

Supporting Information for:

Simple Solution-Phase Syntheses of Tetrahalodiboranes(4) and their Labile Dimethylsulfide Adducts

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Synthetic Details

General considerations

All manipulations were performed under an inert atmosphere of dry argon using either standard Schlenk-line or glovebox techniques. Deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles prior to use. All other solvents were distilled from appropriate drying agents.¹ Solvents were stored under argon over activated molecular sieves. The syntheses of B_2I_4 and $B_2I_4(SMe_2)_2$ were carried out in brown-glass Schlenk flasks to exclude light. NMR spectra were recorded on a Bruker Avance I 400 (1H , 400.1 MHz; ^{13}C , 100.6 MHz; ^{31}P , 162.0 MHz) and/or a Bruker Avance I 500 NMR spectrometer (1H 500.1 MHz; ^{13}C 125.8 MHz; ^{31}P 202.5 MHz) at 298 K. Chemical shifts are given in ppm and were referenced to solvent (1H , $^{13}C\{^1H\}$) or referenced to external $BF_3 \cdot OEt_2$ (^{11}B , $^{11}B\{^1H\}$). Elemental analyses were obtained with an Elementar Vario MICRO cube instrument. $B_2(NMe_2)_4$ was a generous gift from AllyChem Co. Ltd. B_2Br_4 was prepared by following the 1981 procedure of Nöth closely,² and making sure that after the 30 min reaction time at room temperature, the product is kept at or below $-40\text{ }^\circ\text{C}$ at all times (including during NMR characterization) to prevent decomposition. $BCl_3(SMe_2)^3$ and $BBr_3(SMe_2)^3$ were prepared according to literature procedures. Dimethylsulfide, BI_3 , $GaCl_3$ and SbF_3 were purchased from commercial sources and used without further purification.

Syntheses of tetrahalodiboranes(4)

Synthesis of B₂F₄: B₂Br₄ (480 mg, 1.41 mmol) was dissolved in cold hexane (10 mL). This solution was dropped slowly to a solution of SbF₃ (336 mg, 1.88 mmol) in hexane (10 mL) at -78 °C. The suspension was stirred for 30 min at -78 °C and for 1 h at ambient temperature. The B₂F₄ solution was vacuum distilled from the remaining Sb salts (ca. 1 mbar) and stored at -30 °C to yield B₂F₄ as a colorless hexane solution (neat B₂F₄ is a colorless gas). This solution can be used as a stock solution of B₂F₄ by assuming complete conversion. Alternatively, B₂F₄ can be prepared by the same procedure using B₂Cl₄. ¹¹B NMR (128.4 MHz, hexane): δ = 22 (s) ppm. ¹⁹F NMR (376.5 MHz, hexane): δ = -55 (s) ppm.

Synthesis of B₂Cl₄: B₂Br₄ (1.50 g, 4.40 mmol) was dissolved in cold hexane (10 mL). This solution was dropped slowly into a solution of GaCl₃ (1.03 g, 5.87 mmol) in hexane (10 mL) at -78 °C. The suspension was stirred for 30 min at -78 °C and for 1 h at ambient temperature. The B₂Cl₄ solution was vacuum distilled from the remaining Ga salts and stored at -30 °C to yield B₂Cl₄ as a colorless hexane solution (neat B₂Cl₄ is a colorless liquid). This solution can be used as a stock solution of B₂Cl₄ by assuming complete conversion. ¹¹B NMR (128.4 MHz, hexane): δ = 62 (s) ppm.

Synthesis of B₂I₄: BI₃ (450 mg, 1.14 mmol) was suspended in hexane (4 mL) and a cooled solution of B₂Cl₄ in hexane (4.11 mL, 0.21 molL⁻¹, 864 μmol) was added at -78 °C. The suspension was stirred for 30 min at -78 °C and for 1.5 h at ambient temperature. After cooling to -78 °C all volatiles were slowly removed under vacuum (2·10⁻¹ mbar) to yield B₂I₄ (359 mg, 678 μmol, 78%) as a colorless solid, which was subsequently stored at -30 °C under exclusion of light to prevent decomposition. Alternatively, B₂I₄ can be prepared by the same procedure using B₂Br₄. ¹¹B NMR (128.4 MHz, d₈-toluene): δ = 70 (s) ppm.

Syntheses of tetrahalodiborane(4) thioether adducts

Synthesis of B₂Cl₄(SMe₂)₂: To a benzene solution of B₂(NMe₂)₄ (1.00 g, 5.05 mmol) was added a benzene solution of BCl₃(SMe₂) (3.62 g, 20.2 mmol, 4 equiv) at room temperature. After 2 h stirring at room temperature the mixture was heated at 80 °C overnight. ¹¹B NMR data of the reaction mixture showed one broad resonance at 7.3 ppm corresponding to B₂Cl₄(SMe₂)₂, and two sharp resonances at 30.5 and 10.7 ppm, corresponding to the by-product BCl₂(NMe₂) and its dimer, [BCl₂(NMe₂)]₂, respectively. Removal of all volatiles *in vacuo* at 50 °C (to prevent BCl₂(NMe₂) from dimerizing) yielded a ca. 1:3 mixture of B₂Cl₄(SMe₂)₂ and [BCl₂(NMe₂)]₂. The latter was removed by two consecutive fractional crystallizations from 30 mL of toluene at –30 °C. The remaining filtrate was dried *in vacuo* to yield B₂Cl₄(SMe₂)₂ as a colorless, highly air-sensitive solid (0.98 g, 3.41 mmol, 67% yield). Note: B₂Cl₄(SMe₂)₂ may be similarly obtained by reacting B₂Cl₂(NMe₂)₂ with two equivalents of BCl₃(SMe₂) at 80 °C. **Route B (from B₂Cl₄):** Dimethylsulfide (0.1 mL, 1.37 mmol) was added dropwise to a solution of B₂Cl₄ (78.4 mg, 479 μmol) in hexane (4 mL) at –78 °C. The mixture was stirred for 1 h at room temperature and all volatiles were removed under reduced pressure. The compound was washed three times with 0.5 mL pentane, yielding pure B₂Cl₄(SMe₂)₂ (113 mg, 438 μmol, 91%) as colorless solid. ¹H NMR (C₆D₆, 298 K, 500 MHz): 2.22 ppm. ¹³C{¹H} NMR (C₆D₆, 298 K, 125.7 MHz): 19.6 ppm. ¹¹B NMR (C₆D₆, 298 K, 160.4 MHz): 7 ppm. **Elemental analysis** calculated for [C₄H₁₂B₂Cl₄S₂]: C 16.70; H 4.34; S 22.29%; found: C 17.13; H 4.34; S 21.84%.

Synthesis of B₂Br₄(SMe₂)₂ – Route A (from B₂(NMe₂)₄): To a solution of BBr₃(SMe₂) (20.0 g, 64.0 mmol, 1 equiv) in 150 mL toluene was added B₂(NMe₂)₄ (12.7 g, 64.0 mmol) at room temperature. After 2 h heating at 80 °C, ¹¹B NMR data of the reaction mixture showed full conversion to B₂Br₂(NMe₂)₂ (38 ppm) and the by-product BBr(NMe₂)₂ (27.5 ppm). A further two equivalents of BBr₃(SMe₂) (40.0 g, 128 mmol) and 1.0 mL dry and degassed dimethylsulfide were added and the reaction mixture heated at 80 °C overnight, after which ¹¹B NMR data showed ca. 60 % conversion to B₂Br₄(SMe₂)₂ (broad resonance at –0.3 ppm) alongside the by-products BBr(NMe₂)₂ and BBr₂(NMe₂) (25.6 ppm). Removal of all volatiles *in vacuo* over the course of 5 hours at 50 °C and washing of the residue with 5 x 20 mL pentane yielded B₂Br₄(SMe₂)₂ as a colorless, highly air-sensitive solid (18.5 g, 39.8 mmol, 62% yield). **Route B (from B₂Br₄):** Dimethylsulfide (0.1 mL, 1.37 mmol) was added dropwise to a solution of B₂Br₄ (100 mg, 293 μmol) in pentane (10 mL) at –78 °C. The

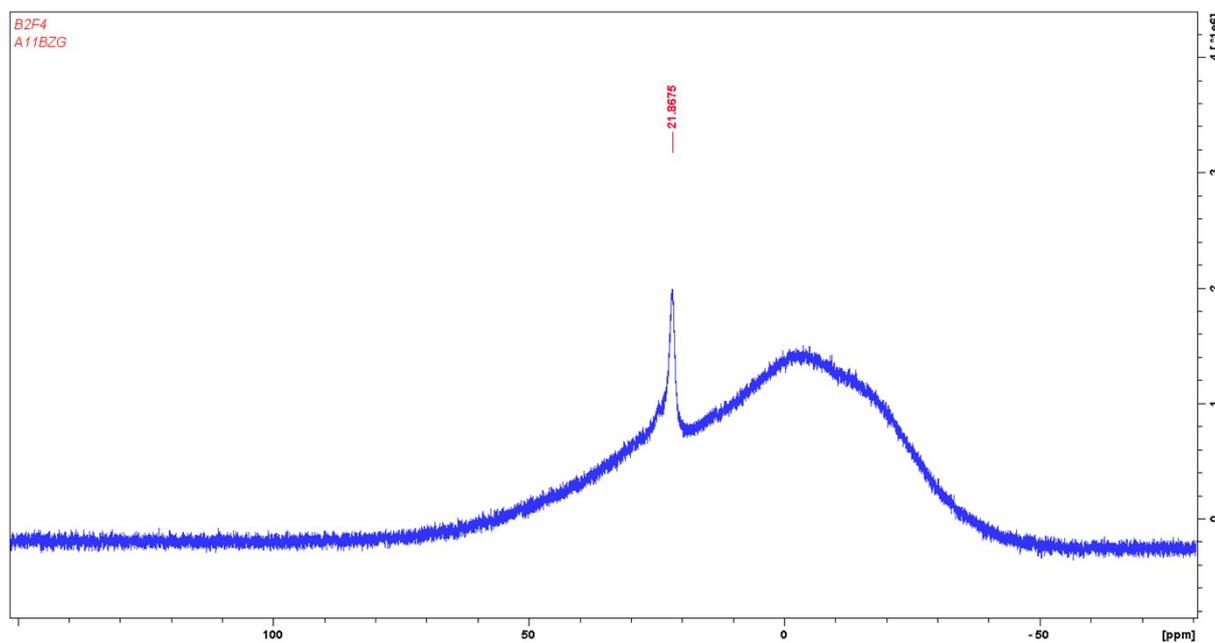
mixture was stirred for 1 h at room temperature and all volatiles were removed under reduced pressure. The compound was crystallized via slow evaporation of a hexane solution and washed three times with 0.5 mL pentane, yielding pure $\text{B}_2\text{Br}_4(\text{SMe}_2)_2$ (118 mg, 254 μmol , 87%) as colorless crystals. $^1\text{H NMR}$ (C_6D_6 , 298 K, 500 MHz): 1.82 ppm. $^{11}\text{B NMR}$ (C_6D_6 , 298 K, 160.4 MHz): 0 ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 298 K, 125.7 MHz): 21.3 ppm. **Elemental analysis** calculated for $[\text{C}_4\text{H}_{12}\text{B}_2\text{Br}_4\text{S}_2]$: C 10.32; H 2.60; S 13.77%; found: C 10.36; H 2.62; S 13.57%.

Synthesis of $\text{B}_2\text{I}_4(\text{SMe}_2)_2$: B_2I_4 (100 mg, 188 μmol) was dissolved in toluene (0.6 mL) and SMe_2 (23.5 mg, 0.1 mL, 378 μmol) was added at dropwise at -78°C . The mixture was stirred for 2 h before all volatiles were removed under reduced pressure. The resulting colorless solid was washed with hexane and slow evaporation of a saturated toluene solution provided $\text{B}_2\text{I}_4(\text{SMe}_2)_2$ (109 mg, 167 μmol , 89%) as colorless crystals, one of which was used for single-crystal X-ray crystallography. $^1\text{H NMR}$ (400.1 MHz, d_8 -toluene): $\delta = 1.79$ (s, 12 H) ppm. $^{11}\text{B NMR}$ (128.4 MHz, d_8 -toluene): $\delta = -20$ (s) ppm. $^{13}\text{C NMR}$ (100.6 MHz, d_8 -toluene): $\delta = 24.5$ (s) ppm. **Elemental analysis** calculated for $[\text{C}_4\text{H}_{12}\text{B}_2\text{I}_4\text{S}_2]$: C 7.35; H 1.85; S 9.81%; found: C 7.53; H 1.73; S 9.86%.

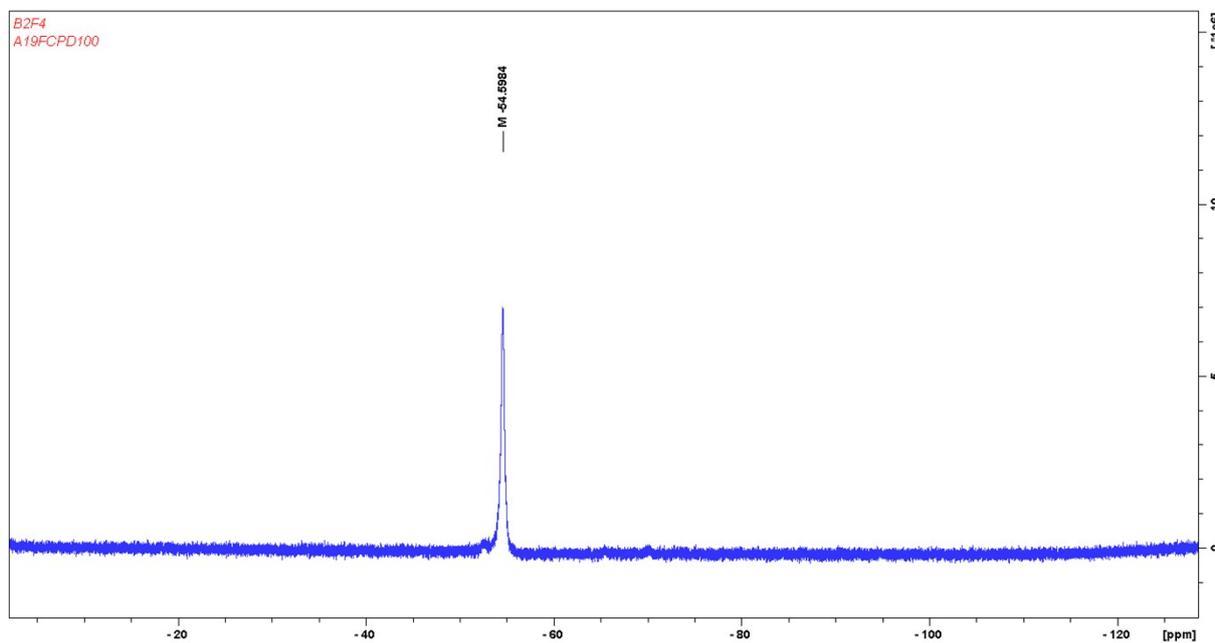
NMR Spectra



^{11}B NMR (hexane)

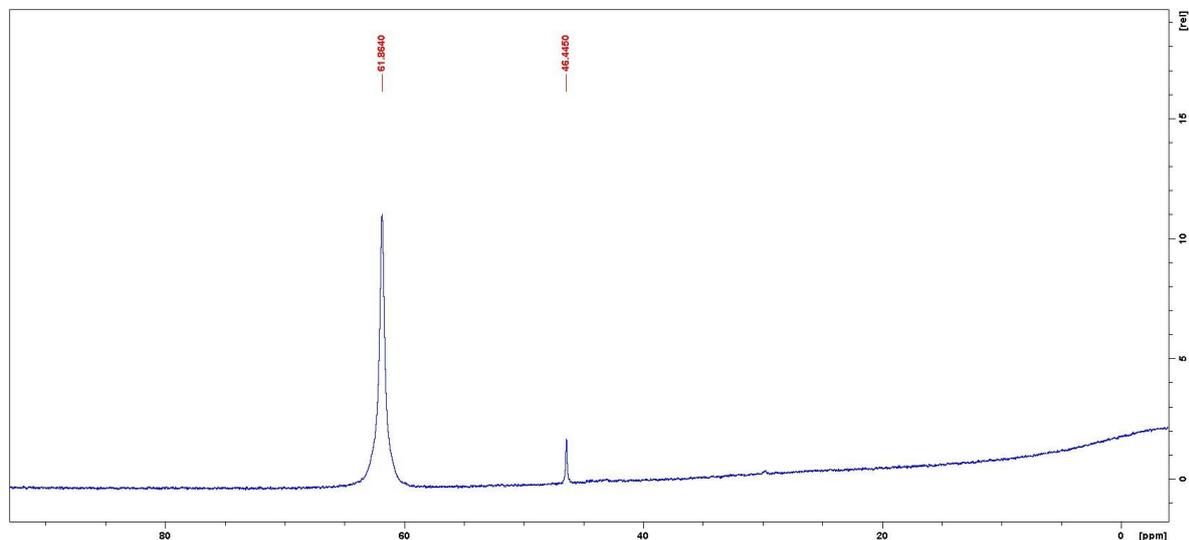


^{19}F NMR (hexane)



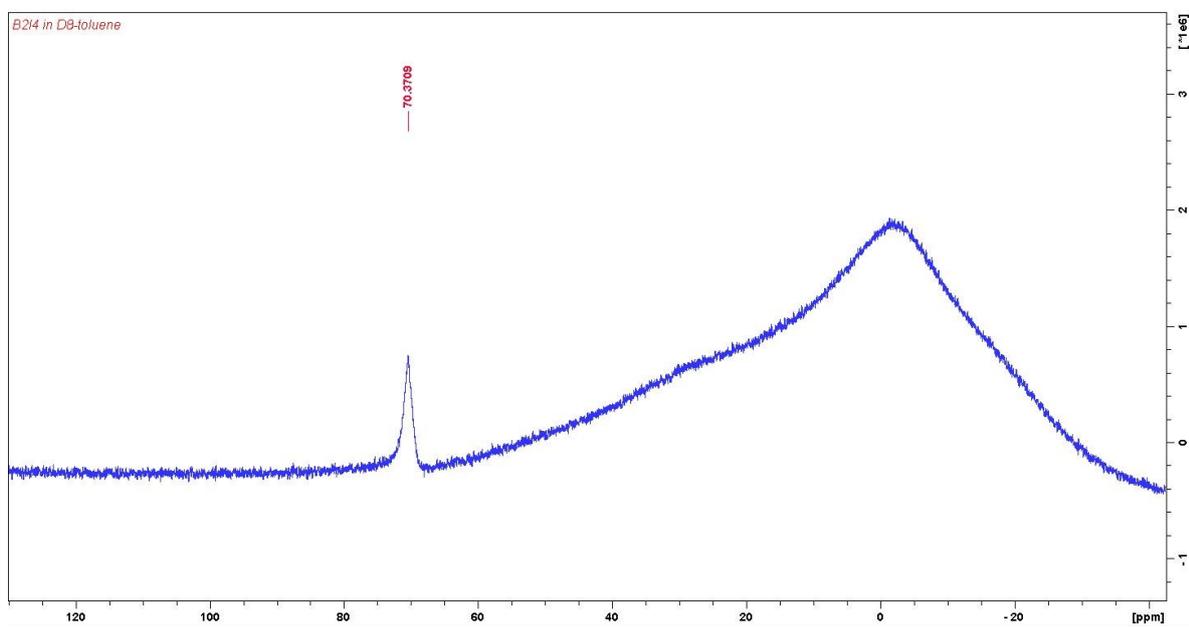
B_2Cl_4

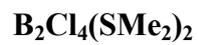
^{11}B NMR (hexane) (the minor signal is the unavoidable BCl_3 impurity)



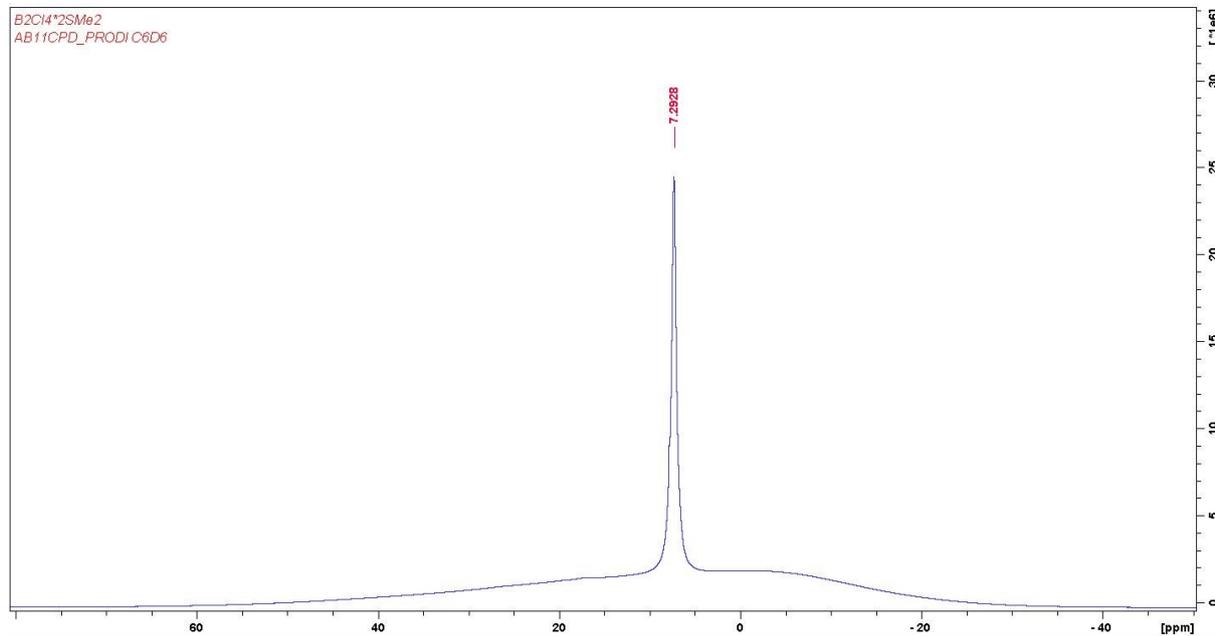
B_2I_4

^{11}B NMR (d_8 -toluene)

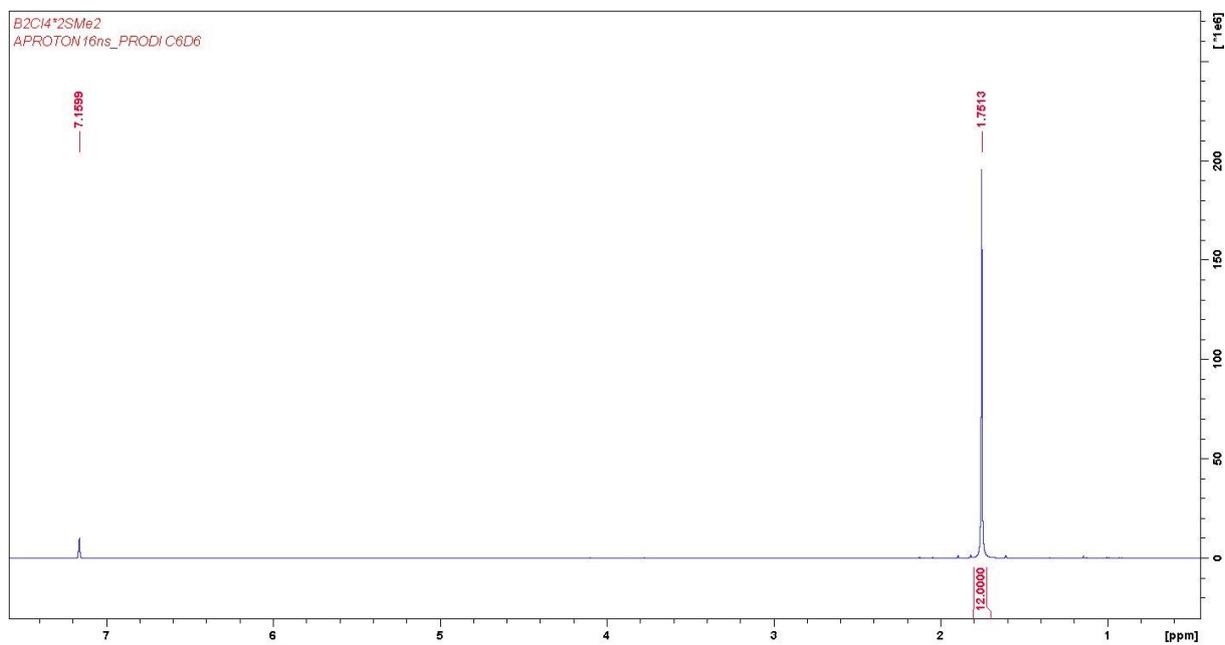




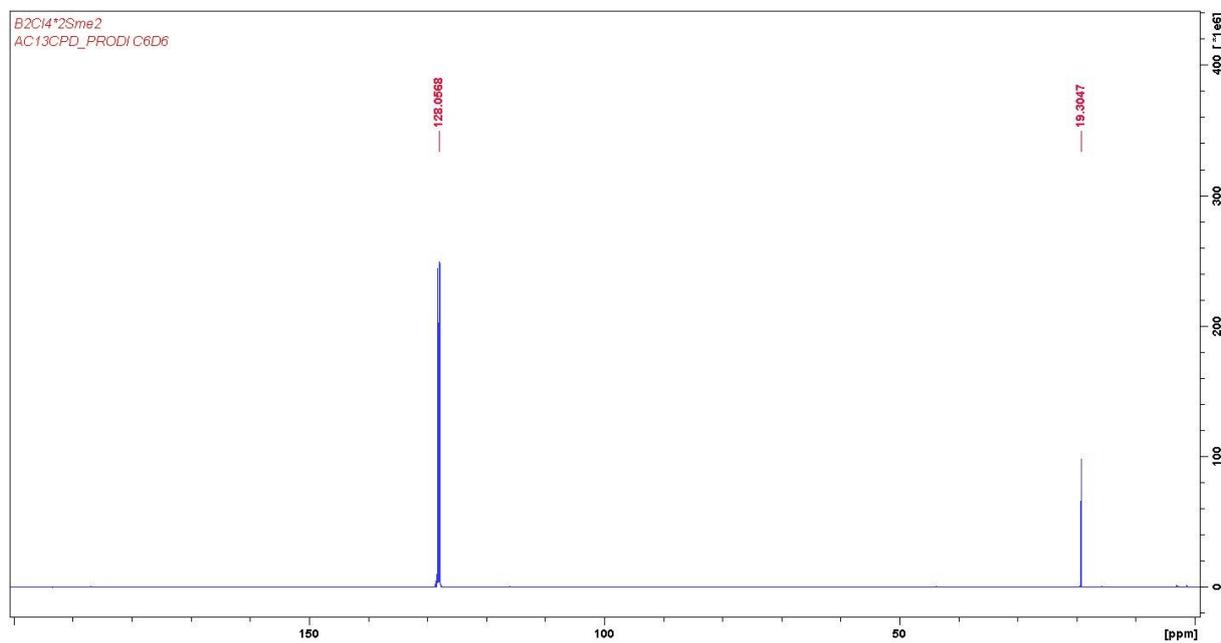
¹¹B NMR (C₆D₆)



¹H NMR (C₆D₆)

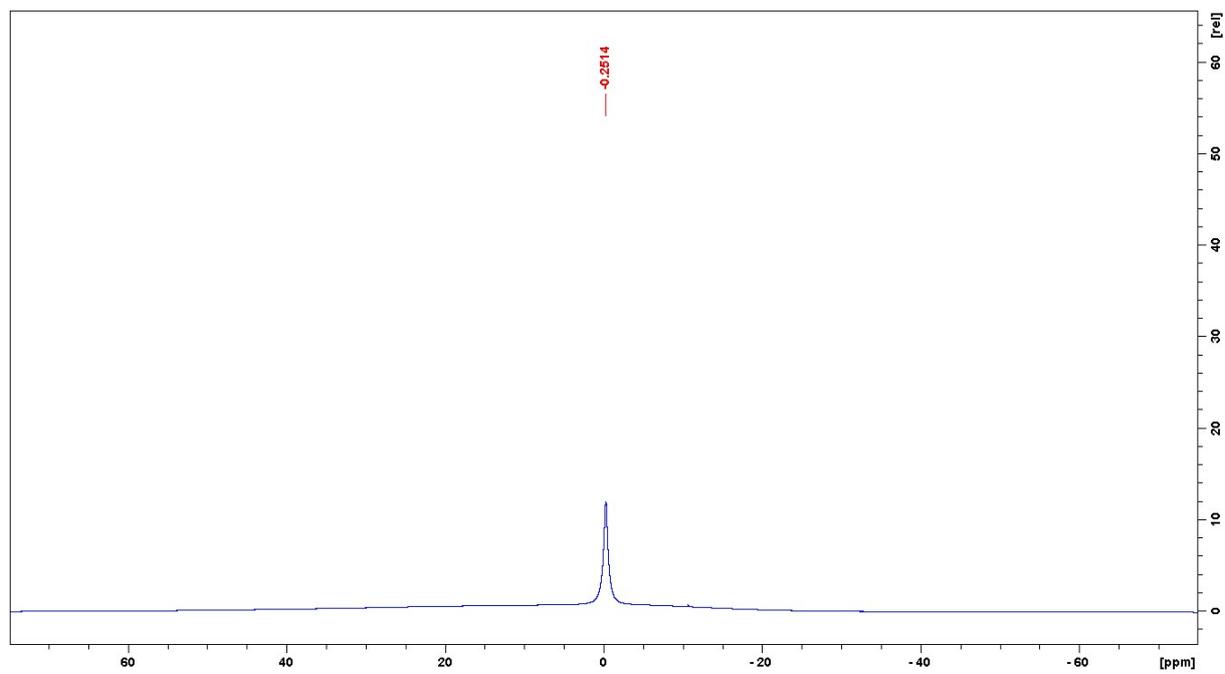


$^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6)

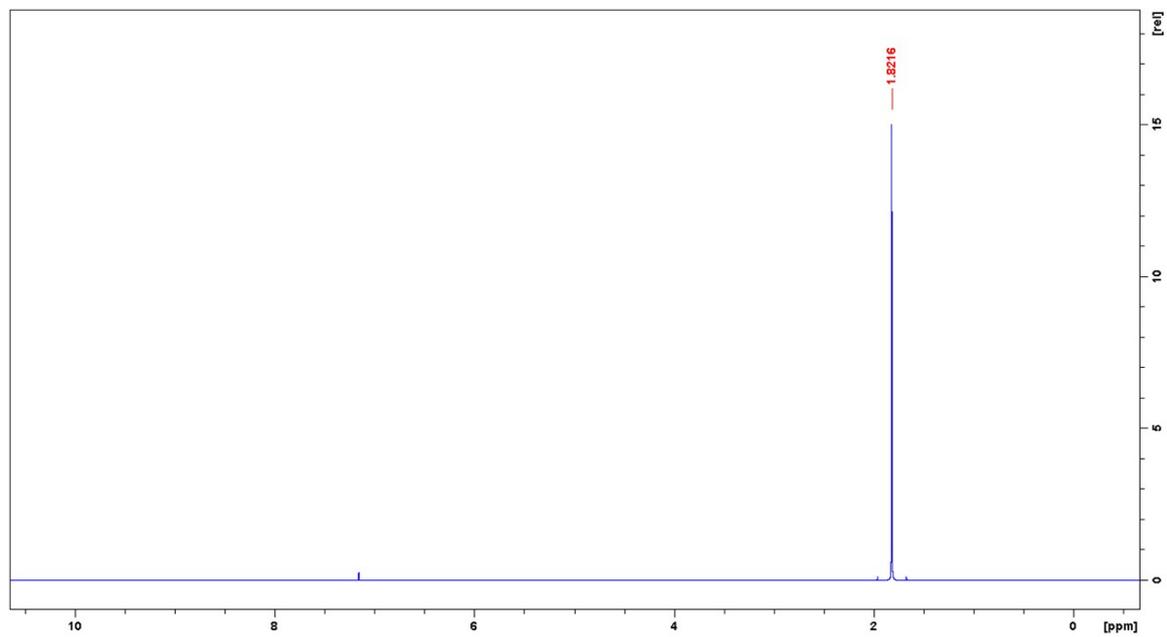


$\text{B}_2\text{Br}_4(\text{SMe}_2)_2$

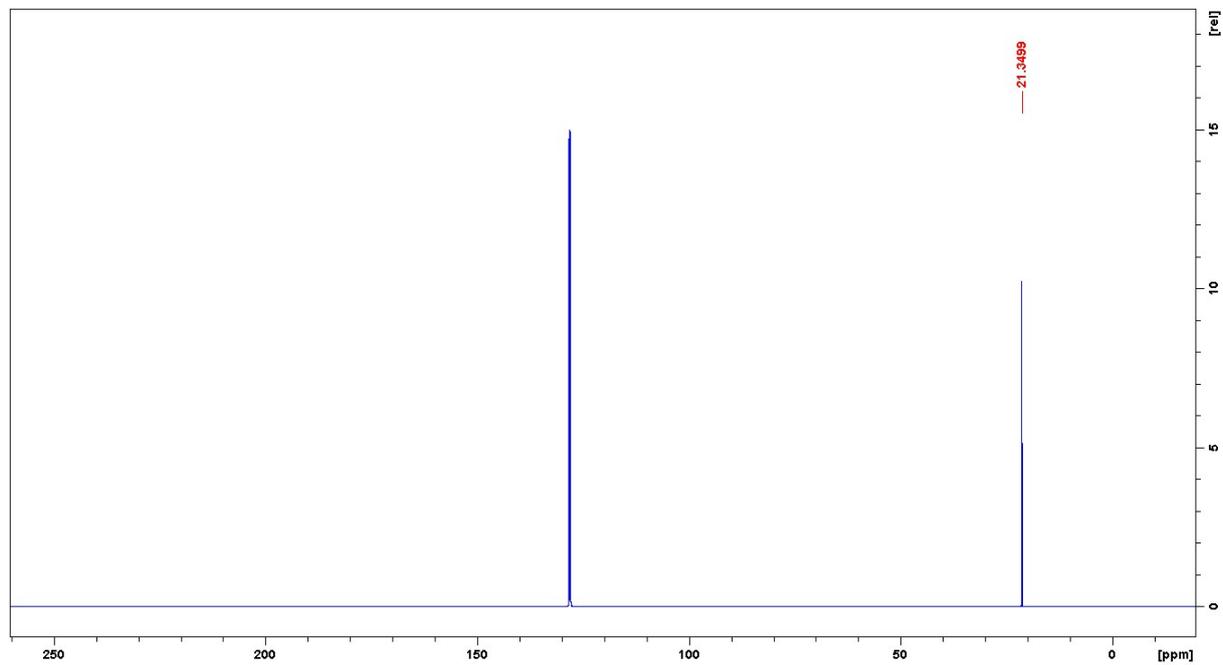
^{11}B NMR (C_6D_6)



^1H NMR (C_6D_6)

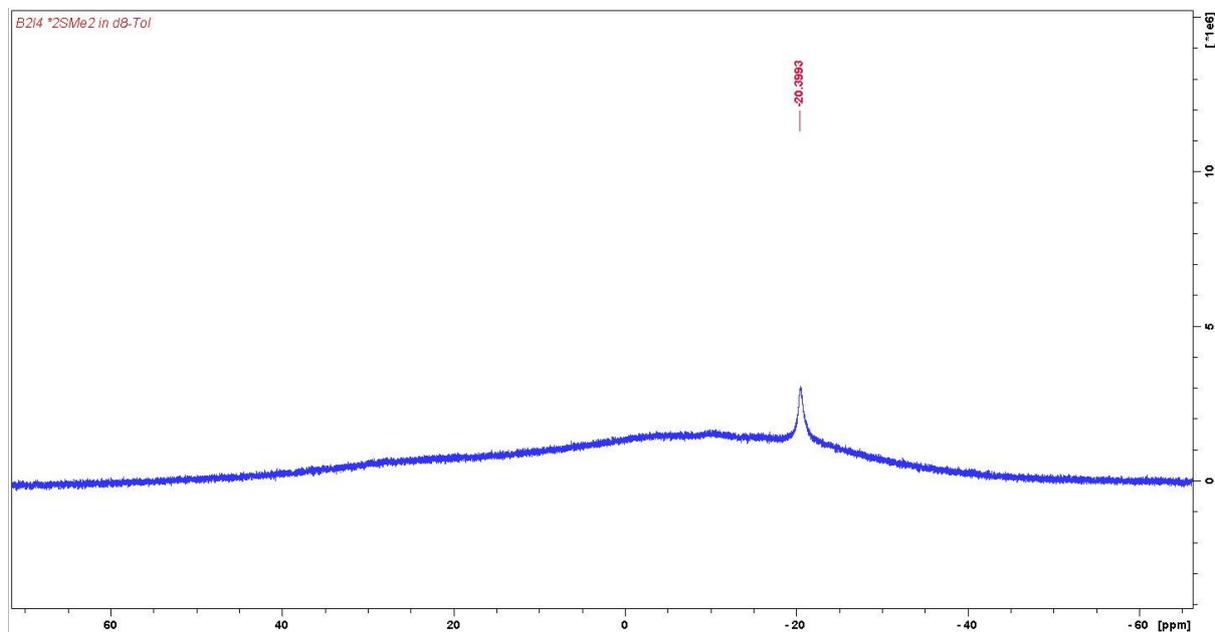


$^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6)

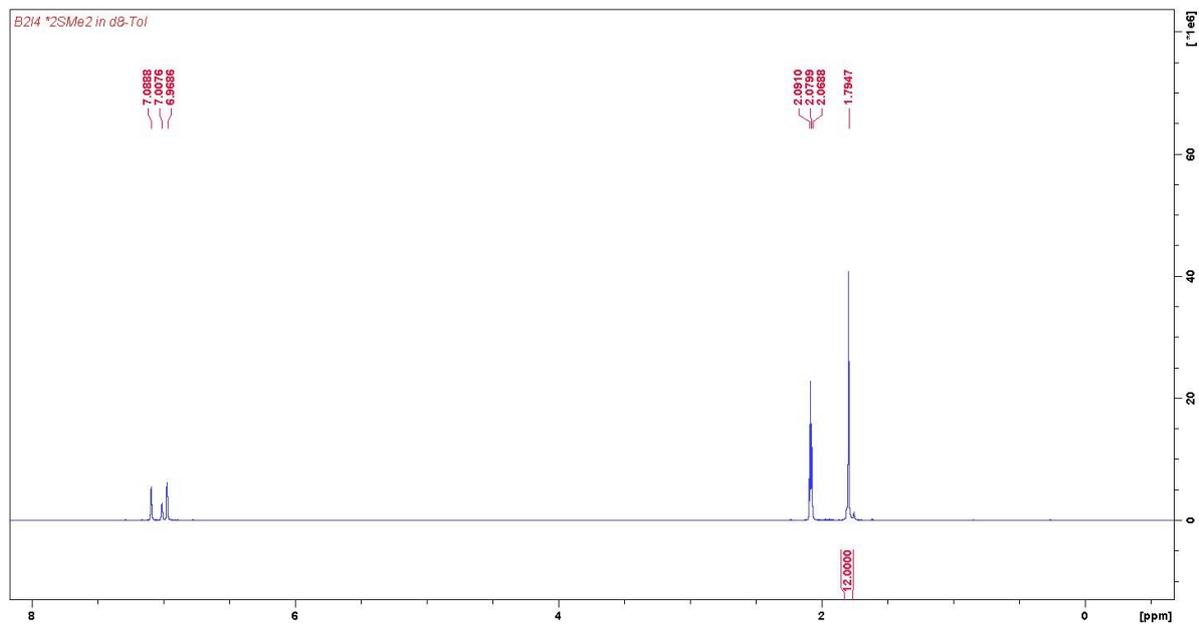


$B_2I_4(SMe_2)_2$

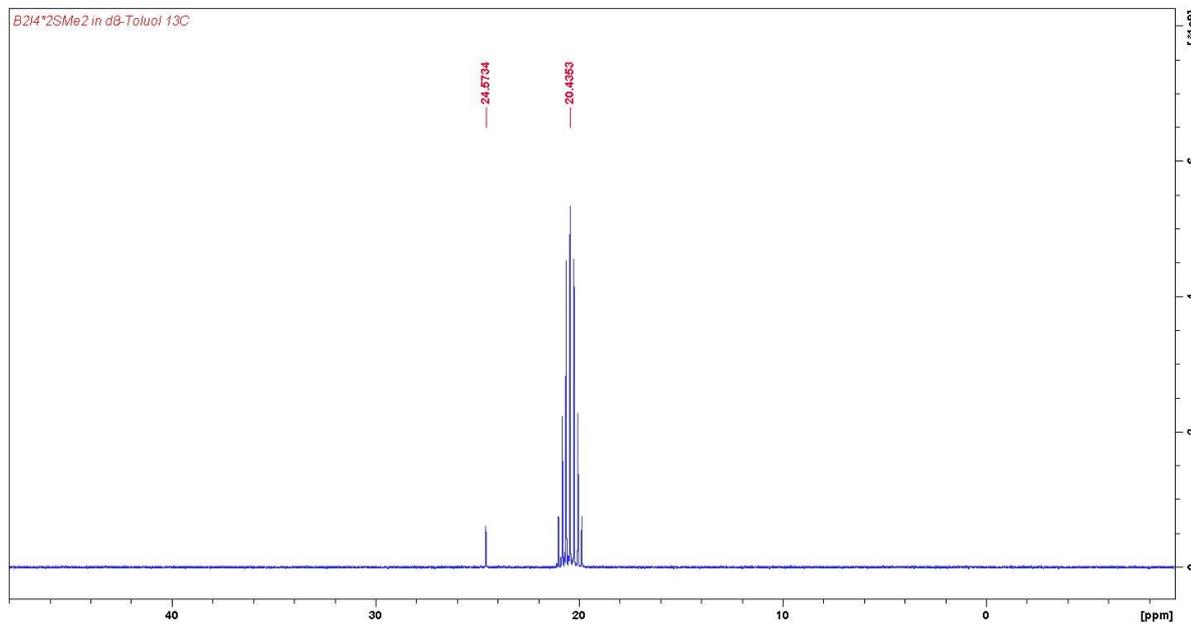
^{11}B NMR (d_8 -toluene)



1H NMR (d_8 -toluene)



$^{13}\text{C}\{^1\text{H}\}$ NMR (d_8 -toluene)



Crystallographic Details

The crystal data of **2a** were collected on a BRUKER X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated Mo_{K α} radiation. The structure was solved using intrinsic phasing method,⁴ refined with the SHELXL program⁵ and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions. Crystal data for **2a**: C₄H₁₂B₂Cl₄S₂, $M_r = 287.68$, colourless plate, 0.60×0.50×0.30 mm³, orthorhombic space group *Pbca*, $a = 9.9144(6)$ Å, $b = 10.8859(7)$ Å, $c = 11.2982(7)$ Å, $V = 1219.38(13)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.567$ g·cm⁻³, $\mu = 1.261$ mm⁻¹, $F(000) = 584$, $T = 100(2)$ K, $R_I = 0.0168$, $wR^2 = 0.0441$, 1290 independent reflections [$2\theta \leq 53.33^\circ$] and 57 parameters. CCDC-1545630.

The crystal data of **2c** were collected on a BRUKER X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated Mo_{K α} radiation. The structure was solved using intrinsic phasing method,⁴ refined with the SHELXL program⁵ and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions. Crystal data for **2c**: C₄H₁₂B₂Br₄S₂, $M_r = 465.52$, colourless plate, 0.30×0.16×0.10 mm³, monoclinic space group *P2₁/n*, $a = 7.4726(4)$ Å, $b = 7.2585(4)$ Å, $c = 12.3850(8)$ Å, $\beta = 107.281(2)^\circ$, $V = 641.44(6)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 2.410$ g·cm⁻³, $\mu = 12.825$ mm⁻¹, $F(000) = 436$, $T = 103(2)$ K, $R_I = 0.0157$, $wR^2 = 0.0380$, 1300 independent reflections [$2\theta \leq 52.742^\circ$] and 57 parameters. CCDC-1545631.

The crystal data of **2d** were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated Mo_{K α} radiation. The crystal data of **2d** were collected on a BRUKER X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated Mo_{K α} radiation. The structures were solved using the intrinsic phasing method,⁴ refined with the SHELXL program⁵ and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealised geometric positions. Crystal data for **2d**: C₄H₁₂B₂I₄S₂, $M_r = 653.48$, colourless block, 0.09×0.08×0.08 mm³, monoclinic space group *P2₁/n*, $a = 7.556(4)$ Å, $b = 7.455(5)$ Å,

$c = 13.174(8) \text{ \AA}$, $\beta = 104.89(3)^\circ$, $V = 717.2(7) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 3.026 \text{ g}\cdot\text{cm}^{-3}$, $\mu = 8.938 \text{ mm}^{-1}$, $F(000) = 580$, $T = 103(2) \text{ K}$, $R_I = 0.0178$, $wR^2 = 0.0405$, 1532 independent reflections [$2\theta \leq 53.46^\circ$] and 57 parameters. CCDC-1545629.

References

- 1 D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 3rd ed., 1988.
- 2 H. Nöth and H. Pommerening, *Chem. Ber.*, 1981, **114**, 398-399.
- 3 H. C. Brown and N. Ravindran, *Inorg. Chem.*, 1977, **16**, 2938-2940.
- 4 G. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3–8.
- 5 G. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112–122.