XLVIII. Crystal data for bis-chelated [$(LiBF_4)(DME)_2$] complex **24.**

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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
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 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
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 The BF4 group is disorderd: it rotates along Li-F1-B line.
 The crystal melting piont is below room temperature.
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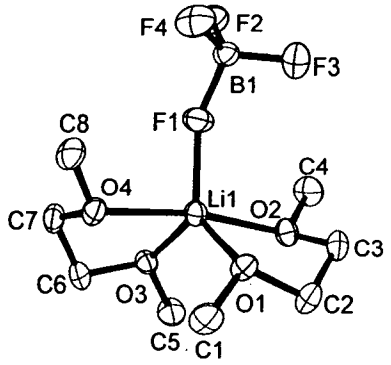


$LiBF_4(DME)_2$; **24**

XLIX. Preparation of Ligands **K, N, O, Q, R, BB,** and **LL.**

N,N-Dimethyl-2-(1-methoxy-2-methyl)propylamine (**K**). Amino ether **K** was prepared from commercially available 2-amino-2-methyl-1-propanol in two steps:

Step A. 2-Amino-2-methyl-1-propanol (25 mL, 0.26 mol) was cooled to 0 °C in a 2-L round-bottom flask containing a stir bar. Following dropwise addition of 88% aqueous formic acid (47 mL, 0.91 mol), 37% aqueous formaldehyde (56 mL, 0.69 mol) was added. Controlled heating to 60 °C initiated rapid gas evolution. The reaction was allowed to proceed without further heating until gas evolution decreased and was then heated to 80 °C for 24 h. The reaction mixture was cooled, acidified with 20% aqueous HCl, and extracted three times with 100-mL portions of ether. The aqueous layer was stirred in a salt/ice bath and brought to pH 12 by dropwise addition of 40% aqueous NaOH without allowing the internal temperature to exceed 25 °C. Following separation of the resulting amine/aqueous layers, the aqueous layer was further extracted three times with 100-mL portions of ether. The combined organic layers were dried over Na_2SO_4 and the solvent evaporated under reduced pressure. The resulting crude was subjected to fractional distillation under full vacuum to afford 2-dimethylamino-2-methyl-1-propanol (14 g, 46% yield).

Step B. After drying over molecular sieves (4 Å), the amino alcohol (10 g, 0.084 mol) was dissolved in THF (25 mL) and added dropwise over a slurry of NaH (5 g, 0.21 mol) in THF (100 mL) cooled to 0 °C. The mixture was further stirred at room temperature for 4 h. Dimethyl sulfate (4.4 mL, 5.8 g, 0.046 mol) in THF (15 mL) was added via syringe pump over 24 h. The excess of NaH was quenched with methanol, and most of the solvents evaporated under reduced pressure. 25 mL of water were added, and the aqueous solution extracted with diethyl ether (4 x 25 mL). The separated organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The obtained crude was distilled to yield *N,N*-dimethyl-2 (1-methoxy-2-methyl)propylamine, b.p. 134-135 °C, >95% pure by GC. Further purification was achieved by crystallization of its hydrochloride from a mixture of 2-propanol-THF (ratio 1:9), drying the HCl salt

under full vacuum at 60 °C for 2 h, and liberating the free base by vacuum transfer from KOH (3.8 g, 35% yield). ^{1}H NMR ($CDCl_3$, ppm) δ 3.35 (3H, s), 3.23 (2H, s), 2.26 (6H, s), 1.02 (6H, s). ^{13}C NMR ($CDCl_3$, ppm) δ 79.1, 59.1, 56.3, 38.6, 38.6, 20.0, 20.0.

N,N-Dimethyl-1-methoxy-2-butylamine (**N**) was prepared by the same procedure as amino ether **K** from commercially available 2-amino-1-butanol. Ligand **N** was liberated by vacuum transfer from KOH (17% yield): b.p. 139-140 °C. ^{1}H NMR ($CDCl_3$, ppm) δ 3.45 (1H, dd, J = 9.6, 6.8 Hz), 3.34 (3H, s), 3.32 (1H, dd, J = 9.6, 4.4 Hz), 2.50-2.45 (1H, m), 2.31 (6H, s), 1.58-1.48 (1H, m), 1.38-1.27 (1H, m), 0.93 (3H, t, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$, ppm) δ 71.9, 64.9, 58.6, 41.0, 41.0, 19.7, 11.4.

N,N-Dimethyl-2-(1-methoxy-3-methyl)butylamine (**O**) was prepared by the same procedure as amino ether **K** from commercially available 2-amino-3-methyl-1-butanol. Ligand **O** was liberated by vacuum transfer from KOH (22% yield): b.p. 155-156 °C. ^{1}H NMR ($CDCl_3$, ppm) δ 3.50-3.40 (2H, m), 3.31 (3H, s), 2.32 (6H, s), 2.17-2.13 (1H, m), 1.91-1.80 (1H, m), 0.97 (3H, d, J = 6.6 Hz), 0.91 (3H, d, J = 6.6 Hz). ^{13}C NMR ($CDCl_3$, ppm) δ 70.1, 69.2, 58.4, 41.9, 41.9, 27.5, 21.0, 19.3.

N,N-Dimethyl-2-methoxybutylamine (**Q**) was prepared from commercially available 2-methoxybutylamine with use of the Eschweiler-Clark methylation followed in step A for the preparation of amino ether **K**. Ligand **Q** was liberated by vacuum transfer from KOH (35% yield): b.p. 133-134 °C. ^{1}H NMR ($CDCl_3$, ppm) δ 3.37 (3H, s), 3.28-3.20 (1H, m), 2.41 (1H, dd, J = 13.1, 7.0 Hz), 2.26 (6H, s), 2.22 (1H, dd, J = 13.1, 4.4 Hz), 1.64-1.46 (2H, m), 0.91 (3H, t, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$) δ 79.8, 62.7, 56.5, 46.1, 46.1, 24.5, 9.0.

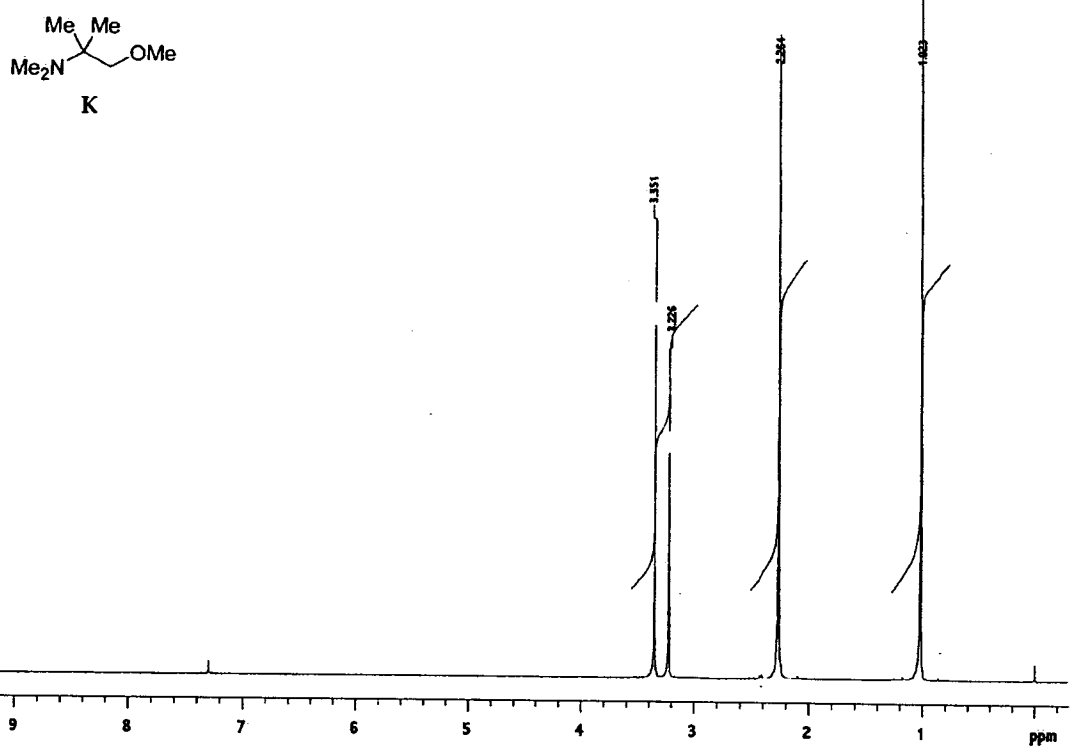
N,N-Dimethyl-1-methoxy-3-methylbutylamine (**R**). To a solution of 2-methoxy-3-methylbutanoic acid[ref2] (5.0 g, 37.9 mmol) in CH_2Cl_2 (100 mL) cooled to 0 °C were added catalytic DMAP (0.1 mL) and oxalyl chloride (3.6 mL, 38.0 mmol). The resulting solution was stirred for 2 h at room temperature. Then the reaction was cooled to 0 °C and a solution of Me_2NH (2.0 M) in THF (22.5 mL, 45.0 mmol), and triethylamine (18.8 mL, 135.0 mmol) were added. The reaction

was warmed to room temperature and stirred for 2 h. The reaction mixture was washed with NH_4Cl and $NaHCO_3$ and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was dissolved in diethyl ether (25 mL). To the resulting solution cooled to 0 °C, was added $LiAlH_4$ (1.1 g, 28.5 mmol) and the mixture was stirred for 3 h at room temperature. The reaction was cooled to 0 °C, quenched with water, stirred for 15 min, and filtered through a plug of Celite. The crude product was purified by flash chromatography (silica gel, diethyl ether) to yield 2.5 g (42% yield) of a yellow oil. ^{1}H NMR ($CDCl_3$, ppm) δ 3.33 (3H, s), 3.05 (1H, m), 2.12-2.38 (2H, m), 2.21 (6H, s), 1.89 (1H, m), 0.85 (6H, d, J = 6.9 Hz). ^{13}C NMR ($CDCl_3$, ppm) δ 83.6, 60.2, 57.5, 46.1, 29.2, 17.6, 17.5.

N,N-Dimethyl-(1-methoxycyclohexyl)methylamine (**BB**) was prepared from (1-methoxycyclohexyl)methylamine[ref3] with use of the Eschweiler-Clark methylation followed in step A for the preparation of aminoether **K**. Ligand **BB** was liberated by vacuum transfer from KOH (35% yield): b.p. 69-70 °C/35 mm. ^{1}H NMR ($CDCl_3$, ppm) δ 3.04 (3H, s), 2.17 (6H, s), 2.13 (2H, s), 1.64-1.56 (2H, m), 1.46-1.08 (8H, m). ^{13}C NMR ($CDCl_3$, ppm) δ 75.8, 62.6, 47.8, 47.6, 32.4, 32.4, 25.7, 21.6, 21.6.

N,N-Bis(2-methoxyethyl)methylamine (**LL**) was prepared from commercially available *N,N*-bis(2-methoxyethyl)amine with use of the Eschweiler-Clark methylation followed in step A for the preparation of amino ether **K**. Ligand **LL** was liberated by vacuum transfer from KOH (40% yield): b.p. 120-122 °C/35 mm. ^{1}H NMR ($CDCl_3$, ppm) δ 3.50 (4H, t, J = 6.0 Hz), 3.35 (6H, s), 2.64 (4H, t, J = 6.0 Hz), 2.33 (3H, s). ^{13}C NMR ($CDCl_3$, ppm) δ 70.5, 58.7, 57.0, 43.0.

L. ^{1}H and ^{13}C NMR spectra for ligands **K, N, O, Q, R, BB** , and **LL**.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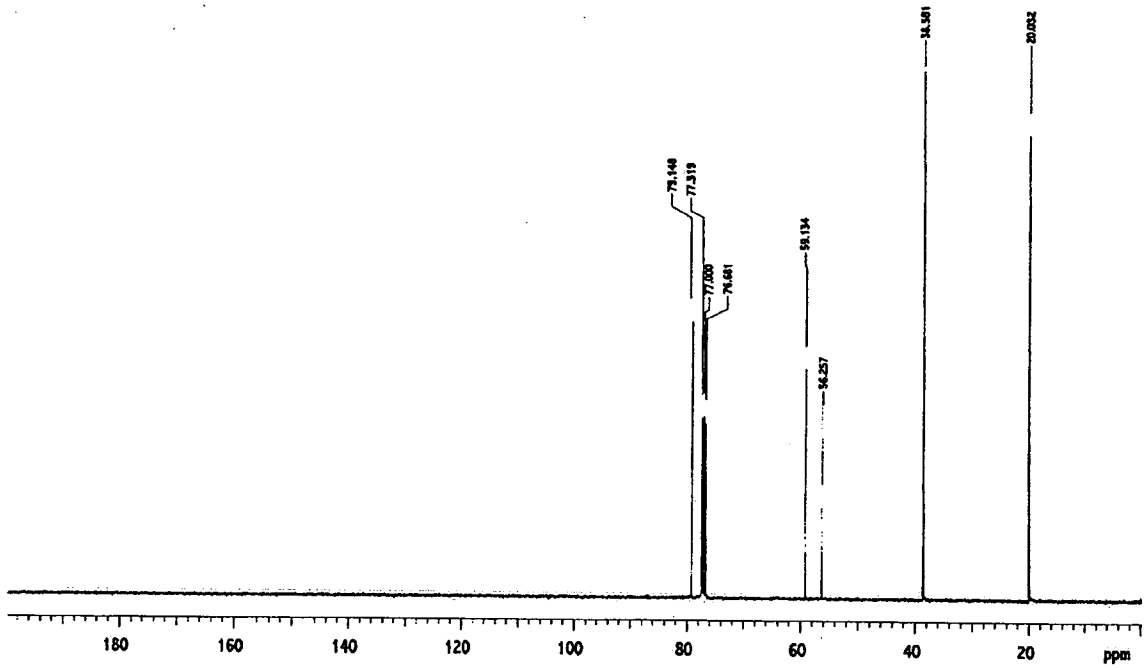
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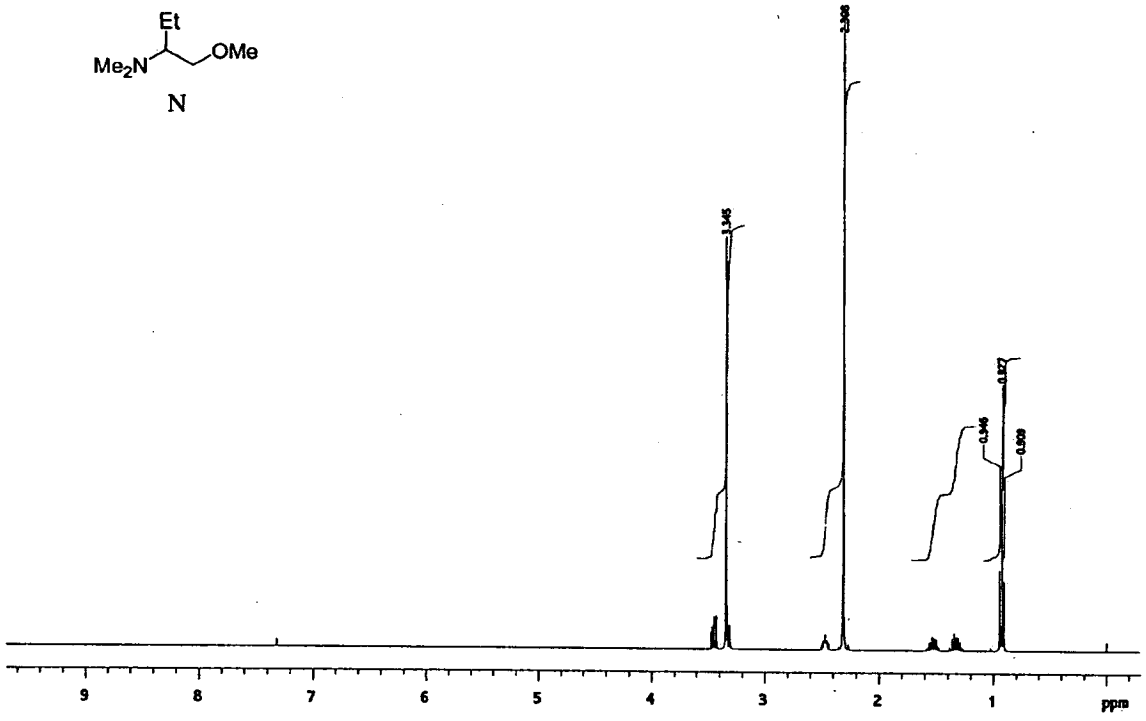

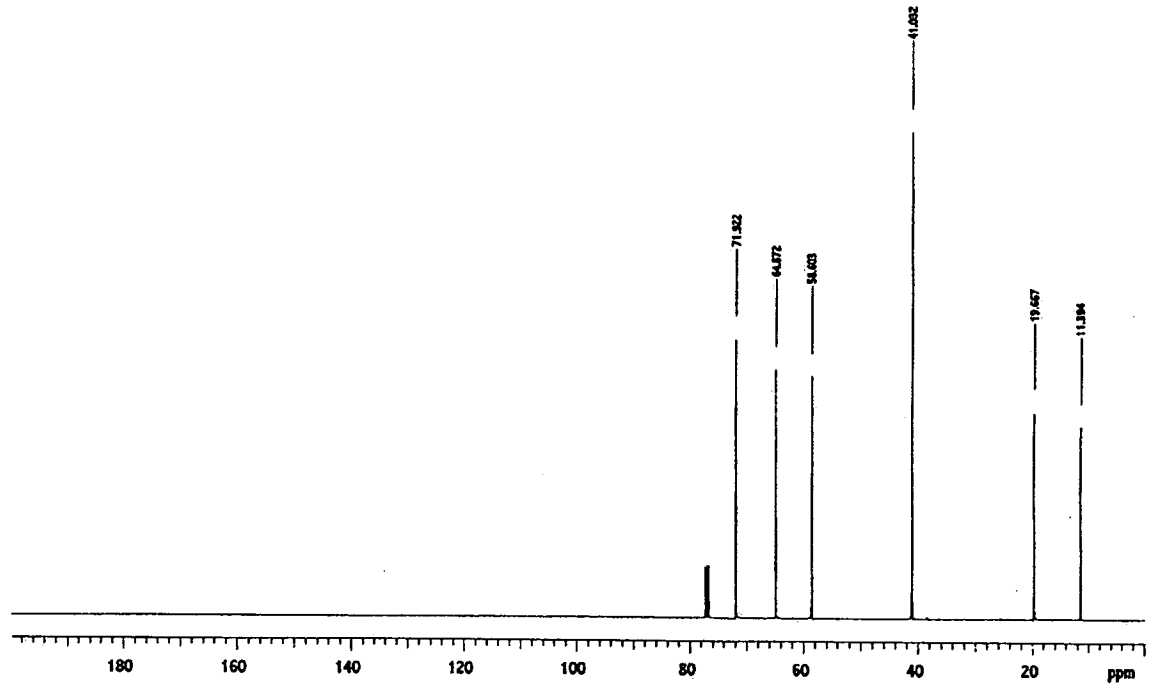

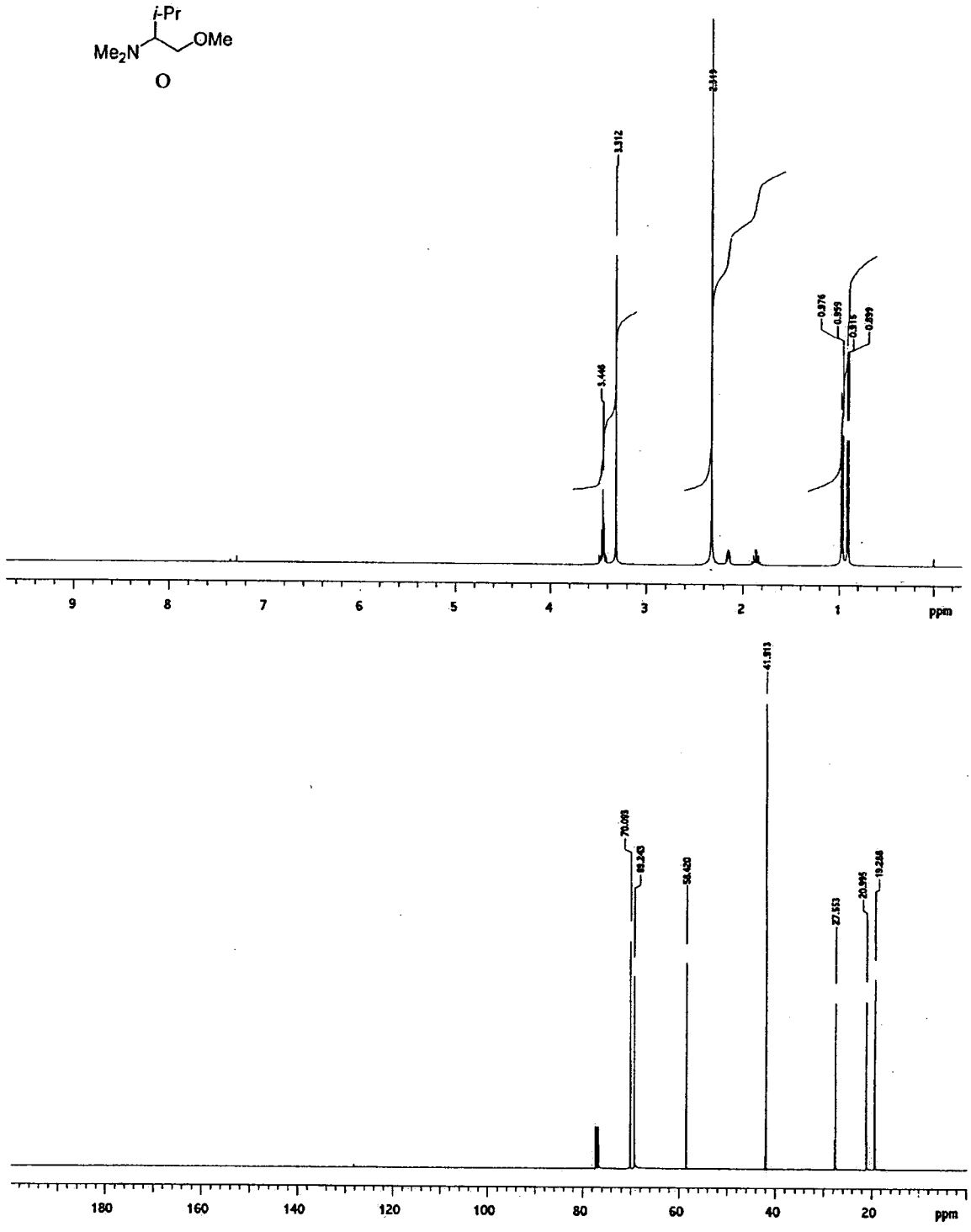

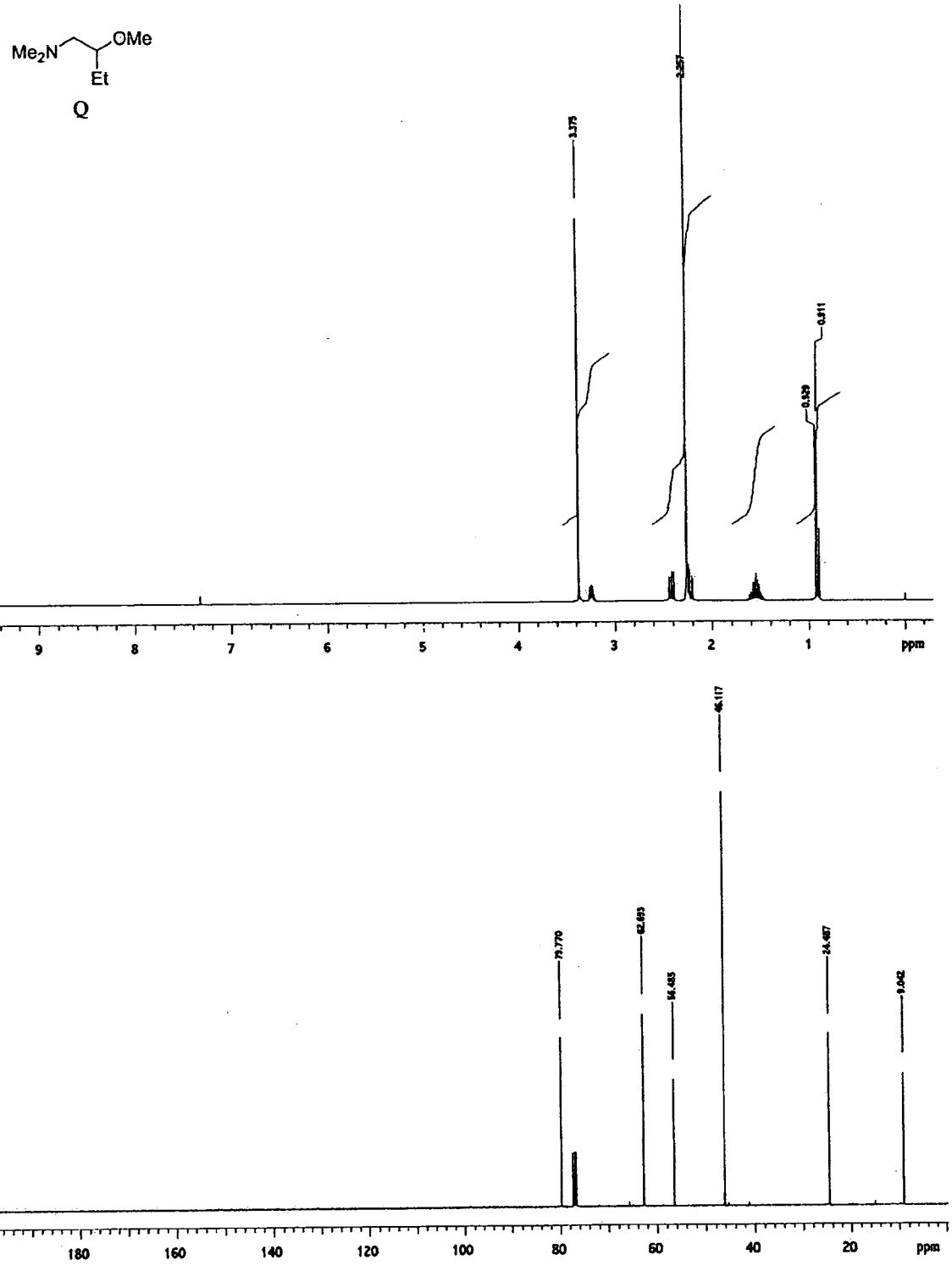
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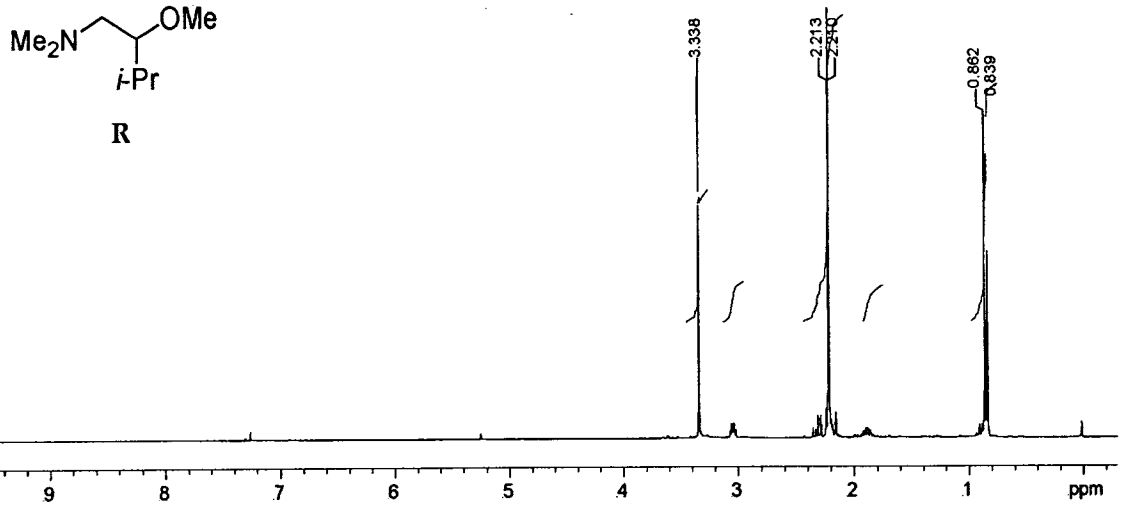
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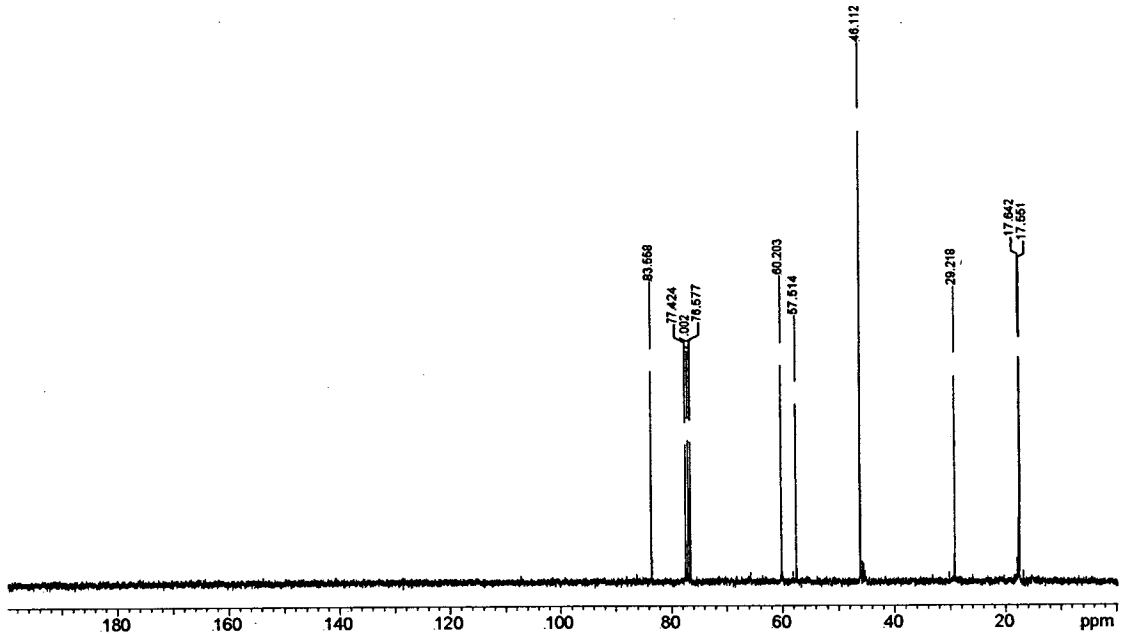
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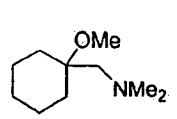
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NMe2

BB

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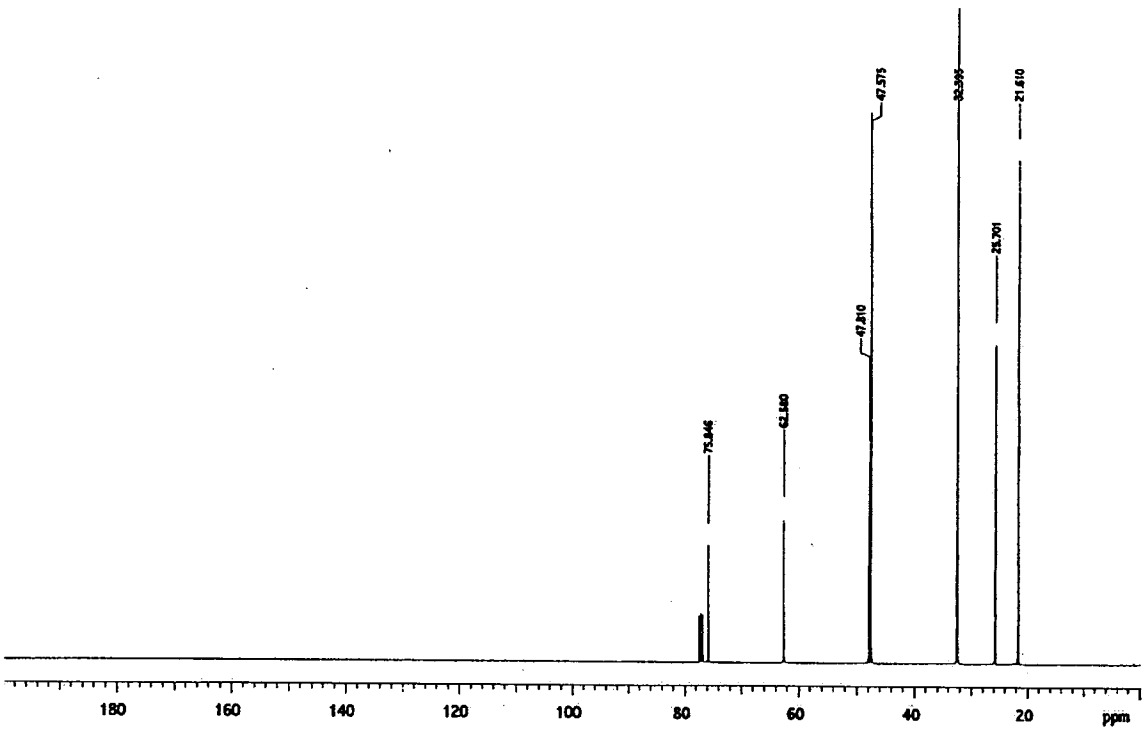
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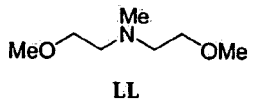
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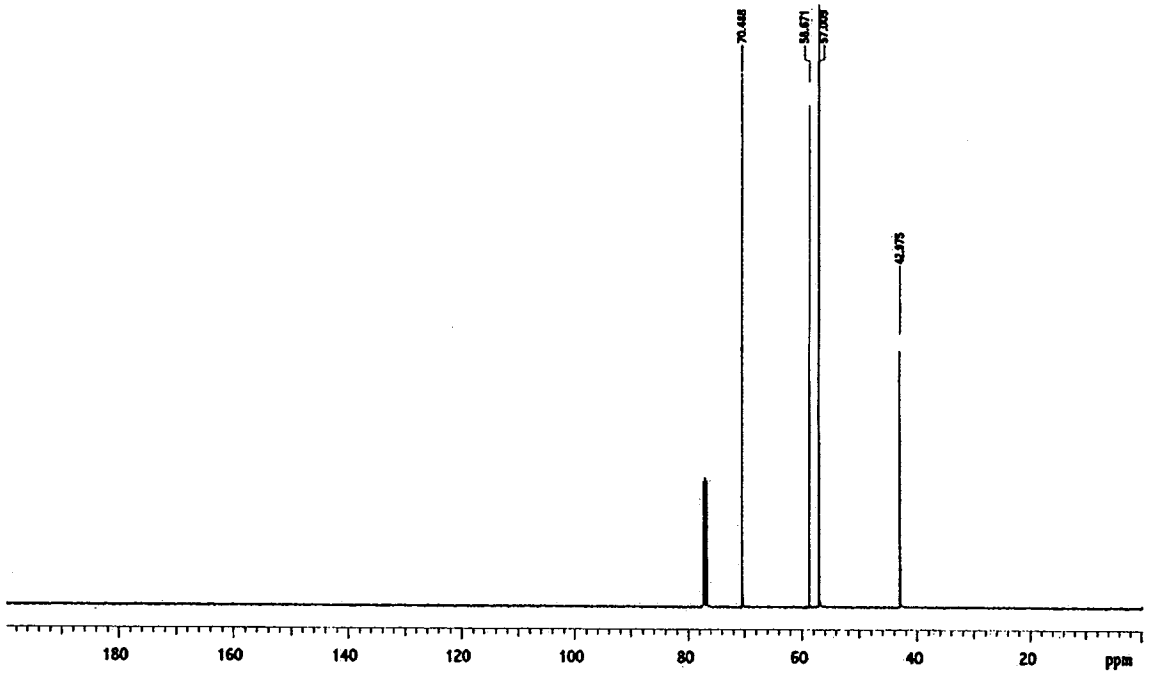
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60
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20
ppm

References:

1. Calculated enthalpies (MNDO, kcal/mol) for six-membered chelates of Me_2NLi: with ligand **W**, $\Delta H_1 = 9.7$, $\Delta H_2 = -6.8$, $\Delta H_3 = 2.9$; with ligand **X**, $\Delta H_1 = 8.4$, $\Delta H_2 = -5.7$, $\Delta H_3 = 2.8$. $H_{f(W)} = -48.3$; $H_{f(X)} = -42.0$.
2. Compere, E. L., Jr.; Shockravi, A. *J. Org. Chem.* **1978**, *43*, 2702.
3. Leonard, N. J.; Jann, K. *J. Am. Chem. Soc.* **1962**, *84*, 4806.