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Supplementary Information for:

Supramolecular Aggregation in Dithia-arsoles: Chlorides, Cations and *N*-centred Paddlewheels

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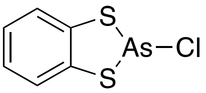
S1. Experimental procedure and compound characterisation

S1.1 General experimental

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk and glove box techniques. With the exception of THF, all solvents used were dried by passing through an alumina column incorporated into an MB SPS-800 solvent purification system, degassed and finally stored in an ampoule fitted with a Teflon valve under a dinitrogen atmosphere. THF was dried over molten potassium for three days and distilled over argon. Deuterated solvents were distilled and/or dried over molecular sieves and stored in a glove box before use. Chemicals were purchased from commercial suppliers and used as received. ^{1}H, ^{13}C{^{1}H} and ^{27}Al NMR spectra were recorded on a Bruker Ascend 500 spectrometer. Chemical shifts are expressed as parts per million (ppm, δ) and are referenced to $CDCl_3$ (7.26/77.16 ppm) or C_6D_6 (7.16/128.06 ppm) as internal standards with ^{27}Al NMR being referenced to $Al(NO_2)_3$. The description of signals include: s = singlet, d = doublet and m = multiplet. All coupling constants are absolute values and are expressed in Hertz (Hz). IR-Spectra were measured on a Shimadzu IRAffinity-1 photospectrometer. Mass spectra were measured on a Waters LCT Premier/XE or a Waters GCT Premier spectrometer.

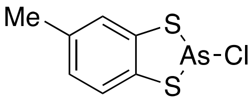
S1.2 Synthesis

Synthesis of 2-chlorobenzo-1,3,2-dithiarsole (**1**).



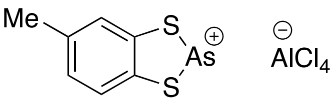
Benzene-1,2-dithiol (0.2 ml, 1.5 mmol, 1 equiv.) was added to a solution of $AsCl_3$ (0.13 ml, 1.5 mmol, 1 equiv.) in THF (10 mL) and left to stir for 20 hours, resulting in a yellow solution. The majority of the solvent was removed under vacuum to give a saturated solution (*ca*. 3 ml). Storage at ambient temperature gave colourless crystals of the product 2-chlorobenzo-1,3,2-dithiarsole (**1**). M.p. 86–89 °C. Yield: 85 mg, 0.34 mmol, 23%. **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 7.62 (dd, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 3.3 Hz, 2H, Ar–H), 7.24 (dd, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 3.3 Hz, 2H, Ar–H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 295 K) δ/ppm: 139.4 (2C, Ar), 127.0 (2C, Ar), 126.3 (2C, Ar). **IR** (Nujol, NaCl windows) $\tilde{\nu}$/cm^{-1}: 1713 (s), 1305 (m), 1151 (m), 968 (m), 934 (m), 863 (m), 740 (s) and 722 (s). **Elem. Anal.** (%) calculated for ($C_6H_4AsClS_2\cdot 0.30\ C_4H_8O$): C: 31.8, H: 2.4; found C: 31.7, H: 2.5.

Synthesis of 2-chloro-5-methylbenzo-1,3,2-dithiarsole (**2**).



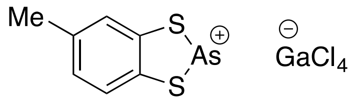
$AsCl_3$ (1.16 g 6.4 mmol, 1 equiv.) was added to a solution of toluene-3,4-dithiol (1.00 g, 6.4 mmol) in CH_2Cl_2 (40 mL). The mixture was stirred at reflux under nitrogen at 40 °C for 1.5 hrs, affording a yellow solution. The solvent was removed *in vacuo* to yield 2-chlorobenzo-1,3,2-dithiarsole (**2**) as a pale yellow solid (1.389 g, 5.25 mmol, 82%). **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 7.49 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Ar–H), 7.43 (s, 1H, Ar–H), 7.05 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Ar–H), 2.37 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 295 K) δ/ppm: 139.6 (1C, Ar), 136.7 (1C, Ar), 136.1 (1C, Ar), 127.5 (1C, Ar), 127.4 (1C, Ar), 126.7 (1C, Ar), 20.9 (1C, CH_3). **Elem. Anal.** (%) calculated for ($C_7H_6AsClS_2$): C: 31.77, H: 2.29; found C: 32.00, H: 2.16. Analyses agree with literature known values.[1] Recrystallisation of **2** from cooling a saturated MeOH solution to −20 °C for 24 h afforded crystals of **2α** suitable for X-ray diffraction and structurally the same as those reported previously [CSD code: DAXLOD].[1] **MP** 81 – 82 °C. A saturated solution of **2** in MeCN (4 mL) stored overnight at – 20 °C afforded crystals of **2β** suitable for X-ray diffraction. **MP** 67–69 °C.

Synthesis of [MeC$_6$H$_3$S$_2$As][AlCl$_4$] (**3a**).



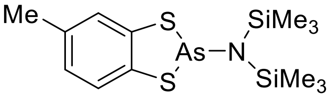
$AlCl_3$ (33 mg, 0.25 mmol, 1 equiv.) dissolved in CH_2Cl_2 (5 mL) was slowly added to 2-chloro-5-methylbenzo-1,3,2-dithiarsole (**2**) (66 mg, 0.25 mmol, 1 equiv.) dissolved in CH_2Cl_2 (5 mL). A dark red solution immediately formed, which was left to stir for 16 hours. The solvent was removed *in vacuo* and the resulting red solid was washed with pentane (3 × 5 mL). Further drying *in vacuo* afforded the product $[MeC_6H_3S_2As][AlCl_4]$ (**3a**) as a red solid. Yield: 89 mg, 0.22 mmol, 89%. **^{1}H NMR** (500 MHz, C_6D_6, 295 K) δ/ppm: 7.03 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Ar–H), 6.88 (s, 1H, Ar–H), 6.47 (d, $^3J_{HH}$ = 8.1 Hz, 1H, Ar–H), 1.82 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6, 295 K) δ/ppm: 141.1 (1C, Ar), 137.6 (1C, Ar), 136.5 (1C, Ar), 127.5 (1C, Ar), 127.4 (1C, Ar), 126.6 (1C, Ar), 20.4 (1C, CH_3). **^{27}Al NMR** (130 MHz, C_6D_6, 295 K) δ/ppm: 104.6 (s, $AlCl_4^-$). **IR** (Nujol, NaCl windows) $\tilde{\nu}$/cm^{-1}: 1579 (w), 1528 (w), 1259 (s), 1210 (w), 1042 (s), 918 (w), 895 (s), 808 (s), 686 (s), 618 (s) and 123 (w). **HRMS** (EI$^+$) *m*/*z* calculated for $[M]^+$ $[C_7H_6S_2As]^+$: 228.9121, found: 228.9131. **Elem. Anal.** (%) calculated for ($C_7H_6AlAsCl_4S_2$): C: 21.13, H: 1.52; found C: 21.09, H: 1.80.

Synthesis of [$MeC_6H_3S_2As$][$GaCl_4$] (**3b**).



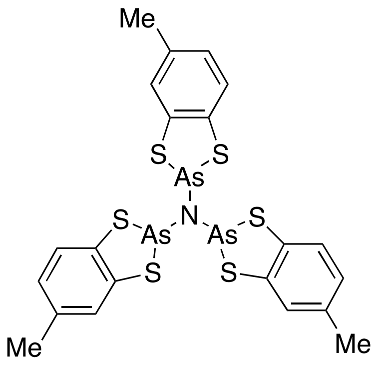
$GaCl_3$ (40 mg, 0.23 mmol, 1 equiv.) dissolved in CH_2Cl_2 (5 mL) was slowly added to 2-chloro-5-methylbenzo-1,3,2-dithiarsole (**2**) (61 mg, 0.23 mmol, 1 equiv.) dissolved in CH_2Cl_2. A dark red solution immediately formed, which was left to stir for 16 hours. The solvent was removed *in vacuo* and the resulting red/orange solid was washed with pentane (3 × 5 mL). Further drying *in vacuo* afforded the product [$MeC_6H_3S_2As$][$GaCl_4$] (**3b**). M.p. 128–129 °C. Yield: 83 mg, 0.19 mmol, 82%. **^{1}H NMR** (500 MHz, C_6D_5Br, 295 K) δ/ppm: 7.03 (d, $^3J_{HH}$ = 8.5 Hz, 1H, Ar–H), 6.81 (s, 1H, Ar–H), 6.52 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, Ar–H), 1.61 (s, 1H, Ar–H). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_5Br, 295 K) δ/ppm: 151.8 (1C, Ar), 148.7 (1C, Ar), 140.3 (1C, Ar), 130.3 (1C, Ar), 127.6 (1C, Ar), 127.3 (1C, Ar), 20.7 (1C, CH_3). **IR** ṽ/cm^{-1}: 1585 (s), 1528 (s), 1444 (s), 1371 (s), 1256 (s), 1101 (s), 808 (s), 750 (s), 689 (s), 538 (w) and 432 (s). **HRMS** (EI$^+$) *m*/*z* calculated for [M]$^+$ [$C_7H_6S_2As$]$^+$: 228.9121; found 228.9132. **Elem. Anal.** (%) calculated for ($C_7H_6AsCl_4GaS_2$): C: 19.08, H: 1.37; found: C: 18.52, H: 1.64.

Synthesis of $MeC_3H_3S_2AsN(SiMe_3)_2$ (**4′**).



2-chlorobenzo-1,3,2-dithiarsole (**2**) (0.519 g, 1.96 mmol, 1 equiv.) dissolved in toluene (10 mL) was added dropwise to a solution of $LiN(SiMe_3)_2$ (0.328 g, 1.96 mmol, 1 equiv.) in toluene (10 mL). The resulting mixture was warmed to ambient temperature and stirred overnight. LiCl was removed *via* cannula filtration and the transferred solvent was removed *in vacuo* to give the product $MeC_3H_3S_2AsN(SiMe_3)_2$ as a yellow oil. Yield: 0.252 g, 0.65 mmol, 33%. **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 7.25 (s, 1H, Ar–H), 7.20 (s, 1H, Ar–H), 6.84 (d, $^3J_{HH}$ = 7.4 Hz, 1H, Ar–H), 2.28 (s, 3H, Ar–CH_3), 0.16 (s, 18H, Si–CH_3). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 295 K) δ/ppm: 141.6 (1C, Ar), 138.1 (1C, Ar), 134.8 (1C, Ar), 126.4 (1C, Ar), 126.0 (1C, Ar), 125.7 (1C, Ar), 20.8 (1C, Ar–$\underline{C}H_3$), 4.7 (6C, Si–$\underline{C}H_3$). **IR** ṽ/cm^{-1}: 1458 (s), 1252 (w), 907 (s), 827 (w), 681 (w) and 496 (s).

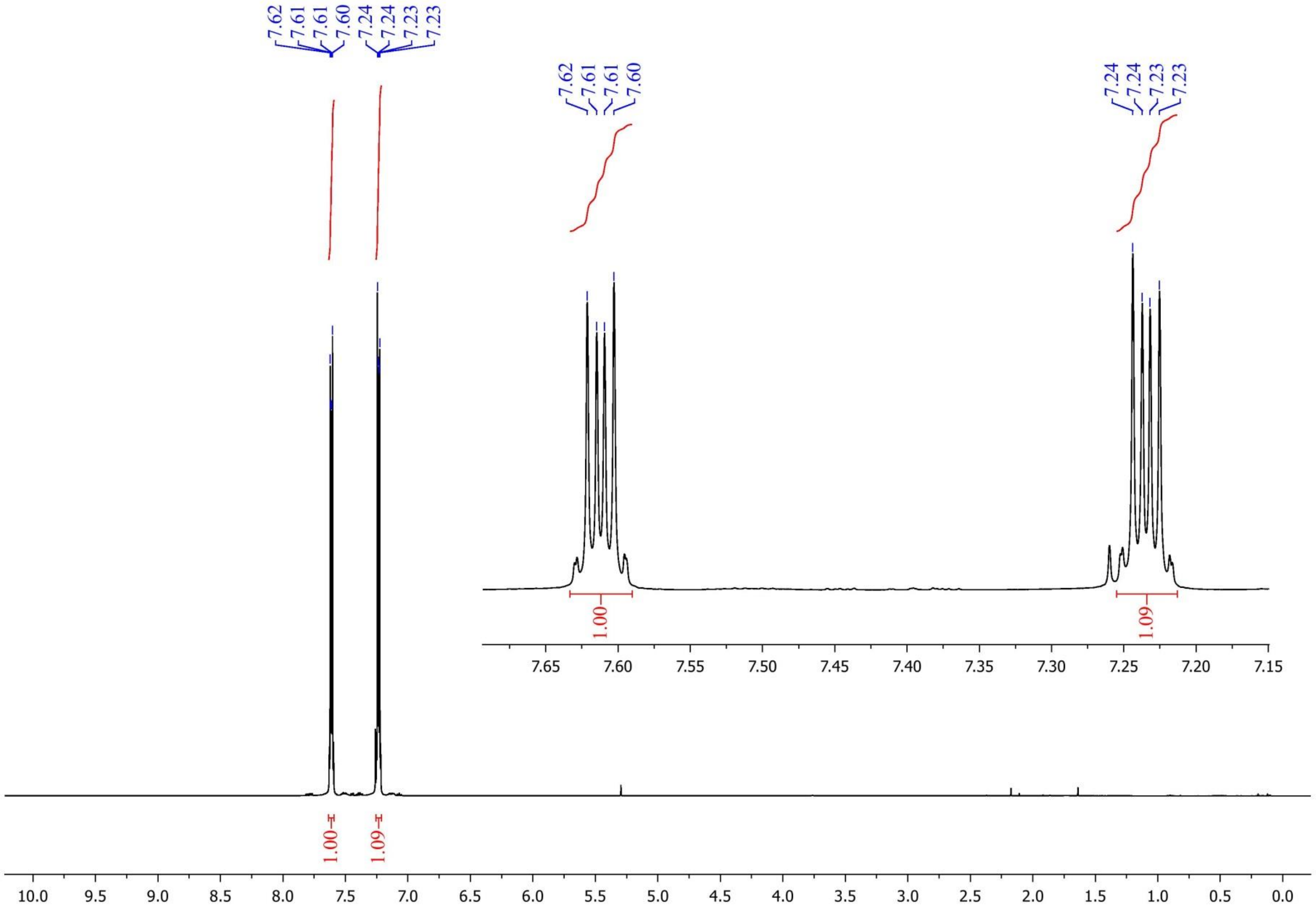
Synthesis of $N(MeC_6H_3S_2As)_3$ (**4**).



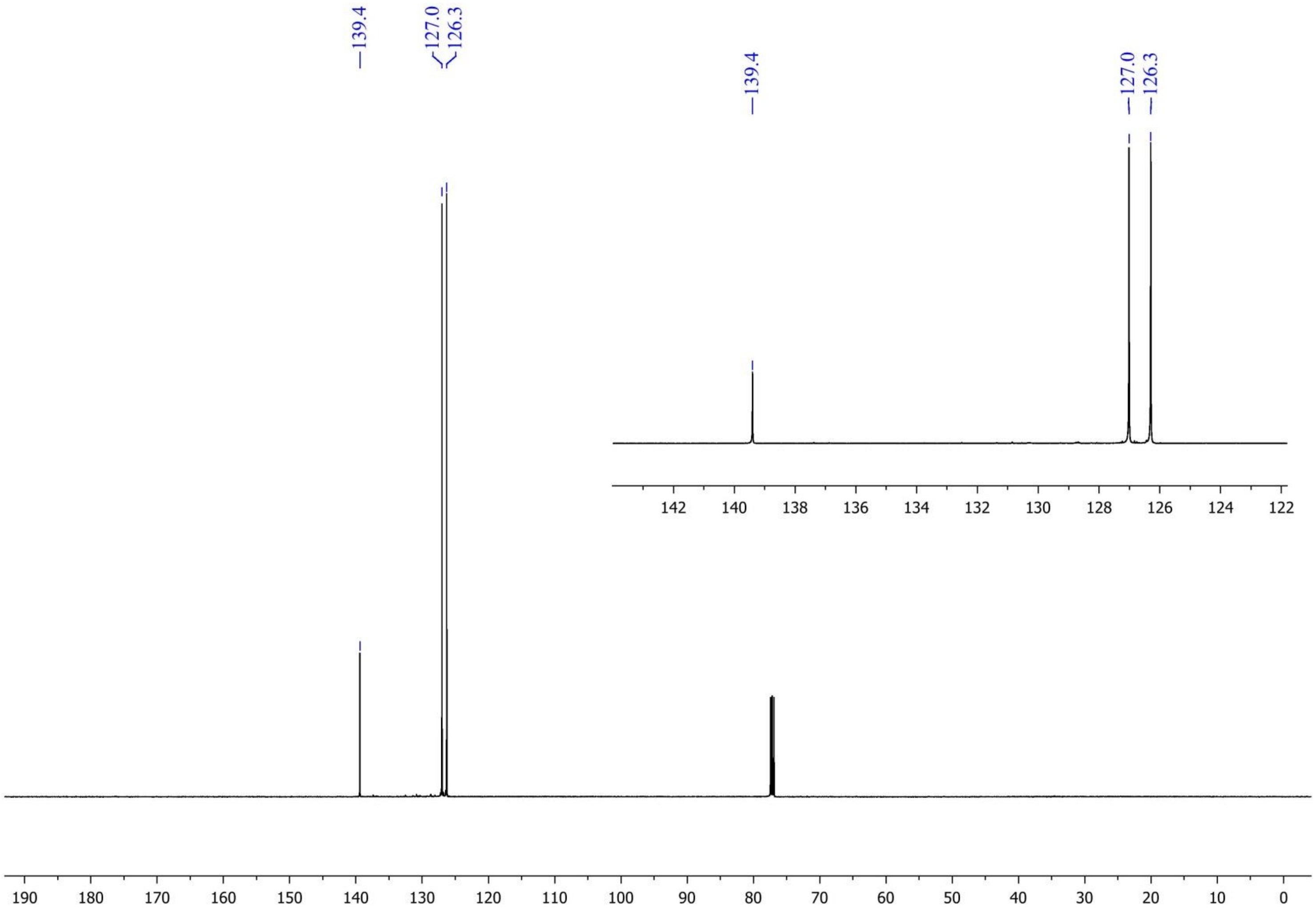
$MeC_6H_3S_2AsN(SiMe_3)_2$ (**4′**) (0.287 g, 0.737 mmol, 1 equiv.) in MeCN (5 mL) was added dropwise to a solution $MeC_6H_3S_2AsCl$ (0.389 g, 1.47 mmol, 2 equiv.) in MeCN (5 mL) at 0 °C. The resulting solution was slowly allowed to reach ambient temperature before being heated at reflux overnight, which produced a white precipitate after *ca*. 1 hour. The mixture was cooled to ambient temperature and then placed in an ice bath for 3 hours, which afforded a white precipitate. The MeCN solvent was removed by filter cannula, after which the white precipitate was washed with dry MeCN (3 × 5 mL) to give the product $N(MeC_6H_3S_2As)_3$ (**4**). **M.p.** 78–82 °C. Yield: 0.208 g, 0.30 mmol, 40%. **^{1}H NMR** (500 MHz, $CDCl_3$, 295 K) δ/ppm: 7.35 (d, $^3J_{HH}$ = 8.1 Hz, 3H, Ar–H), 7.28 (s, 3H, Ar–H), 6.92 (d, $^3J_{HH}$ = 8.1 Hz, 3H, Ar–H), 2.32 (s, 9H, CH_3). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 295 K) δ/ppm: 140.6 (3C, Ar), 137.1 (3C, Ar), 135.9 (3C, Ar), 126.9 (3C, Ar), 126.7 (3C, Ar), 126.0 (3C, Ar), 20.9 (3C, CH_3). **IR** ṽ/cm^{-1}: 1456 (w), 1256 (w), 1032 (w), 860 (w), 796 (s), and 692 (s) and 442 (s). **HRMS** (ES$^+$) *m*/*z* calculated for [M+H]$^+$ [$C_{21}H_{19}S_6As_3N$]$^+$: 701.7490; found 701.7516. **Elem. Anal.** (%) calculated for ($C_{21}H_{18}NAs_3S_6$): C: 35.95, H: 2.59, N: 2.00; found: C: 34.93, H: 2.43, N: 1.91.

S2. NMR spectra of products

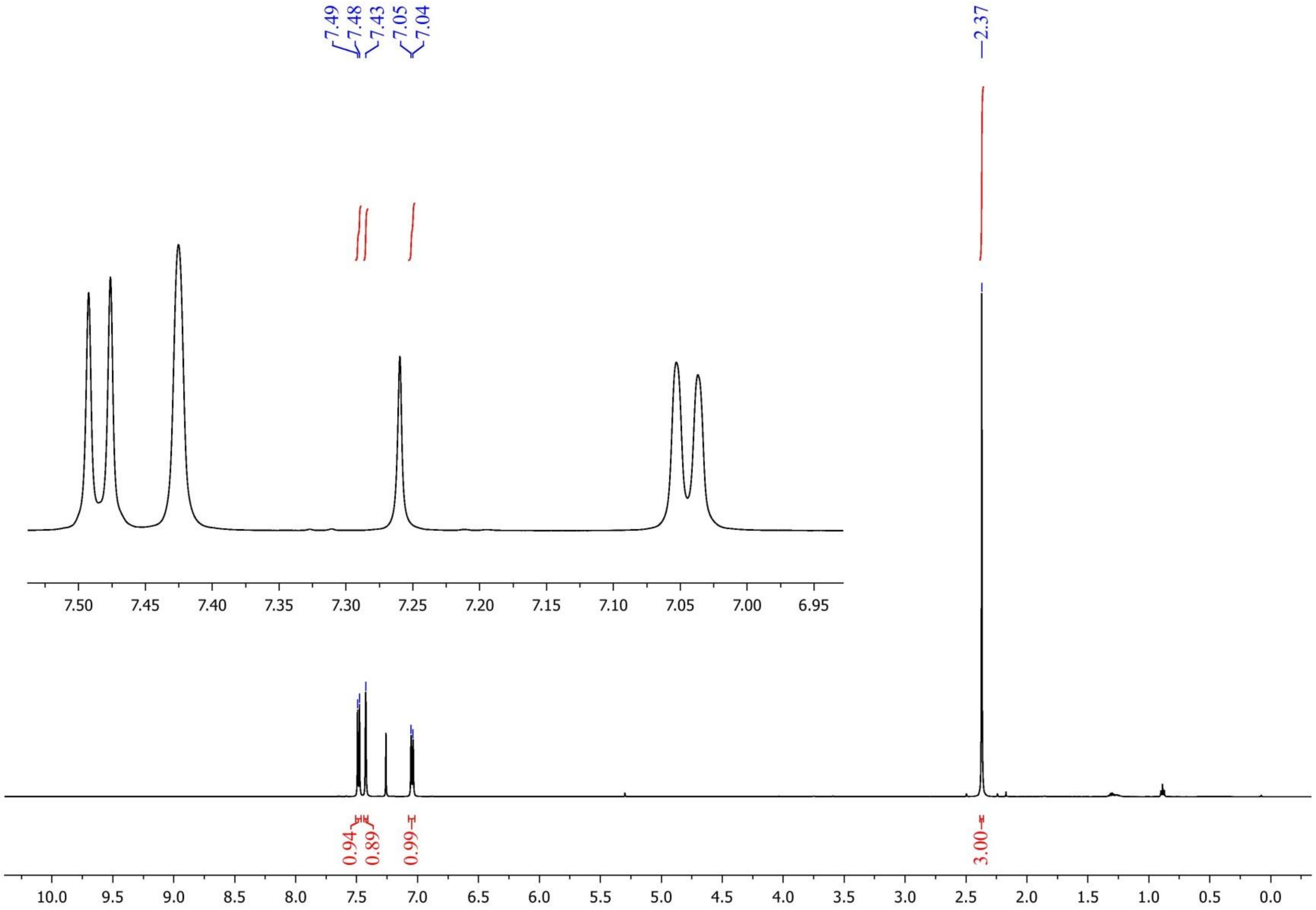
S2.1. ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of 2-chlorobenzo-1,3,2-dithiarsole (**1**).



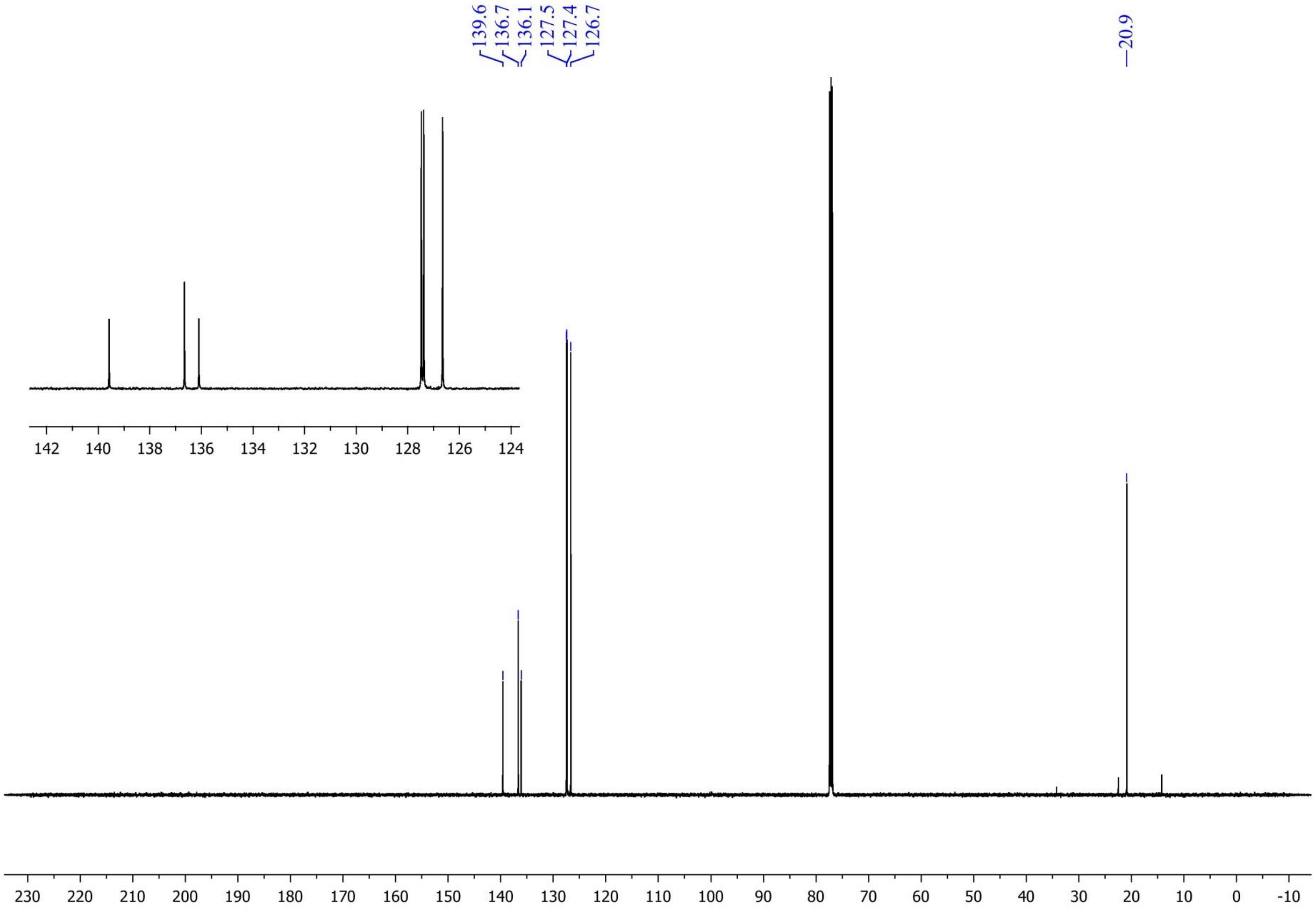
S2.2 $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of 2-chlorobenzo-1,3,2-dithiarsole (**1**).



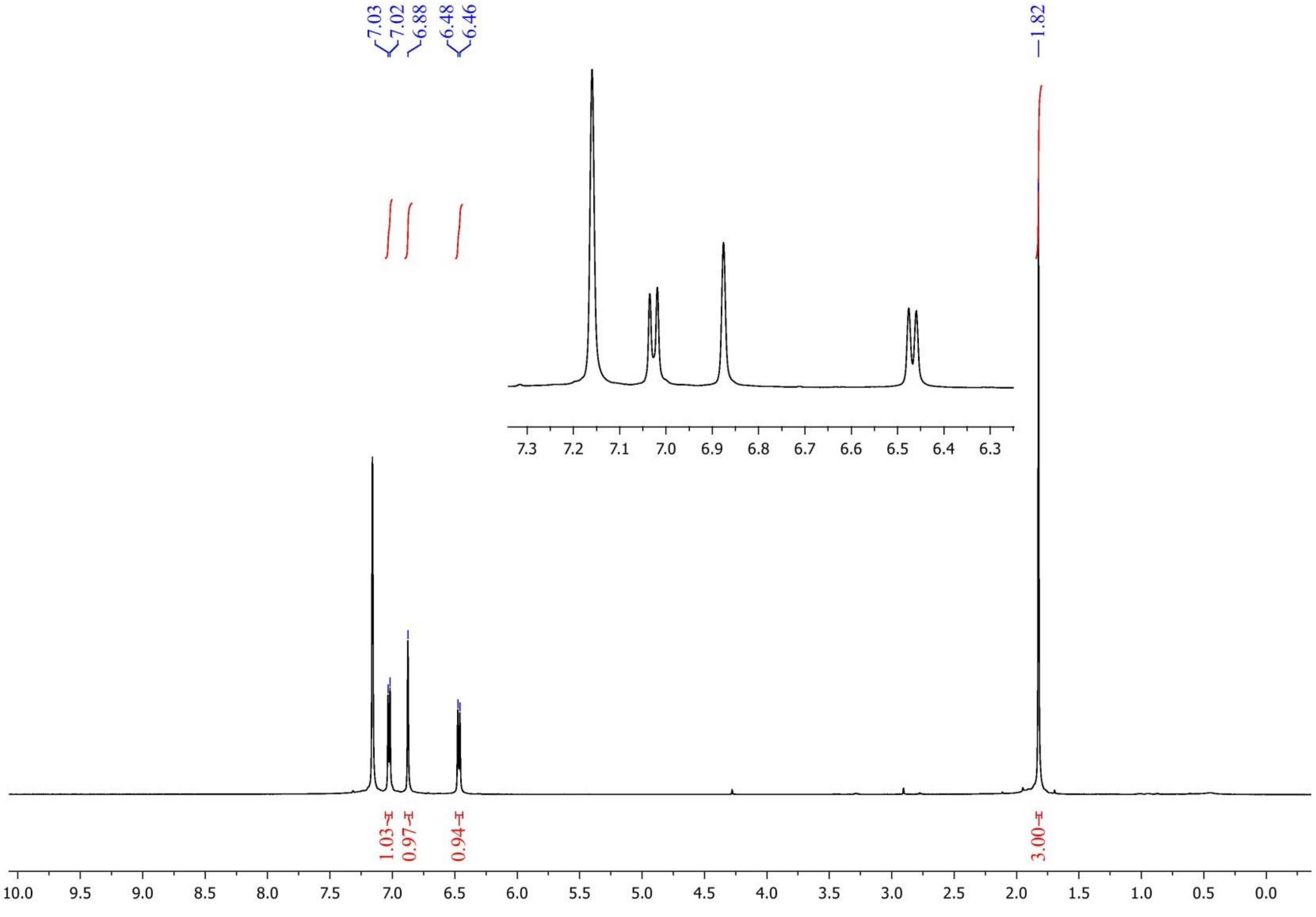
S2.3 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of 2-chloro-5-methylbenzo-1,3,2-dithiarsole (**2**).



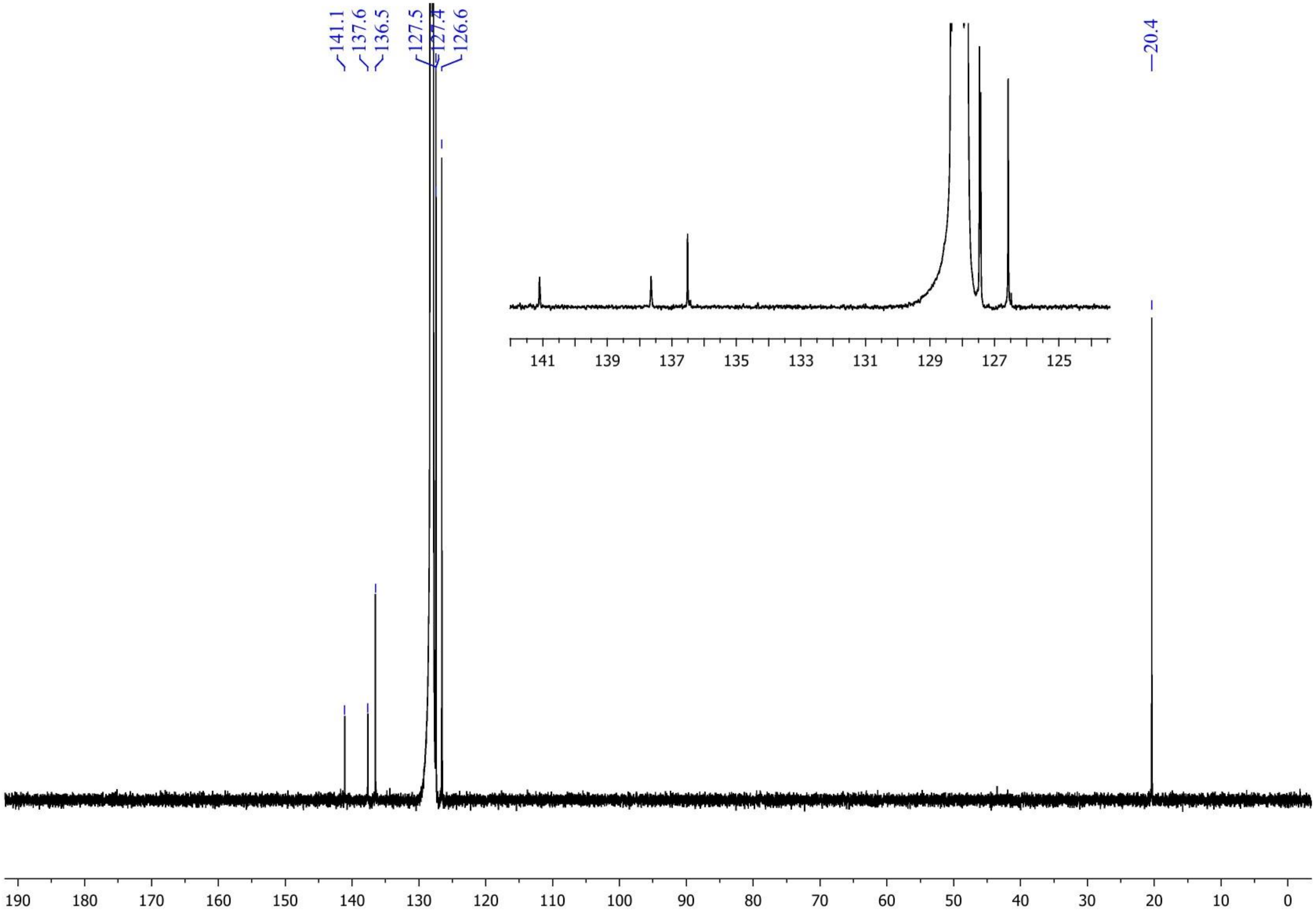
S2.4 $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of 2-chloro-5-methylbenzo-1,3,2-dithiarsole (**2**).



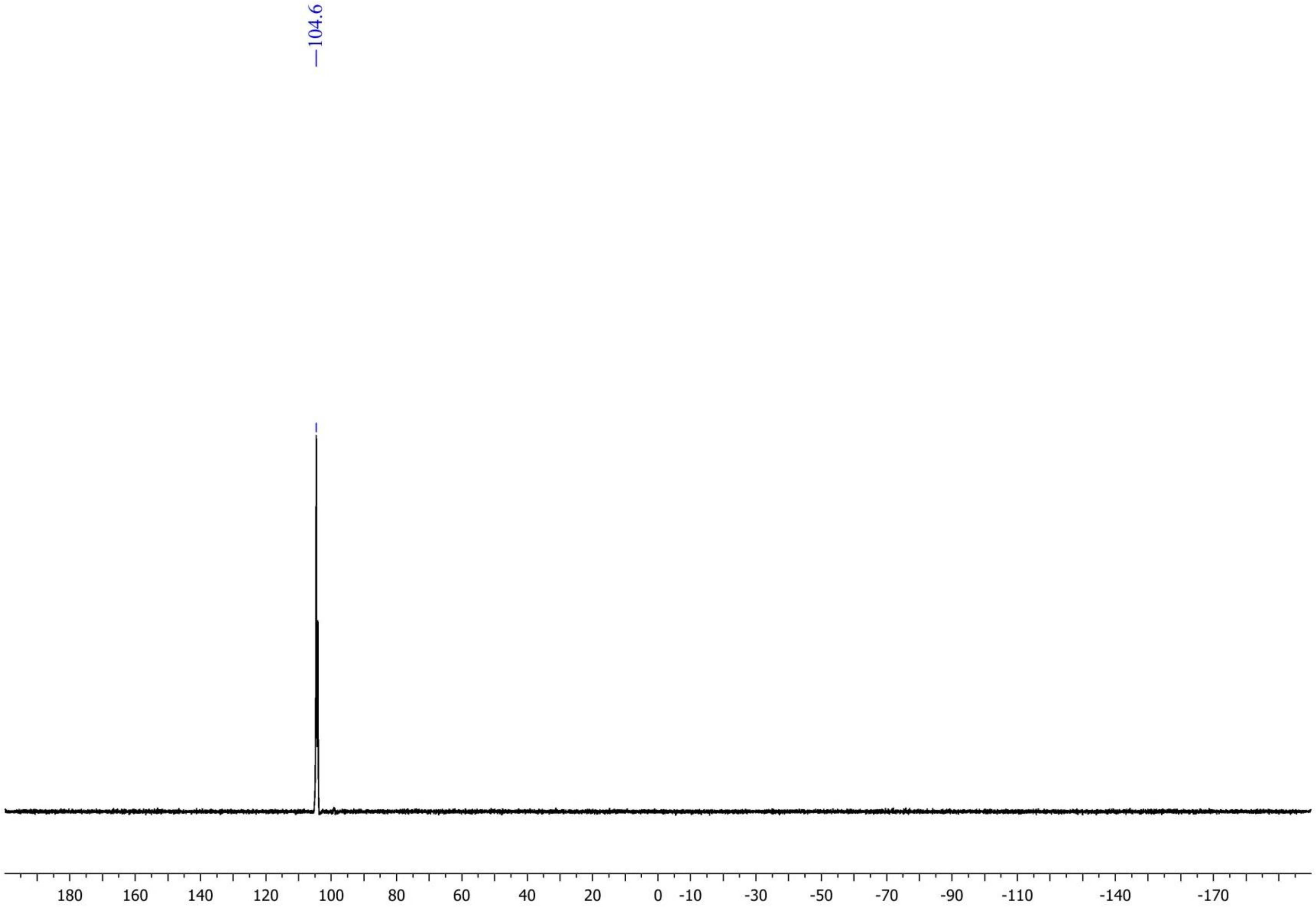
S2.5 ^{1}H NMR (500 MHz, C_6D_6, 295 K) spectrum of [$MeC_6H_3S_2As$][$AlCl_4$] (**3a**).



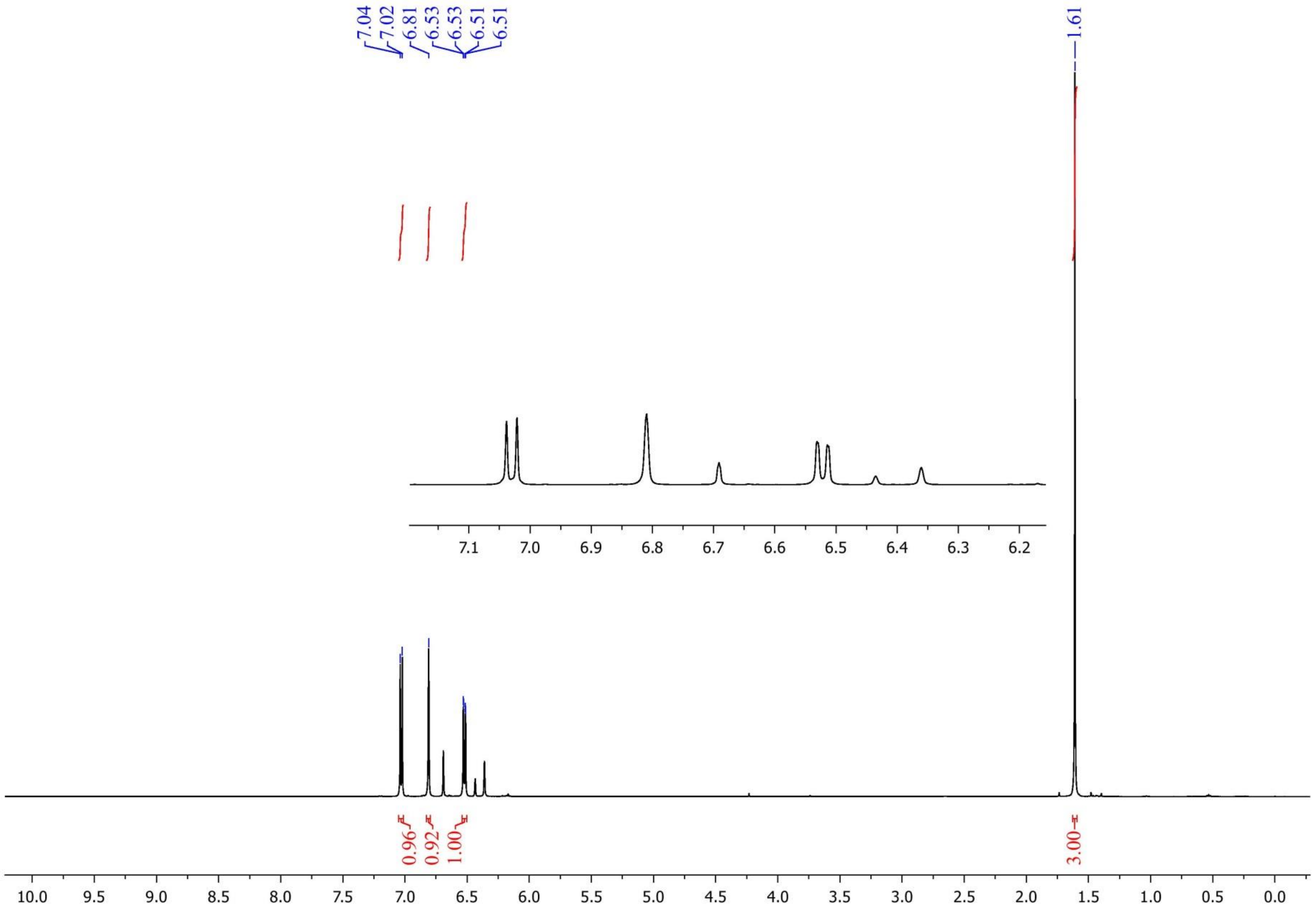
S2.6 $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 295 K) spectrum of $[MeC_6H_3S_2As][AlCl_4]$ (**3a**).



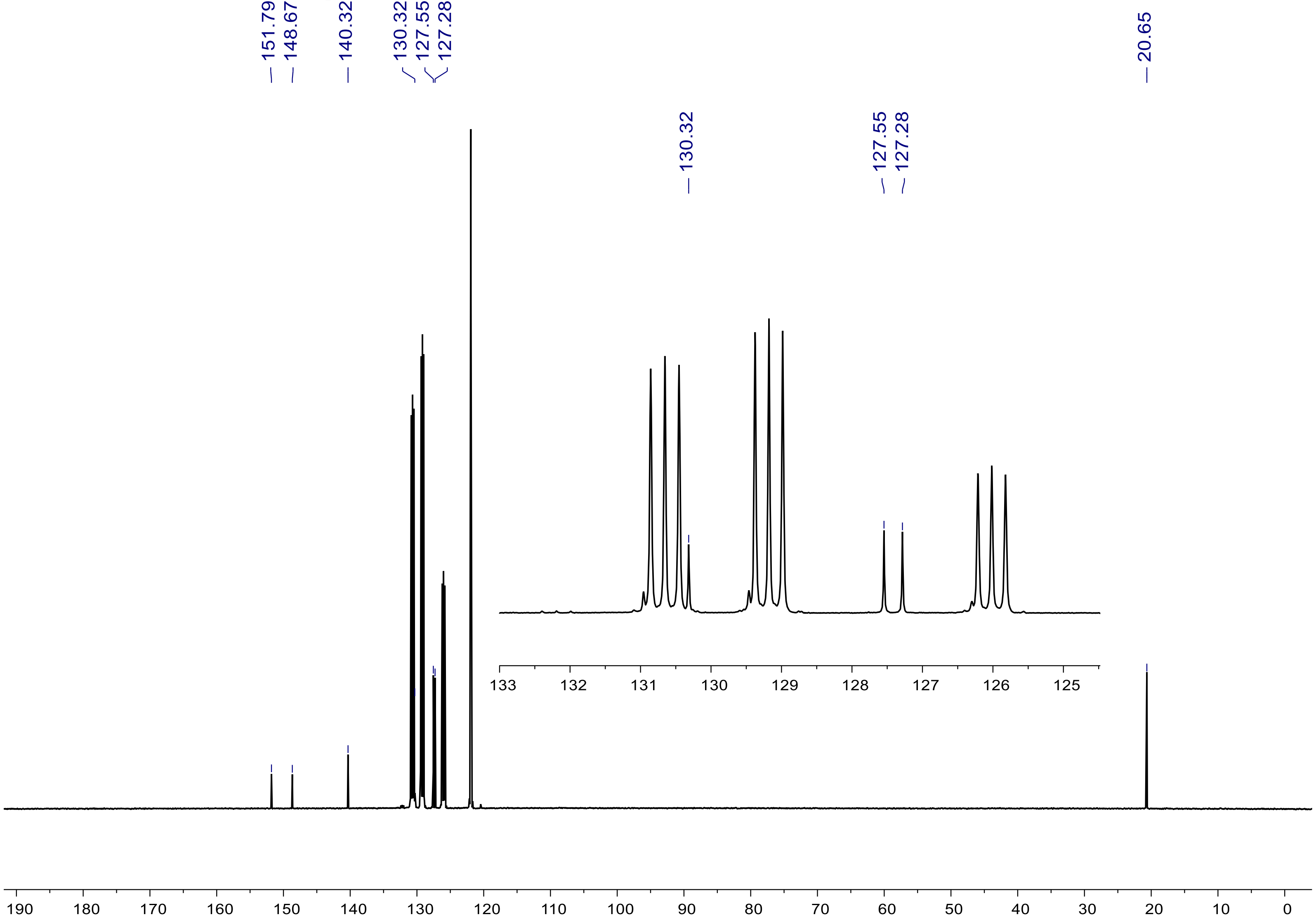
S2.7 ^{27}Al NMR (130 MHz, C_6D_6, 295 K) spectrum of $[MeC_6H_3S_2As][AlCl_4]$ (**3a**).



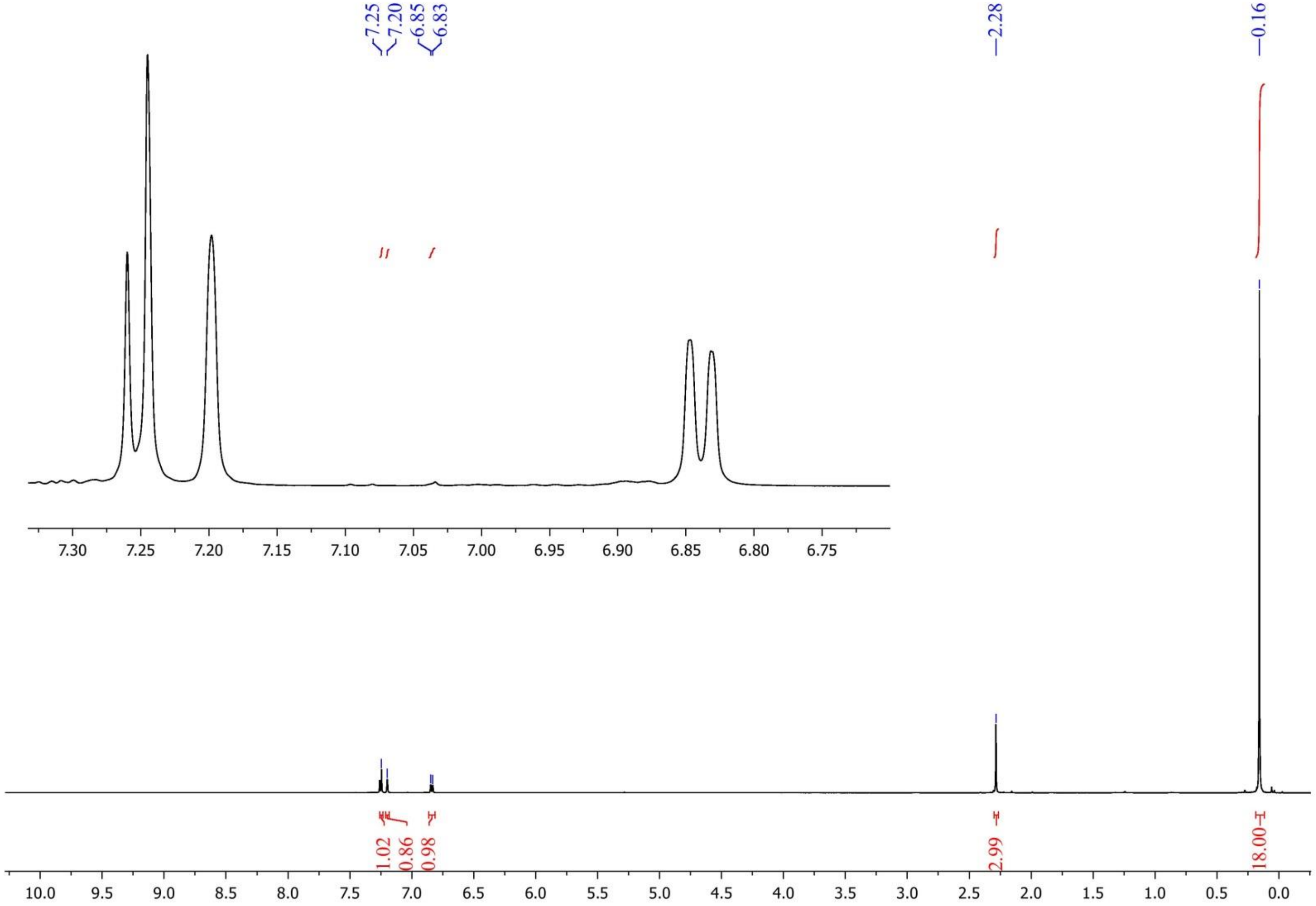
S2.8 ^{1}H NMR (500 MHz, C_6D_5Br, 295 K) spectrum of $[MeC_6H_3S_2As][GaCl_4]$ (**3b**).



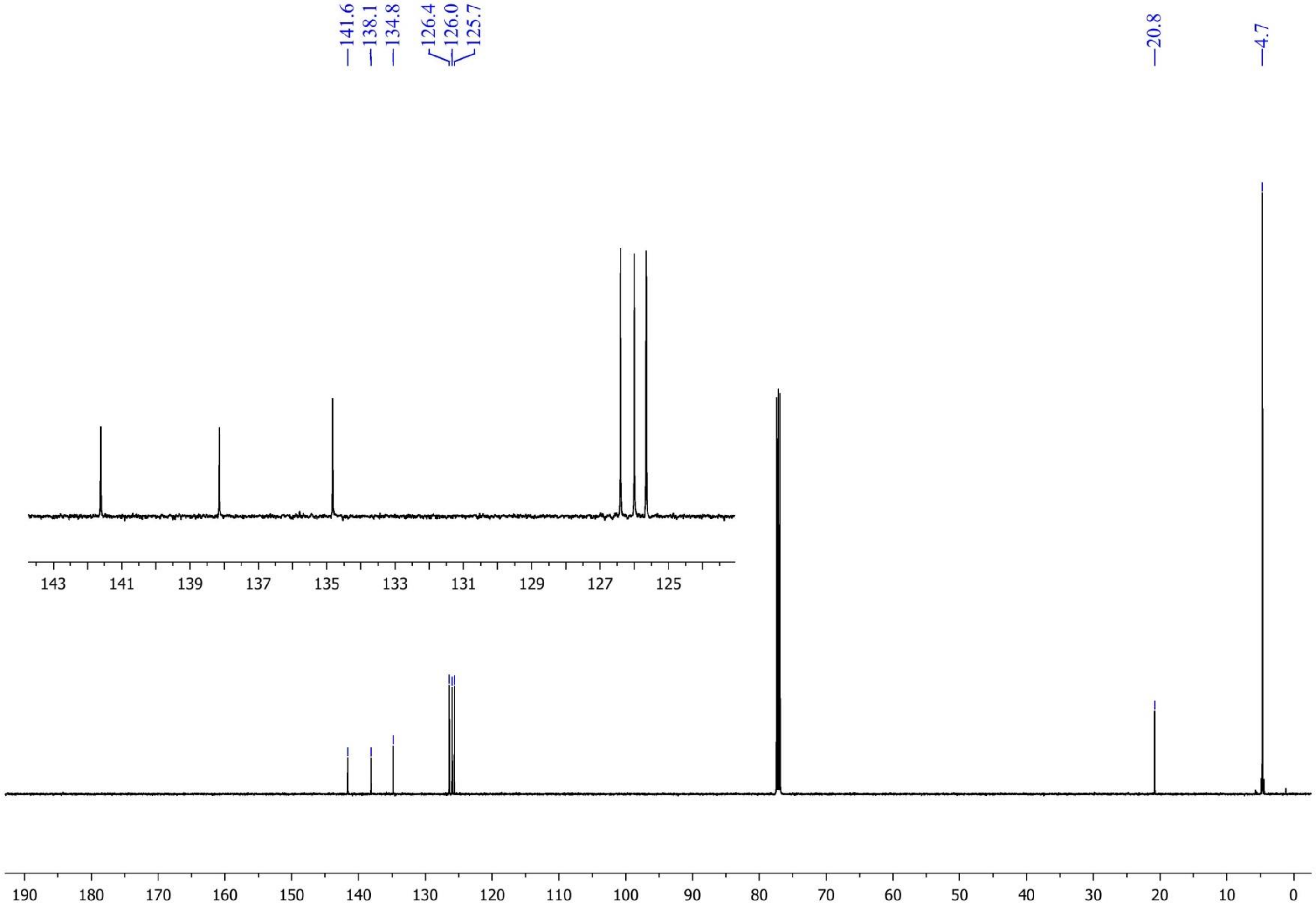
S2.9 $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_5Br, 295 K) spectrum of $[MeC_6H_3S_2As][GaCl_4]$ (**3b**).



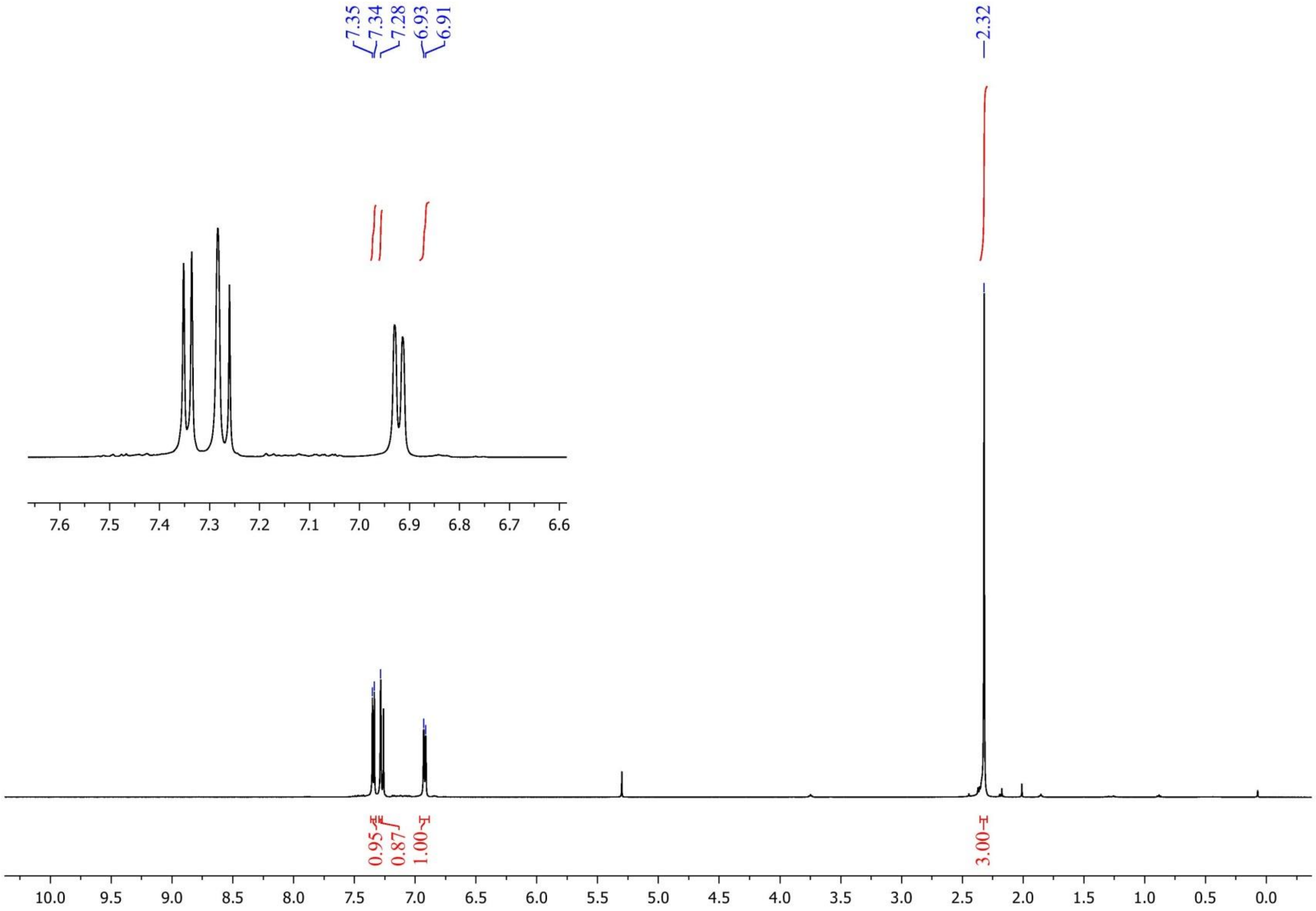
S2.10 ^{1}H NMR (500 MHz, $CDCl_3$, 295 K) spectrum of $MeC_3H_3S_2AsN(SiMe_3)_2$ (**4’**).



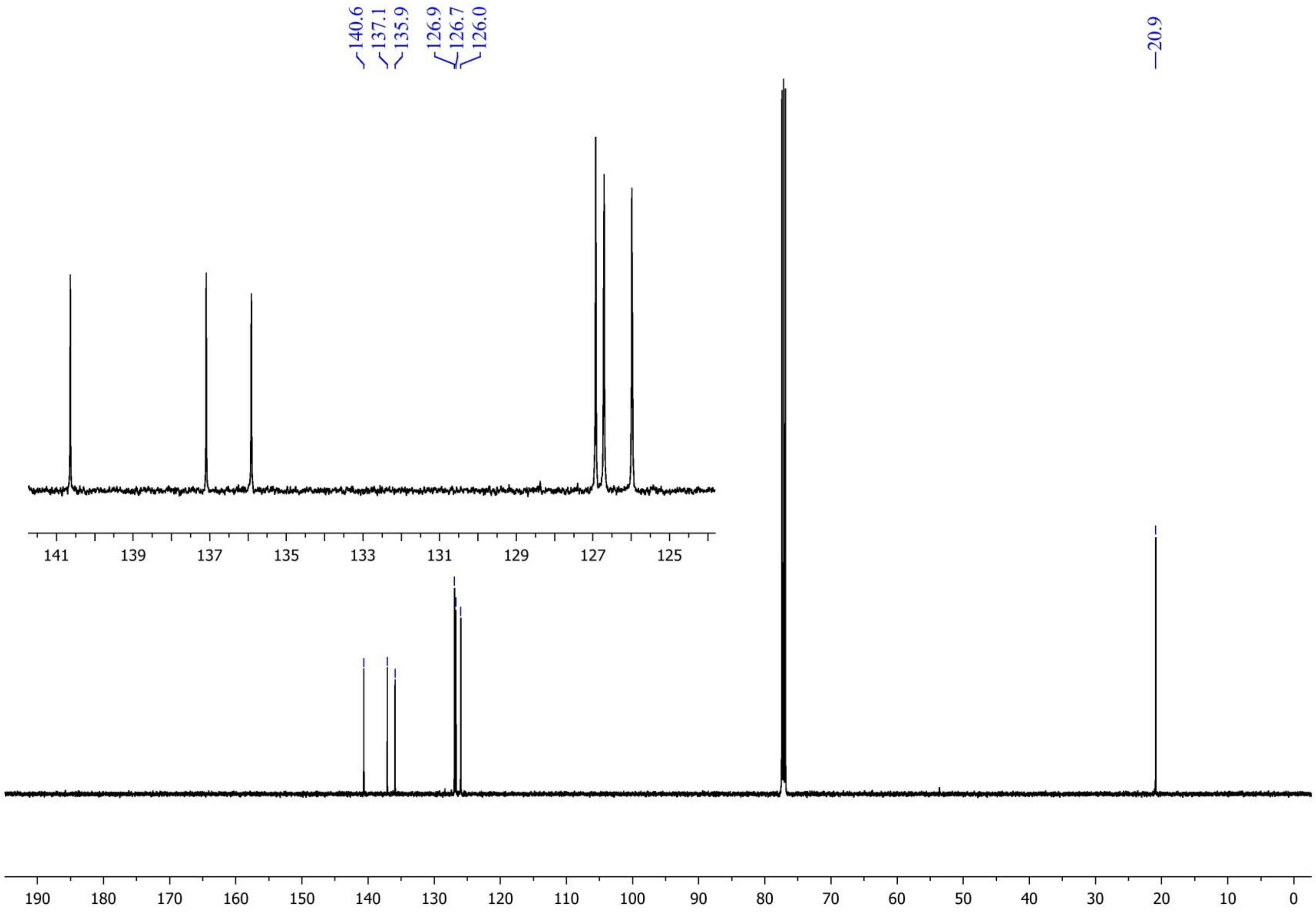
S2.11 $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of $MeC_3H_3S_2AsN(SiMe_3)_2$ (**4'**).



S2.12 1H NMR (500 MHz, CDCl3, 295 K) spectrum of N($MeC_6H_3S_2As$)$_3$ (**4**).



S2.13 $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 295 K) spectrum of $N(MeC_6H_3S_2As)_3$ (**4**).



S3. X-ray crystallographic studies

Single crystals of **1**, **2**, **3a**, **3b** and **4** were grown under a dinitrogen inert atmosphere. Crystallographic studies were undertaken on single crystal mounted in paratone and studied on a Nonius Kappa CCD (**1**, β-**2**, **3a**) or a Bruker APEX diffractometer (α-**2**, **3b**, **4**) using CCD detectors. Data for **1**, β-**2**, **3a** were measured using COLLECT[2] and processed using Denzo and Scalepack[3] whereas for α-**2**, **3b**, **4** data were collected and processed with SAINT.[4] Absorption corrections for all structures were applied using the multi-scan approach of Blessing[5] (**1**, β-**2**, **3a**) or through Sadabs.[6] All structures were solved by direct methods to reveal all non-H atoms which were refined anisotropically except where stated within SHELXL-2014/7.[7] H atoms were added at calculated positions and refined with a riding model.

For **1** multiple crystals were examined which all diffracted weakly but which all revealed the same large unit cell. Full data collections employed 80s frames but provided poor intensity statistics to high angle. Structure solution and refinement revealed a total of 17 crystallographically independent molecules in the asymmetric unit. Consideration of the original frames did not reveal any evidence for non-merohedral twinning and an examination of the data within PLATON[8] revealed only pseudo-symmetry and, with a prime number (Z' = 17) of molecules in the asymmetric unit, there appeared no obvious missing symmetry element. Structure refinement with Z' = 17 proceeded smoothly with S, As and Cl atoms all anisotropic. However, given the paucity of data the remaining C atoms in the ring were refined isotropically with chemically equivalent C atoms sharing a common U_{iso}.

For **2α** and **2β** there were no particular crystallographic points of merit. Refinement proceeds smoothly with all non-H atoms refined anisotropically and H atoms added at calculated positions.

For **3a** the crystals were very small and proved weakly diffracting. Data were collected using 9 minute (540s) frames but still provided very small numbers of observed reflections. Nevertheless, the data were adequate to solve the structure but, like **1**, the C atoms were refined isotropically. The correctness of the structure was confirmed by the superior refinement for **3b** which proved to be isomorphous and provided much better quality data.

Crystals of **3b** provided excellent data. The asymmetric unit comprises two cation-anion pairs with the cations and anions each located on a crystallographic mirror plane. All the cation non-H atoms were located on the mirror plane such that the H atoms of the methyl group were therefore inherently disordered over two sites. The $GaCl_4^-$ anions were also located on mirror planes with the Ga and two Cl atoms located on the mirror pane and the remaining crystallographically independent Cl on a general position.

Crystals of **4** refined adequately with one molecule of **4** in the asymmetric unit along with one CH_2Cl_2 solvate molecule. The solvent molecule was disordered over two sites via pivoting around one Cl atom. The position of the half-weight C and Cl atoms were refined freely with common C-Cl bond lengths (SADI). The half-weight solvent C centers were refined isotropically and H atoms added to them at calculated positions and refined with a riding model.

The structures have been deposited with the Cambridge Structural Database (CCDC deposition numbers CCDC 1546788-1546793). These can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

S3.1 X-ray refinement data

Compound	**1**	**2α**	**2β**
Empirical Formula	$C_6H_4AsClS_2$	$C_7H_6AsClS_2$	$C_7H_6AsClS_2$
Crystal System	Triclinic	Monoclinic	Triclinic
Space Group	*P*-1	$P2_1/c$	*P*-1
a/Å	12.4186(2)	6.0319(5)	9.2240(2)
b/Å	22.4845(4)	15.6876(14)	9.6289(3)
c/Å	26.7287(4)	9.6731(6)	10.8161(3)
α/Å	76.8040(10)	90	81.120(2)
β/Å	80.2820(10)	90.601(8)	76.281(2)
γ/Å	76.7200(10)	90	84.486(2)
V/Å^3	7018.4(2)	915.28(13)	920.29(4)
Z	34	4	4
T /K	180(2)	150(2)	180(2)
D_c/g.cm^{-3}	2.016	1.920	1.910
Crystal size/mm	0.140 x 0.050 x 0.020	0.660 x 0.270 x 0.170	0.230 x 0.070 x 0.020
Total data	104496	25149	8175
Unique data	32107	2772	3932
R_{int}	0.1695	0.0118	0.0427
$R_1[F^2>2\ \sigma(F^2)]$	0.0778	0.0191	0.0311
wR2 (all data)	0.1884	0.0484	0.0804
GoF	1.010	1.261	1.031
ρ_{min}/ρ_{max}/eÅ^{-3}	-0.683/0.645	-0.316/0.530	-0.683/0.428
CCDC code	1546791	1546788	1546789

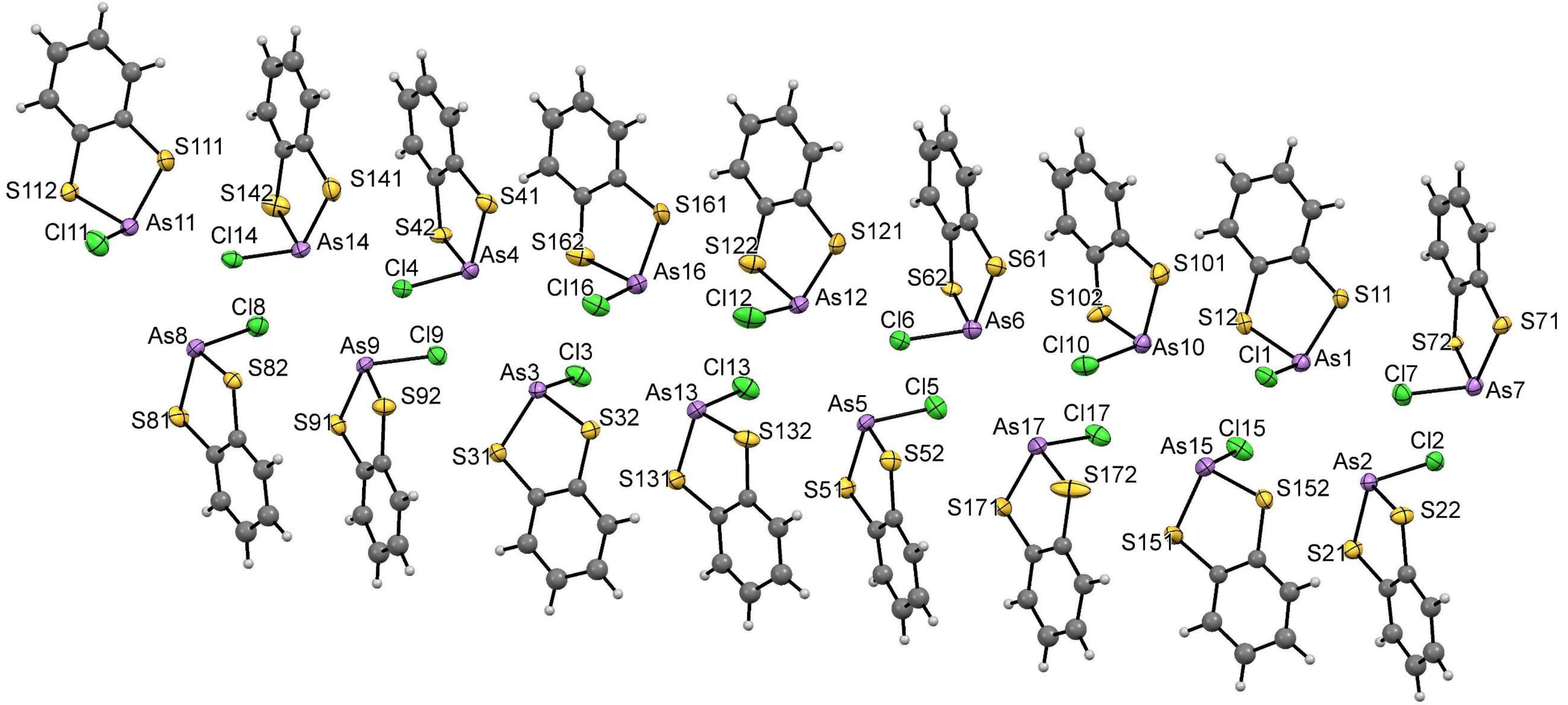
Compound	**3a**	**3b**	**4**
Empirical Formula	$C_7H_6AlAsCl_4S_2$	$C_7H_6AsCl_4GaS_2$	$C_{22}H_{20}As_3Cl_2NS_6$
Crystal System	Monoclinic	Monoclinic	Triclinic
Space Group	*P*21/*m*	*P*21/*m*	*P*-1
a/Å	11.4720(7)	11.409(4)	11.221(8)
b/Å	7.0562(5)	7.015(2)	11.615(8)
c/Å	17.819(2)	17.742(6)	11.965(8)
α/Å	90	90	76.144(8)
β/Å	102.135(3)	102.483(3)	67.962(7)
γ/Å	90	90	87.166(8)
V/Å^3	1410.2(2)	1386.4(8)	1402.1(16)
Z	4	4	2
T /K	180(2)	150(2)	150(2)
D_c/g.cm^{-3}	1.874	2.111	1.863
Crystal size/mm	0.140 x 0.020 x 0.010	0.300 x 0.030 x 0.020	0.130 x 0.050 x 0.020
Total data	7859	15885	14770
Unique data	1959	3415	5673
R_{int}	0.0973	0.0312	0.0858
$R_1[F^2>2\ \sigma(F^2)]$	0.0973	0.0218	0.0806
wR2 (all data)	0.2366	0.0547	0.1545
GoF	1.203	1.071	1.203
ρ_{min}/ρ_{max}/eÅ^{-3}	-0.641/2.393	-0.428/ 0.516	-1.520/1.065
CCDC code	1546790	1546793	1546792

3.2 Experimental bond lengths for compound 1.

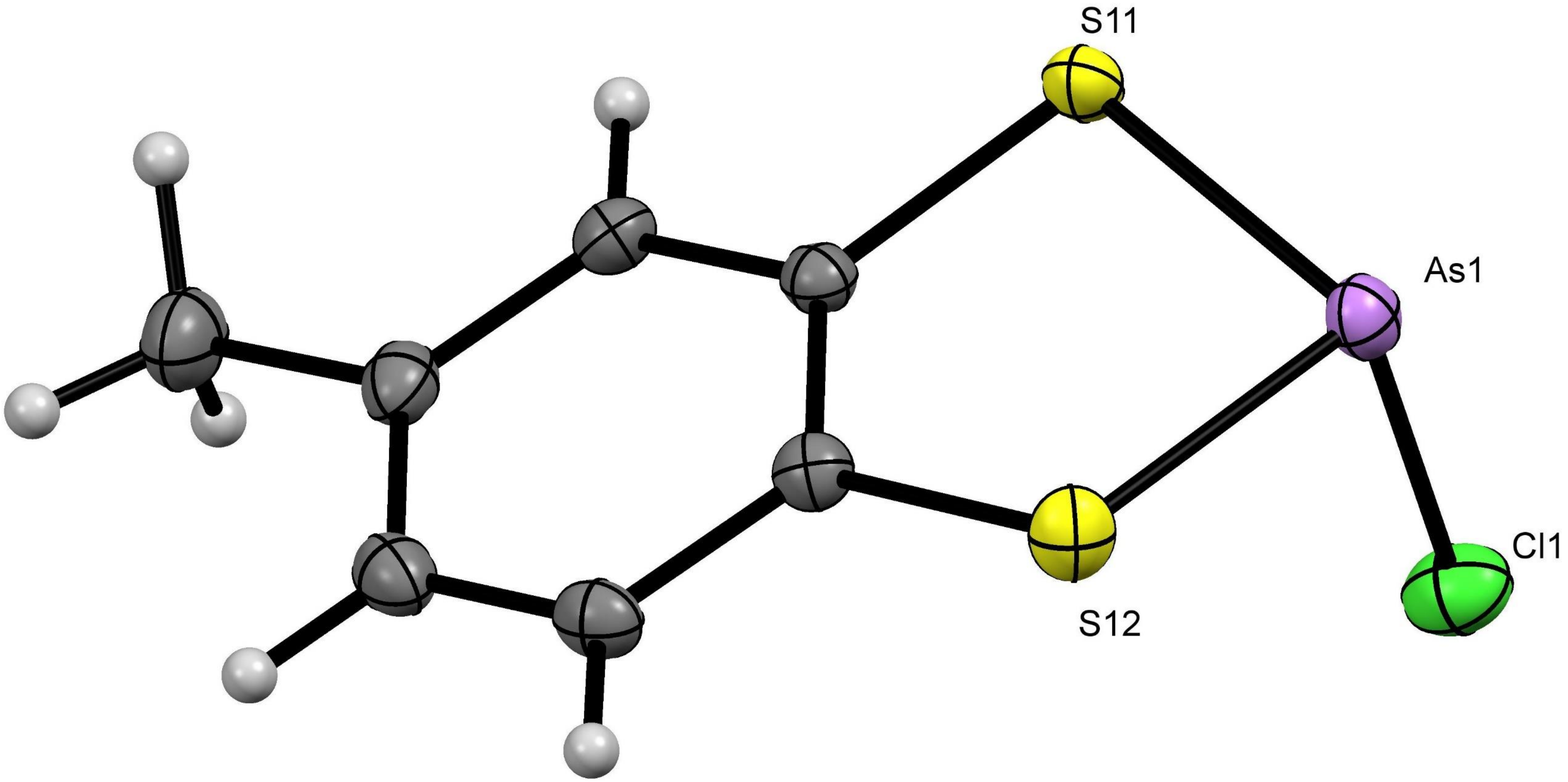
Bond	Length (Å)
As1–S11	2.199(6)
As1–S12	2.233(8)
As1–Cl1	2.283(6)
As2–S21	2.206(6)
As2–S22	2.217(6)
As2–Cl2	2.298(7)
As3–S31	2.205(6)
As3–S32	2.209(7)
As3–Cl3	2.287(7)
As4–S41	2.211(6)
As4–S42	2.208(6)
As4–Cl4	2.285(7)
As5–S51	2.210(6)
As5–S52	2.217(6)
As5–Cl5	2.283(8)
As6–S61	2.211(6)
As6–S62	2.204(6)
As6–Cl6	2.301(8)
As7–S71	2.211(6)
As7–S72	2.206(6)
As7–Cl7	2.314(8)
As8–S81	2.208(6)
As8–S82	2.205(6)
As8–Cl8	2.286(7)
As9–S91	2.199(6)
As9–S92	2.207(6)
As9–Cl9	2.295(8)

Bond	Length (Å)
As10–S101	2.208(6)
As10–S102	2.219(7)
As10–Cl10	2.284(7)
As11–S111	2.213(6)
As11–S112	2224(7)
As11–Cl11	2.277(6)
As12–S121	2.185(7)
As12–S122	2.196(7)
As12–Cl12	2.274(7)
As13–S131	2.203(6)
As13–S132	2.222(7)
As13–Cl13	2.285(7)
As14–S141	2.208(6)
As14–S142	2.189(6)
As14–Cl14	2.284(8)
As15–S151	2.200(7)
As15–S152	2.215(7)
As15–Cl15	2.275(6)
As16–S161	2.216(7)
As16–S162	2.207(7)
As16–Cl16	2.285(7)
As17–S171	2.214(6)
As17–S172	2.188(7)
As17–Cl17	2.285(7)

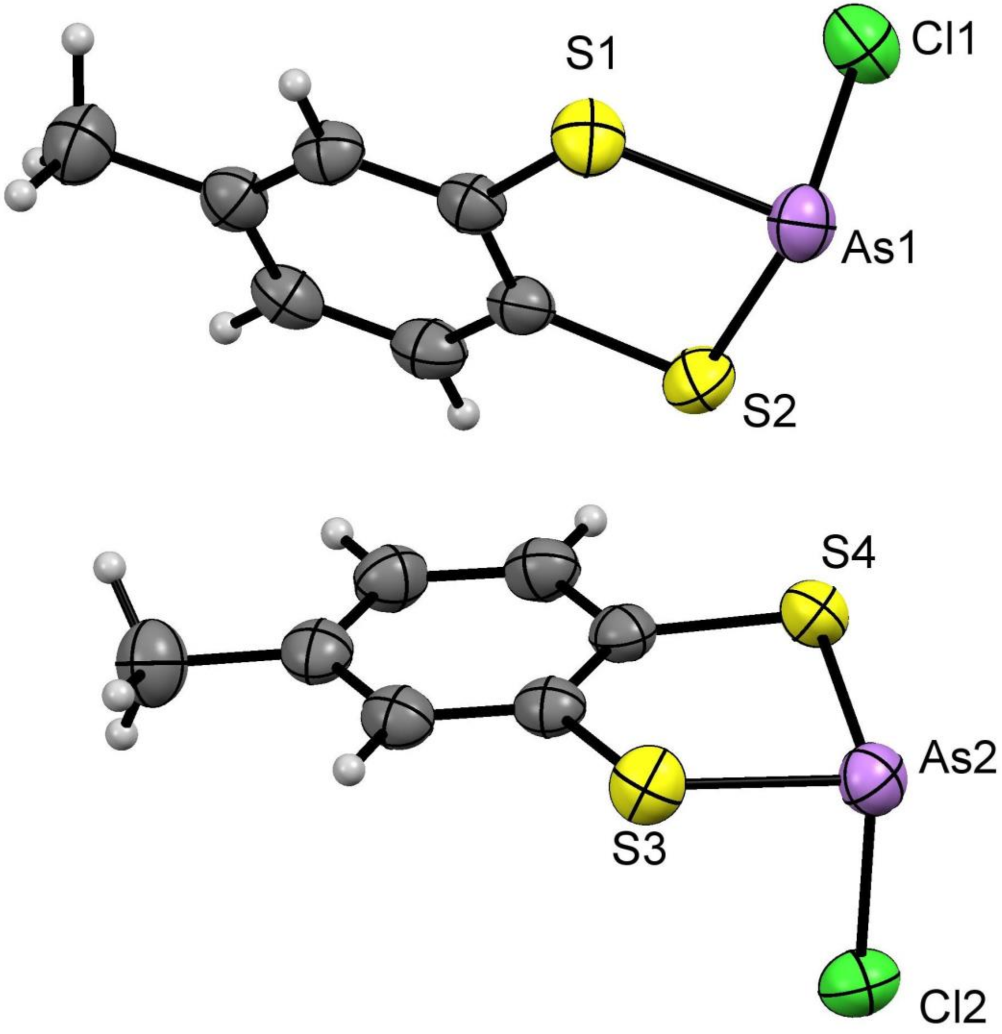
S3.3.1 Solid-state structure of 2-chlorobenzo-1,3,2-dithiarsole (**1**).



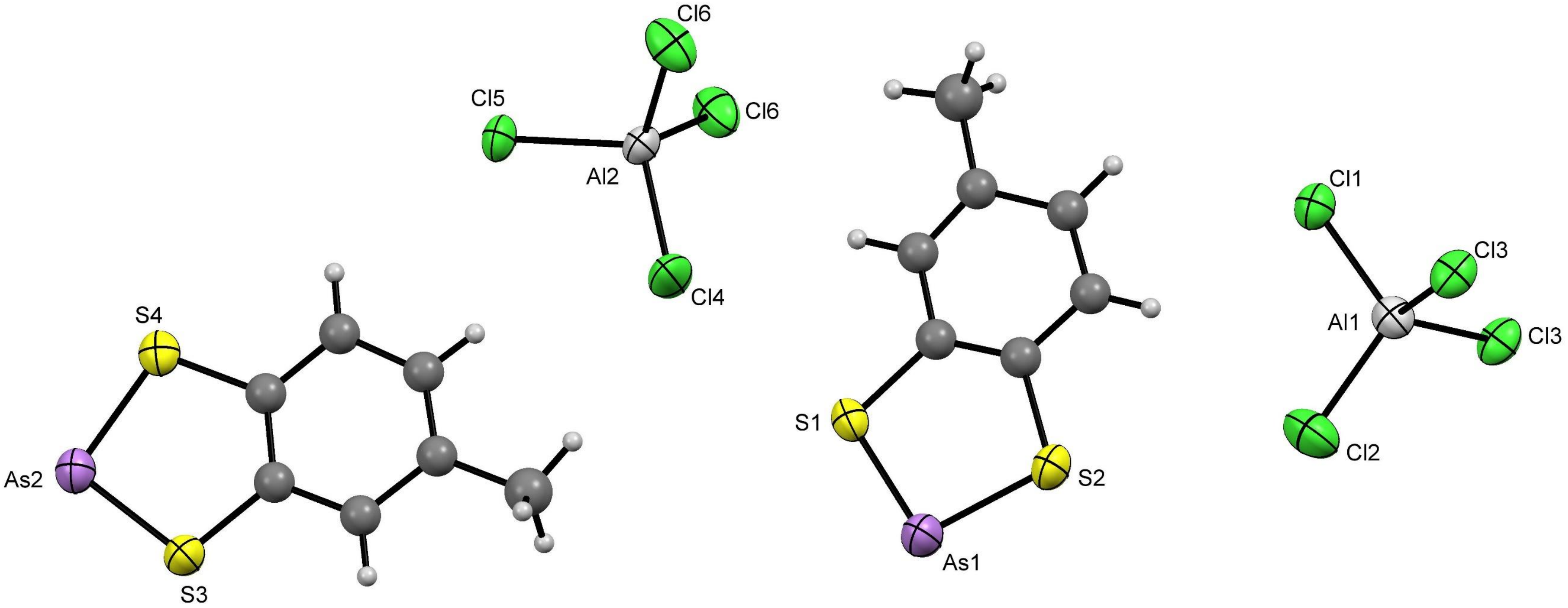
S3.3.2 Solid-state structure of 2-chloro-5-methylbenzo-1,3,2-dithiarsole (α-**2**).



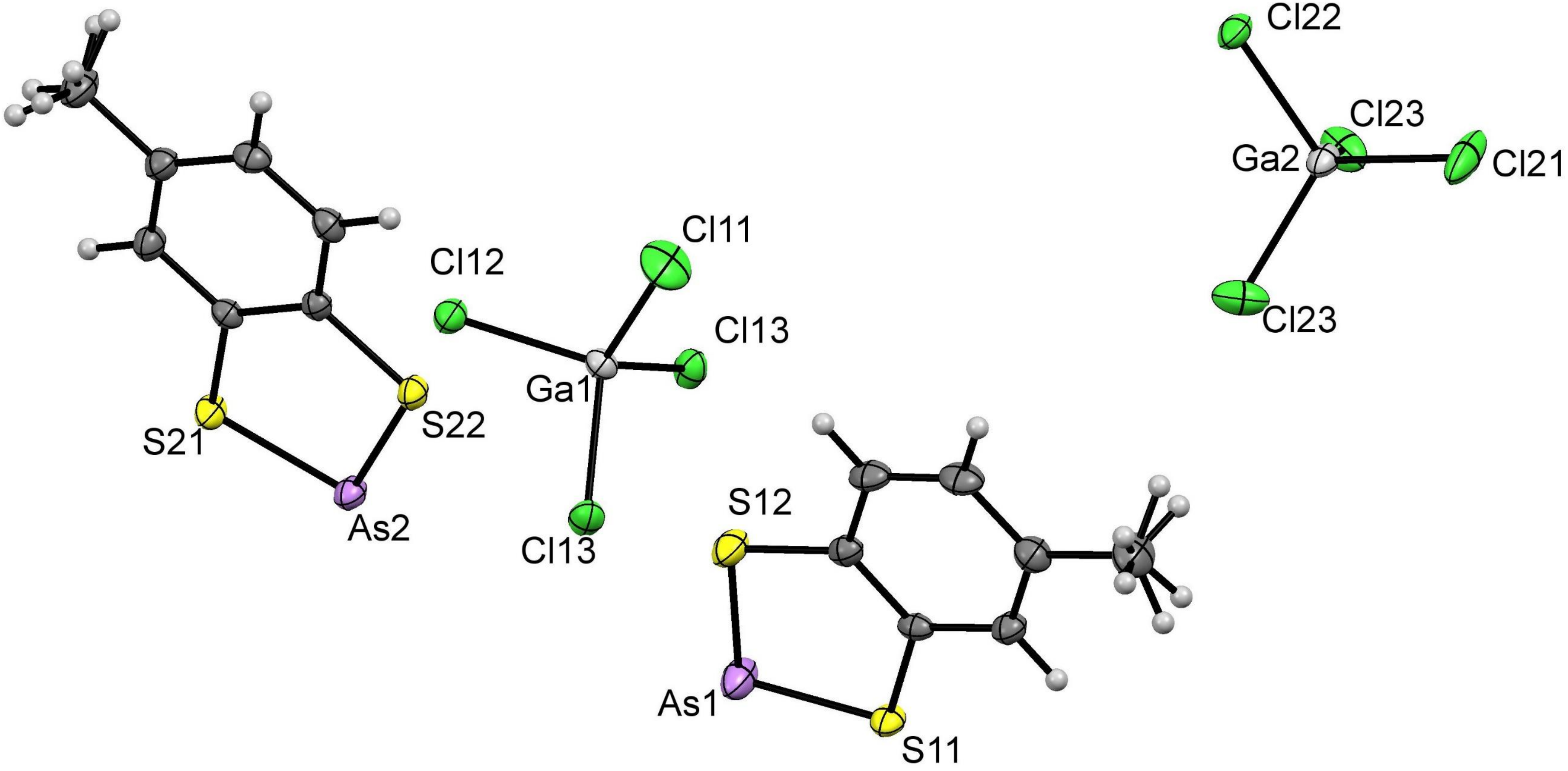
S3.3.3 Solid-state structure of 2-chloro-5-methylbenzo-1,3,2-dithiarsole (β-**2**).



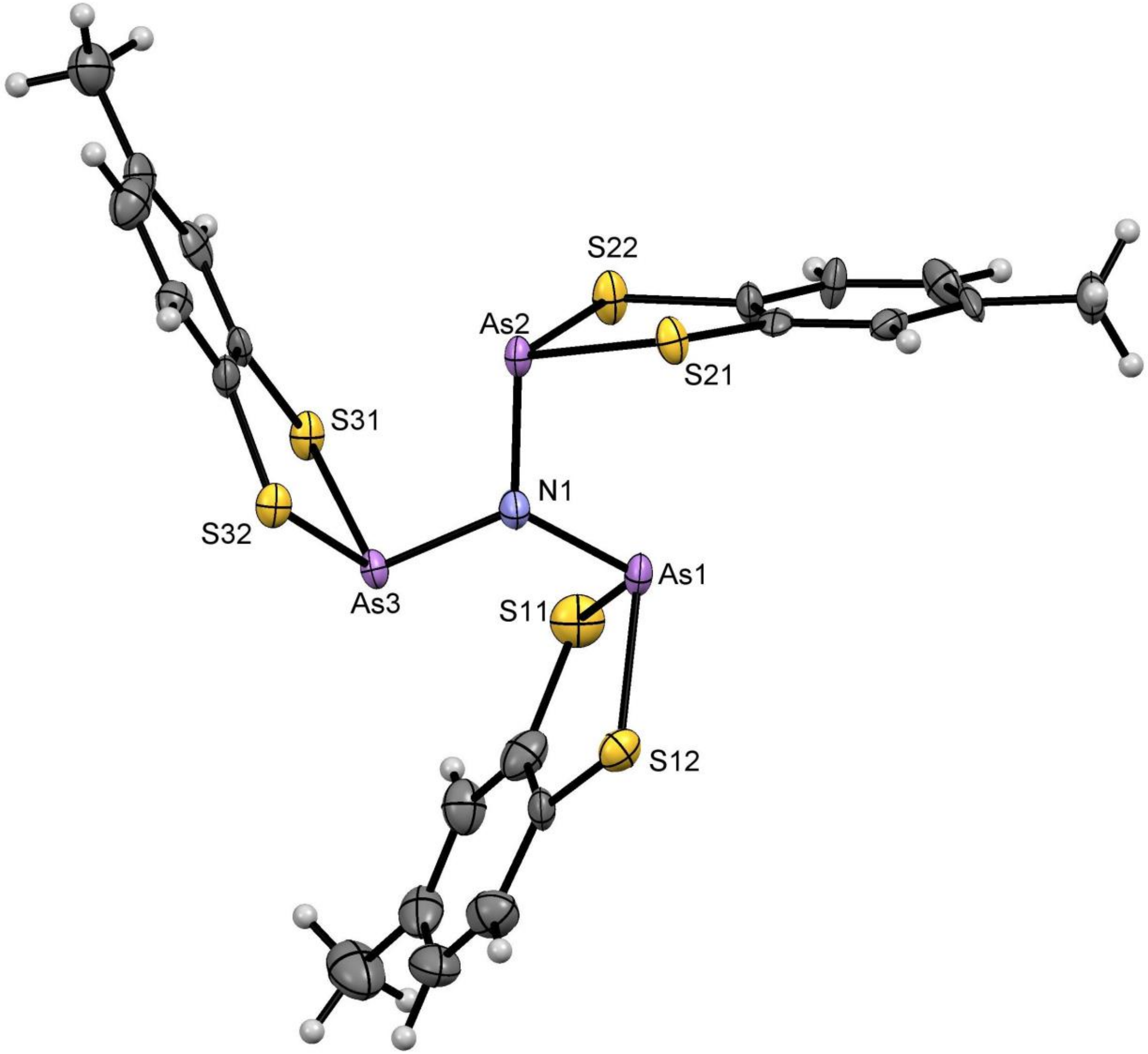
S3.3.4 Solid state structure of [$MeC_6H_3S_2As$][$AlCl_4$] (**3a**).



S3.3.5 Solid state structure of [$MeC_6H_3S_2As$][$GaCl_4$] (**3b**).



S3.3.6 Solid state structure of N(MeC$_6$H$_3$S$_2$As)$_3$ (**4**) (disordered CH$_2$Cl$_2$ solvate molecule omitted for clarity).

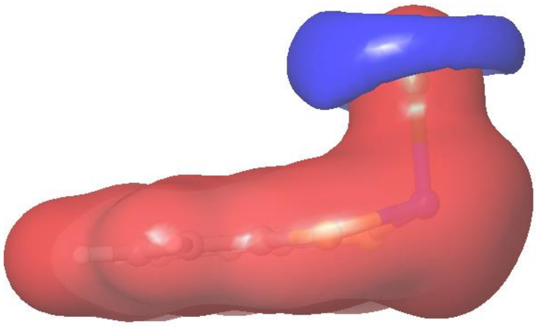


S4. Computational studies on $C_6H_4S_2AsCl$.

Geometry optimisations were undertaken using the B3LYP-D3 functional and the cc-PVTZ-PP(-F) triple zeta valence polarised basis set for **1** using the crystallographically determined geometry as a starting point. The molecular electrostatic isopotential surface for **1** is displayed in Fig. S4.1 and reflects the build-up of positive charge at As and negative charge at Cl. The charge distribution on the heteroatoms (averaged for the two S atoms) based on the MEP and NBO analysis are presented in Table S4.2. although the partial charges extracted from these two methods differ somewhat, they both clearly point to the strongly polar nature of the As−Cl bond, reflected in the NAO bond order of 0.59 and Wiberg bond index of 0.78. There was no evidence for a σ-hole in the electrostatic potential map.

Additional studies using the same basis set and correction for dispersion were made on a dimer pair to consider the strength of the $[As\text{-}Cl]_2$ dimerisation process. Starting from a dimer pair extracted from the crystallographic structure, the gas phase geometry-optimised dimer (Fig. S4.3) was found to be a minimum on the potential energy surface with no imaginary frequencies. The As—Cl bond lengths and As…Cl contacts were found to be comparable with those determined experimentally (Table S4.4). The dimer $(\mathbf{1})_2$ was favoured by -33.4 kJ.mol^{-1} of which dispersion was the major component (-23.6 kJ.mol^{-1}).

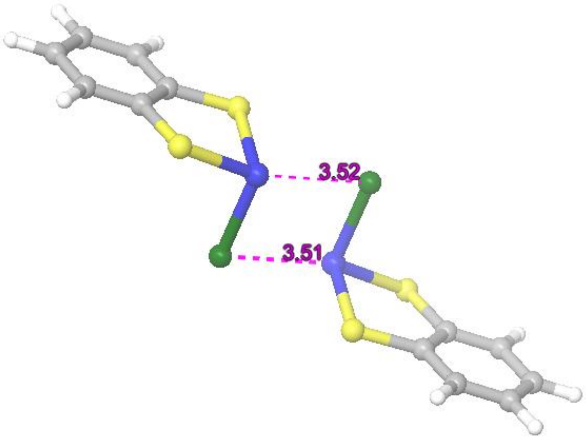
S4.1 Molecular electrostatic isopotential surface (-16 kcal)



S4.2 Atomic point charges Determined

Atom	MEP charge	NBO charge
Cl	-0.22	-0.40
As	+0.33	+0.70
S	-0.12	0.00

S4.3 Geometry-optimised structure of $[C_6H_4S_2AsCl]_2$ for the dimer $[C_6H_4S_2AsCl]_2$



S4.4 Key geometric parameters

Bonds	Exp	Calc.
As-Cl	2.27 – 2.31	2.31
As-S	2.19 – 2.23	2.25 – 2.26
As…Cl	3.36 – 3.58	3.51 – 3.52

S5. References.

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