

Complete numbering scheme for X-ray structures 1-3

X-ray-Crystallgraphy

Unit cell dimensions and intensity data (Tables 1, 2, and 3) for all the structures were obtained on a Siemens CCD SMART diffractometer at $-100\text{ }^{\circ}\text{C}$, with monochromatic $\text{Mo-K}\alpha$ X-rays ($\lambda = 0.71073\text{ \AA}$). The data collections nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different ϕ angle for the crystal and each exposure covered 0.3° in ω . The crystal to detector distance was 5.0 cm. The data sets were corrected empirically for absorption using SADABS.¹ All the structures were solved using the Bruker SHELXTL software package for the PC, using the direct methods option of SHELXS. The space groups for all of the structures were determined from an examination of the systematic absences in the data, and the successful solution and refinement of the structures confirmed these assignments. Except for the phenolic hydrogen and bridging methyl hydrogen atoms, all hydrogen atoms were assigned idealized locations and were given a thermal parameter

equivalent to 1.2 or 1.5 times the thermal parameter of the carbon atom to which it was attached. For the methyl groups, where the location of the hydrogen atoms was uncertain, the AFIX 137 card was used to allow the hydrogen atoms to rotate to the maximum area of residual density, while fixing their geometry. In several cases, the crystals contained severely disordered solvate molecules and in instances where a suitable model could not be constructed for the solvates, their contribution to the diffraction were removed ("squeezed") from the data by the Platon for Windows software program.

1•C₅H₁₂·2H₂O: Single crystals were grown from the evaporation of a saturated pentane solution at room temperature. The structure has been reported and complete experimental data is available in the supplementary material for the previous publication.² Unit cell parameters are reported in Table 1.

2•2.75CH₃CN: Single crystals were grown from the evaporation of a saturated Et₂O/CH₃CN mixture at room temperature. One phenolic arm was disordered with the oxygen atom residing in two unique positions with site occupancies of 0.85 and 0.15. The dominate position was orientated toward the center of the molecule. The phenolic hydrogens were found in the Fourier difference maps and refined isotropically. Several of the *t*-butyl groups were disordered across two distinct positions with several different occupancy factors. Unit cell parameters are reported in Table 1.

3: Single crystals were grown from the evaporation of a saturated Et₂O mixture at room temperature. The phenolic hydrogens were found in the Fourier difference maps and refined isotropically. One phenolic arm was disordered with the oxygen atom residing in two unique positions with site occupancies of 0.85 and 0.15. The dominate position was orientated toward

the center of the molecule. Several of the *t*-butyl groups were disordered across two distinct positions with several different occupancy factors. Unit cell parameters are reported in Table 1.

4•C₅H₁₂: Single crystals were grown from the evaporation of a saturated pentane solution at room temperature. The phenolic hydrogens were found in the Fourier difference maps and refined isotropically. One *t*-butyl group was occupied two distinct orientations with site occupancy factors of 0.5. The pentane solvate was severely disordered and the carbon atoms Unit cell parameters are reported in Table 1.

5•3(Me)₂CO: Single crystals were grown from a saturated acetone solution at room temperature. Disordered solvates were removed ("squeezed") from the data by the Platon for Windows software program. All disordered *tert*-butyl groups were modeled over two positions and refined with appropriate site occupancy factors. The phenolic hydrogens were found in the Fourier difference maps and refined isotropically. Unit cell parameters are reported in Table 2.

6•2C₅H₁₂: Single crystals were grown from a saturated pentane solution at -35°C. The structure has been reported and complete experimental data is available in the supplementary material for the previous publication. Unit cell parameters are reported in Table 2.

7•3CH₂Cl₂: Single crystals were grown from a concentrated methylene chloride solution at -35°C. The hydrogens attached to the bridging alkyl groups were found in the Fourier difference maps and refined isotropically. Unit cell parameters are reported in Table 2.

8•3CH₂Cl₂: Single crystals were grown from a saturated methylene chloride solution at room temperature. One severely disordered methylene chloride molecule was removed ("squeezed") from the data by the Platon for Windows software program. The remaining two solvates were well ordered. Two of *tert*-butyl groups occupied equally two distinct positions. Unit cell information is located in Table 2.

9·3C₅H₁₂: Single crystals were grown from a concentrated pentane solution at -35°C. One *tert*-butyl group was refined isotropically. Two of the three pentane molecules, C(75)-C(84), were refined with partial site occupancy. Unit cell parameters are reported in Table 2.

10·C₅H₁₂·CH₂Cl₂: Single crystals were grown from a pentane-methylene chloride diffusion at -35°C. A disordered pentane and dichloromethane solvate were both removed ("squeezed") from the data by the Platon for Windows software program. One of the *tert*-butyl group was modelled with two orientations and was isotropically refined with site occupancy factors of 0.5. The hydrogens on the bridging methyl groups were found in the Fourier difference maps and refined isotropically.

11·CH₂Cl₂·C₅H₁₂: Single crystals were grown by a diffusion of pentane into a saturated methylene chloride solution at room temperature. The structure has been reported and complete experimental data is available in the supplementary material for the previous publication. Unit cell parameters are reported in Table 2.

12·1½CH₂Cl₂: Single crystals were grown from a saturated methylene chloride solution at -35°C. Four *tert*-butyl group were disordered over two positions (0.7 and 0.3 site occupancies) and these carbon atoms were all refined isotropically. One disordered methylene chlorine molecule was "squeezed" from the structure with the Platon for Windows software program while the remaining solvate molecule was disordered across an inversion symmetry position with an overall occupancy factor of 0.25 on this site.

13·CH₂Cl₂·¼C₇H₈: Single crystals were grown from a saturated methylene chloride/pentane solution at -35°C containing a few drops of toluene. The asymmetric unit contained two complete aluminum species, two ordered disordered and two ordered tetraethylammonium cations, two 0.75 occupancy and one 0.5 occupancy dichloromethane

solvates, and one half occupancy toluene molecule. Several of the *tert*-butyl groups were disordered over two positions and they were refined with the necessary site occupancy factors. Experimental unit cell data for the data collection are contained in Table 3.

14•2CH₂Cl₂: Single crystals were grown from a saturated methylene chloride solution at -35°C. Two disordered dichloromethane solvate molecules were removed ("squeezed") from the data by the Platon for Windows software program. Three of the *tert*-butyl group were disordered in two positions: two groups were modeled with site occupancies of 0.5 while one had occupancy factors of 0.7 and 0.3. Metric parameters are contained in Table 3.

15•C₅H₁₂: Single crystals were grown from a saturated methylene chloride/pentane solution at -35°C. A *tert*-butyl group was disordered over two positions and refined with the necessary site occupancy factors. Both **15** and a pentane solvate reside on 2-fold positions. Unit cell information can be located in Table 3.

16•2½CH₂Cl₂: Single crystals were grown from a saturated methylene chloride solution at -35°C. All disordered *tert*-butyl groups have been modeled over two positions with appropriate occupancy factors. A methylene chloride solvent molecule was modeled at half occupancy while one disordered solvate was removed ("squeezed") from the data by the Platon for Windows software program. Unit cell data is listed in Table 3.

17•2CH₂Cl₂: Single crystals were grown from a saturated methylene chloride solution at -35°C. One disordered dichloromethane solvate molecule was removed ("squeezed") from the data by the Platon for Windows software program. Disordered *tert*-butyl group were modeled over two positions and refined with various site occupancy factors. Unit cell information is located in Table 3.

19•4CH₂Cl₂: Single crystals were grown from a saturated methylene chloride solution at -35°C. Unit cell parameters are reported in Table 3.

a) A.L.Spek (2001) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands b) van der Sluis, P; Spek, A. L. *Acta Cryst.* **1990**, *A46*, 194-201

S-

8

Table 1. X-ray data^a for ligand crystal structures 1 - 4.

	1-C ₅ H ₁₂ -2H ₂ O	2-3CH ₃ CN	3	4-C ₅ H ₁₂
Total reflections	17704	19999	36640	16426
Unique reflections [R(int)]	11264[0.0820]	12179[0.0506]	11534[0.0431]	11048[0.0352]
Temperature (K)	173(2)	173(2)	173(2)	173(2)
Chemical formula	C ₇₇ H ₁₂₆ O ₆	C ₇₀ H ₉₂ N ₃ O ₅	C ₈₄ H ₁₁₁ O ₆	C ₆₃ H ₈₀ O ₅
Formula weight	1147.78	1055.47	1216.73	917.27
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
$\mu(\text{Mo-K}\alpha)$ (mm ⁻¹)	0.070	0.062	0.075	0.069
<i>a</i> (Å)	14.4377(12)	14.5377(8)	13.8114(9)	12.4045(8)
<i>b</i> (Å)	15.1326(13)	15.6387(9)	29.9961(18)	13.0644(8)
<i>c</i> (Å)	15.7110(14)	18.5314(11)	15.809(1)	18.2881(12)
α (°)	77.820(2)	111.716(1)	-	106.0450(10)
β (°)	86.244(2)	91.874(1)	91.207(1)	101.4220(10)
γ (°)	80.759(2)	114.121(1)	-	97.8750(10)
<i>V_c</i> (Å ³)	3309.9(5)	3487.3(3)	6548.1	2733.4(3)
<i>Z</i>	2	2	4	2
<i>R</i> ₁ [<i>I</i> ≥ 2σ(<i>I</i>) data] ^b	0.0962 [4181]	0.689[8290]	0.0479[8474]	0.0705[6240]
<i>wR</i> ₂ (all data) ^c	0.2375	0.1913	0.1323	0.2217
Largest diff. peak, hole	0.359, -0.256	0.530, -0.389	0.339, -0.204	0.555, -0.286

^aObtained with monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å) at 173K. ^b $R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|$.^c $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]\}^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (XP)^2 + YP]$ where $P = (F_o^2 + 2F_c^2)/3$.

8

S- 9

Table 2. X-ray structural data^a for compounds 5 - 11.

	5-3OCMe ₂	6-2C ₃ H ₁₂	7-3CH ₂ Cl ₂	8-3CH ₂ Cl ₂	9-3C ₃ H ₁₂	10-C ₃ H ₁₂ -CH ₂ Cl ₂	11-C ₃ H ₁₂ -CH ₂ Cl ₂
total reflections	19250	22127	42749	44504	18990	33009	45513
uniq. reflections	11705	13827	13377	13646	11472	9926	14664
<i>R</i> (int)	0.0452	0.0816	0.0993	0.1054	0.0868	0.0790	0.0437
Θ_{\max}°	24.74	24.00	24.00	25.00	23.00	22.50	25.00
chemical formula	C ₇₇ H ₁₀₄ O ₇	C ₉₀ H ₁₃₈ O ₄ Al ₄	C ₈₁ H ₁₁₈ O ₅ Al ₄ Cl ₆	C ₇₈ H ₁₀₆ O ₅ Al ₂ Cl ₆	C ₈₉ H ₁₃₂ O ₄ Al ₂	C ₇₈ H ₁₀₄ O ₅ Al ₂ Cl ₂	C ₈₇ H ₁₂₈ O ₄ Al ₂ Cl ₃ N ₁
formula weight	1141.60	1391.92	1492.37	1390.29	1319.91	1246.47	1412.21
crystal system	triclinic	triclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
μ (Mo-K α) (mm ⁻¹)	0.069	0.098	0.289	0.291	0.082	0.155	0.178
<i>a</i> (Å)	13.3480(8)	13.6213(7)	16.1000(11)	14.7565(18)	13.652(4)	14.5373(10)	15.1245(7)
<i>b</i> (Å)	16.5313(10)	17.3859(9)	20.8304(14)	43.043(5)	15.532(5)	23.7780(17)	21.2736(10)
<i>c</i> (Å)	17.2102(10)	21.1789(11)	26.6007(18)	13.4321(16)	21.088(6)	22.6129(16)	26.0590(11)
α (°)	80.230(1)	111.891(1)	-	-	72.037(5)	-	-
β (°)	73.329(1)	98.218(1)	107.3370(10)	114.592(2)	77.508(6)	103.481(2)	95.246(1)
γ (°)	71.513(1)	101.501(1)	-	-	82.443(6)	-	-
<i>V</i> _c (Å ³)	3437.3(4)	4428.3(4)	8515.8(10)	7557.8(16)	4143(2)	7601.2(9)	8349.4(7)
<i>Z</i>	2	2	4	4	2	4	4
<i>R</i> ₁ [<i>I</i> ≥ 2 σ (<i>I</i>) data] ^b	0.0622 [5861]	0.0912 [8243]	0.0914 [8210]	0.0878 [7097]	0.0890 [7699]	0.0668 [4998]	0.0660 [10122]
<i>wR</i> ₂ (all data) ^c	0.1705	0.2510	0.2354	0.2104	0.2480	0.1910	0.2004
Larg. diff. peak, hole	0.373, -0.250	0.369, -0.508	0.464, -0.392	0.424, -0.760	0.583, -0.310	0.751, -0.332	0.907, -0.434

^aObtained with monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). ^b $R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|$. ^c $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2 / \Sigma [w(F_o^2)]]\}^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (XP)^2 + YP]$ where $P = (F_o^2 + 2F_c^2)/3$.

9

S- 10

Table 3. X-ray structural data^a for compounds 12–17, and 19.

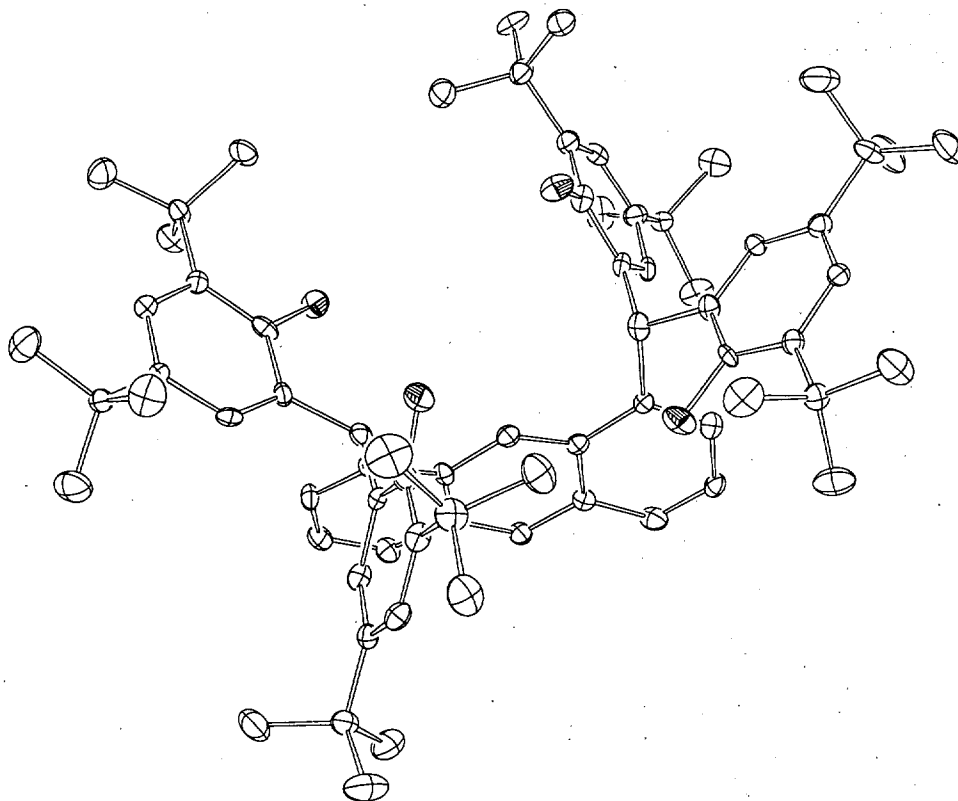
	12-1 $\frac{1}{2}$ CH ₂ Cl ₂	13-CH ₂ Cl ₂ · $\frac{1}{4}$ C ₇ H ₈	14-2CH ₂ Cl ₂	15-C ₃ H ₁₂	16-2 $\frac{1}{2}$ CH ₂ Cl ₂	17-2CH ₂ Cl ₂	19-4CH ₂ Cl ₂
total reflections	72704	45097	50022	31360	20481	22602	22522
uniq. reflects.	11586	26207	15819	11338	11098	14925	13660
<i>R</i> (int)	0.0943	0.0582	0.0647	0.0550	0.0578	0.0433	0.1508
Θ_{\max}°	23.50	22.50	25.00	28.31	23.50	28.34	24.75
chemical formula	C _{81.125} H _{116.25} NO ₅ Al ₂ Cl _{3.125}	C _{93.75} H ₁₄₄ Al ₂ Cl ₄ N ₂ O ₅	C ₈₆ H ₁₁₅ O ₆ Al ₂ Cl ₄ Na	C ₁₀₁ H ₁₃₆ O ₆ Al ₂	C _{77.5} H ₁₀₀ O ₆ AlCl ₅	C ₆₅ H ₈₃ O ₆ Al ₃ Cl ₄	C ₈₁ H ₁₀₂ O ₅ Al ₂ Cl ₈
formula weight	1350.24	1574.87	1463.53	1500.06	1331.81	1183.05	1493.19
crystal system	orthorhombic	triclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic
space group	<i>Pbca</i>	$P\bar{1}$	<i>C2/c</i>	<i>P2₁/n</i>	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
μ (Mo-K α) (mm ⁻¹)	0.192	0.181	0.202	0.082	0.290	0.278	0.351
<i>a</i> (Å)	25.8599(15)	15.4309(7)	61.323(4)	16.6001(12)	14.214(3)	13.0989(14)	14.723(3)
<i>b</i> (Å)	19.8675(12)	25.6420(13)	13.5423(8)	11.9328(9)	15.116(3)	13.2760(14)	15.462(3)
<i>c</i> (Å)	30.5878(18)	28.1895(14)	21.6684(11)	24.8710(18)	20.095(4)	18.315(2)	19.938(4)
α (°)	-	112.4720(1)	-	-	104.122(5)	95.047(2)	69.973(4)
β (°)	-	102.0080(1)	93.043(1)	109.180(2)	106.091(4)	91.299(2)	72.995(4)
γ (°)	-	90.4490(1)	-	-	105.057(4)	94.424(2)	74.811(4)
<i>V_c</i> (Å ³)	15715.1(16)	10034.3(8)	17969.3(17)	4653.1(6)	3766.5(13)	3161.9(6)	4011.3(12)
<i>Z</i>	8	4	8	2	2	2	2
<i>R</i> ₁ [<i>I</i> ≥ 2 σ (<i>I</i>)] ^b	0.0849 [8757]	0.0887 [14595]	0.0596 [10021]	0.0586 [7689]	0.0929 [6166]	0.0535 [9964]	0.0697 [3091]
<i>wR</i> ₂ (all data) ^c	0.2043	0.2770	0.1706	0.1687	0.2981	0.1538	0.1656
diff. peak, hole	0.476, -0.459	1.066, -0.555	0.761, -0.286	0.364, -0.378	0.862, -0.544	0.524, -0.633	0.614, -0.519

^aObtained with monochromatic Mo K α radiation ($\lambda = 0.71073$ Å) at 173 K. ^b $R_1 = \Sigma |F_o| - |F_c| / \Sigma |F_o|$. ^c $wR_2 = \{\Sigma [w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]\}^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (XP)^2 + YP]$ where $P = (F_o^2 + 2F_c^2)/3$.

10

Crystallographic Diagrams

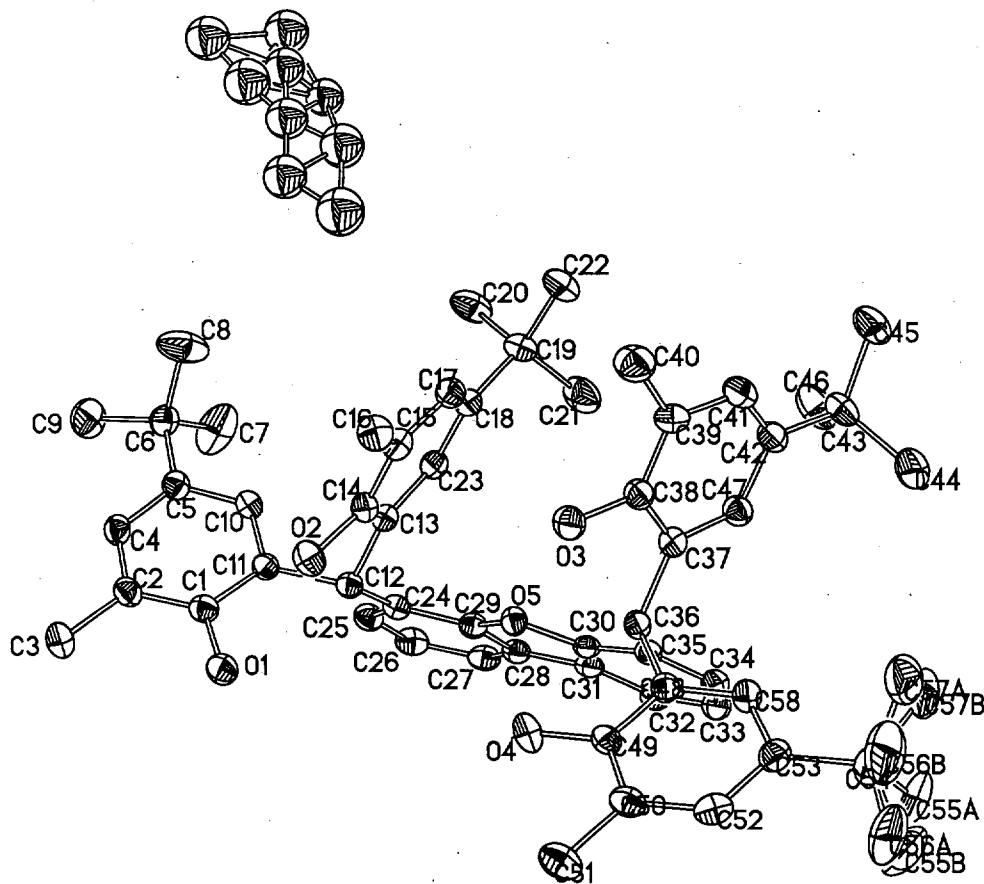
The following diagrams are drawn with 30% probability ellipsoids for all atoms in the asymmetric unit of the structure including the solvate molecules. Hydrogen atoms have been omitted for clarity



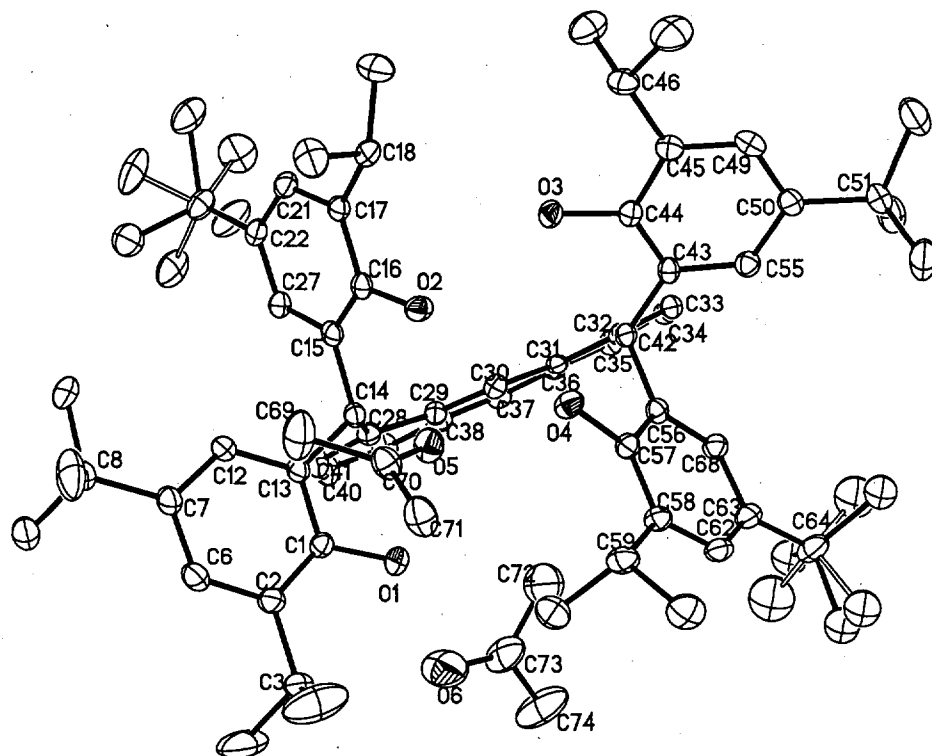
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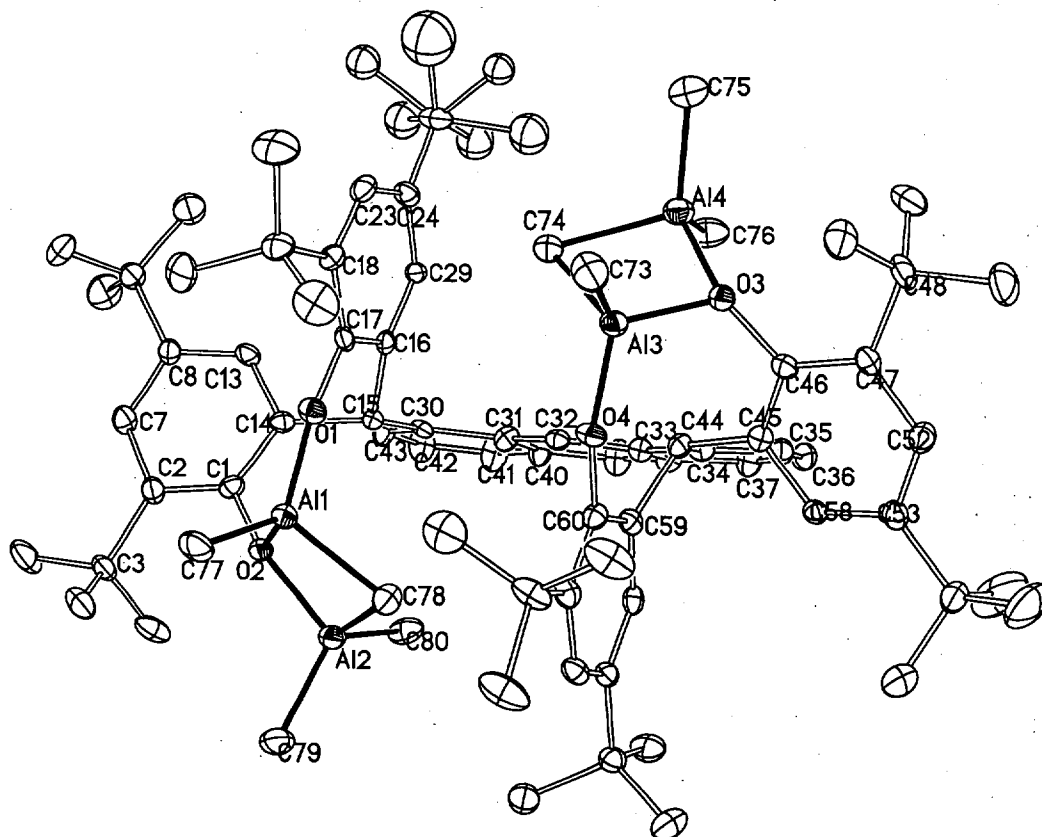
S- 13



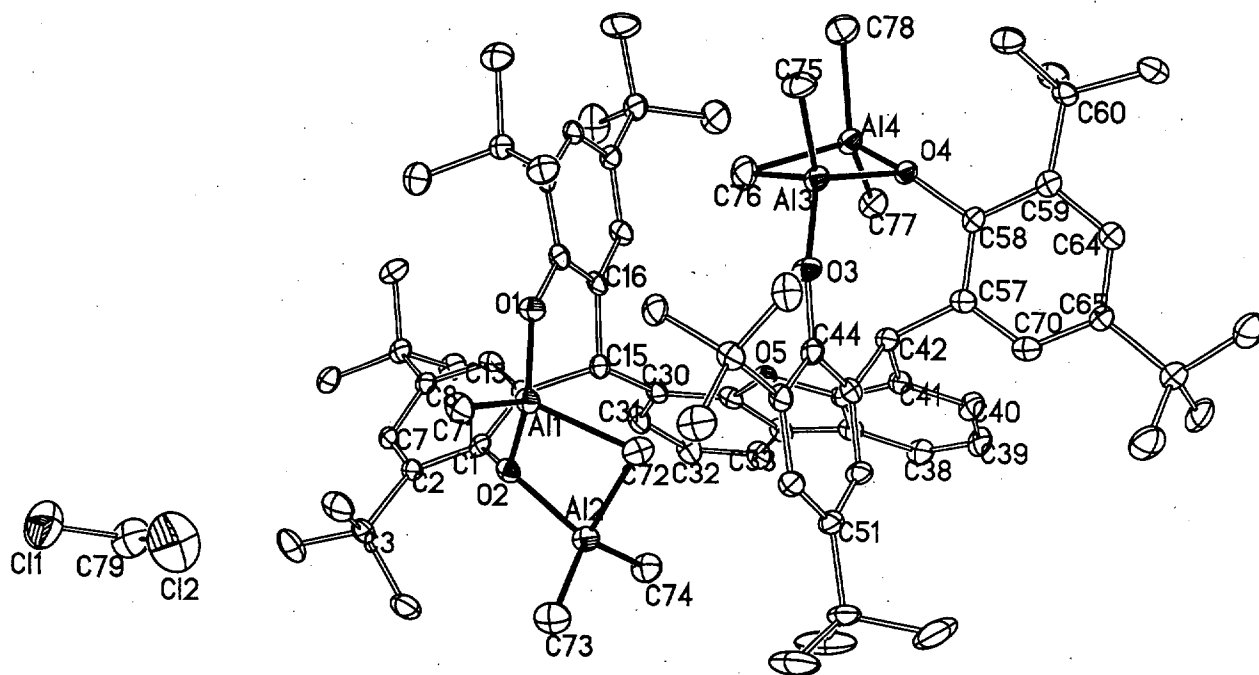
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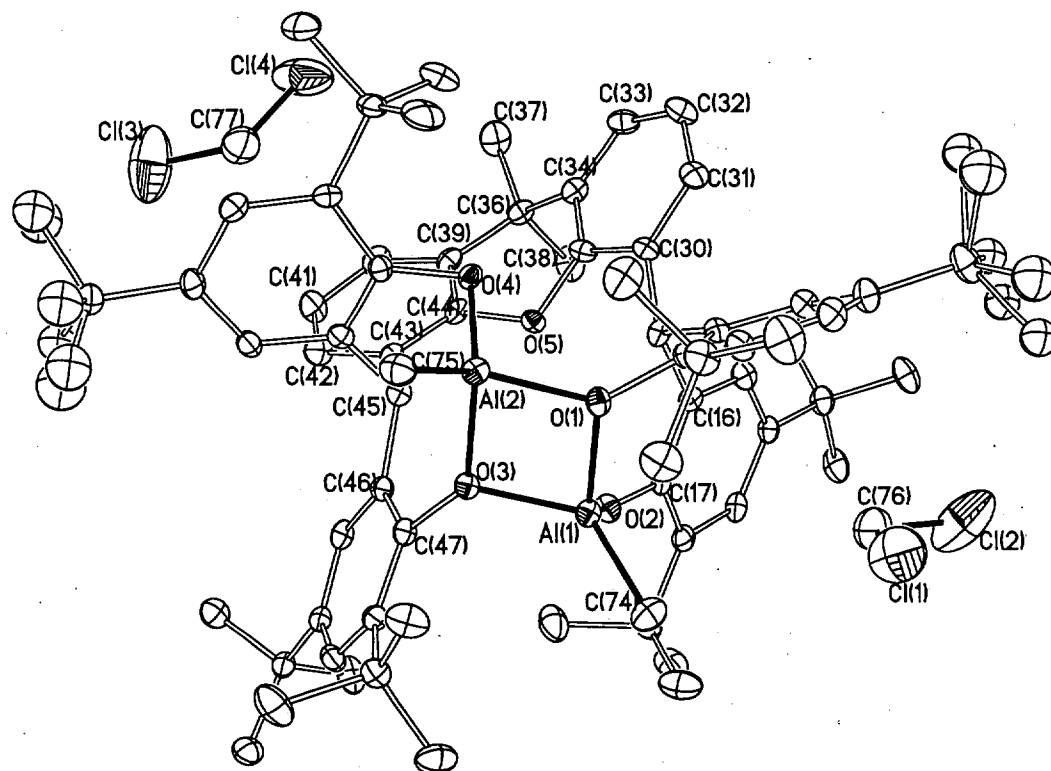
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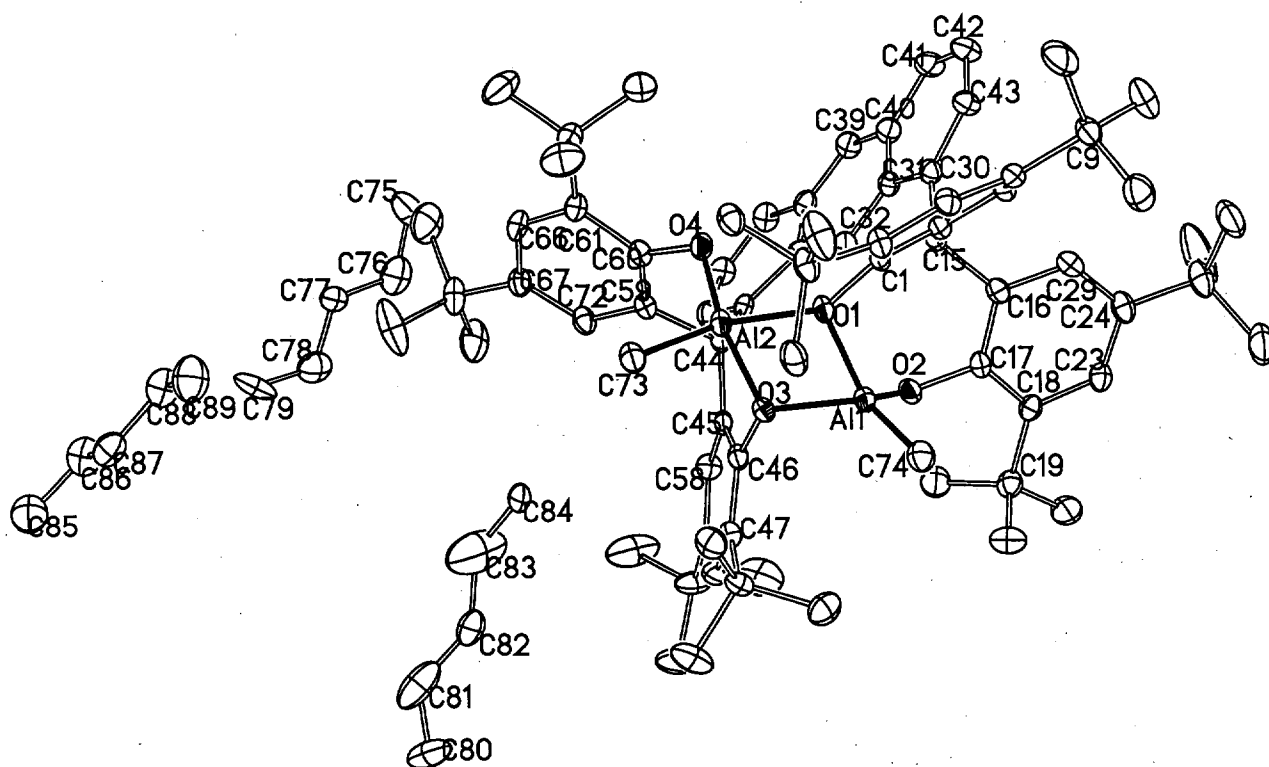
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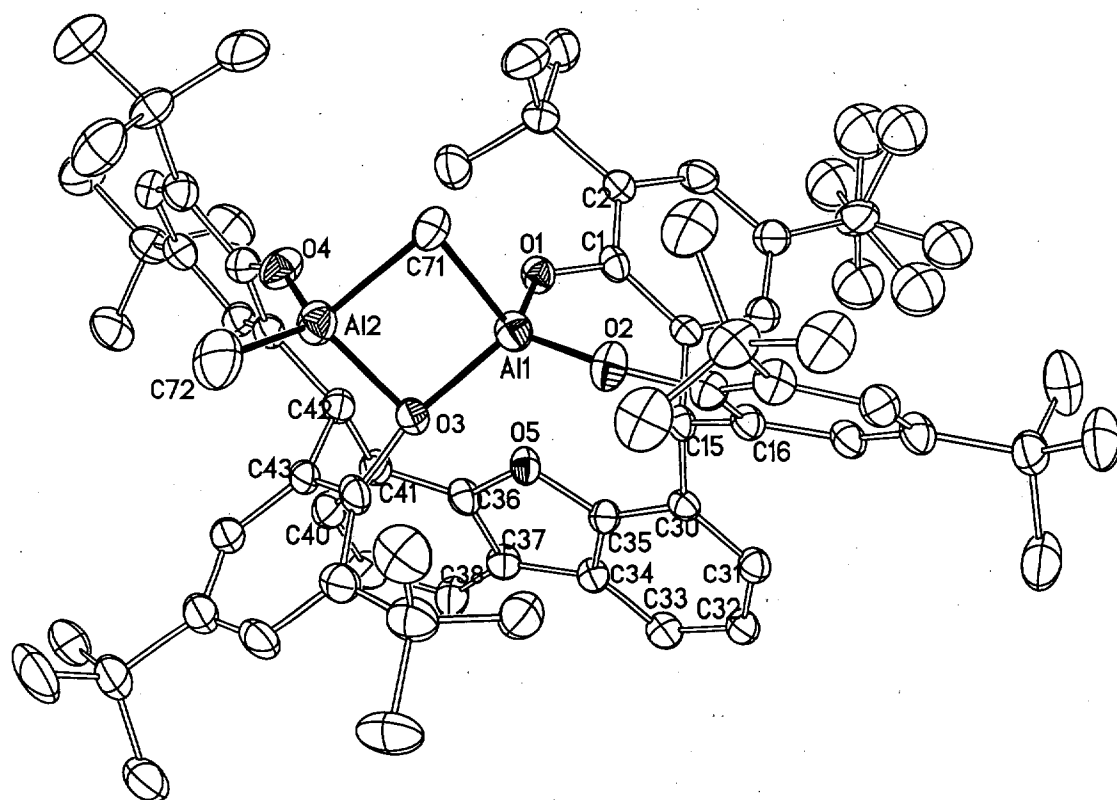
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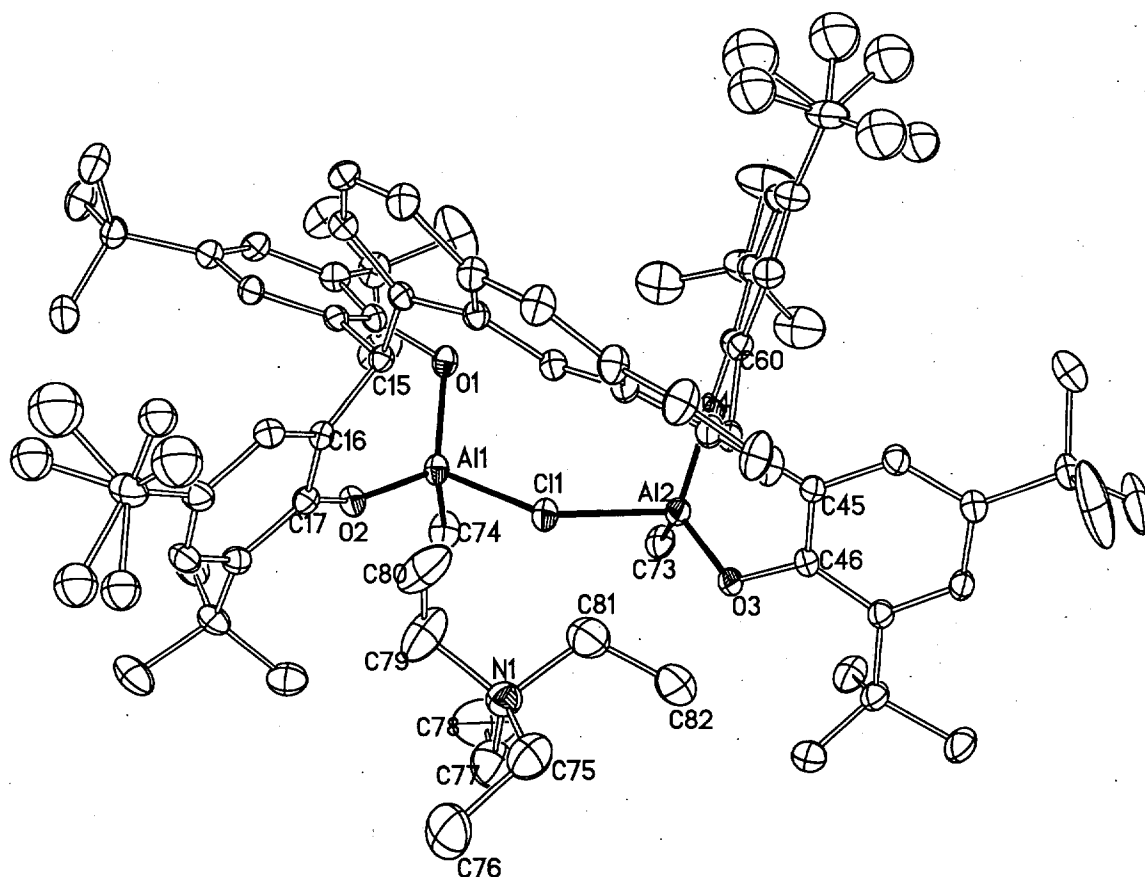
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Compound 9

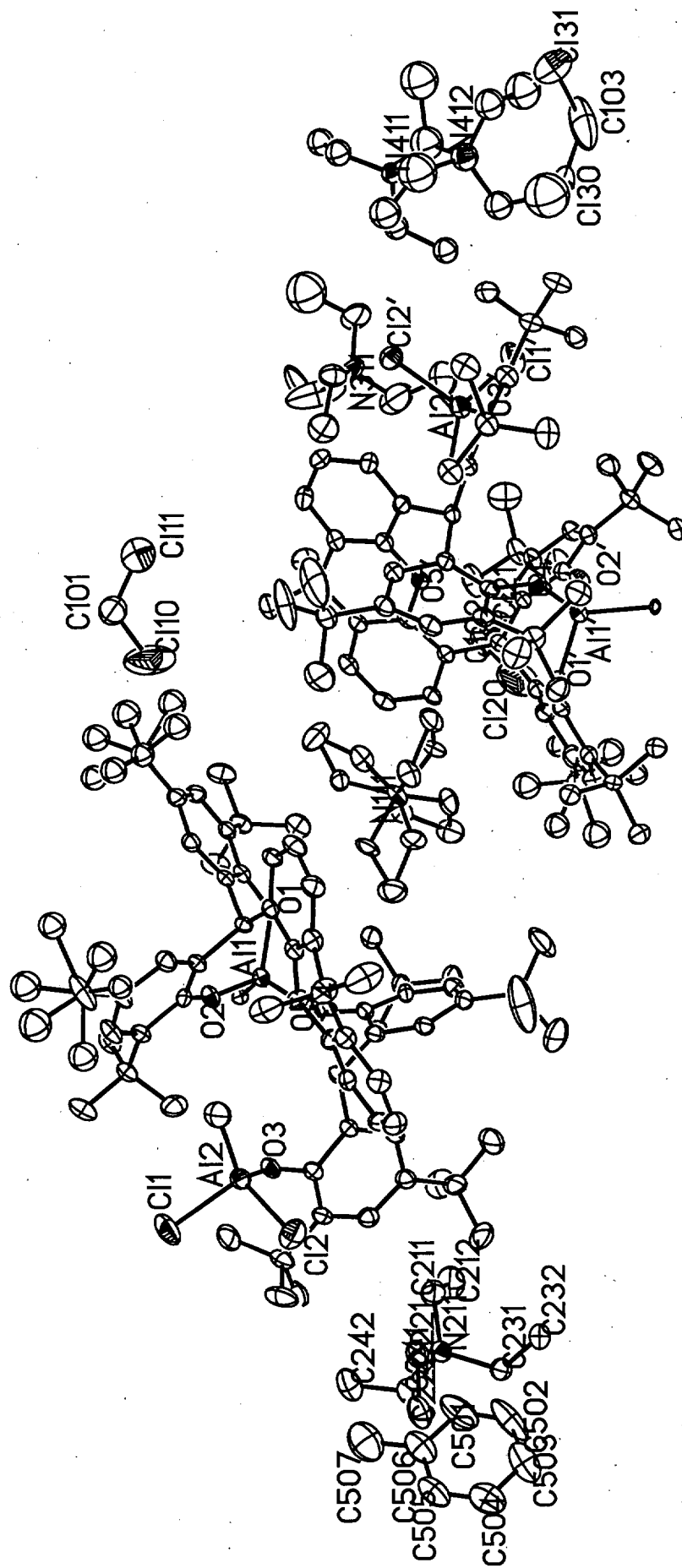


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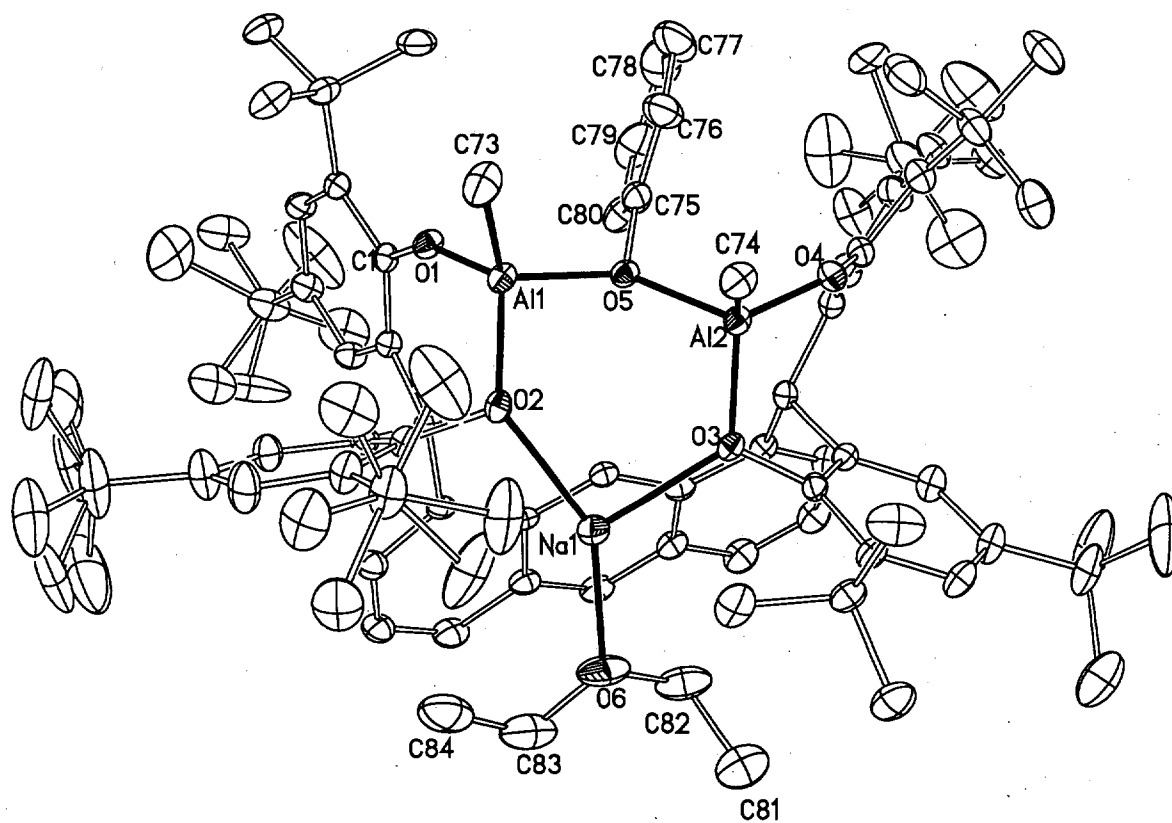


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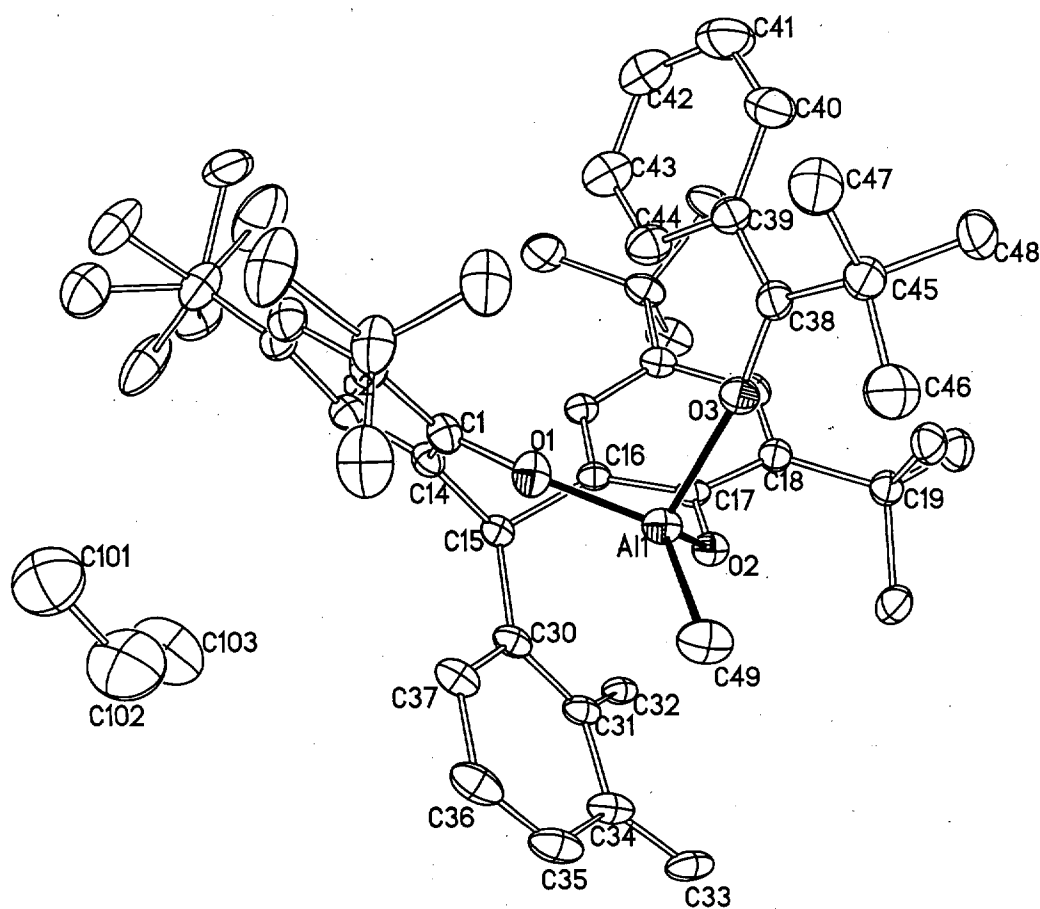




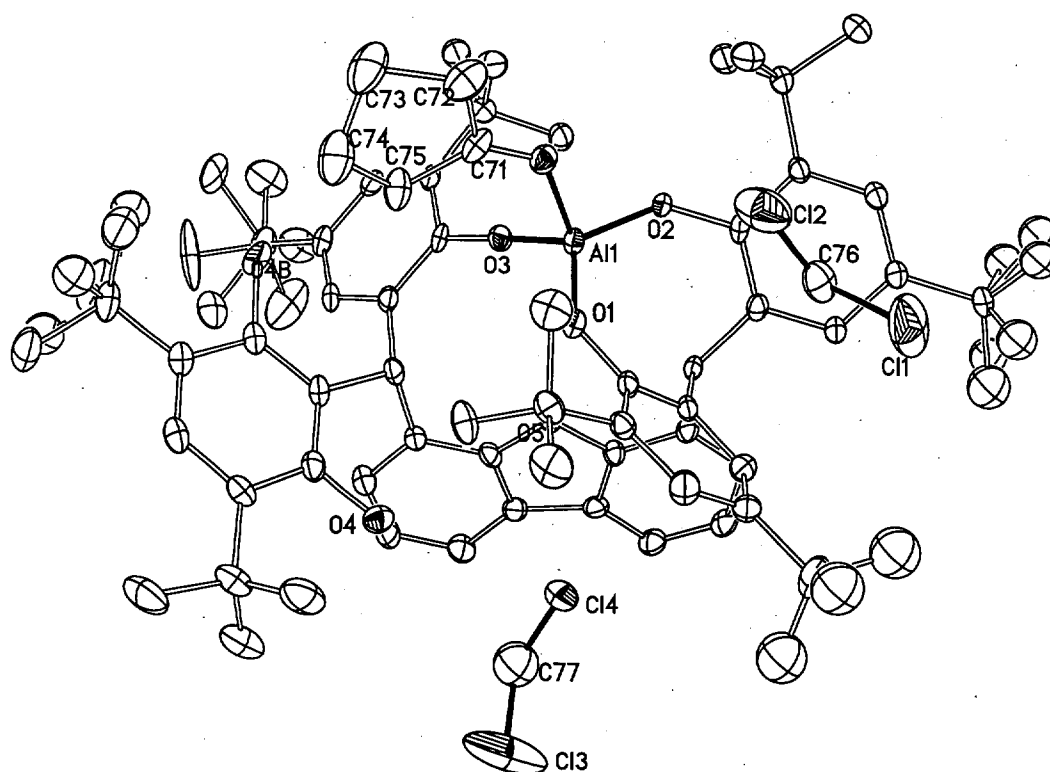
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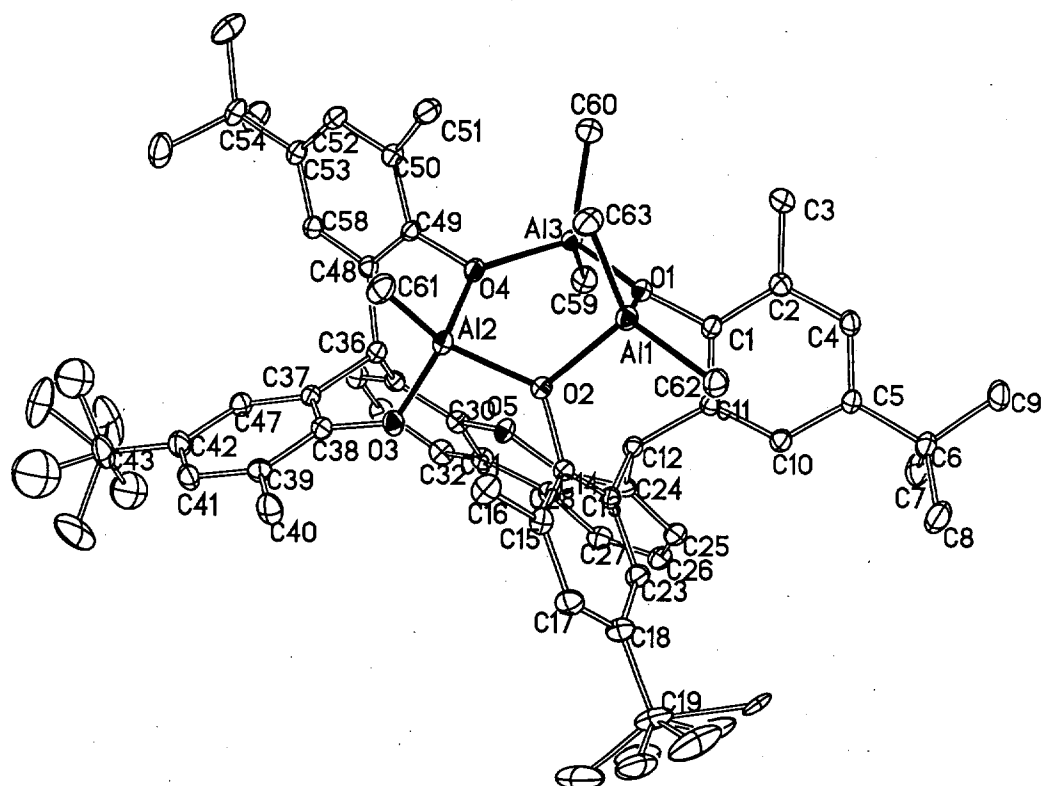
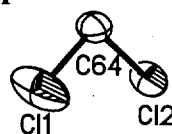
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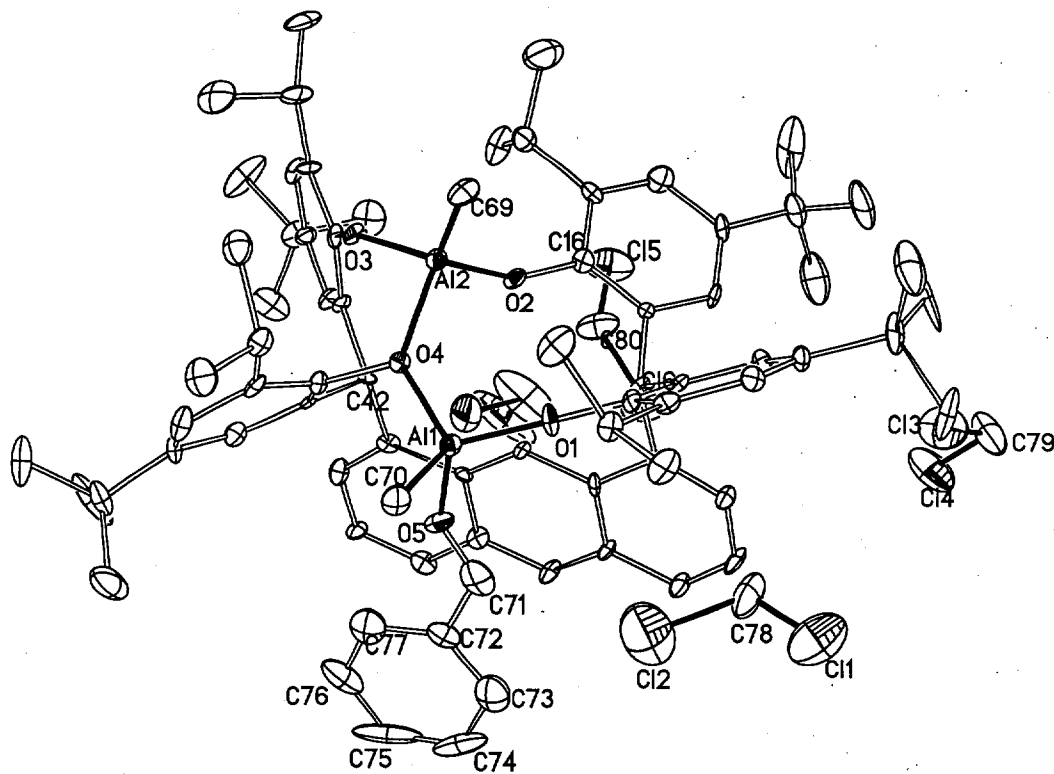
Compound 15



Compound 16



Compound 17



Compound 19

¹. Blessing, R. H. *Acta Cryst., Sect. A*, **1995**, *51*, 33-38.

² Cottone, A; Scott, M. J. *Organometallics* **2000**, *19*, 5254-5256.