**Supplementary Material**

1. **Cyclic Voltammetric (CV) kinetic studies**
   
   1.1 General information ................................................................. 3
   
   1.2 Experimental details ...................................................................... 3
   
   1.3 Data analysis .................................................................................. 3
   
   1.4 General procedure A – Determination of the rate constant of bismuth(III)-acetylide – copper(I) complex formation ................................................................. 4
   
   1.5 General procedure B – Determination of the apparent rate constant of the bismuth(III) triazolide[X] formation ................................................................. 7
      
      1.5.1 Determination of reaction rate parameters .............................................. 11
      
      1.5.2 Derivatization of the catalyst concentration at the equilibrium ([cat]eq.).................. 15
      
      1.5.3 Standard deviations ........................................................................ 15

2. **^1^H NMR kinetic reactivity studies** .......................................................... 17
   
   2.1 General information ........................................................................ 17
   
   2.2 Experimental details ........................................................................ 17
   
   2.3 Data analysis .................................................................................... 17
   
   2.4 General procedure C – Independent bismuth(III)-acetylide reactivity experiments ..... 18
      
      2.4.1 Determination of reaction rate parameters .............................................. 21
   
   2.5 General procedure D - Rate orders experiments ........................................ 24
   
   2.6 Dynamic NMR spectroscopy .............................................................. 30
   
   2.7 General Procedure E - Protoalkyne/ bismuth(III) acetylide competitive experiments .. 32
   
   2.8 Moisture compatibility experiments...................................................... 34
   
   2.9 General procedure F – catalyst robustness experiments ........................... 35

3. **Synthesis and characterization of bismuth(III)-acetylides and 5-bismuth-1,2,3-triazolides**
   
   3.1 General Procedure 1. Synthesis of diphenyl sulfides ..................................... 39
   
   3.2 General Procedure 2. Synthesis of sulfonyldibenzenes ................................ 43
   
   3.3 General Procedure 3. Synthesis of 10-phenyl-10H-dibenzo[b,e][1,4]thiabismine 5,5- diooxides ................................................................. 48
   
   3.4 General Procedure 4. Synthesis of 10-iodo-10H-dibenzo[b,e][1,4]thiabismine 5,5- diooxides ................................................................. 53

S1
3.5 General Procedure 5. Synthesis of bismuth(III) acetylides with a diphenyl sulfone scaffold ................................................................. 58
3.6 General Procedure 6. Synthesis of 5-bismuth(III) triazolides................................. 68
4. 4. X-Ray Crystallographic Details ........................................................................ 74
5. 5. $^1$H, $^{13}$C and $^{19}$F NMR Spectra .................................................................... 131
6. 6. References ........................................................................................................ 175
1. **Cyclic Voltammetric (CV) kinetic studies**

1.1 **General information**

Anhydrous DMSO was purchased from MilliporeSigma and used without further purification. Copper(I) trifluoromethanesulfonate toluene complex (≥99.7%) was purchased from Sigma-Aldrich.

1.2 **Experimental details**

All glassware was oven-dried (140°C) and purged by vacuum-N₂ cycles in the antechamber of the glovebox before use. All electrochemical measurements were performed inside a glovebox under a nitrogen atmosphere. Anhydrous DMSO served as the solvent. A 3-electrode glass cell with a glassy carbon working electrode (BASi, MF-2012), copper foil as the counter and reference electrodes, and copper(I) triflate in anhydrous DMSO) was used for the measurements.

Electrochemical data was collected on a multi-channel potentiostat (AMETEK Scientific Instruments, VersaSTAT 4). Voltammogram at a scan rate of 100 mV s⁻¹ was performed on the copper compound between -0.3 V and 0.8 V vs. Cu⁺/Cu⁰.

¹H NMR spectra were obtained on a Varian 600 MHz. Chemical shifts were reported in ppm referenced at 2.5 ppm of DMSO-d₆ solvent.

1.3 **Data analysis**

Kinetic cyclic voltammetry measurements were processed as current versus time dependences. Graphical interpretation of processed experimental data was performed in Origin 9.0 data analysis and graphing software package (OriginLab Corporation) or Microsoft Excel 2016.
1.4 General procedure A – Determination of the rate constant of
bismuth(III)-acetylide – copper(I) complex formation

Independent reactivity experiments: Stock solutions of the corresponding bismuth(III) acetylides (0.075 M), and copper(I) triflate (0.016 M) was prepared in anhydrous DMSO. 0.5 mL of the copper(I) triflate toluene complex stock solution and 6.0 mL of DMSO were transferred into the 3-electrode cell, agitated, and used to performed cyclic voltammetry studies of three redox cycles (to ensure reproducibility of the data and the stability of copper(I) triflate complex).

Kinetic CV measurements were recorded in the same 3-electrode cell with a glassy carbon working electrode, copper foils as counter, and reference electrodes. A solution of the bismuth(III) acetylide[ X] stock solution in anhydrous DMSO (0.5 mL) was introduced into the electrochemical cell and agitated for some time before the start of the electrochemistry data acquisition. Continuous electrochemical data collection at 100 mV s⁻¹ was performed until no further changes in the redox cycles were observed.
**Table S1.** Reactions conditions of experiments following general procedure A.

| Entry | A[X], mM | AX, µmol | [cat], mM | cat, µmol | T, °C |
|-------|---------|----------|-----------|-----------|-------|
| 1     | [1], 5.35 | [1], 37.5 |           |           |       |
| 2     | [2], 5.35 | [2], 37.5 |           |           |       |
| 3     | [3], 5.35 | [3], 37.5 | 1.16      | 8.12      | 28.0  |
| 4     | [4], 5.35 | [4], 37.5 |           |           |       |
| 5     | [5], 5.35 | [5], 37.5 |           |           |       |
| 6     | [6], 5.35 | [6], 37.5 |           |           |       |
Figure S1. Kinetic profiles A-F of the cyclic voltammograms were obtained by following general procedure A.
1.5 **General procedure B – Determination of the apparent rate constant of the bismuth(III) triazolide[X] formation**

Kinetic CV experiments were recorded in a 3-electrode cell with a glassy carbon working electrode, copper foils as counter and reference electrodes. A solution of the (2-azidoethyl)benzene (0.135M) in anhydrous DMSO (0.5 mL) was introduced to an electrochemical cell with already preformed π-intermediate (general procedure A). The mixture was agitated for some time before the start of the electrochemistry data acquisition. Continuous electrochemical data collection at 100 mV s$^{-1}$ was performed until no further changes in the redox cycles were observed. Electrochemical measurements were recorded at 100 mV s$^{-1}$ between −0.3 V and 0.8 V vs. Cu$^+$/Cu. An aliquot sample was taken and analyzed by $^1$H NMR to confirm the conversion rate of the reaction.
Table S2. Reactions conditions of experiments following general procedure B.

| Entry | A[X], mM | AX, μmol | [Z], mM | Z, μmol | [cat], mM | cat, μmol | [ex], mM | ex, μmol | T, °C |
|-------|----------|-----------|---------|---------|-----------|-----------|---------|---------|-------|
| 1     | [1], 5.0 | [1], 37.5 | 9.0     | 67.5    |           |           |         |         |       |
| 2     | [2], 5.0 | [2], 37.5 | 9.0     | 67.5    |           |           |         |         |       |
| 3     | [3], 5.0 | [3], 37.5 | 9.0     | 67.5    |           | 1.08      | 8.12    | 4.0     | 30.0  |
| 4     | [4], 5.0 | [4], 37.5 | 9.0     | 67.5    |           |           |         |         |       |
| 5     | [5], 5.0 | [5], 37.5 | 9.0     | 67.5    |           |           |         |         |       |
| 6     | [6], 5.0 | [6], 37.5 | 9.0     | 67.5    |           |           |         |         |       |
**Figure S2.** Kinetic profiles A-F of the cyclic voltammograms were obtained by following general procedure B.
Figure S3. Final cyclic voltammograms A-F were obtained after the kinetic studies by following general procedures A and B.
1.5.1 Determination of reaction rate parameters

The development and validation of the theoretical kinetic model of the catalytic reaction were achieved using self-developed program (C++).

Rate of [1]

Kinetic data was obtained following general procedures A and B using 10-((4-methoxyphenyl)ethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (bismuth(III) acetylide[1]). The equilibrium rate constant of the [A·cat] complex formation was calculated as a quotient of the forward (k_A) and reverse (k_A') rate constants. Following Eq. S4 and Eq. 6: k_A = 2.39 (M⁻¹ sec⁻¹), k_A' = 2.81E-3(sec⁻¹), [cat]_eq. = 24.32E-5(M).

![Figure S3a](image)

*Figure S3a.* Concentration and current changes of the Cu⁺/Co⁰ redox pair for the General Procedure A. Table S1, entry 1.

Rate of [2]

Kinetic data was obtained following general procedures A and B using 10-((4-(tert-butyl)phenyl)ethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (bismuth(III) acetylide[2]). The equilibrium rate constant of the [A·cat] complex formation was calculated as a quotient of the forward (k_A) and reverse (k_A') rate constants. Following Eq. S4 and Eq. 6: k_A = 1.95 (M⁻¹ sec⁻¹), k_A' =1.39E-3(sec⁻¹), [cat]_eq. = 16.32E-5(M).
**Rate of [3]**

Kinetic data was obtained following general procedures A and B using 10-(p-tolylethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (bismuth(III) acetylide[3]). The equilibrium rate constant of the [A·cat] complex formation was calculated as a quotient of the forward (k_A) and reverse (k_A^-1) rate constants. Following Eq.S4 from Eq. 6: k_A = 2.80 (M⁻¹ sec⁻¹), k_A^-1 = 3.97E-3 (sec⁻¹), [cat]_eq = 27.97E-5 (M).

**Figure S3b.** Concentration and current changes of the Cu⁺/Co⁰ redox pair for the General Procedure A. Table S1, entry 2.

**Figure S3c.** Concentration and current changes of the Cu⁺/Co⁰ redox pair for the General Procedure A. Table S1, entry 3.
**Rate of [4]**

Kinetic data was obtained following general procedures A and B using 10-(phenylethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (bismuth(III) acetylide[4]). The equilibrium rate constant of the [A·cat] complex formation was calculated as a quotient of the forward ($k_A$) and reverse ($k_{-A}$) rate constants. Following Eq.S4, from Eq.6: $k_A = 3.44 \, (M^{-1} \, sec^{-1})$, $k_{-A} = 3.73E-3 \, (sec^{-1})$, $[\text{cat}]_{eq.} = 22.88E-5 \, (M)$.

**Figure S3d.** Concentration and current changes of the Cu$^+$/Co$^0$ redox pair for the General Procedure A. Table S1, entry 4.

**Rate of [5]**

Kinetic data was obtained following general procedures A and B using 10-((4-bromophenyl)ethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (bismuth(III) acetylide[5]). The equilibrium rate constant of the [A·cat] complex formation was calculated as a quotient of the forward ($k_A$) and reverse ($k_{-A}$) rate constants. Following Eq.S4, from Eq.6: $k_A = 4.97 \, (M^{-1} \, sec^{-1})$, $k_{-A} = 3.65E-3 \, (sec^{-1})$, $[\text{cat}]_{eq.} = 16.75E-5 \, (M)$. 
**Figure S3e.** Concentration and current changes of the Cu$^+/Co^0$ redox pair for the General Procedure A. Table S1, entry 5.

**Rate of [6]**

Kinetic data was obtained following general procedures A and B using 10-((4-bromophenyl)ethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (bismuth(III) acetylde[6]). The equilibrium rate constant of the \([A\cdot\text{cat}]\) complex formation was calculated as a quotient of the forward \((k_A)\) and reverse \((k_A^-)\) rate constants. Following Eq.S4, from Eq.6: \(k_A = 4.36 \text{ (M}^{-1} \text{ sec}^{-1})\), \(k_A^- = 6.15 \text{E-3(}\text{sec}^{-1})\), \([\text{cat}]_{eq} = 27.83\text{E-4(M)}\).

**Figure S3f.** Concentration and current changes of the Cu$^+/Co^0$ redox pair for the General Procedure A. Table S1, entry 6.
1.5.2 Derivatization of the catalyst concentration at the equilibrium ([cat]eq.)

When reaching equilibrium conditions (General Procedure A):

\[
\frac{d[\text{cat}]}{dt} = 0 \quad \text{(Eq.S1)}
\]

From Eq. (2) at the equilibrium conditions:

\[
\frac{d[\text{cat}]}{dt} = 0 = -k_A([A]_0 - [\text{cat}]_0 + [\text{cat}]) + k_{-A}([\text{cat}]_0 - [\text{cat}]) \quad \text{(Eq.S2)}
\]

The equilibrium concentration \([\text{cat}]_{\text{eq}}\) can be determined as a solution to the following quadratic expression:

\[
k_A[\text{cat}]_{\text{eq}}^2 + (k_{-A} + k_A([A]_0 - [\text{cat}]_0))[\text{cat}]_{\text{eq}} - k_{-A}[\text{cat}]_0 = 0 \quad \text{(Eq.S3)}
\]

The positive value solution for the equilibrium concentration \([\text{cat}]_{\text{eq}}\) is defined as:

\[
[\text{cat}]_{\text{eq}} = -\frac{1}{2}\left(\frac{k_{-A}}{k_A} + [A]_0 - [\text{cat}]_0\right) + \frac{1}{4}\left(\frac{k_{-A}}{k_A} + [A]_0 - [\text{cat}]_0\right)^2 + \frac{k_{-A}}{k_A}[\text{cat}]_0^{1/2} \quad \text{(Eq.S4)}
\]

1.5.3 Standard deviations

The standard deviations were calculated for each sample taking into account a 0.01 mL volume error when dissolving and the \(5 \cdot 10^{-5}\) g accuracy of the balance weighing.

Table S3a. Standard deviations for initial concentrations \([\text{cat}]_0\) and \([A]_0\).

| Entry | \([\text{cat}]_0 \cdot 10^{-3}\text{M}\) | \(\sigma([\text{cat}]_0) \cdot 10^{-5}\text{M}\) | \([A]_0 \cdot 10^{-3}\text{M}\) | \(\sigma([A]_0) \cdot 10^{-5}\text{M}\) |
|-------|----------------------------------|----------------------------------|-----------------|----------------------------------|
| [1], \(R = \text{OMe}\) | 1.16 | 1.80 | 5.35 | 5.50 |
| [2], \(R = \text{tBu}\) | | | | 5.48 |
| [3], \(R = \text{Me}\) | | | | 5.51 |
| [4], \(R = \text{H}\) | | | | 5.52 |
| [5], \(R = \text{Br}\) | | | | 5.47 |
| [6], \(R = \text{CF}_3\) | | | | 5.48 |
The estimation of the standard deviations for the rate parameters $k_A$, $k_A$, $K_A$, and $[\text{cat}]_{\text{eq}}$ derived from electrochemical experimental data was done following the reported procedure by Alper et al.. Thus, the repetitive model simulations have been accomplished using Monte Carlo generated noise consisting of normal-distributed values with zero mean and appropriate variance determined by standard deviations for $[\text{cat}]_0$, $[A]_0$. The Box-Muller method was applied to obtain Gaussian-distributed values.

**Table S3b.** Best fit parameter values $k_A$, $k_A$, $K_A$, and $[\text{cat}]_{\text{eq}}$ and their standart deviations $\sigma(k_A)$, $\sigma(k_A)$, $\sigma(K_A)$ and $\sigma([\text{cat}]_{\text{eq}})$. The confidence intervals should be taken as $2 \times \sigma$ to satisfy the 95% level of confidence.

| Entry | $k_A$ M$^{-1}$ sec$^{-1}$ | $\sigma(k_A)$ M$^{-1}$ sec$^{-1}$ | $k_A \cdot 10^3$ sec$^{-1}$ | $\sigma(k_A) \cdot 10^3$ sec$^{-1}$ | $K_A \cdot 10^5$ M$^{-1}$ | $\sigma(K_A) \cdot 10^5$ M$^{-1}$ | $[\text{cat}]_{\text{eq}} \cdot 10^4$ M | $\sigma([\text{cat}]_{\text{eq}}) \cdot 10^4$ M |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| [1], R = OMe | 2.39 | 0.0598 | 2.81 | 0.009 | 0.85 | 0.0215 | 24.32 | 0.033 |
| [2], R = tBu | 1.95 | 0.0415 | 1.39 | 0.007 | 1.40 | 0.0344 | 16.32 | 0.020 |
| [3], R = Me | 2.80 | 0.0754 | 3.97 | 0.012 | 0.70 | 0.0189 | 27.97 | 0.016 |
| [4], R = H | 3.44 | 0.0749 | 3.73 | 0.019 | 0.92 | 0.0240 | 22.88 | 0.015 |
| [5], R = Br | 4.97 | 0.0923 | 3.65 | 0.025 | 1.36 | 0.0337 | 16.75 | 0.016 |
| [6], R = CF$_3$ | 4.36 | 0.0965 | 6.15 | 0.031 | 0.71 | 0.0190 | 27.83 | 0.013 |
2. **¹H NMR kinetic reactivity studies**

2.1 **General information**

DMSO-d6 was purchased in ampules from Cambridge Isotope Laboratories, Inc., opened inside a glovebox, and stored over molecular sieves. Copper(I) trifluoromethanesulfonate toluene complex (≥99.7%) was purchased from Sigma-Aldrich. 1,4-dimethoxybenzene and 1,2,3,4,5,6-hexamethyl benzene were obtained from commercial sources (Sigma-Aldrich).

2.2 **Experimental details**

Kinetic experiments were carried out in 5mm thin wall precision NMR tubes (7”, 600 MHz, 535-PP-7, Wilmad LabGlass). All glassware was oven-dried (140 C) and purged by three vacuum-N₂ cycles in the antechamber of the glovebox before use. Stock solutions of corresponding bismuth(III) acetylides, (2-azidoethyl)benzene, and copper(I) trifluoromethanesulfonate toluene complex were prepared using 1 mL volumetric flasks volume and stored in LCMS-capped vials for the duration of one batch of experiments. ¹H NMR spectra were recorded on a Varian VNMRS-600 spectrometer. Chemical shifts are reported in ppm referenced to the residual peak of DMSO-d₅ at 2.5 ppm.

2.3 **Data analysis**

For manipulation and analysis of the NMR data and signal peak integration, MestReNova (Version 9.0.0, Mestrelab Research S.L.) was used. The substrates rate orders from the excess experiments were derived in the frames of the first kinetic regime (initial rates).
2.4 General procedure C – Independent bismuth(III)-acetylide reactivity experiments

For independent reactivity experiments: Stock solutions for the corresponding bismuth(III) acetylides (0.100 M), (2-azidoethyl)benzene (0.688 M), 1,4-dimethoxybenzene (internal standard) (54 mM) and copper(I) triflate (20 mM) were prepared in DMSO-d6. Of these stock solutions: 200 μL of the alkyne, 50 μL of the azide, and 50 μL of the reference stock solutions were transferred to an NMR tube and diluted with 450 μL of DMSO-d6 capped with a gas-tight rubber NMR septum and agitated. Lastly, 50 μL of the copper(I) trifluoromethanesulfonate toluene complex catalyst solution was added to the NMR tube and immediately agitated. The total volume in the NMR tube for one experiment was 800 μL.

Kinetic NMR measurements were recorded on a Varian VNMRS-600 spectrometer. The sample spinning rate was 20 Hz. 1H-NMR data were collected with the following acquisition parameters: 1 transient (scans), 5 sec. relaxation delay time, acquisition time of 5.824 sec. Between the spectra was a 1 sec pre-acquisition delay. Data was collected at 60.0°C. The temperature was calibrated against a temperature standard (ethylene glycol). Each experiment was performed twice. All reagents were dried before use. All manipulations were performed in the dry nitrogen atmosphere of a glove box. Reaction conversions were integrated relative to an internal reference standard.
**Table S4.** Comparison of acetylene group C(1)≡C(2) IR stretching vibration frequencies of the derivatized bismuth(III) acetylides.

| Bismuth(III)-acetylde | IR* (v[cm⁻¹]) | Bismuth(III)-acetylde | IR* (v[cm⁻¹]) |
|-----------------------|---------------|-----------------------|---------------|
| para-phenyl substituted bismuth(III)acetylides | | | |
| [1], R = OMe          | 2099          | [2], R = ‘Bu          | 2108          |
| [3], R = Me           | 2099          | [4], R = H            | 2111          |
| [5], R = Br           | 2105          | [6], R = CF₃          | 2114          |
| diphenylsulfone substituted bismuth(III)acetylides | | | |
| [7], R’ = CF₃         | 2045          | [8], R’ = Cl          | 2098          |
| [9], R’ = OMe         | 2107          | [10], R’ = OMe, OMe   | 2051          |

* FT-IR spectra were taken in the mid-infrared (MIR) range of 400–4000 cm⁻¹ using attenuated total reflectance (ATR).*
Table S5 Reactions conditions of experiments following general procedure C. Independent bismuth(III)-acetylide reactivity experiment.

| Entry | A [X], mM | [Z], mM | [cat], mM | [ref], mM | [ex], mM | Time (avg), sec | T, °C | Conv, % |
|-------|-----------|---------|-----------|-----------|--------|-----------------|-------|---------|
| 1     | [1], 25   | 43      |           |           |        | 14400           | 60    | 100.0   |
| 2     | [2], 25   | 43      |           |           |        | 9300            | 60    | 100.0   |
| 3     | [3], 25   | 43      |           |           |        | 1350            | 60    | 100.0   |
| 4     | [4], 25   | 43      | 1.25      | 3.375     | 18     | 2100            | 60    | 100.0   |
| 5     | [5], 25   | 43      |           |           |        | 22200           |       | 94.6    |
| 6     | [6], 25   | 43      |           |           |        | 1510            |       | 100.0   |
2.4.1 Determination of reaction rate parameters

Rate of [1]
Kinetic data was obtained by following general procedure C; using 10-((4-methoxyphenyl)ethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (bismuth(III) acetylide[1]). The rate constant $k = 1.19E-5(0.70E-7)$ was derived as the slope of the initial rate curve.

![Figure S4a](image)

Figure S4a. Concentration in substrates [A] and [Z] and the product [P] for the General Procedure C. Table S4, entry 1.

Rate of [2]
Kinetic data was obtained by following general procedure C; using 10-((4-(tert-butyl)phenyl)ethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (bismuth(III) acetylide[2]). The rate constant $k=0.81E-5$ (0.63E-7) was derived as the slope of the initial rate curve.
Figure S4b. Concentration in substrates [A] and [Z] and the product [P] for the General Procedure C. Table S4, entry 2.

Rate of [3]

Kinetic data was obtained by following general procedure C; using 10-\(p\)-tolylethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (bismuth(III) acetylide[3]). The rate constant \(k=2.31\times10^{-5}\) (1.53E-7) was derived as the slope of the initial rate curve.

Figure S4c. Concentration in substrates [A] and [Z] and the product [P] for the General Procedure C. Table 4, entry 3.

Rate of [4]

Kinetic data was obtained by following general procedure C; using 10-(phenylethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (bismuth(III) acetylide[4]). The rate constant \(k=2.24\times10^{-5}\) (1.47E-7) was derived as the slope of the initial rate curve.
Figure S4d. Concentration in substrates [A] and [Z] and the product [P] for the General Procedure C. Table S4, entry 4.

Rate of [5]

Kinetic data was obtained by following general procedure C; using 10-((4-bromophenyl)ethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (bismuth(III) acetylide[5]). The rate constant $k=0.34\times10^{-5}$ ($0.17E{-7}$) was derived as the slope of the initial rate curve.

Figure S4e. Concentration in substrates [A] and [Z] and the product [P] for the General Procedure C. Table S4, entry 5.

Rate of [6]

Kinetic data was obtained by following general procedure C; using 10-((4-bromophenyl)ethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (bismuth(III) acetylide[6]). The rate constant $k=1.43\times10^{-5}$ ($0.70E{-7}$) was derived as the slope of the initial rate curve.
Figure S4f. Concentration in substrates [A] and [Z] and the product [P] for the General Procedure C. Table S4, entry 6.

2.5 General procedure D - Rate orders experiments

Evaluation of 1-bismuth(III) acetylide component rate order: Stock solutions of (2-azidoethyl)benzene (0.6 M), of bismuth(III) acetylide[2], 1,2,3,4,5,6-hexamethylbenzene (0.230 M, as internal standard) and copper(I) triflate (0.300 M) were prepared in DMSO-d6. Of these stock solutions: x μL of the bismuth(III) acetylide, 200 μL of azide, 50 μL of reference stock solution were solutions were transferred to an NMR tube and diluted with (150+180+200-x) μL of DMSO-d6 agitated and closed with a gas-tight rubber NMR septum. Lastly, 20 μL of the copper(I) trifluoromethanesulfonate toluene complex catalyst solution was added to the NMR tube and immediately agitated. The total volume in the NMR tube for one experiment was 800 μL.

Kinetic NMR measurements were recorded on a Varian VNMRS-600 spectrometer. The sample spinning rate was 20 Hz. 1H-NMR data were collected with the following acquisition parameters: 3 transients (scans), 5 sec. relaxation delay time, acquisition time of 2.7263 sec. Between the spectra was a 1 sec pre-acquisition delay. Data was collected at 69.0˚C. The temperature was calibrated against a temperature standard (ethylene glycol). Each experiment was performed twice. All reagents were dried before use. All manipulations were performed in the dry nitrogen
atmosphere of a glove box. Reaction conversions were integrated relative to an internal reference standard.
Table S6. Reactions conditions of experiments following general procedure D. Variable [Alkyne] concentration experiment. Kinetic profiles are shown in Figure S5.

| Entry | A[2], M | [Z], M | [cat], mM | [excess], M | Time (avg), sec | Conv, % |
|-------|---------|--------|-----------|-------------|----------------|---------|
| 1     | 0.063   | 0.150  |           | 0.087       | 3300           | 100.0   |
| 2     | 0.096   | 0.150  |           | 0.054       | 6400           | 100.0   |
| 3     | 0.126   | 0.150  | 7.5       | 0.024       | 16000          | 100.0   |
| 4     | 0.160   | 0.150  |           | -0.10       | 30000          | 100.0   |
| 5     | 0.181   | 0.150  |           | -0.31       | 45000          | 100.0   |
Figure S5. Kinetic profiles of reactions studied following general procedure D.
**Figure S5a.** Substrate rate order kinetic study performed following general procedure D. Method of initial rates. (A-E) Product P[2] concentration vs. time.
Figure S5b. Substrate rate order kinetic study performed following general procedure D. Method of initial rates. LN(rate) vs. LN([A]).
2.6 Dynamic NMR spectroscopy

The experiment was performed by recording \(^1\)H-NMR of one identical sample at different temperatures. No quantitative interpretation of the changes in the spectra was performed. Bismuth(III) triazolide [2] in DMF-d7 was chosen as a representative sample. A restricted rotation around the C(sp\(^2\))-Bi bond was confirmed by the variability of resonances for slow, intermediate, and fast exchange regions. At low temperatures all aromatic protons of the diphenyl sulfone unit exhibit different unique chemical shifts. As the temperature gradually raises, a similar observation was made for the two methylene groups of the ‘azido’ fragment. Close to room temperature these signals are broad and overlapping. The existence of two structural isomers is supported by the fact of two characteristic singlets representing the ‘Bu substituent.
**Figure S6.** $^1$H NMR signal coalescence/decoalescence demonstrate intermolecular processes of bond rotations as a function of temperature for 5-bismuth(III) triazole[2].
2.7 General Procedure E - Protoalkyne/ bismuth(III) acetylide competitive experiments

Evaluation of catalytic activity in the presence of terminal acetylenes: Stock solutions of the corresponding bismuth(III) acetylides (60 mM), terminal alkyne (60 mM), (2-azidoethyl)benzene (60 mM), 1,4-dimethoxybenzene (12 mM, internal standard) and copper(I) triflate (5.0 mM) were prepared in DMSO-d6. Of these stock solutions: 200 μL of bismuth(III)-acetylide, 200 μL of terminal alkyne, and 50 μL of reference the stock solutions were transferred into an NMR tube, diluted with 300 μL of DMSO-d6 agitated and closed with a gas-tight rubber NMR septum. Lastly, 50 μL of the copper(I) trifluoromethanesulfonate toluene complex catalyst solution was added to the NMR tube and immediately agitated. The total volume in the NMR tube for one experiment was 800 μL.

Kinetic NMR measurements were recorded on a Varian VNMRS-600 spectrometer. The sample spinning rate was 20 Hz. ¹H-NMR data were collected with the following acquisition parameters: 1 transient (scan), 5 sec. relaxation delay time, acquisition time of 5.824 sec. Between the spectra was a 1 sec pre-acquisition delay. Data was collected at 27.0°C. After about 1 hour of data acquisition, the temperature was raised to 69.0°C. After which 200 μL of the (2-azidoethyl)benzene stock solution were injected and immediately agitated. The total volume inside the NMR tube experiment increased to 1 mL. Temperatures were calibrated against a temperature standard (ethylene glycol). Each experiment was performed twice. All reagents were dried before use. All manipulations were performed in the dry nitrogen atmosphere of a glove box. Reaction conversions were integrated relative to an internal reference standard.
Table S7. Reactions conditions of experiments following general procedure E. Kinetic profiles are shown in Figure S7.

| Entry | [A][X], mM | [A][Y], M | [Z], M | [cat], mM | yield A, % |
|-------|------------|-----------|--------|-----------|------------|
| 1     | [-Br], 12  | [-H], 12  |        |           | 100.0      |
| 2     | [-H], 12   | [-Br], 12 | 12     | 0.250     | 58.33      |
| 3     | [-Me], 12  | [-H], 12  |        |           | 100.0      |
| 4     | [-H], 12   | [-Me], 12 |        |           | 100.0      |

Figure S7. Kinetic profiles of reactions studied following general procedure E.
2.8 Moisture compatibility experiments

Table S8. Moisture compatibility experiment. Reaction conditions of experiments following general procedure C.

| №  | A [6], mM | [Z], mM | [cat], mM | Water, % | [Ref], mM | Time, sec | T, °C | Conv, % |
|----|-----------|---------|-----------|----------|-----------|-----------|------|--------|
| 1  | 25        | 43      | 1.25      | 2% H₂O   | 3.375     | 1509      | 60   | 100.0  |
| 2  |           |         |           | 12% H₂O  |           | 1685      |      | 100.0  |

Figure S8. Kinetic profiles of reactions studied following general procedure C. (A) Conversion profiles of reactions (Table S7), entries 1 and 2; (B) dry and (C) ‘wet’ DMSO-d6 as solvent.
2.9 General procedure F – catalyst robustness experiments

Evaluation of catalyst rate order: Stock solutions of bismuth(III)-acetylide[4] (60 mM), of 2-azidoethylbenzene (60 mM), 1,4-dimethoxybenzene (25 mM) and copper(I) triflate (6.2 mM) were prepared in DMSO-d6. Of these stock solutions: 160 μL of bismuth(III)-acetylide, 200 μL of azide, 100 μL of reference stock solution transferred to an NMR tube, diluted with 240 μL (entry 1) or 140 μL (entry 2) of pure DMSO-d6 agitated and closed with a gas-tight rubber NMR septum. Lastly, 100 μL (entry 1) or 200 μL (entry 2) of the copper(I) trifluoromethanesulfonate toluene complex catalyst solution was added to the NMR tube and immediately agitated. The total volume in the NMR tube for one experiment was 800 μL.

Kinetic NMR measurements were recorded on a Varian VNMRS-600 spectrometer. The sample spinning rate was 20 Hz. $^1$H-NMR data were collected with the following acquisition parameters: 2 transients (scans), 5 sec. relaxation delay time, acquisition time of 5.824 sec. Between the spectra was a 1 sec pre-acquisition delay. Data was collected either collected at 60.0°C. The temperature was calibrated against a temperature standard (ethylene glycol). Each experiment was performed twice. All reagents were dried before use. All manipulations were performed in the dry nitrogen atmosphere of a glove box. Reaction conversions were integrated relative to an internal reference standard.

Table S9. Catalyst robustness experiments. Reactions conditions of the experiments following general procedure F.

| Entry | A [4], M | [Z], M | [cat], mM | [Ref], mM | [excess], M | Time (averaged), sec | T, °C | Conv, % |
|-------|----------|--------|-----------|-----------|-------------|----------------------|-------|---------|
| 1     | 0.012    | 0.015  | 0.775     | 3.1       | 0.003       | 4436                 | 60    | 100.0   |

S35
Figure S9. Kinetic profiles for experiments performed following general procedure F. (A) [cat]=0.775 mM; (B) [cat]=1.550 mM, (C) rate/[cat] vs. [Z].
3. Synthesis and characterization of bismuth(III)-acetylides and 5-bismuth-1,2,3-triazolides

All reactions were carried out under a nitrogen atmosphere with dry solvents ensuring anhydrous reaction conditions unless otherwise stated. Dry tetrahydrofuran (THF), acetone, diethyl ether (Et₂O), and methylene chloride (CH₂Cl₂) were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Chemical reagents were purchased at the highest commercially available purity and used without further purification unless otherwise stated. Copper(I) iodide (98% purity), bismuth(III) bromide (98% purity), copper(I) trifluoromethanesulfonate toluene complex (90% technical grade) were purchased from Sigma-Aldrich. Triphenyl bismuth (99+% purity) and 3-chloroperbenzoic acid (<77% purity) were purchased from Alfa Aesar. Anhydrous potassium carbonate and ethylene glycol were purchased from Fischer Scientific. LCMS grade 2-propanol, hexane, and ethyl acetate were purchased from Fischer Scientific and used directly without drying or degassing. Aryl thiols and aryl halides were used as received and without additional purification. Silica gel (230-400 mesh) was purchased from Merck. Reactions progress was monitored both by thin-layer chromatography (TLC) on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as a visualizing agent and by Agilent LC/MSD as well as Agilent HPLC/DAD spectrometer. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. NMR spectra were recorded on Varian Mercury 400, Varian VNMRS-500, or Varian VNMRS-600 spectrometer. Chemical shifts were referenced to residual solvent signals (Chloroform-d: δH = 7.26 ppm, δC = 77.16 ppm) as an internal reference. ¹⁹F NMR spectra were externally referenced to 80% CFCl₃ in chloroform-d. The following abbreviations were used to describe NMR signal multiplicities: s = singlet, d =
doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, b = broad. Infrared spectra were recorded in the range 4000-400 cm\(^{-1}\) on Bruker Alpha spectrometer using a diamond ATR unit. IR intensities are described as vw (very weak), w (weak), m (medium), s (strong), vs (very strong). X-ray crystallographic analysis was performed at UCSD on a Bruker Apex II Ultra2 CCD diffractometer equipped with Mo K\(\alpha\) radiation (crystallographic details for all structures are given in section 4). ORTEP drawings were prepared using the Mercury CSD program.\(^3\) Further crystallographic details can be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the deposition no CCDC 2124668-2124680. Yields refer to chromatographically and spectroscopically (\(^1\)H NMR) pure materials unless otherwise is stated.
3.1 General Procedure 1. Synthesis of diphenyl sulfides

Adapted from a procedure of S. L. Buchwald and co-workers⁴.

(4-methoxyphenyl)(phenyl) sulfide 1. A dry 12-mL screw-capped glass vial sealed with rubber septum was purged with dry nitrogen, equipped with a magnetic stirring bar, and charged with copper(I) iodide (70.0 mg, 0.35 mmol), potassium carbonate (1.95 g, 14.0 mmol), and 1-iodo-4-methoxybenzene (1.30 g, 7.0 mmol). The vial and its contents were exposed to three vacuum-nitrogen cycles. Subsequently, 2-propanol (7.0 mL) and ethylene glycol (0.77 mL) were added together with the 4-methoxybenzenethiol (0.77 mg, 7.0 mmol) with a syringe. The stirred reaction mixture was heated up to 80°C and kept at this temperature overnight. The reaction mixture was allowed to cool to room temperature, filtered, and concentrated to give yellow liquid, which was purified by flashed column chromatography to yield a pale-yellow liquid as a product (yield: 0.65 g, 43 %). NMR characterization data were consistent with those previously reported⁵.

phenyl(p-tolyl) sulfide. Synthesized from 4-methylbenzenethiol (0.87 g, 7.0 mmol) and iodobenzene (1.43 g, 7.0 mmol) following general procedure 1, 1.08 g, 77 %, overnight, colorless liquid. NMR characterization data is consistent with those previously reported⁵.
**(4-chlorophenyl)(phenyl) sulfide.** Synthesized from benzenethiol (0.77 g, 7.0 mmol) and 1-chloro-4-iodobenzene (1.97 g, 7.0 mmol) using the general procedure 1, 1.5 g, 97 %, overnight, colorless liquid. NMR characterization data is consistent with those previously reported⁶.

**phenyl(4-(trifluoromethyl)phenyl) sulfide.** Synthesized from benzenethiol (0.77 g, 7.0 mmol) and 1-iodo-4-(trifluoromethyl)benzene (1.90 g, 7.0 mmol) following general procedure 1, 0.88 g, 50 %, overnight, colorless liquid:

IR (υ[cm⁻¹]) 3089 (vw), 3050 (vw), 2921 (vw), 1926 (vw), 1602 (m), 1582 (m), 1568 (w), 1496 (vw), 1477 (m), 1440 (m), 1401 (m), 1320 (s), 1189 (w), 1161 (s), 1127 (s), 1106 (vs), 1094 (vs), 1061 (vs), 1024 (m), 1011 (s), 997 (m), 959 (m), 908 (m), 833 (vs), 778 (w), 743 (vs), 727 (s), 695 (s), 687 (s), 631 (m), 615 (w), 592 (m), 522 (m), 494 (m), 480 (s), 435 (m), 403 (w).

¹H NMR (500 MHz, Chloroform-d) δ 7.50 – 7.46 (m, 4H), 7.42 – 7.36 (m, 3H), 7.28 (d, J = 0.9 Hz, 2H).
$^{13}$C NMR (126 MHz, Chloroform-d) δ 142.97, 133.68, 132.65, 129.82, 128.66, 128.18 (q, J = 32.5 Hz), 125.95 (q, J = 3.8 Hz), 124.37 (q, J = 273.7 Hz).

$^{19}$F NMR (470 MHz, Chloroform-d) δ -62.51.

(4-methoxyphenyl)(4-(trifluoromethyl)phenyl) sulfide. Synthesized from 4-methoxybenzenethiol (0.98 g, 7.0 mmol) and 1-iodo-4-(trifluoromethyl)benzene (1.90 g, 7.0 mmol) following general procedure 1, 1.20 g, 60 %, overnight, colorless liquid:

IR (υ[cm$^{-1}$]) 3086 (vw), 3029 (w), 2973 (w), 2948 (w), 2846 (w), 2084 (vw), 2054 (vw), 1923 (w), 1670 (vw), 1601 (m), 1588 (m), 1569 (m), 1490 (m), 1466 (m), 1451 (m), 1441 (m), 1400 (m), 1356 (vw), 1327 (s), 1288 (m), 1252 (m), 1189 (m), 1165 (s), 1107 (vs), 1082 (vs), 1060 (s), 1030 (s), 1009 (s), 957 (m), 830 (vs), 811 (s), 799 (m), 776 (m), 724 (m), 699 (m), 644 (m), 627 (m), 590 (m), 532 (m), 505 (m), 492 (m), 430 (m).

$^{1}$H NMR (500 MHz, Chloroform-d) δ 7.47 (d, J = 8.9 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 6.96 (d, J = 8.9 Hz, 2H), 3.85 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 160.77, 144.97, 136.85, 127.35 (q, J = 32.7 Hz), 126.55, 125.77 (q, J = 3.8 Hz), 124.32 (q, J = 271.7 Hz), 121.82, 115.52, 55.57.

$^{19}$F NMR (470 MHz, Chloroform-d) δ -62.39.
**bis(4-(trifluoromethyl)phenyl) sulfide.** Synthesized from 4-(trifluoromethyl)benzenethiol (0.89 g, 5.0 mmol) and 1-iodo-4-(trifluoromethyl)benzene (1.36 g, 5.0 mmol) following general procedure 1, 1.21 g, 75 %, overnight, colorless solid:

![](image)

IR (υ[cm⁻¹]) 3094 (vw), 3063 (vw), 2924 (vw), 1604 (m), 1574 (w), 1496 (w), 1401 (m), 1318 (vs), 1162 (s), 1119 (vs), 1103 (vs), 1082 (s), 1060 (vs), 1012 (s), 951 (w), 824 (s), 778 (m), 724 (w), 699 (m), 632 (w), 590 (m), 515 (m), 486 (m), 414 (w).

$^1$H NMR (500 MHz, Chloroform-d) δ 7.60 (d, J = 8.2 Hz, 1H), 7.46 (d, J = 8.5 Hz, 1H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 139.68, 131.17, 129.85 (q, J = 32.8 Hz), 126.42 (q, J = 3.8 Hz), 124.06 (q, J = 272.0 Hz).

$^{19}$F NMR (470 MHz, Chloroform-d) δ -62.77.
3.2 General Procedure 2. Synthesis of sulfonyldibenzenes

Adapted from a procedure of J. Thomas and co-workers\(^7\).

**1-methoxy-4-(phenylsulfonyl)benzene.** To a 50 mL round-bottom flask equipped with a magnetic stir bar, 1.00 g (4.62 mmol, 1.00 eq.) of (4-methoxyphenyl)(phenyl) sulfide in 25 mL of reagent grade DCM were added. To the clear solution, 5.56 g (46.2 mmol, 10.0 eq.) of anhydrous MgSO\(_4\) were added followed by the slow addition of 2.40 g of m-CPBA (oxidizing reagent) (13.86 mmol, 3.00 eq.). The reaction mixture was stirred at room temperature for 8 hours. Complete conversion of starting material was ensured monitoring of the reaction progress by TLC (hexane, Rf(product)=0.5, Rf (reagent)=0.4). The reaction mixture was transferred to a 250 mL separatory funnel and washed with sat. NaHCO\(_3\) (2×40 mL) to ensure complete removal of any residual m-CPBA. The organic phase was dried over MgSO\(_4\), filtered, and concentrated in vacuo to yield a pale yellow oil. The crude material was purified by flash column chromatography using hexane as eluent to give 1-methoxy-4-(phenylsulfonyl)benzene as a pale yellow solid (0.70 g, 98% yield).
IR (υ[cm⁻¹]) 3076 (w), 2847 (w), 2655 (w), 2595 (w), 2550 (w), 1689 (m), 1591 (m), 1574 (m), 1497 (m), 1468 (w), 1446 (m), 1416 (m), 1298 (s), 1261 (s), 1192 (w), 1183 (w), 1148 (s), 1105 (s), 1071 (m), 1018 (m), 997 (m), 914 (m), 897 (m), 850 (m), 833 (m), 803 (m), 748 (s), 730 (s), 719 (s), 711 (m), 687 (m), 667 (m), 656 (m), 627 (m), 575 (s), 554 (vs), 493 (m), 451 (w), 416 (w).

¹H NMR (500 MHz, Chloroform-d) δ 7.92 (d, J = 8.3 Hz, 2H), 7.88 (d, J = 8.2 Hz, 2H), 7.56 – 7.51 (m, 1H), 7.48 (t, J = 7.5 Hz, 2H), 6.96 (d, J = 9.0 Hz, 2H), 3.84 (s, 3H).

¹³C NMR (126 MHz, Chloroform-d) δ 163.51, 142.52, 133.28, 132.96, 130.04, 129.33, 127.46, 114.65, 55.79.

1-chloro-4-(phenylsulfonyl)benzene. Synthesized from (4-chlorophenyl)(phenyl) sulfide (0.80 g, 3.60 mmol) following general procedure 2, 0.91 g, 98%, 4 hours, colorless solid. NMR characterization data is consistent with those previously reported⁸.

IR (υ[cm⁻¹]) 3091 (w), 3068 (w), 2956 (w), 2923 (w), 2853 (w), 1693 (m), 1596 (w), 1576 (m), 1474 (m), 1446 (m), 1417 (w), 1390 (m), 1319 (m), 1308 (s), 1279 (m), 1263 (m), 1176 (w), 1152 (s), 1106 (m), 1084 (s), 1069 (s), 1049 (m), 1026 (m), 1011 (m), 998 (m), 953 (w), 932 (w), 897 (w), 851 (w), 833 (m), 823 (m), 765 (m), 747 (vs), 718 (s), 700 (m), 685 (s), 653 (w), 608 (vs), 564 (vs), 521 (m), 496 (s), 486 (m), 467 (m), 435 (m).
1-(phenylsulfonyl)-4-(trifluoromethyl)benzene. Synthesized from phenyl(4-(trifluoromethyl)phenyl) sulfide (0.88 g, 3.40 mmol) following general procedure 2, 0.89 g, 91%, 4 hours, colorless solid.

IR (υ[cm⁻¹]) 3108 (vw), 3090 (vw), 3063 (vw), 1608 (vw), 1583 (vw), 1500 (vw), 1477 (vw), 1446 (w), 1404 (m), 1317 (s), 1296 (m), 1145 (s), 1106 (s), 1071 (s), 1058 (s), 1017 (m), 998 (m), 978 (w), 967 (w), 928 (w), 846 (m), 839 (m), 787 (m), 758 (m), 742 (m), 720 (s), 700 (s), 684 (s), 593 (vs), 557 (s), 497 (w), 480 (w), 456 (w), 421 (m).

¹H NMR (500 MHz, Chloroform-d) δ 8.07 (d, J = 8.2 Hz, 2H), 7.96 (d, J = 7.6 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 7.63 – 7.56 (m, 1H), 7.53 (t, J = 7.6 Hz, 2H).

¹³C NMR (126 MHz, Chloroform-d) δ 145.33, 140.65, 134.89 (q, J=33.2 Hz), 133.89, 129.64, 128.28, 127.98, 126.54 (q, J=3.7 Hz), 123.20 (q, J=273.5 Hz).

4,4'-sulfonylbis(methoxybenzene). Synthesized from 4,4'-sulfonyldiphenol (0.50 g, 2.0 mmol) and iodomethane (2.84 g, 20.0 mmol) following a literature procedure⁹, 0.54 g, 97 %, 4 hours, colorless solid:
IR (υ[cm⁻¹]) 2996 (w), 2982 (w), 2949 (w), 2921 (w), 2841 (w), 1592 (m), 1576 (m), 1496 (m), 1458 (s), 1437 (s), 1386 (vs), 1317 (s), 1295 (s), 1253 (vs), 1185 (m), 1178 (m), 1145 (s), 1103 (s), 1020 (s), 973 (m), 939 (w), 846 (s), 829 (m), 819 (m), 801 (s), 717 (m), 677 (s), 642 (w), 630 (m), 623 (w), 566 (s), 547 (vs), 484 (m), 411 (vw).

¹H NMR (500 MHz, Chloroform-d) δ 7.85 (d, J = 9.1 Hz, 4H), 6.95 (d, J = 9.0 Hz, 4H), 3.83 (s, 6H).

¹³C NMR (126 MHz, Chloroform-d) δ 163.22, 134.13, 129.66, 114.55, 55.76.

1-methoxy-4-((4-(trifluoromethyl)phenyl)sulfonyl)benzene. Synthesized from (4-methoxyphenyl)(4-(trifluoromethyl)phenyl) sulfide (1.20 g, 3.70 mmol) following general procedure 2, 1.16 g, 99 %, 4 hours, colorless solid:

![Chemical Structure](image)

IR (υ[cm⁻¹]) 3101 (vw), 2955 (vw), 2850 (vw), 1591 (m), 1575 (m), 1497 (m), 1463 (w), 1445 (w), 1415 (w), 1403 (m), 1322 (s), 1302 (m), 1261 (s), 1188 (m), 1155 (s), 1122 (s), 1105 (vs), 1074 (m), 1058 (vs), 1014 (s), 959 (w), 944 (w), 838 (m), 801 (m), 734 (w), 721 (s), 706 (s), 661 (s), 627 (w), 590 (vs), 549 (s), 515 (m), 479 (m), 424 (s).

¹H NMR (500 MHz, Chloroform-d) δ 8.04 (d, J = 9.0 Hz, 2H), 7.89 (d, J = 8.7 Hz, 2H), 7.74 (d, J = 8.9 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H).

¹³C NMR (126 MHz, Chloroform-d) δ 164.00, 146.13, 134.65 (q, J = 33.1 Hz), 132.11, 130.31, 127.99, 126.50 (q, J = 3.8 Hz), 123.26 (q, J = 273.0 Hz), 114.92, 55.86.
4,4'-sulfonylbis((trifluoromethyl)benzene). Synthesized from bis(4-(trifluoromethyl)phenyl) sulfide (1.0 g, 3.10 mmol) following general procedure 2, 0.55 g, 50 %, 4 hours, colorless solid:

![Chemical structure](image)

IR (υ[cm⁻¹]) 3105 (vw), 3056 (vw), 2927 (vw), 1609 (m), 1316 (s), 1158 (s), 1129 (vs), 1105 (vs), 1073 (s), 1058 (vs), 1015 (s), 962 (m), 840 (s), 790 (m), 734 (m), 716 (s), 703 (s), 676 (w), 616 (s), 600 (s), 560 (s), 499 (w), 471 (w), 427 (s).

¹H NMR (500 MHz, Chloroform-d) δ 8.08 (d, J = 8.2 Hz, 4H), 7.81 (d, J = 8.4 Hz, 4H).

¹³C NMR (126 MHz, Chloroform-d) δ 144.34, 135.59 (q, J = 33.2 Hz), 128.60, 126.85 (q, J = 3.7 Hz), 123.11 (q, J = 273.2 Hz).

¹⁹F NMR (470 MHz, Chloroform-d) δ -63.34.
3.3 General Procedure 3. Synthesis of 10-phenyl-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxides

Adapted from a procedure of Suzuki H. and co-workers\textsuperscript{10}.

2-methoxy-10-phenyl-10H-dibenzo[b,e][1,4]thiabismine \textit{5,5-dioxide}. Synthesized from 1-methoxy-4-(phenylsulfonyl)benzene (0.65 g, 2.60 mmol) following a literature procedure\textsuperscript{10}, 1.23 g, 87 \%, 4 hours, colorless solid:

IR (\textit{u}[cm\textsuperscript{-1}]) 3047 (w), 3005 (vw), 2958 (w), 2922 (m), 2851 (w), 1720 (w), 1567 (s), 1496 (vw), 1460 (m), 1427 (m), 1291 (s), 1265 (s), 1236 (m), 1221 (s), 1183 (w), 1145 (s), 1116 (s), 1094 (s), 1074 (s), 1025 (s), 1011 (s), 996 (m), 909 (w), 874 (m), 828 (m), 760 (m), 727 (vs), 715 (s), 706 (m), 695 (s), 661 (m), 650 (s), 582 (s), 561 (vs), 543 (s), 513 (m), 495 (m), 483 (m), 460 (m), 445 (m), 431 (m).
$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.34 (d, $J$ = 7.7 Hz, 1H), 8.32 (d, $J$ = 8.6 Hz, 1H), 7.85 (d, $J$ = 7.2 Hz, 1H), 7.79 (d, $J$ = 7.9 Hz, 2H), 7.47 – 7.40 (m, 2H), 7.42 – 7.35 (m, 3H), 7.33 (t, $J$ = 7.4 Hz, 1H), 6.85 (dd, $J$ = 8.6, 2.6 Hz, 1H), 3.69 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 167.88, 166.20, 163.65, 160.47, 142.74, 138.80, 137.61, 133.32, 133.22, 130.99, 129.11, 128.73, 128.24, 126.73, 123.51, 112.90, 55.68.

**10-phenyl-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide.** Synthesized from diphenyl sulfone (1.8 g, 8.5 mmol) following general procedure 3, 2.07 g, 63 %, overnight, colorless solid. NMR characterization data is consistent with those previously reported$^{11}$.

![Image of 10-phenyl-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide](image.png)

**2-chloro-10-phenyl-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide.** Synthesized from 1-chloro-4-(phenylsulfonyl)benzene (0.78 g, 3.10 mmol) following general procedure 3, 0.79 g, 47 %, overnight, colorless solid:

![Image of 2-chloro-10-phenyl-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide](image.png)
IR (υ[cm⁻¹]) 3056 (w), 3039 (w), 2978 (vw), 2932 (vw), 1651 (vw), 1548 (m), 1474 (w), 1427 (m), 1362 (w), 1284 (m), 1249 (m), 1150 (s), 1122 (m), 1086 (s), 1075 (s), 1055 (m), 1012 (m), 996 (m), 953 (w), 912 (w), 877 (w), 851 (w), 821 (m), 780 (m), 754 (m), 728 (s), 711 (m), 694 (s), 649 (m), 638 (m), 612 (vs), 568 (vs), 527 (m), 502 (m), 476 (m), 467 (m), 442 (m), 426 (m).

^1^H NMR (500 MHz, Chloroform-d) δ 8.37 (d, J = 7.6 Hz, 1H), 8.30 (d, J = 8.3 Hz, 1H), 7.87 (d, J = 7.0 Hz, 1H), 7.82 (d, J = 2.0 Hz, 1H), 7.78 (d, J = 1.9 Hz, 2H), 7.47 (t, J = 7.7 Hz, 2H), 7.45 – 7.34 (m, 4H).

^1^3^C NMR (126 MHz, Chloroform-d) δ 166.45, 159.23, 141.67, 140.90, 140.15, 138.74, 137.74, 137.32, 133.82, 131.29, 129.04, 128.51, 128.48, 128.41, 127.41.

**10-phenyl-2-(trifluoromethyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide.** Synthesized from 1-(phenylsulfonyl)-4-(trifluoromethyl)benzene (2.44 g, 8.52 mmol) following general procedure 3, 1.22 g, 25 %, overnight, colorless solid:

![Structure Image](image)

IR (υ[cm⁻¹]) 3069 (w), 3052 (w), 1954 (w), 1911 (vw), 1852 (vw), 1786 (vw), 1587 (w), 1562 (m), 1475 (w), 1447 (w), 1427 (m), 1383 (m), 1320 (s), 1288 (s), 1256 (m), 1154 (s), 1118 (vs), 1097 (s), 1079 (s), 1064 (vs), 1022 (m), 1012 (m), 996 (m), 964 (m), 909 (w), 898 (m), 877 (w), 851 (w), 821 (m), 780 (m), 754 (m), 728 (s), 711 (m), 694 (s), 649 (m), 638 (m), 612 (vs), 568 (vs), 527 (m), 502 (m), 476 (m), 467 (m), 442 (m), 426 (m).
855 (w), 834 (m), 802 (m), 766 (m), 741 (m), 724 (s), 709 (s), 699 (s), 651 (m), 638 (w), 622 (m), 601 (s), 559 (s), 513 (m), 492 (w), 469 (m), 450 (w), 438 (m), 428 (m), 404 (w).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.47 (d, $J = 8.1$ Hz, 1H), 8.40 (dd, $J = 7.6$, 1.5 Hz, 1H), 8.09 (s, 1H), 7.90 (dd, $J = 7.2$, 1.3 Hz, 1H), 7.76 (dd, $J = 8.0$, 1.4 Hz, 2H), 7.67 (d, $J = 8.1$ Hz, 1H), 7.50 – 7.33 (m, 5H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 166.48, 159.71, 145.43, 141.01, 138.67, 137.82, 134.80 (q, $J = 32.4$ Hz), 134.50 (q, $J = 3.6$ Hz), 134.02, 131.31, 129.15, 128.62, 127.79, 127.35, 127.20, 125.49 (q, $J = 3.7$ Hz), 123.55 (q, $J = 273.2$ Hz).

$^{19}$F NMR (470 MHz, Chloroform-$d$) $\delta$ -62.92.

**2,8-dimethoxy-10-phenyl-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide.** Synthesized from 4,4'-sulfonylbis(methoxybenzene) (1.0 g, 3.60 mmol) following general procedure 3, 1.20 g, 59 %, overnight, colorless solid:

![Structure](./structure.png)

IR ($\nu$[cm$^{-1}$]) 3107 (w), 3059 (w), 2934 (w), 1609 (w), 1593 (w), 1570 (m), 1497 (w), 1460 (w), 1427 (w), 1406 (m), 1314 (s), 1265 (m), 1221 (m), 1156 (s), 1128 (vs), 1104 (vs), 1074 (s), 1058 (s), 1015 (s), 963 (m), 839 (s), 791 (m), 734 (m), 716 (s), 704 (m), 680 (m), 654 (w), 616 (m), 600 (m), 560 (s), 503 (w), 472 (w), 452 (vw), 427 (m).
$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.28 (d, J = 8.6 Hz, 2H), 7.81 (d, J = 7.9 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.39 – 7.35 (m, 3H), 6.84 (dd, J = 8.6, 2.5 Hz, 2H), 3.69 (s, 6H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 172.32, 163.52, 160.04, 138.80, 134.23, 131.00, 128.76, 128.59, 123.50, 112.75, 55.68.

**2,4-dimethoxy-10-phenyl-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide.** Synthesized from 2,4-dimethoxy-1-(phenylsulfonyl)benzene (0.80 g, 2.80 mmol ) following general procedure 3, 0.75 g, 47 %, 4 hours, colorless solid:

![Structure of 2,4-dimethoxy-10-phenyl-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide](image)

IR (υ[cm$^{-1}$]) 3086 (vw), 3051 (w), 3033 (w), 2999 (w), 2980 (w), 2941 (w), 2829 (w), 2067 (vw), 1955 (vw), 1878 (vw), 1820 (vw), 1574 (m), 1556 (s), 1473 (w), 1462 (m), 1445 (m), 1419 (m), 1399 (m), 1298 (s), 1272 (vs), 1208 (s), 1181 (m), 1173 (m), 1142 (vs), 1109 (s), 1083 (m), 1067 (s), 1029 (s), 1009 (s), 995 (m), 951 (m), 923 (m), 854 (s), 845 (s), 754 (m), 728 (vs), 708 (s), 698 (s), 636 (s), 607 (s), 587 (vs), 576 (s), 537 (m), 512 (s), 484 (m), 449 (m), 426 (m), 414 (m).

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.35 (d, J = 6.4 Hz, 1H), 7.75 (d, J = 7.3 Hz, 1H), 7.65 (dd, J = 7.9, 1.5 Hz, 2H), 7.54 (d, J = 2.2 Hz, 1H), 7.37 – 7.20 (m, 5H), 6.54 (d, J = 2.2 Hz, 1H), 3.82 (s, 3H), 3.25 (s, 3H).
\[ ^{13}\text{C} \text{ NMR (101 MHz, Chloroform-d)} \delta \ 164.39, 162.32, 162.13, 157.19, 143.07, 141.64, 138.06, \\
137.90, 137.04, 133.27, 130.29, 128.02, 127.67, 126.57, 104.29, 103.03, 55.94, 55.57. \]

### 3.4 General Procedure 4. Synthesis of 10-iodo-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxides

![Chemical Structure](image)

Adapted from a procedure of H. Suzuki and co-workers.  

**10-iodo-2-methoxy-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide.** Synthesized from 2-methoxy-10-phenyl-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (0.06 g, 11.4 mmol) following a literature procedure, 0.61 g, 10.8 mmol, 92 %, 4 hours, off-white solid:

![Chemical Structure](image)

IR (υ [cm⁻¹]) 2969 (m), 2953 (m), 2928 (m), 1592 (s), 1551 (s), 1496 (m), 1470 (m), 1445 (m), 1425 (s), 1384 (vs), 1267 (s), 1198 (m), 1145 (s), 1106 (m), 1090 (m), 1070 (m), 1017 (m), 962 (w), 898 (w), 874 (w), 831 (m), 803 (w), 760 (m), 731 (s), 684 (m), 671 (m), 658 (m), 577 (m), 513 (s), 430 (w), 408 (w).
$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 9.21 – 9.18 (m, 1H), 8.81 (d, $J = 2.4$ Hz, 1H), 8.27 (d, $J = 7.6$ Hz, 1H), 8.24 (d, $J = 8.4$ Hz, 1H), 7.60 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 1H), 6.91 (dd, $J = 8.5, 2.4$ Hz, 1H), 3.89 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 166.31, 165.77, 163.62, 141.19, 140.29, 135.75, 131.12, 129.68, 128.84, 127.21, 126.39, 114.23, 56.02.

10-iodo-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide. Synthesized from 10-phenyl-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (3.310 g, 6.0 mmol) following general procedure 4, 2.07 g, 63 %, 4 hours, colorless solid. NMR characterization data is consistent with those previously reported$^{11}$.

![Diagram 30](image)

2-chloro-10-iodo-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide. Synthesized from 2-chloro-10-phenyl-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (0.65 g, 1.11 mmol) following general procedure 4, 0.66 g, 69 %, 4 hours, off-white solid:

![Diagram 31](image)
IR (υ[cm\(^{-1}\)]) 3076 (w), 3046 (vw), 3031 (vw), 1547 (m), 1437 (w), 1423 (m), 1362 (w), 1302 (s), 1285 (m), 1248 (m), 1146 (m), 1135 (m), 1116 (m), 1087 (s), 1066 (s), 1024 (m), 1007 (m), 957 (w), 884 (m), 832 (m), 781 (m), 760 (s), 728 (m), 709 (m), 648 (m), 636 (w), 612 (s), 567 (vs), 524 (m), 500 (m), 483 (m), 463 (s), 424 (m).

\(^1\)H NMR (500 MHz, Chloroform-d) δ 9.23 (d, J = 7.4 Hz, 1H), 9.13 (dd, J = 2.0, 1.0 Hz, 1H), 8.30 (d, J = 7.7 Hz, 1H), 8.21 (d, J = 8.2 Hz, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.45 – 7.42 (m, 1H).

\(^{13}\)C NMR (126 MHz, Chloroform-d) δ 163.84, 157.42, 143.99, 140.65, 140.54, 140.11, 138.41, 136.28, 129.22, 129.10, 128.70, 127.86.

**10-iodo-2-(trifluoromethyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide.** Synthesized from 10-phenyl-2-(trifluoromethyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (1.0 g, 1.75 mmol) following general procedure 4, 0.46 g, 42 %, 4 hours, off-white solid:

![Chemical Structure](image)

IR (υ[cm\(^{-1}\)]) 3105 (vw), 3062 (vw), 3031 (vw), 1561 (w), 1440 (w), 1425 (w), 1390 (w), 1311 (vs), 1294 (m), 1254 (m), 1173 (s), 1148 (s), 1118 (vs), 1093 (m), 1073 (m), 1064 (s), 1029 (m), 1010 (m), 985 (w), 971 (w), 894 (m), 878 (w), 844 (m), 823 (w), 802 (w), 762 (m), 738 (m), 723 (m), 707 (m), 652 (w), 638 (w), 623 (m), 601 (m), 588 (m), 558 (s), 526 (w), 513 (m), 491 (w), 470 (m), 442 (m), 428 (m).
$^1$H NMR (500 MHz, Chloroform-d) δ 9.41 (s, 1H), 9.28 – 9.21 (m, 1H), 8.41 – 8.29 (m, 2H), 7.75 (d, J = 7.9 Hz, 1H), 7.67 (tt, J = 7.5, 1.5 Hz, 1H), 7.56 – 7.49 (m, 1H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 143.63, 140.51, 137.56, 136.36 129.07, 128.10, 127.38, 126.05, 123.36 (q, J = 274 Hz), 77.25, 76.99, 76.74.

$^{19}$F NMR (470 MHz, Chloroform-d) δ -62.81.

**10-iodo-2,8-dimethoxy-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide.** Synthesized from 2,8-dimethoxy-10-phenyl-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (0.56 g, 1.78 mmol) following general procedure 4, 0.56 g, 51%, 4 hours, colorless solid:

IR (υ[cm$^{-1}$]) 3083 (w), 3011 (w), 2968 (w), 2930 (w), 2829 (w), 1561 (s), 1472 (w), 1452 (m), 1424 (m), 1400 (m), 1317 (m), 1294 (s), 1269 (s), 1223 (vs), 1189 (m), 1178 (s), 1157 (m), 1139 (m), 1124 (s), 1102 (s), 1071 (s), 1020 (s), 954 (m), 884 (m), 876 (m), 819 (vs), 712 (m), 681 (s), 652 (m), 636 (m), 581 (m), 567 (vs), 548 (s), 539 (vs), 504 (s), 466 (m), 435 (m).

$^1$H NMR (600 MHz, Chloroform-d) δ 8.79 (d, J = 2.4 Hz, 2H), 8.20 (d, J = 8.6 Hz, 2H), 6.89 (dd, J = 8.5, 2.5 Hz, 2H), 3.89 (s, 6H).

$^{13}$C NMR (151 MHz, Chloroform-d) δ 166.14, 165.60, 132.21, 129.12, 126.33, 114.08, 56.00.
10-iodo-2-methoxy-8-(trifluoromethyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide.

Synthesized from 2-methoxy-10-phenyl-8-(trifluoromethyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (0.40 g, 0.67 mmol) following general procedure 4, 0.16 g, 10.8 mmol, 37%, 4 hours, off-white solid:

IR (υ[cm⁻¹]) 3107 (w), 3015 (w), 2969 (w), 2934 (w), 2833 (w), 1566 (m), 1455 (m), 1425 (m), 1397 (m), 1381 (m), 1318 (s), 1302 (s), 1271 (s), 1255 (s), 1227 (s), 1177 (m), 1145 (s), 1122 (vs), 1103 (s), 1075 (s), 1064 (vs), 1019 (s), 1006 (s), 974 (m), 950 (m), 893 (m), 882 (m), 849 (m), 826 (m), 817 (s), 802 (m), 731 (w), 717 (s), 708 (m), 664 (m), 652 (s), 621 (m), 594 (s), 558 (m), 548 (s), 516 (m), 494 (m), 474 (m), 440 (m), 421 (w), 411 (w).

¹H NMR (500 MHz, Chloroform-d) δ 9.39 (s, 1H), 8.84 (d, J = 2.5 Hz, 1H), 8.34 (d, J = 8.2 Hz, 1H), 8.26 (d, J = 8.6 Hz, 1H), 7.73 (d, J = 8.5 Hz, 1H), 6.94 (dd, J = 8.6, 2.4 Hz, 1H), 3.91 (s, 3H).

¹³C NMR (126 MHz, Chloroform-d) δ 166.72, 166.21, 163.06, 137.58 (q, J = 3.6 Hz), 137.07 (q, J = 33.0 Hz), 130.26, 130.16, 126.98, 126.70, 126.16 (q, J = 3.7 Hz), 123.44 (q, J = 272.8 Hz), 114.52, 56.11.

10-iodo-2,4-dimethoxy-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide. Synthesized from 2,4-dimethoxy-10-phenyl-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (0.75 g, 1.33 mmol) following general procedure 4, 0.8 g, 98 %, 4 hours, olive solid:
IR (υ[cm⁻¹]) 3079 (w), 2998 (vw), 2954 (w), 2929 (w), 2828 (w), 1575 (m), 1554 (m), 1463 (m), 1456 (m), 1421 (m), 1397 (s), 1278 (vs), 1251 (m), 1212 (s), 1189 (m), 1180 (m), 1160 (m), 1139 (s), 1108 (s), 1083 (m), 1073 (m), 1038 (s), 1027 (m), 1004 (m), 944 (m), 931 (m), 838 (s), 756 (m), 724 (s), 696 (m), 635 (m), 602 (vs), 572 (s), 541 (m), 511 (s), 473 (m), 449 (w), 432 (m).

¹H NMR (500 MHz, Chloroform-d) δ 10.33 (d, J = 7.7 Hz, 1H), 8.04 –7.96 (m, 1H), 7.81 (dd, J = 2.7, 1.0 Hz, 1H), 7.68 (d, J = 4.8 Hz, 2H), 6.66 (d, J = 1.7 Hz, 1H), 3.97 (s, 3H), 3.87 (s, 3H).

¹³C NMR (126 MHz, Chloroform-d) δ 161.84, 159.81, 148.80, 142.97, 142.39, 140.57, 130.45, 129.61, 110.15, 108.33, 103.94, 57.34, 56.40.

3.5 General Procedure 5. Synthesis of bismuth(III) acetylides with a diphenyl sulfone scaffold

Adapted from a procedure of H Suzuki and co-workers¹⁰.
10-((4-methoxyphenyl)ethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide. Synthesized from 1-ethynyl-4-methoxybenzene and 30 (0.90 g, 1.63 mmol) following a literature procedure\textsuperscript{10}, 0.72 g, 79%, 4 hours, colorless solid:

![Chemical Structure]

IR (υ[cm\textsuperscript{-1}]) 3036 (w), 2972 (w), 2939 (w), 2844 (w), 2099 (m), 1601 (m), 1561 (m), 1504 (m), 1459 (m), 1438 (m), 1285 (s), 1248 (s), 1208 (m), 1182 (m), 1171 (m), 1164 (m), 1143 (s), 1114 (m), 1085 (m), 1069 (m), 1025 (s), 1010 (m), 951 (m), 830 (s), 807 (m), 757 (m), 737 (s), 715 (s), 700 (m), 637 (m), 587 (vs), 563 (vs), 536 (m), 510 (m), 466 (m), 423 (m).

\textsuperscript{1}H NMR (500 MHz, Chloroform-d) δ 8.74 (d, J = 7.5 Hz, 2H), 8.33 (d, J = 7.7 Hz, 2H), 7.52 (t, J = 7.4 Hz, 2H), 7.46 – 7.36 (m, 4H), 6.83 (d, J = 8.2 Hz, 2H), 3.81 (s, 3H).

\textsuperscript{13}C NMR (126 MHz, Chloroform-d) δ 160.60, 159.91, 141.21, 138.19, 134.17, 133.71, 128.53, 127.65, 115.61, 114.06, 112.85, 83.62, 55.43.

10-((4-(tert-butyl)phenyl)ethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide.

Synthesized from 1-ethynyl-4-tert-butylbenzene and 30 (1.0 g, 1.81 mmol) following general procedure 5, 0.80 g, 76%, 4 hours, colorless solid:
IR (\(\text{cm}^{-1}\)) 3044 (vs), 2960 (vs), 2108 (vs), 1562 (vs), 1501 (vs), 1461 (vs), 1438 (vs), 1393 (vs), 1364 (vs), 1301 (s), 1287 (s), 1268 (vs), 1251 (vs), 1209 (vs), 1183 (vs), 1147 (s), 1133 (vs), 1117 (vs), 1106 (vs), 1086 (vs), 1072 (vs), 1012 (vs), 952 (vs), 874 (vs), 831 (vs), 793 (vs), 759 (vs), 737 (s), 715 (vs), 701 (vs), 654 (vs), 637 (vs), 586 (s), 561 (s), 511 (s), 464 (s), 423 (vs).

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 8.74 (d, \(J = 7.2\) Hz, 2H), 8.33 (d, \(J = 7.7\) Hz, 2H), 7.51 (t, \(J = 7.4\) Hz, 2H), 7.45 – 7.37 (m, 4H), 7.32 (d, \(J = 8.2\) Hz, 2H), 1.30 (s, 9H).

\(^1\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 160.66, 152.01, 141.19, 138.21, 134.19, 131.97, 128.53, 127.66, 125.45, 120.46, 112.80, 83.96, 34.95, 31.31.

**10-(p-tolylethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide.** Synthesized from 1-ethynyl-4-methylbenzene and 30 (0.77 g, 1.39 mmol) following general procedure 5, 0.41 g, 54%, 4 hours, colorless solid:

IR (\(\text{cm}^{-1}\)) 3025 (w), 2956 (w), 2924 (w), 2099 (m), 1603 (w), 1562 (m), 1503 (m), 1436 (m), 1375 (w), 1285 (s), 1250 (m), 1201 (m), 1178 (m), 1163 (m), 1144 (s), 1117 (m), 1105 (m), 1086 (m).
Nazarova et al. Electrochemical Mechanistic Elucidation of BiCuAAC

(m, 1069 (m), 1027 (m), 1010 (m), 941 (m), 833 (w), 811 (m), 756 (s), 739 (s), 715 (s), 700 (m), 637 (m), 586 (vs), 563 (vs), 529 (m), 511 (m), 486 (m), 463 (m), 415 (m).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.75 (d, $J = 7.4$ Hz, 2H), 8.33 (d, $J = 7.7$ Hz, 2H), 7.52 (t, $J = 7.4$ Hz, 2H), 7.43 (t, $J = 7.6$ Hz, 2H), 7.35 (d, $J = 7.6$ Hz, 2H), 7.11 (d, $J = 7.9$ Hz, 2H), 2.35 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 160.64, 141.20, 138.85, 138.20, 134.20, 132.11, 129.84, 129.19, 128.54, 127.67, 120.42, 112.89, 21.66.

**10-(phenylethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide.** Synthesized from ethynylbenzene and 30 (1.0 g, 1.81 mmol) following general procedure 5, 0.85 g, 90%, 4 hours, colorless solid:

![Image of molecule](image)

IR ($\nu$[cm$^{-1}$]) 3054 (vw), 3036 (vw), 2111 (w), 1634 (vw), 1596 (w), 1561 (w), 1486 (m), 1437 (m), 1299 (s), 1287 (m), 1249 (m), 1204 (m), 1177 (w), 1165 (w), 1147 (s), 1133 (m), 1116 (m), 1087 (m), 1071 (m), 1026 (m), 1011 (m), 951 (w), 919 (w), 875 (w), 844 (w), 800 (w), 785 (m), 758 (s), 738 (s), 712 (m), 692 (m), 636 (m), 585 (vs), 562 (vs), 538 (m), 530 (m), 509 (m), 465 (m), 424 (m).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.75 (d, $J = 7.3$ Hz, 2H), 8.33 (d, $J = 7.7$ Hz, 2H), 7.52 (t, $J = 7.4$ Hz, 2H), 7.49 – 7.40 (m, 4H), 7.32 – 7.29 (m, 3H).
$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 160.66, 141.19, 140.45, 138.18, 134.23, 132.20, 128.95, 128.58, 128.44, 127.70, 123.51, 112.53.

**10-((4-bromophenyl)ethyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide.** Synthesized from 1-bromo-4-ethynylbenzene and 30 (1.0 g, 1.81 mmol) following general procedure 5, 0.86 g, 79%, 4 hours, colorless solid:

![Structure A][5]

IR ($\nu$ [cm$^{-1}$]) 3056 (vw), 3038 (vw), 2105 (w), 1636 (w), 1582 (w), 1562 (w), 1482 (m), 1466 (w), 1438 (m), 1391 (w), 1285 (s), 1250 (m), 1200 (m), 1177 (w), 1165 (w), 1143 (m), 1118 (m), 1106 (m), 1086 (m), 1069 (m), 1028 (m), 1009 (m), 943 (w), 819 (m), 785 (w), 759 (m), 741 (s), 715 (m), 700 (m), 637 (m), 598 (m), 586 (vs), 563 (vs), 525 (m), 512 (m), 463 (m), 421 (w), 408 (w).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.73 (d, J = 7.3 Hz, 2H), 8.34 (d, J = 7.7 Hz, 2H), 7.53 (t, J = 7.4 Hz, 2H), 7.44 (t, J = 7.6 Hz, 4H), 7.31 (d, J = 7.7 Hz, 2H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 160.66, 141.17, 138.18, 134.28, 133.60, 131.71, 128.65, 127.78, 127.71, 122.86, 122.48, 115.55, 111.21.

**10-((4-bromophenyl)ethyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide.** Synthesized from 1-ethynyl-4-(trifluoromethyl)benzene and 30 (1.0 g, 1.81 mmol) following general procedure 5, 0.60 g, 56%, 4 hours, colorless solid:
IR (υ[cm⁻¹]) 3056 (vw), 2960 (vw), 2921 (vw), 2114 (vw), 1609 (m), 1562 (w), 1509 (vw), 1437 (w), 1427 (w), 1403 (w), 1319 (s), 1299 (m), 1285 (s), 1254 (m), 1207 (m), 1179 (m), 1166 (m), 1151 (s), 1123 (s), 1103 (s), 1087 (m), 1064 (s), 1027 (m), 1014 (m), 946 (w), 869 (vw), 845 (m), 838 (m), 815 (w), 769 (m), 760 (m), 737 (s), 713 (m), 700 (m), 638 (w), 596 (m), 585 (vs), 564 (vs), 523 (m), 514 (m), 464 (s), 422 (m).

¹H NMR (500 MHz, Chloroform-d) δ 8.74 (d, J = 7.3 Hz, 2H), 8.35 (d, J = 7.7 Hz, 2H), 7.58 – 7.51 (m, 6H), 7.44 (t, J = 7.6 Hz, 2H).

¹³C NMR (126 MHz, Chloroform-d) δ 160.80, 141.13, 138.08, 134.31, 132.37, 130.17 (q, J = 32.6 Hz), 128.68, 127.80, 127.33, 125.35 (q, J = 3.5 Hz), 123.97 (q, J = 272.3 Hz), 115.72, 110.58.

¹⁹F NMR (470 MHz, Chloroform-d) δ -62.85.

2,8-dimethoxy-10-(p-tolyethyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide.

Synthesized from 1-ethynyl-4-methylbenzene and 33 (0.50 g, 0.82 mmol) following general procedure 5, 0.30 g, 0.550 mmol, 61 %, overnight, pale yellow solid:
IR (υ[cm⁻¹]) 3062 (w), 2937 (w), 2838 (w), 2051 (vw), 1592 (m), 1573 (m), 1494 (s), 1457 (m), 1438 (m), 1414 (m), 1318 (m), 1308 (m), 1292 (s), 1256 (vs), 1176 (m), 1146 (vs), 1102 (vs), 1072 (s), 1014 (s), 831 (m), 804 (s), 717 (m), 679 (s), 637 (m), 626 (m), 553 (vs), 486 (m), 436 (w), 414 (vw).

¹H NMR (500 MHz, Chloroform-d) δ 8.30 (d, J = 2.5 Hz, 2H), 8.22 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2H), 7.11 (d, J = 7.8 Hz, 2H), 6.86 (dd, J = 8.6, 2.5 Hz, 2H), 3.84 (s, 6H), 2.35 (s, 3H).

¹³C NMR (126 MHz, Chloroform-d) δ 164.22, 162.21, 138.85, 133.46, 132.05, 129.23, 129.01, 123.81, 120.45, 113.49, 113.15, 110.15, 55.84, 21.66.

2-chloro-10-(p-tolylethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide. Synthesized from 1-ethynyl-4-methylbenzene and 31 (0.20 g, 0.34 mmol) following general procedure 5, 0.13 g, 66%, overnight, pale-yellow solid:
IR (ν [cm⁻¹]) 2957 (m), 2920 (vs), 2851 (s), 2098 (w), 1710 (w), 1601 (m), 1548 (m), 1504 (w), 1461 (m), 1439 (w), 1376 (w), 1305 (m), 1285 (m), 1248 (m), 1147 (m), 1117 (m), 1086 (s), 1071 (s), 1010 (m), 956 (w), 915 (vw), 884 (w), 854 (vw), 818 (m), 779 (m), 761 (s), 728 (m), 711 (m), 650 (w), 638 (w), 611 (vs), 568 (vs), 526 (m), 477 (m), 465 (m), 420 (w).

¹H NMR (500 MHz, Chloroform-d) δ 8.75 (d, J = 7.3 Hz, 1H), 8.71 (d, J = 2.0 Hz, 1H), 8.32 (d, J = 7.7 Hz, 1H), 8.24 (d, J = 8.2 Hz, 1H), 7.54 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.40 (dd, J = 8.3, 2.0 Hz, 1H), 7.37 (d, J = 7.7 Hz, 2H), 7.13 (d, J = 8.6 Hz, 2H), 2.36 (s, 3H).

¹³C NMR (126 MHz, Chloroform-d) δ 161.88, 161.16, 161.14, 141.75, 141.04, 139.42, 139.07, 138.24, 138.10, 134.45, 132.14, 129.25, 128.74, 120.14, 113.80, 113.16, 21.68.

2-trifluoro-10-(p-tolylethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide. Synthesized from 1-ethynyl-4-methylbenzene and 32 (0.20 g, 0.32 mmol) following general procedure 5, 0.10 g, 51%, overnight, pale-yellow solid:

IR (ν [cm⁻¹]) 3099 (w), 3081 (w), 3062 (w), 2045 (vw), 1607 (vw), 1582 (vw), 1476 (w), 1446 (m), 1403 (m), 1321 (vs), 1294 (s), 1156 (vs), 1122 (s), 1104 (vs), 1071 (s), 1060 (vs), 1016 (m), 997 (m), 962 (w), 849 (m), 838 (m), 787 (w), 764 (m), 740 (m), 720 (vs), 701 (m), 689 (m), 604 (s), 593 (s), 557 (s), 422 (m).
$^1$H NMR (500 MHz, Chloroform-d) δ 9.02 (s, 1H), 8.76 (d, $J = 7.3$ Hz, 1H), 8.41 (d, $J = 8.0$ Hz, 1H), 8.35 (d, $J = 7.5$ Hz, 1H), 7.70 (d, $J = 8.0$ Hz, 1H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.46 (t, $J = 7.5$ Hz, 1H), 7.34 (d, $J = 7.8$ Hz, 2H), 7.12 (d, $J = 7.8$ Hz, 2H), 2.36 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 161.60, 161.51, 144.74, 140.40, 139.13, 138.33, 135.38, 135.18 (q, $J = 3.27$ Hz), 134.69, 132.07, 129.27, 128.86, 128.23, 127.53, 125.78 (q, $J = 3.67$ Hz), 120.03, 113.88, 77.16, 21.68.

$^{19}$F NMR (470 MHz, Chloroform-d) δ -62.80.

**2-methoxy-10-(p-tolylethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide.** Synthesized from 1-ethynyl-4-methylbenzene and 29 (0.47 g, 0.80 mmol) following general procedure 5, 0.35 g, 60%, overnight, colorless solid:

![Structure](image)

IR (υ [cm$^{-1}$]) 3063 (w), 2943 (w), 2846 (w), 2107 (w), 1591 (m), 1571 (m), 1497 (m), 1459 (m), 1446 (m), 1312 (s), 1297 (s), 1262 (vs), 1229 (m), 1192 (w), 1183 (w), 1148 (vs), 1105 (vs), 1070 (s), 1017 (s), 997 (m), 931 (w), 862 (w), 833 (s), 821 (m), 803 (m), 764 (m), 755 (m), 730 (s), 710 (m), 687 (m), 657 (m), 627 (m), 575 (s), 554 (vs), 485 (m), 454 (m), 424 (w).

$^1$H NMR (500 MHz, Chloroform-d) δ 8.72 (d, $J = 6.1$ Hz, 1H), 8.32 (d, $J = 2.5$ Hz, 1H), 8.29 (d, $J = 6.4$ Hz, 1H), 8.26 (d, $J = 8.6$ Hz, 1H), 7.92 (d, $J = 7.0$ Hz, 0.5H), 7.88 (d, $J = 8.8$ Hz, 0.5H), 7.50
(t, J = 8.2 Hz, 1H), 7.41 (td, J = 7.6, 1.2 Hz, 1.5H), 7.35 (d, J = 7.9 Hz, 2H), 7.11 (d, J = 7.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 0.5H), 6.87 (dd, J = 8.6, 2.5 Hz, 1H), 3.84 (s, 3H), 2.35 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 164.36, 162.60, 160.29, 142.14, 138.85, 138.11, 133.96, 132.08, 130.03, 129.53, 129.33, 129.21, 128.48, 127.46, 127.15, 123.80, 120.43, 114.64, 113.64, 113.01, 55.85, 21.66.
3.6 General Procedure 6. Synthesis of 5-bismuth(III) triazolides

Adapted from a procedure of B. T. Worrell and co-workers\textsuperscript{11}.

10-(4-(4-methoxyphenyl)-1-phenoxy-1H-1,2,3-triazol-5-yl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide. To a 50 mL round-bottom flask equipped with a magnetic stir bar, 0.139 g (0.25 mmol, 1.00 equiv.) of 10-((4-methoxyphenyl)ethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide A[1] and 0.055 g (0.37 mmol, 1.50 equiv.) of (2-azidoethyl)benzene in 3 mL of reagent grade dry THF were added. 1 mL of a copper(I) trifluoromethanesulfonate toluene complex solution in dry THF (0.05 mmol, 0.2 equiv.) was injected directly into the clear solution of A[1] and (2-azidoethyl)benzene. Immediately, the solution turned bright yellow (for all substrates) signalizing the formation of bismuth(III)-acetylenide-Cu(I) \( \pi \)-complex. The reaction mixture was stirred for 2-3 hours at room temperature. After this time, the reaction mixture was dissolved with reagent grade DCM (30 mL), transferred to a 250 mL separatory funnel, and washed with brine:N\textsubscript{4}OH(10%) solution (5:1) 2\( \times \)30 mL N\textsubscript{4}OH to ensure complete removal of any residual catalytic species. The organic phase was dried over MgSO\textsubscript{4}, filtered, and concentrated \textit{in vacuo}. The residue was dissolved in 1 mL of dry DCM and added dropwise to 200 mL of vigorously stirred hexanes. The formed precipitate was filtered.
and dried in a vacuum to yield a colorless solid (0.113 g, 64 %). Due to the mediocre performance of recrystallization as a purification technique, the observable yields are considered to be higher.

IR (υ[cm⁻¹]) 3032 (w), 2991 (w), 2957 (w), 2929 (w), 2851 (w), 2834 (w), 1614 (m), 1576 (w), 1561 (w), 1536 (m), 1498 (m), 1440 (m), 1427 (m), 1398 (w), 1336 (w), 1306 (m), 1290 (m), 1243 (s), 1197 (w), 1174 (m), 1152 (s), 1120 (m), 1106 (m), 1087 (m), 1073 (m), 1037 (m), 1023 (m), 1011 (m), 982 (m), 950 (w), 909 (w), 876 (vw), 834 (m), 810 (m), 775 (w), 759 (m), 734 (s), 717 (m), 696 (s), 669 (m), 636 (w), 614 (m), 586 (vs), 564 (vs), 547 (m), 532 (m), 512 (m), 498 (m), 462 (m), 426 (w).

¹H NMR (500 MHz, Chloroform-d) δ 8.53 (d, J = 7.7 Hz, 2H), 7.97 (s, 2H), 7.51 (t, J = 7.9 Hz, 2H), 7.41 (s, 2H), 7.26 (s, 4H), 6.72 (s, 5H), 3.88 (s, 5H), 3.11 (s, 2H).

¹³C NMR (126 MHz, Chloroform-d) δ 159.54, 157.08, 156.44, 152.42, 141.10, 138.05, 137.30, 134.01, 129.55, 129.23, 128.73, 128.60, 127.78, 127.05, 124.89, 113.82, 77.16, 55.39, 53.34, 36.74.

10-(4-(4-(tert-butyl)phenyl)-1-phenethyl-1H-1,2,3-triazol-5-yl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide. Synthesized from (2-azidoethyl)benzene and A2 (0.146 g, 0.25 mmol) following general procedure 6, 0.127 g, 70 %, 2 hours, colorless solid.
IR (υ[cm⁻¹]) 3062 (vw), 3034 (w), 2950 (m), 2903 (w), 2866 (w), 1561 (m), 1494 (m), 1472 (m), 1458 (m), 1442 (m), 1427 (m), 1404 (m), 1365 (m), 1333 (m), 1305 (s), 1289 (m), 1270 (m), 1256 (m), 1228 (w), 1199 (m), 1178 (m), 1153 (m), 1134 (m), 1119 (m), 1106 (m), 1088 (m), 1074 (m), 1051 (w), 1027 (m), 1011 (m), 983 (m), 912 (w), 889 (w), 878 (w), 842 (m), 764 (m), 740 (s), 715 (m), 697 (s), 637 (m), 585 (vs), 576 (s), 565 (vs), 518 (m), 509 (m), 501 (m), 461 (m), 426 (w).

¹H NMR (500 MHz, Chloroform-d) δ 8.40 (d, J = 7.7 Hz, 2H), 7.85 (s, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.29-7.27 (m, 2H), 7.12 (s, 6H), 6.55 (s, 2H), 3.82 (s, 2H), 2.97 (s, 2H), 1.28 (s, 9H).

¹³C NMR (126 MHz, Chloroform-d) δ 156.95, 156.59, 152.39, 150.98, 141.04, 137.88, 137.17, 133.90, 129.32, 129.22, 128.60, 128.45, 127.93, 127.67, 126.91, 125.24, 77.02, 53.21, 36.49, 34.52, 31.26.

10-(1-phenethyl-4-(p-tolyl)-1H-1,2,3-triazol-5-yl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide. Synthesized from (2-azidoethyl)benzene and A[3] (0.135, 0.25 mmol) following general procedure 6, 0.121 g, 71 %, 4 hours, colorless solid:
1181 (w), 1151 (s), 1135 (m), 1120 (m), 1087 (m), 1073 (m), 1029 (m), 1011 (m), 984 (m), 964 (w), 949 (w), 909 (w), 900 (w), 876 (w), 839 (w), 823 (m), 797 (w), 780 (m), 759 (m), 733 (s), 716 (m), 694 (s), 669 (w), 636 (m), 612 (w), 587 (vs), 564 (vs), 542 (m), 510 (m), 479 (w), 462 (m), 425 (w), 408 (w).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.54 (s, 2H), 8.00 (s, 2H), 7.67 – 7.28 (m, 7H), 7.19 – 6.22 (m, 6H), 3.95 (s, 2H), 3.09 (s, 2H), 2.43 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 157.28, 156.71, 152.80, 141.05, 138.01, 137.23, 133.98, 129.45, 129.13, 128.64, 128.50, 128.22, 127.71, 126.95, 77.37, 77.16, 53.25, 36.59, 21.20.

10-(1-phenethyl-4-phenyl-1H-1,2,3-triazol-5-yl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide. Synthesized from (2-azidoethyl)benzene and A[4] (0.138 g, 0.25 mmol) following general procedure 6, 0.10 g, 59 %, 4 hours, colorless solid:

IR (υ[cm$^{-1}$]) 3062 (w), 3026 (w), 2950 (w), 1605 (w), 1581 (w), 1562 (w), 1497 (w), 1483 (w), 1447 (m), 1427 (m), 1395 (w), 1372 (w), 1298 (s), 1286 (m), 1251 (m), 1223 (m), 1179 (m), 1151 (s), 1106 (m), 1087 (m), 1073 (m), 1050 (m), 1026 (m), 1013 (m), 999 (m), 977 (m), 912 (w), 845 (w), 760 (s), 727 (s), 714 (m), 697 (vs), 690 (vs), 637 (m), 586 (vs), 562 (vs), 517 (m), 508 (m), 462 (m), 427 (w), 404 (vw).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.53 (d, $J = 7.8$ Hz, 2H), 8.00 (s, 2H), 7.51 (t, $J = 8.0$ Hz, 2H), 7.41 (s, 3H), 7.36-7.11 (m, 6H), 6.70 (s, 3H), 3.98 (s, 2H), 3.11 (s, 2H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 157.20, 156.67, 152.74, 141.10, 137.99, 137.24, 134.06, 132.37, 129.32, 128.71, 128.56, 128.40, 128.33, 128.08, 127.80, 127.03, 77.16, 53.34, 36.66.
10-(4-(4-bromophenyl)-1-phenethyl-1H-1,2,3-triazol-5-yl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide. Synthesized from (2-azidoethyl)benzene and A[5] (0.151 g, 0.25 mmol) following general procedure 6, 0.075 g, 40 %, 2 hours, pale-yellow solid:

IR (υ[cm⁻¹]) 3118 (vw), 3091 (vw), 3055 (w), 2918 (vw), 2855 (vw), 1599 (w), 1564 (w), 1498 (w), 1481 (w), 1454 (m), 1402 (w), 1364 (w), 1334 (w), 1301 (m), 1288 (m), 1254 (m), 1222 (m), 1178 (w), 1148 (s), 1133 (m), 1117 (m), 1106 (m), 1088 (m), 1070 (m), 1051 (m), 1028 (m), 1011 (m), 977 (m), 838 (m), 824 (m), 756 (m), 739 (s), 712 (m), 697 (s), 637 (m), 584 (vs), 564 (vs), 507 (m), 480 (m), 461 (m), 443 (m), 423 (w).

¹H NMR (500 MHz, Chloroform-d) δ 8.38 (d, J = 7.7 Hz, 2H), 7.68 (s, 2H), 7.38 (t, J = 7.4 Hz, 2H), 7.23 – 7.15 (m, 4H), 7.08 – 6.42 (m, 7H), 4.33 (s, 2H), 3.18 (s, 2H).

¹³C NMR (126 MHz, Chloroform-d) δ 157.26, 154.98, 152.45, 141.67, 140.85, 137.41, 134.01, 131.28, 131.04, 129.53, 129.29, 129.05, 128.97, 127.91, 127.45, 121.99, 77.16, 53.75, 37.28.

10-(1-phenethyl-4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazol-5-yl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide. Synthesized from (2-azidoethyl)benzene and A[6] (0.297 g, 0.5 mmol) following general procedure 5, 0.298 g, 80 %, 3 hours, colorless solid:
Nazareva et al. Electrochemical Mechanistic Elucidation of BiCuAAC

IR (u[cm⁻¹]) 3036 (w), 2941 (w), 2873 (vw), 1618 (w), 1493 (w), 1457 (w), 1436 (w), 1427 (w), 1413 (w), 1323 (s), 1310 (s), 1256 (m), 1196 (w), 1168 (m), 1152 (s), 1134 (s), 1106 (s), 1088 (s), 1063 (s), 1029 (m), 1011 (m), 983 (m), 915 (w), 878 (w), 850 (m), 781 (w), 761 (m), 737 (s), 714 (m), 699 (s), 665 (m), 636 (m), 608 (w), 586 (vs), 564 (vs), 509 (m), 488 (w), 463 (m), 452 (m), 425 (w).

¹H NMR (600 MHz, Chloroform-d) δ 8.33 (d, J = 7.8 Hz, 2H), 7.71 – 7.55 (m, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.4 Hz, 2H), 7.15 (t, J = 7.3 Hz, 3H), 7.13 – 7.06 (m, 6H), 4.58 (s, 2H), 3.23 (s, 2H).

¹³C NMR (126 MHz, Chloroform-d) δ 157.65, 154.29, 152.81, 140.70, 137.98, 137.40, 135.87, 133.89, 129.29, 129.05, 127.99, 127.74, 127.47, 127.29 (q, J=4.9 Hz), 124.53, 123.94 (q, J=272.1 Hz), 77.16, 53.78, 37.35.

¹⁹F NMR (470 MHz, Chloroform-d) δ -63.00.
4. X-Ray Crystallographic Details

X-Ray Crystallographic Analysis of bismuth(III) acetylide A[1]

A clear colourless blade-like specimen of C_{21}H_{15}BiO_{3}S, approximate dimensions 0.016 mm x 0.143 mm x 0.226 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker APEX DUO system equipped with a TRIUMPH curved-crystal monochromator and a MoKα fine-focus tube (λ = 0.71073 Å). The total exposure time was 14.00 hours. The frames were integrated with the Bruker SAINT software package using a SAINT V8.34A (Bruker AXS, 2013) algorithm. The integration of the data using a triclinic unit cell yielded a total of 22944 reflections to a maximum θ angle of 31.44° (0.68 Å resolution), of which 5725 were independent (average redundancy 4.008, completeness = 93.6%, R_{int} = 3.31%, R_{sig} = 3.01%) and 5300 (92.58%) were greater than 2σ(F^2). The final cell constants of a = 8.5311(12) Å, b = 9.7298(13) Å, c = 12.6454(17) Å, α = 69.541(2)°, β = 75.212(2)°, γ = 71.666(2)°, volume = 921.0(2) Å^3, are based upon the refinement of the XYZ-centroids of 9959 reflections above 20 σ(I) with 4.613° < 2θ < 62.75°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.738. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.2180 and 0.8600.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P-1, with Z = 2 for the formula unit, C_{21}H_{15}BiO_{3}S. The final anisotropic full-matrix least-squares refinement on F^2 with 236 variables converged at R1 = 1.92%, for the observed data and wR2 = 4.28% for all data. The goodness-of-fit was 1.057. The largest peak in the final difference electron density synthesis was 1.128 e/Å^3 and the largest hole was -1.282 e/Å^3 with an RMS deviation of 0.131 e/Å^3. On the basis of the final model, the calculated density was 2.006 g/cm^3 and F(000), 528 e-.

![Asymmetric unit in the crystal structure of compound A[1]](image)

Figure S.1 Asymmetric unit in the crystal structure of compound A[1].
Table S.10 Crystal data and structure refinement for compound A[1].

| Parameter                              | Value                        |
|----------------------------------------|------------------------------|
| Chemical formula                       | C21H15BiO3S                  |
| Formula weight                         | 556.37 g/mol                 |
| Temperature                            | 100(2) K                     |
| Wavelength                             | 0.71073 Å                    |
| Crystal size                           | 0.016 x 0.143 x 0.226 mm     |
| Crystal habit                          | clear colourless blade       |
| Crystal system                         | triclinic                    |
| Space group                            | P - t                        |
| Unit cell dimensions                   | a = 8.5311(12) Å             |
|                                       | b = 9.7298(13) Å             |
|                                       | c = 12.6454(17) Å            |
| Volume                                 | 921.0(2) Å                   |
| Z                                      | 2                            |
| Density (calculated)                   | 2.006 g/cm³                  |
| Absorption coefficient                 | 9.703 mm⁻¹                   |
| F(000)                                 | 528                          |
| Diffractometer                         | Bruker APEX DUO              |
| Radiation source                       | fine-focus tube, MoKα        |
| Theta range for data collection        | 1.74 to 31.44°               |
| Index ranges                           | -12≤h≤12, -13≤k≤14, -18≤l≤18 |
| Reflections collected                  | 22944                        |
| Independent reflections                | 5725 [R(int) = 0.0331]       |
| Coverage of independent reflections    | 93.6%                        |
| Absorption correction                  | multi-scan                   |
| Max. and min. transmission             | 0.8600 and 0.2180            |
| Structure solution technique           | direct methods               |
| Structure solution program             | SHELXTL XT 2014/4 (Bruker AXS, 2014) |
| Refinement method                      | Full-matrix least-squares on F2 |
| Refinement program                     | SHELXTL XL 2014/7 (Bruker AXS, 2014) |
| Function minimized                     | Σ w(Fo² - Fc²)²              |
| Data / restraints / parameters         | 5725 / 0 / 236               |
| Goodness-of-fit on F2                  | 1.057                        |
| Δ/σmax                                 | 0.001                        |
| Final R indices                        | 5300 data; I>2σ(I) R1 = 0.0192, wR2 = 0.0417 |
| all data                               | R1 = 0.0229, wR2 = 0.0428    |
| Weighting scheme                       | w=1/[σ²(Fo²)+(0.0199P)²+0.2424P] |
| where P=(Fo²+2Fc²)/3                   |                             |
| Largest diff. peak and hole            | 1.128 and -1.282 eÅ⁻³        |
| R.M.S. deviation from mean             | 0.131 eÅ⁻³                   |

Table S.11 Bond lengths [Å] and angles [°] for compound A[7].

| Bond          | Length (Å) | Bond          | Length (Å) |
|---------------|------------|---------------|------------|
| C1-C2         | 1.391(3)   | C1-C6         | 1.395(3)   |
| C1-S1         | 1.768(2)   | C2-C3         | 1.391(4)   |
| C2-H2         | 0.95       | C3-C4         | 1.392(4)   |
| C3-H3         | 0.95       | C4-C5         | 1.396(3)   |
| Bond          | Length (Å) | Bond          | Length (Å) |
|---------------|------------|---------------|------------|
| C4-H4         | 0.95       | C5-C6         | 1.393(3)   |
| C5-H5         | 0.95       | C6-Bi1        | 2.277(2)   |
| C7-C12        | 1.388(3)   | C7-C8         | 1.393(3)   |
| C7-S1         | 1.773(2)   | C8-C9         | 1.398(3)   |
| C8-Bi1        | 2.287(2)   | C9-C10        | 1.394(4)   |
| C9-H9         | 0.95       | C10-C11       | 1.396(4)   |
| C10-H10       | 0.95       | C11-C12       | 1.387(3)   |
| C11-H11       | 0.95       | C12-H12       | 0.95       |
| C13-C14       | 1.180(4)   | C13-Bi1       | 2.243(2)   |
| C14-C15       | 1.453(3)   | C15-C16       | 1.396(3)   |
| C15-C20       | 1.406(3)   | C16-C17       | 1.388(3)   |
| C16-H16       | 0.95       | C17-C18       | 1.389(4)   |
| C17-H17       | 0.95       | C18-O3        | 1.368(3)   |
| C18-C19       | 1.391(4)   | C19-C20       | 1.388(4)   |
| C19-H19       | 0.95       | C20-H20       | 0.95       |
| C21-O3        | 1.437(3)   | C21-H21A      | 0.98       |
| C21-H21B      | 0.98       | C21-H21C      | 0.98       |
| O1-S1         | 1.4399(18) | O2-S1         | 1.4586(17) |
| C2-C1-C6      | 123.1(2)   | C2-C1-S1      | 119.83(19) |
| C6-C1-S1      | 117.05(17) | C1-C2-C3      | 118.2(2)   |
| C1-C2-H2      | 120.9      | C3-C2-H2      | 120.9      |
| C2-C3-C4      | 120.0(2)   | C2-C3-H3      | 120.0      |
| C4-C3-H3      | 120.0      | C3-C4-C5      | 120.8(2)   |
| C3-C4-H4      | 119.6      | C5-C4-H4      | 119.6      |
| C6-C5-C4      | 120.3(2)   | C6-C5-H5      | 119.9      |
| C4-C5-H5      | 119.9      | C5-C6-C1      | 117.6(2)   |
| C5-C6-Bi1     | 123.36(18) | C1-C6-Bi1     | 119.00(17) |
| C12-C7-C8     | 123.5(2)   | C12-C7-S1     | 119.31(18) |
| C8-C7-S1      | 117.14(18) | C7-C8-C9      | 117.3(2)   |
| C7-C8-Bi1     | 118.75(17) | C9-C8-Bi1     | 123.99(17) |
| C10-C9-C8     | 120.2(2)   | C10-C9-H9     | 119.9      |
| C8-C9-H9      | 119.9      | C9-C10-C11    | 120.9(2)   |
| C9-C10-H10    | 119.9      | C11-C10-H10   | 119.6      |
| C12-C11-C10   | 119.9(2)   | C12-C11-H11   | 120.1      |
| C10-C11-H11   | 120.1      | C11-C12-C7    | 118.2(2)   |
| C11-C12-H12   | 120.9      | C7-C12-H12    | 120.9      |
| C14-C13-Bi1   | 160.3(2)   | C13-C14-C15   | 176.5(3)   |
| C16-C15-C20   | 118.4(2)   | C16-C15-C14   | 119.1(2)   |
| C20-C15-C14   | 122.4(2)   | C17-C16-C15   | 121.4(2)   |
| C17-C16-H16   | 119.3      | C15-C16-H16   | 119.3      |
| C16-C17-C18   | 119.5(2)   | C16-C17-H17   | 120.3      |
| C18-C17-H17   | 120.3      | O3-C18-C17    | 124.3(2)   |
| O3-C18-C19    | 115.5(2)   | C17-C18-C19   | 120.2(2)   |
| C20-C19-C18   | 120.2(2)   | C20-C19-H19   | 119.9      |
| C18-C19-H19   | 119.9      | C19-C20-C15   | 120.3(2)   |
| C19-C20-H20   | 119.8      | C15-C20-H20   | 119.8      |
| O3-C21-H21A   | 109.5      | O3-C21-H21B   | 109.5      |
| Bond                  | Angle (°) | Bond                  | Angle (°) |
|-----------------------|-----------|-----------------------|-----------|
| H21A-C21-H21B         | 109.5     | O3-C21-H21C           | 109.5     |
| H21A-C21-H21C         | 109.5     | H21B-C21-H21C         | 109.5     |
| C18-O3-C21            | 117.0(2)  | O1-S1-O2              | 118.52(11)|
| O1-S1-C1              | 110.79(11)| O2-S1-C1              | 106.15(11)|
| O1-S1-C7              | 110.19(11)| O2-S1-C7              | 105.66(11)|
| C1-S1-C7              | 104.51(11)| C13-Bi1-C6            | 89.61(8)  |
| C13-Bi1-C8            | 94.75(8)  | C6-Bi1-C8             | 85.94(8)  |
X-Ray Crystallographic Analysis of bismuth(III) acetylide A[2]

The single-crystal X-ray diffraction studies were carried out on a Bruker Kappa Apex II CCD diffractometer equipped with Mo Kα radiation (λ = 0.71073). A 0.180 x 0.125 x 0.060 mm colorless crystal was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using φ and ω scans. Crystal-to-detector distance was 40 mm using exposure time 15s with a scan width of 0.60°. Data collection was 100.0% complete to 25.242° in θ. A total of 24144 reflections were collected covering the indices, -12<=h<=12, -10<=k<=10, -30<=l<=30. 4322 reflections were found to be symmetry independent, with a Rint of 0.0350. Indexing and unit cell refinement indicated a Primitive, Monoclinic lattice. The space group was found to be P21/c. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Notes: Proposed structure in agreement with model derived from diffraction data. Excellent data and refinement Disorder on the t-Bu group, SADI, RIGU…

Figure S.11 Asymmetric unit in the crystal structure of compound A[2].

Table S.12 Crystal data and structure refinement for A[2].

| Property              | Value          |
|-----------------------|----------------|
| Empirical formula     | C24 H21 Bi O2 S|
| Molecular formula     | C24 H21 Bi O2 S|
| Formula weight        | 582.45         |
| Temperature           | 100.0 K        |
| Wavelength            | 0.71073 Å      |
Crystal system: Monoclinic
Space group: P 1 2 1/c 1
Unit cell dimensions:
- \( a = 10.2166(5) \text{ Å} \), \( 90^\circ \)
- \( b = 8.6731(4) \text{ Å} \), \( 97.570(2)^\circ \)
- \( c = 24.1194(11) \text{ Å} \), \( 90^\circ \)
Volume: \( 2118.58(17) \text{ Å}^3 \)
Z: 4

Density (calculated): \( 1.826 \text{ Mg/m}^3 \)
Absorption coefficient: \( 8.437 \text{ mm}^{-1} \)
F(000): 1120
Crystal size: \( 0.18 \times 0.125 \times 0.06 \text{ mm}^3 \)
Crystal color, habit: colorless plank

Theta range for data collection: 2.011 to 26.371°
Index ranges:
- \(-12 \leq h \leq 12\)
- \(-10 \leq k \leq 10\)
- \(-30 \leq l \leq 30\)
Reflections collected: 24144
Independent reflections: 4322 \([R(int) = 0.0350]\)
Completeness to theta = 25.242°: 100.0%
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 0.2607 and 0.1603

Refinement method: Full-matrix least-squares on \( F^2 \)
Data / restraints / parameters: 4322 / 76 / 296

Goodness-of-fit on \( F^2 \): 1.028
Final R indices [I>2sigma(I)]: R1 = 0.0198, wR2 = 0.0336
R indices (all data): R1 = 0.0321, wR2 = 0.0364
Largest diff. peak and hole: 0.481 and -0.415 e.Å\(^{-3}\)

**Table S.13** Bond lengths [Å] and angles [°] for A[2].

| Bond | Length [Å] |
|------|------------|
| Bi(1)-C(1) | 2.277(3) |
| Bi(1)-C(12) | 2.274(3) |
| Bi(1)-C(13) | 2.225(3) |
| S(1)-O(1) | 1.453(2) |
| S(1)-O(2) | 1.440(2) |
| S(1)-C(6) | 1.769(3) |
| S(1)-C(7) | 1.766(3) |
| C(1)-C(2) | 1.389(4) |
| C(1)-C(6) | 1.390(4) |
| C(2)-H(2) | 0.9500 |
| C(2)-C(3) | 1.391(4) |
| C(3)-H(3) | 0.9500 |
| C(3)-C(4) | 1.392(5) |
| C(4)-H(4) | 0.9500 |
| C(4)-C(5) | 1.382(5) |
| C(5)-H(5) | 0.9500 |
| C(5)-C(6) | 1.391(4) |
| C(7)-C(8) | 1.387(4) |
C(7)-C(12)  1.399(4)
C(8)-H(8)  0.9500
C(8)-C(9)  1.390(4)
C(9)-H(9)  0.9500
C(9)-C(10)  1.389(4)
C(10)-H(10)  0.9500
C(10)-C(11)  1.387(4)
C(11)-H(11)  0.9500
C(11)-C(12)  1.385(4)
C(13)-C(14)  1.195(4)
C(14)-C(15)  1.453(4)
C(15)-C(16)  1.397(4)
C(15)-C(20)  1.395(4)
C(16)-H(16)  0.9500
C(16)-C(17)  1.384(4)
C(17)-H(17)  0.9500
C(17)-C(18)  1.399(5)
C(18)-C(19)  1.400(4)
C(18)-C(21)  1.535(7)
C(18)-C(21B)  1.531(7)
C(19)-H(19)  0.9500
C(19)-C(20)  1.382(4)
C(20)-H(20)  0.9500
C(21)-C(22)  1.533(7)
C(21)-C(23)  1.526(7)
C(21)-C(24)  1.535(7)
C(22)-H(22A)  0.9800
C(22)-H(22B)  0.9800
C(22)-H(22C)  0.9800
C(23)-H(23A)  0.9800
C(23)-H(23B)  0.9800
C(23)-H(23C)  0.9800
C(24)-H(24A)  0.9800
C(24)-H(24B)  0.9800
C(24)-H(24C)  0.9800
C(21B)-C(22B)  1.538(7)
C(21B)-C(23B)  1.529(7)
C(21B)-C(24B)  1.530(7)
C(22B)-H(22D)  0.9800
C(22B)-H(22E)  0.9800
C(22B)-H(22F)  0.9800
C(23B)-H(23D)  0.9800
C(23B)-H(23E)  0.9800
C(23B)-H(23F)  0.9800
C(24B)-H(24D)  0.9800
C(24B)-H(24E)  0.9800
C(24B)-H(24F)  0.9800
C(20)-C(15)-C(14)  121.8(3)  
C(20)-C(15)-C(16)  118.1(3)  
C(15)-C(16)-H(16)  119.7  
C(17)-C(16)-C(15)  120.6(3)  
C(17)-C(16)-H(16)  119.7  
C(16)-C(17)-H(17)  119.0  
C(16)-C(17)-C(18)  121.9(3)  
C(18)-C(17)-H(17)  119.0  
C(17)-C(18)-C(19)  116.7(3)  
C(17)-C(18)-C(21)  123.6(5)  
C(17)-C(18)-C(21B)  120.7(5)  
C(19)-C(18)-C(19)  118.9(5)  
C(19)-C(18)-C(21B)  122.5(5)  
C(19)-C(18)-H(17)  119.7  
C(19)-C(18)-H(19)  121.9(3)  
C(19)-C(18)-H(20)  119.6  
C(20)-C(19)-C(18)  119.1  
C(20)-C(19)-H(19)  119.6  
C(20)-C(19)-H(20)  119.6  
C(20)-C(19)-C(15)  104.6(13)  
C(21)-C(20)-C(19)  112.4(7)  
C(21)-C(20)-H(19)  112.1(13)  
C(21)-C(20)-H(20)  108.5(11)  
C(18)-C(21)-C(22)  110.6(8)  
C(18)-C(21)-C(23)  112.8(11)  
C(18)-C(21)-C(24)  112.3(11)  
C(18)-C(21)-C(24A)  114.7(15)  
C(19)-C(21)-C(18)  113.1(8)  
C(19)-C(21)-C(22)  109.7(12)  
C(19)-C(21)-C(22B)  108.0(9)  
C(19)-C(21)-C(24)  105.2(8)

C(22)-C(21)-C(18)  110.6(8)  
C(22)-C(21)-C(23)  112.8(11)  
C(22)-C(21)-C(24)  112.3(11)  
C(22)-C(21)-C(24A)  114.7(15)  
C(18)-C(21B)-C(22B)  113.1(8)  
C(23B)-C(21B)-C(18)  109.7(12)  
C(23B)-C(21B)-C(22B)  108.0(9)  
C(23B)-C(21B)-C(24B)  105.2(8)
C(24B)-C(21B)-C(22B)  105.5(14)
C(21B)-C(22B)-H(22D) 109.5
C(21B)-C(22B)-H(22E)  109.5
C(21B)-C(22B)-H(22F)  109.5
H(22D)-C(22B)-H(22E)  109.5
H(22D)-C(22B)-H(22F)  109.5
H(22E)-C(22B)-H(22F)  109.5
C(21B)-C(23B)-H(23D)  109.5
C(21B)-C(23B)-H(23E)  109.5
C(21B)-C(23B)-H(23F)  109.5
H(23D)-C(23B)-H(23E)  109.5
H(23D)-C(23B)-H(23F)  109.5
H(23E)-C(23B)-H(23F)  109.5
C(21B)-C(24B)-H(24D)  109.5
C(21B)-C(24B)-H(24E)  109.5
C(21B)-C(24B)-H(24F)  109.5
H(24D)-C(24B)-H(24E)  109.5
H(24D)-C(24B)-H(24F)  109.5
H(24E)-C(24B)-H(24F)  109.5
X-Ray Crystallographic Analysis of bismuth(III) acetylide A[3]

The single-crystal X-ray diffraction studies were carried out on a Bruker APEX II ULTRA CCD diffractometer equipped with Mo Kα radiation ($\lambda = 0.71073$ Å). Crystals of the subject compound were used as received. A 0.220 x 0.160 x 0.110 mm colorless block crystal was mounted on a Cryoloop with Paratone N oil. Data were collected in a nitrogen gas stream at 100(2) K using $\phi$ and $\omega$ scans. Crystal-to-detector distance was 40 mm using an exposure time of 5 seconds with a scan width of 1.5°. Data collection was 99.9% complete to 25.242° in $\theta$. A total of 11108 reflections were collected. 4447 reflections were found to be symmetry independent, with a Rint of 0.0314. Indexing and unit cell refinement indicated a Primitive Triclinic lattice. The space group was found to be P-1. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Notes: Excellent data and refinement. There is one molecule per asymmetric unit.

**Figure S.2** Asymmetric unit in the crystal structure of compound A[3].

**Table S.14** Crystal data and structure refinement for compound A[3].

| Property          | Value     |
|-------------------|-----------|
| Empirical formula | C21 H15 Bi O2 S |
| Formula weight    | 540.37    |
| Temperature       | 100.0 K   |
| Wavelength        | 0.71073 Å |
| Crystal system    | Triclinic |
| Space group       | P-1       |
Nazarova et al. Electrochemical Mechanistic Elucidation of BiCuAAC

Unit cell dimensions

- \( a = 8.4656(5) \, \text{Å} \)
- \( \alpha = 70.606(2)^\circ \)
- \( b = 9.4514(5) \, \text{Å} \)
- \( \beta = 87.545(2)^\circ \)
- \( c = 12.2813(6) \, \text{Å} \)
- \( \gamma = 75.602(2)^\circ \)

Volume

- \( 896.93(8) \, \text{Å}^3 \)

Z

- \( 2 \)

Density (calculated)

- \( 2.001 \, \text{Mg/m}^3 \)

Absorption coefficient

- \( 9.956 \, \text{mm}^{-1} \)

F(000)

- \( 512 \)

Crystal size

- \( 0.22 \times 0.16 \times 0.11 \, \text{mm}^3 \)

Theta range for data collection

- \( 1.760 \) to \( 28.292^\circ \)

Index ranges

- \(-11 \leq h \leq 11\)
- \(-12 \leq k \leq 12\)
- \(-16 \leq l \leq 16\)

Reflections collected

- \( 11108 \)

Independent reflections

- \( 4447 \) \([R(int) = 0.0314]\)

Completeness to theta = \( 25.242^\circ \)

- \( 99.9 \% \)

Absorption correction

- Semi-empirical from equivalents

Max. and min. transmission

- \( 0.7457 \) and \( 0.5814 \)

Refinement method

- Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters

- \( 4447 / 0 / 227 \)

Goodness-of-fit on \( F^2 \)

- \( 1.038 \)

Final R indices \([I>2\sigma(I)]\)

- \( R1 = 0.0205, \, wR2 = 0.0463 \)

R indices (all data)

- \( R1 = 0.0242, \, wR2 = 0.0472 \)

Extinction coefficient

- \( \text{n/a} \)

Largest diff. peak and hole

- \( 1.429 \) and \( -0.802 \, \text{e.Å}^{-3} \)

**Table S.15** Bond lengths [Å] and angles [°] for compound A\(^3\).

| Bond                  | Length [Å] |
|-----------------------|------------|
| Bi(1)-C(9)            | 2.256(3)   |
| Bi(1)-C(10)           | 2.274(3)   |
| Bi(1)-C(16)           | 2.275(3)   |
| S(1)-O(1)             | 1.445(2)   |
| S(1)-O(2)             | 1.459(2)   |
| S(1)-C(15)            | 1.767(3)   |
| S(1)-C(17)            | 1.771(3)   |
| C(1)-H(1A)            | 0.9800     |
| C(1)-H(1B)            | 0.9800     |
| C(1)-H(1C)            | 0.9800     |
| C(1)-C(2)             | 1.520(4)   |
| C(2)-C(3)             | 1.391(5)   |
| C(2)-C(7)             | 1.391(5)   |
| C(3)-H(3)             | 0.9500     |
| C(3)-C(4)             | 1.387(4)   |
| C(4)-H(4)             | 0.9500     |
| C(4)-C(5)             | 1.400(5)   |
| C(5)-C(6)             | 1.396(5)   |
| C(5)-C(8)             | 1.483(5)   |
| C(6)-H(6)             | 0.9500     |
| C(6)-C(7)             | 1.377(4)   |
C(7)-H(7) 0.9500
C(8)-C(9) 1.135(5)
C(10)-C(11) 1.391(4)
C(10)-C(15) 1.399(4)
C(11)-H(11) 0.9500
C(11)-C(12) 1.397(5)
C(12)-H(12) 0.9500
C(12)-C(13) 1.392(4)
C(13)-H(13) 0.9500
C(13)-C(14) 1.392(4)
C(14)-H(14) 0.9500
C(14)-C(15) 1.381(4)
C(16)-C(17) 1.390(4)
C(16)-C(21) 1.399(4)
C(17)-C(18) 1.393(4)
C(18)-H(18) 0.9500
C(18)-C(19) 1.384(4)
C(19)-H(19) 0.9500
C(19)-C(20) 1.395(4)
C(20)-H(20) 0.9500
C(20)-C(21) 1.395(4)
C(21)-H(21) 0.9500

C(9)-Bi(1)-C(10) 91.74(11)
C(9)-Bi(1)-C(16) 94.53(11)
C(10)-Bi(1)-C(16) 86.35(11)
O(1)-S(1)-O(2) 118.94(13)
O(1)-S(1)-C(15) 110.15(14)
O(1)-S(1)-C(17) 109.64(14)
O(2)-S(1)-C(15) 106.19(14)
O(2)-S(1)-C(17) 106.05(14)
C(15)-S(1)-C(17) 104.92(14)
H(1A)-C(1)-H(1B) 110.5
H(1A)-C(1)-H(1C) 109.5
H(1B)-C(1)-H(1C) 109.5
C(2)-C(1)-H(1A) 109.5
C(2)-C(1)-H(1B) 109.5
C(2)-C(1)-H(1C) 109.5
C(3)-C(2)-C(1) 121.4(3)
C(7)-C(2)-C(1) 120.6(3)
C(7)-C(2)-C(3) 117.9(3)
C(2)-C(3)-H(3) 119.2
C(4)-C(3)-C(2) 121.6(3)
C(4)-C(3)-H(3) 119.2
C(3)-C(4)-H(4) 120.0
C(3)-C(4)-C(5) 119.9(3)
C(5)-C(4)-H(4) 120.0
C(4)-C(5)-C(8) 120.2(3)
C(6)-C(5)-C(4) 118.5(3)
C(6)-C(5)-C(8) 121.2(3)
C(5)-C(6)-H(6) 119.6
C(7)-C(6)-C(5) 120.8(3)
C(7)-C(6)-H(6) 119.6
C(2)-C(7)-H(7) 119.4
C(6)-C(7)-C(2) 121.2(3)
C(6)-C(7)-H(7) 119.4
C(9)-C(8)-C(5) 178.3(4)
C(8)-C(9)-Bi(1) 161.7(3)
C(11)-C(10)-Bi(1) 123.0(2)
C(11)-C(10)-C(15) 117.3(3)
C(15)-C(10)-Bi(1) 119.7(2)
C(10)-C(11)-H(11) 119.8
C(10)-C(11)-C(12) 120.5(3)
C(12)-C(11)-H(11) 119.8
C(11)-C(12)-H(12) 119.6
C(13)-C(12)-C(11) 120.9(3)
C(13)-C(12)-H(12) 119.6
C(12)-C(13)-H(13) 120.2
C(12)-C(13)-C(14) 119.5(3)
C(14)-C(13)-H(13) 120.2
C(13)-C(14)-H(14) 120.7
C(15)-C(14)-C(13) 118.6(3)
C(15)-C(14)-H(14) 120.7
C(10)-C(15)-S(1) 116.9(2)
C(14)-C(15)-S(1) 119.8(2)
C(14)-C(15)-C(10) 123.3(3)
C(17)-C(16)-Bi(1) 118.9(2)
C(17)-C(16)-C(21) 117.3(3)
C(21)-C(16)-Bi(1) 123.8(2)
C(16)-C(17)-S(1) 118.1(2)
C(16)-C(17)-C(18) 123.2(3)
C(18)-C(17)-S(1) 118.7(2)
C(17)-C(18)-H(18) 120.8
C(19)-C(18)-C(17) 118.4(3)
C(19)-C(18)-H(18) 120.8
C(18)-C(19)-H(19) 120.0
C(18)-C(19)-C(20) 120.0(3)
C(20)-C(19)-H(19) 120.0
C(19)-C(20)-H(20) 119.7
C(19)-C(20)-C(21) 120.6(3)
C(21)-C(20)-H(20) 119.7
C(16)-C(21)-H(21) 119.8
C(20)-C(21)-C(16) 120.5(3)
C(20)-C(21)-H(21) 119.8
X-Ray Crystallographic Analysis of bismuth(III) acetylide A[4]

The single-crystal X-ray diffraction studies were carried out on a Bruker Kappa Apex II CCD diffractometer equipped with Mo Kα radiation (λ = 0.71073). A 0.120 x 0.050 x 0.040 mm colorless crystal was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using φ and ϖ scans. Crystal-to-detector distance was 40 mm using exposure time 20s with a scan width of 0.70°. Data collection was 100.0% complete to 25.242° in A total of 26572 reflections were collected covering the indices, -10<=h<=10, -12<=k<=12, -25<=l<=25. 3488 reflections were found to be symmetry independent, with a R_int of 0.0413. Indexing and unit cell refinement indicated a Primitive, Monoclinic lattice. The space group was found to be P2_1/c. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Notes: Proposed structure in agreement with model derived from diffraction data. Excellent data and refinement

Figure S.3 Asymmetric unit in the crystal structure of compound A[4].

Table S.16 Crystal data and structure refinement for compound A[4].

| Property                        | Value                  |
|---------------------------------|------------------------|
| Empirical formula               | C20 H13 Bi O2 S        |
| Molecular formula               | C20 H13 Bi O2 S        |
| Formula weight                  | 526.34                 |
| Temperature                     | 100.0 K                |
| Wavelength                      | 0.71073 Å              |
| Crystal system                  | Monoclinic             |
| Space group                     | P 1 21/c 1             |

S88
Unit cell dimensions

\[ a = 8.535(4) \, \text{Å} \quad a = 90°. \]
\[ b = 9.906(5) \, \text{Å} \quad \beta = 94.941(17)°. \]
\[ c = 20.213(11) \, \text{Å} \quad \gamma = 90°. \]

Volume

1702.7(15) Å³

Z

4

Density (calculated)

2.053 Mg/m³

Absorption coefficient

10.486 mm⁻¹

F(000)

992

Crystal size

0.12 x 0.05 x 0.04 mm³

Crystal color, habit

colorless plank

Theta range for data collection

2.023 to 26.359°.

Index ranges

\(-10 \leq h \leq 10, -12 \leq k \leq 12, -25 \leq l \leq 25\)

Reflections collected

26572

Independent reflections

3488 [R(int) = 0.0413]

Completeness to theta = 25.242°

100.0 %

Absorption correction

Semi-empirical from equivalents

Max. and min. transmission

0.4910 and 0.3028

Refinement method

Full-matrix least-squares on F²

Data / restraints / parameters

3488 / 0 / 217

Goodness-of-fit on F²

1.029

Final R indices [I>2sigma(I)]

R1 = 0.0172, wR2 = 0.0348

R indices (all data)

R1 = 0.0232, wR2 = 0.0364

Largest diff. peak and hole

0.594 and -0.485 e.Å⁻³

Table S.17 Bond lengths [Å] and angles [°] for compound A[4].

| Bond                  | Length [Å] |
|-----------------------|------------|
| Bi(1)-C(13)           | 2.236(3)   |
| Bi(1)-C(1)            | 2.288(3)   |
| Bi(1)-C(12)           | 2.290(3)   |
| S(1)-O(2)             | 1.456(2)   |
| S(1)-O(1)             | 1.444(2)   |
| S(1)-C(7)             | 1.766(3)   |
| S(1)-C(6)             | 1.772(3)   |
| C(13)-C(14)           | 1.202(4)   |
| C(3)-H(3)             | 0.9500     |
| C(3)-C(4)             | 1.395(5)   |
| C(3)-C(2)             | 1.393(4)   |
| C(1)-C(2)             | 1.400(4)   |
| C(1)-C(6)             | 1.396(4)   |
| C(7)-C(12)            | 1.406(4)   |
| C(7)-C(8)             | 1.394(4)   |
| C(17)-H(17)           | 0.9500     |
| C(17)-C(16)           | 1.402(4)   |
| C(17)-C(18)           | 1.363(4)   |
| C(14)-C(15)           | 1.450(4)   |
| C(4)-H(4)             | 0.9500     |
| C(4)-C(5)             | 1.381(4)   |
| C(5)-H(5)             | 0.9500     |
C(5)-C(6) 1.398(4)
C(2)-H(2) 0.9500
C(20)-H(20) 0.9500
C(20)-C(15) 1.406(4)
C(20)-C(19) 1.379(5)
C(16)-H(16) 0.9500
C(16)-C(15) 1.406(4)
C(12)-C(11) 1.393(5)
C(11)-H(11) 0.9500
C(11)-C(10) 1.395(5)
C(10)-H(10) 0.9500
C(10)-C(9) 1.385(5)
C(8)-H(8) 0.9500
C(8)-C(9) 1.385(5)
C(18)-H(18) 0.9500
C(18)-C(19) 1.380(5)
C(19)-H(19) 0.9500
C(9)-H(9) 0.9500

C(13)-Bi(1)-C(1) 92.23(11)
C(13)-Bi(1)-C(12) 90.07(12)
C(1)-Bi(1)-C(12) 86.04(11)
O(2)-S(1)-C(7) 105.90(14)
O(2)-S(1)-C(6) 106.96(14)
O(1)-S(1)-O(2) 119.21(14)
O(1)-S(1)-C(7) 110.45(15)
O(1)-S(1)-C(6) 109.92(15)
C(7)-S(1)-C(6) 103.15(15)
C(14)-C(13)-Bi(1) 170.0(3)
C(4)-C(3)-H(3) 119.5
C(2)-C(3)-H(3) 119.5
C(2)-C(3)-C(4) 121.0(3)
C(2)-C(1)-Bi(1) 123.6(2)
C(6)-C(1)-Bi(1) 119.4(2)
C(6)-C(1)-C(2) 117.0(3)
C(12)-C(7)-S(1) 117.8(2)
C(8)-C(7)-S(1) 120.1(3)
C(8)-C(7)-C(12) 122.1(3)
C(16)-C(17)-H(17) 119.9
C(18)-C(17)-H(17) 119.9
C(18)-C(17)-C(16) 120.3(3)
C(13)-C(14)-C(15) 177.4(3)
C(3)-C(4)-H(4) 120.0
C(5)-C(4)-C(3) 120.1(3)
C(5)-C(4)-H(4) 120.0
C(4)-C(5)-H(5) 121.0
C(4)-C(5)-C(6) 118.1(3)
C(6)-C(5)-H(5) 121.0
C(3)-C(2)-C(1) 120.4(3)
C(3)-C(2)-H(2) 119.8
C(1)-C(2)-H(2) 119.8
C(15)-C(20)-H(20) 120.2
C(19)-C(20)-H(20) 120.2
C(19)-C(20)-C(15) 119.6(3)
C(17)-C(16)-H(16) 120.1
C(17)-C(16)-C(15) 119.8(3)
C(15)-C(16)-H(16) 120.1
C(7)-C(12)-Bi(1) 118.6(2)
C(11)-C(12)-Bi(1) 123.1(2)
C(11)-C(12)-C(7) 118.2(3)
C(20)-C(15)-C(14) 119.5(3)
C(20)-C(15)-C(16) 118.8(3)
C(16)-C(15)-C(14) 121.6(3)
C(12)-C(11)-H(11) 120.2
C(12)-C(11)-C(10) 119.7(3)
C(10)-C(11)-H(11) 120.2
C(1)-C(6)-S(1) 117.3(2)
C(1)-C(6)-C(5) 123.5(3)
C(5)-C(6)-S(1) 119.2(2)
C(11)-C(10)-H(10) 119.4
C(9)-C(10)-C(11) 121.3(3)
C(9)-C(10)-H(10) 119.4
C(7)-C(8)-H(8) 120.7
C(9)-C(8)-C(7) 118.6(3)
C(9)-C(8)-H(8) 120.7
C(17)-C(18)-H(18) 119.9
C(17)-C(18)-C(19) 120.2(3)
C(19)-C(18)-H(18) 119.9
C(20)-C(19)-C(18) 121.3(3)
C(20)-C(19)-H(19) 119.4
C(18)-C(19)-H(19) 119.4
C(10)-C(9)-H(9) 119.9
C(8)-C(9)-C(10) 120.1(3)
C(8)-C(9)-H(9) 119.9
X-Ray Crystallographic Analysis of bismuth(III) acetylide A[5]

The single-crystal X-ray diffraction studies were carried out on a Bruker APEX II ULTRA CCD diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å). Crystals of the subject compound were used as received. A 0.150 x 0.050 x 0.050 mm colorless prism crystal was mounted on a Cryoloop with Paratone N oil. Data were collected in a nitrogen gas stream at 100(2) K using ϖ scans. Crystal-to-detector distance was 40 mm using an exposure time of 8 seconds with a scan width of 1°. Data collection was 100.0% complete to 25.242° in θ. A total of 23898 reflections were collected. 3274 reflections were found to be symmetry independent, with a Rint of 0.0319. Indexing and unit cell refinement indicated a Primitive Triclinic lattice. The space group was found to be P-1. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Notes: Excellent data and refinement. There is a minor chemical disorder at the Br1 atom (93 % Br, 7 %H).

![Asymmetric unit in the crystal structure of compound A[5]](image)

**Figure S.4** Asymmetric unit in the crystal structure of compound A[5].

**Table S.18** Crystal data and structure refinement for compound A[5].

| Property                  | Value          |
|---------------------------|----------------|
| Empirical formula         | C20 H12.07 Bi Br0.92 O2 S |
| Formula weight            | 599.17         |
| Temperature               | 100.0 K        |
| Wavelength                | 0.71073 Å      |
| Crystal system            | Triclinic      |
| Space group               | P-1            |
Unit cell dimensions

\[a = 8.3788(8) \text{ Å} \quad \alpha = 69.917(3)^\circ.\]

\[b = 9.4899(9) \text{ Å} \quad \beta = 87.930(3)^\circ.\]

\[c = 12.4028(11) \text{ Å} \quad \gamma = 74.563(3)^\circ.\]

Volume

\[891.15(15) \text{ Å}^3\]

Z

2

Density (calculated)

2.233 Mg/m3

Absorption coefficient

12.093 mm-1

F(000)

559

Crystal size

0.15 x 0.05 x 0.05 mm3

Theta range for data collection

1.751 to 25.393°.

Index ranges

-10 \leq h \leq 10, -11 \leq k \leq 11, -14 \leq l \leq 14

Reflections collected

23898

Independent reflections

3274 [R(int) = 0.0319]

Completeness to theta = 25.242°

100.0 %

Absorption correction

Semi-empirical from equivalents

Max. and min. transmission

0.4901 and 0.3629

Refinement method

Full-matrix least-squares on F2

Data / restraints / parameters

3274 / 0 / 228

Goodness-of-fit on F2

1.074

Final R indices [I \geq 2\sigma(I)]

R1 = 0.0168, wR2 = 0.0320

R indices (all data)

R1 = 0.0205, wR2 = 0.0329

Extinction coefficient

n/a

Largest diff. peak and hole

0.733 and -0.509 e.Å-3

**Table S.19** Bond lengths [Å] and angles [°] for compound A[5].

| Bond | Length (Å) |
|------|------------|
| Bi(1)-C(8) | 2.231(3) |
| Bi(1)-C(9) | 2.271(3) |
| Bi(1)-C(20) | 2.281(3) |
| Br(1)-C(1) | 1.900(3) |
| S(1)-O(1) | 1.437(2) |
| S(1)-O(2) | 1.456(2) |
| S(1)-C(14) | 1.767(3) |
| S(1)-C(15) | 1.763(3) |
| C(1)-C(2) | 1.380(5) |
| C(1)-C(6) | 1.380(5) |
| C(2)-C(3) | 1.381(5) |
| C(3)-C(4) | 1.402(5) |
| C(4)-C(5) | 1.390(5) |
| C(4)-C(7) | 1.458(5) |
| C(5)-C(6) | 1.377(5) |
| C(7)-C(8) | 1.175(5) |
| C(9)-C(10) | 1.390(5) |
| C(9)-C(14) | 1.388(4) |
| C(10)-C(11) | 1.396(5) |
| C(11)-C(12) | 1.389(5) |
| C(12)-C(13) | 1.373(5) |
| C(13)-C(14) | 1.394(5) |
| Bond                  | Distance (Å) |
|-----------------------|--------------|
| C(15)-C(16)           | 1.391(4)     |
| C(15)-C(20)           | 1.393(4)     |
| C(16)-C(17)           | 1.385(5)     |
| C(17)-C(18)           | 1.384(5)     |
| C(18)-C(19)           | 1.392(5)     |
| C(19)-C(20)           | 1.387(5)     |
| C(8)-Bi(1)-C(9)       | 90.76(12)    |
| C(8)-Bi(1)-C(20)      | 95.13(12)    |
| C(9)-Bi(1)-C(20)      | 87.10(11)    |
| O(1)-S(1)-O(2)        | 119.00(14)   |
| O(1)-S(1)-C(14)       | 110.21(15)   |
| O(1)-S(1)-C(15)       | 109.69(15)   |
| O(2)-S(1)-C(14)       | 105.80(14)   |
| O(2)-S(1)-C(15)       | 105.77(14)   |
| C(15)-S(1)-C(14)      | 105.48(15)   |
| C(15)-S(1)-C(14)      | 119.9(3)     |
| C(2)-C(1)-Br(1)       | 118.5(3)     |
| C(2)-C(1)-C(6)        | 121.6(3)     |
| C(6)-C(1)-Br(1)       | 119.1(3)     |
| C(1)-C(2)-C(3)        | 119.1(3)     |
| C(2)-C(3)-C(4)        | 120.5(3)     |
| C(3)-C(4)-C(7)        | 119.9(3)     |
| C(5)-C(4)-C(3)        | 118.8(3)     |
| C(5)-C(4)-C(7)        | 121.3(3)     |
| C(6)-C(5)-C(4)        | 121.0(3)     |
| C(5)-C(5)-C(1)        | 119.0(3)     |
| C(8)-C(7)-C(4)        | 178.2(4)     |
| C(7)-C(8)-Bi(1)       | 159.8(3)     |
| C(10)-C(9)-Bi(1)      | 123.1(2)     |
| C(14)-C(9)-Bi(1)      | 119.3(2)     |
| C(14)-C(9)-C(10)      | 117.7(3)     |
| C(9)-C(10)-C(11)      | 120.3(3)     |
| C(12)-C(11)-C(10)     | 120.3(3)     |
| C(13)-C(12)-C(11)     | 120.4(3)     |
| C(12)-C(13)-C(14)     | 118.4(3)     |
| C(9)-C(14)-S(1)       | 117.8(2)     |
| C(9)-C(14)-C(13)      | 122.8(3)     |
| C(13)-C(14)-S(1)      | 119.3(2)     |
| C(16)-C(15)-S(1)      | 118.8(2)     |
| C(16)-C(15)-C(15)     | 122.6(3)     |
| C(20)-C(15)-S(1)      | 118.6(2)     |
| C(17)-C(16)-C(15)     | 118.6(3)     |
| C(18)-C(17)-C(16)     | 119.8(3)     |
| C(17)-C(18)-C(19)     | 120.9(3)     |
| C(20)-C(19)-C(18)     | 120.3(3)     |
| C(15)-C(20)-Bi(1)     | 118.3(2)     |
| C(19)-C(20)-Bi(1)     | 123.9(2)     |
| C(19)-C(20)-C(15)     | 117.8(3)     |
X-Ray Crystallographic Analysis of bismuth(III) acetylide A[6]

The single-crystal X-ray diffraction studies were carried out on a Bruker APEX II ULTRA CCD diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å). Crystals of the subject compound were used as received. A 0.190 x 0.100 x 0.050 mm colorless prism crystal was mounted on a Cryoloop with Paratone N oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and θ scans. Crystal-to-detector distance was 45 mm using an exposure time of 2 seconds with a scan width of 0.70°. Data collection was 100.0% complete to 25.242° in θ. A total of 18762 reflections were collected. 3830 reflections were found to be symmetry independent, with a Rint of 0.0335. Indexing and unit cell refinement indicated a Primitive Monoclinic lattice. The space group was found to be P21/c. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Notes: Excellent data and refinement. There is a minor chemical disorder with approximately 3% of the iodo-Bi starting material present.

Figure S.55 Asymmetric unit in the crystal structure of compound A[6].

Table S.20 Crystal data and structure refinement for compound A[6].

| Property                  | Value                  |
|---------------------------|------------------------|
| Empirical formula         | C21 H12 Bi F3 I0.03 O2 S |
| Formula weight            | 598.15                 |
| Temperature               | 100.0 K                |
| Wavelength                | 0.71073 Å              |
| Crystal system            | Monoclinic             |
Space group: P 1 21/c 1
Unit cell dimensions:
\[ a = 7.7441(5) \text{ Å} \quad \alpha = 90^\circ. \]
\[ b = 9.9411(7) \text{ Å} \quad \beta = 98.4280(10)^\circ. \]
\[ c = 24.6103(16) \text{ Å} \quad \gamma = 90^\circ. \]
Volume: 1874.2(2) Å³
Z: 4
Density (calculated): 2.120 Mg/m³
Absorption coefficient: 9.611 mm⁻¹
F(000): 1126
Crystal size: 0.19 x 0.1 x 0.05 mm³
Theta range for data collection: 1.673 to 26.368°.
Index ranges:
\[ -9 \leq h \leq 8, \quad -12 \leq k \leq 12, \quad -30 \leq l \leq 30 \]
Reflections collected: 18762
Independent reflections: 3830 [R(int) = 0.0335]
Completeness to theta = 25.242°: 100.0 %
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 0.2607 and 0.1551
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 3830 / 0 / 258
Goodness-of-fit on F²: 1.079
Final R indices [I>2sigma(I)]: R1 = 0.0189, wR2 = 0.0412
R indices (all data): R1 = 0.0219, wR2 = 0.0420
Extinction coefficient: n/a
Largest diff. peak and hole: 0.985 and -0.521 e.Å⁻³

**Table S.21** Bond lengths [Å] and angles [°] for compound A[6].

| Bond                  | Length (Å) |
|-----------------------|------------|
| Bi(1)-C(10)           | 2.263(3)   |
| Bi(1)-C(16)           | 2.267(3)   |
| Bi(1)-C(9)            | 2.210(5)   |
| Bi(1)-I(1)            | 2.931(17)  |
| S(1)-O(2)             | 1.449(2)   |
| S(1)-O(1)             | 1.439(2)   |
| S(1)-C(15)            | 1.765(3)   |
| S(1)-C(21)            | 1.778(3)   |
| F(1)-C(1)             | 1.322(4)   |
| C(15)-C(10)           | 1.393(4)   |
| C(15)-C(14)           | 1.393(4)   |
| F(3)-C(1)             | 1.325(5)   |
| F(2)-C(1)             | 1.333(5)   |
| C(5)-C(4)             | 1.395(5)   |
| C(5)-C(6)             | 1.403(5)   |
| C(5)-C(8)             | 1.434(5)   |
| C(5)-I(1)             | 2.122(17)  |
| C(10)-C(11)           | 1.384(4)   |
| C(16)-C(21)           | 1.382(4)   |
| C(16)-C(17)           | 1.390(4)   |
| C(21)-C(20)           | 1.390(4)   |
C(20)-H(20)  0.9500
C(20)-C(19)  1.385(5)
C(14)-H(14)  0.9500
C(14)-C(13)  1.385(5)
C(12)-H(12)  0.9500
C(12)-C(13)  1.380(5)
C(12)-C(11)  1.394(5)
C(18)-H(18)  0.9500
C(18)-C(19)  1.382(5)
C(18)-C(17)  1.393(5)
C(4)-H(4)    0.9500
C(4)-C(3)    1.383(5)
C(13)-H(13)  0.9500
C(2)-C(7)    1.392(5)
C(2)-C(3)    1.383(5)
C(2)-C(1)    1.477(5)
C(19)-H(19)  0.9500
C(9)-C(8)    1.222(7)
C(7)-H(7)    0.9500
C(7)-C(6)    1.366(5)
C(17)-H(17)  0.9500
C(6)-H(6)    0.9500
C(3)-H(3)    0.9500
C(11)-H(11)  0.9500

C(10)-Bi(1)-C(16)  85.21(10)
C(10)-Bi(1)-I(1)    89.2(3)
C(16)-Bi(1)-I(1)    89.6(3)
C(9)-Bi(1)-C(10)    92.67(13)
C(9)-Bi(1)-C(16)    92.72(12)
O(2)-S(1)-C(15)    106.45(13)
O(2)-S(1)-C(21)    106.44(14)
O(1)-S(1)-O(2)     118.82(14)
O(1)-S(1)-C(15)    110.52(15)
O(1)-S(1)-C(21)    109.77(14)
C(15)-S(1)-C(21)   103.72(14)
C(10)-C(15)-S(1)   117.5(2)
C(14)-C(15)-S(1)   119.8(3)
C(14)-C(15)-C(10)  122.7(3)
C(4)-C(5)-C(6)     118.6(3)
C(4)-C(5)-C(8)     121.1(3)
C(4)-C(5)-I(1)     115.3(5)
C(6)-C(5)-C(8)     120.1(3)
C(6)-C(5)-I(1)     125.9(4)
C(15)-C(10)-Bi(1)  119.0(2)
C(11)-C(10)-Bi(1)  123.2(2)
C(11)-C(10)-C(15)  117.8(3)
C(21)-C(16)-Bi(1)  118.9(2)
| Bond         | Angle     |
|--------------|-----------|
| C(21)-C(16)-C(17) | 117.6(3)  |
| C(17)-C(16)-Bi(1)   | 123.4(2)  |
| C(16)-C(21)-S(1)    | 117.7(2)  |
| C(16)-C(21)-C(20)   | 123.0(3)  |
| C(20)-C(21)-S(1)    | 119.4(2)  |
| C(21)-C(20)-H(20)   | 120.9     |
| C(19)-C(20)-C(21)   | 118.2(3)  |
| C(19)-C(20)-H(20)   | 120.9     |
| C(15)-C(14)-H(14)   | 121.0     |
| C(13)-C(14)-C(15)   | 118.0(3)  |
| C(13)-C(14)-H(14)   | 121.0     |
| C(13)-C(12)-H(12)   | 119.6     |
| C(13)-C(12)-C(11)   | 120.8(3)  |
| C(11)-C(12)-H(12)   | 119.6     |
| C(19)-C(18)-H(18)   | 119.9     |
| C(19)-C(18)-C(17)   | 120.3(3)  |
| C(17)-C(18)-H(18)   | 119.9     |
| C(5)-C(4)-H(4)      | 120.0     |
| C(3)-C(4)-C(5)      | 120.0(3)  |
| C(3)-C(4)-H(4)      | 120.0     |
| C(14)-C(13)-H(13)   | 119.8     |
| C(12)-C(13)-C(14)   | 120.4(3)  |
| C(12)-C(13)-H(13)   | 119.8     |
| C(7)-C(2)-C(1)      | 120.1(3)  |
| C(3)-C(2)-C(7)      | 119.8(3)  |
| C(3)-C(2)-C(1)      | 120.1(3)  |
| C(20)-C(19)-H(19)   | 119.8     |
| C(18)-C(19)-C(20)   | 120.4(3)  |
| C(18)-C(19)-H(19)   | 119.8     |
| C(8)-C(9)-Bi(1)     | 160.8(4)  |
| C(2)-C(7)-H(7)      | 120.1     |
| C(6)-C(7)-C(2)      | 119.8(3)  |
| C(6)-C(7)-H(7)      | 120.1     |
| C(16)-C(17)-C(18)   | 120.6(3)  |
| C(16)-C(17)-H(17)   | 119.7     |
| C(18)-C(17)-H(17)   | 119.7     |
| C(5)-C(6)-H(6)      | 119.4     |
| C(7)-C(6)-C(5)      | 121.2(3)  |
| C(7)-C(6)-H(6)      | 119.4     |
| C(4)-C(3)-H(3)      | 119.7     |
| C(2)-C(3)-C(4)      | 120.6(3)  |
| C(2)-C(3)-H(3)      | 119.7     |
| C(9)-C(8)-C(5)      | 175.0(4)  |
| C(10)-C(11)-C(12)   | 120.3(3)  |
| C(10)-C(11)-H(11)   | 119.9     |
| C(12)-C(11)-H(11)   | 119.9     |
| F(1)-C(1)-F(3)      | 106.2(3)  |
| F(1)-C(1)-F(2)      | 104.3(4)  |
| Bond                        | Distance (Å) |
|-----------------------------|--------------|
| F(1)-C(1)-C(2)             | 113.7(3)     |
| F(3)-C(1)-F(2)             | 105.8(4)     |
| F(3)-C(1)-C(2)             | 112.7(3)     |
| F(2)-C(1)-C(2)             | 113.3(3)     |
| C(5)-I(1)-Bi(1)            | 141.4(7)     |
X-Ray Crystallographic Analysis of bismuth(III) acetylide A[7]

The single-crystal X-ray diffraction studies were carried out on a Bruker Apex II Ultra2 CCD diffractometer equipped with Mo Kα radiation (λ = 0.71073). A 0.090 x 0.070 x 0.040 mm colorless crystal was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using φ and ϖ scans. Crystal-to-detector distance was 40 mm using exposure time 1.0s with a scan width of 0.80°. Data collection was 100.0% complete to 25.242° in θ. A total of 32975 reflections were collected covering the indices, -16<=h<=16, -9<=k<=9, -25<=l<=20. 4097 reflections were found to be symmetry independent, with a Rint of 0.0705. Indexing and unit cell refinement indicated a Primitive, Monoclinic lattice. The space group was found to be P21/c. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Notes: Proposed structure in agreement with model derived from diffraction data. Excellent data and refinement

Figure S.16 Asymmetric unit in the crystal structure of compound A[7].

Table S.22 Crystal data and structure refinement for compound A[7].

| Property                  | Value                                      |
|---------------------------|--------------------------------------------|
| Empirical formula         | C22 H17 Bi O3 S                            |
| Molecular formula         | C22 H17 Bi O3 S                            |
| Formula weight            | 570.39                                     |
| Temperature               | 100.0 K                                    |
| Wavelength                | 0.71073 Å                                  |
| Crystal system            | Monoclinic                                 |
| Space group               | P 1 21/c 1                                 |
| Unit cell dimensions      | a = 12.7269(4) Å  α = 90°.                 |
|                           | b = 7.4850(2) Å  β = 104.6713(8)°.         |
Table S.23 Bond lengths [Å] and angles [°] for compound A[7].

| Bond              | Length [Å] |
|-------------------|------------|
| Bi(1)-C(1)        | 2.294(3)   |
| Bi(1)-C(12)       | 2.270(3)   |
| Bi(1)-C(14)       | 2.230(3)   |
| S(1)-O(1)         | 1.453(2)   |
| S(1)-O(2)         | 1.437(2)   |
| S(1)-C(6)         | 1.764(3)   |
| S(1)-C(7)         | 1.768(3)   |
| O(3)-C(3)         | 1.365(3)   |
| O(3)-C(13)        | 1.430(4)   |
| C(9)-H(9)         | 0.9500     |
| C(9)-C(8)         | 1.390(5)   |
| C(9)-C(10)        | 1.390(5)   |
| C(2)-H(2)         | 0.9500     |
| C(2)-C(1)         | 1.390(4)   |
| C(2)-C(3)         | 1.401(4)   |
| C(21)-H(21)       | 0.9500     |
| C(21)-C(20)       | 1.393(5)   |
| C(21)-C(16)       | 1.391(4)   |
| C(1)-C(6)         | 1.393(4)   |
| C(3)-C(4)         | 1.395(4)   |
| C(13)-H(13A)      | 0.9800     |
| C(13)-H(13B)      | 0.9800     |
| C(13)-H(13C)      | 0.9800     |
| C(8)-H(8)         | 0.9500     |
C(8)-C(7) 1.399(4)
C(15)-C(16) 1.440(4)
C(15)-C(14) 1.210(4)
C(20)-H(20) 0.9500
C(20)-C(19) 1.384(5)
C(12)-C(11) 1.386(4)
C(12)-C(7) 1.395(4)
C(6)-C(5) 1.393(4)
C(19)-C(22) 1.503(4)
C(19)-C(18) 1.392(5)
C(16)-C(17) 1.404(4)
C(10)-H(10) 0.9500
C(10)-C(11) 1.400(4)
C(4)-H(4) 0.9500
C(4)-C(5) 1.385(4)
C(11)-H(11) 0.9500
C(5)-H(5) 0.9500
C(17)-H(17) 0.9500
C(17)-C(18) 1.382(4)
C(22)-H(22A) 0.9800
C(22)-H(22B) 0.9800
C(22)-H(22C) 0.9800
C(18)-H(18) 0.9500
C(12)-Bi(1)-C(1) 86.77(9)
C(14)-Bi(1)-C(1) 88.38(11)
C(14)-Bi(1)-C(12) 92.22(10)
O(1)-S(1)-C(6) 106.17(14)
O(1)-S(1)-C(7) 106.10(14)
O(2)-S(1)-O(1) 120.01(14)
O(2)-S(1)-C(6) 110.18(13)
O(2)-S(1)-C(7) 110.24(14)
C(6)-S(1)-C(7) 102.69(13)
C(3)-O(3)-C(13) 117.5(2)
C(8)-C(9)-H(9) 120.0
C(8)-C(9)-C(10) 120.0(3)
C(10)-C(9)-H(9) 120.0
C(1)-C(2)-H(2) 120.4
C(1)-C(2)-C(3) 119.3(3)
C(3)-C(2)-H(2) 120.4
C(20)-C(21)-H(21) 120.0
C(16)-C(21)-H(21) 120.0
C(16)-C(21)-C(20) 120.0(3)
C(2)-C(1)-Bi(1) 122.6(2)
C(2)-C(1)-C(6) 119.0(3)
C(6)-C(1)-Bi(1) 118.1(2)
O(3)-C(3)-C(2) 124.1(3)
O(3)-C(3)-C(4) 115.0(2)
| Bond                  | Length (Å) |
|----------------------|------------|
| C(4)-C(3)-C(2)      | 120.9(3)   |
| O(3)-C(13)-H(13A)   | 109.5      |
| O(3)-C(13)-H(13B)   | 109.5      |
| O(3)-C(13)-H(13C)   | 109.5      |
| H(13A)-C(13)-H(13B) | 109.5      |
| H(13A)-C(13)-H(13C) | 109.5      |
| H(13B)-C(13)-H(13C) | 109.5      |
| C(9)-C(8)-H(8)      | 120.9      |
| C(9)-C(8)-C(7)      | 118.3(3)   |
| C(7)-C(8)-H(8)      | 120.9      |
| C(14)-C(15)-C(16)   | 174.9(3)   |
| C(21)-C(20)-H(20)   | 119.4      |
| C(19)-C(20)-C(21)   | 121.2(3)   |
| C(19)-C(20)-H(20)   | 119.4      |
| C(11)-C(12)-Bi(1)   | 123.5(2)   |
| C(11)-C(12)-C(7)    | 117.6(3)   |
| C(7)-C(12)-Bi(1)    | 118.7(2)   |
| C(1)-C(6)-S(1)      | 117.6(2)   |
| C(1)-C(6)-C(5)      | 122.0(3)   |
| C(5)-C(6)-S(1)      | 120.4(2)   |
| C(20)-C(19)-C(22)   | 120.4(3)   |
| C(20)-C(19)-C(18)   | 118.5(3)   |
| C(18)-C(19)-C(22)   | 121.0(3)   |
| C(21)-C(16)-C(15)   | 122.0(3)   |
| C(21)-C(16)-C(17)   | 118.5(3)   |
| C(17)-C(16)-C(15)   | 119.2(3)   |
| C(9)-C(10)-H(10)    | 119.7      |
| C(9)-C(10)-C(11)    | 120.6(3)   |
| C(11)-C(10)-H(10)   | 119.7      |
| C(3)-C(4)-H(4)      | 120.0      |
| C(5)-C(4)-C(3)      | 119.9(3)   |
| C(5)-C(4)-H(4)      | 120.0      |
| C(12)-C(11)-C(10)   | 120.7(3)   |
| C(12)-C(11)-H(11)   | 119.7      |
| C(10)-C(11)-H(11)   | 119.7      |
| C(6)-C(5)-H(5)      | 120.6      |
| C(4)-C(5)-C(6)      | 118.8(3)   |
| C(4)-C(5)-H(5)      | 120.6      |
| C(8)-C(7)-S(1)      | 119.9(2)   |
| C(12)-C(7)-S(1)     | 117.3(2)   |
| C(12)-C(7)-C(8)     | 122.8(3)   |
| C(16)-C(17)-H(17)   | 119.7      |
| C(18)-C(17)-C(16)   | 120.6(3)   |
| C(18)-C(17)-H(17)   | 119.7      |
| C(19)-C(22)-H(22A)  | 109.5      |
| C(19)-C(22)-H(22B)  | 109.5      |
| C(19)-C(22)-H(22C)  | 109.5      |
| H(22A)-C(22)-H(22B) | 109.5      |
| Bond                        | Angle (°) |
|-----------------------------|-----------|
| H(22A)-C(22)-H(22C)        | 109.5     |
| H(22B)-C(22)-H(22C)        | 109.5     |
| C(15)-C(14)-Bi(1)          | 156.9(2)  |
| C(19)-C(18)-H(18)          | 119.6     |
| C(17)-C(18)-C(19)          | 120.7(3)  |
| C(17)-C(18)-H(18)          | 119.6     |
X-Ray Crystallographic Analysis of bismuth(III) acetylide A[8]

The single-crystal X-ray diffraction studies were carried out on a Bruker Apex II Ultra2 CCD diffractometer equipped with Mo Kα radiation (λ = 0.71073). A 0.160 x 0.140 x 0.040 mm colorless crystal was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using φ and ω scans. Crystal-to-detector distance was 40 mm using exposure time 1.0s with a scan width of 0.80°. Data collection was 100.0% complete to 25.242° in θ. A total of 18974 reflections were collected covering the indices, −16≤h≤16, −9≤k≤9, −20≤l≤25. 3886 reflections were found to be symmetry independent, with a R_int of 0.0508. Indexing and unit cell refinement indicated a Primitive, Monoclinic lattice. The space group was found to be P21/c. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Notes: Proposed structure in agreement with model derived from diffraction data. Excellent data and refinement

Figure S.67 Asymmetric unit in the crystal structure of compound A[8].

Table S.24 Crystal data and structure refinement for compound A[8].

| Property                  | Value          |
|---------------------------|----------------|
| Empirical formula         | C21 H14 Bi Cl O2 S |
| Molecular formula         | C21 H14 Bi Cl O2 S |
| Formula weight            | 574.81         |
| Temperature               | 100.0 K        |
| Wavelength                | 0.71073 Å      |
| Crystal system            | Monoclinic     |
Nazarova et al. Electrochemical Mechanistic Elucidation of BiCuAAC

Space group P 1 21/c 1
Unit cell dimensions
\(a = 12.7458(6) \text{ Å} \quad \alpha = 90^\circ.\)
\(b = 7.3360(3) \text{ Å} \quad \beta = 105.2780(10)^\circ.\)
\(c = 20.2483(8) \text{ Å} \quad \gamma = 90^\circ.\)
Volume 1826.37(14) Å³
Z 4
Density (calculated) 2.090 Mg/m³
Absorption coefficient 9.927 mm⁻¹
F(000) 1088
Crystal size 0.16 x 0.14 x 0.04 mm³
Crystal color, habit colorless irregular
Theta range for data collection 1.656 to 26.730°.
Index ranges
\(-16 <= h <= 16, -9 <= k <= 9, -20 <= l <= 25\)
Reflections collected 18974
Independent reflections 3886 [R(int) = 0.0508]
Completeness to theta = 25.242° 100.0 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.2612 and 0.1459
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 3886 / 0 / 236
Goodness-of-fit on F² 1.050
Final R indices [I>2sigma(I)] R1 = 0.0194, wR2 = 0.0487
R indices (all data) R1 = 0.0214, wR2 = 0.0499
Largest diff. peak and hole 1.068 and -0.449 e.Å⁻³

**Table S.25** Bond lengths [Å] and angles [°] for compound A[8].

| Bond | Length [Å] |
|------|------------|
| Bi(1)-C(1) | 2.284(3) |
| Bi(1)-C(12) | 2.270(3) |
| Bi(1)-C(13) | 2.230(3) |
| Cl(1)-C(3) | 1.749(3) |
| S(1)-O(2) | 1.452(2) |
| S(1)-O(1) | 1.436(2) |
| S(1)-C(6) | 1.770(3) |
| S(1)-C(7) | 1.767(3) |
| C(20)-H(20) | 0.9500 |
| C(20)-C(19) | 1.395(5) |
| C(20)-C(15) | 1.391(5) |
| C(6)-C(1) | 1.394(4) |
| C(6)-C(5) | 1.389(4) |
| C(17)-H(17) | 0.9500 |
| C(17)-C(18) | 1.395(5) |
| C(17)-C(16) | 1.382(4) |
| C(21)-H(21A) | 0.9800 |
| C(21)-H(21B) | 0.9800 |
| C(21)-H(21C) | 0.9800 |
| C(21)-C(18) | 1.500(4) |
| C(1)-C(2) | 1.393(4) |
C(11)-H(11) 0.9500
C(11)-C(12) 1.384(4)
C(11)-C(10) 1.396(4)
C(12)-C(7) 1.397(4)
C(5)-H(5) 0.9500
C(5)-C(4) 1.395(4)
C(8)-H(8) 0.9500
C(8)-C(9) 1.386(4)
C(8)-C(7) 1.394(4)
C(9)-H(9) 0.9500
C(9)-C(10) 1.392(5)
C(3)-C(2) 1.386(4)
C(3)-C(4) 1.383(4)
C(14)-C(13) 1.196(4)
C(14)-C(15) 1.444(4)
C(19)-H(19) 0.9500
C(19)-C(18) 1.391(5)
C(2)-H(2) 0.9500
C(10)-H(10) 0.9500
C(4)-H(4) 0.9500
C(15)-C(16) 1.401(4)
C(16)-H(16) 0.9500
C(12)-Bi(1)-C(1) 86.63(9)
C(13)-Bi(1)-C(1) 87.84(11)
C(13)-Bi(1)-C(12) 94.46(10)
O(2)-S(1)-C(6) 105.40(13)
O(2)-S(1)-C(7) 106.16(14)
O(1)-S(1)-O(2) 119.79(14)
O(1)-S(1)-C(6) 110.36(13)
O(1)-S(1)-C(7) 110.34(14)
C(7)-S(1)-C(6) 103.46(13)
C(19)-C(20)-H(20) 119.8
C(15)-C(20)-H(20) 119.8
C(15)-C(20)-C(19) 120.4(3)
C(1)-C(6)-S(1) 117.0(2)
C(5)-C(6)-S(1) 120.2(2)
C(5)-C(6)-C(1) 122.8(3)
C(18)-C(17)-H(17) 119.6
C(16)-C(17)-H(17) 119.6
C(16)-C(17)-C(18) 120.8(3)
H(21A)-C(21)-H(21B) 109.5
H(21A)-C(21)-H(21C) 109.5
H(21B)-C(21)-H(21C) 109.5
C(18)-C(21)-H(21A) 109.5
C(18)-C(21)-H(21B) 109.5
C(18)-C(21)-H(21C) 109.5
C(6)-C(1)-Bi(1) 118.7(2)
C(2)-C(1)-Bi(1) 123.0(2)
C(2)-C(1)-C(6) 118.2(3)
C(12)-C(11)-H(11) 119.8
C(12)-C(11)-C(10) 120.5(3)
C(10)-C(11)-H(11) 119.8
C(11)-C(12)-Bi(1) 123.6(2)
C(11)-C(12)-C(7) 117.9(3)
C(7)-C(12)-Bi(1) 118.4(2)
C(6)-C(5)-H(5) 120.7
C(6)-C(5)-C(4) 118.6(3)
C(4)-C(5)-H(5) 120.7
C(9)-C(8)-H(8) 120.8
C(9)-C(8)-C(7) 118.3(3)
C(7)-C(8)-H(8) 120.8
C(8)-C(9)-H(9) 119.9
C(8)-C(9)-C(10) 120.1(3)
C(10)-C(9)-H(9) 119.9
C(2)-C(3)-Cl(1) 118.1(2)
C(4)-C(3)-Cl(1) 118.9(2)
C(4)-C(3)-C(2) 123.0(3)
C(13)-C(14)-C(15) 176.4(3)
C(14)-C(13)-Bi(1) 155.6(3)
C(20)-C(19)-H(19) 119.5
C(18)-C(19)-C(20) 121.0(3)
C(18)-C(19)-H(19) 119.5
C(1)-C(2)-H(2) 120.6
C(3)-C(2)-C(1) 118.8(3)
C(3)-C(2)-H(2) 120.6
C(17)-C(18)-C(21) 120.9(3)
C(19)-C(18)-C(17) 118.3(3)
C(19)-C(18)-C(21) 120.7(3)
C(11)-C(10)-H(10) 119.8
C(9)-C(10)-C(11) 120.5(3)
C(9)-C(10)-H(10) 119.8
C(12)-C(7)-S(1) 117.7(2)
C(8)-C(7)-S(1) 119.7(2)
C(8)-C(7)-C(12) 122.6(3)
C(5)-C(4)-H(4) 120.7
C(3)-C(4)-C(5) 118.6(3)
C(3)-C(4)-H(4) 120.7
C(20)-C(15)-C(14) 121.9(3)
C(20)-C(15)-C(16) 118.4(3)
C(16)-C(15)-C(14) 119.5(3)
C(17)-C(16)-C(15) 120.9(3)
C(17)-C(16)-H(16) 119.6
C(15)-C(16)-H(16) 119.6
X-Ray Crystallographic Analysis of 2,8-dimethoxy-10-(p-tolylethynyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide A[9]

The single-crystal X-ray diffraction studies were carried out on a Bruker Apex II Ultra CCD diffractometer equipped with Mo Kα radiation (λ = 0.71073). Crystals of the subject compound were used as received. A 0.140 x 0.140 x 0.050 mm colorless crystal was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ω scans. Crystal-to-detector distance was 40 mm using exposure time 5 s with a scan width of 0.70°. Data collection was 100.0% complete to 25.242° in θ. A total of 25165 reflections were collected covering the indices, -9 ≤ h ≤ 9, -23 ≤ k ≤ 23, -16 ≤ l ≤ 16. 3952 reflections were found to be symmetry independent, with a Rint of 0.0281. Indexing and unit cell refinement indicated a Primitive, Monoclinic lattice. The space group was found to be P21/c. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Notes: Proposed structure in agreement with model derived from diffraction data. Minor disorder or chemical impurity/co-crystallized has not been modeled.

![Crystal structure](image)

**Figure S.18** Crystal structure of compound A[9].

**Table S.26** Crystal data and structure refinement for compound A[9].

| Property            | Value     |
|---------------------|-----------|
| Empirical formula   | C23 H19 Bi O4 S |
| Molecular formula   | C23 H19 Bi O4 S |
| Formula weight      | 600.42    |
| Temperature         | 100.0 K   |
| Wavelength          | 0.71073 Å |
Nazarova et al. Electrochemical Mechanistic Elucidation of BiCuAAC

Crystal system: Monoclinic
Space group: P 1 21/c 1
Unit cell dimensions:
- \( a = 7.6537(3) \) Å, \( \alpha = 90^\circ \)
- \( b = 19.4904(8) \) Å, \( \beta = 90.9170(10)^\circ \)
- \( c = 13.9017(6) \) Å, \( \gamma = 90^\circ \)
Volume: 2073.50(15) Å³
Z: 4
Density (calculated): 1.923 Mg/m³
Absorption coefficient: 8.630 mm⁻¹
F(000): 1152
Crystal size: 0.14 x 0.14 x 0.05 mm³
Crystal color, habit: colorless block
Theta range for data collection: 1.799 to 25.680°
Index ranges:
- \(-9 \leq h \leq 9\)
- \(-23 \leq k \leq 23\)
- \(-16 \leq l \leq 16\)
Reflections collected: 25165
Independent reflections: 3952 [R(int) = 0.0281]
Completeness to theta = 25.242°: 100.0%
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 0.0926 and 0.0606
Refinement method: Full-matrix least-squares on F²
Data / restraints / parameters: 3952 / 15 / 265
Goodness-of-fit on F²: 1.088
Final R indices [I>2sigma(I)]: R1 = 0.0261, wR2 = 0.0606
R indices (all data): R1 = 0.0305, wR2 = 0.0624
Largest diff. peak and hole: 3.365 and -1.161 e.Å⁻³

Table S.27 Bond lengths [Å] and angles [°] for compound A[9].

| Bond | Length [Å] |
|------|------------|
| Bi(1)-C(1) | 2.287(4) |
| Bi(1)-C(12) | 2.266(5) |
| Bi(1)-C(15) | 2.221(5) |
| S(1)-O(1) | 1.450(3) |
| S(1)-O(2) | 1.443(3) |
| S(1)-C(6) | 1.761(5) |
| S(1)-C(7) | 1.764(5) |
| O(3)-C(3) | 1.360(6) |
| O(3)-C(13) | 1.430(6) |
| O(4)-C(10) | 1.362(5) |
| O(4)-C(14) | 1.431(6) |
| C(1)-C(2) | 1.382(7) |
| C(1)-C(6) | 1.399(6) |
| C(2)-H(2) | 0.9500 |
| C(2)-C(3) | 1.401(7) |
| C(3)-C(4) | 1.395(7) |
| C(4)-H(4) | 0.9500 |
| C(4)-C(5) | 1.386(7) |
| C(5)-H(5) | 0.9500 |
| C(5)-C(6) | 1.389(7) |
C(7)-C(8) 1.385(6)
C(7)-C(12) 1.397(6)
C(8)-H(8) 0.9500
C(8)-C(9) 1.384(7)
C(9)-H(9) 0.9500
C(9)-C(10) 1.390(7)
C(10)-C(11) 1.398(6)
C(11)-H(11) 0.9500
C(11)-C(12) 1.400(6)
C(13)-H(13A) 0.9800
C(13)-H(13B) 0.9800
C(13)-H(13C) 0.9800
C(14)-H(14A) 0.9800
C(14)-H(14B) 0.9800
C(14)-H(14C) 0.9800
C(15)-C(16) 1.153(6)
C(16)-C(17) 1.478(7)
C(17)-C(18) 1.398(7)
C(17)-C(22) 1.393(7)
C(18)-H(18) 0.9500
C(18)-C(19) 1.385(7)
C(19)-H(19) 0.9500
C(19)-C(20) 1.390(8)
C(20)-C(21) 1.399(8)
C(20)-C(23) 1.507(7)
C(21)-H(21) 0.9500
C(21)-C(22) 1.385(7)
C(22)-H(22) 0.9500
C(23)-H(23A) 0.9800
C(23)-H(23B) 0.9800
C(23)-H(23C) 0.9800
C(12)-Bi(1)-C(1) 85.38(16)
C(15)-Bi(1)-C(1) 87.64(16)
C(15)-Bi(1)-C(12) 89.16(17)
O(1)-S(1)-C(6) 107.4(2)
O(1)-S(1)-C(7) 106.9(2)
O(2)-S(1)-O(1) 119.0(2)
O(2)-S(1)-C(6) 109.6(2)
O(2)-S(1)-C(7) 109.7(2)
C(6)-S(1)-C(7) 103.0(2)
C(3)-O(3)-C(13) 118.3(4)
C(10)-O(4)-C(14) 118.4(4)
C(2)-C(1)-Bi(1) 122.9(3)
C(2)-C(1)-C(6) 117.9(4)
C(6)-C(1)-Bi(1) 118.7(3)
C(1)-C(2)-H(2) 119.7
C(1)-C(2)-C(3) 120.7(4)
C(3)-C(2)-H(2) 119.7
O(3)-C(3)-C(2) 115.2(4)
O(3)-C(3)-C(4) 124.2(4)
C(4)-C(3)-C(2) 120.5(5)
C(3)-C(4)-H(4) 120.4
C(5)-C(4)-C(3) 119.3(4)
C(5)-C(4)-H(4) 120.4
C(4)-C(5)-H(5) 120.3
C(4)-C(5)-C(6) 119.5(4)
C(6)-C(5)-H(5) 120.3
C(1)-C(6)-S(1) 116.9(4)
C(5)-C(6)-S(1) 120.8(4)
C(5)-C(6)-C(1) 122.1(4)
C(8)-C(7)-S(1) 121.3(3)
C(8)-C(7)-C(12) 121.9(4)
C(12)-C(7)-S(1) 116.6(3)
C(7)-C(8)-H(8) 120.5
C(9)-C(8)-C(7) 119.0(4)
C(9)-C(8)-H(8) 120.5
C(8)-C(9)-C(10) 120.1(4)
C(10)-C(9)-H(9) 120.0
O(4)-C(10)-C(9) 115.6(4)
O(4)-C(10)-C(11) 123.4(4)
C(9)-C(10)-C(11) 121.0(4)
C(10)-C(11)-H(11) 120.4
C(10)-C(11)-C(12) 119.2(4)
C(12)-C(11)-H(11) 120.4
C(7)-C(12)-Bi(1) 119.4(3)
C(7)-C(12)-C(11) 118.8(4)
C(11)-C(12)-Bi(1) 121.5(3)
O(3)-C(13)-H(13A) 109.5
O(3)-C(13)-H(13B) 109.5
O(3)-C(13)-H(13C) 109.5
H(13A)-C(13)-H(13B) 109.5
H(13A)-C(13)-H(13C) 109.5
H(13B)-C(13)-H(13C) 109.5
O(4)-C(14)-H(14A) 109.5
O(4)-C(14)-H(14B) 109.5
O(4)-C(14)-H(14C) 109.5
H(14A)-C(14)-H(14B) 109.5
H(14A)-C(14)-H(14C) 109.5
H(14B)-C(14)-H(14C) 109.5
C(16)-C(15)-Bi(1) 168.9(4)
C(15)-C(16)-C(17) 172.4(5)
C(18)-C(17)-C(16) 121.7(4)
C(22)-C(17)-C(16) 119.2(4)
C(22)-C(17)-C(18) 119.0(5)
C(17)-C(18)-H(18) 119.8
C(19)-C(18)-C(17) 120.4(5)
C(19)-C(18)-H(18) 119.8
C(18)-C(19)-H(19) 119.5
C(18)-C(19)-C(20) 120.9(5)
C(20)-C(19)-H(19) 119.5
C(19)-C(20)-C(21) 118.3(5)
C(19)-C(20)-C(23) 121.3(5)
C(21)-C(20)-C(23) 120.4(5)
C(20)-C(21)-H(21) 119.4
C(22)-C(21)-C(20) 121.2(5)
C(22)-C(21)-H(21) 119.4
C(17)-C(22)-H(22) 119.9
C(21)-C(22)-C(17) 120.1(5)
C(21)-C(22)-H(22) 119.9
C(20)-C(23)-H(23A) 109.5
C(20)-C(23)-H(23B) 109.5
C(20)-C(23)-H(23C) 109.5
H(23A)-C(23)-H(23B) 109.5
H(23A)-C(23)-H(23C) 109.5
H(23B)-C(23)-H(23C) 109.5
**X-Ray Crystallographic Analysis of bismuth(III) acetylide A[10]**

The single-crystal X-ray diffraction studies were carried out on a Bruker Apex II Ultra CCD diffractometer equipped with Mo Kα radiation (λ = 0.71073). A 0.220 x 0.15 x 0.125 mm colorless crystal was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using φ and ϖ scans. Crystal-to-detector distance was 40 mm using exposure time 1s with a scan width of 0.80°. Data collection was 100.0% complete to 25.242° in θ. A total of 31005 reflections were collected covering the indices, -17<=h<=17, -12<=k<=12, -18<=l<=18. 3995 reflections were found to be symmetry independent, with a Rint of 0.0705. Indexing and unit cell refinement indicated a Primitive, Monoclinic lattice. The space group was found to be P2₁/c. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Notes: Proposed structure in agreement with model derived from diffraction data. Slightly higher residual density 3.38 e.Å⁻³ possibly due to minor disorder

**Figure S.197** Asymmetric unit in the crystal structure of compound A[10].

**Table S.28** Crystal data and structure refinement for compound A[10].

| Property                        | Value     |
|---------------------------------|-----------|
| Empirical formula               | C22 H14 Bi F3 O2 S |
| Molecular formula               | C22 H14 Bi F3 O2 S |
| Formula weight                  | 608.37    |
| Temperature                     | 100.0 K   |
| Wavelength                      | 0.71073 Å |
Nazarova et al. Electrochemical Mechanistic Elucidation of BiCuAAC

Crystal system: Monoclinic
Space group: P 1 21/c 1
Unit cell dimensions:
- \( a = 14.1582(7) \, \text{Å} \)  \( \alpha = 90^\circ \)
- \( b = 9.6556(5) \, \text{Å} \)  \( \beta = 100.4560(10)^\circ \)
- \( c = 14.5266(7) \, \text{Å} \)  \( \gamma = 90^\circ \)
Volume: 1952.90(17) \, \text{Å}^3
Z: 4
Density (calculated): 2.069 Mg/m3
Absorption coefficient: 9.179 mm\(^{-1}\)
F(000): 1152
Crystal size: 0.22 x 0.15 x 0.125 mm\(^3\)
Crystal color, habit: colorless irregular
Theta range for data collection: 1.463 to 26.370\(^\circ\)
Index ranges:
- \(-17 \leq h \leq 17\)
- \(-12 \leq k \leq 12\)
- \(-18 \leq l \leq 17\)
Reflections collected: 31005
Independent reflections: 3995 \([R(int) = 0.0705]\)
Completeness to theta = 25.242\(^\circ\): 100.0 %
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 0.2607 and 0.1761
Refinement method: Full-matrix least-squares on \( F^2 \)
Data / restraints / parameters: 3995 / 0 / 263
Goodness-of-fit on \( F^2 \): 1.031
Final R indices \([I>2\sigma(I)]\):  R1 = 0.0242, \( wR2 = 0.0628 \)
R indices (all data):  R1 = 0.0264, \( wR2 = 0.0639 \)
Largest diff. peak and hole: 3.380 and -0.951 e.Å\(^{-3}\)

Table S.29 Bond lengths [Å] and angles [°] for compound A[10].

| Bond                  | Length [Å] |
|-----------------------|------------|
| Bi(1)-C(1)            | 2.277(4)   |
| Bi(1)-C(12)           | 2.271(4)   |
| Bi(1)-C(14)           | 2.209(4)   |
| S(1)-O(1)             | 1.446(3)   |
| S(1)-O(2)             | 1.439(3)   |
| S(1)-C(6)             | 1.768(4)   |
| S(1)-C(7)             | 1.763(4)   |
| F(1)-C(13)            | 1.322(5)   |
| F(2)-C(13)            | 1.331(5)   |
| F(3)-C(13)            | 1.349(5)   |
| C(1)-C(2)             | 1.394(5)   |
| C(1)-C(6)             | 1.398(5)   |
| C(2)-C(3)             | 1.390(5)   |
| C(3)-C(4)             | 1.384(6)   |
| C(3)-C(13)            | 1.497(6)   |
| C(4)-C(5)             | 1.397(6)   |
| C(5)-C(6)             | 1.388(5)   |
| C(7)-C(8)             | 1.390(5)   |
| C(7)-C(12)            | 1.398(5)   |
| C(8)-C(9)             | 1.388(6)   |
C(9)-C(10) 1.388(6)
C(10)-C(11) 1.397(6)
C(11)-C(12) 1.396(5)
C(14)-C(15) 1.198(6)
C(15)-C(16) 1.447(6)
C(16)-C(17) 1.404(6)
C(16)-C(21) 1.401(6)
C(17)-C(18) 1.380(6)
C(18)-C(19) 1.384(6)
C(19)-C(20) 1.396(6)
C(19)-C(22) 1.509(6)
C(20)-C(21) 1.387(5)
C(12)-Bi(1)-C(1) 86.56(13)
C(14)-Bi(1)-C(1) 86.97(14)
C(14)-Bi(1)-C(12) 92.50(14)
O(1)-S(1)-C(6) 105.38(17)
O(1)-S(1)-C(7) 107.05(18)
O(2)-S(1)-O(1) 119.73(17)
O(2)-S(1)-C(6) 109.47(18)
O(2)-S(1)-C(7) 110.08(18)
C(7)-S(1)-C(6) 103.93(18)
C(2)-C(1)-Bi(1) 122.3(3)
C(2)-C(1)-C(6) 117.2(3)
C(6)-C(1)-Bi(1) 120.2(3)
C(3)-C(2)-C(1) 120.1(4)
C(2)-C(3)-C(13) 120.8(4)
C(4)-C(3)-C(2) 121.9(4)
C(4)-C(3)-C(13) 117.3(4)
C(3)-C(4)-C(5) 119.0(4)
C(6)-C(5)-C(4) 118.5(4)
C(1)-C(6)-S(1) 118.1(3)
C(5)-C(6)-S(1) 118.6(3)
C(5)-C(6)-C(1) 123.3(3)
C(8)-C(7)-S(1) 118.8(3)
C(8)-C(7)-C(12) 122.9(4)
C(12)-C(7)-S(1) 118.3(3)
C(9)-C(8)-C(7) 118.6(4)
C(10)-C(9)-C(8) 119.7(4)
C(9)-C(10)-C(11) 121.2(4)
C(12)-C(11)-C(10) 120.1(4)
C(7)-C(12)-Bi(1) 120.5(3)
C(11)-C(12)-Bi(1) 122.0(3)
C(11)-C(12)-C(7) 117.5(4)
F(1)-C(13)-F(2) 108.1(4)
F(1)-C(13)-F(3) 105.9(3)
F(1)-C(13)-C(3) 113.5(3)
F(2)-C(13)-F(3) 105.0(3)
F(2)-C(13)-C(3) 112.6(3)
| Bond                  | Angle (°) |
|----------------------|-----------|
| F(3)-C(13)-C(3)      | 111.2(3)  |
| C(15)-C(14)-Bi(1)    | 166.1(4)  |
| C(14)-C(15)-C(16)    | 176.1(4)  |
| C(17)-C(16)-C(15)    | 119.9(4)  |
| C(21)-C(16)-C(15)    | 121.9(4)  |
| C(21)-C(15)-C(17)    | 118.1(4)  |
| C(18)-C(17)-C(16)    | 120.8(4)  |
| C(17)-C(18)-C(19)    | 121.2(4)  |
| C(18)-C(19)-C(20)    | 118.4(4)  |
| C(18)-C(19)-C(22)    | 121.0(4)  |
| C(20)-C(19)-C(22)    | 120.6(4)  |
| C(21)-C(20)-C(19)    | 121.1(4)  |
| C(20)-C(21)-C(16)    | 120.4(4)  |
X-Ray Crystallographic Analysis of 10-phenyl-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide 26

The single-crystal X-ray diffraction studies were carried out on a Bruker Apex II Ultra CCD diffractometer equipped with Mo Kα radiation (λ = 0.71073). Crystals of the subject compound were used as received. A 0.200 x 0.030 x 0.030 mm colorless crystal was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 50 mm using exposure time 4s with a scan width of 0.70°. Data collection was 99.9% complete to 25.242° in θ. A total of 23456 reflections were collected covering the indices, -30<=h<=29, -17<=k<=17, -6<=l<=6. 3614 reflections were found to be symmetry independent, with a Rint of 0.0393. Indexing and unit cell refinement indicated a Primitive, Orthorhombic lattice. The space group was found to be Pna21. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Notes: Proposed structure in agreement with model derived from diffraction data. Minor twin component tried hkl5 but return to single domain integration.

**Figure S.8** Crystal structure of compound 26.

**Table S.30** Crystal data and structure refinement for compound 26.

| Property                  | Value          |
|---------------------------|----------------|
| Empirical formula         | C19 H12 Bi F3 O2 S |
| Molecular formula         | C19 H12 Bi F3 O2 S |
| Formula weight            | 570.33         |
| Temperature               | 100.0 K        |
| Wavelength                | 0.71073 Å      |
| Crystal system            | Orthorhombic   |
| Space group               | Pna21          |
Unit cell dimensions

\[
\begin{align*}
    a &= 24.2413(8) \text{ Å} \quad \alpha = 90^\circ. \\
    b &= 14.1185(5) \text{ Å} \quad \beta = 90^\circ. \\
    c &= 5.1234(2) \text{ Å} \quad \gamma = 90^\circ.
\end{align*}
\]

Volume

\[1753.49(11) \text{ Å}^3\]

Z

4

Density (calculated)

\[2.160 \text{ Mg/m}^3\]

Absorption coefficient

\[10.214 \text{ mm}^{-1}\]

F(000)

1072

Crystal size

0.2 x 0.03 x 0.03 mm³

Crystal color, habit

colorless plank

Theta range for data collection

1.669 to 26.437°.

Index ranges

-30 ≤ h ≤ 29, -17 ≤ k ≤ 17, -6 ≤ l ≤ 6

Reflections collected

23456

Independent reflections

3614 [R(int) = 0.0393]

Completeness to theta = 25.242°

99.9 %

Absorption correction

Semi-empirical from equivalents

Max. and min. transmission

0.0452 and 0.0204

Refinement method

Full-matrix least-squares on F²

Data / restraints / parameters

3614 / 37 / 235

Goodness-of-fit on F²

1.092

Final R indices [I>2\sigma(I)]

R1 = 0.0259, wR2 = 0.0546

R indices (all data)

R1 = 0.0290, wR2 = 0.0566

Absolute structure parameter

-0.007(6)

Largest diff. peak and hole

1.276 and -2.343 e.Å⁻³

Table S.31 Bond lengths [Å] and angles [°] for compound 26.

| Bond          | Length [Å] |
|---------------|------------|
| Bi(1)-C(1)    | 2.292(9)   |
| Bi(1)-C(12)   | 2.260(8)   |
| Bi(1)-C(14)   | 2.273(9)   |
| S(1)-O(1)     | 1.436(10)  |
| S(1)-O(2)     | 1.439(6)   |
| S(1)-C(6)     | 1.778(9)   |
| S(1)-C(7)     | 1.752(8)   |
| F(1)-C(13)    | 1.285(13)  |
| F(2)-C(13)    | 1.308(13)  |
| F(3)-C(13)    | 1.261(12)  |
| C(1)-C(2)     | 1.390(12)  |
| C(1)-C(6)     | 1.396(12)  |
| C(2)-C(3)     | 1.398(15)  |
| C(3)-C(4)     | 1.383(13)  |
| C(3)-C(13)    | 1.501(13)  |
| C(4)-C(5)     | 1.389(12)  |
| C(5)-C(6)     | 1.395(12)  |
| C(7)-C(8)     | 1.401(11)  |
| C(7)-C(12)    | 1.398(11)  |
| C(8)-C(9)     | 1.395(12)  |
| C(9)-C(10)    | 1.383(12)  |
| Bond                | Distance (Å) |
|---------------------|--------------|
| C(10)-C(11)         | 1.423(11)    |
| C(11)-C(12)         | 1.395(12)    |
| C(14)-C(15)         | 1.383(11)    |
| C(14)-C(19)         | 1.398(11)    |
| C(15)-C(16)         | 1.383(13)    |
| C(16)-C(17)         | 1.367(13)    |
| C(17)-C(18)         | 1.377(12)    |
| C(18)-C(19)         | 1.390(12)    |
| C(12)-Bi(1)-C(1)   | 86.4(3)      |
| C(12)-Bi(1)-C(14)  | 97.7(3)      |
| C(14)-Bi(1)-C(1)   | 89.3(3)      |
| O(1)-S(1)-O(2)     | 118.8(3)     |
| O(1)-S(1)-C(6)     | 105.7(3)     |
| O(1)-S(1)-C(7)     | 107.7(4)     |
| O(2)-S(1)-C(6)     | 109.9(4)     |
| O(2)-S(1)-C(7)     | 109.9(4)     |
| C(7)-S(1)-C(6)     | 103.7(4)     |
| C(2)-C(1)-Bi(1)    | 121.9(7)     |
| C(2)-C(1)-C(6)     | 117.5(8)     |
| C(6)-C(1)-Bi(1)    | 120.6(6)     |
| C(1)-C(2)-C(3)     | 120.1(8)     |
| C(2)-C(3)-C(13)    | 119.2(8)     |
| C(4)-C(3)-C(2)     | 121.2(8)     |
| C(4)-C(3)-C(13)    | 119.6(10)    |
| C(3)-C(4)-C(5)     | 119.9(9)     |
| C(4)-C(5)-C(6)     | 118.1(8)     |
| C(1)-C(6)-S(1)     | 117.4(7)     |
| C(5)-C(6)-S(1)     | 119.5(7)     |
| C(5)-C(6)-C(1)     | 123.1(8)     |
| C(8)-C(7)-S(1)     | 118.9(6)     |
| C(12)-C(7)-S(1)    | 118.9(6)     |
| C(12)-C(7)-C(8)    | 122.2(8)     |
| C(9)-C(8)-C(7)     | 119.1(8)     |
| C(10)-C(9)-C(8)    | 120.2(8)     |
| C(9)-C(10)-C(11)   | 120.0(8)     |
| C(12)-C(11)-C(10)  | 120.6(8)     |
| C(7)-C(12)-Bi(1)   | 120.1(6)     |
| C(11)-C(12)-Bi(1)  | 122.1(6)     |
| C(11)-C(12)-C(7)   | 117.9(8)     |
| F(1)-C(13)-F(2)    | 103.0(11)    |
| F(1)-C(13)-C(3)    | 111.6(10)    |
| F(2)-C(13)-C(3)    | 113.2(9)     |
| F(3)-C(13)-F(1)    | 107.4(10)    |
| F(3)-C(13)-F(2)    | 106.1(11)    |
| F(3)-C(13)-C(3)    | 114.7(9)     |
| C(15)-C(14)-Bi(1)  | 125.0(6)     |
| C(15)-C(14)-C(19)  | 119.5(8)     |
| Bond                  | Angle (°)  |
|----------------------|-----------|
| C(19)-C(14)-Bi(1)    | 115.4(6)  |
| C(16)-C(15)-C(14)    | 119.3(9)  |
| C(17)-C(16)-C(15)    | 121.7(11) |
| C(16)-C(17)-C(18)    | 119.2(10) |
| C(17)-C(18)-C(19)    | 120.5(8)  |
| C(18)-C(19)-C(14)    | 119.6(8)  |
X-Ray Crystallographic Analysis of 10-phenyl-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide 28

The single-crystal X-ray diffraction studies were carried out on a Bruker Kappa Apex II CCD diffractometer equipped with Mo Ka radiation (λ = 0.71073). A 0.180 x 0.150 x 0.130 mm colorless crystal was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using φ and ω scans. Crystal-to-detector distance was 40 mm using exposure time 2s with a scan width of 0.70°. Data collection was 99.9% complete to 25.242° in θ. A total of 13836 reflections were collected covering the indices, -12<=h<=11, -12<=k<=9, -13<=l<=10. 3650 reflections were found to be symmetry independent, with a Rint of 0.0323. Indexing and unit cell refinement indicated a Primitive, Triclinic lattice. The space group was found to be P-1. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Notes: Proposed structure in agreement with model derived from diffraction data. Excellent data and refinement

Figure S.219 Crystal structure of compound 28.

Table S.32 Crystal data and structure refinement for compound 28.

| Property                  | Value       |
|---------------------------|-------------|
| Empirical formula         | C20 H17 Bi O4 S |
| Molecular formula         | C20 H17 Bi O4 S |
| Formula weight            | 562.38      |
| Temperature               | 100.0 K     |
| Wavelength                | 0.71073 Å   |
Nazarova et al. Electrochemical Mechanistic Elucidation of BiCuAAC

Crystal system
Triclinic
Space group
P-1
Unit cell dimensions
\( a = 9.9992(7) \text{ Å} \quad \alpha = 69.723(2)^\circ. \)
\( b = 10.2711(7) \text{ Å} \quad \beta = 86.066(2)^\circ. \)
\( c = 10.5288(7) \text{ Å} \quad \gamma = 62.662(2)^\circ. \)
Volume
895.70(11) Å³
Z
2
Density (calculated)
2.085 Mg/m³
Absorption coefficient
9.982 mm⁻¹
\( F(000) \)
536
Crystal size
0.175 x 0.035 x 0.02 mm³
Crystal color, habit
colorless plank
Theta range for data collection
2.074 to 26.372°.
Index ranges
\(-12 \leq h \leq 11, -12 \leq k \leq 9, -13 \leq l \leq 10 \)
Reflections collected
13836
Independent reflections
3650 [R(int) = 0.0323]
Completeness to theta = 25.242°
99.9 %
Absorption correction
Semi-empirical from equivalents
Max. and min. transmission
0.2607 and 0.1758
Refinement method
Full-matrix least-squares on F²
Data / restraints / parameters
3650 / 0 / 237
Goodness-of-fit on F²
1.050
Final R indices [I>2sigma(I)]
R1 = 0.0164, wR2 = 0.0359
R indices (all data)
R1 = 0.0183, wR2 = 0.0364
Largest diff. peak and hole
0.638 and -0.661 e.Å⁻³

Table S.33 Bond lengths [Å] and angles [°] for compound 28.

| Bond                  | Length [Å] |
|-----------------------|------------|
| Bi(1)-C(1)            | 2.263(3)   |
| Bi(1)-C(12)           | 2.288(3)   |
| Bi(1)-C(15)           | 2.265(3)   |
| S(1)-O(3)             | 1.450(2)   |
| S(1)-O(4)             | 1.441(2)   |
| S(1)-C(6)             | 1.778(3)   |
| S(1)-C(7)             | 1.767(3)   |
| O(1)-C(2)             | 1.370(3)   |
| O(1)-C(13)            | 1.439(3)   |
| O(2)-C(4)             | 1.366(3)   |
| O(2)-C(14)            | 1.439(3)   |
| C(1)-C(2)             | 1.399(4)   |
| C(1)-C(6)             | 1.392(4)   |
| C(2)-C(3)             | 1.387(4)   |
| C(3)-H(3)             | 0.9500     |
| C(3)-C(4)             | 1.401(4)   |
| C(4)-C(5)             | 1.392(4)   |
| C(5)-H(5)             | 0.9500     |
| C(5)-C(6)             | 1.387(4)   |
| C(7)-C(8)             | 1.395(4)   |
| Bond                  | Distance (Å) |
|----------------------|--------------|
| C(7)-C(12)           | 1.395(4)     |
| C(8)-H(8)            | 0.9500       |
| C(8)-C(9)            | 1.384(4)     |
| C(9)-H(9)            | 0.9500       |
| C(9)-C(10)           | 1.389(4)     |
| C(10)-H(10)          | 0.9500       |
| C(10)-C(11)          | 1.382(4)     |
| C(11)-H(11)          | 0.9500       |
| C(11)-C(12)          | 1.390(4)     |
| C(13)-H(13A)         | 0.9800       |
| C(13)-H(13B)         | 0.9800       |
| C(13)-H(13C)         | 0.9800       |
| C(14)-H(14A)         | 0.9800       |
| C(14)-H(14B)         | 0.9800       |
| C(14)-H(14C)         | 0.9800       |
| C(15)-C(16)          | 1.390(4)     |
| C(15)-C(20)          | 1.390(4)     |
| C(16)-H(16)          | 0.9500       |
| C(16)-C(17)          | 1.394(4)     |
| C(17)-H(17)          | 0.9500       |
| C(17)-C(18)          | 1.384(4)     |
| C(18)-H(18)          | 0.9500       |
| C(18)-C(19)          | 1.385(4)     |
| C(19)-H(19)          | 0.9500       |
| C(19)-C(20)          | 1.400(4)     |
| C(20)-H(20)          | 0.9500       |
| C(1)-Bi(1)-C(12)     | 87.99(10)    |
| C(1)-Bi(1)-C(15)     | 97.72(10)    |
| C(15)-Bi(1)-C(12)    | 87.27(10)    |
| O(3)-S(1)-C(6)       | 106.45(13)   |
| O(3)-S(1)-C(7)       | 107.06(13)   |
| O(4)-S(1)-O(3)       | 118.80(12)   |
| O(4)-S(1)-C(6)       | 109.07(13)   |
| O(4)-S(1)-C(7)       | 109.00(13)   |
| C(7)-S(1)-C(6)       | 105.69(13)   |
| C(2)-O(1)-C(13)      | 117.8(2)     |
| C(4)-O(2)-C(14)      | 117.0(2)     |
| C(2)-C(1)-Bi(1)      | 121.2(2)     |
| C(6)-C(1)-Bi(1)      | 122.2(2)     |
| C(6)-C(1)-C(2)       | 116.3(2)     |
| O(1)-C(2)-C(1)       | 114.3(2)     |
| O(1)-C(2)-C(3)       | 123.8(3)     |
| C(3)-C(2)-C(1)       | 121.8(3)     |
| C(2)-C(3)-H(3)       | 120.4        |
| C(2)-C(3)-C(4)       | 119.2(3)     |
| C(4)-C(3)-H(3)       | 120.4        |
| O(2)-C(4)-C(3)       | 114.6(2)     |
O(2)-C(4)-C(5) 124.4(3)
C(5)-C(4)-C(3) 121.0(3)
C(4)-C(5)-H(5) 121.4
C(6)-C(5)-C(4) 117.3(3)
C(6)-C(5)-H(5) 121.4
C(1)-C(6)-S(1) 118.3(2)
C(5)-C(6)-S(1) 117.1(2)
C(5)-C(6)-C(1) 124.2(3)
C(8)-C(7)-S(1) 118.9(2)
C(8)-C(7)-C(12) 122.6(3)
C(12)-C(7)-S(1) 118.5(2)
C(7)-C(8)-H(8) 120.8
C(9)-C(8)-C(7) 118.4(3)
C(9)-C(8)-H(8) 120.8
C(8)-C(9)-H(9) 120.1
C(8)-C(9)-C(10) 119.8(3)
C(10)-C(9)-H(9) 120.1
C(9)-C(10)-H(10) 119.6
C(11)-C(10)-C(9) 120.9(3)
C(11)-C(10)-H(10) 119.6
C(10)-C(11)-H(11) 119.6
C(10)-C(11)-C(12) 120.8(3)
C(12)-C(11)-H(11) 119.6
C(7)-C(12)-Bi(1) 121.4(2)
C(11)-C(12)-Bi(1) 121.1(2)
C(11)-C(12)-C(7) 117.3(3)
O(1)-C(13)-H(13A) 109.5
O(1)-C(13)-H(13B) 109.5
O(1)-C(13)-H(13C) 109.5
H(13A)-C(13)-H(13B) 109.5
H(13A)-C(13)-H(13C) 109.5
H(13B)-C(13)-H(13C) 109.5
O(2)-C(14)-H(14A) 109.5
O(2)-C(14)-H(14B) 109.5
O(2)-C(14)-H(14C) 109.5
H(14A)-C(14)-H(14B) 109.5
H(14A)-C(14)-H(14C) 109.5
H(14B)-C(14)-H(14C) 109.5
C(16)-C(15)-Bi(1) 115.8(2)
C(20)-C(15)-Bi(1) 124.6(2)
C(20)-C(15)-C(16) 118.9(3)
C(15)-C(16)-H(16) 119.8
C(15)-C(16)-C(17) 120.5(3)
C(17)-C(16)-H(16) 119.8
C(16)-C(17)-H(17) 119.9
C(18)-C(17)-C(16) 120.2(3)
C(18)-C(17)-H(17) 119.9
C(17)-C(18)-H(18) 120.0
| Bond                  | Angle (°) |
|-----------------------|-----------|
| C(17)-C(18)-C(19)    | 120.0(3)  |
| C(19)-C(18)-H(18)    | 120.0     |
| C(18)-C(19)-H(19)    | 120.2     |
| C(18)-C(19)-C(20)    | 119.6(3)  |
| C(20)-C(19)-H(19)    | 120.2     |
| C(15)-C(20)-C(19)    | 120.7(3)  |
| C(15)-C(20)-H(20)    | 119.7     |
| C(19)-C(20)-H(20)    | 119.7     |
X-Ray Crystallographic Analysis of 10-iodo-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide 33

The single-crystal X-ray diffraction studies were carried out on a Bruker Apex II Ultra CCD diffractometer equipped with Mo Kα radiation (λ = 0.71073). A 0.140 x 0.025 x 0.025 mm colorless crystal was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using φ and ω scans. Crystal-to-detector distance was 60 mm using exposure time 3s with a scan width of 0.60°. Data collection was 99.9% complete to 25.242° in θ. A total of 14363 reflections were collected covering the indices, -11<=h<=11, -6<=k<=6, -44<=l<=29. 3213 reflections were found to be symmetry independent, with a Rint of 0.0204. Indexing and unit cell refinement indicated a Primitive, Monoclinic lattice. The space group was found to be P21/n. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Notes: Proposed structure in agreement with model derived from diffraction data. Excellent data and refinement

Figure S.22 Crystal structure of compound 33.

Table S.34 Crystal data and structure refinement for compound 33.

| Property                | Value          |
|-------------------------|----------------|
| Empirical formula       | C14 H12 Bi I O4 S |
| Molecular formula       | C14 H12 Bi I O4 S |
| Formula weight          | 612.18         |
| Temperature             | 100.0 K        |
| Wavelength              | 0.71073 Å      |
| Crystal system          | Monoclinic     |
| Space group             | P 1 21/n 1     |
Unit cell dimensions

\[ a = 9.1914(6) \text{ Å} \quad \alpha = 90^\circ. \]
\[ b = 4.8207(3) \text{ Å} \quad \beta = 91.7600(10)^\circ. \]
\[ c = 35.739(2) \text{ Å} \quad \gamma = 90^\circ. \]

Volume

1582.82(18) Å³

\( Z = 4 \)

Density (calculated)

2.569 Mg/m³

Absorption coefficient

13.232 mm⁻¹

F(000)

1120

Crystal size

0.14 x 0.025 x 0.025 mm³

Crystal color, habit

colorless plank

Theta range for data collection

2.272 to 26.372°.

Index ranges

\(-11 \leq h \leq 11, -6 \leq k \leq 6, -44 \leq l \leq 29\)

Reflections collected

14363

Independent reflections

3213 \([R(\text{int}) = 0.0204]\)

Completeness to theta = 25.242°

99.9 %

Absorption correction

Semi-empirical from equivalents

Max. and min. transmission

0.2607 and 0.1503

Refinement method

Full-matrix least-squares on F²

Data / restraints / parameters

3213 / 0 / 192

Goodness-of-fit on F²

1.251

Final R indices \([I>2\sigma(I)]\)

R1 = 0.0186, wR2 = 0.0395

R indices (all data)

R1 = 0.0190, wR2 = 0.0396

Largest diff. peak and hole

0.855 and -1.101 e.Å⁻³

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**Table S.35 Bond lengths [Å] and angles [°] for compound 33.**

| Bond                  | Length  [Å] |
|-----------------------|------------|
| Bi(1)-I(1)            | 2.8715(3)  |
| Bi(1)-C(1)            | 2.275(4)   |
| Bi(1)-C(12)           | 2.270(4)   |
| S(1)-O(2)             | 1.459(3)   |
| S(1)-O(3)             | 1.433(3)   |
| S(1)-C(6)             | 1.763(4)   |
| S(1)-C(7)             | 1.761(4)   |
| O(1)-C(3)             | 1.363(4)   |
| O(1)-C(13)            | 1.433(4)   |
| O(4)-C(10)            | 1.364(4)   |
| O(4)-C(14)            | 1.434(5)   |
| C(1)-C(2)             | 1.379(5)   |
| C(1)-C(6)             | 1.398(5)   |
| C(2)-H(2)             | 0.9500     |
| C(2)-C(3)             | 1.407(5)   |
| C(3)-C(4)             | 1.392(5)   |
| C(4)-H(4)             | 0.9500     |
| C(4)-C(5)             | 1.394(5)   |
| C(5)-H(5)             | 0.9500     |
| C(5)-C(6)             | 1.384(5)   |
| C(7)-C(8)             | 1.383(5)   |
| C(7)-C(12)            | 1.400(5)   |
| Bond (with atom numbers) | Distance | Units |
|--------------------------|----------|-------|
| C(8)-H(8)                | 0.9500   |       |
| C(8)-C(9)                | 1.395(5) |       |
| C(9)-H(9)                | 0.9500   |       |
| C(9)-C(10)               | 1.391(5) |       |
| C(10)-C(11)              | 1.402(5) |       |
| C(11)-H(11)              | 0.9500   |       |
| C(11)-C(12)              | 1.384(5) |       |
| C(13)-H(13A)             | 0.9800   |       |
| C(13)-H(13B)             | 0.9800   |       |
| C(13)-H(13C)             | 0.9800   |       |
| C(14)-H(14A)             | 0.9800   |       |
| C(14)-H(14B)             | 0.9800   |       |
| C(14)-H(14C)             | 0.9800   |       |
| C(1)-Bi(1)-I(1)          | 91.33(9) |       |
| C(12)-Bi(1)-I(1)         | 93.48(9) |       |
| C(12)-Bi(1)-C(1)         | 87.54(13)|       |
| O(2)-S(1)-C(6)           | 104.41(17)|      |
| O(2)-S(1)-C(7)           | 104.26(17)|      |
| O(3)-S(1)-O(2)           | 119.25(16)|     |
| O(3)-S(1)-C(6)           | 110.53(17)|     |
| O(3)-S(1)-C(7)           | 111.58(17)|     |
| C(7)-S(1)-C(6)           | 105.74(17)|     |
| C(3)-O(1)-C(13)          | 118.3(3) |       |
| C(10)-O(4)-C(14)         | 117.4(3) |       |
| C(2)-C(1)-Bi(1)          | 123.4(3) |       |
| C(2)-C(1)-C(6)           | 118.7(3) |       |
| C(6)-C(1)-Bi(1)          | 117.9(3) |       |
| C(1)-C(2)-H(2)           | 120.2    |       |
| C(1)-C(2)-C(3)           | 119.6(3) |       |
| C(3)-C(2)-H(2)           | 120.2    |       |
| O(1)-C(3)-C(2)           | 114.5(3) |       |
| O(1)-C(3)-C(4)           | 124.2(3) |       |
| C(4)-C(3)-C(2)           | 121.3(3) |       |
| C(3)-C(4)-H(4)           | 120.6    |       |
| C(3)-C(4)-C(5)           | 118.9(3) |       |
| C(5)-C(4)-H(4)           | 120.6    |       |
| C(4)-C(5)-H(5)           | 120.3    |       |
| C(6)-C(5)-C(4)           | 119.4(3) |       |
| C(6)-C(5)-H(5)           | 120.3    |       |
| C(1)-C(6)-S(1)           | 116.9(3) |       |
| C(5)-C(6)-S(1)           | 121.0(3) |       |
| C(5)-C(6)-C(1)           | 122.1(3) |       |
| C(8)-C(7)-S(1)           | 121.0(3) |       |
| C(8)-C(7)-C(12)          | 122.2(3) |       |
| C(12)-C(7)-S(1)          | 116.8(3) |       |
| C(7)-C(8)-H(8)           | 120.4    |       |
| C(7)-C(8)-C(9)           | 119.2(3) |       |
C(9)-C(8)-H(8)  120.4
C(8)-C(9)-H(9)  120.4
C(10)-C(9)-C(8)  119.2(3)
C(10)-C(9)-H(9)  120.4
O(4)-C(10)-C(9)  123.9(3)
O(4)-C(10)-C(11)  115.0(3)
C(9)-C(10)-C(11)  121.1(3)
C(10)-C(11)-H(11)  120.1
C(12)-C(11)-C(10)  119.8(3)
C(12)-C(11)-H(11)  120.1
C(7)-C(12)-Bi(1)  117.9(3)
C(11)-C(12)-Bi(1)  123.6(3)
C(11)-C(12)-C(7)  118.5(3)
O(1)-C(13)-H(13A)  109.5
O(1)-C(13)-H(13B)  109.5
O(1)-C(13)-H(13C)  109.5
H(13A)-C(13)-H(13B)  109.5
H(13A)-C(13)-H(13C)  109.5
H(13B)-C(13)-H(13C)  109.5
O(4)-C(14)-H(14A)  109.5
O(4)-C(14)-H(14B)  109.5
O(4)-C(14)-H(14C)  109.5
H(14A)-C(14)-H(14B)  109.5
H(14A)-C(14)-H(14C)  109.5
H(14B)-C(14)-H(14C)  109.5
5. $^1$H, $^{13}$C and $^{19}$F NMR Spectra
| Parameter       | Value |
|----------------|-------|
| Title           | PROTON,3 |
| Comment         | AN-12  |
| Origin          | Varian |
| Owner           | nazarova |
| Instrument      | vnmrs  |
| Solvent         | cdcl3  |
| Temperature     | 25.0   |
| Pulse Sequence  | s2pu1 |
| Experiment      | 1D     |
| Number of Scans | 8      |
| Receiver Gain   | 44     |
| Relaxation Delay| 2.0000 |
| Pulse Width     | 2.4667 |
| Spectrometer Frequency | 99.76 |
| Spectral Width  | 6020.6 |
| Lowest Frequency| 5111.5 |
| Nucleus         | 1H     |
| Acquired Size   | 16384  |
| Spectral Size   | 65536  |

![Nazarova et al. Electrochemical Mechanistic Elucidation of BiCuAAC](image.png)
Nazarova et al. Electrochemical Mechanistic Elucidation of BiCuAAC
| Parameter          | Value          |
|-------------------|----------------|
| Title             | FLORINE_01     |
| Comment           | AN-10          |
| Origin            | Varian         |
| Owner             | nazarova       |
| Instrument        | vnmr           |
| Solvent           | dcm3           |
| Temperature       | 25.0           |
| Pulse Sequence    | s2pul          |
| Experiment        | 1D             |
| Number of Scans   | 16             |
| Receiver Gain     | 30             |
| Relaxation Delay  | 1.0000         |
| Pulse Width       | 3.3667         |
| Spectrometer Frequency | 470.21      |
| Spectral Width    | 108669.7       |
| Lowest Frequency  | -94318.8       |
| Nucleus           | 19F            |
| Acquired Size     | 65336          |
| Spectra Size      | 121372         |

30  20  10  0  -10  -20  -30  -40  -50  -60  -70  -80  -90  -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
**Electrochemical Mechanistic Elucidation of BiCuAAC**

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### Parameters and Values

| Parameter       | Value |
|-----------------|-------|
| **Title**       | CARBOC_01 |
| **Comment**     |       |
| **Origin**      | Varian |
| **Owner**       | nazrova |
| **Instrument**  | wnmrs |
| **Solvent**     | ddo8 |
| **Temperature** | 25.0  |
| **Pulse Sequence** | ZSPUL  |
| **Experiment**  | TD    |
| **Number of Scans** | 640   |
| **Receiver Gain** | 30   |
| **Relaxation Delay** | 2.0000 |
| **Pulse Width** | 4.9500 |
| **Spectrometer Frequency** | 125.68 |
| **Spectral Width** | 31250.0 |
| **Lowest Frequency** | -1782.0 |
| **Nucleus**     | 13C   |
| **Acquired Size** | 32768 |
| **Spectral Size** | 65536 |

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**Nazarova et al.**
**Nazarova et al.** Electrochemical Mechanistic Elucidation of BiCuAAC

| Parameter          | Value       |
|--------------------|-------------|
| Title              | FLUGRINE_01 |
| Comment            | AN-13       |
| Origin             | Varian      |
| Owner              | nazhova     |
| Instrument         | vnmrs       |
| Solvent            | dcm/03      |
| Temperature        | 25.0        |
| Pulse Sequence     | s2pul       |
| Experiment         | 1D          |
| Number of Scans    | 16          |
| Receiver Gain      | 30          |
| Relaxation Delay   | 2.0000      |
| Pulse Width        | 3.3657      |
| Spectrometer Frequency | 470.21   |
| Spectral Width     | 1086899.7   |
| Lowest Frequency   | -94318.8    |
| Nucleus            | 19F         |
| Acquired Size      | 65536       |
| Spectral Size      | 131072      |

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![Graph Image](image-url)
Nazaro\textit{a} et al. Electrochemical Mechanistic Elucidation of BiCuAAC

| Parameter          | Value   |
|--------------------|---------|
| Title              | FLUDRONE_01 |
| Comment            | AN-18   |
| Origin             | Varian  |
| Owner              | nazaro\textit{a} |
| Instrument         | nmrms   |
| Solvent            | cdcl3   |
| Temperature        | 25.0    |
| Pulse Sequence     | s2pul   |
| Experiment         | 10      |
| Number of Scans    | 16      |
| Receiver Gain      | 92      |
| Relaxation Delay   | 1.0000  |
| Pulse Width        | 3.3667  |
| Spectrometer Freque\textit{cy} | 70.21   |
| Spectral Width     | 108896.7|
| Lowest Frequency   | -94318.8|
| Nucleus            | 1H      |
| Acquired Size      | 65536   |
| Spectral Size      | 131772  |

S147
Nazarova et al. Electrochemical Mechanistic Elucidation of BiCuAAC

Parameter | Value
--- | ---
Title | PROTONS
Comment | AN-21
Orign | Varian
Owner | nazanova
Instrument | mercury
Solvant | dde3
Temperature | 25.0
Slice Sequence | sp2ux
Experiment | 1D
Number of Scans | 8
Receiver Gain | 6
Relaxation Delay | 5.0000
Pulse Width | 3.7500
Spectrometer Frequency | 400.12
Spectral Width | 750.16
Lowest Frequency | -15.4
Nuclei | 1H
Acquired Size | 65536
Spectral Size | 65536

Parameter | Value
--- | ---
Title | CARBON-13
Comment | AN-21
Orign | Varian
Owner | nazanova
Instrument | mercury
Solvant | dde3
Temperature | 25.0
Slice Sequence | sp2ux
Experiment | 1D
Number of Scans | 512
Receiver Gain | 36
Relaxation Delay | 1.0000
Pulse Width | 16.2500
Spectrometer Frequency | 100.62
Spectral Width | 2515.6
Lowest Frequency | -1491.5
Nuclei | 13C
Acquired Size | 32768
Spectral Size | 65536
**Electrochemical Mechanistic Elucidation of BiCuAAC**

| Parameter          | Value |
|--------------------|-------|
| Title              | CARBON_01 | 138.86 |
| Comment            | AN-25  | |
| Origin             | Varian |   |
| Owner              | nazarova |   |
| Instrument         | vnmrs |   |
| Solvent            | cdcl3  |   |
| Temperature        | 25.0   |   |
| Pulse Sequence     | s2pu1  |   |
| Experiment         | 10     |   |
| Number of Scans    | 8      |   |
| Receiver Gain      | 52     |   |
| Relaxation Delay   | 5.0000 |   |
| Pulse Width        | 3.7000 |   |
| Spectrometer Frequency | 999.76 |   |
| Spectral Width     | 5900.0 |   |
| Lowest Frequency   | -6.2   |   |
| Nucleus            | 13C    |   |
| Acquired Size      | 32768  |   |
| Spectral Size      | 60536  |   |

**Parameter**

| Value |
|-------|
| 138.86 |

**Diagram**

![Nazarova et al. Electrochemical Mechanistic Elucidation of BiCuAAC](image)


**Table:**

| Parameter            | Value      |
|----------------------|------------|
| Title                | CARBON_01  |
| Comment              | KN-28      |
| Origin               | Varian     |
| Owner                | nazarova   |
| Instrument           | vnmrs      |
| Solvent              | dd233      |
| Temperature          | 25.0       |
| Pulse Sequence       | zpul       |
| Experiment           | 10         |
| Number of Scans      | 6912       |
| Receiver Gain        | 30         |
| Relaxation Delay     | 3.0000     |
| Pulse Width          | 4.9500     |
| Spectrometer Frequency | 125.68    |
| Spectral Width       | 31220.0    |
| Lowest Frequency     | -1781.6    |
| Nucleus              | 13C        |
| Acquired Size        | 32768      |
| Spectral Size        | 65536      |

**Diagram:**

[Image of a chemical structure and spectra graph]

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S155
Nazarova et al. Electrochemical Mechanistic Elucidation of BiCuAAC
| Parameter                        | Value |
|---------------------------------|-------|
| Title                           | CARBON_01 | 1.0 |
| Comment                         | AN-35  | 1.0 |
| Origin                          | Varian | 1.0 |
| Owner                           | nazarova | 1.0 |
| Instrument                      | vnmrs  | 1.0 |
| Solvent                         | cdc53  | 1.0 |
| Temperature                     | 25.0 | 1.0 |
| Pulse Sequence                  | 32pu   | 1.0 |
| Experiment                      | 1D     | 1.0 |
| Number of Scans                 | 65656  | 1.0 |
| Receiver Gain                   | 30     | 1.0 |
| Relaxation Delay                | 3.0000 | 1.0 |
| Pulse Width                     | 4.9500 | 1.0 |
| Spectrometer Frequency          | 125.68 | 1.0 |
| Spectral Width                  | 31200.0 | 1.0 |
| Lowest Frequency                | -781.6 | 1.0 |
| Nucleus                         | 13C    | 1.0 |
| Acquired Size                   | 32768  | 1.0 |
| Spectral Size                   | 60036  | 1.0 |
Nazarova et al. Electrochemical Mechanistic Elucidation of BiCuAAC

| Parameter       | Value |
|-----------------|-------|
| Title           | CANIBOK_01 |
| Comment         | AM-40 |
| Origin          | Varian |
| Owner           | nazrova |
| Instrument      | vnmrS |
| Solvent         | cdcl3 |
| Temperature     | 25.0 |
| Pulse Sequence  | s2pul |
| Experiment      | 1D |
| Number of Scans | 9216 |
| Receiver Gain   | 10 |
| Relaxation Delay| 3.0000 |
| Pulse Width     | 4.9500 |
| Spectrometer Frequency | 125.68 |
| Spectral Width  | 31250.0 |
| Lowest Frequency| -1801.8 |
| Nucleus         | 13C |
| Acquired Size   | 32768 |
| Spectral Size   | 65536 |

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| Parameter       | Value |
|-----------------|-------|
| Title           | FLUORENE_01 |
| Comment         | AM-40 |
| Origin          | Varian |
| Owner           | nazrova |
| Instrument      | vnmrS |
| Solvent         | cdcl3 |
| Temperature     | 25.0 |
| Pulse Sequence  | s2pul |
| Experiment      | 1D |
| Number of Scans | 16 |
| Receiver Gain   | 60 |
| Relaxation Delay| 1.0000 |
| Pulse Width     | 3.3605 |
| Spectrometer Frequency | 1970.21 |
| Spectral Width  | 108691.7 |
| Lowest Frequency| -94318.8 |
| Nucleus         | 19F |
| Acquired Size   | 65536 |
| Spectral Size   | 131072 |

S166
Nazarova et al. Electrochemical Mechanistic Elucidation of BiCuAAC

| Parameter       | Value |
|-----------------|-------|
| Title           |       |
| Comment         |       |
| Origin          | Varian |
| Owner           | nazara |
| Instrument      | wnmrs |
| Solvent         | cc183 |
| Temperature     | 25.0  |
| Pulse Sequence  | s2pul |
| Experiment      | 1D    |
| Number of Scans | 8     |
| Receiver Gain   | 46    |
| Relaxation Delay| 10.0000 |
| Pulse Width     | 3.7000 |
| Spectrometer Frequency | 949.76 |
| Spectral Width  | 5000.0 |
| Lowest Frequency| -7.1  |
| Nucleus         | 1H    |
| Acquired Size   | 16384 |
| Spectral Size   | 65536 |

![Spectrum 1](image1)

| Parameter       | Value |
|-----------------|-------|
| Title           |       |
| Comment         | AN-H+2 |
| Origin          | Varian |
| Owner           | nazara |
| Instrument      | wnmrs |
| Solvent         | cc183 |
| Temperature     | 25.0  |
| Pulse Sequence  | s2pul |
| Experiment      | 1D    |
| Number of Scans | 14270 |
| Receiver Gain   | 30    |
| Relaxation Delay| 3.0000 |
| Pulse Width     | 4.5500 |
| Spectrometer Frequency | 125.68 |
| Spectral Width  | 31250.0 |
| Lowest Frequency| -1782.2 |
| Nucleus         | 13C   |
| Acquired Size   | 32768 |
| Spectral Size   | 65536 |

![Spectrum 2](image2)
Nazarova et al. Electrochemical Mechanistic Elucidation of BiCuAAC
Nazarova et al. Electrochemical Mechanistic Elucidation of BiCuAAC

| Parameter       | Value          |
|-----------------|----------------|
| Title           | FLUORENE_01    |
| Comment         | AN-48          |
| Origin          | Varian         |
| Owner           | nazhova        |
| Instrument      | vnmr           |
| Solvent         | d6DMSO         |
| Temperature     | 25.0           |
| Pulse Sequence  | s2pol          |
| Experiment      | 1D             |
| Number of Scans | 16             |
| Receiver Gain   | 50             |
| Relaxation Delay| 2.00000        |
| Pulse Width     | 4.5333         |
| Spectrometer Frequency | 499.21 |
| Spectral Width  | 108969.7       |
| Lowest Frequency| -94471.6       |
| Nucleus         | 19F            |
| Acquired Size   | 65536          |
| Spectral Size   | 1311072        |
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