X-RAY CRYSTALLOGRAPHIC STUDIES OF SULFUR/SELENIUM HETEROATOM COMPOUNDS

Junyi Du

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews

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X-ray Crystallographic Studies of Sulfur/Selenium Heteroatom Compounds

By

Junyi Du

A Thesis submitted

In Partial Fulfilment for the award of

Doctor of Philosophy of the University of St Andrews

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DECLARATIONS

I, Junyi Du, hereby certify that this thesis, which is approximately 37000 words in length, has been written by me, that it is the record of work carried out by me and that it has not been submitted in any previous application for a higher degree.

I was admitted as research student in September 2011 and as a candidate for the degree of Doctor of Philosophy in July 2012; the higher study for which this is a record was carried out in the University of St Andrews between 2011 and 2016.

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ABSTRACT

The major aim of research reported on this thesis uses X-ray crystallography to investigate the structural features of a series of pentafluorosulfuranyl (SF_5) containing aromatic compounds, chalcogen amides, 2,4-diaryl-1,3-selenazoles and 2,4-diaryl-1,3-chalcogen azoles bearing SF_5 group and organo phosphorus-chalcogen macrocycles incorporationg double $OP(S)SC_n$ or $OP(Se)SeC_n$ scaffolds. The basic theory of crystallography is introduced in Chapter 1, followed by a general discussion on pentafluorosulfuranyl (SF_5) containing heteroatom compounds and sulfur/selenium heterocycles in Chapter 2.

Ten pentafluorosulfuranyl (SF_5)-containing aromatic compounds have been studied crystallographically in Chapter 3. All S-F bond lengths in these compounds are very similar [1.571(3) to 1.618(3) Å and 178.5(3) to 180.0° for the C-S-F(ax) bond] and the angles of two adjacent F(eq) is approximate to 90°. The intramolecular C_{aryl}-H···F(eq) and intermolecular Caryl-H···O/N/F/Cl interactions, and π-stacking interactions are observed in the packing frameworks.

X-ray crystal structure analysis reveals that in the structures of 2,4-diaryl-1,3-selenazoles in Chapter 4, the five-membered N-C-Se-C-C rings have either planar or near-planar conformations, and exhibit a series of the intramolecular and intermolecular C-H···O/N/Se/Br/Cl) interactions and π-stacking interactions.

The crystal structures of 2,4-diaryl-1,3-chalcogen azoles with both a pentafluorosulfuranyl (SF_5) group and a five-membered N-C-Se-C-C ring have been investigated in Chapter 5. A diverse picture of molecular configuration and intramolecular/intermolecular C-H···N/Se/S and π-stacking interactions information are disclosed in selenamide, thiamides, 1,3-selenazoles and 1,3-thiazoles.

Nine organo phosphorus-chalcogen macrocycles with nine- to fifteen-membered ring incorporating double $OP(S)SC_n$ or $OP(Se)SeC_n$ scaffolds have been discussed crystallographically in Chapter 6. The similar intramolecular and intermolecular C-H···O, C-H···S or C-H···Se interactions are observed to lead to the similar packing networks.

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CHAPTER 1

AN INTRODUCTION TO CRYSTALLOGRAPHY

1.1. Introduction

Solids are very important materials in many fields because of their range of chemical and physical properties, so learning the methods of determining the chemical composition is increasingly important. Solids can be divided into two types: crystalline state and non-crystalline state (or amorphous). The difference between them is whether the arrangement is repeating regularly or not. In a crystalline solid, the arrangement patterns of each individual crystal repeats regularly throughout three-dimension space and the smallest repeating pattern is usually named the unit cell.[1] A crystalline material also can be classified into two kinds of crystals: single crystal and polycrystal. Polycrystals also include monophase and multiphase.

Since the intrinsic properties of crystals can be altered with the change of crystal structures, the invention of special crystal materials becomes possible. Therefore, researching crystal structures is an important topic. There are many ways to study a crystal structure, and most of them involve spectroscopic methods such as IR, NMR, and MS. However, these methods cannot provide detail about the three-dimensional geometry information of materials. Crystallography is a very powerful science to determine and analyse crystal structures and properties by using X-ray or neutron diffraction. X-ray crystallography is a mature science, but it is also an active science. Since *Direct Methods* were developed, solving a structure from single crystal data has become more straightforward, and consequently modern X-ray crystallography has been created. X-ray crystallography also became increasingly accessible as a consequence of the rapid improvements in computing resource.

In order to learn the properties of crystals, the structures must be determined. Crystal structure analysis is mainly divided into crystal growth, crystal choice, data collection, structure solution, structure refinement and post process analysis.

1.2. Basic Background of Crystallography

Crystallography is more than 300 years old. Its development went through six stages: crystal morphology, crystal structure geometry, crystal chemistry, quasi-crystal research, symmetry theory, and modern crystallography, along with the development of maths, physics, chemistry, material science and other modern analysis techniques in parallel. Danish academic N. Steno laid the foundation theory for crystallography. In 1784, French scientist R. J. Hauy discussed crystal structures and proposed the Law of Whole Numbers.[1] He thought crystals were symmetrical. Since then, C. S. Weiss, a German scientist refined symmetry law and suggested the existence of symmetry axis.[2] Another German scientist, J. F. C. Hessel, proposed 32 point groups in 1830.[2] In 1855, French scientist Bravais derived 14 Bravais space lattices (Figure 1-1). In 1890, 230 unique space groups were found, at the same time, the crystal limiting law was claimed.[3]

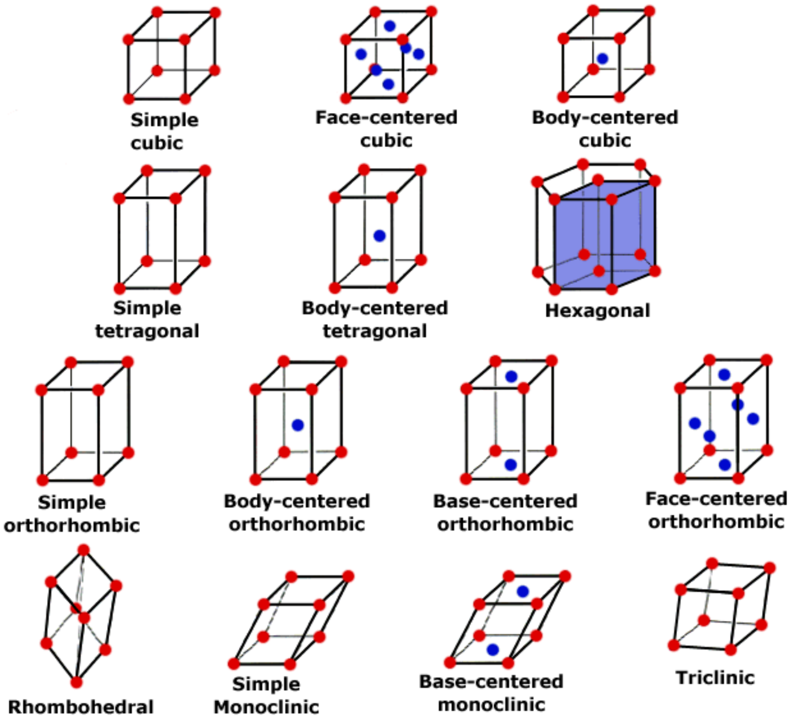

Figure 1-1. 14 Bravais lattices.

In 1895, William Roentgen discovered X-rays.[2]A hypothesis was made by M. V. Laue, suggesting that the interference could be found when an X-ray goes through a crystal in 1909. This hypothesis is very important in the study X-ray crystallography. Since then, W. H. Bragg and W. L. Bragg published the first crystal structure of sodium chloride.[2] All kinds of instruments and software enable the development of

X-ray crystallography because of the rapid development of modern science and technology.

1.2.1. Crystals

A crystal is made up of internal particles (atoms, ions, and molecules) which repeat throughout three-dimensional space (Figure 1-2).[4] There is a simple repeating unit in a crystal called the unit cell. Crystals have two forms: single crystals and polycrystals. Polycrystals are divided into two kinds, regular ones and irregular ones.

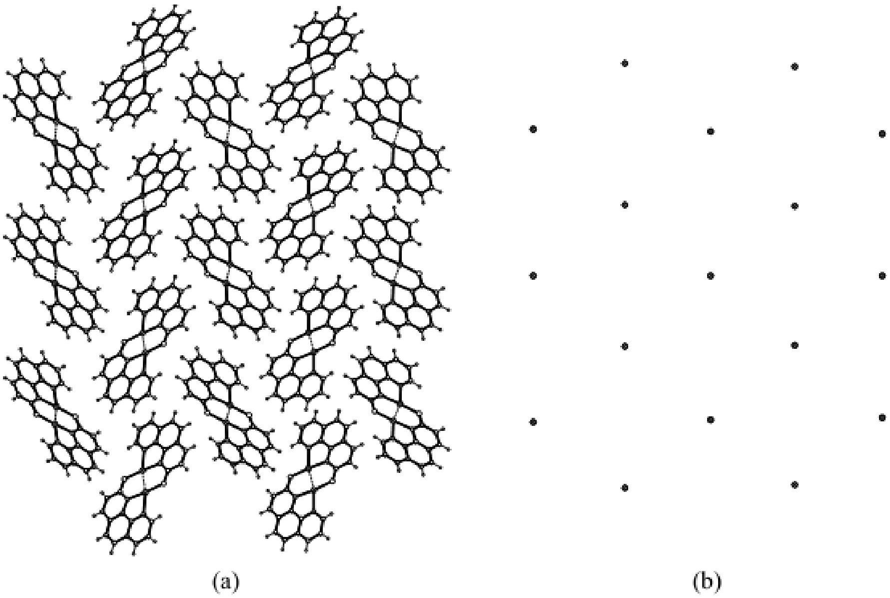

Figure 1-2. The arrangement of unit cell. (a) Molecular arrangement, (b) Abstract lattices.

1.2.2. Four Essentials of Crystal Structures

There are four structural essentials in crystal structures. The first one is particles, the atoms or ions which constitute a crystal. The second one is procession, a line which is made up of repeating particles in one direction. The third is the plane, which can form the unit cell. The last one is unit cell which can be shown in three-dimensional structures. Figure 1-3 displays the simplest repeating unit. The unit cell which gives the complete information of a crystal structure. Any crystal structure is formed by translation of the unit cell in the three-dimensional space.[3]

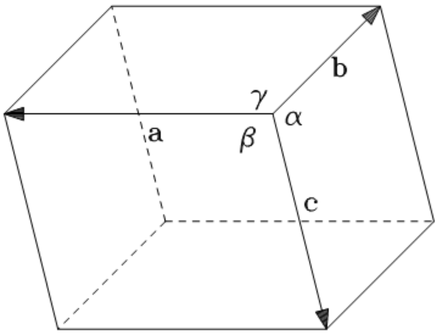

Figure 1-3. The Unit Cell.[5]

1.2.3. The Bragg Equation

The Bragg Equation[6] (Equation 1-1) explains the X-ray diffraction of crystals (Figure 1-4). The equation is shown below, where d is interplanar spacing, θ denotes the Bragg angle, λ is X-ray wavelength and n is the diffraction series:

$$2d\sin\theta = n\lambda \tag{Eqn. 1-1}$$

This equation is the theoretical foundation of single crystal diffraction.

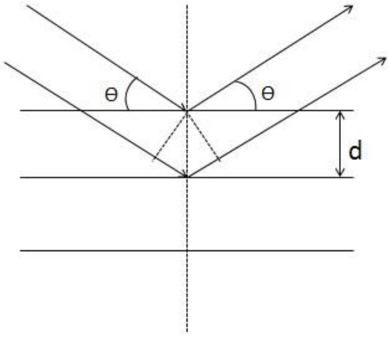

Figure 1-4. Bragg's law.

1.2.4. Space Group

A crystal has an important property called symmetry, and there are two kinds of symmetries present in a crystal: point symmetry [such as inversion center (-1), rotation axes, or mirror planes (m)] and space symmetry [lattice centring (P, C, I, F), screw axis and glide planes (a, b, c, or n)]. Different crystal lattices have different symmetries. They are divided into seven crystal systems according to the minimum symmetry characteristics (such as rotation axes and mirror planes) as shown in Table 1-1, namely, triclinic, monoclinic, orthorhombic, hexagonal, trigonal, tetragonal and cubic. In the field of crystallography, there are 230 space groups, 32 crystallographic point groups or crystal classes and 14 Bravais lattices.[3] Different symmetry operations which are in the crystals provide the space group elements. The symmetry of a crystal is bound up with its optical and electrical properties. Furthermore, a wrong assignment of symmetry can lead to failure in obtaining its structure. In crystallography, Hermann-Mauguin notation is usually used to show symmetric elements, however, in spectroscopy, the general symbol used is the Schoenflies notation.

The symbol of a space group describes all the symmetry information in the unit cell. Seven crystal systems have their own unique axis (or principle axis), for example, the principle axis is b axis in a monoclinic crystal and the principle axis are a, b, c in an orthorhombic crystal. Depending on the above information, each space group can be learned. For example, the $P2_1/c$ space group means the lattice centring is Primitive (P), and there is a screw axis (2_1) along b axis, and a c-glide plane perpendicular to b axis.

The first step in determining space groups is determining the Laue group. When using a diffractometer to test the diffraction data, the intensity of equivalence points can be used to deduce whether the crystallographic axis has symmetry. Due to the translation operations of symmetric elements, some spots disappear regularly in diffraction patterns. This is systematic absence. When systematic absence exists in a crystal, some diffracted intensity can theoretically be zero. All the symmetric elements (e.g. screw, glide plane) which have translation operations can cause systematic absences. The law of systematic absence is a significant foundation to determine a crystal’s space group. The most common systematic absences are shown in Table 1-2. Some software (e.g. PLATON or SHELXTL) can test for systematic absences.

Table 1-1. Seven crystal systems

Crystal System	Lattice Centring	Axial lengths and Angles	Symmetry Elements
Triclinic	P	$a \neq b \neq c; \alpha \neq \beta \neq \gamma$	None
Monoclinic	P, C	$a \neq b \neq c; \alpha = \gamma = 90°, \beta \neq 90°$	One 2-fold axis or mirror plane
Orthorhombic	P, I, C, F	$a \neq b \neq c; \alpha = \beta = \gamma = 90°$	Three 2-fold axis or mirror plane
Tetragonal	P, I	$a = b \neq c; \alpha = \beta = \gamma = 90°$	One 4-fold axis
Hexagonal	P	$a = b \neq c; \alpha = \beta = 90°,$ $\gamma = 120°$	One 6-fold axis
Trigonal	P, R	$a = b = c; \alpha = \beta = \gamma \neq 90°$	One 3-fold axis
Cubic	P, I, F	$a = b = c; \alpha = \beta = \gamma = 90°$	Four 3-fold axis

Table 1-2. Most Common Systematic Absences [1]

Symmetry Element	Affected Reflection	Condition
2-fold Screw (2_1)		
	a h00	h = odd
	b 0k0	k = odd
	c 00l	l = odd
Glide Planes		
b/2 (*b* glide)	a 0kl	k = odd
c/2 (*c* glide)		l = odd
b/2 + c/2 (*n* glide)		k + l = odd
a/2 (*a* glide)	b h0l	h = odd
c/2 (*c* glide)		l = odd
a/2 + c/2 (*n* glide)		h + l = odd
a/2 (*a* glide)	c hk0	h = odd
b/2 (*b* glide)		k = odd
a/2 + b/2 (*n* glide)		h + k = odd
Lattice Centering		
Primitive (**P**)	—	—
C-centered (**C**)	hkl	h + k = odd

1.2.5. The Properties of Crystals

The properties of crystals depend on the chemical composition and crystal structures. Different crystals have different chemical composition and structures. The same crystals must have the same chemical composition and structures. Crystals have symmetry, anisotropy, homogeneity and stability.

Symmetry means the same parts appearing repeatedly in Figure 1-5. The pattern and physical property of a crystal exhibit the crystal symmetry in different directions due to the symmetry of the crystal structure. The crystal properties are different with different directions, and this is crystal anisotropy. Crystal homogeneity is that different parts in a crystal have the some physical property and chemical property.[7] The stability refers to the internal energy in different states. In other words, among the different states of the same substance, the state of a crystal is the most stable because of its least internal energy.

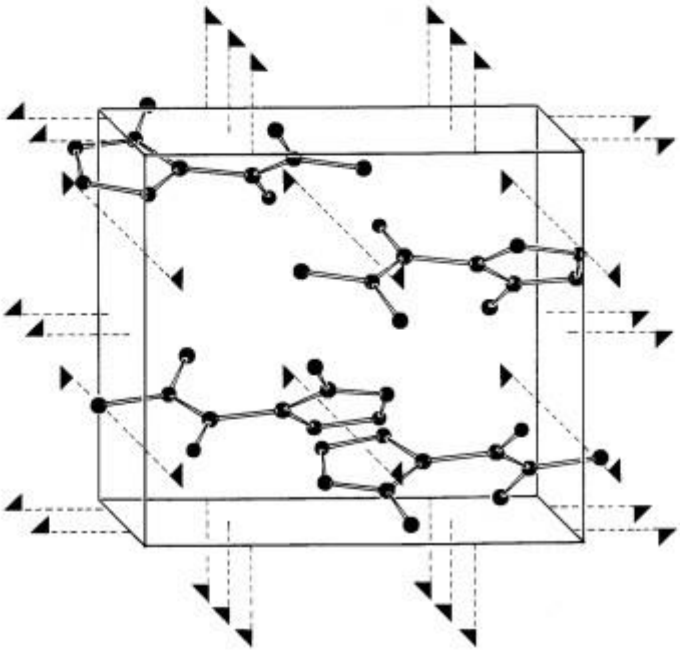

Figure 1-5. The symmetry of a crystal structure.[3]

1.3. Obtaining a Crystal Structure

X-ray crystallographic structure determination is the main method to measure a crystal structure. After that, electron diffraction and neutron diffraction were developed. The method of diffraction can find the structure information from the data, which is collected from the direction and intensity of diffraction (Figure 1-6).

Obtaining a three-dimensional molecular structure by processing the diffraction data from a crystal is the aim of X-ray crystallography.[8]

The wavelength of X-ray beams has an appropriate length that can be diffracted by the electron clouds in the crystal, and some useful information about the atomic arrangement can be obtained. There are two kinds of X-ray wavelength generated from molybdenum (0.71073 Å) and copper (1.54184 Å).[3] When the X-ray beams enter a crystal, the relevant diffraction pattern can be recorded in the detector. In this diffraction pattern, the position and intensity of each reflection can provide the important structural information, such as atom positions, bond lengths and angles, and so on. Three pieces of information can give everything about a crystal: unit cell parameters, space group, and the coordinates of atoms in the asymmetric unit. [1]

There are five main stages in X-ray crystal structure analysis: crystal growth, crystal choice and mounting, data collection, structural solution and crystal refinement. In the following part, the details of crystal structure analysis process will be introduced. (Figure 1-7).

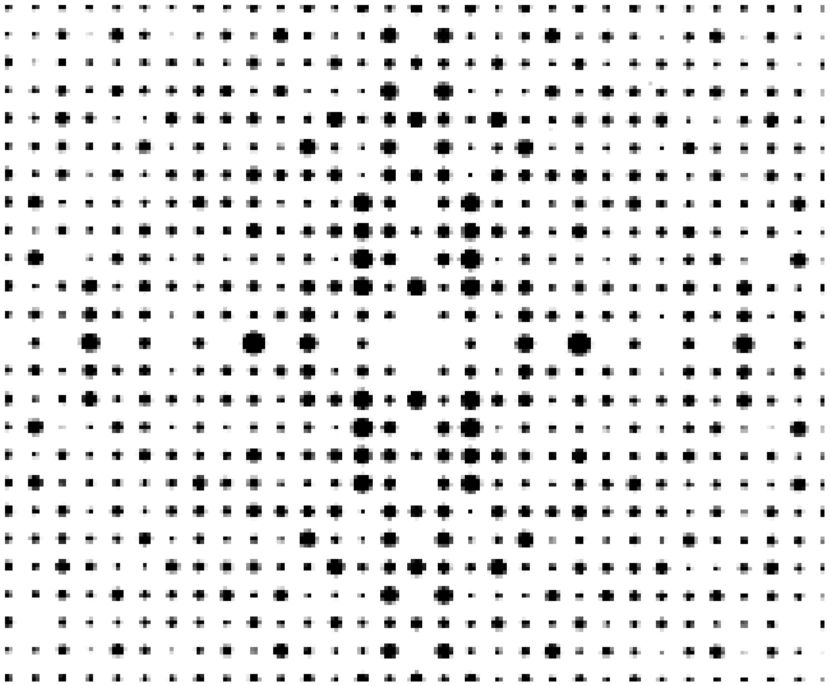

Figure 1-6. Part of an X-ray pattern.[6]

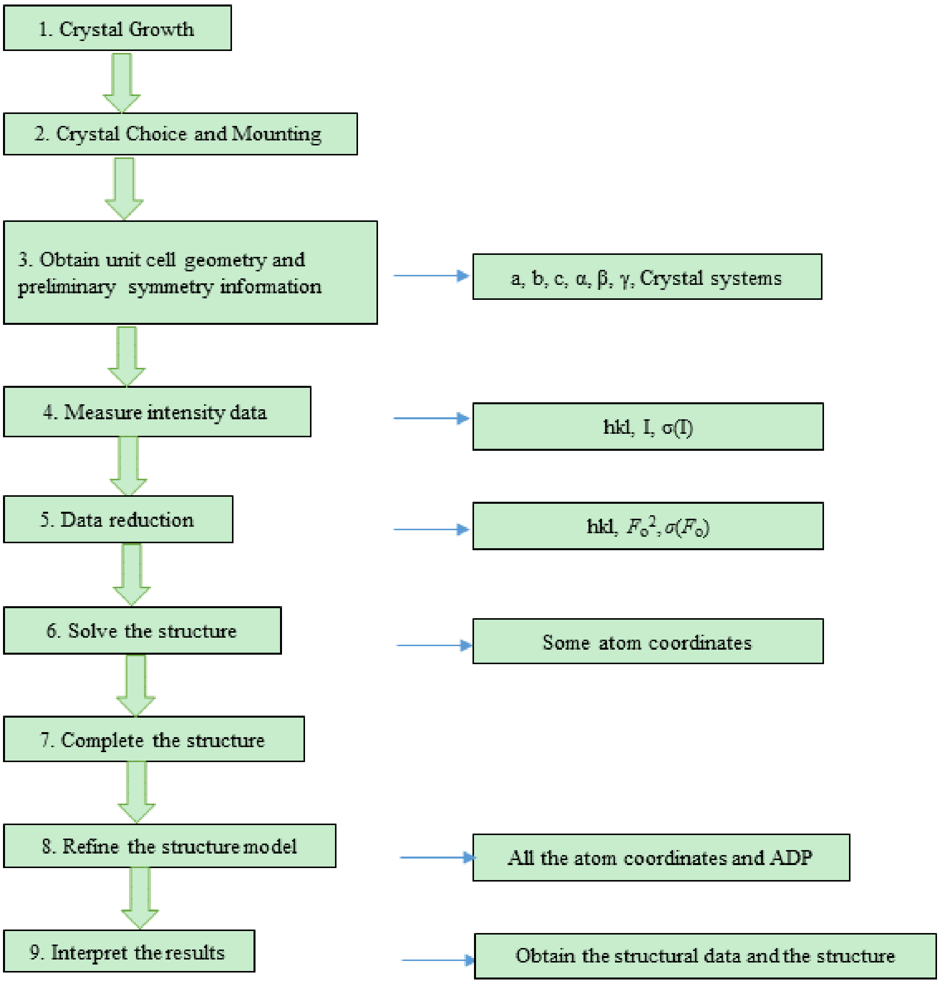

Figure 1-7. A flowchart for the steps involved in a crystal structure determination

1.3.1. Instruments and Software

Modern X-ray single crystallography can be used to analyse a crystal better with the advanced instruments and software. Once, early on, there were oscillation, Weissenburg and precession cameras to record the intensity of diffraction.[9] Then, four-circle diffractometer and area-detector diffractometers appeared. Using computers to control the instruments and obtain the data has improved efficiency. There is a cooling system in the diffraction instrument to reduce the crystal temperature, typically employing liquid nitrogen as the coolant. In St Andrews, the temperature can be reduced to -180°C. There are many kinds of software that can be used to deal with the crystal data. The most useful software packages include SAPI, CRYSTALS, DIRDIF, ORTEP-3, PLATON, SHELX, and SIR.

1.3.2. Crystal Growth

In order to obtain the best diffraction data, a good single crystal is preferable. Therefore, crystal growth is an essential stage. The main methods for purification of compounds are crystallisation and recrystallisation, whilst precipitation method is not a good way to grow a crystal. If the speed of precipitation is too fast, the crystal will be powdery or small. Common methods for crystal growth are liquid diffusion, vapour diffusion, gel diffusion, hydrothermal method and solvothermal method.[10] More details for the methods of crystal growth are as follows. In my experiments, vapour diffusion is the most common method.

The crystallisation of a compound can be achieved most simply through cooling or evaporation and concentration. In order to get the ideal crystals, it is best to use clean and smooth glassware. Do not shake the bottles during crystallisation. If a compound has different solubility in different solvents, we are able to use liquid diffusion to get the crystal, the process is shown in Figure 1-8(a).[10] Commonly, when one solvent spreads into another solvent, a good crystal can be grown near the interface. Vapour diffusion[6] is also a simple method. The first step is choosing two solvents, one in which the crystal is quite soluble and one in which it is less soluble. The compound is put into a small container, and dissolved in the solvent in which it has the greater solubility (Figure 1-8b). The second step is putting the anti-solvent in a large outer container. When the solvents begin to diffuse, the solubility of the compound will be reduced gradually leading to gradual formation of a good quality crystal. Gel diffusion, Hydrothermal methods and Solvothermal methods can also be used to get crystals. Figure 1-9 is a schematic drawing that illustrates the processing steps of gel diffusion.

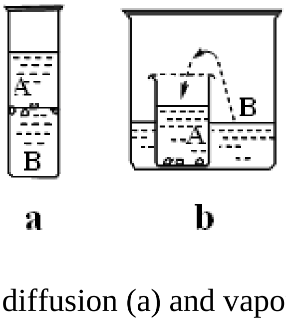

Figure 1-8. Liquid diffusion (a) and vapour diffusion (b).

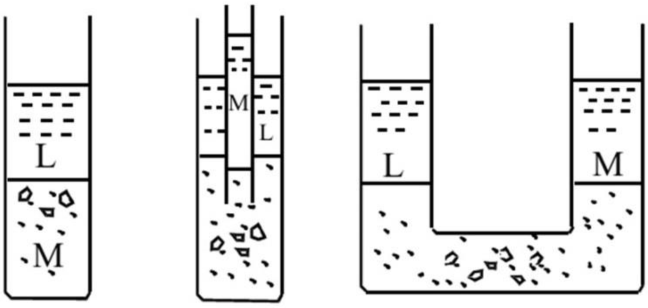

Figure 1-9. A schematic drawing of Gel diffusion.

1.3.3. Crystal Choice and Mounting

Choosing crystals is an important stage. The standards are shapes, size and surfaces of crystals. The internal diameter of the X-ray collimator determines the size of a crystal. Normally, the selected crystals cannot be bigger than the diameter of the X-ray beam. The shape of crystals should ideally be spherical or cubic. A better crystal has a smooth, transparent, clean and gleaming surface. A crystal can be chosen by microscopy at high magnification on a slide. Crystal mounting has three major methods: loop, fibre and capillary. After that, the crystal is placed on the goniometer head (Figure 1-10), and the X-ray beam is centred on the crystal (in our systems this is the centre of the crosshairs on the monitor).

Figure 1-10. A goniometer head.

1.3.4. Data Collection

After the crystal is mounted and centred, the crystal is screened at different angles. This is very important to check the quality of the crystal. These screening pictures can evaluate whether the data can be collected and the exposure time can be determined. If there are too few spots or the spots are poor shape or become circles (Figure 1-11) indicating powder, the crystal is not good enough. A new crystal should be chosen. If the screen pictures show the crystal is suitable for the next step, the data can be collected at low temperature under a nitrogen environment. A poor crystal needs longer exposure time, and longer exposure time or bigger (heavier) atom will produce more intense reflections. In the first stage of the collection, the scope of the data to be collected should be determined. The next step is the full diffraction experiment, which means using an X-ray beam to irradiate the crystal to get a full data set. The CCD detector records the diffraction data (Figure 1-12), which includes the position and intensity of the diffraction spots. The crystallographer can obtain data on the crystal system, the Bravais space lattice, the Miller index of the diffraction in reciprocal space and its intensity.

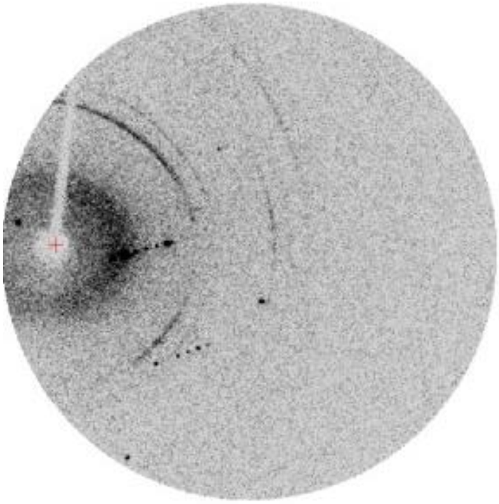

Figure 1-11. A typical image of a bad data collection.

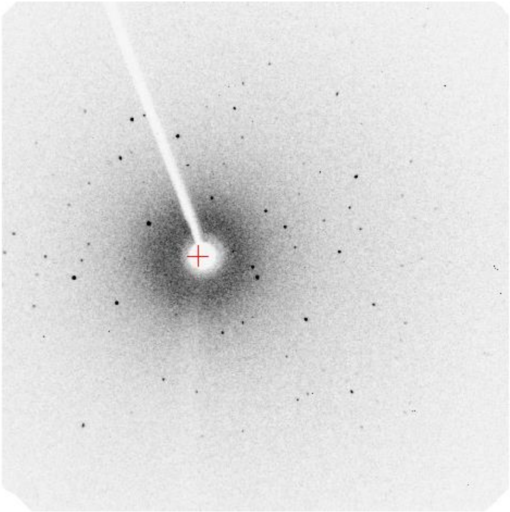

Figure 1-12. A typical image of a good data collection.

1.3.5. Create an Initial Structure

In this step, a set of hkl data is processed on computer. On St Andrews systems before solving the data, the data is processed by CrystalClear (d*TREK or Twinsolve). The value of h, k, l indices and the intensities can be used (solved) to create an electron density map, and then an initial structure can be obtained.

Structural models define all of the coordinates of the atoms. There are two main methods to get a crystal structure. They are Direct Methods, and Patterson Method.[3] Both of the methods need Fourier method. The Fourier method can be divided into the Fourier method and difference Fourier method. If the correct structure models can be afforded, the whole structure model can be determined through Fourier method many times. At the structural solution stage, it is advantageous to use different methods for dealing with different crystals. Normally, Patterson Methods are very useful for heavy metal structure determination; whereas, Direct Methods are good for organic structure solution.

The electron density map is very important in this section. The value of h, k, l positions, structure amplitude, $|F_{h,k,l}|$ and $\sigma(F_{h,k,l})$ can be used to create the relevant electron density map (Figure 1-13). From the hkl data, we only can get unit cell parameters, space group, and diffraction intensity. The accurate positions of atoms cannot be determined from the data, because the phase information of reflections cannot be measured by X-ray diffraction. However, the atom electron density can be obtained from structure factors by Equation 1-2. That means the electron density of all coordinates can be obtained by summation of the observed structure factors, but equation 1-2 is useless without the phase contribution. The contour map is performed using relevant electron densities, and the closer the contourlines are, the higher the electron densities are.

$$\rho_{x,y,z} = \frac{1}{V}\sum_{h,k,l}\left|F_{h,k,l}\right| \cdot e^{(i\phi_{h,k,l})} \cdot e^{[-2\pi i(hx+ky+lz)]}$$ Eqn. 1-2

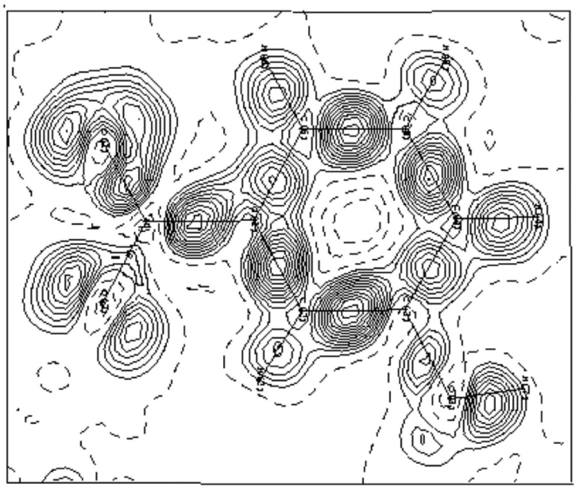

Figure 1-13. Pictorial representation of an electron density map.

1.3.6. Refining the Structure

In order to get an accurate structure, some parameters must be optimised to achieve the best fit. Some atoms need to be added or deleted or changed in this process in order to get a better model. This stage is called structure refinement. Each refinement cycle gives a new set of calculated structure factors, and these phases can produce a calculated diffraction pattern.[1] The model will become closer to the actual structure by structure refinement. The most common method is the least-squares technique. Because of the development of the computer technology, full-matrix refinement can be accomplished. General positions, atomic displacement parameters, overall scale factor and site occupancy are all important parameters. When a refinement is finished, some parameters should be checked, and they are R_1, wR_2, S (Goof), R_{int} and R_{sigma}. The R factor is the residual factor, and relevant calculated equation is shown in Equation 1-3. In this equation, F_o is the observed structure factors and F_c is the calculated structure factors. R-factor shows how good your model fits the diffraction data, and this is the most important value to check a structure. The lower the value of the R-factor is, the better the model is. Generally, in a perfect structure, wR_2 is less than 0.15, R_1 and wR should be less than 0.05, and S is near to 1. Figure 1-14 depicts a typical example of a finished crystal structure in Crystal-structure.[11]

$$R = \frac{\sum||Fo|-|Fc||}{\sum|Fo|} \qquad \text{Eqn. 1-3}$$

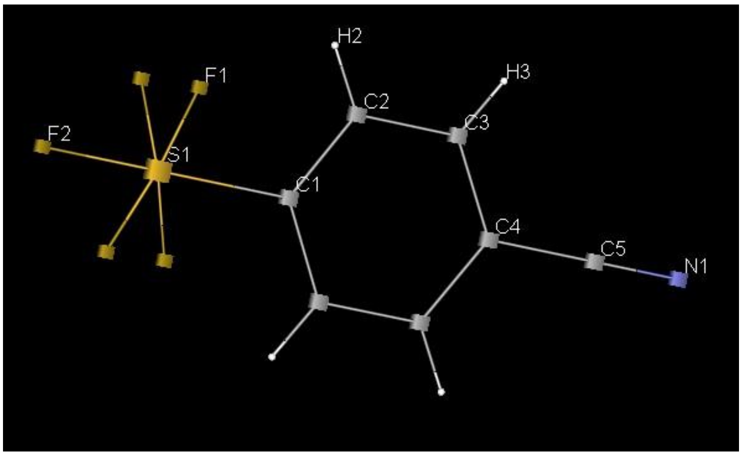

Figure 1-14. X-ray crystal structure of 4-(pentafluorothio)benzonitrile.

1.3.7. Check and Pictures

The final stage is checking the refined structure (IUCR CheckCIF system). Once completed and checked the structure can be submitted as the CIF (Crystallography Information File) to the Cambridge Structure Database. Some kinds of structure figures, for example stick, ball-and-stick, ORTEP, space-filling, polyhedral and stereo, should be provided apart from the CIF. After this, a satisfied model will be created, and some crystallographic information file will be reported, such as a .cif file, .hkl file and .ins file. These files can show all the structural information including parameters, atom positions, distances, angles and diffractions information.

1.4. Conclusions

On the basis of theoretical and experimental analysis, X-ray crystallography can obtain the crystal structures, molecular geometry, electron density and etc. by mathematical calculation. This data provide large quantities of significant information (including cell parameter, crystalline density, bond length, bond angle, etc.) for chemists. X-ray crystallography analysis is connected with the subjects of chemistry, physics and material science through analysing the crystal's solid geometry (the atomic coordinates in a unit cell). Namely, X-ray crystallography is studying the intermolecular interaction. The interaction includes bonding, hydrogen bond, π-π stacking and Van der Waals interactions. The most important parameters are the atomic coordinates, and they are usually showed by fractional coordinates. In a crystal structure, it is also very significant whether it is coplanar, because it may be highly correlated with the crystal's physical and chemical properties. Dihedral angle and torsion angle are the usual parameters describing a crystal's conformation. The above information is the focus on the process of analysing a single crystal.

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CHAPTER 2

INTRODUCTION TO PENTAFLUOROSULFURANYL (SF_5)-CONTAINING COMPOUNDS AND SULFUR/SELENIUM HETEROCYCLES

2.1. Introduction

Chalcogen elements are the main Ⅵ group elements in the Periodic Table, which consist of the elements oxygen (O), sulfur (S), selenium (Se), tellurium (Te), and the radioactive element polonium (Po). Organosulfur compounds and organoselenium compounds in recent years have been discovered and synthetized and used in pharmaceuticals, materials and so on. They can form simple functional group with other oxygen or fluorine atoms, and they also can create simple heterocycles or macrocycles with oxygen, phosphorus, or nitrogen atoms. X-ray crystallography is a technique which has developed rapidly in recent year, and it is very useful for the study of the structures of new compounds. This thesis focus on the structures of pentafluorsulfuranyl (SF_5)-containing compounds, 2,4-diaryl-1,3-chalcogen azoles and organo macrocycles which containing sulfur/selenium atoms by X-ray crystallography. Dr. Hua in Woollins' group has synthesized many relevant compounds. Good crystals can be obtained through crystallization, and their structural data were studied in the following Chapters. In this Chapter, the background of relevant compounds and the research on some published structures will be reviewed.

2.2. Introduction to Pentafluorsulfuranyl (SF_5) Compounds

2.2.1. Organofluorine Chemistry

In 1896, Swarts first described fluoroacetamide, but there is no exact information for the preparation.[1] After that, more and more attention was paid to organofluorine compounds and the range of synthetic methods has increased greatly. Some fluorocarbon compounds have been used as refrigerants since the 1930s,[2] and the 'McMahon Act'[3] in 1946, promoted the development of orgnaofluorine chemistry. In 1943, the toxicity of fluoroacetate was discovered by J. S. C. Marais, and since then the biological activity of organofluorine compounds has been studied.[4] The high-activity fluorouracil (5-FU or f5U) was synthesized in 1950s, it showed that biological activity can be changed by incorporating fluorine atoms into molecules.[5] In recent years, the research of organofluorine has been in a golden period in the fields of biomedicine, pesticide and so on, and 20% of biomedicines and 30% of pesticides contain at least one fluorine atom.[6-7] The importance of the area is demonstrated with a paper in Nature in 2011,[8] additionally, four papers about organofluorine chemistry were published in Science in the same year.[9-12] Compounds containing the trifluoromethyl (CF_3) group or sulfurpentafluoride (SF_5) group are worth studying because of their special properties. Owing to some unique properties such as low surface energy, hydrophobicity, high chemical resistance, high thermal stability and electronegativity,[13] the compounds containing fluorinated groups are used as materials, polymers and organic superconductors.[14-21]

The trifluoromethyl groups possesses strong electron-withdrawing, lipotropy and stable C-F bond, therefore the acidity, dipole moment, polarity, lipotropy, metabolic stability and chemical stability for some compounds can be changed dramatically by introducing trifluoromethyl groups into these compounds. Compounds containing trifluoromethyl groups are widely applied as biomedicines and pesticides, such as prozac, celebrex and januvia (Figure 2-1).

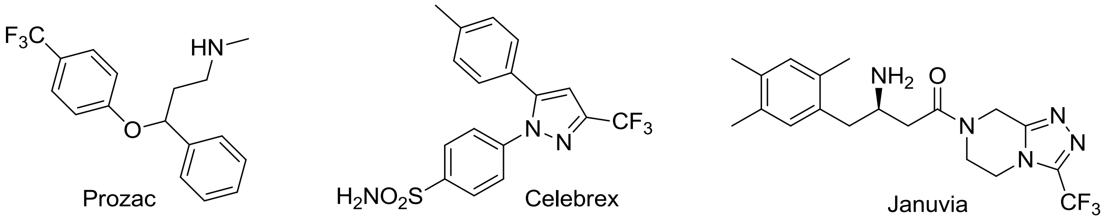
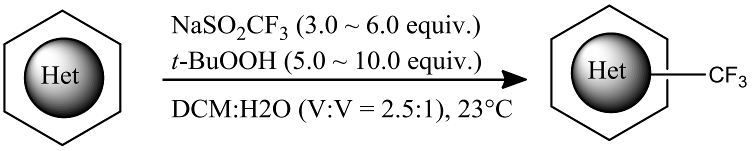


Figure 2-1. Biomedicines containing trifluoromethyl (CF_3) group.

Chemists have created many different types of reactions to insert the trifluoromethyl group into compounds, but these methods have different defects in some aspects, such as strict operational condition and scarce raw materials. In recent years, promoted by the research of organometallic chemistry, trifluoromethylation reactions have made great strides.[22-23] The Baran group used CF_3SO_2Na to insert the fluorine atoms through scheme 2-1, and this reaction can take place at room temperature without any catalyst. They have used this reaction in the biomedicines of caffeine and Varenicline.[24] In 2011, MacMillan, et al. in the University of Princeton published a similar trifluoromethylation reaction in Nature.[25]



Scheme 2-1. The trifluoromethylation reactions.

The sulfurpentafluoride (SF_5) group is well known as 'super-CF_3', and its structure is also very stable. Comparing with the tetrahedron geometry of CF_3 group, the SF_5 group and an aryl carbon atom are in a roughly octahedral environment. Their high density (2.57g/cm^3 for –SF_5 and 2.25 g/cm^3 for –CF_3) means they can be used as energetic oxidizers.[26-27]

2.2.3. Introduction to Pentafluorsulfuranyl (SF_5)

Increasing attention has been paid to organofluorine compounds, such as, benzotrifluoride[28-30] and the compounds containing fluorinated substituents with OCF_3 and CF_3 groups. As discussed above, the trifluoromethyl (CF_3)-containing compounds are usually used as dye-stuffs (eg. fluoro chloro pyrimidene reactive dyes), chemotherapeutic treatment (eg. FdUMP),[29] herbicides (eg. trifluralin)[31] and so on. Currently, some research[28] showed that the structures of pentafluorsulfuranyl (SF_5) derivatives have some similar molecular properties (i.e. dipole moment, density, lipophilicity)[28,30] comparing with fluorinated moieties such as CF_3 and OCF_3, and using the SF_5 group to replace the CF_3 group has been widely patented.[28] Thus, many pentafluorosulfanyl analogues have been synthesized and their herbicidal activity and carcinogenicity were compared with trifluralin.[31] Comparing with trifluoromethyl (CF_3)-containing compounds, the pentafluorsulfuranyl (SF_5)-containing compounds have some better properties like highly fluorinated surfaces, insecticidal activity and chemical stability.[28,29,32] Thus, pentafluorosulfanyl compounds are also named as 'super-CF_3'.[33] Pentafluorsulfuranyl(-SF_5) compounds have wide applications such as surfactants (eg. F_5S-$(CH_2)_n$-X, X is polarity group or polymerizable group),[34] herbicides (Fipronil)[28] and so on. Apart from these, SF_5-aromatic compounds also have a wide application in the fields of surfactants, energetic materials, medicine, pesticides and fungicides.[28,31,38,39] In the beginning, most of them were alkyl sulfurpentafluorides, and the first alkyl sulfurpentafluoride bromide (SF_5Br) was synthesized by C. Merrill.[35] However, Sheppard[36] prepared the first SF_5-aromatic compounds about 50 years ago, and then many kinds of new syntheses have appeared since then. Recently, more and more aromatic SF_5 derivatives have been prepared.[31,33,37,38] The first superconductor which contained a SF_5-aromatic compound was reported in 1996.[38] Although the SF_5-aromatic compounds are very popular, the crystal structures are seldom reported. C. Zarantonello *et al.* published the synthesis of 3- and 4-SF_5 benzoic acid compounds,[28] however, they only reported the X-ray crystal structure of 3-SF_5-C_6H_4-COOH and the structure of another compounds will be analysed in my thesis. The SF_5-group has a unique octahedral environment, so analysing the single crystal structures of pentafluorosulfanyl compounds might be very interesting. The single crystal structures of various pentafluorosulfanyl compounds and derivatives will be discussed below.

2.2.4. Introduction to the X-ray Structures of Sulfurpentafluorides

Pentafluorsulfuranyl (SF_5)-containing compounds are considered to be a derivative of sulphur hexafluoride (SF_6), but sulfur hexafluoride is generally not used to prepare SF_5-containing compounds. There are two main strategies to insert SF_5 group into other organic compounds: (a) using pentafluorsulfuranyl-containing compounds as reactants and (b) fluorination of a thiol, sulphide or disulfide function.[40] More and more pentafluorsulfuranyl (SF_5)-containing compounds are synthesized, but not too many X-ray structures are reported.[1,2,41-53] There are many kinds of pentafluorsulfuranyl (SF_5)-containing compounds, including alkyl SF_5-compounds, alkenyl, alkynyl and acyl SF_5-compounds and aryl SF_5-compounds. In this thesis, I will focus on the structures of aryl-SF_5 compounds (Figure 2-2).

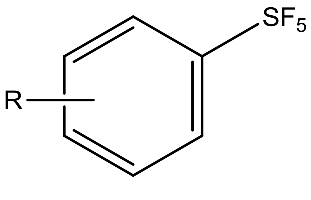


Figure 2-2. The chemical structures of pentafluorsulfuranyl-containing compounds.

In 1977, Bartell and Doun obtained the basic structural information of SF_6 by vapor-phase electron diffraction.[54] In their study, one sulfur atom and six fluorine atoms in SF_6 form a regular octahedron, and the S-F bond distance is 1.561(2) Å, being shorter than the mean S-F bond distance [1.568(1) Å] in SF_5Cl.[55] The X-ray structures of single chain pentafluorsulfuranyl (SF_5)-containing compounds are reported earlier than aromatic SF_5 compounds. The S-F(ax) bond lengths are 1.543(4)[1.546(5)] and

1.553(2) Å in pentafluorosulfanyl isocyanide (SF_5-NC) and pentafluorosulfanyl cyanide (SF_5-CN) with the similar F(ax)-S-F(eq) bond angles [89.5(4) to 90.4(3)°] and F(eq)-S-F(eq) bond angles [89.5(3) to 90.6(3)°], and along with S-F(eq) bond lengths are from 1.515(7) to 1.548(3) Å.[56] There are slight differences in the structures of pentafluorosulfanyl isocyanate (SF_5-NCO), pentafluorosulfanyl isothiocyanate (SF_5-NCS), and N-(pentafluorosulfanyl) (dichloro)methanimine (SF_5-N=CCl_2). The range of S-F(ax) bond distances and S-F(eq) bond distances are 1.556(1) to 1.567(2) and 1.552(2) to 1.577(2) Å.[42] The S-F(ax) bond and S-F(eq) distances are from 1.573(3) to 1.583(3) Å and 1.559(2) to 1.5803(17) Å in pentafluorosulfanylnitramide salts $Z^+SF_5\text{-N-}NO_2^-$ [Z = NH_4 / K / $H_2NC(=NH_2)NH_2$ / $H_2NC(=NH_2)NHNH_2$].[41]

There are several reported X-ray structures of alkyl pentafluorosulfanyl compounds before the year of 2000, but the first X-ray structures of aromatic pentafluorosulfanyl are reported by R. D. Bowden et al. in 2000 (Figure 2-3).[2] In the structures of aromatic pentafluorosulfanyl compounds, the SF_5 group is still essentially in an octahedral environment. The S-F(ax) bond distances range from 1.581(2) to 1.600(2) Å and the S-F(eq) bond distances are from 1.549(2) to 1.5892(16) Å.[1,2,43] The F(eq) atoms are staggered with respect to the aryl-ring, and the F(eq)-S-C-C dihedral angles are from 29.82(19) to 59.87(19).[1,2,43,44-54]

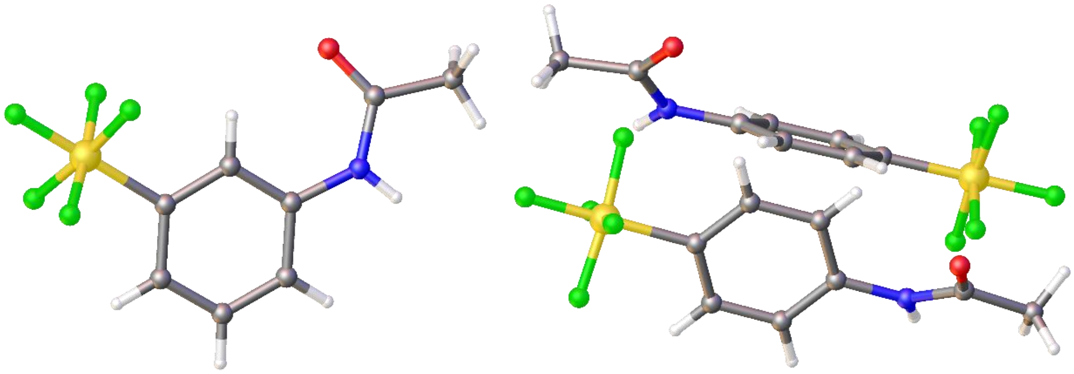


Figure 2-3. The X-ray structures of (3-acetamidophenyl)sulfurpentafluoride (left) and (4-acetamidophenyl)sulfurpentafluoride (right).

The intermolecular and intramolecular interactions are significant features in aromatic pentafluorsulfuranyl (SF_5)-containing compounds. There are many kinds of interactions in this series of compounds, including intramolecular and intermolecular hydrogen bonds and π-stacking interactions. The weak intramolecular interaction distances [2.343(3) to 2.773(3) Å][1,2,43,44-54] between the equatorial fluorine atoms and aromatic hydrogens are marginally shorter than the sum of the van der Waals radii of H and F (2.70 Å), and this C_{aryl}-H···F(eq) intramolecular interaction may support the stability of equatorial fluorine atoms. The intramolecular C_{aryl}-H···F interactions in the structure of 4-Aminophenyl-pentafluoro-sulfur are shown in Figure 2-4.

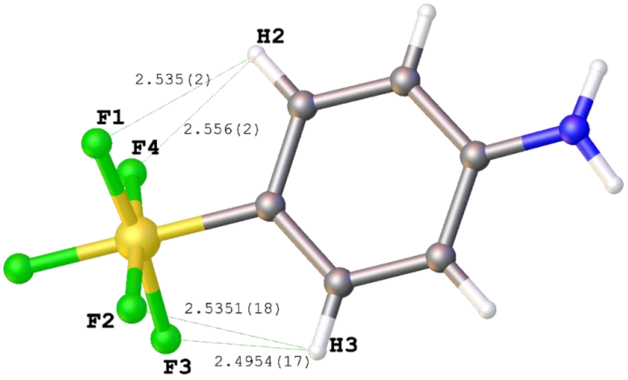


Figure 2-4. A representative 3-D diagram shows the intramolecular C_{aryl}-H···F interactions in the structure of 4-Aminophenyl-pentafluoro-sulfur.

2.3. Introduction to 2,4-Diaryl-1,3-Chalcogen Azoles

Azaheterocycle is a notable structure, and it has many unique properties. This thesis will focus on two kinds of azaheterocycle: selenium-nitrogen heterocyclic compounds and sulfur-nitrogen heterocyclic compounds. Selenazole derivatives are also famous because of their biological efficacy, such as antibiotic and cancerostatic activity.[56-57] For example, selenazofurin was found that it contains significant anti-tumor properties in animals, and it also exhibit broad spectrum antiviral activity in cell culture experiments. Comparing with selenium-nitrogen heterocyclic compounds, sulfur-nitrogen heterocyclic compounds are more popular because of their wide variety of biological and medicinal properties, such as in Riluzole [6-(trifluoromethoxy)benzothiazol-2-amine] and Sulfathiazol [4-amino-N-(1,3-thiazol-2-yl)benzenesulfonamide].

Selenium-nitrogen heterocyclic compounds are famous for their inhibitory effects and their pharmaceutical applications (i.e. antioxidant, anticancer agent, antitumor, antibacterial).[56-59] The main backbone in these compounds is the 1,3-selenazole ring, and the 2,4-diaryl-1,3-selenazoles were synthesized by many synthetic approaches.[60,61] The literature values for the typical C=Se double bond lengths are from 1.81(5) to 1.856(4) Å, and C-N distances range from 1.270(7) to 1.324(8) Å in primary selenoamides (Figure 2-5).[62,63] Nitrogen and selenium atoms are not particularly coplanar with the aryl ring, and the dihedral angles between the Se-C-N mean plane and the aryl ring are from 20.41 to 60.80°, respectively.

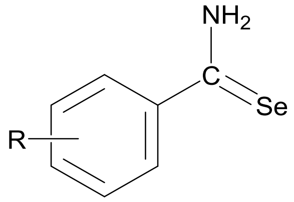


Figure 2-5. The chemical structures of primary selenamides.

Meanwhile, the C-Se bond and C-N bond in azaheterocycles are different to the primary selenoamides. C-Se bond lengths of 1.87 to1.89 Å were observed in 1,3,4-selenadiazoles,[64-67] and the distances in 2,5-diarylselenophenes are very similar [ca. 1.86 to1.89 Å].[68] The C=N and C-N bond distances in reported 1,3-selenazoles are 1.268(11) and 1.384(11) Å, respectively.[61] The C-Se-C bond angles in this kind of azaheterocycles increase from 1,3,4-selenadiazoles [81.9(4) to 82.7(2)°] ‹ 1.3-selenazoles [83.3(5)°] ‹ 2,5-diarylselenophenes [87.8(8)°] (Figure 2-6). The selenium atoms and nitrogen atoms in the five membered ring are nearly coplanar with the azaheterocycle mean plane. The C-N and C-Se bond lengths in 1.3-selenazoles and 2,5-diarylselenophenes are between the typical C-N single bond distance of 1.47 Å and C=N double bond length of 1.29 Å; furthermore, the C-C bond distances also fall in between the typical C-C single-bond length of 1.54 Å and C=C double-bond distance of 1.34 Å, indicating some delocalisation for all bonds in the five-membered N-C-Se-C-C rings.

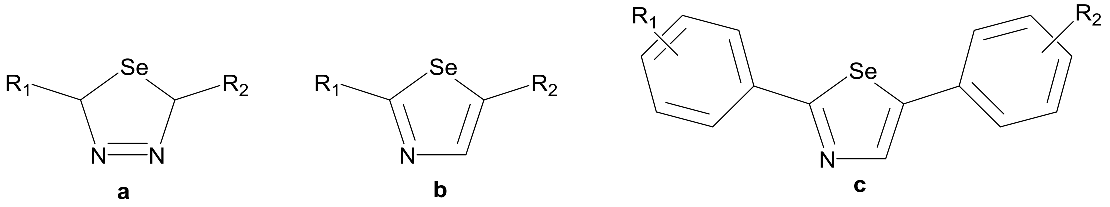


Figure 2-6. The chemical structures of the main framework: (a) 1,3,4-selenadiazoles (b) 1.3-selenazoles and (c) 2,5-diarylselenophenes.

The structures of thiazoles are similar to those of selenazoles (Figure 2-7). Both C-S bond distances [1.6589(5) to 1.769(14) Å] and the C-N bond distances [1.27(1) to 1.415(14) Å] are between the typical single-bond length and double-bond distance [C-

S: 1.83 Å, C=S: 1.63 Å; C-N: 1.47 Å, C=N: 1.29 Å], indicating some delocalisation for all bonds in the five-membered N-C-S-C-C rings.[69-71] The sulfur atoms and nitrogen atoms in the five membered ring are also nearly coplanar with the azaheterocycle mean plane.

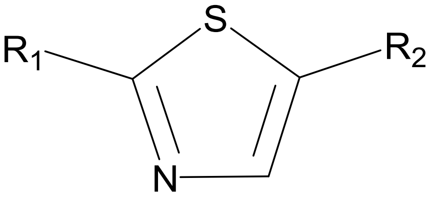


Figure 2-7. The chemical structures for the main framework of thiazoles.

The packing networks for selenazoles and thiazoles are very interesting, and two molecules in some structures form a ‘head to head’ or ‘head to tail’ dimer through hydrogen bonds across an inversion center. Most of them have a very regular multistaged or multisheeted network structures. In the same layer, the molecules are linked by some weak hydrogen interactions, such as N/O/F···H interaction, and that depends on their substituents. The supramolecular aggregation arrangement uses weak intermolecular hydrogen interactions or π-stacking interactions.

2.4. Introduction to Organo Phosphorus Macrocycles

Macrocycles were studied by chemists because of the discovery of crown ether last century, and supramolecular chemistry was developed based on it.[72,73] Organo phosphorus macrocycles occupy an important place in macrocycle chemistry. They not only have various structures, but also they are very stable. The majority of organo phosphorus macrocycles which are based on covalent bonds are created by producing P=N, P-O, P-C and P-Si bonds. They can also form stable coordination complexes with some transition metals in the field of material science. Furthermore, there is work on the wider use of macrocyclic scaffolds in medicinal chemistry to search for new drugs and over 100 compounds approved drugs contain macrocyclic structures.[74] The macrocycles containing twelve-membered ring possess extremely potent biological activity and specificity, but the mactocycles containing bigger than ten-membered ring systems are very hard to be explore.

This thesis will focus on organo phosphorus macrocycles incorporating double P_mE_n (E = S, Se, O, N, C) scaffolds. The Woollins' group has carried out extensive studies on this kind of macrocycle (Figure 2-9) based on the use of Woollins' reagent (Figure 2-8).[75] The P-Se single bond distances are from 2.213 to 2.251 Å with the P=Se bond distances ranging from 2.078 to 2.098 Å, being very similar to the P-Se-Se-P linkage in acyclic systems.[76-77] The transannular P···P (4.793 to 6.890 Å), O···O (2.768 to 5.162 Å) and Se···Se (3.596 to 7.575 Å) distances are longer than that in the four-membered P_2Se_2 ring (3.1 Å) and six-membered P_2Se_4 ring (4.3 Å). The geometry around two phosphorus atoms is nearly tetrahedral, and some weak H···Se hydrogen interactions are observed in the packing networks.

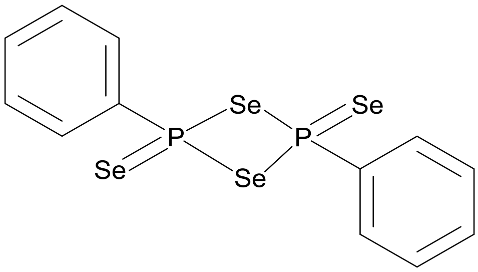


Figure 2-8. The chemical structure of Woollins' Reagent.

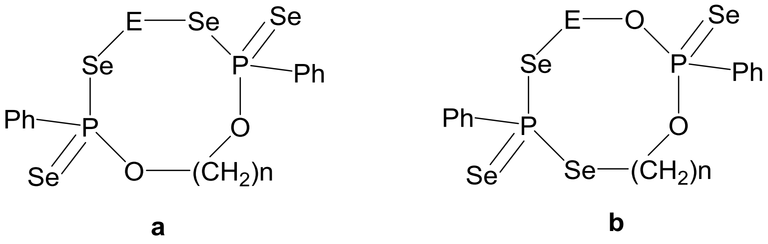


Figure 2-9. The chemical structure of macrocycles.

2.5. Conclusion

Organo-chalcogenide compounds containing sulfur or selenium are playing an increasingly important role in modern chemistry. All of the pentafluorsulfuranyl compounds, selenium/sulfur-nitrogen heterocycles and organo phosphorus macrocycles belong to the general category of organo-chalcogenide compounds. The studies of their structures can help chemist to learn their properties and geometry constructions, and it also can supply some guidance in chemical synthesis. In this thesis, the X-ray single crystal structures of pentafluorsulfuranyl (SF_5)-containing compounds and selenium/sulfur-nitrogen heterocycles are discussed. Our main focus is using X-ray single crystallography to study the new structures and look for the similarities and differences in bond distances, bond angles, and twist angles.

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CHAPTER 3

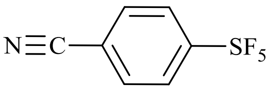
STRUCTURAL STUDIES OF PENTAFLUOROSULFURANYL (SF5)-CONTAINING AROMATIC COMPOUNDS

3.1. Introduction

Organic compounds bearing the SF_5 functional group have attracted vast interest due to their potential application in medicinal and material chemistry.[1-11] The analysis of molecular structure is very important to research the properties and behaviour of matter. Although SF_5 bearing aromatic compounds are very popular, their crystal structures are sparsely reported. Thus, this Chapter will focus on the X-ray structural study of a series of SF_5-substituted compounds with structural similarities and variations, and comparison with the other known similar X-ray structures.

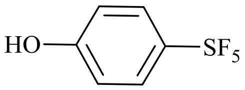
The chemical structures of the aromatic compounds involved in this Chapter are shown in Figure 3-1. In each compound, one important substituent is the SF_5 group. The SF_5 group has a unique umbrella geometry. The sulfur atom is in an approximately octahedral coordination environment. The sixth fluorine position of SF_6 is replaced by an aromatic group. A number of single crystal structures have been reported for the alkyl-sulfurpentafluorides,[12-34] meanwhile, some X-ray structures have been published for the aromatic sulfurpentafluorides.[35-47]

Firstly, the structural similarities will be discussed and next follows a discussion on structural deviations by comparing the organic frameworks, the weak intramolecular and intermolecular interactions, the packing frameworks and etc. Compounds **3.1**–**3.4** were obtained from Apollo Scientific without further purification and compounds **3.5**–**3.10** were prepared by Petr Beier’s group [Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic]. Crystals of all compounds **3.1**–**3.10** suitable for X-ray crystallographic analysis were grown by diffusion of a dichloromethane solution of compound into hexane at room temperature in each case.



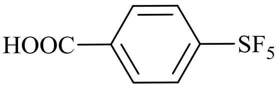
4-(Pentafluoro-l^{6}-sulfanyl)benzonitrile

3.1



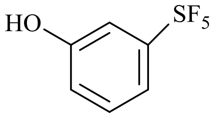
4-(Pentafluoro-l^{6}-sulfanyl)phenol

3.2



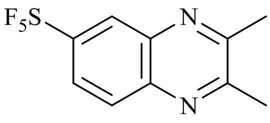
4-(Pentafluoro-l^{6}-sulfanyl)benzoic acid

3.3



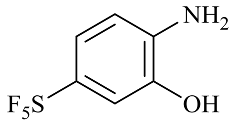
3-(Pentafluoro-l^{6}-sulfanyl)phenol

3.4



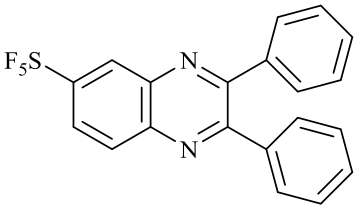
2,3-Dimethyl-6-(pentafluoro-l^{6}-sulfanyl) quinoxaline

3.5



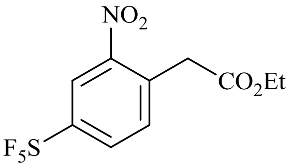
2-Amino-5-(pentafluoro-l^{6}-sulfanyl)phenol

3.6



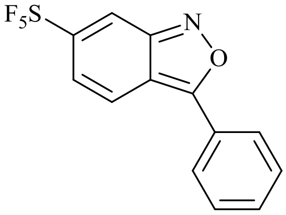
6-(Pentafluoro-l^{6}-sulfanyl)-2,3-diphenyl-quinoxaline

3.7



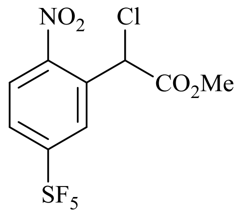
Ethyl 2-(2-nitro-4-(pentafluoro-l^{6}-sulfanyl)-phenyl)acetate

3.8



6-(Pentafluoro-l^{6}-sulfanyl)-3-phenyl-benzo[*c*]isoxazole

3.9



Methyl 2-chloro-2-(2-nitro-5-(pentafluoro-l^{6}-sulfanyl) phenyl)acetate

3.10

Figure 3-1. The chemical structures of compounds **3.1**–**3.10**.

3.2. Crystal Structure Data

The crystal structure data were collected by using a Rigaku SCX-Mini diffractometer (Mercury 2 CCD) at -148℃ with graphite-monochromated Mo-Kα radiation (λ= 0.71073 Å) for compounds **3.1**–**3.5**, **3.7**, **3.8** and **3.10**; using the Mercury diffractometer (Mercury 70) at -148℃ for compound **3.6**, and using the St Andrews Robotic diffractometer (Saturn70 CCD) at -148℃[48-50] for compound **3.9**. Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarization. Absorption effects were corrected on the basis of multiple equivalent reflections by semi-empirical methods. Structures were solved by direct methods and refined by full-matrix least-squares against F2 (SHELXL).[51] Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries.

The details of data collections and refinements for **3.1**–**3.10** are listed in Tables 3-1–3-3. The selected distances (Å) and angles (°) for the structures of **3.1**–**3.10** are shown in Table 3-4–3-6. Compounds **3.1** and **3.2** crystallize in an orthorhombic crystal system; compounds **3.3**, **3.5**, **3.7** and **3.8** in a monoclinic crystal system; compounds **3.4**, **3.9** and **3.10** in a triclinic crystal system, and compound **3.6** in a trigonal crystal system. Compounds **3.2**, **3.3**, **3.4** and **3.9** contain two independent molecules, and compounds **3.1**, **3.5**, **3.6**, **3.7**, **3.8** and **3.10** have a single molecule in the unit cell.

Table 3-1. Relevant crystal data and refinement parameters for compounds **3.1**–**3.4**

Experimental details	**3.1**	**3.2**	**3.3**	**3.4**
Empirical formula	$C_7H_4F_5NS$	$C_6H_5F_5OS$	$C_7H_5F_5O_2S$	$C_6H_4F_5OS$
Formula weight	229.17	220.16	248.17	219.15
Temperature (℃)	-148(1)	-148(1)	-148(1)	-148(1)
Crystal color, habit	Colorless, chip	Colorless, platelet	Colorless, platelet	Colorless, platelet
Crystal dimensions (mm^3)	0.45×0.22×0.10	0.56×0.27×0.10	0.42×0.12×0.03	0.37×0.22×0.07
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Triclinic
Lattice parameters	a = 9.018(11) Å	a = 5.851(8) Å	a = 14.794(3) Å	a = 8.906(12) Å
	b = 13.18(2) Å	b = 18.43(3) Å	b = 7.6423(10) Å	b = 9.97(2) Å
	c = 6.864(8) Å	c = 11.57(2) Å	c = 15.892(3) Å	c = 10.29(2) Å
				α = 85.05(5)°
			β = 100.559(7)°	β = 83.21(6)°
				γ = 66.30(4)°
Volume ($Å^3$)	816(2)	1247(3)	1766.3(5)	830(2)
Space group	*Cmcm*	$P2_12_12$	$P2_1/c$	*P-1*
Z value	4	6	8	4
Dcalc (g/cm^3)	1.865	1.636	1.866	1.754
$F_{(000)}$	456.00	614.46	992.00	436.00
μ(MoKα) (cm^{-1})	4.369	3.776	4.245	4.304
Diffractometer	SCX mini	SCX mini	SCX mini	SCX mini
No. of reflections measured (Total)	5302	15591	14817	10606
Unique	810	4173	3101	5198
R_{int}	0.0338	0.0753	0.1008	0.0600
Friedel pairs		1706		
Min. and max. transmissions	0.890, 0.957	0.771, 0.963	0.736, 0.987	0.814, 0.970
No. of observations (All reflections)	810	4173	3101	5198
No. of variables	46	179	279	235
Reflection/parameter ratio	17.61	23.31	11.11	22.12
Residuals: R_1 (I>2.00σ(I))	0.0386	0.1243	0.0473	0.0539
Residuals: R (all reflections)	0.0493	0.1840	0.1112	0.1206
Residuals: wR_2 (all reflections)	0.1018	0.3626	0.1035	0.1502
Goodness of fit indicator	1.101	1.151	1.010	0.936
Flack parameter	-	-0.0(3)	-	-
Maximum peak in final diff. map ($e^-/Å^3$)	0.36	3.03	0.28	0.44
Minimum peak in final diff. map ($e^-/Å^3$)	-0.49	-0.85	-0.29	-0.43

Table 3-2. Relevant crystal data and refinement parameters for compounds **3.5–3.7**

Experimental details	**3.5**	**3.6**	**3.7**
Empirical formula	$C_{10}H_9F_5N_2S$	$C_6H_6F_5NOS$	$C_{20}H_{13}F_5N_2S$
Formula weight	284.25	232.15	408.39
Temperature (℃)	-148(1)	-148(1)	-148(1)
Crystal color, habit	Colorless, platelet	Colorless, chip	Colorless, chip
Crystal dimensions (mm^3)	0.16×0.11×0.03	0.20×0.08×0.07	0.23×0.20×0.15
Crystal system	Monoclinic	Trigonal	Monoclinic
Lattice parameters	a = 5.8557(10) Å	a = 19.269(4) Å	a = 14.630(4) Å
	b = 23.706(4) Å		b = 8.476(2) Å
	c = 7.8738(14) Å	c = 11.953(4) Å	c = 15.130(4) Å
	β = 92.963(10)°		β = 105.645(9)°
Volume ($Å^3$)	1091.5(3)	3843(2)	1806.7(8)
Space group	$P2_1/n$	$R\text{-}3$	$P2_1/c$
Z value	4	18	4
Dcalc (g/cm^3)	1.730	1.805	1.501
$F_{(000)}$	576.00	2070	832.00
μ(MoKα) (cm^{-1})	3.476	4.270	2.360
Diffractometer	SCX mini	Mercury 70	SCX mini
No. of reflections measured (Total)	9398	11037	15091
Unique	1921	1496	3163
R_{int}	0.1367	0.1326	0.0735
Friedel pairs			
Min. and max. transmissions	0.686, 0.990	0.816, 0.971	0.900, 0.965
No. of observations (All reflections)	1921	1496	3163
No. of variables	163	127	253
Reflection/parameter ratio	11.79	11.78	12.50
Residuals: R_1 (I>2.00σ(I))	0.0535	0.0788	0.0586
Residuals: R (all reflections)	0.1205	0.1257	0.0947
Residuals: wR_2 (all reflections)	0.1403	0.1370	0.1247
Goodness of fit indicator	1.025	1.205	1.110
Flack parameter	-	-	-
Maximum peak in final diff. map ($e^-/Å^3$)	0.31	0.36	0.21
Minimum peak in final diff. map ($e^-/Å^3$)	-0.42	-0.34	-0.28

Table 3-3. Relevant crystal data and refinement parameters for **3.8**–**3.10**

Experimental details	**3.8**	**3.9**	**3.10**
Empirical formula	$C_{10}H_8F_5NO_4S$	$C_{13}H_8F_5NOS$	$C_9H_7F_5NO_4ClS$
Formula weight	333.23	321.26	355.66
Temperature (℃)	-148(1)	-148(1)	-148(1)
Crystal color, habit	Colorless, platelet	Yellow, chip	Colorless, platelet
Crystal dimensions (mm^3)	0.20×0.11×0.03	0.09×0.09×0.06	0.22×0.12×0.03
Crystal system	Monoclinic	Triclinic	Triclinic
Lattice parameters	a = 5.666(13) Å	a = 9.475(5) Å	a = 5.2263(12) Å
	b = 24.94(5) Å	b = 10.296(5) Å	b = 8.7375(12) Å
	c = 9.96(2) Å	c = 13.006(7) Å	c = 14.619(2) Å
		α = 88.80(2)°	α = 78.36(2)°
	β = 97.72(3)°	β = 83.67(3)°	β = 84.85(2)°
		γ = 80.86(2)°	γ = 86.99(2)°
Volume (Å^3)	1396(5)	1245.1(11)	650.8(2)
Space group	$P2_1/c$	P-1	P-1
Z value	4	4	2
Dcalc (g/cm^3)	1.586	1.714	1.815
$F_{(000)}$	672.00	648.00	356.00
μ(MoKα) (cm^{-1})	3.033	3.197	5.295
Diffractometer	SCX mini	Saturn 70	SCX mini
No. of reflections measured (Total)	11333	9578	5703
Unique	2453	4358	2285
R_{int}	0.2357	0.0814	0.1118
Friedel pairs			
Min. and max. transmissions	0.734, 0.991	0.526, 0.981	0.715, 0.984
No. of observations (All reflections)	2453	4358	2285
No. of variables	190	379	190
Reflection/parameter ratio	12.91	11.50	12.03
Residuals: R_1 (I>2.00σ(I))	0.1365	0.0621	0.0571
Residuals: R (all reflections)	0.2696	0.1105	0.1548
Residuals: wR_2 (all reflections)	0.2022	0.2309	0.1493
Goodness of fit indicator	1.148	0.976	0.972
Flack parameter	-	-	-
Maximum peak in final diff. map (e$^-$/Å^3)	0.31	0.53	0.28
Minimum peak in final diff. map (e$^-$/Å^3)	-0.27	-0.48	-0.33

Table 3-4. Selected bond distances (Å) and bond angles (°) for compounds **3.1**–**3.3**

	3.1	**3.2**	**3.3**
S(1)-F(5)	1.588(3)	1.587(7)[1.609(7)]	1.573(3)[1.579(3)]
S(1)-C(1)	1.798(3)	1.814(7)[1.831(9)]	1.795(4)[1.796(4)]
S(1)-F(1)	1.5820(16)	1.573(7)[1.590(5)]	1.577(3)[1.579(2)]
S(1)-F(2)	1.5820(16)	1.587(7)[1.590(5)]	1.590(3)[1.576(3)]
S(1)-F(3)	1.5820(16)	1.597(6)[1.596(5))	1.584(3)[1.573(3)]
S(1)-F(4)	1.5820(16)	1.599(7)[1.596(5)]	1.571(3)[1.578(3)]
C(1)-S(1)-F(5)	180.0	179.4(4)[180.0]	179.56(19)[179.83(18)]
F(5)-S(1)-F(1)	87.49(3)	86.6(4)[87.15(17)]	87.56(13)[87.69(14)]
F(5)-S(1)-F(2)	87.49(3)	86.9(4)[87.15(17)]	87.30(14)[87.83(14)]
F(5)-S(1)-F(3)	87.49(3)	88.3(4)[87.21(18)]	87.64(14[87.49(14)]
F(5)-S(1)-F(4)	87.49(3)	88.9(4)[87.21(18)]	88.24(14)[87.61(14)]
C(1)-S(1)-F(1)	92.51(3)	91.4(4)[92.79(18)]	92.79(16)[92.43(16)]
C(1)-S(1)-F(2)	92.51(3)	92.3(3)[92.79(18)]	92.43(16)[92.06(17)]
C(1)-S(1)-F(3)	92.51(3)	92.8(4)[92.85(17)]	92.01(16)[92.39(16)]
C(1)-S(1)-F(4)	92.51(3)	92.9(4)[92.85(17)]	92.04(17)[92.50(17)]
F-S(1)-F*	89.67(11)	89.3(4)[89.5(4)]	89.65(14)[90.12(14)]
	89.67(11)	89.5(4)[89.5(4)]	89.57(14)[89.78(15)]
	90.11(11)	90.3(4)[90.2(4)]	90.17(14)[89.95(15)]
	90.11(11)	90.5(4)[90.2(4)]	90.24(14)[89.77(15)]
F-S(1)-F**	174.98(6)	174.9(4)[174.4(3)]	175.17(14)[175.18(15)]
	174.98(6)	175.8(4)[174.3(3)]	175.53(14)[175.44(15)]

*The angles between the adjacent F(eq) atoms; **The angles between the opposite F(eq) atoms
Dimensions for second independent molecule in square parentheses.

Table 3-5. Selected bond distances (Å) and bond angles (°) for compounds **3.4**–**3.7**

	3.4	**3.5**	**3.6**	**3.7**
S(1)-F(5)	1.607(3)[1.603(3)]	1.575(3)	1.585(5)	1.597(3)
S(1)-C(1)	1.824(4)[1.824(4)]	1.793(4)	1.801(7)	1.812(4)
S(1)-F(1)	1.590(3)[1.595(3)]	1.575(3)	1.582(6)	1.5851(19)
S(1)-F(2)	1.593(3)[1.598(3)]	1.576(3)	1.591(3)	1.588(2)
S(1)-F(3)	1.603(3)[1.602(3)]	1.575(3)	1.609(5)	1.5923(19)
S(1)-F(4)	1.604(3)[1.607(3)]	1.569(3)	1.618(3)	1.593(2)
C(1)-S(1)-F(5)	179.36(10)[179.74(11)]	179.86(18)	179.1(3)	179.52(13)
F(5)-S(1)-F(1)	87.25(13)[87.30(13)]	87.65(15)	86.57(19)	87.16(11)
F(5)-S(1)-F(2)	87.29(13)[87.67(13)]	87.08(14)	86.9(3)	87.24(12)
F(5)-S(1)-F(3)	87.70(13)[87.67(13)]	87.78(15)	88.0(3)	87.50(12)
F(5)-S(1)-F(4)	87.89(13)[87.80(13)]	87.40(14)	88.18(19)	87.52(11)
C(1)-S(1)-F(1)	92.07(14)[92.08(14)]	92.34(17)	92.4(3)	92.28(13)
C(1)-S(1)-F(2)	92.11(14)[92.26(14)]	92.78(17)	92.6(2)	92.47(13)
C(1)-S(1)-F(3)	92.71(14)[92.45(14)]	92.24(17)	92.6(2)	92.50(13)
C(1)-S(1)-F(4)	92.97(14)[92.76(14)]	92.74(17)	92.7(3)	93.32(13)
F-S(1)-F*	89.44(12)[89.37(13)]	90.33(16)	88.71(19)	89.54(10)
	89.84(13)[89.87(13)]	89.64(16)	89.4(2)	89.75(10)
	89.85(12)[89.98(13)]	90.00(15)	90.6(2)	90.11(10)
	90.45(13)[90.38(13)]	89.59(16)	90.8(3)	90.12(10)
F-S(1)-F**	174.93(13)[174.97(12)]	175.42(15)	174.5(2)	174.40(13)
	175.16(12)[175.43(12)]	174.48(15)	174.9(3)	175.02(13)

*The angles between the adjacent F(eq) atoms; **The angles between the opposite F(eq) atoms
Dimensions for second independent molecule in square parentheses.

Table 3-6. Selected bond distances (Å) and bond angles (°) for compounds **3.8**–**3.10**

	3.8	**3.9**	**3.10**
S(1)-F(5)	1.598(7)	1.576(4)[1.571(4)]	1.568(4)
S(1)-C(1)	1.804(10)	1.791(6)[1.806(6)]	1.795(5)
S(1)-F(1)	1.587(7)	1.570(4)[1.570(4)]	1.572(4)
S(1)-F(2)	1.587(7)	1.572(4)[1.571(4)]	1.579(4)
S(1)-F(3)	1.603(7)	1.573(5)[1.577(4)]	1.582(4)
S(1)-F(4)	1.608(7)	1.577(4)[1.584(4)]	1.579(4)
C(1)-S(1)-F(5)	179.7(4)	178.5(3)[179.0(2)]	179.6(2)
F(5)-S(1)-F(1)	87.7(4)	87.4(2)[87.1(2)]	88.0(2)
F(5)-S(1)-F(2)	87.8(4)	87.8(2)[87.43(19)]	88.3(2)
F(5)-S(1)-F(3)	88.2(4)	88.1(2)[87.5(2)]	88.0(2)
F(5)-S(1)-F(4)	88.4(4)	88.3(2)[88.50(19)]	88.01(19)
C(1)-S(1)-F(1)	91.7(4)	91.2(2)[91.6(2)]	92.2(2)
C(1)-S(1)-F(2)	91.9(4)	91.5(3)[92.4(2)]	91.3(2)
C(1)-S(1)-F(3)	92.0(4)	92.7(2)[92.5(2)]	91.8(2)
C(1)-S(1)-F(4)	92.4(4)	93.1(3)[92.9(3)]	92.4(2)
F-S(1)-F*	89.8(4)	89.63(19)[89.63(19)]	90.4(2)
	89.9(3)	89.8(3)[89.81(18)]	89.6(2)
	89.9(4)	89.9(2)[90.02(19)]	89.79(19)
	90.0(4)	90.3(2)[90.2(2)]	90.0(2)
F-S(1)-F**	175.9(4)	175.4(2)[174.7(2)]	176.0(2)
	176.2(4)	176.1(2)[175.9(2)]	176.3(2)

*The angles between the adjacent F(eq) atoms; **The angles between the opposite F(eq) atoms
Dimensions for second independent molecule in square parentheses.

3.3. X-ray Structure Analysis

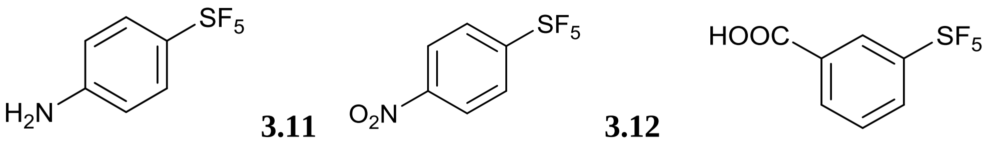
Compounds **3.1**–**3.10** are aromatic compounds with one important moiety SF_5 group in which one aryl carbon occupies the sixth position of octahedral coordination sphere around the sulfur atoms. The S-F(ax) bond is roughly perpendicular to the mean plane of the four equatorial fluorine atoms, which are staggered with the plane of the aryl ring. The C-S-F(ax) angle in **3.1**–**3.10** is very close to 180° [178.5(3) to 180°]. Another important feature is the substituent group on the aryl ring, changing the substituent group makes the compound show different structural characters. The substituent such as -OH, -COOH, and etc. can form intermolecular hydrogen bonds, resulting in stable packing frameworks. It is worth noting that the structure of **3.2** is a chiral configuration (Flack value is -0.0(3) and the space group is $P2_12_12$).

3.3.1. Structural Similarities

Compounds **3.1**–**3.4**, **3.6**, **3.8** and **3.10** consist of only one aryl ring, while, compounds **3.5**, **3.7** and **3.9** have heteroaromatic structure with a fused ring. In crystal structures of **3.1**–**3.10**, the S(1)-F(ax) bond distances are between 1.570(4) to 1.618(3) Å, and the S(1)-C(1) bond distances range from 1.791(6) to 1.824(4) Å. All the equatorial F atoms are in approximately co-plane along with the C(1)-S(1)-F(ax) bond angles of nearly 180°. Although different substituent connected on aromatic ring have a subtle effect on the bond length and angle in the SF_5 group, the SF_5 group is still in a roughly octahedral environment as the previously reported.[7,45]

3.3.2. Pentafluorosulfanyl Benzenes with Mono-Substituted Group

Compounds **3.1**–**3.4** with one simple substituent such as -OH, or -CN or -COOH group on the aryl ring will be described here. Three known compounds with the similar structures (Figure 3-2): 4-aminophenylsulfur pentafluoride **3.11**,[38] 4-nitrophenylsulfur pentafluoride **3.12**[7] and 3-pentafluorosulfanyl benzoic acid **3.13**[45] will be also cited for the comparison. The structures of **3.1** and **3.2** are in the same orthorhombic crystal system, meanwhile, the structures of **3.3** and **3.4** are different from **3.1** and **3.2**, with respective monoclinic and triclinic crystal system. The space groups are *Cmcm*, $P2_12_12$, $P2_1/c$ *and* *P-1* for **3.1**–**3.4**, respectively. The structures of **3.2**–**3.4** have two independent molecules and **3.1** contains one single molecule in the asymmetric unit. The sulfur and oxygen atoms in **3.2**, **3.3** and **3.11** do not lie in the aryl ring plane, however, the sulfur atoms in **3.1** and **3.12** are co-planar with the planes of the aryl rings and these are imposed by the crystallographic symmetry.



3.11 **3.12** **3.13**

Figure 3-2. The chemical structures of the known compounds **3.11**–**3.13**.

The S-F(ax) bond lengths in **3.1**–**3.4** are very similar {1.588(3) Å in **3.1**, 1.587(7)[1.609(7)] Å in **3.2**, 1.573(3)[1.579(3)] Å in **3.3** and 1.607(3)[1.603(3)] Å in **3.4**}, and the values are comparable to that in the known structures of **3.11**–**3.13** [1.600(2) Å in **3.11**, 1.576(2) Å in **3.12** and 1.587(2) Å in **3.13**].[7,38,45] The S-F(eq) bond distances in **3.1**–**3.4** are also very close to each other {1.5820(16) Å in **3.1**, 1.573(7) to 1.599(7) Å in **3.2**, 1.571(3) to 1.590(3) Å in **3.3** and 1.590(3) to 1.607(3) Å in **3.4**, and the longest S(1)-F(eq) distance [1.607(3) Å, from one of two molecules] in **3.4** and the shortest one [1.571(3) Å] in **3.3** are observed. The S-C bond distances [1.795(3) to 1.831(9) Å] in **3.1**–**3.4** are falling in the range of 1.785(3) to 1.812(3) Å for the known structures of **3.11**–**3.13**.[7,38,45] The C-S-F(eq) bond angles in **3.1** [92.51(3)°] are rather close to that in **3.12** [92.18(4)°] due to their very similar and high symmetrical structures.[38] The C-S-F(eq) angles in **3.2** [91.4(4) to 92.9(4)°], in **3.3** [92.01(16) to 92.79(16)°] and in **3.4** [92.07(14) to 92.97(14)°] are also comparable to each other, these values are marginally smaller than that in the structure of **3.11** [92.95(13) to 93.39(12)°].[7] The subtle difference of the bond lengths and angles suggests that the environment of group SF_5 is very similar, attributing to the structural stability of SF_5 group. The different substituent group and group number seem to have limited effect on the bond lengths and angles on SF_5 group in the structures of **3.1**–**3.4**, although the electron withdrawing groups (-CN, -COOH) and the electron donating group (-OH) can somewhat influence the $-SF_5$ group.

The intermolecular and intramolecular interactions are significant features in pentafluorsulfuranyl-containing aromatic compounds. There are different kinds of interactions in **3.1**–**3.4**, including the strong/weak intramolecular hydrogen bonds or interactions, the strong/weak intermolecular hydrogen bonds or interactions and strong π-stacking interactions.

In **3.1** (Figure 3-3), both intermolecular C-H···F hydrogen bonding and intermolecular C-H···N hydrogen bonding are observed with the distances of the H···N and H···F(ax) being respective 2.883(3) and 2.587(3) Å, these values are close to the sum of Van der Walls Radii (2.7 and 2.55 Å) (Figure 3-4). The molecules are packed into multi-layers by these two intermolecular hydrogen bonds in the same layer, however, there is no intermolecular interaction observed between the layers, and the layers are parallel with the interlayer distance of 3.432(4) Å (Figure 3-5).

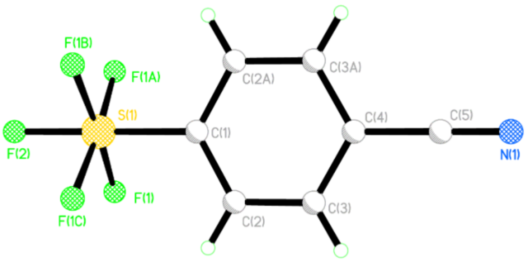


Figure 3-3. X-ray single crystal structure of **3.1**.

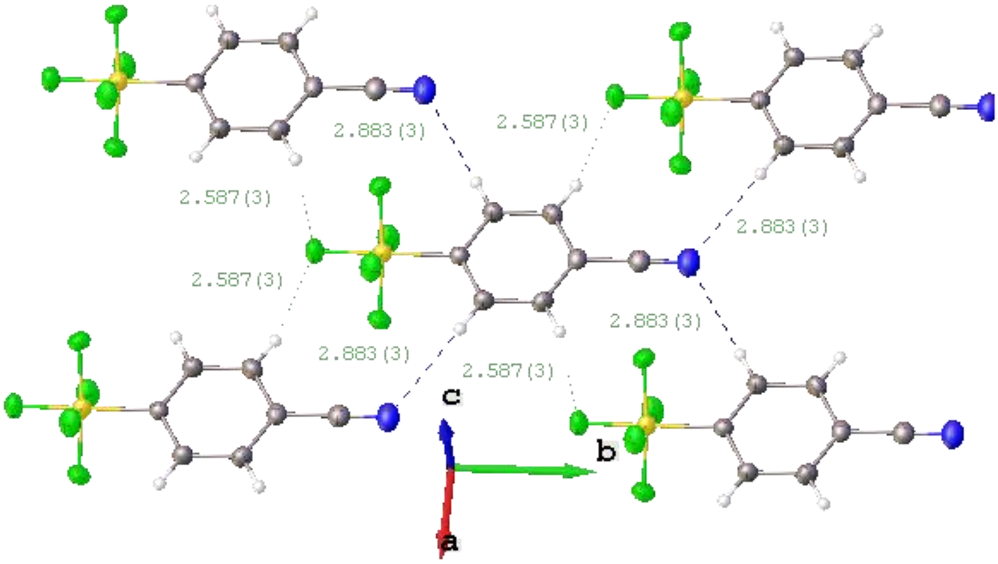


Figure 3-4. Possible intermolecular interactions in structure of **3.1**.

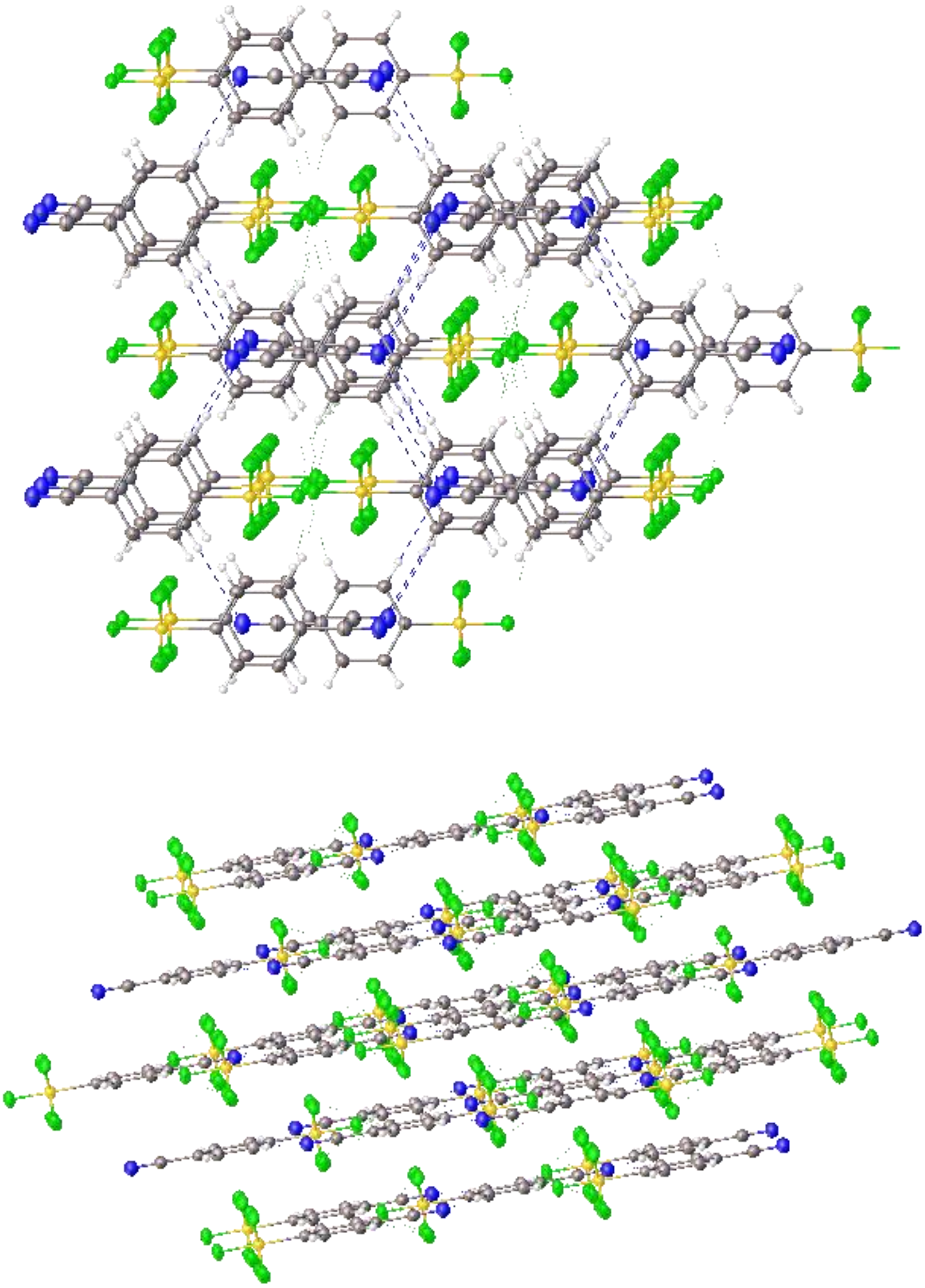


Figure 3-5. View of the layer structure, which builds up the structure in compound **3.1**, formed by the C-H···F hydrogen bonding (green dashed line), C-H···N hydrogen bonding (blue dashed line).

There are some weak intermolecular interactions in **3.2** (Figure 3-6). The three-dimensional networks are built by these weak intermolecular C_{aryl}-H···O and C_{aryl}-H···F(eq) hydrogen bonds. The two molecules are linked by the weak intermolecular C_{aryl}-H···O hydrogen bonding with the H···O distance of 3.008(7) Å along with the

C···O distance of 3.611(11) Å and C-H···O angle of 124.0(5)°, indicating the typical motif for hydrogen bonding.

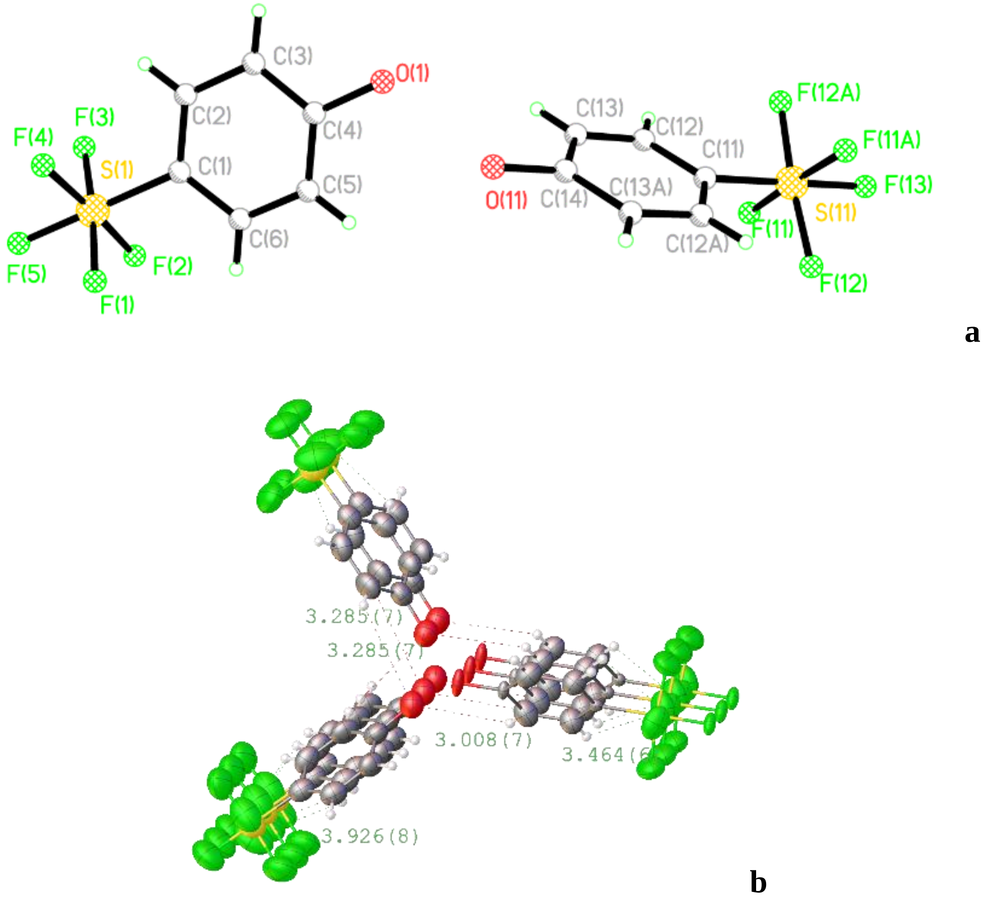


Figure 3-6. (**a**) X-ray crystal structure and (**b**) view of the 3-D network which shows ‘zipper chain’ form in **3.2**.

It is interesting to note that two strong intermolecular O-H···O hydrogen bonds with the H···O distances of 1.65(6) and 1.68(6) Å, which are significantly shorter than the sum of Van der Walls Radii (2.60 Å), are observed between *‘Head to Head’* pairs of molecules in **3.3** (Figure 3-7). The O(2)···O(12) and O(1)···O(11) distances are 2.615(4) and 2.658(4) Å along with the O(2)-H(2A)···O(12) and O(11)-H(11A)···O(1) angles of 174(6) and 175(6)°, meanwhile, there are two weak intermolecular hydrogen bonds existing as shown in Figure 3-7. The intermolecular O(2)-H(2A)···O(11) and O(11)-H(11A)···O(2) hydrogen bonds are almost identical with the H···O distances of 2.79(6) Å, accompanied by the angles of 132(4) and 133(5)°. Furthermore, the molecular sheets are linked by several weak intermolecular interactions: H···S distances range from 3.6234(11) to 4.3212(13) Å, H···F(eq) distances are 2.678(2) and 2.870(2) Å, and H···F(ax) distance is 2.896(3) Å. The layers are packed by the weak intermolecular C_{aryl}-H···F, C_{aryl}-H···S and C_{aryl}-H···O interactions (~3 Å) as shown in Figure 3-8.

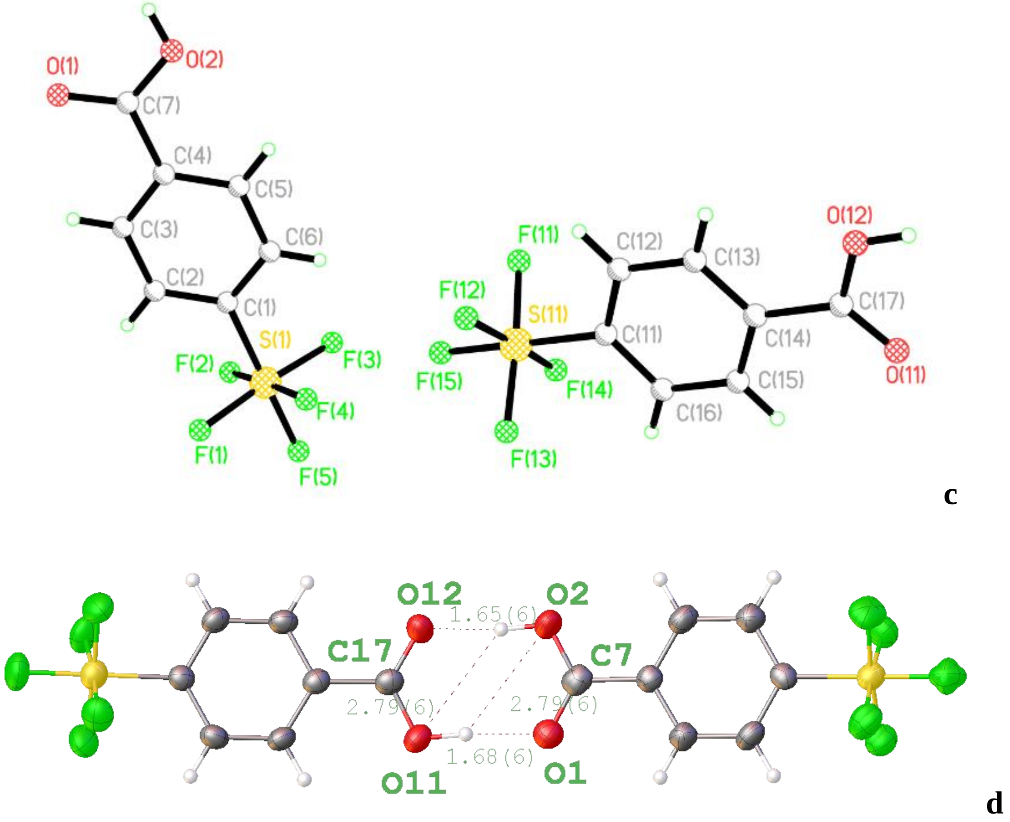
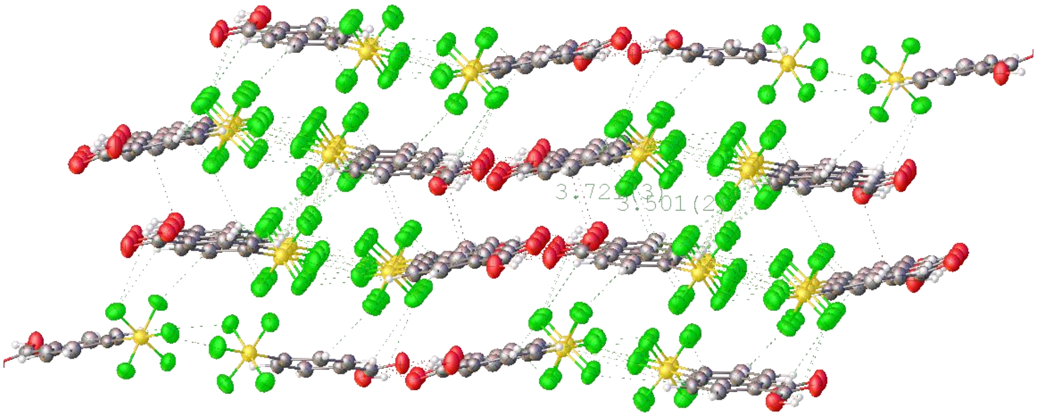


Figure 3-7. (**c**) X-ray crystal structure and (**d**) OLEX drawing of the intermolecular C-O···H interactions [1.65(6) and 2.79(6) Å] in **3.3**.



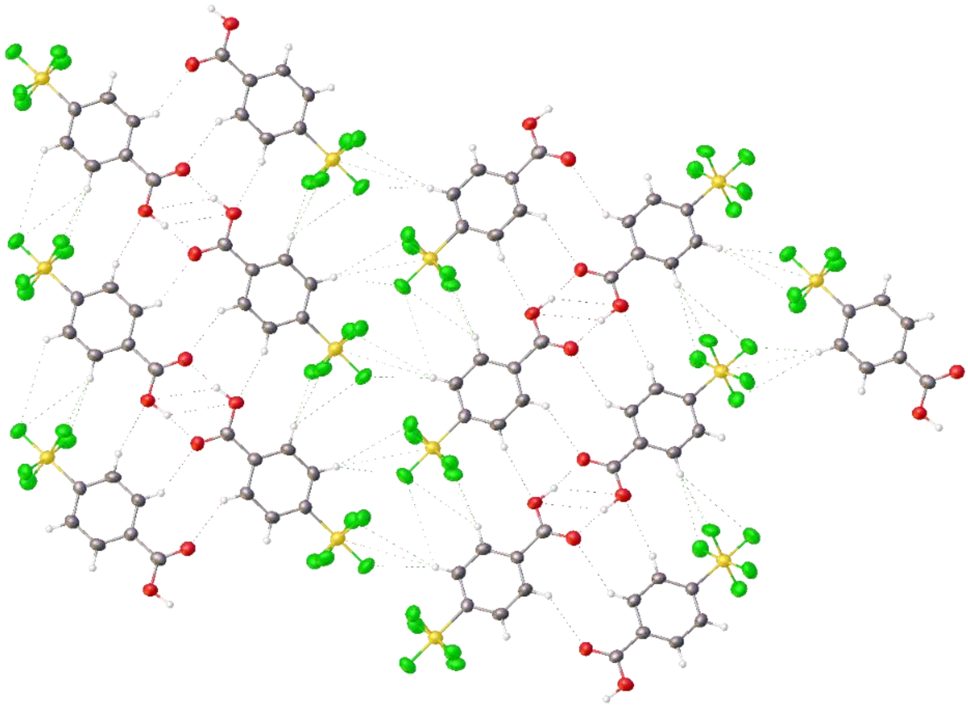


Figure 3-8. The packing network shows the arrangement of layers and a view of network displays clearly intermolecular C-H···O (red dashed line) and C-H···F interactions (green dashed line) in **3.3**.

The X-ray crystal structure and packing network for **3.4** are shown in Figure 3-9, the *'Head to Head'* molecules and '*Tail to Tail'* molecules are spirally arranged by the weak intermolecular C_{aryl}-H···O [2.852(4) and 2.922(4) Å], C_{aryl}-H···F(eq) [2.551(4), 2.649(3) and 2.929(4) Å], C_{aryl}-H···F(ax) [2.619(4) and 2.920(4) Å], and C_{aryl}-H···S [3.564(4) Å] interactions.

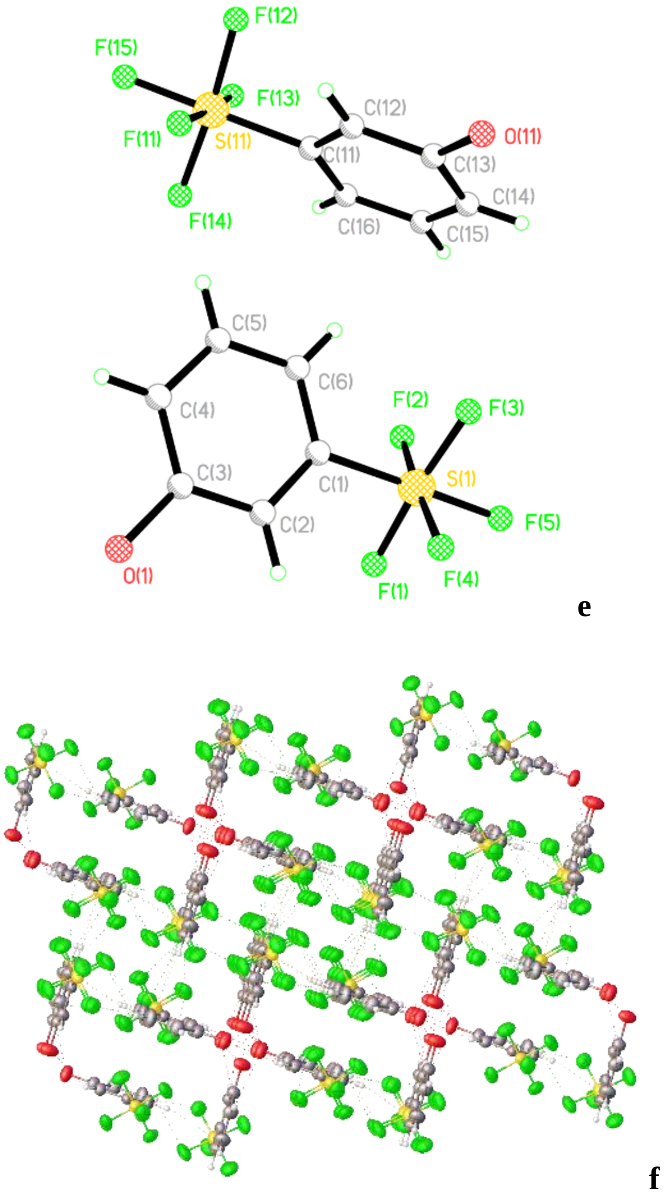


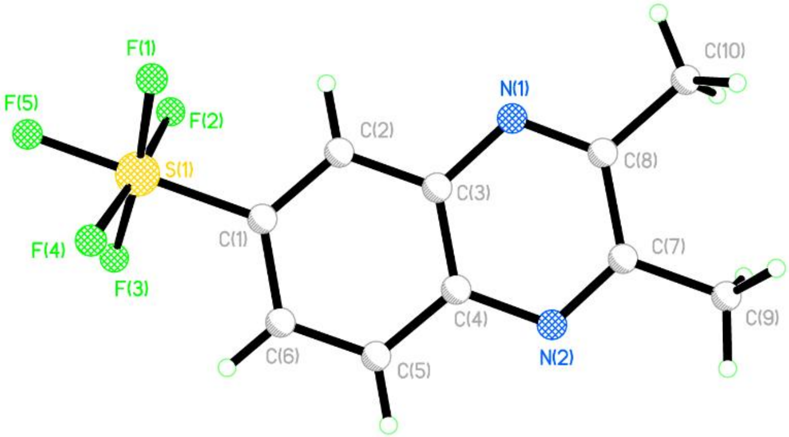
Figure 3-9. (**e**) Single crystal X-ray structure and (**f**) a view of 3-D packing network exhibits the intermolecular C-H···O (red dashed line) and C-H···F (green dashed line) interactions in **3.4**.

Interestingly, though there is no distinct conventional intramolecular hydrogen bonds in **3.1–3.4**, the intramolecular interactions between the equatorial fluorine atoms and aromatic hydrogen atoms are found to be very strong, in which the distances of H···F(eq) are close to the sum of the van der Waals radii (2.55 Å). The intramolecular interaction distances of the F(eq) atoms and the *ortho*-aromatic hydrogen atoms are 2.517(2) Å in **3.1** and 2.536(7) to 2.703(6) Å in **3.2**. The H···F(eq) intrarmolecular interaction distances in **3.4** range from 2.471(3) to 2.648(3) Å. The intramolecular interactions keep the equatorial fluorine atoms staggered relative to the aryl plane.

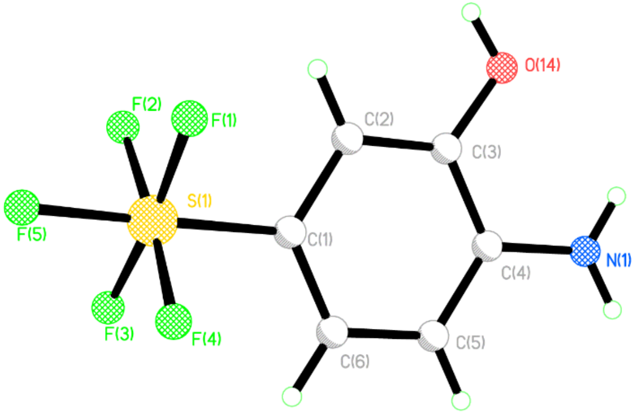
3.3.3. Pentafluorosulfanyl Benzenes with Two or Three Substituted Groups

Pentafluorosulfanyl benzenes with two or three substituted groups will be discussed here. The X-ray single crystal structures of **3.5**–**3.10** are shown in Figure 3-10. Compound **3.5** crystallises in $P2_1/n$ space group, **3.6** in *R-3* space group, **3.7** and **3.8** in the $P2_1/c$ space group, and **3.9** and **3.10** in the *P-1* space group, along with one molecule in the asymmetric unit for all structures except the structure of **3.9** with two molecules in the asymmetric unit. Selected bond lengths and angles are listed in Table 3.5 and 3.6, and further crystal structure data are recorded in **Appendix 1**. These six structures have very similar S-F(ax) bond distances [1.568(4) to 1.598(7) Å], S-C bond distances [1.791(6) to 1.812(4) Å], and S-F(eq) bond distances [1.569(3) to 1.618(3) Å] with the C-S-F(eq) angles from 91.2(2) to 93.32(13)°, being comparable to that in the known pentafluorosulfanyl benzenes with one substituted group. The bond lengths of the S-F single bond and the S-C single bond in **3.5**–**3.10** are comparable to the reported values for the S-C single bond [1.818(1) Å] and the S-F single bond [1.561(2) Å] in SF_6.[53]

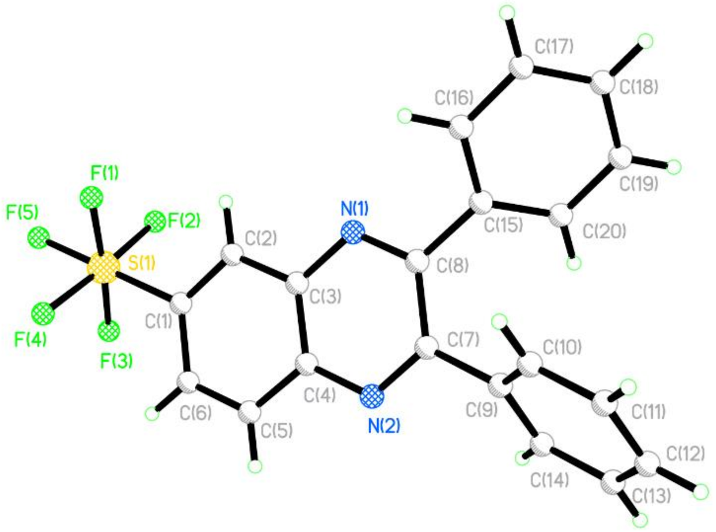
The compounds **3.5** and **3.7** have one pyrazine group adjacent on the aromatic rings; the compound **3.7** contains two phenyl rings connecting with pyrazine. The F(eq)-S(1)-C_{aryl}-C_{aryl} torsion angles in **3.5** and **3.7** are also bigger than that in **3.6**, **3.8**, **3.9** and **3.10**, twisting from 37.7(3) to 52.4(3)° in **3.5** and 37.7(3) to 52.2(2)° in **3.7** (Table 3.4). Two nitrogen atoms deviate 0.004(6) and 0.007(6) Å from the C1-C2-C3-C4-C5-C6 mean plane in **3.5**, and 0.011(5) and -0.008(5) Å in **3.7**. The twisted angles between the N(2)-C(4)-C(3)-N(1)-C(8)-C(7) ring and two phenyl rings in **3.7** are 54.01(12) and 43.71(12)°. The strong intramolecular C_{aryl}-H⋯F(eq) interactions might have some influence on the stability of aromatic-SF5 group. In **3.5**, the intramolecular C_{aryl}-H⋯F(eq) interaction distances are 2.390(3), 2.435(2), 2.619(3) and 2.644(3) Å, and there has also the similar values [2.421(2) to 2.658(2) Å] in **3.7**. The intramolecular C-H(2)⋯N(1) interaction distance [2.560(3) Å] is shorter than that of C-H(5)⋯N(2) [2.583(3) Å] in **3.5** (Figure 3-11). However, the intramolecular C-H(2)⋯N(1) interaction [2.599(3) Å] is similar to the intramolecular C-H(5)⋯N(2) interaction [2.591(3) Å] in **3.7**. Furthermore, the C-H_{aryl}⋯*meta*-N [2.687(2) Å] and C_{aryl}-H⋯*para*-N [2.817(3) Å] interaction distances in **3.7** are considerably longer than that between nitrogen atoms and the relevant H_{methyl} atoms [2.450(3) and 2.430(3) Å] in **3.5** (Figure 3-11).



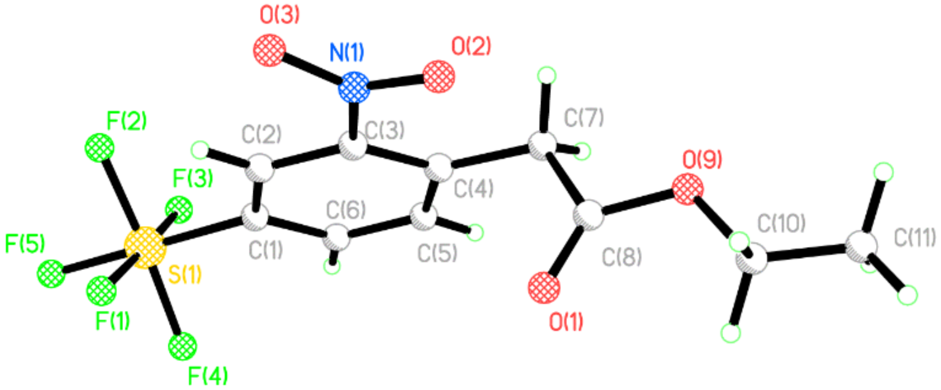
3.5



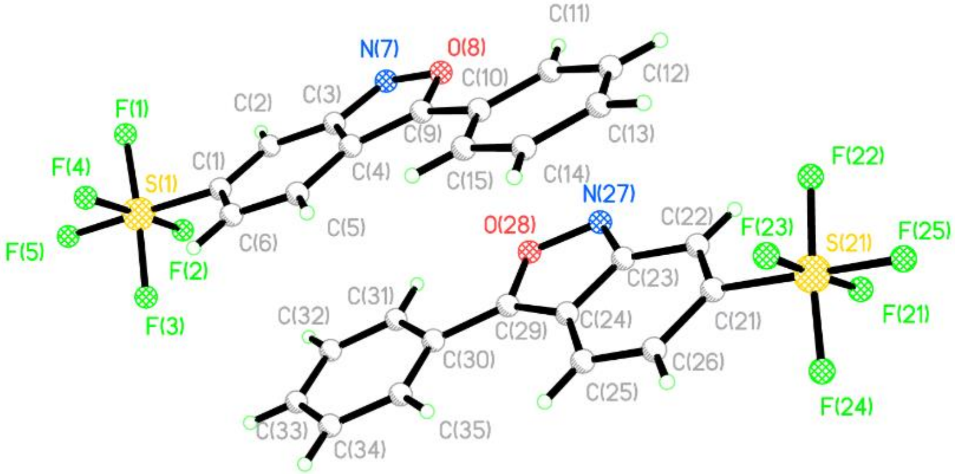
3.6



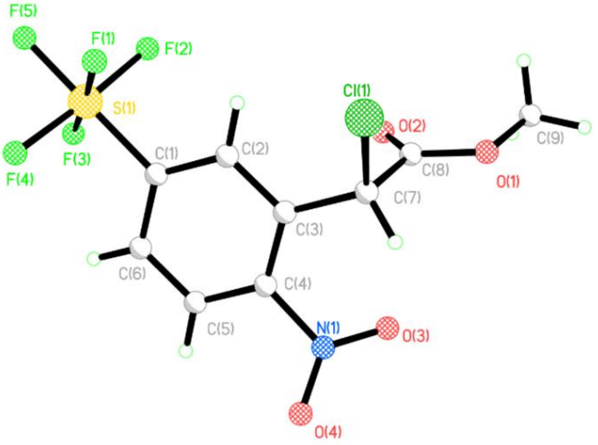
3.7



3.8



3.9



3.10

Figure 3-10. X-ray crystal structures of compounds **3.5**–**3.10**.

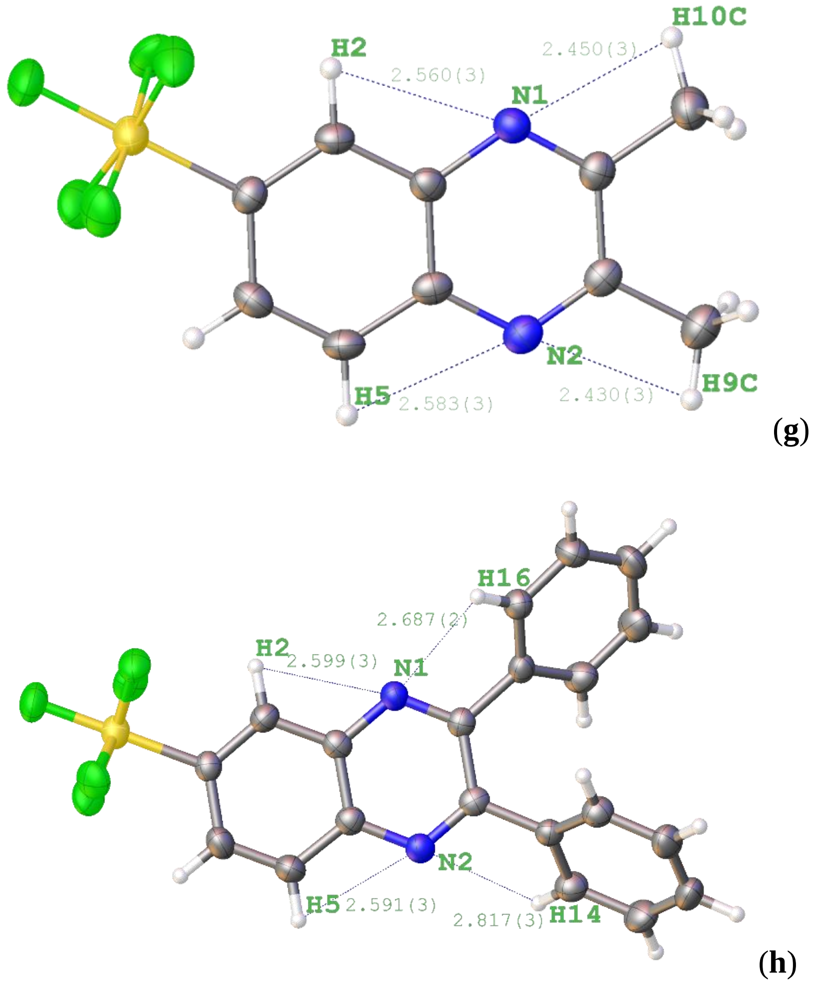


Figure 3-11. Possible intramolecular interactions between nitrogen and hydrogen can be described by the N···H distance in **3.5** (**g**) and **3.7** (**h**).

The intermolecular interactions such as the weak C_{methyl}-H···N, C_{methyl}-H···F and C_{aryl}-H···F hydrogen bonding, are combined with different way giving a variety of packing networks. In the structure of **3.5** (Figure 3-12), the intermolecular H···N interaction distance of 2.744(3) Å is very close to the sum of Van der Walls Radii [2.70 Å] form the multi-layer framework; the intermolecular C_{methyl}-H···F(ax) interaction distance of 2.876(2) Å is longer that the sum of Van der Walls Radii of hydrogen atom and fluorine atom [2.55 Å], being in conjunction with other weak hydrogen bonding between multi-layers; the weak intermolecular C_{methyl}-H···N interactions, the strong intermolecular C_{methyl}-H···F(eq) and C_{aryl}-H···F(eq) interactions Å build up the 3-D packing network, and the chain slots next to each other in a zipper like fashion. In **3.7**, the H···N interaction distances [2.715(3) and 2.661(2) Å] are similar to the H···F(eq) interaction distance [2.793(2) Å]; the intermolecular C_{aryl}-H···F(eq) bonds [2.848(2) and 2.959(2) Å] and the C_{aryl}-H···F(ax) interactions [2.852(3) and 2.953(2) Å] are almost identical in the packing arrangements because the two phenyl rings twist on the quinoxaline ring (Figure 3-13).

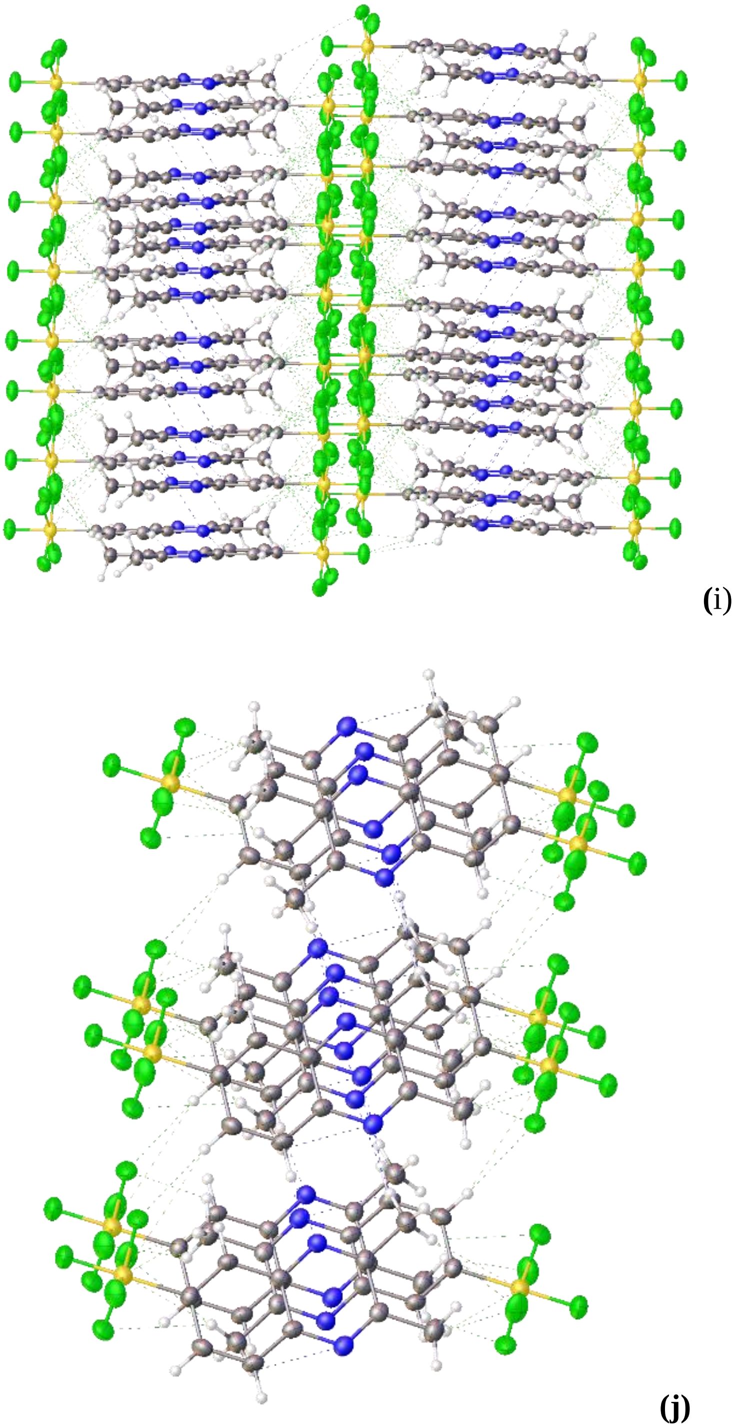


Figure 3-12. (**i**) A view of 3-D packing network displays the intermolecular C-H···N interactions (blue dashed line) and (**j**) the intermolecular C-H···F interactions (green dashed line) in **3.5**.

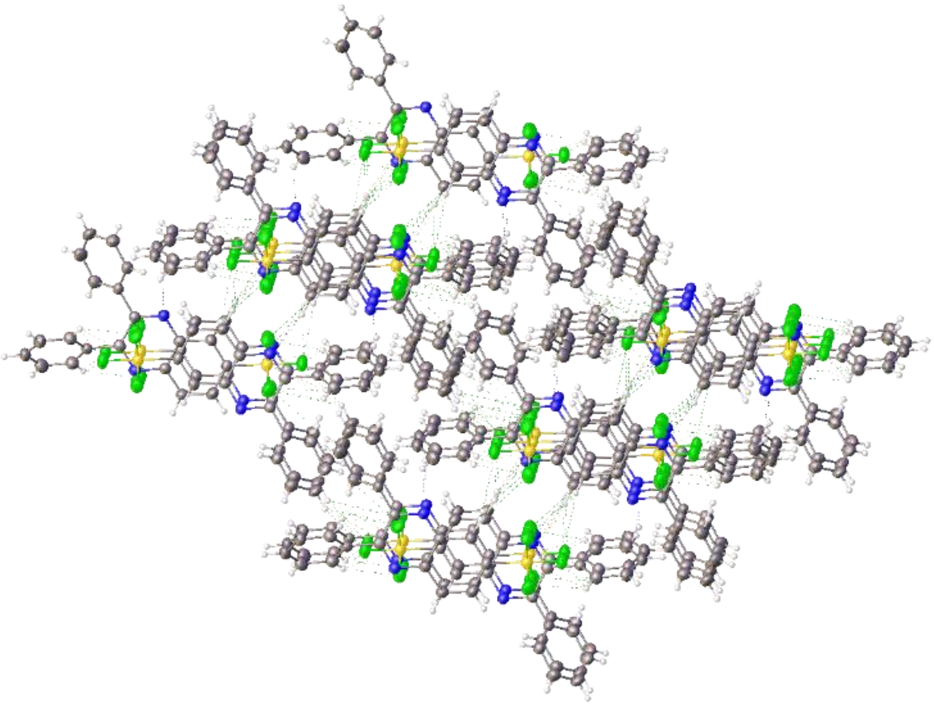


Figure 3-13. A view of 3-D packing network shows the intermolecular C-H···N (blue dashed line) and H···F (green dashed line) interactions in **3.7**.

The structures of **3.6**, **3.8**, **3.9** and **3.10** have a stabilized SF_5-attaching aryl ring with the intramolecular C_{aryl}-H···F(eq) interactions [the distances of 2.385(4) to 2.643(4) Å]. It appears that the intermolecular/intramolecular O···H and N···H interactions could be present in the same time due to these compounds containing oxygen atoms and nitrogen atoms. The distance of H···O is 2.364(3) Å with the N-H···O angle of 101.9(3)° in **3.6**. The distances of H···N are 2.620(6) Å in **3.6**, 2.572(13) Å in **3.8**, 2.706(5) [2.701(5)] Å in **3.9** and 2.557(5) Å in **3.10** (Table 3-5). The intramolecular H_{phenyl}···Cl interaction distance [2.7076(18) Å] is shorter than the sum of Van der Walls Radii [3.0 Å] in **3.10** (Figure 3-14).

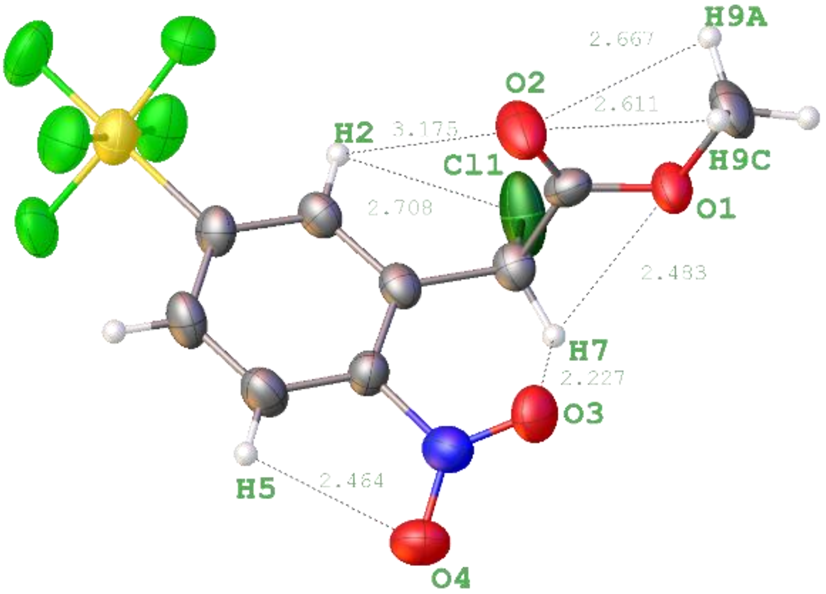


Figure 3-14. Possible intramolecular C-H···O/Cl interaction can be expressed by the H···O/Cl distances in **3.10**.

A variety of slightly different hydrogen bonds, π-stacking interactions and other intermolecular interactions build up the packing arrangement, and the relevant data are listed in Table 3-7. The multi-sheeted supramolecular assemblies in the structures of **3.6** and **3.9** are formed by the strong intermolecular $\mathrm{C_{aryl}}$-H···N hydrogen bonds in conjunction with a series of the weak intermolecular $\mathrm{C_{aryl}}$-H···F, $\mathrm{C_{aryl}}$-H···O interactions and π-stacking interaction (Figure 3-17 and 3-18). There is no stratification and one set of π-stacking interaction is observed in the supramolecular assembly in **3.6** with zero angle, centroid-centroid distance of 3.832 Å, shift distance of 0.432 Å at (1-x, 1-y, -z) (Figure 3-15). These π-stacking arrangements are formed by a combination of the O-H···N [2.063(5) Å], $\mathrm{C_{aryl}}$-H···N [2.977(4) Å], $\mathrm{C_{aryl}}$-H···O [2.543(5) Å], N-H···F(eq) [2.429(3) and 2.450(3) Å] and $\mathrm{C_{aryl}}$-H···F(eq) [2.725(6) Å] hydrogen bonds.

Whilst, four sets of π-stacking interactions intersect to create a complex 3-D network in **3.9** (Figure 3-16). The '*zigzag chain*' polymeric network is built up with '*Head to Tail*' linked by the weak intermolecular $\mathrm{C_{aryl}}$-H···N and $\mathrm{C_{aryl}}$-H···F(eq) interaction. The π-stacking interaction between the aryl rings at (x, y, z) and (-x, -y, 2-z) position in **3.9** is not parallel, having a centroid-centroid distance of 3.774 Å with the angle of 2.462° and shift distance of 1.557 Å. The π-stacking interaction between the aryl rings at (x, y, z) and (+x, +y, +z) position has a centroid-centroid distance of 3.873 Å with the angle of 4.058° and shift distance of 1.606 Å. The other π-stacking interactions have the centroid-centroid distances of 3.708 and 3.835 Å with the dihedral angles of 9.024 and 3.187°. The significant intermolecular interactions can be observed in the same layer in **3.9** because the C_{aryl}-H···F(eq) interaction distance is shorter than 2.55 Å [the sum of Van der Walls Radii of hydrogen atom and fluorine atom] and the C_{aryl}-H···N interaction distance is 2.429 Å, which is significantly shorter than the sum of Van der Walls Radii of hydrogen atom and nitrogen atom (2.8 Å). There are also some weak intermolecular C_{aryl}-H···O and C_{aryl}-H···F(eq) interactions present within one layer.

The intermolecular C_{aryl}-H···O-N interaction distances [2.470(9) Å] in **3.8** is shorter than that in **3.10**. The intermolecular C_{aryl}-H···O(1) [2.645(8) to 2.748(8) Å] and C_{alkyl}-H···F(eq) [2.583(8) to 2.767(8) Å] interactions are found in **3.8** and the molecules are linked by 'zigzag' form in 'S*ingle Molecule Sheet*'. In **3.10**, there are some weak intermolecular C_{alkyl}-H···O/Cl interactions and a strong intermolecular C_{alkyl}-H···O=C [2.183(4) Å] interaction present in the layers, meanwhile, the '*Head to Head*' and '*Tail to Tail*' molecules lead to the packing arrangement by the 'zipper' form, in which the intermolecular O···H interaction distances are from 2.737(4) to 2.829(5) Å within one layer.

Table 3-7. Selected intramolecular or intermolecular interactions (Å) and angles (°) for compounds **3.5–3.10**

	3.5	**3.6**	**3.7**	**3.8**	**3.9**	**3.10**
Intramolecular interactions						
F(1)···H(2)	2.619(3)	2.499(4)	2.421(2)	2.597(8)	2.517(4)[2.645(4)]	2.471(3)
F(2)···H(2)	2.390(3)	2.533(3)	2.628(2)	2.554(8)	2.461(4)[2.385(4)]	2.520(3)
F(3)···H(6)	2.644(3)	2.538(4)	2.453(2)	2.528(8)	2.529(4)[2.643(4)]	2.491(4)
F(4)···H(6)	2.435(2)	2.552(4)	2.658(2)	2.521(8)	2.490(5)[2.415(4)]	2.503(3)
C_{aryl}-H···N	2.560(3) 2.583(3)	2.620(6)	2.599(3) 2.591(3)	2.572(13)	2.706(5)[2.701(5)]	2.557(5)
C_{phenyl}-H···N			2.687(2) 2.817(3)			
C_{aryl}-H···O		2.653(4)		2.342(9)	2.410(4)[2.402(4)]	2.464(4)
C_{alkyl}-H···O						2.227(5)
N-H···O		2.364(3)				
Intermolecular interactions						
C-H···N	2.744(3)					
O-H···N		2.063(5)				
C_{aryl}-H···N		2.977(4)	2.661(2) 2.715(3)		2.429(5)	
C_{aryl}-H···O		2.543(5)		2.645(8) 2.748(8)	2.917(4) 2.942(4)	2.737(4) 2.829(5)
C-H···F	2.834(3) 2.630(3) 2.638(2)	2.725(6)	2.793(2)	2.583(8) 2.744(7) 2.767(8)	2.482(3)	
N-H···F		2.429(3)				

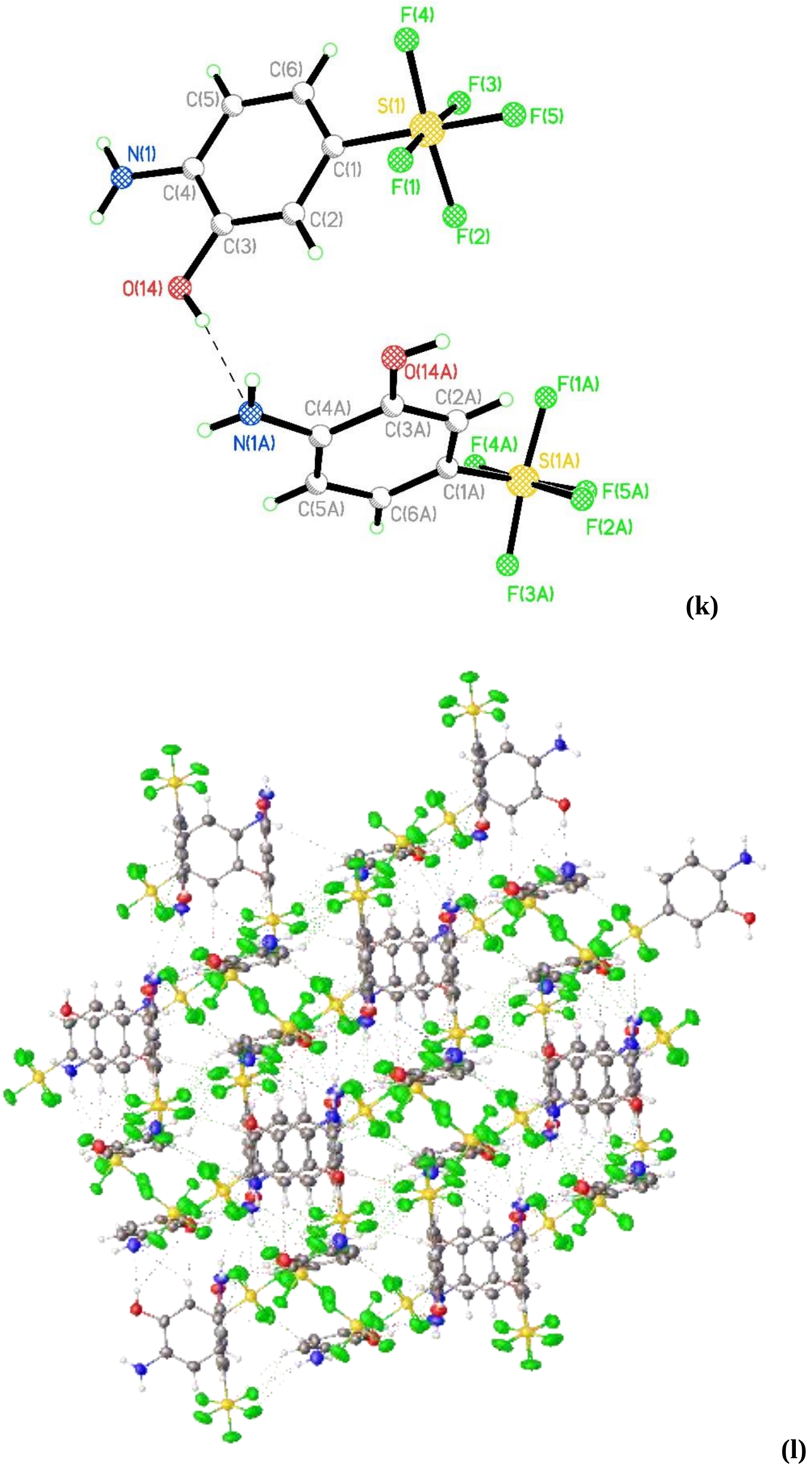


Figure 3-15. (**k**) Intermolecular hydrogen bonding and (**l**) a view of 3-D packing network in **3.6**.

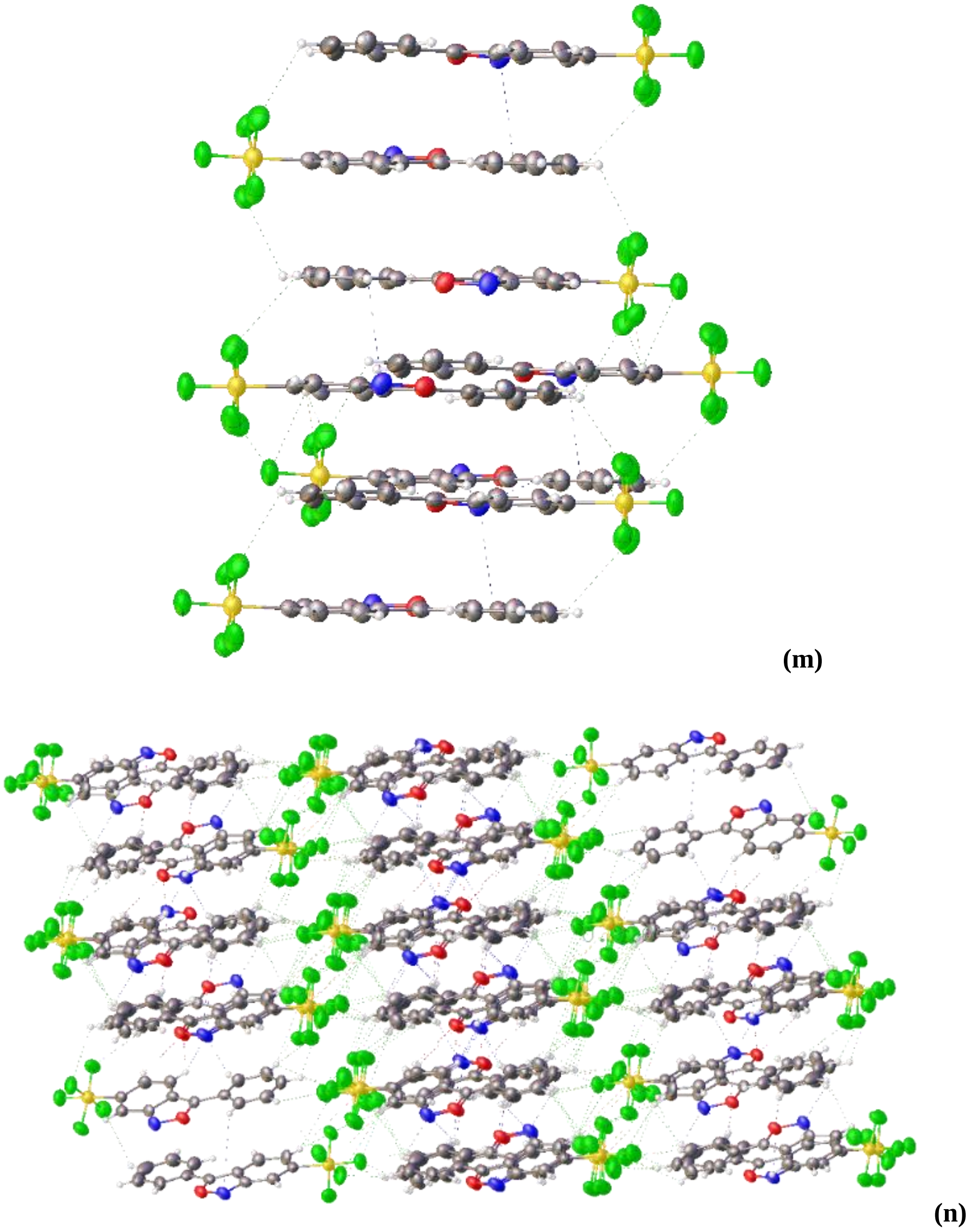


Figure 3-16. 3-D packing network shows ‘Zigzag chain’ polymeric network built up by the intermolecular C-H···N and C-H···F interactions (**m**) and a view of packing network by ‘Zipper’ form (**n**) in **3.9**.

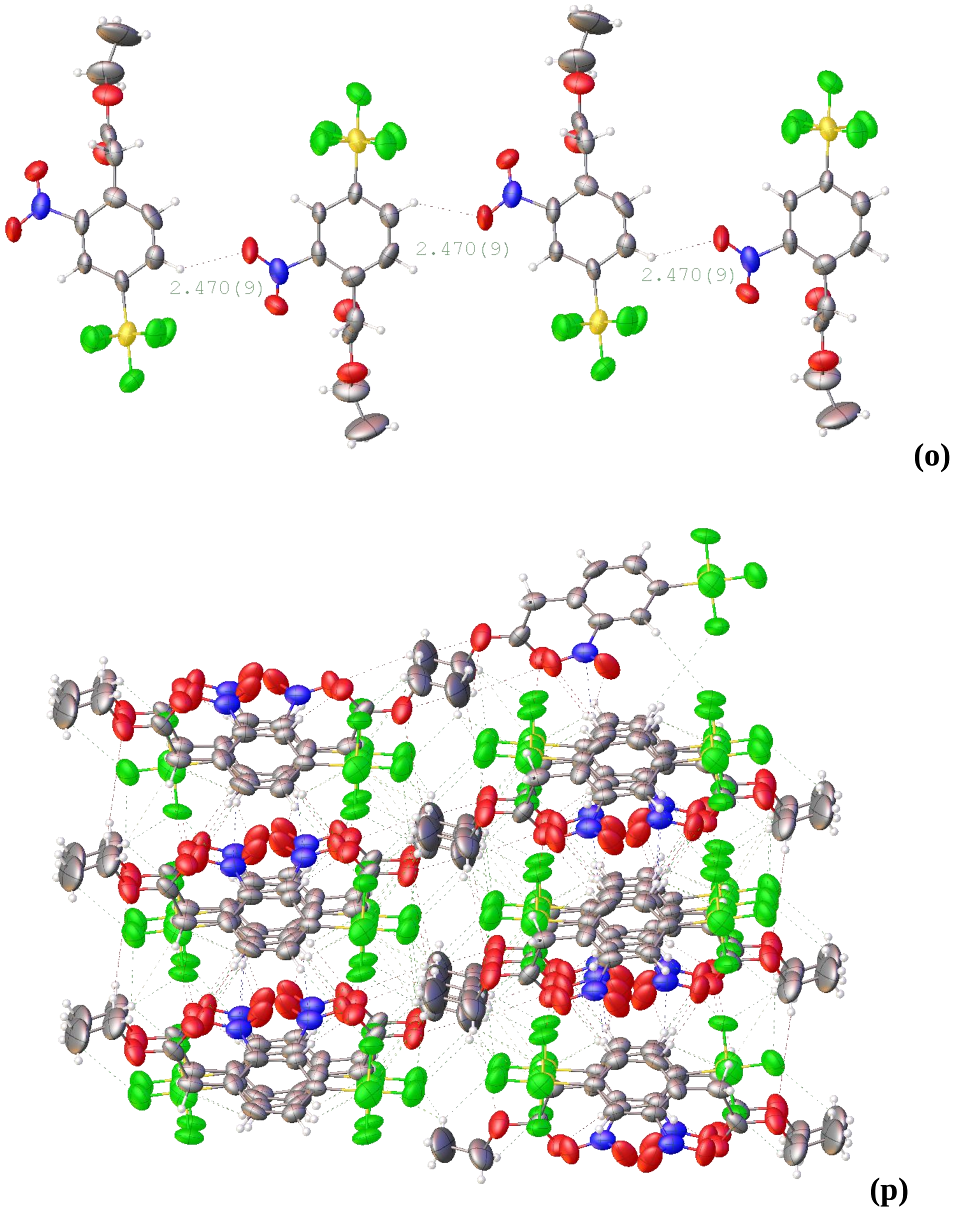


Figure 3-17. 3-D packing network shows ‘Zigzag chain’ polymeric network in a layer (**o**) and a view of 3-D packing network (**p**) in **3.8**.

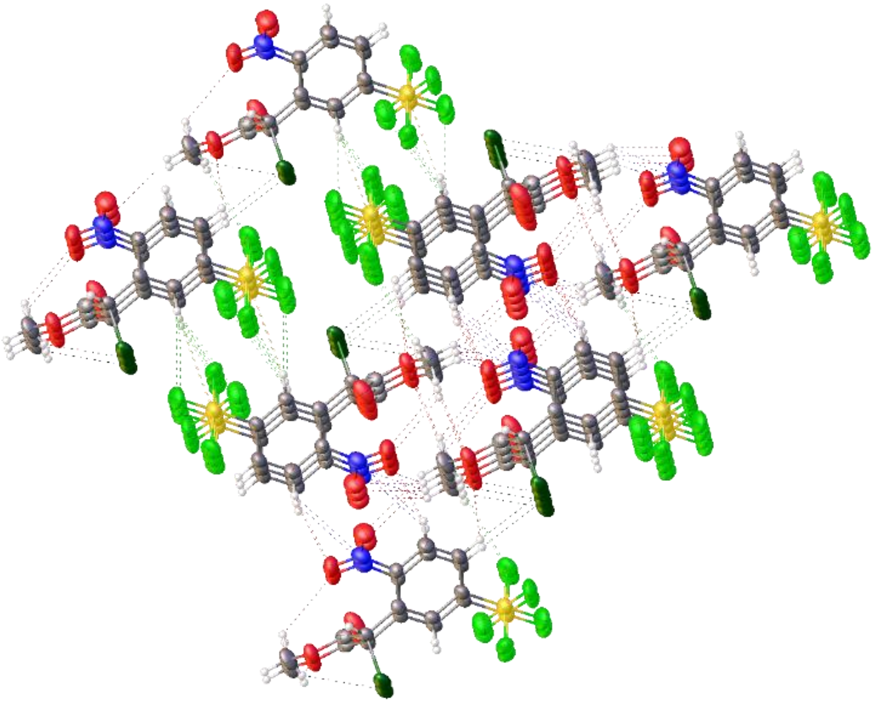


Figure 3-18. A view of 3-D packing network created by the intermolecular C-H···N/O/F/Cl interactions in **3.10**.

3.4. Conclusion

The pentafluorosulfuranyl (SF_5)-containing aromatic compounds **3.1**–**3.10** have been discussed crystallographically. The SF_5 group is stable and there are some slight differences by comparing with the ten compounds and three known structures of SF_5-aromatic compounds. The S-F(ax) bond lengths in these compounds are all ranging from 1.568(4) to 1.607(3) Å with C-S-F(ax) bond angles ranging with 178.5(3) to 180.0°. The S-F(eq) bond lengths are from 1.569(3) to 1.618(3) Å. In each structure, the S-F(ax) bond length and the four S-F(eq) bond lengths are nearly similar. For these ten compounds, the angles of two adjacent F(eq) is approximate 90°. Because of the compounds containing O/N/Cl/F atoms, there are some weak or strong intramolecular interactions appearing in this series of compounds. Especially, the distances of F(eq) and neighbouring H_{aryl} intramolecular interactions [2.385 to 2.703 Å] are falling in the sum of Van der Walls Radii [2.55 Å]. The intramolecular C_{aryl}-H···F(eq) interaction may keep the stability of equatorial fluorine atoms. Packing networks of all ten molecules are directed by some weak or strong intramolecular /intermolecular interactions between aromatic hydrogen atoms or alkyl hydrogen atoms and O/N/F/Cl atoms. Looking at the packing arrangement in compounds **3.6** and **3.9**, the π-stacking interactions are also observed.

3.5. References

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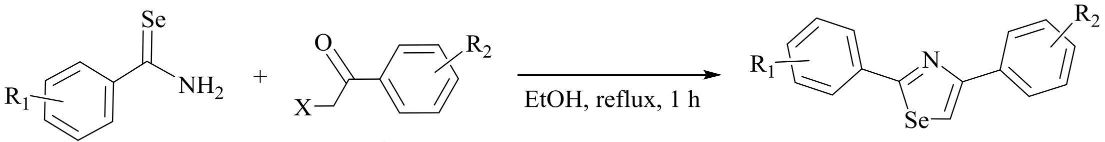
CHAPTER 4

STRUCTURAL STUDIES OF 2,4-DIARYL-1,3-SELENAZOLES

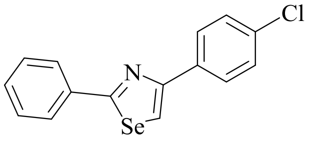
4.1. Introduction

The chemistry of selenium-containing heterocyclic compounds has received significant attention recently due to their interesting synthetic reactivity and their potential pharmaceutical applications, their uses in new materials as well as reagents and catalysts. Among them, the selenazole derivatives are of marked interest because of their anti-tumour, antibacterial and other notable activities.[1-14] This Chapter will focuses on the structural study of a series of new 2,4-diaryl-1,3-selenazoles. The chemical structures of the compounds **4.1**–**4.10** are shown in Figure 4-1. The main backbone in these compounds is 1,3-selenazole ring. The 2,4-diaryl-1,3-selenazoles **4.1**–**4.10** were synthesized in excellent yields from the reaction of aryl-selenamides and the corresponding α-haloketones as shown in Scheme 4-1.[15] All crystals of ten compounds suitable for X-ray crystallographic studies were obtained at room temperature from the diffusion of hexane into a dichloromethane solution. Compounds **4.2**–**4.4** and **4.9** crystallize in monoclinic crystal system, whereas compounds **4.1**, **4.5**–**4.8** and **4.10** crystallize in orthorhombic crystal system.



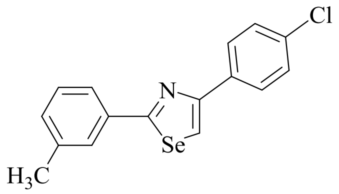
4.1 - 4.10

Scheme 4-1. Synthesis of 2,4-diaryl-1,3-selenazoles **4.1**–**4.10**.



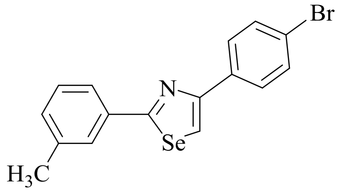
4-(4-Chlorophenyl)-2-phenyl-2*H*-1l^4,3-selenazole

4.1



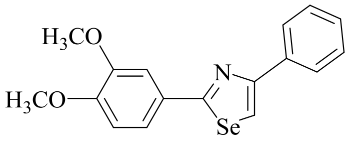
4-(4-Chlorophenyl)-2-(*m*-tolyl)-2*H*-1l^4,3-selenazole

4.2



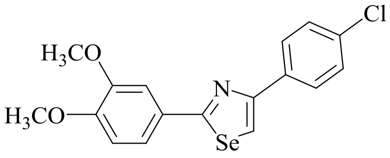
4-(4-Bromophenyl)-2-(*m*-tolyl)-1,3-selenazole

4.3



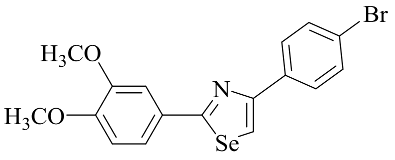
2-(3,4-Dimethoxyphenyl)-4-phenyl-1,3-selenazole

4.4



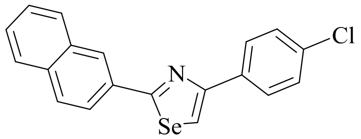
4-(4-Chlorophenyl)-2-(3,4-dimethoxyphenyl)-1,3-selenazole

4.5



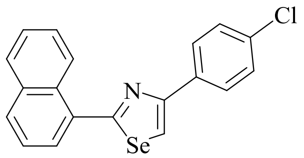
4-(4-Bromophenyl)-2-(3,4-dimethoxyphenyl)-1,3-selenazole

4.6



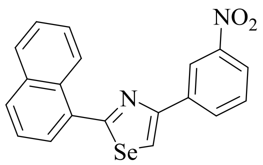
4-(4-Chlorophenyl)-2-(naphthalen-2-yl)-1,3-selenazole

4.7



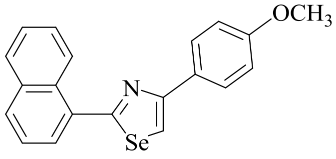
4-(4-Chlorophenyl)-2-(naphthalen-1-yl)-1,3-selenazole

4.8



2-(Naphthalen-1-yl)-4-(3-nitrophenyl)-1,3-selenazole

4.9



4-(4-Methoxyphenyl)-2-(naphthalen-1-yl)-1,3-selenazole

4.10

Figure 4-1. View of the chemical structures of 2,4-diaryl-1,3-selenazoles **4.1**–**4.10**

4.2. Crystal Structure Data

Data for 2,4-diaryl-1,3-selenazoles **4.1**, **4.3** and **4.4** were collected at -148℃ using the St Andrews Robotic diffractometer[16] with graphite-monochromated Mo-Kα radiation (λ = 0.7173 Å). Data for 2,4-diaryl-1,3-selenazoles **4.2** and **4.5–4.10** were also run at either -100℃ or -148℃ using a Rigaku SCX-Mini diffractometer. The unit cell and refinement parameters for compounds **4.1–4.10** are listed in Tables 4.1–4.3. Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorrentz, polarization and absorption effects. Structures were solved by direct methods and refined by full-matrix least-squares again F^2 (SHELXL)[17] using Crystal Structure.[18] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries.

The structures of **4.1–4.10** have a single molecule of the compound in each asymmetric unit. Compounds **4.1–4.3** have both methyl group and halogen substituent on the backbone aryl rings, and crystallize in a $Pca2_1$ (R_1 = 0.0589), $P2_1$ (R_1 = 0.0308) and $P2_1$ (R_1 = 0.0298) space group. Compounds **4.4–4.6** contain two -OCH_3 groups and one halogen substituent, and crystallize in a $P2_1/n$ (R_1 = 0.0827), *Pbca* (R_1 = 0.0530), and *Pbca* (R_1 = 0.0446) space group. The main skeleton structure of compounds **4.7–4.10** differ from compounds **4.1–4.6**, and crystallize in a $Pca2_1$ (R_1 = 0.0303), $P2_12_12_1$ (R_1 = 0.0583), *I2/a* (R_1 = 0.0536), and $P2_12_12_1$ (R_1 = 0.0311) space group, respectively.

Table 4-1. Relevant crystal data and refinement parameters for compounds **4.1**–**4.5**

Experimental details	**4.1**	**4.2**	**4.3**	**4.4**
Empirical formula	$C_{15}H_{10}ClNSe$	$C_{16}H_{12}ClNSe$	$C_{16}H_{12}BrNSe$	$C_{17}H_{15}NO_3Se$
Formula weight	318.66	332.69	377.14	360.27
Temperature (℃)	-148	-100.0	-148.0	-148.0
Crystal color, habit	colorless, platelet	colorless, platelet	colorless, platelet	colorless, platelet
Crystal dimensions (mm^3)	0.15×0.12×0.09	0.23×0.15×0.07	0.15×0.15×0.06	0.25×0.10×0.07
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Lattice parameters	a = 10.608(4) Å	a = 5.9135(7) Å	a = 5.941(3) Å	a = 19.337(18) Å
	b = 15.237(6) Å	b = 7.8207(9) Å	b = 7.744(3) Å	b = 5.100(4) Å
	c = 7.984(3) Å	c = 14.8420(18) Å	c = 14.930(6) Å	c = 19.366(18) Å
	$\alpha = 90^{\mathrm{o}}$	$\alpha = 90^{\mathrm{o}}$	$\alpha = 90^{\mathrm{o}}$	$\alpha = 90^{\mathrm{o}}$
	$\beta = 90^{\mathrm{o}}$	$\beta = 92.839(7)^{\mathrm{o}}$	$\beta = 93.277(11)^{\mathrm{o}}$	$\beta = 114.024(9)^{\mathrm{o}}$
	$\gamma = 90^{\mathrm{o}}$	$\gamma = 90^{\mathrm{o}}$	$\gamma = 90^{\mathrm{o}}$	$\gamma = 90^{\mathrm{o}}$
Volume (Å^3)	1290.6(9)	685.57(14)	685.8(5)	1744(3)
Space group	$Pca2_1$	$P2_1$	$P2_1$	$P2_1/n$
Z value	4	2	2	4
Dcalc (g/cm^3)	1.640	1.612	1.826	1.372
$F_{(000)}$	632.00	332.00	368.00	728.00
μ(MoKα) (cm^{-1})	30.954	29.172	56.441	21.631
Diffractometer	Saturn724	SCX mini	Saturn70	Mercury70
No. of reflections measured	Total: 5382	Total: 5801	Total: 5154	Total: 14003
Unique	1959	2384	2066	3044
R_{int}	0.0646	0.0449	0.0488	0.0991
Friedel pairs	734	1092	771	-
Min. and max. transmissions	0.457, 0.757	0.625, 0.815	0.523, 0.713	0.468, 0.859
No. of observations (All reflections)	1959	2384	2066	3044
No. of variables	163	172	172	199
Reflection/parameter ratio	12.02	13.86	12.01	15.30
Residuals: R_1 (I>2.00σ(I))	0.0589	0.0308	0.0298	0.0827
Residuals: R (all reflections)	0.0815	0.0329	0.0354	0.1127
Residuals: wR_2 (all reflections)	0.2004	0.0591	0.0761	0.2881
Goodness of fit indicator	1.166	1.049	0.997	1.107
Flack parameter	0.11(4)	0.012(10)	0.06(2)	-
Maximum peak in final diff. map (e$^-$/Å^3)	1.16	0.31	0.45	3.72
Minimum peak in final diff. map (e$^-$/Å^3)	-1.11	-0.29	-0.33	-0.67

Table 4-2. Relevant crystal data and refinement parameters for compounds **4.5**–**4.7**

Experimental details	**4.5**	**4.6**	**4.7**
Empirical formula	$C_{17}H_{14}ClNO_2Se$	$C_{17}H_{14}BrNO_2Se$	$C_{19}H_{12}ClNSe$
Formula weight	378.72	423.17	368.72
Temperature (℃)	-148.0	-148.0	-148.0
Crystal color, habit	colorless, chip	colorless, prism	colorless, prism
Crystal dimensions (mm^3)	0.23×0.20×0.10	0.38×0.23×0.07	0.40×0.19×0.10
Crystal system	orthorhombic	orthorhombic	orthorhombic
Lattice parameters	a = 7.45(5) Å	a = 7.475(6) Å	a = 11.190(8) Å
	b = 18.65(12) Å	b = 18.926(15) Å	b = 17.614(12) Å
	c = 22.91(15) Å	c = 22.879(18) Å	c = 7.851(5) Å
	$\alpha = 90^o$	$\alpha = 90^o$	$\alpha = 90^o$
	$\beta = 90^o$	$\beta = 90^o$	$\beta = 90^o$
	$\gamma = 90^o$	$\gamma = 90^o$	$\gamma = 90^o$
Volume ($Å^3$)	3182(37)	3236(4)	1547.5(18)
Space group	*Pbca*	*Pbca*	$Pca2_1$
Z value	8	8	4
Dcalc (g/cm^3)	1.581	1.737	1.583
$F_{(000)}$	1520.00	1664.00	736.00
μ(MoKα) (cm^{-1})	25.333	48.029	25.937
Diffractometer	SCX mini	SCX mini	SCX mini
No. of reflections measured	Total: 25280	Total: 25711	Total: 12673
Unique	2789	2846	2711
R_{int}	0.1267	0.0999	0.0532
Friedel pairs	-	-	1241
Min. and max. transmissions	0.440, 0.776	0.367, 0.714	0.592, 0.772
No. of observations (All reflections)	2789	2846	2711
No. of variables	199	199	199
Reflection/parameter ratio	14.02	14.30	13.62
Residuals: R_1 (I>2.00σ(I))	0.0530	0.0446	0.0303
Residuals: R (all reflections)	0.0834	0.0590	0.0379
Residuals: wR_2 (all reflections)	0.1557	0.1099	0.0757
Goodness of fit indicator	1.025	1.105	1.105
Flack parameter	-	-	-0.018(16)
Maximum peak in final diff. map ($e^-/Å^3$)	0.58	0.59	0.71
Minimum peak in final diff. map ($e^-/Å^3$)	-0.51	-0.60	-0.24

Table 4-3. Relevant crystal data and refinement parameters for compounds **4.8–4.10**

Experimental details	**4.8**	**4.9**	**4.10**
Empirical formula	$C_{19}H_{12}ClNSe$	$C_{19}H_{12}N_2O_2Se$	$C_{20}H_{15}NOSe$
Formula weight	368.72	379.28	364.30
Temperature (℃)	-100.0	-148.0	-100.0
Crystal color, habit	colorless, platelet	yellow, chip	colorless, chip
Crystal dimensions (mm^3)	0.17×0.16×0.07	0.21×0.20×0.10	0.28×0.20×0.15
Crystal system	orthorhombic	monoclinic	orthorhombic
Lattice parameters	a = 7.4657(9) Å	a = 15.380(4) Å	a = 7.3607(6) Å
	b = 8.2812(10) Å	b = 9.2019(14) Å	b = 8.6047(7) Å
	c = 25.225(3) Å	c = 21.514(5) Å	c = 25.1739(19) Å
	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$
	$\beta = 90^{\circ}$	$\beta = 92.896(17)^{\circ}$	$\beta = 90^{\circ}$
	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$
Volume (Å^3)	1559.6(3)	3040.9(12)	1594.4(2)
Space group	$P2_12_12_1$	$I2/a$	$P2_12_12_1$
Z value	4	8	4
Dcalc (g/cm^3)	1.570	1.657	1.518
$F_{(000)}$	736.00	1520.00	736.00
μ(MoKα) (cm^{-1})	25.736	24.839	23.590
Diffractometer	SCX mini	SCX mini	SCX mini
No. of reflections measured	Total: 12750	Total: 12756	Total: 13372
Unique	2746	2673	2799
R_{int}	0.1055	0.1110	0.0445
Friedel pairs	1134	-	1154
Min. and max. transmissions	0.549, 0.835	0.556, 0.780	0.505, 0.702
No. of observations (All reflections)	2746	2673	2799
No. of variables	199	217	208
Reflection/parameter ratio	13.80	12.32	13.46
Residuals: R_1 (I>2.00σ(I))	0.0583	0.0536	0.0311
Residuals: R (all reflections)	0.0836	0.0996	0.0372
Residuals: wR_2 (all reflections)	0.0948	0.1311	0.0634
Goodness of fit indicator	1.076	0.987	1.063
Flack parameter	0.032(17)	-	0.010(11)
Maximum peak in final diff. map (e$^-$/Å^3)	1.00	0.93	0.31
Minimum peak in final diff. map (e$^-$/Å^3)	-0.50	-0.36	-0.27

4.3. X-ray Structure Analysis

There are two phenyl groups in compounds **4.1**–**4.6**, however, there is one phenyl group and one aryl group in compounds **4.7**–**4.10**. The five-membered N(1)-C(2)-Se(3)-C(4)-(5) rings in some structures are approximately coplanar with the aryl rings. The selenium atoms deviate from 0.001 to 0.022 Å and nitrogen atoms deviate from 0.001 to 0.019 Å from the C(2)-C(4)-C(5) mean planes in **4.1**–**4.10**. The dihedral angles between the C(2)-aryl rings and the five-membered N(1)-C(2)-Se(3)-C(4)-(5) mean planes are 11.79, 10.60, 42.09, 13.27 and 37.69° in **4.1**, **4.4**, **4.8**, **4.9** and **4.10**, while the dihedral angles in **4.2**, **4.3**, **4.5**, **4.6** and **4.7** differ from 1.02 to 4.38°. The dihedral angles between C(5)-aryl rings and the five-membered N(1)-C(2)-Se(3)-C(4)-(5) mean planes in **4.4** and **4.8** are 20.38 and 11.41°, the angles vary from 4.24 to 9.87° in **4.1**–**4.3**, **4.5**–**4.7**, **4.9** and **4.10**.

The two kinds of C-Se bond lengths in the structures of **4.1**–**4.10** are slightly different from each other [C(2)-Se(3): 1.886(6) to 1.909(3) Å, C(4)-Se(3): 1.803(13) to 1.856(5) Å]; the Se(3)-C(4) bond length is marginally longer than Se(3)-C(2) bond length, and Se(3)-C(2) bond lengths are also marginally shorter than the C-Se bond lengths in the five-membered ring 1,3,4-selenadiazoles [1.87 to 1.89 Å][19-22] and 2,5-diarylselenophenes [1.86 to 1.89 Å],[23] however, both bond distances are shorter than the typical C-Se single-bond lengths [*ca.* 1.92 to 1.94 Å]. Both C-N bond lengths [1.377(13) to 1.410(9) Å] and C=N double-bond lengths [1.285(14) to 1.311(5) Å] are between the typical C-N single bond distance of 1.47 Å and C=N double bond length of 1.29 Å; furthermore, the C-C bond distances [1.346(13) to 1.377(5) Å] also fall in between the typical C-C single-bond length of 1.54 Å and C=C double-bond distance of 1.34 Å, indicating some delocalisation for all bonds in the five-membered N(1)-C(2)-Se(3)-C(4)-(5) rings.

The C-Se-C bond angles in **4.1**–**4.10** lie in the range of 84.24(15) to 85.2(5)°, which are significantly larger than that in 1,3,4-selenadiazoles [81.9(4) to 82.7(2)°] [19-22] but considerably smaller than that in 2,5-diarylselenophenes [87.8(8)°],[23] suggesting that the size of the C-Se-C bond angles in the five-membered ring is 1,3,4-selenadiazoles < 1,3-selenazoles < 2,5-diarylselenophenes. Furthermore, the angles of C2-N1-C5 range from 112.4(5) to 118.3(4)°.

All ten structures possess rather similar molecular conformations and intermolecular interactions: the five-membered N(1)-C(2)-Se(3)-C(4)-C(5) rings being nearly planar, the weak intermolecular C-H···N/O/Cl/Br/Se interactions and π-stacking interactions being similar to each other. Interestingly enough, some intramolecular C-H···N/Se interactions can be observed in these compounds and the close contacts between Se atoms are found in structures of **4.4**, **4.6** and **4.7**.

4.3.1. Series I

The data for compounds **4.1**–**4.3** is described in this section. All three structures are very similar with a methyl substituent attached to one aryl ring in compounds **4.2** and **4.3**. Compared to compound **4.2**, a bromine atom replaces a chlorine atom in compound **4.3**. The X-ray single crystal structures for **4.1**–**4.3** are shown in Figures 4-2–4-4, and the selected bond distances and angles are listed in Table 4-4**.** More detailed data for **4.1**–**4.3** can be found in Appendix 1.

Because of one more substituent in **4.2** and **4.3**, there are some slight differences in **4.1**. Compounds **4.2** and **4.3** are in the monoclinic crystal system, whereas **4.1** is in the orthorhombic crystal system. Three structures have similar N-C single bond, N=C double bond, Se-C single bond distances. The distances in **4.1** [N-C 1.377(13) Å, N=C 1.285(14) Å, Se(3)-C(4) 1.803(13) Å] are marginally shorter than that in **4.2** [N-C 1.407(4) Å, N=C 1.292(4) Å, Se(3)-C(4) 1.845(3) Å] and **4.3** [N-C 1.406(8) Å, N=C 1.306(8) Å, Se(3)-C(4) 1.825(6) Å]. The Se(3)-C(2) single bond distances range from 1.886(6) to 1.909(3) Å. The C(2)-N(1)-C(5) bond angles [115.0(9)°] and C(2)-Se(3)-C(4) bond angles [85.2(5)°] in **4.1** are bigger than that in **4.2** [113.5(3) and 84.24(15)°] and **4.3** [112.4(5) and 84.8(3)°].

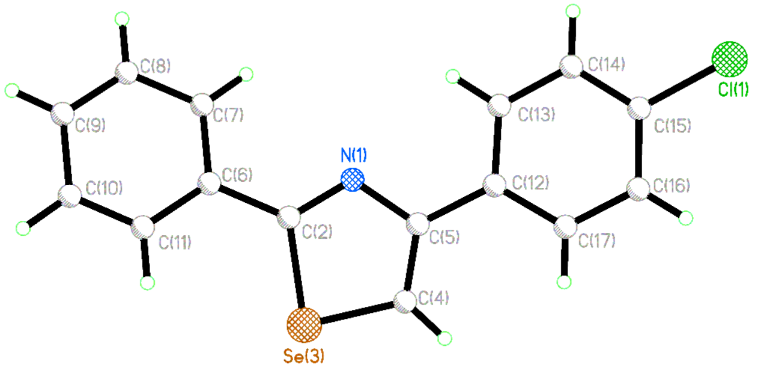


Figure 4-2. X-ray single crystal structure of **4.1**.

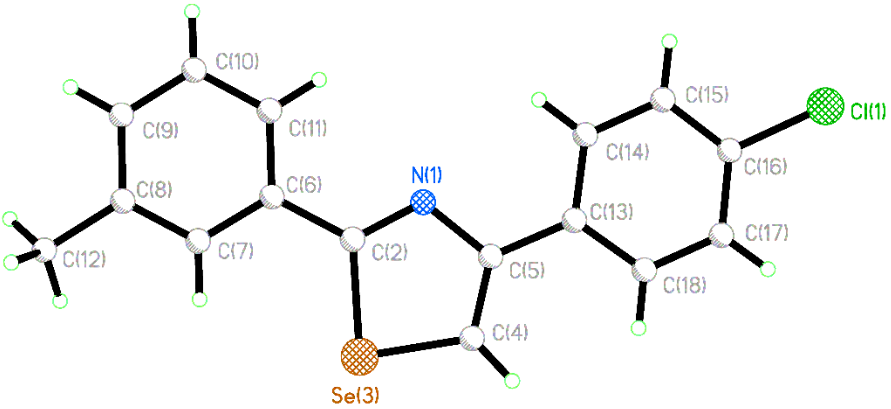


Figure 4-3. X-ray single crystal structure of **4.2**.

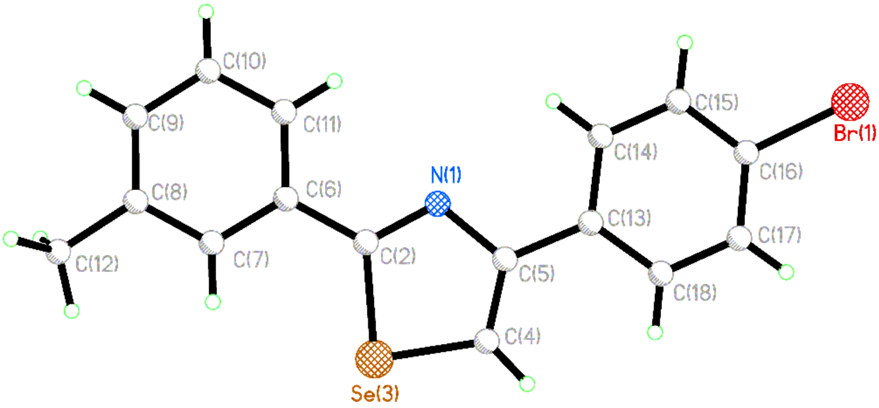


Figure 4-4. X-ray single crystal structure of **4.3**.

The dihedral angle between the five-membered ring N(1)-C(2)-Se(3)-C(4)-C(5) and aromatic ring C(6)…(11) [11.79°] in **4.1** is significantly bigger than that in **4.2** [1.77°] and **4.3** [1.60°]. However, the dihedral angles between the five-membered ring N(1)-C(2)-Se(3)-C(4)-C(5) and the other aromatic ring are similar to each other [4.24 to 5.60°] in **4.1**–**4.3**. The N atoms in **4.1** and **4.2** are approximately co-planar with the C(2)-C(4)-C(5) mean planes, but in **4.3** the N atom deviates 0.013 Å from the C(2)-C(4)-C(5) mean plane. The Se atoms deviate from 0.011 to 0.016 Å from the C(2)-C(4)-C(5) mean planes in these structures in **4.1**–**4.3**.

Table 4-4. Selected bond distances (Å) and bond angles (°) for compounds **4.1**–**4.3**

	4.1	**4.2**	**4.3**
Bond lengths			
N(1)-C(5)	1.377(13)	1.407(4)	1.406(8)
N(1)=C(2)	1.285(14)	1.292(4)	1.306(8)
Se(3)-C(2)	1.893(10)	1.909(3)	1.886(6)
Se(3)-C(4)	1.803(13)	1.845(3)	1.825(6)
C(4)=C(5)	1.369(16)	1.356(5)	1.353(10)
Bond angles			
C(2)-N(1)-C(5)	115.0(9)	113.5(3)	112.4(5)
C(2)-Se(3)-C(4)	85.2(5)	84.24(15)	84.8(3)
Dihedral angles			
Between ring C(2)-aryl and N(1)…C(5) plane	11.79	1.77	1.60
Between ring C(5)-aryl and N(1)…C(5) plane	5.60	4.24	4.56
Deviation distance			
N(1)…C(2)-C(4)-C(5)	0.004(17)	0.005(6)	0.013(11)
Se(3)…C(2)-C(4)-C(5)	-0.01(3)	-0.016(8)	0.016(15)

In order to determine the strength of the intramolecular C_{aryl}-H···N/Se interactions, three parameters have to be considered: (a) the distance between N/Se atom and H atom, (b) the C-C-C-N/Se torsion angle and (c) the deviation of the N/Se atom from the C(2)/C(5)-aryl plane. Therefore, if the H···N/Se distance is shorter than the sum of H···N/Se van der Waals radii, 2.8 Å for N and H, and 3.1 Å for Se and H, and the relevant torsion angle and deviation from the plane is small enough, the interaction can be considered to present in the structure.

The structures of compounds **4.1**–**4.3** have some possible intramolecular C_{aryl}-H···N/Se interactions as shown in Figure 4-5. The selected intramolecular interaction distances and angles for **4.1**–**4.3** are listed in Table 4-5. The intramolecular interaction distances of H···N^a (atom H attached to C(2)-aryl ring) vary from 2.584(5) to 2.654(9) Å (< 2.8 Å), with the C_{aryl}-H···N^a angles ranging from 97.4(7) to 98.7(2)°. The absolute values of N^a-C-C-C torsion angles in **4.2** [1.6(4)°] and **4.3** [1.2(9)°] are much smaller than that in **4.1** [12.9(13)°]. Meanwhile, the deviation distance between N atom and R_1-aryl plane in **4.1** [0.232(15) Å] is also much longer than that in **4.2** [0.030(5) Å] and **4.3** [0.009(11) Å]. Hence, the strength of the intramolecular C_{aryl}-H···N^a interactions increases from **4.1** < **4.2** < **4.3**. For another phenyl arm, the distances and angles for the intramolecular C_{aryl}-H···N^b interactions [atom H attached to C(5)-aryl ring] are similar to each other [2.485(5) to 2.496(3) Å and 101.7(7) to 101.9(4)°]. The absolute value of N^a-C-C-C torsion angle in **4.1** [6.4(11)°] is much bigger than that in **4.2** [2.9(4)°] and **4.3** [1.1(8)°]. The deviation distance between N atom and C(5)-aryl plane in **4.1** [0.0119(15) Å] is also longer than that in **4.2** [0.116(5) Å] and **4.3** [-0.099(10) Å]. Furthermore, this is a slightly different for the H···Se interaction distances [2.7620(12) to 2.8091(13) Å] with the C_{aryl}-H···Se angles [110.4(8) to 111.16(18)°]. The Se-C-C-C torsion angle and deviation distance in **4.1** [11.1(11)°, 0.304(15) Å] are different from that in **4.2** [0.3(3)°, 0.006(4) Å] and **4.3** [0.1(7)°, 0.024(10) Å]. In the five-membered ring N(1)-C(1)-Se(3)-C(4)-(5), N and Se atoms are interacted on each other, so there is some slightly different between the intramolecular C_{aryl}-H···N^a and C_{aryl}-H···N^b interactions. In **4.2** and **4.3**, the strength of the intramolecular C_{aryl}-H···N^a and C_{aryl}-H···Se interactions are slightly stronger than that in **4.1** due to the R_1 substituent influence.

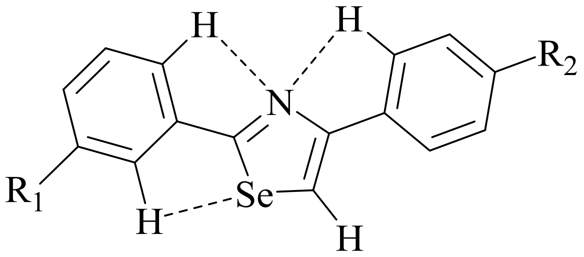


Figure 4-5. Possible intramolecular C_{aryl}-H···N/Se interaction which can be expressed by H···N/Se distance, N/Se-C-C-C torsion angle and nitrogen/ selenium atom deviation from aryl plane in **4.1**–**4.3**.

Table 4-5. Selected intramolecular distances (Å) and angles (°) for compounds **4.1**–**4.3**

	4.1	**4.2**	**4.3**
Intramolecular interaction distances (Å)			
C_{aryl}-H···N^{a}	2.654(9)	2.609(3)	2.584(5)
C_{aryl}-H···N^{b}	2.494(9)	2.496(3)	2.485(5)
C_{aryl}-H···Se	2.8091(13)	2.7630(4)	2.7620(12)
Intramolecular interaction angles (°)			
C_{aryl}-H···N^{a}	97.4(7)	98.7(2)	98.6(4)
C_{aryl}-H···N^{b}	101,7(7)	101.8(2)	101.9(4)
C_{aryl}-H···Se	110.4(8)	111.16(18)	110.8(4)
Torsion angles (°)			
N^{a}-C-C-C	12.9(13)	-1.6(4)	-1.2(9)
N^{b}-C-C-C	-6.4(11)	2.9(4)	-1.1(8)
Se-C-C-C	11.1(11)	0.3(3)	-0.1(7)
Deviation distance (Å)			
N…C(2)-aryl plane	-0.232(15)	0.030(5)	0.009(11)
N…C(5)-aryl plane	-0.0119(15)	0.116(5)	-0.099(10)
Se…C(2)-aryl plane	0.304(15)	-0.006(4)	-0.024(10)

[a] Possible intramolecular interaction between N atom and H atom attached to C(2)-aryl ring

[b] Possible intramolecular interaction between N atom and H atom attached to C(5)-aryl ring

The supramolecular structures for **4.1**–**4.3** are packed by the weak intermolecular C-H···Cl/Br/Se interactions or π-stacking interactions (Figures 4-6–4-8). The relevant selected intermolecular distances and angles are shown in Table 4-6. The structure of **4.1** contains the intermolecular C_{phenyl}-H···Cl, C_{phenyl}-H···N and C_{phenyl}-H···Se interactions; however, π-stacking interaction is absent (Figure 4-9). The distances of H···Cl and H···Se in **4.2** and **4.3** are similar to **4.1**, but the H···N distances is longer than that in **4.1** [3.166(10) Å]. The H···Cl distance in **4.2** is 3.3588(10) Å, along with the C_{methyl}-H···Cl angle of 153.2(2)°. However, the structure **4.3** has a longer H···Br distance with the angle 126.9(5)°, compared to **4.2**. The H···Se distance in **4.3** is 3.1367(11) Å, along with the angle of 142.4(4)°.

Table 4-6. Selected intermolecular distances (Å) and angles (°) for compounds **4.1**–**4.3**

	4.1	**4.2**	**4.3**
Intermolecular interaction distances (Å)			
C_{methyl}-H···Cl/Br		3.3588(10)	3.7133(16)
C_{methyl}-H···Se			3.1367(11)
C_{phenyl}-H···Cl/Br	3.191(4) 3.504(4) 3.509(3)	3.1043(10) 4.1005(10)	3.1405(12) 4.0316(13)
C_{phenyl}-H···N	3.166(10) 3.330(9)	3.593(3) 3.362(3)	3.440(6) 3.652(6) 3.708(6)
C_{phenyl}-H···Se	3.2453(4) 3.3242(19) 3.4327(19) 3.8810(17)	3.1670(5) 3.5502(5) 3.9104(6)	3.1658(11) 3.4907(11) 3.9268(17)
Intermolecular interaction angles (°)			
C_{methyl}-H···Cl/Br		153.2(2)	126.9(5)
C_{methyl}-H···Se			142.4(4)
C_{phenyl}-H···Cl/Br	123.5(7) 149.5(8) 132.7(9)	141.54(19)	142.8(5)
C_{phenyl}-H···N	127.7(7) 131.5(8)	132.6(2) 123.12(19)	129.5(5) 120.3(5) 121.7(4)
C_{phenyl}-H···Se	129.3(9)	122.82(19)	124.4(5)

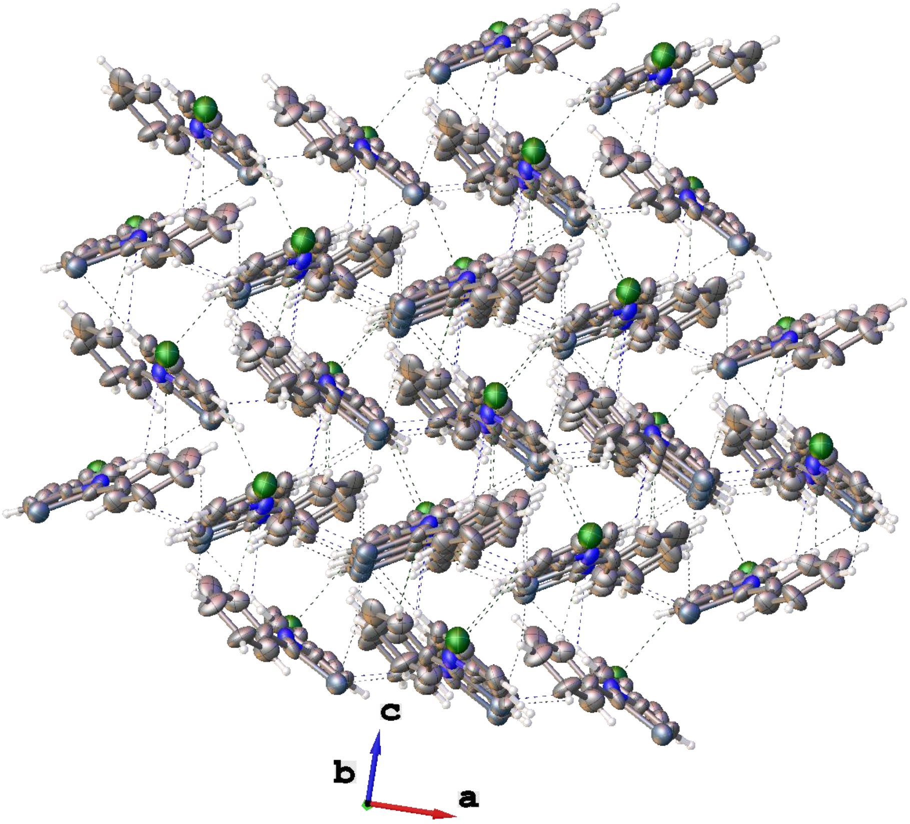


Figure 4-6. View of the 3-D packing network shows the C-H···N/Se/Br hydrogen interactions to build up the structure in **4.1**.

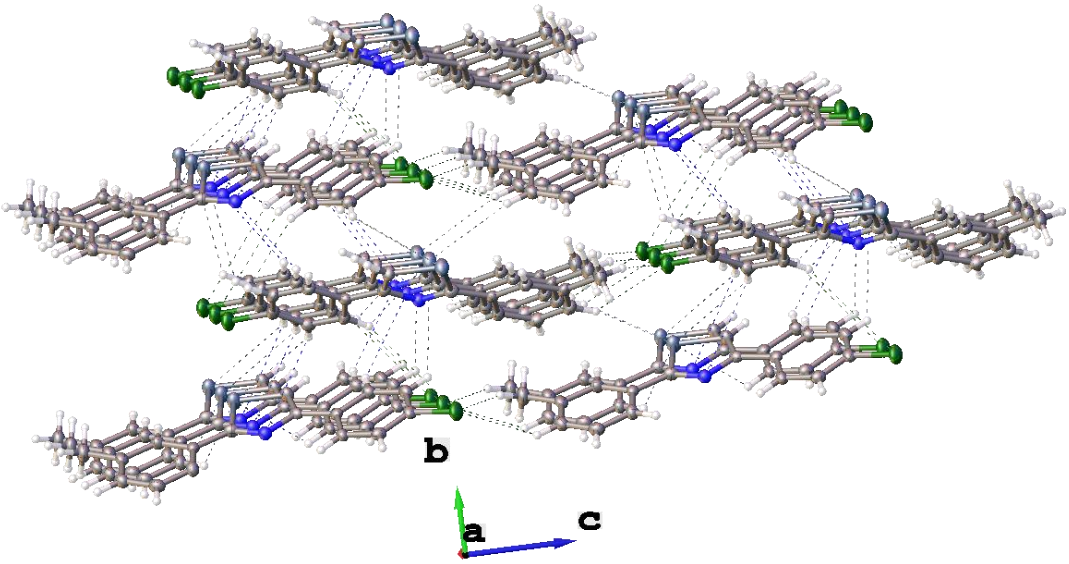


Figure 4-7. View of the 3-D packing network shows the C-H···N/Se/Br hydrogen interactions to build up the structure in **4.2**.

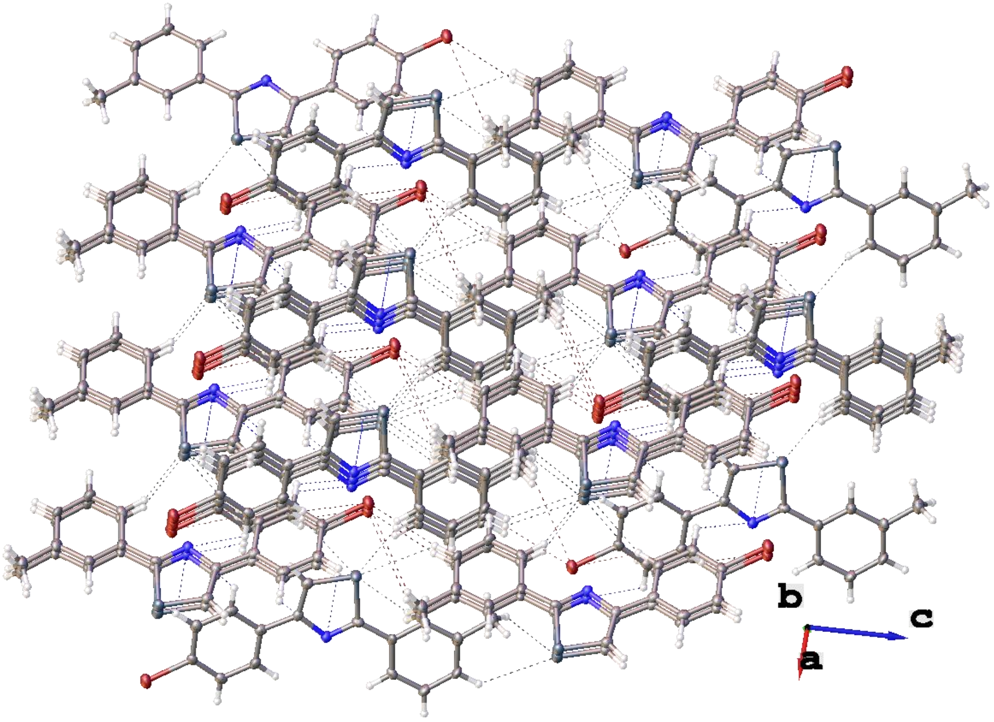


Figure 4-8. View of the 3-D packing network shows C-H···N/Se/Br hydrogen interactions to build up the structure in **4.3**.

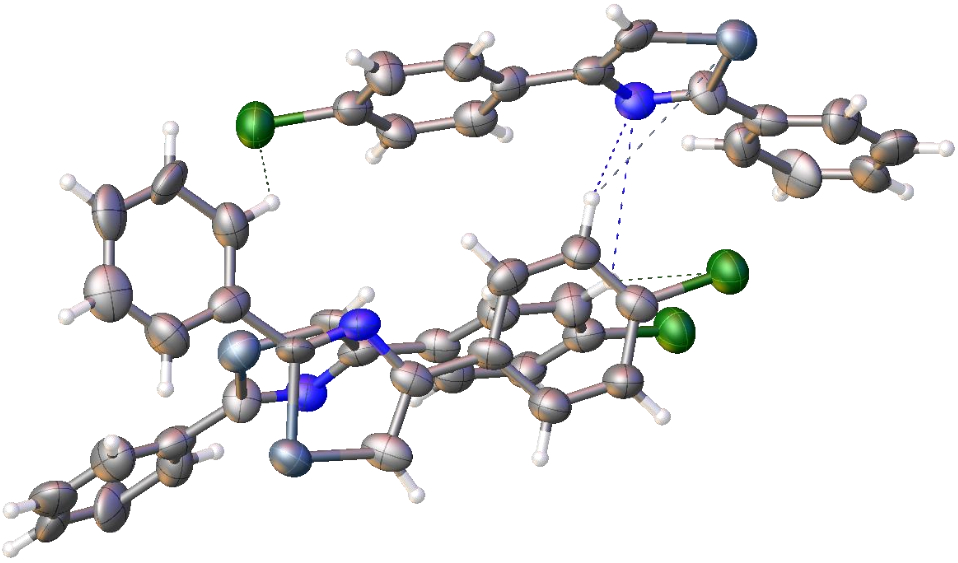


Figure 4-9. Possible intermolecular interactions between molecules in **4.1**.

4.3.2. Series Ⅱ

The structures of compounds **4.4–4.6** are discussed in this section. There are two aryl arms attached to the 1,3-selenazole ring, and one of them has two neighbouring -OCH_3 substituents. In **4.5** and **4.6**, there is one Cl/Br atom attached to the other aryl arm. The X-ray single structures of compounds **4.4–4.6** are shown in Figures 4-10–4-12, respectively. The structural similarities and differences in **4.4–4.6** can be described by comparing the N/Se-C bond lengths and bond angles, the deviations of N/Se atom, torsion angles and dihedral angles between the neighbouring rings. Selected bond lengths, deviations and angles for **4.4–4.6** are listed in Table 4-7.

The Se(3)-C(2) bond lengths in **4.4–4.6** are quite similar to each other [1.894(5) to 1.906(11) Å]. The Se(3)-C(4) bond lengths range from 1.848(10) to 1.856(5) Å, and the average C(2)-Se(3)-C(4) bond angles are 84.7°. The N(1)-C(5) single bond lengths increase from 1.385(9) to 1.410(9) Å and the N(1)=C(2) double bond lengths are 1.293(10) to 1.305(12) Å. These values are almost covered by the range of the typical N(1)-C(5) single bond length (1.47 Å) and N(1)=C(2) double bond length (1.29 Å). The relevant C(2)-N(1)-C(5) bond angles are 117.4(6) to 118.3(4)°. The C(4)=C(5) bond lengths [1.346(13) to 1.375(9) Å] are slightly longer than the usual C=C double bond length [1.34 Å], but much shorter than the usual C-C single bond length. The results indicate that the bond lengths in the five membered ring N(1)-C(2)-Se(3)-C(4)-(5) are not simple typical single bond or double bond because of the conjugated effect. In the structures of **4.1**, **4.2** and **4.5**, which have the same chlorine atom substituent attached on one arm aryl ring, the size for the N(1)-C(5) single bond length, N(1)=C(2) double bond length, and Se(3)-C(4) bond length are similar to each other [N(1)-C(5):1.377(13) Å, N(1)=C(2):1.285(14) Å, Se(3)-C(4):1.803(13) Å in **4.**1, N(1)-C(5):1.407(4) Å, N(1)=C(2):1.292(4) Å, Se(3)-C(4):1.845(3) Å in **4.2** and]N(1)-C(5):1,410(9) Å, N(1)=C(2):1.293(10) Å, Se(3)-C(4):1.855(12) Å in **4.5**].

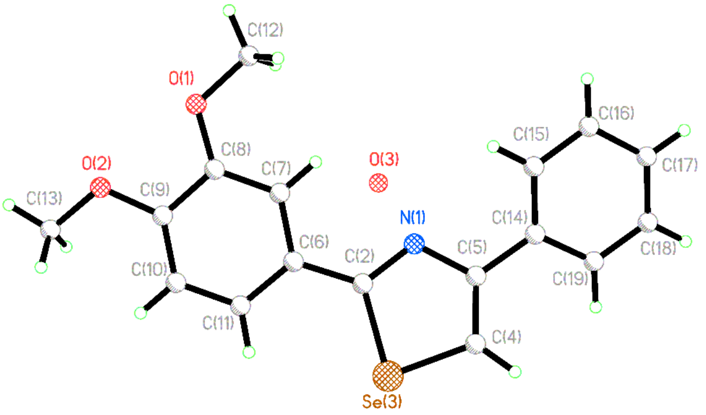


Figure 4-10. X-ray single crystal structure of **4.4**.

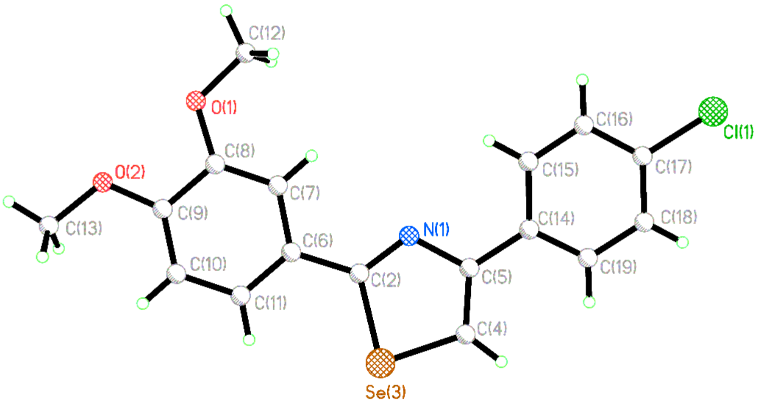


Figure 4-11. X-ray single crystal structure of **4.5**.

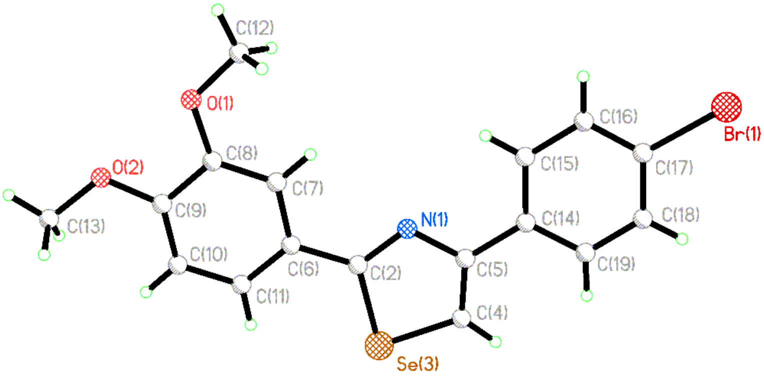


Figure 4-12. X-ray single crystal structure of **4.6**.

The dihedral angles between the five-membered ring N(1)-C(2)-Se(3)-C(4)-C(5) and two aromatic rings [10.60° for C(2)-aryl ring, 20.38° for C(5)-aryl ring] in **4.4** are bigger than that in **4.5** [1.02° for C(2)-aryl ring, 7.47° for C(5)-aryl ring] and in **4.6** [1.16° for R_3-aryl ring, 6.56° for R_4-aryl ring]. The deviations between N(1)/Se(3) atom and C(2)-C(4)-C(5) mean plane are very small [0.006 to 0.019Å], so the N(1)/Se(3) atom can be regarded as coplanar in **4.4–4.6**.

Table 4-7. The selected bond distances (Å) and bond angles (°) for compounds **4.4–4.6**

	4.4	**4.5**	**4.6**
Bond lengths			
N(1)-C(5)	1.385(9)	1.410(9)	1.394(6)
N(1)=C(2)	1.305(12)	1.293(10)	1.301(6)
Se(3)-C(2)	1.898(8)	1.906(11)	1.894(5)
Se(3)-C(4)	1.848(10)	1.855(12)	1.856(5)
C(4)=C(5)	1.346(13)	1.375(9)	1.357(7)
Bond angles			
C(2)-N(1)-C(5)	117.4(6)	117.6(4)	118.3(4)
C(2)-Se(3)-C(4)	85.1(4)	84.6(3)	84.4(2)
Dihedral angles			
Between ring C(2)-aryl and N(1)…C(5) plane	10.60	1.02	1.16
Between ring C(5)-aryl and N(1)…C(5) plane	20.38	7.47	6.56
Deviation distance			
N(1)…C(2)-C(4)-C(5)	0.009(14)	-0.006(7)	-0.019(7)
Se(3)…C(2)-C(4)-C(5)	0.017(19)	0.005(10)	0.012(9)

C(2)-aryl: Two -OCH_3 substituents connecting with left aryl arm; C(5)-aryl: Cl atom in **4.1** and **4.2**, Br atom in **4.3**

Similar to Series I, there are also some possible intramolecular C_{aryl}-H···N/Se interactions present in **4.4–4.6** (Figure 4-13). The intramolecular C_{aryl}-H···N interaction distances increase in the order of **4.4** < **4.6** < **4.5**, whilst the intramolecular C_{aryl}-H···Se interaction increases in the order of **4.6** < **4.5** < **4.4**. The average intramolecular C_{aryl}-H···N and C_{aryl}-H···Se interaction angles are 99.82 to 109.93° in **4.4–4.6**. The absolute value of the N-C-C-C and Se-C-C-C torsion angles are small in **4.5** [0.3(6)°] and **4.6** [8.1(5)°], specially, the N^c-C-C-C torsion angle in **4.5** is the smallest [0.3(6)°], but the N^c-C-C-C and N^d-C-C-C torsion angles are the biggest in **4.4** [11.5(11) and 20.7(11)°], and the Se-C-C-C torsion angle [9.3(9)°] in **4.4** also the biggest, compared to the relevant angles in **4.5** and **4.6**. N atom deviate from 0.011(6)° in **4.6** to 0.459(14)° in **4.4** from one of the aryl planes, and the deviations between the Se atom and the adjacent aryl plane are 0.002(6)° in **4.5** and 0.296(12)° in **4.4**. It can be seen that the N/Se atom deviation distances in **4.4** are obviously longer than that in

4.5 and **4.6**. The details of selected intramolecular distances and angles for compounds **4.4**–**4.6** are shown in Table 4-8.

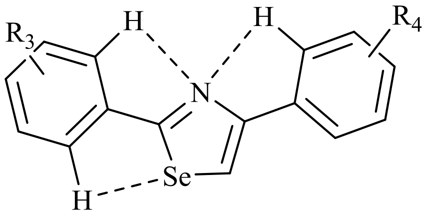


Figure 4-13. Possible intramolecular C_{aryl}-H···N/Se interaction which can be expressed by C_{aryl}-H···N/Se distance, N/Se-C-C-C torsion angle and nitrogen/ selenium atom deviation from aryl plane in **4.4**–**4.6**.

Table 4-8. Selected intramolecular distances (Å) and angles (°) for compounds **4.4**–**4.6**

	4.4	**4.5**	**4.6**
Intramolecular interaction distances (Å)			
C_{aryl}-H···N^c	2.567(6)	2.607(14)	2.599(4)
C_{aryl}-H···N^d	2.514(8)	2.563(13)	2.538(4)
C_{aryl}-H···Se	2.843(2)	2.759(13)	2.7758(17)
Intramolecular interaction angles (°)			
C_{aryl}-H···N^c	99.4(5)	98.9(5)	98.8(3)
C_{aryl}-H···N^d	99.8(7)	101.0(5)	101.0(3)
C_{aryl}-H···Se	108.5(5)	110.7(5)	110.6(3)
Torsion angles (°)			
N^c-C-C-C	-11.5(11)	0.3(6)	-2.0(5)
N^d-C-C-C	20.7(11)	8.1(5)	-7.1(5)
Se-C-C-C	-9.3(9)	1.1(5)	-0.9(4)
Deviation distance (Å)			
N…C(2)-aryl plane	-0.196(13)	0.026(7)	-0.045(6)
N…C(5)-aryl plane	-0.459(14)	-0.189(7)	0.011(6)
Se…C(2)-aryl plane	0.296(12)	-0.002(6)	0.149(6)

[c] Possible intramolecular interaction between N atom and H atom attached to C(2)-aryl ring

[d] Possible intramolecular interaction between N atom and H atom attached to C(5)-aryl ring

The structures of **4.4**–**4.6** display some unique intermolecular interactions in their crystal packing. The selected intermolecular information is listed in Table 4-9. Compared to the sum of H···Se van der Waals radii ~ 3.1 Å and the H···N van der

Waals radii ~ 2.8 Å, the relevant intermolecular hydrogen interaction distances in **4.4**–**4.6** are shorter; however, the C-H···O hydrogen bonding (Figure 4-14) distances are near to the H···O van der Waals radii ~ 2.75 Å. The arrangements of **4.5** and **4.6** are similar with the same orientation, and it is different in **4.4** (Figure 4-15). In Figures 14–16, it can be observed that there is a combination of multiple intermolecular C-H···O, C-H···N, C-H···Se and C-H···Cl/Br interactions and very weak π-stacking interactions to build up the packing networks. Because of the structural similarity in **4.4** and **4.5**, there is no significant difference for the intermolecular interaction distances and angles. There are two kinds of intermolecular C-H···Se interactions in **4.4**–**4.6**: (a) the H···Se distances between the Se atom and H atom attached to the OCH_3 group range from 3.285(17) to 3.301(2) Å with the angles of 120.1(6)° in **4.4**, 174.7(4)° in **4.5** and 176.7(4)° in **4.6**, (b) the C_{aryl}-H···Se distances [3.059(12) Å] in **4.5** and [3.0929(15) Å] in **4.6** are slightly shorter than the C_{methyl}-H···Se intermolecular distances.

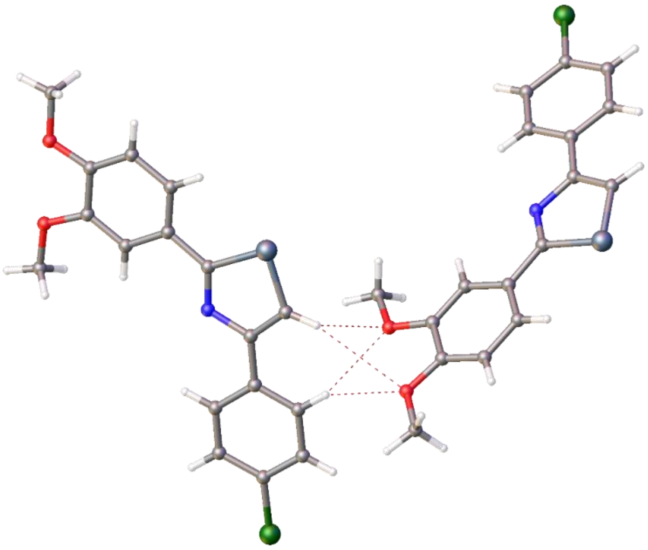


Figure 4-14. The molecules are linked by the intermolecular C-H···O interactions in **4.5**.

Table 4-9. Selected intermolecular distances (Å) and angles (°) for compounds **4.4–4.6**

	4.4	**4.5**	**4.6**
Intermolecular interaction distances (Å)			
C_{methyl}-H···Cl/Br		3.234(15)	3.2548(19)
C_{methyl}-H···N	3.743(9)	3.482(19)	3.579(5)
C_{methyl}-H···Se	3.301(2)	3.285(17)	3.317(2)
C_{methyl}-H···O(1)	2.757(7)	3.65(2)	
C_{methyl}-H···O(2)	3.239(7)	3.95(2)	
C-H4···O(1)	2.578(5)	2.559(13)	2.603(4)
C-H4···O(2)	2.592(6)	3.112(15)	3.131(4)
C_{phenyl}-H···O	2.795(6) 2.934(7)	2.592(14) 2.630(13)	2.599(4) 2.656(4)
C_{phenyl}-H···Cl/Br		2.936(16)	3.062(2)
C_{phenyl}-H···N	3.454(8)	3.50(2)	3.561(5)
C_{phenyl}-H···Se		3.059(12)	3.0929(15)
Intermolecular interaction angles (°)			
C_{methyl}-H···Cl/Br		151.3(4)	154.0(3)
C_{methyl}-H···N	143.9(5)	160.3(4)	159.4(4)
C_{methyl}-H···Se	120.1(6)	174.7(4)	176.7(4)
C_{methyl}-H···O(1)	150.0(5)	148.5(5)	
C_{methyl}-H···O(2)	154.0(7)	177.9(3)	
C-H4···O(1)	176.0(7)	125.7(5)	127.2(3)
C-H4···O(2)	122.3(6)	164.7(3)	165.6(3)
C_{phenyl}-H···O	149.1(7) 143.7(7)	156.5(4) 140.1(4)	155.4(3) 142.2(3)
C_{phenyl}-H···Cl/Br		134.5(4)	133.1(3)
C_{phenyl}-H···N	121.3(6)	140.2(3)	120.9(3)
C_{phenyl}-H···Se		150.6(3)	151.8(3)

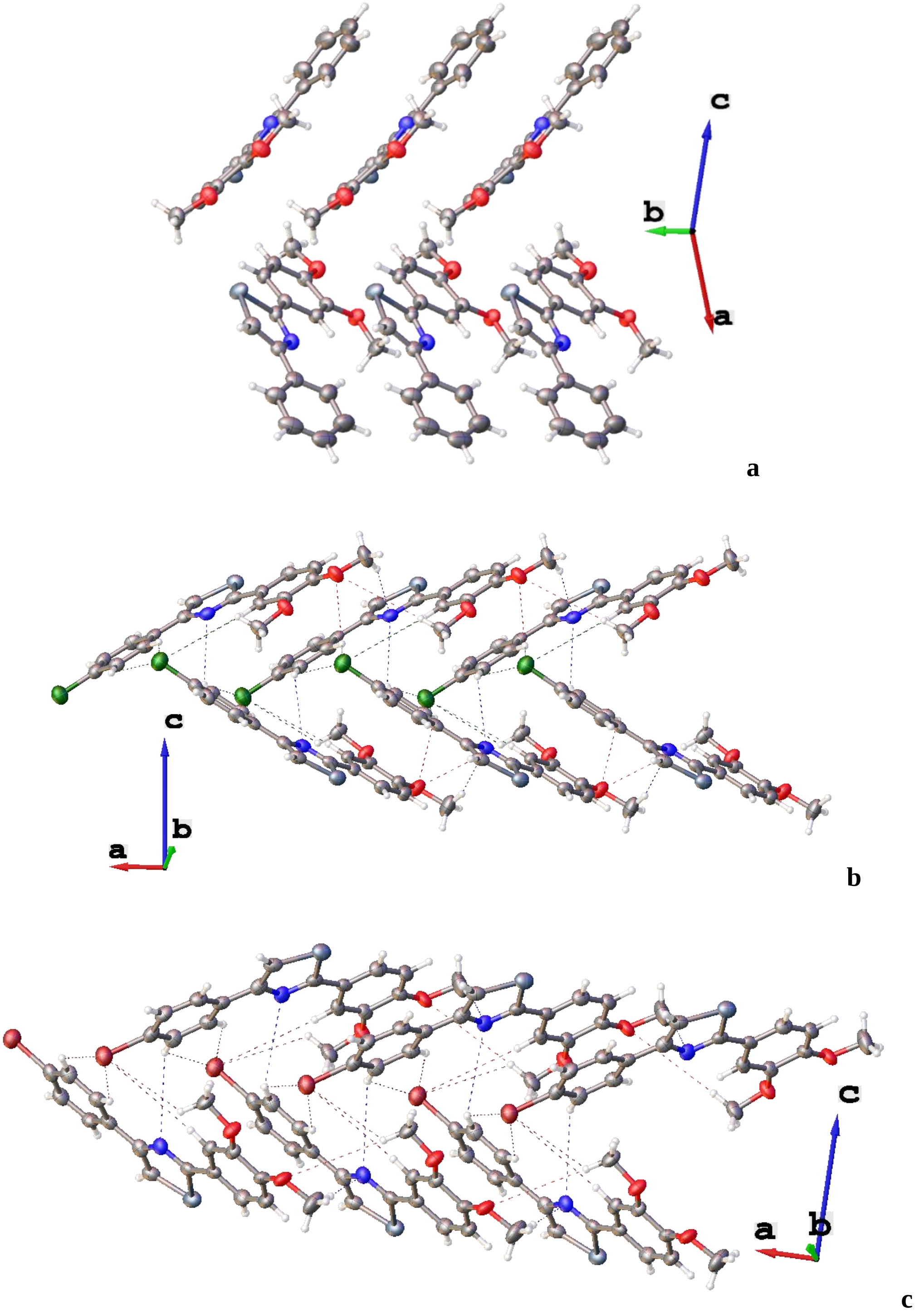


Figure 4-15. Packing arrangements in **4.4** (**a**), **4.5** (**b**) and **4.6** (**c**).

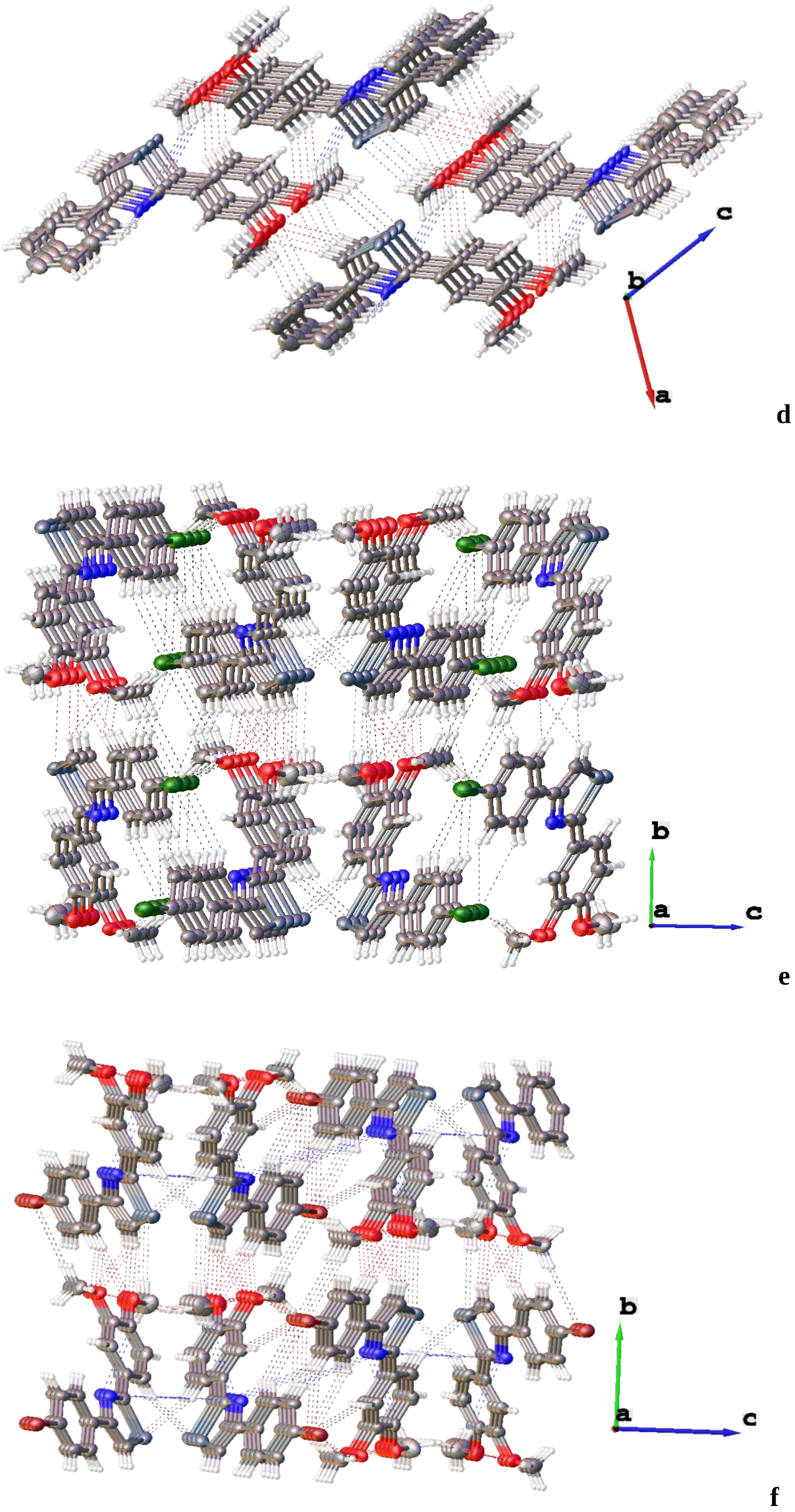


Figure 4-16. View of 3-D packing networks for **4.4** (**d**), **4.5** (**e**) and **4.6** (**f**) display the intermolecular C-H···N/O/Se or C-H···Cl/Br interactions.

4.3.3. Series Ⅲ

The structures of compounds **4.7**–**4.10** are discussed in this section. These structures are a little different from compounds **4.1**–**4.6**, though there are two aryl arms attached to the 1,3-selenazole ring. One aryl substituent is a naphthalene ring, and another six-membered ring has one Cl/NO_2/OCH_3 substituent. The X-ray single structures of compounds **4.7**–**4.10** are shown in Figures 4-17–4-20. The structural similarities and differences in **4.7**–**4.10** will be described by comparing the N/Se-C bond lengths and angles, the deviations of N/Se atom, torsion angles and dihedral angles between the neighbouring rings. Selected bond lengths, deflections and angles for **4.7**–**4.10** are listed in Table 4-10.

The N-C single bond distances are 1.382(7) to 1.393(4) Å and double bond distances are shorter [1.291(6) to 1.311(5) Å] than that in **4.1**–**4.6**, accompanied by the C-N-C bond angles ranging from 113.8(3) to 117.5(2)°. The Se-C bond distances vary from 1.840(4) to 1.908(5) Å, along with the average C2-Se3-C4 bond angle of 84.70°. In **4.7**, the dihedral angles between C(2)/C(5)-aryl ring and the mean plane of the selenazole rings are 4.38 and 4.73°. There are large deviations in **4.8**–**4.10**, especially, the dihedral angles between naphthalene ring and the mean planes of the selenazole rings in **4.8** and **4.10** are 42.09 and 37.69°. The selenazole ring in **4.7**–**4.10** possess similar near-planar conformation with Se and N atoms deviating from 0.001(7) to 0.022(6) Å from the C(2)-C(4)-C(5) mean plane.

Table 4-10. Selected bond distances (Å) and bond angles (°) for compounds **4.7–4.10**

	4.7	**4.8**	**4.9**	**4.10**
Bond lengths				
N(1)-C(5)	1.393(4)	1.382(7)	1.383(7)	1.389(4)
N(1)=C(2)	1.311(5)	1.299(7)	1.291(6)	1.301(4)
Se(3)-C(2)	1.901(4)	1.904(6)	1.908(5)	1.906(3)
Se(3)-C(4)	1.840(4)	1.852(6)	1.843(6)	1.852(3)
C(4)=C(5)	1.377(5)	1.356(8)	1.358(7)	1.360(5)
Bond angles				
C(2)-N(1)-C(5)	113.8(3)	114.3(5)	114.3(4)	117.5(2)
C(2)-Se(3)-C(4)	84.89(15)	84.5(3)	84.9(2)	84.50(14)
Dihedral angles				
Between naphthyl ring and N(1)…C(5) plane	4.38	**42.09**	13.27	**37.69**
Between aryl ring and N(1)…C(5) plane	4.73	11.41	9.39	9.87
Deviation distance				
N(1)…C(2)-C(4)-C(5)	0.011(5)	-0.001(8)	-0.017(9)	0.010(5)
Se(3)…C(2)-C(4)-C(5)	0.001(7)	0.011(11)	0.020(12)	0.022(6)

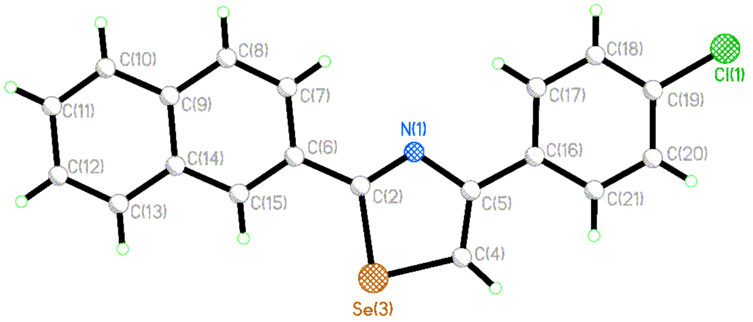


Figure 4-17. X-ray single crystal structure of **4.7**.

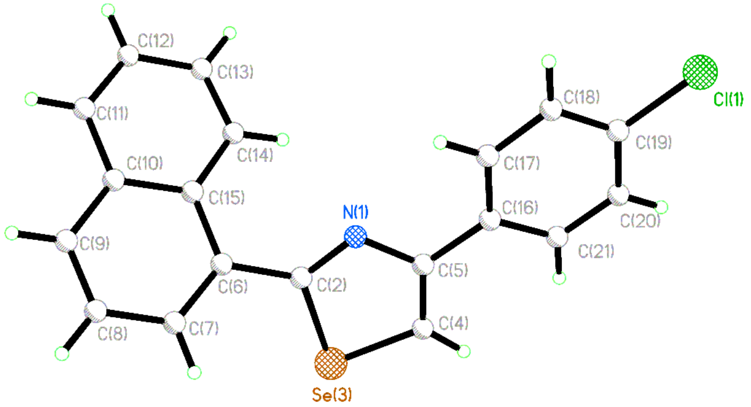


Figure 4-18. X-ray single crystal structure of **4.8**.

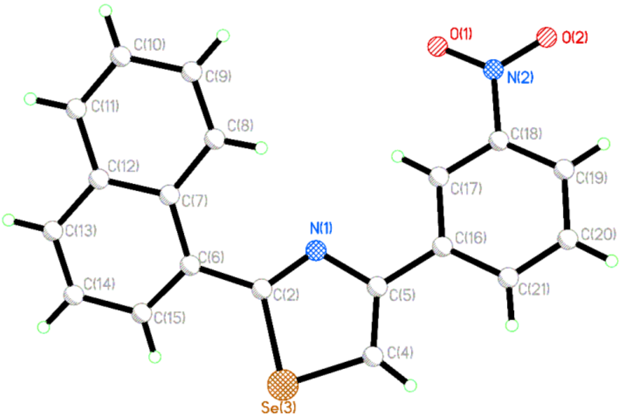


Figure 4-19. X-ray single crystal structure of **4.9**.

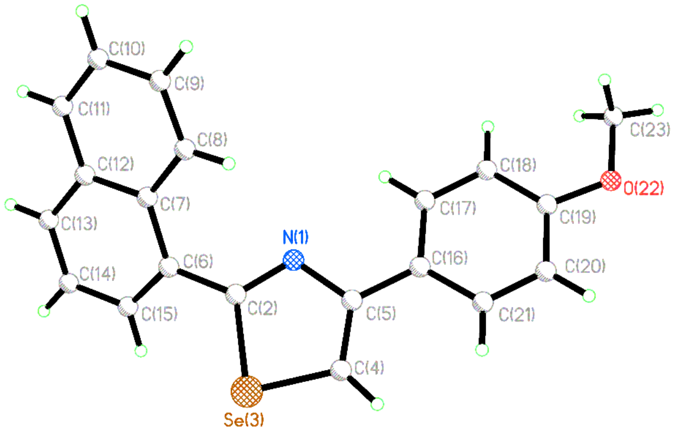


Figure 4-20. X-ray single crystal structure of **4.10**.

The details of possible intramolecular hydrogen interactions in **4.7**–**4.10** are shown in Table 4-11. The hydrogen interaction distances between N atom and H atom attached to the aryl ring range from 2.470(2) to 2.598(3) Å, the exception is the structure **4.9**, in which the distance for the $C_{naphthyl}$-H···N is 2.273(4) Å. The intramolecular C_{aryl}-H···Se interaction distances are 2.6437(9) to 2.9044(6) Å for **4.7**–**4.10**.

In the structures of **4.7**–**4.10**, the naphthalene ring has the smallest deviation in **4.7**, attributed to the differently attached position connecting the selenazole ring. The N-C-C-C (in naphthalene ring) and Se-C-C-C torsion angles in **4.7** are 4.7(5) and 4.8(4)°, meanwhile, the N-C-C-C torsion angle in another aryl ring is 2.2(4)°. In contrast to **4.7**, the structures of **4.8**–**4.10** have a wide range of the N-C-C-C (in naphthalene ring) [15.2(8) to 42.4(6)°] and Se-C-C-C torsion angles [12.7(6) to 39.1(5)°], however, the range for the N-C-C-C torsion angle in another aryl ring [8.5(6) to 10.9(6)°] is smaller. In Table 4-11, the corresponding N/Se deviation distances from the two C-aryl planes in **4.8** [0.812(6) and 0.963(5) Å] and **4.10** [0.790(4) and 0.794(3) Å] are also much longer than that in **4.7** and **4.9**, suggesting that the naphthalene ring in **4.8** and **4.10** has a large deviation from the selenazole ring plane leading to the weaker relevant intramolecular interactions.

There are some intramolecular C-H···O interactions in **4.9** (Figure 4-21), in which the C-H···O interactions distances are 2.390(4) and 2.432(4) Å along with the C-H···O angles of 98.21(3) and 97.2(4)°.

Table 4-11. Selected intramolecular distances (Å) and angles (°) for compounds **4.7–4.10**

	4.7	**4.8**	**4.9**	**4.10**
Intramolecular interaction distances (Å)				
C_{aryl}-H···N^e	2.598(3)	2.490(4)	**2.273(4)**	**2.470(2)**
C_{aryl}-H···N^f	2.490(3)	2.499(4)	2.519(4)	2.533(3)
C_{aryl}-H···Se	2.7932(15)	2.9044(6)	2.6437(9)	2.8117(4)
Intramolecular interaction angles (°)				
C_{aryl}-H···N^e	99.3(2)	119.8(3)	125.5(3)	120.34(19)
C_{aryl}-H···N^f	101.4(2)	101.2(4)	99.7(3)	101.3(2)
C_{aryl}-H···Se	110.7(2)	105.7(3)	113.3(4)	108.71(19)
Torsion angles (°)				
N^c-C-C-C	4.7(5)	**-42.4(6)**	-15.2(8)	**36.7(4)**
N^d-C-C-C	-2.2(4)	-10.9(6)	-8.5(6)	9.1(3)
Se-C-C-C	4.8(4)	**-39.1(5)**	-12.7(6)	**34.1(3)**
Deviation distance (Å)				
N…naphthyl plane	-0.026(4)	**-0.812(6)**	-0.287(7)	**0.790(4)**
N…aryl plane	-0.103(5)	-0.255(7)	0.232(8)	0.141(4)
Se…aryl plane	0.162(4)	**0.963(5)**	0.311(6)	**-0.794(3)**

[e] Possible intramolecular interaction between N atom and H atom attached to naphthalene ring

[f] Possible intramolecular interaction between N atom and H atom attached to another aryl ring

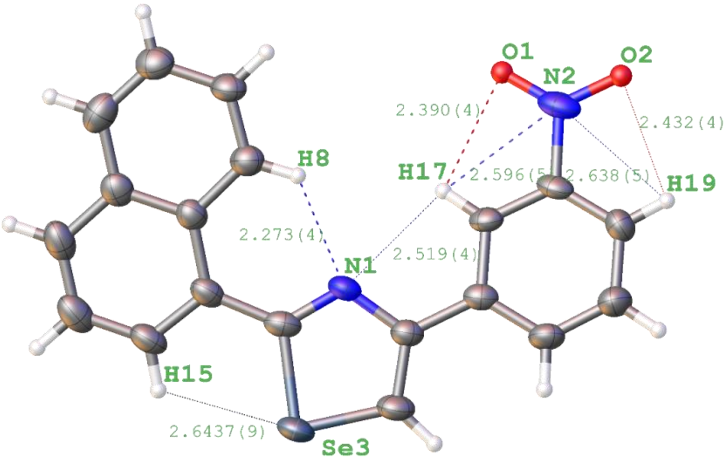


Figure 4-21. Possible intramolecular interactions in **4.9**.

The supramolecular aggregation arrangements for structures of **4.7–4.10** are built up by the multiple weak intermolecular interactions. The multiple C-H···N hydrogen interactions exist in the packing network and C-H···Se hydrogen interactions are found in **4.7**, **4.9** and **4.10**. The C-H···Cl hydrogen interactions also exist in **4.7** and **4.8**, however, the C-H···O hydrogen interactions only present in **4.9**. The structures of **4.8** and **4.10** have very weak π-stacking interactions in conjunctions.

In **4.7**, the 'zigzag chain' polymeric network (Figure 4-22) is built up by some C-H···N hydrogen interactions [2.934(3) to 3.111(4) Å], the C-H···Se hydrogen interactions [3.2887(16) to 3.613(2) Å] and C-H···Cl hydrogen interactions [3.613(2) Å]. The packing networks for **4.8** and **4.10** are very similar to each other [Figures 4-23 and 4-26]. The C-H···N interactions [2.901(4) to 3.970(4) Å] and C-H···Cl hydrogen interactions [2.9159(16) to 4.2234(17) Å] create a complex 3-D network in **4.8**. In the case of **4.10**, the packing network is formed by the C-H···N interactions [2.470(2) to 3.228(2) Å], C-H···O hydrogen interactions [2.720(2) to 3.945(2) Å], and C-H···Se hydrogen interactions [3.4563(4) to 3.8945(4) Å]. In **4.9**, the molecules are linked by the C-H···Se [3.2680(7) Å], C-H···N [3.063(5) and 3.698(5) Å] and C-H···O [2.709(4) to 3.698(5) Å] interactions in a single sheet (Figure 4-24); the intermolecular C-H···Se [3.2144(9) and 4.3056(13) Å] interactions result in the layers in the packing network (Figure 4-25).

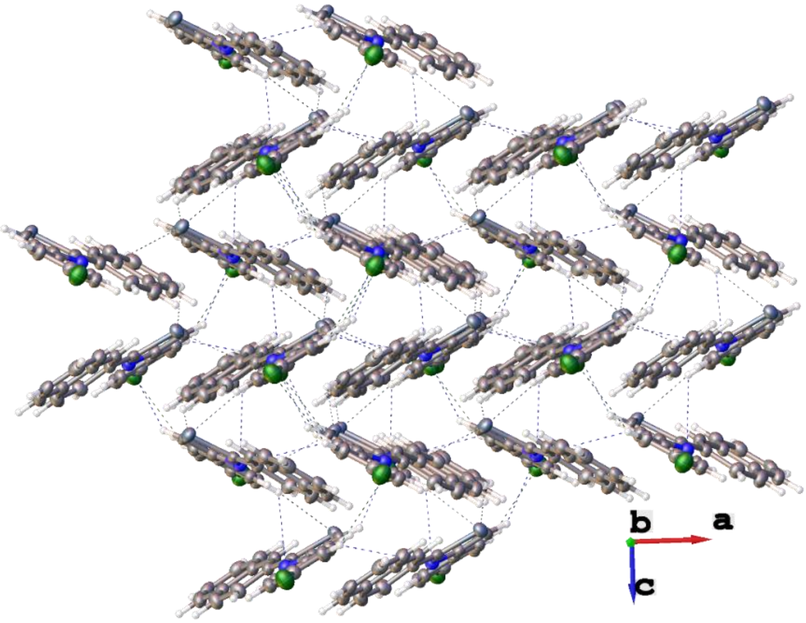


Figure 4-22. 3-D packing network in the structure of **4.7** shows 'Zigzag chain' polymeric network built up by the C-H···N, C-H···Se and C-H···Cl hydrogen interactions.

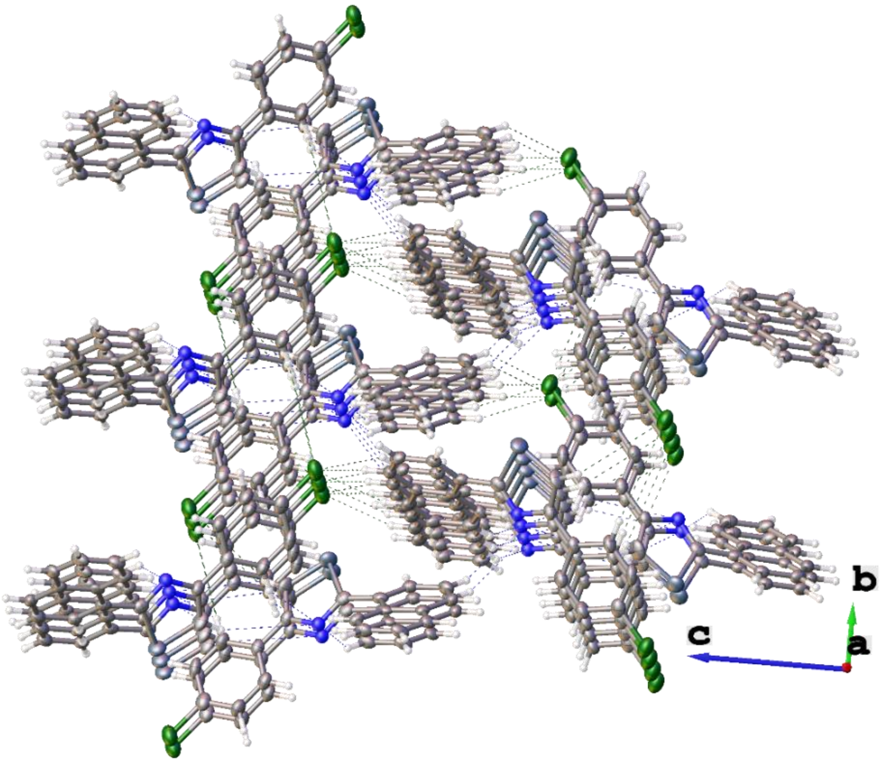


Figure 4-23. A view of 3-D packing network in the structure of **4.8** created by the intermolecular C-H···N/Cl interactions.

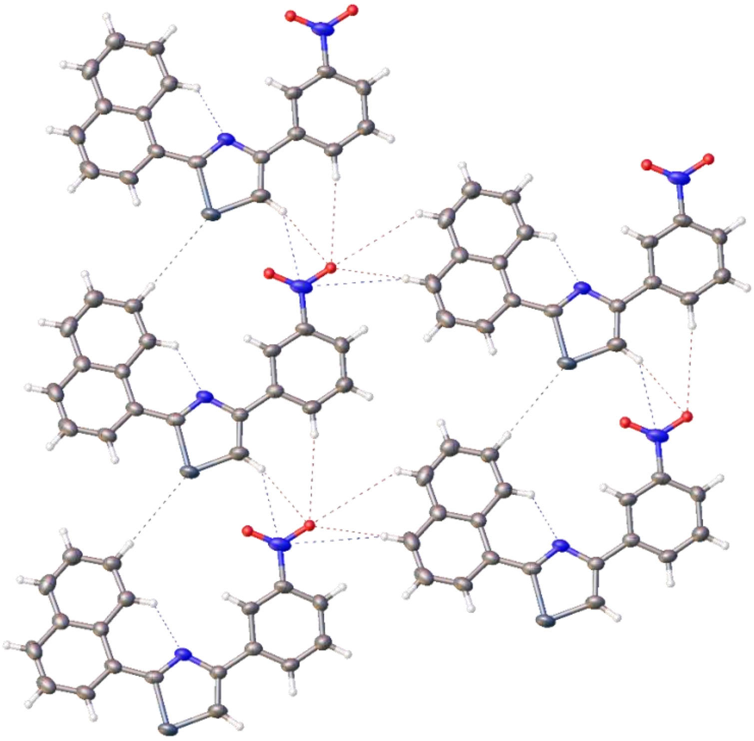


Figure 4-24. A view of 3-D packing network in the structure of **4.9** created by the intermolecular C-H···N/Se/O interactions in the same layer.

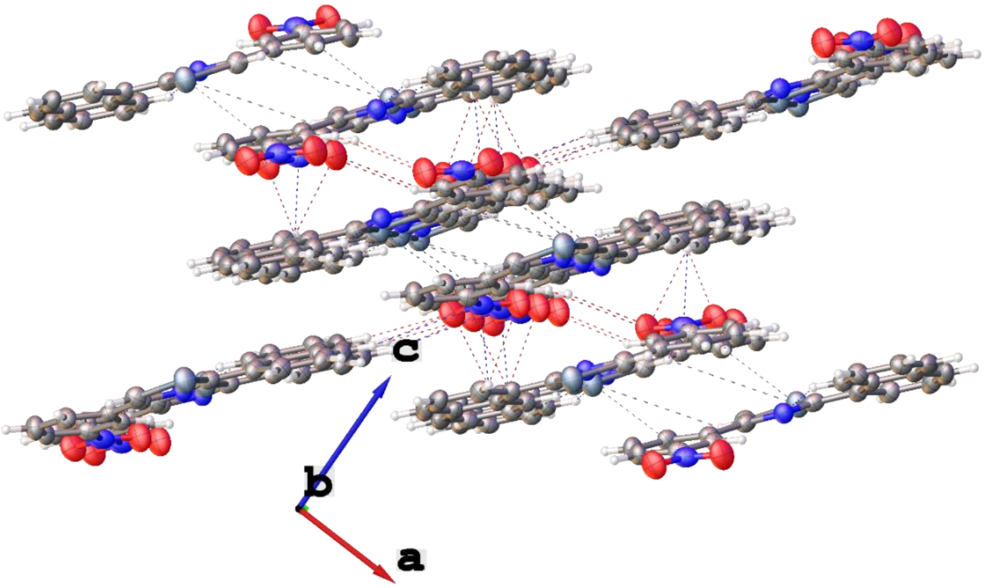


Figure 4-25. A view of 3-D packing network in the structure of **4.9** created by the intermolecular C-H···N/Se/O interactions.

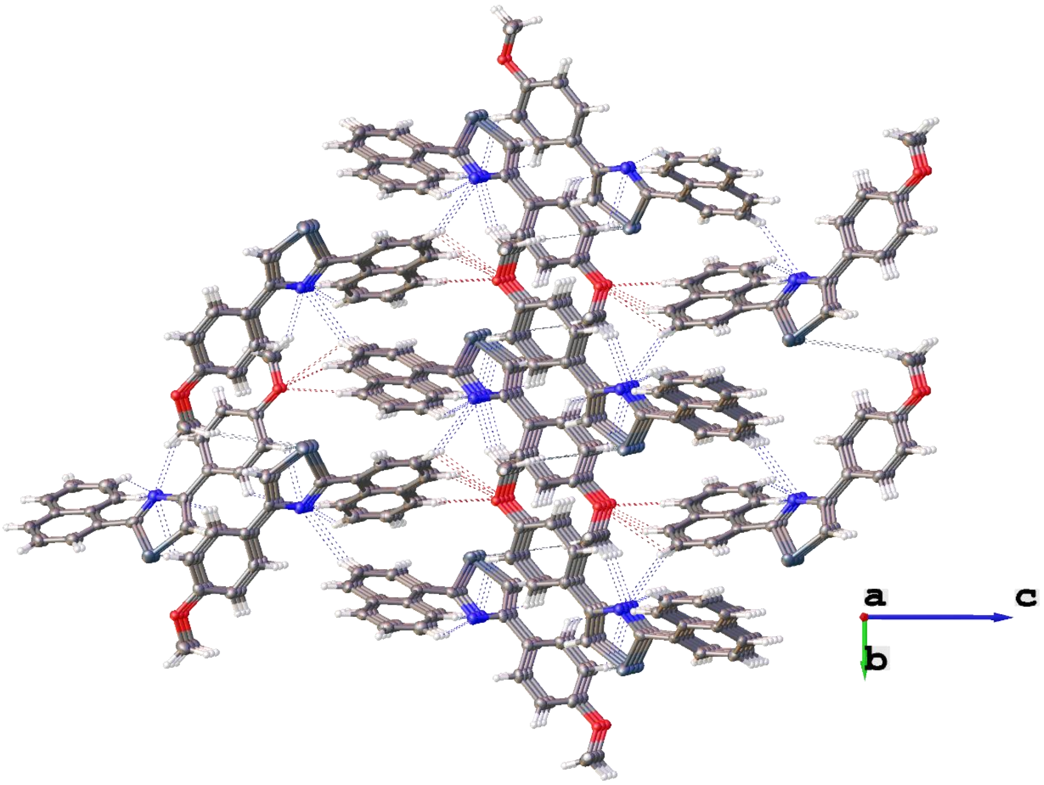


Figure 4-26. A view of 3-D packing network in the structure of **4.10** created by the intermolecular C-H···N/Se/O interactions.

4.4. Conclusion

A series of 2,4-diaryl-1,3-selenazoles have been crystallographically characterised. Ten compounds are very structurally similar though there are some differences resulting from the consequence of the different substituents. The distances between the N atom and the neighbouring C atom range from 1.285(14) to 1.410(9) Å with the C-N-C bond angles from 112.4(5) to 118.3(4)°, meanwhile, the distances between the Se atom and the neighbouring C atom range from 1.803(13) to 1.909(3) Å with the C-Se-C bond angles from 84.24(15) to 85.2(5)°. The values of multiple bond distances in the selenazole ring are between the relevant single bond distance and double bond distance. N atom and Se atom deviate slightly from the C(2)-C(4)-C(5) mean plane less than 0.022(6) Å, therefore, they are nearly flat. There are some differences in the twist angles between the mean planes of the selenazole rings and the two aryl ring substituents, except for **4.8** [42.09°] and **4.10** [37.69°], other distortions are between 1.02 and 20.38°.

The structures of compounds **4.1–4.10** contain some intramolecular and intermolecular interactions depending on the groups connecting to the selenazole moiety. Through some comparisons with these structures, the intramolecular interactions distances, the relevant torsion angles and deviations suggest that there are some possible intramolecular interactions or weak conjugations in these structures. Obviously, the intramolecular C-H···N interactions in **4.9** and **4.10** are very strong [2.273(4) and 2.470(2) Å], but other intramolecular interactions are weak.

Packing frameworks are directed by soft hydrogen bonding interactions, additionally, very weak π-stacking interactions are occurring in some 3-D supramolecular aggregation arrangements. These intermolecular interactions and π-stacking interactions in **4.1–4.10** play an important role in stabilizing the crossed-layer packing network in the solid state.

4.5. References

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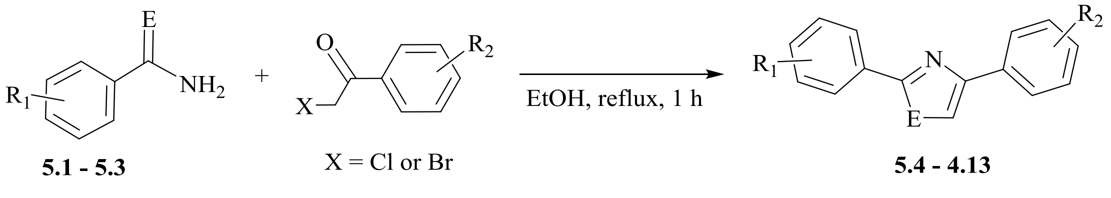
CHAPTER 5

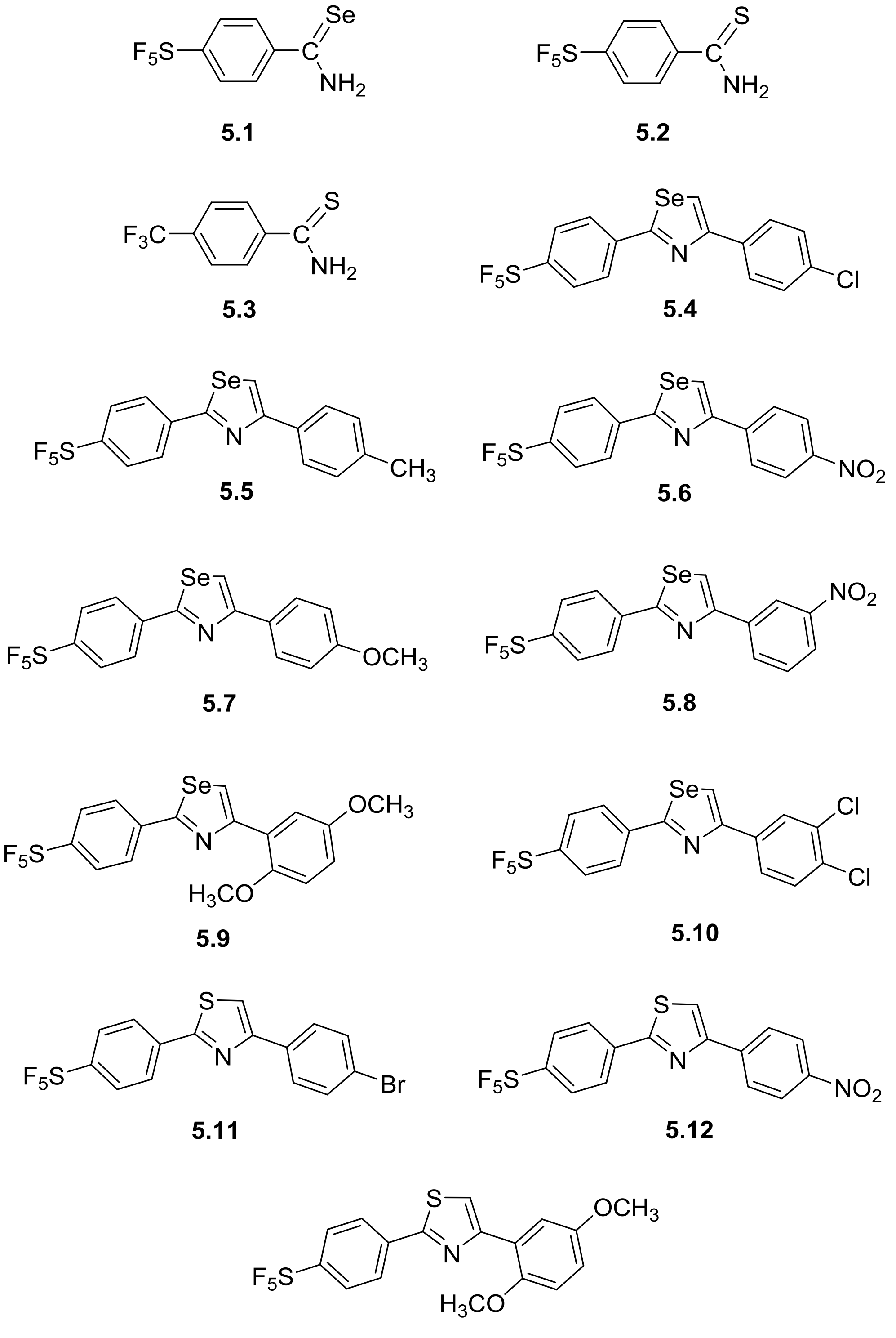
STRUCTURAL STRUCTUAL STUDIES OF CHALCOGEN AMIDES AND 2,4-DIARYL-1,3-CHALCOGEN AZOLES BEARING PENTAFLUOROSULFANYL SF5 GROUP

5.1. Introduction

In Chapter 3 and 4, the structural features of some simple pentafluorosulfuranyl (SF_5)-containing aromatic compounds and 2,4-diaryl-1,3-selenazoles compounds have been discussed. Herein, we focus on the structural characteristic of a series of chalcogen amides and chalcogen azoles incorporating a pentafluorosulfanyl SF_5 group. As it is mentioned in Chapter 3, pentafluorosulfanyl (SF_5)-containing aromatic compounds have some unique characteristic such as high electronegativity, low surface energy, high chemical and metabolic stability, and so on.[1-6] Their wide applications have also been reported as energetic materials, herbicides, liquid crystals and etc.[7-13] Compounds **5.1**–**5.3** were prepared by the reaction of the corresponding nitrile and Woollins' Reagent or Lawesson's Reagent in refluxing toluene solution, followed by hydrolysis with water;[14] the cyclization of selenoamide **5.1** or thioamide **5.2** with an equivalent of α-haloketones gave a series of 1,3-chalcogen azoles **5.4**–**5.13** (Scheme 5-1).[15] The chemical structures of compounds **5.1**–**5.13** are shown in Figure 5-1. All crystals of 13 compounds suitable for X-ray crystallographic studies were obtained at room temperature from the diffusion of hexane into a dichloromethane solution.



Scheme 5-1. Synthesis of 2,4-diaryl-1,3-chalcogen azoles **5.4**–**5.13** from chalcogen amides **5.1**–**5.3**.



5.1 **5.2** **5.3** **5.4** **5.5** **5.6** **5.7** **5.8** **5.9** **5.10** **5.11** **5.12** **5.13**

Figure 5-1. The chemical structures of **5.1**–**5.13**.

5.2. Crystal Structure Data

Structural data were collected at -148℃ on a Rigaku Mercury70 diffractometer using graphite monochromated Mo-Kα radiation for compounds **5.1**, **5.2** and **5.11**, at -148℃ on a Rigaku Saturn70 diffractometer Mo-Kα radiation for compounds **5.3**, **5.6** and **5.12**, at -148℃ using a Rigaku SCX-Mini diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.7173 Å) for compounds **5.4**, **5.5** and **5.7**–**5.9**, at -148℃ on a Rigaku Saturn724 diffractometer using graphite monochromated Mo-Kα radiation for compound **5.10** and at -148℃ on a Rigaku Saturn70 diffractometer Mo-Kα radiation for compound **5.13**. The unit cell and refinement parameters for compounds **5.1**–**5.13** are listed in Tables 5-1–5-4. Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorrentz, polarization and absorption effects. Structures were solved by direct methods and refined by full-matrix least-squares again F2 (SHELXL)[16] using Crystal Structure.[17] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries.

All structures have a single molecule of the compound in each asymmetric unit except **5.3** and **5.9** where the asymmetric unit contains four independent molecules in **5.3**; meanwhile, the asymmetric unit consists of two independent molecules in **5.9**. Compounds **5.1** and **5.2** bearing SF_5 function group crystallize in a $P2_1/c$ space group with R_1 = 0.0620 and 0.0690 respectively; compounds **5.3** with CF_3 functional group crystallizes in a $Pca2_1$ space group with R_1 = 0.0904. Compounds **5.4**–**5.10** have very similar chemical conformation; the only differences between these compounds are the number and position of the substituent on one of two aryl rings. Compounds **5.11**–**5.13** are the sulfur analogues of selenium with very similar conformation to compounds **5.4**–**5.10**. Three compounds **5.4**, **5.11** and **5.12** crystallize in a *Pnma* space group with R_1= 0.0497, 0.0566 and 0.0495, respectively. Compounds **5.5**–**5.10** and **5.13** crystallize in different space groups, namely, $Pna2_1$ with R_1 = 0.0523 for **5.5**, $P2_12_12_1$ with R_1 = 0.0469 for **5.6**, *C2/c* with R_1 = 0.0559 for **5.7**, *P-1* with R_1 = 0.0499 for **5.8** and R_1 = 0.0371 for **5.9**, $P2_1/n$ with R_1 = 0.0706 for **5.10**, and $P2_1/c$ with R_1 = 0.1192 for **5.13**, as shown in Tables 5-1–5-4.

Table 5-1. Relevant crystal data and refinement parameters for **5.1**–**5.3**

Experimental details	**5.1**	**5.2**	**5.3**
Empirical formula	$C_7H_6F_5NSSe$	$C_7H_6F_5NS_2$	$C_8H_6F_3NS$
Formula weight	310.14	263.24	205.20
Temperature (℃)	-148	-148	-148
Crystal color, habit	Colorless, chip	Yellow, platelet	Yellow, chip
Crystal dimensions (mm^3)	0.200 × 0.150 × 0.130	0.200 × 0.090 × 0.030	0.120 × 0.120 × 0.030
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Lattice parameters	a = 17.6082(10) Å	a = 17.3607(10) Å	a = 8.533(2) Å
	b = 5.871(2) Å	b = 5.750(3) Å	b = 20.415(5) Å
	c = 10.079(5) Å	c = 10.038(6) Å	c = 19.854(5) Å
	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$
	$\beta = 106.40(2)^{\circ}$	$\beta = 105.53(3)^{\circ}$	$\beta = 90^{\circ}$
	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$
Volume ($Å^3$)	999.6(6)	965.4(8)	3459(2)
Space group	$P2_1/c$	$P2_1/c$	$Pca2_1$
Z value	4	4	16
Dcalc (g/cm^3)	2.061	1.811	1.576
$F_{(000)}$	600.00	528.00	1664.00
μ(MoKα) (cm^{-1})	40.036	5.902	3.707
Diffractometer	Mercury70	Mercury70	Saturn70
No. of reflections measured	8092	7914	25136
Unique	1745	1685	3135
R_{int}	0.1404	0.3253	0.0904
Friedel pairs	-	-	-
Min. and max. transmissions	0.294, 0.594	0.513, 0.982	0.751, 0.989
No. of observations (All reflections)	1745	1685	3135
No. of variables	136	136	469
Reflection/parameter ratio	12.83	12.39	6.68
Residuals: R_1 (I>2.00σ(I))	0.0620	0.0690	0.0595
Residuals: R (all reflections)	0.1288	0.2486	0.0794
Residuals: wR_2 (all reflections)	0.1682	0.1845	0.1798
Goodness of fit indicator	1.003	0.958	1.133
Flack parameter	-	-	-
Maximum peak in final diff. map ($e^-/Å^3$)	1.17	0.35	0.72
Minimum peak in final diff. map ($e^-/Å^3$)	-0.39	-0.37	-0.57

Table 5-2. Relevant crystal data and refinement parameters for **5.4**–**5.6**

Experimental details	**5.4**	**5.5**	**5.6**
Empirical formula	$C_{15}H_9ClF_5NSSe$	$C_{16}H_{12}F_5NSSe$	$C_{15}H_9F_5N_2O_2SSe$
Formula weight	444.71	424.29	455.26
Temperature (℃)	-148	-148	-148
Crystal color, habit	Colorless, chip	Colorless, platelet	Yellow, platelet
Crystal dimensions (mm^3)	0.220 × 0.100 × 0.100	0.650 × 0.210 × 0.030	0.210 × 0.120 × 0.060
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Lattice parameters	a = 12.536(3) Å	a = 7.789(9) Å	a = 6.761(4) Å
	b = 6.791(2) Å	b = 33.34(4) Å	b = 12.748(7) Å
	c = 18.646(4) Å	c = 6.278(7) Å	c = 18.642(12) Å
	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$
	$\beta = 90^{\circ}$	$\beta = 90^{\circ}$	$\beta = 90^{\circ}$
	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$
Volume ($Å^3$)	1587.3(5)	1630(3)	1606.8(17)
Space group	*Pnma*	$Pna2_1$	$P2_12_12_1$
Z value	4	4	4
Dcalc (g/cm^3)	1.861	1.729	1.882
$F_{(000)}$	872.00	840.00	896.00
μ(MoKα) (cm^{-1})	27.154	24.810	25.350
Diffractometer	SCX mini	SCX mini	Saturn70
No. of reflections measured	12815	10873	12153
Unique	1516	2845	2801
R_{int}	0.0968	0.1044	0.0731
Friedel pairs	-	1274	1164
Min. and max. transmissions	0.533, 0.762	0.521, 0.928	0.511, 0.859
No. of observations (All reflections)	1516	2845	2801
No. of variables	139	217	235
Reflection/parameter ratio	10.91	13.11	11.92
Residuals: R_1 (I>2.00σ(I))	0.0497	0.0523	0.0469
Residuals: R (all reflections)	0.0654	0.0716	0.0586
Residuals: wR_2 (all reflections)	0.0981	0.1184	0.1049
Goodness of fit indicator	1.139	0.989	0.954
Flack parameter	-	-0.008(16)	0.498(19)
Maximum peak in final diff. map ($e^-/Å^3$)	0.41	0.44	0.64
Minimum peak in final diff. map ($e^-/Å^3$)	-0.39	-0.37	-0.48

Table 5-3. Relevant crystal data and refinement parameters for **5.7–5.9**

Experimental details	**5.7**	**5.8**	**5.9**
Empirical formula	$C_{16}H_{12}F_5NOSSe$	$C_{15}H_9F_5N_2O_2SSe$	$C_{17}H_{14}F_5NO_2SSe$
Formula weight	440.29	455.26	470.32
Temperature (℃)	-148	-148	-148
Crystal color, habit	Colorless, platelet	Colorless, platelet	Colorless, chip
Crystal dimensions (mm^3)	0.500 × 0.370 × 0.070	0.360 × 0.200 × 0.070	0.340 × 0.200 × 0.100
Crystal system	Monoclinic	Triclinic	Triclinic
Lattice parameters	a = 35.77(5) Å	a = 7.911(11) Å	a = 9.650(4) Å
	b = 6.207(8) Å	b = 10.425(15) Å	b = 12.717(5) Å
	c = 15.93(2) Å	c = 11.609(16) Å	c = 15.930(7) Å
	$\alpha = 90^{\circ}$	$\alpha = 109.181(3)^{\circ}$	$\alpha = 77.557(12)^{\circ}$
	$\beta = 107.028(14)^{\circ}$	$\beta = 109.088(11)^{\circ}$	$\beta = 75.918(11)^{\circ}$
	$\gamma = 90^{\circ}$	$\gamma = 100.490(13)^{\circ}$	$\gamma = 77.430(13)^{\circ}$
Volume ($Å^3$)	3381(8)	808.4(19)	1823.2(13)
Space group	*C2/c*	*P-1*	*P-1*
Z value	8	2	4
Dcalc (g/cm^3)	1.730	1.870	1.713
$F_{(000)}$	1744.00	448.00	936.00
μ(MoKα) (cm^{-1})	24.003	25.194	22.354
Diffractometer	SCX mini	SCX mini	SCX mini
No. of reflections measured	13593	6780	15741
Unique	2977	2837	6396
R_{int}	0.0611	0.0708	0.0418
Friedel pairs	-	-	-
Min. and max. transmissions	0.658, 0.845	0.550, 0.838	0.542, 0.800
No. of observations (All reflections)	2977	2837	6396
No. of variables	226	235	487
Reflection/parameter ratio	13.17	12.07	13.13
Residuals: R_1 (I>2.00σ(I))	0.0559	0.0499	0.0371
Residuals: R (all reflections)	0.0697	0.0691	0.0511
Residuals: wR_2 (all reflections)	0.1693	0.1207	0.1107
Goodness of fit indicator	1.060	1.043	0.923
Flack parameter	-	-	-
Maximum peak in final diff. map ($e^-/Å^3$)	1.18	0.79	0.37
Minimum peak in final diff. map ($e^-/Å^3$)	-0.66	-0.65	-0.49

Table 5-4. Relevant crystal data and refinement parameters for **5.10–5.13**

Experimental details	**5.10**	**5.11**	**5.12**	**5.13**
Empirical formula	$C_{15}H_8C_{l2}F_5NSSe$	$C_{15}H_9BrF_5NS_2$	$C_{15}H_9F_5N_2O_2S_2$	$C_{17}H_{14}F_5NO_2S_2$
Formula weight	479.15	442.26	408.36	423.42
Temperature (℃)	-148	-148	-148	-148
Crystal color, habit	Colorless, platelet	Colorless, platelet	Yellow, chip	Colorless, block
Crystal dimensions (mm^3)	0.150 × 0.060 × 0.030	0.190 × 0.160 × 0.070	0.240 × 0.060 × 0.060	0.120 × 0.120 × 0.120
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Lattice parameters	a = 15.288(8) Å	a = 12.804(3) Å	a = 12.889(8) Å	a = 12.075(10) Å
	b = 5.682(3) Å	b = 6.7729(16) Å	b = 6.737(4) Å	b = 9.345(7) Å
	c = 19.113(10) Å	c = 18.485(4) Å	c = 18.371(12) Å	c = 16.111(13) Å
	$\alpha = 90^{o}$	$\alpha = 90^{o}$	$\alpha = 90^{o}$	$\alpha = 90^{o}$
	$\beta = 101.979(11)^{o}$	$\beta = 90^{o}$	$\beta = 90^{o}$	$\beta = 106.76(3)^{o}$
	$\gamma = 90^{o}$	$\gamma = 90^{o}$	$\gamma = 90^{o}$	$\gamma = 90^{o}$
Volume ($Å^3$)	1624.1(15)	1603.0(6)	1595.1(18)	1741(3)
Space group	*P2₁/n*	*Pnma*	*Pnma*	*P2₁/c*
Z value	4	4	4	4
Dcalc (g/cm^3)	1.959	1.832	1.700	1.615
$F_{(000)}$	936.00	872.00	824.00	864.00
μ(MoKα) (cm^{-1})	28.204	28.817	4.019	3.697
Diffractometer	Saturn724	Mercury70	Saturn70	Saturn70
No. of reflections measured	11716	13170	11651	12559
Unique	2852	1536	1528	3056
R_{int}	0.1759	0.1718	0.0782	0.1227
Friedel pairs	-	-	-	-
Min. and max. transmissions	0.277, 0.919	0.466, 0.817	0.378, 0.976	0.655, 0.957
No. of observations (All reflections)	2852	1536	1528	3056
No. of variables	226	139	151	244
Reflection/parameter ratio	12.62	11.05	10.12	12.52
Residuals: R_1 (I>2.00σ(I))	0.0706	0.0566	0.0495	0.1192
Residuals: R (all reflections)	0.1368	0.1186	0.0794	0.1860
Residuals: wR_2 (all reflections)	0.2004	0.1510	0.1504	0.3828
Goodness of fit indicator	0.845	1.005	1.053	1.213
Flack parameter	-	-	-	-
Maximum peak in final diff. map ($e^-/Å^3$)	1.01	0.73	0.40	0.79
Minimum peak in final diff. map ($e^-/Å^3$)	-0.55	-0.46	-0.29	-0.78

5.3. X-ray Structure Analysis

X-ray crystal structure analysis of compounds **5.1**–**5.3** reveals that all three structures have very similar structural features along with similar intramolecular/intermolecular C-H···X (X = S, Se, F, N) interactions, weak N-H···E (E= S or Se) hydrogen bonding and the π-stacking interactions. The structures of 2,4-diarylpentafluorosulfanyl-1,3-chalcogen azoles reveal that the five-membered N(1)-C(2)-E(3)-C(4)-C(5) (E = S or Se) ring is either perfectly co-planar with two peripheral aryl ring planes in **5.4**, **5.11** and **5.12**, or nearly planar in **5.5**–**5.10** and **5.13**. Intra/intermolecular C-H···X (X = S, Se, Br, Cl, F, O, N) interactions and π-stacking interactions are observed in the cases of **5.1**–**5.13**.

5.3.1. Chalcogen Amides 5.1–5.3

Compound **5.3** is different from compounds **5.1** and **5.2** with a CF_3 functional group rather than SF_5 functional group. The structures of **5.1** and **5.2** have the same monoclinic crystal systems (Figure 5-2), the structure of **5.3** has an orthorhombic crystal system (Figure 5-3). The selected distances and angles for the structures of **5.1**–**5.3** are listed in Table 5-5.

The C=Se double bond length in **5.1** [1.829(8) Å] is within the range of ordinary C=Se bond distances in reported selenoamides [1.81(5) to 1.856(4) Å],[18-23] but is significantly longer than the C=S double bond distance [ranging from 1.659(8) Å to 1.679(8) Å] in **5.2** and **5.3**. The C-N single bond lengths in **5.1**–**5.3** are very similar [1.312(12) to 1.331(10) Å], accompanied by the similar Se/S(3)-C(2)-N(1) bond angles [119.5(6) to 123.3(6)°]. In the structures of **5.1**–**5.3**, the N atoms deviate from 0.439(17) to 0.705(14) Å with the aryl ring planes, however, the deviation distance between the S/Se(3) atoms in **5.1** [0.264(17) Å] and **5.2** [0.274(15) Å] are significantly smaller than that in **5.3** [0.645(12) to 0.932(13) Å].

The S(1)-F(ax) bond lengths in **5.1** and **5.2** are not significantly different [1.586(5) Å for **5.1** and 1.574(7) Å for **5.2**], as are the S(1)-C(9) bond lengths [1.822(8) Å in **5.1** and 1.799(10) Å in **5.2**]. The S(1)-F(eq) bond distances are also close to each other [1.570(7) to 1.592(7) Å in **5.1** and 1.569(5) to 1.609(5) Å in **5.2**]. The C-S(1)-F(eq) bond angles [91.4(4) to 92.7(3)° in **5.1** and 91.1(4) to 92.4(4)° in **5.2**] are considerably bigger than the F(eq)-S(1)-F(ax) bond angles in **5.1** [87.7(3) to 88.4(3)°] and **5.2** [87.2(3) to 88.9(3)°]. The deviation distance between the S(1) atom and the F(1)-F(2)-

F(3)-F(4) mean plane are 0.055(3) in **5.1** and 0.050(4) Å in **5.2**. The results show that the bond lengths and angles for SF_5 group in **5.1–5.3** are subtly different, though a sulfur atom replaces a selenium atom**,** attributing to the solid stability of SF_5 group.

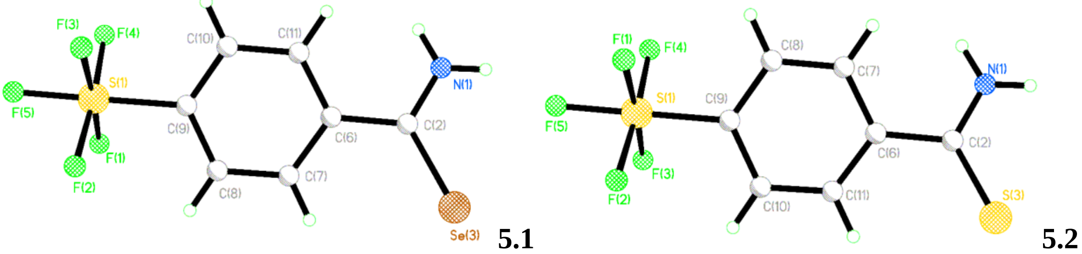


Figure 5-2. X-ray single crystal structures of compounds **5.1** and **5.2**.

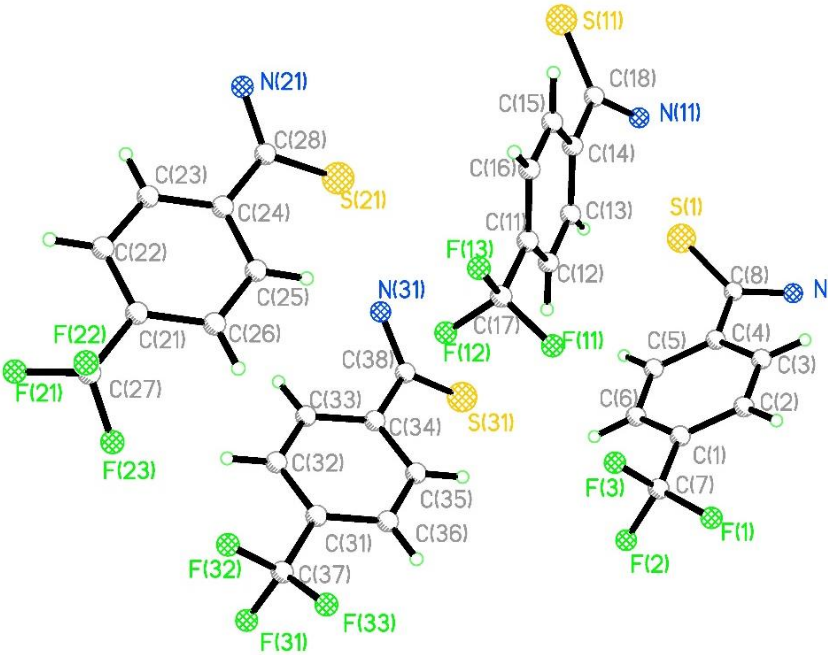


Figure 5-3. X-ray single crystal structure of compound **5.3**.

Table 5-5. Selected bond distances (Å) and angles (°) for compounds **5.1**–**5.3**

	5.1	**5.2**	**5.3**
C(2)=X(3)	1.828(8)	1.662(10)	1.659(8) - 1.679(8)
C(2)-N(1)	1.328(11)	1.312(12)	1.321(10) - 1.331(10)
X(3)-C(2)-N(1)	119.7(6)	121.3(8)	120.9(6) - 123.3(6)
S(1)-C(9)	1.822(8)	1.799(10)	
S(1)-F(5)	1.586(5)	1.574(7)	
S(1)-F(1)	1.585(5)	1.609(5)	
S(1)-F(2)	1.570(7)	1.576(5)	
S(1)-F(3)	1.592(7)	1.581(5)	
S(1)-F(4)	1.586(5)	1.569(5)	
C(9)-S(1)-F(5)	179.4(4)	178.9(4)	
F(5)-S(1)-F(1)	88.4(3)	87.8(3)	
F(5)-S(1)-F(2)	87.7(3)	87.2(3)	
F(5)-S(1)-F(3)	88.1(3)	88.7(3)	
F(5)-S(1)-F(4)	87.9(3)	88.9(3)	
C(9)-S(1)-F(1)	92.1(4)	91.1(4)	
C(9)-S(1)-F(2)	92.7(3)	92.4(4)	
C(9)-S(1)-F(3)	91.4(4)	92.4(4)	
C(9)-S(1)-F(4)	91.8(3)	91.4(4)	
F-S(1)-F*	90.5(3); 88.7(3); 90.0(3); 90.6(3)	88.4(3); 90.5(3); 90.9(3); 90.0(3)	
F-S(1)-F**	176.4(3); 175.4(3)	176.4(4); 175.9(4)	
Deviation distance			
N1… aryl plane	-0.439(18)	0.513(15)	0.486(13) - 0.705(14)
X(3)… aryl plane	0.263(17)	-0.274(15)	-0.645(12) - -0.932(13)
S(1)…F(1)-F(2)-F(3)-F(4) plane	-0.055(3)	-0.050(4)	

* The angles between the adjacent F(eq) atoms; **The angles between the opposite F(eq) atoms; X = S or Se

Intramolecular C_{aryl}-H···N/Se/S/F interactions are present in **5.1**–**5.3** (a representative example is **5.1** as shown in Figure 5-4). The selected intramolecular interaction distances and angles for compounds **5.1**–**5.3** are listed in Table 5-6. The intramolecular H···N/Se/S/F interaction distances in **5.1** and **5.2** are smaller than the sum of H···N/Se/S/F van der Waals radii [2.8 Å for H···N, 3.1 Å for H···Se, 3.0 Å for H···S and 2.7 Å for H···F]. The distances of H···N are 2.552(7) Å in **5.1**, 2.528(9) Å in **5.2,** 2.567(8)[2.632(8), 2.634(8) and 2.666(6)] Å in **5.3**, with the corresponding C_{aryl}-H···N angles of 98.1(5), 97.1(7), 97.6(5)[95.0(5), 95.6(5) and 94.1(5)]°. The relevant absolute values of N-C-C-C torsion angles are 17.0(14), 17.9(9) and 38.1(8)[32.9(8), 27.5(8), 33.0(8)]° in **5.1**–**5.3**. The deviation distances between N atom and C-aryl plane are 0.395(14) Å in **5.1** and 0.441(11) Å in **5.2**, however, the values are bigger in **5.3** [0.501(10) to 0.718(11) Å]. The H···Se interaction distance is 2.7919(13) Å with the C_{aryl}-H···Se angle of 109.2(5)°, the absolute values of Se-C-C-C torsion angle of 13.7(13)° and absolute values of deviation distance of 0.312(12) Å between N atom and C-aryl plane in **5.1**. Compared to **5.1**, the H···S interaction distance of 2.709(3) Å with the C_{aryl}-H···S angle of 106.4(7)° is smaller in **5.2**, though the absolute values of S-C-C-C torsion angle [18.1(9)°] and deviation distance [0.352(10) Å] between S atom and C-aryl plane is similar. Compared to **5.2**, the intramolecular H···S interaction distances [2.759(2) to 2.9112(19) Å] are longer, along with smaller C_{aryl}-H···S angles [94.1(5) to 102.5(5)°] in **5.3**.

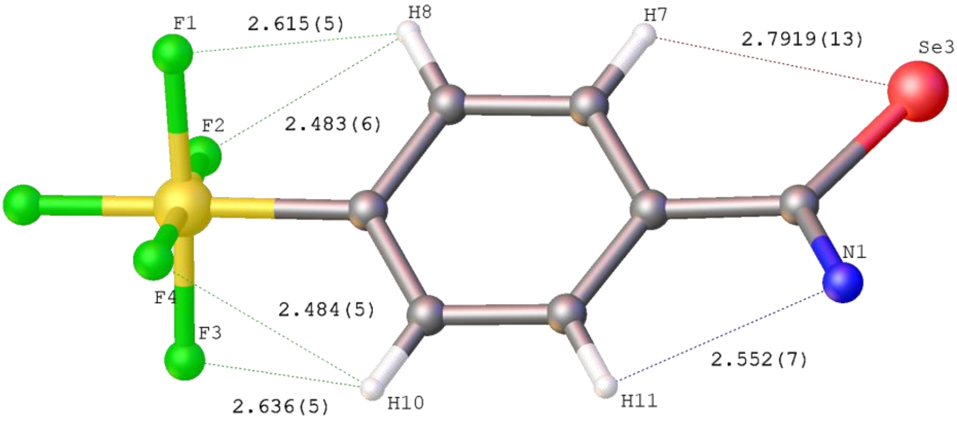


Figure 5-4. A representative 3-D diagram shows the intramolecular C_{aryl}-H···Se, C_{aryl}-H···N and C_{aryl}-H···F interactions in the structure of **5.1**.

In pentafluorosulfuranyl (SF_5)-containing aromatic compounds, the four equatorial fluorine atoms and neighbouring aryl hydrogens form a very important intramolecular interaction. The intramolecular C_{aryl}-H···F(eq) interaction may keep the stability of equatorial fluorine atoms. As shown in Table 5-6, the relevant data for intramolecular C_{aryl}-H···F(eq) interaction in **5.1** and **5.2** are very similar: the distances varying from 2.469(5) to 2.636(5) Å, the angles ranging from 93.0(6) to 98.1(6)°, the absolute values of F(eq)-S-C-C torsion angle differing from 38.9(7) to 51.1(7)° and the equator fluorine atoms deviating from 1.005(9) to 1.227(9) Å from the S-aryl mean plane. Additionally, the intramolecular C_{aryl}-H···F interactions are also found in **5.3**, the shortest distance is 2.432(6) Å with C_{aryl}-H···F angle of 99.1(5)° and F-C-C-C torsion angle of 17.3(9)°.

Table 5-6. Selected intramolecular distances (Å) and angles (°) for **5.1**–**5.3**

	5.1	**5.2**	**5.3**
Intramolecular interaction distances (Å)			
H···Se/S	2.7919(13)	2.709(3)	2.759(2) [2.811(2), 2.826(2), 2.9112(19)]
H···N	2.552(7)	2.528(9)	2.567(8) [2.632(8), 2.634(8), 2.666(6)]
H···F1	2.615(5)	2.614(6)	2.432(6) [2.826(5), 2.490(7), 3.070(9)]
H···F2	2.483(6)	2.492(6)	2.610(7) [2.792(6), 2.558(7), 2.538(7)]
H···F3	2.636(5)	2.593(5)	3.071(7) [2.388(6), 3.191(8), 2.528(7)]
H···F4	2.484(5)	2.469(5)	
Intramolecular interaction angles (°)			
C_{aryl}-H···Se/S	109.2(5)	106.4(7)	94.1(5) [102.5(5), 101.8(5), 99.3(5)]
C_{aryl}-H···N	98.1(5)	97.1(7)	97.6(5) [95.0(5), 95.6(5), 94.1(5)]
C_{aryl}-H···F1	93.2(5)	94.2(6)	99.1(5) [87.8(5), 96.7(5), 81.1(6)]
C_{aryl}-H···F2	98.1(6)	96.7(6)	93.8(5) [88.6(5), 79.2(5), 96.0(5)]
C_{aryl}-H···F3	93.9(5)	93.0(6)	81.4(5) [99.7(5), 94.8(5), 96.3(5)]
C_{aryl}-H···F4	97.1(5)	96.2(5)	
Torsion angles (°)			
Se/S-C-C-C	-13.7(13)	-18.1(9)	37.7(7) [-32.2(7), 23.9(7), 33.3(7)]
N-C-C-C	-17.0(14)	-17.9(9)	38.1(8) [-32.9(8), 27.5(8), 33.0(8)]
F1-S-C-C	-49.4(7)	-51.0(5)	-17.3(9) [43.9(10), -76.3(8), 77.4(10)]
F2-S-C-C	41.2(7)	43.1(5)	61.4(7) [-57.9(10), 0.5(8), -37.5(9)]
F3-S-C-C	-51.1(7)	-47.5(5)	28.0(9) [-90.0(9), -37.0(9), 30.9(9)]
F4-S-C-C	38.9(7)	38.9(7)	
Deviation distance (Å)			
Se/S…C-aryl mean plane	-0.312(12)	-0.352(10)	-0.919(9) [-0.788(9), -0.630(8), -0.773(9)]
N …C-aryl mean plane	0.395(14)	0.441(11)	0.718(11) [0.630(11), 0.501(10), 0.650(11)]
F1…S-aryl mean plane	1.227(9)	-1.197(8)	0.299(12) [1.074(10), -0.522(11), -1.202(10)]
F2…S-aryl mean plane	-1.005(9)	-1.012(8)	0.818(11) [-1.060(9), 1.249(9), 0.678(12)]
F3…S-aryl mean plane	-1.210(9)	1.224(7)	-1.244(11) [-0.03(1), -0.658(12), 0.520(12)]
F4…S-aryl mean plane	1.025(9)	1.042(8)	

Dimensions for other independent molecules in square parentheses.

The supramolecular assemblies in compounds **5.1**–**5.3**, forming three dimensional networks are built by the strong intermolecular N-H···Se/S hydrogen bonds, the weak intermolecular C_{aryl}-H···Se/S, N-H···N and C_{aryl}-H···F interactions and π-stacking interactions as shown in Figures 5-6–5-8. In the same layer there are two strong intermolecular N-H···Se/S hydrogen bonds observed with the H···Se distance of 2.6417(14) Å in **5.1** and H···S distance of 2.520(3) Å in **5.2** between *'Head to Head'* pairs of molecules. The N···Se and N···S distances are 3.503(7) and 3.387(10) Å along with the N-H···Se/S angles of 166.5(5) and 168.6(5)°. Meanwhile, there are two weaker intermolecular hydrogen bonds existing between *'Head to Head'* pairs of molecules as shown in Figure 5-5, and the intermolecular N-H···N interactions are identical with the H···N distances of 3.594(8) Å in **5.1** and 3.426(9) Å in **5.2**, accompanied by the N-H···N angles of 141.8(4) and 139.6(4)°. The two adjacent molecules in the same layer are connected by the strong intermolecular N-H···Se/S interaction [H···Se/S distances 2.7790(13) Å in **5.1** and 2.692(3) Å in **5.2**] and weak intermolecular C_{aryl}-H···Se/S and C_{aryl}-H···F interactions. The packing network is linked by the intermolecular C-H···S and C-H···F interactions in the same layer in **5.3** along with the shortest distances of 2.834(2) and 2.520(8) Å and the corresponding angles of 137.2(6) and 136.7(5)°. Furthermore, the very weak intermolecular C-H···N interaction is also present in the same layer in **5.3** as depicted in Table 5-7.

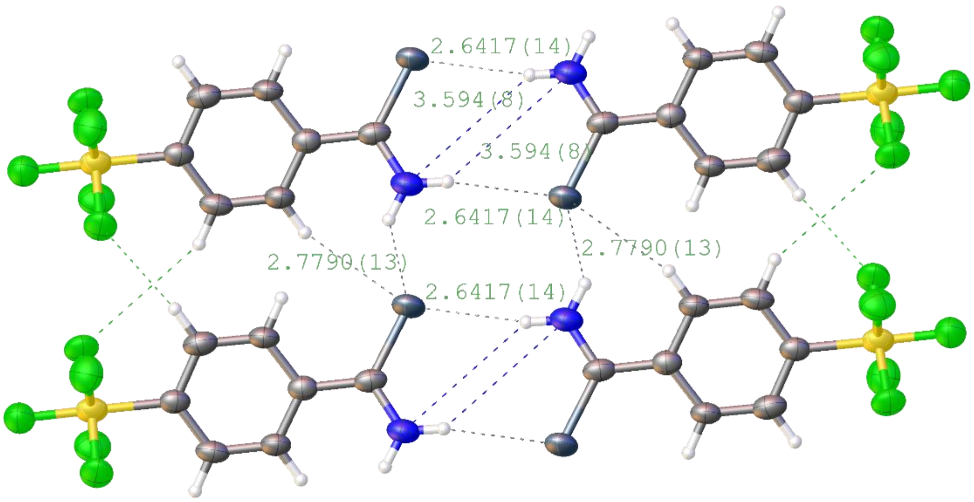


Figure 5-5. A view of 3-D packing network shows the intermolecular C-H···N/Se/F interactions in the same layer in **5.1**.

Table 5-7. Selected intermolecular distances (Å) and angles (°) in the same layer for compounds **5.1**–**5.3**

	5.1	**5.2**	**5.3**
Intermolecular interaction distances (Å)			
H···N	3.594(8)	3.426(9)	
H···Se/S	2.6417(14), 2.7790(13)	2.520(3), 2.692(3)	
H···Se/S	3.8717(16)	3.764(3)	2.834(2), 3.491(2)
H···N			3.882(7)
H···F	3.057(5), 3.926(5)	2.918(6), 3,863(5)	2.520(8), 2.768(6)
Intermolecular interaction angles (°)			
N-H···N	141.8(4)	139.6(4)	
N-H···Se/S	166.5(5), 126.4(5)	168.6(5), 128.9(6)	
C_{aryl}-H···Se/S	125.0(6)	124.9(6)	137.2(6), 155.5(5)
C_{aryl}-H···N			110.2(5)
C_{aryl}-H···F	134.3(7), 134.7(6)	133.8(5), 134.6(5)	136.7(5), 124.8(4)

The structures of the compounds **5.1**–**5.3** pack with weak intermolecular C-H···Se/S/F interactions between the layers (Figures 5-6–5-8). The relevant data are shown in Table 5-8. The networks of **5.1** and **5.2** are very similar with 3-D 'zipper' conformations. The distance of the intermolecular H···N interaction [3.555(9) Å] in **5.1** is very similar to that in **5.2** [3.555(7) Å]. The intermolecular H···Se interaction distances ranging from 3.5231(14) to 3.8937(13) Å in **5.1** are marginally shorter the intermolecular H···S interaction distances of 3.709(3) and 3.900(3) Å in **5.2**. However, the structure of **5.2** has some shorter intermolecular H···S interaction distances [3.517(3) to 3.676(3) Å], compared to the structure of **5.1**. The intermolecular H···F interaction distances of 3.043(6) to 3.840(6) Å in **5.1** is longer than that in **5.2** [2.799(5) Å]. The supramolecular network in **5.3** is formed by the weak intermolecular C-H···S/F/N interactions and π-stacking interactions, however, it is worth noting that the 3-D packing network is not similar to that in **5.1** and **5.2**.

Table 5-8. Selected intermolecular distances (Å) between layers for **5.1**–**5.3**

	5.1	**5.2**	**5.3**
N-H···N	3.555(9)	3.555(7), 3.876(8)	
C_{aryl}-H···Se	3.5231(14), 3.6129(13), 3.8937(13)		3.161(2)
C_{aryl}-H···N			3.081(8), 3.232(7)
C_{aryl}-H···S	3.900(3), 3.709(3)	3.517(3), 3.561(3), 3.676(3), .716(3)	
C_{aryl}-H···F	3.043(6), 3.057(5), 3.365(5) 3.840(6)	2.799(5), 2.988(5), 3.368(5), 3.816(5)	2.686(8), 2.822(7), 2.836(6)

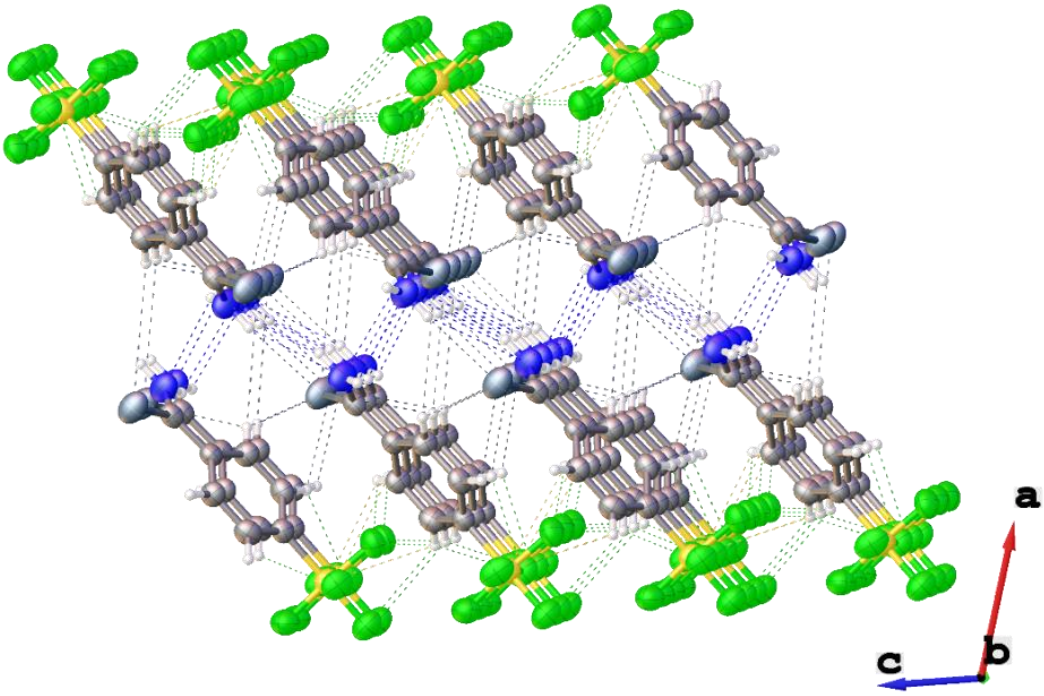


Figure 5-6. A view of 3-D packing network shows the intermolecular C_{aryl}-H···N/Se/S/F interactions and π-stacking interactions in **5.1**.

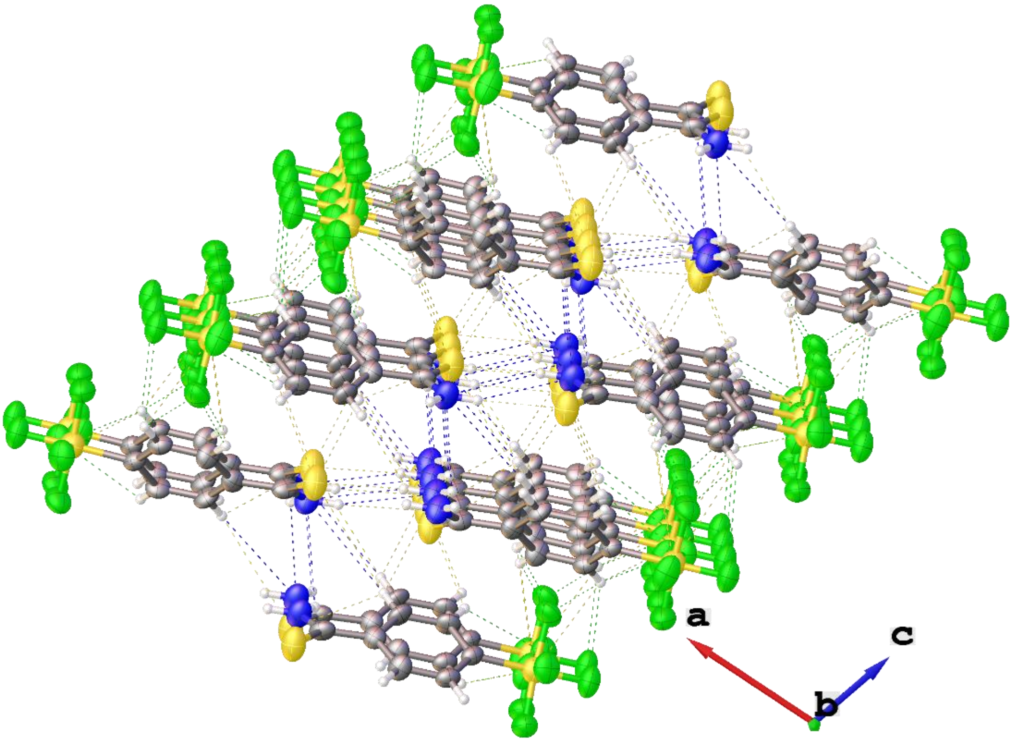


Figure 5-7. A view of 3-D packing network shows the intermolecular C_{aryl}-H···N/S/F interactions and π-stacking interactions in **5.2**.

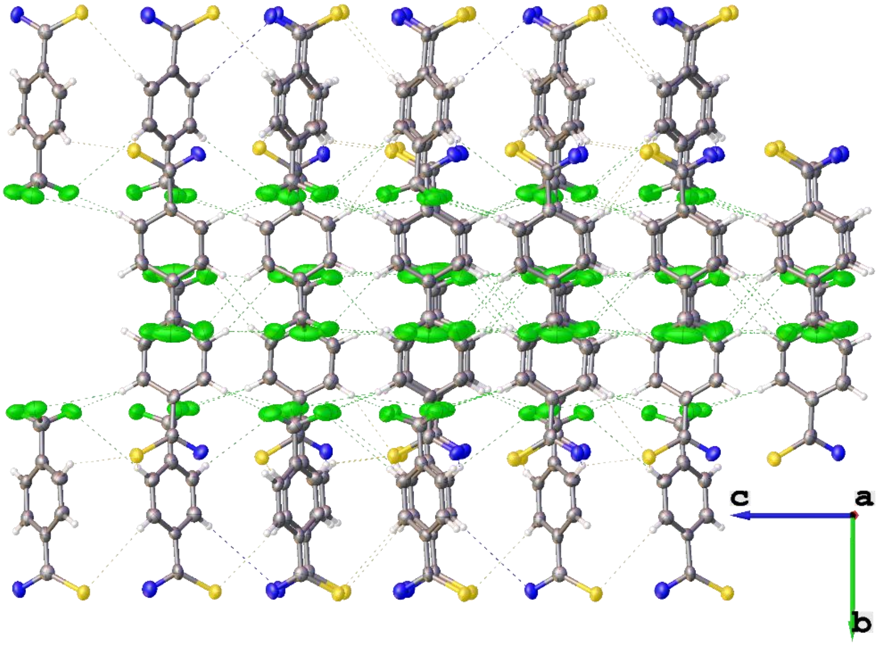


Figure 5-8. A view of 3-D packing network shows the intermolecular C_{aryl}-H···N/S/F interactions and π-stacking interactions in **5.3**.

5.3.2. 2,4-Diaryl-1,3-selenazoles 5.4–5.10

Compounds **5.4**–**5.10** contain a SF_5 functional group and a chalcogen azole ring. 2,4-Diaryl-1,3-selenazoles have been investigated in Chapter 4 and simple SF_5-aromatic compounds have been discussed in Chapter 3. Compounds **5.4**–**5.10** include two aryl-arms [namely, Z1 and Z2 rings as shown in Figure 5-9, the Z1 ring contains one SF_5 group on one of two aryl rings and the Z2 ring has one or two Cl/CH_3/NO_2/OCH_3 groups on the other]. The discussion of the structural similarities and differences in **5.4**–**5.10** will focus on the SF_5 functional group and azole rings. Selected bond lengths and angles for **5.4**–**5.10** are listed in Tables 5-9–5-12. X-ray crystal structures of **5.4**–**5.10** are shown in Figures 5-10–5-16.

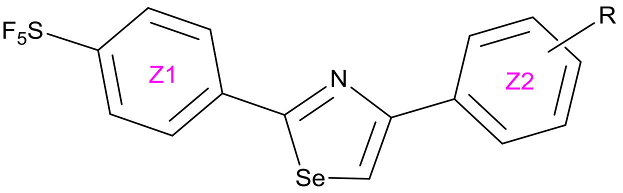


Figure 5-9. Chemical structure of 2,4-diaryl-1,3-selenoazoles **5.4**–**5.10**.

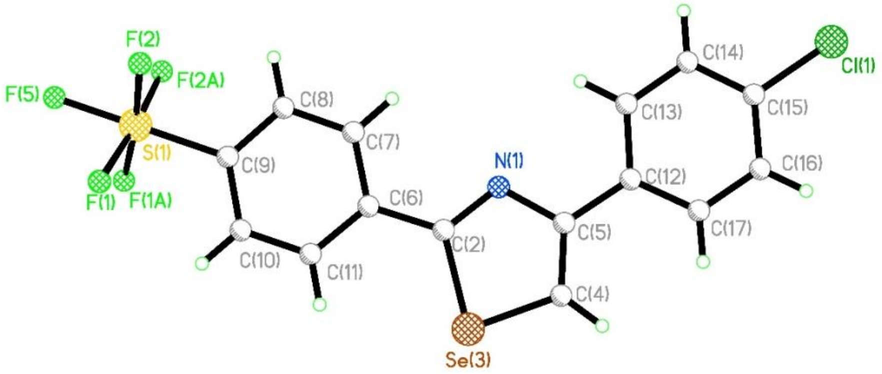


Figure 5-10. X-ray single crystal structure of **5.4**.

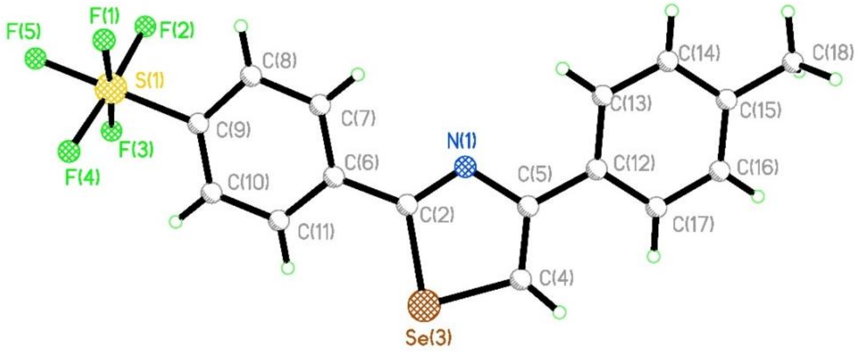


Figure 5-11. X-ray single crystal structure of **5.5**.

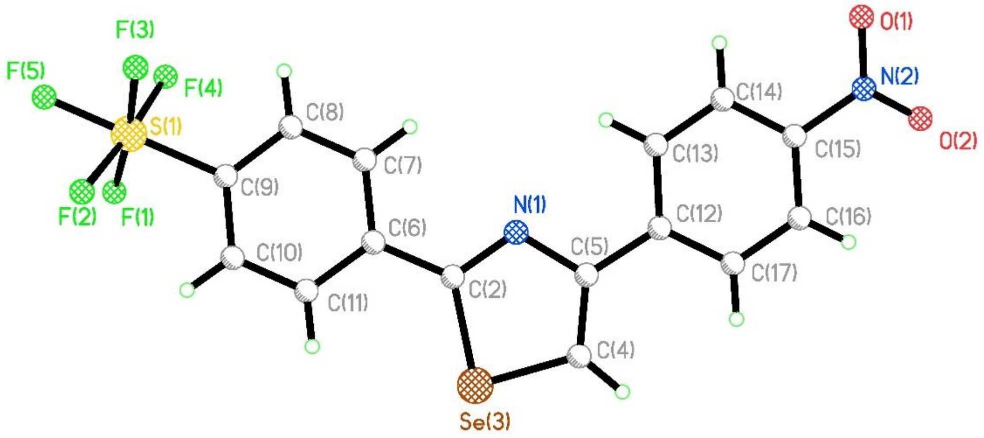


Figure 5-12. X-ray single crystal structure of **5.6**.

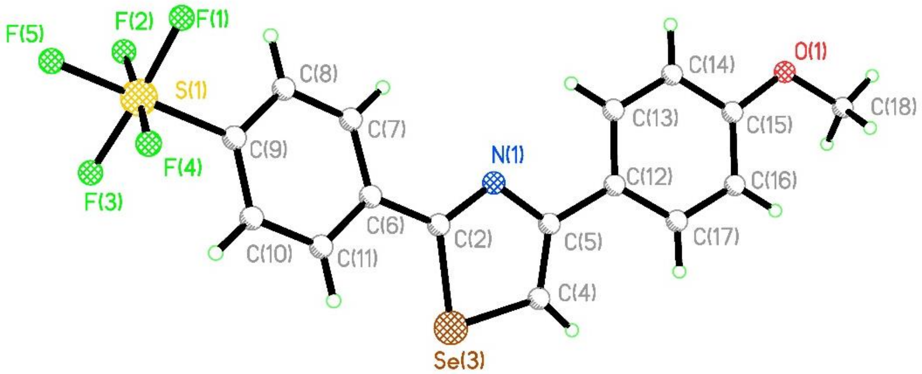


Figure 5-13. X-ray single crystal structure of **5.7**.

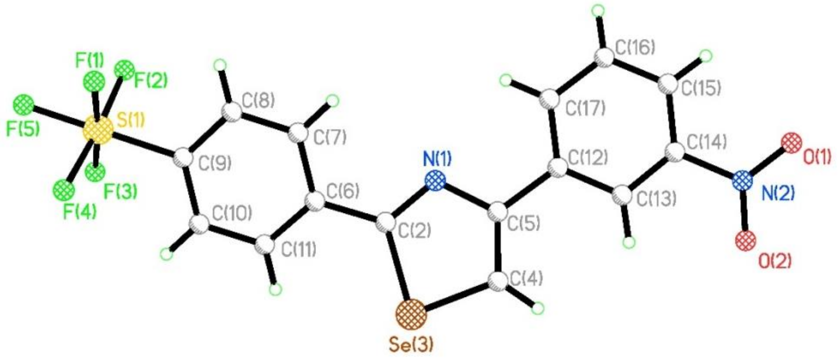


Figure 5-14. X-ray single crystal structure of **5.8.**

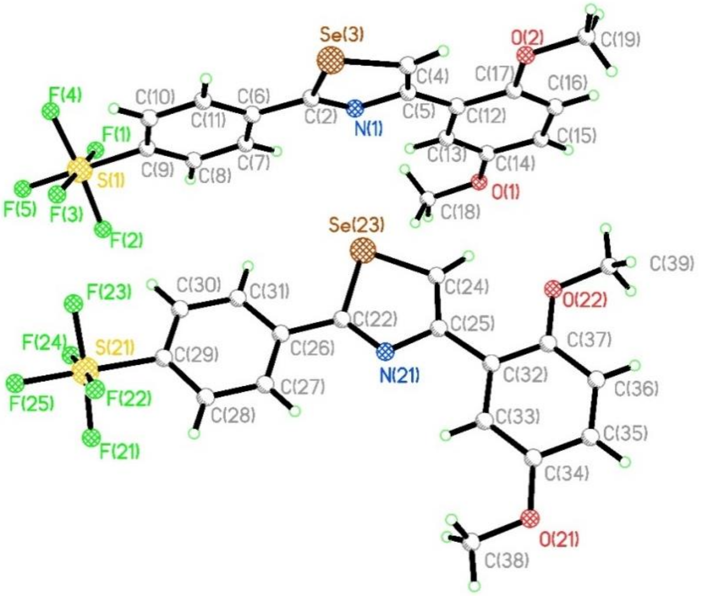


Figure 5-15. X-ray single crystal structure of **5.9**.

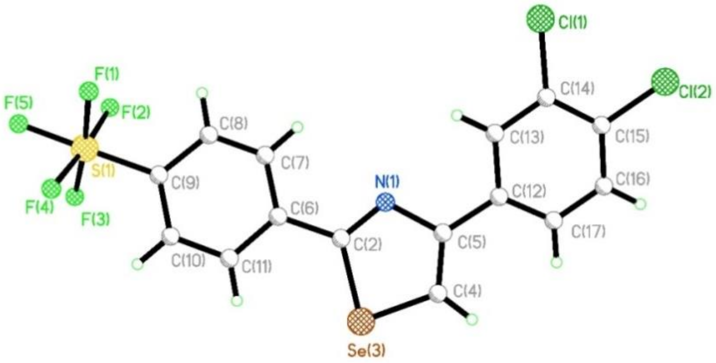


Figure 5-16. X-ray single crystal structure of **5.10**.

The structures of **5.4–5.10** have similar S-F(eq) bond distances [1.558(5) to 1.603(5) Å] with the C-S-F(eq) angles ranging from 91.8(2) to 93.1(2)° and the F(ax)-S-F(eq) angles from 87.1(2) to 88.1(2)°; the S-C bond distances differ from 1.794(11) to 1.834(6) Å and the S-F(ax) bond distances are slightly different from 1.579(7) to 1.593(4) Å with nearly identical C-S-F(ax) angles [179.4(2) to 179.9(3)°] as shown in Tables 5-9 and 5-10.

Table 5-9. Selected bond distances (Å) and angles in the SF5 group (°) for **5.4**–**5.7**

	5.4	**5.5**	**5.6**	**5.7**
S(1)-F(5)	1.593(4)	1.590(5)	1.586(3)	1.587(4)
S(1)-C(9)	1.809(6)	1.834(6)	1.796(4)	1.817(5)
S(1)-F(1)	1.573(3)	1.597(4)	1.582(4)	1.586(4)
S(1)-F(2)	1.572(4)	1.603(5)	1.590(4)	1.591(4)
S(1)-F(3)	1.572(4)	1.593(4)	1.591(5)	1.590(4)
S(1)-F(4)	1.573(3)	1.584(5)	1.583(5)	1.591(4)
C(9)-S(1)-F(5)	179.9(3)	179.9(3)	179.7(2)	179.8(2)
F(5)-S(1)-F(1)	87.16(15)	87.9(2)	87.1(2)	87.7(2)
F(5)-S(1)-F(2)	87.48(15)	87.8(3)	87.1(2)	87.5(2)
F(5)-S(1)-F(3)	87.48(15)	87.9(2)	87.1(2)	87.9(2)
F(5)-S(1)-F(4)	87.16(15)	87.6(2)	87.9(2)	88.1(2)
C(9)-S(1)-F(1)	92.77(17)	92.1(2)	92.8(2)	92.4(2)
C(9)-S(1)-F(2)	92.59(17)	92.1(3)	92.6(2)	92.5(2)
C(9)-S(1)-F(3)	92.59(17)	92.1(3)	93.1(2)	91.9(2)
C(9)-S(1)-F(4)	92.77(17)	92.5(3)	92.3(2)	91.9(2)
F-S(1)-F*	89.95(17)	90.3(3)	89.4(2)	89.6(2)
	90.6(3)	89.7(3)	89.5(2)	90.4(2)
	89.95(17)	89.7(2)	90.3(2)	90.0(2)
	89.0(2)	89.9(2)	90.4(2)	89.7(3)
F-S(1)-F**	174.59(17)	175.8(2)	174.09(19)	175.6(2)
	174.59(17)	175.4(2)	175.02(19)	175.6(2)

*The angles between the adjacent F(eq) atoms; **The angles between the opposite F(eq) atoms.

Table 5-10. Selected bond distances (Å) and angles in the SF5 group (°) for **5.8**–**5.10**

	5.8	**5.9**	**5.10**
S(1)-F(5)	1.585(4)	1.585(3)[1.586(3)]	1.579(7)
S(1)-C(9)	1.803(5)	1.815(4)[1.813(4)]	1.794(11)
S(1)-F(1)	1.575(5)	1.573(3)[1.581(3)]	1.575(6)
S(1)-F(2)	1.573(4)	1.581(2)[1.582(3)]	1.572(6)
S(1)-F(3)	1.558(5)	1.590(3)[1.578(3)]	1.565(6)
S(1)-F(4)	1.589(4)	1.577(3)[1.591(4)]	1.570(6)
C(9)-S(1)-F(5)	179.4(2)	179.34(15)[179.32(18)]	179.8(4)
F(5)-S(1)-F(1)	87.3(2)	87.49(16)[87.19(17)]	87.5(3)
F(5)-S(1)-F(2)	87.7(2)	87.22(14)[87.72(17)]	87.7(3)
F(5)-S(1)-F(3)	87.6(2)	87.13(15)[88.14(17)]	87.8(3)
F(5)-S(1)-F(4)	87.9(2)	87.47(15)[87.56(17)]	87.4(3)
C(9)-S(1)-F(1)	92.2(2)	93.04(16)[92.18(15)]	92.5(4)
C(9)-S(1)-F(2)	92.6(2)	92.39(15)[92.02(17)]	92.5(4)
C(9)-S(1)-F(3)	92.8(2)	92.33(16)[92.49(15)]	92.2(4)
C(9)-S(1)-F(4)	91.8(2)	92.92(16)[92.69(16)]	92.4(4)
F-S(1)-F*	89.5(2)	90.07(15)[89.86(18)]	89.9(3)
	91.0(2)	88.69(14)[90.57(19)]	89.9(3)
	89.9(2)	90.72(16)[89.65(18)]	90.7(3)
	89.2(2)	90.02(16)[89.53(18)]	89.1(3)
F-S(1)-F**	174.89(19)	174.53(18)[175.29(16)]	175.3(4)
	175.5(2)	174.68(16)[175.27(15)]	175.0(4)

*The angles between the adjacent F(eq) atoms; **The angles between the opposite F(eq) atoms
Dimensions for second independent molecule in square parentheses.

In the five-membered N(1)-C(2)-Se(3)-C(4)-(5) ring in **5.4**–**5.10** (Tables 5-11 and 5-12), the Se(3)-C(2) bond lengths range from 1.886(5) to 1.918(7) Å; the Se(3)-C(4) bond lengths differ from 1.820(6) to 1.866(8) Å, and the average C(2)-Se(3)-C(4) bond angles are 84.54°. The N(1)-C(5) single bond lengths increase from 1.384(6) to 1.401(9) Å and the N(1)=C(2) double bond lengths are 1.290(5) to 1.309(9) Å with C2-N1-C5 bond angles from 112.0(4) to 114.6(6)°, these values are quite similar to that in the structures discussed in Chapter 4. The C(4)=C(5) bond lengths [1.344(8) to 1.391(7) Å] are slightly longer than the usual C=C double bond length [1.34 Å]. These results indicated that the conjugated effect in the five-membered N(1)-C(2)-Se(3)-C(4)-(5) ring make the bond lengths not typical single bond or double bond.

The twist angles between the five-membered N(1)-C(2)-Se(3)-C(4)-C(5) ring and two aryl-arm rings are almost 0.0°, indicating that the three rings are nearly co-planar in **5.4**. However, the angles are very different [17.80(16)° for Z1 ring and 3.67(19)° for Z2 ring] in **5.8**. The twist angles in **5.5** [19.84(18)° for Z1 ring and 17.0(2)° for Z2 ring] and in **5.7** [20.22(16)° for Z1 and 15.55(19)° for Z2 ring] are much bigger than that in **5.6** [3.13(18)° for Z1 ring, 5.6(2)° for Z2 ring]. The substituent groups on the Z2 ring are on the *para*-position, the two twist angles are similar but very different in **5.4**–**5.7**. In contrast to **5.6**, the NO_2 group locates on the *meta*-position rather than on the *para*-position resulting in the two twist angles being widely, the deviation between N(1)/Se(3) atom and C(2)-C(4)-C(5) mean plane being very small [0 to 0.037(18)Å], and the N(1)/Se(3) atom being regarded as coplanar with C(2)-C(4)-C(5) mean plane in **5.8**.

Table 5-11. Selected bond distances (Å) and angles (°) in the selenazole ring for **5.4**–**5.7**

	5.4	**5.5**	**5.6**	**5.7**
Bond lengths				
N1-C5	1.388(7)	1.401(9)	1.384(6)	1.397(6)
N1=C2	1.295(7)	1.309(9)	1.292(6)	1.308(6)
Se3-C2	1.891(6)	1.918(7)	1.886(5)	1.899(5)
Se3-C4	1.835(6)	1.866(8)	1.834(5)	1.820(6)
C4=C5	1.344(8)	1.370(10)	1.370(7)	1.391(7)
Bond angles				
C2-N1-C5	113.2(5)	114.6(6)	114.3(4)	112.0(4)
C2-Se3-C4	84.0(3)	84.4(3)	84.9(2)	84.8(2)
Twist angles				
Between Z1 ring and N(1)…C(5) plane	0.0(6)	19.84(18)	3.13(18)	20.22(16)
Between Z2 ring and N(1)…C(5) plane	0	17.0(2)	5.6(2)	15.55(19)
Deviation distance				
N1…C2-C4-C5	0	0.027(10)	-0.002(9)	-0.021(8)
Se3…C2-C4-C5	0	0.002(12)	0.030(13)	-0.014(10)

Table 5-12. Selected bond distances (Å) and angles (°) in the selenazole ring for **5.8–5.10**

	5.8	**5.9**	**5.10**
Bond lengths			
N1-C5	1.386(7)	1.394(5) [1.395(4)]	1.394(13)
N1=C2	1.290(5)	1.300(4),[1.305(4)]	1.300(12)
Se3-C2	1.893(6)	1.894(4)[1.894(3)]	1.890(10)
Se3-C4	1.836(4)	1.846(3)[1.851(4)]	1.831(10)
C4=C5	1.377(8)	1.367(5)[1.374(4)]	1.345(14)
Bond angles			
C2-N1-C5	113.5(4)	114.5(3)[114.3(2)]	114.1(8)
C2-Se3-C4	84.8(2)	84.47(16)[84.61(14)]	84.3(4)
Twist angles			
Between Z1 ring and N(1)…C(5) plane	17.80(16)	176.06(9)[4.32(11)]	2.0(3)
Between Z2 ring and N(1)…C(5) plane	3.67(19)	173.61(10)[5.37(12)]	169.8(3)
Deviation distance			
N1…C2-C4-C5	0.020(8)	-0.008(4)	0.006(14)
Se3…C2-C4-C5	0.015(10)	-0.003(5)	-0.037(18)

The selected intramolecular interaction distances and angles in compounds **5.4–5.10** are listed in Table 5-13 and 5-14. Different intramolecular interactions like C_{aryl}-H⋯F(eq), C_{aryl}-H⋯N and C_{aryl}-H⋯Se are observed. The special intramolecular C_{aryl}-H⋯F(eq) interactions have some effect on the stability of aromatic-SF5 group, and the H···F(eq) distances vary from 2.477(4) to 2.637(4) Å with C_{aryl}-H···F(eq) angles from 93.8(4) to 97.4(4)°. The absolute values of F(eq)-S-C-C torsion angles [41.3(4) to 48.7(3)°] are very similar to that in other SF_5-aromatic compounds. The equator fluorine atoms deviate from 1.036(6) to 1.179(8) Å from the S-aryl mean plane.

In **5.4–5.8**, the intramolecular H···N1^c interaction distances are from 2.531(4) to 2.684(6) Å with the C_{aryl}-H···N1^c angles from 97.7(3) to 99.5(3)°. However, the intramolecular H···N1^d interaction distances [2.409(4) to 2.602(6) Å] are a slightly shorter than that of the intramolecular C_{aryl}-H···N1^c interaction. The intramolecular H···N1 interaction distances are the shortest in **5.6** and the longest in **5.5** as shown in Tables 13 and 14. The intramolecular H···Se interaction distances [2.7963(8) to 2.870(4) Å] are significantly longer than the intramolecular H···N interaction distances, and the relevant angles are from 108.2(2) to 109.7(4)°. The absolute value of the Se3-C2-C6-C11, N1-C2-C6-C7 and N1-C5-C12-C13 torsion angles in **5.4** [-0.0(3), 0 and -0.00(15)°] are close to 0°, but are much smaller than that in **5.6** [4.5(6), 1.9(7) and 5.6(6)°], in **5.5** [19.6(6), 19.7(8) and 17.3(7)°] and in **5.7** [19.3(5), 20.2(6) and 15.9(6)°]. It should be noted that, regarding the intramolecular interaction distances, angles and torsion angles in **5.4**–**5.8**, the intramolecular C_{aryl}-H···Se interaction in **5.4** is the strongest; the intramolecular C_{aryl}-H···N interactions in **5.4** and **5.6** are the strongest.

The intramolecular H···Se interaction distances are 2.7654(13) to 2.8581(13) Å in **5.9** and **5.10**. There are also some intramolecular C_{aryl}-H···O interactions in **5.9** with the H···O distance of 2.223(2)[2.171(3)] Å along with the C_{aryl}-H···O angles of 117.17(19)[118.18(19)]°. The intramolecular H···N1^{c} interaction distances are 2.539(3)[2.610(3)] Å in **5.9** and 2.581(8) Å in **5.10** with the C_{aryl}-H···N1^{c} angles of 99.9(3)[98.9(2)]° and 99.3(6)°, however, the distances are longer than the intramolecular H···N1^{d} interaction distances in **5.9** {2.383(3)[2.416(3)] Å} and in **5.10** [2.496(8) Å]. The absolute value of the Se3-C2-C6-C11 and N1-C2-C6-C7 torsion angles are small in **5.9** {3.7(3)[5.0(3)] and 2.2(9)°}, in **5.10** {3.9(3)[3.7(4)] and 1.7(11)°}. However, compared to **5.9** {-5.9(3)[5.2(3)]°}, the N1-C5-C12-C13 torsion angle in 5**.10** are much wider [11.3(10)°].

A number of slightly different hydrogen bonds, π-stacking interactions and other intermolecular interactions are observed in the packing arrangement. The relevant data for **5.4**–**5.10** are listed in Table 5-15 and 5-16. The 3-D packing networks are formed by the intermolecular C-H···Se, C-H···S and C-H···F interactions in **5.4**–**5.8**. Especially, the strong intermolecular C-H···N and C-H···O interactions are also found in **5.6** and **5.8**. The packing networks in **5.4**, **5.6** and **5.8** have also π-stacking interactions. All structures are very regular and distinct layers. The polymeric networks show '*zigzag chain*' arrangement in **5.5**, **5.7** and **5.8**.

Table 5-13. Selected intramolecular distances (Å) and angles (°) for **5.4**–**5.7**

	5.4	**5.5**	**5.6**	**5.7**
Intramolecular interaction distances (Å)				
H···Se3	2.7963(8)	2.806(3)	2.8338(14)	2.816(3)
H···N1[c]	2.571(5)	2.684(6)	2.531(4)	2.657(5)
H···N1[d]	2.481(4)	2.602(6)	2.409(4)	2.561(4)
H···F1	2.517(3)	2.554(5)	2.516(3)	2.555(5)
H···F2	2.542(3)	2.582(5)	2.522(3)	2.519(5)
H···F3	2.542(3)	2.493(5)	2.540(4)	2.518(5)
H···F4	2.517(3)	2.558(4)	2.637(4)	2.497(5)
Intramolecular interaction angles (°)				
C_{aryl}-H···Se3	109.7(4)	109.0(4)	109.5(3)	108.5(3)
C_{aryl}-H···N1[c]	99.3(3)	97.8(4)	99.5(3)	97.7(3)
C_{aryl}-H···N1[d]	101.6(4)	99.2(4)	102.0(2)	100.4(3)
C_{aryl}-H···F1	96.1(3)	95.7(4)	95.8(3)	95.3(3)
C_{aryl}-H···F2	95.6(3)	95.1(4)	96.0(3)	96.2(3)
C_{aryl}-H···F3	95.6(3)	97.4(4)	96.1(3)	95.5(4)
C_{aryl}-H···F4	96.1(3)	95.9(4)	95.1(3)	96.5(3)
Torsion angles (°)				
Se3-C2-C6-C11	-0.0(3)	-19.6(6)	-4.5(6)	19.3(5)
N1-C2-C6-C7	0	-19.7(8)	-1.9(7)	20.2(6)
N1-C5-C12-C13	-0.00(15)	17.3(7)	5.6(6)	-15.9(6)
F1-S-C-C	44.55(11)	-44.3(4)	-44.2(4)	-46.2(4)
F2-S-C-C	-45.38(14)	46.1(4)	45.3(4)	43.5(3)
F3-S-C-C	-45.38(14)	-43.0(4)	-45.0(4)	45.3(4)
F4-S-C-C	44.55(11)	46.8(4)	45.4(4)	44.8(4)
Deviation distance (Å)				
F1…S-aryl mean plane	1.102(3)	1.100(6)	-1.106(6)	1.128(6)
F2…S-aryl mean plane	1.118(4)	-1.168(7)	1.125(6)	-1.109(5)
F3…S-aryl mean plane	-1.118(4)	-1.096(6)	1.117(7)	-1.137(6)
F4…S-aryl mean plane	-1.102(3)	1.144(6)	-1.133(7)	1.113(6)

[c] Possible intramolecular interaction between N atom and H atom attached to R_3-aryl ring

[d] Possible intramolecular interaction between N atom and H atom attached to R_4-aryl ring

Table 5-14. Selected intramolecular distances (Å) and angles (°) for **5.8–5.10**

	5.8	**5.9**	**5.10**
Intramolecular interaction distances (Å)			
H···Se3	2.870(4)	2.8581(13)[2.7654(13)]	2.7769(16)
H···N1[c]	2.600(6)	2.539(3)[2.610(3)]	2.581(8)
H···N1[d]	2.455(5)	2.383(3)[2.416(3)]	2.496(8)
H···O		2.223(2)[2.171(3)]	
H···F1	2.477(4)	2.528(3)[2.541(3)]	2.536(6)
H···F2	2.569(4)	2.546(2)[2.540(3)]	2.500(7)
H···F3	2.492(5)	2.548(3)[2.532(3)]	2.542(7)
H···F4	2.585(4)	2.532(4)[2.505(3)]	2.515(6)
Intramolecular interaction angles (°)			
C_{aryl}-H···Se3	108.2(2)	108.63(19)[110.2(2)]	109.6(6)
C_{aryl}-H···N1[c]	98.0(4)	99.9(3)[98.9(2)]	99.3(6)
C_{aryl}-H_a···N1[d]	102.1(3)	103.63(18)[103.03(17)]	101.2(5)
C_{aryl}-H···O		117.17(19)[118.18(19)]	
C_{aryl}-H···F1	97.4(3)	96.2(2)[96.5(2)]	94.3(6)
C_{aryl}-H···F2	94.8(3)	95.4(2)[94.46(19)]	96.8(7)
C_{aryl}-H···F3	96.6(4)	95.7(3)[94.8(2)]	96.0(6)
C_{aryl}-H···F4	93.8(4)	96.7(3)[97.6(2)]	95.2(6)
Torsion angles (°)			
Se3-C2-C6-C11	-19.4(5)	3.7(3)[5.0(3)]	2.2(9)
N1-C2-C6-C7	-15.3(6)	3.9(3)[3.7(4)]	1.7(11)
N1-C5-C12-C13	2.8(6)	-5.9(3)[5.2(3)]	11.3(10)
O-N-C-C			
F1-S-C-C	-42.5(3)	-44.0(2)[-46.6(3)]	44.6(6)
F2-S-C-C	47.1(3)	46.2(2)[43.4(3)]	-45.4(6)
F3-S-C-C	-41.3(4)	-46.1(2)[-44.4(3)]	48.1(6)
F4-S-C-C	48.7(3)	44.7(2)[45.4(3)]	-42.7(6)
Deviation distance (Å)			
F1…S-aryl mean plane	1.062(6)	1.096(3)[1.088(4)]	1.179(8)
F2…S-aryl mean plane	-1.154(5)	-1.136(3)[-1.145(5)]	-1.042(9)
F3…S-aryl mean plane	-1.036(6)	-1.132(3)[-1.166(4)]	-1.089(8)
F4…S-aryl mean plane	1.185(5)	1.122(4)[1.066(5)]	1.139(9)

[c] Possible intramolecular interaction between N atom and H atom attached to R_3-aryl ring

[d] Possible intramolecular interaction between N atom and H atom attached to R_4-aryl ring

Dimensions for second independent molecule in square parentheses.

Table 5-15. Selected intermolecular distances (Å) and angles (°) for **5.4**–**5.7**

	5.4	**5.5**	**5.6**	**5.7**
Intermolecular interaction distances (Å)				
H···Se	2.8795(19), 3.000(2)	3.853(3)	3.2422(18)	3.548(3)
H···S	3.6134(17), 4.2941(17)		3.706(2)	4.157(4)
H···F(ax)	2.614(4)		2.583(3)	
H···F(eq)	3.159(3), 3.426(3)		3.448(4), 3.554(4), 3.489(4), 3.178(4)	2.890(5)
H···O			2.291(4), 2.766(4), 3.253(4), 3.928(4)	2.756(5)
H···N			3.394(4), 3.405(4)	
Intermolecular interaction angles (°)				
C_{aryl}-H···Se	156.7(3), 164.2(3)	127.3(4)	170.5(3)	127.7(3)
C_{aryl}-H···S	157.0(3), 174.9(3)		160.0(4)	130.4(5)
C_{aryl}-H···F(ax)	133.7(4)		139.3(4)	
C_{aryl}-H···F(eq)	158.04(13), 160.96(7)		161.2(4), 161.2(4), 154.3(5), 166.2(5)	133.0(4)
C_{aryl}-H···O			140.4(3), 134.1(3), 172.7(3), 162.2(3)	165.7(3)
C_{aryl}-H···N			146.7(2), 153.5(2)	

In the packing network of **5.4**, the relatively strong intermolecular C_{aryl}-H···Se interaction [H···Se distance of 2.8795(19) Å with the C_{aryl}-H···Se angle of 156.7(3)°], intermolecular C-H···F(ax) interactions [H···F(ax) length of 2.614(4) Å with the C-H···F(ax) angle of 133.7(4)°] and the weak intermolecular C_{aryl}-H···S/F(eq) interactions link the adjacent molecules in the same layer. The 3-D packing network (Figure 5-17) is formed by a series of the weak intermolecular C_{aryl}-H···Se, C_{aryl}-H···F, C_{aryl}-H···S interactions and π-stacking interaction. Four sets of π-stacking interactions have the same centroid-centroid distance of 3.730 Å and shift distance of 1.544 Å with the angle of 0°.

Table 5-16. Selected intermolecular distances (Å) and angles (°) for **5.8–5.10**

	5.8	**5.9**	**5.10**
Intermolecular interaction distances (Å)			
H···Se		3.3705(12), 3.4118(11)	4.3129(18)
H···S	3.744(4)	3.5559(14)	
H···F(ax)	2.643(5), 2.734(5)		
H···F(eq)	2.609(4), 3.054(5), 3.554(6), 3.723(6)	2.591(3), 3.044(3)	3.144(6), 3.387(6)
H···O	3.649(6), 2.544(6), 3.010(5)	3.828(3)	
H···N	3.413(6)	3.760(3)	
H···Cl			2.713(3), 2.918(3), 3.034(3)
Intermolecular interaction angles (°)			
C_{aryl}-H···Se		152.4(2), 136.91(17)	124.7(5)
C_{aryl}-H···S	144.1(3)	164.6(2)	
C_{aryl}-H···F(ax)	126.3(2), 122.2(3)		
C_{aryl}-H···F(eq)		157.4(2), 156.4(3)	141.0(3), 139.9(6)
C_{aryl}-H···O	140.6(2), 163.0(3), 158.6(3)	127.1(2)	
C_{aryl}-H···N	159.1(3)	123.9(2)	
C_{aryl}-H···Cl			161.6(6), 156.1(5), 150.1(6)

There is no significant difference for the intermolecular interaction distances and angles due to their structural similarity in **5.5** and **5.7** (Figure 5-18 and 5-20). The molecules in the same layer are conjoint by the relatively strong intermolecular C_{aryl}-H···O, C_{aryl}-H···F(eq) interactions and the weak intermolecular C_{aryl}-H···Se, C_{aryl}-H···S interactions in **5.7**. Only the weak intermolecular C_{aryl}-H···Se interactions are observed in the same layer in **5.5**. There are no π-stacking interactions between the layers in both **5.5** and **5.7**, but the 3-D packing networks are also formed by the intermolecular C_{aryl}-H···Se/S/F/N/O interactions and π-stacking interaction.

The multi-sheeted supramolecular assemblies in the structures of **5.6** and **5.8** (Figure 5-19 and 5-21) are formed by the intermolecular C_{aryl}-H···Se, C_{aryl}-H···S, C_{aryl}-H···F, C_{aryl}-H···O and C_{aryl}-H···N interactions and π-stacking interactions. Especially, the strong intermolecular C_{aryl}-H···F(ax) interactions [2.583(3) Å in **5.6**, 2.643(5) and 2.734(5) Å in **5.8**] and intermolecular C_{aryl}-H···O interactions [2.291(4) Å in **5.6**, 2.544(6) Å in **5.8**] are exist in the same layers. There are also the π-stacking interactions in **5.6** and **5.8**. The π-stacking interaction between the aryl rings in **5.8** have a centroid-centroid distance of 3.951 Å with angle of 16.432° and shift distance of 1.483 Å. There are two sets of π-stacking interactions in **5.6** with the centroid-centroid distances of 3.704 and 3.670 Å and the angle of 1.499° and the shift distances of 1.583 and 1.382 Å.

The supramolecular structure of **5.9** has the multiple intermolecular C_{aryl}-H···Se/F interactions and the simple intermolecular C_{aryl}-H···O/S/N interactions as shown in Figure 5-22: the 'zigzag chain' polymeric network is built up by the intermolecular C_{aryl}-H···N [H···N 3.760(3) Å with the angle of 123.9(2)°], C_{aryl}-H···Se [H···Se 3.3705(12) Å to 4.0043(13) Å], C_{aryl}-H···O [H···O 3.828(3) Å with an angle of 127.1(2)°], C_{aryl}-H···S [H···S 3.5559(14) Å with an angle of 164.6(2)°] and C_{aryl}-H···F [H···F 2.591(3) to 3.044(3) Å] interactions. The interactions C_{aryl}-H···Cl and C_{aryl}-H···Se interactions are found in **5.10** (Figure 5-23): the weak interactions C_{aryl}-H···Se interactions [4.3129(18) Å] and the strong interactions C-H···Cl interaction {2.713(3) Å [161.6(6)°] to 3.034(3) Å [150.1(6)°]}. The 3-D packing network for **5.9** shows 'Zigzag chain' polymeric assembly.

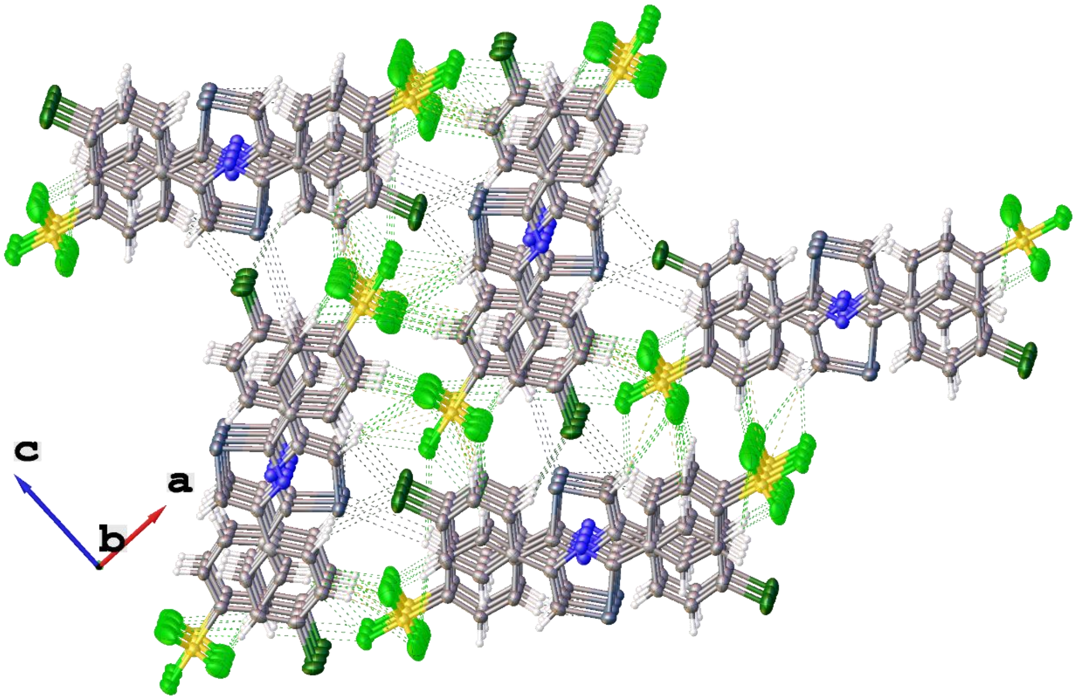


Figure 5-17. View of 3-D packing network shows the intermolecular C_{aryl}-H···Se, C_{aryl}-H···F, C_{aryl}-H···S interactions and π-stacking interactions in **5.4**.

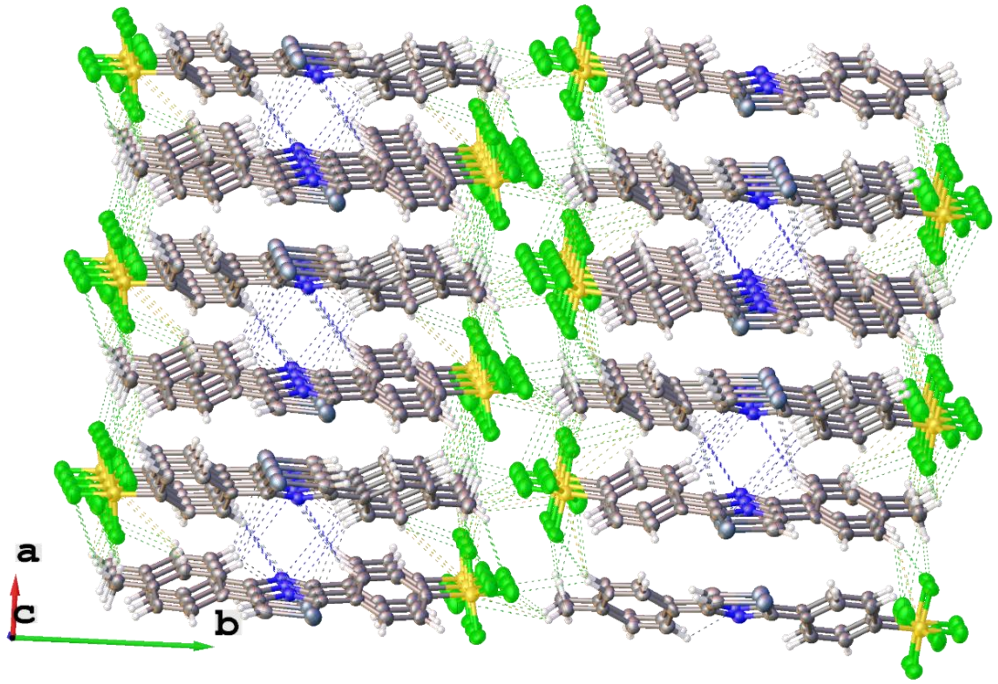


Figure 5-18. View of 3-D packing network show the strong intermolecular C_{aryl}-H···O, C_{aryl}-H···F(eq) and the weak intermolecular C_{aryl}-H···Se, C_{aryl}-H···S interactions and π-stacking interactions in **5.5**.

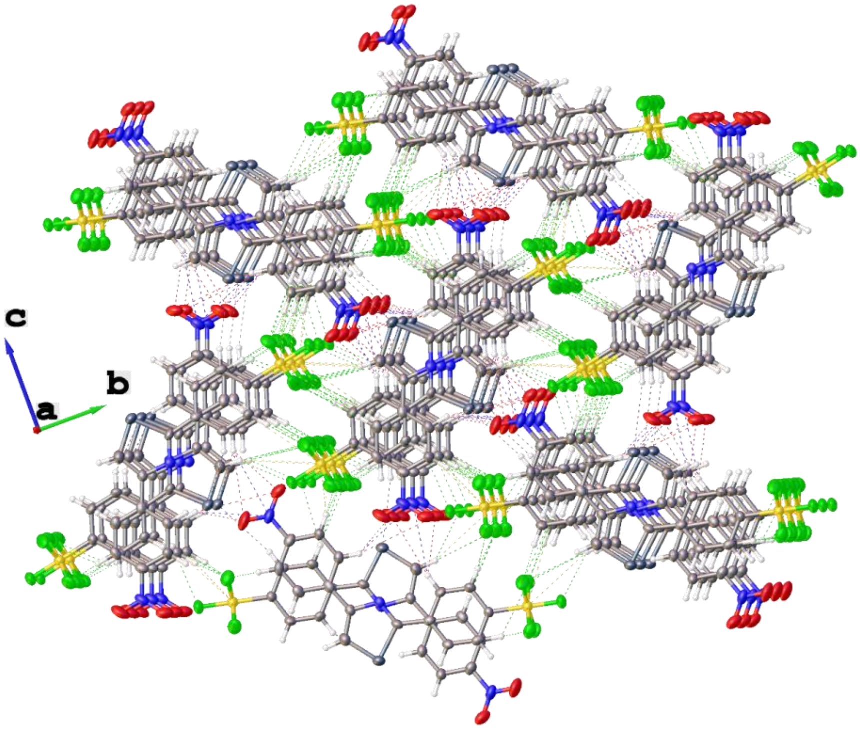


Figure 5-19. View of 3-D packing network shows the intermolecular C_{aryl}-H···Se, C_{aryl}-H···S, C_{aryl}-H···F, C_{aryl}-H···O and C_{aryl}-H···N interactions and π-stacking interactions in **5.6**.

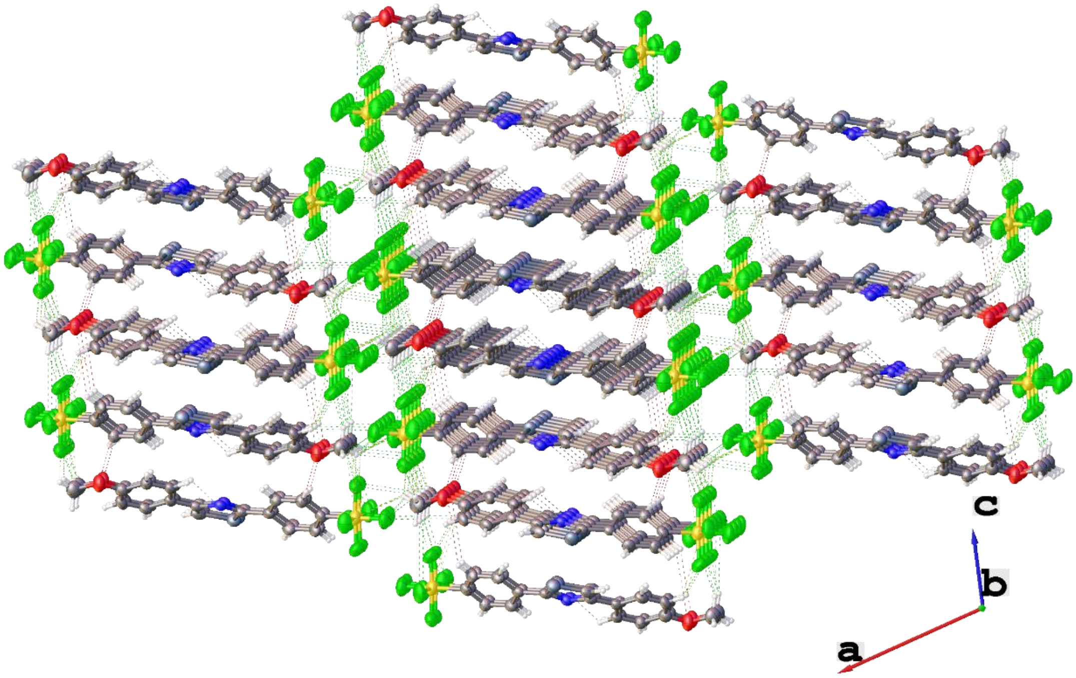


Figure 5-20. View of 3-D packing network shows the strong intermolecular C_{aryl}-H···O, C_{aryl}-H···F(eq) and the weak intermolecular C_{aryl}-H···Se, C_{aryl}-H···S interactions and π-stacking interactions in **5.7**.

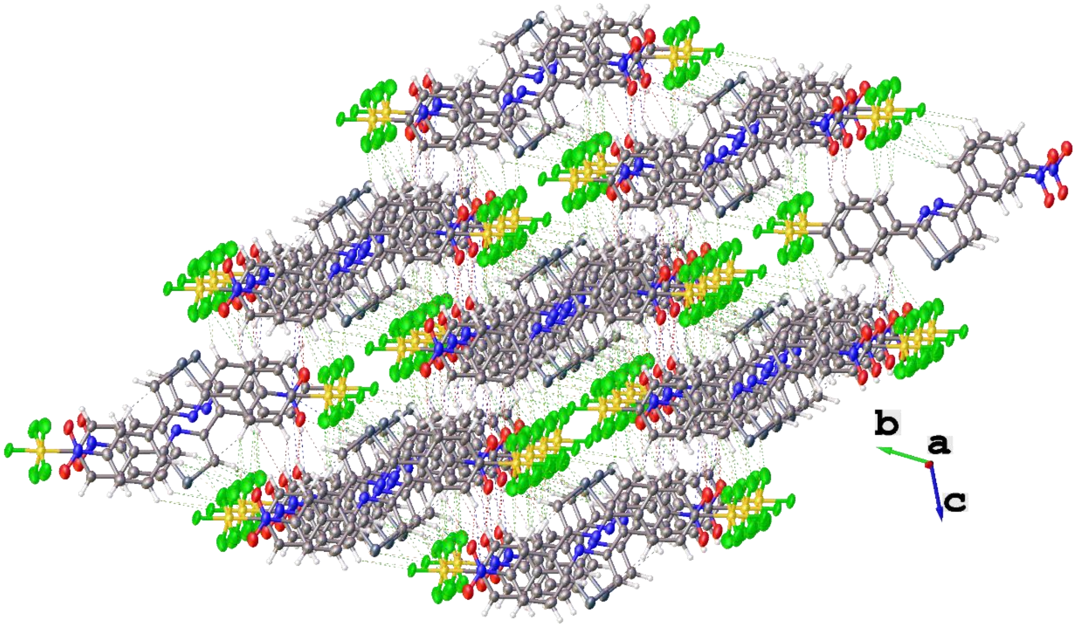


Figure 5-21. View of 3-D packing network shows the intermolecular C_{aryl}-H···Se, C_{aryl}-H···S, C_{aryl}-H···F, C_{aryl}-H···O and C_{aryl}-H···N interactions and π-stacking interactions in **5.8**.

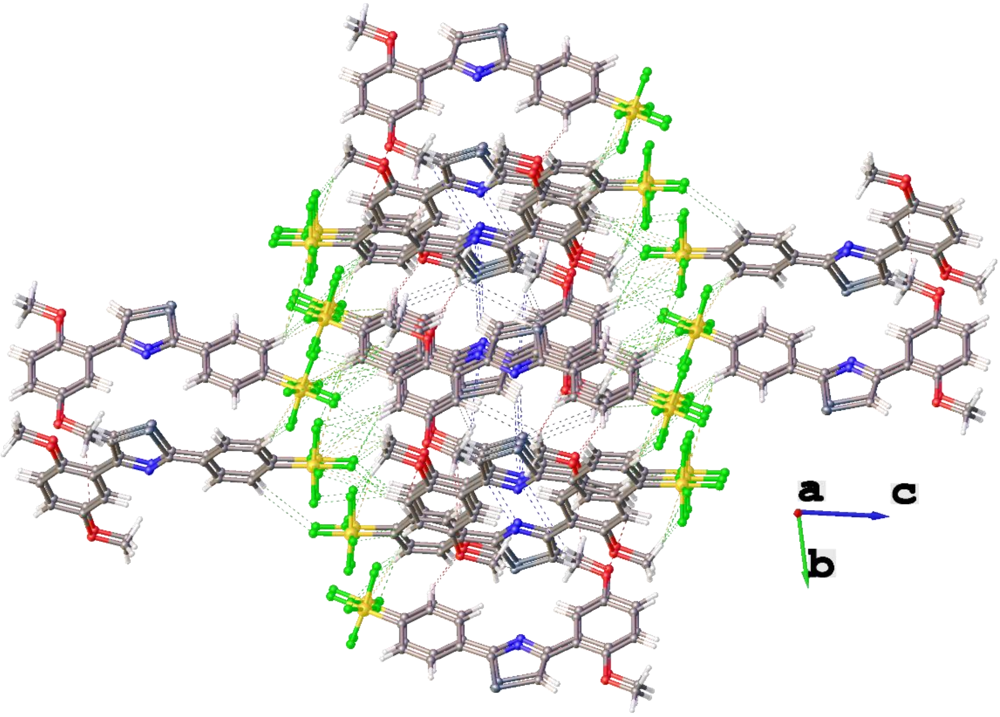
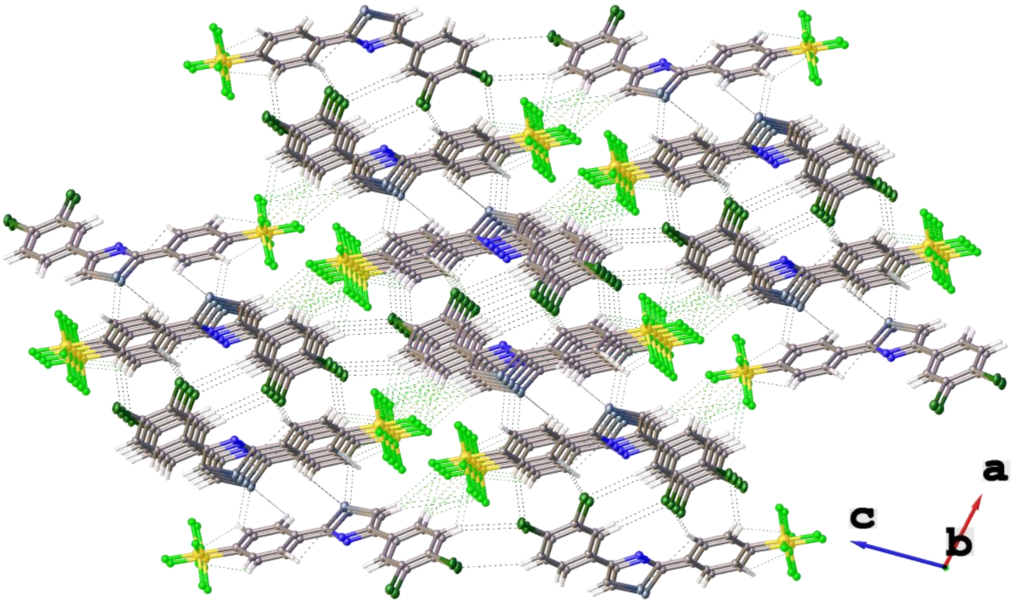


Figure 5-22. A view of 3-D packing network shows the intermolecular C_{aryl}-H···N, C_{aryl}-H···F, C_{aryl}-H···S, C_{aryl}-H···O and C_{aryl}-H···Se interactions and π-stacking interactions in **5.9**.



(d)

Figure 5-23. 3-D packing network shows 'Zigzag chain' polymeric network built up by the intermolecular C_{aryl}-H··Cl and C_{aryl}-H···F interactions in **5.10**.

5.3.3. 2,4-Diaryl-1,3-thiozoles 5.11–5.13

Compounds **5.11**–**5.13** (Figure 5-24) have five-membered N(1)-C(2)-S(3)-C(4)-(5) rings rather than the five-membered N(1)-C(2)-Se(3)-C(4)-(5) rings (Figure 5-9). In this section, the structural similarities and differences between the five-membered N(1)-C(2)-S(3)-C(4)-(5) ring and five-membered N(1)-C(2)-Se(3)-C(4)-(5) ring will be discussed by comparing the N/Se/S-C bond lengths and bond angles, deviation of N/Se/S atom, torsion angles and dihedral angles.

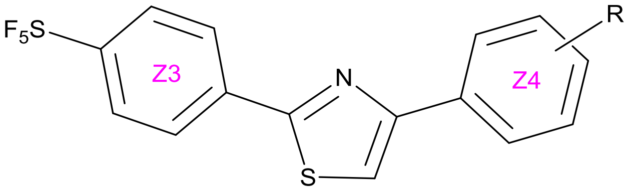


Figure 5-24. Chemical structure of 2,4-diaryl-1,3-thioazoles **5.11**–**5.13**.

Selected bond lengths and angles for **5.11**–**5.13** are listed in Table 5-17. X-ray single crystal structures of **5.11**–**5.13** are shown in Figures 5-25–5-27. The structures of **5.11**–**5.13** have very similar S-F(ax) bond distances [1.585(3) to 1.589(8) Å], S-C bond distances [1.788(8) to 1.815(11) Å], and S-F(eq) bond distances [1.569(5) to 1.608(5) Å] with the average C-S-F(eq) angle of 92.65° and F(ax)-S-F(eq) angle of 87.34°. The angles between the opposite F(eq) atoms range from 174.1(3) to 175.2(4)° and the angles between the adjacent F(eq) atoms range from 88.7(3) to 90.9(3)°, suggesting that in SF_5 group the opposite F(eq) atoms are not collinear, however, the C(9)-S(1)-F(5) angles are nearly 180°.

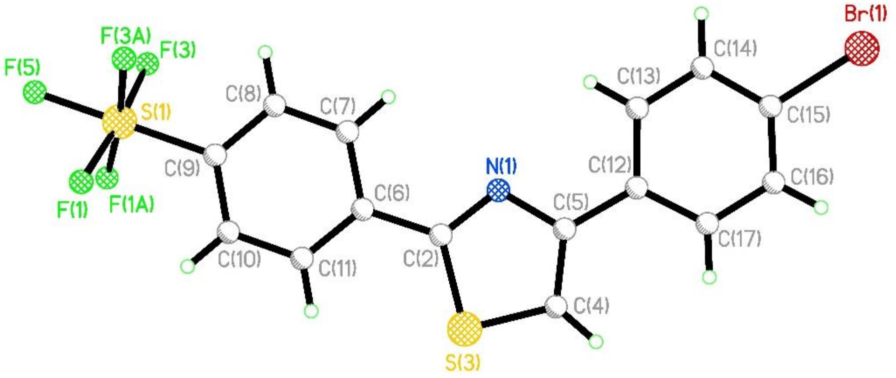


Figure 5-25. X-ray single crystal structure of **5.11**.

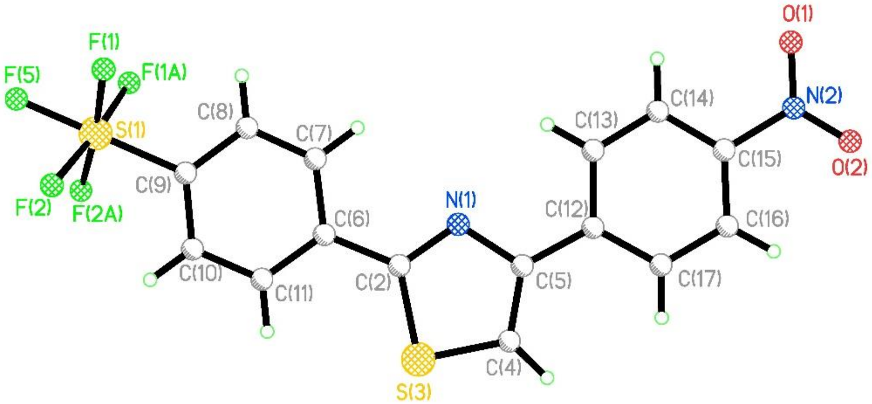


Figure 5-26. X-ray single crystal structure of **5.12**.

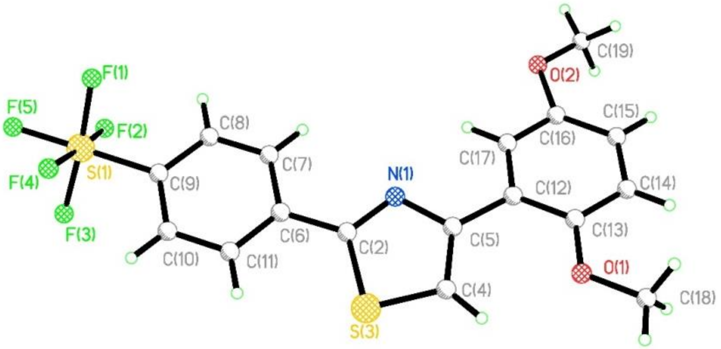


Figure 5-27. X-ray single crystal structure of **5.13**.

The N1-C5 bond distances [1.361(10) to 1.391(14) Å] are longer than the N1-C2 bond distances [1.295(12) - 1.299(13) Å], accompanied by the C-N-C bond angles ranging from 111.3(8) to 112.3(4)° in **5.11**–**5.13**. Compared to **5.4**–**5.10**, the structures of **5.11**–**5.13** have shorter S3-C2 bond distances [1.723(9) to 1.735(10) Å] and shorter S3-C4 bond distances [1.670(9) to 1.701(11) Å] with the bigger C2-S3-C4 angles [89.6(5) to 90.3(5)°]. However, the C4=C5 double bond distances [1.376(7) to 1.395(12) Å] are very similar to that in **5.11**–**5.13**. Compared to the five-membered N(1)-C(2)-Se(3)-C(4)-(5) ring in **5.4**–**5.10**, the five-membered N(1)-C(2)-S(3)-C(4)-(5) ring has shorter S-C bond distances, but there is subtle difference in other bond distances: two S-C bond distances or two N-C bond distances are not identical and not the conventional single bond distances and double bond distance either in **5.11**–**5.13**. The twist angles between two aryl-arm rings and the mean planes of the five-membered rings are approximately to 0° in **5.11** and **5.12**. The five-membered ring possess similar near-planar conformation with S and N atoms deviating from 0 to 0.017(13) Å from the C(2)-C(4)-C(5) mean plane in **5.11**–**5.13** (Table 5-18).

Table 5-17. Selected bond distances (Å) and bond angles (°) in the SF_5 group for **5.11**–**5.13**

	5.11	**5.12**	**5.13**
S(1)-F(5)	1.588(6)	1.585(3)	1.589(8)
S(1)-C(9)	1.788(8)	1.798(4)	1.815(11)
S(1)-F(1)	**1.569(5)**	1.575(3)	1.588(6)
S(1)-F(2)	1.569(5)	1.578(3)	**1.608(5)**
S(1)-F(3)	1.576(6)	1.578(3)	1.596(6)
S(1)-F(4)	1.576(6)	1.575(3)	1.596(6)
C(9)-S(1)-F(5)	179.9(4)	179.7(2)	179.5(4)
F(5)-S(1)-F(1)	86.8(2)	87.70(13)	87.9(4)
F(5)-S(1)-F(2)	86.8(2)	87.10(12)	87.9(4)
F(5)-S(1)-F(3)	87.4(2)	87.10(12)	87.0(4)
F(5)-S(1)-F(4)	87.4(2)	87.70(13)	87.3(4)
C(9)-S(1)-F(1)	93.1(3)	92.49(16)	92.6(4)
C(9)-S(1)-F(2)	**93.1(3)**	92.70(15)	**92.3(4)**
C(9)-S(1)-F(3)	92.7(3)	92.70(15)	92.5(4)
C(9)-S(1)-F(4)	92.7(3)	92.49(16)	92.4(4)
F-S(1)-F*	88.7(3), 90.0(2), 90.7(3), 90.0(2)	89.73(14), 89.50(15), 89.73(14), 90.57(17)	89.6(3), 89.6(3), 89.5(3), 90.9(3)
F-S(1)-F**	174.1(3), 174.1(3)	174.78(14), 174.78(14)	174.9(4), 175.2(4)

*The angles between the adjacent F(eq) atoms; ** The angles between the opposite F(eq) atoms

The details of possible intramolecular interactions in **5.11**–**5.13** are shown in Figure 5-28 (as a representative example for **5.12**) and Table 5-19. The H···N interaction distances [2.531(4) to 2.604(9) Å] involving the Z3 ring are marginally longer than the H···N interaction distances [2.421(4) to 2.511(7) Å] associating with the Z4 ring. The order of H···S3 distance are **5.13** < **5.11** < **5.12**. There are a number of intramolecular C_{aryl}-H···O interactions present in **5.12** and **5.13.** The distances of intramolecular H···O interactions in **5.12** are 2.428(5) and 2.417(6) Å along with the C_{aryl}-H···O angles of 96.6(4) and 96.0(4)° and O-N-C-C torsion angle of 0°. The N-C-C-C and S-C-C-C torsion angles are 0° in both **5.11** and **5.12**. The N-C-C-C torsion angles are also very small [3.3(10) and 6.7(10)°] in **5.13**. The F(eq)-S-C-C torsion angles range from 42.7(6) to 48.1(6)° with the corresponding F atoms deviation distances of 1.042(9) to 1.139(9) Å from the S-aryl plane in **5.11**–**5.13**.

Table 5-18. Selected bond distances (Å) and bond angles (°) in the thiazole ring for **5.11–5.13**

	5.11	**5.12**	**5.13**
Bond lengths			
N1-C5	1.361(10)	1.378(6)	1.391(14)
N1=C2	1.295(12)	1.299(5)	1.299(13)
S3-C2	1.723(9)	1.728(4)	1.735(10)
S3-C4	1.670(9)	1.673(6)	1.701(11)
C4=C5	1.386(13)	1.376(7)	1.395(12)
Bond angles			
C2-N1-C5	111.5(8)	112.3(4)	111.3(8)
C2-S3-C4	90.3(5)	90.1(2)	89.6(5)
Twist angles			
Between Z3 ring and N(1)…C(5) plane	0	0	3.3(3)
Between Z4 ring and N(1)…C(5) plane	0	0	10.5(3)
Deviation distance			
N1…C2-C4-C5	0	0	0.017(13)
S3…C2-C4-C5	0	0	-0.012(15)

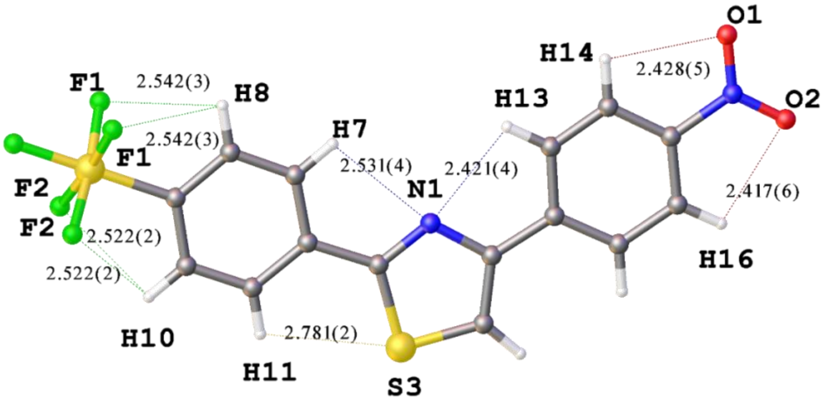


Figure 5-28. A representative 3-D diagram shows the intramolecular C$_{aryl}$-H···S, C$_{aryl}$-H···N, C$_{aryl}$-H···O and C$_{aryl}$-H···F interactions in **5.12**.

The supramolecular aggregation arrangements in structures of **5.11–5.13** are created by multiple weak intermolecular C$_{aryl}$-H···N/S/F interactions and π-stacking interactions. The multiple intermolecular C$_{aryl}$-H···O interactions were also found in **5.12** and **5.13**.

The packing networks for **5.11** and **5.12** are very similar as shown in Figure 5-29 and 5-30. The intermolecular C_{aryl}-H···F [H···F distances from 2.575(5) to 3.752(6) Å], C_{aryl}-H···Br [H···Br distances from 2.8411(13) to 3.1158(15) Å] and C_{aryl}-H···S [H···S distance of 4.1157(15) Å] interactions create a complex 3-D network in **5.11**. In the case of **5.12**, the packing network is formed by the weak intermolecular C_{aryl}-H···N [H···N distances of 3.515(6) and 3.334(6) Å], C_{aryl}-H···S [H···S distances from 3.272(2) to 4.131(2) Å], and multiple C_{aryl}-H···F [H···F distances from 2.536(3) to 3.475(3) Å] and C-H···O [H···O distances from 2.291(5) to 3.745(6) Å] interactions. In **5.13**, the packing molecules are also linked by the intermolecular C_{aryl}-H···S, C_{aryl}-H···F, C_{aryl}-H···N and C_{aryl}-H···O interactions (Figure 5-31).

There are significant intermolecular interactions between the layers in the packing network. The arrangements of **5.11** and **5.12** are very similar, and there are four sets of π-stacking interactions with the same angle of 0.000° and close centroid-centroid distances [3.669 Å in **5.11** and 3.641 Å in **5.12**] and similar shift distance [1.382 Å in **5.11** and 1.487 Å in **5.12**]. The π-stacking interaction between the aryl rings in **5.9** is not parallel, having a centroid-centroid distance of 3.793 Å with an angle of 4.082° and shift distance of 1.441 Å. In the case of **5.13**, a centroid-centroid distance of 3.897 Å with an angle of 10.003° and shift distance of 1.487 Å is observed.

Table 5-19. Selected intramolecular distances (Å) and angles (°) for **5.11–5.13**

	5.11	**5.12**	**5.13**
Intramolecular interaction distances (Å)			
H···S3	2.744(3)	2.781(2)	2.678(3)
H···N1[c]	2.556(6)	2.531(4)	2.604(9)
H···N1[d]	2.511(7)	2.421(4)	2.469(8)
H···O		2.428(5), 2.417(6)	2.231(8)
H···F1	2.505(4)	2.542(3)	2.544(7)
H···F2	2.505(4)	2.522(2)	2.545(7)
H···F3	2.549(4)	2.522(2)	2.541(7)
H···F4	2.549(4)	2.542(3)	2.526((7)
Intramolecular interaction angles (°)			
$\mathrm{C_{aryl}}$-H···Se3/S3	106.4(5)	106.4(3)	107.7(7)
$\mathrm{C_{aryl}}$-H···N1[c]	99.3(6)	100.0(3)	98.4(6)
$\mathrm{C_{aryl}}$-H···N1[d]	101.2(6)	102.2(3)	103.9(6)
$\mathrm{C_{aryl}}$-H···O		96.6(4), 96.0(4)	116.1(6)
$\mathrm{C_{aryl}}$-H···F1	96.2(5)	95.2(3)	96.6(7)
$\mathrm{C_{aryl}}$-H···F2	96.2(5)	95.8(3)	96.8(7)
$\mathrm{C_{aryl}}$-H···F3	95.4(5)	95.8(3)	96.5(7)
$\mathrm{C_{aryl}}$-H···F4	95.4(5)	95.2(3)	96.5(6)
Torsion angles (°)			
S3-C2-C6-C11	-0,00(13)	0.0(6)	3.1(9)
N1-C2-C6-C7	0.00(15)	0	3.3(10)
N1-C5-C12-C13	0.00(2)	0	-6.7(10)
O-N-C-C		0, -0.0(5)	
F1-S-C-C	44.45(17)	-45.34(11)	-44.7(5)
F2-S-C-C	-44.45(17)	44.82(10)	45.0(6)
F3-S-C-C	45.38(19)	-44.82(10)	-45.5(5)
F4-S-C-C	-45.38(19)	45.34(11)	44.1(5)
Deviation distance (Å)			
F1…S-aryl mean plane	1.097(5)	1.119(3)	-1.127(8)
F2…S-aryl mean plane	-1.097(5)	1.111(3)	1.125(8)
F3…S-aryl mean plane	-1.121(6)	-1.111(3)	1.130(8)
F4…S-aryl mean plane	1.121(6)	-1.119(3)	-1.116(8)

[c] Possible intramolecular interaction between N atom and H atom attached to Z3 ring

[d] Possible intramolecular interaction between N atom and H atom attached to Z4 ring

Table 5-20. Selected intermolecular distances (Å) and angles (°) for **5.11–5.13**

	5.11	**5.12**	**5.13**
Intermolecular interaction distances (Å)			
H···S	3.397(3), 3.743(3)	3.272(2)	3.264(4)
H···F	2.575(5), 2.754(5), 2.877(5)	2.536(3), 2.725(3)	2.491(6), 2.743(6)
H···O		2.291(5), 2.725(6)	2.993(7)
H···N		3.334(6)	3.127(8)
H···Br	2.8411(13)		
Intermolecular interaction angles (°)			
C-H···S	168.6(5), 165.7(5)	168.6(3)	153.5(6)
C-H···F	2.575(5), 2.754(5)	154.5(3), 123.6(7)	149.3(6), 163.5(6)
C-H···O		136.8(4), 141.5(3)	129.3(6)
C-H···N		147.9(4)	146.6(6)
C-H···Br	156.8(6)		

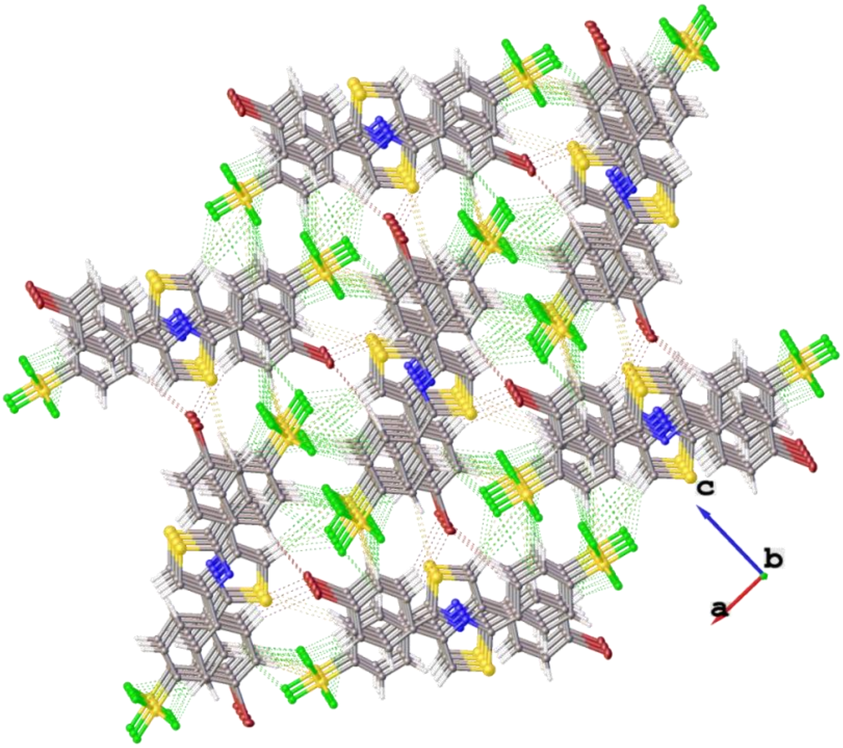


Figure 5-29. 3-D packing network shows ‘Zigzag chain’ polymeric network built up by the intermolecular C_{aryl}-H···F, C_{aryl}-H···Br interactions and π-stacking interactions in **5.11**.

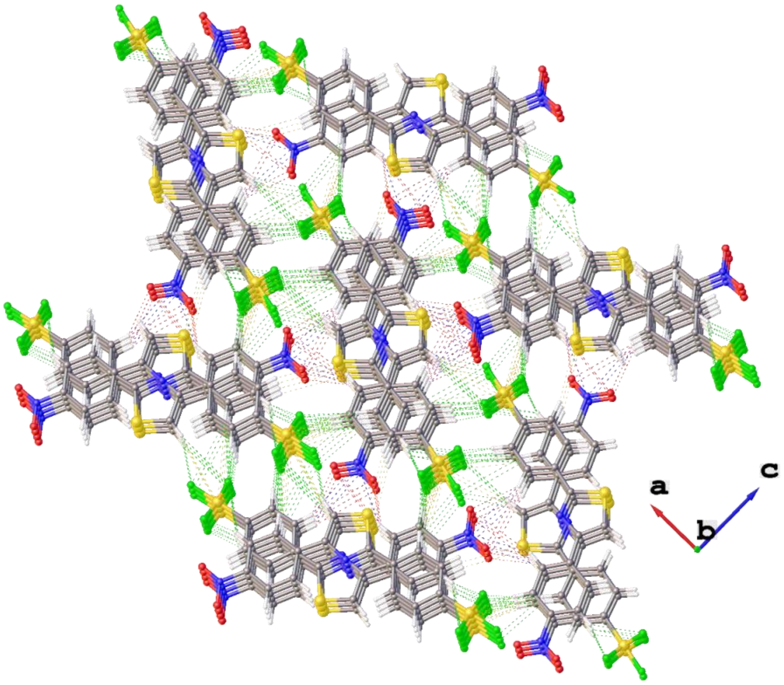


Figure 5-30. 3-D packing network shows the polymeric network built up by the intermolecular C_{aryl}-H···F/O/S/N interactions and π-stacking interactions in **5.12**.

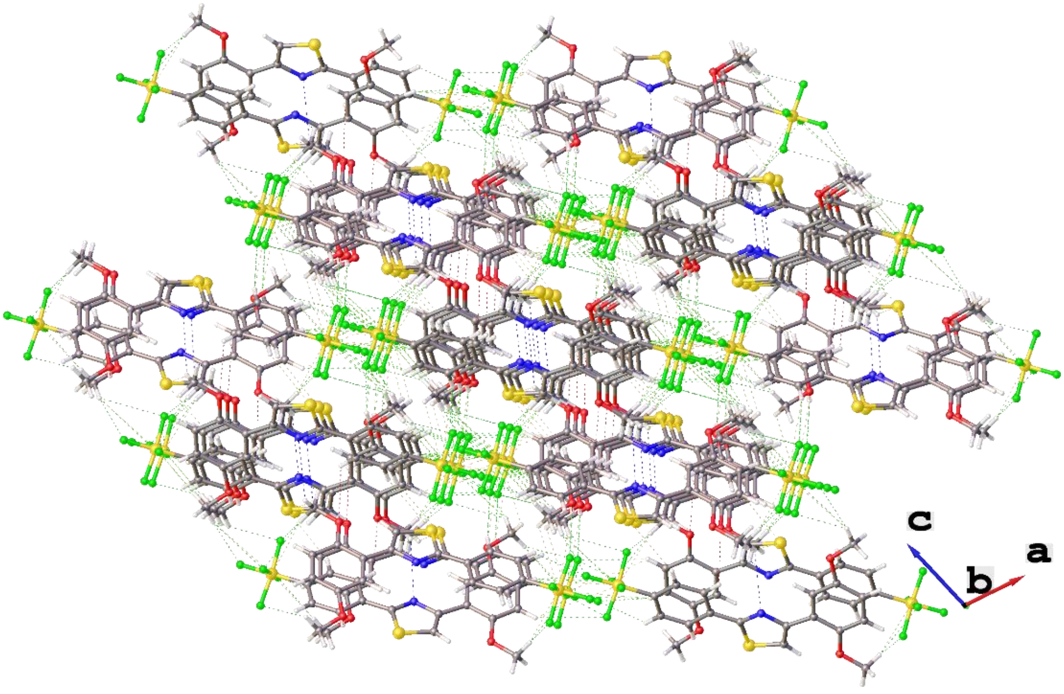


Figure 5-31. A view of 3-D packing network shows the intermolecular C_{aryl}-H···N, C_{aryl}-H···F, C_{aryl}-H···S, C_{aryl}-H···O interactions and π-stacking interactions in **5.13**.

5.4. Conclusion

The crystal structures reveal that compounds **5-4**–**5-13** consist of two important motifs: 2,4-diaryl-1,3-chalcogen azole rings and pentafluorosulfuranyl (SF_5) groups. These compounds are structurally similar though there are some differences from each other attributed to the different substituents. The SF_5 group is structurally stable and the S-F(ax) bond lengths in these compounds are all very similar [1.574(7) to 1.593(4) Å] along with similar C-S-F(ax) bond angles [179.34(15) to 179.9(4)°]. In addition, the angle of two adjacent S-F(eq) is approximate 90°, and the S-F(eq) bond lengths are slightly different [1.558(5) to 1.609(5)] in the structures of **5-1**–**5-13**. The data are comparable with the structures discussed in Chapter 3.

The N-C bond distances in **5.4**–**5.13** range from 1.290(5) to 1.401(9) Å with the C-N-C bond angles of 111.3(8) to 114.6(6)°. The Se-C bond distances in **5.4**–**5.10** [1.820(6) to 1.918(7) Å] are significantly longer than the S-C bond distances in **5.11**–**5.13** [1.670(9) to 1.735(10) Å], however, the C-Se-C bond angles [84.0(3) to 84.9(2)°] are considerably smaller than the C-S-C bond angles [89.6(5) to 90.3(5)°], indicating the effect of two different elements of S and Se in the five-membered rings. The bond distances in the chalcogen azole ring are not typical single bond distance and double bond distance, suggesting the somewhat delocalization of π-electrons and the lone pair electrons within the five-membered ring. N atom and Se/S atom deviating slightly from the C(2)-C(4)-C(5) mean plane [less than 0.037(18) Å] in **5.4**–**5.10** proved that the five-membered rings are approximate flat. The twist angles between the aryl planes and the five-membered planes in compounds **5.4**, **5.6** and **5.9**–**5.13** are smaller than that in **5.5**, **5.7** and **5.8**.

Selenamide **5.1**, thiamides **5.2** and **5.3**, 1,3-selenazoles **5.4**–**5.10** and 1,3-thiazoles **5.11**–**5.13** display a diverse range of molecular configuration and intramolecular/intermolecular interactions information. Especially, from the SF_5 groups in the structures of **5.1**–**5.13**, the distances of F(eq) and neighbouring H_{aryl} intramolecular interactions [2.477(4) to 2.637(4) Å] are falling in the sum of Van der Walls Radii [2.55 Å]. The intramolecular $H_{aryl}\cdots F(eq)$ interaction may keep the stability of equatorial fluorine atoms. The intramolecular C-H···N/Se/S interactions also exit in **5.4**–**5.13**, and compared to other compounds, there are some slightly differences in the intramolecular C-H···N/Se/S interactions in **5.11**–**5.13** because the selenium atom in the 1,3-selenazole ring is replaced by a sulfur atom.

Packing of the molecules is directed by soft hydrogen bonding interactions, additionally, weak π-stacking interactions exist in some 3-D supramolecular aggregation arrangements. These intermolecular interactions and π-stacking interactions can play an important role in stabilizing the crossed-layer packing network in the solid state.

5.5. References

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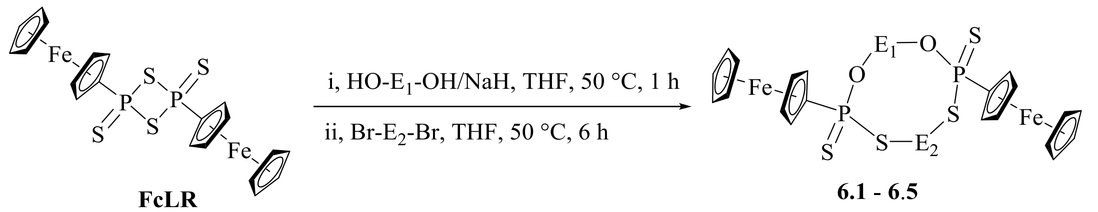
CHAPTER 6

STRUCTUAL STUDIES OF ORGANIC PHOSPHORUS-CHALCOGEN MACROCYCLES INCORPORATING DOUBLE OP(S)SC$_n$ OR OP(Se)SeC$_n$ SCAFFOLDS

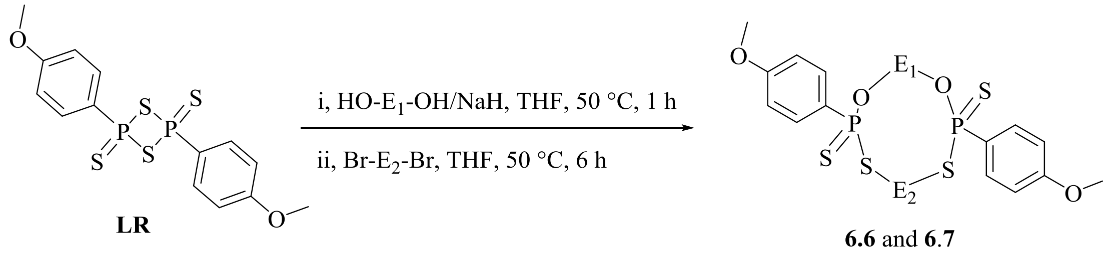
6.1. Introduction

Macrocyclic compounds are widely used in the fields of drug development, material science, and supramolecular chemistry because of their widespread occurrence in nature and intrinsic three-dimensional structures.[1,2] Herein, we will present and study a series of structures which have macro-heterocycles incorporating two phosphorus atoms and two chalcogen atoms and two oxygen atoms [double OP(S)SCn or OP(Se)SeCn scaffolds]. However, the synthesis and structural features of the macrocycles containing bigger than ten-membered ring systems and double OP(S)SCn or OP(Se)SeCn scaffolds are rarely explored.[3] Nine macrocycles were obtained by the three-component condensation reactions of four-membered chalcogenation reagents: 2,4-diferrocenyl-1,3,2,4-diathiadiphosphetane 2,4-disulfide (a ferrocene analogue of Lawesson's Reagent, **FcLR)** or 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide **(**Lawesson's Reagent, **LR**), or 2,4-diphenyl-1,3,2,4-diselenadiphosphetane 2,4-diselenide (Woollins' Reagent, **WR**),[4] disodium alkenyl-diols, and dihalogenated alkanes (Schemes 6-1–6-3). The chemical structures of compounds **6.1**–**6.9** are shown in Figure 6-1. All crystals suitable for X-ray crystallographic studies were obtained at room temperature from the diffusion of hexane into a dichloromethane solution. These macrocycles have close structural similarities along with similar intramolecular and intermolecular interactions or close contacts such as the weak intramolecular/intermolecular C-H···S$_{exo}$, C-H···S$_{endo}$, C-H···Se$_{exo}$, C-H···Se$_{endo}$ and C-H···O interactions; however, the combination of interactions differs in some cases resulting in different packing arrangements.



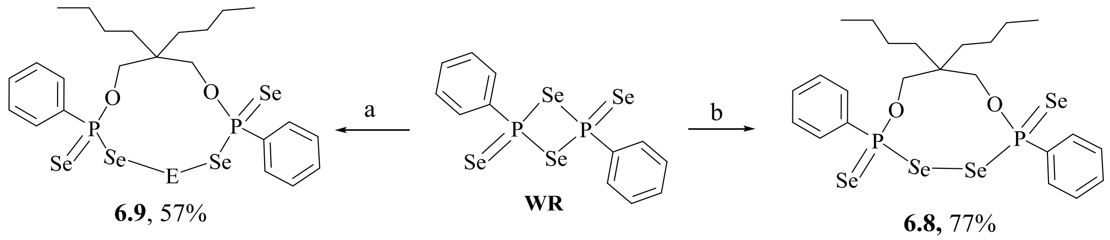
6.1. $E_1 = CH_2CH_2CH_2$, $E_2 =$ *o*-$CH_2C_6H_4CH_2$, 92%
6.2. $E_1 = CH_2CH_2CH_2$, $E_2 =$ *m*-$CH_2C_6H_4CH_2$, 43%
6.3. $E_1 = CH_2CH_2$, $E_2 =$ *p*-$CH_2C_6H_4CH_2$, 54%
6.4. $E_1 = CH(Ph)CH(Ph)$, $E_2 =$ *o*-$CH_2C_6H_4CH_2$, 68%
6.5. $E_1 = CH(Ph)CH(Ph)$, $E_2 =$ *m*-$CH_2C_6H_4CH_2$, 55%

Scheme 6-1. Synthesis of macrocycles **6.1–6.5**.

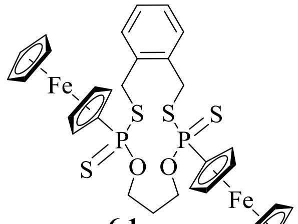


6.6. $E_1 = CH_2CCCH_2$, $E_2 =$ *p*-$CH_2C_6H_4CH_2$, 52%
6.7. $E_1 = CH_2(^nBu)_2CH_2$, $E_2 =$ *o*-$CH_2C_6H_4CH_2$, 62%

Scheme 6-2. Synthesis of macroheterocycles **6.6–6.7**.

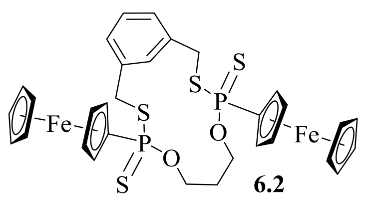


Scheme 6-3. Synthesis of macrocycle **6.8** and **6.9** [a, $HOCH_2C(^nBu)_2CH_2OH$/NaH, THF, 50℃, 1 h / *o*-$BrCH_2C_6H_4CH_2Br$, 50℃, 6h; b, $HOCH_2C(^nBu)_2CH_2OH$/NaH, THF, 50℃, 1h / BrCH(Ph)CH(Ph)Br, 50℃, 6 h].



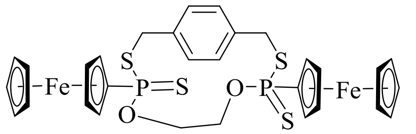
6.1

3,9-Diferrocenyl-1,6,7,11-tetrahydro-5H-benzo[e][1,10]dioxa[3,8]dithia[2,9]diphosphacyclotridecine 3,9-disulfide



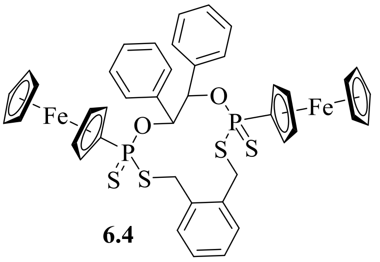
6.2

4,10-Diferrocenyl-5,9-dioxa-3,11-dithia-4,10-diphospha-1(1,3)-benzenacyclododecaphane 4,10-disulfide



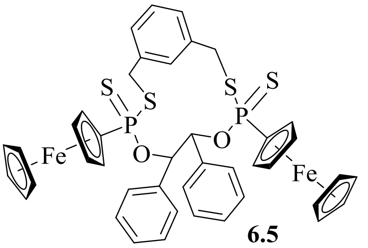
6.3

4,9-Diferrocenyl-5,8-dioxa-3,10-dithia-4,9-diphospha-1(1,4)-benzenacycloundecaphane 4,9-disulfide



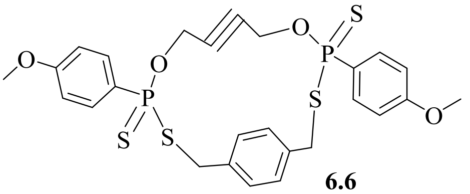
6.4

3,8-Dimethyl-5,6-diphenyl-1,5,6,10-tetrahydrobenzo[e][1,10]dioxa[3,8]dithia[2,9]diphosphacyclododecine 3,8-disulfide



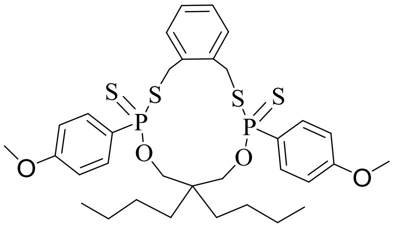
6.5

4,9-Diferrocenyl-6,7-diphenyl-5,8-dioxa-3,10-dithia-4,9-diphospha-1(1,3)-benzenacycloundecaphane 4,9-disulfide



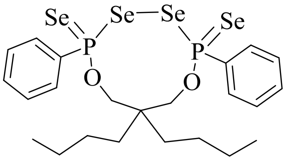
6.6

4,11-Bis(4-methoxyphenyl)-5,10-dioxa-3,12-dithia-4,11-diphospha-1(1,4)-benzenacyclotridecaphan-7-yne 4,11-disulfide



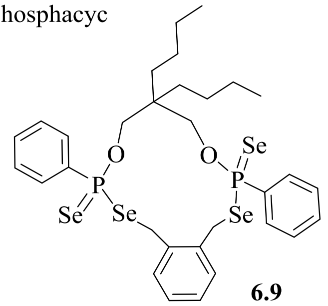
6.7

6,6-Dibutyl-3,9-bis(4-methoxyphenyl)-1,6,7,11-tetrahydro-5H-benzo[e][1,10]dioxa[3,8]dithia[2,9]diphosphacyclotridecine 3,9-disulfide



6.8

8,8-Dibutyl-2,5-diphenyl-1,6,3,4,2,5-dioxadiselenadiphosphonane 2,5-diselenide



6.9

6,6-Dibutyl-3,9-diphenyl-1,6,7,11-tetrahydro-5H-benzo[e][1,10]dioxa[3,8]diselena[2,9]diphosphacyclotridecine 3,9-diselenide

Figure 6-1. View of the chemical structures of macrocycles **6.1**–**6.9**.

6.2. Crystal Structure Data

Data were collected -180℃ using on a Rigaku Mercury70 diffractometer Mo-Kα radiation for **6.1** and **6.3**, and at -148℃ on a Rigaku Saturn70 diffractometer Mo-Kα radiation (λ = 0.7173 Å) for **6.2** and **6.4**–**6.9**. The unit cell and refinement parameters for compounds **6.1**–**6.9** are listed in Tables 6.1 and 6.2. Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz, polarization and absorption effects. Structures were solved by direct methods and refined by full-matrix least-squares again F^2 (SHELXL)[5] using Crystal Structure.[6] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries.

The structures of compounds **6.1**–**6.9** have a single molecule of the compound in each asymmetric unit. Compounds **6.1**, **6.2**, **6.7** and **6.9** crystallize in a monoclinic crystal system with the corresponding R_1 values of 0.0730, 0.0757, 0.0699 and 0.0840, compounds **6.3**, **6.5** and **6.8** in a triclinic crystal system with the respective R_1 values of 0.0728, 0.0604 and 0.0943, and **6.4** and **6.6** in an orthorhombic crystal system with R_1 values of 0.0736 and 0.0897. All data are listed in Tables 6-1–6-3.

Table 6-1. Relevant crystal data and refinement parameters for compounds **6.1**–**6.3**

Experimental details	**6.1**	**6.2**	**6.3**
Empirical formula	$C_{31}H_{32}Fe_2O_2P_2S_4$	$C_{34}H_{38}Fe_2O_3P_2S_4$	$C_{30}H_{30}Fe_2O_2P_2S_4$
Formula weight	738.47	796.55	724.45
Temperature (℃)	-180	-148	-180
Crystal color, habit	Yellow, chip	Yellow, chip	Yellow, platelet
Crystal dimensions (mm^3)	0.12×0.06×0.06	0.12×0.09×0.06	0.12×0.06×0.03
Crystal system	Monoclinic	Monoclinic	Triclinic
Lattice parameters	a = 28.792(9) Å	a = 14.260(3) Å	a = 10.079(2) Å
	b = 7.574(2) Å	b = 10.367(2) Å	b = 10.892(3) Å
	c = 14.883(5) Å	c = 24.945(6) Å	c = 14.675(3) Å
	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$	$\alpha = 79.83(2)^{\circ}$
	$\beta = 94.755(8)\ ^{\circ}$	$\beta = 105.930(6)^{\circ}$	$\beta = 72.080(18)^{\circ}$
	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 86.68(3)^{\circ}$
Volume (Å^3)	3234.5(17)	3545.9(14)	1508.8(7)
Space group	$P2_1/c$	$P2_1/c$	*P-1*
Z value	4	4	2
Dcalc (g/cm^3)	1.516	1.492	1.594
$F_{(000)}$	1520.00	1648.00	744.00
μ(MoKα) (cm^{-1})	12.813	11.768	13.717
Diffractometer	Mercury70	Saturn70	Mercury70
No. of reflections measured	16283	26065	9694
Unique	5544	6212	5134
R_{int}	0.1390	0.1341	0.0975
Friedel pairs	-	-	-
Min. and max. transmissions	0.273, 0.926	0.585, 0.932	0.393, 0.960
No. of observations (All reflections)	5544	6212	5134
No. of variables	370	406	361
Reflection/parameter ratio	14.98	15.30	14.22
Residuals: R_1 (I>2.00σ(I))	0.0730	0.0757	0.0728
Residuals: R (all reflections)	0.1251	0.1288	0.1391
Residuals: wR_2 (all reflections)	0.1717	0.1377	0.2318
Goodness of fit indicator	0.915	1.057	0.876
Flack parameter	-	-	-
Maximum peak in final diff. map (e$^-$/Å^3)	0.90	0.51	0.82
Minimum peak in final diff. map (e$^-$/Å^3)	-0.60	-0.45	-0.65

Table 6-2. Relevant crystal data and refinement parameters for compounds **6.4–6.6**

Experimental details	**6.4**	**6.5**	**6.6**
Empirical formula	$C_{42}H_{38}Fe_2O_2P_2S_4$	$C_{42}H_{38}Fe_2O_2P_2S_4$	$C_{26}H_{26}O_4P_2S_4$
Formula weight	876.64	876.64	592.68
Temperature (℃)	-148	-148	-148
Crystal color, habit	Yellow, chip	Yellow, platelet	Colorless, chip
Crystal dimensions (mm^3)	0.21×0.09×0.03	0.12×0.06×0.03	0.06×0.06×0.06
Crystal system	Orthorhombic	Triclinic	Orthorhombic
Lattice parameters	a = 12.4114(17) Å	a = 10.0572(13) Å	a = 15.528(5) Å
	b = 22.626(3) Å	b = 12.698(2) Å	b = 25.426(8) Å
	c = 28.013(3) Å	c = 16.365(2) Å	c = 7.073(2) Å
	$\alpha = 90^{o}$	$\alpha = 83.638(16)^{o}$	$\alpha = 90^{o}$
	$\beta = 90^{o}$	$\beta = 74.068(16)^{o}$	$\beta = 90^{o}$
	$\gamma = 90^{o}$	$\gamma = 73.326(14)^{o}$	$\gamma = 90^{o}$
Volume ($Å^3$)	7866.7(18)	1924.0(5)	2792.4(15)
Space group	*Pbca*	*P-1*	$Pna2_1$
Z value	8	2	4
Dcalc (g/cm^3)	1.480	1.513	1.410
$F_{(000)}$	3616.00	904.00	1232.00
μ(MoKα) (cm^{-1})	10.669	10.906	4.858
Diffractometer	Saturn70	Saturn70	Saturn70
No. of reflections measured	57019	14862	20858
Unique	6894	6713	4811
R_{int}	0.0836	0.0763	0.1244
Friedel pairs	-	-	2131
Min. and max. transmissions	0.693, 0.969	0.744, 0.968	0.719, 0.971
No. of observations (All reflections)	6894	6713	4811
No. of variables	469	469	325
Reflection/parameter ratio	14.70	14.31	14.80
Residuals: R_1 (I>2.00σ(I))	0.0736	0.0604	0.0897
Residuals: R (all reflections)	0.0829	0.0979	0.1131
Residuals: wR_2 (all reflections)	0.1714	0.1269	0.1489
Goodness of fit indicator	1.261	1.009	1.177
Flack parameter	-	-	0.08(17)
Maximum peak in final diff. map ($e^-/Å^3$)	1.21	0.52	0.40
Minimum peak in final diff. map ($e^-/Å^3$)	-0.42	-0.51	-0.38

Table 6-3. Relevant crystal data and refinement parameters for compounds **6.7**–**6.9**

Experimental details	**6.7**	**6.8**	**6.9**
Empirical formula	$C_{33}H_{44}O_4P_2S_4$	$C_{23}H_{32}O_2P_2Se_4$	$C_{31}H_{40}O_2P_2Se_4$
Formula weight	694.90	718.29	822.44
Temperature (℃)	-148	-148	-148
Crystal color, habit	Colorless, chip	Yellow, platelet	Colorless, platelet
Crystal dimensions (mm^3)	0.15×0.06×0.06	0.15×0.06×0.03	0.15×0.06×0.03
Crystal system	Monoclinic	Triclinic	Monoclinic
Lattice parameters	a = 25.103(11) Å	a = 9.357(4) Å	a = 29.933(9) Å
	b = 13.921(6) Å	b = 12.332(4) Å	b = 9.062(2) Å
	c = 10.351(5) Å	c = 13.609(4) Å	c = 24.805(7) Å
	$\alpha = 90^{o}$	$\alpha = 116.45(2)^{o}$	$\alpha = 90^{o}$
	$\beta = 95.719(9)^{o}$	$\beta = 95.79(4)^{o}$	$\beta = 98.190(8)^{o}$
	$\gamma = 90^{o}$	$\gamma = 93.31(3)^{o}$	$\gamma = 90^{o}$
Volume ($Å^3$)	3599(3)	1389.4(9)	6660(3)
Space group	*C2/c*	*P-1*	*C2/c*
Z value	4	2	8
Dcalc (g/cm^3)	1.282	1.717	1.640
$F_{(000)}$	1472.00	704.00	3264.00
μ(MoKα) (cm^{-1})	3.871	54.147	45.301
Diffractometer	Saturn70	Saturn70	Saturn70
No. of reflections measured	13723	10673	25008
Unique	3156	4848	5845
R_{int}	0.1035	0.0759	0.1048
Friedel pairs	-	-	-
Min. and max. transmissions	0.593, 0.977	0.477, 0.850	0.576, 0.873
No. of observations (All reflections)	3156	4848	5845
No. of variables	195	280	352
Reflection/parameter ratio	16.18	17.31	16.61
Residuals: R_1 (I>2.00σ(I))	0.0699	0.0943	0.0840
Residuals: R (all reflections)	0.0928	0.1272	0.1100
Residuals: wR_2 (all reflections)	0.1994	0.2675	0.2190
Goodness of fit indicator	1.122	1.146	1.163
Flack parameter	-	-	-
Maximum peak in final diff. map ($e^-/Å^3$)	0.32	0.95	0.89
Minimum peak in final diff. map ($e^-/Å^3$)	-0.40	-0.84	-0.78

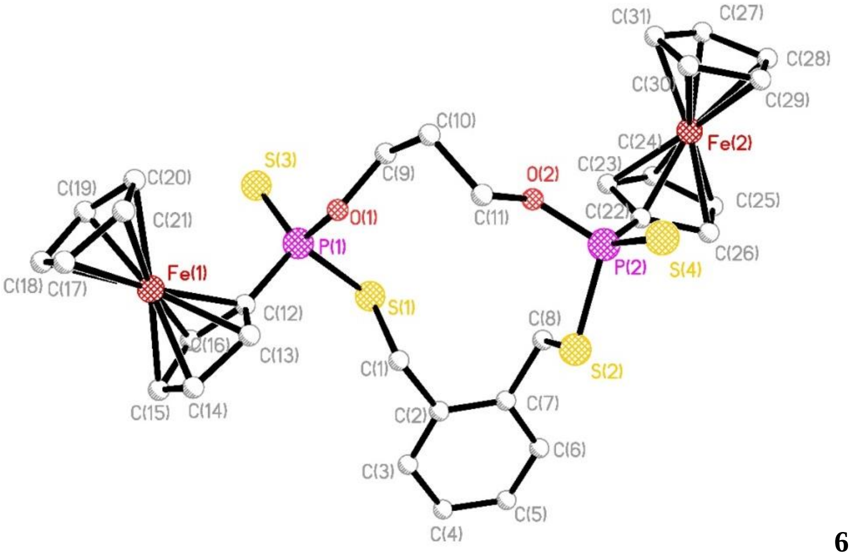
6.3. X-ray Structure Analysis

All structures have a single molecule of the compound in the asymmetric unit. The space groups are *$P2_1/c$* for **6.1** and **6.2**, *P-1* for **6.3**, **6.5** and **6.8**, *Pbca* for **6.4**, *$Pna2_1$* for **6.6**, and *C2/c* for **6.7** and **6.9**. There are two 'outside' ferrocenyl rings attached to two phosphorus atoms in **6.1**–**6.5**, and there are two aryl groups instead of the ferrocenyl groups in **6.6**–**6.9**. Two phosphorus atoms in **6.1**–**6.9** are potentially stereogenic centres, thus, macrocycles **6.1**–**6.9** might be stereotopic with (*R*,*R*), (*S*,*S*), (*S*,*R*) and (*R*,*S*) stereoisomers possible, in fact, a pair of stereoisomers are observed with low diastereoselectivity on the basis of ^{31}P NMR spectra. However, only one of two stereoisomers is obtained and confirmed by single crystallography for macrocycles **6.1**–**6.9**, namely, *SS* stereoisomer for **6.1**, **6.6** and **6.7**; *RR* stereoisomer for **6.2** and **6.8** and *SR* stereoisomer for **6.4**, **6.3**, **6.5** and **6.9**. The inward hetero atoms (S/Se, P, O) are in '*zigzag*' position, suggesting high strains existing in these macrocyclic rings. The geometry around P(1) and P(2) is nearly distorted tetrahedral, and the multi-staged or multi-sheeted network structures are formed by some weak intermolecular C-H···O and C-H···S/Se interactions.

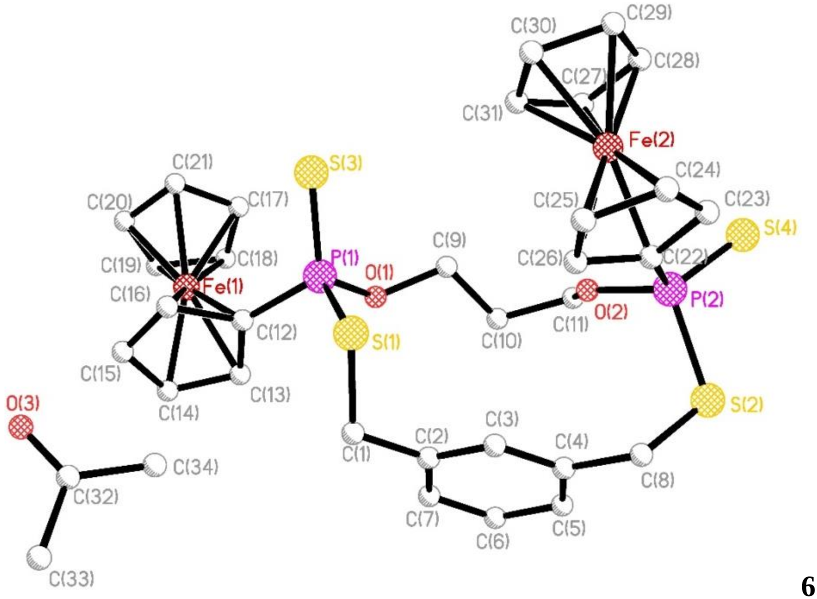
6.3.1. Macrocycles with Two Ferrocene Rings

The data for the structures of compounds **6.1**–**6.5** are listed in Table 6-4, and the X-ray single crystal structures of **6.1**–**6.5** are in Figure 6-2. The X-ray structures confirm the formation of twelve- to fourteen-membered rings in **6.1**–**6.5**. The macrocyclic frameworks are highly puckered with two ferrocene rings on phosphorus atoms on opposite sides of the macro-heterocyclic ring. In these structures, two endocyclic sulfur atoms and two oxygen atoms are in a *trans* orientation, and two exocyclic sulfur atoms are in *trans* orientation as well. The geometry around P(1) and P(2) is distorted tetrahedral, and the P-S single bonds and P=S double bonds are typical of the P(=S)S moiety showing partial double-bond character and resonance delocalization.[7-10] The P-S single bonds are in the range of 2.077(2) to 2.1011(19) Å and P=S double bonds are in the range of 1.9217(18) to 1.936(3) Å similar to that in acyclic structures containing the P-S-S-P linkage. The S(1)-P(1)-S(3)) and S(2)-P(2)-S(4) bond angles are very similar in **6.1** and **6.2** with two similar single bond distances and two similar double bond distances. However, in the cases of **6.3**–**6.5**, these angles are slightly different [S(1)-P(1)-S(3) and S(2)-P(2)-S(4) angles of

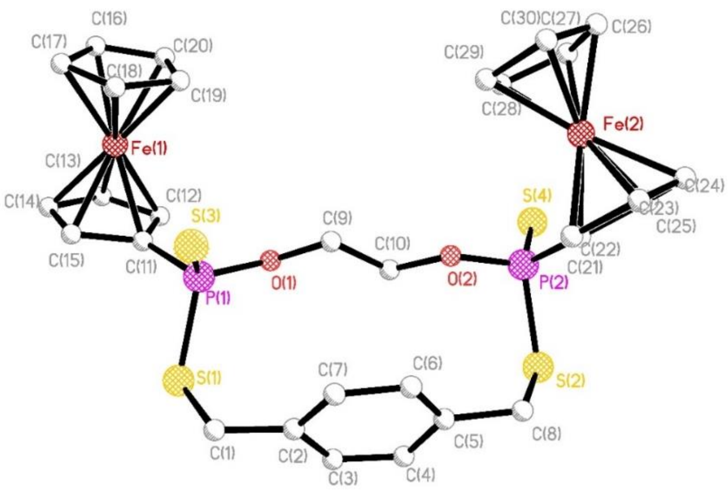
114.38(15) and 107.92(14)° in **6.3**; S(1)-P(1)-S(3) and S(2)-P(2)-S(4) angles of 117.66(9) and 107.45(9)° for **6.4**; S(1)-P(1)-S(3) and S(2)-P(2)-S(4) angles of 113.48(8)° and 115.62(9)° in **6.5**]. The P-S single bond distances are from 2.090(2) to 2.097(3) Å and the P-S double bond distances are 1.926(2) to 1.936(3) Å with S(1)-P(1)-S(3) and S(2)-P(2)-S(4) angles of 107.76(12) and 107.70(12)° in **6.1**, 105.94(10) and 105.47(12)° in **6.2**, respectively. The P-O bond lengths are between 1.592(5) and 1.621(4) Å with the two similar S-P-O bond angles from 106.31(13) to 107.1(3)° in **6.3** and **6.5**, and two different S-P-O bond angles from 99.11(15) to 108.10(17)° for other structures.



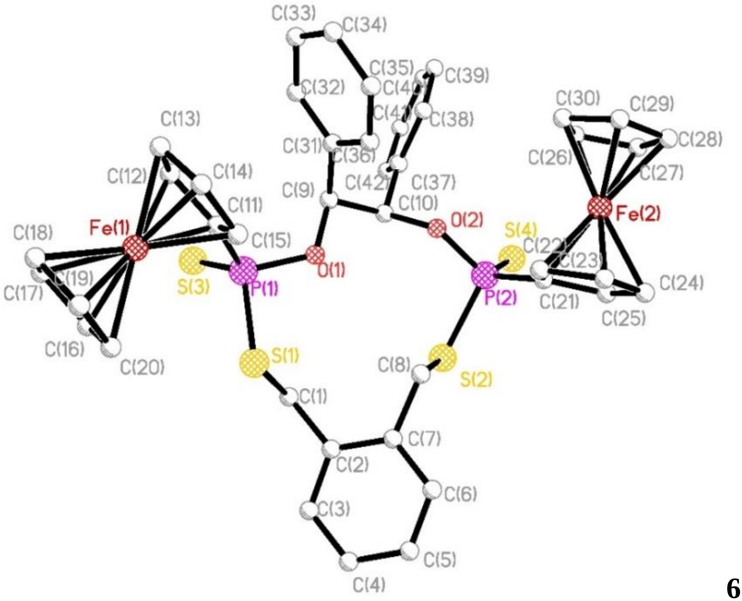
6.1



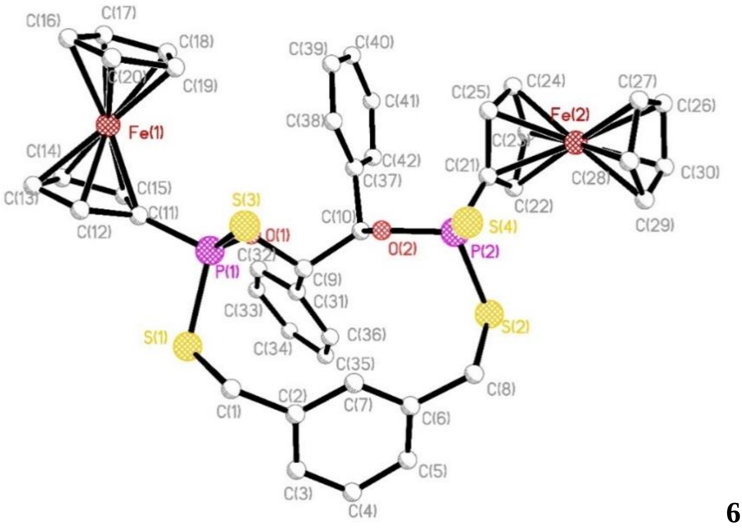
6.2



6.3



6.4



6.5

Figure 6-2. X-ray single crystal structures of compounds **6.1**–**6.5**.

Table 6-4. Selected bond distances (Å) and bond angles (°) for compounds **6.1–6.5**

	6.1	**6.2**	**6.3**	**6.4**	**6.5**
Bond lengths					
P_1-S_1	2.097(3)	2.096(2)	2.097(4)	2.0827(19)	2.1011(19)
P_2-S_2	2.090(3)	2.090(2)	2.087(3)	2.077(2)	2.096(2)
P_1=S_3	1.929(3)	1.926(2)	1.936(3)	1.9291(19)	1.9217(18)
P_2=S_4	1.932(3)	1.936(3)	1.930(3)	1.926(2)	1.9276(17)
P_1-O_1	1.592(5)	1.594(5)	1.603(6)	1.608(4)	1.603(3)
P_2-O_2	1.602(5)	1.595(4)	1.596(5)	1.621(4)	1.601(4)
Bond angles					
S_1-P_1-O_1	105.2(2)	108.10(17)	107.1(3)	99.11(15)	106.31(13)
S_2-P_2-O_2	106.63(19)	106.70(18)	106.9(2)	106.35(14)	106.83(14)
S_1-P_1-S_3	107.76(12)	105.94(10)	114.38(15)	117.66(9)	113.48(8)
S_2-P_2-S_4	107.70(12)	105.47(12)	107.92(14)	107.45(9)	115.62(9)

In the structures of **6.2** and **6.3**, the $S_{exo}\cdots S_{exo}$ lengths are very similar [7.966(3) Å in **6.2** and 7.937(4) Å in **6.3**], however, the transannular $S_{endo}\cdots S_{endo}$ lengths [6.514(3) Å in **6.2** and 7.145(4) Å in **6.3** with the P···P distances of 6.332(3) and 6.398(3) Å] are different. The distances between the two adjacent sulfur atoms are not significantly different [3.213(3) and 3.205(3) Å in **6.2** and 3.390(4) and 3.249(3) Å in **6.3**]. The transannular O···O distance [4.042(6) Å] in **6.2** is significantly longer than that [3.611(8) Å] in **6.3**. In the structures of **6.1** and **6.5** both contain thirteen-membered rings, the distances within the macrocyclic environment are very different: $S_{exo}\cdots S_{endo}$ distances are from 3.249(3) to 3.406(2) Å, and the $S_{exo}\cdots S_{exo}$ lengths [8.969(3) Å] in **6.1** are much longer than that [4.483(3) Å] in **6.5**, however, the transannular $S_{endo}\cdots S_{endo}$ lengths [4.753(3) Å] in **6.1** are shorter than that [6.541(2) Å] in **6.5**. **6.1** also have longer interactional P···P distances [6.094(3) Å] and transannular O···O distances [3.706(6) Å] than that [5.217(2) and 3.041(5) Å] in **6.5**. In the structure of **6.4**, which is similar to **6.5** with a twelve-membered ring, the $S_{exo}\cdots S_{endo}$ distances are 3.229(2) and 3.433(2) Å, the $S_{exo}\cdots S_{exo}$ length is 7.497(2) Å, the transannular $S_{endo}\cdots S_{endo}$ length is 4.8146(19) Å and interactional P···P and transannular O···O distances are 5.554(2) and 2.821(5) Å. The results suggests that it is slightly different in the macrocyclic environment with very similar O-P-S-C_n-S-P-O scaffold, but the macrocyclic environment with various scaffold is very different, even if the structures contain the same membered ring. The P···P distances in all structures are in the range

[4.97 to 6.97 Å] similar to those found in other P-Se containing macrocycles (Table 6-5.[11]

Table 6-5. Selected close contact distances (Å) for compounds **6.1**–**6.5**

	6.1	**6.2**	**6.3**	**6.4**	**6.5**
$S_{exo}\cdots S_{exo}$	8.969(3)	7.966(3)	7.937(4)	7.497(2)	4.483(3)
$S_{endo}\cdots S_{endo}$	4.753(3)	6.514(3)	7.145(4)	4.8146(19)	6.541(2)
$S_1\cdots S_{3\ (adja)}$	3.254(3)	3.213(3)	3.390(4)	3.433(2)	3.3654(19)
$S_2\cdots S_4$	3.249(3)	3.205(3)	3.249(3)	3.229(2)	3.406(2)
P···P	6.094(3)	6.332(3)	6.398(3)	5.554(2)	5.217(2)
O···O	3.706(6)	4.042(6)	3.611(8)	2.821(5)	3.041(5)

The details of possible intramolecular hydrogen interactions in **6.1**, **6.2**, **6.4** and **6.5** are shown in Table 6-6. There are four intramolecular C-H···S and C-H···O interactions present in **6.1**: (a) the intramolecular C-H···S1 interaction distance is 2.9282(19) Å along with the C···S1 distance of 3.642(6) Å and the C-H···S1 angle of 129.8(4)°; (b) the intramolecular C-H···S2 interaction distance is 2.8488(19) Å with the C···S2 distance of 3.588(6) Å and C-H···S2 angle of 132.0(4)°; (c) the intramolecular C-H···S4 interaction distance is 3.115(2) Å with the C···S4 distance of 3.743(8) Å and C-H···S2 angle of 122.0(5)°; (d) the intramolecular C-H···O2 interactions distance is 3.404(5) Å with C···O2 distance of 4.254(8) Å and C-H···O2 angle of 145.1(4)°. The possible intramolecular interactions in **6.1** are shown in Figure 6-3.

6.2 is similar to **6.1** with different possible intramolecular C-H···S interactions, but no obvious intramolecular C-H···O interactions are observed in **6.2**. There are different intramolecular C-H···S interactions in **6.2** [H···S1 distances of 3.1819(19) to 4.1628(19) Å, along with C···S1 distances of 4.042(9) to 4.959(9) Å and C-H···S1 angles of 120.2(5) to 160.9(4)°; H···S3 distance of 2.9769(19) Å with C-H···S3 angle of 167.3(4) ° and C···S3 distance of 3.958(8) Å. The structure of **6.3** is similar to **6.2**, both have a fourteen-membered ring, however, there are no obvious intramolecular interactions in **6.3**.

The intramolecular C-H···S1, C-H···S2, C-H···S4 and C-H···O1 interactions exist in **6.4**. The H···S distances vary from 2.9301(14) to 3.2294(16) Å with C···S distances from 3.625(5) to 3.855(7) Å and C-H···S interaction angles from 122.1(4) to 128.0(3)° in **6.4**. Compared to **6.1**, the intramolecular C-H···O interaction in **6.4** is stronger (Table 6.6). The intramolecular C-H···S2, C-H···S4 and C-H···S3 interactions are observed, however, no obvious intramolecular C-H···O interactions are found in **6.5**.

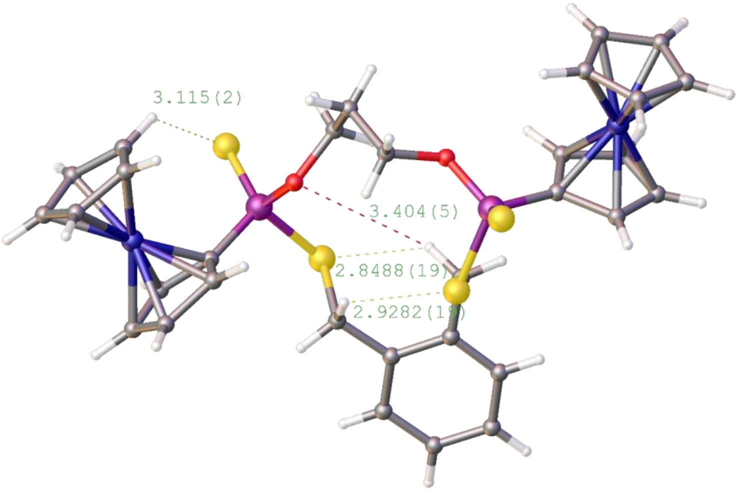


Figure 6-3. Possible intramolecular interactions in **6.1**.

Table 6-6. Selected intramolecular distances (Å) and angles (°) for **6.1**, **6.2**, **6.4** and **6.5**

	6.1	**6.2**	**6.4**	**6.5**
Intramolecular interaction distances (Å)				
H···S1	2.9282(19)	3.1819(19), 3.458(2), 4.1628(19)	2.9301(14)	
C···S1	3.642(6)	4.139(6), 4.042(9), 4.959(9)	3.625(5)	
H···S2	2.8488(19)		2.9559(14)	3.8162(16)
C ···S2	3.588(6)		3.648(6)	4.574(7)
H···S3		2.9769(19)		2.6542(14), 3.2803(17), 3.3475(14), 3.1238(15)
C···S3		3.958(8)		3.364(5), 3.988(6), 4.211(4), 3.793(7)
H···S4	3.115(2)		3.2294(16)	2.7303(15)
C···S4	3.743(8)		3.855(7)	3.450(6)
H···O1			2.513(4)	
C···O1			3.426(6)	
H···O2	3.404(5)			
C···O2	4.254(8)			
Intramolecular interaction angles (°)				
C-H···S1	129.8(4)	160.9(4), 120.2(5), 138.8(5)	128.0(3)	
C-H···S2	132.0(4)		127.8(3)	138.8(3)
C-H···S3		167.3(4)		128.8(3), 132.9(3), 152.2(3), 125.4(3)
C-H···S4	122.0(5)		122.1(4)	129.9(3)
C-H···O1			153.1(4)	
C-H···O2	145.1(4)			

The 3-D packing network contains a combination of various weak intermolecular C-H···S interactions in **6.1** and **6.4** (Figure 6-4 and 6-7). There are also weak intermolecular C-H···O interactions in **6.2**, **6.3** and **6.5** (Figure 6-5, 6-6 and 6-8). Some selected intermolecular interaction distances and angles are listed in Table 6-6. The H···S distances in **6.1** are 2.765(2), 2.878(2) and 2.9882(19) Å, along with C···S distances of 3.713(19), 3.660(9) and 3.642(6) Å and C−H···S angles of 158.4(6), 140.2(5) and 129.8(4)°. The structures of **6.2** and **6.3** are very similar to **6.1**, their supramolecular aggregation arrangements are created by the weak intermolecular

C−H···S and C-H···O interactions. Two strongest intermolecular C−H···S interactions in **6.2** and **6.3** are very similar: H···S distances are 2.9227(19) and 2.9749(18) Å with the angle of 151.7(4) and 156.2(4)° in **6.2**. The H···S distances are 2.910(2) and 3.046(2) Å with the angles of 132.3(5) and 124.2(5)° in **6.3**. The H···O distance [2.716(6) Å] in **6.2** is smaller than that in **6.3** [3.184(5) and 3.391(5) Å]. The intermolecular C−H···S interactions in **6.5** are weaker than that in **6.4**. The intermolecular C-H···O interactions in **6.3** {H···O distances of 3.184(5)[3.391(5)] Å with the C-H···O angles of 154.9(6)[153.9(5)]°} and **6.5** [H···O distance of 3.291(3) Å with the C-H···O angle of 170.1(7)°] are considerably weaker than that in **6.2** [H···O distance of 2.716(6) Å with the C-H···O angle of 146.7(4)°].

Table 6-7. Selected intermolecular distances (Å) and angles (°) for compounds **6.1–6.5**

	6.1	**6.2**	**6.3**	**6.4**	**6.5**
Intermolecular interaction distances (Å) [angles (°)]					
H···S	2.765(2) [158.4(6)]	2.9227(19) [151.7(4)]	2.910(2)[132.3(5)]	2.6706(15)[144.9(3)]	3.0674(15)
	2.878(2) [140.2(5)]	2.9749(18) [156.2(4)]	3.046(2)[124.2(5)]	2.6794(14) [147.0(3)]	3.1753(18)
	2.9882(19) [129.8(4)]	3.372(2)	3.081(3)	2.9559(14)	3.3531(15)
	3.1051(19)		3.123(2)	3.0042(16)	3.4725(15)
	3.115(2)		3.218(2)	3.1204(14)	
	3.1289(19)			3.1928(14)	
	3.198(2)				
C-H···O		2.716(6) [146.7(4)]	3.184(5)[154.9(6)], 3.391(5) [153.9(5)]		3.291(3) [170.1(7)]

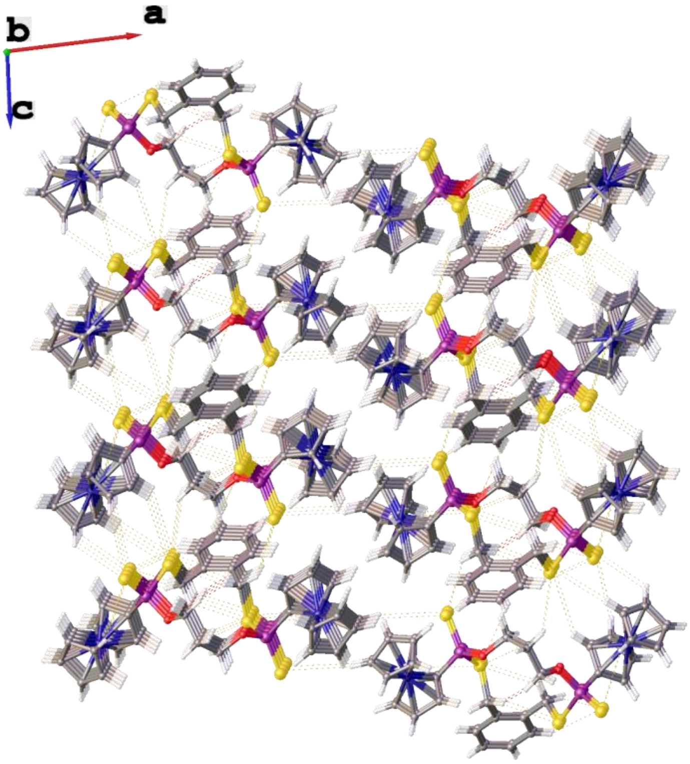


Figure 6-4. A view of 3-D packing network shows the intermolecular H···S interactions in **6.1**.

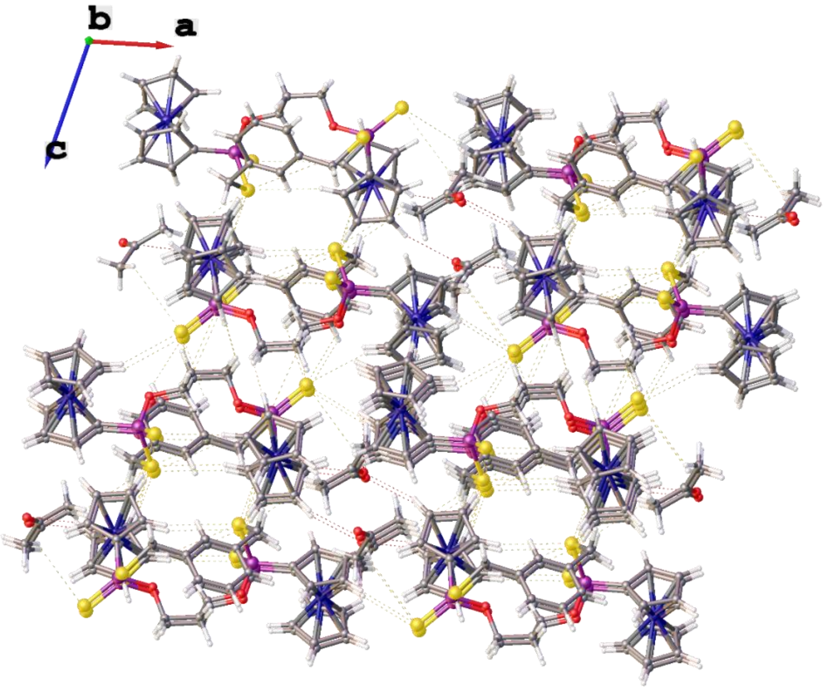


Figure 6-5. A view of 3-D packing network shows the intermolecular H···S/O interactions in **6.2**.

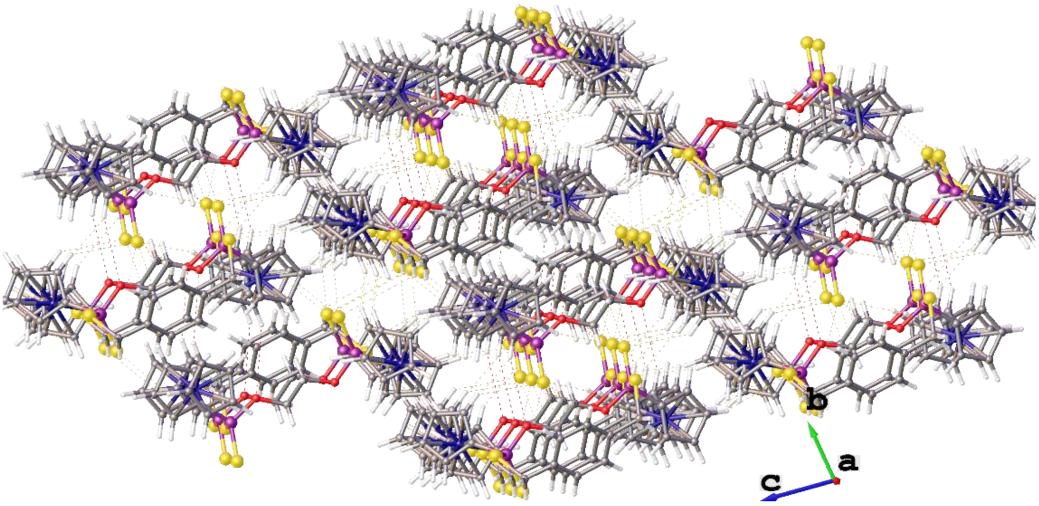


Figure 6-6. A view of 3-D packing network shows the intermolecular H···S/O interactions in **6.3**.

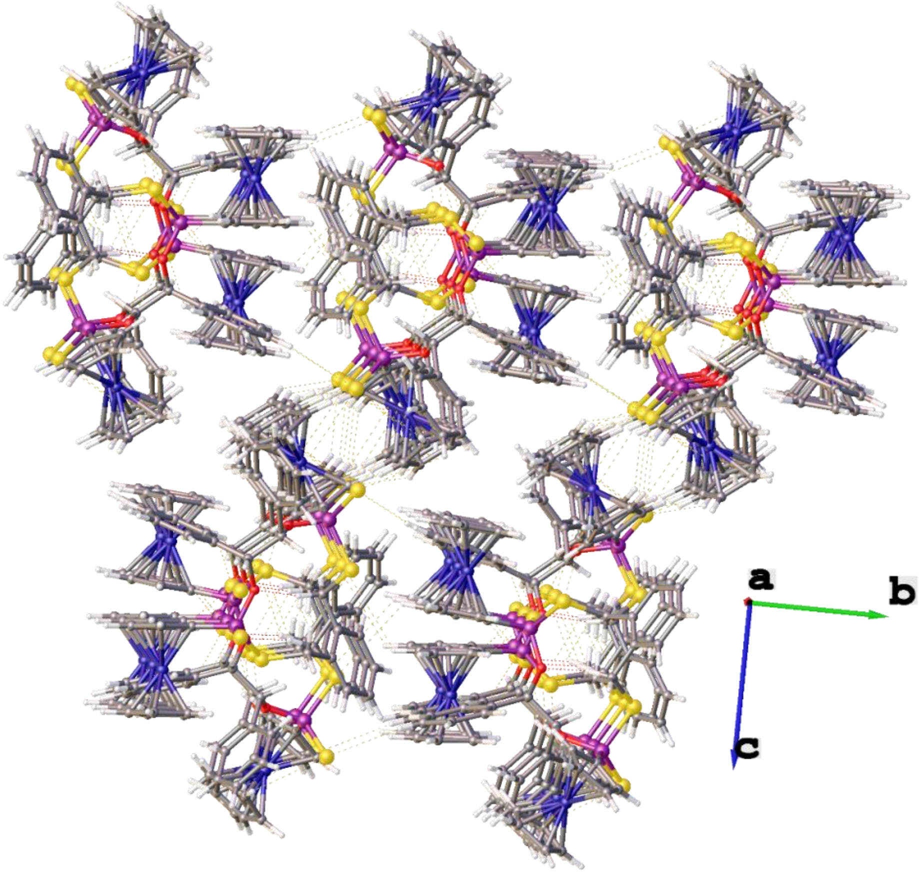


Figure 6-7. A view of 3-D packing network shows the intermolecular H···S interactions in **6.4**.

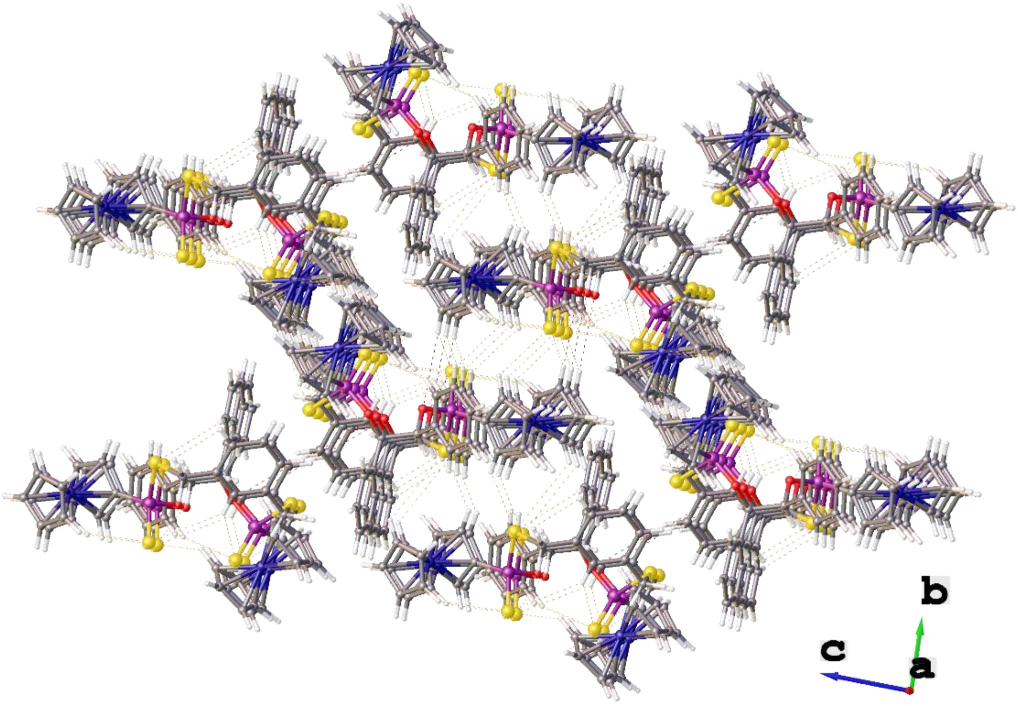
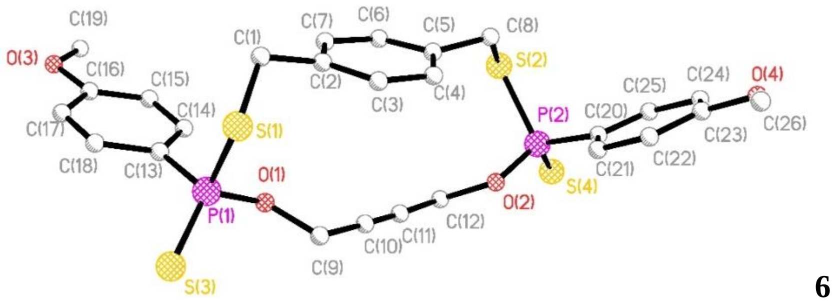


Figure 6-8. A view of 3-D packing network shows the intermolecular H···S/O interactions in **6.5**.

6.3.2. Macrocycles with Two Aryl Rings

Compared to **6.1**–**6.5**, one aryl group is attached to the each phosphorus atom instead of the ferrocene group in **6.6**–**6.9** (Figure 6-9). The geometry around P(1) and P(2) is distorted tetrahedral in **6.6** and **6.7**, along with the similar P-S single bonds from 2.0735(16) to 2.090(3) Å, P=S double bonds in the range of 1.929(3) to 1.934(3) Å and S-P-S bond angles from 106.77(13) to 108.24(7)°. In the cases of **6.8** and **6.9**, the geometry around P(1) and P(2) is the same as **6.6** and **6.7**, however, the P-Se single bond length [2.237(3) to 2.248(3) Å] and P=Se double bond length [2.077(5) to 2.085(3) Å] are longer than the relevant P-S single bond and P=S double bond length. In **6.6**–**6.9**, the P-O bond length range from 1.588(12) to 1.602(5) Å with the bond angles 105.4(3) to 108.8(4)° (Table 6.8). The order of the P···P and $S_{endo}\cdots S_{endo}$ distances are **6.8** [4.643(6) and 2.349(2) Å] < **6.7** [6.056(3) and 4.848(3) Å] and **6.9** [6.392(4) and 4.8281(17) Å] < **6.6** [8.410(4) and 8.150(4) Å]. The sizes of the macrocyclic ring are **6.8** < **6.7** ~ **6.9** < **6.6**. The P···P and $S_{endo}\cdots S_{endo}$ distances of the macrocyclic ring as shown in Table 6-9.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P(2)
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S(4)
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C(12)
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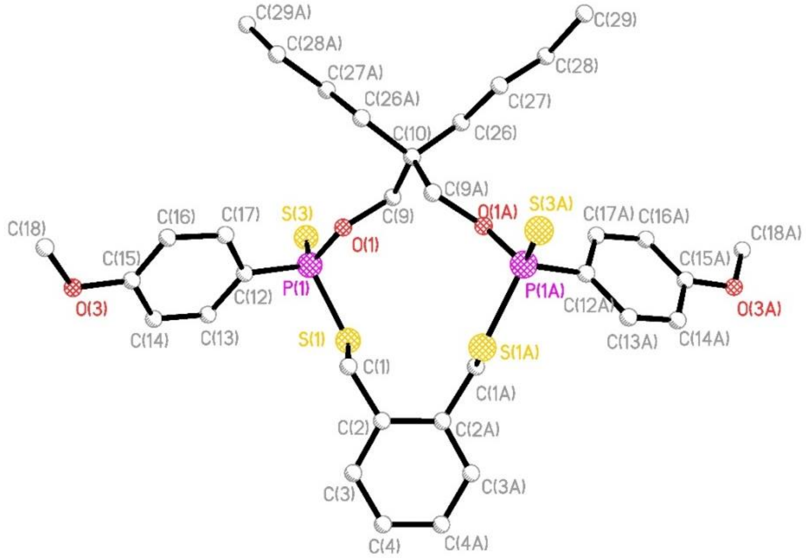
C(9)

6.6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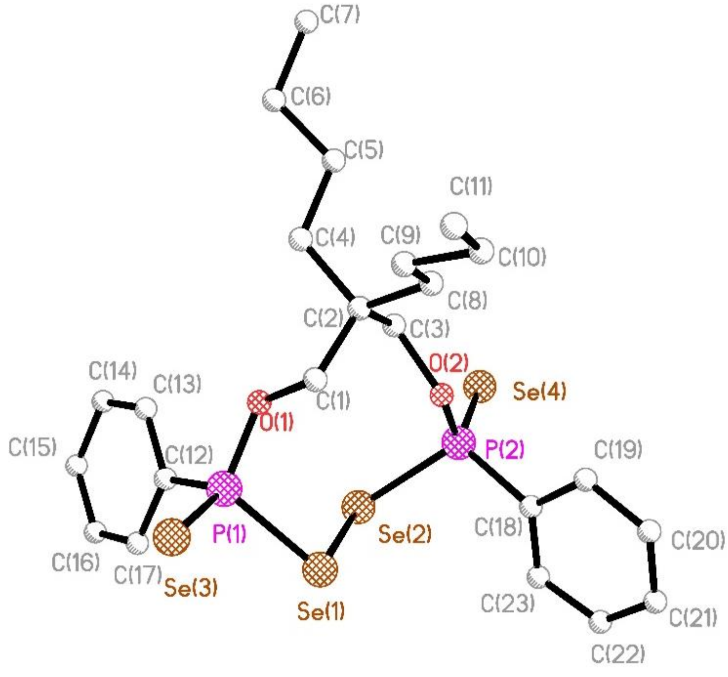
6.7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C(12)
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P(1)
Se(2)
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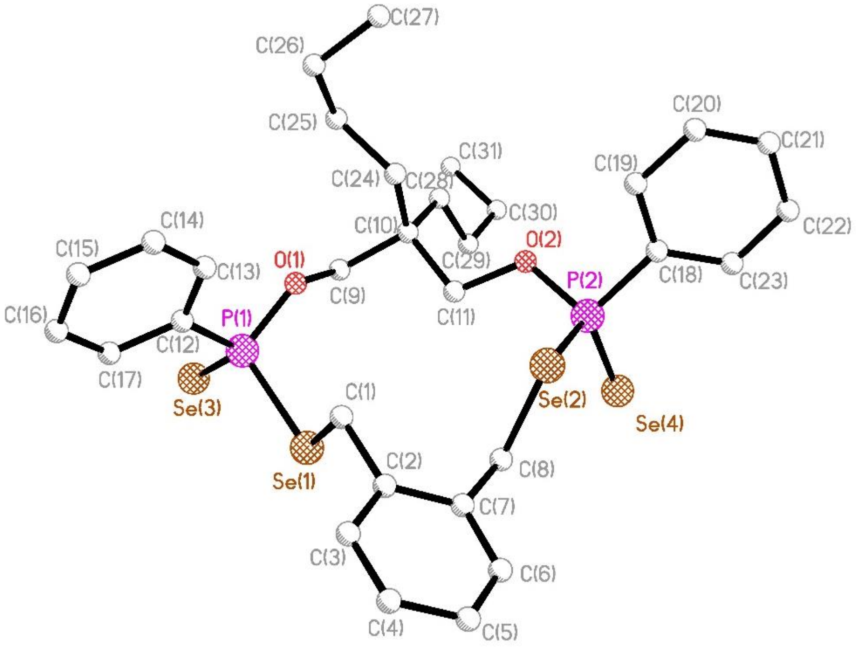
C(22)

6.8



6.9

Figure 6-9. X-ray single crystal structures of **6.6–6.9**.

Table 6-8. Selected bond distances (Å) and bond angles (°) for compounds **6.6–6.9**

	6.6	**6.7**	**6.8**	**6.9**
Bond lengths				
P_1-S_1/Se_1	2.090(3)	2.0735(16)	2.247(4)	2.237(3)
P_2-S_2/Se_2	2.082(3)		2.240(4)	2.248(3)
P_1=S_3/Se_3	1.929(3)	1.9320(16)	2.077(5)	2.085(3)
P_2=S_4/Se_4	1.934(3)		2.084(5)	2.083(3)
P_1-O_1	1.600(5)	1.598(3)	1.595(9)	1.597(7)
P_2-O_2	1.602(5)		1.588(12)	1.598(7)
Bond angles				
S_1/Se_1-P_1-O_1	106.7(2)	107.31(12)	107.7(4)	107.9(3)
S_2/Se_2-P_2-O_2	107.1(2)		108.8(4)	105.4(3)
S_1/Se_1-P_1-S_3/Se_3	106.89(13)	108.24(7)	105.90(17)	107.95(11)
S_2/Se_2-P_2-S_4/Se_4	106.77(13)		102.83(17)	114.59(12)

Table 6-9. Selected close contact distances (Å) for compounds **6.6–6.9**

	6.6	**6.7**	**6.8**	**6.9**
S/Se$_{exo}$···S/Se$_{exo}$	10.970(4)	8.831(4)	8.110(4)	8.147(3)
S/Se$_{endo}$···S/Se$_{endo}$	8.150(4)	4.848(3)	2.349(2)	4.8281(17)
S$_1$/Se$_1$···S$_3$/Se$_3$	3.230(3)	3.2465(18)	3.453(3)	3.4971(18)
S$_2$/Se$_2$···S$_4$/Se$_4$	3.225(3)	3.2465(18)	3.381(3)	3.6459(15)
P···P	8.410(4)	6.056(3)	4.643(6)	6.392(4)
O···O	5.566(7)	3.567(6)	3.234(14)	4.274(11)

In **6.7** and **6.9**, there are some intramolecular interactions such as the intramolecular C-H···S/Se or C-H···O interactions present, however, possible but not obvious close contacts are discovered in **6.6** and **6.8**. The intramolecular C-H···S interactions [H···S distances of 2.9688(16) and 3.666(15) Å with the angles of 127.3(3) and 162.1(3)°] in **6.7** can be also observed, accompanied by the weak intramolecular C-H···O interactions [3.727(3) Å with the angle of 147.2(3)°]. The multiple intramolecular C-H···Se interactions [2.8372(12) and 2.9701(13) Å with the angles of 133.6(6) and 129.0(6)° present in **6.9** (Table 6-10).

The packing frameworks for **6.6–6.9** are shown in Figures 6-10–6-13. The network of **6.7** is arranged in '*zigzag'* conformation. The packing frameworks are connected by a set of two molecules in **6.8** and **6.9**. The packing networks for **6.6–6.9** are combined by the multiple intermolecular C-H···S/Se, C-H···O interactions except **6.8** in which the intermolecular C-H···O interaction is absent. The H···S/Se distances in **6.6** and **6.8** are very similar [2.923(2) Å with the angle 149.8(6)° in **6.6**, and 2.9788(19) Å with the angle 148.0(9)° in **6.8**]. The H···S distance of 2.7916(16) Å with the angle of 135.7(3)°, the H···Se distance of 3.0922(12) Å with the angle of 154.6(7)° and the H···O distance of 2.606(3) Å with the angle 153.7(3)° in **6.7** are shorter than that in **6.6** and **6.9** (Table 6-11).

Table 6-10. Selected intramolecular distances (Å) and angles (°) for **6.6** and **6.9**

	6.7	**6.9**
Intramolecular interaction distances (Å)		
H···S/Se	2.9688(16), 3.6666(15)	2.8372(12), 2.9701(13), 3.3438(12), 3.6704(16)
C···S/Se	3.654(5), 4.619(4)	3.591(12), 3.675(10), 4.085(10), 4.647(12)
H···O	3.727(3)	
C···O	4.590(6)	
Intramolecular interaction angles (°)		
C-H···S	127.3(3), 162.1(3)	133.6(6), 129.0(6), 133.1(6), 169.8(7)
C-H···O	147.2(3)	

Table 6-11. Selected intermolecular distances (Å) and angles (°) for **6.6**–**6.9**

	6.6	**6.7**	**6.8**	**6.9**
Intermolecular interaction distances (Å) [angles (°)]				
H···S/Se	2.923(2)[149.8(6)]	2.7916(16)[135.7(3)]	2.9788(19)[148.0(9)]	3.0922(12)[154.6(7)]
	3.012(2)[155.6(7)]	2.9363(17)[144.4(3)]	3.0771(19)[139.3(7)]	3.1197(12)[127.1(7)]
	3.057(2)[146.0(5)]	3.0866(16)[157.5(3)]	3.1800(17)[154.9(12)]	3.2383(11)[128.9(6)]
	3.152(2)[129.7(5)]		3.190(2)[129.2(9)]	3.2658(12)[122.7(7)]
H···O	2.864(6)[155.1(5)]	2.606(3)[153.7(3)]		2.953(7)[96.2(7)]
	3.030(6)[160.7(5)]			3.730(7)[146.7(5)]
Close contact distances				
C···S/Se	3.801(12), 3.924(11), 3.881(8), 3.830(8)	3.560(5), 3.785(5), 3.981(6)	3.853(14), 3.848(14), 3.861(16)	3.972(11), 3.7701(13), 3.862(12)
C···O	3.95(1)	3.484(5)		4.629(14)
	3.812(11)			4.590(12)

Dimensions for second independent molecule in square parentheses.

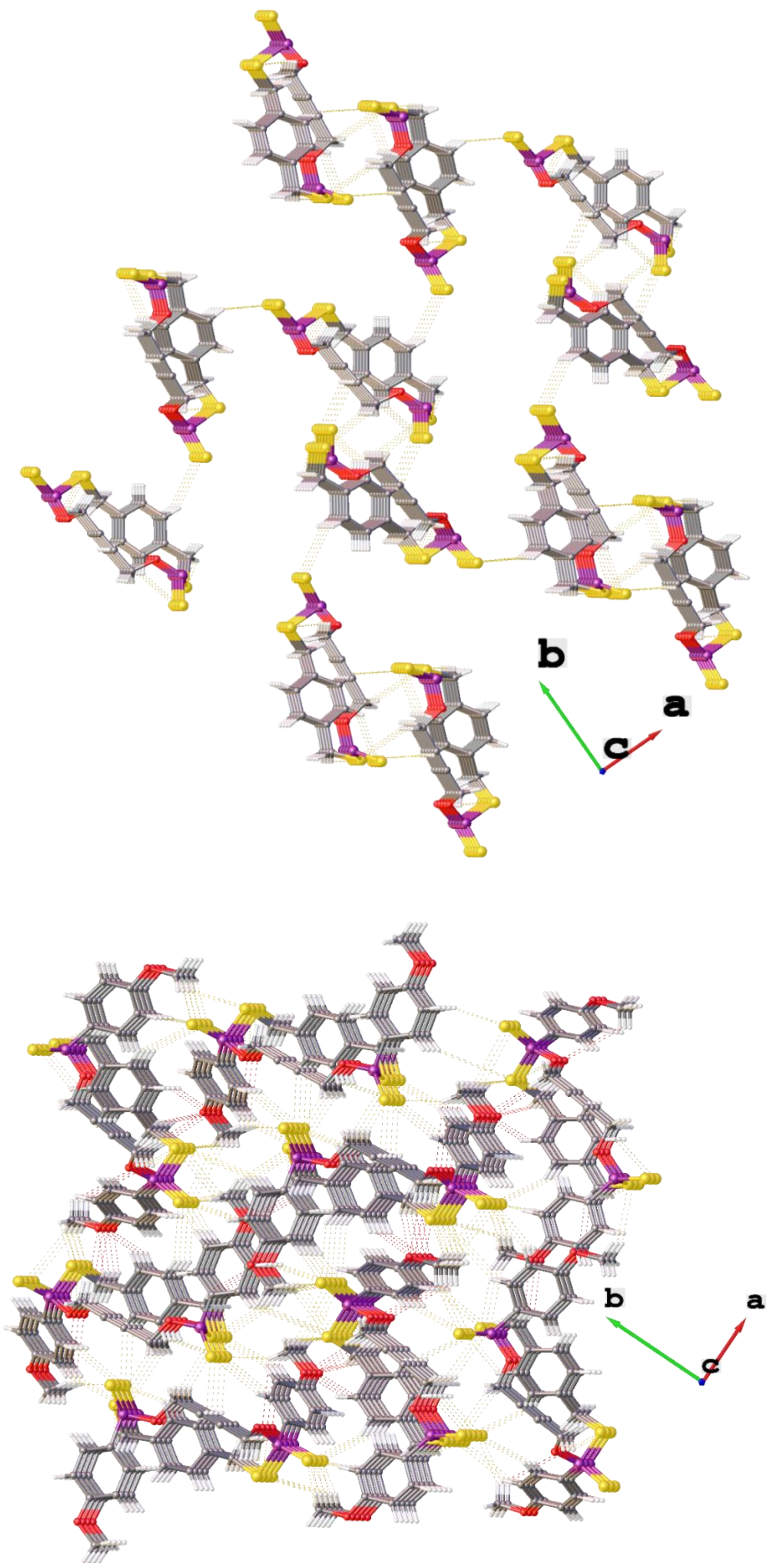


Figure 6-10. A view of 3-D macrocyclic framework (Upper diagram) and packing network (Lower diagram) show the intermolecular H···S/O interactions in **6.6**.

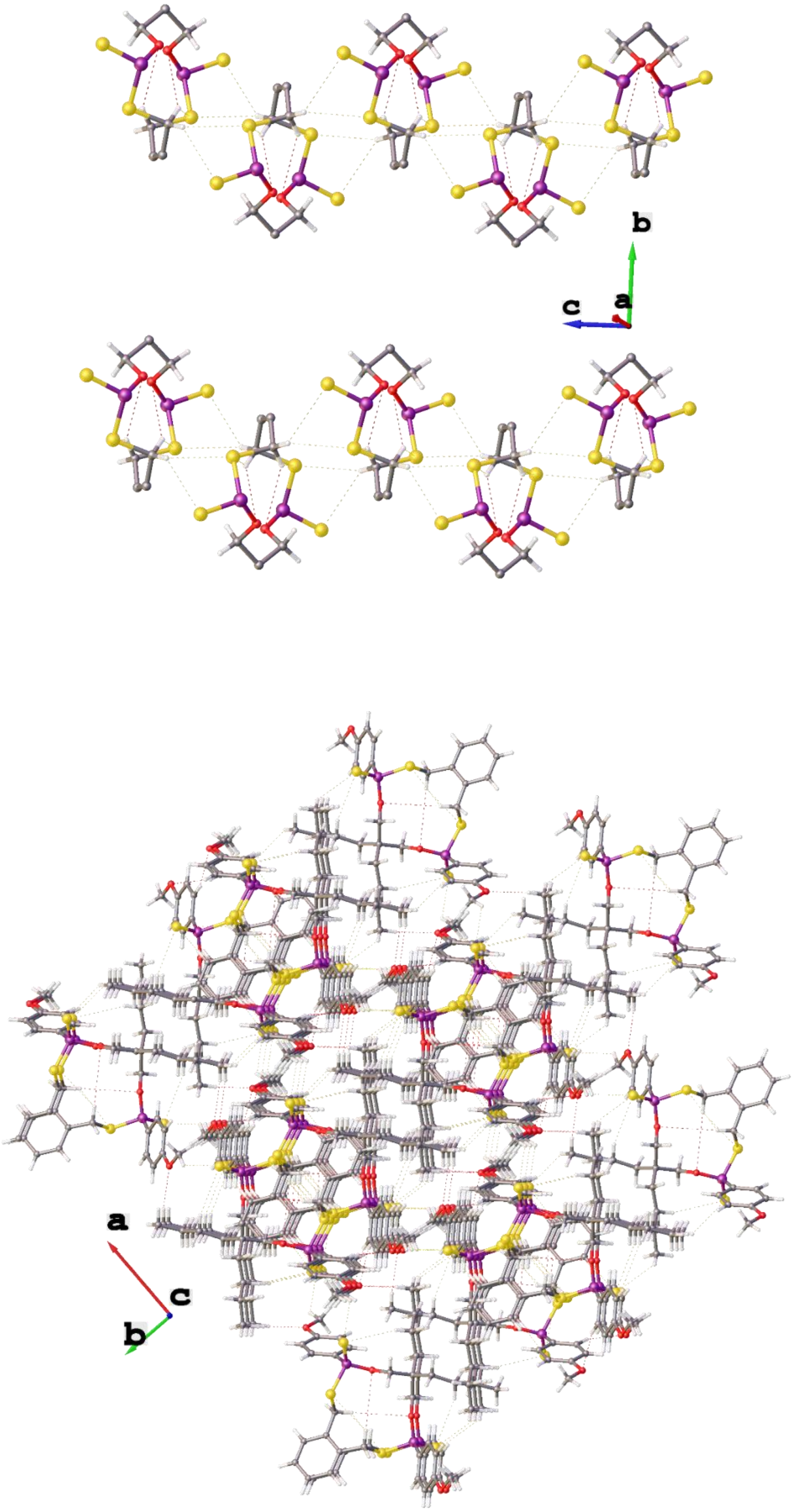


Figure 6-11. A view of 3-D macrocyclic framework (Upper diagram) and packing network (Lower diagram) show the intermolecular H···S/O interactions in **6.7**.

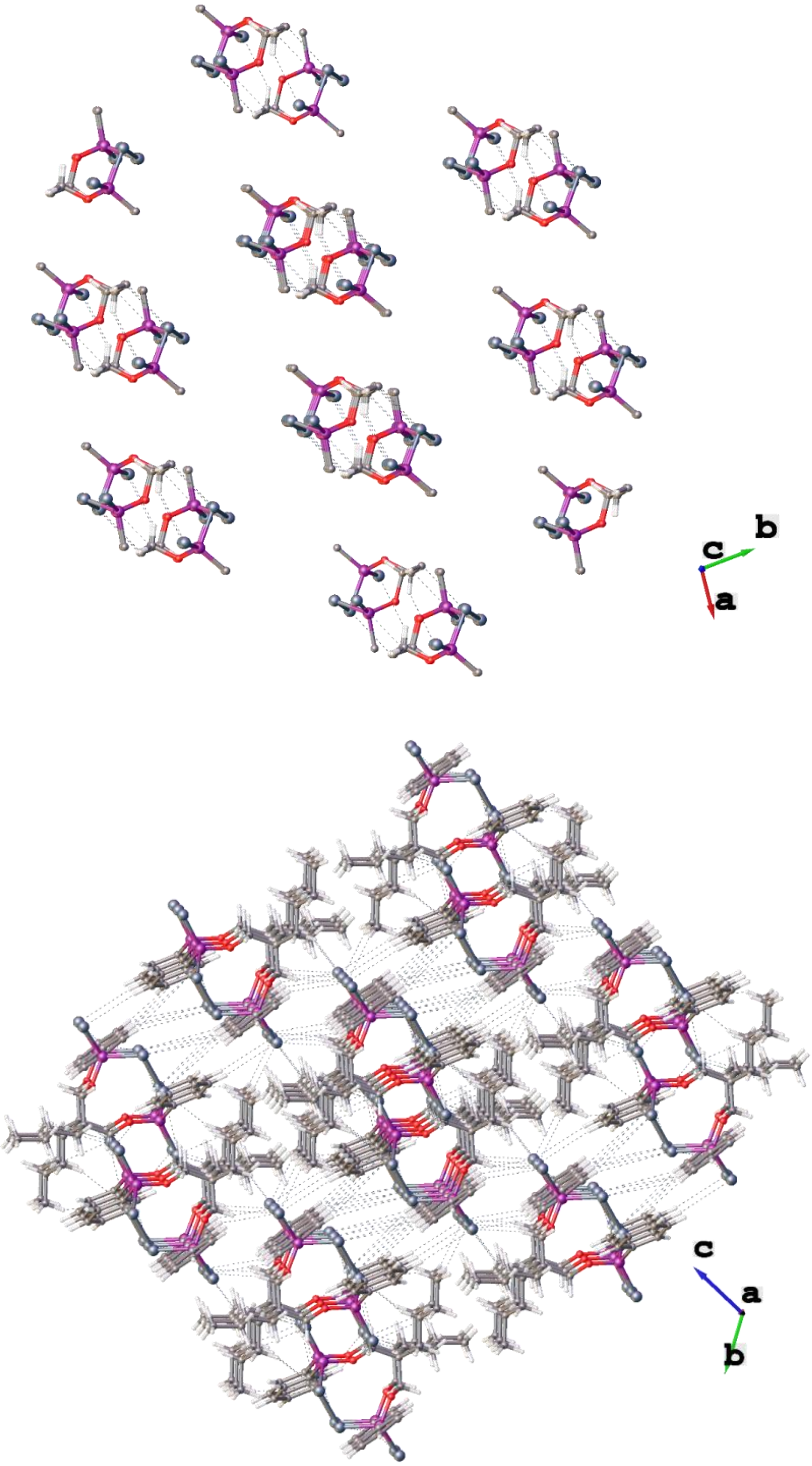


Figure 6-12. A view of 3-D macrocyclic framework (Upper diagram) and packing network (Lower diagram) show the intermolecular H···Se interactions in **6.8**.

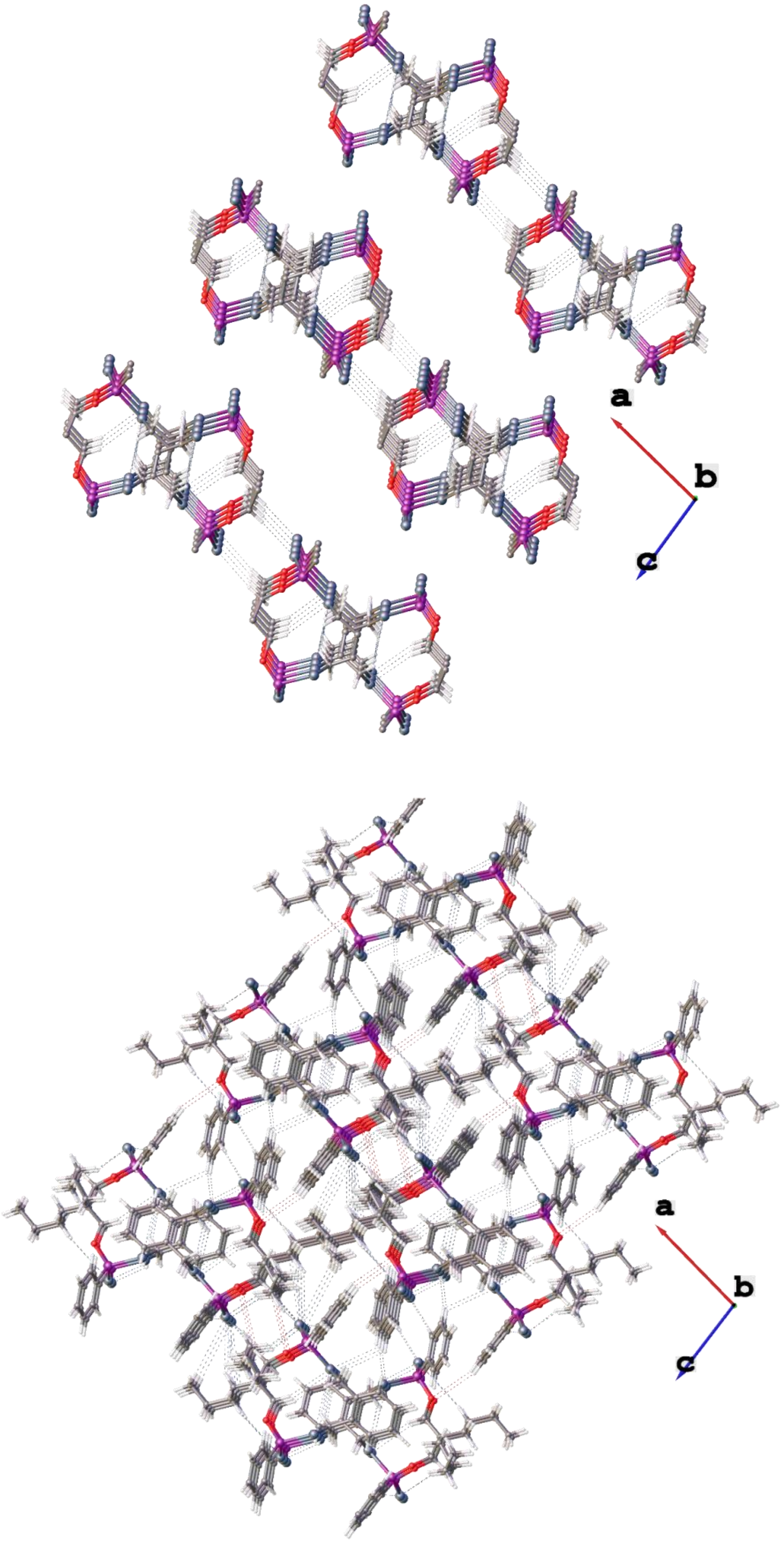


Figure 6-13. A view of 3-D macrocyclic framework (Upper diagram) and packing network (Lower diagram) show the intermolecular H···Se/O interactions in **6.9**.

6.4. Conclusion

The structures of nine macrocycles with nine- to fifteen-membered macro-heterocycles with double OP(S)SC$_n$ or OP(Se)SeC$_n$ scaffolds have been discussed crystallographically, and they are the first large 9-15 macrocycles with this scaffolds to be synthesized and analysed. The P=S bond lengths are in the range of 1.9217(18) to 1.936(3) Å and the P-S bond lengths are ranging from 2.0735(16) to 2.1011(19) Å in **6.1**–**6.7**, being marginally longer than the P=Se bond lengths [2.077(5) to 2.085(3) Å] and P-Se bond lengths [2.237(3) to 2.248(3) Å] in **6.8** and **6.9**. The P-O bond lengths are from 1.592(5) to 1.621(4) Å with the similar corresponding S-P-S [105.47(12) to 117.66(9)°], Se-P-Se [102.83(17) to 114.59(12)°], S-P-O [99.11(15) to 108.10(17)°] and Se-P-O [105.4(3) to 108.8(4)°] angles. The P···P distances are in the range of 4.643(6) to 8.410(4) Å, and the distances between adjacent sulfur atoms [3.205(3) to 3.433(2) Å] in **6.1**–**6.7** are comparable to the Se-Se distances [3.381(1) to 3.6459(15) Å] in **6.8** and **6.9**.

The intramolecular interaction distances and angles suggest that there are some intramolecular C-H···O, C-H···S or C-H···Se interactions in these structures. The packing networks for these structures are formed by the multiple intermolecular C-H···O, C-H···S or C-H···Se interactions. The structures of **6.7** and **6.9** are very similar leading to the similar packing networks.

6.5. References

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CHAPTER 7

CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

Sulfur (S) and selenium (Se) belong to chalcogen elements, and the corresponding organosulfur and organoselenium compounds have a very significant position in organic chemistry. Their compounds are widely used in many fields such as medicine and materials science. It is well known that the structure of substances influences their physical-chemical properties or it might be thought that the physical-chemical properties are also reflections of the structures. The compounds involving in this thesis can be classified into three classes: pentafluorsulfuranyl (SF_5)-containingcompounds, 2,4-diaryl-1,3-chalcogen azoles and organo phosphorus macrocycles bearing multiple selenium or sulfur atoms. This thesis focuses on the structural characterisation and investigation of these series of compounds by means of X-ray crystallography.

Pentafluorsulfuranyl (SF_5)-containing compounds are named as ‘super-CF_3’ analogues and have wide applications such as surfactants, chemotherapeutic treatments, and herbicides. The SF_5 group is a very interesting functional group. It displays a unique umbrella geometry, with the sulfur atom locating in an approximately octahedral coordination environment. The angles between the adjacent F(eq) atoms are near 90° and the C-S-F(ax) angle is near 180°. In all the structures of compounds in Chapter 3 and 5, the S-F bond lengths vary from 1.558(5) to 1.618(3) Å and S-C bond lengths are from 1.791(6) to 1.834(6) Å. Some weak C_{aryl}-H···F(eq) hydrogen bonds existing in the structure help keeping the stability of equatorial fluorine atoms. Many kinds of intermolecular interactions connect the molecules in the packing networks. This has been discussed in detail in Chapter 3 and 5.

Selenazole/sulfur derivatives are also famous because of their biological efficacy, such as antibiotic and cancerostatic activity. Chapter 4 studied the structures of selenium-nitrogen heterocyclic compounds and sulfur-nitrogen heterocyclic compounds. Their main backbone is 1,3-selenazole/sulfur ring, and it is notable that bond distances indicate some delocalisation for all bonds in the five-membered ring. The atoms in 1,3-selenazole/sulfur ring are approximately coplanar. Some twist angles between the mean plane of the selenazole ring and each aryl-ring substituent are near 0°, however, some cases are very big.

In Chapter 5, 2,4-diaryl-1,3-chalcogen azoles bearing the pentafluorosulfanyl (SF_5) group have two functional groups, as has been discussed in Chapter 3 and Chapter 4. They have unique structures, and they are still very stable. In all the structures of compounds in Chapter 4 and 5, the C-N single bond lengths vary from 1.377(13) to 1.410(9) Å, and C=N double bond lengths range from 1.285(14) to 1.311(5) Å with the C-N-C bond angles from 111.3(8) to 118.3(4)°. The Se-C bond distances are from 1.803(13) to 1.918(7) Å with the C-Se-C bond angles from 84.0(3) to 85.2(5)°. In the meanwhile, the S-C bond distances are from 1.670(9) to 1.735(10) Å with the C-S-C bond angles from 89.6(5) to 90.3(5)°. The N-C-Se/S-C-C five membered ring are almost coplanar, and there are some big or small twist angles between the two aryl-arms on this ring in all the structures of Chapter 4 and 5.

Finally, Chapter 6 discussed the structures of macro-heterocycles with double $OP(S)SC_n$ or $OP(Se)SeC_n$ scaffolds. The transannular P···P distance usually reflects the ring size of the macro-heterocycle, and intramolecular hydrogen bonds are present in some structures.

7.2 Future Work

So far, many milestones have been reached in pentafluorosulfanyl chemistry. The compounds bearing pentafluorosulfanyl group are investigated in current research by comparing with the trifluoromethyl (CF_3)-containing compounds which exits in many commercial products. The trifluoromethyl (CF_3)-containing compounds have made enormous impact in the fields of pharmaceuticals, agrochemicals and material sciences,[1] and that means the SF_5 molecules have a large potential to improve the original properties in the fields of drugs and functional materials in the future.[2] Currently, the toxicology and biological feature of pentafluorsulfuranyl (SF_5)-containing compounds are not well understood, and more research about their biotransformation reactions would be worthwhile.[3]

Fluorine chemistry and selenium/sulfur chemistry are very important organic chemistry in the fields of pharmaceuticals and materials. The pentafluorsulfuranyl (SF_5)-containing compounds offer unique chemical properties and biological characteristics, therefore, they have are very promising substituents in current organic chemistry. They can be assembled with other sulfur compounds or selenium-containing compounds in order to create the new compounds which exhibit various chemical properties, because they have very stable structural characteristics.

In general, X-ray crystallography is a very useful technology in modern science. It is the most useful method to accurately determine the 3-D structure of a compound. My future studies will still emphasize the measurement and analysis of the structures of sulfur/selenium heteroatom compounds by using X-ray crystallography. Comparing with the relevant published structures, the similarities and differences of these structures will be further explored. Based on the obtained results and the conclusions, some investigations are now on the way.

Meanwhile, I will try to do some synthetic work, and measure more structures of sulfur/selenium heteroatom compounds by X-ray crystallography. For example, the structures of compounds (in Chapter 5) contain two functional groups with sulfur/selenium atoms: aryl-pentafluorosulfuranyl group and 2,4-diaryl-1,3-selenazoles/thiazoles. I will also investigate how to synthesize some compounds which contain aryl-pentafluorosulfuranyl group and organo phosphorus-chalcogen macrocyclic ring (in Chapter 6), and determine and analyse their structural information.

The aim of my future work is mainly to obtain the structures of compounds using X-ray crystallography, so I hope my study can provide reference and data support for future research and practical application.

7.3 References

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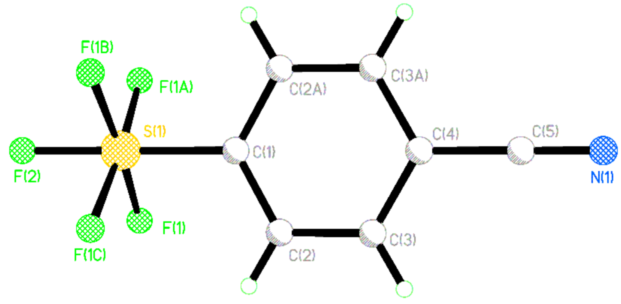
APPENDIX I

CRYSTAL STRUCTURES DISCUSSED IN THIS THESIS

Compound 3.1

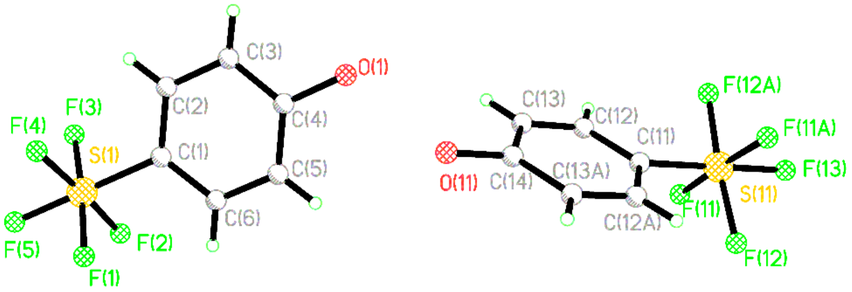
Cmcm

a = 9.018(11) Å
b = 13.18(2) Å
c = 6.864(8) Å
α = 90º
β = 90º
γ = 90º
V = 816(2) Å^3
wR$_2$ = 0.1018
R$_1$ = 0.0386

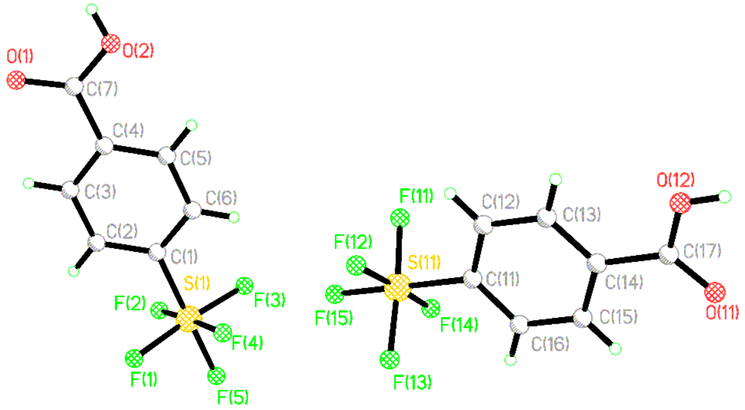


Compound 3.2

P2$_1$2$_1$2$_1$
a = 5.851(8) Å
b = 18.43(3) Å
c = 11.57(2) Å
α = 90º
β = 90º
γ = 90º
V = 1247(3) Å^3
wR$_2$ = 0.3626
R$_1$ = 0.1243

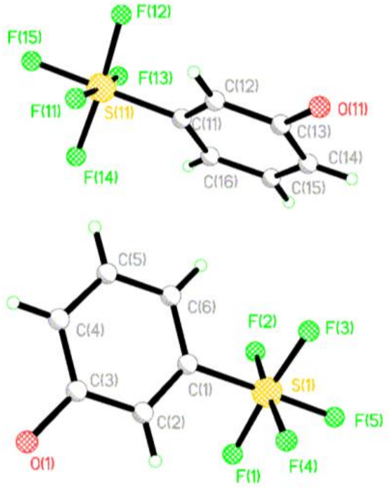


Compound 3.3
P2$_1$/c
a = 14.794(3) Å
b = 7.6423(10) Å
c = 15.892(3) Å
α = 90º
β = 100.559(7)º
γ = 90º
V = 1766.3(5) Å^3
wR$_2$ = 0.1035
R$_1$ = 0.0473



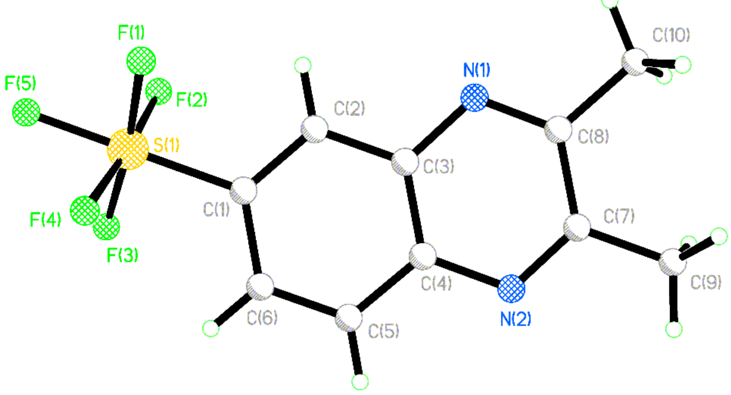
Compound 3.4

P-1
a = 8.906(12) Å
b = 9.97(2) Å
c = 10.29(2) Å
α = 85.05(5)°
β = 83.21(6)°
γ = 66.30(4)°
V = 830(2) Å^3
wR_2 = 0.1502
R_1 = 0.0539



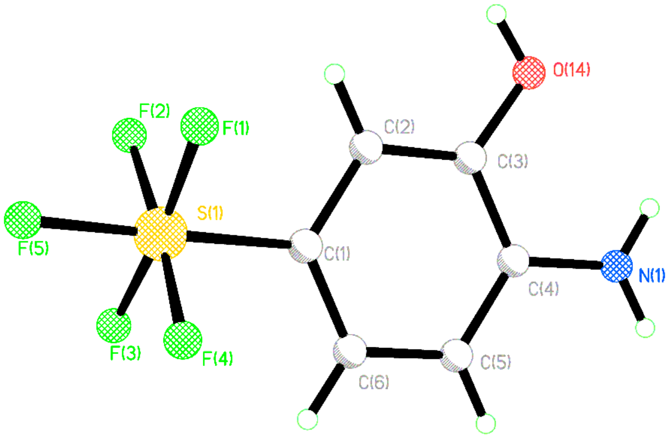
Compound 3.5

$P2_1/n$
a = 5.8557(10) Å
b = 23.706(4) Å
c = 7.8738(14) Å
α = 90°
β = 92.963(10)°
γ = 90°
V = 1091.5(3) Å^3
wR_2 = 0.1403
R_1 = 0.0535



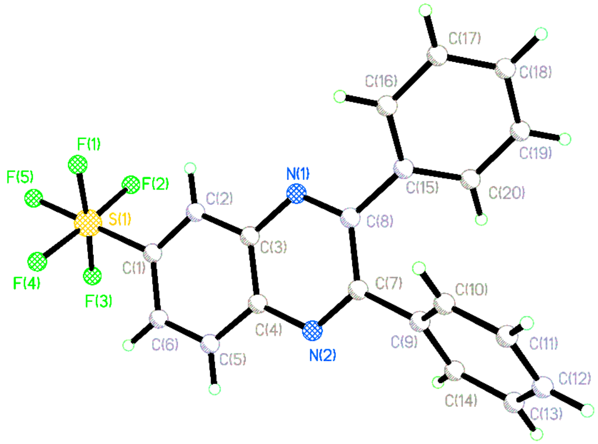
Compound 3.6

R-3
a = 19.269(4) Å
b = 19.269(5) Å
c = 11.953(4) Å
α = 90°
β = 90°
γ = 90°
V = 3843(2) Å^3
wR_2 = 0.1370
R_1 = 0.0788



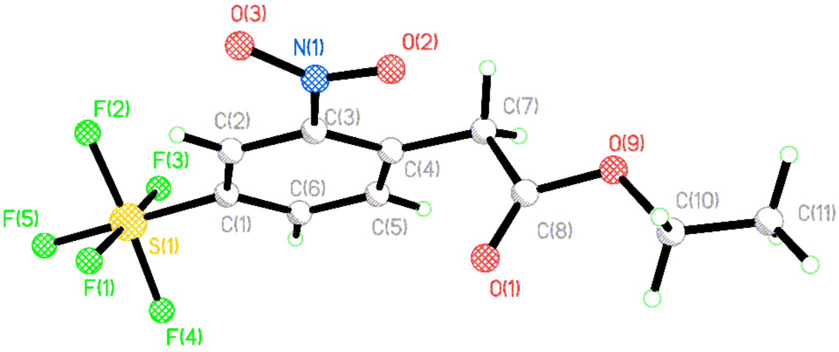
Compound 3.7

$P2_1/c$
a = 14.630(4) Å
b = 8.476(2) Å
c = 15.130(4) Å
α = 90°
β = 105.645(9)°
γ = 90°
V = 1806.7(8) Å^3
wR_2 = 0.1247
R_1 = 0.0586



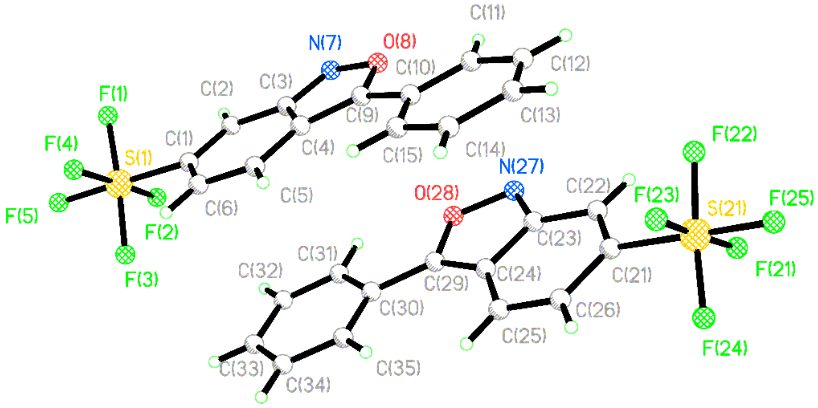
Compound 3.8

$P2_1/c$
a = 5.666(13) Å
b = 24.94(5) Å
c = 9.96(2) Å
α = 90°
β = 97.72(3)°
γ = 90°
V = 1396(5) Å^3
wR_2 = 0.2022
R_1 = 0.1365



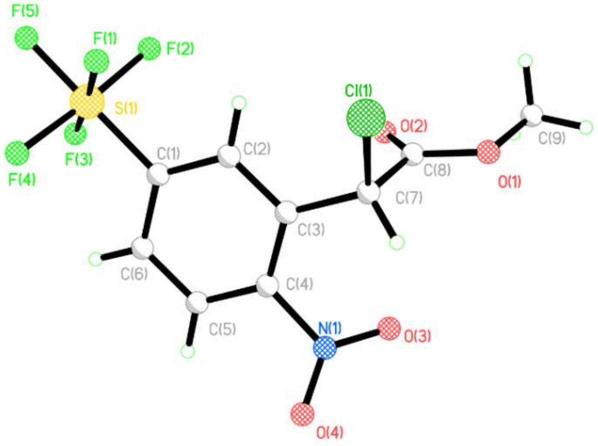
Compound 3.9

P-1
a = 9.475(5) Å
b = 10.296(5) Å
c = 13.006(7) Å
α = 88.80(2)°
β = 83.67(3)°
γ = 80.86(2)°
V = 1245.1(11) Å^3
wR_2 = 0.2309
R_1 = 0.0621



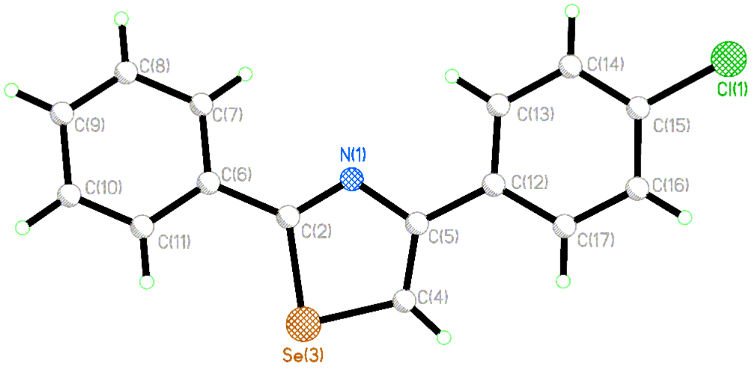
Compound 3.10

P-1
a = 5.2263(12) Å
b = 8.7375(12) Å
c = 14.619(2) Å
α = 78.36(2)º
β = 84.85(2)º
γ = 86.99(2)º
V = 650.8(2) $Å^3$
$wR_2 = 0.1493$
$R_1 = 0.0571$



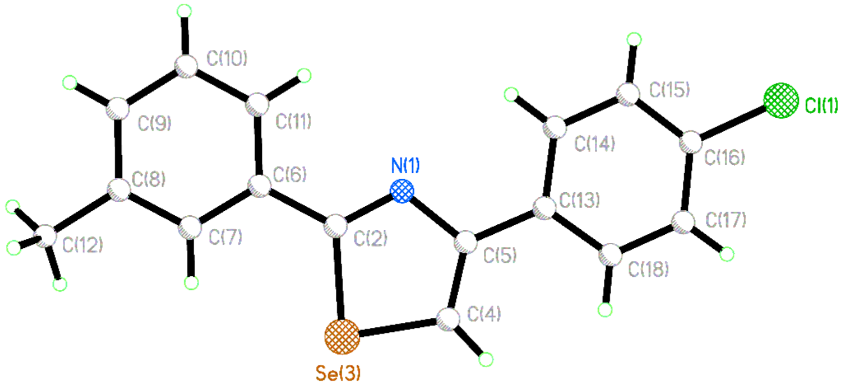
Compound 4.1

$Pca2_1$
a = 10.608(4) Å
b = 15.237(6) Å
c = 7.984(3) Å
α = 90º
β = 90º
γ = 90º
V = 1290.6(9) $Å^3$
$wR_2 = 0.2004$
$R_1 = 0.0589$



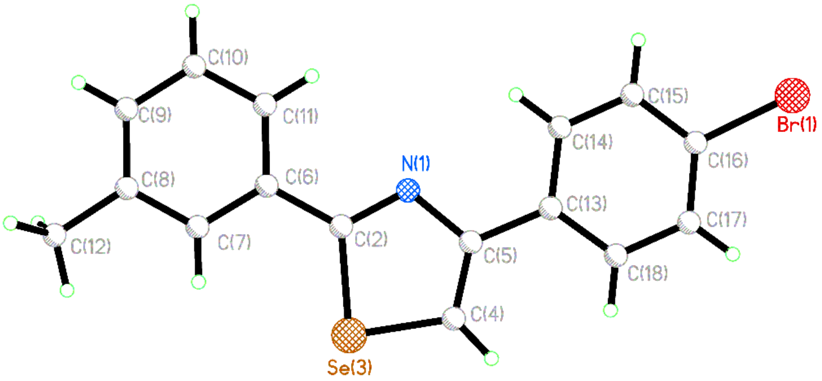
Compound 4.2

$P2_1$
a = 5.9135(7) Å
b = 7.8207(9) Å
c = 14.8420(18) Å
α = 90º
β = 92.839(7)º
γ = 90º
V = 685.57(14) $Å^3$
$wR_2 = 0.0591$
$R_1 = 0.0308$



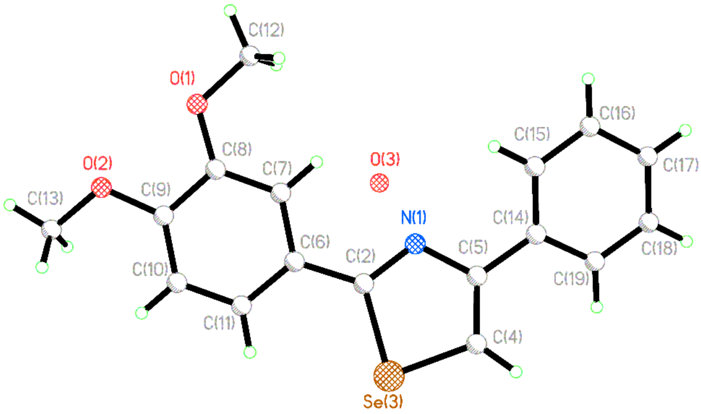
Compound 4.3

$P2_1$
a = 5.941(3) Å
b = 7.744(3) Å
c = 14.930(6) Å
α = 90º
β = 93.277(11)º
γ = 90º
V = 685.8(5) Å^3
wR$_2$ = 0.0761
R$_1$ = 0.0298



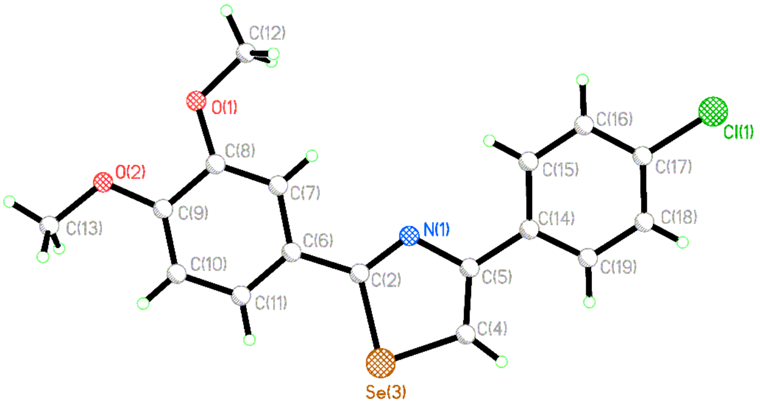
Compound 4.4

$P2_1/n$
a = 19.337(18) Å
b = 5.100(4) Å
c = 19.366(18) Å
α = 90º
β = 114.024(9)º
γ = 90º
V = 1744(3) Å^3
wR$_2$ = 0.2881
R$_1$ = 0.0827



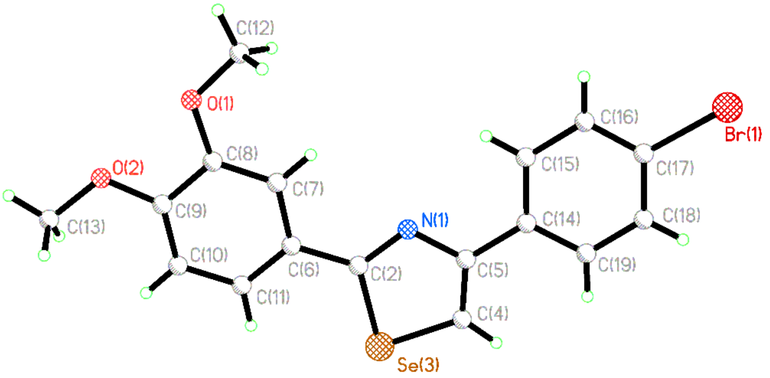
Compound 4.5

Pbca
a = 7.45(5) Å
b = 18.65(12) Å
c = 22.91(15) Å
α = 90º
β = 90º
γ = 90º
V = 3182(37) Å^3
wR$_2$ = 0.1557
R$_1$ = 0.0530



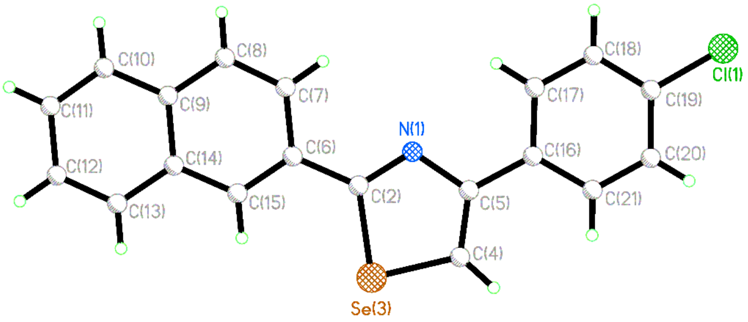
Compound 4.6

Pbca
a = 7.475(6) Å
b = 18.926(15) Å
c = 22.879(18) Å
α = 90º
β = 90º
γ = 90º
V = 3236(4) $Å^3$
wR_2 = 0.1099
R_1 = 0.0446



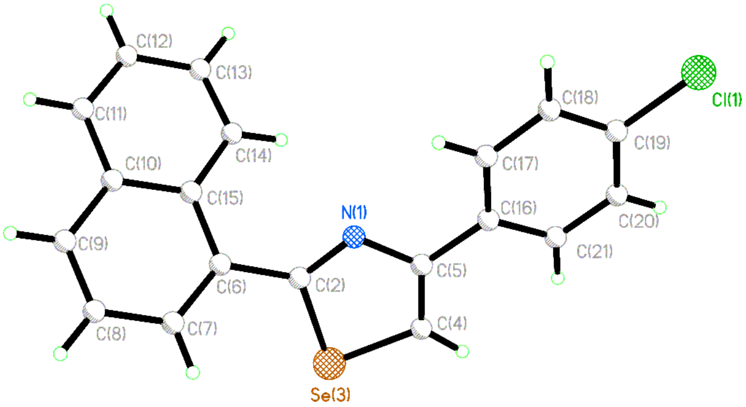
Compound 4.7

Pca2₁
a = 11.190(8) Å
b = 17.614(12) Å
c = 7.851(5) Å
α = 90º
β = 90º
γ = 90º
V = 1547.5(18) $Å^3$
wR_2 = 0.0757
R_1 = 0.0303



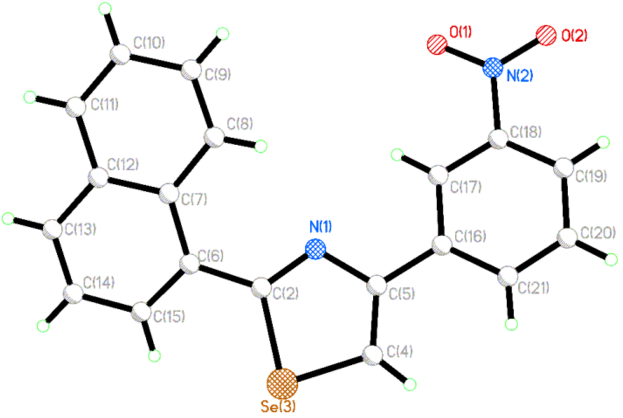
Compound 4.8

$P2_12_12_1$
a = 7.4657(9) Å
b = 8.2812(10) Å
c = 25.225(3) Å
α = 90º
β = 90º
γ = 90º
V = 1559.6(3) $Å^3$
wR_2 = 0.0948
R_1 = 0.0583



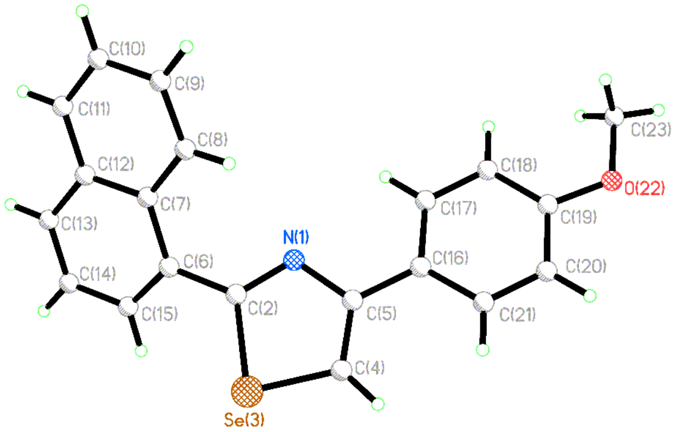
Compound 4.9

I2/a
a = 15.380(4) Å
b = 9.2019(14) Å
c = 21.514(5) Å
α = 90º
β = 92.896(17)º
γ = 90º
V = 3040.9(12) Å^3
wR_2 = 0.1311
R_1 = 0.0536



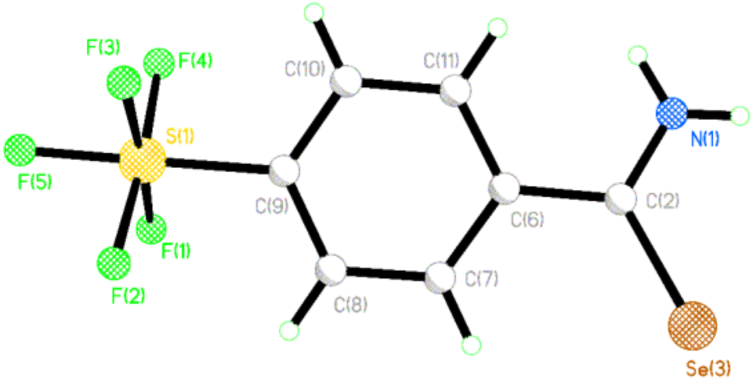
Compound 4.10

$P2_12_12_1$
a = 7.3607(6) Å
b = 8.6047(7) Å
c = 25.1739(19) Å
α = 90º
β = 90º
γ = 90º
V = 1594.4(2) Å^3
wR_2 = 0.0634
R_1 = 0.0311

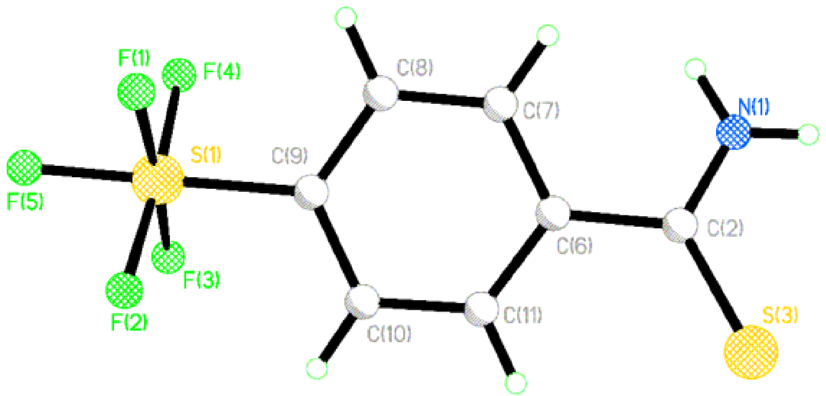


Compound 5.1

$P2_1/c$
a = 17.6082(10) Å
b = 5.871(2) Å
c = 10.079(5) Å
α = 90º
β = 106.40(2)º
γ = 90º
V = 999.6(6) Å^3
wR_2 = 0.1682
R_1 = 0.0620

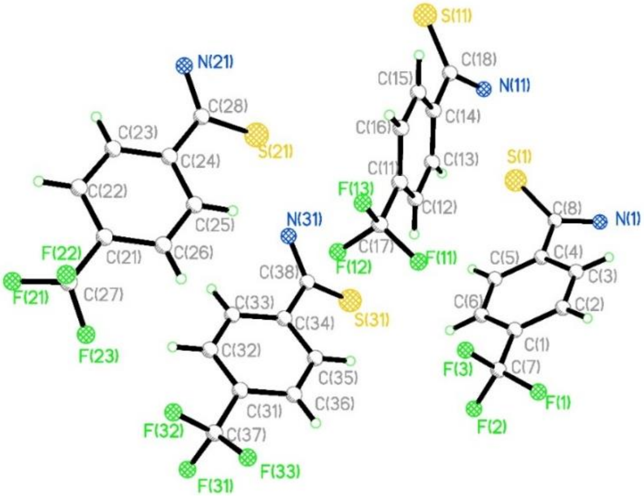


Compound 5.2



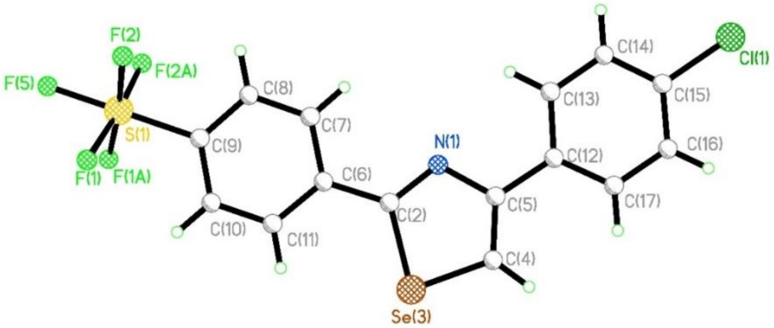
$P2_1/c$
a = 17.3607(10) Å
b = 5.750(3) Å
c = 10.038(6) Å
α = 90º
β = 105.53(3)º
γ = 90º
V = 965.4(8) Å^3
wR$_2$ = 0.1845
R$_1$ = 0.0690

Compound 5.3



$Pca2_1$
a = 8.533(2) Å
b = 20.415(5) Å
c = 19.854(5) Å
α = 90º
β = 90º
γ = 90º
V = 3459(2) Å^3
wR$_2$ = 0.1798
R$_1$ = 0.0595

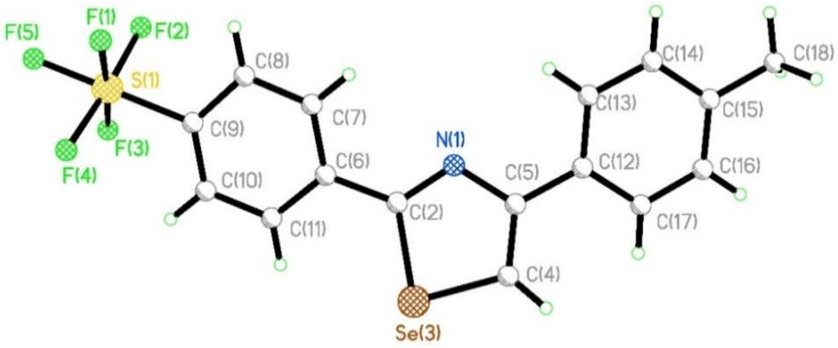
Compound 5.4



$Pnma$
a = 12.536(3) Å
b = 6.791(2) Å
c = 18.646(4) Å
α = 90º
β = 90º
γ = 90º
V = 1587.3(5) Å^3
wR$_2$ = 0.0981
R$_1$ = 0.0497

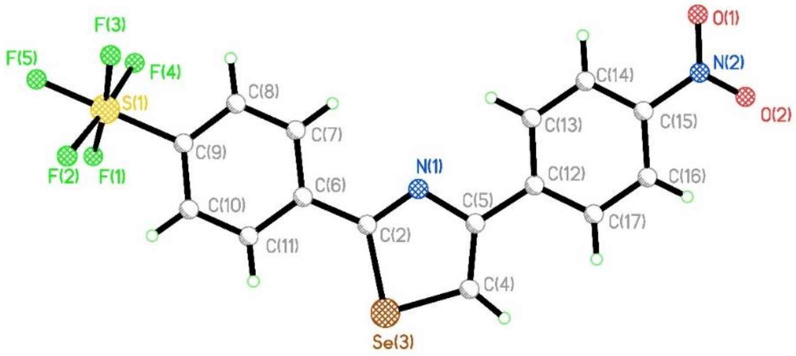
Compound 5.5

$Pna2_1$
a = 7.789(9) Å
b = 33.34(4) Å
c = 6.278(7) Å
α = 90º
β = 90º
γ = 90º
V = 1630(3) Å^3
wR$_2$ = 0.1184
R$_1$ = 0.0523



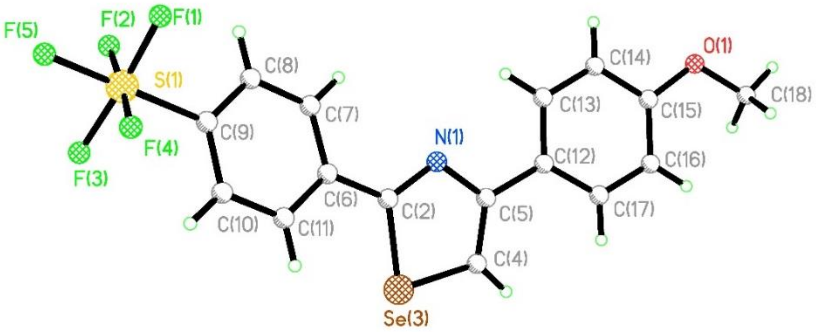
Compound 5.6

$P2_12_12_1$
a = 6.761(4) Å
b = 12.748(7) Å
c = 18.642(12) Å
α = 90º
β = 90º
γ = 90º
V = 1606.8(17) Å^3
wR$_2$ = 0.1049
R$_1$ = 0.0469



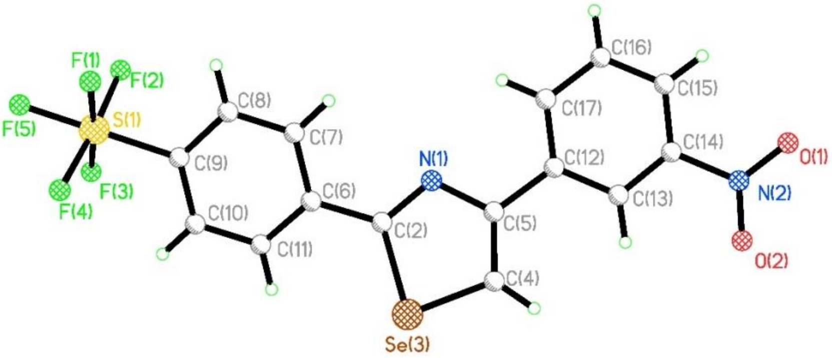
Compound 5.7

$C2/c$
a = 35.77(5) Å
b = 6.207(8) Å
c = 15.93(2) Å
α = 90º
β = 107.028(14)º
γ = 90º
V = 3381(8) Å^3
wR$_2$ = 0.1693
R$_1$ = 0.0559



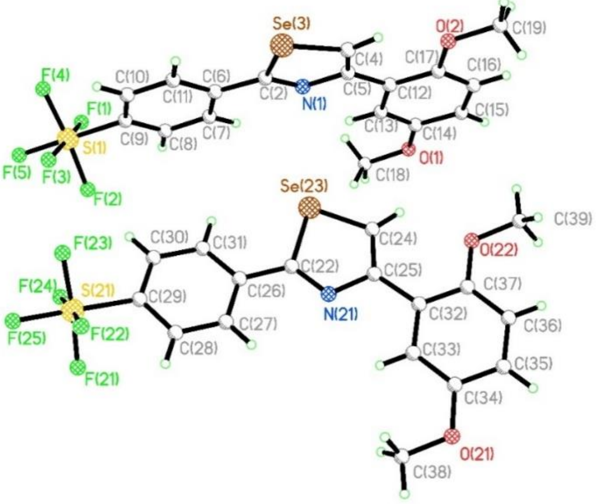
Compound 5.8

P-1
a = 7.911(11) Å
b = 10.425(15) Å
c = 11.609(16) Å
α = 109.181(3)º
β = 109.088(11)º
γ = 100.490(13)º
V = 808.4(19) Å^3
wR$_2$ = 0.1207
R$_1$ = 0.0499



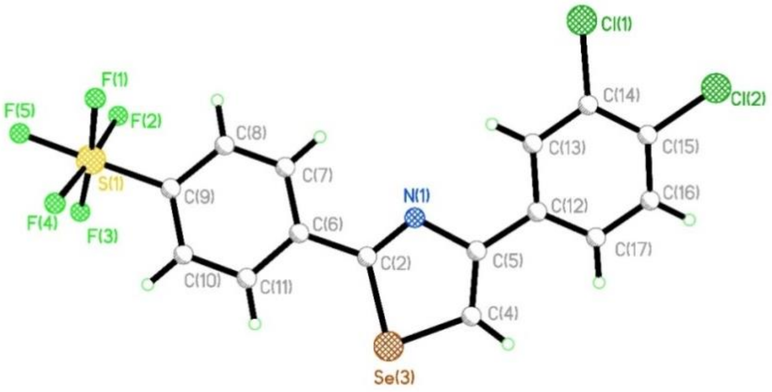
Compound 5.9

P-1
a = 9.650(4) Å
b = 12.717(5) Å
c = 15.930(7) Å
α = 77.557(12)º
β = 75.918(11)º
γ = 77.430(13)º
V = 1823.2(13) Å^3
wR$_2$ = 0.1107
R$_1$ = 0.0371



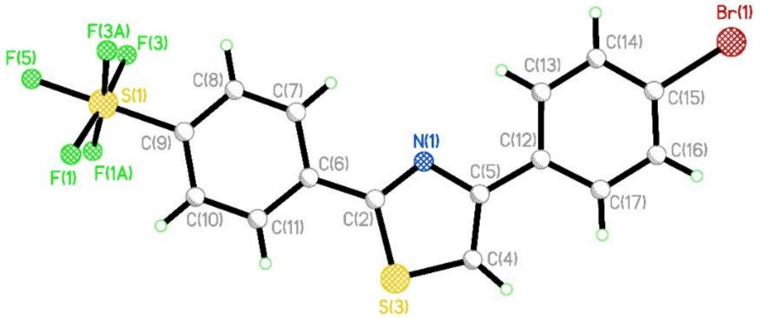
Compound 5.10

$P2_1/n$
a = 15.288(8) Å
b = 5.682(3) Å
c = 19.113(10) Å
α = 90º
β = 101.979(11)º
γ = 90º
V = 1624.1(15) Å^3
wR$_2$ = 0.2004
R$_1$ = 0.0706



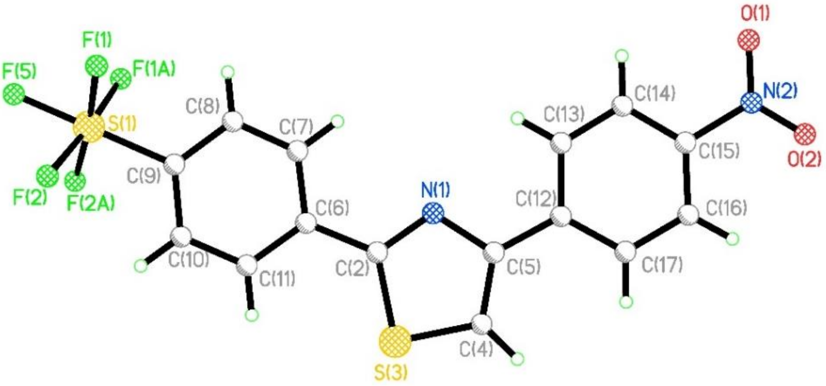
Compound 5.11

Pnma
a = 12.804(3) Å
b = 6.7729(16) Å
c = 18.485(4) Å
α = 90º
β = 90º
γ = 90º
V = 1603.0(6) $Å^3$
wR_2 = 0.1510
R_1 = 0.056



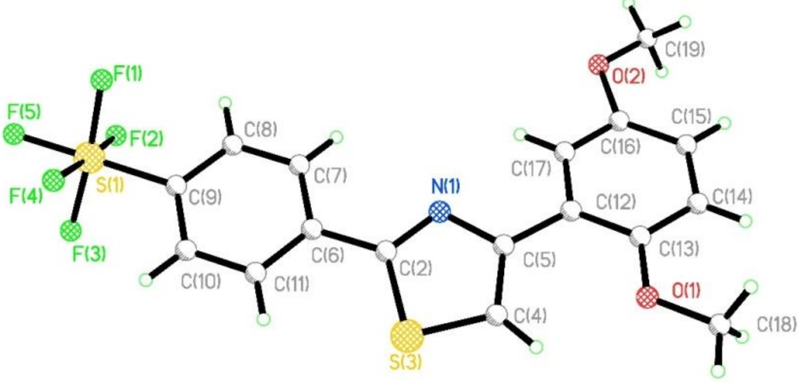
Compound 5.12

Pnma
a = 12.889(8) Å
b = 6.737(4) Å
c = 18.371(12) Å
α = 90º
β = 90º
γ = 90º
V = 1595.1(18) $Å^3$
wR_2 = 0.1504
R_1 = 0.0495



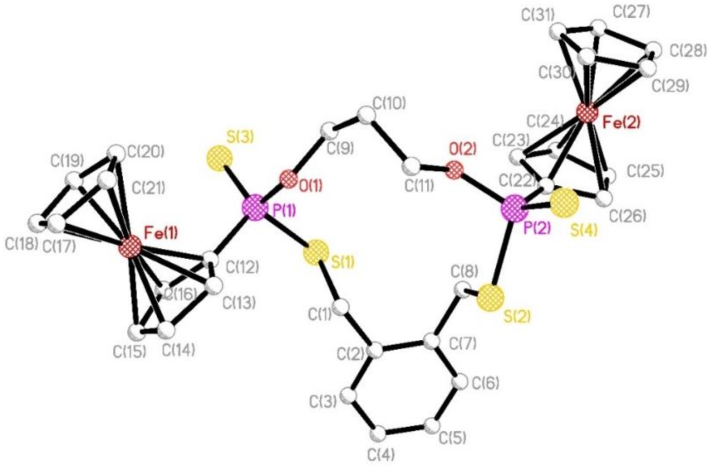
Compound 5.13

$P2_1/c$
a = 12.075(10) Å
b = 9.345(7) Å
c = 16.111(13) Å
α = 90º
β = 106.76(3)º
γ = 90º
V = 1741(3) $Å^3$
wR_2 = 0.3828
R_1 = 0.1192



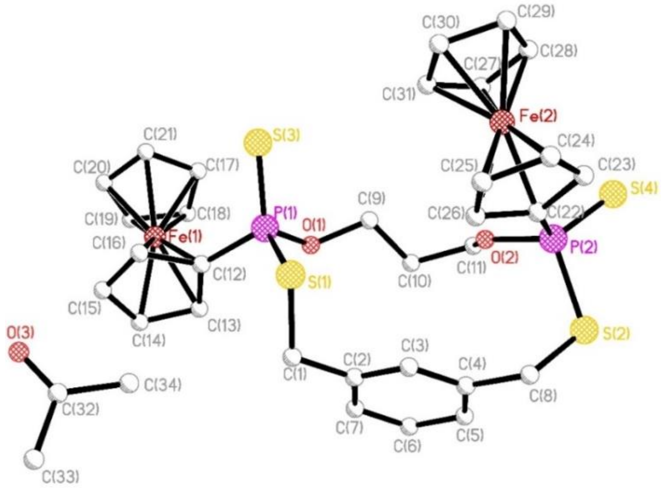
Compound 6.1

$P2_1/c$
a = 28.792(9) Å
b = 7.574(2) Å
c = 14.883(5) Å
α = 90º
β = 94.755(8)º
γ = 90º
V = 3234.5(17) Å^3
wR$_2$ = 0.1717
R$_1$ = 0.0730



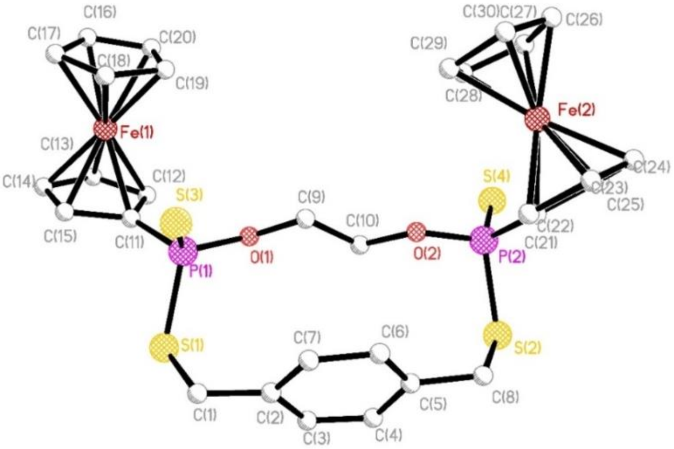
Compound 6.2

$P2_1/c$
a = 14.260(3) Å
b = 10.367(2) Å
c = 24.945(6) Å
α = 90º
β = 105.930(6)º
γ = 90º
V = 3545.9(14) Å^3
wR$_2$ = 0.1377
R$_1$ = 0.0757



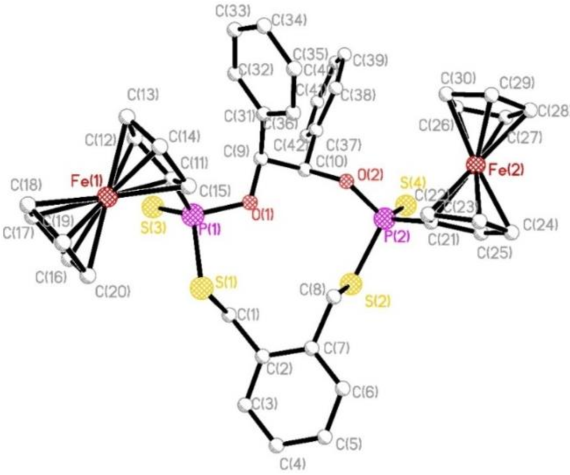
Compound 6.3

$P\text{-}1$
a = 10.079(2) Å
b = 10.892(3) Å
c = 14.675(3) Å
α = 90º
β = 72.080(18)º
γ = 90º
V = 1508.8(7) Å^3
wR$_2$ = 0.2318
R$_1$ = 0.0728



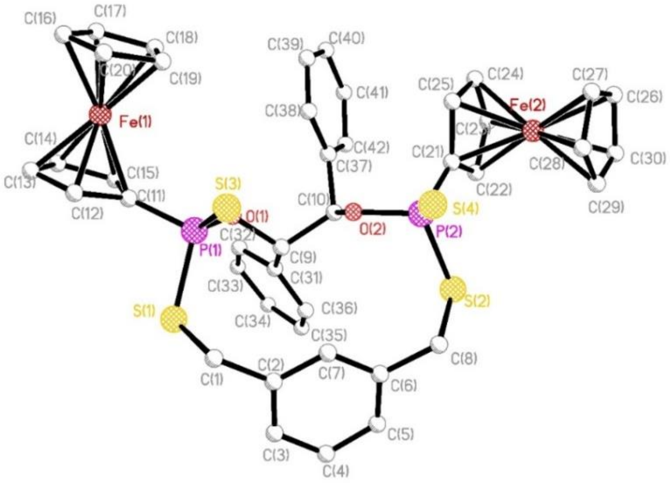
Compound 6.4

Pbca
a = 12.4114(17) Å
b = 22.626(3) Å
c = 28.013(3) Å
α = 90º
β = 90º
γ = 90º
V = 7866.7(18) Å^3
wR$_2$ = 0.1714
R$_1$ = 0.0736



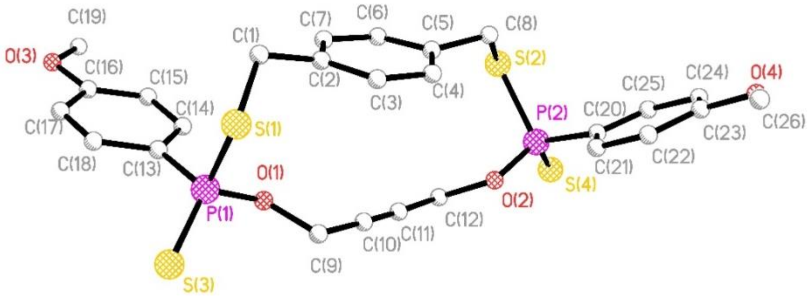
Compound 6.5

P-1
a = 10.0572(13) Å
b = 12.698(2) Å
c = 16.365(2) Å
α = 83.638(16)º
β = 74.068(16)º
γ = 73.326(14)º
V = 1924.0(5) Å^3
wR$_2$ = 0.1269
R$_1$ = 0.0604



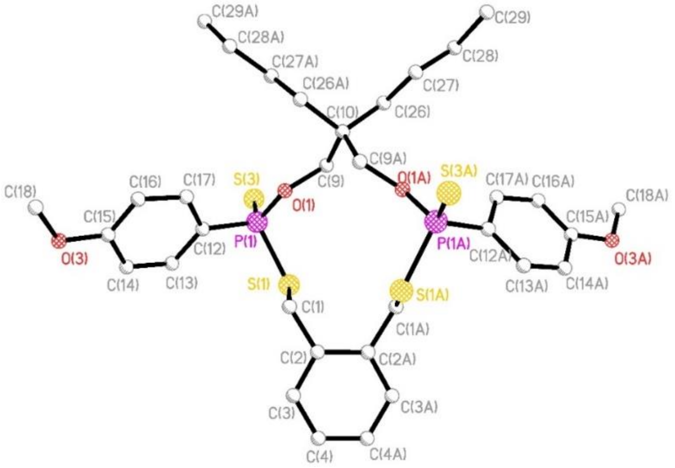
Compound 6.6

Pna21
a = 15.528(5) Å
b = 25.426(8) Å
c = 7.073(2) Å
α = 90º
β = 90º
γ = 90º
V = 2792.4(15) Å^3
wR$_2$ = 0.1489
R$_1$ = 0.0897



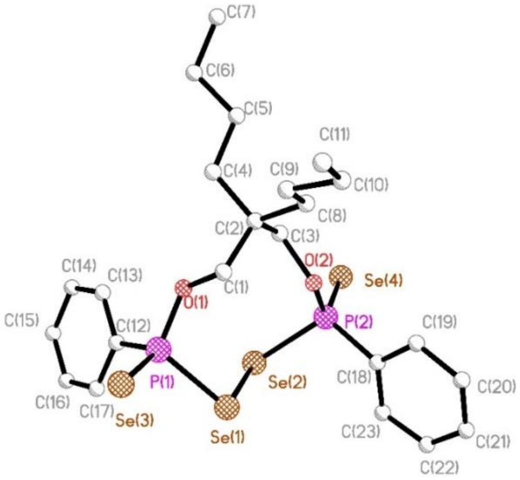
Compound 6.7

C2/c
a = 25.103(11) Å
b = 13.921(6) Å
c = 10.351(5) Å
α = 90º
β = 95.719(9)º
γ = 90º
V = 3599(3) Å^3
$wR_2 = 0.1994$
$R_1 = 0.0699$



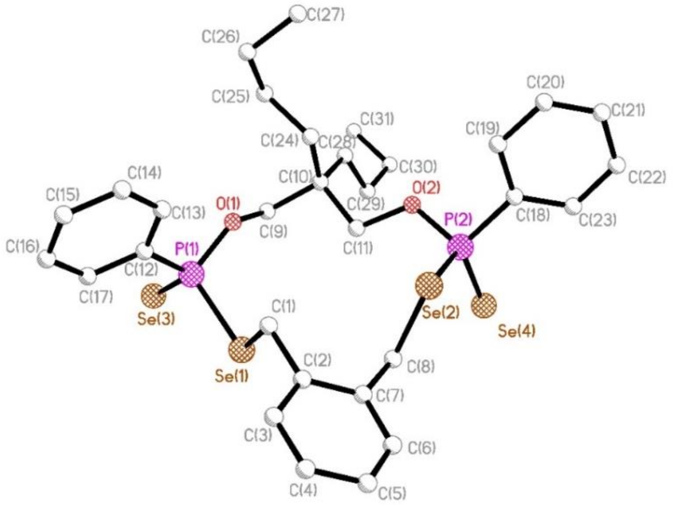
Compound 6.8

P-1
a = 9.357(4) Å
b = 12.332(4) Å
c = 13.609(4) Å
α = 116.45(2)º
β = 95.79(4)º
γ = 93.31(3)º
V = 1389.4(9) Å^3
$wR_2 = 0.2675$
$R_1 = 0.0943$



Compound 6.9

C2/c
a = 29.933(9) Å
b = 9.062(2) Å
c = 24.805(7) Å
α = 90º
β = 98.190(8)º
γ = 90º
V = 6660(3) Å^3
$wR_2 = 0.2190$
$R_1 = 0.0840$

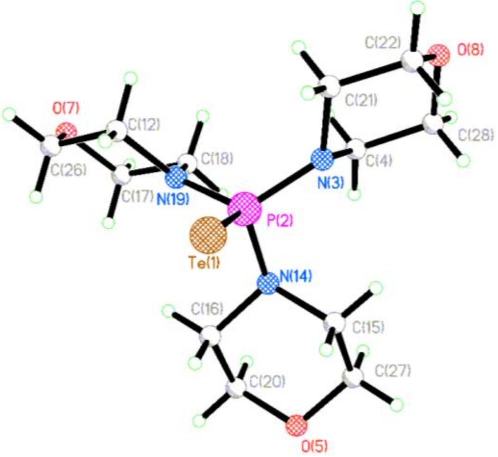


APPENDIX II

CRYSTAL SREUCTURES DETERMINED, NOT DISCUSSED IN THIS THESIS

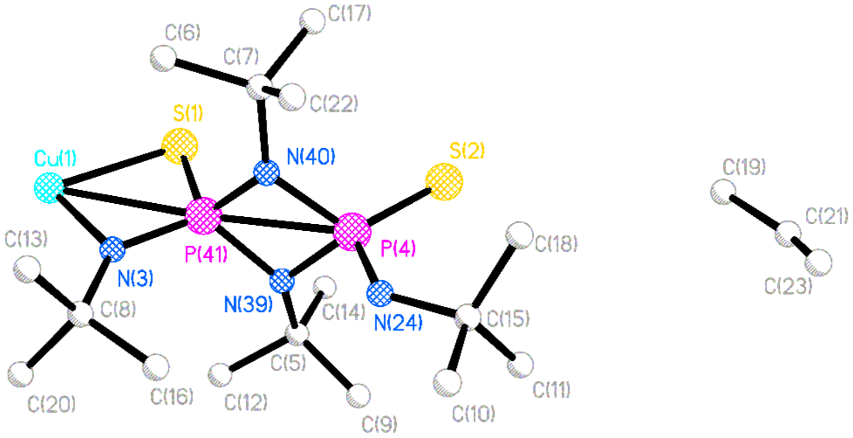
Compound 1

$P2_1/n$
a = 8.736(2) Å
b = 15.160(4) Å
c = 12.033(3) Å
α = 90º
β = 98.281(7)º
γ = 90º
V = 1577.0(7) Å^3
wR$_2$ = 0.1382
R$_1$ = 0.0332



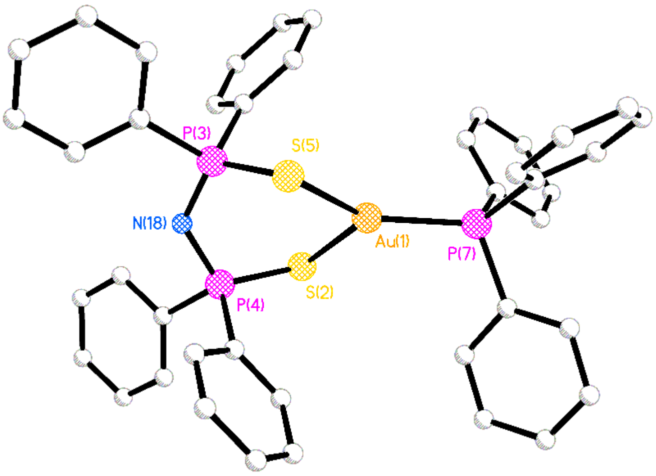
Compound 2

C2/c
a = 25.951(10) Å
b = 16.859(8) Å
c = 12.749(7) Å
α = 90º
β = 96.273(12)º
γ = 90º
V = 5545(4) Å^3
wR$_2$ = 0.2844
R$_1$ = 0.0887



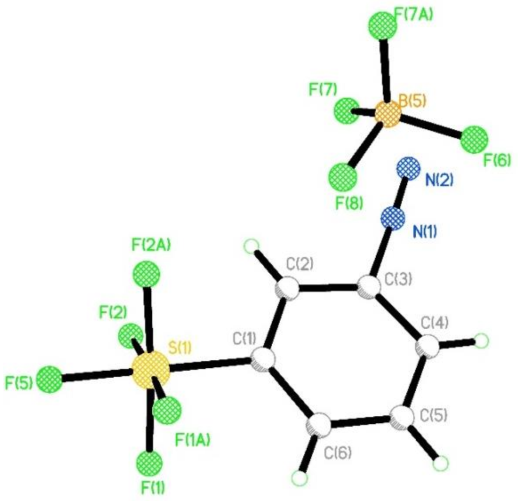
Compound 3

P-1
a = 8.9300(7) Å
b = 12.0100(10) Å
c = 18.480(2) Å
α = 78.000(6)º
β = 80.000(6)º
γ = 74.000(6)º
V = 1849.2(3) Å^3
wR$_2$ = 0.0809
R$_1$ = 0.0374



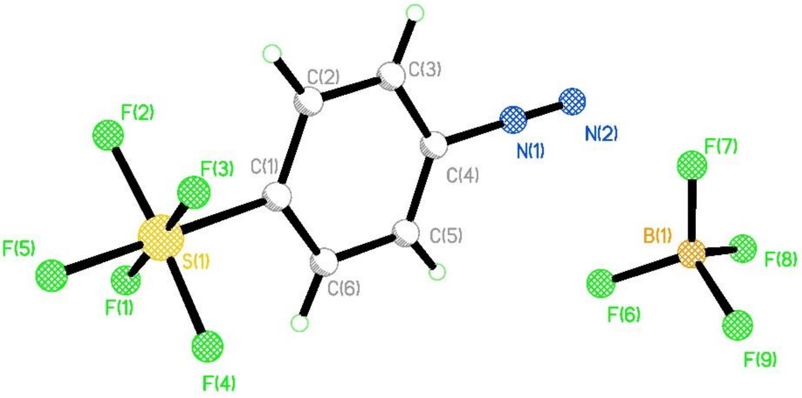
Compound 4

Pnma
a = 16.798(13) Å
b = 7.072(5) Å
c = 9.043(7) Å
α = 90º
β = 90º
γ = 90º
V = 1074.2(14) $Å^3$
wR_2 = 0.2938
R_1 = 0.0806



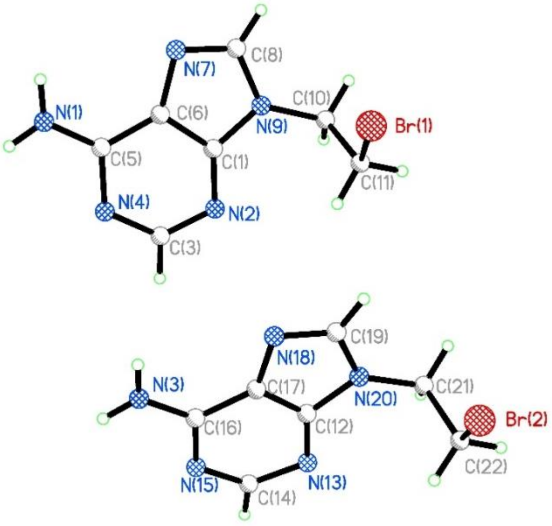
Compound 5

Pbca
a = 10.822(2) Å
b = 17.875(3) Å
c = 34.803(6) Å
α = 90º
β = 90º
γ = 90º
V = 6733(2) $Å^3$
wR_2 = 0.2412
R_1 = 0.1339



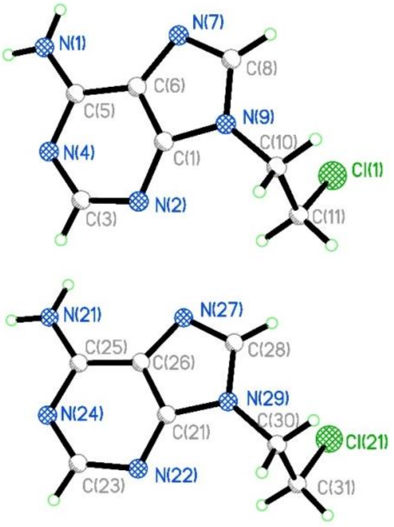
Compound 6

P-1
a = 4.811(6) Å
b = 12.35(2) Å
c = 15.69(2) Å
α = 104.97(4)º
β = 92.97(5)º
γ = 97.57(4)º
V = 889(2) $Å^3$
wR_2 = 0.1620
R_1 = 0.0549



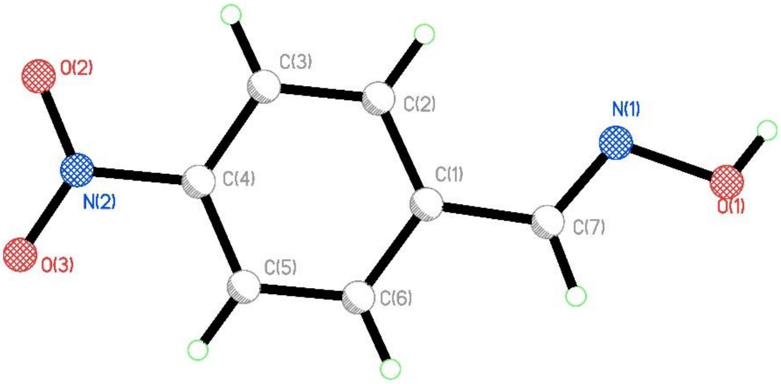
Compound 7

P-1
a = 4.6262(7) Å
b = 12.433(2) Å
c = 15.468(3) Å
α = 104.224(8)º
β = 92.459(7)º
γ = 97.076(7)º
V = 853.4(3) Å^3
wR_2 = 0.1195
R_1 = 0.0665



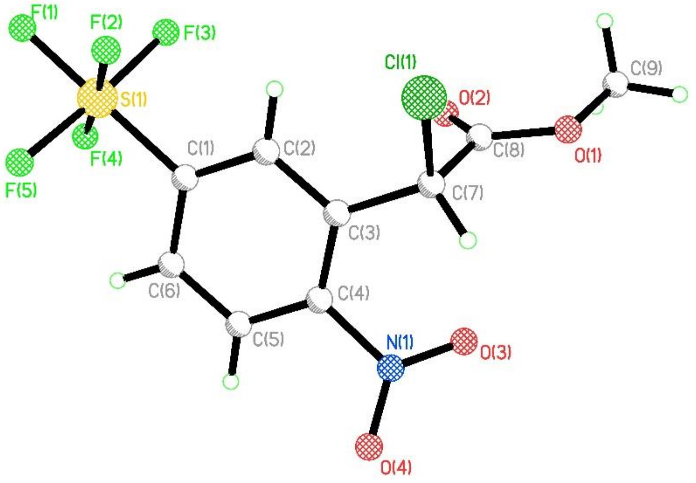
Compound 8

$P2_1/c$
a = 6.268(6) Å
b = 4.872(5) Å
c = 24.53(3) Å
α = 90º
β = 94.681(11)º
γ = 90º
V = 746.7(12) Å^3
wR_2 = 0.1783
R_1 = 0.0649

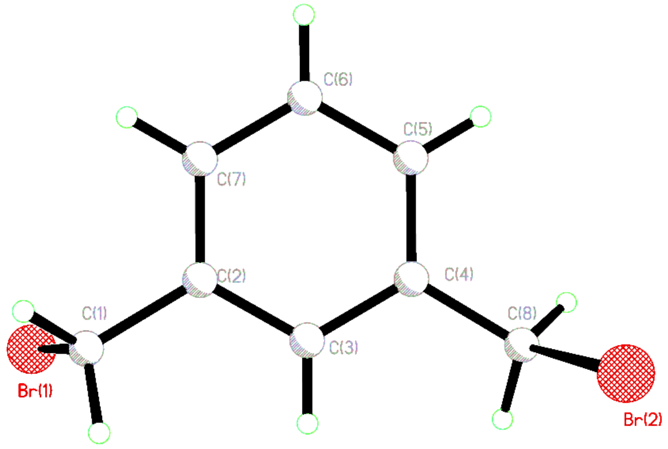


Compound 9

P-1
a = 5.251(10) Å
b = 8.77(2) Å
c = 14.70(3) Å
α = 78.31(4)º
β = 84.85(4)º
γ = 87.02(4)º
V = 660(2) Å^3
wR_2 = 0.1820
R_1 = 0.0878

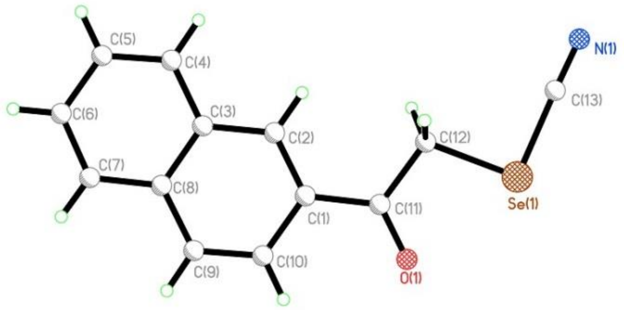


Compound 10



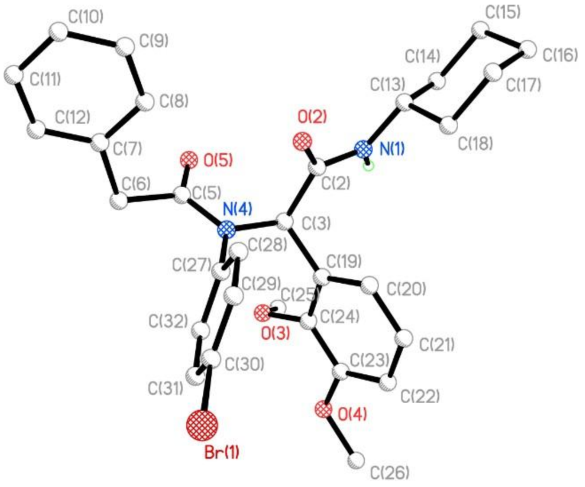
$P2_1/n$
a = 12.947(2) Å
b = 4.4824(6) Å
c = 14.999(2) Å
α = 90º
β = 94.472(7)º
γ = 90º
V = 867.8(2) Å^3
wR_2 = 0.3228
R_1 = 0.1077

Compound 11



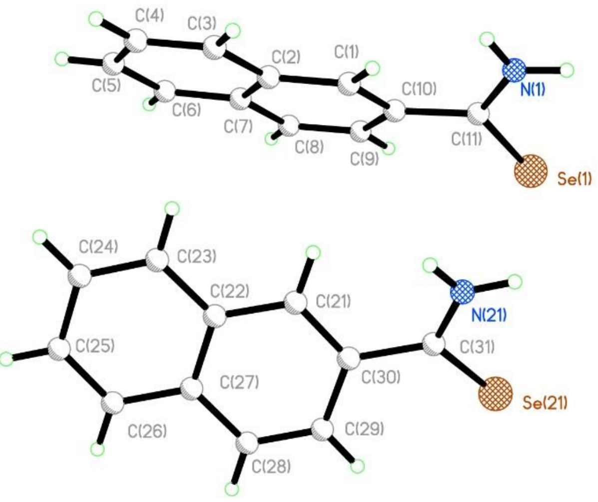
$P2_1/c$
a = 5.0460(7) Å
b = 20.857(3) Å
c = 10.8508(15) Å
α = 90º
β = 94.904(7) º
γ = 90º
V = 1137.8(3) Å^3
wR_2 = 0.1162
R_1 = 0.0662

Compound 12



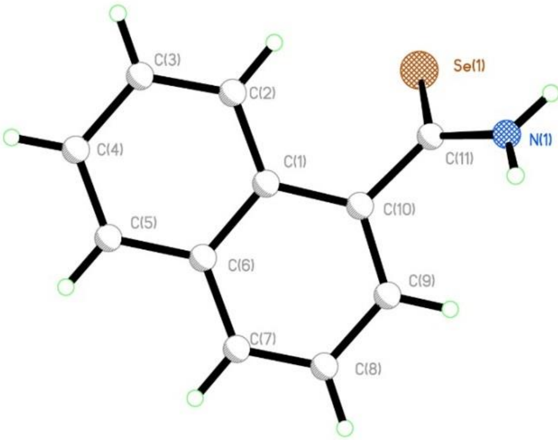
P-1
a = 11.144(15) Å
b = 11.175(14) Å
c = 12.118(13) Å
α = 79.53(4) º
β = 72.75(3) º
γ = 89.49(4) º
V = 1416(3) Å^3
wR_2=0.1831
R_1=0.0677

Compound 13



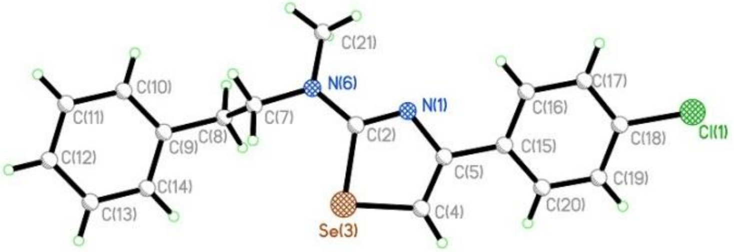
C2/c
a = 21.669(5) Å
b = 6.0922(13) Å
c = 29.488(7) Å
α = 90º
β = 106.496(5)º
γ = 90º
V = 3732.5(15) Å^3
$wR_2 = 0.1348$
$R_1 = 0.0329$

Compound 14



P-1
a = 7.082(4) Å
b = 8.270(4) Å
c = 8.471(5) Å
α = 84.45(4)º
β = 84.17(4)º
γ = 70.41(3)º
V = 464.5(5) Å^3
$wR_2 = 0.1755$
$R_1 = 0.0438$

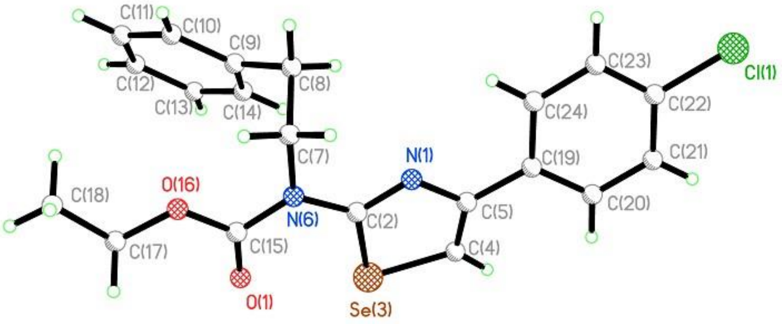
Compound 15



P21
a = 10.657(8) Å
b = 7.525(5) Å
c = 11.320(8) Å
α = 90º
β = 115.852(8)º
γ = 90º
V = 817.0(10) Å^3
$wR_2 = 0.1681$
$R_1 = 0.0574$

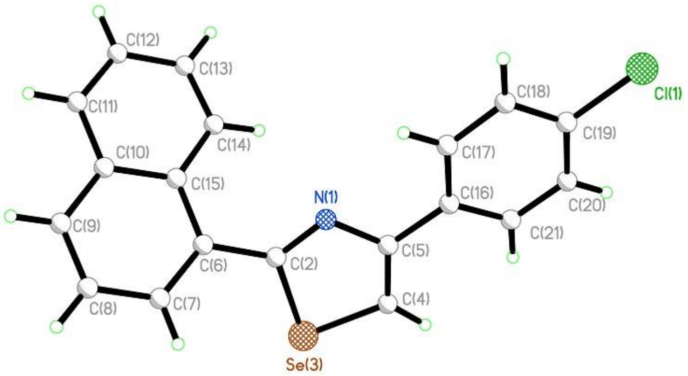
Compound 16

Pbca
a = 27.974(17) Å
b = 17.910(11) Å
c = 7.817(5) Å
α = 90º
β = 90º
γ = 90º
V = 3916(4) Å^3
wR$_2$ = 0.1548
R$_1$ = 0.0637



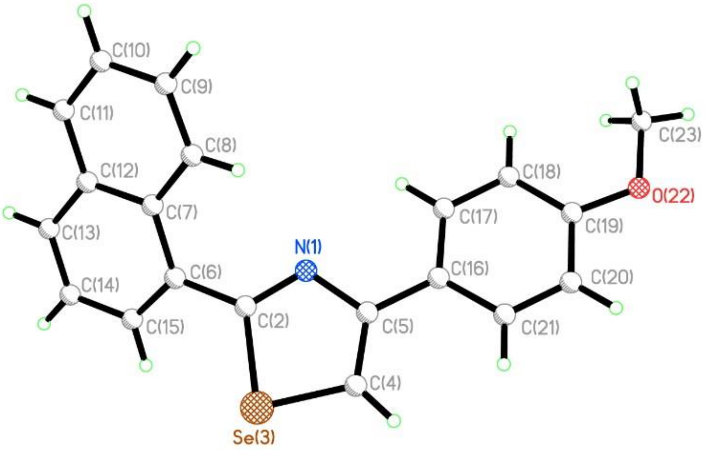
Compound 17

$P2_12_12_1$
a = 7.4657(9) Å
b = 8.2812(10) Å
c = 25.225(3) Å
α = 90º
β = 90º
γ = 90º
V = 1559.5(3) Å^3
wR$_2$ = 0.1985
R$_1$ = 0.0853



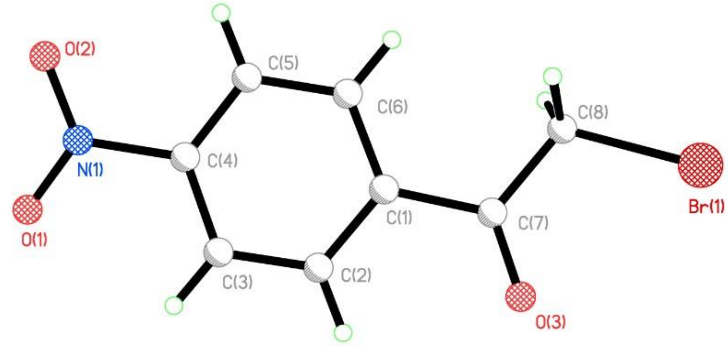
Compound 18

$P2_12_12_1$
a = 7.3607(6) Å
b = 8.6047(7) Å
c = 25.1739(19) Å
α = 90º
β = 90º
γ = 90º
V = 1594.4(2) Å^3
wR$_2$ = 0.1678
R$_1$ = 0.0620



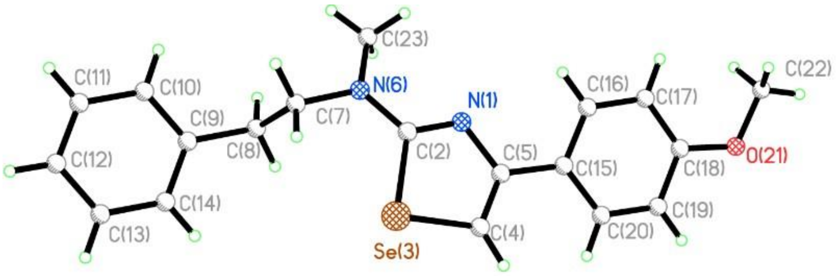
Compound 19

$P2_1/c$
a =7.167(3) Å
b = 10.3149(17) Å
c = 12.359(2) Å
α = 90º
β = 90º
γ = 90º
V = 877.7(4) Å^3
wR$_2$ = 0.0872
R$_1$ = 0.0385



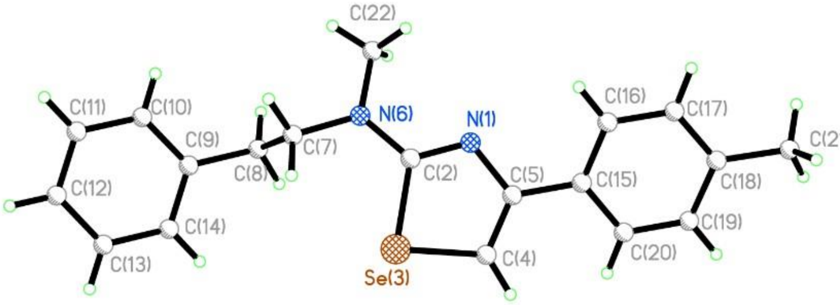
Compound 20

$P2_12_12_1$
a = 6.6544(8) Å
b = 7.8134(10) Å
c = 33.372(4) Å
α = 90º
β = 90º
γ = 90º
V = 1735.1(4) Å^3
wR$_2$ = 0.1279
R$_1$ = 0.0818



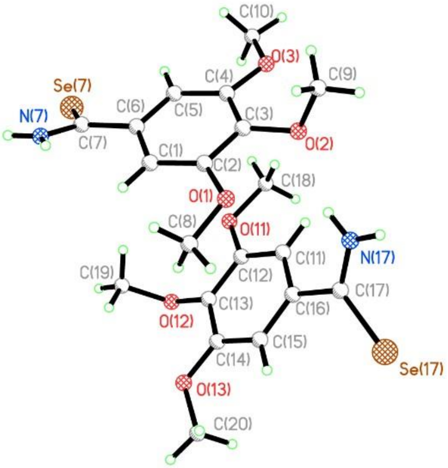
Compound 21

$P2_1$
a = 10.719(4) Å
b = 7.495(3) Å
c = 11.294(4) Å
α = 90º
β = 115.650(7)º
γ = 90º
V = 817.0(5) Å^3
wR$_2$ = 0.1520
R$_1$ = 0.0401



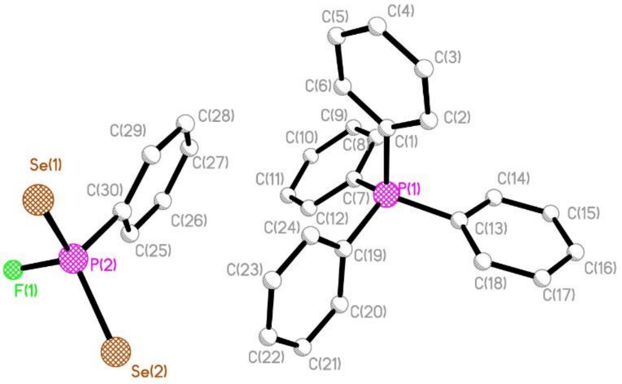
Compound 22

P-1
a = 7.4435(18) Å
b = 8.561(2) Å
c = 19.334(5) Å
α = 101.778(10)º
β = 91.940(7)º
γ = 94.895(15)º
V = 1200.0(5) Å^3
wR_2 = 0.1537
R_1 = 0.0650



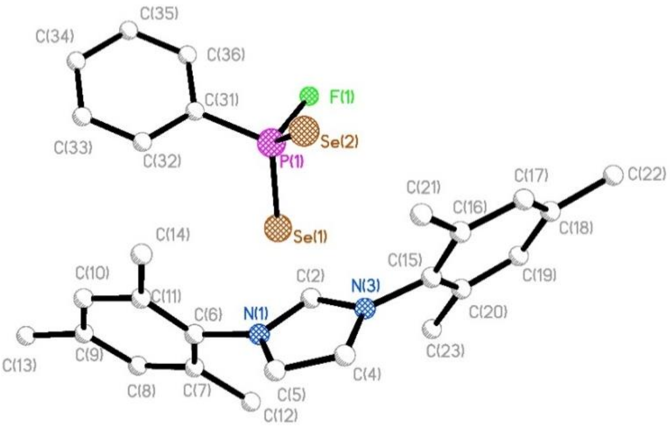
Compound 23

P-1
a = 9.457(6) Å
b = 11.618(7) Å
c = 14.142(7) Å
α = 111.67(4)º
β = 105.41(3)º
γ = 97.26(2)º
V = 1347.7(15) Å^3
wR_2 = 0.1257
R_1 = 0.0470



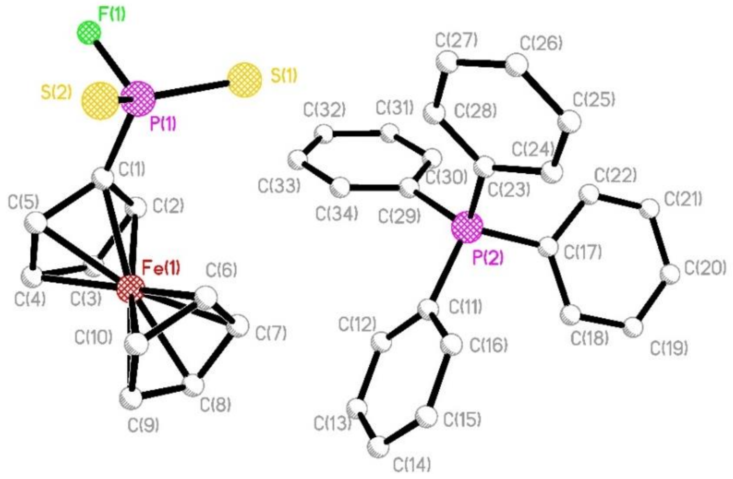
Compound 24

Cc
a = 11.596(5) Å
b = 15.549(6) Å
c = 15.368(7) Å
α = 90º
β = 106.325(11)º
γ = 90º
V = 2659(2) Å^3
wR_2 = 0.1024
R_1 = 0.0563



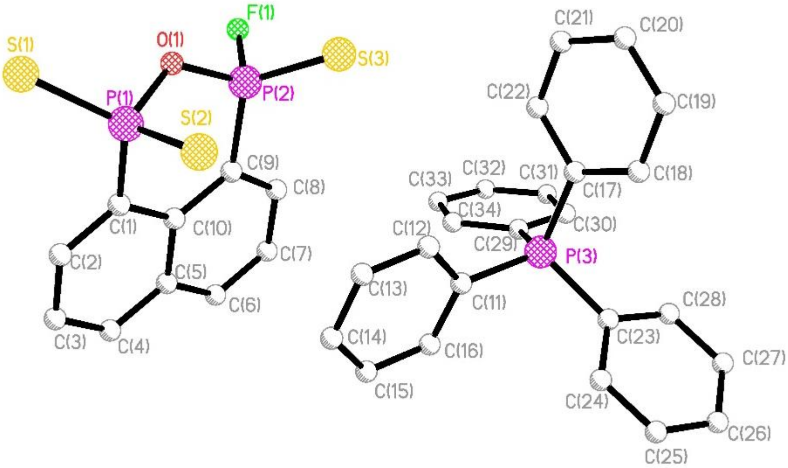
Compound 25

$P2_1/n$
a = 11.704(2) Å
b = 17.994(2) Å
c = 14.981(3) Å
α = 90º
β = 106.902(9)º
γ = 90º
V = 3018.6(9) Å^3
wR$_2$ = 0.1262
R$_1$ = 0.0837



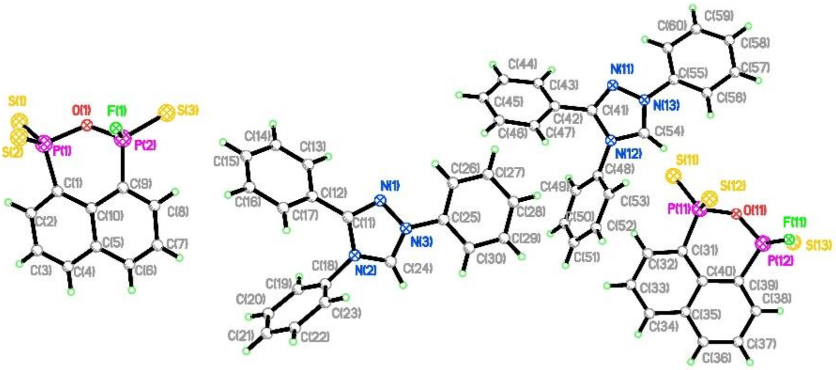
Compound 26

$P2_1/c$
a = 9.563(3) Å
b = 16.876(5) Å
c = 19.258(6) Å
α = 90º
β = 93.820(8)º
γ = 90º
V = 3101(2) Å^3
wR$_2$ = 0.2901
R$_1$ = 0.1053



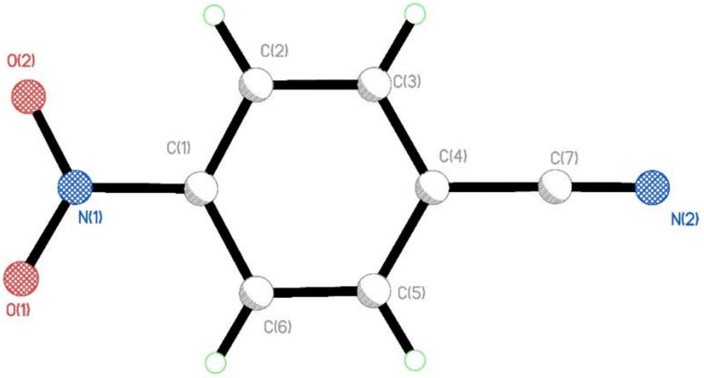
Compound 27

$P\text{-}1$
a = 9.992(5) Å
b = 16.808(8) Å
c = 18.117(8) Å
α = 104.020(12)º
β = 90.270(10)º
γ = 104.404(11)º
V = 2852(3) Å^3
wR$_2$ = 0.3522
R$_1$ = 0.1008



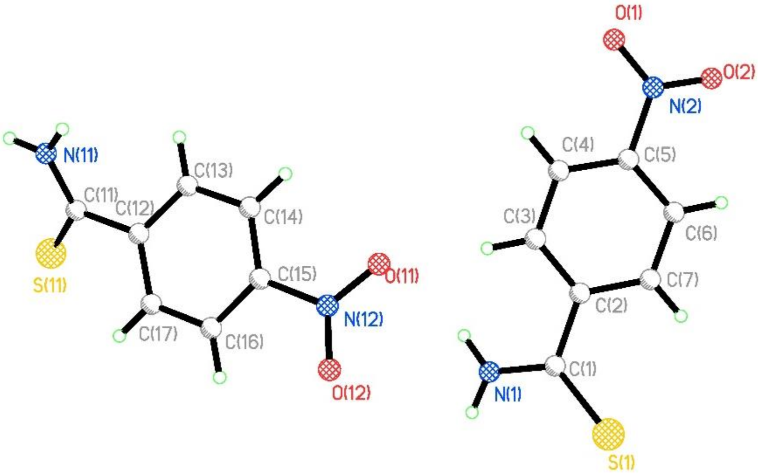
Compound 28

$P2_1$
a = 3.784(2) Å
b = 7.040(4) Å
c = 12.505(7) Å
α = 90º
β = 92.30(2)º
γ = 90º
V = 332.8(3) Å^3
wR_2 = 0.1973
R_1 = 0.0559



Compound 29

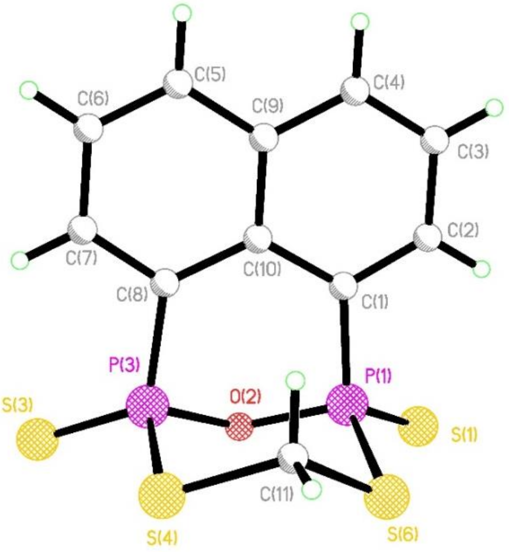
P-1
a = 3.8983(7) Å
b = 12.277(2) Å
c = 16.432(3) Å
α = 86.039(9)º
β = 86.802(8)º
γ = 82.874(7)º
V = 777.6(3) Å^3
wR_2 = 0.1494
R_1 = 0.0468



Compound 30

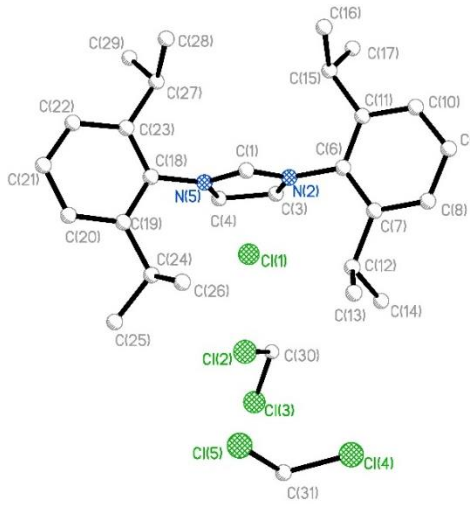
$P2_1/n$
a = 11.171(3) Å

b = 8.618(3) Å
c = 14.122(4) Å
α = 90º
β = 99.002(6)º
γ = 90º
V = 1342.8(7) Å^3
wR_2 = 0.0886
R_1 = 0.0440



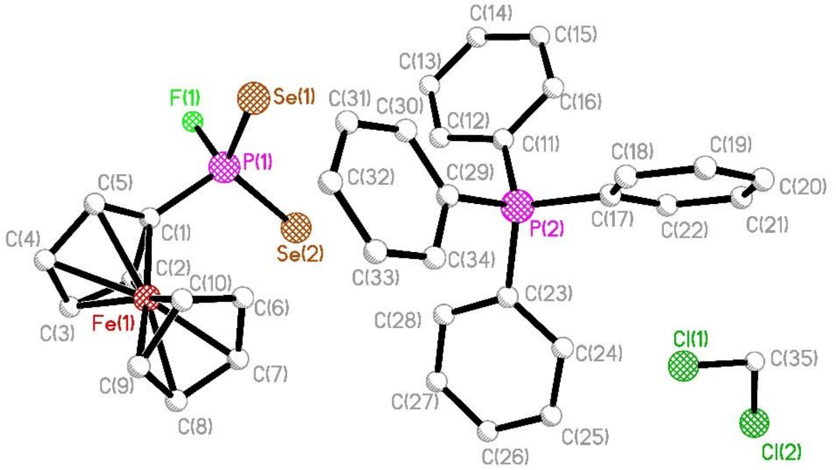
Compound 31

$P2_1/c$
a = 10.895(4) Å
b = 16.471(5) Å
c = 18.191(6) Å
α = 90º
β = 101.104(9)º
γ = 90º
V = 3203(2) Å^3
wR$_2$ = 0.3372
R$_1$ = 0.1346



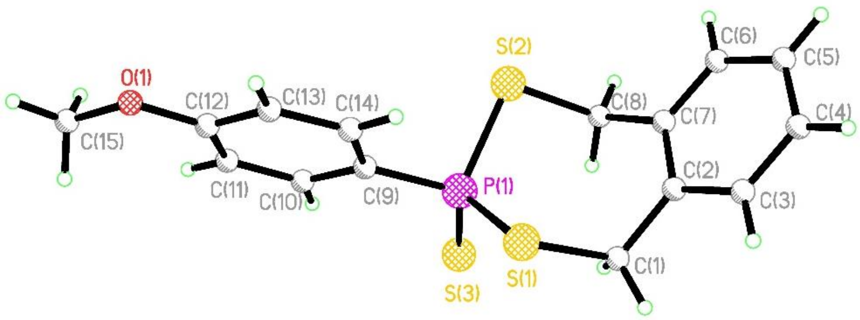
Compound 32

P-1
a = 10.418(2) Å
b = 12.458(2) Å
c = 13.191(2) Å
α = 78.660(8)º
β = 82.532(9)º
γ = 80.240(9)º
V = 1646.0(4) Å^3
wR$_2$ = 0.1598
R$_1$ = 0.0433

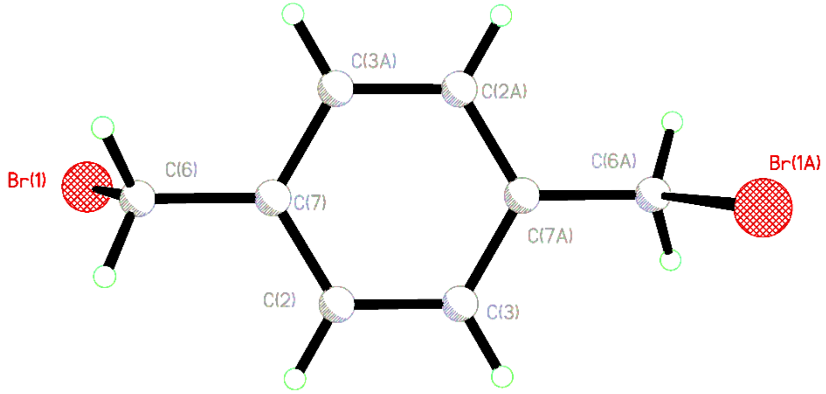


Compound 33

$P2_1/c$
a = 12.876(12) Å
b = 15.374(12) Å
c = 8.382(8) Å
α = 90º
β = 107.58(2)º
γ = 90º
V = 1582(3) Å^3
wR$_2$ = 0.2839
R$_1$ = 0.0883

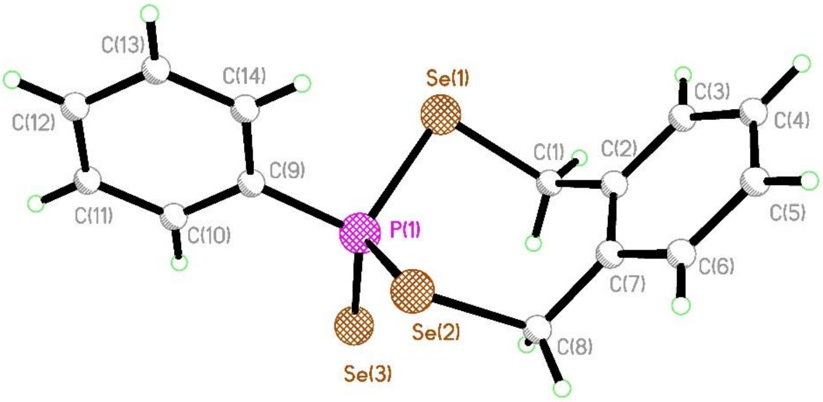


Compound 34



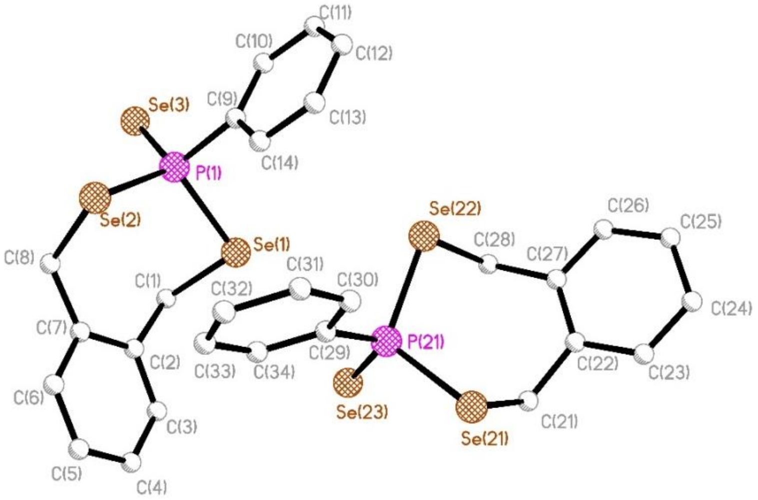
P2$_1$/c
a = 8.697(5) Å
b = 4.612(2) Å
c = 10.658(6) Å
α = 90º
β = 99.489(11)º
γ = 90º
V = 421.6(4) Å^3
wR$_2$ = 0.1822
R$_1$ = 0.0373

Compound 35



P2$_1$/c
a = 8.477(3) Å
b = 8.313(3) Å
c = 20.857(6) Å
α = 90º
β = 90.163(8)º
γ = 90º
V = 1469.8(7) Å^3
wR$_2$ = 0.1136
R$_1$ = 0.0280

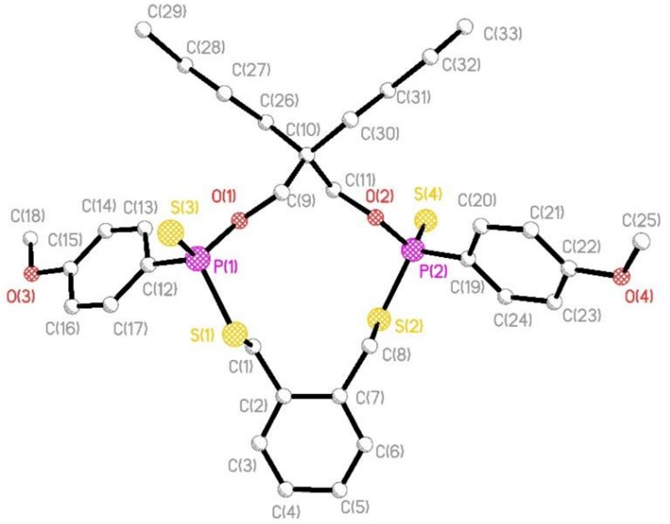
Compound 36



P-1
a = 8.703(3) Å
b = 9.770(6) Å
c = 19.48(2) Å
α = 88.68(5)º
β = 85.01(5)º
γ = 64.08(4)º
V = 1484(2) Å^3
wR$_2$ = 0.2840
R$_1$ = 0.0686

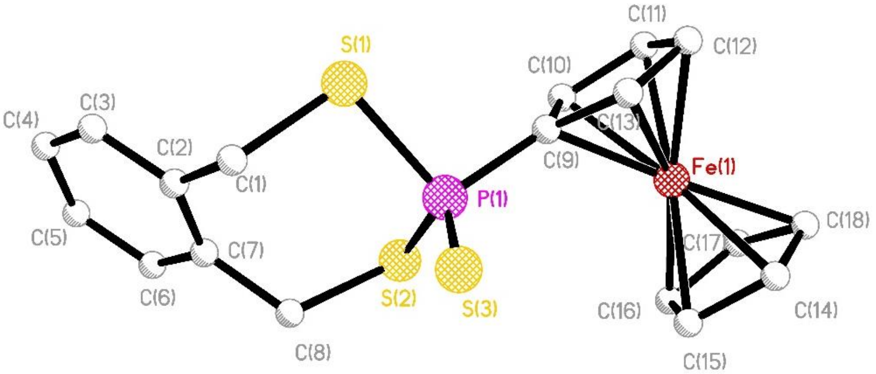
Compound 37

P-1
a = 10.395(4) Å
b = 13.919(7) Å
c = 14.348(6) Å
α = 118.93(4)º
β = 95.008(12)º
γ = 90.016(7)º
V = 1808(2) Å^3
wR_2 = 0.3654
R_1 = 0.1245



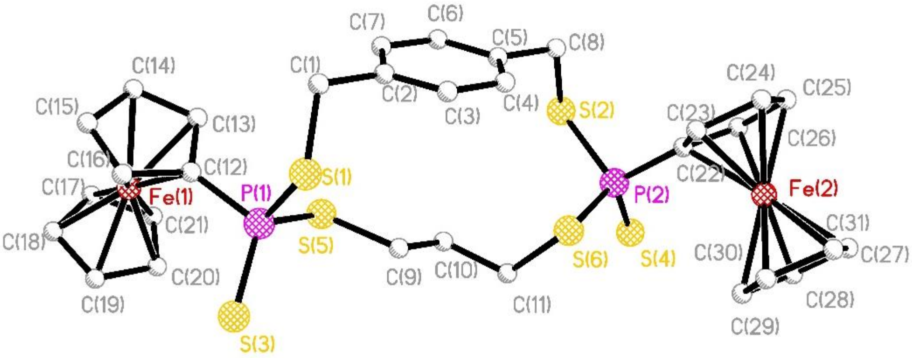
Compound 38

$P2_12_12_1$
a = 10.96(6) Å
b = 12.28(7) Å
c = 12.62(7) Å
α = 90º
β = 90º
γ = 90º
V = 1699(17) Å^3
wR_2 = 0.1688
R_1 = 0.0631



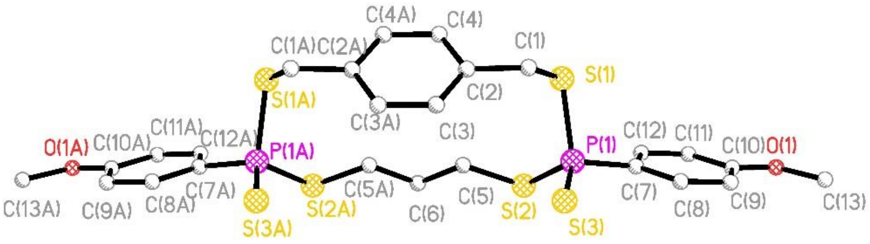
Compound 39

P-1
a = 7.47(4) Å
b = 12.42(7) Å
c = 17.85(11) Å
α = 101(4)º
β = 94(4)º
γ = 99(4)º
V = 1597(37) Å^3
wR_2 = 0.1613
R_1 = 0.0799



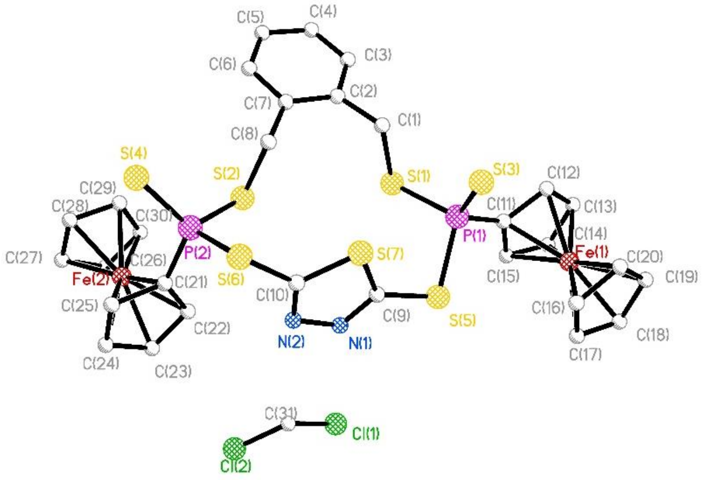
Compound 40

$Cmc2_1$
a = 34.2(2) Å
b = 11.86(8) Å
c = 6.90(5) Å
α = 90º
β = 90º
γ = 90º
V = 2799(33) Å^3
wR_2 = 0.0649
R_1 = 0.0387



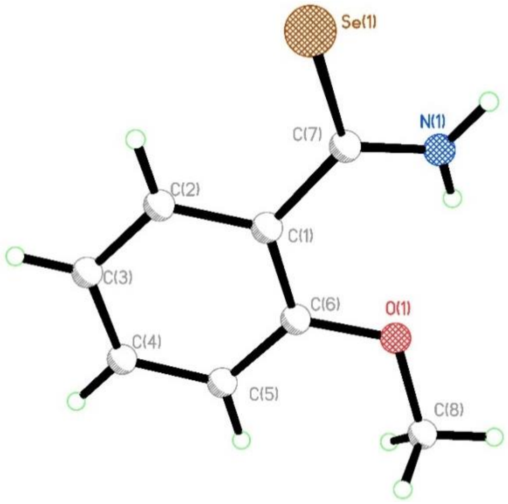
Compound 41

P-1
a = 8.73(5) Å
b = 13.73(7) Å
c = 15.62(8) Å
α = 79(3)º
β = 75(3)º
γ = 78(3)º
V = 1750(35) Å^3
wR_2 = 0.1129
R_1 = 0.0507



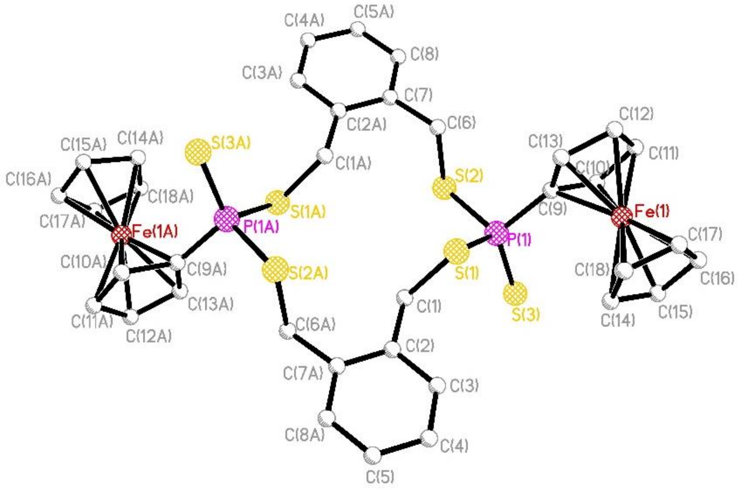
Compound 42

$P2_1/c$
a = 5.965(2) Å
b = 9.969(3) Å
c = 14.141(5) Å
α = 90º
β = 95.646(8) º
γ = 90º
V = 836.8(4) Å^3
wR_2 = 0.1635
R_1 = 0.0421



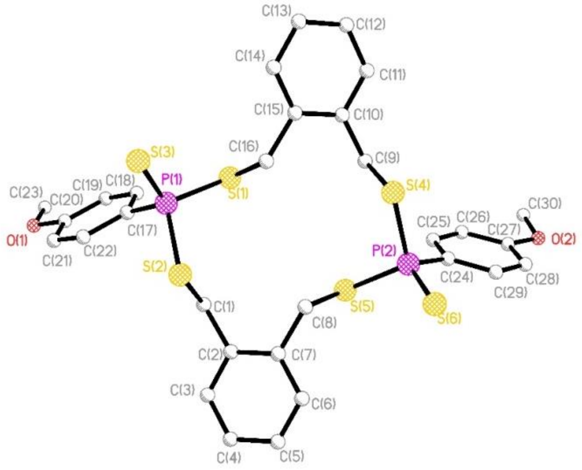
Compound 43

$P2_1/n$
a = 7.515(6) Å
b = 22.102(13) Å
c = 10.965(8) Å
α = 90º
β = 92.82(2)º
γ = 90º
V = 1819(2) Å^3
wR$_2$ = 0.1715
R$_1$ = 0.0934



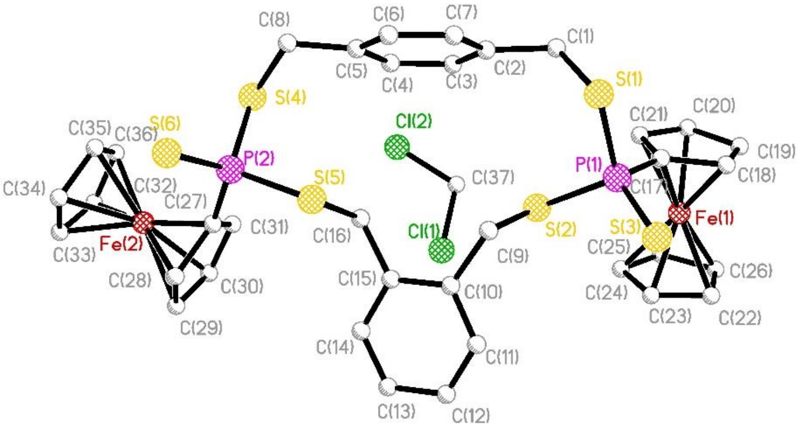
Compound 44

$P\text{-}1$
a = 8.3619(13) Å
b = 16.044(3) Å
c = 24.922(4) Å
α = 93.77(2)º
β = 99.581(13)º
γ = 102.670(12)º
V = 3198.3(9) Å^3
wR$_2$ = 0.3035
R$_1$ = 0.1060



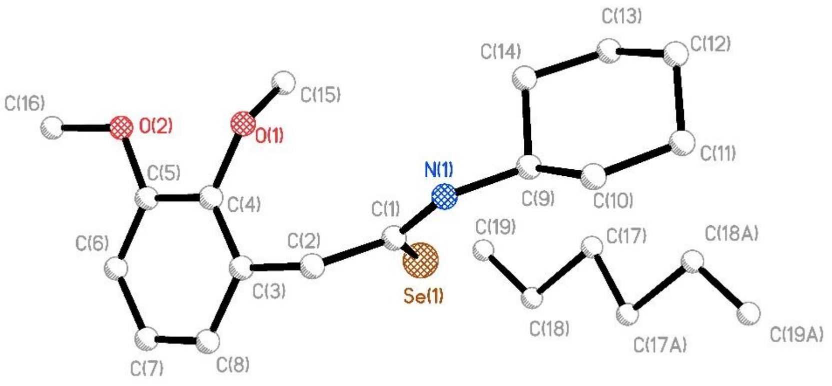
Compound 45

$P2_1/c$
a = 18.848(6) Å
b = 12.694(4) Å
c = 16.584(5) Å
α = 90º
β = 95.752(8)º
γ = 90º
V = 3948(2) Å^3
wR$_2$ = 0.1977
R$_1$ = 0.0743



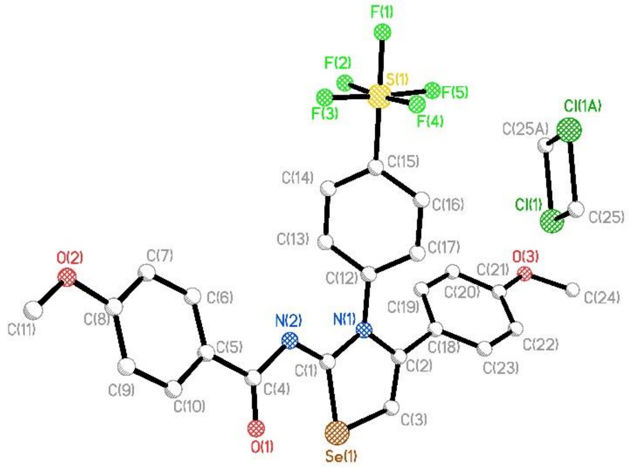
Compound 46

P-1
a = 9.2058(17) Å
b = 10.437(3) Å
c = 10.848(3) Å
α = 87.62(2)º
β = 76.120(18)º
γ = 70.523(15)º
V = 953.1(4) $Å^3$
$wR_2 = 0.2546$
$R_1 = 0.0870$



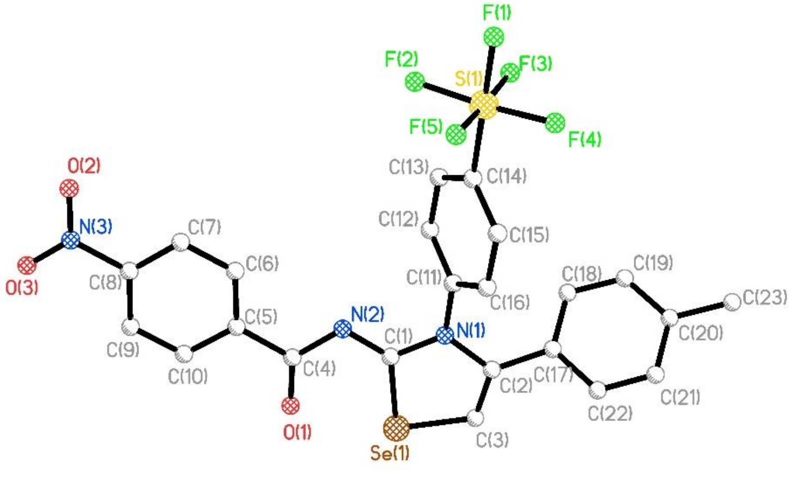
Compound 47

P-1
a = 9.4893(8) Å
b = 10.2641(9) Å
c = 13.4203(11) Å
α = 104.147(14)º
β = 95.793(13)º
γ = 98.240(13)º
V = 1241.7(2) $Å^3$
$wR_2 = 0.1671$
$R_1 = 0.0748$



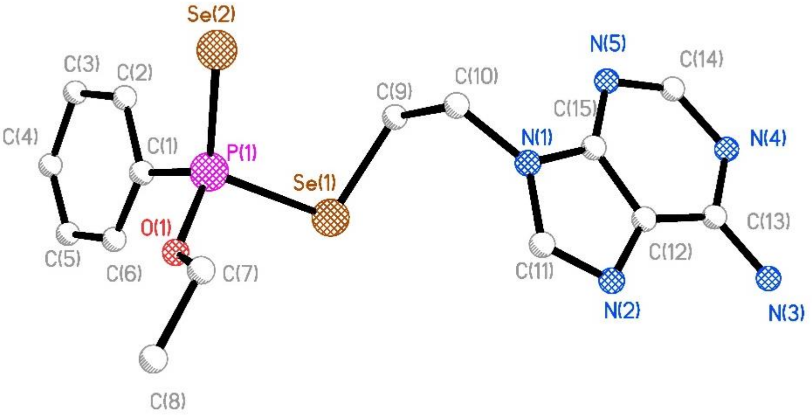
Compound 49

$P2_1/c$
a = 10.2003(7) Å
b = 17.8940(13) Å
c = 12.5877(9) Å
α = 90º
β = 95.325(3)º
γ = 90º
V = 2287.6(3) $Å^3$
$wR_2 = 0.0800$
$R_1 = 0.0408$



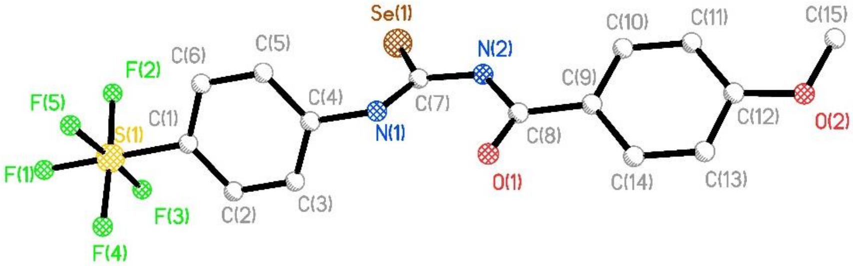
Compound 50

P-1
a = 6.8270(5) Å
b = 7.5233(5) Å
c = 18.5628(13) Å
α = 81.694(9)º
β = 87.199(10)º
γ = 75.331(9)º
V = 912.59(12) Å^3
wR$_2$ = 0.3620
R$_1$ = 0.1145



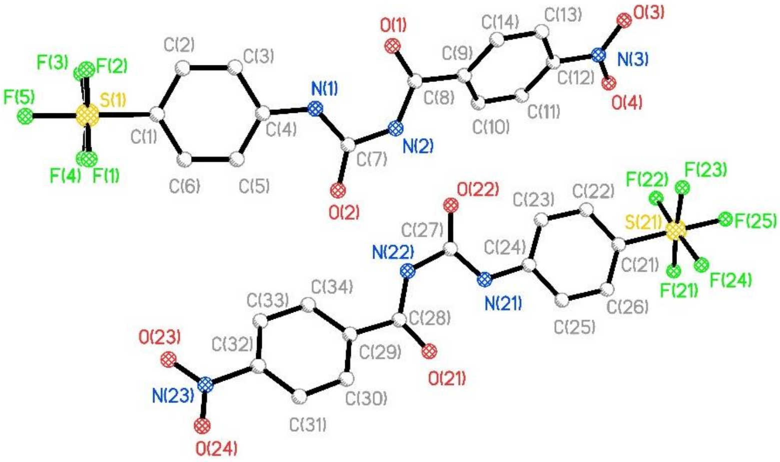
Compound 51

$P2_1/c$
a = 17.4151(11) Å
b = 6.5384(5) Å
c = 15.8481(11) Å
α = 90º
β = 109.850(3)º
γ = 90º
V = 1697.4(2) Å^3
wR$_2$ = 0.1009
R$_1$ = 0.0411



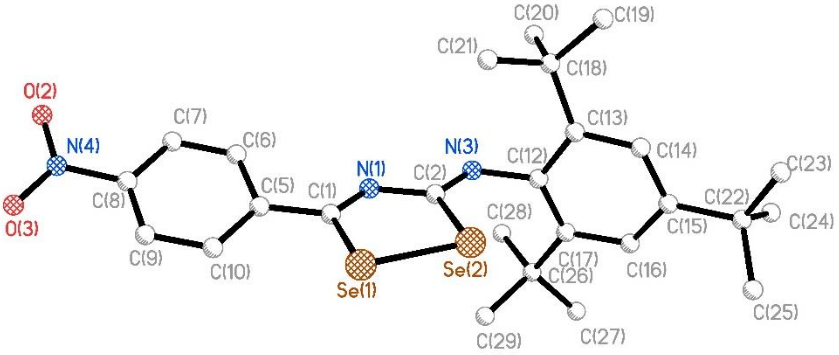
Compound 52

P-1
a = 8.0878(9) Å
b = 13.0950(14) Å
c = 15.6603(17) Å
α = 74.129(11)º
β = 89.090(14)º
γ = 85.272(13)º
V = 1589.9(3) Å^3
wR$_2$ = 0.2967
R$_1$ = 0.0916



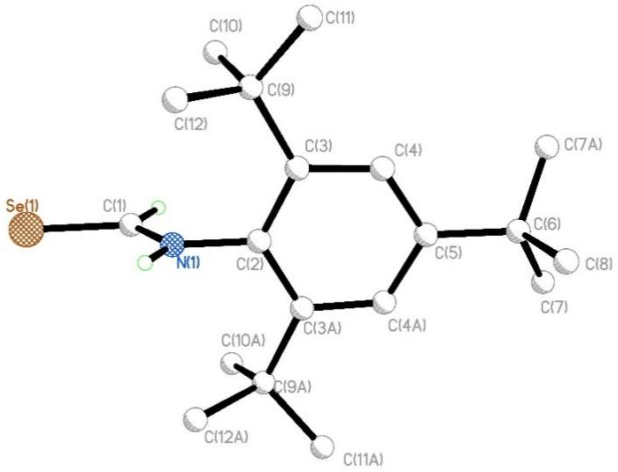
Compound 53

P-1
a = 9.4547(7) Å
b = 11.4917(8) Å
c = 27.2316(19) Å
α = 93.099(6)º
β = 95.470(6)º
γ = 90.116(6)º
V = 2940.9(4) $Å^3$
wR_2 = 0.2090
R_1 = 0.0697



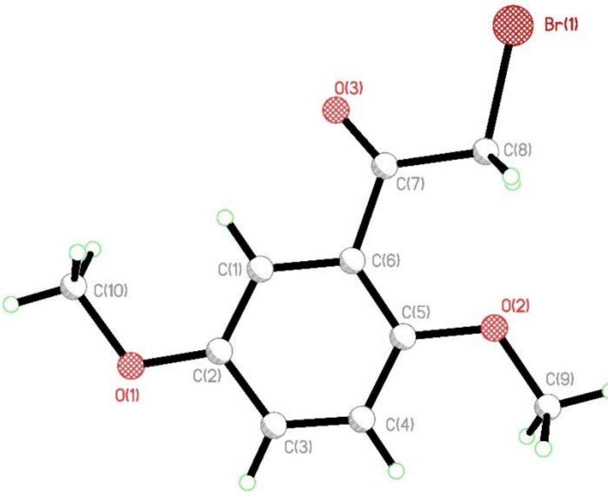
Compound 54

Pnma
a = 20.2224(14) Å
b = 15.2835(11) Å
c = 5.8839(4) Å
α = 90º
β = 90º
γ = 90º
V = 1818.5(2) $Å^3$
wR_2 = 0.1502
R_1 = 0.0435



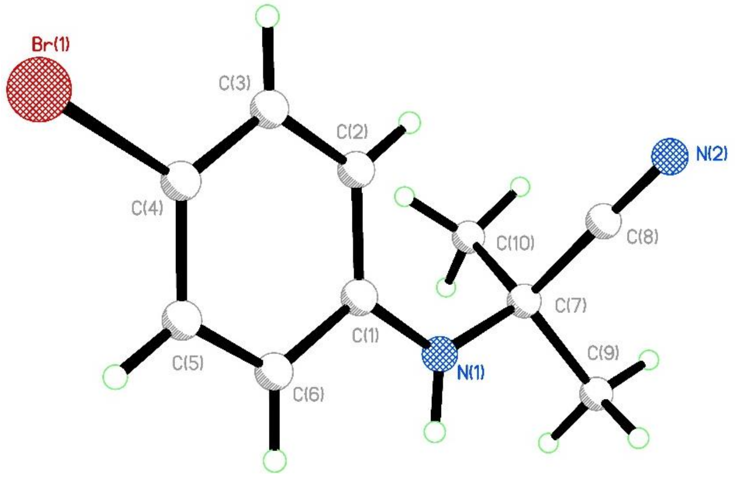
Compound 55

$P2_1/c$
a = 5.0747(4) Å
b = 13.9627(11) Å
c = 14.3270(11) Å
α = 90º
β = 97.223(7)º
γ = 90º
V = 1007.11(14) $Å^3$
wR_2 = 0.3853
R_1 = 0.1108



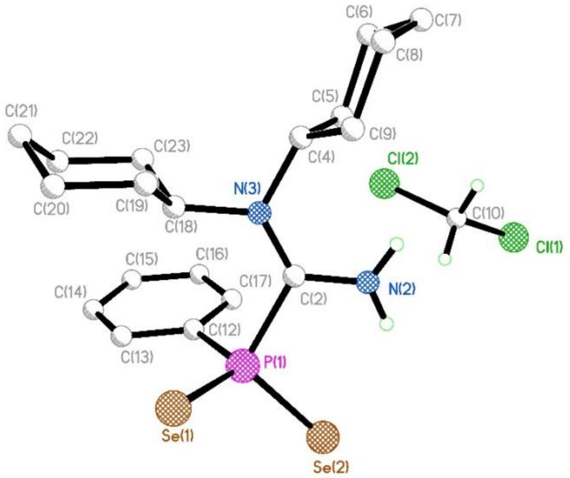
Compound 56

$P2_12_12_1$
a = 6.1079(4) Å
b = 11.9442(9) Å
c = 14.3571(10) Å
α = 90º
β = 90º
γ = 90º
V = 1047.41(13) Å^3
wR$_2$ = 0.0835
R$_1$ = 0.0377



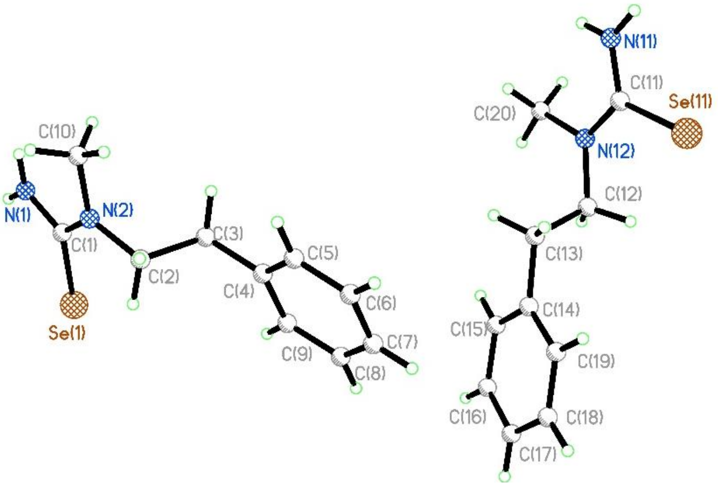
Compound 57

$P2_12_12_1$
a = 10.0785(9) Å
b = 13.1462(11) Å
c = 17.9286(15) Å
α = 90º
β = 90º
γ = 90º
V = 2375.4(4) Å^3
wR$_2$ = 0.1468
R$_1$ = 0.0596



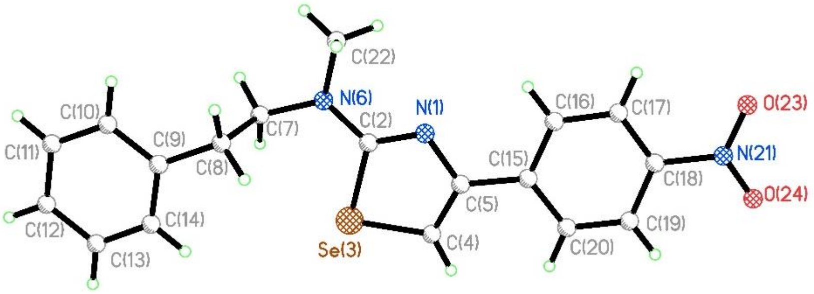
Compound 58

$Pca2_1$
a = 12.0539(9) Å
b = 5.9581(4) Å
c = 29.005(2) Å
α = 90º
β = 90º
γ = 90º
V = 2083.1(3) Å^3
wR$_2$ = 0.1159
R$_1$ = 0.0490



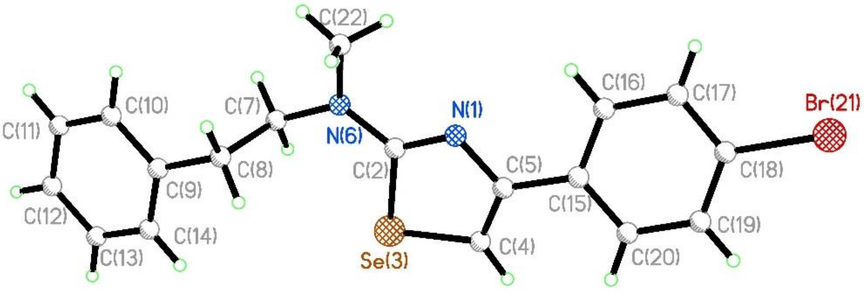
Compound 59

$P2_1/n$
a = 10.5159(7) Å
b = 7.5401(5) Å
c = 20.9330(15) Å
α = 90º
β = 91.879(2)º
γ = 90º
V = 1658.9(2) Å^3
wR$_2$ = 0.1577
R$_1$ = 0.0435



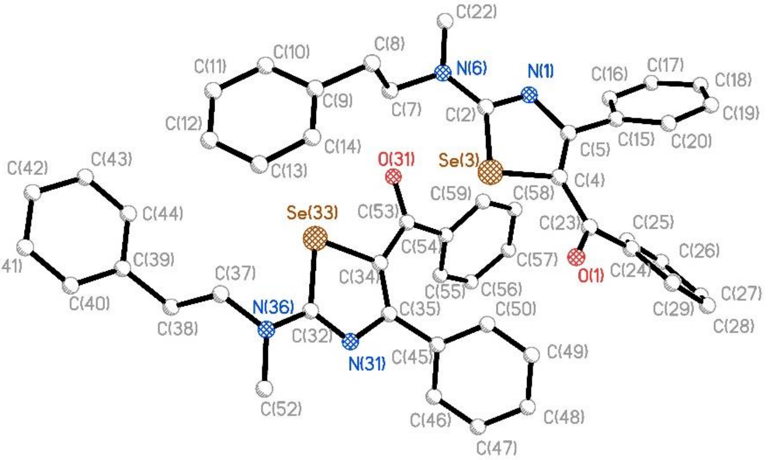
Compound 60

$P2_1$
a = 10.6448(10) Å
b = 7.4660(7) Å
c = 11.5064(11) Å
α = 90º
β = 116.039(3)º
γ = 90º
V = 821.64(14) Å^3
wR$_2$ = 0.0679
R$_1$ = 0.0311



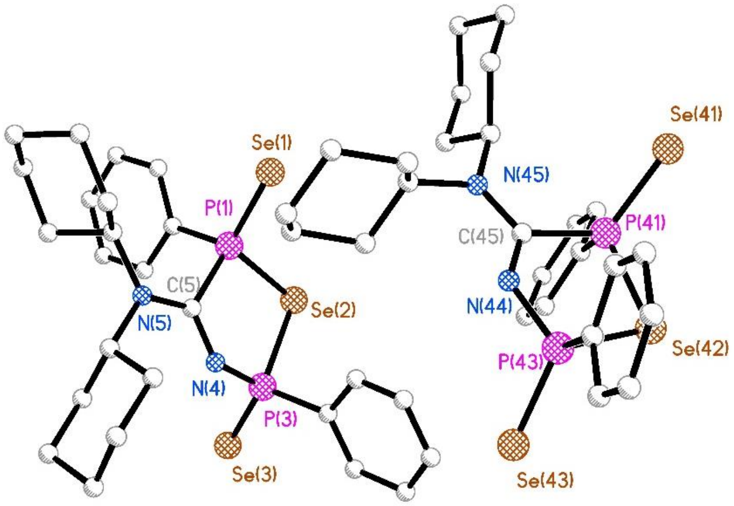
Compound 61

$P2_1/c$
a = 10.1342(7) Å
b = 14.6025(10) Å
c = 27.942(2) Å
α = 90º
β = 90.421(4)º
γ = 90º
V = 4134.9(5) Å^3
wR$_2$ = 0.1775
R$_1$ = 0.0727



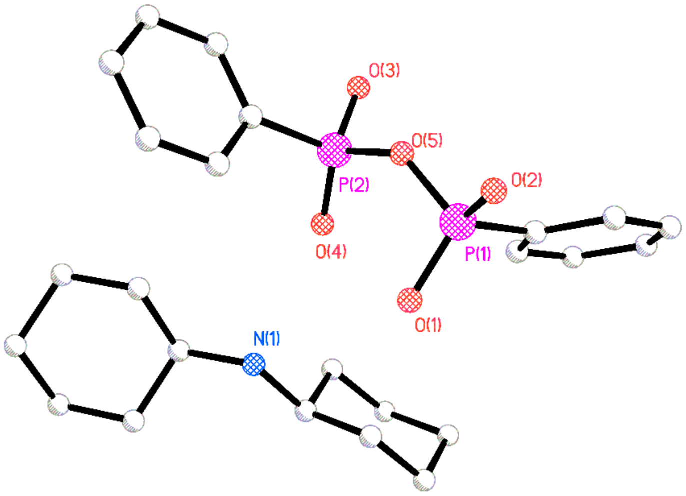
Compound 62

$P2_1/n$
a = 10.2241(7) Å
b = 17.6148(11) Å
c = 30.321(2) Å
α = 90º
β = 99.70620º
γ = 90º
V = 5382.5(6) Å^3
wR_2 = 0.1652
R_1 = 0.0586



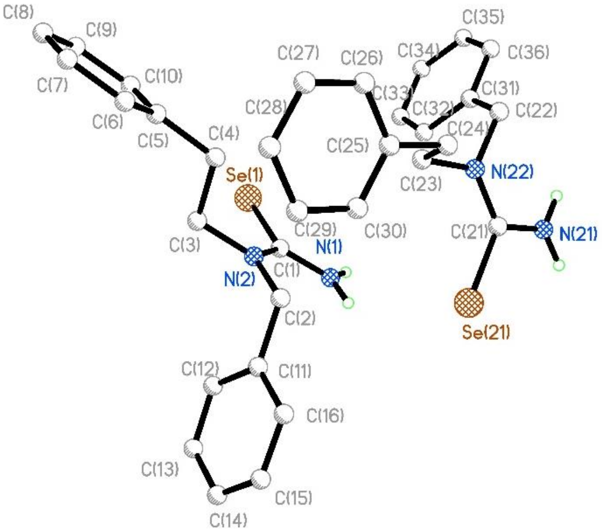
Compound 63

P-1
a = 10.3464(8) Å
b = 11.3332(9) Å
c = 12.6639(10) Å
α = 74.710(19)º
β = 70.999(18)º
γ = 63.139(16)º
V = 1240.5(3) Å^3
wR_2 = 0.1795
R_1 = 0.0956



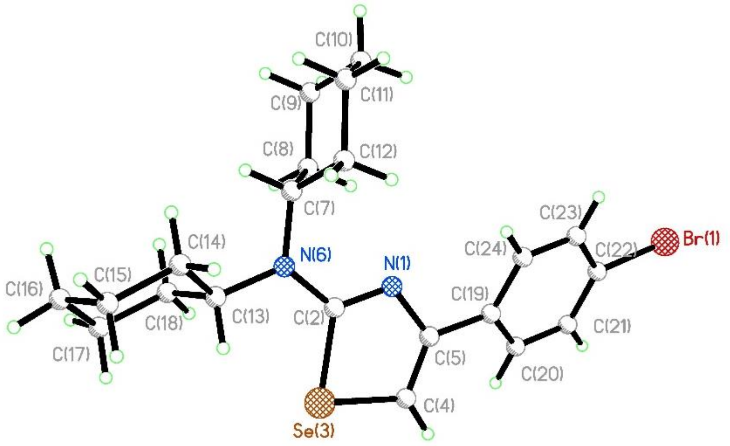
Compound 64

$P2_1/c$
a = 11.2150(8) Å
b = 9.7290(7) Å
c = 27.626(2) Å
α = 90º
β = 98.580(3)º
γ = 90º
V = 2980.6(4) Å^3
wR_2 = 0.1741
R_1 = 0.0619



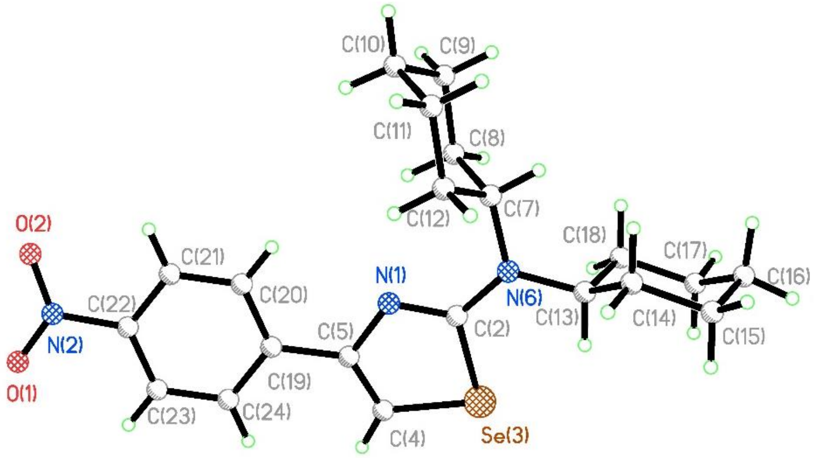
Compound 65

$P2_1/n$
a = 10.6605(8) Å
b = 15.2625(11) Å
c = 12.8472(9) Å
α = 90º
β = 111.4590(17)º
γ = 90º
V = 1945.4(2) Å^3
wR$_2$ = 0.1345
R$_1$ = 0.0460



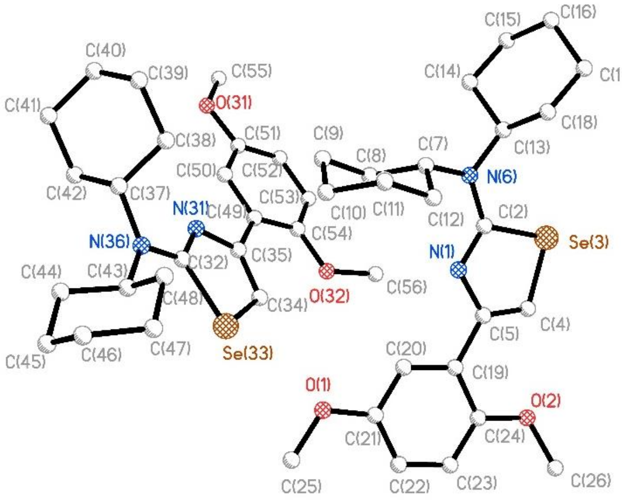
Compound 66

$P2_1/n$
a = 13.8234(10) Å
b = 10.6102(8) Å
c = 15.1033(11) Å
α = 90º
β = 116.047(2)º
γ = 90º
V = 1990.2(3) Å^3
wR$_2$ = 0.1853
R$_1$ = 0.0600

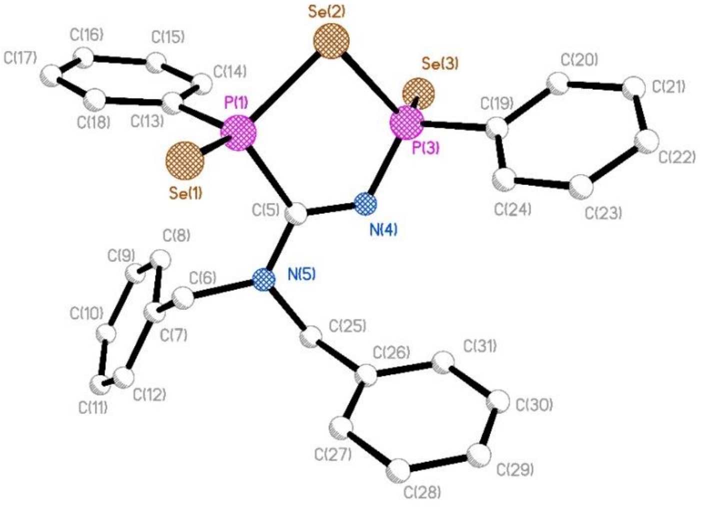


Compound 67

$P2_1/c$
a = 12.5190(9) Å
b = 10.0014(7) Å
c = 33.985(2) Å
α = 90º
β = 98.028(2)º
γ = 90º
V = 4213.5(5) Å^3
wR$_2$ = 0.1417
R$_1$ = 0.0476

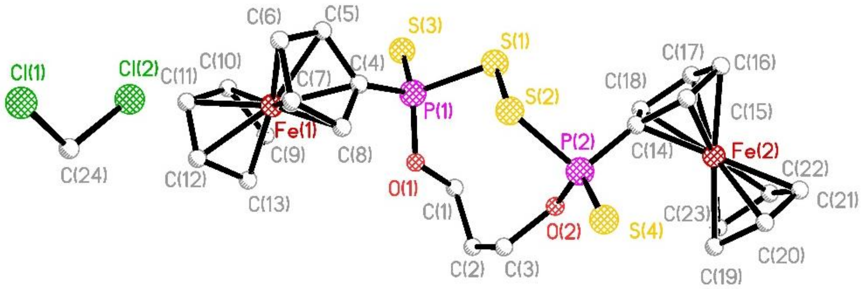


Compound 68



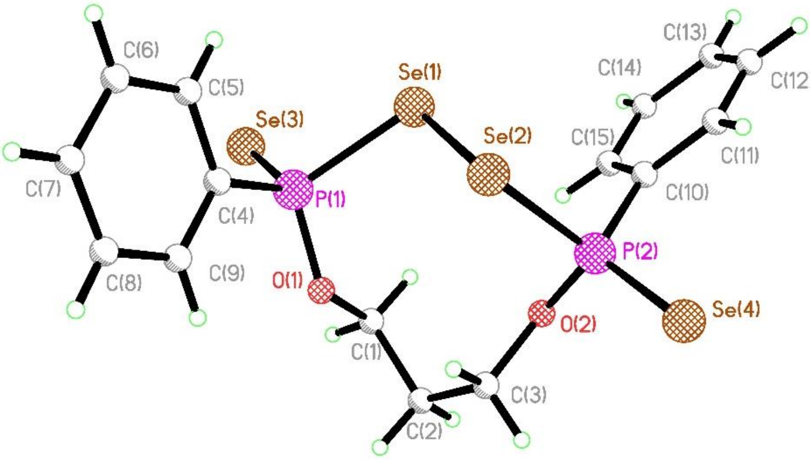
$P2_1/c$
a = 15.5514(11) Å
b = 10.0461(7) Å
c = 16.8283(11) Å
α = 90º
β = 93.574(3)º
γ = 90º
V = 2624.0(3) Å^3
wR$_2$ = 0.1009
R$_1$ = 0.0477

Compound 69



P-1
a = 7.6366(5) Å
b = 11.7048(8) Å
c = 16.7834(11) Å
α = 98.035(5)º
β = 100.985(6)º
γ = 99.739(5)º
V = 1428.35(17) Å^3
wR$_2$ = 0.1849
R$_1$ = 0.0512

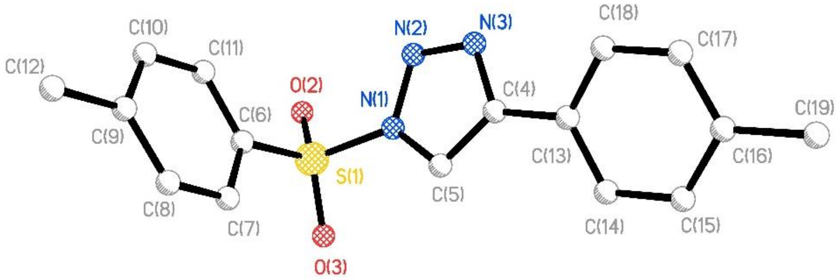
Compound 70



P-1
a = 8.9806(5) Å
b = 9.5256(7) Å
c = 11.8160(8) Å
α = 78.484(9)º
β = 88.1819(10)º
γ = 78.385(9)º
V = 970.14(12) Å^3
wR$_2$ = 0.1985
R$_1$ = 0.0548

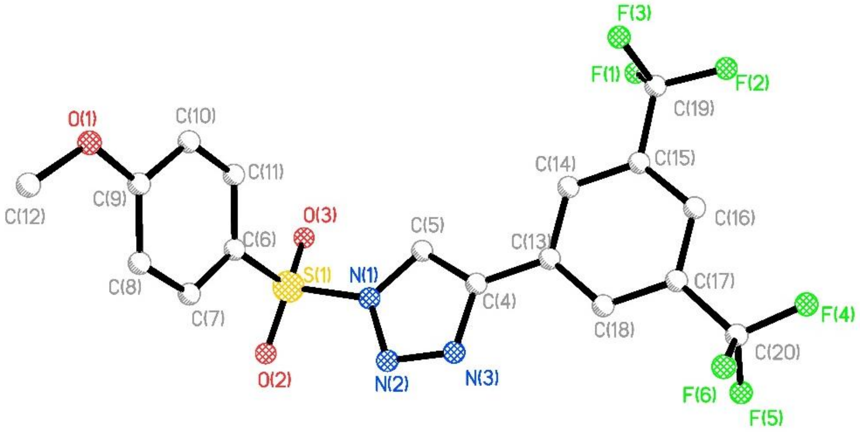
Compound 71

Pbca
a = 19.29(10) Å
b = 15.04(8) Å
c = 10.84(6) Å
α = 90º
β = 90º
γ = 90º
V = 3145(30) Å^3
$wR_2 = 0.1157$
$R_1 = 0.0451$



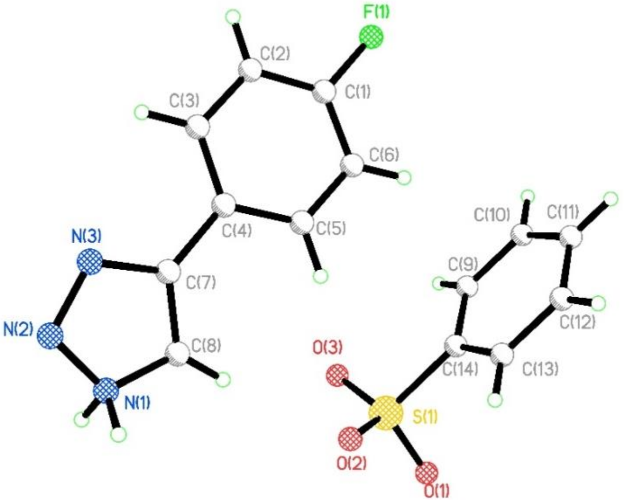
Compound 72

$P2_1/c$
a = 15.493(7) Å
b = 4.742(3) Å
c = 24.111(11) Å
α = 90º
β = 94.179(10)º
γ = 90º
V = 1767(2) Å^3
$wR_2 = 0.2304$
$R_1 = 0.0783$



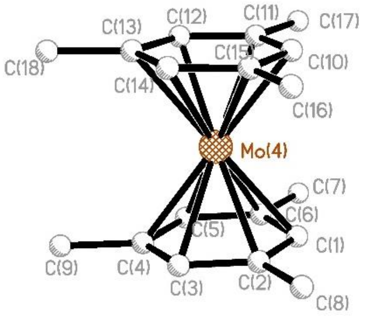
Compound 73

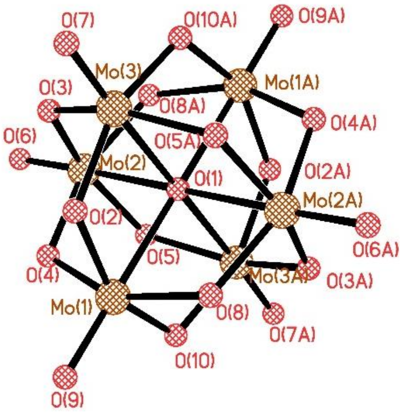
$P2_1/c$
a = 14.5995(11) Å
b = 5.6225(4) Å
c = 18.4716(14) Å
α = 90º
β = 108.236(5)º
γ = 90º
V = 1440.10(19) Å^3
$wR_2 = 0.2263$
$R_1 = 0.0707$



Compound 74

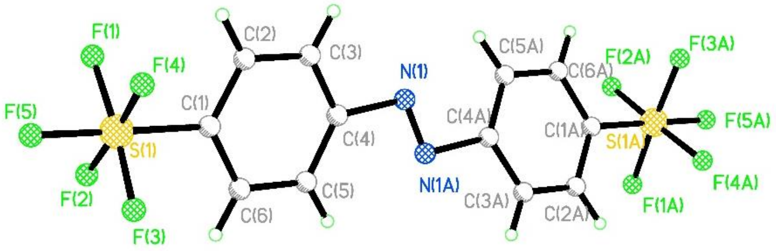
$P2_1/n$
a = 10.674(3) Å
b = 18.504(4) Å
c = 11.591(3) Å
α = 90º
β = 100.995(5)º
γ = 90º
V = 2247.4(8) Å^3
wR$_2$ = 0.1464
R$_1$ = 0.0423





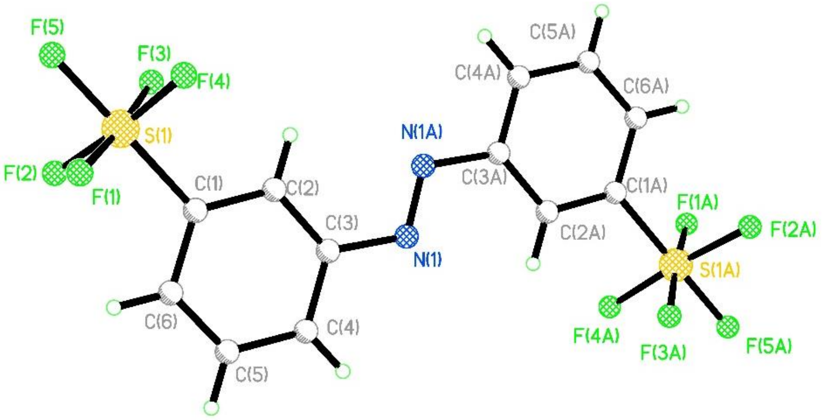
Compound 75

Ibam
a = 15.229(10) Å
b = 15.86(10) Å
c = 19.66(13) Å
α = 90º
β = 90º
γ = 90º
V = 4749(44) Å^3
wR$_2$ = 0.1696
R$_1$ = 0.0599



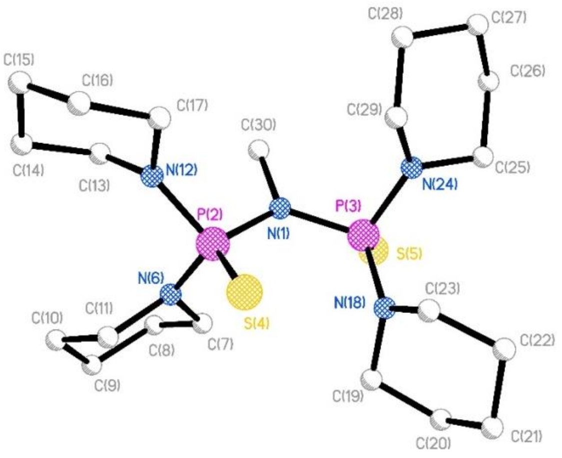
Compound 76

$P2_1/n$
a = 5.774(3) Å
b = 9.071(4) Å
c = 14.398(8) Å
α = 90º
β = 98.90(2)º
γ = 90º
V = 745.1(6) Å^3
wR$_2$ = 0.1929
R$_1$ = 0.0475



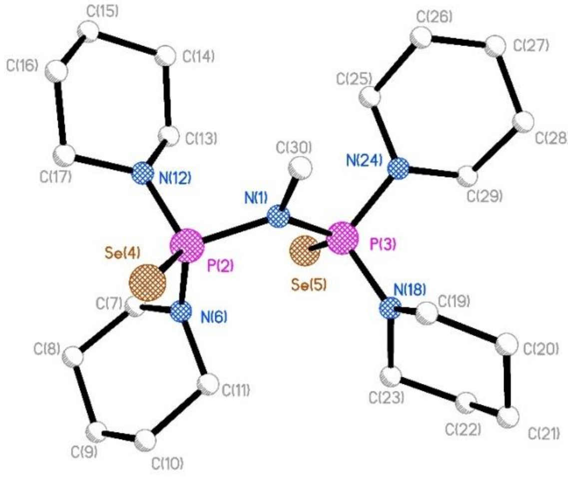
Compound 77

$P2_1/c$
a = 16.366(6) Å
b = 12.442(4) Å
c = 13.653(5) Å
α = 90º
β = 107.638(8)º
γ = 90º
V = 2650(2) Å^3
wR_2 = 0.2302
R_1 = 0.0955



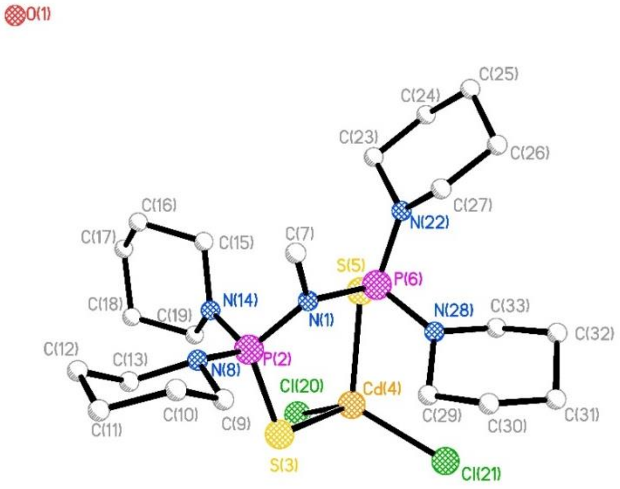
Compound 78

$P\text{-}1$
a = 10.08(4) Å
b = 11.91(5) Å
c = 22.98(10) Å
α = 82(3)º
β = 85(3)º
γ = 73(3)º
V = 2609(49) Å^3
wR_2 = 0.1201
R_1 = 0.0504



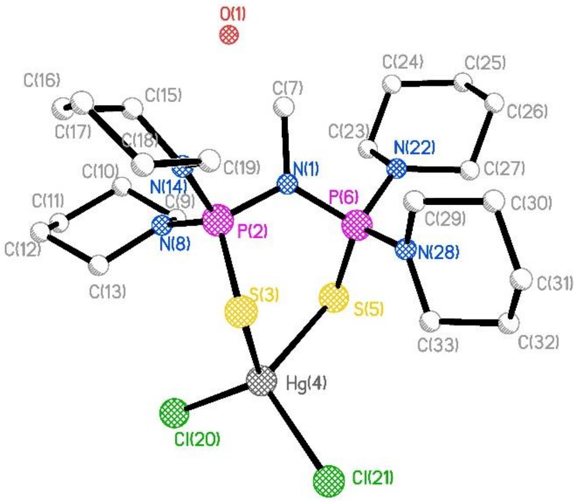
Compound 79

$P2_1/c$
a = 17.27(5) Å
b = 18.30(5) Å
c = 19.26(6) Å
α = 90º
β = 98.2(6)º
γ = 90º
V = 6025(32) Å^3
wR_2 = 0.1667
R_1 = 0.0613



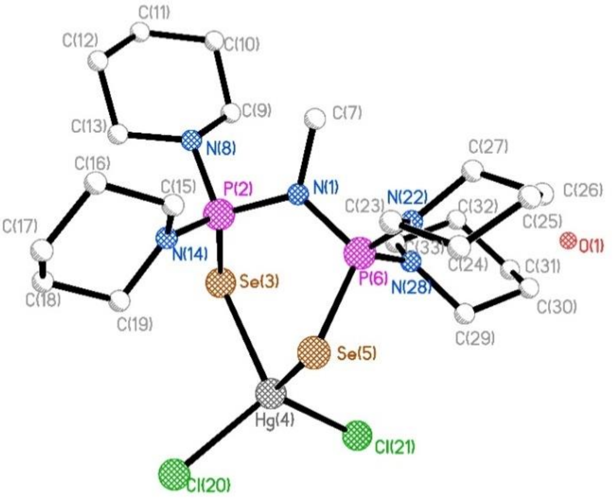
Compound 80

$P2_1/c$
a = 17.26(5) Å
b = 18.22(5) Å
c = 19.27(6) Å
α = 90º
β = 98.2(6)º
γ = 90º
V = 5998(32) $Å^3$
wR_2 = 0.1336
R_1 = 0.0527



Compound 81

Pbca
a = 17.45(5) Å
b = 18.26(5) Å
c = 19.28(5) Å
α = 90º
β = 98.0(6)º
γ = 90º
V = 6084(31) $Å^3$
wR_2 = 0.0996
R_1 = 0.0425



APPENDIX III

PUBLICATIONS TO DATE

1. *Guoxiong Hua,* ***Junyi Du****, David B. Cordes, Alexandra M. Z. Slawin and J. Derek Woollins,* One-Pot Three-Component Condensation Synthesis and Structural Features of Multi-Sulfur Organophosphorus Macrocycles, *J. Org. Chem.* **2016**, (In press). **DOI:** 10.1021/acs.joc.6b00573.
2. *Guoxiong Hua,* ***Junyi Du****, Alexandra M. Z. Slawin and J. Derek Woollins,* One-pot Approach to Organo Phosphorus-Chalcogen Macrocycles Incorporating Double OP(S)SC$_n$ or OP(Se)SeC$_n$ Scaffolds: A Synthetic and Structural Study. *Chem. A Eur. J.* **2016**, (In press). DOI: 10.1002/chem.201504832.
3. *Guoxiong Hua,* ***Junyi Du****, David B. Cordes, Kasun S. A. Arachchige, Alexandra M. Z. Slawin and J. Derek Woollins.* Synthesis and Characterization of Novel Organic Heteroatom Compounds from Reaction of Woollins' Reagent with Various Organic Substrates. *Phosphorus, sulphur, silica and the related elements* **2016**, *191*, 341-346.
4. *Guoxiong Hua,* ***Junyi Du****, Brian. A. Surgenor, Alexandra M. Z. Slawin and J. Derek Woollins*. Novel Fluorinated Phosphorus−Sulfur Heteroatom Compounds: Ferrocenyl- and Aryl-phosphonofluorodithioic Salts, Adducts, and Esters. *Molecules* **2015**, *20(7)*, 12175-12197.
5. *George Iakobson,* ***Junyi Du****, Alex M. Z. Slawin, Petr Beier,* Pyridine-promoted Dediazonation of Aryldiazonim Tetrafluoroboroates: Application to the Synthesis of SF5-substituted Phenylboronic Esters and Iodobenzenes. *Beilstein J. Org. Chem*. **2015**, *11*, 1494-1502.
6. *Guoxiong Hua,* ***Junyi Du****, Alexandra M. Z. Slawin and J. Derek Woollins*. Efficient Synthesis of Novel Chalcogen-Containing Derivatives of DNA Nucleobases. *Tetrahedron* **2015**, *71*, 1792-1798.
7. *Guoxiong Hua,* ***Junyi Du****, Kasun S. A. Arachchige, Alexandra M. Z. Slawin and J. Derek Woollins.* Synthesis, Selenation and X-ray Structures of Tandem Multiomponent Condensation Adducts. *Synlett* **2015**, 26, 839-845.

8. *Guoxiong Hua*, ***Junyi Du***, *Alexandra M. Z. Slawin and J. Derek Woollins*. A Synthetic and Structural Study of Arylselenoamides and 2,4-Diaryl-1,3-Selenazoles. *Synlett* **2014**, *25*, 2189-2195.
9. *Guoxiong Hua*, ***Junyi Du***, *Alexandra M. Z. Slawin and J. Derek Woollins*. 2,4-Diaryl-1,3-Chalcogen Azoles Bearing Pentafulorosulfanyl PF_5 Group: A Synthetic and Structural Study. *J. Org. Chem*. **2014**, 79, 3876-3886.
10. *Guoxiong Hua*, ***Junyi Du***, *Alexandra M. Z. Slawin and J. Derek Woollins,* Novel Fluorinated Phosphorus-selenium Heteroatom Compounds: Phenylphosphonofluorodiselenoic Salts, Adducts and Esters. *Inorg. Chem*. **2013**, *52(14)*, 8214-8217.