Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Bismuth in Dynamic Covalent Chemistry: Access to a Bowl-Type Macrocycle and a Barrel-Type Heptanuclear Complex Cation

*A. Stoy, M. Jürgensen, C. Millidoni, C. Berthold, J. Ramler, S. Martínez, M. R. Buchner, C. Lichtenberg**

Supporting Information

Table of Contents

Experimental

General considerations. All syntheses were performed under an inert argon atmosphere using common Schlenk line techniques or in a glovebox (GS Systems). The synthesized compounds were stored and manipulated in a glovebox. Deuterated solvents were degassed *via* three *'freeze-pump-thaw*' cycles and stored over activated molecular sieves (3 or 4 Å) under argon atmosphere. All other solvents were distilled from appropriate drying agents and stored under an argon atmosphere over activated molecular sieves.[35] All other substances were purchased from common chemical suppliers and used without further purification (except for $BiCl_3$ that was sublimed prior to use).

NMR spectra were recorded on *Bruker* instruments operating at 300, 400 or 500 MHz with respect to ^1H. ^1H and ^{13}C NMR chemical shifts are reported relative to $SiMe_4$ using the residual ^1H and ^{13}C chemical shifts of the solvent as a secondary standard. ^{11}B, ^{19}F, and ^{27}Al NMR chemical shifts are reported relative to $BF_3 \cdot OEt_2$, $CFCl_3$, and $Al(NO_3)_3$ as external standards. NMR spectra were recorded at ambient temperature (typically 23 °C), if not otherwise noted.

Elemental analysis was performed on a *vario MICRO cube* from *Elementar Analysesysteme GmbH*. The sample preparation was executed in a glovebox.

Single-crystals suitable for X-ray diffraction analysis were coated with poly*iso*butylene or perfluorinated polyether oil in a glovebox (GS Systems), transferred to a nylon loop and then to the goniometer of a diffractometer equipped with a molybdenum X-ray tube (Kα λ = 0.71073 Å). The data obtained were integrated with SAINT and a semi-empirical absorption correction from equivalents with SADABS was applied. The structure was solved and refined using the Bruker SHELX 2014 software package.[36] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined isotropically on calculated positions by using a riding model with their U_{iso} values constrained to 1.5 U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 for all other atoms. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers 2257150-2257152.[37] These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

The **UV/vis spectrum** was recorded on an *Analytik Jena* SPECORD S 600 UV/vis spectrometer in a 1 cm quartz cuvette at room temperature with background substraction.

The following compounds were synthesized according to literature:
$[BiMe_2(SbF_6)]$,[21] 2,7-di-*tert*-butyl-4,5-dibromo-9,9-dimethylthioxanthene (Br_2TX),[20] $TlBAr^F$ (BAr^F = $B(3,5\text{-}(CF_3)_2C_6H_3)_4$).[38]
$BiMe_2Cl$ was synthesized by mixing two equivalents of $BiMe_3$[14] (10 g solution in Et_2O, 47%(w), 4.7 g reactant, 18.5 mmol) with one equivalent of freshly sublimed $BiCl_3$ (2.92 g, 9.25 mmol) in DCM (25 mL) at room temperature, stirring overnight and removing all volatiles resulting in a colorless powder in quantitative yields.

In order to identify the individual hydrogen and carbon atoms in the TX-moieties the following naming scheme was used (see **Figure S1**).

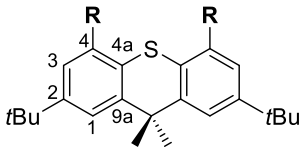


Figure S1. Naming scheme for the used TX-moieties. R = Bi-containing moiety.

Synthetic procedures and characterization of compounds

$(BiMe_2)_2TX$ (1)

a) Synthesis starting from Br_2TX

A 2.5 M *n*-BuLi solution in *n*-hexane (9.95 mmol, 4.0 mL) was added dropwise to a solution of 2,7-di-*tert*-butyl-4,5-dibromo-9,9-dimethylthioxanthene (2.41 g, 4.86 mmol) in toluene (80 mL) cooled to −78 °C and the colorless suspension was allowed to warm to room temperature overnight. The now yellow solution was again cooled to −78 °C and added dropwise to a suspension of $BiMe_2Cl$ (2.67 g, 9.71 mmol) in Et_2O (80 mL) cooled to −78 °C. The resulted colorless suspension was stirred at −78 °C for 1.5 h and then very slowly warmed to room temperature overnight. The solvent was removed under fine vacuum (ca. 10^{-3} mbar; not to dryness), the resulting oil extracted with benzene (3 × 10 mL), and subsequently, all volatile components of the filtrate removed under reduced pressure. Suitable single-crystals for sc-XRD were obtained by slow evaporation of a saturated Et_2O solution of **1** at –30 °C in the glovebox.

Yield: 3.9 g (4.79 mmol, 96%) of a colorless powder.

^{1}H NMR (400.6 MHz, CD_2Cl_2): δ = 1.32 (s, 12H, Bi(CH_3)$_2$), 1.34 (s, 18H, C(CH_3)$_3$), 1.72 (s, 6H, C(CH_3)$_2$), 7.47 (d, 2H, $^4J_{HH}$ = 2.0 Hz, 1-H), 7.72 (d, 2H, $^4J_{HH}$ = 2.0 Hz, 3-H) ppm.

^{13}C{^{1}H} NMR (100.7 MHz, CD_2Cl_2): δ = 3.6 (br.s, Bi(*C*H$_3$)$_2$), 25.1 (C(*C*H$_3$)$_2$), 31.7 (s, C(*C*H$_3$)$_3$), 35.5 (s, *C*(CH$_3$)$_3$), 42.6 (s, *C*(CH$_3$)$_2$), 121.6 (s, 1-C), 130.9 (s, 3-C), 139.0 (s, 2-C), 139.7 (br. s, 4-C), 142.5 (s, 9a-C), 150.8 (s, 4a-C) ppm.

LIFDI-HRMS: Positive mode; calculated (%) for $[C_{27}H_{40}Bi_2S]^+$: m/z = 814.2453; Found: m/z = 814.2438 (5); calculated (%) for $[C_{26}H_{37}Bi_2S]^+$, m/z = 799.2218; Found: m/z = 799.2207 (100).

Elemental Analysis: Calculated (%) for $C_{27}H_{40}Bi_2S$ (814.64 g/mol): C 39.81, H 4.95, S 3.94; Found: C 39.92, H 4.92, S 3.89.

b) Alternative Synthesis from $(BiMe)_2TX_2$ (**3**)

To a solution of $(BiMe)_2TX_2$ (**3**) (20 mg, 17.8 µmol) in 0.6 mL C_6D_6 was added a solution of $BiMe_3$ (92 mg, 364 µmol) in 0.1 mL Et_2O. The colorless solution was stored overnight at room temperature and subsequently all volatiles removed under reduced pressure.

NMR spectroscopic analyses indicated that the residue consist of **1** (85%) and small amounts (15%) of remaining starting material **3**. A higher excess of $BiMe_3$ led to minor increase of the yield. The obtained analytical data is identical to the above discussed values.

c) Spectra of compound **1** in presence of Et_2O

Compound **1** (15.0 mg, 18.4 µmol, 1.00 equiv.) was dissolved in C_6D_6 (0.6 mL), Et_2O (122 mg, 1.66 mmol, 90.0 equiv.) was added, and the ^{1}H NMR spectrum of the mixture was collected.

$(BiMe_2)_2TX$ (**1**) + 90 equiv. Et_2O: **^{1}H NMR** (400.6 MHz, C_6D_6): δ = 1.25 (s, 12H, Bi(CH_3)$_2$), 1.33 (s, 18H, C(CH_3)$_3$), 1.73 (s, 6H, C(CH_3)$_2$), 7.53 (br s, 2H), 7.84 (br s, 2H) ppm.

$[(BiMe)_2TX_2Tl][BAr^F]$ (2)

a) Synthesis starting from $(BiMe_2)_2TX$ (**1**)

A solution of $(BiMe_2)_2TX$ (**1**) (200 mg, 245.5 µmol) in DFB (2 mL) was added to a solution of $TlBAr^F$ (131 mg, 122.8 µmol) in DFB (2 mL). The resulting brown reaction mixture was stirred at room temperature for 20 h and then filtered. The product could be precipitated by adding 45 mL of *n*-pentane and then storing at −30 °C. The *n*-pentane solution was removed and the solid was washed with *n*-pentane (3 x 3.0 mL). A single-crystalline solid was obtained by diffusing *n*-pentane (0.1 mL) into DFB (0.6 mL) at −30 °C. The isolated crystalline solid was washed with *n*-pentane (3 x 0.2 mL) and dried in fine vacuum (ca. 10^{-3} mbar).

Yield: 180 mg (82.2 µmol, 67%) of a beige-brown powder.

^{1}H NMR (500.13 MHz, CD_2Cl_2): δ = 1.30 (s, 36H, C(CH_3)$_3$), 1.41 (s, 6H, 2 x C(CH_3)^a), 1.70 (s, 6H, BiCH_3), 1.93 (s, 6H, 2 x C(CH_3)^b), 7.54 (d, 4H, $^4J_{HH}$ = 1.9 Hz, 1-H), 7.56 (br.s, 4H, 4-$C_6H_3(CF_3)_2$), 7.71 (br.s, 8H, 2,6-$C_6H_3(CF_3)_2$), 8.12 (d, 4H, $^4J_{HH}$ = 1.9 Hz, 3-H) ppm.
^{11}B NMR (96.3 MHz, CD_2Cl_2): δ = –6.6 (s) ppm.
^{13}C{^{1}H} NMR (125.76 MHz, CD_2Cl_2): δ = 20.2 (s, BiCH_3), 24.6 (s, 2 x C(CH_3)^a), 25.3 (s, 2 x C(CH_3)^b), 31.7 (s, C(CH_3)$_3$), 35.9 (s, C(CH$_3$)$_3$), 43.1 (s, C(CH$_3$)$_2$), 117.8-118.0 (m, 4-$C_6H_3(CF_3)_2$), 123.7 (s, 1-C), 123.9 (m, 1-$C_6H_3(CF_3)_2$), 126.1 (s, 3-$C_6H_3(CF_3)$), 129.1-129.2 (m, 3-C), 129.4-129.5 (m, s, 2-$C_6H_3(CF_3)_2$), 131.9 (s, 4a-C), 135.2 (s, 9a-C), 144.0 (s, 4-C), 154.4 (s, 2-C), 161.6 (q, $C_6H_3(CF_3)_2$), 162.0 (q, $C_6H_3(CF_3)_2$), 162.4 (q, $C_6H_3(CF_3)_2$), 161.8 (q, $C_6H_3(CF_3)_2$) ppm.
^{19}F NMR (282.5 MHz, CD_2Cl_2): δ = –62.26 (s) ppm.
LIFDI-HRMS: Positive mode; calculated (%) for $[C_{48}H_{62}Bi_2S_2]^+$: m/z = 1120.3895; Found: m/z = 1120.3876 (100).
Elemental Analysis: Calculated (%) for $C_{92}H_{82}BBi_2F_{28}S_2Tl$ (2416.89 g/mol; **2** + 2 $C_6H_4F_2$): C 45.72, H 3.42; Found: C 45.41, H 3.435.

b) Alternative starting from $(BiMe)_2TX_2$ (**3**)
$(BiMe)_2TX_2$ (**3**) (25 mg, 22.3 µmol) and $TlBAr^F$ (23.8 mg, 22.3 µmol) were dissolved in DFB (2 mL) at room temperature, stirred for 15 min and all volatiles removed under reduced pressure. The obtained orange oil was washed with *n*-pentane (2 x 3.0 mL) and the residue dried *in vacuo*.
Yield: 27 mg (12.3 µmol, 55%) of a beige brown powder.
The obtained analytical data is identical to the values discussed above.

$(BiMe)_2TX_2$ (3)
a) Synthesis starting from $[(BiMe)_2TX_2Tl][BAr^F]$ (**2**)
$[(BiMe)_2TX_2Tl][BAr^F]$ (130 mg, 59.40 µmol) was synthesized, subsequently washed with MeCN (2 x 2.0 mL) and the residue dried under vacuum.
Yield: 61 mg (54.41 µmol, 92%) as an off-white powder.

^{1}H NMR (400 MHz, C_6D_6): δ = 1.30 (s, 6H, BiCH_3), 1.34 (s, 36H, C(CH_3)$_3$), 1.59 (s, 6H, 2 x C(CH_3)^a), 1.64 (s, 6H, 2 x C(CH_3)^b), 7.31 (d, 4H, $^4J_{HH}$ = 1.9 Hz, 1-H), 8.20 (d, 4H, $^4J_{HH}$ = 1.9 Hz, 3-H) ppm.
^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ = 15.9 (s, BiCH_3), 25.1 (s, 2 x C(CH_3)^a), 25.4 (s, 2 x C(CH_3)^b), 31.8 (s, C(CH_3)$_3$), 35.4 (s, C(CH$_3$)$_3$), 42.7 (s, C(CH$_3$)$_2$), 121.4 (s, 1-C), 130.0 (s, 3-C), 139.0 (s, 4a-C), 142.5 (s, 9a-C), 147.5 (s, 4-C), 150.6 (s, 2-C) ppm.
LIFDI-HRMS: Positive mode; calculated (%) for $[C_{48}H_{62}Bi_2S_2]^+$, m/z = 1120.39006; Found: m/z = 1120.39094 (100).
Elemental Analysis: Calculated (%) for $C_{54}H_{68}Bi_2S_2$ (1199.22 g/mol; **3** + C_6H_6): C 54.08, H 5.72, S 5.35; Found: C 53.77, H 5.606, S 5.283.

b) Alternative synthesis starting from $(BiMe_2)_2TX$ (**1**)
$(BiMe_2)_2TX$ (**1**) (30 mg, 36.8 µmol) was dissolved in 0.4 mL C_6D_6 and a solution of $[BiMe_2(SbF_6)]$ (175 µg, 368 nmol) in 0.2 mL C_6D_6 added dropwise at room temperature. The almost colorless reaction mixture was stored for 3 d and analyzed by ^{1}H NMR spectroscopy.
Spectroscopic Yield: 42% by ^{1}H NMR spectroscopy with approx. 7% of starting material left and numerous side products. Larger amounts of $[BiMe_2(SbF_6)]$ did not lead to a significant increase of the yield. The NMR spectroscopic data obtained in these experiments is, aside from the unidentified side products, identical to that of analytically pure compound **3**.

c) Spectra of compound **3** in presence of Et_2O
Compound **3** (10.1 mg, 9.2 µmol, 1.00 equiv.) was dissolved in C_6D_6 (0.6 mL), Et_2O (61.0 mg, 0.83 mmol, 90.0 equiv.) was added, and the ^{1}H NMR spectrum of the mixture was collected.
$(BiMe)_2TX_2$ (**3**) + 90 equiv. Et_2O: **^{1}H NMR** (400 MHz, C_6D_6): δ = 1.28 (s, 6H, BiCH_3), 1.31 (s, 36H, C(CH_3)$_3$), 1.54 (s, 6H, 2 x C(CH_3)), 1.64 (s, 6H, 2 x C(CH_3)), 7.30 (br s, 4H), 8.15 (br s, 4H) ppm.

$[Bi_7Me_4TX_8][BiMe_2(SbF_6)_2]$ (4-Bi)

a) Synthesis starting from $(BiMe)_2TX_2$ (**3**)

To a solution of $(BiMe)_2TX_2$ (**3**) (200 mg, 178 µmol) dissolved in DCM (2 mL) was added a solution $[BiMe_2][SbF_6]$ (21.2 mg, 44.6 µmol) dissolved in DCM (2 mL) dropwise at rt. During this course, the color of the reaction mixture changed to bright red and was stirred at rt overnight. All volatiles were removed under reduced pressure and the residue extracted with *n*-pentane (5 mL). Within 5 h at rt orange to red micro crystals precipitated out of the *n*-pentane solution, were subsequently filtered off, washed with *n*-pentane (3 x 2 mL) and dried under high vacuum. Single crystals suitable for sc-XRD were obtained by slow evaporation of a saturated solution of **4** in DCM at rt overnight. The amount of bound *n*-pentane molecules *m* in the bulk material ranges from 4 to 7 and must be determined for every batch individually.

Yield (*m* = 7): 65 mg (13.1 µmol, 29%) of bright red micro crystals.[i,iv]

^{1}H NMR (500.13 MHz, CD_2Cl_2): δ = 0.14 (s, 6H, Bi(C*H*$_3$)$_2$), 0.27 (s, 18H, C(C*H*$_3$)$_3$), 0.81 (s, 6H, C*H*$_3$), 0.82 (s, 18H, C(C*H*$_3$)$_2$)), 0.90 (s, 6H, Bi(C*H*$_3$)$_2$), 0.93 (s, 18H, C(C*H*$_3$)$_2$)), 0.98 (s, 18H, C(C*H*$_3$)$_2$)), 1.03 (s, 18H, C(C*H*$_3$)$_2$)), 1.08 (s, 18H, C(C*H*$_3$)$_2$)), 1.10 (s, 18H, C(C*H*$_3$)$_2$)), 1.12 (s, 18H, C(C*H*$_3$)$_2$)), 1.27* (s, 6H, C*H*$_3$), 1.31* (s, 6H, Bi(C*H*$_3$)$_2^{anion}$), 1.51 (s, 6H, C*H*$_3$), 1.63 (s, 6H, C*H*$_3$), 1.81 (s, 6H, C*H*$_3$), 1.90 (s, 6H, C*H*$_3$), 1.91 (s, 6H, C*H*$_3$), 1.98 (s, 6H, C*H*$_3$), 5.81 (d, 2H, $^4J_{HH}$ = 1.93 Hz, C*H*), 7.09 (d, 2H, $^4J_{HH}$ = 1.65 Hz, C*H*), 7.17 (d, 2H, $^4J_{HH}$ = 2.02 Hz, C*H*), 7.25 (d, 2H, $^4J_{HH}$ = 1.56 Hz, C*H*), 7.34 (d, 2H, $^4J_{HH}$ = 1.83 Hz, C*H*), 7.42 (d, 2H, $^4J_{HH}$ = 1.93 Hz, C*H*), 7.43 (d, 2H, $^4J_{HH}$ = 1.93 Hz, C*H*), 7.44 (d, 2H, $^4J_{HH}$ = 1.83 Hz, C*H*), 7.46 (d, 2H, $^4J_{HH}$ = 1.83 Hz, C*H*), 7.47 (d, 2H, $^4J_{HH}$ = 2.11 Hz, C*H*), 7.54 (d, 2H, $^4J_{HH}$ = 1.74 Hz, C*H*), 7.59 (d, 2H, $^4J_{HH}$ = 1.92 Hz, C*H*), 7.71 (dd, 4H, $^4J_{HH}$ = 1.59 Hz, $^5J_{HH}$ = 1.48 Hz, C*H*), 8.05 (d, 2H, $^4J_{HH}$ = 1.83 Hz, C*H*), 8.68 (d, 2H, $^4J_{HH}$ = 1.65 Hz, C*H*) ppm.

^{13}C{^{1}H} NMR[ii] (125.76 MHz, CD_2Cl_2): δ = 2.64 (s, Bi(*C*H$_3$)$_2$), 6.42 (s, Bi(*C*H$_3$)$_2$), 24.08 (s, C(*C*H$_3$)$_2$), 24.36 (s, C(*C*H$_3$)$_2$), 24.88 (s, C(*C*H$_3$)$_2$), 25.52 (s, C(*C*H$_3$)$_2$), 25.63 (s, C(*C*H$_3$)$_2$), 25.90 (s, C(*C*H$_3$)$_2$), 26.10 (s, C(*C*H$_3$)$_2$), 26.17 (s, C(*C*H$_3$)$_2$), 26.22 (s, C(*C*H$_3$)$_2$), 26.24 (s, C(*C*H$_3$)$_2$), 30.77 (s, C(*C*H$_3$)$_3$), 31.21 (s, C(*C*H$_3$)$_3$), 31.23 (s, Bi(*C*H$_3$)$_2^{anion}$), 31.41 (s, C(*C*H$_3$)$_3$), 31.44 (s, C(*C*H$_3$)$_3$), 31.51 (s, C(*C*H$_3$)$_3$), 31.54 (s, C(*C*H$_3$)$_3$), 34.07 (s, *C*(CH$_3$)$_3$), 34.85 (s, *C*(CH$_3$)$_3$), 35.07 (s, *C*(CH$_3$)$_3$), 35.20 (s, *C*(CH$_3$)$_3$), 35.23 (s, *C*(CH$_3$)$_3$), 35.33 (s, *C*(CH$_3$)$_3$), 35.51 (s, *C*(CH$_3$)$_3$), 42.96 (s, *C*(CH$_3$)$_2$), 43.06 (s, *C*(CH$_3$)$_2$), 43.16 (s, *C*(CH$_3$)$_2$), 43.31 (s, *C*(CH$_3$)$_2$), 121.46 (*C*H), 121.49 (*C*H), 121.65 (*C*H), 121.86 (*C*H), 121.99 (*C*H), 122.16 (*C*H), 122.48 (*C*H), 123.29 (*C*H), 123.73 (*C*H), 125.12 (*C*H), 127.21 (*C*H), 128.73 (*C*H), 131.80 (*C*H), 132.17 (*C*H), 133.06 (*C*H), 134.10 (*C*H), 134.29 (*C*H), 134.38 (*C*H), 135.47 (*C*H), 135.54 (s, 4-C$_q$), 137.09 (s, 4-C$_q$), 137.29 (s, 4-C$_q$), 137.78 (s, 4-C$_q$), 138.16 (s, 4-C$_q$), 138.51 (s, 4-C$_q$), 138.55 (s, 4-C$_q$), 138.83 (s, 4-C$_q$), 139.18 (s, 4-C$_q$), 141.75 (s, 9a-C$_q$), 143.56 (s, 9a-C$_q$), 143.75 (s, 9a-C$_q$), 144.01 (s, 9a-C$_q$), 144.24 (s, 9a-C$_q$), 144.37 (s, 9a-C$_q$), 144.76 (s, 9a-C$_q$), 148.15 (s, 9a-C$_q$), 151.31 (s, 2-C$_q$), 151.61 (s, 2-C$_q$), 152.40 (s, 2-C$_q$), 152.43 (s, 2-C$_q$), 152.74 (s, 2-C$_q$), 153.35 (s, 2-C$_q$), 153.54 (s, 2-C$_q$), 155.57 (s, 2-C$_q$), 157.28 (s, 4a-C$_q$), 158.19 (s, 4a-C$_q$), 158.47 (s, 4a-C$_q$), 160.31 (s, 4a-C$_q$), 160.37 (s, 4a-C$_q$), 160.55 (s, 4a-C$_q$), 174.32 (s, 4a-C$_q$) ppm.

^{19}F NMR (282.49 MHz, CD_2Cl_2): δ = −123.47 (br s) ppm.[iii]

ESI-HRMS (DCM): Positive mode; calculated (%) for $[C_{189}H_{241}Bi_7S_8]^{2+}$ ($[Bi_7Me_4TX_8]$ + CH_3 + 2 H^+), m/z = 2115.7645; Found: m/z = 2115.7641 (100).

Elemental Analysis: Calculated (%) for $C_{210}H_{290}Bi_8F_{12}S_8Sb_2$ (5214.45 g/mol; **4-Bi** + 4 C_5H_{12})): C 48.37, H 5.61, S 4.92; Found: C 48.72, H 5.83, S 5.37.[iv]

---

[i] The product contains up to nine *solvent* molecules (as determined by ^{1}H NMR spectroscopy), even after prolonged drying in high vacuum. The number of solvent molecules present in a specific sample has been considered for the determination of the yield. Attempts were made to replace the incorporated *n*-pentane with CD_2Cl_2 but the forcing conditions applied led only to partial decomposition of **4**.

*The signals overlap with the intrinsically bound solvent molecules. The assignment was done by ^{13}C-^{1}H HSQC 2D NMR-spectroscopy.

[ii] In the ^{13}C NMR spectroscopic analysis of compounds **4-Bi** and **4-Al**, chemical shifts are listed with two decimal places in order to indicate that some of the resonances remain distinguishable despite their very similar chemical shifts.

[iii] This weak, broad resonance was tentatively assigned to the $(SbF_6)^-$ moieties in the compound (*cf.* Figure S11 and ref. [39]).

[iv] Compound **4** is susceptible to partial loss of *bound solvent molecules*, when dried in vacuo for prolonged periods of time (> 5 h) or stored at ambient temperature for a longer time (> 2 weeks).

b) Alternative synthesis starting from $(BiMe_2)_2TX$ (**1**) with $[BiMe_2SbF_6]$

To a solution of $(BiMe_2)_2TX$ (**1**) (200 mg, 245.5 µmol) in DCM (3 mL) was added a solution of $[BiMe_2][SbF_6]$ (14.6 mg, 30.7 µmol) in DCM (0.7 mL) at room temperature dropwise within 2 min. Upon addition the colorless solution turned intense red. The reaction mixture was stirred over night at room temperature, subsequently all volatiles removed under reduced pressure and the residue extracted with *n*-pentane (3 x 1 mL). The organic solution was then layered with additional 3 mL of *n*-pentane and stored overnight at room temperature. Within this period, red crystals formed on the vessel walls, that were washed with *n*-pentane (5 x 1 mL) and dried *in vacuo* for a short time (< 1 min). The amount of bound *n*-pentane molecules *m* in the bulk material ranges from 5 to 9 and must be determined for every batch individually.

Yield (*m* = 7): 56 mg (10.7 µmol, 35%) of red crystals.[i,iv]

The NMR spectroscopic data is identical to the values discussed above.

ESI-HRMS (DCM): Positive mode; calculated (%) for $[C_{190}H_{242}Bi_8S_8]^{2+}$ ($M^+ + BiMe_2^+$), m/z = 2226.7586; Found: m/z = 2226.7574 (25).

$[Bi_7Me_4TX_8][AlCl_4]$ (4-Al)

To a solution of $(BiMe_2)_2TX$ (**1**) (800 mg, 982.0 µmol) in DCM (5 mL) was added a suspension of $AlCl_3$ (32.8mg, 245.5 µmol) in DCM (2 mL) at room temperature dropwise within 2 min. Upon addition, the colorless solution gradually turned to an intense red reaction mixture. The mixture was stirred overnight at room temperature. Subsequently all volatiles were removed under reduced pressure, the residue was washed with *n*-pentane (5 x 2 mL), dried *in vacuo*, washed with toluene (3 x 2 mL) and dried *in vacuo*. Single-crystals suitable for sc-XRD precipitated out of the *n*-pentane washing solution within 24 h at room temperature. The amount of bound *n*-pentane (*m*) and/or toluene (*o*) molecules in the bulk material ranges from 0.8 to 9 (pentane) and/or 0 to 2.5 (toluene) and must be determined for every batch individually.

Yield (*m* = 0.8, o = 2.12): 181 mg (41.3 µmol, 33%) of a red to orange micro-crystalline powder.[i,iv]

^{1}H NMR (500.13 MHz, CD_2Cl_2): δ = 0.16 (s, 6H, Bi(C*H*$_3$)$_2$), 0.28 (s, 18H, C(C*H*$_3$)$_3$), 0.82 (s, 6H, C(C*H*$_3$)$_2$)), 0.83 (s, 18H, C(C*H*$_3$)$_2$)), 0.91 (s, 6H, Bi(C*H*$_3$)$_2$), 0.94 (s, 18H, C(C*H*$_3$)$_2$)), 0.99 (s, 18H, C(C*H*$_3$)$_2$)), 1.04 (s, 18H, C(C*H*$_3$)$_2$)), 1.08 (s, 18H, C(C*H*$_3$)$_2$)), 1.11 (s, 18H, C(C*H*$_3$)$_2$)), 1.13 (s, 18H, C(C*H*$_3$)$_2$)), 1.28 (s, 6H, C*H*$_3$), 1.51 (s, 6H, C*H*$_3$), 1.64 (s, 6H, C*H*$_3$), 1.82 (s, 6H, C*H*$_3$), 1.90 (s, 6H, C*H*$_3$), 1.92 (s, 6H, C*H*$_3$), 1.99 (s, 6H, C*H*$_3$), 5.82 (d, 2H, $^4J_{HH}$ = 2.00 Hz, C*H*), 7.09 (d, 2H, $^4J_{HH}$ = 1.80 Hz, C*H*), 7.17 (d, 2H, $^4J_{HH}$ = 1.80 Hz, C*H*), 7.26 (d, 2H, $^4J_{HH}$ = 1.80 Hz, C*H*), 7.35 (d, 2H, $^4J_{HH}$ = 1.95 Hz, C*H*), 7.43 (d, 2H, $^4J_{HH}$ = 1.90 Hz, C*H*), 7.44 (d, 2H, $^4J_{HH}$ = 2.00 Hz, C*H*), 7.45 (d, 2H, $^4J_{HH}$ = 1.90 Hz, C*H*), 7.46 (d, 2H, $^4J_{HH}$ = 1.90 Hz, C*H*), 7.47 (d, 2H, $^4J_{HH}$ = 1.95 Hz, C*H*), 7.55 (d, 2H, $^4J_{HH}$ = 1.80 Hz, C*H*), 7.60 (d, 2H, $^4J_{HH}$ = 2.00 Hz, C*H*), 7.73 (d, 2H, $^4J_{HH}$ = 1.95 Hz), 7.73 (d, 2H, $^4J_{HH}$ = 1.85 Hz, C*H*), 8.06 (d, 2H, $^4J_{HH}$ = 1.85 Hz, C*H*), 8.70 (d, 2H, $^4J_{HH}$ = 1.80 Hz, C*H*) ppm.

^{13}C{^{1}H} NMR[ii] (125.76 MHz, CD_2Cl_2): δ = 2.73 (s, Bi(*C*H$_3$)$_2$), 6.56 (s, Bi(C*H*$_3$)$_2$), 24.21 (s, C(*C*H$_3$)$_2$), 24.50 (s, C(*C*H$_3$)$_2$), 24.93 (s, C(*C*H$_3$)$_2$), 25.55 (s, C(*C*H$_3$)$_2$), 25.68 (s, C(*C*H$_3$)$_2$), 26.00 (s, C(*C*H$_3$)$_2$), 26.14 (s, C(*C*H$_3$)$_2$), 26.29 (s, C(*C*H$_3$)$_2$), 30.83 (s, C(*C*H$_3$)$_3$), 31.27 (s, C(*C*H$_3$)$_3$), 31.29 (s, C(*C*H$_3$)$_3$), 31.46 (s, C(*C*H$_3$)$_3$), 31.50 (s, C(*C*H$_3$)$_3$), 31.55 (s, C(*C*H$_3$)$_3$), 31.56 (s, C(*C*H$_3$)$_3$), 31.59 (s, C(*C*H$_3$)$_3$), 34.13 (s, *C*(CH$_3$)$_3$), 34.91 (s, *C*(CH$_3$)$_3$), 35.12 (s, *C*(CH$_3$)$_3$), 35.25 (s, *C*(CH$_3$)$_3$), 35.28 (s, *C*(CH$_3$)$_3$), 35.39 (s, *C*(CH$_3$)$_3$), 35.58 (s, *C*(CH$_3$)$_3$), 43.03 (s, *C*(CH$_3$)$_2$), 43.13 (s, *C*(CH$_3$)$_2$), 43.23 (s, *C*(CH$_3$)$_2$), 43.38 (s, *C*(CH$_3$)$_2$), 121.50 (*C*H), 121.67 (*C*H), 121.90 (*C*H), 122.02 (*C*H), 122.19 (*C*H), 123.35 (*C*H), 125.18 (*C*H), 128.79 (*C*H), 131.87 (*C*H), 132.26 (*C*H), 133.14 (*C*H), 134.18 (*C*H), 134.37 (*C*H), 134.48 (*C*H), 135.56 (*C*H), 135.62 (s, 4-C$_q$), 137.18 (s, 4-C$_q$), 137.36 (s, 4-C$_q$), 137.82 (s, 4-C$_q$), 138.27 (s, 4-C$_q$), 138.41 (s, 4-C$_q$), 138.61 (s, 4-C$_q$), 138.91 (s, 4-C$_q$), 139.24 (s, 4-C$_q$), 141.84 (s, 9a-C$_q$), 143.65 (s, 9a-C$_q$), 143.85 (s, 9a-C$_q$), 144.09 (s, 9a-C$_q$), 144.32 (s, 9a-C$_q$), 144.45 (s, 9a-C$_q$), 144.85 (s, 9a-C$_q$), 148.25 (s, 9a-C$_q$), 151.40 (s, 2-C$_q$), 151.70 (s, 2-C$_q$), 152.50 (s, 2-C$_q$), 152.52 (s, 2-C$_q$), 152.84 (s, 2-C$_q$), 153.44 (s, 2-C$_q$), 153.62 (s, 2-C$_q$), 155.67 (s, 2-C$_q$), 157.39 (s, 4a-C$_q$), 158.32 (s, 4a-C$_q$), 158.58 (s, 4a-C$_q$), 160.32 (s, 4a-C$_q$), 160.67 (s, 4a-C$_q$), 174.57 (s, 4a-C$_q$) ppm.

^{27}Al NMR (130.318 MHz, CD_2Cl_2): δ = 104.0 (s, $AlCl_4^-$) ppm.
ESI-HRMS (DCM): Positive mode; calculated (%) for $[C_{188}H_{236}Bi_7S_8]^+$ ($[Bi_7Me_4TX_8]^+$), m/z = 4214.4722; Found: m/z = 4214.4868 (95).
Elemental Analysis: Calculated (%) for $C_{188}H_{236}AlBi_7Cl_4S_8$ (4384.08 g/mol): C 51.51, H 5.43; Found: C 51.06, H 5.48.

NMR spectra of isolated compounds

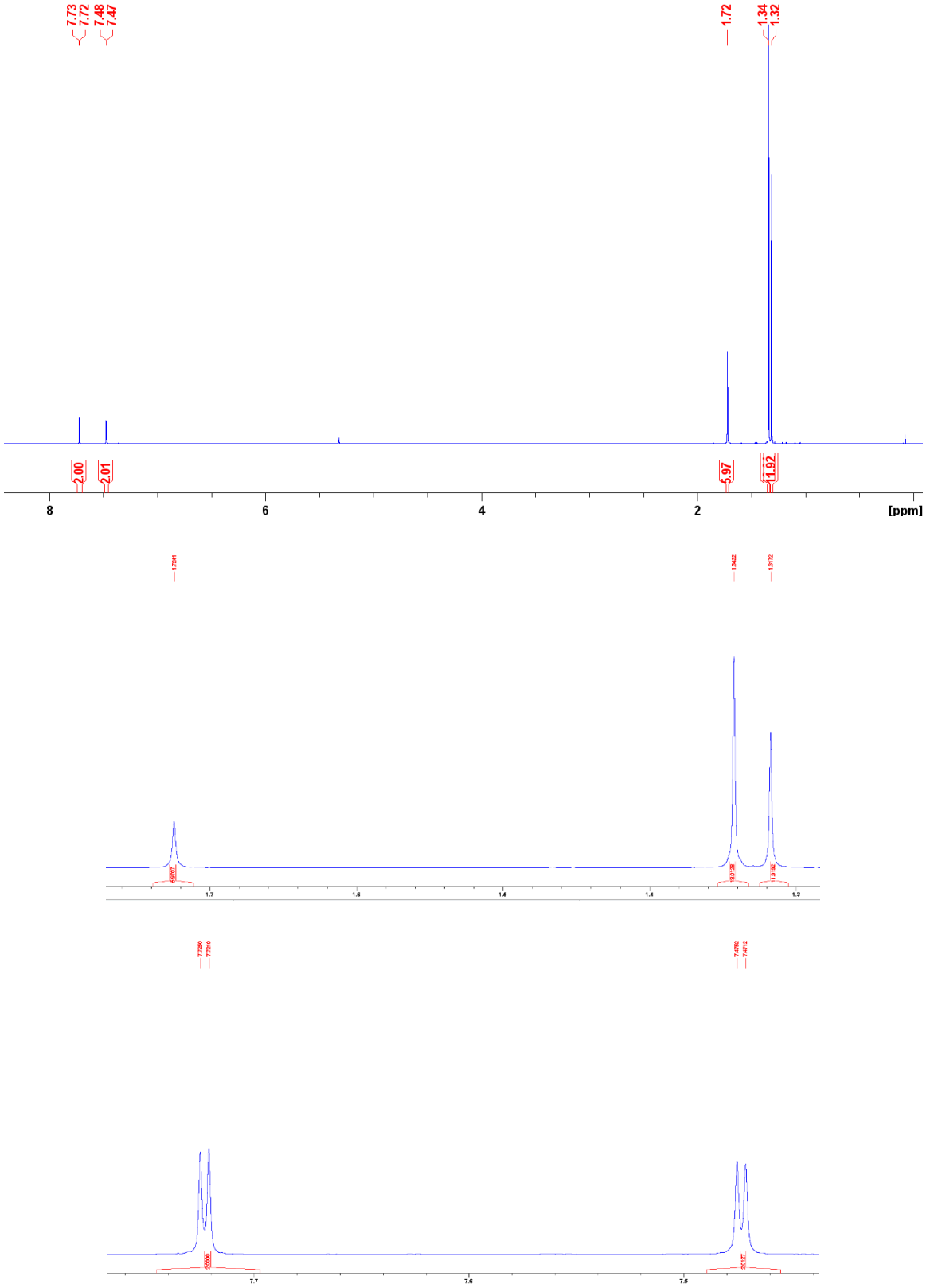


Figure S2. ^{1}H NMR spectrum of compound $(BiMe_2)_2TX$ (**1**) in CD_2Cl_2 (top) with zoom-in on aliphatic (middle) and aromatic region (bottom).

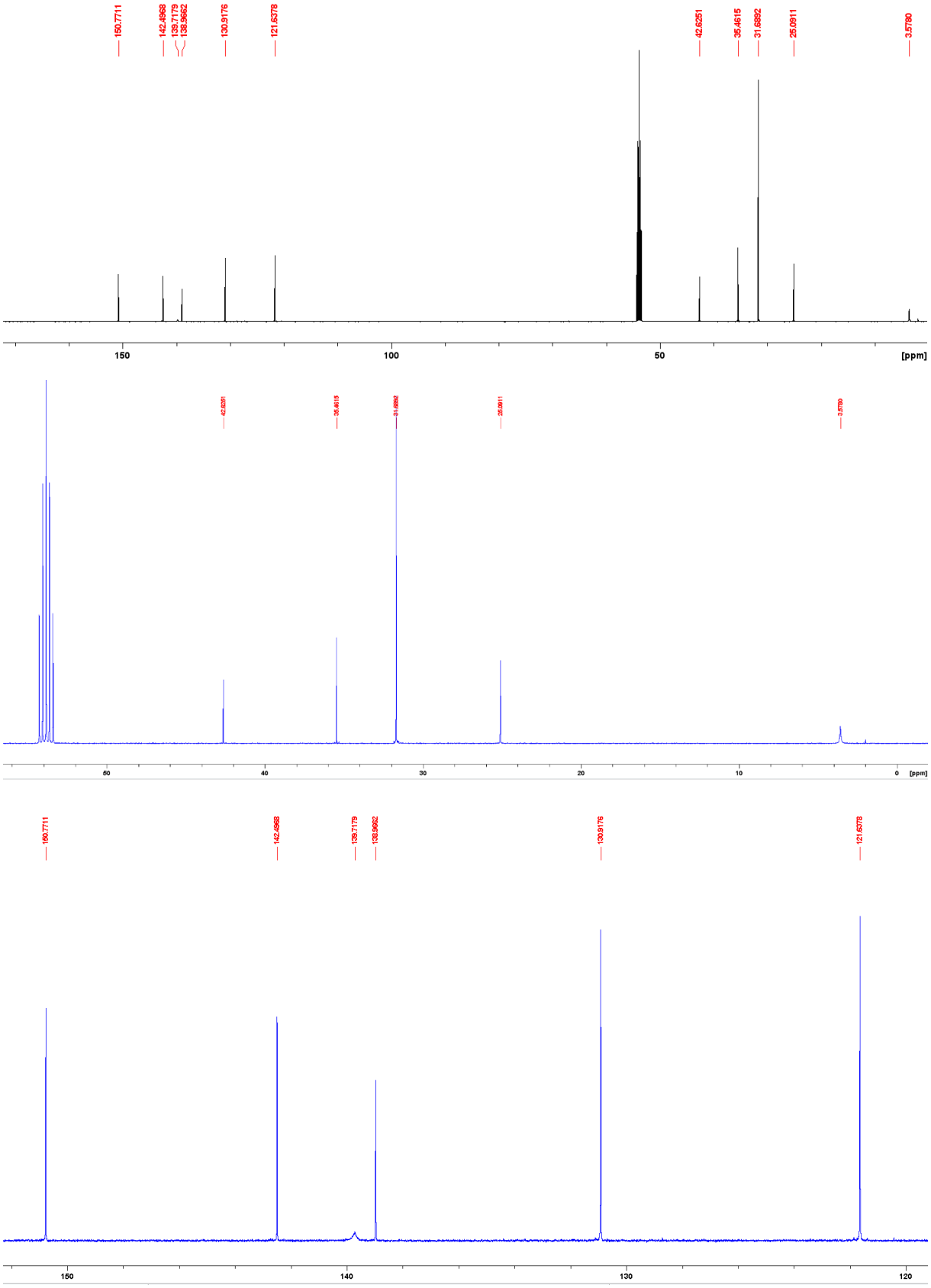


Figure S3. ^{13}C NMR spectrum of compound $(BiMe_2)_2TX$ (**1**) in CD_2Cl_2 (top) with zoom-in on aliphatic (middle) and aromatic region (bottom).

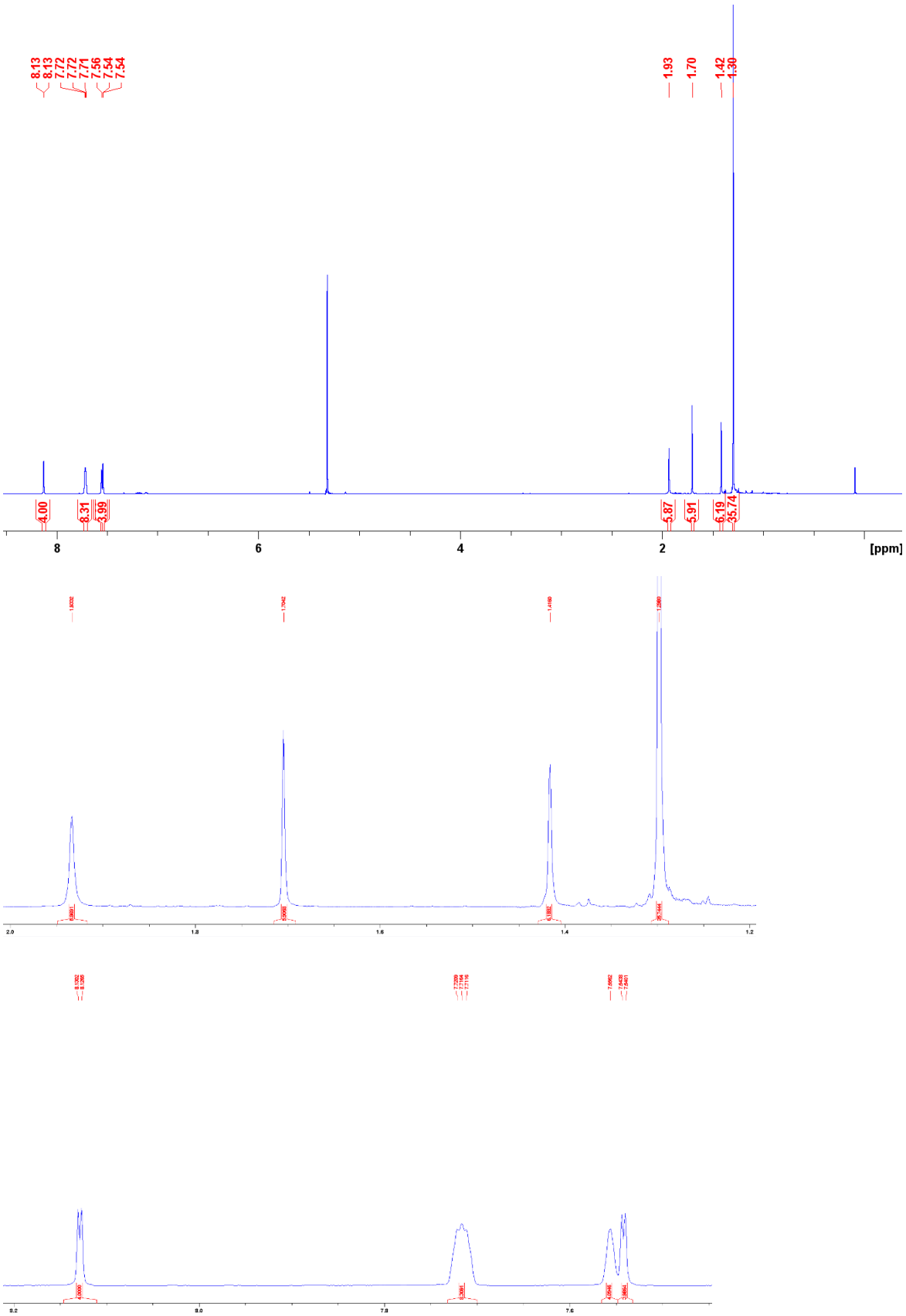


Figure S4. ^{1}H NMR spectrum of compound [$(BiMe)_2TX_2Tl$][BAr^F] (**2**) in CD_2Cl_2 (top) with zoom-in on aliphatic (middle) and aromatic region (bottom).

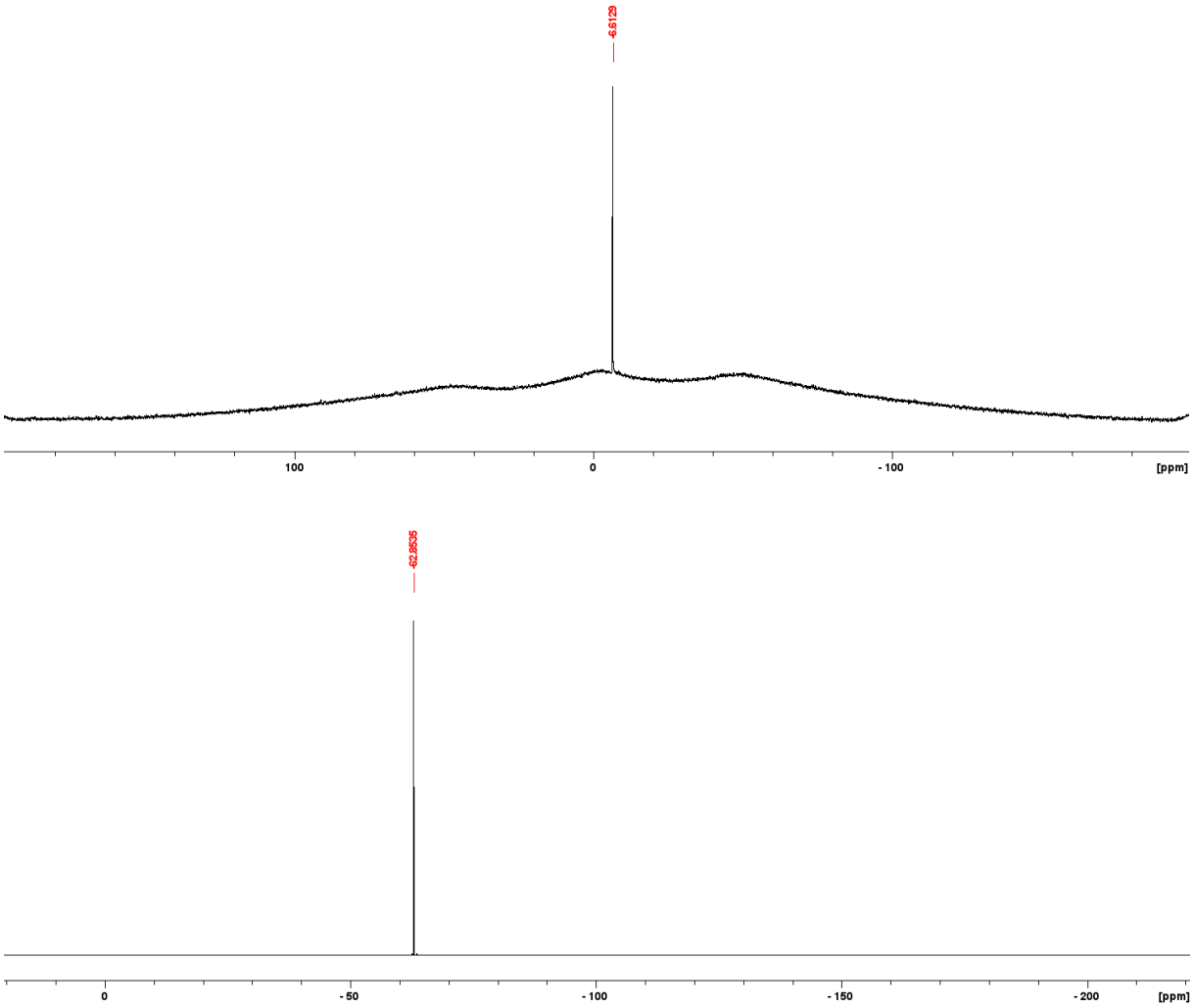


Figure S5. ^{11}B NMR spectrum (top) and ^{19}F NMR spectrum (bottom) of compound $[(BiMe)_2TX_2Tl][BAr^F]$ (**2**) in CD_2Cl_2.

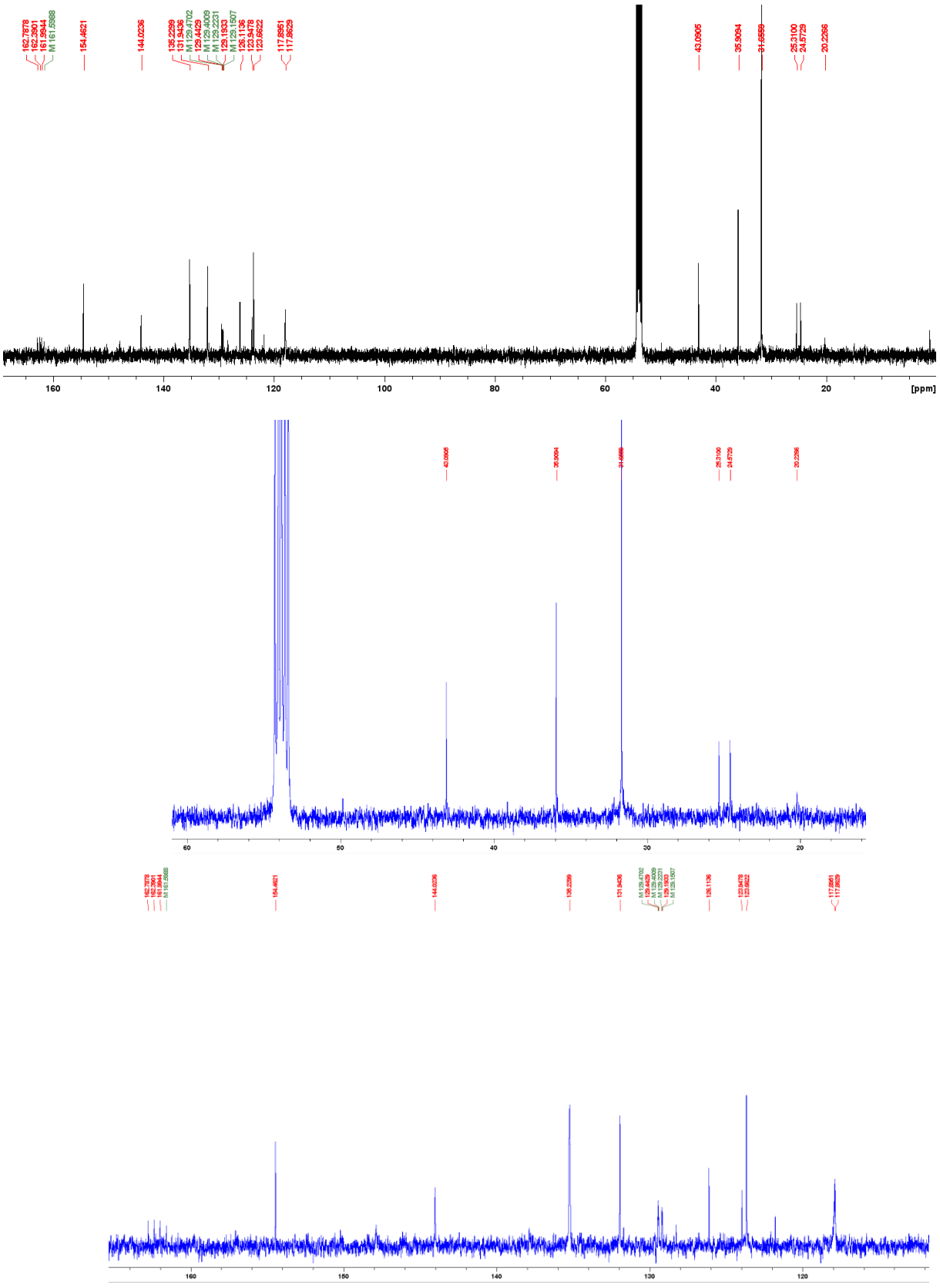


Figure S6. ^{13}C NMR spectrum of compound $[(BiMe)_2TX_2Tl][BArF]$ (**2**) in CD_2Cl_2 (top) with zoom-in on aliphatic (middle) and aromatic region (bottom).

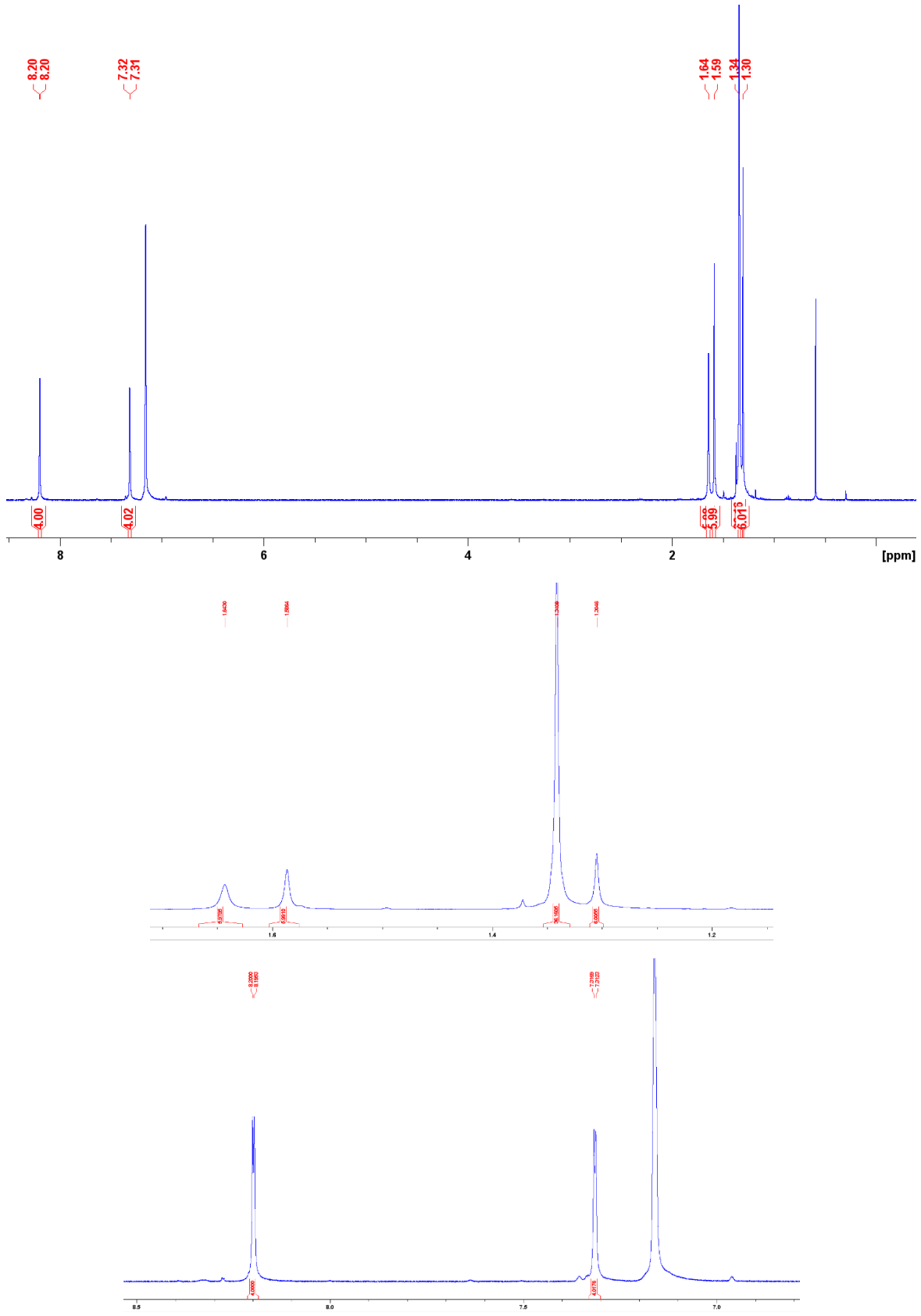


Figure S7. ^{1}H NMR spectrum of compound $(BiMe)_2TX_2$ (**3**) in C_6D_6 (top) with zoom-in on aliphatic (middle) and aromatic region (bottom).

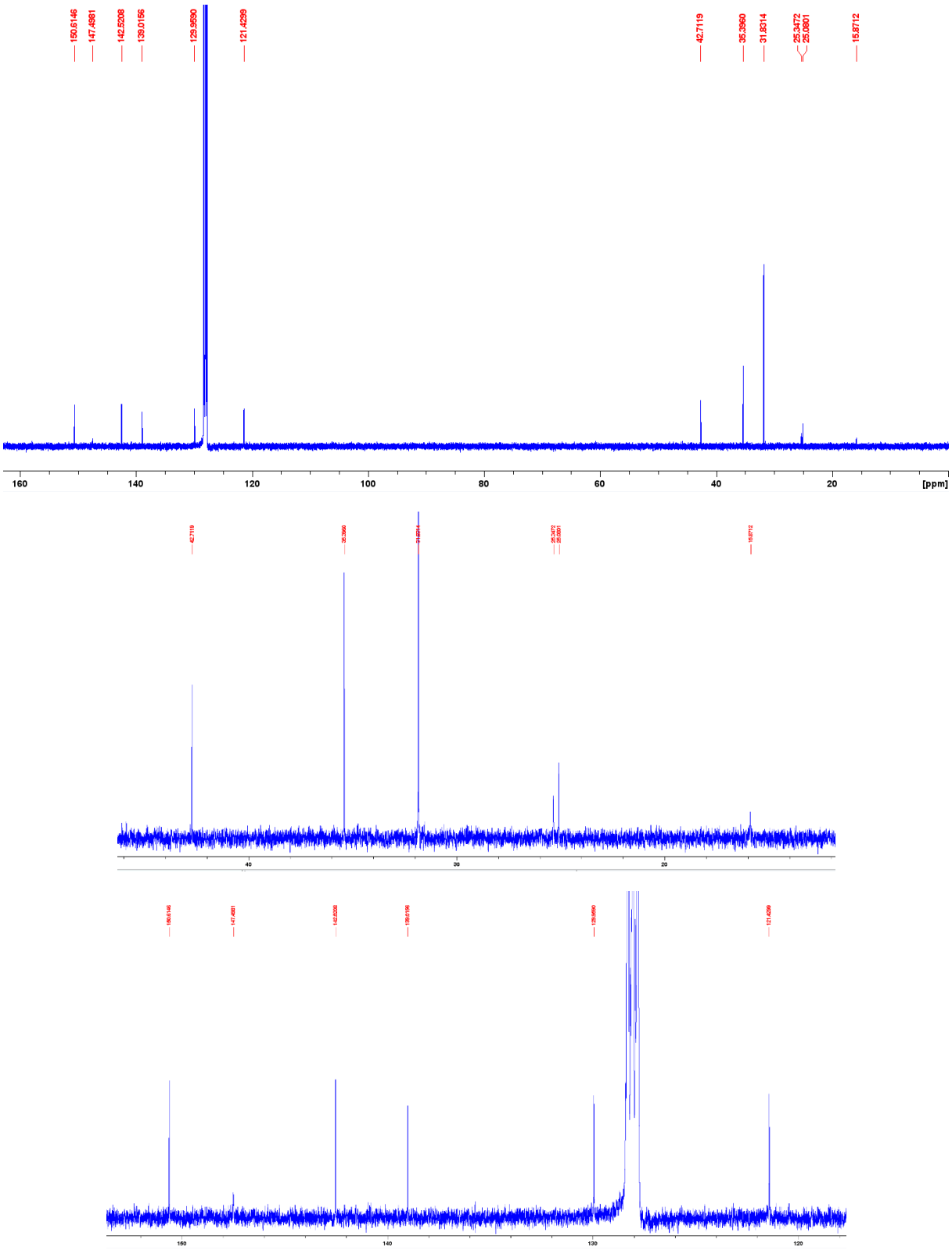


Figure S8. ^{13}C NMR spectrum of compound $(BiMe)_2TX_2$ (**3**) in C_6D_6 (top) with zoom-in on aliphatic (middle) and aromatic region (bottom).

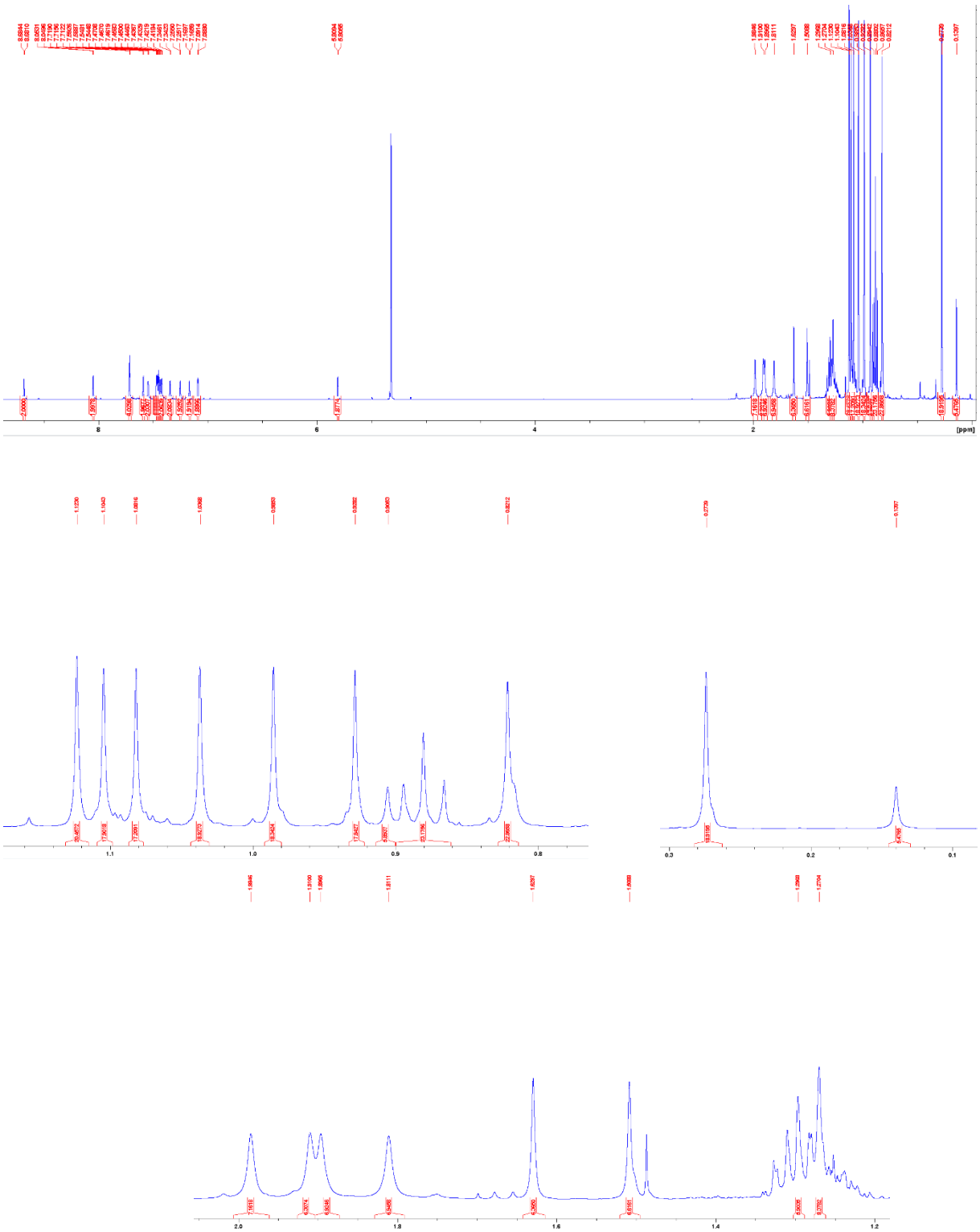


Figure S9. ^{1}H NMR spectrum of compound $[Bi_7Me_4TX_8][BiMe_2(SbF_6)_2]$ (**4-Bi**) in CD_2Cl_2 (top) and zoom-in on aliphatic region (middle and bottom).

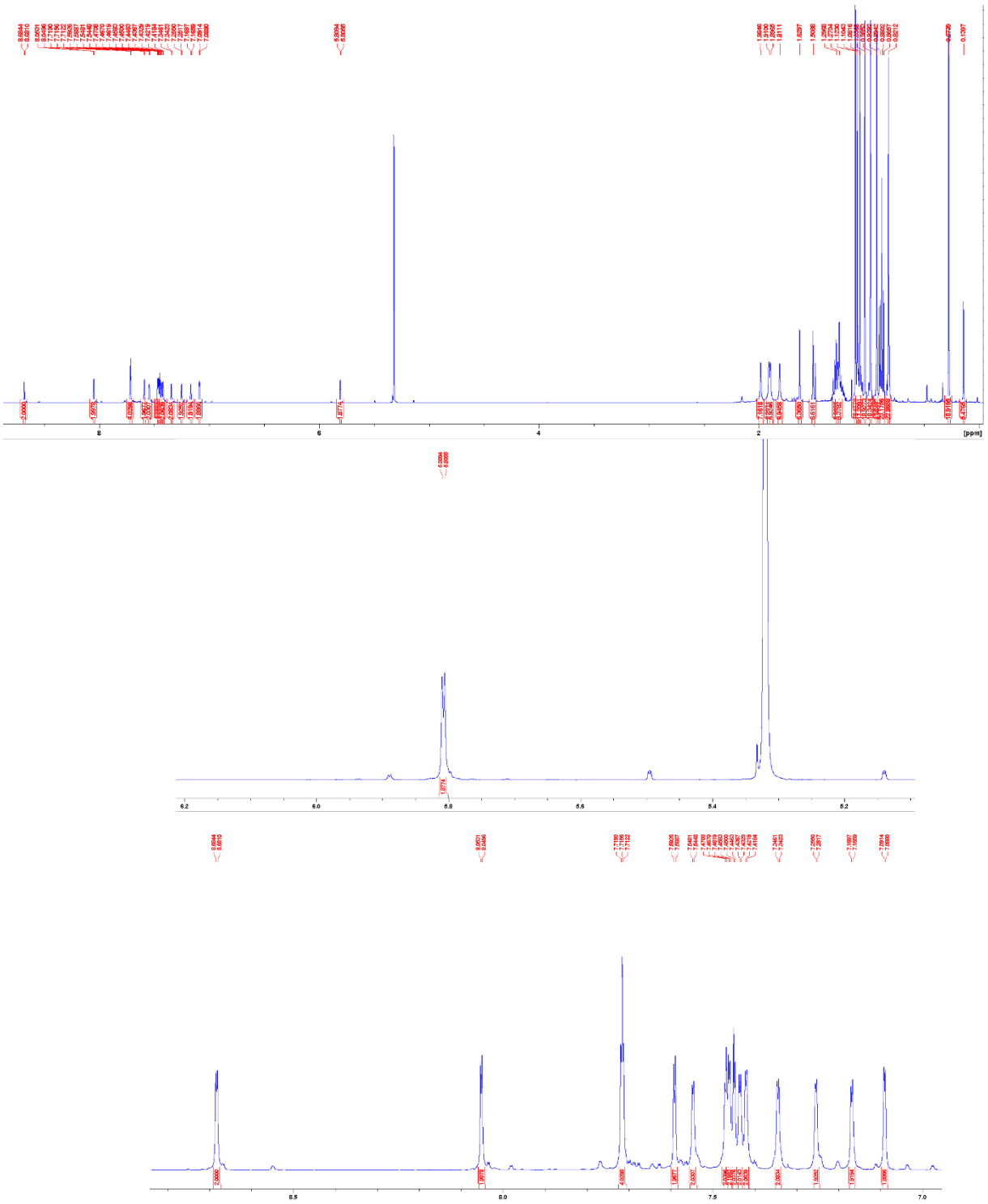


Figure S10. ^{1}H NMR spectrum of compound $[Bi_7Me_4TX_8][BiMe_2(SbF_6)_2]$ (**4-Bi**) in CD_2Cl_2 (top) and zoom-in on aromatic region (middle and bottom).

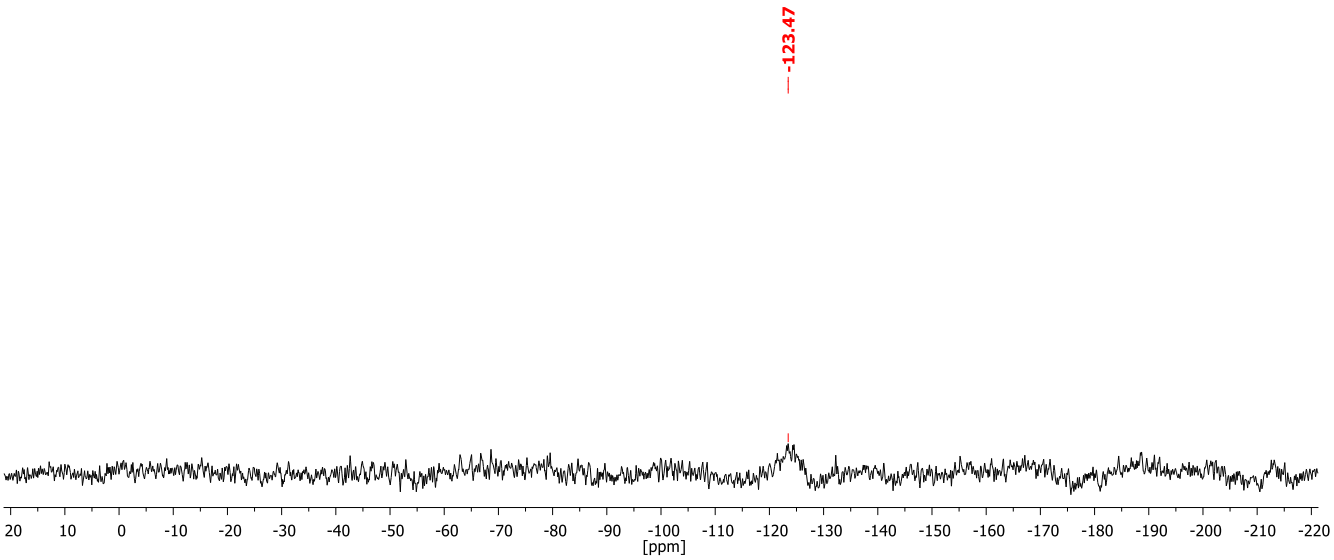


Figure S11. ^{19}F NMR spectrum of compound $[Bi_7Me_4TX_8][BiMe_2(SbF_6)_2]$ (**4-Bi**) in CD_2Cl_2. For a comment concerning the interpretation of this spectrum, see experimental part.

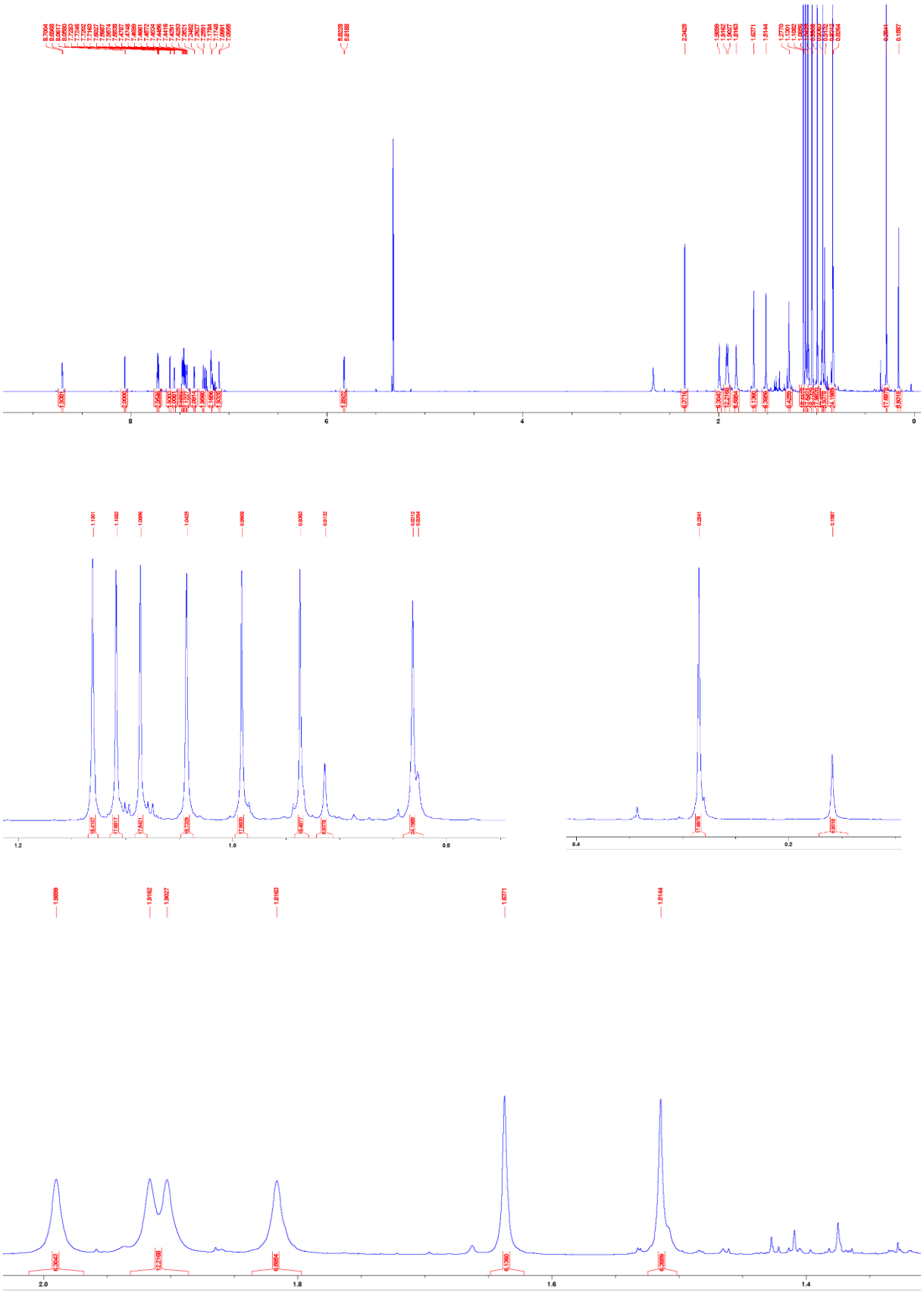


Figure S12. ^{1}H NMR spectrum of compound $[Bi_7Me_4TX_8][AlCl_4]$ (**4-Al**) in CD_2Cl_2 (top) and zoom-in on aliphatic region (middle and bottom).

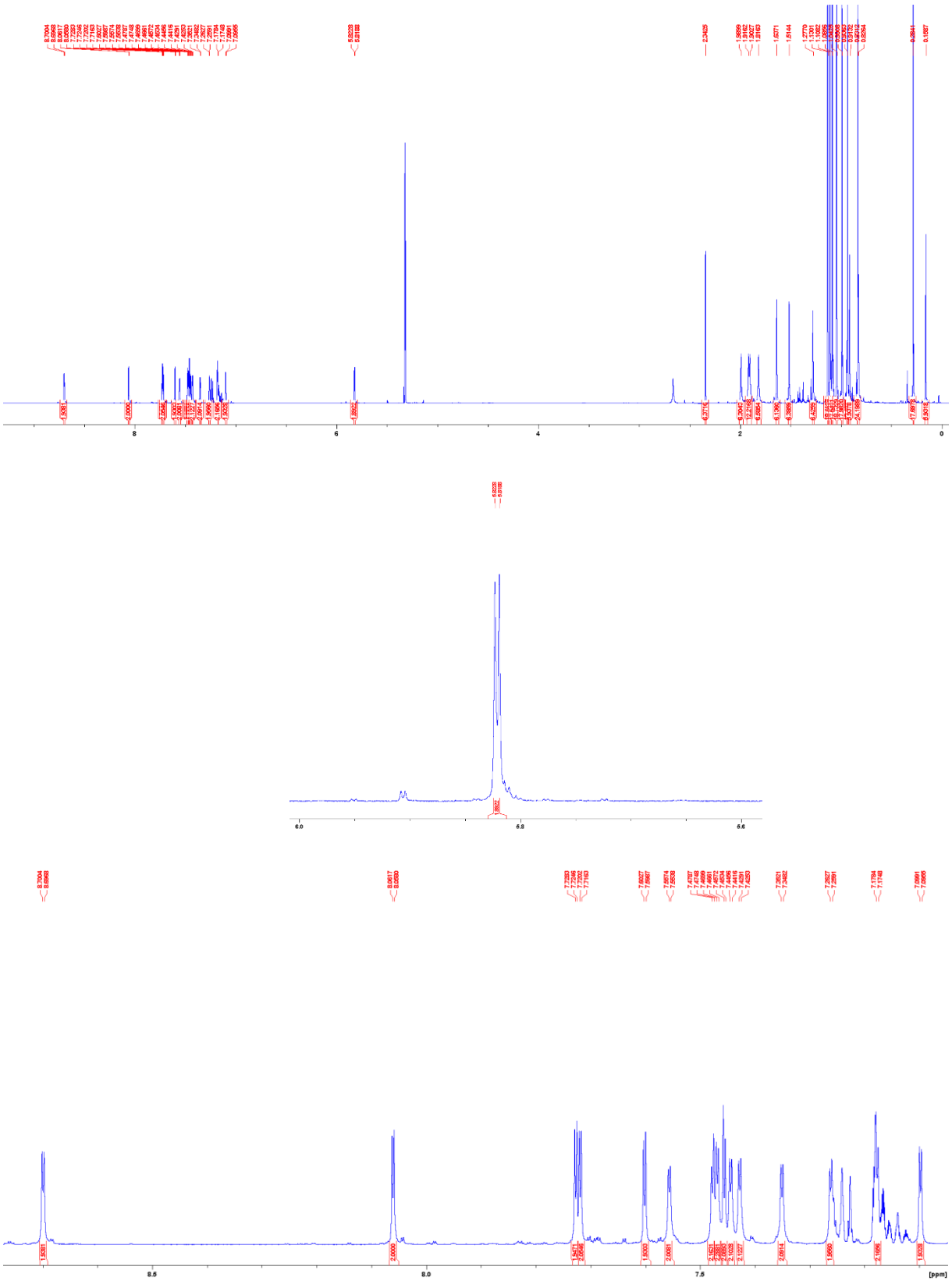


Figure S13. ^{1}H NMR spectrum of compound $[Bi_7Me_4TX_8][AlCl_4]$ (**4-Al**) in CD_2Cl_2 (top) and zoom-in on aromatic region (middle and bottom).

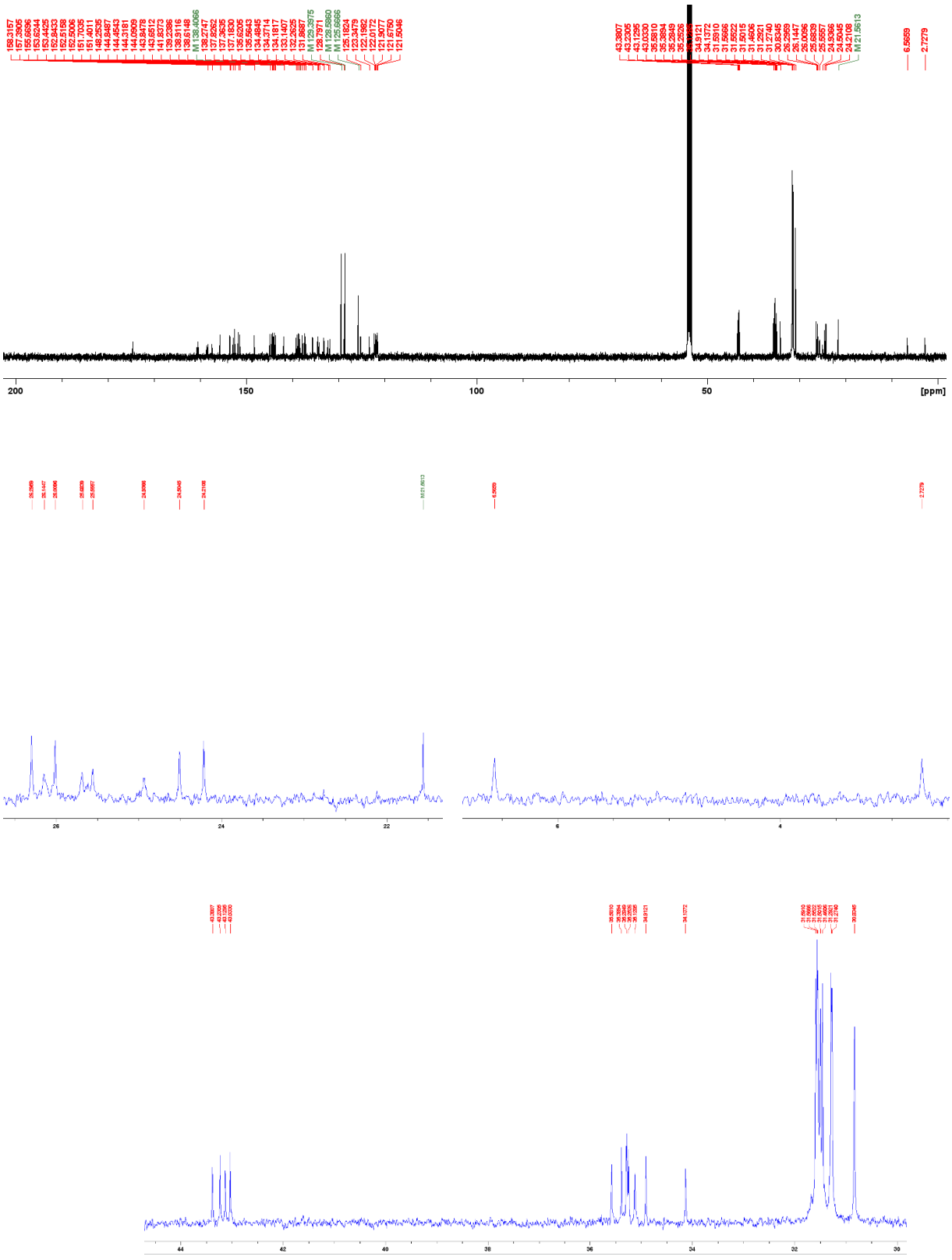


Figure S14. ^{13}C NMR spectrum of compound $[Bi_7Me_4TX_8][AlCl_4]$ (**4-Al**) in CD_2Cl_2 (top) and zoom-in on aromatic region (middle and bottom).

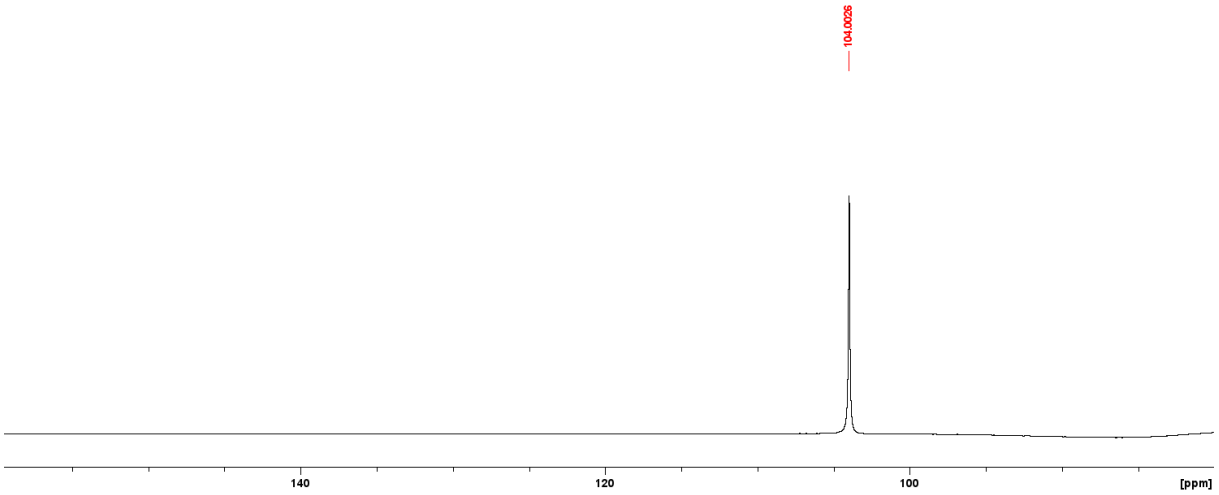
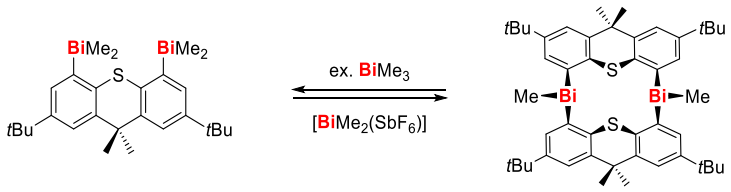


Figure S15. ^{27}Al NMR spectrum of compound $[Bi_7Me_4TX_8][AlCl_4]$ (**4-Al**) in CD_2Cl_2.

NMR spectroscopic reaction monitoring

As described in the main text, the reversible transformation of **1** to **3** and *vice versa* was observed by reacting **3** with an excess of $BiMe_3$ or by treating **1** with stoichiometric or catalytic amounts of $[BiMe_2(SbF_6)]$ in C_6D_6 (see Scheme S1).



1 3

Scheme S1. Reversible transformation of **1** to **3** and *vice versa* by choosing the appropriate bismuth compound as the initiating reagent.

Reactions of **1** with $[BiMe_2(SbF_6)]$ and reactions of **3** with $BiMe_3$ were monitored by NMR spectroscopy. In this context, **3** (14 mg, 12.5 µmol) was dissolved in C_6D_6 (0.4 mL), a solution of $BiMe_3$ (210 mg solution, 47%(w), 75 mg $BiMe_3$, 298 µmol) in Et_2O added dropwise at ambient temperature and immediately after the addition the ^1H NMR experiments started. The kinetic series was collected for 16 h at ambient temperature, with 10 min between each single measurement. This way, the decay shown in Figure S16 (left) was observed, with a half-life of $t_{1/2}$ = 193 min. For the transformation of **1** to **3**, a different approach was chosen. Substance **1** (30 mg, 36.8 µmol) was dissolved in C_6D_6 (0.3 mL), the solution frozen at −30 °C in the glovebox, a solution of $[BiMe_2(SbF_6)]$ (165 µg, 0.37 µmol) in C_6D_6 (0.4 mL) added and subsequently frozen again at −30 °C. This way the reaction could be started in a precisely timed way. The frozen sample was then transported to the NMR spectrometer, warmed just before the measurement so that all of the solid solvent melted, strongly mixed, inserted into the spectrometer, and the NMR experiments started immediately. Figure S17 shows the increase of the relative concentration of **3** over the course of 16 h with a half-life of $t_{1/2}$ = 315 min.

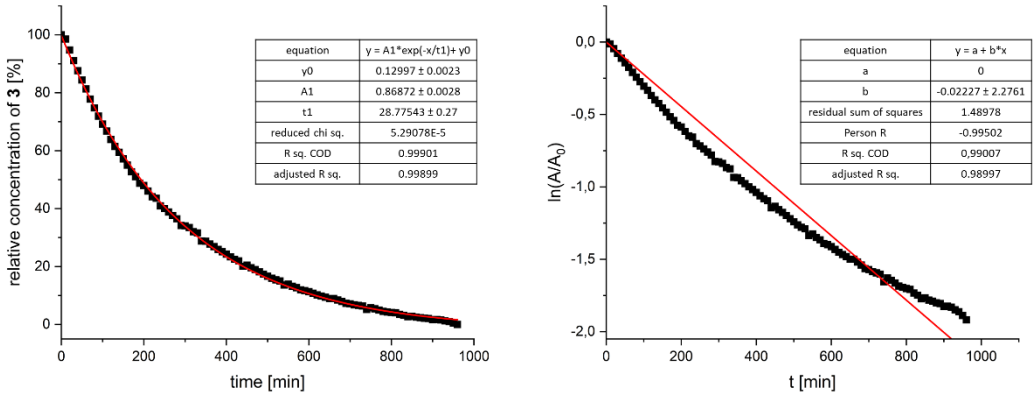


Figure S16. Left: Exponential decay of the relative concentration of **3** over the course of 16 h at ambient temperature - determined by ^1H NMR spectroscopy. The red line represents the best fit of an exponential decay with the given parameters. Right: Plot of the relative concentration of **3** of a logarithmic function over the course of 16 h at ambient temperature. The red line represents the best fit of a line function with the given parameters.

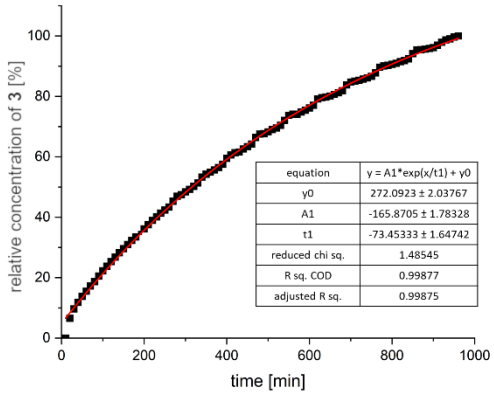


Figure S17. Relative concentration of **3** over the course of 16 h at room temperature - determined by ^{1}H NMR. The red line represents the best fit of an exponential growth with the given parameters.

Attempts were also made to classify the observed reaction patterns by a chemical reaction order, assuming that the rate determining step would be sufficiently isolated and not coupled to other side reactions, so that a simple fit is possible. Unfortunately, a linearization of the relative concentration of **3** over 16 h failed (see in Figure S16 – right) indicating that the reaction is not first order, but presumably a more complex mixture of first and second order. This is likely a result of the relatively large number of elementary steps that must be involved (at least four Bi–C bonds are broken and formed). A first or second order fit was also not possible for the transformation of **1** to **3**; in this case, the side reactions taking place when Tl^+ is not used as a templating agent further complicate the analysis of kinetic data.

In order to investigate the catalytic activity of [$BiMe_2(SbF_6)$], **1** was treated with varying amounts of [$BiMe_2(SbF_6)$], and the reactions were monitored by ^{1}H NMR spectroscopy. The results are summarized in Table S1. Comparison of entries 4 and 5 suggests that the conversion of unidentified side products to compound **3** might be possible.

Table S1. Screening of conditions for reaction of **1** with [$BiMe_2(SbF_6)$] (yields determined via ^{1}H NMR spectroscopy in C_6D_6).

Entry	equiv. [$BiMe_2(SbF_6)$]	reaction time	unreacted 1 [%]	3 [%]	TXH_2 side product [%]	unidentified side products [%][b]
1	1.00	5 min[a]	8	10	9	73
2	0.11	16 h	11	14	11	64
3	0.01	20 min	20	12	2	66
4	0.01	36 h	8	39	3	50
5	0.01	60 h	7	42	3	48

[a] Time between preparation and NMR spectroscopic measurement. [b] The unidentified side products exhibit distinct signal patterns of duplets reminiscent of those found for the aryl groups of **1** or **3**, but with a different chemical shift, indicating that the TX moieties remain intact. The amount of side products was estimated based on the assumption that side products contain one TX moiety.

NMR spectra from reaction monitoring

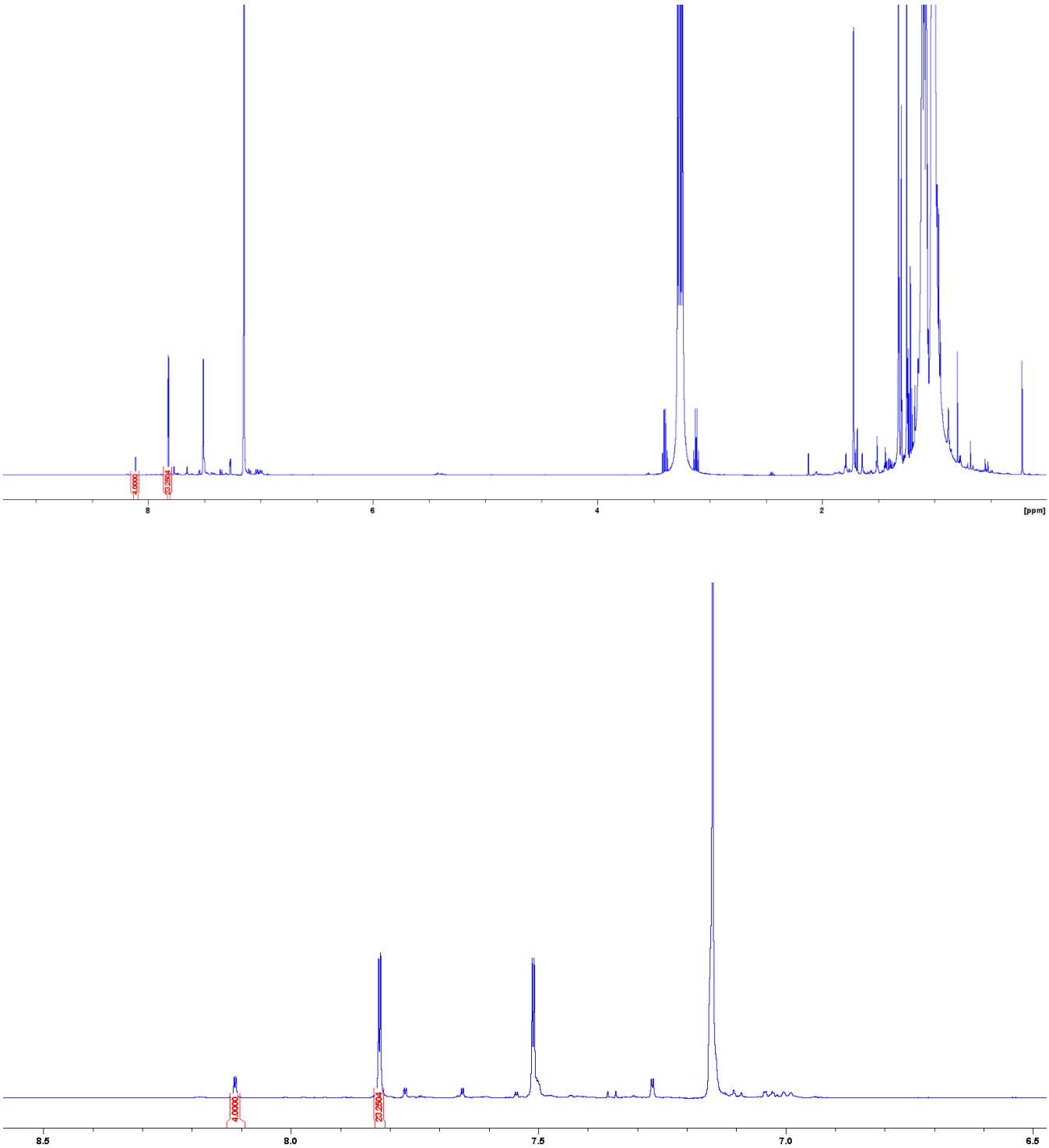


Figure S18. ^{1}H NMR spectrum of reaction between $(BiMe)_2TX_2$ (**3**) and 30 equiv. $BiMe_3$ in C_6D_6 (top) and zoom-in on aromatic region (bottom), showing the presence of **1** and **3**. The slight deviation of chemical shifts of **1** and **3** in benzene from the values observed here is due to the presence of Et_2O from the stock solution of $BiMe_3$, as confirmed by control experiments (see experimental part).

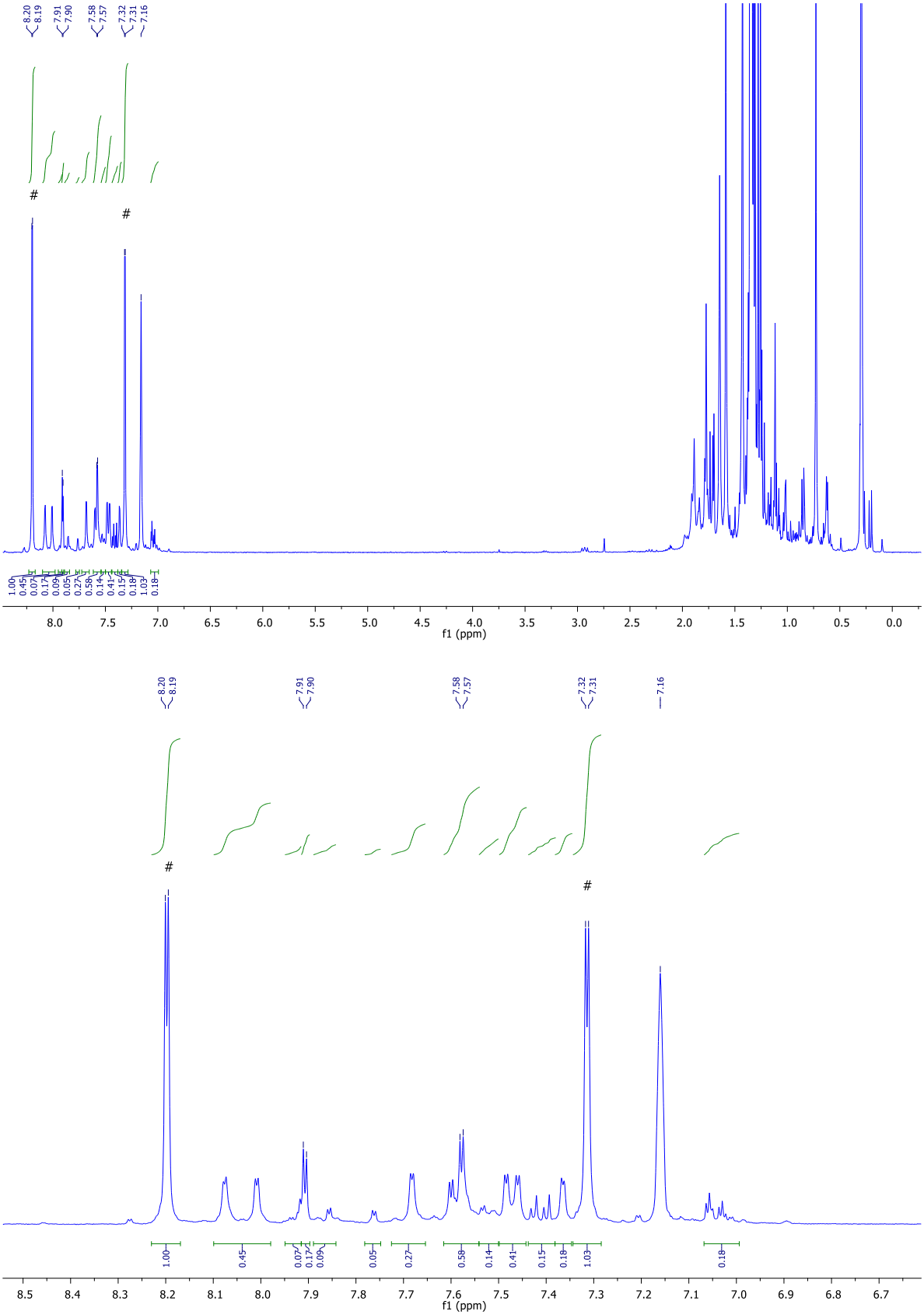


Figure S19. ^{1}H NMR spectrum of reaction between $(BiMe_2)_2TX$ (**1**) and 0.01 equiv. $[BiMe_2(SbF_6)]$ in C_6D_6 (top) and zoom-in on aromatic region (bottom). # denotes resonances due to compound **3**.

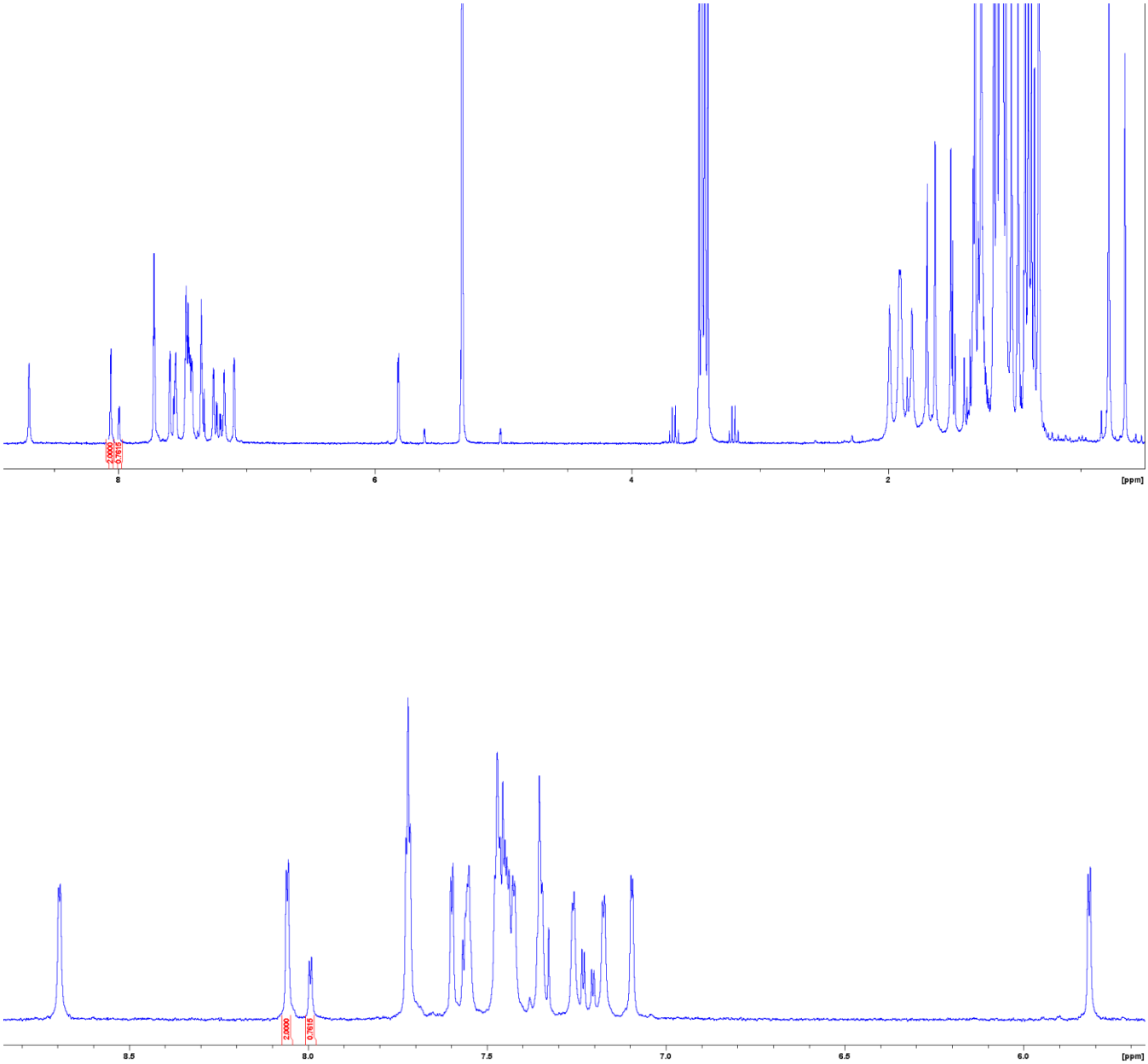


Figure S20. ^{1}H NMR spectrum of reaction between $[Bi_7Me_4TX_8][BiMe_2(SbF_6)_2]$ (**4-Bi**) and 6.2 equiv. $BiMe_3$ in CD_2Cl_2 (top) and zoom-in on aromatic region (bottom). Integrated resonances are due to **4-Bi** and **3**, respectively.

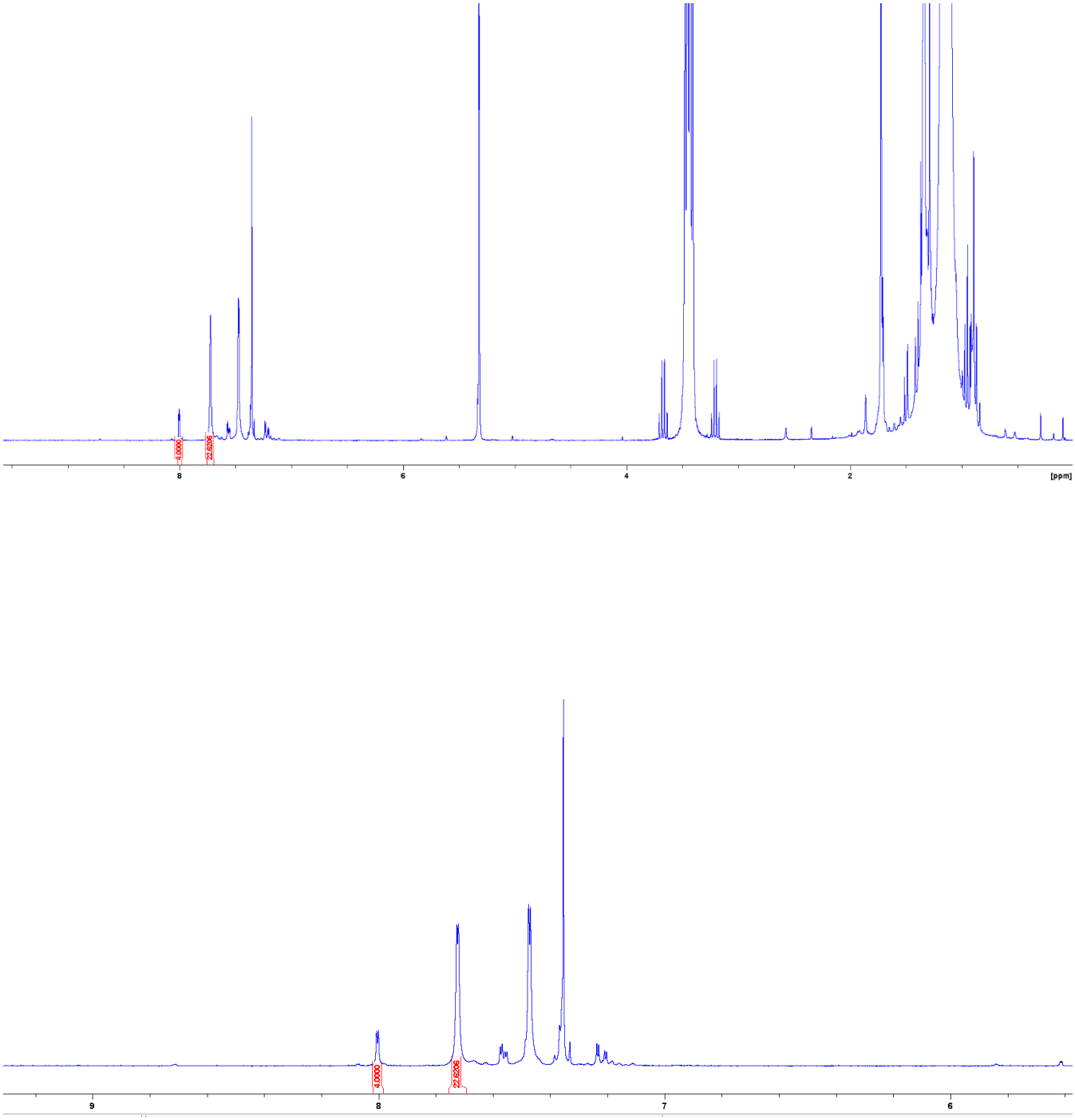


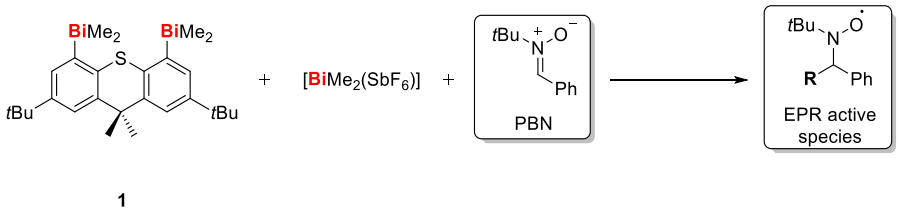
Figure S21. ^{1}H NMR spectrum of reaction between $[Bi_7Me_4TX_8][BiMe_2(SbF_6)_2]$ (**4-Bi**) and 140 equiv. $BiMe_3$ in CD_2Cl_2 (top) and zoom-in on aromatic region (bottom). Integrated resonances are due to **1** and **3**, respectively. Benzene is present from a stock solution of $BiMe_3$.

Mechanistic considerations

As mentioned in the main text, we observed the [$BiMe_2(SbF_6)$]-catalyzed transformation of **1** to form **3** with catalyst loadings as low as 1 mol% (*vide supra* – NMR-kinetic studies). Facile, reversible, non-productive Bi–C bond cleavage/formation in the cationic species [$Me_3Bi{\rightarrow}BiMe_2(SbF_6)$] have been shown to proceed through a polar S_E2 mechanism.[21] In addition, we have shown that Tl^+ central atoms can coordinate two different bismuth compounds via their aryl substituents.[25] This generates a close proximity between these bismuth species, which can be expected to facilitate subsequent reactions between these species through a templating effect. The bismuth atoms and sulfur atoms of compound **1** can also work as coordination points in this scenario. Thus, Bi–C bond cleavage/formation in reactions of **1** with [$BiMe_2(SbF_6)$] to give **3** or **4-Bi** appear reasonable. On the other hand, examples of bismuth-containing compounds that undergo facile homolytic bond dissociation have been reported to the literature (such as bismuth amides,[31] bismuth phosphanides,[31] dibismuthanes,[31] transition-metal bismuthanes,[32] and diaryl(bismuth)alcoholates[33]). Thus, radical pathways in reactions of **1** with [$BiMe_2(SbF_6)$] to give **3** or **4-Bi** were also considered. The relevant EPR spectroscopic experiments revealed that indeed, radical species are generated under the conditions that have been applied for the synthesis of **3** and **4-Bi** (*vide infra* – EPR spectroscopic measurements), leading to an even more complex mechanistic scenario.

EPR spectroscopic measurements

EPR spectroscopic experiments were performed by using phenyl-*N*-tertbutyl-nitrone (PBN) as a spin trap to enable the identification of only short lived intermediate radical species. The reaction conditions were chosen to mimic those that lead to isolable compounds **3** and **4-Bi**, i.e. a mixture of 4:1:4 of **1**:[$BiMe_2(SbF_6)$]:PBN in C_6D_6 or CD_2Cl_2 was used and EPR measurements were conducted for 9 h with a time interval of 30 min between each measurement (see Scheme S2).



Scheme S2. *Via* EPR investigated reaction sequence of a mixture of 4:1:4 (**1**:[$BiMe_2(SbF_6)$]:PBN) in C_6D_6 with the non-bismuth containing radical being trapped via PBN and subsequently detected as a nitroxide-radical species. R = organic residue.

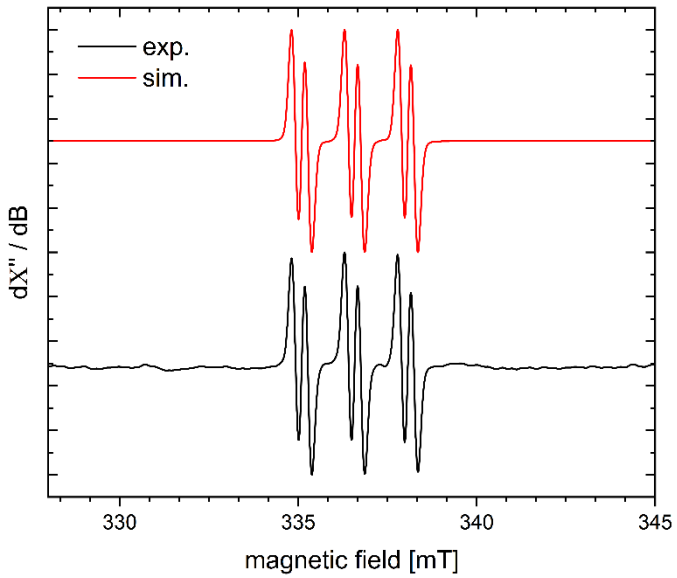


Figure S22. Experimental (black) and simulated (red)[40] continuous-wave (CW) X-band EPR spectra of the 4:1:4 mixture of $(BiMe_2)_2TX$ (**1**), $[BiMe_2(SbF_6)]$, and PBN in benzene (c($[BiMe_2(SbF_6)]$) = 0.017 mol/L; c(PBN) = c(**1**) = 0.070 mol/L). Coupling constants: a(1 × ^{14}N) = 41.6 MHz (14.8 G), a(1 × ^{1}H) = 9.77 MHz (3.5 G), a(1 × ^{13}C) = 11.8 MHz (4.2 G); g_{iso} = 2.0052. Spectrometer settings: microwave frequency = 9.446413 GHz, modulation amplitude = 0.2 mT at 100 kHz, power = 2.0 mW, number of accumulated scans = 24, conversion time = 12.0 ms.

The EPR spectrum (see Figure S22) confirms the formation of radical species in the course of the reactions that must have originated from the bismuth compounds, as no EPR-active species was found by solely mixing C_6D_6 or CD_2Cl_2 and PBN. The EPR spectrum is in good alignment with previously reported data of PBN-trapped alkyl radicals such as $[PBN\text{-}CH_3]^{\bullet}$ (a(1 × ^{1}H) = 10.2 MHz).[41,42] It must be noted that the difference of the hyperfine coupling constants of $[PBN\text{-}CH_3]^{\bullet}$ and $[PBN\text{-}Ar]^{\bullet}$ is only subtle. Furthermore, there is not literature on PBN-trapped TX species. However, the spectra shown in Figure S22 with a(1 × ^{1}H) = 9.77 MHz suggest the presence of $[PBN\text{-}CH_3]^{\bullet}$ (a(1 × ^{1}H) = 10.2 MHz) rather than $[PBN\text{-}Ar]^{\bullet}$ ($[PBN\text{-}Ph]^{\bullet}$: a(1 × ^{1}H) = 5.56 MHz).[41,42] However, the detection of H_2TX[20] as a side product in many reactions suggests that the homolytic cleavage of the Bi–C^{sp2} bonds is also possible in compounds featuring Bi-TX moieties.

After the EPR spectroscopic investigations, the same sample in C_6D_6 was investigated by ^{1}H NMR spectroscopy, confirming the transformation of **1** to **3**, which indicated a mixture of 29% **1** and 71% **3** being obtained after 16 h at room temperature.

Single-Crystal X-Ray Diffraction Analysis

Compound 1

Suitable single-crystals of **1** were obtained by slow evaporation of a saturated Et_2O solution at room temperature. The molecular structure of **1** in the solid state has been discussed in the main text. Additional bond lengths and angles are given in Figure S23. The unit cell contains three multiply disordered Et_2O molecules which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.

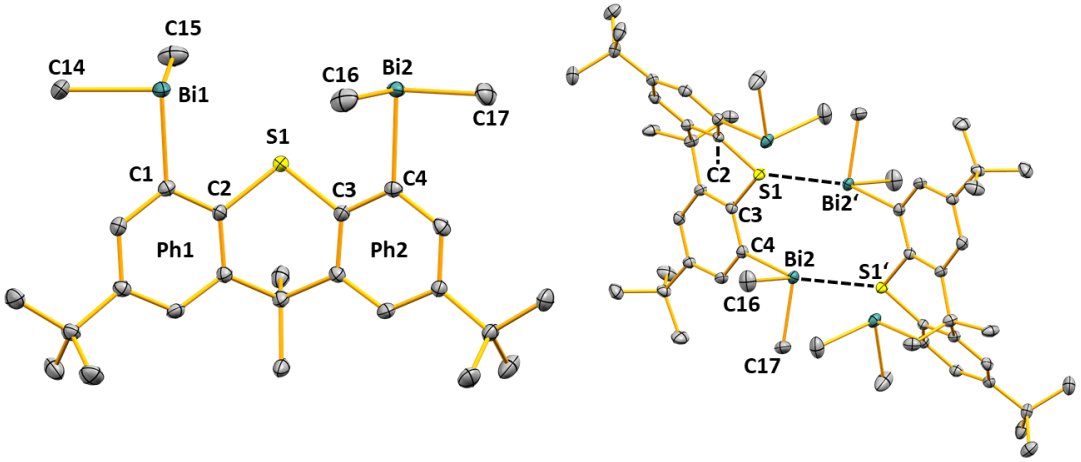


Figure S23. Molecular structure of **1** as a monomeric molecular compound (left) and in the representation of a dimeric packing (right) in the solid state. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Bi1–Bi2, 5.2330(9); Bi1–C1, 2.258(2); Bi1–C14, 2.257(4); Bi1–C15, 2.253(4); C1–C2, 1.397(4); C2–S1, 1.764(3); S1–C3, 1.776(3); C3–C4, 1.395(4); Bi2–C4, 2.266(3); Bi2–C16, 2.256(3); Bi2–C17, 2.257(3); Bi2–S1', 3.699(1); S1–B2', 3.699(1); C14–Bi1–C1, 92.0(1); C1–Bi1–C15, 95.4(1); C15–Bi1–C14, 92.9(1); C16–Bi2–C4, 93.8(1); C4–Bi2–C17, 94.6(1); C17–Bi2–C16, 92.8(1); C2–S1–C3, 100.5(1); C2–S1–Bi2', 138.0(1); C3–S1–Bi2', 83.1(1); C16–Bi2–S1', 167.89(9); C17–Bi2–S1', 82.32(8); $Ph1^{plane}$–$Ph2^{plane}$, 41.87; Σ_{Bi1}, 280.3(1); Σ_{Bi2}, 281.2(1).

Compound 2

Suitable single-crystals for **2** were obtained by diffusing *n*-pentane (0.1 mL) into a DFB solution (0.6 mL) of **2** at −30 °C. The molecular structure of **2** in the solid state has been discussed in the main text. Additional bond lengths and angles are given in Figure S24 alongside the top and side view of the molecule. The main molecule contains a disordered *t*Bu-group on one TX moiety. In addition to that, multiple CF_3 groups of the BAr^F anion and a rotationally disordered 1,2-Difluorobenzene molecule are present in the solid-state structure as well. Furthermore, the coordination sphere of the intercalated Tl(I)-cation is saturated by one benzene molecule (see side view of **2** in Figure S24).

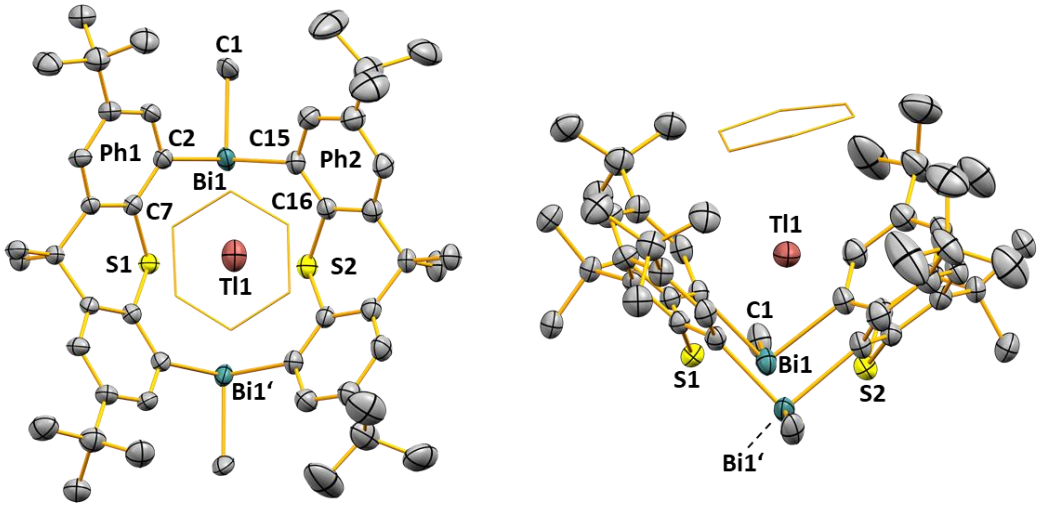


Figure S24. Molecular structure of **2** in the solid state (**left**: top view, **right**: side view with coordinated benzene molecule). Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms, lattice-bound solvent molecules, and split positions of disordered entities, and the BAr^F anion are omitted for clarity. The coordinating benzene ring is shown as a wire frame. Selected bond lengths (Å) and angles (°): Bi1–C1, 2.260(7); Bi1–C2, 2.279(5); Bi1–C15, 2.281(5); C2–C7, 1.400(6); C7–S1, 1.775(5); S1–C7', 1.775(5); C7'–C2', 1.400(6); C2'–B1', 2.279(5); Bi1'–C1', 2.260(7); Bi1'–C15', 2.281(5); C15'–C16', 1.389(8); C16'–S2, 1.786(6); S2–C16, 1.786(6); C16–C15, 1.389(8); C15–Bi1, 2.281(5); Bi1–Tl1, 4.0980; Bi1'–Tl1, 4.0980; Bi1–Bi1', 5.4325(7); S1–Tl1, 3.168(2); S2–Tl1, 3.217; $Ph1^{centro}$–Tl1, 3.795; $Ph2^{centro}$–Tl1, 3.635; C1–Bi1–C2, 94.2(2); C2–Bi1–C15, 93.7(2); C15–Bi1–C1, 94.7(2); C7–S1–C7', 100.7(4); C16–S2–C16', 99.7(4); $Ph1^{plane}$–$Ph1'^{plane}$, 38.6; $Ph2^{plane}$–$Ph2'^{plane}$, 48.59; $Ph1^{plane}$–$Ph2^{plane}$, 75.84; $\Sigma_{Bi1} = \Sigma_{Bi1'}$, 282.6(2).

Compound 4-Bi

Compound **4-Bi** was crystallized by slow evaporation of a saturated solution in DCM at room temperature overnight in the space group *P-1* with two formula units in the unit cell. The unit cell parameters are: a = 19.730(5) Å, b = 19.746(5) Å, c = 28.755(7) Å, α = 88.138(15)°, β = 82.427(11)°, γ = 84.601(19)°, V = 11054(5) $Å^3$. Unfortunately, the quality of the data is not sufficient for a detailed discussion of the bonding parameters but provides a proof of connectivity (see Figure S25).

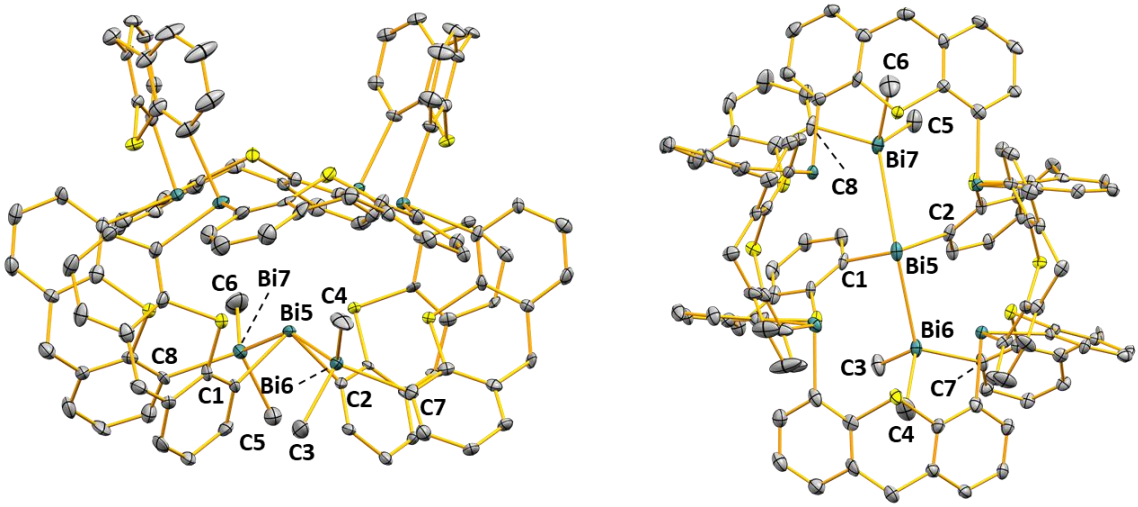


Figure S25. Side view (left) and top view (right) of the molecular structure of **4-Bi** in the solid state. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms, the $[BiMe_2(SbF_6)_2]^-$ anion and all non-bismuth-bound CH_3 and *t*Bu groups are omitted for clarity.

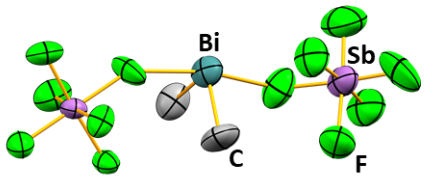


Figure S26. Molecular structure of the $[BiMe_2(SbF_6)_2]^-$ anion in the solid state. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms and split positions of disordered groups are omitted for clarity.

Compound 4-Al

Single-crystals of **4-Al** suitable for sc-XRD precipitated from the *n*-pentane washing solution within 24 h at room temperature. The molecular structure of **4-Al** in the solid state has been discussed in the main text. Additional bond lengths and angles are given in Figure S27. Within the main molecule, multiple disordered *t*Bu-groups are present. Aside from that, the unit cell contains multiple disordered solvent molecules (up to 9 *n*-pentane molecules for single-crystals that grow from the *n*-pentane washing solution) that occupy channels along the crystallographic a and c axis which have been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.

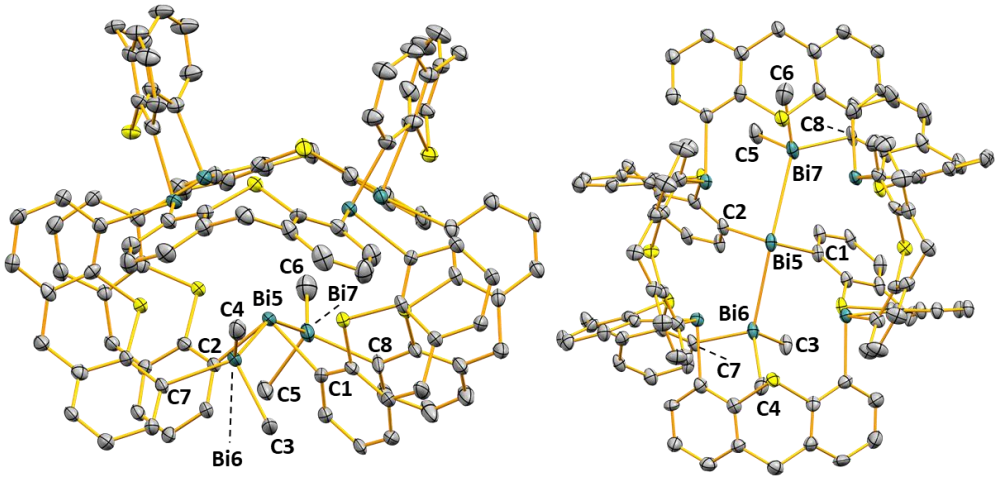


Figure S27. Side view (left) and top view (right) of the molecular structure of **4-Al** in the solid state. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms, the $[BiMe_2(SbF_6)_2]^-$ anion and all non-bismuth-bound CH_3- and *t*Bu-groups are omitted for clarity. Selected bond lengths (Å) and angles (°): Bi7–Bi5, 3.3264(8); Bi6–Bi5, 3.2017(8); Bi6–C7, 2.256(6); Bi6–C4, 2.191(8); Bi6–C3, 2.226(6); Bi7–C5, 2.226(7); Bi7–C6, 2.190(8); Bi7–C8, 2.238(6); Bi5–C1, 2.251(6); Bi5–C2, 2.246(6); Ø Bi(1,2,3,4)–Bi5 5.0137; Ø S(5-8)–Bi5 3.689; Bi6–Bi5–Bi7, 151.983(14); C1–Bi5–C2, 96.7(2); C7–Bi6–C3, 97.7(2); C3–Bi6–C4, 95.9(3); C4–Bi6–C7, 97.4(3); C8–Bi7–C5, 97.0(2); C5–Bi7–C6, 99.2(3); C6–Bi7–C8, 98.0(2).

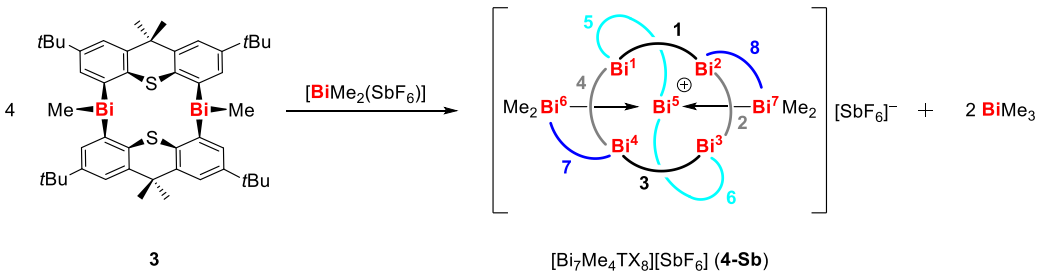
Optimization of the stoichiometric reaction of $[BiMe_2(SbF_6)]$ with $(BiMe)_2TX_2$ (3)

The ideal stoichiometry for the transformation of $(BiMe)_2TX_2$ (**3**) with $[BiMe_2(SbF_6)]$ to form the desired product $[Bi_7Me_4TX_8][BiMe_2(SbF_6)_2]$ (**4-Bi**) should be two equivalents of **3** and one equivalent of the bismuth cation, as presented in the main text. In attempts to optimize the yield of 4-Bi, the impact of varying stoichiometries on the yield of the reaction were investigated. The yield changes only slightly with varying ratios of **3**:$[BiMe_2(SbF_6)]$, but the best results were obtained with sub-stoichiometric amounts of $[BiMe_2(SbF_6)]$ (see Table S2).

Table S2. Impact of varying ratios of the starting materials **3** and $[BiMe_2(SbF_6)]$ on the isolated yield of **4-Bi**. The reactions were performed in DCM.

Entry	equiv. $[BiMe_2(SbF_6)]$	Yield [%]
1	1.0	27
2	0.75	25
3	0.5	22
4	0.25	29

The analysis of simple approaches to the $[Bi_7Me_4TX_8]^+$ cation suggest the reaction shown in Scheme S3 as a straightforward solution. In this approach, a 4:1 stoichiometry of **3** and $[BiMe_2(SbF_6)]$ would generate the desired heptanuclear complex cation with an $[SbF_6]^-$ counteranion, the hypothetical compound **4-Sb**. However, independent of the initial ratio of the starting materials **3** and $[BiMe_2(SbF_6)]$, the more complex $[BiMe_2(SbF_6)_2]^-$ anion instead of the simpler $[SbF_6]^-$ moiety was always observed, i.e. **4-Bi** was isolated and **4-Sb** could not be detected, giving further evidence of the complexity of this reaction.
In attempts to identify the side products formed during the synthesis of **4-Bi**, only H_2TX[20] could unambiguously be identified, a side product that further supports the hypothesis of Bi–aryl homolysis in these reactions.



3 $[Bi_7Me_4TX_8][SbF_6]$ (**4-Sb**)

Scheme S3. Schematic representation of a reasonable reaction of four equivalents of **3** with one equivalent of $[BiMe_2(SbF_6)]$ to form one entity of the characterised $[Bi_7Me_4TX_8]^+$ cation. Note: the shown generic compound **4-Sb** could not be isolated or detected.

Test of potential templating agents

for the condensation reaction of $(BiMe_2)_2TX$ (1)

As noted in the main text, $TlBAr^F$ is used as a templating agent to initiate the condensation reaction of compound **1** to form **2** and subsequently **3**. Other combinations of alkali metal cations such as Li, Na, K, Cs, Tl, Cu, and Ag with weakly coordinating anions like $B(C_6F_5)_4$, BAr^{Cl} (BAr^{Cl} = $B(3,5\text{-}Cl_2C_6H_3)_4$)) and non-innocent anions such as BPh_4^-, OTf^-, NO_3^-, Cp^-, F^-, and I^- were also tested as possible templates (see Table S3). $TlBAr^F$ proved to be the best reagent regarding the yield and purity of the desired product **2** (entry 11). While many of the tested reagents showed some promising results, most of these transformations do not lead to a clean product (e.g.: entry 5-10, 12-14), or proofed to be completely unreactive (e.g.: entry 1-4, 15, 24, 26, 36, 38). The experiments were typically performed in a 1:2 ratio of compound **1** : Lewis acid.

Table S3. Tested combinations of different templating agents, solvents and temperatures with compound **1**. DFB = 1,2-difluorobenzene.

Entry	Reagent	Solvent	Temperature	Observation
1	LiOTf	C_6D_6	rt	[a]
2		C_6H_6 / Et_2O (50:1)	80 °C	[a]
3		C_6H_6	80 °C	[a]
4		C_6H_6 / H_2O (1:4)	80 °C	[a]
5	$LiB(C_6F_5)_4$	CD_2Cl_2 / $CDCl_3$ / Et_2O	rt	[b]
6	$NaBAr^F$	$CDCl_3$	rt	[b]
7	$KB(C_6F_5)_4$	CD_2Cl_2	rt	[f]
8	$CsBAr^{Cl}$	DFB	rt	[d]
9		CD_2Cl_2	60 °C	[e]
10		$CDCl_3$ / THF-D_8	rt / 60 °C	[c]
11	$TlBAr^F$	DFB	rt	selective formation of **3**
12	$TlBAr^{Cl}$	DFB	rt	[d]
13	$TlBPh_4$	DFB	80 °C	[c]
14	$TlNO_3$	DFB	60 °C	[c]
15	TlCp	C_6D_6	rt	[a]
16	$AgNO_3$	CD_2Cl_2	rt	[g]
17		CD_2Cl_2	60 °C	[g]
18		C_6D_6	rt	[g]
19		C_6D_6	80 °C	[f]
20	AgOTf	CD_2Cl_2	rt	[g]
21		CD_2Cl_2	60 °C	[f]
22		C_6D_6	rt	[g]
23		C_6D_6	80 °C	[f]
24	AgF	CD_2Cl_2	rt	[a]
25		CD_2Cl_2	60 °C	[h]
26		C_6D_6	rt	[a]
27		C_6D_6	80 °C	[h]
28	$AgBF_4$	CD_2Cl_2	rt	[f]
29		CD_2Cl_2	60 °C	[f]
30		C_6D_6	rt	[f]
31		C_6D_6	80 °C	[f]
32	$AgSbF_6$	CD_2Cl_2	rt	[f]
33		CD_2Cl_2	60 °C	[f]
34		C_6D_6	rt	[e]
35		C_6D_6	80 °C	[e]
36	CuI	CD_2Cl_2	rt	[a]
37		CD_2Cl_2	60 °C	[h]
38		C_6D_6	rt	[a]
39		C_6D_6	80 °C	[h]
40	$[Cu_2(OTf)_2(C_6H_5CH_3)]$	CD_2Cl_2	rt	[f]
41		CD_2Cl_2	60 °C	[f]
42		C_6D_6	rt	[g]
43		C_6D_6	80 °C	[f]
44	$[Cu(MeCN)_4][OTf]$	CD_2Cl_2	rt	[f]
45		CD_2Cl_2	60 °C	[f]
46		C_6D_6	rt	[f]
47		C_6D_6	80 °C	[f]

[a] no reaction could be observed. [b] mixture of non-converted starting material, $(BiMe)_2TX_2$ (**3**), $[Bi_7Me_4TX_8][A^-]$ (A^- being the corresponding anion) and large amounts of side-products. [c] decomposition. [d] no substance could be isolated. [e] desired product **3** can be observed via ^{1}H NMR spectroscopy, but large amounts of side-products were also detected. [f] mixture of non-converted starting material, desired product **3**, and unidentified side-products. [g] mixture of non-converted starting material, low amounts of desired product **3**, and unidentified side-products. [h] mixture of non-converted starting material and traces of decomposition.

Additional structural details for $[Bi_7Me_4TX_8]^+$ (compound 4-Bi, 4-Al)

Due to the complex constitution of **4-Bi** and **4-Al** only a simplified Lewis and crystal structure was presented in the main text. To emphasize the volumetric ball type structure of the $[Bi_7Me_4TX_8]^+$ cation, all bridging TX moieties are shown in Figure S28, Figure S29, and Figure S30.

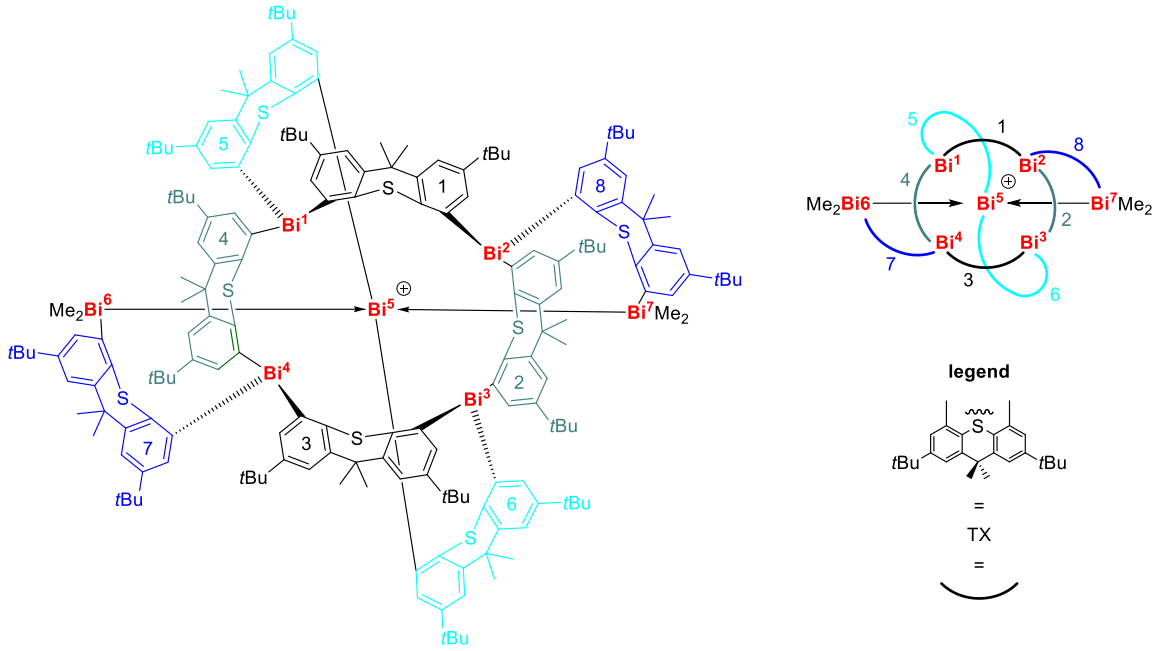


Figure S28. Left: Lewis structure of the $[Bi_7Me_4TX_8]^+$ cation without the corresponding anion ($[BiMe_2(SbF_6)_2]^-$ for **4-Bi**, $AlCl_4^-$ for **4-Al**). Right: Simplified connectivity scheme of the $[Bi_7Me_4TX_8]^+$ cation with color-coding of the different types of bridging thioxanthene moieties. Both illustrations are oriented the same way to emphasize the simplified connectivity scheme used in the main text.

In case of the Lewis structure, the color-coding represents the four different binding types of the TX organic framework that is present in the molecule. Four of the TX substituents are part of a Bi_4TX_4 ring (two TX moieties (TX1 and TX3) are orthogonal to the plane defined by the atoms Bi1-4 and two TX moieties (TX2 and TX4) are oriented along this plane). The other four TX ligands (TX5-8) point away from TX1 and TX3, while two of them are bound to Bi5 (TX5 and TX6) and the other two (TX7 and TX8) are bound to dimethyl bismuthyl units. As a consequence, the bismuth atoms Bi1-4 are each bound to three different TX substituents, whereas bismuth atoms Bi6 and Bi7 are each bound to one TX moiety and two methyl groups. The charge-carrying bismuth atom Bi5 is covalently bound to two TX substituents (TX5 and TX6). At the same time two dative bonds originating from the bismuth atoms Bi6 and Bi7 towards the central cation Bi5 stabilize the bismuth cation.

A representation of the volumetric ball-type structure of the $[Bi_7Me_4TX_8]^+$ cation is shown in Figure S29 and Figure S30. The molecule has a radius of approx. 9 Å, and all bismuth atoms are shielded by the organic framework (see Figure S29).

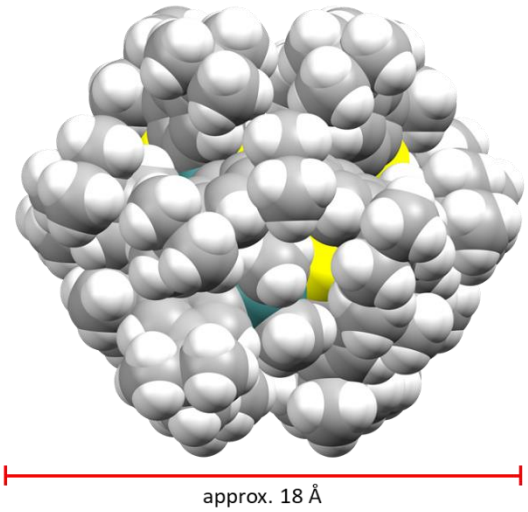


Figure S29. Side view of the space-filled model of $[Bi_7Me_4TX_8][AlCl_4]$ (**4-Al**) without the corresponding anion along the central Bi6–Bi5–Bi7 bond axis (white sphere = hydrogen, grey sphere = carbon, yellow sphere = sulfur, cyan sphere = bismuth).

Figure S30 represents an orientation that allows a look inside the $[Bi_7Me_4TX_8]^+$ molecule. The incorporated void has a volume of 350 $Å^3$ (approximated by an idealized cylinder). The central Bi cation is located at the bottom of a cavity, that is formed by the folded thioxanthene moieties.

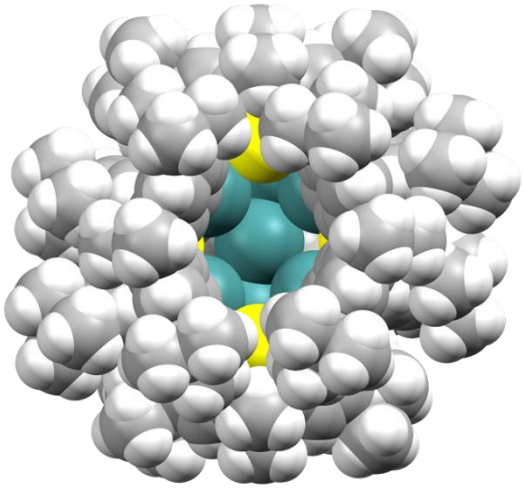


Figure S30. Top view of the space-filled model of$[Bi_7Me_4TX_8][AlCl_4]$ (**4-Al**), without the corresponding anion, towards the central Bi5 cation, emphasizing the void inside the molecule. The four equatorial bismuth atoms Bi1-4 are also clearly visible (white sphere = hydrogen, grey sphere = carbon, yellow sphere = sulfur, cyan sphere = bismuth).

UV/vis-spectrum of 4-Bi

As mentioned in the main text, compound **4-Bi** is intensely red colored. In order to quantify the optical properties, a UV/vis-spectrum was recorded at ambient temperature in THF with a concentration of 0.04825 mmol/mL. The spectrum is shown in Figure S31.

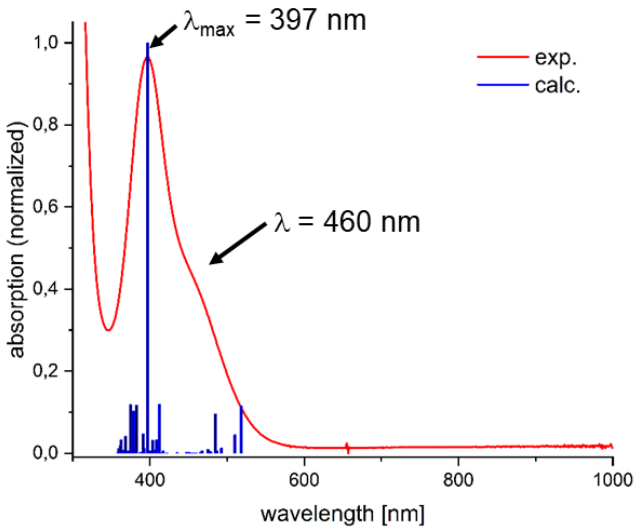


Figure S31. UV/vis spectrum of **4-Bi** in THF at a concentration of 0.04825 mmol/mL. The small signal at λ = 656 nm is attributed to the change of the light source inside the UV/vis spectrometer. The blue bars represent the first 50 calculated main transitions to the overall spectrum (level of theory: B3LYP, 6-31++G / LanL2DZ (Bi), GD3BJ, SCRF=PCM (THF)).

Two distinct features are visible: a main absorption band with its amplitude at λ_{max} = 397 nm and a less pronounced shoulder at λ = 460 nm. These two absorptions are responsible for the red color of the compound. Aside from these signals, the beginning of a strong absorption band at approx. λ = 300 nm, that reaches into the UV region of the electromagnetic spectrum, can be observed and is most likely caused by the absorption of the aromatic ring systems within the molecule.
To get further inside into the optical properties of **4-Bi**, simple quantum chemical calculations (B3LYP, 6-31++G / LanL2DZ (Bi), GD3BJ, SCRF=PCM (THF)) were performed that evaluate the corresponding transitions leading to the observed color. The calculations were performed with all *t*Bu-groups replaced by hydrogen atoms as they massively contribute to the overall complexity of the calculations without improving the quality of the computed properties. They mainly act as solubility-mediating moieties.
As expected, the LUMO+1 is mainly localized at the Bi5-cation with some contributions of the adjacent Bi6 atom, whereas the HOMO-11 has its main contributions by the Bi7-atom and one bismuth moiety of the equatorial plane (see Figure S32 for a graphical representation of the orbitals). Most of the calculated transitions involve the LUMO+1 and the main contribution (32%) to the overall main absorption band is attributed to the HOMO-11 to LUMO+1 transition. Nevertheless, due to the complex molecular structure, many contributions of low-lying HOMO-n orbitals are responsible for the observed optical properties. Further calculations with cam-B3LYP, LC-ωHPBE and wB97XD functionals yielded the same trends with same involved orbitals, but slightly different contributions and absorption maxima.

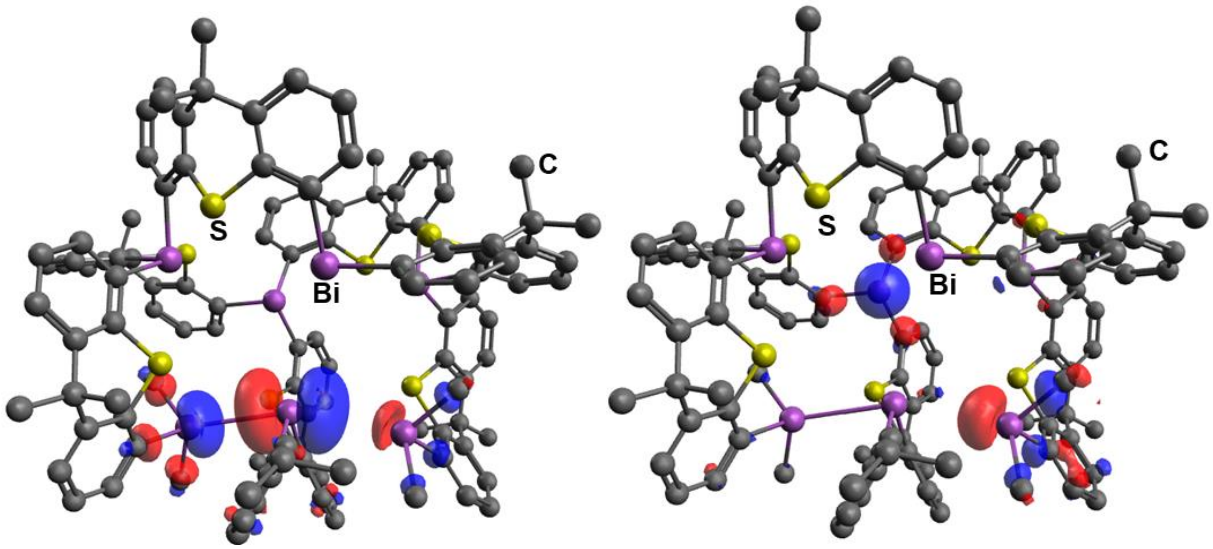
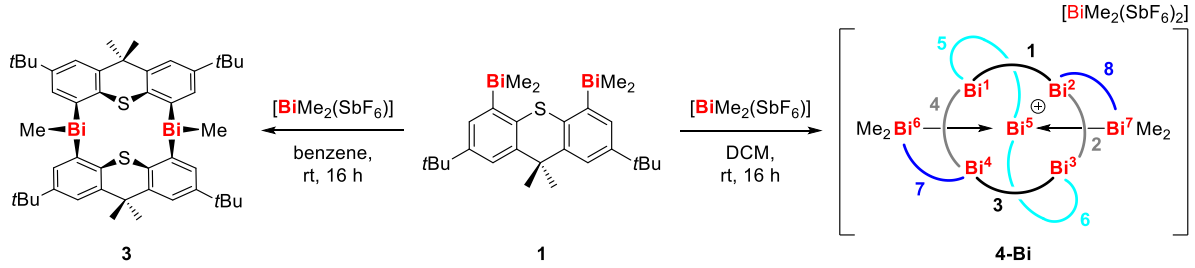


Figure S32. **Left**: LUMO+1 (–2.066 eV) and **right**: HOMO-11 (–6.460 eV) of compound **4-Bi** displayed at an iso-value of 0.04. Parts of one TX moiety and the $[BiMe_2(SbF_6)_2]$ anion were omitted for clarity. Calculated at B3LYP, 6-31++G / LanL2DZ (Bi), GD3BJ, SCRF=PCM (THF) level of theory.

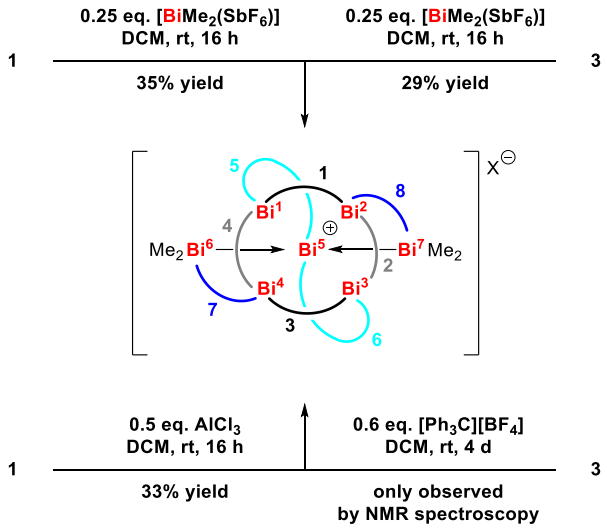
Studies on solvent effects and type of Lewis acid for the transformation of 1 or 3 to $[Bi_7Me_4TX_8][X]$

As mentioned in the main text, different reaction pathways could be observed when treating **1** with $[BiMe_2(SbF_6)]$ in benzene or DCM, respectively, leading either to the formation of **3** or the generation of **4-Bi** (Scheme S4).



Scheme S4. Solvent-dependent product formation of either **3** or **4-Bi** when treating **1** with $[BiMe_2(SbF_6)]$ in benzene or DCM.

This shows that a solvent-dependent reaction pathway is observed. The dependency of product formation on the type of solvent used is widely known in literature. Examples are found for oxidative ring opening reactions,[43] iodoalkynation mediated by Pd(0),[44] ene-reactions,[45] enantiodivergent Friedel crafts and Mannich type reactions,[46] Pt(II) mediated CO_2 reduction,[47] in combinatorial chemistry,[48] and Rh-catalyzed rearrangement reactions,[49] for instance. In the case of bismuth, examples are scarce and have been investigated for the formation of bismuth metal-organic-frameworks.[50] During the formation of compound **4-Bi**, its solubility in weakly coordinating solvents such as DCM seems to be important, which is fostered by the presence of *t*-butyl groups in the ligand backbone. In the reactions leading to **3** and **4-Bi**, the $BiMe_2^+$ cation most likely serves as a strong CH_3-anion-abstractor that initializes the reaction. In order to experimentally confirm this assumption, $[Ph_3C][BF_4]$ was also reacted with **3** and the same color change to a bright red solution was observed (Scheme S5 – bottom right). Similar to **4-Bi** or **4-Al**, characteristic resonances for the $[Bi_7Me_4TX_8]^+$ cation could be detected in the ^1H NMR spectra, but no substance could be isolated in pure form to date.



Scheme S5. Convergent synthetic routs that lead to the observed $[Bi_7Me_4TX_8]$ cation.

Because the $BiMe_2^+$ cation is, aside of its CH_3-anion-abstractor capabilities, also a soft Lewis acid,[21,51] we tested the reaction of **1** with other main group 13 halogenides such as $AlCl_3$, $BBr_3{\bullet}SMe_2$, $GaCl_3$, $InCl_3$, but only in the case of $AlCl_3$ a product could be isolated. In analogy to $[BiMe_2(SbF_6)]$, the reaction of $AlCl_3$ with **1** in DCM leads to the direct conversion of **1** to **4-Al** in yields of 33% after workup (*vide infra*; see Scheme S5 – bottom left). Surprisingly, again the $TX_8Bi_7^+$ cation is formed and only the anion changes (**4-Bi**: $[BiMe_2(SbF_6)_2]$; **4-Al**: $AlCl_4$), leading us to the conclusion that this heptanuclear species may be a

thermodynamic sink of a complex reaction pathway, that is very similar in both cases. To explain the formation of the $AlCl_4$ anion, a simple reaction equation may be used: 8 $(BiMe_2)_2TXMe_4$ (**1**) + 2 $AlCl_3$ → $[Bi_7Me_4TX_8][AlCl_4]$ (**4-Al**) + 9 $BiMe_3$ + $AlMeCl_2$, that also reasons why two equivalents of $AlCl_3$ are necessary for the highest yield of this transformation. Unfortunately, the expected side product $AlMeCl_2$ could not be detected *via* high resolution mass spectrometry so far, as the applied conditions may be too harsh.

Computational details

General Considerations

DFT calculations were performed for $BiMe_3$, **1**, $[(BiMe)_2TX_2Tl]^+$ (compound **2** without the corresponding BAr^F anion), **3** and **4-Bi** with the Gaussian 16, Revision C.01 program package.[52] These were done with the B3LYP,[53] cam-B3LYP,[54] LC-ωHPBE[55] or wB97XD[56] functionals and the 6-311++G(d,p)[57,58,59,60] (H, C, S) and LanL2DZ[61] (Bi, Tl) (for compounds $BiMe_3$, **1**, **2** and **3**) **or** the 6-31++G[57,59,60] (H, C, S, F, Cl, Al) and LanL2DZ[61] (Bi, Sb) (for compound **4-Bi** and **4-Al**) basis sets. All geometries reported herein are characterized as minimum energy structures as no imaginary frequencies were found. In case of the NBO calculations done for the $[(BiMe)_2TX_2Tl]^+$ cation, the NBO 7.0 (NBO = Natural Bond Orbitals) software package was used.[62] Gibbs free energies were calculated at a temperature of 298.15 K and a pressure of 1.00 atm. For compound **4-Bi** and **4-Al**, calculations were performed with all *t*Bu-groups replaced by hydrogen atoms as they massively contribute to the overall complexity of the calculations without improving the quality of the computed properties. All computed energies of the bismuth compounds reported herein are listed in **Table S4**. Cartesian coordinates of optimized structures are provided at the end of this document.

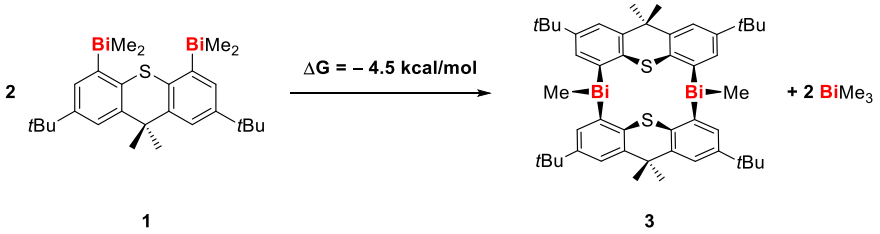
Table S4. Energies of the computed bismuth compounds. Level of theory: B3LYP/6-311++G(d,p); LANL2DZ (Bi, Tl) (for **1**, **2** to **3**) **or** B3LYP/6-31++G; LANL2DZ (Bi, Sb) (for **4-Bi** or **4-Al**).

Entry	Compound	*H* [hartree]	*G* [hartree]
1	$BiMe_3$	-125.097874	-125.141414
2	$(BiMe_2)_2TX$	-1461.715110	-1461.830314
3	$[(BiMe)_2TX_2Tl]^+$	-2724.716064	-2724.878376
4	$(BiMe)_2TX_2$	-2673.231828	-2673.384965
5	$[Bi_7Me_4TX_8][BiMe_2(SbF_6)_2]$[a]	-9304.493026	-9304.876063
6	$[Bi_7Me_4TX_8][AlCl_4]$[a,b]	-10043.257645	-10043.597532
7	$[Bi_7Me_4TX_8]^+$ [a]	-8007.083704	-8006.766960

a: for the calculation of the heptanuclear species, the *t*Bu groups were replaced by H atoms to safe computational resources.
b, the frequency analysis was performed with a 3-21G basis set for C, H, Al, S, Cl atoms (rather than 6-31++G applied in the other cases of heptanuclear species) to safe computational resources.

Stability of 2 and 3

As $TlBAr^F$ does not seem to be necessary for stability of the Tl-containing dinuclear species **2** (see main text for further information), we concluded that the dimerization of two entities of **1** to form **3** is thermodynamically favoured but kinetically hindered (see Scheme S6). To gain further insight into the driving force of this transformation, we compared the relative energies of the starting materials (two entities of **1**) with the respective products (two entities of $BiMe_3$ and one dimer of **3**) and found a small thermodynamic driving force of –4.5 kcal/mol for the calculated free energies.



Scheme S6. Formal dimerization of two molecules of **1** to form one entity of **3** and two $BiMe_3$ moieties. Level of theory: B3LYP, 6-311++G(d,p), LANL2DZ (Bi).

However, as no evidence was found that **1** dimerises by itself even at elevated temperatures of 100 °C (see main text for further information) we concluded that the Tl cation is acting as a necessary template to facilitate the condensation reaction. In order to address this hypothesis, we performed quantum

chemical calculations with subsequent NBO analysis of the corresponding interactions between the Tl-free moiety (formally compound **3**) and the Tl cation (see Figure S33). Interestingly, three distinct interactions could be observed that relate to different parts of the molecule: I.) Bismuth-based donors containing bismuth atoms themselves and corresponding Bi–C bonds acting as donors, II.) Sulfur-based donors and S–C bonds, and III.) Carbon-based donors, and C–C as well as C–H bonds acting as donors. Each class contributes with a different amount (I.: 16.5 kcal/mol, II.: 27.99 kcal/mol, and III.: 43.93 kcal/mol) to the total interaction energy of 88.42 kcal/mol between the $(BiMe)_2TX_2$ moiety and the Tl cation. Nevertheless, the main contributions to the overall interaction originate from the carbon framework and adjacent π-systems of the organic ligand. These findings are in accordance with previous results for a somewhat similar observation of a bismepine acting as a ditopic arene donor for a Tl cation.[25] Because of these circumstances, we assume that the Tl cation is responsible for a pre-coordination of two distinct moieties of **1**, which then dimerize with elimination of two equivalents of $BiMe_3$, without the formation of new strong bonds to the Tl cation during the actual reaction steps.

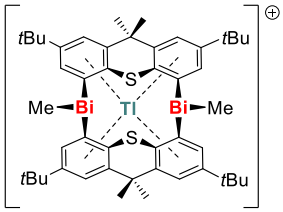


Figure S33. Tl-cation containing dinuclear bismuth species that was used for NBO analysis.

Inversion of 3

Because the ^{1}H- and ^{13}C NMR spectroscopic signals for C5, C5', C6 and C6' atoms indicate, due to their magnetic inequivalence, a non-planar structure in solution, we performed VT NMR studies (see main text for further information) to investigate a possible dynamic behaviour in solution. However, no inversion of the bowl-shaped structure was observed experimentally within the scanned temperature window of room temperature to 100 °C. In order to support these findings with quantum chemical analyses, calculations were performed that scanned the hypersurface by varying one C–Bi–C angle stepwise (see Figure S34 and Table S5).

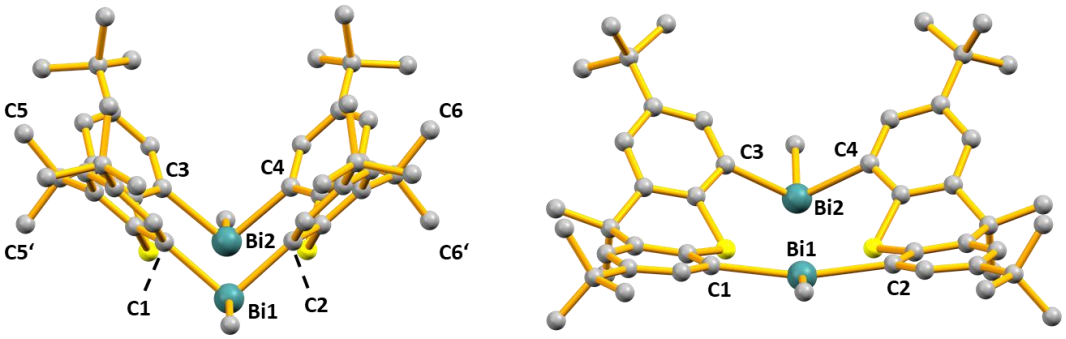


Figure S34. Left: optimised geometry of **3** in the gas phase, whereas the C1–Bi1–C2 angle is 96.0146° and the C3–Bi2–C4 angle is 96.0151°. Right: scanned geometry of **3** with the highest relative energy in the gas phase with an C1–Bi1–C2 angle of 166.0145° and an C3–Bi2–C4 angle of 112.2713°, respectively. Level of theory: B3LYP/6-311++G(d,p); LANL2DZ (Bi, Tl). All hydrogen atoms are included in the calculations but not shown.

As expected, by applying a forced geometry around the bismuth atom Bi1 also leads to modifications in the coordination geometry around Bi2 and to an overall widened structure of the macrocycle. As a result, a significant increase in relative energy is observed, when compared to the non-strained species (see Figure S34 and Table S5). The highest energy within this context was found to be approx. 60.92 kcal/mol

with an C1–Bi1–C2 angle of 166.0145° and an C3–Bi2–C4 angle of 112.2713°, making it very unlikely that a ring inversion will take place even at elevated temperatures.
It must be noted that the geometry of **3** collapsed upon going from step 15 to 16, which can be seen in Table S5 with a sudden decrease of relative energy and a smaller C3–Bi2–C4 angle. Because of this circumstance no further quantum chemical investigations for a possible transition state, concerning the ring inversion, were made.

Table S5. Scanned C1–Bi1–C2 angles of **3** with the corresponding C1–Bi1–C2 angles and the relative energies. Level of theory: B3LYP/6-311++G(d,p); LANL2DZ (Bi).

step	C1–Bi1–C2 angle [°]	C3–Bi2–C4 angle [°]	relative energy [kcal/mol]
1	96.0146	96.0151	0.0
2	101.0145	96.9308	0.430
3	106.0146	97.8399	1.839
4	111.0145	98.8828	3.732
5	116.0145	99.9852	6.264
6	121.0145	101.1543	9.405
7	126.0145	102.3600	13.133
8	131.0145	103.5973	17.426
9	136.0145	104.8606	22.232
10	141.0145	106.1821	27.590
11	146.0145	107.4687	33.441
12	151.0145	108.7441	39.751
13	156.0145	110.0426	46.474
14	161.0146	111.2281	53.557
15	166.0145	112.2713	60.923
16	171.0146	102.2722	51.481
17	176.0144	101.7117	57.750

Bi→Bi donor acceptor interaction

As noted in the main text, an asymmetric binding motif of a Bi→Bi←Bi unit was observed in the solid-state structure of **4-Al**. Due to a similar behaviour of **4-Bi** (for which the bonding parameters can formally not be discussed due to the low quality of the X-ray data) we investigated these findings with quantum chemical calculations to get further inside into the responsible interactions. Interestingly, when optimizing the $[Bi_7Me_4TX_8]$ cation without any adjacent counteranion a fully symmetrical Bi→Bi←Bi unit is obtained, as shown by highly similar Bi–Bi bond lengths of 3.420 Å and 3.421 Å for the Bi→Bi donor-acceptor interactions (see Figure S35). As soon as a counteranion is introduced, the observations made by sc-XRD of **4-Al** are reproduced (see Figure S36). The calculations show a much more pronounced asymmetric binding motif, with the difference in bond lengths (Bi5–Bi6 vs. Bi5–Bi7) being exaggerated by the calculations (**4-Bi**: Δ = 0.3 Å; **4-Al**: Δ = 0.572 Å) in comparison to those obtained from single-crystal XRD analyses (**4-Al**: Δ = 0.125 Å). Nevertheless, the overall trend is confirmed by quantum chemical analysis, whereas the shortest contacts between the Bi-containing heptanuclear cation and the anion are most likely between carbon bound hydrogen atoms and the corresponding halogen (F in case of **4-Bi** and Cl in case of **4-Al**; Figure S36 shows the shortest carbon–halogen distance as no distinct CH-interaction was found for **4-Al**). Interestingly, without a directional interaction with an adjacent counteranion, the Bi–Bi–Bi angle is at its maximum of 162.96° (Figure S35). As soon as an asymmetric Bi→Bi←Bi binding motif is introduced by the corresponding anion, the Bi–Bi–Bi angle becomes more acute (Bi–Bi–Bi **4-Bi**: 161.58°; **4-Al**: 158.32°) with increasing cation-anion interaction strength.

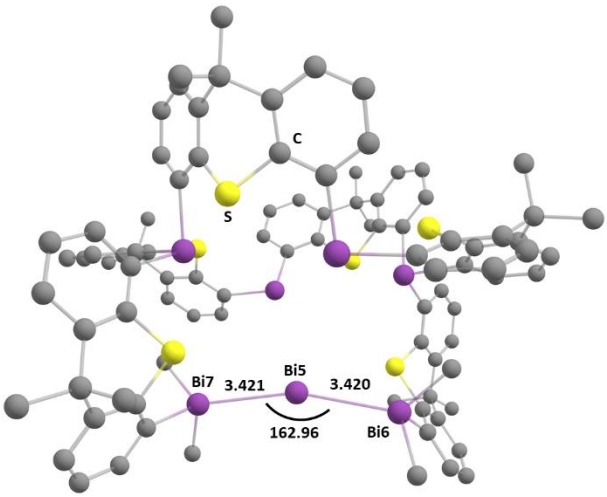


Figure S35. Optimised structure of the [$Bi_7Me_4TX_8$] cation with selected bond distances [Å] and angles [°]. Note: All hydrogen atoms and two TX-moieties that were bound to Bi5 were omitted for clarity. All calculations were done with the corresponding atoms/units. Level of theory: B3LYP/6-31++G; LANL2DZ (Bi). For the calculation of the heptanuclear species, the *t*Bu groups were replaced by H atoms to safe computational resources.

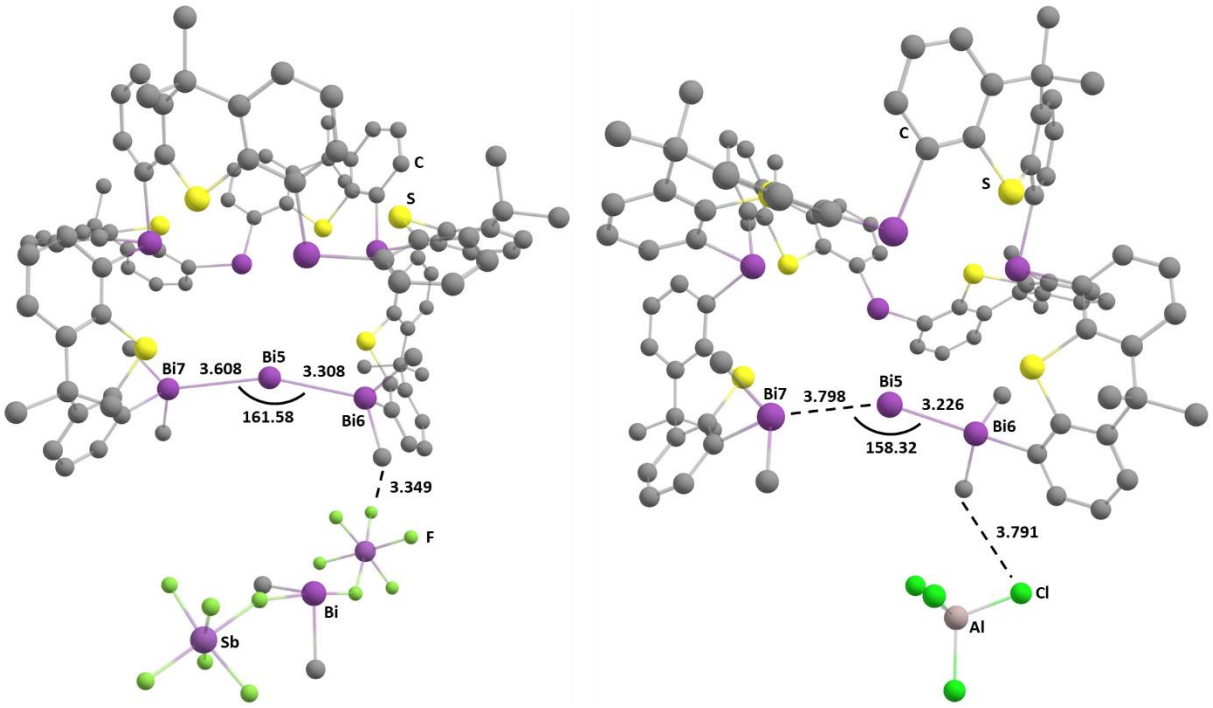


Figure S36. Optimised structure of **4-Bi** (left) and **4-Al** (right) with selected bond distances [Å] and angles [°]. Note: All hydrogen atoms and two TX-moieties that were bound to Bi5 were omitted for clarity. All calculations were done with the corresponding atoms/units. Level of theory: B3LYP/6-31++G; LANL2DZ (Bi, Sb). For the calculation of the heptanuclear species, the *t*Bu groups were replaced by H atoms to safe computational resources.

Cartesian coordinates (Ångstrøm)

$BiMe_3$

Bi	-0.000075000	0.000031000	0.314730000
C	1.128813000	1.531837000	-0.902515000
H	0.762504000	2.531570000	-0.662821000
H	2.192244000	1.477815000	-0.663118000
H	0.984563000	1.336306000	-1.965819000
C	0.762698000	-1.743356000	-0.902345000
H	0.184960000	-2.637692000	-0.662562000
H	0.665009000	-1.520973000	-1.965684000
H	1.811899000	-1.925242000	-0.663101000
C	-1.890873000	0.211263000	-0.902855000
H	-1.648996000	0.185620000	-1.966112000
H	-2.572813000	-0.606846000	-0.664532000
H	-2.376958000	1.158403000	-0.662512000

$(BiMe_2)_2TX$ (1)

Bi	-2,720066000	-2,107735000	-0,144494000
S	0,006812000	-0,240506000	-1,138233000
C	-4,972631000	-2,135480000	0,031477000
H	-5,292054000	-3,178194000	0,089281000
H	-5,420467000	-1,678365000	-0,852214000
H	-5,306952000	-1,612600000	0,928105000
C	-2,546363000	0,159440000	-0,191263000
C	-3,615858000	0,960625000	0,217903000
H	-4,530751000	0,482506000	0,539940000
C	-3,528442000	2,355024000	0,243843000
C	-2,331547000	2,934178000	-0,195610000
H	-2,253355000	4,011720000	-0,189833000
C	-1,246201000	2,185826000	-0,656256000
C	-1,368726000	0,784284000	-0,618486000
C	0,017593000	2,850921000	-1,240301000
C	0,015179000	2,660104000	-2,787238000
H	0,011121000	1,609193000	-3,074076000
H	-0,871198000	3,135090000	-3,216586000
C	0,023202000	4,369698000	-0,990302000
H	0,898060000	4,827839000	-1,454425000
C	2,561717000	0,140770000	-0,192005000
C	3,639063000	0,933454000	0,212781000
H	4,550047000	0,448230000	0,534945000
C	3,563381000	2,328848000	0,235523000
C	2,370379000	2,917404000	-0,201721000
H	2,301038000	3,995569000	-0,197123000
C	1,277876000	2,177210000	-0,658983000
C	1,389379000	0,775139000	-0,620183000
H	0,903986000	3,128711000	-3,218554000
H	0,025456000	4,619653000	0,073615000
H	-0,849493000	4,834096000	-1,452283000

Bi	2,710432000	-2,128120000	-0,151827000
C	4,936682000	-2,184360000	0,229588000
H	5,231014000	-3,230746000	0,335206000
H	5,473120000	-1,752414000	-0,616691000
H	5,194992000	-1,649588000	1,144158000
C	-4,680040000	3,257932000	0,725237000
C	-5,911077000	2,448806000	1,173459000
C	-4,202917000	4,107404000	1,926519000
C	-5,117626000	4,196838000	-0,423498000
H	-6,321613000	1,845284000	0,359446000
H	-5,678924000	1,783966000	2,009874000
H	-6,697378000	3,132579000	1,505044000
H	-3,357076000	4,746557000	1,662802000
H	-5,012023000	4,754413000	2,279994000
H	-3,891587000	3,467586000	2,756840000
H	-5,937352000	4,843565000	-0,094877000
H	-4,300125000	4,840252000	-0,757084000
H	-5,463642000	3,621413000	-1,286631000
C	4,723826000	3,222925000	0,712270000
C	4,257456000	4,077568000	1,914117000
C	5,949714000	2,404390000	1,157480000
C	5,165388000	4,157022000	-0,438856000
H	3,415949000	4,723221000	1,652367000
H	3,943638000	3,441203000	2,746157000
H	5,072894000	4,718407000	2,264277000
H	6,352515000	1,796380000	0,342941000
H	6,742697000	3,082177000	1,485433000
H	5,715055000	1,742540000	1,995538000
H	5,991471000	4,797307000	-0,113552000
H	5,503879000	3,577895000	-1,302499000
H	4,352160000	4,806812000	-0,770504000
C	-2,411774000	-2,238317000	2,088994000
H	-1,365812000	-2,040959000	2,324836000
H	-3,042355000	-1,500901000	2,585647000
H	-2,675672000	-3,241293000	2,429815000
C	2,198320000	-2,279277000	2,042098000
H	2,417212000	-3,289305000	2,393690000
H	2,789015000	-1,555370000	2,603244000
H	1,137384000	-2,070599000	2,180634000

$[(BiMe)_2TX_2Tl]^+$ (2 without the BAr^F anion)

Bi	-2.776272000	-0.003496000	-2.200861000
S	-0.002297000	2.036775000	-1.663579000
C	-5.022591000	-0.007016000	-2.170152000
H	-5.359793000	-0.895927000	-2.705677000
H	-5.362595000	0.880421000	-2.706357000
H	-5.451412000	-0.007332000	-1.169153000
C	-2.550477000	1.681415000	-0.658819000

S	0.002743000	-2.038139000	-1.664235000
C	-3.612964000	2.008838000	0.190273000
H	-4.524632000	1.431682000	0.131415000
C	-3.531914000	3.051993000	1.117646000
C	-2.342265000	3.791892000	1.152574000
H	-2.270070000	4.608897000	1.855269000
C	-1.261164000	3.541622000	0.304401000
C	-1.381130000	2.455297000	-0.586193000
C	-0.005040000	4.437376000	0.290000000
C	-0.005356000	5.293466000	-1.012420000
H	-0.004552000	4.686307000	-1.916639000
H	-0.892162000	5.931427000	-1.032566000
C	-0.006272000	5.431919000	1.464486000
H	0.865742000	6.084841000	1.409627000
C	-2.545323000	-1.686546000	-0.657516000
C	-1.374723000	-2.458666000	-0.585898000
C	-1.252221000	-3.544454000	0.304997000
C	-2.332022000	-3.796007000	1.154460000
H	-2.257846000	-4.612683000	1.857320000
C	-3.522720000	-3.057760000	1.120717000
C	-3.606315000	-2.015082000	0.193022000
H	-4.518831000	-1.439180000	0.135088000
C	-4.673596000	-3.424614000	2.075576000
C	-4.189736000	-3.293623000	3.538973000
H	-4.997005000	-3.556928000	4.227968000
H	-3.880465000	-2.267779000	3.760026000
H	-3.345934000	-3.953905000	3.752609000
C	-5.900117000	-2.512587000	1.891884000
H	-6.316501000	-2.583993000	0.883521000
H	-5.665359000	-1.464045000	2.096437000
H	-6.685085000	-2.812591000	2.590074000
C	-5.115141000	-4.883328000	1.809046000
H	-4.303925000	-5.594988000	1.978685000
H	-5.460441000	-5.006518000	0.779149000
H	-5.937622000	-5.155168000	2.476406000
C	0.005403000	-4.438106000	0.289914000
C	0.005869000	-5.294420000	-1.012351000
H	0.005119000	-4.687450000	-1.916694000
H	0.892709000	-5.932343000	-1.032286000
C	0.006580000	-5.432488000	1.464532000
H	0.006426000	-4.938011000	2.439226000
H	-0.865397000	-6.085465000	1.409672000
C	2.546130000	1.686291000	-0.657620000
C	3.607330000	2.015394000	0.192434000
H	4.520107000	1.439937000	0.134098000
C	3.523614000	3.058047000	1.120130000
C	2.332619000	3.795816000	1.154284000
H	2.258410000	4.612528000	1.857108000

C	1.252629000	3.543794000	0.305215000
C	1.375245000	2.457883000	-0.585533000
H	0.880373000	5.932940000	-1.032003000
H	-0.006230000	4.937558000	2.439243000
H	-0.879305000	6.083424000	1.408994000
C	2.550500000	-1.681715000	-0.658508000
C	1.381378000	-2.455964000	-0.586304000
C	1.261410000	-3.542169000	0.304408000
C	2.342242000	-3.792020000	1.153056000
H	2.269992000	-4.608970000	1.855799000
C	3.531637000	-3.051718000	1.118570000
C	3.612706000	-2.008622000	0.191122000
H	4.524169000	-1.431109000	0.132662000
C	4.683876000	-3.416818000	2.072460000
C	4.200952000	-3.286812000	3.536254000
H	5.009211000	-3.548816000	4.224585000
H	3.890094000	-2.261526000	3.757655000
H	3.358444000	-3.948559000	3.750471000
C	5.908762000	-2.502765000	1.887920000
H	6.324393000	-2.573272000	0.879184000
H	5.672497000	-1.454646000	2.092908000
H	6.694811000	-2.801655000	2.585372000
C	5.127615000	-4.874768000	1.805392000
H	4.317709000	-5.587788000	1.975571000
H	5.472312000	-4.997252000	0.775209000
H	5.951066000	-5.145340000	2.472071000
H	-0.879819000	-5.933956000	-1.031883000
H	0.879662000	-6.083942000	1.409196000
Bi	2.776718000	0.002922000	-2.200677000
C	5.023036000	0.005984000	-2.169968000
H	5.362914000	-0.881621000	-2.705965000
H	5.360355000	0.894728000	-2.705703000
H	5.451861000	0.006456000	-1.168970000
Tl	-0.001226000	0.000572000	1.090336000
C	-4.684454000	3.417653000	2.070981000
C	-5.909555000	2.503983000	1.886052000
C	-4.202187000	3.287725000	3.535005000
C	-5.127548000	4.875695000	1.803468000
H	-6.324788000	2.574540000	0.877148000
H	-5.673742000	1.455795000	2.091214000
H	-6.695795000	2.803179000	2.583171000
H	-3.359604000	3.949292000	3.749488000
H	-5.010680000	3.550052000	4.222937000
H	-3.891711000	2.262384000	3.756697000
H	-5.951235000	5.146669000	2.469699000
H	-4.317485000	5.588475000	1.973930000
H	-5.471716000	4.998149000	0.773095000
C	4.674670000	3.425422000	2.074597000

C	4.191340000	3.294082000	3.538147000
C	5.901552000	2.513998000	1.890406000
C	5.115403000	4.884348000	1.808026000
H	3.347359000	3.954034000	3.752113000
H	3.882540000	2.268094000	3.759188000
H	4.998741000	3.557631000	4.226896000
H	6.317558000	2.585693000	0.881900000
H	6.686637000	2.814304000	2.588348000
H	5.667399000	1.465315000	2.094937000
H	5.938042000	5.156522000	2.475062000
H	5.460228000	5.007814000	0.777994000
H	4.303937000	5.595630000	1.978080000

$(BiMe)_2TX_2$ (3)

Bi	2.691020000	-0.000055000	-2.048718000
S	-0.000041000	-2.087521000	-1.515885000
C	4.948731000	-0.000157000	-2.118697000
H	5.268520000	0.888609000	-2.666147000
H	5.268431000	-0.889090000	-2.665926000
H	5.418483000	-0.000057000	-1.135429000
C	2.541502000	-1.694491000	-0.530901000
S	0.000050000	2.087521000	-1.515889000
C	3.613365000	-1.997503000	0.312386000
H	4.520822000	-1.415678000	0.232110000
C	3.538032000	-3.012566000	1.269303000
C	2.347541000	-3.747094000	1.337908000
H	2.276471000	-4.536897000	2.071702000
C	1.261045000	-3.517973000	0.491883000
C	1.374292000	-2.461135000	-0.431257000
C	-0.000097000	-4.407195000	0.518809000
C	-0.000094000	-5.323162000	-0.742167000
H	-0.000081000	-4.750940000	-1.668918000
H	0.887421000	-5.961827000	-0.734289000
C	-0.000121000	-5.348086000	1.737157000
H	-0.873895000	-6.001299000	1.712672000
C	2.541588000	1.694403000	-0.530917000
C	1.374405000	2.461090000	-0.431273000
C	1.261202000	3.517939000	0.491859000
C	2.347714000	3.747033000	1.337872000
H	2.276677000	4.536847000	2.071657000
C	3.538179000	3.012463000	1.269266000
C	3.613467000	1.997386000	0.312359000
H	4.520903000	1.415529000	0.232084000
C	4.694131000	3.345632000	2.231568000
C	4.222165000	3.152616000	3.691794000
H	5.034129000	3.385217000	4.388179000
H	3.908773000	2.119714000	3.866425000
H	3.378387000	3.802344000	3.935524000

C	5.923247000	2.446504000	2.004890000
H	6.327074000	2.554625000	0.994560000
H	5.691424000	1.391036000	2.171003000
H	6.714227000	2.723715000	2.707215000
C	5.133765000	4.814297000	2.025734000
H	4.318725000	5.514796000	2.221823000
H	5.476090000	4.978396000	1.000191000
H	5.956677000	5.063461000	2.703192000
C	0.000088000	4.407201000	0.518784000
C	0.000101000	5.323133000	-0.742215000
H	0.000087000	4.750885000	-1.668952000
H	-0.887409000	5.961806000	-0.734361000
C	0.000108000	5.348122000	1.737110000
H	0.000077000	4.805786000	2.685918000
H	0.873914000	6.001294000	1.712642000
C	-2.541587000	-1.694405000	-0.530948000
C	-3.613478000	-1.997383000	0.312315000
H	-4.520913000	-1.415526000	0.232023000
C	-3.538206000	-3.012461000	1.269220000
C	-2.347739000	-3.747026000	1.337853000
H	-2.276706000	-4.536823000	2.071657000
C	-1.261215000	-3.517938000	0.491854000
C	-1.374407000	-2.461093000	-0.431286000
H	-0.887622000	-5.961810000	-0.734306000
H	-0.000153000	-4.805726000	2.685952000
H	0.873669000	-6.001280000	1.712720000
C	-2.541501000	1.694487000	-0.530918000
C	-1.374293000	2.461135000	-0.431273000
C	-1.261053000	3.517977000	0.491864000
C	-2.347552000	3.747095000	1.337886000
H	-2.276487000	4.536898000	2.071680000
C	-3.538039000	3.012559000	1.269283000
C	-3.613364000	1.997493000	0.312369000
H	-4.520817000	1.415663000	0.232096000
C	-4.693969000	3.345744000	2.231607000
C	-4.221956000	3.152785000	3.691825000
H	-5.033900000	3.385407000	4.388227000
H	-3.908552000	2.119891000	3.866485000
H	-3.378174000	3.802528000	3.935503000
C	-5.923076000	2.446588000	2.004994000
H	-6.326915000	2.554645000	0.994663000
H	-5.691239000	1.391132000	2.171168000
H	-6.714053000	2.723830000	2.707312000
C	-5.133634000	4.814395000	2.025736000
H	-4.318605000	5.514916000	2.221789000
H	-5.475982000	4.978455000	1.000194000
H	-5.956539000	5.063563000	2.703202000
H	0.887634000	5.961773000	-0.734367000

H	-0.873649000	6.001358000	1.712621000
Bi	-2.691002000	0.000056000	-2.048745000
C	-4.948712000	0.000073000	-2.118748000
H	-5.268447000	0.888859000	-2.666197000
H	-5.268454000	-0.888840000	-2.665987000
H	-5.418476000	0.000193000	-1.135487000
C	4.693965000	-3.345764000	2.231618000
C	5.923129000	-2.446709000	2.004906000
C	4.222011000	-3.152670000	3.691837000
C	5.133516000	-4.814462000	2.025833000
H	6.326965000	-2.554905000	0.994588000
H	5.691353000	-1.391221000	2.170958000
H	6.714088000	-2.723920000	2.707256000
H	3.378193000	-3.802338000	3.935589000
H	5.033961000	-3.385300000	4.388229000
H	3.908686000	-2.119742000	3.866434000
H	5.956409000	-5.063652000	2.703305000
H	4.318433000	-5.514907000	2.221938000
H	5.475839000	-4.978613000	1.000297000
C	-4.694159000	-3.345599000	2.231532000
C	-4.222066000	-3.152904000	3.691759000
C	-5.923133000	-2.446221000	2.005074000
C	-5.134063000	-4.814154000	2.025484000
H	-3.378343000	-3.802776000	3.935303000
H	-3.908540000	-2.120070000	3.866556000
H	-5.034005000	-3.385539000	4.388161000
H	-6.326945000	-2.553994000	0.994700000
H	-6.714176000	-2.723509000	2.707298000
H	-5.691158000	-1.390835000	2.171494000
H	-5.957009000	-5.063268000	2.702918000
H	-5.476436000	-4.978035000	0.999921000
H	-4.319151000	-5.514835000	2.221455000

$[Bi_7Me_4TX_8][BiMe_2(SbF_6)_2]$ (4-Bi)

Bi	4.009825000	-0.843546000	-2.854894000
Bi	3.388992000	-3.623062000	1.670863000
S	5.346415000	-3.604513000	-1.135054000
Bi	3.100886000	4.205404000	-0.465741000
Bi	-0.942571000	-0.263819000	-0.689786000
Bi	1.672593000	1.301056000	3.780635000
Bi	-0.981091000	2.290342000	-3.237990000
Bi	-1.895017000	-2.737560000	1.288759000
C	4.106497000	-0.090465000	-5.979700000
H	3.758439000	-1.111537000	-6.082463000
S	0.637984000	-4.465766000	-0.255091000
S	4.976689000	2.557377000	-2.942334000
S	0.633264000	-1.038808000	-3.640044000
S	3.130911000	4.388740000	2.949499000

S	3.124509000	-1.800018000	4.658133000
S	-0.342552000	4.381186000	-0.617566000
S	-1.526945000	0.786720000	2.509119000
C	3.071896000	-4.469870000	3.758353000
C	3.741337000	-3.561409000	-4.575172000
H	4.807822000	-3.625473000	-4.387201000
C	3.003061000	-2.481663000	-4.061821000
C	-0.129851000	2.638415000	4.094394000
C	-3.111608000	-2.031782000	-2.254296000
H	-3.783843000	-1.748082000	-1.453685000
C	4.308114000	0.455932000	-4.699794000
C	2.913577000	-3.630732000	4.879484000
C	3.019751000	-5.620858000	0.657366000
C	-1.824737000	-1.475278000	-2.356494000
C	-2.782684000	0.804908000	0.000677000
C	4.719525000	4.964143000	2.189583000
C	4.824028000	4.952480000	0.786990000
C	-1.007402000	-1.869063000	-3.436291000
C	1.624826000	-2.436772000	-4.344753000
C	-2.034060000	4.231165000	-2.835928000
C	0.965304000	-3.385442000	-5.152653000
C	6.033795000	5.370612000	0.209343000
H	6.143603000	5.385212000	-0.870124000
C	-2.060786000	-4.774836000	0.400945000
C	2.604920000	-4.122945000	6.166187000
C	-3.539269000	-2.990609000	-3.175791000
C	3.107340000	-4.557983000	-5.323155000
C	-1.383200000	2.324421000	3.536230000
C	1.831950000	6.024648000	0.018022000
C	1.828184000	-5.867421000	-0.044699000
C	-3.814814000	1.148046000	-0.891599000
H	-3.813912000	0.757217000	-1.904360000
C	-2.691041000	-3.391463000	-4.210998000
H	-3.044012000	-4.153141000	-4.892581000
C	6.134698000	-1.635996000	-2.967253000
C	2.452056000	-8.147254000	-0.441438000
H	2.253804000	-9.134286000	-0.837063000
C	5.624438000	-3.922299000	1.638319000
C	-3.291332000	-5.445708000	0.414738000
H	-4.188455000	-4.980143000	0.803755000
C	1.509149000	-7.117246000	-0.614812000
C	2.916728000	-5.854533000	3.949729000
H	3.023661000	-6.532364000	3.112070000
C	4.769772000	1.784556000	-4.617158000
C	3.855978000	5.090303000	-2.420830000
C	6.595999000	-2.649748000	-2.105521000
C	-1.412037000	-2.826838000	-4.386246000
C	2.415733000	7.234448000	0.432736000

H	3.486677000	7.289819000	0.597450000
C	7.102463000	5.761355000	1.021801000
C	-2.837496000	1.314253000	1.314078000
C	-1.005907000	-6.703180000	-0.718627000
C	1.826944000	-1.207522000	5.846837000
C	7.085291000	-0.961239000	-3.753815000
H	6.769554000	-0.184815000	-4.440375000
C	5.091801000	2.553822000	-5.756571000
C	-0.567321000	-2.029305000	-6.639307000
H	-1.601442000	-1.881626000	-6.969653000
H	0.043517000	-2.288575000	-7.511117000
H	-0.195884000	-1.087523000	-6.230367000
C	3.799478000	3.638476000	4.500288000
C	3.951507000	-6.669002000	0.758568000
H	4.894154000	-6.506544000	1.270666000
C	4.550604000	4.313654000	-3.369616000
C	-2.244358000	-7.367589000	-0.631629000
H	-2.346190000	-8.374593000	-1.013170000
C	-4.840703000	2.000407000	-0.479625000
C	-3.370999000	-6.747140000	-0.090052000
C	5.755645000	5.409122000	3.034291000
C	-1.043476000	-4.453028000	-6.315678000
H	-2.057939000	-4.279652000	-6.683767000
H	-1.055933000	-5.332632000	-5.663785000
H	-0.429219000	-4.675899000	-7.192186000
C	2.434723000	-5.512440000	6.296747000
H	2.177155000	-5.938605000	7.256950000
C	-0.947297000	-5.404606000	-0.179367000
C	3.160876000	2.492949000	5.012778000
C	0.386617000	-6.626681000	-2.830013000
H	-0.516872000	-6.783678000	-3.430276000
H	1.241723000	-7.061713000	-3.358724000
H	0.555097000	-5.553017000	-2.736590000
C	4.941974000	4.814961000	-4.629936000
C	3.549705000	6.420195000	-2.761186000
H	3.013041000	7.047687000	-2.060416000
C	-0.510885000	-3.194248000	-5.592652000
C	-0.390583000	7.119994000	0.023806000
C	6.962354000	5.780660000	2.411929000
H	7.804147000	6.101655000	3.011030000
C	4.345071000	0.672270000	-7.125342000
C	7.959284000	-2.990493000	-1.977468000
C	6.321131000	-3.878729000	0.417174000
C	-2.258588000	1.663659000	-4.967337000
H	-2.208466000	2.420486000	-5.754929000
H	-3.294190000	1.533273000	-4.641998000
H	-1.877996000	0.712634000	-5.348138000
C	-2.540869000	3.104681000	3.731515000

C	1.589623000	-1.965623000	7.013900000
C	-1.678791000	5.013304000	-1.724903000
C	-1.142494000	4.644163000	5.023235000
C	-4.861607000	2.504334000	0.825147000
H	-5.686420000	3.145089000	1.099349000
C	0.247183000	8.318189000	0.394672000
H	-0.333600000	9.220980000	0.528743000
C	4.898628000	4.255945000	5.134027000
C	0.214711000	-7.326919000	-1.440502000
C	-3.054693000	4.696279000	-3.678621000
H	-3.369008000	4.114369000	-4.538265000
C	-0.030008000	3.814338000	4.857362000
H	0.915921000	4.083867000	5.314714000
C	7.716052000	-4.052027000	0.322174000
C	-3.869508000	2.162075000	1.763448000
C	1.626039000	8.373511000	0.613131000
C	-2.375865000	4.292355000	4.470174000
H	-3.221061000	4.947591000	4.629792000
C	-4.414586000	1.449480000	4.133171000
H	-5.406714000	1.121218000	3.804982000
H	-4.487087000	1.781958000	5.174465000
H	-3.733065000	0.596895000	4.093017000
C	8.043094000	-5.513941000	-1.721567000
H	8.381462000	-6.338244000	-1.083788000
H	8.542073000	-5.597189000	-2.693621000
H	6.967687000	-5.617639000	-1.875742000
C	5.540302000	5.544876000	4.562466000
C	-0.192871000	-0.387101000	7.564464000
C	3.906895000	6.937966000	-4.007588000
C	-0.022017000	-8.826884000	-1.732016000
H	-0.908811000	-8.955881000	-2.358086000
H	-0.153832000	-9.413218000	-0.816440000
H	0.818321000	-9.242486000	-2.294678000
C	0.114702000	0.381993000	6.439679000
H	-0.438915000	1.294004000	6.249453000
C	1.743299000	-4.466154000	-5.610900000
H	1.289130000	-5.242992000	-6.211030000
C	6.868509000	5.872219000	5.283002000
H	6.693539000	6.028787000	6.350936000
H	7.289011000	6.804399000	4.895774000
H	7.613261000	5.078043000	5.164763000
C	5.749987000	3.948455000	-5.623472000
C	8.443261000	-1.268358000	-3.642715000
C	2.596089000	-6.369293000	5.207222000
C	0.437904000	5.993058000	-0.154924000
C	-3.283402000	6.690480000	-2.317667000
H	-3.780576000	7.635938000	-2.147877000
C	4.586778000	6.141838000	-4.930166000

H	4.844228000	6.567257000	-5.890756000
C	3.907333000	-2.659813000	7.785505000
H	3.823891000	-1.996990000	8.654160000
H	4.396840000	-2.112016000	6.978925000
H	4.540180000	-3.511951000	8.057669000
C	7.214998000	3.779030000	-5.095583000
H	7.688572000	4.763509000	-5.010798000
H	7.792344000	3.175071000	-5.804709000
H	7.252390000	3.294538000	-4.118783000
C	8.872964000	-2.257235000	-2.755597000
H	9.933027000	-2.459550000	-2.681240000
C	-0.887436000	-3.214678000	3.218677000
H	-1.495250000	-3.961352000	3.735783000
H	-0.818859000	-2.301443000	3.813985000
H	0.108384000	-3.615400000	3.024914000
C	4.583865000	6.755978000	4.832832000
H	4.430921000	6.868304000	5.912069000
H	3.609583000	6.628612000	4.357904000
H	5.038458000	7.675387000	4.447107000
C	-3.975454000	-2.526400000	2.048531000
H	-4.149148000	-3.302384000	2.798416000
H	-4.678541000	-2.636982000	1.221874000
H	-4.074220000	-1.537396000	2.501466000
C	-3.936668000	2.641557000	3.235261000
C	-2.292559000	6.244191000	-1.423333000
C	0.700981000	3.121875000	-4.457006000
H	0.278150000	3.723562000	-5.265541000
H	1.285435000	2.293515000	-4.865410000
H	1.335177000	3.746304000	-3.824212000
C	3.662268000	-7.925612000	0.220159000
C	8.419321000	-4.146907000	-1.054979000
C	0.541270000	-1.539637000	7.849506000
H	0.296796000	-2.101695000	8.740792000
C	-2.525249000	6.273401000	1.099766000
H	-3.614842000	6.215888000	1.000438000
H	-2.282814000	6.823107000	2.015809000
H	-2.134610000	5.259682000	1.197689000
C	-3.665295000	5.927927000	-3.423818000
C	8.418578000	-4.197660000	1.533385000
H	9.495291000	-4.303243000	1.525338000
C	7.755602000	-4.225326000	2.763021000
C	-2.573927000	8.432378000	-0.142857000
H	-3.661940000	8.349414000	-0.210291000
H	-2.218489000	9.050379000	-0.974372000
H	-2.359631000	8.952967000	0.794484000
C	4.838829000	1.972904000	-7.012400000
H	5.038480000	2.531198000	-7.917099000
C	1.932973000	-3.919351000	8.619445000

H	1.887149000	-3.243125000	9.477642000
H	2.603686000	-4.736481000	8.899230000
H	0.933674000	-4.333229000	8.448713000
C	9.956963000	-4.152163000	-0.893514000
H	10.269083000	-4.996073000	-0.272147000
H	10.331421000	-3.228175000	-0.440377000
H	10.441115000	-4.284204000	-1.864988000
C	2.484122000	-3.174419000	7.381609000
C	-1.929355000	7.027050000	-0.136304000
C	6.363231000	-4.110361000	2.817500000
H	5.854724000	-4.160572000	3.774863000
C	3.630762000	1.969511000	6.230346000
H	3.156017000	1.098808000	6.666755000
C	5.870647000	4.641736000	-7.000312000
H	6.385994000	5.600650000	-6.897062000
H	4.895926000	4.819872000	-7.466419000
H	6.474450000	4.032329000	-7.678573000
C	-4.988341000	3.762148000	3.402874000
H	-5.979724000	3.424068000	3.097685000
H	-4.741022000	4.652443000	2.815560000
H	-5.066242000	4.050076000	4.455160000
C	5.356151000	3.668245000	6.327013000
H	6.209676000	4.085588000	6.844259000
C	4.723222000	2.551809000	6.877079000
C	1.129294000	-0.019554000	5.552641000
H	9.171402000	-0.731128000	-4.242674000
H	-4.445494000	6.293360000	-4.083870000
H	-5.630344000	2.294674000	-1.159978000
H	-1.053310000	5.563114000	5.594259000
H	-4.323004000	-7.264985000	-0.079501000
H	4.377375000	-8.736804000	0.317831000
H	8.326996000	-4.347184000	3.678146000
H	5.088658000	2.131477000	7.809041000
H	8.044431000	6.062031000	0.573267000
H	3.678712000	-5.401968000	-5.696998000
H	4.163536000	0.248263000	-8.108242000
H	3.650778000	7.961400000	-4.263966000
H	2.084111000	9.309571000	0.918063000
H	-0.993942000	-0.080327000	8.229940000
H	2.464224000	-7.438942000	5.338405000
H	-4.518681000	-3.436372000	-3.063131000
Sb	-6.948165000	-4.237100000	-1.108271000
F	-7.291588000	-3.482778000	-2.830816000
F	-8.255240000	-2.964034000	-0.353367000
F	-5.575526000	-5.346546000	-1.829833000
F	-8.321307000	-5.533447000	-1.292274000
F	-5.714661000	-2.768907000	-0.804293000
F	-6.550063000	-4.796339000	0.679615000

Bi	-8.030208000	-0.709383000	0.302642000
F	-7.992302000	1.554819000	0.630137000
C	-10.248924000	-0.614323000	0.229934000
H	-10.599778000	-1.061372000	-0.703359000
H	-10.680141000	-1.145823000	1.081798000
H	-10.533868000	0.439595000	0.268115000
C	-7.762096000	-0.247165000	-1.850196000
H	-6.734622000	0.080138000	-2.024573000
H	-7.954085000	-1.152613000	-2.430904000
H	-8.462378000	0.548648000	-2.114523000
Sb	-8.896865000	3.305646000	0.333831000
F	-7.398488000	3.745656000	-0.776949000
F	-7.897603000	3.910743000	1.854368000
F	-10.265928000	2.621565000	1.475531000
F	-9.728288000	2.447882000	-1.162633000
F	-9.751790000	4.976408000	0.055035000

[$Bi_7Me_4TX_8$][$AlCl_4$] (4-Al)

Bi	-2.224704000	3.591747000	1.559266000
C	-0.888084000	-0.550043000	5.390645000
Bi	1.359669000	3.235834000	-2.351657000
C	-3.488282000	3.490681000	3.447626000
Bi	0.802046000	-0.614059000	3.866484000
Bi	-4.038915000	-1.258427000	0.441827000
Bi	4.640966000	-0.589097000	0.184851000
Bi	-1.190509000	-1.435041000	-1.063449000
Bi	1.454738000	-2.706525000	-3.474556000
S	-0.682722000	5.597930000	-0.741776000
S	-3.977114000	1.889638000	-0.900761000
S	-0.409131000	0.585406000	-3.733116000
C	-1.327278000	-3.632848000	-0.657264000
C	0.941559000	-2.876079000	3.963986000
C	-2.307450000	-1.352508000	-3.008057000
C	-0.319464000	3.388572000	-3.871826000
C	-5.696565000	-0.303372000	-0.691943000
C	6.092663000	-0.240211000	-1.530203000
C	-1.143767000	-4.099185000	0.661071000
C	0.104787000	-3.686414000	3.174115000
C	-0.922545000	2.234109000	-4.406205000
C	4.735945000	-3.812158000	0.179932000
C	5.440047000	-2.672679000	0.607080000
C	-3.926744000	4.418068000	0.298695000
C	-1.467576000	-4.580735000	-1.685822000
H	-1.650131000	-4.263657000	-2.707043000
C	2.936266000	3.044190000	-3.983475000
C	-1.883063000	2.266329000	-5.438497000
C	2.367697000	-0.133291000	5.435736000
S	4.715577000	2.173668000	-1.979510000

C	-1.390532000	5.648962000	1.967902000
S	3.066505000	-3.568166000	-0.572583000
C	-0.754353000	4.635895000	-4.352322000
H	-0.309484000	5.549753000	-3.971485000
S	4.274300000	-0.979771000	3.569547000
S	-1.079943000	-2.852356000	2.022270000
C	7.065648000	-1.206947000	-1.844069000
H	7.164634000	-2.095670000	-1.232157000
S	-1.320146000	2.128423000	4.621775000
C	1.853543000	-3.518221000	4.819328000
H	2.510250000	-2.931253000	5.453564000
C	3.229501000	-1.694372000	-4.395219000
H	2.905099000	-0.754460000	-4.851318000
H	3.656708000	-2.355013000	-5.154966000
H	3.976760000	-1.487877000	-3.624994000
C	-3.929162000	-0.895871000	-5.254266000
H	-4.587767000	-0.729206000	-6.096539000
C	1.925172000	-4.915329000	4.854466000
C	-5.579422000	1.016783000	-1.158366000
C	5.957219000	0.347714000	1.766702000
C	-1.627168000	0.619757000	5.658022000
C	1.758026000	5.456733000	-2.105728000
C	-4.248169000	-1.920316000	-4.357613000
C	3.743980000	-0.165245000	5.138297000
C	2.607750000	3.371416000	-5.311788000
H	1.595764000	3.668674000	-5.562734000
C	-4.612986000	3.601671000	-0.617053000
C	-2.776123000	-0.101548000	-5.092725000
C	-1.981449000	-0.360870000	-3.958399000
C	6.472640000	0.672241000	4.168315000
C	5.236166000	-5.124909000	0.311439000
C	-6.889248000	-1.006744000	-0.918438000
H	-7.009346000	-2.040027000	-0.609433000
C	-4.796322000	4.009160000	3.454719000
H	-5.186990000	4.509905000	2.576973000
C	-1.384575000	-5.944664000	-1.394949000
C	-1.066020000	-5.465959000	0.987443000
C	-4.882044000	-3.263783000	0.842615000
H	-4.293524000	-3.719781000	1.640666000
H	-4.817068000	-3.878810000	-0.055032000
H	-5.925482000	-3.169394000	1.151186000
C	-3.033475000	2.839362000	4.612328000
C	0.941398000	6.273786000	-1.300041000
C	-4.372174000	5.742434000	0.457903000
H	-3.854638000	6.410922000	1.138836000
C	2.483241000	-4.671001000	-3.073905000
C	6.001357000	0.892962000	-2.362914000
C	-2.309467000	3.541183000	-5.860004000

H	-3.068462000	3.633470000	-6.625868000
C	-3.442465000	-2.150370000	-3.239054000
H	-3.718820000	-2.948492000	-2.558491000
C	4.731000000	0.366038000	5.995827000
C	5.694645000	0.119947000	3.130354000
C	6.504772000	-5.261715000	0.906672000
H	6.949393000	-6.242119000	1.018425000
C	-6.629140000	1.684749000	-1.817359000
C	-5.744428000	4.029166000	-1.343985000
C	0.516313000	-3.322417000	-5.417201000
H	-0.069052000	-2.479104000	-5.794451000
H	-0.149933000	-4.176148000	-5.261915000
H	1.290921000	-3.581946000	-6.145124000
C	7.898054000	-1.047596000	-2.955634000
C	-4.311240000	-0.327012000	2.442996000
H	-3.562448000	-0.731650000	3.127386000
H	-5.317173000	-0.586027000	2.784742000
H	-4.209458000	0.755959000	2.366449000
C	0.104516000	-5.095867000	3.225255000
C	1.062019000	-5.688849000	4.071629000
H	1.133106000	-6.766781000	4.135721000
C	-3.828093000	2.701654000	5.771883000
C	-5.520072000	3.026073000	-3.658731000
H	-5.383215000	4.028553000	-4.079346000
H	-6.002854000	2.390202000	-4.409700000
H	-4.535761000	2.611636000	-3.437318000
C	-0.210274000	7.654818000	1.120787000
C	7.212961000	-4.151052000	1.377542000
C	4.266528000	2.669626000	-3.708737000
C	6.683550000	-2.864289000	1.234736000
H	7.248166000	-2.009450000	1.593386000
C	3.796377000	-6.107217000	-1.540976000
C	-0.761868000	6.370749000	0.936524000
C	1.293503000	7.588991000	-0.927762000
C	0.341429000	8.467149000	-0.077816000
C	-5.495840000	6.199528000	-0.238135000
C	-1.176083000	-1.696554000	6.153940000
H	-0.626699000	-2.615074000	5.980279000
C	-7.830766000	0.966210000	-1.979593000
H	-8.681151000	1.433474000	-2.458976000
C	-6.432279000	3.112075000	-2.388222000
C	-3.524239000	1.258512000	-7.117973000
H	-4.412941000	1.647202000	-6.609678000
H	-3.802464000	0.349655000	-7.658380000
H	-3.207987000	1.983238000	-7.873462000
C	5.279199000	2.663297000	-4.694139000
C	-2.365029000	0.967258000	-6.136383000
C	6.845297000	1.096206000	-3.476820000

C	-7.778588000	3.711502000	-2.856390000
H	-8.494814000	3.819839000	-2.034605000
H	-8.226999000	3.079184000	-3.627777000
H	-7.620218000	4.692367000	-3.313510000
C	1.974715000	0.424780000	6.665964000
H	0.926050000	0.454763000	6.940278000
C	-0.245211000	8.176514000	2.428903000
H	0.189818000	9.145018000	2.638977000
C	-2.590062000	0.697767000	6.688979000
C	7.023950000	1.199009000	1.432290000
H	7.263287000	1.389089000	0.390572000
C	6.236908000	0.269236000	5.646068000
C	-6.179989000	5.347900000	-1.111890000
H	-7.054578000	5.728538000	-1.623057000
C	-1.171548000	-6.375741000	-0.082525000
H	-1.120337000	-7.439737000	0.104216000
C	7.784382000	0.087734000	-3.761859000
H	8.440242000	0.182337000	-4.617293000
C	6.716257000	-1.209748000	5.850818000
H	7.785363000	-1.282442000	5.620175000
H	6.177560000	-1.912715000	5.213182000
H	6.562908000	-1.501563000	6.896193000
C	-7.957019000	-0.359256000	-1.551545000
C	3.120680000	-4.907756000	-1.843307000
C	-5.137106000	3.215349000	5.717789000
H	-5.795350000	3.114901000	6.570622000
C	6.756560000	2.386863000	-4.324029000
C	-0.622306000	-7.447203000	2.530198000
H	0.330721000	-7.690484000	2.048230000
H	-1.415743000	-8.028360000	2.053129000
H	-0.582379000	-7.777470000	3.571928000
C	-5.616225000	3.864654000	4.577511000
C	-1.762396000	4.709390000	-5.320046000
C	1.049079000	9.755653000	0.401614000
H	0.352144000	10.382441000	0.965422000
H	1.378312000	10.349938000	-0.455580000
H	1.918307000	9.543965000	1.033832000
C	4.403439000	-6.352525000	-0.136320000
C	2.927120000	0.964829000	7.535899000
C	-0.859953000	8.934090000	-0.970914000
H	-1.529220000	9.569523000	-0.379536000
H	-1.437844000	8.094873000	-1.361620000
H	-0.480004000	9.517980000	-1.817194000
C	4.891700000	2.968189000	-6.012326000
H	5.621674000	2.949332000	-6.810883000
C	3.572983000	3.312100000	-6.321369000
C	3.841277000	-7.080884000	-2.557769000
H	4.363916000	-8.014317000	-2.393869000

C	-0.846972000	7.474625000	3.478729000
C	7.089009000	1.135619000	6.602209000
H	6.828091000	2.198154000	6.546860000
H	8.151588000	1.024677000	6.367511000
H	6.961852000	0.799131000	7.635134000
C	5.255771000	-7.642415000	-0.116000000
H	6.110456000	-7.589034000	-0.799299000
H	4.642959000	-8.505669000	-0.390971000
H	5.628608000	-7.835368000	0.893993000
C	-0.950087000	-5.937514000	2.458979000
C	-2.342812000	-5.760660000	3.158939000
H	-2.286374000	-6.151794000	4.181169000
H	-3.107398000	-6.318168000	2.607966000
H	-2.649210000	-4.714434000	3.212436000
C	3.239375000	-6.577635000	0.887154000
H	3.658729000	-6.761695000	1.882550000
H	2.653052000	-7.452474000	0.583396000
H	2.569837000	-5.719200000	0.952255000
C	-3.268515000	2.040489000	7.052751000
C	4.283007000	0.950258000	7.195546000
H	4.992365000	1.393097000	7.882416000
C	-1.435746000	6.225886000	3.248190000
H	-1.922437000	5.701887000	4.065011000
C	2.520671000	-5.686967000	-4.042899000
H	2.031162000	-5.551345000	-5.002017000
C	7.506342000	1.549407000	3.785601000
H	8.118277000	2.028961000	4.538569000
C	2.964757000	6.001745000	-2.581702000
H	3.615886000	5.411571000	-3.216849000
C	-1.187098000	0.404856000	-7.005577000
H	-0.904868000	1.145997000	-7.761917000
H	-1.512216000	-0.509164000	-7.515285000
H	-0.304330000	0.173429000	-6.406889000
C	7.778873000	1.812133000	2.438913000
C	7.319015000	3.594288000	-3.497324000
H	7.267042000	4.506460000	-4.102954000
H	8.367924000	3.403439000	-3.242899000
H	6.764951000	3.761350000	-2.572536000
C	-2.212673000	2.992715000	7.713229000
H	-2.694459000	3.940325000	7.980253000
H	-1.372169000	3.207597000	7.051722000
H	-1.825177000	2.528461000	8.627415000
C	-2.863440000	-0.485473000	7.400656000
H	-3.614643000	-0.489303000	8.179415000
C	2.529323000	8.072983000	-1.396547000
H	2.862363000	9.066191000	-1.125116000
C	7.641752000	2.289504000	-5.588365000
H	7.596903000	3.224903000	-6.153831000

H	7.342101000	1.468311000	-6.248359000
H	8.688560000	2.144058000	-5.306183000
C	3.346963000	7.298625000	-2.224835000
C	-2.172622000	-1.670494000	7.134059000
C	-4.378219000	1.838739000	8.110732000
H	-3.956138000	1.406078000	9.022464000
H	-5.183433000	1.186397000	7.756158000
H	-4.811059000	2.802921000	8.392929000
C	3.208606000	-6.879253000	-3.788567000
Cl	-7.886507000	-7.828119000	-2.342340000
Al	-6.771403000	-6.225001000	-1.285521000
Cl	-5.412981000	-5.117905000	-2.722844000
Cl	-8.166206000	-4.680781000	-0.415426000
Cl	-5.475860000	-7.058293000	0.352857000
H	-0.863422000	7.907470000	4.474838000
H	4.287821000	7.705052000	-2.584623000
H	3.302232000	3.546459000	-7.346991000
H	8.633712000	-1.809689000	-3.196564000
H	3.251661000	-7.654019000	-4.548631000
H	-6.630170000	4.254006000	4.563186000
H	-2.402791000	-2.568838000	7.699571000
H	8.182119000	-4.290970000	1.848175000
H	8.587585000	2.488115000	2.176228000
H	2.613129000	1.406923000	8.477086000
H	-5.846046000	7.218064000	-0.096031000
H	-2.112062000	5.677462000	-5.667337000
H	2.647973000	-5.404968000	5.500915000
H	-8.886929000	-0.895879000	-1.710448000
H	-1.504303000	-6.675221000	-2.188057000
H	-5.125902000	-2.538262000	-4.515549000

$[Bi_7Me_4TX_8]^+$ cation of 4-Bi and 4-Al without the corresponding anion

Bi	-0.914403000	-3.532079000	1.337239000
Bi	-3.963936000	0.741952000	1.731323000
S	-3.940236000	-2.507492000	2.787972000
Bi	3.964034000	-0.742836000	1.730901000
Bi	-0.000607000	0.000925000	-2.641810000
Bi	0.914485000	3.531430000	1.338530000
Bi	2.593138000	-2.171515000	-3.148746000
Bi	-2.593075000	2.173237000	-3.148087000
C	0.072654000	-6.493907000	0.546408000
H	-0.903390000	-6.525889000	0.078744000
S	-4.414312000	-0.250096000	-1.577053000
S	2.383295000	-3.764164000	2.601267000
S	-0.770362000	-3.285124000	-2.141184000
S	3.940202000	2.506175000	2.788985000
S	-2.383187000	3.762919000	2.602797000
S	4.414539000	0.251074000	-1.576829000

S	0.770111000	3.286482000	-2.140071000
C	-4.945254000	2.794480000	1.930570000
C	-3.465753000	-5.221957000	0.285016000
H	-3.617864000	-5.377324000	1.346748000
C	-2.372264000	-4.460201000	-0.158081000
C	2.372264000	4.460264000	-0.156397000
C	-1.553681000	-0.833764000	-5.347697000
H	-1.250215000	0.146419000	-5.699270000
C	0.501221000	-5.319040000	1.186435000
C	-4.195833000	3.946280000	2.229043000
C	-5.842267000	-0.195910000	0.835834000
C	-1.087612000	-1.319209000	-4.114520000
C	1.087056000	1.321074000	-4.114028000
C	4.417254000	1.322010000	4.135140000
C	4.498080000	-0.042313000	3.817837000
C	-1.483034000	-2.607224000	-3.707056000
C	-2.205305000	-4.305289000	-1.542715000
C	4.564831000	-1.355473000	-3.858966000
C	-3.046856000	-4.896792000	-2.500638000
C	4.858409000	-0.942774000	4.831024000
H	4.944640000	-2.000734000	4.610943000
C	-4.564696000	1.357389000	-3.858526000
C	-4.761096000	5.235656000	2.261702000
C	-2.428140000	-1.604661000	-6.113695000
C	-4.359866000	-5.771923000	-0.635344000
C	2.205308000	4.305990000	-1.541096000
C	5.842444000	0.195463000	0.836062000
C	-5.932422000	-0.479076000	-0.533147000
C	1.553189000	0.835884000	-5.347275000
H	1.249495000	-0.144102000	-5.699195000
C	-2.835266000	-2.862473000	-5.666139000
H	-3.528185000	-3.426630000	-6.273784000
C	-1.869021000	-4.341244000	3.235514000
C	-8.227331000	-1.123048000	-0.323226000
H	-9.163176000	-1.459244000	-0.746887000
C	-4.498188000	0.040520000	3.817897000
C	-5.164001000	1.835785000	-5.030909000
H	-4.672784000	2.590292000	-5.634176000
C	-7.107042000	-0.943131000	-1.151777000
C	-6.315369000	2.951723000	1.660990000
H	-6.920019000	2.086439000	1.422356000
C	1.769120000	-5.322216000	1.793933000
C	4.945349000	-2.795461000	1.929259000
C	-2.995300000	-3.727840000	3.807812000
C	-2.356277000	-3.408827000	-4.462791000
C	6.974649000	0.435890000	1.632960000
H	6.928917000	0.252272000	2.700201000
C	5.097141000	-0.475904000	6.125192000

C	1.482790000	2.608843000	-3.706078000
C	-6.482004000	-0.141331000	-3.481401000
C	-1.769100000	5.321315000	1.796071000
C	-1.197594000	-5.323386000	3.981544000
H	-0.335151000	-5.826475000	3.562575000
C	2.593407000	-6.464006000	1.827916000
C	-1.486447000	-5.782162000	-4.287286000
H	-1.249238000	-5.768251000	-5.356683000
H	-1.741571000	-6.805566000	-3.993261000
H	-0.605981000	-5.468269000	-3.723257000
C	2.995237000	3.726104000	3.809288000
C	-6.974508000	-0.436778000	1.632565000
H	-6.928827000	-0.253688000	2.699896000
C	4.195924000	-3.947377000	2.227294000
C	-7.070230000	0.392175000	-4.641011000
H	-8.044855000	0.048035000	-4.957284000
C	2.428011000	1.606775000	-6.112866000
C	-6.421131000	1.359545000	-5.409517000
C	4.699659000	1.828621000	5.415077000
C	-3.889239000	-5.412109000	-4.860836000
H	-3.611014000	-5.438335000	-5.918076000
H	-4.799424000	-4.815342000	-4.743236000
H	-4.097385000	-6.443509000	-4.564691000
C	-6.128129000	5.343798000	1.960653000
H	-6.603054000	6.314621000	1.955346000
C	-5.228330000	0.374970000	-3.111786000
C	1.869030000	4.339810000	3.237164000
C	-6.362974000	-2.611585000	-2.913779000
H	-6.408169000	-2.858664000	-3.980893000
H	-6.833366000	-3.416004000	-2.338874000
H	-5.317751000	-2.536147000	-2.612518000
C	4.761160000	-5.236784000	2.259383000
C	6.315440000	-2.952634000	1.659522000
H	6.920087000	-2.087273000	1.421165000
C	-2.717109000	-4.848829000	-4.016653000
C	7.107337000	0.943577000	-1.151127000
C	5.016204000	0.888030000	6.410625000
H	5.214396000	1.218916000	7.420437000
C	0.897455000	-7.618112000	0.505961000
C	-3.453723000	-4.027149000	5.104074000
C	-4.417393000	-1.323939000	4.134611000
C	2.173727000	-3.485661000	-4.927896000
H	2.987988000	-4.206114000	-5.043008000
H	2.082419000	-2.872484000	-5.828385000
H	1.234522000	-4.012965000	-4.746037000
C	3.047038000	4.897679000	-2.498747000
C	-2.593408000	6.463073000	1.830566000
C	5.228560000	-0.373445000	-3.111813000

C	4.360091000	5.771864000	-0.633035000
C	2.835402000	2.864340000	-5.664858000
H	3.528587000	3.428485000	-6.272212000
C	8.227594000	1.123049000	-0.322433000
H	9.163458000	1.459445000	-0.745893000
C	3.453568000	4.024842000	5.105715000
C	-7.147634000	-1.278633000	-2.665204000
C	5.164171000	-1.833456000	-5.031504000
H	4.672924000	-2.587683000	-5.635098000
C	3.465868000	5.221645000	0.287063000
H	3.617973000	5.376527000	1.348867000
C	-4.699917000	-1.831110000	5.414301000
C	2.356356000	3.410459000	-4.461429000
C	8.159462000	0.890404000	1.051914000
C	4.151412000	5.613929000	-2.003607000
H	4.850882000	6.068675000	-2.690530000
C	1.487050000	5.783948000	-4.285358000
H	1.249980000	5.770380000	-5.354791000
H	1.742381000	6.807212000	-3.991027000
H	0.606434000	5.470116000	-3.721531000
C	-5.990299000	-3.972604000	4.990547000
H	-6.890191000	-3.512002000	5.412207000
H	-6.017696000	-5.050262000	5.184839000
H	-5.983618000	-3.808286000	3.911914000
C	4.725717000	3.355050000	5.685190000
C	-0.897582000	7.617723000	0.508918000
C	6.898344000	-4.219125000	1.670028000
C	-8.601434000	-1.525908000	-3.142901000
H	-8.603758000	-1.801167000	-4.201517000
H	-9.234555000	-0.644112000	-3.001130000
H	-9.034629000	-2.367142000	-2.594990000
C	-0.072748000	6.493521000	0.548882000
H	0.903271000	6.525710000	0.081178000
C	-4.151137000	-5.613419000	-2.005841000
H	-4.850484000	-6.068026000	-2.692985000
C	4.868628000	3.648945000	7.200573000
H	4.947407000	4.727091000	7.365713000
H	5.791600000	3.201465000	7.579770000
H	4.020786000	3.260436000	7.773983000
C	3.914348000	-6.475327000	2.635858000
C	-1.626570000	-5.638094000	5.271021000
C	-6.898298000	4.218202000	1.672049000
C	5.932645000	0.479322000	-0.532783000
C	7.070540000	-0.390202000	-4.640931000
H	8.045199000	-0.046003000	-4.957039000
C	6.128173000	-5.344825000	1.958214000
H	6.603085000	-6.315651000	1.952448000
C	-3.584123000	6.437221000	4.170456000

H	-2.993494000	7.322226000	4.430942000
H	-3.023207000	5.544042000	4.448008000
H	-4.520547000	6.456128000	4.738233000
C	3.584344000	-6.439131000	4.167719000
H	4.520822000	-6.458268000	4.735400000
H	2.993736000	-7.324238000	4.427913000
H	3.023455000	-5.546062000	4.445685000
C	-2.726670000	-4.985875000	5.828503000
H	-3.022823000	-5.237633000	6.837040000
C	-3.331982000	3.758802000	-1.736049000
H	-3.975438000	4.437296000	-2.301317000
H	-2.471087000	4.294089000	-1.328751000
H	-3.899549000	3.286255000	-0.932351000
C	5.990153000	3.970246000	4.992345000
H	6.017587000	5.047817000	5.187114000
H	5.983542000	3.806399000	3.913642000
H	6.889990000	3.509413000	5.413870000
C	-2.174114000	3.489105000	-4.926021000
H	-2.988733000	4.209249000	-5.040499000
H	-2.082433000	2.876780000	-5.827049000
H	-1.235176000	4.016675000	-4.743573000
C	2.717453000	4.850250000	-4.014821000
C	6.482318000	0.142874000	-3.481124000
C	3.332867000	-3.758680000	-1.738864000
H	3.976619000	-4.436062000	-2.305122000
H	2.472253000	-4.294933000	-1.332233000
H	3.900248000	-3.286987000	-0.934528000
C	-8.159271000	-0.891046000	1.051238000
C	-4.725941000	-3.357657000	5.683747000
C	-2.136934000	7.602419000	1.147802000
H	-2.746312000	8.494703000	1.122802000
C	6.363549000	2.612908000	-2.912424000
H	6.408806000	2.860436000	-3.979433000
H	6.834031000	3.417021000	-2.337165000
H	5.318317000	2.537468000	-2.611212000
C	6.421368000	-1.357194000	-5.409859000
C	-5.016596000	-0.890955000	6.410216000
H	-5.214904000	-1.222281000	7.419861000
C	-5.097521000	0.473103000	6.125365000
C	8.601881000	1.527092000	-3.141933000
H	8.604276000	1.802709000	-4.200457000
H	9.234939000	0.645206000	-3.000437000
H	9.035109000	2.368106000	-2.593708000
C	2.136858000	-7.603080000	1.144753000
H	2.746210000	-8.495370000	1.119356000
C	-4.704279000	7.786571000	2.399888000
H	-4.098690000	8.644265000	2.706195000
H	-5.605629000	7.794457000	3.019160000

H	-4.992049000	7.908882000	1.350660000
C	-4.868942000	-3.652204000	7.198997000
H	-5.791981000	-3.204962000	7.578314000
H	-4.021175000	-3.263862000	7.772630000
H	-4.947642000	-4.730426000	7.363677000
C	-3.914278000	6.474049000	2.638636000
C	7.148037000	1.279756000	-2.664405000
C	-4.858635000	0.940546000	4.831432000
H	-4.944820000	1.998602000	4.611809000
C	1.197597000	5.321676000	3.983552000
H	0.335218000	5.824991000	3.564724000
C	4.704303000	-7.787763000	2.396468000
H	5.605698000	-7.795952000	3.015670000
H	4.991978000	-7.909604000	1.347160000
H	4.098725000	-8.645581000	2.702448000
C	3.889818000	5.413498000	-4.858703000
H	3.611764000	5.439971000	-5.915983000
H	4.799877000	4.816546000	-4.741072000
H	4.098098000	6.444805000	-4.562332000
C	2.726506000	4.983298000	5.830492000
H	3.022584000	5.234608000	6.839163000
C	1.626489000	5.635817000	5.273196000
C	-0.501239000	5.318392000	1.188486000
H	-1.097206000	-6.387039000	5.849600000
H	6.900384000	-1.743795000	-6.302535000
H	2.805735000	1.224414000	-7.054186000
H	5.215783000	6.338638000	-0.283506000
H	-6.900138000	1.746453000	-6.302063000
H	-9.035704000	-1.059655000	1.667274000
H	-5.355153000	1.170668000	6.914672000
H	1.097122000	6.384550000	5.852048000
H	5.354662000	-1.173820000	6.914226000
H	-5.215491000	-6.338962000	-0.286081000
H	0.567610000	-8.515069000	-0.006748000
H	7.953897000	-4.331674000	1.448225000
H	9.035865000	1.058688000	1.668082000
H	-0.567800000	8.514875000	-0.003488000
H	-7.953863000	4.330823000	1.450341000
H	-2.805797000	-1.222111000	-7.054966000

Funding

Financial support by the DFG (LI2860/5-1) and the LOEWE program is gratefully acknowledged. This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (grant agreements No 946184).