Strong and Confined Acids in Asymmetric Catalysis

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Abstract

This work focuses on the conceptual development of highly confined, super acidic Brønsted acids and their application in asymmetric catalysis. A new synthetic strategy to access imidodiphosphate-derived Brønsted acids based on a toolbox principle has been developed. This methodology proceeds *via* consecutive chloride substitutions of hexachlorobisphosphazonium salts, providing rapid access to privileged catalyst motifs, such as imidodiphosphates (**IDP**), iminoimidodiphosphates (***i*IDP**), and imidodiphosphorimidates (**IDPi**). Furthermore, this approach enables access to previously elusive catalyst scaffolds with particularly high structural confinement, allowing the highly enantioselective transformation of small and structurally unbiased substrates, as exemplarily demonstrated in the asymmetric sulfoxidation of propyl methyl sulfide. To access extremely acidic catalyst motifs, a new synthesis of arylbis(trifluoromethylsulfonylimino)sulfonamides has been developed, which upon implementation into the imidodiphosphate-framework led to the development of imidodiphosphorbis(iminosulfonylimino)imidates (**IDPii**). Combinatorial spectroscopic and experimental data reveal higher acidities of the novel **IDPii** motif than commonly employed super acids, such as trifluoromethanesulfonic acid or bis(trifluoromethanesulfonyl)imide. Most notably, **IDPiis** allow rendering alcohols into strong electrophilic alkylating reagents under silylium activation, as it has been exemplarily demonstrated in the α-methylation of silyl ketene acetals – transforming methanol into a strong electrophilic methyl surrogate. Although the **IDPii** catalyst class displays extreme reactivity and overcomes previous limitations regarding substrate activation, no sufficient enantioinduction was observed in the explored asymmetric transformations. Crystallographic analyses of several **IDPii** catalysts motifs illustrated insufficient BINOL-induced structural confinement. Considered as a solution, a monovalent chiral catalyst scaffold has been conceptually designed, which in combination with the new access of bis(trifluoromethylsulfonylimino)sulfonyl units was believed to give access to a novel extremely Brønsted acidic *and* highly selective catalyst class. This catalyst design focuses on the tetrahydroindacene motif with two adjacent appendages to confine the active site. Herein, a seminal contribution toward the conceptual design, the synthesis and potential application of this unprecedented catalyst scaffold is disclosed.

Kurzzusammenfassung

Der Fokus dieser Arbeit liegt in der konzeptionellen Entwicklung von supersauren, strukturell eingeschränkten Brønsted-Säuren und dessen Anwendung in der asymmetrischen Katalyse. Eine neue Methode, basierend auf dem Baukastenprinzip, wurde für den synthetischen Zugang zu Imidodiphosphat-abgeleiteten Brønsted Säuren entwickelt. Diese Strategie basiert auf einer selektiven und konsekutiven Chloridsubstitution von Hexachlorobisphosphazoniumsalzen und bietet einen schnellen Zugang zu privilegierten Katalysatormotiven, wie beispielsweise Imidodiphosphaten (**IDP**), Iminoimidodiphosphaten (***i*IDP**) und Imidodiphosphorimidaten (**IDPi**). Darüber hinaus ermöglicht dieser Ansatz den Zugang zu bisher schwer zugänglichen Katalysatoren mit besonders hoher struktureller Einschränkung des aktiven Zentrums. Diese Katalysatoren ermöglichen die hochgradig enantioselektive Umwandlung kleiner und strukturell unbefangener Substrate, wie es beispielhaft in der asymmetrischen Sulfoxidation von Propylmethylsulfid demonstriert wurde. Um einen neuen Zugang zu extrem sauren Katalysatormotiven zu erhalten wurde eine neue Synthese von Arylbis(trifluormethylsulfonyl-imino)sulfonamiden entwickelt. Diese fungierten als stark elektronziehende Substituenten und führten, nach Implementierung in das Imidodiphosphat-Gerüst, zur Entwicklung von Imidodiphosphorbis(iminosulfonylimino)imidaten (**IDPii**). Spektroskopische und experimentelle Daten belegen, dass das neuartige **IDPii** Motiv eine höhere Acidität aufweist als die üblicherweise verwendeten Supersäuren, wie beispielsweise Trifluormethansulfonsäure oder Bis(trifluormethansulfonyl)imid. Die hohe Acidität der neuen **IDPii**-Katalysatorklasse ermöglichte, unter Silyliumaktivierung, die Umwandlung von Alkoholen in stark elektrophile Alkylierungsreagenzien. Dies wurde beispielhaft in der α-Methylierung von Silylketenacetalen illustriert, wobei Methanol in ein hochgradig elektrophiles Methylsurrogat umgewandelt wurde. Obwohl die **IDPii**-Katalysatorklasse eine extrem hohe Reaktivität aufweist und frühere Limitierungen hinsichtlich der Substrataktivierung überwindet, wurde bei den untersuchten asymmetrischen Transformationen keine ausreichende Enantioinduktion beobachtet. Kristallographische Analysen mehrerer **IDPii**-Katalysatormotive zeigten eine unzureichende BINOL-induzierte strukturelle Eingrenzung des aktiven Zentrums. Um diese Limitierung zu umgehen, wurde ein monovalentes chirales Katalysatorgerüst konzipiert, das in Kombination mit dem neuen Zugang zu der Bis(trifluormethylsulfonylimino)sulfonyleinheit den Zugang zu einer neuen extrem Brønsted-sauren *und* hochgradig selektiven Katalysatorklasse ermöglichen sollte. Dieses Katalysatordesign basiert auf einem Tetrahydroindacengerüst mit zwei, zum aktiven Zentrum benachbarten benzylischen Substituenten, die das aktive Zentrum umzäunen

sollen. In dieser Arbeit wird das konzeptionelle Design, die Synthese, sowie die potentielle Anwendung dieses neuartigen Katalysatorgerüsts beschrieben.

List of Abbreviations

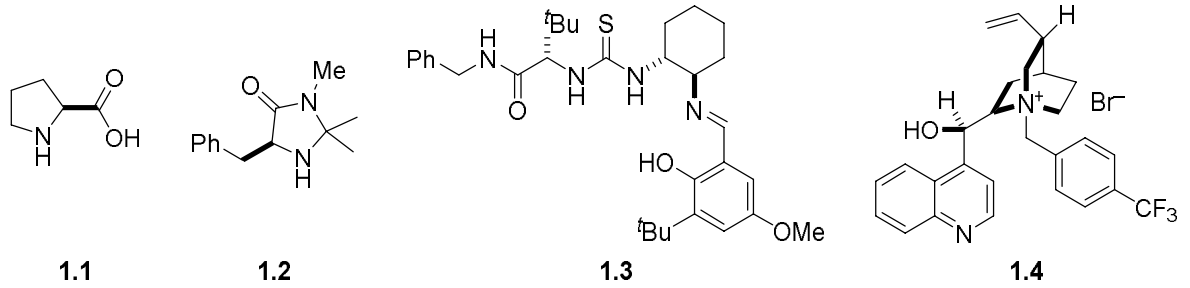
1,2-DCE	1,2-dichloroethan
4-DMAP	4-Dimethylaminopyridine
BINOL	1,1´-Bi-2-naphthol
d.r.	diastereomeric ratio
e.r.	enantiomeric ratio
EI	electron impact
equiv.	equivalents
ESI	electrospray ionization
Et	ethyl
FCC	flash column chromatography
GC	gaschromatography
h	hours
h.v.	high vacuum
HMDS	hexamethyldisilazene
IDP	Imidodiphosphate
IDPi	Imidodiphosphorimidate
IDPii	Imidodiphosphorbis(iminosulfonylimino)imidate
*i*IDP	iminoimidodiphosphate
LDA	lithium diisopropylamide
m/*z*	atomic mass units per change
Me	methyl
min	minutes
NMR	nuclear magnetic resonance spectroscopy
Ph	phenyl

Pr	propyl
r.t.	room temperature
rac	racemic
Tf	triflyl

1 Introduction

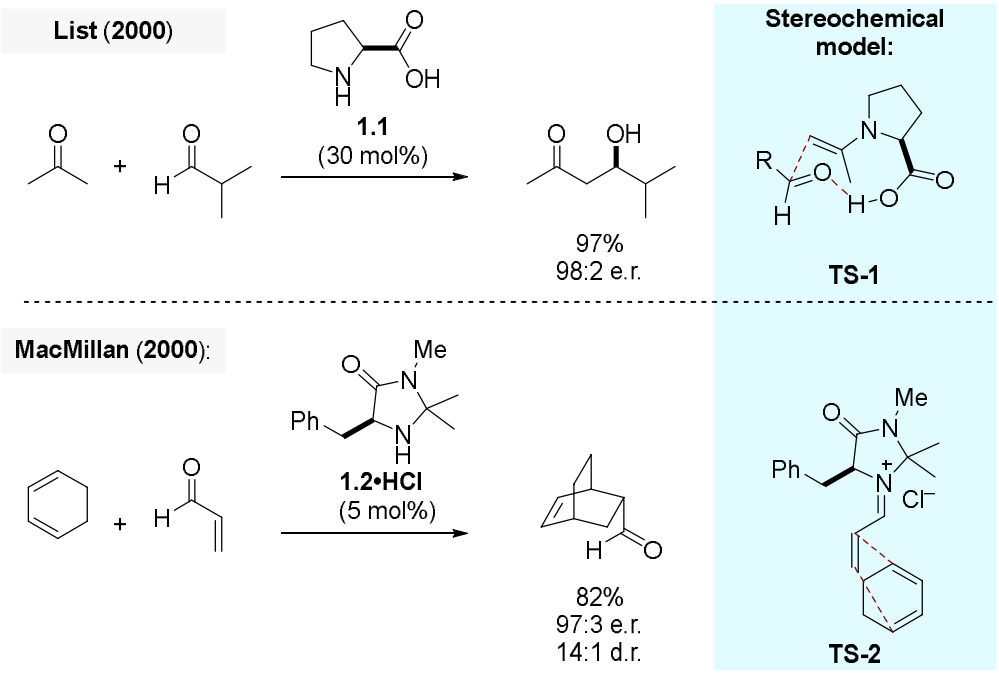
Catalysis - the acceleration of chemical reactions by lowering the required activation energy without the catalyst being consumed during the reaction progress - sounds like a chemical terminology but actually is no less than a fundamental principle of life. For instance, photocatalytic CO_2 fixation converts solar energy into biomass, which in return represents the ultimate energetic foundation for life on earth. Besides the biological perspective, our modern civilization highly depends on technological advancements of our chemical industry, in which the vast majority of chemical processes proceed in the presence of *metal*, *enzyme* or *acid* / *base* catalysis. It is hard to imagine how our modern way of life would look like without catalytic processes, such as the conversion of nitrogen gas into ammonia, representing the feedstock for our modern agriculture supply, without catalytic processes to provide plastic materials, which we encounter in our daily life, or without hydrocarbon cracking, providing our energy and raw material supply. Likewise, these industrial processes require not only a significant amount of our worlds energy production, but considerably account for mankinds greenhouse gas emission. The development of ever more efficient catalytic systems to save energy and reduce waste displays a major on-going scientific research area. Considering aspects such as global warming and dwindling resources a cheap, *catalytic* and industrializable CO_2-fixation with re-utilization as feedstock in our chemical industry would most definitely represent a milestone discovery of the 21th century, which yet needs to be disclosed.

In the context of chemical synthesis, chemists have taken inspiration from nature, in which catalytic biochemical processes *selectively* convert natural building blocks into highly complex molecules and has provided the inspirational foundation for chemists in regard to the development of *selective* catalytic biomimetic total syntheses of complex molecules. These strategies were profoundly dominated by *enzyme* or *metal* catalysis, however, chemists do not only learn from nature, but also start to challenge it. A relatively new field in asymmetric catalysis, namely *organocatalysis*, demonstrates how small and readily available organic molecules may act as catalysts, allowing the highly selective conversion of simple and unbiased substrates into complex molecular frameworks with enzymatic precision, but without the requirement of an entire biopolymeric protein, as nature has taught us to perform selective catalysis.



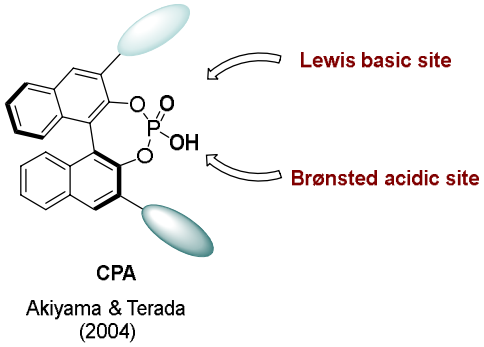
Scheme 1: Early examples of small molecule organocatalysts

In this context, asymmetric milestone transformations, such as the proline (**1.1**) catalyzed intramolecular aldol reaction,[1] the asymmetric Strecker reaction in the presence of thiourea-Schiff base (**1.3**),[2] or the utilization of quinine-derived **(1.4)** ammonium salts as chiral phase-transfer-catalysts (PTC) have been reported (Scheme 1).[3] List and MacMillan identified the utilization of proline (**1.1**) or imidazolidinone (**1.2**), respectively, as readily available and, most notably, highly general catalyst motifs, allowing the activation of carbonyls *via* enamine or iminium ion catalysis (Scheme 2).[4-5] Since then numerous highly selective transformations based on these carbonyl activation strategies have been developed, and thus enriched the repertoire of efficient asymmetric bond-forming reactions. Consequently, the field of *organocatalysis* has established itself and evolved as the third pillar in selective asymmetric catalysis, complementing *metal* and *enzyme* catalysis.[6]



Scheme 2: The proline-catalyzed intermolecular Aldol reaction and the imidazolidinone-catalyzed asymmetric Diels–Alder reaction.

Proline catalysis combines the synergistic activation of carbonyls *via* enamine catalysis with selective acidic activation of the electrophile (Scheme 2. **TS-1**). This bifunctional activation mode, but the requirement of even stronger acids to initiate the transformation of inherently less Lewis basic substrates has inspired future developments. In this regard, Terada and Akiyama independently designed inherently more acidic chiral phosphoric acids (**CPA**)[1] to simultaneously evoke the activation of electrophiles in combination with selective binding of a nucleophile *via* hydrogen-bond interaction (Scheme 3).[7-9]

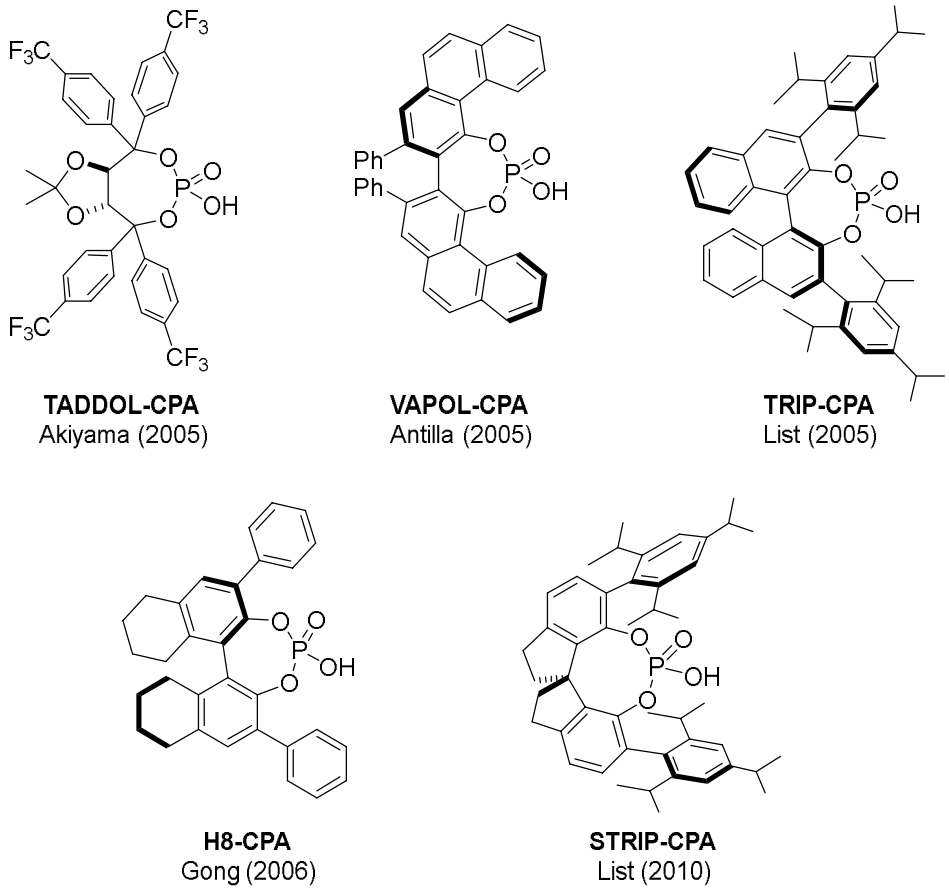


Scheme 3: BINOL-derived phosphoric acids merge a Brønsted acidic and a Lewis basic moiety.

In particular chiral BINOL-derived phosphoric acids (**CPA**) have attracted significant scientific interest due to the general activation mode of a broad variety of substrates,[10] and have enriched the arsenal of efficient asymmetric transformations.[11] Advantageously, enantioenriched BINOLs are readily accessible in both enantiomeric forms, enabling the accessibility of enantioenriched products in both enantiomeric forms. The atropisomers are configurationally stable under standard reaction conditions and the 3,3´-modification with various aryl substituents allow the design of structurally distinct cavities. This partial enclosement of the active center induces the stereofacial bias, dictating the enantioselective transformation.[12] In theory, these attributes represent the ideal platform to design tunable but rigid catalyst motifs to control the vast majority of structurally distinct substrates.[13] Several chiral and non-racemic phosphoric acids, as exemplarily shown in Scheme 4, beyond the BINOL platform, such as e.g. TADDOL-, VAPOL-, H_8-BINOL, SPINOL-, derived backbones have been developed.[14-18] Nevertheless, a single and privileged catalyst structure, which ideally enables the enantioselective transformation of a broad range of substrates, without the necessity of

[1] Ishihara and co-workers revealed that the catalytically active species in Terada´s work was the **CPA** calcium salt, which was isolated after the purification process and not, as initially proposed, the Brønsted acidic phosphoric acid.

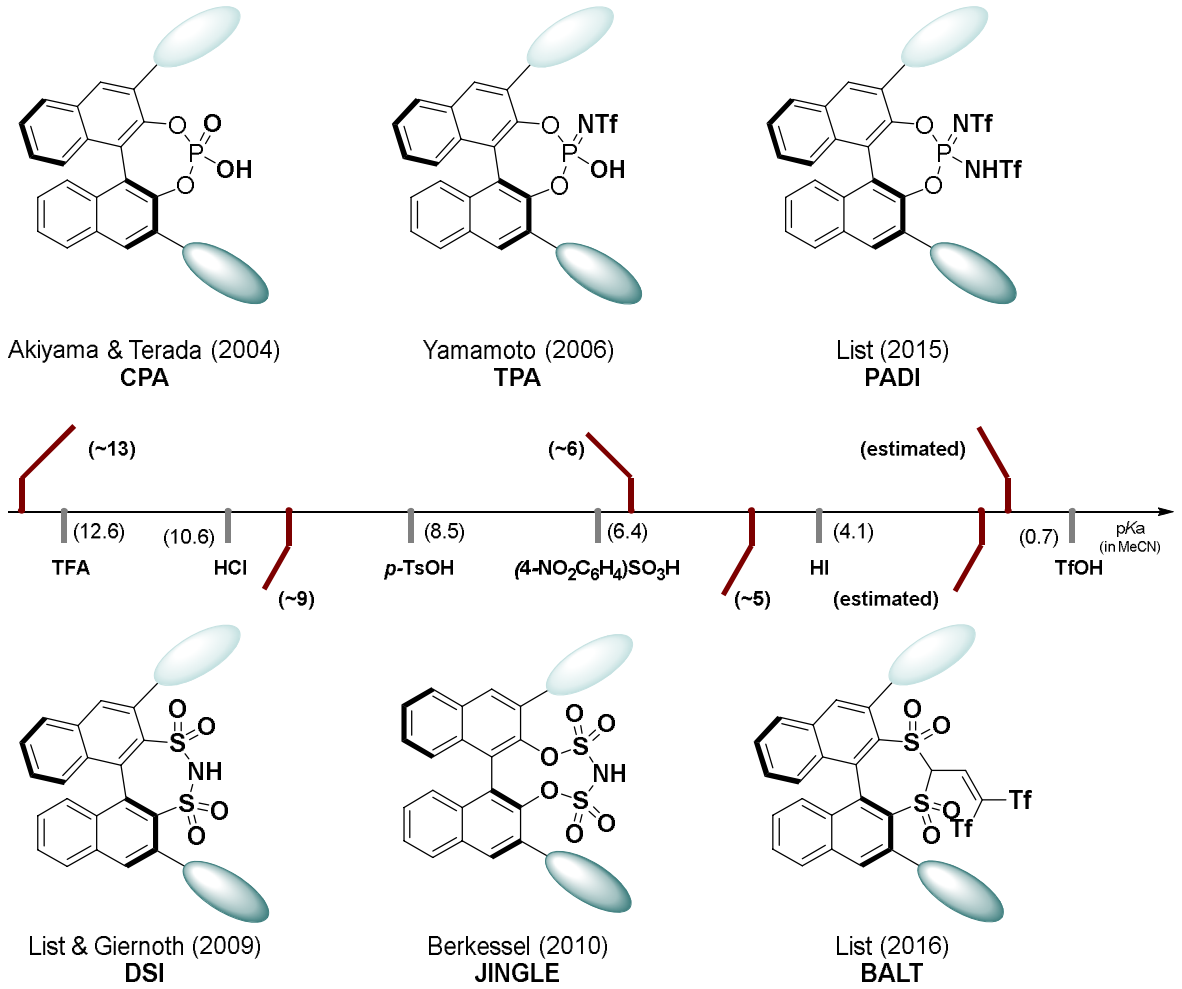
synthesizing a catalyst scaffold for each individual substrate class would be clearly more appealing. In this regard, **TRIP-CPA** has proven to represent a privileged phosphoric acid catalyst and has been widely employed for various enantioselective transformations (Scheme 4).[19]



*Scheme 4: Selected examples of **CPA** catalysts.*

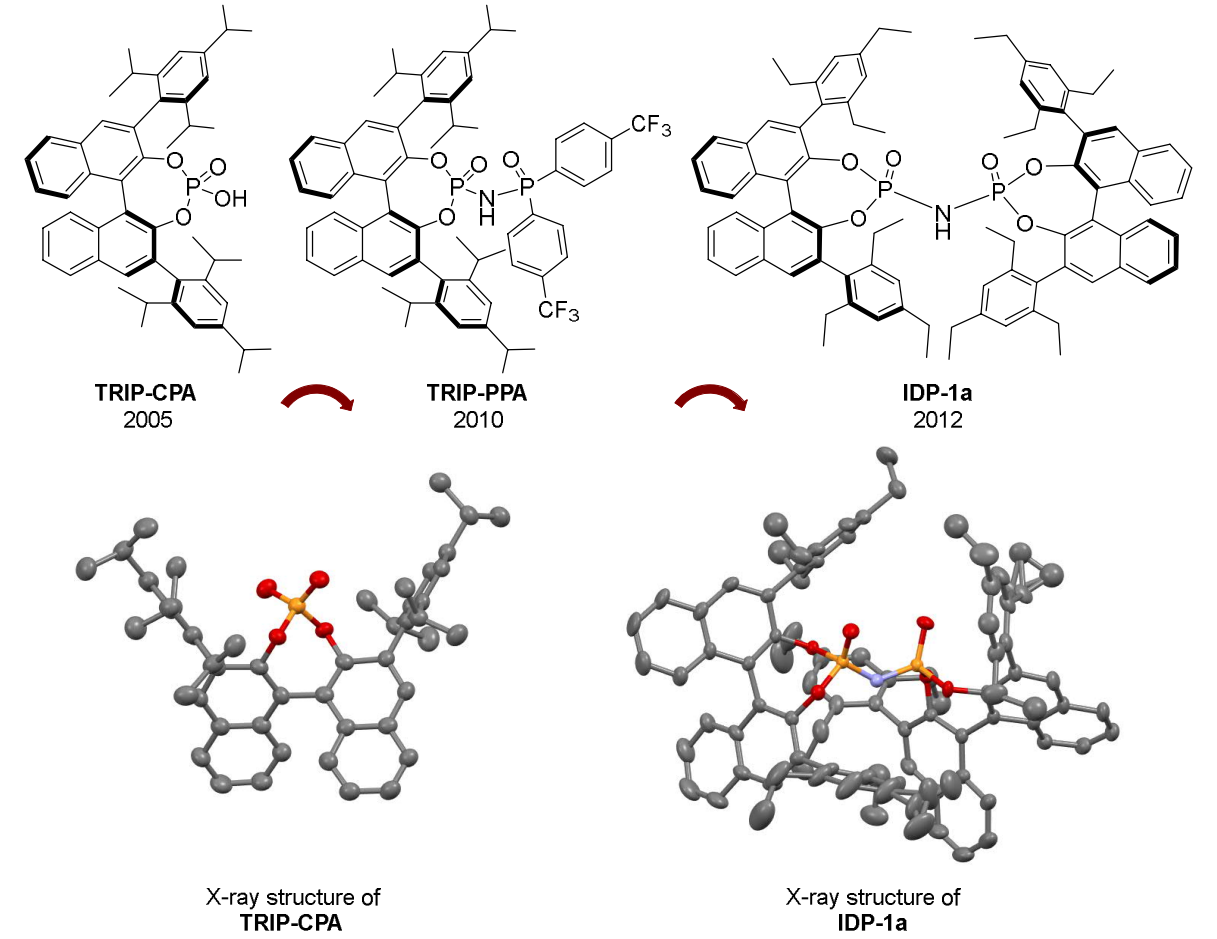
Unfortunately, due to the moderate *acidity* of **CPAs**, their application is limited to relatively Lewis basic substrates, such as imines and certain carbonyl compounds. To overcome this limitation, Yamamoto developed new **CPA**-derived catalysts, in which the replacement of a Lewis basic oxygen (P=**O**) atom with a more electron-withdrawing group (EWG), trifluoromethanesulfonamide ($TfNH_2$), afforded *N*-trilflyl-phosphoramides **TPA** (P=**NTf**).[20] The application of **TPA** has been demonstrated in the previously unprecedented activation of α,β-unsaturated ketones in the context of asymmetric Diels–Alder reactions. To circumvent further reactivity barriers, substantial effort has been devoted to develop ever more acidic catalyst classes.[21-22] New motifs, such as those shown in Scheme 5 have conceptually been designed and cover a broad pK_a range, allowing the activation of the vast majority of distinct

and weakly Lewis basic substrates. In this regard, List *et al.* generalized the underlying principle of asymmetric Brønsted acid catalysis, in which protons resemble the activating mode while chiral, enantiopure anions enable enantiodifferentiation, toward *asymmetric counteranion directed catalysis* (ACDC), which includes all types of cationic activation strategies.[23]



Scheme 5: Development of highly acidic BINOL-derived Brønsted acids.

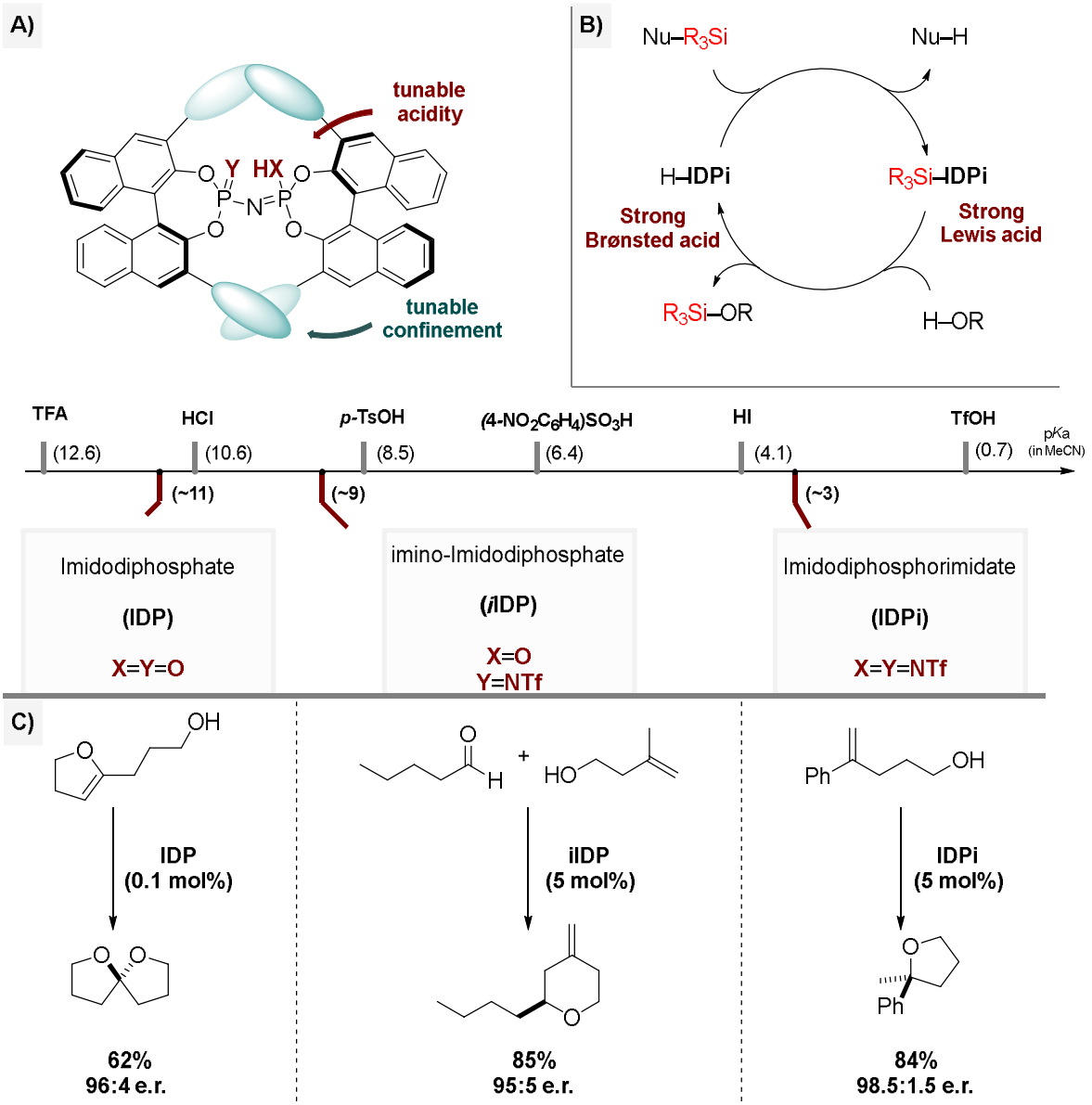
However, due to the installment of additional electron-withdrawing substituents into the catalyst scaffold, the structural size of the active center increases in correlation with the number of electron-withdrawing substituents.[24-25] Consequently, the BINOL-derived microenvironment, resembling the key requisite of stereoinduction from the chiral counteranion, does not efficiently restrain the enlarged active center, and therefore results in a diminished overall stereofacial bias during the reaction progress within the ACDC framework.



*Scheme 6: Development of structurally confined Brønsted acids in the List group. X-ray structures of **TRIP-CPA** and **IDP-1a** are shown. Hydrogen atoms are omitted for clarity, oxygen atoms (red), phosphorus atoms (orange), nitrogen atoms (blue) and carbon atoms (grey).CCDC for **TRIP-CPA** = 777645; CCDC for **IDP-1a** = 864762*

A seminal solution to this problem was realized by the List group in 2010 by replacing a Lewis basic P=O unit of the **CPA** scaffold, with another phosphinyl amide unit to afford *N*-phosphinyl-*N*-phosphoramides (**PPA**).[26] This strategy inspired the dimeric C_2-symmetric imidodiphosphate (**IDP**) scaffold, by replacement of both aryl substituents of **PPA** with another BINOL unit.[27] A constitutional analysis of the X-ray crystal structures of **TRIP-CPA** and **IDP-1a** illustrates the increase of structural enclosement (*confinement)* of the active center (Scheme 6). The active center of **TRIP-CPA** remains partially exposed, whereas the four 3,3´-substituents on the binaphthyl backbone of the **IDP** scaffold provide a well-defined and very tight microenvironment. This confinement effect has enabled the previously unprecedented, long sought-after highly stereoselective conversion of small and structurally unbiased substrates. For example, Nagorny and co-workers described the **TRIP-CPA**-catalyzed spiroketalization of relatively large substrates,[28] whereas the application of highly confined **IDP-1a** allowed the application of small and rather unbiased substrates.[27] Consequently, the

IDP scaffold emerged as a highly privileged catalyst motif within the ACDC framework and led to the realization of several highly stereoselective transformations – resembling enzymatic substrate recognition.[27, 29-48]



*Scheme 7: A) Imidodiphosphate catalysts covers a broad range of pK_a-values. B) The deprotosilylation of **IDPi** to afford highly Lewis acidic catalysts. C) Selected examples of enantioselective transformation for each catalyst motif.*

Although **IDPs** (pK_a ~ 11 in MeCN) are significantly stronger acids than chiral phosphoric acids (**CPAs,** ~13 in MeCN), their acidity is still moderate, limiting once again their applicability to relatively Lewis basic substrates, as experienced in the past with **CPAs**. Inspired by previous developments regarding the establishment of more acidic catalyst scaffolds, the Lewis basic

oxygen atoms (P=**O**) of the imidodiphosphate scaffold have been subsequently replaced by more electron-withdrawing trifluoromethanesulfonamide units (Yagupolskii principle).[49-50]

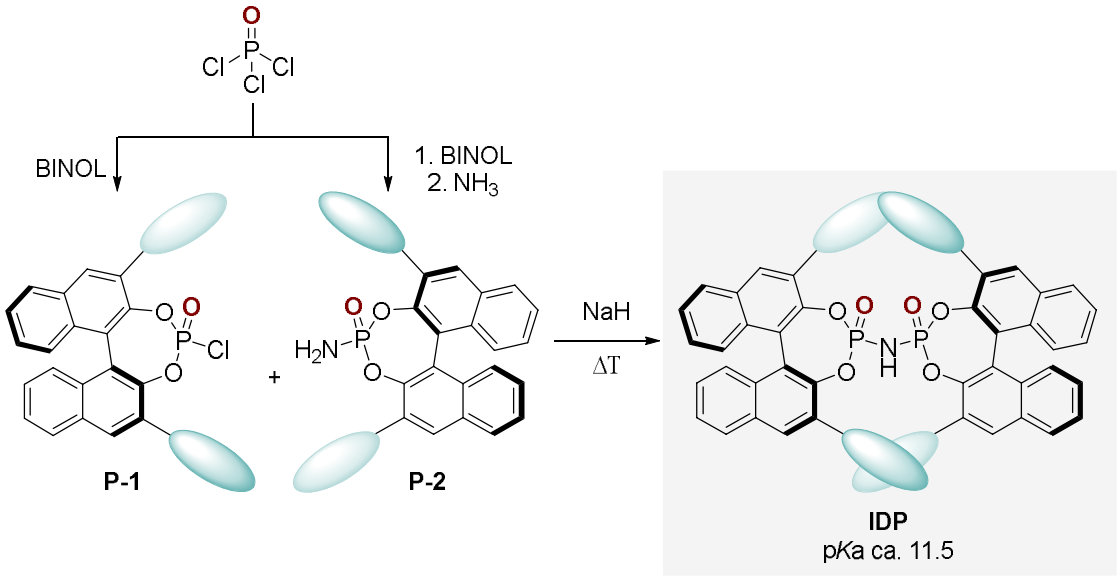
This replacement led to the discovery of iminoimidodiphosphorimidates (***i*IDPs)** and imidodiphosphorimidates (**IDPis)**, respectively, comprising moderate to high acidities (pKa up to ~2 in MeCN) in combination with a structurally confined active site.[51-52] Consequently, imidodiphosphate-derived catalysts evolved as a highly privileged Brønsted acid framework in the context of asymmetric catalysis due to their modular and tunable *confinement* and *acidity* and emanated as an indispensable tool for challenging transformations.[53] Additionally, the high acidity of **IDPis** opened new avenues in silylium Lewis acid catalysis and enabled the activation of weakly Lewis basic substrates in the presence of sacrificial silylating agents, such as allyltrimethylsilane or enol silanes (Scheme 7 B).[54-56] Advantageously, the Lewis acidity correlates with the size of the corresponding silylium ion and therefore provides an additional parameter to tune the Lewis acidity. For example, silylium ACDC with *tert*-butyldimethylsilyl-derived nucleophiles (TBS) often displays higher reactivity in comparison to trimethylsilyl-derived pendants (TMS). This effect may be explained with an increase of steric hindrance, which disfavors the formation of a classical adduct (frustrated Lewis pair) of the silylium cation with the corresponding imidodiphosphazenate anion. Furthermore, no strictly inert reaction conditions are required due to the deprotosilylation ("self-healing" cycle) in the presence of the sacrificial silylating reagent – an advantage, which overcomes common limitations of strong Lewis acids due to their extreme moisture sensitivity and which often destructively react with any nucleophilic impurities, such as water or methanol. Therefore, **IDPi** silylium catalysis may be considered as a powerful, highly versatile and user-friendly approach in direct comparison to other established Lewis acid-catalyzed methodologies.

2 Literature Background

2.1 Established Syntheses of Imidodiphosphoryl-Derived Brønsted Acids

2.1.1 Imidodiphosphates (IDP)

The established synthesis toward **IDPs** relies on a dimerization strategy of two monomeric phosphoryl units.[27] Phosphoryl chloride (**P-1**) is rapidly accessible from the reaction of the desired BINOL[2] with phosphoryl chloride ($POCl_3$) in the presence of an organic base, such as pyridine. The addition of gaseous ammonia to **P-1** affords phosphoryl amide (**P-2**). Both monomeric phosphoryl components **P-1** and **P-2** require a purification step to achieve satisfactory yields in the dimerization event. A careful but fast column chromatography for phosphoryl chloride **P-1** is required to prevent undesired hydrolysis. Subsequently the final dimerization event of **P-1** and **P-2** proceeds under basic reaction conditions to yield the desired imidodiphosphate (**IDP**). Reaction times and yields are highly dependent on the structural properties of the 3,3´-BINOL substituents. Thus, a 3-step reaction sequence, which involves three purification procedures and long reaction times within the dimerization event hamper the catalyst library implementation with diverse 3,3´-substituted BINOL modifications.



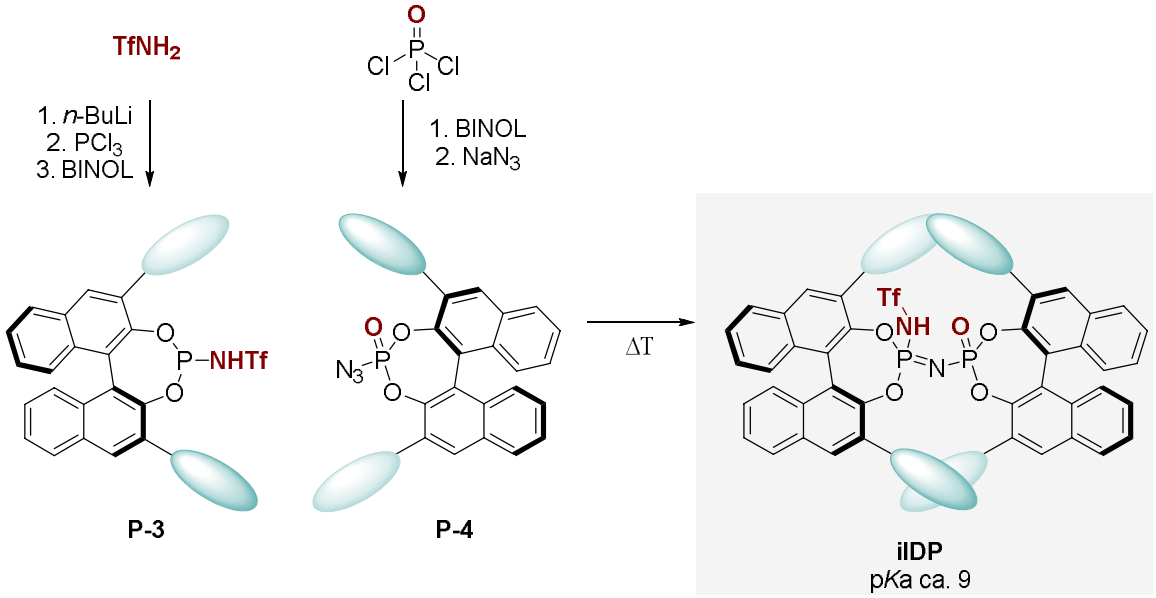
*Scheme 8: Established **IDP** syntheses are based on a dimerization strategy*

[2] Note: The term BINOL installation or utilization of BINOL refers to the application of diverse 3,3´-(aryl)-substituted BINOL derivatives and not solely to the parent 1,1´-Bi-2-naphthol scaffold.

2.1.2 Iminoimidodiphosphates (*i*IDP)

***i*IDP** are synthetically accessible following a 6-step Staudinger approach.[51] This reaction sequence involves the deprotonation of $TfNH_2$ with *n*-BuLi followed by addition of the resulting LiHNTf solution to a second flask containing PCl_3 *via* inert filtration. Subsequently, the BINOL installation event furnishes the *N*-sulfonyl phosphoramidites **P-3**. Meanwhile, another BINOL equivalent needs to be reacted with $POCl_3$ followed by the addition of NaN_3 in the presence of an organic base, to generate phosphoryl azide **P-4**. The solution of freshly prepared phosphoryl azide **P-4** needs to be transferred to a solution of phosphoramidite **P-3** under inert conditions to initiate the Staudinger reaction.

The chemical transformations to afford the phosphoryl azide **P-4** and the phosphoramidite **P-3** are often high yielding steps, but due to the hydrolytic and oxidative sensitivity require careful execution of these experiments. The efficiency of the final Staudinger reaction again highly depends on the steric properties of the utilized BINOLs to achieve high yields.



Scheme 9: Established ***i*IDP** *synthesis via a Staudinger approach.*

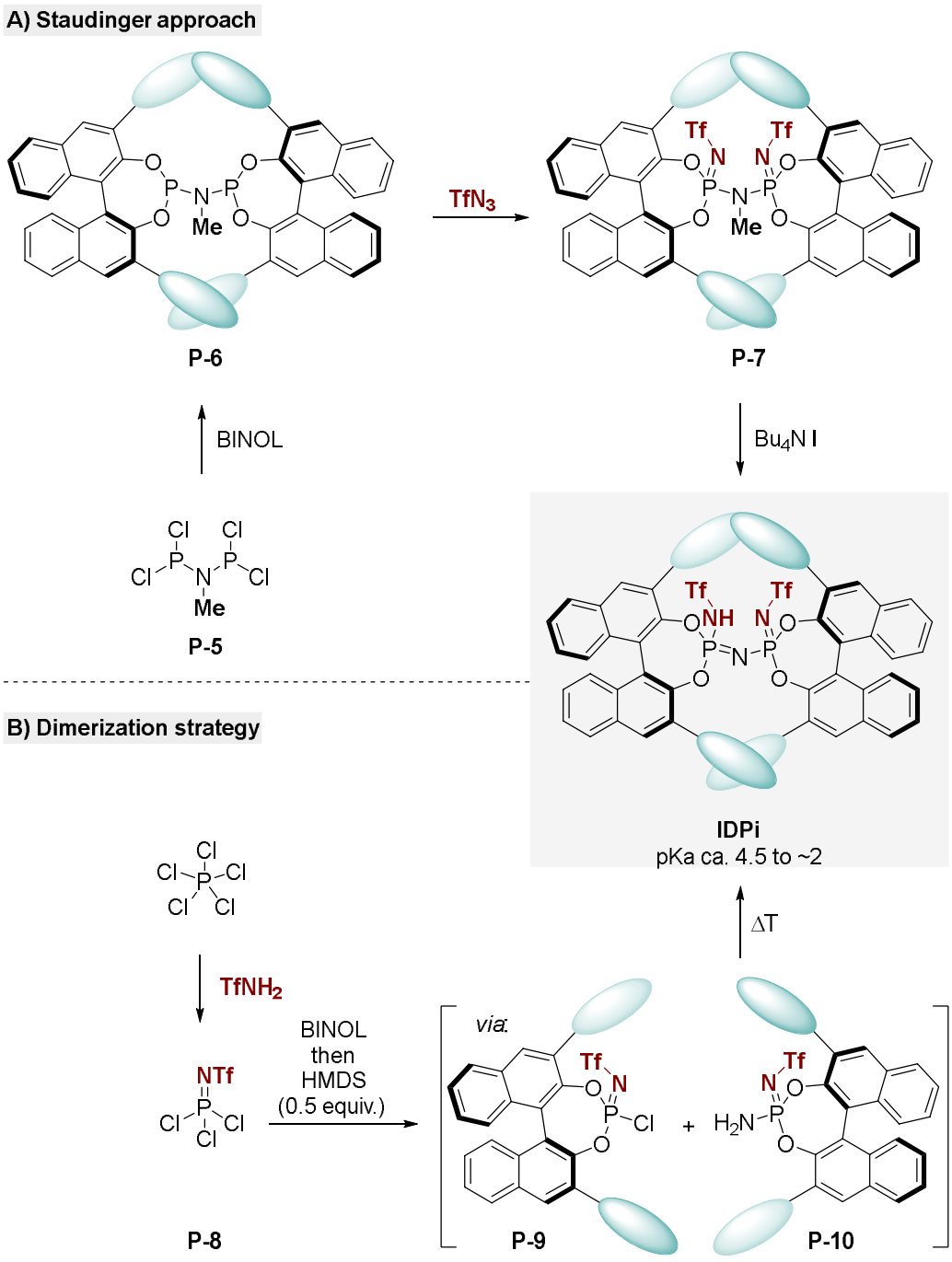
2.1.3 Imidodiphosphorimidates (IDPi)

IDPis were initially prepared based on a Staudinger approach of BINOL-derived *N*-methylbisdiphosphite **P-6** with triflyl azide (TfN_3), followed by demethylation of the pivotal *N*-methyl moiety of **P-7** (Scheme 10 A). Therefore, commercially available bis(dichlorophosphino)-*N*-methylamine **P-5** is first reacted with two equivalents of BINOL under basic reaction conditions, to afford **P-6** which has to be isolated and purified under inert conditions due to oxidative sensitivity. Triflyl azide is rapidly accessible from triflic anhydride or triflyl chloride upon addition of sodium azide but requires extreme caution due to its highly energetic properties and stability issues.[57] The anhydrous transfer of a triflyl azide solution to a pre-cooled solution of **P-7** initiates the desired high yielding Staudinger reaction. The final demethylation of the central *N*-Me unit represents the bottle-neck of this overall sequence due to low yields and undesired side reactions.[58]

The second, more robust and user-friendly route to synthesize **IDPis** relies on a dimerization strategy of two BINOL-derived *N*-sulfonylphosphoryl chlorides **P-9** (Scheme 10 B). In this regard, a new high yielding synthesis of *N*-sulfonylphosphorimidoyl trichloride **P-8** has been developed and provides the ideal building block for this synthetic strategy.[59] **P-8** rapidly reacts with the BINOL to form the *N*-sulfonylphosphoryl chloride **P-9** which smoothly undergoes the chloride to ammonia exchange with ammonia, or HMDS as an ammonia surrogate, to *in situ* generate phosphoryl amide **P-10**. High temperatures favor the dimerization event to afford the desired **IDPi**. The applicability of this strategy has been proven in certain high yielding **IDPi** scaffolds syntheses. Nevertheless, if the dimerization is hampered due to steric reasons, or if the *N*-triflylphosphoryl chloride **P-9** hydrolyzed and generated the corresponding **TPA**, the final purification might be extremely troublesome due to similar polarities of the **IDPi** and the corresponding hydrolysis product *N*-triflyl phosphoramide **TPP**. Additionally, a drawback remains in the *N*-sulfonyl modification, which requires the pre-synthesis of *N*-sulfonylphosphorimidoyl trichloride **P-9** for every core[3] modification. Long reaction times and low yields for some specific **IDPi** motifs hamper the catalyst library implementation and thus impedes the identification of a suitable catalyst scaffold for a specific transformation.

[3] Core modification refers to the replacement of the sulfonyl substituent. Recently, it has been shown that the replacement of commonly employed $TfNH_2$ with other electron-withdrawing groups, such as perfluoroaryl-derived sulfonamides significantly influences the three-dimensional chiral microenvironment. Thus, the modification of 3,3´-substituents from the BINOL residue and the core modification provide tunable parameters to design structurally distinct cavities.

Therefore, a rapid and fast access to **IDPis**, ideally allowing a simple core modification and simplified purification procedures is highly desirable for this highly privileged catalyst class.



*Scheme 10: Synthesis of **IDPis**. A) Synthesis based on a Staudinger approach. B) dimerization strategy*

2.2 Hexachlorobisphosphazonium salts

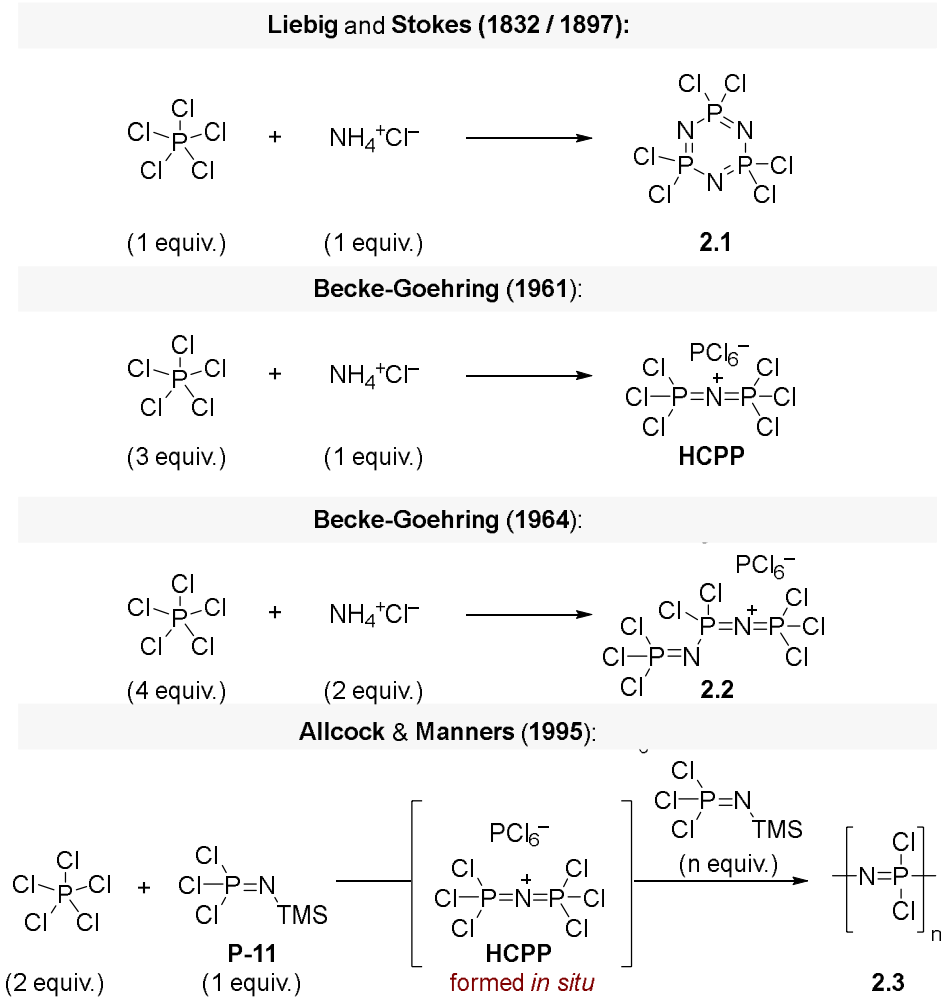
2.2.1 Brief Historical Overview of (poly)Phosphazene Chemistry

Initial reports of the reaction between PCl_5 and ammonia date back to 1832, when Liebig aimed toward the synthesis of phosphoryl amides of the corresponding phosphoric acid.[60] The reaction, however, formed a new, unexpectedly stable compound, which was proposed to consist of the chemical formula $P_3N_3Cl_6$. Notably, the described synthesis was rather low-yielding to afford the described compound after distillation, but apparently was not further investigated. 65 years later, Stokes re-investigated this transformation and assumed that the identified product by Liebig might consist of a cyclic structure of the chemical formula $P_3N_3Cl_6$ and successfully identified a series of cyclic homologues with increasing ring size (Scheme 11).[61] He observed that the obtained product mixture, which consisted of a mixture of cyclic phosphazenes with the general formula of $(NPCl_2)_n$, melted upon heating and then coagulated to form an insoluble "inorganic rubber" material. Allcock and co-workers further investigated this transformation and rationally explained the formation of non-soluble "inorganic rubber" material with the formation of a cross-linked elastomer, resulting from the reaction of $[NPCl_2]_n$ with water. Therefore, performing the same reaction under strictly anhydrous conditions resulted in the formation of soluble and non-cross linked macromolecules consisting of the general formula $[NPCl_2]_n$.[62] These observations have since then attracted significant attention by the chemical community and are considered as the basis for a new era in polymer science.[63] Various poly(organo)phosphazenes with unique structural and physical properties have been synthesized by simple chloride substitution of the $[-N=PCl_2-]$-moiety with suitable nucleophiles. A challenge remained in the synthesis of polyphosphazenes with narrow polydispersity. To overcome this limitation, a collaboration between the Manners and Allcock groups identified phosphoriminoyl ($Cl_3P=NTMS$) as an ideal monomeric building block to access such poly (dichlorophosphazenes). Interestingly, during the polymerization process the formation of hexachlorobisphosphazonium hexachlorophosphate (**HCPP**) was identified as a key intermediate.[64-65]

2.2.2 Hexachlorobisphosphazonium Salts

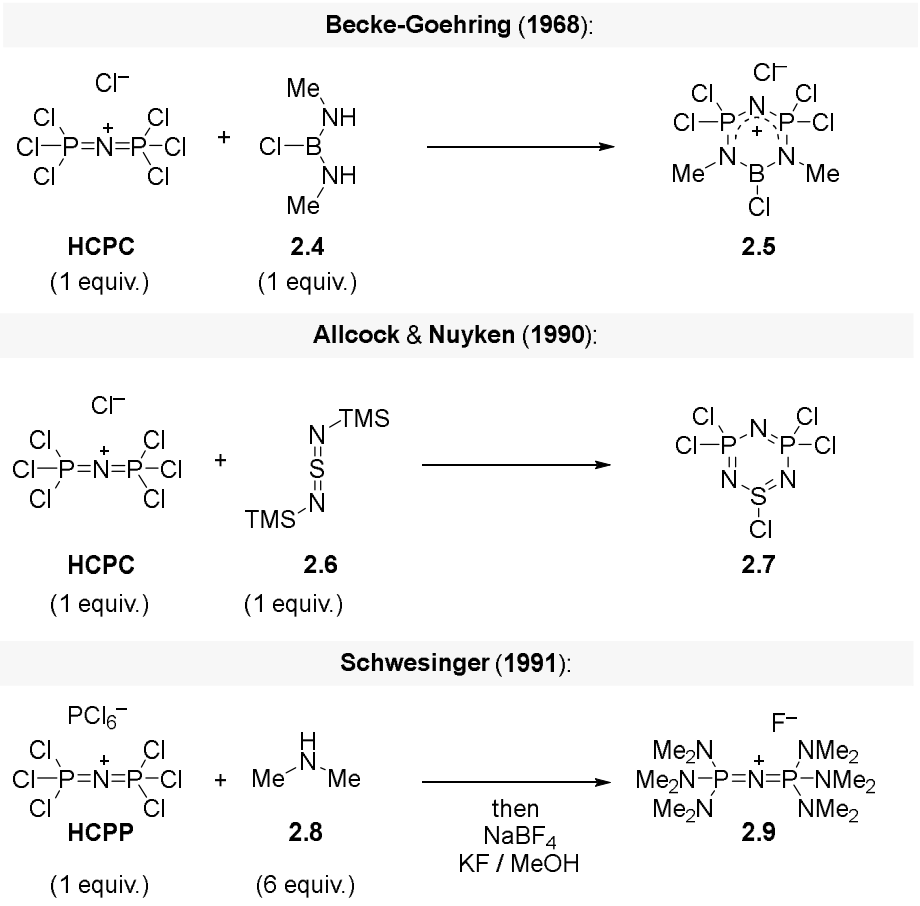
The first synthesis *and* structural identification of hexachlorobisphosphazonium hexachlorophosphate (**HCPP**) was decribed by Becke-Goehring in 1961.[66] Following up on the previous reports by Liebig and Stokes, Becke-Goehring and co-workers systematically investigated the reaction of PCl_5 with stoichiometric and substoichiometric equivalents of NH_4Cl. Under similar reaction conditions to those reported by Liebig and Stokes, a precipitate

formed during the reaction, showing electrical conductivities, thus indicating electrolytic properties due to salt formation. A careful isolation and collaborative NMR spectroscopic investigation with Flucke revealed the formation of an ion pair, which consisted of hexachlorobisphosphazonium hexachlorophosphate (**HCPP**).[67] Moreover, these studies confirmed the formation of **HCPP** as an intermediate in the previously described synthesis of cyclic phosphazenes **2.1** upon reaction with additional NH_4Cl.



Scheme 11: Historical overview of (poly)phosphazenes.

Hexachlorobisphosphazonium salts with various counteranions have been synthesized, with a strong focus toward cationic living polymerization reactions, to afford poly(dichloro)phosphazenes (**2.3**), which have been further functionalized by P-Cl substitution.[68] Only few examples exist in which hexachlorobisphosphazonium salts serve as building blocks to access inorganic heterocycles, such as triazadiphosphaborinane salts **2.5**,[69] thiatriazadiphosphinine **2.7**,[70] or for the synthesis of hexaaminophosphazonium salts **2.9** (Scheme 12).[71-72]



Scheme 12: Applications of hexachlorobisphosphazonium salts as building block.

2.3 The Asymmetric α-Alkylation of Carbonyl Compounds

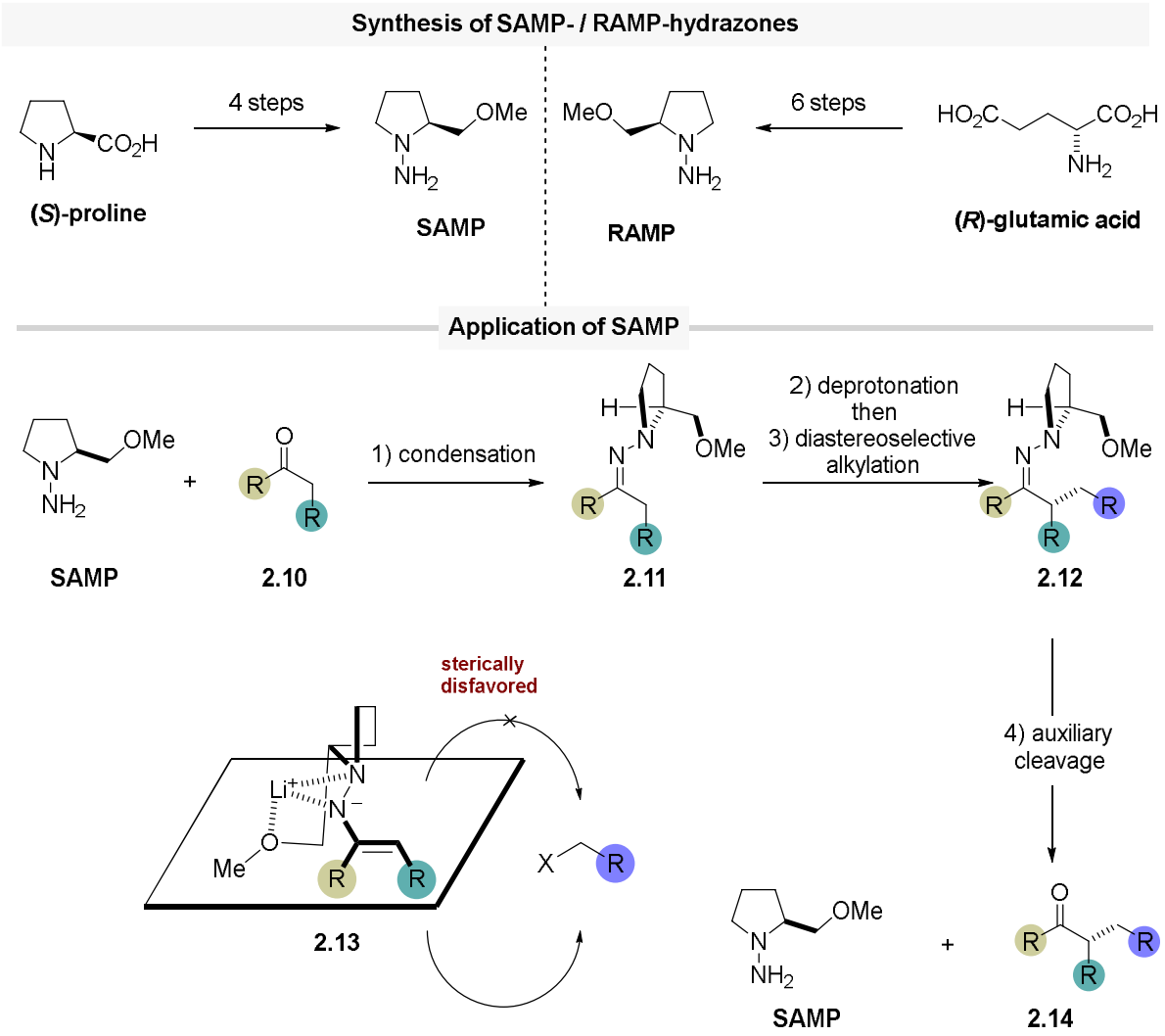
The α-alkylation of carbonyl compounds allows a rapid construction of complex molecules from abundant carbonyl-derived starting materials and alkyl halides or surrogates thereof. Thus, this transformation represents a frequently applied strategy toward the synthesis of natural products, agrochemicals or pharmaceuticals on laboratory but also on technical scale. A standard textbook strategy relies on the activation of carbonyls, for example *via* stoichiometric deprotonation to form enolates, which then rapidly react with electrophilic alkyl halides to deliver the desired α-alkylated product.[73] Despite the great importance, the *direct* enantioselective α-alkylation of carbonyls remains an unsolved challenge. Substantial effort has been devoted to develop novel strategies to overcome these limitations, but yet a *general* strategy needs to be discovered.[74]

The following part focuses on groundbreaking transformations in the field of *i*) auxiliary based strategies and *ii*) catalytic strategies, which over the time have consequently been refined and, moreover, provided the inspiration to develop several more broadly applicable transformations.

2.3.1 Chiral Auxiliary-Based Strategies

Pioneering contribution in the context of diastereoselective α-alkylation strategies arose with the development of 2-methoxymethylpyrrolidine (**SAMP**/**RAMP**) auxiliaries by Enders in 1976. Both hydrazones, now commonly known as Enders reagent,[75] were initially reported in a six-step protocol from abundant and cheap amino acids, such as (*S*)-proline or (*R*)-glutamic acid. A typical reaction procedure for the asymmetric α-alkylation of ketones or aldehydes involves:

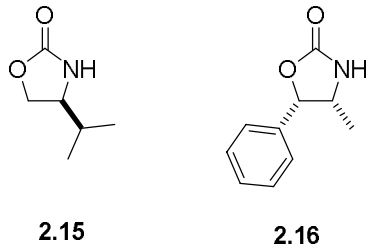
(1) the condensation of e.g. **SAMP** to the carbonyl to form hydrazone **2.11**
(2) formation of azaenolate **2.13** upon deprotonation of hydrazone **2.11**
(3) the diastereoselective alkylation event with alkyl halides to afford **2.12**
(4) and auxiliary cleavage *via* ozonolysis or quaternization with MeI and subsequent hydrolysis under acidic conditions (Scheme 13) to afford the enantioenriched α-alkylated carbonyl compound.[76]



*Scheme 13: Synthesis of **SAMP** / **RAMP**. A general α-alkylation strategy of aldehydes & ketones utilizing **SAMP** auxiliary.*

The applicability of **SAMP**- / **RAMP**-hydrazones has been demonstrated in numerous highly diastereoselective α-alkylation reactions of structurally distinct aldehydes and ketones, and consequently emerged as a common transformation in asymmetric synthesis. Based on this groundbreaking discovery, various C–C and C–heteroatom bond forming reactions have been developed, but also provided the inspiration toward the development of several structurally distinct auxiliaries.[77]

Another class of highly versatile auxiliary (Scheme 14), first described by Evans et. al. in 1981, is based on the oxazolidinone scaffold (**2.15**-**2.16**), and was first applied in the diastereoselective aldol reaction of carboxylic acids,[78] and subsequently found application in the diastereoselective α-alkylation of imido-derived enolates (Scheme 15).[79] Synthetically, these oxazilidonones are readily available in a simple two-step approach, in which enantiopure 1,2-amino alcohols and a suitable carbonate species are condensed, followed by the acylation event to install the desired carbonyl moiety (**2.18**).

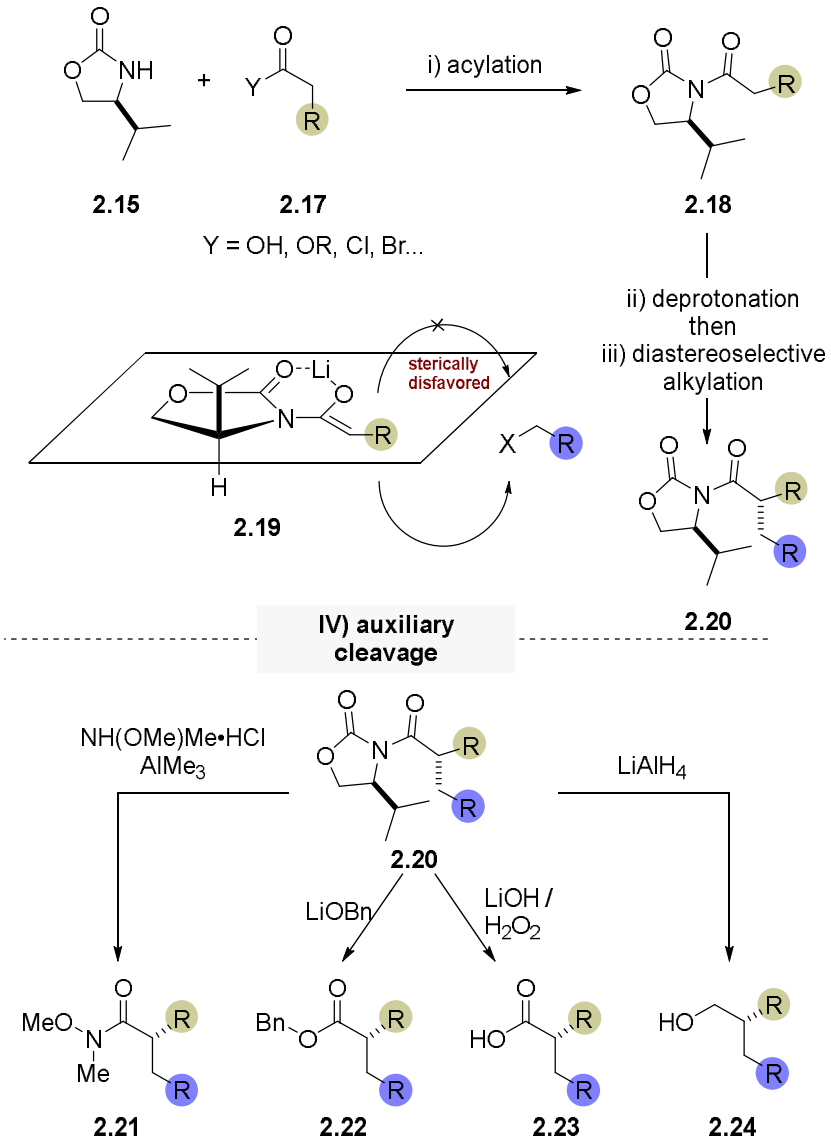


2.15 **2.16**

Scheme 14: First reports of enantiopure oxazilidinones

Upon deprotonation of **2.18**, the geometry of the enolate (*E* vs *Z*) determines the stereochemical outcome of this transformation. Therefore, the utilization of sterically demanding bases, such as LDA, to deprotonate *N*-acyl oxazolidinones represents a useful approach to achieve predominantly *Z*-enolates in high selectivities. Another factor significantly influencing the stereochemical outcome relies in the auxiliary itself. This effect can be rationalized by the bidentate chelation of the Li^+-cation, resulting in the formation of a conformationally constrained form, effectively influencing the facial bias of the electrophilic approach during the C-C-bond forming event (Scheme 15). Most notably, the alkylation step of **2.19** is usually highly diastereoselective and often allows a rapid isolation of a pure diastereoisomer (**2.20**), which, in principle, affords the desired α-alkylated product in enantiopure form upon auxiliary cleavage. Depending on auxiliary cleavage conditions, enantiopure α-alkylated carbonyl products, such as amides (**2.21**), esters (**2.22**), carboxylic acids (**2.23**) as well as alcohols (**2.24**) are readily available, making this strategy highly versatile and truly powerful.[77] The versatility of enenatiopure imidazolidinone- and hydrazone-derived auxiliaries has enormously contributed to the development of efficient asymmetric bond forming reactions. Various chiral auxiliaries have been developed, based on these pioneering contributions and are frequently applied on laboratory but also on technical scale. Furthermore, many of these auxiliaries are commercially available. Although these reaction sequences require a stoichiometric amount of reagents and result in equimolar side product formation, cleaved auxiliaries may easily be

recycled, which, at least in theory, makes this reaction sequence efficient regarding cost / atom economy and sustainability.



Scheme 15: Application of oxazilidinone as chiral auxiliary and selective cleavage.

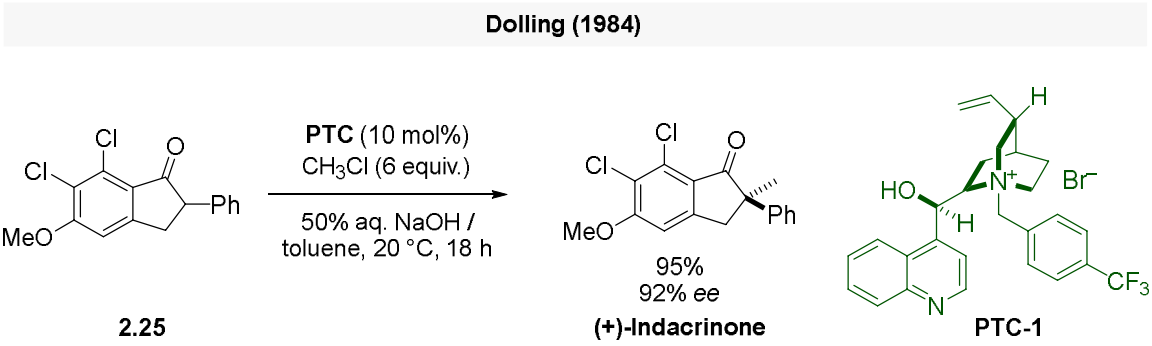
Note: Myers reported the applicability of pseudoephedrine as a chiral auxiliary and is occasionally considered as a more robust alternative in comparison to the Evans auxiliary.[80]

2.3.2. Catalytic Strategies

The development of a catalytic, enantioselective and versatile α-alkylation strategy is often accompanied with inherent challenges, such as:

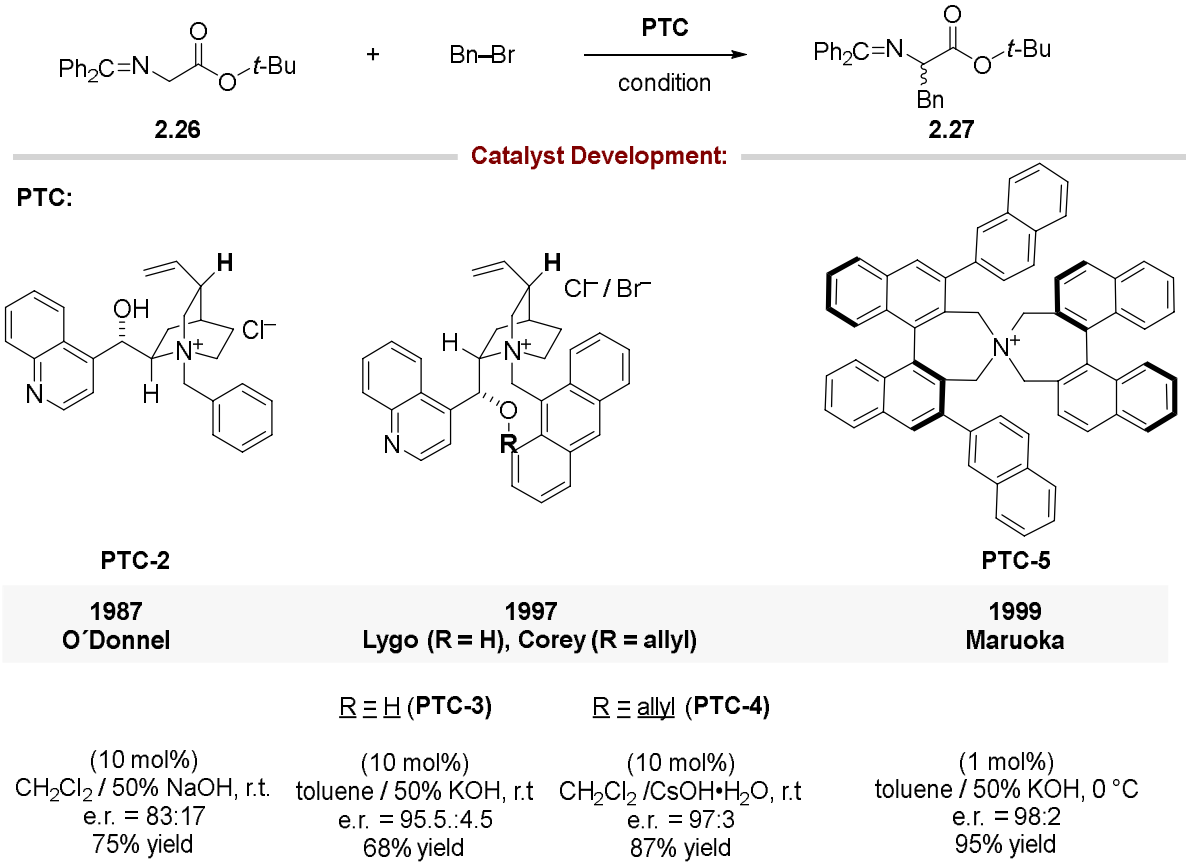
- a potential catalyst alkylation (inhibition) in the presence of strong alkylating reagents,
- the activation of carbonyls on different oxidation levels,
- the overalkylation of the carbonyl,
- the racemization pathway with α-C–H acidic carbonyl compounds.

Nevertheless, a conceptual milestone transformation toward a catalytic α-alkylation strategy has been developed by Dolling and co-workers in the context of asymmetric phase transfer catalysis (PTC). The application of quinine-derived **PTC-1** has been illustrated in the highly enantioselective synthesis of (+)-Indacrinone (Scheme 16).[3] Although this report focuses only on a single substrate, it served as inspiration for the development of several highly efficient α-alkylation strategies of ketones within the **PTC** framework.[81-82]



Scheme 16: Initial report of asymmetric phase-transfer catalysis for the enantioselective α-alkylation.

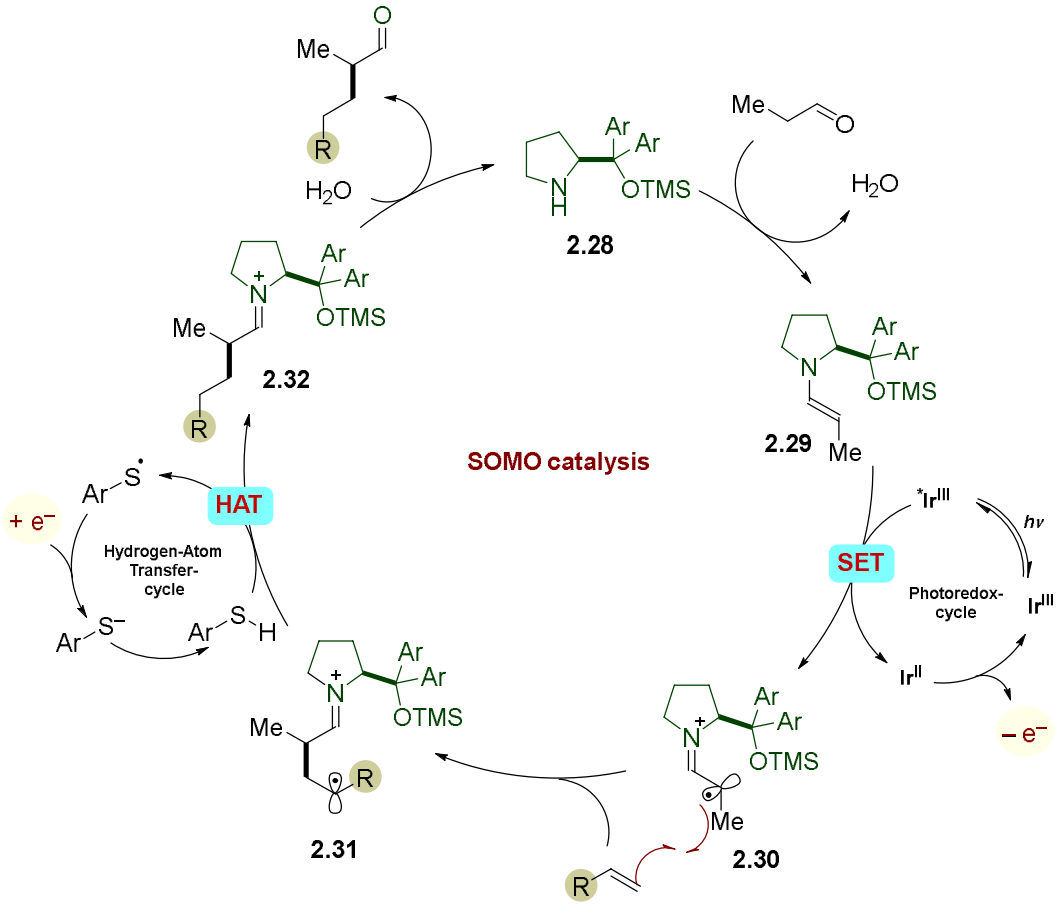
Subsequently, O´Donnel reported the utilization of cinchonine and cinchonidine as phase-transfer catalyst for the enantioselective α-alkylation of glycine Schiff base **2.26** derivatives to afford enantioenriched amino acids.[83] Independently, Lygo and Corey further modified the cinchona alkaloid catalyst scaffold and improved the enantioinduction of the corresponding phase transfer catalyst by introducing an *N*-anthracenylmethyl substituent to afford **PTC-3** and **PTC-4**, respectively (Scheme 17).[84-85] Apart from quinine-derived catalyst scaffolds, Maruoka developed a structurally rigid ammonium salt focusing on an enantiopure 1,1´-bi-2-naphthol scaffold (**PTC-5**), which evolved as a highly active and general **PTC** motif.[86] Its applicability has been demonstrated in several enantioselective C–C and C–heteroatom bond-forming reactions within the concept of phase-transfer catalysis.[87-88]



Scheme 17: Phase-transfer catalyst development for the asymmetric α-benzylation of glycine imine.

A conceptually divergent approach for the asymmetric α-alkylation of ketones has been described by Koga and co-workers in 1994, focusing on the application of chiral, enantioenriched tetraamine ligands, inducing stereoselective bias within the alkylation event of pre-formed enolates.[89] Another commonly employed strategy for the asymmetric α-allylation has been described by Trost focusing on the utility of *in situ* generated η^3-π-allyl palladium complexes, in which enantioenriched phosphine ligands result in the enantiotopic differentiation.[90] Unfortunately, this strategy remains limited to the allylation event. A more general transition-metal-derived α-alkylation strategy has been reported by Jacobsen, utilizing a chiral CrCl(salene) complex as catalyst.[91] This approach allowed the first enantioselective metal-catalyzed application of several alkyl halides with ketone-derived cyclic tin enolates as nucleophilic coupling partner. In this regard, α-alkylations, α-allylations and α-benzylations were achieved, but occasionally delivered the desired product in moderate yield or poor enantioselectivities. Unfortunately, these examples require pre-formed enolates to achieve satisfactory reactivities. Contrarily, the asymmetric α-alkylation via enamine catalysis, reported by List et. al. in 2004, generates a nucleophilic enamine species *in situ*, making this approach, theoretically, more appealing, but unfortunately suffers from inherent reactivity issues.[92-93]

A major development overcoming various limitations regarding reactivity issues, the necessity of pre-formed enolates, or activated alkyl surrogates has been reported by MacMillan and co-workers with the conceptual design of SOMO catalysis. Enamine catalysis in the presence of a single-electron oxidant, such as ceric ammonium nitrate (CAN) or photoredox-catalysis, results in a transient enamine-derived radical cation species (**2.30**) and undergoes C–C-bond forming reactions in the presence of SOMOphiles. This strategy allowed the utilization of various coupling partners, such as allyltrimethylsilane,[94] bromo malonates and derivatives thereof,[95] and to some extend olefins.[96] The concept of SOMO catalysis has profoundly influenced α-alkylation strategies of aldehydes, and has recently been expanded toward ketones as carbonyl partners.[97]



Scheme 18: SOMO catalysis in combination with photoredox and hydrogen-atom transfer catalysis exemplarily illustrated with olefins.

However, the necessity of employing SOMOphiles that efficiently stabilize radical ion pairs limits this methodology regarding suitable alkyl surrogates. For example, the simple α-methylation or α-alkylation with aliphatic and unbranched alkyl-derived reagents will most

likely be extremely challenging due to insufficient stabilization of the corresponding radial ion pairs (Scheme 18).

Nevertheless, the herein illustrated catalytic strategies represent conceptual milestone transformations and consequently led to several advancements in the context of enantioselective α-alkylation of carbonyl compounds. Still, these methods are often limited to certain substrate classes or alkylating reagents. Phase-transfer catalysis, for example, represents a very elegant and straightforward approach, but requires the utilization of relatively α-C–H acidic substrates. Possible racemization pathways due to deprotonation / re-protonation in the presence of stereogenic carbonyl-derived α-C–H units need to be considered. Enamine catalysis remains largely limited to aldehydes as nucleophilc coupling partner, whereas SOMO-catalysis highly depends on the application of suitable SOMOphiles, which efficiently stabilize radical ion pairs to achieve satisfactory yields.

In conclusion, a *direct* and *general* α-alkylation approach in a catalytic and enantioselective fashion for all commonly employed carbonyl compounds, such as aldehydes, ketones or esters with a broad range of tolerated alkyl surrogates remains an on-going challenge in asymmetric catalysis.[74, 98]

2.4 Design of Strong Acids

A general approach to increase the acidity of *neutral* Brønsted acids relies on the installment of electron withdrawing groups into the existing molecular framework. The trifluoromethylsulfonyl group represents one of the strongest and presumably, the most investigated electron-withdrawing unit, due to its inherent stability and non-oxidizing properties. As illustrated in Figure 1 a platform molecule with increasing number of free valencies allows the installment of additional trifluoromethanesulfonyl units and therefore tremendously increases the acidity of the corresponding Brønsted acid.[99]

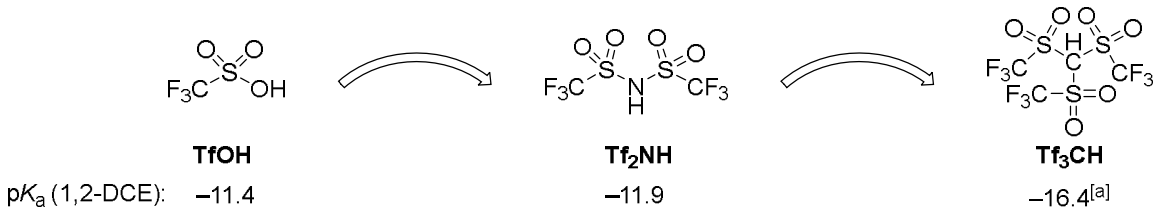


Figure 1: The acidifying-effect of triflyl groups. [a]estimated pKa-value in 1,2-DCE..

However, to further increase the acidity of the structures as shown in Figure 1 electron-withdrawing substituents that exceed the acidifying property of the trifluoromethanesulfonyl unit are required. In this regard, Yagupolskii et al. elaborated a general strategy, in which the acidifying properties of oxygen-containing electron-withdrawing substituents was enhanced by oxygen replacement with *N*-trifluoromethylsulfonyl units (*Yagupolskii principle)*. This replacement led to a significant acidity increase of $CF_3S(\mathbf{O})_2OH$, TfOH (pK_a –11.4 in DCE) to afford $CF_3S(\mathbf{NTf})_2OH$ (**BTISA**), which resembles an extremely strong Brønsted acid with an estimated pK_a of –18 (DCE), thus resulting in an acidity enhancement of ca. 7 pK_a units in comparison to the parent sulfonic acid.

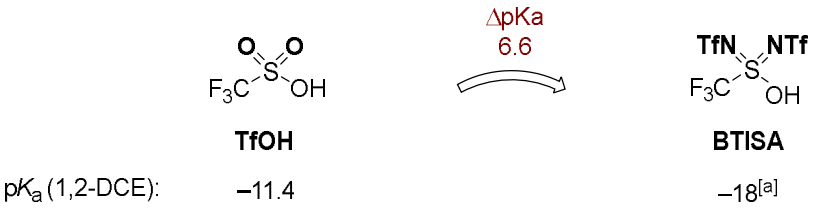


Figure 2: Yagupolskii principle. The acidifying-effect of triflyl groups. [a]estimated pKa-value in 1,2-DCE.

The same acidification principle has been applied to various carboxylic acids and sulfonamides by replacing Lewis basic oxygen-moietys with =NTf units and, at least in theory, represents a general approach to acidify Brønsted acids, bearing oxygen atoms.

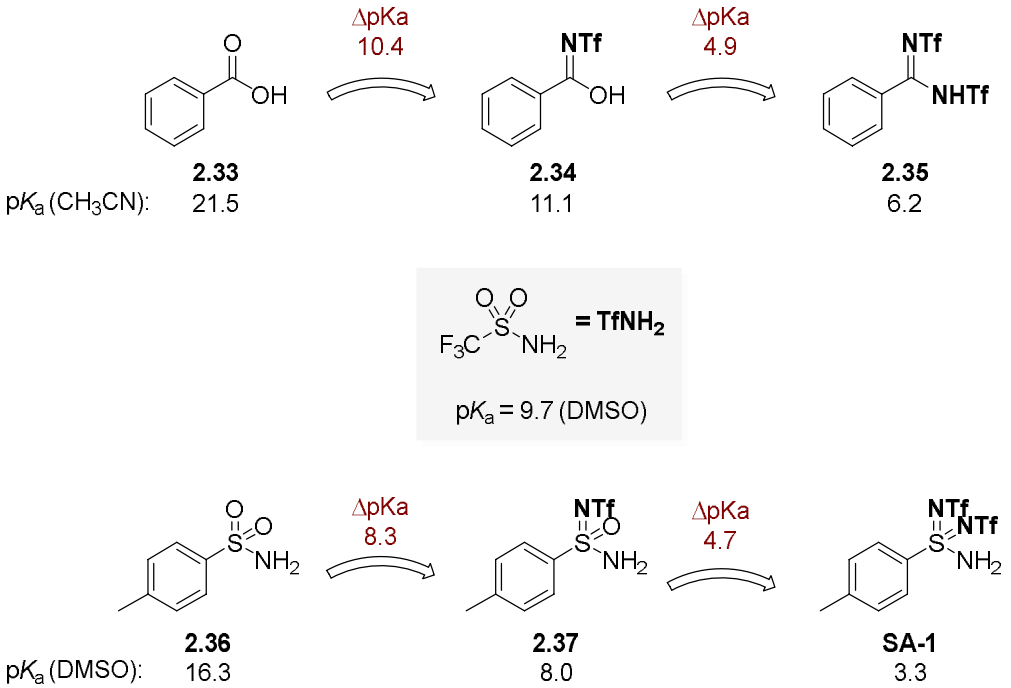


*Figure 3: Yagupolskii principle applied to benzoic acid (**2.33**) and p-toluenesulfonamide (**2.36**).*

As exemplarily shown, the first replacement of Lewis basic =O moieties of benzoic acid **(2.33)** toward **2.34** increases the acidity of *ca.* 10 pK_a units. Subsequent oxygen replacement increases the acidity of ca. 5 pKa units to afford **2.35** and occurs to be more acidic than highly acidic HBr (pKa 6.6).[50, 100] Analogously, the same principle applied to sulfonamides, such as *p*-toluenesulfoneamide (**2.36**), affords bis(trifluoromethylsulfonylimino)sulfonamides **(SA-1)** that exceeds the acidity of $TfNH_2$ by ca. 6 pKa units and, most notably, represents now a stronger acidifying substituent than the parent $TfNH_2$ unit.

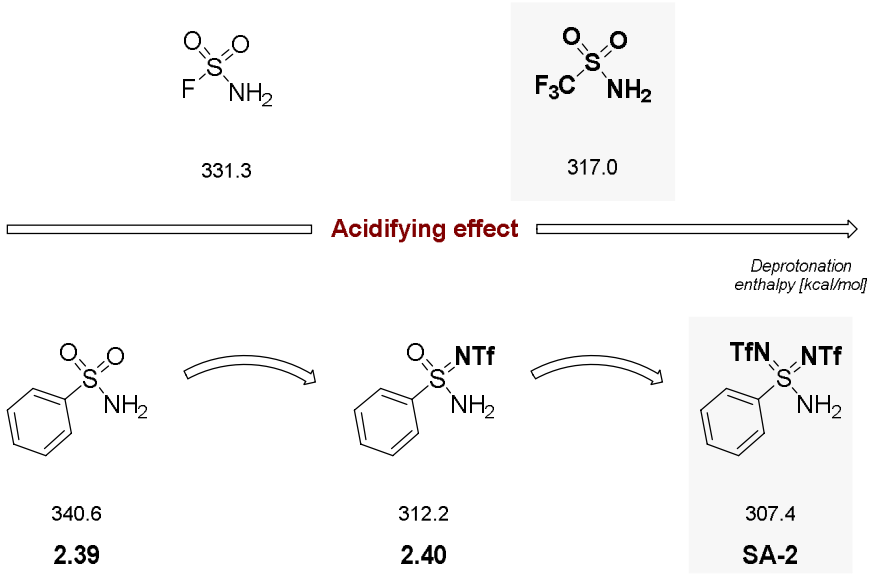
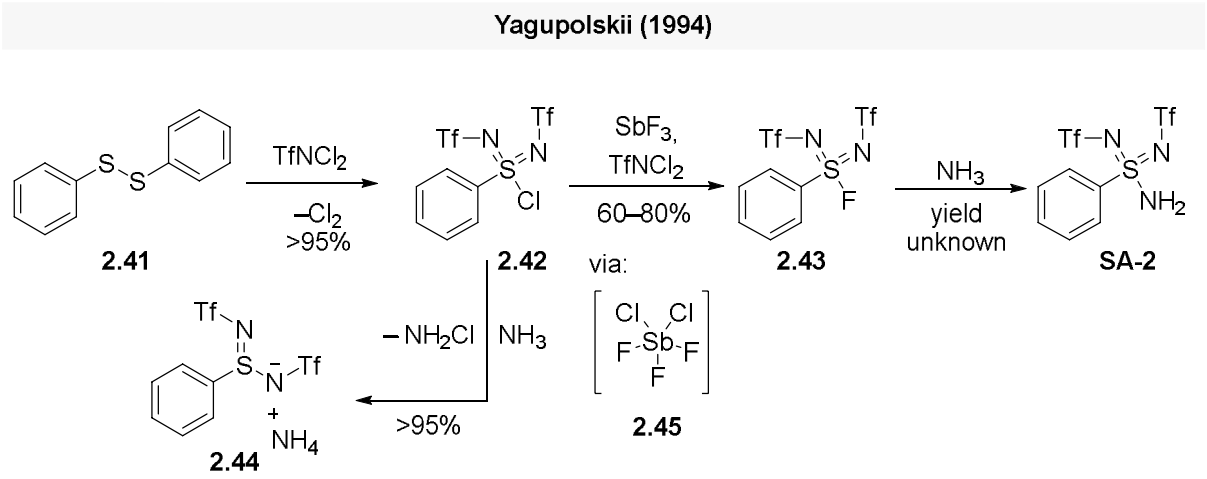


Figure 4: Calculated deprotonation enthalpies of sulfonamides.

Calculated deprotonation enthalpies support this hypothesis in which **SA-2** exceeds the acidification effect of commonly employed $TfNH_2$ by approximately 10 kcal/mol (Figure 4). In return, these new bis(trifluoromethylsulfonylimino)sulfonamides may be re-utilized as new acidifying substituent to replace oxygen units, resulting in even stronger Brønsted acids. Therefore, this principle can theoretically be endlessly executed to prepare ever more acidic Brønsted acids.[101]

From a synthetic perspective, Yagupolskii and co-workers oxidatively installed trifluoromethylsulfonylimino groups utilizing dichlorotrifluoromethanesulfonamide ($TfNCl_2$), which was prepared from trifluoromethanesulfonamide in the presence of chlorine gas under basic aqueous conditions.[4] The reaction of $TfNCl_2$ with phenyl disulfide **2.41** furnished arylbis(trifluoromethanesulfonylimin)sulfonyl chloride (**2.42**). Interestingly, the addition of ammonia to **2.42** did not result in the formation of the desired sulfonamide (S^{VI}) **SA-2**, but served as reductant to afford the corresponding sulfinate (S^{IV}) **2.44**. Therefore, a chloride to fluoride exchange was crucial to access the desired sulfonamide **SA-2** upon addition of ammonia to **2.43** and to prevent any undesired reduction of the sulfonyl moiety. Apparently, the chloride to fluoride exchange only proceeded in the presence of antimony (III) fluoride with additional $TfNCl_2$, whereas commonly employed fluoride salts did not engage in the S–Cl substitution event of **2.42**. Yagupolskii proposed the formation of dichlorotrifluoro antimonate **2.45**, supposedly mediating the desired chloride to fluoride exchange.[102-103]



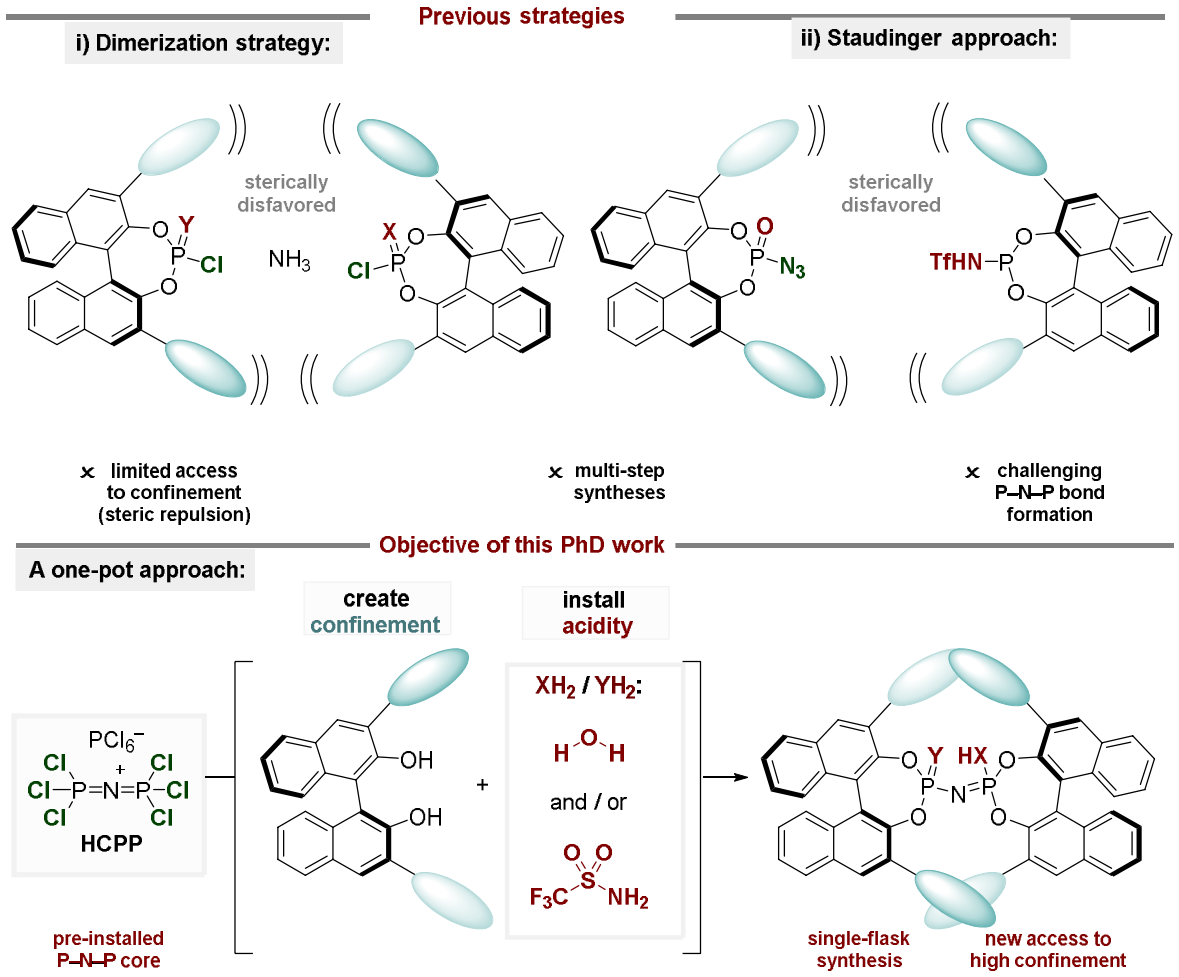
*Scheme 19: Yagupolskii´s synthesis of phenylbis(trifluoromethylsulfonylimino)sulfonamide (**SA-2**)*

[4] Note: $TfNCl_2$ has been reported to spontaneously explode upon distillation at higher temperatures or in the presence of several organic solvents and needs to be handled with extreme caution.

3 Objectives

3.1 A Unified Approach to Imidodiphosphate-Type Brønsted Acids

The synthetic strategies to access imidodiphosphate-derived Brønsted acids are strongly influenced by steric properties of the 3,3´-substituents on the BINOL moieties and occasionally provide unsatisfactory yields, require harsh reaction conditions and/or prolonged reaction times. BINOLs with highly sterically demanding substituents often do not furnish the desired imidodiphosphate motifs due to steric repulsion within the dimerization process. Since we are particularly interested in catalysts possessing extreme confinement in combination with extreme acidities, which we deem a requirement toward controlling very small *and* non-activated substrates in enantioselective processes, we aimed toward a new strategy to address these challenges.



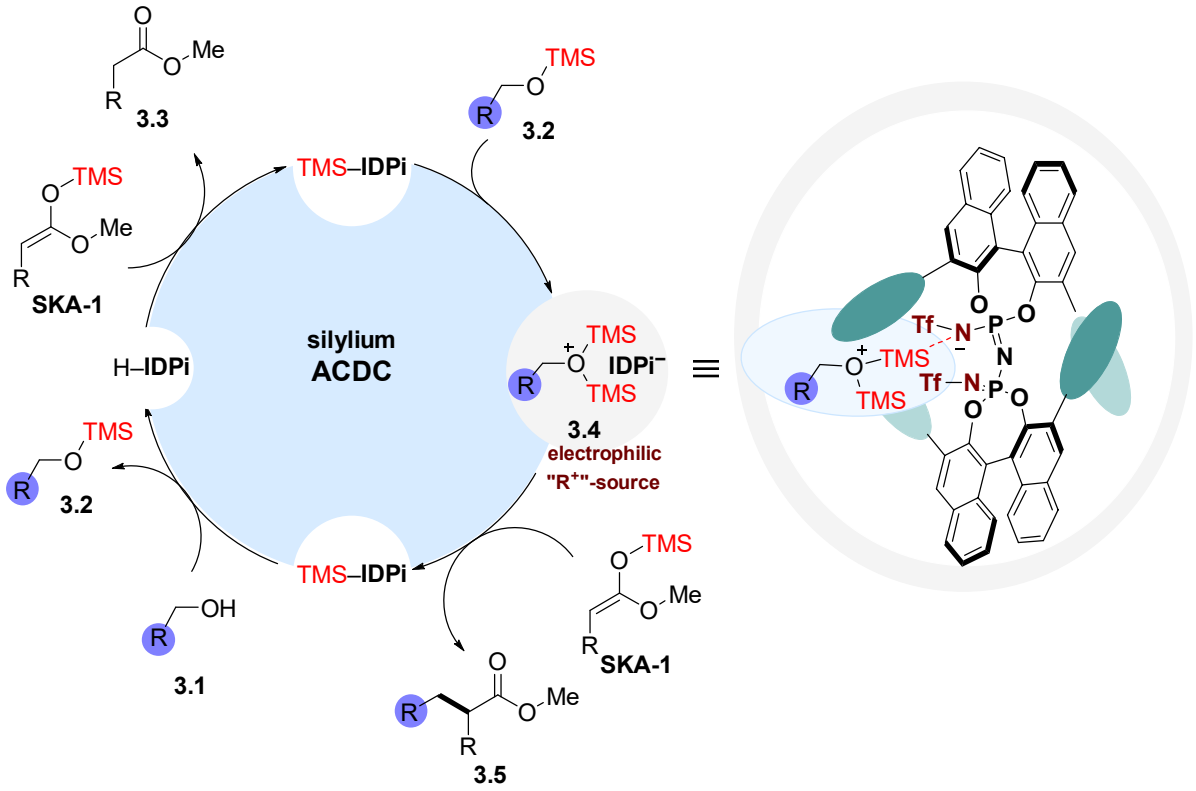
*Scheme 20: Idealized imidodiphosphate-derived Brønsted acid synthesis starting from hexachlorobisphosphazonium hexachlorophosphate (**HCPP**):*

To circumvent the steric repulsion within the dimerization or Staudinger process and to develop a more efficient catalyst synthesis, in which ideally all established catalyst scaffolds are accessible from a common building block, we envisioned hexachlorobisphosphazonium hexachlorophosphate (**HCPP**) as an ideal platform molecule for this purpose. **HCPP** combines a pre-installed P-N-P scaffold, therefore avoiding a dimerization process, and contains six chloride nucleofuges, which due to the high electrophilicity of the bisphosphazonium core were envisioned to react with suitable nucleophiles, such as BINOL and H_2O (or $TfNH_2$).

3.2 Development of a More Acidic Catalyst Motif

The motivation to develop a more acidic Brønsted acid was connected with the development of a catalytic and general strategy for the asymmetric α-alkylation of carbonyl compounds. Typically considered as nucleophiles, alcohols could be rendered electrophilic through silylium-activation to afford a counteranion stabilized bis(trisilyl)alkoxonium ion, which in return was envisioned to represent a strong electrophilic alkylating reagent analogously to Meerwein salts. However, initial studies revealed that the majority of available chiral catalyst motifs did not sufficiently engage in the desired transformation. Therefore, a chiral and more acidic catalyst motif was considered as a necessary condition toward a successful realization of this project.

From a mechanistic perspective, as exemplarily shown with silylated **IDPis**, it was postulated that alcohol (**3.1**) first undergoes the deprotosilylation cycle to generate silyl alkyl ether **3.2**, which in return was envisioned to be Lewis basic enough to react with another equivalent of silylated **IDPi** (Scheme 21**)**.



*Scheme 21: Conceptual design for the asymmetric α-alkylation of silyl-derived nucleophiles within the **IDPi** catalyzed ACDC framework.*

Therefore, a re-silylation of silyl alkyl ether **3.2** would afford a counteranion stabilized bis(silyl)alkoxonium ion **3.4**. Performing this reaction in the presence of nucleophilic silyl

ketene acetals **SKA-1** would most likely result in the desired α-alkylation of an silyl ketene acetal **SKA-1** from the imidodiphosphazenate stabilized bis(silyl)alkoxonium ion **3.4** to afford enantioenriched α-alkylated esters (**3.5**) as terminal product. A successful enantioselective realization of this project, in particular with the utilization of unbiased primary alcohols as unbranched and non-activated alkyl surrogates would complement existing procedures.[104-111] A simple exchange of the silylated nucleophile, for instance, the replacement of silyl ketene acetals with ketone or aldehyde-derived silyl enol ethers would give access to the corresponding enantioenriched α-alkylated carbonyls on distinct oxidation levels. Consequently, this transformation might provide a conceptually general strategy to overcome previous limitations, in which most of the described methodologies are limited to a specific carbonyl class. Furthermore, and upon a successful realization of this project, the replacement of carbonyl-derived nucleophiles with various distinct silylated nucleophiles, such as allyltrimethylsilane, triethylsilane or trimethylsilylcyanide might lead to a more general enantioselective dehydroxyfunctionalization strategy within the ACDC framework. Thus, the potential and high versatility of this concept provided the motivation to design and to develop a novel and highly reactive acid catalyst class to circumvent the initial reactivity issues.

4 Results and Discussion

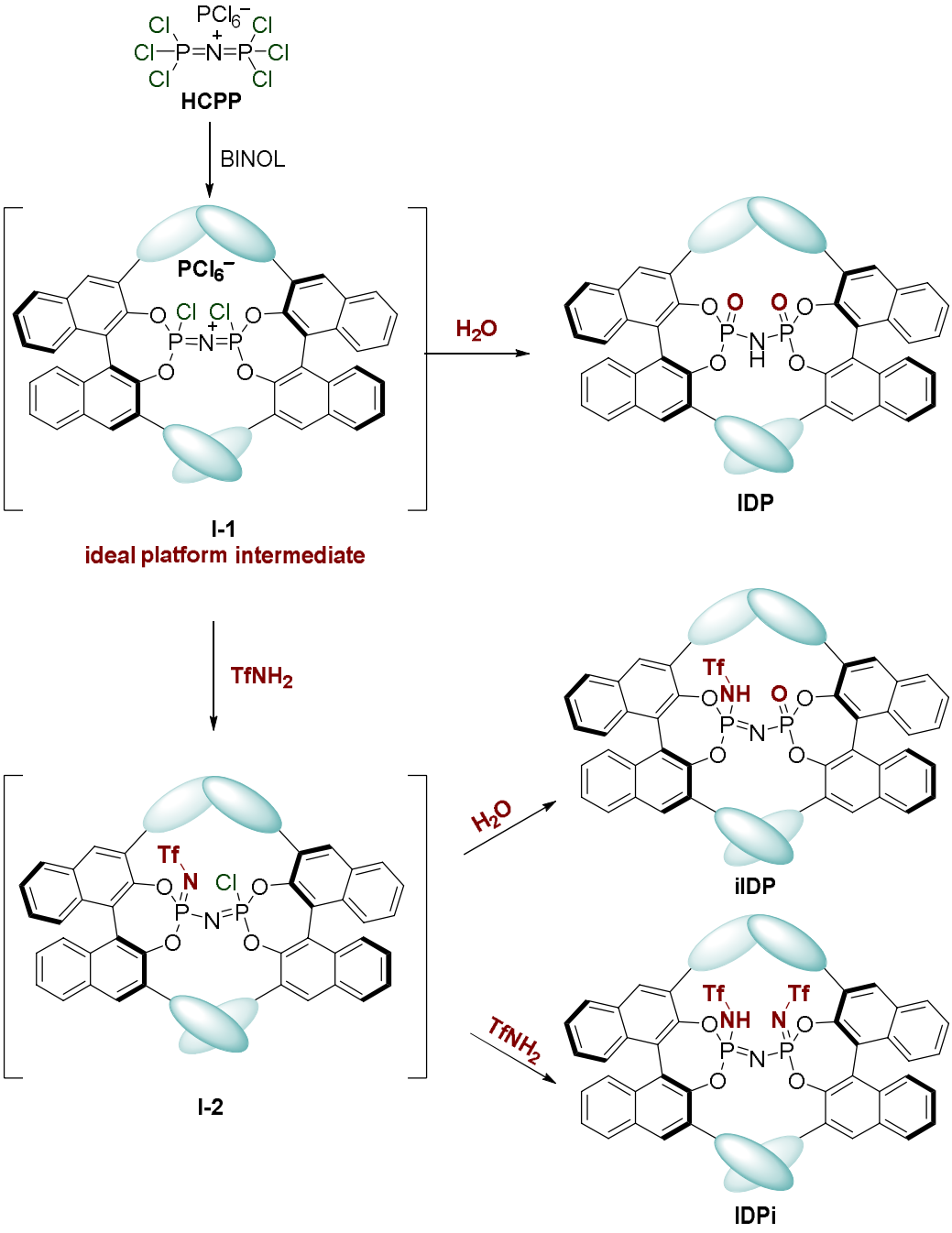
4.1. A Unified Approach to Access Imidodiphosphate Catalysts

For the synthesis of imidodiphosphate catalyst scaffolds, we envisioned two different strategies regarding the nucleophile addition (Scheme 22):

1. Addition of H_2O or $TfNH_2$, followed by BINOL installation to **HCPP**.
2. Addition of two BINOL units followed by H_2O or $TfNH_2$ **to HCPP**.

The first strategy was believed to be synthetically more challenging. Adding two equivalents of water to **HCPP** might result in non-selective chloride substitution, in which more than two chlorides of the corresponding **HCPP** salt might be substituted. This undesired side reactivity would significantly disfavor the subsequent BINOL installation step.

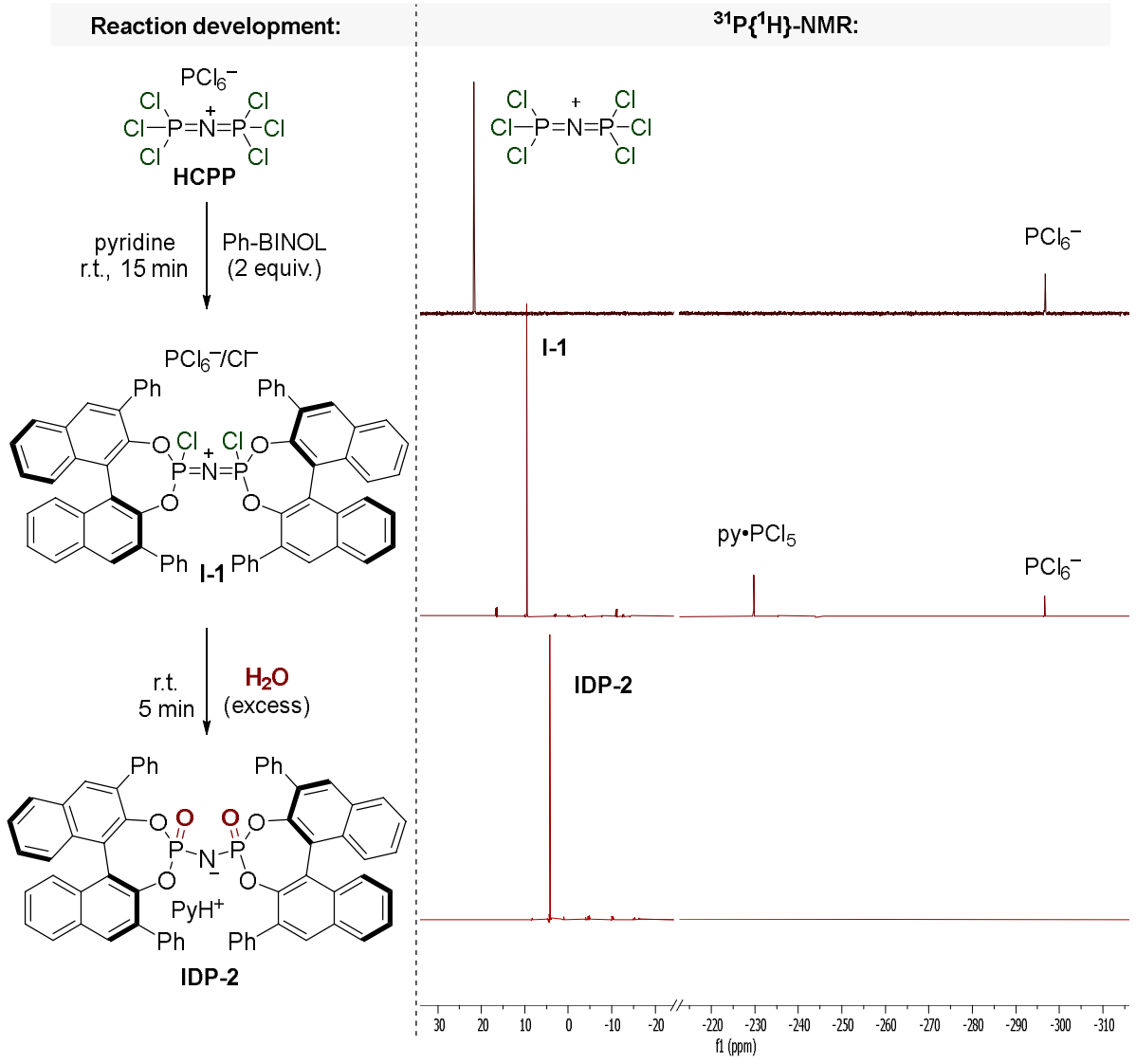
Contrarily, the second strategy, in which first two BINOLs are reacted with **HCPP** might result in an intermediate (**I-1**), as shown in Scheme 22. The two remaining chlorides on intermediate **I-1** were envisioned to undergo subsequent substitution reactions with suitable nucleophiles, such as water (H_2O) or trifluoromethanesulfonamide ($TfNH_2$). Thus, the addition of H_2O to **I-1** was envisioned to give access to **IDPs**, whereas the addition of one equivalent of $TfNH_2$ to **I-1** might provide **I-2**. In return, **I-2** would provide an intermediate, which upon addition of water might lead to the formation of **iIDP**, or upon addition of an additional equivalent of $TfNH_2$ toward the formation of **IDPis**.



*Scheme 22: Idealized stepwise P–Cl substitution of **HCPP** to access imidodiphosphoryl-derived Brønsted acids.*

4.1.1 Synthesis of Imidodiphosphates (IDP)

Initial NMR experiments investigating the reaction of 3,3´-(phenyl)-BINOL (Ph-BINOL) with **HCPP** revealed that solvents such as dichloromethane, toluene and pyridine were suitable solvents for the reaction. Pyridine was the solvent of choice as a result of sufficient and fast reactivity of **HCPP** with BINOL to form intermediate **I-1** (Scheme 23).

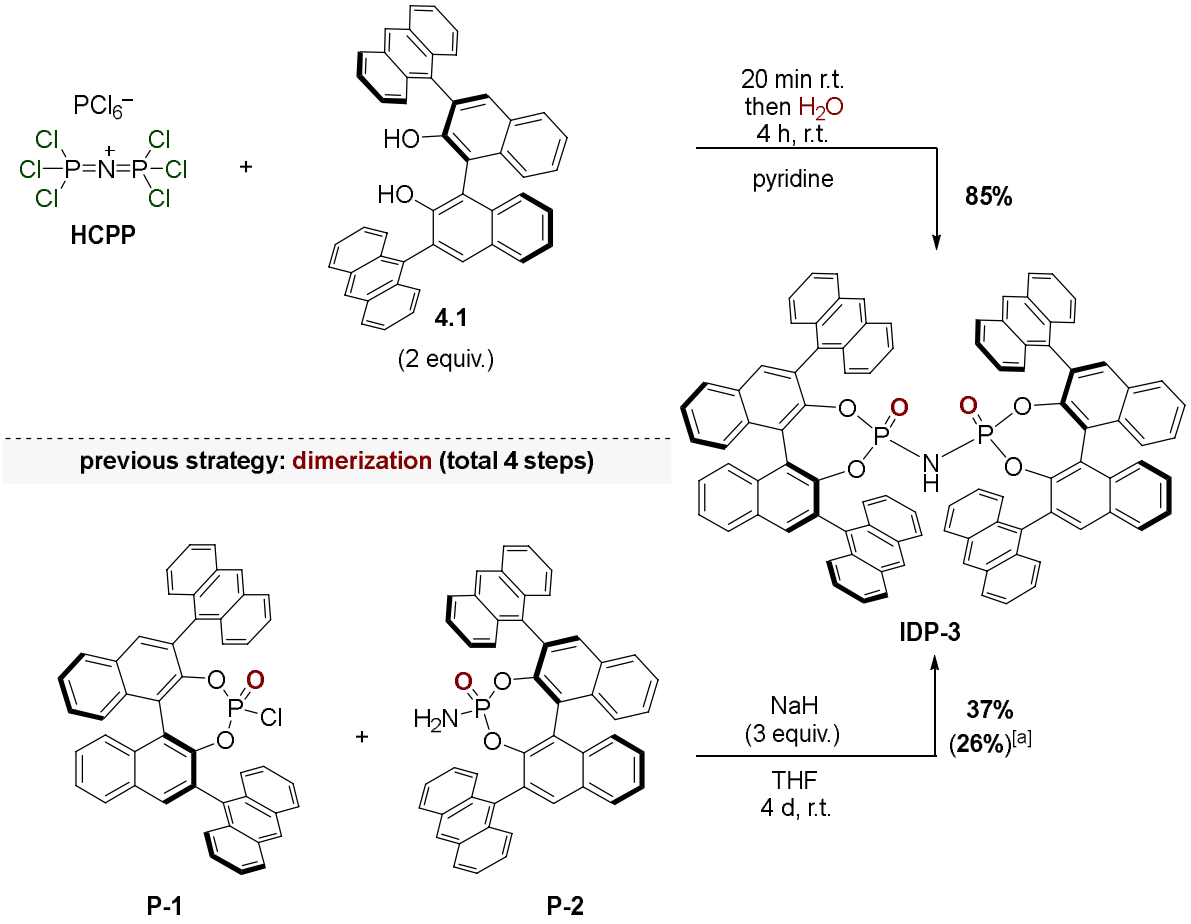


*Scheme 23:Reaction development toward 3,3´-(phenyl)BINOL-derived **IDP-2**. NMR spectra are shown for every intermediate in DCM-d_2.*

Notably, the reaction of two equivalents of BINOL with **HCPP** proceeded too fast to observe any mono-BINOL addition products within our NMR studies. Addition of water to **I-1** resulted in a rapid hydrolysis, substituting both P–Cl units, to afford the desired **IDP** within five minutes at room temperature (Scheme 23). Interestingly, over the course of the reaction, the PCl_6^- counteranion slowly reacted with pyridine, as observed by the formation of a pyridine•PCl_5

adduct, thus presumably expelling a chloride anion.[64] Therefore, salt **I-1** might resemble a mixture of phosphazoniums ions with Cl^- and PCl_6^- counteranions.

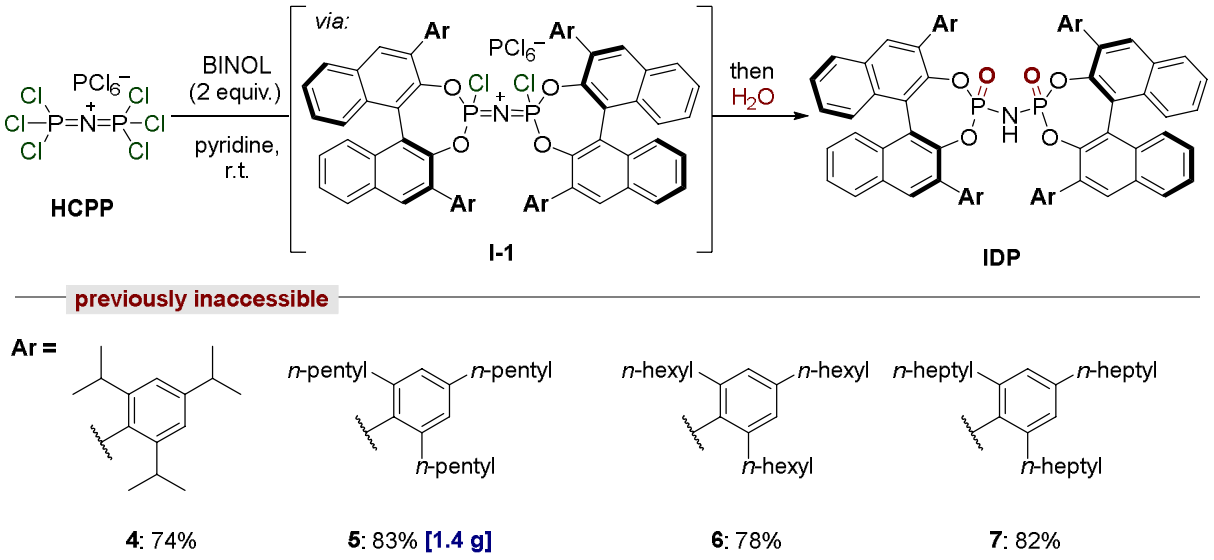
Inspired by these studies, we turned our attention toward a comparison between the previously established dimerization strategy and this new approach. We focused on the synthesis of the anthracenyl-substituted **IDP-3,** which was difficult to access in the past. Based on the previous 4-step reaction sequence, which involved the purification of phosphoryl chloride (**P-1**), phosphoryl amide (**P-2**) and final **IDP** product, the desired **IDP-3** formed in a total yield of 26% based on employed BINOL. Contrarily, our new approach furnished the desired **IDP** within 5 h, required only one simple purification step and resulted in a significantly improved yield of 85%.



*Scheme 24: Synthesis of **IDP-3**, comparing the previous dimerization strategy with the new approach*

Next, we focused on the synthesis of previously elusive catalyst scaffolds with extremely sterically demanding combinations of BINOLs. Inspired by recent advancements of **TRIP-CPA**, we believed the corresponding **TRIP-IDP** (**IDP-4**) to be a highly privileged catalyst scaffold, enabling the control of very small and structurally unbiased substrates in asymmetric

catalysis. In the past, the BINOL-derived *o*,*o*,*p*-triethylphenyl substituted **IDP-1** allowed to control several structurally distinct substrate classes and consequently emerged as a privileged catalyst scaffold.[27, 31, 39, 41] Thus, we assumed that also the elongation of the alkyl chains in the *o*,*o*,*p*-positions of the 3,3'-phenyl substituents may result in an improved enantioinduction of the new **IDP** motifs toward handling challenging substrates.



*Scheme 25: **IDP** catalyst scope of previously elusive catalyst scaffolds.*

To our delight, the new method enabled facile access to these catalyst scaffolds and further enlarged our **IDP** catalyst library. Most notably, these catalysts were previously inaccessible following the traditional dimerization strategy.

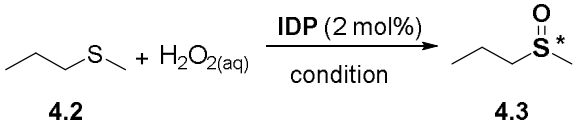
4.1.1.1 The IDP catalyzed asymmetric sulfoxidation

The following work was carried out in collaboration with Natascha Sadlowski.

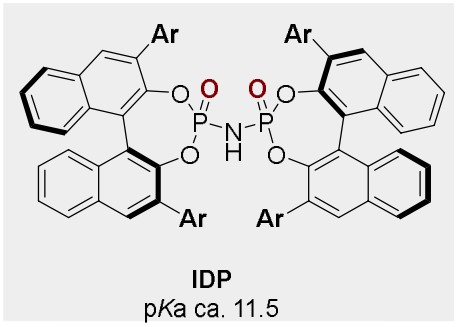
In light of the recently established **IDP**-catalyzed asymmetric sulfoxidation of sulfides, in which **IDP-1** was a privileged catalyst, we wondered if the newly prepared **IDP** catalysts **4-7** with elongated *o*,*o*-*p*-tri(alkyl)phenyl substituents might possibly improve the enantioinduction of small substrates. Especially small sulfides remained challenging to obtain in high enantiomeric enrichments. With a new route to previously inaccessible catalysts, we explored the oxidation of methyl propyl sulfide, under identical reaction conditions to the previously reported procedure.[39]

An initial catalyst screening revealed the superior enantiocontrol of our new catalyst motifs, in direct comparison to the previous benchmark **IDP-1**. Interestingly, **TRIP**-derived **IDP-4**, which was envisioned to resemble a superior motif, delivered the desired, almost racemic product, in poor yield (Table 1 entry 2 and 7). This lack of reactivity and enantioinduction may be explained with a too-encumbered active center, which prevented efficient substrate binding and thus resulted in background reactivity without enantioinduction from the enantiopure counteranion. Nevertheless, our new **IDP** catalysts **5–7** significantly enhanced the enantioinduction from the chiral counteranion, whereas **IDP 6** resulted in the highest enantioinduction (93.6:6.4 e.r.) under previously optimized reaction conditions. Changing the solvent from cyclohexane to dichloromethane allowed lowering the reaction temperature to –20 °C and furnished the desired sulfoxide in a satisfactory enantiomeric ratio of 95.2:4.8. This result confirmed the importance of having an efficient methodology available to access novel and highly confined catalyst motifs, representing an indispensable tool to control structurally unbiased substrates in asymmetric catalysis. It should be noted that this is by far the highest enantioselectivity ever reported with this particular substrate *via* any type of catalytic sulfoxidation.[112-114]

Table 1: Catalyst screening for the asymmetric sulfoxidation of methyl propyl sulfide.

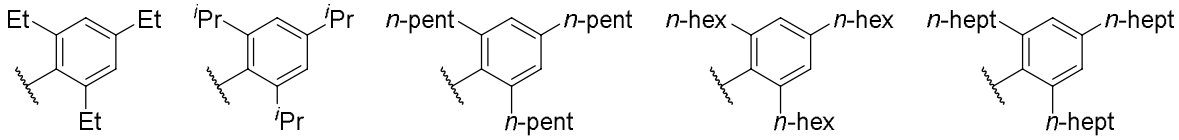


4.2 **4.3**



IDP
p*K*a ca. 11.5

Ar =



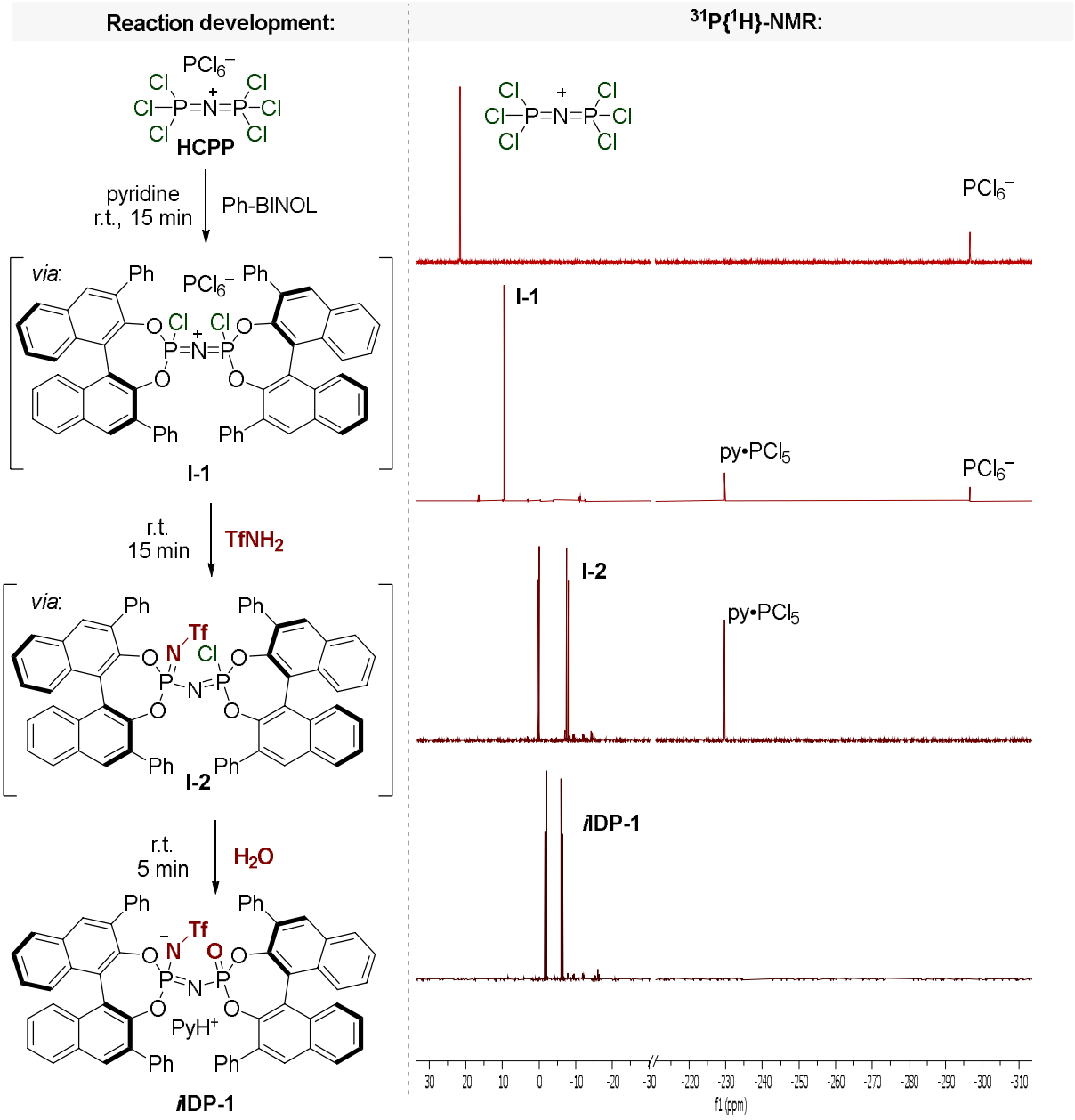
1 **4** **5** **6** **7**

entry	IDP	*Solvent*[b]	temp. [°C]	yield[a]	*e.r.*
1	**1**	*Cyhex*	20	87	**90.3:9.7 (80.6 %ee)**
2	**4**	*Cyhex*	20	29	**51.0:49.0 (2.0 %ee)**
3	**5**	*Cyhex*	20	86	**91.5:8.5 (83.0 %ee)**
4	**6**	*Cyhex*	20	89	**93.6:6.4 (87.2 %ee)**
5	**7**	*Cyhex*	20	88	**92.6:7.4 (85.2 %ee)**
6	**1**	*DCM*	–20	94	**91.5:8.5 (83.0 %ee)**
7	**4**	*DCM*	–20	25	**50.3:49.7 (0.6 %ee)**
8	**5**	*DCM*	–20	95	**95.1:4.9 (90.2 %ee)**
9	**6**	*DCM*	–20	95	**95.2:4.8 (90.4 %ee)**
10	**7**	*DCM*	–20	98	**94.8:5.2 (89.6 %ee)**

[a] yields were determined by NMR with dimethyl sulfone as internal standard
[b] concentreation = 0.1 M. Reaction time in Cyhex = 18 h; in DCM =15 h

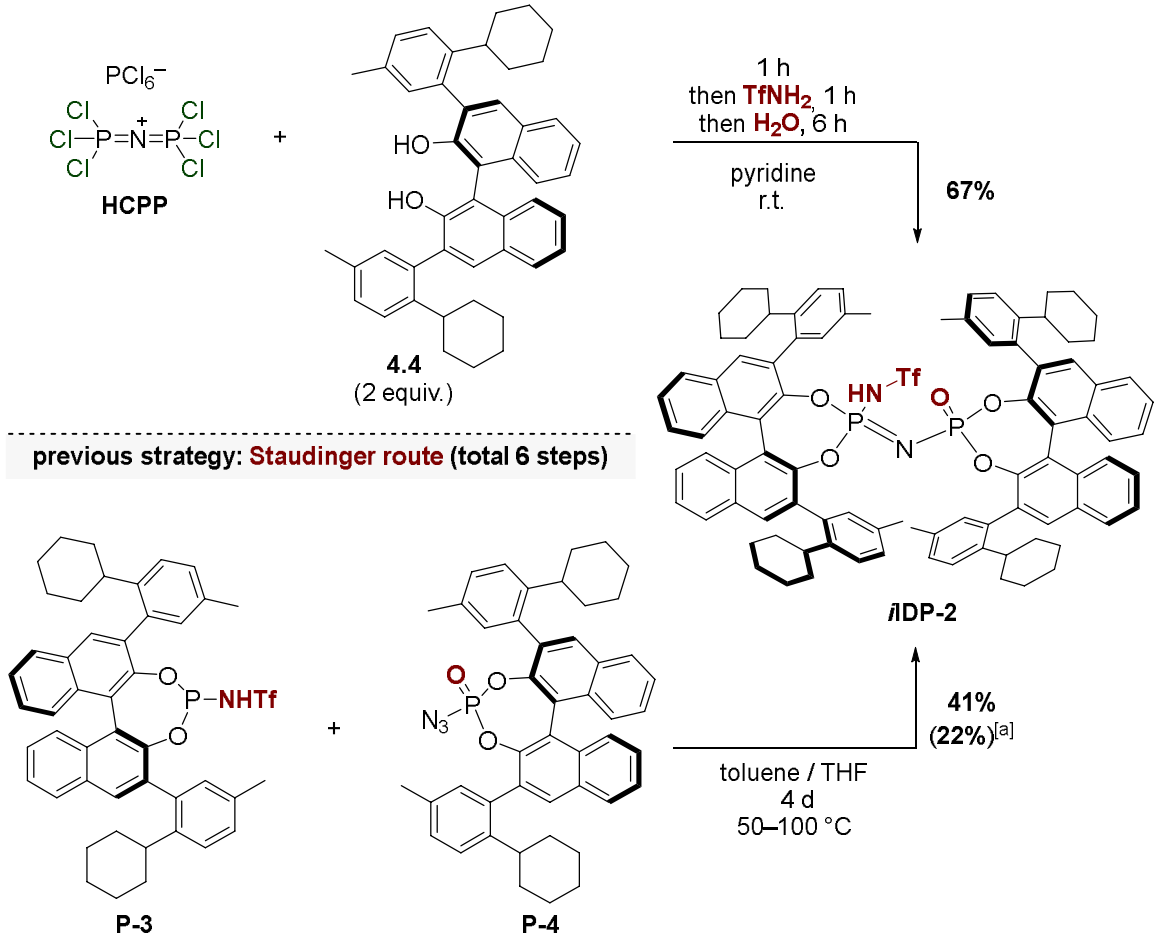
4.1.2 Synthesis of Iminoimidodiphosphates (*i*IDP)

Having identified intermediate **I-1** as a key intermediate, we explored the reaction of **I-1** with sulfonamides to access the proposed intermediate **I-2**, which upon hydrolysis would give access ***i*IDPs**. As expected, initial NMR studies showed rapid formation of intermediate **I-2** upon treatment of **I-1** with $TfNH_2$. **I-2** then rapidly formed ***i*IDP-1** upon hydrolysis. It should be noted that the reaction times were generally very short and the formation of intermediates **I-1** and **I-2**, respectively, were observed within 15 minutes in quantitative conversions.



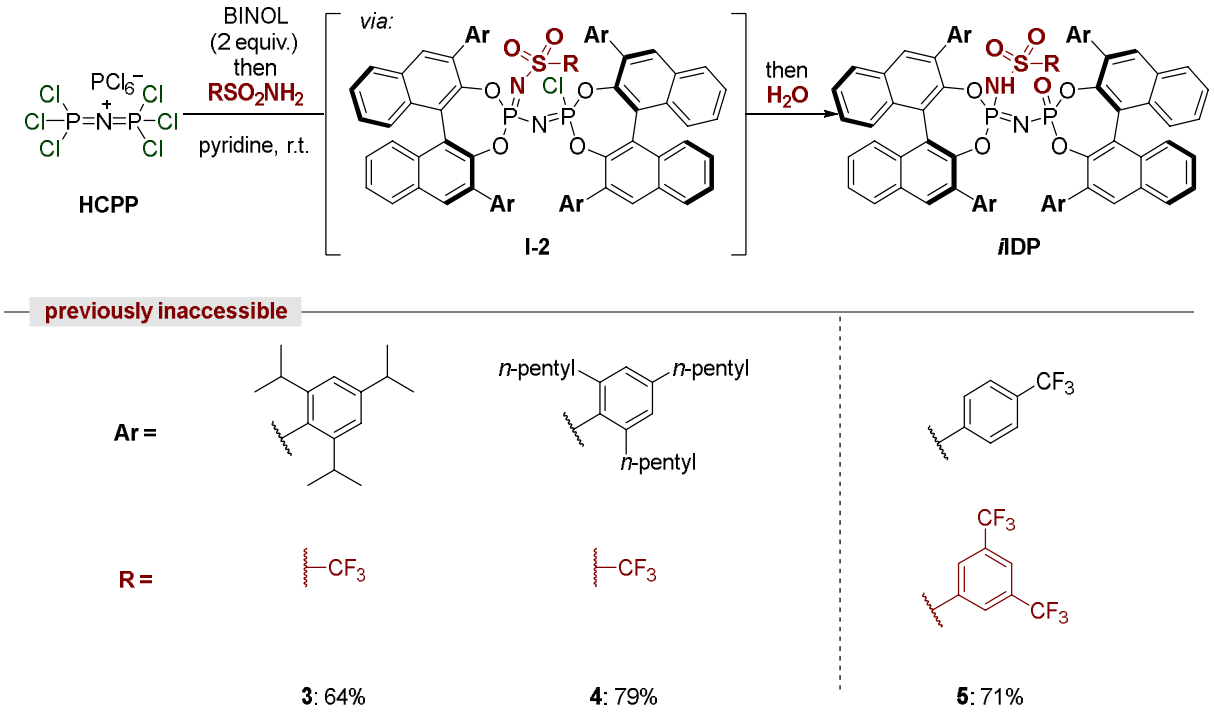
*Scheme 26: Reaction development toward 3,3´-(phenyl)BINOL-derived i**IDP-1**. NMR spectra are shown for every intermediate in DCM-d_2.*

Upon the identification of suitable reaction conditions, we compared this new methodology with the previous Staudinger approach focusing on the synthesis of ***i*IPD-2**, which resembles a privileged catalyst for the ***i*IDP** catalyzed asymmetric Prins cyclization.[51] ***i*IDP-2** was previously synthesized based on a 6-step sequence, yielded the desired product in a total yield of 22% and required several tedious isolation operations throughout the synthesis. In direct comparison, our new approach yielded the desired ***i*IDP** within a significantly shorter reaction time of 8 h, an increased yield of 67% and by applying a single and simplified purification step (Scheme 27).



*Scheme 27: Comparison of the previous Staudinger approach with the new synthesis toward **iIDP-2**. [a]yield refers to BINOL **4.4**. Comparison of the previous Staudinger approach with the new synthesis toward **iIDP-2**.*

We also explored the synthesis of previously inaccessible catalyst scaffolds, such as TRIP-derived ***i*IDP-3** or ***i*IDP**s with elongated alkyl chains in the *o,o,p*-positions of the 3,3´-phenyl substituents (Scheme 28). Gratifyingly, these ***i*IDP**s were all readily available in good yields using the new protocol (***i*IDP 3-4)**. Additionally, this approach allowed the synthesis of ***i*IDP**s with distinct sulfonamides as shown with ***i*IDP-5**.

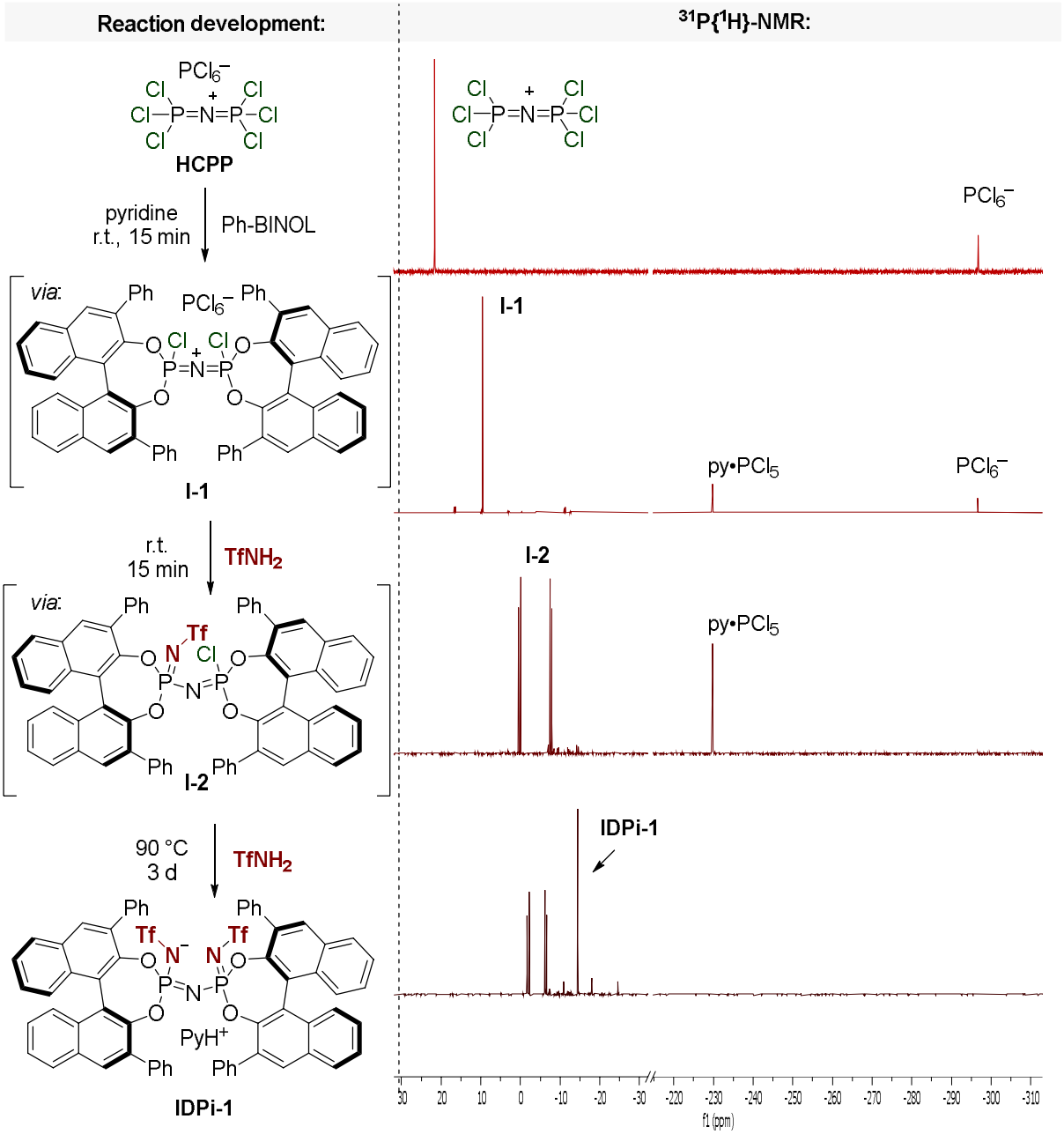


*Scheme 28: Synthesis of new and previously inaccessible **i**IDPs.*

Unambiguously, this new approach provides a fast and reliable access to several ***i*IDP** motifs in a single step, high yields and will most likely evolve as an attractive alternative to the previous 6-step Staudinger strategy.

4.1.3 Synthesis of Imidodiphosphorimidates (IDPi)

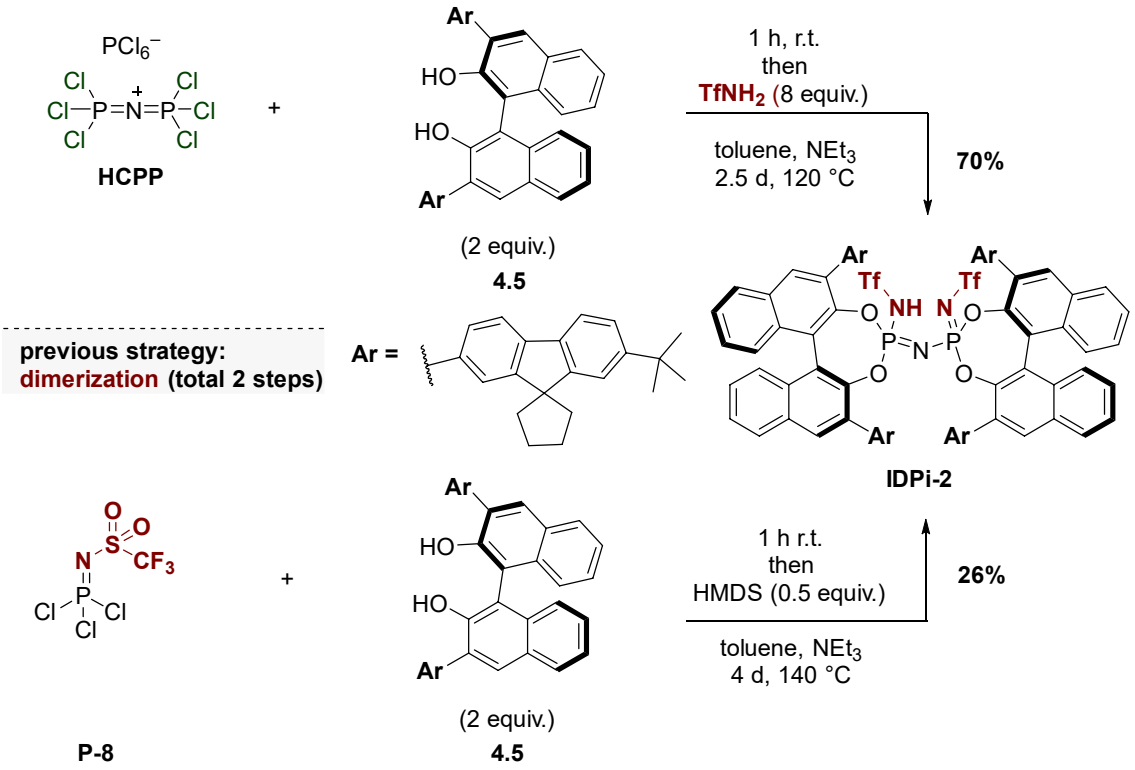
With intermediate **I-2** as key intermediate to give access to ***i*IDPs**, we turned our attention toward the synthesis of the more acidic **IDPi** catalyst class, by the addition of two sulfonamide units to **I-1**. As shown before, the first sulfonamide addition to **I-1** proceeded rapidly within minutes to afford **I-2**. However, the last P-Cl bond substitution with another equivalent of $TfNH_2$ required longer reaction times, also at elevated temperatures of ca. 90 °C.



*Scheme 29: **IDPi** reaction development.*

Conducting the experiment in pyridine above 90 °C resulted in significant **IDPi** decomposition, which was even more predominant in the presence of perfluorinated aromatic sulfonamides,

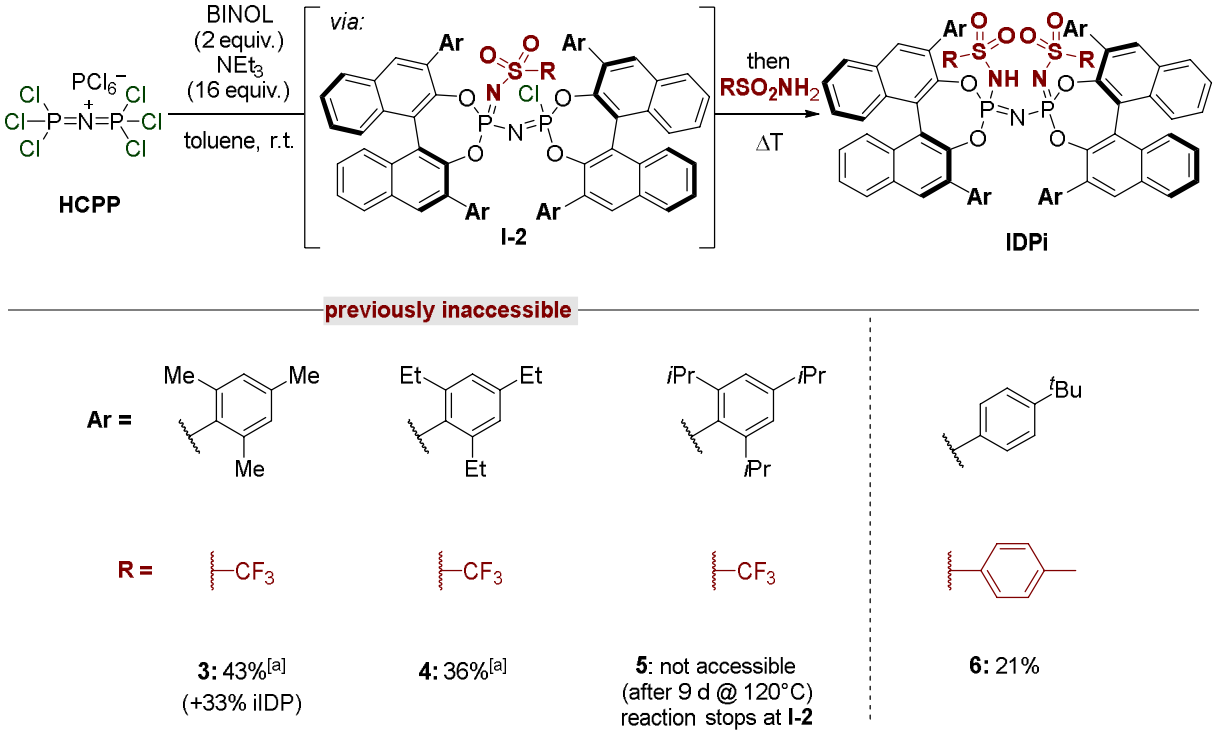
due to undesired S_NAr reactions. To prevent this decomposition pathway in the presence of relatively nucleophilic pyridine, the solvent was exchanged with toluene and triethylamine as a non-nucleophilic organic base was utilized. Under modified reaction conditions we compared the previously established 2-step dimerization strategy with our new approach, focusing on the synthesis of **IDPi-2**, which was previously prepared in an unsatisfactory yield of 26% and required prolonged reaction time of 4 days. To our delight an initial attempt, applying this new strategy afforded the desired **IDPi** in significantly increased yield of 70% and in shorter reaction time of *ca.* 2 days (Scheme 30).



*Scheme 30: Comparison of the previous dimerization strategy with our new methodology toward the synthesis of **IDPi-2**.*

Moreover, this new approach features a simplified purification by flash column chromatography, since the ***i*IDP** side product that forms due to any traces of water present, has a significantly different polarity on silica gel. Contrarily, the dimerization strategy afforded the corresponding *N*-triflylphosphoramide (**TPP**) as the hydrolysis product, which consist of similar polarities to **IDPi** and thus significantly impeded the purification procedure.

Once again, we then turned our attention toward the synthesis of previously elusive **IDPi** catalysts. In particular, **IDPis** that contain *ortho*, *ortho*-substituted aryl substituents on the BINOL moiety remained elusive within the dimerization process. Our new approach, however, smoothly afforded mesityl- and triethyl-derived **IDPis**, as shown with **IDPi-3** and **IDPi-4**.



*Scheme 31: Synthesis of distinct **IDPi** motifs. I**DPi-3** and **IDPi-4** remained elusive under standard dimerization conditions.*

Although the yields were only moderate, the unreacted intermediate **I-2** could be isolated or afforded the corresponding ***i*IDP** upon hydrolysis. Therefore, this approach allowed a rapid catalyst library implementation of distinct imidodiphosphate-derived Brønsted acids in a single one-pot fashion. TRIP-derived **IDPi-5** remained inaccessible under these new reaction conditions. It should be noted that the reaction stopped at the corresponding intermediate **I-2**. Higher temperatures and long reaction times of 14 days did not result in any observable formation of the desired **IDPi-5**. This observation may be explained with the extreme steric congestion of the 3,3´-TRIP substituents.

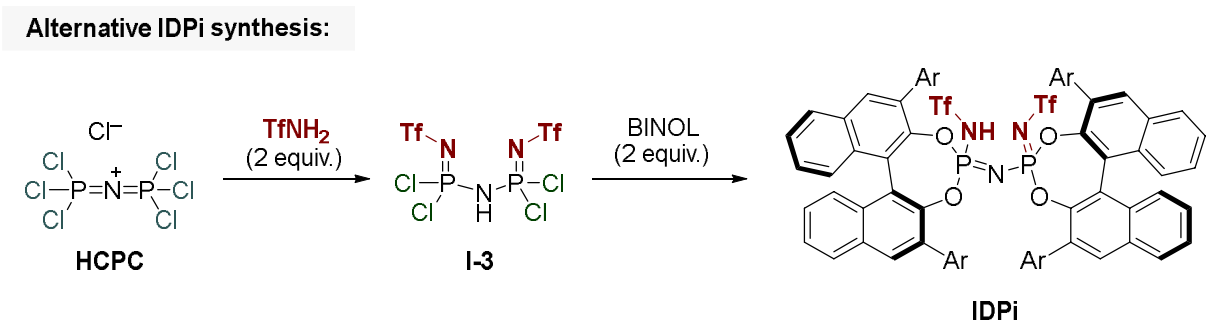
On the other hand, the synthesis of **IDPi-6** illustrates that the N-sulfonyl groups are readily exchangeable, simply by replacing $TfNH_2$ with other sulfonamides within the P–Cl substitution event of intermediate **I-2**. In contrast, the previous **IDPi** synthesis with distinct sulfonamide modifications required the synthesis of *N*-sulfonylphosphoriminoyl trichloride prior to the dimerization strategy.

4.1.4 Alternative IDPi Synthesis

The following work was developed in combination with the synthesis of a new catalyst class, namely, **IDPii.** A more detailed description of the reaction development and synthetic difficulties are thoroughly discussed in chapter 4.2.3.1 **HCPC** as building block to access **IDPii**.

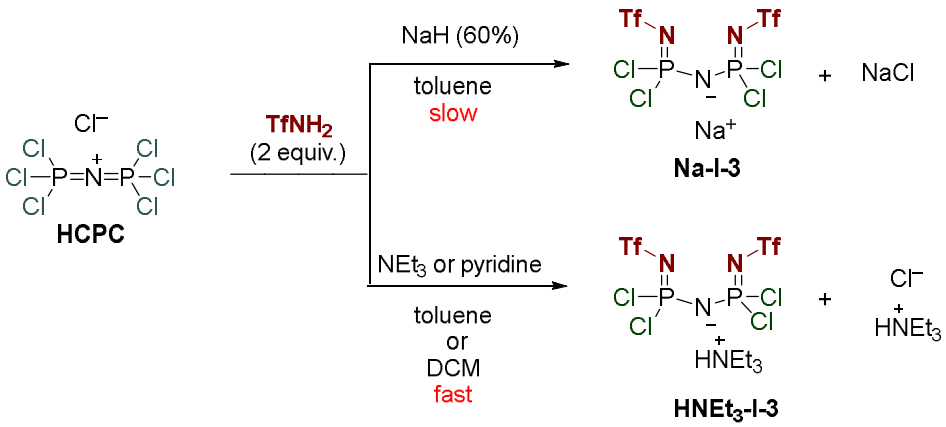
Although increased yields of certain catalyst motifs of the highly privileged **IDPi** motif and previously elusive catalyst scaffolds are now available, we realized that the last chloride substitution in intermediate **I-2** with sulfonamides remains troublesome. Often these reactions resulted in hydrolysis products to afford the corresponding **IDP** and / or ***i*IDP**. This effect might be beneficial on small laboratory scales, since all three imidodiphosphoryl- derived Brønsted acids represent privileged catalysts classes and are separable by flash column chromatography, and thus allows a fast catalyst library implementation. However, to address large-scale **IDPis** syntheses without the necessity of tedious purification procedures, this new method might not represent the ideal approach. Therefore, we aimed toward a new synthesis, which provides the desired **IDPi** motif as main product and ideally only requires a simple crystallization technique as the purification step. To realize this approach, side products, which might form during the reaction progress need to possess significantly different polarities to enable a simple crystallization protocol.

To circumvent the discussed difficulties on installing the last sulfonamide substituent by substitution with the chloride in **I-2**, we changed the order of nucleophile addition to **HCPP**. It was postulated that installing both desired sulfonamides first, followed by the addition of chosen BINOLs, might be a suitable alternative (Scheme 32). This strategy would circumvent the issues of **IDP** and ***i*IDP** formation, since the electron-withdrawing substituents are pre-installed. Furthermore, hydrolysis of Intermediate **I-3** might result in a highly polar compound, and eventually precipitates from the reaction mixture, whereas the stepwise BINOL addition to **I-3** gradually increases the lipophilicity of the intermediate compounds. The final **IDPi** should have the highest lipophilic character in comparison to other formed side products. Therefore, a simple **IDPi** isolation by extraction with solvents, such as diethylether, followed by a simple re-precipitation of **IDPi** from the organic phase by addition of non-polar solvents, such as hexane, might be feasible.



*Scheme 32: Alternative strategy to access **IDPi**.*

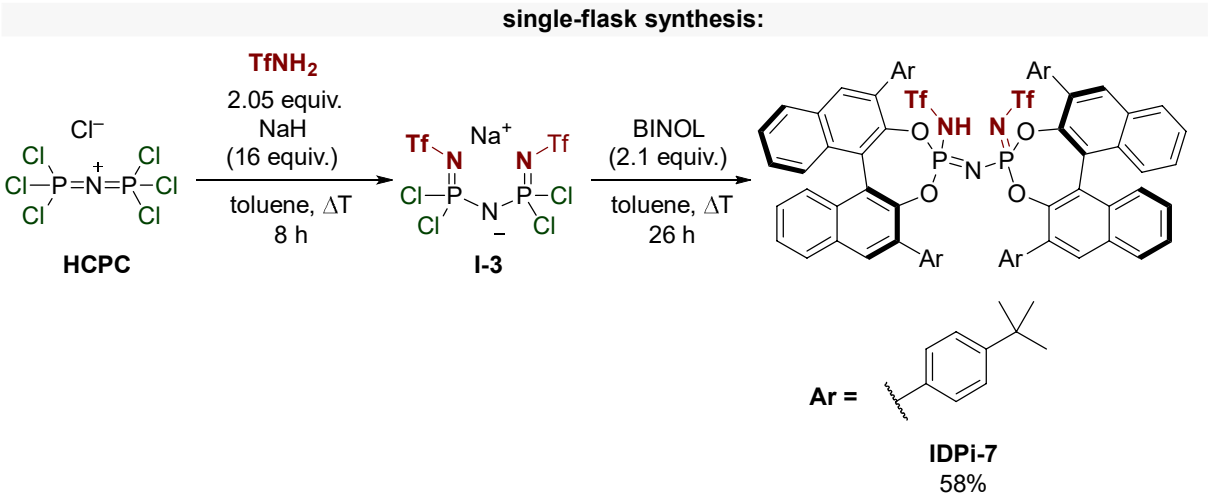
Initial experiments, in which $TfNH_2$ was reacted with **HCPC**[5] under neat reaction conditions and elevated temperatures, did not result in the formation of the desired intermediate **I-3**.[6] The addition of an inorganic base, such as NaH, slowly yielded the desired intermediate **I-3**, whereas the addition of organic bases, such as triethylamine or pyridine, resulted in spontaneous formation of **I-3** (Scheme 33).



*Scheme 33: Synthesis of di(N-trifluoromethylsulfonyl)tetrachloridophosphazenate **I-3**.*

Initial **IDPi** syntheses with **I-3** as the key intermediate were explored with triethylamine or pyridine as base. Unfortunately, these experiments were not successful due to either insufficient nucleophilicity of the BINOL or undesired decomposition of **I-3** in the presence of nucleophilic catalysts, such as 4-DMAP. We reasoned that intermediate **I-3** possesses significantly reduced electrophilic properties, most likely due to the stabilized negative charge on the phosphazenate moiety and thus disfavors the chloride substitution with BINOL. To increase the nucleophilicity of BINOL and to generate BINOLate *in situ*, we reinvestigated on the utilization of NaH as the base. Although the formation of **I-3** proceeded much slower, initial experiments, in which intermediate **I-3** formed *in situ* followed by BINOL addition showed promising results. After some optimizations, we found suitable reaction conditions to afford the desired **IDPi-7** in 58% yield. Additionally **IDPi-7** was easily isolable by simple filtration through a plug of silica (Scheme 34).

[5] The counteranion PCl_6^- was exchanged with Cl^- to prevent any undesired formation of $TfN{=}PCl_3$.
[6] Only mono NTf addition was observed to form an intermediate analogously to **I-5** (cf. 4.2.3.1 HCPC as building block to access IDPii)



*Scheme 34: Modified synthesis of **IDPi-7**.*

Note: this reaction suffered from reproducibility issues due to the poor solubility of NaH, **HCPC** and $TfNH_2$, which are sparingly soluble in toluene and resulted in a heterogenous reaction mixture. Due to the high electrophilicity of **HCPC**, only non-polar solvents, such as toluene or dichloromethane, could be utilized. THF for example rapidly polymerized in the presence of **HCPC**. However, it was found that THF could be used as solvent with pre-formed intermediate **I-3** and enhanced the solubility and facilitated the desired BINOL installation step.

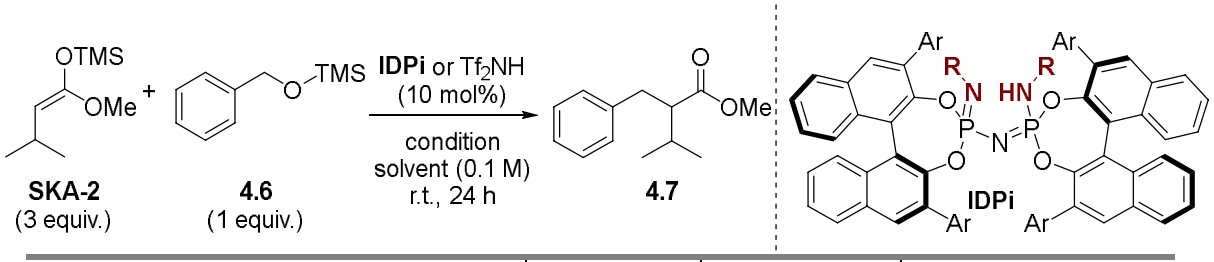
Toward a successful implementation of this strategy additional optimization studies and the identification of suitable **IDPi** isolation protocols on large scale will be further investigated.

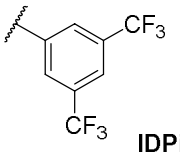
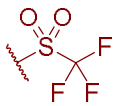
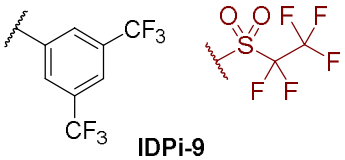
4.2 Development and Application of a More Acidic Brønsted Acid

4.2.1 Motivation: The IDPi Catalyzed α-Alkylation of Silyl Ketene Acetal

Initial experiments with our privileged (*m*,*m*-$(CF_3)_2C_6H_3$)-substituted **IDPi-8** revealed promising reactivities and furnished the desired α-benzylated ester **4.7** in *ca*. 10% yield, albeit in poor enantiomeric enrichment of 54:46. These results were considered as a suitable platform to further optimize this transformation. However, additional condition and **IDPi** catalyst screening with elongated perfluoroalkyl groups at the sulfonyl moiety (**IDPi-9**) did not sufficiently enhance the reactivity and enantioselectivity. Additionally, all other catalyst classes, which were known to be suitable catalyst motifs under silylium conditions, such as DSI and BALT were explored but did not engage in the desired transformation.[115-116] PADIs on the other hand, furnished the desired product, albeit without any enantioselectivity.[117]

*Table 2: Initial catalyst and condition screening for the enantioselective α-benzylation of **SKA-2**.*

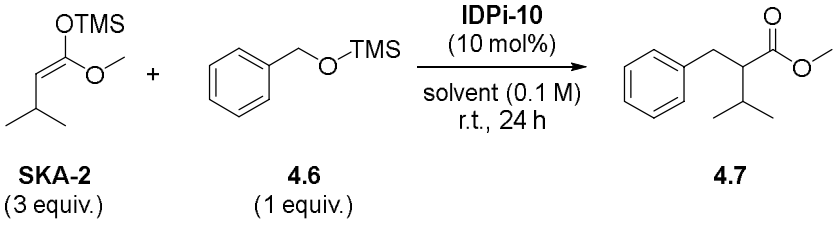


Catalyst	Solvent	conversion	e.r.
Tf-N(H)-Tf	$DCM\text{-}d_2$	68%	racemate
Ar =  R =  **IDPi-8**	$DCM\text{-}d_2$	$12^{[a]}$	54:46
	$CDCl_3$	$11^{[a]}$	55.5:44.5
	Et_2O	n.r.	n.d.
	CyHex	traces	n.d.
	C_6D_6	n.r.	n.d.
 **IDPi-9**	$DCM\text{-}d_2$	11	54:46

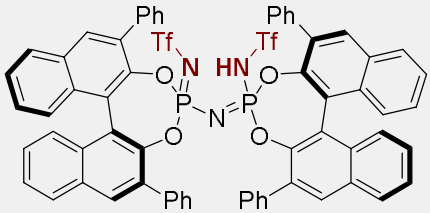
The reaction with **IDPi-8** and **IDPi-9** ceased at approximately 10% conversion with 10 mol-% catalyst loading, thus indicating a catalyst inhibition pathway (Table 2). Additional catalysts were tested and another solvent screening, as exemplarily shown with **IDPi-10** was performed.

However, under all tested reaction conditions no desired or enhanced product formation was observable. Additionally, the exchange of **SKA-2** with **SKA-3** or **SKA-4** and bis-silyl ketene acetal **BSKA-1** did not result in the desired product formation. The replacement of the trimethylsily moiety (TMS) with triethylsilyl (TES, **4.8**), *tert*-butyldimethylsilyl (TBS, **4.9**) on the electrophile moiety, or utilizing dibenzylether **4.10**, did not beneficially influence the reaction (Table 3). These results were disappointing, since only the privileged (*m*,*m*-$(CF_3)_2C_6H_3$)-derived **IDPis** (**8-9**) resulted in the desired transformation, albeit in low yields and no catalyst turnover numbers. Contrarily, Tf_2NH as catalyst smoothly afforded the desired product in 68% yield under non-optimized reaction conditions.

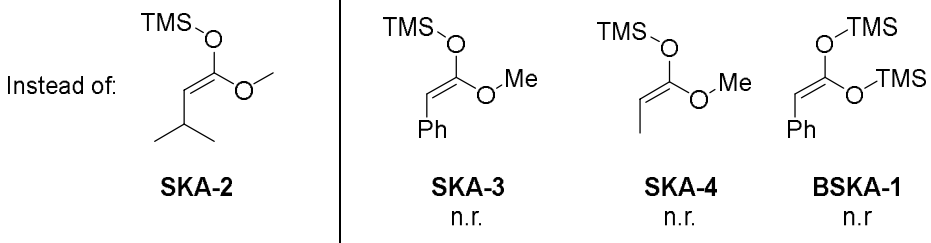
*Table 3: Attempts to optimize the α-benzylation with **IDPi-10**.*

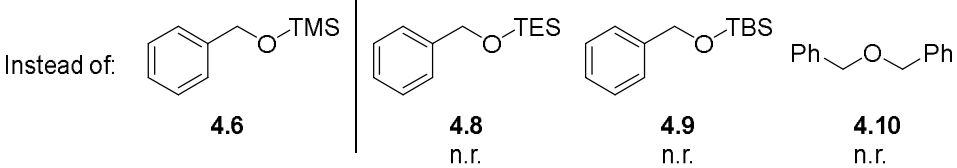


Solvent	conversion	e.r.
DCM	traces	n.d.
$CDCl_3$	traces	n.d.
Et_2O, CyHex, benzene, dioxane, CD_3CN, TMs_2O, DMSO, EtOAc	n.r.	n.d.



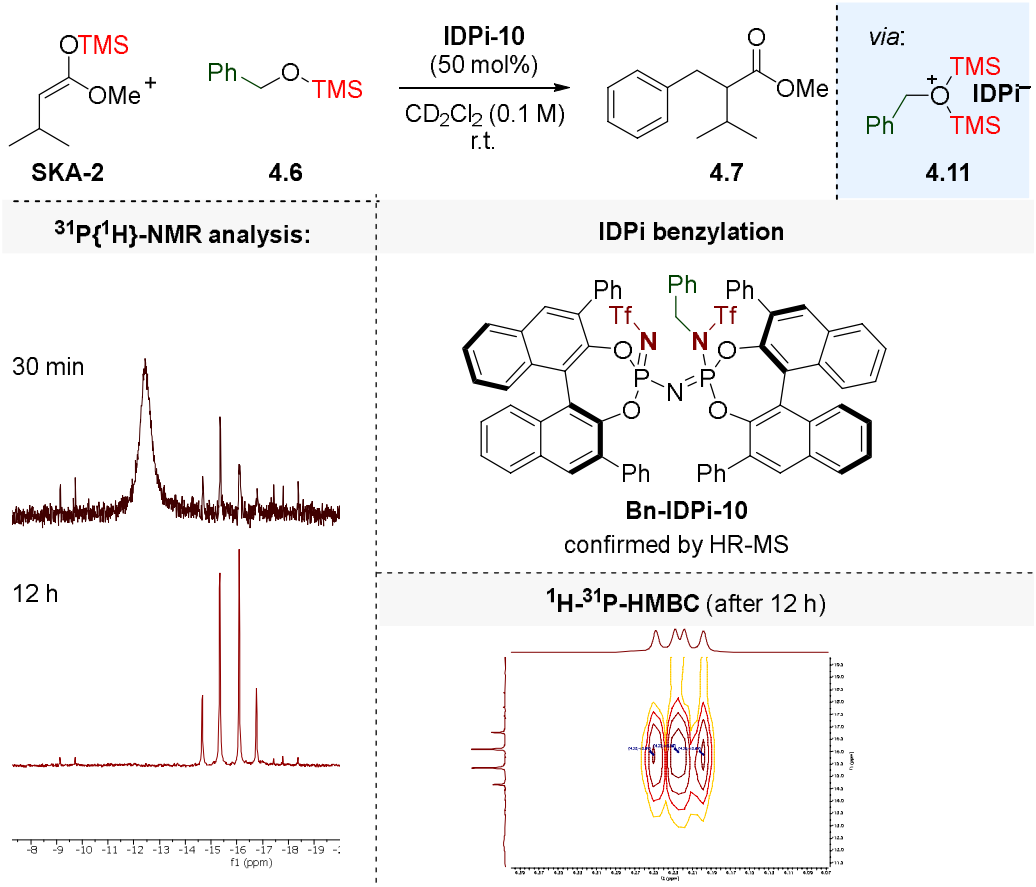
Reagent screening





Additional NMR studies were performed to elucidate the limitations and challenges of this transformation. The initial intention of these studies relied on the spectroscopical analysis of the proposed bis(trimethylsilyl)benzyloxonium salt **4.11**. Surprisingly, during the reaction

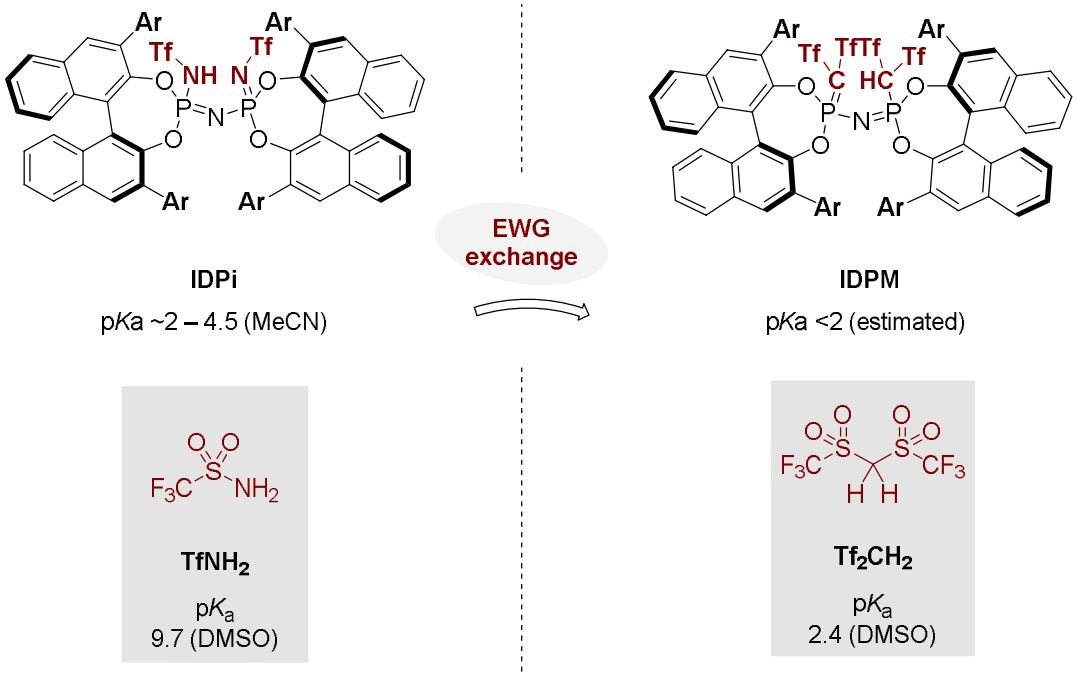
progress the corresponding **IDPi 10** turned into a non C_2-symmetric species and was identified to represent the corresponding benzylated **IDPi 10**, presumably upon **IDPi** benzylation from the proposed intermediate **4.11**. This result clearly indicated that the missing product formation during the reaction screening did not result from a lack of Lewis acidity of **IDPi-10** but rather from insufficient stabilization of the proposed ion pair **4.11** as a result from the relatively high nucleophilicity of the imidodiphosphazenate anion (Scheme 35).



*Scheme 35: Reaction was monitored by ^{31}P-NMR. Formation the **Bn-IDPi-10** was observed by NMR studies and MS analysis.*

However, the application of bistriflimide ($HNTf_2$) as catalyst illustrated that a more acidic catalyst with a corresponding less nucleophilic counteranion was capable of catalyzing the desired transformation. Therefore, a new catalyst motif to overcome the reactivity barrier has been envisioned as a necessary condition toward a successful realization of this project. Furthermore, it was believed that a more acidic catalyst motif based on the imidodiphosphate scaffold might evolve as a new privileged catalyst class and may enable new avenues to develop further novel asymmetric transformation, which require the stabilization of highly reactive intermediates.

4.2.2 Imidodiphosphormethide (IDPM)

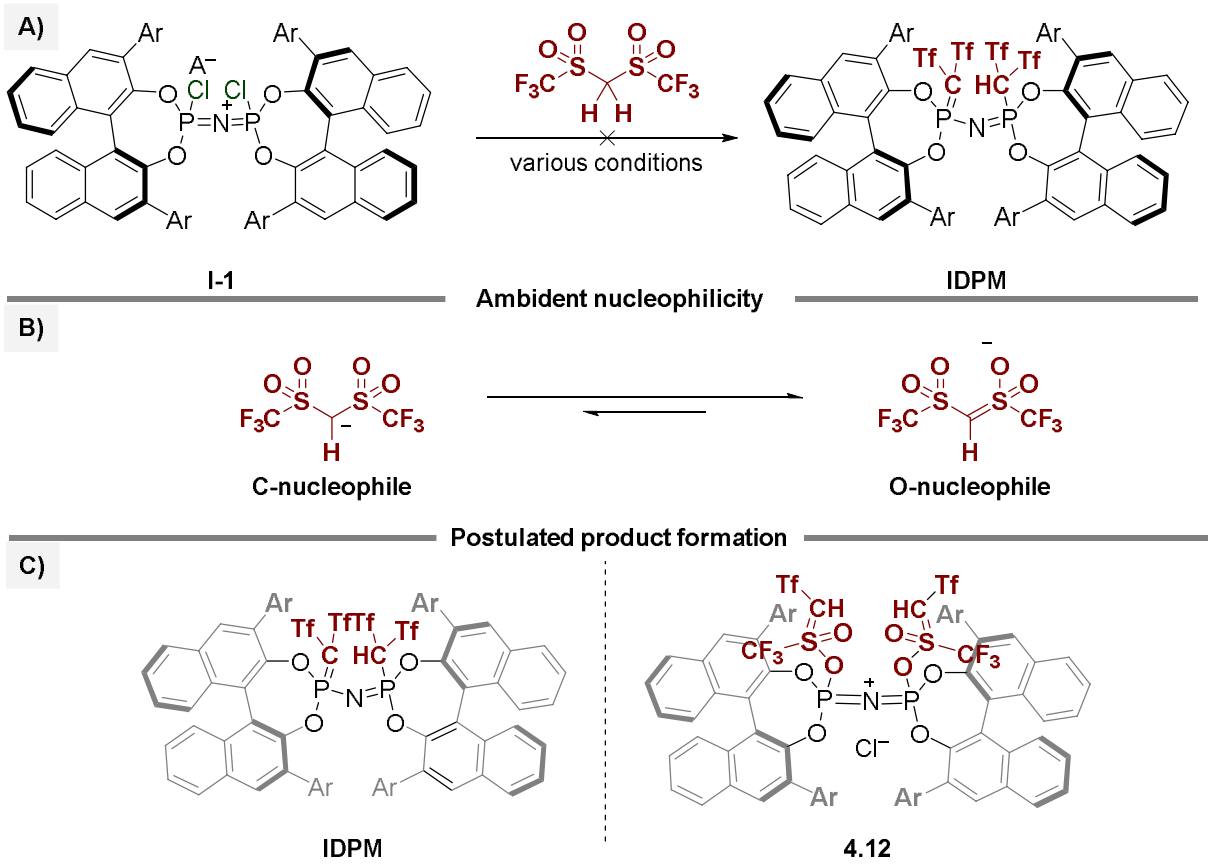


Scheme 36: Design of a more acidic catalyst motif based on the imidodiphosphoryl platform

In light of the recently developed super Brønsted acid tetratriflylpropene (**TTP**),[118] the installment of bis(triflyl)methane (Tf_2CH_2) as acidifying substituent within the imidodiphosphate scaffold was explored. It was believed that the pKa difference of $TfNH_2$ (9.7 in DMSO) vs. Tf_2CH_2 (2.4 in DMSO) would reflect a significant acidity enhancement of the corresponding imidodiphosphate-derived catalyst.

Based on previous success, in which **HCPP** has been utilized as building block to access dimeric imidodiphosphate catalysts, we believed that the addition of Tf_2CH_2 to intermediate **I-1** might be a viable strategy to afford the desired catalyst motif, imidodiphosphorbismethide (**IDPM**). Unfortunately, under identical reaction conditions as shown for the synthesis of **IDPi** starting from **HCPP** as building block (chapter 2.1.3 Imidodiphosphorimidates (**IDPi**)) no formation of the desired catalyst motif **IDPM** could be observed. Instead the corresponding **IDP** formed as main product. First, we assumed that the **IDP** formation was caused by hydrolysis. However, careful drying of all reagents and performing the reaction under strictly inert reaction conditions did not positively influence the final product distribution. NMR studies under inert reaction conditions illustrated a reaction progress of intermediate **I-1** upon addition of Tf_2CH_2, as it was followed by the formation of new ^{31}P-NMR signals. However, when the reaction was exposed to air, **IDP** formed immediately. Based on these NMR studies, we

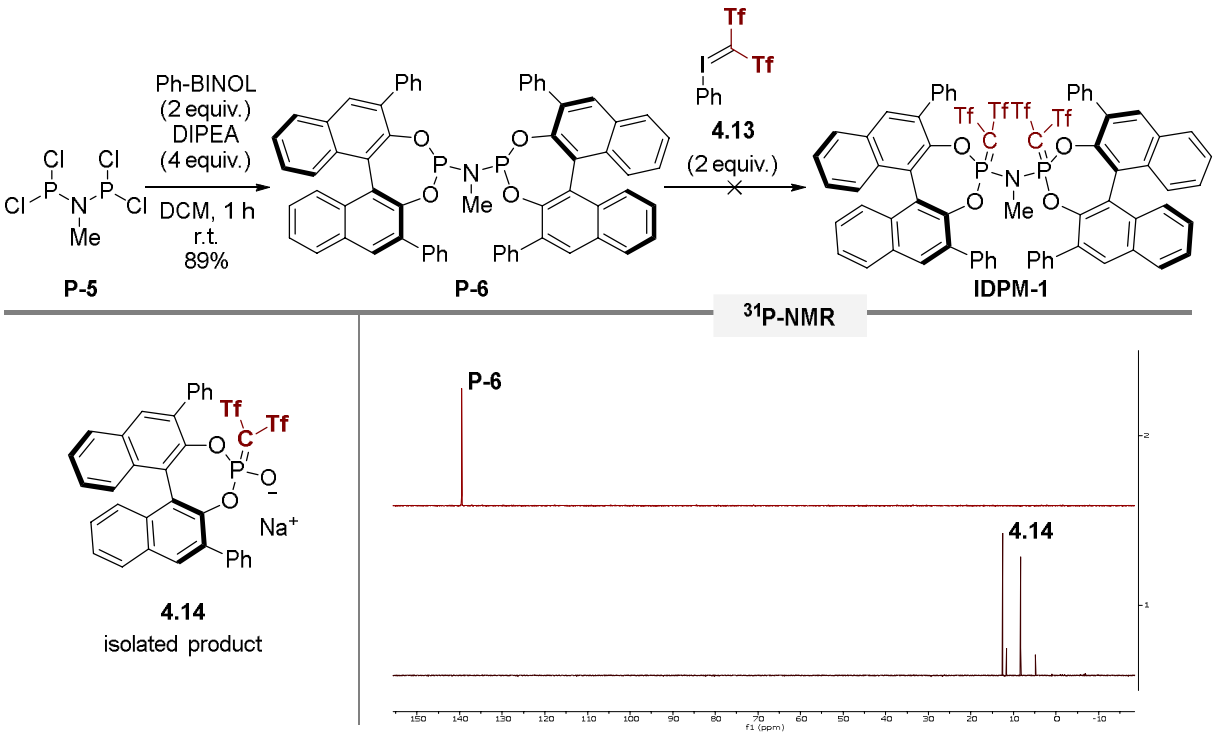
suggested that bistriflylmethane may not only react as the envisioned carbon-nucleophile, but also as an oxygen nucleophile. Considering the statistical distribution of four oxygen atoms vs. one carbon atom of Tf_2CH_2, in combination with the oxophilicity of phosphorous, the O-nucleophilic P-Cl replacement of **I-1** with Tf_2CH_2 was considered as a plausible explanation. Furthermore, this kind of reactivity would result in an extremely moisture sensitive anhydridic salt, as exemplarily visualized with structure **4.12**, and most likely rapidly hydrolyzes in the presence of water (Scheme 37 C)



*Scheme 37: A) Functionalization of intermediate **I-1** with bis(triflyl)methane. B) Proposed ambident character of bis(triflyl)methane. C) Proposed structures resulting from C- vs O-nucleophilic P–Cl replacement.*

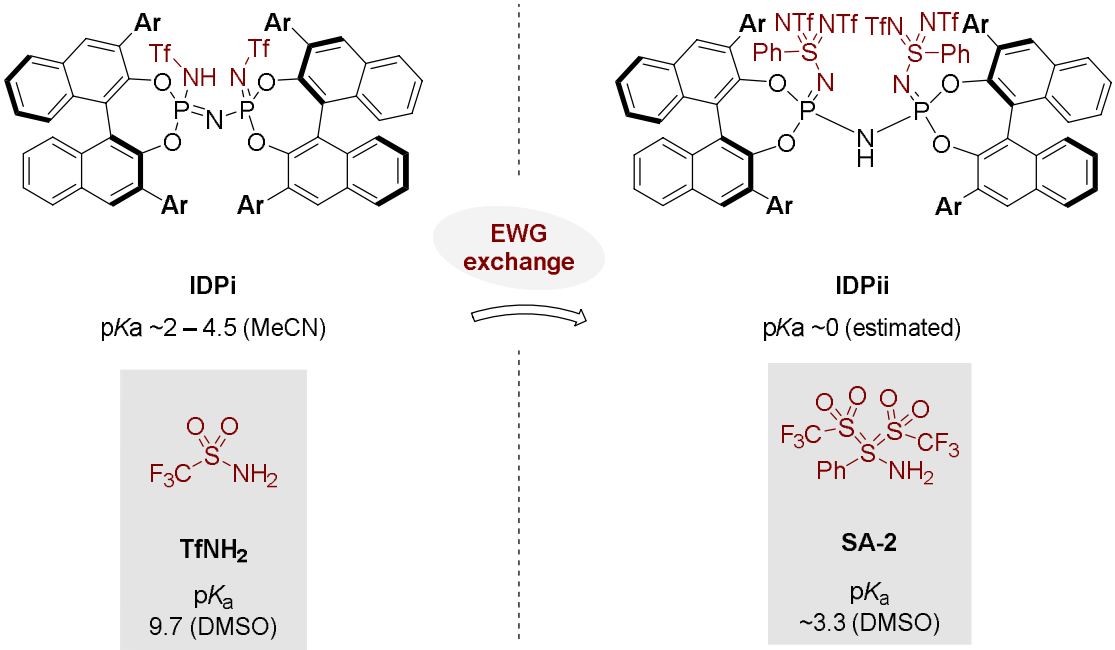
To circumvent the ambiphilicity of Tf_2CH_2, we focused on the application of phenyliodonium bis(triflyl)methide (**4.13**). This reagent has been utilized as bistriflylmethide-transfer reagent to oxidatively install the desired bis(triflyl)methide unit to triphenylphosphine (PPh_3) to afford $Ph_3P{=}CTf_2$.[119] Noteworthy, this reagent dictates the reactivity site of bistriflylmethane and thus avoids the action as oxygen nucleophile. To explore this strategy we followed the previous **IDPi** strategy, in which bis(dichlorophosphinyl)-*N*-methylamine **P-5** served as building block (Scheme 38). **P-5** smoothly reacted with BINOL to afford the desired intermediate **P-6**. The addition of **4.13** to **P-6** clearly indicated the envisioned oxidation of P(III) to P(V), as it was

observed in ^{31}P-NMR studies. Again, the formed products directly reacted upon exposure to air, which significantly impeded the isolation of the formed product. Crystallization attempts to obtain **IDPM-1** remained unsuccessful due to the relatively high lipophilicity. A hydrolysis product, in which bistriflylmethane was installed could be isolated in traces upon several crystallizations attempts due to the increased polarity of **4.14**. However, acidification attempts were not successful due to full hydrolysis to the corresponding phosphoric acid **CPA**. We explained the high sensitivity due to the ylide-type character of the formed bistriflylmethide-derived phosphoryl units. Considering aspects, such as the synthesis of various 3,3´-substituted catalysts to enable a catalyst library synthesis in combination with the high sensitivity, which would additionally hamper the catalyst storage, consequently made this catalyst design less appealing.



*Scheme 38: Reaction profile toward the synthesis of **IDPM-1**.*

4.2.3 Imidodiphosphorbis(iminosulfonylimino)imidate (IDPii)



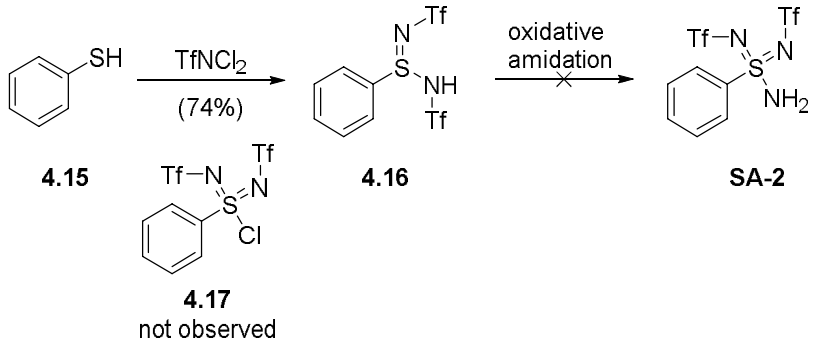
Scheme 39 Conceptualization of a more acidic imidodiphosphazene-derived catalyst by electron-withdrawing group replacement.

The next catalyst design focused on the application of phenylbis(trifluoromethylsulfonyl-imino)sulfonamide, $PhS(NTf)_2NH_2$ (**SA-2**) as electron-withdrawing substituent within the imidodiphosphate framework. The pKa difference of $TfNH_2$ (9.7 in DMSO) to **SA-2** (ca. 3.3 in DMSO) should, theoretically, result in a significantly more acidic imidodiphosphate catalyst. Notably, the utilization of $PhS(NTf)_2NH_2$ as core modification may not only enhance the acidity, but simultaneously installs another sterical element, besides the 3,3´-BINOL modification. Ideally these additional steric elements allow a more flexible and modular implementation of structural confinement. Based on this reasoning the application of $PhS(NTf)_2NH_2$ as electron-withdrawing substituent was further investigated in this work.

Unfortunately, initial experiments to access **SA-2** following the described literature did not furnish the desired sulfonamide (cf. chapter 2.4 Design of Strong Acids). We started with phenyl disulfide under identical reaction conditions as reported by Yagupolskii in the presence of freshly prepared $TfNCl_2$.[7] However, this reaction yielded phenyl(trifluoromethylsulfonyl-imino)sulfinic acid, PhS(NTf)OH and phenylbis(trifluoromethylsulfonylimino)sulfinic acid,

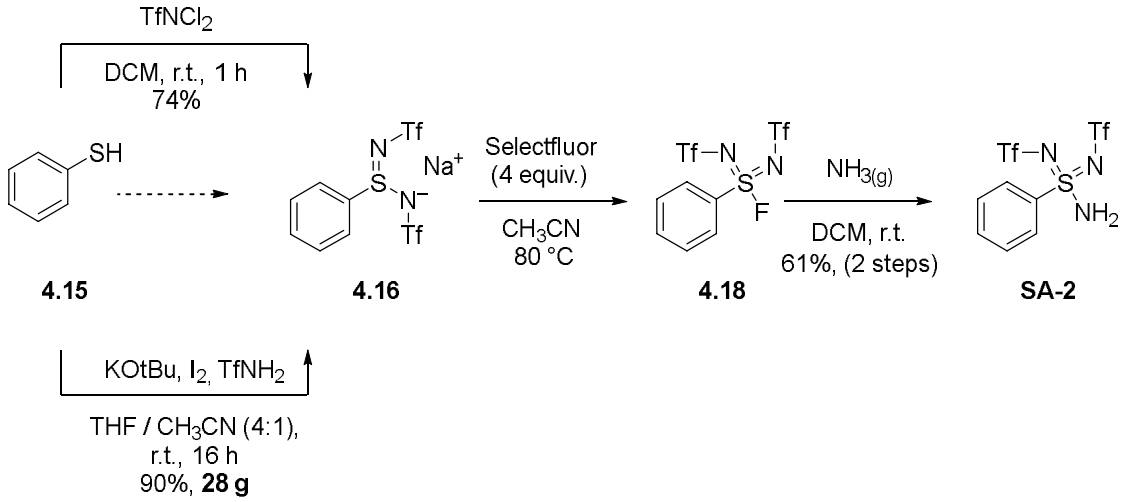
[7] Note: $TfNCl_2$ has been reported to spontaneously explode upon distillation at higher temperatures or in the presence of several organic solvents and needs to be handled with extreme caution.

PhS(NTf)NHTf **4.16**, respectively, as only products, without the observation of the described sulfonyl chloride (**4.17)**. Analogously, thiophenol (**4.15**) readily reacted with $TfNCl_2$ to afford PhS(NTf)NHTf$_2$ **4.16**. Based on these results the development of a new synthetic strategy to oxidatively access sulfonamide **SA-2** (S^{VI}) from **4.16** (S^{IV}) seemed to be necessary. With **4.16** in hand, we explored the oxidative amidation with commonly employed electrophilic aminating reagents, such as dinitrohydroxylamine or aminium carbamates, but did not result in promising reactivities.



Scheme 40: Initial attempts to obtain phenylbis(trifluoromethylsulfonylimino)sulfonamide.

Meanwhile, screening various oxidative fluorinating reagents revealed that Selectfluor® smoothly oxidized the sodium salt of **4.16** to the corresponding sulfonyl fluoride (**4.18**), which was readily available in analytically pure form by simple filtration through a plug of Celite. Sulfonyl fluoride **4.16** was directly converted into sulfonamide **SA-2** upon addition of ammonia gas.



*Scheme 41: New synthesis of phenylbis(trifluoromethylsulfonylimino)sulfonamides **SA-2**.*

The final sulfonamide was easily purified by common crystallization techniques, affording a crystalline material and allowed additional structural analysis by single crystal X-ray crystallography.

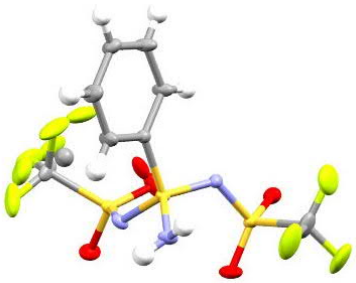
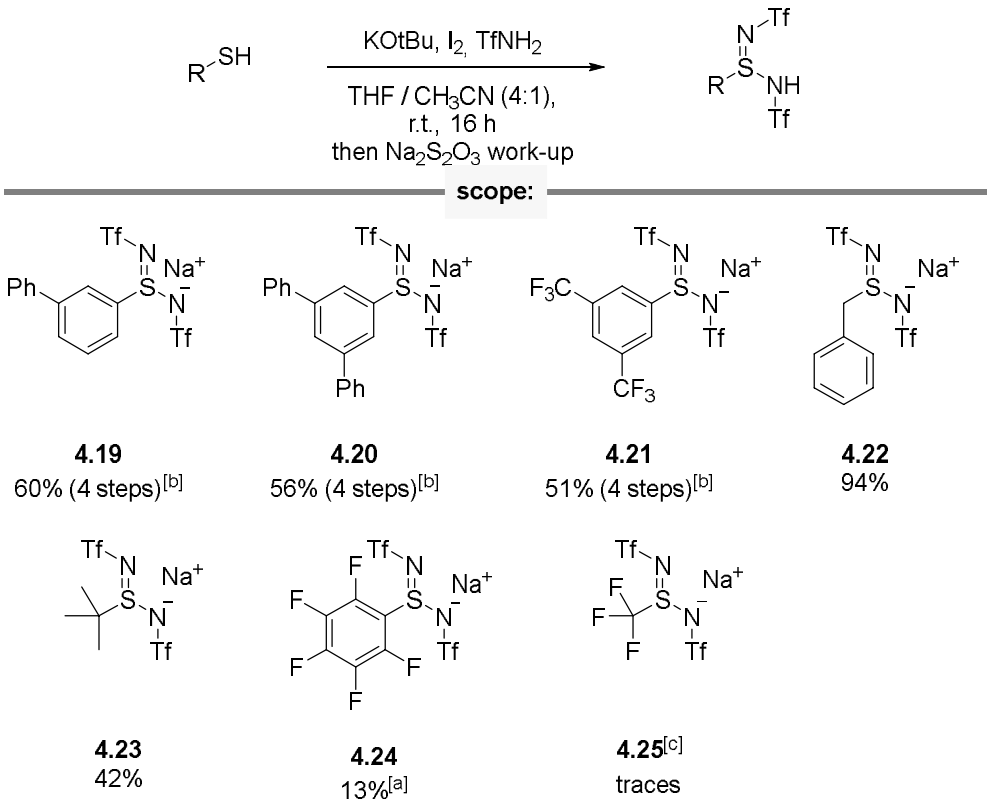


*Figure 5: X-ray structure of phenylbis(trifluoromethylsulfonylimino)sulfonamide **SA-2**. Carbon (grey), fluorine (green), oxygen (red), nitrogen (blue), sulfur (yellow).*

Nevertheless, this synthesis still relied on the utilization and isolation of dichlorotriflamide, which due to the high energetic properties limited scale-up experiments for safety reasons. More importantly, the utilization of $TfNCl_2$ released Cl_2 as side product during the reaction progress, resulting in partial aromatic chlorination, and significantly impeded the purification of the desired products. Therefore, an alternative strategy to oxidatively install NTf units on electron-rich thiols and to obtain the desired sulfinate **4.16** was desirable. Based on the strategy to *in situ* generate sulfenyl halides followed by halide substitution with $TfNH_2$, several oxidants were investigated. Fortunately, suitable reaction conditions were found, utilizing *in situ* generated *tert*-butyl hypoiodide (I-O^{t}Bu), serving as oxidant to form the envisioned sulfenyl iodide, followed by iodide substitution with $TfNH_2$ (Scheme 41). This protocol afforded phenylbis(trifluoromethylsulfonylimino)sulfinate **4.16** as sodium salt after an aqueous thiosulfate workup, provided high yields and was easily scalable to decagram scales. Subsequent electrophilic fluorination, followed by amidation furnished the required sulfonamide **SA-2** in reliably good yields.

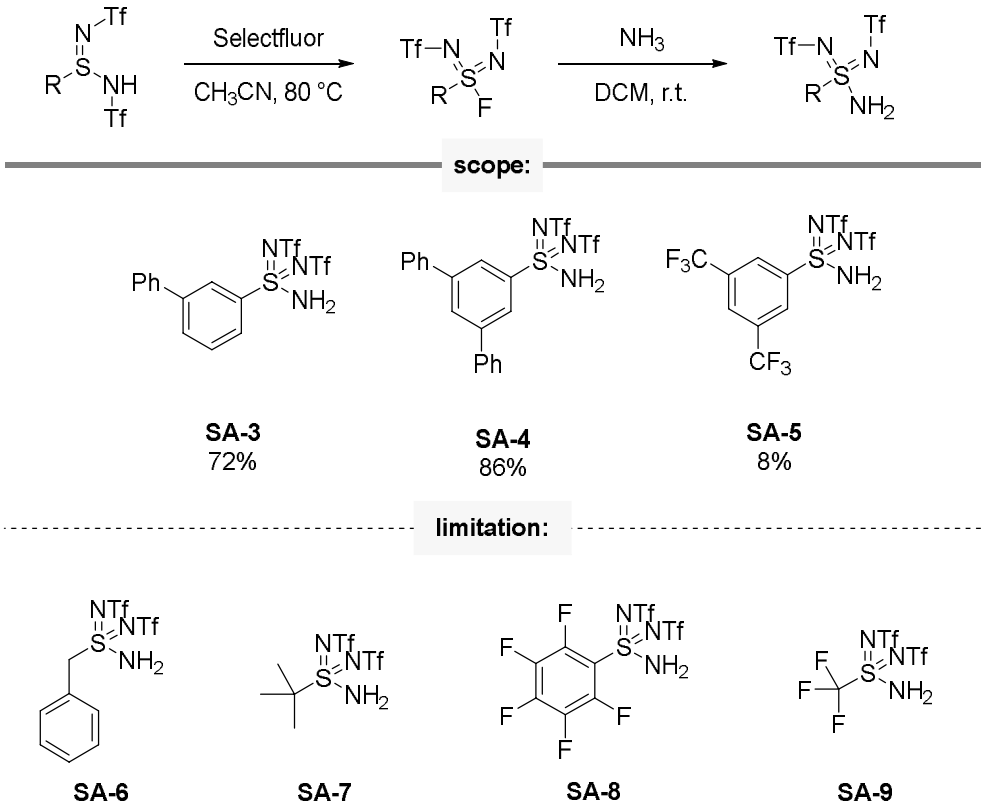
This new method also rapidly allowed the synthesis of distinct aryl-derived sodium bis(trifluoromethylsulfonylimino)sulfinates as shown in Scheme 42. These products were commonly isolated as sodium salts and directly converted into the desired bis(trifluoromethylsulfonylimino)sulfonamides following the new oxidative fluorination and amidation procedure. Noteworthy, the first oxidation step to afford sodium bis(trifluoromethylsulfonyl)sulfinates **4.19** to **4.23** proceeded smoothly with aryl, and alkyl derived thiols. The oxidation of pentafluorothiophenol **4.24** required the application of

dichlorotriflamide ($TfNCl_2$) to oxidatively install the trifluoromethylsulfonylimino groups. Trifluoromethyl disulfide was also explored, but only yielded traces of the desired product **4.25** (Scheme 42).



Scheme 42: Synthesis of sodium bis(trifluoromethylsulfonylimino)sulfinic acids [a] $TfNCl_2$ was used instead of KOtBu / I_2 / $TfNH_2$. [b] Yield refers to a 4-step sequence starting aryl bromides: including i) Grignard-formation ii) addition of sulfur (S_8) iii) $LiAlH_4$ reduction iiii) oxidative NTf-installment. [c] Trifluoromethyl disulfide instead of the corresponding thiol was applied as substrate.

The follow-up oxidation procedure to afford sulfonyl fluorides proceeded persuasively well with aryl-derived sulfinates to yield the desired sulfonamides **SA-3** to **SA-5** (Scheme 43). The same reaction protocol with benzyl-derived sulfinate **4.22** and tert-butyl-derived sulfinate **4.23** unfortunately did not afford the desired sulfonyl fluoride, but resulted in several unidentified side products. The oxidative fluorination of **4.24** did not proceed under standard reaction conditions. However, microwave irradiation at 120 °C for 24 h partially yielded the desired sulfonyl fluoride. Unfortunately, the final amidation with ammonia gas to access **SA-8** afforded several side products, presumably due to S_NAr reaction of ammonia with the perfluorinated aryl moiety. Trifluoromethyl-derived sulfinate **4.25** was not convertible into sulfonyl fluoride under various reaction conditions.

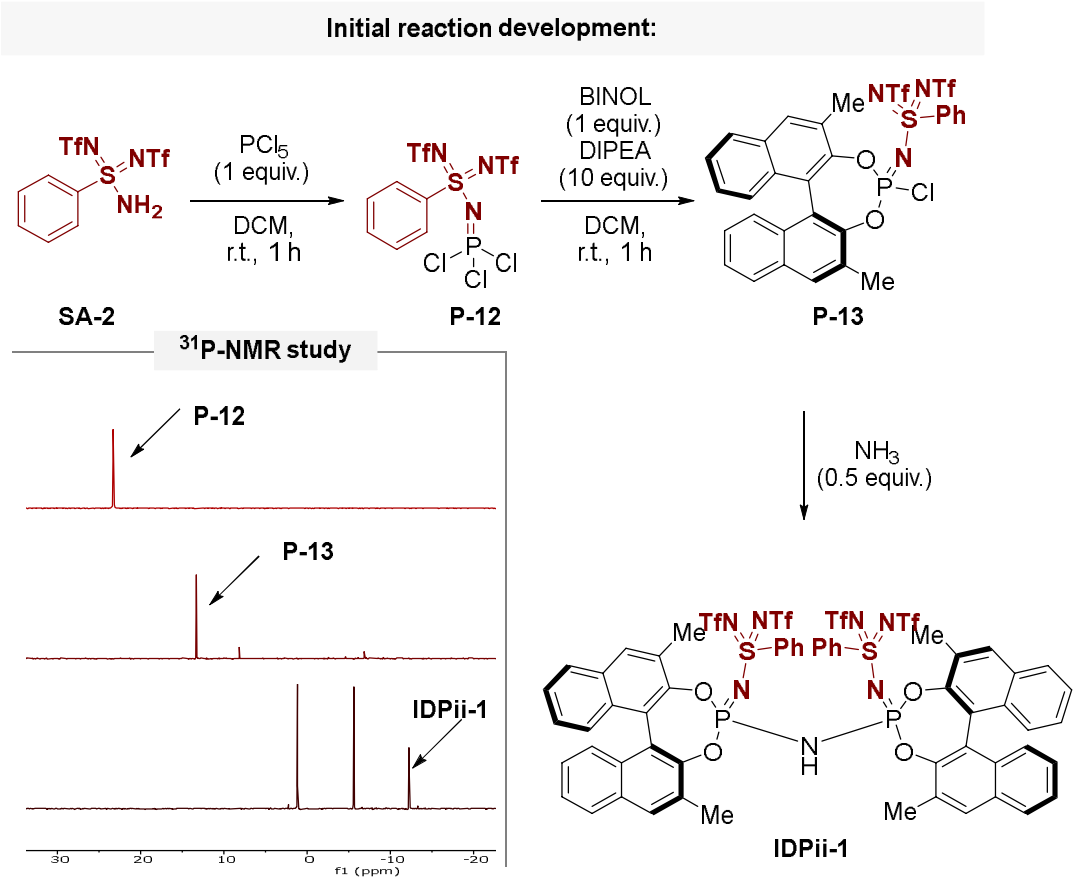


Scheme 43: Synthesis of bis(trifluoromethylsulfonylimino)sulfonamides. Scope and limitations.

With the new catalyst design and an efficient method to prepare sulfonamide **SA-2 to SA-5** in hand, we evaluated the synthesis of imidodiphosphorbis(iminosulfonylimino)imidate, **IDPii**. Two different strategy toward the **IDPii** motif have been explored. It should be noted that the first strategy, the standard dimerization strategy, provided a fast access to the desired motif. However, later it was found that **HCPC** as building block provided a more reliable synthetic strategy regarding yield and catalyst accessibility. The initial difficulties and challenges for each independent synthetic strategy are discussed in the following part.

4.2.3.1 Dimerization Strategy

Based on the previous **IDPi** dimerization strategy, we considered the formation of (*N*-sulfonyl)phosphoriminoyltrichloride **P-12** as crucial building block to access **IDPii**. Interestingly, sulfonamide **SA-2** readily reacted with PCl_5 in dichloromethane at r.t. liberating HCl gas. The gas development ceased after ca. 30 minutes and ^{31}P-NMR studies suggested quantitiative formation of **P-12** from PCl_5. Contrarily, the synthesis of *N*-(trifluoromethylsulfonyl)phosphorimoyl trichloride **P-8** requires higher temperatures and a more sophisticated protocol.[59] This reactivity difference may correlate with the acidity of the acidity of the utilized sulfonamides.



*Scheme 44: Initial reaction development of **IDPii** with 3,3´-(Me)-BINOL. ^{31}P-NMR spectra are shown for each intermediate.*

With **P-12** in hand, we followed the typical dimerization process. The addition of 3,3´-(Me)-BINOL in the presence of an organic base, such as DIPEA, smoothly furnished the desired phosphoryl chloride **P-13**, of which the formation was followed by ^{31}P-NMR. The addition of ammonia yielded the desired **IDPii** motif and a single crystal structure analysis of the sodium salt of **IDPii-1** confirmed the desired **IDPii** formation (Figure 6).

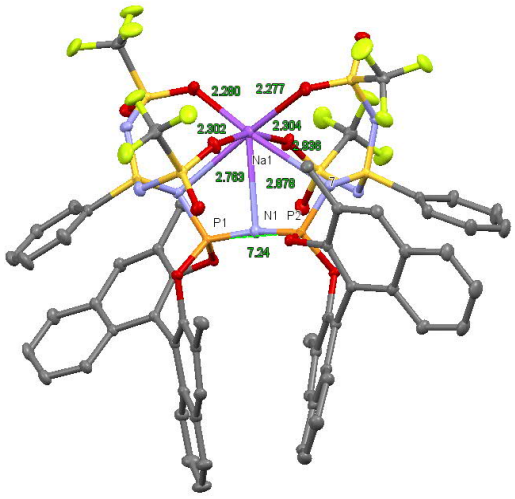
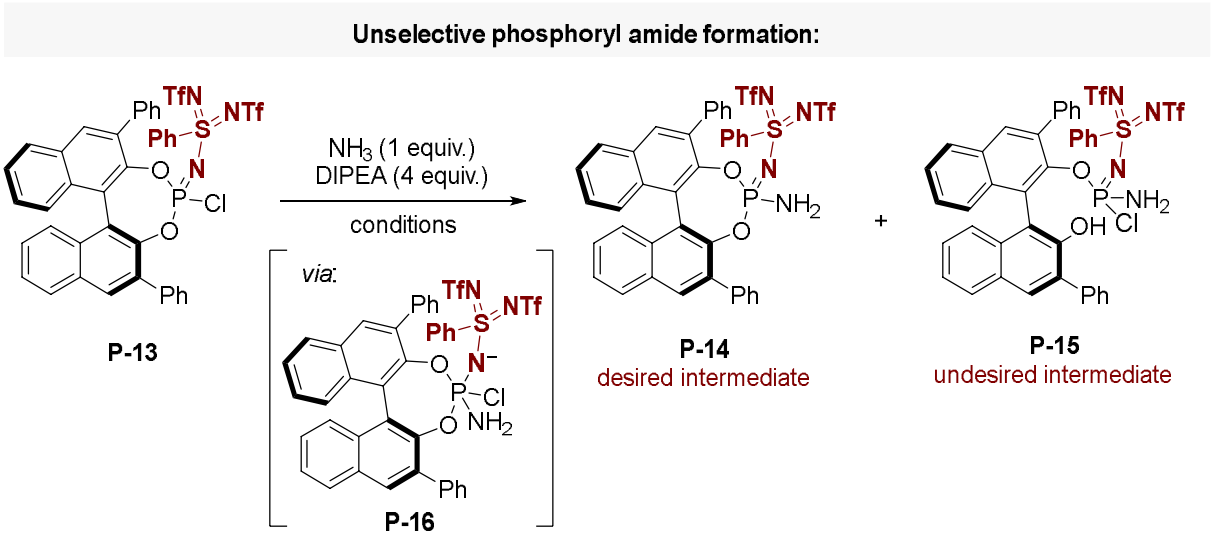


*Figure 6: crystal X-ray structure of **IDPii-1**. Carbon (grey), nitrogen (blue), oxygen (red), fluorine (green), phosphorous (orange), sodium (purple).*

Additional **IDPii** syntheses with structurally distinct 3,3´-aryl substituted BINOLs, however, were extremely low yielding. Therefore, optimization studies were performed and the formed side products further analyzed. It was believed that these side products (or unreacted intermediates) represent phosphoryl amide (**P-14**) and the corresponding phosphoric acid, which might have formed due to hydrolysis. However, additional studies revealed that the amide formation (**P-14**) remained the limiting step. The addition of ammonia or HMDS to phosphoryl chloride **P-13** did not selectively result in the P–Cl substitution, but resulted in a P–O bond cleavage of the BINOL-derived phosphoryl unit to afford **P-15**, presumably proceeding via intermediate **P-16**.



*Scheme 45: Proposed side product formation upon addition of ammonia to phosphoryl chloride **P-13**.*

A crystallographic analysis of a single crystal X-ray structure of hydrolyzed side product **P-15** supports our proposed pathway (Figure 7).

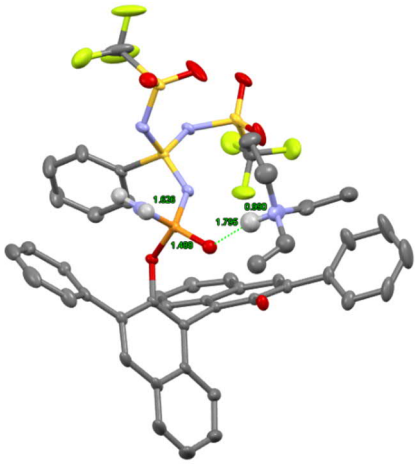
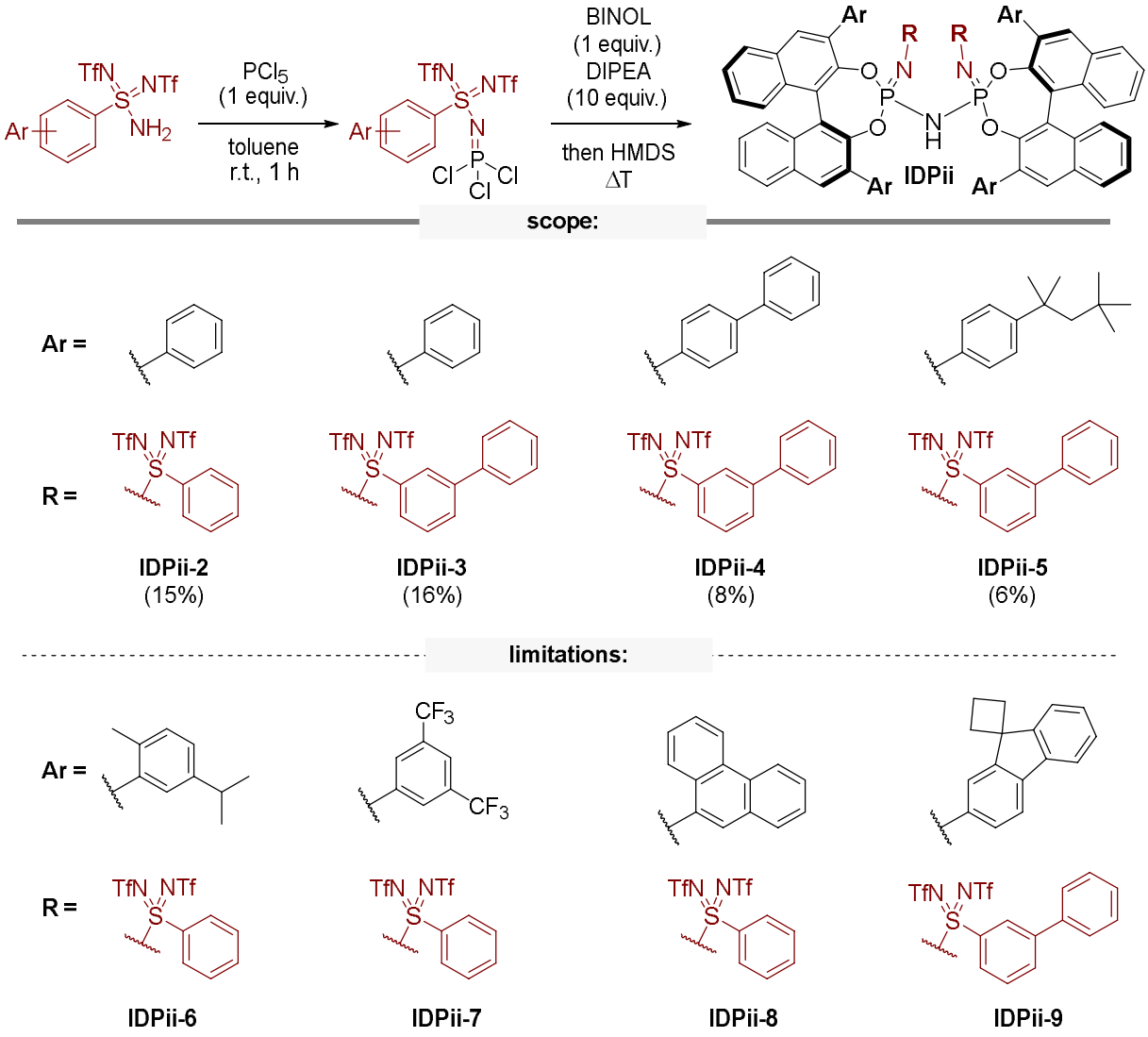


*Figure 7: Crystal structure of hydrolyzed side product **P-15** as DIPEA salt. Carbon (grey). nitrogen (blue), oxygen (red), fluorine (green), phosphorous (orange).*

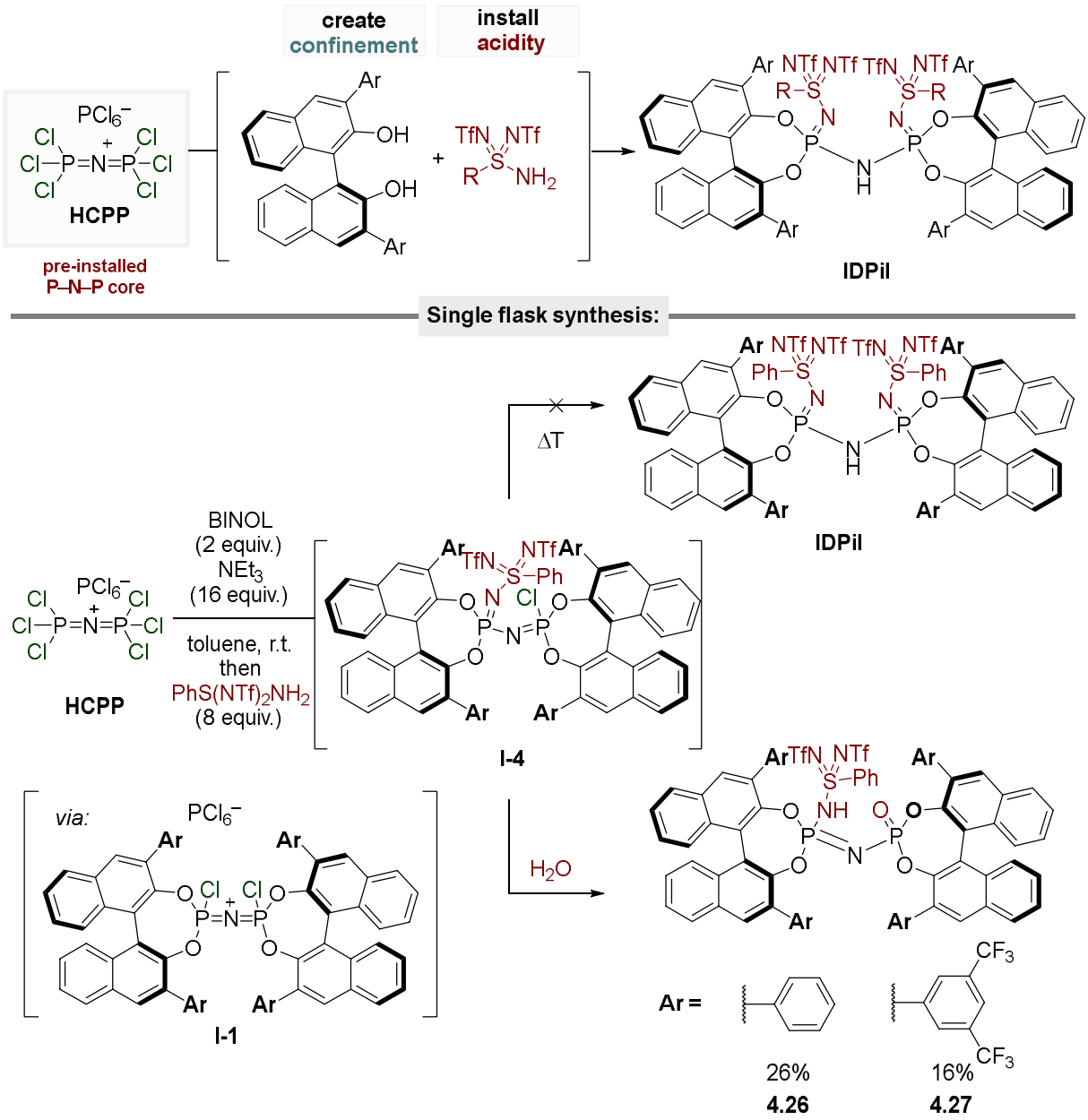
Ammonia and HMDS (TMS_2NH) equally afforded the undesired intermediate as major side product. An extensive solvent screening did not significantly improve the desired amide (**P-14**) formation. Nevertheless, toluene represented the solvent of choice due to a slightly enhanced phosphoryl amide **P-14** formation. With slightly improved reaction conditions the applicability of various 3,3´-substituted BINOLs and distinct aryl bis(trifluoromethylsulfonylimino)-sulfonamides was explored (Scheme 46). **IDPiis 2-5** were accessible, albeit in low yields due to the described side product formation. Unfortunately, *ortho*- or *meta*-substituents on the 3,3´-BINOL substituent did not yield the desired **IDPii** motifs, as shown with structures **IDPii 6-9** and therefore significantly diminished the catalyst accessibility.



*Scheme 46 Synthesis of structurally distinct **IDPii** motifs. Successful catalyst scaffolds and selected limitations are shown.*

4.2.3.1 HCPC as building block to access IDPii

To circumvent the inherent challenge of dimerizing two monomeric phosphoryl units in combination with an unselective phosphoryl amide **P-14** formation we investigated the applicability of hexachlorobisphosphazonium salts as building block. As shown for the synthesis of **IDPi** (chapter 2.1.3 Imidodiphosphorimidates (IDPi), a stepwise P–Cl substitution of intermediate **I-1** with our new sulfonamide **SA-2** was envisioned.



*Scheme 47: Idealized **IDPii** synthesis with **HCPP** as building block. Unsuccessful attempts to access **IDPii** from **HCPP** led to the synthesis of a new catalyst motifs **4.26** and **4.27**, respectively.*

Based on our previous success on synthesizing **IDPi** starting from **HCPP**, identical reaction conditions toward the synthesis of **IDPii** were investigated. Interestingly, the P-Cl substitution

of intermediate **I-1** was significantly slower, whereas the final chloride substitution of **I-4** with **SA-2** was not observable under identical reaction conditions (Scheme 47). This reactivity trend might be explainable with the reduced nucleophilicity of sulfonamide **SA-2** and the increased steric demand, hampering the P-Cl substitution of **I-1** and **I-4,** respectively. Although **IDPii** was not accessible under these reaction conditions, hydrolysis of intermediate **I-4** furnished novel non-C_2 symmetric (trifluoromethylsulfonylimino)iminoimidodiphosphates **4.26** and **4.27** in moderate yields of 26% and 16% yield. The molecular structure of **4.26**, coordinated to a water molecule was confirmed by single crystal X-ray structure analysis, illustrating the bifunctional property.

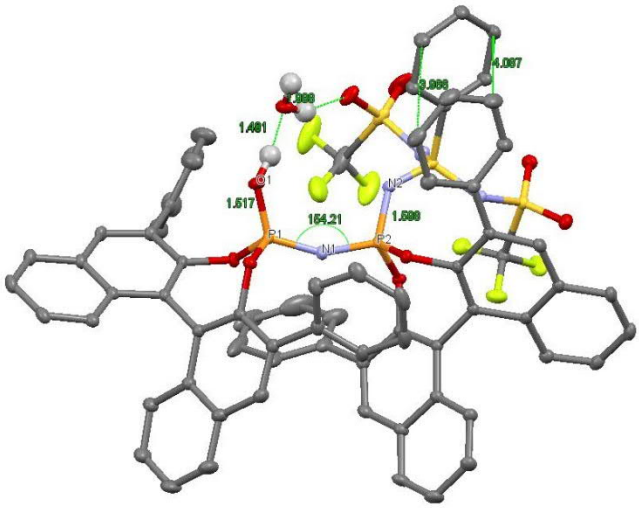
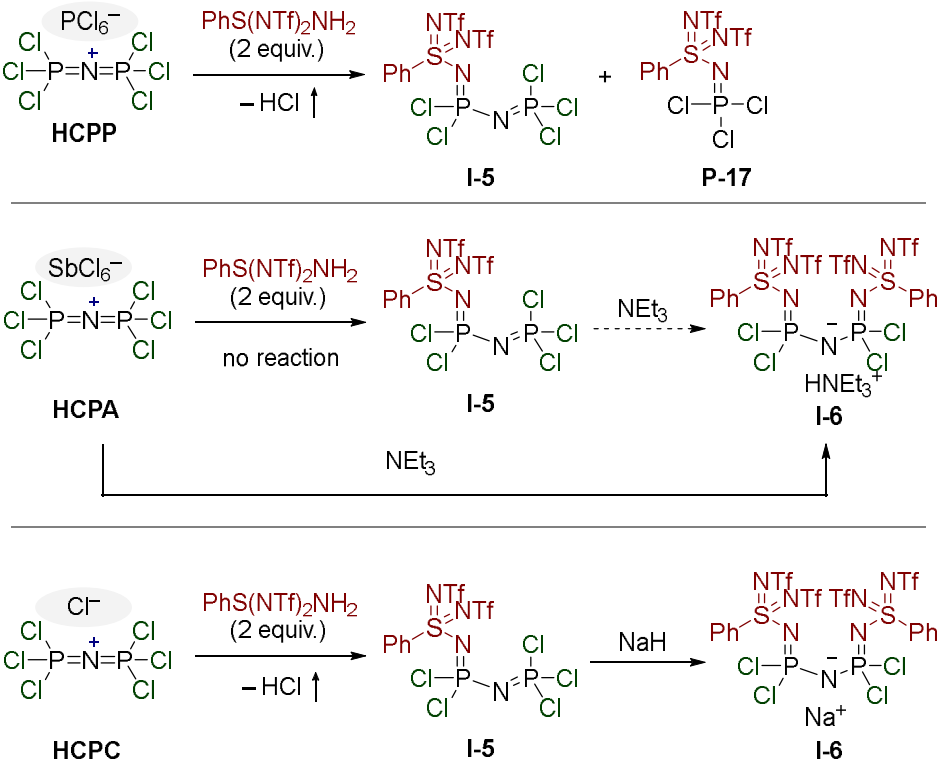


*Figure 8: Single crystal X-ray strucutre of **4.26**. Most hydrogen atoms are omitted for clarity. Hydrogen (light grey), carbon (grey), nitrogen (blue), oxygen (red), fluorine (green), phosphorous (orange).*

To circumvent the limitation of reacting weakly nucleophilic sulfonamide **SA-2** with weakly electrophilic intermediate **I-4**, it was assumed that the direct reaction of sulfonamide **SA-2** with **HCPP**, exploiting the immense electrophilic character of this reagent, followed by BINOL installation would be more effective (Scheme 48). To our delight, we observed the desired transformation of **HCPP** with sulfonamide **SA-2**, liberating HCl gas to form **I-5**, without the requirement of a base. Unexpectedly, the corresponding PCl_6^- counteranion also reacted with sulfonamide **SA-2**, to afford *N*-(phenylbis(trifluoromethylsulfonylimino)sulfonyl)-phosphoriminoyltrichloride **P-17** as undesired side product, which would most likely interfere in the BINOL-installation step. Therefore, the PCl_6^- counteranion of **HCPP** has been exchanged with a less nucleophilic hexachloroantimonate counteranion to afford **HCPA**. Interestingly, **HCPA** did not react with sulfonamide **SA-2** under identical reaction conditions, indicating that the basicity of the corresponding counteranion has a significant impact on the reaction with

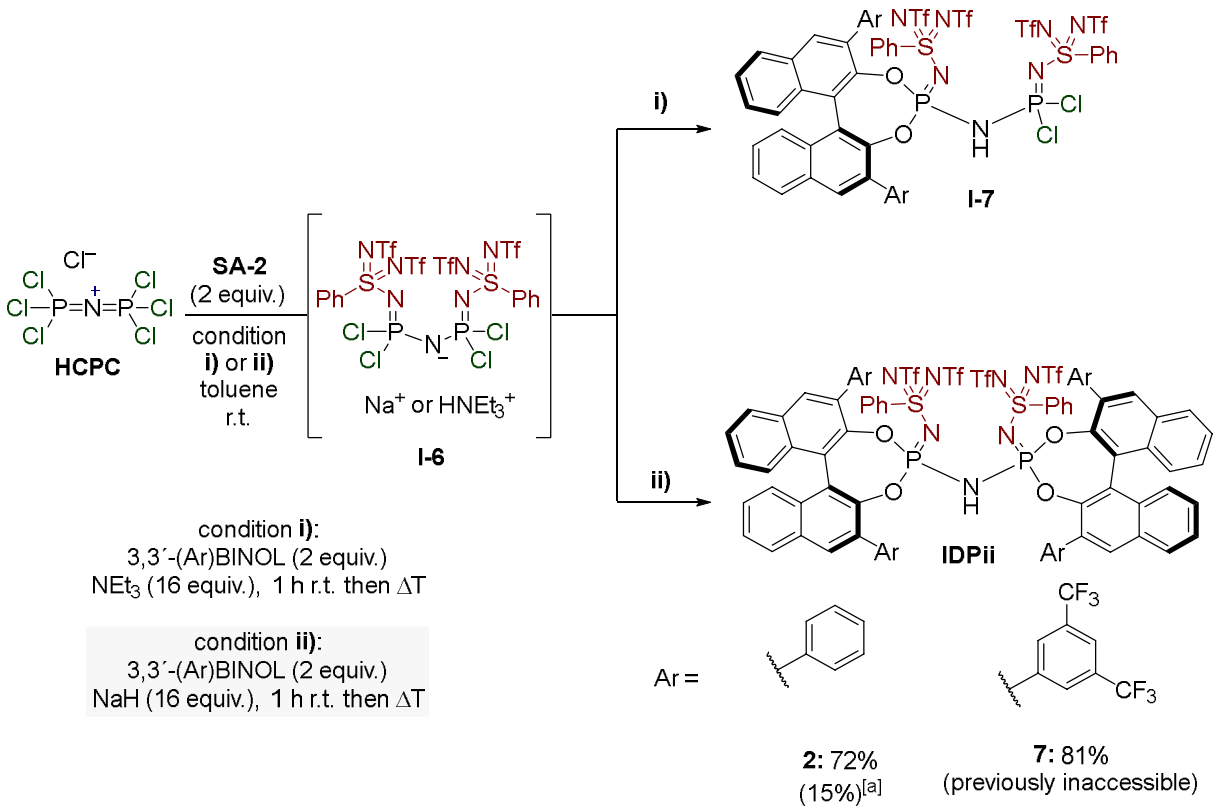
acidic sulfonamide **SA-2**. Addition of organic bases, such as NEt_3 immediately furnishes intermediate **I-6**, in which two sulfonyl units have been installed onto the phosphazen core. Contrarily, the replacement of the PCl_6^- counteranion with a chloride counteranion, to provide hexachlorobisphosphazonium chloride **HCPC**, results in a rapid formation of **SA-2** with **HCPC** to yield intermediate **I-5** without any other observable side product formation. Addition of an organic base, such as NEt_3 or DIPEA afforded the desired intermediate **I-6** and was envisioned to represent the ideal building block toward the synthesis of **IDPii** due to the clean reaction profile without the formation of any potentially disturbing side products. **HCPC** was synthesized on multigram-scale based on a combinatorial modified synthesis of Becke-Goehring and Manners.[64, 66]



*Scheme 48: Reaction of sulfonamide **SA-2** with hexachlorobisphosphazonium salts.*

Next, we investigated the BINOL installation event with intermediate **I-6** as starting material. Interestingly, BINOL reacted with **I-6** in the presence of organic bases, such as NEt_3 or DIPEA (Scheme 49). Unfortunately, only a single BINOL addition was observed to afford intermediate **I-7**. High temperatures, catalytic amounts of 4-DMAP or any other nucleophilic catalyst did not improve the reaction outcome. Although the desired **IDPii** did not form under these reaction conditions **I-7** might be of interested for future applications. Nevertheless, we reasoned that the lack of reactivity results from insufficient nucleophilicity of the utilized BINOLs in combination with reduced electrophilicity of the tetrachlorido phosphazenate (**I-6**) scaffold. We

therefore investigated the applicability of sodium hydride (NaH) as strong base to enhance the nucleophilicity of BINOLs to *in situ* afford BINOLates. After conducting additional optimization studies, we found suitable reaction conditions, in which sulfonamide **SA-2** first reacts with **HCPC** in toluene to afford **I-5** and subsequent addition of NaH affords intermediate **I-6**. The addition of BINOL and elevated reaction temperatures readily afforded the desired **IDPii** motif within reaction times of ca. 24 h. Unprecedented high yields (72%) for **IDPii-2** were achieved, whereas the previous dimerization strategy yielded the same catalyst motifs in significantly lower yields after extensive optimizations (15%). Additionally, this new strategy allowed the synthesis of previously inaccessible **IDPii-7** in a satisfactory yield of 81%. Once again, these results underline the superior imidodiphosphate-derived catalyst accessibility by employment of hexachlorobisphosphazonium salts as building block.



*Scheme 49: A single-flask synthesis of **IDPii** with **HCPC** as building block. [a]Yield refers to previous dimerization strategy.*

4.3: Application of IDPii

4.3.1 Lewis Acidity Comparison of Silylated IDPi and IDPii

With these novel catalysts in hand, we aimed toward a reactivity comparison of **IDPi** and **IDPii**, applying the same phenyl-derived BINOL substituent to evaluate the acidifying effect of our new core modification.

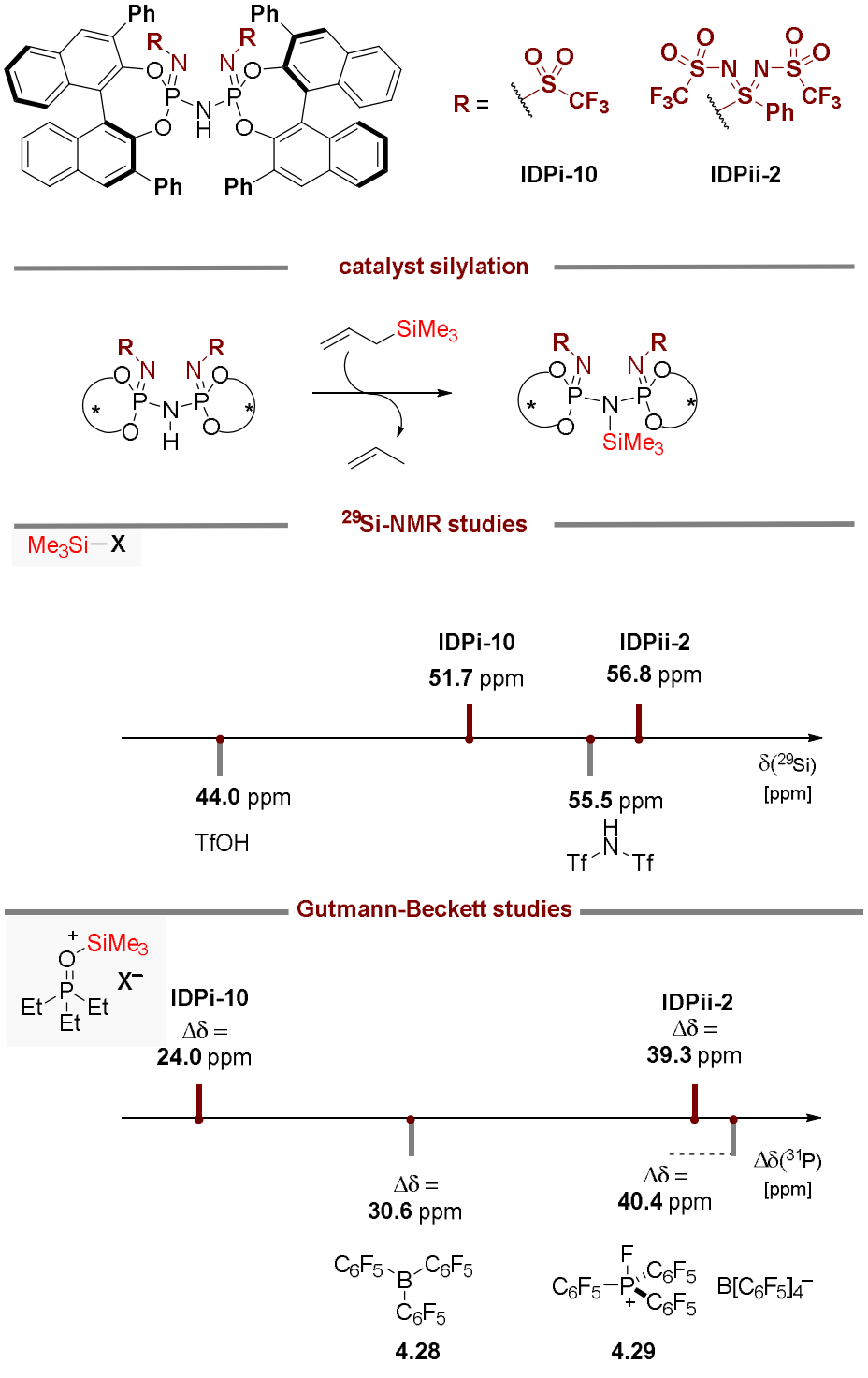
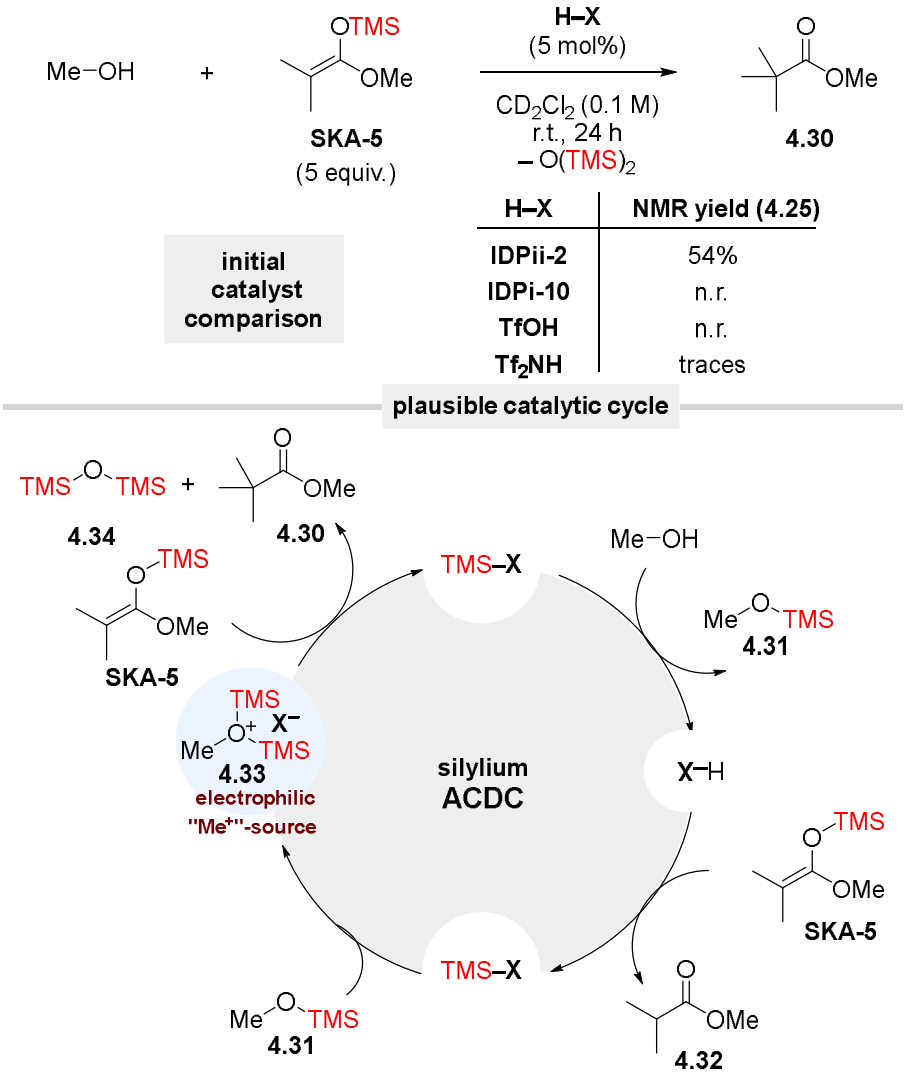


*Figure 9: ^{29}Si-NMR and Gutmann–Beckett studies to compare the Lewis acidities of **IDPii** and **IDPi**.*

In light of recent ^{29}Si-NMR studies from Oestreich and our group in combination with Gutmann–Beckett studies, we focused on a Lewis acidity comparison of **IDPi-10** and **IDPii-2**. Advantageously, these catalyst motifs rapidly react with allyltrimethylsilane to furnish the Lewis acidic silylated imidodiphosphazene catalysts and deprotosilylate any protic nucleophilic impurities, which might negatively influence our Lewis acidity study. It should be noted that **IDPs** and ***i*IDPs** were not included in our studies due to inefficient catalytic activity as Lewis acid. As expected, our new catalyst motif **IDPii-2** illustrated a much higher ^{29}Si-chemical shift, in direct comparison to **IDPi-10,** suggesting a significantly enhanced Lewis acidity. Interestingly, **IDPii-2** exceeded the chemical shift of trimethylsilyl triflate (TMSOTf) and bis(trifluoromethylsulfonyl)imide ($TMSNTf_2$), which are commonly employed super acids in organic synthesis. In agreement with our experience of **IDPi** catalysis, trimethylsilylated **IDPi-10** represents a stronger Lewis acid in comparison to TMSOTf, but remains a significantly weaker Lewis acid than $TMSNTf_2$. The same Lewis acidity trend has been observed in our Gutmann–Beckett study, in which **IDPii-2** resulted in a chemical shift of triethylphosphine oxide of 39.3 ppm, whereas the utilization of **IDPi-10** led to a shift of $\Delta\delta$ = 24.0 ppm. These findings support our hypothesis of an increased Lewis acidity of **IDPiis** in direct comparison to **IDPis**. Interestingly, our Gutmann–Beckett study indicated a Lewis acidity of **IDPii-2,** which was similar to the extremely Lewis acidic fluorophosphonium tetrakis(pentafluoro-phenyl)borate salt **4.29**, initially reported by Stephan *et. al.* and has been successfully utilized for various challenging transformations, proceeding *via* the formation of carbocationic intermediates. Often these extremely Lewis acidic catalysts require strictly inert reaction conditions to prevent catalyst degradation, especially due to hydrolysis pathways in the presence of water or alcohols. In contrast, our catalyst motifs possesses the advantage of extreme Lewis acidity, without the requirement of inert reaction conditions, due to the catalytic deprotosilylation-cycle in the presence of sacrificial silylating reagent. Therefore, **IDPiis** with their high Lewis acidity and simple applicability might evolve as suitable alternatives to conventional Lewis acidities, which most often require sophisticated Schlenk-techniques and suffer from stability issues. Additionally, **IDPiis** might enable previously elusive asymmetric transformation, which require the stabilization of extremely reactive carbocationic intermediates.

4.3.2 Catalytic Applications of IDPii

To demonstrate the advantage of silylium ACDC in combination with the high Lewis acidity of **IDPii** we reinvestigated the α-alkylation of silyl ketene acetals. We were particularly interested in the α-alkylation of silyl ketene acetals utilizing methanol as *electrophilic* methyl surrogate, which is normally an incompatible *nucleophile* for many strong Lewis acids and transition metal catalysts. We performed an initial catalyst screening for the α-methylation of **SKA-5**, comparing **IDPii-2, IDPi-10** with commonly employed super acids TfOH and $HNTf_2$ (Scheme 50). Most notably, the desired transformation proceeded only in the presence of our new **IDPii** motif, whereas all other tested catalysts did not engage in the desired transformation.



Scheme 50: Initial catalyst screening for the α-methylation of a silyl ketene acetal with methanol. [a]Yields were determined by ^{1}H-NMR spectroscopy with mesitylene as internal standard.

Recent unpublished studies from Mathias Turberg revealed that methyl-derived esters might also serve as electrophilic methylating reagent under highly Lewis acidic conditions. Therefore,

we conducted additional NMR studies to elucidate the origin of the methyl group within our α-alkylation strategy. In this regard, the methyl group might result from:

1. methyl ester **4.32**, which formed within the initial deprotosilylation cycle,
2. methyl pivalate **4.30**, which represents the final product,
3. the envisioned bis(trimethylsilyl)methoxonium ion **4.31**.

If the methyl group would result from the envisioned ion pair **4.31** disiloxane **4.34** would consequently form as a stoichiometric side product. Contrarily, if the methyl group originates from methyl esters **4.30** or **4.32**, the corresponding silyl esters would form as terminal side products and should be detectable within our NMR studies.

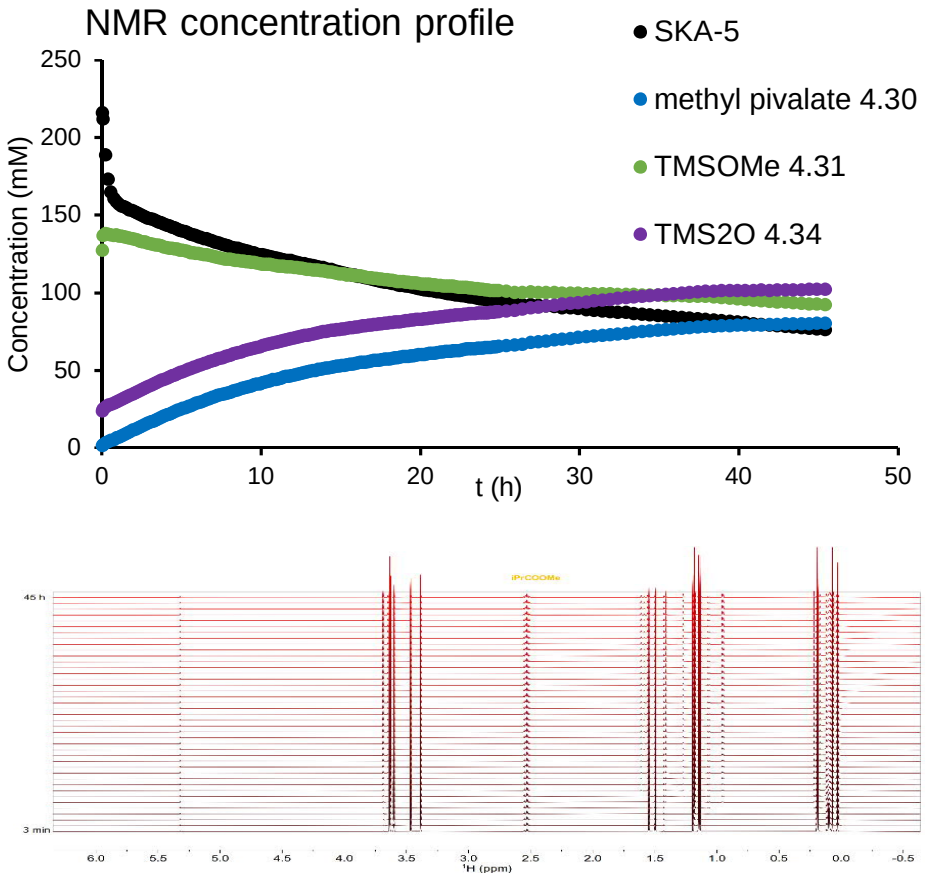


Figure 10: ^{1}H NMR spectra taken at different time points during the reaction.

Based on our NMR concentration profile (Figure 10) we could evidently observe a correlation between the formation of α-alkylated ester **4.30** and disiolxane **4.34**, thus indicating that the methyl group might have resulted from the postulated ion pair **4.33**. The formation of silylated ester was not observed within these studies. [8]

[8] The following NMR studies were performed in collaboration with Dr. Markus Leutzsch

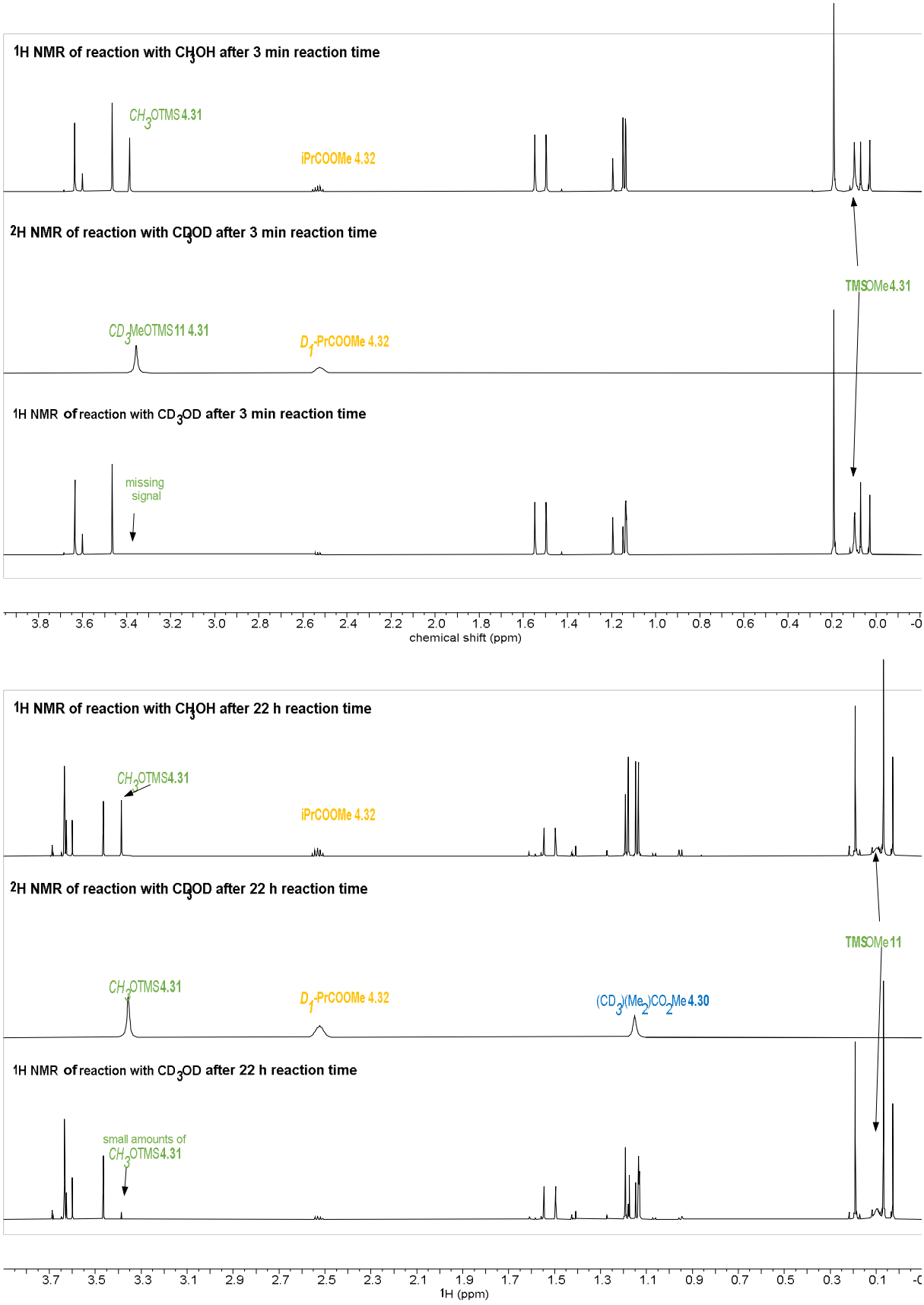
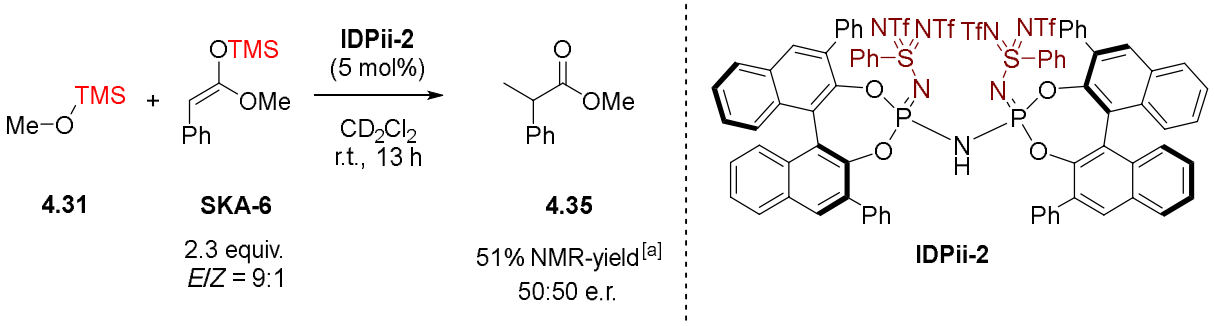


Figure 11: [1]H and [2]H-NMR-spectra after 3 min and 22 h reaction with MeOH and MeOH-d4.

To gain additional information, the same alkylation experiment was performed with deuterated MeOH-d_4. Figure 11 shows ^{1}H and ^{2}H NMR spectra at the beginning of the reaction in comparison to the non-deuterated reaction. The methyl signal of TMSOMe was missing in the ^{1}H-NMR, whereas the ^{2}H-NMR spectrum illustrates the OCD_3 as well as the signal of $Me_2C\underline{D}CO_2Me$, originating from the initial deprotosilylation cycle of $CD_3O\underline{D}$. Additionally the incorporation of the CD_3 group in the final α-alkylated ester **4.31** was observed (*ca.* 1.15 ppm) and thus clearly indicates that the electrophilic methyl group originated from the utilized deuterated methanol-d_4.

These results undeniably support our initial proposed concept of rendering alcohols electrophilic through silylium actvation and illustrate that the *in-situ* generation of ion pairs based on bis(trimethylsilyl)alkoxonium ion provides a suitable platform to develop asymmetric transformations.

We turned our focus toward the enantioselective α-methylation of silyl ketene acetal **SKA-6**. Not surprisingly, initial experiments led to the formation of the desired α-methylated esters **4.35** in 51% NMR-yield, albeit in no enantioenrichment of the desired product (Scheme 51).[9]

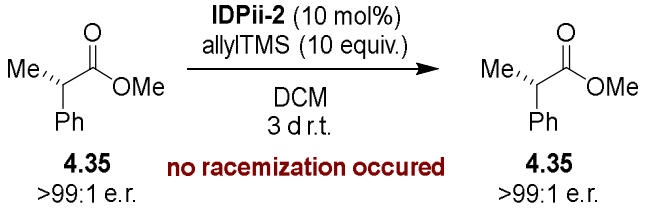


*Scheme 51. Initial experiments toward the enantioselective α-methylation of silyl ketene acetal **SKA-6**. [a] NMR-yield was determined with Ph_3CH as internal standard.*

We wondered if the high Lewis acidity of **IDPii-2** might result in the enolization of esters and would therefore result in a racemization of enantiomerically enriched α-alkylated esters. In this regard, enantiomerically pure ester **4.35** was subjected to the reaction conditions in the presence silylated **IDPii**. Fortunately, no undesired racemization of **4.35** was observed, indicating that enolization due to the strong Lewis acidity of **IDPii** could be neglected and that the lack of

[9] Note: pre-silylated methanol, trimethylsilyl methoxyether was applied to prevent stoichiometric ester side product formation due to the initial deprotosilylation cycle of methanol and to lower the overstoichiometric SKA proportion.

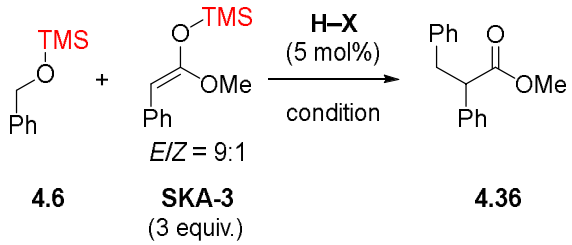
enantioinduction most likely resulted from insufficient stereofacial bias within the reaction progress (Scheme 52**)**.



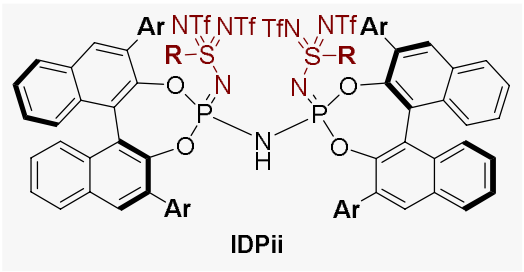
*Scheme 52: Racemization control experiment of enantiomerically enriched ester **4.35** under **IDPii** Lewis acid conditions.*

Considering that the methylation of SKAs with methanol is arguably an extremely challenging transformation regarding efficient stereofacial control from the enantiopure counteranion, we revisited the applicability of the structurally more biased benzyl alcohol-derived trimethylsilyl ether **4.6** (c.f. chapter: 4.2.1 Motivation: The IDPi Catalyzed α-Alkylation of Silyl Ketene Acetal). We considered that the formation of the bis(trimethylsilyl)benzyloxonium phosphazenate ion pair might result in π-π stacking of the benzyl residue with the aromatic site from the catalyst, and thus might result in stereofacial bias. In this context, we hoped to have a suitable platform to further optimize the reaction conditions regarding the identification of a privileged catalyst scaffold, which may induce sufficient levels of enantioselectivity. We also applied trimethylsilyl benzyloxy ether as substrate to avoid the deprotosilylation cycle of the corresponding alcohol and the overstoichiometric excess of sacrificial **SKA-3** as silylating reagent (Table 4). Due to the higher reactivity of **4.6** in direct comparison to methanol, we could lower the reaction temperatures to –50 °C and observed full conversions in all shown experiments. Unfortunately, an extensive solvent and **IDPii** screening did not lead to any considerable enantiomeric enrichment of the desired α-benzylated ester **4.36.** Utilizing silylated benzyl alcohols with enlarged silyl groups, such as triethylsilyl- (TES, **4.8**) and tert-butyldimethylsilyl (TBS, **4.9**) ceased the reactivity. The same reactivity trend was observed with TBS-derived silyl ketene acetal **SKA-7**. Moreover, replacing the nucleophile **SKA-3** with **SKA-2** did not lead to any noteworthy enantioinduction.

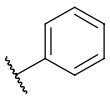
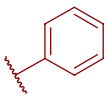
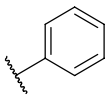
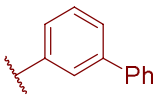
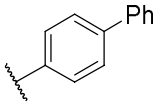
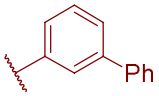
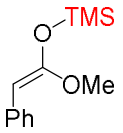
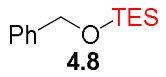
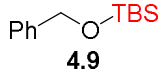
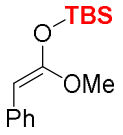
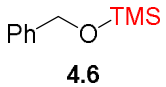
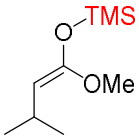
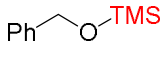
*Table 4: Reaction condition screening for the enantioselective α-benzylation of silyl ketene acetals (selected examples). [a] Conversion refers to the consumption of **4.6**.*



4.6 **SKA-3** (3 equiv.) **4.36**



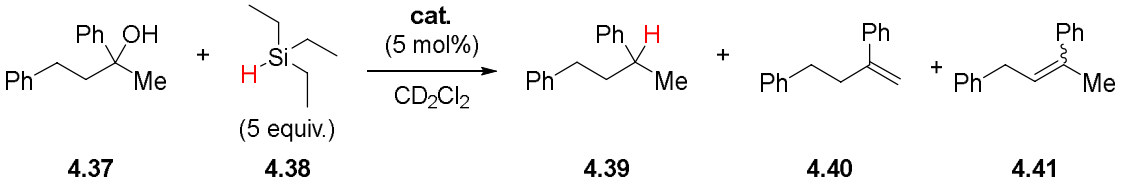
IDPii

catalyst	Solvent	temp. [°C]	conv.[a]	e.r.
Ar =  R =  **IDPii-2**	DCM $CDCl_3$ Et_2O CyHex toluene	0	full	49:51 50:50 50:50 48.5:51.5 51:49
Ar =  R =  **IDPii-3**	DCM $CDCl_3$ Et_2O CyHex toluene	–10	full	50:50 49:51 50:50 51:49 50:50
Ar =  R =  **IDPii-4**	DCM $CDCl_3$ Et_2O CyHex toluene	–50	full	50:50 50:50 49:51 50:50 50:50
nucleophile-	**electrophile variation**			
 **SKA-3**	 **4.8**	DCM	r.t.	n.r.	–
	 **4.9**	DCM	r.t.	n.r.	–
 **SKA-7**	 **4.6**	DCM	r.t.	n.r.	–
 **SKA-2**	 **4.6**	DCM $CDCl_3$ Et_2O CyHex toluene	–50	full	50:50 50:50 50:50 49:51 50:50

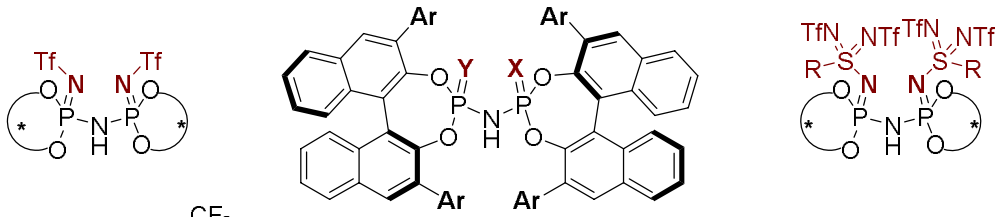
Based on these disappointing results, we revisited the conceptual design for the α-alkylation strategy. As shown before, the formation of Meerwein-type salt, such as **4.31** represents a key intermediate for our α-alkylation strategy. However, the nucleophilic addition of silyl ketene acetals to the ion pair **4.31** proceeds most likely via an S_N2-type mechanism, while the electrophilic site of the ion pair could be located out of reach of the **IDPii** induced chiral microenvironment. We wondered if we could form an ion pair, in which the electrophilic site is closer located within the chiral cavity of the **IDPii** counteranion.

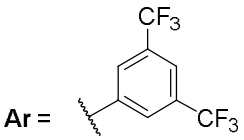
Following the same strategy, tertiary alcohols should undergo the deprotosilylation cycle, followed by re-silylation to afford a bis(trimethylsilyl)alkoxonium ion. However, due to the inherently higher stabilization effect of the ternary alkyl moiety, disiloxane might expel to afford a tertiary carbocation and thus might form a tight ion pair with the corresponding imidodiphosphazenate counteranion and may result in an enhanced stereofacial induction.

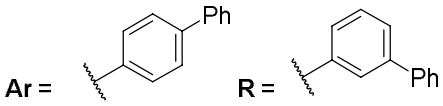
To probe this strategy, we utilized tertiary alcohol **4.37** as substrate and replaced nucleophilic silyl ketene acetals with triethylsilane (**4.38**). Triethylsilane was considered to represent a sterically enlarged nucleophile and additionally prevents any possible issues regarding the *E*/*Z* geometry of the previously utilized silyl ketene acetals (Scheme 53).



Catalyst comparison







IDPi-11

temp.	conv.[a]	4.39	4.40	4.41
r.t.	full	7	39	54

IDPii-4

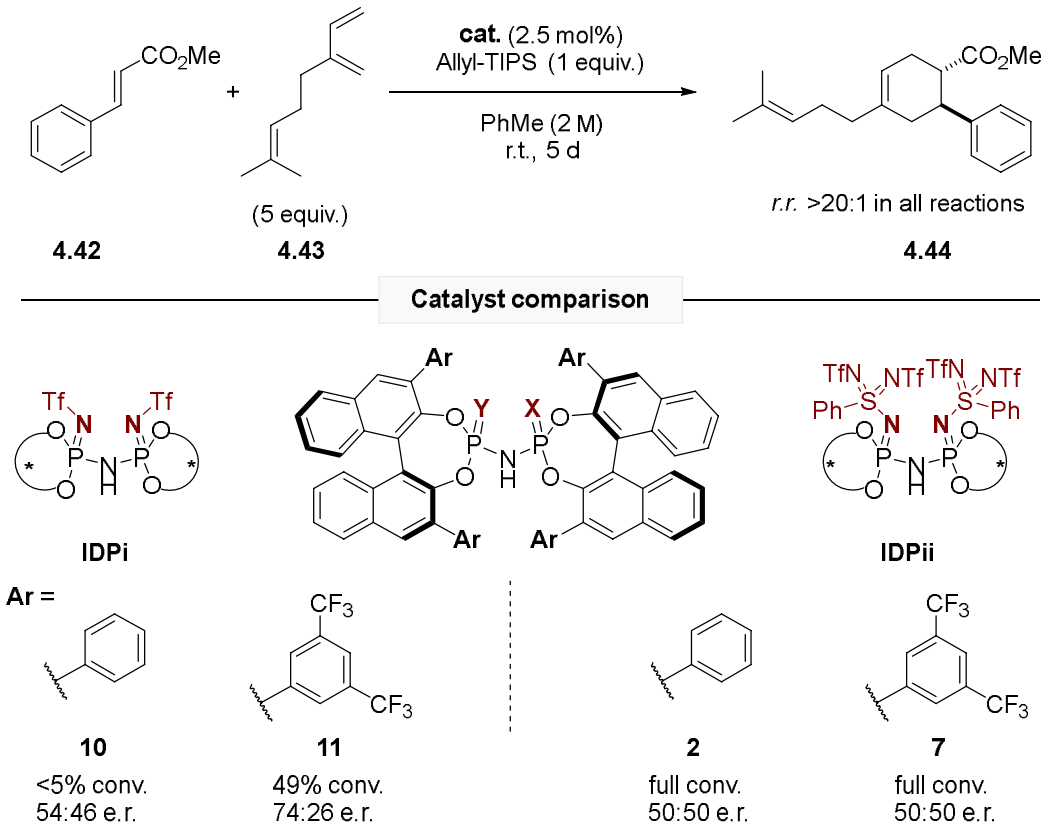
temp.	conv.	4.39	4.40	4.41
r.t.	full	97 e.r. = 49:51	–	**3**
–80°C	full	98 e.r. = 50:50	–	**2**

*Scheme 53: The hydridodehydroxylation in the presence of **IDPi-11** and **IDPii-4** catalysts.*

The efficiency of **IDPi-11** and **IDPii-4** as catalysts were compared at room temperature and the reaction monitored by ^{1}H-NMR analysis. Interestingly, **IDPi-11** resulted predominantly in the dehydrated product to afford olefins **4.40** and **4.41**, presumably due to the comparably high basicity of the corresponding **IDPi** phosphazenate counteranion. Contrarily, **IDPii** afforded the desired hydridodehydroxylated product **4.39** in almost quantitative NMR conversion. The same reaction profile was observed when the temperature was lowered to –80 °C. However, all these experiments did not yield any enantioenriched terminal products.[10]

[10] Triethylsilane as nucleophile was also replaced with allyltrimethylsilane. A similar reactivity trend was observed as shown in Scheme 53. However, also the final products did not show any noteworthy enantioenrichment. Additionally, various alcohols were explored with triethylsilane or allyltrimethylsilane as nucleophile but did not result in enantioinduction in the final products.

Next, we compared the efficiency of **IDPii** with **IDPi** in the Diels–Alder reaction of cinnamate **4.42** with myrcene **4.43** under optimized reaction conditions.[11] As expected, **IDPii-2** displays a significantly higher reactivity, afforded the desired product in high yields, whereas **IDPi-10** afforded traces of the desired product. These results underline again the enhanced reactivity of **IDPii**. Unfortunately again, **IDPiis** did not result in any enantioenriched Diels–Alder products.



*Scheme 54: Comparing the efficiency of **IDPi** and **IDPii** in the Diels–Alder reaction under optimized reaction conditions.*

Note: The herein shown **IDPii** catalyzed transformation represent selected examples. **IDPiis 1-5** have been tested in various other transformation, usually showing the same reactivity trend but without any noteworthy enantioenrichment of the final products.

[11] The Diels–Alder experiment was conducted by Mathias Turberg under optimized reaction conditions. The reactions were simultaneously performed with **IDPi** and **IDPii**, respectively.

4.3.3 Structural analysis of IDPiis

The **IDPii** structures **IDPii-1** to **IDPii-4** were successfully crystallized, enabling crystallographic single crystal X-ray analyses. Based on this analysis, it became vividly evident that replacing the commonly employed electron-withdrawing substituent $TfNH_2$ of the **IDPi** motif with e.g. $PhSNTf_2NH_2$ **SA-2** results in a significantly enlarged active center. The terminal NTf units, which are located at the sulfonyl moiety radiate away from the BINOL induced microenvironment and remain completely exposed, thus may explain the lack of enantioinduction from the chiral but enantiopure counteranion.

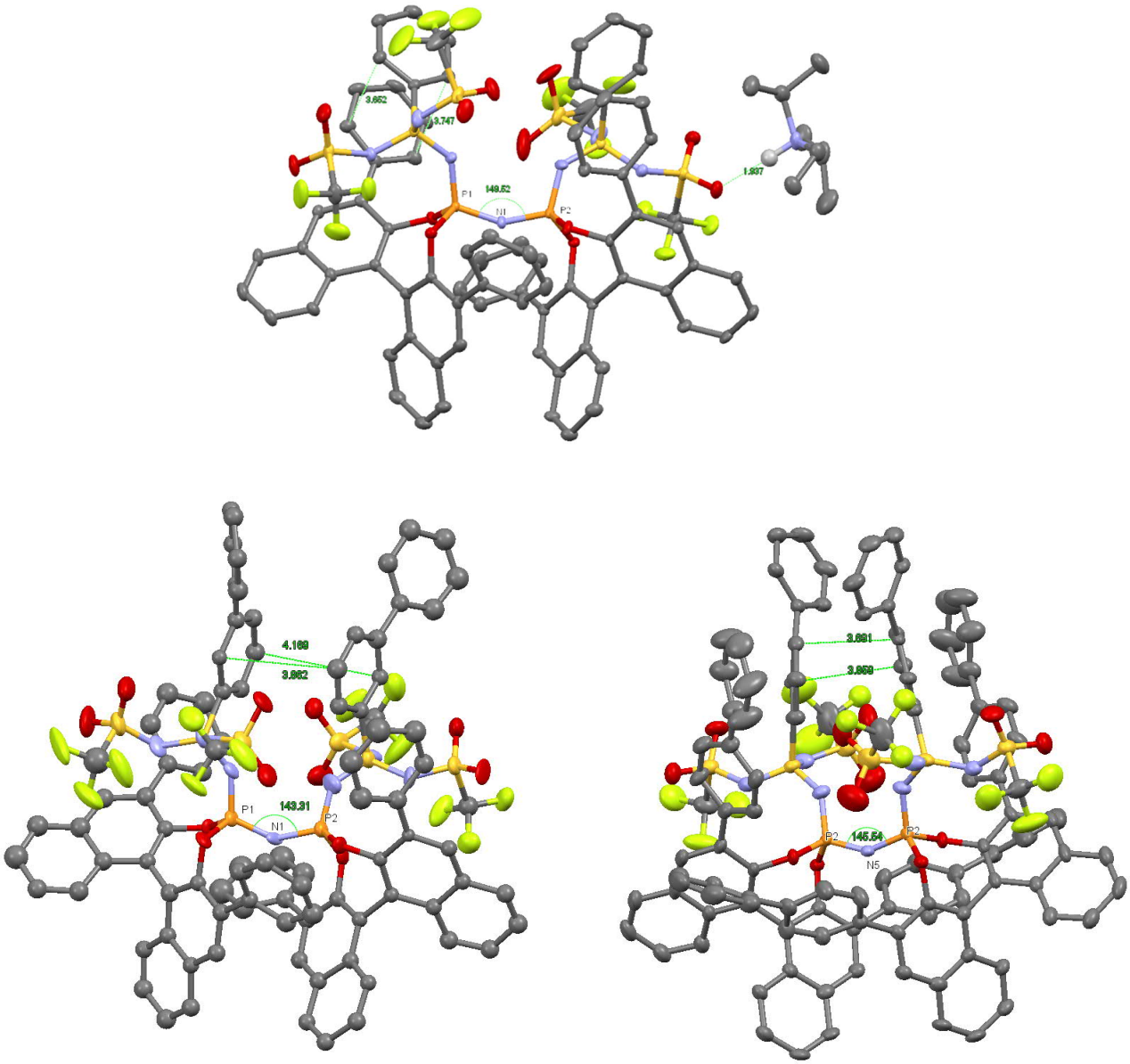
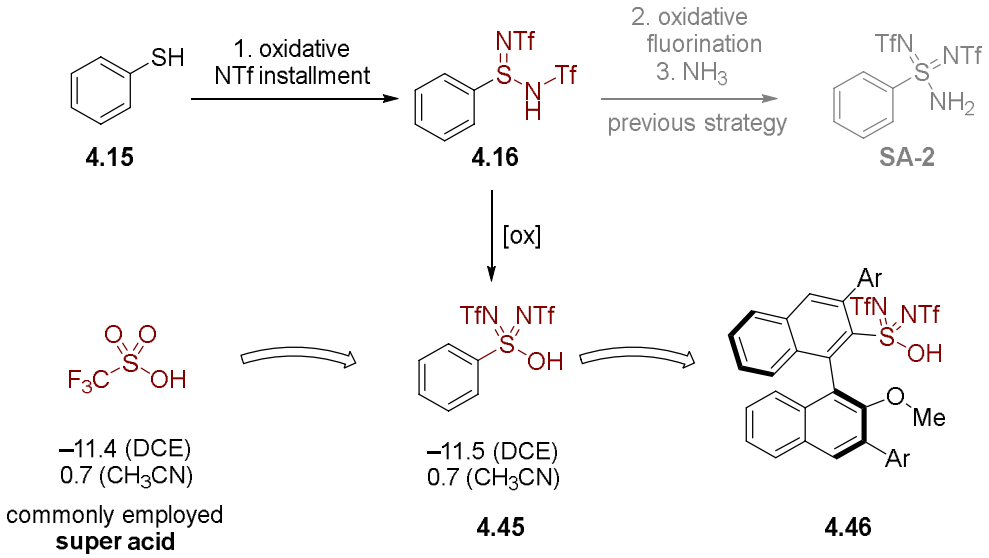


*Figure 12: Single crystal structure analyses of **IDPii-2** (top); **IDPii-3** (bottom left); **IDPii-4** (bottom right).*

Nevertheless, this work demonstrates that the application of arylbis(trifluoromethylsulfonylimino)sulfonyl amide as electron-withdrawing substituent tremendously increases the acidity of imidodiphosphate-derived Brønsted acids. The insufficient confinement of the **IDPii** catalyst motif most likely results from the structural properties of the employed BINOLs. In this regard, future developments and the identification of structurally distinct BINOL substitutes, in combination with the herein disclosed work might lead to the development of an extremely acidic yet highly selective catalyst motif based on the imidodiphosphate framework.

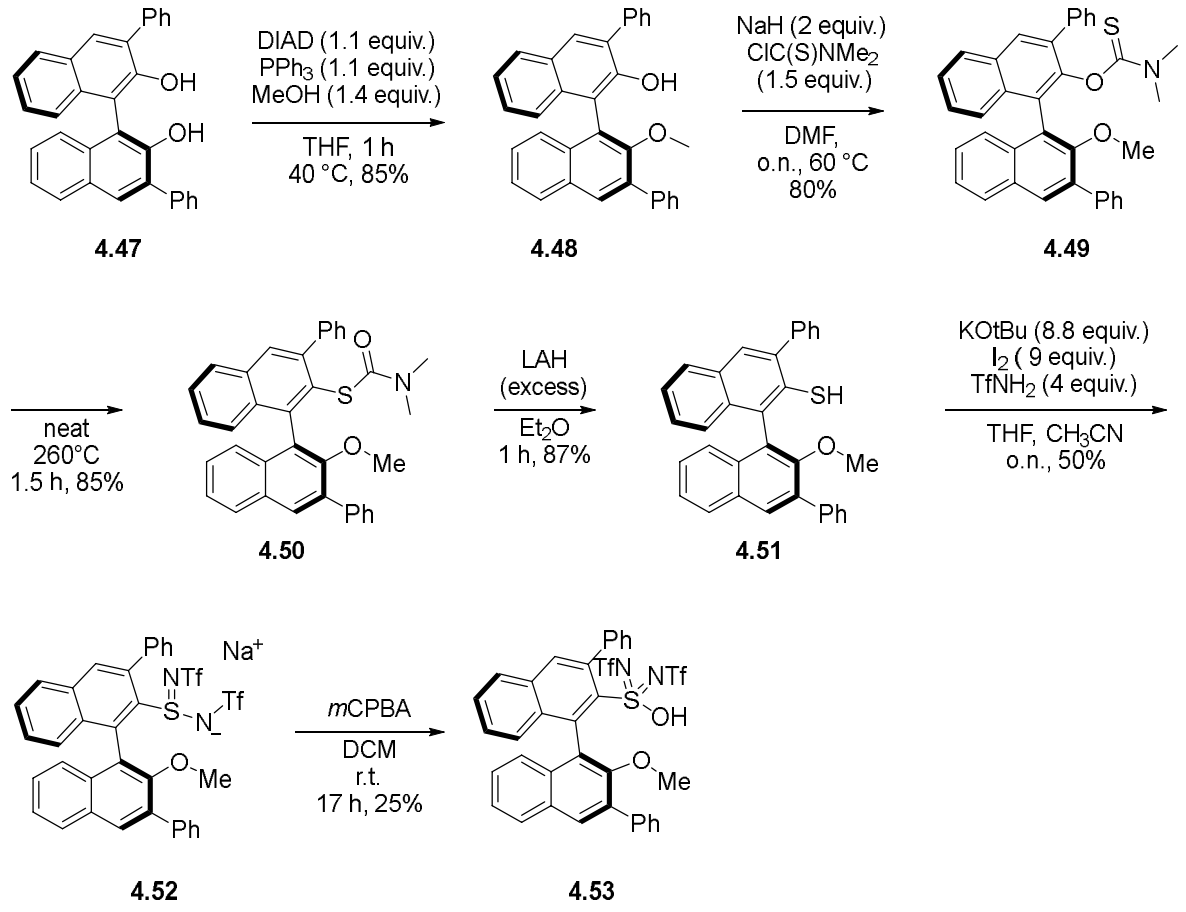
4.4 Toward a Chiral Motif Based on the Tetrahydroindacene Scaffold

Inspired by the remarkable acidifying effect of $PhS(NTf)_2NH_2$, **SA-2** and the previously described work, we wondered if intermediate **4.16** could be converted into the corresponding sulfonic acid **4.45** upon oxidation. As shown by Leito and co-workers, these aryl-derived bis(trifluoromethylsulfonylimino)sulfonic acids display similar, but depending on the aryl substituents, also significantly increased acidities in comparison to the commonly employed Brønsted super acid TfOH (pKa –11.4 in 1,2-DCE).[99] Advantageously, sulfonic acid **4.45** consists of an additional aryl moiety, which in return was envisioned to represent a suitable platform to install a chiral aryl substituent. Following on this strategy, we designed binaphthyl-derived bis(trifluoromethylsulfonylimino)sulfonic acid **4.46**.



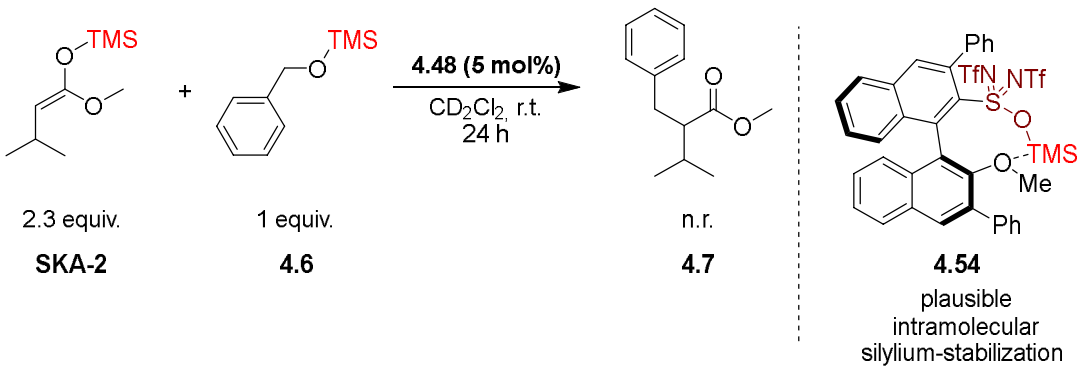
*Scheme 55: Design of chiral bis(trifluoromethylsulfonylimino)sulfonic acid **4.46**.*

We believed that BINOL-derived mercaptophenol **4.51**, first introduced by Miller,[120] would provide the ideal starting material to access the envisioned binaphthyl-derived bis(trifluoromethylsulfonylimino)sulfonic acid **4.46**. Thus, **4.51** was plrepared based on a literature known reaction sequence (Scheme 56). **4.51** smoothly underwent the previously developed oxidative NTf-installment procedure to give rise to binaphthyl-derived bis(trifluoromethylsulfonylimino)sulfinate **4.52**. After oxidant and condition screening we found suitable conditions to obtain the desired sulfonic acid **4.53** in a reasonable yield of 25%.



*Scheme 56: Synthesis of axially chiral binaphthyl-derived bis(trifluoromethylsulfonylimino)sulfonic acid **4.53**.*

With **4.53** in hand, we explored the applicability of this novel catalyst motif in the α-alkylation of silyl ketene acetals. Unfortunately, the tested α-alkylation of SKA, as exemplarily shown with silyl ketene acetal **SKA-2** did not result in any kind of desired reactivity, which we observed previously with our **IDPii** motif (cf. chapter 4.3.2 Catalytic Applications of **IDPii**).



*Scheme 57: Selected example for the α-alkylation of silyl ketene acetal **SKA-2**Proposed reactivity decrease due to intramolecular silylium ion stabilization with the adjacent methoxy moiety (right).*

This lack of reactivity might result from an intramolecular silylium ion stabilization of **4.53** to the adjacent highly Lewis basic methoxy unit, as illustrated in structure **4.54**. To circumvent

this reactivity inhibition, we considered several strategies, such as the replacement of the methoxy unit of **4.53** with an aryl substituent or any other kind of unbiased substituent, which would not hamper the reactivity.

However, based on the previously described structural analysis of **IDPiis**, in which the binaphthyl-framework did not efficiently confine the active center, we considered alternative chiral frameworks to access enantiopure acids based on the bis(trifluoromethylsulfonylimino)-sulfonic acid unit. In this context, the ideal chiral scaffold, which we desired to connect with the sulfonyl unit has to consist of the following properties and should be:

1) Lewis-basic heteroatom-free to prevent any reactivity diminishment;
2) ideally a substituent that results in a (pseudo-)C_2 symmetry of the final acid;
3) providing a structurally confined cavity to encumber the active center;
4) configurationally stable under highly acidic reaction conditions.

In fact, monovalent chiral frameworks fulfilling the mentioned criteria, which we envisioned as indispensable condition to develop a privileged Brønsted acid based on the bis(trifluoromethylsulfonylimino)sulfonic acid framework are scarce. Nevertheless, we became particularly interested in Yamamoto´s design of chiral phenols based on the 2,6-bis(2-alkylphenyl)-3,5-dimethylphenol scaffold **4.55** in which two *ortho*-substituted atropisomeric aryl substituents induce the chirality of the corresponding phenol.[12] Blanchet and co-workers applied the same chiral backbone as platform to access chiral monovalent sulfonic acid **4.56**. Subsequently, Dixon investigated the application of two enantiopure appendages in *ortho*-position to afford sulfonic acid **4.57**.

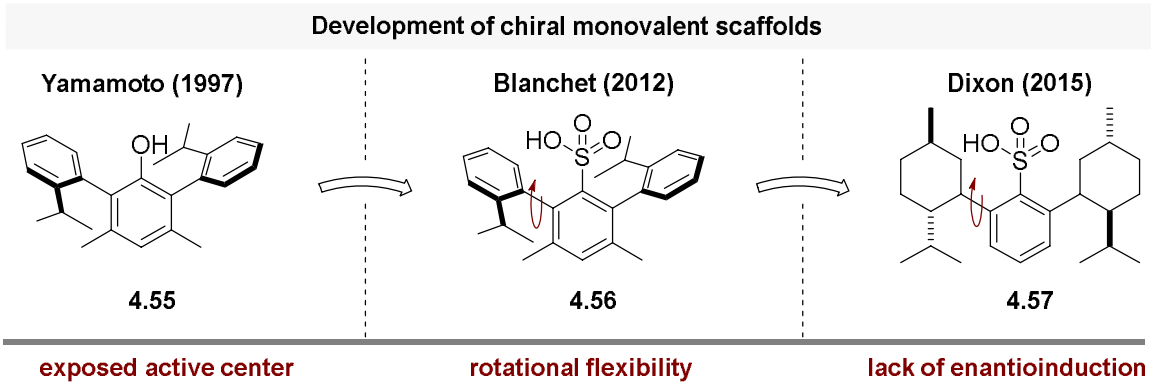
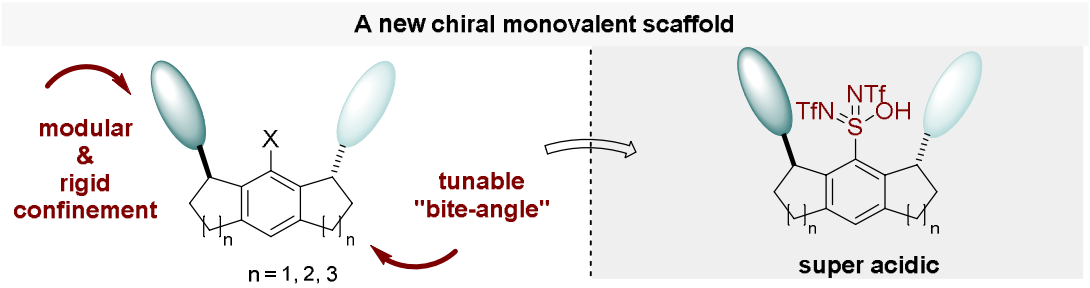


*Figure 13: Development of monovalent chiral sulfonic acid **4.57**.*

[12] These phenols have been utilized for the synthesis and application of enantioenriched aluminium bisphenoxides.

Unfortunately, these sulfonic acids provided unsatisfactory enantioenrichments in several tested transformations, for instance, in the asymmetric 1,3-dipolar cycloaddition of nitrones and ethyl vinyl ethers. Presumably, this lack of enantioinduction correlates with the rotational freedom of both *ortho*-substituents and the resulting flexible microenvironment.

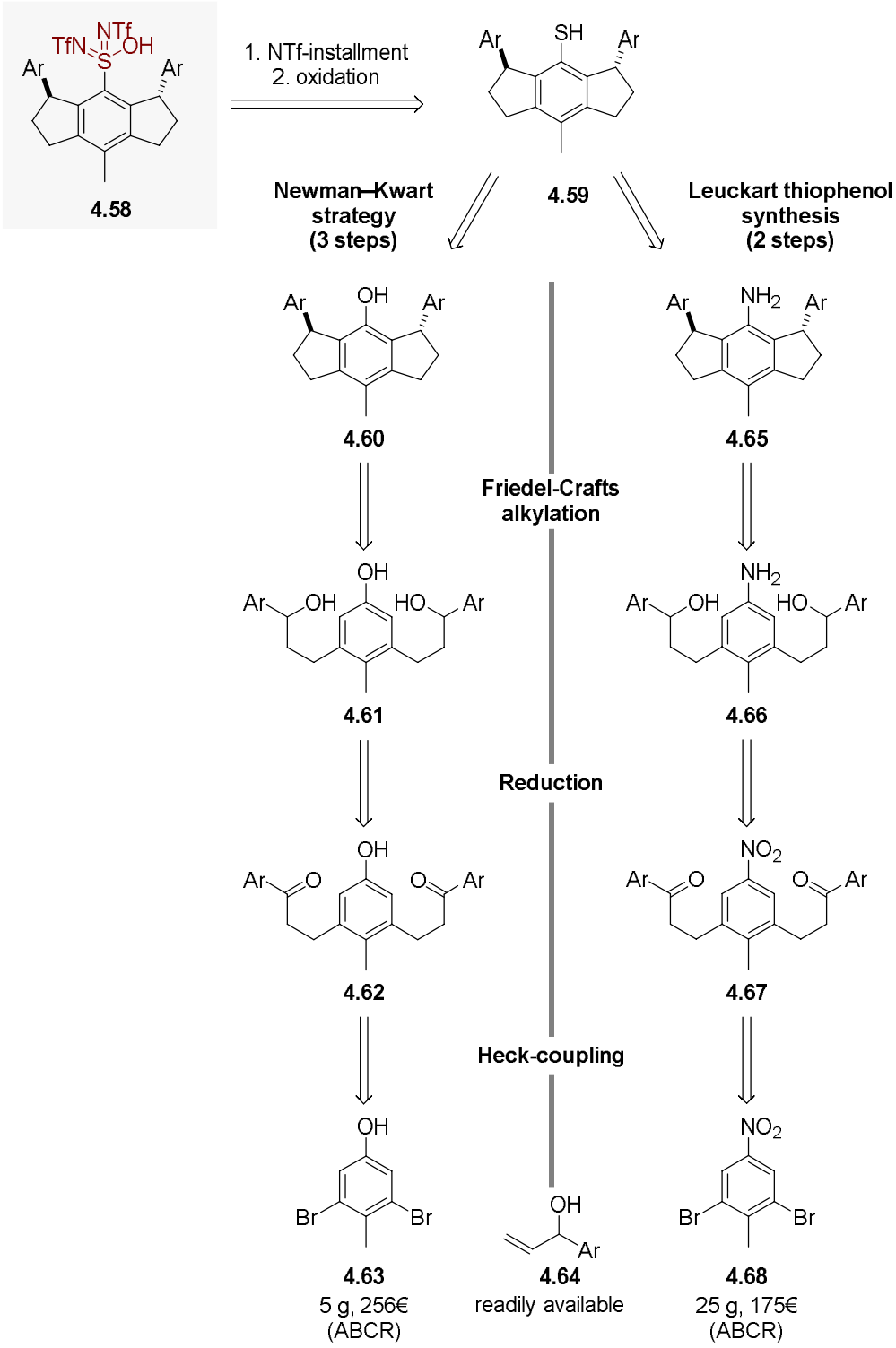
As we are particularly interested in structurally confined Brønsted acids, we revisited this chiral scaffold, which we deemed a requirement to access a confined and highly acidic bis(trifluoromethylsulfonylimino)-derived sulfonic acid. Our conceptual design for a new chiral backbone focuses on two benzylic appendages located adjacent to the sulfonyl functionality and ideally results in the establishment of a chiral cavity, which surrounds the active center. To avoid the possibility of structural flexibility of the *ortho*-appendages due to rotational freedom, we concluded that the tetrahydroindacene scaffold might provide the ideal platform for this purpose (Scheme 58). Additionally, elongating the aliphatic ring size (n) provides an additional parameter to dwindle the structural properties of the induced cavity.



Scheme 58: Conceptual design of a new chiral indacene-derived scaffold.

To access the desired sulfonic acid, and to utilize our new strategy in which we oxidatively install NTf units, we focused on the synthesis of the indacene-derived thiol **4.59** as starting material (Scheme 59). From a retrosynthetic perspective, it was assumed that thiol **4.59** should be easily accessible from the corresponding phenol **4.60** upon following the Newman–Kwart strategy of *O*-thiocarbamates, or from the corresponding aniline **4.65** upon the Leuckart thiophenol synthesis. Both intermediates, phenol **4.60** and aniline **4.65** would be accessible from a common synthetic strategy, in which an intramolecular double Friedel–Crafts alkylation of two benzylic alcohols represents a key step to form the indacene scaffold. Additionally, this intramolecular Friedel–Crafts alkylation could be accomplished stereoselectively in the presence of chiral acids or auxiliaries. To prevent the formation of undesired regioisomers within the alkylation event, the occupation of the *para*-position with a methyl group seemed to be inevitable. These benzylic alcohols would be rapidly available from the corresponding

ketones, which in return should be accessible from a double Heck coupling of commercially available 3,5-dibromo-4-methyl-derived heteroarenes and vinyl alcohols.



*Scheme 59: Retrosynthetic analysis toward tetrahydroindacene-derived phenol (**4.60**) and aniline (**4.65**).*

Furthermore, this synthetic strategy was considerably appealing because chiral phenol **4.60** and aniline **4.65** might not only serve as intermediates towards the synthesis of thiol (**4.59**), but

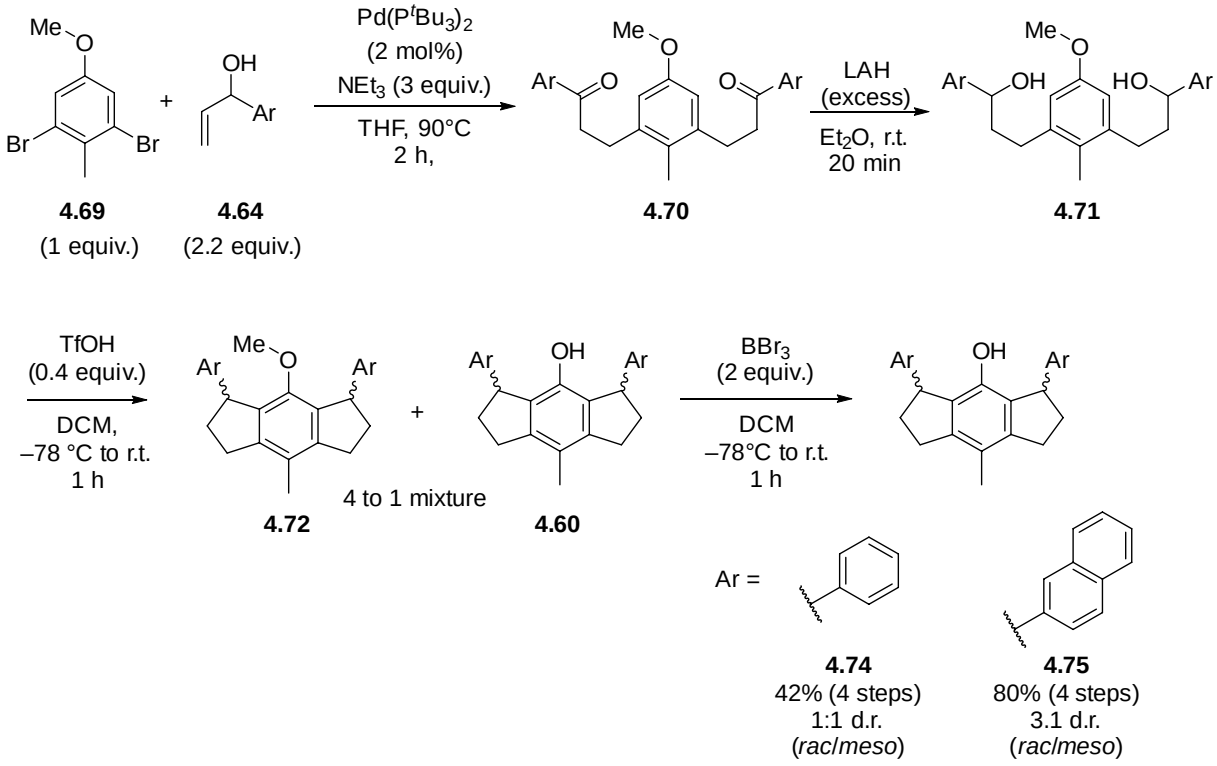
could additionally find future applications in asymmetric synthesis. In particular aniline **4.65** represents an ideal platform molecule to access various heteroatom-functionalized arenes, for instance phosphines, following established functionalization strategies *via* classical diazonium salt chemistry (e.g. Sandmeyer reaction).

Admittedly, the Friedel–Crafts alkylation of the aniline precursor was envisioned to be challenging. Nevertheless, we were confident that suitable reaction conditions could be developed based on inspiring contributions from Coates, Kaneda and Chan, performing Friedel–Crafts alkylations on anilines under Brønsted or Lewis acid conditions.[121-123]

4.4.1 Synthesis of Tetrahydroindacene-Derived Phenols

We explored the synthesis of indacene-derived phenol **4.60** following our postulated strategy. However, the initial Heck coupling proceeded sluggishly with commercially available 3,5-dibromo-4-methylphenol. Therefore, we protected the phenol moiety by simple methylation (**4.69**),[13] which upon double Heck coupling with vinyl alcohol **4.64** provided the desired diketone **4.70** in good yields (Scheme 60). The global reduction with lithium aluminium hydride ($LiAlH_4$) afforded the desired diol **4.71** and subsequently underwent the desired Friedel–Crafts alkylation in the presence of catalytic amounts of TfOH. Interestingly, within the Friedel–Crafts event, the anisole moiety underwent partial demethylation to furnish a mixture of **4.72** and desired phenol **4.60**. This mixture was directly converted to the desired indacene-derived phenol **4.74** upon full demethylation with boron tribromide (BBr_3). Four consecutive steps with a single purification step afforded phenol **4.74** in a good yield of ca. 40% and in a diastereomeric mixture of 1:1. The undesired *meso*-phenol was separable from the racemic product, providing the desired (*rac*)-phenol **4.74** in a yield of ca. 20%. Additionally, the same reaction sequence was applied to access the 2-naphthyl-derived tetrahydroindacenol **4.75**. The reaction sequence was very high yielding and afforded the desired product within short reaction times. Fortunately, with structurally increased aryl substitutents the diastereomeric ratio of 3:1 d.r. increases in favor to the desired racemic naphthyl-derived phenol **4.75**.

[13] 3,5-dibromo-4-methylanisole is commercially available (1 g 121 €, ABCR)



*Scheme 60: Synthesis of tetrahydroindacene-derived phenols **4.74** and **4.75**.*

Moreover, racemic phenyl-derived phenol **4.74** was successfully resolved by preparative HPLC. The corresponding enantiopure material was crystallized and characterized by single crystal X-ray analysis, thus allowing the identification of the absolute stereochemical configuration of **4.74** (Figure 14).

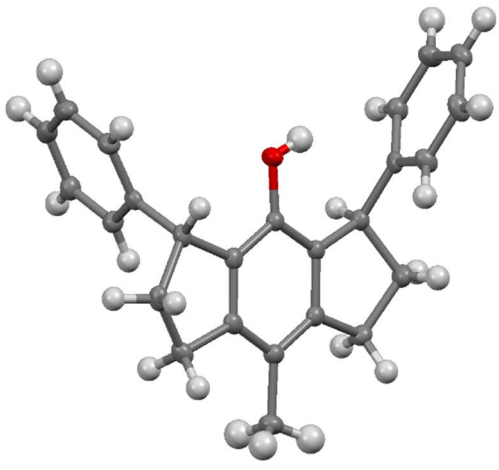
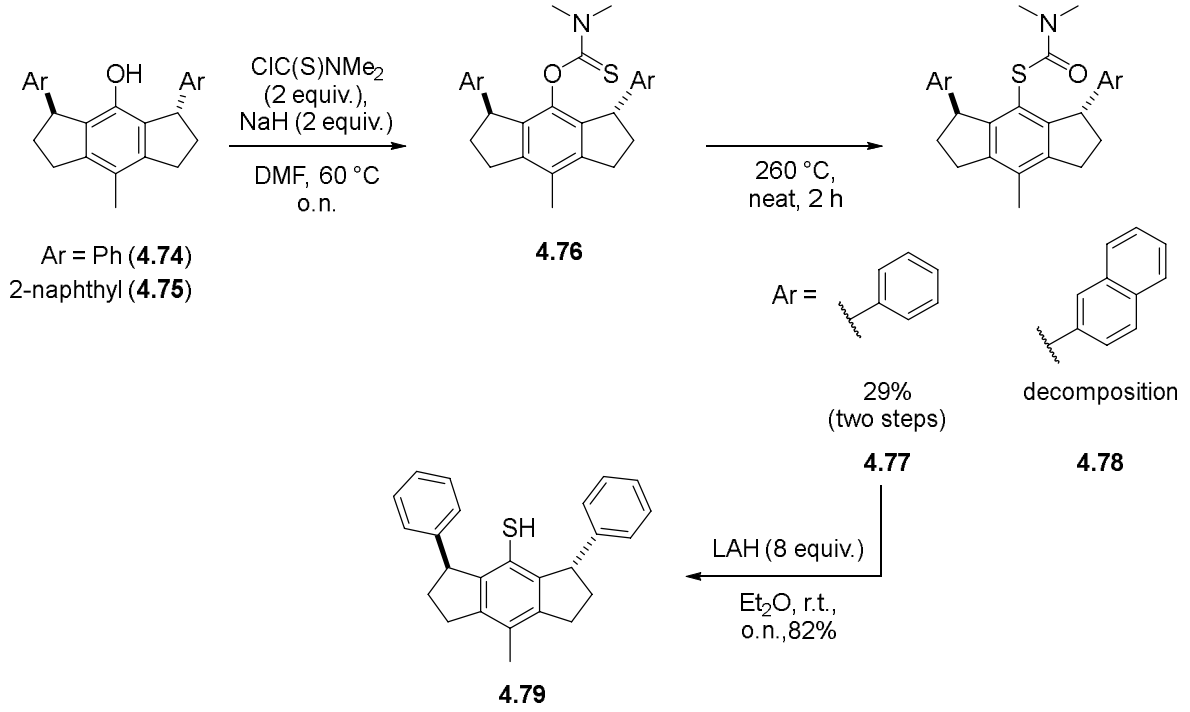


*Figure 14: Crystal Structure of **4.74**. Oxygen (red); carbon (grey), hydrogen (light grey).*

Next, with phenol as intermediate in hand, we evaluated the envisioned Newman–Kwart strategy to transform the phenol moiety into the desired thiol.



Scheme 61: Attempts to synthesize tetrahydroindacene-derived thiols following the Newman–Kwart strategy.

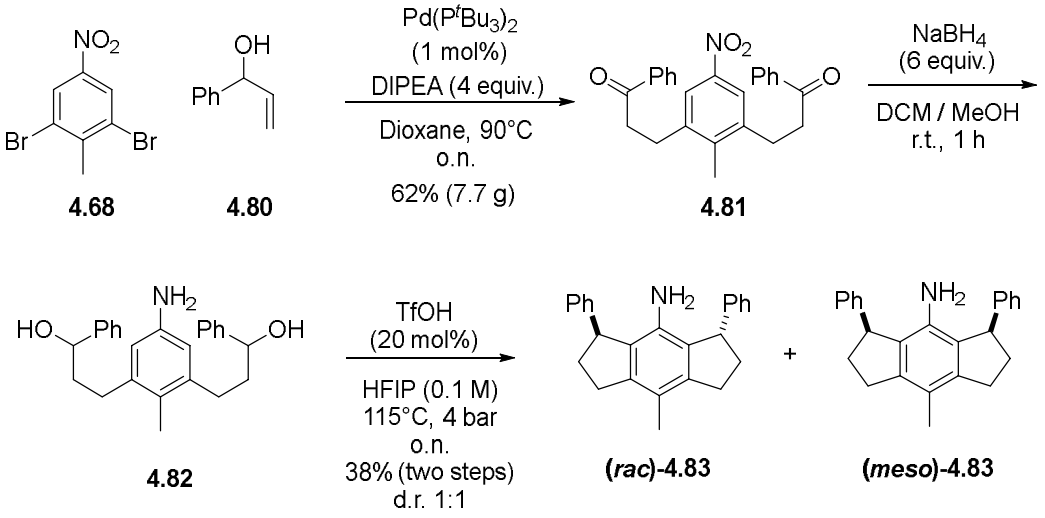
Phenols **4.74** and **4.75** smoothly underwent the carbamoylation with *N*-*N*´-dimethylthiocarbamoylchloride ($Me_2NC(=S)Cl$) to yield **4.76**. The thermal Newman–Kwart strategy turned out to be low yielding to access the corresponding S-thiocarbamates **4.77**. Unfortunately, 2-naphthyl-derived S-thiocarbamate **4.78** was not accessible with this strategy due to decomposition at high temperatures. Nevertheless, **4.77** furnished the desired thiol **4.79** upon reduction in the presence of $LiAlH_4$ and thus provided the envisioned starting material to access the final bis(trifluoromethylsulfonylimino)sulfonic acid **4.58**.

(The follow-up oxidation process is further discussed in Chapter 4.4.3 Toward Indacene-Derived Bis(trifluoromethylsulfonylimino)sulfonic Acid*.)*

Based on these results, in which the Newman–Kwart strategy failed for enlarged aryl-substituents, the development of an alternative strategy on an early stage was considered to be more appealing. A reliable and scalable synthesis toward tetrahydroindacene-derived thiols with diverse aryl modifications was envisioned as an important criteria for a successful implementation of this new chiral backbone.

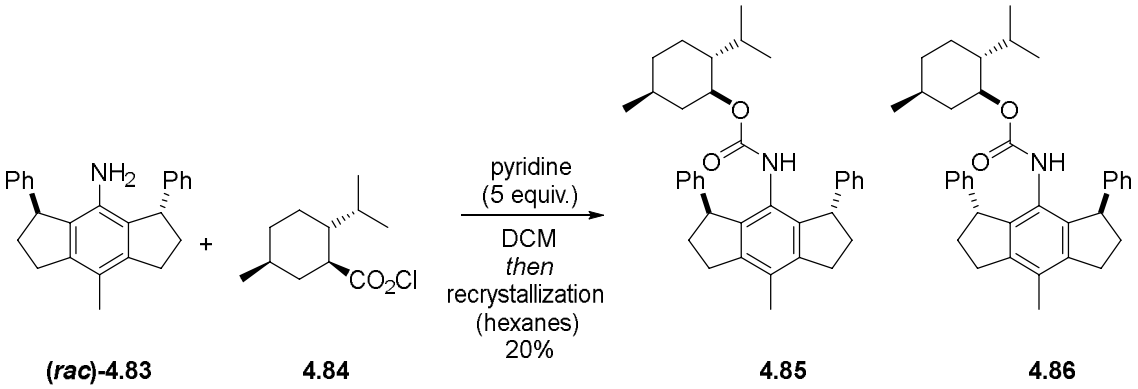
4.4.2 Synthesis of Tetrahydroindacene-Derived Anilines

The second strategy toward thiol **4.59** involved the synthesis of indacene-derived aniline **4.65** followed by subsequent Leuckart thiophenol synthesis. Analogously to the previously described indacene-derived phenol synthesis **4.74**, this synthesis relied on a double Heck coupling in the first step to install the desired aliphatic diketone scaffold. Advantageously, 3,5-dibromo-4-methylnitrobenzene (**4.68**) is significantly cheaper available from commercial suppliers and does not require a protecting group for the initial Heck coupling, thus reducing the total step count by two steps. The first double Heck coupling of **4.68** with phenyl-derived allylic alcohol **4.80** delivered the desired intermediate **4.81** in high yields. Furthermore, the synthesis of **4.81** was readily scalable, afforded frequently high yields and could be easily purified by simple recrystallizations on decagram scales. A global reduction with an excess of sodium borohydride ($NaBH_4$) efficiently reduced both ketones and the nitro functionality to afford the envisioned di(hydroxy)aniline **4.82**. Due to the high hydrophilicity of **4.82** a simple purification protocol has been developed, in which **4.82** was dissolved in an acidic aqueous media, allowing the removal of all undesired side products by simple extraction of the acidic aqueous phase with diethylether or dichloromethane. Subsequent neutralization of the aqueous phase resulted in the precipitation of the desired intermediate **4.82** in analytically pure form. With **4.82** in hand, we explored the double Friedel–Crafts alkylation. Unfortunately literature known procedures, such as the application of Montmorillonite or Lewis acidic tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) resulted into full dehydration to afford a mixture of olefins.[122-123] The same dehydration occurred in the presence of strong Brønsted acids in commonly employed solvents, such as dichloromethane, diethylether or toluene. However, we reasoned that catalytic amounts of highly Brønsted acidic TfOH might protonate the *in situ* generated olefins, resulting in a stabilized benzylic carbocation, which then undergoes the desired hydroarylation (*pseudo* Friedel–Crafts from the benzylic alcohol) transformation. Indeed, after extensive solvent and condition screening, hexafluoroisopropanol (HFIP) was identified to represent a reasonable solvent for this transformation. High temperatures and a pressurized vial increased the yield of the desired tetrahydroindacene-derived aniline **4.83**. This reaction was frequently performed on multigram scales and yielded the desired aniline **4.83** in a diastereomeric mixture of 1:1. Fortunately, the desired racemic product (***rac*-4.84**) was readily separable from the undesired *meso*-side product (***meso*-4.84**) by simple flash column chromatography.



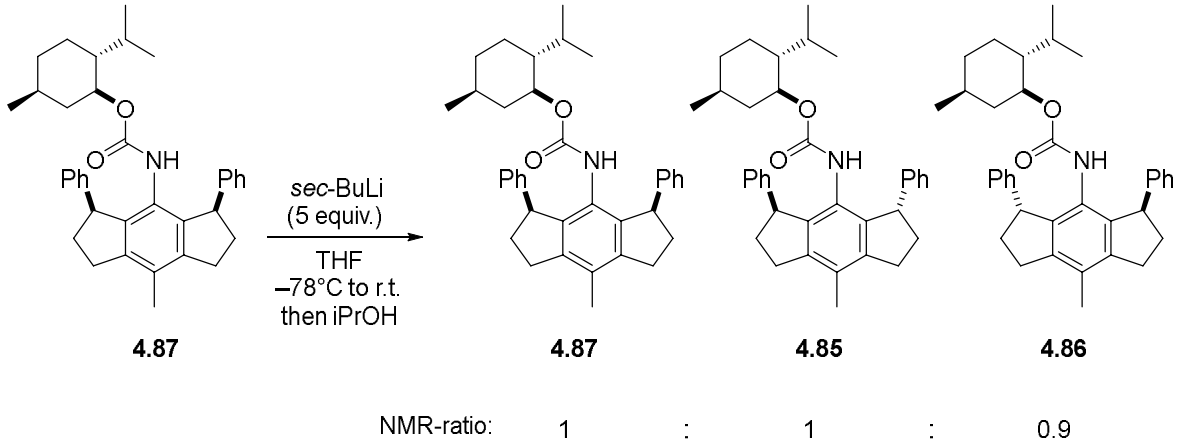
*Scheme 62: Synthesis of tetrahydroindacene-derived aniline **4.83**.*

The resolution of ***rac*-4.83** *via* preparative HPLC turned out to be extremely challenging for this specific aniline due to insufficient baseline separation. However, derivatization of **4.83** with (*1S*)-(+)-menthyl chloroformate (**4.84**) allowed the resolution of diastereomeric carbamates **4.85** and **4.86** *via* crystallization. An initial attempt yielded the diastereomerically pure carbamate in 20% yield. Performing this reaction on larger scales would most like increase the final yield. Initial, NMR-analyses to determine the absolute configuration of each carbamate remained elusive.



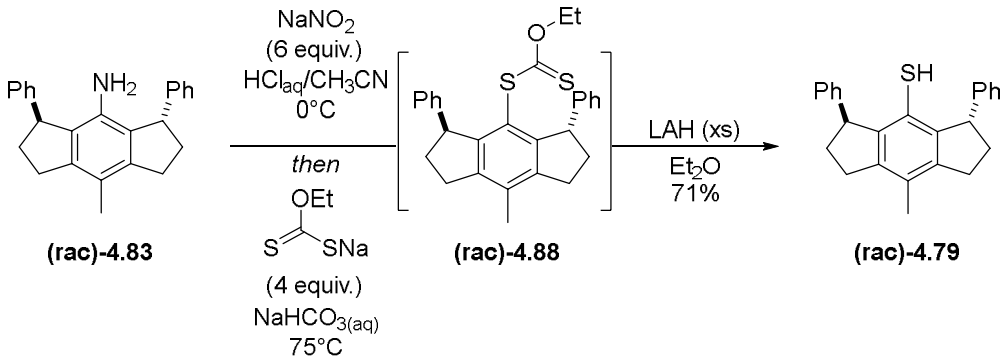
Scheme 63: Resolution of aniline 4.83 via derivatization with menthylchloroformate 4.84.

Moreover, the same strategy was applied to the corresponding *meso*-aniline **4.83** and allowed a simple epimerization upon deprotonation / reprotonation with strong bases, such as *sec*-BuLi and reprotonation with isopropanol, and thus increases the yield of the desired racemic aniline (Scheme 64).



*Scheme 64: Initial epimerization attempt of **meso-4.87**.*

The envisioned Leuckart thiophenol synthesis was first explored with racemic **4.83** and the formed xanthate (**4.88**) cleaved under modified reaction conditions.[14] This approach afforded the desired thiol **4.79** in significantly higher yield of 71% (*cf.* 23% for Newman–Kwart strategy).

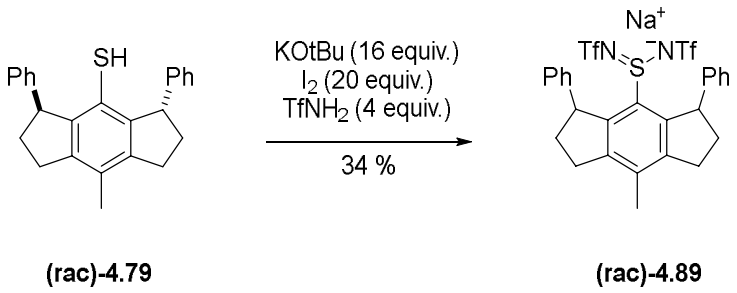


*Scheme 65: Access to racemic tetrahydroindacene-derived thiol **4.79**.*

[14] We used an excess of $LiAlH_4$ to cleave the xanthate, instead of strongly basic reaction conditions to prevent epimerization.

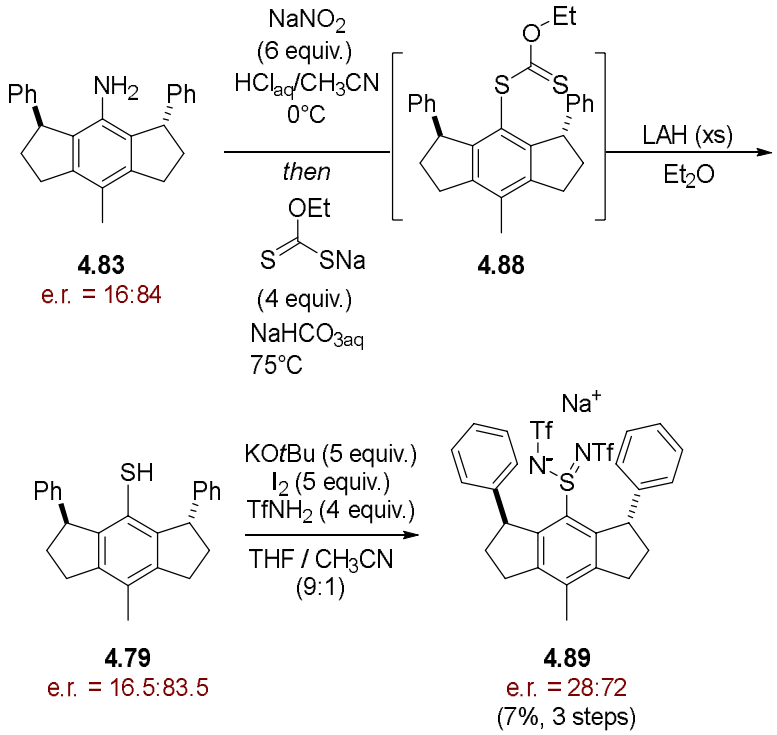
4.4.3 Toward Indacene-Derived Bis(trifluoromethylsulfonylimino)sulfonic Acid

Next the oxidative NTf-installment based on our previously described protocol was explored (cf. chapter 4.2.3 Imidodiphosphorbis(iminosulfonylimino)imidate (IDPii)). Fortunately, we obtained the desired intermediate with two NTf-units installed on sulfur on the sulfinate oxidation level (**4.89**) in moderate yields. Initial attempts to resolve racemic **4.89** on preparative HPLC scale remained elusive due to insufficient baseline separation.



*Scheme 66: Synthesis of racemic tetrahydroindacene-derived sulfinate **4.89**.*

To obtain the enantiomerically enriched sulfinate **4.89**, we repeated the reaction sequence with enantiomerically enriched aniline **4.83**, followed by subsequent Leuckart thiophenol synthesis and the oxidative NTf-installment procedure.



*Scheme 67: Synthesis of tetrahydroindacene-derived sulfinate **4.89**.*

Unfortunately, within this reaction sequence significant epimerization has been detected during the oxidative NTf-installation process. This observation might be explainable with partially active KO^{t}Bu present, which might have resulted in the deprotonation of the benzylic C–H unit. Two different strategies to circumvent this issue have been envisioned.

1. proceeding with the chemical synthesis toward the final racemic indacene-derived bis(trifluoromethylsulfonylimino)sulfonic acid, followed by late-stage resolution
2. avoiding the presence of relatively acidic C–H containing benzylic hydrogen atoms.

An aggravating factor to proceed with the chemical synthesis is the instability of the final sulfonic acid, since preliminary studies indicated that phenylbis(trifluoromethylsulfonylimino)-sulfonic acids slowly decompose in solution. Therefore, the first strategy was considered to be less attractive. Furthermore, this approach would result in a tedious reaction sequence for each individual catalyst synthesis with various aryl modifications in the benzylic position. Strategy 2 would be more appealing, which would allow to start with enantioenriched intermediates, ideally the aniline, without any erosion of the final enantioenrichments.

In this regard, the synthetic strategy to access tetrahydroindacene-derived bis(trifluoromethylsulfonylimino)sulfonic acids needs to be revisited. The ideal precursor to access the desired acid, is exemplarily illustrated in Figuer 15. The two aryl bromides would allow a simple late-stage diversification of the aryl moiety. Additionally the two benzylic methyl units would prohibit the epimerization/racemization of the enantioenriched sulfinate. Thus only the final oxidation from S(IV) to S(VI) to access the desired sulfonic acid would be required. Nevertheless, additional effort needs to be devoted toward a successful realization of this project.

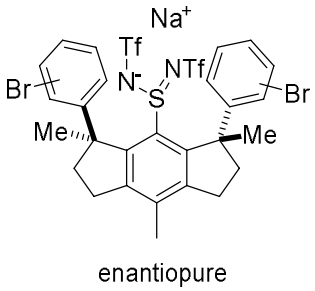


Figure 15: Ideal precursor on the sulfinate oxidation stage to access tetrahydroindacene-derived bis(trifluoromethylsulfonylimino)sulfonic acids.

5 Summary

The imidodiphosphoryl scaffold represents a highly versatile platform to design Brønsted acids, merging enzyme-like substrate recognition with modular acidities and has enabled several, perhaps surprising and unique reactions in asymmetric catalysis over the past years. This doctoral thesis discloses a new user-friendly synthesis of imidodiphosphoryl-based catalysts, in which a hexachlorobisphosphazonium salt serves as a building block and selectively reacts with chosen nucleophiles based on a toolbox principle. This methodology, which proceeds *via* common key intermediates, provides a fast and highly efficient access to privileged Brønsted acids, such as **IDPs**, ***i*IDPs** and **IDPis**, comprising unique and, most notably, previously inaccessible confinement. The new highly confined catalyst motifs allow the highly enantioselective conversion of very small and structurally unbiased substrates within the ACDC framework. In addition, this methodology provides a new foundation toward future developments of novel imidodiphosphoryl-type catalysts, leading to efficient asymmetric transformation in the field of asymmetric catalysis or as ligands in transition-metal catalysis.

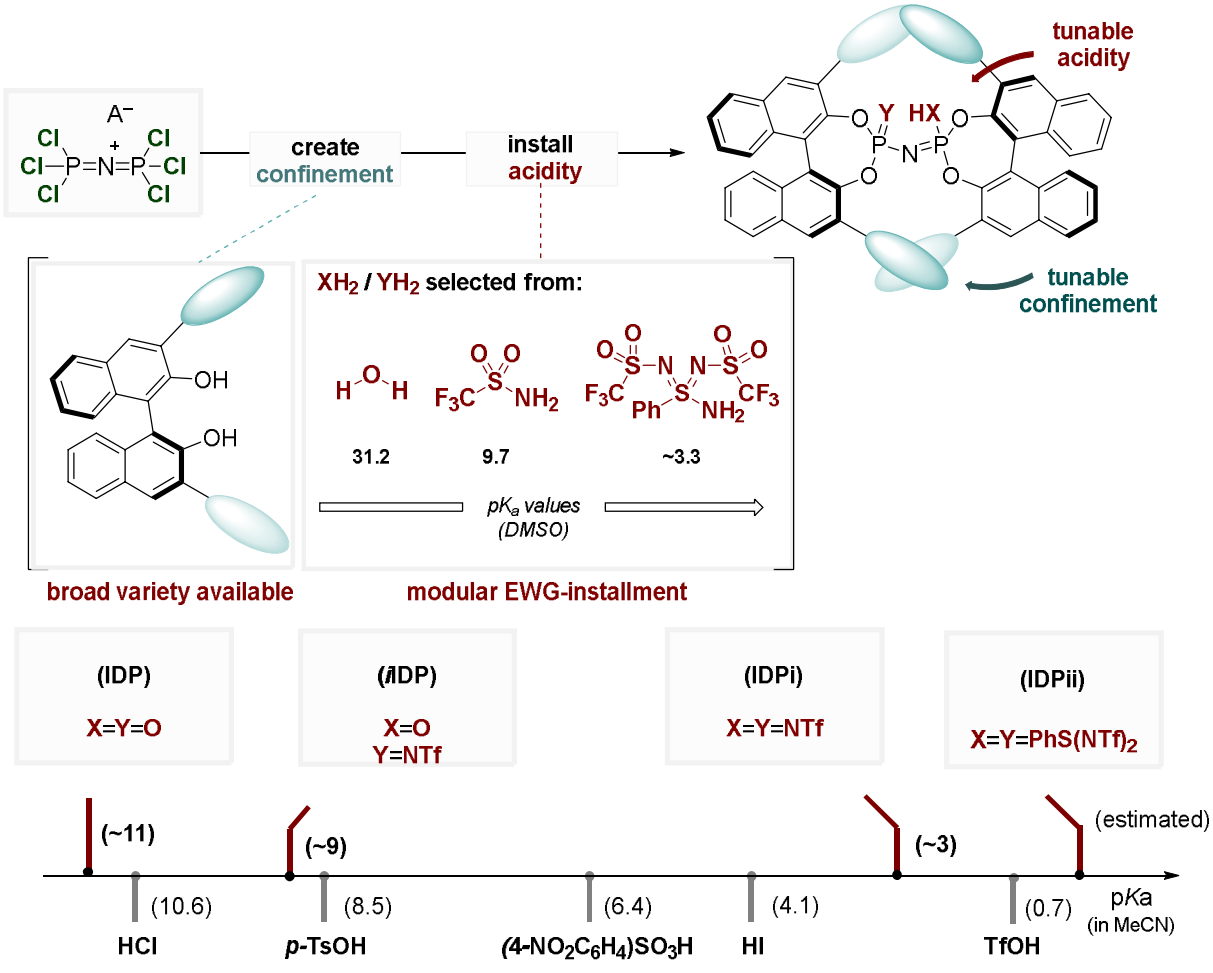
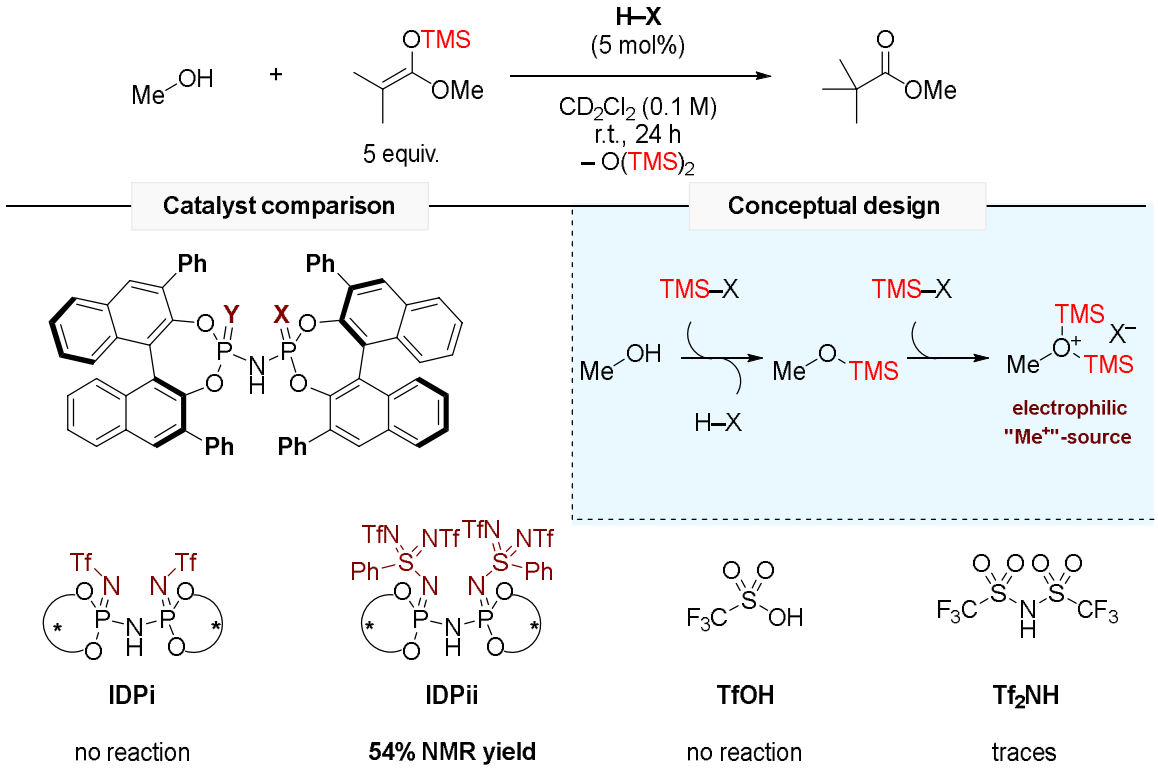


Figure 16: A unified approach to access Imidodiphosphoryl-derived Brønsted acids.

Typically considered as nucleophiles, alcohols could be rendered electrophilic through silylium activation. This concept was investigated within this doctoral work with a strong focus toward the development of a general enantioselective α-alkylation strategy in the presence of carbonyl-derived nucleophiles. However, the required technology regarding catalyst acidity remained elusive, and therefore, a more acidic catalyst motif was considered a necessary condition to overcome remaining reactivity barriers within the context of ACDC.

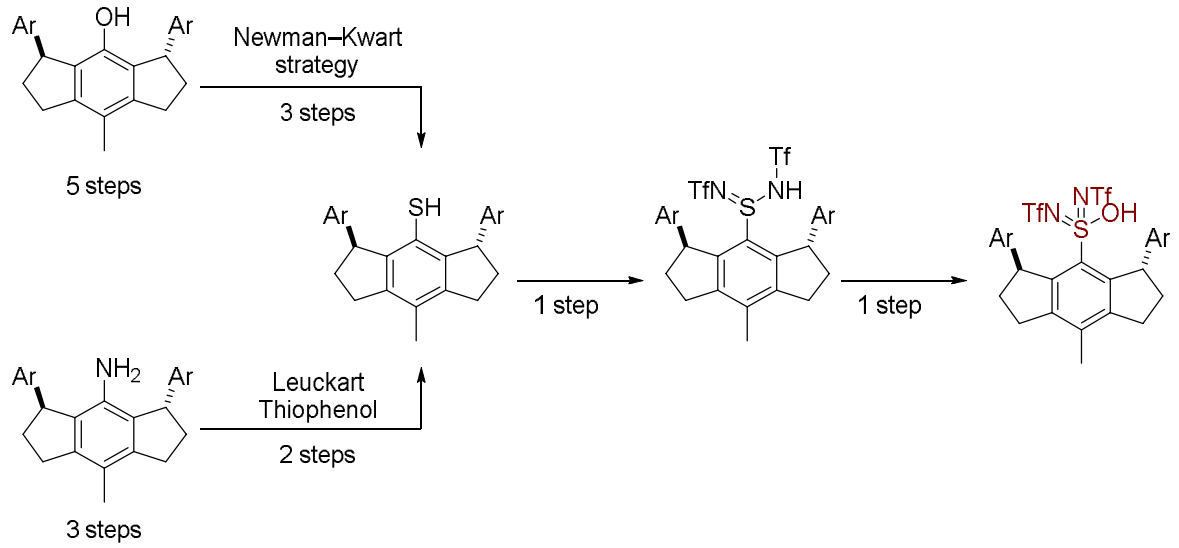
In this context, a new synthetic access of bis(trifluoromethylsulfonylimino)sulfonyl-derived electron-withdrawing groups has been developed and which, upon implementation within the imidodiphosphate framework, led to the conceptually designed and extremely reactive **IDPii** catalyst class. As envisioned, **IDPiis** allowed rendering nucleophilic alcohols into highly electrophilic alkylating reagents, and most impressively, enabled the unprecedented α-methylation of silyl ketene acetals – utilizing methanol as electrophilic methyl surrogate. Contrarily, **IDPi** and commonly employed Brønsted super acids, such as TfOH and Tf_2NH did not engage in the desired transformation.



Scheme 68: A catalyst comparison for the α-methylation of silyl ketene acetal.

The novel **IDPii** catalyst class has overcome previous reactivity barriers of imidodiphosphate-derived catalyst motifs, albeit no significant enantioinduction could be obtained in the herein explored transformation so far.

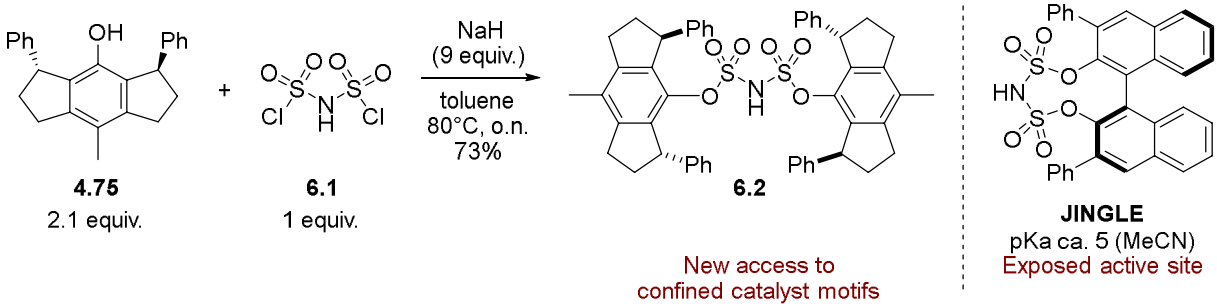
Crystallographic analyses revealed insufficient steric confinement effects from the BINOL-derived chiral microenvironment on the tested **IDPiis**. As a possible approach to address this issue, a structurally distinct monovalent chiral scaffold based on the tetrahydroindacene scaffold has been conceptually developed. Two appendages, located adjacent to the active center were envisioned to provide a superior chiral framework, which in combination with the new methodology to afford bis(imino)sulfonyl units was considered to give access to highly acidic yet selective chiral Brønsted acids. This work provides a seminal contribution to several chiral heteroatom-functionalized tetrahydroindacenes and may lead to the development of numerous novel chiral catalyst motifs and the development of new transformation in the context of asymmetric synthesis.



Scheme 69: Synthesis toward tetrahydroindacene-derived bis(trifluoromethylsulfonylimino)sulfonic acid.

6. Outlook

In contrast to chiral divalent BINOL-derivatives, the herein disclosed monovalent tetrahydroindacene scaffold enables the synthesis of dimeric C_2-symmetric Brønsted acids based on the imidodisulfuryl framework. Analogously to the recently reported JINGLE catalyst class, the shown dimeric and C_2-symmetric disulfurylimide **6.2** comprises relatively high acidity (pK_a *ca.* 5 in MeCN), but comprises of a novel source of chirality ideally providing a structurally confined active site.[24, 124]



*Scheme 70: Synthesis of tetrahydroindacene-derived disulfurylimide **6.2**.*

In analogy to recent developments on the **IDP** scaffold, a subsequent replacement of Lewis basic oxygen atoms with NTf units would tremendously increase the acidity of the target catalyst motif. The new access of bis(trifluoromethylsulfonylimino)sulfonyl units in combination with the new chiral indacene motif provide an ideal starting point to access such dimeric and presumably extremely acidic catalyst motifs based on the disulfonimide scaffold (**6.4**). The successful realization of these novel dimeric catalyst motifs may complement existing catalyst scaffolds on the established imidodiphosphate framework.

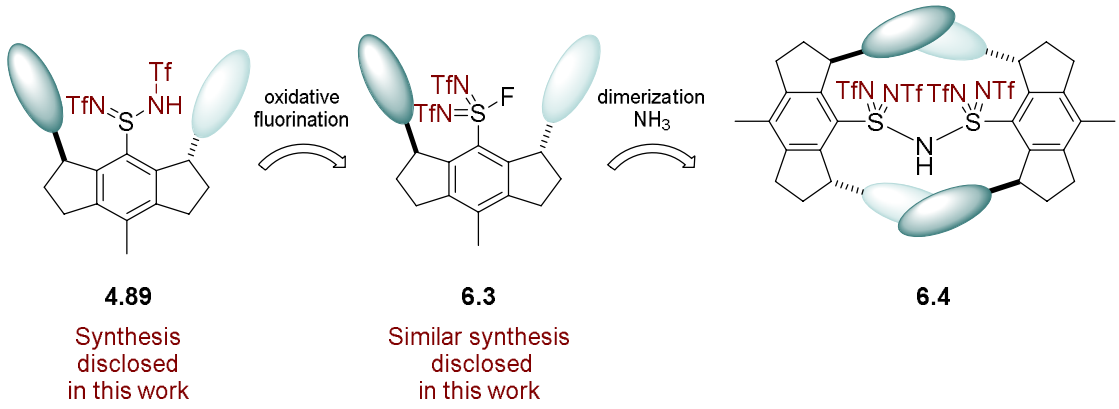


*Figure 17: Dimerization of tetrahydroindacene-derived bis(iminosulfonyl)sulfonyl fluoride **6.3** to access a new class of dimeric catalyst motifs based on the disulfonimide core (**6.4**).*

7 Experimental Section

General Information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Reactions were monitored by thin layer chromatography (TLC) on silica gel pre-coated plastic sheets (0.2 mm, Macherey-Nagel) or glass plates (SIL G-25 UV_{254}, 0.25 mm, Macherey-Nagel). Visualization was accomplished by irradiation with UV light at 254 nm and/or phosphomolybdic acid (PMA) stain. PMA stain: PMA (10 g) in EtOH (100 ml). Flash column chromatography (FCC) was performed on Merck silica gel (60, particle size 0.040–0.063 mm) or on an automated flash purification system: BIOTAGE Isolera^{TM} Four with pre-packed Sfär Silica HC D columns (10 and 25 g). The solvent mixtures used as eluent refer to percentage by volume (vol%). NMR spectra were recorded on a Bruker AV-500 or Bruker AV-600 spectrometer in deuterated solvents. Proton chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ δ=7.26 ppm; CD_2Cl_2 δ=5.32 ppm). NMR solvents were dried and stored over pre-activated 4 Å molecular sieves. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sext = sextet, h = heptet, m = multiplet, br = broad), coupling constants (Hz) and integration. ^{13}C chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ δ=77.16 ppm; CD_2Cl_2 δ=53.84 ppm). ^{19}F, ^{31}P NMR spectra were referenced in ppm from CCl_3F and H_3PO_4, respectively. High resolution mass spectra were determined on a Bruker APEX III FTMS (7 T magnet). The title compounds are named based on a suggestion of ChemDraw Professional (15.0; Cambridgesoft).

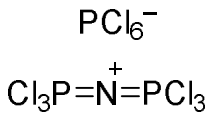
General reaction setup

Unless otherwise stated, all reactions were performed under argon using common Schlenk techniques. Reaction vessels were flame-dried under high vacuum (h.v.), purged with argon and cooled to room temperature (r.t.). Hexachlorobisphosphazonium salts (**HCPP**, **HCPC**, **HCPA**) were stored in a Schlenk flask under argon at r.t.. Hexachlorobisphosphazonium salts were transferred to a tared flame-dried and argonated (1 atm) Schlenk flask and weighted again to determine the amount of hexachlorobisphosphazonium salt transferred to the reaction vessel. All solvents were dried using common drying procedures and stored over pre-activated 4 Å molecular sieves. Acidifications of catalysts in salt form were carried out by dissolving the catalyst (salt form) in CH_2Cl_2 with an equimolar amount of HCl (6 M) and stirring the

corresponding emulsion for 30 minutes at r.t.. The lower organic phase (CH_2Cl_2) needs to be separated and concentrated to dryness to furnish the desired catalyst in acidic form. An alternative acidification procedure relies on a chromatographic acidification, in which the catalyst in salt form was dissolved in a small quantity of CH_2Cl_2 and passed through a plug of pre-acidified DOWEX® 50WX8 (50-100 mesh). DOWEX® 50WX8 was purchased from Sigma-Aldrich and was acidified by washing the resin with aqueous H_2SO_4 (0.125 N) until the elute remains colorless, followed by subsequent washing with methanol, Et_2O and CH_2Cl_2.

7.1 Synthesis of Hexachlorobisphosphazonium Salts

One-step synthesis of hexachlorobisphosphazonium hexachlorophosphate (HCPP)

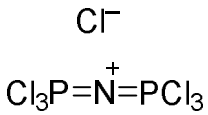


A 250 ml two necked round bottom flask, equipped with a reflux condenser and sulfuric acid filled gas bubbler, was flame-dried under argon. The flask was charged with PCl_5 (53.0 g, 254 mmol, 1 equiv.), NH_4Cl (4.31 g, 80.6 mmol, 0.95 equiv.) and suspended in nitrobenzene (80 ml). The suspension was heated 5.5 h to 130 °C. Within the first 3 h a constant gas development was observed, whereas the gas development slowly ceased after that time and most of the solid dissolved during the reaction progress (Note: sublimed PCl_5 was re-dissolved into the reaction mixture by carefully shaking the glas aparatus). The hot reaction mixture was filtered under inert conditions (argon overpressure through filter paper fitted PE-tube) into a 100 ml Schlenk-flask. Upon cooling to r.t., a colorless precipitate formed from the filtrate. The suspension was left o.n. at r.t. and filtered under inert reaction conditions (argon overpressure through filter paper fitted PE-tube). The beige solid was extensively washed with dry hexanes until the filtrates remain colorless and additionally washed with DCM (100 ml) to afford the desired product as a colorless solid (62%, 28.3 g, 53.2 mmol).

^{31}P NMR (203 MHz, CD_2Cl_2) δ=21.63 (s, 2P), –297.93 ppm (s, 1P).

Reference: *Z. Anorg. Allg. Chem.* **1977**, *433*, 229

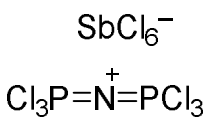
Synthesis of hexachlorobisphosphazonium chloride (HCPC)



A 100 ml Schlenk-flask was charged with hexachlorobisphosphazonium hexachlorophosphate (28.3 g, 53.2 mmol, 1 equiv.), which was then suspended in DCM (60 ml), followed by portion-wise addition of 4-Dimethylaminopyridine (6.50 g, 53.2 mmol, 1 equiv.) to form a dark yellow solution, of which a colorless solid precipitated upon few minutes. The reaction mixture was stirred 1 h at r.t., followed by inert filtration (argon overpressure through filter paper fitted PE-tube). The remaining yellowish solid was washed with DCM (100 ml each run), where each time the solid was suspended and thoroughly stirred in DCM at r.t. and cooled in an ice-bath before the filtration process. The washing process was repeated three times until the filtrate remained colorless to afford the desired product as a colorless solid (87%, 14.9 g, 46.0 mmol).

^{31}P NMR (203 MHz, CD_2Cl_2) δ = –10.1 (s, 2P).
Reference: *Inorg. Chem.* **2004**, *43*, 2765

Synthesis of hexachlorobisphosphazonium hexachloroantimonate (HCPA)

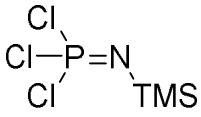


A flame-dried 50 ml Schlenk tube was charged with hexachlorobisphosphazonium hexachlorophosphate, HCPP (2.83 g, 5.32 mmol, 1 equiv.), suspended in DCM (40 ml), cooled to –78°C (dry ice, acetone bath), followed by subsequent addition of antimony pentachloride, SbCl5 (708µl, 5.59 mmol, 1.05 equiv.). The suspension was stirred 10 min at –78°C, allowed to warm to r.t. and stirred o.n.. The next day the colorless suspension was filtered under inert conditions (PE-tube fitted with filter paper, filtration through argon overpressure). The colorless residue was washed with DCM (20 ml), cooled to –78°C and filtered again under inert conditions. The colorless precipitate was dried in h.v. ($1x10^{-3}$ mbar) for 1 h to obtain a colorless solid powder (45%, 1.49 g, 2.39 mmol).

^{31}P NMR (203 MHz, CD_2Cl_2) δ = 21.65.

Alternative two-step synthesis of HCPP

Synthesis of (trimethylsilyl)phosphorimidoyl trichloride

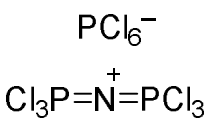


Step 1: A 500 ml flame-dried two-neck round-bottom flask equipped with a dropping funnel was charged with diethylether (200 ml), hexamethyldisilazane (12.5 ml, 60 mmol), cooled to 0 °C (ice bath) followed by dropwise addition of *n*-butyllithium (24 ml, 2.5 M in hexanes, 60 mmol) within 5 minutes at 0 °C. The solution was stirred additional 30 minutes at 0 °C and slowly warmed to r.t. forming a colorless suspension. The suspension was cooled again to 0 °C (ice bath) followed by the dropwise addition of phosphorous trichloride (5.2 ml, 60 mmol) within 2 minutes. The cooling bath was removed after full addition of phosphorous trichloride and the colorless reaction suspension was allowed to warm to r.t. and stirred additional 30 minutes at r.t.. The colorless suspension was cooled to 0 °C (ice bath) followed by the dropwise addition of sulfuryl chloride (6 ml, 60 mmol). The colorless suspension was warmed to r.t. again and stirred additional 60 minutes at r.t. followed by inert filtration over a pad of previously dried celite (Schlenk frit, height 3 cm of celite) to obtain a colorless filtrate which was carefully concentrated (130 mbar to 30 mbar) at 0 °C under inert conditions. The resulting highly viscous oil was then purified by bulb-to-bulb distillation under static vacuum (5 mbar, 25 to 40 °C) condensing the desired product at –78 °C. (Trimethylsilyl)phosphorimidoyl trichloride was isolated as a colorless viscous oil (89%, 12 g, 53 mmol).

^{1}H NMR (501 MHz, CD_2Cl_2) δ= 0.17 ppm (d, $J_{H\text{-}P}$=1.1, 9H). ^{31}P{^{1}H} NMR (203 MHz, CD_2Cl_2) δ –55.35 ppm (s, 1P).

Reference: *Inorg. Chem.* **2002**, *41*, 1690

Synthesis of hexachlorobisphosphazonium hexachlorophosphate (HCPP)



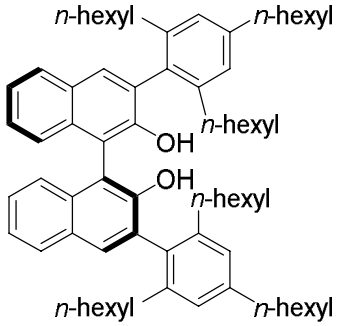
Step 2: A flame-dried 100 ml Schlenk tube was charged with phosphorus pentachloride (16.6 g, 79.8 mmol) followed by the addition of a solution of (trimethylsilyl)phosphorimidoyl trichloride (12.0 g, 53.0 mmol) in dichloromethane (25 ml) at 0 °C to form a colorless suspension which was stirred 2.5 h at r.t.. Additional dichloromethane (20 ml) was added followed by inert filtration through a filter paper fitted PE-tube with argon pressure (1.3 bar). The colorless precipitate was washed followed by inert filtration two times with dichloromethane (40 ml each) and dried in high vacuum ($1x10^{-3}$ mbar) for 5 hours to obtain the desired product, as a colorless powder (15.4 g, 72%).

^{31}P NMR (203 MHz, CD_2Cl_2) δ=21.63 (s, 2P), –297.93 ppm (s, 1P).

Reference: *Inorg. Chem.* **2004**, *43*, 2765

7.2 Synthesis of BINOLs

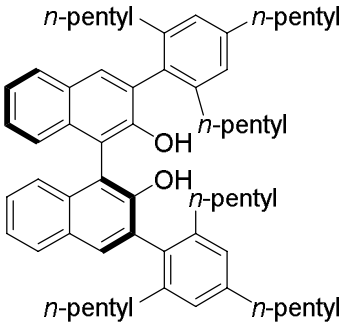
(S)-3,3´-Bis(2,4,6-tri-n-hexylphenyl)-BINOL



An under high vacuum flame-dried 50 ml Schlenk tube was argonated and charged with a freshly prepared solution of (2,4,6-tri-*n*-hexylphenyl)zinc(II)bromide (8.80 ml (c = 0.5 ml), 4.4 mmol, 4 equiv.) and (S)-3,3'-dibromo-2,2'-bis(methoxymethoxy)-1,1'-binaphthalene (585 mg, 1.1 mmol, 1 equiv.) followed by the addition of THF (10 ml). $Pd(P(t\text{-}Bu)_3)_2$ (16.9 mg, 33 µmol, 3 mol%) was added, the solution cooled in liquid nitrogen, degassed by vacuum suction and purged with argon. The reaction was heated to 60 °C for 24 h. HCl in dioxane (4 M, 12 ml, 48 mmol, 43 equiv.) was added and the resulting yellowish solution stirred for additional 24 h at r.t.. All volatiles were removed *in vacuo*, the residue dissolved in CH_2Cl_2, transferred to a separation funnel followed by the addition of water. The aqueous phase was extracted with CH_2Cl_2 (3x30 ml), the combined organic phase dried over sodium sulfate, concentrated to dryness and further purified by FCC (gradient: hexanes / CH_2Cl_2 95:5 to 90:10) to elute the desired product as yellowish oil (845 mg, 82%).

^{1}H NMR (501 MHz, CD_2Cl_2) δ=7.89 (dd, *J*=8.2, 1.3 Hz, 2H), 7.76 (s, 2H), 7.38 (ddd, *J*=8.0, 6.7, 1.2 Hz, 2H), 7.30 (ddd, *J*=8.2, 6.8, 1.3 Hz, 2H), 7.20 (dd, *J*=8.4, 1.1 Hz, 2H), 7.03 (d, *J*=3.6 Hz, 4H), 4.97 (s, 2H), 2.66–2.59 (m, 4H), 2.55–2.46 (m, 2H), 2.46–2.38 (m, 4H), 2.38–2.26 (m, 2H), 1.67 (ddd, *J*=13.0, 8.5, 6.4 Hz, 4H), 1.50–1.29 (m, 20H), 1.26–1.13 (m, 12H), 1.13–1.02 (m, 12H), 0.94–0.86 (m, 6H), 0.78 (t, *J*=7.1 Hz, 6H), 0.68 ppm (t, *J*=6.9 Hz, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ=150.9, 143.4, 142.6, 142.5, 134.0, 132.4, 131.6, 129.6, 129.5, 128.7, 127.4, 127.4, 127.0, 124.6, 124.1, 113.6, 36.3, 34.5, 34.3, 32.2, 32.0, 31.9, 31.5, 31.4, 29.9, 29.6, 29.6, 23.1, 23.0, 22.9, 14.3, 14.2, 14.1 ppm. (other signals not observed or detected). HRMS (ESI): m/z calcd for $C_{68}H_{93}O_2^-$: 941.719160 $[M\text{-}H]^-$, found 941.718105.

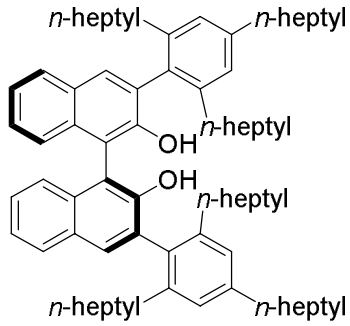
(S)-3,3´-Bis(2,4,6-tri-n-pentylphenyl)-BINOL



The BINOL has been synthesized based on example **4.1.** FCC-conditions: (gradient: hexanes / CH_2Cl_2 95:5 to 80:20); 71% yield (yellowish oil).

^{1}H NMR (501 MHz, CD_2Cl_2) δ=7.89 (dd, *J*=8.3, 1.3 Hz, 2H), 7.76 (s, 2H), 7.38 (ddd, *J*=8.1, 6.7, 1.2 Hz, 2H), 7.30 (ddd, *J*=8.2, 6.7, 1.3 Hz, 2H), 7.20 (dd, *J*=8.4, 1.1 Hz, 2H), 7.03 (d, *J*=4.4 Hz, 4H), 4.98 (s, 2H), 2.66–2.60 (m, 4H), 2.55–2.46 (m, 2H), 2.45–2.36 (m, 4H), 2.32 (dt, *J*=13.7, 7.6 Hz, 2H), 1.72–1.62 (m, 4H), 1.50–1.45 (m, 4H), 1.42 (dd, *J*=8.5, 6.7 Hz, 4H), 1.40–1.36 (m, 8H), 1.21 (qd, *J*=3.7, 1.6 Hz, 8H), 1.09 (dddt, *J*=10.3, 5.5, 3.5, 2.1 Hz, 8H), 0.95–0.90 (m, 6H), 0.82–0.77 (m, 6H), 0.69 ppm (t, *J*=6.9 Hz, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ=151.0, 143.3, 142.5, 142.5, 133.9, 132.4, 131.6, 129.6, 129.5, 128.7, 127.4, 127.3, 127.0, 124.6, 124.1, 113.5, 36.2, 34.4, 34.2, 32.4, 32.1, 32.0, 31.6, 31.2, 31.0, 23.0, 22.8, 22.8, 14.3, 14.2, 14.0 ppm (other signals not observed or detected). HRMS (ESI): m/z calcd for $C_{62}H_{82}O_2^-$: 858.631366 $[M-H]^-$, found 858.631480.

(S)-3,3´-Bis(2,4,6-tri-n-heptylphenyl)-BINOL



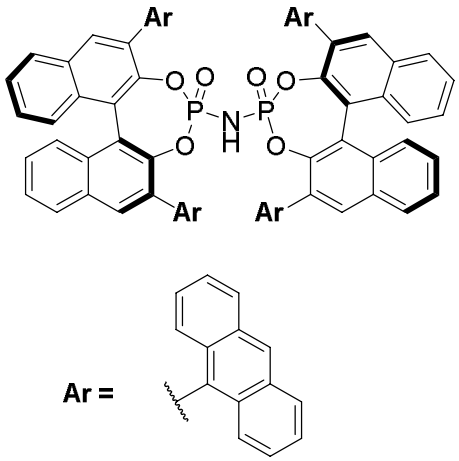
The BINOL has been synthesized based on example **4.1.** FCC-conditions: (gradient: hexanes / CH_2Cl_2 95:5 to 80:20); 53% yield (yellowish oil).

53% yield; ^{1}H NMR (501 MHz, CD_2Cl_2) δ=7.89 (d, *J*=7.7 Hz, 2H), 7.75 (s, 2H), 7.38 (ddd, *J*=8.1, 6.8, 1.3 Hz, 2H), 7.29 (ddd, *J*=8.2, 6.8, 1.3 Hz, 2H), 7.19 (dd, *J*=8.5, 1.1 Hz, 2H), 7.03 (d, *J*=3.9 Hz, 4H), 4.96 (s, 2H), 2.66–2.59 (m, 4H), 2.50 (dt, *J*=13.5, 7.8 Hz, 2H), 2.46–2.36 (m, 4H), 2.36–2.28 (m, 2H), 1.70–1.62 (m, 4H), 1.50–1.42 (m, 4H), 1.42–1.35 (m, 10H), 1.35–1.28 (m, 10H), 1.23–1.14 (m, 16H), 1.13–1.00 (m, 16H), 0.93–0.88 (m, 6H), 0.82–0.77 (m, 6H), 0.76–0.70 ppm (m, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ=146.1, 138.5, 137.7, 137.7, 129.1, 127.5, 126.7, 124.8, 124.6, 123.9, 122.6, 122.2, 119.8, 119.2, 108.8, 31.4, 29.7, 29.4, 27.5, 27.4, 27.3, 27.1, 26.7, 26.6, 25.4, 25.1, 24.8, 24.6, 18.3, 18.2, 18.1, 9.5, 9.4, 9.4 ppm. (other signals not observed or detected). HRMS (ESI): m/z calcd for $C_{74}H_{105}O_2^-$: 1025.812005$[M-H]^-$, found 1025.812920

7.3 Synthesis of Imidodiphosphates (IDP)

5.5 IDP-3

(S,S)-2,6-di(anthracen-9-yl)-4-((-2,6-di(anthracen-9-yl)-4-oxidodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)amino)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide

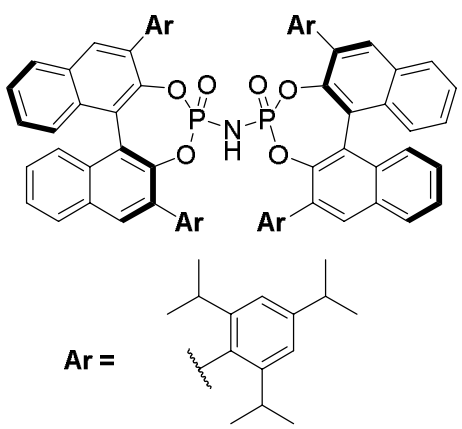


An under high vacuum 5 ml flame-dried Schlenk-tube was charged with hexachlorobisphosphazonium hexachlorophosphate (41 mg, 77 µmol), (*S*)-3,3'-di(anthracen-9-yl)-[1,1'-binaphthalene]-2,2'-diol (98.4 mg, 154 µmol) followed by the addition of pyridine (1 ml). The suspension was stirred for 15 minutes at r.t. followed by the addition of distilled water (250 µl, 13.8 mmol) and was stirred additional 4 h at r.t.. The reaction mixture was poured into aqueous HCl (6 M) solution and extracted with dichloromethane. The combined organic phase was dried over sodium sulfate, concentrated in vacuo and purified by flash column chromatography (dichloromethane) to afford a colorless solid, which was acidified with aqueous 6 M HCl. The solid was dissolved in a small quantitiy of dichloromethane and precipitated with hexanes. After decantation of the organic phase the desired product was obtained as a colorless powder (90 mg, 85%).

^{1}H NMR (501 MHz, CD_2Cl_2) δ = 8.19 (s, 2H), 8.07 – 8.01 (m, 4H), 7.90 (s, 2H), 7.88 – 7.85 (m, 2H), 7.85 – 7.81 (m, 2H), 7.79 (s, 2H), 7.74 – 7.69 (m, 7H), 7.69 – 7.63 (m, 7H), 7.52 (ddd, *J*=8.2, 6.7, 1.3, 2H), 7.49 (s, 2H), 7.48 – 7.43 (m, 4H), 7.41 – 7.37 (m, 2H), 7.36 – 7.32 (m, 2H), 7.31 – 7.24 (m, 6H), 7.14 – 7.07 (m, 4H), 6.88 (ddd, *J*=9.0, 6.5, 1.3, 2H), 5.88 (ddd, *J*=8.7, 6.5, 1.2, 2H), 5.59 – 5.52 (m, 2H), 2.13 ppm (sbr, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 146.57, 134.28, 133.03, 131.88, 131.59, 131.32, 131.18, 130.94, 130.89, 130.62, 129.11, 128.91, 128.83, 128.14, 127.75, 127.67, 127.64, 127.34, 126.55, 126.31, 126.14, 125.31, 125.28, 125.16, 122.61 ppm. ^{31}P NMR (203 MHz, CD_2Cl_2) δ = 12.83 ppm (s). HRMS (ESI): m/z calcd for $C_{96}H_{55}N_1O_6P_2^-$: 1380.358843[M–H]$^+$, found 1380.358390

IDP-4

(S,S)-4,4'-azanediylbis(2,6-bis(2,4,6-triisopropylphenyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide)

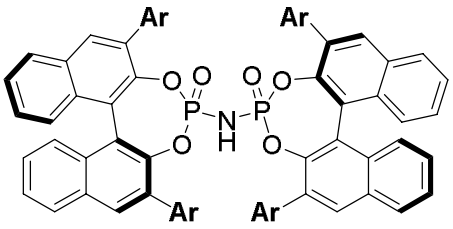


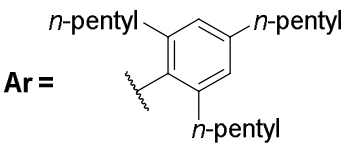
A flame-dried Schlenk was charged with HCPP (58.0 mg, 109 µmol 1 equiv.), (*S*)-TRIP-BINOL (155 mg, 224 µmol, 2.06 equiv.) followed by the addition of pyridine (2.2 ml). The resulting suspension was stirred 22 h at r.t. followed by the addition of water (400 µl, 22.2 mmol, 204 equiv.) and stirred additional 48 h at 50 °C. After cooling to r.t., the reaction mixture was poured into aqueous HCl (6 M, 20 ml) and extracted with CH_2Cl_2 (3x20 ml). The combined organic phase was dried over sodium sulfate, concentrated to dryness and the resulting crude product was purified by FCC (gradient: hexanes / CH_2Cl_2 4:1 up to 2:3) to elute the desired product as a salt. The salt was dissolved in CH_2Cl_2 (15 ml), treated with aqueous HCl (6 M, 15 ml) under vigorous for 30 minutes, the organic phase was separated, concentrated to dryness and dried o.n. in h.v. to furnish the desired product in acidic form as a colorless solid (120 mg, 74%)

^{1}H NMR (501 MHz, CD_2Cl_2) δ=7.89 (d, *J*=8.2 Hz, 2H), 7.87–7.80 (m, 4H), 7.54 (s, 2H), 7.48 (ddd, *J*=8.1, 6.7, 1.1 Hz, 2H), 7.44 (ddd, *J*=8.2, 6.8, 1.1 Hz, 2H), 7.27 (ddd, *J*=8.3, 6.8, 1.3 Hz, 2H), 7.19 (ddd, *J*=8.4, 6.8, 1.3 Hz, 4H), 6.99 (d, *J*=8.9 Hz, 2H), 6.97 (t, *J*=2.5 Hz, 4H), 6.84 (d, *J*=1.8 Hz, 2H), 6.75 (d, *J*=1.8 Hz, 2H), 5.58 (s, 3H), 2.84 (p, *J*=6.9 Hz, 2H), 2.76 (p, *J*=6.9 Hz, 2H), 2.64–2.48 (m, 4H), 2.43 (p, *J*=6.8 Hz, 2H), 1.28 (d, *J*=6.9 Hz, 6H), 1.23–1.20 (m, 12H), 1.16 (d, *J*=6.9 Hz, 6H), 1.12 (d, *J*=6.9 Hz, 6H), 1.04 (d, *J*=6.8 Hz, 6H), 1.01 (d, *J*=6.8 Hz, 7H), 0.93 (d, *J*=6.7 Hz, 6H), 0.86 (d, *J*=6.8 Hz, 6H), 0.75 (d, *J*=6.8 Hz, 6H), 0.43 (d, *J*=6.8 Hz, 6H), -0.20 ppm (d, *J*=6.8 Hz, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ=149.0, 148.5, 148.3, 147.9, 147.6, 146.9, 146.8, 146.8, 146.1, 133.6, 133.4, 132.9, 132.8, 132.6, 131.7, 131.5, 130.9, 128.8, 128.1, 127.7, 127.2, 126.6, 126.5, 126.0, 126.0, 122.6, 122.4, 121.8, 120.7, 54.4, 54.2, 54.0, 53.8, 53.6, 34.7, 34.6, 31.8, 31.5, 31.2, 31.1, 27.3, 25.9, 25.4, 24.8, 24.6, 24.5, 24.0, 24.0, 23.8, 23.7, 23.3, 22.6 ppm. (other signals not observed or detected). ^{31}P NMR (203 MHz CD_2Cl_2) δ=13.96 (s). HRMS (ESI): m/z calcd for $C_{148}H_{210}N_1O_6P_2$+H^+: 1484.797043 $[M+H]^+$, found 1484.798910

IDP-5

(S,S)-4,4'-azanediylbis(2,6-bis(2,4,6-tripentylphenyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide)





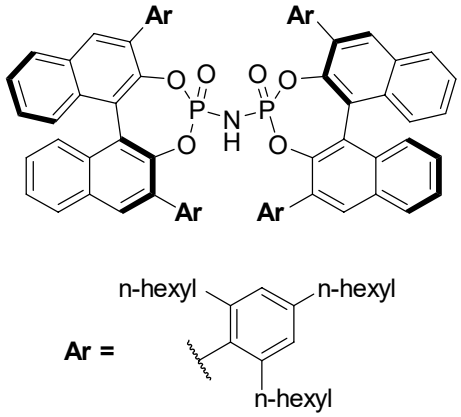
A 50 ml flame-dried and argonated Schlenk tube was charged with HCPP (509 mg, 0.95 mmol), dissolved in pyridine (10 ml) followed by immediate addition of a solution of (S)-3,3´-bis(2,4,6-tri-n-pentylphenyl)-BINOL (1.69 g, 1.96 mmol, 2.05 equiv.) in pyridine (10 ml). The slightly yellowish solution was stirred at r.t. for 18 h followed by the addition of water (5 ml, 290 equiv.) and stirred additional 4 h at 60 °C until full conversion was observed by ^{31}P-NMR. The reaction mixture was diluted with additional water (15 ml) resulting in the formation of a colorless suspension which upon addition of CH_2Cl_2 (20 ml) formed an emulsion, which was transferred to a separation funnel. The aqueous phase was extracted with CH_2Cl_2 (twice 100 ml each) and EtOAc (50 ml). The combined organic phase was washed with sat. $NaHCO_3$, dried over sodium sulfate, concentrated to dryness and further purified by FCC (gradient: hexanes / CH_2Cl_2 (4:1) up to hexanes / CH_2Cl_2 (1:1) to elute the desired product as a colorless foam. The product in salt form was dissolved in CH_2Cl_2 (10 ml) followed by the addition of HCl 6 N (10 ml) and the resulting emulsion stirred vigorously for 30 minutes. The CH_2Cl_2layer was isolated, concentrated to dryness and dried o.n. in h.v. at r.t. to furnish the desired product in acidic form as a highly viscous oil (83% yield, 1.45 g).

^{1}H NMR (501 MHz, CD_2Cl_2) δ=7.90–7.82 (m, 4H), 7.77 (s, 2H), 7.56 (s, 2H), 7.49 (ddd, *J*=8.1, 6.5, 1.4 Hz, 2H), 7.45–7.38 (m, 4H), 7.36 (ddd, *J*=8.3, 6.6, 1.3 Hz, 2H), 7.18 (ddd, *J*=8.3, 6.8, 1.3 Hz, 2H), 7.01 (d, *J*=8.6 Hz, 2H), 6.92 (d, *J*=1.8 Hz, 2H), 6.80 (t, *J*=2.0 Hz, 4H), 6.38 (d, *J*=1.8 Hz, 2H), 5.19 (s, 1H), 2.51 (ddd, *J*=16.1, 8.6, 6.1 Hz, 8H), 2.36 (ddd, *J*=14.2, 8.1, 6.5 Hz, 2H), 2.21 (ddd, *J*=14.2, 8.1, 6.7 Hz, 2H), 2.15 (t, *J*=8.2 Hz, 4H), 2.09–2.02 (m, 2H), 1.99 (ddd, *J*=9.4, 6.4, 2.6 Hz, 4H), 1.67–1.47 (m, 12H), 1.47–1.39 (m, 2H), 1.39–1.25 (m, 20H), 1.24–1.03 (m, 20H), 0.90–0.83 (m, 18H), 0.79 (dt, *J*=11.0, 7.0 Hz, 18H), 0.64 (t, *J*=7.3 Hz, 6H), 0.61–0.50 (m, 6H), 0.45 (t, *J*=6.8 Hz, 6H), 0.33–0.23 ppm (m, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ=146.7, 146.0, 142.9, 142.6, 141.6, 141.5, 133.4, 133.2, 133.0, 133.0, 132.6, 132.5, 132.4, 131.6, 131.1, 128.5, 128.5, 127.7, 127.2, 127.1, 126.8, 126.4, 126.2, 126.2, 125.9, 125.7, 122.7, 122.1, 36.3, 36.0, 34.4, 34.2, 34.1, 33.6, 32.6, 32.4, 32.3, 32.1, 32.1, 31.8, 31.6, 31.5,

31.2, 31.0, 23.3, 23.0, 23.0, 22.9, 22.5, 14.3, 14.3, 14.2, 14.1, 13.8 ppm. (other signals not observed or detected). ^{31}P NMR (203 MHz, CD_2Cl_2) δ=4.68 ppm. HRMS (ESI): *m*/*z* calcd for $C_{124}H_{160}N_1O_6P_2^-$: 1821.172643 [*M*–H]$^-$; found: 1821.174180

IDP-6

(S,S)-4,4'-azanediylbis(2,6-bis(2,4,6-trihexylphenyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide)



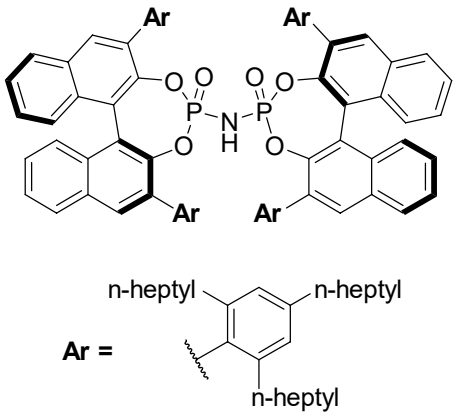
A 10 ml flame-dried and argonated Schlenk tube was charged with HCPP (46 mg, 86,4 µmol) and dissolved in a solution of (*S*)-(o,o,p-tri(n-hexyl)phenyl)BINOL (163 mg, 0,17 mmol 2 equiv. in 1.5 ml pyridine). The reaction was stirred for 19 h at r.t. followed by the addition of water (300 µl, 16.6 mmol, 192 equiv.) and stirred additional 5 h at 80 °C until ^{31}P-NMR analysis shows clean hydrolysis to the desired product. After cooling to r.t. the reaction mixture was poured into 30 ml $HCl_{(aq)}$ and extracted with CH_2Cl_2 (3x30 ml). The combined organic phases were dried over sodium sulfate, concentrated to dryness and purified by FCC (Biotage, gradient: hexanes up to hexanes / CH_2Cl_2 (1:1)) to elute the desired product as a salt. Acidification was carried out by dissolving the salt in CH_2Cl_2 (3 ml) followed by the addition of HCl 6 N (3 ml) and the resulting emulsion stirred vigorously for 30 minutes. The organic phase was isolated, concentrated to dryness followed by drying o.n. in h.v. to furnish the desired product in acidic form as a colorless viscous oil (78%, 172 mg)

^{1}H NMR (501 MHz, CD_2Cl_2) δ=7.86 (dd, *J*=13.8, 8.2 Hz, 4H), 7.77 (s, 2H), 7.56 (s, 2H), 7.49 (dd, *J*=8.3, 6.6 Hz, 2H), 7.42 (dd, *J*=16.8, 8.6 Hz, 4H), 7.37–7.33 (m, 2H), 7.17 (ddd, *J*=8.3, 6.7, 1.3 Hz, 2H), 7.01 (d, *J*=8.6 Hz, 2H), 6.92 (s, 2H), 6.80 (dd, *J*=4.8, 1.7 Hz, 4H), 6.37 (d, *J*=1.6 Hz, 2H), 6.05 (sbr, 1H), 2.59–2.43 (m, 8H), 2.33 (dt, *J*=14.2, 7.2 Hz, 2H), 2.23 (dt, *J*=14.1, 7.3 Hz, 2H), 2.16 (t, *J*=8.2 Hz, 4H), 2.08–1.92 (m, 6H), 1.65–1.48 (m, 12H), 1.46–1.39 (m, 3H), 1.38–1.26 (m, 28H), 1.25–1.09 (m, 28H), 1.08–0.98 (m, 6H), 0.95–0.82 (m, 20H), 0.82–0.74 (m, 23H), 0.57 (t, *J*=7.1 Hz, 12H), 0.32 ppm (dd, *J*=12.3, 6.7 Hz, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ=146.3, 145.6, 142.4, 142.1, 141.1, 141.0, 133.0, 132.8, 132.6, 132.5, 132.2, 132.1, 132.0, 131.1, 130.7, 128.1, 128.1, 127.3, 126.7, 126.5, 126.3, 126.0, 125.8, 125.7, 125.6, 125.5, 125.2, 122.3, 121.7, 36.0, 35.6, 34.1, 33.7, 33.7, 33.2, 32.2, 32.0, 31.8, 31.8, 31.7, 31.7, 31.5, 31.4, 31.2, 31.0, 31.0, 31.0, 29.6, 29.4, 29.3, 29.2, 28.8, 28.2, 22.7, 22.6, 22.5, 22.5, 22.3,

14.0, 13.9, 13.8, 13.8, 13.5 ppm. (other signals not observed or detected). ^{31}P NMR (203 MHz, CD_2Cl_2) δ=4.73 ppm (s, 2P). HRMS (ESI): m/z calcd for $C_{136}H_{186}N_1O_6P_2$+H^+: 1991.374993 $[M+H]^+$, found 1991.375490

IDP-7

(S,S)-4,4'-azanediylbis(2,6-bis(2,4,6-triheptylphenyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide)



A 10 ml flame-dried and argonated Schlenk tube was charged with HCPP (117 mg, 220 µmol) and dissolved in a solution of *(S)*-(o,o,p-tri(n-heptyl)phenyl)BINOL (490 mg, 0.48 mmol 2.1 equiv. in 4 ml pyridine). The reaction was stirred for 19 h at r.t. followed by the addition of water (800 µL, 44.4 mmol, 202 equiv.) and stirred additional 5 h at 80 °C until ^{31}P-NMR analysis shows clean hydrolysis to the desired product. After cooling to r.t. the reaction mixture was poured into 30 ml $HCl_{(aq)}$ and extracted with CH_2Cl_2 (3x30 ml). The combined organic phases were dried over sodium sulfate, concentrated to dryness and purified by FCC (Biotage, gradient: hexanes up to hexanes / CH_2Cl_2 (3:2)) to elute the desired product as a salt. Acidification was carried out by dissolving the salt in CH_2Cl_2 (5 ml) and $HCl_{(aq)}$ (6 M, 5 ml). The organic phase was isolated, concentrated to dryness followed by drying o.n. in h.v. to furnish the desired product as a colorless viscous oil (82%, 389 mg)

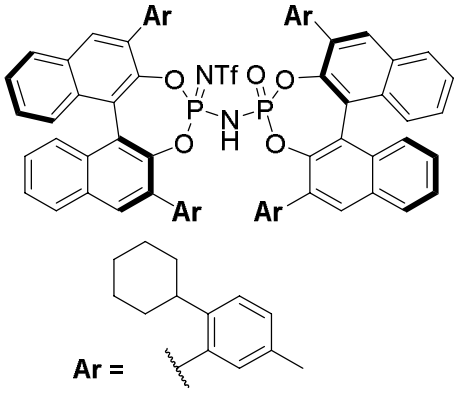
^{1}H NMR (501 MHz, CD_2Cl_2) δ=7.85 (dd, *J*=14.4, 7.9 Hz, 4H), 7.77 (s, 2H), 7.56 (s, 2H), 7.49 (ddd, *J*=8.1, 6.5, 1.3 Hz, 2H), 7.45–7.41 (m, 2H), 7.41–7.36 (m, 2H), 7.36–7.32 (m, 2H), 7.17 (ddd, *J*=8.3, 6.8, 1.4 Hz, 2H), 7.01 (d, *J*=8.6 Hz, 2H), 6.91 (d, *J*=1.7 Hz, 2H), 6.80 (dd, *J*=7.3, 1.7 Hz, 4H), 6.37 (d, *J*=1.7 Hz, 2H), 4.10 (sbr, 1H), 2.58–2.44 (m, 8H), 2.34 (dt, *J*=14.2, 7.2 Hz, 2H), 2.22 (dt, *J*=14.2, 7.3 Hz, 2H), 2.15 (t, *J*=8.2 Hz, 4H), 2.09–2.00 (m, 4H), 1.96 (ddd, *J*=13.5, 10.5, 5.8 Hz, 2H), 1.63–1.49 (m, 12H), 1.36–1.24 (m, 38H), 1.24–1.12 (m, 36H), 1.04–0.95 (m, 8H), 0.93–0.75 (m, 50H), 0.70 (t, *J*=7.1 Hz, 6H), 0.62–0.48 (m, 6H), 0.30 ppm (dt, *J*=11.8, 7.6 Hz, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ=146.8, 146.7, 146.7, 146.0, 146.0, 146.0, 142.9, 142.6, 142.5, 141.6, 141.4, 133.5, 133.2, 133.1, 133.0, 133.0, 132.6, 132.5, 132.4, 131.5, 131.1, 128.6, 128.5, 127.7, 127.2, 127.1, 126.8, 126.4, 126.2, 126.2, 126.1, 125.9, 125.7, 122.7,

122.1, 36.4, 36.1, 34.5, 34.2, 34.1, 33.7, 32.5, 32.4, 32.3, 32.3, 32.2, 32.0, 31.9, 31.5 (d, *J*=2.5), 30.3, 30.1, 30.1, 29.9, 29.7, 29.7, 29.6, 29.6, 29.5, 29.2, 28.9, 23.3, 23.1, 23.1, 23.1, 22.8, 14.4, 14.3, 14.3, 14.3, 14.3, 14.2 ppm. (other signals not observed or detected). ^{31}P NMR (203 MHz, CD_2Cl_2) δ=4.02 ppm (s, 2P). HRMS (ESI): m/z calcd for $C_{148}H_{210}N_1O_6P_2$+H^+: 2159.562792 $[M+H]^+$, found 2159.561040

7.4 Synthesis of iminoimidodiphosphate (*i*IDP)

*i*IDP-2

(*S*,*S*)-N-(4-((2,6-bis(2-cyclohexyl-5-methylphenyl)-4-oxidodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)amino)-2,6-bis(2-cyclohexyl-5-methylphenyl)-4l5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-ylidene)-1,1,1-trifluoromethanesulfonamide



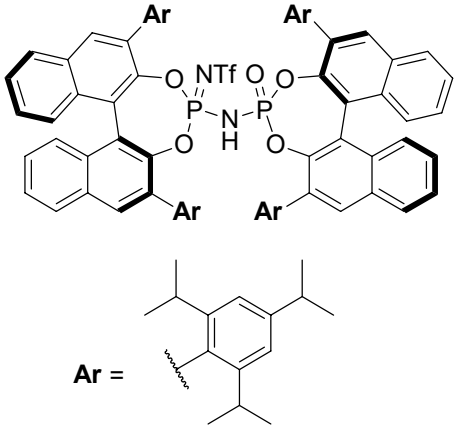
A 25 ml flame dried Schlenk-tube was charged with HCPP (265 mg, 498 µmol, 1 equiv.), 3,3'-bis(2-cyclohexyl-5-methylphenyl)-[1,1'-binaphthalene]-2,2'-diol (628 mg, 996 µmol, 2 equiv.) followed by addition of pyridine (10 ml) to form a yellowish solution. The reaction was stirred 50 min at r.t., followed by addition of $TfNH_2$ (371 mg, 2.49 mmol (5 equiv.) and stirred 1 h at r.t.. Water (1 ml, 55.5 mmol, 112 equiv.) was added and the resulting suspension stirred 6 h at r.t.. The reaction mixture was poured into ice-cooled $HCl_{(aq)}$ (6 M, 100 ml), transferred to a separation funnel and the aqueous phase extracted with DCM (3 x 40 ml). The combined organic phase was dried over sodium sulfate, concentrated to dryness and the crude product purified by FCC (DCM / EtOAc 4:1) to elute the desired product as salt. The salt was dissolved in a small quantitiy of DCM (ca. 4 ml), overlayered with pentane and stand for 3 d in a freezer (–20 °C) to form colorless crystals. The organic phase was decanted and the colorless crystals dissolved in 20 ml DCM followed by addition of HCl (6 M, 20 ml) and stirred for 30 min at r.t.. The DCM phase was isolated, concentrated to dryness and further dried in h.v o.n. to afford the desired product in acidic form as a colorless solid (67 %, 503 mg, 498 µmol). [NMR analysis shows two sets of signals, which indicate the presence of rotamers (ratio 9:1). The main signals are listed below]

^{1}H NMR (501 MHz, CD_2Cl_2) δ = 7.87 – 7.80 (m, 4H), 7.80 – 7.74 (m, 2H), 7.57 (ddd, *J*=19.1, 11.3, 7.6, 4H), 7.37 (dt, *J*=8.7, 7.3, 4H), 7.27 – 7.16 (m, 2H), 7.13 (ddd, *J*=12.3, 7.3, 2.7, 2H), 7.03 (dd, *J*=13.2, 8.4, 2H), 6.94 – 6.83 (m, 7H), 6.78 (s, 1H), 6.51 (s, 1H), 6.29 (d, *J*=2.0, 1H), 5.98 (d, *J*=1.9, 1H), 5.97 – 5.89 (sbr, 1H), 5.66 (d, *J*=2.0, 1H), 2.73 – 2.66 (m, 1H), 2.05 (s, 3H), 1.87 (s, 3H), 1.83 (s, 2H), 1.76 – 1.67 (m, 5H),1.52 (t, *J*=10.3, 4H), 1.43 (d, *J*=18.4, 6H), 1.37 (td, *J*=12.1, 11.2, 2.8, 2H), 1.31 – 1.06 (m, 14H), 1.04 – 0.94 (m, 3H), 0.92 – 0.50 (m, 11H), 0.43 – 0.29 (m, 1H), 0.07 – -0.06 ppm (m, 1H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 145.64, 145.53, 145.35, 145.27, 144.88, 144.80, 144.06, 144.00, 143.94, 143.76, 143.58, 143.47, 135.37, 135.26, 134.78, 134.72, 134.30, 134.22, 134.15, 133.37, 133.10, 132.93, 132.78, 132.74, 132.72, 132.57, 132.17, 132.14, 131.98, 131.93, 131.78, 131.63, 131.58, 131.41, 131.09, 130.23, 129.83, 129.58, 129.51, 129.31, 129.07, 128.98, 128.22, 127.54, 127.46, 127.17, 127.04, 126.99, 126.96, 126.63, 126.55, 126.43, 126.22, 125.12, 122.74, 122.44, 122.44, 121.80, 121.73, 54.27, 54.06, 53.84, 53.62, 53.41, 41.38, 41.29, 41.07, 40.03, 37.56, 37.07, 35.99, 35.67, 33.55, 33.50, 33.18, 31.98, 31.01, 27.65, 27.56, 27.48, 27.42, 27.13, 27.10, 26.92, 26.77, 26.56, 26.51, 26.32, 21.66, 21.46, 20.79, 20.57 ppm. (other signals not detected or observed. ^{19}F NMR (471 MHz, CD_2Cl_2) δ = –80.32 ppm (s, 3F). ^{31}P NMR (203 MHz, CD_2Cl_2) δ = –3.79 (d, *J*=117.4), –8.44 ppm (d, *J*=117.4). HRMS (ESI): *m*/*z* calcd for $C_{93}H_{88}F_3N_2O_7P_2S_1^-$: 1495.574514 [*M*–H]$^-$; found: 1495.574410

*i*IDP-3

(S,S)-1,1,1-trifluoro-N-(4-((4-oxido-2,6-bis(2,4,6-triisopropylphenyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)amino)-2,6-bis(2,4,6-triisopropylphenyl)-4l5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-ylidene)methanesulfonamide



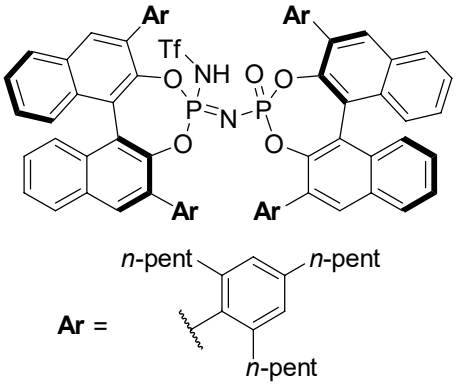
A flame-dried 10 ml Young-Schlenk tube was charged with HCPP (99.0 mg, 186 µmol), *(S)*- 3,3'-di(2,4,6-triisopropylphenyl)-[1,1'-binaphthalene]-2,2'-diol (268 mg, 388 µmol 2.1 equiv.) followed by the addition of toluene (2 ml) and subsequent dropwise addition of NEt_3 (109 µL, 781 µmol, 4.2 equiv.) to form a colorless suspension, which was stirred additional 1.5 h at r.t.. $TfNH_2$ (243 mg, 1.63 mmol, 8.76 equiv.) was added in one portion followed by addition of additional NEt_3 (415 µL, 2.98 mmol, 16 equiv.) and the suspension stirred additional 25 h at 80 °C. 4-DMAP (20.5 mg, 0.167 µmol, 0.9 equiv.) was

added and the reaction mixture stirred 17 h at 110 °C. Water (2 ml) and CH_2Cl_2 (2 ml) were added and the emulsion stirred additional 16 h at r.t., followed by isolation of the organic phase, which was dried over sodium sulfate, concentrated to dryness and the resulting crude product was purified by FCC (hexanes / EtOAc 9:1) to elute the desired product as a salt. The salt was dissolved in CH_2Cl_2 (10 ml) and acidified with HCl (6 M, 10 ml) for 30 min at r.t. The organic phase was isolated, concentrated to dryness and dried in high vacuum o.n. to afford the desired product in acidic form (64%, 194 mg, 186 µmol).

^{1}H NMR (501 MHz, CD_2Cl_2) δ=7.92–7.82 (m, 5H), 7.78 (s, 1H), 7.66 (s, 1H), 7.54 (s, 1H), 7.52–7.40 (m, 4H), 7.26 (dddd, *J*=16.7, 8.3, 6.8, 1.3 Hz, 2H), 7.18 (dddd, *J*=20.9, 8.4, 6.8, 1.3 Hz, 2H), 7.12 (d, *J*=1.8 Hz, 1H), 7.08 (d, *J*=1.7 Hz, 1H), 7.02 (d, *J*=8.5 Hz, 1H), 6.98 (d, *J*=1.8 Hz, 1H), 6.95 (d, *J*=1.8 Hz, 1H), 6.93 (d, *J*=1.7 Hz, 1H), 6.90 (d, *J*=8.6 Hz, 1H), 6.88–6.84 (m, 2H), 6.78 (d, *J*=8.7 Hz, 1H), 6.76 (d, *J*=1.8 Hz, 1H), 6.73 (d, *J*=1.7 Hz, 1H), 5.15 (s, 1H), 3.03 (p, *J*=6.6 Hz, 1H), 2.91–2.80 (m, 4H), 2.80–2.73 (m, 2H), 2.63–2.55 (m, 2H), 2.55–2.49 (m, 1H), 2.42 (p, *J*=6.8 Hz, 1H), 2.25 (p, *J*=6.8 Hz, 1H), 1.30 (dd, *J*=6.2 Hz, 6H), 1.27–1.22 (m, 9H), 1.22–1.20 (m, 9H), 1.20–1.16 (m, 9H), 1.08 (d, *J*=6.8 Hz, 3H), 1.04 (d, *J*=6.7 Hz, 3H), 0.94 (d, *J*=6.8 Hz, 3H), 0.92–0.87 (m, 9H), 0.79 (d, *J*=6.8 Hz, 6H), 0.73 (d, *J*=6.8 Hz, 3H), 0.67 (d, *J*=6.8 Hz, 3H), 0.38 (d, *J*=6.8 Hz, 3H), –0.08 (d, *J*=6.8 Hz, 3H), –0.28 ppm (d, *J*=6.8 Hz, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 149.4, 149.2, 149.1, 148.7, 148.5, 148.1, 147.8, 147.5, 147.4, 147.2, 147.1, 146.6, 146.1, 146.0, 145.9, 145.8, 145.8, 145.3, 145.2, 134.2, 134.0, 133.7, 133.6, 133.5, 133.2, 133.1, 132.8, 132.8, 132.2, 132.2, 132.0, 132.0, 131.8, 131.8, 131.8, 131.7, 131.6, 131.6, 131.5, 131.3, 131.0, 130.9, 130.7, 128.6, 128.4, 128.1, 127.9, 127.1, 127.1, 127.0, 126.9, 126.8, 126.8, 126.4, 126.3, 126.3, 126.2, 122.8, 122.7, 122.7, 122.6, 122.6, 122.5, 122.5, 122.0, 121.8, 121.5, 121.3, 121.3, 121.2, 120.9, 120.7, 120.7, 120.5, 34.7, 34.6, 34.6, 34.4, 31.5, 31.5, 31.3, 30.9, 30.8, 30.7, 27.9, 26.8, 25.7, 25.3, 25.1, 25.0, 24.9, 24.8, 24.8, 24.7, 24.4, 24.3, 24.2, 24.1, 24.0, 24.0, 23.9, 23.8, 23.6, 23.5, 23.4, 23.0, 22.5, 21.7 ppm (other signals not observed or detected).^{19}F NMR (471 MHz, CD_2Cl_2) δ=–77.67 (s, 3F). ^{31}P NMR (203 MHz, CD_2Cl_2) δ=3.08 (d, *J*=80.5 Hz, 1P), –1.58 (d, *J* = 80.5 Hz, 1P). HRMS (ESI): *m/z* calcd for $C_{101}H_{112}F_3N_2O_7P_2S_1^-$: 1615.762314 [*M*–H]$^-$; found: 1615.762680

iIDP-4

1,1,1-trifluoro-N-((2s)-4-((4-oxido-2,6-bis(2,4,6-tripentylphenyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)imino)-2,6-bis(2,4,6-tripentylphenyl)-4l5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)methanesulfonamide



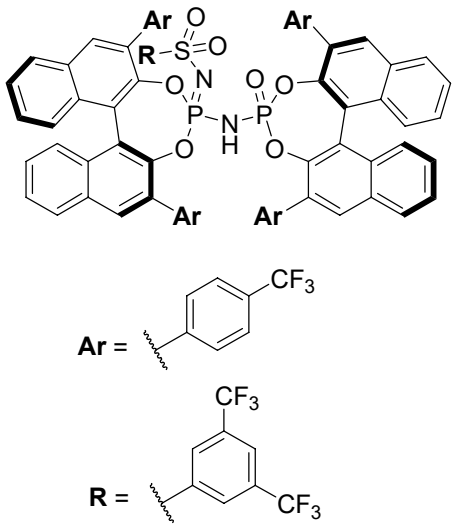
A 10 ml round bottom flask with argon adapter was charged (S)-3,3´-bis(2,4,6-tri-n-pentylphenyl)-BINOL (256 mg, 298 µmol, 2 equiv.), HCPP (82 mg, 154 µmol, 1 equiv.) followed by subsequent addition of toluene and Net3 (249 µl, 1.79 mmol, 12 equiv.) to form a yellowish suspension which was stirred for 3 h at r.t.. TfNH2 (177 mg, 1.19 mmol, 8 equiv.) was added and the reaction stirred for 23 h at r.t. followed by addition of H_2O (268 µl, 14.9 mmol, 100 equiv.), pyridine (1 ml, to increase the solubility and facilitate the hydrolysis) and stirred 3 h at 70°C. The reaction mixture was poured into aqueous HCl (6 M) and extracted with DCM. The combined organic DCM phase was concentrated to dryness and purified by FCC (Biotage, gradient: hexanes / DCM 100:0 up to 0:100; product elution with 60:40) to furnish the desired product as salt, which was acidified by dissolving in DCM (3 ml) and emulsion in HCl (6M, 3 ml). The emulsion was stirred for 30 min, the organic phase isolated, concentrated to dryness and dried o.n. in h.v. to afford the desired product in acidic form (79%, 231 mg, 149 µmol).

[Note: the final product contains hexanes, which could not be removed after extensive drying in h.v..]^{1}H NMR (501 MHz, CD_2Cl_2) δ = 7.94 (d, *J*=8.4, 1H), 7.90 (dd, *J*=8.0, 6.1, 2H), 7.87 (s, 1H), 7.83 (s, 1H), 7.76 (d, *J*=8.0, 1H), 7.71 (s, 1H), 7.60 (t, *J*=7.5, 1H), 7.56 (d, *J*=8.0, 1H), 7.47 (dq, *J*=13.7, 6.9, 6H), 7.25 (ddd, *J*=8.5, 6.8, 1.3, 1H), 7.21 (dddd, *J*=8.5, 6.8, 5.1, 1.4, 2H), 7.12 (d, *J*=8.5, 1H), 7.05 (d, *J*=8.7, 1H), 6.95 (d, *J*=1.9, 1H), 6.93 (d, *J*=8.7, 1H), 6.85 (dd, *J*=4.6, 1.9, 2H), 6.82 (d, *J*=1.9, 1H), 6.79 (d, *J*=1.9, 1H), 6.73 (d, *J*=1.9, 1H), 6.62 (d, *J*=2.0, 1H), 6.10 (d, *J*=1.9, 1H), 2.61 (ddt, *J*=16.4, 9.8, 7.0, 2H), 2.50 (ddd, *J*=9.5, 5.8, 2.5, 5H), 2.47 – 2.39 (m, 5H), 2.35 – 2.25 (m, 2H), 2.23 – 2.10 (m, 5H), 2.01 – 1.86 (m, 5H), 1.83 (dd, *J*=8.0, 5.4, 2H), 1.75 – 1.59 (m, 9H), 1.59 – 1.41 (m, 13H), 1.37 (td, *J*=6.4, 5.5, 3.0, 11H), 1.30 – 1.14 (m, 24H), 1.14 – 1.04 (m, 7H), 1.04 – 0.90 (m, 17H), 0.84 (dq, *J*=13.7, 7.1, 21H), 0.78 – 0.68 (m, 12H), 0.59 (dtd, *J*=10.7, 7.4, 3.5, 4H), 0.55 – 0.48 (m, 2H), 0.45 (t, *J*=7.2, 4H), 0.40 (td, *J*=7.2, 3.5, 10H), 0.30 – 0.22 (m, 1H), 0.17 ppm (dq, *J*=15.6, 5.6, 1H). ^{13}C NMR (126 MHz,

CD_2Cl_2) δ 143.85, 143.12, 142.39, 142.22, 142.00, 141.79, 141.69, 141.22, 141.06, 134.28, 134.04, 133.28, 132.87, 132.71, 132.55, 132.24, 131.93, 131.79, 129.12, 128.74, 128.48, 128.16, 127.67, 127.45, 127.35, 127.16, 126.90, 126.84, 126.59, 126.49, 126.43, 126.20, 125.99, 54.27, 54.06, 53.84, 53.62, 53.41, 36.34, 36.09, 35.89, 34.86, 34.41, 34.35, 34.23, 33.85, 33.64, 33.10, 32.81, 32.69, 32.64, 32.59, 32.44, 32.42, 32.38, 32.17, 32.07, 32.04, 31.72, 31.48, 31.38, 31.22, 31.16, 31.08, 30.79, 23.56, 23.35, 23.07, 23.03, 22.96, 22.81, 22.50, 22.45, 14.37, 14.34, 14.30, 14.24, 14.19, 14.15, 13.81, 13.69 ppm (other signals not observed or detected). ^{19}F NMR (471 MHz, CD_2Cl_2) δ = –79.07 ppm (s, CF3). ^{31}P NMR (203 MHz, CD_2Cl_2) δ = 4.39 (d, *J*=89.5, 1P), –3.79 ppm (d, *J*=88.0, 1P). HRMS (ESI): *m*/*z* calcd for $C_{125}H_{160}F_3N_2O_7P_2S_1^-$: 1952.137914 [*M*–H]$^-$; found: 1952.138740

*i*IDP-5

(S,S)-N-(4-((4-oxido-2,6-bis(4-(trifluoromethyl)phenyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)amino)-2,6-bis(4-(trifluoromethyl)phenyl)-4l5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-ylidene)-3,5-bis(trifluoromethyl)benzenesulfonamide



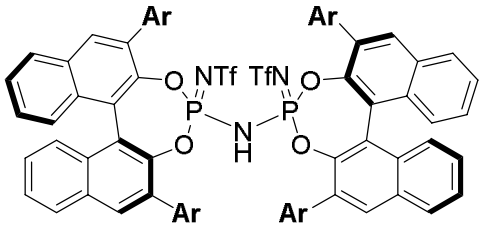
An under high vacuum flame-dried and argonated Schlenk flask was charged with HCPP (67.3 mg, 0.126 mmol,1.0 equiv.), *(S)*-3,3'-bis(4 trifluoromethylphenyl)-BINOL (161 mg, 0.253 mmol, 2.0 equiv.) followed by the addition of pyridine (1 ml) to form a clear yellow solution, which was stirred until full consumption of BINOL (1 h) resulting in the formation of a suspension. 3,5-bis(trifluoromethyl)benzenesulfonamide (94.2 mg, 0.632 mmol, 4.9 equiv.) was added and the reaction mixture stirred additional 16 h at r.t.. Water (0.15 ml) was added and the reaction stirred additional 4 h, at r.t., followed by the addition of an excess of HCl (4 N, 10 ml) to quench the reaction. The aqueous phase was extracted with CH_2Cl_2 and the combined organic layers were washed with brine, dried over $NaSO_4$ and concentrated to dryness. The obtained solid was purified by column chromatography (pentane:Et_2O with a gradient of 4:1 to 2:1) to furnish the desired product as a salt, which was further acidified by dissolving in a small quantitiy of CH_2Cl_2 and passing through a pad of DOWEX 50WX-8 to obtain the desired product as a colorless solid in acidic form (65%, 51.3 mg, 0,094 mmol).

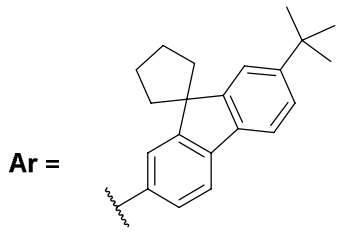
^{1}H NMR (501 MHz, CD_2Cl_2) δ=8.25–8.21 (m, 2H), 8.16 (s, 1H), 8.08 (d, *J*=8.3 Hz, 1H), 8.03 (s, 1H), 8.00 (d, *J*=8.3 Hz, 1H), 7.87 (s, 1H), 7.85–7.77 (m, 5H), 7.75 (s, 1H), 7.69–7.50 (m, 12H), 7.47 (d, *J*=8.5 Hz, 1H), 7.45–7.40 (m, 3H), 7.38 (d, *J*=8.1 Hz, 2H), 7.09 (s), 6.91 (s, 4H), 6.88 (d, *J*=8.2 Hz, 2H), 6.81 ppm (d, *J*=8.1 Hz, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ=145.4, 145.4, 144.3, 144.3, 143.8, 143.8, 143.5, 143.5, 140.3, 140.1, 140.0, 133.1, 133.1, 133.0, 133.0, 132.9, 132.8, 132.5, 132.5, 132.4, 132.3, 132.3, 132.2, 132.1, 131.9, 131.8, 131.7, 131.5, 131.3, 130.3, 130.2, 130.0, 129.9, 129.7, 129.6, 129.5, 129.4, 129.3, 129.2, 129.2, 128.3, 128.1, 127.8, 127.8, 127.6, 127.5, 127.4, 127.4, 127.1, 127.1, 127.0, 126.9, 126.7, 126.7, 126.0, 126.0, 125.8, 125.3, 125.3, 125.2, 125.2, 125.2, 125.1, 125.1, 124.9, 124.9, 124.9, 124.8, 124.8, 124.1, 124.1, 124.1, 124.0, 123.6, 122.9, 122.9, 122.7, 121.9 ppm. (other signals not detected or observed). ^{19}F NMR (471 MHz, CD_2Cl_2) δ=–62.63 (s, CF_3), –62.72 (s, CF_3), –62.88 (s, CF_3), –63.04 (s, CF_3), –63.12 ppm (s, $2CF_3$). ^{31}P NMR (203 MHz, CD_2Cl_2) δ=0.3 (d, *J*=103.5 Hz), –4.75 ppm (d, *J*=103.5 Hz). HRMS (ESI) m/z calculated for $C_{76}H_{39}F_{18}N_2O_7P_2S_1^-$ $(M–H)^-$: 1527.1671, found: 1527.1676.

7.5 Synthesis of Imidodiphosphorimidates (IDPi)

IDPi-2

(*S*,*S*)-N,N'-(azanediylbis(2,6-bis(2'-(tert-butyl)spiro[cyclopentane-1,9'-fluoren]-7'-yl)-4l5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-yl-4-ylidene))bis(1,1,1-trifluoromethanesulfonamide)





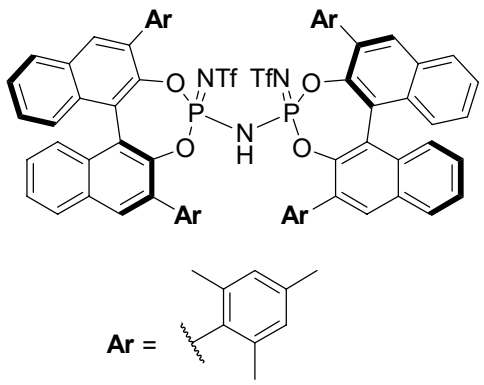
10 ml flame-dried and argonated Schlenk tube was charged with HCPP (30 mg, 56 µmol, 1.0 equiv.) and (*S*)-3,3'-bis(2'-(tert-butyl)spiro[cyclopentane-1,9'-fluoren]-7'-yl)-BINOL (64 mg, 116 µmol, 2.05 equiv.) and dissolved in 0.8 ml toluene. To the solution was added NEt_3 (35 µl, 254 µmol, 4.5 equiv.) dropwise under vigorous stirring. The resulting yellow suspension was stirred for 60 min at r.t. followed by the addition of H_2NTf (327 mg, 2.19 mmol, 8 equiv.). The mixture was heated to 120 °C under stirring for 36h. The crude mixture was purified without work-up by FCC (gradient: hexanes / EtOAc 1:0 to 9:1) to elute the desired product as a salt. Acidification was carried out by dissolving the salt in Et_2O (3 ml) and flushing the solution through a 5 cm pad of DOWEX® 50WX2. The organic phase was concentrated to dryness to furnish the desired product as a colorless solid (70%, 392 mg)

^{1}H NMR (501 MHz, CD_2Cl_2) δ = 8.94 (sbr, 1H), 8.11 (s, 2H), 8.08 (dd, *J*=8.1, 6.2, 4H), 7.86 (ddd, *J*=8.2, 6.8, 1.3, 2H), 7.79 (d, *J*=7.9, 2H), 7.69 (ddd, *J*=8.4, 6.8, 1.3, 2H), 7.61 (ddd, *J*=8.2, 6.1, 1.9, 2H), 7.52 (d, *J*=1.9, 2H), 7.47 (d, *J*=8.4, 4H), 7.41 (dd, *J*=8.0, 1.9, 4H), 7.35 (dd, *J*=4.8, 3.1, 4H), 7.30 – 7.22 (m, 8H), 7.11 (s, 2H), 6.62 (d, *J*=8.0, 2H), 6.49 (dd, *J*=8.0, 1.7, 2H), 6.26 – 6.21 (m, 2H), 2.22 – 2.14 (m, 2H), 2.12 – 1.92 (m, 22H), 1.88 – 1.81 (m, 2H), 1.81 – 1.71 (m, 4H), 1.71 – 1.63 (m, 2H), 1.32 (s, 18H), 1.31 ppm (s, 18H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 154.81, 154.67, 154.46, 154.00, 151.32, 150.72, 143.81, 142.79, 139.60, 138.91, 136.19, 135.99, 134.66, 134.43, 133.91, 133.86, 132.15, 131.74, 131.52, 131.30, 129.11, 128.64, 128.32, 127.41, 126.81, 126.77, 126.73, 126.48, 123.91, 123.73, 123.57, 123.26, 121.83, 119.65, 119.52, 119.16, 118.58, 118.43, 118.06, 57.91, 57.81, 40.03, 39.99, 39.11, 38.91, 34.84, 34.77, 31.30, 30.57, 26.97, 26.74, 26.54, 26.37 ppm (other signals not observed or detected). ^{19}F NMR (471 MHz, CD_2Cl_2) δ = –78.75 ppm (s, 6F). ^{31}P NMR (203 MHz, CD_2Cl_2) δ = –17.10

ppm (s, 2P). HRMS (ESI): m/z cald for $C_{94}H_{86}N_3O_8P_2S_2^-$: 2034.707586 $[M-H]^-$, found 2034.727460

IDPi-3

(S,S)-N,N'-(azanediylbis(2,6-dimesityl-4l5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-yl-4-ylidene))bis(1,1,1-trifluoromethanesulfonamide)



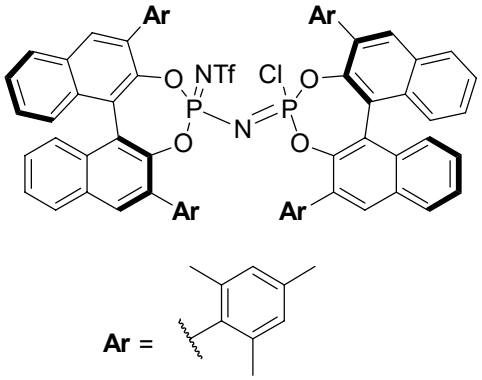
A 10 ml flame-dried Schlenk tube was charged with phosphazene (129 mg, 0.24 mmol, 1 equiv.), *(S)*-3,3´-bis(mesityl)-BINOL (271 mg, 0.52 mmol, 2.1 equiv.) and suspended in toluene (5 ml). Triethylamine (150 µl, 1,09 mmol, 4.5 equiv.) was added dropwise via a Hamilton syringe under vigorous stirring forming a slightly orange suspension which faded away within 5 minutes at r.t.. The resulting colorless suspension was stirred additional 60 minutes at r.t. followed by the addition of $TfNH_2$ (289 mg, 1.94 mmol, 8 equiv.) additional triethylamine (0.54 ml, 3.88 mmol, 16 equiv.) and stirred 26 h at 80 °C. The orange suspension was cooled to r.t. followed by addition of 4-dimethylaminopyridine (26.6 mg, 220 µmol, 0.9 equiv.) and stirred for additional 6 d at 100 °C. The reaction mixture was then analyzed by NMR (a small aliquote was transferred to an NMR tube under inert conditions, all volatiles were removed in high vacuum followed by the addition of CD_2Cl_2) showing a conversion of approximately 60% to the desired product. The reaction mixture was then quenched with ca. 1 ml aqueous HCl (6 M) followed by dilution with dichloromethane (ca. 10 ml). The organic phase was washed with HCl (6 M, 10 ml) followed by washing with sat. $NaHCO_{3(aq)}$ (2x10ml). The organic phase was dried over sodium sulfate, concentrated to dryness followed by FCC (Biotage, gradient: n-hexane/EtOAc (100/0) up to (60/40) to elute the desired product as salt (m = 126 mg, 44 % yield referred to the sodium salt). The corresponding intermediate **I-2** was isolated and stored for further transformations (114 mg, 36 %). 46 mg of the salt was dissolved in a small quantitiy of dichloromethane and passed through a Pasteur pipette filled (ca 3 cm height) with Dowex40W-X8 (acidic form) to elute the desired product in acidic form (m = 42 mg, 90 % yield).

^{1}H NMR (501 MHz, CD_2Cl_2) δ = 8.0 – 7.9 (m, 2H), 7.9 – 7.8 (m, 2H), 7.8 (s, 2H), 7.6 (ddd, *J*=8.2, 6.8, 1.3, 2H), 7.5 – 7.5 (m, 4H), 7.4 (ddd, *J*=8.4, 6.9, 1.4, 2H), 7.4 – 7.3 (m, 2H), 7.2 (ddd, *J*=8.4, 6.8, 1.4, 2H), 7.1 (d, *J*=8.0, 2H), 6.9 (s, 2H), 6.8 (s, 2H), 6.7 (s, 2H), 6.4 (s, 2H),

4.5 (s, 1H), 2.2 (s, 6H), 2.2 (s, 6H), 2.2 (s, 6H), 1.9 (s, 6H), 1.8 (s, 6H), 0.9 (s, 6) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2) δ 145.1, 145.1, 145.1, 144.7, 144.7, 144.6, 138.0, 137.4, 137.32 137.1, 136.9, 135.6, 134.2, 133.2, 132.9, 132.8, 132.6, 132.4, 132.3, 132.3, 132.3, 129.2, 128.8, 128.6, 128.5, 128.2, 128.2, 127.4, 127.4, 127.2, 127.1, 126.7, 126.7, 122.4, 122.2, 21.7, 21.4, 21.0, 20.6, 19.8, 19.5 ppm (other signals not detected or observed). ^{19}F NMR (471 MHz, CD_2Cl_2) δ=–78.71 ppm (s, $2CF_3$); ^{31}P NMR (203 MHz, CD_2Cl_2) δ –10.65 ppm (s); HRMS: calcd for $C_{78}H_{64}F_6N_3O_8P_2S_2^-$ [M–H]–: 1410.351986; found: 1410.351340

7.5.1 Intermediate I-2

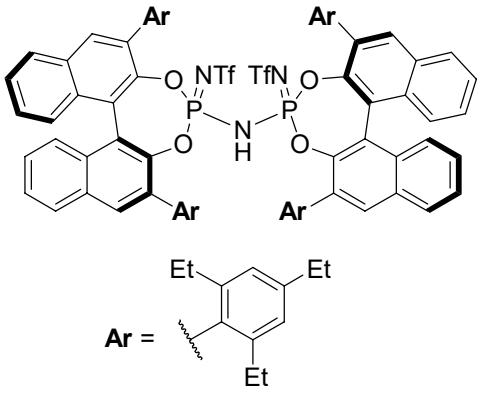
(S,S)-N-(4-((4-chloro-2,6-dimesityl-4l5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-ylidene)amino)-2,6-dimesityl-4l5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-ylidene)-1,1,1-trifluoromethanesulfonamide



^{1}H NMR (600 MHz, CD_2Cl_2) δ = 8.0 – 7.9 (m, 2H), 7.9 (ddd, *J*=8.2, 2.0, 1.0, 2H), 7.9 (t, *J*=1.1, 1H), 7.8 (d, *J*=1.0, 1H), 7.6 – 7.6 (m, 1H), 7.6 – 7.5 (m, 2H), 7.5 – 7.5 (m, 3H), 7.5 – 7.4 (m, 3H), 7.4 – 7.3 (m, 1H), 7.3 – 7.2 (m, 2H), 7.2 – 7.2 (m, 1H), 7.0 (d, *J*=8.5, 1H), 6.9 – 6.9 (m, 1H), 6.9 – 6.9 (m, 1H), 6.8 – 6.8 (m, 2H), 6.8 – 6.8 (m, 1H), 6.7 – 6.6 (m, 1H), 6.3 (d, *J*=1.3, 1H), 6.2 – 6.2 (m, 1H), 2.2 (s, 3H), 2.2 (s, 3H), 2.2 (s, 3H), 2.1 (s, 3H), 2.1 (s, 5H), 1.9 (s, 3H), 1.8 (s, 3H), 1.8 (s, 3H), 1.6 (s, 3H), 0.8 (s, 3H), 0.7 (s, 3H) ppm. ^{13}C NMR (151 MHz, CD_2Cl_2) δ = 145.9, 145.8, 145.2, 145.2, 145.2, 145.0, 144.9, 138.4, 138.2, 137.9, 137.7, 137.5, 137.3, 137.2, 137.2, 136.9, 136.2, 135.8, 135.6, 134.3, 133.3, 133.3, 133.2, 133.1, 133.0, 132.9, 132.8, 132.7, 132.5, 132.4, 132.3, 132.2, 132.2, 132.2, 132.1, 132.0, 131.8, 129.2, 129.0, 128.8, 128.7, 128.6, 128.6, 128.5, 128.2, 128.1, 128.0, 127.7, 127.6, 127.4, 127.3, 127.2, 127.2, 127.1, 126.9, 126.9, 126.7, 126.3, 126.2, 122.3, 122.2, 122.1, 30.1, 21.9, 21.5, 21.3, 21.2, 21.1, 21.0, 20.3, 20.1, 19.9, 19.8, 19.5, 19.4 (other signals not detected or observed). ^{19}F NMR (565 MHz, CD_2Cl_2) δ = –80.0 ppm (s, CF_3). ^{31}P NMR (243 MHz, CD_2Cl_2) δ = 8.0 (d, *J*=79.3, 1P), –1.9 (d, *J*=78.5, 1P) ppm. HRMS: calculated for $C_{77}H_{64}Cl_1F_3N_2O_6P_2S_1Na_1^+$ ([M + Na]$^+$): 1321.348650; found: 1321.349321

IDPi-4

(S,S)-N,N'-(azanediylbis(2,6-bis(2,4,6-triethylphenyl)-4l5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-yl-4-ylidene))bis(1,1,1-trifluoromethanesulfonamide)

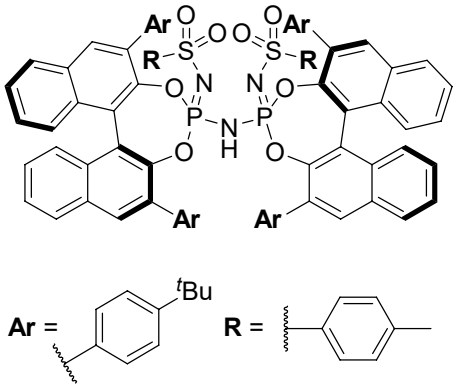


A 10 ml flame-dried and argonated Schlenk tube was charged with HCPP (45 mg, 0,085 mmol, 1.0 equiv.) and *(S)*-3,3´-(*o,o,p*-tri(n-ethyl)phenyl)BINOL (110 mg, 0.18 mmol, 2.2 equiv.) and dissolved in 1 ml toluene. To the solution was added NEt_3 (53 µl, 0.38 mmol, 4.5 equiv.) dropwise under vigorous stirring. The resulting yellow suspension was stirred for 60 min at r.t. followed by the addition of H_2NTf (100 mg, 0.68 mmol, 8 equiv.) and NEt_3 (195 µl, 137 mg, 1.35 mmol, 16,0 equiv.). The mixture was heated to 80 °C under stirring for 15 h and subsequently 4-DMAP (9.3 mg, 0.076 mmol, 0.9 equiv.) was added at r.t.. The reaction was stirred for 120 h at 120 °C. The crude mixture was purified without work-up by FCC (Biotage, gradient: hexanes up to hexanes / EtOAc (5:1)) to elute the desired product as a salt. Acidification was carried out by dissolving the salt in Et_2O (3 ml) and flushing the solution through a 5 cm pad of DOWEX® 50WX2. The organic phase was concentrated to dryness furnish the desired product as a colorless solid (36%, 48 mg)

^{1}H NMR (600 MHz, CD_2Cl_2) δ = 7.9 (dd, *J*=18.3, 8.3, 4H), 7.8 (s, 2H), 7.6 (s, 2H), 7.5 (t, *J*=7.6, 2H), 7.5 (t, *J*=7.5, 2H), 7.4 (t, *J*=7.8, 2H), 7.3 (d, *J*=8.4, 2H), 7.2 (t, *J*=7.7, 2H), 7.0 (s, 2H), 6.9 (s, 1H), 6.9 (s, 3H), 6.8 (s, 2H), 6.5 (s, 2H), 2.7 – 2.6 (m, 6H), 2.6 – 2.5 (m, 6H), 2.4 – 2.2 (m, 6H), 2.2 – 2.1 (m, 2H), 2.1 – 2.0 (m, 2H), 1.7 – 1.6 (m, 2H), 1.2 (t, *J*=7.6, 6H), 1.2 (t, *J*=7.6, 6H), 1.2 (t, *J*=7.4, 6H), 0.9 (t, *J*=7.5, 6H), 0.8 (t, *J*=7.5, 6H), 0.0 (t, *J*=7.6, 6H) ppm. ^{13}C NMR (151 MHz, CD_2Cl_2) δ = 144.9, 144.7, 144.6, 144.5, 144.0, 143.4, 143.0, 142.7, 142.4, 134.7, 133.2, 132.5, 132.0, 131.8, 131.7, 131.7, 128.7, 128.7, 127.5, 127.2, 127.1, 126.8, 126.7, 126.2, 126.1, 125.8, 124.8, 122.5, 122.0, 119.9, 117.8, 30.1, 29.1, 28.7, 28.1, 27.5, 27.3, 26.8, 16.4, 16.2, 15.9, 15.5, 15.0, 14.4 ppm (other signals not observed or detected). ^{19}F NMR (565 MHz, CD_2Cl_2) δ = –78.4 ppm (2 CF_3). ^{31}P NMR (243 MHz, CD_2Cl_2) δ = –10.2 (s, 2P). HRMS (ESI): m/z calcd for $C_{90}H_{88}F_3N_3O_8P_2S_2^-$: 1578.539786 $[M-H]^-$, found 1578.540540.

IDPi-6

(S,S)-N-(4-((2,6-bis(4-(tert-butyl)phenyl)-4-((4-methylphenyl)sulfonamido)-4l5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-ylidene)amino)-2,6-bis(4-(tert-butyl)phenyl)-4l5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-ylidene)-4-methylbenzenesulfonamide

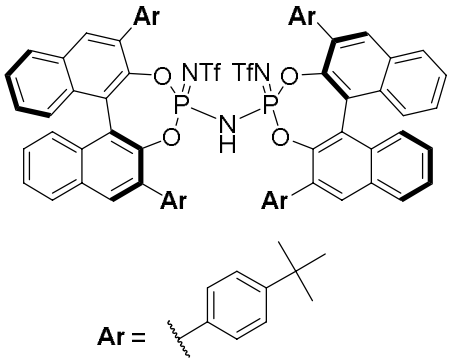


A 10 ml flame-dried and argonated Schlenk tube was charged with HCPP (30 mg, 56 µmol, 1.0 equiv.) and *(S)*-3,3´-di(*p*-^{t}Bu-phenyl)BINOL (64 mg, 116 µmol, 2.05 equiv.) and dissolved in 0.8 ml toluene. To the solution was added NEt_3 (35 µl, 254 µmol, 4.5 equiv.) dropwise under vigorous stirring. The resulting yellow suspension was stirred for 60 min at r.t. followed by the addition of 4-methylbenzenesulfonamide (77.2 mg, 451 µmol, 8.0 equiv.) and NEt_3 (126 µl, 91.2 mg, 902 µmol, 16.0 equiv.). The mixture was heated to 110 °C under stirring for 120 h. The crude mixture was purified without work-up by FCC (Biotage, hexanes / EtOAc (5:1)) to elute the desired product as a salt. Acidification was carried out by dissolving the salt in Et_2O (3 ml) and flushing the solution through a 5 cm pad of DOWEX® 50WX2. The organic phase was concentrated to dryness to furnish the desired product as a colorless solid (21%, 18 mg)

^{1}H NMR (501 MHz, CD_2Cl_2) δ = 8.1 (d, *J*=8.0, 2H), 7.9 (d, *J*=7.9, 2H), 7.9 (s, 2H), 7.7 (t, *J*=7.3, 2H), 7.6 (s, 2H), 7.5 – 7.5 (m, 4H), 7.5 – 7.4 (m, 2H), 7.4 – 7.3 (m, 12H), 7.2 – 7.2 (m, 4H), 6.9 – 6.8 (m, 4H), 6.7 – 6.7 (m, 4H), 6.6 – 6.5 (m, 4H), 2.3 (sbr, 1H), 2.2 (s, 6H), 1.2 (s, 18H), 1.0 (s, 18H) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 150.9, 150.4, 144.7, 142.7, 134.5, 133.6, 133.5, 133.2, 132.5, 132.3, 132.3, 132.0, 131.2, 131.2, 129.8, 129.2, 129.1, 128.9, 127.7, 127.3, 126.9, 126.8, 126.7, 126.3, 126.0, 125.8, 124.9, 124.0, 122.6, 34.7, 34.6, 31.3, 31.3 ppm (other signals not observed or detected). ^{31}P NMR (203 MHz, CD_2Cl_2) δ = –8.9 ppm (s, 2P). HRMS (ESI): m/z cald for $C_{94}H_{86}N_3O_8P_2S_2^-$: 1510.533715 $[M-H]^-$, found 1510.533940

IDPi-7

N,N'-(azanediylbis(2,6-bis(4-(tert-butyl)phenyl)-4l5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-yl-4-ylidene))bis(1,1,1-trifluoromethanesulfonamide)



A 10 ml flame dried and argonated schlenk flask was charged with hexachlorobisphosphazonium chloride (42 mg, 130 µmol, 1 equiv.), $TfNH_2$ (38.6 mg, 259µmol, 2 equiv.) and suspended in toluene (1 ml). The suspension was stirred for 1 h at r.t. followed by addition of sodium hydride (dispersion in mineral oil, 60%, 82.9 mg, 2.07 mmol, 16 equiv.) and stirred 6 h at 100 °C followed by addition of (S)-3,3´-(4-*tert*-butylphenyl)BINOL (173 mg, 314µmol, 2.4 equiv.) and further stirred for 34 h at 100°C. The reaction mixture was then carefully poured into sat. $NaHCO_3$ and the aqueous layer extracted with DCM. The combined organic phases were washed with brine, dried over sodium sulfate and concentrated to dryness followed by purification by filtration through a plug of silica (gradient 1. DCM then DCM / EtOAc 9:1) to elute the desired product as a salt. The organic phase was concentrated to dryness to furnish the desired product in salt form (56%, 107 mg). NMR-spectroscopical data match to previously reported NMR data.

^{1}H NMR (501 MHz, CD_2Cl_2) δ = 8.20 (d, *J*=8.4, 2H), 8.05 (s, 2H), 8.01 (d, *J*=8.0, 2H), 7.84 (s, 2H), 7.76 – 7.70 (m, 2H), 7.58 – 7.49 (m, 10H), 7.49 – 7.42 (m, 6H), 7.35 (ddd, *J*=8.4, 6.8, 1.4, 2H), 6.69 – 6.63 (m, 4H), 6.63 – 6.57 (m, 4H), 1.65 (sbr, 1H), 1.31 (s, 18H), 0.97 (s, 18H) ppm. ^{19}F NMR (471 MHz, CD_2Cl_2) δ = –78.79 (s, 6F) ppm. ^{31}P NMR (203 MHz, CD_2Cl_2) δ = -4.40 ppm (2P).

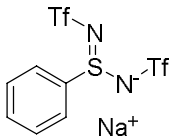
7.6 Synthesis of IDPii

7.6.1 Synthesis of Bis(trifluoromethylsulfonylimino)sulfonamides

8.1 Sodium phenylbis(trifluoromethylsulfonylimino)sulfinate 5

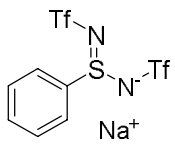
Synthesis of 4.15

sodium-(S-phenyl-N-((trifluoromethyl)sulfonyl)sulfinimidoyl)((trifluoromethyl)sulfonyl)amide



Synthesis utilizing $TfNCl_2$: A 50 ml schlenk tube was charged with an aqueous solution of $TfNH_2$ (2.50 g, 16.8 mmol) and NaOH (2.50 g, 62.5 mmol) and cooled to –20 °C (ethanol, dry ice). Chlorine gas was bubbled through the solution maintaining the temperature between –20 to –10°C for 15 minutes to form a slightly yellowish emulsion, which forms two phases upon standing. The emulsion was carefully transferred to a pre-cooled 50 ml dropping funnel, connected to a 10 ml schlenk-tube, which is charged with a solution of thiophenol (PhSH 550 mg, 5 mmol) in 5 ml anhydrous dichloromethane and cooled to –30 °C. The lower yellowish phase (containing $TfNCl_2$ of the dropping funnel was slowly added to the cooled dichloromethane solution (highly exothermic, few drops in a 10 second intervall). The dichloromethane solution was stirred 1 h at r.t. and quenched with water. The organic phase was isolated, and concentrated to dryness to obtain a highly viscous oil. This oil was dissolved in a small quantity of dichloromethane and loaded on silica followed by FCC (gradient: 1. pure dichloromethane to remove $TfNH_2$ impurites followed by DCM/acetone (3/2) to elute the desired product which was isolated as a colorless solid. The solid was dissolved in diethylether, washed with sat. $NaHCO_{3(aq)}$, the organic phase dried over sodium sulfate and concentrated to dryness to afford the desired product as a beige solid (74%, 1.50 g, 3,71 mmol).

^{1}H NMR (501 MHz, CD_3CN) δ = 7.86 – 7.78 (m, 2H), 7.64 – 7.55 (m, 3H) ppm. ^{13}C NMR (126 MHz, CD_3CN) δ = 142.68, 132.90 (d, *J*=326.1), 130.56, 126.76, 119.97 (q, *J*=322.2) ppm. ^{19}F NMR (471 MHz, CD_3CN) δ = –79.34 (s, 6F) ppm. HRMS: calculated for $C_8H_5F_6N_2O_4S_3$ ($[M – H]^-$): 402.932380; found: 402.932121

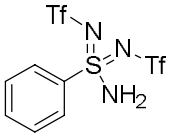


Alternative Synthesis: A 1 L flame dried two necked flask with 250 ml dropping funnel was charged with potassium *tert*-butoxide (45.1 g, 402 mmol, 5.5 equiv.), THF (500 ml) and cooled to 0°C (ice bath). Iodine (108 g, 424 mmol 5.8 equiv) was added in small portions under vigorous stirring of the resulting dark brown suspension. After full addition the resulting dark brown suspension was stirred additional 1 h at 0°C. The dropping funnel was charged with a solution of trifluoromethanesulfonamide (22.5 g, 146 mmol, 2 equiv.) and thiophenol (8.05 g, 73.0.mmol, 1 equiv.) in acetonitrile (200 mL). The solution of the dropping funnel was added dropwise within 30 minutes to the dark brown suspension under vigorous stirring at 0°C. After full addition the resulting dark brown suspension was stirred additional 17 h at r.t. followed by the addition of a saturated aqueous solution of sodium thiosulfate until the dark brown suspension turned into a slightly yellow suspension. The suspension was transferred to a 1 L separating funnel. The 1 L two necked round bottom flask was rinsed with diethylether (300 ml) and added to the dropping funnel. The organic phase was washed with sodium thiosulfate (twice, 200 ml each), brine (200 ml), dried over sodium sulfate and concentrated to dryness. After flash column chromatography (gradient, pure dichloromethane then dichloromethane / acetone (3:2) to elute the product) the desired product was isolated as a colorless solid (90%, 28 g).

^{1}H NMR (501 MHz, CD_3CN) δ = 7.86 – 7.78 (m, 2H), 7.64 – 7.55 (m, 3H) ppm. ^{13}C NMR (126 MHz, CD_3CN) δ = 142.68, 132.90 (d, *J*=326.1), 130.56, 126.76, 119.97 (q, *J*=322.2) ppm. ^{19}F NMR (471 MHz, CD_3CN) δ = –79.34 (s, 6F) ppm. HRMS: calculated for $C_8H_5F_6N_2O_4S_3$ ($[M – H]^-$): 402.932380; found: 402.932121

Synthesis of SA-2

N,N'-(amino(phenyl)-l6-sulfanediylidene)bis(1,1,1-trifluoromethanesulfonamide)

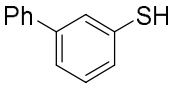


A 100 ml schlenk flask was charged with sodium phenylbis(trifluoromethylsulfinate) (5.33 g, 12.5 mmol), Selectfluor (13.6 g, 38. 5 mmol, 3 equiv.) and suspended in 30 ml acetonitrile. The suspension was stirred 16 h at 80 °C to form a yellowish suspension. An aliquote of the solution was taken, concentrated under inert conditions and analyzed by NMR (CD_3CN). ^{19}F-NMR indicated full conversion of the starting material to the desired sulfonyl fluoride (^{19}F NMR (471 MHz CD_2Cl_2 δ = 69.7 (s, 1F), –75.0 (s, 6F) ppm). All volatiles were removed in high vacuum under inert reaction conditions and the resulting solid residue re-suspended in anhydrous DCM (40 ml). The suspension was transferred to a schlenk-frit, which is filled with a plug of silica and connected to a 250 ml schlenk-flask, by cannula with argon overpressure and washed with additional DCM (3x20 ml). The combined DCM phase containing the desired sulfonyl fluoride was amidated with ammonia gas for 10 minutes to form a colorless suspension. The suspension was poured into a 250 ml round-bottom flask and all volatiles were removed in vacuum (Rotavap). The residue was dissolved in a mixture of diethylether (100 ml) and $HCl_{(aq)}$ (6M). The organic phase was additionally washed with $HCl_{(aq)}$ (6M, 2 x 100 ml), washed with brine and concentrated to dryness to yield the desired product as a beige solid, which was further purified by recrystallization from toluene to afford the desired product as a crystalline solid (88%, 4.60 g, 12.5 mmol).

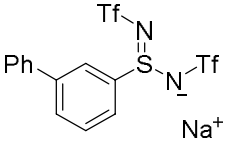
^{1}H NMR (501 MHz, CD_3CN) δ = 8.2 – 8.1 (m, 2H), 7.9 – 7.9 (m, 1H), 7.8 – 7.7 (m, 2H), 7.4 (s br, 2H) ppm. ^{13}C NMR (126 MHz, CD_3CN) δ = 137.5, 137.4, 131.2, 129.0, 119.8 (q, *J*=960.8) ppm. ^{19}F NMR (471 MHz, CD_3CN) δ = –79.3 (s) ppm. HRMS (ESI): m/z cald for $C_8H_6F_6N_3O_4S_3^-$: 417.943020 $[M-H]^-$, found 417.942700

Synthesis of 4.19

sodium (E)-(S-([1,1'-biphenyl]-3-yl)-N-((trifluoromethyl)sulfonyl)sulfinimidoyl)-((trifluoromethyl)sulfonyl)amide



Step 1-3: A two necked 100 ml round bottom flask equipped with a 100 ml dropping funnel and a reflux cooler connected to an argon adapter was charged with pre-activated magnesium tunings (600 mg, 24.7 mmol, 1 equiv.) followed by the addition of THF (ca 5 ml). A dropping funnel was charged with *m*-(phenyl)bromobenzene (5.75 g, 24.7 mmol). Few drops of this bromo arene were added to the magnesium tunings and the Grignard was started with heating the reaction mixture with a heatgun. THF (20 ml) was added to the dropping funnel and the corresponding solution dropwise added to the reaction mixture to afford a constant reflux of the reaction. Upon full addition of the bromo arene the black suspension was refluxed additional 45 min (bath temp: 90 °C). The oil bath was replaced with an ice bath followed by the addition of elemtal sulfur (1.58 g, 49.4 mmol, 2 equiv.) and stirred 1 h at r.t.. Lithium aluminium hydride (1 M in THF, 10 ml) was carefully added the reaction mixture stirred additional 1 h at r.t. and carefully quenched with water until no exothermic reaction was observed. Et_2O (75 ml) was added and the organic phase washed with HCl (6M, 50 ml, two times). The organic phase was isolated, dried over sodium sulfate and concentrated to dryness. The crude product was used without further purification.

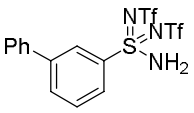


Step 4: A 500 ml round bottom flask equipped with an argon adapter connected to a 100 ml dropping funnel was charged with KOtBu (16.6 g, 148 mmol, 6 equiv.), dissolved in THF (120 ml) and cooled to 0°C: Iodine (37.6 g, 148 mmol, 6 equiv.) was portionwise added to form a dark brown suspension, which upon full addition of iodine was stirred 30 min at r.t.. Meanwhile the dropping funnel was charged with $TfNH_2$ (11.0 g, 74.0 mmol, 3 equiv.) and the previously prepared m-(biphenyl)thiol and dissolved in acetonitrile (40 ml). The solution was added in one portion to the brown suspension and stirred o.n. at r.t., followed by quenching with an aqueous saturated sodium thiosulfate solution to form a slightly yellowish emulsion. The emulsion was transferred to a 250 ml dropping funnel and the organic phase additionally washed with sodium thiosulfate solution (100 ml), brine, isolated, dried over sodium sulfate and concentrated to dryness. The residue was purified by FCC (gradient: DCM (1 l) to remove TfNH2 then DCM/Acetone 4:1 to elute the desired product as a colorless solid (60 %, 7.4 g).

^{1}H NMR (501 MHz, CD_3CN) δ 8.04 (t, *J* = 1.9 Hz, 1H), 7.86 (ddd, *J* = 7.7, 1.8, 1.0 Hz, 1H), 7.82 (ddd, *J* = 8.0, 2.0, 1.1 Hz, 1H), 7.70 – 7.65 (m, 3H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.46 – 7.41 (m, 1H).^{19}F NMR (471 MHz, CD_3CN) δ -79.24. ^{13}C NMR (126 MHz, CD_3CN) δ 207.63, 143.02, 142.94, 140.00, 131.08, 130.92, 129.89, 129.00, 127.75, 125.39, 124.77, 119.97.HRMS (ESI): m/z cald for $C_{14}H_9F_6N_2O_4S_3^-$: 478.963421 $[M-H]^-$, found 478.963930

Synthesis of SA-3

N,N'-([1,1':3',1''-terphenyl]-5'-yl(amino)-l6-sulfanediylidene)bis(1,1,1-trifluoromethanesulfonamide)

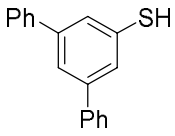


A 20 ml microwave vial was charged with Na[m-biPhS($NTf)_2$] (**4.19**) (1.30 g, 2.59 mmol), Selectfluor (4.45 g, 12.5 mmol) and suspended in acetonitrile (10 ml). The reaction was irradiated under microwave conditions to reach a temperature of 100 °C for 1 h. NMR analysis shows ca. 90 % conversion to the desired sulfonyl fluoride. The reaction mixture was poured into a 100 ml round-bottom flask connected to an argon adapter and concentrated under inert conditions (cooling trap with liquid nitrogen). The yellowish residue was suspended in DCM (20 ml) and filtered through a plug of silica followed by washing with DCM (20 ml) and the organic filtrate was collected in a 100 ml schlenk-flask. Ammonia gas was bubbled into the DCM solution for ca. 20 min, forming a colorless suspension. This suspension was transferred to a 100 ml round bottom flask and concentrated to dryness (Rotavap). The residue was dissolved in a mixture of Et_2O HCl (6 M) 1/1 vol% and transferred to a separation funnel. The organic phase was additionally washed with HCl (6 M, three times, 30 ml) and concentrated to dryness to afford the desired product (95% purity by 1H-NMR). The product was additionally recrystallized from toluene / hexanes to afford the title product (72%, 979 mg, 1.34 mmol) as a colorless solid.

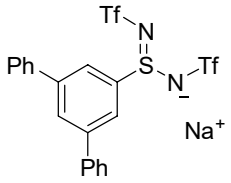
^{1}H NMR (501 MHz, CD_3CN) δ = 2.72 (t, *J*=2.0, 1H), 2.53 (ddt, *J*=8.2, 3.8, 1.7, 2H), 2.23 (t, *J*=8.0, 1H), 2.11 – 2.01 (m, 2H), 1.97 – 1.92 (m, 2H), 1.92 – 1.84 (m, 1H), 1.75 (sbr, 2H) ppm. ^{13}C NMR (126 MHz, CD_3CN) δ = 144.03, 139.02, 138.32, 135.77, 131.79, 130.41, 129.97, 128.11, 127.74, 126.77, 120.13 (q, *J*=320.2), 1.65 (other signals not detected or observed) ppm. ^{19}F NMR (471 MHz, CD_3CN) δ = –79.24 (s, CF_3) ppm. HRMS (ESI): m/z cald for $C_{14}H_{10}F_6N_3O_4S_3^-$: 493.974320 $[M-H]^-$, found 493.975000

Synthesis of 4.20

sodium (E)-(S-([1,1':3',1''-terphenyl]-5'-yl)-N-((trifluoromethyl)sulfonyl)sulfinimidoyl)((trifluoromethyl)sulfonyl)amide



Step 1-3: A 100 ml two necked round bottom flask, connected to a reflux condenser and a 50 ml dropping funnel was charged with magnesium tunings (300 mg, 12.3 mmol, 1 equiv) and overlayered with Et_2O. The Grignard reaction was started by adding a small amount of m,m-di(biphenyl)bromide and heated with a heat gun. m,m-di(biphenyl)bromide (3.82 g, 12.3 mmol, 1 equiv.) dissolved in Et_2O (20 ml) was added dropwise to the reaction mixture under constant refluxing conditions. Upon full addition of the aryl bromide, the reaction was additionally refluxed for 1 h at 50 °C and cooled to r.t.. Sulfur (475 mg, 14.8 mmol, 1.2 equiv.) was added in one portion (exothermic) and the reaction mixture stirred additionally 20 minutes at r.t. LAH (1 M, 12.3 ml, 1 equiv.) was added carefully and the reaction mixture stirred 30 min at r.t. until the gas development ceased. The reaction was cooled in an ice-bath and carefully quenched with water until no further gas development was observed, followed by acidification with HCl (6 M). The reaction mixture was transferred to a separation funnel, all the glas ware washed with Et_2O and the combined organic phase washed with HCl (6 M, 2x 30 ml), brine, the organic phase dried over sodium sulfate and concentrated to dryness. NMR analysis shows ca. 80% purity of the desired thiol, which was further reacted in the next step.



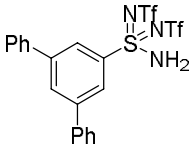
Step 4: A 500 ml two necked flask connected with a 100 ml dropping funnel and an argon adapter was charged with KOtBu (5.78 g, 51.5 mmol, 4.2 equiv.), dissolved in THF (100 ml), cooled in an ice-bath followed by portion-wise addition of I_2 (12.5 g, 49.4 mmol, 4 equiv.) to form a dark brownish suspension, which was additionally stirred 30 min in an ice bath. Meanwhile the dropping funnel was charged with a solution of the thiol from step 1 dissolved in in CH_3CN (30 ml) and $TfNH_2$ (3.68 g, 24.7 mmol, 2 equiv.). This solution was added to the dark brownish suspension and the reaction mixture stirred o.n. at r.t.. Next day (ca. 16 h) the black reaction mixture was diluted with Et_2O (150 ml) and quenched with sat. $Na_2S_2O_{3(aq)}$ until the dark black emulsion turned slightly yellowish. The emulsion was transferred to a 500 ml separation funnel and the organic phase washed additionally with sat. $Na_2S_2O_{3(aq)}$ (200 ml), sat. $NaHCO_3$ (200 ml), brine, dried over sodium sulfate and concentrated to dryness. The crude product was

purified by FCC (DCM/EtOAc 4:1) to afford the desired product as an off-white solid (56%, 3:99 g).

^{1}H NMR (501 MHz, Aceton-d6) δ = 8.02 – 7.98 (m, 3H), 7.73 – 7.67 (m, 4H), 7.47 – 7.40 (m, 4H), 7.37 – 7.30 (m, 2H) ppm. ^{13}C NMR (126 MHz, Acetone) δ = 145.07, 143.67, 140.47, 130.00, 129.24, 129.10, 128.06, 124.03, 122.94, 120.37 (other signals not observed or detected) ppm. ^{19}F NMR (471 MHz, Acetone) δ = –78.90 ppm. HRMS (ESI): m/z cald for $C_{20}H_{13}F_6N_2O_4S_3^-$: 554.994721 $[M-H]^-$, found 554.994810

Synthesis of SA-4

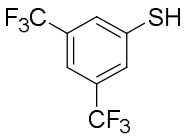
N,N'-([1,1':3',1''-terphenyl]-5'-yl(amino)-l6-sulfanediylidene)bis(1,1,1-trifluoromethanesulfonamide)



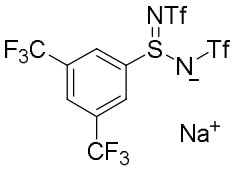
20 ml microwave vial was charged with Na[m,m-di(phenyl)phenylS(NTf)$_2$] (**4.20**) (1.62 g, 2.82 mmol, 1 equiv.), Selectfluor (3.99 g, 11.3 mmol, 4 equiv.) and suspended in acetonitrile (15 ml). The reaction mixture was irradiated for 1 h at 100 °C under microwave conditions and then poured into a 100 ml round-bottom flask connected to an argon adapter and concentrated under inert conditions (cooling trap with liquid nitrogen). The yellowish residue was suspended in DCM (20 ml) and filtered through a plug of silica followed by washing with DCM (20 ml) and the organic filtrate was collected in a 100 ml schlenk-flask. Ammonia gas was bubbled into the DCM solution for ca. 20 min, forming a colorless suspension. This suspension was transferred to a 100 ml round bottom flask and concentrated to dryness (Rotavap). The residue was dissolved in a mixture of Et_2O HCl (6 M) 1/1 vol% and transferred to a separation funnel. The organic phase was additionally washed with HCl (6 M, three times, 30 ml), concentrated to dryness and the crude product recrystallized from toluene / hexanes to afford the title product as a colorless solid (86%, 1.38 g).

^{1}H NMR (501 MHz, Acetone) δ = 8.47 (d, *J*=1.6, 2H), 8.45 (t, *J*=1.6, 1H), 7.88 – 7.86 (m, 2H), 7.86 – 7.84 (m, 2H), 7.63 – 7.57 (m, 4H), 7.57 – 7.50 (m, 2H), 5.42 – 2.63 (sbr, 2H) ppm. ^{13}C NMR (126 MHz, Acetone) δ = 144.55, 140.10, 139.17, 133.58, 130.26, 129.87, 128.19, 125.47, 121.42, 118.87 (other signals not observed or detected) ppm. ^{19}F NMR (471 MHz, Acetone) δ = –79.23 ppm. HRMS (ESI): m/z cald for $C_{20}H_{14}F_6N_3O_4S_3^-$: 570.005620 $[M-H]^-$, found 570.006480

Synthesis of 4.21



Step 1: A two necked 250 ml flask connected with a 50 ml dropping funnel was charged with 3,5-bis(trifluoromethyl)benzenesulfonyl chloride (10.4 g, 33.4 mmol, 1 equiv.) and dissolved in Et_2O (100 ml). $LiAlH_4$ (1M in Et_2O, 100 ml, 100 mmol, 3 equiv) was added dropwise to the reaction mixture at 0 °C and upon full addition stirred additionally for 1 h at 0°C. The reaction was carefully quenched with water to form a milky suspension and upon gas development ceased, aqueous HCl (6M, 100 ml) was added to form a colorless emulsion. The emulsion was transferred to a 500 ml separation funnel, the organic phase washed additionally with aqueous HCl (6M, 2x 150 ml), brine, dried over sodium sulfate and concentrated to dryness. The crude product was utilized without further purifications.

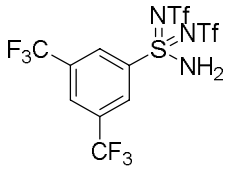


Step 2: A 250 ml two necked flask connected with a 100 ml dropping funnel and an argon adapter was charged with KOtBu (16.9 g, 150 mmol, 4.5 equiv.), dissolved in THF (100 ml), cooled in an ice-bath followed by portion-wise addition of I_2 (42.0 g, 165 mmol, 5 equiv.) to form a dark brownish suspension, which was additionally stirred 30 min in an ice bath. Meanwhile the dropping funnel was charged with a solution of the thiol from **Step 1** dissolved in in CH_3CN (60 ml) and $TfNH_2$ (9.96 g, 66.8 mmol, 2 equiv.). This solution was added to the dark brownish suspension and the reaction mixture stirred o.n. at r.t.. Next day (ca. 16 h) the black reaction mixture was diluted with Et_2O (150 ml) and quenched with sat. $Na_2S_2O_{3(aq)}$ until the dark black emulsion turned slightly yellowish. The emulsion was transferred to a 500 ml separation funnel and the organic phase washed additionally with sat. $Na_2S_2O_{3(aq)}$ (200 ml), sat. $NaHCO_3$ (200 ml), brine, dried over sodium sulfate and concentrated to dryness. The crude product was purified by FCC (gradient: 1. Hexanes 2. DCM 3. DCM / acetone 85:15 to elute the desired product) to afford the desired product (51%, 9.53 g).

^{1}H NMR (501 MHz, CD_3CN) δ = 8.34 (s, 2H), 8.22 (s, 1H). ^{19}F NMR (471 MHz, CD_3CN) δ = – 63.58 (s, 6F), –79.38 (s, 6F). $C_{10}H_3F_{12}N_2O_4S_3^-$: 538.906892 $[M]^-$, found 538.906670

Synthesis of SA-5

N,N'-(amino(3,5-bis(trifluoromethyl)phenyl)-l6-sulfanediylidene)bis(1,1,1-trifluoromethanesulfonamide)

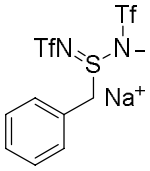


A 100 ml round-bottom flask was charged with Na[m,m-di(CF_3)phenylS($NTf)_2$] (**4.21**) (9.53 g, 16.9 mmol, 1 equiv.), Selectfluor (12.0 g, 33.8 mmol, 1 equiv.) and suspended in acetonitrile (40 ml). The reaction mixture was stirred 48 h at 80°C. All volatiles were removed in h.v. and all volatiles condensed in a cooling trap filled with liquid nitrogen. The yellowish residue was suspended in DCM (20 ml) and filtered through a plug of silica followed by rinsing with DCM (20 ml) and the organic filtrate was collected in a 100 ml schlenk-flask. Ammonia gas was bubbled into the DCM solution for ca. 20 min, forming a colorless suspension. This suspension was transferred to a 100 ml round bottom flask and concentrated to dryness (Rotavap). The residue was dissolved in a mixture of Et_2O HCl (6 M) 1/1 vol% and transferred to a separation funnel. The organic phase was additionally washed with HCl (6 M, 3 x 30 ml), concentrated to to afford the title product as a colorless solid (8%, 760 mg).

^{1}H NMR (501 MHz, CD_3CN) δ = 8.62 (s, 2H), 8.51 (s, 1H), 3.68 (sbr, 2H) ppm. ^{13}C NMR (126 MHz, CD_3CN) δ = 141.46, 133.93 (q, *J*=35.0), 132.67, 130.92 (q, *J*=3.7), 129.59, 129.56, 126.51, 124.34, 122.17, 121.24, 118.70, 118.26 (peaks refer to observed carbon signals) ppm. ^{19}F NMR (471 MHz, CD_3CN) δ = -63.64 (s, 6F), -79.19 (s, 6F) ppm. $C_{10}H_4F_{12}N_3O_4S_3^-$: 553.917791 $[M-H]^-$, found 553.917300

Synthesis of 4.22

sodium (Z)-(S-benzyl-N-((trifluoromethyl)sulfonyl)sulfinimidoyl)((trifluoromethyl)-sulfonyl)amide

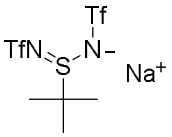


A 500 ml two necked round bottom flask, connected to a 100 ml dropping funnel and an argon adapter, was charged with KO^{t}Bu (14.5 g, 129 mmol, 5.3 equiv.) dissolved in THF (120 ml) and cooled to 0 °C. I_2 (34.3 g, 135 mmol, 5.6 equiv.) was portion-wise added to form a dark brown suspension. Meanwhile the dropping funnel was charged with $TfNH_2$ (7.42 g, 49.8 mmol, 2.1 equiv.) benzylthiol (3.00 g, 24.2 mmol, 1 equiv.) and dissolved in CH_3CN (20 ml). This solution was added to the dark brown suspension and the reaction mixture stirred o.n. (19 h) at r.t.. The black reaction mixture was diluted with Et_2O (50 ml) and the reaction mixture quenched with sat. $Na_2S_2O_{3(aq)}$ until the dark black emulsion turned slightly yellowish. The emulsion was transferred to a 500 ml separation funnel and the organic phase washed additionally with sat. $Na_2S_2O_{3(aq)}$ (200 ml), sat. $NaHCO_3$ (200 ml), brine, dried over sodium sulfate and concentrated to dryness. The crude product was purified by FCC (gradient: 1. DCM (500 ml) then DCM/acetone 4:1) to afford the desired product as a colorless solid (94 %, 9.98 g, 21.3 mmol).

^{1}H NMR (501 MHz, CD_3CN) δ = 7.39 – 7.35 (m, 5H), 4.24 (s, 2H), 2.17 (sbr, 2H) ppm. ^{19}F NMR (471 MHz, CD_3CN) δ – 79.55 ppm. HRMS (ESI): m/z cald for $C_9H_7F_6N_2O_4S_3^-$: 416.947771 $[M-H]^-$, found 416.947930

Synthesis of 4.23

sodium (Z)-(S-(tert-butyl)-N-((trifluoromethyl)sulfonyl)sulfinimidoyl)((trifluoromethyl)sulfonyl)amide

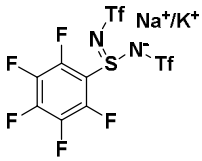


A 500 ml two necked round bottom flask, connected to a 100 ml dropping funnel and an argon adapter, was charged with KO^{t}Bu (6.67 g, 59.4mmol, 5 equiv.) dissolved in THF (80 ml) and cooled to 0 °C. I_2 (15.7 g, 112 mmol, 5.2 equiv.) was portion-wise added to form a dark brown suspension. Meanwhile the dropping funnel was charged with $TfNH_2$ (3.54 g, 23.8 mmol, 2.0 equiv.) tert-butylthiol (1.07 g, 11.9 mmol, 1 equiv.) and dissolved in CH_3CN (20 ml). This solution was added to the dark brown suspension and the reaction mixture stirred o.n. (19 h) at r.t.. The black reaction mixture was diluted with Et_2O (50 ml) and the reaction mixture quenched with sat. $Na_2S_2O_{3(aq)}$ until the dark black emulsion turned slightly yellowish. The emulsion was transferred to a 500 ml separation funnel and the organic phase washed additionally with sat. $Na_2S_2O_{3(aq)}$ (200 ml), sat. $NaHCO_3$ (200 ml), brine, dried over sodium sulfate and concentrated to dryness. The crude product was purified by FCC (gradient: 1. DCM (500 ml) then DCM/acetone 4:1) to afford the desired product as a colorless solid (42 %, 1.92 g, 11.9 mmol).

^{1}H NMR (501 MHz, CD_3CN) δ = 1.28 (s, 9H) ppm. ^{13}C NMR (126 MHz, CD_3CN) δ = 121.53 (q, *J*=322.8), 59.69, 23.05 ppm. ^{19}F NMR (471 MHz, CD_3CN) δ = –78.79 (s) ppm. HRMS (ESI): m/z cald for $C_6H_9F_6N_2O_4S_3^-$: 382.963421 $[M-H]^-$, found 382.963660

Synthesis of 4.24

sodium (Z)-(S-(perfluorophenyl)-N-((trifluoromethyl)sulfonyl)sulfinimidoyl)((trifluoromethyl)-sulfonyl)amide

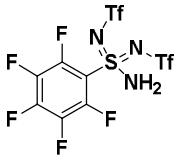


A 50 ml round bottom flask was charged with TfNH2 (5.00 g, 33.5 mmol, 1 equiv.), NaOH (5 g, 125 mmol, 2.8 equiv.) and water (20 ml). The aqueous solution was placed in a cooling bath at –30°C (ethanol, dry ice). Chlorine gas was bubbled into the solution for ca. 10 minutes to form an orange emulsion. This emulsion was carefully transferred to a 50 ml separation funnel. Meanwhile a 25 ml schlenk-tube was charged with pentafluorothiophenol (1.34 g, 6.71 mmol, 0.2 equiv.) and dissolved in DCM (5 ml) and the Schlenk-tube placed in a cooling bath (–78°C, dry ice acetone). The lower dark orange phase of the separation funnel was added to the Schlenk-tube containing the thiol and subsequently allowed to warm to r.t.. The reaction was stirred 1 h at r.t. followed by subsequent addition of sat. NaHCO3 and the aqueous phase extracted with DCM. The DCM phase was dried over sodium sulfate, concentrated to dryness and the crude product purified by FCC (acetone / DCM 1:4) to elute the desired product as a colorless solid (13%, 430 mg, 0.87 mmol).

^{19}F NMR (471 MHz, CD_2Cl_2) δ = –78.15 (6F), –134.86 (2F), –140.82 (2F), –156.36 (1F) ppm. HRMS (ESI): m/z cald for $C_8F_{11}N_2O_4S_3^-$: 492.885013 $[M-H]^-$, found 492.885610

Synthesis of SA-8

N,N'-(amino(perfluorophenyl)-l6-sulfanediylidene)bis(1,1,1-trifluoromethanesulfonamide)



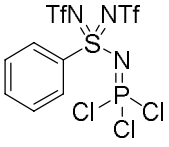
The sulfinate (**4.24**) (247 mg, 478 µmol, 1 equiv.) and Selectfluor (853 mg, 2.41 mmol, 9 equiv.) were placed in a 20 ml microwave vial and suspended in MeCN (4ml). The reaction mixture was irradiated in the microwave for 14 h at 110°C and additional 3 h at 140 °C (4 bar overpressure). The crude mixture was, under inert conditions, transferred to a flask and concentrated in h.v., whereas all volatile compounds were condensed in a cooling trap (liquid nitrogen). The residue was extracted with DCM (40 ml) and the DCM phase filtered through silica (ca. 3cm height) and concentrated under inert conditions in h.v. to obtain a yellow oily liquid. NMR analysis shows the signals of the desired sulfonyl fluoride (^{19}F NMR (471 MHz, CD_3CN) δ = 48.14 (s, 1F), –79.80 (6F), –138.68 – -140.34 (m, 2F), –147.73 – -149.39 (m, 1F), –159.73 – -161.49 (m, 2F) ppm). The sulfonyl fluoride was dissolved in Et_2O (40 ml) and a solution of ammonia in dioxane (0.42 M, 0.73 ml, 306 µmol, 0.64 equiv.) was added via

syringe pump (0.05 ml / min) over night at –72°C. The next day an aliquote was analyzed by NMR, indicating the formation of several unidentified products. The crude product was purified by FCC (Aceton / DCM 1:4) to elute the desired product (79 mg) , albeit in no spectroscopically pure form. The main signals, which belong to the desired product are shown: ^{1}H NMR (501 MHz, CD_3CN) δ = 6.03 (s, 1H). ^{19}F NMR (471 MHz, CD_3CN) δ = –79.48 (6F), –140.49 (dt, J=26.8, 8.1, 2F), –149.73 – –149.98 (m, 1F), –162.40 – –162.68 (m, 2F) ppm.
HRMS (ESI): m/z cald for $C_8H_1F_{11}N_3O_4S_3^-$: 507.895913 $[M-H]^-$, found 507.896140

7.6.2 Synthesis of Imidodiphosphorsulfonyliminoimidates (IDPii)

Synthesis of P-12

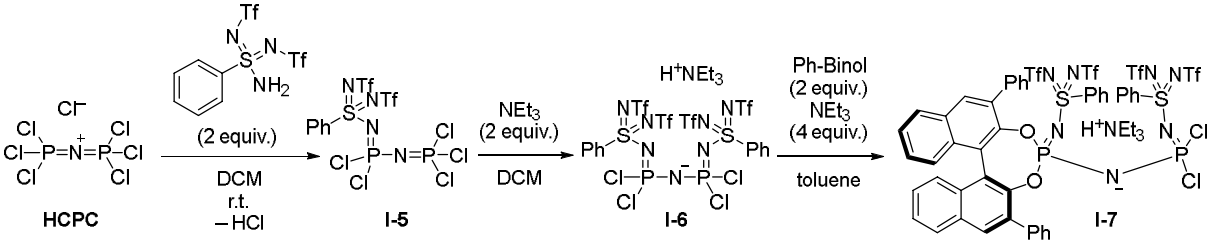
Phenylbis(trifluoromethylsulfonylimino)phosphorimidoyl trichloride



A 10 ml flame dried schlenk tube was charged with phosphorpentachloride (196 mg, 0.94 mmol), phenylbis(imino(trifluoromethanesulfonyl))sulfonamide (395 mg, 0.94 mmol) and suspended in DCM (2ml). The reaction was stirred at 150 rpm under constant gas liberation for 20 minutes, after which the gas development ceased and the reaction suspension turned into a colorless solution. All volatiles were removed in h.v., condensing all volatile compounds into a cooling trap, which is cooled with liquid nitrogen to form a colorless solid (quantitative yield, 522 mg).

^{1}H NMR (501 MHz, CD_2Cl_2) δ = 8.1 – 8.1 (m, 2H), 7.9 – 7.8 (m, 1H), 7.8 – 7.7 (m, 2H) ppm. ^{19}F NMR (471 MHz, CD_2Cl_2) δ = – 78.0 (s, 6F) ppm. ^{31}P NMR (203 MHz, CD_2Cl_2) δ = 23.3 (s, 1P) ppm. HRMS refers to hydrolyzed product within the HR-MS measurement: HRMS (ESI): m/z cald for $C_8H_5F_6N_3O_5S_3Cl_2^-$: 533.841580 [M-H]$^-$, found 533.841460

Stepwise P-Cl substitution of HCPC



A 10 ml flame dried schlenk tube was charged with hexachlorobisphosphazonium chloride (155 mg, 479 µmol, 1 equiv.) and N,N'-(amino(phenyl)-l6-sulfanediylidene)bis(1,1,1-trifluoromethane-sulfonamide) (**SA-2**) (402 mg, 959 µmol, 2 equiv.). DCM (1 ml) was added and the resulting suspension stirred (100 rpm) for 1 h until gas evolution ceased and the suspension turned into a slightly orange solution. An aliquote was analyzed by ^{31}P-NMR, indicating the characteristic signals of the mono sulfonamide addition product **I-5**. Additional DCM (2 ml) was added followed by dropwise addition of NEt_3 (133 µl, 0.96 mmol, 2 equiv.). The reaction was stirred for 10 min at r.t. and analyzed by ^{31}P-NMR, indicating the formation of the desired double sulfonamide addition product **I-6**. All volatiles were removed in vacuo. Toluene (4 ml) and (S)-Phenyl-BINOL (210 mg, 480 µmol, 1 equiv.) was added followed by subsequent addition of NEt_3 (300 µl, 2.16 mmol, 4.5 equiv.). The reaction was stirred 16 h at

90°C and then analyzed by ^{31}P-NMR indicating the characteristic signals of intermediate **I-7** with an ^{31}P-NMR purity of ca. 84%.

^{31}P-NMR spectroscopic data:

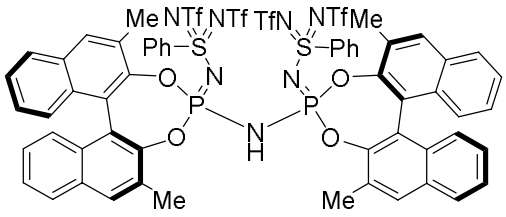
I-5: ^{31}P NMR (203 MHz, CD_2Cl_2) δ = 9.36 (d, ^2J = 31.5 Hz), –5.78 (d, ^2J = 31.5 Hz) ppm.

I-6: ^{31}P NMR (203 MHz, CD_2Cl_2) δ –10.39 (s) ppm.

I-7: 203 MHz, CD_2Cl_2) δ –8.52 (d, ^2J = 60.2 Hz), – 13.90 (d, ^2J = 60.2 Hz) ppm.

Synthesis of IDPii-1

N,N',N'',N'''-(((azanediylbis(2,6-dimethyl-4l5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-yl-4-ylidene))bis(azanylylidene))bis(phenyl-l6-sulfanyldiylidene))tetrakis(1,1,1-trifluoromethanesulfonamide)



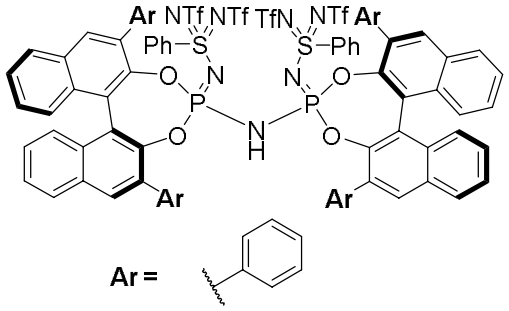
A 10 ml flame dried Schlenk-tube was charged with $PhS(NTf)_2NH_2$ (166 mg, 396 µmol, 1 equiv.) and PCl_5 (81.7 mg, 392 µmol, 0.99 equiv.) followed by addition of DCM (2 ml). The reaction was stirred for 1 h at r.t. (150 rpm). All volatiles were removed in h.v.. 3,3´(Me)-BINOL (125 mg, 397 µmol, 1 equiv.) was added followed by addition of DCM (2ml) and DIPEA (414 µl, 2-38 mmol, 6 equiv.). The reaction was stirred 1 h at r.t. followed by addition of ammonia (c= 0.42 M in dioxane, 282µl, 118 µmol, 0.3 equiv.) and stirred for 3 h r.t.. The reaction was diluted with EtOAc, transferred to a separation funnel, quenched with aqueous HCl (6 M). The organic phase was additionally washed with brine, dried over sodium sulfate, concentrated to dryness and the crude product purified by FCC (DCM/EtOAc 4:1) to afford the desired product as salt. The salt was redissolved in DCM (5 ml), emulgated with HCl 6 M (5 ml) and vigorously stirred for 30 minutes. The DCM phase was separated, concentrated to dryness and the colorless solid dried o.n. in hv. (5%, 30 mg).

^{1}H NMR (501 MHz, CD_2Cl_2) δ = 7.84 (d, *J*=7.4, 2H), 7.78 – 7.73 (m, 2H), 7.71 (s, 2H), 7.51 – 7.42 (m, 4H), 7.33 – 7.29 (m, 4H), 7.26 – 7.22 (m, 2H), 7.16 – 7.09 (m, 2H), 6.92 (d, *J*=8.0, 2H), 6.88 (s, 2H), 6.81 (t, *J*=7.5, 2H), 6.74 (d, *J*=8.8, 2H), 6.44 (t, *J*=7.8, 4H), 3.08 (s, 1H), 2.48 (s, 6H), 2.06 (s, 6H) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2) δ 133.55, 132.51, 131.87, 131.56, 131.37, 131.25, 131.14, 130.22, 129.37, 129.15, 128.56, 128.53, 128.52, 128.07, 127.95, 127.30, 127.16, 126.88, 126.49, 126.28, 126.20, 126.10, 121.18, 17.13 ppm, 16.62 (other signals not observed or detected); ^{19}F NMR (471 MHz, CD_2Cl_2) δ = –77.83 (s, CF_3), –78.67 (s,

CF_3) ppm; ^{31}P NMR (203 MHz, CD_2Cl_2) δ = –14.20 ppm (s, 2P). HRMS (ESI): m/z cald for $C_{60}H_{42}N_7O_{12}S_6F_{12}P_2^-$: 1534.050503 $[M-H]^-$, found 1534.050410

Synthesis of IDPii-2

N,N',N'',N'''-(((azanediylbis(2,6-diphenyl-4l5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-yl-4-ylidene))bis(azanylylidene))bis(phenyl-l6-sulfanyldiylidene))tetrakis(1,1,1-trifluoromethanesulfonamide)



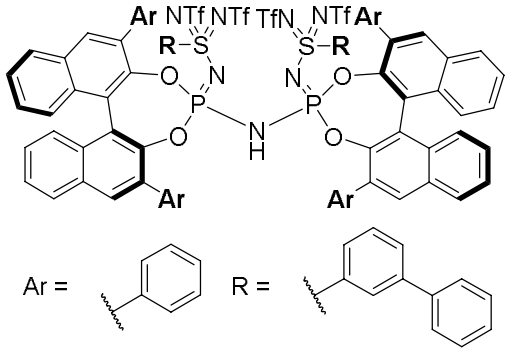
A 25 ml flame dried and argonated schlenk flask was charged with hexachlorobisphosphazonium chloride (132 mg, 407 µmol, 1 equiv.) and of N,N'-(amino(phenyl)-l6-sulfanediylidene)bis(1,1,1-trifluoromethane-sulfonamide) from example 18 (343 mg, 818 µmol, 2 equiv.) and suspended in toluene (4 ml). The suspension was stirred for 15 minutes until gas development ceased. Sodium hydride (dispersion in mineral oil, 60%, 218 mg, 5.45 mmol, 13 equiv.) was added and the reaction mixture stirred 3 h at 60 °C. (S)-3,3´-(Phenyl)BINOL (401 mg, 914 µmol, 2.2 equiv.) was added and the reaction mixture stirred for 23 h at 100 °C. The reaction mixture was then carefully poured into sat. NaHCO3 and the aqueous layer extracted with DCM. The combined organic phases were washed with brine, dried over sodium sulfate and concentrated to dryness followed by purification by FCC (Biotage, gradient DCM up to DCM/MeOH (3:2)) to elute the desired product as a salt. This salt was then acidified by dissolving in a small quantitiy of DCM and flushing through a 5 cm pad of DOWEX® 50WX8. The organic phase was concentrated to dryness to furnish the desired product in acidic form (60%, 437 mg).

^1H NMR (501 MHz, CD_2Cl_2) δ = 8.07 – 7.99 (m, 4H), 7.78 – 7.71 (m, 4H), 7.59 – 7.53 (m, 4H), 7.52 – 7.47 (m, 2H), 7.36 – 7.10 (m, 24H), 7.02 – 6.92 (m, 6H), 6.88 – 6.79 (m, 6H), 5.56 (s br, 1H) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 143.96, 143.76, 143.72, 139.41, 136.09, 134.94, 133.18, 133.06, 132.85, 132.68, 132.61, 132.32, 132.01, 131.87, 130.77, 129.92, 129.83, 129.71, 129.58, 128.99, 128.90, 128.58, 128.39, 128.07, 127.69, 127.53, 127.45, 127.34, 127.11, 126.89, 126.82, 125.82, 123.69, 123.12, 122.82, 120.56, 120.52, 118.00, 115.43 ppm (other signals not observed or detected). ^{19}F NMR (471 MHz, CD_2Cl_2) δ = –77.22

(s, 3F), –77.96 (s, 3F) ppm. ^{31}P NMR (203 MHz, CD_2Cl_2) δ = –20.11 (s, 2P) ppm. HRMS (ESI): m/z calcd for $C_{80}H_{50}F_{12}N_7O_{12}P_2S_6^-$: 1782.113102 [M-H]$^-$, found 1782.110140.

Synthesis of IDPii-3

N,N',N'',N'''-(((azanediylbis(2,6-diphenyl-4l5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-yl-4-ylidene))bis(azanylylidene))bis([1,1'-biphenyl]-3-yl-l6-sulfanyldiylidene))tetrakis(1,1,1-trifluoromethanesulfonamide)

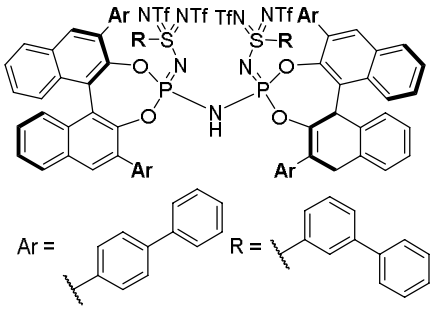


A 10 ml flame dried Schlenk-tube was charged with m-biphenylS(NTf)$_2$NH$_2$ (**SA-3**) (111 mg, 211 µmol, 1 equiv.) and PCl_5 (43.9 mg, 211 µmol, 1 equiv.) followed by addition of DCM (1 ml). The reaction was stirred for 1 h at r.t. (150 rpm). All volatiles were removed in h.v.. 3,3´(phenyl)-BINOL (125 mg, 397 µmol, 1 equiv.) was added followed by addition of toluene (2ml) and NEt_3 (353 µl, 2.53 mmol, 12 equiv.). The reaction was stirred 15 min at r.t. followed by addition of HMDS (22 µl, 105 µmol, 0.5 equiv.) and 4-DMAP (5.15 mg, 42.2 µmol, 0.2 equiv.). The reaction was heated to 110 °C (oil bath), sealed upon reaching the desired temperature and stirred for 46 h. Saturated aqeuous $NaHCO_3$ (*ca.* 1 ml) was added to quench the reaction and transferred to a separation funnel. The aqeuous phase was extracted with DCM (4 x 5 ml), the combined organic phase dried over sodium sulfate and concentrated to dryness. The crude product was purified by flash column chromatography (gradient: 1. Hexanes / EtOAc (1:1) to elute side products then product elution with DCM / EtOAc (1:1) to afford the desired product as salt, which was further acidified by dissolving in a small quantitiy of DCM and passing through a plug of DOWEX50WX80 to yield the desired product in acidic form (18%, 65 mg)

^{1}H NMR (501 MHz, CD_2Cl_2) δ = 8.11 (t, *J*=2.2, 2H), 7.97 (s, 4H), 7.81 – 7.70 (m, 4H), 7.51 (ddd, *J*=14.0, 8.3, 3.2, 10H), 7.42 (dd, *J*=8.5, 6.6, 6H), 7.39 – 7.34 (m, 2H), 7.19 (tdd, *J*=14.3, 7.6, 4.0, 12H), 7.02 (dt, *J*=24.7, 7.3, 12H), 6.83 – 6.73 (m, 4H), 6.55 – 6.51 (sbr, 1H), 6.47 (t, *J*=7.9, 2H) ppm. ^{19}F NMR (471 MHz, CD_2Cl_2) δ = –77.06 (s, 6F), –78.10 (s, 6F). ^{31}P NMR (203 MHz, CD_2Cl_2) δ = –18.45 (s, 2P). HRMS (ESI): m/z cald for $C_{92}H_{58}N_7O_{12}S_6F_{12}P_2^-$: 1934.175702 [M-H]$^-$, found 1934.176920

Synthesis of IDPii-4

N,N',N'',N'''-(((azanediylbis(2,6-di([1,1'-biphenyl]-4-yl)-4l5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-yl-4-ylidene))bis(azanylylidene))bis([1,1'-biphenyl]-3-yl-l6-sulfanyldiylidene))tetrakis(1,1,1-trifluoromethanesulfonamide)



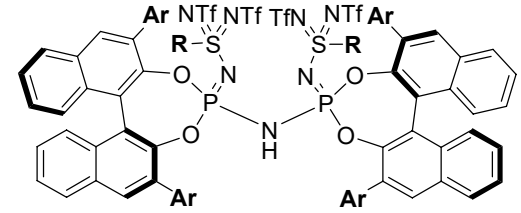
A 10 ml flame dried Schlenk-tube was charged with m-biphenylS(NTf)$_2$NH$_2$ (**SA-3**) (156 mg, 297 µmol, 1 equiv.) and PCl_5 (62.0 mg, 297 µmol, 1 equiv.) followed by addition of DCM (1 ml). The reaction was stirred for 1 h at r.t. (150 rpm). All volatiles were removed in h.v.. (*R*)-3,3´(*p*-biphenyl)-BINOL (176 mg, 298 µmol, 1 equiv.) was added followed by addition of toluene (2ml) and NEt_3 (353 µl, 2.53 mmol, 12 equiv.). The reaction was stirred 15 min at r.t. followed by addition of HMDS (22 µl, 105 µmol, 0.5 equiv.) and 4-DMAP (10.9 mg, 89.3 µmol, 0.3 equiv.). The reaction was heated to 110 °C (oil bath), sealed upon reaching the desired temperature and stirred for 72 h. Saturated aqeuous $NaHCO_3$ (*ca.* 1 ml) was added to quench the reaction and transferred to a separation funnel. The aqueous phase was extracted with DCM (4 x 5 ml), the combined organic phase dried over sodium sulfate and concentrated to dryness. The crude product was purified by flash column chromatography (gradient: 1. hexanes / EtOAc (1:1) to elute side products then product elution with DCM / EtOAc (4:1) to afford the desired product as salt, which was further acidified by dissolving in a small quantitiy of DCM and passing through a plug of DOWEX50WX80 to yield the desired product in acidic form (8%, 52 mg)

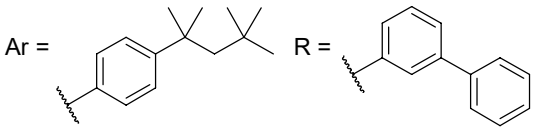
^{1}H NMR (501 MHz, CD_2Cl_2) δ = 8.14 (t, *J*=2.0, 2H), 8.00 – 7.95 (m, 4H), 7.82 (dd, *J*=8.0, 1.3, 2H), 7.77 (ddd, *J*=8.2, 6.2, 1.7, 2H), 7.63 – 7.56 (m, 4H), 7.56 – 7.47 (m, 10H), 7.47 – 7.37 (m, 12H), 7.38 – 7.30 (m, 6H), 7.29 – 7.24 (m, 6H), 7.24 – 7.20 (m, 6H), 7.16 (dt, *J*=10.4, 8.0, 10H), 7.11 (dt, *J*=7.9, 1.1, 2H), 7.05 (d, *J*=8.8, 2H), 6.96 – 6.91 (m, 2H), 6.85 (s, 2H), 6.35 (sbr, 1H), 6.29 (t, *J*=8.0, 2H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 145.38, 145.35, 145.31, 144.46, 144.42, 144.37, 142.07, 142.01, 141.48, 140.78, 140.68, 140.30, 139.33, 139.17, 135.81, 135.63, 133.32, 133.20, 132.70, 132.61, 132.49, 131.83, 131.50, 131.21, 130.49, 130.42, 130.12, 129.81, 129.45, 128.85, 128.80, 128.53, 127.53, 127.44, 127.35, 127.31, 127.17, 127.06, 127.03, 126.92, 126.56, 126.44, 126.34, 126.16, 124.63, 123.75, 123.45, 122.11, 120.89, 118.32 ppm (other signals not observed or detected); ^{19}F NMR (471 MHz, CD_2Cl_2) δ

= –76.91 (s, CF_3), –78.18 (s, CF_3) ppm; ^{31}P NMR (203 MHz, CD_2Cl_2) δ = -16.89 (s, 2P); HRMS (ESI): m/z cald for $C_{116}H_{74}N_7O_{12}S_6F_{12}P_2^-$: 2238.300902 [M-H]$^-$, found 2238.302040

Synthesis of IDPii-5

N,N',N'',N'''-(((azanediylbis(2,6-bis(4-(2,4,4-trimethylpentan-2-yl)phenyl)-4l5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-yl-4-ylidene))bis(azanylylidene))bis([1,1'-biphenyl]-3-yl-l6-sulfanyldiylidene))tetrakis(1,1,1-trifluoromethanesulfonamide)





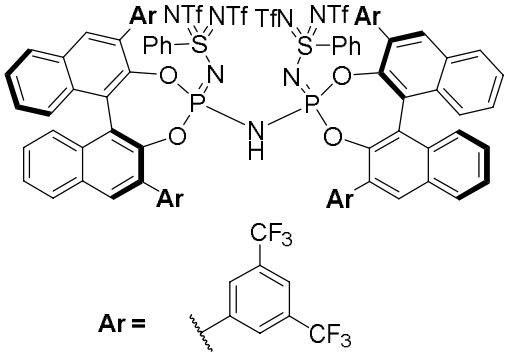
10 ml flame dried Schlenk-tube was charged with m-biphenylS(NTf)$_2$NH$_2$ (**SA-3**) (91.9 mg, 175 µmol, 1.01 equiv.) and PCl_5 (36.0 mg, 173 µmol, 1 equiv.) followed by addition of DCM (1 ml). The reaction was stirred for 1 h at r.t. (150 rpm). All volatiles were removed in h.v.. (*S*)-3,3´(2,4,4-trimethylpentan-2-yl))-BINOL (115 mg, 173 µmol, 1 equiv.) was added followed by addition of toluene (1 ml) and NEt_3 (193 µl, 1.38 mmol, 8 equiv.). The reaction was stirred 15 min at r.t. followed by addition of HMDS (18 µl, 86.4 µmol, 0.5 equiv.) and 4-DMAP (4.22 mg, 34.6 µmol, 0.2 equiv.). The reaction was heated to 120 °C (oil bath), sealed upon reaching the desired temperature and stirred for 72 h. Saturated aqeuous $NaHCO_3$ (*ca.* 1 ml) was added to quench the reaction and transferred to a separation funnel. The aqueous phase was extracted with DCM (4 x 5 ml), the combined organic phase dried over sodium sulfate and concentrated to dryness. The crude product was purified by flash column chromatography (gradient: 1. DCM to elute side products then product elution with DCM / EtOAc (4:1) to afford the desired product as salt, which was further acidified by dissolving in a small quantitiy of DCM and passing through a plug of DOWEX50WX80 to yield the desired product in acidic form (6%, 28 mg).

^{1}H NMR (501 MHz, CD_2Cl_2) δ = 8.01 (t, *J*=2.0, 2H), 7.89 – 7.84 (m, 4H), 7.67 – 7.61 (m, 2H), 7.61 – 7.56 (m, 4H), 7.55 – 7.44 (m, 4H), 7.44 – 7.36 (m, 10H), 7.21 (d, *J*=8.5, 8H), 7.11 (t, *J*=7.9, 8H), 7.07 – 6.98 (m, 6H), 6.63 (d, *J*=9.0, 2H), 6.60 (s, 2H), 6.17 (t, *J*=7.9, 2H).1.86 – 1.71 (m, 8H), 1.45 – 1.22 (m, 24H), 0.92 (sbr, 1H) 0.81 (s, 18H), 0.57 (s, 18H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 150.40, 141.65, 139.03, 135.81, 133.31, 133.14, 132.88, 132.65, 132.49, 132.35, 131.97, 131.82, 131.26, 129.98, 129.77, 129.51, 129.06, 128.75, 127.77,

127.64, 127.58, 127.28, 127.05, 126.94, 126.79, 126.67, 126.44, 125.92, 125.46, 122.51, 66.46, 57.93, 57.58, 47.59, 38.85, 38.78, 32.67, 32.58, 31.98, 31.76, 31.51, 31.36, 30.59, 30.11, 22.77, 19.60, 15.19, 14.50, 11.61, 8.82 ppm (other signals not observed or detected); ^{19}F NMR (471 MHz, CD_2Cl_2) δ = –76.82 (s, 6F), –78.61 (s, 6F) ppm. ^{31}P NMR (203 MHz, CD_2Cl_2) δ = –20.94 (s, 2P) ppm. HRMS (ESI): m/z cald for $C_{124}H_{122}N_7O_{12}S_6F_{12}P_2^-$: 2382.676502 $[M-H]^-$, found 2382.678060

Synthesis of IDPii-7

N,N',N'',N'''-(((azanediylbis(2,6-bis(3,5-bis(trifluoromethyl)phenyl)-4l5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-4-yl-4-ylidene))bis(azanylylidene))bis(phenyl-l6-sulfanyldiylidene))tetrakis(1,1,1-trifluoromethanesulfonamide)



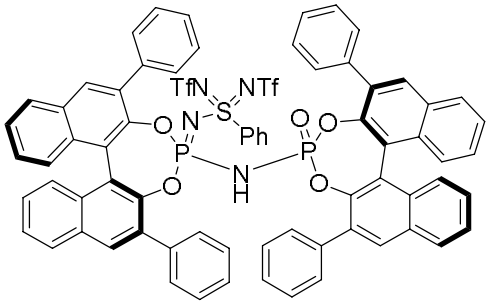
A 10 ml schlenk-tube was charged with HCPC (73.0 mg, 0.23 mmol), phenylbis(trifluoromethylsulfonylimino)sulfonamide (191 mg, 0.46 mmol, 2 equiv.) and suspended in 2 ml toluene. The reaction was stirred 30 min at r.t. (150 rpm) until the gas development ceased. Sodium hydride (dispersion in mineral oil, 60%; 116 mg, 2.90 mmol, 13 equiv.) was added and the resulting suspension stirred for 2 h in a pre-heated metal block to 110 °C. (S,S)-3,3´-(m,m-bistrifluoromethylphenyl)BINOL was added in one portion and the sealed schlenk-flask and 44 h stirred at 110°C. The reaction mixture was cooled to r.t., diluted with DCM and poured into sat. NaHCO3(aq). The aqueous phase was extracted with DCM (4 x 20 ml), the combined organic phase dried over sodium sulfate and concentrated to dryness. Flash column purification (Biotage gradient; DCM / MeOH up to 4 / 1) yields the desired product as a salt, which was acidified by dissolving the product in a small quantitiy of DCM and passing through pre-activated Dowex40WX8 to afford the desired product in acidic form (81%, 426 mg, 0.18 mmol).

^{1}H NMR (600 MHz, CD_2Cl_2) δ = 8.1 (dt, *J*=8.4, 1.1, 2H), 8.0 (m, 6H), 7.9 (s, 2H), 7.8 – 7.7 (m, 6H), 7.7 (ddd, *J*=8.2, 6.8, 1.2, 2H), 7.6 (ddd, *J*=8.1, 6.6, 1.5, 2H), 7.5 (d, *J*=8.6, 2H), 7.3 (ddd, *J*=8.7, 6.8, 1.3, 2H), 7.1 (d, *J*=7.6, 4H), 7.0 – 6.9 (m, 6H), 6.8 – 6.7 (m, 2H), 6.3 (t, *J*=7.8, 4H), 6.3 (s, 2H), 6.1 (sbr, 1H) ppm. ^{13}C NMR (151 MHz, CD_2Cl_2) δ = 143.7, 143.7, 142.6, 142.5,

142.5, 139.3, 139.1, 138.5, 135.3, 134.0, 133.3, 133.2, 132.6, 132.1, 131.8, 131.7, 131.7, 131.6, 131.5, 131.3, 131.3, 131.2, 131.1, 131.1, 130.7, 130.1, 129.9, 129.5, 129.0, 128.9, 128.5, 128.1, 127.7, 127.3, 127.2, 127.1, 126.7, 126.4, 124.9, 124.6, 123.1, 123.0, 122.9, 122.8, 122.1, 121.3, 121.0, 120.8, 120.4, 118.7, 118.3 ppm (other signals not observed or detected.^{19}F NMR (471 MHz, CD_2Cl_2) δ = –62.1 (s, 3F), –62.7 (s, 3F), –74.6 (s, 3F), –78.6 (s, 3F) ppm. ^{31}P NMR (203 MHz, CD_2Cl_2) δ = –19.7 (s, 2P). HRMS (ESI): m/z cald for $C_{88}H_{42}N_7O_{12}S_6F_{36}P_2^-$: 2326.012186 $[M-H]^-$, found 2326.013370

Synthesis of Synthesis of 4.26

(S,S)- N,N'-(((4-((4-oxido-2,6-diphenyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)amino)-2,6-diphenyl-4l5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-ylidene)amino)(phenyl)-l6-sulfanediylidene)bis(1,1,1-trifluoromethanesulfonamide)



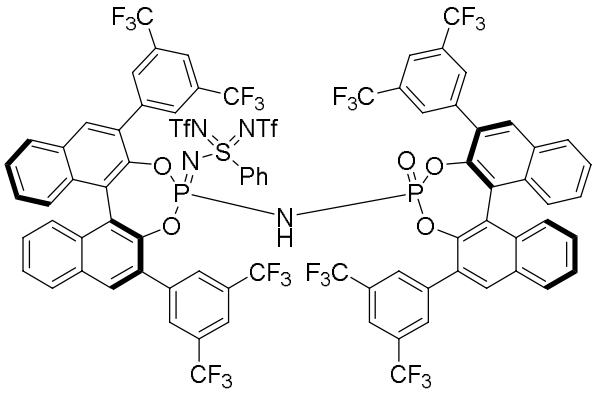
A 5 mL flame dried schlenk tube was charged with hexachlorobisphosphazonium hexachlorophosphate (146 mg, 274 µmol), (S)- 3,3'-bis(phenyl)-[1,1'-binaphthalene]-2,2'-diol (239 mg, 546 µmol) followed by the addition of pyridine (3 mL). The slightly yellow suspension was stirred for 3 h at r.t. followed by the addition of N,N'-(amino(phenyl)-l6-sulfanediylidene)bis(1,1,1-trifluoromethanesulfonamide) (345 mg, 823 µmol) and was stirred 4 d at r.t.. Distilled water (300 µl mL, 16.6 mmol) was added resulting in a beige suspension which was stirred additional 16 h at r.t.. The suspension was poured into a mixture of aqueous 6 M HCl (30 mL) and dichloromethane (30 mL) and was transferred to a separating funnel. The aqueous phase was extracted additional two times with dichloromethane (30 mL each) and the combined organic phase was dried over sodium sulfate and was concentrated to dryness. The crude product was further purified by flash column chromatography (ethyl acetate / hexanes (1:2)) to afford a colorless crystalline solid which was filtered through Dowex 50WX80 (acidic form, 8 cm height) to furnish the desired product as a colorless solid (100 mg, 26%).

^{1}H NMR (501 MHz, CD_2Cl_2) δ = 8.17 (d, *J*=8.0, 1H), 8.14 – 8.08 (m, 2H), 8.05 (d, *J*=8.2, 1H), 7.96 (d, *J*=7.7, 1H), 7.85 – 7.76 (m, 2H), 7.67 – 7.61 (m, 4H), 7.61 – 7.54 (m, 5H), 7.48 (tt, *J*=6.9, 2.2, 3H), 7.44 – 7.34 (m, 7H), 7.32 – 7.09 (m, 7H), 7.01 (td, *J*=7.6, 1.7, 3H), 6.90 (t,

J=7.8, 2H), 6.76 – 6.70 (m, 3H), 6.68 – 6.61 (m, 2H), 6.54 – 6.48 (m, 2H), 1.28 (sbr, 1H) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2) δ 144.64, 144.55, 144.11, 144.03, 143.68, 143.60, 143.06, 142.99, 142.92, 136.08, 136.00, 135.89, 135.71, 134.12, 133.88, 133.81, 133.41, 132.55, 132.39, 132.31, 132.23, 132.18, 132.03, 131.96, 131.54, 131.24, 129.92, 129.71, 129.65, 129.57, 129.25, 129.17, 129.10, 129.02, 128.99, 128.83, 128.38, 128.33, 128.23, 128.07, 127.86, 127.83, 127.56, 127.53, 127.45, 127.32, 127.15, 127.11, 126.98, 126.91, 125.89, 123.97, 123.26, 123.23, 122.39, 120.40 ppm (other signals not observed or detected). ^{19}F NMR (471 MHz, CD_2Cl_2) δ = –77.36 (s, CF_3), –78.77 (s, CF_3) ppm. ^{31}P NMR (203 MHz, CD_2Cl_2) δ = -5.00 (d, *J*=120.3, 1P), -13.85 (d, *J*=120.3, 1P) ppm.

Synthesis of 4.27

(S,S)-N,N'-(((4-((2,6-bis(3,5-bis(trifluoromethyl)phenyl)-4-oxidodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)amino)-2,6-bis(3,5-bis(trifluoromethyl)phenyl)-4l5-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-ylidene)amino)(phenyl)-l6-sulfanediylidene)bis(1,1,1-trifluoromethanesulfonamide)

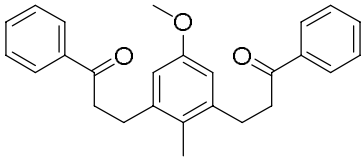


A 25 mL flame dried schlenk tube was charged with hexachlorobisphosphazonium hexachlorophosphate (155 mg, 291 µmol), (S)- 3,3'-bis(3,5-bis(trifluoromethyl)phenyl)-[1,1'-binaphthalene]-2,2'-diol followed by the addition of pyridine (5 mL). The slightly yellow suspension was stirred for 90 minutes at r.t. followed by the addition of N,N'-(amino(phenyl)-l6-sulfanediylidene)bis(1,1,1-trifluoromethanesulfonamide) (420 mg, 1 mmol) and was stirred 72 h at 60°C. After cooling to r.t. distilled water (1 mL, 27 mmol) was added resulting in a beige suspension which was stirred additional 24 h at r.t.. The suspension was poured into a mixture of aqueous 6 M HCl (30 mL) and dichloromethane (30 mL) and was transferred to a separating funnel. The aqueous phase was extracted additional two times with dichloromethane (30 mL each) and the combined organic phase was dried over sodium sulfate and was concentrated to dryness. The crude product was further purified by flash column chromatography (ethyl acetate / hexanes (1:4)) to afford a colorless crystalline solid which was filtered through Dowex 50WX80 (acidic form, 8 cm height) to furnish the desired product as a colorless solid (92 mg, 16%).

^{1}H NMR (501 MHz, CD_2Cl_2) δ = 8.45 (s, 1H), 8.26 (d, *J*=8.4, 1H), 8.01 (d, *J*=8.4, 3H), 7.97 – 7.94 (m, 2H), 7.90 (s, 2H), 7.88 (s, 3H), 7.87 – 7.84 (m, 1H), 7.82 – 7.71 (m, 4H), 7.70 – 7.65 (m, 1H), 7.65 – 7.59 (m, 3H), 7.55 (dd, *J*=8.3, 6.9, 1H), 7.46 – 7.39 (m, 3H), 7.29 (ddt, *J*=8.4, 6.8, 1.4, 1H), 7.05 (dd, *J*=12.8, 8.6, 3H), 7.02 – 6.96 (m, 3H), 6.85 (s, 2H), 6.70 (s, 1H), 6.45 – 6.38 (m, 3H), 5.29 (sbr, 1H) ppm. ^{19}F NMR (471 MHz, CD_2Cl_2) δ = –62.35 (s, 2CF3), –62.79(s, 2CF3), –62.99 (s, 2CF3), –63.13 (s, 2CF3), –77.39 (s, CF3), –79.74 (s, CF3) ppm. ^{31}P NMR (203 MHz, CD_2Cl_2) δ = –10.63 (d, *J*=126.2), –16.83 (d, *J*=126.2) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 143.34, 141.05, 139.41, 139.25, 138.07, 137.75, 133.65, 133.38, 133.16, 132.66, 132.32, 132.10, 131.87, 131.53, 131.47, 131.42, 131.09, 130.90, 130.45, 130.29, 130.15, 129.97, 129.82, 129.51, 129.05, 128.85, 128.72, 128.49, 127.80, 127.77, 127.35, 127.26, 127.20, 127.04, 126.97, 126.87, 126.36, 125.01, 124.81, 124.07, 123.70, 122.84, 122.37, 122.00, 121.13, 54.00, 53.77, 53.56 (other signals not observed or detected) ppm. HRMS (ESI): m/z calcd for $C_{80}H_{37}F_{30}N_4O_9P_2S_3^-$: 1925.072456 $[M-H]^-$, found 1925.074110.

7.7 Synthesis of Tetrahydroindacene-Derivatives

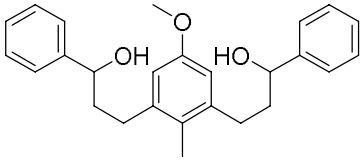
7.7.1. Synthesis of Tetrahydroindacene-Derived Phenols



Synthesis of 4.74

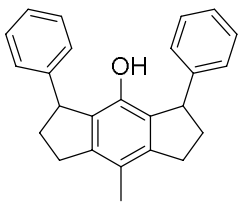
3,3'-(5-methoxy-2-methyl-1,3-phenylene)bis(1-phenylpropan-1-one)

Step 1: A 250 ml round bottom flask with argon adapter was charged with 3,5-dibromo-Step 1: 4-methylanisole (3.74 g, 13.4 mmol, 1 equiv.), followed by subsequent addition of $Pd(P(tBu)_3)_2$ (135 mg, 264 µmol, 2 mol%), THF (100 ml) and 1-phenylprop-2-en-1-ol (3.76 g, 28.0 mmol. 2.1 equiv.) and DIPEA (13.9 ml, 80.1 mmol, 6.0 equiv.). The solution stirred 2 h at 90°C (oil bath) and then allowed to cool to r.t.. The reaction was quenched with aq. HCl (6 M) and the aqueous phase extracted with EtOAc (200 ml). The organic phase was dried over sodium sulfate, concentrated to dryness



3,3'-(5-methoxy-2-methyl-1,3-phenylene)bis(1-phenylpropan-1-ol)

Step 2: The crude product from step 2, placed in a 100 ml round bottom flask was dissolved in DCM / MeOH (1:1 vol-%, 50 ml) followed by portion-wise addition of NaBH4 (1.52 g, 40.1 mmol, 3 equiv.) to form a black solution and under gas development. After 20 min the gas development ceased, the reaction mixture was additionally stirred for 30 minutes and quenched with aqueous HCl (6M,40 ml). The emulsion was transferred to a separation funnel and the aqueous phase extracted with DCM (3 x 40 ml). The combined organic phase was dried over sodium sulfate, concentrated to dryness and analyzed by NMR [^{1}H NMR (501 MHz, CD_2Cl_2) δ = 7.40 – 7.32 (m, 8H), 7.27 (ddt, *J*=6.9, 5.7, 2.1, 2H), 6.55 (s, 2H), 4.71 (ddd, *J*=7.7, 5.3, 3.5, 2H), 3.72 (s, 3H), 2.73 (ddd, *J*=13.9, 10.6, 5.4, 2H), 2.58 (ddd, *J*=14.5, 10.6, 6.0, 1H), 2.02 – 1.94 (m, 2H), 1.91 (ddd, *J*=10.6, 8.1, 5.5, 2H), 1.57 (s, 3H) ppm; ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 157.70, 145.33, 142.21, 128.99, 128.79, 128.34, 127.85, 126.30, 112.79, 74.44, 55.41, 40.10, 30.93, 13.90.



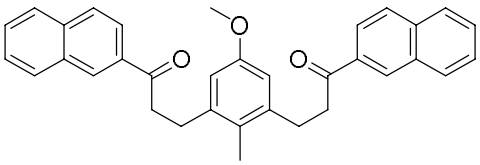
8-methyl-3,5-diphenyl-1,2,3,5,6,7-hexahydro-s-indacen-4-ol

Step 3&4: The crude product from Step 2, placed in a 250 ml round bottom flask connected to an argon adapter, was dissolved in DCM (80 ml), cooled

to –78°C (acetone dry ice) followed by addition of TfOH (500 µl, 5.65 mmol, 0.4 equiv.). The reaction was allowed to warm to r.t. and stirred 1 h. An aliquote was transferred to a GC-vial, all volatiles evaporated, and the residue analyzed by NMR, which indicated full conversion. The reaction was quenched with sat. NaHCO3, the aqueous phase extracted with DCM (3 x 30 ml), the organic phase dried over sodium sulfate and concentrated to dryness. NMR analysis shows partial demethylation of the anisole moiety. The residue was re-dissolved in DCM (80 ml), cooled to –78 °C followed by addition of BBr_3 (1 M in DCM, 10 ml, 10 mmol, 0.8 equiv.). Upon full addition the reaction was warmed to r.t., sturred 30 minutes at r.t. and the reaction mixture quenched with aqueous HCl (6 M, 150 ml) to form a greenish emulsion. This emulsion was transferred to a separation funnel and the aqeuous phase was extracted with DCM (5 x 40 ml). The combined organic phase was dried over sodium sulfate, concentrated to dryness and the crude product purified by FCC (hexane Et_2O 9:1). The desired racemic product (22%, 973 mg) was separated from the meso product (20 %).

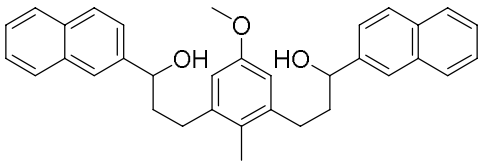
Spectroscopic data of racemic product: ^{1}H NMR (501 MHz, CD_2Cl_2) δ = 7.30 – 7.22 (m, 4H), 7.21 – 7.14 (m, 6H), 4.35 (dd, *J*=8.6, 5.9, 2H), 3.03 (ddd, *J*=15.2, 8.7, 5.9, 2H), 2.87 (ddd, *J*=15.6, 8.7, 6.2, 2H), 2.63 (dtd, *J*=12.8, 8.7, 5.9, 2H), 2.22 (s, 3H), 2.04 (ddt, *J*=12.5, 8.7, 6.1, 2H) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 147.36, 145.86, 144.96, 130.05, 129.07, 127.83, 126.84, 121.76, 49.28, 36.99, 31.01, 15.66 ppm. HRMS (ESI): *m*/*z* calcd for $C_{25}H_{25}O_1$: 341.18990[*M*+H]$^+$; found: 341.189540. HPLC racemate: (OD-3, *n*-hepante/*i*-propanol 99:1, 1 ml/min, 298 K) = $t_{R(enantiomer1)}$ = 4.81 min (50%), $t_{R(enantiomer\ 2)}$ = 5.85 min (50%)

Synthesis of 4.75



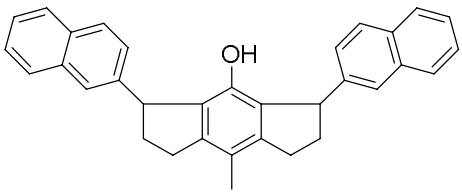
3,3'-(5-methoxy-2-methyl-1,3-phenylene)bis(1-(naphthalen-2-yl)propan-1-one)

Step 1:A 25 ml Schlenk-tube was charged with 3,5-dibromo-Step 4-methylanisole (550 mg, 1.97 mmol, 1 equiv.), followed by subsequent addition of $Pd(P(tBu)_3)_2$ (52 mg, 102 µmol, 5 mol%), 1,4-dioxane (15 ml) and 1-(2-naphthyl)prop-2-en-1-ol (724 mg, 3.93 mmol. 2 equiv.) and NEt_3 (1.64 ml, 11.8 mmol, 6.0 equiv.). The solution stirred 3 h at 90°C (oil bath) and then allowed to cool to r.t.. The reaction was quenched with aq. HCl (6 M) and the aqueous phase extracted with EtOAc (200 ml). The organic phase was dried over sodium sulfate and concentrated to dryness, followed by NMR analysis of the crude product, which was clean enough for the follow-up step [^{1}H NMR (501 MHz, $CDCl_3$) δ = 8.46 (t, *J*=1.1, 2H), 8.04 (td, *J*=8.1, 1.7, 2H), 7.95 – 7.85 (m, 6H), 7.63 – 7.52 (m, 4H), 6.73 (s, 2H), 3.78 (s, 3H), 3.41 – 3.35 (m, 4H), 3.18 – 3.10 (m, 4H), 2.09 (s, 3H) ppm].



3,3'-(5-methoxy-2-methyl-1,3-phenylene)bis(1-(naphthalen-2-yl)propan-1-ol)

Step 2: The crude product was dissolved in DCM (10 ml) followed by addition of $LiAlH_4$ (1M in Et_2O, 5.89 ml, 5.89 mmol, 3 equiv.) and stirred for 45 minutes at r.t. The reaction was carefully quenched with water to form a suspension followed by addition of aqueous HCl (6M, ca. 15 ml) to form an emulsion, in which all solid particles were dissolved. This emulsion was transferred to a dropping funnel and the aqueous phase was extracted with DCM (3 x 20 ml). The combined organic phase was dried over sodium sulfate and concentrated to dryness.



8-methyl-3,5-di(naphthalen-2-yl)-1,2,3,5,6,7-hexahydro-s-indacen-4-ol

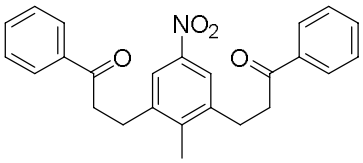
Step 3&4: The crude product from Step 2 was dissolved in DCM (30 ml), cooled to –72°C (dry ice ethanol), followed by subsequent addition of TfOH (174 µl, 1.95 mmol, 1 equiv). The reaction was stirred o.n. in the cooling bath and slowly allowed to reach r.t.. The next day the rxt was quenched with sat. $NaHCO_3$, transferred to a separation funnel and the aqueous phase extracted with DCM (3 x 20 ml). The combined organic DCM phase was dried over sodium sulfate and concentrated

to dryness. The residue, placed in a 100 ml round bottom flask connected to an argon adapter, was dissolved in DCM (40 ml), cooled to –72°C (dry ice, ethanol) followed by addition of BBr_3 (1 M in DCM, 3.93 ml, 3.93 mmol, 2 equiv.). The reaction was allowed to warm to r.t., stirred additional 30 minutes at r.t. and quenched with aqueous HCl (6 M). The emulsion was transferred to a separation funnel, the aqueous phase extracted with DCM (3 x 20 ml), the combined DCM phase dried over sodium sulfate and concentrated to dryness. The crude product was further purified by FCC (hexanes / Et_2O 9:1) to obtain the desired product in a d.r. of 3:1 (*rac*/*meso*). Note: The final product was isolated as mixture of racemic and meso product (61%, 528 mg, 1.20 mmol)

Spectroscopic data of racemic product (main signals): ^{1}H NMR (501 MHz, $CDCl_3$) δ = 7.66 (dd, *J*=9.0, 2.4, 4H), 7.63 – 7.59 (m, 2H), 7.54 – 7.52 (m, 2H), 7.43 – 7.27 (m, 4H), 7.22 (dd, *J*=8.5, 1.7, 2H), 7.16 (s, 1H), 4.47 – 4.41 (m, 2H), 3.04 – 2.95 (m, 2H), 2.84 (dt, *J*=16.1, 7.2, 2H), 2.65 – 2.56 (m, 2H), 2.18 (s, 3H), 2.13 – 2.00 (m, 2H). HRMS (ESI): *m*/*z* calcd for $C_{33}H_{28}O_1Na_1$: 463.203234 $[M+Na]^+$; found: 463.203270. An HPLC-sample was prepared *via* preparative thin-layer-chromatography to get a racemate enriched analytical sample: HPLC: (OD-3, *n*-heptane/*i*-PrOH 98:2, 1 ml/min 297 K, $t_{R(enantiomer\ 1)}$ = 8.45 min (48.0%), $t_{R(meso)}$ = 10.90 min (4%), $t_{R(enantiomer\ 2)}$ = 12.50 min (48%).

7.7.2. Synthesis of Tetrahydroindacene-Derived Aniline

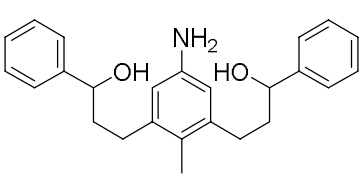
Synthesis of 4.81



3,3'-(2-methyl-5-nitro-1,3-phenylene)bis(1-phenylpropan-1-one)

Step1 :A 250 ml round-bottom flask connected to a schlenk-line was charged with 2,6-dibromo-4-nitrotoluene (9.13 g, 31.0 mmol), evacuated and purged with argon, followed by subsequent addition in the following order 1,4-dioxane (120 ml), bis(tri-tert-butylphosphin)palladium ($Pd[P(^tBu)_3]_2$ (184 mg, 361 µmol, 1 mol%), vinylbenzylalcohol (9.14 g, 68.1 mmol, 2.2 equiv.) and DIPEA (25.2 ml, 144 mmol, 4.6 equiv.). The reaction mixture was heated to 90 °C (oil bath), upon reaching the desired temperature sealed and stirred o.n. (15 h). After cooling to r.t., the reaction was concentrated to dryness, dissolved in DCM (100 ml) and poured into aqueous HCl (6M, 100 ml). The aqeuous phase was additionally extracted with DCM (4 x 100 ml), the combined organic phase dried over sodium sulfate and concentrated to dryness. The dark orange residue was recrystallized from EtOAc to afford the desired product as yellowish solid. Additional product could be recovered from the mother liquor upon standing for several days to obtain the desired product in a total yield of 92% (11.4 g, 28.5 mmol) ^{1}H NMR (501 MHz, $CDCl_3$) δ = 8.01 – 7.94 (m, 6H), 7.62 – 7.53 (m, 2H), 7.48 (t, *J*=7.7, 4H), 3.31 (dd, *J*=8.7, 6.5, 4H), 3.18 (dd, *J*=8.7, 6.6, 4H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 198.52, 146.18, 142.60, 141.73, 136.69, 133.52, 128.87, 128.18, 121.83, 38.62, 28.13, 15.60. HRMS (ESI): *m*/*z* calcd for $C_{25}H_{23}N_1O_4Na_1^+$: 424.151928[*M*+Na]$^+$; found: 424.152240

Synthesis of 4.82

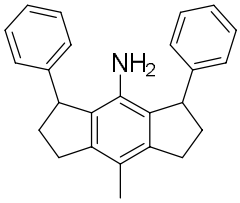


3,3'-(5-amino-2-methyl-1,3-phenylene)bis(1-phenylpropan-1-ol)

Step 2: A 250 ml round-bottom flask was charged with 3,3'-(2-methyl-5-nitro-1,3-phenylene)bis(1-phenylpropan-1-one, Product from **Step 1**) (14.5 g, 36.2 mmol, 1 equiv.) and dissolved in a mixture of DCM / MeOH (1:1 vol-%, 150 ml). NaBH4 (10.9 g, 289 mmol, 8 equiv.) was portion-wise added and upon full addition the black reaction mixture was stirred 1 h at r.t.. The reaction was carefully quenched with water, followed by addition of aqueous HCl (6 M, 100 ml). The emulsion was transferred to a 500 ml separation funnel. The aqueous phase was extracted with Et_2O (200 ml) and additionally with DCM (100 ml) to obtain a colorless aqueous solution. This aqeuous solution was placed in a 300 ml beaker, cooled in an ice-bath and carefully neutralized with sat.

NaOH. Upon reaching neutral pH, additional sat. $NaHCO_3$ was added, resulting in the precipitation of a colorless solid. The solid was isolated by filtration and dried 2 h in vacuum (11.99 g, 88%). ^{1}H NMR (501 MHz, CD_2Cl_2) δ = 7.39 – 7.31 (m, 8H), 7.31 – 7.23 (m, 2H), 6.35 (s, 2H), 4.70 (dd, *J*=7.7, 5.2, 2H), 3.48 – 3.43 (sbr, 2H), 2.65 (ddd, *J*=13.7, 10.5, 5.4, 2H), 2.50 (ddd, *J*=13.6, 10.3, 6.0, 2H), 2.01 (s, 3H), 1.99 – 1.84 (m, 4H) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 145.39, 144.51, 141.85, 128.76, 127.79, 126.30, 123.95, 114.39, 74.47, 40.17, 30.75, 13.74 ppm. HRMS (ESI): *m*/*z* calcd for $C_{25}H_{29}N_1O_2Na_1$: 398.209048 $[M+Na]^+$; found: 398.209260

Synthesis of 4.83



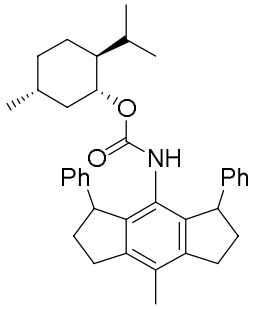
8-methyl-3,5-diphenyl-1,2,3,5,6,7-hexahydro-s-indacen-4-amine

Step 3: A 100 ml round-bottom flask containing 3,3'-(5-amino-2-methyl-1,3-phenylene)bis(1-phenylpropan-1-ol, Product from **Step 2**), (14.4 g, 38.5 mmol, 1 equiv.) placed in a 250 ml round bottom flask was dissolved in HFIP (200 ml). The solution was equally distributed in 20x20 ml Headspace-Vials. The 250 ml flask was additionally rinsed with HFIP (100 ml) and equally distributed in the 20 Headspace vials. TfOH (0.68 ml, 7.69 mmol, 0.2 equiv.) was equally distributed to the 20 reaction vessels (35 µl each). The Headspace vials were sealed with a microwave cap and placed in a metal block, which was subsequently heated to 80°C. The reactions were stirred 24 h at 80°C. An aliquote of one reaction vessel has been taken, concentrated and analyzed by NMR, indicating ca. 80% conversion. The 20 reaction vessels were combined in a 500 ml flask, all microwave vessels rinsed with DCM and the combined organic phase concentrated to dryness. The residue was re-dissolved in DCM (100 ml), transferred to a separation funnel and quenched with sat. $NaHCO_3$ (100 ml). The aqueous phase was extracted with DCM (4 x 100 ml), the combined organic phase dried over sodium sulfate, concentrated to dryness and purified by FCC (dry load, hexanes / Et_2O 9:1). The racemic aniline (23 %, 3.00 g, 8.84 mmol) was separated from the corresponding meso-side product (20%, 2.82 g, 8.3 mmol). The column was flushed with EtOAc to obtain additional 4 g of a brownish solid, which based on NMR analysis contains a significant amount of aniline and could be further purified.

^{1}H NMR (501 MHz, CD_2Cl_2) δ = 7.25 (dtd, *J*=7.4, 6.0, 5.5, 1.3, 4H), 7.20 – 7.14 (m, 2H), 7.12 (dt, *J*=8.0, 1.5, 4H), 4.24 (ddd, *J*=15.6, 8.8, 5.0, 2H), 3.04 – 2.92 (m, 2H), 2.89 – 2.77 (m, 2H), 2.64 (dtdd, *J*=12.8, 8.8, 6.7, 1.6, 2H), 2.58 – 2.41 (sbr, 2H), 2.20 (s, 3H), 2.00 (dddt, *J*=14.0, 10.1, 8.7, 5.2, 2H) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 146.11, 145.75, 144.29, 144.09,

137.79, 137.46, 129.06, 129.02, 129.01, 128.87, 127.79, 127.72, 126.66, 126.62, 119.23, 119.16, 49.77, 49.58, 37.14, 36.87, 30.78, 30.63, 15.62. HRMS (ESI): *m*/*z* calcd for $C_{25}H_{26}N_1$: 340.205974 $[M+H]^+$; found: 340.206180, HPLC: (OD-3, *n*-heptane/*i*-PrOH 98:2, 1 ml/min 297 K, $t_{R(meso)}$ = 3.20 min (46%), $t_{R(enantiomer\ 1)}$ = 3.63 min (27%), $t_{R(enantiomer\ 2)}$ = 4.20 min (27%),

Synthesis of 4.85&4.86



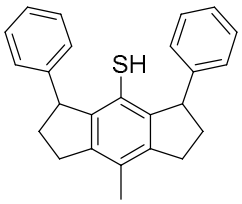
(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl (8-methyl-3,5-diphenyl-1,2,3,5,6,7-hexahydro-s-indacen-4-yl)carbamate

A 25 ml round-bottom flask with argon adapter was charged with (*rac*)-(8-methyl-3,5-diphenyl-1,2,3,5,6,7-hexahydro-s-indacen-4-amine, product from **Step 3**) (500 mg, 1.47 mmol, 1 equiv.), dissolved in DCM (20 ml), followed by addition of (*1S*)-(+)-menthyl chloroformate (644 mg, 2.95 mmol, 2 equiv.) and under vigorous stirring, pyridine (0.59 ml, 7.36 mmol, 5 equiv.) was added. The reaction was stirred for 1 h at r.t., quenched with sat. NH_4Cl and transferred to a 100 ml separation funnel. The aqueous phase was extracted with DCM (4 x 20 ml), dried over sodium sulfate and concentrated to dryness. The crude product was purified by FCC (Biotage, gradient: 1: DCM/hexanes (1:4) to elute side products, 2. DCM / hexanes (1:1) to elute the desired product. The obtained product was placed in a 250 ml round-bottom flask, followed by portion-wise addition of hexanes to obtain a colorless solution upon refluxing (ca. 120 ml). The solution was stored in a fridge. The precipitated crystalline material was isolated via decantation (20%, 152 mg, 291 µmol) and analyzed by NMR. The mother liquor was concentrated to dryness (360 mg) and recrystallized following the same procedure.

Spectroscopic data of clean diastereoisomer: ^{1}H NMR (501 MHz, CD_2Cl_2) δ = 7.16 (dd, *J*=8.2, 6.8, 4H), 7.16 – 7.05 (m, 2H), 7.00 – 6.94 (m, 4H), 5.45 (s, 1H), 4.39 (dd, *J*=9.1, 5.2, 2H), 4.18 (td, *J*=10.6, 4.1, 1H), 3.09 – 3.03 (m, 1H), 3.05 – 2.99 (m, 1H), 2.91 (ddd, *J*=15.7, 9.1, 5.6, 2H), 2.62 (dtd, *J*=13.0, 9.1, 6.5, 2H), 2.28 (s, 3H), 1.97 (ddt, *J*=13.0, 8.9, 5.4, 2H), 1.64 – 1.52 (m, 2H), 1.52 (s, 3H), 1.30 – 1.24 (m, 1H), 0.96 (ddd, *J*=25.0, 15.1, 11.7, 2H), 0.83 (dd, *J*=21.7, 6.7, 6H), 0.78 (d, *J*=6.9, 2H), 0.75 – 0.66 (m, 1H), 0.32 (q, *J*=12.0, 1H) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 146.71, 144.38, 140.65, 128.65, 127.44, 126.31, 50.45, 47.32, 41.46, 36.40, 34.61, 31.59, 30.88, 25.93, 23.52, 22.15, 20.99, 16.54, 16.24 ppm (other signals not observed or detected). HRMS (ESI): *m*/*z* calcd for $C_{36}H_{44}N_1O_2$: 522.336654 $[M+H]^+$; found: 522.336670

7.7.3 Synthesis of Tetrahydroindacene-Derived Thiol

Synthesis of 4.79



8-methyl-3,5-diphenyl-1,2,3,5,6,7-hexahydro-s-indacene-4-thiol

Leuckart thiophenol synthesis: A 50 ml round-bottom flask was charged with (*rac*)-(8-methyl-3,5-diphenyl-1,2,3,5,6,7-hexahydro-s-indacen-4-amine (1.81 g, 5.34 mmol, 1 equiv.), suspended in a mixture of acetonitrile (20 ml) and aqeuous HCl (6 M, 8.9 ml, 53.4 mmol, 10 equiv.) and placed in an ice-bath. $NaNO_2$ (737 mg, 10.7 mmol. 2 equiv.) was placed in a 10 ml Vial and dissolved in water (ca. 1 ml). This solution was dropwise added to the reaction mixture via Pasteur-pipette to form a dark brownish solution. The solution was stirred 25 minutes in the ice bath.

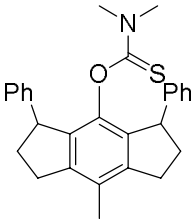
Meanwhile a 250 ml round-bottom flask was charged with sodium potassium ethyl xanthate (1.71 g, 10.7 mmol, 2 equiv.) and dissolved in aqueous sat. $NaHCO_3$ (ca. 100 ml) and heated to 80°C (oil bath.)

The diazonium solution was poured into the pre-heated solution of aqueous ethyl xanthate and stirred 1 h at 80°C resulting in the formation of an emulsion. After cooling to r.t., the reaction mixture was poured into a separation funnel and the aqueous phase extracted with DCM (5 x 50 ml). The combined DCM extract was dried over sodium sulfate and concentrated to dryness. The residue was re-dissolved in Et_2O (50 ml), followed by careful addition of $LiAlH_4$ (1 M in Et_2O, 10.5 ml, 10.5 mmol, 10.5 equiv.) and the reaction stirred o.n. at r.t.. The next day the reaction was carefully quenched with water to form a suspension. Addition of aqueous HCl (6 M) results in the formation of an emulsion, which was transferred to a separation funnel. The aqueous phase was extracted with DCM (4 x 40 ml). The combined organic phase was dried over sodium sulfate, concentrated to dryness and the crude product further purified by FCC (hexanes/Et_2O 9:1) to elute the desired product (91%, 1.73 g, 4.86 mmol).

^{1}H NMR (501 MHz, CD_2Cl_2) δ = 7.28 – 7.23 (m, 4H), 7.21 – 7.12 (m, 2H), 7.03 (ddd, *J*=8.0, 4.7, 1.5, 4H), 4.39 (ddd, *J*=9.5, 6.6, 2.9, 2H), 3.02 (dq, *J*=17.3, 8.8, 2H), 2.97 – 2.85 (m, 2H), 2.80 (s, 1H), 2.70 – 2.57 (m, 2H), 2.28 (s, 3H), 2.12 – 2.01 (m, 2H) ppm. Additional spectroscopical data can be found in the thiol synthesis via Newman–Kwart strategy.

Newman–Kwart strategy:

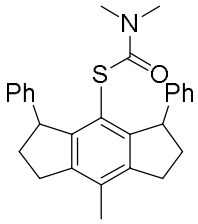
Synthesis of 4.76



O-(8-methyl-3,5-diphenyl-1,2,3,5,6,7-hexahydro-s-indacen-4-yl) dimethylcarbamothioate

Step 1: A 100 ml round-bottom flask connected with an argon adapter was charged with 8-methyl-3,5-diphenyl-1,2,3,5,6,7-hexahydro-s-indacen-4-ol (mixture of racemate & meso (1:1) 635 mg,1.87 mmol, 1 equiv.) and dissolved in DMF (25 ml). NaH (dispersion in mineral oil, 60%, 89.5 mg, 3.7 mmol, 2 equiv.) was added portion-wise. Dimethylthiocarbamoyl chloride (461 mg, 3.73 mmol, 2 equiv.) was added in one portion and the reaction was stirred o.n. at 60°C. The next day the reaction mixture was poured into water (50 ml) and the resulting brown suspension was extracted with EtOAc (4 x 40 ml). The combined organic phase was washed with brine, dried over sodium sulfate and concentrated to dryness. The crude product was purified by FCC (hexanes/EtOAc 9:1) to elute the desired product as diastereomeric mixture.

Synthesis of 4.77

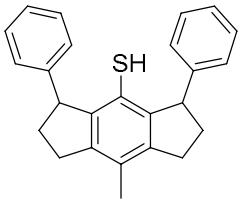


S-(8-methyl-3,5-diphenyl-1,2,3,5,6,7-hexahydro-s-indacen-4-yl) dimethylcarbamothioate

Step 2: the diastereomeric mixture of **Step 1** was placed in a 20 ml microwave vial, sealed and heated in a pre-heated metal block at 260°C for 2 h. After cooling to r.t., the reaction mixture was purified by FCC (hexanes/EtOAc 4:1) to elute the desired racemic product (Note: the diastereoisomers were easily separable by FCC). The first eluted spot represented the desired racemic product (28 %, 230 mg, 1.86 mmol)

Spectroscopic data of racemic product: ^{1}H NMR (501 MHz, CD_2Cl_2) δ = 7.21 – 7.14 (m, 4H), 7.14 – 7.07 (m, 2H), 7.00 – 6.94 (m, 4H), 4.49 (dd, *J*=9.1, 3.3, 2H), 3.05 (dt, *J*=16.6, 8.4, 3H), 2.98 – 2.92 (m, 1H), 2.63 (dq, *J*=12.8, 9.0, 2H), 2.55 (s, 6H), 2.33 (s, 3H), 2.04 (ddt, *J*=12.9, 8.2, 3.3, 2H). HPLC: (IA-3, *n*-heptane/*i*-PrOH 98:2, 1 ml/min 297 K, $t_{R(enantiomer\ 1)}$ = 5.55 min (50%), $t_{R(enantiomer\ 2)}$ = 7.11 min (50%),

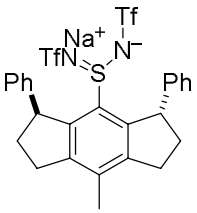
Synthesis of 4.79



8-methyl-3,5-diphenyl-1,2,3,5,6,7-hexahydro-s-indacene-4-thiol

Step 3: A 25 ml round bottom flask was charged with racemic S-aryl thiocarabamte (product from **Step 2**) (35 mg, 81.9 µmol, 1 equiv.) and dissolved in Et_2O (5 ml). $LiAlH_4$ (1 M in Et_2O, 0.7 ml, 0.7 mmol, 8.5 equiv.) was added and the reaction stirred o.n. at r.t.. The next day the reaction was carefully quenched with water followed by subsequent addition of aqueous HCl (6M, 5 ml). The emulsion was transferred to a separation funnel and the aqueous phase was extracted with DCM (5 x 5 ml). The combined organic phase was dried over sodium sulfate, concentrated to dryness and purified by FCC (hexane/Et_2O, 9:1) to elute the desired product (82%, 24 mg, 81.9 µmol)

^{1}H NMR (501 MHz, CD_2Cl_2) δ = 7.29 – 7.23 (m, 4H), 7.22 – 7.15 (m, 2H), 7.04 – 7.00 (m, 4H), 4.38 (dd, *J*=9.3, 2.8, 2H), 3.01 (dd, *J*=16.2, 7.9, 2H), 2.91 (ddd, *J*=16.1, 9.1, 3.0, 2H), 2.64 (ddq, *J*=12.9, 10.9, 9.1, 2H), 2.54 (s, 1H), 2.27 (s, 3H), 2.11 – 1.97 (m, 2H) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 145.66, 143.97, 143.03, 128.93, 128.23, 128.08, 127.93, 127.25, 126.55, 51.66, 36.06, 30.73, 16.19 ppm. HRMS (ESI): *m*/*z* calcd for $C_{25}H_{23}S_1$: 355.152597 [*M*–H]$^-$; found: 355.152370



A 50 ml round-bottom flask connected with an argon adapter was charged with KOtBu (326 mg, 2.91 mmol, 10.0 equiv.) and dissolved in THF (10 ml). Iodine (740 mg, 2.92 mmol, 10.4 equiv.) was added portion-wise to form a dark purple suspension. Meanwhile a 10 ml vial connected to an argon adapter was charged with 8-methyl-3,5-diphenyl-1,2,3,5,6,7-hexahydro-s-indacen-4-thiol (100 mg, 280 µmol, 1 equiv), $TfNH_2$ (167 mg, 1.12 mmol, 4 equiv.) and dissolved in MeCN (5 ml). This solution was added to the reaction mixture and the reaction mixture stirred o.n. at 50°C. The next day the reaction was quenched with sat. aqueous $Na_2S_2O_3$ to form a slightly yellowish emulsion, which was transferred to a separation funnel and diluted with additional Et_2O (50 ml). The organic phase was washed with sat. $NaHCO_3$ (2 x 30 ml), brine, dried over sodium sulfate and concentrated to dryness. The crude product was purified by FCC (gradient: 1. DCM to elute side products 2. DCM/EtOAc (4:1) to elute the desired product as yellowish solid. NMR analysis of the purified product indicates several broad signals due to a lack of solubility in commonly employed deuterated NMR solvents. NMR data from the crude reaction mixture are given:

^{1}H NMR (501 MHz, CD_2Cl_2) δ = 7.29 – 6.67 (m, 10H), 5.38 (dd, *J*=5.0, 2.2, 2H), 3.04 – 2.76 (m, 2H), 2.36 – 2.24 (s, 3H), 2.04 – 1.86 (m, 2H), 1.80 – 1.68 (m, 4H). ^{19}F NMR (471 MHz, CD_2Cl_2) δ = – 79.04 (s, CF_3), – 79.16 (s, CF_3) ppm. HRMS (ESI): *m*/*z* calcd for $C_{27}H_{23}N_2O_4S_3F_6$: 649.072971 [*M*–H]$^-$; found: 649.073220

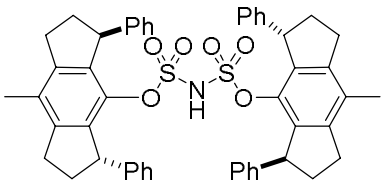
Additional LC-MS and chiral HPLC studies were performed.

Achiral LC-MS: 50 mm Eclipse Plus C18 1.8 µm, 30 mm i.D. USDEA 04251 (MeCN/0.1 TFA-Gradient 50 % C-5´-80% B; 0.5 ml/min, 14.3 MPa, 308 K; UV 220nm): $t_{R(\text{minor side product})}$ 3.88 min (10.6 %); $t_{R(\text{meso product})}$ = 4.93 min (4.4%); $t_{R(\text{racemate})}$ = 5 min (82 %).

Chiral HPLC = 150 mm Chiralpak IC-3, 4.6 mm i.D., MeCN/0.1 TFA = 45:55, 1 ml/min, 21.1 MPa, 298 K, 220 nm: $t_{R(\text{first enantiomer+meso})}$ = 11.2 min (47%), $t_{R(\text{second enantiomer})}$ 12.3 min (42%) (Note: remaining 11% refer to the side product).

Synthesis of 6.2

O,O-bis((3S,5S)-8-methyl-3,5-diphenyl-1,2,3,5,6,7-hexahydro-s-indacen-4-yl) iminodisulfate



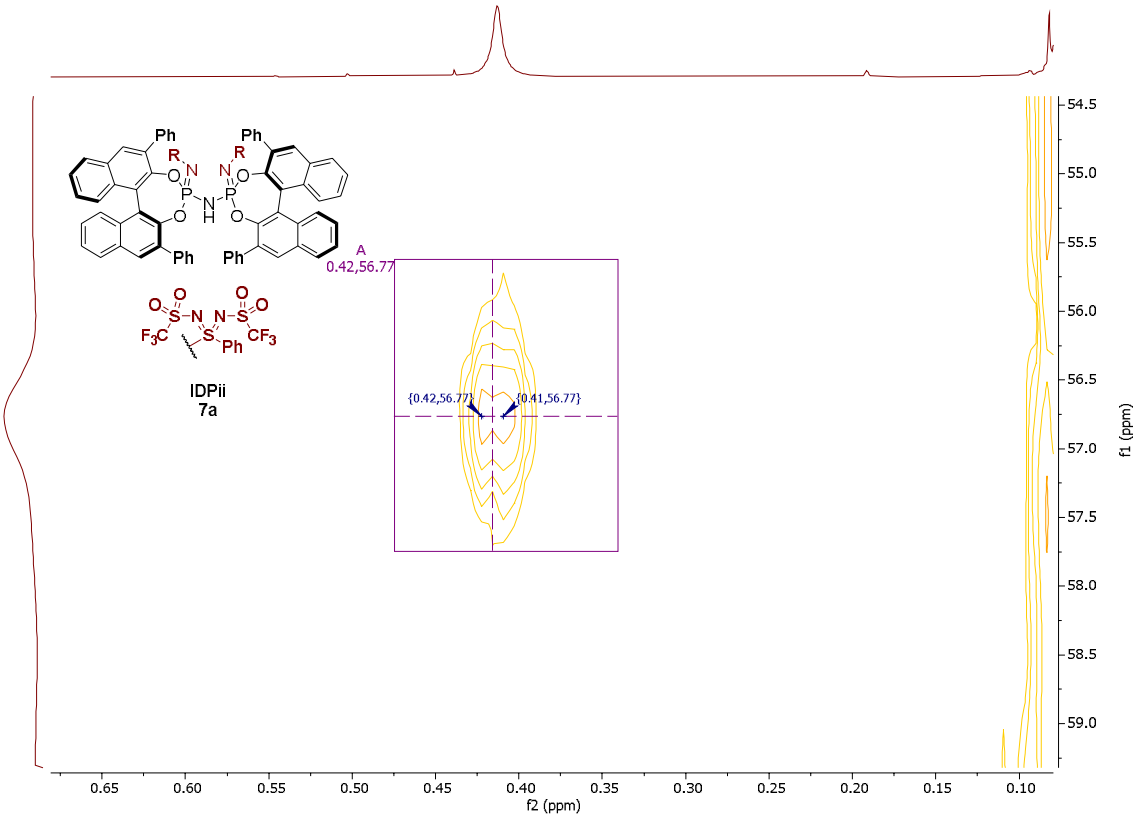
A 5 ml flame dried Schlenk-tube was charged with enantioenriched 3S,5S)-8-methyl-3,5-diphenyl-1,2,3,5,6,7-hexahydro-s-indacen-4-ol (70 mg, 206 µmol, 2.1 equiv.) and dissolved in toluene (1 ml). NaH (60% dispersion oil, 35 mg, 875 µmol, 8.9 equiv.) was added. Meanwhile a second 5 ml Schlenk-tube was charged with imidodi(sulfurylchloride) (21 mg, 98.1 µmol, 1 equiv.) and dissolved in toluene (0.5 ml). The solution of imidodi(sulfurylchloride) was transferred to the reaction mixture via an PE-tube and argon overpressure. During this transfer the reaction mixture turned into a dark purple suspension, which turned dark black within minutes. The reaction was stirred o.n. at r.t., poured into sat. $NaHCO_3$ (5 ml) and extracted with DCM (5 x 5 ml). The combined organic phase was dried over sodium sulfate, concentrated to dryness and the crude product purified by FCC (Biotage gradient DCM / EtOAc 1:0 up to 1:4) to elute the desired product as a salt, which was acidified by emulation in DCM HCl (6 M, 1:1, 10 ml). The emulsion was thoroughly stirred for 30 minutes, the DCM phase isolated, concentrated to dryness and additionally dried o.n. in h.v.. to furnish the desired product in acidic form (73%, 84.5 mg, 103 µmol).

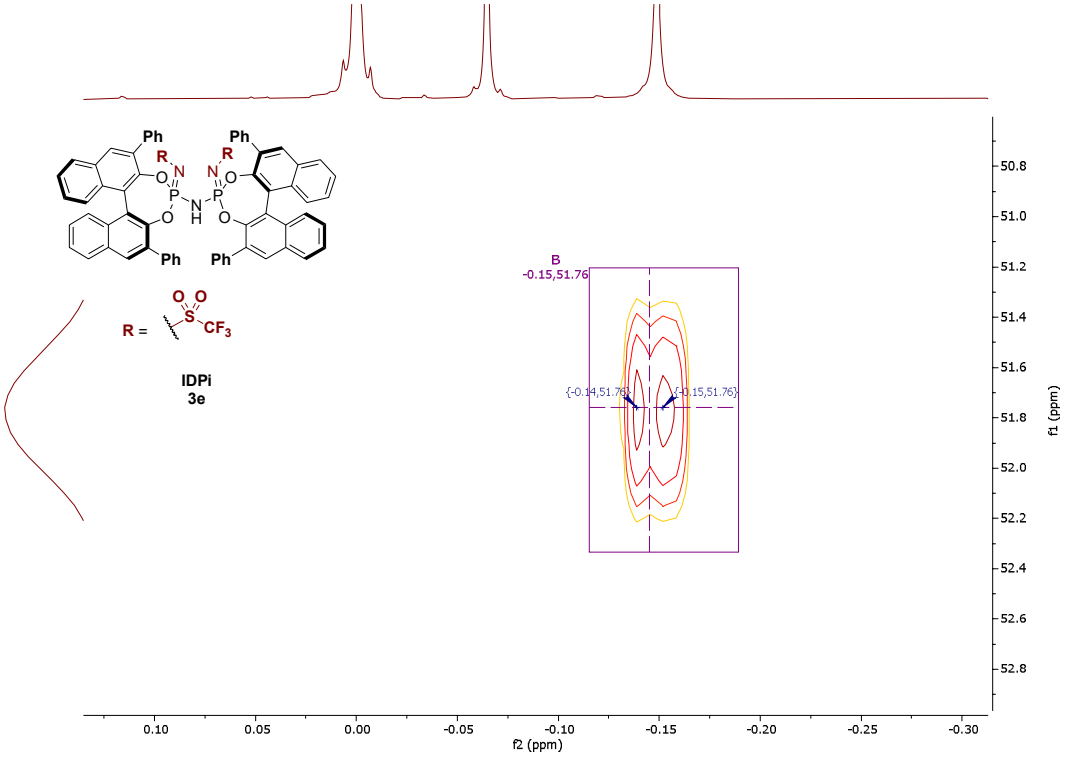
^{1}H NMR (501 MHz, CD_2Cl_2) δ = 7.19 – 7.08 (m, 12H), 6.88 – 6.83 (m, 8H), 4.52 (dd, *J*=8.7, 2.2, 4H), 2.96 – 2.80 (m, 8H), 2.57 (ddt, *J*=12.8, 9.9, 8.8, 4H), 2.26 (s, 6H), 1.99 (ddt, *J*=12.6, 7.6, 2.5, 4H), 1.52 (sbr, 1H) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 146.71, 145.00, 142.69, 136.59, 130.04, 128.83, 127.53, 126.72, 48.99, 36.80, 30.23, 16.34 ppm. HRMS (ESI): *m*/*z* calcd for $C_{50}H_{46}N_1O_6S_2$: 820.277209 $[M–H]^-$; found: 820.278330

7.8 Lewis Acidity Measurement

7.8.1 ^{29}Si NMR Studies

NMR tubes were charged with the corresponding catalyst, IDPi, IDPii, TfOH, Tf_2NH (0.01 mmol each), evacuated and purged with argon. Meanwhile a stock solution of allyltrimethylsilane (137 mg, 1.2 mmol) in anhydrous CD_2Cl_2 (3 ml) was prepared. 500 µl of this stock solution was added to each (four different with the corresponding catalyst) NMR tube, sealed and analyzed by NMR. ^{29}Si-NMR shifts were measured by ^{1}H-^{29}Si-HMBC




Ph
R
N
O
P
N
H
O
Ph
R =
O O
S
CF3
IDPi
3e
B
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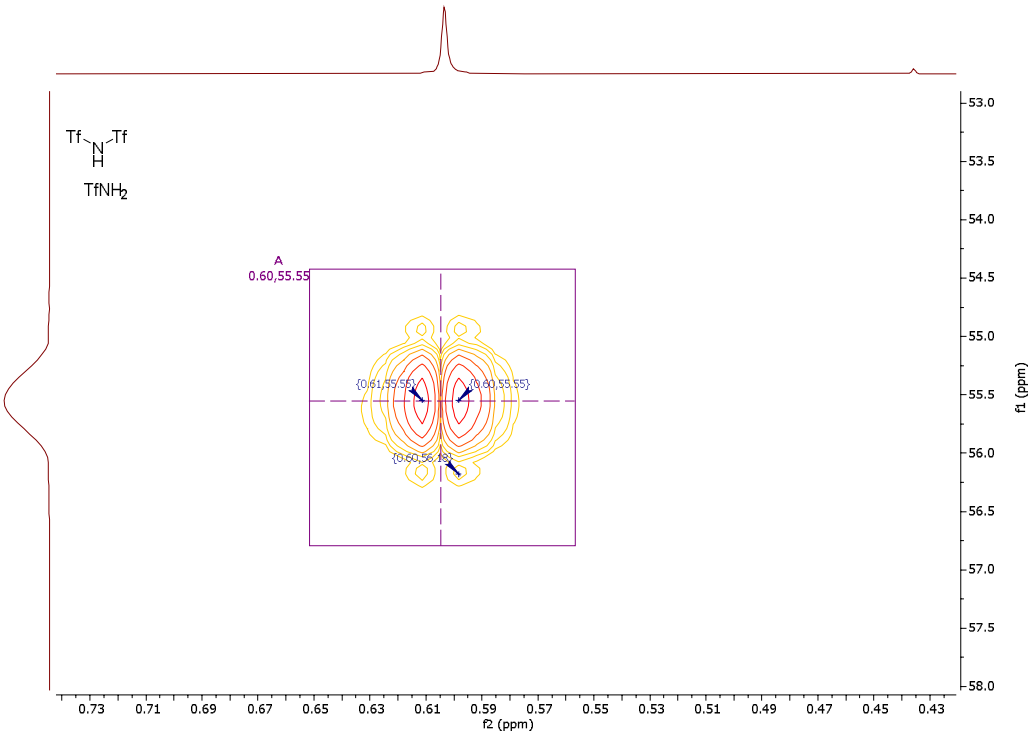
{-0.14,51.76}
{-0.15,51.76}
f1 (ppm)
f2 (ppm)


Tf
N
H
Tf
TfNH2
A
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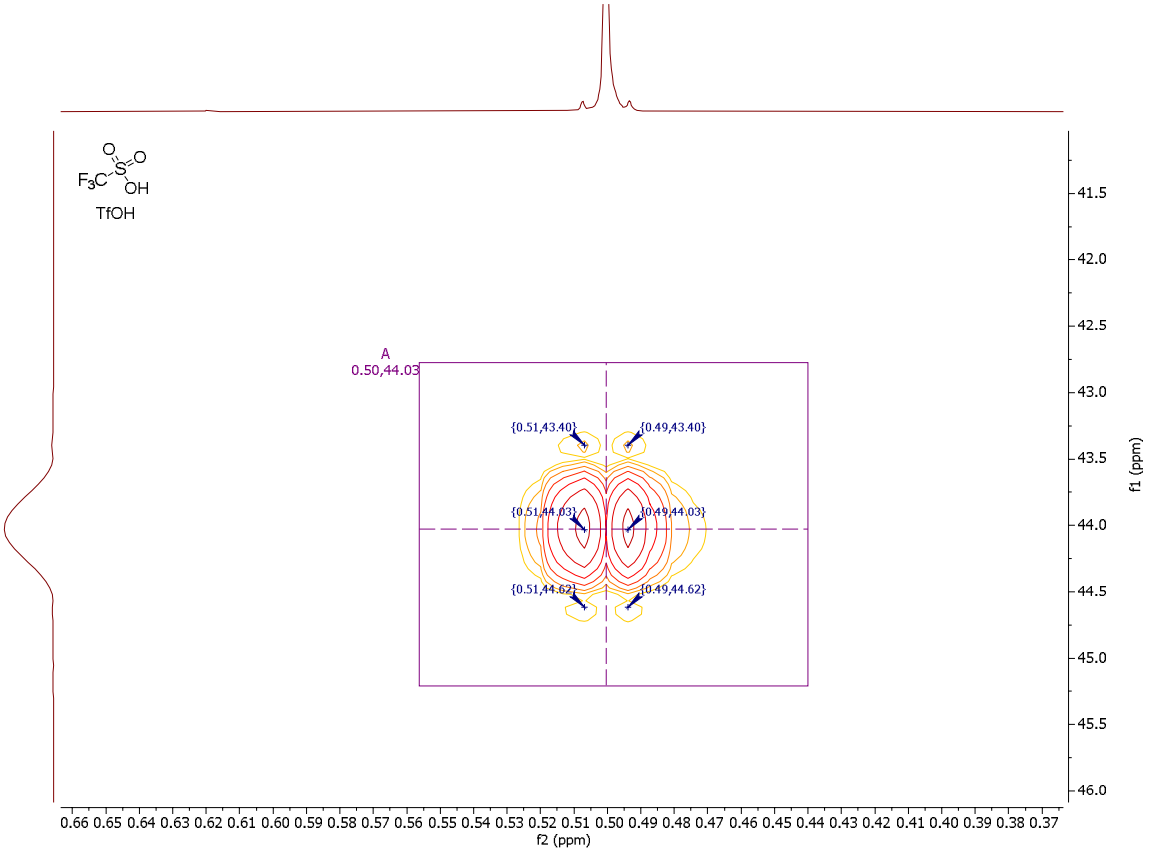
f1 (ppm)
f2 (ppm)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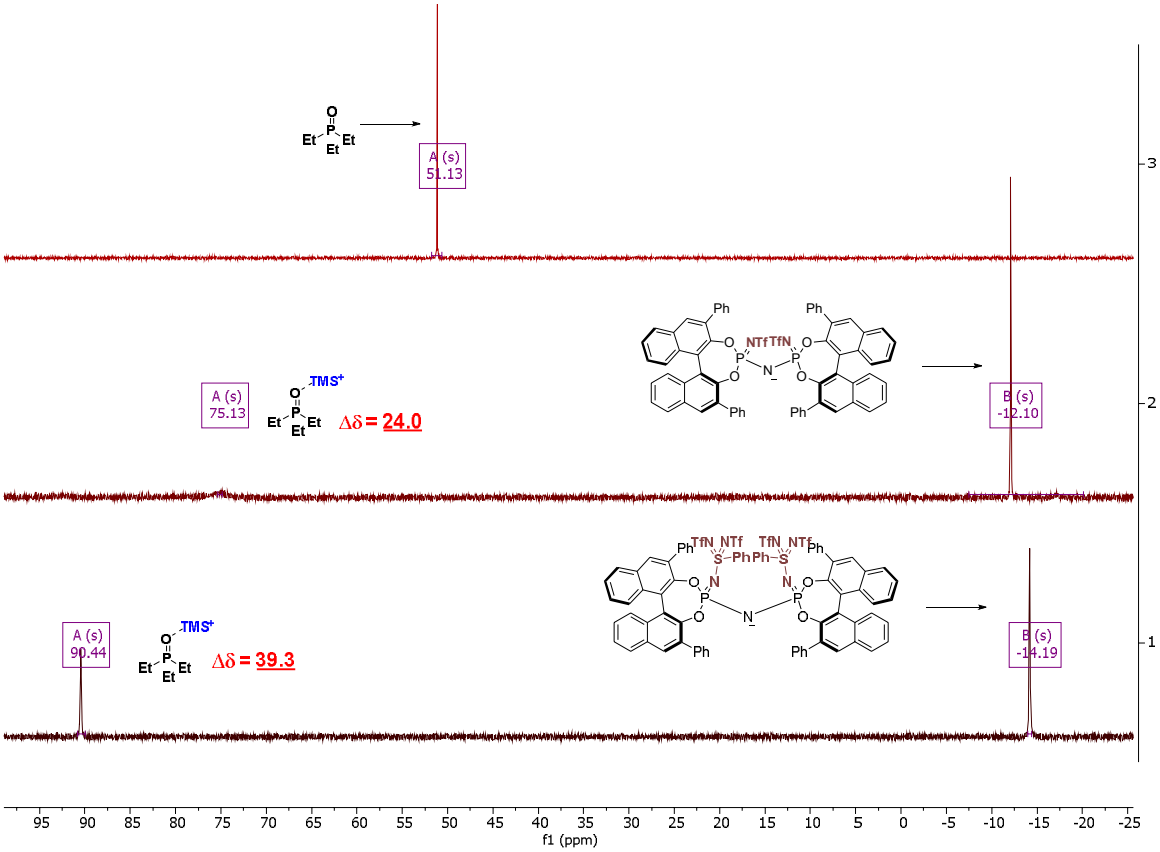
f1 (ppm)
f2 (ppm)

7.8.1 Gutmann-Beckett Studies

Two NMR tubes were charged with **IDPii-2** (17.8 mg, 10 µmol) or **IDPi-10** (12.7 mg, 10 µmol), dissolved in 200 µl anhydrous CD_2Cl_2 followed by subsequent addition of allyltrimethylsilane (8 µl, 50 µmol). A stock solution containing triethylphosphinoxide $Et_3P{=}O$ in anhydrous CD_2Cl_2 was prepared (3.8 mg, in 900 µl CD_2Cl_2). Of this stock solution, 300 µl were transferred to each NMR-tube containing the catalyst, respectively (1.27 mg, $Et_3P{=}O$, 9.5 µmol were transferred to each NMR-sample). Meanwhile, $Et_3P{=}O$ was measured by NMR. The NMR samples containing the Lewis acid and Et_3PO were NMR-spectroscopically analyzed after 30 minutes.



7.9 Supplementary Data

7.9.1 X-ray Data for Compound SA-2

Table 1. Crystal data and structure refinement.

Identification code	12241	
Empirical formula	$C_8 H_7 F_6 N_3 O_4 S_3$	
Color	colourless	
Formula weight	419.35 g·mol^{-1}	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	*P*-1, (No. 2)	
Unit cell dimensions	a = 10.4242(7) Å	α= 88.846(2)°.
	b = 11.0369(7) Å	β= 73.910(2)°.
	c = 13.8643(9) Å	γ = 86.750(2)°.
Volume	1530.13(17) Å^3	
Z	4	
Density (calculated)	1.820 Mg·m^{-3}	
Absorption coefficient	0.573 mm^{-1}	
F(000)	840 e	
Crystal size	0.114 x 0.111 x 0.110 mm^3	
θ range for data collection	1.529 to 33.869°.	
Index ranges	-16 ≤ h ≤ 16, -17≤ k ≤ 17, -20 ≤ l ≤ 21	
Reflections collected	57397	
Independent reflections	12191 [R_{int} = 0.0262]	
Reflections with I>2σ(I)	10697	
Completeness to θ = 25.242°	99.5 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.95756 and 0.94732	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12191 / 0 / 494	
Goodness-of-fit on F^2	1.123	
Final R indices [I>2σ(I)]	R_1 = 0.0408	wR^2 = 0.1032
R indices (all data)	R_1 = 0.0471	wR^2 = 0.1059
Extinction coefficient	n/a	
Largest diff. peak and hole	0.700 and -0.552 e·Å^{-3}	

Table 2. Bond lengths [Å] and angles [°].

C(1)-C(6)	1.388(2)	C(1)-C(2)	1.395(2)
C(1)-S(1)	1.7561(15)	C(2)-C(3)	1.386(2)
C(2)-H(2)	0.9500	C(3)-C(4)	1.391(3)
C(3)-H(3)	0.9500	C(4)-C(5)	1.384(3)
C(4)-H(4)	0.9500	C(5)-C(6)	1.386(2)
C(5)-H(5)	0.9500	C(6)-H(6)	0.9500
C(7)-F(4)	1.317(3)	C(7)-F(5)	1.327(3)
C(7)-F(6)	1.324(2)	C(7)-S(3)	1.836(2)
C(8)-F(2)	1.319(3)	C(8)-F(3)	1.324(3)
C(8)-F(1)	1.830(2)	C(8)-S(2)	1.386(2)
C(11)-C(16)	1.386(2)	C(11)-C(12)	1.7579(16)
C(11)-S(4)	1.386(3)	C(12)-C(13)	1.385(3)
C(12)-H(12)	0.9500	C(13)-C(14)	1.373(3)
C(13)-H(13)	0.9500	C(14)-C(15)	1.388(2)
C(14)-H(14)	0.9500	C(15)-C(16)	1.308(3)
C(15)-H(15)	0.9500	C(16)-H(16)	0.9500
C(17)-F(9)	1.323(3)	C(17)-F(8)	1.325(3)
C(17)-S(5)	1.843(2)	N(1)-S(1)	1.5939(14)
N(1)-H(1A)	0.85(3)	N(1)-H(1B)	0.84(3)
N(2)-S(1)	1.5521(13)	N(2)-S(2)	1.6003(14)
N(3)-S(1)	1.5608(13)	N(3)-S(3)	1.5892(14)
N(4)-S(4)	1.5897(14)	N(4)-H(4A)	0.85(3)
N(4)-H(4B)	0.77(3)	N(5)-S(4)	1.5452(14)
N(5)-S(5)	1.5995(14)	N(6)-S(6)	1.5676(14)
N(6)-S(6)	1.5832(14)	O(1)-S(2)	1.4243(13)
O(2)-S(2)	1.4220(13)	O(3)-S(3)	1.4233(13)
O(4)-S(3)	1.4253(13)	O(5)-S(5)	1.4217(14)
O(6)-S(5)	1.4319(13)	O(8)-S(6)	1.4210(13)	S(6)-

O(7A)	1.388(5)	S(6)-O(7B)	
1.486(5)	S(6)-C(18B)	1.759(5)	S(6)-
C(18A)	1.899(6)	C(18A)-F(12A)	
1.306(7)	C(18A)-F(10A)	1.316(6)	
C(18A)-F(11A)	1.338(7)	C(18B)-F(12B)	
1.306(8)	C(18B)-F(10B)	1.323(7)	C(18B)-
F(11B)	1.330(7)		
C(6)-C(1)-C(2)	122.78(15)	C(6)-C(1)-S(1)	
120.85(12)	C(2)-C(1)-S(1)	116.36(12)	C(3)-
C(2)-C(1)	117.86(16)	C(3)-C(2)-H(2)	121.1
C(1)-C(2)-H(2)	121.1	C(2)-C(3)-C(4)	
120.30(16)	C(2)-C(3)-H(3)	119.9	C(4)-
C(3)-H(3)	119.9	C(5)-C(4)-C(3)	
120.59(16)	C(5)-C(4)-H(4)	119.7	C(3)-
C(4)-H(4)	119.7	C(4)-C(5)-C(6)	
120.48(17)	C(4)-C(5)-H(5)	119.8	C(6)-
C(5)-H(5)	119.8	C(5)-C(6)-C(1)	
117.99(16)	C(5)-C(6)-H(6)	121.0	C(1)-
C(6)-H(6)	121.0	F(4)-C(7)-F(5)	
109.08(19)	F(4)-C(7)-F(6)	108.96(19)	F(5)-
C(7)-F(6)	109.1(2)	F(4)-C(7)-S(3)	
110.98(18)	F(5)-C(7)-S(3)	108.38(14)	F(6)-
C(7)-S(3)	110.31(15)	F(2)-C(8)-F(3)	
108.98(19)	F(2)-C(8)-F(1)	108.6(2)	F(3)-
C(8)-F(1)	109.5(2)	F(2)-C(8)-S(2)	
110.17(18)	F(3)-C(8)-S(2)	108.48(16)	F(1)-
C(8)-S(2)	111.12(15)	C(16)-C(11)-C(12)	
122.11(15)	C(16)-C(11)-S(4)	121.22(12)	C(12)-
C(11)-S(4)	116.67(12)	C(13)-C(12)-C(11)	
118.81(17)	C(13)-C(12)-H(12)	120.6	C(11)-
C(12)-H(12)	120.6	C(14)-C(13)-C(12)	
119.84(17)	C(14)-C(13)-H(13)	120.1	C(12)-
C(13)-H(13)	120.1	C(15)-C(14)-C(13)	
120.36(17)	C(15)-C(14)-H(14)	119.8	C(13)-
C(14)-H(14)	119.8	C(14)-C(15)-C(16)	
121.12(17)	C(14)-C(15)-H(15)	119.4	C(16)-
C(15)-H(15)	119.4	C(11)-C(16)-C(15)	

117.73(16)	C(11)-C(16)-H(16)	121.1	C(15)-
C(16)-H(16)	121.1	F(9)-C(17)-F(7)	
109.6(2)	F(9)-C(17)-F(8)	109.6(2)	F(7)-
C(17)-F(8)	108.71(19)	F(9)-C(17)-S(5)	
110.38(15)	F(7)-C(17)-S(5)	110.15(16)	F(8)-
C(17)-S(5)	108.44(17)	S(1)-N(1)-H(1A)	
112.2(18)	S(1)-N(1)-H(1B)	113.6(19)	H(1A)-
N(1)-H(1B)	116(3)	S(1)-N(2)-S(2)	
123.10(8)	S(1)-N(3)-S(3)	123.06(9)	S(4)-
N(4)-H(4A)	112.6(18)	S(4)-N(4)-H(4B)	114(2)
H(4A)-N(4)-H(4B)	119(3)	S(4)-N(5)-S(5)	
123.65(9)	S(4)-N(6)-S(6)	123.91(9)	N(2)-
S(1)-N(3)	121.77(7)	N(2)-S(1)-N(1)	
111.03(8)	N(3)-S(1)-N(1)	99.93(7)	N(2)-
S(1)-C(1)	102.13(7)	N(3)-S(1)-C(1)	
110.73(8)	N(1)-S(1)-C(1)	111.47(7)	O(2)-
S(2)-O(1)	120.20(9)	O(2)-S(2)-N(2)	
114.46(8)	O(1)-S(2)-N(2)	107.74(8)	O(2)-
S(2)-C(8)	106.27(11)	O(1)-S(2)-C(8)	
104.24(10)	N(2)-S(2)-C(8)	101.79(9)	O(3)-
S(3)-O(4)	119.67(9)	O(3)-S(3)-N(3)	
107.70(8)	O(4)-S(3)-N(3)	114.26(7)	O(3)-
S(3)-C(7)	104.44(10)	O(4)-S(3)-C(7)	
104.93(11)	N(3)-S(3)-C(7)	104.19(9)	N(5)-
S(4)-N(6)	120.04(8)	N(5)-S(4)-N(4)	
113.06(8)	N(6)-S(4)-N(4)	99.46(8)	N(5)-
S(4)-C(11)	101.87(7)	N(6)-S(4)-C(11)	
113.37(8)	N(4)-S(4)-C(11)	109.12(8)	O(5)-
S(5)-O(6)	119.81(9)	O(5)-S(5)-N(5)	
115.11(8)	O(6)-S(5)-N(5)	108.04(7)	O(5)-
S(5)-C(17)	107.30(11)	O(6)-S(5)-C(17)	
104.46(10)	N(5)-S(5)-C(17)	99.60(9)	O(7A)-
S(6)-O(8)	128.1(2)	O(8)-S(6)-O(7B)	
110.63(19)	O(7A)-S(6)-N(6)	113.7(2)	O(8)-
S(6)-N(6)	108.91(8)	O(7B)-S(6)-N(6)	
113.94(19)	O(8)-S(6)-C(18B)	107.9(2)	O(7B)-
S(6)-C(18B)	106.0(3)	N(6)-S(6)-C(18B)	
109.3(2)	O(7A)-S(6)-C(18A)	104.2(3)	O(8)-

S(6)-C(18A)	98.73(17)	N(6)-S(6)-C(18A)	96.7(2)
F(12A)-C(18A)-F(10A)	110.0(6)	F(12A)-C(18A)-F(11A)	
108.8(5)	F(10A)-C(18A)-F(11A)	109.3(5)	F(12A)-
C(18A)-S(6)	111.0(4)	F(10A)-C(18A)-S(6)	
111.5(4)	F(11A)-C(18A)-S(6)	106.2(4)	F(12B)-
C(18B)-F(10B)	108.8(6)	F(12B)-C(18B)-F(11B)	
109.2(5)	F(10B)-C(18B)-F(11B)	108.6(6)	F(12B)-
C(18B)-S(6)	109.8(5)	F(10B)-C(18B)-S(6)	
110.5(4)	F(11B)-C(18B)-S(6)	110.0(4)	

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7.9.2 X-Ray Data for IDPii-1

Table 1. Crystal data and structure refinement.

Identification code	12107	
Empirical formula	$C_{61}H_{44}Cl_2F_{12}N_7NaO_{12}P_2S_6$	
Color	colourless	
Formula weight	1643.22 g · mol^{-1}	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**$P2_1$, (no. 4)**	
Unit cell dimensions	a = 11.5416(3) Å	α= 90°.
	b = 19.2739(15) Å	β= 104.682(5)°.
	c = 15.6880(12) Å	γ = 90°.
Volume	3375.9(4) $Å^3$	
Z	2	
Density (calculated)	1.617 Mg · m^{-3}	
Absorption coefficient	0.436 mm^{-1}	
F(000)	1668 e	
Crystal size	0.27 x 0.18 x 0.08 mm^3	
θ range for data collection	2.736 to 33.158°.	
Index ranges	$-17 \le h \le 17$, $-29 \le k \le 29$, $-24 \le l \le 24$	
Reflections collected	67058	
Independent reflections	25595 [R_{int} = 0.0297]	
Reflections with I>2σ(I)	23795	
Completeness to θ = 25.242°	99.7 %	
Absorption correction	Gaussian	

Max. and min. transmission	0.98 and 0.93	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	25595 / 1 / 932	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2σ(I)]	R_1 = 0.0305	wR^2 = 0.0673
R indices (all data)	R_1 = 0.0361	wR^2 = 0.0704
Absolute structure parameter	-0.018(12)	
Largest diff. peak and hole	0.4 and -0.4 e · $Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°].

S(1)-N(2)	1.5520(16)	S(1)-N(3)	1.5610(18)
S(1)-N(4)	1.7691(19)	S(1)-C(23)	1.4353(16)
S(2)-O(5)	1.4314(17)	S(2)-O(6)	1.5827(18)
S(2)-C(29)	1.832(2)	S(3)-O(3)	1.4253(16)
S(3)-O(4)	1.4362(15)	S(3)-N(4)	1.5891(18)
S(3)-C(30)	1.833(2)	S(4)-N(5)	1.5408(17)
S(4)-N(6)	1.5754(17)	S(4)-N(7)	1.5702(17)
S(4)-C(53)	1.7683(19)	S(5)-O(11)	1.4378(15)
S(5)-O(12)	1.4226(16)	S(5)-N(6)	1.5884(17)
S(5)-C(59)	1.837(2)	S(6)-O(9)	1.4362(15)
S(6)-O(10)	1.4228(16)	S(6)-N(7)	1.5765(17)
S(6)-C(60)	1.838(2)	P(1)-O(1)	1.5734(14)
P(1)-O(2)	1.5804(14)	P(1)-N(1)	1.5440(17)
P(1)-N(2)	1.6128(16)	P(2)-O(7)	1.5787(14)
P(2)-O(8)	1.5779(14)	P(2)-N(1)	1.5408(17)
P(2)-N(5)	1.6058(17)	Na(1)-O(4)	2.3018(17)
Na(1)-O(5)	2.2804(18)	Na(1)-O(9)	2.2764(17)
Na(1)-O(11)	2.3039(17)	Na(1)-N(1)	2.878(2)
Na(1)-N(2)	2.7627(18)	Na(1)-N(5)	2.9363(19)
F(1)-C(29)	1.322(3)	F(2)-C(29)	1.320(3)
F(3)-C(29)	1.317(3)	F(4)-C(30)	1.319(3)
F(5)-C(30)	1.331(3)	F(6)-C(30)	1.326(3)
F(7)-C(59)	1.320(3)	F(8)-C(59)	1.326(3)
F(9)-C(59)	1.317(3)	F(10)-C(60)	1.326(3)
F(11)-C(60)	1.327(3)	F(12)-C(60)	1.320(2)	O(1)-

C(1)	1.413(2)	O(2)-C(11)	
1.415(2)	O(7)-C(31)	1.419(2)	O(8)-
C(41)	1.413(2)	C(1)-C(2)	
1.414(3)	C(1)-C(10)	1.374(3)	C(2)-
C(3)	1.371(3)	C(2)-C(21)	
1.506(3)	C(3)-C(4)	1.417(3)	C(4)-
C(5)	1.419(3)	C(4)-C(9)	
1.423(3)	C(5)-C(6)	1.364(3)	C(6)-
C(7)	1.407(3)	C(7)-C(8)	
1.368(3)	C(8)-C(9)	1.416(3)	C(9)-
C(10)	1.434(3)	C(10)-C(20)	
1.491(3)	C(11)-C(12)	1.420(3)	C(11)-
C(20)	1.370(3)	C(12)-C(13)	
1.369(3)	C(12)-C(22)	1.507(3)	C(13)-
C(14)	1.418(3)	C(14)-C(15)	
1.421(3)	C(14)-C(19)	1.422(3)	C(15)-
C(16)	1.368(3)	C(16)-C(17)	
1.418(3)	C(17)-C(18)	1.374(3)	C(18)-
C(19)	1.419(3)	C(19)-C(20)	
1.437(3)	C(23)-C(24)	1.391(3)	C(23)-
C(28)	1.384(3)	C(24)-C(25)	
1.387(3)	C(25)-C(26)	1.386(4)	C(26)-
C(27)	1.388(4)	C(27)-C(28)	
1.396(3)	C(31)-C(32)	1.413(3)	C(31)-
C(40)	1.379(3)	C(32)-C(33)	
1.372(3)	C(32)-C(52)	1.506(3)	C(33)-
C(34)	1.418(3)	C(34)-C(35)	
1.421(3)	C(34)-C(39)	1.424(3)	C(35)-
C(36)	1.367(3)	C(36)-C(37)	
1.413(4)	C(37)-C(38)	1.372(3)	C(38)-
C(39)	1.416(3)	C(39)-C(40)	
1.437(3)	C(40)-C(50)	1.490(3)	C(41)-
C(42)	1.411(3)	C(41)-C(50)	
1.377(3)	C(42)-C(43)	1.373(3)	C(42)-
C(51)	1.502(3)	C(43)-C(44)	
1.415(3)	C(44)-C(45)	1.420(3)	C(44)-
C(49)	1.425(3)	C(45)-C(46)	
1.365(3)	C(46)-C(47)	1.411(3)	C(47)-

C(48) 1.375(3) C(48)-C(49) 1.415(3) C(49)-C(50) 1.433(3) C(53)-C(54) 1.386(3) C(53)-C(58) 1.390(3) C(54)-C(55) 1.393(3) C(55)-C(56) 1.384(3) C(56)-C(57) 1.389(3) C(57)-C(58) 1.388(3) Cl(1)-C(99) 1.758(3) Cl(2)-C(99) 1.762(3)

N(2)-S(1)-N(3) 108.42(9) N(2)-S(1)-N(4) 116.85(9) N(2)-S(1)-C(23) 111.10(9) N(3)-S(1)-N(4) 110.92(10) N(3)-S(1)-C(23) 107.68(9) N(4)-S(1)-C(23) 101.41(9) O(5)-S(2)-N(3) 114.09(10) O(5)-S(2)-C(29) 104.74(10) O(6)-S(2)-O(5) 117.52(11) O(6)-S(2)-N(3) 114.49(10) O(6)-S(2)-C(29) 106.04(10) N(3)-S(2)-C(29) 96.75(10) O(3)-S(3)-O(4) 118.92(10) O(3)-S(3)-N(4) 109.67(10) O(3)-S(3)-C(30) 104.01(10) O(4)-S(3)-N(4) 114.37(9) O(4)-S(3)-C(30) 105.12(11) N(4)-S(3)-C(30) 102.74(10) N(5)-S(4)-N(6) 115.82(9) N(5)-S(4)-N(7) 111.53(9) N(5)-S(4)-C(53) 112.02(9) N(6)-S(4)-C(53) 101.03(9) N(7)-S(4)-N(6) 111.60(9) N(7)-S(4)-C(53) 103.73(9) O(11)-S(5)-N(6) 114.15(9) O(11)-S(5)-C(59) 104.66(10) O(12)-S(5)-O(11) 119.26(10) O(12)-S(5)-N(6) 109.92(10) O(12)-S(5)-C(59) 104.02(10) N(6)-S(5)-C(59) 102.73(9) O(9)-S(6)-N(7) 115.25(9) O(9)-S(6)-C(60) 104.39(10) O(10)-S(6)-O(9) 119.23(10) O(10)-S(6)-N(7) 108.43(9) O(10)-S(6)-C(60) 104.20(10) N(7)-S(6)-C(60) 103.39(9) O(1)-P(1)-O(2) 106.92(7) O(1)-P(1)-N(2) 109.93(8) O(2)-P(1)-N(2) 105.89(8) N(1)-P(1)-O(1) 105.57(8) N(1)-P(1)-O(2) 116.66(9) N(1)-P(1)-N(2) 111.72(9) O(7)-

P(2)-N(5) 107.85(8) O(8)-P(2)-O(7) 106.50(7) O(8)-P(2)-N(5) 106.14(8) N(1)-P(2)-O(7) 107.52(8) N(1)-P(2)-O(8) 115.38(9) N(1)-P(2)-N(5) 113.06(9) O(4)-Na(1)-O(11) 163.45(7) O(4)-Na(1)-N(1) 80.76(6) O(4)-Na(1)-N(2) 73.88(6) O(4)-Na(1)-N(5) 92.59(6) O(5)-Na(1)-O(4) 98.88(7) O(5)-Na(1)-O(11) 93.16(6) O(5)-Na(1)-N(1) 128.93(6) O(5)-Na(1)-N(2) 75.49(6) O(5)-Na(1)-N(5) 168.51(6) O(9)-Na(1)-O(4) 94.02(6) O(9)-Na(1)-O(5) 111.85(7) O(9)-Na(1)-O(11) 91.99(6) O(9)-Na(1)-N(1) 119.15(6) O(9)-Na(1)-N(2) 166.99(7) O(9)-Na(1)-N(5) 66.26(5) O(11)-Na(1)-N(1) 82.85(6) O(11)-Na(1)-N(2) 98.44(6) O(11)-Na(1)-N(5) 75.76(5) N(1)-Na(1)-N(5) 53.66(5) N(2)-Na(1)-N(1) 55.14(5) N(2)-Na(1)-N(5) 108.75(5) C(1)-O(1)-P(1) 117.08(12) C(11)-O(2)-P(1) 121.01(12) S(3)-O(4)-Na(1) 146.51(10) S(2)-O(5)-Na(1) 128.18(10) C(31)-O(7)-P(2) 115.55(11) C(41)-O(8)-P(2) 119.53(12) S(6)-O(9)-Na(1) 134.17(10) S(5)-O(11)-Na(1) 143.30(10) P(1)-N(1)-Na(1) 94.63(8) P(2)-N(1)-P(1) 165.52(13) P(2)-N(1)-Na(1) 96.18(8) S(1)-N(2)-P(1) 128.07(11) S(1)-N(2)-Na(1) 109.07(8) P(1)-N(2)-Na(1) 97.44(7) S(1)-N(3)-S(2) 124.90(11) S(1)-N(4)-S(3) 120.74(11) S(4)-N(5)-P(2) 128.28(11) S(4)-N(5)-Na(1) 105.51(8) P(2)-N(5)-Na(1) 92.51(7) S(4)-N(6)-S(5) 121.28(10) S(4)-N(7)-S(6) 129.71(11) O(1)-C(1)-C(2) 116.88(16) C(10)-C(1)-O(1) 118.24(16) C(10)-C(1)-C(2) 124.87(17) C(1)-C(2)-C(21) 121.09(17) C(3)-C(2)-C(1) 116.63(17) C(3)-C(2)-C(21) 122.25(18) C(2)-C(3)-C(4) 121.95(18) C(3)-C(4)-C(5) 120.94(19) C(3)-C(4)-C(9) 119.91(17) C(5)-

C(4)-C(9)	119.04(18)	C(6)-C(5)-C(4)	
120.9(2)	C(5)-C(6)-C(7)	119.97(19)	C(8)-
C(7)-C(6)	120.7(2)	C(7)-C(8)-C(9)	
120.8(2)	C(4)-C(9)-C(10)	118.57(17)	C(8)-
C(9)-C(4)	118.48(17)	C(8)-C(9)-C(10)	
122.85(18)	C(1)-C(10)-C(9)	117.65(17)	C(1)-
C(10)-C(20)	121.34(17)	C(9)-C(10)-C(20)	
120.90(17)	O(2)-C(11)-C(12)	116.04(16)	C(20)-
C(11)-O(2)	118.97(17)	C(20)-C(11)-C(12)	
124.81(17)	C(11)-C(12)-C(22)	121.06(17)	C(13)-
C(12)-C(11)	116.67(18)	C(13)-C(12)-C(22)	
122.24(18)	C(12)-C(13)-C(14)	121.82(18)	C(13)-
C(14)-C(15)	121.00(19)	C(13)-C(14)-C(19)	
119.97(18)	C(15)-C(14)-C(19)	119.02(19)	C(16)-
C(15)-C(14)	120.9(2)	C(15)-C(16)-C(17)	
120.1(2)	C(18)-C(17)-C(16)	120.3(2)	C(17)-
C(18)-C(19)	120.7(2)	C(14)-C(19)-C(20)	
118.57(18)	C(18)-C(19)-C(14)	118.92(18)	C(18)-
C(19)-C(20)	122.50(18)	C(11)-C(20)-C(10)	
121.22(17)	C(11)-C(20)-C(19)	117.55(17)	C(19)-
C(20)-C(10)	121.18(17)	C(24)-C(23)-S(1)	
115.77(16)	C(28)-C(23)-S(1)	121.97(17)	C(28)-
C(23)-C(24)	122.25(19)	C(25)-C(24)-C(23)	
118.5(2)	C(26)-C(25)-C(24)	120.4(2)	C(25)-
C(26)-C(27)	120.2(2)	C(26)-C(27)-C(28)	
120.5(2)	C(23)-C(28)-C(27)	118.2(2)	F(1)-
C(29)-S(2)	107.97(15)	F(2)-C(29)-S(2)	
110.74(15)	F(2)-C(29)-F(1)	108.68(19)	F(3)-
C(29)-S(2)	110.64(16)	F(3)-C(29)-F(1)	
109.20(19)	F(3)-C(29)-F(2)	109.56(19)	F(4)-
C(30)-S(3)	111.75(16)	F(4)-C(30)-F(5)	
109.2(2)	F(4)-C(30)-F(6)	109.32(19)	F(5)-
C(30)-S(3)	107.90(15)	F(6)-C(30)-S(3)	
109.93(16)	F(6)-C(30)-F(5)	108.64(19)	C(32)-
C(31)-O(7)	116.41(16)	C(40)-C(31)-O(7)	
118.07(16)	C(40)-C(31)-C(32)	125.51(17)	C(31)-
C(32)-C(52)	121.00(17)	C(33)-C(32)-C(31)	
116.19(18)	C(33)-C(32)-C(52)	122.82(18)	C(32)-

C(33)-C(34) 122.07(18) C(33)-C(34)-C(35) 120.48(19) C(33)-C(34)-C(39) 119.31(19) C(35)-C(34)-C(39) 120.6(2) C(35)-C(36)-C(37) 120.6(2) C(36)-C(35)-C(34) 120.2(2) C(38)-C(37)-C(36) 120.7(2) C(34)-C(39)-C(40) 118.64(18) C(37)-C(38)-C(39) 118.47(17) C(38)-C(39)-C(34) 122.77(18) C(31)-C(40)-C(39) 120.10(17) C(38)-C(39)-C(40) 117.32(17) C(31)-C(40)-C(50) 122.52(17) C(42)-C(41)-O(8) 118.37(17) C(39)-C(40)-C(50) 116.62(17) C(50)-C(41)-O(8) 124.96(18) C(41)-C(42)-C(51) 116.73(18) C(50)-C(41)-C(42) 120.65(18) C(43)-C(42)-C(41) 122.61(19) C(42)-C(43)-C(44) 121.13(19) C(43)-C(42)-C(51) 121.81(19) C(43)-C(44)-C(45) 120.04(18) C(45)-C(44)-C(49) 121.2(2) C(43)-C(44)-C(49) 118.8(2) C(46)-C(45)-C(44) 120.0(2) C(48)-C(47)-C(46) 120.9(2) C(45)-C(46)-C(47) 120.4(2) C(47)-C(48)-C(49) 118.61(18) C(48)-C(49)-C(44) 122.57(18) C(44)-C(49)-C(50) 118.77(18) C(48)-C(49)-C(50) 120.78(17) C(41)-C(50)-C(49) 121.68(17) C(41)-C(50)-C(40) 117.52(18) C(49)-C(50)-C(40) 118.70(15) C(54)-C(53)-C(58) 119.00(15) C(54)-C(53)-S(4) 122.04(18) C(58)-C(53)-S(4) 118.58(19) C(56)-C(55)-C(54) 120.5(2) C(53)-C(54)-C(55) 120.1(2) C(55)-C(56)-C(57) 120.2(2) C(57)-C(58)-C(53) 111.33(15) C(58)-C(57)-C(56) 118.5(2) F(7)-C(59)-S(5) 107.92(19) F(8)-C(59)-S(5) 110.66(15) F(7)-C(59)-F(8) 109.54(15) F(9)-C(59)-S(5) 109.13(19) F(9)-C(59)-F(8) 109.94(15) F(9)-C(59)-F(7) 108.17(19) F(10)-C(60)-S(6) 108.50(18) F(11)-C(60)-S(6) 109.44(16) F(10)-C(60)-F(11) 111.35(14) F(12)-C(60)-S(6) 108.78(18) F(12)-C(60)-F(11) 112.27(15) F(12)-C(60)-F(10) 108.77(19) Cl(1)-C(99)-Cl(2)

7.9.3 X-Ray Data for IDPii-2

Table 1. Crystal data and structure refinement.

Identification code	12144	
Empirical formula	C_{89} H_{72} Cl_2 F_{12} N_8 O_{12} P_2 S_6	
Color	colourless	
Formula weight	1998.74 g·mol^{-1}	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$, (No. 19)	
Unit cell dimensions	a = 13.169(2) Å	α= 90°.
	b = 15.101(3) Å	β= 90°.
	c = 44.396(7) Å	γ = 90°.
Volume	8829(3) Å^3	
Z	4	
Density (calculated)	1.504 Mg·m^{-3}	
Absorption coefficient	0.344 mm^{-1}	
F(000)	4104 e	
Crystal size	0.109 x 0.083 x 0.032 mm^3	
θ range for data collection	1.613 to 33.578°.	
Index ranges	$-20 \le h \le 20$, $-23 \le k \le 23$, $-69 \le l \le 68$	
Reflections collected	264447	
Independent reflections	34630 [R_{int} = 0.0663]	
Reflections with I>2σ(I)	30152	
Completeness to θ = 25.242°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.98987 and 0.96681	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	34630 / 6 / 1214	
Goodness-of-fit on F^2	1.134	
Final R indices [I>2σ(I)]	R_1 = 0.0549	wR^2 = 0.1251
R indices (all data)	R_1 = 0.0674	wR^2 = 0.1301
Absolute structure parameter	0.021(10)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.750 and -0.607 e·Å^{-3}	

Table 2. Bond lengths [Å] and angles [°].

C(1)-C(2)	1.374(4)	C(1)-C(16)	1.429(4)
C(1)-C(17)	1.412(3)	C(2)-O(1)	1.415(4)
C(2)-C(3)	1.388(4)	C(3)-C(4)	1.387(4)
C(3)-C(10)	1.492(4)	C(4)-C(5)	1.391(5)
C(4)-C(9)	1.397(4)	C(5)-C(6)	1.394(5)
C(5)-H(5)	0.9500	C(6)-C(7)	1.387(5)
C(6)-H(6)	0.9500	C(7)-C(8)	1.389(5)
C(7)-H(7)	0.9500	C(8)-C(9)	1.418(5)
C(8)-H(8)	0.9500	C(9)-H(9)	0.9500
C(10)-C(11)	1.415(4)	C(10)-H(10)	0.9500
C(11)-C(12)	1.364(5)	C(11)-C(16)	1.431(4)
C(12)-C(13)	1.411(5)	C(12)-H(12)	0.9500
C(13)-C(14)	1.374(4)	C(13)-H(13)	0.9500
C(14)-C(15)	1.425(4)	C(14)-H(14)	0.9500
C(15)-H(15)	0.9500	C(15)-C(16)	1.433(4)
C(17)-C(18)	1.372(4)	C(17)-C(32)	1.424(4)
C(18)-O(2)	1.418(4)	C(18)-C(19)	1.387(4)
C(19)-C(20)	1.397(4)	C(19)-C(26)	1.492(4)
C(20)-C(21)	1.410(4)	C(20)-C(25)	1.398(4)
C(21)-H(21)	0.9500	C(21)-C(22)	1.384(5)
C(22)-H(22)	0.9500	C(22)-C(23)	1.394(6)
C(23)-H(23)	0.9500	C(23)-C(24)	1.383(4)
C(24)-H(24)	0.9500	C(24)-C(25)	1.411(4)
C(25)-H(25)	0.9500	C(26)-C(27)	1.424(4)
C(26)-H(26)	0.9500	C(27)-C(28)	1.406(5)
C(27)-C(32)	1.416(4)	C(28)-H(28)	0.9500
C(28)-C(29)	1.367(5)	C(29)-H(29)	0.9500
C(29)-C(30)	1.371(4)	C(30)-H(30)	0.9500
C(30)-C(31)	1.406(5)		

C(31)-C(32)	1.424(4)	C(31)-H(31)	0.9500
C(33)-C(34)	1.376(4)	C(33)-C(48)	
1.438(4)	C(33)-C(49)	1.485(4)	C(34)-
C(35)	1.414(4)	C(34)-O(7)	
1.415(3)	C(35)-C(42)	1.379(4)	C(35)-
C(36)	1.484(4)	C(36)-C(41)	
1.398(4)	C(36)-C(37)	1.398(4)	C(37)-
C(38)	1.388(5)	C(37)-H(37)	0.9500
C(38)-C(39)	1.383(6)	C(38)-H(38)	0.9500
C(39)-C(40)	1.390(5)	C(39)-H(39)	0.9500
C(40)-C(41)	1.386(5)	C(40)-H(40)	0.9500
C(41)-H(41)	0.9500	C(42)-C(43)	
1.414(4)	C(42)-H(42)	0.9500	C(43)-
C(44)	1.419(4)	C(43)-C(48)	
1.423(4)	C(44)-C(45)	1.373(4)	C(44)-
H(44)	0.9500	C(45)-C(46)	
1.414(5)	C(45)-H(45)	0.9500	C(46)-
C(47)	1.372(4)	C(46)-H(46)	0.9500
C(47)-C(48)	1.422(4)	C(47)-H(47)	0.9500
C(49)-C(50)	1.378(4)	C(49)-C(64)	
1.442(4)	C(50)-O(8)	1.402(3)	C(50)-
C(51)	1.419(4)	C(51)-C(58)	
1.380(4)	C(51)-C(52)	1.479(4)	C(52)-
C(53)	1.396(4)	C(52)-C(57)	
1.407(4)	C(53)-C(54)	1.391(4)	C(53)-
H(53)	0.9500	C(54)-C(55)	
1.381(5)	C(54)-H(54)	0.9500	C(55)-
C(56)	1.397(5)	C(55)-H(55)	0.9500
C(56)-C(57)	1.386(4)	C(56)-H(56)	0.9500
C(57)-H(57)	0.9500	C(58)-C(59)	
1.410(4)	C(58)-H(58)	0.9500	C(59)-
C(64)	1.416(4)	C(59)-C(60)	
1.427(4)	C(60)-C(61)	1.365(4)	C(60)-
H(60)	0.9500	C(61)-C(62)	
1.413(5)	C(61)-H(61)	0.9500	C(62)-
C(63)	1.370(4)	C(62)-H(62)	0.9500
C(63)-C(64)	1.418(4)	C(63)-H(63)	0.9500
C(65)-C(66)	1.389(4)	C(65)-C(70)	

1.391(4)	C(65)-S(1)	1.769(3)	C(66)-
C(67)	1.380(4)	C(66)-H(66)	0.9500
C(67)-C(68)	1.397(5)	C(67)-H(67)	0.9500
C(68)-C(69)	1.388(5)	C(68)-H(68)	0.9500
C(69)-C(70)	1.382(4)	C(69)-H(69)	0.9500
C(70)-H(70)	0.9500	C(71)-C(72)	
1.379(4)	C(71)-C(76)	1.392(4)	C(71)-
S(4)	1.767(3)	C(72)-C(73)	
1.391(4)	C(72)-H(72)	0.9500	C(73)-
C(74)	1.384(5)	C(73)-H(73)	0.9500
C(74)-C(75)	1.388(5)	C(74)-H(74)	0.9500
C(75)-C(76)	1.389(4)	C(75)-H(75)	0.9500
C(76)-H(76)	0.9500	C(77)-F(2)	
1.314(4)	C(77)-F(3)	1.323(5)	C(77)-
F(1)	1.343(4)	C(77)-S(2)	
1.841(4)	C(78)-F(5)	1.308(7)	C(78)-
F(6)	1.327(6)	C(78)-F(4)	
1.327(5)	C(78)-S(3)	1.844(4)	C(79)-
F(8)	1.322(4)	C(79)-F(9)	
1.328(4)	C(79)-F(7)	1.340(4)	C(79)-
S(5)	1.836(3)	C(81)-N(8)	
1.515(5)	C(81)-C(82)	1.522(5)	C(81)-
H(81A)	0.9900	C(81)-H(81B)	0.9900
C(82)-H(82A)	0.9800	C(82)-H(82B)	0.9800
C(82)-H(82C)	0.9800	C(83)-N(8)	
1.509(5)	C(83)-C(85)	1.535(7)	C(83)-
C(84)	1.546(6)	C(83)-H(83)	1.0000
C(84)-H(84A)	0.9800	C(84)-H(84B)	0.9800
C(84)-H(84C)	0.9800	C(85)-H(85A)	0.9800
C(85)-H(85B)	0.9800	C(85)-H(85C)	0.9800
C(86)-C(87)	1.521(6)	C(86)-C(88)	
1.524(6)	C(86)-N(8)	1.541(5)	C(86)-
H(86)	1.0000	C(87)-H(87A)	0.9800
C(87)-H(87B)	0.9800	C(87)-H(87C)	0.9800
C(88)-H(88A)	0.9800	C(88)-H(88B)	0.9800
C(88)-H(88C)	0.9800	C(89)-Cl(2)	
1.753(5)	C(89)-Cl(1)	1.761(5)	C(89)-
H(89A)	0.9900	C(89)-H(89B)	0.9900

N(1)-P(2)	1.539(3)	N(1)-P(1)	
1.545(2)	N(2)-S(1)	1.531(2)	N(2)-
P(1)	1.583(2)	N(3)-S(1)	
1.573(3)	N(3)-S(2)	1.582(2)	N(4)-
S(1)	1.567(3)	N(4)-S(3)	
1.587(3)	N(5)-S(4)	1.530(3)	N(5)-
P(2)	1.588(3)	N(6)-S(5)	
1.567(3)	N(6)-S(4)	1.583(3)	N(7)-
S(4)	1.551(3)	N(7)-S(6A)	
1.582(3)	N(7)-S(6B)	1.666(4)	N(8)-
H(8A)	1.0000	O(1)-P(1)	
1.591(2)	O(2)-P(1)	1.593(2)	O(3)-
S(2)	1.431(3)	O(4)-S(2)	
1.432(3)	O(5)-S(3)	1.422(3)	O(6)-
S(3)	1.424(3)	O(7)-P(2)	
1.588(2)	O(8)-P(2)	1.584(2)	O(9)-
S(5)	1.442(3)	O(10)-S(5)	
1.426(2)	C(80A)-F(10A)	1.309(7)	
C(80A)-F(11A)	1.321(10)	C(80A)-F(12A)	
1.333(7)	C(80A)-S(6A)	1.831(6)	
O(11A)-S(6A)	1.438(7)	O(12A)-S(6A)	
1.426(6)	C(80B)-F(10B)	1.276(17)	C(80B)-
F(11B)	1.334(16)	C(80B)-F(12B)	
1.339(16)	C(80B)-S(6B)	1.819(14)	
O(11B)-S(6B)	1.40(2)	O(12B)-S(6B)	
1.411(12)			

C(2)-C(1)-C(16)	118.5(3)	C(2)-C(1)-C(17)	
119.9(2)	C(16)-C(1)-C(17)	121.6(3)	C(1)-
C(2)-O(1)	117.6(2)	C(1)-C(2)-C(3)	
124.7(3)	O(1)-C(2)-C(3)	117.8(3)	C(10)-
C(3)-C(2)	116.0(3)	C(10)-C(3)-C(4)	
121.0(3)	C(2)-C(3)-C(4)	123.0(3)	C(9)-
C(4)-C(5)	119.1(3)	C(9)-C(4)-C(3)	
119.4(3)	C(5)-C(4)-C(3)	121.4(3)	C(6)-
C(5)-C(4)	120.4(3)	C(6)-C(5)-H(5)	119.8
C(4)-C(5)-H(5)	119.8	C(5)-C(6)-C(7)	
120.0(3)	C(5)-C(6)-H(6)	120.0	C(7)-

C(6)-H(6) 120.0 C(8)-C(7)-C(6) 119.5(3) C(8)-C(7)-H(7) 120.3 C(6)-C(7)-H(7) 120.3 C(7)-C(8)-C(9) 120.4(3) C(7)-C(8)-H(8) 119.8 C(9)-C(8)-H(8) 120.6(3) C(4)-C(9)-H(9) 119.7 C(8)-C(9)-H(9) 121.8(3) C(3)-C(10)-H(10) 119.1 C(11)-C(10)-H(10) 120.4(3) C(16)-C(11)-C(12) 119.2(3) C(10)-C(11)-C(12) 120.2(3) C(13)-C(12)-H(12) 119.9 C(11)-C(12)-H(12) 120.7(3) C(12)-C(13)-H(13) 119.7 C(14)-C(13)-H(13) 120.7(3) C(15)-C(14)-H(14) 119.6 C(13)-C(14)-H(14) 120.0(3) C(14)-C(15)-H(15) 120.0 C(16)-C(15)-H(15) 119.2(3) C(11)-C(16)-C(1) 118.3(3) C(15)-C(16)-C(1) 122.4(3) C(18)-C(17)-C(32) 118.8(3) C(18)-C(17)-C(1) 120.8(3) C(32)-C(17)-C(1) 120.4(2) C(17)-C(18)-O(2) 118.4(2) C(17)-C(18)-C(19) 123.5(3) O(2)-C(18)-C(19) 118.1(2) C(26)-C(19)-C(18) 117.0(3) C(26)-C(19)-C(20) 119.1(3) C(18)-C(19)-C(20) 123.9(3) C(21)-C(20)-C(25) 119.0(3) C(21)-C(20)-C(19) 123.0(3) C(25)-C(20)-C(19) 117.9(3) C(20)-C(21)-C(22) 120.0(3) C(20)-C(21)-H(21) 120.0 C(22)-C(21)-H(21) 120.0 C(23)-C(22)-C(21) 120.4(3) C(23)-C(22)-H(22) 119.8 C(21)-C(22)-H(22) 119.8 C(22)-C(23)-C(24) 119.9(3) C(22)-C(23)-H(23) 120.1 C(24)-C(23)-H(23) 120.1 C(25)-C(24)-C(23) 120.2(3) C(25)-C(24)-H(24) 119.9 C(23)-C(24)-H(24) 119.9 C(24)-C(25)-C(20) 120.4(3) C(24)-C(25)-H(25) 119.8 C(20)-

C(25)-H(25)	119.8	C(19)-C(26)-C(27)	
122.0(3)	C(19)-C(26)-H(26)	119.0	C(27)-
C(26)-H(26)	119.0	C(26)-C(27)-C(32)	
119.7(3)	C(26)-C(27)-C(28)	120.7(3)	C(32)-
C(27)-C(28)	119.6(3)	C(29)-C(28)-C(27)	
120.4(3)	C(29)-C(28)-H(28)	119.8	C(27)-
C(28)-H(28)	119.8	C(28)-C(29)-C(30)	
120.4(3)	C(28)-C(29)-H(29)	119.8	C(30)-
C(29)-H(29)	119.8	C(31)-C(30)-C(29)	
120.4(3)	C(31)-C(30)-H(30)	119.8	C(29)-
C(30)-H(30)	119.8	C(30)-C(31)-C(32)	
120.9(3)	C(30)-C(31)-H(31)	119.6	C(32)-
C(31)-H(31)	119.6	C(27)-C(32)-C(31)	
118.2(3)	C(27)-C(32)-C(17)	118.9(3)	C(31)-
C(32)-C(17)	122.9(3)	C(34)-C(33)-C(48)	
118.0(3)	C(34)-C(33)-C(49)	120.8(2)	C(48)-
C(33)-C(49)	121.3(3)	C(33)-C(34)-C(35)	
124.4(2)	C(33)-C(34)-O(7)	117.5(2)	C(35)-
C(34)-O(7)	118.1(2)	C(42)-C(35)-C(34)	
116.8(3)	C(42)-C(35)-C(36)	119.8(3)	C(34)-
C(35)-C(36)	123.4(2)	C(41)-C(36)-C(37)	
118.6(3)	C(41)-C(36)-C(35)	119.3(3)	C(37)-
C(36)-C(35)	122.0(3)	C(38)-C(37)-C(36)	
120.1(3)	C(38)-C(37)-H(37)	119.9	C(36)-
C(37)-H(37)	119.9	C(39)-C(38)-C(37)	
120.7(3)	C(39)-C(38)-H(38)	119.7	C(37)-
C(38)-H(38)	119.7	C(38)-C(39)-C(40)	
119.8(3)	C(38)-C(39)-H(39)	120.1	C(40)-
C(39)-H(39)	120.1	C(41)-C(40)-C(39)	
119.7(3)	C(41)-C(40)-H(40)	120.1	C(39)-
C(40)-H(40)	120.1	C(40)-C(41)-C(36)	
121.0(3)	C(40)-C(41)-H(41)	119.5	C(36)-
C(41)-H(41)	119.5	C(35)-C(42)-C(43)	
122.1(3)	C(35)-C(42)-H(42)	119.0	C(43)-
C(42)-H(42)	119.0	C(42)-C(43)-C(44)	
121.0(3)	C(42)-C(43)-C(48)	119.8(3)	C(44)-
C(43)-C(48)	119.2(3)	C(45)-C(44)-C(43)	
120.5(3)	C(45)-C(44)-H(44)	119.7	C(43)-

C(44)-H(44)	119.7	C(44)-C(45)-C(46)	
120.4(3)	C(44)-C(45)-H(45)	119.8	C(46)-
C(45)-H(45)	119.8	C(47)-C(46)-C(45)	
120.3(3)	C(47)-C(46)-H(46)	119.9	C(45)-
C(46)-H(46)	119.9	C(46)-C(47)-C(48)	
120.8(3)	C(46)-C(47)-H(47)	119.6	C(48)-
C(47)-H(47)	119.6	C(47)-C(48)-C(43)	
118.7(3)	C(47)-C(48)-C(33)	122.6(3)	C(43)-
C(48)-C(33)	118.6(3)	C(50)-C(49)-C(64)	
118.3(3)	C(50)-C(49)-C(33)	120.5(3)	C(64)-
C(49)-C(33)	121.1(2)	C(49)-C(50)-O(8)	
118.2(2)	C(49)-C(50)-C(51)	123.8(3)	O(8)-
C(50)-C(51)	117.9(2)	C(58)-C(51)-C(50)	
117.0(2)	C(58)-C(51)-C(52)	119.2(2)	C(50)-
C(51)-C(52)	123.7(3)	C(53)-C(52)-C(57)	
118.6(3)	C(53)-C(52)-C(51)	122.6(3)	C(57)-
C(52)-C(51)	118.5(3)	C(54)-C(53)-C(52)	
120.5(3)	C(54)-C(53)-H(53)	119.8	C(52)-
C(53)-H(53)	119.8	C(55)-C(54)-C(53)	
120.6(3)	C(55)-C(54)-H(54)	119.7	C(53)-
C(54)-H(54)	119.7	C(54)-C(55)-C(56)	
119.6(3)	C(54)-C(55)-H(55)	120.2	C(56)-
C(55)-H(55)	120.2	C(57)-C(56)-C(55)	
120.2(3)	C(57)-C(56)-H(56)	119.9	C(55)-
C(56)-H(56)	119.9	C(56)-C(57)-C(52)	
120.4(3)	C(56)-C(57)-H(57)	119.8	C(52)-
C(57)-H(57)	119.8	C(51)-C(58)-C(59)	
121.9(3)	C(51)-C(58)-H(58)	119.0	C(59)-
C(58)-H(58)	119.0	C(58)-C(59)-C(64)	
120.3(3)	C(58)-C(59)-C(60)	120.2(3)	C(64)-
C(59)-C(60)	119.5(3)	C(61)-C(60)-C(59)	
120.4(3)	C(61)-C(60)-H(60)	119.8	C(59)-
C(60)-H(60)	119.8	C(60)-C(61)-C(62)	
120.0(3)	C(60)-C(61)-H(61)	120.0	C(62)-
C(61)-H(61)	120.0	C(63)-C(62)-C(61)	
120.6(3)	C(63)-C(62)-H(62)	119.7	C(61)-
C(62)-H(62)	119.7	C(62)-C(63)-C(64)	
120.8(3)	C(62)-C(63)-H(63)	119.6	C(64)-

C(63)-H(63) 119.6 C(59)-C(64)-C(63) 118.4(3) C(59)-C(64)-C(49) 118.4(2) C(63)-C(64)-C(49) 123.1(3) C(66)-C(65)-C(70) 121.8(3) C(66)-C(65)-S(1) 120.2(2) C(70)-C(65)-S(1) 118.0(2) C(67)-C(66)-C(65) 118.4(3) C(67)-C(66)-H(66) 120.8 C(66)-C(67)-C(68) 120.6(3) C(66)-C(67)-H(67) 119.7 C(69)-C(68)-C(67) 120.1(3) C(69)-C(68)-H(68) 119.9 C(70)-C(69)-C(68) 119.9(3) C(70)-C(69)-H(69) 120.0 C(69)-C(70)-C(65) 119.2(3) C(69)-C(70)-H(70) 120.4 C(72)-C(71)-C(76) 122.3(3) C(72)-C(71)-S(4) 117.9(2) C(71)-C(72)-C(73) 118.5(3) C(71)-C(72)-H(72) 120.8 C(74)-C(73)-C(72) 120.3(3) C(74)-C(73)-H(73) 119.9 C(73)-C(74)-C(75) 120.5(3) C(73)-C(74)-H(74) 119.8 C(74)-C(75)-C(76) 120.1(3) C(74)-C(75)-H(75) 120.0 C(75)-C(76)-C(71) 118.4(3) C(75)-C(76)-H(76) 120.8 F(2)-C(77)-F(3) 108.4(3) F(2)-C(77)-F(1) 108.0(3) F(3)-C(77)-S(2) 113.2(3) F(3)-C(77)-S(2) 108.4(3) F(5)-C(78)-F(6) 109.6(4) F(5)-C(78)-F(4) 107.8(5) F(6)-C(78)-S(3) 111.4(4) F(6)-C(78)-S(3) 109.0(3) F(8)-C(79)-F(9) 109.0(3) F(8)-C(79)-F(7) 107.8(3) F(9)-C(79)-S(5) 112.7(2) F(9)-C(79)-S(5) 111.0(2) F(7)-

C(79)-S(5)	107.7(2)	N(8)-C(81)-C(82)	
111.7(3)	N(8)-C(81)-H(81A)	109.3	C(82)-
C(81)-H(81A)	109.3	N(8)-C(81)-H(81B)	109.3
C(82)-C(81)-H(81B)	109.3	H(81A)-C(81)-H(81B)	107.9
C(81)-C(82)-H(82A)	109.5	C(81)-C(82)-H(82B)	109.5
H(82A)-C(82)-H(82B)	109.5	C(81)-C(82)-H(82C)	109.5
H(82A)-C(82)-H(82C)	109.5	H(82B)-C(82)-H(82C)	109.5
N(8)-C(83)-C(85)	107.7(3)	N(8)-C(83)-C(84)	
111.5(3)	C(85)-C(83)-C(84)	111.8(4)	N(8)-
C(83)-H(83)	108.6	C(85)-C(83)-H(83)	108.6
C(84)-C(83)-H(83)	108.6	C(83)-C(84)-H(84A)	109.5
C(83)-C(84)-H(84B)	109.5	H(84A)-C(84)-H(84B)	109.5
C(83)-C(84)-H(84C)	109.5	H(84A)-C(84)-H(84C)	109.5
H(84B)-C(84)-H(84C)	109.5	C(83)-C(85)-H(85A)	109.5
C(83)-C(85)-H(85B)	109.5	H(85A)-C(85)-H(85B)	109.5
C(83)-C(85)-H(85C)	109.5	H(85A)-C(85)-H(85C)	109.5
H(85B)-C(85)-H(85C)	109.5	C(87)-C(86)-C(88)	
112.8(4)	C(87)-C(86)-N(8)	112.1(3)	C(88)-
C(86)-N(8)	109.4(3)	C(87)-C(86)-H(86)	107.4
C(88)-C(86)-H(86)	107.4	N(8)-C(86)-H(86)	107.4
C(86)-C(87)-H(87A)	109.5	C(86)-C(87)-H(87B)	109.5
H(87A)-C(87)-H(87B)	109.5	C(86)-C(87)-H(87C)	109.5
H(87A)-C(87)-H(87C)	109.5	H(87B)-C(87)-H(87C)	109.5
C(86)-C(88)-H(88A)	109.5	C(86)-C(88)-H(88B)	109.5
H(88A)-C(88)-H(88B)	109.5	C(86)-C(88)-H(88C)	109.5
H(88A)-C(88)-H(88C)	109.5	H(88B)-C(88)-H(88C)	109.5
Cl(2)-C(89)-Cl(1)	111.2(2)	Cl(2)-C(89)-H(89A)	109.4
Cl(1)-C(89)-H(89A)	109.4	Cl(2)-C(89)-H(89B)	109.4
Cl(1)-C(89)-H(89B)	109.4	H(89A)-C(89)-H(89B)	108.0
P(2)-N(1)-P(1)	149.51(18)	S(1)-N(2)-P(1)	
132.89(17)	S(1)-N(3)-S(2)	127.92(17)	S(1)-
N(4)-S(3)	123.71(17)	S(4)-N(5)-P(2)	
132.80(18)	S(5)-N(6)-S(4)	126.90(17)	S(4)-
N(7)-S(6A)	121.63(19)	S(4)-N(7)-S(6B)	
128.6(2)	C(83)-N(8)-C(81)	111.7(3)	C(83)-
N(8)-C(86)	114.0(3)	C(81)-N(8)-C(86)	
110.7(3)	C(83)-N(8)-H(8A)	106.6	C(81)-
N(8)-H(8A)	106.6	C(86)-N(8)-H(8A)	106.6

C(2)-O(1)-P(1)	114.73(17)	C(18)-O(2)-P(1)	
122.81(18)	C(34)-O(7)-P(2)	115.81(17)	C(50)-
O(8)-P(2)	121.95(19)	N(1)-P(1)-N(2)	
114.71(14)	N(1)-P(1)-O(1)	111.12(13)	N(2)-
P(1)-O(1)	107.95(12)	N(1)-P(1)-O(2)	
105.77(13)	N(2)-P(1)-O(2)	112.65(13)	O(1)-
P(1)-O(2)	104.18(11)	N(1)-P(2)-O(8)	
107.25(13)	N(1)-P(2)-O(7)	111.18(13)	O(8)-
P(2)-O(7)	103.82(11)	N(1)-P(2)-N(5)	
114.27(15)	O(8)-P(2)-N(5)	111.54(15)	O(7)-
P(2)-N(5)	108.29(13)	N(2)-S(1)-N(4)	
114.55(15)	N(2)-S(1)-N(3)	110.61(14)	N(4)-
S(1)-N(3)	108.58(14)	N(2)-S(1)-C(65)	
104.63(14)	N(4)-S(1)-C(65)	110.72(14)	N(3)-
S(1)-C(65)	107.51(14)	O(3)-S(2)-O(4)	
119.05(16)	O(3)-S(2)-N(3)	107.89(15)	O(4)-
S(2)-N(3)	116.09(15)	O(3)-S(2)-C(77)	
103.16(17)	O(4)-S(2)-C(77)	105.13(17)	N(3)-
S(2)-C(77)	103.46(15)	O(5)-S(3)-O(6)	
119.61(17)	O(5)-S(3)-N(4)	109.72(17)	O(6)-
S(3)-N(4)	114.79(15)	O(5)-S(3)-C(78)	
104.6(2)	O(6)-S(3)-C(78)	103.2(2)	N(4)-
S(3)-C(78)	102.68(18)	N(5)-S(4)-N(7)	
115.99(18)	N(5)-S(4)-N(6)	110.47(15)	N(7)-
S(4)-N(6)	107.84(15)	N(5)-S(4)-C(71)	
104.59(14)	N(7)-S(4)-C(71)	110.09(16)	N(6)-
S(4)-C(71)	107.56(14)	O(10)-S(5)-O(9)	
117.35(15)	O(10)-S(5)-N(6)	117.28(14)	O(9)-
S(5)-N(6)	107.35(15)	O(10)-S(5)-C(79)	
105.05(16)	O(9)-S(5)-C(79)	102.32(15)	N(6)-
S(5)-C(79)	105.75(15)	F(10A)-C(80A)-F(11A)	
110.5(6)	F(10A)-C(80A)-F(12A)	107.6(6)	F(11A)-
C(80A)-F(12A)	109.0(6)	F(10A)-C(80A)-S(6A)	
111.4(5)	F(11A)-C(80A)-S(6A)	110.6(4)	F(12A)-
C(80A)-S(6A)	107.6(5)	O(12A)-S(6A)-O(11A)	
117.9(4)	O(12A)-S(6A)-N(7)	116.3(3)	
O(11A)-S(6A)-N(7)	112.7(3)	O(12A)-S(6A)-C(80A)	
106.7(4)	O(11A)-S(6A)-C(80A)	106.8(4)	N(7)-

S(6A)-C(80A)	92.4(2)	F(10B)-C(80B)-F(11B)	
110.3(12)	F(10B)-C(80B)-F(12B)	108.0(11)	F(11B)-
C(80B)-F(12B)	106.9(11)	F(10B)-C(80B)-S(6B)	
109.9(10)	F(11B)-C(80B)-S(6B)	110.1(9)	F(12B)-
C(80B)-S(6B)	111.6(10)	O(11B)-S(6B)-O(12B)	
117.7(9)	O(11B)-S(6B)-N(7)	110.9(8)	
O(12B)-S(6B)-N(7)	119.8(5)	O(11B)-S(6B)-C(80B)	
105.0(10)	O(12B)-S(6B)-C(80B)	105.9(6)	N(7)-
S(6B)-C(80B)	93.3(4)		

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7.9.4 X-Ray Data for P-15

Table 1. Crystal data and structure refinement.

Identification code	12218	
Empirical formula	$C_{184}\ H_{172}\ F_{24}\ N_{20}\ O_{28}\ P_4\ S_{12}$	
Color	colourless	
Formula weight	4076.01 $g \cdot mol^{-1}$	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$, (No. 4)	
Unit cell dimensions	a = 21.1925(9) Å	α= 90°.
	b = 21.2447(9) Å	β= 100.625(2)°.
	c = 21.9090(10) Å	γ = 90°.
Volume	9694.9(7) $Å^3$	
Z	2	
Density (calculated)	1.396 $Mg \cdot m^{-3}$	
Absorption coefficient	0.264 mm^{-1}	
F(000)	4216 e	
Crystal size	0.150 x 0.128 x 0.110 mm^3	
θ range for data collection	1.369 to 33.833°.	
Index ranges	$-33 \le h \le 33$, $-32 \le k \le 33$, $-33 \le l \le 33$	
Reflections collected	343907	
Independent reflections	76008 [R_{int} = 0.0546]	
Reflections with I>2σ(I)	55747	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.98356 and 0.97644	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	76008 / 1 / 2456	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2σ(I)]	R_1 = 0.0556	wR^2 = 0.1224
R indices (all data)	R_1 = 0.0894	wR^2 = 0.1380
Absolute structure parameter	0.04(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.066 and -0.668 $e \cdot Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°].

S(10)-N(14)	1.498(4)	S(10)-N(13)	1.570(4)
S(10)-N(15)	1.766(3)	S(10)-C(153)	1.418(4)
S(11)-O(30)	1.426(3)	S(11)-O(29)	1.565(4)
S(11)-C(159)	1.394(6)	S(11)-N(13)	1.827(5)
S(12)-O(32B)	1.433(3)	S(12)-O(32A)	1.565(3)
S(12)-O(31)	1.519(6)	S(12)-N(15)	1.703(9)
S(12)-C(1A)	1.490(3)	S(12)-C(1D)	1.992(9)
P(4)-O(26)	1.592(2)	P(4)-O(25)	1.615(3)
P(4)-N(14)	1.626(3)	P(4)-N(16)	1.311(5)
F(19)-C(159)	1.317(5)	F(20)-C(159)	1.312(6)
F(21)-C(159)	1.122(10)	F(22A)-C(1D)	1.310(10)
F(23A)-C(1D)	1.282(10)	F(23B)-C(1A)	0.811(9)
F(24B)-C(1A)	1.399(4)	N(16)-H(16A)	0.8700
N(16)-H(16B)	0.8700	O(25)-C(122)	1.381(4)
O(28)-C(132)	1.368(4)	O(32A)-H(32A)	0.8300
C(121)-C(122)	1.433(4)	C(121)-C(130)	1.487(4)
C(121)-C(131)	1.423(4)	C(122)-C(123)	1.384(4)
C(123)-C(124)	1.482(4)	C(123)-C(141)	1.413(4)
C(124)-C(125)	1.422(4)	C(124)-H(124)	0.9400
C(125)-C(126)	1.366(5)	C(125)-C(130)	1.429(4)
C(126)-C(127)	1.411(5)	C(126)-H(126)	0.9400
C(127)-C(128)	0.9400	C(127)-H(127)	1.374(5)
C(128)-C(129)	1.419(4)	C(128)-H(128)	0.9400
C(129)-H(129)	0.9400	C(131)-C(132)	1.376(4)
C(131)-C(140)	1.429(4)	C(132)-C(133)	1.429(4)
C(133)-C(134)	1.371(4)	C(133)-C(147)	1.491(4)
C(134)-C(135)	1.418(4)	C(134)-	

H(134)	0.9400	C(135)-C(136)	
1.419(4)	C(135)-C(140)	1.424(4)	C(136)-
C(137)	1.368(5)	C(136)-H(136)	0.9400
C(137)-C(138)	1.409(5)	C(137)-H(137)	0.9400
C(138)-C(139)	1.384(5)	C(138)-H(138)	0.9400
C(139)-C(140)	1.411(4)	C(139)-H(139)	0.9400
C(141)-C(146)	1.397(4)	C(141)-C(142)	
1.399(5)	C(142)-C(143)	1.389(4)	C(142)-
H(142)	0.9400	C(143)-C(144)	
1.372(6)	C(143)-H(143)	0.9400	C(144)-
C(145)	1.387(6)	C(144)-H(144)	0.9400
C(145)-C(146)	1.395(5)	C(145)-H(145)	0.9400
C(146)-H(146)	0.9400	C(147)-C(152)	
1.389(4)	C(147)-C(148)	1.393(4)	C(148)-
C(149)	1.391(5)	C(148)-H(148)	0.9400
C(149)-C(150)	1.382(5)	C(149)-H(149)	0.9400
C(150)-C(151)	1.393(5)	C(150)-H(150)	0.9400
C(151)-C(152)	1.390(5)	C(151)-H(151)	0.9400
C(152)-H(152)	0.9400	C(153)-C(158)	
1.376(6)	C(153)-C(154)	1.376(5)	C(154)-
C(155)	1.391(5)	C(154)-H(154)	0.9400
C(155)-C(156)	1.366(6)	C(155)-H(155)	0.9400
C(156)-C(157)	1.382(7)	C(156)-H(156)	0.9400
C(157)-C(158)	1.395(6)	C(157)-H(157)	0.9400
C(158)-H(158)	0.9400	S(1)-N(1)	
1.525(3)	S(1)-N(3)	1.572(3)	S(1)-
N(2)	1.581(3)	S(1)-C(33)	
1.766(3)	S(2)-O(8)	1.431(3)	S(2)-
O(7)	1.440(3)	S(2)-N(2)	
1.573(3)	S(2)-C(39)	1.808(5)	S(3)-
O(5)	1.418(3)	S(3)-O(6)	
1.425(3)	S(3)-N(3)	1.574(3)	S(3)-
C(40)	1.834(4)	P(1)-O(2)	
1.490(2)	P(1)-O(1)	1.599(2)	P(1)-
N(1)	1.625(3)	P(1)-N(4)	
1.625(3)	F(1)-C(39)	1.305(6)	F(2)-
C(39)	1.329(6)	F(3)-C(39)	
1.318(5)	F(4)-C(40)	1.315(5)	F(5)-

C(40)	1.338(4)	F(6)-C(40)	
1.332(5)	O(1)-C(2)	1.395(3)	N(4)-
H(4A)	0.8700	N(4)-H(4B)	0.8700
O(4)-C(12)	1.375(4)	C(1)-C(2)	
1.370(4)	C(1)-C(10)	1.440(4)	C(1)-
C(11)	1.495(4)	C(2)-C(3)	
1.419(4)	C(3)-C(4)	1.379(4)	C(3)-
C(21)	1.487(4)	C(4)-C(5)	
1.418(4)	C(4)-H(4)	0.9400	C(5)-
C(10)	1.420(5)	C(5)-C(6)	
1.420(4)	C(6)-C(7)	1.368(5)	C(6)-
H(6)	0.9400	C(7)-C(8)	
1.404(5)	C(7)-H(7)	0.9400	C(8)-
C(9)	1.376(5)	C(8)-H(8)	0.9400
C(9)-C(10)	1.419(4)	C(9)-H(9)	0.9400
C(11)-C(12)	1.371(4)	C(11)-C(20)	
1.431(4)	C(12)-C(13)	1.435(5)	C(13)-
C(14)	1.356(5)	C(13)-C(27)	
1.487(5)	C(14)-C(15)	1.409(5)	C(14)-
H(14)	0.9400	C(15)-C(16)	
1.423(5)	C(15)-C(20)	1.428(4)	C(16)-
C(17)	1.361(5)	C(16)-H(16)	0.9400
C(17)-C(18)	1.403(5)	C(17)-H(17)	0.9400
C(18)-C(19)	1.369(5)	C(18)-H(18)	0.9400
C(19)-C(20)	1.413(4)	C(19)-H(19)	0.9400
C(21)-C(26)	1.394(4)	C(21)-C(22)	
1.401(4)	C(22)-C(23)	1.387(5)	C(22)-
H(22)	0.9400	C(23)-C(24)	
1.388(6)	C(23)-H(23)	0.9400	C(24)-
C(25)	1.384(6)	C(24)-H(24)	0.9400
C(25)-C(26)	1.395(5)	C(25)-H(25)	0.9400
C(26)-H(26)	0.9400	C(27)-C(32)	
1.381(6)	C(27)-C(28)	1.399(6)	C(28)-
C(29)	1.387(6)	C(28)-H(28)	0.9400
C(29)-C(30)	1.345(8)	C(29)-H(29)	0.9400
C(30)-C(31)	1.384(7)	C(30)-H(30)	0.9400
C(31)-C(32)	1.400(6)	C(31)-H(31)	0.9400
C(32)-H(32)	0.9400	C(33)-C(38)	

1.385(5)	C(33)-C(34)	1.387(5)	C(34)-
C(35)	1.385(5)	C(34)-H(34)	0.9400
C(35)-C(36)	1.379(5)	C(35)-H(35)	0.9400
C(36)-C(37)	1.376(5)	C(36)-H(36)	0.9400
C(37)-C(38)	1.396(5)	C(37)-H(37)	0.9400
C(38)-H(38)	0.9400	S(7)-N(11)	
1.531(3)	S(7)-N(9)	1.564(3)	S(7)-
N(10)	1.582(3)	S(7)-C(113)	
1.772(3)	S(8)-O(22)	1.427(3)	S(8)-
O(21)	1.427(2)	S(8)-N(10)	
1.574(3)	S(8)-C(119)	1.832(4)	S(9)-
O(23)	1.424(3)	S(9)-O(24)	
1.426(2)	S(9)-N(9)	1.582(3)	S(9)-
C(120)	1.836(3)	P(3)-O(19)	
1.488(2)	P(3)-O(17)	1.600(2)	P(3)-
N(11)	1.622(3)	P(3)-N(12)	
1.633(3)	F(13)-C(119)	1.342(4)	F(14)-
C(119)	1.326(5)	F(15)-C(119)	
1.323(4)	F(16)-C(120)	1.308(5)	F(17)-
C(120)	1.329(5)	F(18)-C(120)	
1.328(4)	O(17)-C(82)	1.406(4)	N(12)-
H(12A)	0.8700	N(12)-H(12B)	0.8700
O(20)-C(92)	1.370(4)	C(81)-C(82)	
1.375(4)	C(81)-C(90)	1.429(4)	C(81)-
C(91)	1.498(4)	C(82)-C(83)	
1.424(4)	C(83)-C(84)	1.384(5)	C(83)-
C(101)	1.491(5)	C(84)-C(85)	
1.405(5)	C(84)-H(84)	0.9400	C(85)-
C(90)	1.422(4)	C(85)-C(86)	
1.429(5)	C(86)-C(87)	1.370(5)	C(86)-
H(86)	0.9400	C(87)-C(88)	
1.410(5)	C(87)-H(87)	0.9400	C(88)-
C(89)	1.372(5)	C(88)-H(88)	0.9400
C(89)-C(90)	1.418(4)	C(89)-H(89)	0.9400
C(91)-C(92)	1.382(4)	C(91)-C(100)	
1.430(4)	C(92)-C(93)	1.423(4)	C(93)-
C(94)	1.365(5)	C(93)-C(107)	
1.486(5)	C(94)-C(95)	1.412(5)	C(94)-

H(94)	0.9400	C(95)-C(96)	
1.418(5)	C(95)-C(100)	1.421(4)	C(96)-
C(97)	1.361(5)	C(96)-H(96)	0.9400
C(97)-C(98)	1.409(5)	C(97)-H(97)	0.9400
C(98)-C(99)	1.375(5)	C(98)-H(98)	0.9400
C(99)-C(100)	1.415(4)	C(99)-H(99)	0.9400
C(101)-C(102)	1.396(5)	C(101)-C(106)	
1.403(5)	C(102)-C(103)	1.395(5)	C(102)-
H(102)	0.9400	C(103)-C(104)	
1.382(6)	C(103)-H(103)	0.9400	C(104)-
C(105)	1.358(7)	C(104)-H(104)	0.9400
C(105)-C(106)	1.406(6)	C(105)-H(105)	0.9400
C(106)-H(106)	0.9400	C(107)-C(112)	
1.387(6)	C(107)-C(108)	1.396(5)	C(108)-
C(109)	1.400(5)	C(108)-H(108)	0.9400
C(109)-C(110)	1.381(6)	C(109)-H(109)	0.9400
C(110)-C(111)	1.375(6)	C(110)-H(110)	0.9400
C(111)-C(112)	1.390(6)	C(111)-H(111)	0.9400
C(112)-H(112)	0.9400	C(113)-C(114)	
1.386(4)	C(113)-C(118)	1.389(4)	C(114)-
C(115)	1.388(5)	C(114)-H(114)	0.9400
C(115)-C(116)	1.388(6)	C(115)-H(115)	0.9400
C(116)-C(117)	1.387(5)	C(116)-H(116)	0.9400
C(117)-C(118)	1.394(5)	C(117)-H(117)	0.9400
C(118)-H(118)	0.9400	S(4)-N(7)	
1.528(3)	S(4)-N(6)	1.560(3)	S(4)-
N(5)	1.591(3)	S(4)-C(73)	
1.774(3)	S(5)-O(13)	1.420(3)	S(5)-
O(14)	1.423(2)	S(5)-N(5)	
1.572(3)	S(5)-C(79)	1.833(5)	S(6)-
O(15)	1.420(3)	S(6)-O(16)	
1.428(3)	S(6)-N(6)	1.588(3)	S(6)-
C(80)	1.836(4)	P(2)-O(11)	
1.488(2)	P(2)-O(9)	1.606(2)	P(2)-
N(7)	1.608(3)	P(2)-N(8)	
1.626(3)	F(7)-C(79)	1.327(5)	F(8)-
C(79)	1.322(6)	F(9)-C(79)	
1.334(5)	F(10)-C(80)	1.344(5)	F(11)-

C(80)	1.316(5)	F(12)-C(80)	
1.320(5)	O(9)-C(42)	1.403(4)	N(8)-
H(8A)	0.8700	N(8)-H(8B)	0.8700
O(12)-C(52)	1.377(4)	C(41)-C(42)	
1.373(4)	C(41)-C(50)	1.429(4)	C(41)-
C(51)	1.499(4)	C(42)-C(43)	
1.434(4)	C(43)-C(44)	1.379(5)	C(43)-
C(61)	1.476(5)	C(44)-C(45)	
1.405(5)	C(44)-H(44)	0.9400	C(45)-
C(50)	1.422(5)	C(45)-C(46)	
1.425(5)	C(46)-C(47)	1.361(7)	C(46)-
H(46)	0.9400	C(47)-C(48)	
1.416(7)	C(47)-H(47)	0.9400	C(48)-
C(49)	1.371(5)	C(48)-H(48)	0.9400
C(49)-C(50)	1.416(5)	C(49)-H(49)	0.9400
C(51)-C(52)	1.385(4)	C(51)-C(60)	
1.425(4)	C(52)-C(53)	1.419(4)	C(53)-
C(54)	1.389(5)	C(53)-C(67)	
1.488(4)	C(54)-C(55)	1.402(5)	C(54)-
H(54)	0.9400	C(55)-C(60)	
1.419(4)	C(55)-C(56)	1.421(5)	C(56)-
C(57)	1.365(5)	C(56)-H(56)	0.9400
C(57)-C(58)	1.404(5)	C(57)-H(57)	0.9400
C(58)-C(59)	1.381(5)	C(58)-H(58)	0.9400
C(59)-C(60)	1.416(4)	C(59)-H(59)	0.9400
C(61)-C(66)	1.403(5)	C(61)-C(62)	
1.403(5)	C(62)-C(63)	1.395(6)	C(62)-
H(62)	0.9400	C(63)-C(64)	
1.379(7)	C(63)-H(63)	0.9400	C(64)-
C(65)	1.376(6)	C(64)-H(64)	0.9400
C(65)-C(66)	1.390(5)	C(65)-H(65)	0.9400
C(66)-H(66)	0.9400	C(67)-C(68)	
1.391(5)	C(67)-C(72)	1.395(5)	C(68)-
C(69)	1.402(5)	C(68)-H(68)	0.9400
C(69)-C(70)	1.359(7)	C(69)-H(69)	0.9400
C(70)-C(71)	1.398(8)	C(70)-H(70)	0.9400
C(71)-C(72)	1.383(6)	C(71)-H(71)	0.9400
C(72)-H(72)	0.9400	C(73)-C(78)	

1.378(5)	C(73)-C(74)	1.391(4)	C(74)-
C(75)	1.393(5)	C(74)-H(74)	0.9400
C(75)-C(76)	1.380(6)	C(75)-H(75)	0.9400
C(76)-C(77)	1.381(6)	C(76)-H(76)	0.9400
C(77)-C(78)	1.395(6)	C(77)-H(77)	0.9400
C(78)-H(78)	0.9400	N(20)-C(219)	
1.493(6)	N(20)-C(223)	1.504(5)	N(20)-
C(221)	1.506(6)	N(20)-H(20)	0.9900
C(23A)-C(219)	1.497(10)	C(23A)-H(23A)	0.9700
C(23A)-H(23B)	0.9700	C(23A)-H(23C)	0.9700
C(23B)-C(219)	1.528(11)	C(23B)-H(23D)	0.9700
C(23B)-H(23E)	0.9700	C(23B)-H(23F)	0.9700
C(23C)-C(221)	1.424(10)	C(23C)-H(23G)	0.9700
C(23C)-H(23H)	0.9700	C(23C)-H(23I)	0.9700
C(23D)-C(221)	1.609(13)	C(23D)-H(23J)	0.9700
C(23D)-H(23K)	0.9700	C(23D)-H(23L)	0.9700
C(219)-H(21C)	0.9800	C(219)-H(21D)	0.9800
C(219)-H(21A)	0.9800	C(219)-H(21B)	0.9800
C(221)-H(22C)	0.9800	C(221)-H(22D)	0.9800
C(221)-H(22A)	0.9800	C(221)-H(22B)	0.9800
C(223)-C(224)	1.488(6)	C(223)-H(22E)	0.9800
C(223)-H(22F)	0.9800	C(224)-H(22G)	0.9700
C(224)-H(22H)	0.9700	C(224)-H(22I)	0.9700
N(19)-C(22A)	1.431(8)	N(19)-C(213)	
1.485(5)	N(19)-C(215)	1.710(8)	N(19)-
C(22B)	1.783(11)	N(19)-H(19A)	0.9900
C(22A)-C(22D)	1.532(12)	C(22A)-H(22J)	0.9800
C(22A)-H(22K)	0.9800	C(22B)-C(22C)	
1.393(14)	C(22B)-H(22L)	0.9800	C(22B)-
H(22M)	0.9800	C(22C)-H(22N)	0.9700
C(22C)-H(22O)	0.9700	C(22C)-H(22P)	0.9700
C(22D)-H(22Q)	0.9700	C(22D)-H(22R)	0.9700
C(22D)-H(22S)	0.9700	C(213)-C(214)	
1.516(6)	C(213)-H(21E)	0.9800	C(213)-
H(21F)	0.9800	C(214)-H(21G)	0.9700
C(214)-H(21H)	0.9700	C(214)-H(21I)	0.9700
C(215)-C(216)	1.375(9)	C(215)-H(21J)	0.9800
C(215)-H(21K)	0.9800	C(216)-H(21L)	0.9700

C(216)-H(21M)	0.9700	C(216)-H(21N)	0.9700
N(18)-C(21B)	1.475(11)	N(18)-C(207)	
1.494(6)	N(18)-C(209)	1.500(6)	N(18)-
C(21A)	1.566(11)	N(18)-H(18A)	0.9900
C(21A)-C(21C)	1.239(13)	C(21A)-H(21O)	0.9800
C(21A)-H(21P)	0.9800	C(21B)-C(21D)	
1.261(16)	C(21B)-H(21Q)	0.9800	C(21B)-
H(21R)	0.9800	C(21C)-H(21S)	0.9700
C(21C)-H(21T)	0.9700	C(21C)-H(21U)	0.9700
C(21D)-H(21V)	0.9700	C(21D)-H(21W)	0.9700
C(21D)-H(21X)	0.9700	C(207)-C(208)	
1.516(6)	C(207)-H(20A)	0.9800	C(207)-
H(20B)	0.9800	C(208)-H(20C)	0.9700
C(208)-H(20D)	0.9700	C(208)-H(20E)	0.9700
C(209)-C(210)	1.506(7)	C(209)-H(20F)	0.9800
C(209)-H(20G)	0.9800	C(210)-H(21Y)	0.9700
C(210)-H	0.9700	C(210)-HA	0.9700
N(17)-C(205)	1.504(4)	N(17)-C(203)	
1.505(4)	N(17)-C(201)	1.514(5)	N(17)-
H(17A)	0.9900	C(201)-C(202)	
1.502(6)	C(201)-H(20H)	0.9800	C(201)-
H(20I)	0.9800	C(202)-H(20J)	0.9700
C(202)-H(20K)	0.9700	C(202)-H(20L)	0.9700
C(203)-C(204)	1.508(5)	C(203)-H(20M)	0.9800
C(203)-H(20N)	0.9800	C(204)-H(20O)	0.9700
C(204)-H(20P)	0.9700	C(204)-H(20Q)	0.9700
C(205)-C(206)	1.516(5)	C(205)-H(20R)	0.9800
C(205)-H(20S)	0.9800	C(206)-H(20T)	0.9700
C(206)-H(20U)	0.9700	C(206)-H(20V)	0.9700

N(14)-S(10)-N(13)	119.6(2)	N(14)-S(10)-N(15)	
116.03(18)	N(13)-S(10)-N(15)	104.6(2)	N(14)-
S(10)-C(153)	104.72(17)	N(13)-S(10)-C(153)	
100.17(19)	N(15)-S(10)-C(153)	110.46(16)	O(30)-
S(11)-O(29)	118.2(2)	O(30)-S(11)-N(13)	
110.9(3)	O(29)-S(11)-N(13)	116.3(2)	O(30)-
S(11)-C(159)	104.1(2)	O(29)-S(11)-C(159)	
105.5(2)	N(13)-S(11)-C(159)	98.9(2)	

O(32B)-S(12)-O(31)	125.5(3)	O(31)-S(12)-O(32A)	
108.7(3)	O(32B)-S(12)-N(15)	112.3(3)	O(31)-
S(12)-N(15)	116.12(15)	O(32A)-S(12)-N(15)	
110.9(2)	O(31)-S(12)-C(1D)	106.5(3)	
O(32A)-S(12)-C(1D)	106.8(4)	N(15)-S(12)-C(1D)	
107.3(3)	O(32B)-S(12)-C(1A)	98.2(4)	O(31)-
S(12)-C(1A)	105.0(3)	N(15)-S(12)-C(1A)	90.3(3)
O(26)-P(4)-O(25)	109.93(14)	O(26)-P(4)-N(14)	
112.78(19)	O(25)-P(4)-N(14)	103.14(15)	O(26)-
P(4)-N(16)	111.13(15)	O(25)-P(4)-N(16)	
108.08(13)	N(14)-P(4)-N(16)	111.40(15)	C(122)-
O(25)-P(4)	121.84(18)	P(4)-N(16)-H(16A)	120.0
P(4)-N(16)-H(16B)	120.0	H(16A)-N(16)-H(16B)	120.0
S(12)-O(32A)-H(32A)	109.5	S(10)-N(14)-P(4)	
137.8(2)	S(11)-N(13)-S(10)	125.4(2)	S(12)-
N(15)-S(10)	121.79(19)	F(24B)-C(1A)-F(23B)	
127.5(11)	F(24B)-C(1A)-S(12)	117.1(9)	F(23B)-
C(1A)-S(12)	113.3(6)	F(22A)-C(1D)-F(23A)	
108.0(8)	F(22A)-C(1D)-S(12)	140.2(8)	F(23A)-
C(1D)-S(12)	110.8(6)	C(122)-C(121)-C(130)	
118.5(3)	C(122)-C(121)-C(131)	122.0(3)	C(130)-
C(121)-C(131)	119.4(3)	C(121)-C(122)-O(25)	
118.1(3)	C(121)-C(122)-C(123)	123.5(3)	O(25)-
C(122)-C(123)	118.4(2)	C(124)-C(123)-C(122)	
117.6(3)	C(124)-C(123)-C(141)	121.1(3)	C(122)-
C(123)-C(141)	121.3(3)	C(123)-C(124)-C(125)	
121.5(3)	C(123)-C(124)-H(124)	119.2	C(125)-
C(124)-H(124)	119.2	C(124)-C(125)-C(130)	
119.6(3)	C(124)-C(125)-C(126)	121.3(3)	C(130)-
C(125)-C(126)	119.1(3)	C(127)-C(126)-C(125)	
120.2(3)	C(127)-C(126)-H(126)	119.9	C(125)-
C(126)-H(126)	119.9	C(126)-C(127)-C(128)	
120.5(3)	C(126)-C(127)-H(127)	119.8	C(128)-
C(127)-H(127)	119.8	C(129)-C(128)-C(127)	
121.0(3)	C(129)-C(128)-H(128)	119.5	C(127)-
C(128)-H(128)	119.5	C(128)-C(129)-C(130)	
120.0(3)	C(128)-C(129)-H(129)	120.0	C(130)-
C(129)-H(129)	120.0	C(129)-C(130)-C(125)	

119.2(3)	C(129)-C(130)-C(121)	121.5(3)	C(125)-
C(130)-C(121)	119.3(3)	C(132)-C(131)-C(140)	
119.7(3)	C(132)-C(131)-C(121)	120.9(3)	C(140)-
C(131)-C(121)	119.3(3)	C(131)-C(132)-O(28)	
120.4(3)	C(131)-C(132)-C(133)	121.9(3)	O(28)-
C(132)-C(133)	117.6(3)	C(134)-C(133)-C(132)	
118.2(3)	C(134)-C(133)-C(147)	119.8(3)	C(132)-
C(133)-C(147)	122.0(3)	C(133)-C(134)-C(135)	
122.1(3)	C(133)-C(134)-H(134)	119.0	C(135)-
C(134)-H(134)	119.0	C(134)-C(135)-C(136)	
121.5(3)	C(134)-C(135)-C(140)	119.1(3)	C(136)-
C(135)-C(140)	119.4(3)	C(137)-C(136)-C(135)	
121.0(3)	C(137)-C(136)-H(136)	119.5	C(135)-
C(136)-H(136)	119.5	C(136)-C(137)-C(138)	
119.4(3)	C(136)-C(137)-H(137)	120.3	C(138)-
C(137)-H(137)	120.3	C(139)-C(138)-C(137)	
121.2(3)	C(139)-C(138)-H(138)	119.4	C(137)-
C(138)-H(138)	119.4	C(138)-C(139)-C(140)	
120.3(3)	C(138)-C(139)-H(139)	119.9	C(140)-
C(139)-H(139)	119.9	C(139)-C(140)-C(135)	
118.6(3)	C(139)-C(140)-C(131)	122.6(3)	C(135)-
C(140)-C(131)	118.8(3)	C(146)-C(141)-C(142)	
118.8(3)	C(146)-C(141)-C(123)	120.1(3)	C(142)-
C(141)-C(123)	121.1(3)	C(143)-C(142)-C(141)	
120.0(3)	C(143)-C(142)-H(142)	120.0	C(141)-
C(142)-H(142)	120.0	C(144)-C(143)-C(142)	
120.9(4)	C(144)-C(143)-H(143)	119.6	C(142)-
C(143)-H(143)	119.6	C(143)-C(144)-C(145)	
120.0(3)	C(143)-C(144)-H(144)	120.0	C(145)-
C(144)-H(144)	120.0	C(144)-C(145)-C(146)	
119.8(3)	C(144)-C(145)-H(145)	120.1	C(146)-
C(145)-H(145)	120.1	C(145)-C(146)-C(141)	
120.4(4)	C(145)-C(146)-H(146)	119.8	C(141)-
C(146)-H(146)	119.8	C(152)-C(147)-C(148)	
118.4(3)	C(152)-C(147)-C(133)	121.4(3)	C(148)-
C(147)-C(133)	120.1(3)	C(149)-C(148)-C(147)	
121.1(3)	C(149)-C(148)-H(148)	119.4	C(147)-
C(148)-H(148)	119.4	C(150)-C(149)-C(148)	

119.8(3)	C(150)-C(149)-H(149)	120.1	C(148)-
C(149)-H(149)	120.1	C(149)-C(150)-C(151)	
120.0(3)	C(149)-C(150)-H(150)	120.0	C(151)-
C(150)-H(150)	120.0	C(152)-C(151)-C(150)	
119.6(3)	C(152)-C(151)-H(151)	120.2	C(150)-
C(151)-H(151)	120.2	C(147)-C(152)-C(151)	
121.1(3)	C(147)-C(152)-H(152)	119.5	C(151)-
C(152)-H(152)	119.5	C(158)-C(153)-C(154)	
122.0(3)	C(158)-C(153)-S(10)	118.2(3)	C(154)-
C(153)-S(10)	119.7(3)	C(153)-C(154)-C(155)	
118.6(4)	C(153)-C(154)-H(154)	120.7	C(155)-
C(154)-H(154)	120.7	C(156)-C(155)-C(154)	
119.9(4)	C(156)-C(155)-H(155)	120.0	C(154)-
C(155)-H(155)	120.0	C(155)-C(156)-C(157)	
121.4(4)	C(155)-C(156)-H(156)	119.3	C(157)-
C(156)-H(156)	119.3	C(156)-C(157)-C(158)	
119.1(4)	C(156)-C(157)-H(157)	120.5	C(158)-
C(157)-H(157)	120.5	C(153)-C(158)-C(157)	
118.9(4)	C(153)-C(158)-H(158)	120.5	C(157)-
C(158)-H(158)	120.5	F(19)-C(159)-F(21)	
108.9(5)	F(19)-C(159)-F(20)	107.4(4)	F(21)-
C(159)-F(20)	109.2(4)	F(19)-C(159)-S(11)	
108.8(3)	F(21)-C(159)-S(11)	111.1(3)	F(20)-
C(159)-S(11)	111.4(3)	N(1)-S(1)-N(3)	
110.15(15)	N(1)-S(1)-N(2)	116.20(15)	N(3)-
S(1)-N(2)	106.23(16)	N(1)-S(1)-C(33)	
103.43(15)	N(3)-S(1)-C(33)	112.90(16)	N(2)-
S(1)-C(33)	108.10(15)	O(8)-S(2)-O(7)	
116.58(19)	O(8)-S(2)-N(2)	116.05(16)	O(7)-
S(2)-N(2)	112.49(17)	O(8)-S(2)-C(39)	
106.2(2)	O(7)-S(2)-C(39)	105.8(2)	N(2)-
S(2)-C(39)	96.9(2)	O(5)-S(3)-O(6)	
119.02(18)	O(5)-S(3)-N(3)	111.49(16)	O(6)-
S(3)-N(3)	115.46(16)	O(5)-S(3)-C(40)	
104.32(19)	O(6)-S(3)-C(40)	105.17(18)	N(3)-
S(3)-C(40)	98.13(16)	O(2)-P(1)-O(1)	
111.96(12)	O(2)-P(1)-N(1)	109.43(13)	O(1)-
P(1)-N(1)	104.64(13)	O(2)-P(1)-N(4)	

112.62(14) O(1)-P(1)-N(4) 105.01(13) N(1)-P(1)-N(4) 112.86(15) C(2)-O(1)-P(1) 121.42(18) P(1)-N(4)-H(4A) 120.0 P(1)-N(4)-H(4B) 120.0 H(4A)-N(4)-H(4B) 120.0 S(1)-N(1)-P(1) 127.28(18) S(2)-N(2)-S(1) 120.25(19) S(1)-N(3)-S(3) 125.44(18) C(2)-C(1)-C(10) 118.6(3) C(2)-C(1)-C(11) 123.5(3) C(10)-C(1)-C(11) 117.9(3) C(1)-C(2)-O(1) 118.1(3) C(1)-C(2)-C(3) 123.4(3) O(1)-C(2)-C(3) 118.5(2) C(4)-C(3)-C(2) 117.7(3) C(4)-C(3)-C(21) 120.5(3) C(2)-C(3)-C(21) 121.7(3) C(3)-C(4)-C(5) 121.7(3) C(3)-C(4)-H(4) 119.2 C(5)-C(4)-H(4) 119.2 C(4)-C(5)-C(10) 119.5(3) C(4)-C(5)-C(6) 121.3(3) C(10)-C(5)-C(6) 119.2(3) C(7)-C(6)-C(5) 120.3(3) C(7)-C(6)-H(6) 119.8 C(5)-C(6)-H(6) 119.8 C(6)-C(7)-C(8) 120.6(3) C(6)-C(7)-H(7) 119.7 C(8)-C(7)-H(7) 119.7 C(9)-C(8)-C(7) 120.7(3) C(9)-C(8)-H(8) 119.6 C(7)-C(8)-H(8) 119.6 C(8)-C(9)-C(10) 120.0(3) C(8)-C(9)-H(9) 120.0 C(10)-C(9)-H(9) 120.0 C(9)-C(10)-C(5) 119.1(3) C(9)-C(10)-C(1) 121.8(3) C(5)-C(10)-C(1) 119.0(3) C(12)-C(11)-C(20) 120.0(3) C(12)-C(11)-C(1) 120.2(3) C(20)-C(11)-C(1) 119.4(3) C(11)-C(12)-O(4) 120.8(3) C(11)-C(12)-C(13) 121.6(3) O(4)-C(12)-C(13) 117.5(3) C(14)-C(13)-C(12) 118.1(3) C(14)-C(13)-C(27) 119.4(3) C(12)-C(13)-C(27) 122.5(3) C(13)-C(14)-C(15) 122.7(3) C(13)-C(14)-H(14) 118.6 C(15)-C(14)-H(14) 118.6 C(14)-C(15)-C(16) 121.7(3) C(14)-C(15)-C(20) 119.1(3) C(16)-C(15)-C(20) 119.2(3) C(17)-C(16)-C(15) 120.5(3) C(17)-C(16)-H(16) 119.7 C(15)-C(16)-H(16) 119.7 C(16)-C(17)-C(18)

120.1(3)	C(16)-C(17)-H(17)	120.0	C(18)-
C(17)-H(17)	120.0	C(19)-C(18)-C(17)	
121.3(3)	C(19)-C(18)-H(18)	119.4	C(17)-
C(18)-H(18)	119.4	C(18)-C(19)-C(20)	
120.5(3)	C(18)-C(19)-H(19)	119.8	C(20)-
C(19)-H(19)	119.8	C(19)-C(20)-C(15)	
118.4(3)	C(19)-C(20)-C(11)	123.2(3)	C(15)-
C(20)-C(11)	118.4(3)	C(26)-C(21)-C(22)	
119.0(3)	C(26)-C(21)-C(3)	120.1(3)	C(22)-
C(21)-C(3)	120.9(3)	C(23)-C(22)-C(21)	
120.6(3)	C(23)-C(22)-H(22)	119.7	C(21)-
C(22)-H(22)	119.7	C(22)-C(23)-C(24)	
119.9(3)	C(22)-C(23)-H(23)	120.0	C(24)-
C(23)-H(23)	120.0	C(25)-C(24)-C(23)	
120.0(3)	C(25)-C(24)-H(24)	120.0	C(23)-
C(24)-H(24)	120.0	C(24)-C(25)-C(26)	
120.4(3)	C(24)-C(25)-H(25)	119.8	C(26)-
C(25)-H(25)	119.8	C(21)-C(26)-C(25)	
120.0(3)	C(21)-C(26)-H(26)	120.0	C(25)-
C(26)-H(26)	120.0	C(32)-C(27)-C(28)	
118.3(4)	C(32)-C(27)-C(13)	121.5(4)	C(28)-
C(27)-C(13)	120.0(4)	C(29)-C(28)-C(27)	
121.9(5)	C(29)-C(28)-H(28)	119.1	C(27)-
C(28)-H(28)	119.1	C(30)-C(29)-C(28)	
118.7(5)	C(30)-C(29)-H(29)	120.7	C(28)-
C(29)-H(29)	120.7	C(29)-C(30)-C(31)	
121.7(5)	C(29)-C(30)-H(30)	119.2	C(31)-
C(30)-H(30)	119.2	C(30)-C(31)-C(32)	
119.8(5)	C(30)-C(31)-H(31)	120.1	C(32)-
C(31)-H(31)	120.1	C(27)-C(32)-C(31)	
119.6(5)	C(27)-C(32)-H(32)	120.2	C(31)-
C(32)-H(32)	120.2	C(38)-C(33)-C(34)	
122.0(3)	C(38)-C(33)-S(1)	120.7(3)	C(34)-
C(33)-S(1)	117.3(3)	C(35)-C(34)-C(33)	
118.6(3)	C(35)-C(34)-H(34)	120.7	C(33)-
C(34)-H(34)	120.7	C(36)-C(35)-C(34)	
120.4(3)	C(36)-C(35)-H(35)	119.8	C(34)-
C(35)-H(35)	119.8	C(37)-C(36)-C(35)	

120.4(3) C(37)-C(36)-H(36) 119.8 C(35)-C(36)-H(36) 119.8 C(36)-C(37)-C(38) 120.5(3) C(36)-C(37)-H(37) 119.7 C(38)-C(37)-H(37) 119.7 C(33)-C(38)-C(37) 118.1(3) C(33)-C(38)-H(38) 121.0 C(37)-C(38)-H(38) 121.0 F(1)-C(39)-F(3) 108.6(5) F(1)-C(39)-F(2) 108.2(4) F(3)-C(39)-F(2) 108.0(4) F(1)-C(39)-S(2) 110.2(3) F(3)-C(39)-S(2) 113.6(3) F(2)-C(39)-S(2) 108.0(4) F(4)-C(40)-F(6) 108.7(3) F(4)-C(40)-F(5) 107.9(3) F(6)-C(40)-F(5) 107.9(3) F(4)-C(40)-S(3) 112.3(3) F(6)-C(40)-S(3) 110.8(3) F(5)-C(40)-S(3) 109.1(3) N(11)-S(7)-N(9) 112.76(14) N(11)-S(7)-N(10) 112.13(15) N(9)-S(7)-N(10) 114.84(14) N(11)-S(7)-C(113) 110.72(15) N(9)-S(7)-C(113) 101.42(14) N(10)-S(7)-C(113) 104.00(14) O(22)-S(8)-O(21) 119.36(16) O(22)-S(8)-N(10) 115.71(14) O(21)-S(8)-N(10) 108.91(15) O(22)-S(8)-C(119) 104.83(18) O(21)-S(8)-C(119) 103.56(16) N(10)-S(8)-C(119) 102.09(16) O(23)-S(9)-O(24) 119.26(15) O(23)-S(9)-N(9) 116.30(14) O(24)-S(9)-N(9) 108.80(15) O(23)-S(9)-C(120) 104.66(17) O(24)-S(9)-C(120) 101.08(15) O(19)-P(3)-O(17) 112.61(13) O(19)-P(3)-N(11) 111.15(13) O(17)-P(3)-N(11) 104.20(13) O(19)-P(3)-N(12) 111.37(16) O(17)-P(3)-N(12) 103.47(15) N(11)-P(3)-N(12) 113.63(15) C(82)-O(17)-P(3) 119.04(19) P(3)-N(12)-H(12A) 120.0 P(3)-N(12)-H(12B) 120.0 H(12A)-N(12)-H(12B) 120.0 S(7)-N(11)-P(3) 127.42(17) S(8)-N(10)-S(7) 127.21(16) S(7)-N(9)-S(9) 128.00(17) C(82)-C(81)-C(90) 118.6(3) C(82)-C(81)-C(91) 121.9(3) C(90)-C(81)-C(91) 119.5(3) C(81)-C(82)-O(17) 117.3(2) C(81)-C(82)-C(83) 123.8(3) O(17)-C(82)-C(83) 118.9(3) C(84)-

C(83)-C(82) 116.2(3)
C(84)-C(83)-C(101) 121.2(3)
C(82)-C(83)-C(101) 122.5(3)
C(83)-C(84)-C(85) 122.3(3)
C(83)-C(84)-H(84) 118.9
C(85)-C(84)-H(84) 118.9
C(84)-C(85)-C(90) 119.9(3)
C(84)-C(85)-C(86) 121.1(3)
C(90)-C(85)-C(86) 119.0(3)
C(87)-C(86)-C(85) 120.6(3)
C(87)-C(86)-H(86) 119.7
C(85)-C(86)-H(86) 119.7
C(86)-C(87)-C(88) 120.1(3)
C(86)-C(87)-H(87) 120.0
C(88)-C(87)-H(87) 120.0
C(89)-C(88)-C(87) 120.8(3)
C(89)-C(88)-H(88) 119.6
C(87)-C(88)-H(88) 119.6
C(88)-C(89)-C(90) 120.6(3)
C(88)-C(89)-H(89) 119.7
C(90)-C(89)-H(89) 119.7
C(89)-C(90)-C(85) 118.8(3)
C(89)-C(90)-C(81) 122.6(3)
C(85)-C(90)-C(81) 118.5(3)
C(92)-C(91)-C(100) 119.6(3)
C(92)-C(91)-C(81) 119.3(3)
C(100)-C(91)-C(81) 121.0(3)
O(20)-C(92)-C(91) 120.6(3)
O(20)-C(92)-C(93) 117.9(3)
C(91)-C(92)-C(93) 121.5(3)
C(94)-C(93)-C(92) 118.5(3)
C(94)-C(93)-C(107) 120.5(3)
C(92)-C(93)-C(107) 121.0(3)
C(93)-C(94)-C(95) 122.2(3)
C(93)-C(94)-H(94) 118.9
C(95)-C(94)-H(94) 118.9
C(94)-C(95)-C(96) 121.5(3)
C(94)-C(95)-C(100) 119.3(3)
C(96)-C(95)-C(100) 119.2(3)
C(97)-C(96)-C(95) 121.5(3)
C(97)-C(96)-H(96) 119.3
C(95)-C(96)-H(96) 119.3
C(96)-C(97)-C(98) 119.3(3)
C(96)-C(97)-H(97) 120.3
C(98)-C(97)-H(97) 120.3
C(99)-C(98)-C(97) 120.9(3)
C(99)-C(98)-H(98) 119.5
C(97)-C(98)-H(98) 119.5
C(98)-C(99)-C(100) 120.7(3)
C(98)-C(99)-H(99) 119.6
C(100)-C(99)-H(99) 119.6
C(99)-C(100)-C(95) 118.2(3)
C(99)-C(100)-C(91) 123.1(3)
C(95)-C(100)-C(91) 118.6(3)
C(102)-C(101)-C(106) 118.1(3)
C(102)-C(101)-C(83) 121.7(3)
C(106)-C(101)-C(83) 120.1(4)
C(103)-C(102)-C(101)

121.1(3)	C(103)-C(102)-H(102)	119.4	C(101)-
C(102)-H(102)	119.4	C(104)-C(103)-C(102)	
120.0(4)	C(104)-C(103)-H(103)	120.0	C(102)-
C(103)-H(103)	120.0	C(105)-C(104)-C(103)	
119.8(4)	C(105)-C(104)-H(104)	120.1	C(103)-
C(104)-H(104)	120.1	C(104)-C(105)-C(106)	
121.4(4)	C(104)-C(105)-H(105)	119.3	C(106)-
C(105)-H(105)	119.3	C(101)-C(106)-C(105)	
119.6(4)	C(101)-C(106)-H(106)	120.2	C(105)-
C(106)-H(106)	120.2	C(112)-C(107)-C(108)	
119.5(3)	C(112)-C(107)-C(93)	121.2(3)	C(108)-
C(107)-C(93)	119.2(3)	C(107)-C(108)-C(109)	
119.9(3)	C(107)-C(108)-H(108)	120.1	C(109)-
C(108)-H(108)	120.1	C(110)-C(109)-C(108)	
119.8(3)	C(110)-C(109)-H(109)	120.1	C(108)-
C(109)-H(109)	120.1	C(111)-C(110)-C(109)	
120.3(4)	C(111)-C(110)-H(110)	119.8	C(109)-
C(110)-H(110)	119.8	C(110)-C(111)-C(112)	
120.4(4)	C(110)-C(111)-H(111)	119.8	C(112)-
C(111)-H(111)	119.8	C(107)-C(112)-C(111)	
120.1(4)	C(107)-C(112)-H(112)	120.0	C(111)-
C(112)-H(112)	120.0	C(114)-C(113)-C(118)	
122.2(3)	C(114)-C(113)-S(7)	121.7(2)	C(118)-
C(113)-S(7)	116.1(2)	C(113)-C(114)-C(115)	
118.2(3)	C(113)-C(114)-H(114)	120.9	C(115)-
C(114)-H(114)	120.9	C(114)-C(115)-C(116)	
120.6(3)	C(114)-C(115)-H(115)	119.7	C(116)-
C(115)-H(115)	119.7	C(117)-C(116)-C(115)	
120.4(3)	C(117)-C(116)-H(116)	119.8	C(115)-
C(116)-H(116)	119.8	C(116)-C(117)-C(118)	
119.8(3)	C(116)-C(117)-H(117)	120.1	C(118)-
C(117)-H(117)	120.1	C(113)-C(118)-C(117)	
118.7(3)	C(113)-C(118)-H(118)	120.7	C(117)-
C(118)-H(118)	120.7	F(15)-C(119)-F(14)	
108.1(3)	F(15)-C(119)-F(13)	108.3(3)	F(14)-
C(119)-F(13)	107.5(3)	F(15)-C(119)-S(8)	
111.2(3)	F(14)-C(119)-S(8)	111.2(3)	F(13)-
C(119)-S(8)	110.4(2)	F(16)-C(120)-F(18)	

109.6(3)	F(16)-C(120)-F(17)	109.2(3)	F(18)-
C(120)-F(17)	107.0(3)	F(16)-C(120)-S(9)	
111.1(3)	F(18)-C(120)-S(9)	109.2(3)	F(17)-
C(120)-S(9)	110.8(2)	N(7)-S(4)-N(6)	
112.71(14)	N(7)-S(4)-N(5)	112.32(15)	N(6)-
S(4)-N(5)	114.88(14)	N(7)-S(4)-C(73)	
111.35(15)	N(6)-S(4)-C(73)	101.93(15)	N(5)-
S(4)-C(73)	102.64(15)	O(13)-S(5)-O(14)	
119.54(18)	O(13)-S(5)-N(5)	115.74(16)	O(14)-
S(5)-N(5)	108.94(15)	O(13)-S(5)-C(79)	
106.4(3)	O(14)-S(5)-C(79)	102.30(19)	N(5)-
S(5)-C(79)	101.29(19)	O(15)-S(6)-O(16)	
119.94(18)	O(15)-S(6)-N(6)	116.21(15)	O(16)-
S(6)-N(6)	109.10(16)	O(15)-S(6)-C(80)	
105.7(2)	O(16)-S(6)-C(80)	103.34(17)	N(6)-
S(6)-C(80)	99.45(17)	O(11)-P(2)-O(9)	
109.72(13)	O(11)-P(2)-N(7)	113.73(14)	O(9)-
P(2)-N(7)	102.93(13)	O(11)-P(2)-N(8)	
110.62(15)	O(9)-P(2)-N(8)	109.89(14)	N(7)-
P(2)-N(8)	109.67(15)	C(42)-O(9)-P(2)	
120.67(19)	P(2)-N(8)-H(8A)	120.0	P(2)-
N(8)-H(8B)	120.0	H(8A)-N(8)-H(8B)	120.0
S(4)-N(7)-P(2)	130.69(17)	S(5)-N(5)-S(4)	
126.00(17)	S(4)-N(6)-S(6)	127.69(18)	C(42)-
C(41)-C(50)	118.9(3)	C(42)-C(41)-C(51)	
122.1(3)	C(50)-C(41)-C(51)	119.1(3)	C(41)-
C(42)-O(9)	118.5(3)	C(41)-C(42)-C(43)	
123.5(3)	O(9)-C(42)-C(43)	118.0(3)	C(44)-
C(43)-C(42)	116.3(3)	C(44)-C(43)-C(61)	
121.3(3)	C(42)-C(43)-C(61)	122.3(3)	C(43)-
C(44)-C(45)	122.6(3)	C(43)-C(44)-H(44)	118.7
C(45)-C(44)-H(44)	118.7	C(44)-C(45)-C(50)	
119.8(3)	C(44)-C(45)-C(46)	122.1(3)	C(50)-
C(45)-C(46)	118.1(4)	C(47)-C(46)-C(45)	
121.8(4)	C(47)-C(46)-H(46)	119.1	C(45)-
C(46)-H(46)	119.1	C(46)-C(47)-C(48)	
119.4(4)	C(46)-C(47)-H(47)	120.3	C(48)-
C(47)-H(47)	120.3	C(49)-C(48)-C(47)	

120.9(4)	C(49)-C(48)-H(48)	119.6	C(47)-
C(48)-H(48)	119.6	C(48)-C(49)-C(50)	
120.4(4)	C(48)-C(49)-H(49)	119.8	C(50)-
C(49)-H(49)	119.8	C(49)-C(50)-C(45)	
119.4(3)	C(49)-C(50)-C(41)	122.0(3)	C(45)-
C(50)-C(41)	118.6(3)	C(52)-C(51)-C(60)	
119.9(3)	C(52)-C(51)-C(41)	119.1(3)	C(60)-
C(51)-C(41)	120.8(3)	O(12)-C(52)-C(51)	
120.2(3)	O(12)-C(52)-C(53)	117.8(3)	C(51)-
C(52)-C(53)	122.0(3)	C(54)-C(53)-C(52)	
117.6(3)	C(54)-C(53)-C(67)	120.3(3)	C(52)-
C(53)-C(67)	122.0(3)	C(53)-C(54)-C(55)	
122.0(3)	C(53)-C(54)-H(54)	119.0	C(55)-
C(54)-H(54)	119.0	C(54)-C(55)-C(60)	
120.0(3)	C(54)-C(55)-C(56)	120.8(3)	C(60)-
C(55)-C(56)	119.2(3)	C(57)-C(56)-C(55)	
120.7(3)	C(57)-C(56)-H(56)	119.6	C(55)-
C(56)-H(56)	119.6	C(56)-C(57)-C(58)	
120.2(3)	C(56)-C(57)-H(57)	119.9	C(58)-
C(57)-H(57)	119.9	C(59)-C(58)-C(57)	
120.7(3)	C(59)-C(58)-H(58)	119.6	C(57)-
C(58)-H(58)	119.6	C(58)-C(59)-C(60)	
120.3(3)	C(58)-C(59)-H(59)	119.9	C(60)-
C(59)-H(59)	119.9	C(59)-C(60)-C(55)	
118.8(3)	C(59)-C(60)-C(51)	122.8(3)	C(55)-
C(60)-C(51)	118.4(3)	C(66)-C(61)-C(62)	
117.8(3)	C(66)-C(61)-C(43)	121.3(3)	C(62)-
C(61)-C(43)	120.8(3)	C(63)-C(62)-C(61)	
120.6(4)	C(63)-C(62)-H(62)	119.7	C(61)-
C(62)-H(62)	119.7	C(64)-C(63)-C(62)	
120.6(4)	C(64)-C(63)-H(63)	119.7	C(62)-
C(63)-H(63)	119.7	C(65)-C(64)-C(63)	
119.5(4)	C(65)-C(64)-H(64)	120.2	C(63)-
C(64)-H(64)	120.2	C(64)-C(65)-C(66)	
120.8(4)	C(64)-C(65)-H(65)	119.6	C(66)-
C(65)-H(65)	119.6	C(65)-C(66)-C(61)	
120.7(3)	C(65)-C(66)-H(66)	119.7	C(61)-
C(66)-H(66)	119.7	C(68)-C(67)-C(72)	

118.4(3)	C(68)-C(67)-C(53)	121.9(3)	C(72)-
C(67)-C(53)	119.7(3)	C(67)-C(68)-C(69)	
120.5(4)	C(67)-C(68)-H(68)	119.8	C(69)-
C(68)-H(68)	119.8	C(70)-C(69)-C(68)	
120.5(4)	C(70)-C(69)-H(69)	119.8	C(68)-
C(69)-H(69)	119.8	C(69)-C(70)-C(71)	
119.8(4)	C(69)-C(70)-H(70)	120.1	C(71)-
C(70)-H(70)	120.1	C(72)-C(71)-C(70)	
120.0(5)	C(72)-C(71)-H(71)	120.0	C(70)-
C(71)-H(71)	120.0	C(71)-C(72)-C(67)	
120.8(4)	C(71)-C(72)-H(72)	119.6	C(67)-
C(72)-H(72)	119.6	C(78)-C(73)-C(74)	
122.0(3)	C(78)-C(73)-S(4)	121.6(3)	C(74)-
C(73)-S(4)	116.4(2)	C(73)-C(74)-C(75)	
118.9(3)	C(73)-C(74)-H(74)	120.6	C(75)-
C(74)-H(74)	120.6	C(76)-C(75)-C(74)	
119.4(4)	C(76)-C(75)-H(75)	120.3	C(74)-
C(75)-H(75)	120.3	C(75)-C(76)-C(77)	
121.4(4)	C(75)-C(76)-H(76)	119.3	C(77)-
C(76)-H(76)	119.3	C(76)-C(77)-C(78)	
119.9(4)	C(76)-C(77)-H(77)	120.1	C(78)-
C(77)-H(77)	120.1	C(73)-C(78)-C(77)	
118.6(3)	C(73)-C(78)-H(78)	120.7	C(77)-
C(78)-H(78)	120.7	F(8)-C(79)-F(7)	
109.6(5)	F(8)-C(79)-F(9)	109.6(4)	F(7)-
C(79)-F(9)	108.0(4)	F(8)-C(79)-S(5)	
110.6(3)	F(7)-C(79)-S(5)	109.9(3)	F(9)-
C(79)-S(5)	109.1(4)	F(11)-C(80)-F(12)	
109.6(4)	F(11)-C(80)-F(10)	109.1(3)	F(12)-
C(80)-F(10)	107.8(3)	F(11)-C(80)-S(6)	
111.1(3)	F(12)-C(80)-S(6)	111.1(3)	F(10)-
C(80)-S(6)	108.0(3)	C(219)-N(20)-C(223)	
112.3(3)	C(219)-N(20)-C(221)	113.2(4)	C(223)-
N(20)-C(221)	113.1(3)	C(219)-N(20)-H(20)	105.8
C(223)-N(20)-H(20)	105.8	C(221)-N(20)-H(20)	105.8
C(219)-C(23A)-H(23A)	109.5	C(219)-C(23A)-H(23B)	109.5
H(23A)-C(23A)-H(23B)	109.5	C(219)-C(23A)-H(23C)	109.5
H(23A)-C(23A)-H(23C)	109.5	H(23B)-C(23A)-H(23C)	109.5

C(219)-C(23B)-H(23D)	109.5	C(219)-C(23B)-H(23E)	109.5
H(23D)-C(23B)-H(23E)	109.5	C(219)-C(23B)-H(23F)	109.5
H(23D)-C(23B)-H(23F)	109.5	H(23E)-C(23B)-H(23F)	109.5
C(221)-C(23C)-H(23G)	109.5	C(221)-C(23C)-H(23H)	109.5
H(23G)-C(23C)-H(23H)	109.5	C(221)-C(23C)-H(23I)	109.5
H(23G)-C(23C)-H(23I)	109.5	H(23H)-C(23C)-H(23I)	109.5
C(221)-C(23D)-H(23J)	109.5	C(221)-C(23D)-H(23K)	109.5
H(23J)-C(23D)-H(23K)	109.5	C(221)-C(23D)-H(23L)	109.5
H(23J)-C(23D)-H(23L)	109.5	H(23K)-C(23D)-H(23L)	109.5
N(20)-C(219)-C(23A)	112.7(5)	N(20)-C(219)-C(23B)	
115.9(5)	N(20)-C(219)-H(21C)	108.3	C(23B)-
C(219)-H(21C)	108.3	N(20)-C(219)-H(21D)	108.3
C(23B)-C(219)-H(21D)	108.3	H(21C)-C(219)-H(21D)	107.4
N(20)-C(219)-H(21A)	109.0	C(23A)-C(219)-H(21A)	109.0
N(20)-C(219)-H(21B)	109.0	C(23A)-C(219)-H(21B)	109.0
H(21A)-C(219)-H(21B)	107.8	C(23C)-C(221)-N(20)	
123.1(6)	N(20)-C(221)-C(23D)	105.7(6)	C(23C)-
C(221)-H(22C)	106.6	N(20)-C(221)-H(22C)	106.6
C(23C)-C(221)-H(22D)	106.6	N(20)-C(221)-H(22D)	106.6
H(22C)-C(221)-H(22D)	106.5	N(20)-C(221)-H(22A)	110.6
C(23D)-C(221)-H(22A)	110.6	N(20)-C(221)-H(22B)	110.6
C(23D)-C(221)-H(22B)	110.6	H(22A)-C(221)-H(22B)	108.7
C(224)-C(223)-N(20)	112.8(3)	C(224)-C(223)-H(22E)	109.0
N(20)-C(223)-H(22E)	109.0	C(224)-C(223)-H(22F)	109.0
N(20)-C(223)-H(22F)	109.0	H(22E)-C(223)-H(22F)	107.8
C(223)-C(224)-H(22G)	109.5	C(223)-C(224)-H(22H)	109.5
H(22G)-C(224)-H(22H)	109.5	C(223)-C(224)-H(22I)	109.5
H(22G)-C(224)-H(22I)	109.5	H(22H)-C(224)-H(22I)	109.5
C(22A)-N(19)-C(213)	124.9(4)	C(22A)-N(19)-C(215)	
107.5(4)	C(213)-N(19)-C(215)	106.7(3)	C(213)-
N(19)-C(22B)	92.1(4)	C(215)-N(19)-C(22B)	
144.4(5)	C(213)-N(19)-H(19A)	102.5	C(215)-
N(19)-H(19A)	102.5	C(22B)-N(19)-H(19A)	102.5
N(19)-C(22A)-C(22D)	109.0(6)	N(19)-C(22A)-H(22J)	109.9
C(22D)-C(22A)-H(22J)	109.9	N(19)-C(22A)-H(22K)	109.9
C(22D)-C(22A)-H(22K)	109.9	H(22J)-C(22A)-H(22K)	108.3
C(22C)-C(22B)-N(19)	109.6(7)	C(22C)-C(22B)-H(22L)	109.7
N(19)-C(22B)-H(22L)	109.7	C(22C)-C(22B)-H(22M)	109.7

N(19)-C(22B)-H(22M)	109.7	H(22L)-C(22B)-H(22M)	108.2
C(22B)-C(22C)-H(22N)	109.5	C(22B)-C(22C)-H(22O)	109.5
H(22N)-C(22C)-H(22O)	109.5	C(22B)-C(22C)-H(22P)	109.5
H(22N)-C(22C)-H(22P)	109.5	H(22O)-C(22C)-H(22P)	109.5
C(22A)-C(22D)-H(22Q)	109.5	C(22A)-C(22D)-H(22R)	109.5
H(22Q)-C(22D)-H(22R)	109.5	C(22A)-C(22D)-H(22S)	109.5
H(22Q)-C(22D)-H(22S)	109.5	H(22R)-C(22D)-H(22S)	109.5
N(19)-C(213)-C(214)	115.2(3)	N(19)-C(213)-H(21E)	108.5
C(214)-C(213)-H(21E)	108.5	N(19)-C(213)-H(21F)	108.5
C(214)-C(213)-H(21F)	108.5	H(21E)-C(213)-H(21F)	107.5
C(213)-C(214)-H(21G)	109.5	C(213)-C(214)-H(21H)	109.5
H(21G)-C(214)-H(21H)	109.5	C(213)-C(214)-H(21I)	109.5
H(21G)-C(214)-H(21I)	109.5	H(21H)-C(214)-H(21I)	109.5
C(216)-C(215)-N(19)	115.1(5)	C(216)-C(215)-H(21J)	108.5
N(19)-C(215)-H(21J)	108.5	C(216)-C(215)-H(21K)	108.5
N(19)-C(215)-H(21K)	108.5	H(21J)-C(215)-H(21K)	107.5
C(215)-C(216)-H(21L)	109.5	C(215)-C(216)-H(21M)	109.5
H(21L)-C(216)-H(21M)	109.5	C(215)-C(216)-H(21N)	109.5
H(21L)-C(216)-H(21N)	109.5	H(21M)-C(216)-H(21N)	109.5
C(21B)-N(18)-C(207)	102.5(5)	C(21B)-N(18)-C(209)	
121.0(5)	C(207)-N(18)-C(209)	114.3(4)	C(207)-
N(18)-C(21A)	120.5(5)	C(209)-N(18)-C(21A)	
102.9(5)	C(207)-N(18)-H(18A)	106.0	C(209)-
N(18)-H(18A)	106.0	C(21A)-N(18)-H(18A)	106.0
C(21C)-C(21A)-N(18)	119.3(9)	C(21C)-C(21A)-H(21O)	107.5
N(18)-C(21A)-H(21O)	107.5	C(21C)-C(21A)-H(21P)	107.5
N(18)-C(21A)-H(21P)	107.5	H(21O)-C(21A)-H(21P)	107.0
C(21D)-C(21B)-N(18)	139.6(11)	C(21D)-C(21B)-H(21Q)	102.2
N(18)-C(21B)-H(21Q)	102.2	C(21D)-C(21B)-H(21R)	102.2
N(18)-C(21B)-H(21R)	102.2	H(21Q)-C(21B)-H(21R)	104.8
C(21A)-C(21C)-H(21S)	109.5	C(21A)-C(21C)-H(21T)	109.5
H(21S)-C(21C)-H(21T)	109.5	C(21A)-C(21C)-H(21U)	109.5
H(21S)-C(21C)-H(21U)	109.5	H(21T)-C(21C)-H(21U)	109.5
C(21B)-C(21D)-H(21V)	109.5	C(21B)-C(21D)-H(21W)	
109.5	H(21V)-C(21D)-H(21W)	109.5	C(21B)-
C(21D)-H(21X)	109.5	H(21V)-C(21D)-H(21X)	109.5
H(21W)-C(21D)-H(21X)	109.5	N(18)-C(207)-C(208)	
112.8(4)	N(18)-C(207)-H(20A)	109.0	C(208)-

C(207)-H(20A)	109.0	N(18)-C(207)-H(20B)	109.0
C(208)-C(207)-H(20B)	109.0	H(20A)-C(207)-H(20B)	107.8
C(207)-C(208)-H(20C)	109.5	C(207)-C(208)-H(20D)	109.5
H(20C)-C(208)-H(20D)	109.5	C(207)-C(208)-H(20E)	109.5
H(20C)-C(208)-H(20E)	109.5	H(20D)-C(208)-H(20E)	109.5
N(18)-C(209)-C(210)	112.9(4)	N(18)-C(209)-H(20F)	109.0
C(210)-C(209)-H(20F)	109.0	N(18)-C(209)-H(20G)	109.0
C(210)-C(209)-H(20G)	109.0	H(20F)-C(209)-H(20G)	107.8
C(209)-C(210)-H(21Y)	109.5	C(209)-C(210)-H	109.5
H(21Y)-C(210)-H	109.5	C(209)-C(210)-HA	109.5
H(21Y)-C(210)-HA	109.5	H-C(210)-HA	109.5
C(205)-N(17)-C(203)	113.5(3)	C(205)-N(17)-C(201)	
111.8(3)	C(203)-N(17)-C(201)	111.5(3)	C(205)-
N(17)-H(17A)	106.5	C(203)-N(17)-H(17A)	106.5
C(201)-N(17)-H(17A)	106.5	C(202)-C(201)-N(17)	
112.7(3)	C(202)-C(201)-H(20H)	109.1	N(17)-
C(201)-H(20H)	109.1	C(202)-C(201)-H(20I)	109.1
N(17)-C(201)-H(20I)	109.1	H(20H)-C(201)-H(20I)	107.8
C(201)-C(202)-H(20J)	109.5	C(201)-C(202)-H(20K)	109.5
H(20J)-C(202)-H(20K)	109.5	C(201)-C(202)-H(20L)	109.5
H(20J)-C(202)-H(20L)	109.5	H(20K)-C(202)-H(20L)	109.5
N(17)-C(203)-C(204)	113.2(3)	N(17)-C(203)-H(20M)	108.9
C(204)-C(203)-H(20M)	108.9	N(17)-C(203)-H(20N)	108.9
C(204)-C(203)-H(20N)	108.9	H(20M)-C(203)-H(20N)	107.7
C(203)-C(204)-H(20O)	109.5	C(203)-C(204)-H(20P)	109.5
H(20O)-C(204)-H(20P)	109.5	C(203)-C(204)-H(20Q)	109.5
H(20O)-C(204)-H(20Q)	109.5	H(20P)-C(204)-H(20Q)	109.5
N(17)-C(205)-C(206)	114.2(3)	N(17)-C(205)-H(20R)	108.7
C(206)-C(205)-H(20R)	108.7	N(17)-C(205)-H(20S)	108.7
C(206)-C(205)-H(20S)	108.7	H(20R)-C(205)-H(20S)	107.6
C(205)-C(206)-H(20T)	109.5	C(205)-C(206)-H(20U)	109.5
H(20T)-C(206)-H(20U)	109.5	C(205)-C(206)-H(20V)	109.5
H(20T)-C(206)-H(20V)	109.5	H(20U)-C(206)-H(20V)	109.5

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7.9.5 X-Ray Data for IDPii-3

Table 1. Crystal data and structure refinement.

Identification code	12396	
Empirical formula	$C_{92}\ H_{59}\ Cl_{0.50}\ F_{12}\ N_7\ O_{12}\ P_2\ S_6$	
Color	colourless	
Formula weight	1954.48 $g \cdot mol^{-1}$	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*1, (No. 1)	
Unit cell dimensions	a = 14.783(20) Å	α= 81.89(6)°.
	b = 14.837(6) Å	β= 83.33(10)°.
	c = 26.61(4) Å	γ = 64.16(5)°.
Volume	5190(10) $Å^3$	
Z	2	
Density (calculated)	1.251 $Mg \cdot m^{-3}$	
Absorption coefficient	0.254 mm^{-1}	
F(000)	1997 e	
Crystal size	0.17 x 0.07 x 0.05 mm^3	
θ range for data collection	2.652 to 28.282°.	
Index ranges	$-19 \le h \le 19$, $-19 \le k \le 18$, $-35 \le l \le 35$	
Reflections collected	71895	
Independent reflections	47055 [R_{int} = 0.0946]	
Reflections with I>2σ(I)	23430	
Completeness to θ = 25.242°	99.7 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.98904 and 0.96993	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	47055 / 3 / 1494	
Goodness-of-fit on F^2	1.013	
Final R indices [I>2σ(I)]	R_1 = 0.1250	wR^2 = 0.2879
R indices (all data)	R_1 = 0.2152	wR^2 = 0.3501
Absolute structure parameter	0.07(7)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.194 and -0.838 $e \cdot Å^{-3}$	
Additional comments	Solvent mask (SQUEEZE) was used	

Table 2. Bond lengths [Å] and angles [°].

S(8)-N(13)	1.582(11)	S(8)-N(9)	1.537(12)
S(8)-N(14)	1.778(14)	P(3)-O(13)	1.570(9)
P(3)-O(14)	1.527(12)	P(3)-N(10)	1.612(12)
S(7)-N(12)	1.549(12)	S(7)-N(10)	1.500(11)
S(7)-C(169)	1.548(12)	S(1)-N(2)	1.537(12)
S(1)-N(7)	1.773(14)	S(11)-O(22)	1.408(11)
S(11)-O(21)	1.581(12)	S(11)-C(184)	1.802(18)
P(2)-O(2)	1.561(10)	P(2)-N(1)	1.545(12)
P(2)-N(2)	1.585(10)	P(4)-O(16)	1.595(10)
P(4)-N(8)	1.559(12)	S(9)-O(17)	1.451(10)
S(9)-N(11)	1.407(10)	S(9)-C(181)	1.830(19)
P(1)-O(3)	1.604(9)	P(1)-N(3)	1.587(12)
P(1)-N(1)	1.522(13)	S(2)-C(77)	1.782(14)
S(2)-N(5)	1.576(13)	S(2)-N(4)	1.423(11)
S(4)-O(6)	1.595(11)	S(4)-C(92)	1.814(17)
S(10)-N(12)	1.447(10)	S(10)-O(19)	1.401(12)
S(10)-C(182)	1.411(11)	S(12)-O(24)	1.597(11)
S(12)-N(13)	1.422(10)	S(12)-C(183)	1.845(16)
S(6)-O(11)			

1.411(13)	S(6)-O(12)	1.435(10)	S(6)-
N(5)	1.602(12)	S(6)-C(90)	
1.814(17)	S(3)-O(7)	1.433(11)	S(3)-
N(6)	1.583(12)	S(3)-C(91)	
1.863(17)	S(3)-O(8)	1.440(13)	S(5)-
O(9)	1.449(15)	S(5)-N(4)	
1.591(14)	S(5)-O(10)	1.432(14)	S(5)-
C(89)	1.80(2)	O(15)-C(128)	
1.392(16)	O(13)-C(93)	1.412(15)	O(14)-
C(96)	1.430(15)	O(2)-C(1)	
1.401(15)	O(1)-C(18)	1.396(15)	O(16)-
C(125)	1.419(15)	O(3)-C(33)	
1.435(15)	F(6)-C(92)	1.328(18)	F(11)-
C(90)	1.331(18)	O(4)-C(36)	
1.421(16)	F(17)-C(181)	1.34(2)	F(23)-
C(184)	1.355(19)	F(22)-C(184)	
1.359(19)	F(10)-C(90)	1.315(19)	F(19)-
C(183)	1.305(18)	N(8)-H(8)	0.8800
F(5)-C(92)	1.309(18)	F(13)-C(182)	1.31(2)
F(12)-C(90)	1.35(2)	F(20)-C(183)	
1.340(18)	F(24)-C(184)	1.298(18)	F(18)-
C(181)	1.25(2)	F(4)-C(92)	
1.346(19)	F(21)-C(183)	1.291(18)	F(3)-
C(91)	1.30(2)	F(14)-C(182)	1.29(2)
C(140)-C(141)	1.435(18)	C(140)-C(139)	
1.395(17)	C(140)-C(126)	1.452(19)	C(6)-
C(1)	1.447(17)	C(6)-C(5)	
1.387(17)	C(6)-C(7)	1.426(19)	C(45)-
C(37)	1.52(2)	C(45)-C(50)	1.34(2)
C(45)-C(46)	1.42(2)	C(129)-C(130)	
1.323(19)	C(129)-C(128)	1.464(18)	C(129)-
C(151)	1.489(19)	C(83)-C(81)	
1.492(19)	C(83)-C(88)	1.41(2)	C(83)-
C(84)	1.378(19)	C(97)-C(120)	
1.472(17)	C(97)-C(98)	1.373(19)	C(97)-
C(96)	1.419(18)	F(16)-C(181)	1.36(2)
F(15)-C(182)	1.36(2)	C(141)-H(141)	0.9500
C(141)-C(142)	1.396(19)	C(53)-C(54)	

1.409(19)	C(53)-C(52)	1.44(2)	C(53)-
C(58)	1.436(19)	C(173)-C(175)	
1.511(19)	C(173)-C(172)	1.342(19)	C(173)-
C(174)	1.44(2)	C(105)-C(113)	1.47(2)
C(105)-C(93)	1.431(19)	C(105)-C(106)	
1.345(19)	C(99)-C(100)	1.417(19)	C(99)-
C(98)	1.366(19)	C(99)-C(104)	1.47(2)
C(1)-C(2)	1.382(17)	N(1)-H(1)	0.8800
C(77)-C(82)	1.378(19)	C(77)-C(78)	
1.369(19)	C(81)-C(82)	1.397(18)	C(81)-
C(80)	1.368(19)	C(26)-H(26)	0.9500
C(26)-C(21)	1.425(18)	C(26)-C(25)	
1.366(19)	C(130)-H(130)	0.9500	C(130)-
C(131)	1.375(19)	C(120)-C(119)	
1.392(19)	C(120)-C(121)	1.361(19)	F(9)-
C(89)	1.37(2)	C(128)-C(127)	
1.364(18)	C(70)-H(70)	0.9500	C(70)-
C(65)	1.407(18)	C(70)-C(69)	1.37(2)
C(119)-H(119)	0.9500	C(119)-C(124)	
1.377(19)	F(2)-C(91)	1.320(19)	C(100)-
C(95)	1.433(18)	C(100)-C(101)	
1.445(18)	C(108)-C(94)	1.408(18)	C(108)-
C(107)	1.400(19)	C(108)-C(109)	
1.455(18)	C(4)-C(3)	1.439(19)	C(4)-
C(5)	1.382(18)	C(4)-C(13)	1.45(2)
F(1)-C(91)	1.35(2)	C(143)-H(143)	0.9500
C(143)-C(142)	1.399(18)	C(143)-C(144)	
1.375(19)	C(169)-C(174)	1.346(19)	C(169)-
C(170)	1.379(19)	C(51)-C(33)	
1.407(19)	C(51)-C(52)	1.368(19)	C(51)-
C(59)	1.52(2)	C(3)-C(2)	
1.424(18)	C(3)-C(16)	1.417(19)	C(151)-
C(152)	1.40(2)	C(151)-C(156)	1.41(2)
C(54)-C(55)	1.42(2)	C(54)-C(34)	
1.443(19)	C(163)-C(159)	1.468(19)	C(163)-
C(164)	1.42(2)	C(163)-C(168)	1.45(2)
C(175)-C(180)	1.33(2)	C(175)-C(176)	1.39(2)
C(137)-C(145)	1.488(19)	C(137)-C(125)	

1.433(17)	C(137)-C(138)	1.404(19)	C(5)-
H(5)	0.9500	C(145)-C(150)	1.39(2)
C(145)-C(146)	1.38(2)	C(21)-C(22)	
1.447(19)	C(21)-C(20)	1.408(19)	F(8)-
C(89)	1.34(3)	C(162)-H(162)	0.9500
C(162)-C(157)	1.38(2)	C(162)-C(161)	1.40(2)
F(7)-C(89)	1.31(2)	C(17)-C(22)	
1.397(17)	C(17)-C(2)	1.505(18)	C(17)-
C(18)	1.403(18)	C(152)-H(152)	0.9500
C(152)-C(153)	1.39(2)	C(94)-C(93)	
1.397(19)	C(94)-C(95)	1.513(18)	C(125)-
C(126)	1.365(18)	C(82)-H(82)	0.9500
C(37)-C(38)	1.36(2)	C(37)-C(36)	1.38(2)
C(114)-H(114)	0.9500	C(114)-C(113)	1.42(2)
C(114)-C(115)	1.38(2)	C(22)-C(23)	
1.432(18)	C(87)-H(87)	0.9500	C(87)-
C(88)	1.35(2)	C(87)-C(86)	1.44(2)
C(40)-C(35)	1.44(2)	C(40)-C(39)	1.46(2)
C(40)-C(41)	1.42(2)	C(98)-H(98)	0.9500
C(23)-H(23)	0.9500	C(23)-C(24)	
1.345(18)	C(80)-H(80)	0.9500	C(80)-
C(79)	1.40(2)	C(142)-H(142)	0.9500
C(139)-C(138)	1.391(18)	C(139)-C(144)	1.45(2)
C(35)-C(36)	1.374(18)	C(35)-C(34)	1.42(2)
C(79)-H(79)	0.9500	C(79)-C(78)	1.37(2)
C(38)-H(38)	0.9500	C(38)-C(39)	1.44(2)
C(157)-C(158)	1.390(18)	C(39)-C(44)	1.38(2)
C(12)-H(12)	0.9500	C(12)-C(7)	1.46(2)
C(12)-C(11)	1.33(2)	C(172)-H(172)	0.9500
C(172)-C(171)	1.36(2)	C(121)-H(121)	0.9500
C(121)-C(122)	1.35(2)	C(68)-H(68)	0.9500
C(68)-C(67)	1.40(2)	C(68)-C(69)	1.38(2)
C(78)-H(78)	0.9500	C(159)-C(158)	
1.414(18)	C(159)-C(160)	1.372(19)	C(158)-
H(158)	0.9500	C(150)-H(150)	0.9500
C(150)-C(149)	1.42(2)	C(104)-H(104)	0.9500
C(104)-C(103)	1.40(2)	C(33)-C(34)	1.40(2)
C(7)-C(8)	1.43(2)	C(65)-C(66)	

1.375(19)	C(50)-H(50)	0.9500	C(50)-
C(49)	1.40(2)	C(88)-H(88)	0.9500
C(138)-H(138)	0.9500	C(113)-C(118)	1.40(2)
C(24)-H(24)	0.9500	C(24)-C(25)	1.43(2)
C(126)-C(127)	1.482(18)	C(52)-H(52)	0.9500
C(127)-C(132)	1.435(18)	C(156)-H(156)	0.9500
C(156)-C(155)	1.36(2)	C(174)-H(174)	0.9500
C(103)-H(103)	0.9500	C(103)-C(102)	1.40(2)
C(131)-C(132)	1.439(19)	C(131)-C(136)	1.43(2)
C(102)-H(102)	0.9500	C(102)-C(101)	1.37(2)
C(59)-C(60)	1.359(19)	C(59)-C(64)	1.41(2)
C(67)-H(67)	0.9500	C(67)-C(66)	1.34(2)
C(60)-H(60)	0.9500	C(60)-C(61)	1.40(2)
C(180)-H(180)	0.9500	C(180)-C(179)	1.40(2)
C(46)-H(46)	0.9500	C(46)-C(47)	1.36(2)
C(49)-H(49)	0.9500	C(49)-C(48)	1.41(2)
C(20)-H(20)	0.9500	C(20)-C(19)	
1.376(18)	C(160)-H(160)	0.9500	C(160)-
C(161)	1.39(2)	C(55)-H(55)	0.9500
C(55)-C(56)	1.331(19)	C(58)-H(58)	0.9500
C(58)-C(57)	1.38(2)	C(170)-H(170)	0.9500
C(170)-C(171)	1.44(2)	C(96)-C(95)	
1.375(17)	C(18)-C(19)	1.471(19)	C(112)-
H(112)	0.9500	C(112)-C(107)	1.42(2)
C(112)-C(111)	1.34(2)	C(69)-C(71)	1.52(2)
C(25)-H(25)	0.9500	C(164)-H(164)	0.9500
C(164)-C(165)	1.42(2)	C(115)-H(115)	0.9500
C(115)-C(116)	1.38(3)	C(124)-H(124)	0.9500
C(124)-C(123)	1.38(2)	C(107)-C(106)	1.42(2)
C(132)-C(133)	1.43(2)	C(27)-C(19)	1.46(2)
C(27)-C(28)	1.37(2)	C(27)-C(32)	1.41(2)
C(57)-H(57)	0.9500	C(57)-C(56)	1.40(2)
C(71)-C(72)	1.38(2)	C(71)-C(76)	1.36(2)
C(14)-H(14)	0.9500	C(14)-C(13)	1.29(2)
C(14)-C(15)	1.42(2)	C(144)-H(144)	0.9500
C(133)-H(133)	0.9500	C(133)-C(134)	1.41(2)
C(161)-H(161)	0.9500	C(171)-H(171)	0.9500
C(106)-H(106)	0.9500	C(146)-H(146)	0.9500

C(146)-C(147)	1.44(2)	C(134)-H(134)	0.9500
C(134)-C(135)	1.45(2)	C(56)-H(56)	0.9500
C(118)-H(118)	0.9500	C(118)-C(117)	1.40(3)
C(86)-H(86)	0.9500	C(86)-C(85)	1.35(2)
C(136)-H(136)	0.9500	C(136)-C(135)	1.33(2)
C(147)-H(147)	0.9500	C(147)-C(148)	1.35(2)
C(64)-H(64)	0.9500	C(64)-C(63)	1.40(2)
C(61)-H(61)	0.9500	C(61)-C(62)	1.41(2)
C(178)-H(178)	0.9500	C(178)-C(179)	1.35(2)
C(178)-C(177)	1.34(3)	C(109)-H(109)	0.9500
C(109)-C(110)	1.342(19)	C(28)-H(28)	0.9500
C(28)-C(29)	1.41(3)	C(66)-H(66)	0.9500
C(123)-H(123)	0.9500	C(123)-C(122)	1.38(2)
C(101)-H(101)	0.9500	C(149)-H(149)	0.9500
C(149)-C(148)	1.38(2)	C(42)-H(42)	0.9500
C(42)-C(41)	1.35(2)	C(42)-C(43)	1.40(2)
C(168)-H(168)	0.9500	C(168)-C(167)	1.39(2)
C(13)-H(13)	0.9500	C(41)-H(41)	0.9500
C(148)-H(148)	0.9500	C(111)-H(111)	0.9500
C(111)-C(110)	1.41(2)	C(122)-H(122)	0.9500
C(32)-H(32)	0.9500	C(32)-C(31)	1.41(3)
C(16)-H(16)	0.9500	C(16)-C(15)	1.36(2)
C(135)-H(135)	0.9500	C(62)-H(62)	0.9500
C(62)-C(63)	1.34(2)	C(154)-H(154)	0.9500
C(154)-C(153)	1.36(3)	C(154)-C(155)	1.42(3)
C(11)-H(11)	0.9500	C(11)-C(10)	1.44(3)
C(47)-H(47)	0.9500	C(47)-C(48)	1.42(2)
C(166)-H(166)	0.9500	C(166)-C(167)	1.25(2)
C(166)-C(165)	1.41(2)	C(176)-H(176)	0.9500
C(176)-C(177)	1.37(2)	C(153)-H(153)	0.9500
C(179)-H(179)	0.9500	C(15)-H(15)	0.9500
C(63)-H(63)	0.9500	C(48)-H(48)	0.9500
C(177)-H(177)	0.9500	C(9)-H(9)	0.9500
C(9)-C(10)	1.35(3)	C(9)-C(8)	1.43(3)
C(117)-H(117)	0.9500	C(117)-C(116)	1.37(3)
C(10)-H(10)	0.9500	C(74)-H(74)	0.9500
C(74)-C(73)	1.43(2)	C(74)-C(75)	1.36(2)
C(110)-H(110)	0.9500	C(84)-H(84)	0.9500

C(84)-C(85)	1.41(2)	C(44)-H(44)	0.9500
C(44)-C(43)	1.40(2)	C(8)-H(8A)	0.9500
C(85)-H(85)	0.9500	C(73)-H(73)	0.9500
C(73)-C(72)	1.37(2)	C(155)-H(155)	0.9500
C(72)-H(72)	0.9500	C(29)-H(29)	0.9500
C(29)-C(30)	1.35(3)	C(116)-H(116)	0.9500
C(43)-H(43)	0.9500	C(30)-H(30)	0.9500
C(30)-C(31)	1.35(3)	C(76)-H(76)	0.9500
C(76)-C(75)	1.38(2)	C(167)-H(167)	0.9500
C(75)-H(75)	0.9500	C(31)-H(31)	0.9500
C(165)-H(165)	0.9500	Cl(1)-C(186)	2.05(6)
Cl(2)-C(185)	1.45(3)	Cl(2)-Cl(4)	2.32(4)
C(2AA)-C(1BA)	1.47(3)	C(2AA)-C(3AA)	1.51(4)
C(185)-Cl(4)	1.31(4)	C(186)-Cl(3)	1.61(5)
C(1BA)-C(2BA)	1.47(3)	C(0BA)-C(3AA)	1.46(4)

N(13)-S(8)-C(157)	109.3(6)	N(9)-S(8)-N(13)	
109.4(6)	N(9)-S(8)-N(14)	116.0(6)	N(9)-
S(8)-C(157)	103.3(6)	N(14)-S(8)-N(13)	
107.9(6)	N(14)-S(8)-C(157)	110.9(6)	O(13)-
P(3)-O(14)	104.3(5)	O(13)-P(3)-N(10)	
111.4(5)	O(14)-P(3)-N(10)	108.0(5)	N(8)-
P(3)-O(13)	106.2(6)	N(8)-P(3)-O(14)	
113.0(6)	N(8)-P(3)-N(10)	113.6(6)	N(12)-
S(7)-N(11)	106.7(6)	N(12)-S(7)-C(169)	
111.6(6)	N(11)-S(7)-C(169)	109.1(6)	N(10)-
S(7)-N(12)	110.0(6)	N(10)-S(7)-N(11)	
116.7(6)	N(10)-S(7)-C(169)	102.8(7)	N(6)-
S(1)-N(7)	107.3(6)	N(6)-S(1)-C(65)	
111.7(6)	N(2)-S(1)-N(6)	119.1(7)	N(2)-
S(1)-N(7)	108.6(7)	N(2)-S(1)-C(65)	
101.6(7)	N(7)-S(1)-C(65)	107.9(7)	O(22)-
S(11)-N(14)	114.2(6)	O(22)-S(11)-C(184)	
104.6(7)	O(21)-S(11)-O(22)	118.8(7)	O(21)-
S(11)-N(14)	113.0(6)	O(21)-S(11)-C(184)	
103.9(8)	N(14)-S(11)-C(184)	99.4(7)	O(1)-
P(2)-O(2)	104.1(5)	N(1)-P(2)-O(2)	
106.0(6)	N(1)-P(2)-O(1)	110.7(6)	N(2)-

P(2)-O(2)	111.6(7)	N(2)-P(2)-O(1)	
109.1(6)	N(2)-P(2)-N(1)	114.8(7)	O(15)-
P(4)-O(16)	104.5(5)	N(8)-P(4)-O(15)	
106.6(5)	N(8)-P(4)-O(16)	111.3(5)	N(8)-
P(4)-N(9)	113.1(6)	N(9)-P(4)-O(15)	
113.9(5)	N(9)-P(4)-O(16)	107.2(5)	O(17)-
S(9)-N(11)	112.1(6)	O(17)-S(9)-C(181)	
100.7(8)	N(11)-S(9)-C(181)	101.6(7)	O(18)-
S(9)-O(17)	120.9(7)	O(18)-S(9)-N(11)	
114.8(6)	O(18)-S(9)-C(181)	103.0(9)	O(3)-
P(1)-O(4)	105.1(5)	N(3)-P(1)-O(3)	
108.1(5)	N(3)-P(1)-O(4)	110.1(5)	N(1)-
P(1)-O(3)	111.4(6)	N(1)-P(1)-O(4)	
105.8(6)	N(1)-P(1)-N(3)	115.8(6)	N(3)-
S(2)-C(77)	102.8(6)	N(3)-S(2)-N(5)	
118.5(7)	N(3)-S(2)-N(4)	108.6(6)	N(5)-
S(2)-C(77)	109.2(7)	N(5)-S(2)-N(4)	
107.0(6)	N(4)-S(2)-C(77)	110.7(7)	O(5)-
S(4)-O(6)	118.9(7)	O(5)-S(4)-N(7)	
108.5(7)	O(5)-S(4)-C(92)	102.5(7)	O(6)-
S(4)-N(7)	114.8(6)	O(6)-S(4)-C(92)	
105.6(8)	N(7)-S(4)-C(92)	104.7(7)	N(12)-
S(10)-C(182)	104.8(8)	O(20)-S(10)-N(12)	
114.7(6)	O(20)-S(10)-C(182)	103.0(8)	O(19)-
S(10)-N(12)	109.8(6)	O(19)-S(10)-O(20)	
119.5(7)	O(19)-S(10)-C(182)	102.9(8)	O(23)-
S(12)-N(13)	107.3(7)	O(23)-S(12)-O(24)	
119.0(7)	O(23)-S(12)-C(183)	102.7(7)	N(13)-
S(12)-C(183)	104.2(7)	O(24)-S(12)-N(13)	
116.3(6)	O(24)-S(12)-C(183)	105.4(8)	O(11)-
S(6)-O(12)	117.6(7)	O(11)-S(6)-N(5)	
114.1(7)	O(11)-S(6)-C(90)	108.4(8)	O(12)-
S(6)-N(5)	113.5(7)	O(12)-S(6)-C(90)	
105.4(7)	N(5)-S(6)-C(90)	94.6(8)	O(7)-
S(3)-N(6)	113.9(6)	O(7)-S(3)-C(91)	
104.3(7)	O(7)-S(3)-O(8)	119.6(7)	N(6)-
S(3)-C(91)	96.3(7)	O(8)-S(3)-N(6)	
114.3(7)	O(8)-S(3)-C(91)	104.4(9)	O(9)-

S(5)-N(4) 108.2(8) O(9)-S(5)-C(89) 103.6(11) N(4)-S(5)-C(89) 104.7(9) O(10)-S(5)-O(9) 119.5(9) O(10)-S(5)-N(4) 115.3(7) O(10)-S(5)-C(89) 103.6(11) C(128)-O(15)-P(4) 121.4(9) C(93)-O(13)-P(3) 123.7(9) C(96)-O(14)-P(3) 113.7(8) C(1)-O(2)-P(2) 121.9(8) C(18)-O(1)-P(2) 115.1(8) C(125)-O(16)-P(4) 114.0(7) C(33)-O(3)-P(1) 112.1(7) C(36)-O(4)-P(1) 120.8(8) S(7)-N(12)-S(10) 125.3(7) P(3)-N(8)-P(4) 145.2(8) P(3)-N(8)-H(8) 107.4 P(4)-N(8)-H(8) 107.4 S(8)-N(13)-S(12) 122.8(7) S(8)-N(9)-P(4) 137.5(8) S(7)-N(11)-S(9) 124.0(7) S(2)-N(3)-P(1) 137.6(7) S(7)-N(10)-P(3) 138.2(8) S(1)-N(6)-S(3) 126.8(8) S(8)-N(14)-S(11) 127.6(7) C(141)-C(140)-C(126) 120.6(11) C(139)-C(140)-C(141) 119.7(13) C(139)-C(140)-C(126) 119.5(12) C(5)-C(6)-C(1) 115.2(11) C(5)-C(6)-C(7) 120.1(12) C(7)-C(6)-C(1) 124.7(11) C(50)-C(45)-C(37) 122.8(13) C(50)-C(45)-C(46) 118.5(14) C(46)-C(45)-C(37) 118.6(13) C(130)-C(129)-C(128) 117.9(12) C(130)-C(129)-C(151) 120.7(12) C(128)-C(129)-C(151) 121.3(11) C(88)-C(83)-C(81) 119.6(12) C(84)-C(83)-C(81) 122.8(12) C(84)-C(83)-C(88) 117.6(13) C(98)-C(97)-C(120) 120.6(12) C(98)-C(97)-C(96) 114.4(12) C(96)-C(97)-C(120) 124.8(12) C(140)-C(141)-H(141) 120.5 C(142)-C(141)-C(140) 119.1(12) C(142)-C(141)-H(141) 120.5 C(54)-C(53)-C(52) 120.2(12) C(54)-C(53)-C(58) 120.9(13) C(52)-C(53)-C(58) 118.9(13) C(172)-C(173)-C(175) 124.0(13) C(172)-C(173)-C(174) 117.5(13) C(174)-C(173)-C(175) 118.4(12) C(93)-C(105)-C(113) 122.1(12) C(106)-C(105)-C(113) 121.3(13) C(106)-C(105)-C(93) 116.6(13) C(100)-C(99)-C(104) 120.7(12) C(98)-C(99)-C(100) 118.5(13) C(98)-C(99)-C(104) 120.5(13) O(2)-

C(1)-C(6) 117.9(10) C(2)-C(1)-O(2) 119.1(11) C(2)-C(1)-C(6) 123.1(11) P(2)-N(1)-P(1) 143.4(7) P(2)-N(1)-H(1) 108.3 P(1)-N(1)-H(1) 108.3 C(82)-C(77)-S(2) 117.8(10) C(78)-C(77)-S(2) 120.5(11) C(78)-C(77)-C(82) 121.6(12) C(82)-C(81)-C(83) 120.0(12) C(80)-C(81)-C(83) 122.1(12) C(80)-C(81)-C(82) 117.8(13) C(21)-C(26)-H(26) 119.8 C(25)-C(26)-H(26) 119.8 C(25)-C(26)-C(21) 120.4(13) S(2)-N(5)-S(6) 121.6(8) C(129)-C(130)-H(130) 117.9 C(129)-C(130)-C(131) 124.3(13) C(131)-C(130)-H(130) 117.9 C(119)-C(120)-C(97) 122.1(12) C(121)-C(120)-C(97) 120.1(12) C(121)-C(120)-C(119) 117.4(12) F(19)-C(183)-S(12) 110.7(11) F(19)-C(183)-F(20) 107.5(13) F(20)-C(183)-S(12) 109.1(11) F(21)-C(183)-S(12) 111.9(11) F(21)-C(183)-F(19) 110.3(14) F(21)-C(183)-F(20) 107.2(14) O(15)-C(128)-C(129) 119.1(11) C(127)-C(128)-O(15) 119.8(11) C(127)-C(128)-C(129) 120.9(12) C(65)-C(70)-H(70) 120.8 C(69)-C(70)-H(70) 120.8 C(69)-C(70)-C(65) 118.4(13) C(120)-C(119)-H(119) 119.9 C(124)-C(119)-C(120) 120.3(13) C(124)-C(119)-H(119) 119.9 C(99)-C(100)-C(95) 119.5(11) C(99)-C(100)-C(101) 117.2(12) C(95)-C(100)-C(101) 123.3(12) C(94)-C(108)-C(109) 122.1(12) C(107)-C(108)-C(94) 119.9(13) C(107)-C(108)-C(109) 117.9(12) C(3)-C(4)-C(13) 117.1(12) C(5)-C(4)-C(3) 120.0(12) C(5)-C(4)-C(13) 122.7(13) C(142)-C(143)-H(143) 120.6 C(144)-C(143)-H(143) 120.6 C(144)-C(143)-C(142) 118.8(14) C(174)-C(169)-S(7) 119.1(11) C(174)-C(169)-C(170) 123.5(14) C(170)-C(169)-S(7) 117.0(11) C(33)-C(51)-C(59) 121.2(12) C(52)-C(51)-C(33) 118.7(14) C(52)-C(51)-C(59) 120.1(13) S(2)-N(4)-S(5) 124.6(8) C(2)-C(3)-C(4) 117.7(11) C(16)-C(3)-C(4) 118.1(12) C(16)-C(3)-C(2) 124.0(13) C(152)-C(151)-C(129) 122.1(12) C(152)-

C(151)-C(156) 116.0(14) C(156)-C(151)-C(129) 121.8(14) C(53)-C(54)-C(55) 117.2(12) C(53)-C(54)-C(34) 119.6(13) C(55)-C(54)-C(34) 123.2(13) C(164)-C(163)-C(159) 122.0(13) C(164)-C(163)-C(168) 119.4(14) C(168)-C(163)-C(159) 118.6(12) C(180)-C(175)-C(173) 121.3(14) C(180)-C(175)-C(176) 119.2(14) C(176)-C(175)-C(173) 119.4(12) C(125)-C(137)-C(145) 124.7(12) C(138)-C(137)-C(145) 120.3(12) C(138)-C(137)-C(125) 115.0(12) C(6)-C(5)-H(5) 118.1 C(4)-C(5)-H(5) 123.8(13) C(4)-C(5)-H(5) 118.1 C(150)-C(145)-C(137) 115.5(13) C(146)-C(145)-C(137) 122.5(13) C(146)-C(145)-C(150) 121.9(14) C(26)-C(21)-C(22) 120.1(13) C(20)-C(21)-C(26) 121.2(13) C(20)-C(21)-C(22) 118.7(12) C(157)-C(162)-H(162) 121.1 C(157)-C(162)-C(161) 117.8(15) C(161)-C(162)-H(162) 121.1 C(22)-C(17)-C(2) 124.0(12) C(22)-C(17)-C(18) 119.0(12) C(18)-C(17)-C(2) 117.0(11) C(151)-C(152)-H(152) 118.5 C(153)-C(152)-C(151) 122.9(14) C(153)-C(152)-H(152) 118.5 S(1)-N(2)-P(2) 137.7(9) C(108)-C(94)-C(95) 122.8(12) C(93)-C(94)-C(108) 118.3(12) C(93)-C(94)-C(95) 118.8(12) O(16)-C(125)-C(137) 116.1(10) C(126)-C(125)-O(16) 116.7(11) C(126)-C(125)-C(137) 127.0(12) C(77)-C(82)-C(81) 119.5(12) C(77)-C(82)-H(82) 120.2 C(81)-C(82)-H(82) 120.2 C(38)-C(37)-C(45) 119.1(14) C(38)-C(37)-C(36) 115.9(13) C(36)-C(37)-C(45) 124.6(13) C(113)-C(114)-H(114) 118.3 C(115)-C(114)-H(114) 118.3 C(115)-C(114)-C(113) 123.4(16) C(17)-C(22)-C(21) 119.9(12) C(17)-C(22)-C(23) 123.2(12) C(23)-C(22)-C(21) 116.5(11) C(1)-C(2)-C(3) 119.6(12) C(1)-C(2)-C(17) 119.9(11) C(3)-C(2)-C(17) 120.4(11) C(88)-C(87)-H(87) 119.6 C(88)-C(87)-C(86) 120.8(15) C(86)-C(87)-H(87) 119.6 C(35)-C(40)-C(39) 120.6(13) C(41)-C(40)-C(35)

124.4(14) C(41)-C(40)-C(39) 114.8(14) C(97)-
C(98)-H(98) 117.3 C(99)-C(98)-C(97)
125.4(14) C(99)-C(98)-H(98) 117.3 C(22)-
C(23)-H(23) 119.1 C(24)-C(23)-C(22)
121.8(13) C(24)-C(23)-H(23) 119.1 C(81)-
C(80)-H(80) 118.5 C(81)-C(80)-C(79)
123.0(13) C(79)-C(80)-H(80) 118.5 C(141)-
C(142)-C(143) 122.3(13) C(141)-C(142)-H(142) 118.9
C(143)-C(142)-H(142) 118.9 C(140)-C(139)-C(144)
118.8(12) C(138)-C(139)-C(140) 122.2(13) C(138)-
C(139)-C(144) 118.7(12) C(36)-C(35)-C(40)
115.4(12) C(36)-C(35)-C(34) 124.4(13) C(34)-
C(35)-C(40) 120.2(12) C(80)-C(79)-H(79) 121.2
C(78)-C(79)-C(80) 117.5(14) C(78)-C(79)-H(79) 121.2
C(37)-C(38)-H(38) 118.3 C(37)-C(38)-C(39)
123.3(15) C(39)-C(38)-H(38) 118.3 C(162)-
C(157)-S(8) 117.9(11) C(162)-C(157)-C(158)
122.7(13) C(158)-C(157)-S(8) 118.7(10) C(38)-
C(39)-C(40) 115.9(14) C(44)-C(39)-C(40)
122.2(14) C(44)-C(39)-C(38) 121.4(15) C(7)-
C(12)-H(12) 118.7 C(11)-C(12)-H(12) 118.7
C(11)-C(12)-C(7) 122.6(15) C(173)-C(172)-H(172) 118.3
C(173)-C(172)-C(171) 123.4(15) C(171)-C(172)-H(172) 118.3
C(120)-C(121)-H(121) 118.2 C(122)-C(121)-C(120)
123.6(15) C(122)-C(121)-H(121) 118.2 C(67)-
C(68)-H(68) 119.4 C(69)-C(68)-H(68) 119.4
C(69)-C(68)-C(67) 121.1(14) C(77)-C(78)-C(79)
120.3(14) C(77)-C(78)-H(78) 119.9 C(79)-
C(78)-H(78) 119.9 C(158)-C(159)-C(163)
119.5(11) C(160)-C(159)-C(163) 121.8(12) C(160)-
C(159)-C(158) 117.9(13) C(157)-C(158)-C(159)
119.1(12) C(157)-C(158)-H(158) 120.5 C(159)-
C(158)-H(158) 120.5 C(145)-C(150)-H(150) 120.6
C(145)-C(150)-C(149) 118.8(15) C(149)-C(150)-H(150) 120.6
C(99)-C(104)-H(104) 121.6 C(103)-C(104)-C(99)
116.8(14) C(103)-C(104)-H(104) 121.6 C(51)-
C(33)-O(3) 120.2(12) C(34)-C(33)-O(3)
116.1(11) C(34)-C(33)-C(51) 123.7(13) S(1)-

N(7)-S(4) 124.7(8) C(6)-C(7)-C(12) 122.2(13) C(6)-C(7)-C(8) 123.0(13) C(8)-C(7)-C(12) 114.7(14) C(70)-C(65)-S(1) 116.2(10) C(66)-C(65)-S(1) 121.8(10) C(66)-C(65)-C(70) 121.9(13) C(45)-C(50)-H(50) 118.7 C(45)-C(50)-C(49) 122.5(15) C(49)-C(50)-H(50) 118.7 C(83)-C(88)-H(88) 119.5 C(87)-C(88)-C(83) 121.0(14) C(87)-C(88)-H(88) 119.5 C(137)-C(138)-H(138) 119.5 C(139)-C(138)-C(137) 120.9(12) C(139)-C(138)-H(138) 119.5 C(114)-C(113)-C(105) 123.1(14) C(118)-C(113)-C(114) 116.5(15) C(118)-C(113)-C(105) 120.2(14) C(25)-C(24)-H(24) 119.3 C(23)-C(24)-H(24) 121.5(14) F(4)-C(92)-S(4) 112.3(11) F(6)-C(92)-F(4) 103.8(13) F(5)-C(92)-S(4) 107.9(13) F(5)-C(92)-F(4) 108.7(13) C(125)-C(126)-C(127) 123.9(11) C(125)-C(126)-C(140) 115.4(11) C(51)-C(52)-H(52) 119.7 C(51)-C(52)-C(53) 120.5(13) C(132)-C(127)-C(126) 118.7(11) C(128)-C(127)-C(132) 118.9(12) C(155)-C(156)-H(156) 118.8 C(155)-C(156)-C(151) 122.3(16) C(169)-C(174)-H(174) 120.3 C(169)-C(174)-C(173) 119.3(13) C(102)-C(103)-H(103) 118.2 C(104)-C(103)-C(102) 123.6(16) C(136)-C(131)-C(132) 118.4(12) C(130)-C(131)-C(136) 124.7(13) C(94)-C(93)-C(105) 119.2(12) O(13)-C(93)-C(105) 120.7 C(94)-C(93)-O(13) 118.2(12) C(101)-C(102)-H(102) 122.7(13) C(101)-C(102)-C(103) 118.5(14) C(64)-C(59)-C(51) 120.7 C(103)-C(60)-C(59)-C(51) 118.6(14) C(60)-C(59)-C(64) 118.3(13) C(68)-

C(67)-H(67) 120.1
C(66)-C(67)-C(68) 119.8(15)
C(66)-C(67)-H(67) 120.1
C(59)-C(60)-H(60) 119.7
C(59)-C(60)-C(61) 120.7(14)
C(61)-C(60)-H(60) 119.7
C(175)-C(180)-H(180) 118.3
C(175)-C(180)-C(179) 123.4(17)
C(179)-C(180)-H(180) 118.3
C(45)-C(46)-H(46) 118.8
C(47)-C(46)-C(45) 122.4(16)
C(47)-C(46)-H(46) 118.8
C(50)-C(49)-H(49) 120.9
C(50)-C(49)-C(48) 118.2(15)
C(48)-C(49)-H(49) 120.9
C(21)-C(20)-H(20) 118.0
C(19)-C(20)-C(21) 124.0(13)
C(19)-C(20)-H(20) 118.0
C(159)-C(160)-H(160) 118.7
C(159)-C(160)-C(161) 122.5(14)
C(161)-C(160)-H(160) 118.7
C(54)-C(55)-H(55) 119.6
C(56)-C(55)-C(54) 120.8(14)
C(56)-C(55)-H(55) 119.6
C(53)-C(58)-H(58) 120.4
C(57)-C(58)-C(53) 119.2(14)
C(57)-C(58)-H(58) 120.4
C(169)-C(170)-H(170) 122.0
C(169)-C(170)-C(171) 116.1(13)
C(171)-C(170)-H(170) 122.0
C(97)-C(96)-O(14) 119.5(10)
C(95)-C(96)-O(14) 115.7(11)
C(95)-C(96)-C(97) 124.7(12)
C(100)-C(95)-C(94) 120.7(11)
C(96)-C(95)-C(100) 117.0(12)
C(96)-C(95)-C(94) 122.2(12)
O(1)-C(18)-C(17) 119.3(11)
O(1)-C(18)-C(19) 117.9(11)
C(17)-C(18)-C(19) 122.7(11)
C(107)-C(112)-H(112) 119.2
C(111)-C(112)-H(112) 119.2
C(111)-C(112)-C(107) 121.6(16)
C(70)-C(69)-C(68) 119.4(13)
C(70)-C(69)-C(71) 119.1(13)
C(68)-C(69)-C(71) 121.4(13)
C(26)-C(25)-C(24) 119.6(13)
C(26)-C(25)-H(25) 120.2
C(24)-C(25)-H(25) 120.2
C(163)-C(164)-H(164) 120.9
C(163)-C(164)-C(165) 118.1(15)
C(165)-C(164)-H(164) 120.9
C(37)-C(36)-O(4) 118.0(11)
C(35)-C(36)-O(4) 114.2(12)
C(35)-C(36)-C(37) 127.8(13)
C(114)-C(115)-H(115) 120.8
C(114)-C(115)-C(116) 118.3(18)
C(116)-C(115)-H(115) 120.8
C(119)-C(124)-H(124) 119.8
C(119)-C(124)-C(123)

120.3(14)	C(123)-C(124)-H(124)	119.8	C(108)-
C(107)-C(112)	119.7(14)	C(108)-C(107)-C(106)	
118.8(13)	C(112)-C(107)-C(106)	121.5(14)	C(127)-
C(132)-C(131)	118.7(12)	C(133)-C(132)-C(127)	
121.7(12)	C(133)-C(132)-C(131)	119.0(12)	C(28)-
C(27)-C(19)	123.9(15)	C(28)-C(27)-C(32)	
117.4(16)	C(32)-C(27)-C(19)	118.5(13)	C(35)-
C(34)-C(54)	122.8(14)	C(33)-C(34)-C(54)	
116.8(13)	C(33)-C(34)-C(35)	120.1(13)	C(20)-
C(19)-C(18)	115.3(13)	C(20)-C(19)-C(27)	
121.5(13)	C(27)-C(19)-C(18)	123.2(12)	C(58)-
C(57)-H(57)	120.9	C(58)-C(57)-C(56)	
118.3(15)	C(56)-C(57)-H(57)	120.9	C(72)-
C(71)-C(69)	121.2(13)	C(76)-C(71)-C(69)	
121.0(13)	C(76)-C(71)-C(72)	117.7(14)	C(13)-
C(14)-H(14)	119.3	C(13)-C(14)-C(15)	
121.3(15)	C(15)-C(14)-H(14)	119.3	C(143)-
C(144)-C(139)	121.3(13)	C(143)-C(144)-H(144)	119.4
C(139)-C(144)-H(144)	119.4	C(132)-C(133)-H(133)	119.7
C(134)-C(133)-C(132)	120.6(14)	C(134)-C(133)-H(133)	119.7
C(162)-C(161)-H(161)	120.1	C(160)-C(161)-C(162)	
119.8(15)	C(160)-C(161)-H(161)	120.1	C(172)-
C(171)-C(170)	119.4(14)	C(172)-C(171)-H(171)	120.3
C(170)-C(171)-H(171)	120.3	C(105)-C(106)-C(107)	
123.4(14)	C(105)-C(106)-H(106)	118.3	C(107)-
C(106)-H(106)	118.3	F(17)-C(181)-S(9)	
110.2(12)	F(17)-C(181)-F(16)	102.7(15)	F(18)-
C(181)-S(9)	112.0(14)	F(18)-C(181)-F(17)	
114.2(17)	F(18)-C(181)-F(16)	109.0(16)	F(16)-
C(181)-S(9)	108.3(13)	C(145)-C(146)-H(146)	121.4
C(145)-C(146)-C(147)	117.3(15)	C(147)-C(146)-H(146)	121.4
C(133)-C(134)-H(134)	120.0	C(133)-C(134)-C(135)	
120.0(16)	C(135)-C(134)-H(134)	120.0	C(55)-
C(56)-C(57)	123.7(16)	C(55)-C(56)-H(56)	118.2
C(57)-C(56)-H(56)	118.2	C(113)-C(118)-H(118)	120.2
C(117)-C(118)-C(113)	119.5(16)	C(117)-C(118)-H(118)	120.2
C(87)-C(86)-H(86)	120.5	C(85)-C(86)-C(87)	
119.0(15)	C(85)-C(86)-H(86)	120.5	C(131)-

C(136)-H(136) 117.2
C(135)-C(136)-C(131) 125.5(14)
C(135)-C(136)-H(136) 119.0
C(146)-C(147)-H(147) 121.9(17)
C(148)-C(147)-C(146) 119.0
C(148)-C(147)-H(147) 119.3
C(59)-C(64)-H(64) 121.3(15)
C(63)-C(64)-C(59) 119.3
C(63)-C(64)-H(64) 120.3
C(60)-C(61)-H(61) 119.3(15)
C(60)-C(61)-C(62) 120.3
C(62)-C(61)-H(61) 118.0
C(179)-C(178)-H(178) 118.0
C(177)-C(178)-C(179) 124.0(19)
C(177)-C(178)-H(178) 120.5
C(108)-C(109)-H(109) 118.9(13)
C(110)-C(109)-H(109) 120.5
C(27)-C(28)-H(28) 119.5
C(27)-C(28)-C(29) 121.1(18)
C(29)-C(28)-H(28) 120.3
C(65)-C(66)-H(66) 119.4(13)
C(67)-C(66)-C(65) 120.3
C(67)-C(66)-H(66) 120.5
C(124)-C(123)-H(123) 119.1(15)
C(122)-C(123)-C(124) 120.5
C(122)-C(123)-H(123) 118.5
C(100)-C(101)-H(101) 123.0(14)
C(102)-C(101)-C(100) 118.5
C(102)-C(101)-H(101) 119.9
C(150)-C(149)-H(149) 120.1(16)
C(148)-C(149)-C(150) 119.9
C(148)-C(149)-H(149) 119.9
C(41)-C(42)-H(42) 120.3(16)
C(41)-C(42)-C(43) 119.9
C(43)-C(42)-H(42) 122.2
C(163)-C(168)-H(168) 115.7(14)
C(167)-C(168)-C(163) 122.2
C(167)-C(168)-H(168) 118.9
C(4)-C(13)-H(13) 122.3(15)
C(14)-C(13)-C(4) 118.9
C(14)-C(13)-H(13) 118.5
C(40)-C(41)-H(41) 123.0(15)
C(42)-C(41)-C(40) 118.5
C(42)-C(41)-H(41) 120.0(17)
C(147)-C(148)-C(149) 120.0
C(147)-C(148)-H(148) 120.0
C(149)-C(148)-H(148) 120.0
C(112)-C(111)-H(111) 120.6
C(112)-C(111)-C(110) 118.7(15)
C(110)-C(111)-H(111) 120.6
C(121)-C(122)-C(123) 119.1(15)
C(121)-C(122)-H(122) 120.4
C(123)-C(122)-H(122) 120.4
C(27)-C(32)-H(32) 119.7
C(27)-C(32)-C(31) 120.5(17)
C(31)-C(32)-H(32) 119.7
C(3)-C(16)-H(16) 119.3
C(15)-C(16)-C(3) 121.4(14)
C(15)-C(16)-H(16) 119.3
C(134)-C(135)-H(135) 121.1
C(136)-C(135)-C(134)

117.9(15)	C(136)-C(135)-H(135)	121.1	C(61)-
C(62)-H(62)	119.4	C(63)-C(62)-C(61)	
121.1(17)	C(63)-C(62)-H(62)	119.4	C(153)-
C(154)-H(154)	119.6	C(153)-C(154)-C(155)	
120.8(18)	C(155)-C(154)-H(154)	119.6	C(12)-
C(11)-H(11)	119.2	C(12)-C(11)-C(10)	
121.7(17)	C(10)-C(11)-H(11)	119.2	C(46)-
C(47)-H(47)	121.1	C(46)-C(47)-C(48)	
117.9(16)	C(48)-C(47)-H(47)	121.1	C(167)-
C(166)-H(166)	119.4	C(167)-C(166)-C(165)	
121.2(19)	C(165)-C(166)-H(166)	119.4	C(175)-
C(176)-H(176)	120.8	C(177)-C(176)-C(175)	
118.5(16)	C(177)-C(176)-H(176)	120.8	C(152)-
C(153)-H(153)	120.6	C(154)-C(153)-C(152)	
118.7(18)	C(154)-C(153)-H(153)	120.6	C(180)-
C(179)-H(179)	122.5	C(178)-C(179)-C(180)	
115.1(17)	C(178)-C(179)-H(179)	122.5	C(14)-
C(15)-H(15)	120.2	C(16)-C(15)-C(14)	
119.6(14)	C(16)-C(15)-H(15)	120.2	C(64)-
C(63)-H(63)	120.6	C(62)-C(63)-C(64)	
118.7(17)	C(62)-C(63)-H(63)	120.6	F(3)-
C(91)-S(3)	113.0(12)	F(3)-C(91)-F(2)	
109.1(17)	F(3)-C(91)-F(1)	108.7(14)	F(2)-
C(91)-S(3)	111.9(12)	F(2)-C(91)-F(1)	
106.8(14)	F(1)-C(91)-S(3)	107.1(12)	C(49)-
C(48)-C(47)	120.5(16)	C(49)-C(48)-H(48)	119.8
C(47)-C(48)-H(48)	119.8	C(178)-C(177)-C(176)	120(2)
C(178)-C(177)-H(177)	120.1	C(176)-C(177)-H(177)	120.1
C(10)-C(9)-H(9)	119.4	C(10)-C(9)-C(8)	
121.3(18)	C(8)-C(9)-H(9)	119.4	F(23)-
C(184)-S(11)	113.0(11)	F(23)-C(184)-F(22)	
106.2(13)	F(22)-C(184)-S(11)	111.0(12)	F(24)-
C(184)-S(11)	112.9(12)	F(24)-C(184)-F(23)	
106.4(14)	F(24)-C(184)-F(22)	106.8(13)	C(118)-
C(117)-H(117)	119.1	C(116)-C(117)-C(118)	122(2)
C(116)-C(117)-H(117)	119.1	C(11)-C(10)-H(10)	120.8
C(9)-C(10)-C(11)	118.3(18)	C(9)-C(10)-H(10)	120.8
C(73)-C(74)-H(74)	118.4	C(75)-C(74)-H(74)	118.4

C(75)-C(74)-C(73) 123.2(17)
C(109)-C(110)-C(111) 123.1(15)
C(109)-C(110)-H(110) 118.5
C(111)-C(110)-H(110) 118.5
C(83)-C(84)-H(84) 118.9
C(83)-C(84)-C(85) 122.1(14)
C(85)-C(84)-H(84) 118.9
F(13)-C(182)-S(10) 107.9(14)
F(13)-C(182)-F(15) 108.7(16)
F(14)-C(182)-S(10) 111.5(14)
F(14)-C(182)-F(13) 111.3(16)
F(14)-C(182)-F(15) 109.9(18)
F(15)-C(182)-S(10) 107.5(13)
C(39)-C(44)-H(44) 120.6
C(39)-C(44)-C(43) 118.9(17)
C(43)-C(44)-H(44) 120.6
C(7)-C(8)-C(9) 120.9(16)
C(7)-C(8)-H(8A) 119.6
C(9)-C(8)-H(8A) 119.6
C(86)-C(85)-C(84) 119.5(13)
C(86)-C(85)-H(85) 120.3
C(84)-C(85)-H(85) 120.3
C(74)-C(73)-H(73) 122.0
C(72)-C(73)-C(74) 116.1(16)
C(72)-C(73)-H(73) 122.0
C(156)-C(155)-C(154) 119.1(17)
C(156)-C(155)-H(155) 120.4
C(154)-C(155)-H(155) 120.4
C(71)-C(72)-H(72) 118.8
C(73)-C(72)-C(71) 122.4(15)
C(73)-C(72)-H(72) 118.8
C(28)-C(29)-H(29) 120.0
C(30)-C(29)-C(28) 120(2)
C(30)-C(29)-H(29) 120.0
C(115)-C(116)-H(116) 119.9
C(117)-C(116)-C(115) 120(2)
C(117)-C(116)-H(116) 119.9
F(11)-C(90)-S(6) 110.7(12)
F(11)-C(90)-F(12) 106.2(13)
F(10)-C(90)-S(6) 110.7(14)
F(10)-C(90)-F(12) 108.4(15)
F(12)-C(90)-S(6) 119.7
C(42)-C(43)-H(43) 120.6(18)
C(44)-C(43)-H(43) 119.4
C(29)-C(30)-H(30) 119.4
C(31)-C(30)-C(29) 121(2)
C(31)-C(30)-H(30) 119.4
C(71)-C(76)-H(76) 117.9
C(71)-C(76)-C(75) 124.2(17)
C(75)-C(76)-H(76) 117.9
C(168)-C(167)-H(167) 116.9
C(166)-C(167)-C(168) 126.2(18)
C(166)-C(167)-H(167) 116.9
C(74)-C(75)-C(76) 116.2(18)
C(74)-C(75)-H(75) 121.9
C(76)-C(75)-H(75) 121.9
C(32)-C(31)-H(31) 120.2
C(30)-C(31)-C(32) 120(2)
C(30)-C(31)-H(31) 120.2
C(164)-C(165)-H(165) 120.5
C(166)-C(165)-C(164) 119.0(16)
C(166)-C(165)-H(165) 120.5
F(9)-C(89)-S(5) 109.1(16)
F(8)-C(89)-S(5)

113.7(16)	F(8)-C(89)-F(9)	108.8(18)	F(7)-
C(89)-S(5)	112.1(16)	F(7)-C(89)-F(9)	
105.6(19)	F(7)-C(89)-F(8)	107.2(19)	C(185)-
Cl(2)-Cl(4)	30.9(14)	C(1BA)-C(2AA)-C(3AA)	
115.4(19)	Cl(4)-C(185)-Cl(2)	114(3)	Cl(3)-
C(186)-Cl(1)	103.4(19)	C(2BA)-C(1BA)-C(2AA)	
108(2)	C(0BA)-C(3AA)-C(2AA)	111(2)	C(185)-
Cl(4)-Cl(2)	34.7(16)		

7.9.5 X-Ray Data for IDPii-4

Table 1. Crystal data and structure refinement.

Identification code	12409	
Empirical formula	$C_{116}H_{74}F_{12}N_7O_{12}P_2S_6 \cdot 0.5\ Et_2O$	
Color	colourless	
Formula weight	2276.67 g · mol^{-1}	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	MONOCLINIC	
Space group	**C2, (no. 5)**	
Unit cell dimensions	a = 18.9991(19) Å	α= 90°.
	b = 25.127(3) Å	β= 96.052(4)°.
	c = 26.813(3) Å	γ = 90°.
Volume	12729(2) $Å^3$	
Z	4	
Density (calculated)	1.188 Mg · m^{-3}	
Absorption coefficient	0.207 mm^{-1}	
F(000)	4678 e	
Crystal size	0.196 x 0.185 x 0.164 mm^3	
θ range for data collection	1.348 to 28.789°.	
Index ranges	$-25 \le h \le 25$, $-33 \le k \le 33$, $-35 \le l \le 36$	
Reflections collected	155849	
Independent reflections	32509 [R_{int} = 0.0464]	
Reflections with I>2σ(I)	24987	
Completeness to θ = 25.242°	99.8 %	
Absorption correction	Gaussian	

Max. and min. transmission	0.98 and 0.97	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	32509 / 1 / 1398	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2σ(I)]	R_1 = 0.0725	wR^2 = 0.1970
R indices (all data)	R_1 = 0.0958	wR^2 = 0.2174
Absolute structure parameter	0.028(14)	
Remarks	**SQUEEZE was applied**	
Largest diff. peak and hole	0.8 and -0.6 e·$Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°].

S(1)-N(2)	1.519(5)	S(1)-N(3)	1.562(5)
S(1)-N(4)	1.547(5)	S(1)-C(53)	1.403(5)
S(2)-O(3)	1.426(5)	S(2)-N(3)	1.852(8)
S(2)-O(4)	1.569(5)	S(2)-C(65)	1.425(6)
S(3)-O(5)	1.442(6)	S(3)-O(6)	1.590(5)
S(3)-N(4)	1.841(8)	S(3)-C(66)	1.590(4)
P(1)-O(1)	1.581(4)	P(1)-O(2)	1.548(2)
P(1)-N(1)	1.585(5)	P(1)-N(2)	1.311(10)
F(1)-C(65)	1.346(9)	F(2)-C(65)	1.300(10)
F(3)-C(65)	1.300(11)	F(4)-C(66)	1.312(10)
F(5)-C(66)	1.336(10)	F(6)-C(66)	1.478(11)
O(1)-C(1A)	1.368(11)	O(1)-C(1B)	1.386(6)
O(2)-C(31)	1.347(17)	C(1A)-C(2A)	1.441(15)
C(1A)-C(10A)	1.385(17)	C(1B)-C(2B)	1.422(17)
C(1B)-C(10B)	1.460(15)	C(2A)-C(32)	1.437(15)
C(2A)-C(3A)	1.366(13)	C(2B)-C(3B)	1.628(14)
C(2B)-C(32)	1.400(17)	C(3A)-C(4A)	1.450(15)
C(3A)-C(8A)	1.387(18)	C(3B)-C(8B)	1.376(16)
C(3B)-C(4B)	1.434(17)	C(4A)-C(5A)	1.414(18)
C(4B)-C(5B)	1.434(18)	C(5A)-C(6A)	1.40(2)
C(5B)-C(6B)	1.342(18)	C(6A)-C(7A)	1.34(2)
C(6B)-C(7B)	1.410(15)	C(7A)-C(8A)	1.457(17)
C(7B)-C(8B)	1.337(17)	C(8A)-C(9A)	1.366(18)
C(8B)-C(9B)	1.428(16)	C(9A)-C(10A)	1.364(18)
C(9B)-C(10B)	1.653(14)	C(10A)-C(11)	1.242(16)
C(10B)-C(11)	1.389(11)	C(11)-C(12)	

C(16) 1.396(9) C(12)-C(13) 1.410(10) C(14)-C(15) 1.376(9) C(14)-C(17A) 1.327(15) C(15)-C(16) 1.393(11) C(17A)-C(18A) 1.43(2) C(17B)-C(18B) 1.328(19) C(17B)-C(22B) 1.42(2) C(18A)-C(19A) 1.44(3) C(18B)-C(19B) 1.42(2) C(19A)-C(20A) 1.26(3) C(19B)-C(20B) 1.40(2) C(20A)-C(21A) 1.48(3) C(20B)-C(21B) 1.33(2) C(21A)-C(22A) 1.30(2) C(21B)-C(22B) 1.46(2) C(31)-C(32) 1.371(9) C(31)-C(40) 1.423(9) C(32)-C(33) 1.418(8) C(33)-C(34) 1.442(10) C(33)-C(38) 1.429(11) C(34)-C(35) 1.367(9) C(35)-C(36) 1.431(14) C(36)-C(37) 1.329(13) C(37)-C(38) 1.430(10) C(38)-C(39) 1.376(11) C(39)-C(40) 1.397(8) C(40)-C(41) 1.504(9) C(41)-C(42) 1.375(9) C(41)-C(46) 1.405(9) C(42)-C(43) 1.397(11) C(43)-C(44) 1.358(11) C(44)-C(45) 1.433(10) C(44)-C(47B) 1.540(11) C(44)-C(47A) 1.417(14) C(45)-C(46) 1.370(10) C(47B)-C(52B) 1.3900 C(47B)-C(48B) 1.3900 C(52B)-C(51B) 1.3900 C(51B)-C(50B) 1.3900 C(50B)-C(49B) 1.3900 C(49B)-C(48B) 1.3900 C(49A)-C(48A) 1.3900 C(49A)-C(50A) 1.3900 C(48A)-C(47A) 1.3900 C(47A)-C(52A) 1.3900 C(52A)-C(51A) 1.3900 C(51A)-C(50A) 1.3900 C(53)-C(54) 1.374(8) C(53)-C(58) 1.401(8) C(54)-C(55) 1.382(9) C(55)-C(56) 1.387(10) C(56)-C(57) 1.382(9) C(57)-C(58) 1.412(8) C(57)-C(59) 1.480(8) C(59)-C(60) 1.377(12) C(59)-C(64) 1.399(10) C(60)-C(61) 1.362(11) C(61)-C(62) 1.366(16) C(62)-

C(63)	1.356(17)	C(63)-C(64)	
1.420(13)	S(4)-N(6)	1.525(5)	S(4)-
N(7)	1.552(5)	S(4)-N(8)	
1.572(5)	S(4)-C(123)	1.769(5)	S(5)-
O(9)	1.400(6)	S(5)-O(10)	
1.442(8)	S(5)-N(7)	1.612(6)	S(5)-
C(135)	1.762(10)	S(6)-O(11)	
1.424(5)	S(6)-O(12)	1.427(5)	S(6)-
N(8)	1.586(5)	S(6)-C(136)	
1.833(7)	P(2)-O(7)	1.592(4)	P(2)-
O(8)	1.579(3)	P(2)-N(5)	
1.530(2)	P(2)-N(6)	1.590(4)	F(7)-
C(135)	1.359(13)	F(8)-C(135)	
1.371(12)	F(9)-C(135)	1.240(12)	F(10)-
C(136)	1.303(9)	F(11)-C(136)	
1.315(9)	F(12)-C(136)	1.332(8)	O(7)-
C(71)	1.406(6)	O(8)-C(101)	
1.401(6)	C(71)-C(72)	1.371(7)	C(71)-
C(80)	1.410(7)	C(72)-C(73)	
1.443(7)	C(72)-C(102)	1.508(7)	C(73)-
C(74)	1.441(7)	C(73)-C(78)	
1.398(8)	C(74)-C(75)	1.382(8)	C(75)-
C(76)	1.386(9)	C(76)-C(77)	
1.394(9)	C(77)-C(78)	1.415(7)	C(78)-
C(79)	1.410(8)	C(79)-C(80)	
1.383(7)	C(80)-C(81)	1.482(7)	C(81)-
C(82)	1.387(8)	C(81)-C(86)	
1.377(9)	C(82)-C(83)	1.379(8)	C(83)-
C(84)	1.393(9)	C(84)-C(85)	
1.372(9)	C(84)-C(87)	1.466(9)	C(85)-
C(86)	1.400(9)	C(87)-C(88)	
1.378(11)	C(87)-C(92)	1.424(11)	C(88)-
C(89)	1.411(10)	C(89)-C(90)	
1.342(13)	C(90)-C(91)	1.390(13)	C(91)-
C(92)	1.371(11)	C(101)-C(102)	
1.351(7)	C(101)-C(110)	1.432(7)	C(102)-
C(103)	1.425(7)	C(103)-C(104)	
1.387(8)	C(103)-C(108)	1.433(8)	C(104)-

C(105) 1.384(8) C(105)-C(106) 1.428(10) C(106)-C(107) 1.344(10) C(107)-C(108) 1.404(8) C(108)-C(109) 1.410(9) C(109)-C(110) 1.365(7) C(110)-C(111) 1.487(8) C(111)-C(112) 1.391(7) C(111)-C(116) 1.391(8) C(112)-C(113) 1.389(9) C(113)-C(114) 1.357(9) C(114)-C(115) 1.393(8) C(114)-C(117) 1.496(9) C(115)-C(116) 1.398(8) C(117)-C(118) 1.362(11) C(117)-C(122) 1.386(11) C(118)-C(119) 1.402(12) C(119)-C(120) 1.320(13) C(120)-C(121) 1.358(15) C(121)-C(122) 1.404(13) C(123)-C(124) 1.385(8) C(123)-C(128) 1.379(7) C(124)-C(125) 1.402(8) C(125)-C(126) 1.382(8) C(126)-C(127) 1.388(8) C(127)-C(128) 1.387(7) C(127)-C(129) 1.484(7) C(129)-C(130) 1.413(7) C(129)-C(134) 1.386(8) C(130)-C(131) 1.377(8) C(131)-C(132) 1.395(10) C(132)-C(133) 1.375(10) C(133)-C(134) 1.396(8) O(99)-C(151) 1.438(10) O(99)-C(153) 1.407(12) C(151)-C(152) 1.483(13) C(153)-C(154) 1.496(17)

N(2)-S(1)-N(3) 110.4(3) N(2)-S(1)-N(4) 117.1(3) N(2)-S(1)-C(53) 102.0(3) N(3)-S(1)-C(53) 110.0(3) N(4)-S(1)-N(3) 107.7(3) N(4)-S(1)-C(53) 109.5(3) O(3)-S(2)-O(4) 118.6(4) O(3)-S(2)-N(3) 110.6(3) O(3)-S(2)-C(65) 103.4(4) O(4)-S(2)-N(3) 115.3(3) O(4)-S(2)-C(65) 103.7(4) N(3)-S(2)-C(65) 102.8(3) O(5)-S(3)-O(6) 117.6(4) O(5)-S(3)-N(4) 114.4(3) O(5)-S(3)-C(66) 106.1(4) O(6)-S(3)-N(4) 113.6(3) O(6)-S(3)-C(66)

105.6(4) P(1)-O(1) 110.2(2) P(1)-O(2) 114.9(3) O(1)-P(1) 119.8(6) N(1)-P(1)#1 136.0(3) N(4)-S(3) 123.0(9) C(10A)-C(1A)-O(1) 111.5(9) C(1B)-C(10B) 118.7(10) C(2A)-C(3A) 119.2(10) C(2B)-C(32) 122.4(11) C(3A)-C(2A) 122.2(11) C(3B)-C(2B) 120.4(11) C(5A)-C(6A) 121.7(14) C(6B)-C(5B) 121.9(11) C(8A)-C(3A) 120.3(10) C(8B)-C(7B) 120.0(10) C(9A)-C(10A) 126.7(12) C(10A)-C(1A) 123.2(9) C(10B)-C(1B) 121.5(12) C(11)-C(16)

N(4)-S(3)-C(66) 103.7(2) N(1)-P(1)-O(1) 107.05(17) N(2)-P(1)-O(1) 108.1(5) C(31)-O(2)-P(1) 145.2(5) S(1)-N(3)-S(2) 121.0(3) C(2A)-C(1A)-C(10A) 111.8(9) O(1)-C(1B)-C(10B) 124.5(10) C(1A)-C(2A)-C(32) 124.4(11) C(1B)-C(2B)-C(32) 117.0(10) C(4A)-C(3A)-C(8A) 117.1(11) C(4B)-C(3B)-C(8B) 115.9(11) C(3B)-C(4B)-C(5B) 119.1(12) C(7A)-C(6A)-C(5A) 119.1(14) C(6B)-C(7B)-C(8B) 117.1(10) C(9A)-C(8A)-C(7A) 115.3(11) C(9B)-C(8B)-C(7B) 124.6(11) C(1A)-C(10A)-C(11) 113.5(11) C(9B)-C(10B)-C(1B) 125.0(11) C(10B)-C(11)-C(12) 124.1(9)

96.3(3) O(2)-P(1)-N(2) 110.7(2) N(1)-P(1)-N(2) 109.6(2) C(1B)-O(1)-P(1) 121.8(4) S(1)-N(2)-P(1) 128.2(3) C(2A)-C(1A)-O(1) 125.1(10) O(1)-C(1B)-C(2B) 123.7(10) C(1A)-C(2A)-C(3A) 116.9(9) C(1B)-C(2B)-C(3B) 122.9(9) C(4A)-C(3A)-C(2A) 120.4(10) C(4B)-C(3B)-C(2B) 122.0(10) C(5A)-C(4A)-C(3A) 118.4(12) C(6B)-C(5B)-C(4B) 121.1(11) C(6A)-C(7A)-C(8A) 123.2(13) C(9A)-C(8A)-C(3A) 122.6(10) C(9B)-C(8B)-C(3B) 124.6(11) C(10B)-C(9B)-C(8B) 123.2(9) C(9A)-C(10A)-C(11) 113.1(13) C(11)-C(10B)-C(9B) 117.9(8) C(12)-C(11)-C(10A)

O(2)-N(1)-C(1A)-P(1) S(1)-N(2)-C(2B)-C(32) C(3B)-C(8A)-C(4A)-C(7B) C(7A)-C(3B)-C(8A)-C(9A) C(8A)-C(10B)-C(9A)-C(11) C(10B)-

124.2(7)	C(12)-C(11)-C(16)	117.6(8)	C(16)-
C(11)-C(10A)	118.2(7)	C(13)-C(12)-C(11)	
120.7(7)	C(12)-C(13)-C(14)	121.8(7)	C(13)-
C(14)-C(17A)	122.6(7)	C(15)-C(14)-C(13)	
117.9(8)	C(15)-C(14)-C(17A)	119.0(7)	C(17B)-
C(14)-C(13)	117.2(8)	C(17B)-C(14)-C(15)	
123.7(8)	C(14)-C(15)-C(16)	119.8(6)	C(15)-
C(16)-C(11)	121.8(7)	C(18A)-C(17A)-C(14)	
117.1(13)	C(18A)-C(17A)-C(22A)	118.5(14)	
C(22A)-C(17A)-C(14)	123.9(10)	C(14)-C(17B)-C(18B)	
128.0(14)	C(14)-C(17B)-C(22B)	114.4(12)	C(18B)-
C(17B)-C(22B)	117.2(14)	C(17A)-C(18A)-C(19A)	
119.2(17)	C(17B)-C(18B)-C(19B)	122.6(16)	
C(20A)-C(19A)-C(18A)	123.2(17)	C(20B)-C(19B)-C(18B)	
120.7(14)	C(19A)-C(20A)-C(21A)	117.2(17)	C(21B)-
C(20B)-C(19B)	118.7(15)	C(22A)-C(21A)-C(20A)	
122.0(19)	C(20B)-C(21B)-C(22B)	120.4(18)	
C(21A)-C(22A)-C(17A)	119.7(17)	C(17B)-C(22B)-C(21B)	
119.5(15)	O(2)-C(31)-C(40)	117.2(5)	C(32)-
C(31)-O(2)	119.7(5)	C(32)-C(31)-C(40)	
123.1(5)	C(2A)-C(32)-C(31)	117.8(7)	C(2A)-
C(32)-C(33)	122.7(7)	C(31)-C(32)-C(2B)	
120.5(6)	C(31)-C(32)-C(33)	119.4(6)	C(33)-
C(32)-C(2B)	119.2(7)	C(32)-C(33)-C(34)	
122.5(6)	C(32)-C(33)-C(38)	119.1(6)	C(38)-
C(33)-C(34)	118.2(6)	C(35)-C(34)-C(33)	
120.6(8)	C(34)-C(35)-C(36)	120.2(8)	C(37)-
C(36)-C(35)	120.2(7)	C(36)-C(37)-C(38)	
122.4(8)	C(33)-C(38)-C(37)	118.2(7)	C(39)-
C(38)-C(33)	118.4(6)	C(39)-C(38)-C(37)	
123.3(7)	C(38)-C(39)-C(40)	124.4(6)	C(31)-
C(40)-C(41)	125.3(5)	C(39)-C(40)-C(31)	
115.3(6)	C(39)-C(40)-C(41)	119.3(6)	C(42)-
C(41)-C(40)	118.8(6)	C(42)-C(41)-C(46)	
118.2(6)	C(46)-C(41)-C(40)	123.0(6)	C(41)-
C(42)-C(43)	120.4(6)	C(44)-C(43)-C(42)	
122.8(7)	C(43)-C(44)-C(45)	116.7(7)	C(43)-
C(44)-C(47B)	117.8(8)	C(43)-C(44)-C(47A)	

125.1(9)	C(45)-C(44)-C(47B)	125.2(7)	
C(47A)-C(44)-C(45)	118.0(8)	C(46)-C(45)-C(44)	
120.8(6)	C(45)-C(46)-C(41)	121.0(6)	C(52B)-
C(47B)-C(44)	121.0(7)	C(52B)-C(47B)-C(48B)	120.0
C(48B)-C(47B)-C(44)	118.6(7)	C(47B)-C(52B)-C(51B)	120.0
C(50B)-C(51B)-C(52B)	120.0	C(51B)-C(50B)-C(49B)	120.0
C(50B)-C(49B)-C(48B)	120.0	C(49B)-C(48B)-C(47B)	120.0
C(48A)-C(49A)-C(50A)	120.0	C(47A)-C(48A)-C(49A)	120.0
C(48A)-C(47A)-C(44)	119.4(10)	C(52A)-C(47A)-C(44)	
120.5(10)	C(52A)-C(47A)-C(48A)	120.0	
C(47A)-C(52A)-C(51A)	120.0	C(50A)-C(51A)-C(52A)	120.0
C(51A)-C(50A)-C(49A)	120.0	C(54)-C(53)-S(1)	
119.7(4)	C(54)-C(53)-C(58)	123.0(5)	C(58)-
C(53)-S(1)	117.2(4)	C(53)-C(54)-C(55)	
117.4(6)	C(54)-C(55)-C(56)	121.2(6)	C(57)-
C(56)-C(55)	121.6(6)	C(56)-C(57)-C(58)	
118.0(5)	C(56)-C(57)-C(59)	122.0(6)	C(58)-
C(57)-C(59)	120.0(6)	C(53)-C(58)-C(57)	
118.6(5)	C(60)-C(59)-C(57)	120.6(6)	C(60)-
C(59)-C(64)	120.2(7)	C(64)-C(59)-C(57)	
119.2(7)	C(61)-C(60)-C(59)	119.6(8)	C(60)-
C(61)-C(62)	122.4(11)	C(63)-C(62)-C(61)	
118.6(9)	C(62)-C(63)-C(64)	121.6(9)	C(59)-
C(64)-C(63)	117.5(9)	F(1)-C(65)-S(2)	
111.7(5)	F(1)-C(65)-F(2)	107.4(7)	F(2)-
C(65)-S(2)	107.1(6)	F(3)-C(65)-S(2)	
111.6(6)	F(3)-C(65)-F(1)	109.1(7)	F(3)-
C(65)-F(2)	109.8(6)	F(4)-C(66)-S(3)	
111.7(6)	F(4)-C(66)-F(5)	110.2(7)	F(4)-
C(66)-F(6)	110.8(7)	F(5)-C(66)-S(3)	
108.5(6)	F(5)-C(66)-F(6)	110.2(8)	F(6)-
C(66)-S(3)	105.4(6)	N(6)-S(4)-N(7)	
116.2(3)	N(6)-S(4)-N(8)	110.0(3)	N(6)-
S(4)-C(123)	102.9(3)	N(7)-S(4)-N(8)	
107.7(3)	N(7)-S(4)-C(123)	109.9(3)	N(8)-
S(4)-C(123)	110.1(2)	O(9)-S(5)-O(10)	
117.0(5)	O(9)-S(5)-N(7)	115.3(3)	O(9)-
S(5)-C(135)	107.7(5)	O(10)-S(5)-N(7)	

112.2(4) O(10)-S(5)-C(135) 102.6(5) N(7)-S(5)-C(135) 99.5(4) O(11)-S(6)-O(12)
119.3(3) O(11)-S(6)-N(8) 115.4(3) O(11)-S(6)-C(136) 105.9(3) O(12)-S(6)-N(8)
108.7(3) O(12)-S(6)-C(136) 102.7(3) N(8)-S(6)-C(136) 102.7(3) O(8)-P(2)-O(7)
104.02(19) O(8)-P(2)-N(6) 113.6(2) N(5)-P(2)-O(7) 111.7(2) N(5)-P(2)-O(8)
105.68(16) N(5)-P(2)-N(6) 112.8(3) N(6)-P(2)-O(7) 108.8(2) C(71)-O(7)-P(2)
115.3(3) C(101)-O(8)-P(2) 123.3(3) P(2)-N(5)-P(2)#2 145.5(4) S(4)-N(6)-P(2)
135.0(3) S(4)-N(7)-S(5) 126.3(4) S(4)-N(8)-S(6) 123.4(3) O(7)-C(71)-C(80)
118.4(4) C(72)-C(71)-O(7) 117.8(4) C(72)-C(71)-C(80) 123.8(5) C(71)-C(72)-C(73)
117.6(5) C(71)-C(72)-C(102) 120.2(4) C(73)-C(72)-C(102) 122.0(4) C(74)-C(73)-C(72)
121.7(5) C(78)-C(73)-C(72) 119.7(5) C(78)-C(73)-C(74) 118.4(5) C(75)-C(74)-C(73)
120.3(5) C(74)-C(75)-C(76) 120.5(5) C(75)-C(76)-C(77) 120.6(5) C(76)-C(77)-C(78)
119.9(5) C(73)-C(78)-C(77) 120.2(5) C(73)-C(78)-C(79) 119.6(5) C(79)-C(78)-C(77)
120.2(5) C(80)-C(79)-C(78) 121.6(5) C(71)-C(80)-C(81) 123.1(5) C(79)-C(80)-C(71)
117.4(5) C(79)-C(80)-C(81) 119.5(4) C(82)-C(81)-C(80) 120.5(5) C(86)-C(81)-C(80)
124.2(5) C(86)-C(81)-C(82) 115.3(5) C(83)-C(82)-C(81) 122.9(6) C(82)-C(83)-C(84)
120.3(6) C(83)-C(84)-C(87) 121.4(6) C(85)-C(84)-C(83) 118.1(6) C(85)-C(84)-C(87)
120.3(6) C(84)-C(85)-C(86) 119.9(6) C(81)-C(86)-C(85) 123.1(6) C(88)-C(87)-C(84)
121.8(7) C(88)-C(87)-C(92) 116.8(6) C(92)-C(87)-C(84) 121.4(7) C(87)-C(88)-C(89)
120.9(8) C(90)-C(89)-C(88) 121.2(8) C(89)-C(90)-C(91) 119.4(7) C(92)-C(91)-C(90)

120.5(8)	C(91)-C(92)-C(87)	121.2(8)	O(8)-
C(101)-C(110)	115.5(4)	C(102)-C(101)-O(8)	
119.4(4)	C(102)-C(101)-C(110)	125.1(4)	C(101)-
C(102)-C(72)	120.8(4)	C(101)-C(102)-C(103)	
118.8(4)	C(103)-C(102)-C(72)	120.4(5)	C(102)-
C(103)-C(108)	117.6(5)	C(104)-C(103)-C(102)	
123.5(5)	C(104)-C(103)-C(108)	118.9(5)	C(105)-
C(104)-C(103)	120.8(6)	C(104)-C(105)-C(106)	
119.7(6)	C(107)-C(106)-C(105)	120.0(5)	C(106)-
C(107)-C(108)	121.4(6)	C(107)-C(108)-C(103)	
119.1(6)	C(107)-C(108)-C(109)	120.7(5)	C(109)-
C(108)-C(103)	120.2(5)	C(110)-C(109)-C(108)	
122.4(5)	C(101)-C(110)-C(111)	124.6(4)	C(109)-
C(110)-C(101)	115.6(5)	C(109)-C(110)-C(111)	
119.8(5)	C(112)-C(111)-C(110)	119.8(5)	C(116)-
C(111)-C(110)	121.8(5)	C(116)-C(111)-C(112)	
118.3(5)	C(113)-C(112)-C(111)	119.7(6)	C(114)-
C(113)-C(112)	122.9(5)	C(113)-C(114)-C(115)	
117.7(6)	C(113)-C(114)-C(117)	122.2(5)	C(115)-
C(114)-C(117)	120.1(6)	C(114)-C(115)-C(116)	
120.7(5)	C(111)-C(116)-C(115)	120.6(5)	C(118)-
C(117)-C(114)	121.4(6)	C(118)-C(117)-C(122)	
119.6(7)	C(122)-C(117)-C(114)	119.0(7)	C(117)-
C(118)-C(119)	120.0(8)	C(120)-C(119)-C(118)	
121.6(9)	C(119)-C(120)-C(121)	118.6(8)	C(120)-
C(121)-C(122)	122.6(9)	C(117)-C(122)-C(121)	
117.2(9)	C(124)-C(123)-S(4)	117.4(4)	C(128)-
C(123)-S(4)	120.0(4)	C(128)-C(123)-C(124)	
122.6(5)	C(123)-C(124)-C(125)	117.9(5)	C(126)-
C(125)-C(124)	118.9(5)	C(125)-C(126)-C(127)	
123.0(5)	C(126)-C(127)-C(129)	122.5(4)	C(128)-
C(127)-C(126)	117.6(5)	C(128)-C(127)-C(129)	
119.7(5)	C(123)-C(128)-C(127)	119.9(5)	C(130)-
C(129)-C(127)	121.1(5)	C(134)-C(129)-C(127)	
121.1(5)	C(134)-C(129)-C(130)	117.8(5)	C(131)-
C(130)-C(129)	121.1(6)	C(130)-C(131)-C(132)	
119.7(6)	C(133)-C(132)-C(131)	120.1(5)	C(132)-
C(133)-C(134)	119.9(6)	C(129)-C(134)-C(133)	

121.1(5) C(135)-F(8)	F(7)-C(135)-S(5) 105.4(11)	110.3(8) F(8)-C(135)-S(5)	F(7)-
111.1(5) C(135)-F(7)	F(9)-C(135)-S(5) 110.4(8)	112.8(9) F(9)-C(135)-F(8)	F(9)-
106.5(9) C(136)-F(11)	F(10)-C(136)-S(6) 107.3(6)	112.8(5) F(10)-C(136)-F(12)	F(10)-
108.3(7) C(136)-F(12)	F(11)-C(136)-S(6) 108.3(6)	109.9(5) F(12)-C(136)-S(6)	F(11)-
110.1(5) C(151)-C(152) 110.1(10)	C(153)-O(99)-C(151) 114.4(8)	111.1(7) O(99)-C(153)-C(154)	O(99)-

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Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+2 #2 -x+1,y,-z+1

7.9.6 X-Ray Data for 4.74

Table 1. Crystal data and structure refinement.

Identification code	13078	
Empirical formula	C_{25} H_{24} O	
Color	colourless	
Formula weight	340.44 g·mol^{-1}	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 2_1 2_1 2, (No. 18)	
Unit cell dimensions	a = 15.4353(12) Å	α= 90°.
	b = 21.594(5) Å	β= 90°.
	c = 5.5403(15) Å	γ = 90°.
Volume	1846.7(7) Å^3	
Z	4	
Density (calculated)	1.225 Mg·m^{-3}	
Absorption coefficient	0.073 mm^{-1}	
F(000)	728 e	
Crystal size	0.26 x 0.14 x 0.05 mm^3	
θ range for data collection	2.639 to 33.150°.	
Index ranges	-23 ≤ h ≤ 23, -33≤ k ≤ 33, -8 ≤ l ≤ 8	
Reflections collected	51130	
Independent reflections	7059 [R_{int} = 0.0958]	
Reflections with I>2σ(I)	4712	
Completeness to θ = 25.242°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99655 and 0.98497	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7059 / 0 / 237	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2σ(I)]	R_1 = 0.0524	wR^2 = 0.1060
R indices (all data)	R_1 = 0.0986	wR^2 = 0.1206
Absolute structure parameter	0.0(9)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.241 and -0.239 e·Å^{-3}	

Table 2. Bond lengths [Å] and angles [°].

O(1)-C(1)	1.375(2)	C(6)-C(1)	
1.395(3)	C(6)-C(5)	1.405(3)	C(6)-
C(7)	1.520(3)	C(1)-C(2)	
1.397(3)	C(19)-C(24)	1.394(3)	C(19)-
C(20)	1.393(3)	C(19)-C(18)	
1.523(3)	C(5)-C(4)	1.397(3)	C(5)-
C(9)	1.515(3)	C(10)-C(15)	
1.394(3)	C(10)-C(11)	1.398(3)	C(10)-
C(7)	1.514(3)	C(4)-C(3)	
1.405(3)	C(4)-C(25)	1.510(3)	C(3)-
C(2)	1.393(3)	C(3)-C(16)	
1.513(3)	C(2)-C(18)	1.522(3)	C(9)-
C(8)	1.544(3)	C(24)-C(23)	
1.390(3)	C(20)-C(21)	1.389(3)	C(15)-
C(14)	1.394(3)	C(23)-C(22)	
1.384(3)	C(13)-C(12)	1.384(3)	C(13)-
C(14)	1.388(3)	C(8)-C(7)	
1.547(3)	C(18)-C(17)	1.560(3)	C(11)-
C(12)	1.390(3)	C(16)-C(17)	
1.546(3)	C(22)-C(21)	1.385(3)	
C(1)-C(6)-C(5)	120.10(18)	C(1)-C(6)-C(7)	
128.61(17)	C(5)-C(6)-C(7)	110.95(17)	O(1)-
C(1)-C(6)	124.19(17)	O(1)-C(1)-C(2)	
117.33(17)	C(6)-C(1)-C(2)	118.48(17)	C(24)-
C(19)-C(18)	120.41(18)	C(20)-C(19)-C(24)	
118.02(19)	C(20)-C(19)-C(18)	121.57(18)	C(6)-
C(5)-C(9)	109.71(17)	C(4)-C(5)-C(6)	
122.41(19)	C(4)-C(5)-C(9)	127.77(18)	C(15)-
C(10)-C(11)	118.25(19)	C(15)-C(10)-C(7)	
119.99(19)	C(11)-C(10)-C(7)	121.76(19)	C(5)-
C(4)-C(3)	116.19(18)	C(5)-C(4)-C(25)	
122.16(19)	C(3)-C(4)-C(25)	121.59(18)	C(4)-
C(3)-C(16)	127.48(18)	C(2)-C(3)-C(4)	
122.25(19)	C(2)-C(3)-C(16)	110.23(18)	C(1)-

C(2)-C(18)	126.62(17)	C(3)-C(2)-C(1)	
120.56(18)	C(3)-C(2)-C(18)	112.61(17)	C(5)-
C(9)-C(8)	103.21(17)	C(23)-C(24)-C(19)	
120.92(19)	C(21)-C(20)-C(19)	121.2(2)	C(10)-
C(15)-C(14)	120.9(2)	C(22)-C(23)-C(24)	
120.2(2)	C(12)-C(13)-C(14)	119.5(2)	C(9)-
C(8)-C(7)	105.55(16)	C(19)-C(18)-C(17)	
114.05(16)	C(2)-C(18)-C(19)	111.66(17)	C(2)-
C(18)-C(17)	102.08(16)	C(12)-C(11)-C(10)	
120.8(2)	C(3)-C(16)-C(17)	104.33(16)	C(6)-
C(7)-C(8)	101.69(16)	C(10)-C(7)-C(6)	
117.71(17)	C(10)-C(7)-C(8)	113.30(17)	C(13)-
C(12)-C(11)	120.5(2)	C(23)-C(22)-C(21)	
119.6(2)	C(13)-C(14)-C(15)	120.2(2)	C(16)-
C(17)-C(18)	107.38(17)	C(22)-C(21)-C(20)	
120.0(2)			

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8.0 Bibliography

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9 Appendix

9.1 Erklärung

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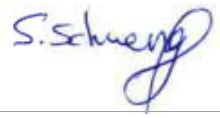

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1. “Unified Approach to Imidodiphosphate-Type Brønsted Acids with Tunable Confinement and Acidity” S. A. Schwengers, Chandra Kanta De, Oleg Grossmann, Joyce A. A. Grimm, Natascha R. Sadlowski, Gabriela G. Gerosa, B. List, *J. Am. Chem. Soc.* **2021** DOI: 10.1021/jacs.1c07067

2. “Process for Preparing Dimeric Phosphazene Derived Brønsted Acids.” S. A. Schwengers, C. K. De, Y. Li, B. List, (EP20200632), **2020**, Assignee: Studiengesellschaft Kohle mBH.

3. „Homologation of the Fischer Indolization: A Quinoline Synthesis via Homo-Diaza-Cope Rearrangement.” G. G. Gerosa, S. A. Schwengers, R. Maji, C. K. De, B. List, *Angew. Chem. Int. Ed.* **2020**, *59*, 20485

9.2 Lebenslauf

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