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Structure and Reactivity of N-Heterocyclic Alkynyl Hypervalent Iodine Reagents

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Dedicated to Prof. Antonio Togni on the occasion of his retirement and as a tribute to his immense contribution to the chemistry of hypervalent iodine.

Abstract: Ethynylbenziodoxol(on)e (EBX) cyclic hypervalent iodine reagents have become popular reagents for the alkynylation of radicals and nucleophiles, but only offer limited possibilities for further structure and reactivity fine-tuning. Herein, the synthesis of new N-heterocyclic hypervalent iodine reagents with increased structural flexibility based on amide, amidine and sulfoximine scaffolds is reported. Solid-state structures of the reagents are reported and the analysis of the I–C_{alkyne} bond lengths allowed assessing the *trans*-effect of the different substituents. Molecular electrostatic potential (MEP) maps of the reagents, derived from DFT computations, revealed less pronounced σ-hole regions for sulfonamide-based compounds. Most reagents reacted well in the alkynylation of β-ketoesters. The alkynylation of thiols afforded more variable yields, with compounds with a stronger σ-hole reacting better. In metal-mediated transformations, the N-heterocyclic hypervalent iodine reagents gave inferior results when compared to the O-based EBX reagents.

Introduction

In the last decades, hypervalent iodine reagents (HIR) have been established as versatile and environmentally benign oxidants and mainstream reagents for functional group transfer in organic chemistry.[1] Among them, cyclic HIRs bearing a benzene ring and incorporating the iodine atom in a heterocycle exhibit higher stability. The most studied cyclic HIRs belong to the benziodoxol(on)e (BX) class of reagents characterized by an I–O bond in the iodoheterocycle (Figure 1A).[2] Iodine(V) reagents, such as the Dess-Martin Periodinane (R=$(OAc)_3$, Y=O), have found widespread application as mild

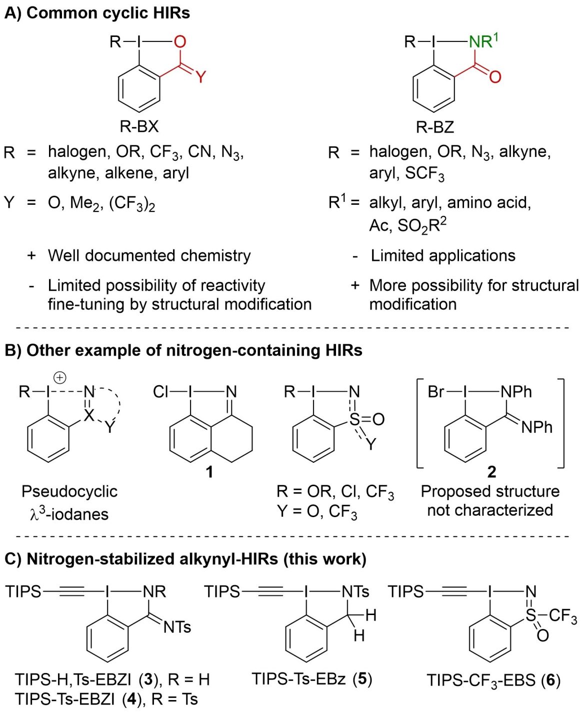

Figure 1. A) Established BX reagents and BZ reagents. B) Other examples of nitrogen-stabilized HIR. C) New alkynyl reagents synthesized in this work.

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/chem.202101475 and stable oxidants.[3] In contrast, iodine(III) reagents, such as CN–BX,[4] N_3–BX,[5] CF_3–BX (Togni's reagent),[6] (hetero)Ar–BX,[7] EBX (R = alkynyl),[8] and VBX (R = alkene)[9] have found their main applications in functional group transfer reactions. Despite their success, these reagents offer only limited options for fine-tuning their reactivity by structural modification, as the oxygen in the heterocycle can have only one substituent. The replacement of the oxygen by a nitrogen atom in the iodoheterocycle was therefore considered by several researchers.[10] The benziodazol(on)e (BZ) class of reagent was discovered in the late 60's and most reports focused on the determination and the study of their X-ray structure (Figure 1A).[11] The first synthetic application of this type of HIR was reported only recently with a radical dehydrogenative olefination of $C(sp^3)$–H bonds using an alanine derived BZ reagent.[12] Later our group reported the first synthesis of EBZ (R = alkyne) reagents and studied their reactivity towards nucleophiles and in the oxyalkynylation of diazo compounds.[13] Interestingly, although it had been computed that the benziodoxole-based SCF_3-reagent would not be stable,[14] Zhang and coworkers reported in 2020 the synthesis of SCF_3-BZ reagents and employed them for the trifluoromethylthiolation of various nucleophiles.[15]

Moreover, other types of nitrogen-stabilized (pseudo)-cyclic HIR have been reported in the literature (Figure 1B). The groups of Zhdankin,[16] Nachtsheim[17] and Tsarevsky[18] studied the synthesis, the stability and the reactivity of (pseudo)cyclic N-heterocycle hypervalent iodine compounds in oxidative transformations. Compound **1**[19] and benziodathiazole reagents (Y=O)[20] were also reported in the literature but their reactivity was not investigated. More recently, the Magnier and Togni groups disclosed the synthesis of sulfoximine based reagents ($Y=CF_3$) and studied their reactivity in trifluoromethylation reactions.[21] Finally, Braddock and coworkers speculated on the formation of an amidine-derived bromoiodinane reagent **2** when performing the bromolactonization of alkenes.[22]

Our initial goal when designing the first EBZ reagents was to develop an atom-economical aminoalkynylation of diazo compounds that would have led to α-amino acid derivatives.[13] Unfortunately only oxyalkynylation products were obtained through the reaction of the oxygen atom on the amide. Removing the nucleophilic amide oxygen appeared therefore as a promising strategy and reagents bearing amidine, amine and sulfoximine core structures were envisioned. More generally, access to these unprecedented reagents was expected to further increase our understanding on the structure-reactivity relationship of cyclic alkynyl hypervalent iodine reagents. Herein, we report the first synthesis of ethynylbenziodazolimine (EBZI, **3** and **4**), ethynylbenziodazole (EBz, **5**) and ethynylbenziodosulfoximine (EBS, **6**) (Figure 1C).[23] Their structures as well as their reactivity in standard reactions were compared to already reported EBX and EBZ reagents. Although these reagents did not allow to develop the desired aminoalkynylation of diazo compounds, they were competent alkyne-transfer reagents towards several nucleophiles.

Results and Discussion

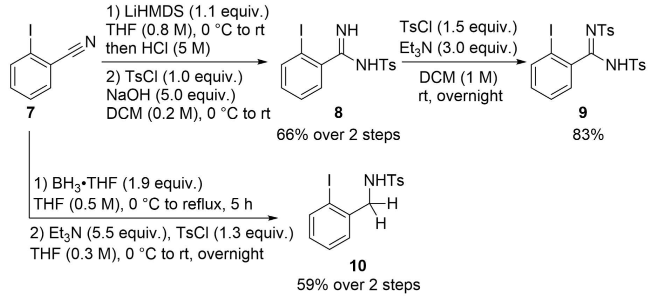
Synthesis of the precursors

In order to access the amidine-based and the benziodazole reagents, iodine(I) precursors **8**, **9** and **10** were obtained from commercially available 2-iodobenzonitrile (**7**) (Scheme 1). Nucleophilic addition of LiHMDS onto the nitrile group followed by hydrolysis and tosyl protection afforded **8** in 66% yield over two steps.[24] A second tosyl protection led to compound **9** in 83% yield. A stepwise protection procedure was favored as it would allow to finely tune the properties of the amidine-based reagents by adding two different electron-withdrawing groups. Reducing the electron-density on the nitrogen atom bound to the iodine was expected to be essential to obtain stable reagents.[11l,25] Other protecting groups such as benzoyl or Boc were introduced using similar conditions. However they were not tolerated under the reaction conditions required to form hypervalent iodine reagents and only hydrolysis of the amidine was observed in most cases. Tosyl-protected 2-iodobenzylamine (**10**) could be obtained in 59% yield in two steps via borane-reduction according to a reported procedure,[26] followed by tosylation.

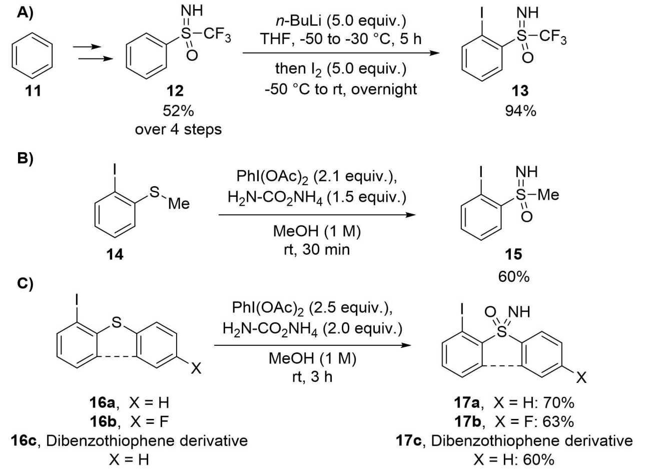
The sulfoximine precursor **12** was synthesized on multigram scale from benzene (**11**), in 52% yield over 4 steps according to our previous methodology (Scheme 2A, see Supporting Information for details).[21a,27] Finally, *ortho*-iodination afforded racemic sulfoximine precursor **13** in 94% yield. Both enantiomers of the iodosulfoximine **13** could be separated by preparative chiral HPLC and were configurationally stable (see Supporting Information for details). Four other *ortho*-iodinated sulfoximines were synthesized from the corresponding sulfides **14** and **16a**–**16c** in good yields (Scheme 2B and C respectively, see Supporting Information for the preparation of sulfides).[28] With both alkyl substituted sulfoximine **15** and aryl-substituted sulfoximines **17a**–**17c** in hand, the influence of the group linked to the sulfur atom was then investigated.

Synthesis and structure of the new reagents

We started our investigation on the synthesis of amidine-based hypervalent iodine reagents by attempting the one-pot oxidation-alkynylation protocol reported to convert 2-iodoben-



Scheme 1. Synthesis of precursors **8**, **9** and **10** from 2-iodobenzonitrile (**7**).



Scheme 2. Synthesis of A) Trifluoromethyl-substituted sulfoximine **13**, B) Methyl-substituted sulfoximine **15**, and C) Aryl-substituted sulfoximines **17a**–**17c**.

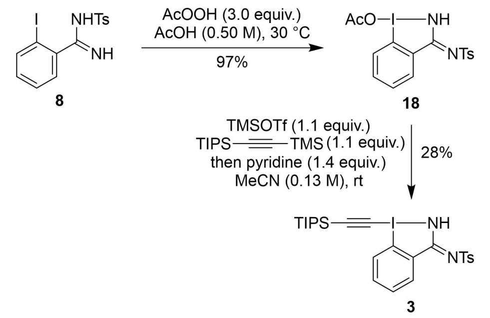
zamides into EBZs.[13] Unfortunately, only degradation and hydrolysis of amidines **8** and **9** was observed under these conditions. Hence, we decided to follow a stepwise oxidation, ligand exchange strategy.[8b,11i] Acetoxylation of monoprotected amidine **8** followed by ligand exchange after activation with trimethylsilyl triflate led to the formation of TIPS-H,Ts-EBZI (**3**) in 27% yield over the two steps (Scheme 3).

The structure of **3** was unambiguously established by X-ray analysis (Figure 2).[29] Similarly to what was observed by Zhdankin and coworkers with benziodazolone reagents, the isomer with the endocyclic free nitrogen atom was formed.[11i] Moreover, the presence of a hydrogen-bond between one of the oxygen of the sulfonyl group and the hydrogen on the endocyclic nitrogen might enhance the donating ability of the nitrogen.

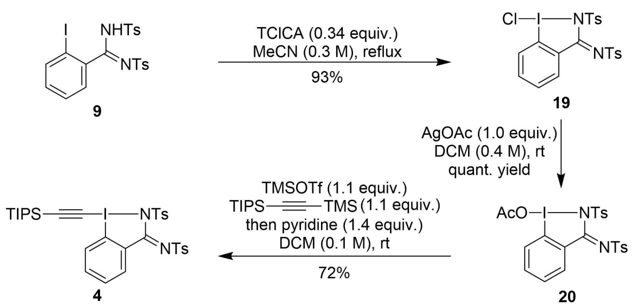
Unfortunately, bis-tosylated amidine **9** was degraded in a peracetic acid-acetic acid solution and no hypervalent iodine reagent was detected. However, a sequence of chlorination followed by two ligand exchanges afforded TIPS-Ts-EBZI (**4**) in 67% yield over three steps (Scheme 4).

The structure of **4** was determined by X-ray diffraction (Figure 3).[29] The presence of a potential secondary interaction between the iodine atom and an oxygen atom from a tosyl protecting group might help to stabilize the hypervalent iodine reagent.

To our delight, EthynylBenziodazole (EBz) reagent (**5**) and EthynylBenziodoSulfoximine (**6**) (EBS) could be obtained following a one-pot two steps procedure in 49% and 75% yield respectively (Scheme 5).[13] Moreover, starting from enantiopure sulfoximine precursor **13**, a chiral alkynyl hypervalent iodine reagent was obtained in good yield and high enantiopurity. Only few chiral alkynyl hypervalent iodine reagents have been reported so far.[30] Despite our efforts, no other HIR with a sulfoximine motif was obtained starting from **15** or **17a**–**17c**,



Scheme 3. Synthesis of TIPS-H,Ts-EBZI (**3**).



Scheme 4. Synthesis of TIPS-Ts-EBZI (**4**).

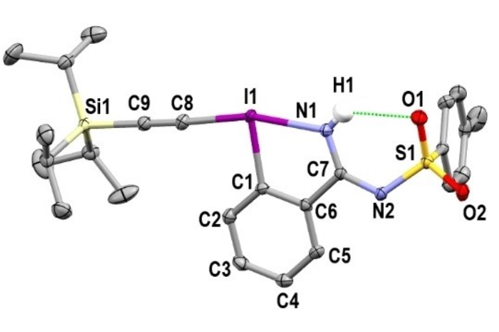


Figure 2. Structure of TIPS-H,Ts-EBZI (**3**) (see Table 1 for structural properties). H atoms (except H1) are omitted for clarity; thermal ellipsoids given at 50% probability.

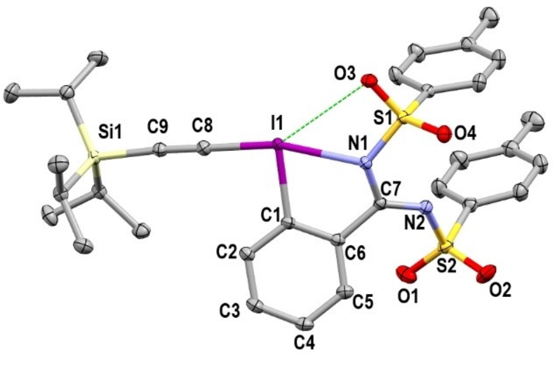
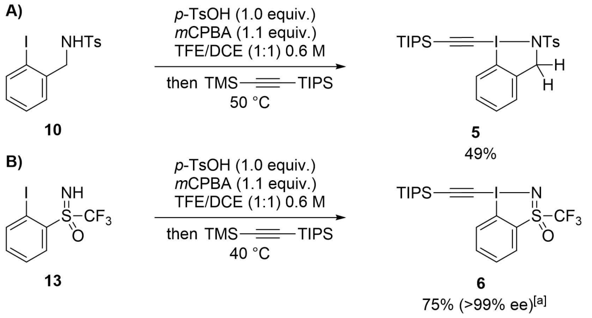


Figure 3. Structure of TIPS-Ts-EBZI (**4**) (see Table 1 for structural properties). H atoms are omitted for clarity; thermal ellipsoids given at 50% probability.



Scheme 5. A) Synthesis of TIPS-Ts-EBz (**5**) B) Synthesis of TIPS-CF_3-EBS (**6**).

highlighting the essential role of the CF_3 group of **13** for successful synthesis.

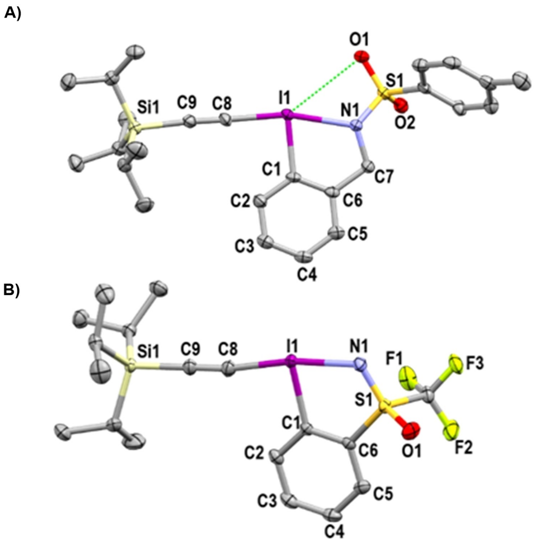


Figure 4. A) Structure of TIPS-Ts-EBz (**5**) B) Structure of TIPS-CF_3-EBS (**6**) (see Table 1 for structural properties). H atoms are omitted for clarity; thermal ellipsoids given at 50% probability.

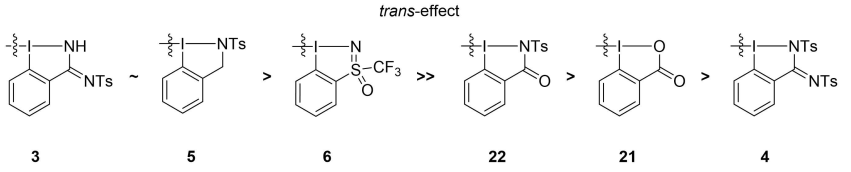
The structure of both reagents **5** and **6** was also established by X-ray analysis (Figure 4).[29] As previously observed in reagent **4** a potential secondary interaction between an oxygen atom and the iodine atom might stabilize **5**.

The structural features of the newly obtained hypervalent iodine reagents were compared to that of the reported TIPS-EBX (**21**) and TIPS-Ts-EBZ (**22**) (Table 1).[13] The comparison of the I1–C8 bond lengths between the different species allows to assess the relative *trans* effects of the substituents.[11l,25] This parameter plays an important role in the stability of hypervalent iodine species and is usually related to the donating ability of the ligands along the 3c–4e$^-$ bond. The longer the I1–C8 bond, the higher the *trans* influence of the corresponding ligand. From the measured values, we can conclude that the monoprotected amidine **3** and the sulfonamide **5** are the ligands having the higher *trans* influence of the studied substituents (entries 1 and 2). The sulfoximine ligand in **6** has a slightly lower influence (entry 3, I1–C8 = 2.089(3) Å vs. 2.102(3) and 2.100(3) for **3** and **5**). The benziodazolone and benziodoxolone moieties have similar *trans* effect (I1–C8 = 2.060(9) Å and 2.054(2) for **22** and **21** respectively, entries 4 and 5). Finally the diprotected amidine has the lower *trans* influence (I1–C8 = 2.046(2) Å for **4**, entry 6). The iodine-heteroatom bond length is similar for EBz (**5**), EBS (**6**) and EBX (**21**) (2.333(3), 2.337(2), 2.338(1) Å respectively, entries 2, 3 and 5). On the other hand, for the TIPS-Ts-EBZI (**4**) reagent, this bond is significantly longer (2.443(1) Å, entry 6), probably due to higher steric hindrance. As observed in TIPS-EBX (**21**) and TIPS-Ts-EBZ (**22**) (entries 5 and 4), the hypervalent bond in the new reagents was close to linearity with X1–I1–C8 angle ranging from 164.74(9)° for **3** (entry 1) to 171.23(1)° for **6** (entry 3). The C1–I1–C8 angles between the alkyne and the benzene range from 90.0(1)° for **3** (entry 1) to 93.03(6)° for **4** (entry 6). These angles are fully coherent with the T-shape structure expected for hypervalent iodine reagents. The torsion angle (C8–I1–C1–C2) showed that in most cases the alkynyl bond is in the plane of the aromatic ring from −8.33(2)° for **21** (entry 5) to 3.44(2)° in **3** (entry 1). In the case of TIPS-Ts-EBZI (**4**) the torsion angle is relatively high −16.56(1)° (entry 6). Finally, in reagents **5**, **22** and **4** the short distance between one oxygen atom of the tosyl protecting group and the iodine

Table 1. Comparison of bond lengths and bond angles in alkynyl hypervalent iodine reagents obtained from single crystal X-ray diffraction. X=O or N. The torsion angle corresponds to C8–I1–C1–C2.

Entry	Reagent	I1–C8 [Å]	I1–X1 [Å]	X1–I1–C8 [°]	C1–I1–C8 [°]	Torsion [°]	I–$O_{sulfonyl}$ [Å]
1	TIPS-H,Ts-EBZI (**3**)	2.102(3)	2.317(2)	164.74(9)	90.0(1)	3.44(2)	–
2	TIPS-Ts-EBz (**5**)	2.100(3)	2.333(3)	165.99(1)	90.77(1)	−0.49(3)	3.246(3)
3	TIPS-CF_3-EBS (**6**)	2.089(3)	2.337(2)	171.23(1)	90.31(1)	2.85(2)	–
4[a]	TIPS-Ts-EBZ (**22**)	2.060(9)	2.387(6)	165.79(3)	92.08(3)	−6.63(7)	3.285(5)
5[a]	TIPS-EBX (**21**)	2.054(2)	2.338(1)	166.11(6)	91.37(7)	−8.33(2)	–
6	TIPS-Ts-EBZI (**4**)	2.046(2)	2.443(1)	165.51(5)	93.03(6)	−16.56(1)	3.319(1)

[a] Data taken from the literature.[13]



center (3.246(3) Å for **5**, 3.285(5) Å for **22**, 3.319(1) Å for **4**, entries 2, 4 and 6) indicated a possible interaction.

In order to get a deeper understanding on the electronic effects of the different substituents next to the iodine atom, molecular electrostatic potential (MEP) maps were generated (Figure 5, see Supporting Information for details). A strong polarization towards the ligand is observed in almost all the reagents. The calculated molecular dipole moment is higher for **21** (8.30 D) followed by **22** (8.03 D). The new reagents have lower calculated dipole moment, 7.97 D for monoprotected amidine **3**, 7.17 D for the sulfoximine **6**, 6.03 D for the diprotected amidine **4** and finally 5.82 D for the benziodazole **5**. The MEPs allowed also to visualize the σ-hole regions of the reagents. These regions of positive charge at the iodine atom play an important role on the strength and the directionality of reagent-solvent or -substrate interactions.[31] The most extended positive regions are observed for TIPS-EBX (**21**), TIPS-EBS (**6**) and TIPS-H,Ts-EBZI (**3**), while the reagents having a tosyl group on the heteroatom bound to the iodine atom (TIPS-Ts-EBz (**5**), TIPS-Ts-EBZ (**22**) and TIPS-Ts-EBZI (**4**)) have a less extended σ-hole region. As observed in the X-ray structures of these reagents, the secondary interaction between one of the oxygen of the tosyl group and the iodine atom might weaken the σ-hole. From the MEPs plots, local potential maximum ($V_{x,max}$) around the atoms can also be extracted. In all the reagents the potential maximum around the C(sp) bound to the iodine atom ($V_{c,max}$) and around the iodine ($V_{I,max}$) are similar (between −0.002 and +0.005 and +0.032 and +0.052 au respectively, see Supporting Information). The iodoheterocycle structure seems to have an impact on the spatial extension of the σ-hole region, but not on the potential maximum on the iodine. While the oxygen atom bound to iodine from TIPS-EBX (**21**) and the nitrogen atom bound to iodine from **6** have a significant negative electron density, the nitrogen bound to iodine in the other reagents is almost neutral. The negative charge seems in fact transferred to the oxygen of the sulfonamide for TIPS-Ts-EBz (**5**) and TIPS-Ts-EBZI (**4**) or on the other heteroatom present in the iodoheterocycle for TIPS-H,Ts-EBZI (**3**) and TIPS-Ts-EBZ (**22**). The higher electron-density on the oxygen in TIPS-Ts-EBZ (**22**) reagent might explain why only oxyalkynylation was observed with diazo compounds and not the targeted aminoalkynylation.[13] Overall, these observations might indicate that the major resonance structures for these reagents are not the one drawn, but instead ionic structures with a positively charged iodine atom and a negative charge on the oxygen atoms.

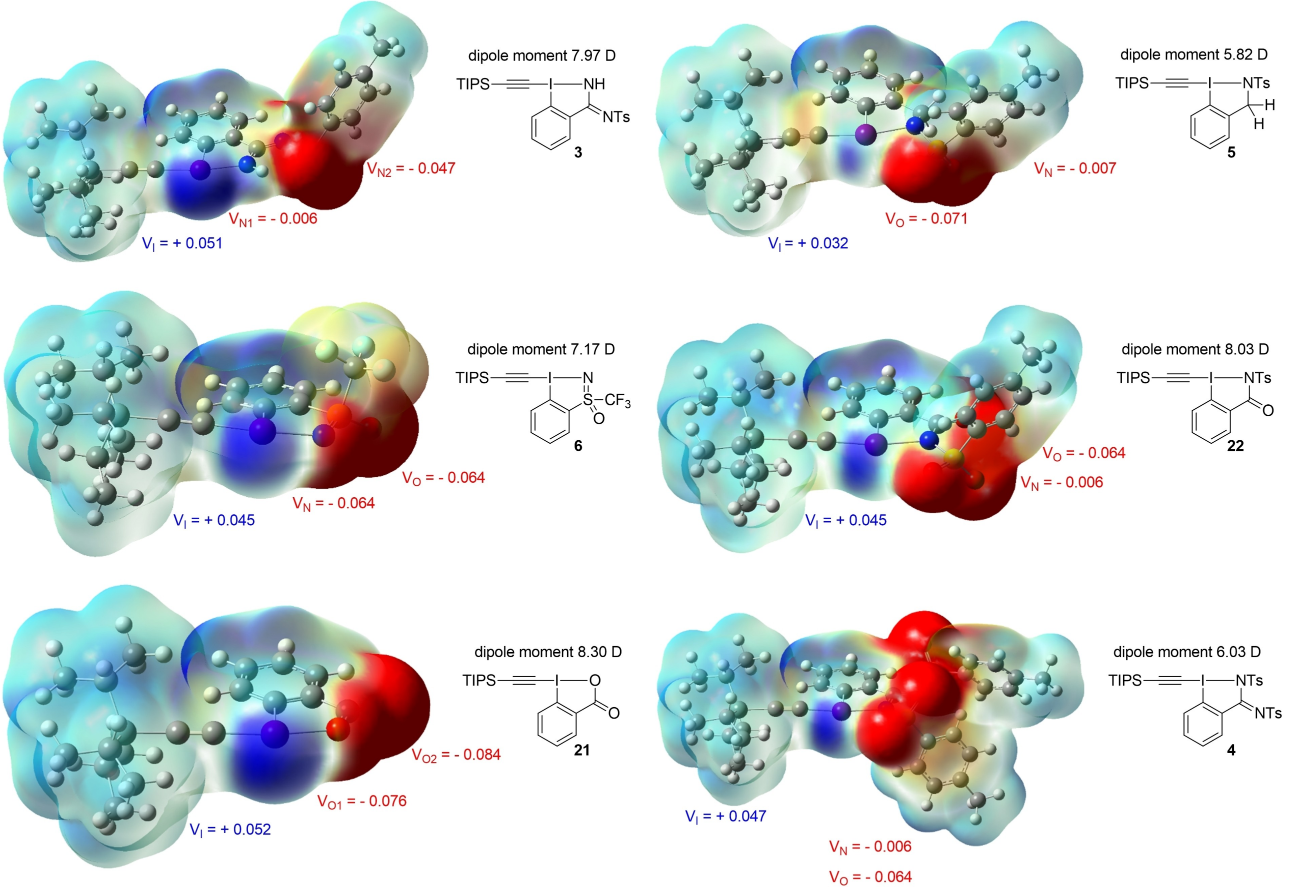
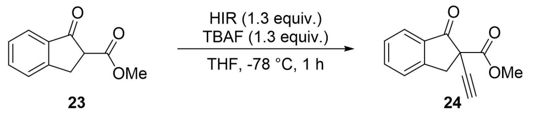


Figure 5. Molecular electrostatic potential (MEP) maps computed at the M06/def2-SVP level. MEPs were mapped onto the 0.001 au isodensity surface. V_X represents the potential maximum around the atom X and is given in au (see Supporting Information for details).

Comparison of the reactivity of the new reagents

With the new reagents in hand, we investigated their reactivity in electrophilic alkynylations and compared them to the already existing reagents TIPS-EBX (**21**) and TIPS-Ts-EBZ (**22**). First, we focused our attention on the alkynylation of β-ketoester **23** (Scheme 6).[32] In the case of the monoprotected amidine-based reagent **3**, only degradation of the reagent was observed. In the case of reagent **5**, alkyne-transfer was observed, but the side product *ortho*-iodobenzylamine could not be separated from the desired product **24**. The sulfoximine-based reagent **6** afforded **24** in 90% yield. Unfortunately, when using enantiopure sulfoximine reagent **6**, only racemic alkyne **24** was obtained. Probably, the chiral center in the reagent is too far from the reactive site to induce any selectivity. Finally, reagents **22**, **21** and **4** afforded **24** in quantitative yield.

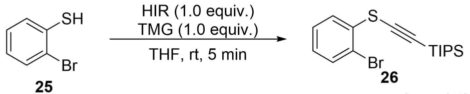
Next, we studied the thioalkynylation of *ortho*-bromothiophenol (**25**) following our reported procedure (Scheme 7).[32] When using the monoprotected amidine based reagent **3**, the desired product was not detected and only degradation of the reagent was observed. Alkynylated product **26** could be obtained in low yield from TIPS-Ts-EBz (**5**). Reagents with more pronounced σ-hole regions TIPS-CF_3-EBS (**6**), TIPS-Ts-EBZ (**22**)[13] and TIPS-EBX (**21**)[33] afforded **26** in good to excellent yields. Finally, TIPS-Ts-EBZI (**4**) led to the formation of **26** in 46% yield. Computations suggested that the accessibility of the σ-hole was key for success in this transformation.[34] The lower yields often observed with tosylated reagents (with the exception of **22**) with a smaller σ-hole region is in accordance with this hypothesis.



23 **24**

with TIPS-H,Ts-EBZI (**3**) : degradation of reagent
with TIPS-Ts-EBz (**5**) : ND (79% NMR yield)[a]
with TIPS-CF_3-EBS (**6**) : 90% yield[b]
with TIPS-Ts-EBZ (**22**) : quant. yield[13]
with TIPS-EBX (**21**) : quant. yield
with TIPS-Ts-EBZI (**4**) : quant. yield

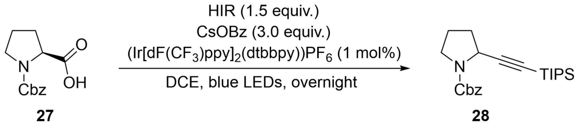
Scheme 6. Alkynylation of keto ester **23**. [a] The desired product could not be separated from side-products, CH_2Br_2 was used as internal standard. [b] No stereoinduction was observed when enantiopure reagent **6** was employed.



25 **26**

with TIPS-H,Ts-EBZI (**3**) : degradation of reagent
with TIPS-Ts-EBz (**5**) : 22% yield
with TIPS-CF_3-EBS (**6**) : 73% yield
with TIPS-Ts-EBZ (**22**) : 79% yield[13]
with TIPS-EBX (**21**) : 97% yield[32]
with TIPS-Ts-EBZI (**4**) : 46% yield

Scheme 7. Alkynylation of thiol **25**.



27 **28**

with TIPS-H,Ts-EBZI (**3**) : degradation of reagent
with TIPS-Ts-EBz (**5**) : ~10% yield
with TIPS-CF_3-EBS (**6**) : ~10% yield
with TIPS-EBX (**21**) : 90% yield[34]
with TIPS-Ts-EBZI (**4**) : degradation of reagent

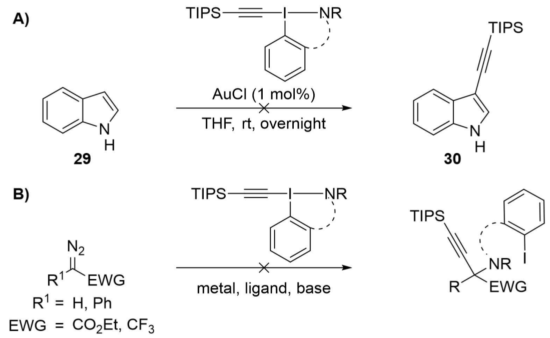
Scheme 8. Photoredox-catalyzed decarboxylative-alkynylation of Cbz-proline **27**.

The photoredox-catalyzed decarboxylative alkynylation of carboxylic acids was then investigated (Scheme 8).[35] The procedure developed for EBX reagents afforded alkynylated proline **28** in 90% yield with TIPS-EBX (**21**). Unfortunately, these conditions were not suitable for the amidine based reagents as only degradation was observed with **3** and **4**. When benzylamine or sulfoximine based reagents **5** and **6** were submitted to the reaction conditions, around 10% of the desired alkynylated proline **28** was obtained.

Finally, the gold-catalyzed alkynylation of indole (**29**)[36] was studied using the newly developed reagents, but no C3-alkynylated indole **30** was isolated (Scheme 9A). Likewise, all attempts to employ these reagents in the atom-economical aminoalkynylation of diazo compounds under the conditions developed for oxyalkynylation[13,37] did not afford promising results (Scheme 9B). The lack of reactivity could be linked to the lack of nitrogen nucleophilicity observed on the MEP maps.

Conclusions

In summary, we have synthesized four new N-heterocyclic alkynyl hypervalent iodine reagents and elucidated their solid-sate structures via X-ray crystallography. We demonstrated the possibility to modulate the iodine-alkyne bond length by modifying the iodoheterocycle and fine-tuning the *trans* effect. The modification of the iodoheterocycle had also a clear impact on the distribution of the electron density on the reagents. Computed MEP maps showed a transfer of electron-density away from the nitrogen bound to the iodine, and a diminished σ-hole region in the case of tosylated reagents. Finally, the reactivity of the new hypervalent compounds was compared to



Scheme 9. Unsuccessful A) Alkynylation of indole (**29**) and B) Aminoalkynylation of diazo compounds.

the already established EBX and EBZ reagents. The alkynylation of β-ketoester was successful with all new reagents, except for the unstable reagent **3** bearing an unprotected amidine group. On the other hand, only reagents with more pronounced σ-hole regions reacted well in the thioalkynylation reaction. Transfer to radical intermediates was possible in low yield for the benzylamine and sulfoximine based reagents in the photoredox-catalyzed decarboxylative alkynylation of proline.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: alkynyl transfer · density functional calculations · heterocycles · hypervalent iodine · sulfoximine

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[23] Reagents Nomenclature: TIPS-H,Ts-EBZI (**3**) = substituent on alkyne-substituent on the nitrogen linked to the iodine, substituent on the other nitrogen-EthynylBenziodazolImine; TIPS-Ts-EBZI (**4**) = substituent on alkyne-substituent on both nitrogen-EthynylBenziodazolImine; TIPS-Ts-EBz (**5**) = substituent on alkyne-substituent on the nitrogen linked to

the iodine-EthynylBenziodazole; TIPS-CF_3-EBS (**6**) = substituent on alkyne-substituent on the sulfoximine-EthynylBenziodoSulfoximine.

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1. General methods

All reactions were carried out in oven dried glassware under an atmosphere of nitrogen, unless for the oxidative decarboxylation and if stated otherwise. For flash chromatography, distilled technical grade solvents were used. THF, CH_3CN, toluene and CH_2Cl_2 were dried by passage over activated alumina under nitrogen atmosphere (H_2O content < 10 ppm, Karl-Fischer titration). All chemicals were purchased from Acros, Aldrich, Fluka, VWR, TCI, Merck or Bachem and used as such unless stated otherwise. All dipeptides starting materials were commercially available and used as received. Chromatographic purification was performed as flash chromatography using Macherey-Nagel silica 40-63, 60 Å, using the solvents indicated as eluent with 0.1-0.5 bar pressure. TLC was performed on Merck silica gel 60 F254 TLC aluminum or glass plates and visualized with UV light and $KMnO_4$ stain. ^{1}H-NMR spectra were recorded on a Brucker DPX-400 400 MHz spectrometer in chloroform-d, DMSO-d^6 or acetonitrile-d^3, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm, the internal DMSO signal at 2.50 ppm or the internal acetonitrile signal at 1.94 ppm as standard. The data is being reported as (s = singlet, d = doublet, t= triplet, q = quadruplet, qi = quintet, m = multiplet or unresolved, br = broad signal, app = apparent, coupling constant(s) in Hz, integration, interpretation).^{13}C-NMR spectra were recorded with ^{1}H-decoupling on a Brucker DPX-400 100 MHz spectrometer in chloroform-d, DMSO-d^6 or acetonitrile-d^3, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm, the internal DMSO signal at 39.5 ppm or the internal acetonitrile signals at 1.32 and 118.26 ppm as standard. Infrared spectra were recorded on a JASCO FT-IR B4100 spectrophotometer with an ATR PRO410-S and a ZnSe prisma and are reported as cm-1 (w = weak, m = medium, s = strong, br = broad).

High resolution mass spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL on a MICROMASS (ESI) Q-TOF Ultima API. MS-MS analyses were performed on a LTQ Orbitrap FTMS instrument (LTQ Orbitrap Elite FTMS, Thermo Scientific, Bremen, Germany) operated in the positive mode coupled with a robotic chip-based nano-ESI source (TriVersa Nanomate, Advion Biosciences, Ithaca, NY, U.S.A.). A standard data acquisition and instrument control system was utilized (Thermo Scientific) whereas the ion source was controlled by Chipsoft 8.3.1 software (Advion BioScience). Samples were loaded onto a 96-well plate (Eppendorf, Hamburg, Germany) within an injection volume of 5µl. The experimental conditions for the ionization voltage was +1.4kV and the gas pressure was set at 0.30 psi. The temperature of ion transfer capillary was 275 °C, tube voltages. FTMS spectra were obtained in the 80-1000 *m/z* range in the reduce profile mode with a resolution set to 120,000. In all spectra one microscan was acquired with a maximum injection time value of 1000ms. Typical CID experiments were carried out using Normalized collision energy values of 26-28 and 5 Da of isolation width.

Versailles instrumentation

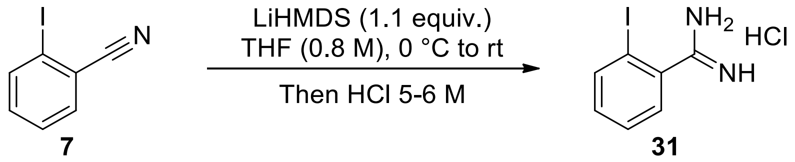
NMR spectra were collected on a Bruker AC-300 spectrometer operating at the denoted spectrometer frequency given in MHz for the specified nucleus. Reported coupling constants and chemicals shifts were based on a first order analysis. $CFCl_3$ (0.00 ppm) was used as internal reference for ^{19}F NMR spectra. High resolution mass spectrometry (HRMS) was recorded on a Mass Spectrometer XEVO-QTOF in the Institute Lavoisier of Versailles – University of Versailles Saint Quentin.

Photoredox catalyzed reactions were performed in test tubes (5 and 10 mL), which were hold using a rack for test tubes placed at the center of a crystallization flask. On this flask were attached the blue LEDs (RUBAN LED 5MÈTRES - 60LED/M - 3528 BLEU - IP65 with Transformateur pour Ruban LED 24W/2A/12V, bought directly on RubanLED.com). The distance between the LEDs and the test tubes was approximatively 2 cm for the test tubes and 5 cm for the Schlenk flasks. Long irradiation resulted in temperature increasing up to 37°C during overnight reactions.

HPLC analysis on chiral stationary phase was performed on a Agilent Acquity instrument using a Daicel CHIRALPAK IA, IB-N5 and IC chiral columns. The exact conditions for the analyses are specified within the characterization section. HPLC traces were compared to racemic samples prepared by running the reactions using racemic substrates. Absolute values of enantiomeric excesses are reported.

2. Preparation of precursors

2-Iodobenzamidine hydrochloride (31)

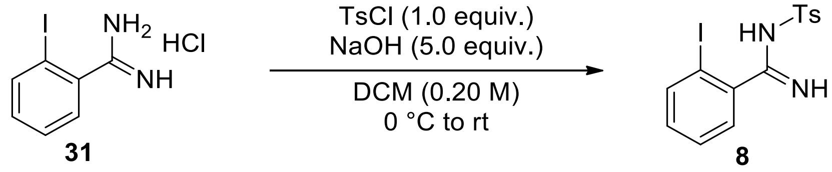


Following a reported procedure,[1] an oven-dried 250 mL flask was charged with LiHMDS (22 mL, 22 mmol, 1.1 equiv.) and cooled to 0 °C and a solution of 2-iodobenzonitrile (**7**) (4.6 g, 20 mmol, 1.0 equiv.) in 2.5 mL of dry THF was added dropwise and the reaction mixture was stirred at this temperature for 15 min. The reaction mixture was then stirred at room temperature for 4h. After cooling the reaction mixture to 0 °C, HCl (5 M in isopropanol, 12 mL, 60 mmol, 3.0 equiv.) was added dropwise. The reaction mixture was stirred at 0 °C and let warm up to rt. The precipitated product was filtered, washed with Et_2O and dry on the filter for 1 h to afford the title compound (**31**) as a white solid (5.1 g, 18 mmol, 90% yield).

^1H NMR (400 MHz, DMSO-d6) δ 8.90 (br s, 4H, N*H*$_2$), 8.01 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar*H*), 7.63-7.49 (m, 2H, Ar*H*), 7.35 (ddd, *J* = 7.9, 7.2, 2.0 Hz,1H, Ar*H*). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.7, 139.4, 136.0, 132.9, 129.0, 128.4, 94.9.

The characterization data corresponded to the reported values.[2]

2-Iodo-N-tosylbenzimidamide (8)



Following a slightly modified reported procedure,[3] a round bottom flask was loaded with 2-iodobenzimidamide.HCl (2.1 g, 7.4 mmol, 1.0 equiv.), *p*-toluenesulfonyl chloride (1.4 g, 7.4 mmol, 1.0 equiv.) and DCM (37 mL). Subsequently, the solution was cooled down to 0 °C and a 10 M aqueous solutiom of NaOH (3.7 ml, 37 mmol, 5.0 equiv.) was added slowly. The reaction mixture was stirred for 5 h at room temperature. The mixture was washed with HCl 1M (3X20 mL), the organic layer was dried over MgSO4 and concentrated under vacuum The crude mixture was purified by flash column chromatography (Pentane/EtOAC 1:2 to 1:1) to afford the title compound (**8**) as a white solid (2.2 g, 5.5 mmol, 74% yield)

R_f = 0.3 (Pentane/EtOAc 2:1). Mp: 136-138 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.37 (br s, 1H, *H*NTs), 7.88 (d, *J* = 8.2 Hz, 2H, Ar*H*), 7.81 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.37 (qd, *J* = 7.7, 1.5 Hz, 2H, Ar*H*), 7.29 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.13-7.06 (m, 1H, Ar*H*), 6.05 (br s, 1H, C=N*H*), 2.41 (s, 3H, C*H*$_3$). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.1, 143.4, 140.2, 139.9, 138.4, 131.9, 129.5, 128.9, 128.5, 127.1, 92.9, 21.7. IR(ν_{max}, cm^{-1}) 3369 (w), 3284 (w), 3121 (w), 3057 (w), 1629 (m), 1535 (m), 1416 (w), 1297 (m), 1142 (s), 1082 (s), 1018 (w), 835 (m), 806 (m), 788 (m), 751 (s), 716 (s), 685 (s), 656 (s). HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{13}IN_2NaO_2S^+$ 422.9635; Found 422.9641.

2-Iodo-N,N'-ditosylbenzimidamide (9)

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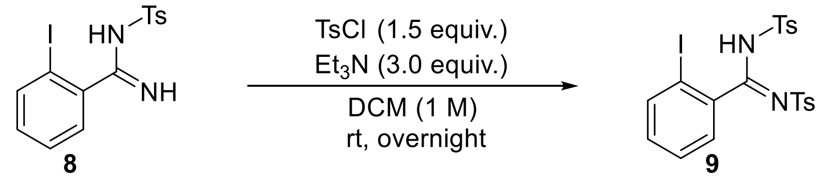
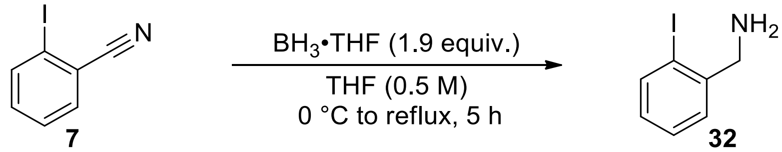


Following a slightly modified procedure,[4] an oven-dried 10 mL microwave vial was charged with 2-iodo-N-tosylbenzimidamide (1.5 g, 3.8 mmol, 1.0 equiv) and triethylamine (0.80 mL, 5.6 mmol, 1.5 equiv) and 1.9 mL of dry DCM. After 10mins a solution of *p*-toluenesulfonyl chloride (1.1 g, 5.6 mmol, 1.50 equiv) and triethylamine (0.80 mL, 5.6 mmol, 1.5 equiv) in 1.9 mL of dry DCM was added dropwise to the reaction mixture. The reaction mixture was stirred at rt overnight. The reaction mixture was then diluted with DCM (10 mL), and the mixture was washed 1M HCL (3X 10 mL). The organic phase was combined with a dichloromethane extract of the aqueous phase, dried (MgSO4), and concentrated under vacuum. The crude mixture was purified by flash column chromatography using DCM/MeOH 2% as mobile phase to afford the title compound as a yellowish solid (**9**) (1.7 g, 3.1 mmol, 83% yield).

R_f = 0.27 (DCM/MeOH 4%). Mp: 185-187 °C. ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 9.36 (s, 1H, N*H*), 7.84 (dd, *J* = 8.0, 0.7 Hz, 1H, Ar*H*), 7.62 (br s, 4H, Ar*H*), 7.47 (td, *J* = 7.6, 1.1 Hz, 1H, Ar*H*), 7.36-7.12 (m, 6H), 2.43 (s, 6H, C*H*$_3$). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 161.8, 139.8, 138.6, 132.7, 130.3, 129.8, 128.8, 128.0, 94.1, 21.7.[5] IR (ν_{max}, cm^{-1}) 3667 (w), 2978 (m), 2902 (m), 1603 (m), 1454 (m), 1352 (m), 1311 (m), 1168 (s), 1146 (s), 1083 (s), 932 (m), 818 (m), 768 (m), 720 (s), 682 (s). HRMS (APPI/LTQ-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{21}H_{20}IN_2O_4S_2^+$ 554.9904; Found 554.9902.

2-Iodobenzylamine (32)



Following a slightly modified procedure,[6] in an oven dried round-bottom flask 2-iodobenzonitrile (5.0 g, 22 mmol, 1.0 equiv.) and dry THF (44 mL) were mixed together, then borane-THF complex (41 ml, 41 mmol, 1.9 equiv.) was added dropwise to the solution at 0 °C. The mixture was refluxed under stirring for 5 h, then it was hydrolyzed at 0 °C with HCl 6 N until pH ~ 1; after, it was made basic with KOH until pH ~ 13 and extracted with DCM. The combined organic phases were washed with brine, dried over $MgSO_4$ and the solvent was removed under vacuum. The crude mixture was purified by flash column chromatography (DCM to DCM/MeOH 20:1) to afford the title compound as green oil (**32**) (3.1 g, 13 mmol, 61% yield)

Rf = 0.36 (DCM/MeOH 9:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.42-7.28 (m, 2H, Ar*H*), 6.95 (td, *J* = 7.7, 1.9 Hz, 1H, Ar*H*), 3.87 (s, 2H, ArC*H*$_2$NH$_2$), 1.64 (s, 2H, N*H*$_2$). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.2, 139.6, 128.8, 128.7, 128.6, 99.1, 51.5.

The characterization data corresponded to the reported values.[7]

N-(2-iodobenzyl)-4-methylbenzenesulfonamide (10)

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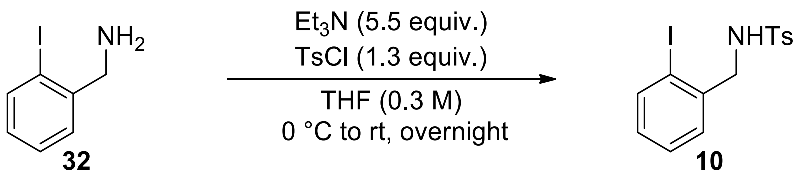
[4] A. Guzmán, M. Romero, F. X. Talamás, R. Villena, R. Greenhouse, J. M. Muchowski, *J. Org. Chem.* **1996**, *61*, 2470–2483.

[5] 2 carbons were not resolved by ^{13}C in acetonitrile-d_3

[6] L. A. Aronica, G. Albano, L. Giannotti, E. Meucci, *Eur. J. Org. Chem.* **2017**, *2017*, 955–963.

[7] T. Fukuyama, T. Bando, I. Ryu, *Synthesis* **2018**, *50*, 3015–3021.

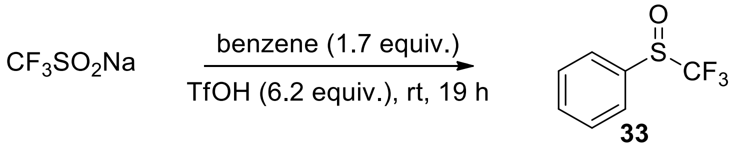


Following a slightly modified procedure,[6] in an oven dried round-bottom flask 2-iodobenzylamine (1.0 g, 4.3 mmol, 1.0 equiv.) triethylamine (3.3 ml, 24 mmol, 5.5 equiv.) and dry THF (14 mL) were mixed together, then *p*-toluenesulfonyl chloride (1.1 g, 5.6 mmol, 1.3 equiv.) was added to the solution at 0 °C. The solution was left under stirring overnight at room temperature, then it was extracted with EtOAc. The combined organic phases were washed with H_2O and brine, dried over $MgSO_4$ and the solvent was removed under vacuum. The crude mixture was purified by flash column chromatography (Pentane/EtOAc 10:1) to afford the title compound as a white solid (**10**) (1.6 g, 4.2 mmol, 97% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75-7.70 (m, 3H, Ar*H*), 7.32-7.22 (m, 4H, Ar*H*), 6.94 (td, *J* = 7.6, 1.9 Hz, 1H, Ar*H*), 4.90 (t, *J* = 6.4 Hz, 1H, N*H*), 4.18 (d, *J* = 6.5 Hz, 2H, ArCH_2NHTs), 2.41 (s, 3H, CH_3). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.6, 139.6, 138.7, 137.0, 130.2, 129.8(3C), 128.7, 127.3, 98.9, 51.9, 21.7.

The characterization data corresponded to the reported values.[6]

((trifluoromethyl)sulfinyl)benzene (33)



A dry 1 L, three-necked, round-bottomed flask equipped with a thermometer and a mechanical stirrer was charged with sodium trifluoromethanesulfinate (90 g, 0.58 mol, 1.0 equiv.) and dried under vacuum for 24 h prior to use. The flask is placed in a cold-water bath and trifluoromethanesulfonic acid (0.32 L, 3.6 mol, 6.2 equiv.) is added, under argon, in three portions with vigorous stirring (around 100 mL each), in order to keep the temperature under 50 °C. After the addition, the reaction is stirred for 20−30 min until the temperature decreases to room temperature. Then, benzene (90 mL, 1.0 mol, 1.7 equiv.) is added in one portion and the solution is stirred at room temperature for 19 h under an inert atmosphere. The reaction is quenched by pouring the reaction medium on ice (900 g), extracted with dichloromethane (3 × 100 mL), and washed with a saturated solution of $NaHCO_3$ (3 × 60 mL). The organic phase is dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The product is purified by distillation under reduced pressure (78−80 °C at 15 mmHg) to afford the title compound as a colorless oil (**33**) (78 g, 0.40 mol, 69% yield).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.4 Hz, 2H, Ar*H*), 7.70−7.49 (m, 3H, Ar*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6 (q, *J* = 1.7 Hz), 133.6, 129.6, 125.9, 124.7 (q, *J* = 335 Hz, CF_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ −75.0 (s, 3F).

The characterization data corresponded to the reported values.[8]

(S-(trifluoromethyl)sulfonimidoyl)benzene (12)

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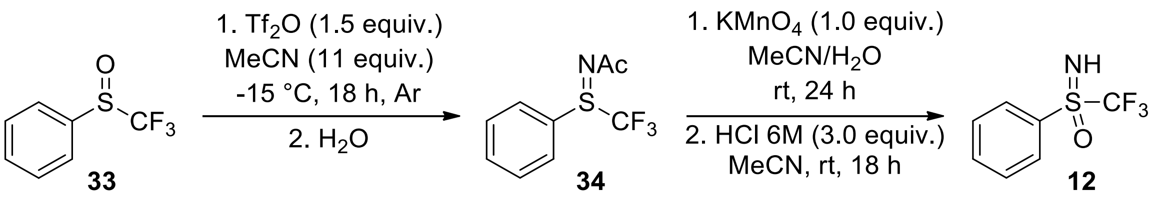
[8] A.-L. Barthelemy, V. Certal, G. Dagousset, E. Anselmi, L. Bertin, L. Fabien, B. Salgues, P. Courtes, C. Poma, Y. El-Ahmad, E. Magnier, *Org. Process Res. Dev.* **2020**, *24*, 704–712.

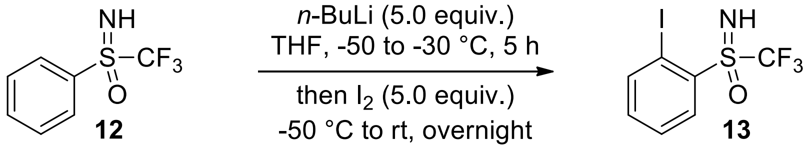


In a dry 500 mL two-necked round-bottomed flask equipped with a dropping-funnel and a thermometer, a solution of phenyl trifluoromethyl sulfoxide **33** (40.0 g, 206 mmol, 1.00 equiv.) in dry acetonitrile (120 mL, 2.28 mol, 11.0 equiv.) is cooled to −15 °C under argon. Tf_2O (52.0 mL, 309 mmol, 1.50 equiv.) is introduced into the dropping-funnel and added dropwise to the solution, keeping the temperature around −15 °C. The solution is then left at −15 °C for 18 h under argon in a freezer. The reaction is quenched by pouring the reaction media on ice (400 g), extracted with dichloromethane (3 × 80 mL), and washed with a saturated solution of NaHCO3 (3 × 40 mL). The organic phase is dried over $MgSO_4$, filtered, and concentrated under reduced pressure. To a solution of this crude product in acetonitrile (160 mL) and water (40 mL) is added $KMnO_4$ (32.6 g, 206 mmol, 1.00 equiv.) portionwise. The reaction is stirred at room temperature for 18 h and diluted with H2O (150 mL), and a saturated solution of $Na_2S_2O_4$ is added until complete discoloration of the solution. The product is extracted with dichloromethane (3 × 70 mL), and the organic phase is dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product is dissolved in acetonitrile (184 mL), and HCl 6 M (67.2 mL) is added. The reaction is stirred at room temperature for 18 h. Then, water (100 mL) is added and the organic phase is extracted with dichloromethane (3 × 50 mL), washed with a solution of saturated NaHCO3 (3 × 20 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The product is filtered on silica (200 g) using petroleum ether/ethyl acetate 8/2 as eluent to afford the title compound as a white solid (**12**) (32.8 g, 157 mmol, 76%).

^1H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.5 Hz, 2H, Ar*H*), 7.84−7.72 (m, 1H, Ar*H*), 7.63 (dd, *J* = 8.5, 7.1 Hz, 2H, Ar*H*), 3.53 (s, br s, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6, 131.6, 130.7, 129.6, 121.0 (q, *J* = 333 Hz, CF_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ −79.3 (s, 3F).

The characterization data corresponded to the reported values.[8]

1-iodo-2-(*S*-(trifluoromethyl)sulfonimidoyl)benzene (13)



A solution of 2.5 M *n*-BuLi in hexane (96 mL, 0.24 mol, 5.0 equiv.) was added dropwise to a solution of (S-(trifluoromethyl)sulfonimidoyl)benzene **12** (10 g, 48 mmol, 1.0 equiv.) in freshly distilled THF (300 mL) at -50 °C. The reaction temperature was slowly increased to -30°C over 5 h. The reaction mixture was cooled to -50 °C, and solid I_2 (61 g, 0.24 mol, 5.0 equiv.) was added portion-wise. The reaction mixture was allowed to warm to room temperature overnight and subsequently quenched with a saturated aqueous NH_4Cl solution (200 mL). The aqueous layer was extracted with Et_2O (3 x 200 mL), dried with anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography using toluene/MeOH (98/2) as eluent to give the title compound as a pale yellow solid **13** (15 g, 45 mmol, 94% yield).

^1H NMR (300 MHz, CD_3CN, 298 K): δ 8.40 (dd, *J* = 8.1, 1.3 Hz, 1H, Ar*H*), 8.32 (dd, *J* = 7.9, 0.9 Hz, 1H, Ar*H*), 7.72-7.67 (m, 1H, Ar*H*), 7.43 (td, *J* = 7.7, 1.5 Hz, 1H, Ar*H*), 4.98 (br. s, 1H, N*H*). ^{13}C NMR (75 MHz, CD_3CN, 298 K): δ 145.8, 137.2, 135.5, 135.2, 130.5, 121.8 (q, *J* = 333 Hz), 95.0. ^{19}F NMR (282 MHz, CD_3CN, 298 K): δ -75.4.

The characterization data corresponded to the reported values.[9]

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[9] J. Kalim, T. Duhail, T.-N. Le, N. Vanthuyne, E. Anselmi, A. Togni, E. Magnier, *Chem. Sci.* **2019**, *10*, 10516–10523.

Semi-preparative separation of **13**:

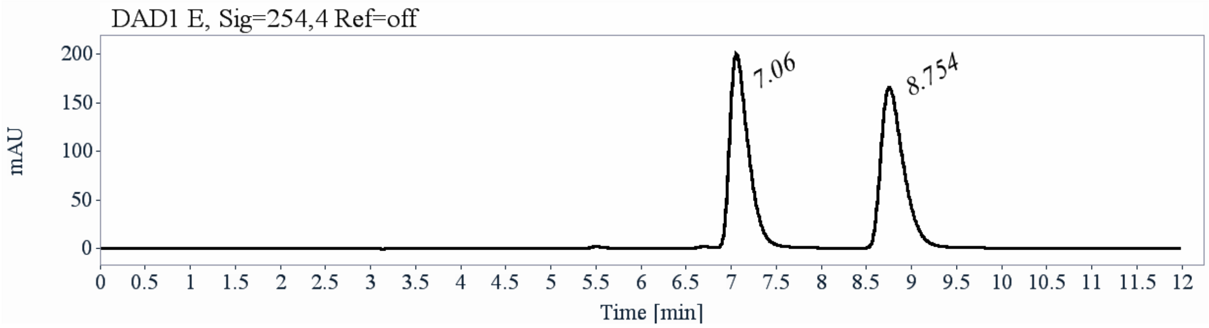


Figure S1: *HPLC trace of racemic **13**. Chromatographic conditions: Chiralpak AS-H (250 x 10 mm), n-hexane/isopropanol (80/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 270 nm. Retention times: 7.06 min [(+)-**13**], 8.75 min [(–)-**13**].*

RT [min]	Area	Area%
7.06	2830	49.46
8.75	2891	50.54

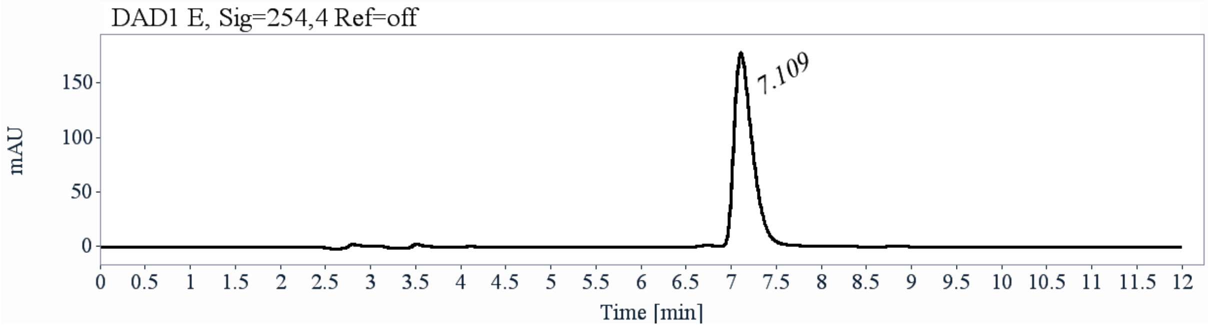


Figure S2: *HPLC trace of enantiopure (+)-**13**. Chromatographic conditions: Chiralpak AS-H (250 x 10 mm), n-hexane/isopropanol (80/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 270 nm.*

RT [min]	Area	Area%
7.11	2474	100.00

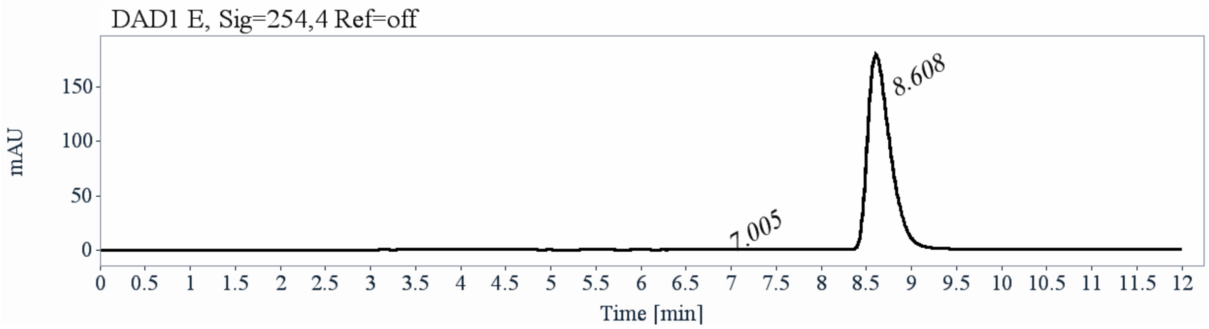
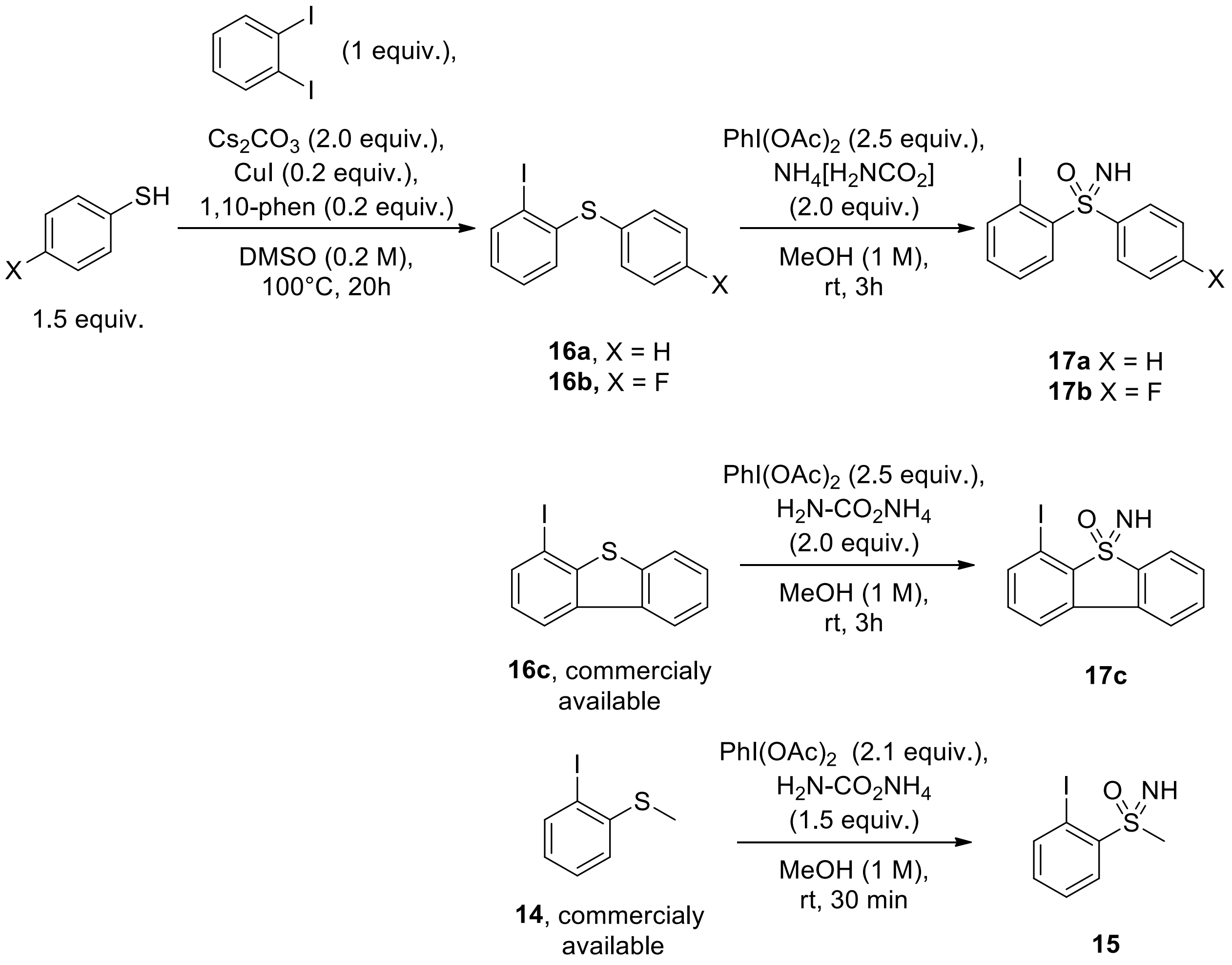


Figure S3: *HPLC trace of enantiopure (–)-**13**. Chromatographic conditions: Chiralpak AS-H (250 x 10 mm), n-hexane/isopropanol (80/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 270 nm*

RT [min]	Area	Area%

7.00	7	0.23
8.61	3159	99.77

Other sulfoximines 15, 17a, 17b and 17c



16a, X = H
16b, X = F

17a X = H
17b X = F

16c, commercialy available

17c

14, commercialy available

15

Sulfides 16a and 16b

Following a reported procedure,[10] a round bottom flask was charged with thiol aryl (1.5 equiv.), 1,2-diiodobenzene (1.0 equiv), Cs_2CO_3 (2.0 equiv.), CuI (0.2 equiv.), and 1,10-phenanthroline (0.2 equiv.) in DMSO (0.2 M) and heated at 100°C for 20h. The reaction mixture was then cooled at room temperature and diluted with water, extracted with EtOAc and dry over $MgSO_4$. The desired sulfide was isolated after column chromatography on silica gel (100% pentane) as a solid ; **16a** and **16b** were respectively obtained in 55% and 30% yield starting from thiophenol and 4-fluorothiophenol respectively. The characterization data corresponded to the reported values.[10]

Sulfoximines 15, 17a, 17b and 17c

Following a reported procedure,[11] a round bottom flask was charged with sulfide (1.0 equiv.) and MeOH (1 M). PIDA (2.5 equiv.) and ammonium carbamate (2.0 equiv.) were successively added, the flask well closed to maintain an ammoniac atmosphere and the reaction mixture stirred at room temperature for 3h (only 30 min were necessary for the transformation of **14** in **15**, and quantity of PIDA and ammonium carbamate could be reduced respectively to 1.5 equiv. and 2.1 equiv. in this case). Chromatography on silica gel (P/EtOAc 1/1) afforded the desired *ortho*-

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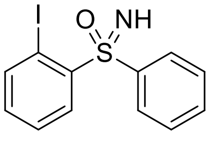
[10] Y. Liu, H. Wang, X. Cao, Z. Feng, J.-P. Wan, *Synthesis* **2013**, *45*, 2977-2982.

[11] A. Tota, M. Zenzola, S. J. Chawner, S. St John-Campbell, C. Carlucci, G. Romanazzi, L. Degennaro, J. A. Bull, R. Luisi, *Chem. Commun.* **2017**, *53*, 348-351.

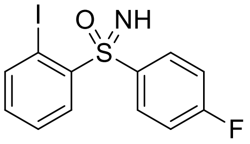
iodinated sulfoximine as solid. **15**, **17a**, **17b** and **17c** were respectively obtained in 60%, 70%, 63% and 60 yield starting from **14**, **16a**, **16b** and **16c** respectively.

1-iodo-2-(phenylsulfonimidoyl)benzene 17a



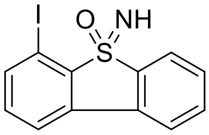
^{1}H NMR (300 MHz, CD_3CN) δ 8.46 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 8.1 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 3.25 – 2.20 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, CD_3CN) δ 145.8, 144.2, 141.7, 134.6, 133.7, 131.6, 130.2, 129.9, 129.7, 129.6, 128.6, 93.9 (*C*-I). HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{12}H_{11}INOS^+$ 343.9601; Found 343.9594.

1-(4-fluorophenylsulfonimidoyl)-2-iodobenzene 17b



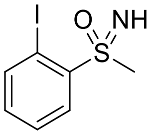
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.0 Hz, 1H), 8.09 – 7.91 (m, 3H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.14 (t, *J* = 8.5 Hz, 3H), 3.24 (s, 1H, *N*H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.28 (d, *J* = 255.4 Hz, *C*-F), 144.7, 143.3, 135.90 (d, *J* = 3.1 Hz), 133.7, 132.1, 131.9, 130.6, 128.8, 116.1, 115.8, 93.2 (*C*-I). ^{19}F NMR (282 MHz, $CDCl_3$) δ -105.5 (td, *J* = 8.4, 4.2 Hz). HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{12}H_{11}INOSF^+$ 361.9506; Found 361.9485.

5-imino-4-iododibenzo[b,d]thiophene 5-oxide 17c



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.7 Hz, 1H), 7.85 – 7.71 (m, 3H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.21 (dd, *J* = 8.5, 6.9 Hz, 1H), 3.81 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4, 140.0, 138.9, 133.9, 133.8, 133.3, 130.8, 130.8, 122.8, 121.4, 121.3, 85.7 (*C*-I). HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{12}H_9INOS^+$ 341.9444; Found 341.9456.

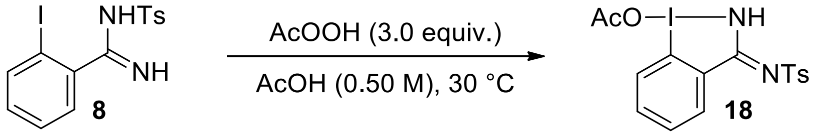
1-iodo-2-(S-methylsulfonimidoyl)benzene 15



^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.9 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 3.25 (s, 3H), 2.85 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.4, 143.0, 133.8, 130.5, 129.0, 93.2 (*C*-I), 42.5 (CH_3). HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_7H_9INOS^+$ 281.9444; Found 281.9446.

3. Preparation of hypervalent iodine reagents

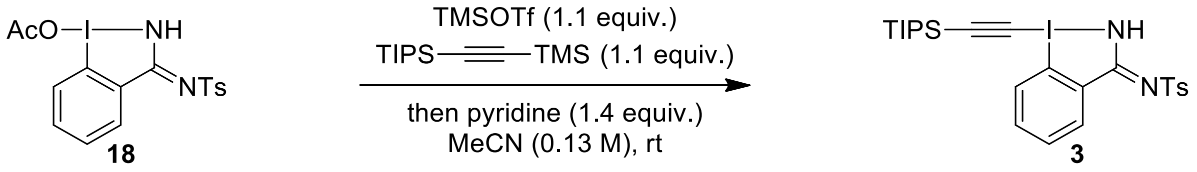
3-(Tosylimino)-2,3-dihydro-1H-1λ^3-benzo[d][1,2]iodazol-1-yl acetate (AcO-H,Ts-BZI, 15)



Following a slightly modified reported procedure,[12] in a round bottom flask, 2-iodo-N-tosylbenzimidamide **8** (2.0 g, 5.0 mmol, 1.0 equiv.) was dissolved in acetic acid (10 mL). The reaction mixture was cooled to 0 °C and peracetic acid (39% in acetic acid, 2.6 mL, 15 mmol, 3.0 equiv) was added dropwise to the aluminium foil covered flask. The reaction mixture was stirred at 30 °C for 2 h. The reaction was quenched by the addition of water (5 mL) and the precipitate was filtrated and washed with cold water (4X 5 mL) and with cold Et_2O (3X 5 mL). The precipitate was dried under vacuum and afforded the title compound as a white solid (**18**) (2.2 g, 4.8 mmol, 97% yield).

Mp > 166 °C (decomposition). ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.97 (s, 1H, N*H*), 8.00 (d, *J* = 7.9 Hz, 1H, Ar*H*), 7.86-7.81 (m, 2H, Ar*H*), 7.73 (d, *J* = 8.2 Hz, 3H, Ar*H*), 7.22 (d, *J* = 8.0 Hz, 2H, Ar*H*), 2.32 (s, 3H, ArCH_3), 1.91 (s, 3H, OCCH_3). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.1, 169.0, 144.2, 142.5, 140.1, 132.3, 131.9, 129.6, 129.0, 128.5, 126.5, 121.0, 21.1, 20.9. IR (vmax, cm^{-1}) 3336 (w), 3064 (w), 2979 (w), 2920 (w), 1611 (w), 1576 (m), 1516 (s), 1363 (m), 1318 (s), 1158 (m), 1136 (s), 1082 (s), 1016 (m), 873 (s), 781 (s), 734 (m), 660 (s). HRMS (nanochip-ESI/LTQ-Orbitrap) m/z: [M + H]$^+$ Calcd for $C_{16}H_{16}IN_2O_4S^+$ 458.9870; Found 458.9854.

4-Methyl-N-(1-((triisopropylsilyl)ethynyl)-1,2-dihydro-3H-1λ^3-benzo[d][1,2]iodazol-3-ylidene)benzenesulfonamide (TIPS-H,Ts-EBZI, 3)



Following a reported procedure,[15] an oven-dried round-bottom flask equipped with magnetic stirring bar was charged with AcO-H,Ts-BZI **18** (1.0 g, 2.2 mmol, 1.0 equiv.) and MeCN (17 mL). TMS-OTf (0.43 mL, 2.4 mmol, 1.1 equiv.) was added to the solution and the resulting mixture was stirred at rt for 1 h. Then triisopropyl((trimethylsilyl)ethynyl)silane (0.61 g, 2.4 mmol, 1.1 equiv.) was added to the reaction mixture. After stirring at rt for 18 h, pyridine (0.25 mL, 3.1 mmol, 1.4 equiv.) was added and the reaction mixture was stirred vigorously for 1 h. The crude mixture was filtered and the precipitate washed with MeCN. The filtrate was concentrated under vacuum and purified by flash column chromatography using DCM/MeOH 99:1 as mobile phase to afford the title compound as a white solid (**3**) (0.36 g, 0.61 mmol, 28% yield).

R_f = 0.20 (DCM/MeOH 1%). Mp > 162 °C (decomposition). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (dd, *J* = 5.8, 3.2 Hz, 2H, N*H* and Ar*H*), 8.48-8.41 (m, 1H, Ar*H*), 7.86 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.71 (q, *J* = 5.2, 3.5 Hz, 2H, Ar*H*), 7.21 (d, *J* = 8.0 Hz, 2H, Ar*H*), 2.36 (s, 3H, CH_3), 1.13 (m, 21H, TIPS). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.9, 142.0, 141.0, 134.1, 133.1, 131.4, 131.3, 129.2, 127.2, 126.4, 113.8, 110.2, 78.1, 21.6, 18.7, 11.4. IR (vmax, cm-1) 3329 (w), 2948 (w), 2870 (w), 1579 (w), 1517 (m), 1375 (m), 1271 (m), 1167 (w), 1135 (m), 1078 (m), 1002 (w), 876 (m), 812 (m), 773 (m), 662 (s). HRMS (ESI/QTOF) m/z: [M + H]$^+$ Calcd for $C_{25}H_{34}IN_2O_2SSi^+$ 581.1149; Found 581.1148.

N-(1-chloro-2-tosyl-1,2-dihydro-3H-1λ^3-benzo[d][1,2]iodazol-3-ylidene)-4-methyl-

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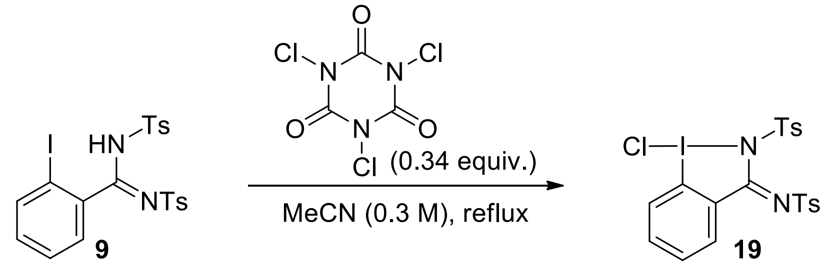
[12] V. V. Zhdankin, R. M. Arbit, B. J. Lynch, P. Kiprof, V. G. Young, *J. Org. Chem.* **1998**, *63*, 6590–6596.

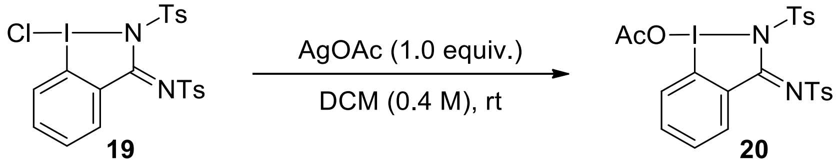
-benzenesulfonamide (Cl-Ts-BZI, 19)



Following a reported procedure,[13] an oven-dried round-bottom flask equipped with magnetic stirring bar was charged under Ar with solid 2-iodo-N,N'-ditosylbenzimidamide (**9**) (1.1 g, 2.0 mmol, 1.0 equiv.) and anhydrous MeCN (7.0 mL) was added. The resulting stirred suspension was heated to 75 °C. A solution of trichloroisocyanuric acid (0.19 g, 0.80 mmol, 0.40 equiv, 1.2 equiv. in "Cl") in 1.0 mL of anhydrous MeCN was added dropwise. After addition was complete, the reaction mixture was refluxed for an additional 15 min. The reaction mixture was vacuum-filtered over a sintered-glass funnel and the precipitate was rinsed with additional hot MeCN (10−20 mL), the precipitate was air-dried. Then the precipitate was washed on a filter with DCM until only isocyanuric acid was left on the filter. The filtrate was concentrated under vacuum to afford the title compound (**19**) as a yellowish solid (1.1 g, 1.9 mmol, 93 %yield).

Mp > 223 °C (decomposition). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.36 (dd, *J* = 7.4, 2.1 Hz, 1H, Ar*H*), 8.45-8.36 (m, 1H, Ar*H*), 7.88 (ddd, *J* = 6.8, 4.6, 1.7 Hz, 2H, Ar*H*), 7.84 (d, *J* = 8.3 Hz, 2H, Ar*H*), 7.40 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.32 (d, *J* = 8.3 Hz, 2H, Ar*H*), 6.94 (d, *J* = 8.1 Hz, 2H, Ar*H*), 2.53 (s, 3H, CH_3), 2.35 (s, 3H, CH_3). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.5, 145.3, 143.3, 140.0, 136.7, 136.6, 134.0, 132.2, 130.7, 129.5, 129.4, 129.1, 128.5, 127.0, 114.9, 21.9, 21.8. IR (ν_{max}, cm^{-1}) 3086 (w), 1553 (m), 1444 (w), 1303 (m), 1256 (w), 1151 (m), 1082 (m), 1002 (w), 951 (w), 837 (m), 809 (m), 714 (s), 656 (m). Despite many attempts, the mass of the compound was not found by HRMS.

2-Tosyl-3-(tosylimino)-2,3-dihydro-1H-1λ^3-benzo[d][1,2]iodazol-1-yl acetate (AcO-Ts-BZI, 20)



Following a reported procedure,[14] an oven-dried round-bottom flask equipped with magnetic stirring bar was charged under N_2 with N-(1-chloro-2-tosyl-1,2-dihydro-3H-1λ^3-benzo[d][1,2]iodazol-3-ylidene)-4-methylbenzenesulfonamide (**19**) (1.0 g, 1.7 mmol, 1.0 equiv.) and 8.0 mL of dry DCM was added. The flask was covered with aluminium foil to protect it from light. Silver acetate (0.28 g, 1.7 mmol, 1.0 equiv.) was added in one portion and the reaction mixture was stirred at rt for 22 h. The solution was filtered over a sintered-glass funnel and washed with DCM. The filtrate was concentrated under vacuum to afford the title compound (**20**) as a white solid (1.0 g,1.7 mmol, quant. yield).

Mp > 190 °C (decomposition). ^{1}H NMR (400 MHz, Methylene Chloride-d_2) δ 9.28 (dd, *J* = 8.0, 1.6 Hz, 1H, Ar*H*), 8.14 (dd, *J* = 8.3, 1.1 Hz, 1H, Ar*H*), 7.87 (td, *J* = 8.4, 7.9, 1.6 Hz, 1H, Ar*H*), 7.83-7.78 (m, 1H, Ar*H*), 7.75 (d, *J* = 8.3 Hz, 2H, Ar*H*), 7.41 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.33 (d, *J* = 8.4 Hz, 2H, Ar*H*), 6.97 (d, *J* = 8.1 Hz, 2H, Ar*H*), 2.53 (s, 3H, ArCH_3), 2.36 (s, 3H, ArCH_3), 2.25 (s, 3H, OCCH_3). ^{13}C NMR (101 MHz, Methylene Chloride-d_2) δ 176.7, 155.0, 145.7, 143.8, 140.7, 136.8, 136.7, 134.7, 131.8, 131.2, 130.9, 129.8(X2), 129.3, 127.1, 117.5, 22.0, 21.9, 21.0. IR (ν_{max}, cm^{-1}) 3076 (w), 2924 (w), 2751 (w), 1700 (w), 1540 (m), 1447 (w), 1326 (m), 1257 (m), 1209 (m),

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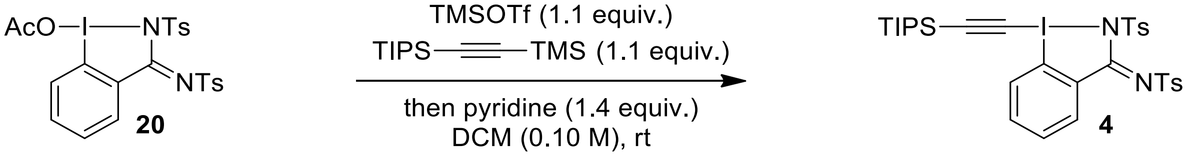
[13] V. Matoušek, E. Pietrasiak, R. Schwenk, A. Togni, *J. Org. Chem.* **2013**, *78*, 6763–6768.

[14] Y. Kita, S. Akai, T. Okuno, M. Egi, T. Takada, H. Tohma, *HETEROCYCLES* **1996**, *42*, 47.

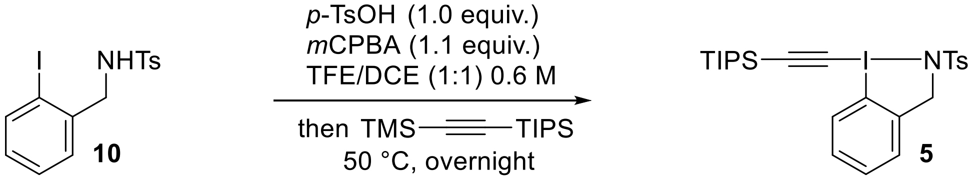
1149 (m), 1081 (m), 955 (w), 832 (m), 727 (s), 663 (s) HRMS (APPI/LTQ-Orbitrap) m/z: [M + H]+ Calcd for $C_{23}H_{22}IN_2O_6S_2^+$ 612.9959; Found 612.9946.

4-Methyl-N-(2-tosyl-1-((triisopropylsilyl)ethynyl)-1,2-dihydro-3H-1λ³-benzo[d][1,2] iodazol-3-ylidene)benzenesulfonamide (TIPS-Ts-EBZI, 4)



Following a reported procedure,[15] an oven-dried round-bottom flask equipped with magnetic stirring bar was charged with AcO-Ts-BZI **20** (0.61 g, 1.0 mmol, 1.0 equiv.) and DCM (7.7 mL). TMS-OTf (0.20 mL, 1.1 mmol, 1.1 equiv.) was added to the solution and the resulting mixture was stirred at rt for 1 h. Then triisopropyl((trimethylsilyl)ethynyl)silane (0.28 g, 1.1 mmol, 1.1 equiv.) was added to the reaction mixture. After stirring at rt for 3 h, pyridine (0.11 mL, 1.4 mmol, 1.4 equiv.) was added and the reaction mixture was stirred vigorously for 30 min. The crude mixture was filtered and the precipitate washed with DCM. The filtrate was concentrated under vacuum and purified by flash column chromatography using DCM/MeOH 99.5:0.5 as mobile phase to afford the title compound as a white solid (**4**) (0.53 g, 0.72 mmol, 72% yield). R_f = 0.32 (DCM/MeOH 1%). Mp > 192 °C (decomposition). ^{1}H NMR (400 MHz, Chloroform-d) δ 9.31 (dd, *J* = 7.9, 1.5 Hz, 1H, Ar*H*), 8.49 (dd, *J* = 8.4, 0.9 Hz, 1H, Ar*H*), 7.86-7.67 (m, 4H, Ar*H*), 7.35 (br d, *J* = 27.6 Hz, 4H, Ar*H*), 6.86 (br s, 2H, Ar*H*), 2.48 (br s, 3H, ArCH_3), 2.30 (br s, 3H, ArCH_3), 1.27-1.10 (m, 21H, TIPS). ^{13}C NMR (101 MHz, Chloroform-d) δ 153.0, 142.1, 141.1, 139.8, 135.6, 135.1, 134.3, 130.6, 130.5, 127.9 (X2), 127.2 (X2), 125.6, 114.3, 114.2, 67.8, 20.6 (X2), 17.5, 10.2. IR (vmax, cm^{-1}) 2949 (w), 2866 (w), 1523 (m), 1456 (w), 1351 (w), 1279 (m), 1147 (m), 1079 (s), 945 (w), 845 (m), 690 (s). HRMS (ESI/QTOF) m/z: [M + H]$^+$ Calcd for $C_{32}H_{40}IN_2O_4S_2Si^+$ 735.1238; Found 735.1248.

2-Tosyl-1-((triisopropylsilyl)ethynyl)-2,3-dihydro-1H-1λ³-benzo[d][1,2]iodazole (TIPS-Ts-EBz, 5)



Following a slightly modified reported procedure,[16] in a sealed tube, N-(2-iodobenzyl)-4-methylbenzenesulfonamide (1.0 g, 2.6 mmol, 1.0 equiv.), *p*-TsOH (0.49 g, 2.6 mmol, 1.0 equiv.) and *m*CPBA (0.64 g, 2.8 mmol, 1.1 equiv) were suspended in DCE:TFE (Ratio: 1:1, Volume: 4.4 mL) and heated up to 50 °C for 60 min. Triisopropyl(2-trimethylsilylethynyl)silane (0.92 g, 3.6 mmol, 1.4 equiv) was added at this temperature. The reaction mixture was stirred at this temperature overnight. The reaction mixture was concentrated under vacuum. The crude mixture was dissolved in 5 mL of DCM and washed with sat. $NaHCO_3$ (3 X 5 mL) and brine (5 mL). The organic layer was dried over $MgSO_4$ and the solvent were evaporated under vacuum. The crude mixture was purified by flash column chromatography using DCM/MeOH 99.5:0.5 as mobile phase to afford the title compound as a white solid (**5**) (0.71 g, 1.3 mmol, 49% yield).

R_f = 0.29 (DCM/MeOH 1%). Mp > 133 °C (decomposition). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31-8.25 (m, 1H, Ar*H*), 7.78-7.73 (m, 2H, Ar*H*), 7.49 (td, *J* = 7.3, 1.0 Hz, 1H, Ar*H*), 7.40-7.33 (m, 1H, Ar*H*), 7.25-7.17 (m, 3H, Ar*H*), 4.32 (s, 2H, ArCH_2N), 2.37 (s, 3H, ArCH_3), 1.13 (m, 21H, TIPS). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.7, 139.1, 138.3, 130.8, 130.2, 129.7, 129.4, 128.8,

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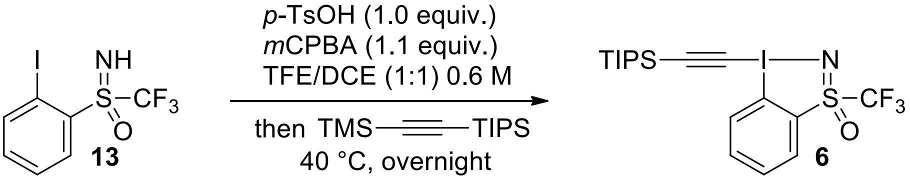
[15] V. V. Zhdankin, C. J. Kuehl, A. P. Krasutsky, J. T. Bolz, A. J. Simonsen, *J. Org. Chem.* **1996**, *61*, 6547–6551.

[16] D. P. Hari, P. Caramenti, L. Schouwey, M. Chang, S. Nicolai, D. Bachert, T. Wright, C. Orella, J. Waser, *Org. Process Res. Dev.* **2020**, *24*, 106–110.

127.0, 111.3, 109.9, 75.8, 46.5, 21.6, 18.7, 11.4. IR (ν_{max}, cm^{-1}) 2940 (m), 2864 (m), 1461 (m), 1273 (s), 1253 (m), 1151 (s), 1135 (s), 1087 (s), 999 (m), 915 (s), 883 (m), 811 (m), 747 (s), 674 (s). HRMS (ESI/QTOF) m/z: [M + H]$^+$ Calcd for $C_{25}H_{35}INO_2SSi^+$ 568.1197; Found 568.1202.

3-(Trifluoromethyl)-1-((triisopropylsilyl)ethynyl)-1H-1λ^3,3λ^4-benzo[d][1,3,2]iodathiazole 3-oxide (TIPS-CF_3-EBS, 6)

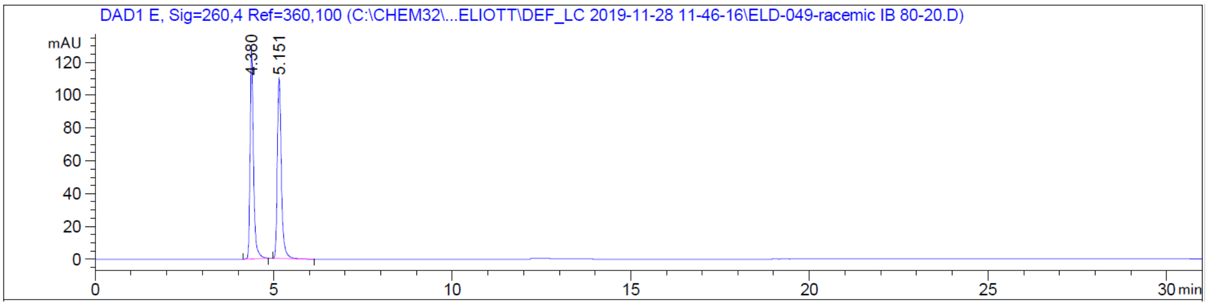


Following a slightly modified reported procedure,[16] in a sealed tube 1-iodo-2-(S-(trifluoromethyl)sulfonimidoyl)benzene **13** (1.0 g, 3.0 mmol, 1.0 equiv.), *p*-TsOH (0.57 g, 3.0 mmol, 1.0 equiv.) and *m*CPBA (0.74 g, 3.3 mmol, 1.1 equiv.) were suspended in DCE:TFE (Ratio: 1:1, Volume: 5.0 mL) and heated up to 40 °C for 60 min. Triisopropyl((trimethylsilyl)ethynyl)silane (1.1 g, 4.2 mmol, 1.4 equiv.) was added at this temperature. The reaction mixture was stirred at this temperature overnight. pyridine (0.34 mL, 4.2 mmol, 1.4 equiv.) was added and the mixture was stirred vigorously for 10 min. The reaction mixture was concentrated under vacuum. The crude mixture was dissolved in 5 mL of DCM and washed with sat. $NaHCO_3$ (3 X 5 mL) and brine (5 mL). The organic layer was dried over $MgSO_4$ and the solvent were evaporated under vacuum. The crude mixture was purified by flash column chromatography using DCM/MeOH 99:1 as mobile phase to afford the title compound as a slightly yellow solid (**6**) (1.2 g, 2.2 mmol, 75 % yield).

R_f = 0.21 (DCM/MeOH 1%). Mp > 125 °C (decomposition). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.79-8.74 (m, 1H, Ar*H*), 8.22 (d, *J* = 7.3 Hz, 1H, Ar*H*), 7.95-7.84 (m, 2H, Ar*H*), 1.15 (m, 21H, TIPS). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.5, 132.4, 131.4, 129.9, 129.0, 122.6 (q, *J* = 337.2 Hz), 120.9, 110.8, 76.1, 18.7, 11.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -77.8. IR (ν_{max}, cm^{-1}) 3076 (m), 2945 (m), 2867 (m), 1559 (m), 1464 (m), 1434 (m), 1301 (s), 1254 (m), 1189 (s), 1169 (s), 1096 (m), 1063 (s), 883 (m), 690 (s). HRMS (ESI/QTOF) m/z: [M + H]$^+$ Calcd for $C_{18}H_{26}F_3INOSSi^+$ 516.0496; Found 516.0494.

For the enantiomer **6** prepared from (-)-**13**: $[\alpha]_{\lambda}^{20}$ ($CHCl_3$, c = 0.5, λ = 589 nm): +12

HPLC trace of racemic **13**, Chiralpak IB 80:20 Hexane/iPrOH, 1.0 ml/min, 31 min



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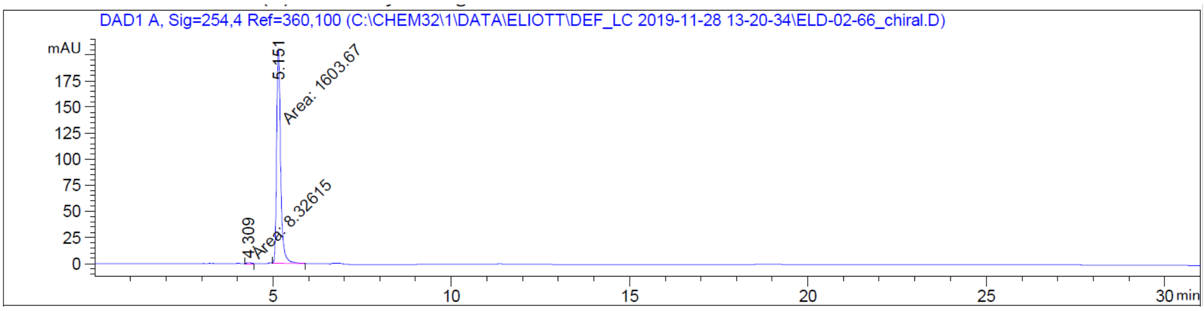
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.380 BB    0.0987  858.55957  130.60844  49.9553
   2   5.151 BB    0.1197  860.09583  109.41880  50.0447
```

HPLC trace of enantiopure (+)-**6** obtained from (-)-**13**, Chiralpak IB 80:20 Hexane/iPrOH, 1.0 ml/min, 31 min



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Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.309 MM    0.1568    8.32615 8.84966e-1   0.5165
   2   5.151 MM    0.1303 1603.67468  205.11935  99.4835
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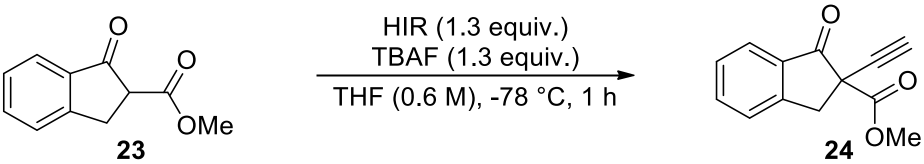
4. Reactivity investigation

Alkynylation of β-ketoesters



23 **24**

Following a reported procedure,[17] a solution of methyl 1-oxo-2,3-dihydro-1H-indene-2-carboxylate (20 mg, 0.10 mmol, 1.0 equiv.) and hypervalent iodine reagent (0.13 mmol, 1.30 equiv.) in dry THF (1.7 mL) was stirred at -78 °C for 5 min under nitrogen. After this period of time, TBAF (0.13 mL, 0.13 mmol, 1.3 equiv.) was added and the mixture was vigorously stirred at -78 °C. The reaction was monitored by TLC analysis (Pentane/EtOAc, 4:1, UV and p-anisaldehyde) and was complete at -78 °C in 1 hour. The reaction was quenched by addition of water at rt and aqueous layer was extracted with DCM. The combined layer were dried over MgSO4 and concentrated under vacuum. The crude mixture was purified by PrepTLC (Pentane/EtOAc 5/1) to afford the title **24** as a yellow oil.

Starting from TIPS-H,Ts-EBZI **3** (75 mg, 0.13 mmol, 1.3 equiv.), **24** was not observed.

Starting from TIPS-Ts-EBz **5** (74 mg, 0.13 mmol, 1.3 equiv.), **24** could not be isolated from the degradation products of **5** (79% NMR yield using CH_2Br_2 as internal standard).

Starting from racemic TIPS-EBS **6** (67 mg, 0.13 mmol, 1.3 equiv.), **24** (20 mg, 90 µmol, 90% yield) was obtained as a racemic mixture.

Starting from enantiopure TIPS-EBS **(+)-6** (67 mg, 0.13 mmol, 1.3 equiv.), **24** (20 mg, 90 µmol, 90% yield) was obtained as a racemic mixture.

Starting from TIPS-EBX **21** (56 mg, 0.13 mmol, 1.3 equiv.), **24** (21 mg, 0.10 mmol, quant. Yield) was obtained.

Starting from TIPS-Ts-EBZI **4** (96 mg, 0.13 mmol, 1.3 equiv.), **24** (21 mg, 0.10 mmol, quant. Yield) was obtained.

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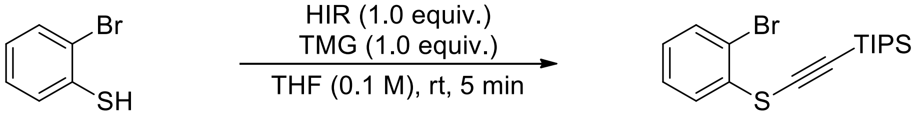
[17] D. Fernández González, J. P. Brand, R. Mondière, J. Waser, *Advanced Synthesis & Catalysis* **2013**, *355*, 1631–1639.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.70-7.64 (m, 1H, Ar*H*), 7.50 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.47-7.41 (m, 1H, Ar*H*), 3.94 (d, *J* = 17.1 Hz, 1H, ArC*H*$_2$), 3.80 (s, 3H, OC*H*$_3$), 3.52 (d, *J* = 17.1 Hz, 1H, ArC*H*$_2$), 2.42 (s, 1H, CC*H*).

The ^{1}H NMR data corresponds to literature data.[17]

Alkynylation of thiol



25 **26**

Following a reported procedure,[18] a 5 mL microwave vial was charged with a magnetic stir bar, 2-bromobenzenethiol (12 µL, 0.10 mmol, 1.0 equiv.), 1,1,3,3-tetramethylguanidine (13 µL, 0.10 mmol, 1.0 equiv.) and THF (1.0 mL). After stirring the resulting solution for 5 minutes at room temperature, hypervalent iodine reagent (0.10 mmol, 1.0 equiv.) was added as a solid in one portion. The resulting reaction mixture was stirred with an open flask for 5 minutes at room temperature. Next, the mixture was diluted with water (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in vacuo. The reaction mixture was purified by PrepTLC using pentane as mobile phase affording **26** as a clear colourless oil.

Starting from TIPS-H,Ts-EBZI **3** (58 mg, 0.10 mmol, 1.0 equiv.), **26** was not observed.

Starting from TIPS-Ts-EBz **5** (57 mg, 0.10 mmol, 1.0 equiv.), **26** (8 mg, 2 µmol, 22% yield)

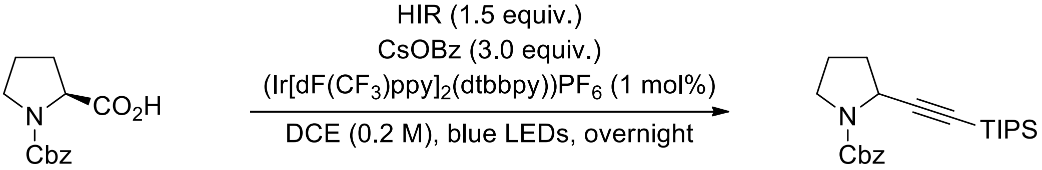
Starting from racemic TIPS-EBS **6** (52 mg, 0.10 mmol, 1.0 equiv.), **26** (27 mg, 73 µmol, 73% yield) was obtained.

Starting from TIPS-Ts-EBZI **4** (74 mg, 0.10 mmol, 1.0 equiv.), **26** (17 mg, 46 µmol, 46% yield) was obtained.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (dd, *J* = 8.0, 1.1 Hz, 1H, Ar*H*), 7.51-7.47 (m, 1H, Ar*H*), 7.40-7.31 (m, 1H, Ar*H*), 7.08 (td, *J* = 7.9, 1.3 Hz, 1H, Ar*H*), 1.13 (m, 21H, TIPS).

The ^{1}H NMR data corresponds to literature data.[18]

Decarboxylative-alkynylation of proline



27 **28**

Following a reported procedure,[19] dry degassed DCE (0.50 mL) was added in a flame dried 1.5 mL test tube containing a teflon coated stirring bar, Cbz-Pro-OH (25 mg, 0.10 mmol, 1.0 equiv.), hypervalent iodine reagent (0.15 mmol, 1.5 equiv.), CsOBz (76 mg, 0.30 mmol, 3.0 equiv.) and $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (1.1 mg, 1.0 µmol, 0.01 equiv.) under N_2. The reaction mixture was again degassed by bubbling N_2 inside the test tube via syringe for 5 min before being irradiated using blue light LEDs for 22 h at rt. The reaction mixture was filtered over celite, eluting with ethyl acetate, and evaporated under reduced pressure. The crude product was purified by preparative TLC (Pentane/Ethyl Acetate 8/2) directly without any further work-up.

Starting from TIPS-H,Ts-EBZI **3** (87 mg, 0.15 mmol, 1.5 equiv.), **28** was not observed.

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[18] R. Frei, J. Waser, *J. Am. Chem. Soc.* **2013**, *135*, 9620–9623.

[19] F. Le Vaillant, T. Courant, J. Waser, *Angew. Chem. Int. Ed.* **2015**, *54*, 11200–11204.

Starting from TIPS-Ts-EBz **5** (85 mg, 0.15 mmol, 1.5 equiv.), **28** (4 mg, 10 µmol, 10% yield)

Starting from racemic TIPS-EBS **6** (77 mg, 0.15 mmol, 1.5 equiv.), **28** (4 mg, 10 µmol, 10% yield) was obtained.

Starting from TIPS-Ts-EBZI **4** (110 mg, 0.150 mmol, 1.5 equiv.), **28** was not observed.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45-7.27 (m, 5H, Ar*H*), 5.17 (s, 2H, OCH_2Ph), 4.66-4.52 (m, 1H, CbzNC*H*CC), 3.63-3.49 (m, 1H, $CbzNCH_2$), 3.48-3.29 (m, 1H, $CbzNCH_2$), 2.24-1.86 (m, 4H, $CbzNCH_2CH_2CH_2CH$), 1.03 (s, 21H, TIPS).

The ^{1}H NMR data corresponds to literature data.[19]

5. X-ray crystallographic data

5.1. Single Crystal X-Ray Diffraction for the compound 3

Crystals of the compound **3** were obtained from slow evaporation of a DCM solution.

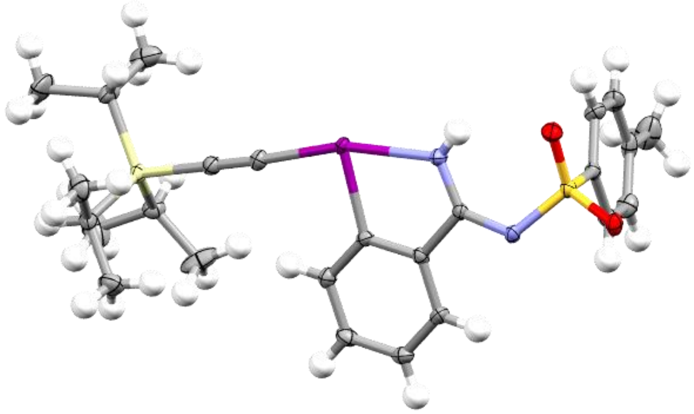


Table 1. Crystal data and structure refinement for **3.**

Identification code	CCDC 2072273	
Empirical formula	$C_{25}H_{33}IN_2O_2SSi$	
Formula weight	580.58	
Temperature	140.02(18) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.6983(5) Å	α= 90°.
	b = 16.7909(6) Å	β= 99.201(3)°.
	c = 13.5441(4) Å	γ = 90°.
Volume	2626.17(17) $Å^3$	
Z	4	
Density (calculated)	1.468 Mg/m^3	
Absorption coefficient	1.368 mm^{-1}	
F(000)	1184	
Crystal size	0.297 x 0.108 x 0.044 mm^3	
Θ range for data collection	2.426 to 32.970°.	
Index ranges	$-17 \leq h \leq 17$, $-25 \leq k \leq 25$, $-20 \leq l \leq 20$	
Reflections collected	15787	
Independent reflections	15787	
Completeness to θ = 25.242°	99.2 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.698	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15787 / 0 / 303	
Goodness-of-fit on F^2	0.924	
Final R indices [I > 2σ(I)]	R_1 = 0.0417, wR_2 = 0.0763	
R indices (all data)	R_1 = 0.0646, wR_2 = 0.0802	

Largest diff. peak and hole	1.534 and -0.833 e.Å^{-3}

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

	x	y	z	U(eq)
I(1)	4059(1)	2950(1)	6360(1)	16(1)
S(1)	1736(1)	2795(1)	9443(1)	16(1)
Si(1)	7029(1)	3841(1)	4150(1)	17(1)
O(1)	1211(2)	2191(1)	8754(1)	23(1)
O(2)	1646(2)	2685(1)	10488(1)	21(1)
N(1)	2987(2)	2750(2)	7636(2)	22(1)
N(2)	3082(2)	2946(1)	9413(1)	16(1)
C(1)	5013(2)	3517(2)	7631(2)	16(1)
C(2)	6015(2)	3944(2)	7589(2)	21(1)
C(3)	6553(2)	4326(2)	8449(2)	23(1)
C(4)	6095(2)	4284(2)	9324(2)	23(1)
C(5)	5097(2)	3847(2)	9359(2)	20(1)
C(6)	4541(2)	3450(2)	8512(2)	16(1)
C(7)	3445(2)	3003(2)	8518(2)	15(1)
C(8)	5319(2)	3297(2)	5501(2)	21(1)
C(9)	5986(2)	3516(2)	4973(2)	20(1)
C(10)	7205(3)	4952(2)	4302(2)	23(1)
C(11)	7308(4)	5251(2)	5379(2)	47(1)
C(12)	8213(3)	5265(2)	3814(3)	50(1)
C(13)	8391(2)	3251(2)	4531(2)	23(1)
C(14)	8986(3)	3415(2)	5605(2)	35(1)
C(15)	8145(3)	2356(2)	4405(2)	33(1)
C(16)	6306(3)	3558(2)	2846(2)	23(1)
C(17)	7122(3)	3523(3)	2070(2)	49(1)
C(18)	5256(3)	4088(2)	2489(2)	38(1)
C(19)	1077(2)	3713(2)	9046(2)	16(1)
C(20)	1459(2)	4405(2)	9560(2)	21(1)
C(21)	976(3)	5128(2)	9247(2)	26(1)
C(22)	101(3)	5183(2)	8419(2)	25(1)
C(23)	-274(3)	4485(2)	7928(2)	28(1)
C(24)	209(2)	3751(2)	8223(2)	23(1)
C(25)	-413(3)	5974(2)	8067(2)	40(1)

Table 3. Bond lengths [Å] and angles [°] for **3.**

I(1)-C(8)	2.102(3)
I(1)-C(1)	2.122(2)
I(1)-N(1)	2.317(2)
S(1)-O(1)	1.4467(19)
S(1)-O(2)	1.4471(18)
S(1)-N(2)	1.601(2)
S(1)-C(19)	1.768(3)
Si(1)-C(9)	1.863(3)
Si(1)-C(13)	1.877(3)
Si(1)-C(10)	1.884(3)
Si(1)-C(16)	1.892(3)
N(1)-C(7)	1.299(3)
N(2)-C(7)	1.351(3)
C(1)-C(2)	1.382(4)
C(1)-C(6)	1.398(3)
C(2)-C(3)	1.390(4)
C(3)-C(4)	1.379(4)
C(4)-C(5)	1.386(4)
C(5)-C(6)	1.395(3)
C(6)-C(7)	1.487(4)
C(8)-C(9)	1.196(4)
C(10)-C(11)	1.529(4)
C(10)-C(12)	1.534(4)
C(13)-C(14)	1.534(4)
C(13)-C(15)	1.535(4)
C(16)-C(17)	1.530(4)
C(16)-C(18)	1.531(4)
C(19)-C(24)	1.384(4)
C(19)-C(20)	1.391(4)
C(20)-C(21)	1.378(4)
C(21)-C(22)	1.395(4)
C(22)-C(23)	1.384(4)
C(22)-C(25)	1.504(4)
C(23)-C(24)	1.388(4)
C(8)-I(1)-C(1)	89.99(10)
C(8)-I(1)-N(1)	164.74(9)
C(1)-I(1)-N(1)	74.76(9)
O(1)-S(1)-O(2)	116.81(12)
O(1)-S(1)-N(2)	114.36(12)

O(2)-S(1)-N(2)	105.72(11)
O(1)-S(1)-C(19)	107.15(12)
O(2)-S(1)-C(19)	108.19(12)
N(2)-S(1)-C(19)	103.72(12)
C(9)-Si(1)-C(13)	106.79(13)
C(9)-Si(1)-C(10)	107.15(13)
C(13)-Si(1)-C(10)	114.83(13)
C(9)-Si(1)-C(16)	104.33(12)
C(13)-Si(1)-C(16)	110.92(13)
C(10)-Si(1)-C(16)	112.05(13)
C(7)-N(1)-I(1)	116.46(19)
C(7)-N(2)-S(1)	119.06(17)
C(2)-C(1)-C(6)	122.1(2)
C(2)-C(1)-I(1)	122.61(18)
C(6)-C(1)-I(1)	115.31(18)
C(1)-C(2)-C(3)	118.6(2)
C(4)-C(3)-C(2)	120.7(3)
C(3)-C(4)-C(5)	120.1(2)
C(4)-C(5)-C(6)	120.6(2)
C(5)-C(6)-C(1)	117.9(2)
C(5)-C(6)-C(7)	121.7(2)
C(1)-C(6)-C(7)	120.3(2)
N(1)-C(7)-N(2)	131.2(2)
N(1)-C(7)-C(6)	112.9(2)
N(2)-C(7)-C(6)	115.9(2)
C(9)-C(8)-I(1)	176.1(2)
C(8)-C(9)-Si(1)	179.1(3)
C(11)-C(10)-C(12)	110.5(3)
C(11)-C(10)-Si(1)	114.9(2)
C(12)-C(10)-Si(1)	111.7(2)
C(14)-C(13)-C(15)	109.3(2)
C(14)-C(13)-Si(1)	113.7(2)
C(15)-C(13)-Si(1)	110.6(2)
C(17)-C(16)-C(18)	111.3(3)
C(17)-C(16)-Si(1)	114.6(2)
C(18)-C(16)-Si(1)	111.4(2)
C(24)-C(19)-C(20)	120.0(3)
C(24)-C(19)-S(1)	120.9(2)
C(20)-C(19)-S(1)	119.08(19)
C(21)-C(20)-C(19)	119.9(2)
C(20)-C(21)-C(22)	121.2(3)
C(23)-C(22)-C(21)	117.7(3)

C(23)-C(22)-C(25)	121.0(3)
C(21)-C(22)-C(25)	121.2(3)
C(22)-C(23)-C(24)	122.0(3)
C(19)-C(24)-C(23)	119.1(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3)for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	17(1)	19(1)	11(1)	0(1)	4(1)	-1(1)
S(1)	16(1)	19(1)	15(1)	1(1)	4(1)	0(1)
Si(1)	20(1)	18(1)	16(1)	0(1)	6(1)	-2(1)
O(1)	23(1)	22(1)	24(1)	-3(1)	4(1)	-5(1)
O(2)	22(1)	25(1)	18(1)	5(1)	9(1)	2(1)
N(1)	18(1)	33(2)	15(1)	-3(1)	5(1)	-8(1)
N(2)	16(1)	22(1)	12(1)	2(1)	4(1)	1(1)
C(1)	16(1)	16(1)	15(1)	-2(1)	0(1)	1(1)
C(2)	22(2)	23(2)	17(1)	1(1)	6(1)	-1(1)
C(3)	18(2)	25(2)	27(1)	1(1)	2(1)	-6(1)
C(4)	22(2)	25(2)	20(1)	-3(1)	-2(1)	-2(1)
C(5)	20(1)	26(2)	13(1)	-1(1)	2(1)	0(1)
C(6)	14(1)	17(1)	16(1)	2(1)	2(1)	1(1)
C(7)	15(1)	17(1)	13(1)	0(1)	3(1)	2(1)
C(8)	22(2)	23(2)	17(1)	0(1)	5(1)	0(1)
C(9)	21(1)	21(2)	17(1)	-1(1)	4(1)	0(1)
C(10)	26(2)	20(2)	23(1)	0(1)	3(1)	-3(1)
C(11)	84(3)	23(2)	29(2)	-7(1)	-7(2)	0(2)
C(12)	46(2)	29(2)	81(3)	3(2)	27(2)	-11(2)
C(13)	20(1)	24(2)	27(1)	-2(1)	10(1)	-1(1)
C(14)	26(2)	40(2)	35(2)	-4(1)	-3(1)	6(2)
C(15)	32(2)	26(2)	40(2)	-3(1)	9(2)	6(1)
C(16)	31(2)	23(2)	16(1)	-2(1)	5(1)	-4(1)
C(17)	57(3)	72(3)	19(2)	-3(2)	14(2)	-7(2)
C(18)	47(2)	32(2)	31(2)	-5(1)	-10(2)	4(2)
C(19)	14(1)	19(2)	15(1)	2(1)	4(1)	0(1)
C(20)	21(2)	23(2)	19(1)	1(1)	0(1)	-2(1)
C(21)	33(2)	20(2)	27(2)	-2(1)	9(1)	-1(1)
C(22)	30(2)	27(2)	22(1)	7(1)	15(1)	9(1)
C(23)	25(2)	36(2)	21(1)	6(1)	2(1)	8(1)
C(24)	24(2)	28(2)	16(1)	-2(1)	1(1)	-1(1)
C(25)	53(2)	34(2)	35(2)	12(2)	14(2)	18(2)

Table 5. Hydrogen bonds for **3** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(1)	0.80(4)	2.32(3)	2.915(3)	132(3)

Symmetry transformations used to generate equivalent atoms:

5.2. Single Crystal X-Ray Diffraction for the compound 4

Crystals of the compound **4** were obtained from slow evaporation of a DCM solution.

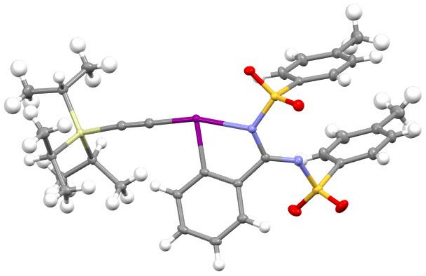


Table 1. Crystal data and structure refinement for **4**.

Identification code	CCDC 2072274	
Empirical formula	$C_{32}H_{39}IN_2O_4S_2Si$	
Formula weight	734.76	
Temperature	100.01(11) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 11.3588(3) Å	α= 112.064(3)°.
	b = 11.8051(3) Å	β= 98.385(2)°.
	c = 14.2418(4) Å	γ = 105.326(2)°.
Volume	1641.46(8) $Å^3$	
Z	2	
Density (calculated)	1.487 Mg/m^3	
Absorption coefficient	1.178 mm^{-1}	
F(000)	752	
Crystal size	0.545 x 0.213 x 0.093 mm^3	
Θ range for data collection	2.553 to 32.959°.	
Index ranges	$-15 \leq h \leq 16$, $-17 \leq k \leq 13$, $-15 \leq l \leq 20$	
Reflections collected	19613	
Independent reflections	10888 [R_{int} = 0.0177]	

Completeness to θ = 25.242°	99.9 %
Absorption correction	Gaussian
Max. and min. transmission	1.000 and 0.407
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10888 / 0 / 387
Goodness-of-fit on F^2	1.052
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0244$, $wR_2 = 0.0561$
R indices (all data)	$R_1 = 0.0276$, $wR_2 = 0.0576$
Largest diff. peak and hole	0.617 and -0.488 e.Å^{-3}

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

	x	y	z	U(eq)
I(1)	6733(1)	4017(1)	4753(1)	13(1)
S(2)	5691(1)	5825(1)	3530(1)	15(1)
S(3)	6788(1)	3414(1)	721(1)	19(1)
Si(1)	7675(1)	1355(1)	6694(1)	14(1)
O(1)	5449(1)	6165(1)	4556(1)	19(1)
O(2)	6128(1)	6855(1)	3227(1)	21(1)
O(3)	7338(1)	4211(1)	234(1)	29(1)
O(4)	7344(1)	2475(1)	792(1)	27(1)
N(1)	6734(1)	5121(1)	3607(1)	15(1)
N(2)	6656(1)	4381(1)	1835(1)	16(1)
C(1)	7134(1)	4505(1)	2770(1)	15(1)
C(2)	8164(1)	4066(1)	3131(1)	14(1)
C(3)	9201(1)	4063(1)	2708(1)	18(1)
C(4)	10170(1)	3723(2)	3111(1)	19(1)
C(5)	10107(1)	3340(2)	3917(1)	20(1)
C(6)	9103(1)	3360(1)	4372(1)	17(1)
C(7)	8172(1)	3753(1)	3982(1)	15(1)
C(8)	7100(1)	2987(2)	5568(1)	17(1)
C(9)	7313(1)	2391(1)	6059(1)	17(1)
C(10)	6457(1)	1116(2)	7434(1)	19(1)
C(11)	5093(2)	539(2)	6732(2)	29(1)
C(12)	6663(2)	309(2)	8030(2)	32(1)
C(13)	9312(1)	2304(1)	7634(1)	18(1)
C(14)	9337(2)	3559(2)	8520(1)	26(1)
C(15)	10342(1)	2609(2)	7086(1)	23(1)
C(16)	7560(1)	-204(1)	5569(1)	17(1)
C(17)	8217(2)	-1016(2)	5929(1)	25(1)
C(18)	8052(2)	-4(2)	4672(1)	22(1)
C(19)	4265(1)	4664(1)	2589(1)	16(1)
C(20)	3690(2)	3498(2)	2639(1)	23(1)
C(21)	2539(2)	2638(2)	1916(1)	24(1)
C(22)	1935(2)	2923(2)	1155(1)	21(1)
C(23)	2521(2)	4097(2)	1126(1)	25(1)
C(24)	3679(2)	4966(2)	1836(1)	23(1)
C(25)	656(2)	1999(2)	401(1)	31(1)
C(26)	5179(1)	2536(2)	13(1)	18(1)
C(27)	4572(2)	1386(2)	66(2)	26(1)

C(28)	3352(2)	614(2)	-579(2)	28(1)
C(29)	2736(2)	979(2)	-1270(1)	22(1)
C(30)	3339(2)	2165(2)	-1277(1)	26(1)
C(31)	4557(2)	2948(2)	-635(1)	23(1)
C(32)	1448(2)	88(2)	-2020(2)	33(1)

Table 3. Bond lengths [Å] and angles [°] for **4**.

I(1)-C(8)	2.0460(15)
I(1)-C(7)	2.1233(14)
I(1)-N(1)	2.4425(12)
S(2)-O(2)	1.4319(10)
S(2)-O(1)	1.4510(11)
S(2)-N(1)	1.6289(12)
S(2)-C(19)	1.7643(15)
S(3)-O(3)	1.4366(12)
S(3)-O(4)	1.4401(13)
S(3)-N(2)	1.6248(13)
S(3)-C(26)	1.7627(15)
Si(1)-C(9)	1.8644(15)
Si(1)-C(10)	1.8830(15)
Si(1)-C(13)	1.8839(15)
Si(1)-C(16)	1.8886(16)
N(1)-C(1)	1.3558(18)
N(2)-C(1)	1.3001(19)
C(1)-C(2)	1.499(2)
C(2)-C(7)	1.3937(19)
C(2)-C(3)	1.3983(19)
C(3)-C(4)	1.386(2)
C(4)-C(5)	1.388(2)
C(5)-C(6)	1.393(2)
C(6)-C(7)	1.387(2)
C(8)-C(9)	1.205(2)
C(10)-C(11)	1.530(2)
C(10)-C(12)	1.532(2)
C(13)-C(14)	1.534(2)
C(13)-C(15)	1.537(2)
C(16)-C(18)	1.539(2)
C(16)-C(17)	1.540(2)
C(19)-C(24)	1.387(2)
C(19)-C(20)	1.392(2)
C(20)-C(21)	1.386(2)
C(21)-C(22)	1.392(2)
C(22)-C(23)	1.389(2)
C(22)-C(25)	1.510(2)
C(23)-C(24)	1.387(2)
C(26)-C(31)	1.384(2)
C(26)-C(27)	1.386(2)

C(27)-C(28)	1.387(2)
C(28)-C(29)	1.386(2)
C(29)-C(30)	1.392(2)
C(29)-C(32)	1.508(2)
C(30)-C(31)	1.387(2)

C(8)-I(1)-C(7)	93.03(6)
C(8)-I(1)-N(1)	165.51(5)
C(7)-I(1)-N(1)	72.48(5)
O(2)-S(2)-O(1)	117.76(7)
O(2)-S(2)-N(1)	111.63(6)
O(1)-S(2)-N(1)	102.12(6)
O(2)-S(2)-C(19)	108.56(7)
O(1)-S(2)-C(19)	106.92(7)
N(1)-S(2)-C(19)	109.48(7)
O(3)-S(3)-O(4)	117.65(8)
O(3)-S(3)-N(2)	107.30(7)
O(4)-S(3)-N(2)	114.31(7)
O(3)-S(3)-C(26)	108.37(7)
O(4)-S(3)-C(26)	106.74(7)
N(2)-S(3)-C(26)	101.04(7)
C(9)-Si(1)-C(10)	106.76(7)
C(9)-Si(1)-C(13)	106.42(7)
C(10)-Si(1)-C(13)	110.61(7)
C(9)-Si(1)-C(16)	104.94(7)
C(10)-Si(1)-C(16)	113.47(7)
C(13)-Si(1)-C(16)	113.96(7)
C(1)-N(1)-S(2)	122.81(10)
C(1)-N(1)-I(1)	109.18(9)
S(2)-N(1)-I(1)	119.32(6)
C(1)-N(2)-S(3)	127.42(11)
N(2)-C(1)-N(1)	121.61(13)
N(2)-C(1)-C(2)	129.39(13)
N(1)-C(1)-C(2)	108.99(12)
C(7)-C(2)-C(3)	117.23(13)
C(7)-C(2)-C(1)	119.87(12)
C(3)-C(2)-C(1)	122.65(13)
C(4)-C(3)-C(2)	120.58(14)
C(3)-C(4)-C(5)	120.56(14)
C(4)-C(5)-C(6)	120.29(14)
C(7)-C(6)-C(5)	117.92(14)
C(6)-C(7)-C(2)	123.22(13)

C(6)-C(7)-I(1)	119.73(11)
C(2)-C(7)-I(1)	116.93(10)
C(9)-C(8)-I(1)	179.13(14)
C(8)-C(9)-Si(1)	174.04(14)
C(11)-C(10)-C(12)	110.60(13)
C(11)-C(10)-Si(1)	112.83(11)
C(12)-C(10)-Si(1)	112.60(11)
C(14)-C(13)-C(15)	110.53(12)
C(14)-C(13)-Si(1)	111.13(11)
C(15)-C(13)-Si(1)	113.24(11)
C(18)-C(16)-C(17)	109.17(13)
C(18)-C(16)-Si(1)	114.08(10)
C(17)-C(16)-Si(1)	112.99(11)
C(24)-C(19)-C(20)	120.23(14)
C(24)-C(19)-S(2)	118.93(11)
C(20)-C(19)-S(2)	120.71(11)
C(21)-C(20)-C(19)	119.06(14)
C(20)-C(21)-C(22)	121.60(15)
C(23)-C(22)-C(21)	118.27(15)
C(23)-C(22)-C(25)	120.77(15)
C(21)-C(22)-C(25)	120.93(15)
C(24)-C(23)-C(22)	121.05(15)
C(19)-C(24)-C(23)	119.78(14)
C(31)-C(26)-C(27)	120.60(14)
C(31)-C(26)-S(3)	120.40(11)
C(27)-C(26)-S(3)	118.89(12)
C(26)-C(27)-C(28)	119.31(15)
C(29)-C(28)-C(27)	120.94(15)
C(28)-C(29)-C(30)	118.87(15)
C(28)-C(29)-C(32)	120.49(15)
C(30)-C(29)-C(32)	120.62(15)
C(31)-C(30)-C(29)	120.73(15)
C(26)-C(31)-C(30)	119.43(14)

Symmetry transformations used to generate equivalent atoms:

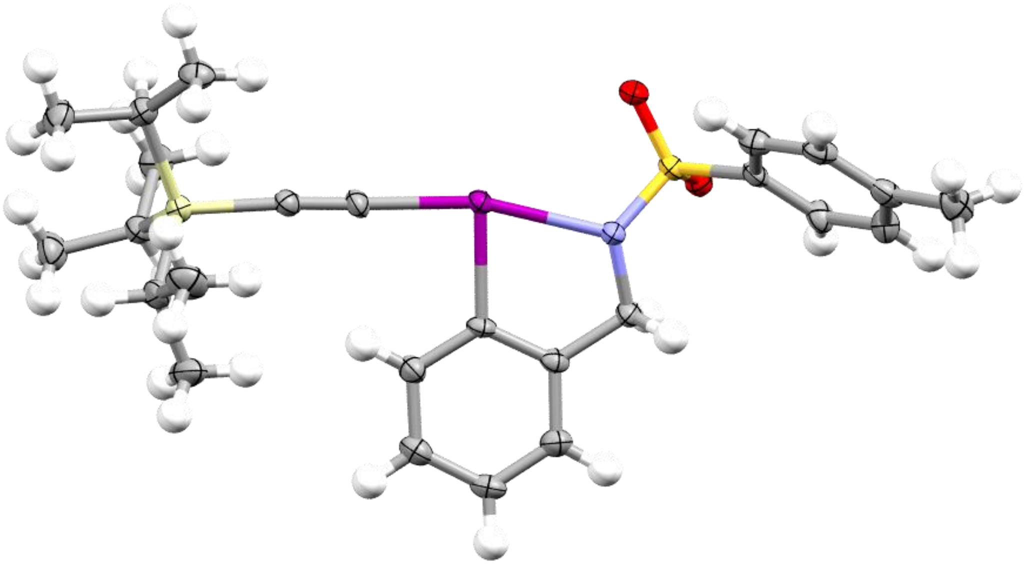
Table 4. Anisotropic displacement parameters (Å^{2}x 10^3)for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	13(1)	15(1)	14(1)	8(1)	5(1)	7(1)
S(2)	17(1)	15(1)	18(1)	10(1)	8(1)	8(1)
S(3)	17(1)	22(1)	16(1)	7(1)	6(1)	6(1)
Si(1)	15(1)	14(1)	15(1)	8(1)	4(1)	7(1)
O(1)	20(1)	20(1)	20(1)	9(1)	9(1)	10(1)
O(2)	25(1)	17(1)	28(1)	14(1)	10(1)	9(1)
O(3)	26(1)	36(1)	22(1)	13(1)	11(1)	2(1)
O(4)	23(1)	28(1)	25(1)	4(1)	4(1)	14(1)
N(1)	16(1)	17(1)	17(1)	10(1)	7(1)	9(1)
N(2)	18(1)	18(1)	16(1)	9(1)	6(1)	8(1)
C(1)	13(1)	14(1)	18(1)	9(1)	6(1)	5(1)
C(2)	14(1)	14(1)	16(1)	6(1)	5(1)	6(1)
C(3)	16(1)	18(1)	19(1)	7(1)	7(1)	5(1)
C(4)	16(1)	19(1)	22(1)	6(1)	7(1)	8(1)
C(5)	15(1)	18(1)	24(1)	7(1)	4(1)	9(1)
C(6)	16(1)	17(1)	19(1)	8(1)	4(1)	8(1)
C(7)	13(1)	15(1)	18(1)	7(1)	5(1)	6(1)
C(8)	18(1)	19(1)	18(1)	9(1)	6(1)	8(1)
C(9)	18(1)	18(1)	17(1)	8(1)	6(1)	8(1)
C(10)	21(1)	19(1)	20(1)	10(1)	8(1)	8(1)
C(11)	18(1)	37(1)	32(1)	16(1)	9(1)	8(1)
C(12)	35(1)	40(1)	35(1)	28(1)	16(1)	16(1)
C(13)	18(1)	17(1)	18(1)	8(1)	3(1)	7(1)
C(14)	25(1)	23(1)	21(1)	4(1)	6(1)	6(1)
C(15)	18(1)	22(1)	27(1)	9(1)	6(1)	7(1)
C(16)	16(1)	17(1)	18(1)	8(1)	3(1)	7(1)
C(17)	29(1)	21(1)	26(1)	8(1)	1(1)	14(1)
C(18)	22(1)	22(1)	20(1)	7(1)	8(1)	10(1)
C(19)	16(1)	18(1)	18(1)	10(1)	7(1)	9(1)
C(20)	21(1)	22(1)	29(1)	16(1)	2(1)	8(1)
C(21)	21(1)	22(1)	31(1)	14(1)	3(1)	7(1)
C(22)	20(1)	26(1)	17(1)	8(1)	5(1)	11(1)
C(23)	28(1)	34(1)	20(1)	17(1)	5(1)	13(1)
C(24)	27(1)	27(1)	22(1)	16(1)	7(1)	11(1)
C(25)	27(1)	35(1)	23(1)	9(1)	1(1)	10(1)
C(26)	19(1)	19(1)	16(1)	7(1)	5(1)	6(1)
C(27)	22(1)	29(1)	33(1)	21(1)	4(1)	7(1)

C(28)	22(1)	24(1)	38(1)	16(1)	5(1)	5(1)
C(29)	20(1)	23(1)	17(1)	4(1)	3(1)	7(1)
C(30)	26(1)	33(1)	22(1)	15(1)	4(1)	13(1)
C(31)	25(1)	22(1)	24(1)	13(1)	6(1)	9(1)
C(32)	24(1)	34(1)	26(1)	2(1)	0(1)	7(1)

5.3. Single Crystal X-Ray Diffraction for the compound 5

Crystals of the compound **5** were obtained from slow evaporation of a DCM solution.



Compound	**TIPS-Ts-EBz**
Identification code	CCDC 2072275
Formula	$C_{25}H_{34}INO_2SSi$
$D_{calc.}$/ g cm^{-3}	1.476
μ/mm^{-1}	11.226
Formula Weight	567.58
Colour	clear colourless
Shape	plate
Size/mm^3	0.75×0.30×0.07
T/K	100.00(10)
Crystal System	triclinic
Space Group	$P\bar{1}$
a/Å	8.3150(5)
b/Å	9.5571(4)
c/Å	16.2727(8)
α/°	95.596(4)
β/°	91.566(5)
γ/°	96.709(4)
V/Å^3	1277.18(11)
Z	2
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu $K\alpha$
Θ_{min}/°	2.731
Θ_{max}/°	76.215
Measured Refl's.	10120
Ind't Refl's	5160
Refl's with I > 2(I)	5087
R_{int}	0.0292
Parameters	288
Restraints	0
Largest Peak/e Å^{-3}	2.075
Deepest Hole/e Å^{-3}	-1.586
GooF	1.085
wR_2 (all data)	0.1245
wR_2	0.1242
R_1 (all data)	0.0444
R_1	0.0442

Table 1: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	**x**	**y**	**z**	U_{eq}
I1	5659.6(2)	2441.2(2)	4424.6(2)	19.74(12)
S1	6563.5(11)	1786.3(9)	6388.6(5)	22.85(19)
Si1	3192.6(12)	2995.4(10)	1545.0(6)	22.9(2)
O1	5870(3)	2555(3)	7073.0(16)	27.5(5)
O2	5584(4)	547(3)	5977.2(17)	29.8(6)
N1	7138(4)	2744(3)	5681.9(19)	22.6(6)
C1	6827(4)	4574(3)	4508(2)	20.8(6)
C2	6638(5)	5404(4)	3865(2)	25.8(7)
C3	7477(5)	6760(4)	3928(2)	28.0(7)
C4	8486(5)	7237(4)	4611(3)	26.7(8)
C5	8614(5)	6405(4)	5252(2)	26.2(7)
C6	7770(4)	5044(3)	5220(2)	21.1(6)
C7	7864(4)	4185(4)	5943(2)	23.8(7)
C8	8338(4)	1225(4)	6798(2)	23.1(7)
C9	9033(5)	119(4)	6385(2)	29.6(8)
C10	10461(5)	-269(4)	6687(3)	29.7(8)
C11	11259(5)	438(4)	7404(3)	29.2(8)
C12	10549(5)	1550(4)	7812(2)	30.3(8)
C13	9095(5)	1948(4)	7515(2)	27.3(7)

Atom	x	y	z	U_{eq}
C14	12835(5)	48(5)	7728(3)	38.4(9)
C15	4632(5)	2656(4)	3257(2)	23.9(7)
C16	4059(4)	2735(4)	2576(2)	23.3(7)
C17	4870(5)	3896(4)	953(2)	29.8(8)
C18	5596(6)	5332(5)	1398(3)	42.0(10)
C19	6218(6)	2971(6)	757(3)	43.6(10)
C20	1595(5)	4218(4)	1754(2)	27.8(7)
C21	936(6)	4788(5)	986(3)	38.8(9)
C22	206(5)	3545(5)	2246(3)	35.8(9)
C23	2305(5)	1213(4)	1019(2)	27.6(7)
C24	1980(6)	1261(5)	88(3)	38.8(9)
C25	3313(5)	2(4)	1158(3)	33.2(8)

Table 2: Anisotropic Displacement Parameters (×10^4) for **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	22.37(16)	16.17(16)	21.29(16)	3.46(9)	-0.64(9)	3.98(9)
S1	26.1(4)	18.5(4)	24.4(4)	5.9(3)	-2.8(3)	2.6(3)
Si1	24.4(5)	22.5(5)	22.0(4)	4.8(3)	-1.9(3)	2.0(4)
O1	25.7(12)	29.6(13)	28.5(12)	5.9(10)	-0.7(9)	6.2(10)
O2	36.5(14)	19.7(12)	32.4(13)	7.1(10)	-6.6(11)	-2.6(11)
N1	27.8(15)	16.3(15)	23.1(14)	4.4(11)	-5.2(11)	0.4(12)
C1	22.8(15)	12.6(14)	27.5(16)	3.5(12)	3.6(12)	2.3(12)
C2	31.8(18)	22.9(17)	23.0(16)	4.1(13)	1.4(13)	3.5(14)
C3	32.6(19)	22.5(17)	30.5(17)	7.4(13)	6.8(14)	5.2(14)
C4	28.4(18)	17.7(17)	34.3(19)	4.0(14)	9.6(14)	0.9(14)
C5	23.7(17)	22.6(18)	32.1(18)	1.7(13)	2.8(13)	1.9(14)
C6	21.2(15)	15.5(15)	27.5(16)	3.2(12)	2.7(12)	5.2(12)
C7	26.5(17)	19.0(16)	25.9(16)	3.0(12)	-4.0(12)	4.0(13)
C8	29.1(17)	17.4(15)	24.4(16)	8.3(12)	0.6(13)	4.0(13)
C9	34(2)	20.7(17)	34.2(19)	2.2(14)	2.2(14)	1.8(15)
C10	29.5(18)	18.9(16)	42(2)	6.7(14)	4.0(15)	4.5(14)
C11	25.8(18)	26.4(19)	39(2)	15.1(15)	7.8(15)	6.2(15)
C12	30.8(19)	35(2)	26.1(17)	4.8(14)	-1.8(14)	7.7(16)
C13	32.3(19)	24.3(18)	27.3(17)	3.2(13)	-1.4(14)	11.7(15)
C14	27.2(19)	43(2)	50(2)	16.7(19)	4.1(17)	11.8(17)
C15	29.8(18)	21.3(17)	22.1(16)	6.7(12)	-1.7(13)	5.9(14)
C16	23.9(17)	19.4(16)	27.2(17)	5.0(13)	-1.0(13)	3.1(13)
C17	34.9(19)	30.7(19)	23.0(16)	6.6(14)	0.9(14)	-3.2(16)
C18	52(3)	36(2)	34(2)	3.4(17)	2.0(18)	-15(2)
C19	34(2)	47(3)	51(3)	13(2)	13.8(19)	1.0(19)
C20	30.5(18)	23.6(17)	29.2(17)	3.5(13)	-3.4(14)	3.1(14)
C21	43(2)	37(2)	39(2)	9.6(17)	-8.6(17)	13.4(18)
C22	32(2)	38(2)	38(2)	3.3(17)	3.1(16)	7.9(17)
C23	27.3(17)	26.2(18)	28.3(17)	1.5(13)	-1.3(13)	0.8(14)
C24	45(2)	38(2)	31(2)	-2.1(16)	-8.9(16)	3.3(19)
C25	37(2)	24.3(18)	38(2)	0.6(15)	3.4(16)	4.1(16)

Table 3: Bond Lengths in Å for **5**.

Atom	Atom	Length/Å
I1	N1	2.333(3)
I1	C1	2.143(3)
I1	C15	2.101(4)
S1	O1	1.445(3)
S1	O2	1.450(3)
S1	N1	1.588(3)
S1	C8	1.763(4)
Si1	C16	1.858(4)
Si1	C17	1.889(4)
Si1	C20	1.885(4)
Si1	C23	1.888(4)
N1	C7	1.456(5)
C1	C2	1.389(5)
C1	C6	1.388(5)
C2	C3	1.391(5)
C3	C4	1.381(6)
C4	C5	1.381(6)
C5	C6	1.399(5)
C6	C7	1.505(5)
C8	C9	1.389(5)

Atom	Atom	Length/Å
C8	C13	1.390(5)
C9	C10	1.377(6)
C10	C11	1.399(6)
C11	C12	1.397(6)
C11	C14	1.499(5)
C12	C13	1.397(5)
C15	C16	1.206(6)
C17	C18	1.537(6)
C17	C19	1.528(6)
C20	C21	1.524(5)
C20	C22	1.539(6)
C23	C24	1.539(5)
C23	C25	1.537(6)

Table 4: Bond Angles in ° for **5.**

Atom	Atom	Atom	Angle/°
C1	I1	N1	75.34(12)
C15	I1	N1	165.99(14)
C15	I1	C1	90.77(14)
O1	S1	O2	117.43(18)
O1	S1	N1	113.44(17)
O1	S1	C8	105.69(16)
O2	S1	N1	106.12(16)
O2	S1	C8	107.65(17)
N1	S1	C8	105.81(17)
C16	Si1	C17	107.69(17)
C16	Si1	C20	105.63(16)
C16	Si1	C23	108.48(17)
C20	Si1	C17	109.67(18)
C20	Si1	C23	112.00(17)
C23	Si1	C17	113.02(17)
S1	N1	I1	118.84(17)
C7	N1	I1	115.4(2)
C7	N1	S1	117.0(2)
C2	C1	I1	120.1(3)
C6	C1	I1	116.5(2)
C6	C1	C2	123.4(3)
C1	C2	C3	118.2(3)
C4	C3	C2	119.9(3)
C5	C4	C3	120.5(4)
C4	C5	C6	121.4(4)
C1	C6	C5	116.5(3)
C1	C6	C7	123.1(3)
C5	C6	C7	120.4(3)
N1	C7	C6	108.2(3)
C9	C8	S1	120.4(3)
C9	C8	C13	119.8(3)
C13	C8	S1	119.7(3)
C10	C9	C8	120.1(4)
C9	C10	C11	121.6(4)
C10	C11	C14	122.1(4)
C12	C11	C10	117.7(4)
C12	C11	C14	120.2(4)
C11	C12	C13	121.2(4)
C8	C13	C12	119.5(3)
C16	C15	I1	177.7(3)
C15	C16	Si1	175.9(3)
C18	C17	Si1	112.2(3)
C19	C17	Si1	113.0(3)
C19	C17	C18	109.8(4)
C21	C20	Si1	114.3(3)
C21	C20	C22	110.8(4)
C22	C20	Si1	111.9(3)
C24	C23	Si1	111.9(3)
C25	C23	Si1	114.2(3)
C25	C23	C24	109.7(3)

Table 5: Torsion Angles in ° for **5.**

Atom	Atom	Atom	Atom	Angle/°
I1	N1	C7	C6	-12.9(3)
I1	C1	C2	C3	-177.1(3)
I1	C1	C6	C5	176.1(2)
I1	C1	C6	C7	-5.9(4)
S1	N1	C7	C6	-160.1(2)
S1	C8	C9	C10	176.8(3)
S1	C8	C13	C12	-176.5(3)
O1	S1	N1	I1	-108.64(19)
O1	S1	N1	C7	37.4(3)
O1	S1	C8	C9	160.5(3)
O1	S1	C8	C13	-23.2(3)
O2	S1	N1	I1	21.8(2)
O2	S1	N1	C7	167.8(3)
O2	S1	C8	C9	34.3(3)
O2	S1	C8	C13	-149.5(3)
N1	S1	C8	C9	-78.9(3)
N1	S1	C8	C13	97.4(3)
C1	C2	C3	C4	1.1(5)

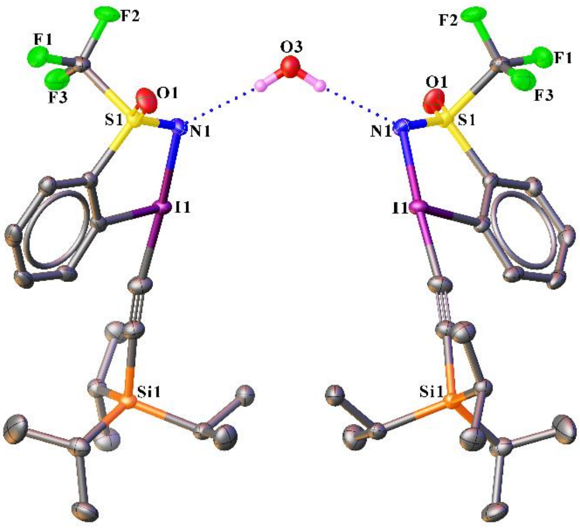
Atom	Atom	Atom	Atom	Angle/°
C1	C6	C7	N1	12.7(4)
C2	C1	C6	C5	-3.0(5)
C2	C1	C6	C7	175.0(3)
C2	C3	C4	C5	-3.0(6)
C3	C4	C5	C6	1.9(6)
C4	C5	C6	C1	1.0(5)
C4	C5	C6	C7	-177.0(3)
C5	C6	C7	N1	-169.4(3)
C6	C1	C2	C3	2.0(5)
C8	S1	N1	I1	135.94(18)
C8	S1	N1	C7	-78.0(3)
C8	C9	C10	C11	-0.8(6)
C9	C8	C13	C12	-0.2(6)
C9	C10	C11	C12	0.6(6)
C9	C10	C11	C14	-178.5(4)
C10	C11	C12	C13	-0.2(6)
C11	C12	C13	C8	0.0(6)
C13	C8	C9	C10	0.6(6)
C14	C11	C12	C13	178.9(4)
C16	Si1	C17	C18	-59.2(4)
C16	Si1	C17	C19	65.6(3)
C16	Si1	C20	C21	169.5(3)
C16	Si1	C20	C22	-63.4(3)
C16	Si1	C23	C24	-164.5(3)
C16	Si1	C23	C25	-39.1(3)
C17	Si1	C20	C21	53.7(3)
C17	Si1	C20	C22	-179.2(3)
C17	Si1	C23	C24	-45.2(3)
C17	Si1	C23	C25	80.2(3)
C20	Si1	C17	C18	55.3(4)
C20	Si1	C17	C19	-179.9(3)
C20	Si1	C23	C24	79.3(3)
C20	Si1	C23	C25	-155.3(3)
C23	Si1	C17	C18	-179.0(3)
C23	Si1	C17	C19	-54.2(4)
C23	Si1	C20	C21	-72.6(3)
C23	Si1	C20	C22	54.5(3)

Table 6: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for **5**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	**x**	**y**	**z**	U_{eq}
H2	5954.44	5054.22	3394.55	31
H3	7356.31	7356.14	3502.18	34
H4	9097.72	8146.18	4639.93	32
H5	9288.2	6763.8	5723.98	31
H7A	9009.03	4185.94	6127.55	29
H7B	7274.23	4596.55	6409.93	29
H9	8521.76	-370.31	5892.56	36
H10	10915.91	-1034.68	6400.92	36
H12	11063.88	2045.12	8301.91	36
H13	8626.86	2706.67	7799.49	33
H14A	13686.96	840.17	7701.63	58
H14B	13119.99	-787.91	7390.94	58
H14C	12726.62	-164.31	8302.27	58
H17	4378.91	4085.64	413.54	36
H18A	6444.77	5767.9	1065.52	63
H18B	6064.27	5189.39	1938.58	63
H18C	4743.45	5953.45	1473.81	63
H19A	6762.1	2798.19	1272.8	65
H19B	7004.68	3456.4	410.97	65
H19C	5751.08	2066.13	461.47	65
H20	2131.77	5057.23	2115.85	33
H21A	1826.8	5306.45	716.81	58
H21B	132.3	5426.75	1145.54	58
H21C	424.56	3997.48	601.93	58
H22A	-426.74	2770.52	1895.13	54
H22B	-497.47	4262.59	2424.2	54
H22C	656.04	3173.86	2731.48	54
H23	1229.46	972.47	1264.11	33
H24A	1270.27	1988.27	3.06	58
H24B	1455.41	336.8	-155.98	58
H24C	3009.04	1489.38	-177.66	58
H25A	4312.61	120.67	853.49	50
H25B	2685.3	-906.78	960.36	50
H25C	3585.51	18.5	1749.08	50

5.4. Single Crystal X-Ray Diffraction for the compound 6

Crystals of the compound **6** were obtained from slow evaporation of a DCM solution.



Compound	**TIPS-CF_3-EBS**
Identification code	CCDC 2072276
Formula	$C_{72}H_{102}F_{12}I_4N_4O_5S_4Si_4$
$D_{calc.}$/ g cm^{-3}	1.610
μ/mm^{-1}	1.681
Formula Weight	2079.77
Colour	clear colourless
Shape	prism
Size/mm^3	0.79×0.39×0.29
T/K	140.00(10)
Crystal System	tetragonal
Flack Parameter	-0.003(5)
Space Group	$I4_1$
a/Å	19.07771(12)
b/Å	19.07771(12)
c/Å	23.5685(2)
α/°	90
β/°	90
γ/°	90
V/Å^3	8577.97(14)
Z	4
Z'	0.5
Wavelength/Å	0.71073
Radiation type	Mo $K\alpha$
Θ_{min}/°	2.539
Θ_{max}/°	32.974
Measured Refl's.	52957
Ind't Refl's	14808
Refl's with I > 2(I)	13940
R_{int}	0.0271
Parameters	490
Restraints	1
Largest Peak/e Å^{-3}	0.412
Deepest Hole/e Å^{-3}	-0.496
GooF	1.022
wR_2 (all data)	0.0478
wR_2	0.0465
R_1 (all data)	0.0263
R_1	0.0228

Table 7: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **6**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	**x**	**y**	**z**	**U_{eq}**
I1	3852.3(2)	6136.9(2)	4292.4(2)	18.24(4)
S1	2931.5(3)	5223.6(3)	5161.7(3)	17.47(12)
Si1	4120.7(4)	7403.1(4)	2380.8(3)	18.00(14)
F1	1828.5(10)	5661.6(11)	5773.2(8)	36.8(4)
F2	2831.1(10)	5712.8(11)	6194.8(7)	34.5(4)
F3	2568.8(11)	6464.7(10)	5550.2(8)	35.5(5)
O1	2699.8(12)	4536.8(11)	5340.6(10)	29.9(5)
N1	3675.1(12)	5429.4(13)	5085.2(10)	21.5(5)
C1	2789.2(13)	5845.6(13)	4129.6(11)	17.2(5)
C2	2452.2(13)	5481.5(13)	4554.4(11)	16.6(5)
C3	1744.6(14)	5296.6(15)	4494.8(12)	22.2(5)
C4	1389.7(15)	5501.7(17)	4009.4(13)	27.4(6)
C5	1743.0(17)	5857.4(16)	3583.1(13)	27.1(6)
C6	2450.8(16)	6033.7(14)	3635.0(12)	22.3(6)
C7	2507.0(15)	5797.3(15)	5701.1(12)	24.1(5)
C8	3871.4(17)	6686.7(16)	3524.0(12)	27.1(6)
C9	3953.8(16)	6981.6(16)	3081.0(12)	25.1(6)

Atom	x	y	z	U_{eq}
C10	4256.3(15)	8373.4(15)	2506.9(12)	21.9(5)
C11	4639.9(18)	8553.4(17)	3058.1(14)	31.1(7)
C12	4610.0(19)	8734.9(17)	2002.5(15)	33.3(7)
C13	3328.8(15)	7233.2(16)	1924.1(12)	25.8(6)
C14	2701.1(18)	7681(3)	2102.0(19)	53.8(12)
C15	3470.6(19)	7324(2)	1287.5(14)	38.0(8)
C16	4907.7(15)	6935.4(15)	2084.7(12)	22.7(5)
C17	5569.8(16)	7052.2(17)	2435.4(13)	28.6(6)
C18	4759.5(19)	6144.5(17)	2020.9(16)	35.0(7)
I2	3994.7(2)	3555.5(2)	5697.6(2)	17.93(4)
S2	4825.4(3)	2565.3(3)	4828.2(3)	16.80(12)
Si2	2772.3(4)	4065.3(4)	7590.8(3)	17.12(14)
F4	3553.4(9)	2352.3(11)	4432.4(8)	35.1(4)
F5	4333.5(11)	2561.9(10)	3796.2(7)	33.8(4)
F6	4273.4(11)	1541.9(10)	4182.9(8)	36.9(5)
O2	5482.4(10)	2260.0(11)	4648.7(10)	27.9(5)
N2	4700.0(12)	3325.5(12)	4908.5(10)	20.2(4)
C19	4179.0(13)	2472.0(13)	5854.8(11)	15.9(5)
C20	4520.3(13)	2102.4(14)	5433.2(11)	16.4(5)
C21	4658.1(15)	1389.3(15)	5500.9(13)	22.6(5)
C22	4431.2(16)	1060.9(15)	5991.9(13)	26.1(6)
C23	4091.2(15)	1437.8(16)	6415.6(13)	25.5(6)
C24	3963.7(14)	2150.3(15)	6350.3(11)	20.7(5)
C25	4210.3(15)	2225.9(15)	4279.4(13)	24.0(5)
C26	3450.1(15)	3638.6(16)	6463.8(12)	23.9(6)
C27	3183.4(15)	3809.8(15)	6906.0(12)	23.7(6)
C28	3270.4(15)	4840.1(16)	7878.3(12)	23.1(6)
C29	4051.7(18)	4660(2)	7962.6(16)	40.0(8)
C30	3195(2)	5507.0(18)	7528.1(15)	37.0(8)
C31	1818.6(14)	4245.8(14)	7439.3(12)	20.5(5)
C32	1444.6(17)	4601.0(18)	7942.7(13)	29.8(6)
C33	1679.8(17)	4651.6(17)	6886.8(13)	29.8(6)
C34	2876.9(16)	3293.3(15)	8081.3(12)	24.1(6)
C35	2803.1(19)	3484.1(18)	8712.4(13)	31.9(7)
C36	2365(2)	2705.5(18)	7936.1(18)	47.0(10)
O3	5000	5000	5677.3(15)	27.5(6)

Table 8: Anisotropic Displacement Parameters (×10^4) for **6**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11}+ ... +2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	20.68(8)	19.96(8)	14.06(7)	0.21(6)	0.56(6)	-4.30(6)
S1	18.4(3)	16.6(3)	17.4(3)	4.1(2)	-0.3(2)	2.1(2)
Si1	19.4(3)	19.7(3)	14.9(3)	2.5(3)	1.2(3)	-2.1(3)
F1	24.2(9)	59.7(13)	26.5(10)	0.6(9)	5.3(8)	6.4(8)
F2	36.6(11)	52.3(13)	14.5(8)	3.4(8)	-3.4(7)	1.1(9)
F3	54.9(13)	23.6(9)	28.1(10)	-1.7(7)	4.4(9)	10.9(9)
O1	31.6(11)	19.6(10)	38.5(12)	13.4(9)	-1.0(10)	1.3(8)
N1	18.5(10)	28.7(12)	17.3(10)	5.1(9)	-1.2(9)	1.1(9)
C1	19.3(12)	14.2(11)	18.1(12)	-4.2(9)	-4.8(9)	0.6(9)
C2	19.0(11)	14.0(11)	16.9(11)	-1.8(9)	-2.3(9)	1.7(9)
C3	18.8(12)	23.5(13)	24.3(13)	-4.4(11)	0.1(10)	-0.1(10)
C4	18.0(13)	32.5(15)	31.7(15)	-12.3(13)	-8.1(11)	3.6(11)
C5	32.1(15)	26.4(15)	22.6(14)	-6.1(11)	-12.0(12)	8.5(12)
C6	33.8(15)	17.3(12)	16.0(12)	-1.6(10)	-4.9(11)	2.9(11)
C7	25.7(13)	30.7(14)	15.9(11)	3.7(12)	0.2(11)	2.8(11)
C8	34.7(16)	25.3(14)	21.2(13)	1.6(11)	4.5(12)	-5.4(12)
C9	28.0(14)	25.4(14)	21.8(14)	0.5(11)	2.2(11)	-2.5(11)
C10	22.5(13)	21.1(12)	22.0(13)	1.8(10)	0.5(10)	-0.6(10)
C11	36.4(17)	26.9(15)	30.0(16)	-3.1(12)	-4.0(13)	-2.3(13)
C12	41.9(19)	24.1(14)	33.9(16)	7.1(13)	3.4(14)	-5.2(13)
C13	23.1(13)	30.7(15)	23.6(14)	1.4(11)	-3.3(11)	-8.5(11)
C14	19.5(16)	90(3)	52(2)	-21(2)	-3.0(16)	2.1(18)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C15	37.6(19)	52(2)	24.5(15)	1.7(15)	-10.3(14)	-2.7(16)
C16	25.4(13)	25.3(13)	17.3(12)	0.2(11)	1.3(11)	2.5(11)
C17	25.3(14)	33.4(16)	27.1(15)	-1.0(13)	-0.3(12)	6.4(12)
C18	39.6(18)	25.4(15)	39.9(19)	-7.2(14)	-1.0(15)	2.5(13)
I2	21.17(8)	18.42(8)	14.21(7)	-0.63(6)	2.39(6)	3.74(6)
S2	15.7(3)	18.2(3)	16.5(3)	0.2(2)	4.6(2)	-0.7(2)
Si2	18.6(3)	18.7(3)	14.0(3)	-1.5(3)	2.0(3)	1.4(3)
F4	21.2(8)	56.9(13)	27.3(9)	-4.9(9)	-0.3(7)	-6.6(8)
F5	48.7(12)	38.5(11)	14.3(8)	1.9(7)	2.7(8)	-5.5(9)
F6	57.6(13)	25.3(9)	27.7(10)	-7.3(8)	2.9(9)	-12.1(8)
O2	19.7(9)	28.8(11)	35.1(12)	0.5(9)	12.1(9)	3.3(8)
N2	24.6(11)	19.1(11)	16.8(10)	0.6(9)	4.9(9)	-1.3(9)
C19	13.5(11)	18.6(11)	15.6(11)	0.8(9)	-2.4(9)	-1.2(9)
C20	15.1(11)	18.2(11)	15.9(11)	2.1(9)	-1.5(9)	-1.1(9)
C21	21.9(13)	19.2(12)	26.7(14)	0.6(11)	-2.8(11)	1.8(10)
C22	27.9(15)	19.8(13)	30.7(15)	7.7(12)	-5.1(12)	-2.6(11)
C23	23.8(14)	30.1(15)	22.6(13)	9.5(12)	-2.8(11)	-7.0(11)
C24	18.0(12)	27.1(14)	17.0(12)	3.4(10)	0.2(10)	-2.1(10)
C25	30.6(14)	25.5(13)	16.0(11)	-2.2(11)	2.6(12)	-5.3(11)
C26	23.7(13)	27.1(14)	21.0(13)	-3.2(11)	0.4(11)	3.7(11)
C27	25.2(13)	27.2(14)	18.5(13)	-1.8(11)	1.1(10)	3.5(11)
C28	23.9(14)	28.7(14)	16.6(12)	-2.4(11)	1.5(10)	-5.1(11)
C29	25.9(16)	54(2)	40.4(19)	-4.1(17)	-3.1(14)	-7.8(15)
C30	48(2)	30.7(17)	32.1(17)	0.6(14)	-2.4(15)	-16.8(15)
C31	20.3(12)	21.0(12)	20.2(12)	-0.6(10)	0.9(10)	1.2(10)
C32	25.8(15)	35.9(17)	27.5(15)	-2.6(13)	4.8(12)	4.7(12)
C33	30.3(15)	33.4(16)	25.8(15)	4.7(13)	-5.7(12)	4.7(12)
C34	28.7(14)	21.3(13)	22.3(14)	1.1(10)	0.0(11)	6.7(11)
C35	42.7(19)	32.9(17)	20.0(14)	7.2(12)	2.1(13)	3.3(14)
C36	73(3)	19.8(15)	48(2)	4.2(15)	-15(2)	-4.4(16)
O3	27.4(15)	25.4(14)	29.8(15)	0	0	5.0(12)

Table 9: Bond Lengths in Å for **6**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	N1	2.330(2)	I2	N2	2.337(2)
I1	C1	2.138(3)	I2	C19	2.129(3)
I1	C8	2.093(3)	I2	C26	2.090(3)
S1	O1	1.446(2)	S2	O2	1.445(2)
S1	N1	1.483(2)	S2	N2	1.482(2)
S1	C2	1.768(3)	S2	C20	1.775(3)
S1	C7	1.863(3)	S2	C25	1.863(3)
Si1	C9	1.863(3)	Si2	C27	1.859(3)
Si1	C10	1.893(3)	Si2	C28	1.883(3)
Si1	C13	1.883(3)	Si2	C31	1.886(3)
Si1	C16	1.881(3)	Si2	C34	1.883(3)
F1	C7	1.331(3)	F4	C25	1.326(3)
F2	C7	1.327(3)	F5	C25	1.328(3)
F3	C7	1.327(3)	F6	C25	1.330(3)
C1	C2	1.378(4)	C19	C20	1.382(4)
C1	C6	1.380(4)	C19	C24	1.382(4)
C2	C3	1.402(4)	C20	C21	1.395(4)
C3	C4	1.386(4)	C21	C22	1.385(4)
C4	C5	1.387(5)	C22	C23	1.391(5)
C5	C6	1.397(4)	C23	C24	1.389(4)
C8	C9	1.196(4)	C26	C27	1.205(4)
C10	C11	1.530(4)	C28	C29	1.542(4)
C10	C12	1.531(4)	C28	C30	1.523(4)
C13	C14	1.530(5)	C31	C32	1.541(4)
C13	C15	1.534(4)	C31	C33	1.538(4)
C16	C17	1.526(4)	C34	C35	1.538(4)
C16	C18	1.543(4)	C34	C36	1.526(5)

Table 10: Bond Angles in ° for **6**.

Atom	Atom	Atom	Angle/°
C1	I1	N1	81.70(9)
C8	I1	N1	170.68(10)
C8	I1	C1	89.51(11)
O1	S1	N1	124.61(13)
O1	S1	C2	109.28(13)
O1	S1	C7	101.57(13)
N1	S1	C2	108.82(13)
N1	S1	C7	110.07(14)
C2	S1	C7	99.45(12)
C9	Si1	C10	107.84(13)
C9	Si1	C13	107.15(13)
C9	Si1	C16	105.09(13)
C13	Si1	C10	111.58(13)
C16	Si1	C10	114.40(13)
C16	Si1	C13	110.29(13)
S1	N1	I1	112.93(12)
C2	C1	I1	116.33(18)
C2	C1	C6	121.8(3)
C6	C1	I1	121.9(2)
C1	C2	S1	119.1(2)
C1	C2	C3	120.2(2)
C3	C2	S1	120.6(2)
C4	C3	C2	118.8(3)
C3	C4	C5	119.9(3)
C4	C5	C6	121.6(3)
C1	C6	C5	117.6(3)
F1	C7	S1	113.3(2)
F2	C7	S1	108.93(19)
F2	C7	F1	108.5(2)
F3	C7	S1	110.0(2)
F3	C7	F1	107.9(2)
F3	C7	F2	108.1(2)
C9	C8	I1	173.2(3)
C8	C9	Si1	176.7(3)
C11	C10	Si1	114.7(2)
C11	C10	C12	110.3(3)
C12	C10	Si1	112.3(2)
C14	C13	Si1	112.0(2)
C14	C13	C15	110.1(3)
C15	C13	Si1	113.5(2)
C17	C16	Si1	113.0(2)
C17	C16	C18	110.3(2)
C18	C16	Si1	110.7(2)
C19	I2	N2	82.02(9)
C26	I2	N2	171.23(10)
C26	I2	C19	90.31(11)
O2	S2	N2	124.87(13)
O2	S2	C20	108.60(13)
O2	S2	C25	101.71(14)
N2	S2	C20	109.36(13)
N2	S2	C25	109.09(14)
C20	S2	C25	100.27(12)
C27	Si2	C28	107.77(13)
C27	Si2	C31	106.88(13)
C27	Si2	C34	106.44(13)
C28	Si2	C31	114.31(13)
C34	Si2	C28	109.86(13)
C34	Si2	C31	111.18(13)
S2	N2	I2	112.22(12)
C20	C19	I2	116.63(18)
C20	C19	C24	121.4(2)
C24	C19	I2	121.9(2)
C19	C20	S2	118.6(2)
C19	C20	C21	120.3(2)
C21	C20	S2	121.0(2)
C22	C21	C20	118.5(3)
C21	C22	C23	120.8(3)
C24	C23	C22	120.5(3)
C19	C24	C23	118.4(3)
F4	C25	S2	110.1(2)
F4	C25	F5	108.2(3)
F4	C25	F6	108.1(2)
F5	C25	S2	108.44(19)
F5	C25	F6	108.1(2)
F6	C25	S2	113.7(2)
C27	C26	I2	168.0(3)
C26	C27	Si2	179.5(3)
C29	C28	Si2	111.0(2)
C30	C28	Si2	114.4(2)
C30	C28	C29	110.3(3)
C32	C31	Si2	112.4(2)
C33	C31	Si2	114.7(2)
C33	C31	C32	110.5(2)
C35	C34	Si2	113.5(2)
C36	C34	Si2	111.7(2)
C36	C34	C35	109.4(3)

Table 11: Torsion Angles in ° for **6**.

Atom	Atom	Atom	Atom	Angle/°
I1	C1	C2	S1	-5.2(3)
I1	C1	C2	C3	177.14(19)
I1	C1	C6	C5	-176.0(2)
S1	C2	C3	C4	-179.2(2)
O1	S1	N1	I1	140.17(14)
O1	S1	C2	C1	-142.1(2)
O1	S1	C2	C3	35.5(3)
O1	S1	C7	F1	-49.0(2)
O1	S1	C7	F2	71.9(2)

Atom	Atom	Atom	Atom	Angle/˚
O1	S1	C7	F3	-169.9(2)
N1	S1	C2	C1	-3.1(2)
N1	S1	C2	C3	174.6(2)
N1	S1	C7	F1	177.2(2)
N1	S1	C7	F2	-61.9(2)
N1	S1	C7	F3	56.4(2)
C1	C2	C3	C4	-1.6(4)
C2	S1	N1	I1	8.94(17)
C2	S1	C7	F1	63.1(2)
C2	S1	C7	F2	-176.1(2)
C2	S1	C7	F3	-57.8(2)
C2	C1	C6	C5	1.6(4)
C2	C3	C4	C5	2.7(4)
C3	C4	C5	C6	-1.7(4)
C4	C5	C6	C1	-0.4(4)
C6	C1	C2	S1	177.1(2)
C6	C1	C2	C3	-0.6(4)
C7	S1	N1	I1	-99.07(14)
C7	S1	C2	C1	112.0(2)
C7	S1	C2	C3	-70.3(2)
C9	Si1	C10	C11	35.8(3)
C9	Si1	C10	C12	162.8(2)
C9	Si1	C13	C14	73.9(3)
C9	Si1	C13	C15	-160.7(2)
C9	Si1	C16	C17	-64.9(2)
C9	Si1	C16	C18	59.4(2)
C10	Si1	C13	C14	-43.9(3)
C10	Si1	C13	C15	81.5(3)
C10	Si1	C16	C17	53.2(2)
C10	Si1	C16	C18	177.5(2)
C13	Si1	C10	C11	153.2(2)
C13	Si1	C10	C12	-79.8(2)
C13	Si1	C16	C17	179.9(2)
C13	Si1	C16	C18	-55.7(2)
C16	Si1	C10	C11	-80.7(2)
C16	Si1	C10	C12	46.3(3)
C16	Si1	C13	C14	-172.3(3)
C16	Si1	C13	C15	-46.9(3)
I2	C19	C20	S2	4.2(3)
I2	C19	C20	C21	-179.6(2)
I2	C19	C24	C23	178.7(2)
S2	C20	C21	C22	177.5(2)
O2	S2	N2	I2	-141.17(14)
O2	S2	C20	C19	143.9(2)
O2	S2	C20	C21	-32.2(3)
O2	S2	C25	F4	169.0(2)
O2	S2	C25	F5	-72.8(2)
O2	S2	C25	F6	47.5(2)
N2	S2	C20	C19	4.6(3)
N2	S2	C20	C21	-171.4(2)
N2	S2	C25	F4	-57.5(2)
N2	S2	C25	F5	60.8(2)
N2	S2	C25	F6	-178.9(2)
C19	C20	C21	C22	1.5(4)
C20	S2	N2	I2	-10.11(17)
C20	S2	C25	F4	57.3(2)
C20	S2	C25	F5	175.5(2)
C20	S2	C25	F6	-64.1(2)
C20	C19	C24	C23	-0.7(4)
C20	C21	C22	C23	-1.8(4)
C21	C22	C23	C24	1.0(4)
C22	C23	C24	C19	0.3(4)

Atom	Atom	Atom	Atom	Angle/°
C24	C19	C20	S2	-176.3(2)
C24	C19	C20	C21	-0.2(4)
C25	S2	N2	I2	98.64(14)
C25	S2	C20	C19	-109.9(2)
C25	S2	C20	C21	74.0(2)
C27	Si2	C28	C29	-58.6(2)
C27	Si2	C28	C30	67.1(3)
C27	Si2	C31	C32	-168.8(2)
C27	Si2	C31	C33	-41.4(2)
C27	Si2	C34	C35	160.2(2)
C27	Si2	C34	C36	-75.6(3)
C28	Si2	C31	C32	-49.7(2)
C28	Si2	C31	C33	77.7(2)
C28	Si2	C34	C35	43.8(3)
C28	Si2	C34	C36	168.0(2)
C31	Si2	C28	C29	-177.2(2)
C31	Si2	C28	C30	-51.6(3)
C31	Si2	C34	C35	-83.8(3)
C31	Si2	C34	C36	40.5(3)
C34	Si2	C28	C29	57.0(2)
C34	Si2	C28	C30	-177.3(2)
C34	Si2	C31	C32	75.4(2)
C34	Si2	C31	C33	-157.2(2)

Table 12: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **6.** U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H3	1512.74	5035.38	4782.1	27
H4	905.08	5398.86	3968.68	33
H5	1497.7	5984.06	3247.63	32
H6	2690.58	6274.5	3340.41	27
H10	3778.12	8584.14	2539.62	26
H11A	4403.52	8325.5	3377.88	47
H11B	4636.61	9062.38	3113.91	47
H11C	5125.27	8387.48	3035.5	47
H12A	5082.73	8543.98	1951.43	50
H12B	4639.85	9239.9	2074.79	50
H12C	4333.87	8652.28	1658.29	50
H13	3192.69	6732.49	1984.28	31
H14A	2616.2	7622.13	2509.3	81
H14B	2284.97	7533.61	1889.59	81
H14C	2800.1	8175.42	2021.12	81
H15A	3613.54	7807.98	1211.69	57
H15B	3043.35	7216.88	1073.49	57
H15C	3845.65	7003.47	1170.76	57
H16	4996.82	7127.84	1696.71	27
H17A	5489.22	6893.85	2825.57	43
H17B	5687.55	7552.2	2436.6	43
H17C	5957.95	6785.49	2269.32	43
H18A	5158.9	5917.6	1834.72	52
H18B	4337.13	6076.96	1790.65	52
H18C	4688.43	5936.47	2396.68	52
H21	4902.28	1134.38	5216.57	27
H22	4508.57	572.53	6039.75	31
H23	3945.08	1206.28	6752.29	31
H24	3733.84	2410.16	6639.51	25
H28	3073.32	4943.44	8262.42	28
H29A	4092.42	4223.27	8179.31	60
H29B	4282.44	5040.24	8170.45	60
H29C	4276.54	4601.38	7591.8	60

Atom	x	y	z	U_{eq}
H30A	3341.57	5414.61	7136.55	56
H30B	3491.52	5875.58	7690.71	56
H30C	2705.04	5659.76	7531.78	56
H31	1590.39	3777.67	7391.13	25
H32A	1488.47	4305.28	8280.83	45
H32B	947.62	4665.09	7851.2	45
H32C	1659.96	5058.47	8016.09	45
H33A	1860.34	5130.31	6923.73	45
H33B	1174.33	4667.06	6813.73	45
H33C	1916.28	4415.9	6570.75	45
H34	3361.16	3104.94	8025.12	29
H35A	3154.15	3838.09	8812.44	48
H35B	2875.17	3063.97	8944.41	48
H35C	2332.79	3671.78	8782.39	48
H36A	2427.48	2567.66	7538.74	70
H36B	1883.49	2869.96	7994.02	70
H36C	2454.71	2301.35	8182.25	70
H3A	5340(20)	4870(20)	5490(17)	49(13)

Table 13: Hydrogen Bond information for **6**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O3	H3A	N1[1]	0.82(4)	2.18(4)	3.001(3)	172(4)

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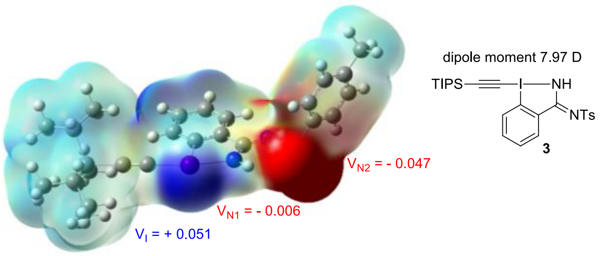
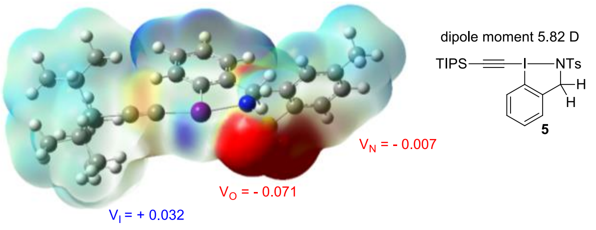
[1] 1-x,1-y,+

6. DFT calculations and coordinates

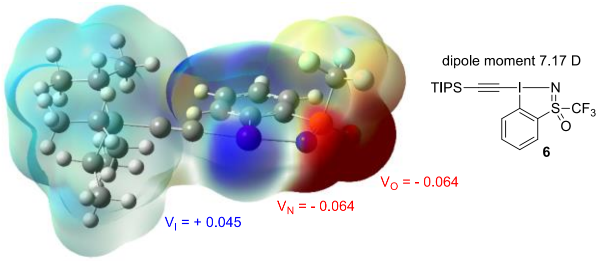
Geometries of the hypervalent iodine reagents were first optimized at the M06/def2-SVP level in Gaussian09.[20] Electrostatic potential maps and corresponding surface values were obtained using GaussView 5.0.9 via mapping onto the isodensity surface at 0.001au.[21] Reported dipole moments were obtained from the M06/def2-SVP computations on the optimized structures.



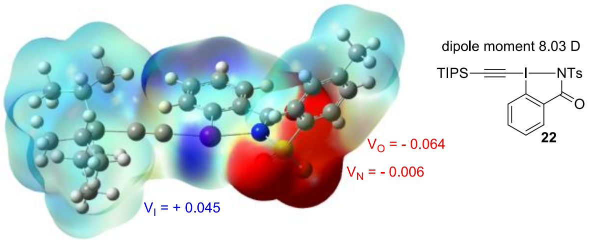
3



5



6



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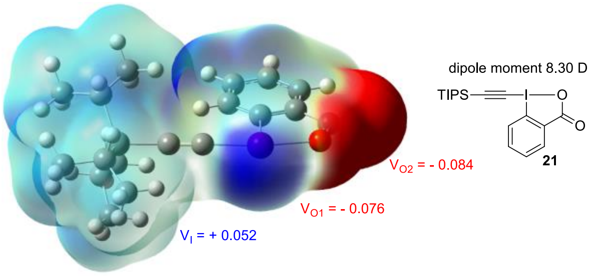

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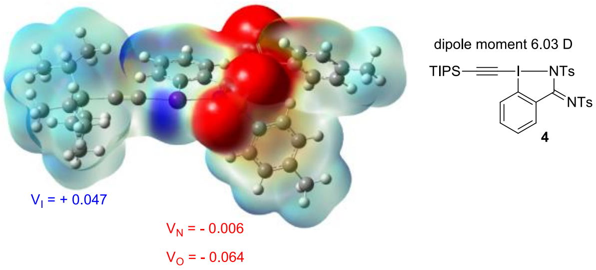

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[20] (a) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor. Chem. Acc.* **2008**, *120*, 215–241. (b) Zhao, Y.; Truhlar, D. G. Density Functionals with Broad Applicability in Chemistry. *Acc. Chem. Res.* **2008**, *41*, 157–167. (c) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305. (d) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian09, Revision D.01*; Gaussian, Inc.: Wallingford CT, 2016.

[21] Dennington, R.; Keith, T. A.; Millam, J. M. *GaussView 5.0.9*; Semichem Inc.: Shawnee Mission, KS, 2009.

Entry	**Reagent**	**$V_{C,max}$ (au)**
1	TIPS-H,Ts-EBZI **3**	+0.003
2	TIPS-Ts-EBz **5**	-0.001
3	TIPS-CF_3-EBS **6**	-0.002
4	TIPS-Ts-EBZ[a] **22**	-0.001
5	TIPS-EBX[a] **21**	+0.005
6	TIPS-Ts-EBZI **4**	+0.003

Table S1. Molecular electrostatic potential (MEP) maps computed at the M06/def2-SVP level. MEPs were mapped onto the 0.001 au isodensity surface. V_X represents the potential maximum around the atom X and is given in au.

Cartesian coordinate

TIPS-H,Ts-EBZI 3

I	-0.472028	-1.183486	0.031751
C	0.098391	0.762558	-0.619019
C	1.462638	0.911244	-0.851468
C	1.914538	2.160660	-1.283516
C	1.016931	3.205660	-1.467327
C	-0.823236	1.782111	-0.794340
C	-0.344247	3.018674	-1.224986
C	2.385894	-0.238980	-0.636831
H	2.987529	2.266548	-1.466993
H	1.379875	4.179835	-1.806089
H	-1.887984	1.620934	-0.600745
H	-1.049982	3.841210	-1.371072
C	-2.514316	-0.583112	0.154293
N	1.750199	-1.330190	-0.237310
C	-3.708085	-0.324438	0.283153
N	3.659153	-0.009656	-0.870700
Si	-5.512553	0.088600	0.468670
C	-5.657650	1.612144	1.610512
C	-6.184090	0.448374	-1.272124
C	-6.310955	-1.407716	1.329794
C	-7.829147	-1.280232	1.403605
C	-5.891622	-2.762028	0.769751
H	-5.907887	-1.333438	2.361748
H	-7.226641	0.797254	-1.122658
C	-5.394121	1.568666	-1.943165
C	-6.209741	-0.792367	-2.157459
C	-6.932045	2.413265	1.354867
H	-5.730974	1.169008	2.625551

C	-4.435000	2.524264	1.591101
H	-8.276063	-2.123869	1.958889
H	-8.154155	-0.354424	1.907667
H	-8.284105	-1.284641	0.396552
H	-6.272024	-3.584103	1.401654
H	-6.293294	-2.926950	-0.244376
H	-4.795994	-2.866638	0.709185
H	-6.536592	-0.542692	-3.182565
H	-5.205249	-1.246817	-2.239494
H	-6.893708	-1.568121	-1.776759
H	-5.808134	1.806390	-2.939085
H	-5.394651	2.503491	-1.357868
H	-4.340036	1.273039	-2.095596
H	-4.538866	3.340113	2.328320
H	-3.503646	1.980841	1.819189
H	-4.301613	3.002663	0.603466
H	-7.054774	3.213088	2.106404
H	-6.905569	2.906318	0.367186
H	-7.846511	1.797303	1.384768
H	2.356890	-2.126442	-0.014387
S	4.772785	-1.216925	-0.740016
O	5.251497	-1.574548	-2.069332
O	4.308726	-2.294302	0.155992
C	6.092075	-0.369208	0.099517
C	6.088839	-0.294056	1.490124
C	7.120558	0.380310	2.131170
C	8.158749	0.976809	1.402738
C	7.109375	0.209265	-0.650653
C	8.135428	0.881212	0.007497
H	5.284896	-0.773558	2.055768
H	7.128947	0.444891	3.224825
C	9.279343	1.672851	2.110200
H	7.088172	0.119127	-1.740055
H	8.941715	1.341714	-0.573590
H	9.836702	2.338486	1.434229
H	8.913092	2.272657	2.958470
H	10.001001	0.946081	2.521750

TIPS-Ts-EBZI 4

I	-1.266280	0.616041	-0.546623
C	-0.920032	-1.278108	0.387459
C	0.421181	-1.637651	0.595844
C	0.655051	-2.829222	1.294343
C	-0.401669	-3.631896	1.709422
C	-1.987695	-2.061331	0.791627
C	-1.716391	-3.260018	1.450130
C	1.518586	-0.746765	0.110697
H	1.678136	-3.124018	1.537719
H	-0.188320	-4.558668	2.247785
H	-3.018267	-1.747385	0.604009
H	-2.548181	-3.893995	1.770349
C	-3.351000	0.335677	-0.472820
N	1.016871	0.419205	-0.350900
C	-4.574694	0.253157	-0.424943
N	2.799232	-0.937988	0.118479
Si	-6.423540	0.115395	-0.237288
C	-6.948478	-1.642652	-0.766176
C	-6.784905	0.433130	1.601987
C	-7.188643	1.386163	-1.425094
C	-8.696033	1.504196	-1.220932
C	-6.513281	2.752652	-1.413117
H	-7.009212	0.931766	-2.422047
H	-7.869490	0.238960	1.733726
C	-6.008822	-0.541360	2.484124
C	-6.496754	1.872388	2.014042
C	-8.225720	-2.098140	-0.064875
H	-7.172734	-1.534857	-1.847534
C	-5.846780	-2.688037	-0.625025
H	-9.143035	2.214764	-1.938359
H	-9.218477	0.541390	-1.351681
H	-8.936734	1.875566	-0.208301
H	-6.913684	3.396412	-2.216045
H	-6.683849	3.285965	-0.462503

H	-5.422837	2.680457	-1.556962
H	-6.641515	2.010291	3.100211
H	-5.451303	2.152435	1.788431
H	-7.151189	2.596684	1.502857
H	-6.234666	-0.377971	3.552732
H	-6.236317	-1.597127	2.260672
H	-4.918724	-0.404721	2.361304
H	-6.187193	-3.673407	-0.989913
H	-4.940699	-2.418465	-1.191836
H	-5.547935	-2.825311	0.430466
H	-8.583369	-3.058680	-0.476072
H	-8.059291	-2.256914	1.015070
H	-9.053702	-1.375909	-0.161917
S	1.936548	1.557132	-1.171280
O	2.718412	0.958062	-2.239558
O	0.920168	2.567219	-1.486137
C	3.033325	2.224626	0.049829
C	2.517571	3.108003	0.996815
C	3.369471	3.629960	1.960423
C	4.728175	3.284683	1.986784
C	4.376565	1.863586	0.045512
C	5.215360	2.403347	1.015872
H	1.460022	3.385730	0.963479
H	2.979578	4.328846	2.708437
C	5.627437	3.837684	3.046942
H	4.749545	1.165765	-0.710384
H	6.276270	2.131166	1.022851
H	6.689000	3.703926	2.791605
H	5.445655	4.911501	3.212272
H	5.455596	3.332747	4.013144
S	3.672063	-2.318024	0.316283
O	3.829108	-2.654005	1.734493
O	3.196690	-3.349249	-0.603063
C	5.232864	-1.711809	-0.271782
C	5.383459	-1.456970	-1.634776
C	6.591436	-0.949515	-2.091024
C	7.654785	-0.701379	-1.208511

C	6.262967	-1.475946	0.628204
C	7.472523	-0.973424	0.150039
H	4.548397	-1.641928	-2.316248
H	6.721795	-0.739411	-3.158169
C	8.951403	-0.163722	-1.728217
H	6.108232	-1.688341	1.689421
H	8.296040	-0.789696	0.848590
H	9.682663	-0.008380	-0.921302
H	9.401759	-0.852275	-2.462497
H	8.807336	0.799088	-2.246092

TIPS-Ts-EBz 5

I	0.377718	-0.323221	-0.249244
C	0.302202	1.813452	-0.076826
C	1.488826	2.482861	-0.365529
C	1.470453	3.878497	-0.273270
C	0.315800	4.561158	0.090537
C	-0.865507	2.466816	0.295581
C	-0.852011	3.856557	0.379051
C	2.732792	1.744803	-0.773731
H	2.392462	4.427685	-0.494236
H	0.327470	5.652513	0.155502
H	-1.773170	1.899271	0.521904
H	-1.762181	4.385817	0.675341
C	-1.723247	-0.425673	0.064092
N	2.544929	0.350417	-0.490671
C	-2.935010	-0.555488	0.216271
Si	-4.783132	-0.663407	0.373893
C	-5.305304	0.213851	1.989269
C	-5.501695	0.208417	-1.156401
C	-5.222875	-2.509102	0.502671
C	-6.730160	-2.732672	0.436029
C	-4.476711	-3.407327	-0.476978
H	-4.879361	-2.772071	1.525147
H	-6.601063	0.224096	-1.006702
C	-5.004868	1.649215	-1.245102

C	-5.198458	-0.540418	-2.449166
C	-6.720798	0.781500	1.914373
H	-5.304357	-0.601411	2.742250
C	-4.321047	1.279567	2.461801
H	-6.982977	-3.802128	0.546298
H	-7.274531	-2.189136	1.226790
H	-7.143712	-2.402938	-0.534320
H	-4.669687	-4.473013	-0.260161
H	-4.793907	-3.231634	-1.518774
H	-3.386437	-3.250271	-0.437081
H	-5.551228	0.026641	-3.329033
H	-4.111384	-0.694247	-2.576919
H	-5.679559	-1.531112	-2.485368
H	-5.456542	2.174012	-2.105688
H	-5.237924	2.240893	-0.343449
H	-3.909312	1.680963	-1.387790
H	-4.633227	1.704468	3.432598
H	-3.300581	0.881336	2.583611
H	-4.261505	2.123753	1.750316
H	-7.040185	1.182967	2.892510
H	-6.783313	1.614662	1.192053
H	-7.472593	0.034134	1.610291
S	3.508162	-0.739981	-1.214802
O	3.959502	-0.293453	-2.532977
O	2.788623	-2.012866	-1.072954
C	4.955525	-0.816437	-0.176170
C	4.840801	-1.377834	1.096074
C	5.957848	-1.424708	1.916614
C	7.195136	-0.919866	1.486821
C	6.166893	-0.309072	-0.629080
C	7.280240	-0.362979	0.208830
H	3.876647	-1.777141	1.425159
H	5.879996	-1.866734	2.916307
C	8.389547	-0.990761	2.385862
H	6.227085	0.111341	-1.636796
H	8.240591	0.031044	-0.140869
H	9.272176	-0.519231	1.929104

H	8.197747	-0.489683	3.349198
H	8.650505	-2.036536	2.619964
H	2.931760	1.935563	-1.850783
H	3.596740	2.175716	-0.221712

TIPS-CF$_3$-EBS 6

I	1.009131	-1.287240	-0.419930
C	1.559970	0.803625	-0.428349
C	2.918121	1.053510	-0.480110
C	3.396120	2.359299	-0.551196
C	2.482504	3.409278	-0.537845
C	0.633884	1.835192	-0.420611
C	1.114899	3.144975	-0.469867
S	4.037915	-0.366607	-0.543353
H	4.474363	2.530026	-0.620567
H	2.837665	4.441839	-0.588606
H	-0.440070	1.629048	-0.382713
H	0.398290	3.971395	-0.464223
C	-1.018050	-0.675036	-0.110907
N	3.179760	-1.585379	-0.738421
C	-2.206636	-0.426533	0.075988
O	5.229170	-0.003052	-1.312174
Si	-4.001679	-0.006403	0.307333
C	-4.119199	1.449688	1.538140
C	-4.673577	0.467127	-1.407549
C	-4.824518	-1.538244	1.079485
C	-6.340727	-1.393215	1.158593
C	-4.423348	-2.865347	0.445715
H	-4.422155	-1.529067	2.114348
H	-5.716048	0.809383	-1.242587
C	-3.875578	1.623042	-2.005063
C	-4.696987	-0.720691	-2.362384
C	-5.382030	2.281024	1.328560
H	-4.196579	0.953251	2.527673
C	-2.880785	2.340148	1.564910
H	-6.802605	-2.266422	1.652619

H	-6.652609	-0.499886	1.725698
H	-6.791090	-1.319199	0.152190
H	-4.799370	-3.715442	1.042171
H	-4.842909	-2.978180	-0.568369
H	-3.329504	-2.973465	0.362293
H	-5.027243	-0.415606	-3.371300
H	-3.691480	-1.167191	-2.471016
H	-5.376875	-1.518308	-2.022398
H	-4.263970	1.903722	-3.000224
H	-3.901732	2.530030	-1.377695
H	-2.814156	1.344516	-2.139724
H	-2.976441	3.128763	2.332448
H	-1.963196	1.769225	1.782362
H	-2.727406	2.853266	0.597298
H	-5.491038	3.046118	2.117561
H	-5.353323	2.819284	0.365014
H	-6.304761	1.676706	1.333320
C	4.676354	-0.321359	1.225436
F	5.526198	-1.309357	1.398762
F	5.270982	0.825458	1.511879
F	3.644262	-0.480718	2.044956

TIPS-EBX 21

I	-1.845691	-1.392926	-0.171230
C	-2.513024	0.627011	0.014079
C	-3.894271	0.713958	0.071633
C	-4.456918	1.984585	0.202294
C	-3.638656	3.107353	0.267533
C	-1.660130	1.716711	0.074537
C	-2.250256	2.974755	0.202644
C	-4.758287	-0.530074	-0.008578
H	-5.548437	2.046343	0.247561
H	-4.083183	4.101266	0.369613
H	-0.573681	1.599321	0.023213
H	-1.610134	3.860419	0.251375
C	0.162605	-0.785442	-0.170353

O	-4.057795	-1.614608	-0.130683
C	1.348038	-0.468457	-0.177388
O	-5.963700	-0.442596	0.041881
Si	3.137210	0.051674	-0.146420
C	3.369318	1.450257	-1.426247
C	3.493568	0.649288	1.622099
C	4.144879	-1.464459	-0.692058
C	5.644542	-1.226521	-0.542707
C	3.718560	-2.778128	-0.046532
H	3.912531	-1.533798	-1.775375
H	4.519524	1.070527	1.594108
C	2.527990	1.760028	2.026328
C	3.460503	-0.483458	2.641618
C	4.520906	2.384444	-1.063093
H	3.647160	0.908696	-2.354228
C	2.100492	2.245616	-1.714260
H	6.225678	-2.095351	-0.898997
H	5.993172	-0.349468	-1.113760
H	5.924650	-1.065415	0.514115
H	4.246601	-3.631850	-0.506985
H	3.953351	-2.800868	1.030953
H	2.636479	-2.960976	-0.149908
H	3.596457	-0.097275	3.667390
H	2.489882	-1.012353	2.621171
H	4.249803	-1.232715	2.467654
H	2.757613	2.138503	3.038091
H	2.556154	2.623673	1.341182
H	1.486938	1.389722	2.050195
H	2.272988	2.994691	-2.507410
H	1.267438	1.601346	-2.038974
H	1.760811	2.802012	-0.821466
H	4.721573	3.101133	-1.878890
H	4.284735	2.983823	-0.166226
H	5.465394	1.853088	-0.858201

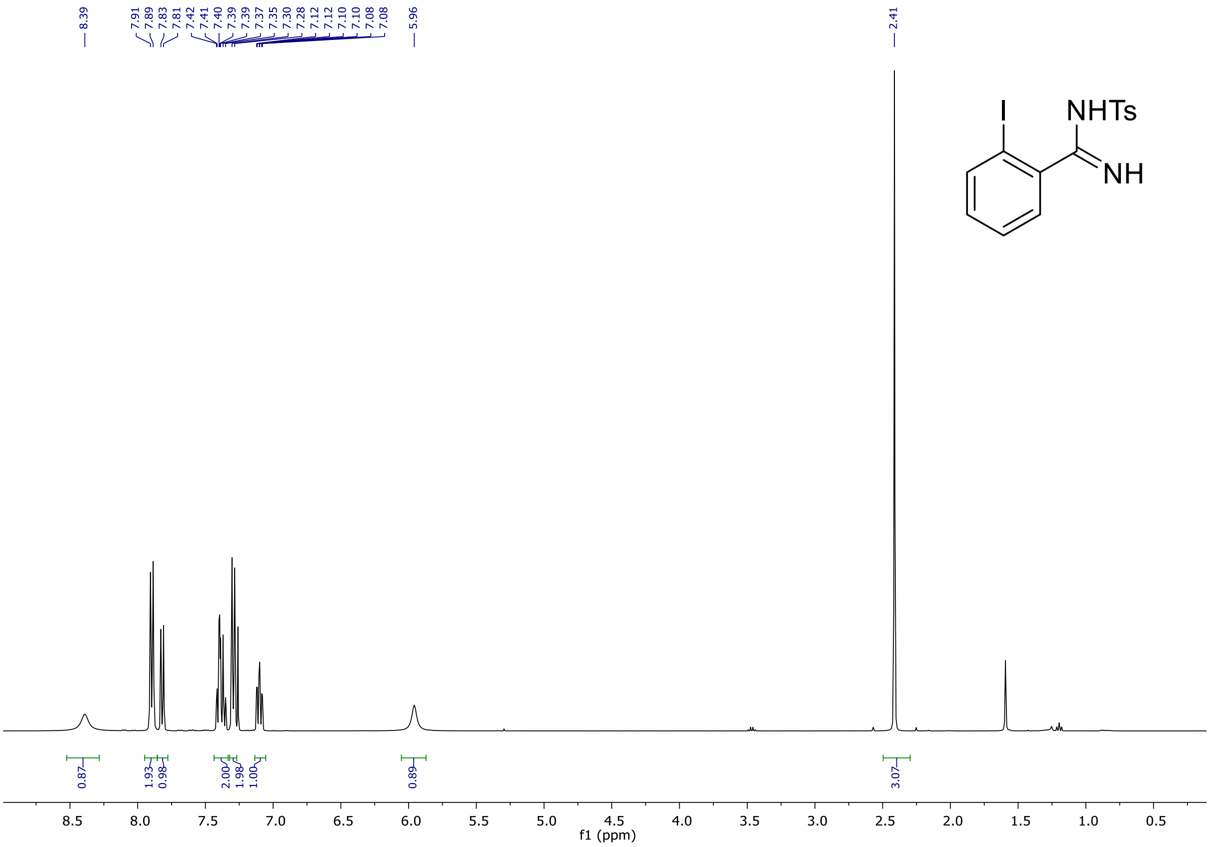
TIPS-Ts-EBZ 22

I	0.289822	-0.256924	-0.573182
C	0.306662	1.816342	-0.043805
C	1.553766	2.436711	-0.112302
C	1.629086	3.789750	0.222814
C	0.488375	4.486456	0.605456
C	-0.848627	2.484762	0.329433
C	-0.744487	3.836574	0.656962
C	2.793144	1.701222	-0.541110
H	2.614412	4.262287	0.165095
H	0.556617	5.546604	0.863679
H	-1.811993	1.967651	0.363939
H	-1.644461	4.383048	0.953872
C	-1.772948	-0.379240	-0.147029
N	2.477960	0.412103	-0.836615
C	-2.968902	-0.509560	0.097374
O	3.883116	2.236845	-0.577712
Si	-4.800017	-0.648906	0.413241
C	-5.202360	0.313443	2.013931
C	-5.658017	0.110891	-1.102950
C	-5.152890	-2.496367	0.689694
C	-6.648147	-2.788519	0.771598
C	-4.454756	-3.427267	-0.295513
H	-4.710760	-2.678348	1.691877
H	-6.739892	0.130861	-0.858838
C	-5.186262	1.544369	-1.328827
C	-5.459868	-0.726959	-2.361015
C	-6.643603	0.816780	2.041854
H	-5.090155	-0.450076	2.811330
C	-4.230485	1.448877	2.317552
H	-6.835114	-3.855284	0.987720
H	-7.153428	-2.206573	1.560841
H	-7.158065	-2.562687	-0.182530
H	-4.582393	-4.483006	0.002307
H	-4.868191	-3.330749	-1.313627
H	-3.372706	-3.228137	-0.361784
H	-5.918431	-0.239697	-3.239627
H	-4.386473	-0.861549	-2.588369

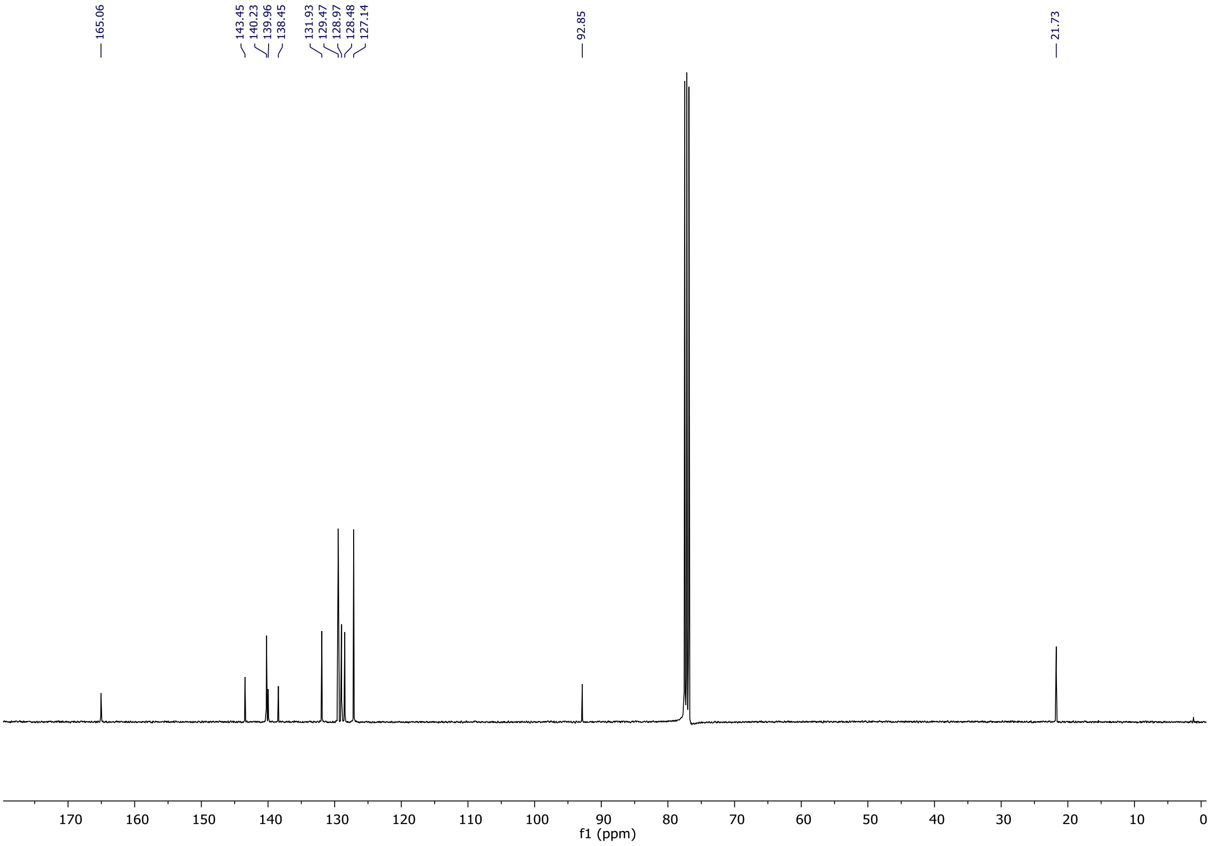
H	-5.906932	-1.730294	-2.271987
H	-5.684751	1.996164	-2.204671
H	-5.387542	2.200148	-0.465493
H	-4.098642	1.577439	-1.523099
H	-4.469175	1.927442	3.284104
H	-3.184217	1.105573	2.365058
H	-4.284290	2.241129	1.548770
H	-6.889045	1.260765	3.022786
H	-6.808908	1.604354	1.285659
H	-7.385250	0.023512	1.850032
S	3.549799	-0.699823	-1.457483
O	4.238302	-0.178152	-2.624231
O	2.714918	-1.902739	-1.562332
C	4.739409	-0.960511	-0.165479
C	4.504369	-1.962066	0.774904
C	5.432015	-2.162792	1.788975
C	6.590776	-1.379222	1.873024
C	5.878727	-0.162514	-0.109170
C	6.795071	-0.380239	0.914678
H	3.606217	-2.580181	0.693256
H	5.262201	-2.948910	2.532911
C	7.595776	-1.627437	2.953667
H	6.027268	0.622417	-0.854694
H	7.694529	0.241599	0.973199
H	8.292458	-0.783277	3.063409
H	7.109467	-1.801749	3.926675
H	8.199198	-2.524911	2.733440

7. NMR spectra

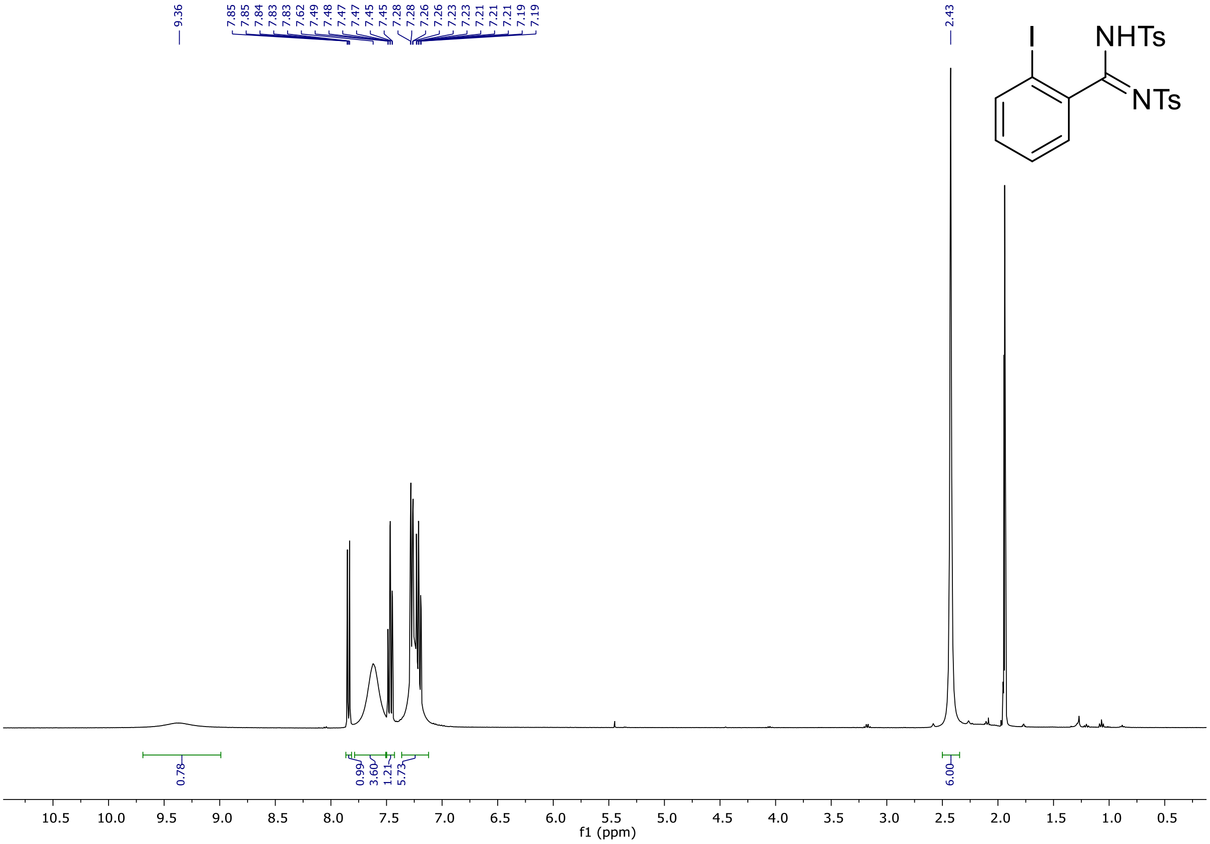
^{1}H-NMR (400 MHz, Chloroform-*d*) (8)



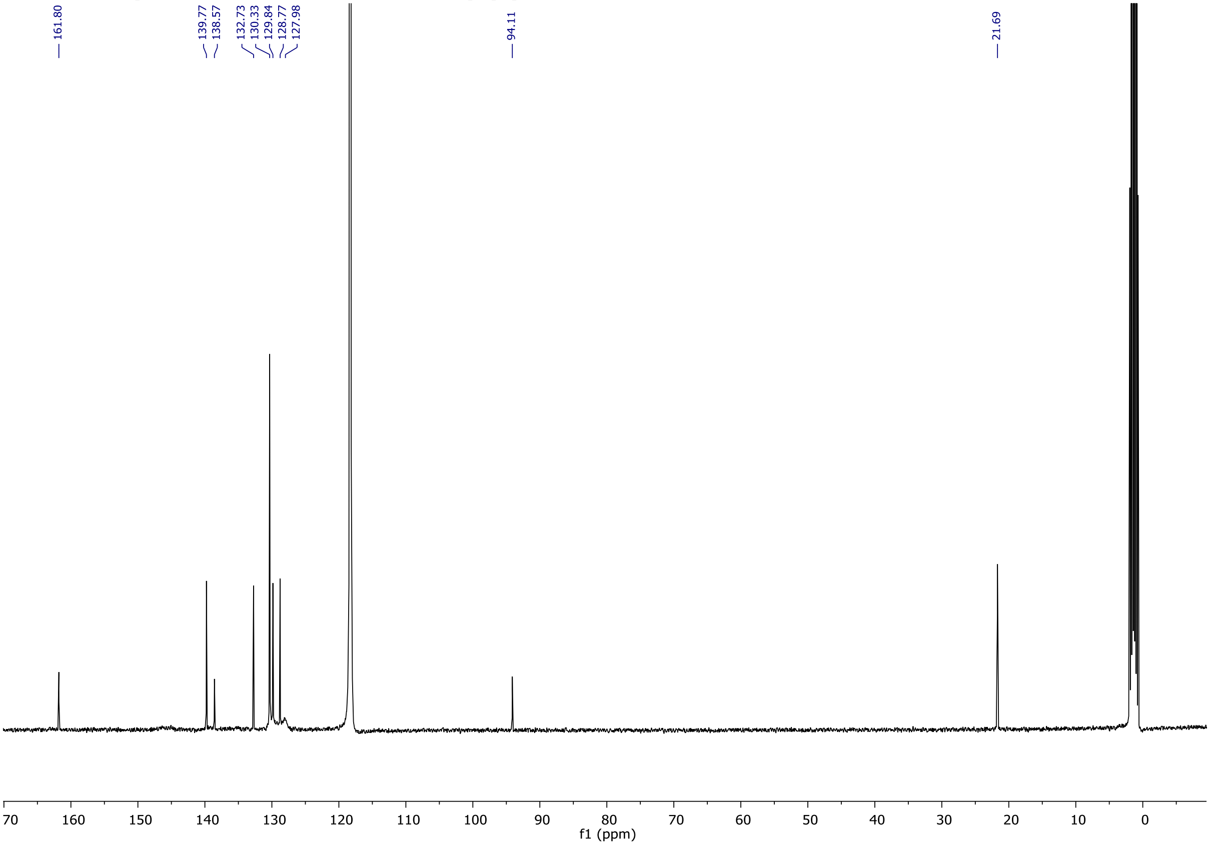
^{13}C-NMR (101 MHz, Chloroform-*d*) (8)



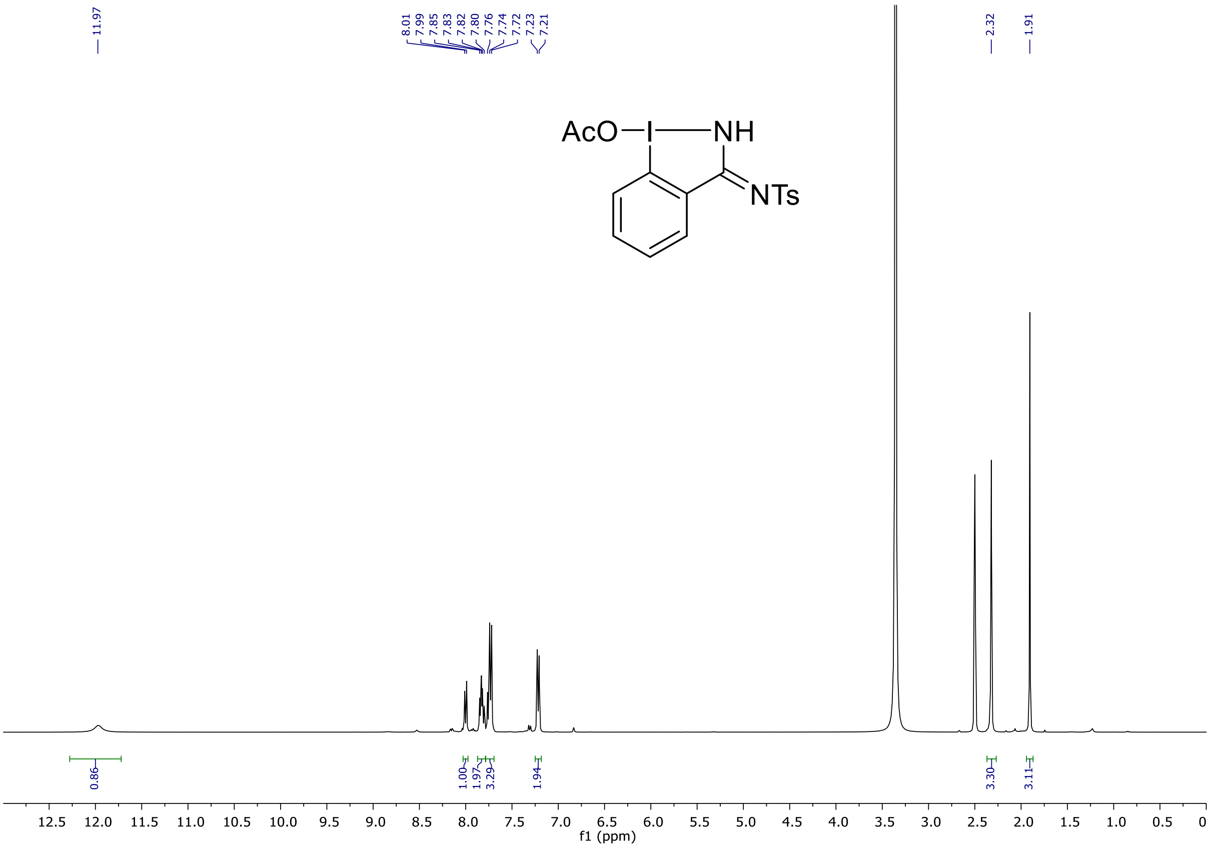
^{1}H-NMR (400 MHz, acetonitrile-d_3) (9)



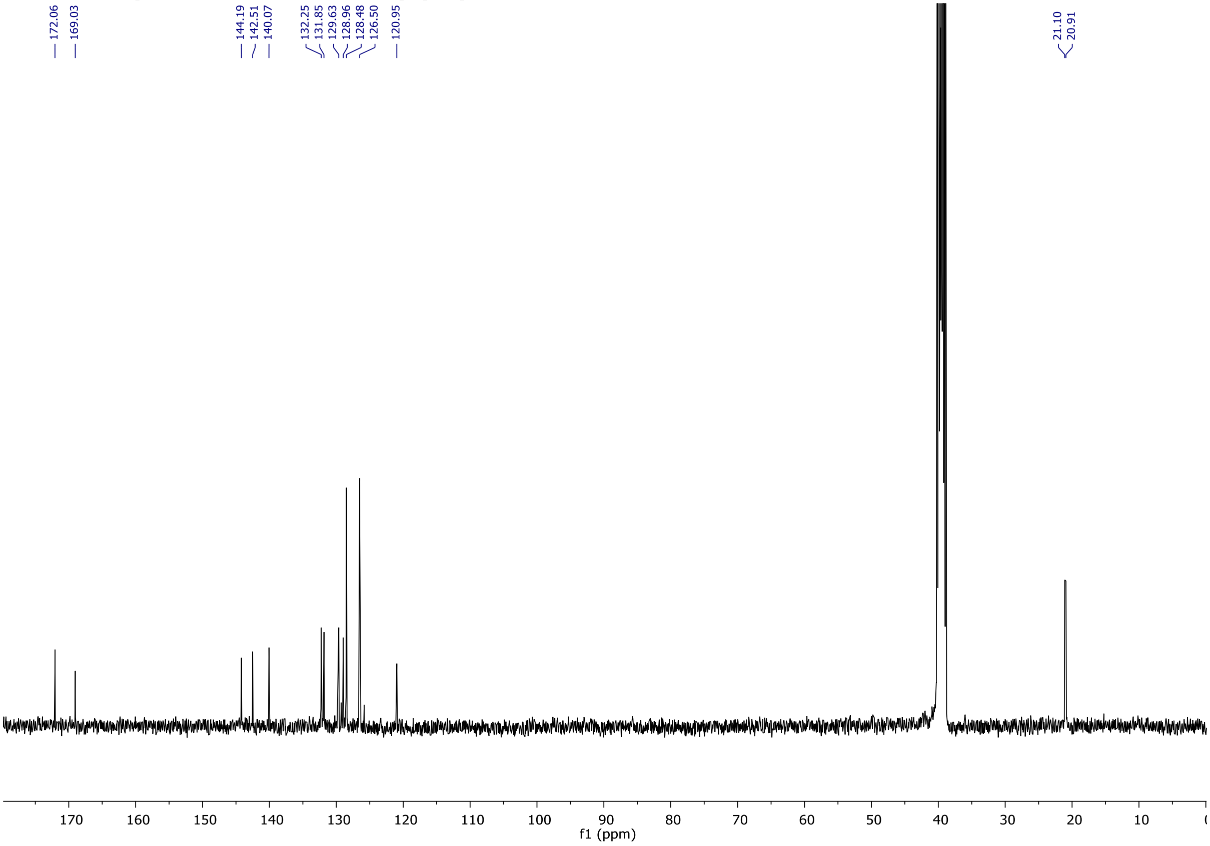
^{13}C-NMR (101 MHz, acetonitrile-d_3) (9)



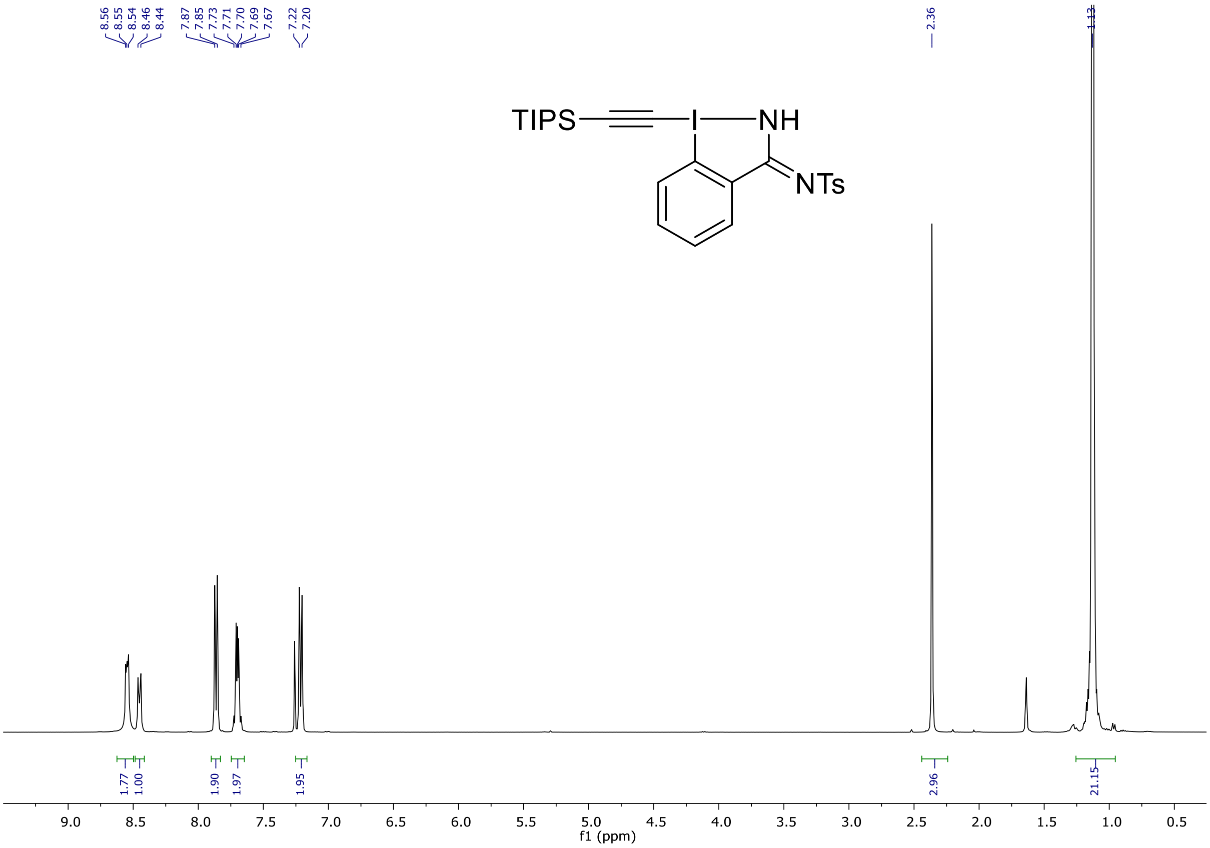
^{1}H-NMR (400 MHz, DMSO-d_6) (18)



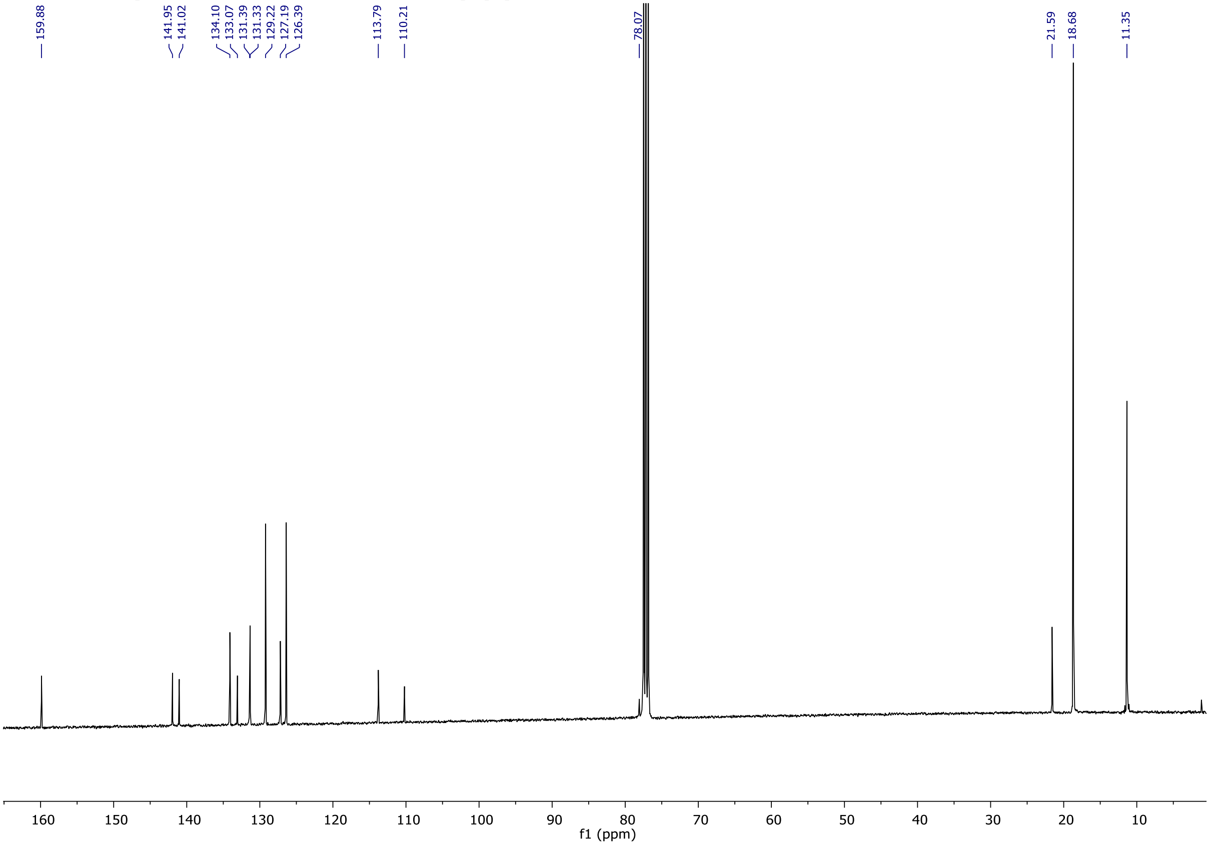
^{13}C-NMR (101 MHz, DMSO-d_6) (18)



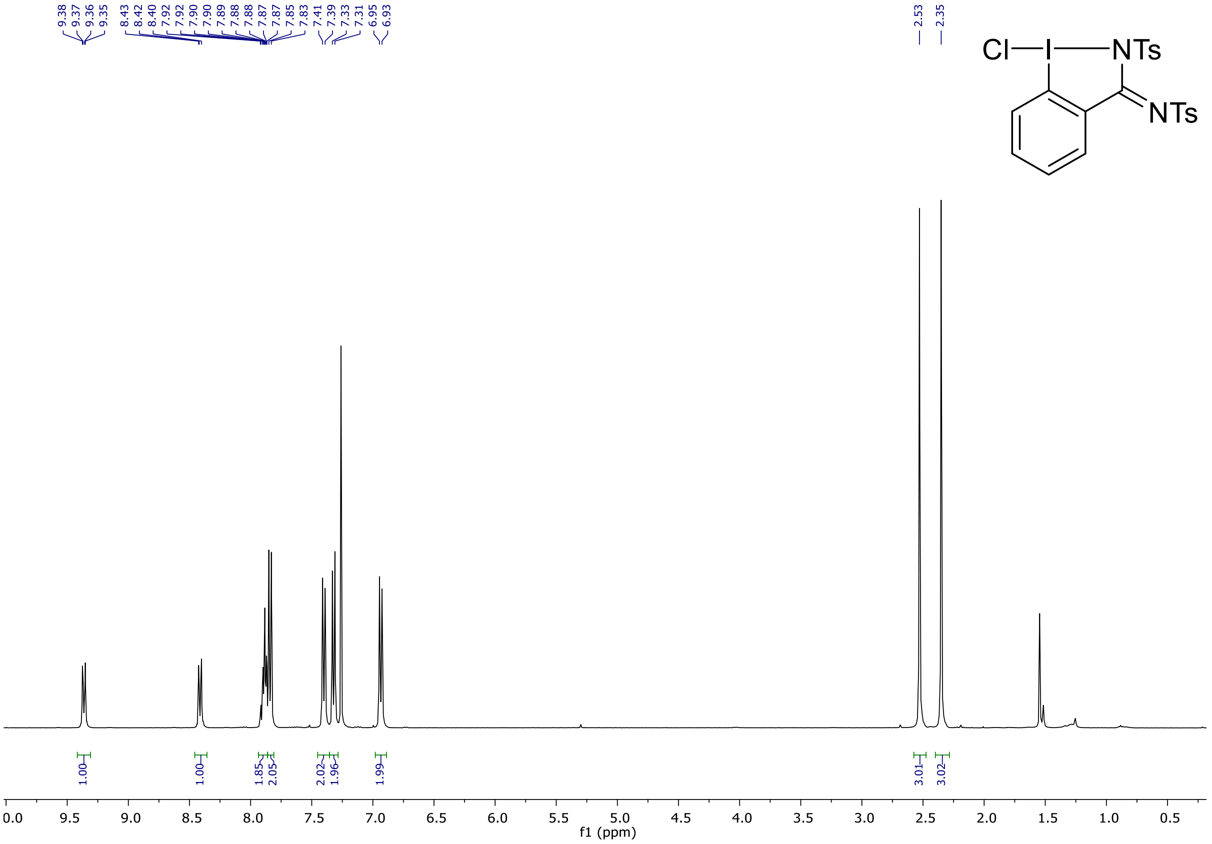
^{1}H-NMR (400 MHz, Chloroform-*d*) (3)



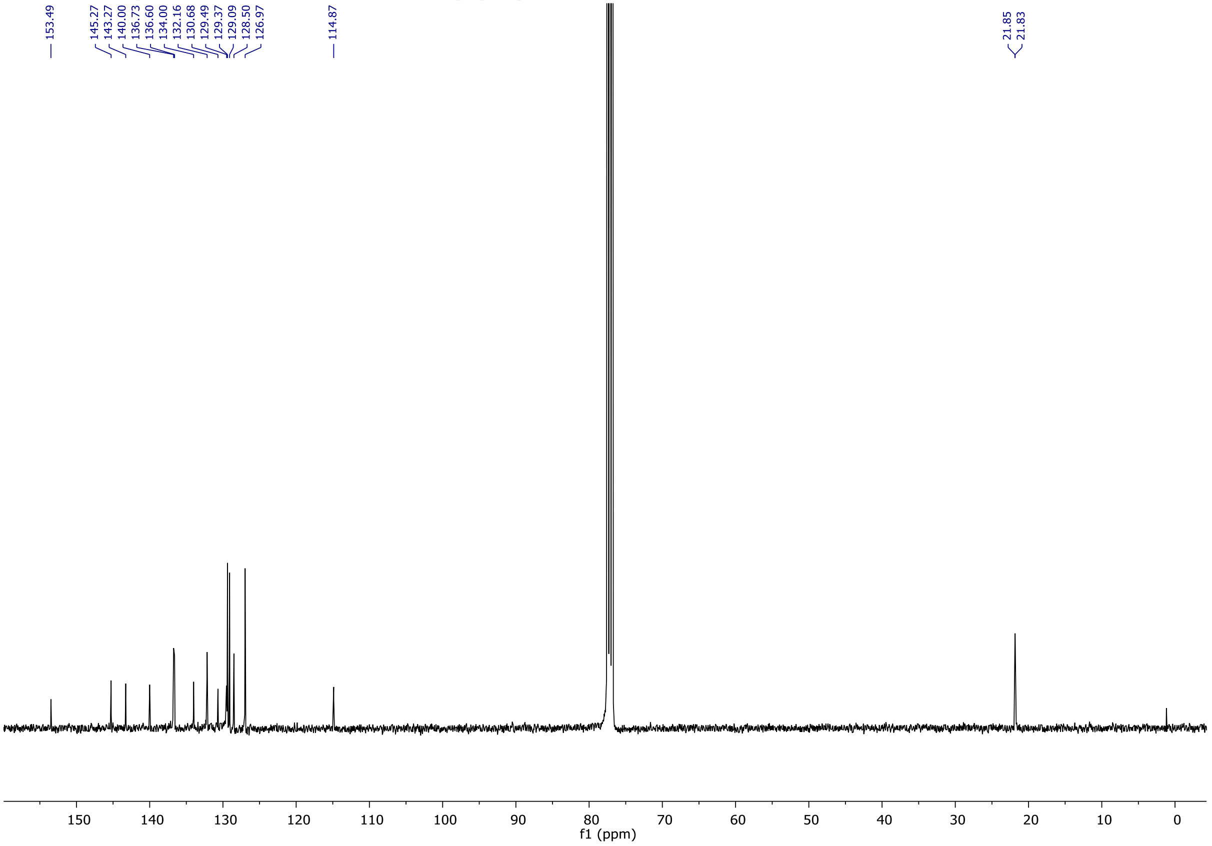
^{13}C-NMR (101 MHz, Chloroform-*d*) (3)



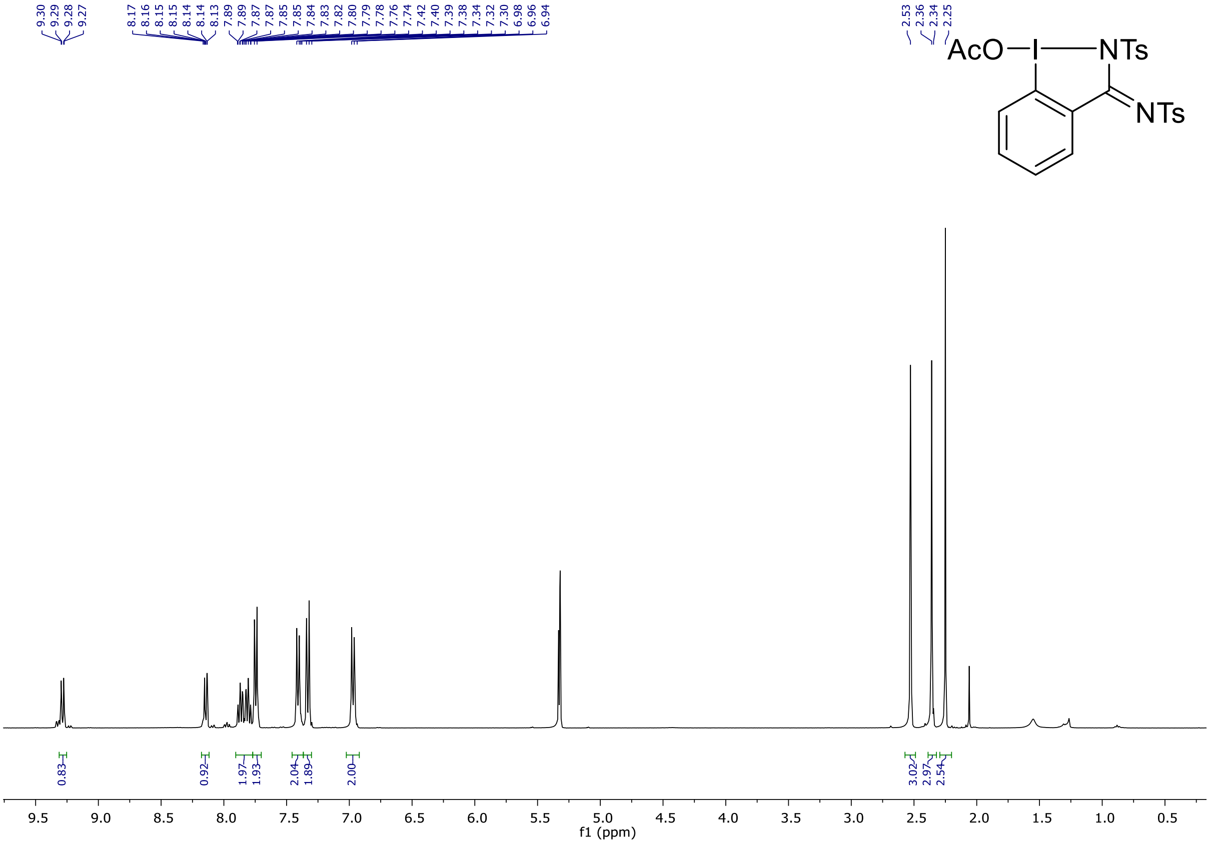
^{1}H-NMR (400 MHz, chloroform-*d*) (19)



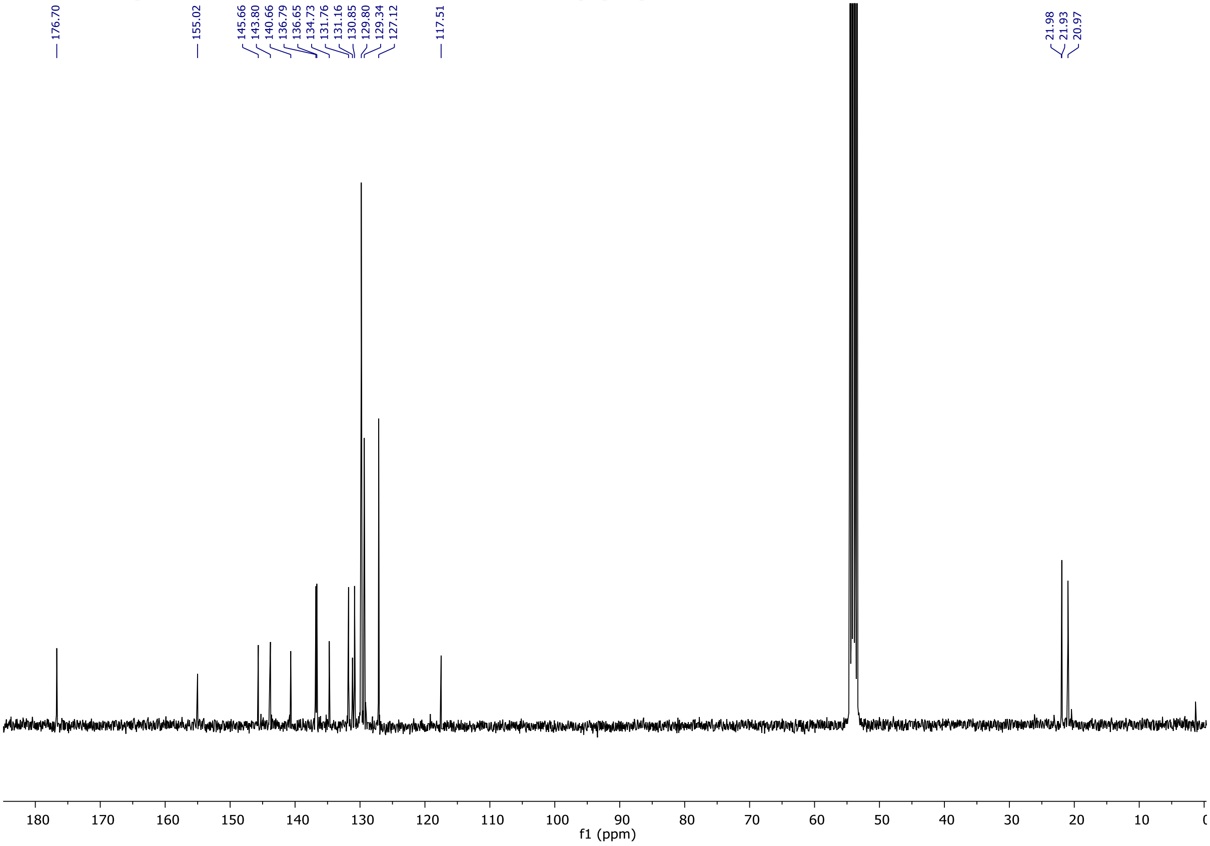
^{13}C-NMR (101 MHz, chloroform-*d*) (19)



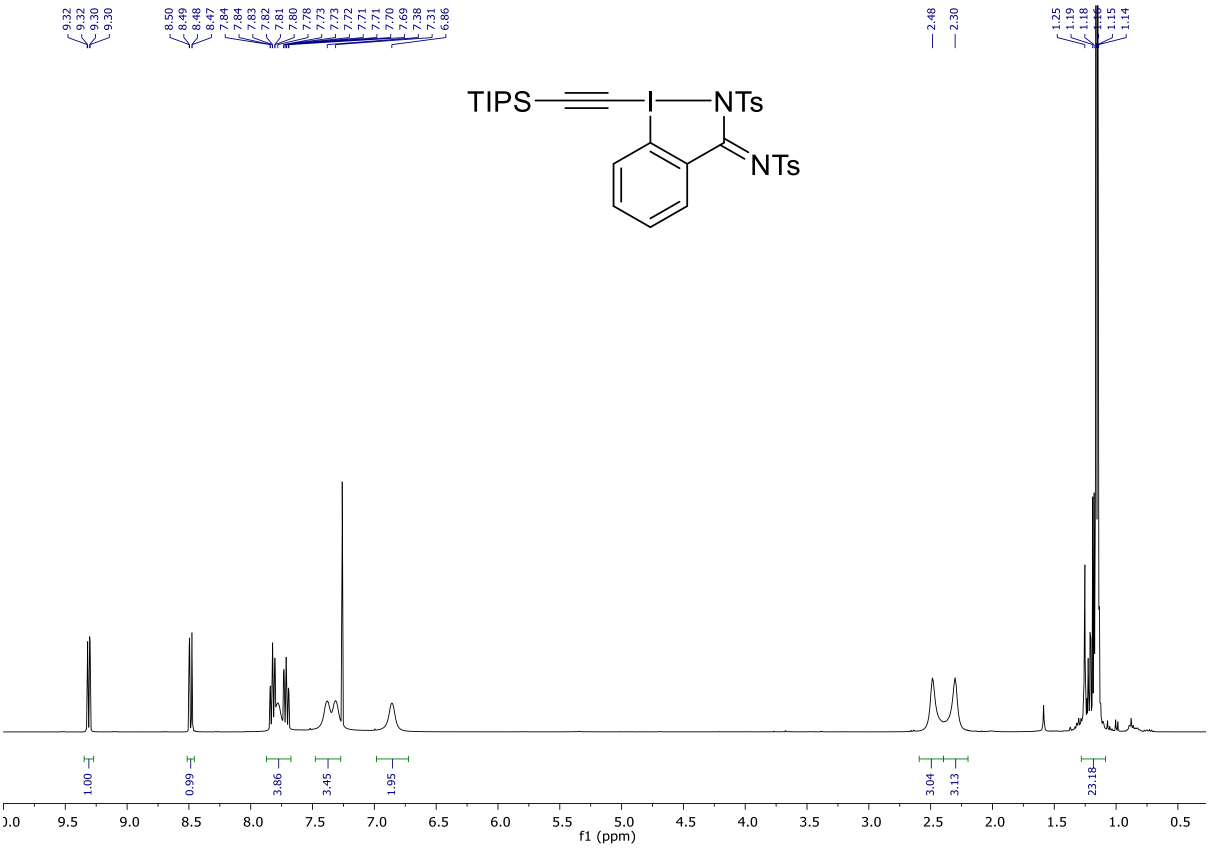
^{1}H-NMR (400 MHz, methylene chloride-d_2) (20)



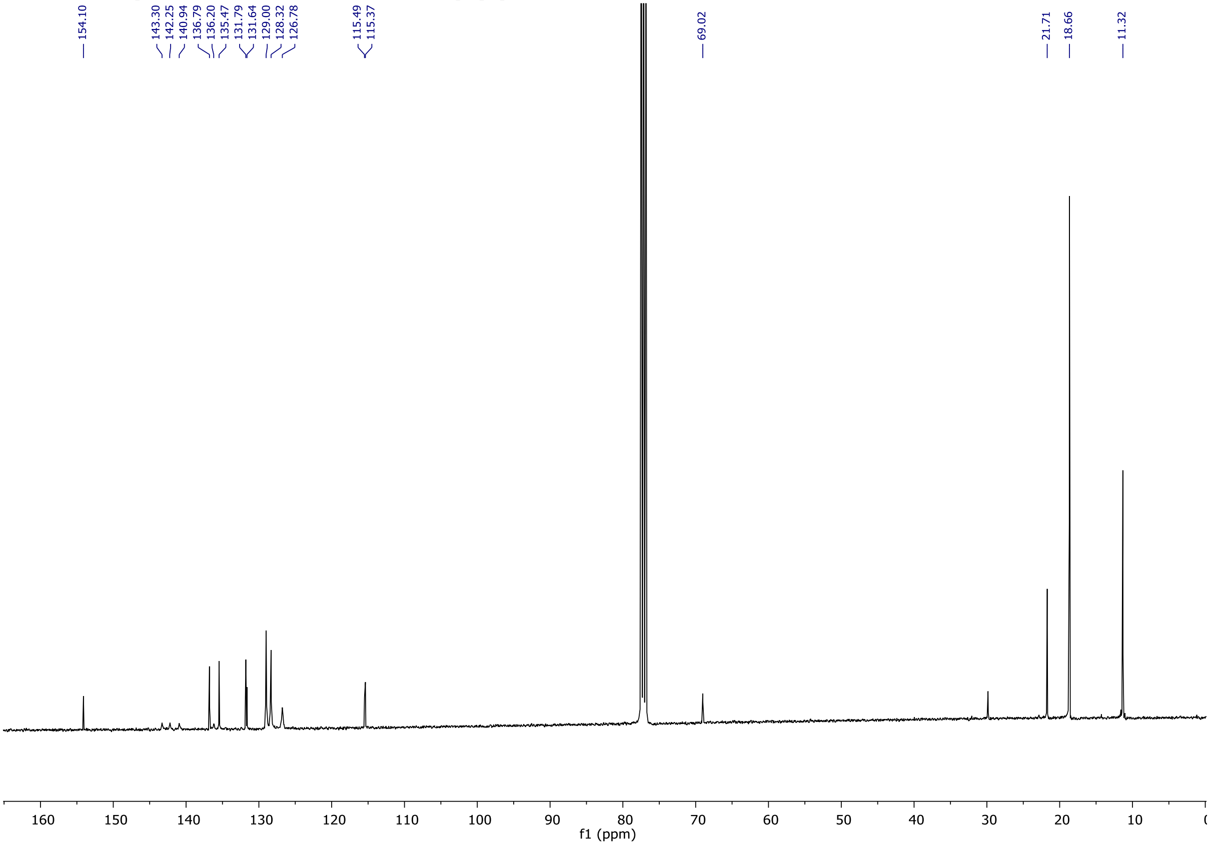
^{13}C-NMR (101 MHz, methylene chloride-d_2) (20)



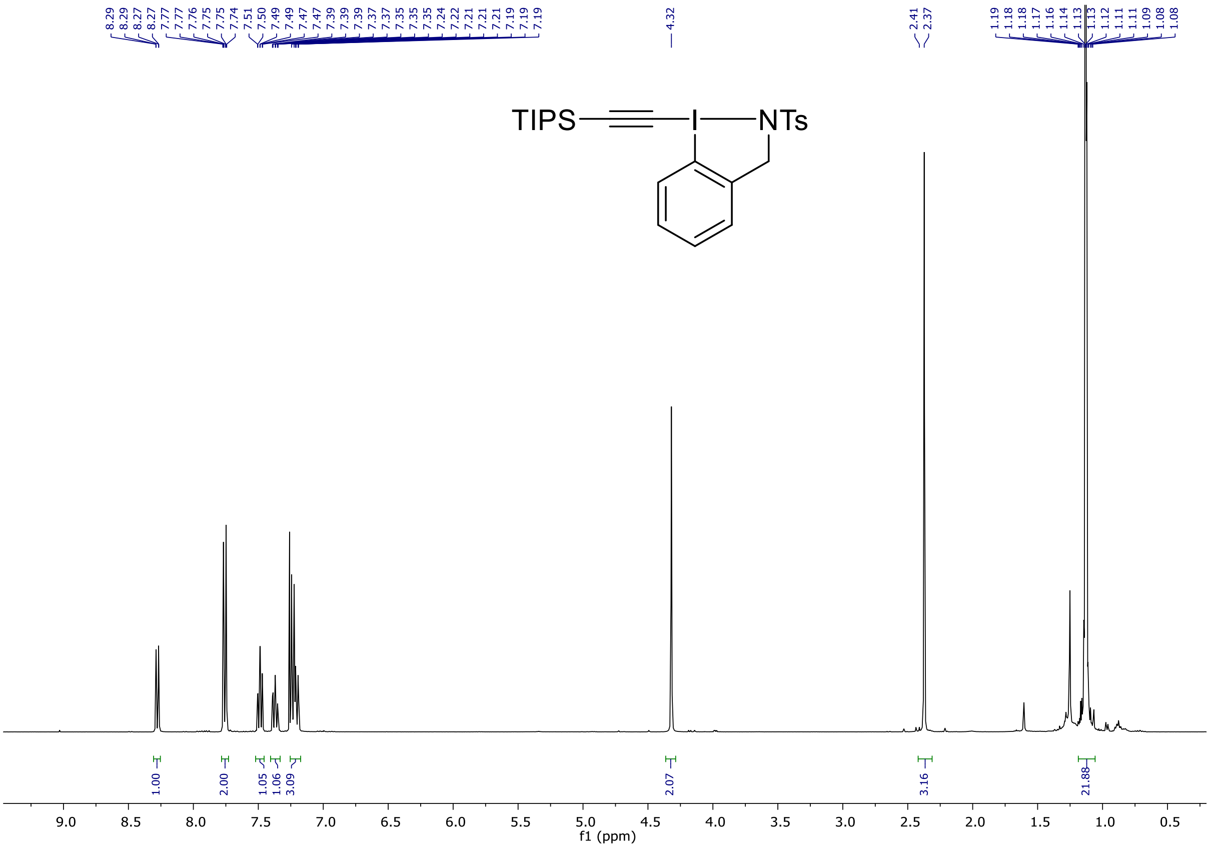
^{1}H-NMR (400 MHz, chloroform-*d*) (4)



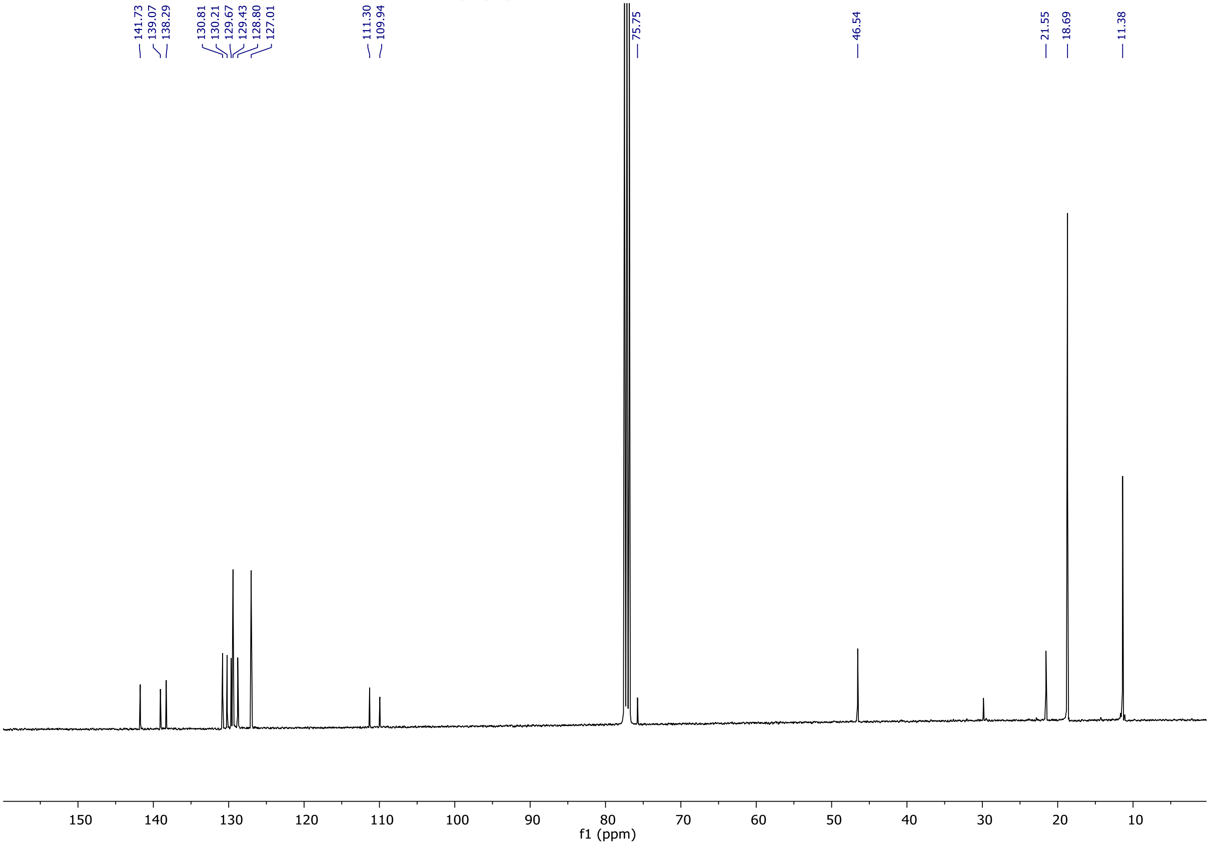
^{13}C-NMR (101 MHz, chloroform-*d*) (4)



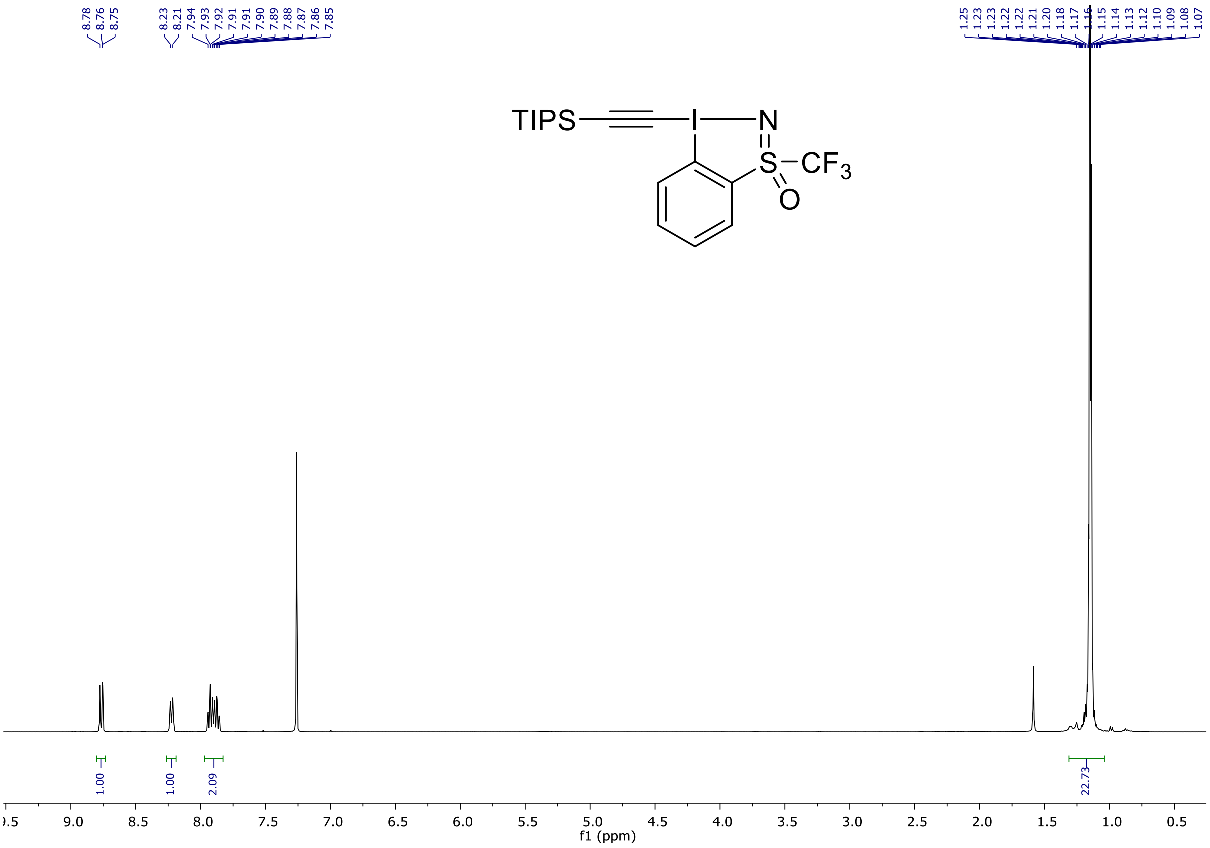
^{1}H-NMR (400 MHz, Chloroform-*d*) (5)



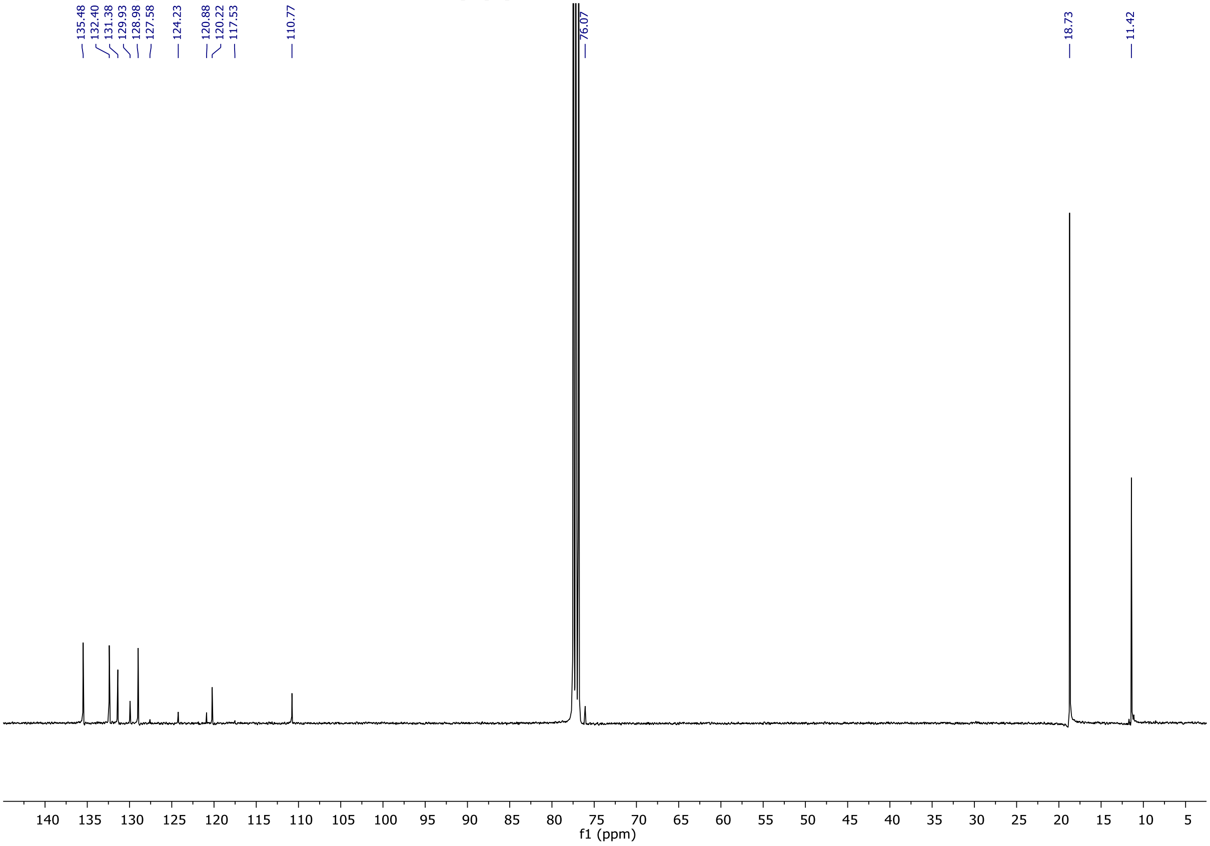
^{13}C-NMR (101 MHz, Chloroform-*d*) (5)



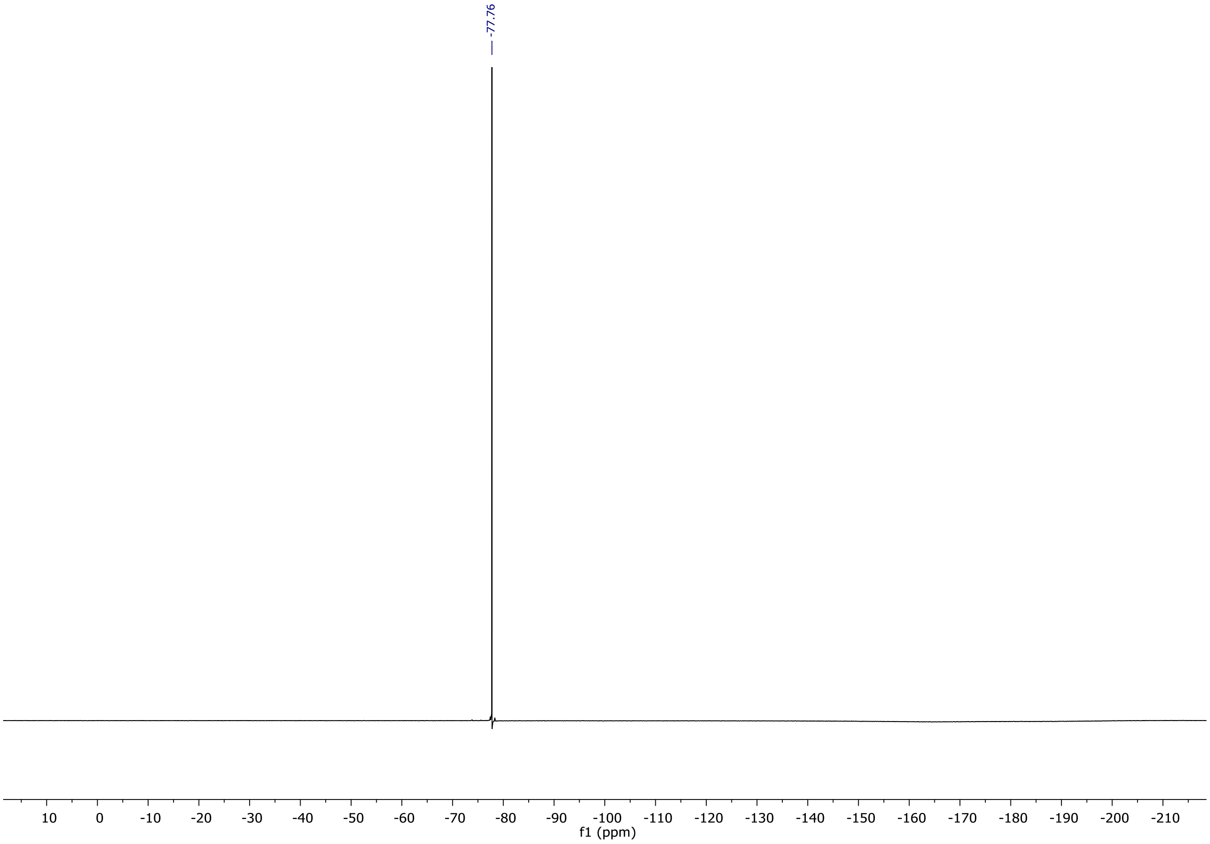
^{1}H-NMR (400 MHz, Chloroform-*d*) (6)



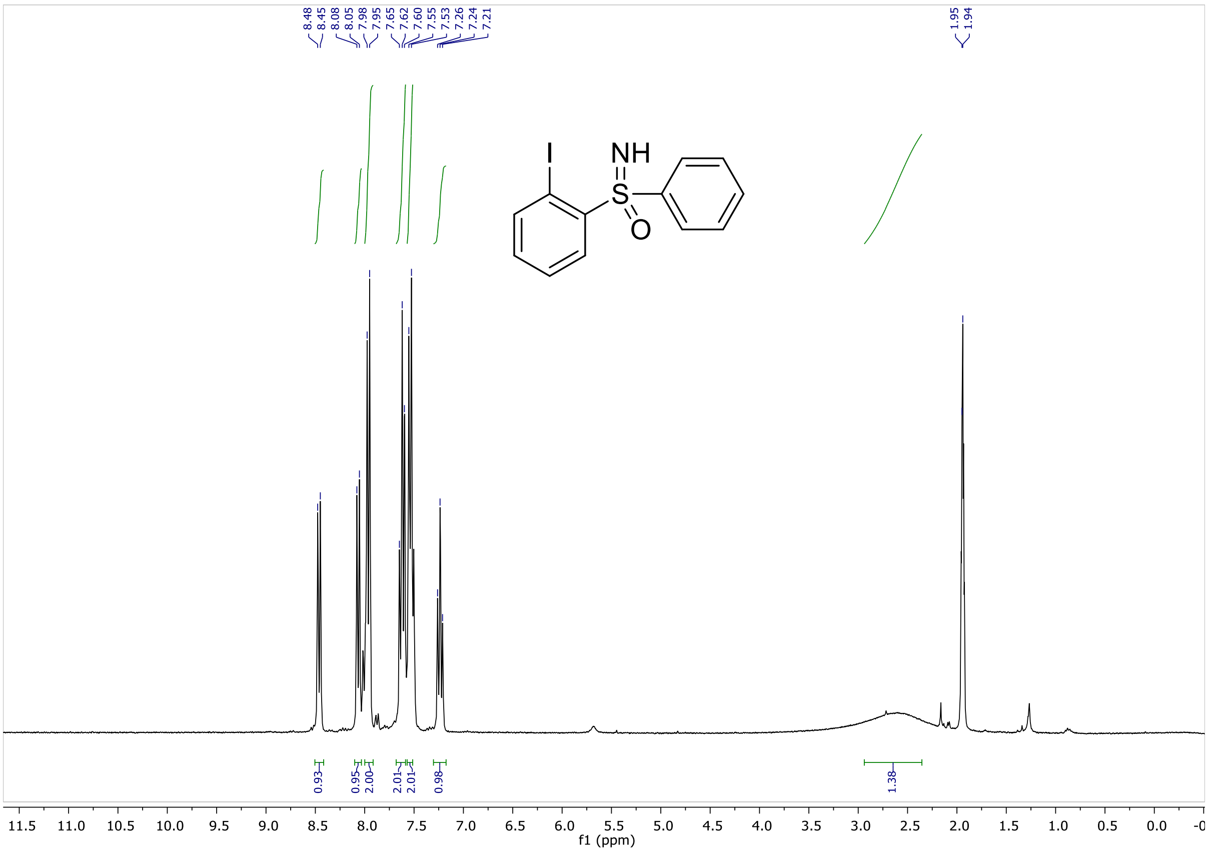
^{13}C-NMR (101 MHz, Chloroform-*d*) (6)



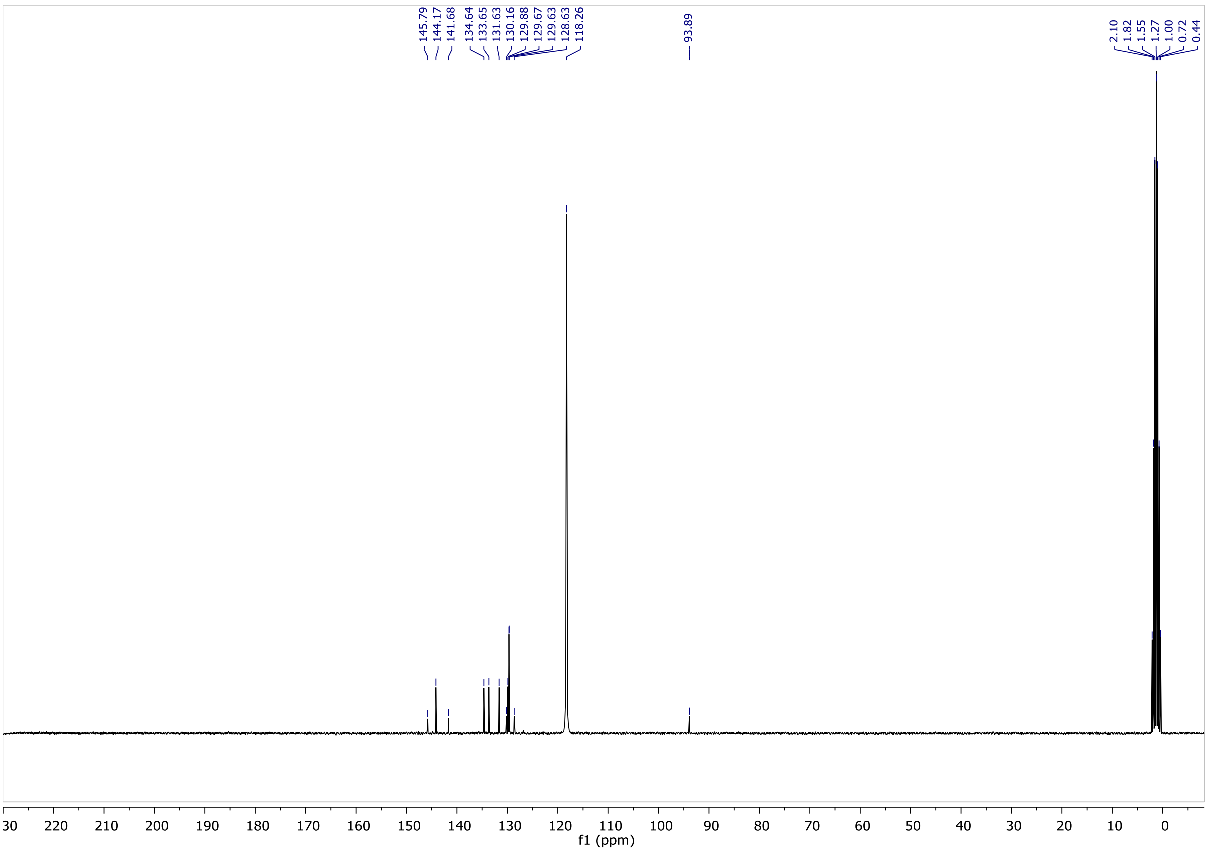
^{19}F-NMR (376 MHz, Chloroform-*d*) (6)



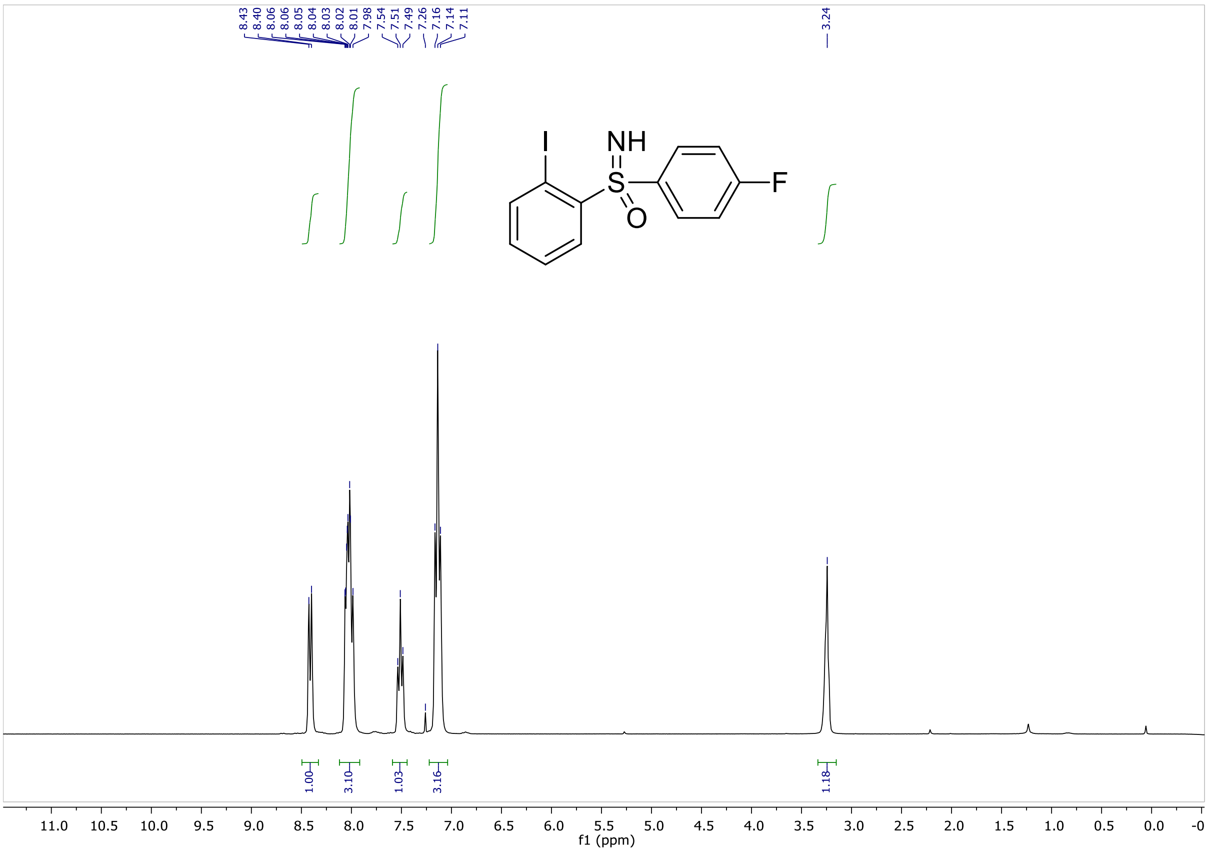
^{1}H-NMR (300 MHz, acetonitrile-*d*$_3$) 17a



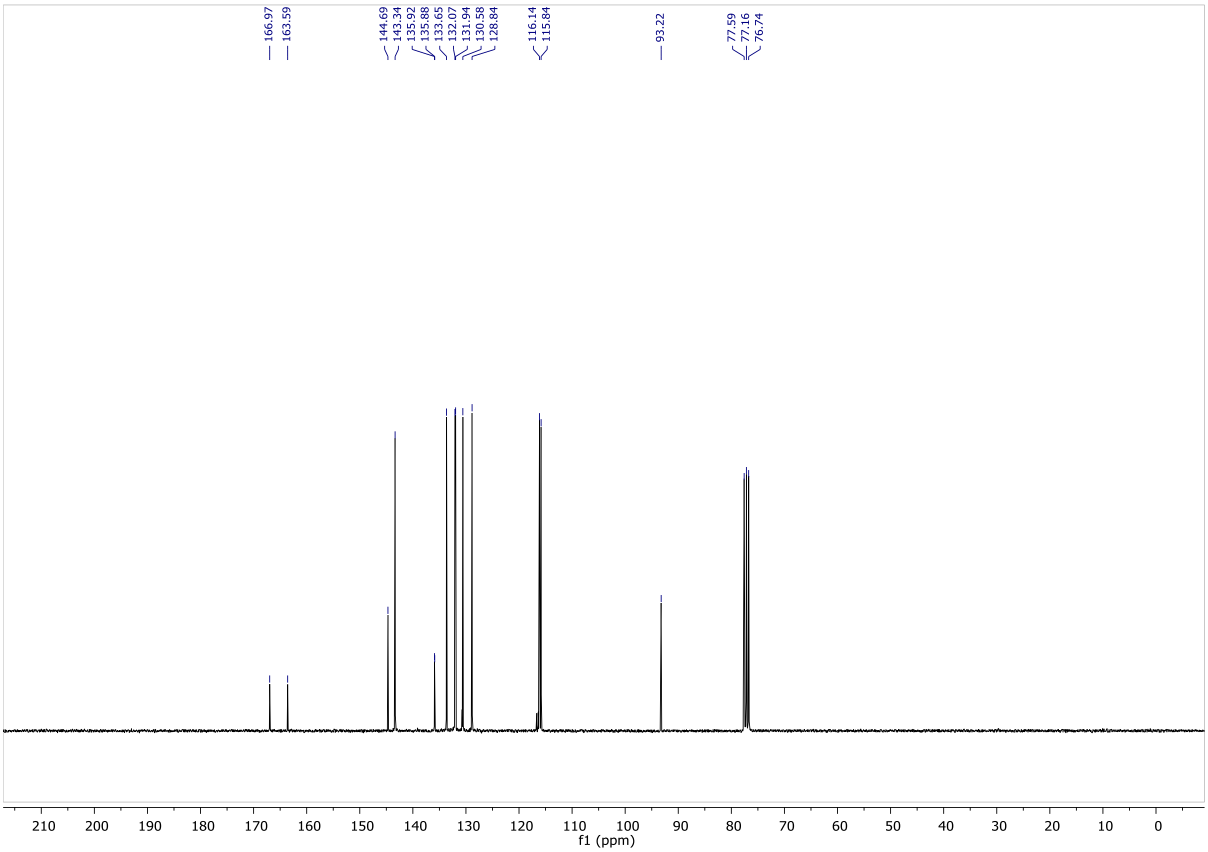
^{13}C-NMR (75 MHz, acetonitrile-*d*$_3$) 17a



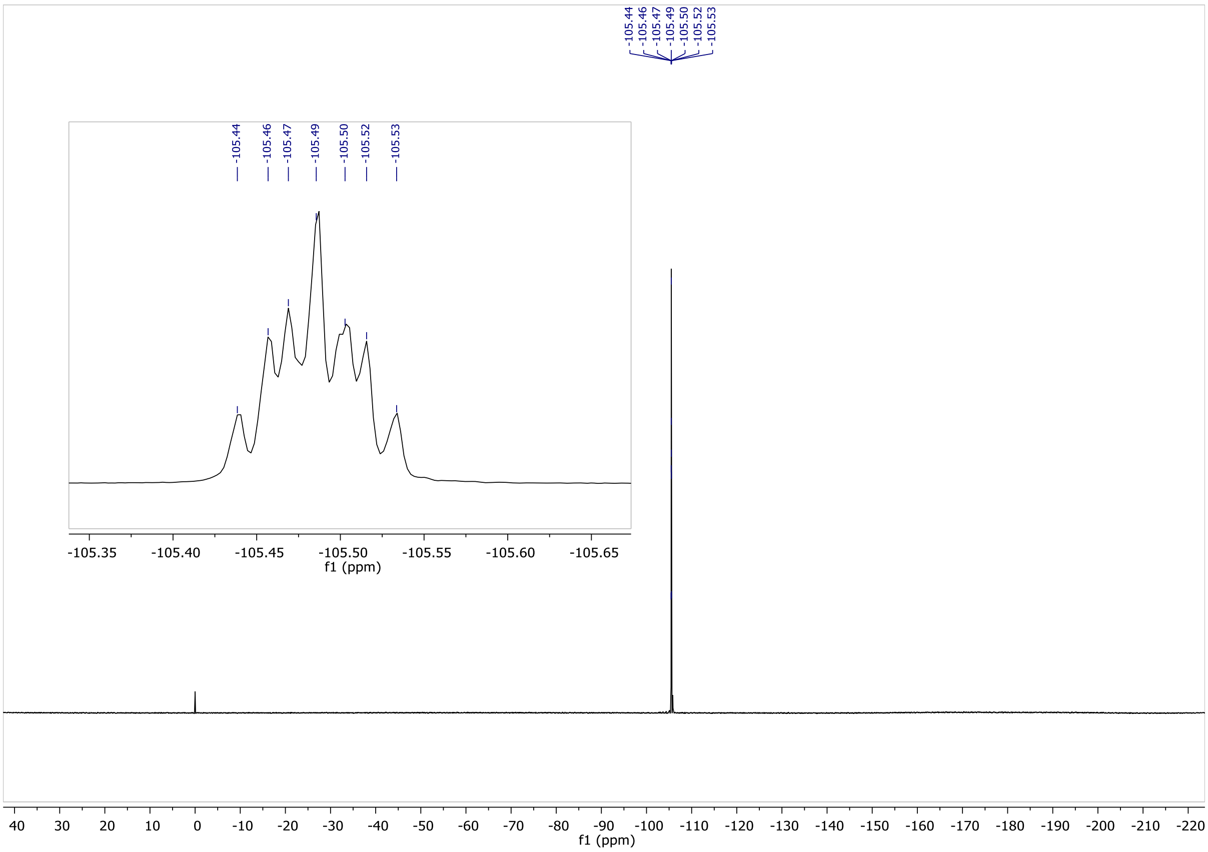
^{1}H-NMR (300 MHz, Chloroform-*d*) 17b



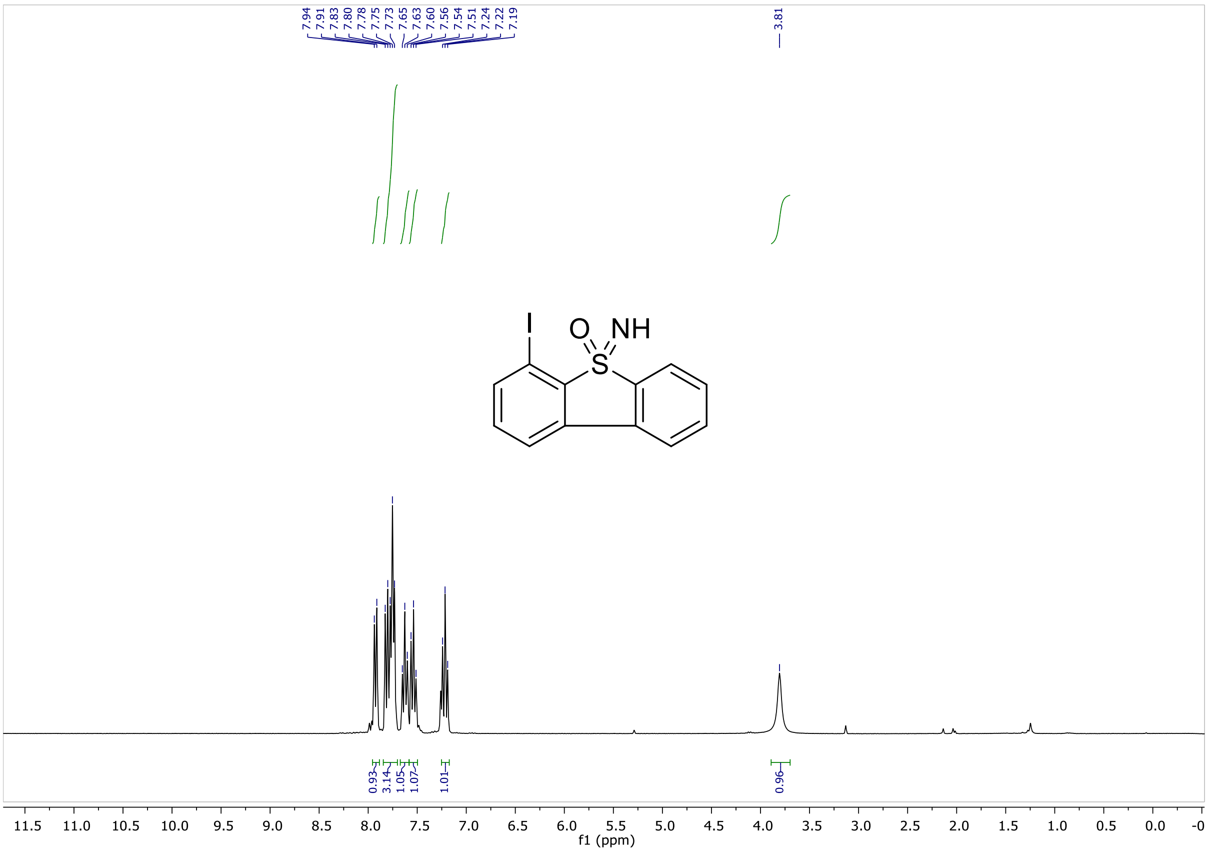
^{13}C-NMR (75 MHz, Chloroform-*d*) 17b



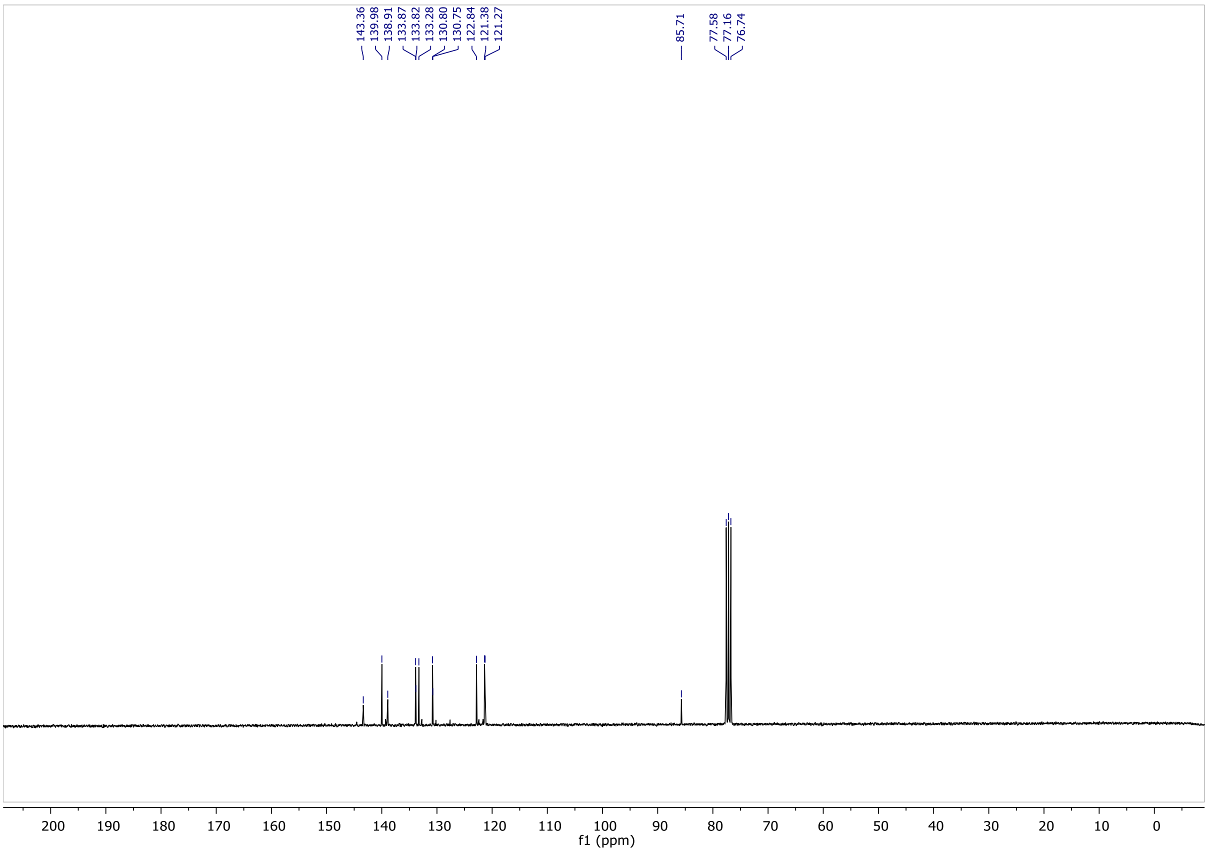
^{19}F-NMR (188 MHz, Chloroform-*d*) 17b



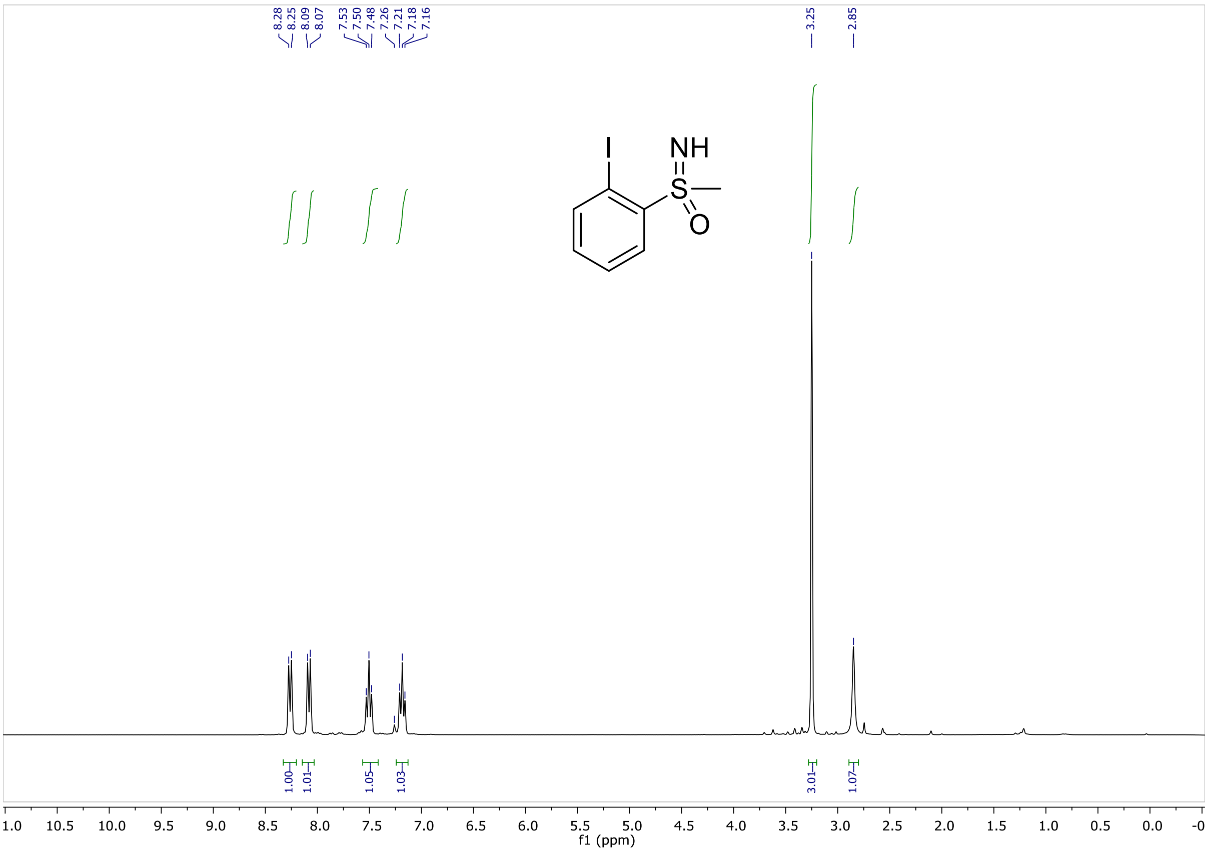
^{1}H-NMR (300 MHz, Chloroform-*d*) 17c



^{13}C-NMR (75 MHz, Chloroform-*d*) 17c



^{1}H-NMR (300 MHz, Chloroform-*d*) 15



^{13}C-NMR (75 MHz, Chloroform-*d*) 15