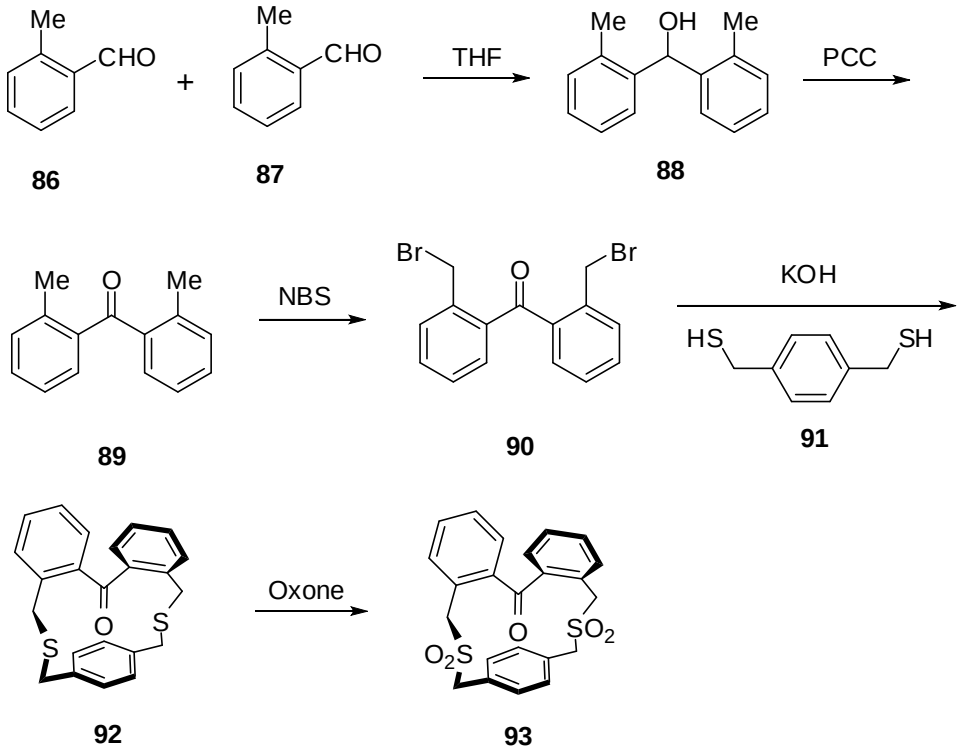
The "molecular iron maidens" with the biggest functional group pointing *in* so far are the *in*-methylcyclophanes **84** and **85** made in Pascal's group by Song et al. in 2005.[33] Cyclophane **84** was made by condensation of 1,3,5-tris(mercaptomethyl)benzene (**15**) with a mixture of the *anti* and *syn* isomers of tris(bromomethyl)-9-methyltriptycene (**82** and **83** respectively), which was made by addition of 3-methylbenzyne to 1,8,9-trimethylanthracene (**78**) followed by NBS bromination (Scheme 17).

Scheme 17. Synthesis of *in*-methylcyclophanes



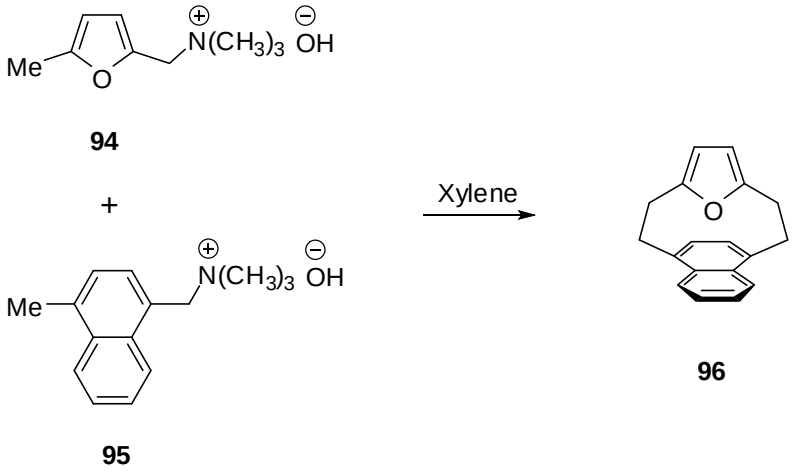
The ^{1}H NMR spectrum of **84** exhibits an *in*-methyl resonance at δ 2.52, about 1 ppm upfield from the 9-methyl resonances of **81** (δ 3.16) and **83** (δ 3.85). The *in*-methyl ^{13}C NMR resonance in **84** appears at δ 14.8, significantly upfield from any of the methyl resonances in precursors **80**, **81**, **82**, or **83** ($\delta_C \geq 18.4$). Large crystals of **84** were difficult to obtain, so **84** was oxidized to the trisulfone **85** by boiling in H_2O_2 and acetic acid. The two independent structures of **85** showed that the C_{methyl}-ring centroid distances are 2.896(5) Å and 2.869(5) Å, respectively, which remains the new "world record" for such a contact.

Scheme 18. Synthesis of *in*-keto cyclophane **93**



The first *in*-keto cyclophane **93**, which does not have a C_3 framework, was synthesized by Pascal's group in 2010.[34] The ketone group projected directly toward an aromatic ring. It was made by condensation of 2,2'-bis(bromomethyl)benzophenone (**90**) with 1,4-bis(mercaptomethyl)benzene (**91**), followed by oxidization with excess oxone (Scheme 18). The crystal structure showed that the molecule has C_2 symmetry and the C---Ar contact distance is 2.91 Å. The electron cloud of the ketone oxygen is projected into the π-cloud of the benzene ring. The closest contacts fall exactly at the sum of the van der Waals radii of carbon and oxygen (3.2 Å), so there is no great steric compression of the carbonyl group.

Scheme 19. Synthesis of furanophane **96**



The shortest O---Ar distance known at present is found in furanophane **96** made by Keehn and coworkers. It was made by pyrolysis of an equimolar mixture of **94** and **95**

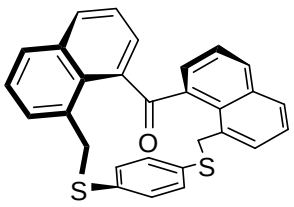
(Scheme 19). The O---Ar contact is observed to be 2.55 Å in the crystal structure.[35][36]

1.2 Results and Discussion

Will any structural relative of **93** contain a more highly congested ketone or even a new world record for a C---O nonbonded contact distance? If so, will the ketone still point directly at the basal benzene ring, or it will point sideways as in **92**? DFT calculations have shown that, with bulky substituents and short linking arms to a basal aromatic ring, the ketone may be prevented from lying parallel to the basal ring, and ultimately may be forced to point directly at it. This was exactly how Qin et al. made the *in*-keto cyclophane **93**. In order to design a new kind of *in*-keto cyclophane which is more congested, the linking arms have to be shorter and bulkier.

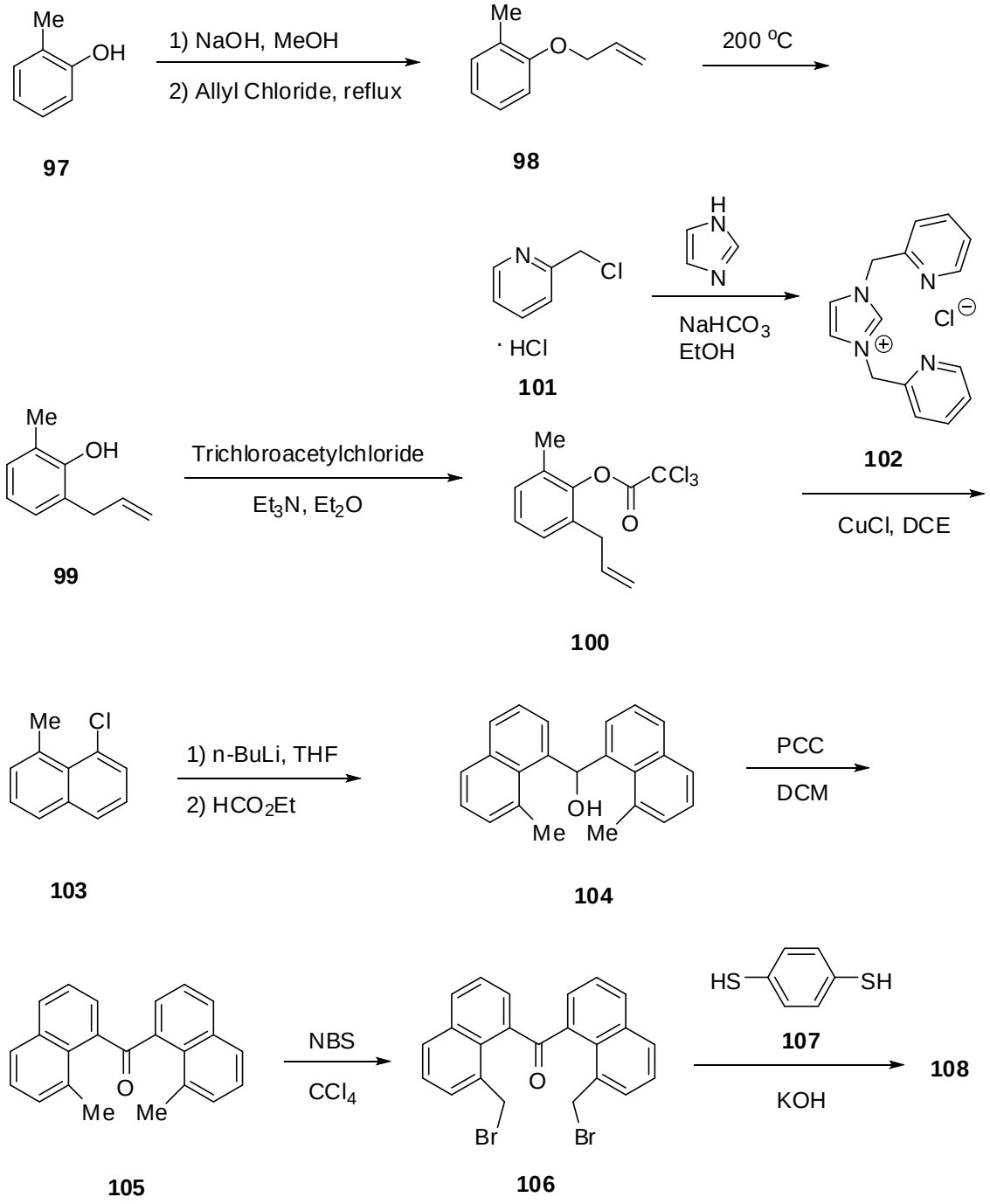
1.2.1 First Attempted Synthesis of *in*-Keto Cyclophane

Computational studies (B3PW91/6-31G*) show that the C---O distance in cyclophane **108** is 2.60 Å, which is very close to the world record of 2.55 Å, and the ketone group is pointing directly at the basal benzene ring. There is no doubt that cyclophane **108** is a good candidate to be the most congested *in*-keto cyclophane.



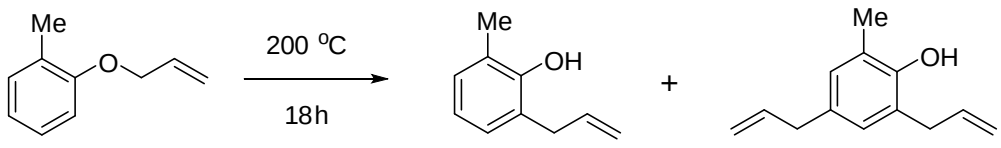
108

Scheme 20. Proposed synthesis of *in*-keto cyclophane **108**



In order to synthesize cyclophane **108**, the above route was designed (Scheme 20). Compound **99** can be prepared by alkylation of *o*-cresol (**97**) to give ether **98**, followed by Claisen rearrangement. After acylation with trichloroacetyl chloride, compound **100** can undergo benzannulation, catalyzed by compound **102** and CuCl, to give the key intermediate naphthalene **103**.[37] Transmetallation with *n*-BuLi followed by a double addition to ethyl formate will give alcohol **104**. After oxidation with pyridinium chlorochromate (PCC) and bromination with N-bromosuccinimide (NBS), the doubly brominated ketone **106** may be made. The last step is simply the standard cyclization of **106** with 1,4-benzenedithiol (**107**) in benzene, ethanol and KOH to give *in*-keto cyclophane **108**.

The proposed route seems long but easy, but problems were encountered in practice. 1-(Allyloxy)-2-methylbenzene (**98**) was made from *o*-cresol (**97**) in 73% yield. When **98** was subjected to Claisen rearrangement, alcohol **99** was the major product, but much alcohol **109** was also present in the reaction mixture, which gave trouble during purification. Finally, alcohol **99** was separated using vacuum distillation in 40% yield. Acylation was easy and compound **100** was formed in 90% yield.



98 **99** **109**

For the cyclization, some byproduct **110** formed after reflux for 14 h, but after 86 h, about half of compound **110** was converted to **103**, and after 110 h, conversion to **103** was complete (Scheme 21). The yields of the conversions of **110** to **103** are shown in Table 1.

Scheme 21. Benzannulation reaction of compound **100**

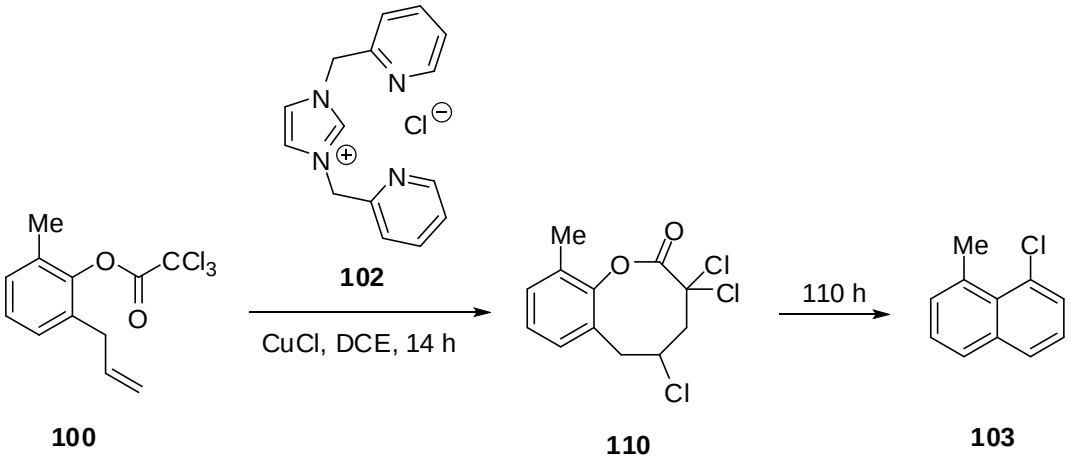
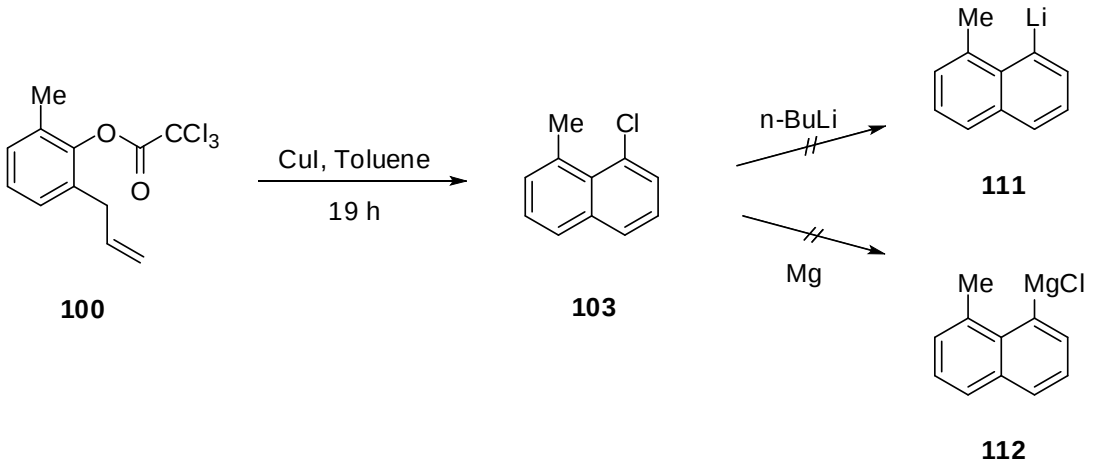


Table 1. Conversions of **110** to **103**

Reaction Time	% of **103** in the mixture of **103** and **110**
14 h	0
86 h	50
110 h	100

In order to avoid such a long reaction time, the solvent was changed from dichloroethane to toluene and catalyst from CuCl to CuI. The reaction time was reduced to 19 h, with an isolated yield of 30%. However, compound **103** did not react with either *n*-BuLi or Mg to form the anion **111** or **112** (Scheme 22), so alcohol **104** could not be made in this way.

Scheme 22. Optimized benzannulation reaction and attempted transmetallation

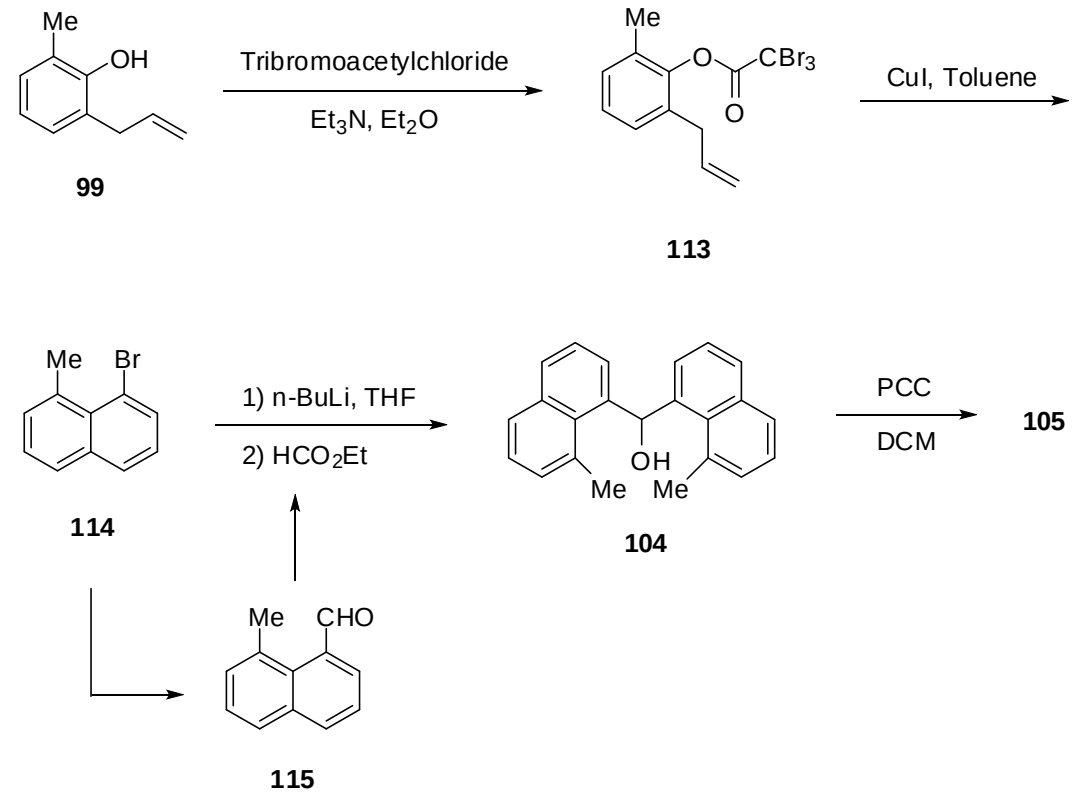


100 **103** **111** **112**

In order to increase the reactivity of the halogen atom on the naphthalene ring, the brominated derivative **114** was made in a similar way (Scheme 23). Acylation with tribromoacetylchloride gave compound **113** in 81% yield, which was then subjected to benzannulation to make 1-bromo-8-methylnaphthalene (**114**) in 34% yield. Transmetallation of **114** with *n*-BuLi gave the anion, which then reacted with ethyl formate to give alcohol **104** in 48% yield. In some preparations, aldehyde **115** formed in the reaction, which was reacted with the anion again to obtain alcohol **104**. Alcohol **104**

was oxidized with PCC to obtain ketone **105** in 84% yield, for which ^{1}H NMR, ^{13}C NMR, MS, X-ray and IR data were collected. The crystal structure is shown in Figure 1.

Scheme 23. Synthesis of ketone **105**



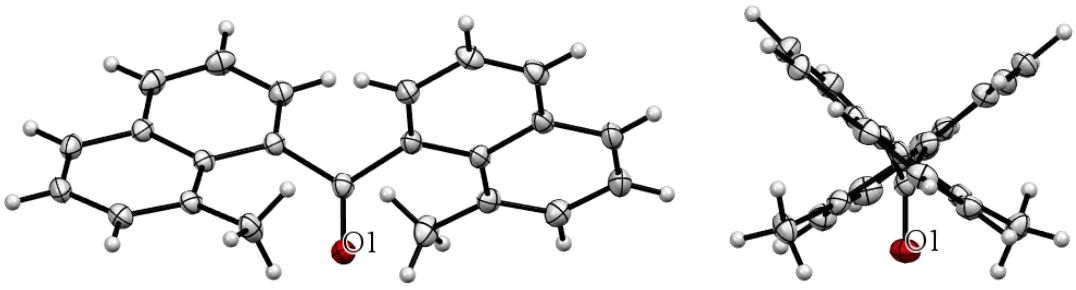
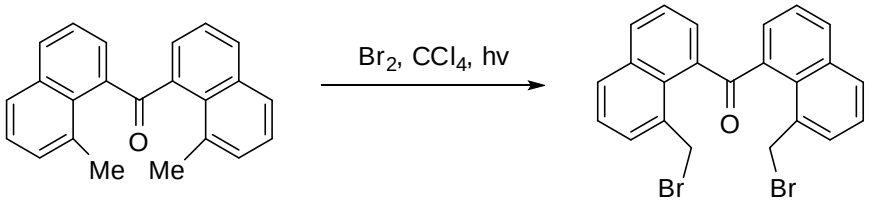


Figure 1. Molecular structure of compound **105**; thermal ellipsoids have been drawn at the 50% probability level.

Scheme 24. Bromination reactions of ketone **105**



105 **106**

Conditions:

1) NBS, CCl_4, hv

2) NBS, CCl_4, Na_2CO_3, hv

3) Br_2, CCl_4, hv

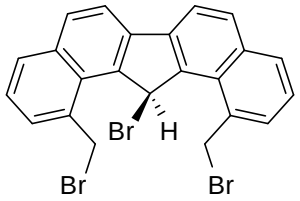
4) Br_2, CCl_4, Na_2CO_3, hv

5) NBS, Benzene, hv

6) NBS, CCl_4, BPO

7) NBS, CCl_4, AIBN

+



116

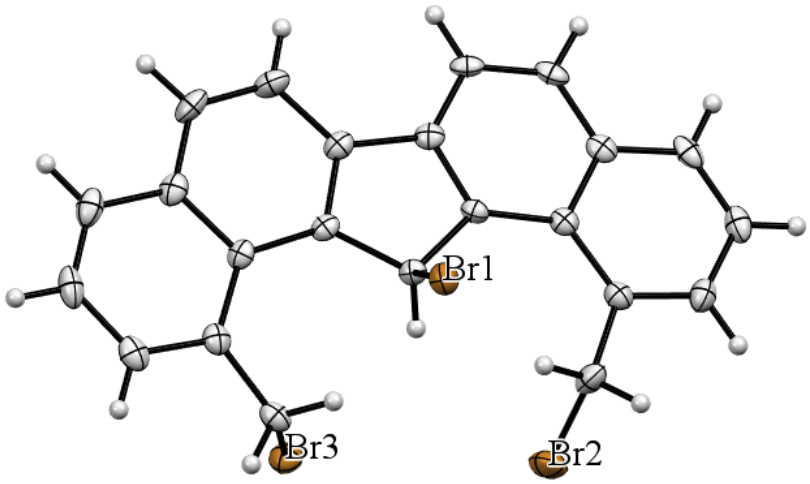
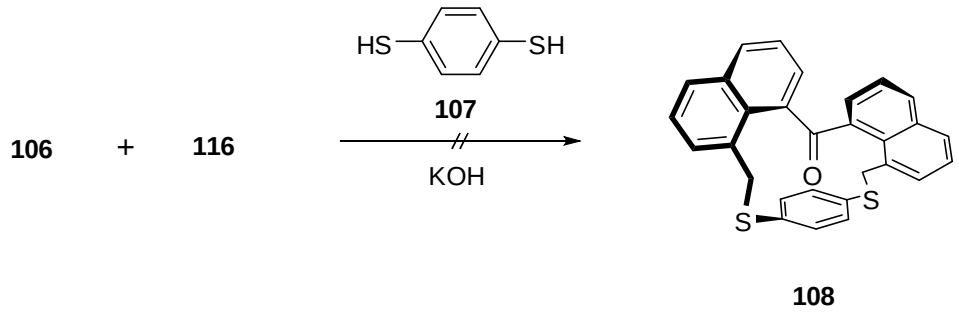


Figure 2. Molecular structure of compound **116**; thermal ellipsoids have been drawn at the 50% probability level.

Bromination of **105** with NBS is problematic, and various conditions were tried as shown in Scheme 24. The reaction with bromine in CCl_4 with illumination by a tungsten lamp gave the desired compound **106** in very low yield, and the pentacyclic compound **116** was also found among the products. The crystal structure of compound **116** is shown in Figure 2. The whole reaction mixture was subjected to the cyclization conditions, but no cyclophane **108** was isolated from the reaction (Scheme 25).

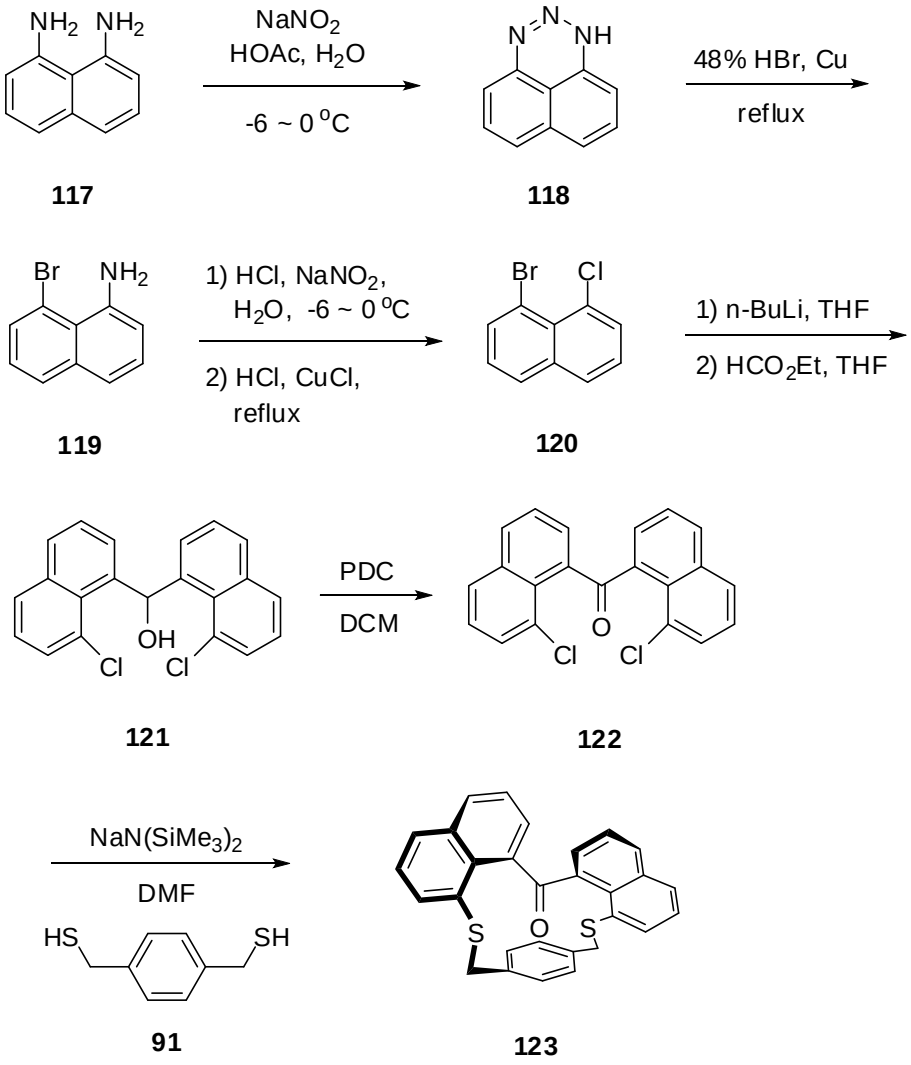
Scheme 25. Attempted cyclization reaction



1.2.2 Second Attempted Synthesis of *in*-Keto Cyclophane

In order to make a highly congested ketone, the synthesis of an alternative *in*-keto cyclophane **123** was designed (Scheme 26). 1-Bromo-8-aminonaphthalene (**119**) can be made by diazotisation of 1,8-diaminonaphthalene (**117**) followed by treatment with hydrobromic acid and copper. Compound **119** may be subjected to Sandmeyer conditions to form 1-bromo-8-chloronaphthalene (**120**), which can be carried through a route similar to that in Scheme 18 to form alcohol **121** and ketone **122**. 1,4-Bis(mercaptomethyl)benzene (**91**) could then be used for nucleophilic aromatic

Scheme 26. Proposed synthesis of *in*-keto cyclophane **123**



substitution on ketone **122** to form cyclophane **123**.

In the actual experiments, the triazine **118** was carried on without purification, and the yield from **117** to **119** was 16%. Sandmeyer reaction of **119** gave **120** in 92% yield. As the reactivity of the chlorine is less than bromine, the monoanion was formed with chlorine remaining on the naphthalene ring. This was added twice to ethyl formate to

form alcohol **121** in 55% yield. Oxidation was not complete, with either PCC or PDC, but starting material can be recycled, and the combined yield was 79%. The ketone **122** was characterized by ^{1}H NMR, ^{13}C NMR, MS and X-ray analysis. The crystal structure of compound **122** is shown in Figure 3.

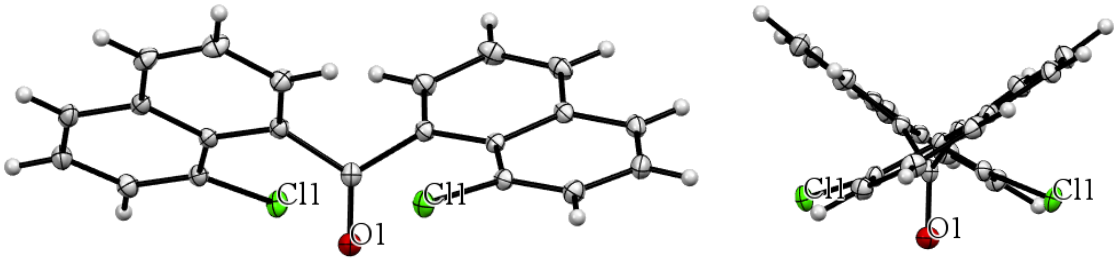
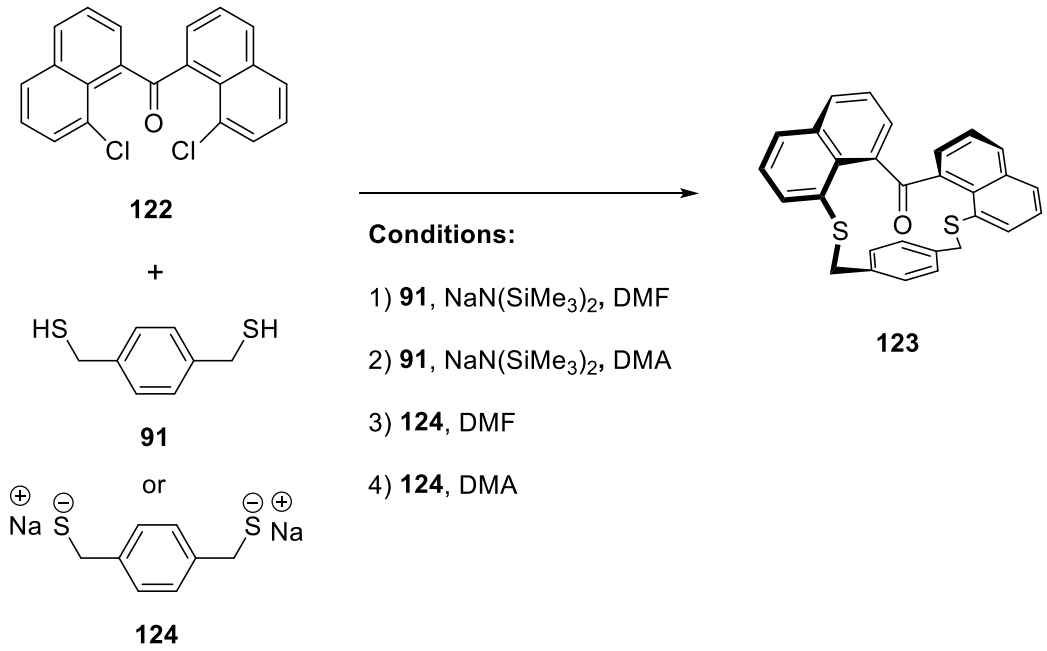


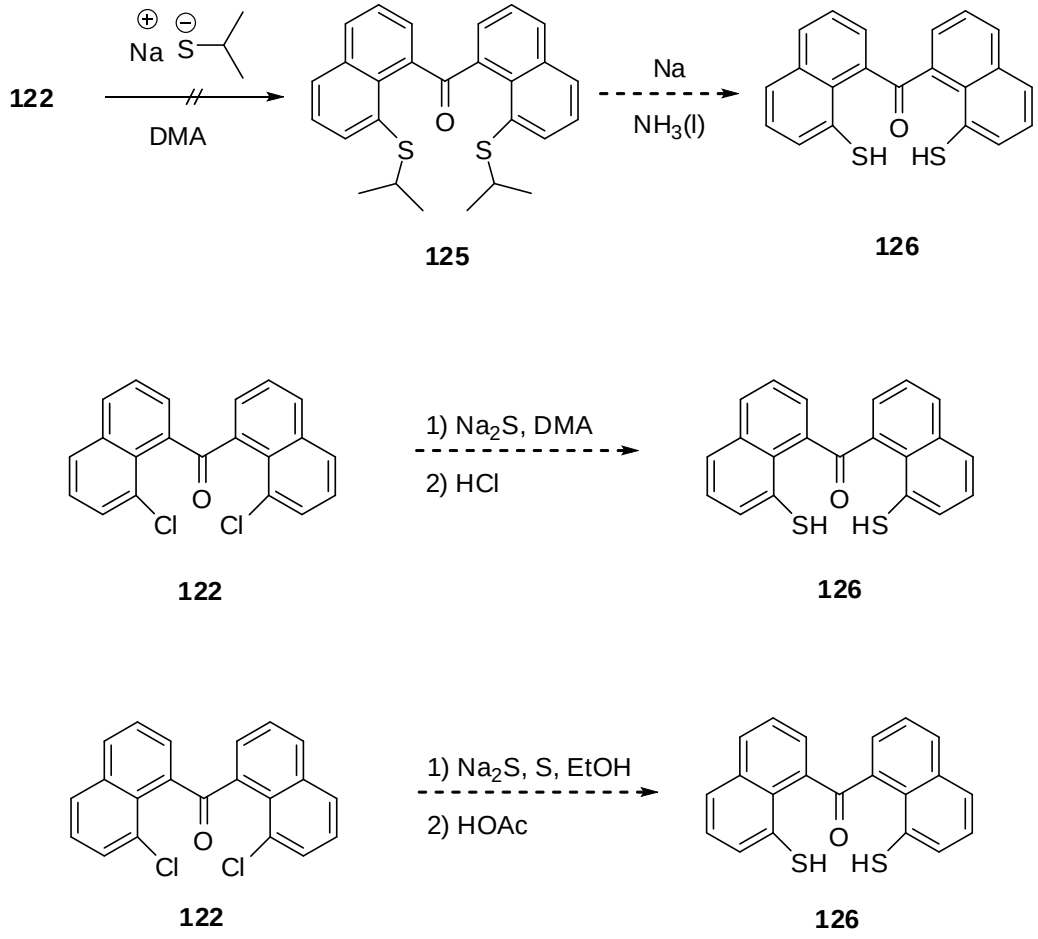
Figure 3. Molecular structure of compound **122**; thermal ellipsoids have been drawn at the 50% probability level.

Scheme 27. Attempted cyclization reactions



Condensation of ketone **122** and dithiol **91** is not a facile step. Various solvents were tried, such as DMF and DMA, with $NaN(SiMe_3)_2$ as base, but the reactions all failed. The disodium salt **124** was also made so as to increase its nucleophilicity, but this did not help either (Scheme 27).

Scheme 28. Attempted reactions to make dithiol **126**



Another attempt was the reaction of ketone **122** with sodium isopropylthiolate to make dithioether **125**, followed by elimination of the isopropyl group with sodium and liquid ammonia to achieve dithiol **126**. However, dithioether **125** was not formed. Other attempts to substitute chlorine with sulfur were unsuccessful, including the use of sodium sulfide in DMA and in ethanol (Scheme 28). The steric crowding in ketone **122** might be a problem.

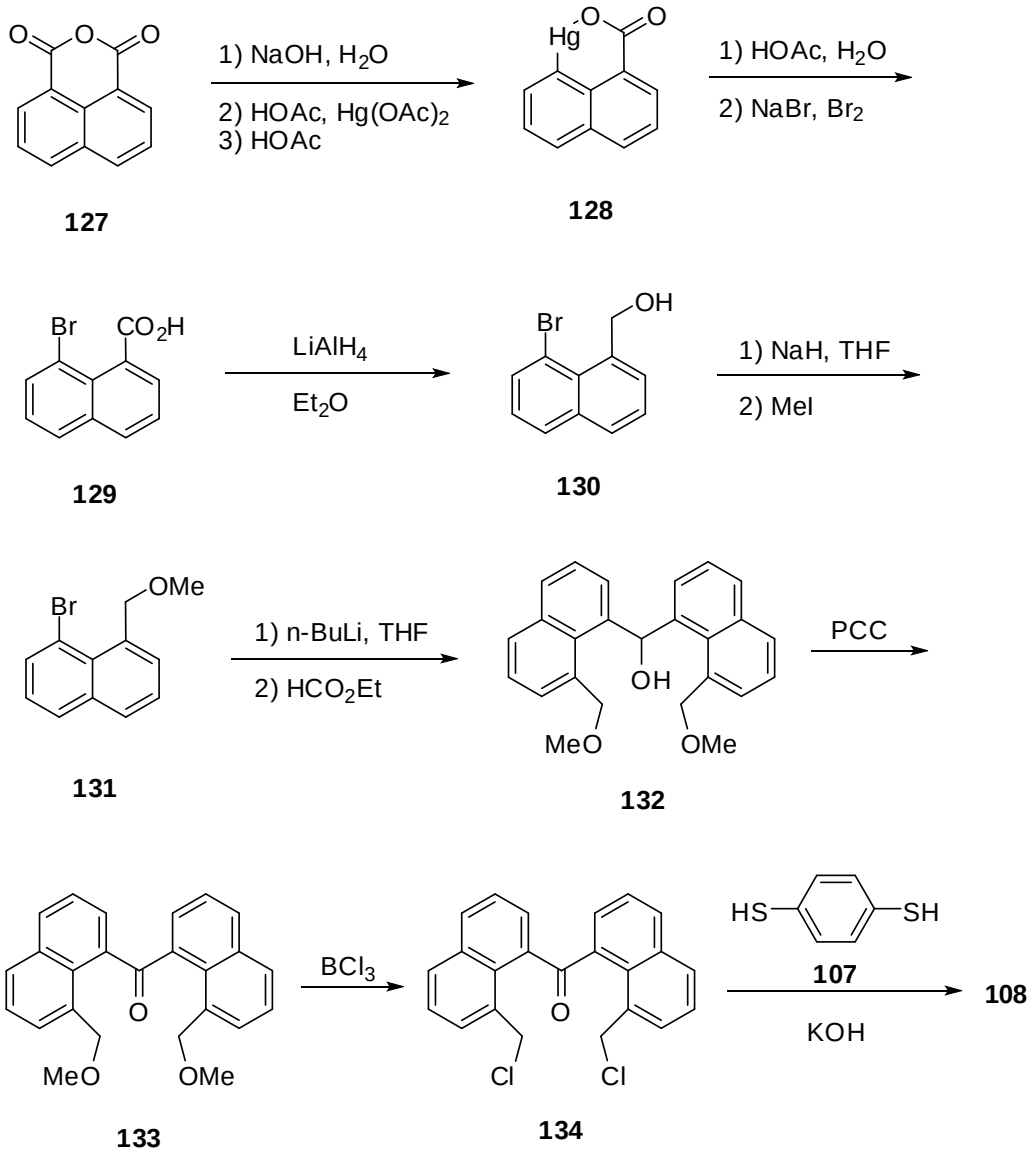
1.2.3 Third Attempted Synthesis of *in*-Keto Cyclophane

The previous failure led to the design of another route for the synthesis of *in*-keto cyclophane **108** that would avoid the need for a free radical bromination (Scheme 29). Mercuration of 1,8-naphthalic anhydride (**127**) will give anhydro-8-(hydroxymercuri)-1-naphthoic acid (**128**), which can then be subjected to demercuration to form 8-bromo-1-naphthoic acid (**129**). Compound **129** can be reduced by $LiAlH_4$ to give alcohol **130**. Methylation of alcohol **130** with methyl iodide gives the key intermediate 1-bromo-8-(methoxymethyl)- naphthalene (**131**), which can then be converted to alcohol **132** and ketone **133** through a route similar to that in Scheme 1. The methoxy group could be replaced by reaction with boron trichloride to form the dichloro derivative **134**. In the last step, ketone **134** can be subjected to the cyclization conditions described before to give *in*-keto cyclophane **108**.

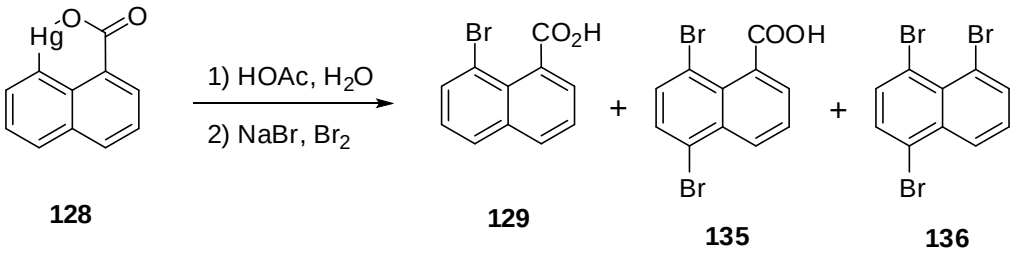
In the actual experiments, the first step worked well, and the mercury compound **128** was made in 84% yield. Demercuration did not work well at first, with a large amount of

the overbrominated product **135** and the decarboxylation product **136** formed as by-products (Scheme 30). The reaction conditions were optimized with less bromine added to the reaction mixture and ultimately 8-bromo-1-naphthoic acid (**129**) was formed in 69% yield.

Scheme 29. Proposed synthesis of *in*-keto cyclophane **108**

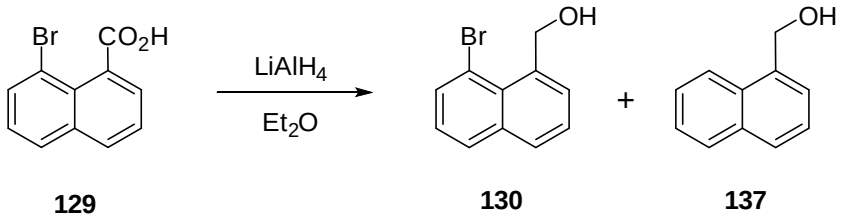


Scheme 30. Demercuration reaction of compound **128**

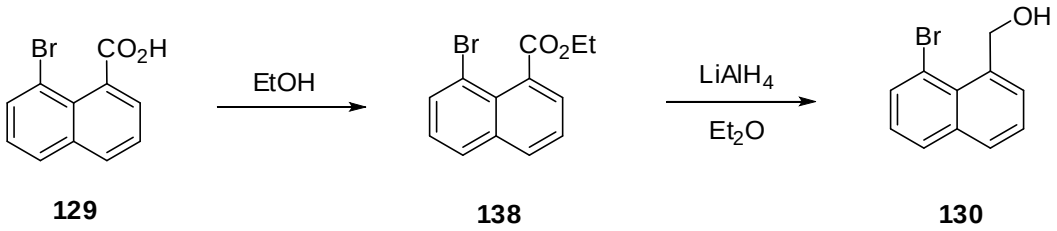


128 **129** **135** **136**

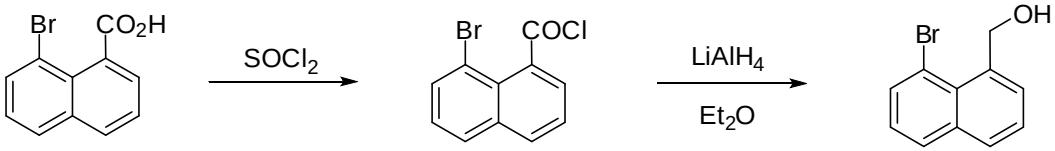
Scheme 31. Reduction of compound **129** to **130**



129 **130** **137**



129 **138** **130**



129 **139** **130**

With compound **129** in hand, the initial attempt was to treat it directly with $LiAlH_4$ to make (8-bromonaphthalen-1-yl)methanol (**130**). However, this reaction also led to some loss of bromine, and a large amount of naphthalen-1-ylmethanol (**137**) was detected in the reaction mixture, which was difficult to separate. Esterification with ethanol to make ester **138** followed by reduction with $LiAlH_4$ did not work well either. Finally, treatment

with thionyl chloride ($SOCl_2$) and reduction with $LiAlH_4$ gave the acyl chloride **139** and alcohol **130** in high yields, 94% and 86%, respectively (Scheme 31). Methylation with MeI and NaH was quantitative. The lithiation of **131** and formation of **132** proceeded in 15% yield, probably due to the steric hinderance of the compound. Alcohol **132** was characterized by ^{1}H NMR, ^{13}C NMR, MS and X-ray analysis.

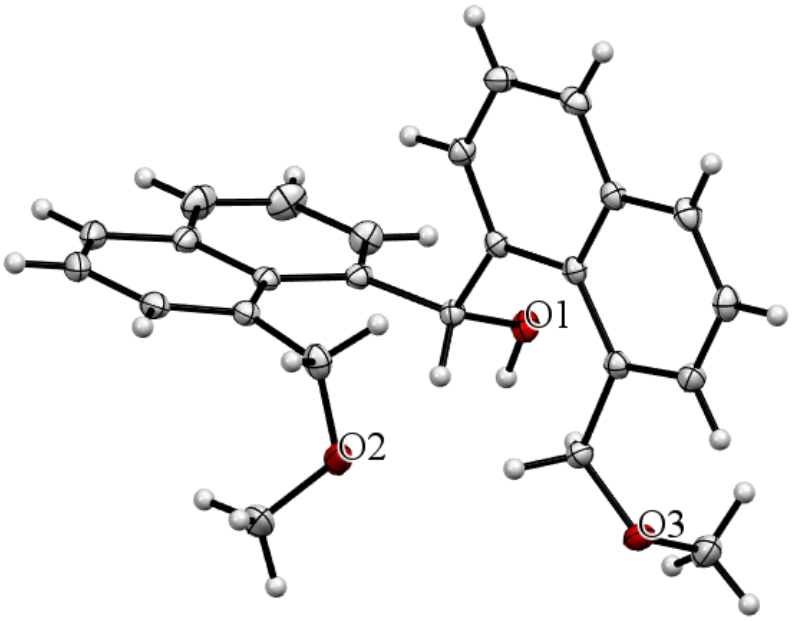
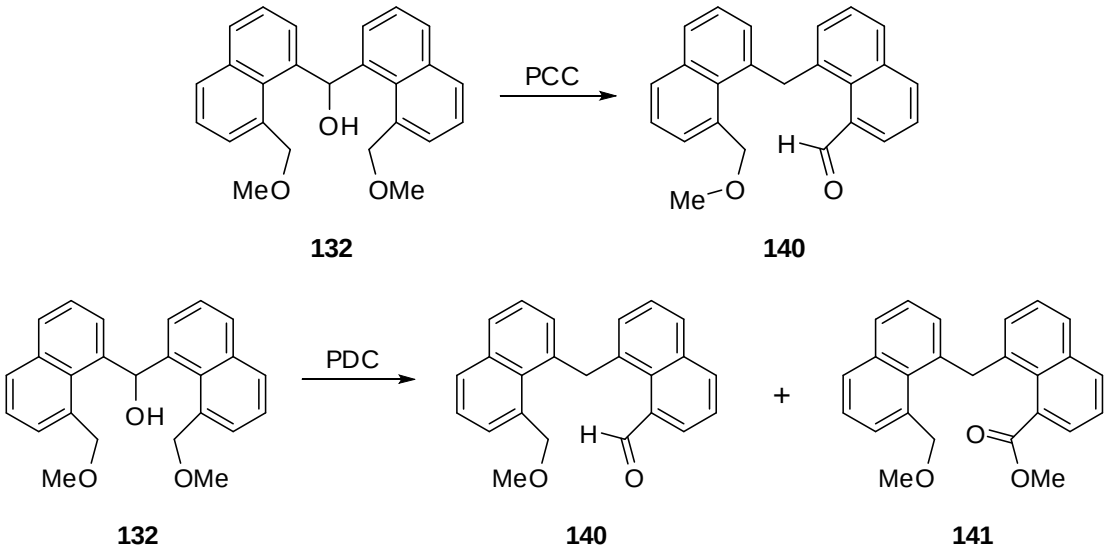


Figure 4. Molecular structure of compound **132**; thermal ellipsoids have been drawn at the 50% probability level.

Scheme 32. Attempted oxidation reaction of compound **132**



Oxidation of alcohol **132** is problematic. The oxidation with PCC did not give the desired ketone **133**, but the rearranged aldehyde **140** instead. The crystal structure of compound **140** is shown in Figure 5. Changing the oxidizing agent to PDC did not succeed either, and the reaction mixture contained both the rearranged aldehyde **140** and ester **141** (Scheme 32). The crystal structure of compound **141** is shown in Figure 6.

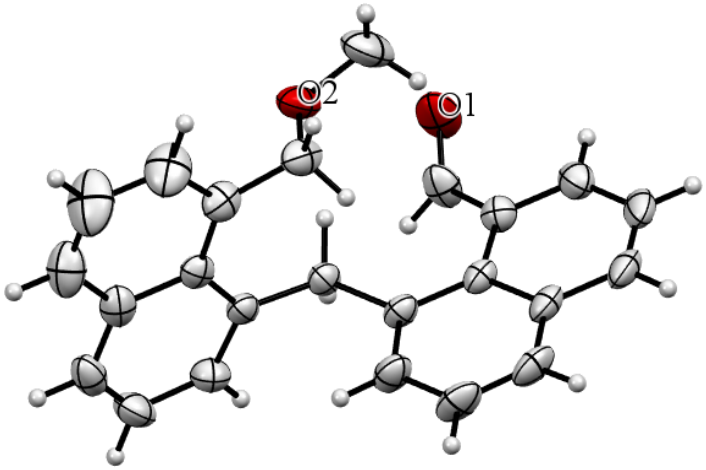


Figure 5. Molecular structure of compound **140**; thermal ellipsoids have been drawn at the 50% probability level.

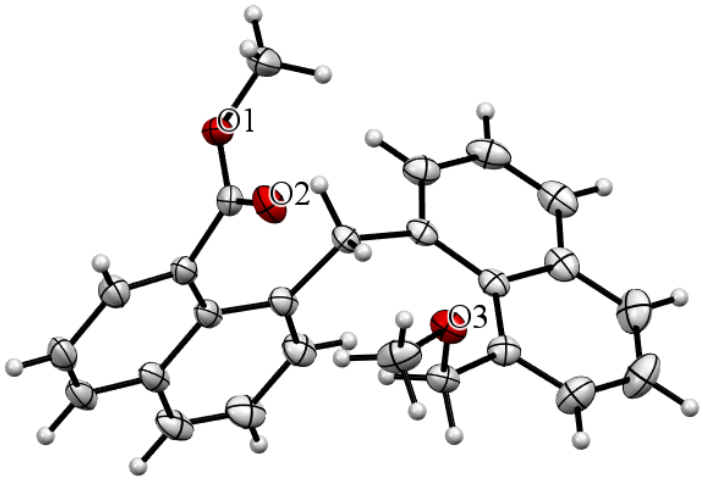
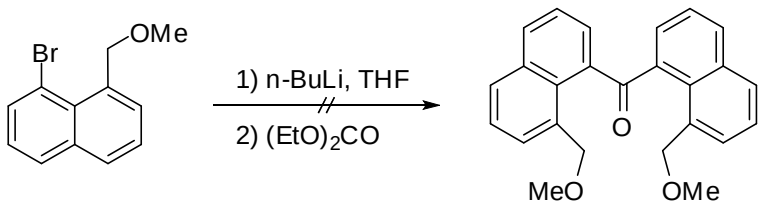


Figure 6. Molecular structure of compound **141**; thermal ellipsoids have been drawn at the 50% probability level.

Scheme 33. Attempted synthesis of ketone **133**



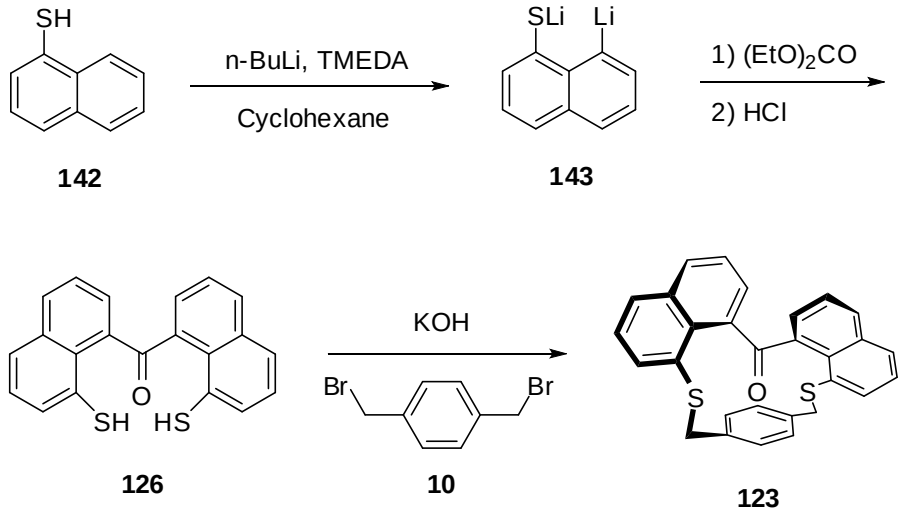
131 **133**

In order to avoid preparing alcohol **132** first, followed by oxidation to ketone **133**, another route was proposed. However, transmetallation of compound **131** followed by direct addition to diethyl carbonate still gave no desired product **133** (Scheme 33).

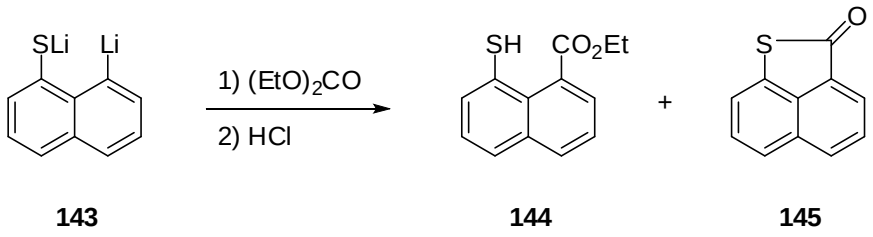
1.2.4 Fourth Attempted Synthesis of *in*-Keto Cyclophane

All these routes are tedious and problematic, but is there some other possible short synthesis of congested *in*-keto cyclophanes **108** or **123**? Inspired by Block's method to make the dilithium derivative of thiophenol (**35**), a dilithium derivative of 1-thionaphthol (**143**) might be made in similar way. Dilithium salt **143** could be added twice to diethyl carbonate to form the dithiol **126**, which could cyclize with 1,4-bis(bromomethyl)benzene (**10**) to make *in*-keto cyclophane **123** (Scheme 34). This route has the great advantage that it needs only three steps to yield the target molecule.

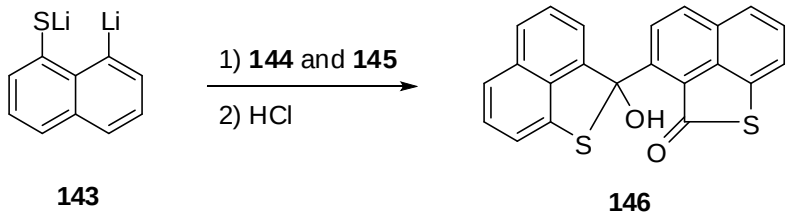
Scheme 34. Proposed synthesis of *in*-keto cyclophane **123**



Scheme 35. Reaction of compound **143** with diethyl carbonate



Scheme 36. Reaction of compound **143** with compound **144** and **145**



In the actual experiment, dilithium salt **143** was made and carried on without purification. In the addition reaction, ethyl 8-mercapto-1-naphthoate (**144**) and thiolactone **145** were formed, instead of ketone **126** (Scheme 35). The dilithium salt **143** was once again added to the mixture of **144** and **145**, which formed a mysterious compound that was revealed by X-ray crystallography to be the dimer **146** (Scheme 36). The crystal structure of compound **146** is shown in Figure 7.

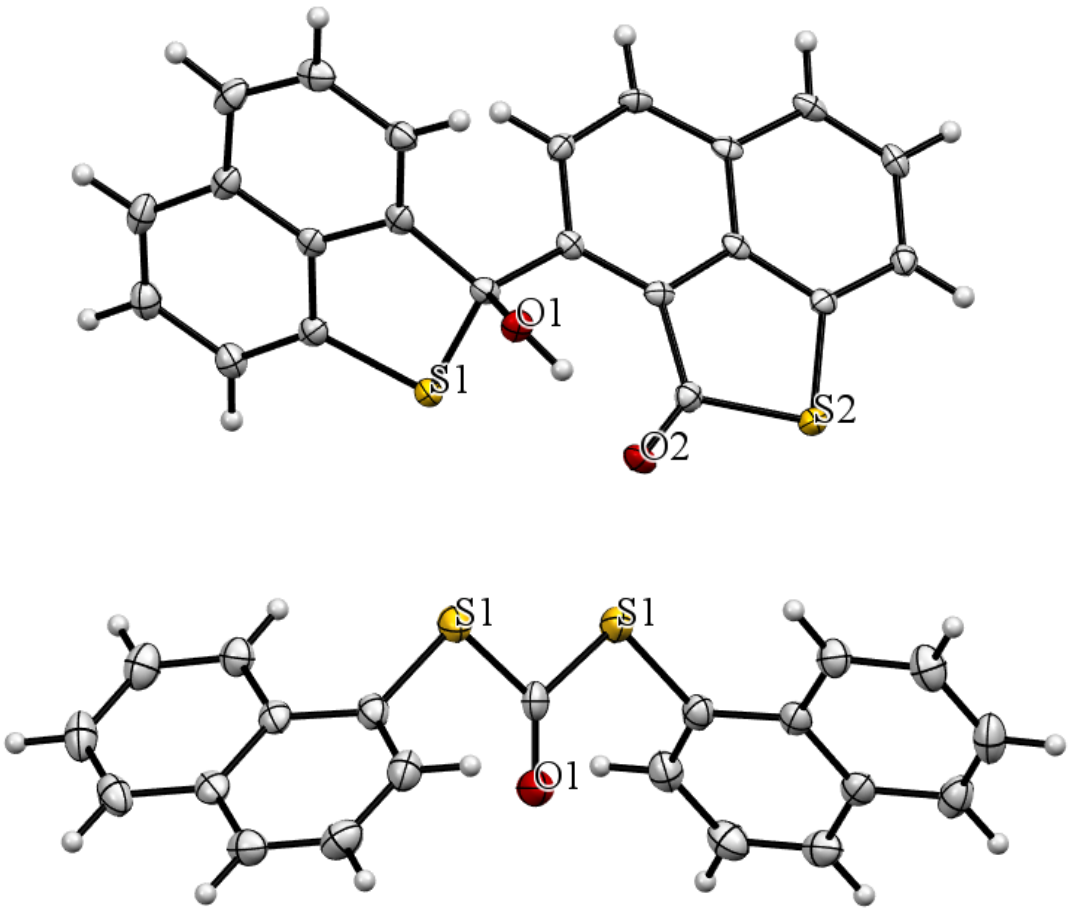
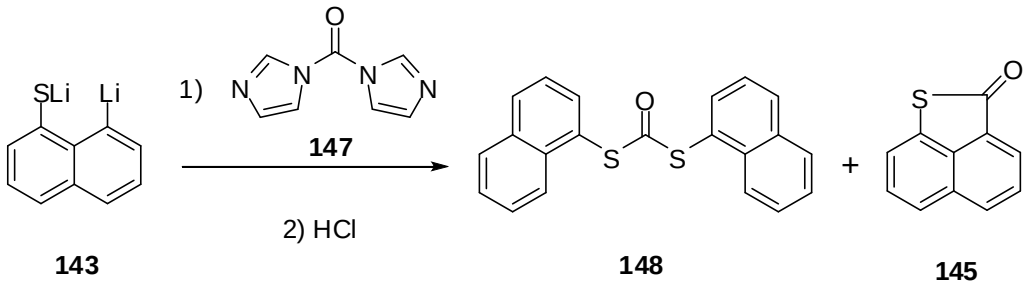


Figure 7. Molecular structure of compound **146** (top) and compound **148** (bottom); thermal ellipsoids have been drawn at the 50% probability level.

Scheme 37. Reaction of compound **143** with carbonyldiimidazole



143 **148** **145**

Similarly, by making the dilithium salt **143** first, followed by reaction with carbonyldiimidazole (**147**), it might be possible to make dithiol **126**, which might cyclize with 1,4-bis(bromomethyl)benzene (**10**) to make *in*-keto cyclophane **123**. In the actual experiment, a mixture of compound **148** and **145** was separated, instead of ketone **126** (Scheme 37). The crystal structure of compound **148** is shown in Figure 7.

1.3 Conclusion

Many attempts to synthesize *in*-keto cyclophanes **108** and **123** were made. Several important precursors were synthesized and fully characterized. However, none of the cyclization reactions gave either **108** or **123**. The nonbonded interaction between the ketone oxygen and basal benzene ring may be so close as to prevent the formation of an *in*-keto cyclophane.

Chapter 2: Sterically Congested Macrobicycles

2.1 Introduction

A bicyclic molecule is a molecule that features two fused rings. There are three kinds of ring fusions. They can be fused across a bond between two atoms, as in decalin (**150**), which has a C-C bond shared between two cyclohexane rings. They can also be fused across a sequence of atoms, as in norbornane (**151**), which can be viewed as a pair of cyclopentane rings that share three of the five carbon atoms. Fusion can also happen at a single atom to form spiro compounds, such as spiro[5.5]undecane (**152**), which has a carbon atom shared between two cyclohexane rings (Figure 8).

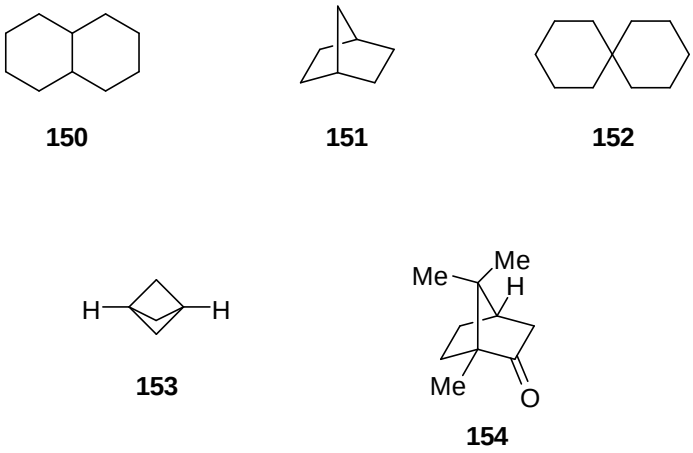
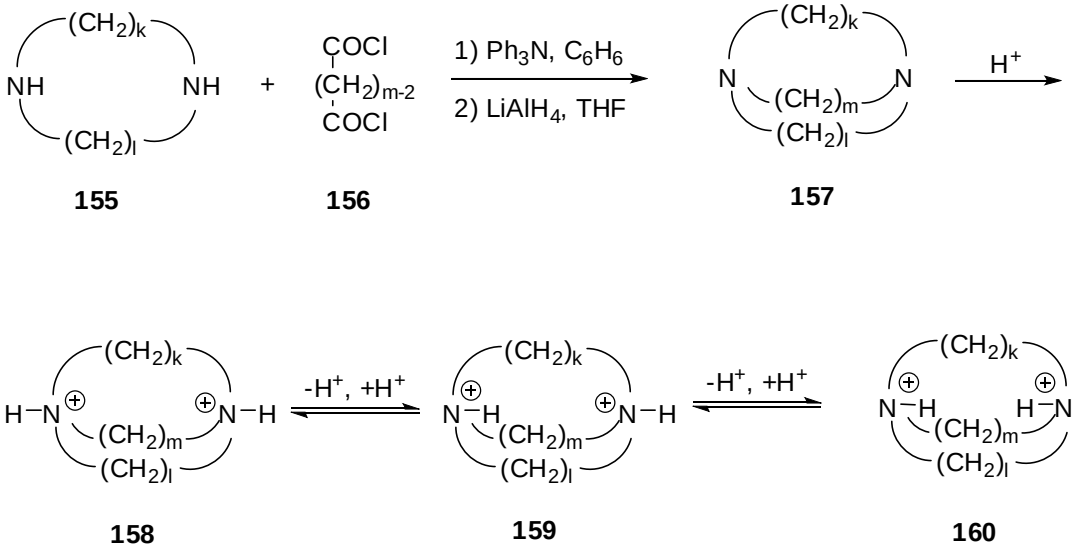


Figure 8. Examples of bicyclic molecules

Usually bridgehead substituents point outward in common, small, bridged bicyclic compounds. Representative examples are bicyclo[1.1.1]pentane (**153**) and camphor (**154**).

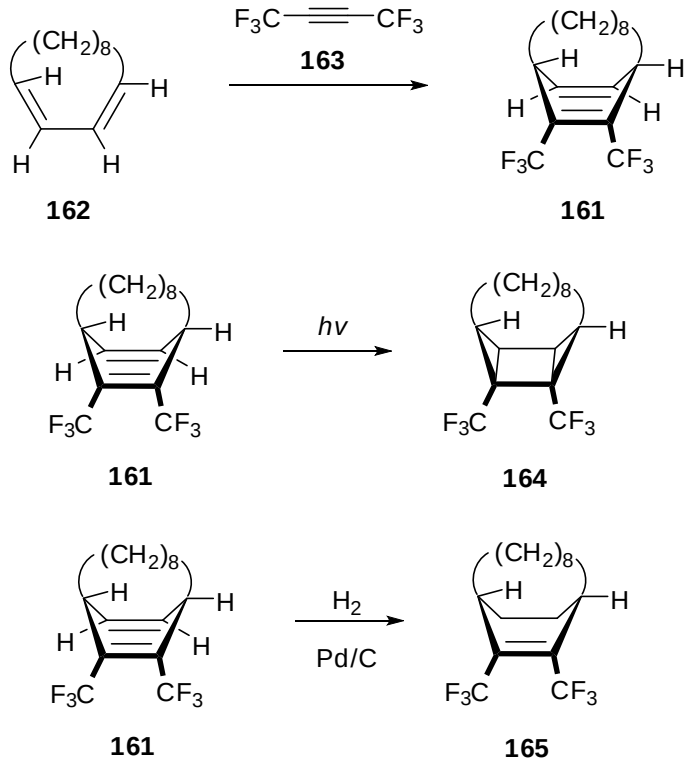
This was thought to be always true until macrocyclic diammonium ions were prepared by Simmons and Park in 1968.[38][39][40][41] The bridgehead nitrogen atoms show *in* and *out* configurations and nitrogen inversion appeared to occur in [8.8.8]-**157**, with an activation energy of 7.7 kcal/mol and $k = 1.4 \times 10^7$ sec^{-1} at 25 ℃ (Scheme 38).

Scheme 38. Macrocyclic diammonium ions prepared by Simmons and Park

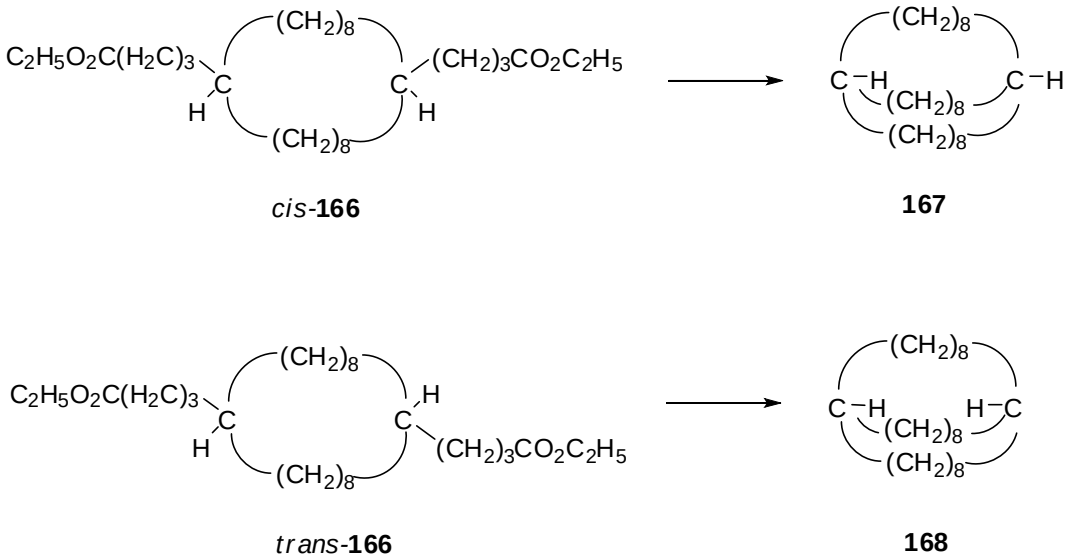


The earliest compounds with *in*-CH bridgeheads were reported simultaneously by Gassman and Thummel,[42][43] and by Park and Simmons,[44] using different approaches. Gassman and Thummel made compound **161** by Diels-Alder reaction of *cis,trans*-1,3-cyclodecadiene (**162**) and the powerful dienophile hexafluoro-2-butyne (**163**). Intramolecular 2+2 cycloaddition of **161** gave compound **164**. Catalytic hydrogenation of **161** yielded compound **165**, in which the disubstituted double bond was reduced with the tetrasubstituted double bond unchanged (Scheme 39).

Scheme 39. Preparation of compound **161** and its reactions

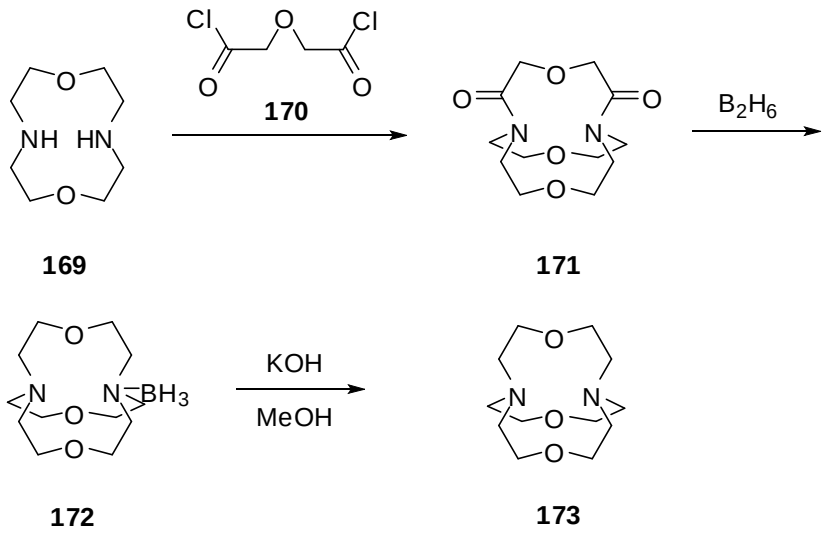


Scheme 40. Synthesis of *in,out*- and *in,in*- bicyclo[8.8.8]hexacosane



In quite a different approach, Park and Simmons used the acyloin condensation of *cis*- and *trans*- isomers of **166** to obtain *in,out*- and *in,in*- bicyclo[8.8.8]hexacosane (**167** and **168**, respectively) (Scheme 40).

Scheme 41. Synthesis of cryptand **173**

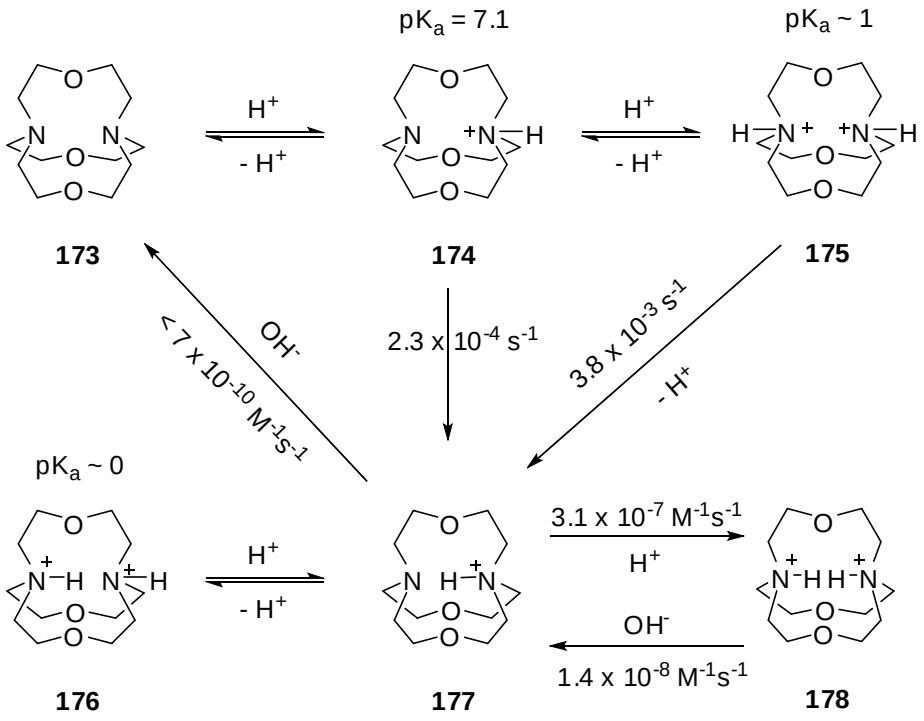


The first small molecule with both nitrogen lone pairs pointing *in* is cryptand **173** made by Cheney et al. in 1978.[45] It was made by condensation of cyclic diamine **169** with diglycolic acid dichloride (**170**), followed by reduction with diborane and treatment with KOH (Scheme 41). Cryptand **173** presents very unusual proton transfer properties; it was the thermodynamically strongest and kinetically slowest base known at that time.[46]

The structure of the cryptand **173** and its inside protonated species **177** and **178** have been determined by X-ray analysis.[47] The N-H bond lengths in **177** and **178** are 0.916

and 0.844 Å respectively, which suggested that N-H in **178** is stronger than **177**. Also, **178** possesses a highly symmetrical structure and leaves no possibilities for the attack of nucleophiles and electrophiles, which makes it suitable for the fixation of tritium (Scheme 42).

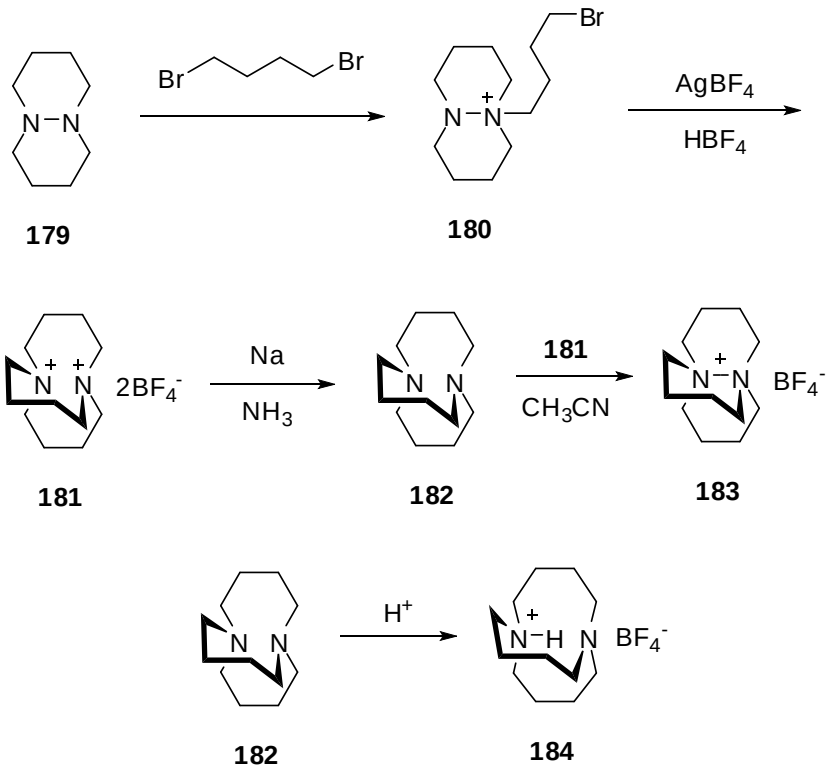
Scheme 42. Protonation and deprotonation of cryptand **173** and its derivatives



The smaller *in,in* diamine **182** was made by Alder and coworkers at 1979.[48][49] It was made by alkylation of 1,6-diazabicyclo[4.4.0]decane (**179**) with 1,4-dibromobutane, followed by cyclization with $AgBF_4$ in 40% aqueous HBF_4 and reduction with Na/NH_3 solution. Diamine **182** and dication salt **181** react stoichiometrically in CH_3CN to give

183, which is stable for months in organic or aqueous solution without base. Inside protonation of **182** is thermodynamically favorable but kinetically difficult; *in*-monoprotonated ion **184** was formed in moderately strongly acidic media for more than a week. The inside protonated ion **184** is extraordinarily inert to deprotonation or further protonation (Scheme 43).

Scheme 43. Synthesis of *in,in* diamine **182** and its reactions



Diamines (**185**-**190**) with even shorter linkers were also made.[50][51][52][53][54][55][56] However, the nitrogen atoms in these molecules point barely *in* (Figure 9).

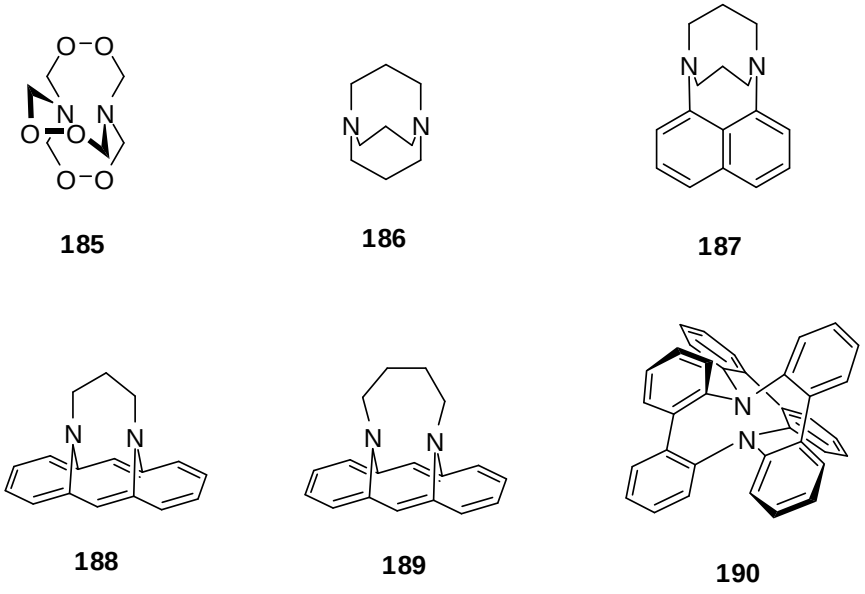
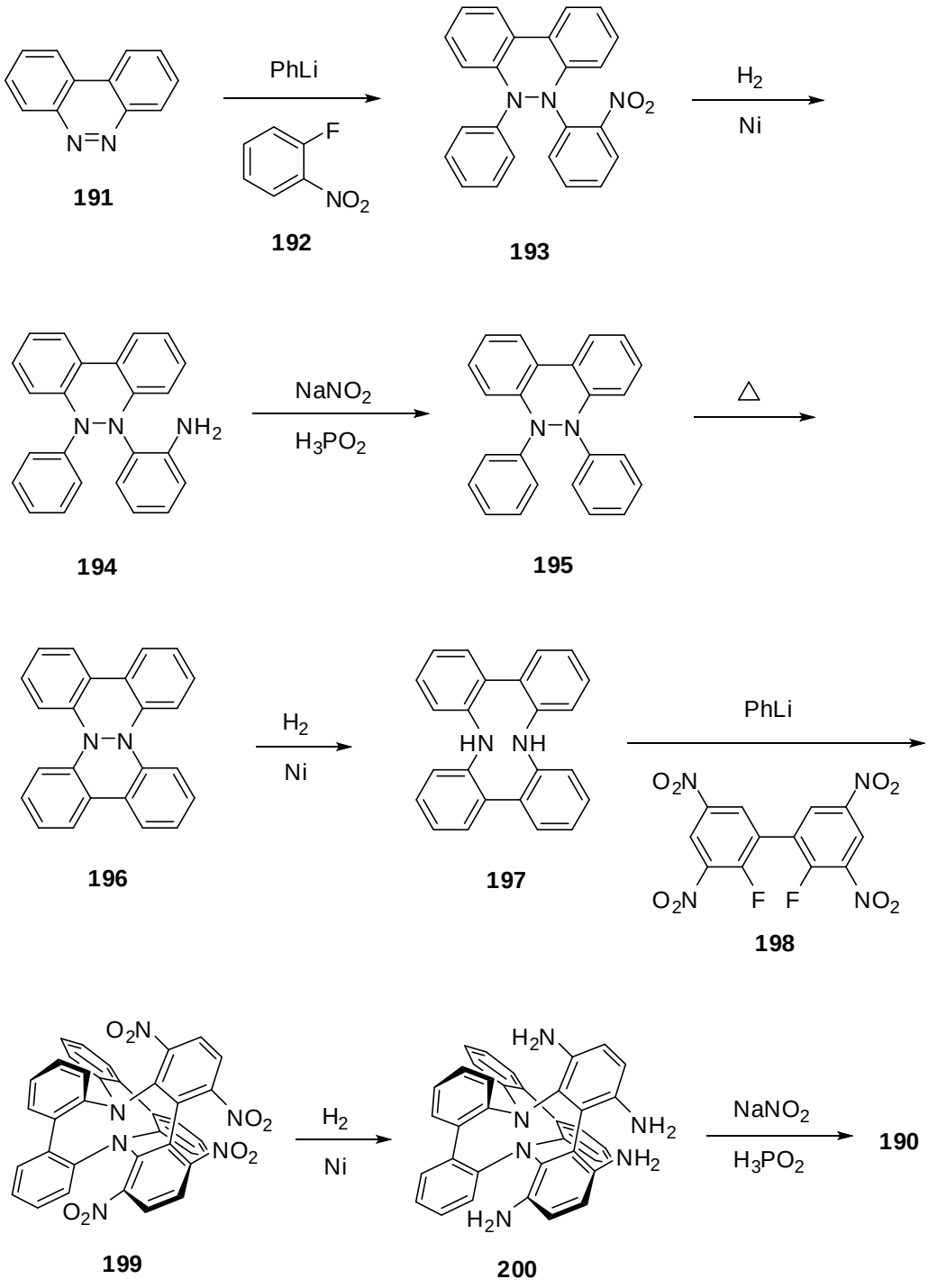


Figure 9. Other *in,in* diamines.

The most interesting molecule is the triphenylamine double decker **190** made by Neugebauer and Kuhnhaeuser in 1985. The reaction of the dilithium salt of **197** with **198** gave precursor **199**. Catalytic hydrogenation with Raney nickel and H_2 gave **200**, which was immediately diazotized in phosphinic acid to give the triphenylamine double decker **190** (Scheme 44). ^{1}H NMR showed that the aromatic protons were shielded and the nitrogen is nearly planar. The N---N nonbonded contact in this propeller molecule is about 2.5 Å.

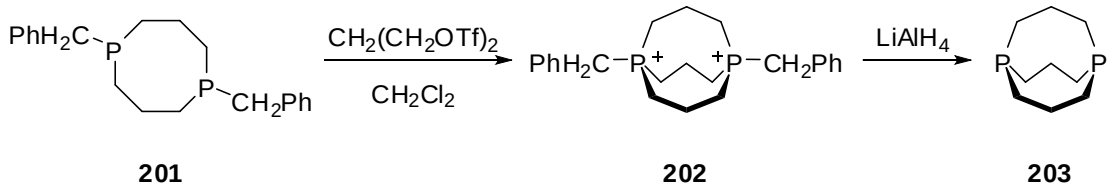
Scheme 44. Synthesis of triphenylamine double decker **190**



A very limited number of interactions involving phosphorus have been studied. Most

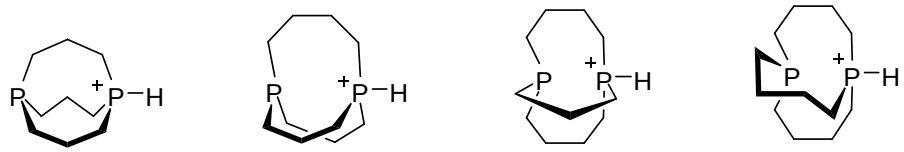
of these molecules contain *out*-P.[57] Alder et al. made *out,out*-diphosphine **203** by mixing solutions of **201** and $CH_2(CH_2OTf)_2$ in CH_2Cl_2, followed by debenzylation with $LiAlH_4$ (Scheme 45).[58]

Scheme 45. Synthesis of *out,out*-diphosphine **203**

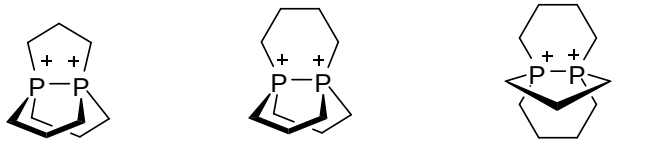


201 **202** **203**

203 **204** **205** **206**



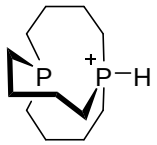
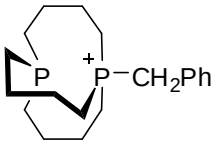
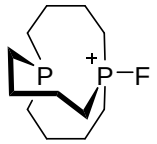
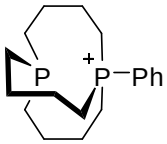
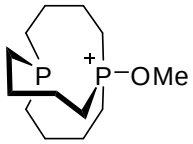
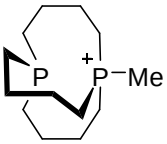
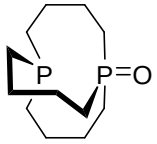
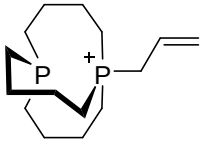
207 **208** **209** **210**



211 **212** **213** **214**

Figure 10. Diphosphines, protonated diphosphines and diphosphonium dications made by Alder et al.

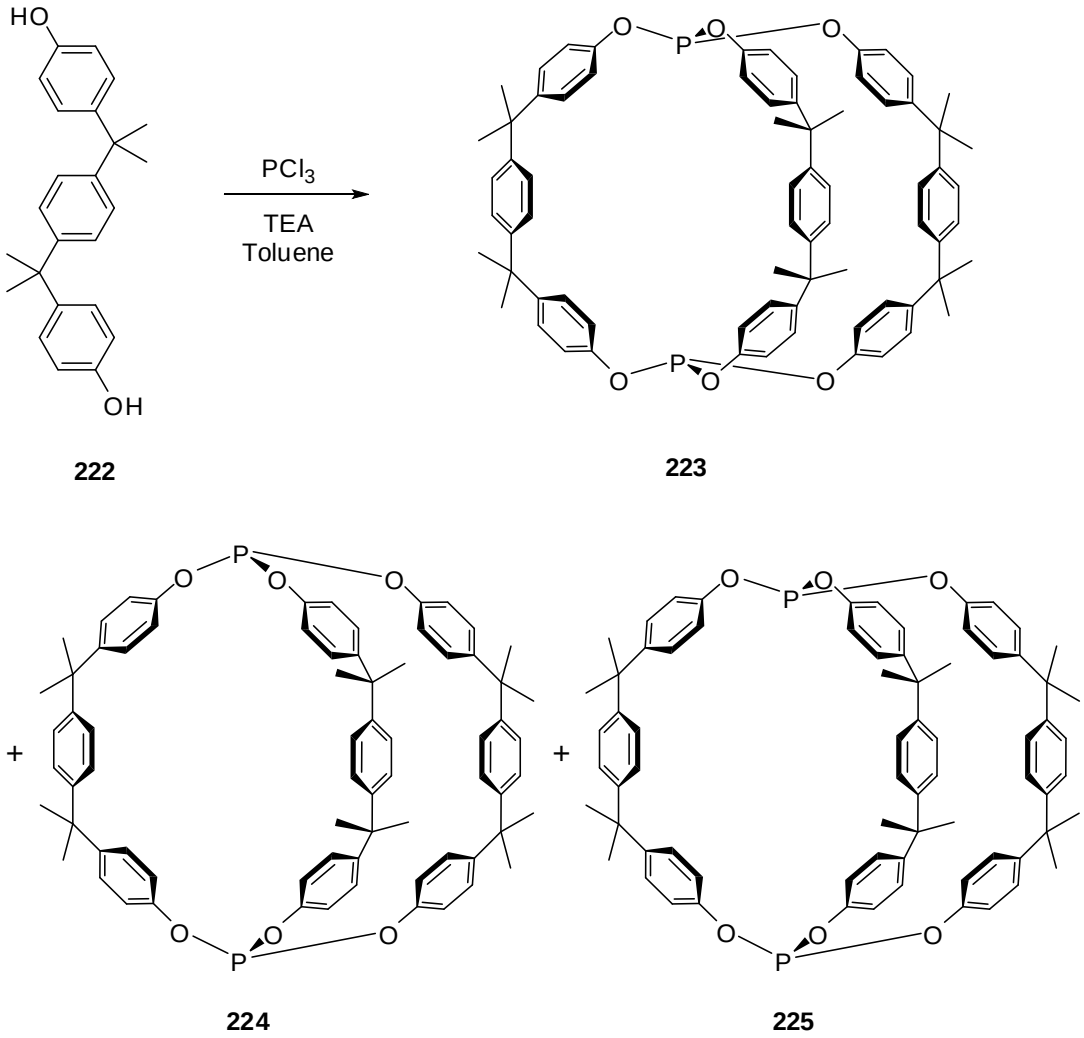
Table 2. P-P coupling constants in *in,out*-adducts

Adduct	J_{PP}/Hz	Adduct	J_{PP}/Hz
 **210**	178	 **218**	46
 **215**	198	 **219**	46
 **216**	139	 **220**	57
 **217**	108	 **221**	67

They also made various other diphosphines (**203**-**206**), all of which display *out,out*-isomers and are extremely strong bases.[59][60][61][62] The protonation of medium-ring *out,out*-bisphosphines can give remarkable *out*-protonated *in,out*-isomers (**207**-**210**). They also made a series of diphosphonium dications (**211**-**214**) in which phosphrous atoms are bonded to each other and exhibit an *in,in* conformation (Figure 10).

These diphosphonium dications undergo addition reactions with a range of nucleophiles, and these adducts may retain some P-P interactions. Examples are shown in Table 2.

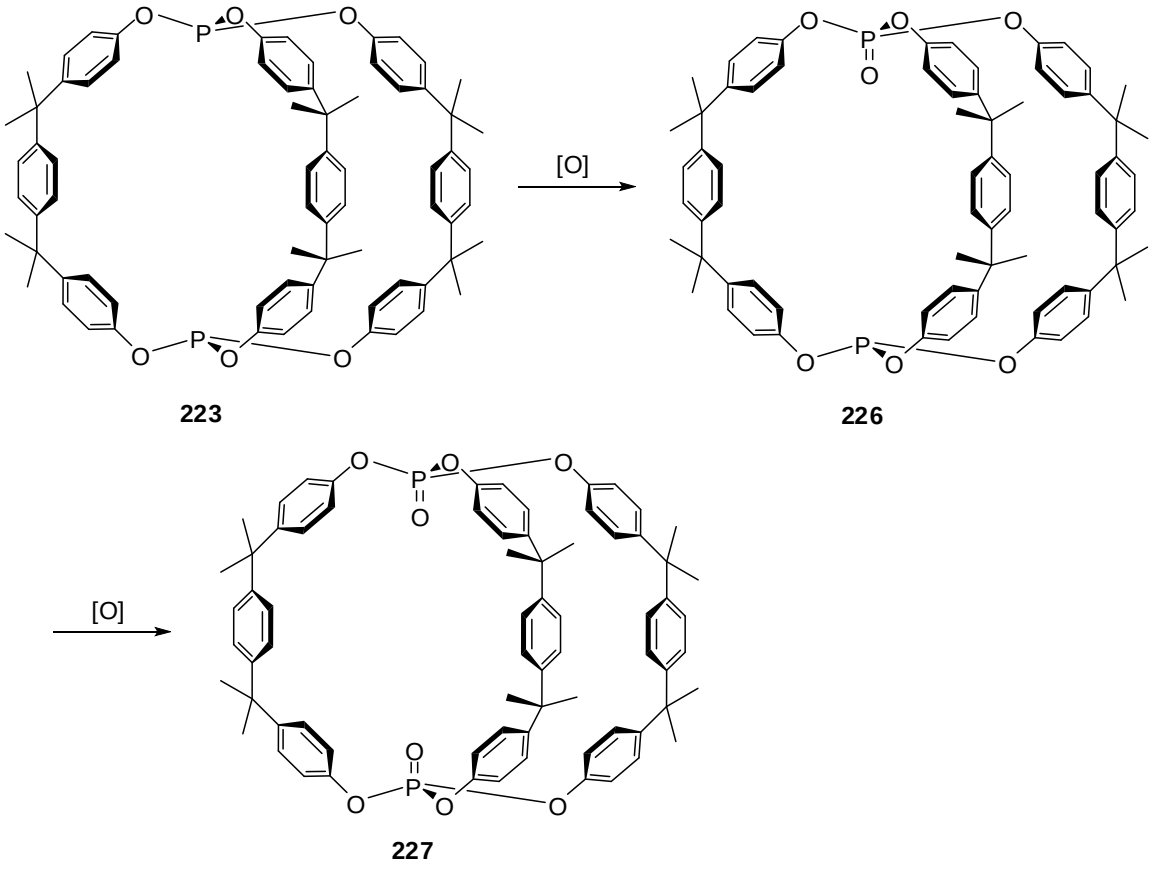
Scheme 46. Synthesis of *in,out* isomers **223**, **224** and **225**



Is there any bicyclic molecule with two phosphorous bridgehead atoms both pointing in? The answer is yes. There exist two examples of very large, macrobicyclic *in,in*-diphosphites made by Bauer et al.[63][64] The *in,in*-diphosphite **223** was made by a one-pot

tripod capping method starting from bisphenol **222** and PCl_3 in 2.9% yield, while *out,out*-diphosphite **224** and *in,out*-diphosphite **225** formed at the same time in 5% and 4.4% yield, respectively (Scheme 46).[31]P NMR showed that the *in*- and *out*-P atoms are remarkably different in chemical shift [**223**: δ 142.7 (*in*); **224**: δ 121.6 (*out*); **225**: δ 143.1 (*in*), 121.6 (*out*)]. The crystal structures of **223** and **224** revealed that compound **223** does not have C_3 symmetry in solid state. The P---P contact distances of *in,in*-isomer **223** are 8.5 Å and 8.3 Å in the two independent molecules, both are shorter than that of the *out,out*-isomer **224** (10.5 Å).

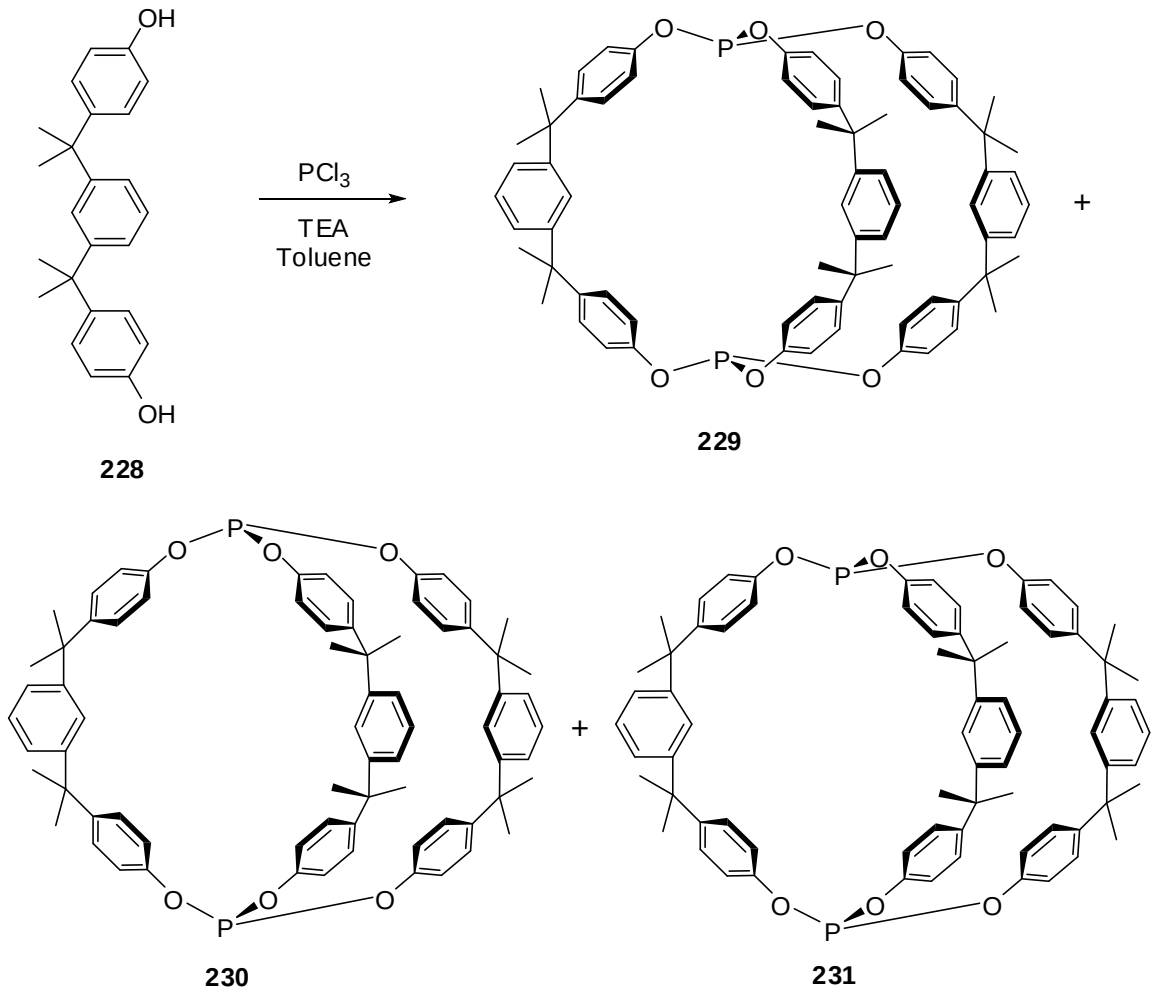
Scheme 47. Oxidation of *in,in*-diphosphite **223**



223 **226** **227**

The *in*-P atoms have a decreased reactivity, and they are more slowly oxidized by cumene hydroperoxide than *out*-P atoms (Scheme 47). The *in,in*-isomer **223** was most slowly oxidized, when compared with *out,out*-isomer **224** and *in,out*-isomer **225**. ^{31}P NMR of **226** showed two peaks at δ 141.9 and -12.3, while **227** showed only one peak at δ -12.7, about 7 ppm downfield from the *out*-phosphate oxide.

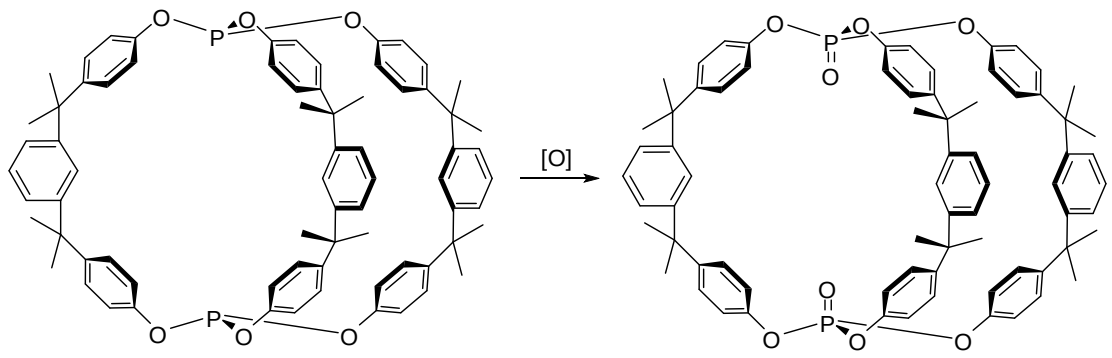
Scheme 48. Synthesis of *in,out* isomers **229**, **230** and **231**



228 **229** **230** **231**

The other *in,in*-diphosphite **229** was made by a similar method starting from bisphenol **228** and PCl_3 in 3% yield, while *out,out*-diphosphite **230** and *in,out*-diphosphite **231** formed at the same time in 6% and 10% yield, respectively (Scheme 48). ^{31}P NMR resonances are in the same range as in **223**-**225**. The crystal structure showed that the P---P contact distances of the *in,in*-isomer **229** are 4.47 Å and 5.33 Å in the two independent molecules, whereas the distance in *out,out*-isomer **230** is only 4.94 Å due to distortion. Oxidation of *in,in*-isomer **229** with cumene hydroperoxide is faster than **223**, which means that the lone pairs can point more or less out of the cavity (Scheme 49).

Scheme 49. Oxidation of *in,in*-diphosphite **223**



229 **232**

2.2 Results and Discussion

2.2.1 *In,in*-Diphosphine

Can the lone pair of two phosphorous atoms point into each other in a smaller molecule? If so, how close will the P---P nonbonding contact distance be? How reactive will they be compared with cyclophanes **40**,[65] **223**[66] and **234**[67] previously made in our lab (Figure 11)?

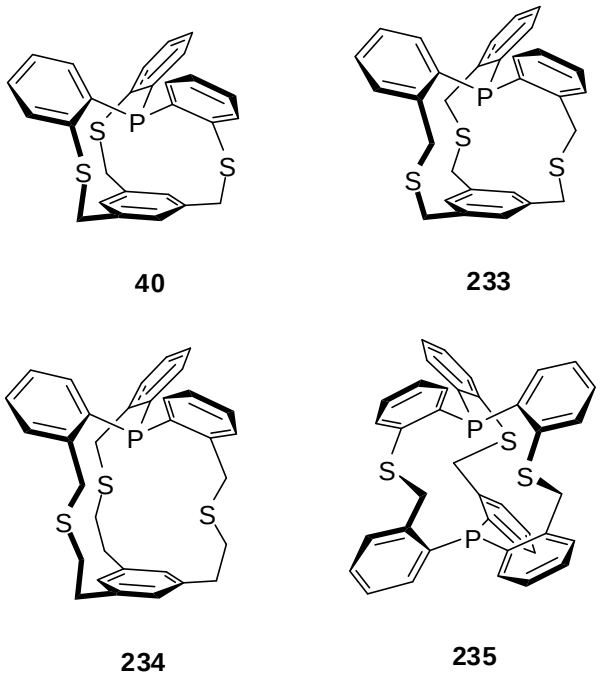
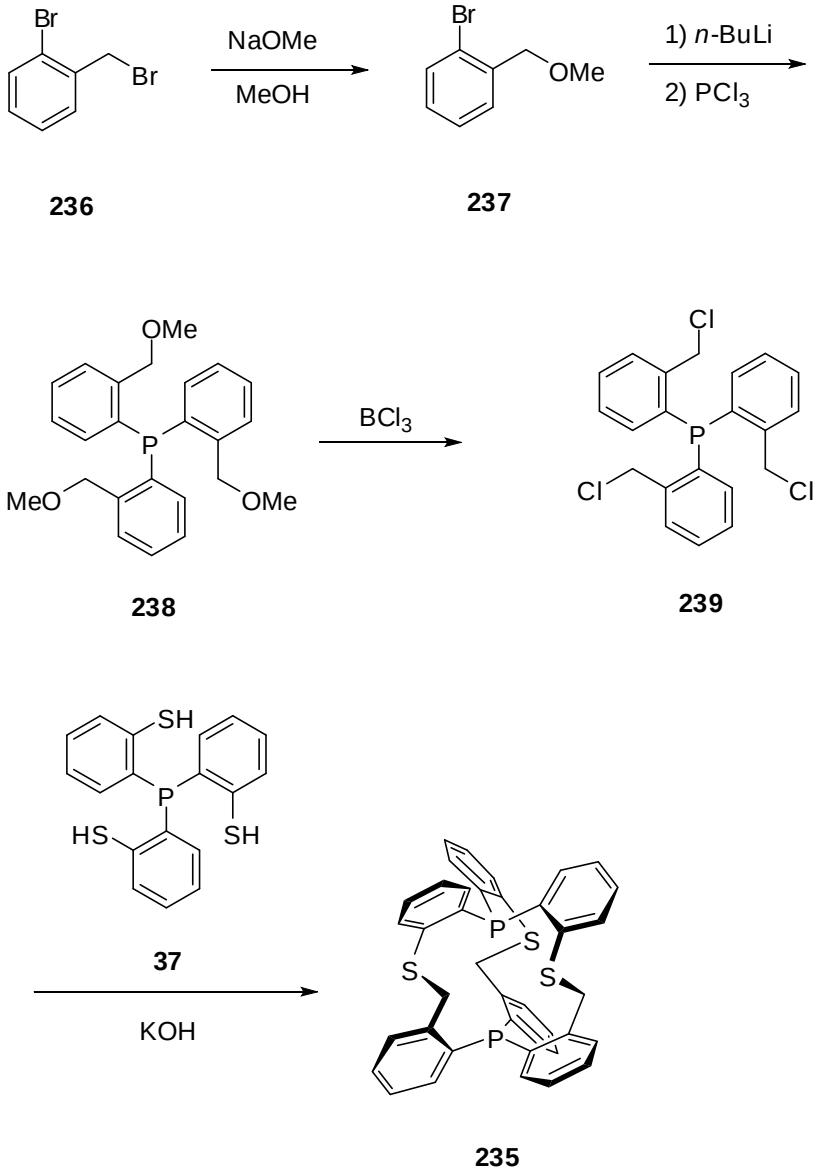


Figure 11. Cyclophanes previously made in Pascal's lab (**40**, **233**, **234**) and the proposed target molecule (**235**)

B3PW91/6-31G(d) calculations showed that diphosphine **235** would likely possess only high-energy *out,out*- and *in,out*-isomers, thus permitting the study of face-to-face,

interacting phosphines. The *in,in*-diphosphine **235** is more than 18 kcal/mol lower in energy than either *in,out*-isomer, and fully 30 kcal/mol lower than the *out,out*-isomer, therefore the *in,in*-isomer is the expected product of synthesis.

Scheme 50. Synthesis of *in,in*-diphosphine **235**



The synthesis of *in,in*-diphosphine **235** is shown in Scheme 50. 2-Bromobenzyl bromide (**236**) was reacted with sodium methoxide to get 1-bromo-2-(methoxymethyl)benzene (**237**). Compound **237** was treated with *n*-BuLi to form the anion and then reacted with phosphorus trichloride to give tris[2-(methoxymethyl)phenyl]phosphine (**238**), which was then treated with boron trichloride to form tris[2-(chloromethyl)- phenyl]phosphine (**239**).[68] Tris(2-mercaptophenyl)phosphine (**37**) was made by treating thiophenol with two equivalents of *n*-BuLi to form the dianion, followed by reaction with phosphorus trichloride.[69][70] Trichloride **239** and trithiol **37** was subjected to base induced cyclization at high dilution to provide *in,in*-diphosphine **235** in 10% yield.

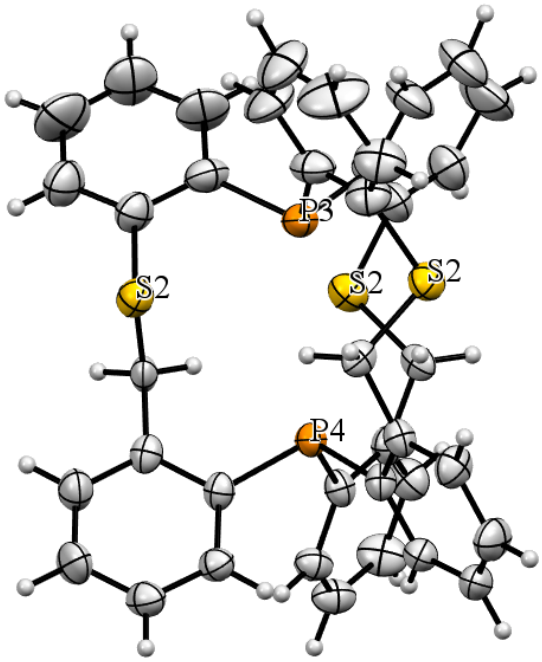


Figure 12. Molecular structure of *in,in*-diphosphine **235**; 50% thermal ellipsoids have been employed.

Single crystals of compound **235** suitable for X-ray analysis were obtained from $CHCl_3$-MeOH. The structure contains two independent molecules, each with crystallographic C_3 symmetry. The molecular structure of one of these is illustrated in Figure 12. As expected, the diphosphine adopts an *in,in*-conformation, with P---P nonbonding contact distances of 3.72 Å and 3.58 Å in the two independent molecules, both somewhat shorter than the calculated distance of 3.79 Å at the B3PW91/6-31G(d) level, as DFT methods commonly overestimate the contact distances in stained cyclophanes.[71]

Are there any interactions between the two phosphorus atoms pointing to each other? The answer is yes! The ^{31}P NMR spectrum shows a pair of doublets with J_{PP} = 175 Hz (Figure 13), comparable to the J_{PP} = 178 Hz for compound **210**, where the P---P contact distance is only 2.58 Å. Spectroscopic data reveal strong spin-spin coupling between the phosphorus atoms and the diastereotopic methylene protons (J_{PH} = 3 Hz at δ 4.06 and J_{PH} = 5 Hz at δ 5.16, respectively) and the methylene carbons (J_{PC} = 32 Hz, 2 Hz at δ 43.4).

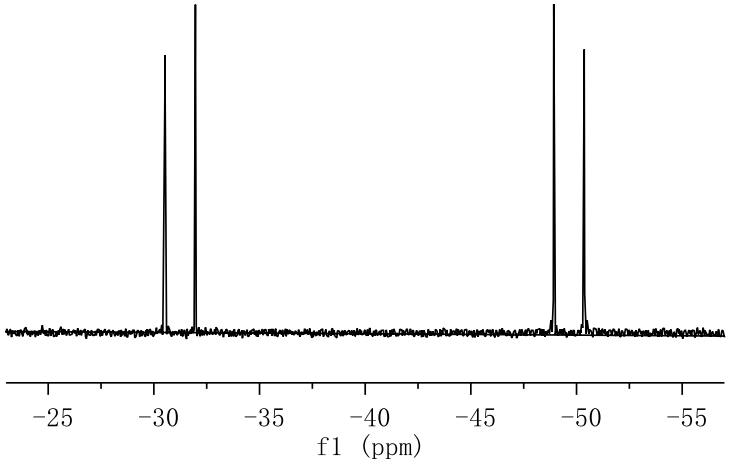


Figure 13. Proton-decoupled ^{31}P NMR spectrum of compound **235**.

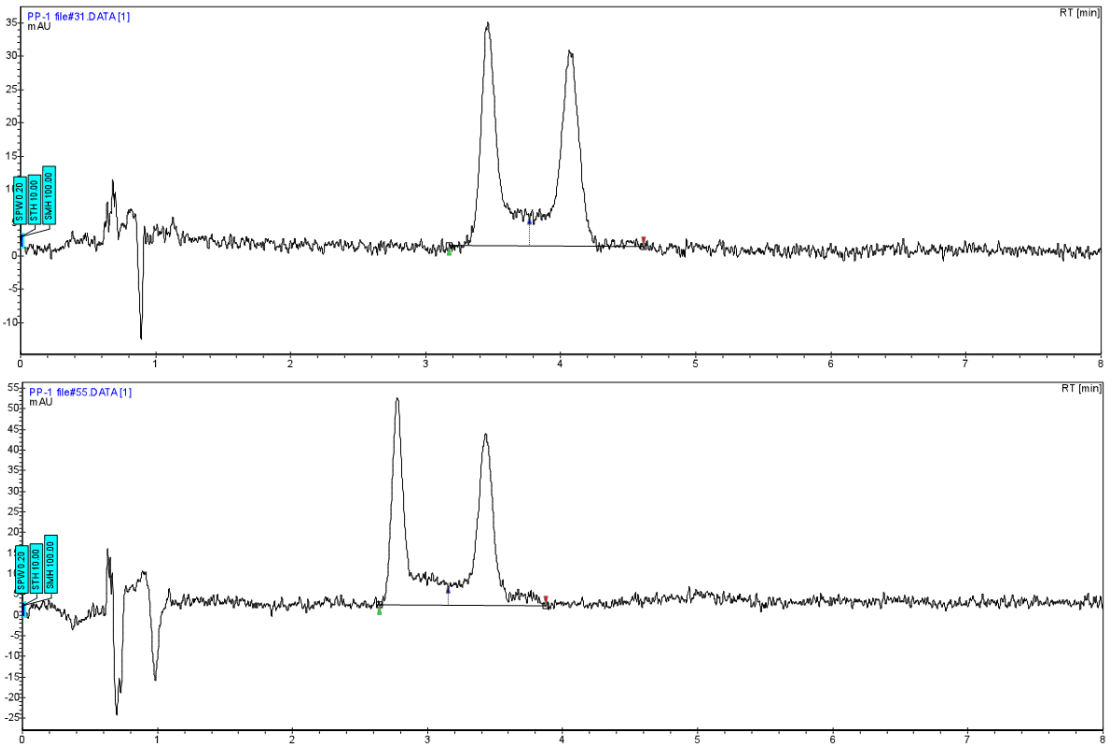
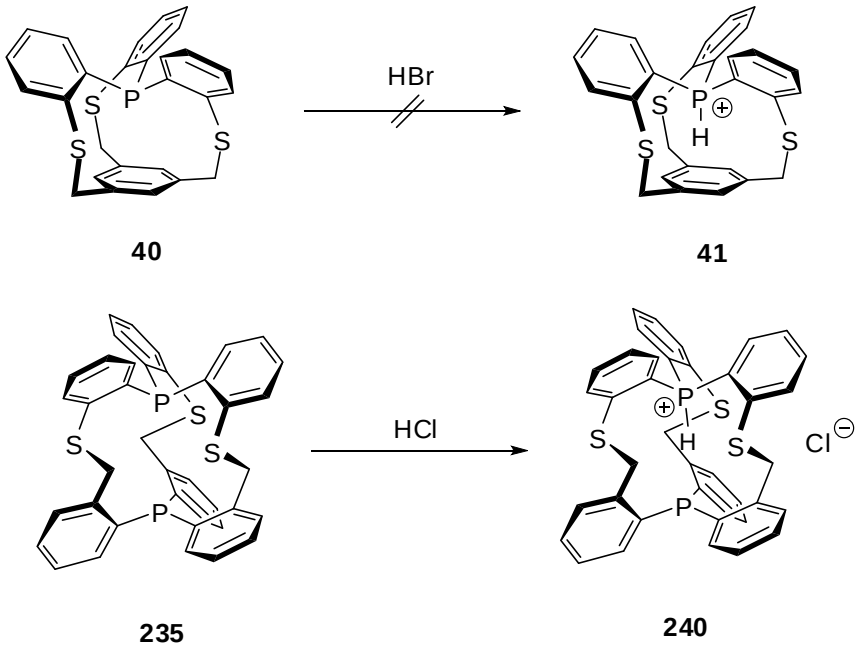


Figure 14. Resolution of Compound **235** by Chiral Supercritical Fluid Chromatography. (1) Chiralpak IA (15 cm × 0.46 cm), 40% ethanol (0.1% diethylamine)/CO_2, 3 mL/min, 220 nm (Top); (2) Chiralpak IA, (15 cm × 0.46 cm), 40% isopropanol (0.1% diethylamine)/CO_2, 3 mL/min, 220 nm (Bottom).

Compound **235** is a chiral molecule with twin molecular propellers. The barrier to racemization of diphosphine **235** can not be determined by dynamic NMR methods as a result of the high barrier, which was indicated by no coalescence or even broadening of its diastereotopic methylene resonances at δ 4.06 and δ 5.16 in high temperature ^{1}H NMR spectra.[72][73] The enantiomers were resolved by using supercritical fluid chromatography (SFC) on a Chiralpak IA column with both EtOH/CO_2 and *i*PrOH/CO_2 as mobile phases. However, both chromatograms show a "bridge" between the two enantiomer peaks (Figure 14), indicating that significant racemization occurs during the separation. Using the dynamic chromatography method of Trapp,[74] the barrier is calculated to be 20.7 kcal/mol from a resolution in EtOH/CO_2 and 20.6 kcal/mol from a resolution in *i*PrOH/CO_2 at 22 ℃, which corresponds to a half-life of about 7 min. Therefore, it is impossible to do a preparative resolution of diphosphine **235** at this temperature.

Scheme 51. Protonation reactions of cyclophane **40** and **235**



40 **41**

235 **240**

The phosphorus atom of **40** is extremely unreactive. It can not be protonated by anhydrous HBr to form compound **41**. However, when HCl gas was bubbled into chloroform solutions of compound **235**, protonation occurred and *in,in*-diphosphine hydrochloride **240** was obtained, as indicated by the new proton resonance (δ 14.08) in the ^{1}H NMR spectrum (Scheme 51). The protonation is a first-order process with half-life of 26 min, as monitored by ^{1}H NMR.

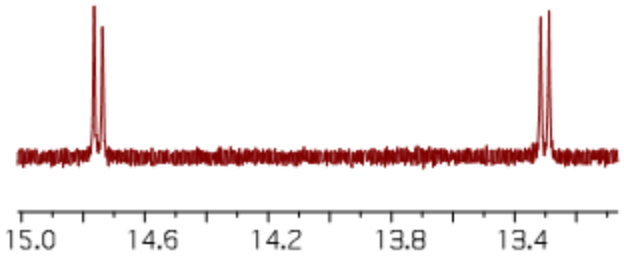


Figure 15. Low-field region of the ^{1}H NMR spectrum of compound **240**

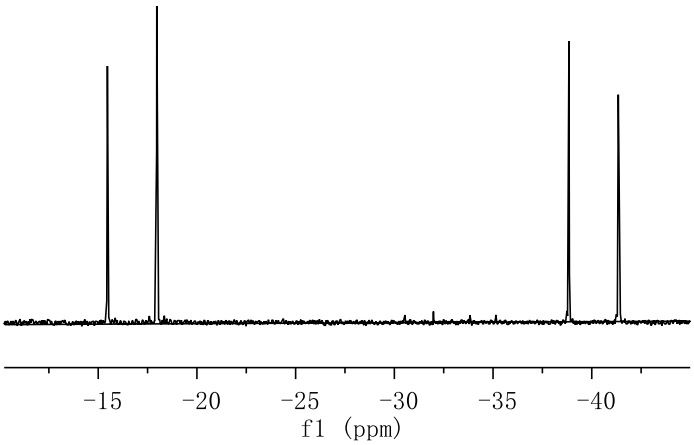


Figure 16. Proton-decoupled ^{31}P NMR spectrum of compound **240**

There are some interactions between the atoms on the central axis in **240**, similar to those in compound **235**. The new proton resonance at δ 14.08 is a doublet of doublets, with a coupling of J_{PH} = 584 Hz between the *in*-proton and the protonated phosphorous atom and a through space coupling of J_{PH} = 13 Hz between the the *in*-proton and the opposite phosphorous atom (Figure 15). This clearly indicated an asymmetric protonation of the diphosphine. The coupling between the two phosphorous atoms (J_{PP}) increased to 304 Hz (Figure 16), which is nearly double that in compounds **235** (J_{PP} = 175 Hz) and **210** (J_{PP} = 178 Hz).

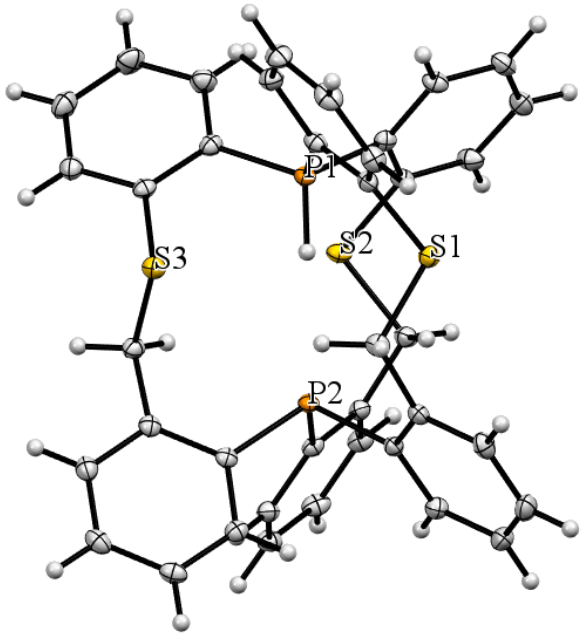
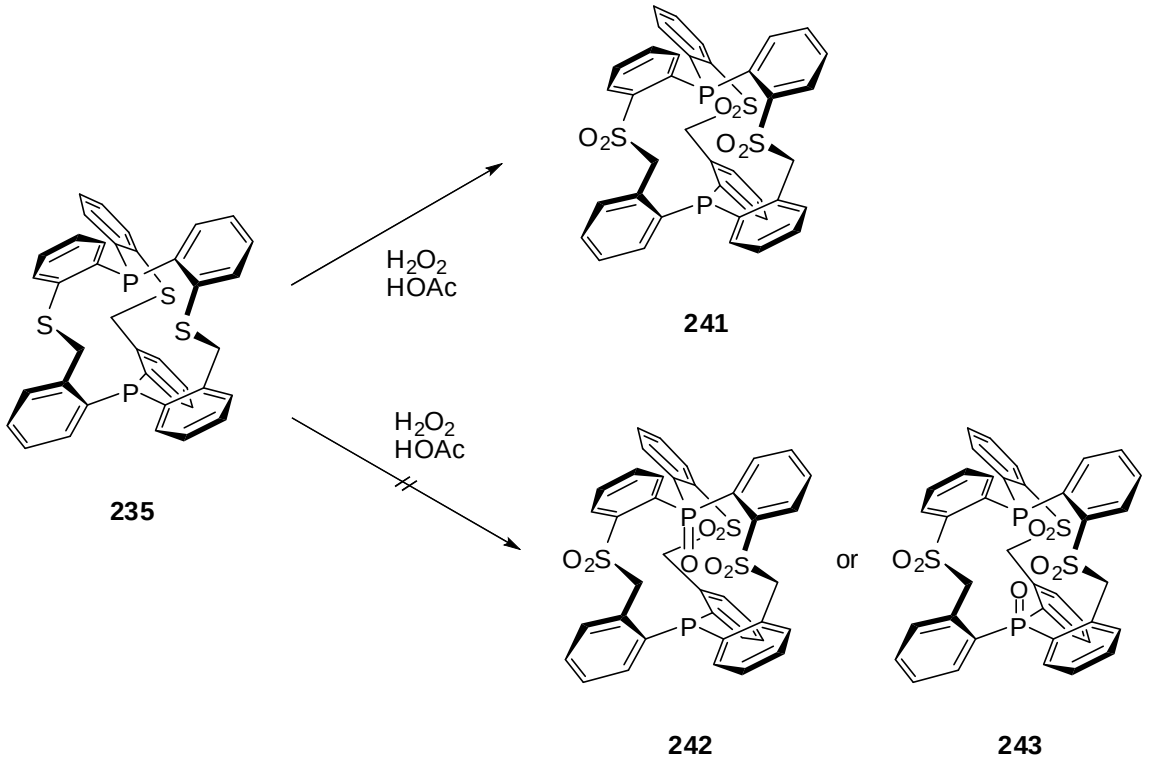


Figure 17. Molecular structure of compound **240**; thermal ellipsoids have been drawn at the 50% probability level.

Single crystals of compound **240** suitable for X-ray analysis were obtained by slow evaporation of a solution in $CHCl_3$-MeOH. The X-ray structure showed protonation on the sulfur-substituted triaryl phosphine, which is more basic due to the electron donating effect of sulfur. The proton's position was refined in the X-ray structure, with P-H bond distance of 1.29 Å and P---H nonbonding distance of 2.59 Å, which is a reasonable hydrogen bond distance. However, the P-H bond distance is likely to be underestimated, because the peak of the hydrogen electron density is displaced slightly toward the phosphorus as a result of there being no core electrons on hydrogen.[75] The actual P-H distance is probably about 1.4 Å.

Scheme 52. Oxidation reaction of *in,in*-diphosphine **235**



When compound **40** was treated with refluxing hydrogen peroxide and acetic acid, only the corresponding trisulfone **42** formed, without formation of phosphine oxide **43** (Scheme 10). As compound **235** shows higher reactivity in protonation, it would be interesting to know if it can react with hydrogen peroxide, which would insert a larger atom into the cavity.

Compound **235** was heated in a refluxing solution of acetic acid and 30% H_2O_2. Hexaoxide **241** was detected by MALDI-TOF mass spectrometric analysis without evidence of either heptaoxide **242** or **243**. Compound **235** was also heated in a refluxing

solution of THF and 30% H_2O_2, followed by a refluxing solution of acetic acid and 30% H_2O_2, but there was still no evidence of formation of a phosphine oxide (Scheme 52).

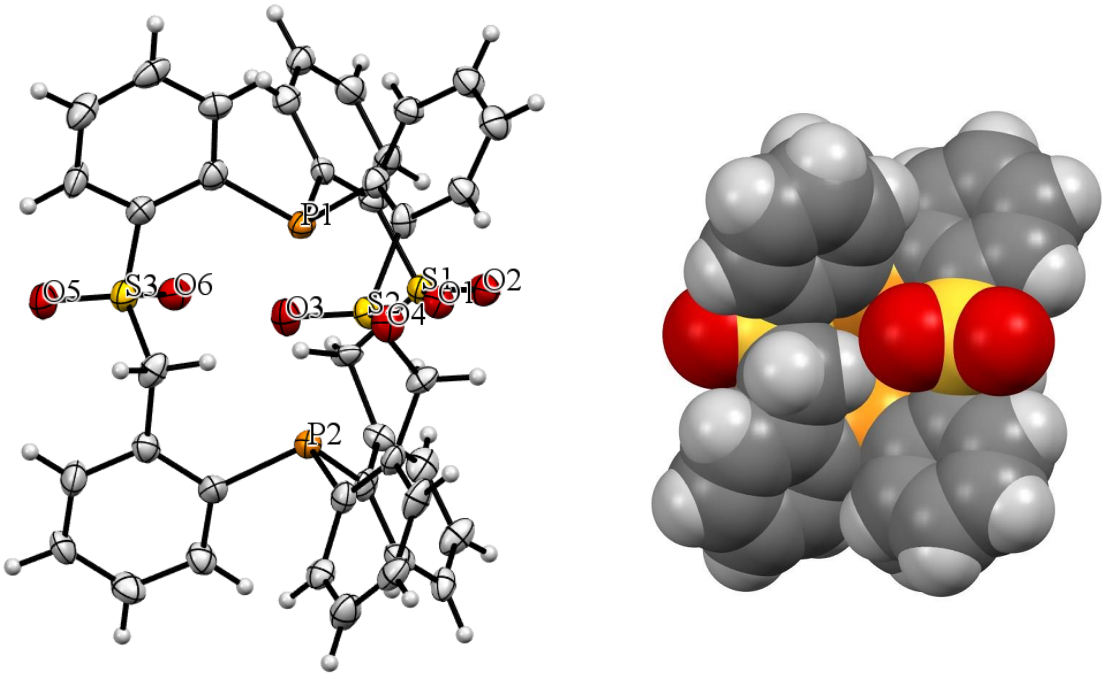
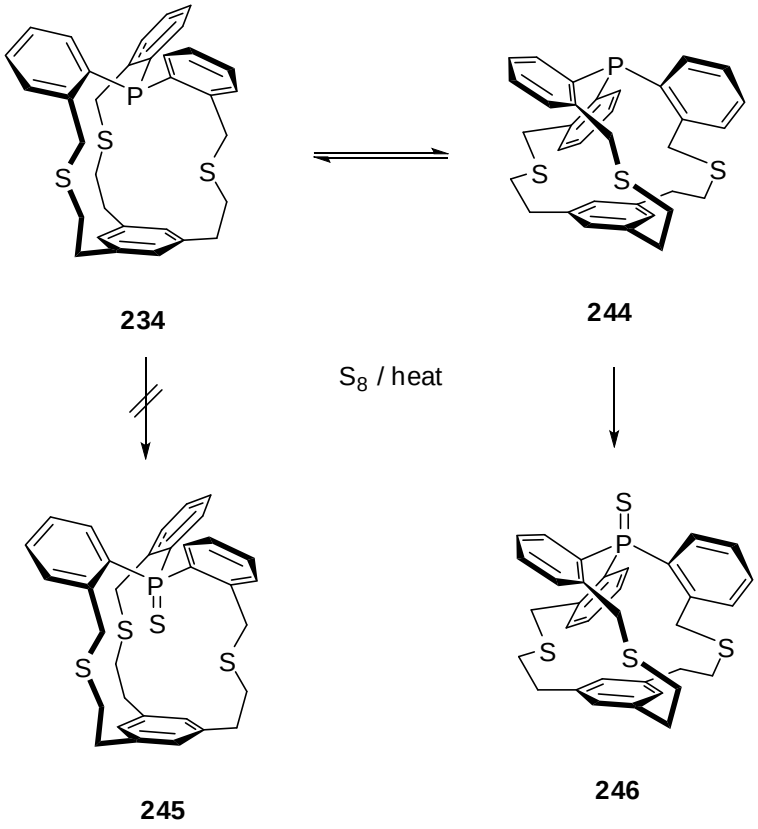


Figure 18. Molecular structure of hexaoxide **241**, 50% thermal ellipsoids have been employed in the left image; the right image is a space-filling model.

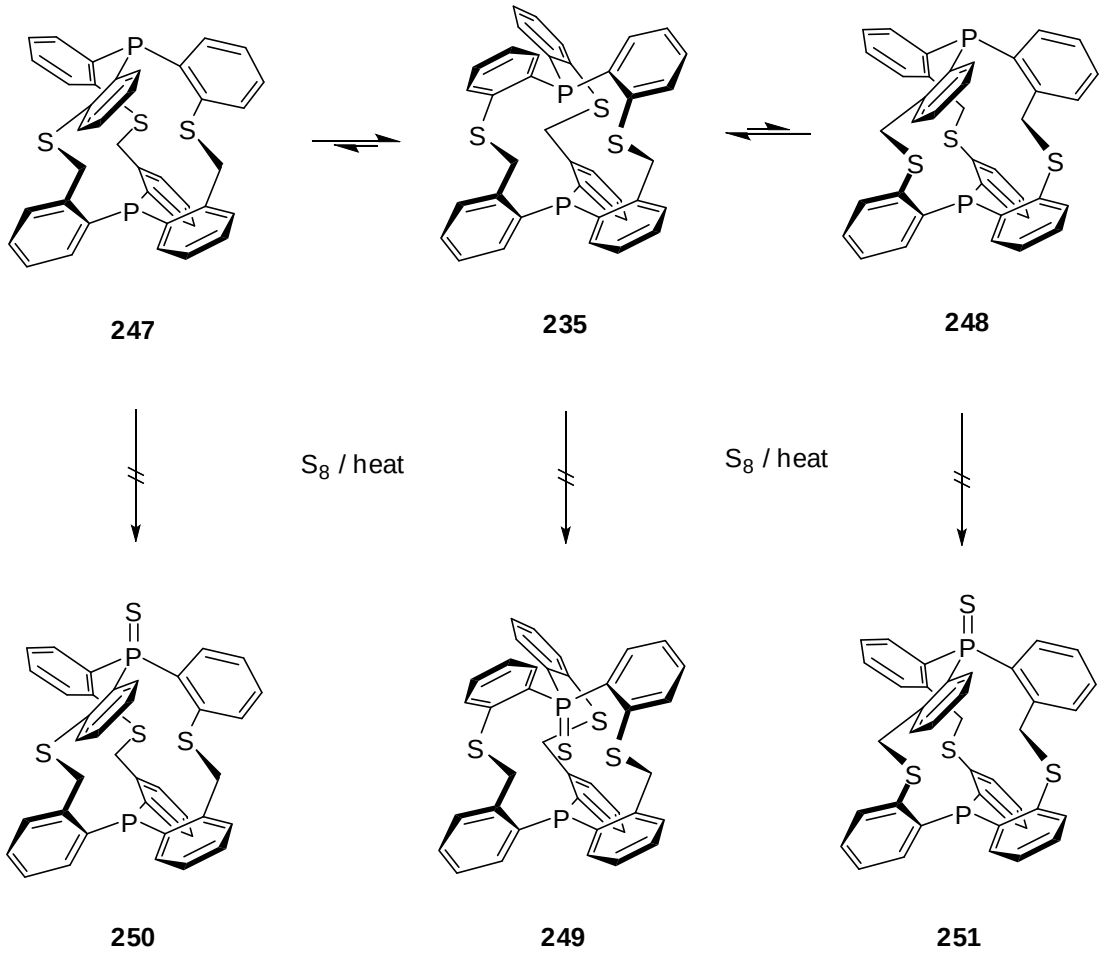
Hexaoxide **241** is a relatively insoluble compound. It was dissolved in hot DMSO and upon cooling crystals suitable for X-ray analysis was obtained. X-ray analysis confirmed that it is the trisulfone **241**. The crystal structure of compound **241** is shown in Figure 18. The distance between the inner sulfone oxygen and the nearest methylene proton is about 2.2-2.5 Å in X-ray structure. Thus, the interior phosphorous lone pairs are sterically shielded from further reactions.

Scheme 53. Sulfuration reaction of compound **234**



Phosphine **234** was made by Chen et al. in Pascal's group in 1999.[67] When it was heated at 200 ℃ for several days, which would overcome even a 40 kcal/mol barrier to inversion, no *out*-isomer **244** was produced. HF/STO-3G calculations showed that **234** is 28.0 kcal/mol more stable than **244**, so it is impossible to produce significant amounts of **244** in a simple thermal isomerization. However, when phosphine **234** was heated with sulfur in CS_2 at 185 ℃ in a sealed tube, *out*-phosphine sulfide **246** was formed rather than *in*-phosphine sulfide **245** (Scheme 53). This means that the *in*-phosphine **234** can be inverted under these conditions, and when *out*-phosphine **244** formed it reacted with sulfur to yield *out*-phosphine sulfide **246**.

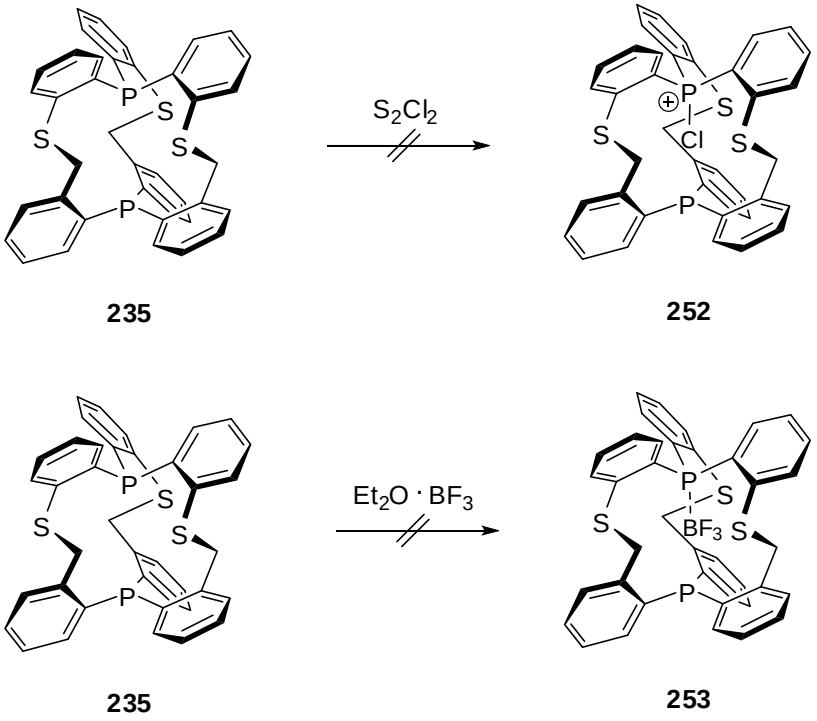
Scheme 54. Sulfuration reaction of *in,in*-diphosphine **235**



Similar *in,out*-isomerism might happen in diphosphine **235** upon heating, and compound **235** has two *in,out*-isomers (**247** and **248**). However, when **235** was heated with sulfur in CS_2 at about 180 ℃, neither the *in*-phosphine sulfide **249** nor the *out*-phosphine sulfides **250** or **251** were detected by mass spectrometric analysis. Benzene and toluene were also used as solvents for this reaction, but there was no evidence of addition of sulfur (Scheme 54). The transition states for inversion of

in,in-**235** to give each of the *in,out*-isomers was located at the B3PW91/6-31G(d) level, and the $\Delta G^{\neq}_{inv}$ for these processes were calculated to be 26.2 and 28.8 kcal/mol. This means that the formation of *out*-atom adducts would be very slow at best, and the existence of the *in,out*-isomers, which have barriers of only 8-10 kcal/mol to return to the *in,in* ground state, would be fleeting.

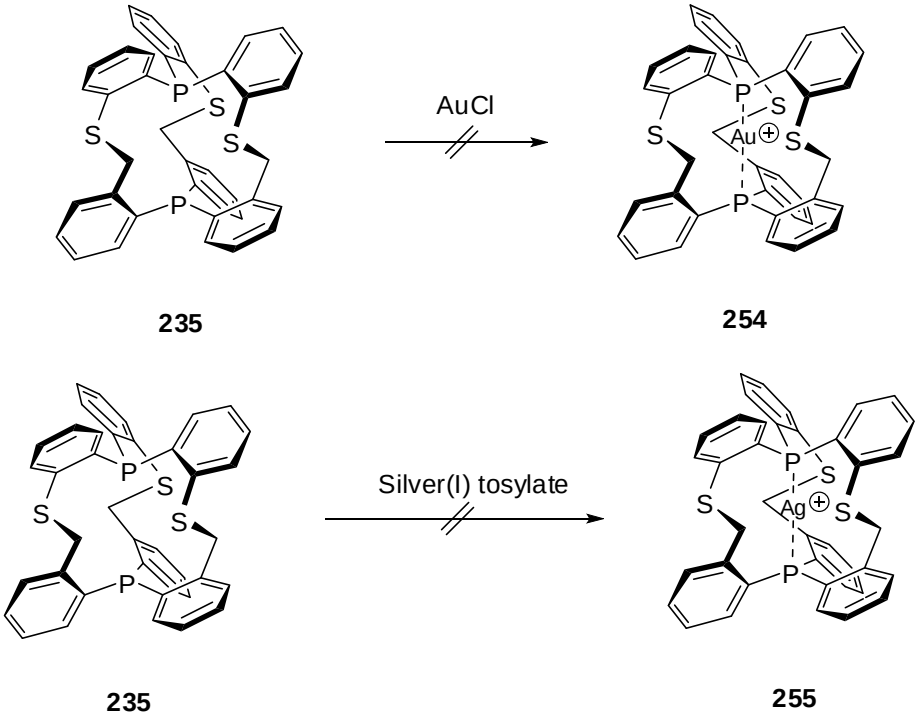
Scheme 55. Other attempted *in*-functionalization experiments



235 **252** **235** **253**

Other *in*-functionalization experiments were also attempted (Scheme 55). Compound **235** was dissolved in chloroform, to which sulfur monochloride was added, but phosphine chloride **252** was not obtained. In another attempt, compound **235** was heated with boron trifluoride diethyl etherate in chloroform, but complex **253** was not formed either.

Scheme 56. Attempted experiments with compound **235** and divalent metals



235 **254**

235 **255**

Divalent metals, such as Ag^{I} or Au^{I}, might be captured between the phosphines to form linear metal complexes **254** and **255** (Scheme 56). Compound **235** and gold(I) chloride were mixed in acetone stirred at room temperature overnight under protection of argon, but mass spectrometric analysis showed no evidence of gold addition. A similar reaction was carried out with compound **235** and silver(I) *p*-toluenesulfonate but it was also unsuccessful. It appears that the cavity is too tight for these big groups or atoms to fit inside.

2.2.2 *In,in*-Aminophosphine

The *in*-aminophane **56** was recently synthesized in the group.[76] The substitution of nitrogen for phosphorus in a triaryl-element-capped cyclophane results in reduced inward pyramidalization of the apical nitrogen, but it is just as unreactive as phosphine **40**. Interestingly, while phosphine **40** possesses distinct *in*- and *out*-conformations, aminophane **56** has only a single, low-energy conformation. This suggested the idea of making the mixed *in,in*-P,N cyclophanes **256** or **257** (Figure 19). They have both nitrogen and phosphorus pointing inward towards each other, which may result in some interesting properties.

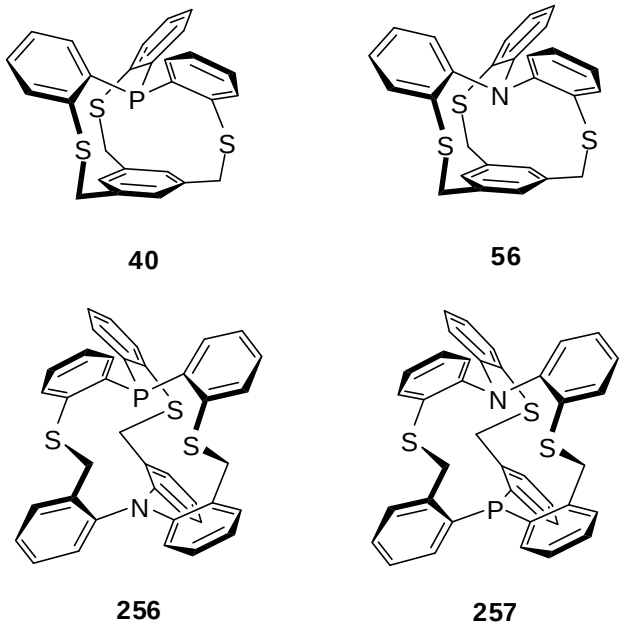
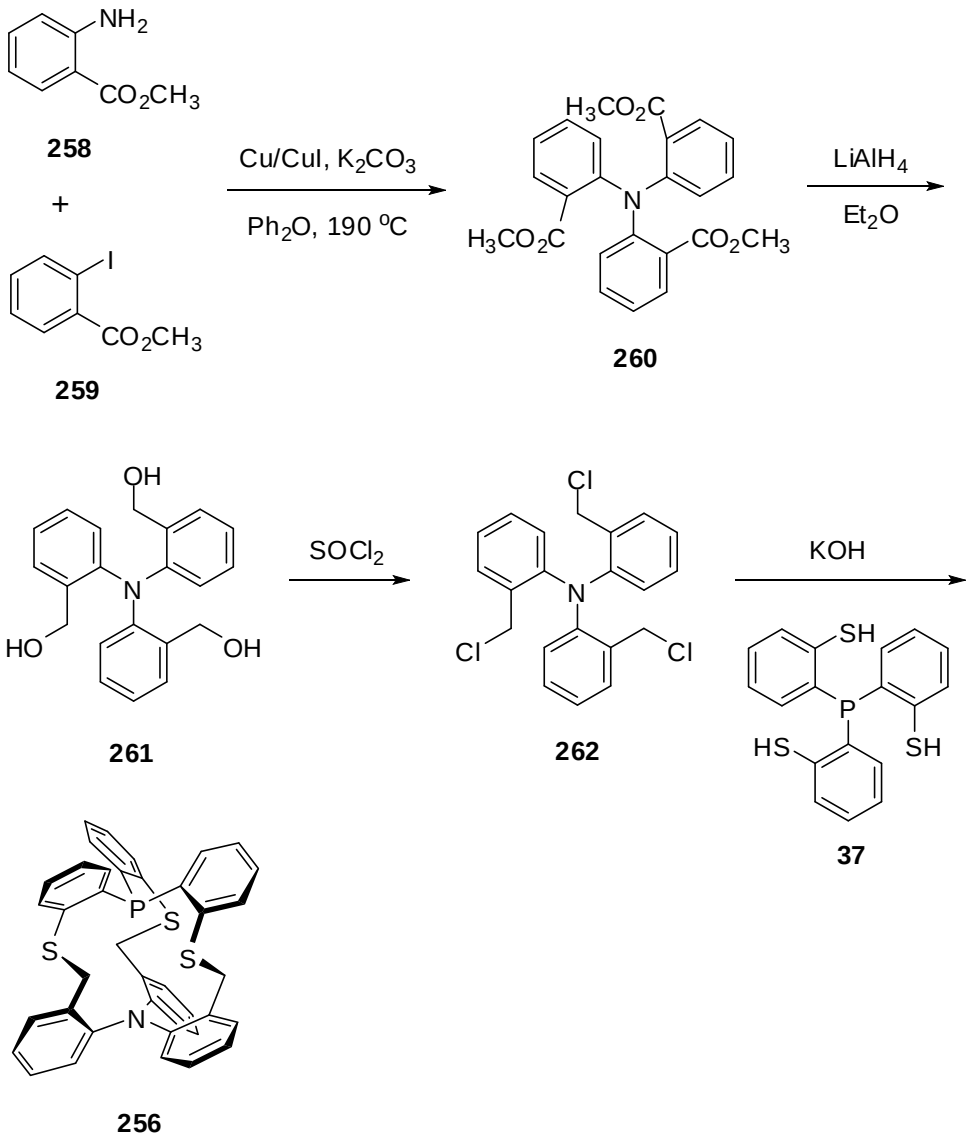


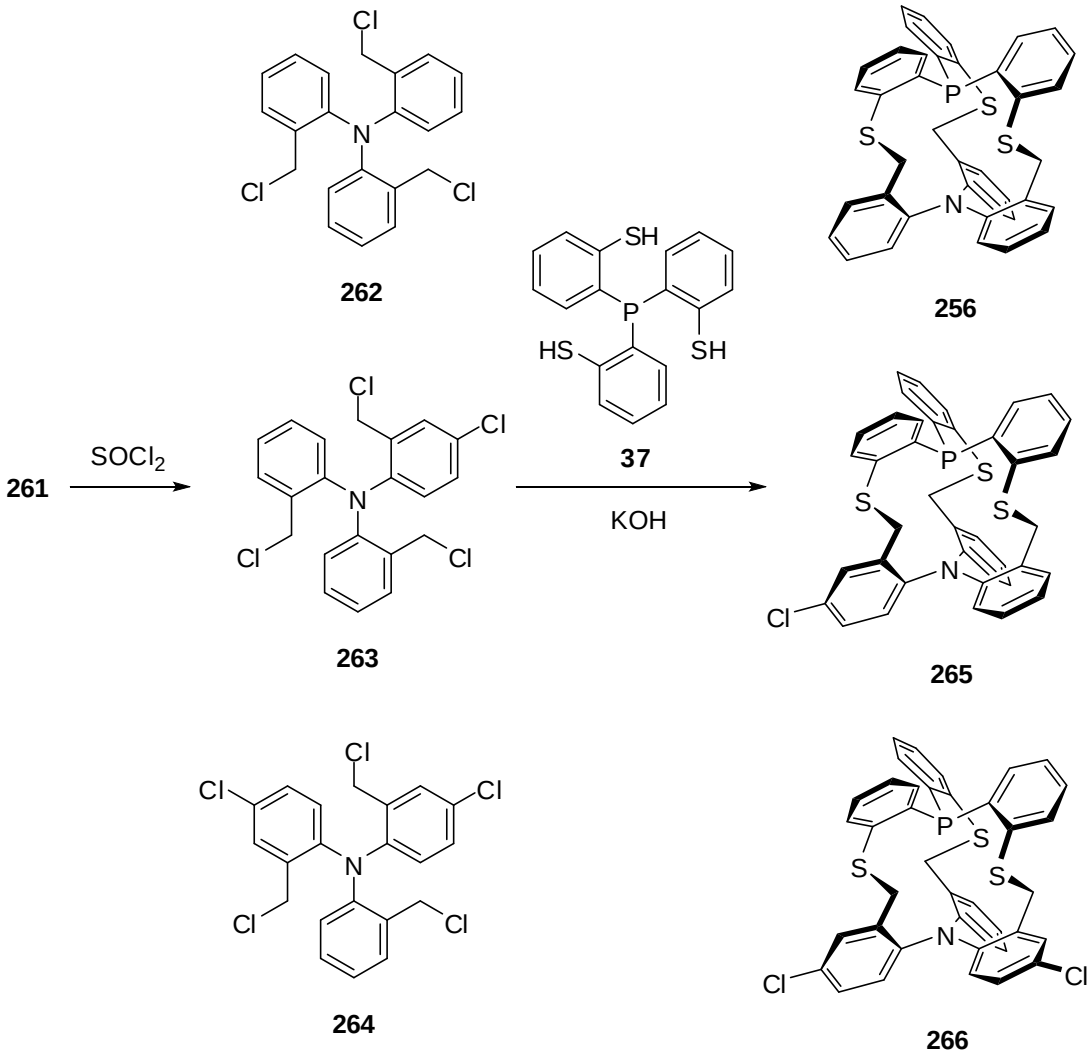
Figure 19. Cyclophanes previsously made in Pascal's lab (**40**, **56**) and proposed *in,in*-P,N cyclophanes

Scheme 57. Synthesis of *in,in*-P,N cyclophane **256**



The initially designed synthesis of *in,in*-P,N cyclophane **256** is shown in Scheme 57. Triester **260** can be made by Ullmann reaction of methyl anthranilate (**258**) and methyl 2-iodobenzoate (**259**).[77] Reduction with $LiAlH_4$ followed by chlorination would give trichloride **262**, which may cyclize with trithiol **37** to provide *in,in*-P,N cyclophane **256**.

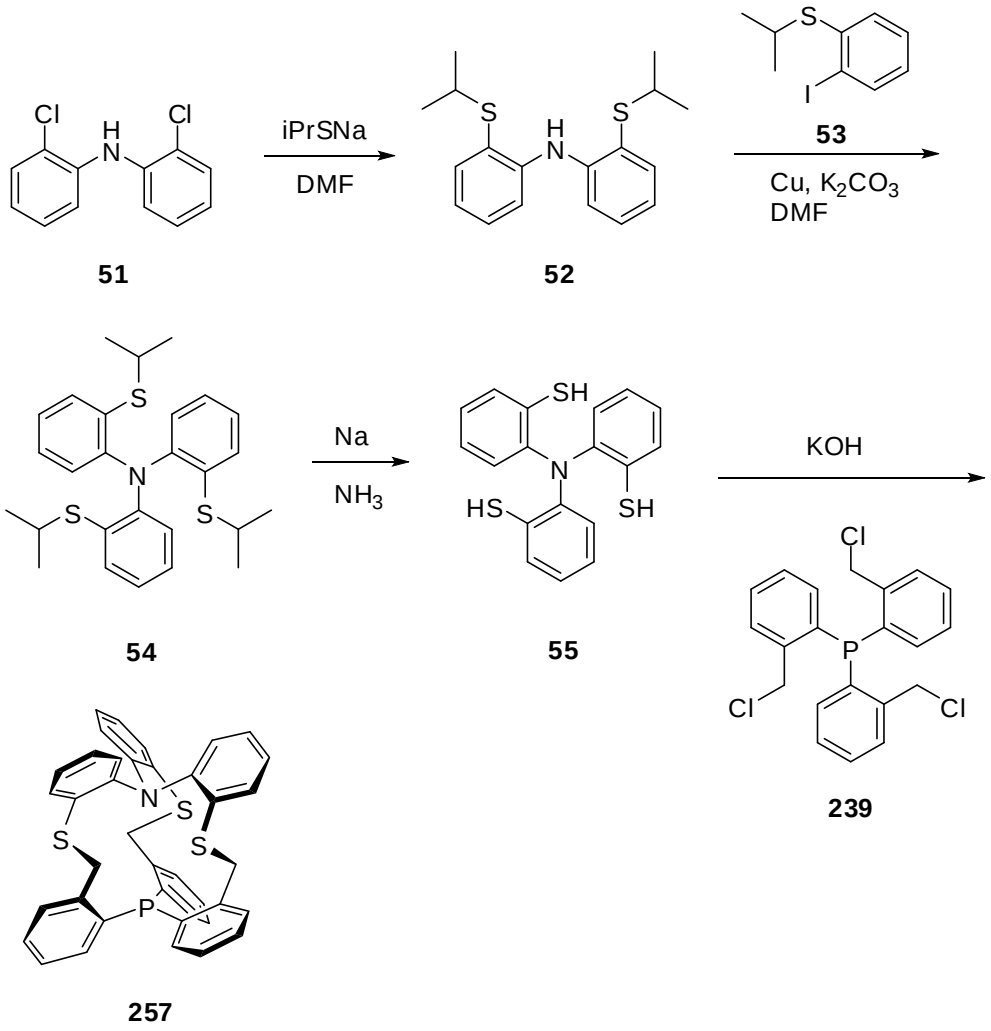
Scheme 58. Reactions of compound **261** in the actual experiment



The Ullmann reaction and reduction with $LiAlH_4$ succeeded and triol **261** was obtained. When **261** was heated with $SOCl_2$, trichloride **262** was made along with substantial amounts of tetrachloride **263** and pentachloride **264**. This mixture and trithiol **37** was subjected to base induced cyclization at high dilution, and a mixture of **256**, **265** and **266** was obtained (Scheme 58). Single crystals formed by slow evaporation of a solution in $CHCl_3$-MeOH. The X-ray structure is end-to-end disordered, but there is no

doubt that the *in,in*-P,N cyclophane **256** is present in the reaction mixture, which was supported by NMR and MALDI-TOF mass spectrometric analysis.

Scheme 59. Synthesis of *in,in*-P,N cyclophane **257**



The other *in,in*-P,N cyclophane **257** was made by the method shown in Scheme 59. The triphenylamine trithiol **55** was made by Ullmann reaction of thioethers **52** and **53** to achieve trithioether **54**, followed by Birch reduction. Thioethers **52** and **53** were made by

reacting sodium isopropylthiolate with the corresponding halogenated precursors. Condensation of trithiol **55** with trichloride **239** gave *in,in*-P,N cyclophane **257** in 15.5% yield and the product was easily isolated by chromatography.[76]

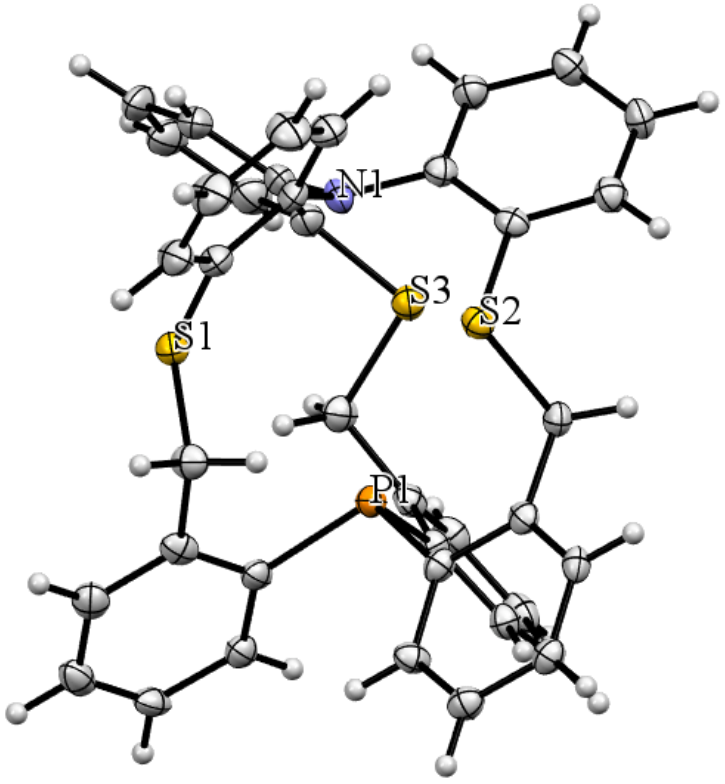


Figure 20. Molecular structure of compound **257**; 50% thermal ellipsoids has been employed.

Single crystals of compound **257** suitable for X-ray analysis were obtained from $CHCl_3$-MeOH. The molecular structure is illustrated in Figure 20. Compound **257** possesses C_3 symmetry in gas phase calculations, and it adopts an *in,in*-conformation with approximate C_3 symmetry in the solid state. The amine is more nearly planar than

the highly pyramidalized phosphine. The P---N nonbonding contact distance is 4.17 Å, substantially longer than the P---P nonbonding contact distance (3.58 Å and 3.72 Å in two independent molecules) observed in the structures of diphosphine **235**. It would be interesting to know if there is any coupling between the nitrogen and phosphorous atoms, but a highly concentrated solution of **257** is not easy to make.

Compound **257** is a propeller-like chiral molecule similar to diphosphine **235**, and it can be easily resolved by supercritical fluid chromatography (SFC) on Chiralpak 1A with 40% EtOH/CO_2 as mobile phase (Figure 18). 25 mg of **257** were resolved into pure enantiomers, and these samples yielded specific rotations ($[\alpha]_D^{25}$) of +132 and –122 for the faster and slower eluting components, respectively.

When diphosphine **235** was resolved, significant racemization occured during the separation. However, there is no "bridge" between the two enantiomer peaks during resolution of **257** (Figure 21). Also, no racemization of enantiomerically pure (–)-**257** was observed upon heating for 24 h at 100 ℃ in toluene, which indicates that the barrier to racemization is at least 31 kcal/mol. Heating for 24 h at 180 ℃ in DMSO showed complete decomposition to unknown products. This barrier is much higher than the 20.7 kcal/mol barrier estimated for diphosphine **235**. The reason for this difference is not at all obvious, and racemization pathways for both molecules have yet to be defined computationally, despite numerous attempts and the expenditure of an enormous amount of computer time.

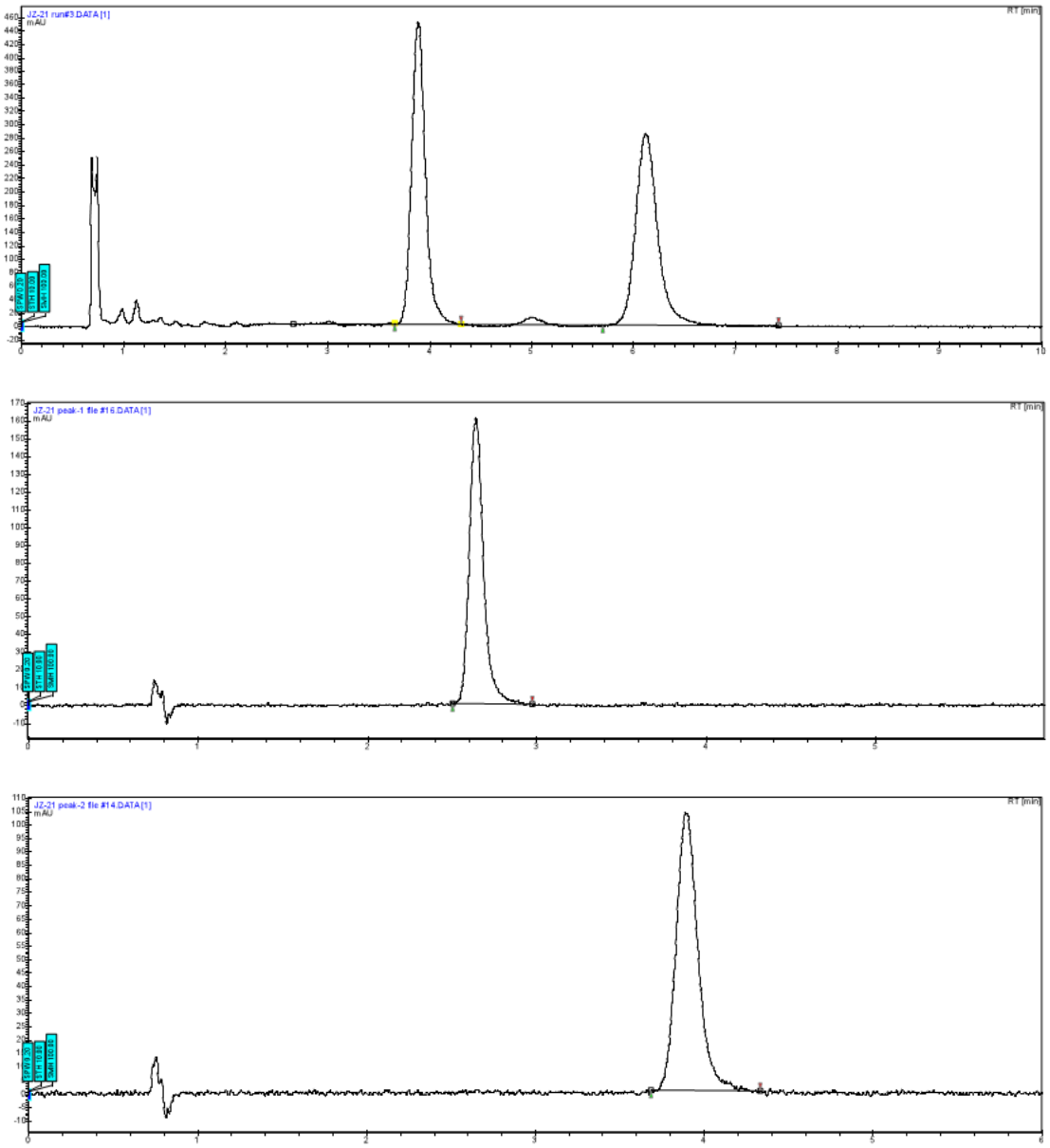
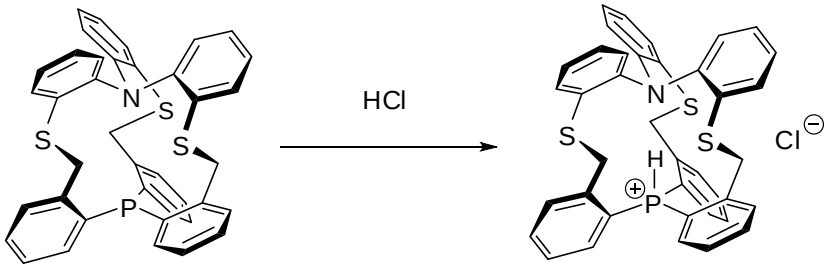


Figure 21. Resolution of Compound **257** by Chiral Supercritical Fluid Chromatography (Chiralpak 1A, 40% EtOH/CO_2, 100 bar) (Top); Analytical Chiral SFC of (+)-**257** (Middle); Analytical Chiral SFC of (–)-**257** (Bottom).

When HCl was added to cyclophane **56**, there was no evidence of a protonated cyclophane **57** (Scheme 12). No materials were available for other reactions, such as oxidation, due to the low yield formation of compound **56**. Protonation of compound **235**

is first order at a first-order process with half-life of 26 min, and it would be interesting to see if the larger cavity will increase the protonation rate. When HCl gas was bubbled into chloroform solutions of compound **257**, protonation occurred on the phosphorous atom to form *in,in*-P,N hydrochloride **267** (Scheme 60), as indicated by the new proton resonance at δ 11.97 with a coupling constant of 532 Hz in the ^{1}H NMR spectrum. The protonation is a first-order process with half-life of 26 min, which means the larger cavity did not increase the protonation rate. Single crystals formed by slow evaporation of a solution in $CHCl_3$-MeOH. However, the proton position was not defined due to poor diffraction in the X-ray experiments.

Scheme 60. Protonation reaction of compound **257**

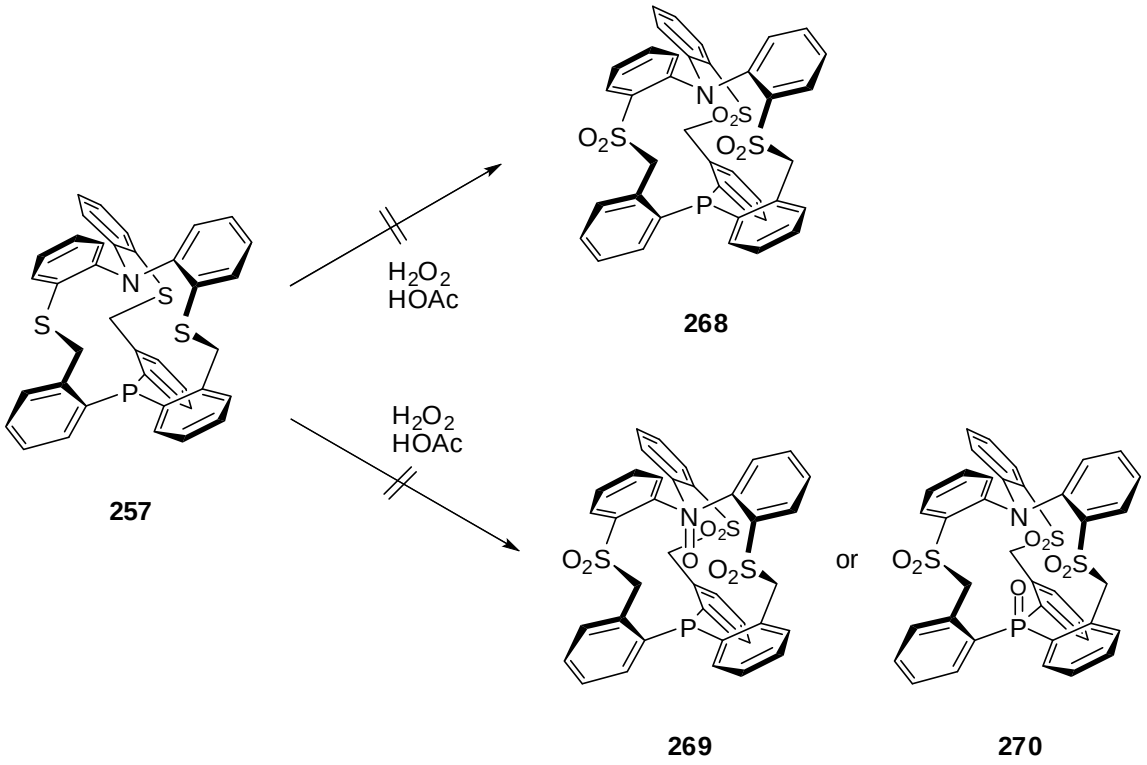


257 **267**

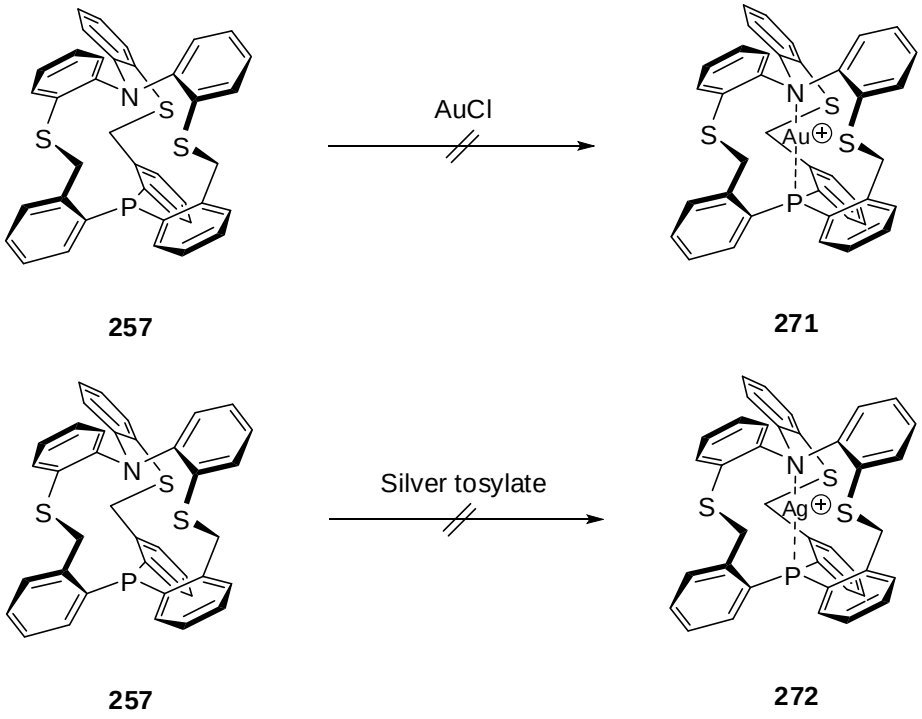
An oxidation reaction was also carried out. Compound **257** was heated in refluxing solution of acetic acid and 30% H_2O_2. Neither hexaoxide **268** nor heptaoxides **269** and **270** were detected by MALDI-TOF mass spectrometric analysis (Scheme 61). Instead, it showed only low molecular weight peaks which indicated decomposition of compound

257. Reaction of compound **257** with gold(I) chloride or silver(I) tosylate under conditions similar to those used for diphosphine **235** did not give metal adducts (Scheme 62). The relatively flat, non-basic amine might cause problems in these reactions even though it increases the size of the cavity.

Scheme 61. Attempted oxidation reaction of compound **257**



Scheme 62. Attempted complexation experiments of compound **257** with divalent metals



257 **271**

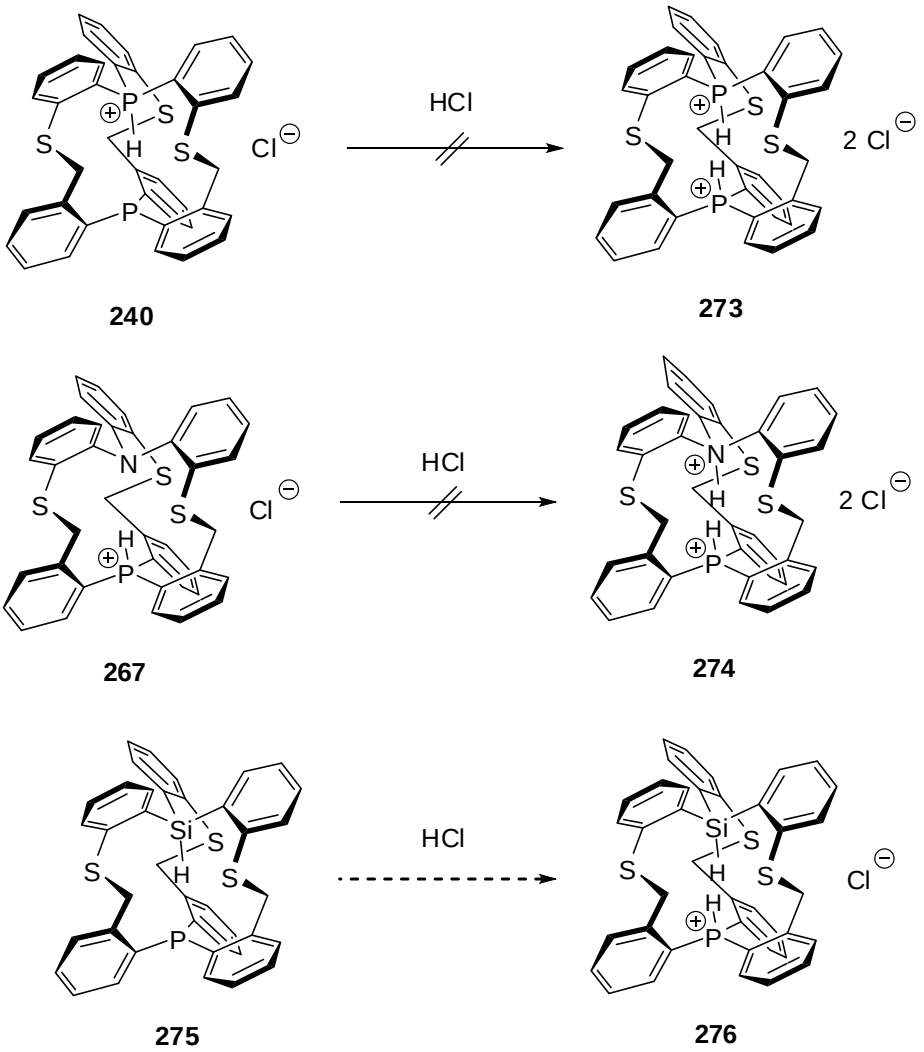
257 **272**

2.2.3 *In,in*-Phosphinosilane

As stated above, protonation of compounds **235** and **257** gave monoprotonated hydrochloride salts **240** and **267**, respectively. Further protonation might produce the more congested cyclophanes **273** and **274**, which necessitates very close H---H nonbonding contacts (Scheme 63). However, a second protonation was not detected in either **240** or **267**. One must admit that the monoprotonated versions of the cyclophanes are more congested, leaving less room for the second proton to attach. Also, the positive charge on phosphorous is repulsive to protons, which makes the second protonation even more difficult.

Silicon is similar in size to phosphorous, and it would be interesting to see if *in,in*-phosphinosilane **275** could be made. Since there is no charge on **275**, it might be a better candidate than **240** for the internal protonation reaction.

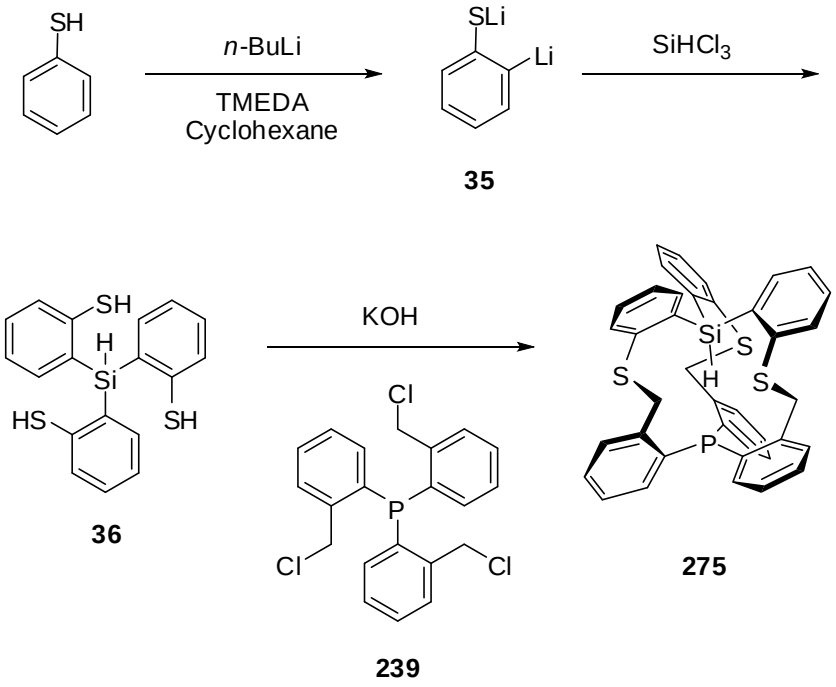
Scheme 63. Proposed protonation reactions



The precursor trithiol **36** was made by converting thiophenol to its dilithium salt **35**, followed by reaction with $SiHCl_3$. Condensation of trithiol **36** with trichloride **239** gave

in,in-P,HSi cyclophane **275** in 0.7% yield, and the product was isolated by chromatography (Scheme 64).

Scheme 64. Synthesis of *in,in*-phosphinosilane **275**



Single crystals of compound **275** suitable for X-ray analysis were obtained from $CHCl_3$-CH_2Cl_2-MeOH. The molecular structure is illustrated in Figure 22. Compound **275** adopts an *in,in*-conformation with crystallographic C_3 symmetry, and it is similar as the hydrochloride salt **240**. The P---Si distance in compound **275** is 4.08 Å, longer than the P---P distance in hydrochloride salt **240**, which is only 3.88 Å. One reason is that Si-H bonds are slightly longer than P-H bonds. Also, the P^+-H---P interaction in **240** is an attractive hydrogen bond, but the Si-H---P interaction in **275** is essentially repulsive.

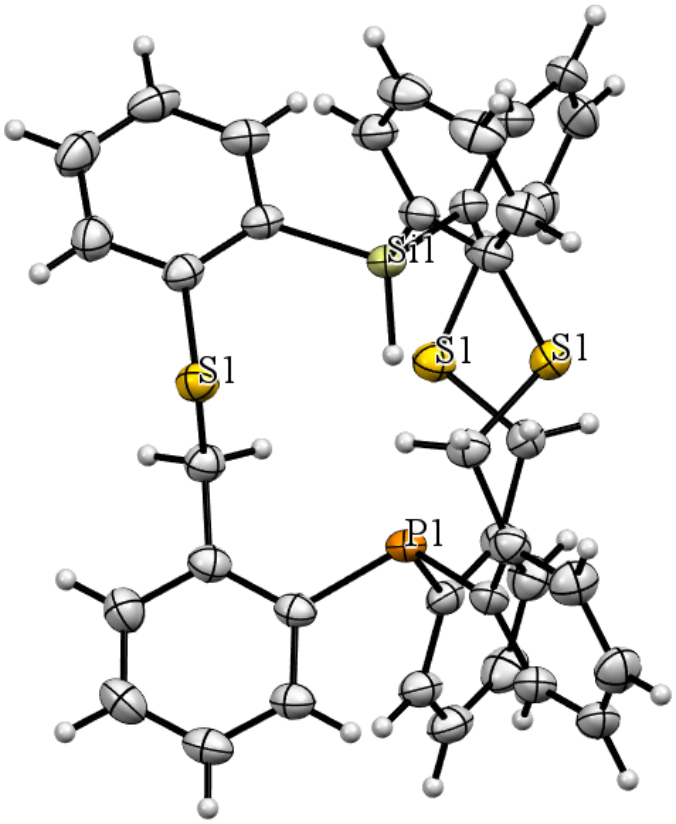


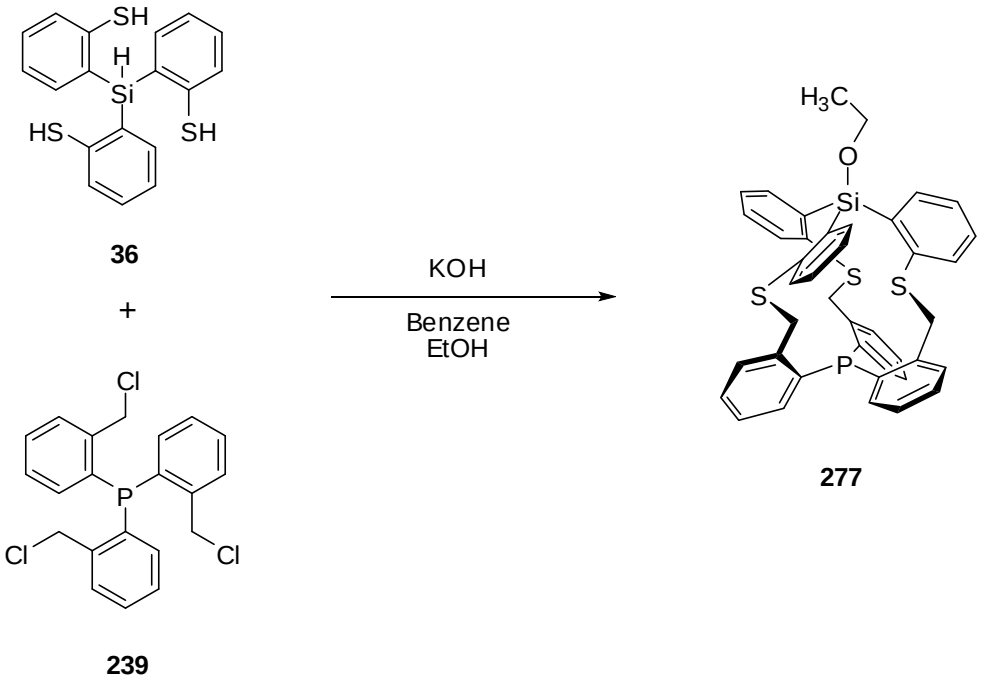
Figure 22. Molecular structure of compound **275**; thermal ellipsoids have been drawn at the 50% probability level.

Spin-spin coupling among the central atoms (P, H, and Si) in compound **275** is observed. The ^{1}H NMR spectrum of **275** showed a doublet (δ 9.31, J_{PH} = 25 Hz) for the central proton resonance due to coupling with the phosphorus. In addition, the easily visible ^{29}Si side bands indicated a coupling of J_{SiH} = 248 Hz between silicon and the central hydrogen. Most interesting is the proton-decoupled ^{29}Si NMR spectrum of **275**, consisting of a lone doublet with strong coupling to phosphorus (J_{SiP} = 76 Hz).

Despite of the low yield of compound **275**, there was enough to attempt protonation. Compound **275** was treated with HCl gas in chloroform solution at room temperature,

and protonation did eventually occur. However, no X-ray structure of the desired product was obtained. What happened upon protonation is still a mystery.

Scheme 65. Synthesis of *in,out*-P, EtOSi cyclophane **277**



The Si-H functional group is not completely stable, since a byproduct **277** was detected in the cyclization reaction of trithiol **36** with trichloride **239** (Scheme 65). Single crystals of compound **277** suitable for X-ray analysis were obtained from $CHCl_3$-CH_2Cl_2-MeOH. The *in,out*- macrobicycle is 'screwed together' more tightly than the *in,in*-isomers. The P---Si distance in **277** is 4.90 Å, longer than the *in,in*-isomers.

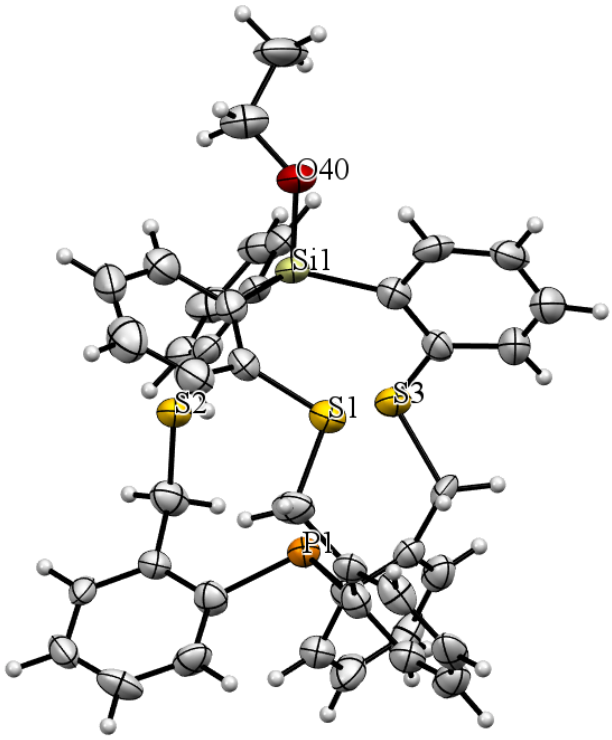
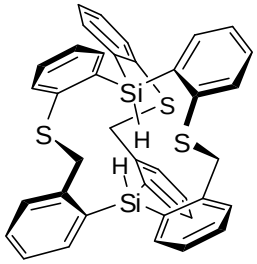
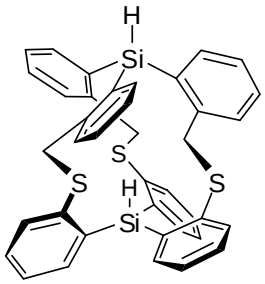
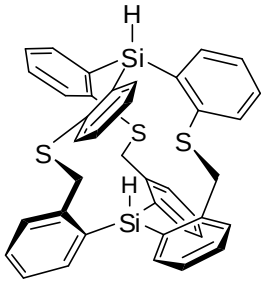
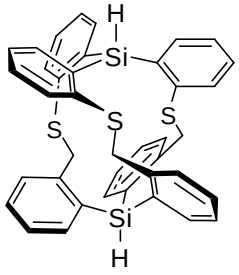


Figure 23. Molecular structure of compound **277**; thermal ellipsoids have been drawn at the 50% probability level.

2.2.4 *In,in*-Bis(hydrosilane)

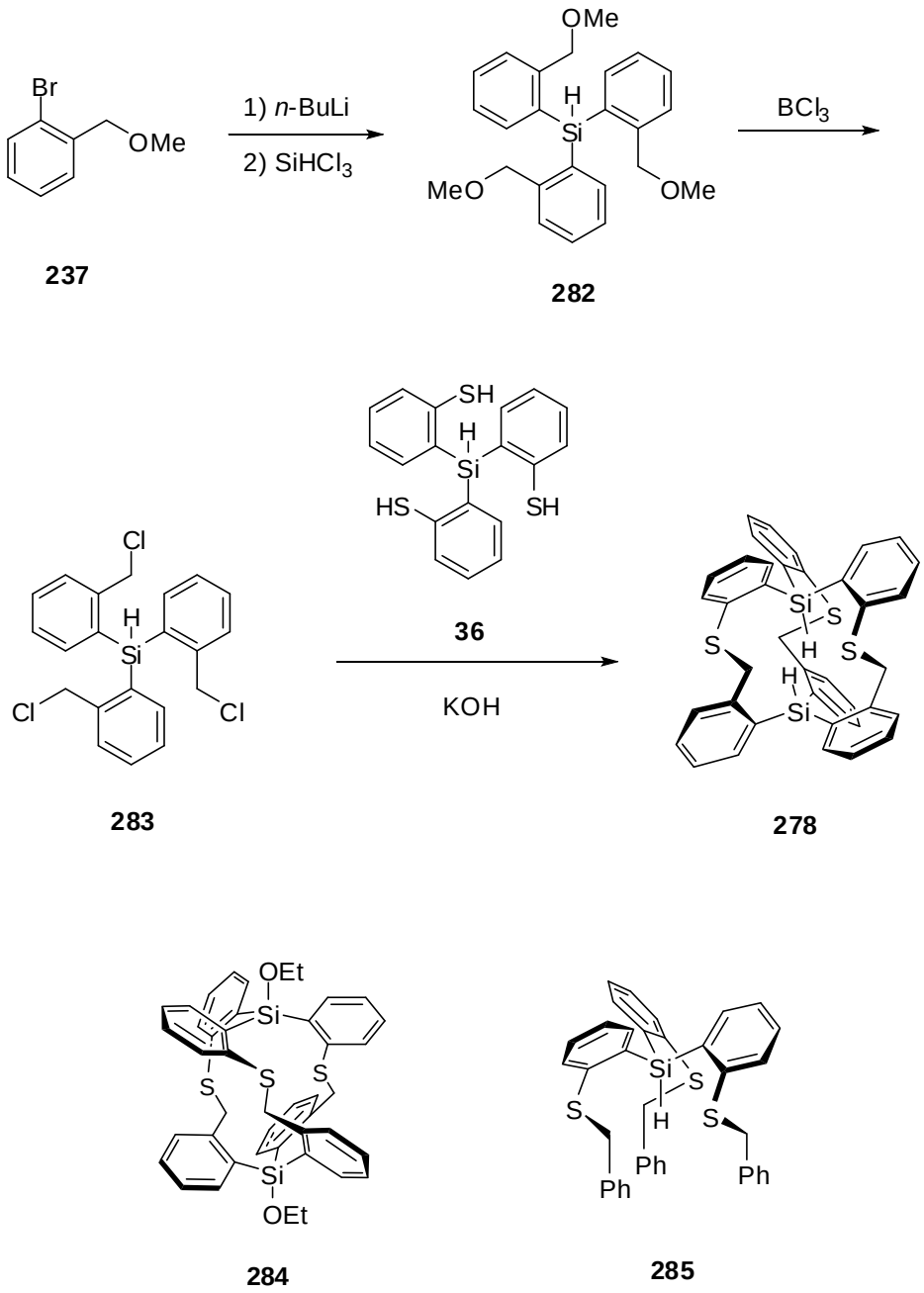
Since the stability of hydrosilanes is a potential problem, fewer steps are helpful in the formation of hydrosilane-containing cyclophanes. Most interesting is the *in,in*-bis(hydrosilane) **278**. The B3PW91/6-31G(d) calculations in Table 3 show that the *in,in* geometry of **278** is only about 6 kcal/mol more favorable than the possible *in,out*-isomers and 10.4 kcal/mol more favorable than the *out,out*-isomer. Can the *in,in*-isomer be made and how close is the H---H nonbonded contact?

Table 3. Calculated relative energies of *in/out* isomers of bis(hydrosilane)

Compound	**E + ZPE (au)**[a]	**△E (kcal/mol)**
 **278**	-3277.599416	0.0
 **279**	-3277.589307	+6.3
 **280**	-3277.590474	+5.6
 **281**	-3277.582801	+10.4

[a]All calculations were performed at the B3PW91/6-31G(d) level; all compounds possessed C_3 symmetry and displayed zero imaginary frequencies.

Scheme 66. Synthesis of bis(hydrosilane) **278**



Tris[2-(methoxymethyl)phenyl]silane (**282**) was made by transmetallation of compound **237** followed by addition to $SiHCl_3$ three times in 66% yield. Chlorination of **282** with boron trichloride gave the trichloride precursor **283** in 17% yield. Cyclization of

trichloride **283** with trithiol **36** at high dilution in benzene/ethanol in the presence of KOH gave a very complex mixture, which was composed of oligomeric and polymeric products and other cyclophanes, such as the *in,out*-isomers of cyclophanes with mixed hydrosilane and ethoxysilane bridgehead functionality and the *out,out*-bis(ethoxysilane) **284**. However, the *in,in*-bis(hydrosilane) **278** was present in the mixture and was separated by chromatography in 0.4% yield (Scheme 66).

The *in,in*-bis(hydrosilane) **278** is exceptional sterically congested. First, the ^{1}H NMR spectrum showed steric deshielding of the Si-H resonances, which were shifted approximately 2 ppm downfield (to δ 8.24 and δ 8.57) from the silane proton resonance in the nonmacrocyclic model compound **285** (δ 6.21). Second, the IR spectrum of **278** shows one strong band in the Si-H region (2325 cm^{-1}), roughly 150 cm^{-1} higher in frequency than the Si-H stretch in model **285** (2177 cm^{-1}). This is a clear case of compressional frequency enhancement.

Single crystals of compound **278** suitable for X-ray analysis were obtained from benzene-$CHCl_3$-MeOH. The molecule possesses crystallographic C_3 symmetry (Figure 24), in agreement with the calculated structure. The *in,in* geometry is confirmed, as is the unique "head-on collision" of the two *in*-hydrogen atoms. The hydrogen atom positions were refined and the distance between the two hydrogen atoms in X-ray structure is 1.89 Å. However, due to the foreshortening of the Si-H distances, the actual H---H distance ($d_{H\text{-}H}$) is shorter. The distance of between silicon atoms is 4.43 Å, about 0.8 Å greater than the distance between phosphorus atoms in **235** (3.58 Å and 3.71 Å in two

independent molecules), which is another indication of steric congestion. If a standard Si-H bond distance of 1.48 Å were employed,[78] then $d_{H\text{-}H}$ would be only 1.47 Å, but there must be some compression of the Si-H bond in this environment.

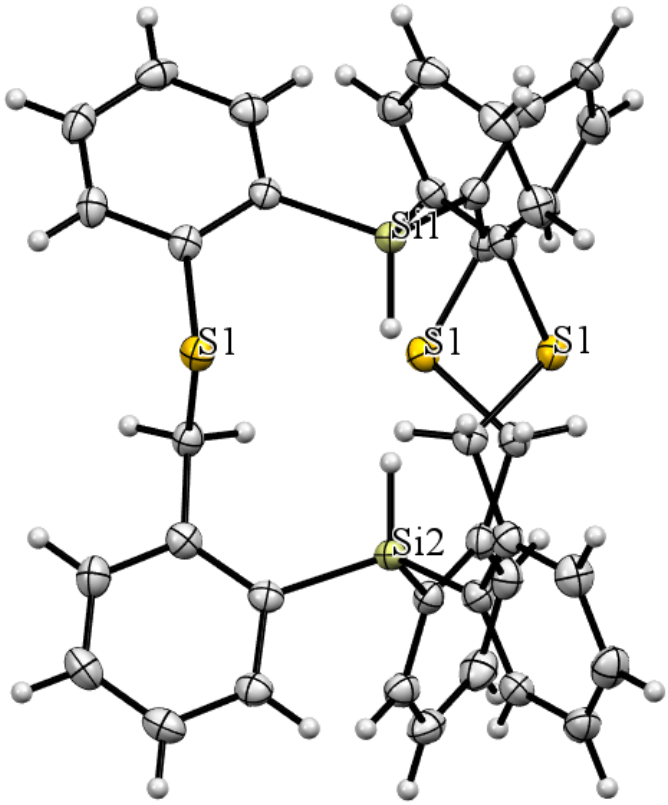


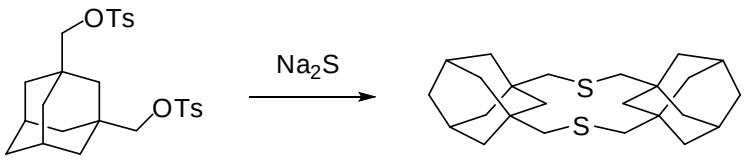
Figure 24. Molecular structure of compound **278**; thermal ellipsoids have been drawn at the 50% probability level.

The computational methods listed in Table 4 gave Si-H bond distances ranging from 1.44 Å to 1.46 Å and $d_{H\text{-}H}$ values ranging from 1.56 Å to 1.62 Å. However, all of these methods significantly overestimated $d_{Si\text{-}Si}$,[79] so the actual $d_{H\text{-}H}$ or the Si-H bond distances must be shorter still.

Table 4. Experimental and calculated interatomic distances for the core atoms of compound **278**

Method	$d_{Si\text{-}Si}$ (Å)	$d_{H\text{-}H}$ (Å)
X-ray	4.433(2)	1.89(10)
B3LYP/6-31G(d)	4.535	1.623
B3LYP/6-311+G(2d,p)	4.518	1.618
B3PW91/6-31G(d)	4.501	1.576
B3PW91/6-311+G(2d,p)	4.484	1.570
M062X/6-31G(d)	4.474	1.568
M062X/6-311+G(2d,p)	4.449	1.560
MP2(FC)/6-31G(d)	4.458	1.556

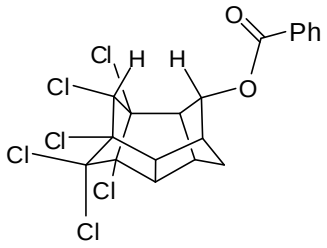
Scheme 67. Synthesis of bisadamantyl-containing cyclophane **287**



286 **287**

Extensive searches of the Cambridge Structural Database (CSD) found several compounds with very short H---H nonbonded contact. One of these compounds is the bisadamantyl-containing cyclophane **287** made by Vögtle and coworkers in 1994 (Scheme 67).[80] A B3PW91/6-31G(d) calculation gave an H---H contact of 1.637 Å.

The “world record” for the shortest experimentally determined H---H nonbonded contact is 1.617(3) Å via neutron diffraction for a cage pentacyclododecane **288**.[81] This distance is in almost perfect agreement with the results of modern calculations [e.g., B3PW91/6-31G(d), 1.616 Å; MP2/6-31G(d), 1.622 Å].

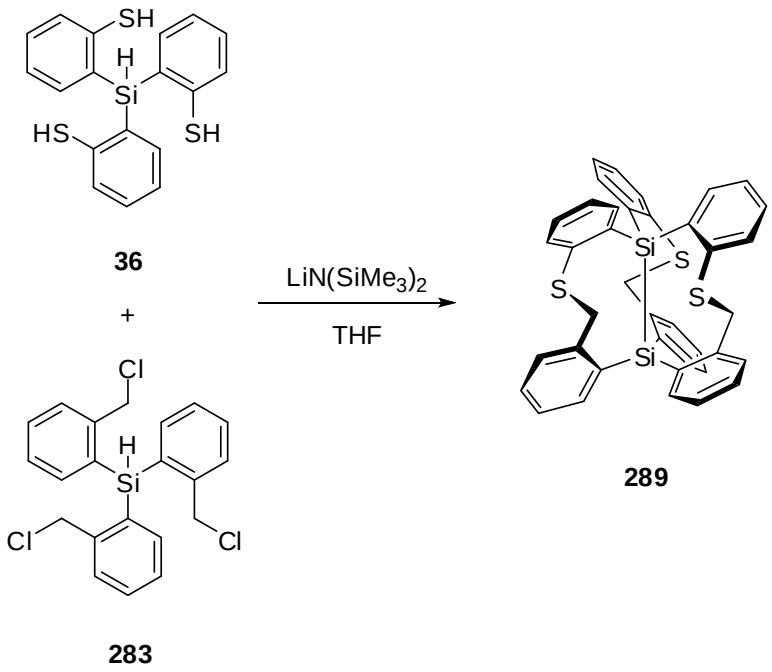


288

There can be little doubt that $d_{H\text{-}H}$ in compound **278** is significantly shorter, on the order of 1.56 Å, but direct experimental confirmation awaits a large enough crystal for a neutron diffraction experiment.

Since the two hydrogens on the central axis of **278** are so close, one reaction that might happen is loss of hydrogen gas under some conditions. The bond energy of Si-H is 393 kJ/mol, compared with Si-Si 340 kJ/mol and H-H 432 kJ/mol, thus the formation of compound **289** is favored by14 kJ/mol (in the absence of any added strain). Cyclization of **36** and **283** in THF at the presence of $LiN(SiMe_3)_2$ appeared to give compound **289** based on ^1H NMR analysis (Scheme 68), but the confirmation of this structure awaits a single crystal suitable for X-ray analysis.

Scheme 68. Synthesis of cyclophane **289**



In compounds **235** and **275**, there is through space spin-spin coupling among the atoms on the central axes of the molecules. However, the Si-H resonances of **278** are singlets. Still, there might be a small coupling of the two atoms, and an NMR experiment was carried out to measure the possible coupling. First, in a good quality spectrum where the chloroform peak width was 0.4 Hz, the hydrogen signals at δ 8.57 and δ 8.24 are singlets with line widths of 2.4 Hz and 2.7 Hz respectively. Second, irradiation of the peak at δ 8.57 did not change the peak width of the δ 8.24 resonance (Figure 25). A COSY experiment did show slight coupling between these two hydrogens (Figure 26), but the coupling constant could not be determined. It seems that even if these two hydrogens are coupled to each other, the coupling constant is sertainly less than 0.5 Hz.

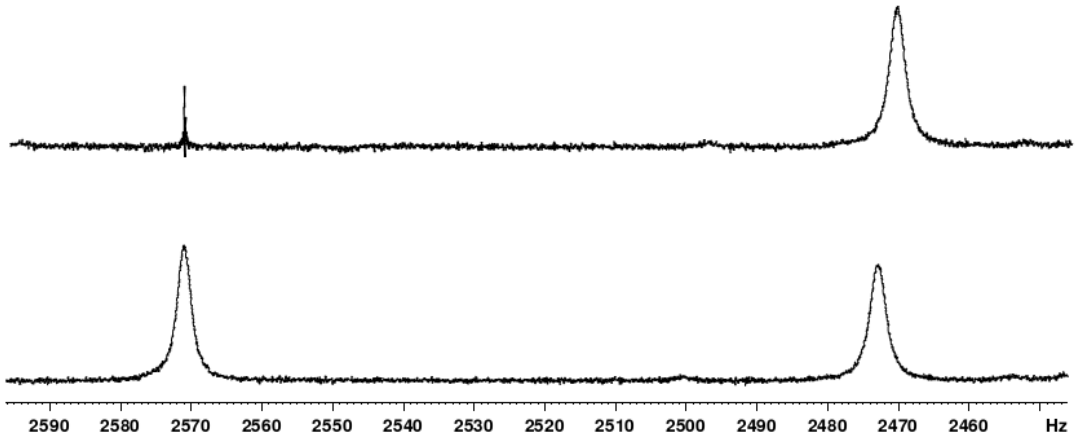


Figure 25. Decoupling experiment of compound **278**

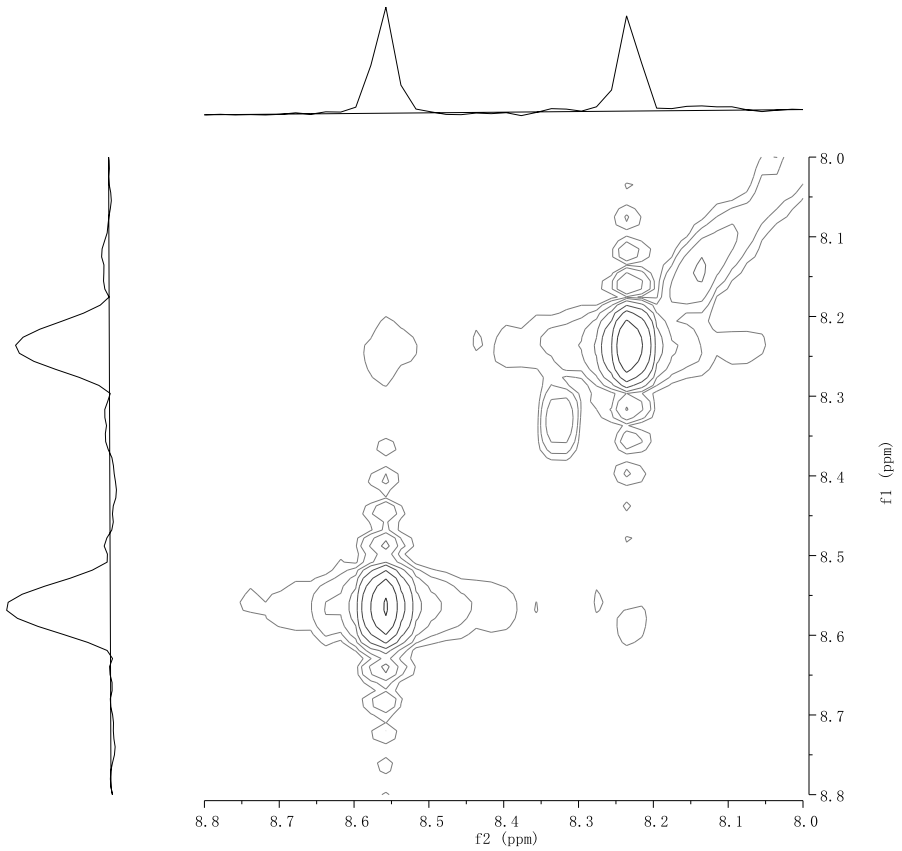


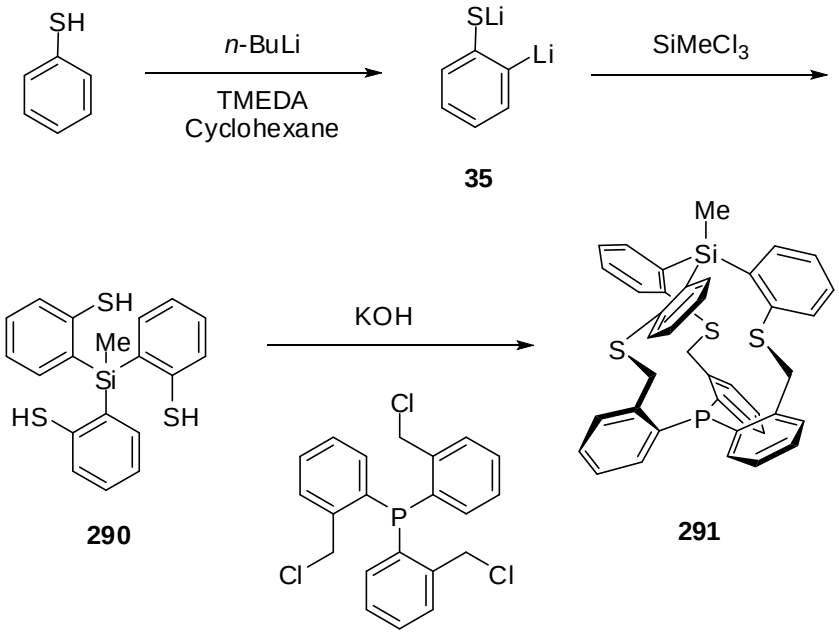
Figure 26. Low-field region of the COSY spectrum of compound **278**

2.2.5 *In,out*-Phosphinomethylsilane

Another interesting question for this kind of molecular cage is: what is the largest functional group to fit into the cavity? In order to explore this, Block's synthesis was used to synthesize the methylsilane trithiol **290**, which was utilized in a cyclization with trichloride **239**. Compound **291** was isolated in 2.2% yield, and single crystals suitable for X-ray analysis were obtained from benzene-$CHCl_3$-MeOH (Scheme 69). In contrast with the results obtained before with lone pairs and protons as bridgehead substituents, compound **291** gave an *in,out* conformation. B3PW91/6-31G(d) calculations showed that the observed *out,in*-MeSi,P (**291**) is about 35 kcal/mol more stable than *in,in*-MeSi,P and *in,out*-MeSi,P cyclophanes.

Since the bridgehead silicon adopts an *out* conformation, the cavity is larger than those in the *in,in*-isomers. The P---Si distance is measured to be 4.90 Å, about 0.7 Å longer than *in,in*-N,P (**257**) and 1.3 Å longer than *in,in*-P,P (**235**). It was expected that this will allow higher reactivity of the phosphorous atom, but it is not the case. Protonation of **291** is even slower than **235** and **257**, and eventually gave more than three new methyl resonances in the ^{1}H NMR spectrum. No good-quality crystals were obtained from this mixture, and the characterization of these products, which must result in part from ring fragmentation at silicon, was not pursued (Scheme 70).

Scheme 69. Synthesis of *in,out*-phosphinosilane **291**



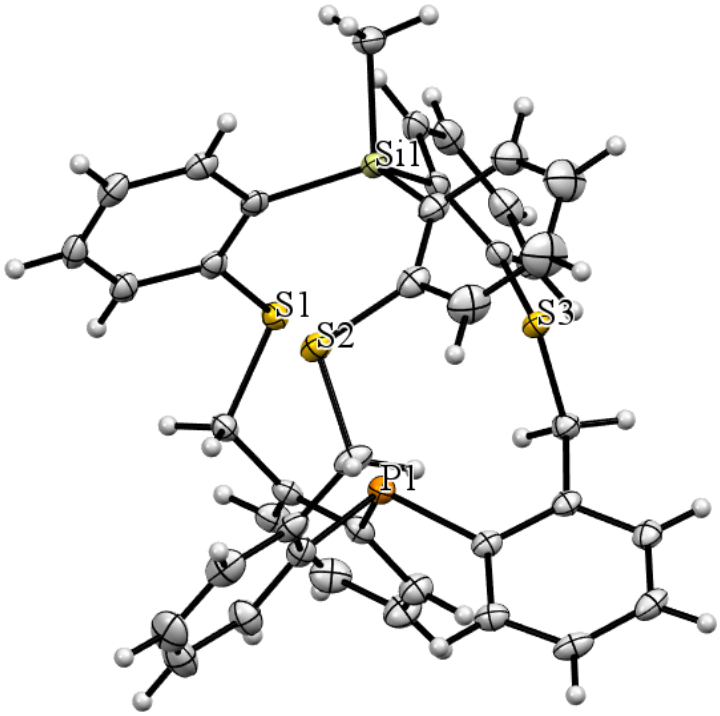
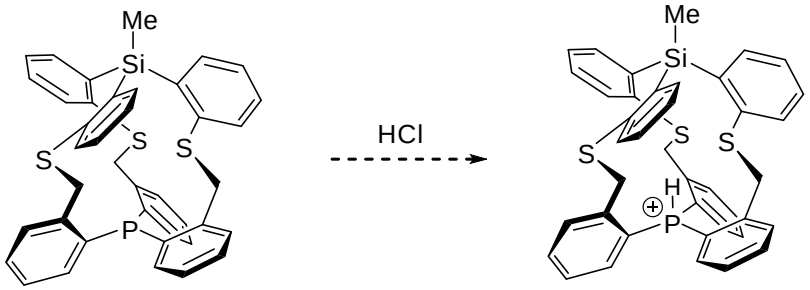


Figure 27. Molecular structure of compound **291**; thermal ellipsoids have been drawn at the 50% probability level.

Scheme 70. Proposed protonation of cyclophane **291**



291 **292**

2.3 Conclusion

The calculated relative energies of the various cyclophanes are summarized in Table 5. In this kind of cage molecule, only lone pair and protons bridgehead substituents have a low enough energy to form *in,in*-isomers, and larger substitutions, such as methyl group, only permit formation of the *in,out*-isomers. In order to put methyl or larger groups inside, some different synthetic methods must be developed.

Table 5. Calculated relative energies of *in/out* isomers of bis(triarylelement) cyclophanes

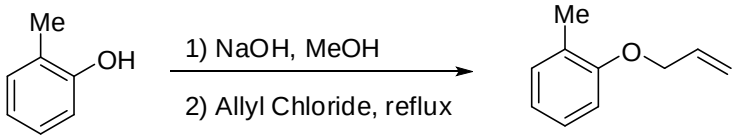
Compound	**E + ZPE (au)**[a]	**△E (kcal/mol)**
in,in-P,P (**1**)	-3380.091662	0.0
in,out-P,P-A	-3380.062618	+18.2
in,out-P,P-B	-3380.061870	+18.7
out,out-P,P	-3380.043331	+30.3
in,in-N,P (**2**)	-3093.505473	0.0
in,out-N,P	-3093.481031	+15.3
out,in-N,P	*not a potential minimum*	
out,out-N,P	*not a potential minimum*	
in,in-HSi,P (**3**)	-3328.848381	0.0
in,out-HSi,P	-3328.817926	+19.1
out,in-HSi,P	-3328.832399	+10.0
out,out-HSi,P	-3328.813156	+22.1
in,in-MeSi,P	-3368.054971	+35.7
in,out-MeSi,P	-3368.056685	+34.6
out,in-MeSi,P (**4**)	-3368.111798	0.0
out,out-MeSi,P	-3368.092861	+11.9
in,in-HSi,HSi (**5**)	-3277.599416	0.0
in,out-HSi,HSi-A	-3277.589307	+6.3
in,out-HSi,HSi-B	-3277.590474	+5.6
out,out-HSi,HSi	-3277.582801	+10.4

[a]All calculations were performed at the B3PW91/6-31G(d) level; all compounds possessed C_3 symmetry and displayed zero imaginary frequencies.
[b]For isomer A, the carbon-substituted triarylelement is *out*; for isomer B, the sulfur-substituted triarylelement is *out*.

In conclusion, several macrobicyclic, bis(triarylelement)-containing cyclophanes have been synthesized and fully characterized, each bearing two different bridgehead heteroatoms. Computational studies accurately predicted that when the bridgehead substituents are small (lone pairs or protons), an *in,in* bridgehead stereochemistry is strongly favored, but larger bridgehead substituents favor the formation of *in,out* stereoisomers. Besides, compound **235**, **240** and **275** show through-space spin-spin coupling between atoms along the central axis. Even compound **278** only shows small through-space spin-spin coupling between the two hydrogens, a combination of crystallographic and computational data indicate that the hydrogen-hydrogen nonbonded contact distance is approximately 1.56 Å, a new "world record" for such contact in any crystallographically characterized compound.

Chapter 3: Experimental Procedures and Selected Spectras

Synthesis of allyl *o*-tolyl ether (98)

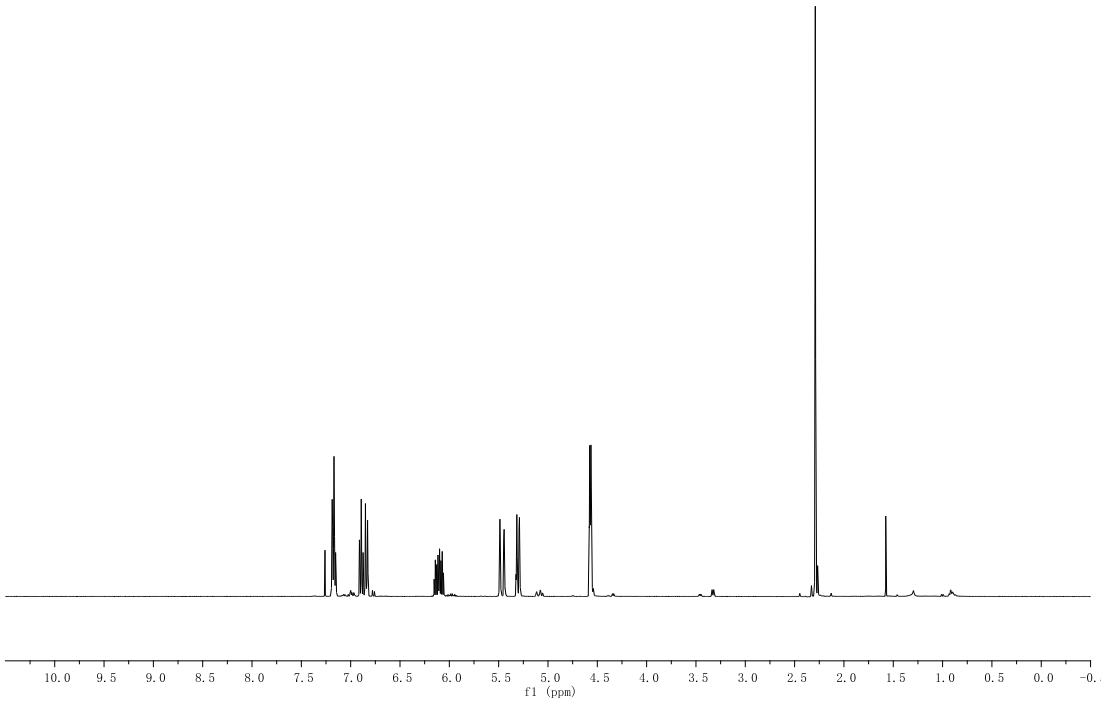


97 **98**

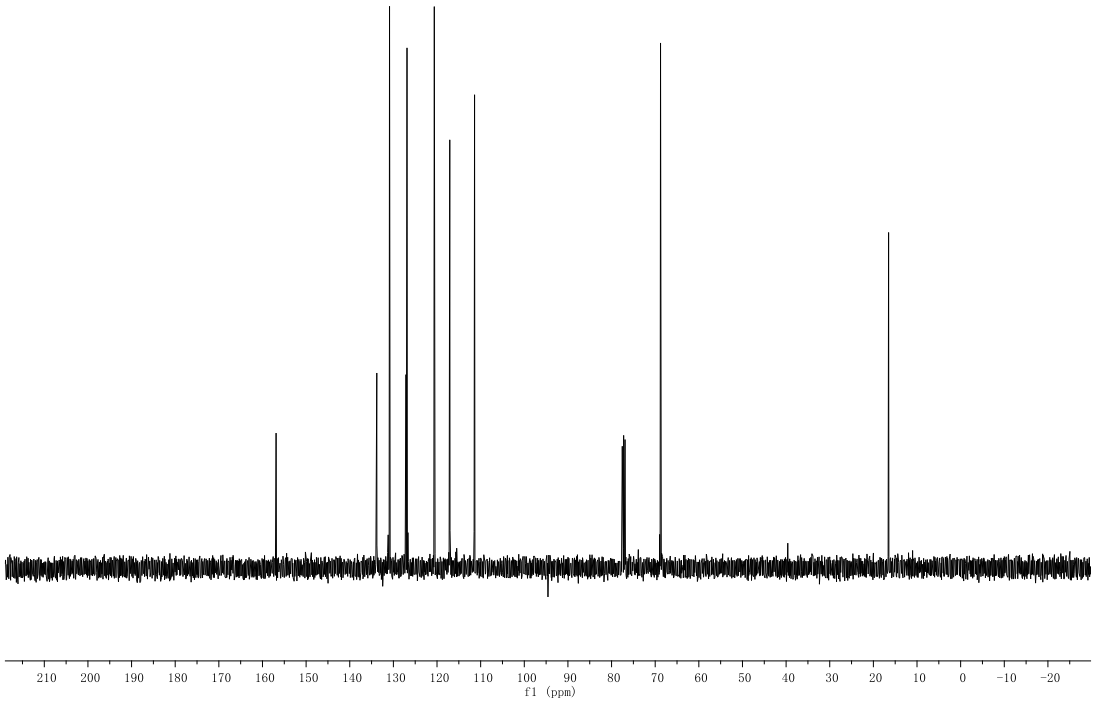
$C_{10}H_{12}O$
Exact Mass: 148.09
Molecular Weight: 148.20
C, 81.04; H, 8.16; O, 10.80

To a solution of NaOH (0.40 g, 10 mmol) in MeOH (5 mL), *o*-cresol (1.08 g, 10 mmol) was added dropwise. After 2 h, allyl chloride (0.92 g, 12 mmol) was added and the mixture was heated to reflux for 4 h. Upon cooling, water was added and the mixture was extracted with chloroform 3 times. The organic layer was washed with brine and dried over Na_2SO_4. Removal of the solvent under vacuum gave a residue, which was chromatographed on silica gel. Elution with hexanes yielded compound **98** as a light yellow liquid (1.08 g, 7.3 mmol, 73%). ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 3 H), 4.56 (d, *J* = 5 Hz, 2 H), 5.30 (d, *J* = 11 Hz, 1 H), 5.46 (d, *J* = 17 Hz, 1 H), 6.10 (m, 1 H), 6.84 (d, *J* = 8 Hz, 1 H), 6.89 (t, *J* = 8 Hz, 1 H), 7.17 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 16.5, 68.8, 111.4, 117.1, 120.6, 126.9, 127.1, 130.9, 133.8, 156.9 (10 of 10 expected resonances).

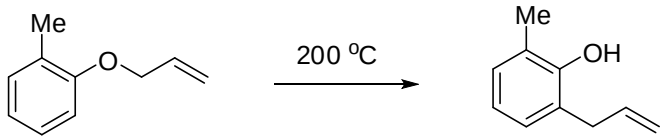
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **98**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **98**



Synthesis of 2-allyl-6-methylphenol (99)

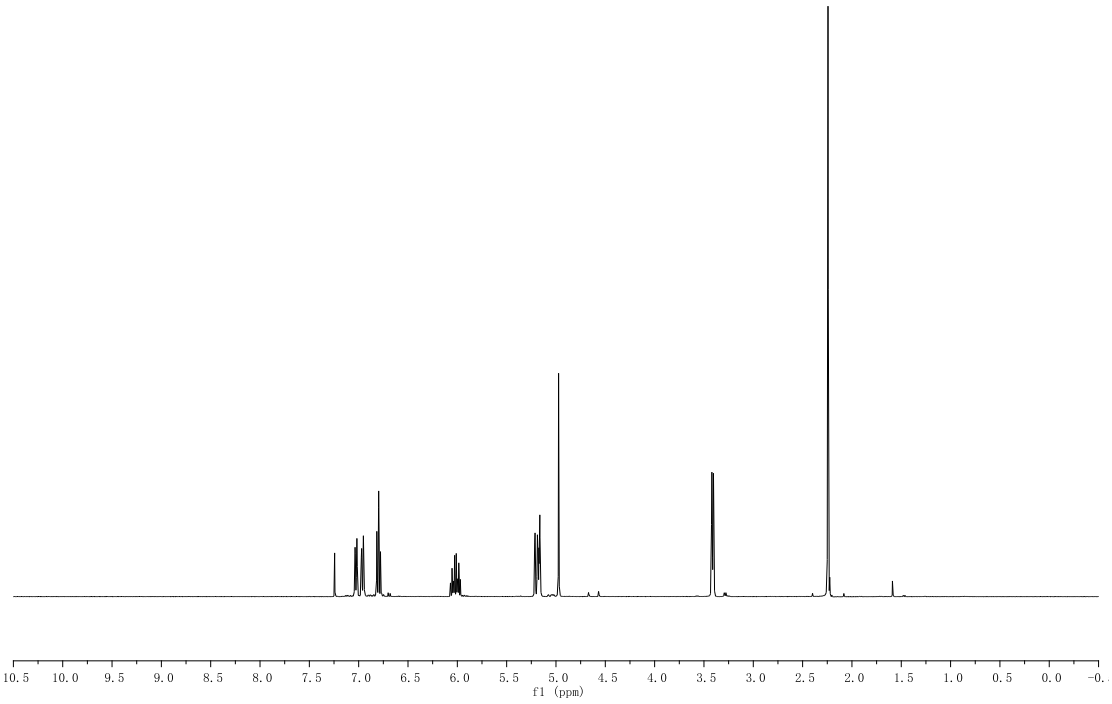


98 **99**

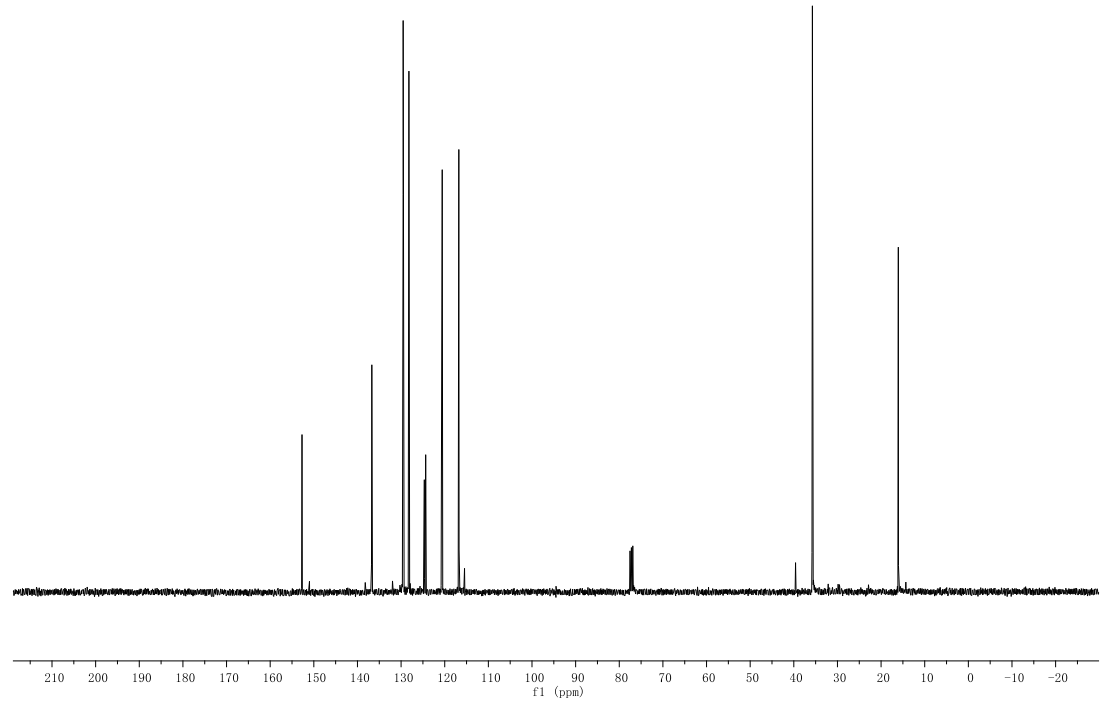
$C_{10}H_{12}O$
Exact Mass: 148.09
Molecular Weight: 148.20
C, 81.04; H, 8.16; O, 10.80

Allyl *o*-tolyl ether (**98**, 9.14 g, 61.7 mmol) was placed in a round bottom flask and heated at 200 ℃ for 18 h. The reaction mixture was subjected to vacuum distillation. The desired product **99** distilled from 80 to 85 ℃ under vacuum as a colorless liquid (3.66 g, 24.7 mmol, 40%). ^{1}H NMR ($CDCl_3$) δ 2.26 (s, 3 H), 3.43 (d, *J* = 6 Hz, 2 H), 4.99 (s, 1 H), 5.21 (m, 2 H), 6.01 (m, 1 H), 6.81 (t, *J* = 8 Hz, 1 H), 6.98 (d, *J* = 7 Hz, 1 H), 7.04 (d, *J* = 8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 16.1, 35.8, 116.8, 120.6, 124.4, 124.7, 128.2, 129.5, 136.7, 152.7 (10 of 10 expected resonances).

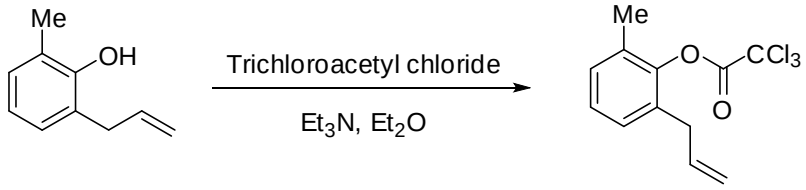
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **99**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **99**



Synthesis of 2-allyl-6-methylphenyl trichloroacetate (100)



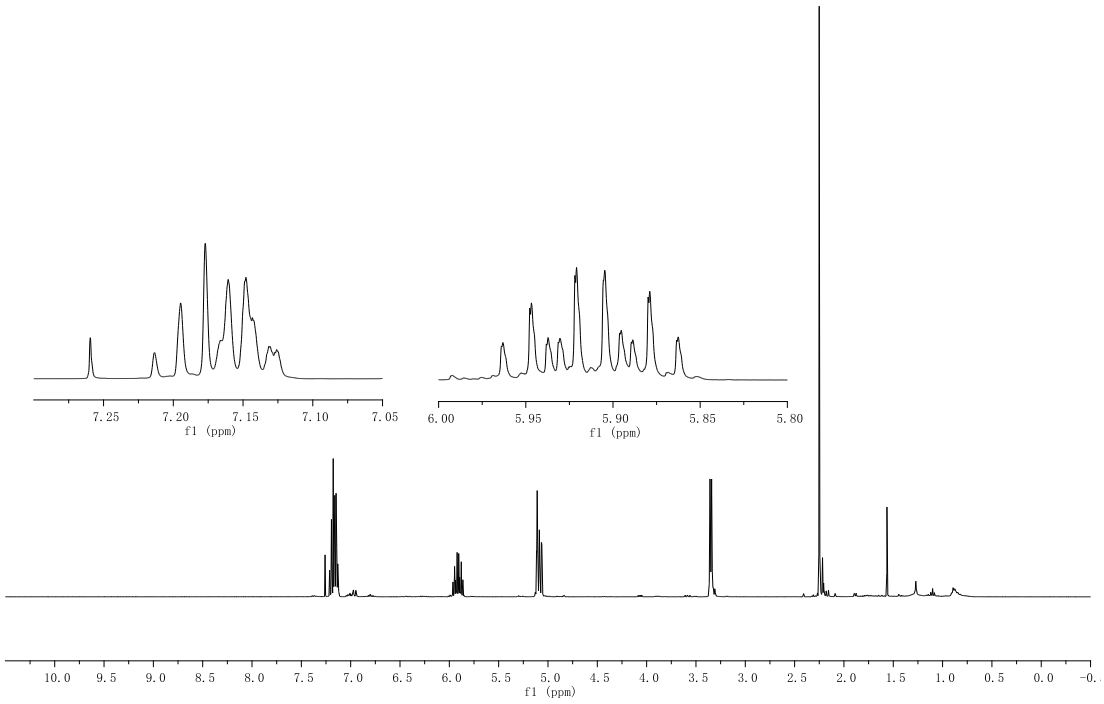
99

100

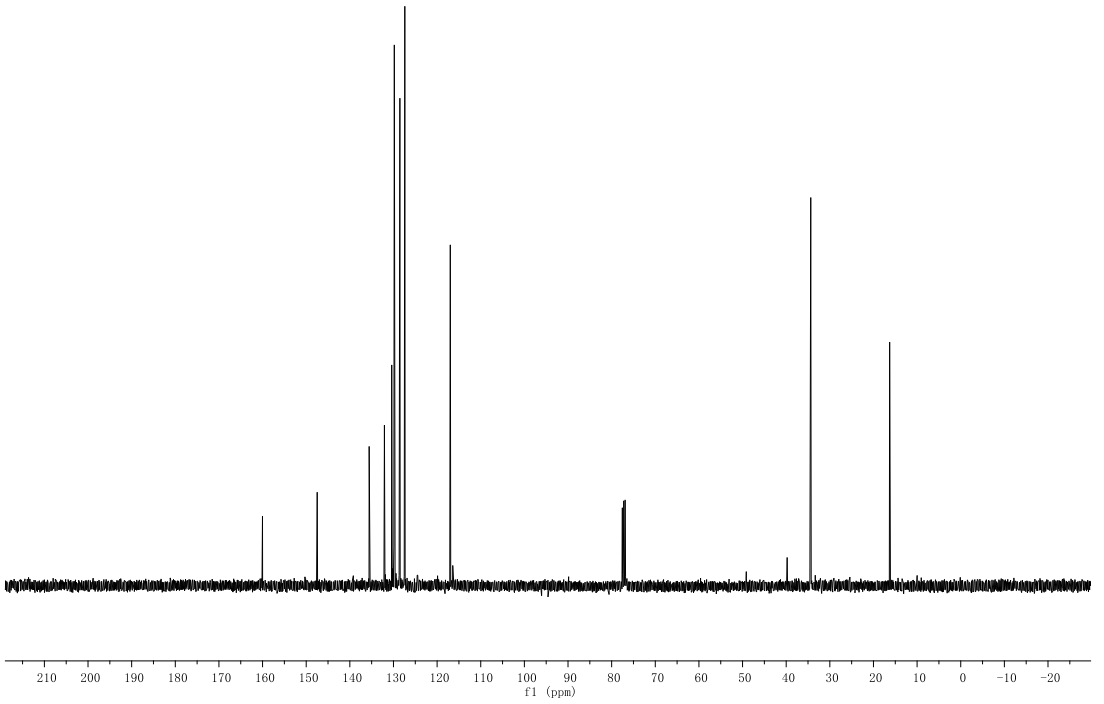
$C_{12}H_{11}Cl_3O_2$
Exact Mass: 291.98
Molecular Weight: 293.57
C, 49.09; H, 3.78; Cl, 36.23; O, 10.90

To a solution of compound **99** (3.55 g, 24.0 mmol) in ether (100 mL), trichloroacetyl chloride (4.36 g, 24.0 mmol) was added. The mixture was stirred at room temperature overnight. Water was added to the reaction mixture, which was extracted with ether three times. The organic layer was combined and dried with Na_2SO_4. After removal of solvent, compound **100** was obtained as light yellow liquid (6.33 g, 21.6 mmol, 90%). ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3 H), 3.35 (d, J = 7 Hz, 2 H), 5.09 (m, 2 H), 5.91 (m, 1 H), 7.16 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 16.3, 34.4, 117.0, 127.4, 128.5, 129.8, 130.4, 132.1, 135.6, 147.5, 160.0 (11 of 11 expected resonances).

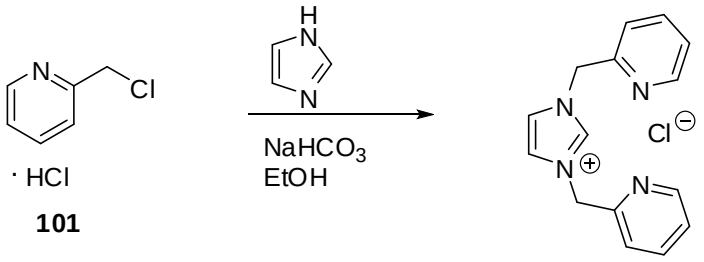
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **100**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **100**



Synthesis of 1,3-di(2-picolyl)imidazolium chloride (102)

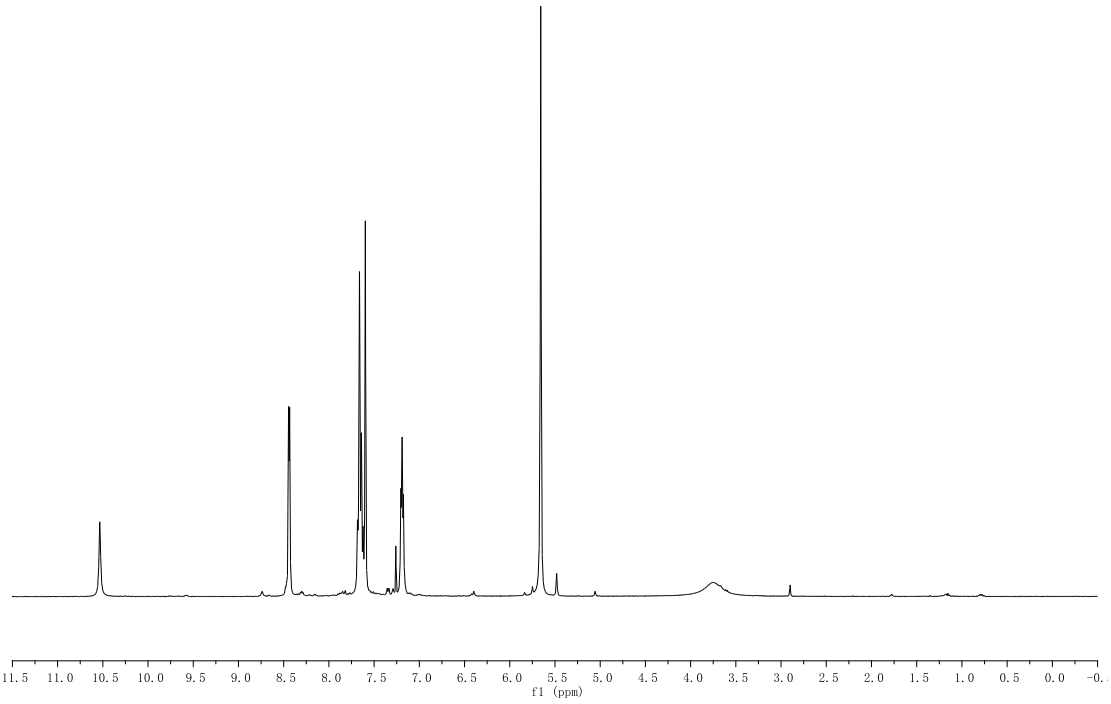


102

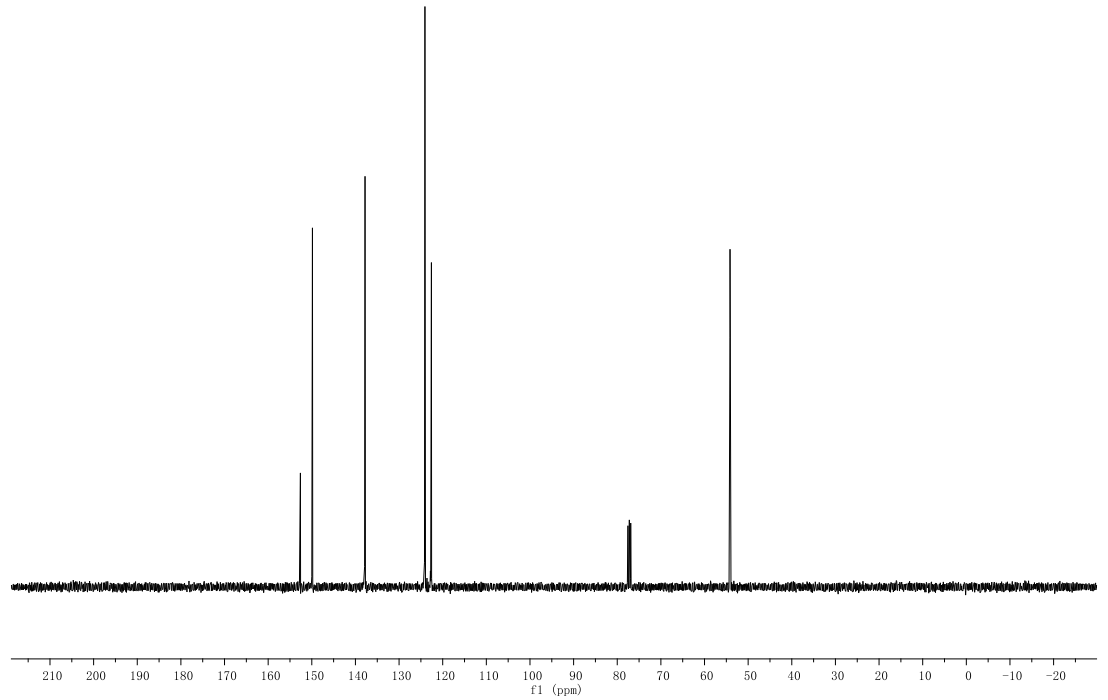
$C_{15}H_{15}ClN_4$
Exact Mass: 286.10
Molecular Weight: 286.76
C, 62.83; H, 5.27; Cl, 12.36; N, 19.54

Compound **102** was prepared by the method of Alison et al.[82] Picolylchloride hydrochloride (**101**, 1.18 g, 7.2 mmol), imidazole (0.25 g, 3.6 mmol) and $NaHCO_3$ (0.91 g, 11.2 mmol) were taken up in ethanol (10 mL) and heated at reflux for 2 days. The solvent was removed in vacuo, and the residue was taken up in dichloromethane and dried over Na_2SO_4. Removal of the DCM in vacuo gave an oil that was triturated with 4 mL THF to give a powder, which was further washed with THF (20 mL) twice and dried in vacuo. Yield: 687 mg (66%). ^{1}H NMR ($CDCl_3$) δ 5.66 (s, 4 H), 7.19 (t, J = 6 Hz, 2 H), 7.64 (m, 6 H), 8.44 (d, J = 4 Hz, 2 H), 10.53 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 54.2, 122.6, 124.1, 137.8, 149.9, 152.6 (6 of 8 expected resonances).

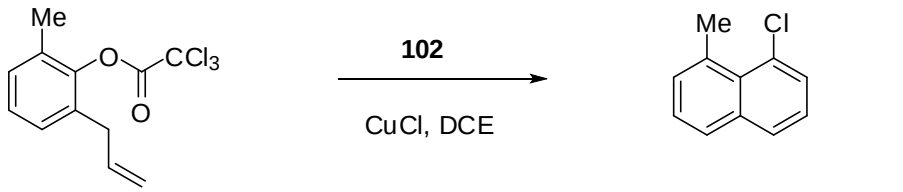
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **102**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **102**



Synthesis of 1-chloro-8-methylnaphthalene (103)



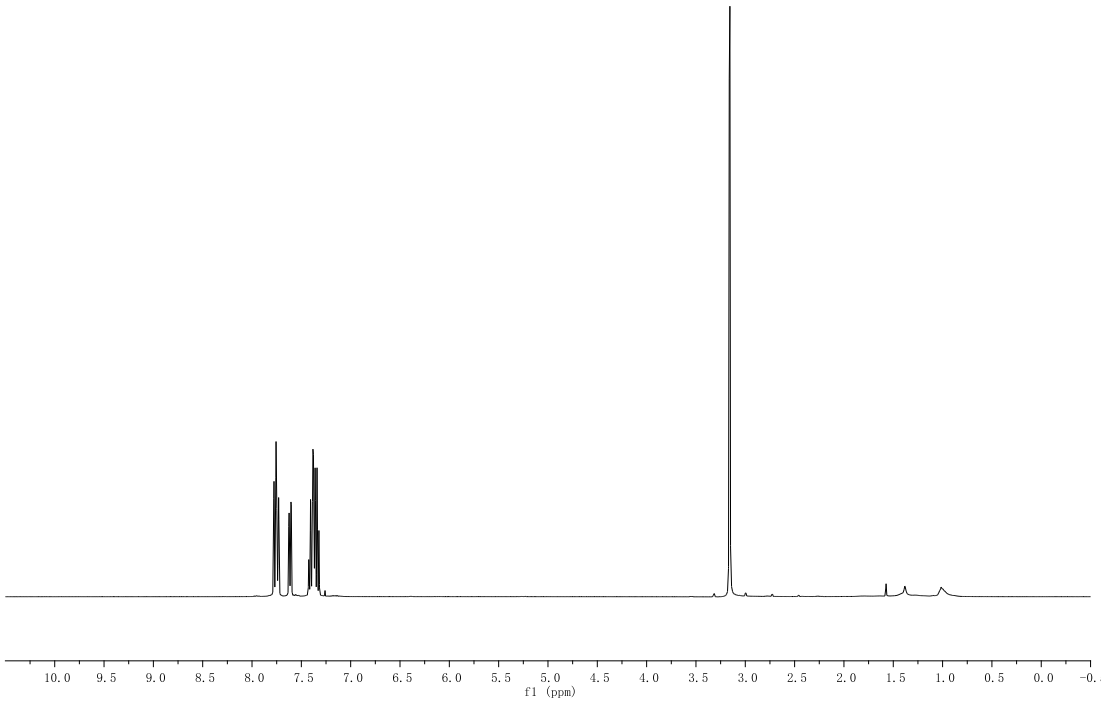
100

103

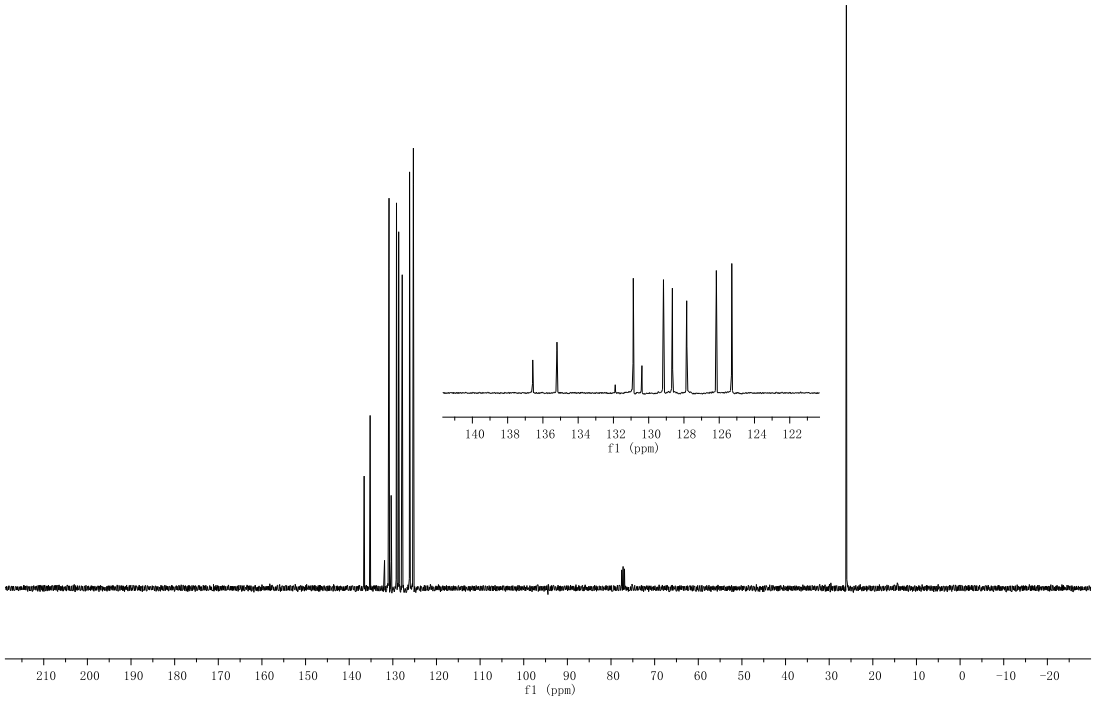
$C_{11}H_9Cl$
Exact Mass: 176.04
Molecular Weight: 176.64
C, 74.79; H, 5.14; Cl, 20.07

A solution of the trichloroacetate **100** (119 mg, 0.40 mmol) in degassed toluene (1 mL) containing CuCl (1.8 mg, 0.018 mmol) and the ligand **102** (5.5 mg, 0.018 mmol) was sealed under nitrogen in a screw capped tube and heated at 160 ℃ for 19 h. On cooling the reaction to ambient temperature the solvent was removed in vacuo and the black residue fractionated by column chromatography (silica gel; eluent: hexanes) to afford 1-chloro-8-methylnaphthalene (**103**) (21 mg, 0.12 mmol, 30%). ^{1}H NMR ($CDCl_3$) δ 3.16 (s, 3 H), 7.38 (m, 3 H), 7.61 (m, 1 H), 7.75 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 26.1, 125.3, 126.2, 127.8, 128.7, 129.2, 130.4, 130.9, 131.9, 135.2, 136.6 (11 of 11 expected resonances).

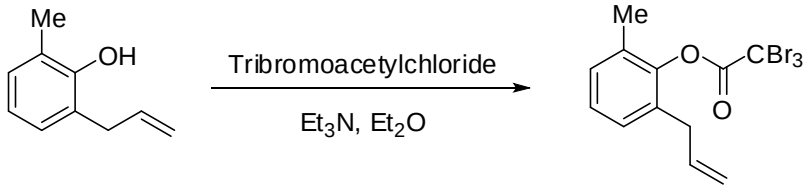
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **103**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **103**



Synthesis of 2-allyl-6-methylphenyl tribromoacetate (133)



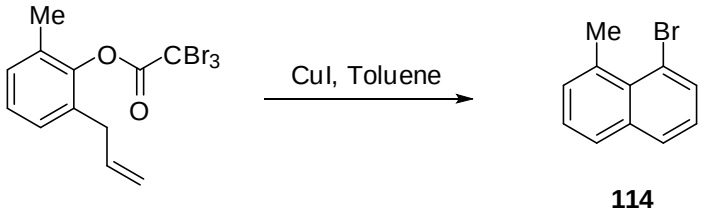
99

113

$C_{12}H_{11}Br_3O_2$
Exact Mass: 423.83
Molecular Weight: 426.93
C, 33.76; H, 2.60; Br, 56.15; O, 7.50

The preparation of compound **113** is adapted from the method of Strazzolini et al.,[83] who prepared the corresponding trichloroacetate. Tribromoacetyl chloride (4.49 g, 14.2 mmol) was added to a solution of compound **99** (2.11 g, 14.2 mmol) in Et_2O (60 mL). Et_3N (1.98 mL, 14.2 mmol) was added afterwards and the mixture was stirred at room temperature for 16 h. Water was added to the reaction mixture, which was then extracted with Et_2O (20 mL) three times. The combined organic layers were dried over Na_2SO_4 and concentrated to afford compound **113** as yellow liquid (4.92 g, 11.5 mmol, 81%).

Synthesis of 1-bromo-8-methylnaphthalene (114)



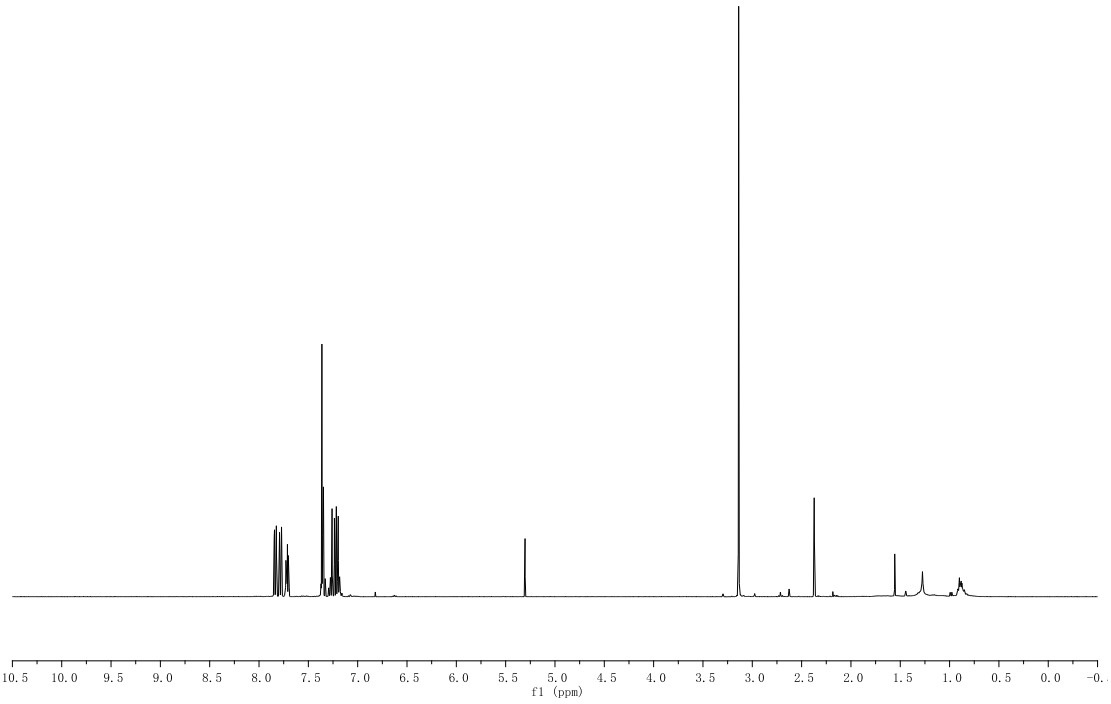
113

114

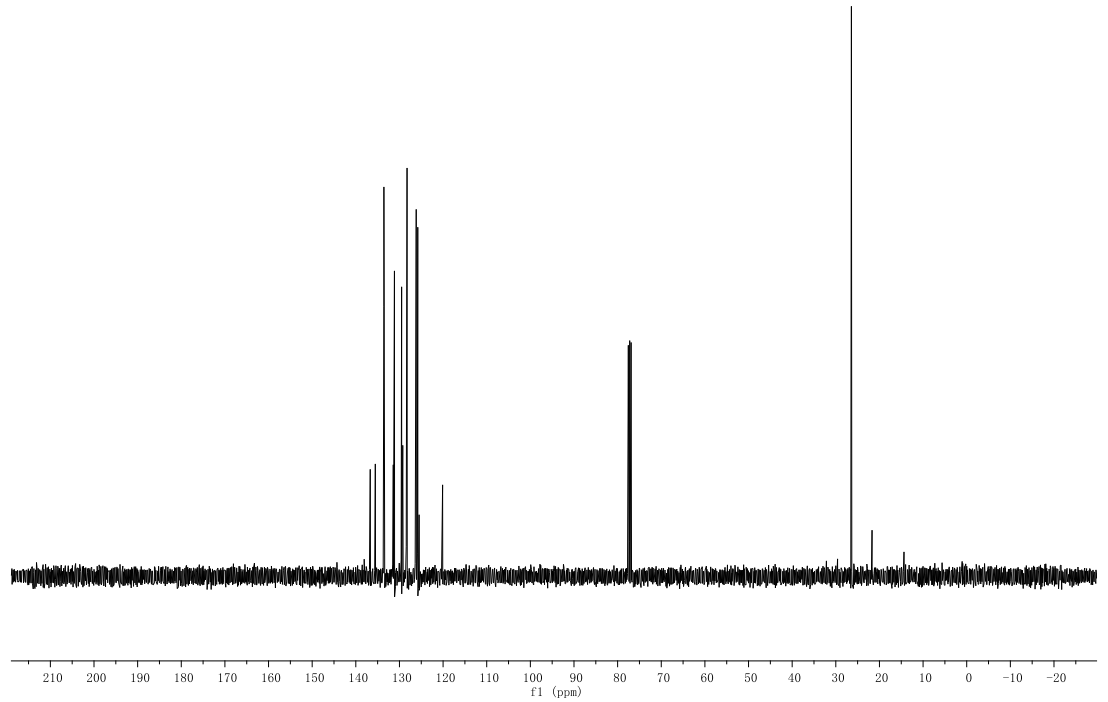
$C_{11}H_9Br$
Exact Mass: 219.99
Molecular Weight: 221.09
C, 59.76; H, 4.10; Br, 36.14

The preparation of compound **114** is adapted from the method of Bull et al.,[4] who prepared 1-chloro-8-methylnaphthalene. CuI (30 mg, 0.158 mmol) was added to a solution of compound **113** (1.50 g, 3.51 mmol) in toluene (25 mL), and the mixture was heated at reflux for 18 h. The solvent was removed and the resulting material was fractionated by silica gel column chromatography (solvent, hexanes) to give compound **113** as white crystals (0.26 g, 1.18 mmol, 34%). ^{1}H NMR ($CDCl_3$) δ 3.14 (s, 3 H), 7.21 (m, 1 H), 7.36 (m, 2 H), 7.71 (m, 1H), 7.78 (ddd, *J* = 8 Hz, *J* = 1 Hz, *J* = 0.5 Hz, 1 H), 7.83 (dd, *J* = 8 Hz, *J* = 1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 26.4, 120.1, 125.8, 126.2, 128.3, 128.4, 129.5, 131.2, 133.6, 135.5, 136.7 (11 of 11 expected resonances); MS (EI) *m/z* 220 (M^+, 75), 141 (M – Br, 100).

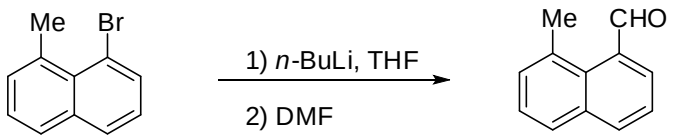
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **114**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **114**



Synthesis of 8-methyl-1-naphthaldehyde (115)

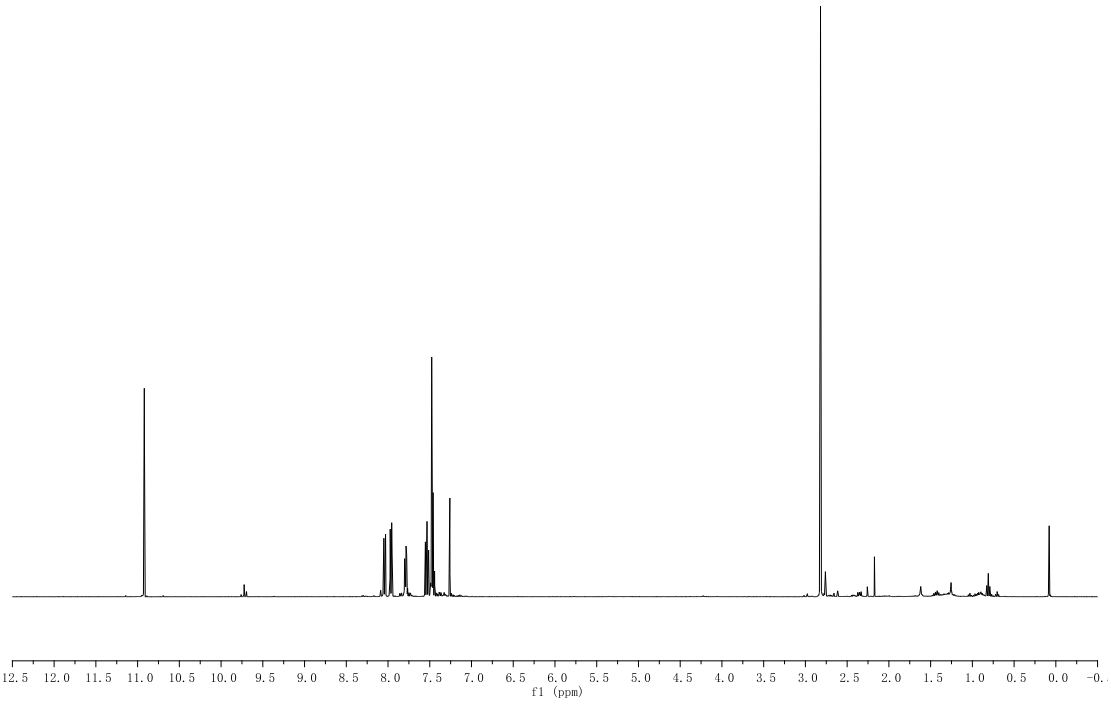


114 **115**

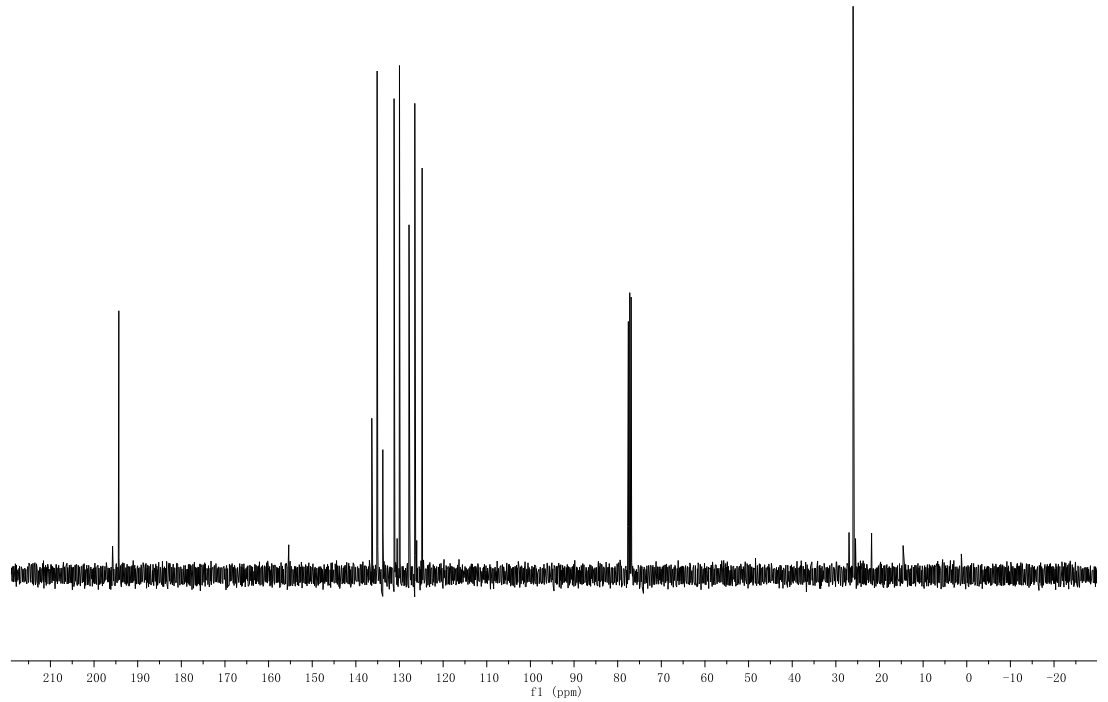
$C_{12}H_{10}O$
Exact Mass: 170.07
Molecular Weight: 170.21
C, 84.68; H, 5.92; O, 9.40

Compound **114** (55 mg, 0.25 mmol) was dissolved in THF (3 mL) and the solution was cooled to -78 ℃. *n*-BuLi (2.5 *M* in THF, 0.5 mL, 1.25 mmol) was added, and the solution was stirred at -78 ℃ for 30 min. DMF (0.20 mL, 2.5 mmol) was added, and the reaction mixture was stirred at room temperature for 4 h. Aqueous NH_4Cl was then added, and the resulting mixture was extracted with ether. The organic phase was dried over Na_2SO_4, and the solvent was stripped off. The resulting material was purified by silica gel column chromatography (solvent, hexanes then CH_2Cl_2) to give compound **115** as a yellow liquid (9 mg, 0.053 mmol, 21%). ^{1}H NMR ($CDCl_3$) δ 2.82 (s, 3 H), 7.46 (m, 2 H), 7.53 (t, *J* = 8 Hz, 1 H), 7.79 (m, 1 H), 7.96 (dd, *J* = 7 Hz, 2 Hz, 1 H), 8.04 (dd, *J* = 8 Hz, 1 Hz, 1 H), 10.92 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 26.1, 124.8, 126.5, 127.8, 130.0, 131.2, 131.3, 133.8, 135.0, 135.1, 136.4, 194.3 (12 of 12 expected resonances); MS (EI) *m/z* 170 (M^+, 100), 141 (M – CHO, 70).

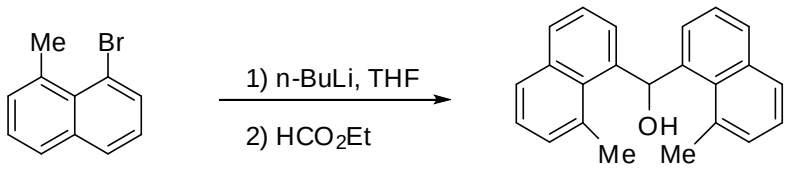
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **115**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **115**



Synthesis of bis(8-methylnaphthalen-1-yl)methanol (104)

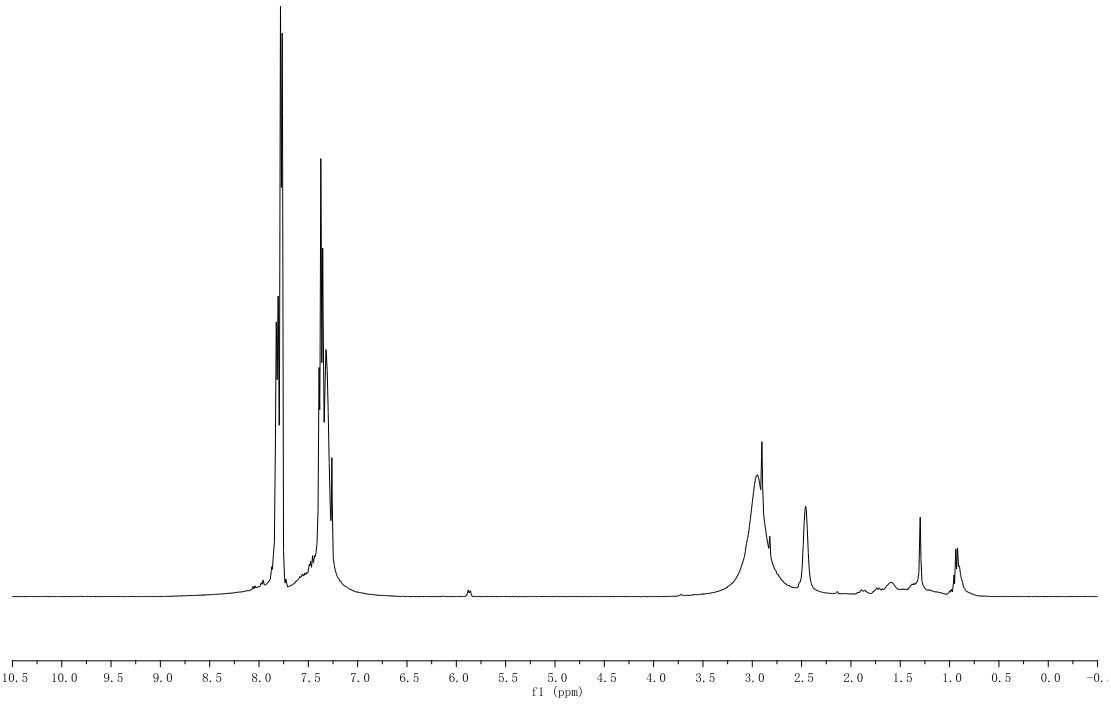


114 **104**

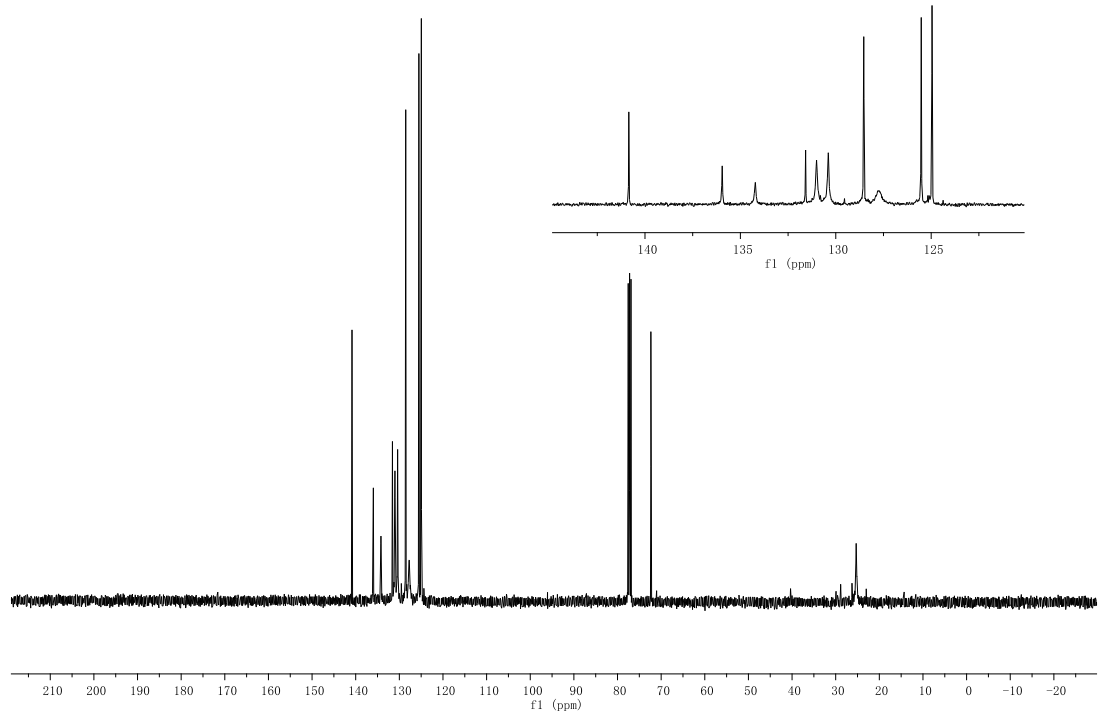
$C_{23}H_{20}O$
Exact Mass: 312.15
Molecular Weight: 312.40
C, 88.43; H, 6.45; O, 5.12

Compound **114** (1.10 g, 4.97 mmol) was dissolved in THF (4 mL) and the solution was cooled to -78 ℃. *n*-BuLi (2.5 *M* in THF, 2.0 mL, 5 mmol) was added, and the solution was stirred at -78 ℃ for 30 min. Ethyl formate (0.20 mL, 2.5 mmol) was added, and the reaction mixture was stirred at room temperature for 4 h. Aqueous NH_4Cl was then added, and the resulting mixture was extracted with ether. The organic phase was dried over Na_2SO_4, and the solvent was stripped off. The resulting material was purified by silica gel column chromatography (solvent, 3:1 hexanes-CH_2Cl_2) to give compound **104** as a yellow liquid (0.753 g, 2.41 mmol, 48%). ^{1}H NMR ($CDCl_3$) δ 2.46 (br s, 1 H), 3.10 (m, 6 H), 7.41 (m, 7 H), 7.81 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 72.4, 125.0, 125.5, 127.7, 128.5, 130.4, 131.0, 131.6, 134.2, 136.0, 140.9 (11 of 12 expected resonances); MS (EI) *m/z* 312 (M^+, 60), 294 (M – H_2O, 100).

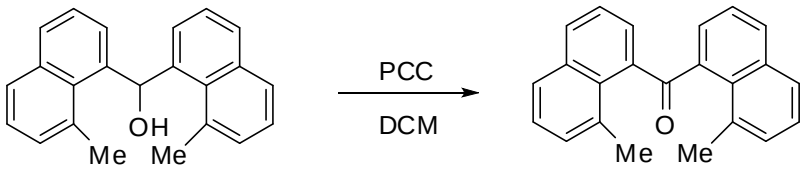
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **104**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **104**



Synthesis of bis(8-methylnaphthalen-1-yl)methanone (105)

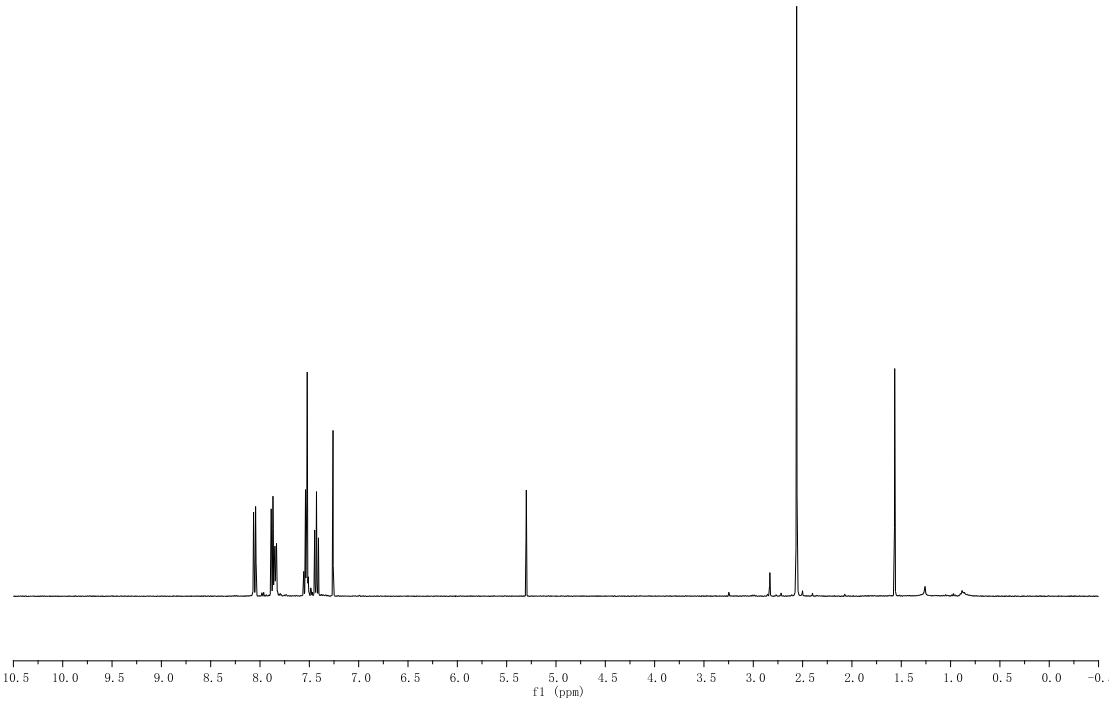


104 **105**

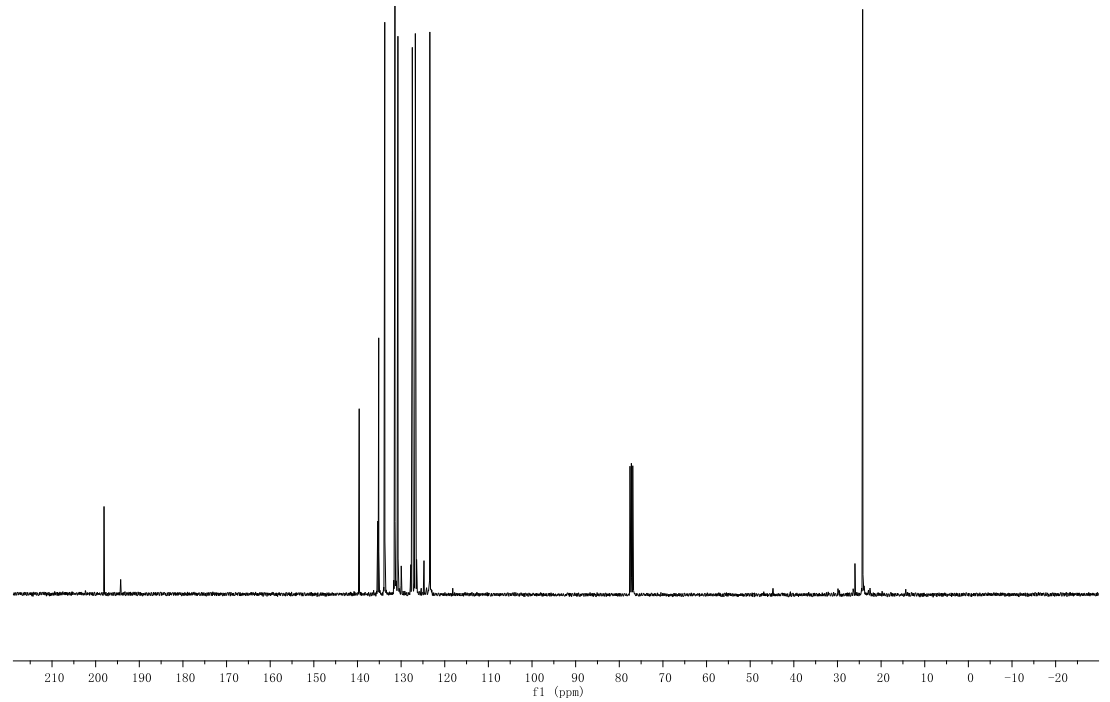
$C_{23}H_{18}O$
Exact Mass: 310.14
Molecular Weight: 310.39
C, 89.00; H, 5.85; O, 5.15

Compound **104** (100 mg, 0.32 mmol) and PCC (70 mg, 0.32 mmol) were stirred in CH_2Cl_2 (40 mL) at room temperature for 4 h. Ether and celite were added, and the mixture was filtered through a short column of silica gel. The filtrate was concentrated to yield compound **105** as white solid (84 mg, 0.27 mmol, 88%). Single crystals, suitable for X-ray analysis, were obtained from hexanes-CH_2Cl_2. ^{1}H NMR ($CDCl_3$) δ 2.56 (s, 6 H), 7.43 (t, *J* = 8 Hz, 2 H), 7.53 (m, 4 H), 7.84 (dd, *J* = 6.5 Hz, 2.5 Hz, 2 H), 7.88 (dd, *J* = 7 Hz, 1 Hz, 2 H); 8.05 (dd, *J* = 8 Hz, 1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 24.2, 123.4, 126.7, 127.4, 130.7, 130.8, 131.4, 133.8, 135.1, 135.3, 139.6, 198.1 (12 of 12 expected resonances); MS (EI) *m/z* 310 (M^+, 50), 292 (M – H_2O, 100).

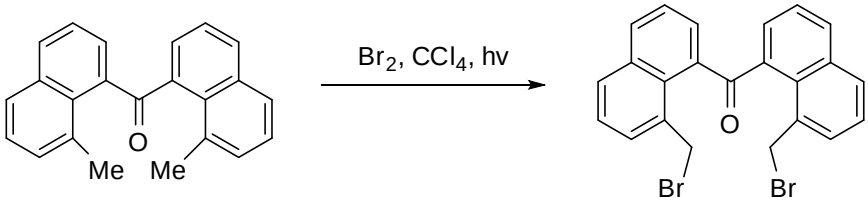
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **105**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **105**



Synthesis of bis[8-(bromomethyl)naphthalen-1-yl]methanone (106) and 13-bromo-1,12-bis(bromomethyl)-13H-dibenzo[a,i]fluorene (116)

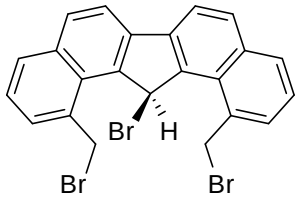


105

106

$C_{23}H_{16}Br_2O$
Exact Mass: 465.96
Molecular Weight: 468.18
C, 59.00; H, 3.44; Br, 34.13; O, 3.42

+



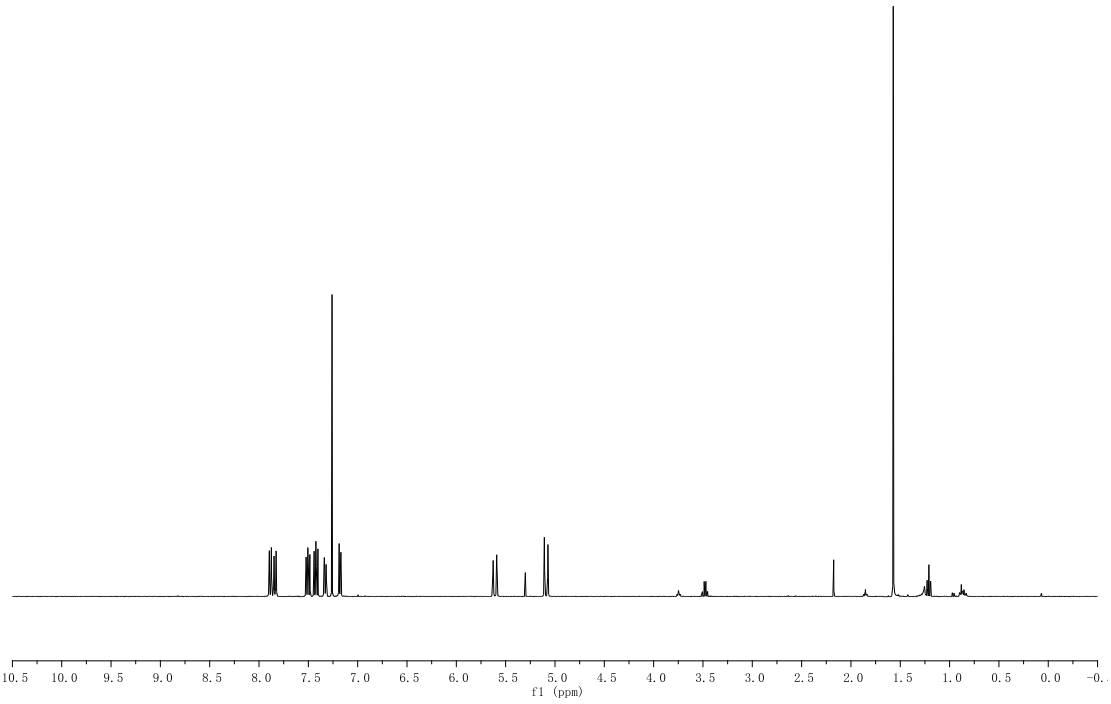
116

$C_{23}H_{15}Br_3$
Exact Mass: 527.87
Molecular Weight: 531.08
C, 52.02; H, 2.85; Br, 45.14

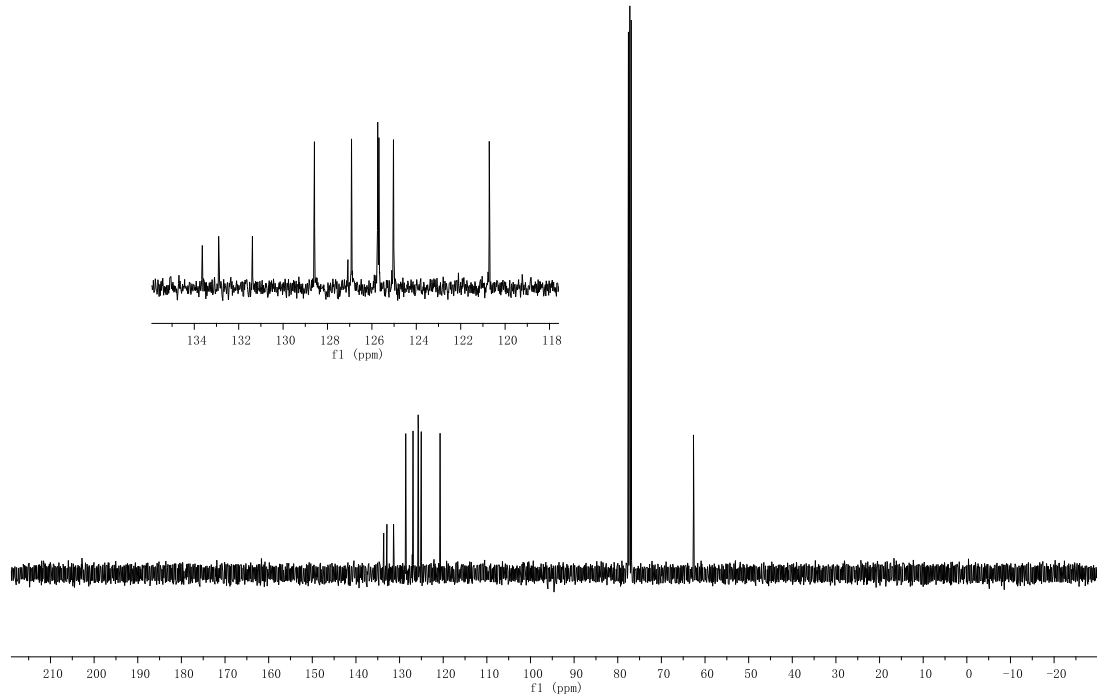
To a refluxing solution of ketone **105** (30 mg, 0.097 mmol) in CCl_4 (5 mL) under illumination with a tungsten lamp, in the presence of a small amount of anhydrous Na_2CO_3, a solution of bromine (0.015 mL Br_2 in 5 mL CCl_4) was added dropwise. After complete addition of Br_2, the mixture was heated at reflux for another 20 min with light. The mixture was then poured into dilute $NaHCO_3$, and the aqueous layer was extracted

with $CHCl_3$ (3X). The combined organics were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified on preparative TLC with 1:1 hexanes-CH_2Cl_2 as eluate to yield ketone **106** (1 mg, 2 μmol, 2.1%) and pentacyclic compound **116**. For **106**: ^{1}H NMR ($CDCl_3$) δ 5.09 (d, *J* = 14.5 Hz, 2 H), 5.61 (d, *J* = 14.5 Hz, 2 H), 7.18 (dd, *J* = 7 Hz, 1 Hz, 2 H), 7.33 (dd, *J* = 7 Hz, 1 Hz, 2 H), 7.42 (dd, *J* = 8 Hz, 7 Hz, 2 H), 7.50 (dd, *J* = 8 Hz, 7 Hz, 2 H), 7.84 (d, *J* = 8 Hz, 2 H), 7.89 (dd, *J* = 8 Hz, 1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 62.6, 120.7, 125.0, 125.7, 125.8, 126.9, 127.1, 128.6, 131.4, 132.9, 133.6, 202.8 (12 of 12 expected resonances).

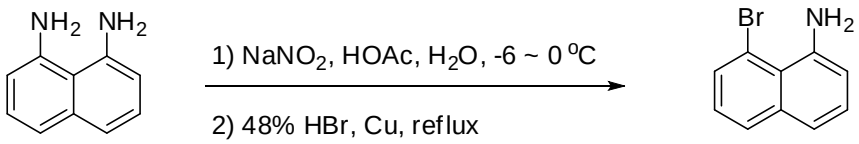
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **106**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **106**



Synthesis of 1-amino-8-bromonaphthalene (119)



117 **119**

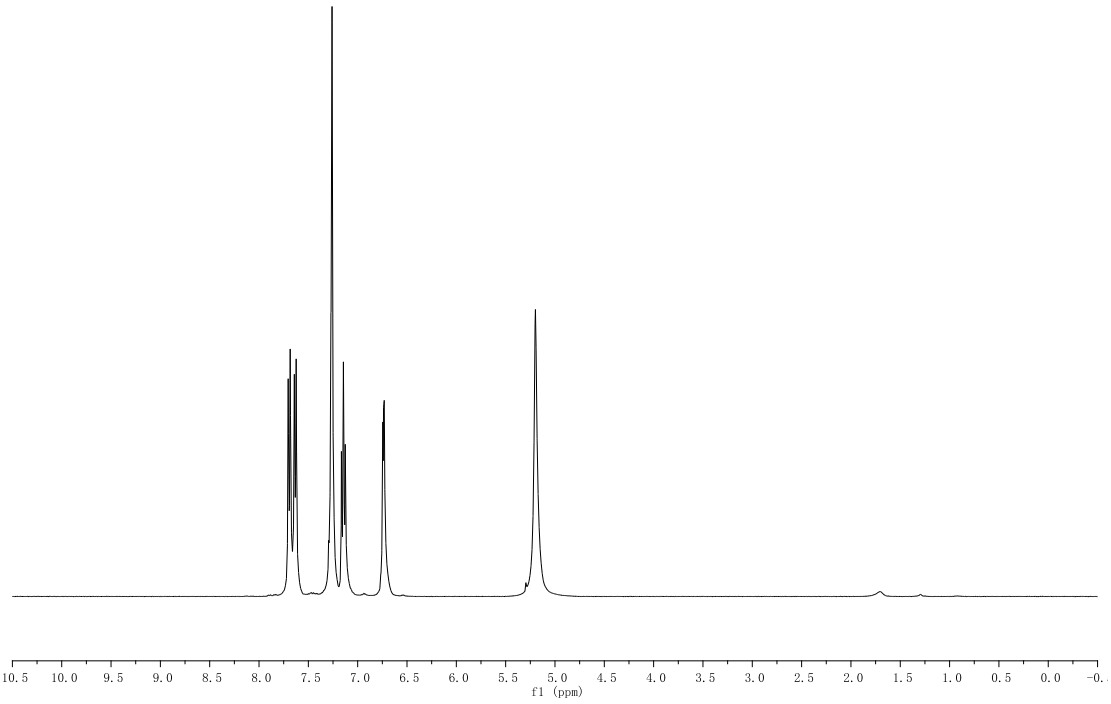
$C_{10}H_8BrN$
Exact Mass: 220.98
Molecular Weight: 222.08
C, 54.08; H, 3.63; Br, 35.98; N, 6.31

Compound **119** was prepared by the method of Jurok et al.[84] A solution of $NaNO_2$ (9.12 g, 132 mmol) in water (53 mL) was added to a solution of naphthalene-1,8-diamine (20.00 g, 126 mmol) in a mixture of acetic acid (240 mL) and water (175 mL) at –6 ℃. Then the reaction mixture was diluted with water (40 mL) and stirred at 0 ℃ for 45 min. The brown precipitate was filtered off, washed with water and dried at room temperature to give compound **118** as brown powder, which was sufficiently pure for the next synthesis.

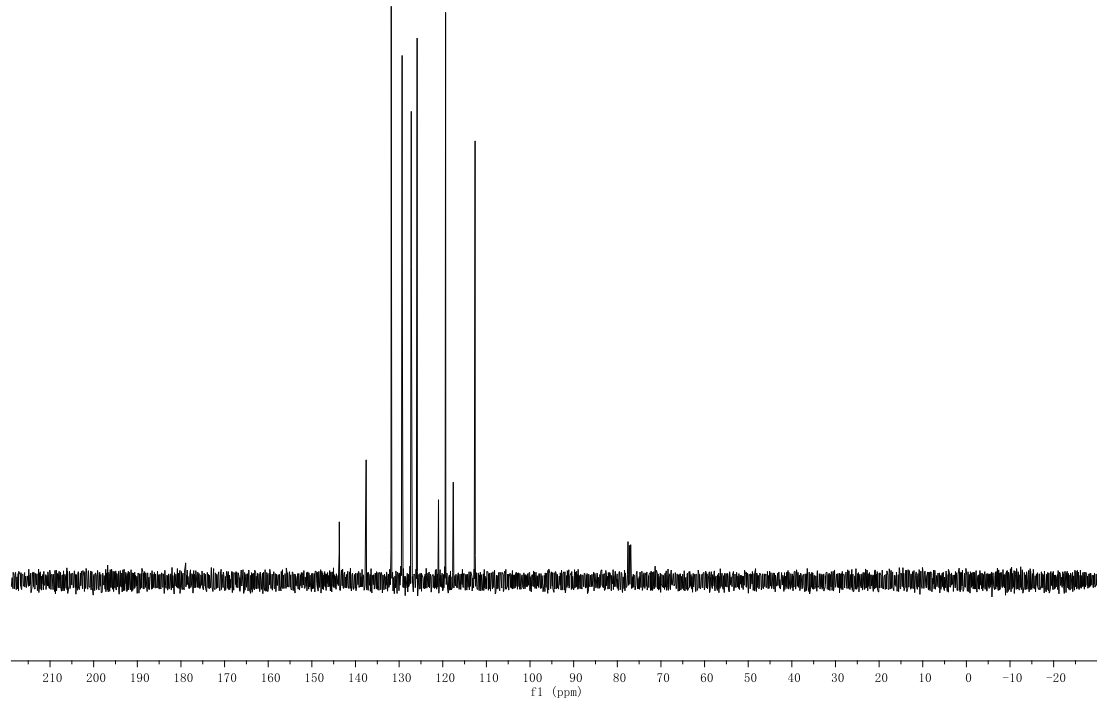
Copper powder (6.00 g, 94 mmol), activated by iodine, was added to a vigorously stirring solution of compound **118** in aqueous HBr (48%, 140 mL) at 50 ℃. When the intense evolution of nitrogen had finished, the mixture was heated at reflux. The mixture was diluted with water (300 mL), heated to boiling and filtered. The residue was washed with boiling water (150 mL). The combined filtrates were neutralised with ammonia and

extracted with diethyl ether. The ethereal solution was washed with water, filtered to remove suspended solid, and dried with Na_2SO_4. The crude product obtained after solvent evaporation was purified by column chromatography with 3:2 CH_2Cl_2-hexanes as elute to afford **119** (4.59 g; 20.7 mmol, 16%) as a pink solid. ^{1}H NMR ($CDCl_3$) δ 5.20 (s, 2 H), 6.74 (dd, *J* = 6 Hz, 3 Hz, 1 H), 7.15 (t, *J* = 8 Hz, 1 H), 7.26 (m, 2 H), 7.63 (dd, *J* = 8 Hz, 1 Hz, 1 H), 7.70 (dd, *J* = 8 Hz, 1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 112.6, 117.6, 119.4, 121.0, 125.9, 127.2, 129.3, 131.8, 137.6, 143.7 (10 of 10 expected resonances).

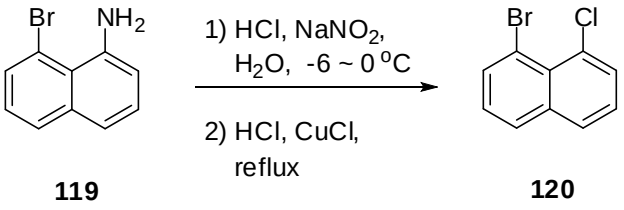
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **119**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **119**



Synthesis of 1-bromo-8-chloronaphthalene (120)

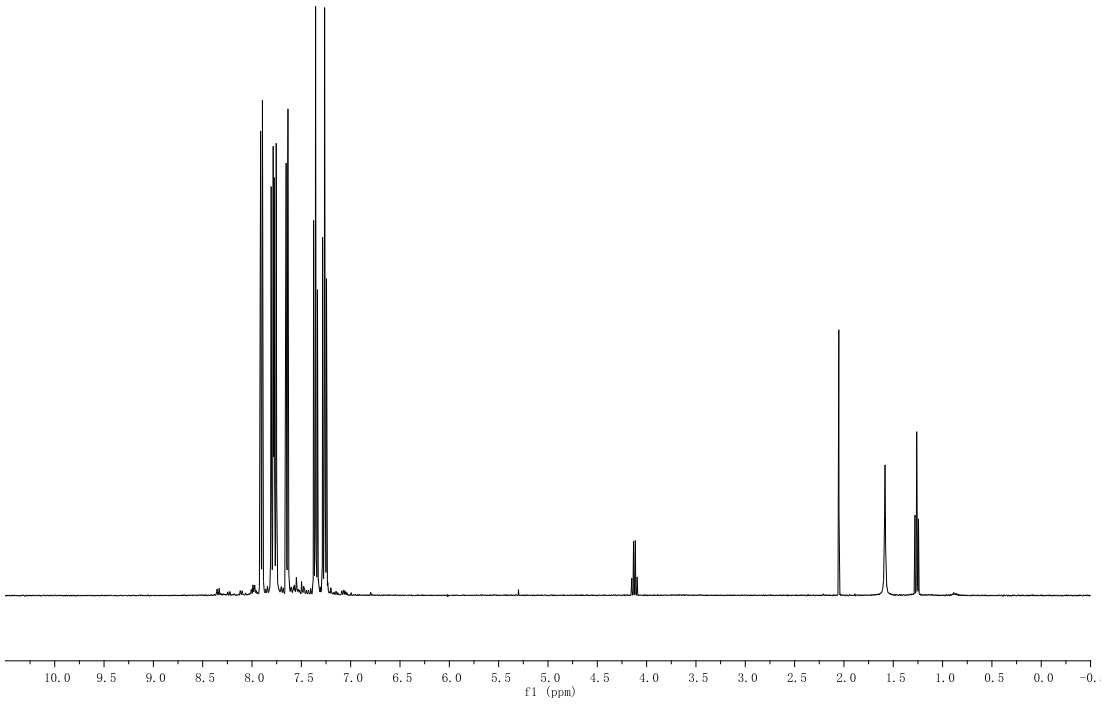


119 **120**

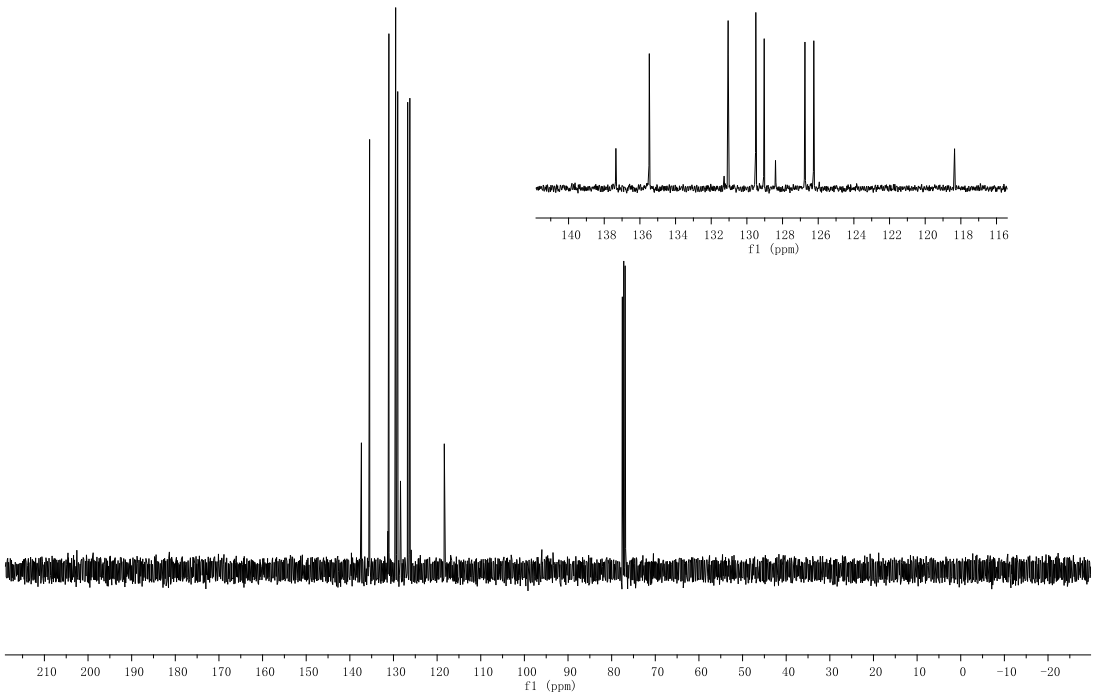
$C_{10}H_6BrCl$
Exact Mass: 239.93
Molecular Weight: 241.51
C, 49.73; H, 2.50; Br, 33.08; Cl, 14.68

A solution of $NaNO_2$ (1.15 g, 16.7 mmol) in water (4 mL) was added to a cold solution (kept between -6 and 0 ℃) of 1-amino-8-bromonaphthalene (**119**, 1.5 g, 6.75 mmol) in conc. HCl (10 mL) and water (8.5 mL). CuCl (4.62 g, 46.7 mmol) was dissolved in conc. HCl (20 mL), and it was added to the reaction mixture. The reaction was brought to room temperature and stirred at 70 ℃ for 1 h. EtOAc (200 mL) was added, and the organic layer was separated. This solution was washed with water, aqueous Na_2CO_3, and brine, and it was dried over Na_2SO_4. The solvent was stripped away to afford compound **120** (1.5 g, 6.2 mmol, 92%) as a dark brown solid. ^{1}H NMR ($CDCl_3$) δ 7.26 (t, *J* = 8 Hz, 1 H), 7.36 (t, *J* = 8 Hz, 1 H), 7.65 (dd, *J* = 7 Hz, *J* = 1 Hz, 1 H), 7.76 (d, *J* = 8 Hz, 1 H), 7.80 (d, *J* = 8 Hz, 1 H), 7.90 (dd, *J* = 7.5 Hz, *J* = 1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 118.4, 126.3, 126.8, 128.4, 129.0, 129.5, 131.1, 131.3, 135.5, 137.4 (10 of 10 expected resonances); MS (EI) *m/z* 242 (M^+, 100), 161 (M – Br, 50).

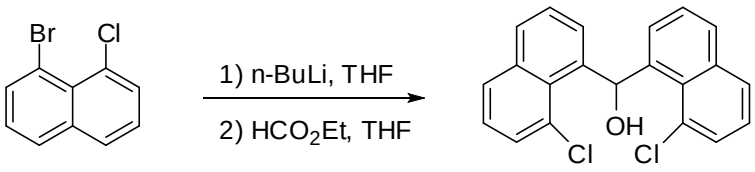
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **120**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **120**



Synthesis of bis(8-chloronaphthalen-1-yl)methanol (121)



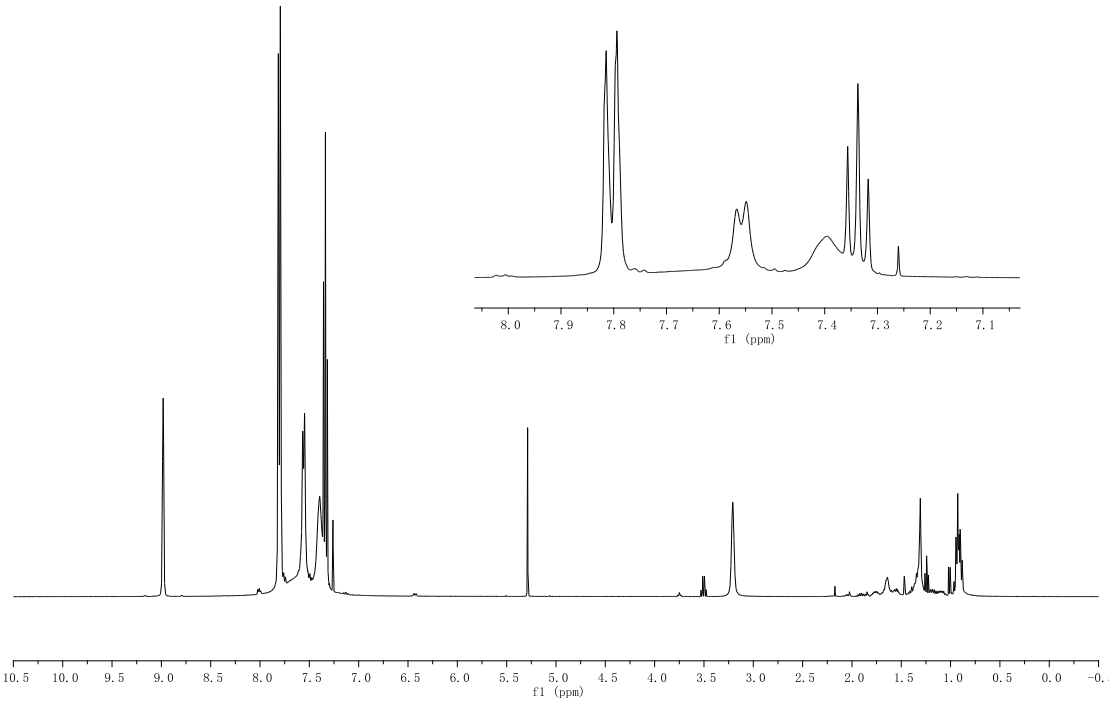
120

121

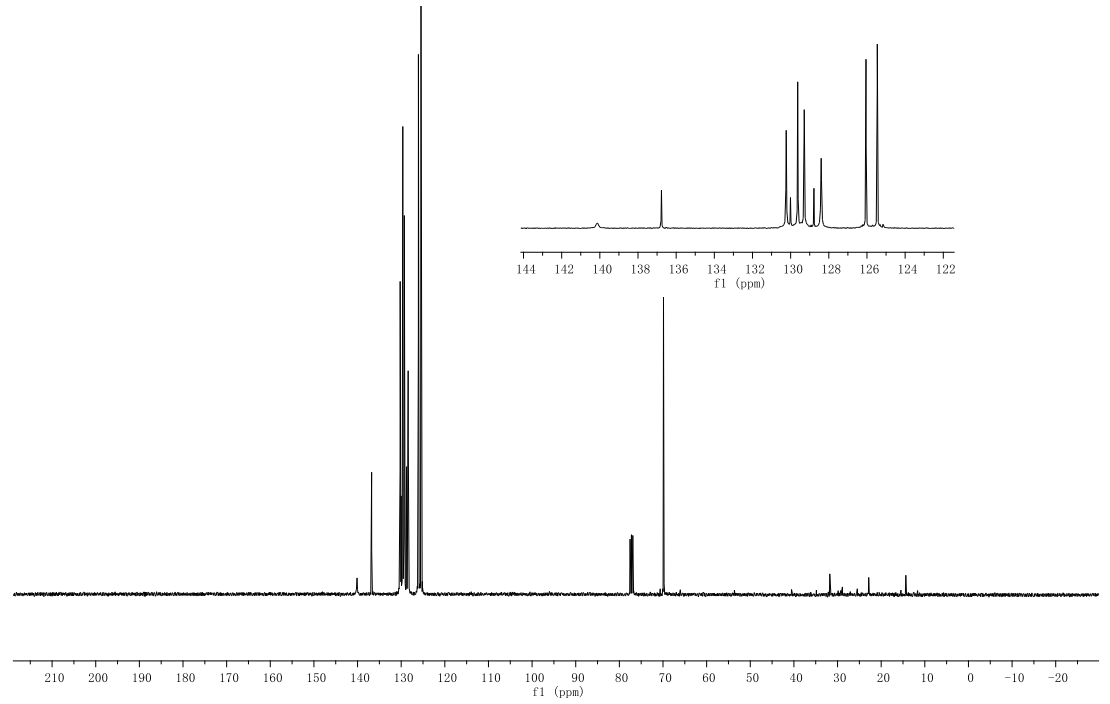
$C_{21}H_{14}Cl_2O$
Exact Mass: 352.04
Molecular Weight: 353.24
C, 71.40; H, 3.99; Cl, 20.07; O, 4.53

Compound **120** (120 mg, 0.497 mmol) was dissolved in 1 mL THF and cooled to -78 ℃. *n*-BuLi (2.5 *M* in THF, 0.2 mL, 0.5 mmol) was added and the solution was stirred at -78 ℃ for 30 min. Ethyl formate (0.020 mL, 0.25 mmol) was added, and the reaction mixture was stirred at room temperature for a further 4 h. Aqueous NH_4Cl was then added, and the resulting mixture was extracted with ether. The organic phase was dried over Na_2SO_4, and the solvent was stripped away to leave compound **121** as yellow liquid (97 mg, 0.275 mmol, 55%). ^{1}H NMR ($CDCl_3$) δ 3.21 (s, 1H), 7.34 (t, *J* = 8 Hz, 3 H), 7.40 (br s, 2 H), 7.56 (d, *J* = 8 Hz, 3 H), 7.80 (d, *J* = 8 Hz, 4 H), 8.98 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 69.9, 125.5, 126.0, 128.4, 128.8, 129.3, 129.6, 130.0, 130.2, 136.8, 140.1 (11 of 11 expected resonances); MS (EI) *m/z* 352 (M^+, 20), 317 (M – Cl, 30), 282 (M – 2Cl, 20), 189 (100).

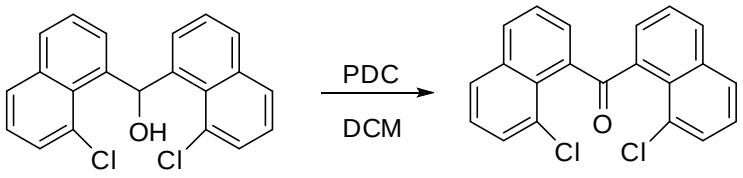
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **121**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **121**



Synthesis of bis(8-chloronaphthalen-1-yl)methanone (122)

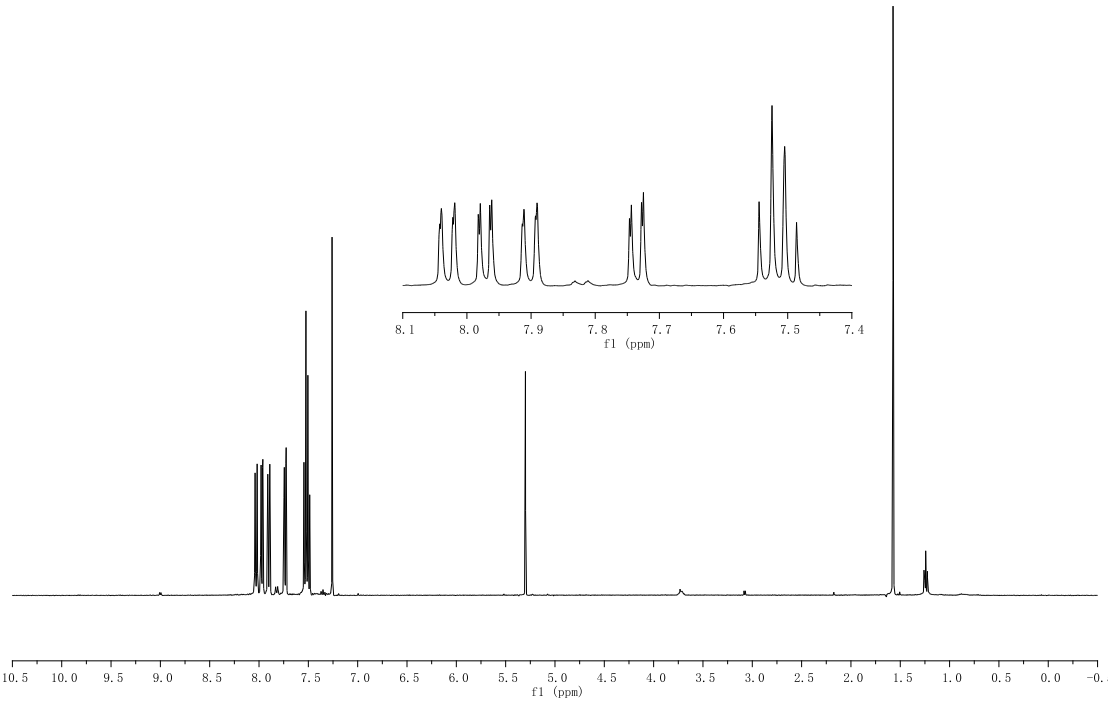


121 **122**

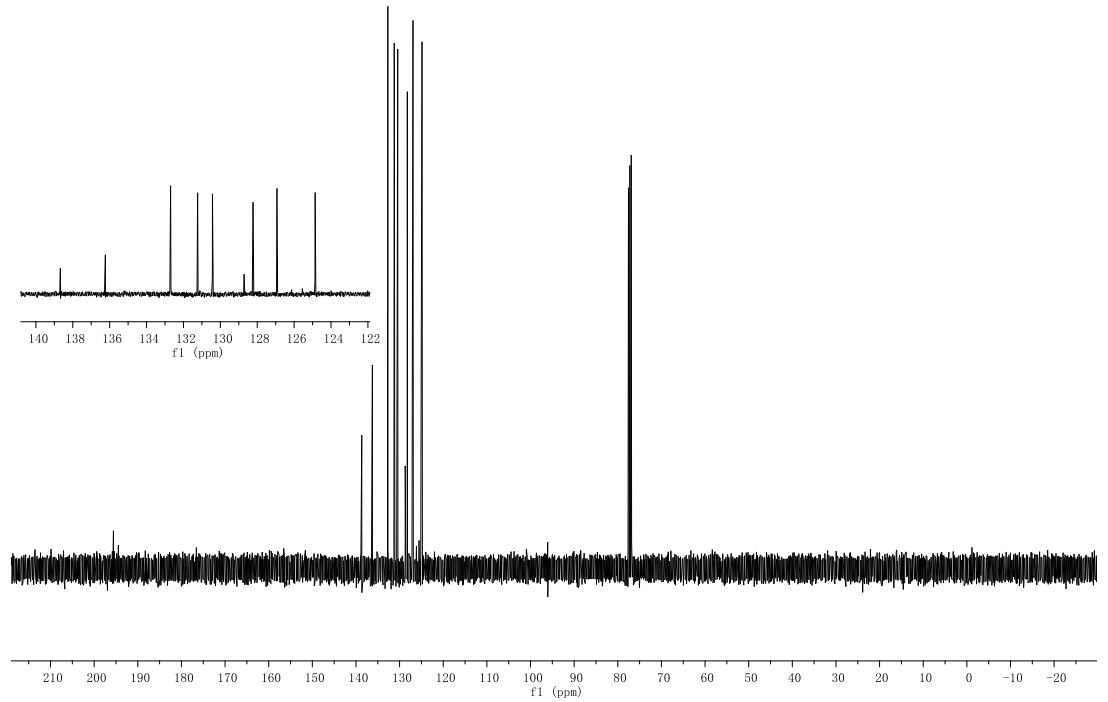
$C_{21}H_{12}Cl_2O$
Exact Mass: 350.03
Molecular Weight: 351.23
C, 71.81; H, 3.44; Cl, 20.19; O, 4.56

Compound **121** (1.51 g, 4.27 mmol) and PDC (0.965 g, 2.56 mmol) were stirred in CH_2Cl_2 (150 mL) at room temperature for 4 h. Ether and celite were added, and the mixture was filtered through a short column of silica gel. The filtrate was concentrated to dryness and the residue was recrystallized from CH_2Cl_2 to give compound **122** as white solid (1.18 g, 3.36 mmol, 79%). Single crystals, suitable for X-ray analysis, were obtained from hexanes-CH_2Cl_2. ^{1}H NMR ($CDCl_3$) δ 7.50 (t, *J* = 8 Hz, 2 H), 7.53 (t, *J* = 8 Hz, 2 H), 7.74 (dd, *J* = 8 Hz, *J* = 1.2 Hz, 2 H), 7.90 (dd, *J* = 8 Hz, *J* = 1.2 Hz, 2 H), 7.97 (dd, *J* = 8 Hz, *J* = 1 Hz, 2 H), 8.03 (dd, *J* = 8 Hz, *J* = 1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 124.9, 126.9, 128.2, 128.7, 130.4, 131.2, 131.3, 132.7, 136.2, 138.7, 195.6 (11 of 11 expected resonances); MS (EI) *m/z* 315 (M – Cl, 100).

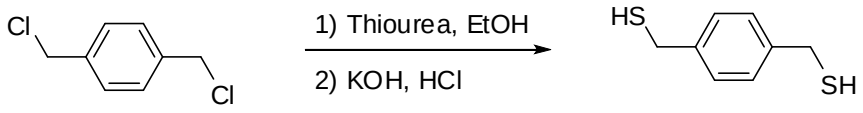
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **122**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **122**



Synthesis of 1,4-bis(mercaptomethyl)benzene (91)

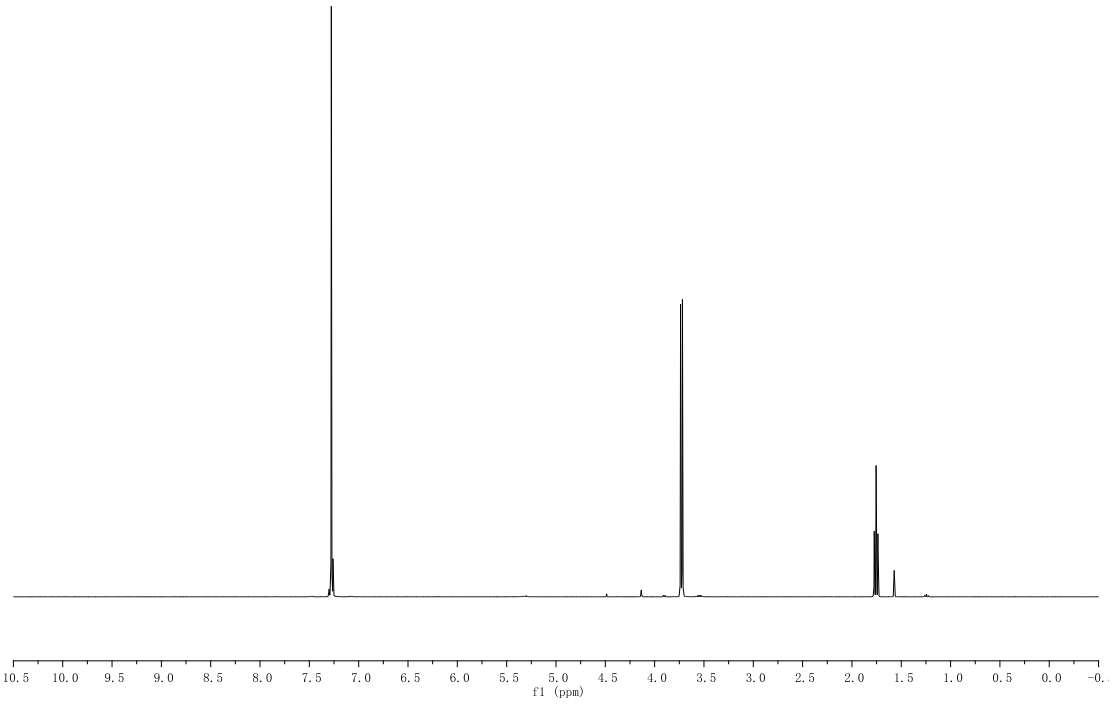


91

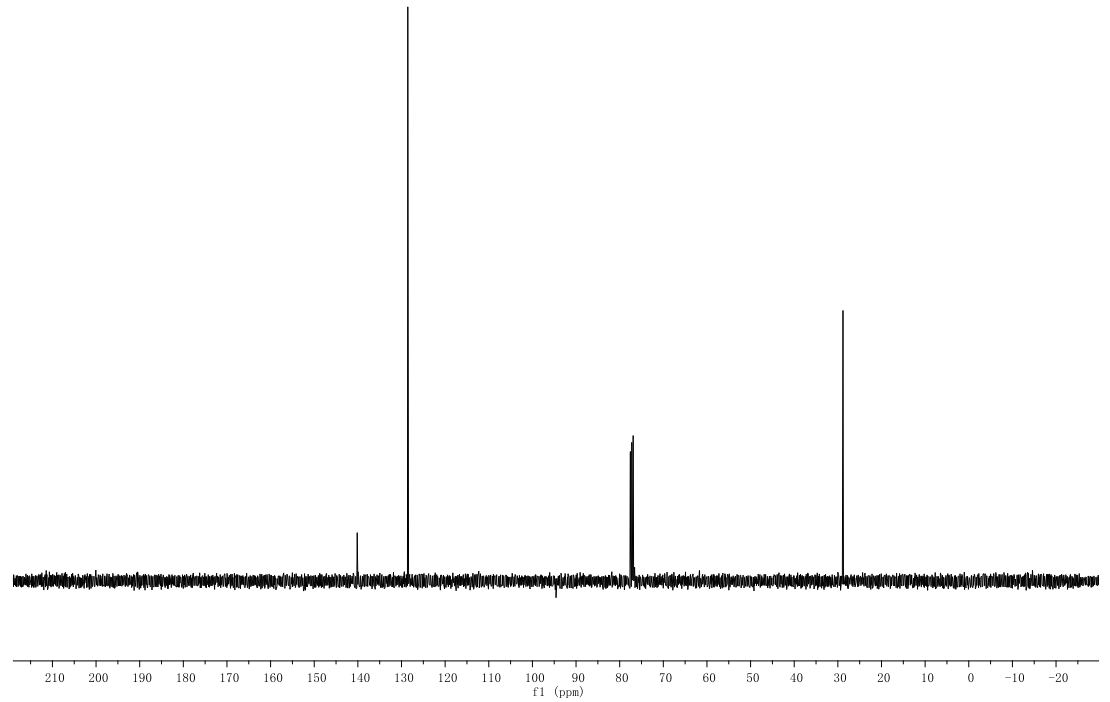
$C_8H_{10}S_2$
Exact Mass: 170.02
Molecular Weight: 170.29
C, 56.42; H, 5.92; S, 37.66

A solution of 1,4-bis(chloromethyl)benzene (1.75 g, 10 mmol) and thiourea (1.52 g, 20 mmol) in ethanol was heated at reflux overnight. After cooling, the solvent was removed. To the remaining white salt was added aqueous KOH (4.4 g, 70 mL water) under argon. This solution was heated at reflux for 5 h, cooled to room temperature, acidified with 1 N HCl and extracted with CH_2Cl_2 (3X). The combined extracts were dried over Na_2SO_4 and concentrated in vacuo to give the desired dithiol **91** (1.50 g, 8.8 mmol, 88%); ^{1}H NMR ($CDCl_3$) δ 1.75 (t, *J* = 8 Hz, 2 H), 3.73 (d, *J* = 8 Hz, 4 H), 7.28 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 28.8, 128.6, 140.2 (3 of 3 expected resonances).

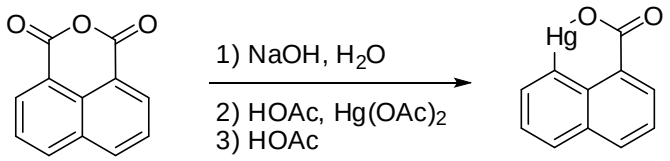
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **91**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **91**



Synthesis of anhydro-8-(hydroxymercuri)-1-naphthoic acid (128)

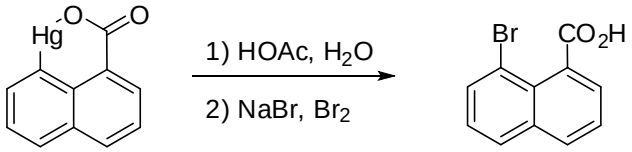


127 **128**

$C_{11}H_6HgO_2$
Exact Mass: 372.01
Molecular Weight: 370.75
C, 35.63; H, 1.63; Hg, 54.10; O, 8.63

Compound **128** was prepared by the method of Bailey et al.[85] 1,8-Naphthalic anhydride (**127**, 19.8 g, 0.10 mol) was suspended in aqueous sodium hydroxide (14.0 g, 0.35 mol, in 600 mL of water) and refluxed until the solid material dissolved. The excess base was neutralized with glacial acetic acid (10 mL), and a solution of mercuric acetate, prepared by dissolving mercuric oxide (22.0 g, 0.10 mol) in hot glacial acetic acid (50 mL) and diluting with water (100 mL), was added in one portion. After the mixture had been heated at reflux for 30 min, additional glacial acetic acid (18 mL) was added to the white slurry, resulting in the slow evolution of carbon dioxide. The slurry was heated at reflux for 48 h, cooled, and filtered. The highly insoluble solid was washed with water and then dried to give compound **128** as a tan powder (31.1 g, 0.10 mol, 84%), which was used without further purification.

Synthesis of 8-bromo-1-naphthoic acid (129)

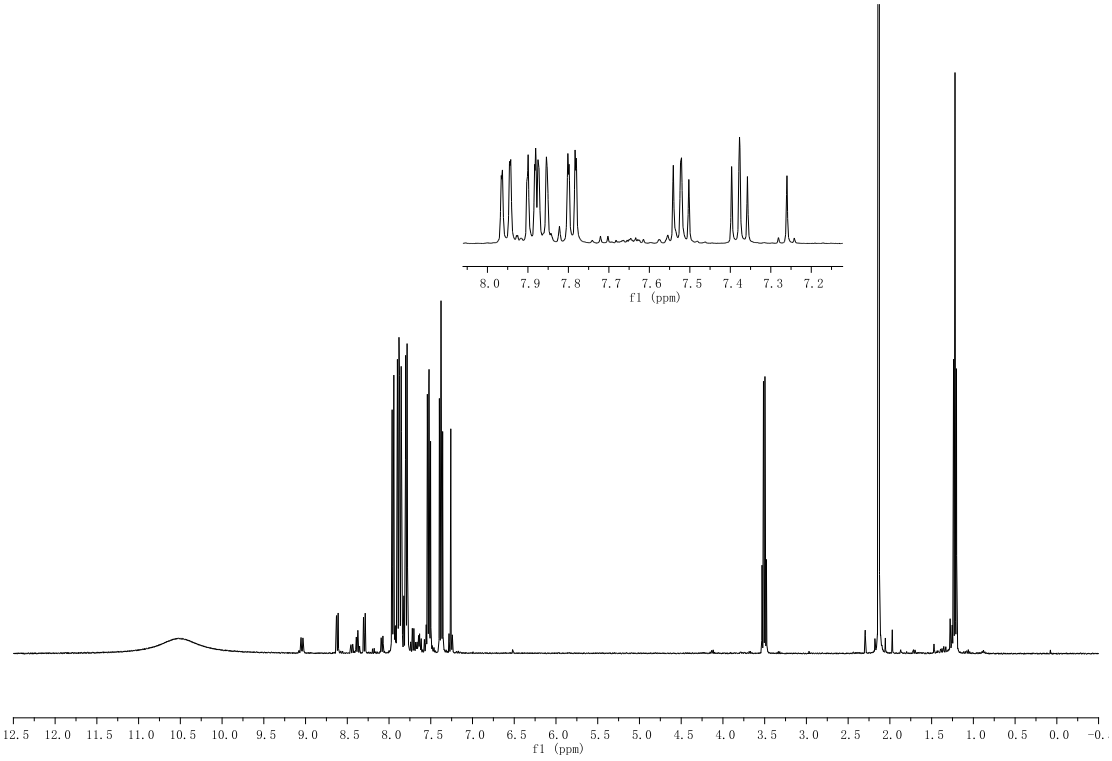


128 **129**

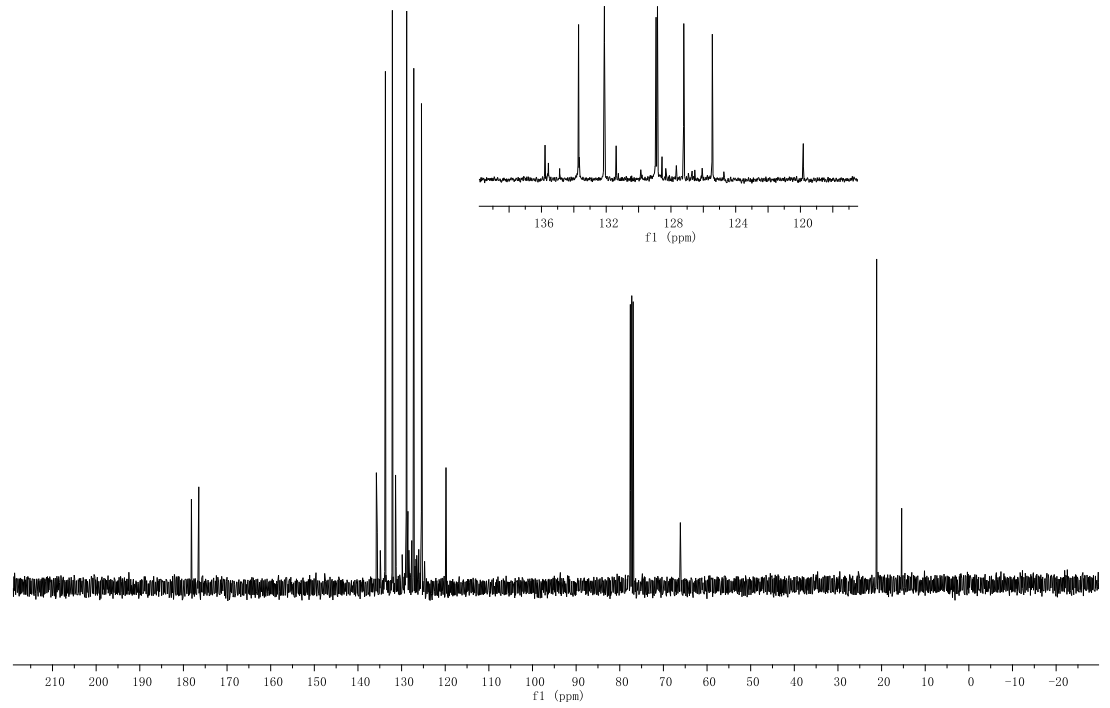
$C_{11}H_7BrO_2$
Exact Mass: 249.96
Molecular Weight: 251.08
C, 52.62; H, 2.81; Br, 31.82; O, 12.74

Compound **129** was prepared by the method of Bailey et al.[85] Compound **128** (31.12 g, 84 mmol) suspended in glacial acetic acid (123 mL) and water (20 mL), and the mixture was stirred vigorously at 0 ℃. Sodium bromide (55.82 g, 0.54 mol) in water (100 mL) and bromine (4.09 g, 79 mmol) were added slowly all together while the reaction temperature was maintained at 0-5 ℃. The resulting slurry was then slowly heated to 100 ℃ and poured on ice. The precipitate was washed with water, dissolved in hot aqueous sodium hydroxide (19.6 g, in 40 mL of water), and filtered through Celite. When the filtrate was acidified with concentrated hydrochloric acid (40 mL) and cooled, it was extracted with ether. The organic layer was dried with Na_2SO_4 and concentrated in vacuo to give compound **129** as white solid (14.5 g, 57.8 mmol, 69%). ^{1}H NMR ($CDCl_3$) δ 7.38 (t, *J* = 8 Hz, 1 H), 7.52 (dd, *J* = 8 Hz, 7 Hz, 1 H), 7.79 (dd, *J* = 7 Hz, 1 Hz, 1 H), 7.86 (d, *J* = 8 Hz, 1 H), 7.89 (dd, *J* = 8 Hz, 1 Hz, 1 H), 7.95 (dd, *J* = 8 Hz, 1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 119.8, 125.4, 127.2, 128.5, 128.8, 128.9, 131.4, 132.1, 133.7, 135.8, 176.5 (11 of 11 expected resonances).

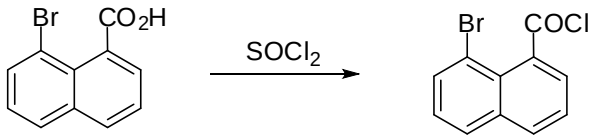
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **129**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **129**



Synthesis of 8-bromo-1-naphthoyl chloride (139)

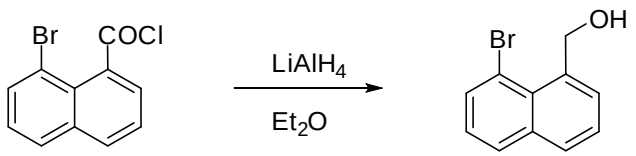


129 **139**

$C_{11}H_6BrClO$
Exact Mass: 267.93
Molecular Weight: 269.52
C, 49.02; H, 2.24; Br, 29.65; Cl, 13.15; O, 5.94

8-Bromonaphthoic acid (**129**, 14.5 g, 58 mmol) was placed in a round bottom flask to which thionyl chloride (12.5 mL, 172 mmol) was added. The mixture was heated under refluxed for 3 h. After the mixture had cooled to room temperature, it was concentrated under reduced pressure to yield 8-bromo-1-naphthoyl chloride (**139**) as a yellow solid (15.43 g, 57 mmol, 98%). The crude product was used without further purification.

Synthesis of (8-bromonaphthalen-1-yl)methanol (130)

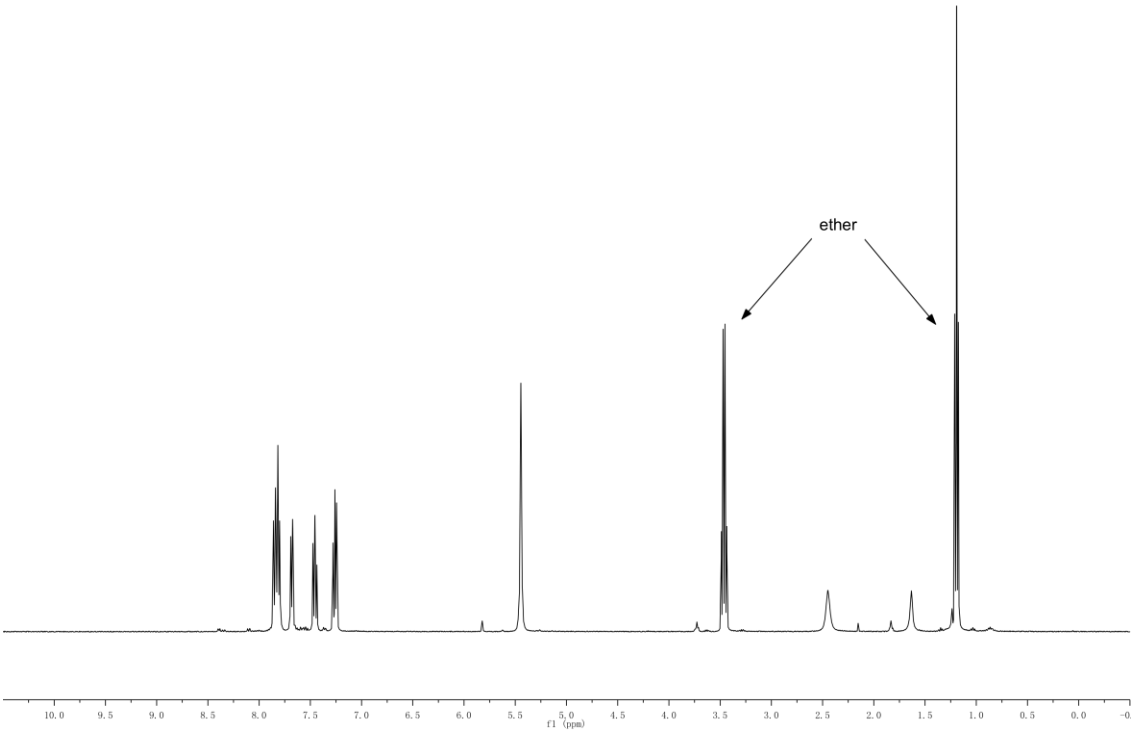


139 **130**

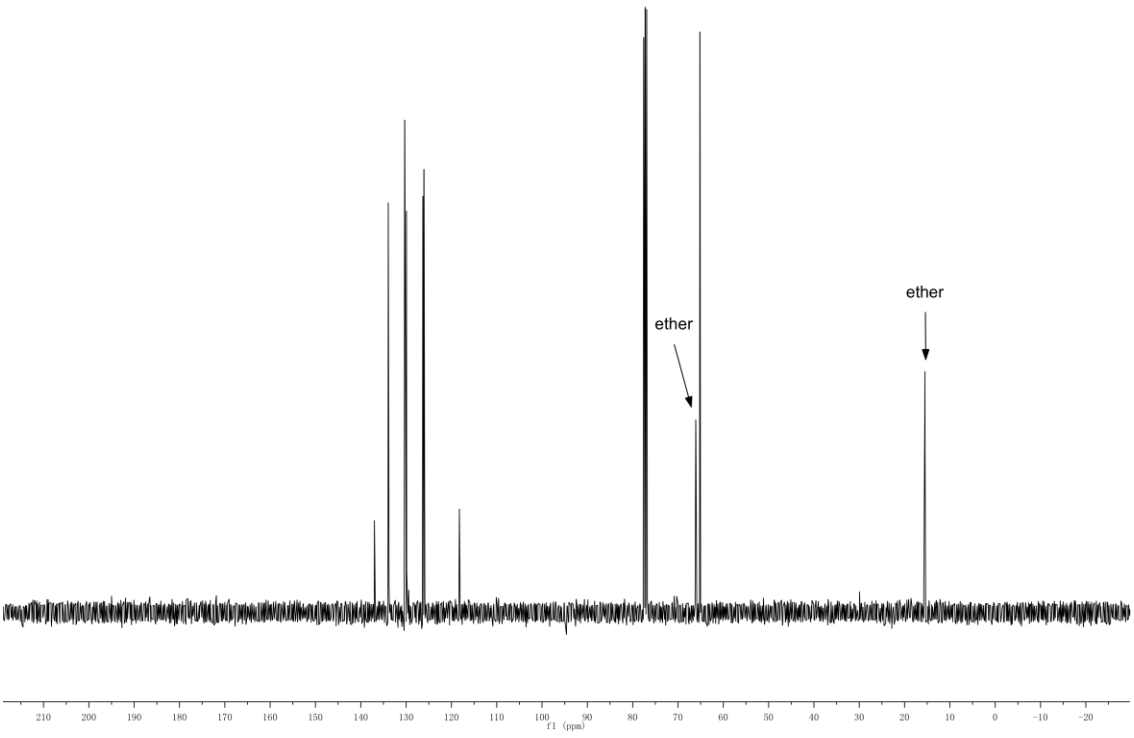
$C_{11}H_9BrO$
Exact Mass: 235.98
Molecular Weight: 237.09
C, 55.72; H, 3.83; Br, 33.70; O, 6.75

8-Bromo-1-naphthoyl chloride (**139**, 15.43 g, 57 mmol) was dissolved in ether (150 mL) to which $LiAlH_4$ (1.65 g, 44 mmol) was added. The reaction mixture was heated to reflux for 2 h. After the reaction mixture had cooled to room temperature, water was added and the mixture was filtered. The filtrate was extracted with ether and dried with Na_2SO_4. Solvent was removed under reduced pressure and compound **130** was obtained as a light yellow solid (11.67 g, 49 mmol, 86%). ^{1}H NMR ($CDCl_3$) δ 2.46 (s, 1 H), 5.46 (s, 2 H), 7.27 (t, *J* = 8 Hz, 1 H), 7.47 (t, *J* = 8 Hz, 1 H), 7.70 (d, *J* = 8 Hz, 1 H), 7.85 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 65.2, 118.2, 126.1, 126.3, 129.9, 130.3, 130.4, 133.9, 136.9, 137.0 (10 of 11 expected resonances); MS (EI) *m/z* 236 (M^+, 20), 219 (M – OH, 15), 156 (M – HBr, 50), 128 (100).

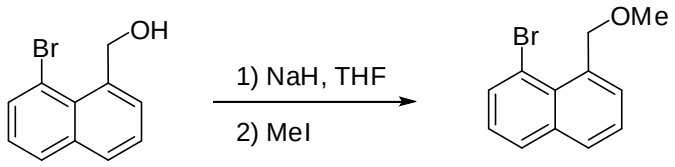
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **130**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **130**



Synthesis of 1-bromo-8-(methoxymethyl)naphthalene (131)

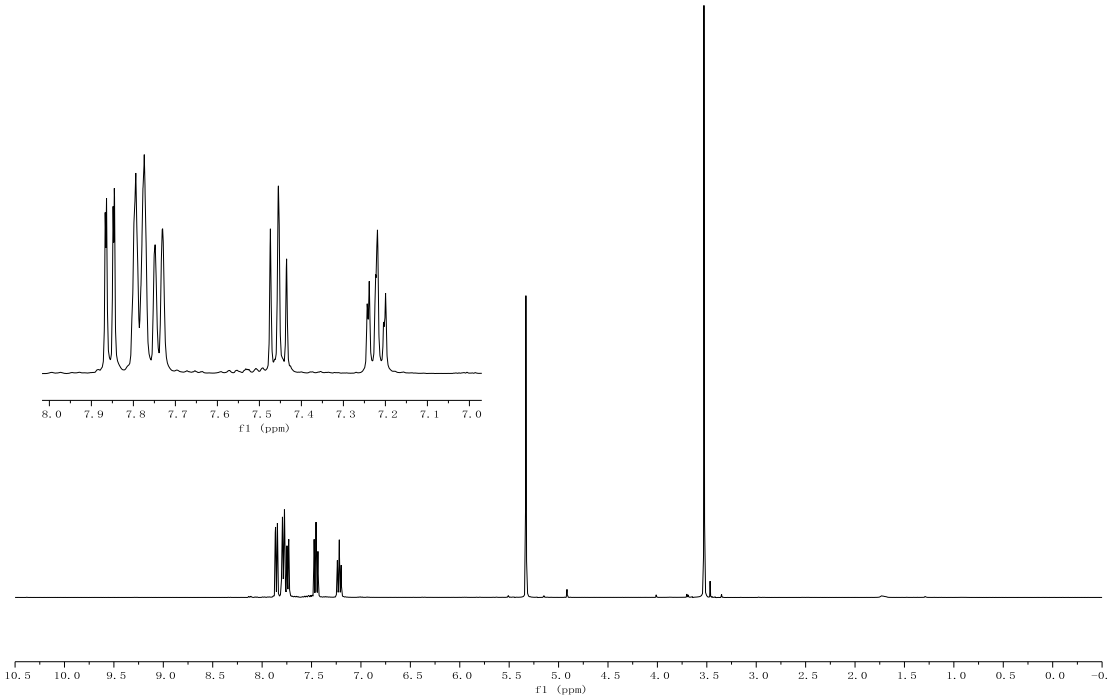


130 **131**

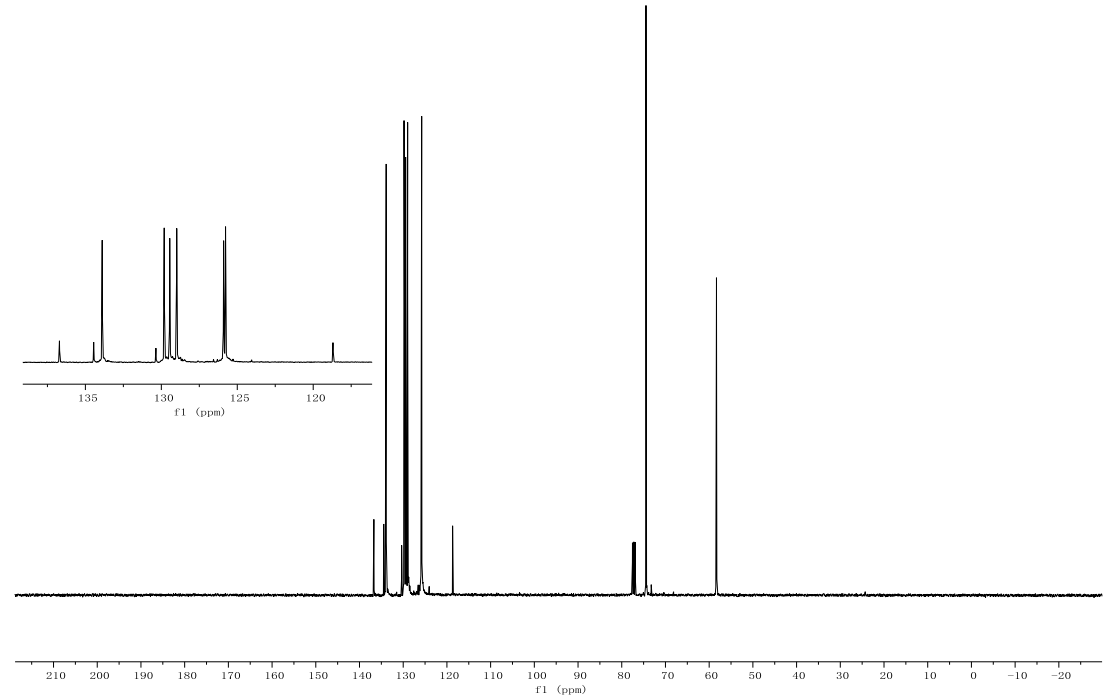
$C_{12}H_{11}BrO$
Exact Mass: 250.00
Molecular Weight: 251.12
C, 57.39; H, 4.42; Br, 31.82; O, 6.37

(8-Bromonaphthalen-1-yl)methanol (**130**, 11.67 g, 49 mmol) was dissolved in THF (300 mL), to which NaH (57%-63%) powder (2.51 g, 60-66 mmol) was added. The reaction mixture was heated at reflux for 2 h. Iodomethane (3.62 g, 58 mmol) was added to the cooled solution at 0 ℃ and the reaction mixture was heated at reflux for 2 h. Water was added to the reaction mixture, and it was extracted with ether, and the extract was dried with Na_2SO_4. Solvent was removed under reduced pressure and compound **131** was obtained as a brown oily liquid (12.24 g, 49 mmol, 99%), which solidified in the refrigerator. ^{1}H NMR ($CDCl_3$) δ 3.53 (s, 3 H), 5.33 (s, 2 H), 7.22 (td, *J* = 8 Hz, 2 Hz, 1 H), 7.46 (t, *J* = 8 Hz, 1 H), 7.74 (d, *J* = 7 Hz, 1 H), 7.78 (d, *J* = 8 Hz, 2 H), 7.86 (dd, *J* = 8 Hz, 1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 58.3, 74.5, 118.7, 125.8, 125.9, 129.0, 129.5, 129.8, 130.4, 133.9, 134.5, 136.7 (12 of 12 expected resonances); MS (EI) *m/z* 250 (M^+, 10), 219 (M – OMe, 20), 171 (M – Br, 100).

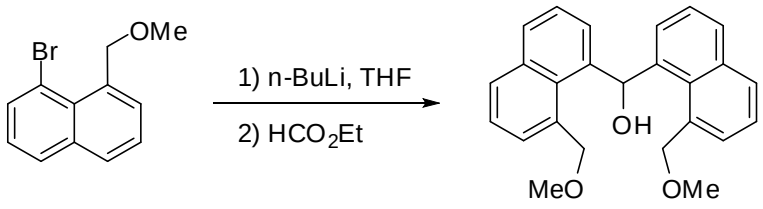
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **131**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **131**



Synthesis of bis[8-(methoxymethyl)naphthalen-1-yl]methanol (132)

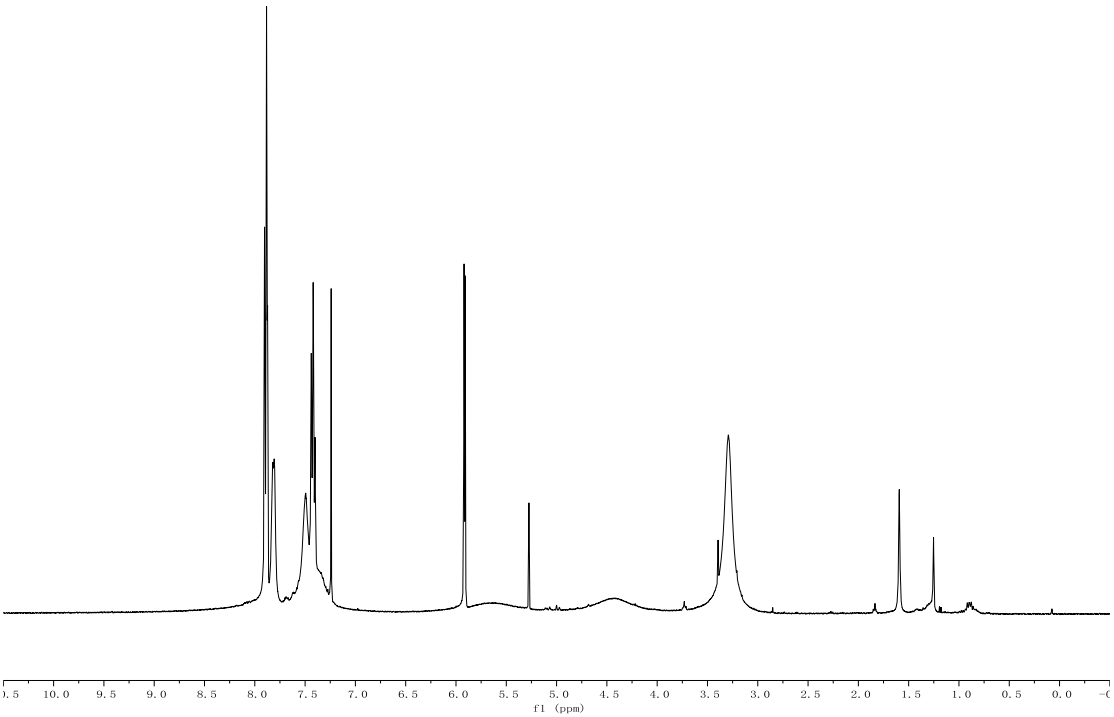


131 **132**

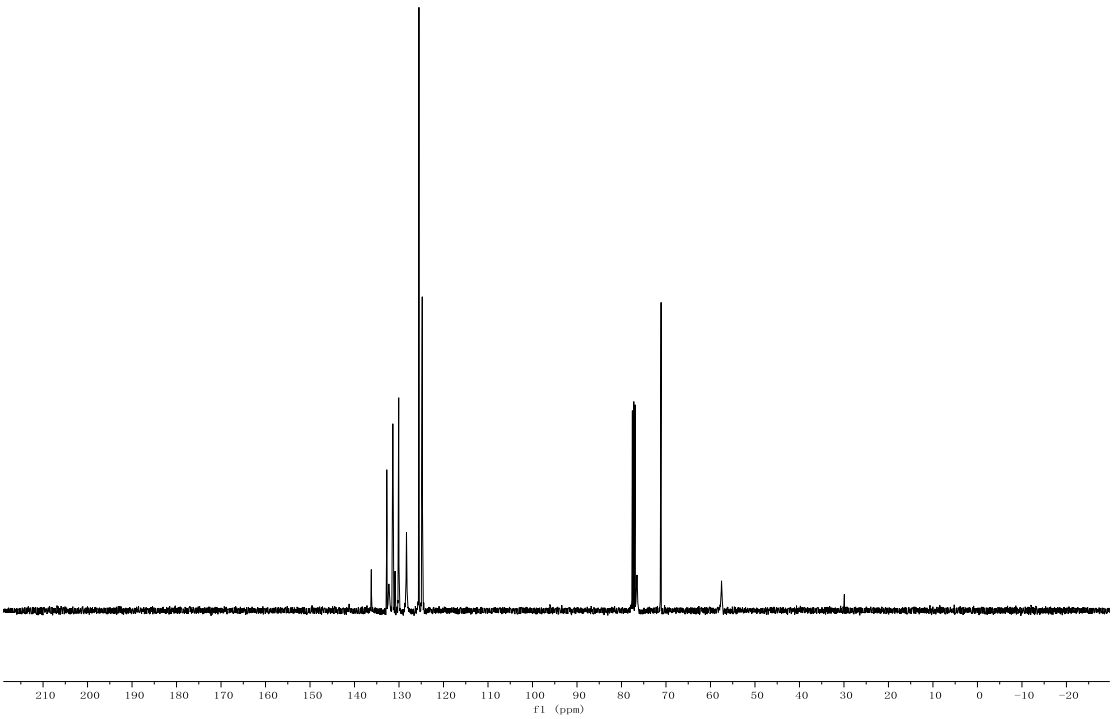
$C_{25}H_{24}O_3$
Exact Mass: 372.17
Molecular Weight: 372.46
C, 80.62; H, 6.49; O, 12.89

Compound **131** (126 mg, 0.5 mmol) was dissolved in 1 mL THF and cooled to -78 ℃. *n*-BuLi (2.5 *M* in THF, 0.2 mL, 0.5 mmol) was added and the solution was stirred at -78 ℃ for 30 min. Ethyl formate (0.020 mL, 0.25 mmol) was added, and the reaction mixture was stirred at room temperature overnight. Aqueous NH_4Cl was then added, and the resulting mixture was extracted with ether. The organic phase was dried over Na_2SO_4, and the solvent was stripped away to leave compound **132** as a yellow liquid (14 mg, 0.038 mmol, 15%). ^{1}H NMR ($CDCl_3$) δ 3.31 (br, 6 H), 4.45 (br, 2 H), 5.66 (br, 2 H), 5.93 (d, *J* = 4 Hz, 1 H), 7.44 (t, *J* = 8 Hz, 2 H), 7.52 (br, 3 H), 7.83 (m, 2 H), 7.91 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 57.5, 71.1, 76.5, 124.8, 125.5 (double intensity), 128.3, 130.1, 130.9, 131.4, 132.3, 132.8, 136.2 (13 of 13 expected resonances).

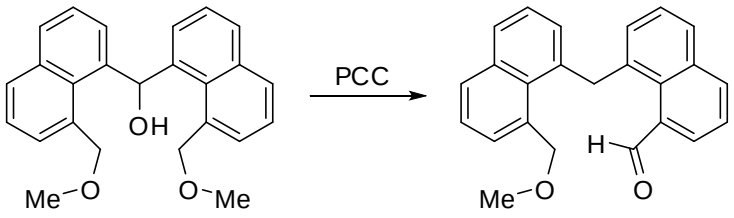
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **132**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **132**



Synthesis of compound 140

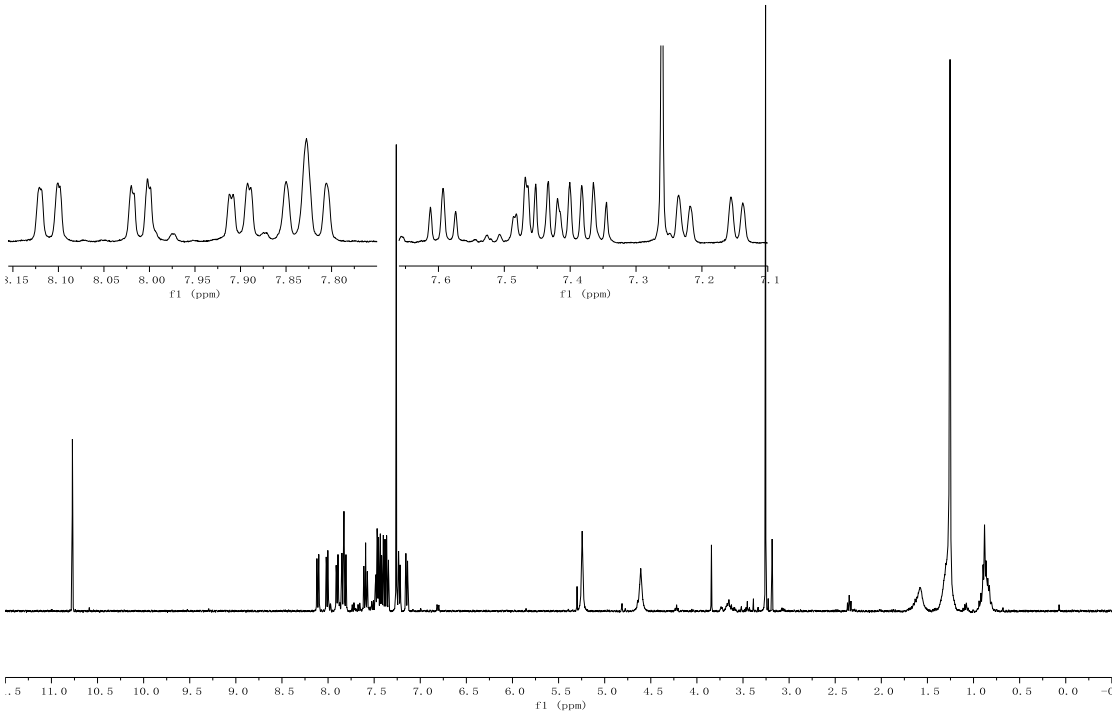


132 **140**

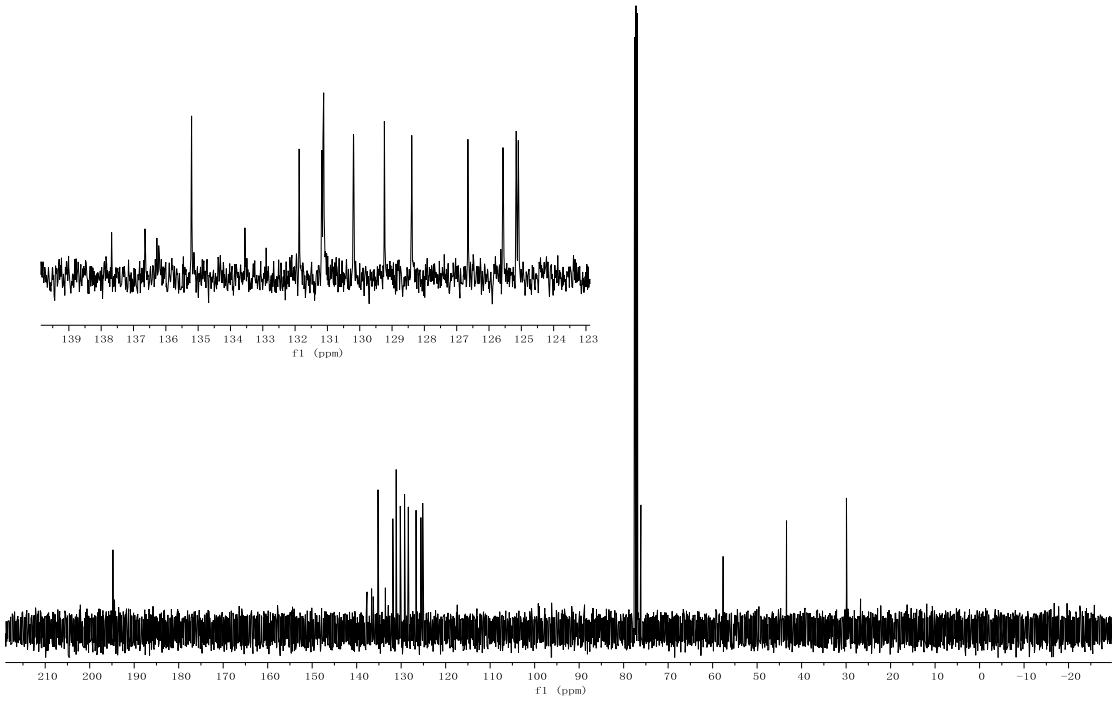
$C_{24}H_{20}O_2$
Exact Mass: 340.15
Molecular Weight: 340.41
C, 84.68; H, 5.92; O, 9.40

Compound **132** (125 mg, 0.34 mmol) was dissolved in dichloromethane (10 mL), to which PCC (80 mg, 0.37 mmol) was added. The reaction mixture was stirred at room temperature overnight. Precipitated solid was filtered away and the solvent was removed under reduced pressure. The product was purified by preparative TLC (silica gel, dichloromethane) to give compound **140** as a yellow solid. Crystallization from $CHCl_3$-MeOH yielded compound **140** as crystals suitable for X-ray analysis. ^{1}H NMR ($CDCl_3$) δ 3.26 (s, 3 H), 4.61 (br, 2 H), 5.24 (s, 2 H), 7.15 (d, *J* = 7 Hz, 1 H), 7.24 (d, *J* = 8 Hz, 1 H), 7.41 (m, 5 H), 7.59 (t, *J* = 8 Hz, 1 H), 7.83 (t, *J* = 9 Hz, 2 H), 7.90 (dd, *J* = 8 Hz, 2 Hz, 1 H), 8.01 (dd, *J* = 8 Hz, 1 Hz, 1 H), 8.11 (dd, *J* = 8 Hz, 1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 43.4, 57.7, 76.1, 125.1, 125.2, 125.6, 126.7, 128.4, 129.2, 130.2, 131.0, 131.1, 131.2, 131.9, 133.6, 135.2, 136.6, 137.7, 194.8 (19 of 24 expected resonances).

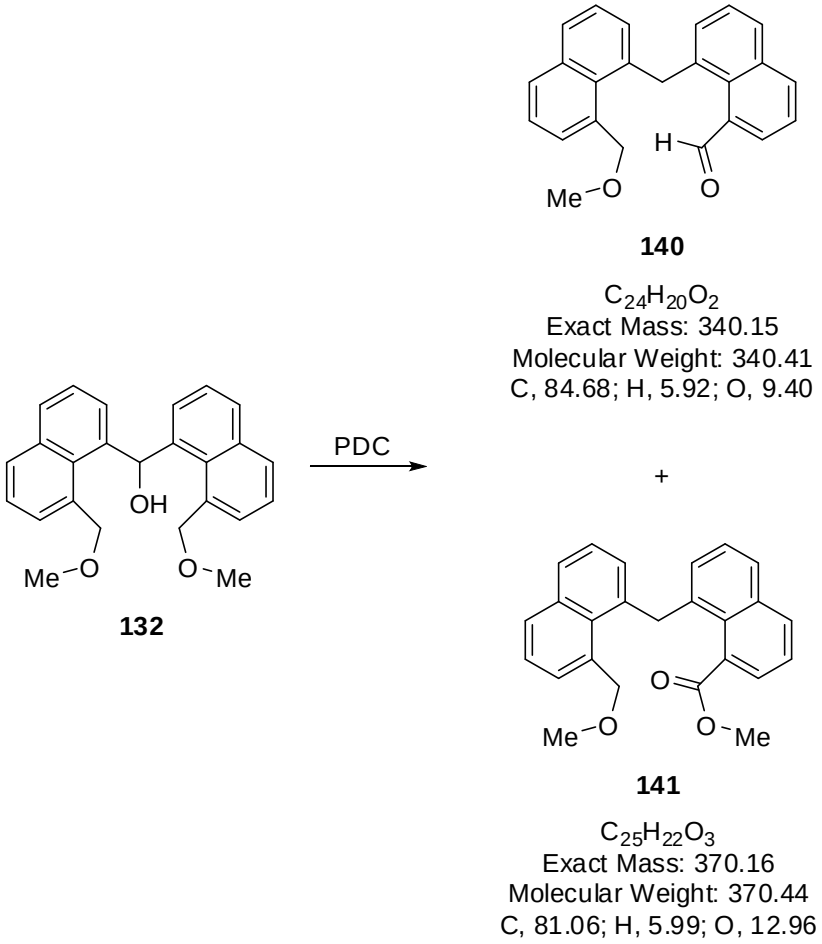
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **140**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **140**



Synthesis of compound 140 and compound 141



132

140

$C_{24}H_{20}O_2$
Exact Mass: 340.15
Molecular Weight: 340.41
C, 84.68; H, 5.92; O, 9.40

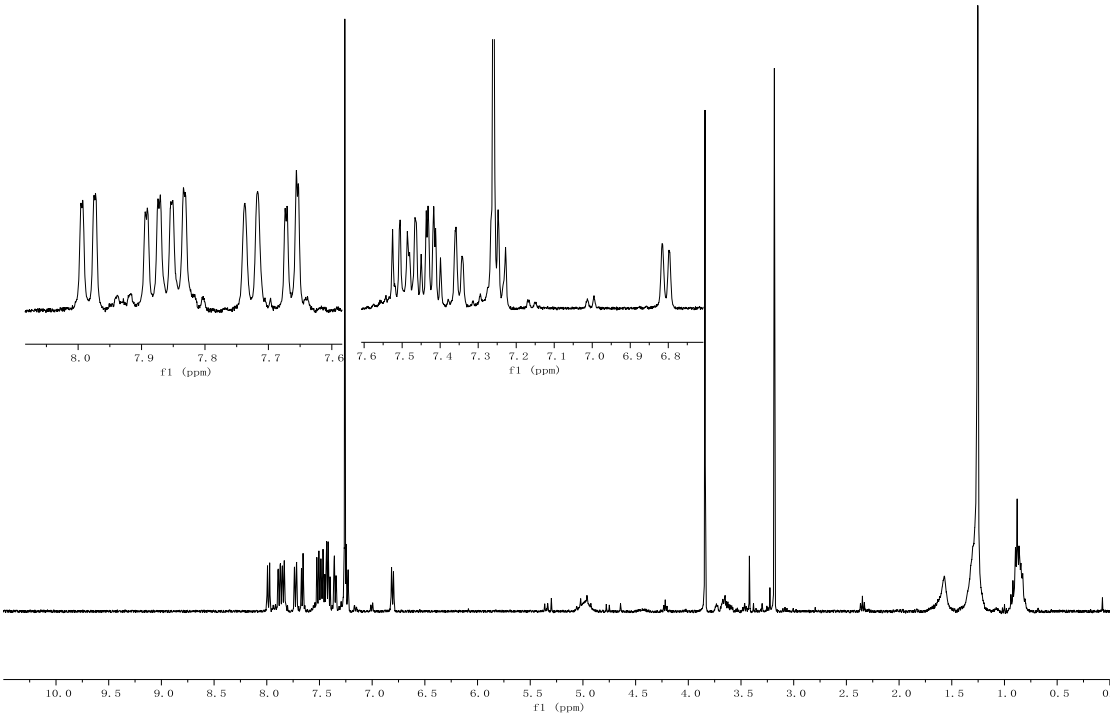
141

$C_{25}H_{22}O_3$
Exact Mass: 370.16
Molecular Weight: 370.44
C, 81.06; H, 5.99; O, 12.96

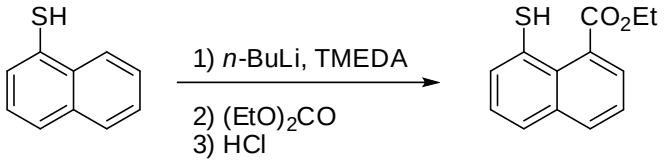
Compound **132** (60 mg, 0.16 mmol) was dissolved in dichloromethane (10 mL), to which PDC (60 mg, 0.16 mmol) and celite was added. The reaction mixture was stirred at room temperature overnight. Precipitated solid was filtered away, and the solvent was removed under reduced pressure. The product was purified by preparative TLC (silica gel, dichloromethane) to give compound **140** and compound **141** as yellow solids. Crystallization from $CHCl_3$ yielded compound **141** as crystals suitable for X-ray analysis. ^{1}H NMR ($CDCl_3$) δ 3.18 (s, 3 H), 3.84 (s, 3 H), 4.97 (br, 2 H), 6.80 (d, J = 7 Hz, 1 H),

7.25 (t, *J* = 8 Hz, 2 H), 7.35 (dd, *J* = 7 Hz, 1 Hz, 1 H), 7.46 (m, 5 H), 7.66 (dd, *J* = 7 Hz, 2 Hz, 1 H), 7.73 (d, *J* = 8 Hz, 1 H), 7.84 (dd, *J* = 8 Hz, 2 Hz, 1 H), 7.88 (dd, *J* = 8 Hz, 2 Hz, 1 H), 7.98 (dd, *J* = 8 Hz, 2 Hz, 1 H).

^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **141**



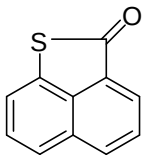
Synthesis of ethyl 8-mercapto-1-naphthoate (144) and 2H-naphtho[1,8-bc]-thiophen-2-one (141)



142 **144**

$C_{13}H_{12}O_2S$
Exact Mass: 232.06
Molecular Weight: 232.30
C, 67.21; H, 5.21; O, 13.77; S, 13.80

+



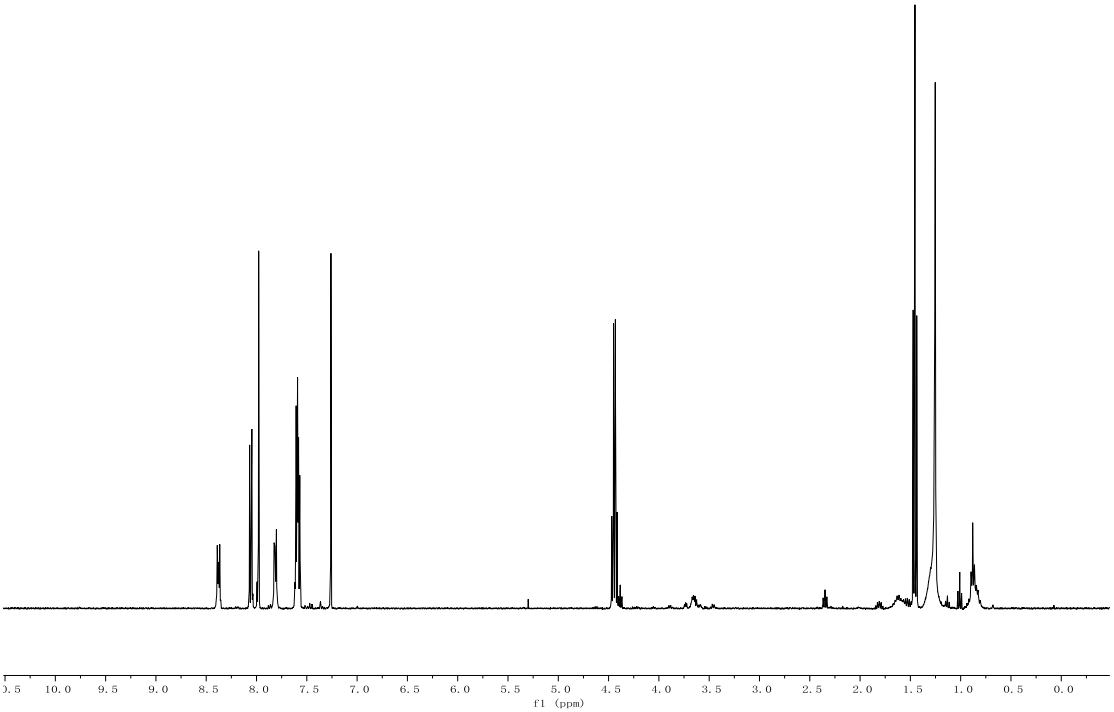
145

$C_{11}H_6OS$
Exact Mass: 186.01
Molecular Weight: 186.23
C, 70.94; H, 3.25; O, 8.59; S, 17.22

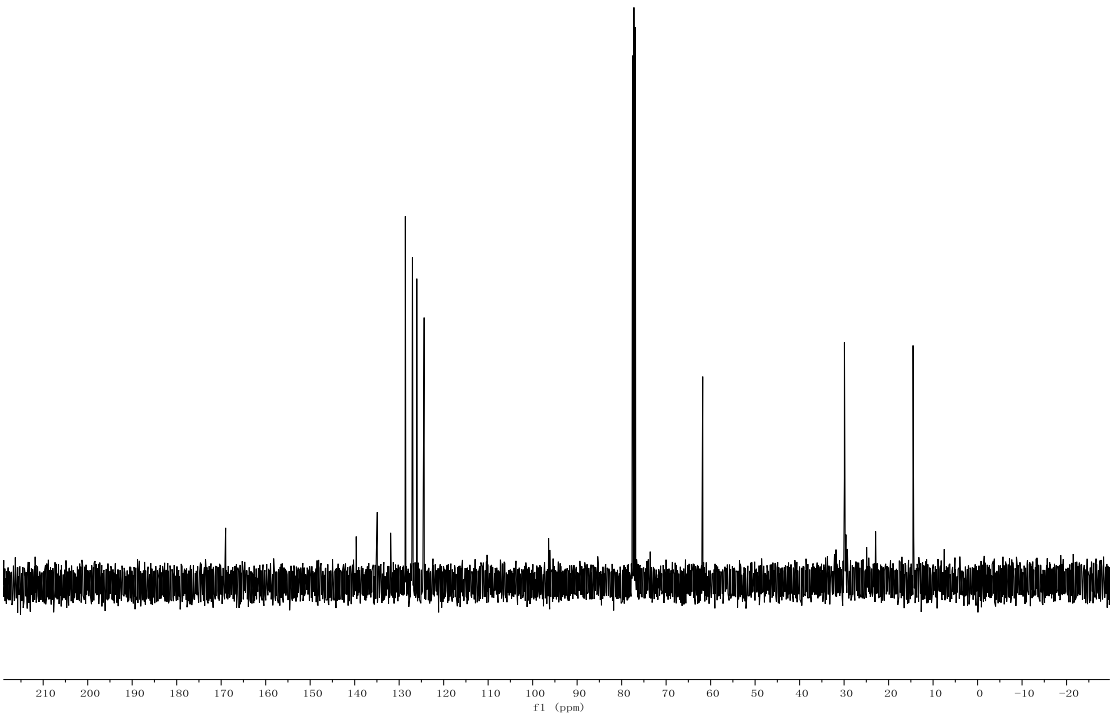
Through an addition funnel, a three-necked flask was charged with cyclohexane (14 mL), TMEDA (2 mL) and *n*-BuLi (2.5 M in hexane, 5.4 mL, 13.5 mmol). (The *n*-BuLi was added dropwise to the reaction flask in an ice bath.) 1-Thionaphthol (1 g, 6.24 mmol) in cyclohexane (3 mL) was added to the flask at 0 ℃. The reaction was warmed to room temperature and stirred overnight. Cyclohexane was removed from the reaction flask, and the precipitate was washed with cyclohexane. When the precipitate settled, cyclohexane was removed again. Freshly distilled THF (6 mL) was added to the precipitate and the

reaction mixture was cooled to -78 ℃. Diethyl carbonate (0.34 mL, 2.8 mmol) diluted with THF (1 mL) was added and the mixture was warmed to room temperature for 20 hours. The reaction mixture was acidified with hydrochloric acid and extracted with dichloromethane. The organic layer was dried with Na_2SO_4 and concentrated in vacuo to yield yellow oil. The product was purified by silica gel column chromatography (solvent, 4:1 hexanes-dichloromethane) to give compound **144** as greenish needles (86 mg, 0.37 mmol, 6%) and compound **145** as yellow needles (180 mg, 0.97 mmol, 15%). For compound **144**: ^{1}H NMR ($CDCl_3$) δ 1.46 (t, *J* = 7 Hz, 3 H), 4.44 (q, *J* = 7 Hz, 2 H), 7.59 (m, 3 H), 7.81 (m, 1 H), 7.98 (s, 1 H), 8.06 (d, *J* = 9 Hz, 1 H), 8.38 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.5, 61.8, 124.4, 126.0, 126.9, 127.0, 128.5, 128.6, 131.9, 134.9, 139.7, 169.0 (12 of 13 expected resonances). For compound **145**: ^{1}H NMR ($CDCl_3$) δ 7.61 (m, 2 H), 7.77 (t, *J* = 8 Hz, 1 H), 7.83 (m, 1 H), 8.15 (d, *J* = 8 Hz, 1 H), 8.18 (d, *J* = 8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 122.7, 125.2, 125.7, 128.1, 128.5, 131.2, 132.2, 133.4, 133.5, 134.0, 193.6 (11 of 11 expected resonances).

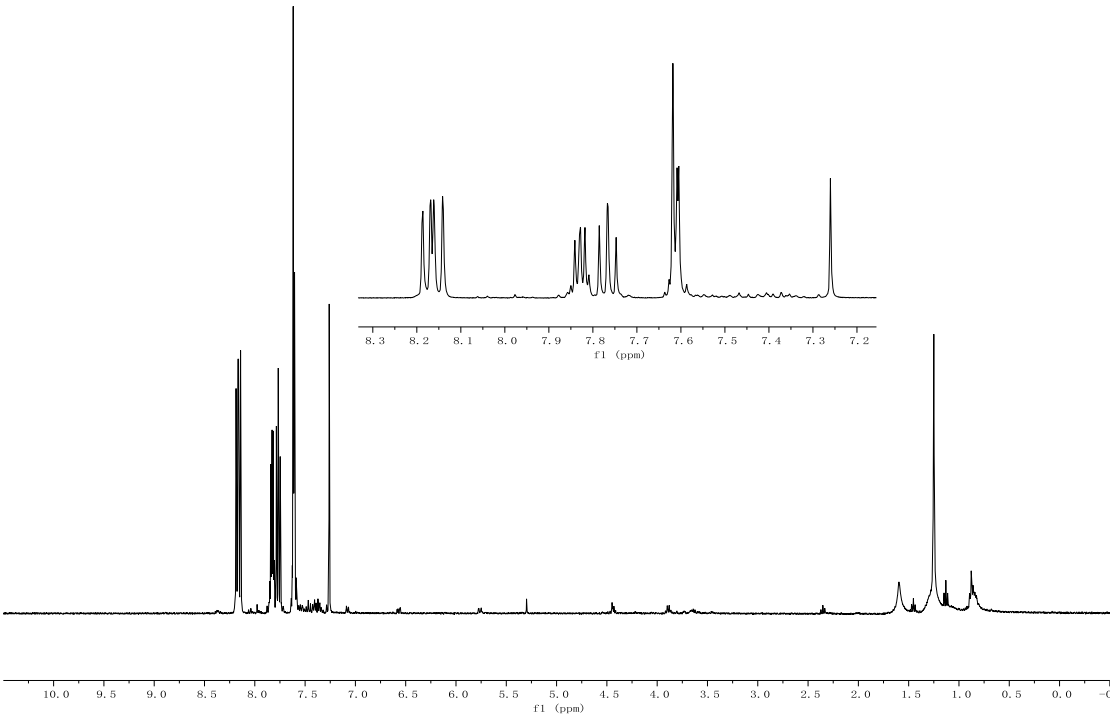
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **144**



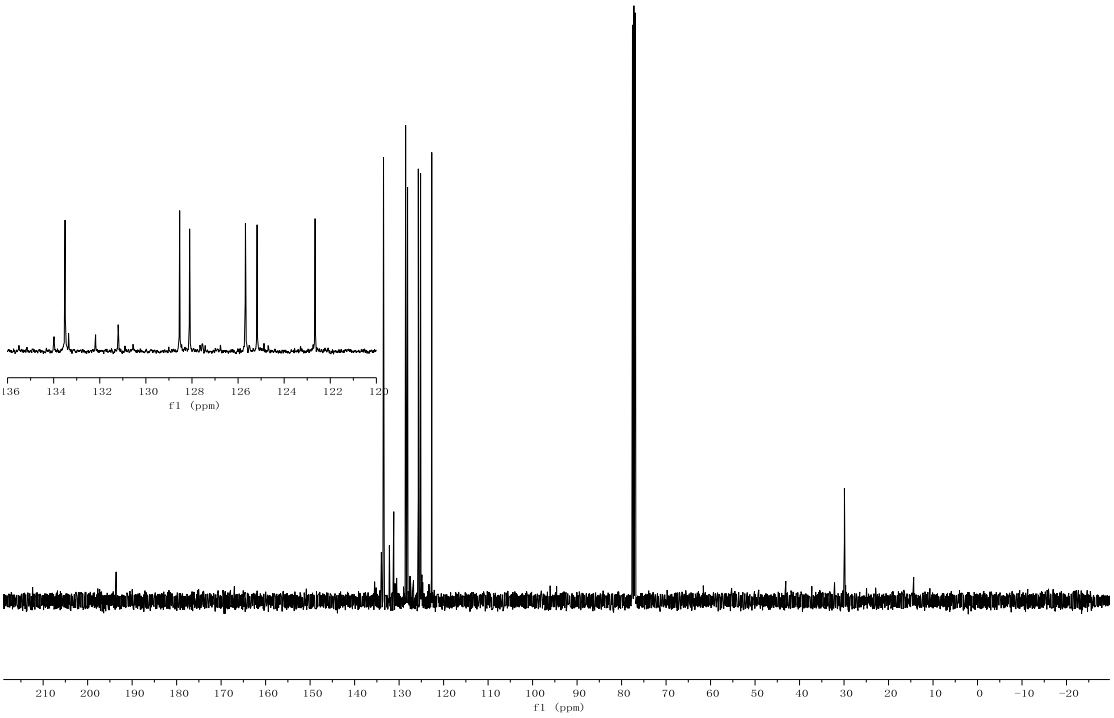
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **144**



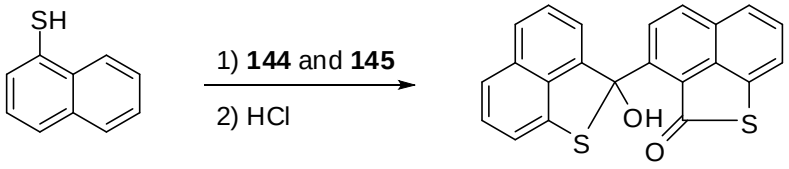
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **145**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **145**



Synthesis of dimer 146



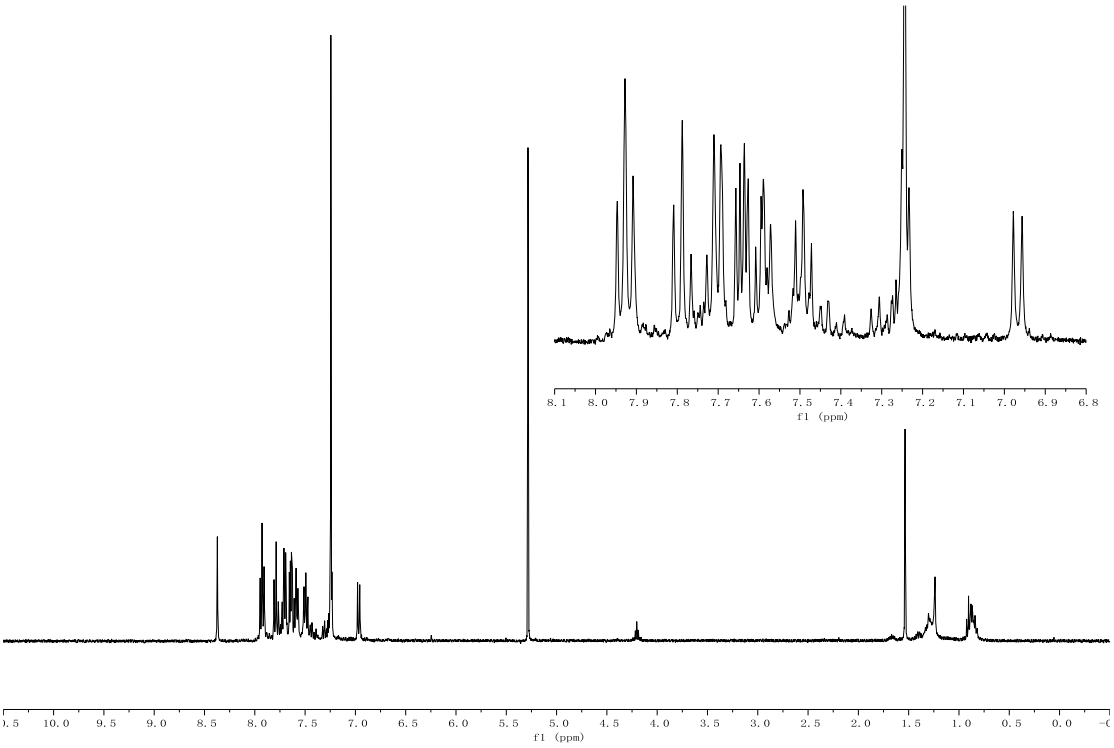
142 **146**

$C_{22}H_{12}O_2S_2$
Exact Mass: 372.03
Molecular Weight: 372.46
C, 70.94; H, 3.25; O, 8.59; S, 17.22

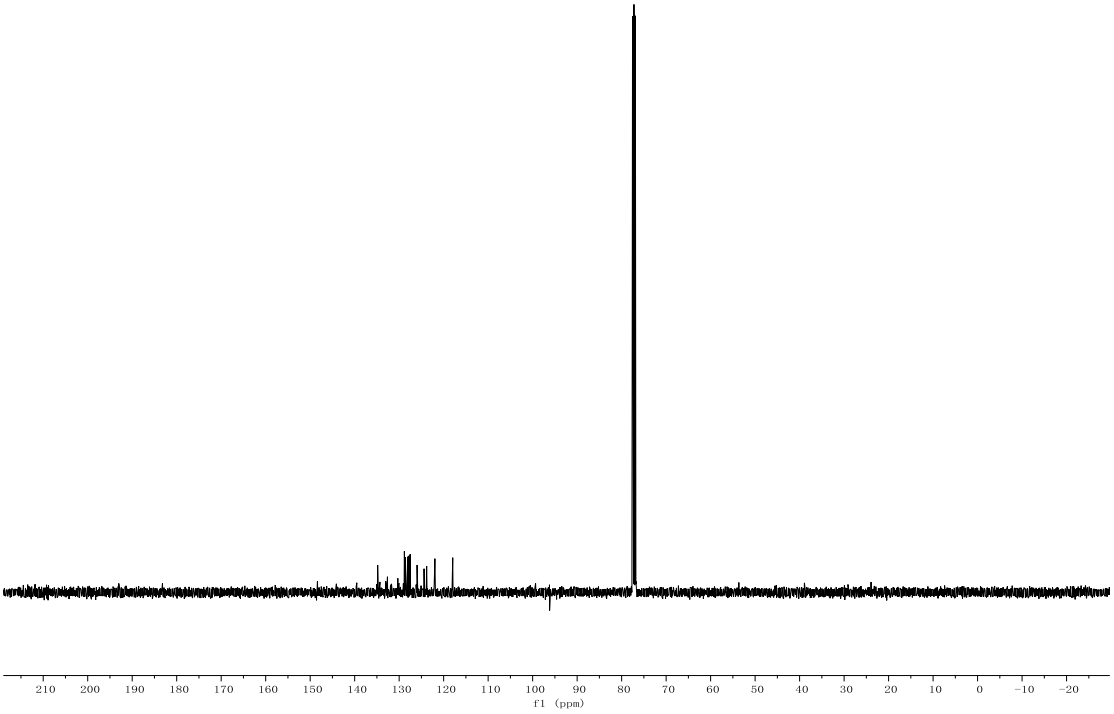
Through an addition funnel, a three-necked flask was charged with cyclohexane (14 mL), TMEDA (2 mL) and *n*-BuLi (2.5 M in hexane, 5.4 mL, 13.5 mmol). (The *n*-BuLi was added dropwise to the reaction flask in an ice bath.) 1-Thionaphthol (1 g, 6.24 mmol) in cyclohexane (3 mL) was added to the flask at 0 ℃. The reaction was warmed to room temperature and stirred overnight. Cyclohexane was removed from the reaction flask, and the precipitate was washed with cyclohexane. When the precipitate settled, cyclohexane was removed again. Freshly distilled THF (6 mL) was added to the precipitate and the reaction mixture was cooled to -78 ℃. Diethyl carbonate (0.34 mL, 2.8 mmol) diluted with THF (1 mL) was added and the mixture was warmed to room temperature for 20 hours. The reaction mixture was acidified with hydrochloric acid and extracted with dichloromethane. The organic layer was dried with Na_2SO_4 and concentrated in vacuo to yield a yellow oil. The product was purified by preparative TLC (silica gel, dichloromethane) to give compound **146** as a yellow solid. Crystallization from

$CHCl_3$-CH_2Cl_2-MeOH yielded compound **146** as crystals suitable for X-ray analysis. The ^1H NMR and ^{13}C NMR spectra of compound **146** are illustrated on the next page.

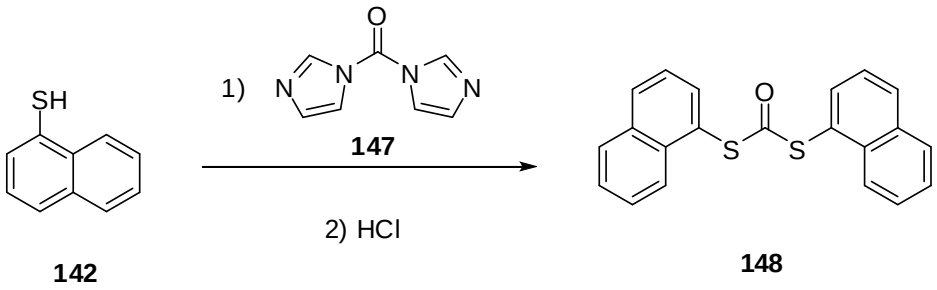
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **146**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **146**



Synthesis of carbonodithioate 148



142

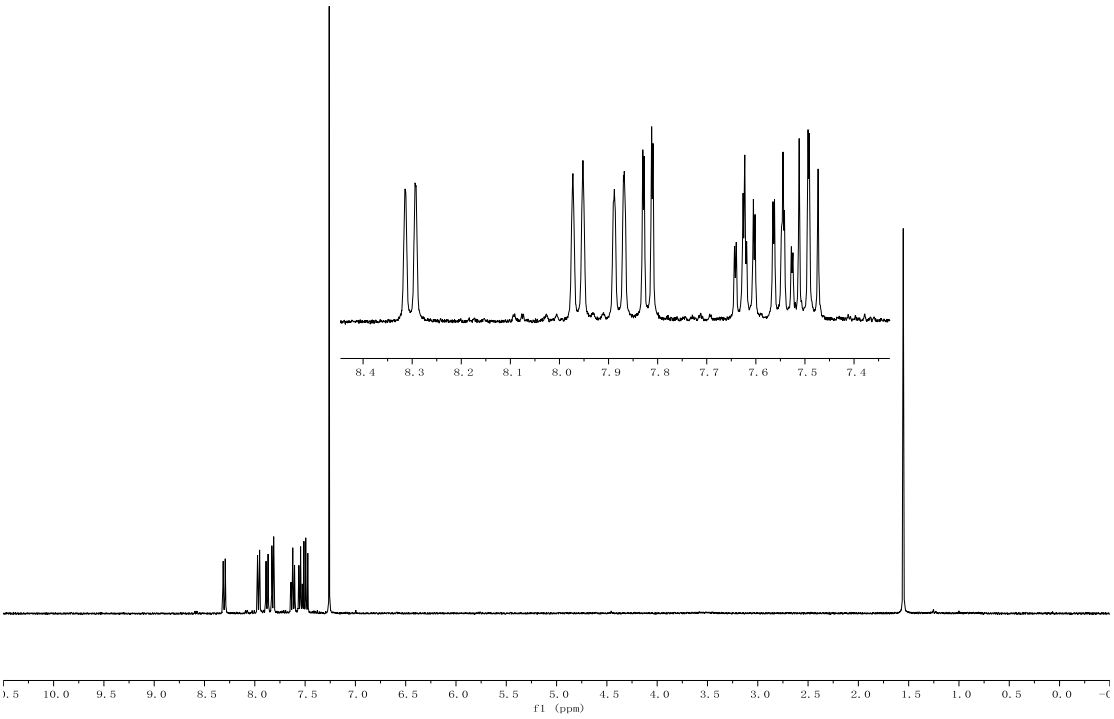
148

$C_{21}H_{14}OS_2$
Exact Mass: 346.05
Molecular Weight: 346.47
C, 72.80; H, 4.07; O, 4.62; S, 18.51

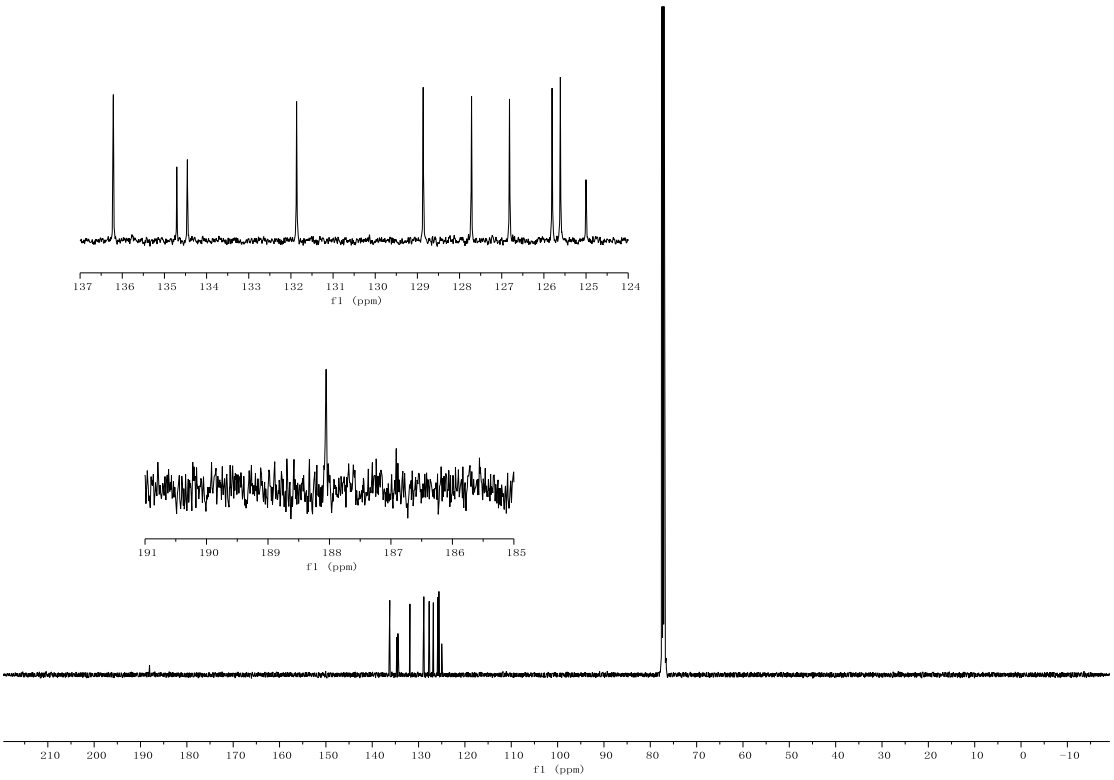
Through an addition funnel, a flask was charged with cyclohexane (28 mL), TMEDA (4 mL) and *n*-BuLi (2.5 M in hexane, 10.8 mL, 13.5 mmol). (The *n*-BuLi was added dropwise to the reaction flask in an ice bath.) 1-Thionaphthol (2 g, 12.5 mmol) in cyclohexane (6 mL) was added to the flask at 0 ℃. The reaction was warmed to room temperature and stirred overnight. Cyclohexane was removed from the reaction flask, and the precipitate was washed with cyclohexane. When the precipitate settled, cyclohexane was removed again. Freshly distilled THF (6 mL) was added to the precipitate and the reaction mixture was cooled to -78 ℃. A solution of 1,1'-carbonyldiimidazole (908 mg, 5.6 mmol) in THF was added and the mixture was warmed to room temperature overnight. The reaction mixture was acidified with hydrochloric acid and extracted with dichloromethane. The organic layer was dried with Na_2SO_4 and concentrated in vacuo. The product was purified by silica gel column chromatography then by preparative TLC

to give compound **148** as a yellow solid (95 mg, 0.27 mmol, 2.2%). ^{1}H NMR ($CDCl_3$) δ 7.48 (d, *J* = 7 Hz, 1 H), 7.50 (d, *J* = 7 Hz, 1 H), 7.54 (dd, *J* = 7 Hz, 2 Hz, 1 H), 7.56 (dd, *J* = 7 Hz, 1 Hz, 1 H), 7.60 (dd, *J* = 7 Hz, 2 Hz, 1 H), 7.63 (dd, *J* = 7 Hz, 1 Hz, 1 H), 7.82 (dd, *J* = 7 Hz, 1 Hz, 2 H), 7.88 (dd, *J* = 8 Hz, 1 Hz, 2 H), 7.96 (d, *J* = 8 Hz, 2 H), 8.30 (dd, *J* = 7 Hz, 1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 125.0, 125.6, 125.8, 126.8, 127.7, 128.9, 131.9, 134.5, 134.7, 136.2, 188.1 (11 of 11 expected resonances); MS (EI) *m/z* 346 (M^+, 5), 159 (M – OCNpSH, 95), 115 (100).

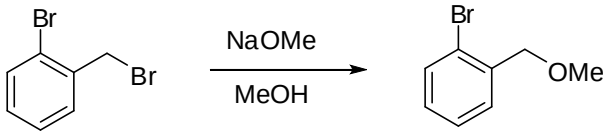
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **148**



^{13}C NMR Spectrum (126 MHz, $CDCl_3$) of Compound **148**



Synthesis of *o*-bromobenzyl methyl ether (237)

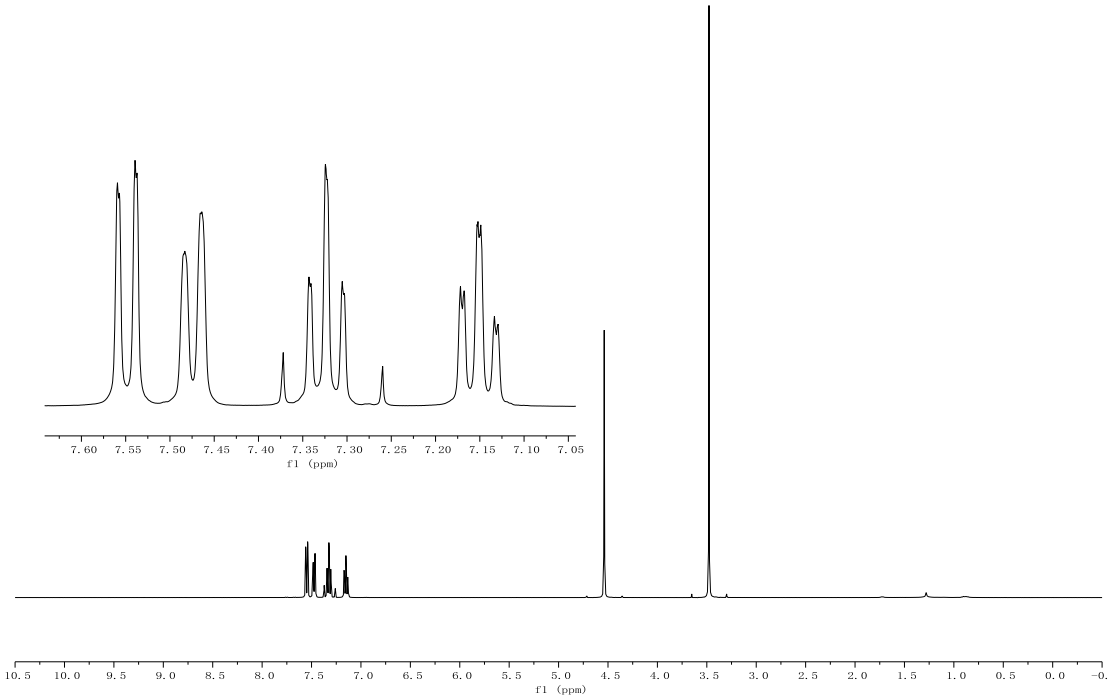


236 **237**

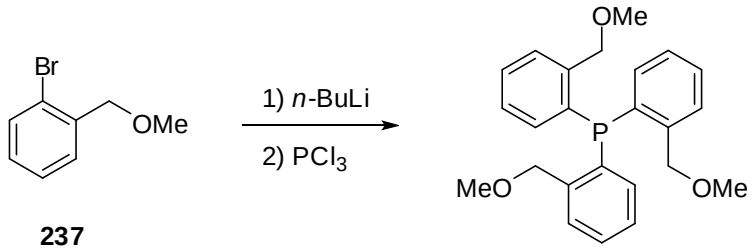
C_8H_9BrO
Exact Mass: 199.98
Molecular Weight: 201.06
C, 47.79; H, 4.51; Br, 39.74; O, 7.96

After sodium (2.0 g, 87 mmol) was dissolved in methanol (40 mL), 2-bromobenzyl bromide, diluted in methanol (20 mL), was added. The resulting solution was stirred in an ice bath for 10 minutes and then heated to reflux for 1 h. After cooling the solution, conc. HCl was added until the bubbling ceased. The methanol was evaporated under reduced pressure. Water was added to the residue, and the aqueous layer was extracted twice with chloroform. The combined chloroform layers were washed with water, dried over Na_2SO_4, and concentrated to give a yellow liquid. The product was distilled under vacuum to give **237** as a clear liquid (11.0 g, 55 mmol, 96%).^{1}H NMR ($CDCl_3$) δ 3.48 (s, 3 H), 4.54 (s, 2 H), 7.15 (td, *J* = 8 Hz, 2 Hz, 1 H), 7.32 (td, *J* = 8 Hz, 1 Hz, 1 H), 7.47 (d, *J* = 8 Hz, 1 H), 7.55 (dd, *J* = 8 Hz, 1 Hz, 1 H).

^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **237**



Synthesis of tris[2-(methoxymethyl)phenyl]phosphine (238).



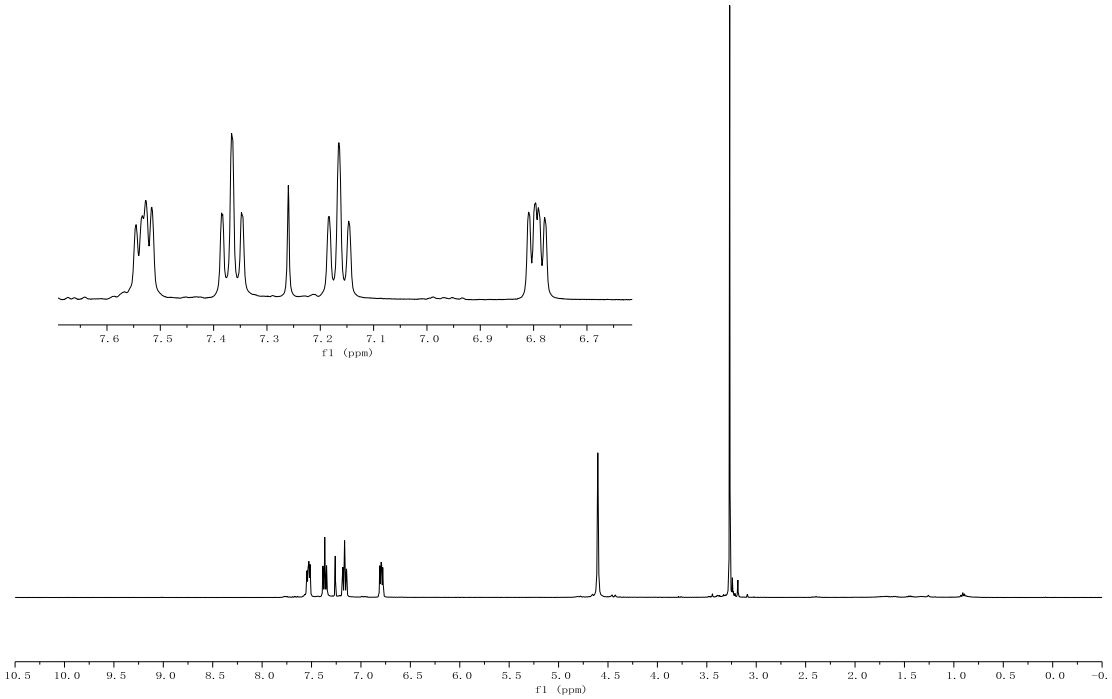
237

238

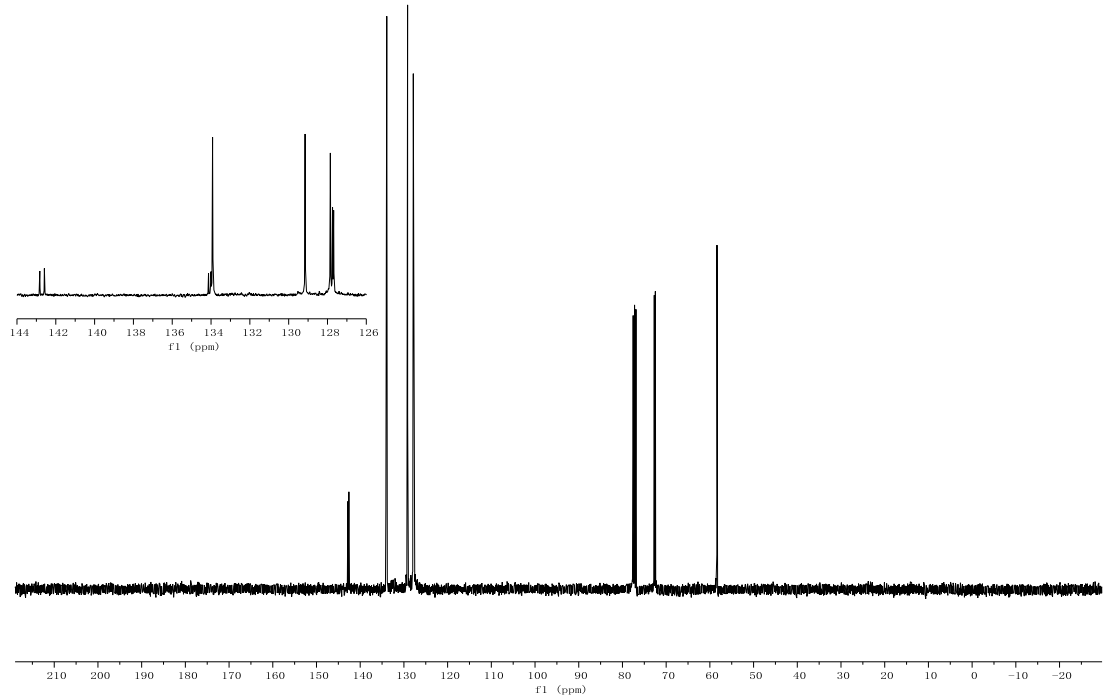
$C_{24}H_{27}O_3P$
Exact Mass: 394.17
Molecular Weight: 394.44
C, 73.08; H, 6.90; O, 12.17; P, 7.85

n-BuLi (2.5 *M* in hexane, 10.5 mL, 26 mmol) was added dropwise to a stirred solution of *o*-bromobenzyl methyl ether (**237**, 4.8 g, 24 mmol) in THF (18 mL) at -78 ℃ under argon. After the solution was stirred for 2 hours, phosphrous trichloride (0.69 mL, 8 mmol) diluted with THF (2 mL) was added dropwise. The reaction was stirred at room temperature for 20 hours and refluxed for 1 hour. The reaction mixure was cooled and then saturated with NH_4Cl. The organic layer was separated and the water layer was again extracted with ether. The combined ether extracts were dried over Na_2SO_4 and concentrated to leave beige crystals. Recrystallization from ethanol gave **238** as a white solid (1.8 g, 4.6 mmol, 57%). ^{1}H NMR ($CDCl_3$) δ 3.27 (s, 9 H), 4.60 (s, 6 H), 6.79 (dd, *J* = 8 Hz, 5 Hz, 3 H), 7.17 (t, *J* = 8 Hz, 3 H), 7.37 (t, *J* = 8 Hz, 3 H), 7.53 (dd, *J* = 8 Hz, 5 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 58.4 (s), 72.6 (d, J_{PC} = 25 Hz), 127.7 (d, J_{PC} = 6 Hz), 127.9 (s), 129.2 (s), 133.9 (s), 134.1 (d, J_{PC} = 13 Hz), 142.7 (d, J_{PC} = 23 Hz) (8 of 8 expected resonances); MS (EI) *m/z* 394 (M^+, 20), 379 (M – CH_3), 347 (75), 178 (100).

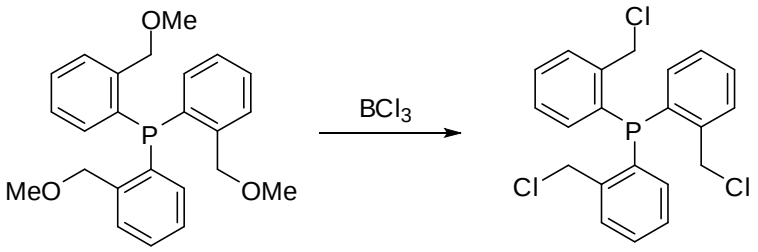
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **238**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **238**



Synthesis of tris[2-(chloromethyl)phenyl]phosphine (239).

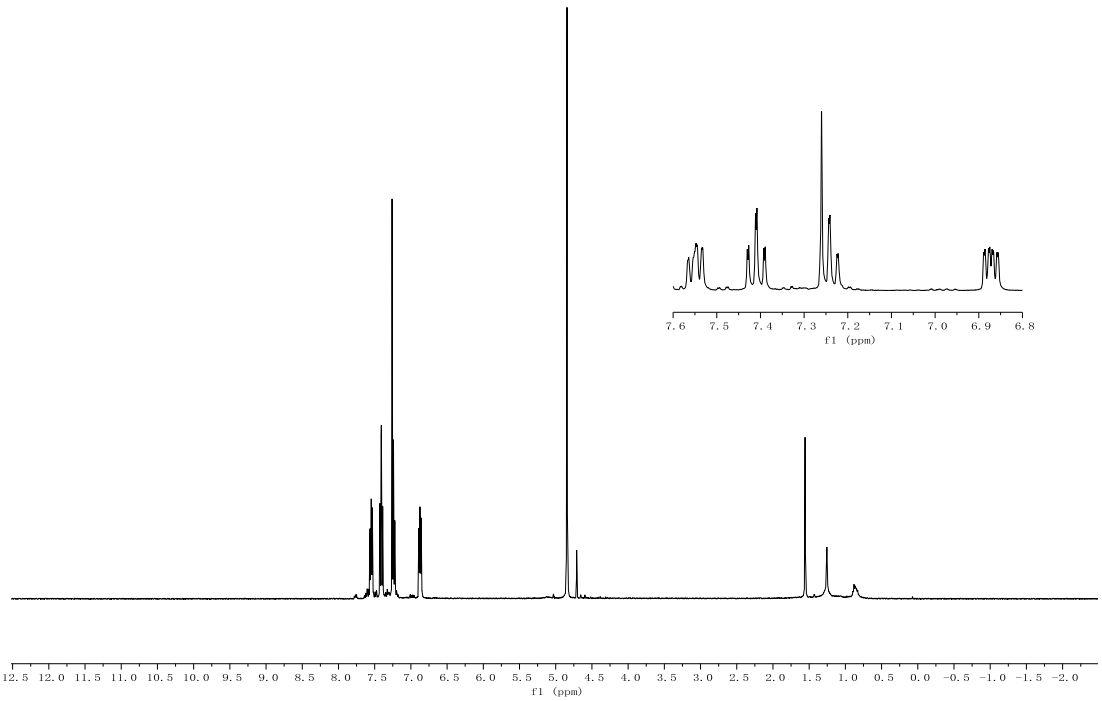


238 **239**

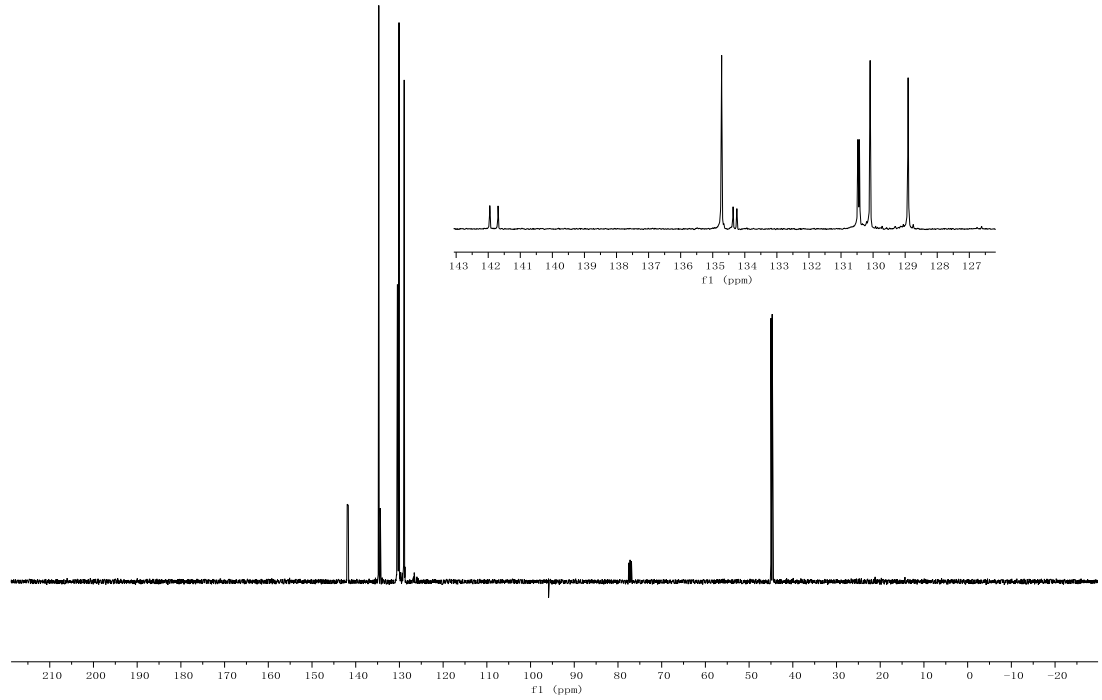
$C_{21}H_{18}Cl_3P$
Exact Mass: 406.02
Molecular Weight: 407.70
C, 61.87; H, 4.45; Cl, 26.09; P, 7.60

Boron trichloride (1 *M* in heptane, 10 mL, 10 mmol) was added to tris[2-(methoxymethyl)phenyl]phosphine (**238**, 176 mg, 0.45 mmol) in round bottom flask under argon. The reaction mixture was stirred at room temperature for 1 hour and then heated at reflux for 3 hours. When the mixture was cooled to room temperature, chloroform and water were added. The organic layer was separated and the water layer was again extracted with chloroform. The combined chloroform extracts were dried over Na_2SO_4 and concentrated to dryness. The lime-colored crystals were chromatographed on silica gel (solvent, chloroform) to give **239** as a light yellow solid (82 mg, 0.20 mmol, 45%). ^{1}H NMR ($CDCl_3$) δ 4.85 (d, *J* = 2 Hz, 6 H), 6.87 (ddd, *J* = 8 Hz, 5 Hz, 1 Hz, 3 H), 7.24 (ddd, *J* = 8 Hz, 8 Hz, 1 Hz, 3 H), 7.41 (ddd, *J* = 8 Hz, 8 Hz, 1 Hz, 3 H), 7.54 (ddd, *J* = 5 Hz, 5 Hz, 1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 44.9 (d, J_{PC} = 28 Hz), 128.9 (s), 130.1 (s), 130.5 (d, J_{PC} = 5 Hz), 134.3 (d, J_{PC} = 12 Hz), 134.7 (s), 141.8 (d, J_{PC} = 26 Hz) (7 of 7 expected resonances); MS (EI) *m/z* 406 (M^+, 100), 357 (M-CH_2Cl, 30), 178 (100).

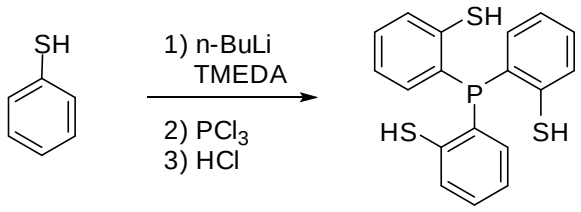
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **239**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **239**



Synthesis of tris(2-mercaptophenyl)phosphine (37)



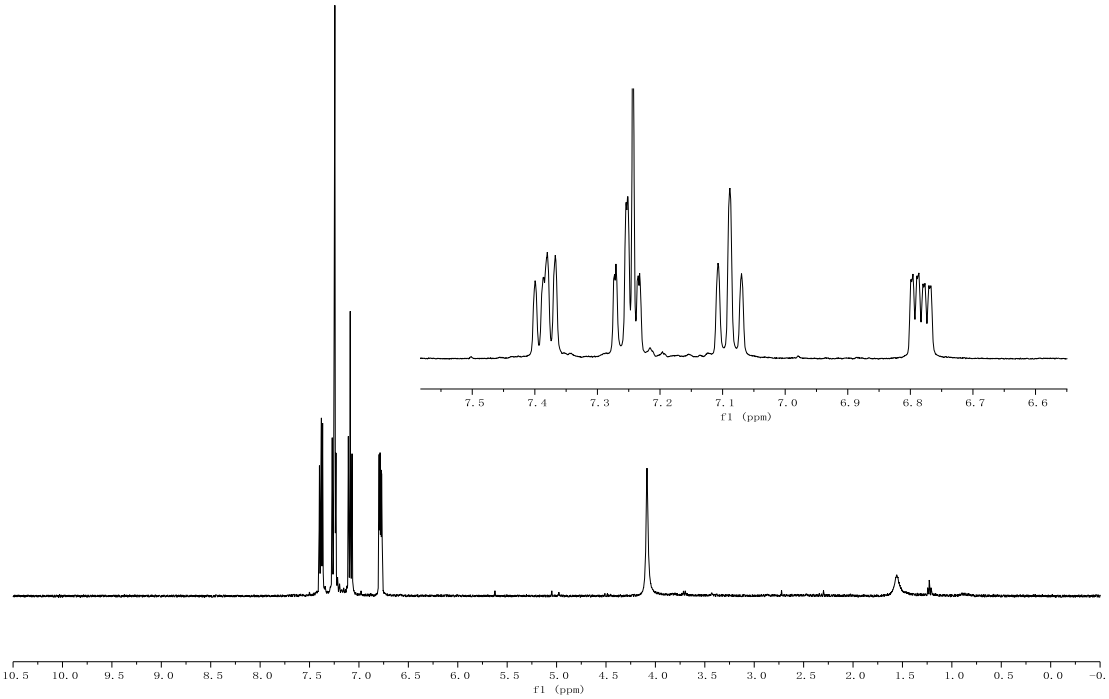
37

$C_{18}H_{15}PS_3$
Exact Mass: 358.01
Molecular Weight: 358.48
C, 60.31; H, 4.22; P, 8.64; S, 26.83

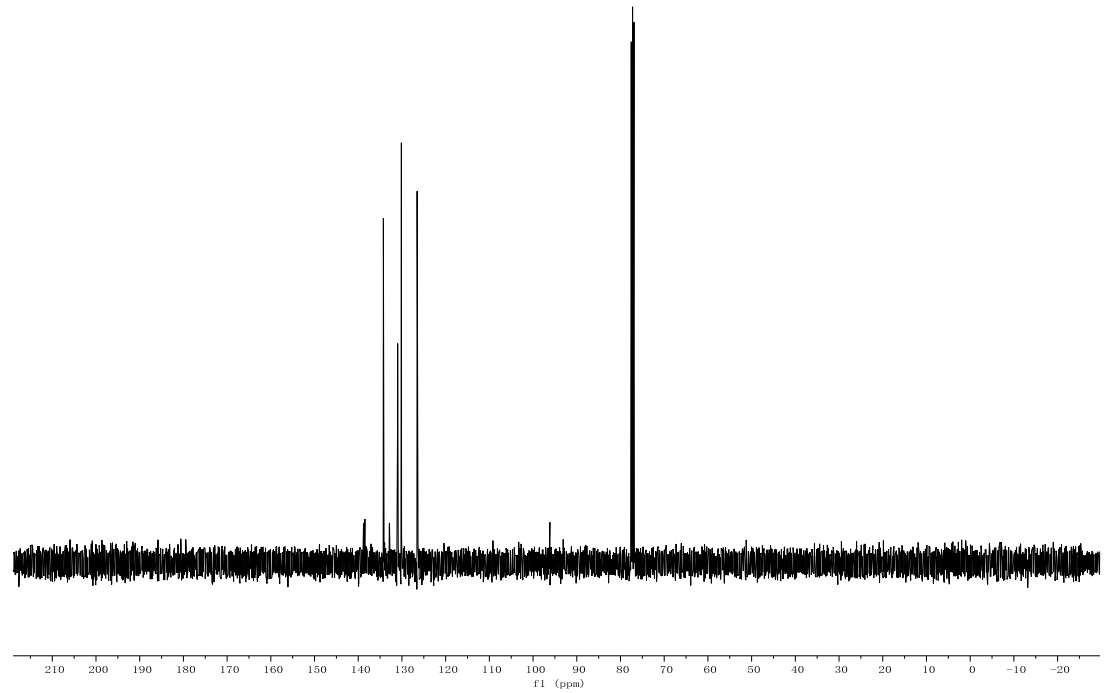
Through an addition funnel, a flask was charged with cyclohexane (55 mL), TMEDA (7.9 mL) and *n*-BuLi (2.5 M in hexane, 21 mL, 52.5 mmol). Thiophenol (2.5 mL, 24.4 mmol) in cyclohexane (20 mL) was added to the flask at 0 ℃. The reaction was warmed to room temperature over the next two days. Cyclohexane was removed from the reaction flask and the precipitate was washed with cyclohexane. When the precipitate settled, cyclohexane was removed again. THF (24 mL) was added to the precipitate, to which PCl_3 (0.5 mL) diluted with THF (5 mL) was added dropwise. The mixture was warmed to room temperature for 20 hours and then acidified with 10% sulfuric acid (100 mL). The mixture was concentrated in vacuo to remove THF, and the water solution was extracted with CH_2Cl_2 three times. The organic layer was dried with Na_2SO_4 and concentrated in vacuo to yield a yellow oil. Recrystallization from ethanol gave **37** as a white solid (830 mg, 2.3 mmol, 28%). ^{1}H NMR ($CDCl_3$) δ 4.10 (s, 3 H), 6.80 (ddd, *J* = 8 Hz, 4 Hz, 1 Hz, 3 H), 7.10 (t, *J* = 8 Hz, 3 H), 7.27 (ddd, *J* = 8 Hz, 8 Hz, 1 Hz, 3 H), 7.40 (dd, *J* = 8 Hz, 5

Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 126.5 (s), 130.1 (s), 131.0 (d, J_{PC} = 4 Hz), 132.9 (d, J_{PC} = 4 Hz), 134.3 (s), 138.6 (d, J_{PC} = 32 Hz) (6 of 6 expected resonances); MS (EI) *m/z* 324 (M – H_2S, 25), 215 (100).

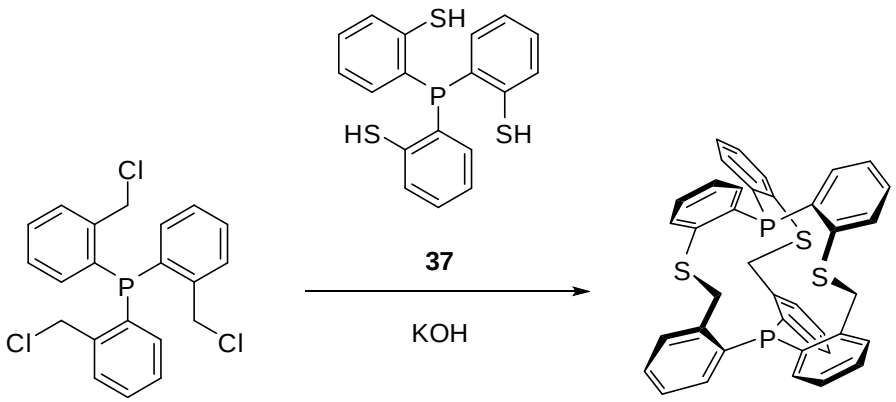
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **37**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **37**



Synthesis of *in,in*-diphosphine 235



239

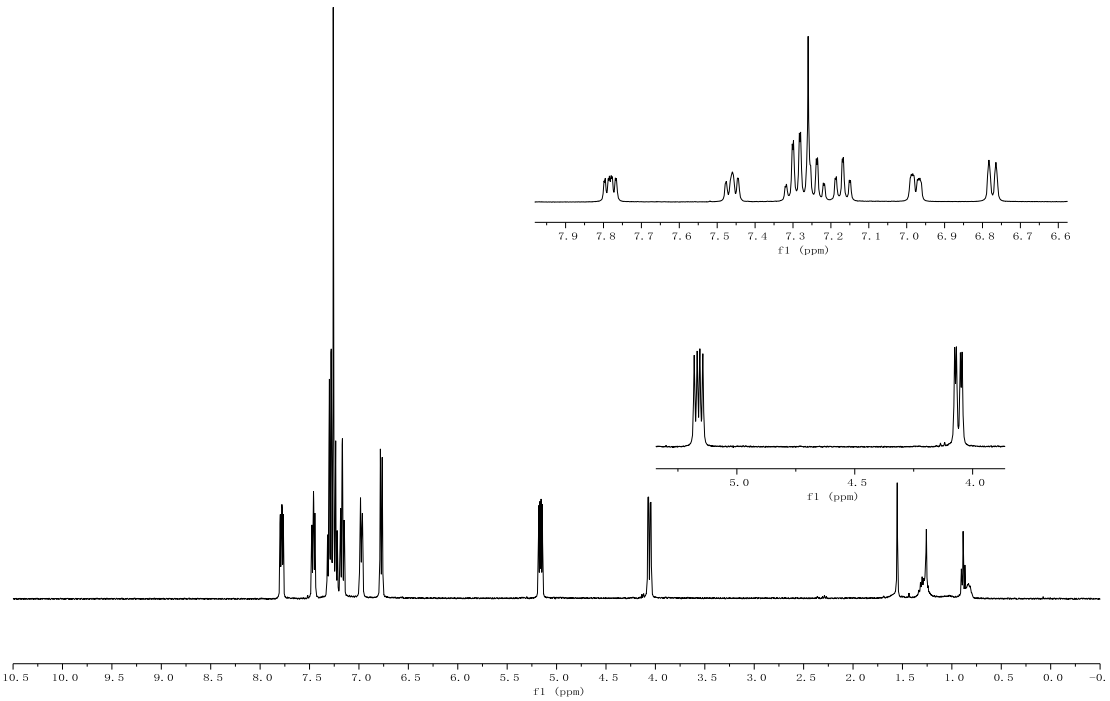
235

$C_{39}H_{30}P_2S_3$
Exact Mass: 656.10
Molecular Weight: 656.80
C, 71.32; H, 4.60; P, 9.43; S, 14.65

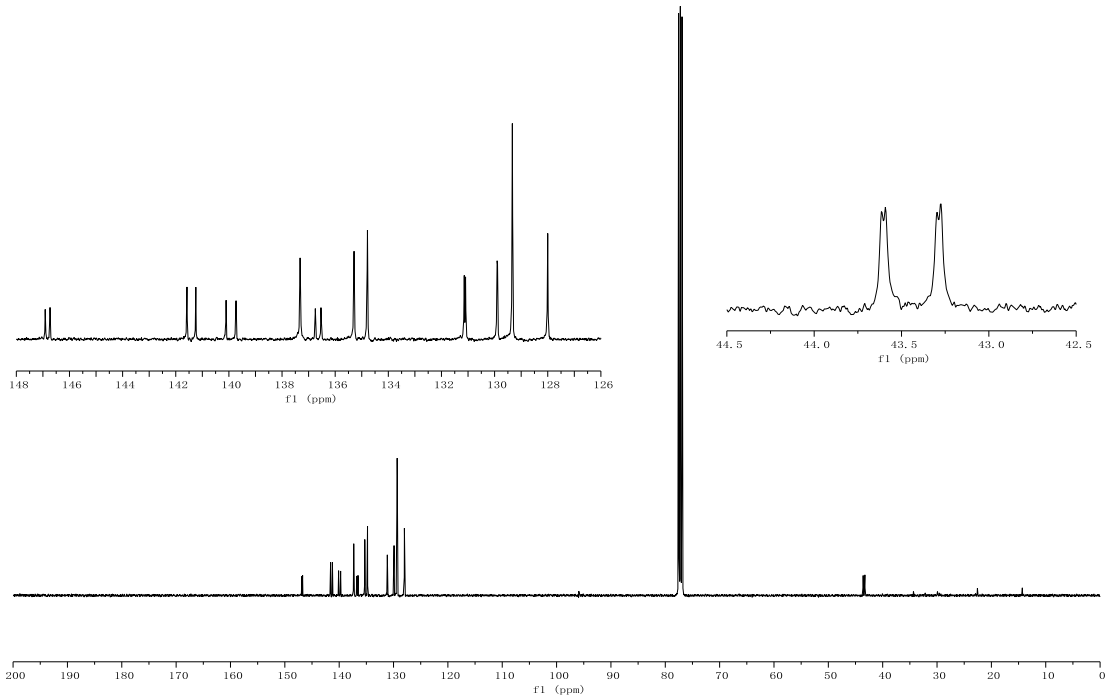
Tris[2-(chloromethyl)phenyl]phosphine (**239**, 101.9 mg, 0.250 mmol) and tris(2-mercaptophenyl)phosphine (**37**, 89.6 mg, 0.250 mmol) were mixed in 2:1 benzene-ethanol (220 mL), and the solution was heated to reflux. An argon-saturated solution of KOH (67 mg, 1.2 mmol) in ethanol (10 mL) was added slowly over 3 hours. After 20 hours, the solution was cooled, and the solvent was evaporated under reduced pressure to leave a white precipitate. The precipitate was extracted twice with chloroform. The combined extracts were concentrated and the resulting light yellow liquid was chromatographed on silica gel (solvent, 2:1 hexane-benzene) to yield phosphaphane **235** as a white solid (16.6 mg, 0.0253 mmol, 10.1%). Crystals suitable for X-ray analysis were obtained from $CHCl_3$-MeOH. ^{1}H NMR ($CDCl_3$) δ 4.06 (dd, J = 10 Hz, 3 Hz, 3 H),

5.16 (dd, J = 10 Hz, 5 Hz, 3 H), 6.77 (d, J = 8 Hz, 3 H), 6.97 (dd, J = 8 Hz, 1 Hz, 3 H), 7.17 (ddd, J = 8 Hz, 8 Hz, 1 Hz, 3 H), 7.27 (m, 9 H), 7.46 (dd, J = 6 Hz, 6 Hz, 3 H), 7.78 (ddd, J = 7 Hz, 4 Hz, 1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 43.4 (dd, J_{PC} = 32 Hz, 2 Hz), 128.0 (s), 129.3 (s, double intensity), 129.9 (d, J_{PC} = 1 Hz), 131.1 (d, J_{PC} = 5 Hz), 134.8 (s), 135.3 (s), 136.6 (dd, J_{PC} = 21 Hz, 1 Hz), 137.3 (d, J_{PC} = 2 Hz), 139.9 (d, J_{PC} = 37 Hz), 141.4 (d, J_{PC} = 34 Hz), 146.8 (d, J_{PC} = 18 Hz) (13 of 13 expected resonances); ^{31}P NMR ($CDCl_3$) δ -49.6 (d, J = 175 Hz), -31.2 (d, J = 175 Hz); MS (MALDI-TOF) *m/z* 657 (M + H, 100); HRMS (ESI) *m/z* 657.1061 (M + H), calcd for $C_{39}H_{31}P_2S_3$ 657.1058.

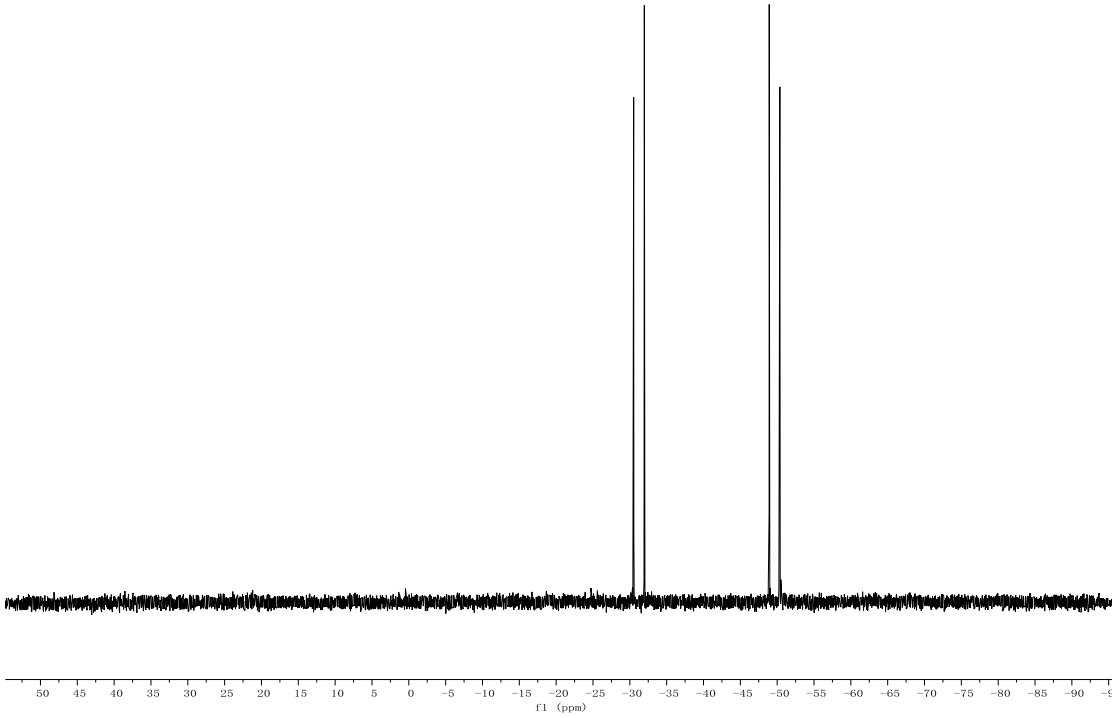
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **235**



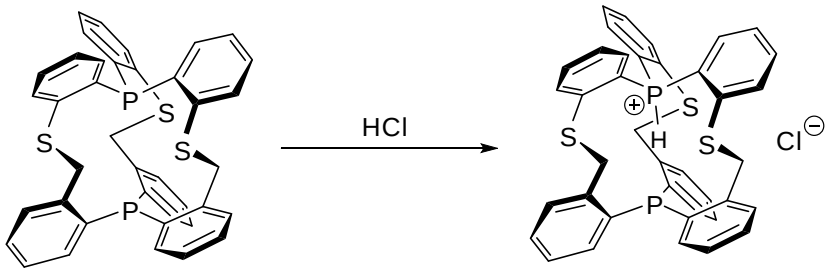
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **235**



^{31}P NMR Spectrum (121 MHz, $CDCl_3$) of Compound **235**



Synthesis of *in,in*-diphosphine hydrochloride 240



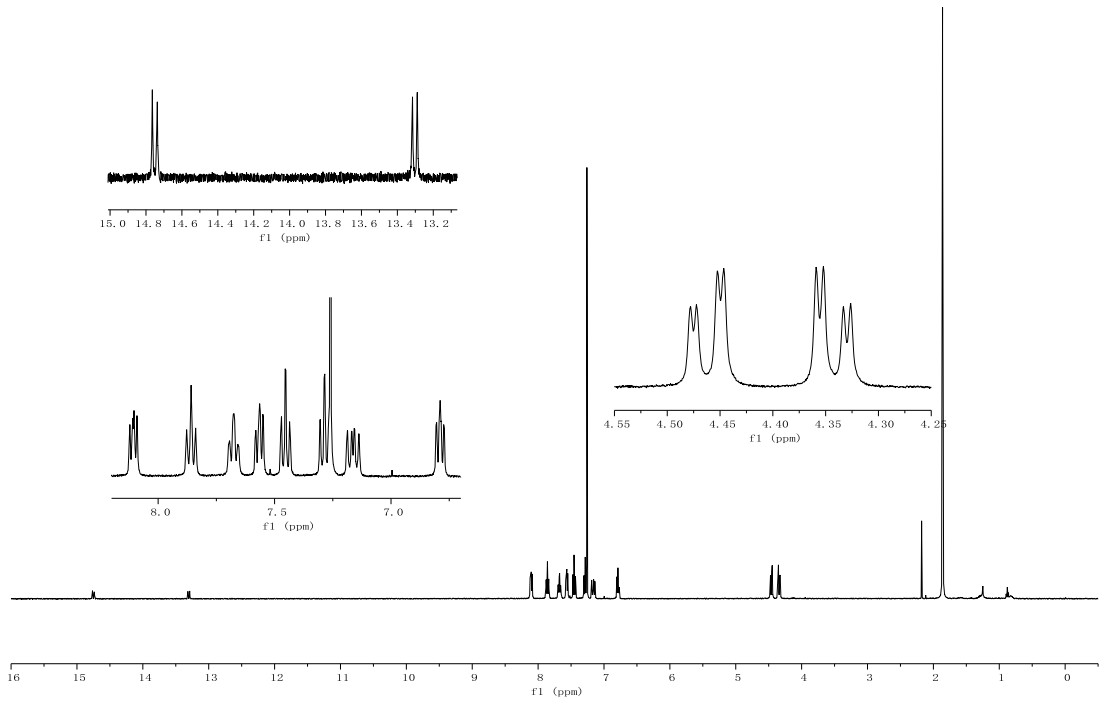
235 **240**

$C_{39}H_{31}ClP_2S_3$
Exact Mass: 692.08
Molecular Weight: 693.26
C, 67.57; H, 4.51; Cl, 5.11; P, 8.94; S, 13.88

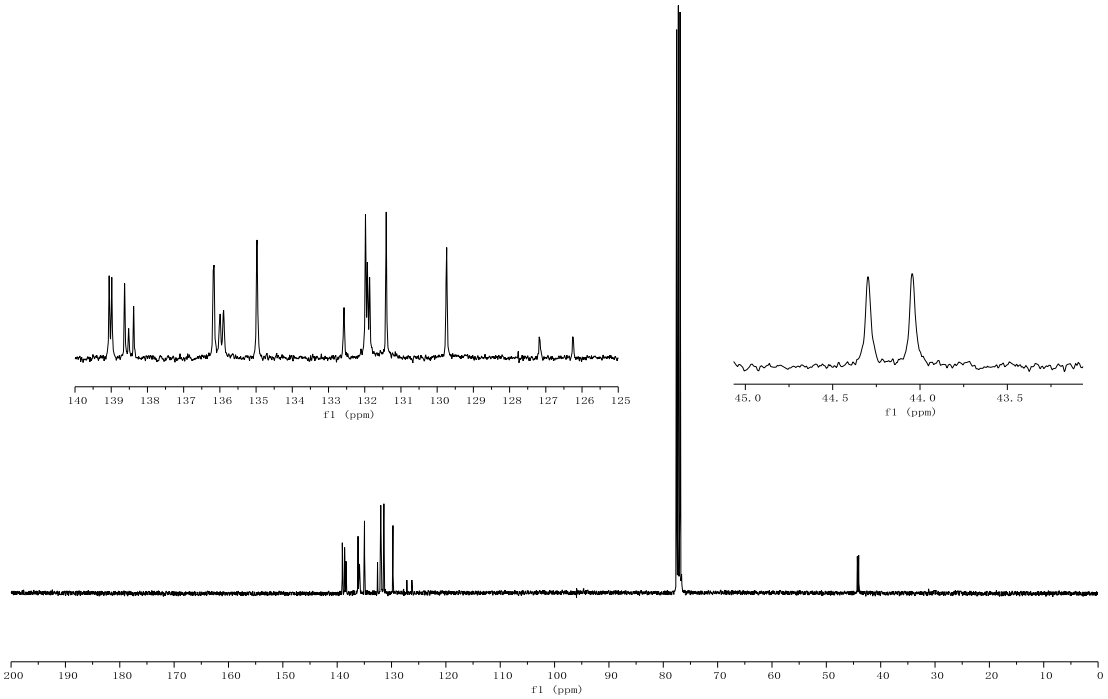
A stream of HCl gas was bubbled into a solution of diphosphine **235** (11 mg, 0.017 mmol) in $CDCl_3$ (1 mL) for 20 seconds. The resulting solution was left in a capped 5 mm NMR tube for 100 h at room temperature; at this time, ^{1}H NMR analysis indicated that protonation was complete. (Subsequent studies showed that protonation is complete in under 6 h.) Crystals of the hydrochloride **240** suitable for X-ray analysis were obtained by slow evaporation of a solution in $CHCl_3$-MeOH. ^{1}H NMR ($CDCl_3$) δ 4.37 (dd, J = 10 Hz, 2 Hz, 3 H), 4.44 (dd, J = 10 Hz, 2 Hz, 3 H), 6.77 (dd, J = 6 Hz, 6 Hz, 3 H), 7.09 (dd, J = 12 Hz, 8 Hz, 3 H), 7.28 (dd, J = 7 Hz, 7 Hz, 3 H), 7.44 (dd, J = 7 Hz, 7 Hz, 3 H), 7.57 (dd, J = 6 Hz, 6 Hz, 3 H), 7.68 (dd, J = 7 Hz, 7 Hz, 3 H), 7.88 (dd, J = 8 Hz, 8 Hz, 3 H), 8.14 (dd, J = 7 Hz, 5 Hz, 3 H), 14.08 (dd, J = 584 Hz, 13 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 44.2 (d, J_{PC} = 25 Hz), 126.7 (d, J_{PC} = 93 Hz), 129.7 (s), 131.4 (s), 131.9 (d, J_{PC} = 6 Hz), 132.0 (s), 132.6 (s), 135.0 (s), 135.9 (d, J_{PC} = 9 Hz), 136.2 (d, J_{PC} = 2 Hz),

138.5 (d, J_{PC} = 25 Hz), 138.6 (d, J_{PC} = 11 Hz), 139.0 (d, J_{PC} = 7 Hz) (13 of 13 expected resonances); ^{31}P NMR ($CDCl_3$) δ -16.7 (d, *J* = 303 Hz), -40.1 (d, *J* = 303 Hz); HRMS (ESI) *m/z* 657.1056 (M – Cl), calcd for $C_{39}H_{31}P_2S_3$ 657.1058.

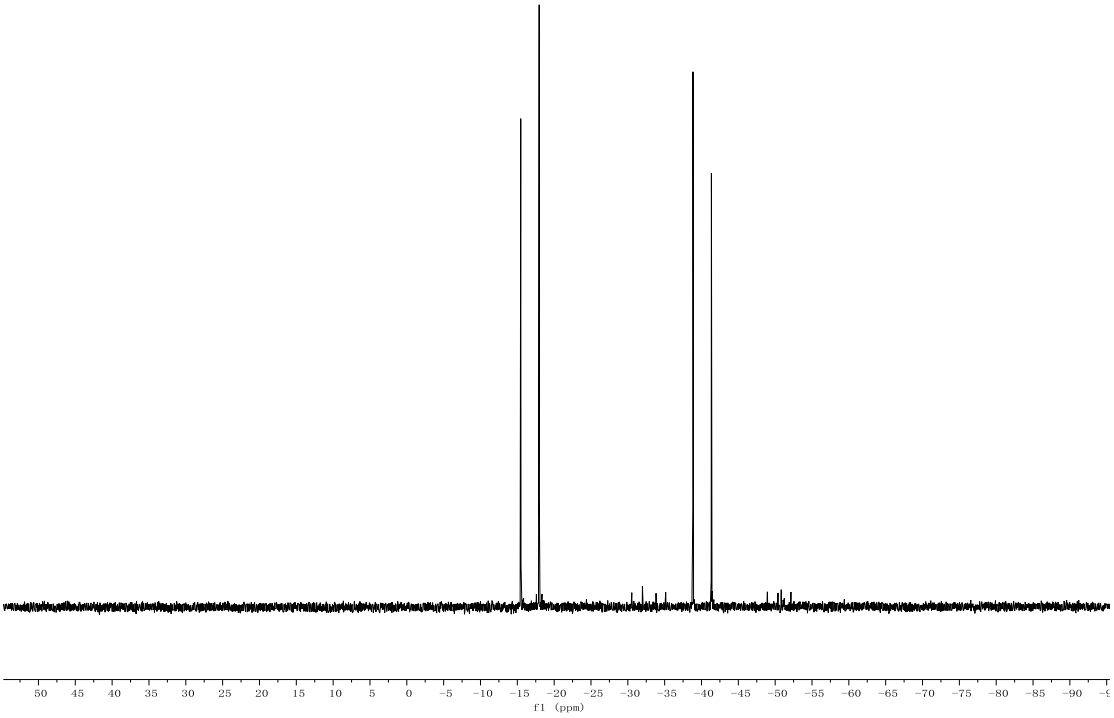
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **240**



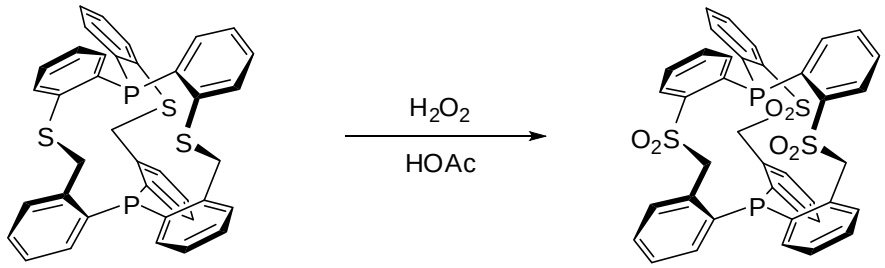
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **240**



^{31}P NMR Spectrum (121 MHz, $CDCl_3$) of Compound **240**



Synthesis of *in,in*-diphosphine hexaoxide 241

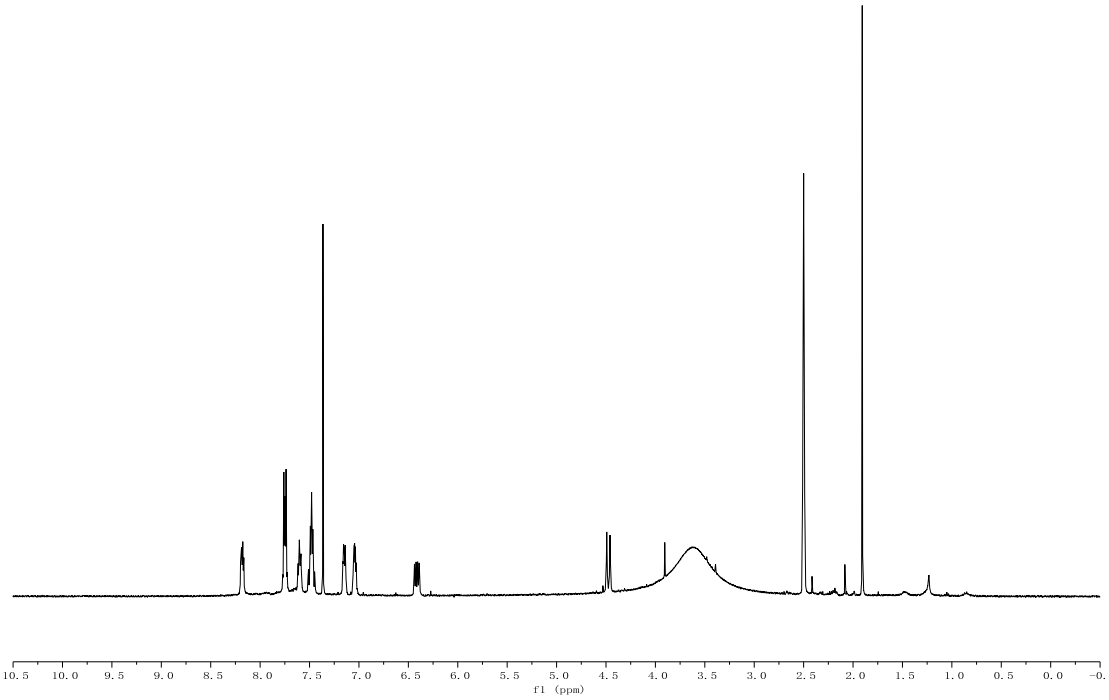


235 **241**

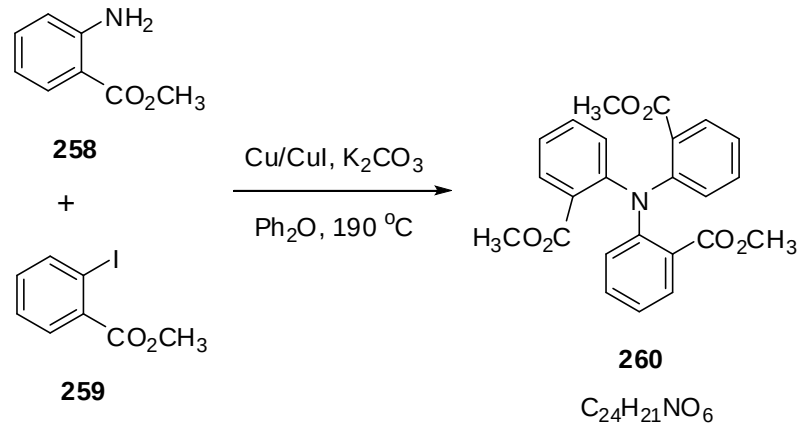
$C_{39}H_{30}O_6P_2S_3$
Exact Mass: 752.07
Molecular Weight: 752.79
C, 62.22; H, 4.02; O, 12.75; P, 8.23; S, 12.78

Diphosphine (**235**, 11 mg, 0.017 mmol), acetic acid (2 mL), and 30% H_2O_2 (1 mL) were heated at reflux for 20 h. Evaporation of the solvent left the relatively insoluble trisulfone **241** (~12 mg). Recrystallization of this material from hot DMSO gave crystals suitable for X-ray analysis. ^{1}H NMR ($CDCl_3$-DMSO-d_6) δ 4.48 (d, *J* = 13 Hz, 3 H), 6.31 (dd, *J* = 13 Hz, 6 Hz, 3 H), 7.04 (m, 3 H), 7.15 (m, 3 H), 7.48 (m, 6 H), 7.60 (m, 3 H), 7.75 (m, 6 H), 8.18 (m, 3 H); MS (MALDI-TOF) *m/z* 753 (M + H, 100); HRMS (ESI) *m/z* 753.0753 (M + H), calcd for $C_{39}H_{31}O_6P_2S_3$ 753.0753.

^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **241**



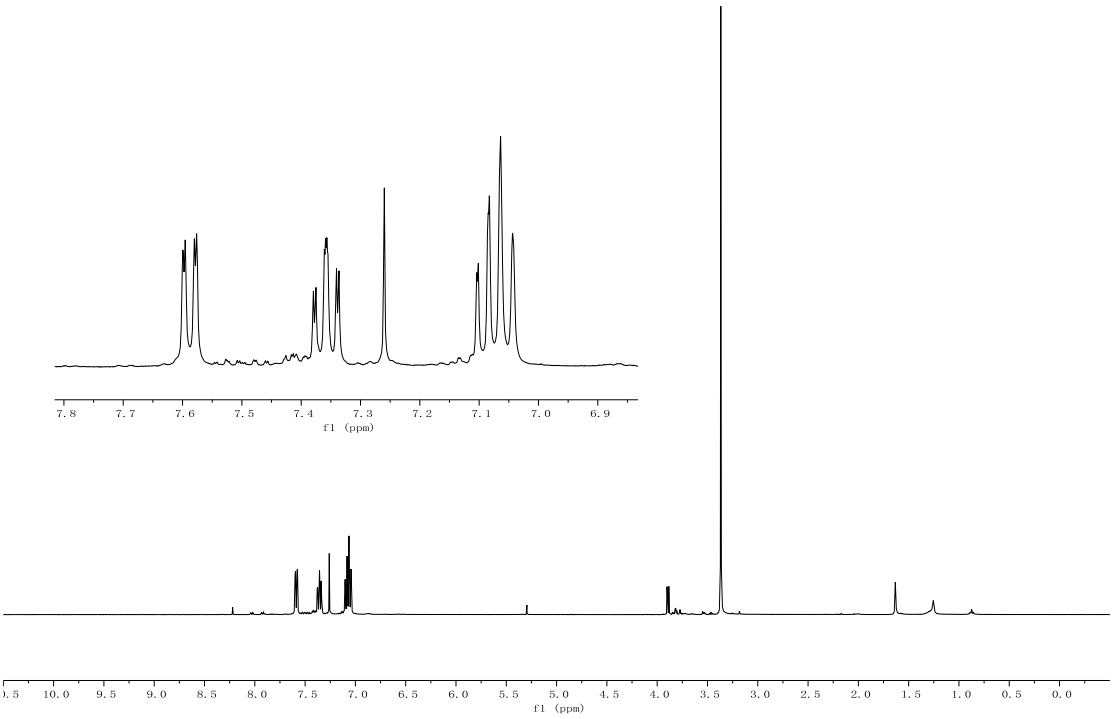
Synthesis of tris[2-(methoxycarbonyl)phenyl]amine (260)



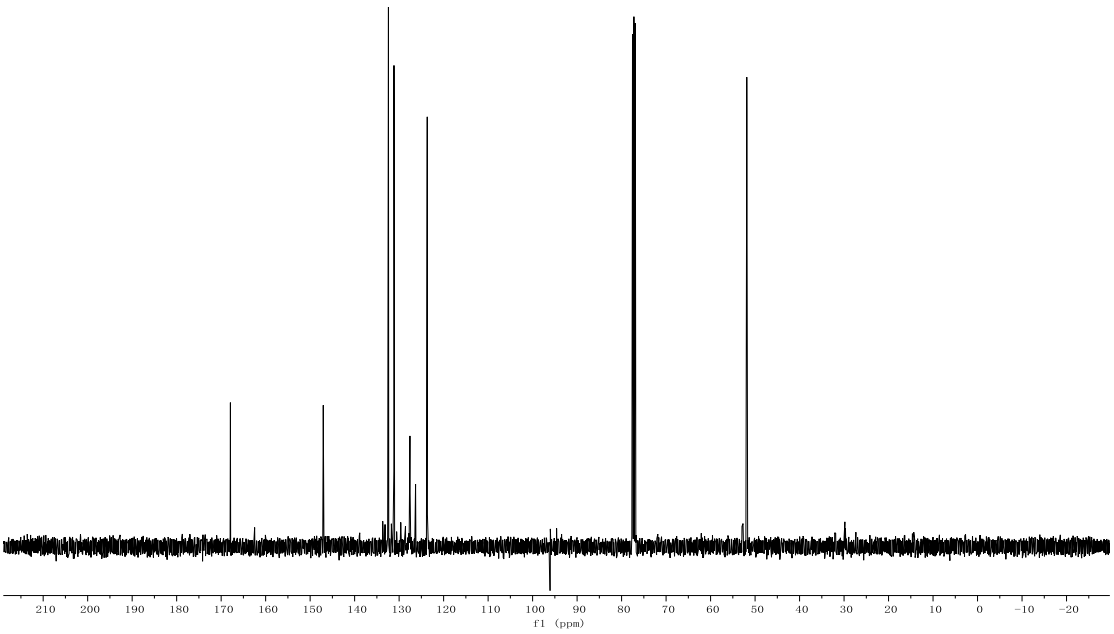
$C_{24}H_{21}NO_6$
Exact Mass: 419.14
Molecular Weight: 419.43
C, 68.73; H, 5.05; N, 3.34; O, 22.89

A mixture of methyl anthranilate (**258**, 9 ml), methyl 2-iodobenoate (**259**, 30 ml), K_2CO_3 (22 g), Cu (0.9 g) and CuI (1.3 g) in diphenyl ether (80 ml) was heated at 190 ℃ under Ar for 48 hours. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel using 4:1 hexane/ethyl acetate as eluent to yield compound **260** as a yellow solid (22.1 g, 75%). ^{1}H NMR ($CDCl_3$) δ 3.37 (s, 9 H), 7.08 (m, 6H), 7.36 (m, 3 H), 7.59 (dd, *J* = 8 Hz, 2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 51.9, 123.7, 126.3, 127.6, 131.2, 132.4, 147.1, 167.9, 171.9 (8 of 8 expected resonances).

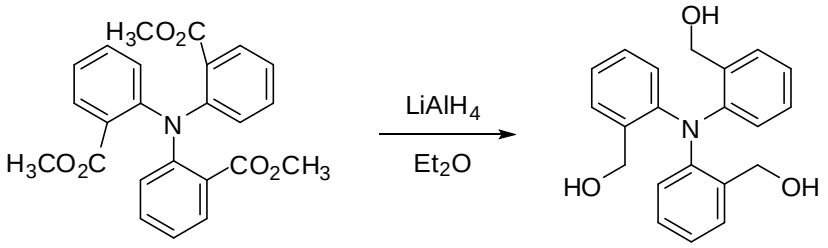
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **260**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **260**



Synthesis of tris[2-(hydroxymethyl)phenyl]amine (261)

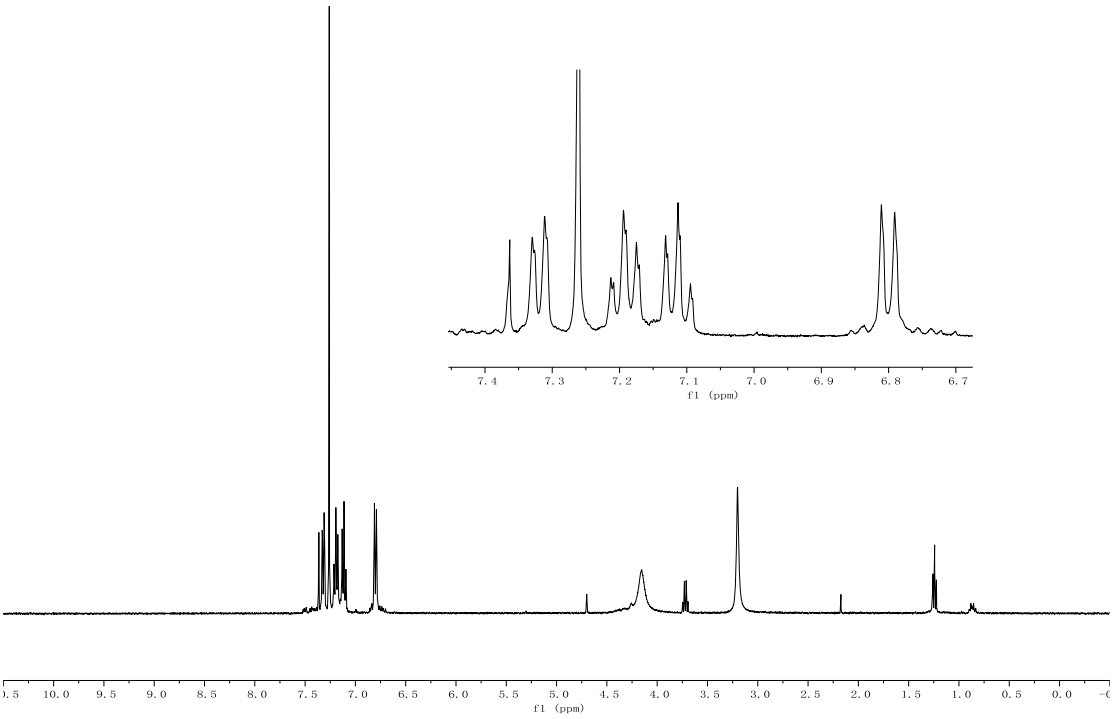


260 **261**

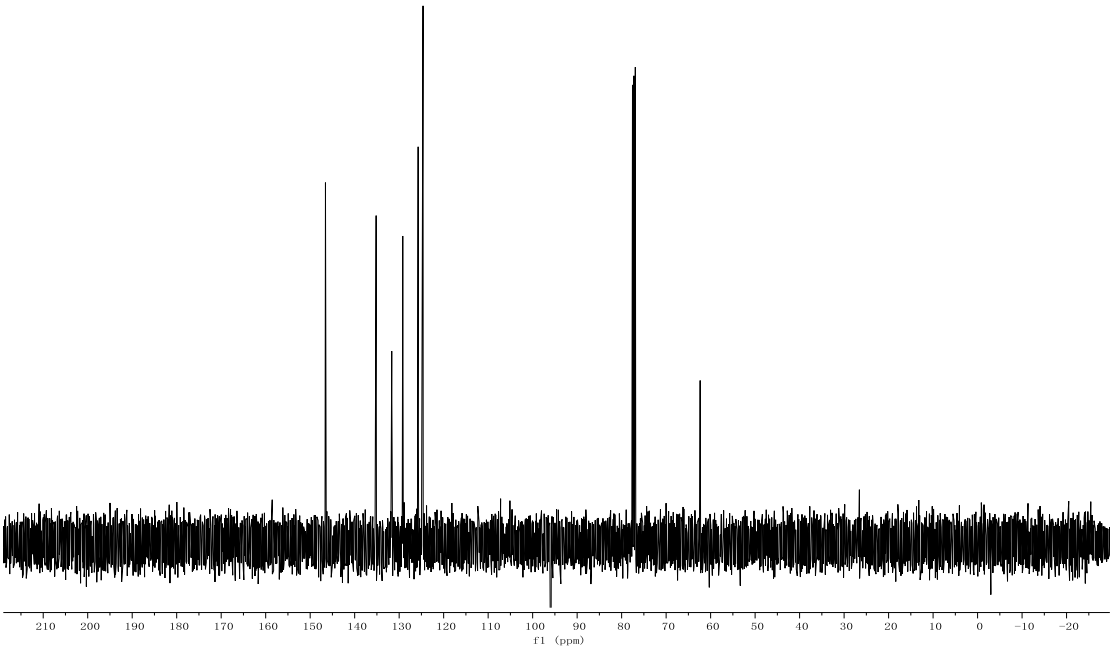
$C_{21}H_{21}NO_3$
Exact Mass: 335.15
Molecular Weight: 335.40
C, 75.20; H, 6.31; N, 4.18; O, 14.31

A solution of tris[2-(methoxycarbonyl)phenyl]amine (**260**, 2.67 g, 6.4 mmol) in 75 ml of THF was added dropwise to a suspension of lithium aluminum hydride (1.28 g, 34 mmol) in 15 mL of tetrahydrofuran with stirring. The mixture was heated at a gentle reflux for 3 hours, and then water was added to the reaction mixture, followed by addition of dilute hydrochloric acid. The organic phase was extracted three times with chloroform. The combined organic phase was dried with sodium sulfate and the solvent was removed under vacuum. The crude solid was recrystallized with 1:1 acetone-ethanol to give compound **261** as light yellow crystals (1.43 g, 4.3 mmol, 67%). ^{1}H NMR ($CDCl_3$) δ 3.20 (br, 3 H), 4.16 (br, 6 H), 6.80 (d, *J* = 8 Hz, 3 H), 7.11 (ddd, *J* = 7 Hz, 7 Hz, 1 Hz, 3 H), 7.19 (t, *J* = 8 Hz, 2 Hz, 3 H), 7.32 (dd, *J* = 8 Hz, 2 Hz, 3 H) ; ^{13}C NMR ($CDCl_3$) δ 62.4, 124.6, 125.7, 129.2, 131.7, 135.2, 146.6 (7 of 7 expected resonances).

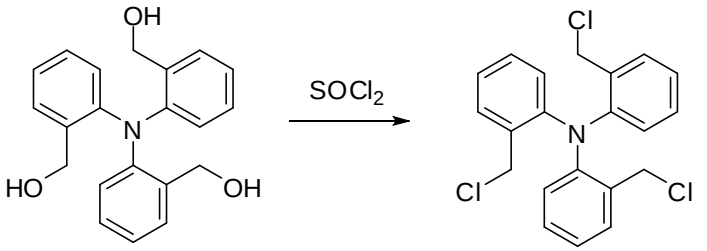
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **261**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **261**



Synthesis of tris[2-(chloromethyl)phenyl]amine (262)

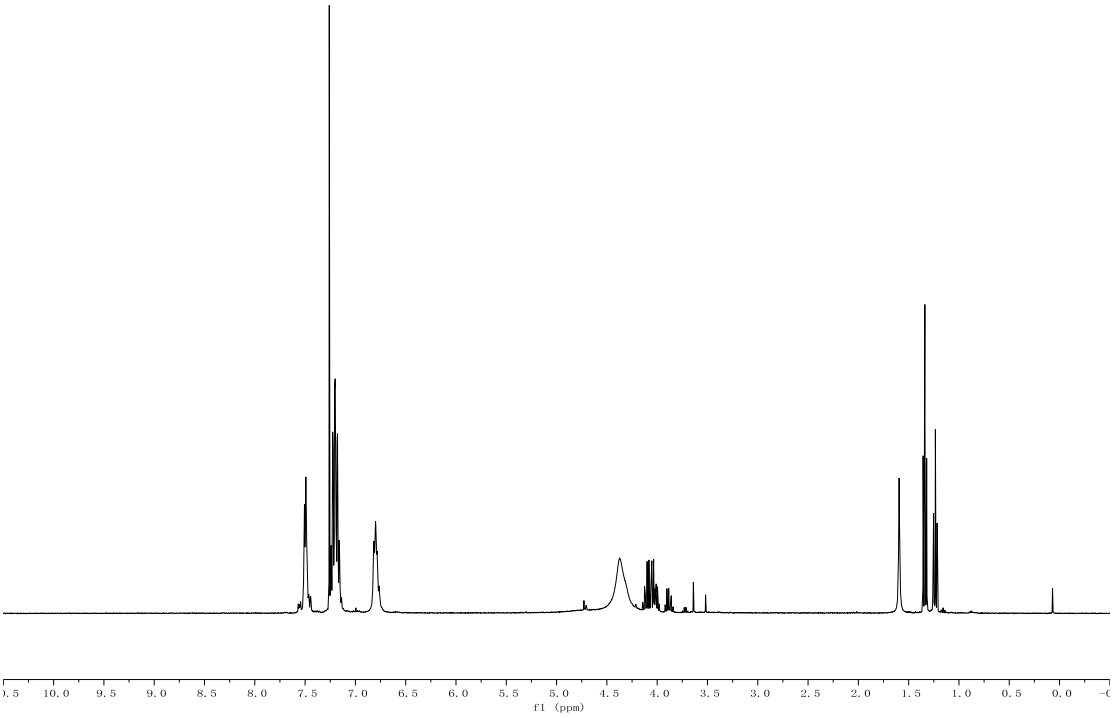


261 **262**

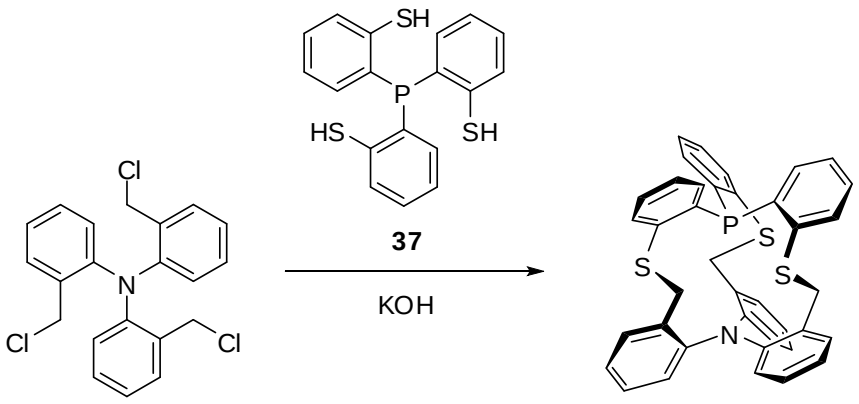
$C_{21}H_{18}Cl_3N$
Exact Mass: 389.05
Molecular Weight: 390.73
C, 64.55; H, 4.64; Cl, 27.22; N, 3.58

To a solution of compound **261** (606 mg, 1.8 mmol) in chloroform (25 mL), thionyl chloride (0.4 mL) was added dropwise. The reaction mixture was refluxed overnight. After the reaction mixture was cooled to room temperature, water was added and the mixture was extracted with chloroform three times. The combined organic layer was dried with Na_2SO_4. The solvent was removed to yield compound **262** as a yellow solid. ^{1}H NMR ($CDCl_3$) δ 4.37 (br, 6 H), 6.80 (m, 3 H), 7.20 (m, 6 H), 7.50 (dd, *J* = 8 Hz, 2 Hz, 3 H).

^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **262**



Synthesis of *in,in*-P,N cyclophane 256



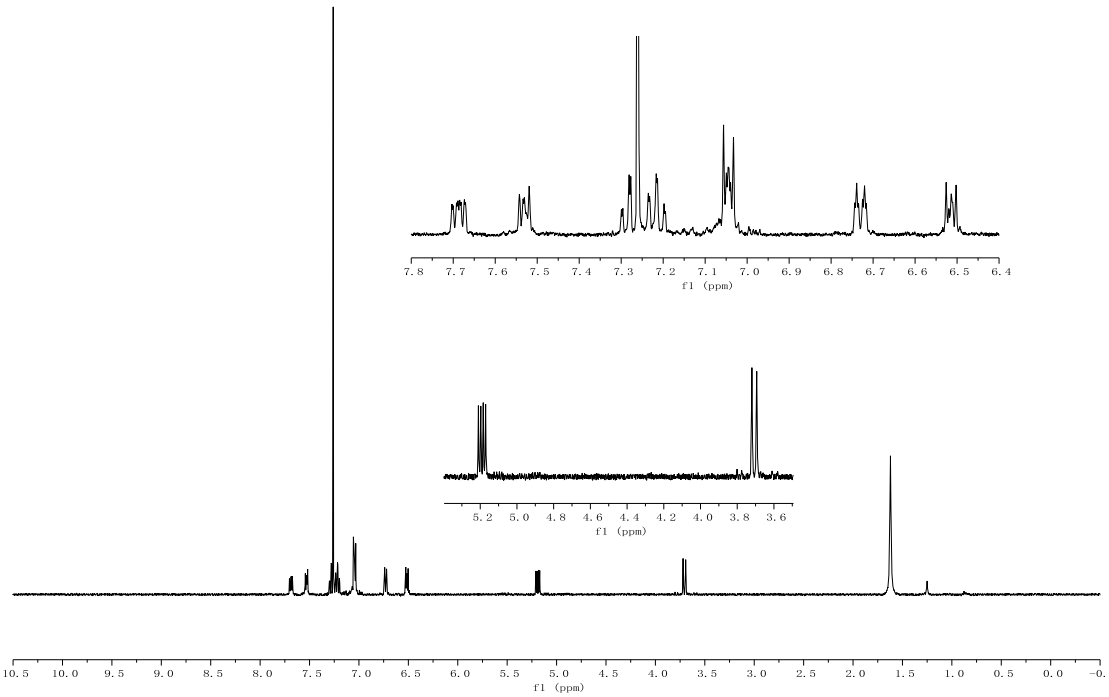
262 **256**

$C_{39}H_{30}NPS_3$
Exact Mass: 639.13
Molecular Weight: 639.83
C, 73.21; H, 4.73; N, 2.19; P, 4.84; S, 15.03

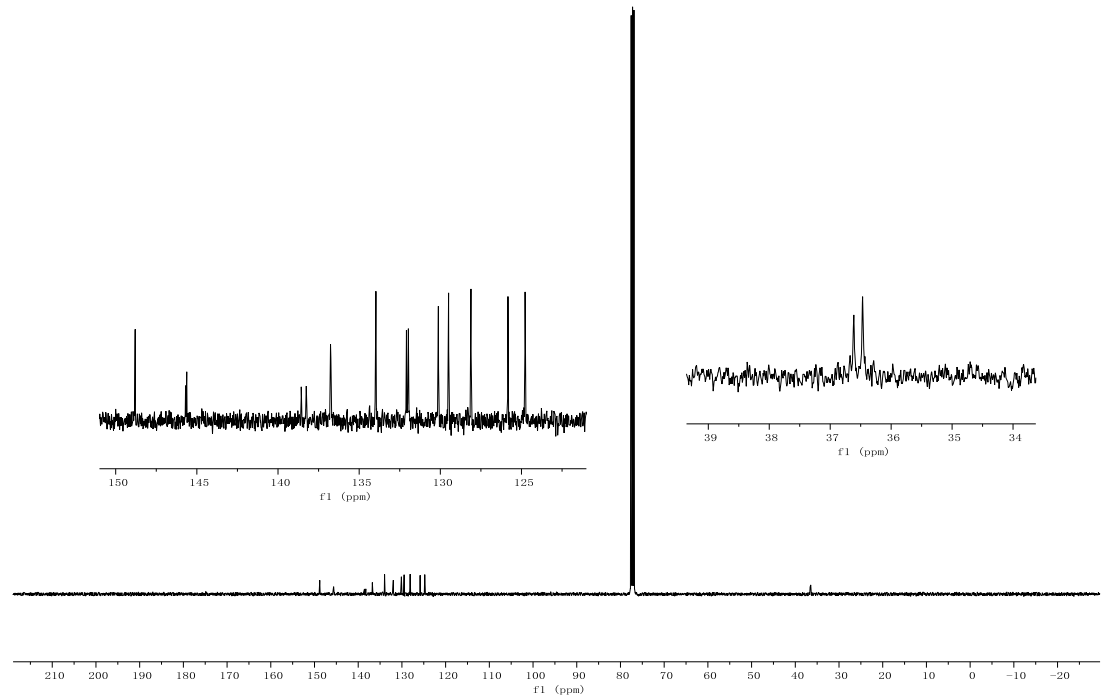
Tris[2-(chloromethyl)phenyl]amine (**262**, 170 mg, 0.44 mmol) and tris(2-mercaptophenyl)phosphine (**37**, 156 mg, 0.44 mmol) were mixed in 2:1 benzene-ethanol (400 mL), and the solution was heated to reflux. An argon-saturated solution of KOH (117 mg, 2.1 mmol) in ethanol (50 mL) was added slowly over 6 hours. After 18 hours, the solution was cooled, and the solvent was evaporated under reduced pressure to leave a white precipitate. The precipitate was extracted twice with chloroform. The combined extracts were concentrated and the resulting light yellow liquid was chromatographed on silica gel (solvent, 2:1 hexanes-benzene) to yield compound **256** as a white solid. ^{1}H NMR ($CDCl_3$) δ 3.71 (d, *J* = 10 Hz, 3 H), 5.19 (dd, *J* = 10 Hz, 5 Hz, 3 H), 6.51 (m, 3 H), 6.73 (ddd, *J* = 8 Hz, 2 Hz, 2 Hz, 3 H), 7.04 (m, 6 H), 7.22 (td, *J* = 8

Hz, 8 Hz, 1 Hz, 3 H), 7.28 (ddd, J = 8 Hz, 8 Hz, 1 Hz, 3 H), 7.53 (m, 3 H), 7.69 (ddd, J = 7 Hz, 4 Hz, 1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 36.5 (d, J_{PC} = 14 Hz), 124.8, 125.8, 128.1, 129.5, 130.1, 132.0 (d, J_{PC} = 12 Hz), 134.0, 136.8, 138.3, 138.6, 145.6 (d, J_{PC} = 7 Hz), 148.8 (13 of 13 expected resonances); MS (MALDI-TOF) *m/z* 640 (M + H, 100).

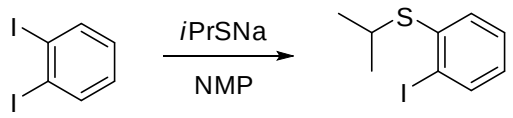
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **256**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **256**



Synthesis of 1-iodo-2-(isopropylthio)benzene (53)

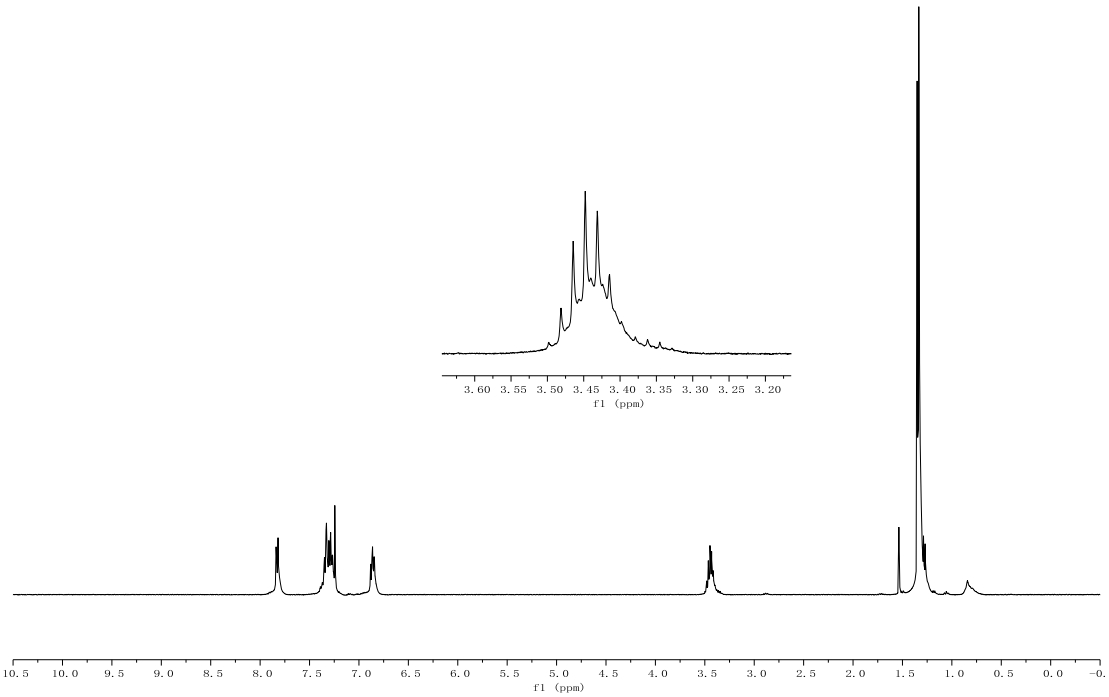


53

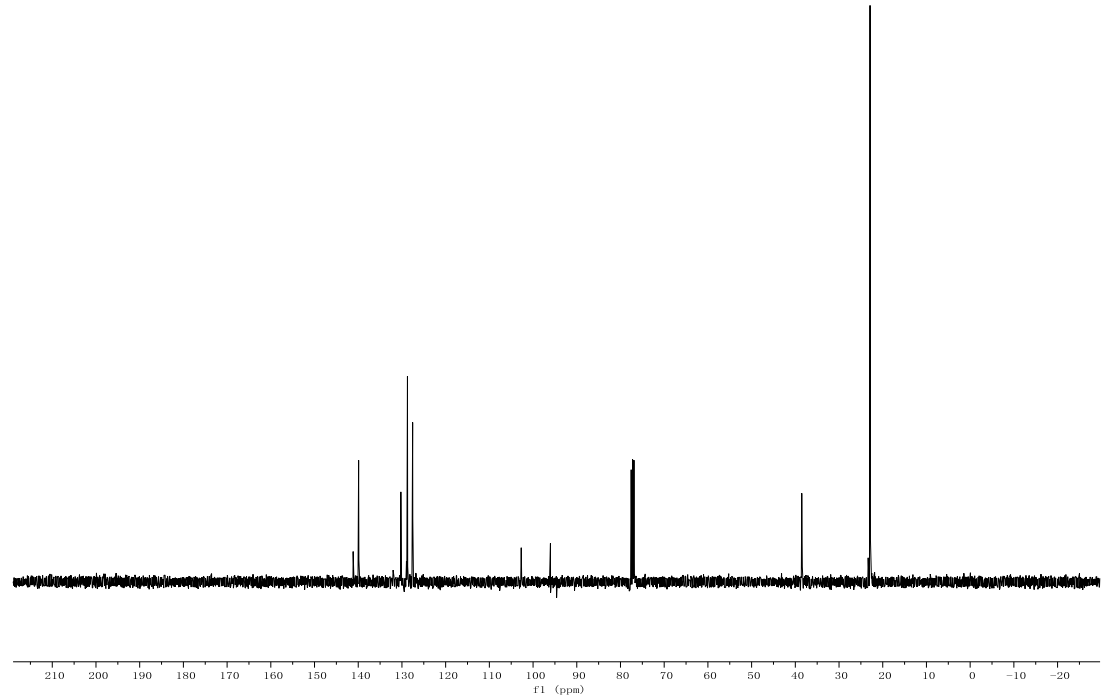
$C_9H_{11}IS$
Exact Mass: 277.96
Molecular Weight: 278.15
C, 38.86; H, 3.99; I, 45.62; S, 11.53

1,2-Diiodobenzene (11.8 mL, 90 mmol) and sodium 2-propanethiolate (9.0 g, 92 mmol) were dissolved in argon-saturated NMP (70 mL) and heated to 110 ℃ under argon. After 24 h, the solution was cooled to room temperature, diluted with water, and extracted three times with hexanes. The combined organics were washed twice with water and dried over Na_2SO_4. The solvent was stripped off, and the resulting material was fractionated on a silica gel column (solvent: hexanes) to yield compound **53** as a colorless oil (8.19 g, 29.4 mmol, 32%). ^{1}H NMR ($CDCl_3$) δ 1.36 (d, J = 7 Hz, 6 H), 3.46 (septet, J = 7 Hz, 1 H), 6.88 (m, 1 H), 7.32 (m, 2 H), 7.85 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.0, 38.5, 102.7, 127.6, 128.8, 130.2, 139.9, 141.2 (8 of 8 expected resonances); MS (EI) *m/z* 278 (M^+, 75), 236 (M – propene, 100).

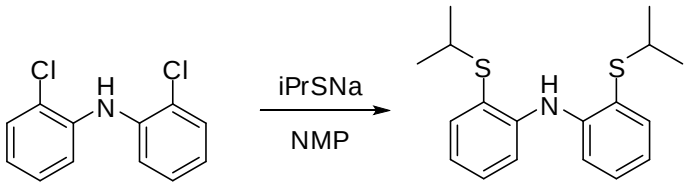
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **53**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **53**



Synthesis of bis(2-isopropylthiophenyl)amine (52)

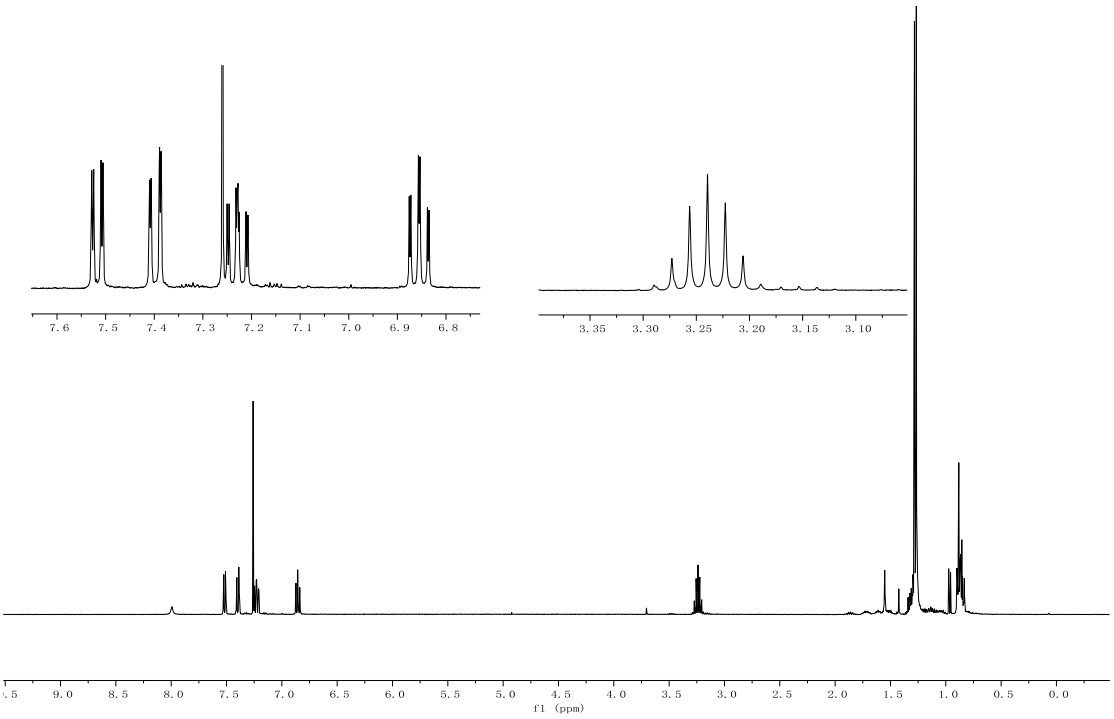


51 **52**

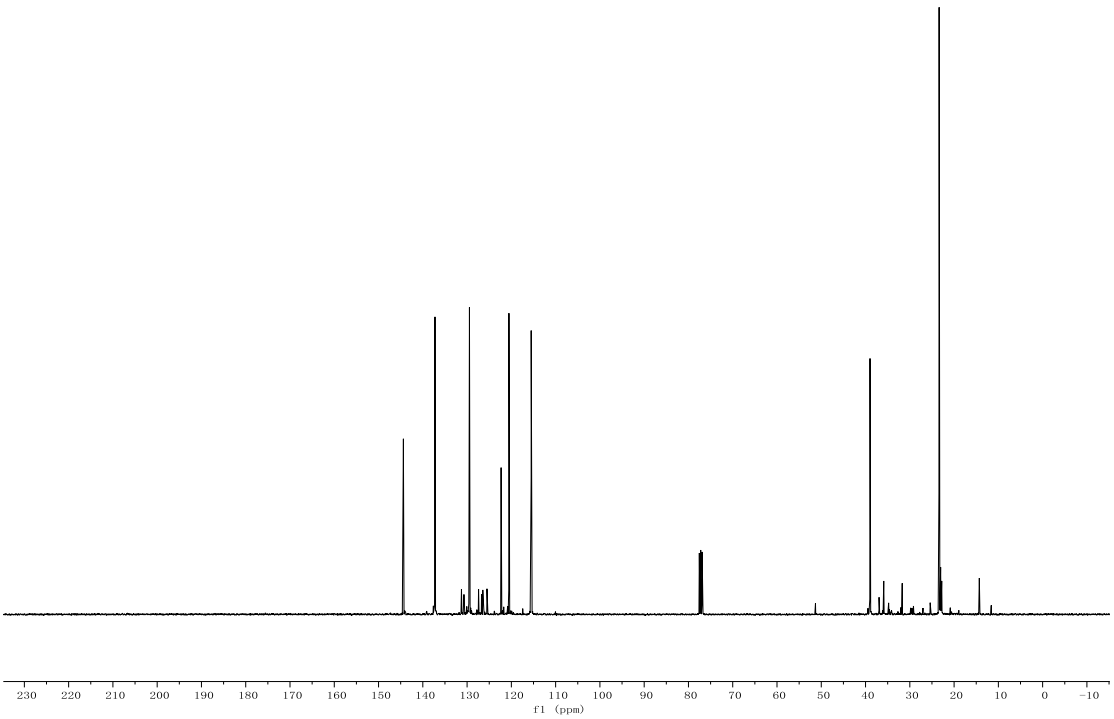
$C_{18}H_{23}NS_2$
Exact Mass: 317.13
Molecular Weight: 317.51
C, 68.09; H, 7.30; N, 4.41; S, 20.20

Bis(2-chlorophenyl)amine (**51**, 10.0 g, 42 mmol) and sodium 2-propanethiolate (8.4 g, 86 mmol) were dissolved in argon-saturated NMP (50 mL) and heated to 120 ℃ under argon. After 24 h, the solution was cooled to room temperature, diluted with water, and extracted three times with hexanes. The combined organics were washed twice with water and dried over Na_2SO_4. The solvent was stripped off, and the resulting material was fractionated on a silica gel column (solvent: hexanes) to yield compound **52** as a yellow oil (4.00 g, 12.6 mmol, 30%). ^{1}H NMR ($CDCl_3$) δ 1.27 (d, *J* = 7 Hz, 12 H), 3.24 (septet, *J* = 7 Hz, 2 H), 6.86 (m, 2 H), 7.23 (m, 2 H), 7.40 (dd, *J* = 8 Hz, 1 Hz, 2 H), 7.52 (dd, *J* = 8 Hz, 1.5 Hz, 2 H), 8.00 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.6, 39.2, 115.7, 120.8, 122.5, 129.7, 137.5, 144.6 (8 of 8 expected resonances); MS (EI) *m/z* 317 (M^+, 50), 242 (M – Me_2CHS, 45), 199 (M – Me_2CHS – Me_2CH, 100).

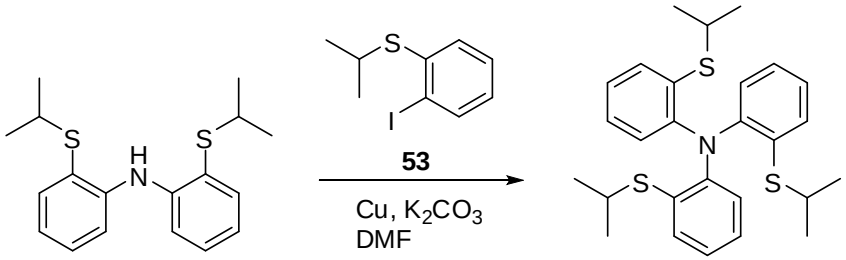
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **52**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **52**



Synthesis of tris(2-isopropylthiophenyl)amine (54)

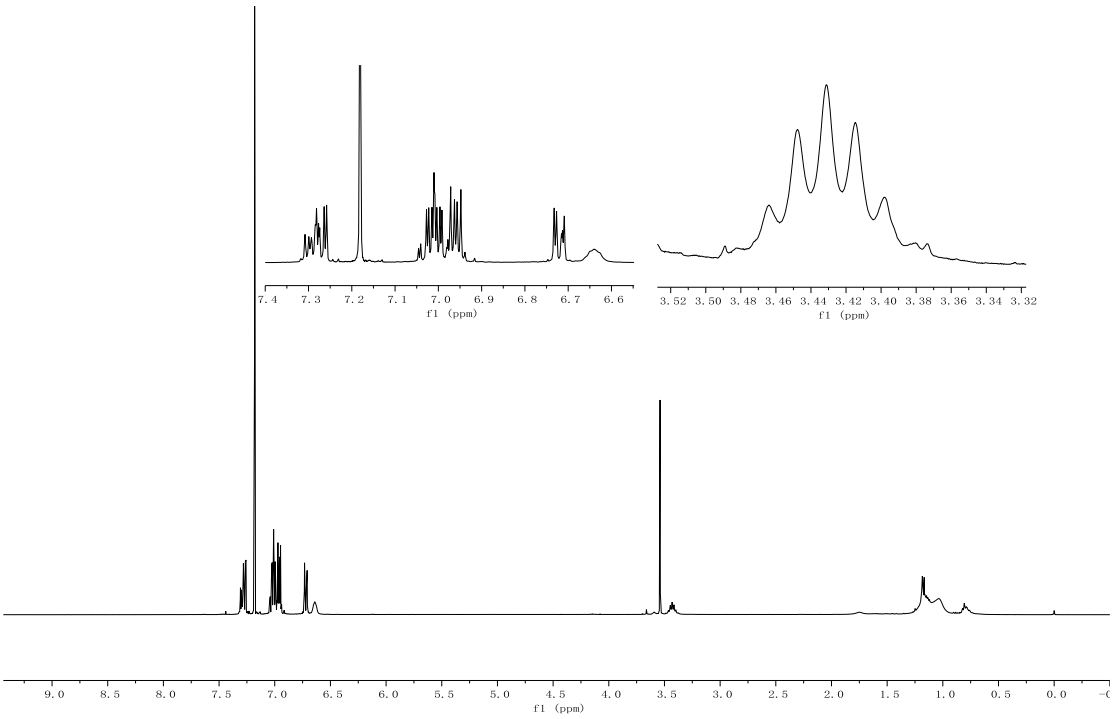


52 **54**

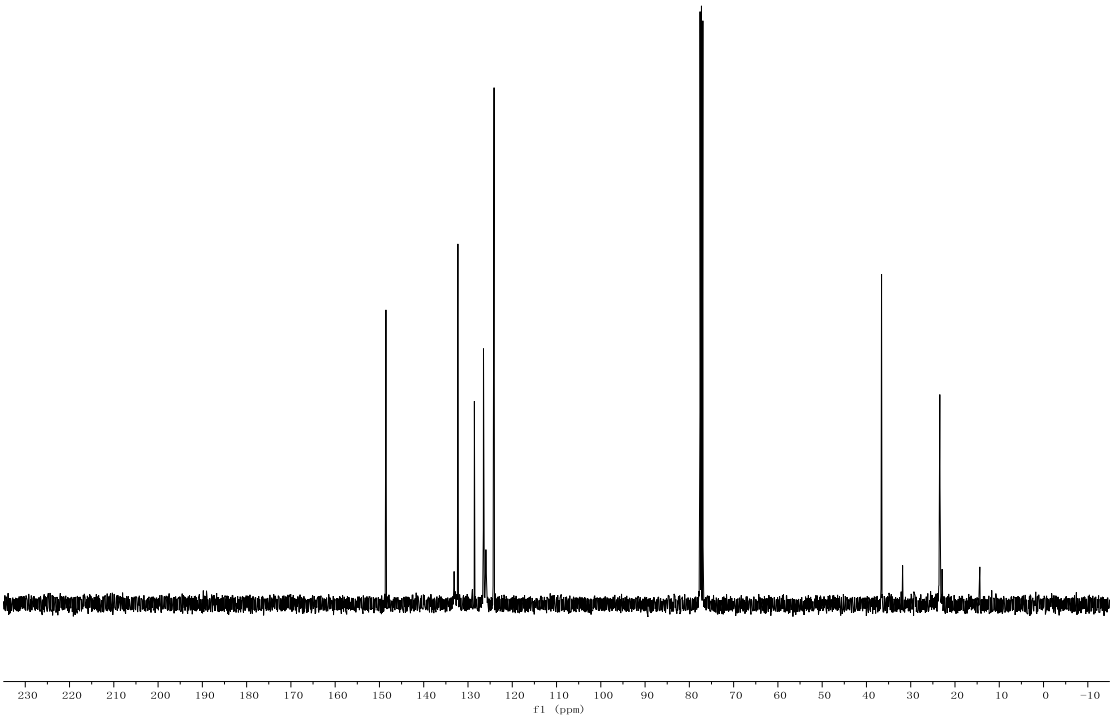
$C_{27}H_{33}NS_3$
Exact Mass: 467.18
Molecular Weight: 467.75
C, 69.33; H, 7.11; N, 2.99; S, 20.57

Bis(2-isopropylthiophenyl)amine (**52**, 4.00 g, 12.6 mmol), 1-iodo-2-(isopropylthio)benzene (**53**, 3.56 g, 12.8 mmol), Cu powder (0.83 g, 13 mmol), and K_2CO_3 (1.8 g, 13 mmol) were mixed in DMF (20 mL) and heated at reflux for 60 h. After cooling to room temperature, the mixture was diluted with water and extracted three times with hexanes. The combined organics were washed twice with water and dried over Na_2SO_4. The solvent was stripped off, and the resulting oil was fractionated on a silica gel column (solvent: hexanes, then 3:1 hexanes-benzene). Concentration of the appropriate fractions gave compound **54** as colorless crystals (0.850 g, 1.82 mmol, 14.4%), mp 91-94 ℃. ^{1}H NMR ($CDCl_3$) δ 1.16 (br, 18 H), 3.48 (septet, *J* = 7 Hz, 3 H), 6.71 (m, 3 H), 7.03 (m, 6 H), 7.37 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 23.4, 36.6, 124.1, 126.5, 128.6, 132.3, 148.5 (7 of 8 expected resonances); MS (EI) *m/z* 467 (M^+, 7.5), 392 (M – Me_2CHS, 35), 349 (M – Me_2CHS – Me_2CH, 100).

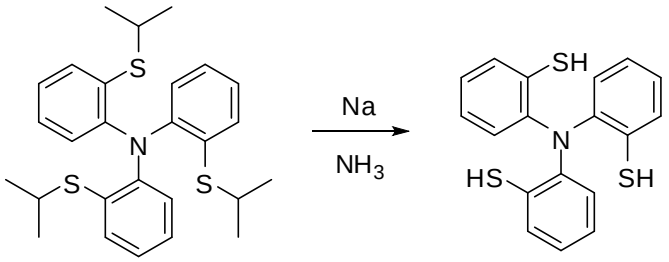
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **54**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **54**



Synthesis of tris(2-mercaptophenyl)amine (55)

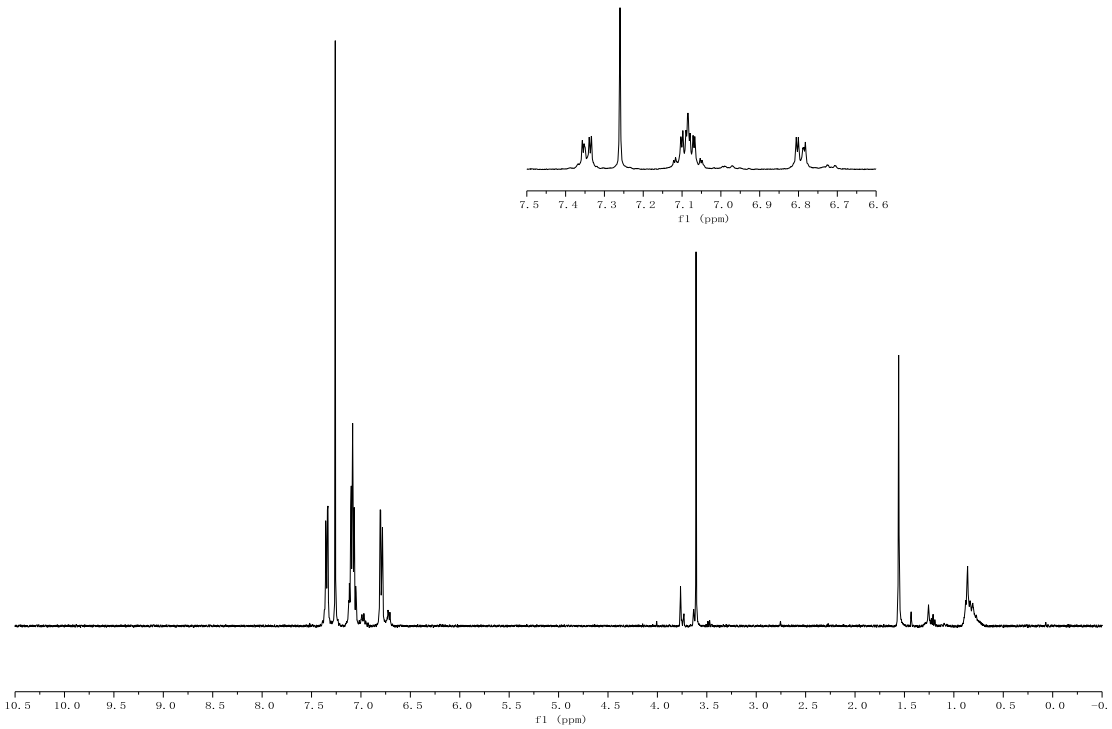


54 **55**

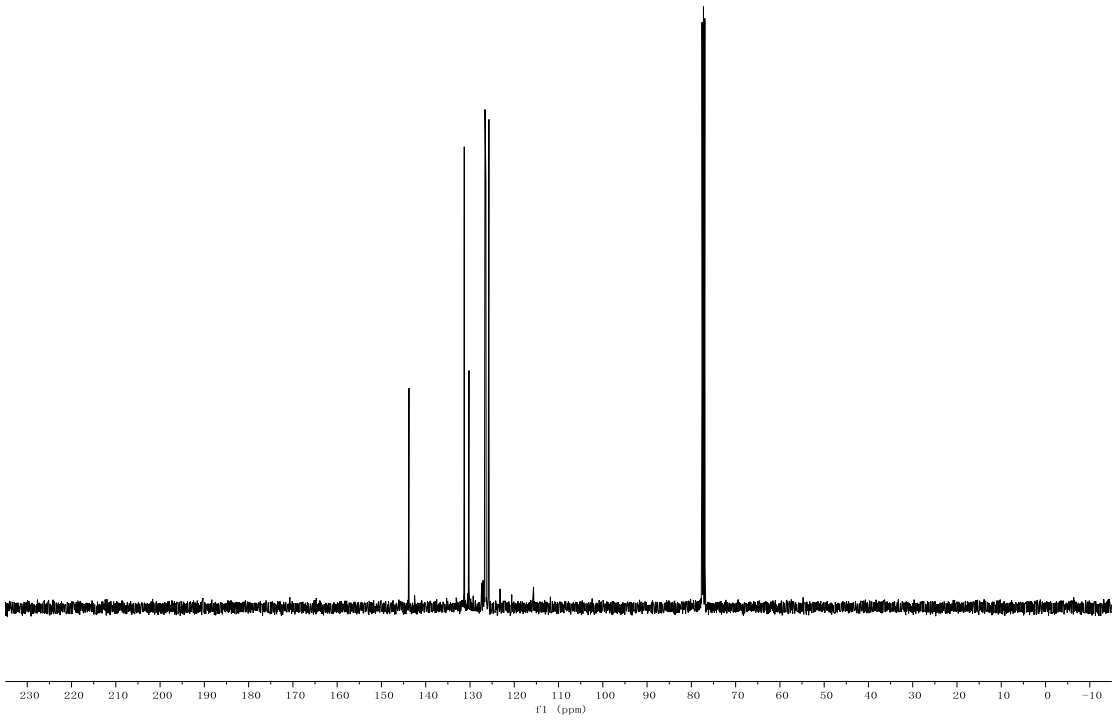
$C_{18}H_{15}NS_3$
Exact Mass: 341.04
Molecular Weight: 341.51
C, 63.30; H, 4.43; N, 4.10; S, 28.17

A three-necked flask equipped with a dry ice condenser was charged with tris(2-isopropylthiophenyl)amine (**54**, 0.77 g, 1.7 mmol) in hexanes (10 mL). Liquid ammonia was added until the total volume of solution was approximately 50 mL. Sodium (0.49 g, 21 mmol) was added, almost immediately yielding a dark blue solution. After six hours, the reaction was quenched with ammonium chloride (1.2 g, 22 mmol), and the ammonia was allowed to evaporate overnight. Aqueous HCl was then added, and the mixture was extracted three times with chloroform. The combined organics were dried over Na_2SO_4, and concentration of this solution gave compound **55** as a white solid (0.47 g, 1.4 mmol, 84%). ^{1}H NMR ($CDCl_3$) δ 3.62 (s, 3 H), 6.81 (m, 3 H), 7.09 (m, 6 H), 7.35 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 125.7, 126.4, 126.6, 130.2, 131.3, 143.8 (6 of 6 expected resonances); MS (EI) *m/z* 307 (M – H_2S, 100), 273 (M – $2H_2S$, 50).

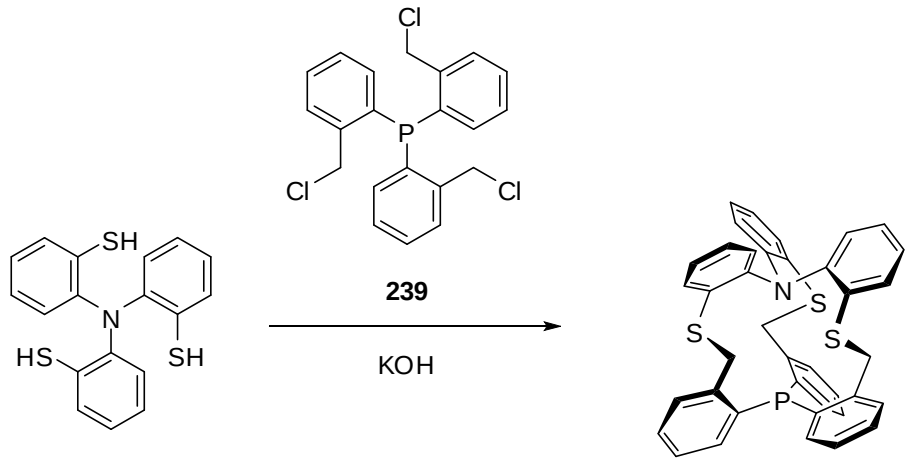
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **55**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **55**



Synthesis of *in,in*-N,P cyclophane 257



55

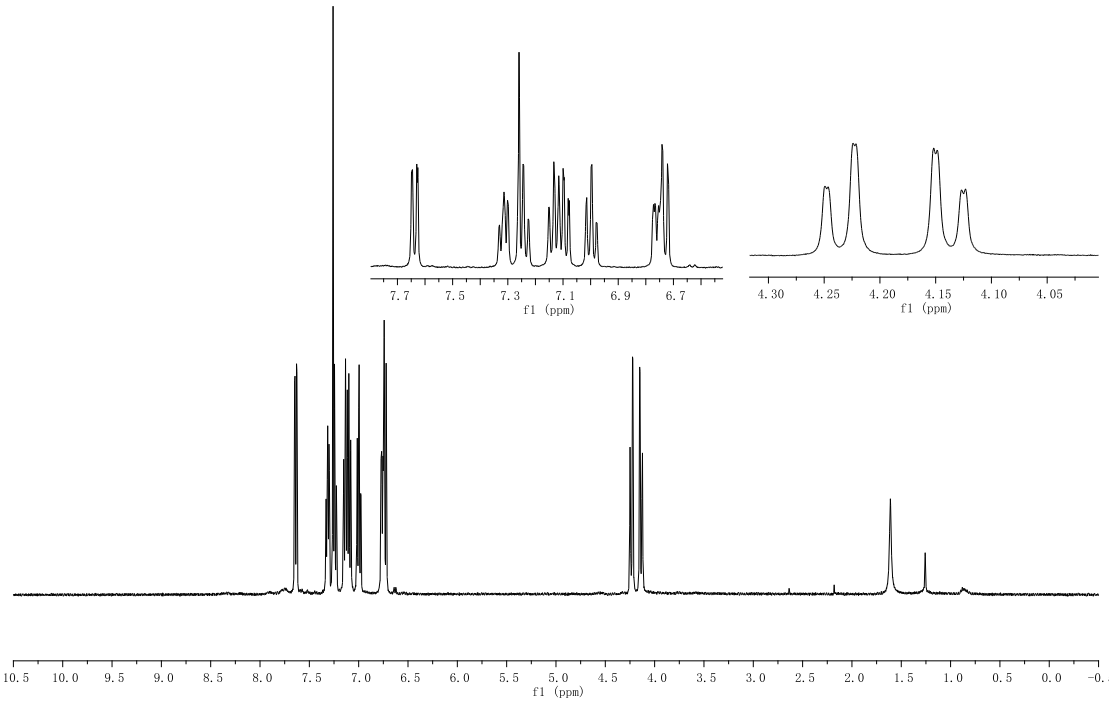
257

$C_{39}H_{30}NPS_3$
Exact Mass: 639.13
Molecular Weight: 639.83
C, 73.21; H, 4.73; N, 2.19; P, 4.84; S, 15.03

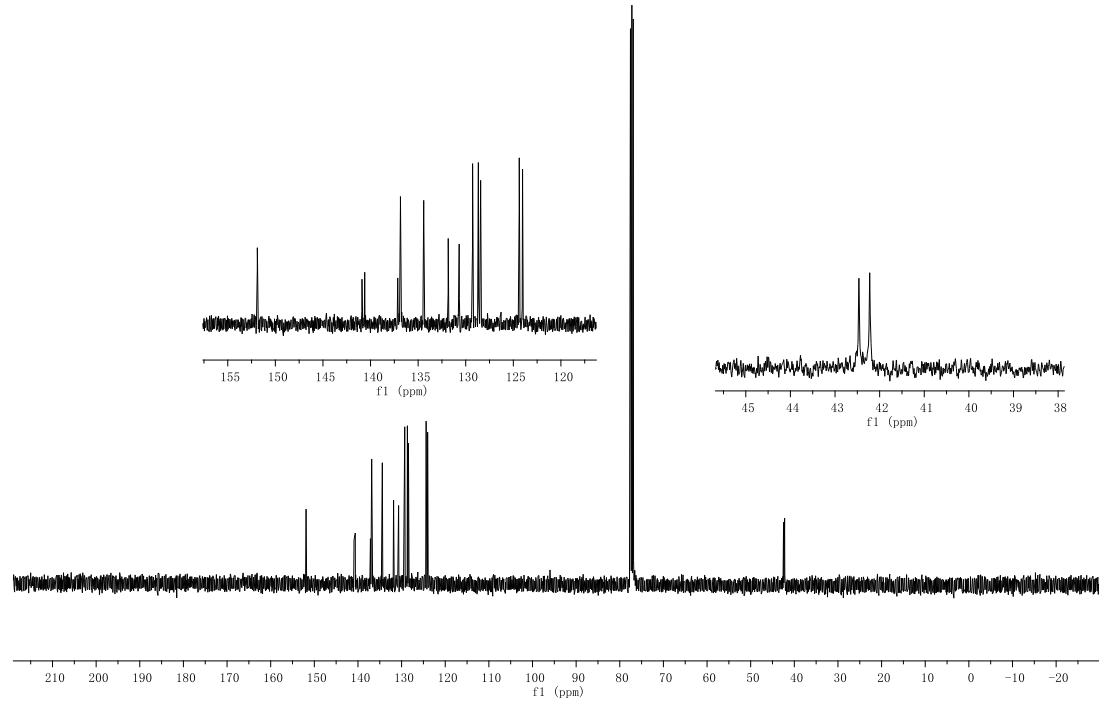
Tris[2-(chloromethyl)phenyl]phosphine (**239**, 561 mg, 1.38 mmol) and tris(2-mercaptophenyl)amine (**55**, 470 mg, 1.38 mmol) were mixed in 2:1 benzene-ethanol (1.2 L), and the solution was heated to reflux. An argon-saturated solution of KOH (372 mg, 6.62 mmol) in ethanol (55 mL) was added slowly over 5.5 hours. After 17 hours, the solution was cooled, and the solvent was evaporated under reduced pressure to leave a white precipitate. The precipitate was extracted twice with chloroform. The combined extracts were concentrated and the resulting light yellow liquid was chromatographed on silica gel (solvent, 2:1 hexane-benzene) and the fractions containing compound **257** were combined and further purified by preparative TLC (silica

gel, 1:1 hexanes-benzene) to give cyclophane **257** as a white solid (136.8 mg, 0.21 mmol, 15.5%). Single crystals, suitable for X-ray analysis, were obtained from $CHCl_3$-MeOH. ^1H NMR ($CDCl_3$) δ 4.14 (dd, *J* = 10 Hz, 2 Hz, 3 H), 4.23 (dd, *J* = 10 Hz, 1 Hz, 3 H), 6.73 (dd, *J* = 8 Hz, 1 Hz, 3 H), 6.76 (dd, *J* = 8 Hz, 2 Hz, 3 H), 7.00 (td, *J* = 8 Hz, *J* = 1 Hz, 3 H), 7.10 (m, 6 H), 7.24 (td, *J* = 8 Hz, *J* = 1 Hz, 3 H), 7.30 (m, 3 H), 7.64 (dd, *J* = 8 Hz, *J* = 2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 42.3 (d, J_{PC} = 25 Hz), 124.0, 124.4, 128.4, 128.7, 129.3, 130.7 (d, J_{PC} = 5 Hz), 131.8, 134.4, 136.9, 137.0 (d, J_{PC} = 28 Hz), 140.8 (d, J_{PC} = 29 Hz), 151.9 (13 of 13 expected resonances); HRMS (ESI) *m/z* 640.1350 (M + H), calcd for $C_{39}H_{31}NPS_3$ 640.1351.

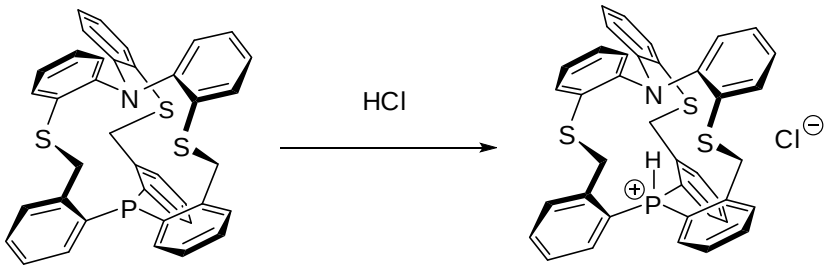
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **257**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **257**



Synthesis of *in,in*-N,P cyclophane hydrochloride 267

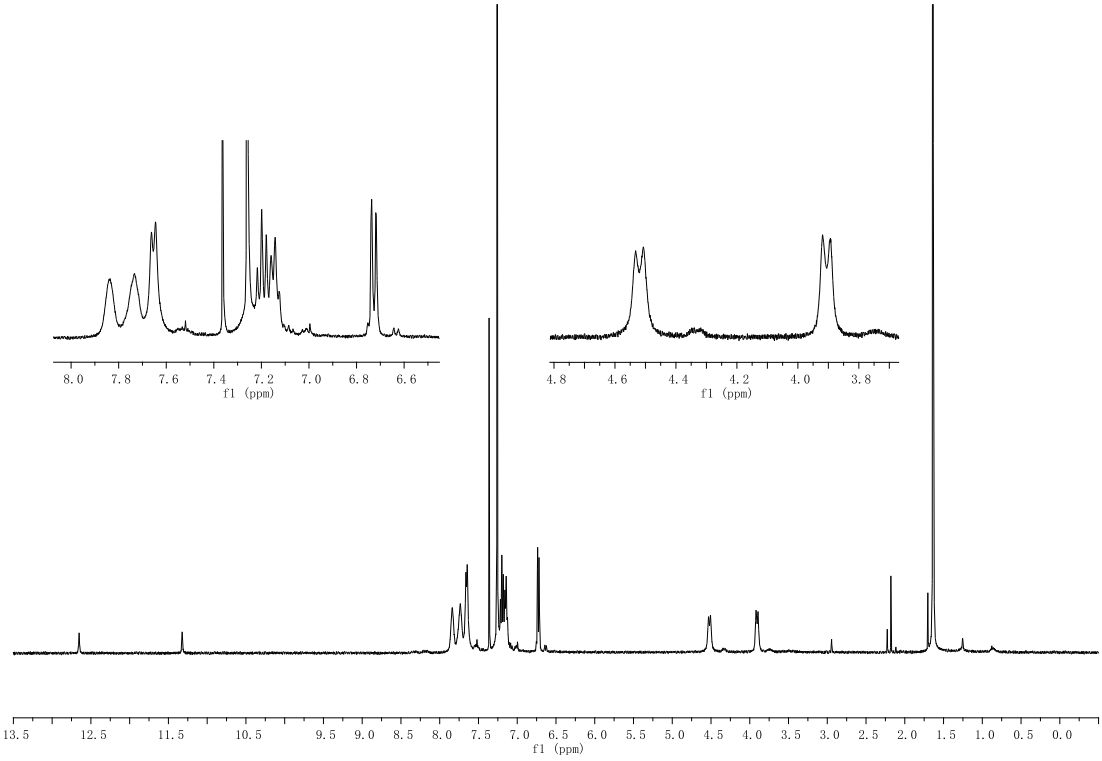


257 **267**

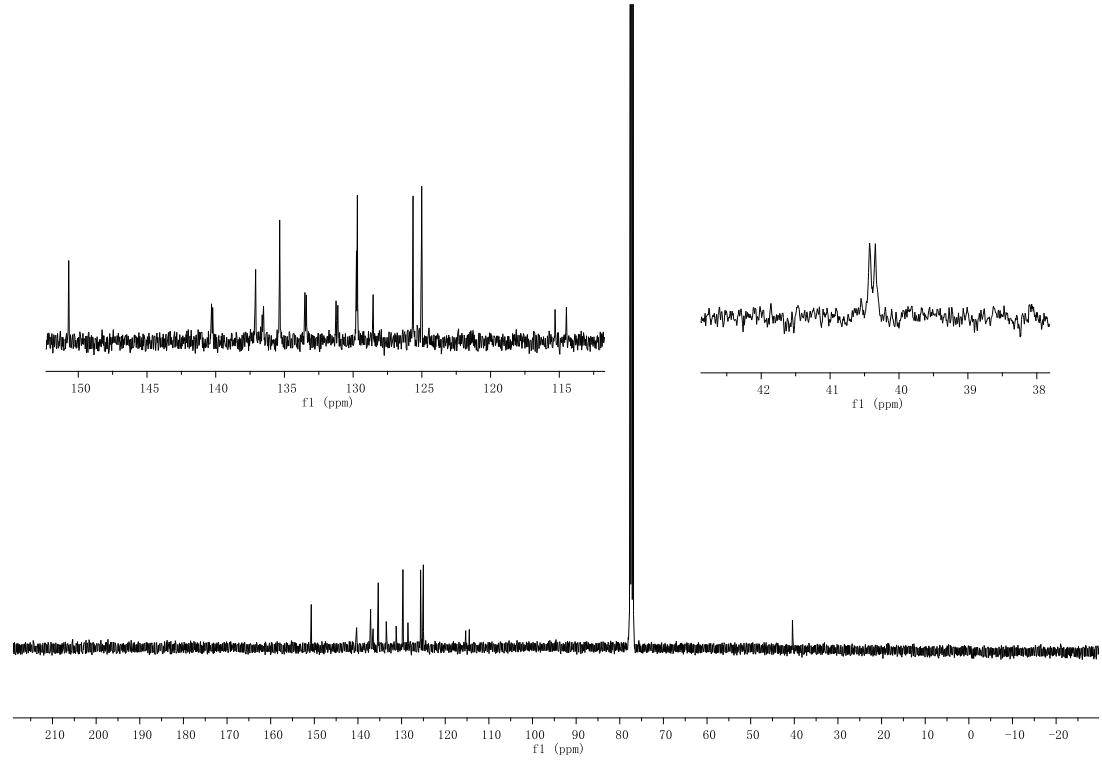
$C_{39}H_{31}ClNPS_3$
Exact Mass: 675.10
Molecular Weight: 676.29
C, 69.26; H, 4.62; Cl, 5.24; N, 2.07; P, 4.58; S, 14.22

A stream of HCl gas was bubbled into an NMR tube containing a $CDCl_3$ solution of cyclophane **257** for 5 s, and then the ^1H NMR spectra were recorded at intervals. Protonation was a slow process ($t_{1/2}$ = 26 min), but it was essentially complete in 6 h. Crystals of the hydrochloride **267** suitable for X-ray analysis were obtained by slow evaporation of a solution in $CHCl_3$-MeOH. ^1H NMR ($CDCl_3$) δ 3.91 (d, J = 10 Hz, 3 H), 4.52 (br d, J = 10 Hz, 3 H), 6.73 (br d, J = 7 Hz, 3 H), 7.18 (m, 9 H), 7.65 (br d, J = 7 Hz, 6 H), 7.73 (br s, 3 H), 7.84 (br s, 3 H), 11.99 (d, J = 532 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 40.4 (d, J_{PC} = 8 Hz), 114.9 (d, J_{PC} = 84 Hz), 125.0, 125.6, 129.7, 129.8, 131.2 (d, J = 13 Hz), 133.5 (d, J = 10 Hz), 135.4, 136.6 (d, J = 10 Hz), 137.1, 140.3 (d, J = 9 Hz), 150.7 (13 of 13 expected resonances); HRMS (ESI) *m/z* 640.1352 (M - Cl), calcd for $C_{39}H_{31}NPS_3$ 640.1351.

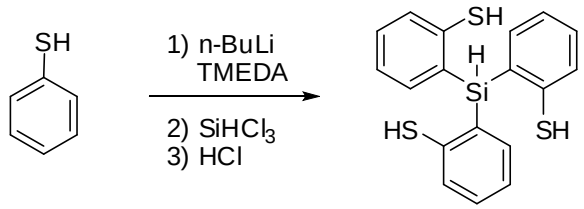
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **267**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **267**



Synthesis of tris(2-mercaptophenyl)silane (36)



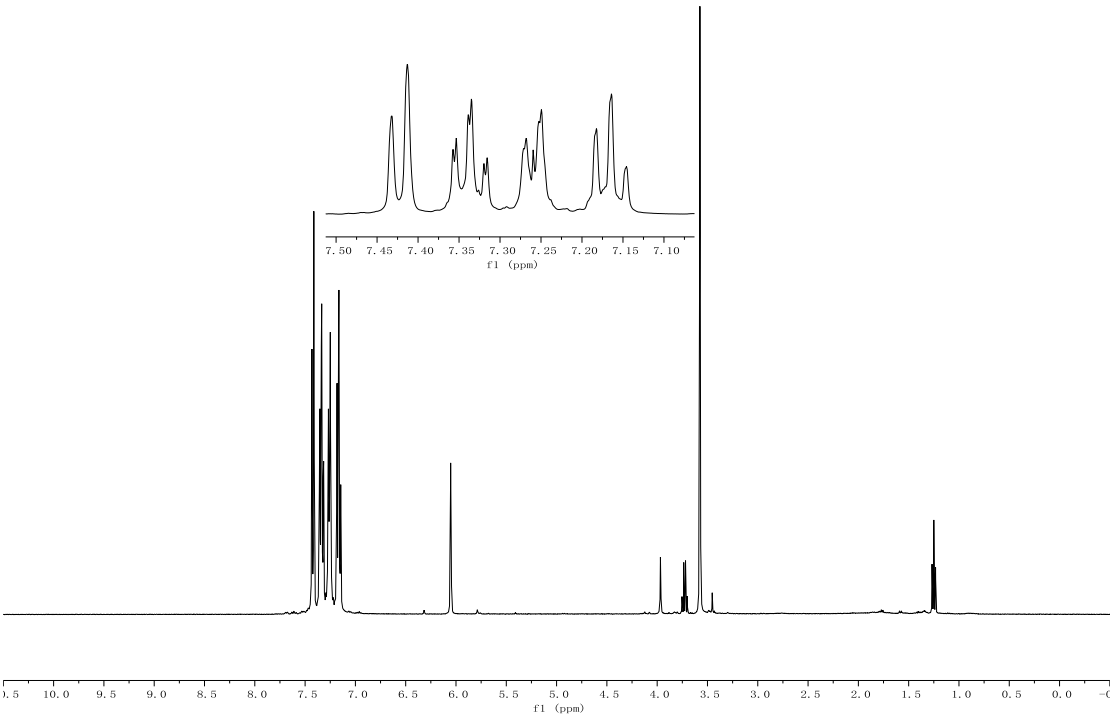
36

$C_{18}H_{16}S_3Si$
Exact Mass: 356.02
Molecular Weight: 356.60
C, 60.63; H, 4.52; S, 26.98; Si, 7.88

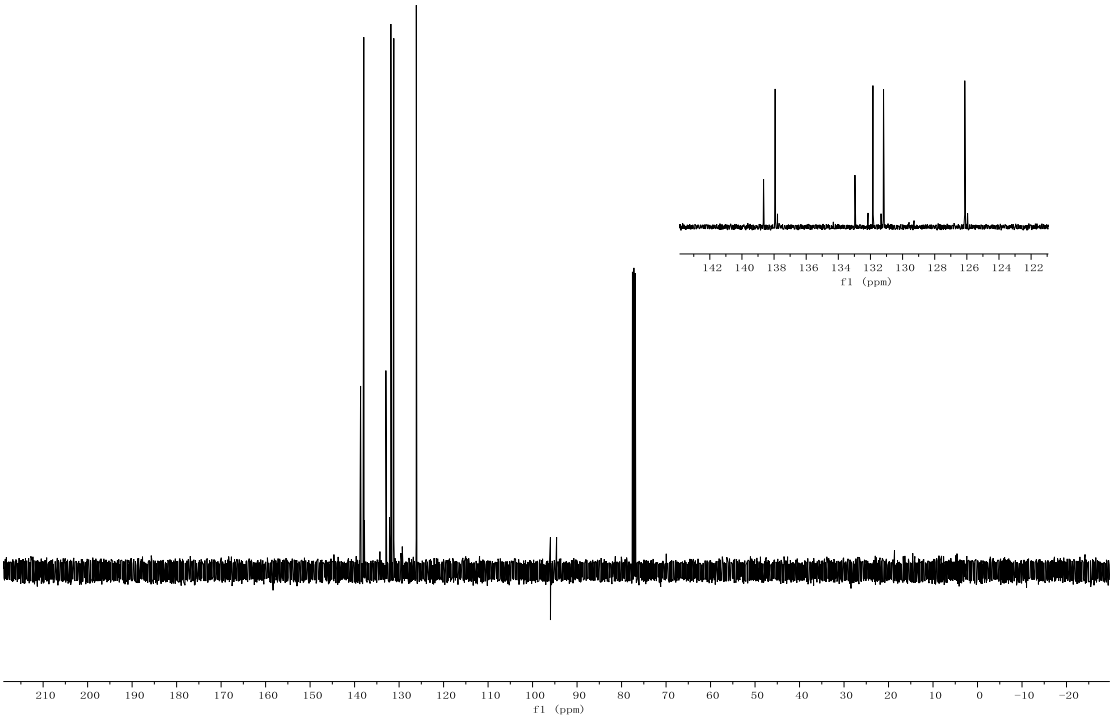
Through an addition funnel, a flask was charged with cyclohexane (55 mL), TMEDA (7.9 mL) and *n*-BuLi (2.5 M in hexane, 21 mL, 52.5 mmol). Thiophenol (2.5 mL, 24.4 mmol) in cyclohexane (20 mL) was added to the flask at 0 ℃. The reaction was warmed to room temperature over the next two days. Cyclohexane was removed from the reaction flask and precipitate was washed with cyclohexane. When the precipitate settled, cyclohexane was removed again. THF (24 mL) was added to the precipitate, in which $SiHCl_3$ (0.6 mL) diluted with THF (5 mL) was added dropwise. The mixture was warmed to room temperature for 20 hours and then acidified with 10% sulfuric acid (100 mL). The mixture was concentrated in vacuo to remove THF, and the water solution was extracted with CH_2Cl_2 three times. The organic layer was dried with Na_2SO_4 and concentrated in vacuo to yield a yellow oil. Recrystallization from ethanol gave **36** as a white solid (880 mg, 2.5 mmol, 30%). ^{1}H NMR ($CDCl_3$) δ 3.58 (s, 3 H), 6.05 (s, 1 H), 7.17 (td, *J* = 8 Hz, 1 Hz, 3 H), 7.26 (dd, *J* = 8 Hz, 2 Hz, 3 H), 7.34 (td, *J* = 8 Hz, 2 Hz, 3

H), 7.42 (d, J = 8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 126.1, 131.2, 131.9, 133.0, 137.9, 138.7 (6 of 6 expected resonances).

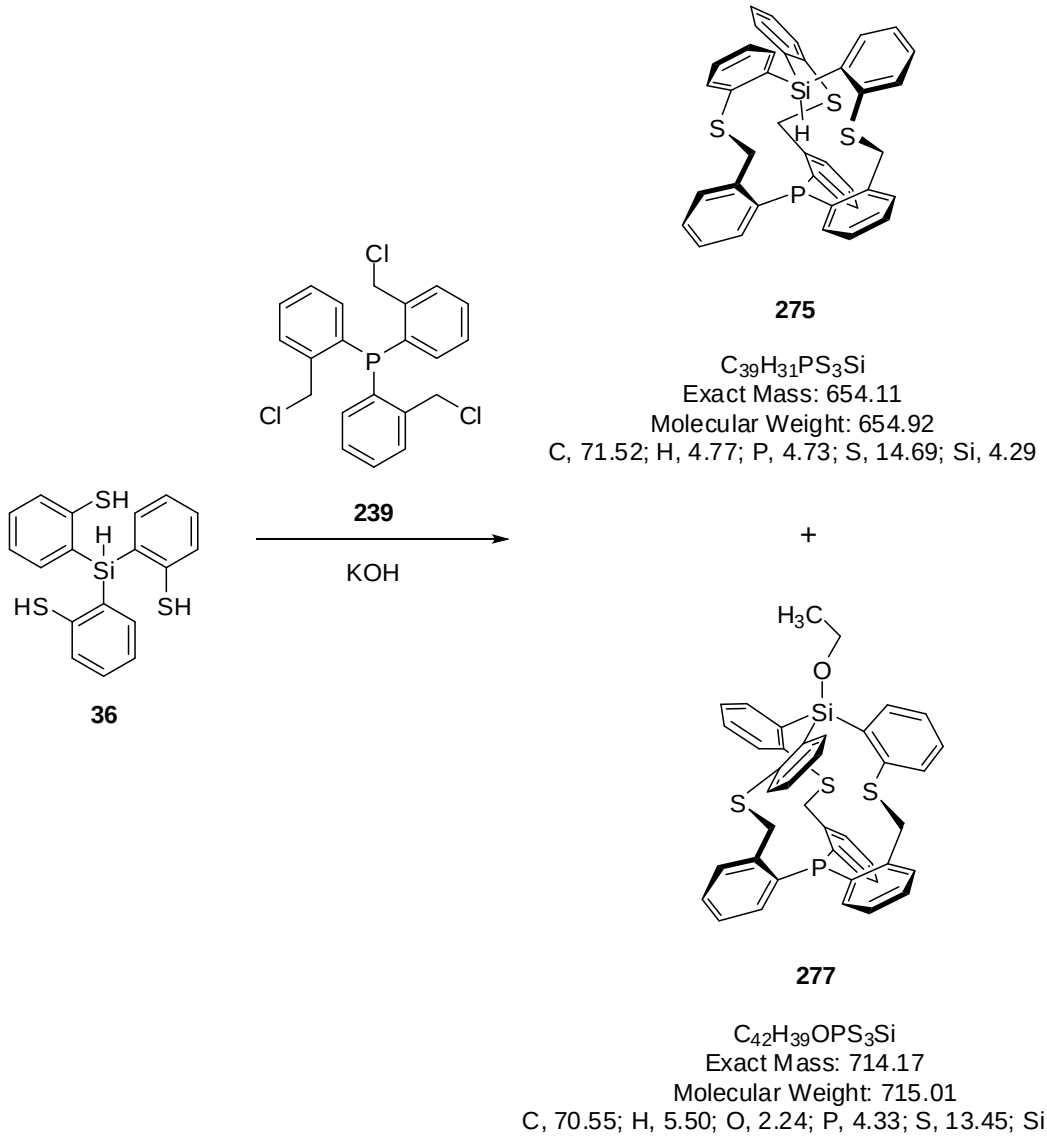
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **36**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **36**



Synthesis of *in,in*-HSi,P cyclophane 257 and *out,in*-EtOSi,P cyclophane 277



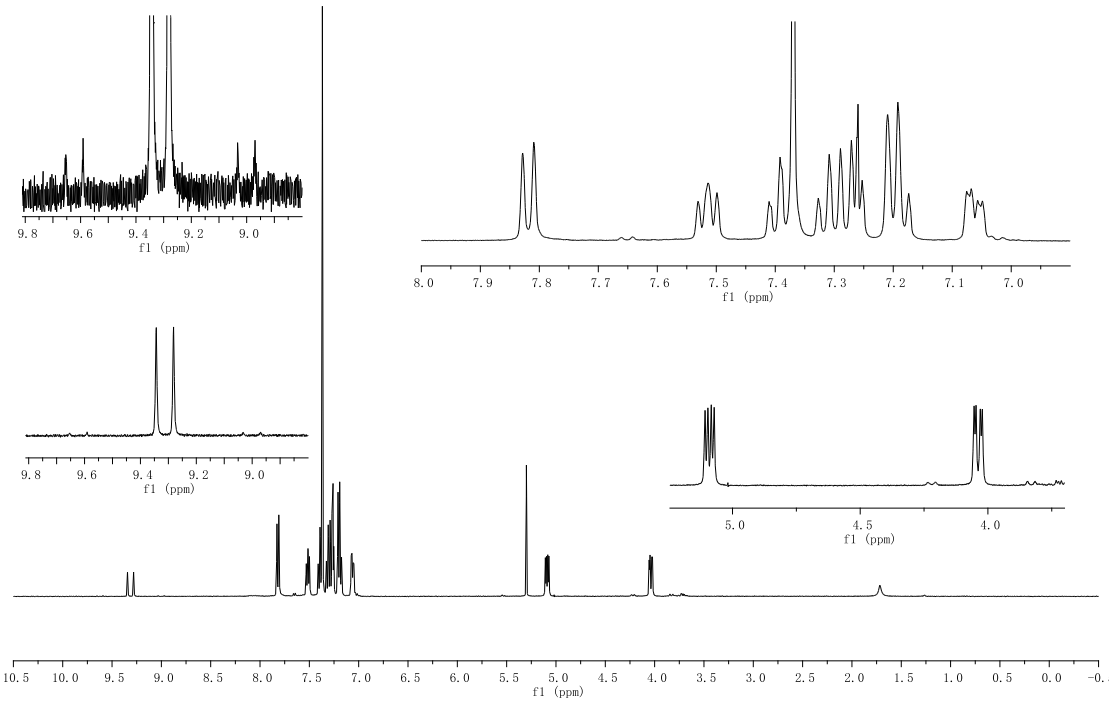
Tris[2-(chloromethyl)phenyl]phosphine (**239**, 563 mg, 1.38 mmol) and tris(2-mercaptophenyl)silane (**36**, 493 mg, 1.38 mmol) were mixed in 2:1 benzene-ethanol (1.2 L), and the solution was heated to reflux. An argon-saturated solution of KOH (376 mg, 6.70 mmol) in ethanol (55 mL) was added slowly over 6 hours.

After 18 hours, the solution was cooled, and the solvent was evaporated under reduced pressure to leave a white precipitate. The precipitate was extracted twice with chloroform. The combined extracts were concentrated and the resulting light yellow liquid was chromatographed on silica gel (solvent, 1:1 hexane-benzene) and the fractions containing compound **275** were combined and further purified by preparative TLC (silica gel, 1:1 hexanes-benzene) to give cyclophane **275** as a white solid. This material exhibited a single component by TLC, but the ^{1}H NMR spectrum clearly indicated the presence of significant impurities. Further chromatographic purification was unsuccessful, but careful crystallization from $CHCl_3$-CH_2Cl_2-MeOH gave cyclophane **275** (6 mg, 9.2 μmol, 0.66%) as crystals suitable for X-ray analysis. ^{1}H NMR ($CDCl_3$) δ 4.04 (dd, *J* = 10 Hz, 3 Hz, 3 H), 5.09 (dd, *J* = 10 Hz, 5 Hz, 3 H), 7.06 (dd, *J* = 8 Hz, 3 Hz, 3 H), 7.19 (m, 6 H), 7.29 (m, 6 H), 7.39 (m, 3 H), 7.51 (m, 3 H), 7.82 (d, *J* = 8 Hz, 3 H), 9.31 (d, *J* = 25 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 43.7 (d, J_{PC} = 29 Hz), 128.0, 128.6, 129.6, 130.6, 131.7 (d, J_{PC} = 6 Hz), 135.36, 135.40 (d, J_{PC} = 17 Hz), 137.4, 137.6, 141.7 (d, J_{PC} = 34 Hz), 141.8, 143.6 (d, J_{PC} = 2 Hz) (13 of 13 expected resonances); ^{31}P NMR ($CDCl_3$) δ -48.9; ^{29}Si NMR ($CDCl_3$) δ -35.8 (d, J_{PSi} = 76 Hz); HRMS (ESI) *m/z* 655.1173 (M + H), calcd for $C_{39}H_{32}PS_3Si$ 655.1168.

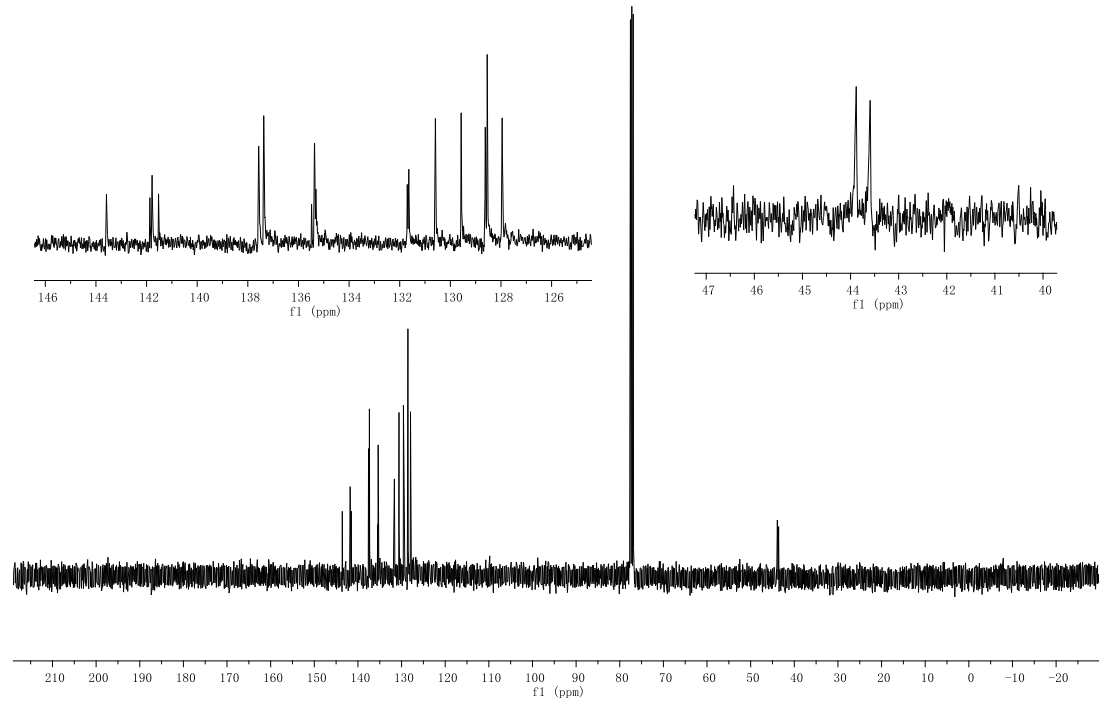
A second component proved to be the out,in compound **277**. Crystallization from $CHCl_3$-CH_2Cl_2-MeOH yielded cyclophane **277** (15 mg, 21 μmol, 1.6%) as crystals suitable for X-ray analysis. ^{1}H NMR ($CDCl_3$) δ 1.21 (t, *J* = 7 Hz, 3 H), 3.65 (d, *J* = 11 Hz, 3 H), 3.84 (dq, *J* = 10 Hz, 7 Hz, 1 H), 3.93 (dq, *J* = 10 Hz, 7 Hz, 1 H), 4.20 (d, *J* = 11 Hz,

3 H), 6.68 (dd, J = 7 Hz, 2.5 Hz, 3 H), 7.11 (td, J = 7 Hz, 2 Hz, 3 H), 7.16 (td, J = 7 Hz, 2 Hz, 3 H), 7.25 (m, 12 H), 7.65 (dd, J = 7.5 Hz, 1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 18.8, 41.6 (d, J_{PC} = 18 Hz), 60.3, 125.2, 128.6, 129.1, 130.4, 130.6, 130.9 (d, J_{PC} = 6 Hz), 133.2, 135.9, 136.9 (d, J_{PC} = 26 Hz), 139.7, 140.2 (d, J_{PC} = 27 Hz), 145.5 (15 of 15 expected resonances); HRMS (ESI) *m/z* 699.1430 (M + H), calcd for $C_{41}H_{36}OPS_3Si$ 699.1435.

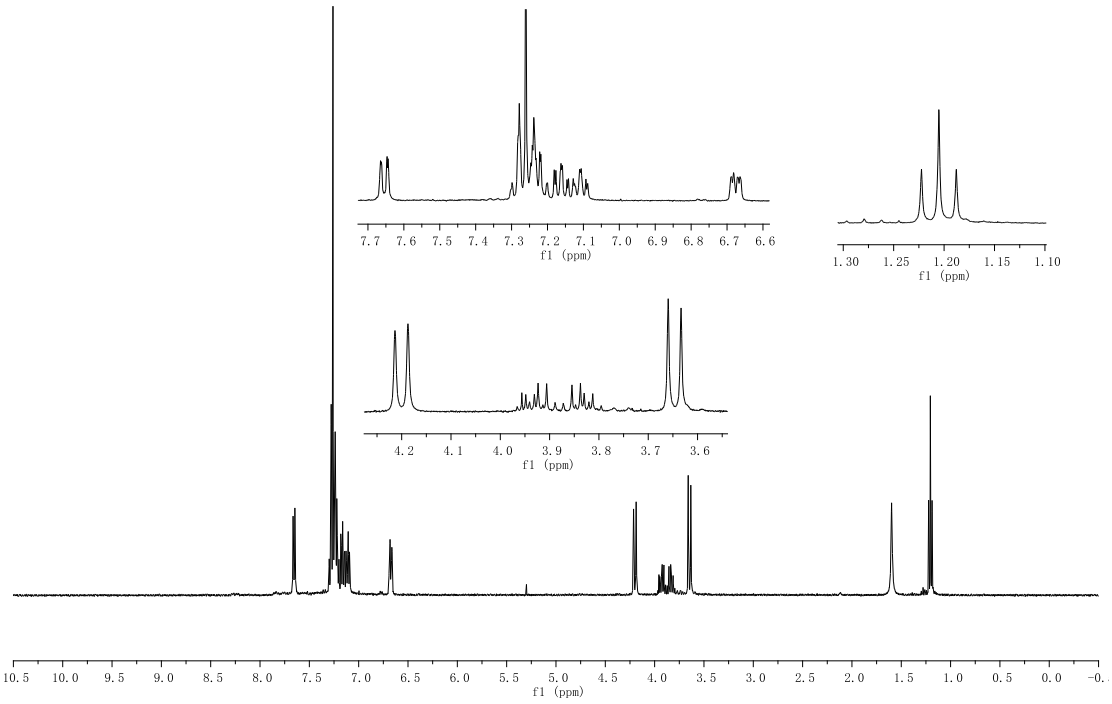
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **275**



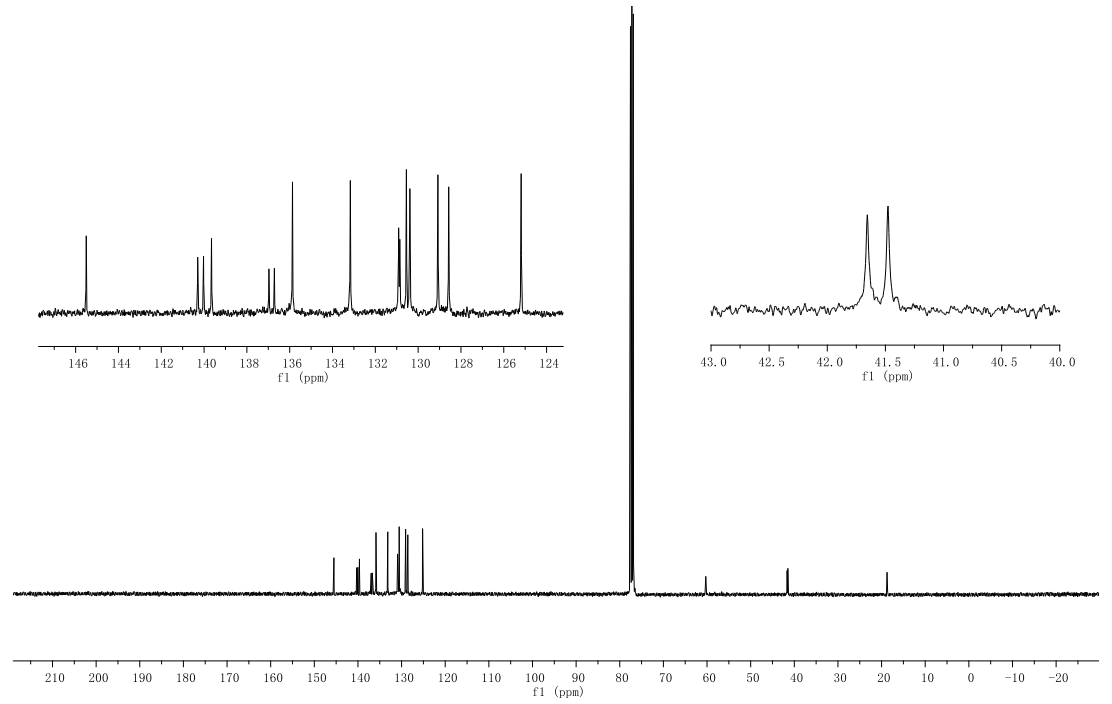
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **275**



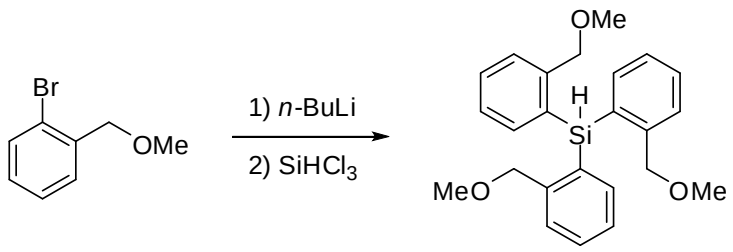
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **277**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **277**



Synthesis of tris[2-(methoxymethyl)phenyl]silane (282)

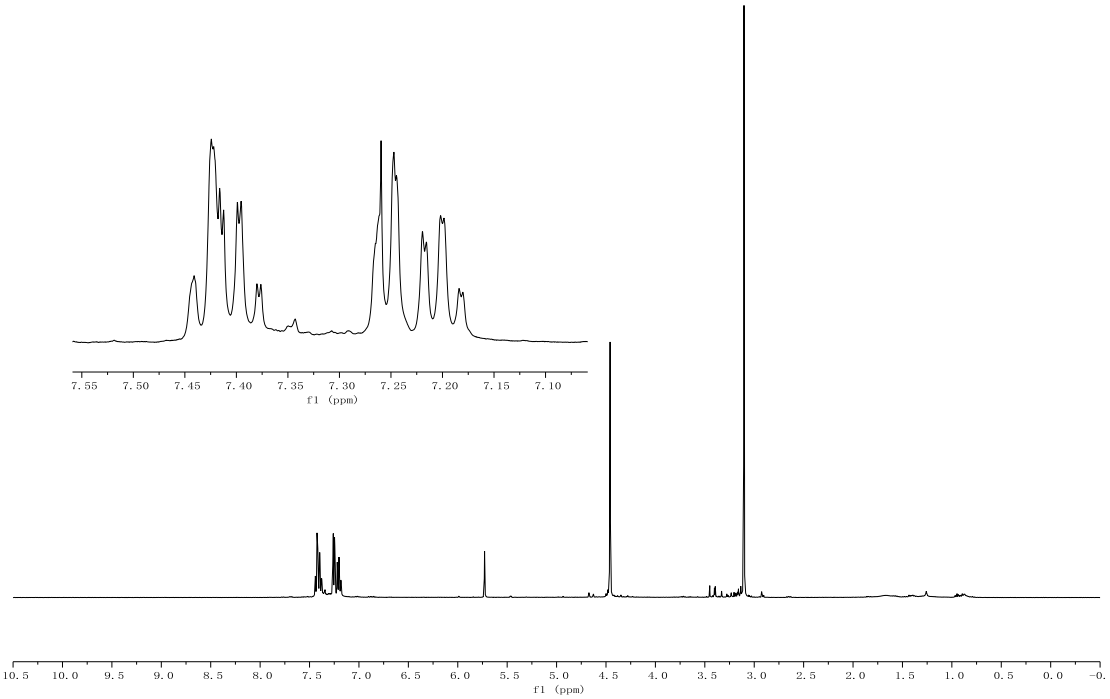


237 **282**

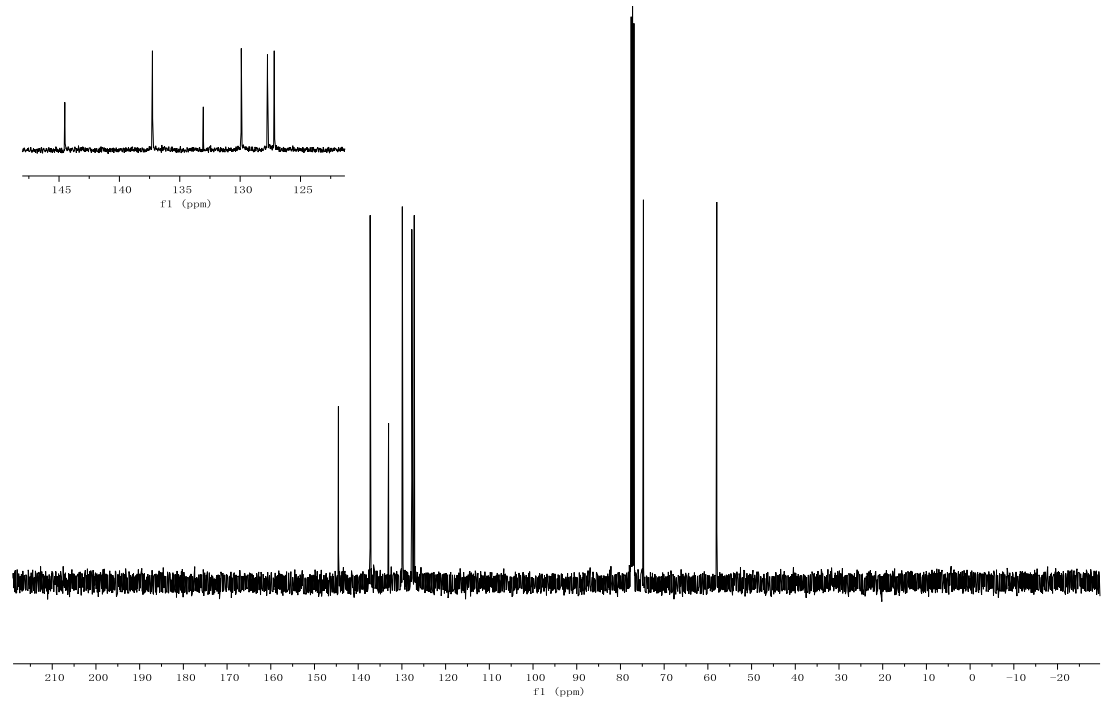
$C_{24}H_{28}O_3Si$
Exact Mass: 392.18
Molecular Weight: 392.56
C, 73.43; H, 7.19; O, 12.23; Si, 7.15

n-BuLi (2.5 *M* in hexane, 11 mL, 27.5 mmol) was added dropwise to a stirred solution of *o*-bromobenzyl methyl ether (5.33 g, 26.5 mmol) in THF (30 mL) at -78 ℃ under argon. After the solution was stirred for 2 hours, trichlorosilane (0.89 mL, 8.8 mmol) diluted with THF (5 mL) was added dropwise. The reaction was stirred at room temperature for 24 hours and refluxed for 1 hour. The reaction mixure was cooled and then saturated with NH_4Cl. The organic layer was separated and the water layer was again extracted with ether. The combined ether extracts were dried over Na_2SO_4 and concentrated to leave 3.40 g white solid. Recrystallization from ethanol gave **282** as a white solid (2.29 g, 5.8 mmol, 66%). ^{1}H NMR ($CDCl_3$) δ 3.10 (s, 9 H), 4.46 (s, 6 H), 5.73 (s, 1 H), 7.20 (td, *J* = 7 Hz, 1 Hz, 3 H), 7.25 (dd, *J* = 6 Hz, 1 Hz, 3 H), 7.40 (td, *J* = 8 Hz, 2 Hz, 3 H), 7.43 (d, *J* = 8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 58.0, 74.7, 127.2, 127.7, 129.9, 133.1, 137.3, 144.5 (8 of 8 expected resonances).

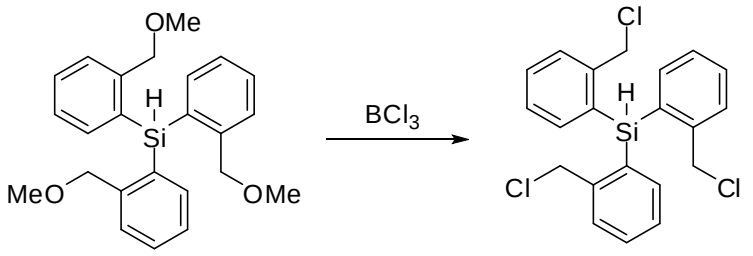
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **282**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **282**



Synthesis of tris[2-(chloromethyl)phenyl]silane (283)

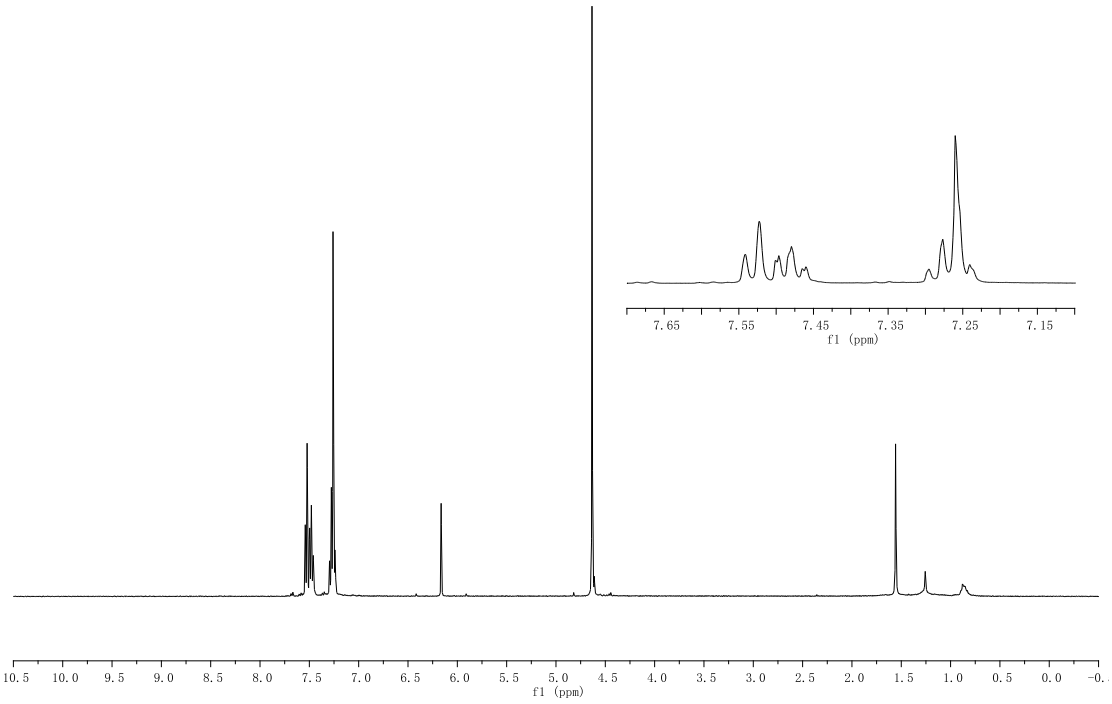


282 **283**

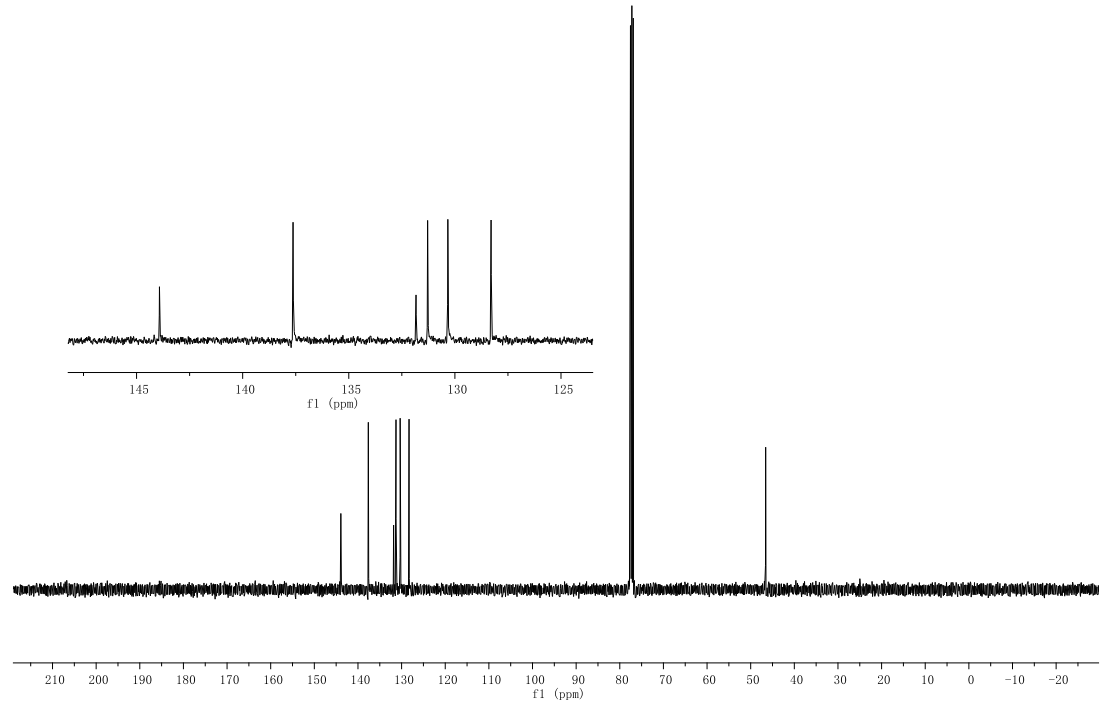
$C_{21}H_{19}Cl_3Si$
Exact Mass: 404.03
Molecular Weight: 405.82
C, 62.15; H, 4.72; Cl, 26.21; Si, 6.92

Boron trichloride (1 *M* in heptane, 100 mL, 100 mmol) was added to tris[2-(methoxymethyl)phenyl]silane (**282**, 1.76 g, 4.5 mmol) in round bottom flask under argon. The reaction mixture was stirred at room temperature for 2 hour and then heated at reflux for 3 hours. When the mixture had cooled to room temperature, chloroform and water were added. The organic layer was separated and the water layer was again extracted with chloroform. The combined chloroform extracts were dried over Na_2SO_4 and concentrated to dryness. The white solid was chromatographed on silica gel (solvent, chloroform) to give **283** as a white solid (306 mg, 0.75 mmol, 16.7%). ^{1}H NMR ($CDCl_3$) δ 4.64 (s, 6 H), 6.16 (s, 1 H), 7.27 (m, 6 H), 7.48 (td, *J* = 7 Hz, 2 Hz, 3 H), 7.53 (d, *J* = 7.5 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 46.6, 128.3, 130.3, 131.3, 131.8, 137.6, 143.9 (7 of 7 expected resonances).

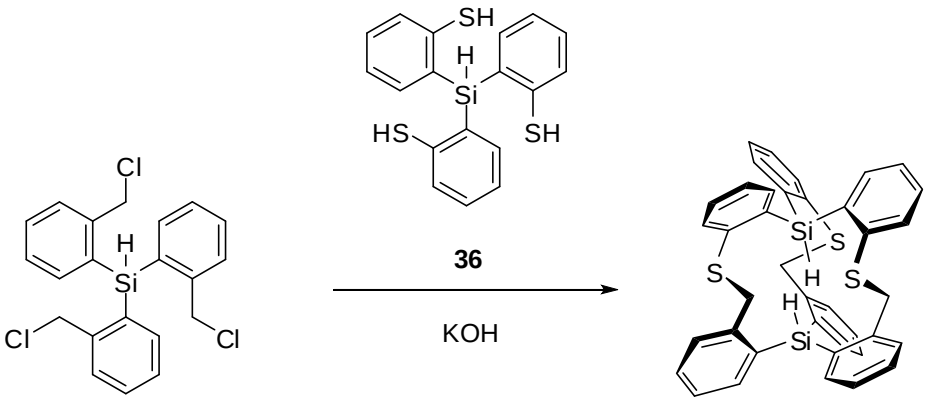
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **283**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **283**



Synthesis of *in,in*-bis(hydrosilane) 278



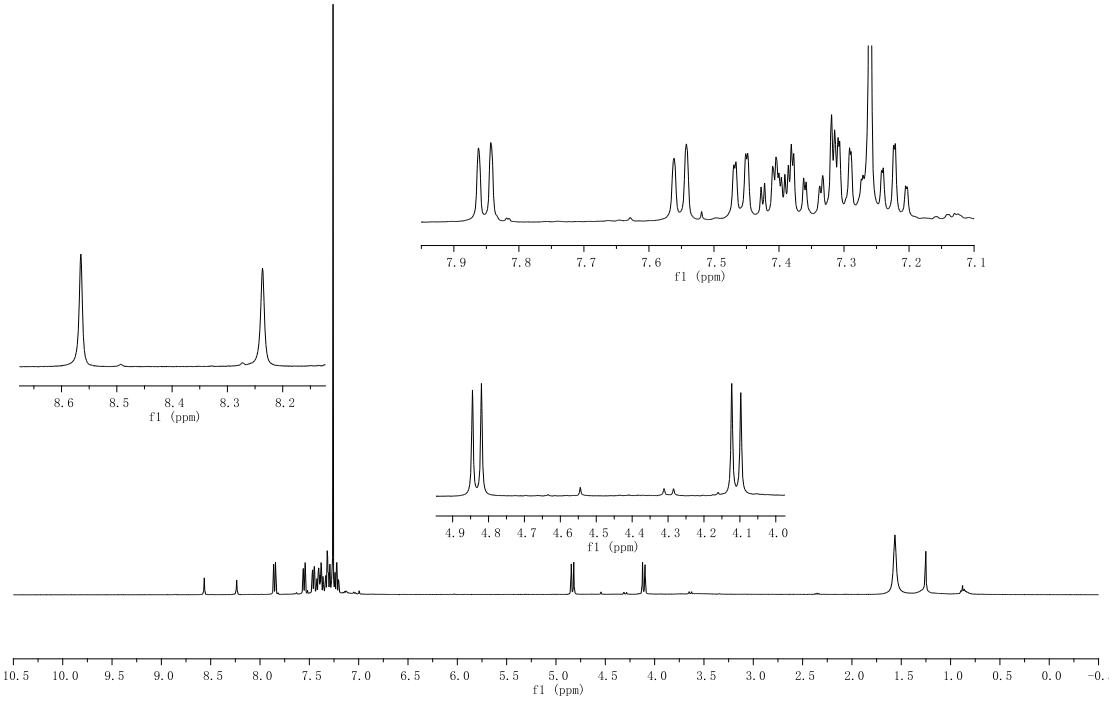
283 **278**

$C_{39}H_{32}S_3Si_2$
Exact Mass: 652.12
Molecular Weight: 653.04
C, 71.73; H, 4.94; S, 14.73; Si, 8.60

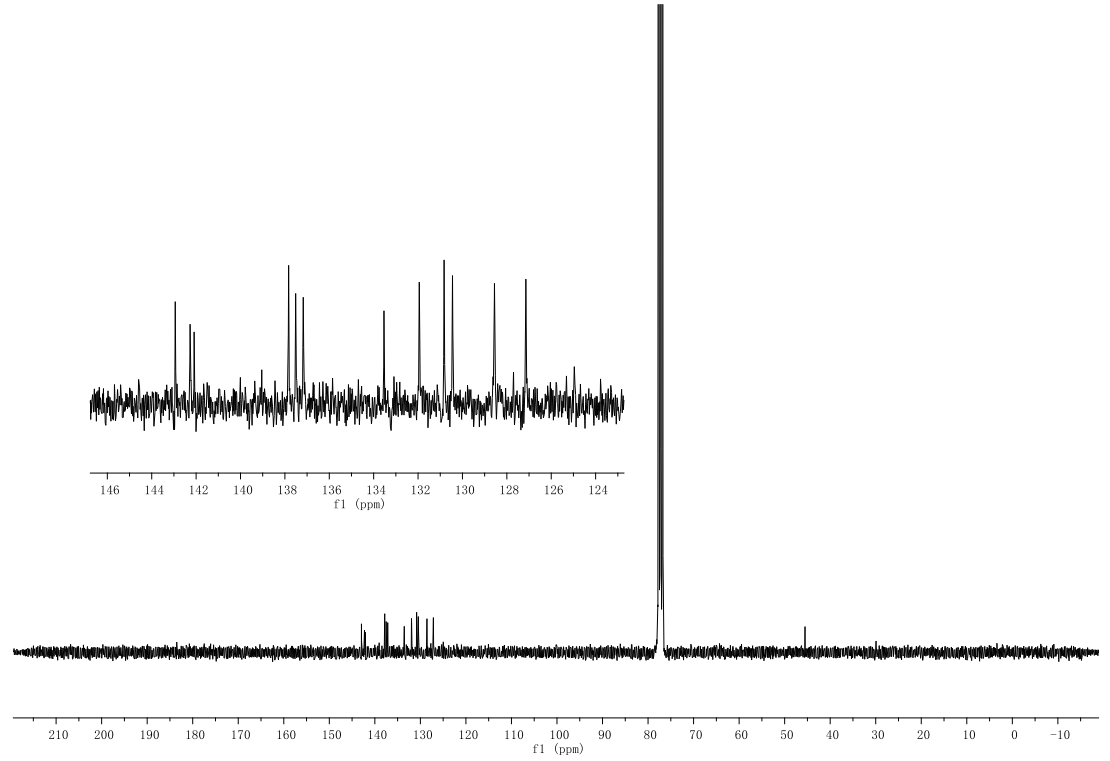
Tris[2-(chloromethyl)phenyl]silane (**283**, 300 mg, 0.74 mmol) and tris(2-mercaptophenyl)silane (**36**, 264 mg, 0.74 mmol) were mixed in 2:1 benzene-ethanol (700 mL), and the solution was heated to reflux. An argon-saturated solution of KOH (200 mg, 3.56 mmol) in ethanol (60 mL) was added slowly over 10 hours. After 12 hours, the solution was cooled, and the solvent was evaporated under reduced pressure to leave a white precipitate. The precipitate was extracted twice with chloroform. The combined extracts were concentrated and the resulting light yellow liquid was chromatographed on silica gel (solvent, 1:1 hexane-benzene) and the fractions containing compound **278** were combined and further purified by preparative TLC (silica gel, 1:1 hexanes-benzene) to give cyclophane **278** as a light yellow solid. This material

exhibited a single component by TLC, but its ^{1}H NMR spectrum indicated that some impurities were present. Crystallization from benzene-$CHCl_3$-MeOH yielded cyclophane **278** as crystals suitable for X-ray analysis, and after the structure determination, the crystals were combined and again subjected to preparative TLC (silica gel, 2:1 hexanes-benzene) to give cyclophane **278** as a white solid (2.0 mg, 3.1 μmol, 0.41%). ^{1}H NMR ($CDCl_3$) δ 4.11 (d, *J* = 10 Hz, 3 H), 4.83 (d, *J* = 10 Hz, 3 H), 7.22 (td, *J* = 7.5 Hz, 1 Hz, 3 H), 7.28-7.43 (m, 12 H), 7.46 (dd, *J* = 7.5 Hz, 1 Hz, 3 H), 7.55 (d, *J* = 7.5 Hz, 3 H), 7.85 (d, *J* = 7.5 Hz, 3 H), 8.24 (s, 1 H), 8.57 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 45.5, 127.1, 128.6, 130.5, 130.8, 132.0, 133.5, 137.2, 137.5, 137.8, 142.1, 142.3, 143.0 (13 of 13 expected resonances); ^{29}Si NMR ($CDCl_3$) δ -32.3, -40.4; MS (MALDI-TOF) *m/z* 653 (M + H, 20), 652 (M^+, 40), 651 (M - H, 100); HRMS (ESI-TOF) *m/z* 653.12767 (M + H), calcd for $C_{39}H_{33}S_3Si_2$ 653.12774.

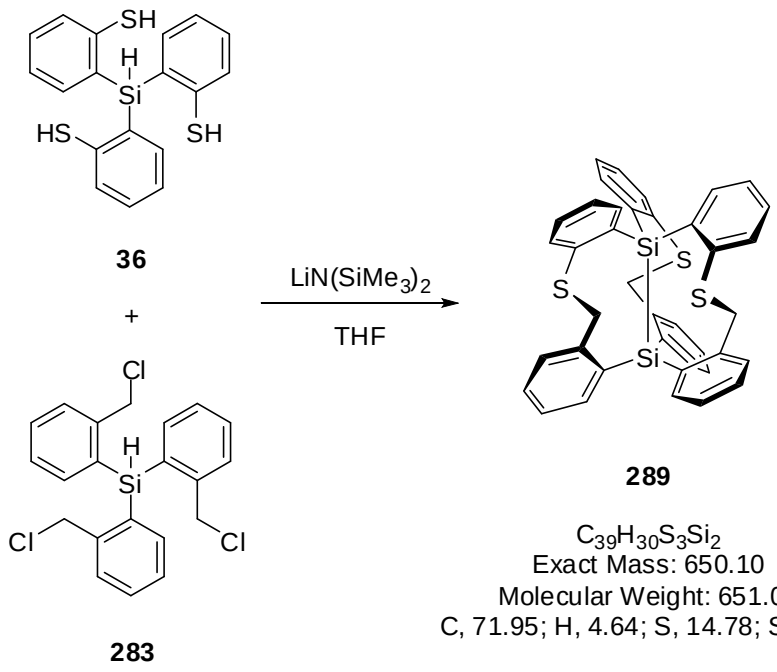
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **278**



^{13}C NMR Spectrum (75 MHz, $CDCl_3$) of Compound **278**



Synthesis of compound 289

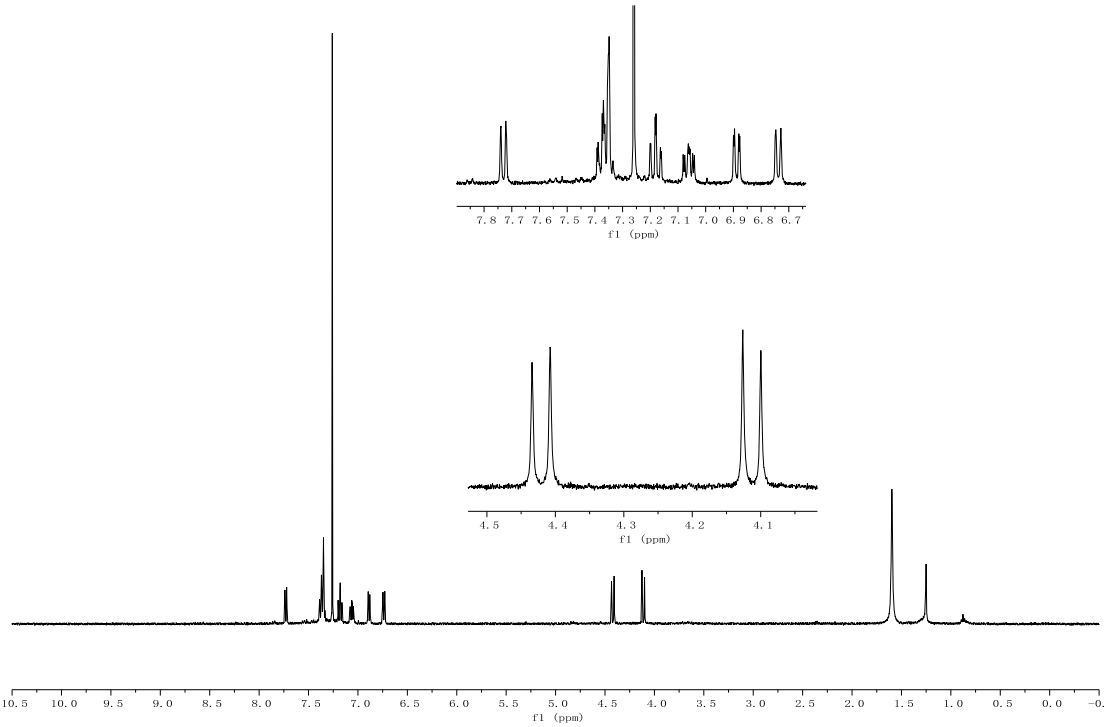


$C_{39}H_{30}S_3Si_2$
Exact Mass: 650.10
Molecular Weight: 651.02
C, 71.95; H, 4.64; S, 14.78; Si, 8.63

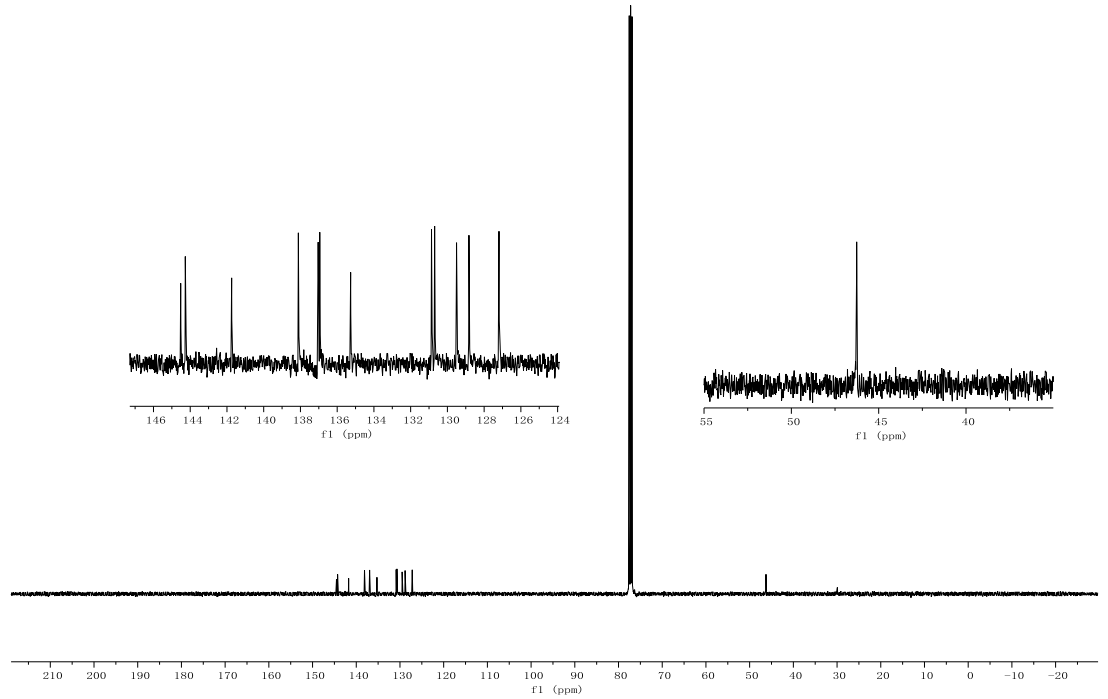
Tris[2-(chloromethyl)phenyl]silane (**283**, 101 mg, 0.25 mmol) and tris(2-mercaptophenyl)silane (**36**, 89 mg, 0.25 mmol) were mixed in THF (250 mL), and the solution was heated to reflux. An argon-saturated solution of $Li[N(SiMe_3)_2]$ (2.5 *M* in THF, 1.0 mL, 1.0 mmol) in THF (30 mL) was added slowly over 6 hours. After 16 hours, the solution was cooled, and the solvent was evaporated under reduced pressure to leave a white precipitate. The precipitate was extracted twice with chloroform. The combined extracts were concentrated and the resulting light yellow liquid was chromatographed on silica gel (solvent, 1:1 hexane-benzene) and the fractions containing compound **289** were combined and further purified by preparative TLC (silica gel, 1:1 hexanes-benzene) to

give cyclophane **289** as a white solid (10 mg, 15 μmol, 6%). ^{1}H NMR ($CDCl_3$) δ 4.13 (d, *J* = 10 Hz, 3 H), 4.42 (d, *J* = 10 Hz, 3 H), 6.74 (d, *J* = 7 Hz, 3 H), 6.89 (dd, *J* = 8 Hz, 1 Hz, 3 H), 7.06 (m, 3 H), 7.18 (td, *J* = 8 Hz, 1 Hz, 3 H), 7.37 (m, 9 H), 7.73 (dd, *J* = 8 Hz, 1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 46.3, 127.2, 128.8, 129.5, 130.7, 130.9, 135.3, 136.9, 137.0, 138.1, 141.7, 144.3, 144.5 (13 of 13 expected resonances).

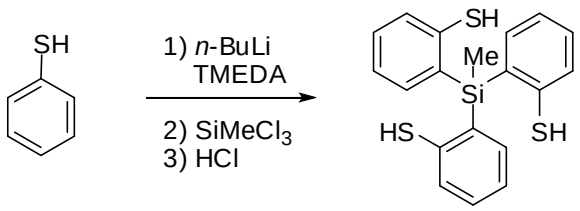
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **289**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **289**



Synthesis of tris(2-mercaptophenyl)methylsilane (290)



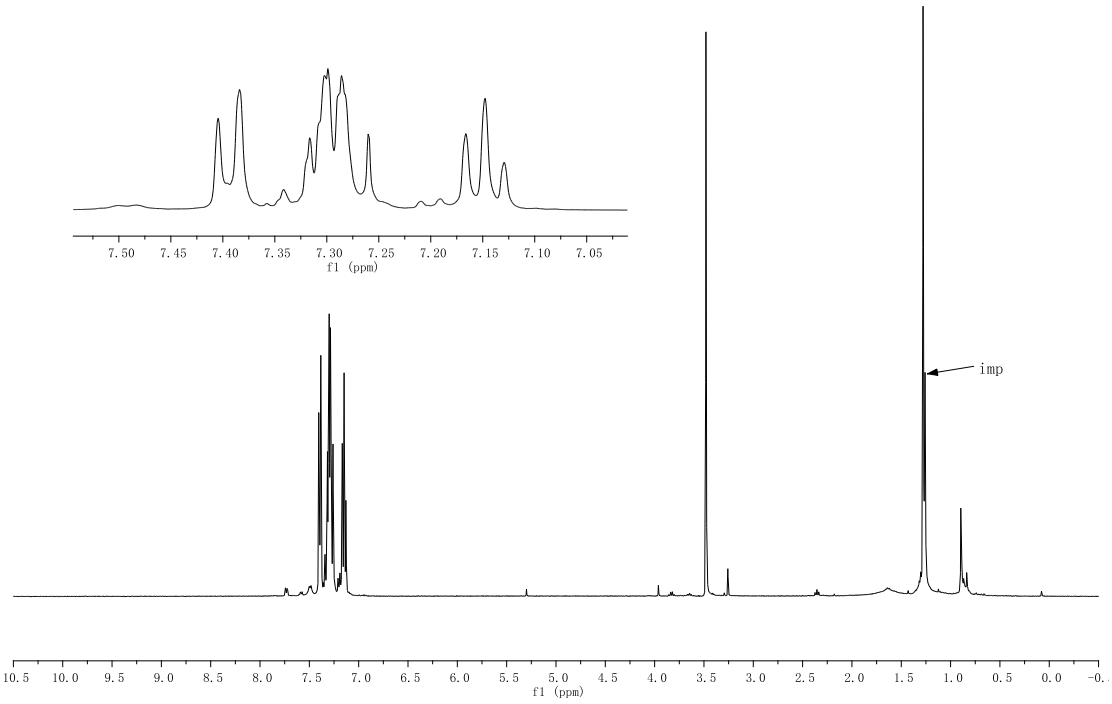
290

$C_{19}H_{18}S_3Si$
Exact Mass: 370.03
Molecular Weight: 370.63
C, 61.57; H, 4.90; S, 25.95; Si, 7.58

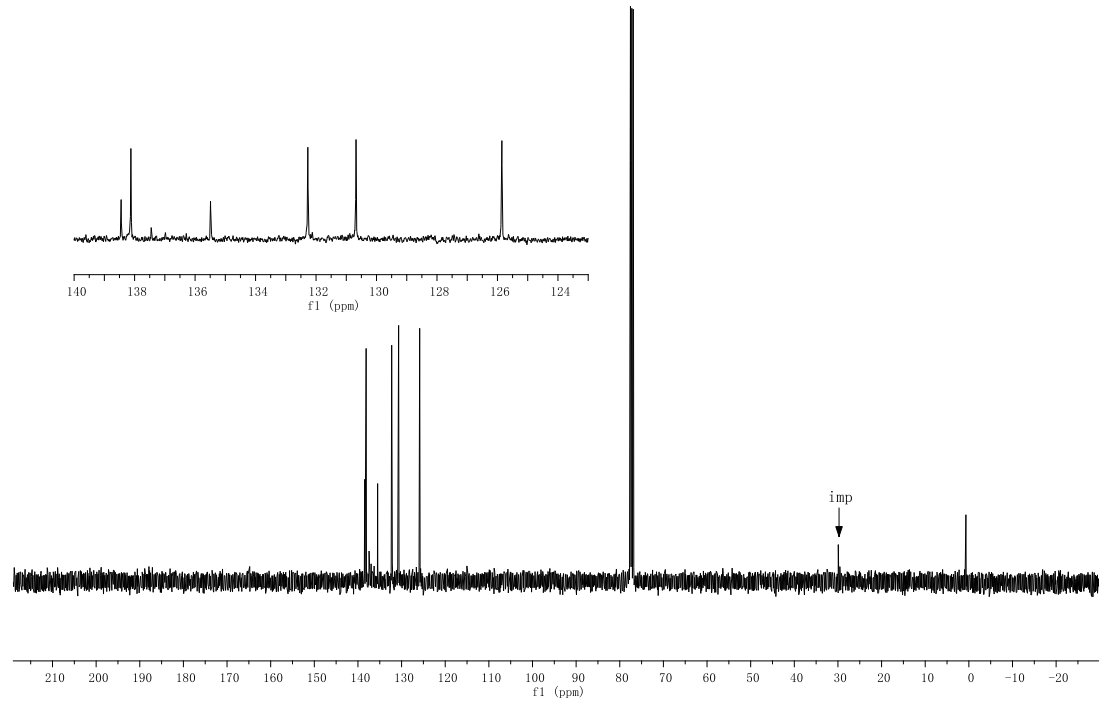
Through an addition funnel, a flask was charged with cyclohexane (110 mL), TMEDA (15.7 mL) and *n*-BuLi (2.5 M in hexane, 40.7 mL, 101.8 mmol). Thiophenol (5 mL, 48.9 mmol) in cyclohexane (20 mL) was added to the flask at 0 ℃. The reaction was warmed to room temperature over the next two days. Cyclohexane was removed from the reaction flask and the precipitate was washed with cyclohexane. When the precipitate settled, cyclohexane was removed again. THF (55 mL) was added to the precipitate, in which $MeSiCl_3$ (1.35 mL) diluted with THF (15 mL) was added dropwise. The mixture was warmed to room temperature for 20 hours and then acidified with 10% sulfuric acid (100 mL). The mixture was concentrated in vacuo to remove THF and the water solution was extracted with $CHCl_3$ three times. The organic layer was dried with Na_2SO_4 and concentrated in vacuo to yield yellow oil. This was purified by column chromatography on silica gel (3:1, then 1:1, hexanes-benzene) to give compound **290** as gummy yellow oil

(0.39 g, 1.1 mmol, 6.7%). ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 3 H), 3.48 (s, 3 H), 7.15 (t, *J* = 8 Hz, 3 H), 7.29 (m, 6 H), 7.40 (d, *J* = 8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 0.68, 125.9, 130.7, 132.3, 135.5, 138.1, 138.5 (7 of 7 expected resonances); MS (EI) *m/z* 336 (M – H_2S, 24), 321 (M – H_2S – CH_3, 12), 227 (M – H_2S – C_6H_4SH, 100).

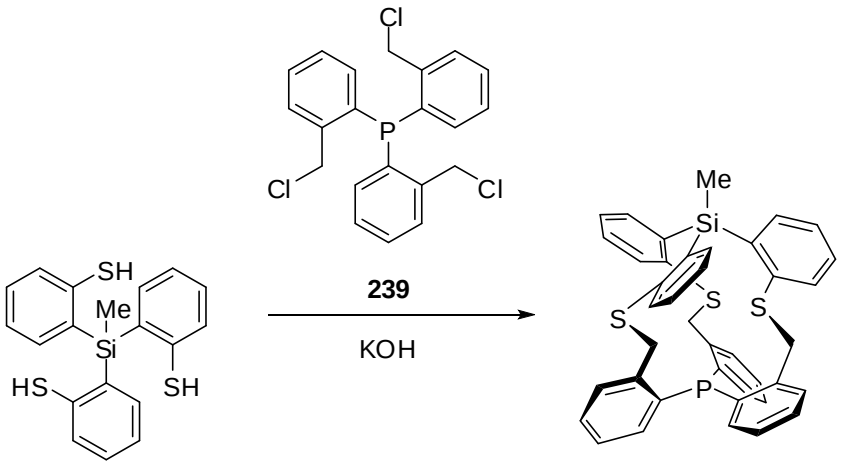
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **290**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **290**



Synthesis of *out,in*-MeSi,P cyclophane 291



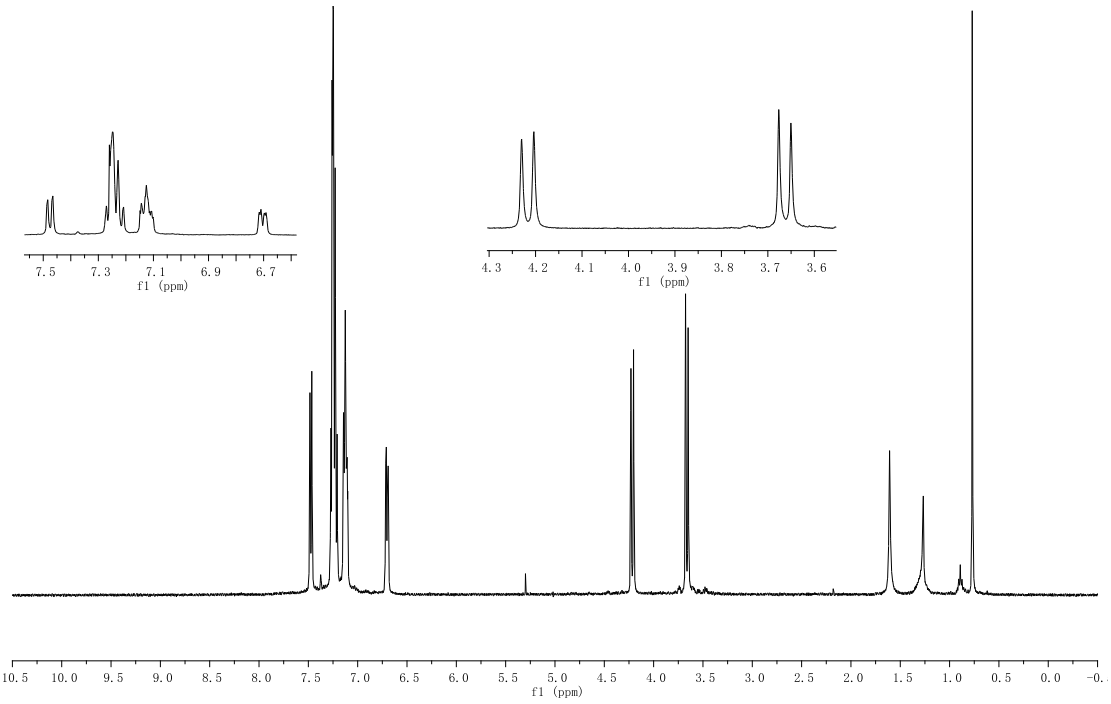
290 **291**

$C_{41}H_{37}PS_3Si$
Exact Mass: 684.16
Molecular Weight: 684.99
C, 71.89; H, 5.44; P, 4.52; S, 14.04; Si, 4.10

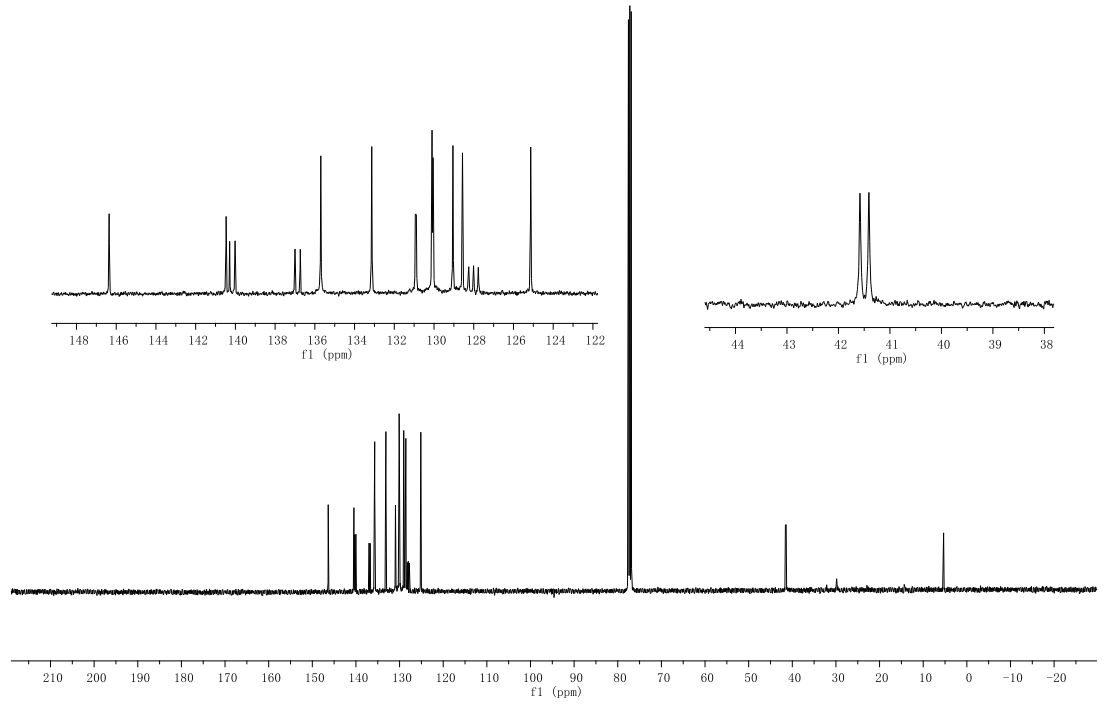
Tris[2-(chloromethyl)phenyl]phosphine (**239**, 413 mg, 1.01 mmol) and tris(2-mercaptophenyl)methylsilane (**290**, 376 mg, 1.01 mmol) were mixed in 2:1 benzene-ethanol (900 mL), and the solution was heated to reflux. An argon-saturated solution of KOH (280 mg, 4.99 mmol) in ethanol (100 mL) was added slowly over 9 hours. After another 15 hours, the solution was cooled, and the solvent was evaporated under reduced pressure to leave a white precipitate. The precipitate was extracted twice with chloroform. The combined extracts were concentrated and the resulting light yellow liquid was chromatographed on silica gel (solvent, 1:1 hexane-benzene) and the fractions containing compound **291** were combined and further purified by preparative TLC (silica

gel, 1:1 hexanes-benzene) to give cyclophane **291** as a white solid (15 mg, 0.022 mmol, 2.2%). Single crystals, suitable for X-ray analysis, were obtained from benzene-$CHCl_3$-MeOH. ^{1}H NMR ($CDCl_3$) δ 0.77 (s, 3 H), 3.66 (d, J = 10 Hz, 3 H), 4.22 (d, J = 10 Hz, 3 H), 6.70 (dd, J = 8 Hz, 2 Hz, 3 H), 7.12 (m, 6 H), 7.24 (m, 12 H), 7.47 (d, J = 8 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 5.3, 41.5 (d, J_{PC} = 18 Hz), 125.1, 128.6, 129.0, 130.0, 130.1, 130.9 (d, J_{PC} = 5 Hz), 133.1, 135.7, 136.9 (d, J_{PC} = 26 Hz), 140.2 (d, J_{PC} = 27 Hz), 140.5, 146.4 (14 of 14 expected resonances); HRMS (ESI) *m/z* 669.1324 (M + H), calcd for $C_{40}H_{34}PS_3Si$ 669.1324.

^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **291**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of Compound **291**



Appendix: Selected Crystallographic Data

Table 6. Crystallographic data for compounds **105**, **116** and **122**

	105	**116**	**122**
Chemical Formula	$C_{23}H_{18}O$	$C_{23}H_{15}Br_3$	$C_{21}H_{12}Cl_2O$
Formula Weight	310.37	531.08	351.21
Crystal Color	colourless	yellow	colourless
Crystal Size	0.33×0.16×0.12	0.23×0.16×0.04	0.33×0.24×0.12
Crystal System	Triclinic	Orthorhombic	Monoclinic
Space Group	$P\bar{1}$	*Pbca*	*C2/c*
a, Å	8.266(2)	16.3574(12)	14.5661(19)
b, Å	8.448(2)	7.9047(6)	7.9339(10)
c, Å	13.400(3)	28.285(2)	14.7343(19)
α, deg	95.512(4)	90.000	90.000
β, deg	97.575(3)	90.000	117.006(2)
γ, deg	119.437(3)	90.000	90.000
V, Å^3	793.7(3)	3657.2(5)	1517.1(3)
Z	2	8	4
ρ_{calcd}, g/cm^3	1.299	1.929	1.538
μ, mm^{-1}	0.078	6.622	0.432
T, K	100(2)	100(2)	100(2)
λ, Å	0.71073	0.71073	0.71073
Reflections			
total	25945	56967	12746
unique	7503	4206	1976
observed	6398	3543	1880
$R(F)$ (obs.)^a	0.0501	0.0351	0.0306
$wR(F^2)$ (obs.)^b	0.1350	0.0839	0.0833
$R(F)$ (all)^a	0.0584	0.0455	0.0317
$wR(F^2)$ (all)^b	0.1460	0.0884	0.0844
S (all)^c	1.016	1.077	1.096

Table 7. Crystallographic data for compounds **132**, **140** and **141**

	132	**140**	**141**
Chemical Formula	$C_{25}H_{24}O_3$	$C_{24}H_{20}O_2$	$C_{25}H_{22}O_3$
Formula Weight	372.44	340.40	370.43
Crystal Color	colourless	colourless	colourless
Crystal Size	0.25×0.22×0.17	0.40×0.27×0.07	0.23×0.13×0.13
Crystal System	Orthorhombic	Monoclinic	Monoclinic
Space Group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
a, Å	8.2015(13)	21.013(3)	8.242(3)
b, Å	10.0526(16)	8.1467(12)	11.029(4)
c, Å	23.091(4)	21.507(3)	21.340(7)
α, deg	90.000	90.000	90.000
β, deg	90.000	105.097(2)	99.449(4)
γ, deg	90.000	90.000	90.000
V, Å^3	1903.8(5)	3554.6(9)	1913.4(11)
Z	4	8	4
ρ_{calcd}, g/cm^3	1.299	1.272	1.286
μ, mm^{-1}	0.084	0.080	0.083
T, K	100(2)	100(2)	100(2)
λ, Å	0.71073	0.71073	0.71073
Reflections			
total	33677	56735	32115
unique	4814	8142	4591
observed	4548	6434	3795
$R(F)$ (obs.)[a]	0.0348	0.0659	0.0444
$wR(F^2)$ (obs.)[b]	0.0860	0.1522	0.1151
$R(F)$ (all)[a]	0.0376	0.0835	0.0550
$wR(F^2)$ (all)[b]	0.0882	0.1616	0.1233
S (all)[c]	1.040	1.107	1.063

Table 8. Crystallographic data for compounds **146**, **148** and **235**

	146	**148**	**235**
Chemical Formula	$C_{22}H_{12}O_2S_2$	$C_{21}H_{14}OS_2$	$C_{39}H_{30}P_2S_3$
Formula Weight	372.44	346.44	656.75
Crystal Color	yellow	light yellow	colourless
Crystal Size	0.14×0.10×0.03	0.219×0.132×0.057	0.21×0.10×0.06
Crystal System	Monoclinic	Monoclinic	Trigonal
Space Group	*P2₁/c*	*C2/c*	*P321*
a, Å	6.8452(3)	15.817(2)	14.810(5)
b, Å	9.0996(4)	11.6854(15)	14.810(5)
c, Å	25.8139(12)	8.9861(12)	21.949(8)
α, deg	90.000	90.000	90.000
β, deg	95.864(2)	98.861(2)	90.000
γ, deg	90.000	90.000	120.000
V, Å^3	1599.50(12)	1641.1(4)	4169(3)
Z	4	4	4
ρ_{calcd}, g/cm^3	1.547	1.402	1.046
μ, mm^{-1}	3.134	0.328	0.277
T, K	100(2)	150(2)	100(2)
λ, Å	1.54178	0.71073	0.71073
Reflections			
total	4490	14773	36419
unique	4490	2130	6414
observed	4048	1686	5455
$R(F)$ (obs.)[a]	0.0463	0.0401	0.0603
$wR(F^2)$ (obs.)[b]	0.1036	0.0912	0.1726
$R(F)$ (all)[a]	0.0541	0.0553	0.0683
$wR(F^2)$ (all)[b]	0.1067	0.1024	0.1779
S (all)[c]	1.152	1.039	1.068

Table 9. Crystallographic data for compounds **240 • 2($CHCl_3$) • H_2O**, **241 • 1.5(C_2H_6OS)** and **257**

	240 • 2($CHCl_3$) • H_2O	**241 • 1.5(C_2H_6OS)**	**257**
Chemical Formula	$C_{41}H_{35}Cl_7OP_2S_3$	$C_{42}H_{39}O_{7.5}P_2S_{4.5}$	$C_{39}H_{30}NPS_3$
Formula Weight	949.96	869.94	639.79
Crystal Color	colourless	clear colourless	colourless
Crystal Size	0.38×0.16×0.15	0.12×0.12×0.06	0.20×0.19×0.16
Crystal System	Monoclinic	Orthorhombic	Tetragonal
Space Group	*P2₁/n*	*Pna2₁*	*P4/n*
a, Å	13.157(2)	17.7602(7)	18.6366(14)
b, Å	19.846(4)	10.5542(4)	18.6366(14)
c, Å	16.443(3)	21.7285(8)	19.3600(16)
α, deg	90.000	90.000	90.000
β, deg	94.875(3)	90.000	90.000
γ, deg	90.000	90.000	90.000
V, Å^3	4277.9(13)	4072.9(3)	6724.2(9)
Z	4	4	8
ρ_{calcd}, g/cm^3	1.475	1.419	1.264
μ, mm^{-1}	0.719	3.556	2.676
T, K	100(2)	100(2)	100(2)
λ, Å	0.71073	1.54178	1.54178
Reflections			
total	75153	60991	60690
unique	11199	6947	4993
observed	9721	5756	4306
$R(F)$ (obs.)[a]	0.0344	0.0843	0.0623
$wR(F^2)$ (obs.)[b]	0.0850	0.2269	0.1858
$R(F)$ (all)[a]	0.0412	0.1015	0.0705
$wR(F^2)$ (all)[b]	0.0900	0.2412	0.1919
S (all)[c]	1.042	1.071	1.088

Table 10. Crystallographic data for compounds **275** and **277 • 0.125(CH_2Cl_2)**

	275	**277 • 0.125(CH_2Cl_2)**
Chemical Formula	$C_{39}H_{31}PS_3Si$	$C_{41.12}H_{35.25}Cl_{0.25}OPS_3Si$
Formula Weight	654.88	709.54
Crystal Color	colourless	colourless
Crystal Size	0.17×0.16×0.11	0.18×0.18×0.06
Crystal System	Trigonal	Triclinic
Space Group	$P\bar{3}$	*P1*
a, Å	13.8326(3)	12.9706(5)
b, Å	13.8326(3)	13.2671(5)
c, Å	11.3205(3)	13.8130(5)
α, deg	90.000	64.212(2)
β, deg	90.000	64.706(2)
γ, deg	120.000	62.734(2)
V, Å^3	1875.87(8)	1823.65(13)
Z	2	2
ρ_{calcd}, g/cm^3	1.159	1.292
μ, mm^{-1}	0.297	2.999
T, K	200(2)	100(2)
λ, Å	0.71073	1.54178
Reflections		
total	17748	16294
unique	2577	16294
observed	2188	13264
$R(F)$ (obs.)[a]	0.0351	0.0846
$wR(F^2)$ (obs.)[b]	0.0947	0.2158
$R(F)$ (all)[a]	0.0415	0.1035
$wR(F^2)$ (all)[b]	0.0975	0.2364
S (all)[c]	1.131	1.039

Table 11. Crystallographic data for compounds **278 • 0.5(C_6H_6) • $CHCl_3$** and **291 • C_6H_6**

	278 • 0.5(C_6H_6) • $CHCl_3$	**291 • C_6H_6**
Chemical Formula	$C_{43}H_{36}Cl_3S_3Si_2$	$C_{46}H_{39}PS_3Si$
Formula Weight	811.43	747.01
Crystal Color	colourless	colourless
Crystal Size	0.25×0.14×0.02	0.22×0.15×0.10
Crystal System	Trigonal	Triclinic
Space Group	$P\bar{3}$	$P\bar{1}$
a, Å	14.0183(5)	11.4759(4)
b, Å	14.0183(5)	13.1277(5)
c, Å	11.3948(5)	13.7216(5)
α, deg	90.000	88.006(1)
β, deg	90.000	70.561(1)
γ, deg	120.000	79.884(1)
V, Å^3	1939.22(16)	1918.42(12)
Z	2	2
ρ_{calcd}, g/cm^3	1.39	1.293
μ, mm^{-1}	4.482	2.702
T, K	100(2)	100(2)
λ, Å	1.54178	1.54178
Reflections		
total	4981	21842
unique	4981	6870
observed	4366	6544
$R(F)$ (obs.)[a]	0.0822	0.0294
$wR(F^2)$ (obs.)[b]	0.2456	0.0757
$R(F)$ (all)[a]	0.0905	0.0307
$wR(F^2)$ (all)[b]	0.2544	0.0766
S (all)[c]	1.109	1.030

[a] $R(F) = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; [b] $wR(F^2) = [\Sigma w(F_o^2 - F_c^2) / \Sigma w(F_o^2)^2]^{1/2}$; $w = 1 / [\sigma^2(F_o^2) + (xP)^2]$, where $P = (F_o^2 + 2F_c^2) / 3$; [c] S = goodness-of-fit on $F^2 = [\Sigma w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined.

Table 12. Atomic coordinates and equivalent isotropic displacement parameters for compound **105**

Atom	X	Y	Z	U_{equiv}
O1	0.62191(10)	-0.11389(9)	0.26417(5)	0.0261
C1	0.91980(13)	0.02557(12)	0.21308(7)	0.0195
C2	0.89365(13)	-0.10387(12)	0.12579(7)	0.0183
C3	0.72433(13)	-0.20653(12)	0.04734(7)	0.0202
C4	0.71649(14)	-0.32932(13)	-0.03124(7)	0.0233
H4	0.60340	-0.39830	-0.08240	0.0280
C5	0.86961(15)	-0.35649(13)	-0.03857(8)	0.0259
H5	0.85760	-0.44600	-0.09230	0.0310
C6	1.03568(14)	-0.25323(13)	0.03213(8)	0.0248
H6	1.14040	-0.26900	0.02630	0.0300
C7	1.05328(13)	-0.12305(13)	0.11393(7)	0.0207
C8	1.23038(14)	-0.01091(14)	0.18371(7)	0.0250
H8	1.33360	-0.02860	0.17670	0.0300
C9	1.25418(14)	0.12127(14)	0.26029(7)	0.0263
H9	1.37520	0.20080	0.30390	0.0320
C10	1.09784(14)	0.13905(13)	0.27431(7)	0.0232
H10	1.11540	0.23210	0.32760	0.0280
C11	0.78839(13)	0.21499(12)	0.29413(7)	0.0197
C12	0.81431(14)	0.32143(13)	0.21909(7)	0.0227
H12	0.84220	0.28580	0.15720	0.0270
C13	0.80039(14)	0.48170(13)	0.23188(7)	0.0256
H13	0.81680	0.55180	0.17880	0.0310
C14	0.76332(14)	0.53499(13)	0.32079(8)	0.0245
H14	0.75000	0.64070	0.32870	0.0290
C15	0.74416(13)	0.43504(12)	0.40220(7)	0.0207
C16	0.70643(14)	0.49431(14)	0.49425(8)	0.0261
H16	0.69340	0.60020	0.50090	0.0310
C17	0.68864(15)	0.40095(15)	0.57346(8)	0.0287
H17	0.65700	0.43790	0.63360	0.0340
C18	0.71734(14)	0.24962(14)	0.56576(7)	0.0263
H18	0.71070	0.18960	0.62280	0.0320
C19	0.75462(13)	0.18569(13)	0.47867(7)	0.0215
C20	0.76009(12)	0.27294(12)	0.39131(7)	0.0188
C21	0.76306(13)	0.02816(13)	0.25741(7)	0.0201
C22	0.55780(14)	-0.17787(13)	0.04244(8)	0.0257
H22A	0.48020	-0.22590	-0.02720	0.0380
H22B	0.60380	-0.04550	0.06060	0.0380

H22C	0.48090	-0.24350	0.09070	0.0380
C23	0.79896(16)	0.03320(15)	0.48198(8)	0.0279
H23A	0.83200	0.02470	0.55340	0.0420
H23B	0.90610	0.06010	0.44870	0.0420
H23C	0.68760	-0.08450	0.44590	0.0420

Table 13. Atomic coordinates and equivalent isotropic displacement parameters for compound **116**

Atom	X	Y	Z	U_{equiv}
Br1	0.12378(2)	0.17571(4)	0.666895(12)	0.0210
Br2	0.11622(3)	-0.38363(5)	0.602935(14)	0.0318
Br3	-0.07426(2)	-0.26073(4)	0.688098(14)	0.0257
C1	0.0343(2)	0.0751(4)	0.62741(11)	0.0157
H1	0.03650	-0.03480	0.63550	0.0190
C2	0.0505(2)	0.1123(4)	0.57601(11)	0.0157
C3	0.1084(2)	0.0416(4)	0.54326(12)	0.0170
C4	0.1677(2)	-0.0867(4)	0.55205(12)	0.0192
C5	0.1803(2)	-0.1726(5)	0.59870(13)	0.0250
H5A	0.16370	-0.09520	0.62450	0.0300
H5B	0.23900	-0.19870	0.60280	0.0300
C6	0.2172(2)	-0.1429(5)	0.51594(13)	0.0233
H6	0.25670	-0.22800	0.52260	0.0280
C7	0.2117(2)	-0.0795(5)	0.46985(13)	0.0240
H7	0.24650	-0.12180	0.44570	0.0290
C8	0.1559(2)	0.0431(5)	0.45990(13)	0.0221
H8	0.15230	0.08690	0.42870	0.0270
C9	0.1034(2)	0.1063(4)	0.49544(12)	0.0187
C10	0.0451(2)	0.2300(4)	0.48317(13)	0.0208
H10	0.04390	0.27100	0.45160	0.0250
C11	-0.0095(2)	0.2927(4)	0.51485(12)	0.0190
H11	-0.04870	0.37530	0.50580	0.0230
C12	-0.0060(2)	0.2311(4)	0.56136(12)	0.0178
C13	-0.0611(2)	0.2710(4)	0.60039(12)	0.0187
C14	-0.1261(2)	0.3882(4)	0.60054(13)	0.0239
H14	-0.13910	0.45230	0.57310	0.0290
C15	-0.1696(2)	0.4065(5)	0.64127(14)	0.0248
H15	-0.21240	0.48770	0.64230	0.0300
C16	-0.1533(2)	0.3084(4)	0.68215(13)	0.0216
C17	-0.1991(2)	0.3365(5)	0.72373(14)	0.0263
H17	-0.24020	0.42130	0.72410	0.0310
C18	-0.1849(2)	0.2433(5)	0.76328(14)	0.0277
H18	-0.21410	0.26700	0.79150	0.0330
C19	-0.1272(2)	0.1122(5)	0.76244(13)	0.0236
H19	-0.11980	0.04470	0.78990	0.0280
C20	-0.0809(2)	0.0788(4)	0.72277(13)	0.0200
C21	-0.0264(2)	-0.0728(4)	0.72508(13)	0.0215

H21A	-0.01950	-0.10820	0.75840	0.0260
H21B	0.02810	-0.04380	0.71220	0.0260
C22	-0.0896(2)	0.1825(4)	0.68160(12)	0.0173
C23	-0.0426(2)	0.1728(4)	0.63919(12)	0.0169

Table 14. Atomic coordinates and equivalent isotropic displacement parameters for compound **122**

Atom	X	Y	Z	U_{equiv}
Cl1	1.136682(19)	0.33081(3)	0.475485(19)	0.0171
O1	1.00000	0.42006(14)	0.25000	0.0175
C1	1.00000	0.2667(2)	0.25000	0.0138
C2	0.93996(8)	0.16683(13)	0.29254(8)	0.0136
C3	0.86563(9)	0.06404(14)	0.22153(8)	0.0176
H3	0.86770	0.04210	0.15910	0.0210
C4	0.78668(9)	-0.00953(15)	0.23861(9)	0.0196
H4	0.73680	-0.08030	0.18840	0.0240
C5	0.78252(8)	0.02185(14)	0.32792(9)	0.0179
H5	0.72740	-0.02260	0.33810	0.0210
C6	0.86005(8)	0.12055(14)	0.40574(8)	0.0145
C7	0.85513(9)	0.14866(14)	0.49856(9)	0.0174
H7	0.79890	0.10440	0.50710	0.0210
C8	0.93012(9)	0.23864(15)	0.57600(9)	0.0189
H8	0.92420	0.26120	0.63640	0.0230
C9	1.01608(9)	0.29760(15)	0.56582(8)	0.0170
H9	1.07010	0.35470	0.62090	0.0200
C10	1.02192(8)	0.27268(13)	0.47633(8)	0.0138
C11	0.94248(8)	0.19078(13)	0.39038(8)	0.0127

Table 15. Atomic coordinates and equivalent isotropic displacement parameters for compound **132**

Atom	X	Y	Z	U_{equiv}
O1	0.10309(11)	0.22263(9)	0.11632(4)	0.0178
H1	0.02260	0.20960	0.08790	0.0210
O2	0.36420(13)	-0.08059(9)	0.02152(4)	0.0254
O3	0.41052(12)	0.33930(9)	-0.02058(4)	0.0194
C1	0.3513(2)	-0.18978(14)	-0.01761(6)	0.0302
H1A	0.45760	-0.23350	-0.02130	0.0450
H1B	0.31620	-0.15730	-0.05560	0.0450
H1C	0.27110	-0.25360	-0.00280	0.0450
C2	0.41955(16)	-0.12099(13)	0.07781(6)	0.0203
H2A	0.44610	-0.04080	0.10080	0.0240
H2B	0.52080	-0.17360	0.07350	0.0240
C3	0.29509(15)	-0.20309(12)	0.11051(5)	0.0160
C4	0.32658(17)	-0.33812(13)	0.11182(5)	0.0203
H4	0.42450	-0.36960	0.09460	0.0240
C5	0.22078(19)	-0.43126(13)	0.13738(6)	0.0237
H5	0.24630	-0.52340	0.13720	0.0280
C6	0.08134(18)	-0.38638(13)	0.16238(6)	0.0226
H6	0.00850	-0.44830	0.17960	0.0270
C7	0.04216(16)	-0.24883(13)	0.16336(5)	0.0184
C8	-0.10344(17)	-0.20919(15)	0.19157(6)	0.0252
H8	-0.17320	-0.27480	0.20780	0.0300
C9	-0.14457(17)	-0.07862(15)	0.19571(6)	0.0262
H9	-0.24240	-0.05290	0.21470	0.0310
C10	-0.04060(16)	0.01813(14)	0.17159(6)	0.0208
H10	-0.06950	0.10920	0.17530	0.0250
C11	0.10132(15)	-0.01376(12)	0.14280(5)	0.0148
C12	0.14886(15)	-0.15189(12)	0.13740(5)	0.0149
C13	0.20005(15)	0.10398(11)	0.11881(5)	0.0141
H13	0.23840	0.08160	0.07890	0.0170
C14	0.34759(15)	0.14070(11)	0.15608(5)	0.0136
C15	0.35424(15)	0.08851(12)	0.21111(5)	0.0164
H15	0.27200	0.02740	0.22250	0.0200
C16	0.47671(16)	0.12108(13)	0.25132(6)	0.0193
H16	0.47690	0.08260	0.28890	0.0230
C17	0.59493(16)	0.20880(13)	0.23538(5)	0.0191
H17	0.67670	0.23330	0.26250	0.0230
C18	0.59779(15)	0.26421(12)	0.17877(5)	0.0156

C19	0.72936(16)	0.34919(13)	0.16424(6)	0.0189
H19	0.81120	0.36770	0.19220	0.0230
C20	0.73955(16)	0.40459(13)	0.11061(6)	0.0201
H20	0.82760	0.46200	0.10120	0.0240
C21	0.61869(16)	0.37604(12)	0.06931(5)	0.0180
H21	0.62580	0.41680	0.03230	0.0220
C22	0.49021(14)	0.29127(12)	0.08031(5)	0.0149
C23	0.47399(14)	0.23153(12)	0.13709(5)	0.0137
C24	0.37965(15)	0.25814(12)	0.02910(5)	0.0171
H24A	0.39530	0.16360	0.01840	0.0200
H24B	0.26460	0.26970	0.04100	0.0200
C25	0.30518(19)	0.45162(13)	-0.02356(6)	0.0250
H25A	0.19260	0.42150	-0.02900	0.0380
H25B	0.33730	0.50810	-0.05620	0.0380
H25C	0.31310	0.50260	0.01250	0.0380

Table 16. Atomic coordinates and equivalent isotropic displacement parameters for compound **140**

Atom	X	Y	Z	U_{equiv}
O1	0.29918(11)	0.8177(3)	0.53325(11)	0.0606
O2	0.28820(8)	0.8994(2)	0.35518(11)	0.0519
C1	0.41400(12)	0.5705(3)	0.43036(11)	0.0324
C2	0.44821(14)	0.4826(3)	0.39543(13)	0.0443
H2	0.47930	0.53790	0.37780	0.0530
C3	0.43862(16)	0.3121(3)	0.38484(14)	0.0508
H3	0.46360	0.25380	0.36100	0.0610
C4	0.39373(14)	0.2321(3)	0.40884(13)	0.0464
H4	0.38570	0.11870	0.39980	0.0560
C5	0.35876(12)	0.3151(3)	0.44715(12)	0.0370
C6	0.31317(13)	0.2277(3)	0.47256(14)	0.0466
H6	0.30710	0.11360	0.46390	0.0560
C7	0.27798(13)	0.3027(4)	0.50891(14)	0.0491
H7	0.24710	0.24210	0.52510	0.0590
C8	0.28746(13)	0.4702(4)	0.52239(13)	0.0428
H8	0.26230	0.52300	0.54740	0.0510
C9	0.33273(12)	0.5606(3)	0.50015(11)	0.0357
C10	0.36965(11)	0.4866(3)	0.46009(11)	0.0313
C11	0.34362(14)	0.7295(3)	0.52692(13)	0.0448
H11	0.38740	0.77040	0.53970	0.0540
C12	0.42297(11)	0.7574(3)	0.43463(12)	0.0322
H12A	0.37880	0.80860	0.42550	0.0390
H12B	0.44650	0.78580	0.47950	0.0390
C13	0.46007(11)	0.8336(3)	0.38997(12)	0.0317
C14	0.52585(12)	0.8590(3)	0.41704(13)	0.0423
H14	0.54390	0.82430	0.46020	0.0510
C15	0.56802(13)	0.9331(4)	0.38465(15)	0.0498
H15	0.61360	0.94550	0.40520	0.0600
C16	0.54291(13)	0.9871(3)	0.32352(14)	0.0450
H16	0.57110	1.03880	0.30130	0.0540
C17	0.47519(13)	0.9675(3)	0.29240(12)	0.0400
C18	0.45049(18)	1.0342(4)	0.23027(14)	0.0578
H18	0.47960	1.09040	0.21030	0.0690
C19	0.3862(2)	1.0196(5)	0.19867(16)	0.0804
H19	0.37010	1.06460	0.15680	0.0960
C20	0.34378(18)	0.9376(5)	0.22828(16)	0.0672
H20	0.29880	0.92680	0.20530	0.0800

C21	0.36388(13)	0.8712(3)	0.28929(13)	0.0414
C22	0.43170(11)	0.8862(3)	0.32464(11)	0.0314
C23	0.31100(12)	0.7895(3)	0.31367(14)	0.0452
H23A	0.27380	0.75810	0.27690	0.0540
H23B	0.32870	0.68850	0.33760	0.0540
C24	0.22992(14)	0.8377(5)	0.3696(2)	0.0702
H24A	0.19410	0.83260	0.32990	0.1060
H24B	0.21720	0.91080	0.40050	0.1060
H24C	0.23850	0.72750	0.38810	0.1060
O3	1.09982(9)	0.0934(2)	0.47725(9)	0.0432
C25	0.92259(11)	0.3406(3)	0.38833(10)	0.0285
C26	0.86860(12)	0.4311(3)	0.35643(12)	0.0366
H26	0.82780	0.37640	0.33980	0.0440
C27	0.87182(14)	0.6023(3)	0.34752(12)	0.0410
H27	0.83330	0.66140	0.32620	0.0490
C28	0.92977(13)	0.6821(3)	0.36942(11)	0.0374
H28	0.93200	0.79670	0.36210	0.0450
C29	0.98718(12)	0.5973(3)	0.40304(10)	0.0301
C30	1.04697(12)	0.6843(3)	0.42542(11)	0.0344
H30	1.04780	0.79880	0.41720	0.0410
C31	1.10311(13)	0.6088(3)	0.45830(11)	0.0349
H31	1.14290	0.66920	0.47290	0.0420
C32	1.10154(12)	0.4392(3)	0.47045(11)	0.0315
H32	1.14090	0.38570	0.49320	0.0380
C33	1.04456(11)	0.3488(3)	0.45023(10)	0.0274
C34	0.98407(11)	0.4242(3)	0.41456(9)	0.0265
C35	1.05128(11)	0.1758(3)	0.47422(10)	0.0303
H35	1.01580	0.12840	0.48770	0.0360
C36	0.91486(11)	0.1563(3)	0.39398(10)	0.0274
H36A	0.95280	0.10230	0.38310	0.0330
H36B	0.91750	0.13030	0.43950	0.0330
C37	0.85203(11)	0.0809(3)	0.35250(10)	0.0280
C38	0.80126(12)	0.0615(3)	0.38135(12)	0.0353
H38	0.80730	0.09960	0.42420	0.0420
C39	0.74100(12)	-0.0119(3)	0.35036(13)	0.0402
H39	0.70660	-0.01920	0.37150	0.0480
C40	0.73224(11)	-0.0723(3)	0.28989(12)	0.0374
H40	0.69190	-0.12470	0.26910	0.0450
C41	0.78276(11)	-0.0578(3)	0.25751(11)	0.0323
C42	0.77169(13)	-0.1262(4)	0.19542(12)	0.0450
H42	0.73140	-0.18140	0.17690	0.0540

C43	0.81769(15)	-0.1142(4)	0.16200(13)	0.0536
H43	0.81010	-0.16140	0.12030	0.0640
C44	0.87673(14)	-0.0312(4)	0.18950(12)	0.0446
H44	0.90840	-0.02140	0.16520	0.0530
C45	0.89086(11)	0.0363(3)	0.24987(10)	0.0321
C46	0.84336(10)	0.0242(3)	0.28729(10)	0.0265
O4	1.00256(9)	-0.0017(3)	0.30780(9)	0.0335
C47	0.95716(12)	0.1164(3)	0.27085(11)	0.0371
H47A	0.97190	0.15160	0.23280	0.0450
H47B	0.95490	0.21440	0.29740	0.0450
C48	1.06858(15)	0.0508(5)	0.31680(16)	0.0462
H48A	1.09850	-0.03130	0.34210	0.0690
H48B	1.07500	0.15590	0.33970	0.0690
H48C	1.07800	0.06420	0.27480	0.0690
O4A	1.0088(5)	0.0959(16)	0.3180(5)	0.0335
C47A	0.95716(12)	0.1164(3)	0.27085(11)	0.0371
H47C	0.97440	0.10790	0.23230	0.0450
H47D	0.94650	0.23400	0.27390	0.0450
C48A	1.0459(8)	-0.025(2)	0.2890(9)	0.0462
H48D	1.08610	-0.05730	0.32120	0.0690
H48E	1.05760	0.02570	0.25210	0.0690
H48F	1.01830	-0.12150	0.27470	0.0690

Table 17. Atomic coordinates and equivalent isotropic displacement parameters for compound **141**

Atom	X	Y	Z	U_{equiv}
O1	0.16814(12)	0.32517(10)	0.53675(4)	0.0363
O2	0.22060(12)	0.15313(9)	0.48760(5)	0.0352
O3	0.24310(11)	0.17628(8)	0.31974(4)	0.0305
C1	-0.05703(15)	0.22505(12)	0.47687(6)	0.0255
C2	-0.13773(17)	0.14049(13)	0.50806(7)	0.0329
H2	-0.07600	0.08970	0.53920	0.0390
C3	-0.30997(18)	0.12797(14)	0.49461(7)	0.0357
H3	-0.36390	0.06970	0.51670	0.0430
C4	-0.39810(16)	0.19947(13)	0.44995(7)	0.0331
H4	-0.51450	0.19220	0.44170	0.0400
C5	-0.32031(15)	0.28519(12)	0.41509(6)	0.0282
C6	-0.41632(16)	0.35229(13)	0.36578(7)	0.0340
H6	-0.53240	0.34230	0.35790	0.0410
C7	-0.34420(16)	0.43090(14)	0.32964(7)	0.0357
H7	-0.40940	0.47530	0.29660	0.0430
C8	-0.17196(16)	0.44603(12)	0.34155(7)	0.0306
H8	-0.12320	0.50180	0.31630	0.0370
C9	-0.07169(14)	0.38293(12)	0.38847(6)	0.0248
C10	-0.14481(14)	0.29981(11)	0.42777(6)	0.0244
C11	0.12500(15)	0.22929(12)	0.49919(6)	0.0253
C12	0.11410(14)	0.39893(12)	0.39632(6)	0.0243
H12A	0.15460	0.42430	0.44060	0.0290
H12B	0.16390	0.31910	0.39000	0.0290
C13	0.17548(14)	0.48940(11)	0.35217(6)	0.0237
C14	0.21000(16)	0.60373(12)	0.37699(7)	0.0308
H14	0.18970	0.62020	0.41870	0.0370
C15	0.27388(18)	0.69706(13)	0.34331(7)	0.0360
H15	0.29500	0.77480	0.36200	0.0430
C16	0.30510(17)	0.67518(13)	0.28378(7)	0.0351
H16	0.35100	0.73730	0.26130	0.0420
C17	0.26960(16)	0.56017(12)	0.25491(6)	0.0293
C18	0.3001(2)	0.54239(15)	0.19221(7)	0.0416
H18	0.34650	0.60650	0.17120	0.0500
C19	0.2645(2)	0.43551(16)	0.16144(7)	0.0480
H19	0.28330	0.42540	0.11900	0.0580
C20	0.1995(2)	0.34039(14)	0.19312(7)	0.0391
H20	0.17460	0.26590	0.17130	0.0470

C21	0.17030(16)	0.35042(12)	0.25478(6)	0.0268
C22	0.20273(14)	0.46403(11)	0.28839(6)	0.0234
C23	0.10852(15)	0.23602(12)	0.28147(6)	0.0270
H23A	0.02300	0.25600	0.30740	0.0320
H23B	0.05900	0.18210	0.24640	0.0320
C24	0.1957(2)	0.06020(13)	0.33973(7)	0.0407
H24A	0.10690	0.06970	0.36480	0.0610
H24B	0.29030	0.02110	0.36580	0.0610
H24C	0.15720	0.00990	0.30240	0.0610
C25	0.34387(18)	0.34016(18)	0.55712(7)	0.0467
H25A	0.38770	0.26960	0.58220	0.0700
H25B	0.36420	0.41360	0.58310	0.0700
H25C	0.39830	0.34750	0.51980	0.0700

Table 18. Atomic coordinates and equivalent isotropic displacement parameters for compound **146**

Atom	X	Y	Z	U_{equiv}
S1	0.37484(14)	0.52056(10)	0.39416(3)	0.0179
S2	0.24690(14)	0.76533(10)	0.56860(3)	0.0172
O1	-0.0189(4)	0.5598(3)	0.40043(10)	0.0185
O2	0.1945(4)	0.5505(3)	0.49926(9)	0.0198
C1	0.4126(5)	0.5185(4)	0.32782(13)	0.0174
C2	0.5656(5)	0.4582(4)	0.30490(14)	0.0209
H2	0.67120	0.41130	0.32520	0.0250
C3	0.5622(6)	0.4677(4)	0.25042(14)	0.0239
H3	0.66800	0.42640	0.23420	0.0290
C4	0.4127(6)	0.5340(4)	0.21978(14)	0.0240
H4	0.41680	0.53870	0.18310	0.0290
C5	0.2512(5)	0.5959(4)	0.24261(13)	0.0184
C6	0.0857(6)	0.6651(4)	0.21549(14)	0.0227
H6	0.07800	0.67480	0.17870	0.0270
C7	-0.0636(6)	0.7181(4)	0.24190(14)	0.0223
H7	-0.17470	0.76210	0.22290	0.0270
C8	-0.0554(5)	0.7087(4)	0.29661(14)	0.0203
H8	-0.16050	0.74540	0.31420	0.0240
C9	0.1050(5)	0.6462(4)	0.32416(13)	0.0174
C10	0.2556(5)	0.5879(4)	0.29696(13)	0.0153
C11	0.1423(5)	0.6326(4)	0.38300(13)	0.0156
C12	0.1839(5)	0.7809(4)	0.41047(13)	0.0140
C13	0.1988(5)	0.9113(4)	0.38082(13)	0.0161
H13	0.18680	0.90380	0.34390	0.0190
C14	0.2297(5)	1.0481(4)	0.40302(13)	0.0160
H14	0.23920	1.13140	0.38120	0.0190
C15	0.2475(5)	1.0665(4)	0.45734(13)	0.0141
C16	0.2748(5)	1.2021(4)	0.48440(14)	0.0172
H16	0.28280	1.29100	0.46540	0.0210
C17	0.2896(5)	1.2053(4)	0.53746(14)	0.0172
H17	0.30550	1.29720	0.55490	0.0210
C18	0.2818(5)	1.0746(4)	0.56750(13)	0.0172
H18	0.29320	1.07870	0.60450	0.0210
C19	0.2575(5)	0.9422(4)	0.54179(13)	0.0146
C20	0.2382(5)	0.9373(4)	0.48727(13)	0.0138
C21	0.2089(5)	0.7974(4)	0.46435(13)	0.0136

C22	0.2113(5)	0.6823(4)	0.50513(13)	0.0160
H1	0.004(6)	0.545(5)	0.4332(18)	0.0300

Table 19. Atomic coordinates and equivalent isotropic displacement parameters for compound **148**

Atom	X	Y	Z	U_{equiv}
S1	0.42980(3)	0.79414(4)	0.33605(5)	0.0293
O1	0.50000	0.60228(15)	0.25000	0.0331
C1	0.50000	0.7042(2)	0.25000	0.0232
C2	0.35902(10)	0.69137(14)	0.39613(18)	0.0236
C3	0.38838(11)	0.62200(16)	0.5151(2)	0.0302
H3	0.44610	0.62820	0.56280	0.0360
C4	0.33381(12)	0.54115(16)	0.5678(2)	0.0333
H4	0.35480	0.49320	0.65070	0.0400
C5	0.25082(12)	0.53176(14)	0.4997(2)	0.0302
H5	0.21440	0.47730	0.53600	0.0360
C6	0.21830(11)	0.60202(14)	0.37586(18)	0.0245
C7	0.13210(11)	0.59291(16)	0.3035(2)	0.0310
H7	0.09540	0.53810	0.33850	0.0370
C8	0.10120(12)	0.66159(18)	0.1849(2)	0.0347
H8	0.04350	0.65380	0.13730	0.0420
C9	0.15449(12)	0.74375(18)	0.1329(2)	0.0331
H9	0.13240	0.79190	0.05090	0.0400
C10	0.23798(11)	0.75517(15)	0.19933(19)	0.0268
H10	0.27310	0.81120	0.16280	0.0320
C11	0.27253(10)	0.68471(13)	0.32145(18)	0.0224

Table 20. Atomic coordinates and equivalent isotropic displacement parameters for compound **235**

Atom	X	Y	Z	U_{equiv}
S1	0.4891(4)	0.1246(2)	0.77193(14)	0.0462
C7	0.5527(7)	0.0945(9)	0.7040(3)	0.0391
H7A	0.62970	0.13610	0.70650	0.0470
H7B	0.53120	0.01960	0.70290	0.0470
P1	0.66670	0.33330	0.65886(6)	0.0378
P2	0.66670	0.33330	0.82214(6)	0.0302
C1	0.5527(3)	0.2217(3)	0.62243(16)	0.0454
C2	0.5045(3)	0.2341(4)	0.57236(17)	0.0548
H2	0.53170	0.30000	0.55290	0.0660
C3	0.4109(4)	0.1439(5)	0.5501(2)	0.0831
H3	0.37520	0.15120	0.51620	0.1000
C4	0.3745(5)	0.0532(5)	0.5756(2)	0.0934
H4	0.31250	-0.00520	0.56090	0.1120
C5	0.4272(6)	0.0424(4)	0.6245(2)	0.0889
H5	0.40200	-0.02490	0.64160	0.1070
C6	0.5136(4)	0.1243(3)	0.64902(17)	0.0534
C8	0.5612(3)	0.1189(3)	0.83332(15)	0.0394
C9	0.5358(3)	0.0227(3)	0.85936(18)	0.0481
H9	0.48150	-0.04000	0.84220	0.0580
C10	0.5884(4)	0.0185(3)	0.9091(2)	0.0570
H10	0.56990	-0.04720	0.92660	0.0680
C11	0.6683(4)	0.1082(3)	0.93426(19)	0.0526
H11	0.70800	0.10480	0.96730	0.0630
C12	0.6898(3)	0.2048(3)	0.90994(16)	0.0428
H12	0.74120	0.26710	0.92900	0.0510
C13	0.6392(3)	0.2120(3)	0.85970(14)	0.0322
S2	0.55584(8)	0.72898(8)	0.73240(4)	0.0446
C20	0.5475(2)	0.8154(3)	0.78980(15)	0.0351
H20A	0.60710	0.88730	0.78560	0.0420
H20B	0.48190	0.81710	0.78490	0.0420
P3	0.33330	0.66670	0.67837(6)	0.0384
P4	0.33330	0.66670	0.84769(6)	0.0318
C14	0.4524(4)	0.7670(3)	0.63940(17)	0.0507
C15	0.4519(5)	0.8202(4)	0.5879(2)	0.0704
H15	0.38750	0.80580	0.57030	0.0840
C16	0.5442(5)	0.8940(5)	0.5620(3)	0.0776
H16	0.54220	0.92520	0.52460	0.0930

C17	0.6370(6)	0.9234(5)	0.5879(3)	0.1001
H17	0.69920	0.97960	0.57160	0.1200
C18	0.6401(4)	0.8686(4)	0.6399(2)	0.0631
H18	0.70510	0.88350	0.65690	0.0760
C19	0.5502(3)	0.7951(3)	0.66527(18)	0.0496
C21	0.5504(3)	0.7698(3)	0.85229(15)	0.0363
C22	0.6462(3)	0.7978(3)	0.87759(18)	0.0471
H22	0.70810	0.84430	0.85620	0.0560
C23	0.6535(3)	0.7583(4)	0.9346(2)	0.0543
H23	0.71960	0.77770	0.95170	0.0650
C24	0.5623(3)	0.6903(3)	0.96556(16)	0.0441
H24	0.56600	0.66170	1.00360	0.0530
C25	0.4667(3)	0.6646(3)	0.94127(15)	0.0379
H25	0.40520	0.61960	0.96340	0.0460
C26	0.4577(3)	0.7034(2)	0.88412(15)	0.0338
S1A	0.5835(3)	0.1094(4)	0.71048(17)	0.0462
C7A	0.4948(19)	0.1037(14)	0.7751(8)	0.0391
H7AA	0.47760	0.16000	0.77120	0.0470
H7AB	0.42930	0.03560	0.77590	0.0470

Table 21. Atomic coordinates and equivalent isotropic displacement parameters for compound **240 • 2($CHCl_3$) • H_2O**

Atom	X	Y	Z	U_{equiv}
S1	0.36486(3)	0.222212(19)	0.28046(2)	0.0148
S2	0.33992(3)	0.436643(18)	0.12635(2)	0.0148
S3	0.66815(3)	0.325490(19)	0.19626(2)	0.0147
P1	0.44324(3)	0.293131(19)	0.12577(2)	0.0123
H1P	0.4557(14)	0.3263(10)	0.1936(12)	0.0190
P2	0.47911(3)	0.399897(19)	0.32407(2)	0.0117
C1	0.47085(11)	0.20544(7)	0.14449(9)	0.0141
C2	0.52389(12)	0.16783(8)	0.08975(10)	0.0173
H2	0.54370	0.18790	0.04110	0.0210
C3	0.54726(12)	0.10071(8)	0.10748(11)	0.0206
H3	0.58200	0.07460	0.07010	0.0250
C4	0.52010(12)	0.07170(8)	0.17928(11)	0.0205
H4	0.53830	0.02630	0.19160	0.0250
C5	0.46634(12)	0.10871(8)	0.23346(10)	0.0179
H5	0.44740	0.08840	0.28230	0.0210
C6	0.44037(11)	0.17546(7)	0.21586(9)	0.0143
C7	0.31238(11)	0.30251(7)	0.08626(9)	0.0133
C8	0.25390(12)	0.24673(8)	0.05932(9)	0.0165
H8	0.28540	0.20410	0.05390	0.0200
C9	0.14927(12)	0.25404(8)	0.04050(10)	0.0188
H9	0.10920	0.21630	0.02220	0.0220
C10	0.10352(12)	0.31634(9)	0.04836(10)	0.0202
H10	0.03170	0.32060	0.03750	0.0240
C11	0.16119(12)	0.37256(8)	0.07184(10)	0.0187
H11	0.12960	0.41550	0.07440	0.0230
C12	0.26589(11)	0.36587(8)	0.09164(9)	0.0146
C13	0.53184(11)	0.32513(7)	0.05828(9)	0.0146
C14	0.50369(13)	0.33533(9)	-0.02451(10)	0.0198
H14	0.43710	0.32360	-0.04690	0.0240
C15	0.57333(13)	0.36273(9)	-0.07411(10)	0.0233
H15	0.55460	0.36920	-0.13060	0.0280
C16	0.67048(13)	0.38071(9)	-0.04118(10)	0.0221
H16	0.71720	0.40050	-0.07510	0.0270
C17	0.69947(12)	0.36987(8)	0.04099(10)	0.0179
H17	0.76620	0.38180	0.06290	0.0220
C18	0.63100(11)	0.34152(7)	0.09132(9)	0.0141
C19	0.46055(11)	0.24626(8)	0.36335(9)	0.0147

H19A	0.48550	0.20590	0.39440	0.0180
H19B	0.51940	0.26860	0.34090	0.0180
C20	0.28322(11)	0.45009(8)	0.22367(9)	0.0161
H20A	0.21130	0.46460	0.21340	0.0190
H20B	0.28500	0.40780	0.25570	0.0190
C21	0.67635(12)	0.41352(8)	0.23154(9)	0.0156
H21A	0.73430	0.43620	0.20820	0.0190
H21B	0.61300	0.43780	0.21250	0.0190
C22	0.40842(11)	0.29413(7)	0.41808(9)	0.0137
C23	0.35447(12)	0.26682(8)	0.47994(10)	0.0179
H23	0.35360	0.21940	0.48740	0.0210
C24	0.30212(12)	0.30795(9)	0.53069(10)	0.0208
H24	0.26610	0.28880	0.57270	0.0250
C25	0.30286(12)	0.37729(9)	0.51944(10)	0.0191
H25	0.26700	0.40570	0.55360	0.0230
C26	0.35627(12)	0.40522(8)	0.45799(9)	0.0162
H26	0.35600	0.45270	0.45060	0.0190
C27	0.41023(11)	0.36458(7)	0.40708(9)	0.0128
C28	0.34495(11)	0.50388(8)	0.26973(9)	0.0140
C29	0.31354(12)	0.57080(8)	0.26159(9)	0.0171
H29	0.25200	0.58120	0.22960	0.0210
C30	0.37075(12)	0.62248(8)	0.29958(9)	0.0182
H30	0.34840	0.66790	0.29360	0.0220
C31	0.46073(12)	0.60745(8)	0.34636(10)	0.0174
H31	0.50060	0.64260	0.37200	0.0210
C32	0.49245(12)	0.54080(8)	0.35566(9)	0.0150
H32	0.55380	0.53090	0.38810	0.0180
C33	0.43566(11)	0.48814(7)	0.31814(9)	0.0130
C34	0.69119(11)	0.41580(7)	0.32350(9)	0.0143
C35	0.78962(12)	0.42606(8)	0.36033(10)	0.0177
H35	0.84510	0.43030	0.32720	0.0210
C36	0.80756(12)	0.43019(8)	0.44484(10)	0.0188
H36	0.87490	0.43730	0.46900	0.0220
C37	0.72721(12)	0.42398(8)	0.49387(10)	0.0171
H37	0.73930	0.42660	0.55160	0.0210
C38	0.62877(12)	0.41384(7)	0.45787(9)	0.0148
H38	0.57390	0.40970	0.49160	0.0180
C39	0.60898(11)	0.40966(7)	0.37311(9)	0.0128
Cl1	0.94329(3)	0.46103(2)	0.14743(2)	0.0223
O1	0.07730(11)	0.57292(7)	0.05188(9)	0.0354
H1A	0.03840	0.54570	0.07680	0.0420

H1B	0.07490	0.56190	0.00080	0.0420
C40	0.75977(13)	0.58810(9)	0.16681(10)	0.0211
H40	0.82580	0.56360	0.17840	0.0250
Cl2	0.68867(4)	0.54766(2)	0.08585(3)	0.0311
Cl3	0.78629(4)	0.67227(2)	0.14101(3)	0.0324
Cl4	0.69371(5)	0.58718(3)	0.25530(3)	0.0423
C41	0.03605(13)	0.34297(9)	0.29244(11)	0.0236
H41	0.01720	0.37110	0.24300	0.0280
Cl5	0.14794(3)	0.29758(2)	0.27733(3)	0.0319
Cl6	0.06073(4)	0.39666(3)	0.37784(3)	0.0331
Cl7	-0.06483(4)	0.28719(3)	0.30697(5)	0.0497

Table 22. Atomic coordinates and equivalent isotropic displacement parameters for compound **241 • 1.5(C_2H_6OS)**

Atom	X	Y	Z	U_{equiv}
S1	0.33343(10)	0.66572(17)	0.25323(10)	0.0270
S2	0.04387(10)	0.55636(17)	0.24581(10)	0.0271
S3	0.12172(11)	1.04417(18)	0.25161(11)	0.0316
P1	0.16782(11)	0.76133(18)	0.30979(10)	0.0252
P2	0.17709(11)	0.75532(19)	0.13342(10)	0.0249
O1	0.2668(3)	0.5874(5)	0.2460(3)	0.0297
O2	0.4056(3)	0.6042(5)	0.2506(3)	0.0330
O3	0.0302(3)	0.6916(5)	0.2413(3)	0.0347
O4	-0.0212(3)	0.4740(5)	0.2404(3)	0.0347
O5	0.1035(3)	1.1757(5)	0.2462(3)	0.0390
O6	0.1998(3)	1.0105(5)	0.2502(3)	0.0337
C1	0.2593(4)	0.7896(7)	0.3493(4)	0.0243
C2	0.3280(5)	0.7473(8)	0.3241(4)	0.0263
C3	0.3958(5)	0.7704(8)	0.3527(4)	0.0313
H3	0.44130	0.74100	0.33470	0.0380
C4	0.3977(5)	0.8379(8)	0.4087(4)	0.0337
H4	0.44440	0.85290	0.42870	0.0400
C5	0.3327(5)	0.8814(7)	0.4341(4)	0.0290
H5	0.33420	0.92850	0.47130	0.0340
C6	0.2636(5)	0.8571(8)	0.4055(4)	0.0293
H6	0.21850	0.88650	0.42420	0.0350
C7	0.1393(5)	0.6095(7)	0.3465(4)	0.0280
C8	0.0886(4)	0.5243(7)	0.3184(4)	0.0263
C9	0.0724(5)	0.4059(8)	0.3437(4)	0.0317
H9	0.03950	0.34930	0.32290	0.0380
C10	0.1037(5)	0.3723(9)	0.3981(5)	0.0380
H10	0.09260	0.29190	0.41550	0.0460
C11	0.1515(5)	0.4537(8)	0.4283(4)	0.0327
H11	0.17290	0.42910	0.46650	0.0390
C12	0.1690(5)	0.5724(8)	0.4034(4)	0.0277
H12	0.20130	0.62820	0.42520	0.0330
C13	0.1043(5)	0.8746(7)	0.3507(4)	0.0297
C14	0.0820(5)	0.9880(8)	0.3217(4)	0.0297
C15	0.0257(5)	1.0637(8)	0.3473(4)	0.0343
H15	0.00860	1.13710	0.32630	0.0410
C16	-0.0050(5)	1.0310(9)	0.4038(5)	0.0393
H16	-0.04410	1.08110	0.42110	0.0470

C17	0.0209(5)	0.9262(8)	0.4348(4)	0.0350
H17	0.00280	0.90740	0.47490	0.0420
C18	0.0730(4)	0.8492(8)	0.4074(4)	0.0283
H18	0.08830	0.77470	0.42840	0.0340
C19	0.3313(4)	0.7950(8)	0.1985(4)	0.0247
H19A	0.28450	0.84490	0.20380	0.0300
H19B	0.37480	0.85180	0.20530	0.0300
C20	0.1137(5)	0.5074(8)	0.1901(4)	0.0273
H20A	0.16190	0.55130	0.19830	0.0330
H20B	0.12230	0.41500	0.19340	0.0330
C21	0.0731(5)	0.9579(8)	0.1942(4)	0.0310
H21A	0.07910	0.86580	0.20150	0.0370
H21B	0.01880	0.97840	0.19570	0.0370
C22	0.3345(4)	0.7396(7)	0.1336(4)	0.0247
C23	0.4043(5)	0.7119(8)	0.1087(4)	0.0350
H23	0.44830	0.73240	0.13150	0.0420
C24	0.4120(5)	0.6553(9)	0.0518(4)	0.0363
H24	0.46020	0.63190	0.03680	0.0430
C25	0.3467(5)	0.6329(7)	0.0163(4)	0.0287
H25	0.35100	0.59760	-0.02370	0.0350
C26	0.2774(5)	0.6621(8)	0.0398(4)	0.0320
H26	0.23370	0.64470	0.01600	0.0390
C27	0.2695(5)	0.7172(7)	0.0982(4)	0.0287
C28	0.1136(4)	0.6465(8)	0.0944(4)	0.0283
C29	0.0855(5)	0.6669(8)	0.0338(4)	0.0290
H29	0.10270	0.73850	0.01130	0.0350
C30	0.0340(5)	0.5862(9)	0.0063(5)	0.0387
H30	0.01700	0.60210	-0.03440	0.0470
C31	0.0072(5)	0.4817(9)	0.0387(4)	0.0350
H31	-0.02870	0.42650	0.02050	0.0420
C32	0.0336(5)	0.4589(8)	0.0980(5)	0.0377
H32	0.01560	0.38700	0.11970	0.0450
C33	0.0864(5)	0.5395(7)	0.1268(4)	0.0270
C34	0.1056(5)	0.9933(8)	0.1307(4)	0.0280
C35	0.0878(5)	1.1096(8)	0.1052(5)	0.0357
H35	0.05540	1.16500	0.12720	0.0430
C36	0.1159(5)	1.1480(8)	0.0484(4)	0.0343
H36	0.10440	1.22960	0.03250	0.0410
C37	0.1614(5)	1.0638(9)	0.0153(5)	0.0380
H37	0.18020	1.08750	-0.02400	0.0460
C38	0.1794(5)	0.9461(8)	0.0396(4)	0.0317

H38	0.21090	0.89070	0.01670	0.0380
C39	0.1523(5)	0.9072(8)	0.0965(4)	0.0310
S4	0.79017(15)	0.2869(2)	0.36527(12)	0.0461
O7	0.8352(6)	0.2201(8)	0.4115(4)	0.0740
C40	0.8550(6)	0.3733(11)	0.3203(6)	0.0547
H40A	0.88330	0.43150	0.34670	0.0820
H40B	0.82780	0.42180	0.28890	0.0820
H40C	0.89000	0.31450	0.30020	0.0820
C41	0.7690(6)	0.1752(10)	0.3060(5)	0.0487
H41A	0.81380	0.12380	0.29740	0.0730
H41B	0.75390	0.22040	0.26860	0.0730
H41C	0.72790	0.11990	0.31950	0.0730
S5	0.8299(4)	0.2404(5)	0.0827(3)	0.0550
O8	0.8927(9)	0.2416(12)	0.0473(7)	0.0520
C42	0.8237(8)	0.3814(14)	0.1288(7)	0.0210
H42A	0.83720	0.45520	0.10380	0.0310
H42B	0.85840	0.37470	0.16370	0.0310
H42C	0.77210	0.39110	0.14410	0.0310
C43	0.7942(15)	0.136(2)	0.1274(12)	0.0627
H43A	0.79550	0.05310	0.10720	0.0940
H43B	0.74190	0.15860	0.13670	0.0940
H43C	0.82330	0.13250	0.16570	0.0940

Table 23. Atomic coordinates and equivalent isotropic displacement parameters for compound **257**

Atom	X	Y	Z	U_{equiv}
S1	0.50544(5)	0.56151(5)	0.33257(5)	0.0240
S2	0.32145(4)	0.66905(5)	0.24085(5)	0.0205
S3	0.31328(5)	0.43471(5)	0.27361(5)	0.0231
P1	0.43138(5)	0.53739(5)	0.16926(5)	0.0186
N1	0.34332(16)	0.56807(17)	0.36492(16)	0.0225
C1	0.52762(19)	0.51489(19)	0.16544(18)	0.0206
C2	0.5556(2)	0.4599(2)	0.12403(19)	0.0223
H2	0.52450	0.43340	0.09480	0.0270
C3	0.6283(2)	0.4435(2)	0.1252(2)	0.0253
H3	0.64630	0.40590	0.09700	0.0300
C4	0.6744(2)	0.4816(2)	0.1671(2)	0.0278
H4	0.72430	0.47100	0.16710	0.0330
C5	0.6472(2)	0.5361(2)	0.2095(2)	0.0266
H5	0.67890	0.56210	0.23870	0.0320
C6	0.5743(2)	0.55275(19)	0.20958(19)	0.0221
C7	0.5456(2)	0.6087(2)	0.2589(2)	0.0262
H7A	0.50910	0.63870	0.23560	0.0310
H7B	0.58500	0.64020	0.27490	0.0310
C8	0.4261(2)	0.61155(19)	0.10748(18)	0.0206
C9	0.48160(19)	0.62984(19)	0.0621(2)	0.0219
H9	0.52460	0.60240	0.06250	0.0260
C10	0.4755(2)	0.6872(2)	0.0164(2)	0.0238
H10	0.51380	0.69880	-0.01390	0.0290
C11	0.4128(2)	0.72723(19)	0.01585(19)	0.0220
H11	0.40770	0.76630	-0.01520	0.0260
C12	0.35742(19)	0.71004(19)	0.06071(19)	0.0211
H12	0.31470	0.73790	0.05980	0.0250
C13	0.36249(19)	0.65342(19)	0.10689(18)	0.0206
C14	0.30037(19)	0.6360(2)	0.15377(19)	0.0219
H14A	0.29240	0.58350	0.15500	0.0260
H14B	0.25610	0.65930	0.13650	0.0260
C15	0.39307(19)	0.46382(19)	0.11888(19)	0.0205
C16	0.37766(19)	0.46883(19)	0.0479(2)	0.0216
H16	0.38590	0.51270	0.02420	0.0260
C17	0.3504(2)	0.4098(2)	0.0120(2)	0.0250
H17	0.33840	0.41400	-0.03550	0.0300
C18	0.3409(2)	0.3460(2)	0.0455(2)	0.0275

H18	0.32460	0.30530	0.02050	0.0330
C19	0.3551(2)	0.3400(2)	0.1165(2)	0.0254
H19	0.34770	0.29550	0.13930	0.0310
C20	0.37953(19)	0.39842(19)	0.1535(2)	0.0219
C21	0.3906(2)	0.3921(2)	0.2307(2)	0.0252
H21A	0.43570	0.41640	0.24440	0.0300
H21B	0.39390	0.34090	0.24420	0.0300
C22	0.4583(2)	0.6342(2)	0.37102(19)	0.0246
C23	0.4948(2)	0.6963(2)	0.3883(2)	0.0292
H23	0.54540	0.69820	0.38220	0.0350
C24	0.4593(2)	0.7562(2)	0.4145(2)	0.0360
H24	0.48530	0.79850	0.42530	0.0430
C25	0.3862(2)	0.7536(2)	0.4248(2)	0.0350
H25	0.36140	0.79450	0.44170	0.0420
C26	0.3487(2)	0.6903(2)	0.4102(2)	0.0284
H26	0.29860	0.68800	0.41910	0.0340
C27	0.3839(2)	0.6305(2)	0.38276(19)	0.0221
C28	0.25338(19)	0.62412(19)	0.28826(18)	0.0198
C29	0.1815(2)	0.6325(2)	0.2700(2)	0.0240
H29	0.16930	0.66370	0.23300	0.0290
C30	0.1274(2)	0.5961(2)	0.3046(2)	0.0264
H30	0.07880	0.60150	0.29050	0.0320
C31	0.1443(2)	0.5517(2)	0.3599(2)	0.0262
H31	0.10760	0.52640	0.38370	0.0310
C32	0.2153(2)	0.5447(2)	0.3801(2)	0.0256
H32	0.22660	0.51600	0.41920	0.0310
C33	0.2707(2)	0.5789(2)	0.34418(19)	0.0223
C34	0.3469(2)	0.4362(2)	0.3595(2)	0.0246
C35	0.3607(2)	0.3707(2)	0.3925(2)	0.0310
H35	0.34830	0.32710	0.37010	0.0370
C36	0.3922(2)	0.3686(2)	0.4579(2)	0.0347
H36	0.40140	0.32390	0.47980	0.0420
C37	0.4096(2)	0.4316(3)	0.4900(2)	0.0342
H37	0.43280	0.43040	0.53370	0.0410
C38	0.3938(2)	0.4979(2)	0.4592(2)	0.0294
H38	0.40490	0.54120	0.48290	0.0350
C39	0.36199(19)	0.5009(2)	0.3943(2)	0.0241

Table 24. Atomic coordinates and equivalent isotropic displacement parameters for compound **275**

Atom	X	Y	Z	U_{equiv}
S1	0.80843(3)	0.57753(3)	0.96431(3)	0.0359
P1	0.66670	0.33330	0.74234(5)	0.0299
Si1	0.66670	0.33330	1.09801(5)	0.0283
C1	0.80228(12)	0.44989(13)	1.15714(12)	0.0311
C2	0.84857(14)	0.43783(15)	1.26263(12)	0.0381
H2	0.81430	0.36740	1.30110	0.0460
C3	0.94318(14)	0.52636(16)	1.31190(14)	0.0444
H3	0.97260	0.51630	1.38370	0.0530
C4	0.99453(14)	0.62881(16)	1.25698(15)	0.0474
H4	1.05850	0.68990	1.29160	0.0570
C5	0.95270(14)	0.64269(15)	1.15107(14)	0.0424
H5	0.98910	0.71300	1.11230	0.0510
C6	0.85799(13)	0.55447(13)	1.10147(12)	0.0327
C7	0.87657(13)	0.52735(14)	0.86168(12)	0.0346
H7A	0.95820	0.56780	0.87530	0.0410
H7B	0.84780	0.44660	0.87400	0.0410
C8	0.85112(13)	0.54825(13)	0.73686(12)	0.0339
C9	0.92172(14)	0.65249(15)	0.68636(15)	0.0435
H9	0.98490	0.70610	0.72940	0.0520
C10	0.90118(15)	0.67916(15)	0.57415(15)	0.0462
H10	0.95000	0.75040	0.54090	0.0550
C11	0.80962(14)	0.60162(14)	0.51160(13)	0.0406
H11	0.79500	0.61940	0.43500	0.0490
C12	0.73912(14)	0.49821(14)	0.56013(12)	0.0363
H12	0.67580	0.44570	0.51650	0.0440
C13	0.75876(13)	0.46903(13)	0.67219(12)	0.0311
H1	0.66670	0.33330	0.981(2)	0.0210

Table 25. Atomic coordinates and equivalent isotropic displacement parameters for compound **277 • 0.125(CH_2Cl_2)**

Atom	X	Y	Z	U_{equiv}
S1	0.3356(3)	0.1769(3)	0.7932(3)	0.0454
S2	0.6300(3)	0.1611(3)	0.5146(3)	0.0433
S3	0.3412(3)	0.4593(3)	0.5064(3)	0.0442
P1	0.5231(3)	0.3407(3)	0.6828(3)	0.0365
Si1	0.3462(4)	0.1845(4)	0.5365(4)	0.0469
C1	0.4456(12)	0.3500(13)	0.8284(12)	0.0407
C2	0.4170(14)	0.4496(13)	0.8579(13)	0.0465
H2	0.44890	0.51140	0.80620	0.0550
C3	0.3439(15)	0.4571(14)	0.9604(14)	0.0515
H3	0.32700	0.52510	0.97920	0.0620
C4	0.2920(14)	0.3734(16)	1.0401(13)	0.0529
H4	0.23940	0.38300	1.11110	0.0630
C5	0.3215(13)	0.2711(14)	1.0099(12)	0.0481
H5	0.28850	0.21030	1.06240	0.0570
C6	0.3975(13)	0.2591(12)	0.9057(12)	0.0377
C7	0.4278(16)	0.1481(13)	0.8789(14)	0.0506
H7A	0.41260	0.08410	0.94950	0.0610
H7B	0.51470	0.12130	0.83780	0.0610
C8	0.6826(13)	0.2530(12)	0.6826(12)	0.0399
C9	0.7272(15)	0.2152(13)	0.7737(12)	0.0466
H9	0.67680	0.24180	0.83790	0.0560
C10	0.8433(15)	0.1402(15)	0.7694(13)	0.0514
H10	0.87240	0.11620	0.83120	0.0610
C11	0.9191(13)	0.0983(12)	0.6801(14)	0.0459
H11	0.99890	0.04470	0.67990	0.0550
C12	0.8751(12)	0.1372(11)	0.5884(13)	0.0374
H12	0.92660	0.10970	0.52490	0.0450
C13	0.7600(12)	0.2136(11)	0.5882(11)	0.0356
C14	0.7200(14)	0.2492(15)	0.4866(13)	0.0479
H14A	0.79180	0.23630	0.42140	0.0580
H14B	0.67110	0.33470	0.46840	0.0580
C15	0.5280(13)	0.4917(12)	0.6045(12)	0.0411
C16	0.6300(13)	0.5233(13)	0.5752(13)	0.0454
H16	0.69620	0.46790	0.60460	0.0540
C17	0.6338(15)	0.6340(14)	0.5043(15)	0.0564
H17	0.70220	0.65460	0.48700	0.0680
C18	0.5419(16)	0.7149(13)	0.4582(13)	0.0534

H18	0.54700	0.79020	0.40820	0.0640
C19	0.4384(15)	0.6851(12)	0.4860(13)	0.0477
H19	0.37380	0.74040	0.45430	0.0570
C20	0.4321(12)	0.5745(12)	0.5599(11)	0.0360
C21	0.3201(14)	0.5442(15)	0.5943(17)	0.0568
H21A	0.24980	0.61810	0.58560	0.0690
H21B	0.30350	0.49630	0.67420	0.0690
C22	0.4131(13)	0.0462(13)	0.7514(14)	0.0437
C23	0.4625(15)	-0.0617(14)	0.8211(16)	0.0593
H23	0.44940	-0.06800	0.89640	0.0710
C24	0.5303(17)	-0.1607(16)	0.7854(18)	0.0693
H24	0.57100	-0.23160	0.83330	0.0830
C25	0.5405(15)	-0.1594(16)	0.6827(19)	0.0656
H25	0.58400	-0.22950	0.66000	0.0780
C26	0.4847(14)	-0.0512(15)	0.6106(16)	0.0570
H26	0.49120	-0.04970	0.53890	0.0680
C27	0.4185(13)	0.0567(13)	0.6418(14)	0.0479
C28	0.5759(14)	0.2376(12)	0.3942(13)	0.0407
C29	0.6451(15)	0.2834(14)	0.2914(14)	0.0508
H29	0.72560	0.27350	0.28270	0.0610
C30	0.6009(19)	0.3434(15)	0.2004(15)	0.0629
H30	0.64960	0.37750	0.13000	0.0760
C31	0.4855(17)	0.3547(14)	0.2101(16)	0.0602
H31	0.45450	0.39790	0.14700	0.0730
C32	0.4169(15)	0.3038(13)	0.3103(15)	0.0499
H32	0.33880	0.31080	0.31490	0.0600
C33	0.4574(14)	0.2396(13)	0.4098(14)	0.0468
C34	0.2087(12)	0.4188(12)	0.5805(12)	0.0374
C35	0.0976(14)	0.4991(15)	0.6166(15)	0.0557
H35	0.09190	0.57870	0.59970	0.0670
C36	-0.0022(15)	0.4690(16)	0.6745(15)	0.0592
H36	-0.07490	0.52510	0.70420	0.0720
C37	-0.0021(14)	0.3601(16)	0.6919(14)	0.0548
H37	-0.07470	0.34120	0.73040	0.0650
C38	0.1046(15)	0.2772(14)	0.6530(14)	0.0507
H38	0.10530	0.20040	0.66610	0.0610
C39	0.2153(13)	0.3048(13)	0.5925(13)	0.0460
O40	0.2756(10)	0.1375(10)	0.4990(11)	0.0657
C41	0.3155(18)	0.0602(17)	0.4373(17)	0.0687
H41A	0.31750	-0.02030	0.48920	0.0820
H41B	0.39890	0.05560	0.38830	0.0820

C42	0.2344(19)	0.101(2)	0.3664(19)	0.0868
H42A	0.26580	0.04620	0.32260	0.1300
H42B	0.23180	0.18090	0.31540	0.1300
H42C	0.15260	0.10230	0.41490	0.1300
S4	0.1734(3)	0.6568(3)	0.1562(3)	0.0316
S5	-0.0090(3)	0.9934(3)	0.0019(3)	0.0320
S6	-0.1676(3)	0.8199(3)	0.3255(3)	0.0329
P2	0.0820(3)	0.9083(3)	0.2294(3)	0.0274
Si2	-0.0855(3)	0.7458(3)	0.0814(3)	0.0270
C43	0.2488(11)	0.8438(11)	0.2051(10)	0.0286
C44	0.3203(12)	0.9133(12)	0.1678(11)	0.0360
H44	0.28420	0.99690	0.15420	0.0430
C45	0.4464(12)	0.8592(12)	0.1502(12)	0.0401
H45	0.49560	0.90590	0.12620	0.0480
C46	0.4977(14)	0.7389(13)	0.1680(12)	0.0446
H46	0.58280	0.70220	0.15480	0.0540
C47	0.4257(13)	0.6704(12)	0.2050(12)	0.0399
H47	0.46190	0.58680	0.21860	0.0480
C48	0.3023(11)	0.7222(11)	0.2224(10)	0.0310
C49	0.2269(12)	0.6422(11)	0.2666(11)	0.0335
H49A	0.15660	0.66400	0.33010	0.0410
H49B	0.27650	0.55850	0.29460	0.0410
C50	0.0565(10)	1.0683(10)	0.1709(10)	0.0261
C51	0.0186(12)	1.1410(12)	0.2360(12)	0.0359
H51	0.00980	1.10650	0.31430	0.0430
C52	-0.0069(12)	1.2631(11)	0.1897(12)	0.0381
H52	-0.02910	1.31090	0.23520	0.0450
C53	0.0004(12)	1.3144(12)	0.0772(13)	0.0408
H53	-0.02040	1.39810	0.04470	0.0490
C54	0.0384(13)	1.2417(12)	0.0127(12)	0.0402
H54	0.04630	1.27660	-0.06530	0.0480
C55	0.0651(12)	1.1217(11)	0.0567(11)	0.0310
C56	0.1080(13)	1.0482(12)	-0.0220(11)	0.0359
H56A	0.18200	0.98020	-0.00900	0.0420
H56B	0.12830	1.09790	-0.10090	0.0420
C57	0.0282(12)	0.8858(10)	0.3815(10)	0.0283
C58	0.1042(14)	0.8551(11)	0.4438(12)	0.0401
H58	0.18680	0.84900	0.40690	0.0480
C59	0.0601(14)	0.8330(12)	0.5613(12)	0.0430
H59	0.11150	0.81490	0.60330	0.0520
C60	-0.0580(15)	0.8379(12)	0.6139(12)	0.0451

H60	-0.08770	0.81960	0.69330	0.0550
C61	-0.1349(14)	0.8695(12)	0.5519(11)	0.0386
H61	-0.21710	0.87410	0.58890	0.0470
C62	-0.0918(12)	0.8941(11)	0.4368(11)	0.0342
C63	-0.1827(12)	0.9358(12)	0.3741(12)	0.0358
H63A	-0.17120	1.00570	0.30860	0.0430
H63B	-0.26550	0.96110	0.42400	0.0430
C64	0.0672(12)	0.5809(10)	0.2358(11)	0.0299
C65	0.0822(12)	0.4856(11)	0.3333(11)	0.0338
H65	0.15110	0.46220	0.35650	0.0410
C66	0.0038(13)	0.4264(12)	0.3951(12)	0.0388
H66	0.01750	0.36230	0.46060	0.0460
C67	-0.0992(13)	0.4593(11)	0.3626(11)	0.0356
H67	-0.15600	0.41840	0.40540	0.0430
C68	-0.1151(12)	0.5525(11)	0.2670(11)	0.0324
H68	-0.18400	0.57410	0.24450	0.0390
C69	-0.0357(12)	0.6172(10)	0.2012(10)	0.0290
C70	0.0715(12)	0.8905(12)	-0.0777(10)	0.0314
C71	0.1683(12)	0.9063(13)	-0.1724(11)	0.0378
H71	0.19110	0.97350	-0.19490	0.0460
C72	0.2316(13)	0.8283(14)	-0.2342(12)	0.0418
H72	0.29820	0.84030	-0.29800	0.0510
C73	0.1973(13)	0.7323(13)	-0.2026(12)	0.0427
H73	0.24040	0.67700	-0.24460	0.0500
C74	0.1011(12)	0.7161(12)	-0.1108(11)	0.0374
H74	0.07750	0.65030	-0.09210	0.0440
C75	0.0368(11)	0.7904(11)	-0.0442(10)	0.0310
C76	-0.2504(12)	0.9068(11)	0.2228(11)	0.0305
C77	-0.3520(12)	1.0069(12)	0.2411(12)	0.0386
H77	-0.37780	1.02490	0.30900	0.0460
C78	-0.4153(13)	1.0796(12)	0.1630(13)	0.0428
H78	-0.48570	1.14560	0.17750	0.0510
C79	-0.3741(13)	1.0545(12)	0.0632(13)	0.0414
H79	-0.41350	1.10630	0.00630	0.0500
C80	-0.2758(13)	0.9545(11)	0.0456(12)	0.0368
H80	-0.25080	0.93760	-0.02280	0.0440
C81	-0.2112(11)	0.8763(10)	0.1257(10)	0.0274
O82	-0.1428(8)	0.6864(7)	0.0394(7)	0.0319
C83	-0.1867(13)	0.7321(12)	-0.0527(12)	0.0375
H83A	-0.14410	0.78630	-0.11470	0.0460
H83B	-0.27400	0.77820	-0.03210	0.0460

C84	-0.1682(17)	0.6352(14)	-0.0899(15)	0.0587
H84A	-0.19880	0.66850	-0.15500	0.0880
H84B	-0.21170	0.58250	-0.02880	0.0880
H84C	-0.08160	0.59000	-0.11070	0.0880
C85	0.656(6)	0.418(5)	0.907(7)	0.0776
H85A	0.68000	0.43680	0.82400	0.0920
H85B	0.60030	0.37190	0.93780	0.0920
Cl1	0.7808(15)	0.3274(19)	0.9492(14)	0.0681
Cl2	0.575(2)	0.5469(14)	0.9374(18)	0.0764

Table 26. Atomic coordinates and equivalent isotropic displacement parameters for compound **278 • 0.5(C_6H_6) • $CHCl_3$**

Atom	X	Y	Z	U_{equiv}
S1	0.80616(10)	0.23620(10)	0.52699(11)	0.0234
Si1	0.66670	0.33330	0.3847(2)	0.0195
H1A	0.66670	0.33330	0.496(9)	0.0230
Si2	0.66670	0.33330	0.7738(2)	0.0211
H2A	0.66670	0.33330	0.661(9)	0.0250
C1	0.8027(4)	0.3541(4)	0.3308(4)	0.0211
C2	0.8511(4)	0.4129(4)	0.2282(5)	0.0262
H2	0.81610	0.44590	0.18690	0.0310
C3	0.9490(4)	0.4247(4)	0.1845(5)	0.0287
H3	0.98010	0.46470	0.11420	0.0340
C4	1.0003(4)	0.3773(4)	0.2448(5)	0.0291
H4	1.06660	0.38390	0.21490	0.0350
C5	0.9564(4)	0.3209(4)	0.3475(5)	0.0260
H5	0.99310	0.28970	0.38890	0.0310
C6	0.8578(4)	0.3093(4)	0.3917(4)	0.0214
C7	0.8775(4)	0.3503(4)	0.6316(4)	0.0234
H7A	0.95760	0.39020	0.61520	0.0280
H7B	0.85010	0.40280	0.62320	0.0280
C8	0.8564(4)	0.3042(4)	0.7561(5)	0.0241
C9	0.9274(4)	0.2697(4)	0.8009(5)	0.0302
H9	0.98540	0.27520	0.75300	0.0360
C10	0.9146(5)	0.2281(5)	0.9132(5)	0.0320
H10	0.96480	0.20710	0.94260	0.0390
C11	0.8287(5)	0.2169(4)	0.9831(5)	0.0297
H11	0.81900	0.18750	1.06010	0.0360
C12	0.7570(4)	0.2492(4)	0.9387(5)	0.0258
H12	0.69790	0.24130	0.98650	0.0310
C13	0.7691(4)	0.2935(4)	0.8253(4)	0.0224
C14	0.9494(8)	0.8858(7)	0.5025(12)	0.0868
H14	0.91500	0.80790	0.50940	0.1050
C15	1.00000	1.00000	0.772(2)	0.0931
H15	1.00000	1.00000	0.68460	0.1120
Cl1	0.86847(19)	0.97121(18)	0.8153(3)	0.0894

Table 27. Atomic coordinates and equivalent isotropic displacement parameters for compound **291 • C_6H_6**

Atom	X	Y	Z	U_{equiv}
S1	0.20718(3)	0.10048(2)	0.11729(2)	0.0187
S2	-0.04062(3)	0.26234(3)	0.40241(3)	0.0224
S3	0.01252(3)	0.40940(2)	0.11548(2)	0.0183
P1	0.23372(3)	0.32817(3)	0.22917(2)	0.0165
Si1	-0.11931(3)	0.18920(3)	0.19208(3)	0.0182
C1	-0.03091(13)	0.08391(10)	0.25135(10)	0.0183
C2	-0.10937(14)	0.03879(11)	0.33662(11)	0.0221
H2	-0.19760	0.05940	0.35450	0.0260
C3	-0.06331(15)	-0.03481(11)	0.39602(11)	0.0247
H3	-0.11910	-0.06250	0.45430	0.0300
C4	0.06487(15)	-0.06719(11)	0.36919(11)	0.0242
H4	0.09770	-0.11670	0.40970	0.0290
C5	0.14546(14)	-0.02735(10)	0.28314(11)	0.0214
H5	0.23320	-0.05190	0.26360	0.0260
C6	0.09934(13)	0.04857(10)	0.22459(10)	0.0183
C7	-0.19454(13)	0.30617(11)	0.28162(11)	0.0224
C8	-0.29357(15)	0.36884(12)	0.25864(13)	0.0317
H8	-0.31820	0.34750	0.20410	0.0380
C9	-0.35723(17)	0.46081(14)	0.31226(16)	0.0443
H9	-0.42360	0.50180	0.29420	0.0530
C10	-0.32256(18)	0.49194(14)	0.39247(16)	0.0461
H10	-0.36470	0.55500	0.42950	0.0550
C11	-0.22661(16)	0.43131(13)	0.41873(13)	0.0350
H11	-0.20420	0.45290	0.47450	0.0420
C12	-0.16217(13)	0.33904(11)	0.36476(11)	0.0236
C13	-0.02541(13)	0.22235(10)	0.05704(11)	0.0192
C14	-0.01093(14)	0.14843(11)	-0.01954(12)	0.0243
H14	-0.05540	0.09220	-0.00090	0.0290
C15	0.06564(15)	0.15401(11)	-0.12121(12)	0.0269
H15	0.07410	0.10210	-0.17080	0.0320
C16	0.12957(14)	0.23646(12)	-0.14929(11)	0.0268
H16	0.18430	0.24010	-0.21820	0.0320
C17	0.11398(13)	0.31358(11)	-0.07734(11)	0.0226
H17	0.15600	0.37100	-0.09790	0.0270
C18	0.03702(12)	0.30773(10)	0.02512(10)	0.0186
C19	-0.25455(14)	0.13397(12)	0.17971(13)	0.0281
H19A	-0.29470	0.17930	0.13750	0.0420

H19B	-0.31570	0.12880	0.24850	0.0420
H19C	-0.22360	0.06500	0.14670	0.0420
C20	0.38599(12)	0.28194(11)	0.13097(10)	0.0184
C21	0.46391(13)	0.34868(12)	0.07364(11)	0.0243
H21	0.44250	0.42070	0.09040	0.0290
C22	0.57234(14)	0.31152(12)	-0.00763(12)	0.0296
H22	0.62270	0.35830	-0.04760	0.0360
C23	0.60684(14)	0.20650(13)	-0.03024(12)	0.0290
H23	0.68180	0.18080	-0.08490	0.0350
C24	0.53169(13)	0.13891(12)	0.02710(11)	0.0236
H24	0.55670	0.06670	0.01210	0.0280
C25	0.41978(12)	0.17503(11)	0.10653(10)	0.0187
C26	0.33943(13)	0.09876(11)	0.16493(10)	0.0194
H26A	0.30730	0.11710	0.23970	0.0230
H26B	0.39030	0.02840	0.15540	0.0230
C27	0.26403(13)	0.30012(10)	0.35135(10)	0.0204
C28	0.38274(15)	0.26012(12)	0.35579(11)	0.0270
H28	0.45320	0.25270	0.29410	0.0320
C29	0.39956(17)	0.23093(13)	0.44925(13)	0.0351
H29	0.48100	0.20360	0.45130	0.0420
C30	0.29736(18)	0.24181(14)	0.53921(12)	0.0371
H30	0.30830	0.22060	0.60300	0.0450
C31	0.17929(16)	0.28356(13)	0.53641(11)	0.0314
H31	0.10990	0.29210	0.59890	0.0380
C32	0.15985(14)	0.31352(11)	0.44339(11)	0.0226
C33	0.03022(14)	0.36073(11)	0.44336(11)	0.0242
H33A	0.03540	0.41930	0.39550	0.0290
H33B	-0.02260	0.38760	0.51360	0.0290
C34	0.21962(12)	0.46955(10)	0.22467(10)	0.0182
C35	0.23700(13)	0.52871(11)	0.29990(10)	0.0217
H35	0.27150	0.49510	0.34910	0.0260
C36	0.20452(13)	0.63617(11)	0.30377(11)	0.0247
H36	0.21490	0.67520	0.35640	0.0300
C37	0.15715(13)	0.68596(11)	0.23087(11)	0.0240
H37	0.13300	0.75910	0.23430	0.0290
C38	0.14506(12)	0.62861(11)	0.15280(11)	0.0215
H38	0.11610	0.66330	0.10110	0.0260
C39	0.17464(12)	0.52106(10)	0.14902(10)	0.0183
C40	0.15792(13)	0.46203(11)	0.06356(10)	0.0195
H40A	0.23010	0.40510	0.03650	0.0230
H40B	0.15370	0.50870	0.00610	0.0230

C41	0.43867(18)	0.10423(18)	0.76166(16)	0.0488
H41	0.37750	0.08030	0.81900	0.0590
C42	0.46302(19)	0.2029(2)	0.7629(2)	0.0666
H42	0.41910	0.24740	0.82160	0.0800
C43	0.5515(2)	0.23751(18)	0.6787(3)	0.0706
H43	0.56670	0.30630	0.67930	0.0850
C44	0.61805(17)	0.17256(16)	0.59335(18)	0.0477
H44	0.67960	0.19590	0.53590	0.0570
C45	0.59337(16)	0.07371(15)	0.59347(14)	0.0389
H45	0.63840	0.02810	0.53590	0.0470
C46	0.50361(17)	0.04081(14)	0.67681(15)	0.0408
H46	0.48630	-0.02720	0.67550	0.0490

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