

Supporting Information for:

# Neutral and Cationic Bismuth Compounds Supported by Bis(amidodimethyl)disiloxane Ligands

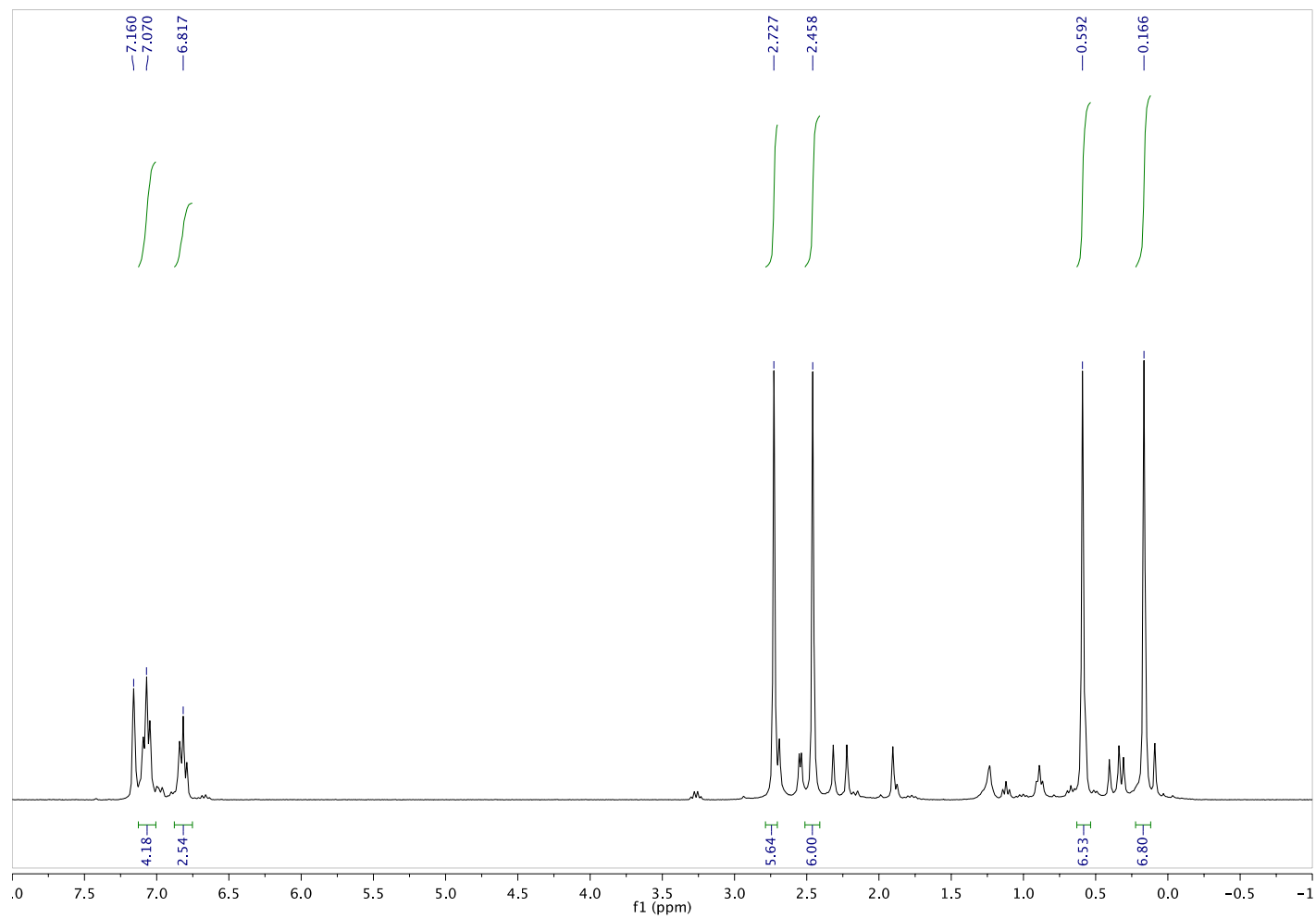
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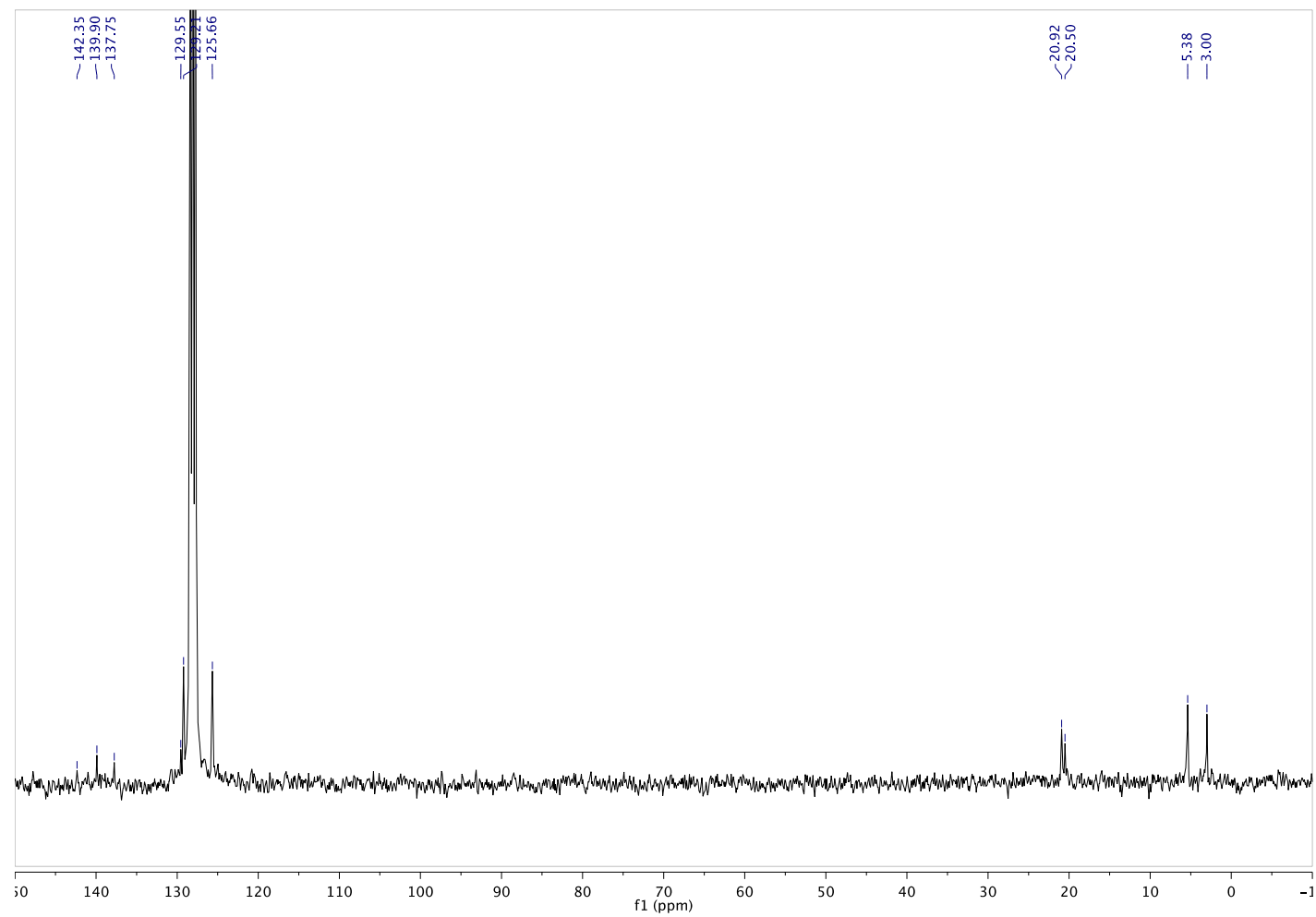
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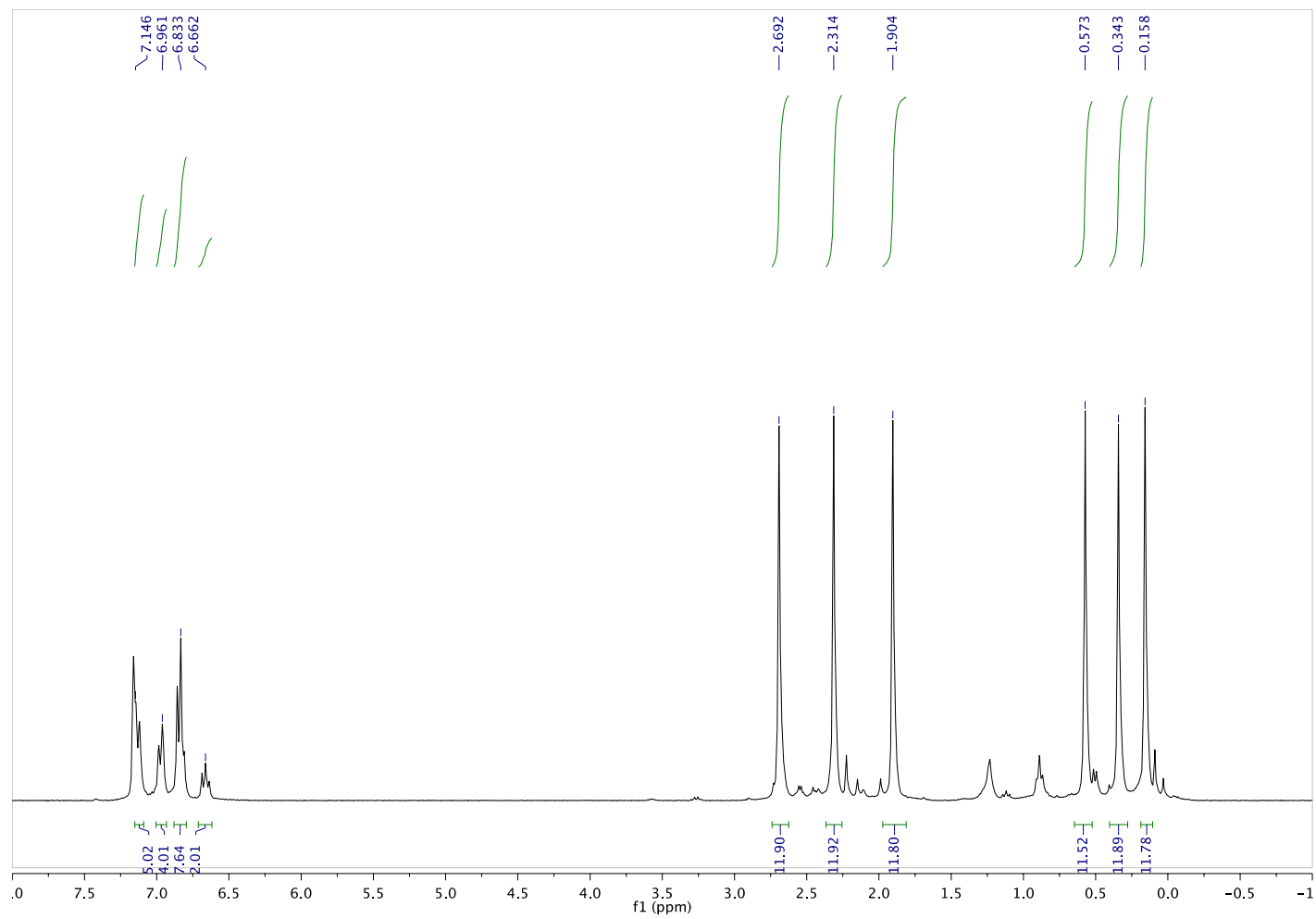
**Figure S1**  $^1\text{H}$  NMR spectrum (300 MHz,  $\text{C}_6\text{D}_6$ ) of  $\text{Bi}(\text{NON}^{\text{Ar}^1})\text{Cl}$  (**1b**)



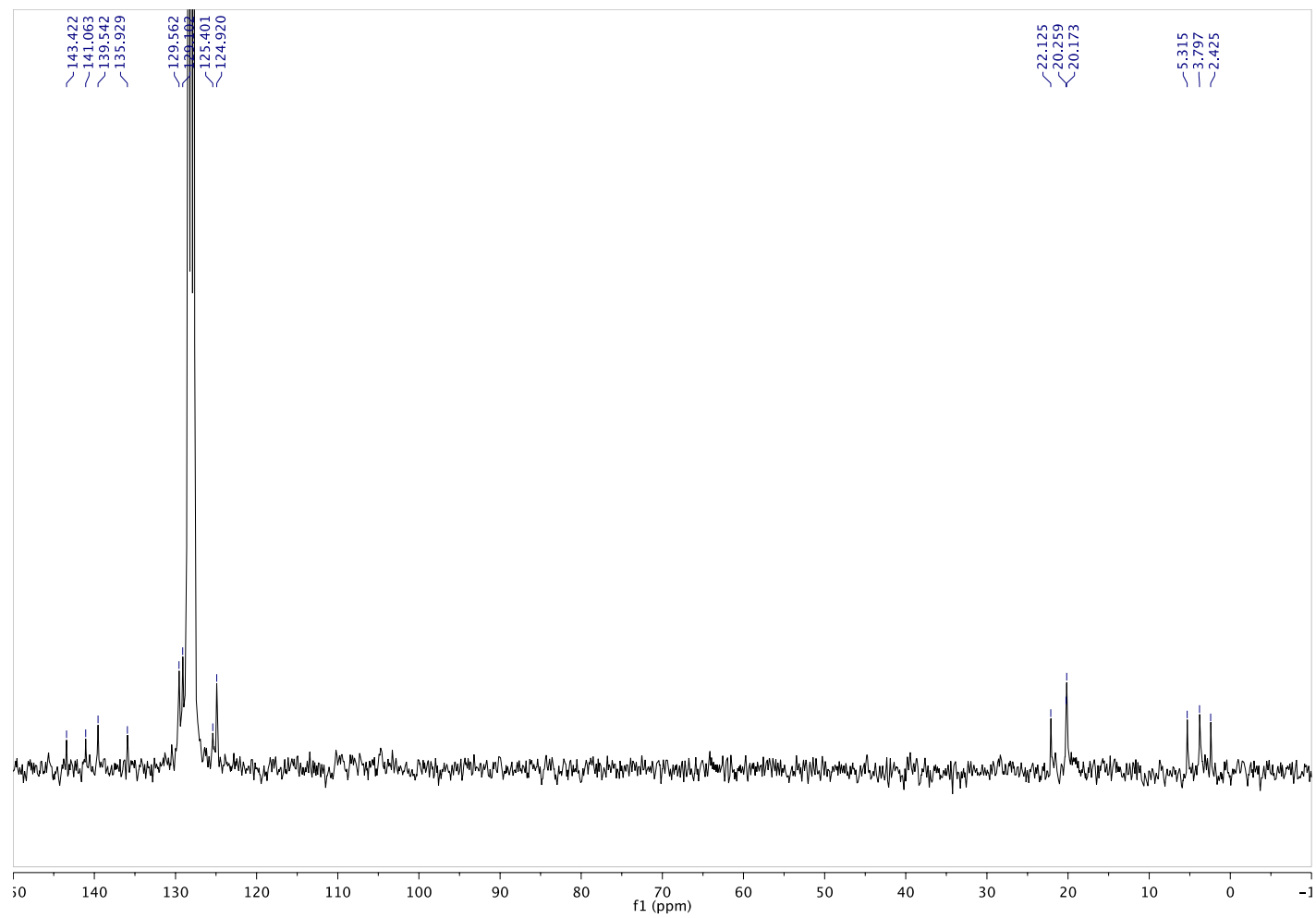
**Figure S2**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (75 MHz,  $\text{C}_6\text{D}_6$ ) of  $\text{Bi}(\text{NON}^{\text{Ar}'})\text{Cl}$  (**1b**)



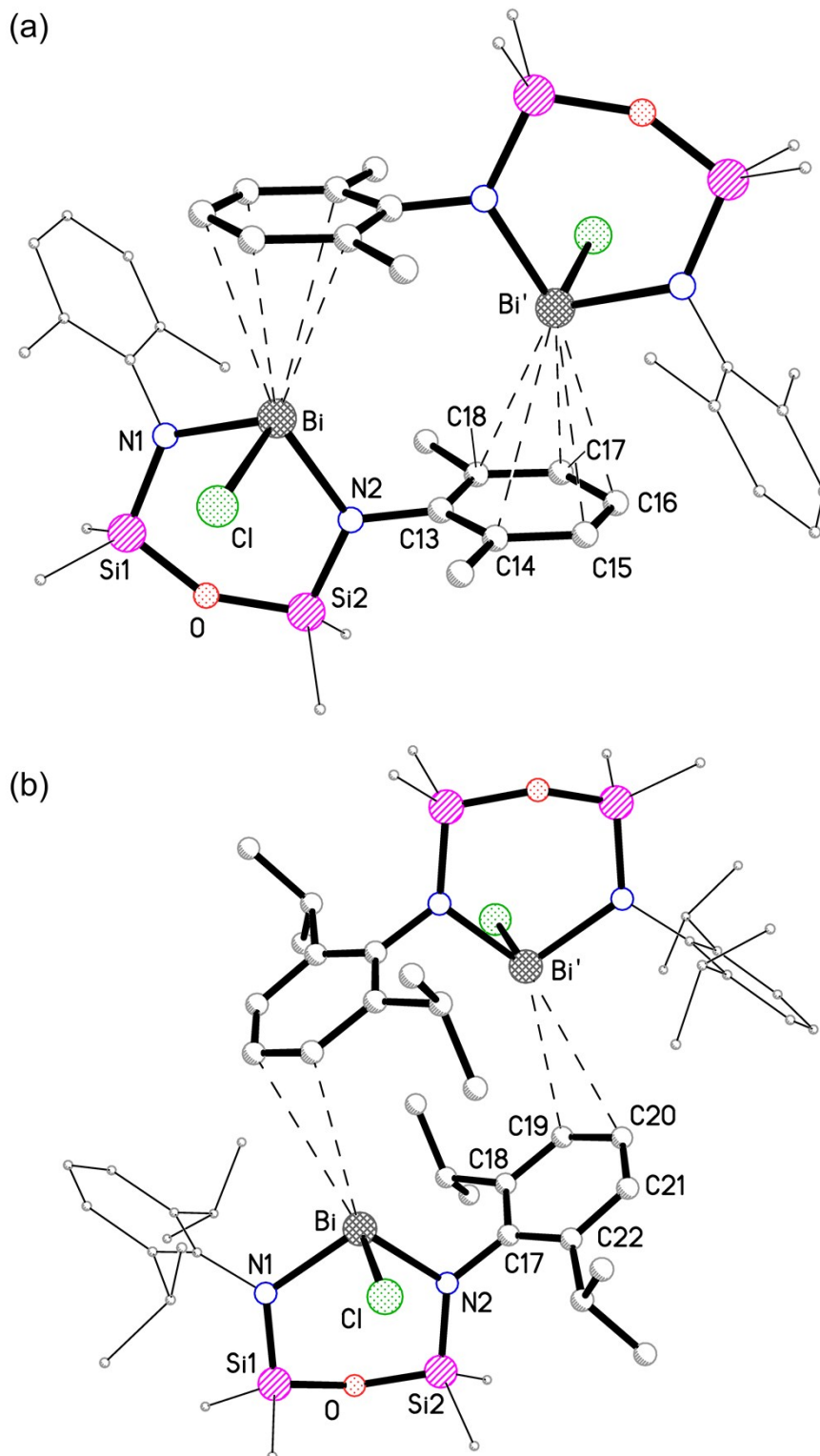
**Figure S3**  $^1\text{H}$  NMR spectrum (300 MHz,  $\text{C}_6\text{D}_6$ ) of  $\{\text{Bi}(\text{NON}^{\text{Ar}'})\}_2(\mu\text{-NON}^{\text{Ar}'})$  (**2b**)



**Figure S4**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (75 MHz,  $\text{C}_6\text{D}_6$ ) of  $\{\text{Bi}(\text{NON}^{\text{Ar}'})\}_2(\mu\text{-NON}^{\text{Ar}'})$  (**2b**)



**Figure S5** Solid-state dimers of **[1b]<sub>2</sub>** (top) and **[1c]<sub>2</sub>** (bottom). (a)  $' = 2-x, 2-y, -z$ . Bi...C14' 3.673(6) Å; Bi...C15' 3.540(6) Å; Bi...C16' 3.489(5) Å; Bi...C17' 3.496(5) Å; Bi...C18' 3.634(6) Å. (b)  $' = 1-x, 1-y, 1-z$ . Bi...C19' 3.715(4) Å; Bi...C20' 3.753(4) Å.



**Table S1** Crystal structure and refinement data for Bi(NON<sup>Ar'</sup>)Cl (**1b**), {Bi(NON<sup>Ar'</sup>)}<sub>2</sub>( $\mu$ -NON<sup>Ar'</sup>) (**2b**), [Bi(NON<sup>Ar'</sup>)][AlCl<sub>4</sub>] $\cdot$ C<sub>7</sub>H<sub>8</sub> (**3c**) and [Bi(NON<sup>Ar'</sup>)][Ga<sub>2</sub>Cl<sub>7</sub>] (**4c**)

	<b>1b</b>	<b>2b</b>	<b>3c</b>	<b>4c</b>
CCDC number	1528433	1528434	1528435	1528436
Empirical formula	C <sub>20</sub> H <sub>30</sub> BiClN <sub>2</sub> OSi <sub>2</sub>	C <sub>60</sub> H <sub>90</sub> Bi <sub>2</sub> N <sub>6</sub> O <sub>3</sub> Si <sub>6</sub>	C <sub>35</sub> H <sub>54</sub> AlBiCl <sub>4</sub> N <sub>2</sub> OSi <sub>2</sub>	C <sub>28</sub> H <sub>46</sub> BiCl <sub>7</sub> Ga <sub>2</sub> N <sub>2</sub> OSi <sub>2</sub>
<i>M<sub>r</sub></i>	615.07	1529.87	952.74	1079.42
Radiation (wavelength [Å])	MoK $\alpha$ ( $\lambda$ = 0.71073)	CuK $\alpha$ ( $\lambda$ = 1.54184)	MoK $\alpha$ ( $\lambda$ = 0.71073)	MoK $\alpha$ ( $\lambda$ = 0.71073)
<i>T</i> [K]	173(2)	120.0(1)	120.01(10)	120.0(1)
Crystal size [mm]	0.10 $\times$ 0.08 $\times$ 0.04	0.21 $\times$ 0.17 $\times$ 0.06	0.46 $\times$ 0.31 $\times$ 0.22	0.41 $\times$ 0.29 $\times$ 0.16
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$ (No.2)	<i>P</i> $\bar{1}$ (No.2)	<i>P</i> $\bar{1}$ (No.2)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No.14)
<i>a</i> [Å]	9.8884(3)	11.7744(3)	10.5351(2)	10.0533(2)
<i>b</i> [Å]	10.6089(4)	15.3339(4)	10.8349(2)	10.2526(3)
<i>c</i> [Å]	12.3277(5)	19.9763(5)	18.5054(3)	39.4446(10)
$\alpha$ [°]	85.527(2)	102.811(2)	87.1030(13)	90
$\beta$ [°]	76.827(2)	90.9255(19)	88.7719(13)	92.9450(19)
$\gamma$ [°]	68.765(2)	107.564(2)	75.1549(15)	90
<i>V</i> [Å <sup>3</sup> ]	1173.70(7)	3339.50(16)	2039.14(6)	4060.27(16)
<i>Z</i>	2	2	2	4
<i>D</i> <sub>calc.</sub> [Mg m <sup>-3</sup> ]	1.74	1.52	1.55	1.77
Absorption coefficient [mm <sup>-1</sup> ]	7.739	11.608	4.695	6.186
$\theta$ range for data collection [°]	1.70 to 27.49	3.11 to 69.99	2.60 to 30.0	2.82 to 26.00
Reflections collected	17593	38204	73699	31043
Independent reflections ( <i>R</i> <sub>int</sub> )	5299 (0.054)	12659 (0.039)	11894 (0.028)	7987 (0.050)
Data/restraints/parameters	5299 / 0 / 248	12659 / 0 / 718	11894 / 0 / 428	7987 / 12 / 400
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.029, <i>wR</i> <sub>2</sub> = 0.062	<i>R</i> <sub>1</sub> = 0.031, <i>wR</i> <sub>2</sub> = 0.080	<i>R</i> <sub>1</sub> = 0.015, <i>wR</i> <sub>2</sub> = 0.038	<i>R</i> <sub>1</sub> = 0.060, <i>wR</i> <sub>2</sub> = 0.105
Final <i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.040, <i>wR</i> <sub>2</sub> = 0.090	<i>R</i> <sub>1</sub> = 0.031, <i>wR</i> <sub>2</sub> = 0.081	<i>R</i> <sub>1</sub> = 0.016, <i>wR</i> <sub>2</sub> = 0.039	<i>R</i> <sub>1</sub> = 0.066, <i>wR</i> <sub>2</sub> = 0.106
GOOF on <i>F</i> <sup>2</sup>	1.466	1.103	1.134	1.367
Largest diff. peak/hole [e. $\cdot$ Å <sup>-3</sup> ]	0.93 and -2.79	1.39 and -2.52	1.00 and -0.55	1.34 and -2.57