Structure and Reactivity of N-Heterocyclic Alkynyl Hypervalent Iodine Reagents

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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$_3$CN, toluene and CH$_2$Cl$_2$ were dried by passage over activated alumina under nitrogen atmosphere (H$_2$O 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 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. CFCI$_3$ (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 approximately 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-Iodobenazamide 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\(_2\)O 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).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 8.90 (br s, 4H, \(\text{NH}_2\)), 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-\(d_6\)) \(\delta\) 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-iodobenazamide.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 solution of NaOH (3.7 ml, 3.7 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\(_t\) = 0.3 (Pentane/EtOAc 2:1). Mp: 136-138 °C. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.37 (br s, 1H, H\(\text{NTs}\)), 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=NH), 2.41 (s, 3H, C\(\text{H}_3\)). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 165.1, 143.4, 140.2, 139.9, 134.8, 131.9, 129.5, 128.2, 128.5, 127.1, 92.9, 21.7. IR(\(\nu_{\text{max}}, \text{cm}^{-1}\)) 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\(_{13}\)N\(_2\)NaO\(_2\)S\(_2\) 422.9635; Found 422.9641.

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

\(^1\)S. Dalai, V. N. Belov, S. Nizamov, K. Rauch, D. Finsinger, A. de Meijere, European Journal of Organic Chemistry 2006, 2006, 2753–2765.
\(^2\)T. Yao, Tetrahedron Letters 2015, 56, 4623–4626.
\(^3\)M. Baeten, B. U. W. Maes, Adv. Synth. Catal. 2016, 358, 826–833.
Following a slightly modified procedure, 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 10 mins 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 1 M 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).

Rf = 0.27 (DCM/MeOH 4%). Mp: 185-187 °C. ¹H NMR (400 MHz, Acetonitrile-d₃) δ 9.36 (s, 1H, NH), 7.84 (dd, J = 8.0, 0.7 Hz, 1H, ArH), 7.62 (br s, 4H, ArH), 7.47 (td, J = 7.6, 1.1 Hz, 1H, ArH), 7.36-7.12 (m, 6H), 2.43 (s, 6H, CH₃). ¹³C NMR (101 MHz, Acetonitrile-d₃) δ 161.8, 139.8, 138.6, 132.7, 130.3, 129.8, 128.8, 128.0, 94.1, 21.7. ²IR (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 C₂₁H₂₀IN₂O₄S₂⁺ 554.9904; Found 554.9902.

2-Iodobenzylamine (32)

Following a slightly modified procedure, 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 MgSO₄ 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). ¹H NMR (400 MHz, Chloroform-d) δ 7.82 (d, J = 7.8 Hz, 1H, ArH), 7.42-7.28 (m, 2H, ArH), 6.95 (td, J = 7.7, 1.9 Hz, 1H, ArH), 3.87 (s, 2H, ArCH₂NH₂), 1.64 (s, 2H, NH₂). ¹³C 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.

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 ¹³C in acetonitrile-d₃
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, 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 H2O and brine, dried over MgSO4 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).

1H NMR (400 MHz, Chloroform-d) δ 7.75-7.70 (m, 3H, ArH), 7.32-7.22 (m, 4H, ArH), 6.94 (td, J = 7.6, 1.9 Hz, 1H, ArH), 4.90 (t, J = 6.4 Hz, 1H, NH), 4.18 (d, J = 6.5 Hz, 2H, ArCH2NHTs), 2.41 (s, 3H, CH3).
13C 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.

((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 NaHCO3 (3 × 60 mL). The organic phase is dried over MgSO4, 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).

1H NMR (300 MHz, CDCl3) δ 7.76 (d, J = 7.4 Hz, 2H, ArH), 7.70–7.49 (m, 3H, ArH). 13C NMR (75 MHz, CDCl3) δ 135.6 (q, J = 1.7 Hz), 133.6, 129.6, 125.9, 124.7 (q, J = 335 Hz, CF3). 19F NMR (282 MHz, CDCl3) δ −75.0 (s, 3F).

The characterization data corresponded to the reported values.

(S-(trifluoromethyl)sulfonylimidoyl)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 $-15 \, ^\circ\text{C}$ under argon. Tf$_2$O (52.0 mL, 309 mmol, 1.50 equiv.) is introduced into the dropping-funnel and added dropwise to the solution, keeping the temperature around $-15 \, ^\circ\text{C}$. The solution is then left at $-15 \, ^\circ\text{C}$ 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 NaHCO$_3$ (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 H$_2$O (150 mL), and a saturated solution of Na$_2$S$_2$O$_4$ 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 NaHCO$_3$ (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%).

$^1$H NMR (300 MHz, CDCl$_3$) δ 8.15 (d, $J$ = 7.5 Hz, 2H, ArH), 7.84−7.72 (m, 1H, ArH), 7.63 (s, br s, 1H, NH). $^{13}$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.

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 $-50 \, ^\circ\text{C}$. The reaction mixture was cooled to $-50 \, ^\circ\text{C}$, 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$_4$Cl solution (200 mL). The aqueous layer was extracted with Et$_2$O (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).

$^1$H NMR (300 MHz, CD$_3$CN, 298 K): δ 8.40 (dd, $J$ = 8.1, 1.3 Hz, 1H, ArH), 8.32 (dd, $J$ = 7.9, 0.9 Hz, 1H, ArH), 7.72−7.67 (m, 1H, ArH). $^{13}$C NMR (75 MHz, CD$_3$CN, 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$_3$CN, 298 K): δ $-$75.4.

The characterization data corresponded to the reported values.

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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% |
|----------|-------|-------|
|          |       |       |
Other sulfoximines 15, 17a, 17b and 17c

Sulfides 16a and 16b

Following a reported procedure, a round bottom flask was charged with thiol aryl (1.5 equiv.), 1,2-diiodobenzene (1.0 equiv.), Cs$_2$CO$_3$ (2.0 equiv.), Cul (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.

Sulfoximines 15, 17a, 17b and 17c

Following a reported procedure, 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

\[
\begin{align*}
\text{O=S} & \\
\text{N} & \\
\text{S} & \\
\text{NH} & \\
\end{align*}
\]

$^1$H NMR (300 MHz, CD$_3$CN) 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, NH). $^{13}$C NMR (75 MHz, CD$_3$CN) 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

\[
\begin{align*}
\text{O=S} & \\
\text{N} & \\
\text{S} & \\
\text{NH} & \\
\text{F} & \\
\end{align*}
\]

$^1$H NMR (300 MHz, CDCl$_3$) δ 8.41 (d, $J = 8.0$ Hz, 1H), 8.09 – 7.91 (m, 3H), 7.51 (t, $J = 8.5$ Hz, 3H), 3.24 (s, 1H, NH). $^{13}$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

\[
\begin{align*}
\text{O=S} & \\
\text{N} & \\
\text{S} & \\
\text{NH} & \\
\end{align*}
\]

$^1$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$_{9}$INOS$^+$ 341.9444; Found 341.9456.

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

\[
\begin{align*}
\text{O=S} & \\
\text{N} & \\
\text{S} & \\
\text{NH} & \\
\end{align*}
\]

$^1$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), 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$_{7}$H$_{8}$INOS$^+$ 281.9444; Found 281.9446.
3. Preparation of hypervalent iodine reagents

3-(Tosylimino)-2,3-dihydro-1H-1λ3-benzo[d][1,2]iodazol-1-yl acetate (AcO-H,Ts-BZI, 15)

Following a slightly modified reported procedure,\(^\text{12}\) 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 stirred at room temperature for 1 h. Then the reaction mixture was cooled to 0 °C and triisopropyl((trimethylsilyl)ethynyl)silane (0.36 g, 0.61 mmol, 28% yield). After stirring at rt for 1 h, the reaction mixture was filtered and washed with cold water (4 × 5 mL) and with cold EtO (3 × 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\(_6\)) \(\delta\) 11.97 (s, 1H, NH), 8.00 (d, \(\text{J} = 7.9\) Hz, 1H, Ar\(H\)), 7.86-7.81 (m, 2H, Ar\(H\)), 7.73 (d, \(\text{J} = 8.2\) Hz, 3H, Ar\(H\)), 7.22 (d, \(\text{J} = 8.0\) Hz, 2H, Ar\(H\)), 2.32 (s, 3H, Ar\(CH_3\)). \(^{13}\)C NMR (101 MHz, DMSO-d\(_6\)) \(\delta\) 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), 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\(_{29}\)H\(_{24}\)N\(_2\)O\(_3\)S\(_2\)I\(_2\): 659.9870; Found 659.9854.

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

Following a reported procedure,\(^\text{15}\) 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(trimethysilyl)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).

\(R_t = 0.20\) (DCM/MeOH 1%). Mp > 162 °C (decomposition). \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 8.55 (dd, \(\text{J} = 5.8, 3.2\) Hz, 2H, NH and Ar\(H\)), 8.48-8.41 (m, 1H, Ar\(H\)), 7.86 (d, \(\text{J} = 8.0\) Hz, 2H, Ar\(H\)), 7.71 (q, \(\text{J} = 5.2, 3.5\) Hz, 2H, Ar\(H\)), 7.21 (d, \(\text{J} = 8.0\) Hz, 2H, Ar\(H\)), 2.36 (s, 3H, C\(CH_3\)). \(^{13}\)C NMR (101 MHz, Chloroform-d) \(\delta\) 159.9, 142.0, 141.0, 134.1, 131.3, 134.1, 131.6, 129.2, 127.2, 126.4, 113.8, 110.2, 78.1, 21.6, 18.7, 11.4, IR (vmax, cm\(^{-1}\)) 3292 (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\(_{24}\)N\(_2\)O\(_3\)SSi\(_2\): 581.1149; Found 581.1148.

N-(1-chloro-2-tosyl-1,2-dihydro-3H-1λ3-benzo[d][1,2]iodazol-3-ylidene)-4-methyl-

\(^{12}\) V. V. Zhdankin, R. M. Arbit, B. J. Lynch, P. Kiprof, V. G. Young, \textit{J. Org. Chem.} 1998, 63, 6590–6596.
Following a reported procedure, an oven-dried round-bottom flask equipped with magnetic stirring bar was charged under Ar with solid 2-ido-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, 0.40 mmol, 0.40 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). ¹H NMR (400 MHz, Chloroform-d) δ 9.36 (dd, J = 7.4, 2.1 Hz, 1H, ArH), 8.45-8.36 (m, 1H, ArH), 7.88 (ddd, J = 6.8, 4.6, 1.7 Hz, 2H, ArH), 7.84 (d, J = 8.3 Hz, 2H, ArH), 7.40 (d, J = 8.1 Hz, 2H, ArH), 7.32 (d, J = 8.3 Hz, 2H, ArH), 6.94 (d, J = 8.1 Hz, 2H, ArH), 2.53 (s, 3H, CArH), 2.35 (s, 3H, CH₃). ¹³C 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 (νmax, cm⁻¹) 3086 (w), 1553 (m), 1444 (w), 1303 (m), 1256 (w), 1151 (m), 1082 (m), 1002 (w), 951 (m), 837 (w), 809 (m), 714 (m), 656 (m). Despite many attempts, the mass of the compound was not found by HRMS.

2-Tosyl-3-(tosylimino)-2,3-dihydro-1H-1λ³-benzo[d][1,2]iodazol-1-yl acetate (AcO-Ts-BZI, 20)

Following a reported procedure, an oven-dried round-bottom flask equipped with magnetic stirring bar was charged under N₂ with N-(1-chloro-2-tosyl-1,2-dihydro-3H-1λ³-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). ¹H NMR (400 MHz, Methylene Chloride-d₂) δ 9.28 (dd, J = 8.0, 1.6 Hz, 1H, ArH), 8.14 (dd, J = 8.3, 1.1 Hz, 1H, ArH), 7.87 (td, J = 8.4, 7.9, 1.6 Hz, 1H, ArH), 7.83-7.78 (m, 1H, ArH), 7.75 (d, J = 8.3 Hz, 2H, ArH), 7.41 (d, J = 8.0 Hz, 2H, ArH), 7.33 (d, J = 8.4 Hz, 2H, ArH), 6.97 (d, J = 8.1 Hz, 2H, ArH), 2.53 (s, 3H, ArCH₃), 2.36 (s, 3H, ArCH₃), 2.25 (s, 3H, OCCH₃). ¹³C NMR (101 MHz, Methylene Chloride-d₂) 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 (νmax, cm⁻¹) 3076 (w), 2924 (w), 2751 (w), 1700 (w), 1540 (m), 1447 (w), 1326 (m), 1257 (m), 1209 (m), 1151 (m), 1082 (m), 1002 (w).

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13. V. Matoušek, E. Pietrasik, 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.
Following a reported procedure,\textsuperscript{15} an oven-dried round-bottom flask equipped with a 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)ethyl)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. 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 (4) (0.53 g, 0.72 mmol, 72% yield). IR (vmax, cm\textsuperscript{-1}) 2949 (w), 2866 (w), 1523 (m), 1456 (w), 1351 (w), 1279 (m), 1147 (m), 1079 (m), 955 (w), 832 (m), 727 (s), 663 (s) HRMS (ESI/QTOF) m/z: [M + H]\textsuperscript{+} Calcd for C\textsubscript{32}H\textsubscript{46}N\textsubscript{2}O\textsubscript{2}S\textsubscript{2}Si\textsuperscript{2+} 735.1238; Found 735.1248.

\textbf{2-Tosyl-1-((triisopropylsilyl)ethynyl)-2,3-dihydro-1H-1λ\textsuperscript{3}-benzo[d][1,2]iodazole (TIPS-Ts-EBz, 5)}

Following a slightly modified reported procedure,\textsuperscript{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 mCPBA (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-trimethylsilyl)ethyl)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\textsubscript{3} (3 X 5 mL) and brine (5 mL). The organic layer was dried over MgSO\textsubscript{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\textsubscript{t} = 0.29 (DCM/MeOH 1%). Mp > 133 °C (decomposition). \textsuperscript{1}H NMR (400 MHz, Chloroform-d) \(\delta\) 8.31-8.25 (m, 1H, ArH), 7.78-7.73 (m, 2H, ArH), 7.49 (td, J = 7.3, 1.0 Hz, 1H, ArH), 7.40-7.33 (m, 1H, ArH), 7.25-7.17 (m, 3H, ArH), 4.32 (s, 2H, ArCH\textsubscript{2}N), 2.37 (s, 3H, ArCH\textsubscript{3}), 1.13 (m, 21H, TIPS). \textsuperscript{13}C NMR (101 MHz, Chloroform-d) \(\delta\) 141.7, 139.1, 138.3, 130.8, 130.2, 129.7, 129.4, 128.8, 128.7, 130.8, 130.2, 129.7, 129.4, 128.8, 128.5, 127.9 (X2), 127.2 (X2), 125.6, 114.3, 114.2, 67.8, 20.6 (X2), 17.5, 10.2. IR (vmax, cm\textsuperscript{-1}) 2949 (w), 2866 (w), 1523 (m), 1456 (w), 1351 (w), 1279 (m), 1147 (m), 1079 (s), 945 (w), 845 (m), 690 (s). HRMS (APPI/LTQ-Orbitrap) m/z: [M + H]\textsuperscript{+} Calcd for C\textsubscript{32}H\textsubscript{46}N\textsubscript{2}O\textsubscript{2}S\textsubscript{2}Si\textsuperscript{2+} 6547.6551; Found 6547.6551.

\textsuperscript{15} V. V. Zhdankin, C. J. Kuehl, A. P. Krasutsky, J. T. Bolz, A. J. Simonsen, J. Org. Chem. 1996, 61, 6547–6551.

\textsuperscript{16} D. P. Hari, P. Carabenti, L. Schouwey, M. Chang, S. Nicolai, D. Bachert, T. Wright, C. Orella, J. Waser, Org. Process Res. Dev. 2020, 24, 106–110.
Following a slightly modified reported procedure, in a sealed tube 1-iodo-2-(S- (trifluoromethyl)sulfinylimidoyl)benzene 13 (1.0 g, 3.0 mmol, 1.0 equiv.), p-TsOH (0.57 g, 3.0 mmol, 1.0 equiv.) and mCPBA (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 NaHCO₃ (3 X 5 mL) and brine (5 mL). The organic layer was dried over MgSO₄ 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).

Rᵣ = 0.21 (DCM/MeOH 1%). Mp > 125 °C (decomposition). ¹H NMR (400 MHz, Chloroform-d) δ 8.79-8.74 (m, 1H, ArH), 8.22 (d, J = 7.3 Hz, 1H, ArH), 7.95-7.84 (m, 2H, ArH), 1.15 (m, 21H, TIPS). ¹³C 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. ¹⁹F 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 C₂₅H₃₅INO₂SSi+ 568.1197; Found 568.1202.

For the enantiomer 6 prepared from (-)-13: [α] D° (CHCl₃, c = 0.5, λ = 589 nm): +12

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

| 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
4. Reactivity investigation

Alkynylation of β-ketoesters

Following a reported procedure,\textsuperscript{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 CH₂Br₂ 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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\textsuperscript{17} D. Fernández González, J. P. Brand, R. Mondière, J. Waser, \textit{Advanced Synthesis & Catalysis} \textbf{2013}, 355, 1631–1639.
1H NMR (400 MHz, Chloroform-d) δ 7.83 (d, J = 7.7 Hz, 1H, ArH), 7.70-7.64 (m, 1H, ArH), 7.50 (d, J = 7.7 Hz, 1H, ArH), 7.47-7.41 (m, 1H, ArH), 3.94 (d, J = 17.1 Hz, 1H, ArC2H), 3.80 (s, 3H, OCH3), 3.52 (d, J = 17.1 Hz, 1H, ArC2H), 2.42 (s, 1H, CCH).

The 1H NMR data corresponds to literature data.17

Alkynylation of thiol

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, 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 MgSO4, 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.

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

The 1H NMR data corresponds to literature data.18

Decarboxylative-alkynylation of proline

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(CF3)ppy)2(dtbppy)PF6 (1.1 mg, 1.0 μmol, 0.01 equiv.) under N2. The reaction mixture was again degassed by bubbling N2 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.

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, ArH), 5.17 (s, 2H, OCH$_2$Ph), 4.66-4.52 (m, 1H, CbzNCHCC), 3.63-3.49 (m, 1H, CbzNCH$_2$), 3.48-3.29 (m, 1H, CbzNCH$_2$), 2.24-1.86 (m, 4H, CbzNCH$_2$CH$_2$CH$_2$CH), 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$_{2}$O$_{2}$Si |
| 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   |
|                              | $b = 16.7909(6)$ Å   |
|                              | $c = 13.5441(4)$ Å   |
|                              | $\alpha = 90^\circ$. |
|                              | $\beta = 99.201(3)^\circ$. |
| 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$^3$ |
| $\Theta$ range for data collection | 2.426 to 32.970°. |
| Index ranges                 | -17 ≤ h ≤ 17, -25 ≤ k ≤ 25, -20 ≤ l ≤ 20 |
| Reflections collected        | 15787                 |
| Independent reflections      | 15787                 |
| Completeness to $\theta = 25.242^\circ$ | 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 > 2$\sigma$(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 eÅ⁻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.

| Bond                  | Length/Angle       |
|-----------------------|--------------------|
| 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)           |
| N(1)-C(16)            | 1.892(3)           |
| N(2)-C(7)             | 1.299(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)
| Bond                                      | Angle (°) |
|-------------------------------------------|-----------|
| 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 ($\text{Å}^2 \times 10^3$) for 3. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [ h^2 a^* a^* U^{11} + ... + 2 h k a^* b^* U^{12} ]$

|       | 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)   |
| 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.

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Table 1. Crystal data and structure refinement for 4.

| Identification code | CCDC 2072274 |
|---------------------|--------------|
| Empirical formula   | C₃₂H₃₉N₂O₄S₂Si |
| 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  \(\alpha = 112.064(3)^\circ\). |
|                     | b = 11.8051(3) Å  \(\beta = 98.385(2)^\circ\). |
|                     | c = 14.2418(4) Å  \(\gamma = 105.326(2)^\circ\). |
| Volume              | 1641.46(8) Å³ |
| Z                   | 2             |
| Density (calculated)| 1.487 Mg/m³   |
| Absorption coefficient| 1.178 mm⁻¹   |
| F(000)              | 752           |
| Crystal size        | 0.545 x 0.213 x 0.093 mm³ |
| \(\Theta\) 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 0 = 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 > 2σ(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$$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.

| Bond                  | Length [Å]     |
|-----------------------|----------------|
| 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(1)-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: \(-2\pi^2 h^2 a^* U^{11} + ... + 2 h k a^* b^* U^{12}\)

|     | U\(^{11}\) | U\(^{22}\) | U\(^{33}\) | U\(^{12}\) | U\(^{13}\) | U\(^{23}\) |
|-----|-----------|-----------|-----------|-----------|-----------|-----------|
| 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)     | 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)      |
| 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)     | 24(1)     | 17(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**

| **Identification code** | CCDC 2072275 |
|-------------------------|---------------|
| **Formula** | C_{25}H_{34}INO_{2}SSi |
| **D_{calc} / g cm⁻³** | 1.476 |
| **µ/mm⁻¹** | 11.226 |
| **Formula Weight** | 567.58 |
| **Colour** | clear colourless |
| **Shape** | plate |
| **Size/mm³** | 0.75×0.30×0.07 |
| **T/K** | 100.00(10) |
| **Crystal System** | triclinic |
| **Space Group** | P̅1 |
| **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/Å³** | 31277.18(11) |
| **Z** | 2 |
| **Z'** | 1 |
| **Wavelength/Å** | 1.54184 |
| **Radiation type** | Cu Kα |
| **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_{I} (all data)** | 0.0444 |
| **R_{I}** | 0.0442 |

**Table 1**: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 5. \( U_{eq} \) is defined as 1/3 of the trace of the orthogonalised \( U_{ij} \).
### Table 2: Anisotropic Displacement Parameters (×10^2) for 5. The anisotropic displacement factor exponent takes the form: -2π^2[bhka^* × b^* × U_11 + ... + 2hka^* × b^* × U_12]

| Atom | U_{11}  | U_{22}  | U_{33}  | U_{12}  |
|------|---------|---------|---------|---------|
| I1   | 22.37(16)| 16.17(16)| 21.29(16)| 3.46(9) |
| S1   | 26.1(4) | 18.5(4) | 24.4(4) | 5.9(3) |
| Si1  | 24.4(5) | 22.5(5) | 22.0(4) | 4.8(3) |
| O1   | 25.7(12) | 29.6(13) | 28.5(12) | 5.9(10) |
| O2   | 36.5(14) | 19.7(12) | 32.4(13) | 7.1(10) |
| N1   | 27.8(15) | 16.3(15) | 23.1(14) | 4.4(11) |
| C1   | 22.8(15) | 12.6(14) | 27.5(16) | 3.5(12) |
| C2   | 31.8(18) | 22.9(17) | 23.0(16) | 4.1(13) |
| C3   | 32.6(19) | 22.5(17) | 30.5(17) | 7.4(13) |
| C4   | 28.4(18) | 17.7(17) | 34.3(19) | 4.0(14) |
| C5   | 23.7(17) | 22.6(18) | 32.1(18) | 1.7(13) |
| C6   | 21.2(15) | 15.5(15) | 27.5(16) | 3.2(12) |
| C7   | 26.5(17) | 19.0(16) | 25.9(16) | 3.0(12) |
| C8   | 29.1(17) | 17.4(15) | 24.4(16) | 8.3(12) |
| C9   | 34(2) | 20.7(17) | 34.2(19) | 2.2(14) |
| C10  | 29.5(18) | 18.9(16) | 42(2) | 6.7(14) |
| C11  | 25.8(18) | 26.4(19) | 39(2) | 15.1(15) |
| C12  | 30.8(19) | 35(2) | 26.1(17) | 4.8(14) |
| C13  | 32.3(19) | 24.3(18) | 27.3(17) | 3.2(13) |
| C14  | 27.2(19) | 43(2) | 50(2) | 16.7(19) |
| C15  | 29.9(18) | 21.3(17) | 22.1(16) | 6.7(12) |
| C16  | 23.9(17) | 19.4(16) | 27.2(17) | 5.0(13) |
| C17  | 34.9(19) | 30.7(19) | 23.0(16) | 6.6(14) |
| C18  | 52(3) | 36(2) | 34(2) | 3.4(17) |
| C19  | 34(2) | 47(3) | 51(3) | 13(2) |
| C20  | 30.5(18) | 23.6(17) | 29.2(17) | 3.5(13) |
| C21  | 43(2) | 37(2) | 39(2) | 9.6(17) |
| C22  | 32(2) | 38(2) | 38(2) | 3.3(17) |
| C23  | 27.3(17) | 26.2(18) | 28.3(17) | 1.5(13) |
| C24  | 45(2) | 38(2) | 31(2) | -2.1(16) |
| C25  | 37(2) | 24.3(18) | 38(2) | 0.6(15) |

### Table 3: Bond Lengths in Å for 5.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| I1   | N1   | 2.33(3)  | Si1  | C23  | 1.888(4) |
| I1   | C1   | 2.14(3)  | N1   | C7   | 1.456(5) |
| I1   | C15  | 2.101(4) | C1   | C2   | 1.389(5) |
| S1   | O1   | 1.445(3) | C1   | C6   | 1.388(5) |
| S1   | O2   | 1.450(3) | C2   | C3   | 1.391(5) |
| S1   | N1   | 1.588(3) | C3   | C4   | 1.381(6) |
| S1   | C8   | 1.763(4) | C4   | C5   | 1.381(6) |
| Si1  | C16  | 1.858(4) | C5   | C6   | 1.399(5) |
| Si1  | C17  | 1.889(4) | C6   | C7   | 1.505(5) |
| Si1  | C20  | 1.885(4) | 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) |

| Atom | Atom | Length/Å |
|------|------|----------|
| 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) |

**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) |
| C9   | C8   | 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 | 3099.04| 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$_{4}$N$_{4}$O$_{5}$S$_{4}$Si$_{4}$

**$D_{calc}$/ g cm$^{-3}$**

1.610

**$\mu$/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)

**$\alpha^o$**

90

**$\beta^o$**

90

**$\gamma^o$**

90

**$V$/Å$^3$**

8577.97(14)

**Z**

4

**Z’**

0.5

**Wavelength/Å**

0.71073

**Radiation type**

Mo $K\alpha$

**$\Theta_{min}$/$^o$**

2.539

**$\Theta_{max}$/$^o$**

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

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**Table 7:** Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2\times10^3$) 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     | Ueq  |
|------|-------|-------|-------|------|
| 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) |
| I1   | 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) | 5919.1(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(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) | 6868.6(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: -2π²[α^a*α^a* × U11*+ ... +2hkα^a* × b^* × U12]
### Table 9: Bond Lengths in Å for 6.

| Atom | Atom | Length/Å |
|------|------|----------|
| C15  | N1   | 2.330(2) |
| C16  | C1   | 2.138(3) |
| C17  | C8   | 2.093(3) |
| S1   | O1   | 1.446(2) |
| S1   | N1   | 1.483(2) |
| S1   | C2   | 1.768(3) |
| S1   | C7   | 1.863(3) |
| S1   | C9   | 1.863(3) |
| S1   | C10  | 1.893(3) |
| S1   | C13  | 1.883(3) |
| S1   | C16  | 1.881(3) |
| F1   | C7   | 1.331(3) |
| F2   | C7   | 1.327(3) |
| F3   | C7   | 1.327(3) |
| C1   | C2   | 1.378(4) |
| C1   | C6   | 1.380(4) |
| C2   | C3   | 1.402(4) |
| C3   | C4   | 1.386(4) |
| C4   | C5   | 1.387(5) |
| C5   | C6   | 1.397(4) |
| C8   | C9   | 1.196(4) |
| C10  | C11  | 1.530(4) |
| C10  | C12  | 1.531(4) |
| C13  | C14  | 1.530(5) |
| C13  | C15  | 1.534(4) |
| C16  | C17  | 1.526(4) |
| C16  | C18  | 1.543(4) |

| Atom | Atom | Length/Å |
|------|------|----------|
| C15  | N2   | 2.337(2) |
| C16  | C19  | 2.129(3) |
| C17  | C26  | 2.090(3) |
| S1   | O2   | 1.445(2) |
| S1   | N2   | 1.482(2) |
| S1   | C20  | 1.775(3) |
| S1   | C25  | 1.863(3) |
| S1   | C27  | 1.859(3) |
| S1   | C28  | 1.883(3) |
| S1   | C31  | 1.886(3) |
| S1   | C34  | 1.883(3) |
| F1   | C5   | 1.326(3) |
| F2   | C25  | 1.328(3) |
| F3   | C25  | 1.330(3) |
| C1   | C20  | 1.382(4) |
| C2   | C21  | 1.395(4) |
| C3   | C22  | 1.385(4) |
| C4   | C23  | 1.391(5) |
| C5   | C24  | 1.389(4) |
| C8   | C27  | 1.205(4) |
| C10  | C29  | 1.542(4) |
| C10  | C30  | 1.523(4) |
| C13  | C32  | 1.541(4) |
| C13  | C33  | 1.538(4) |
| C16  | C35  | 1.538(4) |
| C16  | 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) |
| S1   | N1   | H   | 112.93(12) |
| C2   | C1   | H   | 116.33(18) |
| C2   | C1   | C6   | 121.8(3) |
| C6   | C1   | H   | 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   | G6   | 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) |
| 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) |
| Atom | Atom | Atom | Angle/° |
| 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   | C1   | C6   | C5   | 1.6(4) |
| C2   | C1   | C12  | C11  | 162.8(2) |
| C2   | C1   | C13  | C12  | 73.9(3) |
| C2   | C1   | C13  | C15  | 160.7(2) |
| C2   | C16  | C17  | C18  | -64.9(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) |
| C10  | Si1  | C10  | C11  | 162.8(2) |
| C10  | Si1  | C10  | C12  | -79.8(2) |
| C10  | Si1  | C16  | C17  | 179.9(2) |
| C10  | Si1  | C16  | C18  | -55.7(2) |
| C10  | Si1  | C10  | C11  | -80.7(2) |
| C10  | Si1  | C10  | C12  | 46.3(3) |
| C16  | Si1  | C13  | C14  | 53.2(2) |
| C16  | Si1  | C13  | C15  | -172.3(3) |
| C16  | Si1  | C13  | C15  | -46.9(3) |
| I2   | C19  | C20  | S2   | 4.2(3) |
| I2   | C19  | C20  | C21  | -179.6(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  | 0.5(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) |
| C28  | Si2  | C31  | C35  | 160.2(2) |
| C28  | Si2  | C31  | C36  | -75.6(3) |
| C28  | Si2  | C31  | C32  | -49.7(2) |
| C28  | Si2  | C31  | C33  | 77.7(2) |
| C27  | Si2  | C34  | C35  | 43.8(3) |
| C27  | 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 \( U_{ij} \).
### 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<sup>1</sup> | 0.82(4)  | 2.18(4)  | 3.001(3) | 172(4)    |

<sup>1</sup>-x,1-y,+

**Table:**

| Atom | x     | y     | z     | U<sub>eq</sub> |
|------|-------|-------|-------|---------------|
| 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)        |
6. DFT calculations and coordinates

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

\textsuperscript{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. \textit{Theor. Chem. Acc.} \textbf{2008}, \textit{120}, 215–241. (b) Zhao, Y.; Truhlar, D. G. Density Functionals with Broad Applicability in Chemistry. \textit{Acc. Chem. Res.} \textbf{2008}, \textit{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. \textit{Phys. Chem. Chem. Phys.} \textbf{2005}, \textit{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. \textit{Gaussian09, Revision D.01}; Gaussian, Inc.: Wallingford CT, 2016.

\textsuperscript{21} Dennington, R.; Keith, T. A.; Millam, J. M. \textit{GaussView 5.0.9}; Semichem Inc.: Shawnee Mission, KS, 2009.
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**

| 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\(_{22}\) | -0.001 |
| 5     | TIPS-EBX\(_{21}\) | +0.005 |
| 6     | TIPS-Ts-EBZI 4   | +0.003 |

| 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 | -2.760208 | 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
| Atom | X  | Y  | Z   |
|------|----|----|-----|
| 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**

| Atom | X  | Y  | Z   |
|------|----|----|-----|
| I    | 0.377718  | -0.323211  | -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  -0.907061   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-CF₃-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
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
|    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**
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-\textit{d}) (4)

$^{13}$C-NMR (101 MHz, chloroform-\textit{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
$^{19}\text{F-NMR (188 MHz, Chloroform-d)}$ 17b
$^1$H-NMR (300 MHz, Chloroform-<i>d</i>) 17c

$^{13}$C-NMR (75 MHz, Chloroform-<i>d</i>) 17c
$^1$H-NMR (300 MHz, Chloroform-$d$) 15

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