

Supplementary Information For;

**Tris(imidazolin-2-ylidene-1-yl)borate Complexes of the
Heavier Alkaline Earths: Synthesis and Structural Studies**

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Aminoalkene synthesis and NMR scale hydroamination reactions.

NMR Spectra of products of reactions to form compounds **4** and **8**

Figure S1: ¹H NMR spectrum of **4** in d₈-toluene

Figure S2: Enhanced view of the BH signal region for compound **4** in d₈-toluene

Figure S3: ¹H NMR spectrum of a mixture of **2** and **8** in d₈-toluene

Aminoalkene synthesis

Representative procedure:¹ To a suspension of LiNMe₂ or LDA (1.1 equiv.) in THF at -78 °C was added to the nitrile (1 equiv.). The reaction was stirred for 30 min and warmed to room temperature, dimethylamine evolution was observed. The electrophile (1.2 equiv.) was added via syringe and the reaction mixture stirred overnight. The reaction was cooled in an ice-water bath and quenched with H₂O, extraction with ether (3 x 100 mL), drying over MgSO₄ and removal of the solvent gave the crude nitrile as a colourless or light yellow oil. The latter was characterised solely by ¹H NMR spectroscopy and useful without further purification. To a suspension of LiAlH₄ (2.5 equiv.) in diethyl ether under an inert atmosphere was added the nitrile (1 equiv.) as a solution in the same solvent. The mixture was stirred for 30 min at room temperature, then refluxed for 3 h and finally cooled and left to stir overnight at room temperature. The reaction was quenched by slow addition to a 95:5 mixture of THF:H₂O cooled to -20 °C (ice-acetone bath). The solid was filtered, and washed with several portions of diethyl ether (3 x 50 mL). The combined filtrates were washed with H₂O, dried over MgSO₄ and the solvent removed under reduced pressure to give the crude aminoalkene. The latter could be purified by bulb-to-bulb distillation or by flash column chromatography using silica gel and a gradient eluent system of 100:0 → 70:30 petroleum spirit (40-60 °C) : EtOAc. The pure substrates were distilled from CaH₂ or KOH, and stored under nitrogen.

Catalytic Intramolecular Hydroamination of Aminoalkenes

NMR scale experiments: In a glove box, a solution of the aminoalkene (40 µL) and a known amount of TMSS (2-5 mg, internal standard) in C₆D₆ (500 mg) was transferred to a Youngs tap NMR tube. A ¹H NMR spectrum was run to calculate the concentration of the substrate. The NMR tube was pumped back into the glovebox and the catalyst (2-20 mol %) added, the reaction was then monitored by NMR spectroscopy.

Figure S1: ^1H NMR spectrum of **4** in d_8 -toluene

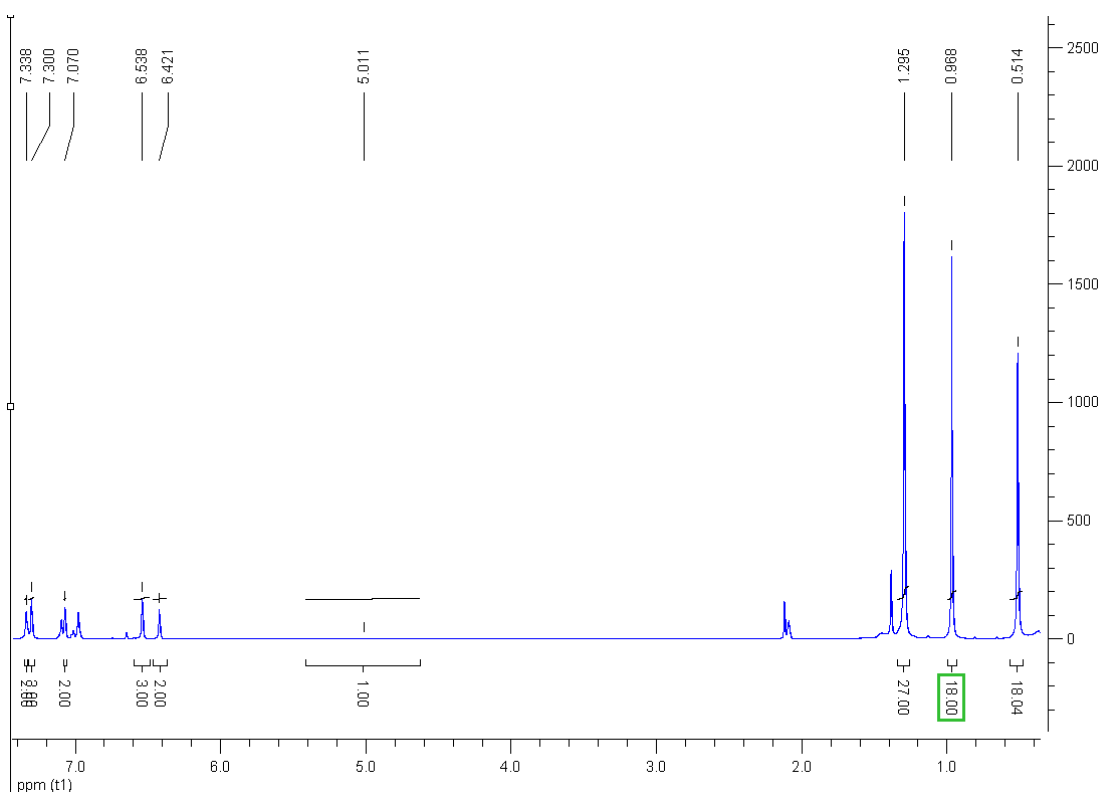


Figure S2: Enhanced view of the BH signal region for compound **4** in d_8 -toluene

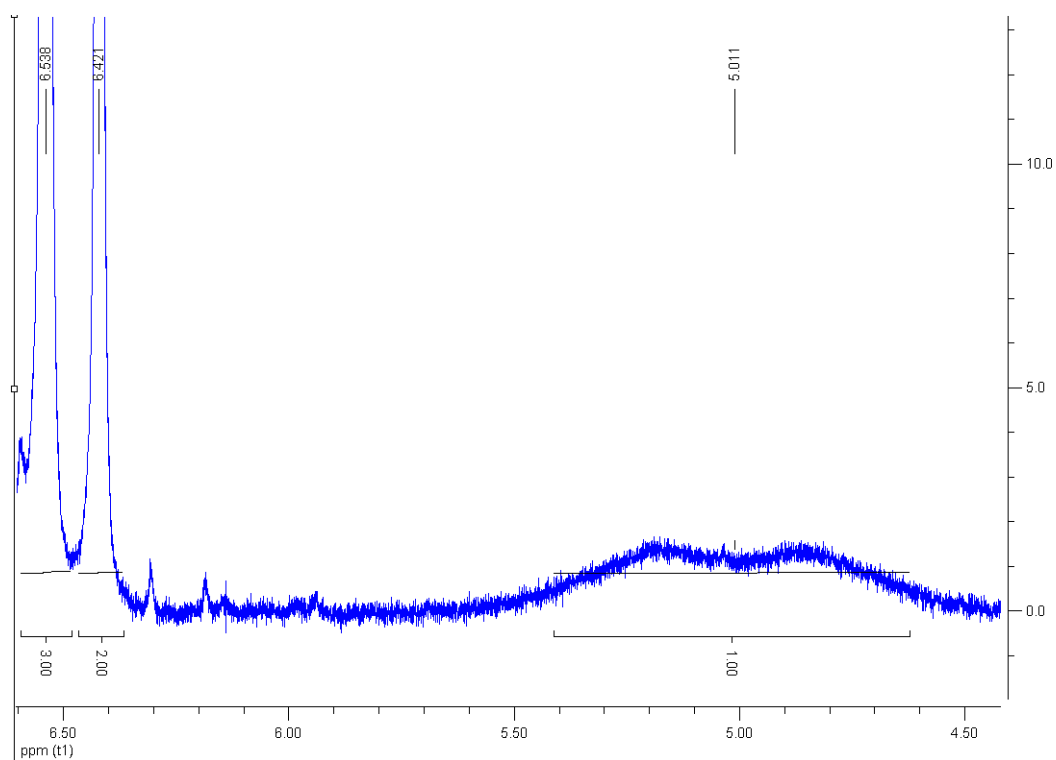
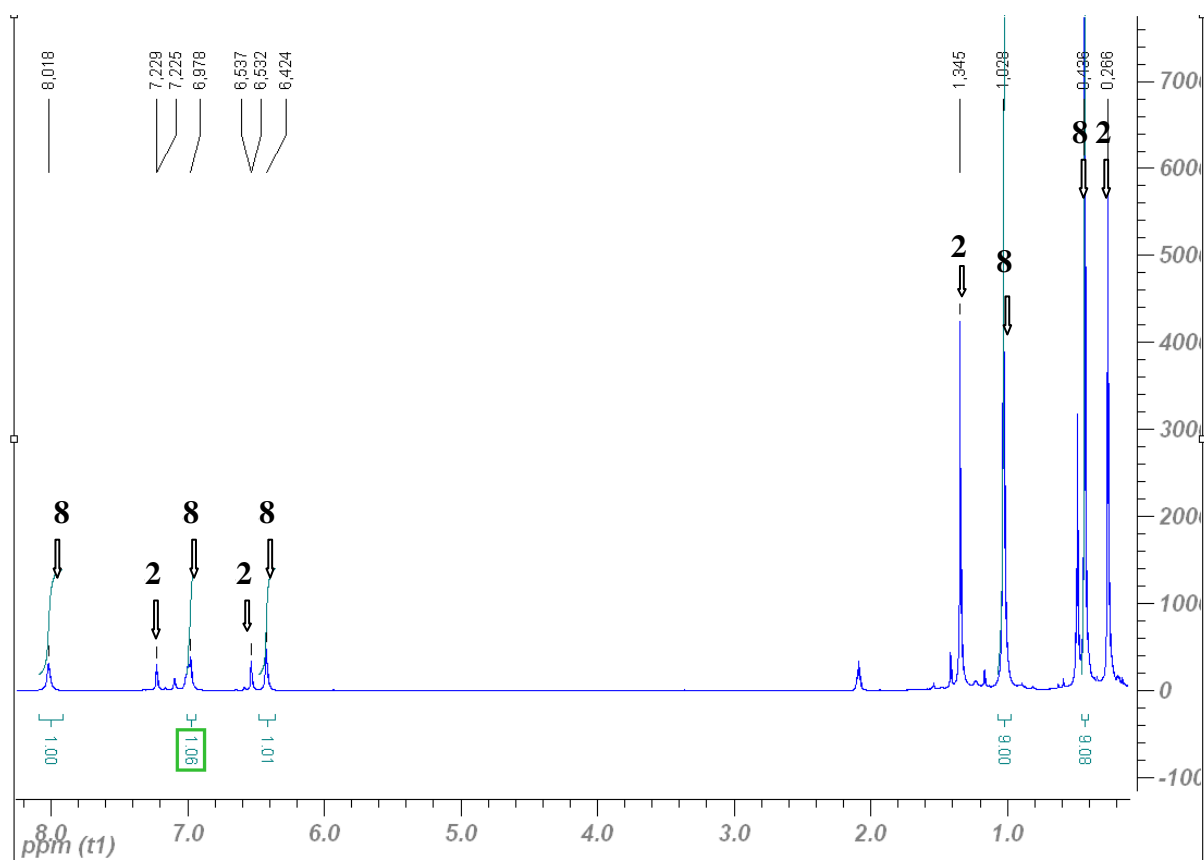


Figure S3: ^1H NMR spectrum of a mixture of **2** and **8** in d_8 -toluene



References

- (1) Gagne, M. R.; Stern, C. L.; Marks, T. J., *J. Am. Chem. Soc.* **1992**, *114*, 275.