Note added 15th January 2018: This version of the Electronic Supplementary Information including the accompanying script files replaces the previous version first published on-line on the 30th November 2017.

Solution and gas phase evidence of anion binding through the secondary bonding interactions of a bidendate antimony(III) compound.

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Supplementary Information

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S1 Experimental Details

S1.1 General Methods

The starting materials, antimony(III) trichloride (99%, Strem Chemicals), catechol (99%, Alfa Aesar), and 4-tert-butyl-catechol (99%, Acros Organics) were used as purchased. Methanol (99.9%, Fisher Chemicals) was used as purchased without any further drying. Potassium hydroxide (86%, Fisher Chemicals) for synthesis was heated to 100 °C, dried under vacuum and transferred inside a N2 purged glovebox before being ground into a powder. Anhydrous toluene was obtained by passing HPLC grade toluene over a bed of activated molecular sieves in a commercial (LC Technologies Solutions Inc.) solvent purification system (SPS). Pyridine (99%, EMD Chemicals) was dried over calcium hydride, distilled under nitrogen, transferred onto pre-activated 4 Å molecular sieves and allowed to sit for two days before being used in synthesis. Compounds **1** (2,2'-bi-(1,3,2-benzodioxastibole) oxide) and **2** (2,2'-bi-(1,3-dioxa-4-tertbutylbenzo-2-stibole) oxide) were prepared according to published literature procedure.[1] Salts tetrabutylammonium chloride (TBACl, 95%), tetraphenylphosphonium chloride (TPPCl, 98%), and tetrabutylammonium bromide (TBABr, 98%) were purchased from Acros Organics. Tetrabutylammonium iodide (TBAI, 98%) was purchased from Alfa Aesar, and tetrabutylammonium hexafluorophosphate was purchased from Oakwood Chemicals. The salts (TBACl, TBABr, and TPPCl) were dried under high vacuum for more than 8 hours prior to use. Tris(pentafluorophenyl)borane (BCF, 97%) was purchase from Strem Chemicals. Deuterated solvent d_6-DMSO (99.9% Deuterium), purchased from Cambridge Isotopes Laboratory, was degassed using the freeze-pump-thaw cycles before being transferred onto freshly activated 4 Å molecular sieves. After sitting on the sieves for two days it was again transferred onto freshly activated sieves for storage. Air sensitive manipulations were performed either in an N_2 purged inert atmosphere box (LC Technology Solutions Inc.) or on a glass inert atmosphere line with N_2 purge. All NMR spectra were collected on a JEOL ECS 400 MHz NMR spectrometer.

S1.2 NMR Titrations of 2 with Anions

*S1.2.1 ^{1}H NMR Test of chemical reversibility of interaction of **2** with chloride*

A 0.40 mL d_6-DMSO solution of **2** (0.010 g, 0.017 mmol) and TPPCl (0.0064 g, 0.017 mmol) was made and its ^{1}H NMR spectrum was recorded (See Figure S12 in Section S2). Two equivalents (0.018 g, 0.035 mmol) of BCF was then added to the solution and the ^{1}H NMR spectrum was recorded again. An additional aliquot of BCF was added to the solution and a final ^{1}H NMR spectrum was recorded.

S1.2.2 ^{1}H NMR Titration Procedure

^{1}H NMR titration were performed by adding stock solutions of tetrabutylammonium salts (1.0 M in d_6-DMSO) to 0.50 mL of a solution of **2** in d_6-DMSO (0.0340 M) up to 20 equivalents (where 1.0 eq. = 17.0 µL) of salt solutions. Data points were collected at 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 10.0, 15.0, and 20.0 equivalents of halide solutions added. All halide titrations were performed in triplicate.

S1.2.3 Data Processing and Extraction

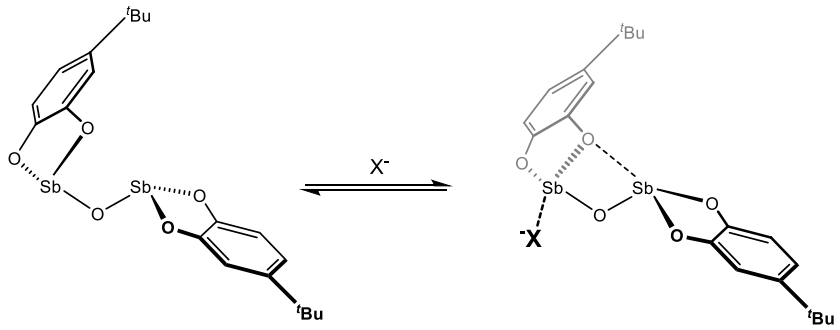
MestReNova 10.0.2[2] was used for all data processing and extraction. FIDs were treated with an exponential multiplication value of 0.3 prior to Fourier transformation. Phasing was performed manually and a multipoint baseline correction was applied. All peaks were fit with a minimal number of Laurentian-Gaussian functions. Initially, one function per feature (peak or shoulder) was added and the fit was refined until no change was observed. If a significant residual remained than an additional function was added. Peak positions were determined from the center of the multiplet or peak according to the Laurentian-Gaussian function positions. Peak areas were determined by summing the areas of the Laurentian-Gaussian functions.

S1.2.4 Data Analysis and Fitting

Peak positions (and intensities) for the aromatic peaks of **2** (and complexes) were recorded as a function of added concentration. Various models were used to fit this data by varying parameters such as binding constants and chemical shifts. The models, including parameters, are described below for the various likely systems that could be represented in the data (corresponding to equations 1-6 in the manuscript). Maple 2016[3] was used to simplify the equations. The host/guest terminology is used here. Host (H) represents **2** and guest (G) represents that halide anion. It is assumed that cation/anion pairing of the tert-butyl ammonium cation with the halide is negligible in DMSO. The binding of DMSO to **2** is also not explicitly modelled.

S1.2.4.1 Model for 1:1 binding of H:G

$H + G \rightleftharpoons HG$ (H = **2**, G = X^-, HG = **2**·X^-)



Scheme S1. Proposed 1:1 binding model of H + G ⇌ HG.

(S1.1) $K = \frac{[HG]}{[H][G]}$

(S1.2) $[H_0] = [H] + [HG], \quad [HG] = [H_0] - [H]$

(S1.3) $[G_0] = [G] + [HG], \quad [G] = [G_0] - [HG]$

Solve for [G], [H], or [HG] with Maple 2016 using equations S1.1-S1.3.

eliminate$(\{K\cdot H\cdot G - HG, H + HG - H0, G + HG - G0\}, \{HG, G\})$;

(S1.4) $\left[\{G = H - H0 + G0, HG = -H + H0\}, \{G0\,H\,K + H^2\,K - H\,H0\,K + H - H0\}\right]$

eliminate$(\{K\cdot H\cdot G - HG, H + HG - H0, G + HG - G0\}, \{HG, H\})$;

(S1.5) $\left[\{H = G - G0 + H0, HG = -G + G0\}, \{G^2\,K - G\,G0\,K + G\,H0\,K + G - G0\}\right]$

eliminate({K· H·G − HG, H + HG − H0, G + HG − G0}, {H, G});

(S1.6) $[\{G = -HG + G0, H = -HG + H0\}, \{G0\,H0\,K - G0\,HG\,K - H0\,HG\,K + HG^2\,K - HG\}]$

From equation set S1.4:

$$[H]^2 + \left([G_0] - [H_0] + \frac{1}{K}\right)[H] - \frac{[H_0]}{K} = 0$$

$$[H] = \frac{-\left([G_0] - [H_0] + \frac{1}{K}\right) \pm \sqrt{\left([G_0] - [H_0] + \frac{1}{K}\right)^2 + 4\frac{[H_0]}{K}}}{2}$$

$[H_0]$ – known experimental quantity (original concentration of host)

$[G_0]$ – known experimental quantity (original concentration of guest)

K – 1:1 binding constant, a refined parameter

NMR – Fast exchange of resonances associated with host compound

$$\delta_{obs} = \frac{\delta_H[H]}{[H_0]} + \frac{\delta_{HG}[HG]}{[Sb_0]}$$

δ_H is the chemical shift of the host, a known experimental quantity

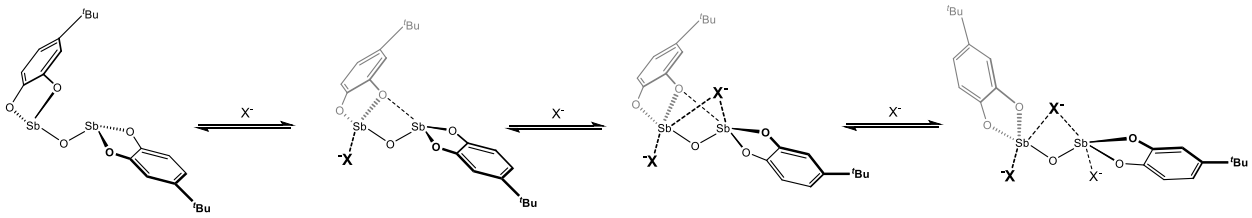
δ_{HG} is the chemical shift of the complex, a refined parameter

S1.2.4.2 Model for 1:1, 1:2 and 1:3 binding of H:G

H + G ⇌ HG (H = **2**, G = X^-, HG = **2**·X^-)

HG + G ⇌ HG_2 (HG_2 = **2**·2X^-)

HG_2 + G ⇌ HG_3 (HG_3 = **2**·3X^-)



Scheme S2. Proposed 1:1, 1:2, and 1:3 binding model of H, G, HG, HG_2, and HG_3.

(S2.1) $K_{11} = \frac{[HG]}{[H][G]}$

(S2.2) $K_{12} = \frac{[HG_2]}{[HG][G]}$

(S2.3) $K_{13} = \frac{[HG_3]}{[HG_2][G]}$

(S2.4) $\beta_{12} = \frac{[HG_2]}{[H][G]^2} = K_{11} \cdot K_{12}$

(S2.5) $\beta_{13} = \frac{[HG_3]}{[H][G]^3} = K_{11} \cdot K_{12} \cdot K_{13}$

(S2.6) $[H_0] = [H] + [HG] + [HG_2] + [HG_3]$

(S2.7) $[G_0] = [G] + [HG] + 2[HG_2] + 3[HG_3]$

Solve for [G] with Maple 2016 using equations S2.1-S2.3, S2.6-S2.7.

```
eliminate({K11·H·G − HG, K12·HG·G − HGG, K13·HGG·G − HGGG, H + HG + HGG
    + HGGG − H0, G + HG + 2·HGG + 3·HGGG − G0}, {HG, HGG, HGGG, H});
```

(S2.8)

$$\left[\left\{H = -\frac{G - G0}{(3\,G^2\,K12\,K13 + 2\,G\,K12 + 1)\,G\,K11},\ HG = -\frac{G - G0}{3\,G^2\,K12\,K13 + 2\,G\,K12 + 1},\ HGG = -\frac{G\,K12\,(G - G0)}{3\,G^2\,K12\,K13 + 2\,G\,K12 + 1},\ HGGG = -\frac{G^2\,K12\,K13\,(G - G0)}{3\,G^2\,K12\,K13 + 2\,G\,K12 + 1}\right\},\ \{G^4\,K11\,K12\,K13 - G^3\,G0\,K11\,K12\,K13 + 3\,G^3\,H0\,K11\,K12\,K13 + G^3\,K11\,K12 - G^2\,G0\,K11\,K12 + 2\,G^2\,H0\,K11\,K12 + G^2\,K11 - G\,G0\,K11 + G\,H0\,K11 + G - G0\}\right]$$

From equation set S2.8:

$$(K_{11}K_{12}K_{13})[G]^4 + (K_{11}K_{12} - [G_0]K_{11}K_{12}K_{13} + 3[H_0]K_{11}K_{12}K_{13})[G]^3 + (K_{11} - [G_0]K_{11}K_{12} + 2[H_0]K_{11}K_{12})[G]^2 + \left(1 - [G_0]K_{11} + [H_0]K_{11}\right)[G] - [G_0] = 0$$

for: $a[G]^4 + b[G]^3 + c[G]^2 + d[G] + e$

$a = (K_{11}K_{12}K_{13})$

$b = (K_{11}K_{12} - [G_0]K_{11}K_{12}K_{13} + 3[H_0]K_{11}K_{12}K_{13})$

$c = (K_{11} - [G_0]K_{11}K_{12} + 2[H_0]K_{11}K_{12})$

$d = \left(1 - [G_0]K_{11} + [H_0]K_{11}\right)$

$e = -[G_0]$

$[H_0]$ – known experimental quantity (original concentration of host)

$[G_0]$ – known experimental quantity (original concentration of guest)

K_{11} – 1:1 stepwise binding constant, a refined parameter

K_{12} – 1:2 stepwise binding constant, a refined parameter

K_{13} – 1:3 stepwise binding constant, a refined parameter

NMR – 4 species, 2 sets in fast exchange of resonances associated with host compound

H/HG and HG_2/ HG_3 in fast exchange

$$\delta(\mathrm{H/HG})_{obs} = \frac{\delta_{\mathrm{H}}[\mathrm{H}]}{[\mathrm{H}] + [\mathrm{HG}]} + \frac{\delta_{\mathrm{HG}}[\mathrm{HG}]}{[\mathrm{H}] + [\mathrm{HG}]}$$

$$\delta(\mathrm{HG_2/HG_3})_{obs} = \frac{\delta_{\mathrm{HG_2}}[\mathrm{HG_2}]}{[\mathrm{HG_2}] + [\mathrm{HG_3}]} + \frac{\delta_{\mathrm{HG_3}}[\mathrm{HG_3}]}{[\mathrm{HG_2}] + [\mathrm{HG_3}]}$$

$$\frac{I(\mathrm{H/HG})_{obs}}{I_{total}} = \frac{[\mathrm{H}]}{[\mathrm{H_0}]} + \frac{[\mathrm{HG}]}{[\mathrm{H_0}]}$$

$$\frac{I(\mathrm{HG_2/HG_3})_{obs}}{I_{total}} = \frac{[\mathrm{HG_2}]}{[\mathrm{H_0}]} + \frac{[\mathrm{HG_3}]}{[\mathrm{H_0}]}$$

H/HG_2 and HG/HG_3 in fast exchange

$$\delta(\mathrm{H/HG_2})_{obs} = \frac{\delta_{\mathrm{H}}[\mathrm{H}]}{[\mathrm{H}] + [\mathrm{HG_2}]} + \frac{\delta_{\mathrm{HG_2}}[\mathrm{HG_2}]}{[\mathrm{H}] + [\mathrm{HG_2}]}$$

$$\delta(\mathrm{HG/HG_3})_{obs} = \frac{\delta_{\mathrm{HG}}[\mathrm{HG}]}{[\mathrm{HG}] + [\mathrm{HG_3}]} + \frac{\delta_{\mathrm{HG_3}}[\mathrm{HG_3}]}{[\mathrm{HG}] + [\mathrm{HG_3}]}$$

$$\frac{I(\mathrm{H/HG_2})_{obs}}{I_{total}} = \frac{[\mathrm{H}]}{[\mathrm{H_0}]} + \frac{[\mathrm{HG_2}]}{[\mathrm{H_0}]}$$

$$\frac{I(\mathrm{HG/HG_3})_{obs}}{I_{total}} = \frac{[\mathrm{HG}]}{[\mathrm{H_0}]} + \frac{[\mathrm{HG_3}]}{[\mathrm{H_0}]}$$

H/HG_3 and HG/HG_2 in fast exchange

$$\delta(\mathrm{H/HG_3})_{obs} = \frac{\delta_{\mathrm{H}}[\mathrm{H}]}{[\mathrm{H}] + [\mathrm{HG_3}]} + \frac{\delta_{\mathrm{HG_3}}[\mathrm{HG_3}]}{[\mathrm{H}] + [\mathrm{HG_3}]}$$

$$\delta(\mathrm{HG/HG_2})_{obs} = \frac{\delta_{\mathrm{HG}}[\mathrm{HG}]}{[\mathrm{HG}] + [\mathrm{HG_2}]} + \frac{\delta_{\mathrm{HG_2}}[\mathrm{HG_2}]}{[\mathrm{HG}] + [\mathrm{HG_2}]}$$

$$\frac{I(\mathrm{H/HG_3})_{obs}}{I_{total}} = \frac{[\mathrm{H}]}{[\mathrm{H_0}]} + \frac{[\mathrm{HG_3}]}{[\mathrm{H_0}]}$$

$$\frac{I(\mathrm{HG/HG_2})_{obs}}{I_{total}} = \frac{[\mathrm{HG}]}{[\mathrm{H_0}]} + \frac{[\mathrm{HG_2}]}{[\mathrm{H_0}]}$$

δ_{H} is the chemical shift of the host, a known experimental quantity

δ_{HG} is the chemical shift of the 1:1 complex, a refined parameter

$\delta_{\mathrm{HG_2}}$ is the chemical shift of the 1:2 complex, a refined parameter

$\delta_{\mathrm{HG_3}}$ is the chemical shift of the 1:3 complex, a refined parameter

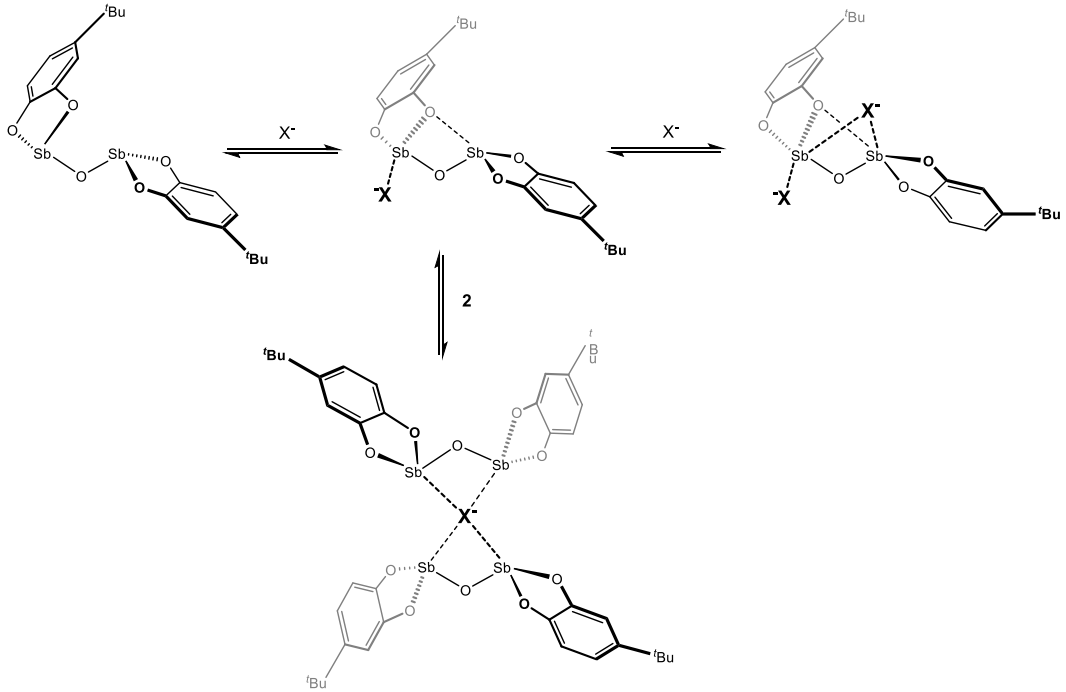
I is the experimental integrated intensity

S1.2.4.3 Model for 1:1, 1:2 and 2:1 binding of H:G

H + G ⇌ HG (H = **2**, G = X^-, HG = **2**·X^-)

HG + G ⇌ HG_2 (HG_2 = **2**·$2X^-$)

HG + H ⇌ H_2G (H_2G =$\mathbf{2}_2$·X^-)



Scheme S3. Proposed 1:1, 1:2, and 2:1 binding model of H, G, HG, HG_2, and H_2G.

(S3.1) $\mathrm{K_{11}} = \frac{[\mathrm{HG}]}{[\mathrm{H}][\mathrm{G}]}$

(S3.2) $K_{12} = \frac{[HG_2]}{[HG][G]}$

(S3.3) $K_{21} = \frac{[H_2G]}{[HG][H]}$

(S3.4) $\beta_{12} = \frac{[HG_2]}{[H][G]^2} = K_{11} \cdot K_{12}$

(S3.5) $\beta_{21} = \frac{[H_2G]}{[H]^2[G]} = K_{11} \cdot K_{21}$

(S3.6) $[H_0] = [H] + [HG] + [HG_2] + 2[H_2G]$

(S3.7) $[G_0] = [G] + [HG] + 2[HG_2] + [H_2G]$

Solve for [H] with Maple 2016 using equations S3.1-S3.3, S3.6-S3.7.

```
eliminate({K11·H·G − HG, K12·HG·G − HGG, K21·HG·H − HHG, H + HG + HGG + 2
    · HHG − H0, G + HG + 2·HGG + HHG − G0}, {HG, HHG, HGG, G});
```

(S3.8)

$$\left[\left\{G = -\frac{G0 + 2H - 2H0}{3H^2 K11 K21 + HK11 - 1}, HG = -\frac{HK11\,(G0 + 2H - 2H0)}{3H^2 K11 K21 + HK11 - 1}, HGG\right.\right.$$
$$= \frac{1}{3H^2 K11 K21 + HK11 - 1}\left(2\,G0\,H^2 K11 K21 + H^3 K11 K21 - H^2 H0 K11 K21\right.$$
$$\left. + G0\,HK11 + H^2 K11 - HH0 K11 + H - H0\right), HHG =$$
$$\left.\left. -\frac{H^2 K11 K21\,(G0 + 2H - 2H0)}{3H^2 K11 K21 + HK11 - 1}\right\}, \{-6\,G0\,H^4 K11^2 K21^2 - 3H^5 K11^2 K21^2\right.$$
$$+ 3H^4 H0 K11^2 K21^2 - 5\,G0\,H^3 K11^2 K21 - 4H^4 K11^2 K21 + 4H^3 H0 K11^2 K21$$
$$+ G0^2 HK11 K12 - G0\,H^2 K11^2 + 4\,G0\,H^2 K11 K12 + 2\,G0\,H^2 K11 K21$$
$$- 4\,G0\,HH0 K11 K12 - H^3 K11^2 + 4H^3 K11 K12 - 2H^3 K11 K21 + H^2 H0 K11^2$$
$$\left. - 8H^2 H0 K11 K12 + 2H^2 H0 K11 K21 + 4HH0^2 K11 K12 + G0\,HK11 + H - H0\}\right]$$

From equation set S3.8:

$$\left\{-3H^5 K11^2 K21^2 - 6\left(\frac{2}{3} + \left(G0 - \frac{1}{2}H0\right)K21\right)K21\,K11^2 H^4 - 5K11\left(\left(\frac{1}{5} + \left(G0\right.\right.\right.\right.$$
$$\left.\left.\left.\left. - \frac{4}{5}H0\right)K21\right)K11 - \frac{4}{5}K12 + \frac{2}{5}K21\right)H^3 - K11\,((G0 - H0)\,K11 + (-2\,G0$$
$$- 2H0)\,K21 - 4\,(G0 - 2H0)\,K12)\,H^2 + \left(1 + \left(G0^2 K12 + (-4H0\,K12 + 1)\,G0\right.\right.$$
$$\left.\left. + 4H0^2 K12\right)K11\right)H - H0\}$$

for: $a[H]^5 + b[H]^4 + c[H]^3 + d[H]^2 + e[H] + f$

a = $\left(-3{K_{11}}^2{K_{21}}^2\right)$

b = $\left(-6\left(\frac{2}{3}+\left([\mathrm{G_0}]-\frac{1}{2}[\mathrm{H_0}]\right)\mathrm{K_{21}}\right)\mathrm{K_{11}}^2\mathrm{K_{21}}\right)$

c = $\left(-5\mathrm{K_{11}}\left(\left(\frac{1}{5}+\left([\mathrm{G_0}]-\frac{4}{5}[\mathrm{H_0}]\right)\mathrm{K_{21}}\right)\mathrm{K_{11}}-\frac{4}{5}\mathrm{K_{12}}+\frac{2}{5}\mathrm{K_{21}}\right)\right)$

d = $\left(-\mathrm{K_{11}}\left(([\mathrm{G_0}]-[\mathrm{H_0}])\mathrm{K_{11}}+(-2[\mathrm{G_0}]-2[\mathrm{H_0}])\mathrm{K_{21}}-4([\mathrm{G_0}]-2[\mathrm{H_0}])\mathrm{K_{12}}\right)\right)$

e = $(1+([\mathrm{G_0}]^2\mathrm{K_{12}}+(-4[\mathrm{H_0}]\mathrm{K_{12}}+1)[\mathrm{G_0}]+4[\mathrm{H_0}]^2\mathrm{K_{12}})\mathrm{K_{11}})$

f = $-[\mathrm{H_0}]$

$[\mathrm{H_0}]$ – known experimental quantity (original concentration of host)

$[\mathrm{G_0}]$ – known experimental quantity (original concentration of guest)

$\mathrm{K_{11}}$ – 1:1 stepwise binding constant, a refined parameter

$\mathrm{K_{12}}$ – 1:2 stepwise binding constant, a refined parameter

$\mathrm{K_{21}}$ – 2:1 stepwise binding constant, a refined parameter

NMR – 4 species, 2 sets in fast exchange of resonances associated with host compound

H/HG and $\mathrm{HG_2}$/$\mathrm{H_2G}$ in fast exchange

$$\delta(\mathrm{H/HG})_{obs}=\frac{\delta_{\mathrm{H}}[\mathrm{H}]}{[\mathrm{H}]+[\mathrm{HG}]}+\frac{\delta_{\mathrm{HG}}[\mathrm{HG}]}{[\mathrm{H}]+[\mathrm{HG}]}$$

$$\delta(\mathrm{HG_2/H_2G})_{obs}=\frac{\delta_{\mathrm{HG_2}}[\mathrm{HG_2}]}{[\mathrm{HG_2}]+2[\mathrm{H_2G}]}+2\frac{\delta_{\mathrm{H_2G}}[\mathrm{H_2G}]}{[\mathrm{HG_2}]+2[\mathrm{H_2G}]}$$

$$\frac{I(\mathrm{H/HG})_{obs}}{I_{total}}=\frac{[\mathrm{H}]}{[\mathrm{H_0}]}+\frac{[\mathrm{HG}]}{[\mathrm{H_0}]}$$

$$\frac{I(\mathrm{HG_2/H_2G})_{obs}}{I_{total}}=\frac{[\mathrm{HG_2}]}{[\mathrm{H_0}]}+2\frac{[\mathrm{H_2G}]}{[\mathrm{H_0}]}$$

H/$\mathrm{HG_2}$ and HG/$\mathrm{H_2G}$ in fast exchange

$$\delta(\mathrm{H/HG_2})_{obs}=\frac{\delta_{\mathrm{H}}[\mathrm{H}]}{[\mathrm{H}]+[\mathrm{HG_2}]}+\frac{\delta_{\mathrm{HG_2}}[\mathrm{HG_2}]}{[\mathrm{H}]+[\mathrm{HG_2}]}$$

$$\delta(\mathrm{HG/H_2G})_{obs}=\frac{\delta_{\mathrm{HG}}[\mathrm{HG}]}{[\mathrm{HG}]+2[\mathrm{H_2G}]}+2\frac{\delta_{\mathrm{H_2G}}[\mathrm{H_2G}]}{[\mathrm{HG}]+2[\mathrm{H_2G}]}$$

$$\frac{I(\mathrm{H/HG_2})_{obs}}{I_{total}} = \frac{[\mathrm{H}]}{[\mathrm{H_0}]} + \frac{[\mathrm{HG_2}]}{[\mathrm{H_0}]}$$

$$\frac{I(\mathrm{HG/H_2G})_{obs}}{I_{total}} = \frac{[\mathrm{HG}]}{[\mathrm{H_0}]} + 2\frac{[\mathrm{H_2G}]}{[\mathrm{H_0}]}$$

H/H_2G and HG/HG_2 in fast exchange

$$\delta(\mathrm{H/H_2G})_{obs} = \frac{\delta_{\mathrm{H}}[\mathrm{H}]}{[\mathrm{H}] + 2[\mathrm{H_2G}]} + 2\frac{\delta_{\mathrm{H_2G}}[\mathrm{H_2G}]}{[\mathrm{H}] + 2[\mathrm{H_2G}]}$$

$$\delta(\mathrm{HG/HG_2})_{obs} = \frac{\delta_{\mathrm{HG}}[\mathrm{HG}]}{[\mathrm{HG}] + [\mathrm{HG_2}]} + \frac{\delta_{\mathrm{HG_2}}[\mathrm{HG_2}]}{[\mathrm{HG}] + [\mathrm{HG_2}]}$$

$$\frac{I(\mathrm{H/H_2G})_{obs}}{I_{total}} = \frac{[\mathrm{H}]}{[\mathrm{H_0}]} + 2\frac{[\mathrm{H_2G}]}{[\mathrm{H_0}]}$$

$$\frac{I(\mathrm{HG/HG_2})_{obs}}{I_{total}} = \frac{[\mathrm{HG}]}{[\mathrm{H_0}]} + \frac{[\mathrm{HG_2}]}{[\mathrm{H_0}]}$$

δ_{H} is the chemical shift of the host, a known experimental quantity

δ_{HG} is the chemical shift of the 1:1 complex, a refined parameter

$\delta_{\mathrm{HG_2}}$ is the chemical shift of the 1:2 complex, a refined parameter

$\delta_{\mathrm{H_2G}}$ is the chemical shift of the 2:1 complex, a refined parameter

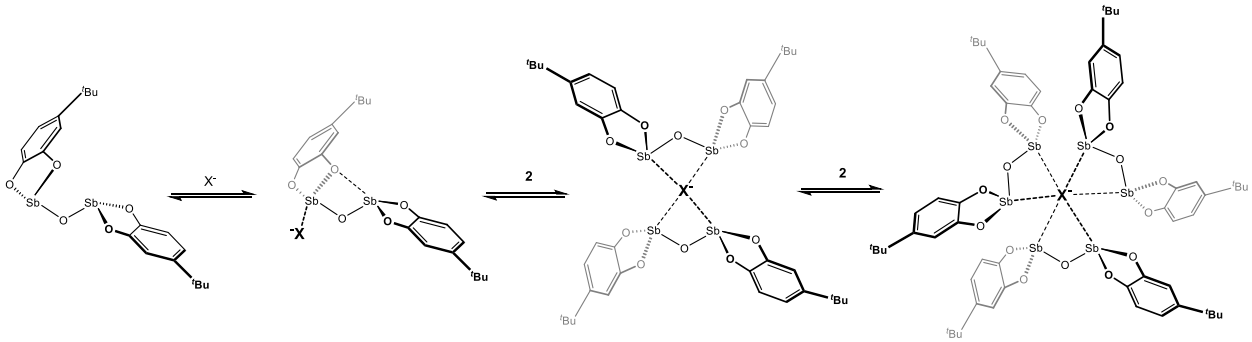
I is the experimental integrated intensity

S1.2.4.4 Model for 1:1, 2:1 and 3:1 binding of H:G

H + G ⇌ HG (H = **2**, G = X^-, HG = **2**·X^-)

HG + G ⇌ H_2G (H_2G = $\mathbf{2}_2$·X^-)

H_2G + G ⇌ H_3G (H_3G = $\mathbf{2}_3$·X^-)



Scheme S4. Proposed 1:1, 2:1, and 3:1 binding model of H, G, HG, H_2G, and H_3G.

(S4.1) $$K_{11} = \frac{[HG]}{[H][G]}$$

(S4.2) $$K_{21} = \frac{[H_2G]}{[HG][H]}$$

(S4.3) $$K_{31} = \frac{[H_3G]}{[H_2G][H]}$$

(S4.4) $$\beta_{21} = \frac{[H_2G]}{[H]^2[G]} = K_{11} \cdot K_{21}$$

(S4.5) $$\beta_{31} = \frac{[H_3G]}{[H]^3[G]} = K_{11} \cdot K_{21} \cdot K_{31}$$

(S4.6) $$[H_0] = [H] + [HG] + 2[H_2G] + 3[H_3G]$$

(S4.7) $$[G_0] = [G] + [HG] + [H_2G] + [H_3G]$$

Solve for [H] with Maple 2016 using equations S4.1-S4.3, S4.6-S4.7.

$$eliminate(\{K11 \cdot H \cdot G - HG,\ K21 \cdot HG \cdot H - HHG, K31 \cdot HHG \cdot H - HHHG,\ H + HG + 2 \cdot HHG + 3 \cdot HHHG - H0, G + HG + HHG + HHHG - G0\}, \{HG, HHG, HHHG, G\});$$

(S4.8)
$$\left[\left\{G = -\frac{H - H0}{\left(3H^2 K21\,K31 + 2H K21 + 1\right) K11\,H}, HG = -\frac{H - H0}{3H^2 K21\,K31 + 2H K21 + 1},\right.\right.$$
$$\left.HHG = -\frac{H K21\,(H - H0)}{3H^2 K21\,K31 + 2H K21 + 1}, HHHG = -\frac{H^2 K21\,K31\,(H - H0)}{3H^2 K21\,K31 + 2H K21 + 1}\right\},$$
$$\{3\,G0\,H^3 K11\,K21\,K31 + H^4 K11\,K21\,K31 - H^3 H0\,K11\,K21\,K31 + 2\,G0\,H^2 K11\,K21$$
$$\left.+ H^3 K11\,K21 - H^2 H0\,K11\,K21 + G0\,H K11 + H^2 K11 - H H0\,K11 + H - H0\}\right]$$

From equation set S4.8:

$$(K_{11}K_{21}K_{31})[H]^4 + (K_{11}K_{21} + 3[G_0]K_{11}K_{21}K_{31} - [H_0]K_{11}K_{21}K_{31})[H]^3$$
$$+ (K_{11} + 2[G_0]K_{11}K_{21} - [H_0]K_{11}K_{12})[H]^2 + \left(1 + [G_0]K_{11} - [H_0]K_{11}\right)[H] - [H_0]$$
$$= 0$$

for: $a[H]^4 + b[H]^3 + c[H]^2 + d[H] + e$

$a = (K_{11}K_{21}K_{31})$

$b = (K_{11}K_{21} + 3[G_0]K_{11}K_{21}K_{31} - [H_0]K_{11}K_{21}K_{31})$

$c = (K_{11} + 2[G_0]K_{11}K_{21} - [H_0]K_{11}K_{12})$

$d = \left(1 + [G_0]K_{11} - [H_0]K_{11}\right)$

$e = -[H_0]$

$[H_0]$ – known experimental quantity (original concentration of host)

$[G_0]$ – known experimental quantity (original concentration of guest)

K_{11} – 1:1 stepwise binding constant, a refined parameter

K_{21} – 2:1 stepwise binding constant, a refined parameter

K_{31} – 3:1 stepwise binding constant, a refined parameter

NMR – 4 species in fast exchange of resonances associated with host compound

$$\delta_{obs} = \frac{\delta_H[H]}{[H_0]} + \frac{\delta_{HG}[HG]}{[H_0]} + 2\frac{\delta_{H_2G}[H_2G]}{[H_0]} + 3\frac{\delta_{H_3G}[H_3G]}{[H_0]}$$

δ_H is the chemical shift of the host, a known experimental quantity

δ_{HG} is the chemical shift of the 1:1 complex, a refined parameter

δ_{H_2G} is the chemical shift of the 2:1 complex, a refined parameter

δ_{H_3G} is the chemical shift of the 3:1 complex, a refined parameter

NMR – 4 species, 2 sets in fast exchange of resonances associated with host compound

H/HG and H_2G/ H_3G in fast exchange

$$\delta(\mathrm{H/HG})_{obs} = \frac{\delta_{\mathrm{H}}[\mathrm{H}]}{[\mathrm{H}] + [\mathrm{HG}]} + \frac{\delta_{\mathrm{HG}}[\mathrm{HG}]}{[\mathrm{H}] + [\mathrm{HG}]}$$

$$\delta(\mathrm{H_2G/H_3G})_{obs} = 2\frac{\delta_{\mathrm{H_2G}}[\mathrm{H_2G}]}{2[\mathrm{H_2G}] + 3[\mathrm{H_3G}]} + 3\frac{\delta_{\mathrm{H_3G}}[\mathrm{H_3G}]}{2[\mathrm{H_2G}] + 3[\mathrm{H_3G}]}$$

$$\frac{I(\mathrm{H/HG})_{obs}}{I_{total}} = \frac{[\mathrm{H}]}{[\mathrm{H_0}]} + \frac{[\mathrm{HG}]}{[\mathrm{H_0}]}$$

$$\frac{I(\mathrm{H_2G/H_3G})_{obs}}{I_{total}} = 2\frac{[\mathrm{H_2G}]}{[\mathrm{H_0}]} + 3\frac{[\mathrm{H_3G}]}{[\mathrm{H_0}]}$$

H/HG_2 and HG/HG_3 in fast exchange

$$\delta(\mathrm{H/H_2G})_{obs} = \frac{\delta_{\mathrm{H}}[\mathrm{H}]}{[\mathrm{H}] + 2[\mathrm{H_2G}]} + 2\frac{\delta_{\mathrm{H_2G}}[\mathrm{H_2G}]}{[\mathrm{H}] + 2[\mathrm{H_2G}]}$$

$$\delta(\mathrm{HG/H_3G})_{obs} = \frac{\delta_{\mathrm{HG}}[\mathrm{HG}]}{[\mathrm{HG}] + 3[\mathrm{H_3G}]} + 3\frac{\delta_{\mathrm{H_3G}}[\mathrm{H_3G}]}{[\mathrm{HG}] + 3[\mathrm{H_3G}]}$$

$$\frac{I(\mathrm{H/H_2G})_{obs}}{I_{total}} = \frac{[\mathrm{H}]}{[\mathrm{H_0}]} + 2\frac{[\mathrm{H_2G}]}{[\mathrm{H_0}]}$$

$$\frac{I(\mathrm{HG/H_3G})_{obs}}{I_{total}} = \frac{[\mathrm{HG}]}{[\mathrm{H_0}]} + 3\frac{[\mathrm{H_3G}]}{[\mathrm{H_0}]}$$

H/HG_3 and HG/HG_2 in fast exchange

$$\delta(\mathrm{H/H_3G})_{obs} = \frac{\delta_{\mathrm{H}}[\mathrm{H}]}{[\mathrm{H}] + 3[\mathrm{H_3G}]} + 3\frac{\delta_{\mathrm{H_3G}}[\mathrm{H_3G}]}{[\mathrm{H}] + 3[\mathrm{H_3G}]}$$

$$\delta(\mathrm{HG/H_2G})_{obs} = \frac{\delta_{\mathrm{HG}}[\mathrm{HG}]}{[\mathrm{HG}] + 2[\mathrm{H_2G}]} + 2\frac{\delta_{\mathrm{H_2G}}[\mathrm{H_2G}]}{[\mathrm{HG}] + 2[\mathrm{H_2G}]}$$

$$\frac{I(\mathrm{H/H_3G})_{obs}}{I_{total}} = \frac{[\mathrm{H}]}{[\mathrm{H_0}]} + 3\frac{[\mathrm{H_3G}]}{[\mathrm{H_0}]}$$

$$\frac{I(\mathrm{HG/H_2G})_{obs}}{I_{total}} = \frac{[\mathrm{HG}]}{[\mathrm{H_0}]} + 2\frac{[\mathrm{H_2G}]}{[\mathrm{H_0}]}$$

δ_{H} is the chemical shift of the host, a known experimental quantity

δ_{HG} is the chemical shift of the 1:1 complex, a refined parameter

δ_{HG_2} is the chemical shift of the 1:2 complex, a refined parameter

δ_{H_3G} is the chemical shift of the 3:1 complex, a refined parameter

I is the experimental integrated intensity

S1.2.4.5 Fitting Procedure

Scripts were written in R (version 3.4.0)[4] to minimize the above models against the data by varying the parameters. A bootstrapping method was implemented to obtain deviations. Within R, the nlminb routine in the optimx[5,6] package was used for the minimization and the rootSolve[7,8] package was used to find the lowest positive roots. For each dataset, initial guesses were performed until a set of real roots were obtained. A set number of initial guesses (100 in the final runs) were performed and the best guess was passed on to the optimization routine which minimized the sum of the square of the differences between the modelled and experimental values. The peak position data was weighted more heavily than the integrated intensity data due to the inherent inaccuracies in obtaining good intensities (particularly under intermediate exchange conditions).[9] This process was repeated a set number of times (1000 in the final runs) with the different randomly selected bootstrapping datasets. Bounding conditions were given for both the initial guesses and the minimization. The binding constants were restricted to being non-negative. The bounding conditions for the chemical shift were set to be chemically reasonable. The aromatic resonances had a lower bound of 4 ppm and an upper bound of 10 ppm. For the final average and standard deviations, 1000 bootstrapping cycles were run (each with 20 initial guesses). Only the results that were within 10% of the lowest sum of square of differences were used as the remainder were deemed to likely be local minima. It should be noted that including all the data did not change the order of magnitude of any of the binding constants.

S1.2.4.6 Selecting the correct model for the bromide and chloride titrations.

Preliminary fitting runs over the 9 possible models for each of the TBABr and TBACl titrations were performed. During each run 100 minimizations with 20 initial guess cycles were performed. Data of all three replicates are displayed below with the exception of TBABr, where the aromatic peaks in one of the trials could not be resolved. The different stepwise equilibria are reiterated in equations S5.1-S5.5.

$$\mathbf{2} + \mathbf{2}_2\cdot X^- \rightleftharpoons \mathbf{2}_3\cdot X^- \qquad K_{3:1} \qquad \text{(S5.1)}$$

$$\mathbf{2} + \mathbf{2}\cdot X^- \rightleftharpoons \mathbf{2}_2\cdot X^- \qquad K_{2:1} \qquad \text{(S5.2)}$$

$$\mathbf{2} + X^- \rightleftharpoons \mathbf{2}\cdot X^- \qquad K_{1:1} \qquad \text{(S5.3)}$$

$$\mathbf{2}\cdot X^- + Br^- \rightleftharpoons \mathbf{2}\cdot [X^-]_2 \qquad K_{1:2} \qquad \text{(S5.4)}$$

$$\mathbf{2}\cdot [X^-]_2 + Br^- \rightleftharpoons \mathbf{2}\cdot [X^-]_3 \qquad K_{1:3} \qquad \text{(S5.5)}$$

Table S1. Data fitting from modelling titration of **2** with TBABr according to equations 3-5 from manuscript (S5.3-S5.5 from above). The 3 different possible pairings of species for fast exchange are shown.

Fast exchange pairs	Trial #	Fit*	K_{11}	K_{12}	K_{13}	$\delta_{\mathbf{2}}$	$\delta_{\mathbf{2}\cdot Br^-}$	$\delta_{\mathbf{2}\cdot [Br^-]_2}$	$\delta_{\mathbf{2}\cdot [Br^-]_3}$
2/**2**·Br^- and **2**·$[Br^-]_2$/**2**·$[Br^-]_3$	1	1.3980	5.1428	68.7971	1.1942	6.6327	6.6034	6.6041	6.3140
	2	1.6109	7.5172	84.9627	1.5295	6.6316	6.6077	6.6063	6.3538
	Average	1.5044	6.3300	76.8799	1.3619	6.6321	6.6055	6.6052	6.3339
2/**2**·$[Br^-]_2$ and **2**·Br^-/**2**·$[Br^-]_3$	1	0.4653	12.8183	5.4227	12.4273	6.6305	6.6021	6.6122	6.5149
	2	0.9966	15.1896	3.6046	15.2391	6.6290	6.6035	6.6113	6.5107
	Average	0.7310	14.0039	4.5137	13.8332	6.6297	6.6028	6.6118	6.5128
2/**2**·$[Br^-]_3$and **2**·$[Br^-]_2$/**2**·Br^-	1	0.4254	9.5411	5.8392	1.3073	6.6288	6.6177	6.4816	6.6064
	2	0.9734	12.1346	4.5335	1.0568	6.6276	6.6169	6.4678	6.6053
	Average	0.6994	10.8378	5.1864	1.1821	6.6282	6.6173	6.4747	6.6058

* Evaluated from sum of square of differences

Table S2. Data fitting from modelling titration of **2** with TBABr according to equations 2-4 from manuscript (S5.2-S5.4 from above). The 3 different possible pairings of species for fast exchange are shown.

Fast exchange pairs	Trial #	Fit	K_{11}	K_{12}	K_{21}	$\delta_{\mathbf{2}}$	$\delta_{\mathbf{2}\cdot Br^-}$	$\delta_{\mathbf{2}\cdot[Br^-]_2}$	$\delta_{\mathbf{2}_2\cdot Br^-}$
2/**2**·Br^- and $\mathbf{2}_2\cdot Br^-$/**2**·$[Br^-]_2$	1	0.4347	0.6233	71.7231	331.6848	6.6314	6.5272	6.5213	6.6096
	2	0.4326	0.8082	56.0102	257.2867	6.6315	6.5476	6.5206	6.6098
	Average	0.4337	0.7157	63.8667	294.4858	6.6314	6.5374	6.5210	6.6097
2/**2**·$[Br^-]_2$ and $\mathbf{2}_2\cdot Br^-$/**2**·Br^-	1	0.6475	1.7192	0.2048	153.2082	6.6288	6.2602	6.2629	6.6452
	2	0.3807	11.5576	0.4056	0.8807	6.6291	6.5212	6.5838	8.4110
	Average	0.5141	6.6384	0.3052	77.0445	6.6290	6.3907	6.4233	7.5281
2/$\mathbf{2}_2$·Br^- and **2**·Br^-/**2**·$[Br^-]_2$	1	1.1853	14.0822	0.5067	23.3115	6.6399	6.6035	6.0791	6.5940
	2	1.1082	11.4577	0.2741	5.0030	6.6365	6.6036	5.6865	6.5245
	Average	1.1467	12.7700	0.3904	14.1572	6.6382	6.6035	5.8828	6.5593

Table S3. Data fitting from modelling titration of **2** with TBABr according to equations 1-3 from manuscript (S5.1-S5.3 from above). The 3 different possible pairings of species for fast exchange are shown.

Fast exchange pairs	Trial #	Fit	K_{11}	K_{21}	K_{31}	$\delta_{\mathbf{2}}$	$\delta_{\mathbf{2}\cdot Br^-}$	$\delta_{\mathbf{2}_2\cdot Br^-}$	$\delta_{\mathbf{2}_3\cdot Br^-}$
2/**2**·Br^- and $\mathbf{2}_2\cdot Br^-$/$\mathbf{2}_3\cdot Br^-$	1	0.8333	0.4248	570.2641	9.9973	6.6312	6.4988	6.4861	6.9314
	2	1.5533	0.2860	884.5654	15.8699	6.6297	6.4593	6.4772	6.8404
	Average	1.1933	0.3554	727.4147	12.9336	6.6304	6.4791	6.4817	6.8859
2/$\mathbf{2}_2$·Br^- and **2**·Br^-/$\mathbf{2}_3\cdot Br^-$	1	0.7361	6.2092	0.7524	764.6840	6.6351	6.5209	5.7966	6.6790
	2	1.5345	9.8475	6.2707	78.1411	6.6347	6.5340	6.5386	6.6999
	Average	1.1353	8.0283	3.5115	421.4126	6.6349	6.5275	6.1676	6.6894
2/$\mathbf{2}_3$·$Br^-$and **2**·Br^- /$\mathbf{2}_2$·Br^-	1	1.1330	31.5232	17.0084	568.8184	6.5904	6.5215	6.8426	6.6497
	2	1.5708	39.4896	11.0608	832.6499	6.5950	6.5293	6.9606	6.6450
	Average	1.3519	35.5064	14.0346	700.7342	6.5927	6.5254	6.9016	6.6474

Table S4 . Data fitting from modelling titration of **2** with TBACl according to equations 3-5 from manuscript (S5.3-S5.5 from above). The 3 different possible pairings of species for fast exchange are shown.

Fast exchange pairs	Trial #	Fit	K_{11}	K_{12}	K_{13}	$\delta_{\mathbf{2}}$	$\delta_{\mathbf{2}\cdot Cl^-}$	$\delta_{\mathbf{2}\cdot[Cl^-]_2}$	$\delta_{\mathbf{2}\cdot[Cl^-]_3}$
2/**2**·Cl^- and **2**·$[Cl^-]_2$/**2**·$[Cl^-]_3$	1	2.6932	36.9381	10980.7079	55.6620	6.6368	6.5854	6.5742	6.4769
	2	2.2699	9.0504	5317.4456	24.8384	6.6362	6.5647	6.5847	6.4620
	3	8.4157	32.8355	25701.9169	96.3963	6.6361	6.5850	6.5785	6.4901
	Average	4.4596	26.2746	14000.0235	58.9656	6.6364	6.5784	6.5791	6.4763
2/**2**·$[Cl^-]_2$ and **2**·Cl^-/**2**·$[Cl^-]_3$	1	0.9263	116.9299	1.0960	6.0949	6.6360	6.5580	6.5834	6.3477
	2	1.0119	108.3735	1.6384	211.7847	6.6358	6.5811	6.5825	6.4738
	3	1.9804	136.1477	1.8173	5.1370	6.6374	6.5625	6.5909	6.3769
	Average	1.3062	120.4837	1.5172	74.3389	6.6364	6.5672	6.5856	6.3995
2/**2**·$[Cl^-]_3$ and **2**·$[Cl^-]_2$/**2**·Cl^-	1	0.4455	107.4845	10.6799	1.2874	6.6337	6.5825	6.4415	6.5843
	2	0.5955	94.0712	12.8443	1.1847	6.6341	6.5945	6.4451	6.5853
	3	1.8342	113.3564	4.6042	1.9860	6.6340	6.5798	6.3950	6.5844
	Average	0.9584	104.9707	9.3762	1.4860	6.6339	6.5856	6.4272	6.5847

Table S5. Data fitting from modelling titration of **2** with TBACl according to equations 2-4 from manuscript (S5.2-S5.4 from above). The 3 different possible pairings of species for fast exchange are shown.

Fast exchange pairs	Trial #	Fit	K_{11}	K_{12}	K_{21}	$\delta_{\mathbf{2}}$	$\delta_{\mathbf{2}\cdot Cl^-}$	$\delta_{\mathbf{2}\cdot[Cl^-]_2}$	$\delta_{\mathbf{2}_2\cdot Cl^-}$
2/**2**·Cl^- and $\mathbf{2}_2\cdot Cl^-$/**2**·$[Cl^-]_2$	1	3.5782	0.9845	968.5116	397.0708	6.6364	6.3972	6.4976	6.6267
	2	2.6291	0.9563	839.3614	361.4960	6.6372	6.3840	6.5031	6.6337
	3	5.1197	0.9879	640.1485	935.7188	6.6293	6.4620	6.5429	6.5264
	Average	3.7756	0.9762	816.0072	564.7619	6.6343	6.4144	6.5145	6.5956
2/**2**·$[Cl^-]_2$ and $\mathbf{2}_2\cdot Cl^-$/**2**·Cl^-	1	3.2480	25.4771	0.1697	3.9976	6.6314	6.4999	6.4756	6.9019
	2	2.2171	23.7147	0.0441	4.0824	6.6318	6.4765	6.1514	7.1189
	3	10.2343	16.2089	0.1642	12.2975	6.6313	6.4479	6.4286	6.8093
	Average	5.2332	21.8002	0.1260	6.7925	6.6315	6.4747	6.3519	6.9434
2/$\mathbf{2}_2\cdot Cl^-$ and **2**·Cl^-/**2**·$[Cl^-]_2$	1	3.5969	28.1164	33.0500	1.2842	6.5845	6.6093	6.4751	8.7625
	2	3.4829	32.1948	9.6208	0.0148	6.6242	6.5977	6.4319	6.7343
	3	7.7392	48.6449	25.3860	0.0110	6.6238	6.5318	6.5480	6.6180
	Average	4.9397	36.3187	22.6856	0.4367	6.6108	6.5796	6.4850	7.3716

Table S6. Data fitting from modelling titration of **2** with TBACl according to equations 1-3 from manuscript (S5.1-S5.3 from above). The 3 different possible pairings of species for fast exchange are shown.

Fast exchange pairs	Trial #	Fit	K_{11}	K_{21}	K_{31}	$\delta_{\mathbf{2}}$	$\delta_{\mathbf{2}\cdot Cl^-}$	$\delta_{\mathbf{2}_2\cdot Cl^-}$	$\delta_{\mathbf{2}_3\cdot Cl^-}$
2/**2**·Cl^- and $\mathbf{2}_2\cdot Cl^-$/$\mathbf{2}_3\cdot Cl^-$	1	0.6999	1.6182	1373.2497	16.2057	6.6391	6.4817	6.4539	6.9104
	2	0.4576	0.5580	3037.8711	17.2147	6.6378	6.2990	6.4479	6.9037
	3	0.7092	1.2301	1796.5293	19.8428	6.6391	6.4529	6.4470	6.8886
	Average	0.6222	1.1354	2069.2167	17.7544	6.6387	6.4112	6.4496	6.9009
2/$\mathbf{2}_2\cdot Cl^-$ and **2**·Cl^-/$\mathbf{2}_3\cdot Cl^-$	1	1.2620	16.1638	3.0796	2329.0098	6.6494	6.4507	6.0350	6.5985
	2	1.0235	13.4021	3.0287	2245.3761	6.6474	6.4380	6.0258	6.6087
	3	1.5794	15.4759	15.1372	719.8104	6.6517	6.4392	6.4710	6.6001
	Average	1.2883	15.0139	7.0818	1764.7321	6.6495	6.4426	6.1773	6.6024
2/$\mathbf{2}_3\cdot Cl^-$and **2**·Cl^-/$\mathbf{2}_2\cdot Cl^-$	1	0.8110	56.1467	39.5547	22.8395	6.5679	6.4669	6.6769	6.8708
	2	0.8584	114.2117	32.1380	84.3343	6.5766	6.4864	6.7234	6.7152
	3	2.0631	58.2844	67.7166	21.6099	6.5675	6.4589	6.6552	6.8267
	Average	1.2442	76.2142	46.4697	42.9279	6.5707	6.4707	6.6852	6.8042

S1.2.4.7 Fitting of data from titration of **2** with TBAI.

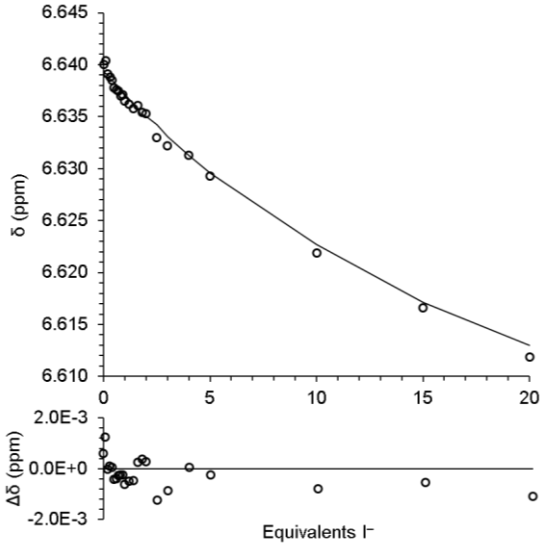


Figure S1. Fit of modelled chemical shift from for 1:1 binding (eq. 3/eq. S4.3) of **2**:I^- (line) to the experimental chemical shift (open circles) from titration of **2** with TBAI. Difference shown below.

S1.2.4.8 Fitting of data from titration of **2** with TBABr.

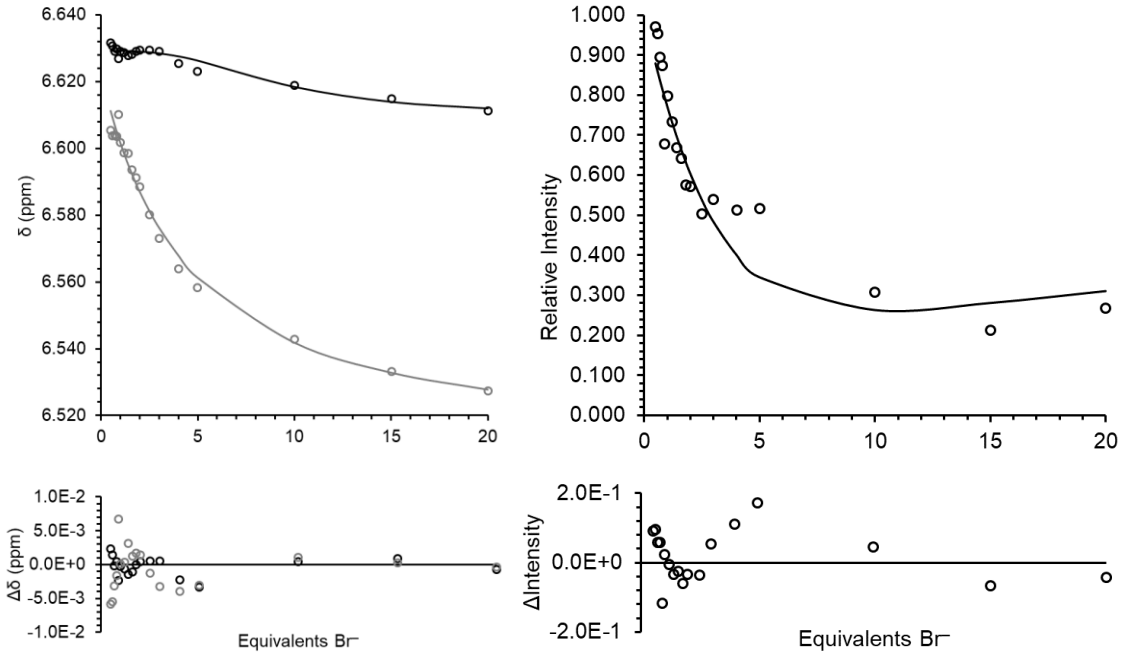


Figure S2. Fit of modelled chemical shift from for 1:1, 1:2 and 1:3 binding (eq. 1-3/eq. S4.1-S4.3) of **2**:Br^- (line) to the experimental chemical shift (black represents fast exchange between **2** and **2**·$[Br^-]_3$, grey represents fast exchange between **2**·Br^- and **2**·$[Br^-]_2$) (open circles, chart on the left) and intensity data (open circles for **2**/**2**·$[Br^-]_3$, chart on the right) from titration of **2** with TBABr. Differences shown below each graph.

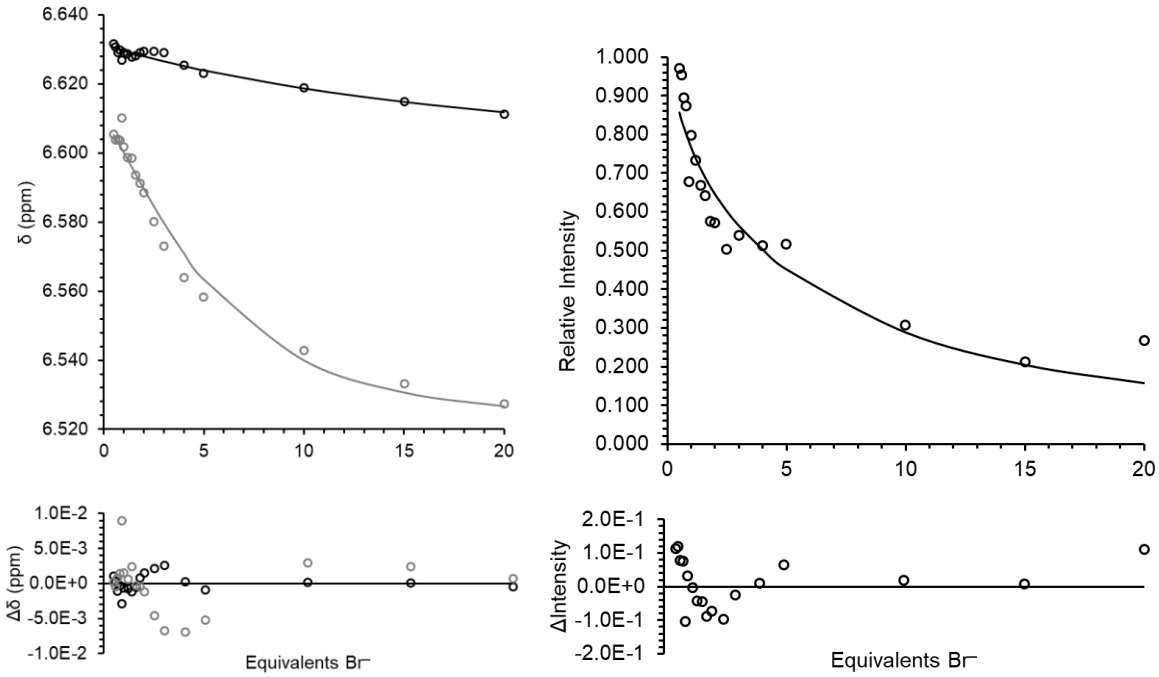


Figure S3. Fit of modelled chemical shift from for 1:1, 1:2 and 2:1 binding (eq. 2-4/eq. S4.2-S4.4) of **2**:Br^- (line) to the experimental chemical shift (black represents fast exchange between **2** and **2**·Br^-, grey represents fast exchange between **2**·$[Br^-]_2$and $\mathbf{2}_2$·Br^-) (open circles, chart on the left) and intensity data (open circles for **2**/**2**·Br^-, chart on the right) from titration of **2** with TBABr. Differences shown below each graph.

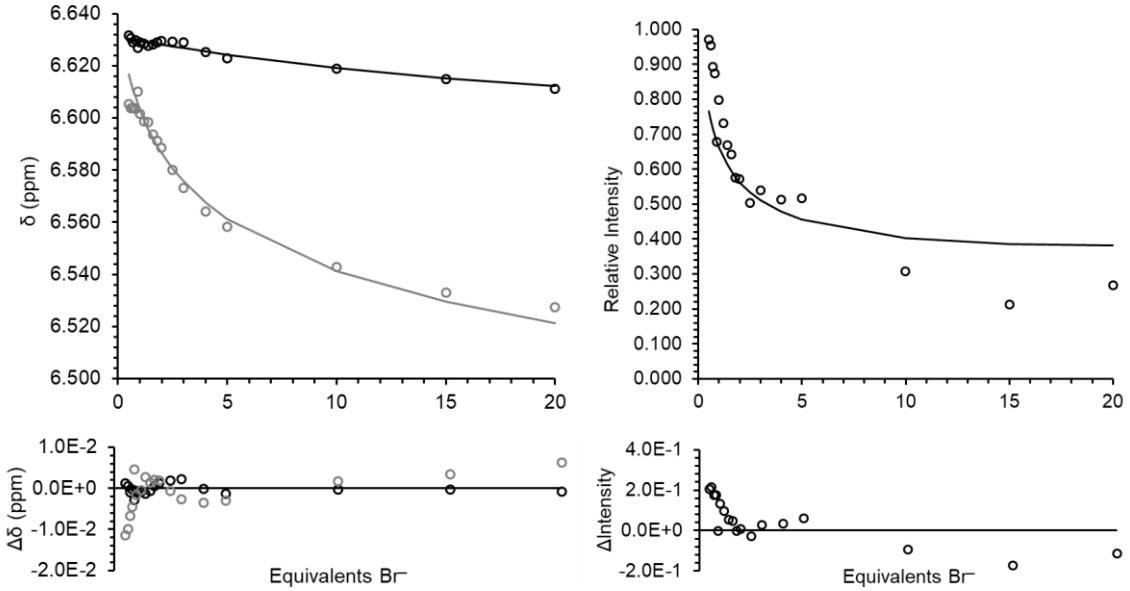


Figure S4. Fit of modelled chemical shift from for 1:1, 2:1 and 3:1 binding (eq. 3-5/eq. S4.3-S4.5) of **2**:Br^- (line) to the experimental chemical shift (black represents fast exchange between **2** and **2**·Br^-, grey represents fast exchange between $\mathbf{2}_2$·Br^- and $\mathbf{2}_3$·Br^-) (open circles, chart on the left) and intensity data (open circles for **2**/**2**·Br^-, chart on the right) from titration of **2** with TBABr. Differences shown below each graph.

S1.2.4.9 Fitting of data from titration of **2** with TBACl

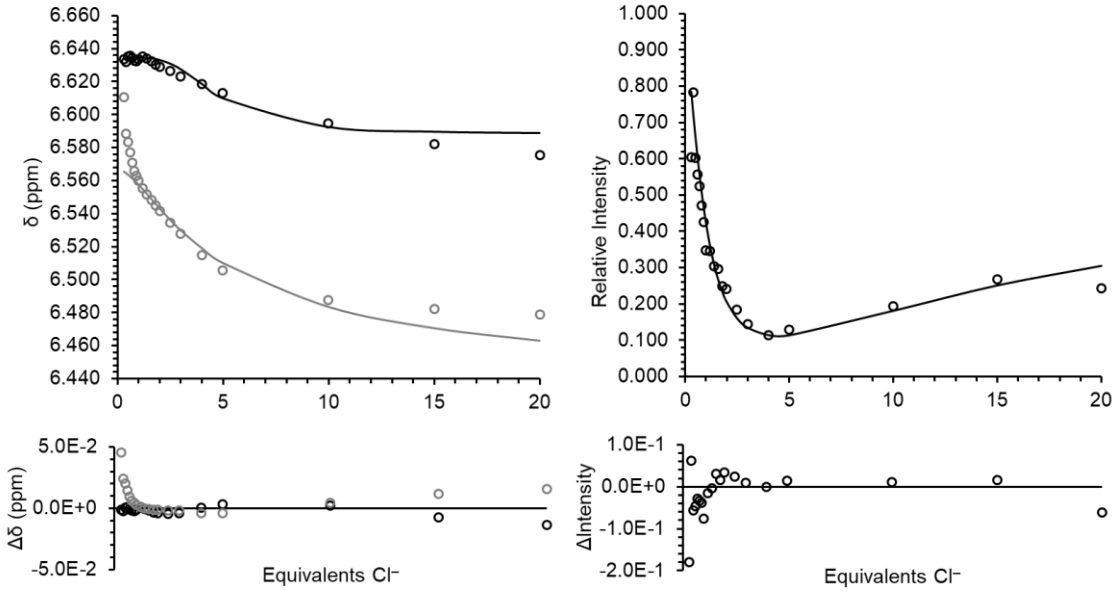


Figure S5. Fit of modelled chemical shift from for 1:1, 1:2 and 1:3 binding (eq. 1-3/eq. S4.1-S4.3) of **2**:Cl^- (line) to the experimental chemical shift (black represents fast exchange between **2** and **2**·$[Cl^-]_3$, grey represents fast exchange between **2**·Cl^- and **2**·$[Cl^-]_2$) (open circles, chart on the left) and intensity data (open circles for **2/2**·$[Cl^-]_3$, chart on the right) from titration of **2** with TBACl. Differences shown below each graph.

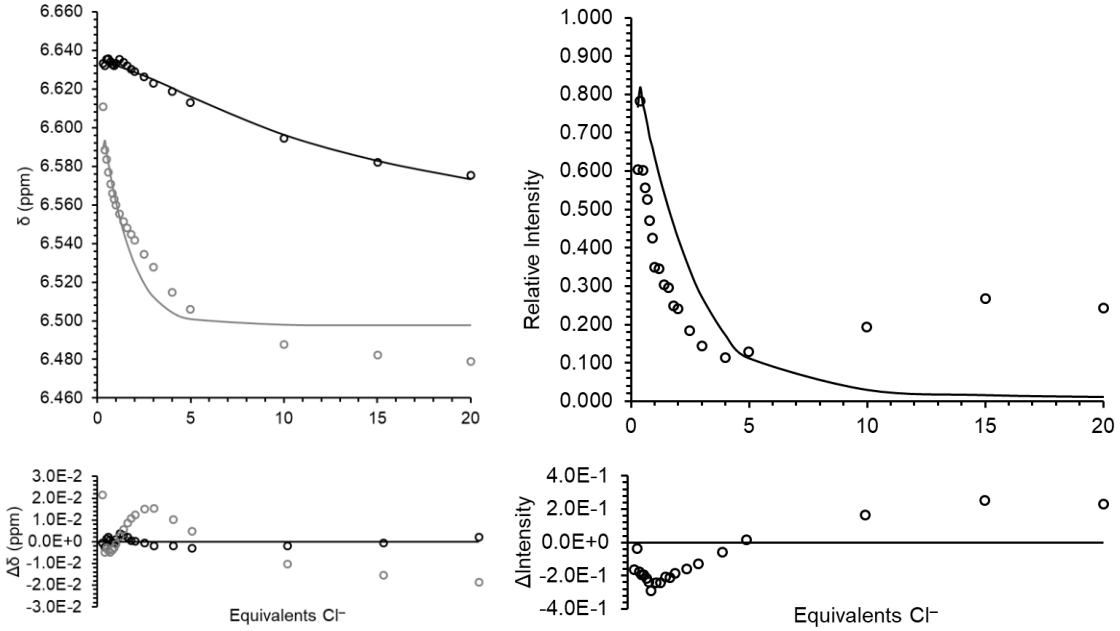


Figure S6. Fit of modelled chemical shift from for 1:1, 1:2 and 2:1 binding (eq. 2-4/eq. S4.2-S4.4) of **2**:Cl^- (line) to the experimental chemical shift (black represents fast exchange between **2** and **2**·Cl^-, grey represents fast exchange between **2**·$[Cl^-]_2$ and $\mathbf{2}_2$·Cl^-) (open circles, chart on the left) and intensity data (open circles for **2/2**·Cl^-, chart on the right) from titration of **2** with TBACl. Differences shown below each graph.

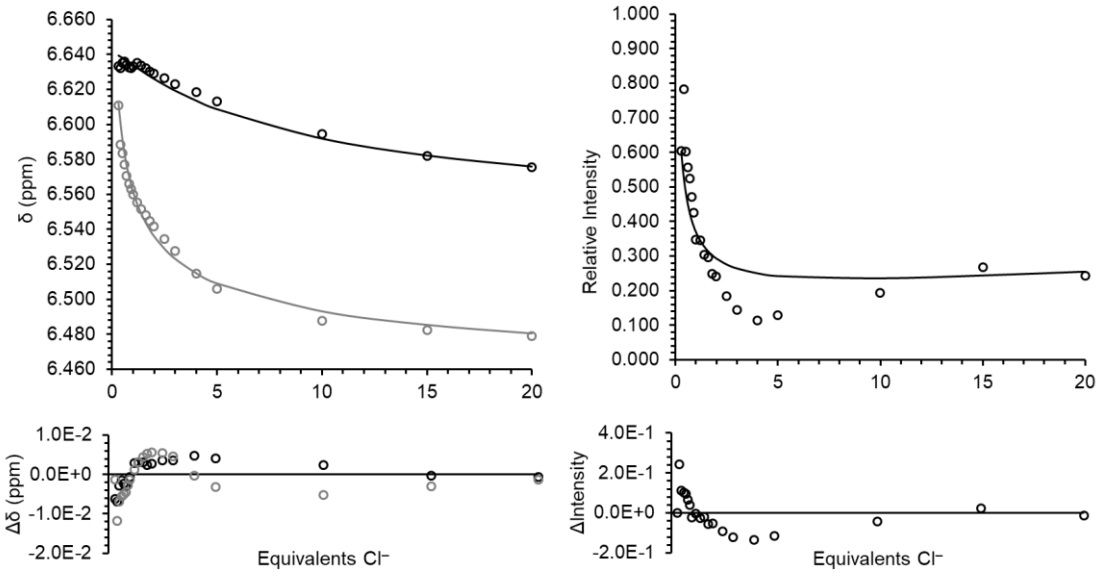


Figure S7. Fit of modelled chemical shift from for 1:1, 2:1 and 3:1 binding (eq. 3-5/eq. S4.3-S4.5) of **2**:Cl^- (line) to the experimental chemical shift (black represents fast exchange between **2** and **2**·Cl^-, grey represents fast exchange between $\mathbf{2}_2$·Cl^-, and $\mathbf{2}_3$·Cl^-) (open circles, chart on the left) and intensity data (open circles for **2**/**2**·Cl^-, chart on the right) from titration of **2** with TBACl. Differences shown below each graph.

S1.3 ESI-MS Details

ESI-MS experiments were performed on Waters Synapt G2 mass spectrometer under the following conditions: ESI capillary voltage, 3.0 kV; sample cone voltage, 20 V; extraction cone voltage, 0.1 V; cone gas flow, 10 L/h; desolvation gas flow, 700 L/h (N_2); source gas control, 0 mL/min; trap gas control, 2 mL/min; Helium cell gas control, 100 mL/min; sample flow rate, 5 μL/min. Source temperature and desolvation temperature were used at 100 ºC and 120 ºC, respectively.

All the initial solutions were prepared at concentration of 0.5 mg/mL in acetonitrile. The samples were prepared by mixing **2** with TBAX (X = Cl or Br) in 1:1, 1:2 and 1:3 molar ratios, respectively. Some precipitates formed after the mixing. A 100 uL aliquot of each was taken, filtered, diluted to 500 uL using acetonitrile and was used directly for ESI test. The data were recorded under negative mode. In both cases a base peak that corresponds to the m/z of the spirocyclic anion $[Sb(O_2C_6H_3C(CH_3)_3)_2]^-$ which likely results from fragmentation of the parent ion(s).[10]

S1.4 Computational Details

S1.4.1 Methods and Functionals

Calculations were performed using the ORCA 4.0 quantum chemistry program package from the development team at the Max Planck Institute for Bioinorganic Chemistry.[11] The starting geometry for optimization of the neutral **1** and its complexes with X^- were based on our previous computational studies.[1] All calculations were carried out with the Zero-Order Regular Approximation (ZORA).[12,13] For geometry optimizations, frequencies, and thermochemistry the B97-D3 functional[14] and def2-TZVPP[15,16] with SARC/J basis sets[17] were used for hydrogen atoms and all other atoms respectively. Spin-restricted Kohn–Sham determinants[18] were chosen to describe the closed shell wavefunctions, employing the RI approximation[19] and the tight SCF convergence criteria provided by ORCA. The basis set superposition error (BSSE) was corrected using the Boys and Bernardi procedures.[20] The conductor-like polarizable continuum model (CPCM)[21] was adopted to evaluate the dielectric effects of solvents (DMSO, THF, and chloroform). All reported secondary bonding distances were obtained from gas-phase calculations.

*S1.4.2 Geometry of **1** and X^- Complexes*

Complex stoichiometries of 2:1, 1:1, and 1:2 for **1**:X^- were probed. For the 2:1 complex, over 15 starting geometric conformations were considered for Cl^-, but none converged with all positive vibrational frequencies, which indicated that the global minima was not located likely due to a rather flat potential energy surface. Given the rotation flexibility of **1** at the Sb—O—Sb bridge centre, many possible structures could be constructed, and the effort spent in searching for the true global minimal could be well beyond the purpose of this paper. Although 3:1 complexes were possible according to ^{1}H NMR data fitting, they were not probed by DFT calculations. We report two possible conformations for $\mathbf{1}_2 \cdot Cl^-$ (Figure S8) that converged with the lowest energies and their five lowest calculated vibrational frequencies (See Section S3). Note that the structure with self-assembled dimeric **1** and Cl^- interacting with only one of the two molecules of **1** gave large negative ΔG values (Section S3). Other geometries that contain one or more

solvent molecules explicitly bound through SBIs might lead to more appropriate energetics. The second structure, gave more positive ΔG values.

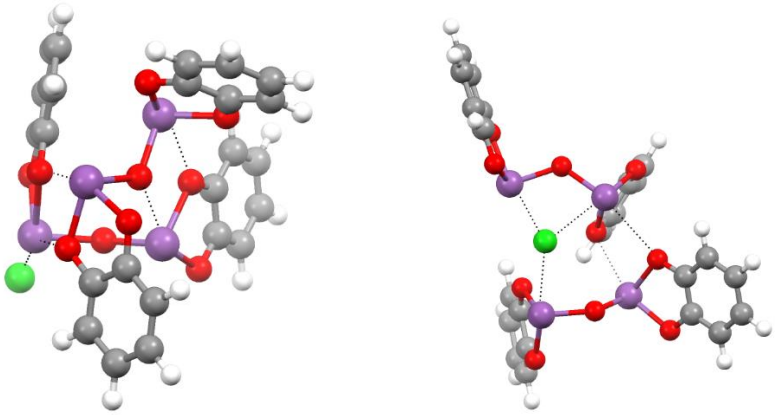


Figure S8 DFT minimized structures of $\mathbf{1}_2 \cdot Cl^-$. Intermolecular SBIs are depicted with black dotted lines. Left: structure of dimeric, self-assembled **1** units and Cl^- interacting with only one of the two molecules of **1** units (denoted as $\mathbf{1}_{2(dimer)} \cdot Cl^-$). Right: structure of Cl^- interacting with both molecules of **1**.

Table S7. SBI distances (in Å) of DFT-minimized $\mathbf{1}_2 \cdot X^-$complexes.

Geometry	SBI distances (in Å)				
	$Sb_1 \cdots X_1$	$Sb_2 \cdots X_1$	$Sb_3 \cdots X_1$	$Sb_4 \cdots X_1$	Average Intermolecular Sb···O
$\mathbf{1}_{2(dimer)} \cdot Cl^-$	2.49	--	--	--	2.40
$\mathbf{1}_2 \cdot Cl^-$	2.62	--	3.10	3.70	2.47

Three possible geometries were considered for the $\mathbf{1} \cdot X^-$ complexes (Figure S9): 1) X^- interacting with two Sb(III) centres (forming a bridge) and the catecholate rings in a cis arrangement (denoted as cis-$\mathbf{1} \cdot X_b^-$); 2) X^- interacting with two Sb(III) centres (forming a bridge) with the catecholate rings in a trans arrangement (denoted as trans-$\mathbf{1} \cdot X_b^-$); 3) X^- interacting with only one Sb(III) centre (in a terminal position) and the other Sb(III) forming an intramolecular SBI with one oxygen atom on the opposite catecholate ring (denoted as $\mathbf{1} \cdot X_t^-$). For the cis-$\mathbf{1} \cdot Cl_b^-$ structure, one negative vibrational frequency still existed in the minimized structure indicating that it does not represent a global minimum. As a result, the energetics and bond distances for cis-$\mathbf{1} \cdot Cl_b^-$ were not reported.

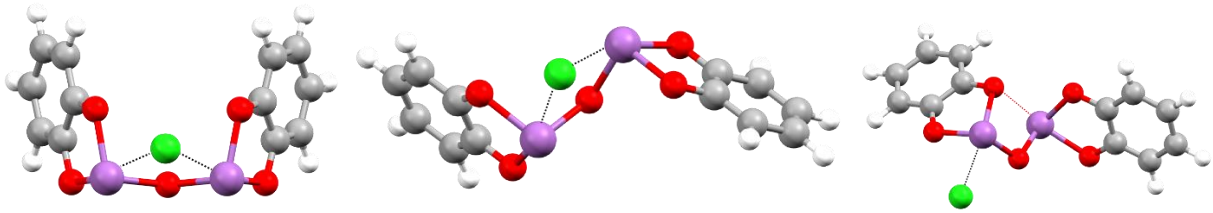


Figure S9. DFT-probed structures of **1**·X^- (Cl^- shown). Intermolecular SBIs are shown in black dotted lines, while intramolecular SBIs are shown in red dotted lines. Left: cis-**1**·X_b^-; middle: trans-**1**·X_b^-; right: **1**·X_t^-.

Table S8. SBI distances (in Å) of DFT-minimized **1**·X^-complexes.

Geometry	SBI distances (in Å)		
	$Sb_1\cdots X_1$	$Sb_2\cdots X_1$	Intramolecular Sb···O
cis-**1**·Br_b^-	3.04	3.04	--
cis-**1**·I_b^-	3.32	3.32	--
1·Cl_t^-	2.49	--	2.38
1·Br_t^-	2.67	--	2.39
1·I_t^-	2.94	--	2.41
trans-**1**·Cl_b^-	2.85	2.85	--
trans-**1**·Br_b^-	3.03	3.03	--
trans-**1**·I_b^-	3.32	3.31	--

In the same manner, three possible geometries were considered for the **1**·$[Cl^-]_2$ complexes (Figure S10): 1) both X^- interacting with two Sb(III) centres (forming two bridges) and the catecholate rings in a cis arrangement (denoted as **1**·$[Cl_b^-]_2$); 2) one X^- interacting with two Sb(III) centres (forming two bridge) but the other X^- interacts only one Sb(III) (in terminal position); the catecholate rings were in a trans arrangement (denoted as **1**·Cl_b^-·Cl_t^-); 3) both X^- interacting with only one Sb(III) centre (in terminal positions); each Sb(III) forms intramolecular SBI with one oxygen atom on the opposite catecholate ring (denoted as **1**·$[Cl_t^-]_2$). Only **1**·$[Cl_t^-]_2$ gave all positive vibrational frequencies according to the calculation results, thus the energetics and bond distances of the other two alternative structures were not reported. Both Sb···Cl^- SBI distances were 2.63 Å, with two additional intramolecular Sb···O SBI of 3.13 Å in **1**·$[Cl_t^-]_2$. Because no **1**·$[Br^-]_2$ complex was observed by ESI-MS and that it was not favourable structure in

solution according to ^{1}H NMR fitting, **1**·[Br^-]$_2$ was not studied by DFT calculations. The **1**·[I^-]$_2$ complex, was also not studied, since it showed simple binding forming only **1**·I^- in solutions according to ^{1}H NMR data.

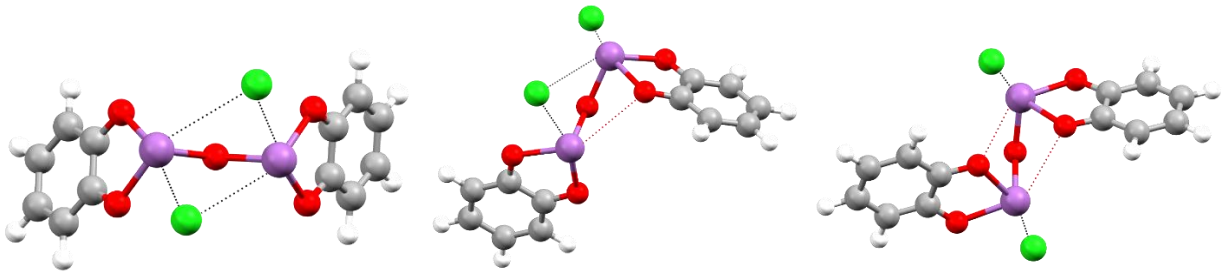


Figure S10. DFT-probed structures of **1**·[Cl^-]$_2$ (Cl^- shown). Intermolecular SBIs are shown in black dotted lines, while intramolecular SBIs are shown in red dotted lines.
Left: **1**·[Cl_b^-]$_2$; middle: **1**·Cl_b^-·Cl_t^-; right: **1**·[Cl_t^-]$_2$.

The **1**·[DMSO]$_2$ and **1**·DMSO·X^- were constructed according to the reported crystal structure of **1**·[pyridine]$_2$ (Figure S11).[10] The **1**·[DMSO]$_2$ structure was analogous to the **1**·[X_t^-]$_2$, where the DMSO molecules were in terminal positions with respect to the Sb(III) centres and each of the Sb(III) centres formed one pair of SBI with the oxygen on the opposite catecholate ring. The structure of **1**·DMSO·X^- had the DMSO and X^- both at terminal positions and only one pair of intermolecular SBIs. The **1**·DMSO·I^- yielded one small negative vibrational frequency (See Section S3 for details) consistent with a very flat potential energy surface for a weak SBI.

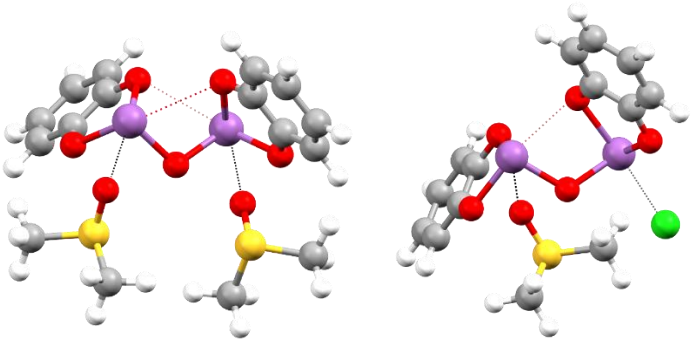


Figure S11. DFT minimized structures of **1**·$[DMSO]_2$ (left) and **1**·DMSO·X^- (right; Cl^- shown). Intermolecular SBIs are shown in black dotted lines, while intramolecular SBIs are shown in red dotted lines.

Table S9. SBI distances (in Å) of DFT-minimized **1**·$[DMSO]_2$ and **1**·DMSO·X^-complexes.

Geometry	SBI distances (in Å)			
	$Sb_1\cdots X_1$	$Sb_1\cdots O_{DMSO}$	$Sb_2\cdots O_{DMSO}$	Intramolecular Sb···O
1·$[DMSO]_2$	--	2.43	2.42	2.91
1·DMSO·Cl^-	2.55	--	2.58	2.71
1·DMSO·Br^-	2.75	--	2.56	2.76
1·DMSO·I^-	3.14	--	2.43	3.45

S2 Spectroscopic (^{1}H NMR) and Spectrometric (ESI-MS) Data

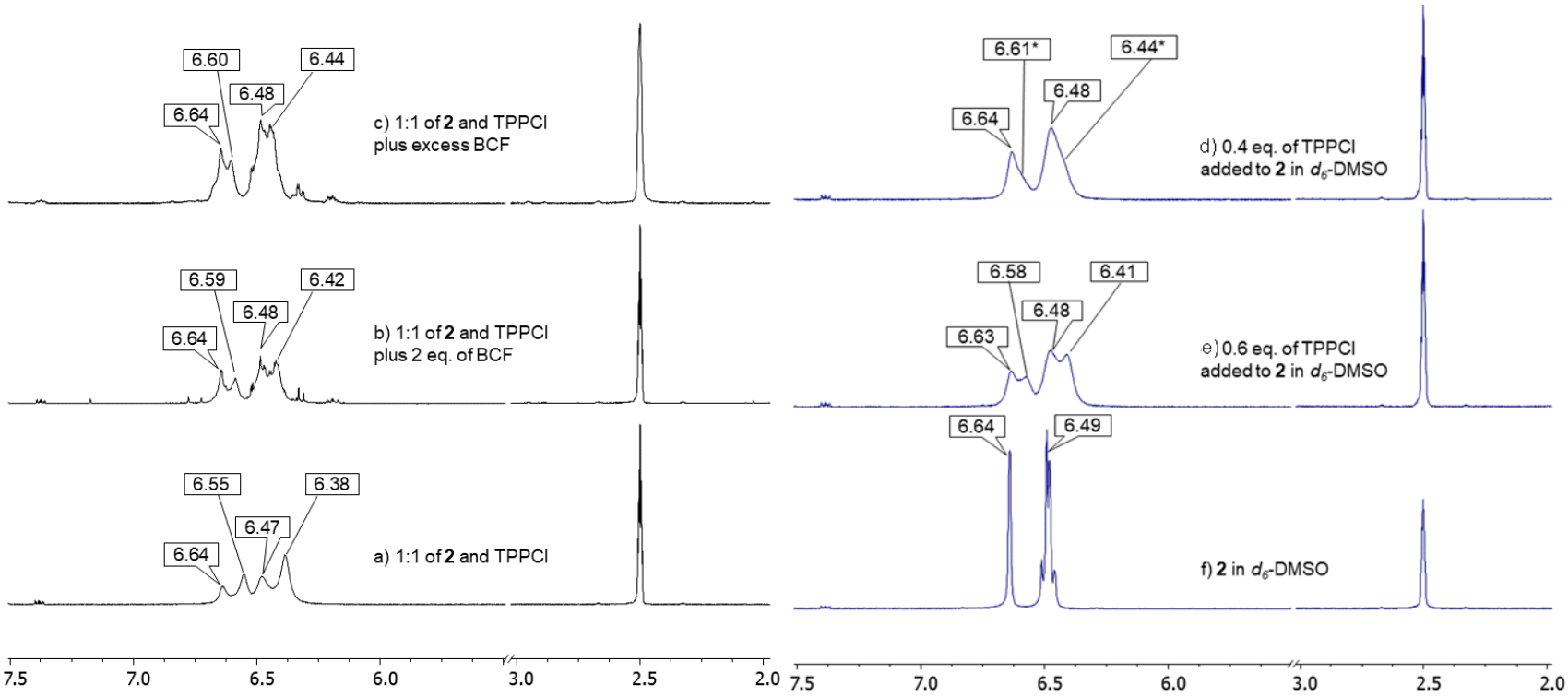


Figure S12. ^{1}H NMR spectra (2.0-7.5 ppm; peak positions are denoted on spectra) of a) 1:1 mix of **2** (0.010 g) and tetraphenylphosphonium chloride (TPPCl; 0.0064 g) in 0.40 mL d_6-DMSO, showing a pattern of two sets of fast exchange pairs in solution; b) 2 equivalents (0.018 g) of BCF added to the 1:1 mixture of **2** and TPPCl to competitively bind Cl^-. c) excess (>>2 eq.) of BCF added to the 1:1 mixture of **2** and TPPCl. d) 0.6 eq. of TPPCl (10.2 µL, 1.0 M) added to **2** (0.034 M) in d_6-DMSO to illustrate the similar peak positions to b); e) 0.4 eq. of TPPCl (6.8 µL, 1.0 M) added to **2** (0.034 M) in d_6-DMSO to illustrate the similar peak positions to c) (*peak positions are assigned according to line fitting in MestReNova); f) free **2** (0.034 M) in d_6-DMSO.

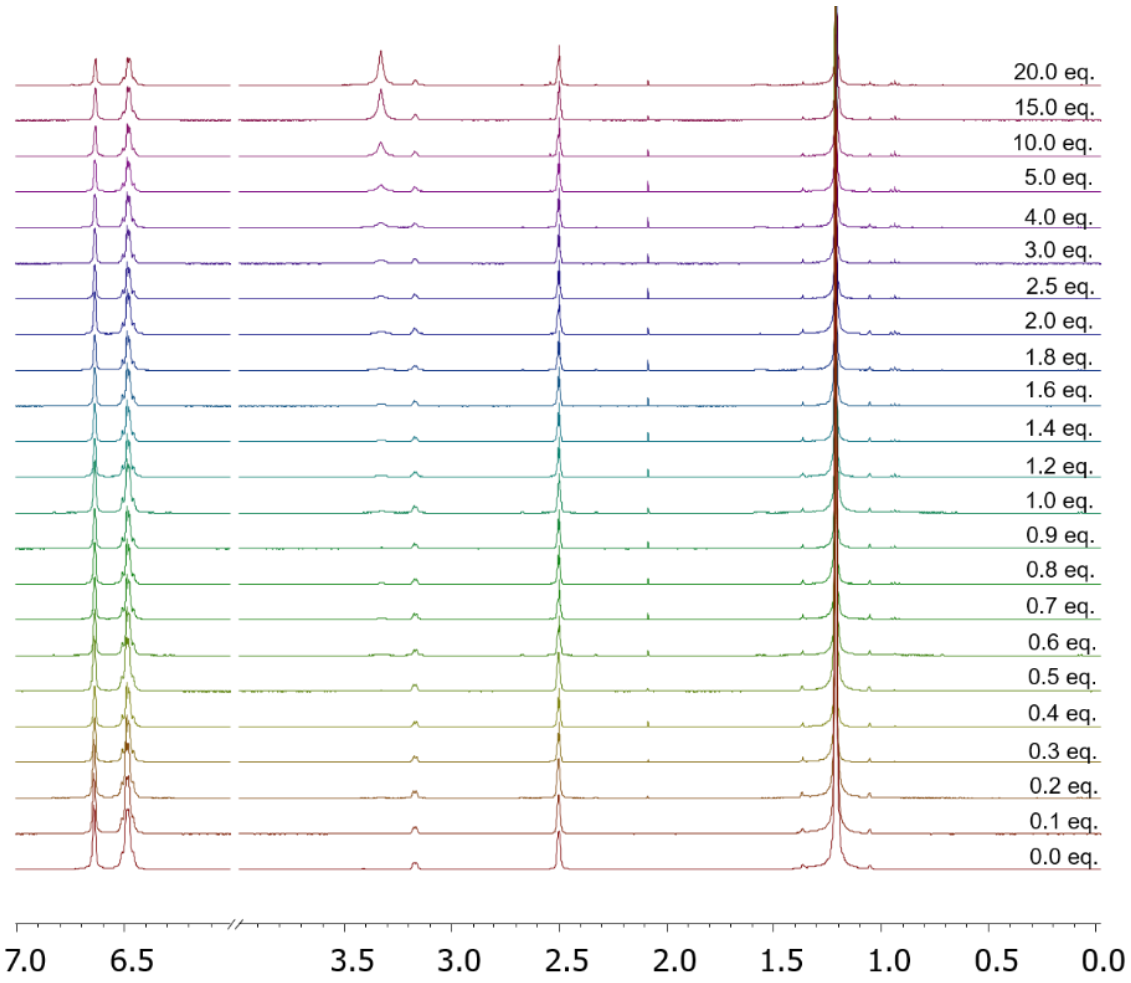


Figure S13. ^{1}H NMR spectra (0.0-7.0 ppm) of titration of 0.50 mL 0.034 M solution of **2** in d_6-DMSO with d_6-DMSO (1 equiv. added = 17.0 μL). Added amounts are provided on figure.

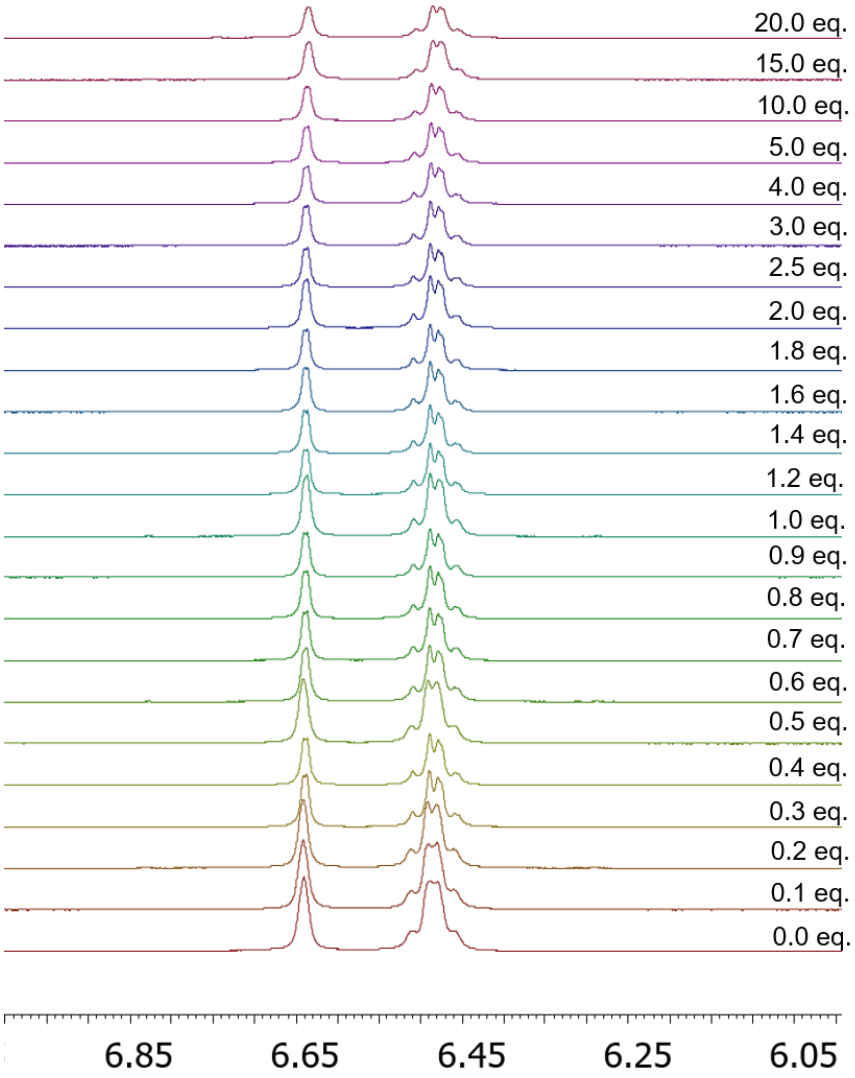


Figure S14. ^{1}H NMR spectra (6.0-7.0 ppm) of titration of 0.50 mL 0.034 M solution of **2** in d_6-DMSO with d_6-DMSO (1 equiv. added = 17.0 μL). Added amounts are provided on figure.

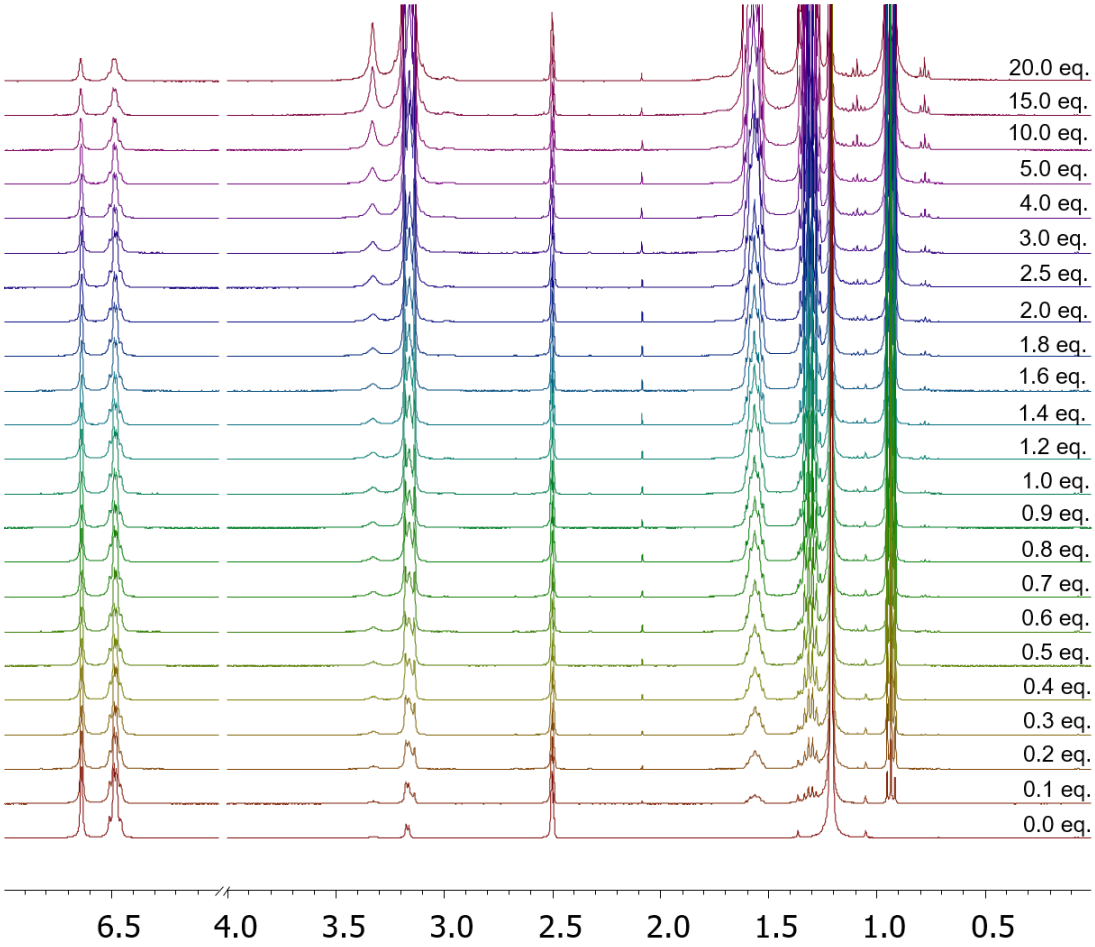


Figure S15. ^{1}H NMR spectra (0.0-7.0 ppm) of titration of 0.50 mL 0.034 M solution of **2** in d_6-DMSO with a 1.0 M solution of TBA(PF_6) in d_6-DMSO. Added equivalents of anion are provided on figure.

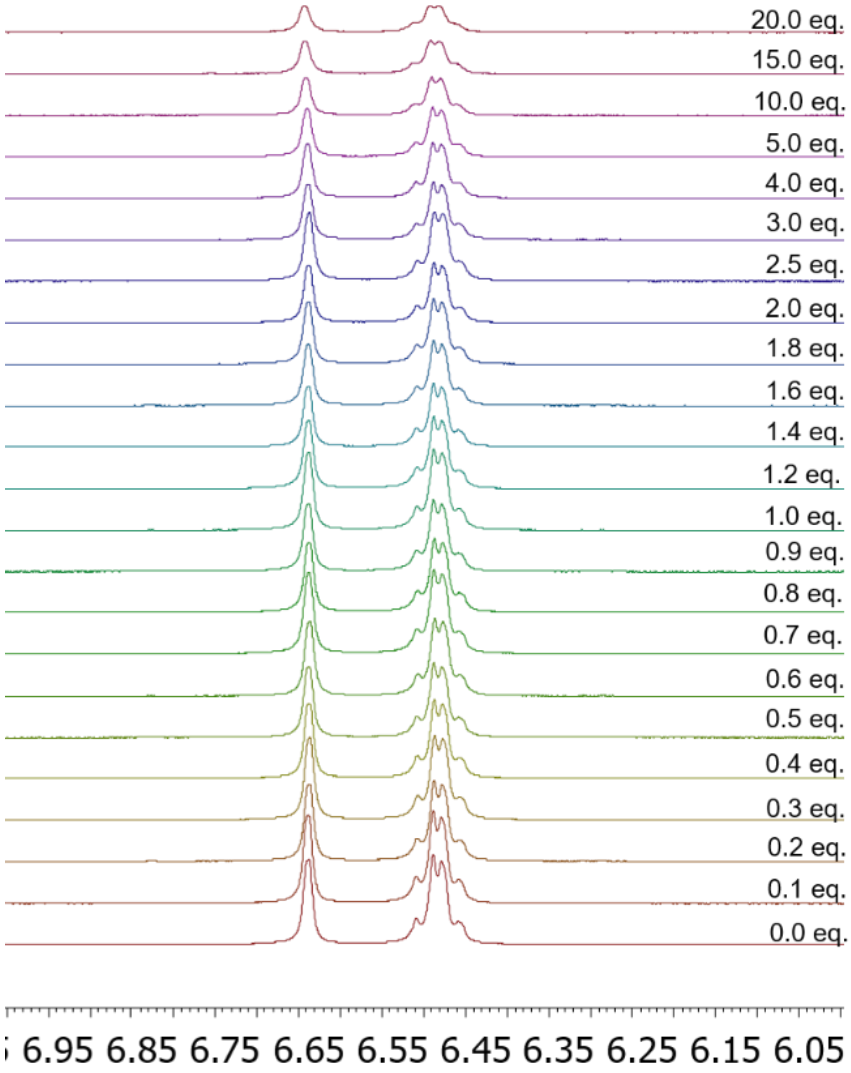


Figure S16. ^{1}H NMR spectra (6.0-7.0 ppm) of titration of 0.50 mL 0.034 M solution of **2** in d_6-DMSO with a 1.0 M solution of TBA(PF_6) in d_6-DMSO. Added equivalents of anion are provided on figure.

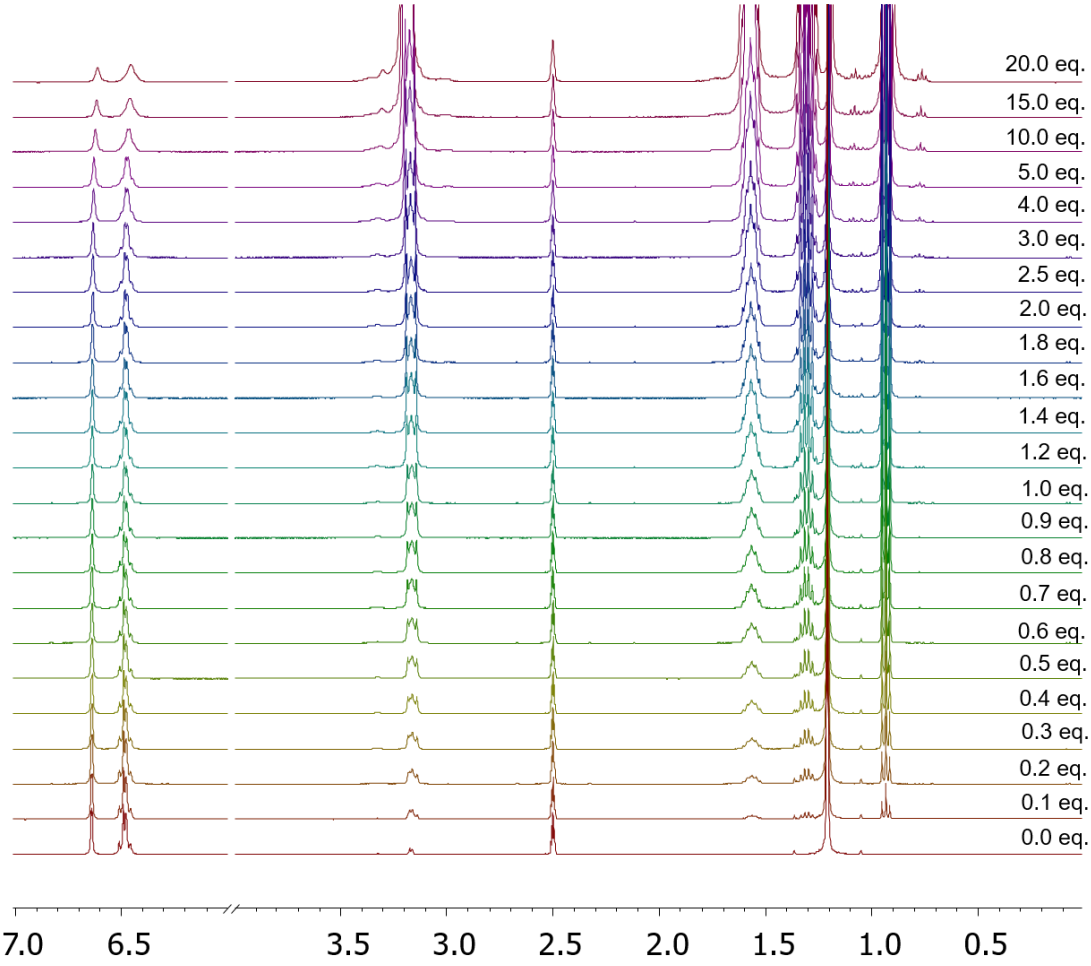


Figure S17 ^{1}H NMR spectra (0.0-7.0 ppm) of titration of 0.50 mL 0.034 M solution of **2** in d_6-DMSO with a 1.0 M solution of TBAI in d_6-DMSO. Added equivalents of anion are provided on figure.

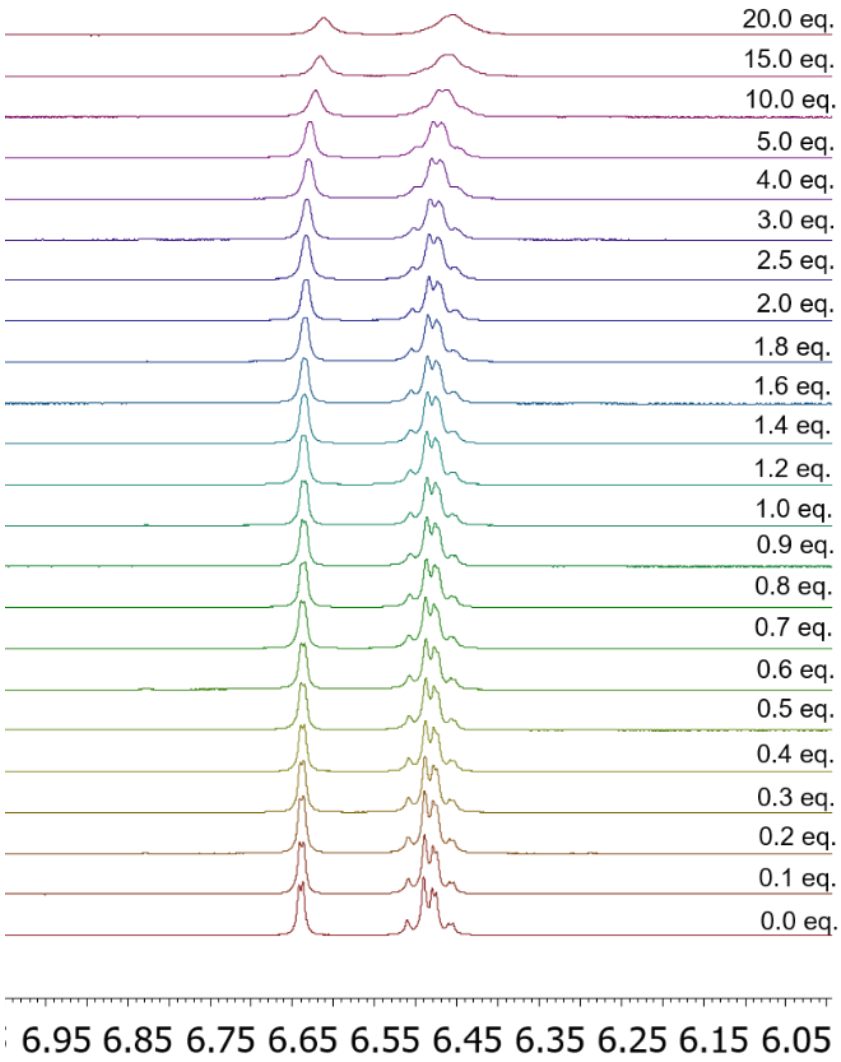


Figure S18 ^{1}H NMR spectra (6.0-7.0 ppm) of titration of 0.50 mL 0.034 M solution of **2** in d_6-DMSO with a 1.0 M solution of TBAI in d_6-DMSO. Added equivalents of anion are provided on figure.

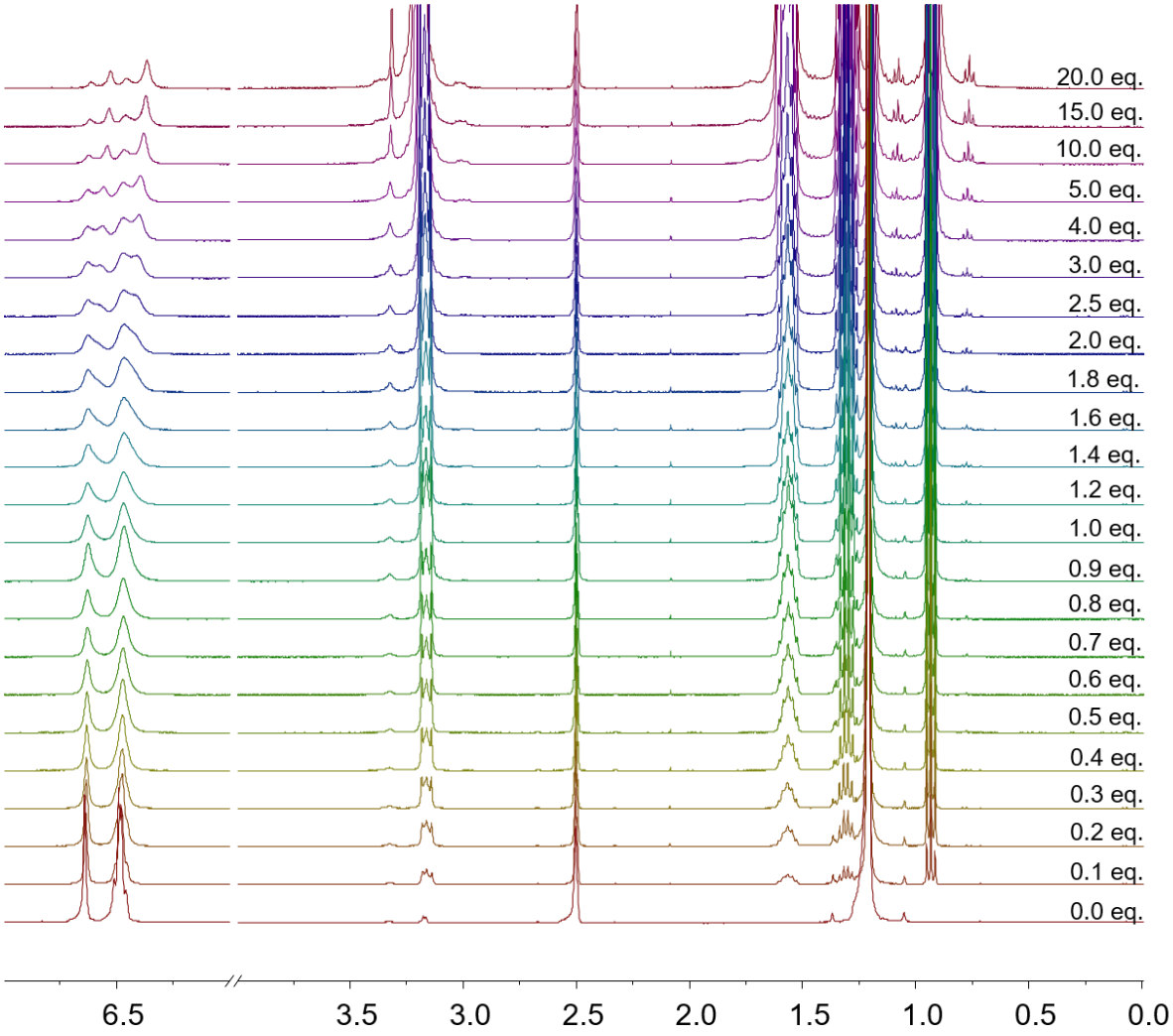


Figure S19. ^{1}H NMR spectra (0.0-7.0 ppm) of titration of 0.50 mL 0.034 M solution of **2** in d_6-DMSO with a 1.0 M solution of TBABr in d_6-DMSO. Added equivalents of anion are provided on figure.

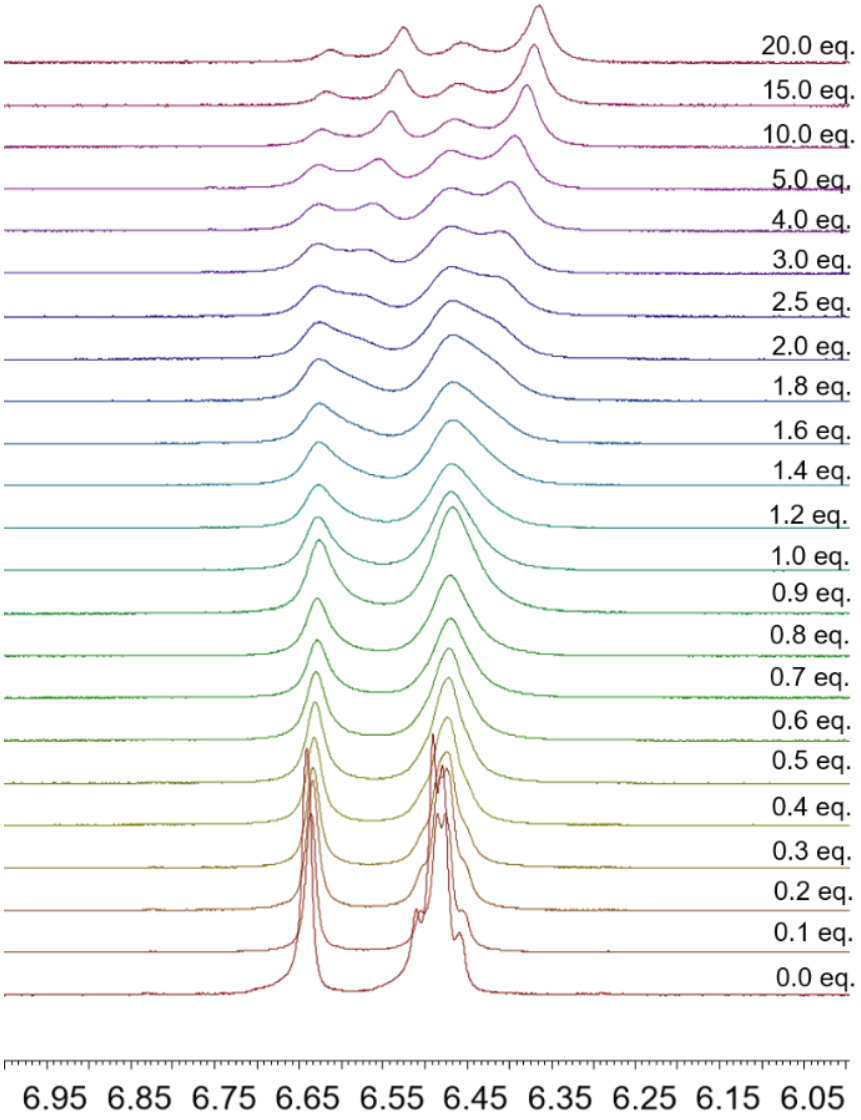


Figure S20. ^{1}H NMR spectra (6.0-7.0 ppm) of titration of 0.50 mL 0.034 M solution of **2** in d_6-DMSO with a 1.0 M solution of TBABr in d_6-DMSO. Added equivalents of anion are provided on figure.

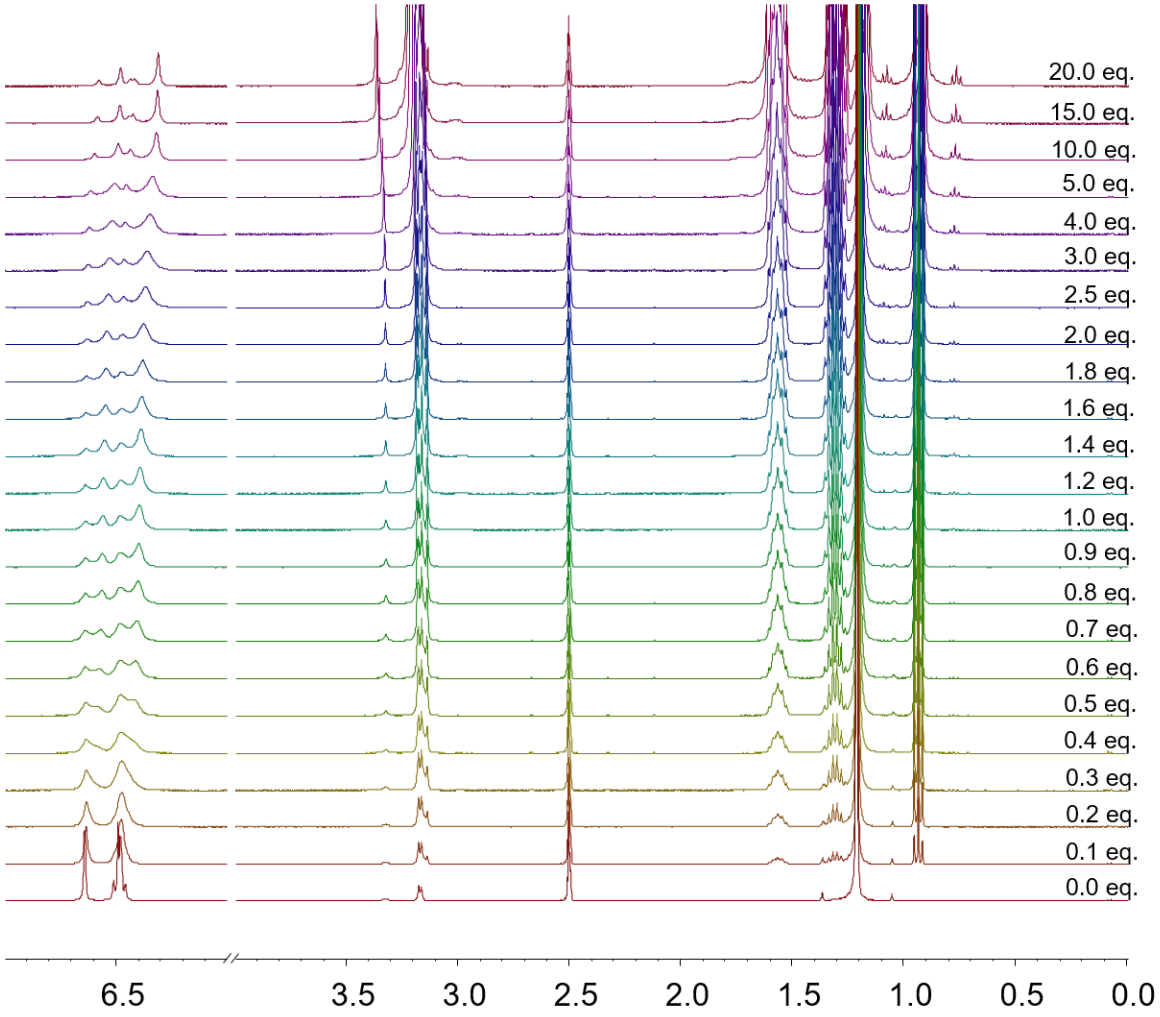


Figure S21. ^{1}H NMR spectra (0.0-7.0 ppm) of titration of 0.50 mL 0.034 M solution of **2** in d_6-DMSO with a 1.0 M solution of TBACl in d_6-DMSO. Added equivalents of anion are provided on figure.

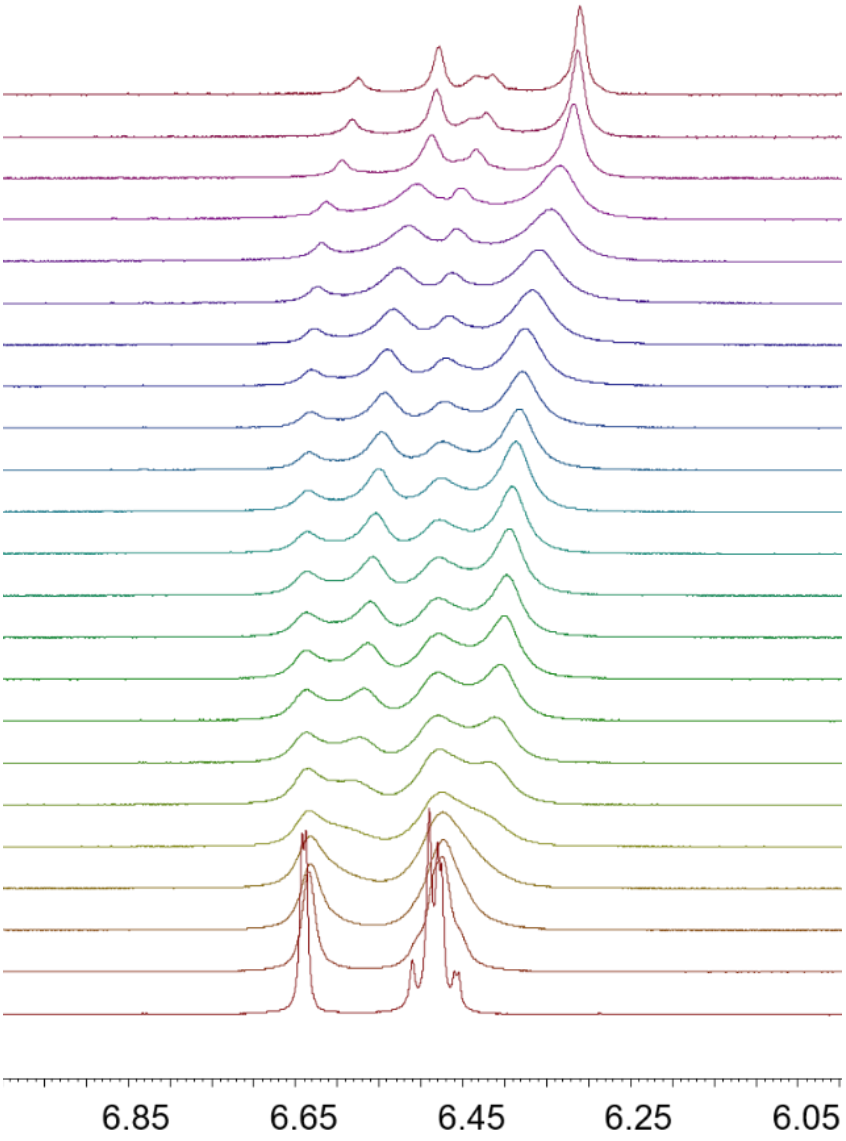


Figure S22. ^{1}H NMR spectra (6.0-7.0 ppm) of titration of 0.50 mL of a 0.034 M solution of **2** in d_6-DMSO with a 1.0 M solution of TBACl in d_6-DMSO. Added equivalents of anion are provided on figure.

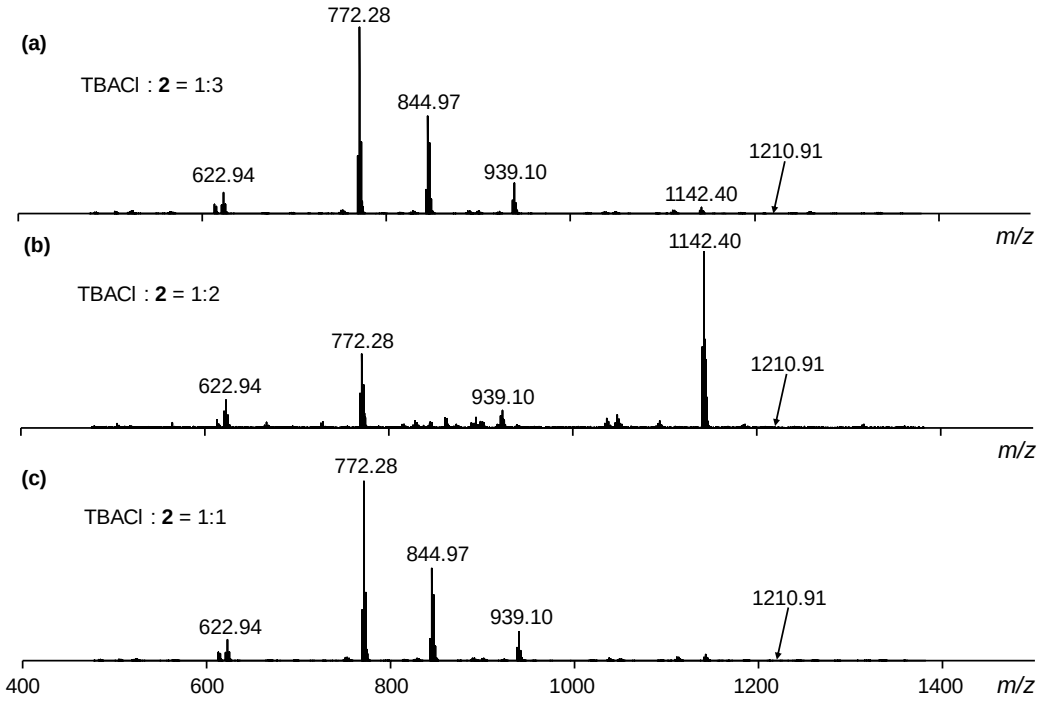


Figure S23. ESI-MS of TBACl with 1, 2 or 3 equivalents of **2** – full window.

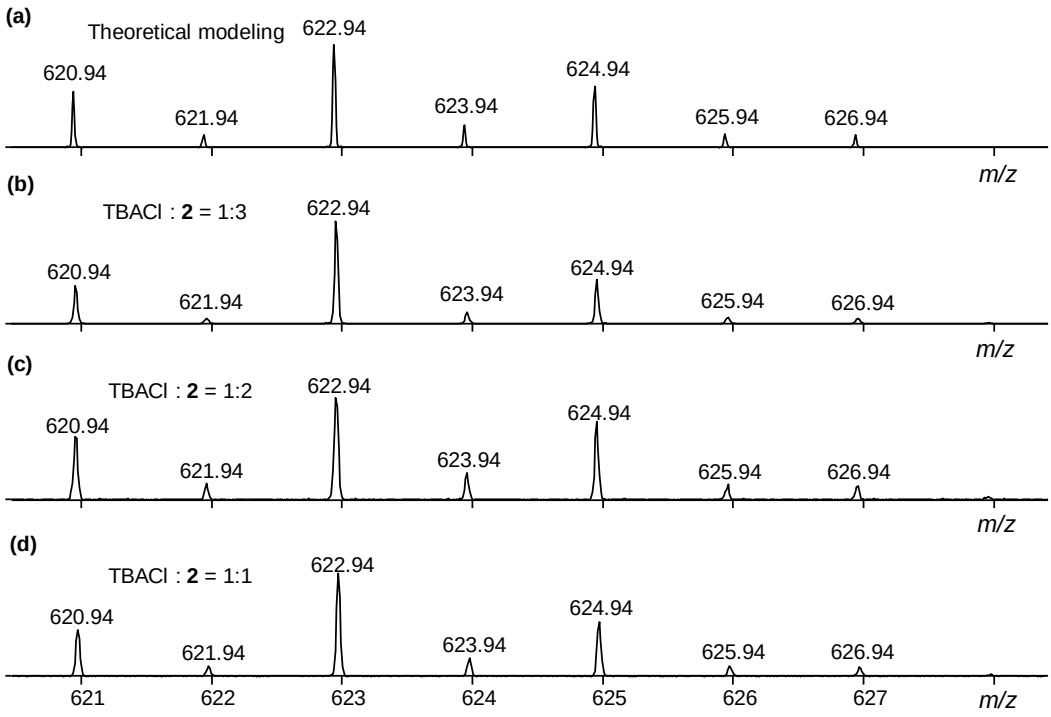


Figure S24. Theoretical modelling (a) and isotopic distribution of **2**·Cl^- when mixing TBACl with 1 (b),2 (c) or 3 (d) equivalents of **2** from ESI-MS.

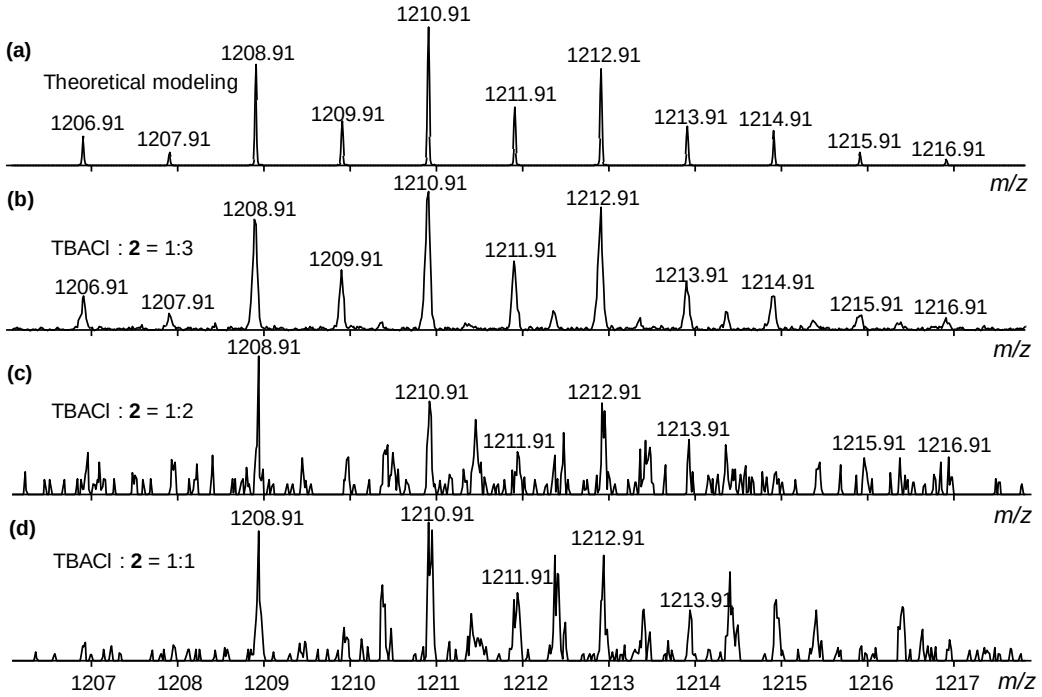


Figure S25. Theoretical modelling (a) and isotopic distribution of $\mathbf{2}_2 \cdot Cl^-$ when mixing TBACl with 1 (b), 2 (c) or 3 (d) equivalents of **2** from ESI-MS.

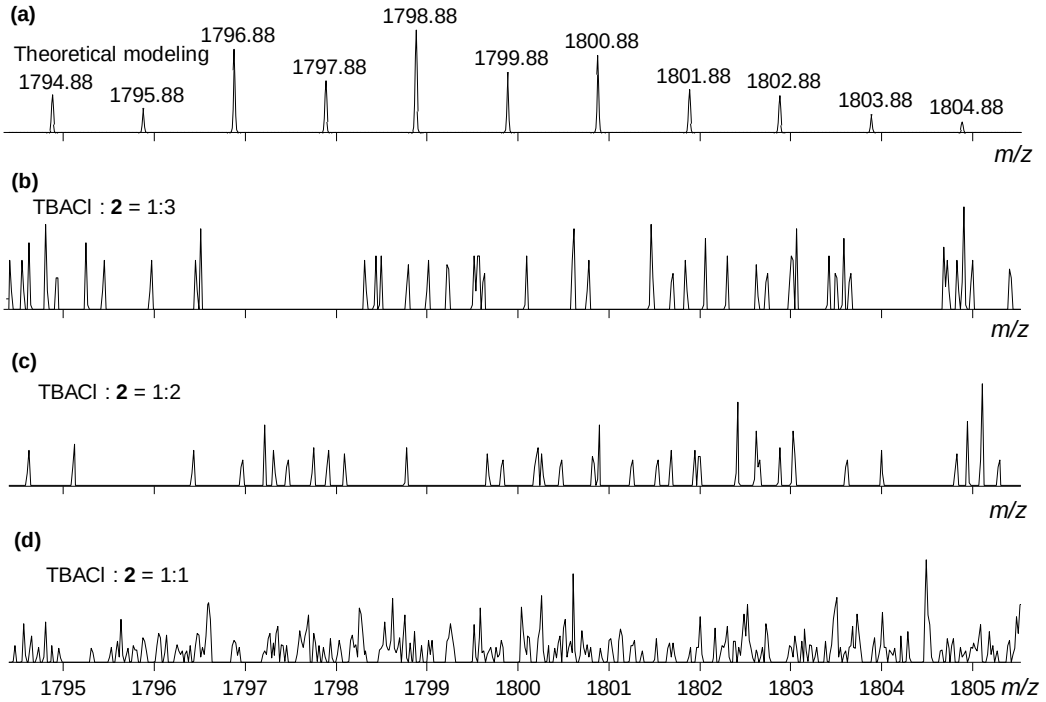


Figure S26. Theoretical modelling (a) and isotopic distribution of $\mathbf{2}_3 \cdot Cl^-$ when mixing TBACl with 1 (b), 2 (c) or 3 (d) equivalents of **2** from ESI-MS.

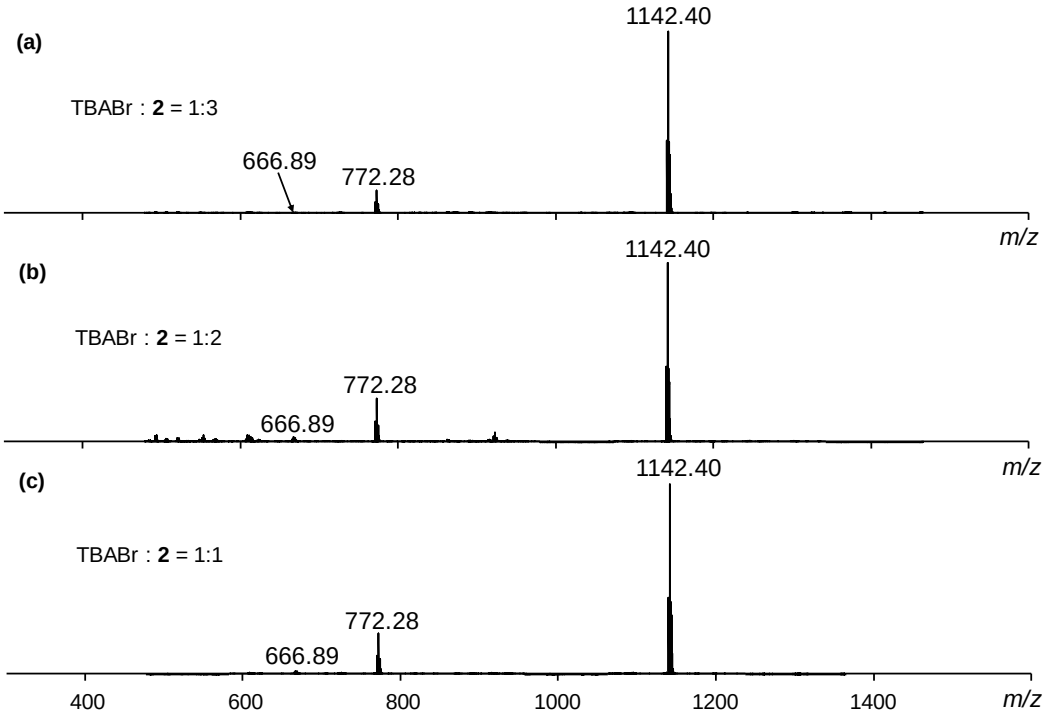


Figure S27. ESI-MS of TBABr with 1 (a), 2 (b) or 3 (c) equivalents of **2** – full window.

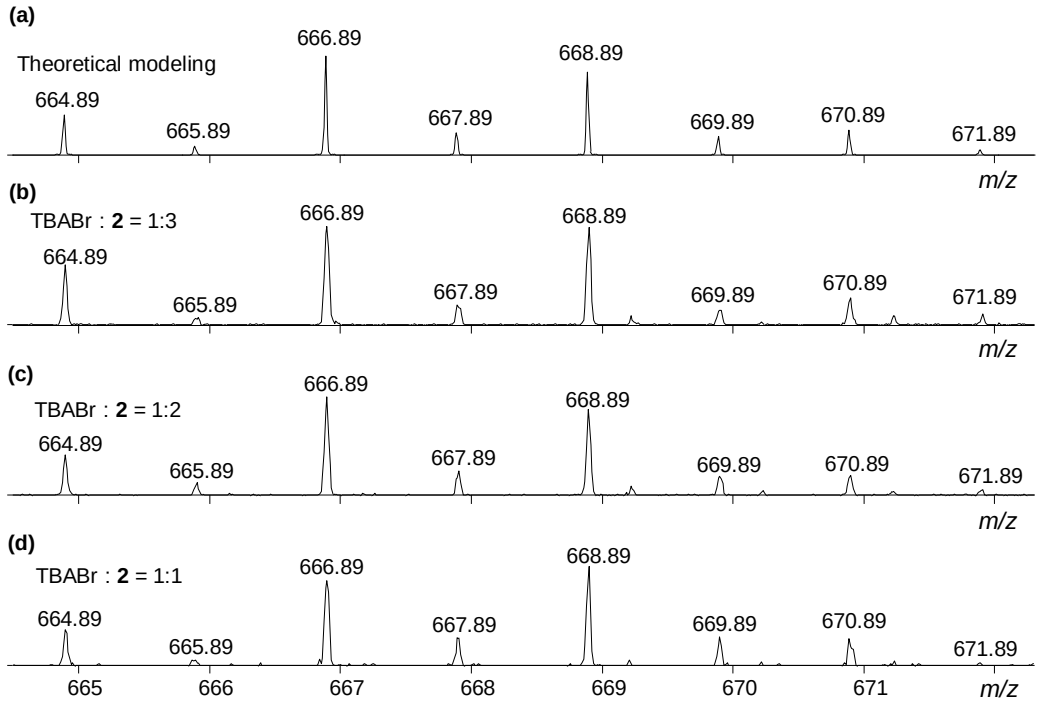


Figure S28. Theoretical modelling (a) and isotopic distribution of **2**·Br^- when mixing TBABr with 1 (b) ,2 (c) or 3 (d) equivalents of **2** from ESI-MS.

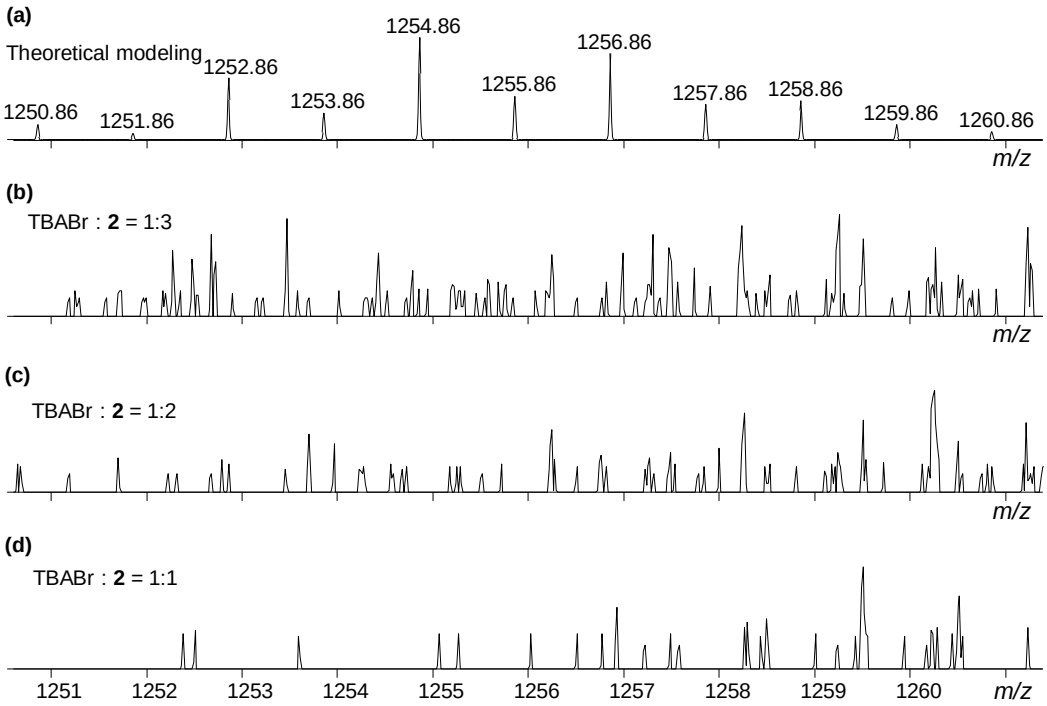


Figure S29. Theoretical modelling (a) and isotopic distribution of $\mathbf{2}_2 \cdot Br^-$ when mixing TBABr with 1 (b), 2 (c) or 3 (d) equivalents of **2** from ESI-MS.

S3 DFT Energetics

Table S10. Final DFT single point energies (in Hartree) of proposed equilibrium structures. The lowest-energy isomers (those discussed in the manuscript) are highlighted in yellow.

	Final Single Point Energy (Hartree)			
	Gas-phase	CPCM(DMSO)	CPCM(THF)	CPCM($CHCl_3$)
1	-13989.65051	-13989.67708	-13989.67324	-13989.67112
$\mathbf{1}_{2(dimer)}\cdot Cl^-$ *	-28442.01184	-28442.09312	--	--
$\mathbf{1}_2\cdot Cl^-$ *	-28442.00337	-28442.08780	--	--
$\mathbf{1}\cdot Cl_t^-$	-14452.29226	-14452.37151	-14452.36095	-14452.35516
trans-$\mathbf{1}\cdot Cl_b^-$	-14452.29162	-14452.37126	-14452.36083	-14452.35505
$\mathbf{1}\cdot[Cl_t^-]_2$	-14914.81167	-14915.05455	--	--
cis-$\mathbf{1}\cdot Br_b^-$	-16615.45742	-16615.53871	-16615.52805	-16615.52216
$\mathbf{1}\cdot Br_t^-$	-16615.46037	-16615.53885	-16615.52841	-16615.52261
trans-$\mathbf{1}\cdot Br_b^-$	-16615.46029	-16615.53886	-16615.52853	-16615.52286
cis-$\mathbf{1}\cdot I_b^-$	-21216.91519	-21216.99521	-21216.98470	-21216.97890
$\mathbf{1}\cdot I_t^-$	-21216.91764	-21216.99491	-21216.98454	-21216.97888
trans-$\mathbf{1}\cdot I_b^-$	-21216.91776	-21216.99517	-21216.98497	-21216.97942
$\mathbf{1}\cdot[DMSO]_2$	-15099.88486	-15099.92405	--	--
$\mathbf{1}\cdot DMSO\cdot Cl^-$	-15007.40164	-15007.49018	--	--
$\mathbf{1}\cdot DMSO\cdot Br^-$	-17170.57062	-17170.65791	--	--
$\mathbf{1}\cdot DMSO\cdot I^-$ *	-21772.03001	-21772.11607	--	--

*not global minima (negative vibrational frequencies obtained). For $\mathbf{1}_2$(dimer)$\cdot Cl^-$ the five lowest vibrational frequencies were: -20.23 cm^{-1} (imaginary mode), -10.20 cm^{-1} (imaginary mode), 7.64 cm^{-1}, 20.57 cm^{-1}, and 25.18 cm^{-1}. For $\mathbf{1}_2\cdot Cl^-$ the five lowest vibrational frequencies were: -26.11 cm^{-1} (imaginary mode), -21.30 cm^{-1} (imaginary mode), -14.94 cm^{-1} (imaginary mode), -12.17 cm^{-1} (imaginary mode), and 16.76 cm^{-1}. For $\mathbf{1}\cdot DMSO\cdot I^-$, the the five lowest vibrational frequencies were: -10.59 (imaginary mode), 22.20 cm^{-1}, 25.75 cm^{-1}, 34.25 cm^{-1}, and 37.43 cm^{-1}.

Table S11. Calculated enthalpy (with BSSE) and T*S (gas-phase) in Hartree.

	H (Hartree, with BSSE)				T*S (Hartree)
	Gas-phase	CPCM(DMSO)	CPCM(THF)	CPCM($CHCl_3$)	Gas-phase
1	-13989.45632	-13989.4829	-13989.47905	-13989.47694	0.06197
$\mathbf{1}_{2(dimer)}\cdot Cl^-$	-28441.62156	-28441.70284	--	--	0.10100
$\mathbf{1}_2\cdot Cl^-$	-28441.61518	-28441.69962	--	--	0.09698
$\mathbf{1}\cdot Cl_t^-$	-14452.09616	-14452.1754	-14452.16485	-14452.15906	0.06655
trans-$\mathbf{1}\cdot Cl_b^-$	-14452.09553	-14452.17517	-14452.16474	-14452.15896	0.06723
$\mathbf{1}\cdot 2Cl_t^-$	-14914.61425	-14914.8571	--	--	0.07361
cis-$\mathbf{1}\cdot Br_b^-$	-16615.2614	-16615.3427	-16615.33203	-16615.32614	0.06843
$\mathbf{1}\cdot Br_t^-$	-16615.26435	-16615.34283	-16615.33239	-16615.32659	0.06748
trans-$\mathbf{1}\cdot Br_b^-$	-16615.26424	-16615.34282	-16615.33249	-16615.32682	0.06817
cis-$\mathbf{1}\cdot I_b^-$	-21216.71915	-21216.79918	-21216.78867	-21216.78287	0.06932
$\mathbf{1}\cdot I_t^-$	-21216.72159	-21216.79886	-21216.78849	-21216.78283	0.06842
trans-$\mathbf{1}\cdot I_b^-$	-21216.72171	-21216.79911	-21216.78891	-21216.78336	0.06924
$\mathbf{1}\cdot$2DMSO	-15099.51566	-15099.55485	--	--	0.09118
$\mathbf{1}\cdot DMSO\cdot Cl^-$	-15007.11828	-15007.20682	--	--	0.08140
$\mathbf{1}\cdot DMSO\cdot Br^-$	-17170.2873	-17170.37459	--	--	0.08246
$\mathbf{1}\cdot DMSO\cdot I^-$	-21771.74753	-21771.83358	--	--	0.08055

Table S12. Calculated Gibbs free energy (in Hartree).

	G (Hartree, with BSSE)			
	Gas-phase	CPCM(DMSO)	CPCM(THF)	CPCM($CHCl_3$)
1	-13989.51829	-13989.54487	-13989.54102	-13989.53891
$\mathbf{1}_{2(dimer)}\cdot Cl^-$	-28441.72256	-28441.80385	--	--
$\mathbf{1}_2\cdot Cl^-$	-28441.71217	-28441.7966	--	--
$\mathbf{1}\cdot Cl_t^-$	-14452.16271	-14452.24195	-14452.2314	-14452.22561
trans-$\mathbf{1}\cdot Cl_b^-$	-14452.16276	-14452.24240	-14452.23197	-14452.22619
$\mathbf{1}\cdot[Cl_t^-]_2$	-14914.68786	-14914.93071	--	--
cis-$\mathbf{1}\cdot Br_b^-$	-16615.32983	-16615.41112	-16615.40046	-16615.39457
$\mathbf{1}\cdot Br_t^-$	-16615.33183	-16615.41031	-16615.39987	-16615.39407
trans-$\mathbf{1}\cdot Br_b^-$	-16615.33241	-16615.41098	-16615.40066	-16615.39498
cis-$\mathbf{1}\cdot I_b^-$	-21216.78847	-21216.8685	-21216.85799	-21216.85219
$\mathbf{1}\cdot I_t^-$	-21216.79001	-21216.86728	-21216.85692	-21216.85125
trans-$\mathbf{1}\cdot I_b^-$	-21216.79095	-21216.86835	-21216.85815	-21216.8526
1·2DMSO	-15099.60684	-15099.64603	--	--
1·DMSO·Cl^-	-15007.19967	-15007.28821	--	--
1·DMSO·Br^-	-17170.36975	-17170.45705	--	--
1·DMSO·I^-	-21771.82808	-21771.91414	--	--

Table S13. Binding energy ΔE, ΔH, T*ΔS (gas-phase), and ΔG (in KJ/mol). Calculated according to Equation 6 in manuscript: **1**·$[DMSO]_2$ + X^- ⇌ **1**·DMSO·X^- + DMSO.

	Binding Energy (kJ/mol, with BSSE)		ΔH (kJ/mol, with BSSE)		T*ΔS (kJ/mol)	ΔG (kJ/mol, with BSSE)	
	Gas-phase	DMSO	Gas-phase	DMSO	Gas-phase	Gas-phase	DMSO
1·DMSO·Cl^-	-106.0	39.4	-122.0	23.4	17.4	-139.5	6.0
1·DMSO·Br^-	-79.0	44.9	-95.2	28.7	17.2	-112.3	11.5
1·DMSO·I^-	-54.0	50.4	-72.4	32.0	10.5	-82.9	21.6

Table S14. Binding energy ΔE, ΔH, T*ΔS (gas-phase), and ΔG (in KJ/mol). Calculated according to Equation 7 in manuscript: **1**·$[DMSO]_2$ + X^- ⇌ **1**·X^- + 2 DMSO. The most favourable isomers were highlighted in yellow.

	Binding Energy (kJ/mol, with BSSE)		ΔH (kJ/mol, with BSSE)		T*ΔS (kJ/mol)	ΔG (kJ/mol, with BSSE)	
	Gas-phase	DMSO	Gas-phase	DMSO	Gas-phase	Gas-phase	DMSO
1$_{2(dimer)}$·Cl^-	-73.5	77.2	-106.5	44.2	95.9	-202.5	-51.8
1$_2$·Cl^-	-42.5	99.9	-81.0	61.4	85.4	-166.4	-24.0
1·Cl_t^-	-56.1	74.8	-77.4	53.5	67.2	-144.6	-13.7
trans-**1**·Cl_b^-	-48.4	81.5	-69.7	60.2	69.0	-138.7	-8.8
1·$[Cl_t^-]_2$	45.6	60.8	27.8	43.1	40.1	-12.3	3.0
cis-**1**·Br_b^-	-14.0	86.7	-35.5	65.2	69.2	-104.7	-4.0
1·Br_t^-	-25.0	83.1	-46.6	61.5	66.7	-113.2	-5.1
trans-**1**·Br_b^-	-21.4	86.4	-42.9	65.0	68.5	-111.3	-3.5
cis-**1**·I_b^-	12.8	94.2	-8.6	72.7	69.8	-78.4	3.0
1·I_t^-	2.9	91.5	-18.5	70.1	67.4	-86.0	2.7
trans-**1**·I_b^-	6.2	94.5	-15.2	73.0	69.6	-84.8	3.5

Table S15. Binding energy ΔE (in kJ/mol) calculated according to **1** + X^- ⇌ **1**·X^-. The most favourable isomers are highlighted in yellow. Dispersion contribution to ΔE was summarized, and it shows a trend of Cl^- < Br^- < I^- in terms of magnitude of such contribution. It should be noted that when implicit solvation in DMSO was modelled, the dispersion contribution of forming **1**·Cl^- counts only 26.9% of total ΔE, whereas it contributes to 50.2% of total ΔE towards forming **1**·I^-.

	Binding Energy (kJ/mol, with BSSE)							
	Gas-phase		DMSO		THF		CHCl3	
	ΔE (kJ/mol)	Dispersion Contribution (kJ/mol)	ΔE (kJ/mol)	Dispersion Contribution (kJ/mol)	ΔE (kJ/mol)	Dispersion Contribution (kJ/mol)	ΔE (kJ/mol)	Dispersion Contribution (kJ/mol)
1·Cl_t^-	-218.8	-11.1	-43.2	-11.6	-63.0	-11.5	-74.6	-11.4
trans-**1**·Cl_b^-	-211.0	0.0	-36.5	-0.2	-56.6	-0.3	-68.2	0.1
1·$[Cl_t^-]_2$	-117.0	-21.2	-57.2	-29.1	--	--	--	--
cis-**1**·Br_b^-	-176.6	-13.2	-31.3	-16.8	-47.9	-16.6	-57.6	-16.4
1·Br_t^-	-187.7	-12.3	-35.0	-12.4	-52.2	-12.3	-62.1	-12.3
trans-**1**·Br_b^-	-184.1	-0.7	-31.6	-1.2	-49.1	-1.1	-59.3	-0.7
cis-**1**·I_b^-	-149.8	-15.6	-23.8	-19.2	-38.1	-18.7	-46.4	-18.4
1·I_t^-	-159.8	-13.8	-26.5	-13.3	-41.2	-13.5	-49.9	-13.5
trans-**1**·I_b^-	-156.5	-1.9	-23.6	-6.3	-38.7	-3.3	-47.7	-4.5

Table S16. ΔH, T*ΔS (gas-phase), and ΔG (in kJ/mol) calculated according to **1** + X^- ⇌ **1**·X^-. The most favourable isomers are highlighted in yellow.

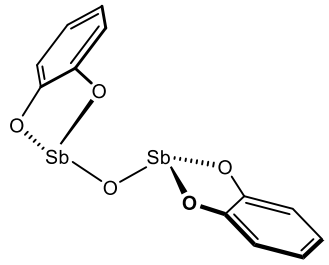
	ΔH (kJ/mol, with BSSE)				T*ΔS (kJ/mol)	ΔG (kJ/mol, with BSSE)			
	Gas-phase	DMSO	THF	CHCl3	Gas-phase	Gas-phase	DMSO	THF	CHCl3
1$_{2(dimer)}$·Cl^-	-393.8	-153.8	--	--	-105.9	-287.9	-47.9	--	--
1$_2$·Cl^-	-368.3	-136.6	--	--	-116.5	-251.9	-20.1	--	--
1·Cl_t^-	-213.7	-38.1	-57.9	-69.5	-33.7	-180.0	-4.4	-24.3	-35.8
trans-**1**·Cl_b^-	-206.0	-31.4	-51.6	-63.2	-31.9	-174.1	0.4	-19.7	-31.3
1·[Cl_t^-]$_2$	-108.5	-48.6	--	--	-60.8	-47.7	12.3	--	--
cis-**1**·Br_b^-	-171.8	-26.5	-54.4	-52.7	-31.8	-140.1	5.3	-11.3	-21.0
1·Br_t^-	-182.9	-30.1	-41.8	-57.3	-34.3	-148.7	4.1	-13.1	-23.0
trans-**1**·Br_b^-	-179.2	-26.7	-36.0	-54.4	-32.4	-146.7	5.8	-11.8	-22.0
cis-**1**·I_b^-	-145.0	-18.9	-33.2	-41.6	-31.1	-113.8	12.2	-2.1	-10.4
1·I_t^-	-154.9	-21.6	-36.3	-45.0	-33.5	-121.4	11.9	-2.8	-11.5
trans-**1**·I_b^-	-151.6	-18.6	-33.8	-42.8	-31.3	-120.2	12.7	-2.4	-11.4

S4 Cartesian Coordinates of Optimized Structures

In the following tables X = Cl, Br, or I., X_t^- is used to denote that the halide is in a terminal position on one of the antimony atoms, X_b^- is used to denote that the halide is bridging between the two antimony atoms, and cis and trans refer to the relative positions of the aryl rings with respect to the Sb-O-Sb core.

S4.1 Gas-phase Structures

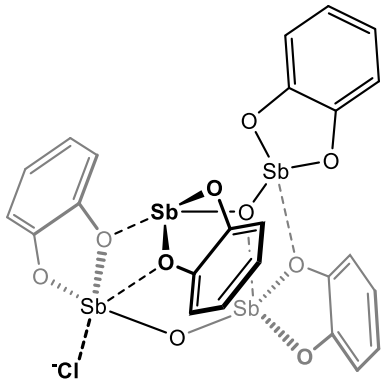
Table S17. Cartesian coordinates (in Å) of **1**



Atom	x	y	z
Sb	-2.29219321001255	6.94765900080427	3.49924328227843
Sb	-1.67144985190040	5.48739159904945	0.29129523979088
O	-1.44138054912600	6.83805555954375	1.67950175539993
O	-1.01867879007253	5.69067687946830	4.41998406476215
O	-0.99635826723911	8.35254371261029	4.14067341425338
O	-1.91092490081157	3.94455408165817	1.57401763941336
O	-3.70156496551838	5.52383352827545	0.36317196541989
C	0.10870459670777	6.36130967402165	4.82469918037195
C	1.20424462639865	5.70212305761232	5.37689250054608
C	2.31480609481515	6.44816791260175	5.78261364777608
C	2.32752826970704	7.83676627101280	5.63724931416810
C	1.23035510818272	8.50299787323496	5.08361270072777
C	0.12104281328556	7.76486061791124	4.67783263582245
C	-4.09637924458603	4.88845839223275	1.50868473423748
C	-5.37452695425613	5.03663690686394	2.04646417217214
C	-5.69268879204979	4.38822044968559	3.24315119427447
C	-4.74251111565659	3.60618839111609	3.90343139457545
C	-3.45977158857019	3.44729147863305	3.37175686958999
C	-3.13860134435411	4.07414998915139	2.16639597483956
H	1.17625992986801	4.62208364269644	5.48178371934319
H	3.17195476969966	5.93809897156026	6.21221945100655
H	3.19459815519516	8.40881625514269	5.95405133703750
H	1.22313858713430	9.58161369515318	4.96236237082285
H	-6.09650381562051	5.66105780813893	1.52984647746636

H	-6.68508833827221	4.50931032320916	3.66665696293464
H	-4.99318010868082	3.12310313185634	4.84272365681522
H	-2.70397011426711	2.85357879675573	3.87426934415416

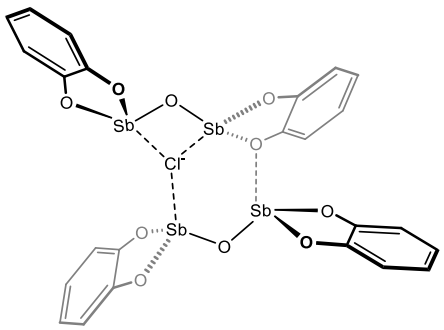
Table S18. Cartesian coordinates (in Å) of $\mathbf{1}_{2(\text{dimer})}\cdot Cl^-$



Atom	x	y	z
Sb	-2.70016440183566	6.82374010365114	4.20772563205176
Sb	0.24533863091005	8.69792548755019	4.87860481548288
O	-1.08446818428170	7.87126463246635	3.57064038143572
O	-3.76220665828597	7.20261786414817	2.48853965708735
O	-2.07965243997564	5.22470748336532	3.01145896865890
O	-0.11850281377719	7.03576657073786	6.09585256996282
O	1.74233324307016	7.47193661207795	4.21557592916890
C	-3.29384318501178	6.48392438143562	1.43059216909207
C	-3.64306128258986	6.77865410862991	0.11313064270854
C	-3.08422240098120	6.03215470600805	-0.93080548818961
C	-2.18332690891621	5.00171777692435	-0.65472096458071
C	-1.82620718437726	4.70229238186545	0.66415148735556
C	-2.37997986263881	5.43601068422231	1.71745308286426
C	1.61038294204647	6.20614835027535	4.69616405035567
C	2.40565250492000	5.15304166472587	4.24570552111909
C	2.21988937724598	3.86899120234655	4.76985205984441
C	1.24255405489031	3.63679472933596	5.73827454322788
C	0.44074419970659	4.68749586896797	6.19674892365795
C	0.62285462482686	5.97292518373726	5.68599379778570
H	-4.32269160839715	7.60167762373236	-0.08487820586924
H	-3.34497830603516	6.27127539762164	-1.95782135736953
H	-1.74374606837844	4.43252661831473	-1.46971083562513
H	-1.11391403000361	3.91533878571471	0.89413979624867
H	3.15422485586032	5.34984455359613	3.48356528848322
H	2.83729605425255	3.04986917667455	4.41040727462673
H	1.09496883157453	2.63644641537870	6.13668468349283

H	-0.32789960068784	4.52537779931167	6.94754185186893
Cl	-4.24563720374090	12.25424500418150	0.96594245070683
Sb	-3.82532163078428	10.25170380990420	2.38398405607032
Sb	-0.65965704145060	8.58344071402608	1.29314869798240
O	-2.22419585366474	9.74078859024319	1.36319829788035
O	-3.51667071599010	9.00725391480369	4.53002110318856
O	-2.77429676006670	11.48342491643840	3.64933772302005
O	0.49272562588598	9.68266697995713	2.66580259135802
O	0.35698130075483	9.91026831811060	0.04687845432727
C	-2.76103379138700	9.76905802627674	5.33381026008405
C	-2.33968994471888	9.36973989230307	6.61499783063908
C	-1.52565258738307	10.19875954682990	7.39912268403729
C	-1.11424720633011	11.43498765442510	6.90327116820490
C	-1.52350372546781	11.85387701200630	5.63341038109130
C	-2.35535233273987	11.04899008613510	4.84455845100885
C	1.00365795049657	10.88805711961010	0.71153750290838
C	1.59262263543592	11.98651749528920	0.07978956807941
C	2.26274941940128	12.95204913916850	0.83808505977376
C	2.34620584950753	12.83424498618200	2.22583530030218
C	1.75886765897475	11.74089023254400	2.87387780790160
C	1.09660504390304	10.77964613304700	2.11989516277491
H	-2.65956185505244	8.40398318723646	6.99449238181495
H	-1.20814884163104	9.86175855613459	8.38142983564358
H	-0.46984952626905	12.07697077758480	7.49779427794266
H	-1.20906702934140	12.81028192581790	5.22653220529716
H	1.51197976120715	12.07217864188200	-0.99988362196471
H	2.71400944004604	13.80516722559890	0.33765388719707
H	2.86009430269744	13.59182858467420	2.81115168417425
H	1.80173267457711	11.64025236677220	3.95457352360987

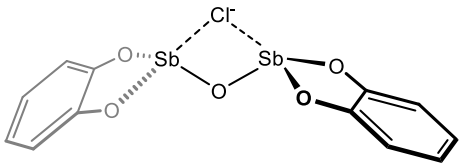
Table S19. Cartesian coordinates (in Å) of $\mathbf{1}_2 \cdot Cl^-$



Atom	x	y	z
Sb	-2.3282437427720	7.8523225963387	2.2234916538559
Sb	-0.8277539455902	4.9574680950934	0.8709489843861
O	-1.1373687504507	6.2855962682745	2.2782792262746
O	-2.2062366602567	8.0963375522646	4.2888005264284
O	-0.7669673453830	9.2182472770788	2.3862457968194
O	-1.0791453076964	6.3253575492718	-0.6319853270255
O	1.1470989051413	5.4736786265484	0.5949740313377
C	-1.1536806595432	8.8674494176066	4.6915870730677
C	-0.8332217745548	9.0772956109329	6.0277563256205
C	0.2739353873313	9.8716637335757	6.3509133192721
C	1.0451659163495	10.4426834198049	5.3379808672814
C	0.7246876111090	10.2309554009715	3.9928096994731
C	-0.3812071958025	9.4462791699822	3.6555807389105
C	1.2519572323992	6.5688740208794	-0.2015438605120
C	2.4541433273479	7.2486891509255	-0.3994937486102
C	2.4948651657626	8.3537770343577	-1.2564958709442
C	1.3395979788818	8.7824593433989	-1.9113824949793
C	0.1277909400184	8.1101279037657	-1.7175358984531
C	0.0791225926626	7.0096475137467	-0.8637058384887
H	-1.4370262477310	8.6144914472599	6.8032452856499
H	0.5299205545045	10.0353745693037	7.3941538271348
H	1.9073532681428	11.0544334137492	5.5916033482709
H	1.3195479599302	10.6631901880179	3.1935795629473
H	3.3417986310015	6.9067122325733	0.1248818226757
H	3.4327001548687	8.8836338675623	-1.4025938227148
H	1.3727132070014	9.6475698835899	-2.5685087208159
H	-0.7845557192677	8.4335587770656	-2.2104413009311
Cl	-3.9097370331536	4.9747659772539	0.5141817552553
Sb	-4.2437066030169	7.0469031959355	5.2921270822348
Sb	-4.5445561314415	4.5551050523097	3.0192571461284
O	-3.9780555401521	6.4614026347907	3.3448134994010
O	-5.0514076378389	8.8206349166827	4.6386340180832
O	-6.2307659361114	6.4680470504850	5.1265415046461
O	-2.7359211508701	3.5954712219515	3.0476165262236
O	-4.1135930677136	4.4638607663930	5.1708195974850
C	-6.3442931274136	8.6725096057370	4.2520624178478
C	-7.0593880945167	9.6924019804833	3.6243099798604
C	-8.3931032831501	9.4815520105253	3.2556555054697
C	-9.0091865971115	8.2556178383605	3.5097464887118
C	-8.2989469431030	7.2251691752363	4.1369893678173
C	-6.9703940448983	7.4268199261701	4.5118615168554
C	-2.8357647566916	4.0545854129086	5.3801412396375

C	-2.2197900331552	4.0922355221120	6.6322511683977
C	-0.8946615543125	3.6642777977788	6.7703085321627
C	-0.1875002024939	3.2003505106825	5.6614978773629
C	-0.7947447370937	3.1637545321112	4.4019173780995
C	-2.1119140979245	3.5951363851479	4.2555792473769
H	-6.5618715109164	10.6382734052011	3.4296866377385
H	-8.9453669632382	10.2785855437787	2.7645923983969
H	-10.0434890434867	8.0931362886727	3.2176765098255
H	-8.7611464832607	6.2631659457753	4.3409921922340
H	-2.7875240830075	4.4515177071951	7.4863219499148
H	-0.4180357694592	3.6998631451835	7.7460925936438
H	0.8436138197357	2.8751191333768	5.7676236376698
H	-0.2532408776084	2.8099632538208	3.5290570255886

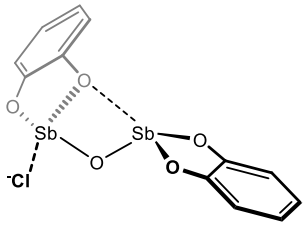
Table S20. Cartesian coordinates (in Å) of trans-**1**·Cl_b^-



Atom	x	y	z
Sb	-0.20709856637274	2.18635901897626	-1.14692779028355
Sb	-0.42380371720554	-0.94046003051393	-2.61839130288166
O	-1.21474585804956	0.81024289161218	-2.14782048751698
O	0.87104253572895	2.91490007620332	-2.72811120901474
O	-1.51042358690969	3.68857602822274	-1.78256268900152
O	-0.81822262363307	-1.89045373843053	-0.84837496450215
O	-2.30290831788791	-1.73110862704275	-3.06948173711440
C	0.17047231725351	3.83331560672015	-3.44280623223562
C	0.66406184690007	4.38416143716321	-4.62520021743376
C	-0.09695127178989	5.32884630699542	-5.32568052771147
C	-1.34646543034249	5.72016770820588	-4.84367400051453
C	-1.85017027412078	5.17272497759952	-3.65741047170905
C	-1.09911941298842	4.23366957937050	-2.94593299191971
C	-2.87238076712785	-2.29161693407331	-1.98238577664296
C	-4.17821884028269	-2.78835098027852	-1.97448149152267
C	-4.69399113445326	-3.38638160675427	-0.81818003430351
C	-3.91193466547226	-3.48489361221931	0.33309561614104
C	-2.60325712077577	-2.98546533510188	0.34072916132830
C	-2.08092778634891	-2.38821842542646	-0.80632210180870
H	1.63740348279890	4.06263367533018	-4.98592004722967
H	0.29111704448304	5.75253067752546	-6.24886862373406

H	-1.93803892733412	6.45110231534222	-5.39021690089015
H	-2.82276754151505	5.46454032882916	-3.27018530648009
H	-4.77514401940788	-2.70139119360456	-2.87842287528781
H	-5.71115767518430	-3.77128036760996	-0.82177352350072
H	-4.31509271337477	-3.94664878500539	1.23122910097788
H	-1.97962901633148	-3.04778921629082	1.22843807325514
Cl	1.77342003974396	0.14304622425543	-1.16742964846289

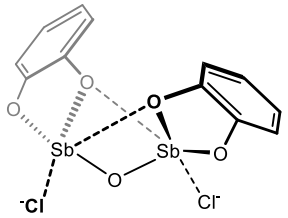
Table S21. Cartesian coordinates (in Å) of **1**·Cl_t^-



Atom	x	y	z
H	-5.07849298808623	6.78040782623898	0.18865819472314
H	-6.52682435972731	8.69685187620940	0.87309985591968
H	5.34813307475428	9.28576026680458	4.43905932149725
C	-4.70564269272033	7.54681194179434	0.86265228940369
H	6.08898675040908	10.12194492411850	2.21491872533715
C	-5.50847688195464	8.62606284918691	1.24817059735442
O	-2.60914728258721	6.40300045689045	0.96164641875367
C	4.61748979753934	9.49223975094085	3.66070583450289
C	-3.39338853793246	7.43747412201064	1.33313469611862
C	5.03194563942214	9.96047306627127	2.41362589624175
H	2.91392957445833	8.90923997185413	4.87863889072963
C	3.25648717199419	9.27926290972254	3.91588649800746
C	-5.00584639197604	9.60609040867567	2.10372268490771
C	4.09294798242026	10.22112789538450	1.40811767044776
H	4.40018068774669	10.58391640003140	0.43081250747939
H	-5.62742441615121	10.44693350789180	2.40163316959216
Sb	-0.67082013524087	6.35839001891942	1.64941002197167
C	-2.88322003885236	8.42880870280142	2.21484410636160
C	2.31418245660247	9.53428386580539	2.92005590899020
C	-3.69389610919916	9.50761990620730	2.58144805932991
C	2.73174668496836	10.01930694128510	1.65086439904364
O	0.15968882640693	7.83911945371675	0.62562395405978
O	-1.61092491541664	8.28722852890280	2.64811756771983
O	0.98513645457984	9.33713382069760	3.11749822821791
O	1.77273737906489	10.28375581679230	0.74147411075677
H	-3.28304127574509	10.25649463957250	3.25429461897257
Cl	-0.18389528891458	4.72150707464421	-0.16400235964620

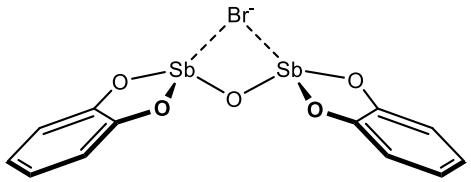
Sb	-0.10554416586262	9.64742305662889	1.40674313320597

Table S22. Cartesian coordinates (in Å) of **1**·$[Cl_t^-]_2$



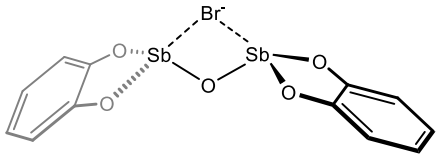
Atom	x	y	z
H	-5.20855581037853	8.27945221453744	-0.23877363507226
H	-6.70596317144713	7.43038361248179	1.58205095081456
H	5.81184792817018	8.44087169379978	1.80525188721715
C	-4.79295591376689	7.90818478541054	0.69570331638094
H	6.00885986164000	10.88550333834000	2.25940024188628
C	-5.62578360871990	7.43276169429093	1.72141368461132
O	-2.58374523404322	8.36355531774246	-0.11362092496083
C	4.94064718957936	9.01218036575318	2.12414106342029
C	-3.40521623552286	7.92546695051983	0.85637528547348
C	5.05159005435918	10.37938938763130	2.37613690789476
H	3.59925403436757	7.30253745414706	2.07026166390060
C	3.70342004417524	8.36749376959941	2.26823376717758
C	-5.06714427557816	6.97585781782765	2.91485293802063
C	3.92138765480260	11.11164948334240	2.77379461154129
H	3.98354531372358	12.18092089024060	2.96498712778003
H	-5.70907193635849	6.61601079267595	3.71828582016978
Sb	-0.56384021629293	8.41760978331801	0.38978798877542
C	-2.82459355402358	7.45043328290585	2.07595010811831
C	2.56352044068006	9.07811889008635	2.67452840465088
C	-3.67579971492523	6.98894511626279	3.09183667990800
C	2.68284896622537	10.48295951583390	2.92412067729121
O	-0.58390190015989	10.11674430417570	1.41468295413448
O	-1.50106374177999	7.46603757320197	2.17688923481435
O	1.37261682028762	8.51856330582051	2.85023102766817
O	1.58773061961901	11.15725864182080	3.31620810542171
H	-3.22476743663628	6.64103007357666	4.01905099725567
Cl	-0.29419503406061	9.66200355418060	-1.90626568096983
Sb	-0.17333454078668	10.04683041091650	3.35482780094823
Cl	-1.31774960314940	12.36538397955950	3.81095999572781

Table S23. Cartesian coordinates (in Å) of cis-**1**·Br_b^-



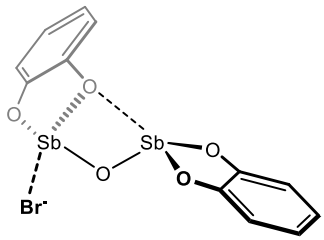
Atom	x	y	z
H	-3.72418731875984	9.47017353565355	3.99765405062128
O	-2.42271304532325	7.18931431593770	4.45545794743644
O	0.41214819120107	6.88321182691590	4.99022650425877
C	-3.16630316173820	9.08358304525410	3.14891345922891
H	2.45453660871539	11.38002038198450	4.37903543580175
O	2.62084087500177	8.74954052351438	4.77956676575127
Sb	-1.01110590552388	5.66387718009730	4.34966325026210
C	-2.44530978947683	7.89765189005621	3.30180583345980
Sb	2.33978204320927	6.69764658579676	4.57368500965100
H	-3.70709006988339	10.68436917005700	1.81171620632770
C	2.32324312967919	10.77232187925950	3.48771604517604
C	-3.15102707893460	9.75625769962359	1.92127205574320
C	2.38380887095884	9.38239126354861	3.60630535504512
Br	1.40297354012040	3.98052380372295	3.58483240880104
C	-1.70258309082099	7.38445391311037	2.20725641865467
O	-1.01810395747881	6.22321722279971	2.39380085465355
H	2.02991268165609	12.43927920273770	2.15435461565140
C	2.08519702665462	11.35643293810390	2.23797722918353
C	2.20233755440844	8.57370863274862	2.45479516220933
C	-2.41521550483940	9.25022383950907	0.84915904663405
O	2.27269575387824	7.22382584347688	2.61022544862971
C	-1.68829911889392	8.06281769553741	0.99022448005418
H	-2.38855572129491	9.78515741739609	-0.09680302152438
C	1.90320769605637	10.55689243096280	1.10906160540531
C	1.96085156696387	9.16267801637790	1.21533411528937
H	-1.09247608365692	7.66285175047850	0.17539102929644
H	1.69801614023820	11.01230349430260	0.14353163498909
H	1.80172216788320	8.52135950103602	0.35370005330934

Table S24. Cartesian coordinates (in Å) of trans-**1**·Br_b^-



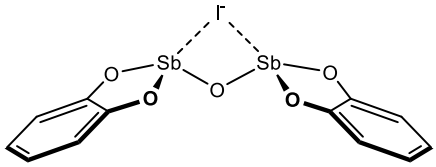
Atom	x	y	z
Sb	-0.16113781235664	2.19487560047257	-1.13199242715334
Sb	-0.38679329044739	-0.96376728771646	-2.60472379713175
O	-1.14778049843141	0.79641829933324	-2.12222678666718
O	0.89339253341272	2.93501512101597	-2.72251145288904
O	-1.49525435196321	3.66799463809625	-1.76404558985627
O	-0.80649464123660	-1.91811413243978	-0.84403839606573
O	-2.27458284810611	-1.71597362759587	-3.07225113415395
C	0.16892018651910	3.83318390921635	-3.43970993974966
C	0.64198733175460	4.38353780290215	-4.63061541968719
C	-0.14261415320366	5.30870170288365	-5.33079064426127
C	-1.39473520687143	5.68094289113144	-4.84026298174316
C	-1.87783390165511	5.13356537987884	-3.64554174951983
C	-1.10309827810951	4.21359486478727	-2.93484886797542
C	-2.86190090840612	-2.27130229572620	-1.99082348504890
C	-4.17706820271712	-2.74230725100726	-1.99456413363931
C	-4.71239951008924	-3.33357857825629	-0.84383466972908
C	-3.94047557028771	-3.45102981576283	0.31260806622717
C	-2.62228975124798	-2.97806555112145	0.33127906301180
C	-2.08047303855389	-2.38812900094310	-0.81045213106314
H	1.61788251974708	4.07726071240472	-4.99740933970483
H	0.22920086720933	5.73244009213105	-6.26056466515110
H	-2.00445885158663	6.39663010220223	-5.38692190598248
H	-2.85218300767228	5.41017247256645	-3.25178700634994
H	-4.76572670068904	-2.64022398230339	-2.90225082377450
H	-5.73693372526584	-3.69805764095434	-0.85563519750573
H	-4.35920269298324	-3.90735859957936	1.20631970044322
H	-2.00610923942647	-3.05586502118208	1.22284244110266
Br	2.01323074266382	0.09219719556626	-1.08831572598201

Table S25. Cartesian coordinates (in Å) of **1**·Br_t^-



Atom	x	y	z
H	-4.86863947841569	8.46141900376298	-0.27158881268204
H	-6.47443920138192	7.19771569522281	1.16817292740721
H	5.21827161246416	8.12727695260089	1.33936338591260
C	-4.53239576447776	7.96404631438286	0.63425033624284
H	5.84017593178353	10.49869293917750	1.78343030189648
C	-5.42455039461298	7.25337836212642	1.44626673344438
O	-2.26155350651235	8.67790310156168	0.22543482107354
C	4.50261283530920	8.80598932125042	1.79682852731732
C	-3.18093445081232	8.04204208093379	0.98003172312901
C	4.84991256635580	10.13370722770360	2.04567581387111
H	2.93576103791157	7.31141215719048	1.95745700424964
C	3.22598305794159	8.34382002151143	2.13671591308918
C	-4.97342119983026	6.62442734080844	2.60702736842856
C	3.92635633933929	11.00675689815310	2.63082095772542
H	4.17724078119088	12.04630877492870	2.82286044937937
H	-5.66834683872784	6.07654915601556	3.23875843197076
Sb	-0.40972797413083	8.75552676355741	1.18753770606606
C	-2.72701979058448	7.40770445494494	2.16781147800235
C	2.29626064392266	9.20147854825411	2.73258274073539
C	-3.62238848044978	6.70025259883934	2.96920811131780
C	2.64841227273037	10.55639779397610	2.97553071947521
O	-0.87651168081820	10.46122971562240	2.09621232180456
O	-1.40924032974419	7.51530594064954	2.48050628506656
O	1.05046914131735	8.80585832696495	3.07817021784638
O	1.74857466089668	11.39042063066930	3.54077212245713
H	-3.25229781435153	6.22277075859397	3.87256337993650
Sb	-0.13386998311035	10.65518048205400	3.92489830349105
Br	-0.97317399320257	13.18633863854280	4.10719073134565

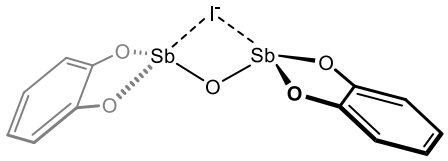
Table S26. Cartesian coordinates (in Å) of cis-**1**·I_b^-



Atom	x	y	z
Sb	-2.05445321597209	6.72081577252523	4.89433412310626
Sb	-1.80761210151570	5.66351174031326	1.50785842696388
O	-2.43850612547443	6.85238331001516	2.95757899089824
O	-0.08795607450995	7.22600094633450	4.83799357115828
O	-2.24897759369123	8.77573750222967	5.12363751049714
O	-1.91790140995723	7.20786310212890	0.12477104908018

O	0.14586198567676	6.22115638284684	1.51255148243055
C	0.07945927905689	8.57283219716898	4.73396500667026
C	1.32577997472391	9.14594839763498	4.49026777084032
C	1.44266027254885	10.53724664307630	4.39903135306312
C	0.31826867323861	11.34956645992450	4.55048225708391
C	-0.93801888189970	10.78117144078090	4.79131274369091
C	-1.06678383987000	9.39423968120583	4.88386383059211
C	0.32900765552288	7.39857302871319	0.85353499171772
C	1.54248591397284	8.08248034582723	0.88576186198998
C	1.67899914189113	9.28494739564851	0.18370711583835
C	0.60672731354280	9.80017648021066	-0.54555532058870
C	-0.61707782537523	9.12152916405923	-0.57912518658908
C	-0.76520422857256	7.92147816616360	0.11847812492010
H	2.18397956597390	8.49457855154058	4.35583166723472
H	2.41331284508541	10.98033855896530	4.19132870590761
H	0.41064775503423	12.42994832840310	4.46887319511091
H	-1.82578097621772	11.39846826470380	4.89922476210304
H	2.35761929878145	7.67472732041198	1.47567986798396
H	2.62155407137352	9.82476043693364	0.22528919653456
H	0.71305299792488	10.74004146504120	-1.08198662342209
H	-1.46603557258009	9.51476354578250	-1.13185019915744
I	-0.97680589871214	3.69080037141014	4.05901972434125

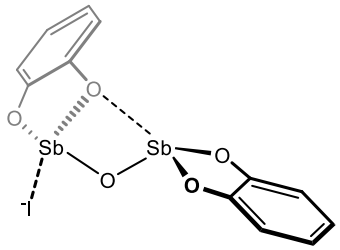
Table S27. Cartesian coordinates (in Å) of trans-**1**·I_b^-



Atom	x	y	z
Sb	-2.29465821224350	8.72975595605499	3.38902704114751
Sb	-0.14515821575342	6.51491782084896	1.67586278740177
O	-0.66533222282999	8.29659774086046	2.35649924861149
O	-1.57087425440417	8.19429975932591	5.22512554286713
O	-1.52092942245748	10.56634124578720	3.98524585637044
O	-1.24718308941417	6.57680694281803	-0.04509591873608
O	1.28114587846543	7.33411929845439	0.40247469598480
C	-0.85583171355711	9.19707379295349	5.79953921500708
C	-0.17607896876205	9.02506138729467	7.00521938181231
C	0.54198664303682	10.09266020513620	7.55798165946610
C	0.57940792585320	11.32644776567260	6.90696609832729
C	-0.09999541208192	11.50818556037060	5.69656482440533
C	-0.82272831169157	10.45210668664680	5.13711268827225

C	0.74671514761032	7.63310168070162	-0.80265402967178
C	1.45492031503275	8.29993339828318	-1.80500629987957
C	0.84703253885529	8.55269251478775	-3.04044129788995
C	-0.46668506150835	8.14545639329634	-3.27609981058802
C	-1.18859212582484	7.48008878068436	-2.27765550558884
C	-0.59091797123248	7.22401121599825	-1.04381255368016
H	-0.21425521913465	8.05554317770041	7.49405947774590
H	1.07309396562736	9.95268972886658	8.49631879805653
H	1.14083672343755	12.15319954655600	7.33571019422740
H	-0.07901658290954	12.46133378557190	5.17524879437927
H	2.47590234884471	8.61283810398544	-1.60382986756435
H	1.40486310299282	9.07271203815535	-3.81565985440416
H	-0.93794971563264	8.34550610955298	-4.23530664482303
H	-2.21363471125621	7.15838422518084	-2.43978667338240
I	-2.97668237906208	5.50236213845428	3.07351115212577

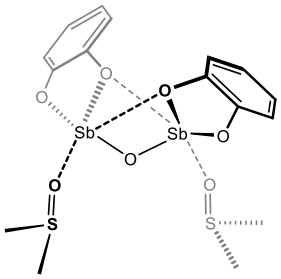
Table S28. Cartesian coordinates (in Å) of **1**·I_t^-



Atom	x	y	z
H	-5.35291077342856	8.40002119066737	-0.02297093615676
H	-6.49468415267483	7.81472129463816	2.12048958880766
H	5.89221539162863	8.47520752007016	2.55287699059730
C	-4.78019528145536	8.09183994480919	0.84722485269109
H	5.84936688972536	10.95480385634120	2.75860379269321
C	-5.41058194888074	7.76515051129345	2.05272302313616
O	-2.76469750078090	8.34298183879349	-0.41731144285878
C	4.94392559954425	9.00174503968114	2.62681279877831
C	-3.38750028963599	8.03309433280099	0.74115167327397
C	4.91912702581566	10.39198284873420	2.74174748333282
H	3.74438817949054	7.19326641675922	2.50355195215879
C	3.74645610341214	8.27571752588276	2.59907240244625
C	-4.65499802327910	7.38289990276604	3.16126284974647
C	3.69907935924030	11.07269910671730	2.83108436988560
H	3.66239395740798	12.15518640585970	2.91837440270615
H	-5.14384472069507	7.13242082732310	4.09945145410950
Sb	-0.70919148189247	8.31496854926876	-0.42569522144944
C	-2.61721082734820	7.63553492965757	1.86584057704631

C	2.52651651717224	8.94558173387647	2.68515975310409
C	-3.25993518952983	7.32193071145627	3.06711264751567
C	2.49776304592022	10.36009234146320	2.81145062470153
O	-0.26256722794226	9.90177458923148	0.67453997217469
O	-1.27208181529497	7.59961721581185	1.72311943550576
O	1.33804045798468	8.28672659482560	2.65558543450863
O	1.28891788134203	10.94905997056720	2.93099923145206
H	-2.65145360539467	7.02157994542128	3.91659295641370
I	-0.79770323301475	9.90584311494051	-2.90192607706145
Sb	-0.25294433743634	9.57889174034214	2.63765541074068

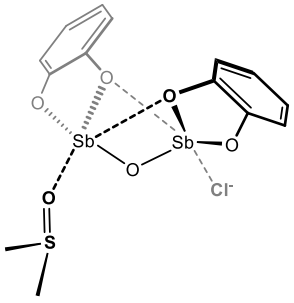
Table S29. Cartesian coordinates (in Å) of **1**·$(DMSO)_2$



Atom	x	y	z
H	-8.0694326716870	7.8176304494023	0.8854128195121
H	-7.4166908567885	10.2155573341102	0.9886677666474
C	-7.0223383267827	8.0948644874598	0.9690480340572
C	-6.6565907630286	9.4402034588275	1.0282676251518
H	-6.0202787380334	8.9302930484560	4.5002926391251
H	-4.4217377555012	9.0524532159746	3.6975642587133
H	-6.3134753195946	6.0425858421930	0.9522840623683
C	-6.0452406230127	7.0937968321242	1.0068923847741
C	-5.3081557549943	9.7992923169332	1.1381394398210
H	-5.0044164331672	10.8409381144004	1.1940592981784
C	-4.9837145917924	9.2563427301288	4.6055185620060
H	-4.9188285148258	10.3152056323344	4.8691124954426
C	-4.6962588958338	7.4397992070630	1.1056483864310
C	-4.3284534810591	8.8078236896132	1.1891819606006
S	-4.1923484360878	8.2830743718670	5.9166707449955
H	-5.1441905118810	9.8290423618890	7.4963231470013
O	-4.6097128694027	6.8151716814246	5.6589724419180
H	-6.3170546249571	8.5453377696420	7.0155869182364
C	-5.2839951745511	8.7641541839838	7.2927076561645
O	-3.7028601498084	6.5171575158802	1.1460617062738
O	-3.0077930091276	9.1072204860725	1.3471988520291
H	-4.9837389499723	8.1686399436497	8.1560959929050

Sb	-3.3587291035591	5.4899093589202	4.0448855049414
O	-2.6512140191733	7.3009980690559	3.5999642624787
Sb	-1.9035302906337	7.4288659007255	1.7367230817197
O	-1.7208451507947	4.7766672290106	2.9309306397059
O	-2.0259840661842	5.2350279101927	5.5690280907066
H	-0.2099399187618	11.7810849210248	3.6660481104928
O	-0.4624510082198	9.0021157800843	2.8884723044346
C	-0.6040746275618	4.7661961037512	3.7085044192405
H	-0.1097228738809	11.4796934256270	5.4315459909188
C	-0.7675747907793	4.9918049252142	5.0979623067581
C	0.0694527266125	11.0617739995831	4.4373657245709
S	-0.9998891096361	9.6058795626465	4.2078352899475
H	0.7830908534590	4.3903139107702	2.1195046842868
C	0.6732833071560	4.5560982814030	3.1873292378991
H	-0.8195725158955	7.6051428934961	5.4474159244784
H	1.1102750072425	10.7543942849259	4.3177784664661
C	0.3419953428744	4.9760241363890	5.9427423006780
H	0.1944708207023	5.1382981518597	7.0068145635969
C	-0.3061377741057	8.5618111824398	5.5219826584990
H	-0.5110570293262	9.0337930686277	6.4865208715458
C	1.7821540887340	4.5523506430716	4.0402645188913
C	1.6175877931427	4.7568908152382	5.4105358517784
H	0.7651219634038	8.4429704283654	5.3495235117957
H	2.7732778621167	4.3844834184846	3.6287369110505
H	2.4791869649574	4.7440709256631	6.0721675807664

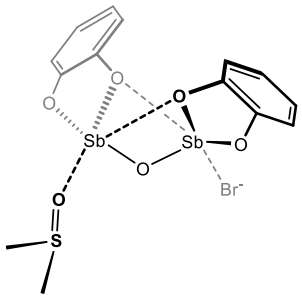
Table S30. Cartesian coordinates (in Å) of **1**·DMSO·Cl_t^-



Atom	x	y	z
H	-2.27986254358398	3.86824803468776	8.50148730824800
H	-4.57311250303506	4.81156230842210	8.73210852901879
C	-2.75937945976927	4.35468801686052	7.65520847813047
C	-4.04359648680403	4.88288589636105	7.78502410484352
H	-1.07588629413657	4.04777778400749	6.31870892727443
C	-2.07843790203052	4.45136987583277	6.43592229566914

C	-4.65529024633810	5.51577691726686	6.69531836682849
H	-5.65273558183688	5.94010055405071	6.77729906632130
C	-2.67955344870792	5.07047586892921	5.33336172013077
H	-4.30459275420636	9.25333899511628	6.64567428514854
C	-3.98638830203512	5.61389384250311	5.47417624703617
O	-1.57649973323919	9.15785002823208	5.97185802077777
H	-4.30971795284705	8.46360338966835	5.02787986782543
O	-2.07178835466969	5.20614009132492	4.14358760335247
H	-2.88866536604887	11.21249041364180	7.31232944079929
C	-4.21825810885078	9.40523918582361	5.56710514086974
Sb	-0.49599208646234	7.38697216868131	4.43886568969186
O	-4.55086303980477	6.23221277864051	4.40970603843231
H	-4.96005556128263	10.11415885944840	5.19004377176581
S	-2.56042463110928	10.06369012705310	5.20802318233735
C	-2.67032863275359	11.53592351808480	6.29172562288419
O	-2.14819162447937	7.88380464310040	3.43743345961578
H	-1.69635618050519	12.02656813517440	6.24681955271378
O	0.41109901134119	6.60593845990300	2.73070511824166
O	0.48988329251779	9.07653668754463	3.76893221190797
Sb	-3.33282674687502	6.45681835960061	2.75490505992219
H	-3.44950366901723	12.20211115572220	5.91073021784546
C	0.99566033204884	7.57655505567854	1.99584536422849
C	1.03730251681731	8.88791803566716	2.54533629540006
Cl	-5.01484274475326	8.25373016297673	2.06975685926741
H	1.51546240289419	6.33028797909609	0.33346056830138
C	1.55957921268980	7.33706388711050	0.74061898683855
H	1.65976222384440	10.91730188469720	2.26232507400737
C	1.64181233174320	9.92111306432989	1.82781988387118
C	2.16621085305096	8.38151901168635	0.03104406839054
C	2.20759106221362	9.66679349593811	0.57149254076752
H	2.60131409476419	8.18478448517213	-0.94609717393567
H	2.67508662125661	10.47835984196480	0.01876420523045

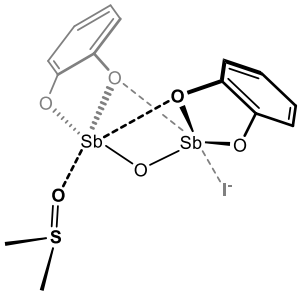
Table S31. Cartesian coordinates (in Å) of **1**·DMSO·Br_t^-



Atom	x	y	z
H	-5.70856728833876	8.81573209294467	7.20204444090381
H	-4.37133908085714	7.91807882193387	7.99422076832929
H	-4.25842706360266	9.69904895599677	7.81476775653587
C	-4.62927069164958	8.77294173078346	7.36652523709539
H	-5.55895423857586	9.92511337309574	4.96892238039604
H	-4.06554921923397	10.86491321857700	5.39421666935565
S	-3.78860898729461	8.51096673374740	5.76208293768967
C	-4.46841201693484	9.96913968427475	4.91481291607360
O	-4.54945776801420	7.30410319740007	5.17730807999294
H	-7.78573563053408	6.61080289992553	0.27397256337295
H	-8.21815709448655	8.98526086953162	0.88744903734579
C	-6.96099097028345	7.26374075083932	0.54980055411389
C	-7.20378805992245	8.59356954455844	0.89323127209405
H	-4.12227473267200	9.92679405084088	3.88244933015006
H	-5.44890682111990	5.72483892003783	0.30222539127574
C	-5.65499014812568	6.76007656089660	0.56208182083224
C	-6.14053541854247	9.43029512281581	1.25527359509580
H	-6.30847077514161	10.46807514885140	1.53157788805232
Sb	-3.15953454298464	6.00720973663355	3.46996734069221
O	-2.19887173475842	5.45829922047844	5.21072902863707
C	-4.57987817788260	7.58594009264942	0.91129742408429
C	-4.83440869354326	8.93893970386690	1.26502461137064
O	-2.26710663699895	7.79228291467918	3.46278868469849
H	-0.38488369084516	4.79410771796320	7.02522048158354
O	-3.30764583941411	7.15633463073774	0.96035725001353
O	-3.78700116516797	9.72303053356305	1.61745324121161
C	-0.96554409833345	4.95181341079639	4.96993941957846
C	-0.07899724059125	4.62364350579322	5.99616320985959
O	-1.48563435802122	5.06240349560526	2.65778755380877
Sb	-1.96807191943482	8.75283032046831	1.76344624400751
Br	-1.19368449284450	10.97143649183570	3.19805044266152
C	-0.58832400891614	4.74319560008218	3.61487405728526
C	1.17955583656674	4.08845903938315	5.69195852334480

H	1.86535308513043	3.83715901148608	6.49762442323409
C	0.67124116511095	4.21330857129263	3.32483730157117
C	1.55214592033527	3.88511780438269	4.36319647371910
H	0.94638368598264	4.06412844035719	2.28395491991220
H	2.53067891194027	3.47356608089447	4.12664073002104

Table S32. Cartesian coordinates (in Å) of **1**·DMSO·I_t^-

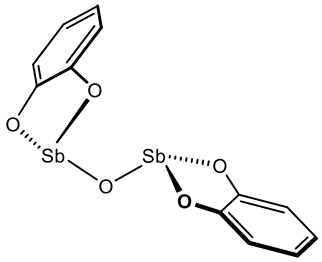


Atom	x	y	z
H	-6.64467739088130	6.13876072748118	7.42858419552785
H	-7.44153973365540	6.33854230501485	5.82752938324741
H	-7.10400817702008	4.68778556405525	6.45414641259357
C	-6.76369798328930	5.72635888831650	6.42382610334800
H	-4.23930297732502	5.39738055760942	7.73080499495936
H	-4.50270158184452	3.85946497322963	6.79595106250416
S	-5.16429544977734	5.78937512421953	5.55014476741729
C	-4.15702071104170	4.89488610871787	6.76372765989689
O	-4.71067974707077	7.26273357059908	5.72012016788605
H	-0.05850125597299	10.72237450095560	6.00387360154264
H	-0.49761607802325	9.05686399644758	7.80054787614350
C	-0.39778506349534	9.72097693118868	5.74928685194608
C	-0.64258534595333	8.78739244938500	6.75730126299040
H	-3.14132464245374	4.92978147104013	6.36778866966716
H	-0.41123823171942	10.09562351002770	3.60995152068874
C	-0.59309631606133	9.37910562868596	4.40662640201593
C	-1.08956341980735	7.50146341143650	6.43108354940495
H	-1.29623207145719	6.76685209081287	7.20430894764059
Sb	-4.50908313257938	8.44885628088452	3.60988126379894
O	-6.50864258294509	7.95151062272907	3.68567796516287
C	-1.03195956404143	8.09422693336935	4.06381127167212
C	-1.28557578512980	7.14946076483347	5.09622248988412
O	-3.98162472897677	6.70309180002638	2.84461089414274
H	-9.01621917972780	7.31173440666227	3.10165249302236
O	-1.24341779785724	7.69855266804436	2.79848403746619
O	-1.72006369421743	5.91755446899520	4.73062946335475
C	-7.14837196968107	8.18094085435947	2.51126063423512

C	-8.47608077251514	7.81148573486494	2.30145742542875
O	-5.14639960670351	9.18402027209576	1.75223243333312
Sb	-2.23073672738065	5.79626107269498	2.73212702453205
I	-3.37690410864502	2.98519601410229	3.55994129630768
C	-6.41657036689677	8.83066849847539	1.48078031693043
C	-9.09003278269312	8.07925596064516	1.07101348264944
H	-10.12431018908880	7.78461638129668	0.91112735023778
C	-7.04019483616928	9.08791564695468	0.25661855017206
C	-8.37433204772980	8.71372366112577	0.05538767904414
H	-6.46882565959490	9.58003803558213	-0.52591112775311
H	-8.84994429057754	8.91815111303476	-0.90102437304214

S4.2 Structures with solvation model (CPCM) in DMSO

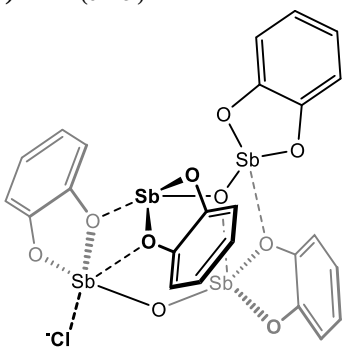
Table S33. Cartesian coordinates (in Å) of **1**



Atom	x	y	z
Sb	-2.30799149365049	6.95939800442239	3.46064287737762
Sb	-1.67604828891690	5.50086439664015	0.23769239976731
O	-1.40886204282388	6.82322103782416	1.67725692743367
O	-1.02712752928258	5.70575024465328	4.42350440692660
O	-0.96579801257198	8.36394262944143	4.08376930547352
O	-1.91844215037308	3.95541542119578	1.54836179047164
O	-3.71500019185498	5.56731387760236	0.38986068756312
C	0.09810906874809	6.37076300627246	4.82882611367371
C	1.18131817857951	5.71221361816239	5.41017734455370
C	2.29767533697649	6.45234649869695	5.81826806375403
C	2.32934118229434	7.83804386402771	5.64478537570005
C	1.24526571477645	8.50468404844095	5.06084836749180
C	0.13014341320362	7.77314685319037	4.65245344663878
C	-4.09867262701596	4.91232914610274	1.52538321742064
C	-5.37144402061844	5.05581473516502	2.08147864277242
C	-5.68525636666043	4.37705346500492	3.26299852103659
C	-4.73543281445276	3.56676969067050	3.89119916815025
C	-3.45834795606547	3.41437564223168	3.34227938823575
C	-3.13898231842439	4.07535834341812	2.15276567677347
H	1.14246082537289	4.63439549331615	5.53928326781696

H	3.14177899063598	5.93949229607758	6.27033432369395
H	3.19810240951519	8.40790570045293	5.96172953040827
H	1.25718468851138	9.58159300557423	4.91950108973468
H	-6.09482525766482	5.70180074346974	1.59322123931738
H	-6.67234507229760	4.49651108419440	3.69939265303246
H	-4.98123795624826	3.05682277272154	4.81771440543383
H	-2.70870470969197	2.79222238102998	3.82085676934781

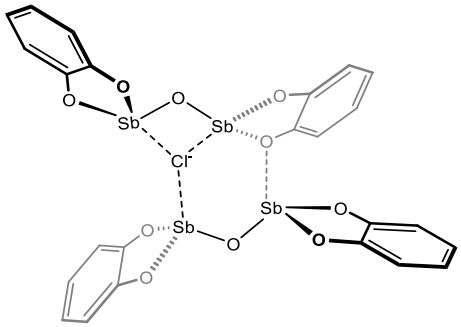
Table S34. Cartesian coordinates (in Å) of $\mathbf{1}_{2(\text{dimer})}\cdot Cl^-$



Atom	x	y	z
Sb	-2.63944992215019	6.80723584324987	4.23570545759108
Sb	0.31424014339038	8.68323720879954	4.92650599998040
O	-1.01657742536459	7.86052806478533	3.59649446220839
O	-3.68815491256470	7.19491011883104	2.50824456084170
O	-2.01368705279319	5.20966148972522	3.05718920530339
O	-0.09919000346174	7.02499205114772	6.12887137306950
O	1.77523754988046	7.41075246732888	4.25123389087428
C	-3.21604150073582	6.46468892855735	1.45524502897005
C	-3.56288113095173	6.74738779968930	0.13388817814534
C	-3.00749988944541	5.98435460951921	-0.90023695192122
C	-2.11370380363797	4.94971302480154	-0.61121231973957
C	-1.76107221306570	4.66254493216433	0.71234287255072
C	-2.31166475370361	5.41481112871005	1.75388252092544
C	1.57790740657249	6.13736237080189	4.69926502605142
C	2.31208615523008	5.05538226971482	4.21371855720813
C	2.05565157480840	3.76860278542006	4.70336178831636
C	1.06975219923376	3.56418157174974	5.67115025235062
C	0.32947002920432	4.64538506017807	6.16430733764951
C	0.58448702840421	5.93155726517578	5.68709383285091
H	-4.24422571267190	7.56644085845967	-0.07510068059180
H	-3.26925996463772	6.20907375719713	-1.92999717296301
H	-1.68007201075192	4.36515030817300	-1.41773474507106
H	-1.05879469477835	3.86768423885900	0.94711764026833

H	3.07032193140767	5.22582810354406	3.45422543015065
H	2.62704818268620	2.92762867258400	4.32025869833740
H	0.87001173482872	2.56371812867139	6.04473618396280
H	-0.44344313574745	4.50263947526015	6.91473335708178
Cl	-3.96278349942681	12.29098100349130	0.83467372827704
Sb	-3.69866088793357	10.20752895668350	2.41648933156376
Sb	-0.54340596914349	8.48982627049562	1.34836735178204
O	-2.12764505110078	9.64127595230738	1.37895261497767
O	-3.43823952457827	9.10841340725587	4.46307294993855
O	-2.59655110673992	11.51161578780640	3.57432041468569
O	0.60875342635696	9.63191062283024	2.68014793268538
O	0.38289424046343	9.88529860358301	0.06842711316606
C	-2.66950463869670	9.84846056421194	5.28788659562793
C	-2.30235025853700	9.43766986547593	6.57955081639686
C	-1.47832966557694	10.24830692920660	7.37412698315248
C	-1.01002808704011	11.46536422214710	6.87796624160351
C	-1.37043582343822	11.88978608878700	5.59398624728682
C	-2.20735656670170	11.10127522865720	4.79674531899727
C	0.95000882622590	10.91401561131320	0.73598737832411
C	1.41009800649403	12.07704715711540	0.11041695323577
C	1.99536929650013	13.09557762269550	0.87320121655423
C	2.12107334039254	12.96395061339530	2.25784376463522
C	1.66341854128902	11.80478606260060	2.89881372147940
C	1.08555673368961	10.79275491231540	2.14002938572510
H	-2.67645395551344	8.49250941090522	6.96111271018254
H	-1.20157899228990	9.91522526246394	8.36952079800592
H	-0.35987510071391	12.08904142726930	7.48423353485655
H	-1.01022732336460	12.83407565857250	5.19660240986938
H	1.30521570171141	12.17458659974320	-0.96679915476205
H	2.34952183250044	13.99594379330390	0.37850130131157
H	2.56979061514109	13.75936031382340	2.84588948092501
H	1.74495008084609	11.69145651844480	3.97575807511463

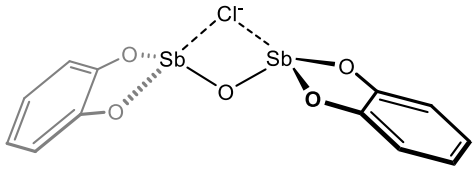
Table S35. Cartesian coordinates (in Å) of $\mathbf{1}_2 \cdot Cl^-$



Atom	x	y	z
Sb	-3.16361477746532	7.91371392896627	1.84198201603901
Sb	-0.47326720711135	5.84208701842923	2.80785606581719
O	-1.83200205016132	6.50464863185769	1.49564154230611
O	-2.32370691700140	8.16319772632099	3.78194038720709
O	-1.85854735598942	9.56405466758256	1.59227904333359
O	0.62050888952767	5.06955657956934	1.25632071192414
O	0.81709613462063	7.41116744671664	2.53891968997055
C	-1.45379734644626	9.21545387301480	3.89546779162242
C	-0.82518331080802	9.54419184300188	5.09040568376472
C	0.09558049744791	10.60003911290630	5.10982161755443
C	0.37061997327250	11.30927792891000	3.93828026677593
C	-0.26943773039928	10.98027969019550	2.73814435314783
C	-1.19268951521965	9.93098349185057	2.70474252764312
C	1.51000515027213	7.27583002830575	1.37655891848647
C	2.30148480396999	8.29820074440027	0.85202734840040
C	3.00886224363926	8.08328287615900	-0.33794659813709
C	2.92103259896587	6.85635997616161	-0.99990432862729
C	2.12265397346477	5.82710072307237	-0.48317106233858
C	1.41361510744656	6.03467427020593	0.70001891456616
H	-1.04114078645754	8.97181363653915	5.98830720952151
H	0.59395731945336	10.86026083220750	6.03914994907610
H	1.08825411348037	12.12529035415830	3.95373003020721
H	-0.05618210398030	11.52483781723000	1.82241650412341
H	2.35271083557841	9.24770908590794	1.37717876773456
H	3.62415169181477	8.88041433406348	-0.74600828444982
H	3.46985129100070	6.69355541782110	-1.92327797016510
H	2.04269691974762	4.87007053362872	-0.99136421009925
Cl	-5.81024351296995	5.65939468298589	0.77586550362695
Sb	-3.89722851711625	7.07360994199185	5.36355447434312
Sb	-5.37148362874200	4.86607779652753	3.22327626225605
O	-4.29100452809345	6.58805419281376	3.40893604068686
O	-4.79814444257215	8.90473598121488	5.12630534829603

O	-5.87625638624349	6.53410950215892	5.73950986477802
O	-3.87075791773413	3.75775848376644	2.36580758641529
O	-4.08706649320355	4.38754301900469	4.96787533668938
C	-6.15595062339370	8.80073104196855	5.08863521037298
C	-6.97816306304093	9.87464380530444	4.74562218757517
C	-8.36801516088131	9.70166818103438	4.71912605416571
C	-8.93179552695648	8.46221825943328	5.02994793545648
C	-8.11272706591196	7.37959097138484	5.37501445485855
C	-6.72814713812611	7.54667970556762	5.41117253333909
C	-2.92602939465969	3.84527550862541	4.55281396235348
C	-1.84141554717644	3.61026274260702	5.40536861878515
C	-0.67073825856749	3.02103926299651	4.91241818911810
C	-0.56756812322187	2.68091579385238	3.56241211560254
C	-1.63727982223028	2.93352521472586	2.68680172504075
C	-2.81762579353100	3.50679189083482	3.17526038651423
H	-6.52656930499047	10.83172348769950	4.49925991262658
H	-9.00559507388285	10.53906367503430	4.44983698242099
H	-10.00976538840100	8.33023936557421	5.00333293955786
H	-8.53617530618404	6.40842857868116	5.61615356689177
H	-1.92952392292827	3.88414796672861	6.45297841174421
H	0.16171815025259	2.83939714475177	5.58530722742272
H	0.34238124450545	2.23287686300224	3.17607271820853
H	-1.56984189666157	2.67954437054516	1.63331756544851

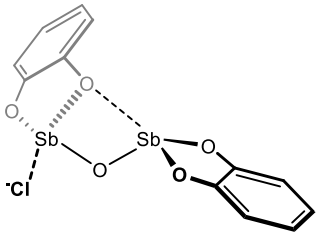
Table S36. Cartesian coordinates (in Å) of trans-**1**·Cl_b^-



Atom	x	y	z
Sb	-0.17326573139890	2.33519065774553	-0.94030211729463
Sb	-0.43332021626149	-0.74749549987570	-2.59703255492059
O	-1.22073806190139	0.93091061702343	-1.88175276413269
O	0.88305582282996	2.93805036900000	-2.59437665941721
O	-1.48261089617269	3.78810567157736	-1.66133527298687
O	-0.76812804559510	-1.88093823370424	-0.92073666497954
O	-2.34425401749844	-1.44431588210244	-3.04374718960394
C	0.15884115640651	3.79125416423014	-3.37469825046932
C	0.62033781542607	4.23085018841694	-4.61600412635632
C	-0.16275956445947	5.10894395739862	-5.37701358980076
C	-1.40017093054089	5.54379738130155	-4.89741138887593
C	-1.87003578644371	5.10637111585311	-3.65230971252158
C	-1.09562090807544	4.23317856867838	-2.88418071006101

C	-2.88061311157779	-2.11940515913196	-1.99453350872841
C	-4.19691261386057	-2.58745019118045	-1.98836925069411
C	-4.67924753678820	-3.29652732934009	-0.88056722274466
C	-3.85225802369919	-3.53512365259637	0.21911399313044
C	-2.53204286057801	-3.06580806247748	0.22479176066710
C	-2.04470196893312	-2.35865831966627	-0.87504959220923
H	1.58423177063490	3.88258158569607	-4.97734871418469
H	0.19904244134156	5.44734834374395	-6.34396376671113
H	-2.00675093530076	6.22427602381172	-5.48882419194206
H	-2.83082648421978	5.43883843373872	-3.26827171441782
H	-4.83081784099250	-2.39670681716745	-2.85026496792801
H	-5.70305879668682	-3.66038495813345	-0.88308181090569
H	-4.22798250631625	-4.08504668625315	1.07750781764696
H	-1.87776142767858	-3.24276488287364	1.07421130396070
Cl	1.82343725834014	0.21368659628719	-0.99751813351895

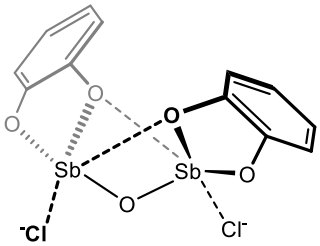
Table S37. Cartesian coordinates (in Å) of **1**·Cl_t^-



Atom	x	y	z
H	-4.99466479264376	6.75285646128800	0.14901195792032
H	-6.50258042728659	8.62937287551385	0.79703108677674
H	5.34532663497877	9.14242463289765	4.36954037069900
C	-4.65579848547391	7.52303176786229	0.83669901151614
H	6.08132515408444	9.95987191220024	2.13560088476593
C	-5.49602901777295	8.58111528292746	1.20338377284432
O	-2.52275094550273	6.43394709578502	1.00332915674755
C	4.61064749295335	9.39567488626163	3.61024089934698
C	-3.35910189919730	7.44797301245413	1.35260803274040
C	5.02282227621818	9.85306496079276	2.35696645948286
H	2.91069324355043	8.89747614600038	4.86633655283128
C	3.24602972582851	9.25614666206539	3.89680254082289
C	-5.04427545289003	9.56791846198827	2.08166094892329
C	4.07702458279303	10.17683370435580	1.37539359720694
H	4.38643706159163	10.53553516745470	0.39715449660198
H	-5.69506046531427	10.39085061208850	2.36349909751303
Sb	-0.62546427144118	6.49609931640538	1.79435478582821
C	-2.90384754850626	8.44198614488993	2.25354860968874
C	2.29865044050381	9.57516390155326	2.92362818497436

C	-3.74698248622456	9.50020008552221	2.60360012503682
C	2.71366996234366	10.04545123960810	1.65178421392088
O	0.14439748226707	7.96364852312562	0.68991850362958
O	-1.63295444144581	8.33063859613007	2.72582895665941
O	0.95978048833526	9.45031312104502	3.14918579913723
O	1.74610481049211	10.36624966453080	0.75624246023814
H	-3.37794605363836	10.26001802847970	3.28769350577149
Cl	-0.01982392806895	4.84777558133750	-0.09718872641479
Sb	-0.13862214053352	9.79703215543606	1.44699971479029

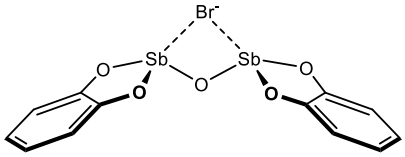
Table S38. Cartesian coordinates (in Å) of **1**·$[Cl_t^-]_2$



Atom	x	y	z
H	-4.94341401277590	8.38900375736471	-0.28463160921652
H	-6.53146359371219	7.84609174101379	1.56302167038972
H	5.64555085193281	8.59120452923655	1.55035507905890
C	-4.57605057807500	8.02495788903882	0.67172589327820
H	5.70355884742603	11.03936901857920	2.00946185828751
C	-5.46269083525526	7.72007837522595	1.71421860763991
O	-2.30827449457336	8.15819338254556	-0.12880474741668
C	4.77087339312040	9.09295259064445	1.95608439890228
C	-3.20079149082235	7.86809079053720	0.85524897202479
C	4.80367877665002	10.46492652841170	2.21228886066343
H	3.57035847230879	7.28561909255940	2.02028750766075
C	3.60887290300583	8.35427529279742	2.21695088428638
C	-4.97355144956750	7.26269221020363	2.93914520886947
C	3.67199513155853	11.11165187817640	2.72911271958808
H	3.68176111355804	12.18065861194880	2.92688548622528
H	-5.65943310625409	7.03247557967980	3.75024131957322
Sb	-0.34401599367825	8.14331772291083	0.51891358604382
C	-2.69961949935884	7.39091355831285	2.09660053338488
C	2.47578890305878	8.98508352169829	2.74224617828622
C	-3.59502422785710	7.10128052649506	3.13213472031168
C	2.50978916937955	10.38375920432640	2.99200246113984
O	-0.51897863821342	9.86453809273847	1.51166036341477
O	-1.36445749663162	7.24656486498214	2.21763274618924
O	1.33275698267573	8.32763840994314	3.02344899118291
O	1.39102813633424	10.97448477325710	3.49025151864354

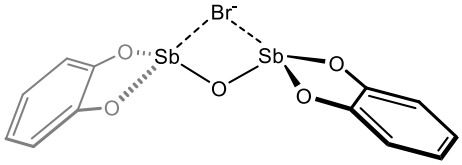
H	-3.20138458548355	6.74743473997814	4.08192147534954
Cl	0.08624060755262	9.63050298300286	-1.70302464102815
Sb	-0.26102001374898	9.72977810729554	3.48589212118931
Cl	-1.64249627255395	12.05660022709540	3.68003083607770

Table S39. Cartesian coordinates (in Å) of cis-**1**·Br_b^-



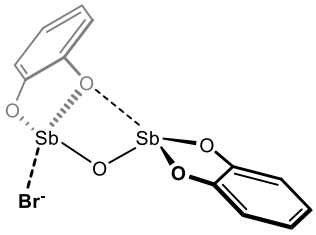
Atom	x	y	z
H	-3.50704073303143	9.60634396921354	4.01027238366206
O	-2.34081105904797	7.24774923324687	4.47412859638234
O	0.43334554834595	6.82395782637500	4.98935341359602
C	-2.97294289300844	9.18304979705340	3.16348555682300
H	2.21616301210610	11.36500792604440	4.37272615154125
O	2.52973535014780	8.74420119408466	4.78216495143291
Sb	-1.03068823582536	5.63427735722054	4.37161797471187
C	-2.32600341076593	7.95424450760274	3.31066591784526
Sb	2.37178063775782	6.67883786828932	4.58653753216973
H	-3.42655098121524	10.80878982888780	1.82429268318590
C	2.11625815493854	10.74592875980280	3.48489146404157
C	-2.92446709759447	9.85112940332171	1.93277674864979
C	2.25824663498528	9.36150716026482	3.59988160475254
Br	1.42190020638009	3.91475492497104	3.50189310502727
C	-1.62470921507526	7.39382115766691	2.21518791395188
O	-1.00815384623954	6.19121708474777	2.40499609593113
H	1.73375314043112	12.39307618204360	2.14976709677811
C	1.84672675551306	11.31547580674540	2.23346527794989
C	2.12636315219808	8.54365949703200	2.45109558468786
C	-2.23272801967960	9.29496633721252	0.85534041989264
O	2.27239880911362	7.19616924466313	2.61133135678835
C	-1.58134067715556	8.06395130778717	0.99403782320957
H	-2.18569982302444	9.82038092670217	-0.09445342251428
C	1.71859881839478	10.50602879559230	1.10333160454300
C	1.85856463047248	9.11739944647812	1.20962523823179
H	-1.02549979376960	7.62756625974217	0.16937141070377
H	1.49696956460519	10.94830681971420	0.13603274875246
H	1.74413537004294	8.47428637749333	0.34204176727233

Table S40. Cartesian coordinates (in Å) of trans-**1**·Br_b^-



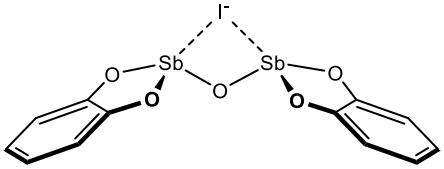
Atom	x	y	z
Sb	-0.11362038326539	2.37623826494948	-0.90138838983219
Sb	-0.40109762030064	-0.72749429968922	-2.56465000285449
O	-1.15838136428757	0.94129267532462	-1.79852310476350
O	0.90323066082057	2.94953388923601	-2.58904997732323
O	-1.44863108771979	3.80114511074773	-1.62140194640988
O	-0.75575503476516	-1.89706615029282	-0.91825333885995
O	-2.31886381410132	-1.37861858803413	-3.03246620057494
C	0.15406104873181	3.77884931271165	-3.37177085963785
C	0.58371182546469	4.19397142324978	-4.63279488197612
C	-0.22376927934850	5.04878336653888	-5.39456640413917
C	-1.45338200083853	5.48501715916274	-4.89650659558091
C	-1.89130892907288	5.07220559475632	-3.63153640051666
C	-1.09226307303188	4.22213692056929	-2.86308632420590
C	-2.86986004583871	-2.07068082846111	-2.00092019463873
C	-4.19411137269277	-2.51517000993183	-2.01033631721752
C	-4.69243120068886	-3.24061113424012	-0.92051294548977
C	-3.87352374691502	-3.51893251478778	0.17593304591555
C	-2.54518595575311	-3.07401023840904	0.19648818730433
C	-2.04189838903212	-2.35105495480427	-0.88568566135317
H	1.54184317479601	3.84496343256171	-5.00837547066050
H	0.11302370764256	5.36821252688713	-6.37688541062526
H	-2.07881600357188	6.14721678995647	-5.48898296123098
H	-2.84574106231942	5.40564190827781	-3.23290474360001
H	-4.82154202012665	-2.29285176652915	-2.86933554492723
H	-5.72263732581936	-3.58563663904612	-0.93414099777562
H	-4.26210605434075	-4.08137759792011	1.02036352776882
H	-1.89694003181622	-3.28227477857275	1.04336434293829
Br	2.06106337819094	0.17332912578881	-0.88514342973337

Table S41. Cartesian coordinates (in Å) of **1**·Br_t^-



Atom	x	y	z
H	-4.87116123600249	8.53619442646070	-0.24163614100326
H	-6.48643594429206	7.34348950955470	1.23917825258293
H	5.26711710709918	8.17912467181768	1.37107181777402
C	-4.52848665080139	8.02602576927445	0.65478298763788
H	5.80770275380721	10.57742510301680	1.77439580647243
C	-5.42931981120612	7.35308208789687	1.49044899112257
O	-2.23785524988439	8.64826436708828	0.18653978653060
C	4.53002495980712	8.83875526807164	1.82030847509971
C	-3.16708882461274	8.04004185426904	0.96798494008485
C	4.83223333915167	10.18313982052520	2.04564183192945
H	3.01885355894628	7.29120293282944	2.00233168694126
C	3.27245877318149	8.33431152952207	2.17236480721119
C	-4.97449311352771	6.69907775730356	2.63732900460257
C	3.88110956643913	11.03488553926040	2.61974606110746
H	4.10313003231016	12.08410430806550	2.79470373321800
H	-5.67489095862378	6.17871982883871	3.28468599108882
Sb	-0.37032026554793	8.65417754975596	1.10491682068350
C	-2.70935139701239	7.38117680675210	2.13694897246361
C	2.32008957716443	9.17360523173673	2.75627225827367
C	-3.61181296253355	6.71130295488579	2.96341408205983
C	2.62366225135829	10.53935010976270	2.97449274214085
O	-0.85599167156538	10.34835316690250	2.06172391737333
O	-1.37421554821609	7.42871551206876	2.41195274592057
O	1.07925929324265	8.73915567083084	3.10951274854984
O	1.68021719557825	11.34658159091450	3.53104798321545
H	-3.24364786779406	6.20981765302562	3.85445593494148
Sb	-0.14163397074405	10.47479656864150	3.91597833691317
Br	-1.10763293572169	13.07503241092770	4.03389542506422

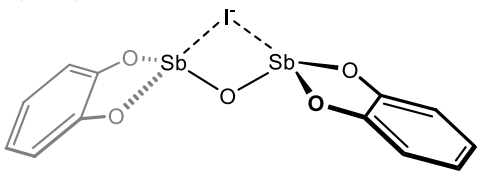
Table S42. Cartesian coordinates (in Å) of cis-**1**·I_b^-



Atom	x	y	z
Sb	-2.05773131205918	6.69982408946925	4.93166478817029
Sb	-1.83755876107805	5.64646844101170	1.49257378141062
O	-2.46191404404075	6.78551551005308	2.99146461168631
O	-0.08296991780714	7.20243899694881	4.81665787432694
O	-2.25012116700934	8.76215861236776	5.04300271043236
O	-1.94402386668279	7.28593569765968	0.22589189864495
O	0.12696349700873	6.19906493315217	1.53287868352352

C	0.08239841945740	8.54754296024853	4.64862695430129
C	1.32681511024196	9.11210736733322	4.37576446134535
C	1.43810695884142	10.49781498011910	4.21583401356901
C	0.31061035176306	11.31309026657930	4.32961932976762
C	-0.94352886668822	10.75270004529440	4.60454047529533
C	-1.06303473237904	9.37096666127784	4.76558966987986
C	0.31954437776206	7.41131758535549	0.93433077586798
C	1.54421802043705	8.07451081705793	0.98223802976043
C	1.68561488088672	9.31359752828612	0.34762740909907
C	0.60798108066649	9.88419139672161	-0.33204428972246
C	-0.62572990743180	9.22268129241962	-0.38549706600166
C	-0.77527884518355	7.98627386364434	0.24578494043747
H	2.19215455937068	8.46408287226537	4.27327182757915
H	2.40721063989460	10.93347450859230	3.98914723231641
H	0.39872095358172	12.38855405309070	4.20059977787730
H	-1.82924534765473	11.37637652496390	4.69339185670294
H	2.36900657431532	7.62637018887227	1.52834222393139
H	2.63759325424320	9.83459642264269	0.39874044220145
H	0.71879907411847	10.84855477868550	-0.82059311491590
H	-1.47273257071696	9.65710465941654	-0.91012983532756
I	-0.86356541385737	3.60876994647037	4.06654053784052

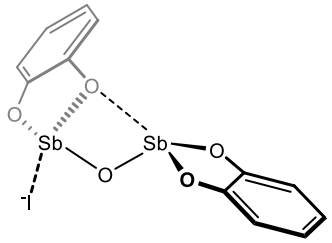
Table S43. Cartesian coordinates (in Å) of trans-**1**·I_b^-



Atom	x	y	z
Sb	-3.02114799951757	8.99917538298087	3.62425123570258
Sb	-0.56399538526517	7.04018407799375	2.07528004178516
O	-1.64463031303483	8.70116273442237	2.22012171802272
O	-1.84704660215223	8.21306797163944	5.11156969690155
O	-2.07127812620860	10.73873810593600	4.23678952984215
O	-1.21901582750157	6.56848434704822	0.19627992201211
O	0.87844076924485	8.03979033178710	0.97999176852603
C	-0.92699387431571	9.12380907271916	5.54903562601068
C	0.09724331292727	8.77483611033316	6.42914963822181
C	1.01373625139202	9.74901637097345	6.84529179220074
C	0.90466466324990	11.06226006317140	6.38260655843575
C	-0.12127098638130	11.41892077067330	5.49832789733878
C	-1.04145280986553	10.45535236425130	5.07976601612772
C	0.59233672898174	8.01393603888790	-0.35055296338268
C	1.34653190741250	8.71008237003682	-1.29724712697688

C	1.00513391468219	8.62736332534141	-2.65320399226669
C	-0.08521610895323	7.85589614996879	-3.06120943506375
C	-0.84912508180857	7.15644916425781	-2.11791945217617
C	-0.51383596065394	7.23313976519503	-0.76587401660277
H	0.17132270727148	7.74835235933632	6.77751857653858
H	1.81276720382043	9.47436159805902	7.52809400688402
H	1.61822366456293	11.81537094005950	6.70510166260787
H	-0.21592883637916	12.43723470598680	5.13106316172451
H	2.19256215669132	9.30690905444650	-0.96745885028545
H	1.59529788168903	9.16967548041404	-3.38670526843823
H	-0.34804619694450	7.79444295497526	-4.11352713596123
H	-1.70090281592560	6.55363832231586	-2.42067557265041
I	-3.57897323701806	5.68257706678895	3.09125396492152

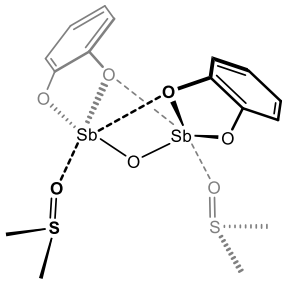
Table S44. Cartesian coordinates (in Å) of **1**·I_t^-



Atom	x	y	z
H	-5.31244349619161	8.50147225520330	-0.03075277822780
H	-6.49316573856041	7.89918250822125	2.08174961973014
H	5.87669226253744	8.50224352379700	2.46662988076752
C	-4.75658220147580	8.14984151621616	0.83412005597789
H	5.82082546550613	10.98712160608540	2.60773528069181
C	-5.41179429209277	7.81138144028843	2.02401426880337
O	-2.69973787392969	8.35574055196287	-0.39498065879887
C	4.92841941613148	9.02311254110842	2.56513645301827
C	-3.36665169595562	8.03734368805157	0.74819104304300
C	4.89660351640757	10.41701699028130	2.64311020731111
H	3.74731975156795	7.20080817739222	2.54689639810250
C	3.73797366102718	8.28560216749507	2.60986186273798
C	-4.68326957373906	7.36682004381660	3.12923327978333
C	3.67508026750505	11.09129822822430	2.76788543901541
H	3.63754930741184	12.17551133854080	2.83184864628075
H	-5.19256760819836	7.10864722203591	4.05337320625464
Sb	-0.65233678868928	8.21102832219935	-0.29292549753613
C	-2.62875546038469	7.57946051321701	1.86555743371094
C	2.51773435528486	8.95064764513344	2.73227689007193
C	-3.29006925848847	7.25310624504486	3.05185443055771
C	2.48319975655517	10.36487649023140	2.81802905361437

O	-0.23644202805468	9.83829130321477	0.77102856575498
O	-1.27407972973369	7.50500898515890	1.73819033149868
O	1.32923976705088	8.28154969872479	2.77496942851078
O	1.26766354029278	10.95579092894560	2.96638388816950
H	-2.70666435559125	6.91182537217055	3.90295480513218
I	-0.65373905878556	9.96695914904724	-2.81583451865599
Sb	-0.26431190740735	9.57365154819115	2.75804298468000

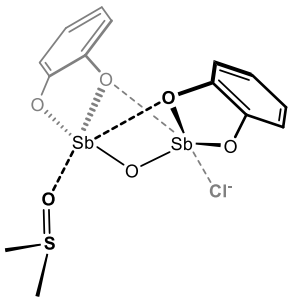
Table S45. Cartesian coordinates (in Å) of **1**·$(DMSO)_2$



Atom	x	y	z
H	-8.02164543194319	7.60902516805962	0.67755836373079
H	-7.51975209636282	10.03706222891570	0.91105243121286
C	-6.99552590540630	7.94631291392618	0.79702601413225
C	-6.71467217386432	9.30749344145329	0.92762111371971
H	-5.90419080305669	9.27666992194480	4.83400148002187
H	-4.41775222150138	9.23688679595509	3.81356811983115
H	-6.16391203679896	5.94241993169415	0.72369430052973
C	-5.95787824016936	7.00516350459270	0.82227118280359
C	-5.39238136521332	9.74153390333827	1.09054573532733
H	-5.16038679424274	10.79664199187370	1.20967257356865
C	-4.82348594923554	9.42574460956413	4.80592340869595
H	-4.54706164327473	10.42352375298870	5.15388768093313
C	-4.63351555434369	7.42638766723130	0.97269314084360
C	-4.35340842096411	8.81071716826544	1.11977006360797
S	-4.04044325075447	8.22199050919660	5.90537224171974
H	-4.69608369897246	9.59749328249915	7.72671505996329
O	-4.63516142891703	6.83867554000016	5.45670471392002
H	-6.02741666686634	8.48861424788272	7.22219841205398
C	-4.95844475733074	8.58192440626466	7.42085052068710
O	-3.58646518299974	6.56797896874757	0.99911236735743
O	-3.05653524451156	9.18620280060071	1.30548434017574
H	-4.62684411186724	7.86145878999945	8.16950906026051
Sb	-3.46034008855121	5.56465986665912	3.89486005133264
O	-2.60717744188848	7.32478502036320	3.51304922808861
Sb	-1.83146805356862	7.57990245419857	1.69681513957983

O	-1.76671539179217	4.72551719810868	2.88687168743377
O	-2.21229650708874	5.21398532691630	5.49240184075151
H	-0.43903867526132	11.93834307341900	3.69961330873861
O	-0.55840126930547	9.17914067066952	2.81721453589093
C	-0.69874718999257	4.70821602994256	3.71867059380302
H	-0.28513446453935	11.57814006649160	5.44977199368789
C	-0.93465042005416	4.95146487289581	5.09784530719993
C	-0.08797901861860	11.21622868715370	4.43779467534475
S	-1.06480313128518	9.71308605683952	4.20597660178674
H	0.78004874988812	4.30514698851872	2.21631335067931
C	0.60674618849722	4.47664402388351	3.27567072298946
H	-0.68505923400664	7.66390351994948	5.30658687463913
H	0.96817162420743	10.98055805399670	4.29688421804741
C	0.12682068642469	4.93509438929309	6.00317158092731
H	-0.07173191159399	5.12789275481273	7.05421674275875
C	-0.24618509709254	8.65348399316566	5.42173657662333
H	-0.46001906631070	9.05947052693947	6.41282678923789
C	1.66749290127099	4.46520402992418	4.19096635443045
C	1.42922208108269	4.69006604403543	5.54796757226450
H	0.82509907998053	8.64597140524133	5.21392608163842
H	2.67850129875055	4.28240612955755	3.83676744589709
H	2.25247532944429	4.68401127203025	6.25713840113234

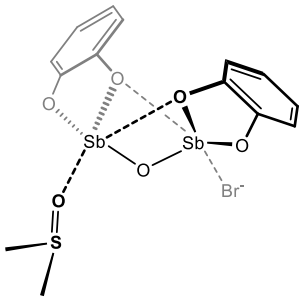
Table S46. Cartesian coordinates (in Å) of **1**·DMSO·Cl_t^-



Atom	x	y	z
H	-2.32122180176622	4.05698501732841	8.55722294044768
H	-4.55098355829004	5.15171641306959	8.74160144829072
C	-2.78970231356277	4.49505387425551	7.67988473139771
C	-4.03989546361622	5.10823418420044	7.78365353227259
H	-1.15223576039670	3.97609348334656	6.35334181017769
C	-2.12889293751172	4.44421146513993	6.44595704190567
C	-4.64023341378985	5.67880054526274	6.65363009382627
H	-5.60750437454961	6.16949824254639	6.72122418747040
C	-2.72215475407823	5.00116555529370	5.30743493525165
H	-4.27939525416868	9.12980872077506	6.64227567170564

C	-3.99122284681446	5.62653421092496	5.41919967932031
O	-1.58178373201832	9.01195955276893	5.88524238339010
H	-4.33740234055609	8.48658603792886	4.95779314670049
O	-2.13133658891175	4.99900451613865	4.09216801966322
H	-2.78269032734985	11.01985145433930	7.40978112709106
C	-4.21846644818033	9.37265556681370	5.57988026631651
Sb	-0.50710850401683	7.40865302867691	4.47635192857168
O	-4.53757374740135	6.17548789413341	4.30117660437360
H	-4.94562692746139	10.13970393976060	5.30228071082036
S	-2.57122476323492	10.03416149861050	5.23224654566791
C	-2.57698259765818	11.40904020281950	6.41084823758517
O	-2.11740605631684	7.72530990603828	3.33524063538743
H	-1.59058276927140	11.87211096273710	6.36088698016106
O	0.53293197161912	6.60884797356006	2.80829779196177
O	0.39433096749239	9.11506270486923	3.75067697634932
Sb	-3.25357893540128	6.24104323269748	2.68566217166651
H	-3.34695515489009	12.11536148717870	6.09173071158549
C	1.04313354850466	7.59211713816689	2.03734574033773
C	0.97780878639897	8.92119238678966	2.53729253405364
Cl	-4.95745847781092	8.10402444042287	1.81433679067109
H	1.67568918488147	6.33850611022533	0.41245553203223
C	1.63261254950189	7.35696484791759	0.79057257005097
H	1.44925022008259	10.98619585133890	2.19110581729206
C	1.50707713502979	9.97634818987017	1.79272241112192
C	2.16218545312760	8.42250733862467	0.04979863980808
C	2.10108649374939	9.72548983183725	0.54747090384820
H	2.62049066377137	8.22756713447032	-0.91622599152525
H	2.51063687486484	10.55174805912130	-0.02725925704872

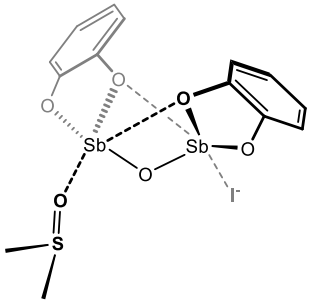
Table S47. Cartesian coordinates (in Å) of **1**·DMSO·Br_t^-



Atom	x	y	z
H	-5.61122573235032	8.72849882437322	7.26262330242781
H	-4.18047455411697	7.84612136322530	7.91260152950393
H	-4.14182131299002	9.63378972886347	7.78735042367260
C	-4.52263768924172	8.71121731474741	7.34283765113280

H	-5.67737729189088	9.88540310054373	5.01001144707983
H	-4.24291711164466	10.89406383065310	5.43988055138953
S	-3.79538483587234	8.57194305698537	5.68984715883689
C	-4.59541801320042	9.99980935556732	4.92083319290887
O	-4.50356955627508	7.33050442514346	5.05591038056817
H	-7.73497024424931	6.60325180638038	0.25460924689076
H	-8.20787810575521	8.89123841409830	1.11684440464457
C	-6.91739681483959	7.25930590303738	0.54093105688126
C	-7.18305493952672	8.54236453940841	1.02418500142399
H	-4.27223060411656	10.01379602267360	3.87982468841180
H	-5.37727382215996	5.80816688586291	0.05775411843797
C	-5.59702952895594	6.80732512632074	0.42491602974334
C	-6.12979986321934	9.38614149332014	1.39976176105792
H	-6.32164745743911	10.38429273280650	1.78406072772053
Sb	-3.20254351687377	6.04669034990365	3.47791984861111
O	-2.21431309323830	5.56630432862755	5.21827788492441
C	-4.53655569344380	7.64396966174439	0.78827016973247
C	-4.81119958104764	8.94473504105007	1.28155943376135
O	-2.15283031625967	7.73963068325058	3.30185183056311
H	-0.36237350609328	5.01361781180754	7.03963631526358
O	-3.23987475027235	7.26283299194344	0.71715508823676
O	-3.75715498396808	9.72949447982730	1.63753714415034
C	-0.99473863126301	5.00784415522615	4.98826622305068
C	-0.08999542393323	4.75341151954012	6.01988755523517
O	-1.58533549345893	4.92527499764973	2.69539878193892
Sb	-1.94658198667051	8.74114200715364	1.60954430083832
Br	-1.08234546284000	10.99716777478540	3.21870588287592
C	-0.66185835872870	4.67375666225281	3.64800340508645
C	1.15186414077561	4.16950566740712	5.73179514405009
H	1.85218095200738	3.97362297896698	6.53919083346748
C	0.58275321034675	4.09713230923725	3.37364474927649
C	1.48545531309507	3.84421458377244	4.41555717109596
H	0.83251733222393	3.84642862067943	2.34560639872073
H	2.44837332748664	3.39268745116347	4.19168316638807

Table S48. Cartesian coordinates (in Å) of **1**·DMSO·I_t^-

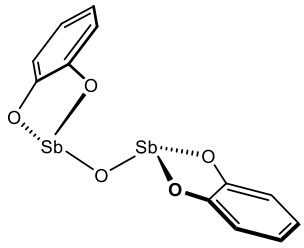


Atom	x	y	z
H	-4.37030632487409	9.66359466996889	6.70907145271750
H	-5.05642271143786	10.46613174064070	5.24251751741621
C	-4.47371614737967	9.62466024566393	5.62327164644671
H	-4.89961795454281	8.67945582705877	5.28686955369138
H	-2.32798215147977	11.15029464314130	6.73286279345045
H	-3.86131761363329	5.41299853497338	9.00764485544648
H	-2.86671470356514	12.06445583674540	5.27350515636327
C	-2.24859001253875	11.24527450035810	5.64852075538591
H	-2.15368134493993	3.70406955737419	8.40693181334149
O	-2.03197176811607	8.59022734781684	5.61528937921742
S	-2.83330245661828	9.71681882945147	4.87454309707339
C	-3.62839957842946	5.21644893849496	7.96473957360763
C	-2.66978762469379	4.25785911185324	7.62736280274397
H	-1.21209482092882	11.37361853349350	5.33448198606979
H	-5.02984872585195	6.69146506443940	7.21207590648628
C	-4.28951584603161	5.93704554323770	6.96253946996653
C	-2.36466253740232	4.00532375066169	6.28452052689204
H	-1.61816492470214	3.26523018071446	6.00874796964021
C	-3.99227568831302	5.69033507283521	5.62199871739806
Sb	-0.69921699178955	7.16067832216389	4.34557874536424
C	-3.02400887151239	4.71405690902087	5.27494949020273
O	-2.15648164294660	7.18400565146433	2.97866969992189
O	-4.60352899475829	6.36409766675402	4.60886198350099
O	0.00419477129441	9.00164219280585	3.75499220219811
O	-2.77532766904345	4.52286786887301	3.95675217023156
I	-5.50629444032605	8.59153022560094	1.87920363269394
H	0.97035610763940	11.07097835215000	2.40106061498314
Sb	-3.72701271119202	6.00797610035601	2.78006536391485
C	0.79207637436763	8.94651735373432	2.64836706174466
O	0.68298493858523	6.59077607659636	2.83171070868561
C	1.25173086207185	10.09740433904890	2.00786090027586
C	1.14467984382100	7.66180416380034	2.15484555817814
C	2.06297352748093	9.98476766621840	0.86990488051628

C	1.95054923907228	7.56422263380658	1.01512490156964
H	2.41780501517423	10.88379261968040	0.37338500152820
C	2.40892779234485	8.72479125541631	0.37728185336002
H	2.21516927255186	6.57905384650735	0.63899318505997
H	3.03674651264345	8.63764082707837	-0.50563892728456

S4.3 Structures with solvation model (CPCM) in THF

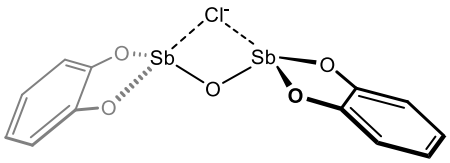
Table S49. Cartesian coordinates (in Å) of **1**.



Atom	x	y	z
Sb	-2.30432518679868	6.95074043160169	3.47285148085597
Sb	-1.67112175586946	5.48859893812197	0.25405487713549
O	-1.41569338487488	6.82040593698662	1.68116580719538
O	-1.01984378591977	5.69958589443905	4.42531210199855
O	-0.97133236934918	8.35850824457906	4.09434988961416
O	-1.91973026209227	3.94751550180124	1.56313650273132
O	-3.71002022381843	5.55221829881298	0.38507327036029
C	0.10556952627427	6.36797486153058	4.82736914498485
C	1.19363684751166	5.71157704424580	5.40126240818458
C	2.30856274884040	6.45520501441983	5.80579125582819
C	2.33377015296772	7.84147509887096	5.63641957271180
C	1.24462840136913	8.50573646287453	5.06007707917260
C	0.13098855566092	7.77054757379223	4.65534352419024
C	-4.09976731984917	4.90473182219889	1.52337101370139
C	-5.37482611203209	5.05231297545587	2.07226855792072
C	-5.69342229359626	4.38318580395368	3.25801537017895
C	-4.74623204373007	3.57889376578976	3.89732002738051
C	-3.46675745839061	3.42201187824417	3.35538049553866
C	-3.14323175545307	4.07263134658740	2.16165581343627
H	1.15908154207551	4.63332414102072	5.52678859290374
H	3.15709336119327	5.94472341950514	6.25213793859884
H	3.20193632536303	8.41353494522678	5.95088207399207
H	1.25074928166818	9.58293171876130	4.92160163976739
H	-6.09613330389194	5.69352405324141	1.57484172299067
H	-6.68262754120679	4.50536226001666	3.68882652531875
H	-4.99598062768091	3.07699018348279	4.82712231353545

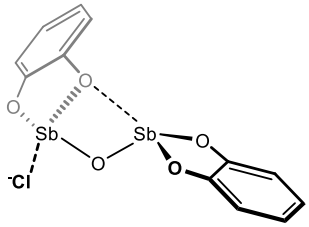
H	-2.71811031837054	2.80530038443880	3.84216599977315

Table S50. Cartesian coordinates (in Å) of trans-**1**·Cl_b^-



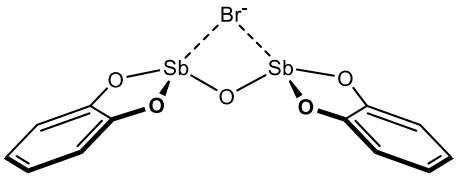
Atom	x	y	z
Sb	-0.17175135400783	2.33034535464027	-0.95083043745213
Sb	-0.43372170576618	-0.75165562688121	-2.58620674981520
O	-1.22600853584649	0.92947601841306	-1.88660893078691
O	0.87931785245198	2.93357039415488	-2.60773343150281
O	-1.47664928683189	3.79471577532604	-1.66262963212574
O	-0.77478756613774	-1.87942408357776	-0.90814510966298
O	-2.33859631592810	-1.46097540177835	-3.04294201500276
C	0.15862667690976	3.79467607572300	-3.38050615947433
C	0.61906113888807	4.23787628329339	-4.62080250953152
C	-0.16112700123954	5.12359696137484	-5.37588600630399
C	-1.39487300763331	5.56263537771418	-4.89115120675257
C	-1.86371455914029	5.12209337123421	-3.64683268948839
C	-1.09231253254438	4.24169931240048	-2.88386787167024
C	-2.87830032838255	-2.13287819320702	-1.99514073356831
C	-4.19212881266819	-2.60778492301740	-1.99466066960232
C	-4.67796271152382	-3.31428564445719	-0.88684397807088
C	-3.85705300271184	-3.54347828871408	0.21918292994797
C	-2.53937744786955	-3.06731612835708	0.23108238404729
C	-2.04833307494826	-2.36285402280593	-0.86864072288158
H	1.57995697056737	3.88506103700886	-4.98559437596581
H	0.19988048659609	5.46428516806397	-6.34245061732776
H	-1.99971130822774	6.24846088052285	-5.47837340584963
H	-2.82202558190726	5.45668206777444	-3.25857972704846
H	-4.82097374884833	-2.42308156378099	-2.86149774440154
H	-5.70011671955724	-3.68305061408180	-0.89398970487147
H	-4.23578092788094	-4.09095056875676	1.07794803342683
H	-1.88917409168695	-3.23568136865432	1.08528811476921
Cl	1.81270449587516	0.22100035042539	-0.99665603303398

Table S51. Cartesian coordinates (in Å) of **1**·Cl_t^-



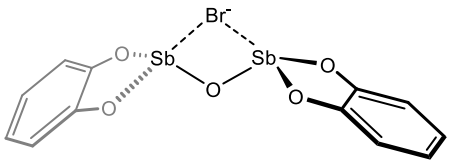
Atom	x	y	z
H	-5.01339259487002	6.76010072299349	0.15605051802078
H	-6.50888734420713	8.64365857410770	0.81560503372214
H	5.34403732932823	9.17284770141942	4.38784236910877
C	-4.66697666610745	7.52872954366514	0.84160861644412
H	6.08430054492449	9.99108261174387	2.15574316509076
C	-5.49945288446254	8.59065797755338	1.21437755063149
O	-2.54068197802403	6.42874918882998	0.99025945314875
C	4.61107456598934	9.41614909659084	3.62355127339134
C	-3.36622981083195	7.44630058655029	1.34672930366815
C	5.02561794285782	9.87414916812051	2.37139220270568
H	2.90819555893537	8.90286598168176	4.87035271321623
C	3.24639232187511	9.26258309464158	3.90223167541908
C	-5.03645431872299	9.57529032547296	2.08897199251827
C	4.08222508837126	10.18451261587550	1.38335299904361
H	4.39241645962222	10.54274490220560	0.40527866460636
H	-5.68112628136095	10.40134659292450	2.37598310167562
Sb	-0.63346811623202	6.46560566477631	1.76115233327311
C	-2.89907293019504	8.43896650619742	2.24450941712238
C	2.30108693720712	9.56790374607620	2.92269322694616
C	-3.73524860220902	9.50091561855678	2.60032641280644
C	2.71867362695410	10.03954973405620	1.65163095677349
O	0.15020938116427	7.93745910395582	0.67390450038028
O	-1.62665584665430	8.32168071141152	2.70615905040205
O	0.96333256133205	9.42905296708335	3.14078339270113
O	1.75335533180175	10.34817518698620	0.75144439313684
H	-3.35694561649592	10.25813446562420	3.28231149732889
Cl	-0.05720790716021	4.82392593041156	-0.11764425784636
Sb	-0.13210975282951	9.76553168048756	1.43425344456444

Table S52. Cartesian coordinates (in Å) of cis-**1**·Br_b^-



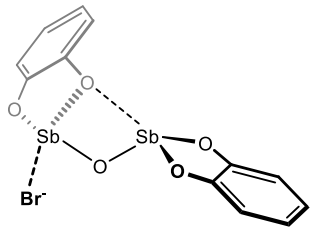
Atom	x	y	z
H	-3.52898216694676	9.59076182680900	4.00929959989605
O	-2.35032008058606	7.23885852172502	4.46993692384579
O	0.43044148504132	6.82936735265930	4.99125657984569
C	-2.99165891236308	9.17243794748354	3.16217049358446
H	2.23857442190665	11.36593179009930	4.37203258136989
O	2.53967736332881	8.74414802503689	4.78006414989817
Sb	-1.02679831609152	5.63601512103058	4.36642802029185
C	-2.33752207489052	7.94747798734355	3.30909728882235
Sb	2.36679742979271	6.67961430126081	4.58313246056022
H	-3.45097101036899	10.79856878835240	1.82536977282087
C	2.13535438048022	10.74803775918900	3.48384431414305
C	-2.94416389476848	9.84322181800439	1.93305933566680
C	2.27000796114191	9.36295743662073	3.59939737622443
Br	1.41899353561876	3.92420805766639	3.52053024656642
C	-1.63005965752006	7.39346692736830	2.21386232374322
O	-1.00691315186064	6.19469880792491	2.40217548394381
H	1.75915260603084	12.39688429559990	2.14903527199692
C	1.86735921773747	11.31871366466120	2.23276365162135
C	2.13199766871040	8.54566276734329	2.45048974386992
C	-2.24595056599545	9.29372280329828	0.85644572832465
O	2.27082157329853	7.19800076362024	2.61006488554601
C	-1.58736614239674	8.06649018361094	0.99434610417086
H	-2.19895994111750	9.82188476954761	-0.09190957066459
C	1.73282147196864	10.50985246352210	1.10304731533019
C	1.86519816240509	9.12053958183133	1.20943150323016
H	-1.02591682038356	7.63455518833370	0.17124476379170
H	1.51125798807629	10.95319401808230	0.13612685790575
H	1.74543146975176	8.47681203197462	0.34311579365404

Table S53. Cartesian coordinates (in Å) of trans-**1**·Br_b^-



Atom	x	y	z
Sb	-0.12166126588778	2.35511250465594	-0.92680145929379
Sb	-0.40323778809434	-0.75182983944897	-2.56934584555150
O	-1.16421748514685	0.92807606945987	-1.83430226696769
O	0.90187441126825	2.95032548526819	-2.60221377357745
O	-1.45334783755449	3.79098061832577	-1.63662536244721
O	-0.76250875689902	-1.90143517193561	-0.91069587182530
O	-2.31732674600929	-1.41796452103365	-3.03790155176126
C	0.15657133009097	3.78715517382222	-3.37901805189287
C	0.59203090699301	4.21590093502478	-4.63329645218133
C	-0.21157431647191	5.07900842328047	-5.38974688441189
C	-1.44338926244865	5.50981820771377	-4.89272315649291
C	-1.88730287201728	5.08333131740521	-3.63448465054078
C	-1.09239583468604	4.22511764569867	-2.87073692003343
C	-2.87097958453752	-2.09543113461794	-1.99983957320208
C	-4.19393015878059	-2.54359489340741	-2.00747540562948
C	-4.69478140333849	-3.25480834469810	-0.90957129455764
C	-3.87964183969574	-3.51530408970013	0.19385757309513
C	-2.55265758081834	-3.06648947218650	0.21319352437820
C	-2.04660641953374	-2.35779906334982	-0.87689894193193
H	1.55188604989047	3.87004608165120	-5.00723876550066
H	0.12972307528791	5.40879329608278	-6.36716221728103
H	-2.06629407987349	6.17798391159656	-5.48133513266379
H	-2.84394393519081	5.41126016951629	-3.23670186013143
H	-4.81808866828623	-2.33402937917317	-2.87198801029691
H	-5.72427646680238	-3.60231209973823	-0.92211859002522
H	-4.27032686216520	-4.06624601443569	1.04499139600164
H	-1.90675697293529	-3.25970969479252	1.06533727321320
Br	2.04822836364291	0.16680187901604	-0.91222672849056

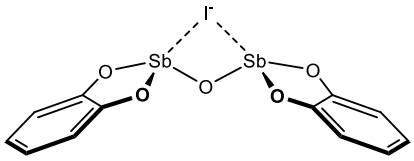
Table S54. Cartesian coordinates (in Å) of **1**·Br_t^-



Atom	x	y	z
H	-4.87470358603154	8.52459394124572	-0.24337672562903
H	-6.48556863043967	7.30998414922968	1.22627410772358
H	5.25596584899698	8.16193300380222	1.37140636706187
C	-4.53198675298249	8.01408284352876	0.65272071436892

H	5.81610415367720	10.55623324858920	1.77305727134117
C	-5.42960546763294	7.32932124331399	1.48203527956761
O	-2.24605053403444	8.66050986251980	0.19741455409120
C	4.52401224109958	8.82833487439497	1.81923738751659
C	-3.17223538083762	8.04158045563858	0.97187166377440
C	4.83711138998340	10.17020220327580	2.04376792082164
H	2.99905814164020	7.29423042141520	2.00273573177449
C	3.26163243588830	8.33551504475221	2.17069908758902
C	-4.97338385949284	6.67698183678238	2.62918342280473
C	3.89254216405925	11.02997982978020	2.61646939085964
H	4.12180460059942	12.07773927666550	2.79045719542623
H	-5.67149233072436	6.14807668158081	3.27217236295284
Sb	-0.38074853355432	8.68183090805219	1.12345331058159
C	-2.71294532258237	7.38418562433855	2.14158837501653
C	2.31504405110668	9.18233268578375	2.75355156803051
C	-3.61250188007228	6.70269225535922	2.96163246725445
C	2.63011673377134	10.54661828528280	2.97113118922882
O	-0.86675820531600	10.37393514148080	2.07485601483211
O	-1.38061308620083	7.44493903670213	2.42313188996048
O	1.07222256093239	8.75934797980023	3.10592519262610
O	1.69627897146328	11.36311108852450	3.52558804876477
H	-3.24241796005175	6.20357194665606	3.85316133137509
Sb	-0.13806424879512	10.52087630800760	3.92147098944888
Br	-1.07129751446942	13.10716982349660	4.04287389083578

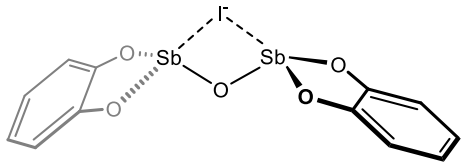
Table S55. Cartesian coordinates (in Å) of cis-**1**·I_b^-



Atom	x	y	z
Sb	-2.05993832913412	6.70314574899646	4.92824142320415
Sb	-1.83018082284846	5.64905799557813	1.49553306799769
O	-2.46200358262001	6.78926720815683	2.98880994304977
O	-0.08592750658484	7.20461160292416	4.82308431953858
O	-2.25152743216810	8.76529605207796	5.05103694758032
O	-1.93750141897351	7.27761132597033	0.21446591445375
O	0.13196740913720	6.20487134004508	1.53516371075322
C	0.08064703589551	8.54963606197706	4.66033526315560
C	1.32601989653959	9.11395741253414	4.39162129613757
C	1.43888822924979	10.50008567807220	4.23649555998146
C	0.31205730031898	11.31611160195520	4.35069108522416

C	-0.94299301225905	10.75603427604090	4.62137862873670
C	-1.06443333222076	9.37408981103089	4.77788740043099
C	0.32334193548419	7.41211158945974	0.92742443202446
C	1.54675594804751	8.07770927476907	0.97268598312516
C	1.68755741035821	9.31201066012760	0.32871505500892
C	0.61054015643745	9.87576970647379	-0.35750223116737
C	-0.62198613389078	9.21205354800238	-0.40819378352786
C	-0.77116404737305	7.98025111479266	0.23186492432006
H	2.19014290084482	8.46459833435934	4.28828567476039
H	2.40885417902566	10.93541115526930	4.01270663684918
H	0.40136606807304	12.39178742184290	4.22419393430006
H	-1.82891294955120	11.37936021047100	4.70915525520361
H	2.37024096607619	7.63445553961706	1.52450783089928
H	2.63871905170795	9.83476378679427	0.37784977228444
H	0.72077740438243	10.83690926205090	-0.85253427984537
H	-1.46933211985952	9.64100044363982	-0.93649706321179
I	-0.90367220409515	3.61411683697040	4.06845329873292

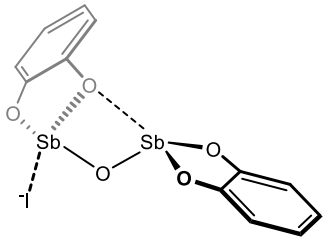
Table S56. Cartesian coordinates (in Å) of trans-**1**·I_b^-



Atom	x	y	z
Sb	-2.65877231483369	8.92356761054319	3.46518460804442
Sb	-0.29101658945971	6.83328802854487	1.87782078786590
O	-1.12951484895449	8.59318464216374	2.24316752868949
O	-1.70389726043701	8.22413460050151	5.13895819101041
O	-1.81256582350037	10.70277717066680	4.12460169755088
O	-1.20407240613777	6.56274787532235	0.06591605999398
O	1.13220084132242	7.72724377467404	0.66830788713421
C	-0.89178796016642	9.17279166726095	5.68717142758884
C	-0.03393358940323	8.88810108314981	6.74995981741275
C	0.77674562658564	9.90150349097221	7.27738222823402
C	0.72924913614803	11.19105780849410	6.74361961429278
C	-0.12974314662563	11.48426780252940	5.67681713857546
C	-0.94381518795161	10.48130346512080	5.14587486681428
C	0.69350875169639	7.82922977390649	-0.61468270573067
C	1.41159241416225	8.49997705231909	-1.60680888584639
C	0.90801553581713	8.55351056016157	-2.91267655653257
C	-0.30767922387565	7.94199075952803	-3.22602101591875

C	-1.03606617778614	7.26877287758746	-2.23675416190908
C	-0.54021356695741	7.21012703419890	-0.93392927575443
H	-0.00529557736231	7.87928323375727	7.15244448712457
H	1.44588101207302	9.67545717397182	8.10300635961047
H	1.36064856129722	11.97513144812180	7.15270271663507
H	-0.17647911183762	12.48365789367490	5.25276558628212
H	2.35555817923201	8.97272219256870	-1.34954882161347
H	1.47045980051176	9.07653675192383	-3.68131301077036
H	-0.69695492119443	7.98628294541168	-4.23942083788723
H	-1.98402883604144	6.78954697103320	-2.46541683123773
I	-3.25862231632085	5.63603131189099	3.06799010034105

Table S57. Cartesian coordinates (in Å) of **1**·I_t^-

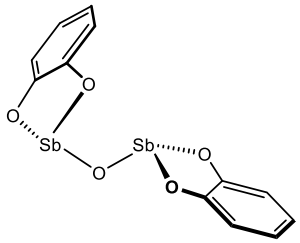


Atom	x	y	z
H	-5.31757009544241	8.47006231258301	-0.03597403554285
H	-6.49620649404966	7.86962768826310	2.07891171373585
H	5.87701411341305	8.49073513145560	2.47161104505167
C	-4.76007725504737	8.13162647248814	0.83302167079396
H	5.82987910071395	10.97474010846500	2.63041298946717
C	-5.41363133241235	7.79486640769738	2.02412823929624
O	-2.70806252993307	8.35625901440923	-0.39530757770443
C	4.93022147809500	9.01459972914152	2.56915170469417
C	-3.36849867564484	8.03688325496710	0.74898452690467
C	4.90328398665280	10.40789820059440	2.65720629217605
H	3.74104376383441	7.19742913100206	2.52996817725225
C	3.73659870827063	8.28168498398517	2.60159099976349
C	-4.68180713595476	7.36880977827235	3.13426230459886
C	3.68374021813686	11.08585180301320	2.78002469487214
H	3.64898493175948	12.16966510852070	2.85069534685717
H	-5.18937859411961	7.11166410877849	4.05973805385612
Sb	-0.65793694424892	8.24045093536462	-0.31266974892576
C	-2.62620707872713	7.59647976016658	1.87175174198159
C	2.51810827860203	8.95020435801701	2.72174369750917
C	-3.28719101739025	7.27236850316567	3.05925494368240
C	2.48844920101067	10.36430490473190	2.81853845908472
O	-0.24720644079801	9.86332665210180	0.76032776837124

O	-1.27272255298125	7.53520290762727	1.74706776825760
O	1.32776434509967	8.28566342463650	2.75181816836344
O	1.27560427581112	10.95707215165100	2.96606579009967
H	-2.70044775539700	6.94394631583105	3.91321473916950
I	-0.67415777657638	9.95257253098393	-2.82264218104672
Sb	-0.26390072267666	9.58134432208594	2.74168270738058

S4.4 Structures with solvation model (CPCM) in chloroform

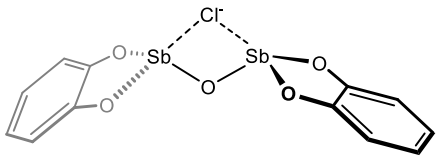
Table S58. Cartesian coordinates (in Å) of **1**.



Atom	x	y	z
Sb	-2.30299000552570	6.94237335207972	3.47957138631083
Sb	-1.66937505011785	5.48593828237684	0.25973125638774
O	-1.41957193992962	6.81929091661357	1.68377700878021
O	-1.01456185753826	5.69313954374613	4.42494117213155
O	-0.97748920084701	8.35317239320477	4.10320296200767
O	-1.91976479519863	3.94468170486590	1.56549066085428
O	-3.70767336386149	5.54671733562756	0.38075373299925
C	0.10936090718217	6.36478740455082	4.82720613329949
C	1.20074833231671	5.71070241740326	5.39698501299700
C	2.31329335904029	6.45749365882390	5.80167371512614
C	2.33269358580268	7.84434350344453	5.63670655595578
C	1.24007427933692	8.50619290792113	5.06464822146169
C	0.12883255475815	7.76778173494773	4.65977786177805
C	-4.09972478609261	4.90183932183432	1.52005109434270
C	-5.37527517351072	5.05141977468210	2.06671437295253
C	-5.69514682018966	4.38643422196601	3.25444323821756
C	-4.74875056817752	3.58456425304616	3.89775224621839
C	-3.46871708416518	3.42547403435829	3.35786987988230
C	-3.14417028122871	4.07163650912947	2.16213422720176
H	1.17038344757423	4.63197756834571	5.51892582672088
H	3.16466419969018	5.94902254827769	6.24484588431305
H	3.19918144023492	8.41874776423150	5.95144245345844
H	1.24133794711425	9.58376488849778	4.92953989414313
H	-6.09580661827217	5.69086651623856	1.56597620603923
H	-6.68487859741722	4.50997311058900	3.68363293779256

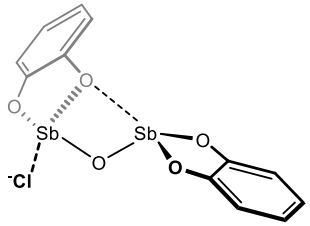
H	-4.99954315534797	3.08618501814661	4.82913836987777
H	-2.72026975563017	2.81102731505089	3.84765268875003

Table S59. Cartesian coordinates (in Å) of trans-**1**·Cl_b^-



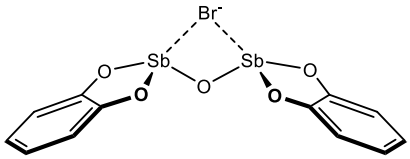
Atom	x	y	z
Sb	-0.17650474812893	2.26321774365746	-1.01281565458229
Sb	-0.40849940222756	-0.83846088796049	-2.61369665241952
O	-1.19872310735243	0.87447346023903	-1.99706873060198
O	0.88683244993617	2.93515940047055	-2.63386459091754
O	-1.49768206468211	3.72715947054446	-1.70063588844815
O	-0.77795404900958	-1.89340565314361	-0.89539282266195
O	-2.31037986305751	-1.56149254760890	-3.06818732713156
C	0.16385713626908	3.80793590594475	-3.39033229094238
C	0.63607595912400	4.29810423978575	-4.60820768546368
C	-0.14676920928945	5.19444502476307	-5.34782594335933
C	-1.39529807819125	5.59716313794657	-4.86989975059774
C	-1.87616275026664	5.10969043699477	-3.64795381047486
C	-1.10242240517296	4.21855478111844	-2.89992474958646
C	-2.86775923473026	-2.18369557816761	-2.00017641207633
C	-4.18362078473245	-2.65283281654869	-1.99687006537028
C	-4.68739739449826	-3.30998260472608	-0.86706272895478
C	-3.88239627265810	-3.49550680970896	0.25847860607056
C	-2.56296946931790	-3.02451519175302	0.26791055054391
C	-2.05393611429257	-2.36885570552531	-0.85355020060872
H	1.60865896970801	3.97276078841476	-4.96754477649627
H	0.22382080637008	5.57184842338541	-6.29704391590649
H	-2.00247775352364	6.29105480846563	-5.44527807821938
H	-2.84632554774432	5.41513075477577	-3.26516703790845
H	-4.79964167812831	-2.50225365955227	-2.87936194892250
H	-5.71113965394659	-3.67454883536187	-0.87228664567543
H	-4.27509600005518	-4.00463561093648	1.13446419394978
H	-1.92463890528732	-3.15872704817826	1.13698222921015
Cl	1.82361716488600	0.18497257266507	-1.06075687244833

Table S60. Cartesian coordinates (in Å) of **1**·Cl_t^-



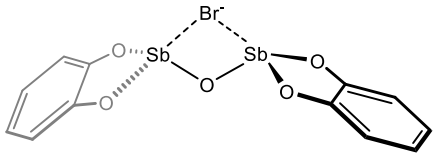
Atom	x	y	z
H	-5.02304029455579	6.76236161849951	0.16196505897241
H	-6.51221788656482	8.64932381979062	0.82749137690273
H	5.34189459978462	9.18887175864691	4.39759361511123
C	-4.67238339672254	7.53075451063723	0.84558188416324
H	6.08519910762106	10.00626640800610	2.16624923279052
C	-5.50096943254519	8.59448940960215	1.22159502510740
O	-2.54894638719876	6.42631197877586	0.98405190628270
C	4.61015570834101	9.42697310669181	3.63040681633559
C	-3.36914559023088	7.44546600049775	1.34417880154577
C	5.02634834641744	9.88454371659087	2.37875293047841
H	2.90541350170579	8.90686434593576	4.87211072443534
C	3.24534097312906	9.26676357403441	3.90466755106670
C	-5.03201147930616	9.57872818196398	2.09326118664197
C	4.08462281741487	10.18774688003060	1.38699786710549
H	4.39585467850899	10.54494405052250	0.40889447497957
H	-5.67373090177790	10.40624160435770	2.38294225600350
Sb	-0.63658932918446	6.45132506254270	1.74404461974556
C	-2.89578027437222	8.43816527728264	2.23928202561482
C	2.30157672014972	9.56495114354381	2.92154910137488
C	-3.72844721701871	9.50186391230725	2.59820444975236
C	2.72078739320015	10.03653542221490	1.65064552581487
O	0.15345372680766	7.92414723447382	0.66422733687032
O	-1.62220380242466	8.31838008530274	2.69513784042348
O	0.96441137472478	9.41890452678512	3.13543389585226
O	1.75740328039725	10.33832031914390	0.74757426537312
H	-3.34533039344963	10.25815817605020	3.27857008364200
Cl	-0.07585938014844	4.81152774420441	-0.12700664155388
Sb	-0.12879946270217	9.74974013156432	1.42645178916766

Table S61. Cartesian coordinates (in Å) of cis-**1**·Br_b^-



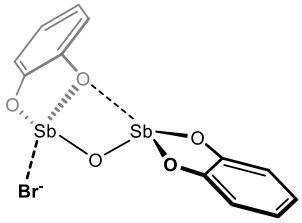
Atom	x	y	z
H	-3.54099171721928	9.58254830180448	4.00887024342937
O	-2.35585120987756	7.23403948392979	4.46784379689338
O	0.42893517311591	6.83273927084054	4.99052765023666
C	-3.00222241623234	9.16664064966993	3.16152241034864
H	2.25104084580350	11.36653277670380	4.37196419605277
O	2.54545778679833	8.74427346513427	4.77913593106472
Sb	-1.02493287282047	5.63756328999359	4.36388629840243
C	-2.34430899732659	7.94374974521211	3.30830652409662
Sb	2.36408243777263	6.68074049117207	4.58145538653411
H	-3.46499005912914	10.79266807634570	1.82577539575515
C	2.14635448829043	10.74933688380850	3.48351218581482
C	-2.95567815457979	9.83855648744015	1.93309276442960
C	2.27698773029644	9.36395027032688	3.59923273159650
Br	1.41734559113405	3.92837072434539	3.53010949188133
C	-1.63372034544144	7.39291121116669	2.21320955738557
O	-1.00694206568538	6.19635476980869	2.40088869357022
H	1.77368367022330	12.39922590450770	2.14899812429953
C	1.87943716064612	11.32075576951740	2.23264063005887
C	2.13589298679737	8.54690727894433	2.45027826152355
C	-2.25441511092549	9.29236358259869	0.85685967721374
O	2.27074001428671	7.19916254344518	2.60958245475147
C	-1.59187239136181	8.06726087614230	0.99442716063992
H	-2.20771257424892	9.82176492753181	-0.09087379601889
C	1.74170055110081	10.51229224985170	1.10310497027649
C	1.86998089814585	9.12261577576181	1.20944412338926
H	-1.02756851672313	7.63773390465495	0.17206704591394
H	1.52036207926319	10.95625454874400	0.13636165976872
H	1.74750901789670	8.47877174059718	0.34363543069150

Table S62. Cartesian coordinates (in Å) of trans-**1**·Br_b^-



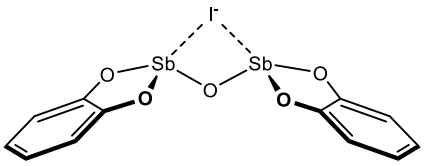
Atom	x	y	z
Sb	-0.15048283543367	2.25845528397671	-1.01455381637706
Sb	-0.37961232752215	-0.87514373717508	-2.62181725438400
O	-1.14105486202991	0.84841804092534	-1.99967585167433
O	0.90208664480430	2.95062825000393	-2.63192211247097
O	-1.49778343664468	3.69264498373313	-1.69816470212136
O	-0.76662769883775	-1.92249574134988	-0.90323551955125
O	-2.29068888025881	-1.56364292026876	-3.07707174571286
C	0.16072843851671	3.80730330141051	-3.38982361800381
C	0.62203348417171	4.30552378473881	-4.60856841682163
C	-0.17902959499755	5.18667644484118	-5.34659680379913
C	-1.43415138175761	5.56613520220347	-4.86660857125083
C	-1.90413117932943	5.07000588743962	-3.64391262553198
C	-1.11206683184191	4.19347089503868	-2.89827424021739
C	-2.86149803008145	-2.17202835053229	-2.00724583598762
C	-4.18668660867102	-2.61386524273895	-2.00463955806847
C	-4.70573040332916	-3.25429201665627	-0.87219547944106
C	-3.90662784328191	-3.45034108096057	0.25593477823598
C	-2.57757377663637	-3.00732890827052	0.26543717340425
C	-2.05334750027028	-2.36894128166205	-0.85890426665245
H	1.60013283007726	3.99877785605644	-4.96906746620814
H	0.18271183449498	5.57097604313318	-6.29642082376762
H	-2.05518453137752	6.24824521075129	-5.44117094679267
H	-2.87931669271038	5.35682244405567	-3.25966716651193
H	-4.79798362912200	-2.45449944944562	-2.88880919447452
H	-5.73696398078536	-3.59700661547407	-0.87715170208157
H	-4.31159534530975	-3.94602172506899	1.13400812591704
H	-1.94355738284468	-3.15031899199383	1.13618453394241
Br	2.05906952100841	0.11460043328895	-1.00913589359704

Table S63. Cartesian coordinates (in Å) of **1**·Br_t^-



Atom	x	y	z
H	-4.87671364613454	8.51724800930312	-0.24423911179939
H	-6.48339848877426	7.29053224985712	1.22037188141421
H	5.24929355635123	8.15319288311493	1.37054898251326
C	-4.53297456614501	8.00757990758513	0.65192962395767
H	5.82096436222708	10.54365994867210	1.77913884295829
C	-5.42803948596239	7.31621226380395	1.47840795046670
O	-2.25044867727616	8.66782838743501	0.20215586177226
C	4.51977451398132	8.82249905077355	1.81819582209614
C	-3.17390432617762	8.04376702477093	0.97355512104501
C	4.83930012489849	10.16204511328770	2.04674571037726
H	2.98629279778931	7.29619426819537	1.99561141040914
C	3.25389737454791	8.33589988448936	2.16565991704469
C	-4.97035031400925	6.66577703143443	2.62591412456076
C	3.89792795561846	11.02518679041090	2.61943586190728
H	4.13164855580723	12.07142059881080	2.79646583939930
H	-5.66653552347442	6.13187507666844	3.26697500475879
Sb	-0.38485709010503	8.69823408417136	1.13172801827641
C	-2.71329687348500	7.38829284998641	2.14425269407444
C	2.30990851735281	9.18589595611063	2.74836228051136
C	-3.61039966631819	6.70024750884479	2.96136918669666
C	2.63180682654012	10.54826003437030	2.97015076660498
O	-0.87212359279892	10.39117804642300	2.07785010955051
O	-1.38267490619380	7.45729310914373	2.42913587533425
O	1.06505570093257	8.76847072727223	3.09737586633533
O	1.70303208923688	11.36897960606710	3.52410483886117
H	-3.23873102344736	6.20311031030931	3.85334983752889
Sb	-0.13984941020313	10.54506860168710	3.92123418766561
Br	-1.05308478477830	13.12396067700070	4.04870349567904

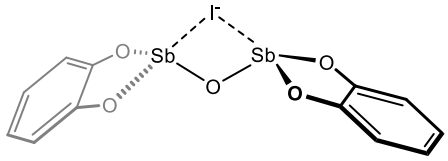
Table S64. Cartesian coordinates (in Å) of cis-**1**·I_b^-



Atom	x	y	z
Sb	-2.05742780195231	6.70317124431890	4.92589858134028
Sb	-1.82726297942717	5.64983716798804	1.49755101665636
O	-2.46194948804290	6.79226825895397	2.98744529567926
O	-0.08468315958963	7.20594278977634	4.82263510963059
O	-2.25044334078327	8.76505127794418	5.05682276086134
O	-1.93539957005471	7.27293335444024	0.20919797630458

O	0.13378250637084	6.20637255291281	1.53487680291433
C	0.08112449092920	8.55126009517700	4.66432527981411
C	1.32618309769731	9.11672777481660	4.39677405124741
C	1.43869721787699	10.50335978095890	4.24620132837054
C	0.31175871219984	11.31871101655220	4.36367976117323
C	-0.94297287530069	10.75748910339510	4.63297636258104
C	-1.06434267469169	9.37505884107898	4.78511258687056
C	0.32437165034737	7.41143934934598	0.92325276591895
C	1.54721175251978	8.07811868245643	0.96715008012253
C	1.68758880988509	9.31031990899157	0.31911473516951
C	0.61063228708667	9.87096159814807	-0.36967719988068
C	-0.62131373362913	9.20626564808897	-0.41889211953275
C	-0.77030094003427	7.97645358151143	0.22500361253834
H	2.18988127103404	8.46729815450795	4.29067043541065
H	2.40841362295575	10.93965631789530	4.02299793637248
H	0.40074861661648	12.39480111827870	4.24014947439267
H	-1.82932894213874	11.37988581379720	4.72251809061051
H	2.37015491355584	7.63689006324972	1.52133690061017
H	2.63825598426123	9.83413441125191	0.36739842368984
H	0.72041810860122	10.83083026659300	-0.86736957480754
H	-1.46907630287883	9.63284677489002	-0.94838179254247
I	-0.91641823341434	3.61800005268022	4.06709131848421

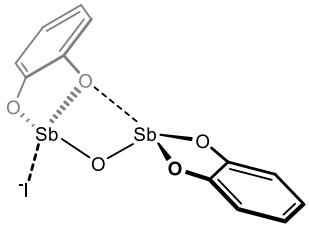
Table S65. Cartesian coordinates (in Å) of trans-**1**·I_b^-



Atom	x	y	z
Sb	-2.86064174266817	8.95920154518939	3.56835863236466
Sb	-0.45220119034444	6.96323263261648	1.96748950696696
O	-1.42393034458041	8.67345426514424	2.22805116323837
O	-1.76421847333287	8.21231583478189	5.13284954828733
O	-1.97148969247195	10.72311632278540	4.21722790524472
O	-1.22119380761092	6.57367565923585	0.11279798505938
O	0.98818471966011	7.91002889528402	0.82012081140043
C	-0.90185803761908	9.14517379508684	5.62961263305102
C	0.05522853308144	8.82807697865251	6.59369364782571
C	0.91607958336943	9.82507063967524	7.07038461738713
C	0.81863311502227	11.13064859605830	6.58472142598222
C	-0.14059322110056	11.45642865464740	5.61758294680156
C	-1.00581843061729	10.47048966095410	5.13802346949952

C	0.63660797111902	7.93245867007452	-0.49247184065418
C	1.38014855660464	8.60817872172410	-1.46209683868734
C	0.96898486619924	8.57533678199040	-2.80061370275354
C	-0.18087731572454	7.87374081504598	-3.16880462954288
C	-0.93499919665343	7.19553069917535	-2.20251825993173
C	-0.53068390916827	7.22203629923739	-0.86746694209219
H	0.12027585817221	7.80697712789452	6.95933079146544
H	1.66284767700757	9.57384312123603	7.81848113591752
H	1.48952948434415	11.90179764623550	6.95346960378523
H	-0.22633883677533	12.46824394376490	5.23071359746441
H	2.27238814944368	9.15086867000074	-1.16189903837590
H	1.55135300973662	9.10209722752069	-3.55171518347562
H	-0.49852864932398	7.85115972330786	-4.20762971059010
H	-1.83290417433001	6.64686959042792	-2.47307312594091
I	-3.43458350143906	5.68417448225194	3.07249885030283

Table S66. Cartesian coordinates (in Å) of **1**·I_t^-



Atom	x	y	z
H	-5.32382020220159	8.46000733482497	-0.03254856214068
H	-6.49515017901191	7.85773415764198	2.08620475430699
H	5.87728043641717	8.48463318144388	2.48829364464706
C	-4.76308018463306	8.12565491456910	0.83591475393666
H	5.83400976310712	10.96858640611990	2.64851202784233
C	-5.41229227819086	7.78806739571085	2.02906538869247
O	-2.71708643769830	8.35833857585586	-0.39831478693371
C	4.93091827715063	9.01033040550908	2.58054682689924
C	-3.37111255206375	8.03789591338152	0.74801508778163
C	4.90611218632663	10.40352754964930	2.66946922926404
H	3.73779404884435	7.19575046469453	2.53223502882525
C	3.73557152478635	8.27994065428843	2.60497634213489
C	-4.67595603481154	7.36776740500969	3.13828302823324
C	3.68720010230340	11.08373977204370	2.78510735541569
H	3.65375073141248	12.16757873504320	2.85583592677871
H	-5.18009525571730	7.10969734643794	4.06544520139448
Sb	-0.66527774978873	8.25346856087774	-0.33176084086897
C	-2.62388905807466	7.60322886312017	1.87031588024940

C	2.51765229261720	8.95059485880616	2.71798328690216
C	-3.28105624796613	7.27826590910043	3.05980038984542
C	2.48997000438302	10.36496230966500	2.81585994083587
O	-0.24772128885822	9.87175178835780	0.74456717803580
O	-1.27125530849015	7.54785069470095	1.74242784245534
O	1.32630019335050	8.28849421948833	2.73992839376997
O	1.27808117199518	10.95912451015180	2.95672609820183
H	-2.69041750561615	6.95367993460611	3.91259036771902
I	-0.69661830521925	9.94897144940945	-2.83468147357161
Sb	-0.26412214435240	9.58569668949197	2.72378168934746

S5 References

(1) Qiu, J.; Unruh, D. K.; Cozzolino, A. F. *J. Phys. Chem. A* **2016**, *120* (46), 9257–9269.
(2) Willcott, M. R. *J. Am. Chem. Soc.* **2009**, *131* (36), 13180–13180.
(3) *Maple*; Maplesoft, a division of Waterloo Maple Inc.: Waterloo, Ontario, 2016.
(4) R Core Team. *R: A Language and Environment for Statistical Computing*; R Foundation for Statistical Computing: Vienna, Austria, 2017.
(5) John C. Nash. *J. Stat. Softw.* **2011**, *43* (9), 1–14.
(6) John C. Nash. *J. Stat. Softw.* **2014**, *40* (2), 1–14.
(7) Karline Soetaert. *rootSolve: Nonlinear root finding, equilibrium and steady-state analysis of ordinary differential equations.*; R-package.
(8) Soetaert, K.; Herman, P. M. J. *A practical guide to ecological modelling: using R as a simulation platform*; Springer: Dordrecht, 2009.
(9) Thordarson, P. *Chem Soc Rev* **2011**, *40* (3), 1305–1323.
(10) Biros, S. M.; Bridgewater, B. M.; Villeges-Estrada, A.; Tanski, J. M.; Parkin, G. *Inorg. Chem.* **2002**, *41* (15), 4051–4057.
(11) Neese, F. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2* (1), 73–78.
(12) van Lenthe, E.; Baerends Evert, J.; Snijders, J. G. *J Chem Phys* **1993**, *99*, 4597–4610.
(13) Heully, J. L.; Lindgren, I.; Lindroth, E.; Lundqvist, S.; Maartensson-Pendrill, A. M. *J Phys B Mol Phys* **1986**, *19*, 2799–2815.
(14) Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, *32* (7), 1456–1465.
(15) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7* (18), 3297–3305.
(16) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97* (4), 2571–2577.
(17) Weigend, F. *Phys. Chem. Chem. Phys.* **2006**, *8* (9), 1057–1065.
(18) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140* (4A), A1133–A1138.
(19) Kendall, R. A.; Früchtl, H. A. *Theor. Chem. Acc.* **1997**, *97* (1–4), 158–163.
(20) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19* (4), 553–566.
(21) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102* (11), 1995–2001.