Ionic Organocatalysis

By
Trevor Adam McGrath

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Approved: Dr. Robert D. Singer
Supervisor

Approved: Dr. Jason Masuda
Acting Chairperson
Department of Chemistry

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Abstract

A method for synthesizing ionic thiourea based organocatalysts was elucidated. Two ionic organocatalysts were then successfully synthesized and fully characterized. A thiourea containing a pyrrolidinium moiety was shown to be catalytically active in a DABCO co-catalyzed Morita-Baylis-Hillman reaction between benzaldehyde and cyclohex-2-en-1-one. The pyrrolidinium tagged organocatalyst was successfully entrained and recycled using the ionic liquid *N*-butyl-*N*-methylpyrrolidiniumbis(trifluoromethane)sulfonamide,[BMPyr][N(Tf)$_2$].

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Finally, I would like to thank my family, who have provided endless support and encouragement my entire time at Saint Mary's.

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Abbreviations

$[BMIM]^+$	1-butyl-3-methylimidazolium
$[BMPyr]^+$	*N*-butyl-*N*-methylpyrrolidinium
DABCO	1,4-Diazabicyclo[2.2.2]octane
DMSO-d^6	deuterated dimethylsulfoxide
$[EMIM]^+$	1-ethyl-3-methylimidazolium
ESI-MS	electrospray ionization mass spectrometry
FT-IR	Fourier transform infrared
IL	ionic liquid
IR	infrared
m.p.	melting point
NMR	nuclear magnetic resonance
$[N(Tf)_2]^-$	bis(trifluoromethane)sulfonimide
$[PF_6]^-$	hexafluorophosphate
Ppm	parts per million
rpm	rotations per minute
RT	room temperature
RTIL	room temperature ionic liquid
S_N2	nucleophilic substitution bi-molecular
THF	tetrahydrofuran
TSIL	task specific ionic liquid
XRD	X-ray diffraction

1.0 Introduction

1.1 Green Chemistry

Green chemistry is a relatively new and emerging field that strives to achieve sustainability at a molecular level. The concept of green chemistry was first formulated just overtwenty years ago in the early 1990s and is defined as the design of chemical processes to eliminate the use and generation of hazardous substances.[1] Since the idea of green chemistry has been put forward there have been a number of international initiatives directed towards adoption of green chemistry such as the US Presidential Green Chemistry Challenge Awards established in 1995, The Green Chemistry Institute founded in 1997 and the publication of the first volume of the Royal Society of Chemistry's Green Chemistry in 1999.[2] An Atlantic Canadian example of adoption of green chemistry is the establishment in 2010of The Atlantic Center for Green Chemistryat Saint Mary's University.

The concept of green chemistry is one which requires a conscious effort. Paul Anastas states that the most important aspect of green chemistry is the concept of design and further states that design is a statement of human intent and cannot be done by accident.[3] Green chemistry strives to achieve sustainability at a molecular level and thus it is not surprising that green chemistry can be applied to a wide array of industrial sectors. The aerospace, cosmetic, electronics, energy, agricultural and pharmaceutical industries have all been touched by green chemistry and there are hundreds of examples of economically competitive and sustainable technologies within these industries.[3]

Anastas has devised twelve principles of green chemistry that are intended to allow chemists to achieve more sustainable practices in chemical synthesis and molecular design. Waste prevention is the first principle of green chemistry. One measure of waste prevention is the Sheldon E Factor and is defined as the ratio of waste mass to the ratio of product mass in kilograms.[4] Ideal processes would have a very low E factor, less than one. The second principle of green chemistry is atom economy. The incorporation of as many atoms fromreactants into the products as possible will facilitate the prevention of waste through minimization of by-products. Principles three, four and five are less hazardous chemical synthesis, designing safer chemicals and safer solvents and auxiliaries. The reduction of chemical toxicity and decreased solvent use are both goals of green chemistry design. Principle six states that chemical processes should be, when possible, carried out at ambient temperature and pressures to reduce energy consumption. The use of renewable feedstock for chemical processes is principle seven. The reduction of unnecessary use of derivatives such as protecting groups, which is principle eight, will help improve atom economy and prevent waste. Catalysis, which is principle nine, can eliminate the need for stoichiometric reagents thus aiding in waste prevention and lowering the E Factor for a process. Designing chemicals for degradation so they can be safely released into the environment at the end of their lifetime is the tenth principle of green chemistry. Real time analysis to allow pollution prevention before a hazardous substance is created in a process is the eleventh principle of green chemistry. The twelfth and final principle of green chemistry is the design of inherently safer chemistry to allow for accident prevention. Following these principles as a guideline allows for chemical processes to be designed to minimize their environmental impact and increase safety.[3]

1.2 Ionic Liquids

Ionic Liquids (ILs) have received considerable attention in chemistry due to their unique and useful properties. Alternative names for ionic liquids that can be found during a literature search include, but are not limited to, low temperature molten salts, ambient temperature molten salts and liquid organic salts.[5] By definition ionic liquids are salts with a melting point below 100°C, the boiling point of water. Furthermore, ionic liquids that are in the liquid phase at room temperature are aptly referred to as room temperature ionic liquids (RTILs). Most ionic liquids are comprised of an organic cation and an inorganic polyatomic ion. The typically large and diffusely charged ions lead to relatively weak intermolecular forces causing the melting points of ionic liquids to fall below the 100°C benchmark.

Due to the number of known cations and anions the potential number of permutations which will afford ILs and potentially possess different properties is immense. Properties such as polarity and viscosity can be altered dramatically by changing the cation or anion. Ionic liquid cations typically contain a nitrogen or a phosphorus atom due to their ability to stabilize charged species.[5] Common nitrogen containing cations include N,N'-dialkylimidazolium, N,N-dialkylpyrrolidinium and tetraalkylammonium. The most common phosphorus containing cation is tetraalkylphosphonium. Common anions include tetrafluoroborate, hexafluorophosphate and bis(trifluoromethanesulfonimide). These are depicted in **Figure 1**.

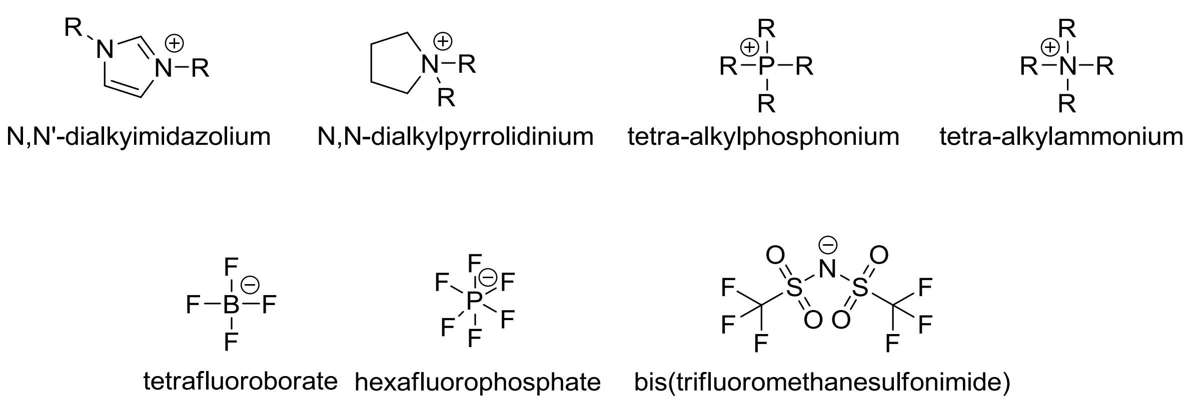


Figure 1. Typical Ionic Liquid Cations and Anions.

1.2.1 History

The first documented incidence of an ionic liquid, although unknown at the time, was made in the mid nineteenth century and was the 'red oil' formed during Friedel-Crafts reactions.[6] When nuclear magnetic resonance spectroscopy became more commonplace the structure of the 'red oil' was determined to be a postulated intermediate in the Friedel-Crafts reaction called the sigma complex (**Figure 2**).

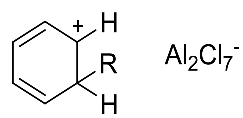


Figure 2. Sigma Complex for $AlCl_3$ Catalyzed Friedel-Crafts Reaction.[6]

Simple alkylammonium nitrates were also found to be liquids in the early twentieth century. Ethylammonium nitrate was found to have a melting point of 12°C; a room temperature ionic liquid by definition.[7]

Further advances in the field of ionic liquids were made when Major (Dr.) Lowell A. King attempted to find a lower melting replacement for the eutectic LiCl-KCl molten salt used in thermal batteries. Although the melting point for this eutectic mixture was considerably lower than most inorganic salts, at 355°C this temperature still caused material problems within the battery.[5] The need for lower melting eutectic salts lead to the discovery of chloroaluminate molten salts. The eutectic composition of NaCl-$AlCl_3$ was found to have a melting point of 107°C, much lower than the previous 355°C achieved using LiCl-KCl.[5]

The modern era of ionic liquids, containing an organic cation and an inorganic anion is marked by the synthesis of 1-butylpyridinium chloride-$AlCl_3$ by Wilkes and Hussey. Due to the ease with which alkylpyridinium cations are reduced, both chemically and electrochemically, a more stable cation was sought after. This lead to the preparation of the 1-ethyl-3-methylimidazolium chloroaluminate, [EMIM]Cl-$AlCl_3$, ionic liquid.[8] While the pyridinium and imidazolium based chloroaluminate ionic liquids were shown to be effective in Friedel-Crafts reactions both as a solvent and a catalyst[9,59] they suffer from the drawback of being reactive with water and thus needed to be handled under anhydrous conditions. In 1990 Dr. Michael Zaworotko took sabbatical leave from Saint Mary’s University to travel to the U.S. Air Force Academy where he and Wilkes prepared water stable ionic liquids using tetrafluoroborate, hexafluorophosphate, nitrate, sulfate and acetate anions. This was a significant advancement in the field.[10] Since the work of these pioneers in the area of ionic liquids the number of publications featuring ionic liquids has experienced exponential growth into the twenty first century (**Figure 3**).[11]

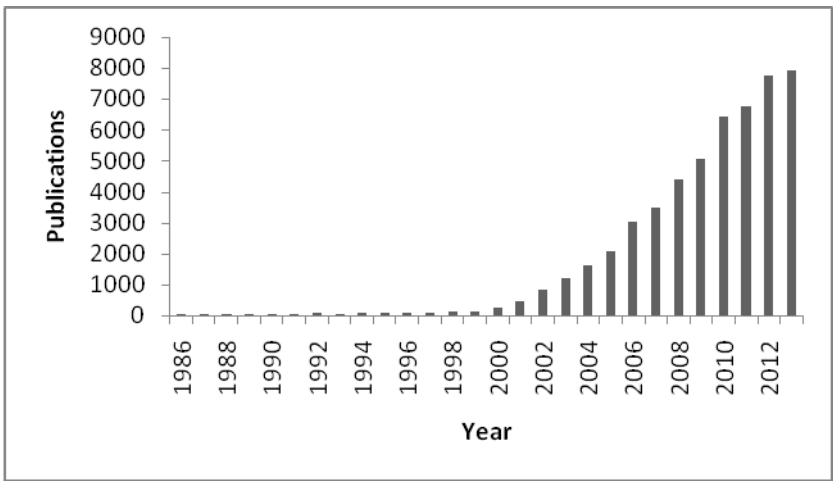


Figure 3. Ionic Liquid Publication Statistics.[11]

1.2.2 Properties

The increased interest in ionic liquids has occurred in large part due to the useful and novel solvent properties ionic liquids possess. Properties that make ionic liquids attractive solvents include negligible vapor pressure, high thermal stability and the ability to solvate a wide array of organic and inorganic materials. Aside from these properties, ionic liquids possess wide liquid ranges and large electrochemical windows making them stable solvents under a potentially wide range of working conditions. The upper temperature limit of ionic liquids is limited only by decomposition, not vaporization, which commonly occurs above 300°C.[12] A potential drawback for ionic liquids in some applications is viscosities that are several orders of magnitude greater than water, although the viscosity of ionic liquids is decreased significantly with heating. Other properties of ionic liquids such as polarity and hydrophobicity can be tuned by altering either the cation or anion.[5]

1.3 Task Specific Ionic Liquids

The properties of an ionic liquid can be tuned by functionalizing either the cation or the anion to afford a task specific ionic liquid (TSIL). Most task specific ionic liquids have functionalized cations, but the same principles can be applied to functionalization of the anion. Due to the non-volatile nature of ionic liquids these task specific ionic liquids have been compared to solid supported reagents. However, the task specific ionic liquids possess kinetic mobility and operational surface area unmatched by their solid-state counterparts.[5] Task specific ionic liquids have been designed and synthesized for a number of applications including catalysis, electrochemistry, metal ion extraction, synthesis of nanomaterials and ion-conducting materials.[13-15,60-61]

1.3.1 TSIL Metal Complexes

Previous work within the Singer Group has been performed designing and synthesizing task specific ionic liquids. Through tuning of the substituents attached to ionic liquid cores the properties of these task specific ionic liquids were able to be tuned, specifically for metal coordination. Imidazolium based salicylaldoxime and salen task specific ionic liquids were designed based upon previously reported ligands lacking the ionic liquids cores.[16] The idea of designing ligands with ionic liquid groups attached to them was inspired by the goal of immobilizing the catalyst within an ionic liquid phase to facilitate recycling of the catalyst. The ionic liquid tagged ligands were complexed a variety of metals including Mn^{III} (**Figure 4**) which was used to perform epoxidations of various alkenes in [BMIM][PF_6].[16]

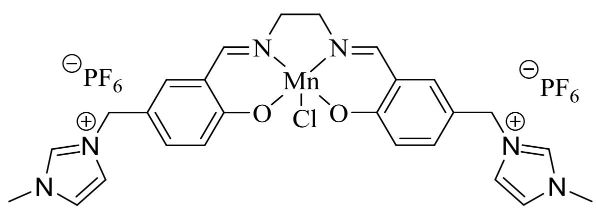


Figure 4. Mn^{III} Salen TSIL Complex.[16]

Similarly, it has also been shown that an ethylamine diacetic acid functionalized imidazolium ionic liquid can be complexed with nickel, copper and cobalt for metal extraction from aqueous media. Altering the length of the R group alkyl chain present on the imidazolium moieties along with careful selection of anion allowed for the hydrophobicity of the chelate complex to be tuned. Sufficiently long alkyl chains caused the chelate complex to become immiscible with water allowing very easy separation of the metal ions from the aqueous medium (**Figure 5**).[13]

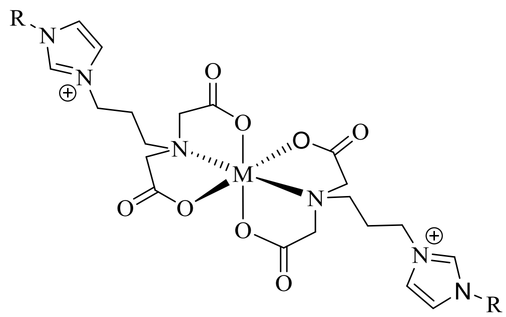


Figure 5. Structure of Ethylene Diacetic Acid TSIL-Metal Complexes.[13]

1.4 Microwave Assisted Organic Synthesis

Since the pioneering work in 1986 by Geyde and co-workers using a domestic microwave oven, the use of microwave irradiation in organic synthesis has grown drastically.[51] Since the year 2000, when dedicated microwave reactors became commercially available, more than 2500 publications have reported the use of microwave irradiation in order to carry out a wide variety of synthetic applications.[52] Many examples in the literature have shown that microwave irradiation can be used to shorten reaction times, increase product yields and even change the distribution of products when compared to conventional heating methods.[52]

Conventional heating methods rely on convection currents and the thermal conductivity of the various materials that must be penetrated in order to heat the reaction mixture, and often result in the temperature of the reaction vessel being higher than that of the reaction mixture itself. These methods of heating result in a transfer of energy that is rather slow and inefficient, leading to prolonged reaction times.[53] In contrast to conventional heating, microwave irradiation results in dielectric heating, which couples the microwave energy with the molecules that are present in the reaction mixture. Microwave irradiation causes heating by the mechanisms of dipolar polarization and ionic conduction.[52] When irradiated with microwave frequencies, the dipoles and ions in the reaction mixture align with the magnetic field, and when the magnetic field direction is alternated, the dipoles and ions realign. During this process energy is lost due to molecular friction and dielectric loss, resulting in the heating of the reaction mixture. Microwave reaction vessels are typically made of microwave transparent materials, materials that contain few dipoles or ions, resulting in efficient heating of the reaction mixture without energy being wasted heating the reaction vessel itself.[53]

The ability of a material to convert microwave energy into heat is measured by a parameter called the loss tangent, defined as tan δ. Generally a reaction medium with a high loss tangent is required for efficient absorption of microwave energy, and thus for efficient heating of the medium. Many molecular solvents such as toluene, dichloromethane, acetonitrile and chloroform have relatively low loss tangents (<0.1) and are inefficient for use in microwave dielectric heating. Polar or ionic additives can be added to poor microwave absorbing molecular solvents to increase the efficiency with which they absorb microwave radiation.[54]

The direct coupling of microwave energy to molecules in a reaction mixture results in a very efficient heating method. Being ionic by definition, ionic liquids absorb microwave energy very efficiently using the ionic conduction mechanism. Ionic liquids have been used as additives to facilitate the efficient use of microwave irradiation as a heating method.[62] Utilizing ionic liquids as reaction media will allow very efficient heating to occur and reduce the amount of energy required to achieve and maintain elevated reaction temperatures.[62] Performing chemistry under mild conditions to minimize energy consumption is the sixth principle of green chemistry and utilizing ionic liquids and microwave irradiation can aid in achieving this aim.

1.5 Catalysis

With the advent of the concept of green chemistry and the development of such metrics as the Sheldon E Factor, the environmental impact of chemical processes is being brought to the forefront of the minds of chemists.[17] Catalysis, the use of a sub-stoichiometric reagent to accelerate a process, in synthesis, often allows for greater atom efficiency and a lower E Factor for processes. Stoichiometric reagents contribute a significant portion to the waste generated from chemical processes. Replacing stoichiometric reagents with catalytic quantities of substances will allow for a reduction of overall waste generated by a process.[1]

The formation of carbon-carbon bondsis vital to organic chemistry. The synthesis of most products, whether it be bulk chemicals, fine chemicals or pharmaceuticals will include a carbon-carbon bond being formed at some point in the synthesis.[17] Carbon-carbon bond forming reactions are numerous and include, among others, Diels-Alder reactions[18], aldol reactions[19], Claisen reactions[20], Michael reactions[21], Heck, Suzuki and Sonogashira coupling reactions[17] as well as the Morita-Baylis-Hillman reaction[22]. Each of these reactions can be catalyzed by transition metals and/or organic molecules.[17]

While transition metal catalyzed carbon-carbon bond forming reactions such as Heck, Suzuki and Sonogashira coupling reactions are inherently not entirely green due to the presence of a palladium catalyst, they provide a marked improvement over stoichiometric reactions. The introduction of the Heck reaction allowed for the coupling of aromatic rings with side chains to be performed under much more mild conditions than the Lewis acid catalyzed Friedel-Crafts method. Suzuki and Sonogashira couplings allow a high yielding and relatively clean linkage of two substituted aromatic rings.[17] In order to make these processes greener and sustainable recovery methods for the palladium catalyst have been devised such as using palladium on a solid support or having the palladium catalyst phase separate from the reaction to allow for easy recyclability.[17]

1.5.1 Organocatalysis

Organocatalysis can be defined as the acceleration of a chemical reaction using a sub-stoichiometric quantity of an organic compound that does not contain a metal atom.[27] The use of non-metallic catalysts to accelerate organic reactions has been known and reported for almost a century.[23] Work by K.J. Pedersen and Frank Westheimer in 1934 demonstrated the iminium catalysis of the decarboxylation of β-keto acids. Subsequently in 1940 Westheimer showed that a retro-aldol reaction could be accelerated by enamine catalysis.[24]Hajos and Parrish used (s)-proline to facilitate an asymmetric aldol cyclization (**Figure 6**).[28] Despite these early reports of organocatalytic transformations, the field of organocatalysis remained dormant for years. This is due to the fact that these early reports focused on the individual reactions and not underlyingprinciples that could be made widely applicable.[24]

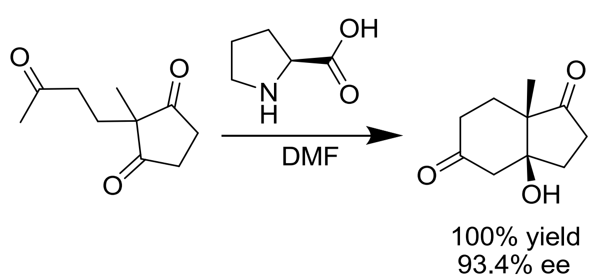


Figure 6. Asymmetric Aldol Cyclization Reported by Hajos and Parrish.[28]

The modern wide reaching field of organocatalysts began at the turn of the twenty first century when reports by David MacMillan[25] and Benjamin List[26] showed that secondary amines could be used to catalyze asymmetric Diels-Alder and aldol reactions respectively. Showing the diverse applicability and potential for tuning organocatalyst activities, MacMillan used the same class of imidazolidinone catalyst shown to be active in Diels-Alder reactions and performed Friedel-Crafts coupling of α,β-unsaturated aldehydes to heterocycles(**Figure 7**). The imidazolidinone catalyst depicted below on the left was shown to be active in reactions using a pyrrole nucleophile but inactive in reactions where N-methylindole was the nucleophile. The imidazolidinone depicted below on the right showed catalytic activity in reactions with N-methylindole as the nucleophile demonstrating that basic principles of organocatalysis could be widely applied by tuning auxiliary moieties of the organocatalyst for specific applications.[29]

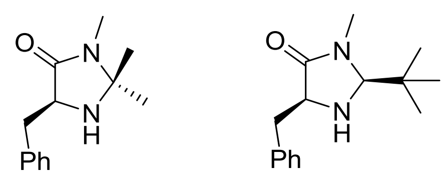


Figure 7. MacMillan Imidazolidinone Organocatalysts.

Since these initial reports the number of publications in the field of organocatalysis has grown exponentially each year (**Figure 8**) and the number of reactions organocatalysts have been applied to has also grown substantially.[27]

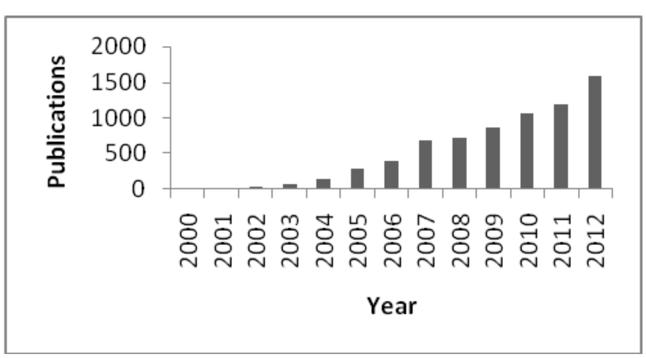


Figure 8. Organocatalysis Publication Statistics.[27]

Continuing upon the pioneering work of MacMillan and List, the modern field of organocatalysis now features reports of metal free catalysis of Claisenreactions[21], Michael reactions[21] and Morita-Baylis-Hillman reactions.[22]

1.6 Thiourea Organocatalysis

Thiourea organocatalysis functions on the principle that Lewis acidic hydrogen atoms can form hydrogen bonds with a Lewis basic heteroatom to facilitate catalysis. One of the first examples of this work was when Hine *et al.* showed in the mid-1980s that conformationally rigid 1,8-biphenylenediol could form two hydrogen bonds to the same oxygen atom of 1,2,6-trimethyl-4-pyridone from X-ray crystal structure analysis (**Figure 9**).[30] Hine and co-workers subsequently showed that twelve-fold rate enhancement over a phenol catalyst for the aminolysis of an epoxide could be achieved using 1,8-biphenylenediol.[31] According to a Brönsted plot created by the authors, a monohydroxylic phenol that is 600 fold more acidic than phenol would be needed to achieve this rate enhancement based on acidity effects alone. The pKa of phenol is 9.98 and the pKa of 1,8-biphenylenediol is 8.00 indicating that having both hydroxyl groups participate in catalysis is significant to the observed rate enhancement.[31]

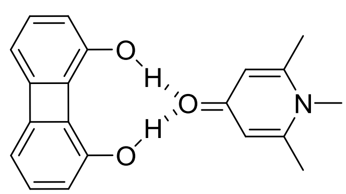


Figure 9. Hydrogen Bonding of 1,8-Biphenylenediol.[30]

In 1990 Kelly and co-workers showed that using a structural analogue of 1,8-biphenylenediol could catalyze a Diels-Alder reaction between cyclopentadiene and α,β-unsaturated aldehydes and proposed double hydrogen bonding interactions with the aldehyde carbonyl group oxygen atom as the reason for the observed rate enhancement.[32]

Also published in 1990 was a report by Etter *et al.* showing that 3,3'-dinitrocarbanilide could doubly hydrogen bond with substrates containing heteroatoms in a variety of functional groups. Tetrahydrofuran, *p*-nitroaniline, benzophenone, dimethyl sulfoxide and triphenylphosphine oxide all bonded to the urea protons *via* their oxygen atom.[33] This work showed that double hydrogen bonding by metal free diprotic species could be applied to a wide variety of substrates. Although the 1,8-biphenylenediols possess a very limited solubility profile limiting their use, the effectiveness of double hydrogen bonding catalysts shown by Hine and Kelly made further exploration of thiourea based double hydrogen bonding catalysts viable.

Since this initial research was performed using double hydrogen bonding catalysts much work has been done by Schreiner and co-workers exploring the use of thiourea based organocatalysts.[34-36] Schreiner and Wittkopp showed, in 2002, that an electron deficient thiourea catalyst (**Figure 10**) could behave like a Lewis acid. Like $AlCl_3$ and $TiCl_4$, Schreiner's electron deficient thiourea catalyzed the reaction between cyclopentadiene and an oxazolidinone which generally do not react with simple dieneophiles at ambient temperatures without the presence of a catalyst.[34]

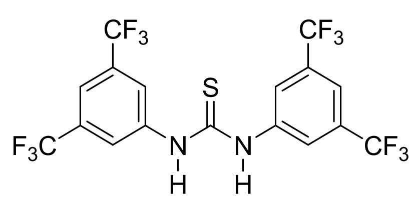


Figure 10. Schreiner's Thiourea.[34]

IR spectroscopy studies performed by Schreiner and Wittkopp shed light onto the interactions of the thiourea catalyst with the oxazolidinone (**Figure 11**). The shift observed in both carbonyl stretching frequencies indicate that the thiourea is bonding to both oxygen atoms in the substrate.[34]

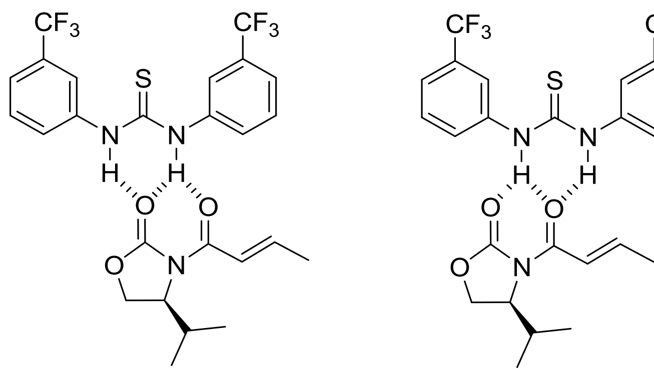
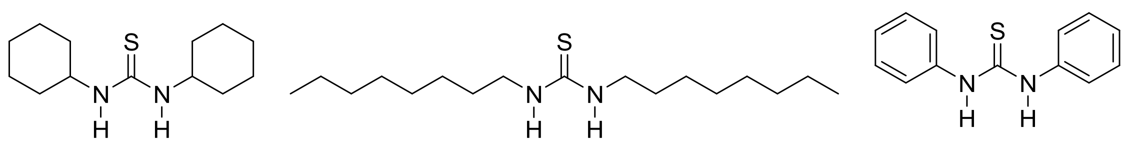


Figure 11. Thiourea-Substrate Binding.[34]

Subsequently, in 2003, Schreiner and Wittkopp elucidated key structural features by systematically varying the substituents of the thiourea backbone. It was found alkyl substituents and unsubstituted phenyl substituents gave very poor catalysts (**Figure 12**).[35,36]



Fi

gure 12. Unsuccessful Thiourea Catalysts.[35,36]

The need for electron deficiency in thiourea catalyst design was made apparent by the fact that N,N'-bis(3-trifluoromethylphenyl)thiourea gave substantial rate enhancement with respect to N,N'-diphenylthiourea.[35] If this rate enhancement were to be attributed to purely electron withdrawing effects and increasing the acidity of the secondary amine protons, then N,N'-bis(2-trifluoromethylphenyl)thiourea should show greater catalytic activity than N,N'-bis(3-

trifluoromethylphenyl)thiourea. However, the opposite was found to be true and having the trifluoromethyl group in an *ortho* position rather than a *meta* position with respect to the secondary amine functionality rendered the catalyst inactive.[35] Computations and crystallographic data published by Schreiner *et al.* in 2012 showed that there were interactions between the *ortho* protons on the phenyl ring possessing *meta* trifluromethyl substitution and the Lewis basic sulfur atom of the thiourea backbone. These rigidifying interactions cause a minimization of entropy loss when the catalyst binds to the substrate, making catalyst binding more thermodynamically favorable, especially since the enthalpic binding between the secondary amine protons and substrate heteroatoms is much weaker than with a conventional Lewis acid.[36]

Based upon the work performed by Schreiner and co-workers key structural features for thiourea catalyst design can be elucidated. Highly acidic amine protons are necessary for any substrate binding to be observed; thus, the thiourea must be electron deficient.[36] Rigidifying effects between *ortho* protons of the phenyl ring and the sulfur atom of the thiourea backbone make catalysis thermodynamically more favorable from an entropy perspective so the phenyl rings of a thiourea catalyst cannot be *ortho* substituted (**Figure 13**). Thus, electron deficient phenyl rings not substituted in the *ortho* position, such as the 3,5-bis(trifluromethyl)phenyl group, are very suitable substituents for thiourea catalysts.[35,36]

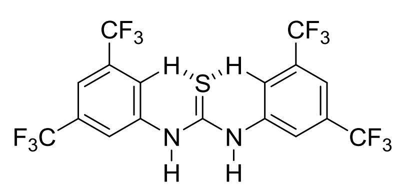


Figure 13. Rigidifying Interactions in Schreiner’s Catalyst.

1.7 Morita-Baylis-Hillman Reaction

1.7.1 Mechanistic Aspects

The Morita-Baylis-Hillman reaction is a carbon-carbon bond forming reaction that occurs between aldehydes and α,β-unsaturated ketones to afford allylic alcohols (**Figure 14**). A nucleophilic base, typically a tertiary amine or phosphine, is needed to catalyze the Morita-Baylis-Hillman Reaction.[37]

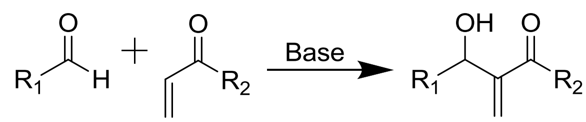


Figure 14. General Morita-Baylis-Hillman Reaction Scheme.

Based upon the work of Hill and Isaacs the Morita-Baylis-Hillman reaction was thought to proceed *via* addition of the nucleophilic base to the α,β-unsaturated ketone to afford a zwitterionic enolate intermediate that added to the aldehyde in the rate determining step, followed by a proton abstraction and elimination of the base (**Figure 15**).[38]

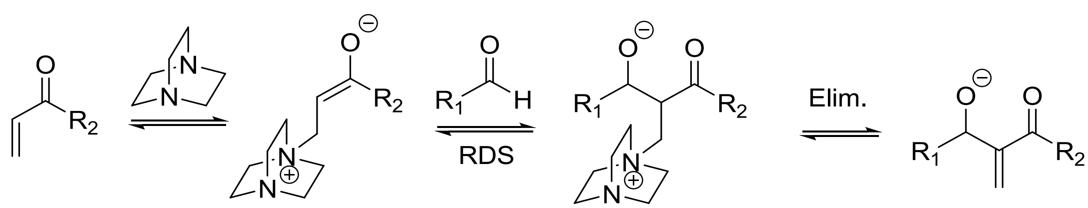


Figure 15. Mechanism Proposed by Hill and Isaacs.[38]

More recent work conducted by the McQuade group showed that the mechanism proposed by Hill and Isaacs needed modification. Kinetic studies showed that the rate determining step was first order with respect to the nucleophilic base and α,β-unsaturated ketone but second order with respect to the aldehyde (**Figure 16**). This is not in agreement with the proposed rate determining step in the mechanism put forward by Hill and Isaacs which is first order with respect to the aldehyde. The mechanism proposed by McQuade was further supported using a primary kinetic isotope effect experiment.[39]McQuade and co-workers further showed that this mechanism is consistent under polar, nonpolar and protic conditions observing the same rate data and kinetic isotope effects in all types of reaction media mentioned.[40]

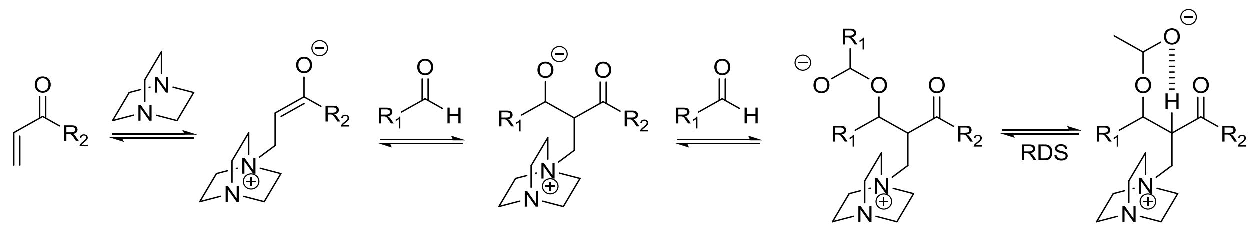


Figure 16. Proposed Mechanism by McQuade.[39]

1.7.2 Rate Acceleration

While the Morita-Baylis-Hillman reaction is very useful with respect to the fact that it affords an atom economical path to densely functionalized allylic alcohols which are useful synthetic building blocks, the reaction suffers from notoriously slow rates of reation.[41] The rates of Morita-Baylis-Hillman reactions have shown to be accelerated in polar solvents such as THF or acetonitrile, owning to the stabilization of the charge separation observed in the enolate intermediate.[42,43] It has been reported in literature that non-imidazolium based ionic liquids, very polar solvents, show rate enhancement of the Morita-Baylis-Hillman reaction.[44,45] When imidazolium ionic liquids were used, rate enhancement seemed to occur due to the disappearance of benzaldehyde but it was shown by Aggarwal and co-workers that under Morita-Baylis-

Hillman conditions the C2 position of the imidazolium ring was being deprotonated and the free carbene was adding to benzaldehyde (**Figure 17**).[46]

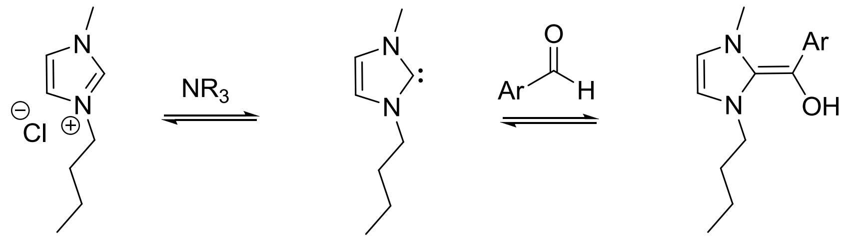


Figure 17.Imidazolium IL Reacting with Benzaldehyde under Basic Conditions.

The Morita-Baylis-Hillman reaction has also been shown to be promoted by Lewis acidic hydrogen bond donating thiourea derivatives.[22,47] The proposed mechanism of action for thiourea co-catalysts in the Morita-Baylis-Hillman reaction is activation of the aldehyde towards nucleophilic attack and stabilization of the negative charge on the oxygen in the enolate intermediate.[22,47]

1.8 Objectives

The observed rate enhancement using both ionic liquids and thiourea hydrogen bonding co-catalysts in the Morita-Baylis-Hillman reaction is very encouraging. Based upon the catalytic strategies previously used within Singer group, the goal of this project is to design and synthesize a thiourea derived co-catalyst for the Morita-Baylis-Hillman reaction containing an ionic liquid tag (**Figure 18**). By choosing the appropriate ionic liquid tag the electron deficient nature of the catalyst can be maintained while allowing for immobilization of the catalyst in an ionic liquid phase to facilitate recycling of the catalyst.

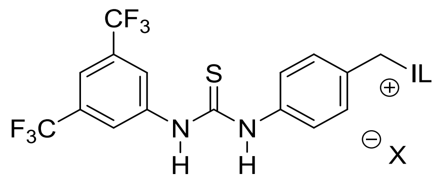


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Figure 18. Ionic Liquid Tagged Thiourea Co-Catalyst Design.

A green synthetic pathway will be elucidated for the preparation of a thiourea co-catalyst for the Morita-Baylis-Hillman reaction containing an IL tag. Upon successful synthesis of the thiourea co-catalyst, the catalytic activity of the molecule will be tested in a Morita-Baylis-Hillman reaction and if successful, immobilization in an ionic liquid phase for use in successive reactions will be attempted. Microwave irradiation with a Morita-Baylis-Hillman reaction in an ionic liquid medium will be used to achieve efficient dielectric heating of the reaction mixture and ideally reduce the long reaction times associated with the Morita-Baylis-Hillman Reaction.

2.0 Results and Discussion

The synthesis of the IL-tagged thiourea, **1**, was designed to be green and economical. The number of synthetic steps was carefully considered along with the reagents and solvents used. *p*-Nitrobenzyl bromide was chosen as the starting material due to its relatively low cost compared to other potential starting materials and it contains functionality that could be easily modified to meet the needs of this synthesis.

Synthesis of 1-methyl-3-(*p*-nitrobenzyl)imidazolium bromide, **2**, was performed reacting *p*-nitrobenzyl bromide (1 eq.) and 1-methylimidazole (1 eq.) in toluene at 80°C for 6 hours. The ionic nature of the product resulted in precipitation of the product in toluene. After filtration and drying under vacuum and the product was obtained in a 47% yield. This yield seemed quite low for a straightforward S_N2 reaction and required further optimization. The synthesis was performed again using acetonitrile (polar, aprotic) as a solvent instead of toluene. The product remained in solution when acetonitrile was used so the solvent was removed *in vacuo* to afford the crude product. This crude product was washed with toluene to remove any unreacted starting material, filtered and dried under vacuum. Using this modified procedure the product was obtained in a 91% yield. The product, **2**, (**Figure 19**) was characterized using ^{1}H and ^{13}C NMR spectroscopy, infrared spectroscopy and ESI-MS.

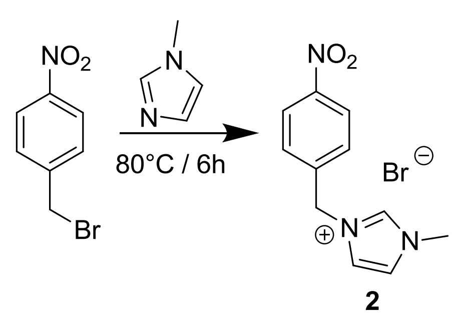

Figure 19. Synthesis of 1-methyl-3-(*p*-nitrobenzyl)imidazolium bromide, **2**.

The synthesis of 1-methyl-3-(*p*-nitrobenzyl)imidazolium bromide, **2**, was repeated under microwave irradiation rather than conventional heating in an attempt to reduce the reaction time. The reaction was performed in an open vessel using a reflux condenser with acetonitrile as the solvent, using microwave heating at 80 °C for 15 minutes. The microwave power was set to 20W but after an initial ramping period of approximately two minutes the microwave reduced the power input to between 2W and 3W to maintain the reaction temperature for the 15 minute duration of the reaction, minimizing energy consumption. The reaction work up was modified so that rather than evaporating the acetonitrile and washing with toluene, an equal volume of ethyl acetate was added to the reaction mixture causing the product to precipitate from solution as a white solid. Using this alternate workup, the product was obtained in an 82% yield upon filtration of the precipitated product. The spectral data matched that previously obtained for 1-methyl-3-(*p*-nitrobenzyl)imidazolium bromide, **2**, obtained via the initial method describe above.

In order to perform the anion metathesis to the PF_6 salt, 1-methyl-3-(*p*-nitrobenzyl)imidazolium bromide, **2**, was dissolved in water and 1.25 equivalents of aqueous HPF_6 was added dropwise. The reaction mixture was allowed to stir at room temperature for three hours. Due to the hydrophobic nature of the hexafluorophosphate salt, the product precipitated from solution, driving the reaction to completion according to Le Chatelier's principle. The product was filtered and dried under vacuum to afford 1-methyl-3-(*p*-nitrobenzyl)imidazolium hexafluorophosphate, **3**, (**Figure 20**)in a 95% yield. The product, **3**, was characterized using ^{1}H,^{13}C and ^{31}P NMR spectroscopy, infrared spectroscopy and ESI-MS. The successful metathesis was confirmed by the septet observed in the ^{31}P NMR spectrum and the peaks in the infrared spectrum at 557 and 843cm^{-1} corresponding to the hexafluorophosphate ion.

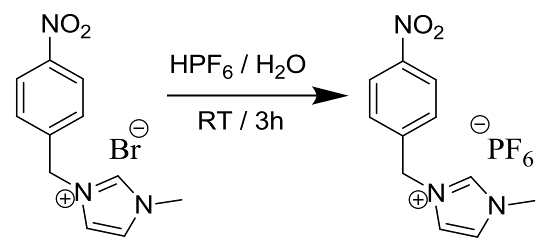

Figure 20. Synthesis of 1-methyl-3-(*p*-nitrobenzyl)imidazolium hexafluorophosphate, **3**.

The synthesis of a thiourea compound can be achieved by reacting an isothiocyanate with an amine. For this approach to be accessible for this synthetic scheme the nitro group present in 1-methyl-3-(*p*-nitrobenzyl)imidazolium hexafluorophosphate, **3**, needed to be reduced to an amino group to afford 1-methyl-3-(*p*-aminobenzyl)imidazolium hexafluorophosphate, **4**. Initially an approach was attempted that used hydrazine hydrate as the reducing agent and ferrous sulphateheptahydrate as a catalyst as reported by Singh *et al*.[48]This failed to yield any of the desired amino compound. A method of reducing nitroarenes reported by Ranu and co-workers using iron(0) in water was then attempted.[49]Hence, ferrous sulphate heptahydrate (3 eq.) and sodium citrate (0.25 eq.) were added to water with stirring and sodium borohydride (5 eq.) was then slowly added to the mixture. The sodium borohydride reduced the iron(II) to iron (0). The stirring was ceased and the iron settled to the bottom of the flask and the water was decanted. The iron was washed twice more with water, stirring and decanting before use. The 1-methyl-3-(*p*-nitrobenzyl)imidazolium hexafluorophosphate, **3**, (1 eq.) was added to the flask containing the iron and water and was stirred for 24 hours at room temperature. After completion of the reaction, the mixture was passed through a medium pore sized glass frit in order to separate the aqueous layer from the iron residues. Following the literature procedure,[49] the aqueous layer was extracted with ethyl acetate but no product was observed due to water insolubility of the product because it remained in the frit along with the iron residues. The iron residues remaining in the frit were washed with acetonitrile and when the acetonitrile was removed *in vacuo*, a yellow solid remained in the flask. This yellow solid was determined to be the desired 1-methyl-3-(*p*-aminobenzyl)imidazolium hexafluorophosphate, **4**. The disappearance of the nitro group stretching peaks at 1352 and 1522cm^{-1}and the appearance of primary amine stretching peaks at 3414 and 3509cm^{-1}confirmed the successful reduction of the nitro group. The product, **4**, was obtained after drying under vacuum in a 61% yield and was further characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, ESI-MS and ESI-HRMS.

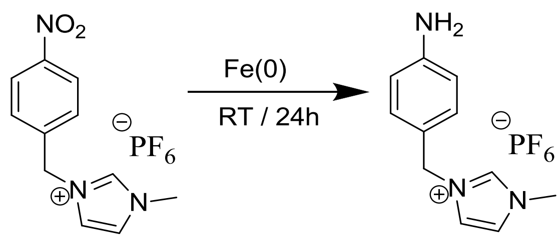

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Figure 21. Synthesis of 1-methyl-3-(*p*-aminobenzyl)imidazolium hexafluorophosphate, **4**.

To synthesize the desired thiourea derivative, 1-methyl-3-(*p*-aminobenzyl)imidazolium hexafluorophosphate, **4**, was mixed in a 1:1 ratio with 3,5-bis(trifluoromethyl)phenyl isothiocynate in acetonitrile and stirred at room temperature for seven days. After completion of the reaction, the acetonitrile and unreacted 3,5-bis(trifluoromethyl)phenyl isothiocyanate were removed *in vacuo* to afford a yellow oil. This was further dried under reduced pressure to remove residual acetonitrile to afford a yellow colored solid. This yellow colored solid, containing a mixture of the desired product, **5**, and 1-methyl-3-(*p*-aminobenzyl)imidazolium hexafluorophosphate, **4**, was purified using silica gel column chromatography with acetone as the eluent. The product moved down the column as a pale yellow band and the 1-methyl-3-(*p*-

aminobenzyl)imidazolium hexafluorophosphate, **4**, remained at the top of the column, allowing for very easy purification of the reaction mixture. The eluent was evaporated *in vacuo* to afford a yellow oil-like substance. This was placed under vacuum to remove residual acetone to afford a pale yellow colored solid. This procedure yields the desired product, **5**, in an 80% yield. The product was characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, FT-IR, ESI-MS, ESI-HRMS and single crystal XRD. The ^{1}H NMR spectrum, showing amine protons at 10.29 and 10.34 ppm, clearly demonstrates that the reaction was successful.

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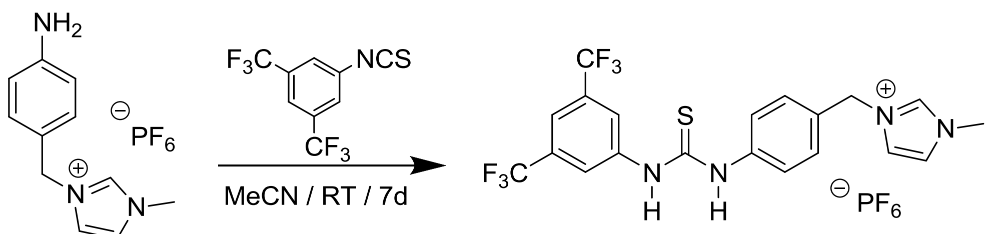

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Figure 22. Reaction Scheme for Synthesis of *N*-3,5-bis(trifluoromethyl)phenyl-*N*'-*p*-(benzyl-1-methylimidaolium)phenylthiourea hexafluorophosphate, **5**.

Thiourea derivatives have been shown to co-crystallize with Lewis basic heteroatom containing molecules with both amine protons of the thiourea being bonded to the heteroatom of the other molecule.[33]Hence, a 1:1 molar mixture of **4** and benzophenone was dissolved in a minimum amount of ethanol. Compound **4** co-crystallized with benzophenone to afford a co-crystal, **6**, but there were no hydrogen bonding interactions present between the amine protons and benzophenone (**Figure 23**).

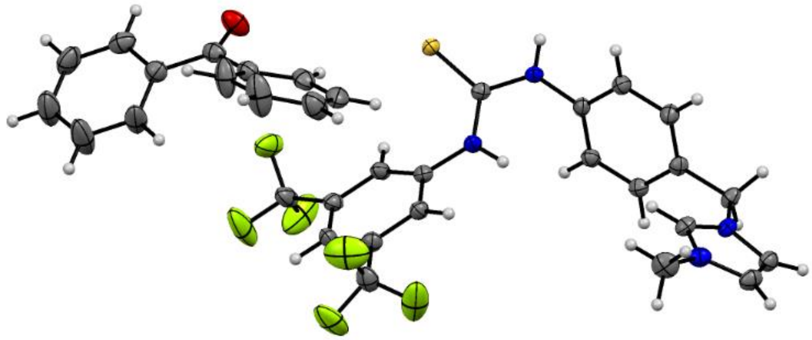

Figure 23.Crystal Structure of **5**·Benzophenone, **6**.

The thiourea co-catalyst *N*-3,5-bis(trifluoromethyl)phenyl-*N*'-*p*-(benzyl-1-methyl imidazolium)phenylthiourea, **5**, contains an imidazolium ionic liquid moiety which has a proton at the C2 position which is sufficiently acidic such that it can be removed under basic conditions present in the Morita-Baylis-Hillman reaction. This free carbene created by deprotonation at the C2 position could add to the carbonyl carbon atom of the aldehyde used in the Morita-Baylis-Hillman reaction causing an unwanted side reaction. Hence, a thiourea derivative containing an imidazolium moiety that has a proton at the C2 position cannot be used for a Morita-Baylis-Hillman reaction due to this structural feature. However, the imidazolium thiourea derivative, **5**, may be useful for accelerating Diels Alder or Friedel Crafts reactions, but the goal of this project was to design and synthesize a thiourea derivative capable of accelerating a Morita-Baylis-Hillman reaction. Hence, the 1-methylimidazolium ionic liquid tag was substituted with an *N*-methylpyrrolidinium ionic liquid tag. *N*-methylpyrroldinium moieties are inert under Baylis-Hillman conditions because they possess no acidic protons.

The four step synthesis used to make the ionic liquid tagged thiourea derivatives is a modular synthesis that allows for easy modification of the ionic liquid tag present. Using a similar synthetic sequence as for *N*-3,5-bis(trifluoromethyl)phenyl-*N*'-*p*-(benzyl-1-

methylimidazolium)phenylthiourea hexafluorophosphate, **5**, the modified derivative *N*-3,5-bis(trifluoromethyl)phenyl-*N*'-*p*-(benzyl-*N*-methylpyrrolidinium)phenylthiourea hexafluorophosphate, **10**, was synthesized.

Hence, *p*-nitrobenzyl bromide was dissolved in acetonitrile and *N*-methylpyrrolidine (1 eq.) was added and the reaction mixture was heated to 80°C for 6 hours using conventional heating. The acetonitrile was removed *in vacuo* and the product was washed with toluene to remove any unreacted starting materials. The product was dried under vacuum and was obtained in a 90% yield. The product, **5**, was characterized using ^{1}H and ^{13}C NMR spectroscopy, infrared spectroscopy and ESI-MS.

Similarly to **2**, the synthesis of *N*-methyl-*N*-(*p*-nitrobenzyl)pyrrolidinium bromide, **7**, (**Figure 24**) was repeated under microwave irradiation using a reaction temperature of 80 °C for 15 minutes with acetonitrile as the solvent. The product, **7**, was precipitated from the reaction mixture using an equal volume of ethyl acetate and obtained in an 81% yield. The spectral data matched that previously obtained for **7**.

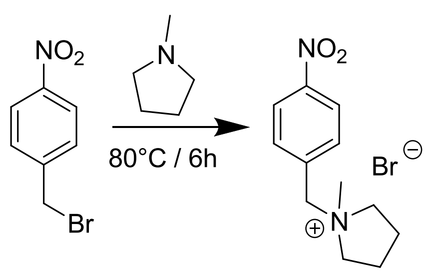

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Figure 24. Reaction Scheme for Synthesis of *N*-methyl-*N*-(*p*-nitrobenzyl)pyrrolidinium bromide, **7**.

N-methyl-*N*-(*p*-nitrobenzyl)pyrrolidinium bromide, **7**, was then dissolved water and aqueous HPF_6 (1.25 eq.) was added dropwise. The product precipitated from solution, was filtered and dried under vacuum to afford *N*-methyl-*N*-(*p*-nitrobenzyl)pyrrolidinium hexafluorophosphate, **8**, (**Figure 25**) in an 85% yield. The product, **8**, was characterized using ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, infrared spectroscopy and ESI-MS. The successful metathesis was confirmed by the septet observed in the ^{31}P NMR spectrum and the peaks in the infrared spectrum at 557 and 834 wavenumbers corresponding to the hexafluorophosphate anion.

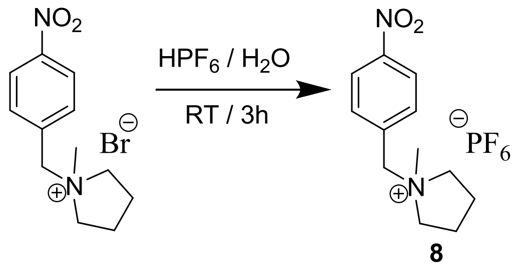

Figure 25. Synthesis of *N*-methyl-*N*-(*p*-nitrobenzyl)pyrrolidinium hexafluorophosphate, **8**.

Reduction of the nitro group in *N*-methyl-*N*-(*p*-nitrobenzyl)pyrrolidinium hexafluorophosphate, **8**, was performed using the same modified iron(0) procedure[49] used to synthesize 1-methyl-3-(*p*-aminobenzyl)imidazolium hexafluorophosphate, **4**. *N*-methyl-*N*-(*p*-aminobenzyl)pyrrolidinium hexafluorophosphate, **9**, (**Figure 26**) was obtained in 73% yield. The disappearance of the nitro group stretching peaks at 1359 and 1530 $cm^{-1}$and the appearance of primary amine stretching peaks at 3401 and 3489 cm^{-1} confirmed the successful reduction of the nitro group. The product, **9**, was further characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR ESI-MS, and ESI-HRMS.

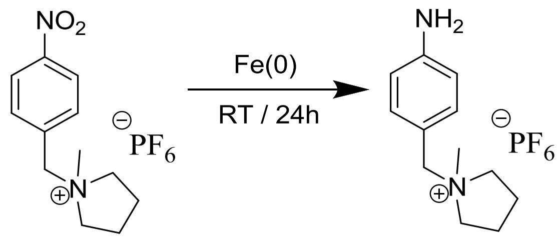

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Figure 26. Synthesis of *N*-methyl-*N*-(*p*-aminobenzyl)pyrrolidinium hexafluorophosphate, **9**.

N-3,5-bis(trifluoromethyl)phenyl-*N*'-*p*-(benzyl-N-methylpyrrolidinium)phenylthiourea hexafluorophosphate, **10**,was synthesized using the same procedure that was used for *N*-3,5-bis(trifluoromethyl)phenyl-*N*'-*p*-(benzyl-1-methylimidazolium)phenylthiourea hexafluorophosphate, **5**. After dissolving *N*-methyl-*N*-(*p*-aminobenzyl)pyrrolidinium hexafluorophosphate, **9**, in acetonitrile, 3,5-bis(trifluoromethyl)phenyl isothiocyanate (1 eq.) was added and the reaction mixture was allowed to stir for seven days at room temperature. After the reaction was completed the product was obtained using column chromatography with acetone as the eluent. The product, **10**, was obtained in an 85% yield and was characterized using ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, FT-IR, ESI-MS, ESI-HRMS and single crystal XRD. The ^{1}H NMR spectrum clearly shows the reaction was successful. The amine protons are observed at 10.35 and 10.45 ppm.

The reaction to synthesize the thiourea backbone of the molecule from the substituted aniline and the isothiocynate is clearly the rate determining step in this synthesis, being seven times longer than the next longest step. In an attempt to alleviate the problem of long reaction time, the reaction between *N*-methyl-*N*-(*p*-aminobenzyl)pyrrolidinium hexafluorophosphate, **9**, and 3,5-bis(trifluoromethyl)phenyl isothiocynate could be significantly shortened using microwave irradiation at 50 °C for only two hours. The product, **10**, was obtained in an 81% yield which is very similar to the 85% yield achieved after a week at room temperature. Microwave heating is very efficient for this reaction since the substituted aniline product itself is ionic and thus the ionic conduction heating mechanism is active. While the microwave is maintaining the temperature at 50 °C for the duration of the reaction the power input is approximately 2-3 Watts.

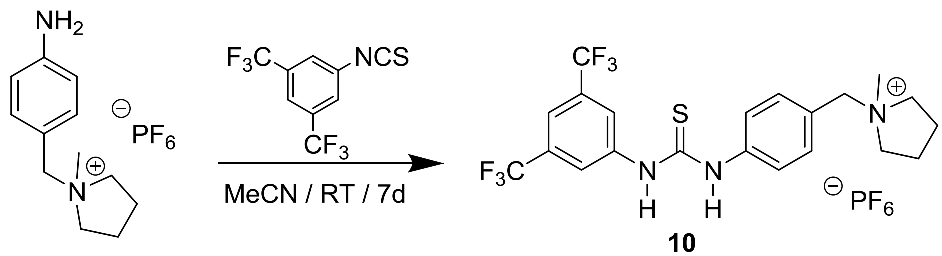


Figure 27. Synthesis of *N*-3,5-bis(trifluoromethyl)phenyl-*N'*-*p*-(benzyl-N-methylpyrrolidinium)phenylthiourea hexafluorophosphate, **10**.

X-ray quality crystals were obtained by dissolving a 1:1 mixture compound **10** and benzophenone in a minimum amount of ethanol and allowing slow evaporation of the solvent. The X-ray crystal structure of the adduct of **10** and ethanol, **11**, was obtained (**Figure 28**).

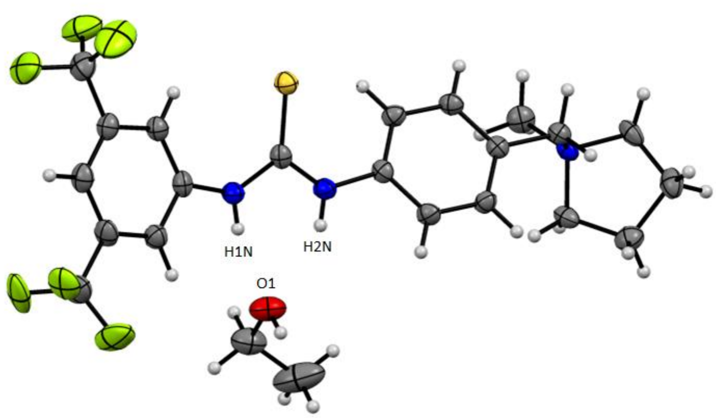


Figure 28. Crystal Structure of **10**·Ethanol, **11**.

The crystal structure of the ethanol adduct with **10** shows that the secondary amine protons are capable of forming two hydrogen bonds with a Lewis basic heteroatom, such as the oxygen atom present in ethanol, which is necessary for catalytic activity of thiourea derivatives. The interatomic distance between H1N and O1 is 2.04(2) Å and the interatomic distance between H2N and O1 is 2.19(2) Å indicating that the amine proton on the side of the molecule with the 3,5-bis(trifluoromethyl)phenyl group is more electron deficient than the amine proton on the side of the molecule with the p-(benzyl-N-methylpyrrolidinium)phenyl group, and both amine protons form medium strength hydrogen bonds with the Lewis basic oxygen atom.[63]

Further X-ray quality crystals were obtained by dissolving **10** in a minimum amount of acetone with crystals forming after several minutes. The X-ray crystal structure of the adduct of**10** and acetone, **12**, was obtained (**Figure 29**).

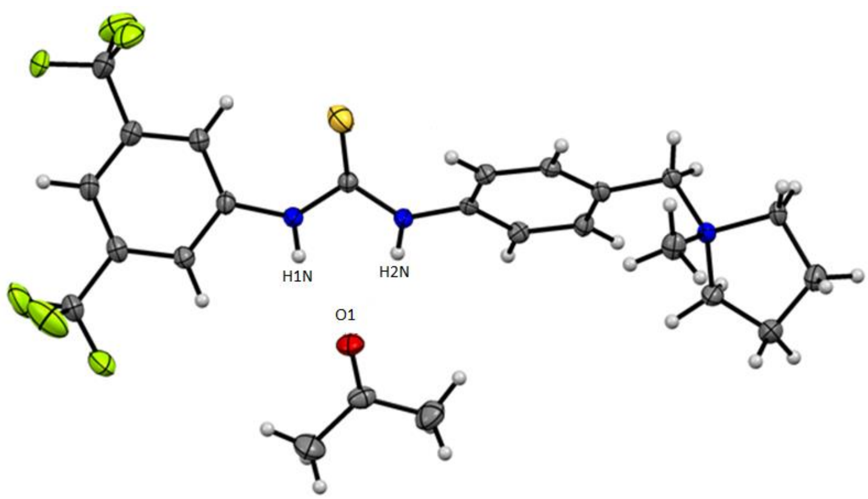


Figure 29. Crystal Structure of **8**·Acetone, **12**.

The crystal structure of the acetone adduct with **10** shows that both secondary amine protons present in the thiourea can hydrogen bond to a carbonyl oxygen atom, which is a postulated activation mode of the Morita-Baylis-Hillman reaction for hydrogen bonding co-catalysts. The interatomic distances between carbonyl oxygen O1 and H1N and H2N are 2.12(2) Å and 2.11(2) Å, respectively, indicative of medium strength hydrogen bonding.[63]

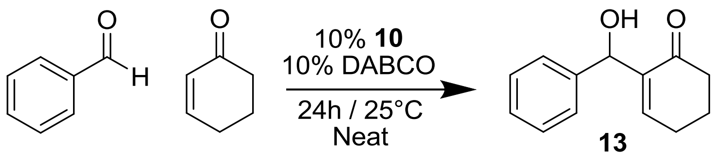
In order to test the catalytic activity of an ionic liquid tagged thiourea derivative in a Morita-Baylis-Hillman reaction, the previously synthesized *N*-methylpyrrolidinium thiourea derivative, **10**, was tested. Morita-Baylis-Hillman reactions have been previously performed under solvent free conditions in literature[22,50], so solvent free conditions were used initially herein. Benzaldehyde is the most commonly used aldehyde reported in literature for Morita-Baylis-Hillman reactions and was also used for this study. Methyl acrylate[50] and cyclohex-2-en-1-one[22] have been reportedly used in literature as the α,β-unsaturated ketone component and both were screened in this study.

Due to the electron withdrawing effects of the oxygen atom adjacent to the carbonyl group of methyl acrylate, the enolate intermediate is stabilized, and the Morita-Baylis-Hillman reaction between benzaldehyde and methyl acrylate proceeds at room temperature using DABCO without the addition of a thiourea co-catalyst. This makes determining the effect of the thiourea co-catalyst non-trivial and thus is not an ideal substrate choice. Also, the methyl acrylate had to be distilled prior to use in this reaction in order to remove the stabilizer, making it susceptible to polymerization and unstable over prolonged periods of storage.

Cyclohex-2-en-1-one, lacking an electron withdrawing group adjacent to the carbonyl group, does not have a stabilized enolate intermediate and the Morita-Baylis-Hillman reaction between benzaldehyde and cyclohex-2-en-1-one does not proceed at room temperature in the presence of DABCO alone without the presence of a thiourea co-catalyst. This makes determining catalytic activity rather straight forward as all product observed can be attributed to the ability of the thiourea derivative present to act as a co-catalyst. Having screened the two common α,β-unsaturated ketones reported in literature it was decided that for the purposes of this study that cyclohex-2-en-1-one was the ideal choice.

For our initial studies, DABCO and thiourea co-catalyst loading used was 10 mol %. The ratio of cyclohex-2-en-1-one to benzaldehyde was varied to determine optimal reaction conditions.

Table 1: Optimization of Reaction Stoichiometry



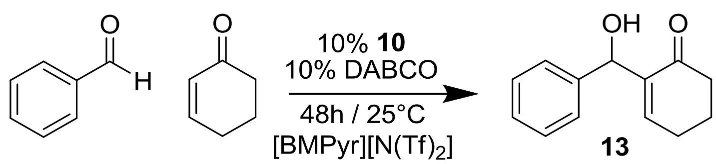
Benzaldehyde (mmol)	Cyclohex-2-en-1-one (mmol)	Yield(%)[a]
1.0	**1.0**	**8**
1.0	**2.5**	**34**
1.0	**5.0**	**80**

a) Yield determined by ^{1}H NMR

It was determined that the cyclohex-2-en-1-one to benzaldehyde ratio that gave the greatest conversion to 2-(hydroxyphenylmethyl)-cyclohex-2-en-1-one, **13**, was5:1 (**Table 1**). The percent conversions have been calculated based on the relative integrations of the benzaldehyde proton that appears at approximately 10 ppm in $CDCl_3$ and the methane proton in the product that occurs at approximately 5.5 ppm in $CDCl_3$. These signals are both clearly separated from all other signals and are clearly resolved. This reagent ratio is best suited for a synthesis where the aldehyde is the more precious, limiting reactant. The percent conversions have been calculated based on the amount of benzaldehyde converted into product and even with 80% conversion under the 5:1 conditions only 16% of the cyclohex-2-en-1-one used was converted into product.

The next step in the catalyst testing process was to determine if the catalyst could be immobilized in an ionic liquid and recycled for multiple uses. In order to perform this study 10 mol % thiourea catalyst was dissolved in 2 mL of [BMPyr][N(Tf)$_2$], **14**. The appropriate amounts of benzaldehyde, cyclohex-2-en-1-one and DABCO were then added to the reaction mixture.

Table 2: Catalyst Recycling Study in an Ionic Liquid



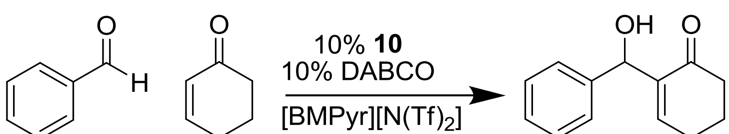
Run	Benzaldehyde (mmol)	Cyclohex-2-en-1-one (mmol)	Yield (%)[a]
1	1.0	5.0	38
2	1.0	5.0	36
3	1.0	5.0	35

a) Yield determined by ^{1}H NMR

Upon completion of the reaction, the reaction mixture was extracted with 5x10 mL portions of diethyl ether which is immiscible with [BMPyr][N(Tf)$_2$], **14**, and preferentially solvates the organic products and unreacted starting materials present. A crude extract aliquot was taken and a ^{1}H NMR was performed on the aliquot to determine % conversion. Again, the aldehyde proton at approximately 10 ppm in benzaldehyde and the methane proton in the product, **13**, at approximately 5.5 ppm were integrated and used to determine conversion percentages. The catalyst and ionic liquid phase were able to be successfully recycled without loss of catalytic activity as the variances in conversion are minimal. This facile method of catalyst recycling shows that the design of the catalyst was indeed successful in causing the ionic liquid tagged thiourea to be preferentially soluble in the ionic liquid phase with respect to the organic ether phase. The reduced yields compared to the neat reaction conditions are believed to be due to a dilution of the reaction mixture, or in other words, a concentration effect.

While the catalyst was shown to be easily recycled using an ionic liquid phase to conduct the reaction followed by extraction of the organic reaction materials with diethyl ether, the decreased yields observed were not optimal. Prolonged periods of conventional heating, while potentially increasing the reaction times, are not entirely efficient, or green, as much energy is consumed to maintain the reaction temperature due to thermal loss to the surroundings. In an effort to reduce the reaction times while maintaining energy efficiency and the green aspect of the catalyst system, microwave heating was employed once again (**Table 3**).

Table 3: Microwave Irradiation of Morita-Baylis-Hillman Reaction



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Benzaldehyde (mmol)	Cyclohex-2-en-1-one (mmol)	[BMPyr][$N(Tf)_2$] (mL)	Temperature (°C)	Time (Hours)	Yield (%)[a]
1.0	5.0	2.0	50	2	8
1.0	5.0	2.0	100	2	14
1.0	5.0	0.5	50	2	38
1.0	5.0	0.5	50	6	78

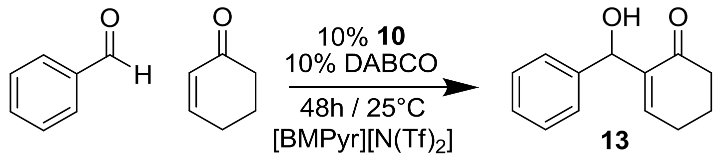
a) Yield determined by ^{1}H NMR

Use of microwave irradiation at 50 °C using the same volume of ionic liquid that was used in the recycling study provided approximately slightly more than a fifth of the conversion observed over the course of forty eight hours in only two hours, a marked improvement. To study the effect of temperature in this system the reaction temperature was raised to 100 °C.

Very little improvement was observed in the conversion and rather than the usual yellow color of the ionic liquid and catalyst solution when the 100 °C run was removed from the microwave reactor the solution was a dark orange color. This was not observed when the catalyst was recycled at room temperature and could hint toward thermal decomposition of the catalyst, reaction materials, IL solvent or all of these. Aside from potential decomposition issues, the slight increase in conversion hardly warrants the extra energy input to increase the reaction temperature by 50 °C. The best conversions were attained when the reaction was performed neat so it appeared that reducing the amount of ionic liquid and thus increasing reagent concentrations could potentially have a much more beneficial influence than increasing reaction temperatures above 50 °C. Hence, decreasing the amount of ionic liquid four-fold proved to be very effective in increasing the conversion to products as very similar conversion was attained after only two hours under microwave irradiation *versus* forty eight hours at room temperature.

To further explore the effect of decreasing the amount of ionic liquid present, a series of reactions were allowed to proceed at room temperature for 48 hours with the usual 10% catalyst loadings while varying the volume of ionic liquid (**Table 4**).

Table 4: Effect of IL Volume on Reaction Efficiency



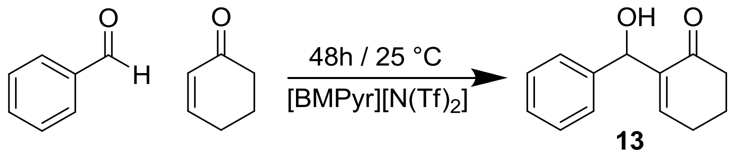
Benzaldehyde (mmol)	Cyclohex-2-en-1-one (mmol)	$[BMPyr][N(Tf)_2]$ (mL)	Yield (%)[a]
1.0	**5.0**	**2.0**	**38**
1.0	**5.0**	**1.0**	**54**
1.0	**5.0**	**0.5**	**96**

a) Yield determined by ^{1}H NMR

Decreasing the amount of ionic liquid used in room temperature reactions had the same effect that was observed in the microwave reactions. The decrease in ionic liquid volume utilized caused a very substantial increase in conversion to product. This is very likely predominantly due to a concentration effect. Decreasing the amount of ionic liquid used increases the concentration of reactant species in solution and therefore makes the reaction proceed much quicker. Use of the IL also promoted microwave irradiative heating.

After nearly full conversion was observed in 48 hours by reducing the amount of ionic liquid used in the reaction, it was then explored if nearly full conversion would be still possible to achieve with reduced catalyst loadings (**Table 5**).

Table 5: Effects ofCatalyst Loading



13

Benzaldehyde (mmol)	Cyclohex-2-en-1-one (mmol)	[BMPyr][N(Tf)$_2$] (mL)	8 (mol %)	DABCO (mol %)	Yield (%)[a]
1.0	**5.0**	**0.5**	**5**	**10**	**72**
1.0	**5.0**	**0.5**	**10**	**10**	**96**
1.0	**5.0**	**0.5**	**10**	**5**	**56**

a) Yield determined by ^{1}H NMR

Decreasing the catalyst loadings caused a decrease in conversion to the product, **13**. This showed that under the reaction conditions used that 10 mol % loading of **10** and DABCO were necessary to obtain near full conversion.

3.0 Conclusion

An ionic pyrrolidinium thiourea derivative was successfully designed and a synthesis elucidated that was very efficient, modular and relatively green with harsh reagents being avoided. Complete characterization of the thiourea derivative was then completed using IR, NMR, ESI-MS, ESI-HRMS and X-ray crystallography. The pyrrolidinium thiourea derivative was shown to be catalytically active as a co-catalyst in the DABCO catalyzed Morita-Baylis-Hillman reaction between benzaldehyde and cyclohex-2-en-1-one to afford 2-(hydroxyphenylmethyl)-cyclohex-2-en-1-one, **13**. Due to the ionic nature of the catalyst it was able to be successfully entrained in an IL, recycled and used in three cycles of the Morita-Baylis-Hillman reaction without loss of catalytic activity. This catalyst and ionic liquid system was able to be made more efficient with reduced reaction times by employing microwave irradiation and performing the reactions in a minimum of ionic liquid. Conversion levels could not be maintained with a reduced catalyst loading under the established conditions. An imidazolium thiourea derivative was also successfully synthesized and characterized using IR, NMR,ESI-MS, ESI-HRMS and X-ray crystallography but has yet to be tested for catalytic activity.

4.0 Future Work

Successful catalysis of a Morita-Baylis-Hillman reaction between benzaldehyde and cyclohex-2-en-1-one was achieved using the ionic organocatalyst, **8**. The substrate scope for the reaction should be explored, using a number of substituted aldehydes and various α,β-unsaturated ketones.

Furthermore, to fully understand the catalytic system a kinetic study would be appropriate to determine the kinetics of the reaction. The mechanism for the Morita-Baylis-Hillman reaction is still debated and not fully understood. A mechanism proposal by Hill and Isaacs provides evidence for a mechanism that is first order with respect to the aldehyde concentration while McQuade provides evidence for a mechanism that is second order with respect to the aldehyde concentration. Work by Kumar showed that a Morita-Baylis-Hillman reaction performed in ionic liquids can be first or second order with respect to aldehyde concentration, depending on the ionic liquid used.[54]

The imidazolium based ionic organocatalyst has yet to be tested for catalytic activity. The catalytic activity of **4** should be tested in reactions that are amenable to imidazolium based ionic liquids such as Diels Alder or Friedel Crafts reactions. Due to the modularity and ease with which different derivatives can be synthesized, several ionic liquid tags can be incorporated into different organocatalysts to design and test a wider range of ionic organocatalysts.

5.0 Experimental

5.1 General Procedures

Syntheses of catalysts and subsequent Morita-Baylis-Hillman reactions were performed in glassware that was cleaned using a Mandel Lancer dishwasher followed by drying in an oven at 110 °C for a minimum one hour. Solvents, including acetonitrile, acetone, toluene and diethyl ether were purchased from Sigma Aldrich and used directly from the bottle without further purification. [BMPyr][N(Tf)$_2$] was prepared using a previously reported procedure.[64]

p-Nitrobenzyl bromide, *N*-methylpyrrolidine, aqueous hexafluorophosphoric acid (60% w/v), iron sulfate heptahydrate, sodium citrate, sodium borohydride, 3,5-bis(trifluoromethyl)phenyl isothiocynate, benzaldehyde, cyclohex-2-en-1-one and DABCO were purchased from Sigma Aldrich and used without further purification.

Nuclear Magnetic Resonance spectra were registered using a Bruker 300 MHz Ultrashield spectrometer. Spectra were processed using Topspin. Deuterated solvents, DMSO-d^6 and $CDCl_3$,were purchased from Cambridge Isotope Laboratories.

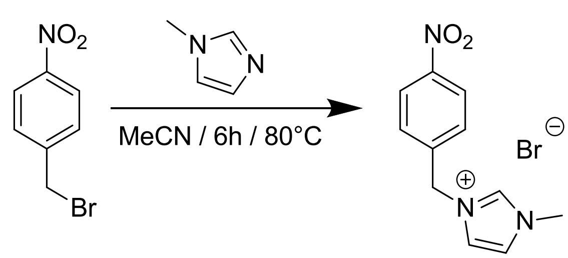
Melting point data was determined using an Electrothermal Mel-Temp 3.0 apparatus. Infrared spectra were recorded as KBr pellets using a Bruker ALPHA Infrared Spectrometer and processed using OPUS software. Electrospray ionization mass spectrometry experiments were performed at Saint Mary's Center for Environmental Analysis and Remediation by Patricia Granados. ESI-MS was performed using an Agilent 1100 LC/MSD Trap.

Crystals were attached to the tip of a 300 μmMicroLoop with paratone-N oil. Measurements were made on a Bruker APEXII CCD equipped diffractometer (30 mA, 50 mV) using monochromated Mo Kαradiation (λ= 0.71073 Å) at 125 K.[55]The initial orientation and unit cell were indexed using a least-squares analysis of a random set of reflections collected from three series of 0.5° ω-scans, 10 seconds per frame and 12 frames per series, that were well distributed in reciprocal space. For data collection, four ω-scan frame series were collected with 0.5° wide scans, 30 second frames and 366 frames per series at varying φ angles (φ = 0°, 90°, 180°, 270°). The crystal to detector distance was set to 6 cm and a complete sphere of data was collected. Cell refinement and data reduction were performed with the Bruker SAINT software, which corrects for beam inhomogeneity, possible crystal decay, Lorentz and polarisation effects.[56] A multi-scan absorption correction was applied.[57] The structures were solved using direct methods (SHELXS-2013)[58] and refined using a full-matrix least-squares method on F^2 with SHELXL-2013.[58]

5.2 Synthesis of the 1-Methylimidazolium Tagged Thiourea, 2

Preparation of 1-methyl-3-(*p*-nitrobenzyl)imidazolium bromide, **2**

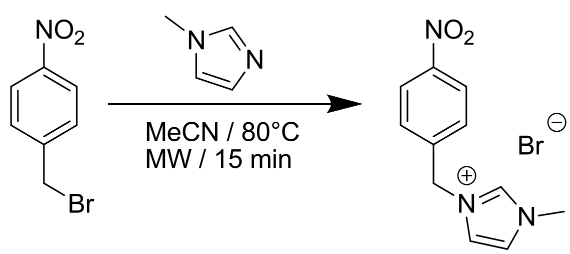
Method A:



2

p-Nitrobenzyl bromide (0.982 g, 4.49 mmol) was dissolved in 50 mL MeCN and 1-methylimidazole (0.36 mL, 4.49 mmol) was added dropwise at ambient temperature. The reaction was then heated and stirred at 80°C for 6 hours. Solvent was removed *in vacuo* followed by suspension of the product in toluene to remove any unreacted starting materials, filtered and dried under vacuum to afford an off white solid. (1.22 g, 91% yield). MP 162-164 °C, IR (KBr): 3090, 2921, 1602, 1510, 1447, 1344 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300MHz) δ 9.44 (s, 1H), 8.25 (d, *J*=8.0 Hz, 2H), 7.90 (s, 1H), 7.81 (s, 1H), 7.72 (d, *J*=8.0 Hz, 2H), 5.69 (s, 2H), 3.89 (s, 3H) ; ^{13}C NMR (DMSO-d_6, 75MHz) δ148.0, 142.7, 137.6, 130.5, 124.6, 124.4, 122.9, 51.2, 36.5; ESI-MS: Positive mode: Found: m/z 218.0 [100%, $(C_{11}H_{12}N_3O_2)^+$]; Calc: 218.1

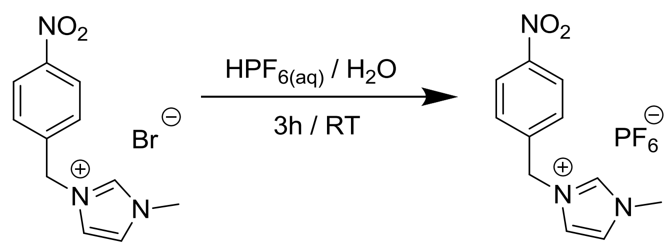
Method B:



2

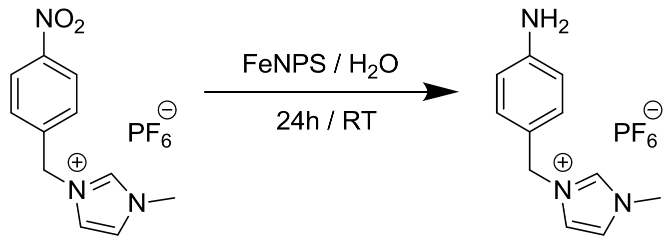
p-Nitrobenzyl bromide (1.00g, 4.77mmol) was dissolved in 10 mL MeCN and 1-methylimidazole (0.38 mL, 4.77mmol) was added dropwise at ambient temperature. The reaction vessel was heated using microwave irradiation to 80 °C and held for fifteen minutes. The product was precipitated from the MeCN upon addition of an equal volume of ethyl acetate, filtered and dried under vacuum. (1.16 g, 82% yield) The characterization data matched that previously obtained using conventional heating methods.

<u>Preparation of 1-methyl-3-(*p*-nitrobenzyl)imidazolium hexafluorophosphate,**3**</u>



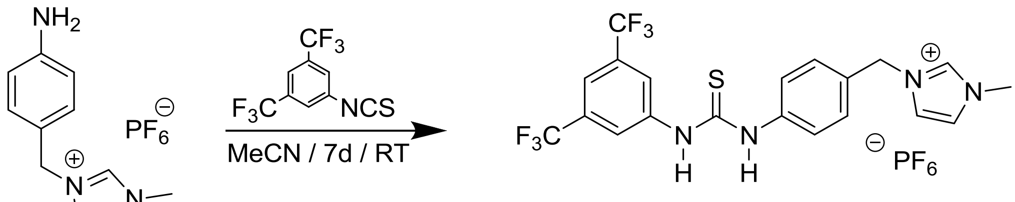
1-Methyl-3-(*p*-nitrobenzyl) imidazolium bromide, **2**,(1.23g, 4.09 mmol) was dissolved in a minimum amount of water and an aqueous solution of HPF_6 (1.25 eq, 0.43 mL) was added dropwise. The product precipitated, was filtered after 3h and dried under vacuum. The product obtained was a white solid. (1.32 g, 89%). MP 99-100 °C, IR (KBr): 3166, 3120, 1610, 1522, 1450, 1352, 843, 557cm^{-1}; ^{1}H NMR (DMSO-d$_6$, 300MHz) δ 9.22 (s, 1H), 8.27 (d, *J*=8.0 Hz, 2H), 7.79 (s, 1H), 7.74 (s, 1H), 7.65 (d, *J*=8.0 Hz, 2H), 5.59 (s, 2H), 3.87 (s, 3H) ; ^{13}C NMR (DMSO-d$_6$, 75MHz) δ148.1, 142.6, 137.6, 129.9, 124.7, 124.5, 123.0, 51.4, 36.4; ^{31}P NMR (DMSO-d$_6$, 121MHz) δ -144.2 (septet, *J*=711.3Hz); ESI-MS: Positive Mode Found: m/z 218.0 [100%, $(C_{11}H_{12}N_3O_2)^+$]; Calc. 218.1; Negative Mode Found: : m/z 144.6 [100%, $(PF_6)^-$]; Calc. 144.9

Preparation of 1-methyl-3-(p-aminobenzyl)imidazoliumhexafluorophosphate **4**



$FeSO_4{\cdot}7H_2O$ (0.384 g, 3 mmol) and sodium citrate (0.055 g, 0.25 mmol) were added to 100 mL of H_2O. $NaBH_4$ (0.200 g , 5 mmol) was added slowly and the iron was reduced to black Fe^0 nanoparticles. The water was decanted and the nanoparticles were washed and decanted twice more with 50 mL of water to remove any excess unreacted starting materials. *N*-methyl-*N*-(*p*-nitrobenzyl)pyrrolidinium hexafluorophosphate (1.26 g, 3.45 mmol) was added and the reaction was stirred at ambient temperature for 24 hours. The reaction mixture was passed through a medium pore size glass frit to remove water and other aqueous impurities. The residue in the frit was washed with 3x20 mL portions of acetonitrile. The acetonitrile from the washings was removed *in vacuo* and the product was dried under vacuum. The product was obtained as a yellow solid. (0.70 g, 61%) MP 116-117 °C, IR (KBr): 3509, 3414, 3169, 3117, 1630, 1459, 841, 557cm^{-1}; ^{1}H NMR (DMSO-d_6, 300MHz) δ 9.03 (s, 1H), 7.63 (s, 1H) 7.59 (s, 1H), 7.13 (d, *J*=8.4 Hz, 2H), 6.61 (d, *J*=8.4 Hz, 2H), 5.29 (s, 2NH), 5.16 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (DMSO-d_6, 75MHz) δ 149.6, 136.5, 130.2, 124.2, 122.4, 121.6, 114.5, 52.6, 36.1; ^{31}P NMR (DMSO-d_6, 121MHz) δ -144.1 (septet, *J*=711.5Hz); ESI-MS: Positive Mode Found m/z 188.0 [22.4%, $(C_{11}H_{14}N_3)^+$]; Calc. 188.2; Negative Mode Found: m/z 144.6 [100%, $(PF_6)^-$]; Calc. 144.9; ESI-HRMS: Positive Mode Found m/z 188.1187 [22.4%, $(C_{11}H_{14}N_3)^+$]; Calc. 188.1188;

Preparation of *N*-3,5-bis(trifluoromethyl)phenyl-*N'*-p-(benzyl-1-methylimidazolium) phenylthiourea hexafluorophosphate, **5**



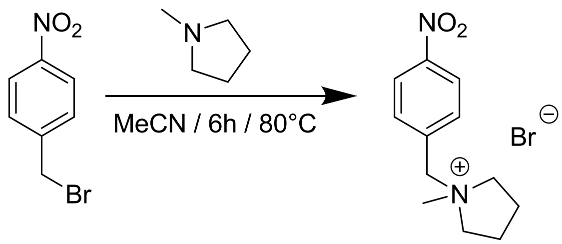
5

1-Methyl-3-(p-aminobenzyl)pyrrolidinium hexafluorophosphate (0.667 g, 2 mmol) was dissolved in 10 mL MeCNand 3,5-bis(trifluoromethyl)phenyl isothiocyanate was added (0.36 mL, 2 mmol) and the reaction stirred at RT for 7 days. Solvent was removed *in vacuo* and after column chromatography with acetone as the eluting solvent the acetone was removed *in vacuo* and after drying under vacuum was obtained as a yellow solid. (0.97 g, 80%) IR (KBr): 3379, 1536, 1473, 1383, 1280, 1169, 1132, 843, 558 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300MHz) δ 10.34 (s, 1NH), 10.29 (s, 1NH), 9.21 (s, 1H), 8.25 (s, 2H), 7.79 (s, 1H), 7.71 (s, 1H), 7.53 (d, *J*=8.4Hz, 2H), 7.49 (s, 1H), 7.43 (d, *J*=8.4Hz, 2H), 5.40 (s,2H), 3.86 (s, 3H); ^{13}C NMR (DMSO-d_6, 75MHz) δ 180.4, 142.2, 139.7, 137.1, 131.9, 130.8, 130.3, 129.3, 126.9, 125.5, 124.7, 124.5, 122.8, 51.9, 36.3 ; ^{31}P NMR (DMSO-d_6, 121MHz) δ -144.2 (septet, *J*=711.4Hz); ESI-MS: Positive Mode Found m/z 459.2 [100%, $(C_{20}H_{17}N_4F_6S)^+$]; Calc. 459.1; Negative Mode Found: m/z 144.7 [100%, $(PF_6)^-$]; Calc. 144.9; ESI-HRMS: Positive Mode Found m/z 459.1075 [100%, $(C_{20}H_{17}N_4F_6S)^+$]; Calc. 459.1078;

5.3 Synthesis of the *N*-Methylpyrrolidinium Tagged Thiourea, 10

Preparation of *N*-methyl-*N*-(p-nitrobenzyl)pyrrolidinium bromide, **7**

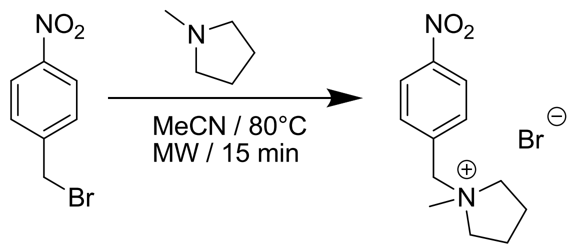
Method A:



7

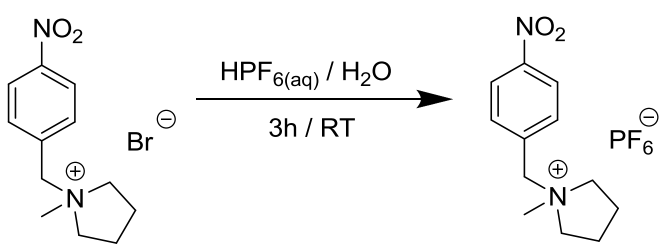
p-Nitrobenzyl bromide (1.08 g, 5.00 mmol) was dissolved in 50 mL MeCNand *N*-methylpyrrolidine (0.52 mL, 5.00 mmol) was added dropwise at ambient temperature. The reaction was then heated and stirred at 80°C for 6 hours. Solvent was removed *in vacuo* then the product was suspended in toluene to wash any unreacted starting materials, filtered and dried under vacuum to afford an off white solid. (1.36 g, 90% yield). MP 168-169 °C, IR (KBr): 2963, 1605, 1528, 1424, 1346 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300MHz) δ 8.35 (d, *J*=8.7Hz, 2H), 7.94 (d, *J*=8.7Hz, 2H), 4.85 (s, 2H), 3.65-3.69 (m, 2H), 3.46-4.51 (m, 2H), 2.97 (s, 3H), 2.14-2.16 (m, 2H),; ^{13}C NMR (DMSO-d_6, 75MHz) δ 149.0, 136.9, 134.6, 124.3, 64.1, 63.5 47.7, 21.2; ESI-MS: Positive Mode Found: m/z 221.9 [100%, $(C_{12}H_{17}N_2O_2)^+$]; Calc. 221.1

Method B:



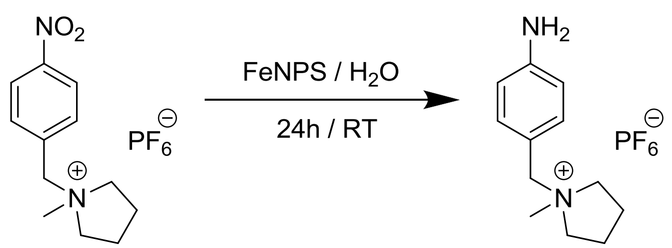
p-Nitrobenzyl bromide (1.00 g, 4.63 mmol) was dissolved in 10 mL MeCN and *N*-methylpyrrolidine (0.48 mL, 4.63mmol) was added dropwise at ambient temperature. The reaction vessel was heated using microwave irradiation to 80 °C and held for fifteen minutes. The product was precipitated from the acetonitrile using an equal volume of ethyl acetate, filtered and dried under vacuum. (1.13 g, 81% yield) The characterization data matched that previously obtained using conventional heating methods.

Preparation of *N*-methyl-*N*-(p-nitrobenzyl)pyrrolidinium hexafluorophosphate, **8**



N-methyl-*N*-(p-nitrobenzyl)pyrrolidinium bromide (1.23 g, 4.08 mmol) was dissolved in a minimum amount of water and an aqueous solution of HPF_6 (1.25 eq, 0.43 mL) was added dropwise. The product precipitated, was filtered off after 3h and dried under vacuum. The product obtained was a white solid. (1.27 g, 85%). , MP 155-156 °C, IR (KBr): 3081, 1610, 1530, 1431, 1359, 834, 557 cm^{-1}; ^{1}H NMR (DMSO-d$_6$, 300MHz) δ 8.34 (d, *J*=8.8Hz, 2H), 7.86 (d, *J*=8.8Hz, 2H), 4.72 (s, 2H), 3.58-3.62 (m, 2H), 3.41-3.47 (m, 2H), 2.93 (s, 3H), 2.14-2.16 (m, 2H); ^{13}C NMR (DMSO-d$_6$, 75MHz) δ 149.0, 136.4, 134.5, 124.3, 64.5, 63.6, 47.8, 21.2; ^{31}P NMR (DMSO-d$_6$, 121MHz) δ -144.2 (septet, *J*=711.4Hz); ESI-MS: Positive Mode Found: m/z 221.1 [100%, $(C_{12}H_{17}N_2O_2)^+$]; Calc. 221.1 Negative mode: m/z 144.6 [100%, $(PF_6)^-$]; Calc. 144.9

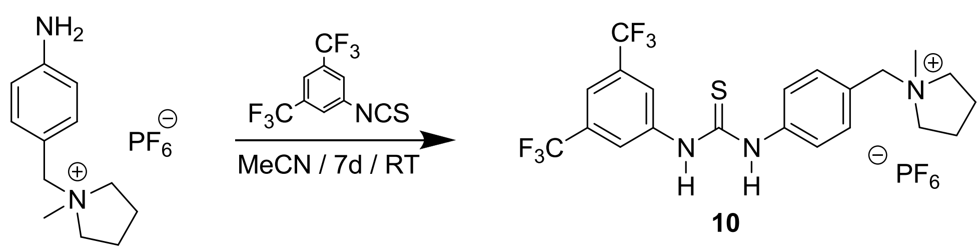
Preparation of N-methyl-N-(p-aminobenzyl)pyrrolidinium hexafluorophosphate, **9**



9

$FeSO_4 \cdot 7H_2O$ (5.75 g, 20.69 mmol) and sodium citrate (0.44 g, 1.72 mmol) were added to 100 mL of H_2O. $NaBH_4$ (1.30 g , 34.49 mmol) was added slowly and the iron was reduced to black Fe^0.[49] The water was decanted and the nanoparticles were washed and decanted twice more with 50 mL of water. *N*-methyl-*N*-(*p*-nitrobenzyl)pyrrolidinium hexafluorophosphate (1.26 g, 3.45 mmol) was added and the reaction was stirred at ambient temperature for 24 hours. The reaction mixture was passed through a vacuum frit to remove water and other aqueous impurities. The residue in the frit was washed with 3x20mL portions of acetonitrile. The acetonitrile from the washings was removed *in vacuo* and the product was dried under vacuum. The product was obtained was a yellow solid. (0.85 g, 73%) MP 143-144 °C, IR (KBr): 3489, 3401, 2981, 1632, 1426, 835, 558 cm^{-1}; ^{1}H NMR (DMSO-d$_6$, 300MHz) δ 7.16 (d, *J*=8.4Hz, 2H), 6.60 (d, *J*=8.4Hz, 2H), 5.53 (s, 2NH), 4.30 (s, 2H), 3.44-3.48 (m, 2H), 3.26-3.30 (m, 2H), 2.83 (s, 3H), 2.09 (s, 2H); ^{13}C NMR ($DMSO-d_6$, 75MHz) δ 150.8, 133.8, 115.4, 114.0, 66.1, 62.3, 47.5, 21.3; ^{31}P NMR ($DMSO-d_6$, 121MHz) δ -144.2 (septet, *J*=711.3Hz); ESI-MS: Positive Mode Found: m/z 191.2 [99.5%, $(C_{12}H_{19}N_2)^+$]; Calc. 191.1 Negative mode: m/z 144.6 [100%, $(PF_6)^-$]; Calc. 144.9; ESI-HRMS: Positive Mode Found: m/z 191.1535 [99.5%, $(C_{12}H_{19}N_2)^+$]; Calc. 191.1548

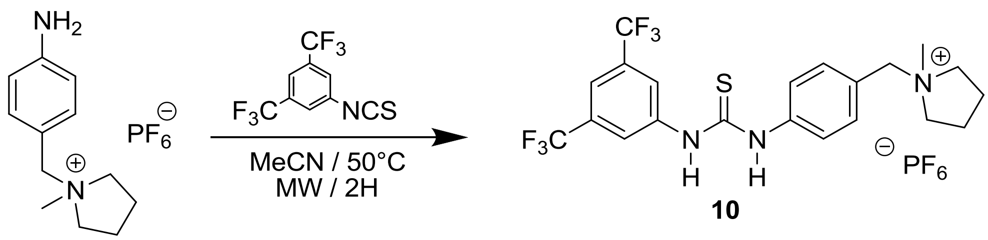
Preparation of *N*-3,5-bis(trifluoromethyl)phenyl-*N'*-p-(benzyl-*N*-methylpyrrolidinium) phenylthiourea hexafluorophosphate, **10**



N-methyl-*N*-(p-aminobenzyl)pyrrolidinium hexafluorophosphate (1.35 g, 4.02 mmol) was dissolved in 10 mL MeCN and 3,5-bis(trifluoromethyl)phenyl isothiocyanate was added (0.74 mL, 4.02 mmol) and the reaction stirred at RT for 7 days. Solvent was removed *in vacuo* and after column chromatography with acetone as the eluting solvent the acetone was removed *in vacuo* and after drying under vacuum was obtained as a yellow solid. (2.08 g, 85%) IR (KBr): 3378, 1614, 1537, 1473, 1384, 1280, 1178, 1133, 841, 558 cm^{-1}; ^{1}H NMR ($DMSO-d_6$, 300MHz) δ 10.46 (s, 1NH), 10.36 (s,1NH), 8.25 (s, 2H), 7.82 (s, 1H), 7.66 (d, *J*=8.6Hz, 2H), 7.56 (d, *J*=8.6Hz, 2H), 4.53 (s, 2H), 3.54-3.58 (m, 2H), 3.36-3.41 (m, 2H), 2.91 (s, 3H), 2.14-2.15 (m, 4H); ^{13}C NMR ($DMSO-d_6$, 75MHz) δ 180.3, 142.1, 141.0, 133.4, 130.8, 130.4, 125.6, 123.9, 121.9, 65.2, 63.1, 47.7, 21.3; ^{31}P NMR ($DMSO-d_6$, 121MHz) δ -144.2 (septet, *J*=711.4Hz); ESI-

MS: Positive Mode Found: m/z 462.3 [100%, $(C_{21}H_{22}N_3F_6S)^+$]; Calc. 462.1; Negative mode: m/z 144.6 [100%, $(PF_6)^-$]; Calc. 144.9; ESI-HRMS: Positive Mode Found: m/z 462.1424 [100%, $(C_{21}H_{22}N_3F_6S)^+$]; Calc. 462.1439

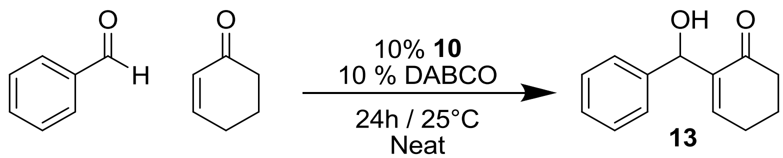
Method B:



N-methyl-*N*-(p-aminobenzyl)pyrrolidinium hexafluorophosphate (0.334g, 0.99mmol) was dissolved in 5 mL MeCN and 3,5-bis(trifluoromethyl)phenyl isothiocyanate was added (0.18 mL, 0.99 mmol) and was heated to 50 °C under microwave irradiation and held for two hours. Solvent was removed *in vacuo* and after column chromatography with acetone as the eluting solvent the acetone was removed *in vacuo* and after drying under vacuum was obtained as a pale yellow solid. (0.49g, 81%) Spectral data matched that previously obtained for this compound.

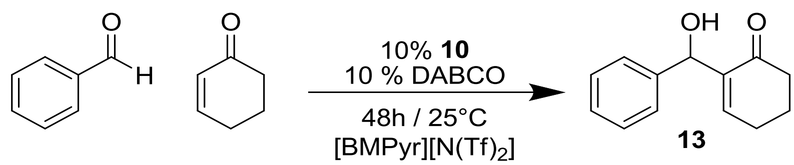
5.4 Morita-Baylis-Hillman Reactions

Solvent-Free Morita-Baylis-Hillman Reaction – General Procedure



N-methylpyrrolidinium tagged thiourea, **10**, (0.304 g, 10 mol %) was placed in a 50 mL round bottom flask and dissolved in cyclohex-2-en-1-one (0.49 mL, 5.00 mmol) with stirring at 300 rpm. Benzaldehyde (0.10 mL, 1.00 mmol) was then added to the reaction mixture followed by the addition of DABCO (0.056 g, 0.50 mmol; 10 mol %). The reaction vessel was filled with nitrogen and left to stir at room temperature (25°C) for 24 hours. Upon completion of the reaction an aliquot was removed and dissolved in $CDCl_3$. The insoluble ionic thiourea co-catalyst was removed *via* gravity filtration and the sample was analyzed *via* ^{1}H NMR to determine percent conversion to 2-(hydroxyphenylmethyl)-cyclohex-2-en-1-one, **13**. Spectroscopic data obtained for **13** agreed with literature reports.[22] Additional solvent-free reactions were performed using the same procedure and are summarized in **Table 1**.

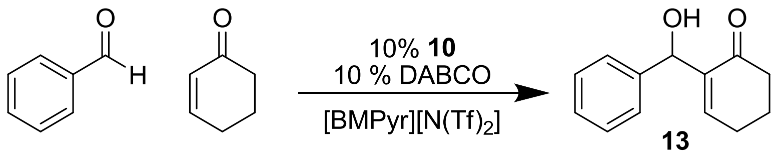
Recycling Study Morita-Baylis Hillman Reaction in [BMPyr][N(Tf)$_2$]– General Procedure



13

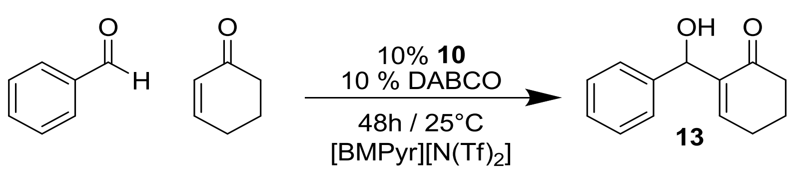
N-methylpyrrolidinium tagged thiourea, **10**, (0.304g, 10 mol %) was placed in a 50 mL round bottom flask and dissolved in 2 mL of [BMPyr][N(Tf)$_2$] with stirring at 300 rpm at room temperature.Cyclohex-2-en-1-one (0.49 mL, 5.00 mmol) and benzaldehyde (0.10 mL, 1.00 mmol) were then added sequentially to the reaction mixture. DABCO (0.056g, 10 mol %) was then added to the reaction mixture. The reaction vessel was filled with nitrogen and left to stir at room temperature (25°C) for 48 hours. Upon completion of the reaction the organic materials were extracted using 5x10mL portions of diethyl ether. An aliquot of the ether extract was dissolved in $CDCl_3$ and the sample was analyzed *via*^{1}H NMR spectroscopy to determine percent conversion to 2-(hydroxyphenylmethyl)-cyclohex-2-en-1-one, **13**. To recycle the ionic liquid phase containing the catalyst the ionic liquid phase was placed under vacuum to remove any residual ether. Benzaldehyde, cyclohex-2-en-1-one and DABCO were added in the same amounts as in the first run. The mixture was stirred for 48 hours and extracted using the same procedure with 5x10 mL portions of diethyl ether. The third consecutive reaction in [BMPyr][N(Tf)$_2$] was performed using the same procedure as the second and results are summarized in **Table 2**.

Microwave Irradiated Morita-Baylis Hillman Reaction in [BMPyr][N(Tf)$_2$] – General Procedure



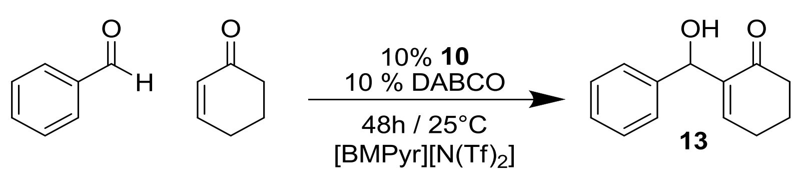
N-methylpyrrolidinium tagged thiourea, **10**, (0.304g, 10 mol %) was placed in a microwave reaction vessel and dissolved in the specified amount of [BMPyr][N(Tf)$_2$] (**Table 3**) using a vortex stirrer.Cyclohex-2-en-1-one (0.49 mL, 5.00 mmol) and benzaldehyde (0.10 mL, 1.00 mmol) were then added to the reaction mixture. DABCO (0.056g, 10 mol %) was then added to the reaction mixture. The reaction vessel was then heated using microwave irradiation for the appropriate duration at the appropriate temperature. Upon completion of the reaction the organic materials were extracted using 5x10mL portions of diethyl ether. An aliquot of the ether extract was dissolved in $CDCl_3$ and the sample was analyzed *via* ^{1}H NMR to determine percent conversion. All microwave irradiated reactions in [BMPyr][N(Tf)$_2$] were performed using the same procedure and are summarized in **Table 3**.

IL Volume Study Morita-Baylis Hillman Reaction in [BMPyr][N(Tf)$_2$] – General Procedure



N-methylpyrrolidinium tagged thiourea, **10**, (0.304 g, 10 mol %) was placed in a 50 mL round bottom flask and dissolved in the appropriate amount of [BMPyr][N(Tf)$_2$] with stirring at 300 rpm. Cyclohex-2-en-1-one (0.49 mL, 5.00 mmol) and benzaldehyde (0.10 mL, 1.00 mmol) were then added to the reaction mixture. DABCO (0.056g, 10 mol %) was then added to the reaction mixture. The reaction vessel was placed under a nitrogen atmosphere and left to stir at room temperature (25°C) for 48 hours. Upon completion of the reaction, the organic materials were extracted using 5x10mL portions of diethyl ether. An aliquot of the ether extract was dissolved in $CDCl_3$ and the sample was analyzed *via* ^1H NMR spectroscopy to determine conversion. To recycle the ionic liquid phase containing the catalyst the ionic liquid phase was placed under vacuum to remove residual ether. Benzaldehyde, cyclohex-2-en-1-one and DABCO were added in the same amounts as in the first run. The mixture was stirred for 48 hours and extracted using the same procedure with 5x10 mL portions of diethyl ether. The third consecutive reaction in [BMPyr][$N(Tf)_2$] was performed using the same procedure as the second and results are summarized in **Table 4**.

Catalyst Loading Study Morita-Baylis Hillman Reaction in [BMPyr][$N(Tf)_2$]



The specified (**Table 5**) amount of *N*-methylpyrrolidinium tagged thiourea, **10**, was placed in a 50 mL round bottom flask and dissolved 0.5 mL of [BMPyr][$N(Tf)_2$] with stirring at 300 rpm. Cyclohex-2-en-1-one (0.49 mL, 5.00 mmol) and benzaldehyde (0.10 mL, 1.00 mmol) were then added to the reaction mixture. The specified (**Table 5**) amount of DABCO was then added to the reaction mixture. The reaction vessel was filled with nitrogen and left to stir at room temperature (25°C) for 48 hours. Upon completion of the reaction the organic materials were extracted using

5x10mL portions of diethyl ether. An aliquot of the ether extract was dissolved in $CDCl_3$ and the sample was analyzed *via* ^{1}H NMR spectroscopy to determine percent conversion. To recycle the ionic liquid phase containing the catalyst the ionic liquid phase was placed under vacuum to remove residual ether. Benzaldehyde, cyclohex-2-en-1-one and DABCO were added in the same amounts as in the first run. The mixture was stirred for 48 hours and extracted using the same procedure with 5x10 mL portions of diethyl ether. The third consecutive reaction in [BMPyr][$N(Tf)_2$] was performed using the same procedure as the second and results are summarized in **Table 5**.

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7.0 Appendix A: X-ray Crystallographic Data

Table 6: Crystal data and structure refinement for compound **11**

Identification code	**11**	
Empirical formula	$C_{23} H_{28} F_{12} N_3 O P S$	
Formula weight	653.51	
Temperature	125(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P* -1	
Unit cell dimensions	*a* = 9.8767(12) Å	α= 86.049(2)°
	b = 11.7841(15) Å	β= 69.8570(10)°
	c = 13.4563(17) Å	γ = 76.0960(10)°
Volume	1427.1(3) $Å^3$	
Z	2	
Density (calculated)	1.521 Mg/m^3	
Absorption coefficient	0.271 mm^{-1}	
F(000)	668	
Crystal size	0.240 x 0.180 x 0.160 mm^3	
Theta range for data collection	2.258 to 28.311°	
Index ranges	-13<=h<=13, -15<=k<=15, -17<=l<=17	
Reflections collected	16892	
Independent reflections	6706 [R(int) = 0.0310]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6856	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6706 / 27 / 408	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0450, wR2 = 0.1023	
R indices (all data)	R1 = 0.0728, wR2 = 0.1146	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.301 and -0.312 $e.Å^{-3}$	

Table 7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **11**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	6842(1)	1287(1)	4258(1)	29(1)
N(1)	4458(2)	888(2)	3903(1)	28(1)
N(2)	3974(2)	2427(2)	4951(1)	28(1)
N(3)	2784(2)	6213(1)	8622(1)	24(1)
F(1A)	4120(20)	-908(18)	121(11)	81(5)
F(2A)	3590(30)	-2222(13)	1280(20)	66(5)
F(3A)	2381(13)	-660(20)	1631(17)	86(5)
F(1B)	4610(8)	-1228(6)	58(3)	50(1)
F(2B)	3353(12)	-2076(7)	1367(8)	87(3)
F(3B)	2699(9)	-191(7)	1183(7)	89(2)
F(4)	8866(2)	-3193(1)	1244(1)	67(1)
F(5)	8965(2)	-2557(2)	2649(1)	62(1)
F(6)	9628(2)	-1652(2)	1208(2)	85(1)
C(1)	5131(2)	24(2)	3102(2)	27(1)
C(2)	4239(3)	-127(2)	2522(2)	31(1)
C(3)	4800(3)	-943(2)	1703(2)	35(1)
C(4)	6233(3)	-1624(2)	1436(2)	33(1)
C(5)	7076(2)	-1492(2)	2034(2)	30(1)
C(6)	6547(2)	-686(2)	2866(2)	27(1)
C(7)	3835(3)	-1118(2)	1108(2)	50(1)
C(8)	8616(3)	-2221(2)	1793(2)	38(1)
C(9)	5052(2)	1532(2)	4379(2)	25(1)
C(10)	4045(2)	3327(2)	5568(2)	24(1)
C(11)	4976(2)	3171(2)	6164(2)	27(1)
C(12)	4910(2)	4094(2)	6777(2)	27(1)
C(13)	3914(2)	5167(2)	6824(2)	24(1)
C(14)	3000(2)	5308(2)	6215(2)	27(1)
C(15)	3061(2)	4397(2)	5591(2)	28(1)
C(16)	3869(2)	6158(2)	7487(2)	24(1)
C(17)	2866(2)	7241(2)	9195(2)	33(1)

C(18)	1967(3)	8302(2)	8815(2)	38(1)
C(19)	851(3)	7832(2)	8478(2)	38(1)
C(20)	1198(2)	6524(2)	8654(2)	30(1)
C(21)	3115(3)	5101(2)	9183(2)	36(1)
P(1)	2187(1)	3786(1)	2096(1)	32(1)
F(7)	3522(2)	4352(1)	1394(1)	52(1)
F(8)	847(2)	3206(1)	2806(1)	52(1)
F(9)	2162(2)	3230(1)	1060(1)	50(1)
F(10)	2220(2)	4324(2)	3136(1)	61(1)
F(11)	1023(2)	4912(1)	1949(1)	57(1)
F(12)	3352(2)	2649(1)	2243(1)	51(1)
C(22)	-1021(3)	2726(3)	5875(2)	81(1)
C(23)	117(3)	1689(3)	5342(2)	51(1)
O(1)	1372(2)	2007(2)	4562(1)	44(1)

Table 8. Bond lengths [Å] and angles [°] for **11**

S(1)-C(9)	1.673(2)
N(1)-C(9)	1.368(2)
N(1)-C(1)	1.405(3)
N(1)-H(1N)	0.831(15)
N(2)-C(9)	1.358(3)
N(2)-C(10)	1.420(2)
N(2)-H(2N)	0.819(15)
N(3)-C(21)	1.490(3)
N(3)-C(20)	1.507(3)
N(3)-C(17)	1.512(2)
N(3)-C(16)	1.530(2)
F(1A)-C(7)	1.278(12)
F(2A)-C(7)	1.369(11)
F(3A)-C(7)	1.355(11)
F(1B)-C(7)	1.352(5)
F(2B)-C(7)	1.309(6)
F(3B)-C(7)	1.346(5)

F(4)-C(8)	1.331(3)
F(5)-C(8)	1.323(3)
F(6)-C(8)	1.333(3)
C(1)-C(6)	1.388(3)
C(1)-C(2)	1.408(3)
C(2)-C(3)	1.385(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.385(3)
C(3)-C(7)	1.496(3)
C(4)-C(5)	1.381(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.391(3)
C(5)-C(8)	1.492(3)
C(6)-H(6)	0.9500
C(10)-C(11)	1.389(3)
C(10)-C(15)	1.390(3)
C(11)-C(12)	1.386(3)
C(11)-H(11)	0.9500
C(12)-C(13)	1.393(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.391(3)
C(13)-C(16)	1.501(3)
C(14)-C(15)	1.384(3)
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(18)	1.518(3)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-C(19)	1.549(3)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-C(20)	1.517(3)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900

C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
P(1)-F(11)	1.5849(15)
P(1)-F(10)	1.5890(15)
P(1)-F(9)	1.5912(14)
P(1)-F(12)	1.5929(15)
P(1)-F(7)	1.5990(14)
P(1)-F(8)	1.6138(14)
C(22)-C(23)	1.475(4)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-O(1)	1.433(3)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
O(1)-H(1O)	0.81(3)

C(9)-N(1)-C(1)	131.31(18)
C(9)-N(1)-H(1N)	114.0(16)
C(1)-N(1)-H(1N)	113.6(16)
C(9)-N(2)-C(10)	130.74(17)
C(9)-N(2)-H(2N)	116.9(16)
C(10)-N(2)-H(2N)	111.9(16)
C(21)-N(3)-C(20)	111.56(16)
C(21)-N(3)-C(17)	111.07(16)
C(20)-N(3)-C(17)	102.39(15)
C(21)-N(3)-C(16)	111.07(16)
C(20)-N(3)-C(16)	111.60(15)
C(17)-N(3)-C(16)	108.82(15)
C(6)-C(1)-N(1)	125.81(19)
C(6)-C(1)-C(2)	119.06(19)
N(1)-C(1)-C(2)	115.11(19)
C(3)-C(2)-C(1)	119.9(2)

C(3)-C(2)-H(2)	120.0
C(1)-C(2)-H(2)	120.0
C(2)-C(3)-C(4)	121.4(2)
C(2)-C(3)-C(7)	119.6(2)
C(4)-C(3)-C(7)	119.0(2)
C(5)-C(4)-C(3)	118.0(2)
C(5)-C(4)-H(4)	121.0
C(3)-C(4)-H(4)	121.0
C(4)-C(5)-C(6)	122.3(2)
C(4)-C(5)-C(8)	120.11(19)
C(6)-C(5)-C(8)	117.63(19)
C(1)-C(6)-C(5)	119.33(19)
C(1)-C(6)-H(6)	120.3
C(5)-C(6)-H(6)	120.3
F(2B)-C(7)-F(3B)	110.5(6)
F(2B)-C(7)-F(1B)	105.5(5)
F(3B)-C(7)-F(1B)	104.1(3)
F(1A)-C(7)-F(3A)	109.2(8)
F(1A)-C(7)-F(2A)	108.0(13)
F(3A)-C(7)-F(2A)	90.3(14)
F(1A)-C(7)-C(3)	122.7(9)
F(2B)-C(7)-C(3)	112.9(5)
F(3B)-C(7)-C(3)	112.9(3)
F(1B)-C(7)-C(3)	110.3(3)
F(3A)-C(7)-C(3)	112.2(6)
F(2A)-C(7)-C(3)	109.5(9)
F(5)-C(8)-F(4)	106.2(2)
F(5)-C(8)-F(6)	106.1(2)
F(4)-C(8)-F(6)	105.34(19)
F(5)-C(8)-C(5)	113.30(18)
F(4)-C(8)-C(5)	113.3(2)
F(6)-C(8)-C(5)	112.0(2)
N(2)-C(9)-N(1)	109.82(17)
N(2)-C(9)-S(1)	124.58(15)
N(1)-C(9)-S(1)	125.58(15)
C(11)-C(10)-C(15)	120.08(18)

C(11)-C(10)-N(2)	123.81(18)
C(15)-C(10)-N(2)	116.04(17)
C(12)-C(11)-C(10)	119.17(19)
C(12)-C(11)-H(11)	120.4
C(10)-C(11)-H(11)	120.4
C(11)-C(12)-C(13)	121.58(18)
C(11)-C(12)-H(12)	119.2
C(13)-C(12)-H(12)	119.2
C(14)-C(13)-C(12)	118.30(18)
C(14)-C(13)-C(16)	120.96(18)
C(12)-C(13)-C(16)	120.70(17)
C(15)-C(14)-C(13)	120.82(19)
C(15)-C(14)-H(14)	119.6
C(13)-C(14)-H(14)	119.6
C(14)-C(15)-C(10)	120.03(19)
C(14)-C(15)-H(15)	120.0
C(10)-C(15)-H(15)	120.0
C(13)-C(16)-N(3)	114.65(15)
C(13)-C(16)-H(16A)	108.6
N(3)-C(16)-H(16A)	108.6
C(13)-C(16)-H(16B)	108.6
N(3)-C(16)-H(16B)	108.6
H(16A)-C(16)-H(16B)	107.6
N(3)-C(17)-C(18)	104.87(16)
N(3)-C(17)-H(17A)	110.8
C(18)-C(17)-H(17A)	110.8
N(3)-C(17)-H(17B)	110.8
C(18)-C(17)-H(17B)	110.8
H(17A)-C(17)-H(17B)	108.8
C(17)-C(18)-C(19)	105.25(18)
C(17)-C(18)-H(18A)	110.7
C(19)-C(18)-H(18A)	110.7
C(17)-C(18)-H(18B)	110.7
C(19)-C(18)-H(18B)	110.7
H(18A)-C(18)-H(18B)	108.8
C(20)-C(19)-C(18)	105.46(18)

C(20)-C(19)-H(19A)	110.6
C(18)-C(19)-H(19A)	110.6
C(20)-C(19)-H(19B)	110.6
C(18)-C(19)-H(19B)	110.6
H(19A)-C(19)-H(19B)	108.8
N(3)-C(20)-C(19)	105.31(16)
N(3)-C(20)-H(20A)	110.7
C(19)-C(20)-H(20A)	110.7
N(3)-C(20)-H(20B)	110.7
C(19)-C(20)-H(20B)	110.7
H(20A)-C(20)-H(20B)	108.8
N(3)-C(21)-H(21A)	109.5
N(3)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
N(3)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
F(11)-P(1)-F(10)	91.68(9)
F(11)-P(1)-F(9)	88.98(8)
F(10)-P(1)-F(9)	179.29(9)
F(11)-P(1)-F(12)	179.70(9)
F(10)-P(1)-F(12)	88.55(9)
F(9)-P(1)-F(12)	90.79(8)
F(11)-P(1)-F(7)	90.38(8)
F(10)-P(1)-F(7)	90.04(9)
F(9)-P(1)-F(7)	90.21(8)
F(12)-P(1)-F(7)	89.82(8)
F(11)-P(1)-F(8)	90.00(8)
F(10)-P(1)-F(8)	89.95(8)
F(9)-P(1)-F(8)	89.79(8)
F(12)-P(1)-F(8)	89.80(8)
F(7)-P(1)-F(8)	179.62(9)
C(23)-C(22)-H(22A)	109.5
C(23)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(23)-C(22)-H(22C)	109.5

H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
O(1)-C(23)-C(22)	111.7(2)
O(1)-C(23)-H(23A)	109.3
C(22)-C(23)-H(23A)	109.3
O(1)-C(23)-H(23B)	109.3
C(22)-C(23)-H(23B)	109.3
H(23A)-C(23)-H(23B)	107.9
C(23)-O(1)-H(1O)	108(2)

Table 9. Anisotropic displacement parameters ($Å^2$x 10^3)for **11**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	28(1)	31(1)	28(1)	-5(1)	-10(1)	-5(1)
N(1)	25(1)	30(1)	30(1)	-7(1)	-10(1)	-4(1)
N(2)	25(1)	31(1)	29(1)	-7(1)	-11(1)	-3(1)
N(3)	26(1)	29(1)	21(1)	-3(1)	-8(1)	-9(1)
F(1A)	114(11)	79(9)	96(8)	41(6)	-90(8)	-39(7)
F(2A)	129(13)	40(6)	75(10)	13(5)	-80(10)	-38(6)
F(3A)	81(7)	99(11)	107(10)	-33(8)	-73(7)	-3(7)
F(1B)	73(3)	59(3)	36(2)	-1(1)	-36(2)	-19(2)
F(2B)	104(4)	134(6)	66(3)	20(4)	-44(3)	-86(5)
F(3B)	86(3)	87(3)	109(4)	-53(3)	-79(3)	33(3)
F(4)	61(1)	59(1)	78(1)	-43(1)	-32(1)	18(1)
F(5)	48(1)	80(1)	48(1)	-20(1)	-23(1)	19(1)
F(6)	39(1)	75(1)	110(2)	10(1)	12(1)	-12(1)
C(1)	36(1)	23(1)	23(1)	-1(1)	-9(1)	-10(1)
C(2)	36(1)	29(1)	32(1)	-2(1)	-16(1)	-6(1)
C(3)	48(1)	32(1)	31(1)	-2(1)	-22(1)	-10(1)
C(4)	45(1)	30(1)	24(1)	-4(1)	-11(1)	-8(1)
C(5)	35(1)	27(1)	24(1)	-1(1)	-7(1)	-7(1)
C(6)	32(1)	26(1)	24(1)	1(1)	-10(1)	-8(1)
C(7)	58(2)	51(2)	51(2)	-17(1)	-32(2)	-4(2)
C(8)	39(1)	38(1)	32(1)	-9(1)	-6(1)	-5(1)

C(9)	33(1)	24(1)	19(1)	1(1)	-10(1)	-9(1)
C(10)	26(1)	28(1)	19(1)	-3(1)	-6(1)	-6(1)
C(11)	28(1)	28(1)	25(1)	-1(1)	-10(1)	-3(1)
C(12)	28(1)	32(1)	23(1)	0(1)	-11(1)	-6(1)
C(13)	24(1)	27(1)	20(1)	0(1)	-6(1)	-8(1)
C(14)	29(1)	25(1)	26(1)	-2(1)	-12(1)	-1(1)
C(15)	30(1)	32(1)	23(1)	-4(1)	-13(1)	-3(1)
C(16)	24(1)	28(1)	22(1)	0(1)	-7(1)	-8(1)
C(17)	35(1)	41(1)	28(1)	-11(1)	-9(1)	-16(1)
C(18)	40(1)	34(1)	35(1)	-10(1)	-4(1)	-10(1)
C(19)	33(1)	41(1)	36(1)	-2(1)	-9(1)	-3(1)
C(20)	22(1)	41(1)	28(1)	-7(1)	-7(1)	-10(1)
C(21)	43(1)	39(1)	27(1)	5(1)	-13(1)	-11(1)
P(1)	28(1)	40(1)	32(1)	5(1)	-16(1)	-9(1)
F(7)	45(1)	69(1)	59(1)	31(1)	-32(1)	-32(1)
F(8)	38(1)	90(1)	42(1)	23(1)	-22(1)	-31(1)
F(9)	54(1)	66(1)	38(1)	-5(1)	-19(1)	-21(1)
F(10)	63(1)	84(1)	48(1)	-15(1)	-29(1)	-19(1)
F(11)	47(1)	50(1)	77(1)	4(1)	-33(1)	2(1)
F(12)	41(1)	46(1)	71(1)	18(1)	-27(1)	-7(1)
C(22)	51(2)	120(3)	54(2)	-4(2)	-19(2)	18(2)
C(23)	40(2)	63(2)	53(2)	6(1)	-18(1)	-15(1)
O(1)	31(1)	63(1)	37(1)	8(1)	-12(1)	-6(1)

Table 10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **11**

	x	y	z	U(eq)
H(1N)	3552(18)	1134(19)	4027(18)	34
H(2N)	3155(19)	2530(20)	4893(18)	34
H(2)	3253	331	2693	38
H(4)	6623	-2166	859	40
H(6)	7149	-622	3269	33
H(11)	5649	2441	6151	32

H(12)	5559	3992	7175	32
H(14)	2326	6037	6226	32
H(15)	2430	4504	5179	33
H(16A)	3599	6903	7137	29
H(16B)	4876	6090	7510	29
H(17A)	3906	7302	9012	40
H(17B)	2436	7162	9971	40
H(18A)	2617	8661	8208	46
H(18B)	1439	8894	9390	46
H(19A)	-181	8197	8914	46
H(19B)	979	7998	7724	46
H(20A)	530	6328	9348	36
H(20B)	1083	6097	8091	36
H(21A)	4152	4924	9147	54
H(21B)	2943	4464	8845	54
H(21C)	2466	5184	9925	54
H(22A)	-1858	2476	6404	122
H(22B)	-1366	3214	5350	122
H(22C)	-593	3177	6224	122
H(23A)	445	1188	5876	61
H(23B)	-322	1230	4998	61
H(1O)	1080(30)	2430(30)	4150(20)	66(10)

Table 11. Torsion angles [°] for **11**

C(9)-N(1)-C(1)-C(6)	25.5(3)
C(9)-N(1)-C(1)-C(2)	-156.1(2)
C(6)-C(1)-C(2)-C(3)	-2.5(3)
N(1)-C(1)-C(2)-C(3)	179.01(19)
C(1)-C(2)-C(3)-C(4)	0.0(3)
C(1)-C(2)-C(3)-C(7)	178.6(2)
C(2)-C(3)-C(4)-C(5)	2.0(3)
C(7)-C(3)-C(4)-C(5)	-176.6(2)
C(3)-C(4)-C(5)-C(6)	-1.6(3)
C(3)-C(4)-C(5)-C(8)	178.8(2)
N(1)-C(1)-C(6)-C(5)	-178.82(19)

C(2)-C(1)-C(6)-C(5)	2.9(3)
C(4)-C(5)-C(6)-C(1)	-0.9(3)
C(8)-C(5)-C(6)-C(1)	178.78(19)
C(2)-C(3)-C(7)-F(1A)	116.9(11)
C(4)-C(3)-C(7)-F(1A)	-64.5(12)
C(2)-C(3)-C(7)-F(2B)	-104.3(6)
C(4)-C(3)-C(7)-F(2B)	74.3(6)
C(2)-C(3)-C(7)-F(3B)	22.0(7)
C(4)-C(3)-C(7)-F(3B)	-159.4(6)
C(2)-C(3)-C(7)-F(1B)	138.0(4)
C(4)-C(3)-C(7)-F(1B)	-43.4(4)
C(2)-C(3)-C(7)-F(3A)	-16.3(14)
C(4)-C(3)-C(7)-F(3A)	162.3(14)
C(2)-C(3)-C(7)-F(2A)	-115.0(13)
C(4)-C(3)-C(7)-F(2A)	63.6(13)
C(4)-C(5)-C(8)-F(5)	-141.8(2)
C(6)-C(5)-C(8)-F(5)	38.5(3)
C(4)-C(5)-C(8)-F(4)	-20.8(3)
C(6)-C(5)-C(8)-F(4)	159.60(19)
C(4)-C(5)-C(8)-F(6)	98.2(3)
C(6)-C(5)-C(8)-F(6)	-81.4(3)
C(10)-N(2)-C(9)-N(1)	-179.33(19)
C(10)-N(2)-C(9)-S(1)	-0.8(3)
C(1)-N(1)-C(9)-N(2)	167.3(2)
C(1)-N(1)-C(9)-S(1)	-11.2(3)
C(9)-N(2)-C(10)-C(11)	-35.8(3)
C(9)-N(2)-C(10)-C(15)	147.1(2)
C(15)-C(10)-C(11)-C(12)	-0.1(3)
N(2)-C(10)-C(11)-C(12)	-177.07(18)
C(10)-C(11)-C(12)-C(13)	1.2(3)
C(11)-C(12)-C(13)-C(14)	-1.7(3)
C(11)-C(12)-C(13)-C(16)	-179.51(18)
C(12)-C(13)-C(14)-C(15)	1.1(3)
C(16)-C(13)-C(14)-C(15)	178.97(18)
C(13)-C(14)-C(15)-C(10)	-0.1(3)
C(11)-C(10)-C(15)-C(14)	-0.4(3)

N(2)-C(10)-C(15)-C(14)	176.77(18)
C(14)-C(13)-C(16)-N(3)	91.2(2)
C(12)-C(13)-C(16)-N(3)	-91.0(2)
C(21)-N(3)-C(16)-C(13)	57.0(2)
C(20)-N(3)-C(16)-C(13)	-68.2(2)
C(17)-N(3)-C(16)-C(13)	179.57(17)
C(21)-N(3)-C(17)-C(18)	-159.01(17)
C(20)-N(3)-C(17)-C(18)	-39.8(2)
C(16)-N(3)-C(17)-C(18)	78.42(19)
N(3)-C(17)-C(18)-C(19)	25.5(2)
C(17)-C(18)-C(19)-C(20)	-1.5(2)
C(21)-N(3)-C(20)-C(19)	157.75(17)
C(17)-N(3)-C(20)-C(19)	38.9(2)
C(16)-N(3)-C(20)-C(19)	-77.35(19)
C(18)-C(19)-C(20)-N(3)	-23.2(2)

Table 12. Hydrogen bonds for **11**[Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1n)...O(1)	0.831(15)	2.045(16)	2.860(2)	167(2)
N(2)-H(2n)...O(1)	0.819(15)	2.183(17)	2.948(2)	156(2)
O(1)-H(1o)...F(8)	0.81(3)	2.03(3)	2.807(2)	163(3)

Table 13. Crystal data and structure refinement for **12**.

Identification code	**12**	
Empirical formula	$C_{51} H_{62} F_{24} N_6 O_3 P_2 S_2$	
Formula weight	1389.12	
Temperature	125(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P* -1	
Unit cell dimensions	*a* = 9.2648(13) Å	□= 82.916(2)°
	b = 10.2545(15) Å	□= 80.708(2)°
	c = 16.746(2) Å	□ = 71.473(2)°
Volume	1484.3(4) $Å^3$	
Z	1	
Density (calculated)	1.554 Mg/m^3	
Absorption coefficient	0.267 mm^{-1}	
F(000)	712	
Crystal size	0.240 x 0.210 x 0.170 mm^3	
Theta range for data collection	2.101 to 28.754°	
Index ranges	-12<=h<=12, -13<=k<=13, -22<=l<=22	
Reflections collected	17868	
Independent reflections	7066 [R(int) = 0.0197]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.6935	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7066 / 117 / 504	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0441, wR2 = 0.1126	
R indices (all data)	R1 = 0.0553, wR2 = 0.1207	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.545 and -0.409 e.$Å^{-3}$	

Table 14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **12**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1A)	949(2)	5381(1)	2120(1)	23(1)
S(1B)	1710(40)	5200(15)	1985(9)	35(3)
F(1)	2245(2)	11148(2)	-1264(1)	53(1)
F(2)	3290(2)	11098(2)	-216(1)	61(1)
F(3)	4427(2)	9713(2)	-1128(1)	62(1)
F(4A)	797(4)	6989(3)	-1664(1)	43(1)
F(5A)	1252(5)	5352(3)	-747(2)	46(1)
F(6A)	-965(6)	6931(5)	-657(3)	53(1)
F(4B)	-197(6)	7642(5)	-1495(3)	83(1)
F(5B)	1418(6)	5749(6)	-1136(4)	98(2)
F(6B)	-724(6)	6422(5)	-480(3)	52(1)
N(1)	1488(2)	7838(2)	1771(1)	24(1)
N(2)	1452(2)	7047(1)	3085(1)	20(1)
N(3)	3460(2)	3547(1)	6505(1)	20(1)
C(1)	1541(2)	8004(2)	922(1)	21(1)
C(2)	2207(2)	9005(2)	532(1)	23(1)
C(3)	2307(2)	9266(2)	-301(1)	25(1)
C(4)	1752(2)	8554(2)	-773(1)	28(1)
C(5)	1086(2)	7574(2)	-380(1)	28(1)
C(6)	968(2)	7287(2)	459(1)	25(1)
C(7)	3073(2)	10300(2)	-719(1)	31(1)
C(8)	480(3)	6770(2)	-865(1)	40(1)
C(9)	1322(2)	6784(2)	2324(1)	19(1)
C(10)	1638(2)	6148(2)	3801(1)	18(1)
C(11)	2442(2)	4740(2)	3800(1)	20(1)
C(12)	2638(2)	3944(2)	4531(1)	21(1)
C(13)	2048(2)	4524(2)	5273(1)	20(1)
C(14)	1281(2)	5935(2)	5265(1)	21(1)
C(15)	1083(2)	6745(2)	4539(1)	20(1)
C(16)	2134(2)	3622(2)	6059(1)	21(1)
C(17)	3370(2)	2653(2)	7295(1)	25(1)

C(18)	4197(3)	3132(2)	7861(1)	33(1)
C(19)	4301(2)	4551(2)	7492(1)	30(1)
C(20)	3349(2)	4921(2)	6792(1)	25(1)
C(21)	4955(2)	2965(2)	5993(1)	28(1)
P(1)	7406(1)	919(1)	3560(1)	30(1)
F(7A)	8186(4)	32(2)	2794(1)	67(1)
F(8A)	6683(3)	1805(2)	4314(1)	58(1)
F(9A)	6327(3)	2063(2)	3005(2)	71(1)
F(10A)	8532(3)	-225(2)	4088(2)	59(1)
F(7B)	7080(30)	399(17)	2793(8)	50(5)
F(8B)	5847(16)	2199(14)	3476(14)	50(5)
F(9B)	7390(30)	1500(30)	4389(11)	72(7)
F(10B)	8780(20)	-391(19)	3650(20)	85(8)
F(11)	6174(2)	110(2)	3794(1)	73(1)
F(12)	8644(2)	1735(2)	3321(1)	56(1)
O(1)	2327(2)	9521(1)	2775(1)	33(1)
C(22)	2102(3)	10601(2)	3978(1)	42(1)
C(23)	2392(2)	10521(2)	3078(1)	27(1)
C(24)	2810(3)	11676(2)	2576(2)	44(1)
O(2A)	4730(30)	6002(16)	775(13)	52(3)
O(2B)	4840(40)	5560(20)	894(18)	73(5)
C(25)	5471(8)	5972(8)	-603(4)	63(2)
C(26)	4873(6)	5344(6)	187(4)	51(1)
C(27)	4349(9)	4098(8)	158(5)	64(2)

Table 15. Bond lengths [Å] and angles [°] for **12**.

S(1A)-S(1B)	0.68(3)
S(1A)-C(9)	1.6679(17)
S(1B)-C(9)	1.697(14)
F(1)-C(7)	1.335(2)
F(2)-C(7)	1.323(2)
F(3)-C(7)	1.323(2)
F(4A)-C(8)	1.329(3)
F(5A)-C(8)	1.407(4)

F(6A)-C(8)	1.289(5)
F(4B)-C(8)	1.390(4)
F(5B)-C(8)	1.212(5)
F(6B)-C(8)	1.323(5)
N(1)-C(9)	1.365(2)
N(1)-C(1)	1.406(2)
N(1)-H(1N)	0.824(16)
N(2)-C(9)	1.366(2)
N(2)-C(10)	1.418(2)
N(2)-H(2N)	0.843(15)
N(3)-C(21)	1.492(2)
N(3)-C(20)	1.512(2)
N(3)-C(16)	1.514(2)
N(3)-C(17)	1.521(2)
C(1)-C(6)	1.394(2)
C(1)-C(2)	1.401(2)
C(2)-C(3)	1.381(2)
C(2)-H(2)	0.9500
C(3)-C(4)	1.391(3)
C(3)-C(7)	1.501(2)
C(4)-C(5)	1.388(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.394(2)
C(5)-C(8)	1.504(3)
C(6)-H(6)	0.9500
C(10)-C(15)	1.395(2)
C(10)-C(11)	1.399(2)
C(11)-C(12)	1.389(2)
C(11)-H(11)	0.9500
C(12)-C(13)	1.397(2)
C(12)-H(12)	0.9500
C(13)-C(14)	1.394(2)
C(13)-C(16)	1.510(2)
C(14)-C(15)	1.389(2)
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500

C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(18)	1.521(3)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-C(19)	1.535(3)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-C(20)	1.520(3)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
P(1)-F(10B)	1.543(13)
P(1)-F(7B)	1.557(11)
P(1)-F(9B)	1.573(13)
P(1)-F(8A)	1.5789(18)
P(1)-F(10A)	1.5847(16)
P(1)-F(11)	1.5884(16)
P(1)-F(9A)	1.5889(17)
P(1)-F(12)	1.5984(15)
P(1)-F(7A)	1.6009(18)
P(1)-F(8B)	1.626(11)
O(1)-C(23)	1.221(2)
C(22)-C(23)	1.495(3)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-C(24)	1.484(3)
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
O(2A)-C(26)	1.23(2)

O(2A)-C(27)#1	1.65(3)
O(2B)-C(26)	1.22(3)
O(2B)-C(25)#1	1.82(3)
O(2B)-C(27)#1	1.84(3)
C(25)-C(26)	1.501(10)
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(25)-H(25D)	0.9800
C(25)-H(25E)	0.9800
C(25)-H(25F)	0.9800
C(26)-C(26)#1	0.950(10)
C(26)-C(27)#1	1.108(9)
C(26)-C(27)	1.513(10)
C(26)-C(25)#1	1.542(10)
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(27)-H(27D)	0.9800
C(27)-H(27E)	0.9800
C(27)-H(27F)	0.9800

S(1B)-S(1A)-C(9)	80.7(12)
S(1A)-S(1B)-C(9)	76.0(14)
C(9)-N(1)-C(1)	131.94(15)
C(9)-N(1)-H(1N)	116.5(15)
C(1)-N(1)-H(1N)	110.9(15)
C(9)-N(2)-C(10)	129.60(14)
C(9)-N(2)-H(2N)	115.0(14)
C(10)-N(2)-H(2N)	115.4(14)
C(21)-N(3)-C(20)	111.23(14)
C(21)-N(3)-C(16)	110.52(13)
C(20)-N(3)-C(16)	112.73(13)
C(21)-N(3)-C(17)	110.16(13)
C(20)-N(3)-C(17)	102.70(13)
C(16)-N(3)-C(17)	109.21(12)

C(6)-C(1)-C(2)	119.22(15)
C(6)-C(1)-N(1)	125.48(15)
C(2)-C(1)-N(1)	115.28(15)
C(3)-C(2)-C(1)	120.34(16)
C(3)-C(2)-H(2)	119.8
C(1)-C(2)-H(2)	119.8
C(2)-C(3)-C(4)	121.35(16)
C(2)-C(3)-C(7)	120.19(17)
C(4)-C(3)-C(7)	118.43(16)
C(5)-C(4)-C(3)	117.76(16)
C(5)-C(4)-H(4)	121.1
C(3)-C(4)-H(4)	121.1
C(4)-C(5)-C(6)	122.25(17)
C(4)-C(5)-C(8)	119.77(16)
C(6)-C(5)-C(8)	117.97(17)
C(5)-C(6)-C(1)	119.08(16)
C(5)-C(6)-H(6)	120.5
C(1)-C(6)-H(6)	120.5
F(2)-C(7)-F(3)	107.01(18)
F(2)-C(7)-F(1)	106.17(17)
F(3)-C(7)-F(1)	105.57(16)
F(2)-C(7)-C(3)	113.32(15)
F(3)-C(7)-C(3)	112.50(16)
F(1)-C(7)-C(3)	111.74(16)
F(5B)-C(8)-F(6B)	108.4(4)
F(6A)-C(8)-F(4A)	111.0(3)
F(5B)-C(8)-F(4B)	109.5(4)
F(6B)-C(8)-F(4B)	99.5(3)
F(6A)-C(8)-F(5A)	107.1(3)
F(4A)-C(8)-F(5A)	101.3(3)
F(5B)-C(8)-C(5)	115.3(3)
F(6A)-C(8)-C(5)	112.6(3)
F(6B)-C(8)-C(5)	114.1(3)
F(4A)-C(8)-C(5)	114.1(2)
F(4B)-C(8)-C(5)	108.8(2)
F(5A)-C(8)-C(5)	109.9(2)

N(1)-C(9)-N(2)	110.87(14)
N(1)-C(9)-S(1A)	125.39(13)
N(2)-C(9)-S(1A)	123.70(12)
N(1)-C(9)-S(1B)	118.0(6)
N(2)-C(9)-S(1B)	125.9(5)
C(15)-C(10)-C(11)	119.52(14)
C(15)-C(10)-N(2)	116.96(14)
C(11)-C(10)-N(2)	123.33(15)
C(12)-C(11)-C(10)	119.73(15)
C(12)-C(11)-H(11)	120.1
C(10)-C(11)-H(11)	120.1
C(11)-C(12)-C(13)	121.19(15)
C(11)-C(12)-H(12)	119.4
C(13)-C(12)-H(12)	119.4
C(14)-C(13)-C(12)	118.39(15)
C(14)-C(13)-C(16)	120.92(15)
C(12)-C(13)-C(16)	120.52(15)
C(15)-C(14)-C(13)	121.04(15)
C(15)-C(14)-H(14)	119.5
C(13)-C(14)-H(14)	119.5
C(14)-C(15)-C(10)	120.07(15)
C(14)-C(15)-H(15)	120.0
C(10)-C(15)-H(15)	120.0
C(13)-C(16)-N(3)	114.90(13)
C(13)-C(16)-H(16A)	108.5
N(3)-C(16)-H(16A)	108.5
C(13)-C(16)-H(16B)	108.5
N(3)-C(16)-H(16B)	108.5
H(16A)-C(16)-H(16B)	107.5
N(3)-C(17)-C(18)	105.81(14)
N(3)-C(17)-H(17A)	110.6
C(18)-C(17)-H(17A)	110.6
N(3)-C(17)-H(17B)	110.6
C(18)-C(17)-H(17B)	110.6
H(17A)-C(17)-H(17B)	108.7
C(17)-C(18)-C(19)	105.96(15)

C(17)-C(18)-H(18A)	110.5
C(19)-C(18)-H(18A)	110.5
C(17)-C(18)-H(18B)	110.5
C(19)-C(18)-H(18B)	110.5
H(18A)-C(18)-H(18B)	108.7
C(20)-C(19)-C(18)	105.57(15)
C(20)-C(19)-H(19A)	110.6
C(18)-C(19)-H(19A)	110.6
C(20)-C(19)-H(19B)	110.6
C(18)-C(19)-H(19B)	110.6
H(19A)-C(19)-H(19B)	108.8
N(3)-C(20)-C(19)	104.54(14)
N(3)-C(20)-H(20A)	110.8
C(19)-C(20)-H(20A)	110.8
N(3)-C(20)-H(20B)	110.8
C(19)-C(20)-H(20B)	110.8
H(20A)-C(20)-H(20B)	108.9
N(3)-C(21)-H(21A)	109.5
N(3)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
N(3)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
F(10B)-P(1)-F(7B)	90.5(13)
F(10B)-P(1)-F(9B)	97.0(14)
F(7B)-P(1)-F(9B)	168.7(12)
F(8A)-P(1)-F(10A)	91.42(12)
F(10B)-P(1)-F(11)	93.7(9)
F(7B)-P(1)-F(11)	69.1(8)
F(9B)-P(1)-F(11)	101.9(10)
F(8A)-P(1)-F(11)	90.14(12)
F(10A)-P(1)-F(11)	89.17(12)
F(8A)-P(1)-F(9A)	90.05(14)
F(10A)-P(1)-F(9A)	177.95(15)
F(11)-P(1)-F(9A)	92.27(12)
F(10B)-P(1)-F(12)	86.3(9)

F(7B)-P(1)-F(12)	110.8(8)
F(9B)-P(1)-F(12)	78.3(10)
F(8A)-P(1)-F(12)	89.96(11)
F(10A)-P(1)-F(12)	90.95(11)
F(11)-P(1)-F(12)	179.84(10)
F(9A)-P(1)-F(12)	87.61(11)
F(8A)-P(1)-F(7A)	178.29(14)
F(10A)-P(1)-F(7A)	87.96(12)
F(11)-P(1)-F(7A)	91.44(12)
F(9A)-P(1)-F(7A)	90.54(14)
F(12)-P(1)-F(7A)	88.46(11)
F(10B)-P(1)-F(8B)	174.3(11)
F(7B)-P(1)-F(8B)	86.6(10)
F(9B)-P(1)-F(8B)	85.1(11)
F(11)-P(1)-F(8B)	80.6(6)
F(12)-P(1)-F(8B)	99.3(6)
C(23)-C(22)-H(22A)	109.5
C(23)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(23)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
O(1)-C(23)-C(24)	121.71(18)
O(1)-C(23)-C(22)	120.81(18)
C(24)-C(23)-C(22)	117.45(17)
C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(26)-C(25)-H(25A)	109.5
C(26)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(26)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5

H(25B)-C(25)-H(25C)	109.5
C(26)-C(25)-H(25D)	109.5
H(25A)-C(25)-H(25D)	141.1
H(25B)-C(25)-H(25D)	56.3
H(25C)-C(25)-H(25D)	56.3
C(26)-C(25)-H(25E)	109.5
H(25A)-C(25)-H(25E)	56.3
H(25B)-C(25)-H(25E)	141.1
H(25C)-C(25)-H(25E)	56.3
H(25D)-C(25)-H(25E)	109.5
C(26)-C(25)-H(25F)	109.5
H(25A)-C(25)-H(25F)	56.3
H(25B)-C(25)-H(25F)	56.3
H(25C)-C(25)-H(25F)	141.1
H(25D)-C(25)-H(25F)	109.5
H(25E)-C(25)-H(25F)	109.5
O(2B)-C(26)-C(25)	132.5(14)
O(2A)-C(26)-C(25)	114.6(12)
O(2B)-C(26)-C(27)	109.6(14)
O(2A)-C(26)-C(27)	127.5(13)
C(25)-C(26)-C(27)	117.5(5)
C(26)-C(27)-H(27A)	109.5
C(26)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(26)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(26)-C(27)-H(27D)	109.5
H(27A)-C(27)-H(27D)	141.1
H(27B)-C(27)-H(27D)	56.3
H(27C)-C(27)-H(27D)	56.3
C(26)-C(27)-H(27E)	109.5
H(27A)-C(27)-H(27E)	56.3
H(27B)-C(27)-H(27E)	141.1
H(27C)-C(27)-H(27E)	56.3
H(27D)-C(27)-H(27E)	109.5

C(26)-C(27)-H(27F)	109.5
H(27A)-C(27)-H(27F)	56.3
H(27B)-C(27)-H(27F)	56.3
H(27C)-C(27)-H(27F)	141.1
H(27D)-C(27)-H(27F)	109.5
H(27E)-C(27)-H(27F)	109.5

Table 16. Anisotropic displacement parameters ($Å^2$x 10^3)for **12**. The anisotropic displacement factor exponent takes the form: -2□^{2}[$h^2a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1A)	37(1)	19(1)	18(1)	0(1)	-6(1)	-14(1)
S(1B)	41(9)	29(5)	33(6)	-1(4)	2(6)	-13(5)
F(1)	60(1)	55(1)	48(1)	33(1)	-17(1)	-31(1)
F(2)	113(1)	59(1)	33(1)	3(1)	-3(1)	-64(1)
F(3)	44(1)	51(1)	81(1)	2(1)	22(1)	-19(1)
F(4A)	74(2)	56(2)	13(1)	-3(1)	-5(1)	-40(2)
F(5A)	73(2)	33(1)	41(2)	-6(1)	-21(2)	-22(1)
F(6A)	42(2)	65(3)	60(2)	-14(2)	-14(2)	-22(2)
F(4B)	121(3)	93(3)	62(2)	23(2)	-60(2)	-58(2)
F(5B)	70(2)	118(3)	118(3)	-89(3)	-6(2)	-19(2)
F(6B)	59(2)	65(3)	48(2)	-17(2)	-4(2)	-39(2)
N(1)	39(1)	21(1)	17(1)	1(1)	-6(1)	-16(1)
N(2)	30(1)	16(1)	16(1)	0(1)	-5(1)	-10(1)
N(3)	22(1)	21(1)	18(1)	3(1)	-5(1)	-9(1)
C(1)	26(1)	21(1)	16(1)	1(1)	-4(1)	-6(1)
C(2)	28(1)	21(1)	21(1)	1(1)	-5(1)	-9(1)
C(3)	28(1)	25(1)	21(1)	4(1)	-2(1)	-8(1)
C(4)	34(1)	34(1)	17(1)	3(1)	-4(1)	-13(1)
C(5)	34(1)	33(1)	20(1)	0(1)	-6(1)	-14(1)
C(6)	32(1)	26(1)	19(1)	2(1)	-4(1)	-13(1)
C(7)	38(1)	34(1)	23(1)	4(1)	-2(1)	-17(1)
C(8)	54(1)	57(1)	20(1)	-2(1)	-6(1)	-32(1)
C(9)	21(1)	19(1)	17(1)	0(1)	-3(1)	-6(1)
C(10)	20(1)	20(1)	17(1)	2(1)	-5(1)	-11(1)

C(11)	24(1)	21(1)	19(1)	-2(1)	-3(1)	-9(1)
C(12)	25(1)	18(1)	21(1)	0(1)	-5(1)	-9(1)
C(13)	20(1)	23(1)	18(1)	3(1)	-5(1)	-10(1)
C(14)	21(1)	26(1)	16(1)	-2(1)	-2(1)	-7(1)
C(15)	20(1)	19(1)	21(1)	-2(1)	-4(1)	-5(1)
C(16)	22(1)	25(1)	20(1)	4(1)	-6(1)	-12(1)
C(17)	32(1)	27(1)	18(1)	8(1)	-8(1)	-13(1)
C(18)	45(1)	32(1)	25(1)	3(1)	-12(1)	-15(1)
C(19)	35(1)	35(1)	25(1)	-1(1)	-6(1)	-17(1)
C(20)	34(1)	21(1)	24(1)	0(1)	-7(1)	-11(1)
C(21)	23(1)	34(1)	25(1)	-1(1)	-3(1)	-5(1)
P(1)	41(1)	22(1)	26(1)	-2(1)	-7(1)	-9(1)
F(7A)	113(2)	56(1)	37(1)	-22(1)	9(1)	-35(1)
F(8A)	73(2)	43(1)	50(1)	-22(1)	18(1)	-11(1)
F(9A)	87(2)	51(1)	85(2)	26(1)	-59(2)	-25(1)
F(10A)	69(1)	41(1)	49(1)	11(1)	-18(1)	8(1)
F(7B)	76(10)	48(7)	34(6)	-11(5)	-14(6)	-21(7)
F(8B)	50(7)	36(6)	57(9)	3(6)	-5(6)	-7(5)
F(9B)	90(12)	76(11)	62(10)	-23(7)	-19(8)	-31(8)
F(10B)	75(10)	70(10)	104(12)	7(8)	-2(8)	-23(7)
F(11)	65(1)	47(1)	115(2)	-8(1)	4(1)	-34(1)
F(12)	56(1)	45(1)	69(1)	-9(1)	7(1)	-23(1)
O(1)	47(1)	24(1)	32(1)	-6(1)	-8(1)	-17(1)
C(22)	54(1)	38(1)	34(1)	-12(1)	-9(1)	-13(1)
C(23)	27(1)	20(1)	34(1)	-5(1)	-9(1)	-4(1)
C(24)	62(2)	28(1)	48(1)	1(1)	-10(1)	-21(1)
O(2A)	58(5)	57(9)	44(6)	-15(6)	-26(4)	-10(7)
O(2B)	72(7)	75(12)	75(9)	-4(8)	-30(6)	-20(10)
C(25)	48(3)	69(4)	60(4)	-12(4)	-4(3)	1(3)
C(26)	35(3)	59(4)	56(4)	-24(2)	-18(2)	3(2)
C(27)	55(4)	59(4)	82(5)	-24(4)	-5(4)	-16(3)

Table 17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **12**.

	x	y	z	U(eq)
H(1N)	1730(20)	8451(19)	1938(13)	29
H(2N)	1420(20)	7863(16)	3134(13)	24
H(2)	2591	9505	843	28
H(4)	1827	8734	-1346	34
H(6)	504	6612	713	30
H(11)	2851	4330	3300	25
H(12)	3184	2988	4526	25
H(14)	888	6349	5764	25
H(15)	569	7708	4544	24
H(16A)	2216	2677	5941	26
H(16B)	1163	3972	6422	26
H(17A)	3878	1667	7204	30
H(17B)	2287	2776	7528	30
H(18A)	5236	2475	7897	39
H(18B)	3614	3204	8413	39
H(19A)	3883	5244	7900	36
H(19B)	5381	4507	7295	36
H(20A)	2269	5436	6976	30
H(20B)	3771	5489	6352	30
H(21A)	4987	2085	5808	42
H(21B)	5798	2815	6314	42
H(21C)	5062	3613	5522	42
H(22A)	1793	9803	4236	62
H(22B)	1280	11451	4111	62
H(22C)	3041	10601	4176	62
H(24A)	2958	11506	2001	66
H(24B)	3763	11746	2723	66
H(24C)	1984	12540	2672	66
H(25A)	5460	6910	-533	95
H(25B)	4819	6004	-1016	95
H(25C)	6525	5412	-777	95

H(25D)	5743	5307	-1017	95
H(25E)	6383	6213	-535	95
H(25F)	4678	6805	-774	95
H(27A)	3602	4030	636	97
H(27B)	5235	3263	155	97
H(27C)	3869	4194	-335	97
H(27D)	4868	3628	-332	97
H(27E)	3236	4395	149	97
H(27F)	4602	3464	639	97

Table 18. Torsion angles [°] for **12**.

C(9)-N(1)-C(1)-C(6)	21.1(3)
C(9)-N(1)-C(1)-C(2)	-160.25(18)
C(6)-C(1)-C(2)-C(3)	-0.6(3)
N(1)-C(1)-C(2)-C(3)	-179.38(16)
C(1)-C(2)-C(3)-C(4)	0.2(3)
C(1)-C(2)-C(3)-C(7)	-177.74(17)
C(2)-C(3)-C(4)-C(5)	0.2(3)
C(7)-C(3)-C(4)-C(5)	178.22(18)
C(3)-C(4)-C(5)-C(6)	-0.2(3)
C(3)-C(4)-C(5)-C(8)	-179.55(19)
C(4)-C(5)-C(6)-C(1)	-0.2(3)
C(8)-C(5)-C(6)-C(1)	179.12(18)
C(2)-C(1)-C(6)-C(5)	0.6(3)
N(1)-C(1)-C(6)-C(5)	179.23(17)
C(2)-C(3)-C(7)-F(2)	-14.2(3)
C(4)-C(3)-C(7)-F(2)	167.80(18)
C(2)-C(3)-C(7)-F(3)	107.4(2)
C(4)-C(3)-C(7)-F(3)	-70.6(2)
C(2)-C(3)-C(7)-F(1)	-134.09(19)
C(4)-C(3)-C(7)-F(1)	47.9(2)
C(4)-C(5)-C(8)-F(5B)	85.5(4)
C(6)-C(5)-C(8)-F(5B)	-93.9(4)
C(4)-C(5)-C(8)-F(6A)	-120.9(3)

C(6)-C(5)-C(8)-F(6A)	59.8(3)
C(4)-C(5)-C(8)-F(6B)	-148.0(3)
C(6)-C(5)-C(8)-F(6B)	32.7(4)
C(4)-C(5)-C(8)-F(4A)	6.8(3)
C(6)-C(5)-C(8)-F(4A)	-172.5(3)
C(4)-C(5)-C(8)-F(4B)	-38.0(4)
C(6)-C(5)-C(8)-F(4B)	142.7(3)
C(4)-C(5)-C(8)-F(5A)	119.8(3)
C(6)-C(5)-C(8)-F(5A)	-59.6(3)
C(1)-N(1)-C(9)-N(2)	175.50(17)
C(1)-N(1)-C(9)-S(1A)	-6.5(3)
C(1)-N(1)-C(9)-S(1B)	19.5(11)
C(10)-N(2)-C(9)-N(1)	-167.01(16)
C(10)-N(2)-C(9)-S(1A)	15.0(3)
C(10)-N(2)-C(9)-S(1B)	-13.4(13)
S(1B)-S(1A)-C(9)-N(1)	78.8(12)
S(1B)-S(1A)-C(9)-N(2)	-103.5(12)
S(1A)-S(1B)-C(9)-N(1)	-115.1(11)
S(1A)-S(1B)-C(9)-N(2)	92.9(14)
C(9)-N(2)-C(10)-C(15)	-152.53(17)
C(9)-N(2)-C(10)-C(11)	32.5(3)
C(15)-C(10)-C(11)-C(12)	1.9(2)
N(2)-C(10)-C(11)-C(12)	176.76(15)
C(10)-C(11)-C(12)-C(13)	-0.1(2)
C(11)-C(12)-C(13)-C(14)	-1.4(2)
C(11)-C(12)-C(13)-C(16)	173.96(15)
C(12)-C(13)-C(14)-C(15)	1.1(2)
C(16)-C(13)-C(14)-C(15)	-174.29(15)
C(13)-C(14)-C(15)-C(10)	0.8(2)
C(11)-C(10)-C(15)-C(14)	-2.3(2)
N(2)-C(10)-C(15)-C(14)	-177.43(15)
C(14)-C(13)-C(16)-N(3)	-86.85(19)
C(12)-C(13)-C(16)-N(3)	97.87(18)
C(21)-N(3)-C(16)-C(13)	-60.78(18)
C(20)-N(3)-C(16)-C(13)	64.40(18)
C(17)-N(3)-C(16)-C(13)	177.88(14)

C(21)-N(3)-C(17)-C(18)	83.69(18)
C(20)-N(3)-C(17)-C(18)	-34.88(18)
C(16)-N(3)-C(17)-C(18)	-154.75(15)
N(3)-C(17)-C(18)-C(19)	17.1(2)
C(17)-C(18)-C(19)-C(20)	7.3(2)
C(21)-N(3)-C(20)-C(19)	-78.44(17)
C(16)-N(3)-C(20)-C(19)	156.77(14)
C(17)-N(3)-C(20)-C(19)	39.37(17)
C(18)-C(19)-C(20)-N(3)	-29.05(19)

Table 19. Hydrogen bonds for **12**[Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(1)	0.824(16)	2.117(17)	2.8980(19)	158(2)
N(2)-H(2N)...F(10B)#2	0.843(15)	2.62(3)	3.104(19)	118.1(17)
N(2)-H(2N)...O(1)	0.843(15)	2.107(17)	2.8654(19)	149.5(19)

Table 20. Crystal data and structure refinement for **6**.

Identification code	**6**	
Empirical formula	C33 H27 F12 N4 O P S	
Formula weight	786.61	
Temperature	125(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 9.1393(8) Å	□= 92.9940(10)°
	b = 10.1924(8) Å	□= 103.2290(10)°
	c = 18.9510(16) Å	□ = 92.1860(10)°
Volume	1713.8(2) $Å^3$	
Z	2	
Density (calculated)	1.524 Mg/m^3	
Absorption coefficient	0.241 mm^{-1}	
F(000)	800	
Crystal size	0.490 x 0.410 x 0.400 mm^3	
Theta range for data collection	2.212 to 28.526°	
Index ranges	-11<=h<=11, -13<=k<=13, -24<=l<=24	
Reflections collected	13704	
Independent reflections	7725 [R(int) = 0.0152]	
Completeness to theta = 25.242°	97.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6723	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7725 / 209 / 584	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0474, wR2 = 0.1237	
R indices (all data)	R1 = 0.0541, wR2 = 0.1290	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.844 and -0.569 e.$Å^{-3}$	

Table 21. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **6**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	199(1)	4416(1)	1163(1)	23(1)
N(1)	1629(2)	6647(2)	1872(1)	27(1)
N(2)	805(2)	6663(2)	639(1)	24(1)
N(3)	4114(2)	12371(1)	794(1)	23(1)
N(4)	6387(2)	12244(2)	1432(1)	28(1)
F1Aa	-373(9)	3191(7)	3415(4)	50(1)
F2Aa	-1123(7)	4869(6)	3879(4)	62(1)
F3Aa	750(6)	3838(7)	4499(2)	62(1)
F1Bb	-14(17)	3109(13)	3480(11)	49(3)
F2Bb	-1236(15)	4808(19)	3652(8)	87(5)
F3Bb	322(14)	4253(11)	4510(5)	56(2)
F4Aa	5001(8)	6889(7)	4954(2)	59(1)
F5Aa	5653(9)	7902(7)	4094(5)	67(2)
F6Aa	6127(7)	5896(6)	4234(3)	58(1)
F4Bb	5241(18)	6643(14)	4952(6)	59(3)
F5Bb	5326(19)	8052(11)	4204(10)	76(4)
F6Bb	6220(16)	6213(16)	4089(9)	88(4)
C(1)	1900(2)	6242(2)	2589(1)	23(1)
C(2)	854(2)	5488(2)	2849(1)	25(1)
C(3)	1229(2)	5133(2)	3565(1)	27(1)
C(4)	2584(2)	5550(2)	4033(1)	29(1)
C(5)	3588(2)	6340(2)	3772(1)	27(1)
C(6)	3263(2)	6682(2)	3055(1)	25(1)
C(7)	120(3)	4282(2)	3834(1)	37(1)
C(8)	5080(2)	6786(2)	4263(1)	38(1)
C(9)	905(2)	5986(2)	1241(1)	21(1)
C(10)	1253(2)	8007(2)	602(1)	22(1)
C(11)	801(2)	9001(2)	1024(1)	25(1)
C(12)	1243(2)	10303(2)	958(1)	24(1)
C(13)	2091(2)	10616(2)	461(1)	22(1)
C(14)	2510(2)	9614(2)	33(1)	26(1)

C(15)	2115(2)	8308(2)	107(1)	25(1)
C(16)	2545(2)	12033(2)	389(1)	25(1)
C(17)	4815(2)	13609(2)	839(1)	29(1)
C(18)	6233(2)	13526(2)	1239(1)	31(1)
C(19)	5082(2)	11567(2)	1161(1)	24(1)
C(20)	7751(2)	11696(2)	1853(1)	39(1)
O(1)	536(2)	552(2)	2509(1)	44(1)
C(21)	1601(2)	606(2)	3032(1)	31(1)
C(22)	1492(2)	-111(2)	3687(1)	33(1)
C(23)	2378(3)	254(3)	4374(1)	51(1)
C(24)	2168(4)	-397(3)	4972(2)	76(1)
C(25)	1094(4)	-1413(3)	4889(2)	70(1)
C(26)	186(3)	-1775(2)	4211(2)	49(1)
C(27)	382(2)	-1128(2)	3612(1)	37(1)
C(28)	2994(2)	1420(2)	3018(1)	31(1)
C(29)	2816(2)	2564(2)	2641(1)	33(1)
C(30)	4052(3)	3372(2)	2615(1)	39(1)
C(31)	5477(3)	3040(3)	2956(1)	49(1)
C(32)	5675(3)	1881(4)	3307(2)	67(1)
C(33)	4435(3)	1073(3)	3340(2)	56(1)
P(1)	6044(1)	7485(1)	1596(1)	38(1)
F7Aa	6375(7)	6478(8)	2190(4)	77(2)
F8Aa	5680(4)	8443(4)	895(2)	44(1)
F9Aa	5241(8)	8436(6)	2016(3)	103(2)
F10Aa	4436(4)	6685(3)	1205(3)	76(1)
F11Aa	6739(5)	6502(3)	1064(2)	54(1)
F12Aa	7517(5)	8247(5)	1869(3)	94(1)
F7Bb	5768(6)	6336(6)	2095(4)	58(1)
F8Bb	6332(7)	8705(5)	1178(3)	81(2)
F9Bb	4590(3)	8221(3)	1771(2)	38(1)
F10Bb	5174(7)	6735(4)	928(2)	88(1)
F11Bb	7531(6)	6866(5)	1517(3)	96(1)
F12Bb	6926(5)	8311(4)	2346(3)	89(1)

Table 22. Bond lengths [Å] and angles [°] for **6**.

S(1)-C(9)	1.6889(17)
N(1)-C(9)	1.358(2)
N(1)-C(1)	1.411(2)
N(1)-H(1N)	0.82(3)
N(2)-C(9)	1.350(2)
N(2)-C(10)	1.425(2)
N(2)-H(2N)	0.83(3)
N(3)-C(19)	1.331(2)
N(3)-C(17)	1.382(2)
N(3)-C(16)	1.482(2)
N(4)-C(19)	1.335(2)
N(4)-C(18)	1.378(3)
N(4)-C(20)	1.466(3)
F1Aa-C(7)	1.333(6)
F2Aa-C(7)	1.321(6)
F3Aa-C(7)	1.367(4)
F1Bb-C(7)	1.328(12)
F2Bb-C(7)	1.348(12)
F3Bb-C(7)	1.253(9)
F4Aa-C(8)	1.328(5)
F5Aa-C(8)	1.319(6)
F6Aa-C(8)	1.351(5)
F4Bb-C(8)	1.297(10)
F5Bb-C(8)	1.316(11)
F6Bb-C(8)	1.310(12)
C(1)-C(2)	1.394(2)
C(1)-C(6)	1.395(2)
C(2)-C(3)	1.392(2)
C(2)-H(2)	0.9500
C(3)-C(4)	1.385(3)
C(3)-C(7)	1.502(3)
C(4)-C(5)	1.389(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.388(2)

C(5)-C(8)	1.503(3)
C(6)-H(6)	0.9500
C(10)-C(11)	1.391(2)
C(10)-C(15)	1.395(2)
C(11)-C(12)	1.393(2)
C(11)-H(11)	0.9500
C(12)-C(13)	1.392(2)
C(12)-H(12)	0.9500
C(13)-C(14)	1.390(3)
C(13)-C(16)	1.509(2)
C(14)-C(15)	1.389(2)
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(18)	1.352(3)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(19)-H(19)	0.9500
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(20)-H(20D)	0.9800
C(20)-H(20E)	0.9800
C(20)-H(20F)	0.9800
O(1)-C(21)	1.217(2)
C(21)-C(22)	1.494(3)
C(21)-C(28)	1.498(3)
C(22)-C(23)	1.391(3)
C(22)-C(27)	1.401(3)
C(23)-C(24)	1.388(3)
C(23)-H(23)	0.9500
C(24)-C(25)	1.377(4)
C(24)-H(24)	0.9500
C(25)-C(26)	1.385(4)
C(25)-H(25)	0.9500

C(26)-C(27)	1.384(3)
C(26)-H(26)	0.9500
C(27)-H(27)	0.9500
C(28)-C(33)	1.386(3)
C(28)-C(29)	1.395(3)
C(29)-C(30)	1.384(3)
C(29)-H(29)	0.9500
C(30)-C(31)	1.378(4)
C(30)-H(30)	0.9500
C(31)-C(32)	1.383(4)
C(31)-H(31)	0.9500
C(32)-C(33)	1.391(4)
C(32)-H(32)	0.9500
C(33)-H(33)	0.9500
P(1)-F10Bb	1.487(4)
P(1)-F12Aa	1.498(4)
P(1)-F9Aa	1.534(5)
P(1)-F7Aa	1.549(8)
P(1)-F8Bb	1.554(5)
P(1)-F11Bb	1.555(4)
P(1)-F7Bb	1.592(6)
P(1)-F11Aa	1.632(3)
P(1)-F12Bb	1.636(4)
P(1)-F9Bb	1.639(3)
P(1)-F10Aa	1.649(3)
P(1)-F8Aa	1.668(4)

C(9)-N(1)-C(1)	129.57(15)
C(9)-N(1)-H(1N)	113.0(17)
C(1)-N(1)-H(1N)	116.6(17)
C(9)-N(2)-C(10)	127.49(15)
C(9)-N(2)-H(2N)	117.3(17)
C(10)-N(2)-H(2N)	115.0(17)
C(19)-N(3)-C(17)	108.76(15)
C(19)-N(3)-C(16)	127.11(14)
C(17)-N(3)-C(16)	124.13(15)

C(19)-N(4)-C(18)	108.56(16)
C(19)-N(4)-C(20)	125.10(17)
C(18)-N(4)-C(20)	126.34(16)
C(2)-C(1)-C(6)	119.97(16)
C(2)-C(1)-N(1)	123.14(16)
C(6)-C(1)-N(1)	116.83(15)
C(3)-C(2)-C(1)	118.84(16)
C(3)-C(2)-H(2)	120.6
C(1)-C(2)-H(2)	120.6
C(4)-C(3)-C(2)	121.88(16)
C(4)-C(3)-C(7)	119.46(17)
C(2)-C(3)-C(7)	118.66(17)
C(3)-C(4)-C(5)	118.40(16)
C(3)-C(4)-H(4)	120.8
C(5)-C(4)-H(4)	120.8
C(6)-C(5)-C(4)	121.02(16)
C(6)-C(5)-C(8)	119.32(17)
C(4)-C(5)-C(8)	119.61(17)
C(5)-C(6)-C(1)	119.81(16)
C(5)-C(6)-H(6)	120.1
C(1)-C(6)-H(6)	120.1
F3Bb-C(7)-F1Bb	114.7(11)
F2Aa-C(7)-F1Aa	104.0(4)
F3Bb-C(7)-F2Bb	102.0(7)
F1Bb-C(7)-F2Bb	106.6(9)
F2Aa-C(7)-F3Aa	108.4(3)
F1Aa-C(7)-F3Aa	104.3(5)
F3Bb-C(7)-C(3)	116.3(5)
F2Aa-C(7)-C(3)	113.9(4)
F1Bb-C(7)-C(3)	108.3(9)
F1Aa-C(7)-C(3)	114.1(4)
F2Bb-C(7)-C(3)	108.1(8)
F3Aa-C(7)-C(3)	111.4(2)
F4Bb-C(8)-F6Bb	105.2(9)
F4Bb-C(8)-F5Bb	105.6(10)
F6Bb-C(8)-F5Bb	105.7(8)

F5Aa-C(8)-F4Aa	109.1(5)
F5Aa-C(8)-F6Aa	105.4(4)
F4Aa-C(8)-F6Aa	105.2(4)
F4Bb-C(8)-C(5)	117.2(8)
F6Bb-C(8)-C(5)	113.3(8)
F5Bb-C(8)-C(5)	109.0(8)
F5Aa-C(8)-C(5)	114.0(4)
F4Aa-C(8)-C(5)	111.6(4)
F6Aa-C(8)-C(5)	111.1(3)
N(2)-C(9)-N(1)	115.21(15)
N(2)-C(9)-S(1)	119.60(12)
N(1)-C(9)-S(1)	125.16(13)
C(11)-C(10)-C(15)	120.62(15)
C(11)-C(10)-N(2)	121.40(15)
C(15)-C(10)-N(2)	117.92(16)
C(10)-C(11)-C(12)	119.26(16)
C(10)-C(11)-H(11)	120.4
C(12)-C(11)-H(11)	120.4
C(13)-C(12)-C(11)	120.61(16)
C(13)-C(12)-H(12)	119.7
C(11)-C(12)-H(12)	119.7
C(14)-C(13)-C(12)	119.42(15)
C(14)-C(13)-C(16)	120.62(16)
C(12)-C(13)-C(16)	119.96(16)
C(15)-C(14)-C(13)	120.72(16)
C(15)-C(14)-H(14)	119.6
C(13)-C(14)-H(14)	119.6
C(14)-C(15)-C(10)	119.32(17)
C(14)-C(15)-H(15)	120.3
C(10)-C(15)-H(15)	120.3
N(3)-C(16)-C(13)	111.53(14)
N(3)-C(16)-H(16A)	109.3
C(13)-C(16)-H(16A)	109.3
N(3)-C(16)-H(16B)	109.3
C(13)-C(16)-H(16B)	109.3
H(16A)-C(16)-H(16B)	108.0

C(18)-C(17)-N(3)	106.85(17)
C(18)-C(17)-H(17)	126.6
N(3)-C(17)-H(17)	126.6
C(17)-C(18)-N(4)	107.33(16)
C(17)-C(18)-H(18)	126.3
N(4)-C(18)-H(18)	126.3
N(3)-C(19)-N(4)	108.48(15)
N(3)-C(19)-H(19)	125.8
N(4)-C(19)-H(19)	125.8
N(4)-C(20)-H(20A)	109.5
N(4)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
N(4)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
N(4)-C(20)-H(20D)	109.5
H(20A)-C(20)-H(20D)	141.1
H(20B)-C(20)-H(20D)	56.3
H(20C)-C(20)-H(20D)	56.3
N(4)-C(20)-H(20E)	109.5
H(20A)-C(20)-H(20E)	56.3
H(20B)-C(20)-H(20E)	141.1
H(20C)-C(20)-H(20E)	56.3
H(20D)-C(20)-H(20E)	109.5
N(4)-C(20)-H(20F)	109.5
H(20A)-C(20)-H(20F)	56.3
H(20B)-C(20)-H(20F)	56.3
H(20C)-C(20)-H(20F)	141.1
H(20D)-C(20)-H(20F)	109.5
H(20E)-C(20)-H(20F)	109.5
O(1)-C(21)-C(22)	119.69(19)
O(1)-C(21)-C(28)	119.60(18)
C(22)-C(21)-C(28)	120.69(16)
C(23)-C(22)-C(27)	119.0(2)
C(23)-C(22)-C(21)	122.42(18)
C(27)-C(22)-C(21)	118.45(18)

C(24)-C(23)-C(22)	120.0(2)
C(24)-C(23)-H(23)	120.0
C(22)-C(23)-H(23)	120.0
C(25)-C(24)-C(23)	120.5(2)
C(25)-C(24)-H(24)	119.8
C(23)-C(24)-H(24)	119.8
C(24)-C(25)-C(26)	120.2(2)
C(24)-C(25)-H(25)	119.9
C(26)-C(25)-H(25)	119.9
C(27)-C(26)-C(25)	119.8(2)
C(27)-C(26)-H(26)	120.1
C(25)-C(26)-H(26)	120.1
C(26)-C(27)-C(22)	120.5(2)
C(26)-C(27)-H(27)	119.7
C(22)-C(27)-H(27)	119.7
C(33)-C(28)-C(29)	118.9(2)
C(33)-C(28)-C(21)	123.51(19)
C(29)-C(28)-C(21)	117.56(18)
C(30)-C(29)-C(28)	120.7(2)
C(30)-C(29)-H(29)	119.7
C(28)-C(29)-H(29)	119.7
C(31)-C(30)-C(29)	120.0(2)
C(31)-C(30)-H(30)	120.0
C(29)-C(30)-H(30)	120.0
C(30)-C(31)-C(32)	120.0(2)
C(30)-C(31)-H(31)	120.0
C(32)-C(31)-H(31)	120.0
C(31)-C(32)-C(33)	120.1(2)
C(31)-C(32)-H(32)	119.9
C(33)-C(32)-H(32)	119.9
C(28)-C(33)-C(32)	120.2(2)
C(28)-C(33)-H(33)	119.9
C(32)-C(33)-H(33)	119.9
F12Aa-P(1)-F9Aa	91.7(3)
F12Aa-P(1)-F7Aa	94.0(3)
F9Aa-P(1)-F7Aa	95.8(4)

F10Bb-P(1)-F8Bb	93.2(3)
F10Bb-P(1)-F11Bb	91.7(3)
F8Bb-P(1)-F11Bb	93.1(3)
F10Bb-P(1)-F7Bb	92.0(3)
F8Bb-P(1)-F7Bb	174.2(3)
F11Bb-P(1)-F7Bb	89.3(3)
F12Aa-P(1)-F11Aa	92.6(3)
F9Aa-P(1)-F11Aa	173.2(3)
F7Aa-P(1)-F11Aa	89.2(3)
F10Bb-P(1)-F12Bb	177.2(3)
F8Bb-P(1)-F12Bb	88.0(3)
F11Bb-P(1)-F12Bb	90.7(3)
F7Bb-P(1)-F12Bb	86.6(3)
F10Bb-P(1)-F9Bb	95.1(3)
F8Bb-P(1)-F9Bb	87.2(2)
F11Bb-P(1)-F9Bb	173.2(3)
F7Bb-P(1)-F9Bb	89.8(2)
F12Bb-P(1)-F9Bb	82.5(2)
F12Aa-P(1)-F10Aa	173.8(3)
F9Aa-P(1)-F10Aa	91.3(3)
F7Aa-P(1)-F10Aa	91.1(3)
F11Aa-P(1)-F10Aa	84.0(2)
F12Aa-P(1)-F8Aa	88.7(2)
F9Aa-P(1)-F8Aa	89.2(3)
F7Aa-P(1)-F8Aa	174.2(4)
F11Aa-P(1)-F8Aa	85.55(19)
F10Aa-P(1)-F8Aa	85.90(19)

Table 23. Anisotropic displacement parameters ($Å^2$x 10^3)for **6**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	28(1)	18(1)	22(1)	1(1)	5(1)	-4(1)
N(1)	33(1)	24(1)	22(1)	2(1)	2(1)	-10(1)
N(2)	32(1)	20(1)	20(1)	0(1)	2(1)	-6(1)
N(3)	24(1)	18(1)	29(1)	1(1)	8(1)	0(1)
N(4)	24(1)	27(1)	32(1)	-2(1)	7(1)	-2(1)
F1Aa	56(3)	48(2)	46(2)	-15(2)	24(2)	-31(2)
F2Aa	57(2)	47(2)	98(3)	-2(2)	56(2)	-10(1)
F3Aa	59(2)	82(3)	41(2)	32(2)	1(1)	-28(2)
F1Bb	54(6)	26(3)	76(7)	-1(3)	37(5)	-14(3)
F2Bb	53(5)	94(7)	129(9)	22(6)	52(5)	-9(4)
F3Bb	68(4)	71(4)	30(3)	-5(2)	22(3)	-28(3)
F4Aa	43(2)	100(4)	25(2)	-14(2)	-5(1)	-13(2)
F5Aa	48(2)	74(3)	62(2)	28(2)	-21(2)	-36(2)
F6Aa	30(2)	74(2)	61(2)	4(2)	-9(1)	10(2)
F4Bb	46(5)	74(5)	47(5)	35(4)	-16(3)	-13(4)
F5Bb	75(8)	36(4)	87(7)	19(4)	-43(5)	-28(4)
F6Bb	36(4)	130(9)	88(7)	-40(6)	6(4)	-4(5)
C(1)	26(1)	20(1)	21(1)	0(1)	5(1)	-1(1)
C(2)	24(1)	25(1)	24(1)	-3(1)	5(1)	-4(1)
C(3)	32(1)	26(1)	25(1)	-1(1)	10(1)	-6(1)
C(4)	35(1)	29(1)	21(1)	2(1)	4(1)	-3(1)
C(5)	27(1)	27(1)	25(1)	1(1)	1(1)	-2(1)
C(6)	25(1)	24(1)	25(1)	1(1)	6(1)	-4(1)
C(7)	45(1)	39(1)	28(1)	-3(1)	14(1)	-16(1)
C(8)	33(1)	45(1)	30(1)	5(1)	-2(1)	-7(1)
C(9)	20(1)	21(1)	22(1)	2(1)	4(1)	-1(1)
C(10)	24(1)	19(1)	20(1)	3(1)	0(1)	-4(1)
C(11)	25(1)	25(1)	24(1)	2(1)	7(1)	-2(1)
C(12)	23(1)	22(1)	25(1)	-1(1)	4(1)	1(1)
C(13)	20(1)	19(1)	27(1)	3(1)	2(1)	-1(1)
C(14)	28(1)	23(1)	28(1)	4(1)	10(1)	0(1)

C(15)	29(1)	20(1)	25(1)	1(1)	7(1)	0(1)
C(16)	23(1)	18(1)	34(1)	3(1)	4(1)	1(1)
C(17)	33(1)	20(1)	37(1)	2(1)	13(1)	-3(1)
C(18)	32(1)	24(1)	38(1)	-2(1)	12(1)	-7(1)
C(19)	24(1)	20(1)	29(1)	-1(1)	7(1)	0(1)
C(20)	25(1)	42(1)	44(1)	0(1)	-2(1)	1(1)
O(1)	33(1)	66(1)	29(1)	4(1)	-1(1)	-1(1)
C(21)	30(1)	33(1)	27(1)	-2(1)	4(1)	5(1)
C(22)	34(1)	29(1)	34(1)	3(1)	3(1)	-1(1)
C(23)	59(2)	48(1)	36(1)	14(1)	-8(1)	-25(1)
C(24)	95(2)	75(2)	40(1)	25(1)	-15(1)	-46(2)
C(25)	87(2)	63(2)	52(2)	27(1)	-1(1)	-34(2)
C(26)	51(1)	34(1)	61(2)	6(1)	9(1)	-14(1)
C(27)	34(1)	31(1)	43(1)	-5(1)	4(1)	-2(1)
C(28)	33(1)	34(1)	26(1)	3(1)	4(1)	3(1)
C(29)	39(1)	34(1)	28(1)	2(1)	10(1)	10(1)
C(30)	55(1)	32(1)	36(1)	2(1)	21(1)	5(1)
C(31)	47(1)	59(2)	40(1)	4(1)	11(1)	-15(1)
C(32)	32(1)	94(2)	70(2)	43(2)	-4(1)	-7(1)
C(33)	33(1)	66(2)	66(2)	39(1)	-1(1)	1(1)
P(1)	43(1)	24(1)	54(1)	8(1)	24(1)	1(1)
F7Aa	101(5)	76(3)	47(2)	28(2)	3(3)	-14(3)
F8Aa	48(2)	31(2)	61(2)	21(2)	22(2)	13(1)
F9Aa	141(4)	83(3)	108(3)	0(2)	73(3)	20(3)
F10Aa	31(2)	42(2)	157(4)	36(2)	20(2)	-2(1)
F11Aa	88(3)	31(1)	63(2)	21(1)	47(2)	28(2)
F12Aa	82(2)	79(2)	96(3)	16(2)	-24(2)	-42(2)
F7Bb	87(4)	37(2)	64(3)	20(2)	41(3)	15(2)
F8Bb	123(5)	35(2)	114(4)	27(3)	83(3)	15(3)
F9Bb	24(1)	44(2)	50(2)	14(1)	14(1)	9(1)
F10Bb	133(3)	55(2)	61(2)	-18(2)	-2(2)	7(2)
F11Bb	87(3)	96(3)	128(3)	22(2)	63(2)	44(2)
F12Bb	81(2)	74(2)	89(2)	-17(2)	-24(2)	2(2)

Table 24. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **6**.

	x	y	z	U(eq)
H(1N)	2080(30)	7330(30)	1810(13)	40
H(2N)	510(30)	6250(30)	241(14)	37
H(2)	-98	5221	2542	30
H(4)	2820	5301	4520	34
H(6)	3966	7214	2883	30
H(11)	197	8794	1354	29
H(12)	963	10985	1255	29
H(14)	3074	9826	-313	31
H(15)	2428	7625	-178	30
H(16A)	2449	12188	-131	30
H(16B)	1856	12613	576	30
H(17)	4382	14372	629	35
H(18)	6985	14222	1365	37
H(19)	4878	10664	1220	29
H(20A)	8556	12389	1988	58
H(20B)	8067	10988	1560	58
H(20C)	7543	11344	2294	58
H(20D)	7555	10759	1906	58
H(20E)	8044	12159	2334	58
H(20F)	8568	11803	1601	58
H(23)	3126	950	4435	61
H(24)	2770	-140	5441	91
H(25)	974	-1867	5299	84
H(26)	-568	-2464	4156	59
H(27)	-241	-1377	3146	45
H(29)	1837	2791	2400	40
H(30)	3918	4155	2362	47
H(31)	6323	3607	2950	59
H(32)	6661	1636	3525	80
H(33)	4575	281	3585	67

Table 25. Torsion angles [°] for **6**.

C(9)-N(1)-C(1)-C(2)	-38.3(3)
C(9)-N(1)-C(1)-C(6)	144.57(19)
C(6)-C(1)-C(2)-C(3)	-3.2(3)
N(1)-C(1)-C(2)-C(3)	179.77(17)
C(1)-C(2)-C(3)-C(4)	2.6(3)
C(1)-C(2)-C(3)-C(7)	-177.99(18)
C(2)-C(3)-C(4)-C(5)	-0.3(3)
C(7)-C(3)-C(4)-C(5)	-179.71(19)
C(3)-C(4)-C(5)-C(6)	-1.4(3)
C(3)-C(4)-C(5)-C(8)	-178.78(19)
C(4)-C(5)-C(6)-C(1)	0.8(3)
C(8)-C(5)-C(6)-C(1)	178.14(18)
C(2)-C(1)-C(6)-C(5)	1.6(3)
N(1)-C(1)-C(6)-C(5)	178.80(17)
C(4)-C(3)-C(7)-F3Bb	16.5(8)
C(2)-C(3)-C(7)-F3Bb	-163.0(7)
C(4)-C(3)-C(7)-F2Aa	112.0(4)
C(2)-C(3)-C(7)-F2Aa	-67.5(4)
C(4)-C(3)-C(7)-F1Bb	-114.4(8)
C(2)-C(3)-C(7)-F1Bb	66.1(8)
C(4)-C(3)-C(7)-F1Aa	-128.8(4)
C(2)-C(3)-C(7)-F1Aa	51.8(5)
C(4)-C(3)-C(7)-F2Bb	130.4(8)
C(2)-C(3)-C(7)-F2Bb	-49.1(8)
C(4)-C(3)-C(7)-F3Aa	-11.0(5)
C(2)-C(3)-C(7)-F3Aa	169.5(4)
C(6)-C(5)-C(8)-F4Bb	168.5(7)
C(4)-C(5)-C(8)-F4Bb	-14.1(7)
C(6)-C(5)-C(8)-F6Bb	-68.6(8)
C(4)-C(5)-C(8)-F6Bb	108.8(8)
C(6)-C(5)-C(8)-F5Bb	48.8(8)
C(4)-C(5)-C(8)-F5Bb	-133.8(8)
C(6)-C(5)-C(8)-F5Aa	29.3(5)

C(4)-C(5)-C(8)-F5Aa	-153.3(4)
C(6)-C(5)-C(8)-F4Aa	153.4(4)
C(4)-C(5)-C(8)-F4Aa	-29.2(4)
C(6)-C(5)-C(8)-F6Aa	-89.6(4)
C(4)-C(5)-C(8)-F6Aa	87.8(4)
C(10)-N(2)-C(9)-N(1)	-5.8(3)
C(10)-N(2)-C(9)-S(1)	176.06(15)
C(1)-N(1)-C(9)-N(2)	178.72(18)
C(1)-N(1)-C(9)-S(1)	-3.3(3)
C(9)-N(2)-C(10)-C(11)	-50.0(3)
C(9)-N(2)-C(10)-C(15)	132.47(19)
C(15)-C(10)-C(11)-C(12)	-1.3(3)
N(2)-C(10)-C(11)-C(12)	-178.70(16)
C(10)-C(11)-C(12)-C(13)	1.9(3)
C(11)-C(12)-C(13)-C(14)	-0.7(3)
C(11)-C(12)-C(13)-C(16)	179.26(16)
C(12)-C(13)-C(14)-C(15)	-1.1(3)
C(16)-C(13)-C(14)-C(15)	178.93(16)
C(13)-C(14)-C(15)-C(10)	1.7(3)
C(11)-C(10)-C(15)-C(14)	-0.5(3)
N(2)-C(10)-C(15)-C(14)	177.02(16)
C(19)-N(3)-C(16)-C(13)	2.6(3)
C(17)-N(3)-C(16)-C(13)	-178.35(16)
C(14)-C(13)-C(16)-N(3)	-80.8(2)
C(12)-C(13)-C(16)-N(3)	99.32(19)
C(19)-N(3)-C(17)-C(18)	0.3(2)
C(16)-N(3)-C(17)-C(18)	-178.84(16)
N(3)-C(17)-C(18)-N(4)	0.3(2)
C(19)-N(4)-C(18)-C(17)	-0.8(2)
C(20)-N(4)-C(18)-C(17)	178.49(19)
C(17)-N(3)-C(19)-N(4)	-0.8(2)
C(16)-N(3)-C(19)-N(4)	178.33(16)
C(18)-N(4)-C(19)-N(3)	1.0(2)
C(20)-N(4)-C(19)-N(3)	-178.28(17)
O(1)-C(21)-C(22)-C(23)	-156.4(2)
C(28)-C(21)-C(22)-C(23)	22.0(3)

O(1)-C(21)-C(22)-C(27)	19.0(3)
C(28)-C(21)-C(22)-C(27)	-162.60(19)
C(27)-C(22)-C(23)-C(24)	0.8(4)
C(21)-C(22)-C(23)-C(24)	176.1(3)
C(22)-C(23)-C(24)-C(25)	0.5(6)
C(23)-C(24)-C(25)-C(26)	-1.5(6)
C(24)-C(25)-C(26)-C(27)	1.2(5)
C(25)-C(26)-C(27)-C(22)	0.1(4)
C(23)-C(22)-C(27)-C(26)	-1.1(4)
C(21)-C(22)-C(27)-C(26)	-176.6(2)
O(1)-C(21)-C(28)-C(33)	-144.8(3)
C(22)-C(21)-C(28)-C(33)	36.8(3)
O(1)-C(21)-C(28)-C(29)	33.2(3)
C(22)-C(21)-C(28)-C(29)	-145.22(19)
C(33)-C(28)-C(29)-C(30)	-2.8(3)
C(21)-C(28)-C(29)-C(30)	179.09(18)
C(28)-C(29)-C(30)-C(31)	0.8(3)
C(29)-C(30)-C(31)-C(32)	1.8(4)
C(30)-C(31)-C(32)-C(33)	-2.5(5)
C(29)-C(28)-C(33)-C(32)	2.2(4)
C(21)-C(28)-C(33)-C(32)	-179.8(3)
C(31)-C(32)-C(33)-C(28)	0.4(5)

Symmetry transformations used to generate equivalent atoms:

Table 26. Hydrogen bonds for **6** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...F9Bb	0.82(3)	2.45(3)	3.143(3)	142(2)
N(1)-H(1N)...C(10)	0.82(3)	2.39(3)	2.800(2)	112(2)
N(1)-H(1N)...C(11)	0.82(3)	2.47(3)	2.983(2)	121(2)
N(2)-H(2N)...S(1)#1	0.83(3)	2.64(3)	3.4359(16)	163(2)