Supporting Information

Bismuthenium-pnictonium Dications [R'BiPnR$_3$]$^{2+}$ (Pn = As, Sb) containing Carbenoid Bismuth Centers and Rare Bi-Sb Bonds

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General: Small scale reactions were carried out in a glove box with an inert N_2 atmosphere. Solvents were dried on an MBraun solvent-purification system and stored over molecular sieves prior to use. Deuterated solvents were purchased from Aldrich and were used as received. All chemicals were purchased from Aldrich and solids sublimed before use. TMSOTf was purchased from Aldrich and distilled prior to use.
NMR spectra were obtained at room temperature, unless otherwise stated, on a Bruker AVANCE 500 ^{1}H (500.13 MHz, 11.7 T) and Bruker/Tecmag AC250 ^{1}H (250.06 MHz, 5.9 T). ^{13}C{^{1}H}-NMR (125.76 MHz) chemical shifts were referenced to δ_{TMS} = 0.00, ^{31}P{^{1}H}-NMR (202.46 MHz, 101.26 MHz) to $\delta_{H3PO4\ (85\%)}$ = 0.00. Chemical shifts (δ) are reported in ppm. IR spectra were obtained on powdered and crystalline samples on CsI plates. Data collection was on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Peaks are reported in wavenumbers (cm^{-1}) with ranked intensities in parentheses beside the value, where a value of one is indicative of the most intense peak in the spectrum. Melting points were recorded on an Electrothermal melting point apparatus in sealed capillary tubes under N_2. Elemental analyses of selected samples were performed by Canadian Microanalytical Services Ltd. Delta, British Columbia, Canada, but data were inconsistent due to degradation of samples by loss of solvent. X-ray diffraction data were collected on Bruker APEX II CCD area detector/D8 diffractometer. Crystals were coated with Paratone-N oil, mounted on glass fibres, and placed in a cold stream of N_2. Structures were solved by direct methods (*SHELXS-97*[S1]) or Patterson search/structure expansion (*DIRDIF-2008*[S2]), and refined using full matrix least squares on F^2 (*SHELXL-97*[S1]) Hydrogen atom positions were calculated from the sp^2 or sp^3 hybridization geometries of their attached atoms. Data for these structures can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/products/csd/request/ CCDC.

Preparation of [Ph$_3$AsBiCl$_2$][OTf] {[**1b**][OTf]•C$_6$H$_6$}$_4$
$BiCl_3$ (157.5 mg, 0.5 mmol) was stirred in benzene and TMSOTf (1.1 mmol) was added dropwise and allowed to stir for 30 minutes. Ph_3As (151.5 mg, 0.5 mmol) was dissolved in benzene and added dropwise over five minutes resulting in a yellow solution. After one hour, the mixture was filtered and crystals formed upon the solution standing at room

temperature overnight. The yellow crystals were washed with pentane (3 x 3 mL), Yield: 42%,136 mg, Melting Point: 159-160 °C; Elemental Analysis Calcd. For $C_{25}H_{21}AsBiCl_2F_3O_3$ (Found): C 38.43 (36.92), H 2.60 (2.43); FTIR (cm^{-1}, ranked intensities): 3062 (6), 2655 (18), 1975 (11), 1898 (13), 1828 (12), 1758 (14), 1660 (15), 1576 (9), 1481 (5), 1436 (4), 1390 (19), 1264 (1), 1166 (2), 1075 16), 1036 (3), 920 (17), 843 (10), 731 (8), 668 (7)., ^{1}H-NMR (C_6D_6, 500 MHz, 293 K): 7.02 (*s*, 6H), 7.09-7.18 (*m*, 9H), 7.38 (*m*, 6H); $^{13}C\{^{1}H\}$-NMR (C_6D_6, 125.8 MHz, 293 K): 128.5(*s*), 130.5 (*s*), 132.0 (*s*), 133.7 (*s*), 134.8 (*s*); 128.6 (s) (C_6H_6).

Preparation of $[Ph_3SbBiCl_2][AlCl_4]$ [**1c**][$AlCl_4$]•PhMe
$BiCl_3$ (126.0 mg, 0.4 mmol) was stirred in toluene and $AlCl_3$ (49.2 mg, 0.4 mmol) was added to the mixture. After 30 minutes, Ph_3Sb (141.2 mg, 0.4 mmol) in toluene was added dropwise. The mixture was stirred for 30 minutes and was then filtered. Crystals were isolated through toluene/hexanes layering at -25 °C over 48 hours and were washed with hexanes (3 x 3 mL) and dried by evaporation, Yield: 50% 179 mg, mp: 79-80 °C, color changes on washing samples precluded acquisition of elemental analyses; FTIR (cm^{-1}, ranked intensities): 3090 (11), 3069 (5), 3030 (4), 2918(10), 2880 (6), 1951 (16), 1856 (17), 1804 (18), 1737 (19), 1607 (9), 1495 (3), 1464 (15), 1432 (8), 1383 (7), 1183 (20), 1085 (13), 1032 (12), 997 (14), 731 (1), 696 (2)., ^{1}H-NMR ($C_6D_5CD_3$, 500 MHz, 293 K): 2.16 (s, 3H), 6.99-7.22 (*m*, 13H), 7.31-7.41 (*m*, 4H), 7.44-7.46 (*m*, 1H), 7.74 (*t*, $^{3}J_{HH}$ = 9 Hz, 1H), 8.99 (*d*, $^{3}J_{HH}$ = 9 Hz, 1H); $^{13}C\{^{1}H\}$-NMR ($C_6D_5CD_3$, 125.8 MHz, 293 K):130.2 (s), 131.6 (s), 134.6 (s), 137.5 (s).

Preparation of $[Ph_3AsBiPh][OTf]_2$ $\{$[**3b**][OTf]$_2\}_2$
$PhBiCl_2$ (0.4 mmol) was stirred in bezene and TMSOTf (1.0 mmol) was added to the mixture and stirred for 1 hour. Ph_3As (151.5 mg, 0.5 mmol) in benzene was added dropwise and the mixture was stirred for 1 hour. Crystals were isolated by benzene/pentane layering at -25°C over 48 hours, and were washed with pentane (3 x 3 mL), Yield: 30%, 106 mg, mp: 203-205°C; samples change color to brown when placed under vacuum and elemental analyses were not obtained; FTIR (cm^{-1}, ranked intensities): 3062 (12), 1968 (13), 1888 (14), 1821 (15), 1765 (16), 1572 (11), 1481 (10), 1432 (8), 1306 (9), 1204 (1), 1162 (3), 1015 (2), 731 (4), 692 (5), 671 (6), 629 (7). ^{1}H-NMR (CD_3CN, 500 MHz, 293 K): 8.35 (*dd*, $^{3}J_{HH}$ = 8.2 Hz, $^{4}J_{HH}$ = 1.3 Hz, 6H), 7.70 (*t*, $^{3}J_{HH}$ = 7.7 Hz, 6H), 7.45-7.36 (*m*, 8H). $^{13}C\{^{1}H\}$-NMR (CD_3CN, 125.8 MHz, 293 K): 138.1 (*s*), 137.3 (*s*), 134.2 (*s*), 132.7 (*s*), 131.1 (*s*), 129.6 (*s*), 129.4 (*s*), 128.8 (*s*).

Preparation of $[Ph_3SbBiCl][AlCl_4]_2$ [**3c**][$AlCl_4$]$_2$•C_6H_6
$SbCl_3$ (91.2 mg, 0.4 mmol) and $AlCl_3$ (123.0 mg, 1.0 mmol) in benzene was stirred for 30 minutes. Ph_3Bi (175.6 mg, 0.4 mmol) in benzene was added dropwise and stirred for 1 hour. The resulting yellow solution was filtered and layered with pentane and stored at -25°C for 48 hours giving orange crystals that were washed with pentane (3 x 3 mL), Yield: 40%, 162 mg; mp: 65-67°C, samples change color to brown when placed under vacuum and elemental analyses were not obtained; FTIR (cm^{-1}, ranked intensities): 3508 (7), 3063 (8), 1814 (16), 1775 (17), 1675 (18), 1617 (15), 1574 (10), 1477 (4), 1431 (3), 1331 (11), 1064 (6), 1019 (9), 997 (5), 730 (1), 693 (2); ^{1}H-NMR (C_6D_6, 500 MHz, 293 K): 6.91 (*m*, 1H), 7.01 (*t*. $^{3}J_{HH}$ = 8 Hz, 3H), 7.05-7.30 (*m*, 12H), 7.59 (*d*, $^{3}J_{HH}$ = 8.0 Hz,

5H); $^{13}C\{^{1}H\}$-NMR (C_6D_6, 125.8 MHz, 293 K): 131.4 (*s*), 132.5 (*s*), 134.0 (*s*), 134.8 (*s*), 137.7 (*s*).

Crystal data for {[**1b**][OTf]}$_4$•4C_6H_6 (CCDC 755446): $C_{100}H_{84}As_4Bi_4Cl_8F_{12}O_{12}S_4$, M_r = 3253.11, yellow prisms, 0.55 x 0.29 x 0.22 mm^3, triclinic, $P\bar{1}$ (No. 2), a = 11.4407(9) Å, b = 15.4984(13) Å, c = 18.1472 (15) Å, α = 67.5168(9)º, β = 74.1484(9)º, γ = 76.2140(10)º, V = 2827.5 (4) Å^3, Z = 1, ρ_{calcd} = 1.911 g cm^{-3}, μ = 7.704 mm^{-1}, Mo Kα (0.71073 Å), T = 173(1) K, $2\theta_{max}$ = 55.10º, 24994 total data collected, 12865 independent data (R_{int} = 0.0200), structure solution: direct methods (*SHELXS-97*[19]), R_1 = 0.0292 (for 11607 data with $I \geq 2\sigma(I)$), wR_2 = 0.0854 (for all 12865 unique data), $\Delta\rho_{min,max}$ = 2.590, –0.704 e Å^{-3}.

Crystal data for [**1c**][$AlCl_4$]•PhMe (CCDC 755447): $C_{25}H_{23}AlBiCl_6Sb$, M_r = 893.84, yellow plates, 0.47 x 0.29 x 0.07 mm^3, triclinic, $P\bar{1}$ (No. 2), a = 10.0275(10) Å, b = 11.0904(11) Å, c = 15.4057(16) Å, α = 92.501(1)º, β = 106.014(1)º, γ = 112.471(1)º, V = 1500.1(3) Å^3, Z = 2, ρ_{calcd} = 1.979 g cm^{-3}, μ = 7.335 mm^{-1}, Mo Kα (0.71073 Å), T = 173(1) K, $2\theta_{max}$ = 55.12º, 13108 total data collected, 6781 independent data (R_{int} = 0.0198), structure solution: direct methods (*SHELXS-97*[19]), R_1 = 0.0301 (for 6142 data with $I \geq 2\sigma(I)$), wR_2 = 0.1059 (for all 0.0788 unique data), $\Delta\rho_{min,max}$ = 2.552, –1.262 e Å^{-3}.

Crystal data for {[**3b**][OTf]$_2$}$_2$ (CCDC 755448): $C_{52}H_{40}As_2Bi_2F_{12}O_{12}S_4$, M_r = 1780.88, colorless blocks, 0.71 x 0.71 x 0.30 mm^3, triclinic, $P\bar{1}$ (No. 2), a = 10.9929(6) Å, b = 14.9895(9) Å, c = 18.7965 (11) Å, α = 77.240(1)º, β = 81.085(1)º, γ = 88.203(1)º, V = 2984.3(3) Å^3, Z = 2, ρ_{calcd} = 1.982 g cm^{-3}, μ = 7.225 mm^{-1}, Mo Kα (0.71073 Å), T = 173(1) K, $2\theta_{max}$ = 54.92º, 26194 total data collected, 13503 independent data (R_{int} = 0.0190), structure solution: direct methods (*SHELXS-97*[19]), R_1 = 0.0231 (for 12538 data with $I \geq 2\sigma(I)$), wR_2 = 0.0587 (for all 13503 unique data), $\Delta\rho_{min,max}$ = 1.158, –1.552 e Å^{-3}.

Crystal data for [**3c**][$AlCl_4$]$_2$•C_6H_6 (CCDC 755449): $C_{24}H_{21}Al_2BiCl_9Sb$, M_r = 1013.15, orange prisms, 0.45 x 0.36 x 0.27 mm^3, triclinic, $P1$ (No. 1), a = 8.9027(4) Å, b = 10.6863 (5) Å, c = 10.7459(5) Å, α = 112.0241(5)º, β = 106.9854(5)º, γ = 101.5107(5)º, V = 849.52(7) Å^3, Z = 1, ρ_{calcd} = 1.980 g cm^{-3}, μ = 6.741 mm^{-1}, Mo Kα (0.71073 Å), T = 173(1) K, $2\theta_{max}$ = 54.98º, 7690 total data collected, 7690 independent data (R_{int} = 0.0000), structure solution: Patterson search/structure expansion (*DIRDIF-2008*[20]), R_1 = 0.0188 (for 7645 data with $I \geq 2\sigma(I)$), wR_2 = 0.0488 (for all 7690 unique data), $\Delta\rho_{min,max}$ = 0.579, –0.748 e Å^{-3}.

[S1] G. M. Sheldrick, *Acta Crystallogr.* 2008, *A64*, 112–122
[S2] P. T. Beurskens, G. Beurskens, R. de Gelder, J. M. M. Smits, S. Garcia-Granda and R. O. Gould (2008). The *DIRDIF-2008* program system. Crystallography Laboratory, Radboud University Nijmegen, The Netherlands

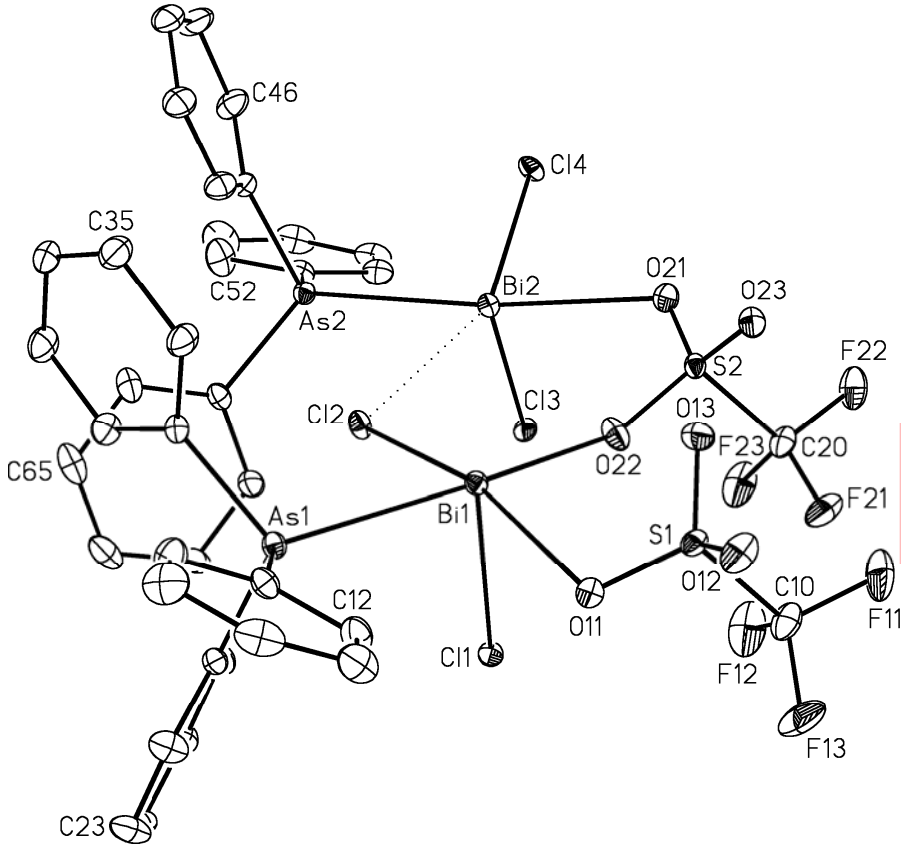

Figure S1: Perspective view of the unique half of the {[**1b**][OTf]}$_4$•4C_6H_6 cluster showing the atom labelling scheme. Non-hydrogen atoms are represented by ellipsoids at the 20% probability level. Hydrogen atoms are not shown.

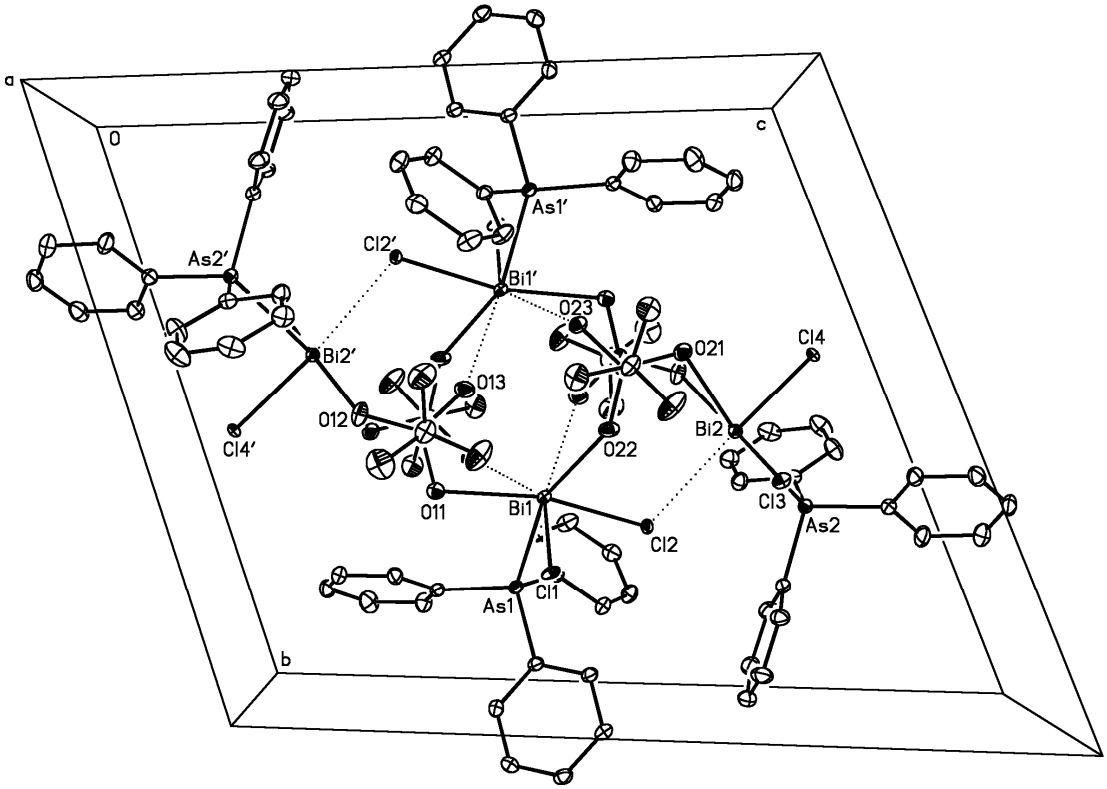

Figure S2: Packing diagram viewed along the crystallographic *a*-axis of {[**1b**][OTf]}$_4$•4C$_6$H$_6$. Non-hydrogen atoms are represented by ellipsoids at the 20% probability level. Hydrogen atoms are not shown.

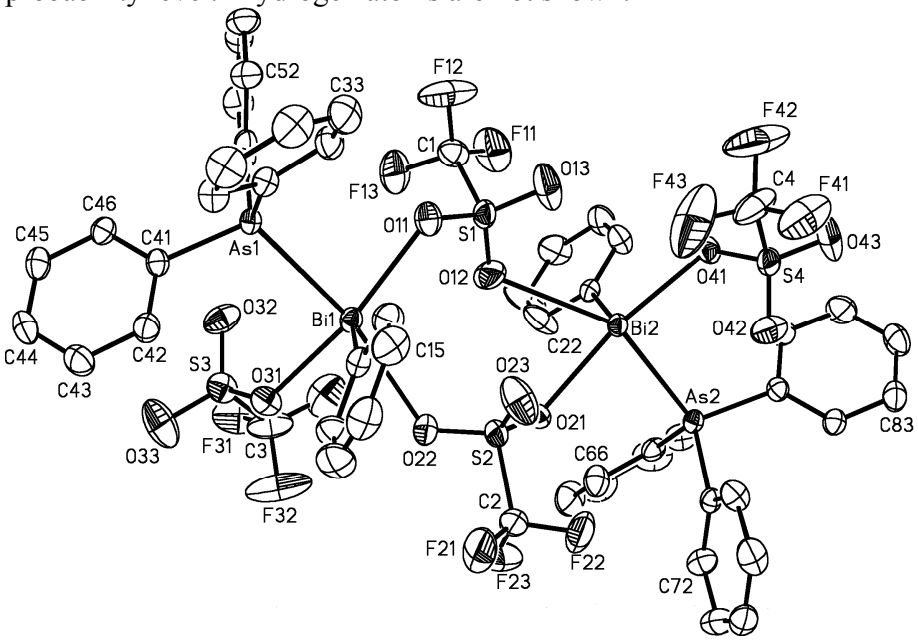

Figure S3: Perspective view of the {[**3b**][OTf]$_2$}$_2$ complex showing the atom labelling scheme. Non-hydrogen atoms are represented by ellipsoids at the 50% probability level. Hydrogen atoms are not shown.

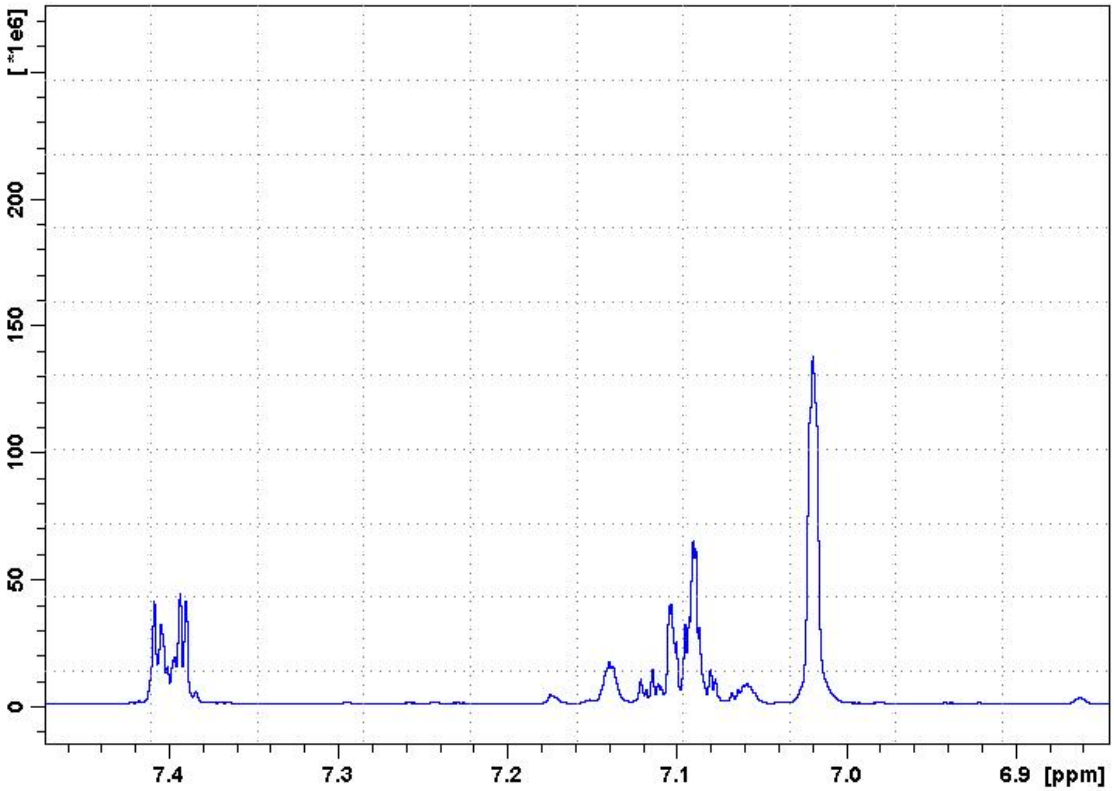

Figure S4: ^{1}H NMR spectra (C_6D_6, 500 MHz, 293 K) of dissolved crystalline material of {[**1b**][OTf]}$_4$•4C_6H_6.

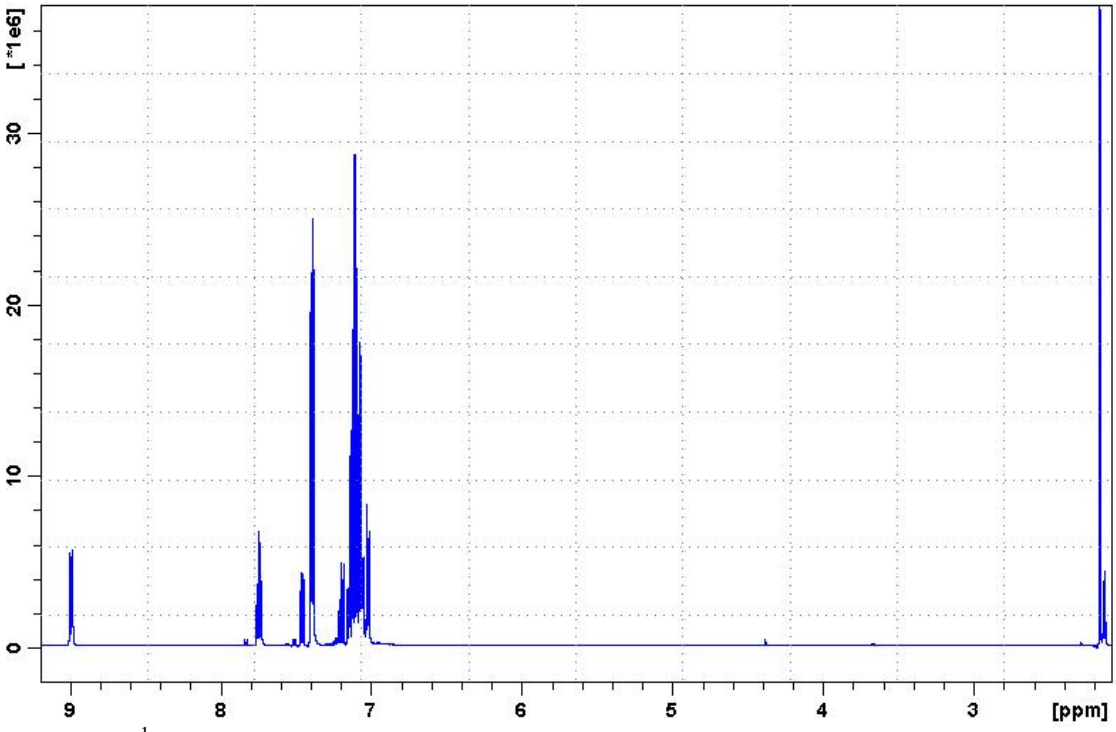

Figure S5: ^{1}H NMR spectra ($C_6D_5CD_3$, 500 MHz, 293 K) of dissolved crystalline material of [**1c**][$AlCl_4$]•PhMe.

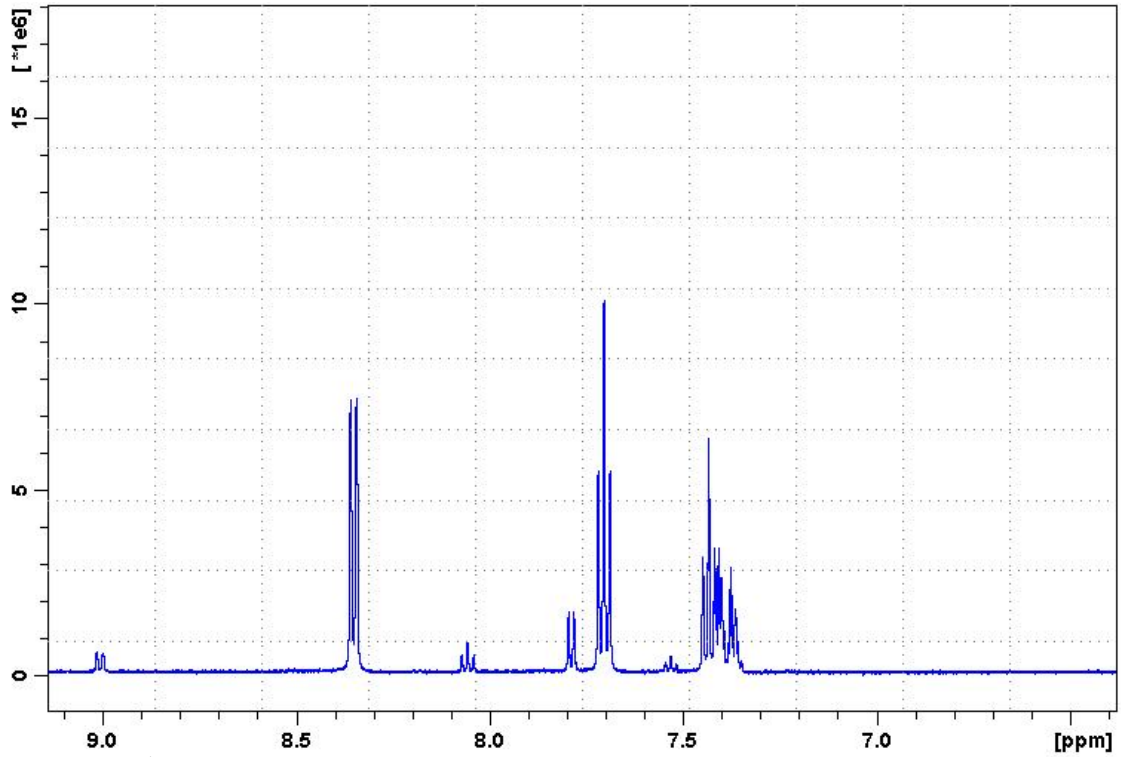

Figure S6: ^{1}H NMR spectra (CD_3CN, 500 MHz, 293 K) of dissolved crystalline material of {[**3b**][OTf]2}2.

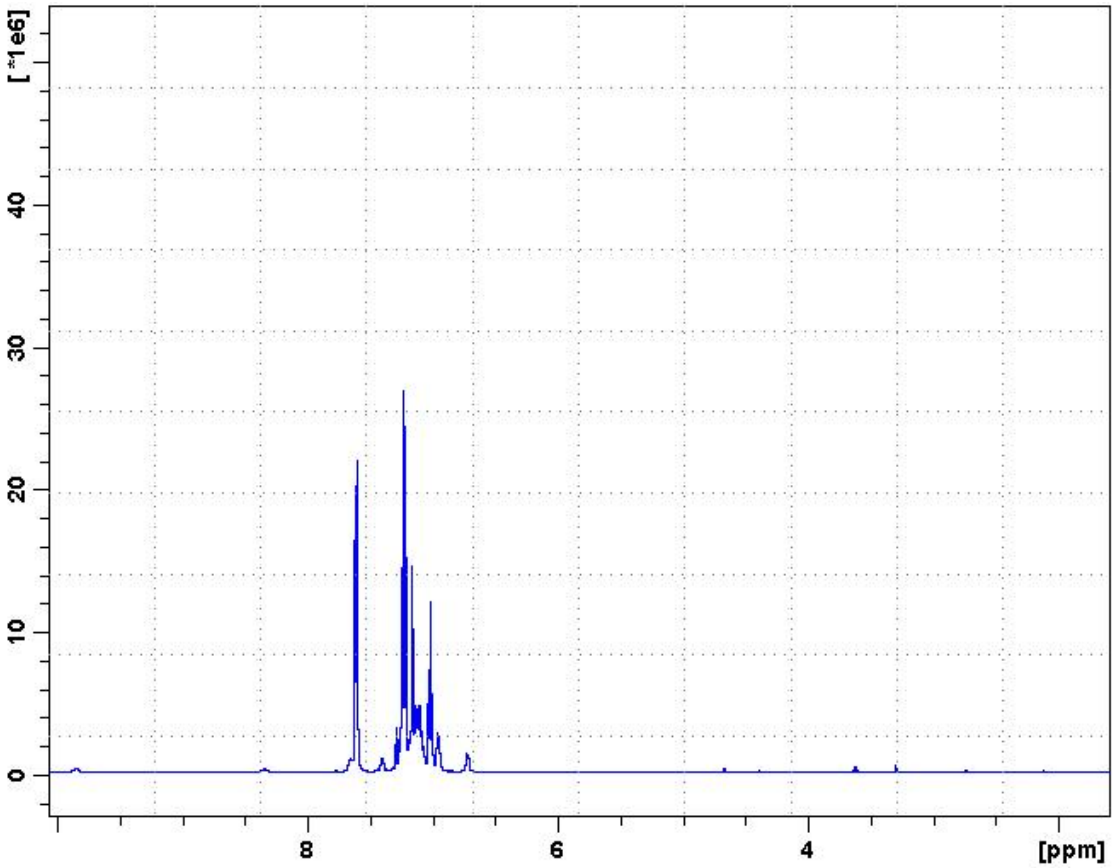

Figure S7: ^{1}H NMR spectra (C_6D_6, 500 MHz, 293 K) of dissolved crystalline material of [**3c**][$AlCl_4$]$_2$•C_6H_6.