Supporting Information

Chromium Precursor for Phillips Ethylene Trimerization Catalyst: (2-Ethylhexanoate)$_2$CrOH

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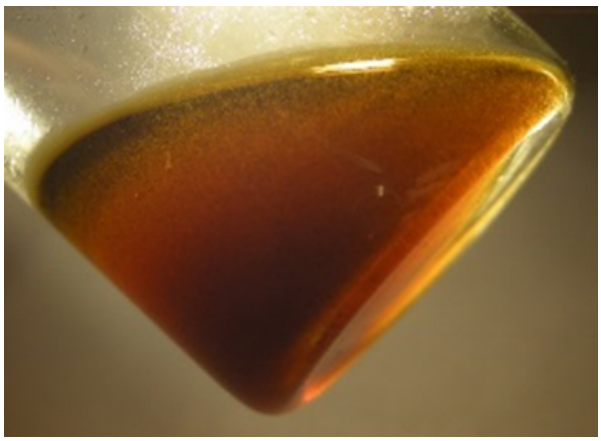
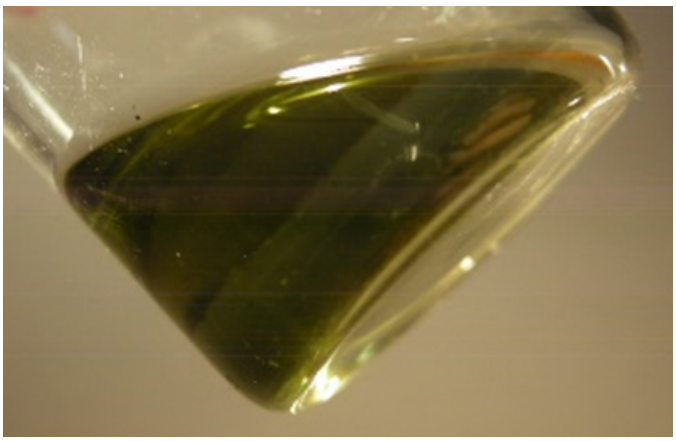


Original Phillips catalyst solution in toluene (entry 1)



Catalyst solution prepared using $(EH)_2CrOH$, $(Me_2C_4H_2N)AlEt_2$, and $Et_3Al{\cdot}ClAlEt_2$. in methylcyclohexane (entry 5)

X-ray crystallography studies of tetranuclear chromium complex. Several pieces of single crystals were fortuitously deposited (ca, 10%) with some oily compounds, when a pentane solution of the catalyst prepared from the three components of $(EH)_2CrOH$, $(Me_2C_4H_2N)Al\mathbf{Me}_2{\cdot}OEt_2$ and $\mathbf{Me}_3Al{\cdot}ClAl\mathbf{Me}_2$ was stored in a glove box for a month: A mixture of Me_3Al (0.162 g, 2.25 mmol) and Me_2AlCl (2.25 mL, 2.25 mmol, 1.0 M in hexane) was added to a solution of $(Me_2C_4H_2N)AlMe_2{\cdot}OEt_2$ (0.190 g, 0.843 mmol) in benzene (2 mL). A solution of $(EH)_2CrOH$ (0.100 g, 0.281 mmol) in benzene (3 mL) was added to the resulting solution. The mixture was stirred for 3 h at room temperature. The solvent was concentrated to 0.5 mL and pentane (5 mL) was layered onto the benzene solution. Green crystals were deposited along with some oily product in 1 month. The crystals were manually collected (7.5 mg, 12%) for X-ray crystallography and testing the activity. Several other trials resulted in formation of tiny crystals in the oily matrix, not allowing manual collection of the crystals.

In the structure refinement (O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339-341; G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112-122), we detected three μ_2-type atoms which were situated in two different conditions. One could be assigned to $-CH_3$ (C28) with little ambiguity: Bond length with Cr(3) was short (2.099 Å), similar to Cr-C bond distances observed for the μ_3-type carbon atoms (2.06~2.07 Å) in this molecule. The other two atoms formed relatively long bond distances with Cr (2.226 Å and 2.242 Å), which were assigned as Cl with half occupancy. When we tried to solve the structure by assigning the μ_3-type atoms as oxygen, R_1 value increased and, moreover, hydrogen atom couldn't be attached. An $AlClMe_2$ fragment was disordered over three orientations with site-occupancy ratio of 0.55 : 0.25 : 0.20. Based upon aforementioned assignment, the structure was refined (CCDC #, 1044534): $C_{28}H_{51}Al_3Cl_4CrN_3$, M = 860.45, monoclinic, a = 11.6198(2), b = 29.9914(7), c = 12.3307(3) Å, β = 111.9370(10)°, V = 3986.04(15) Å^3, T = 100(2) K, space group $P2_1/n$, Z = 4, 6974 unique (R(int) = 0.0977) which were used in all calculations. The final wR_2 was 0.1538 ($I > 2\sigma(I)$). The structure was drawn in Fig. S1 with the selective bond distances and angles.

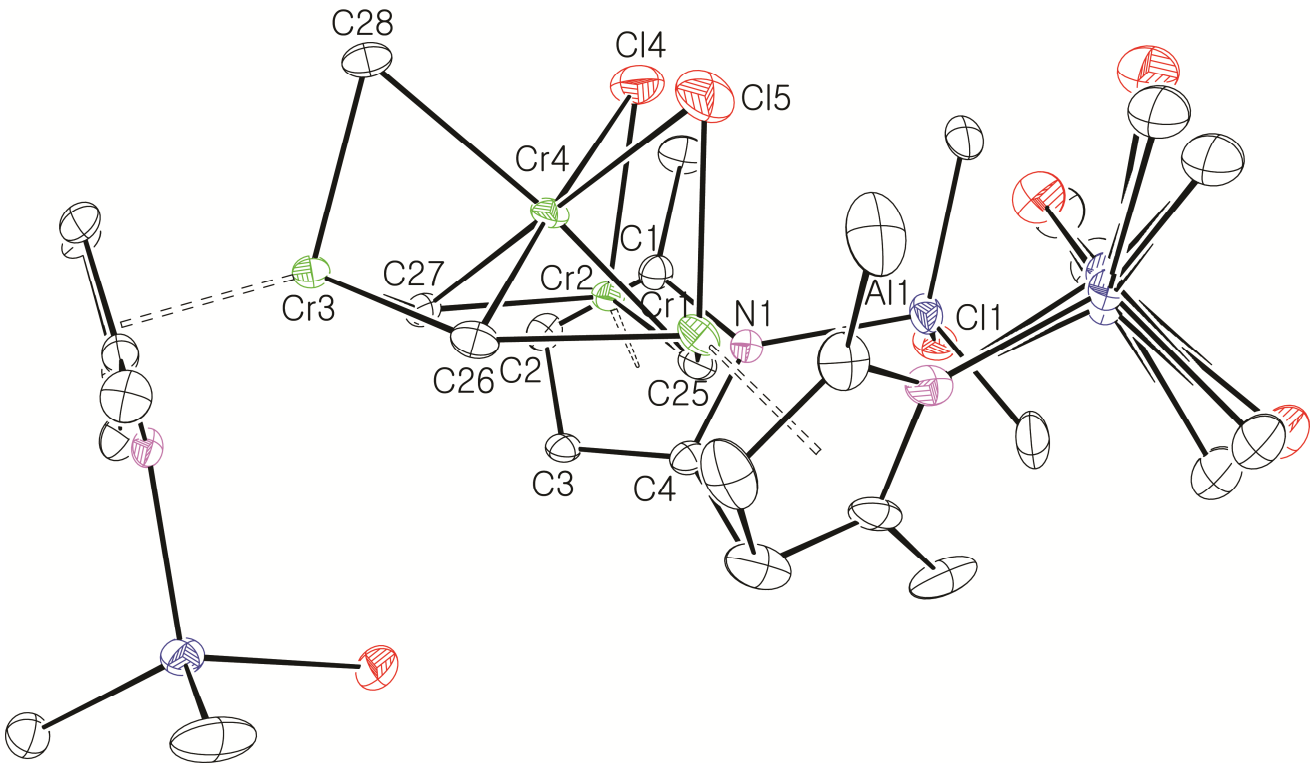
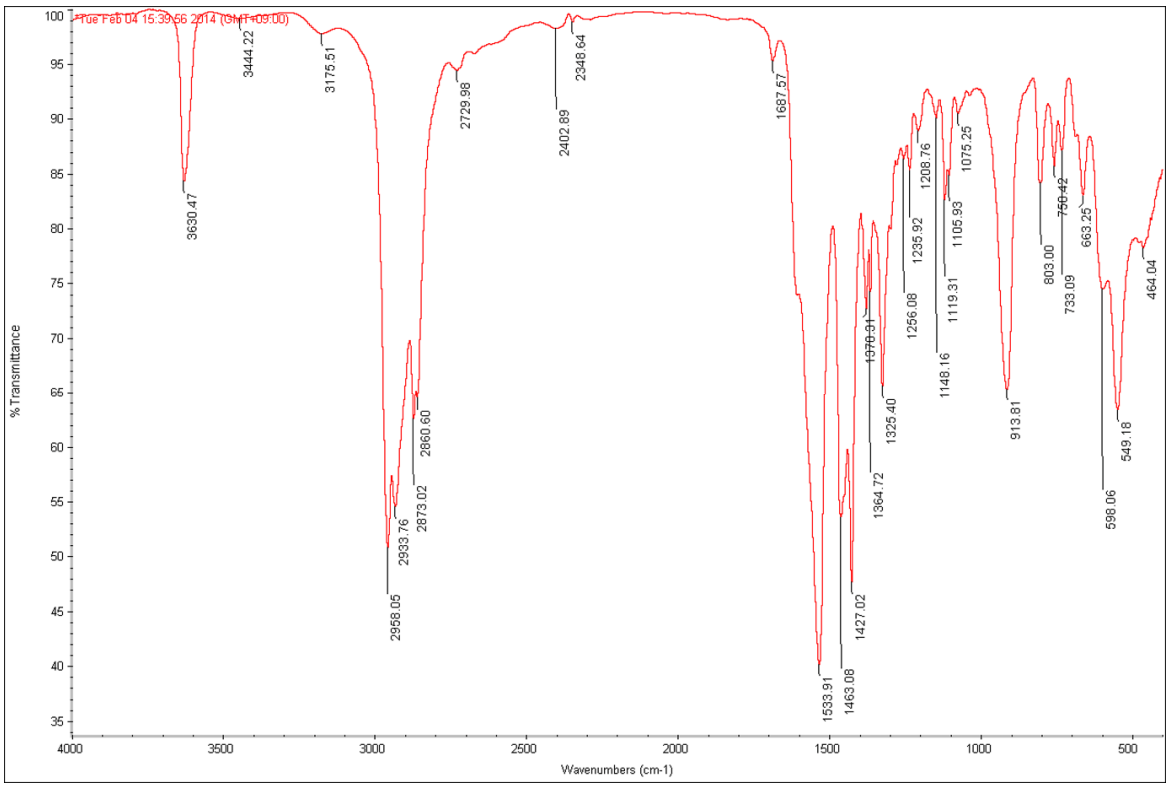


Fig. S1 Thermal ellipsoid plot (30% probability level) of the tetranuclear chromium complex. Cl(4) and Cl(5) atoms are half occupied. Selected bond distances (Å) and angles (°): Cr(1)-Cl(4), 2.240(4); Cr(1)-C(25), 2.089(7); Cr(1)-C(27), 2.065(8); Cr(1)-Cr(4), 2.4330(17); Cr(2)-Cl(5), 2.226(5); Cr(2)-C(25), 2.080(8); Cr(2)-C(26), 2.078(8); Cr(3)-C(28), 2.100(9); Cr(3)-C(26), 2.083(8); Cr(3)-C(27), 2.073(8); Cr(4)-C(25), 2.114(8); Cr(4)-C(26), 2.111(9); Cr(4)-C(27), 2.109(8); Cr(4)-C(28), 2.315(9); Cr(4)-Cl(4), 2.354(5); Cr(4)-Cl(5), 2.363(4); Cr(4)-Cr(2), 2.4386(16); Cr(4)-Cr(3), 2.3921(16); Cr(1)-N(1), 2.278(6); Cr(1)-C(1), 2.301(8); Cr(1)-C(2), 2.322(7); Cr(1)-C(3), 2.310(7); Cr(1)-C(4), 2.296(7); N(1)-Al(1), 1.996(6); C(25)-Cr(4)-C(28), 174.3(3); Cl(4)-Cr(4)-C(26), 176.9 (2); Cl(5)-Cr(4)-C(27), 179.6(3).

<FT-IR spectrum of $(EH)_2CrOH$>



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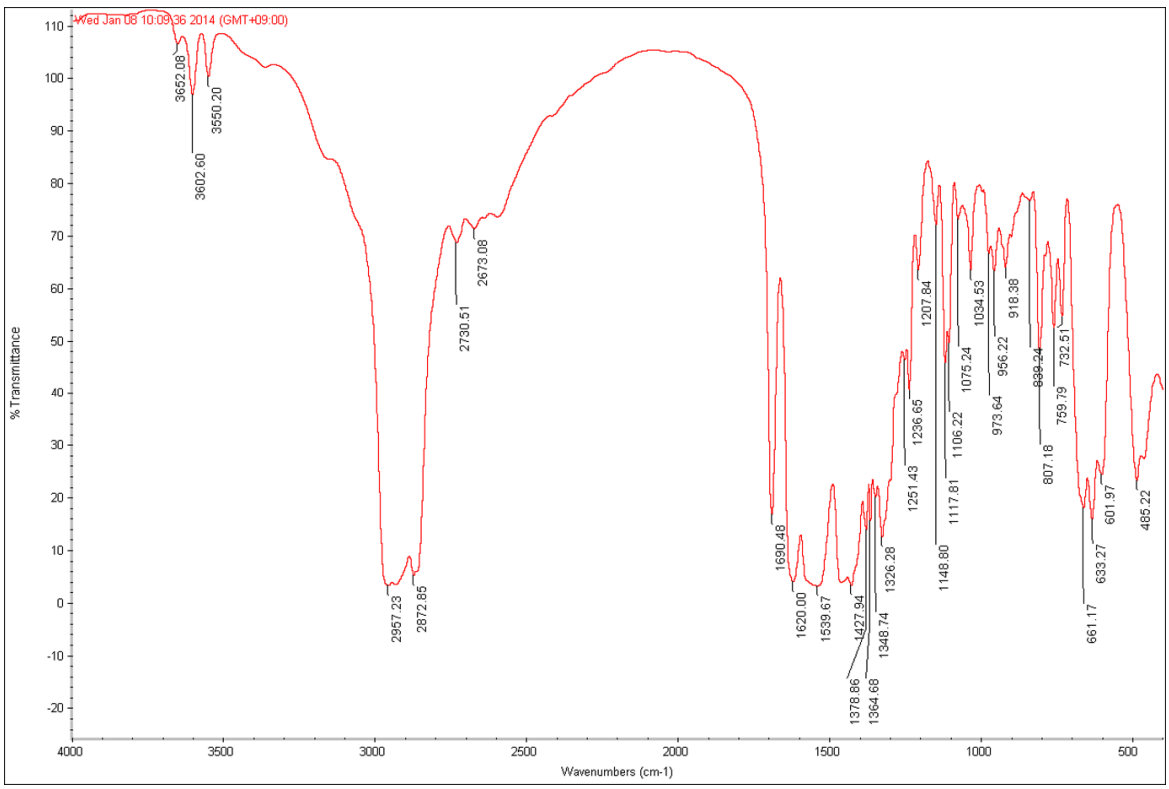

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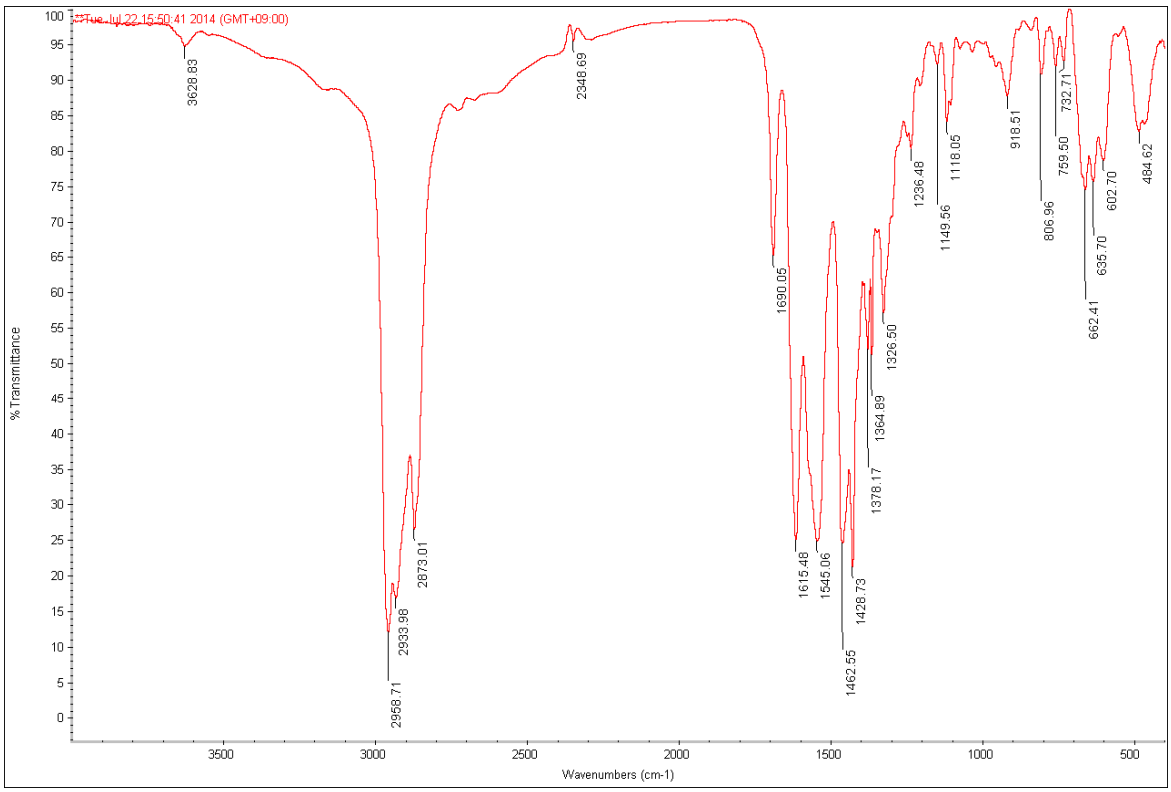
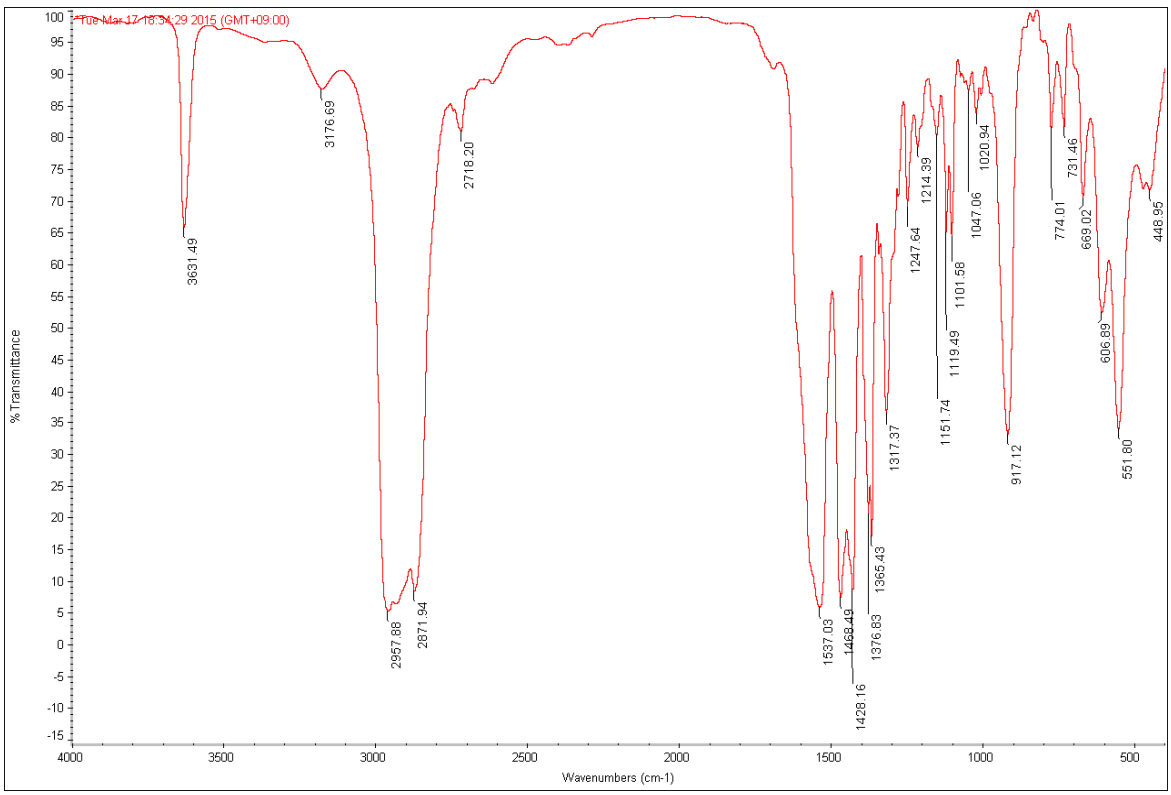
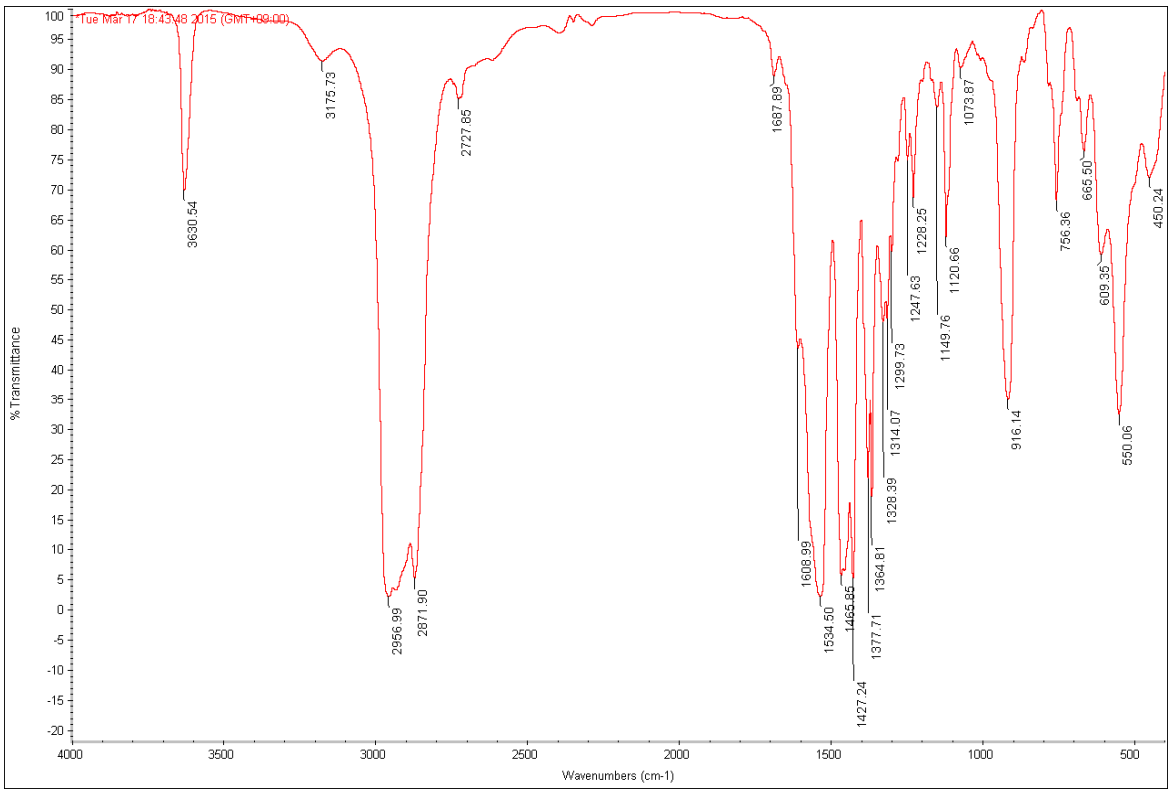


<FT-IR spectrum of **3**>



<FT-IR spectrum of **4**>



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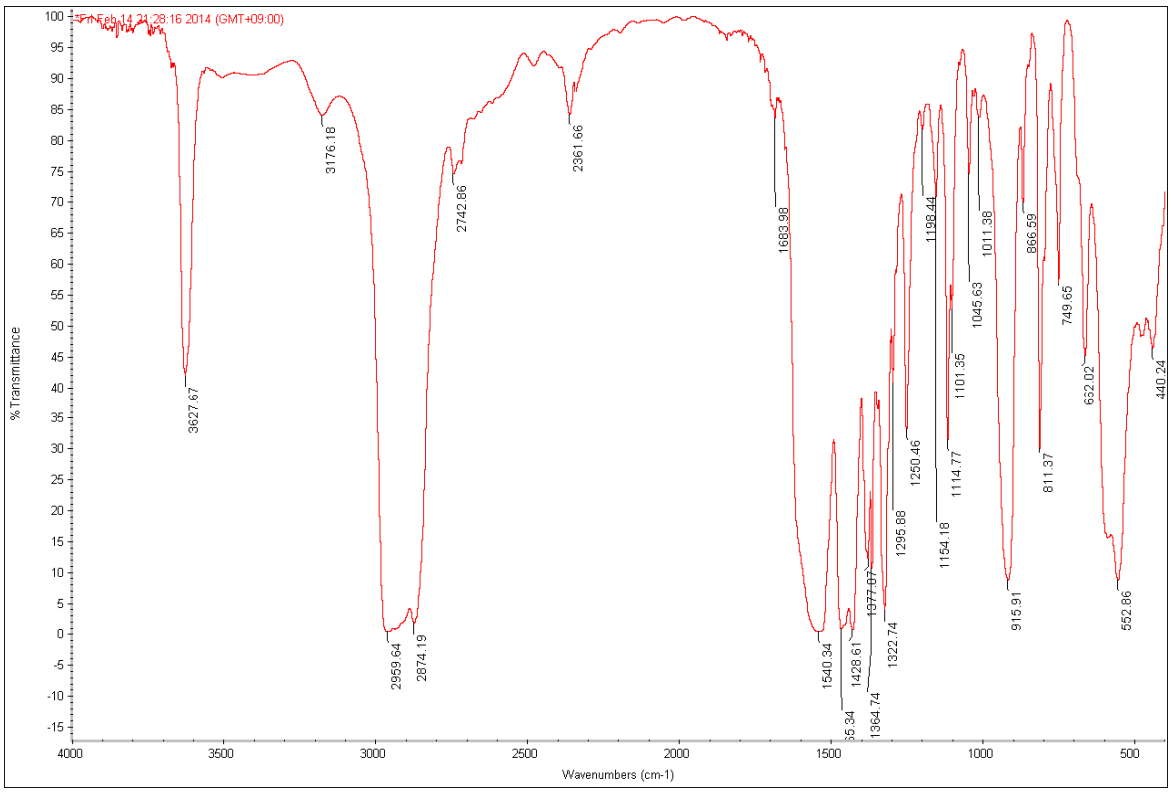

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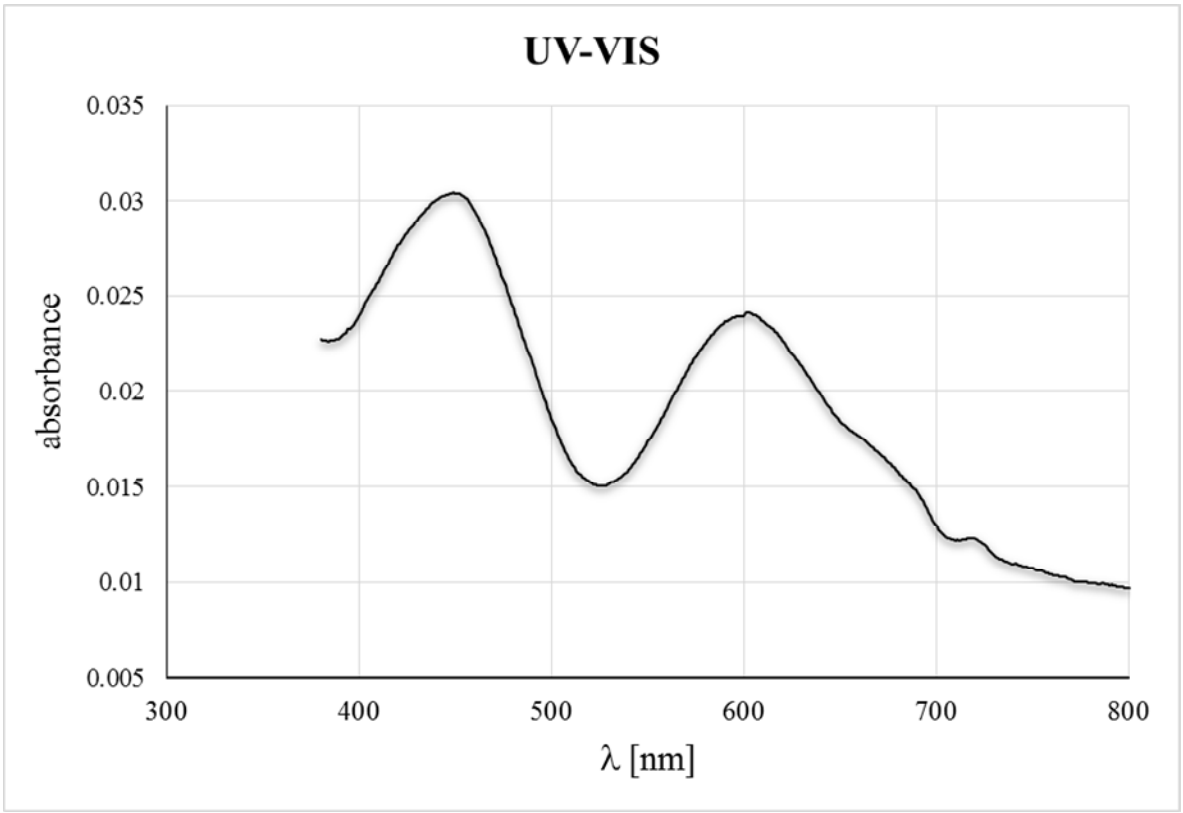

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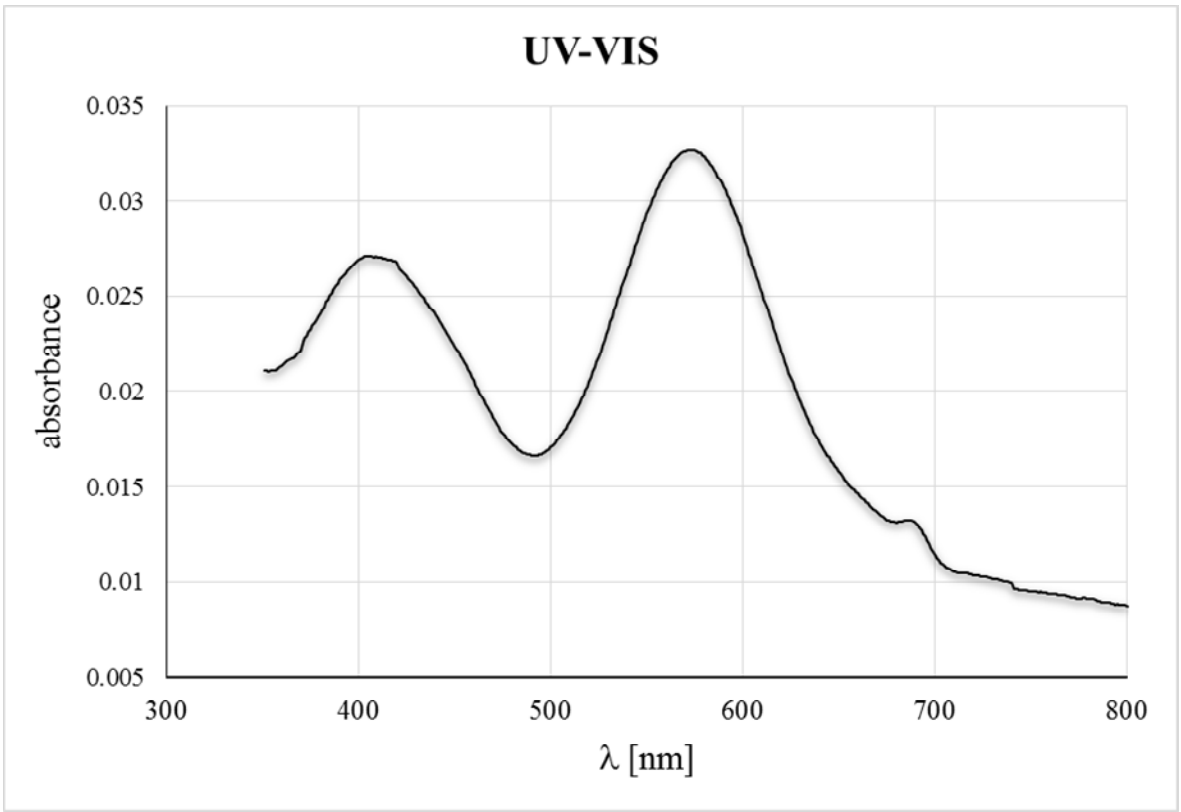

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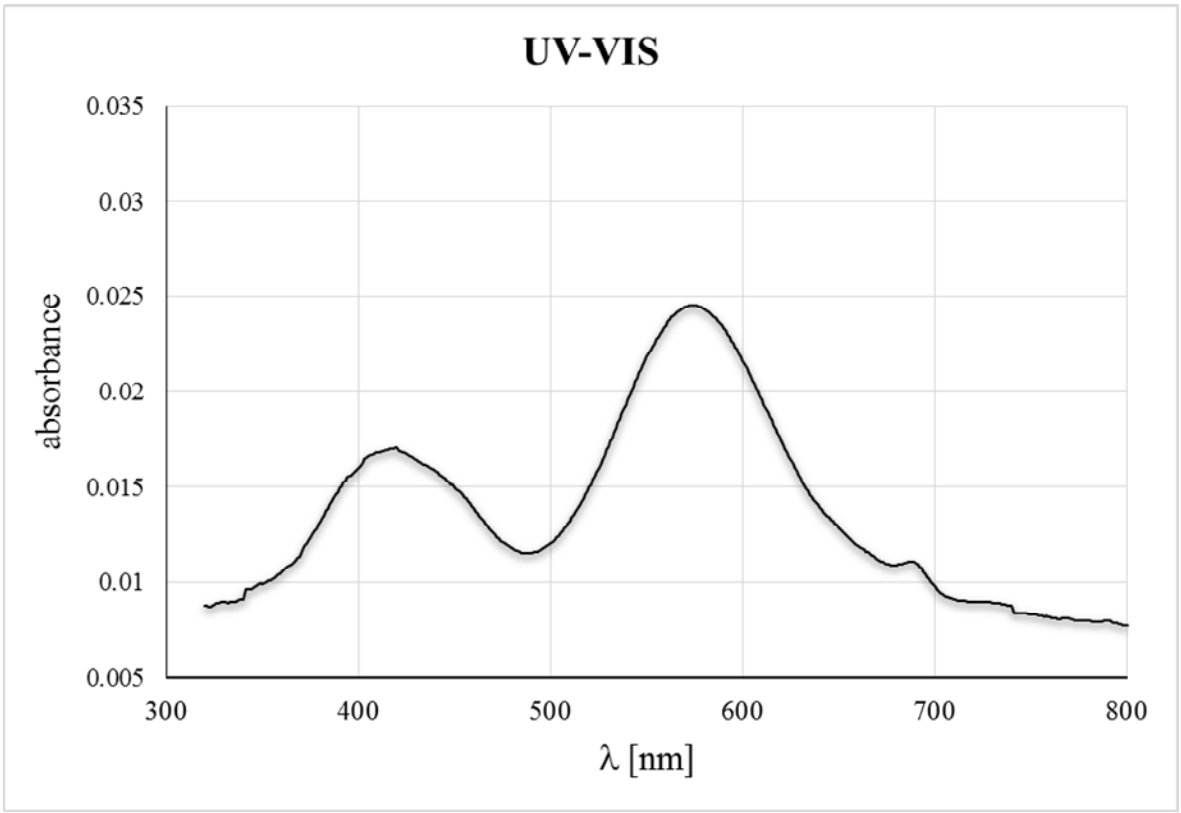

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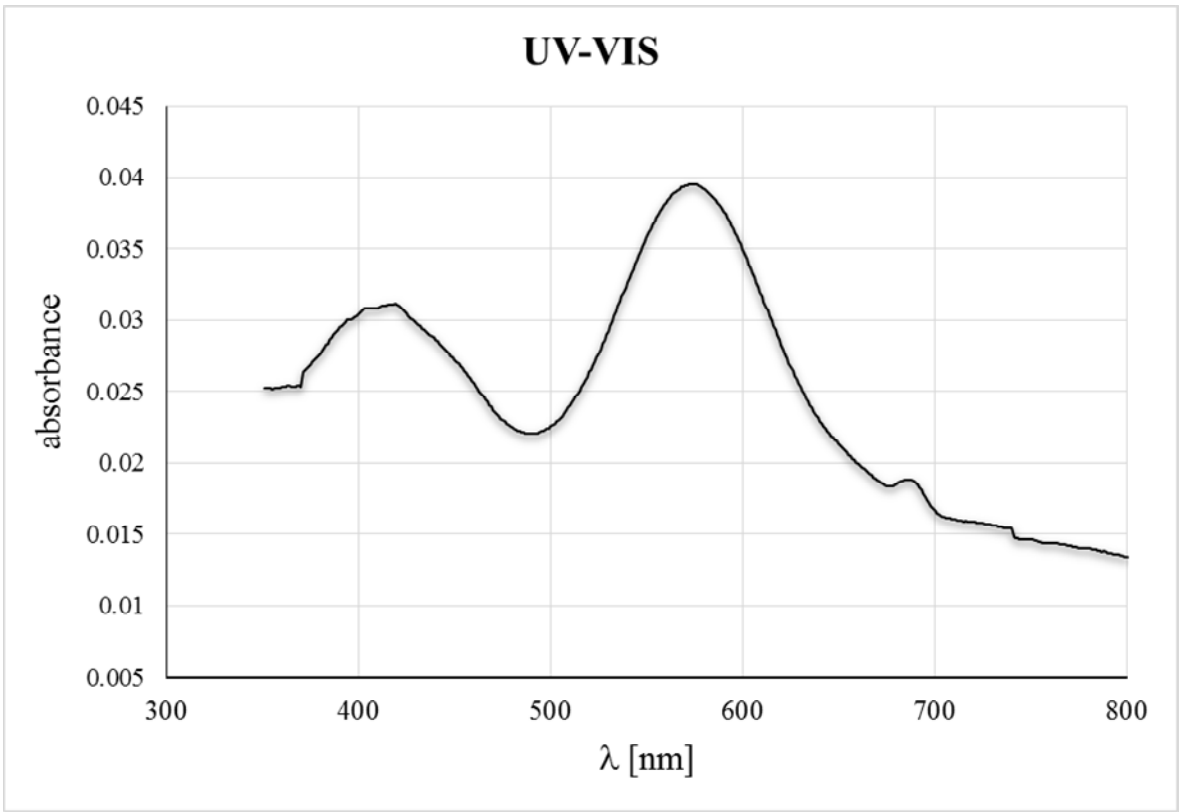

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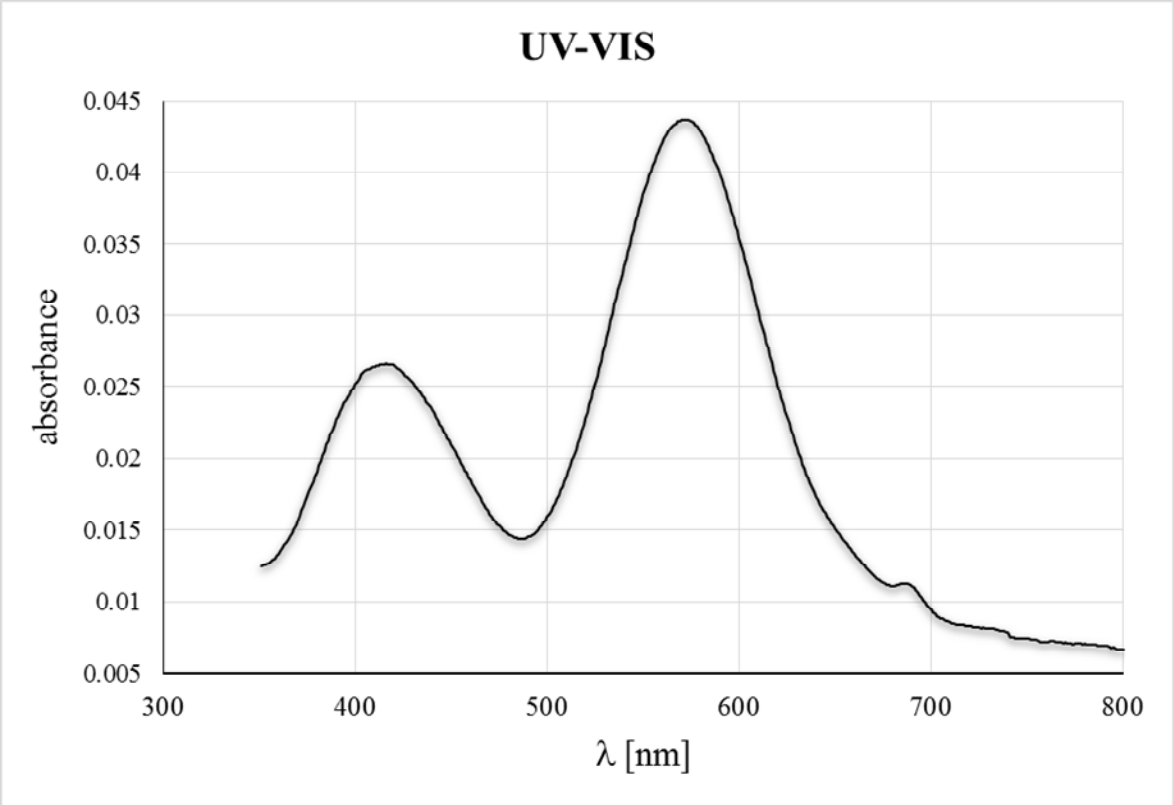
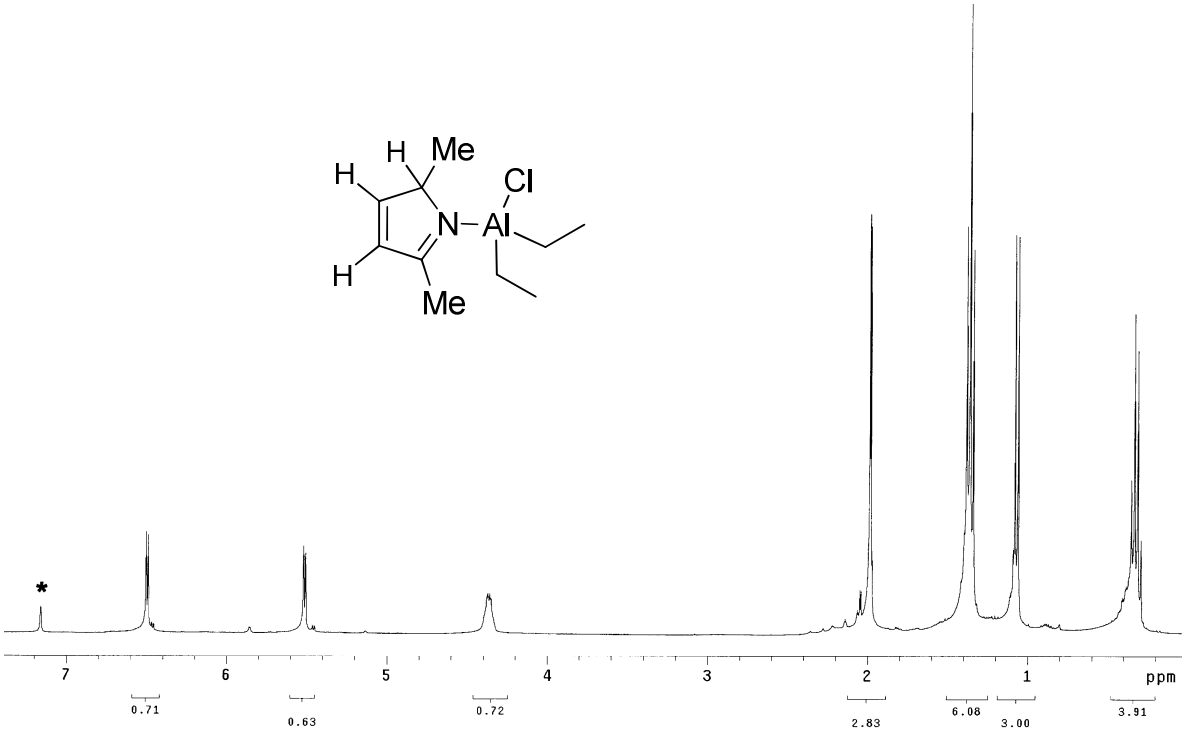
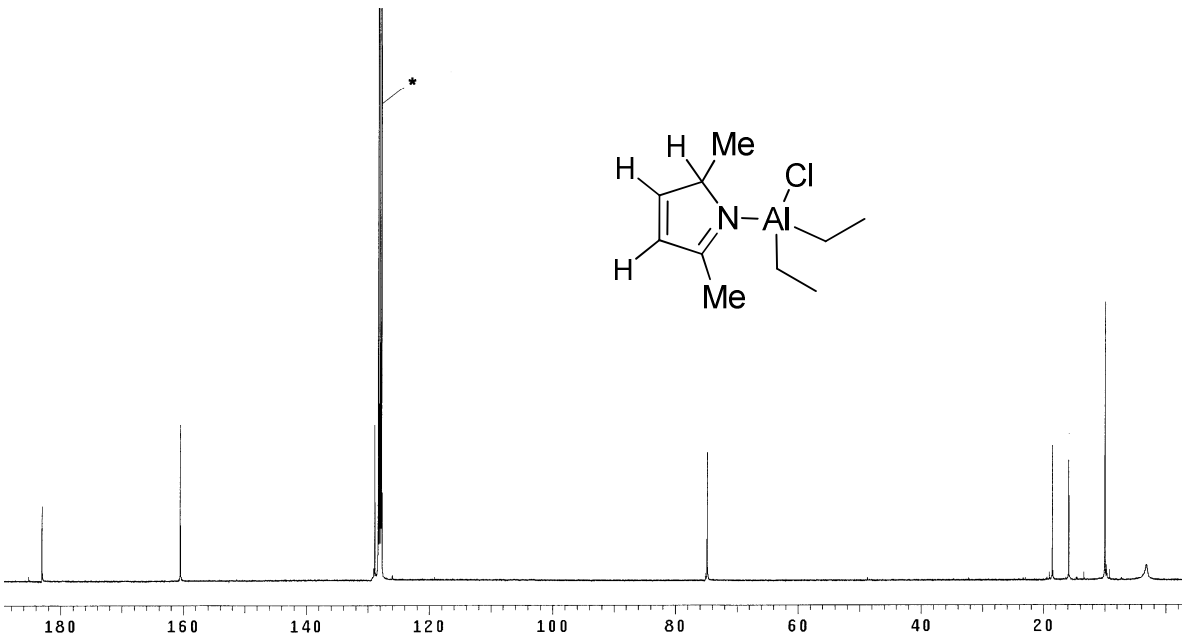


<[1]H NMR spectrum of the sample reacting $Me_2C_4H_2NH$ and Et_2AlCl in C_6D_6 for 4 h>

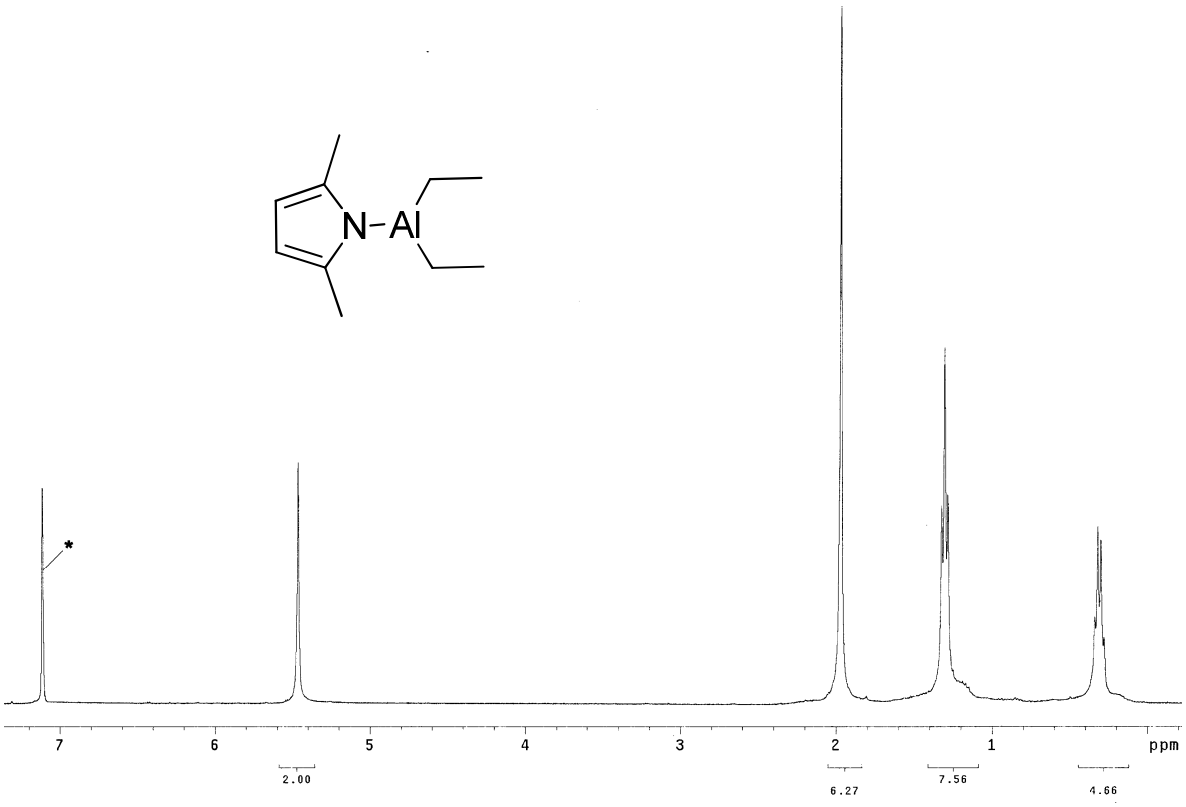


<[13]C NMR spectrum of the sample reacting $Me_2C_4H_2NH$ and Et_2AlCl in C_6D_6 for 4 h >

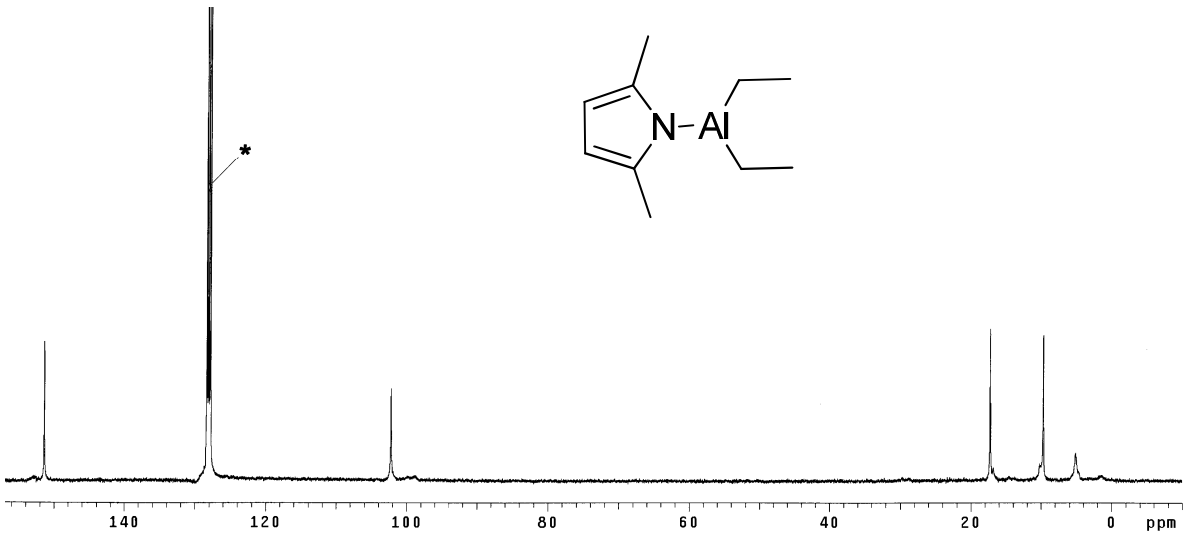


<[1]H NMR spectrum of $(Me_2C_4H_2N)AlEt_2$>

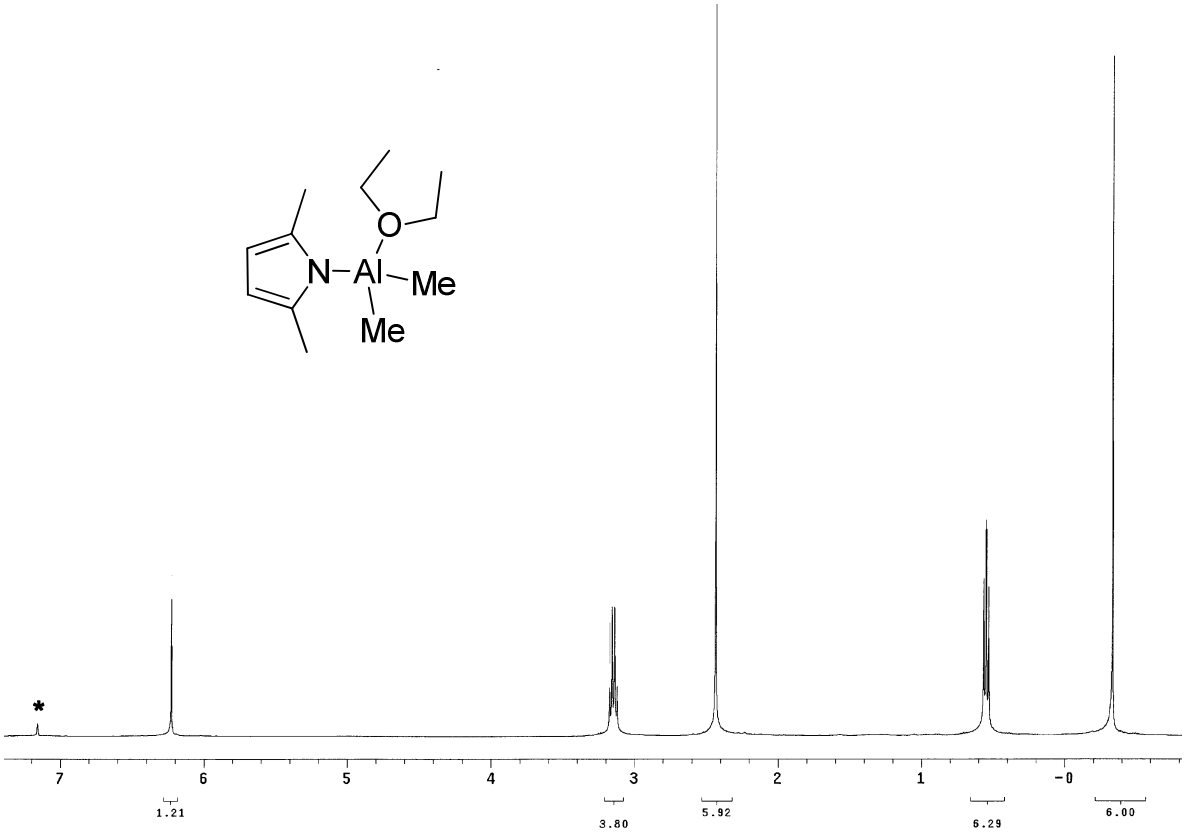
The signal marked with "*" is the C_6D_6 signal.



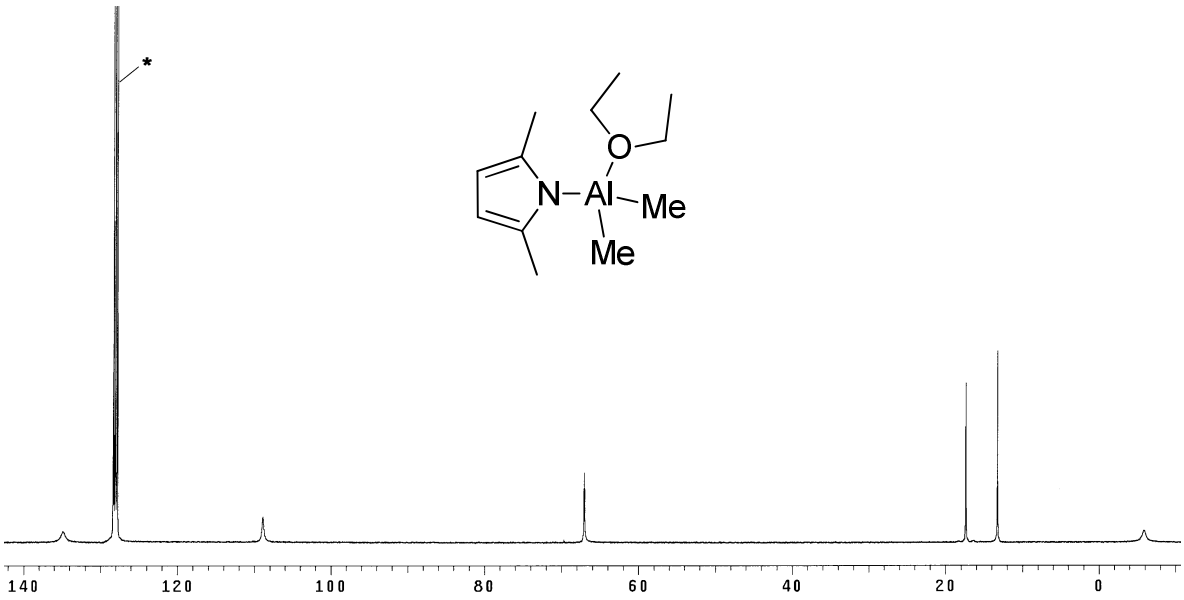
<[13]C NMR spectrum of $(Me_2C_4H_2N)AlEt_2$>



<[1]H NMR spectrum of $(Me_2C_4H_2N)AlMe_2 \cdot OEt_2$>

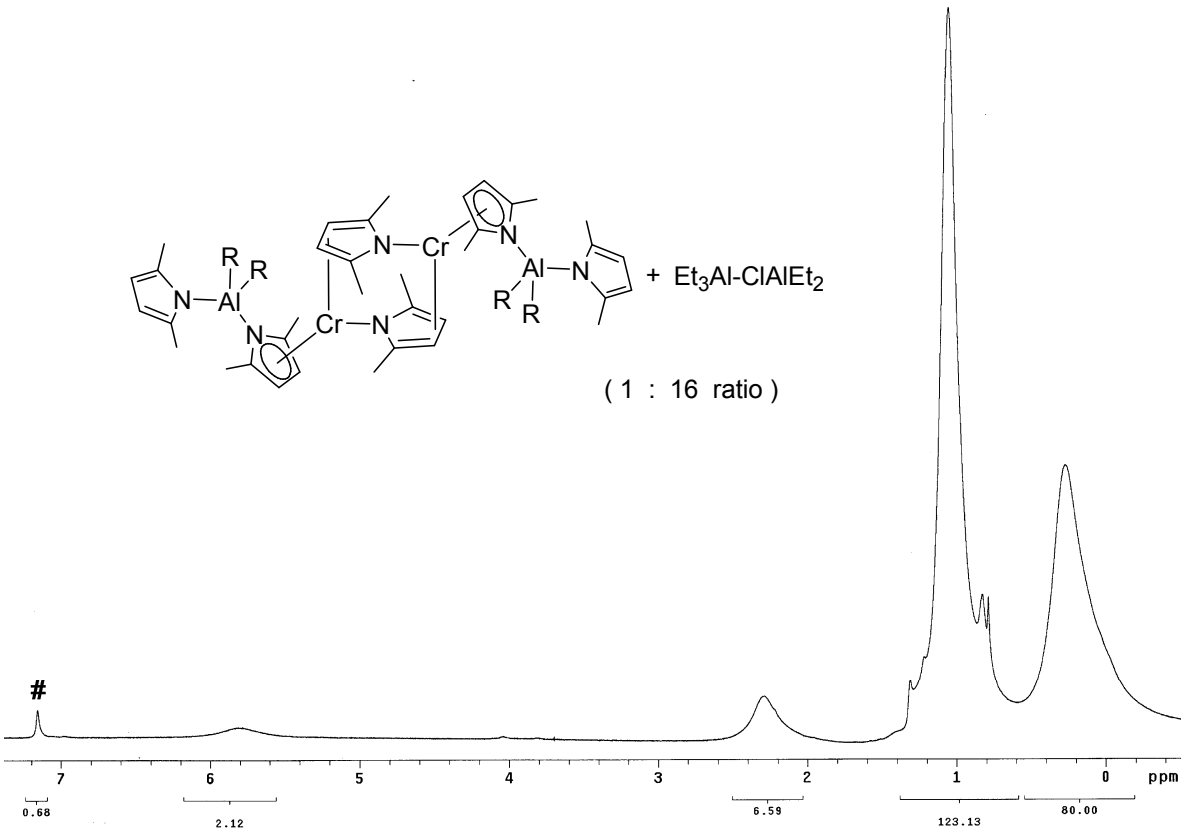


<[13]C NMR spectrum of $(Me_2C_4H_2N)AlMe_2 \cdot OEt_2$>



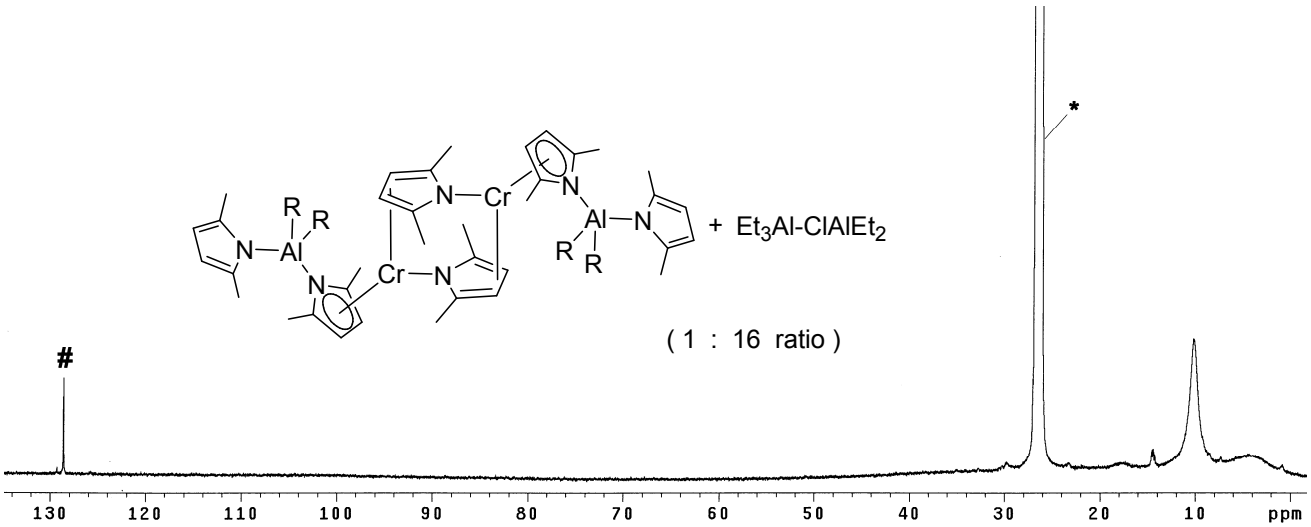
<[1]H NMR spectrum of the sample reacting **4** with 16 equiv $Et_3Al{\cdot}ClAlEt_2$ in C_6D_{12}>

The signals marked with "#" are residual solvent (C_6H_6) signals.



<[13]C NMR spectrum of the sample reacting **4** with 16 equiv $Et_3Al{\cdot}ClAlEt_2$ in C_6D_{12}>

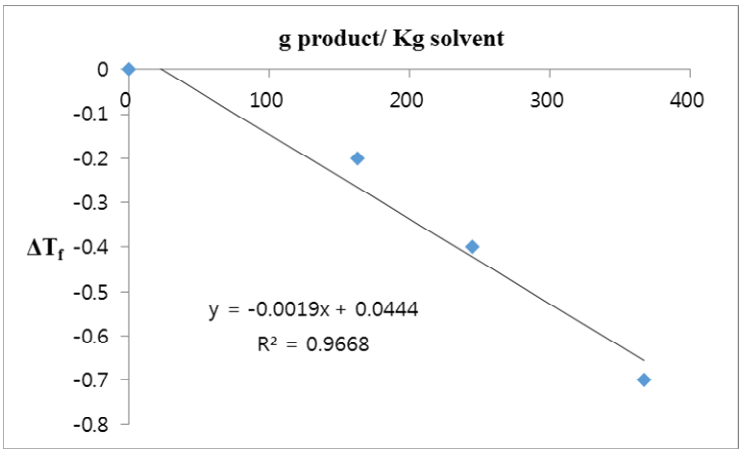
The signals marked with "*" and "#" are the C_6D_{12} and residual solvent (C_6H_6) signals, respectively.



<Cryoscopy measurement of the molecular weight of $Cr(EH)_3$ (Strem) in benzene>

$\Delta T_f = K_f \cdot m \cdot i$ (K_f = cryoscopic constant, m = molality, i = van 't Hoff factor)

$= (K_f/MW) \cdot$ (g-product/Kg-solvent) (K_f = 4.9 K·Kg /mol, MW = molecular weight)



=> MW: 2580

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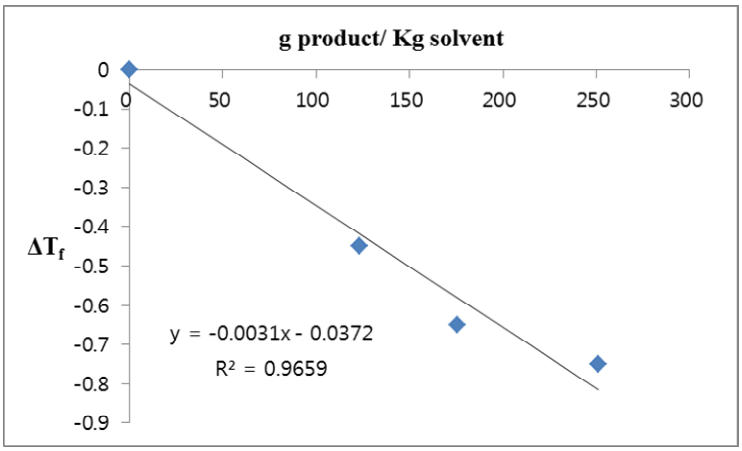

=> MW: 1580

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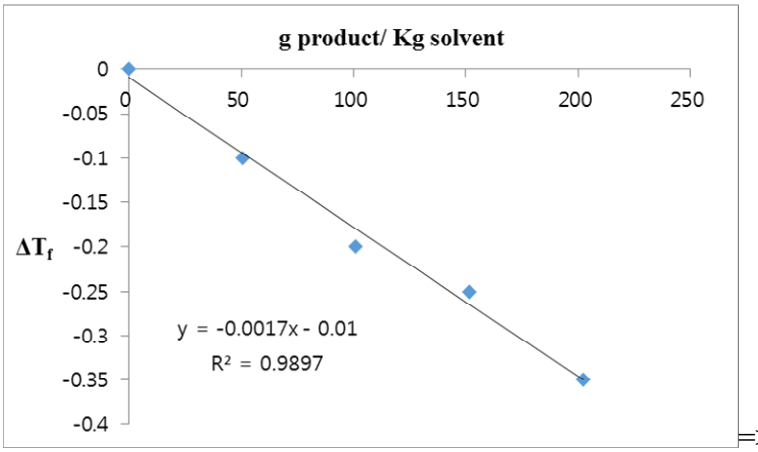

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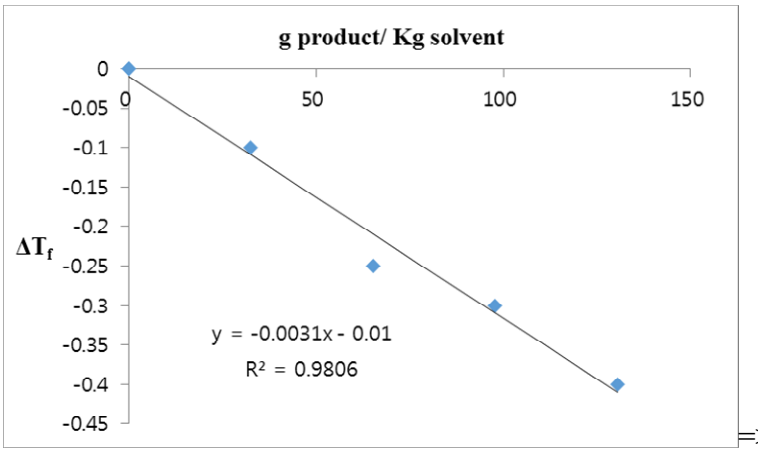
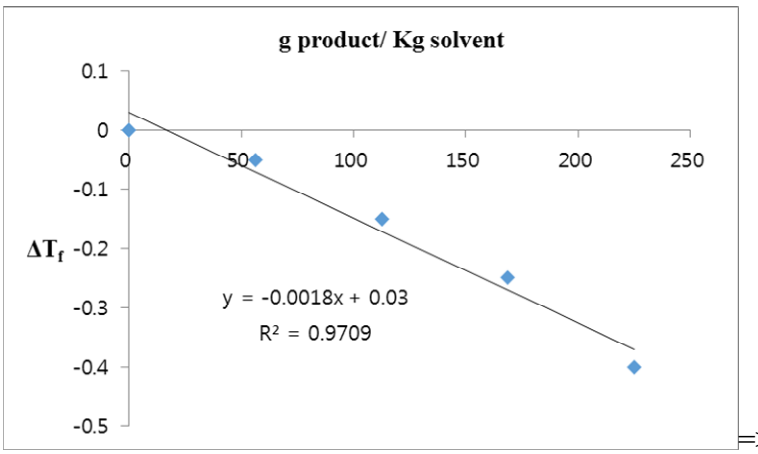


=> MW: 1580

<Cryoscopy measurement of the molecular weight of **5** in benzene>



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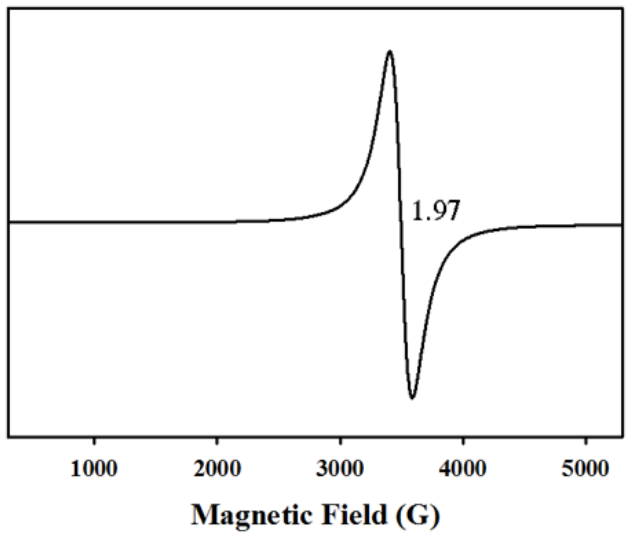
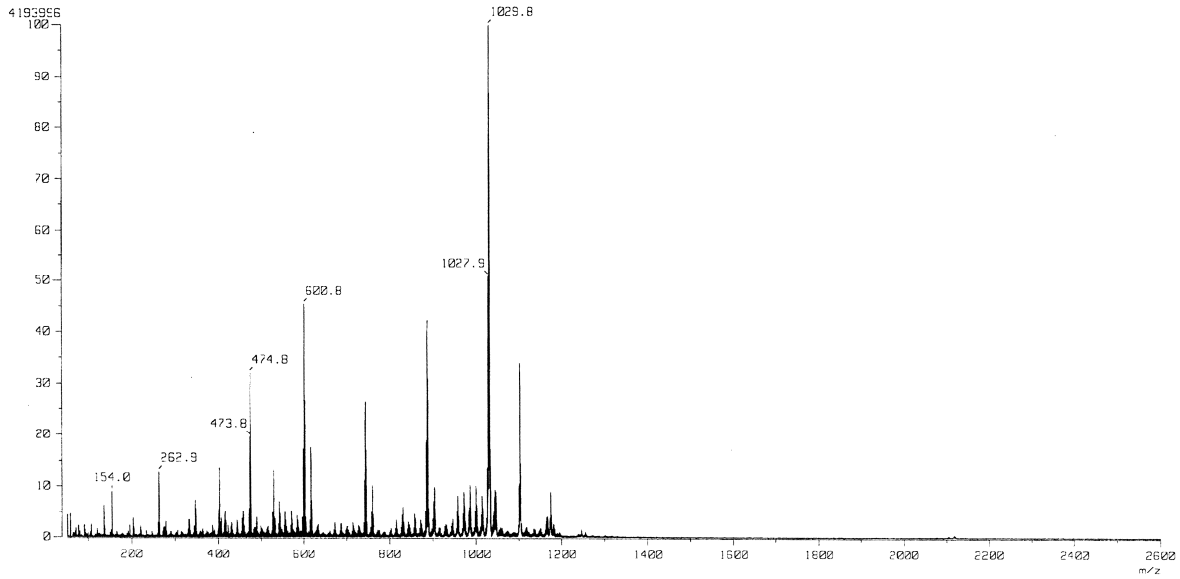
<X-band EPR spectrum of $(EH)_2CrOH$>



<Mass spectrum of $(EH)_2CrOH$>

Ion Mode: FAB+



Ion Mode: EI+