

Electronic Supplementary Information for

Strategic combination of Grignard reagents and allyl-functionalized ionic liquids as an advanced electrolytes for rechargeable magnesium batteries

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Supplementary Table S1

Supplementary Figures S1 to S11

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Supplementary Table

Table S1. Ionic conductivities of electrolytes combining 0.4 M PhMgCl solution with 0 M, 0.1 M, 0.2 M, 0.3 M and 0.4 M of AMPyrrCl in THF, termed as PMC, (PMC)(AMPC)_{0.25}, (PMC)(AMPC)_{0.5}, (PMC)(AMPC)_{0.75} and (PMC)(AMPC)_{1.0}, respectively.

Electrolyte	Ionic conductivity (mS cm ⁻¹)
0.4 M PhMgCl	0.17
(PMC)(AMPC) _{0.25}	0.60
(PMC)(AMPC) _{0.5}	0.61
(PMC)(AMPC) _{0.75}	0.48
(PMC)(AMPC) _{1.0}	0.23

Supplementary Figures

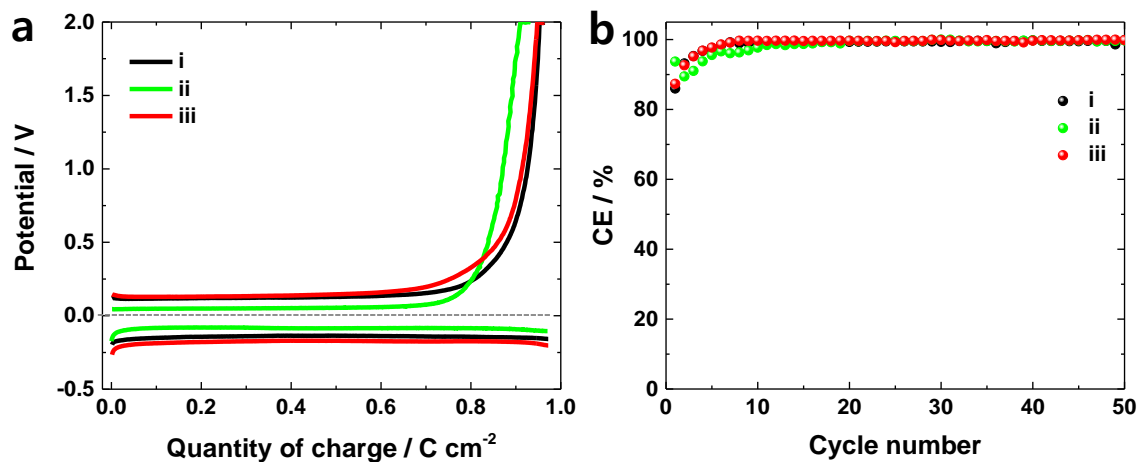


Fig. S1. Characteristics of Mg deposition-stripping reaction for the various electrolytes investigated. a) The chronopotentiograms of the 10th cycle for Mg deposition-stripping and b) the calculated cycling efficiency up to 50 cycles for the electrolytes of 0.4 M PhMgCl solutions combined with i) 0 M, ii) 0.2 M, and iii) 0.4 M of AMPyrrCl in THF. The galvanostatic Mg deposition-stripping was conducted with Ni as the working electrode at a current density of 0.135 mA cm⁻². The coulombic efficiency of the electrolytes reached more than 99.5 % for all electrolytes after 50 cycles.

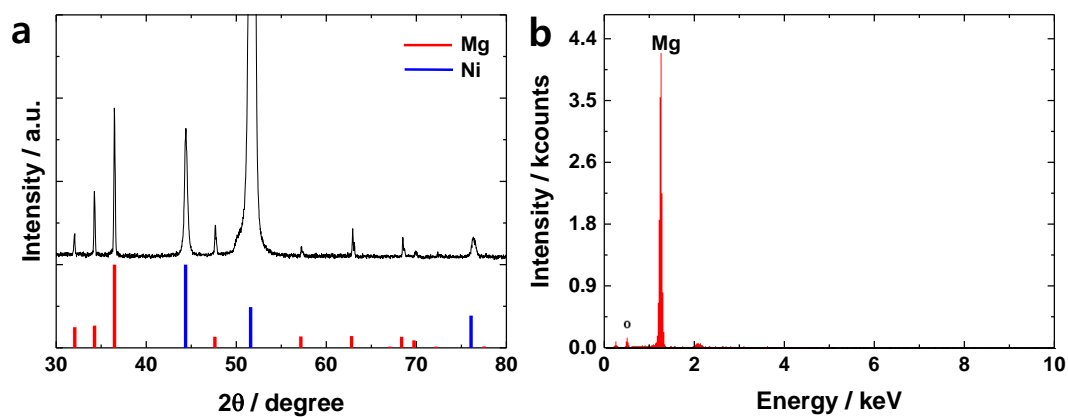


Fig. S2. Identification of the deposit from an equimolar solution (0.4 M) of PhMgCl and AMPyrrCl in THF. a) XRD pattern and b) EDS elemental analysis for the deposit on a Ni substrate. From these data, pure Mg metal was established to be a single dominant deposit from the electrolyte. A small amount of oxygen (~5 %) in the EDS spectrum originates from the metal oxide layer generated following exposure to air during the analysis.

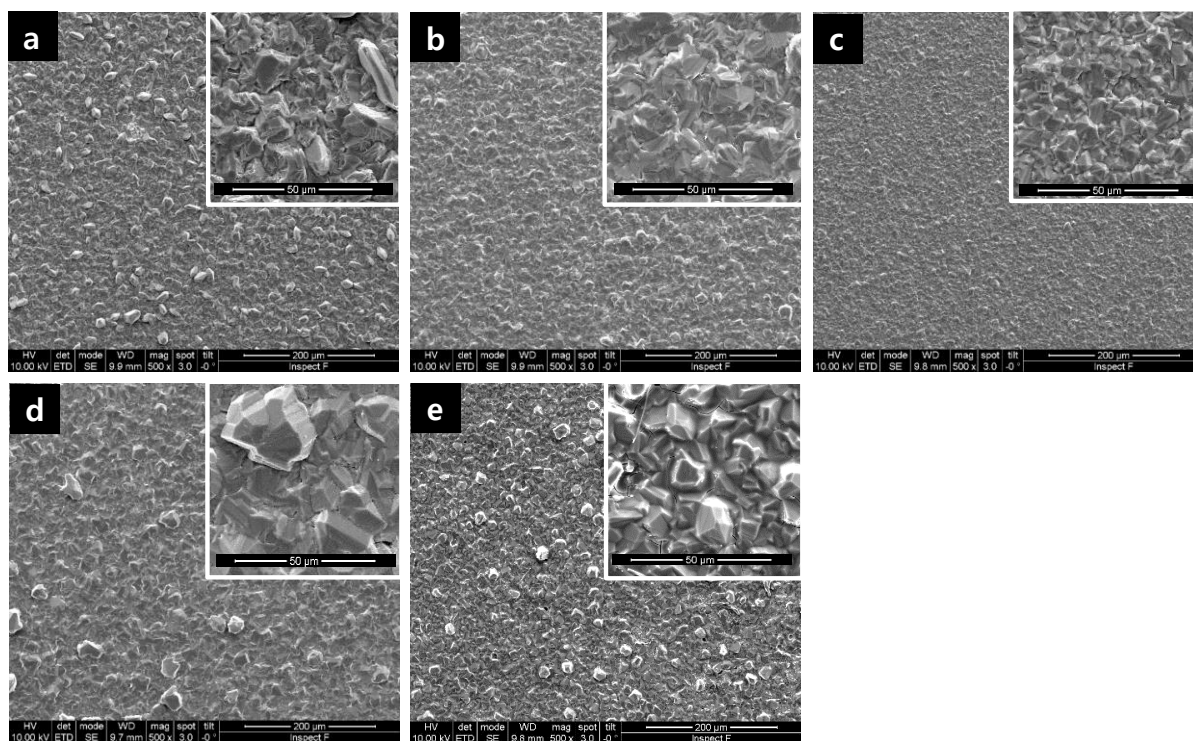


Fig. S3. SEM images showing the morphological features of Mg deposits in the electrolytes containing a) pure 0.4 M PhMgCl, b) (PMC)(AMPC)_{0.25}, c) (PMC)(AMPC)_{0.5}, d) (PMC)(AMPC)_{0.75}, and e) (PMC)(AMPC)_{1.0} after the 1st deposition. All the deposits were obtained on Ni substrates at the total charge of 4.86 C cm⁻² (0.135 mA cm⁻², 10 h). Round and grain-like morphology was observed regardless of the electrolytes and no dendrite was observed for all cases considered.

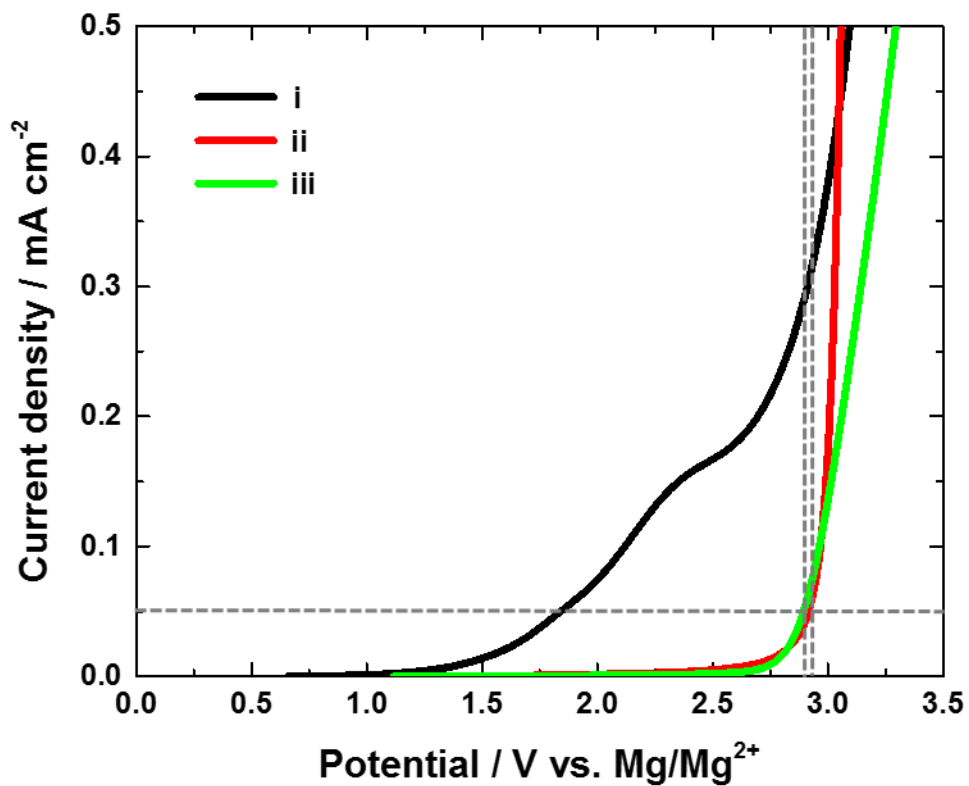
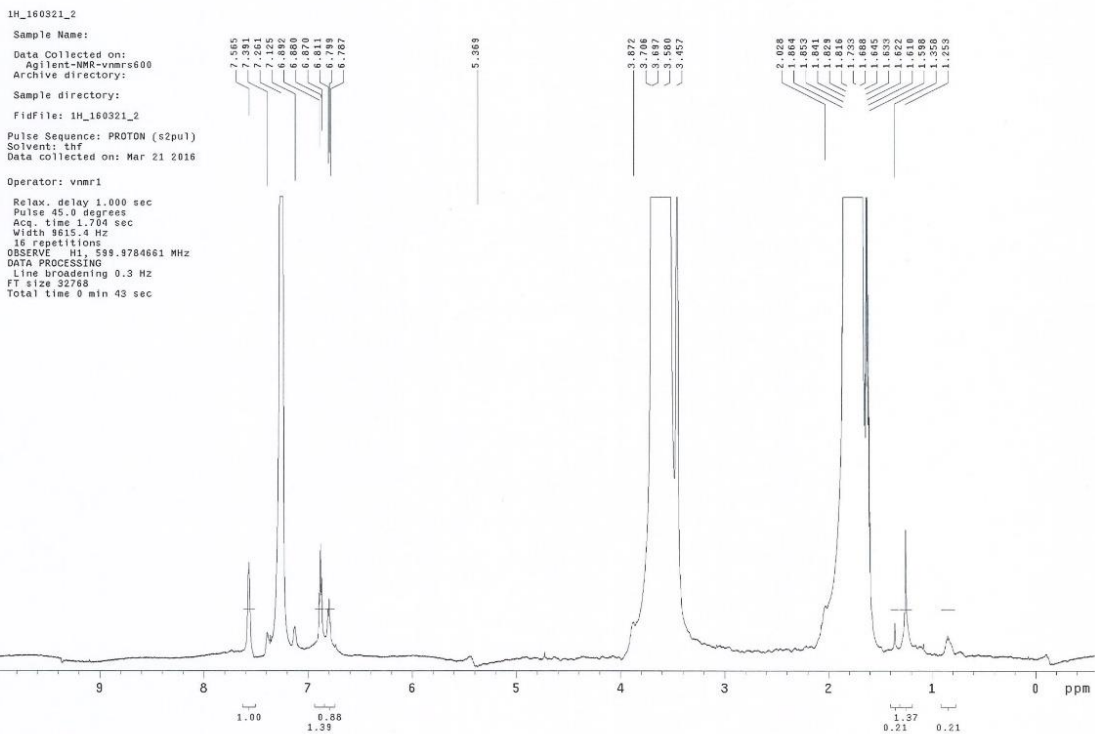
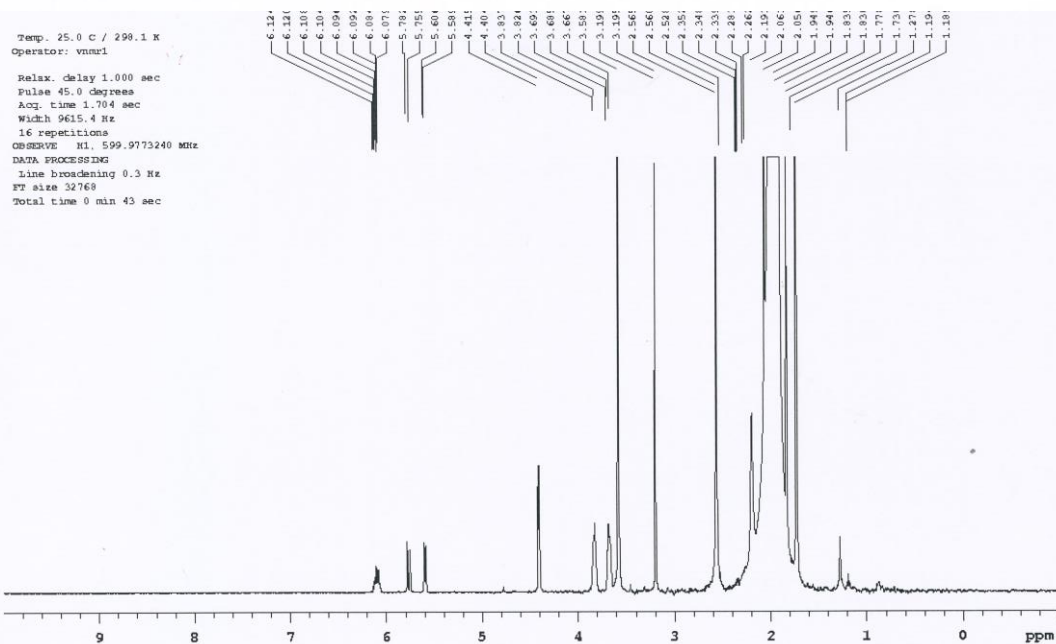


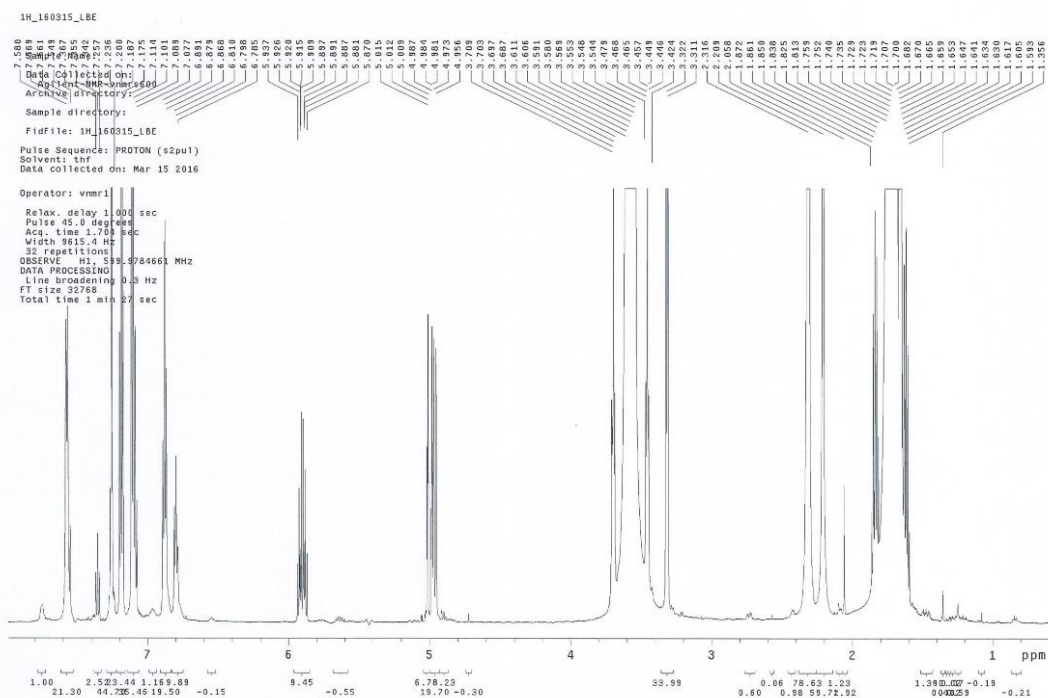
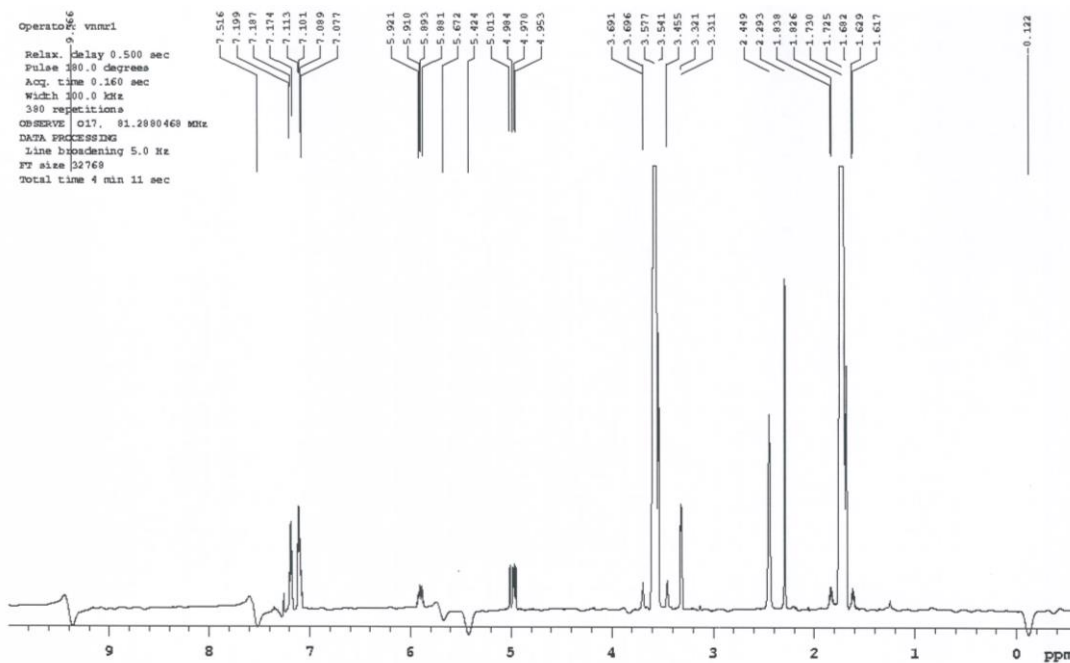
Fig. S4. Comparison in the oxidative stability of the various electrolytes. Linear sweep voltammograms of i) pure 0.4 M PhMgCl and 0.4 M PhMgCl solutions with ii) 0.2 M of AlCl₃ (APC solution) and iii) 0.4 M of AMPyrrCl in THF. All experiments were conducted with a Ni working electrode and Mg counter/reference electrodes at a scan rate of 25 mV s⁻¹. Oxidative stability of the Grignard reagents increases dramatically by adding AlCl₃ or AMPyrrCl up to ~2.9 V vs. Mg/Mg²⁺.

a



b



c**d**

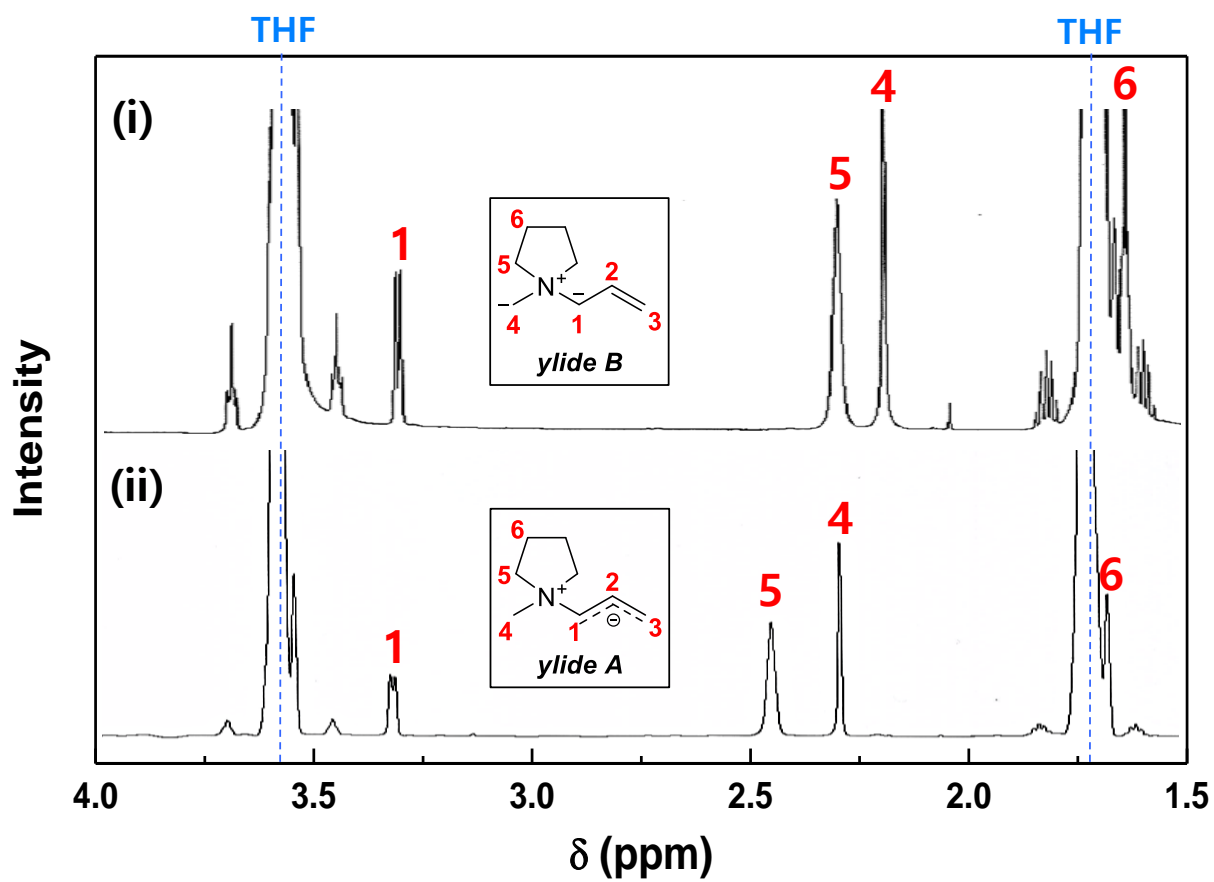


Fig. S6. The enlarged ¹H NMR spectrum (600 MHz, THF-d₈, 25 °C) of (i) 2:1 and (ii) 1:1 molar ratio of the PhMgCl-AMPyrrCl complex in the range of 1.5~4 ppm.

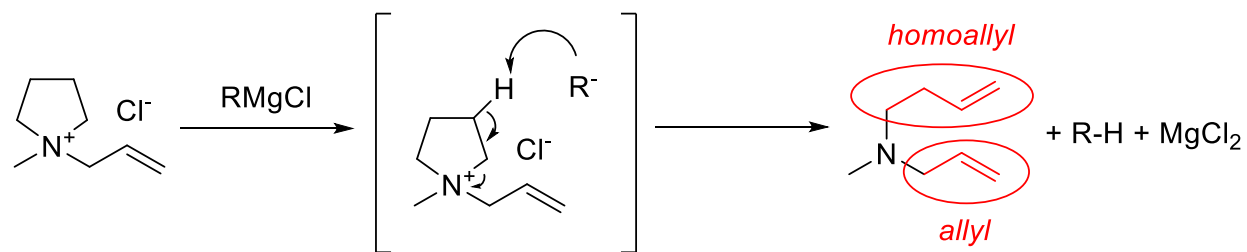


Fig. S7. Plausible reaction mechanism for Hofmann elimination of AMPyrrCl by Grignard reagent. The plausible reaction mechanism predicts the formation of tertiary amine, allyl-homoallyl-methylamine. However, we could not observe ¹H peaks corresponding to individual allyl and homoallyl group in ¹H NMR spectrum, but just one allylic ¹H pattern was observed.

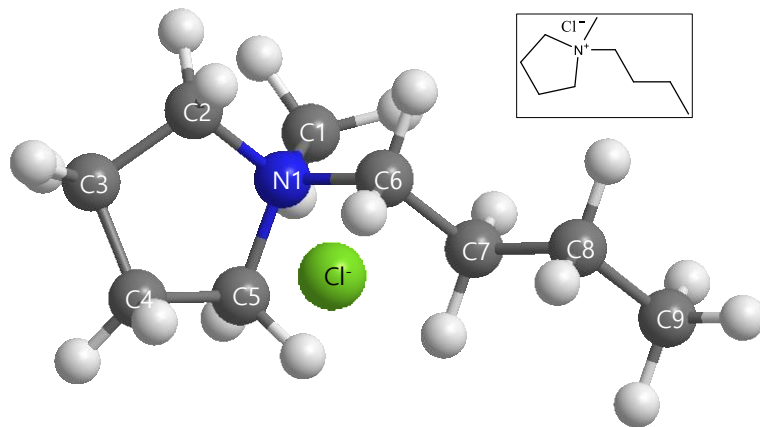


Fig. S8. The molecular structure of *N*-butyl-*N*-methylpyrrolidinium chloride (BMPyrrCl).

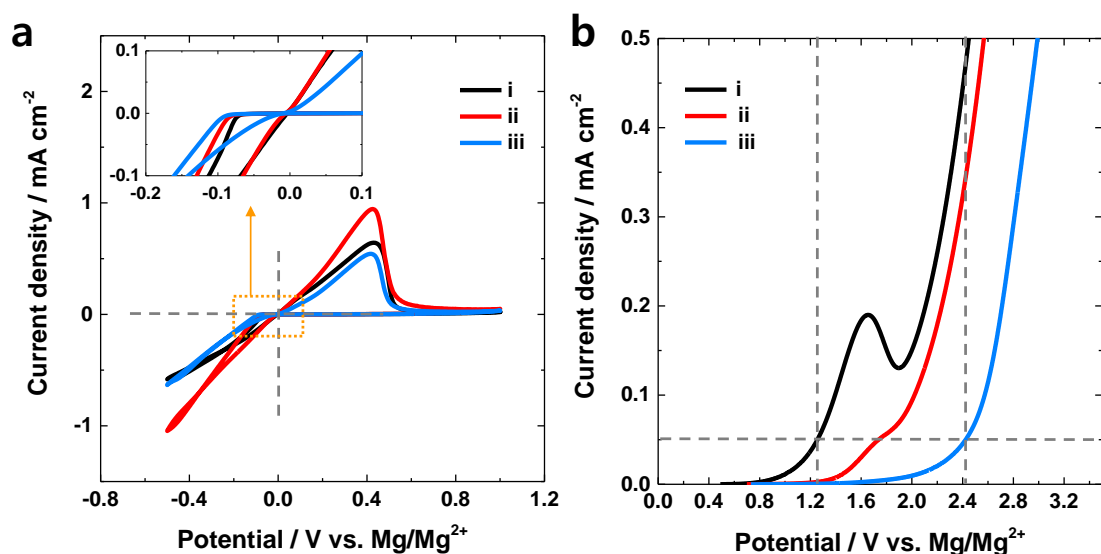


Fig. S9. a) Cyclic voltammograms (5th cycle) and b) linear sweep voltammograms for a series of electrolytes combining 0.4 M of EtMgCl with i) 0 M, ii) 0.1 M and iii) 0.2 M of AMPyrrCl. Inset in a) shows an enlarged picture near the onset of Mg deposition marked with an orange square. All experiments were conducted with a Ni working electrode and Mg counter/reference electrodes at a scan rate of 1 mV s⁻¹ for CV and 25 mV s⁻¹ for LSV.

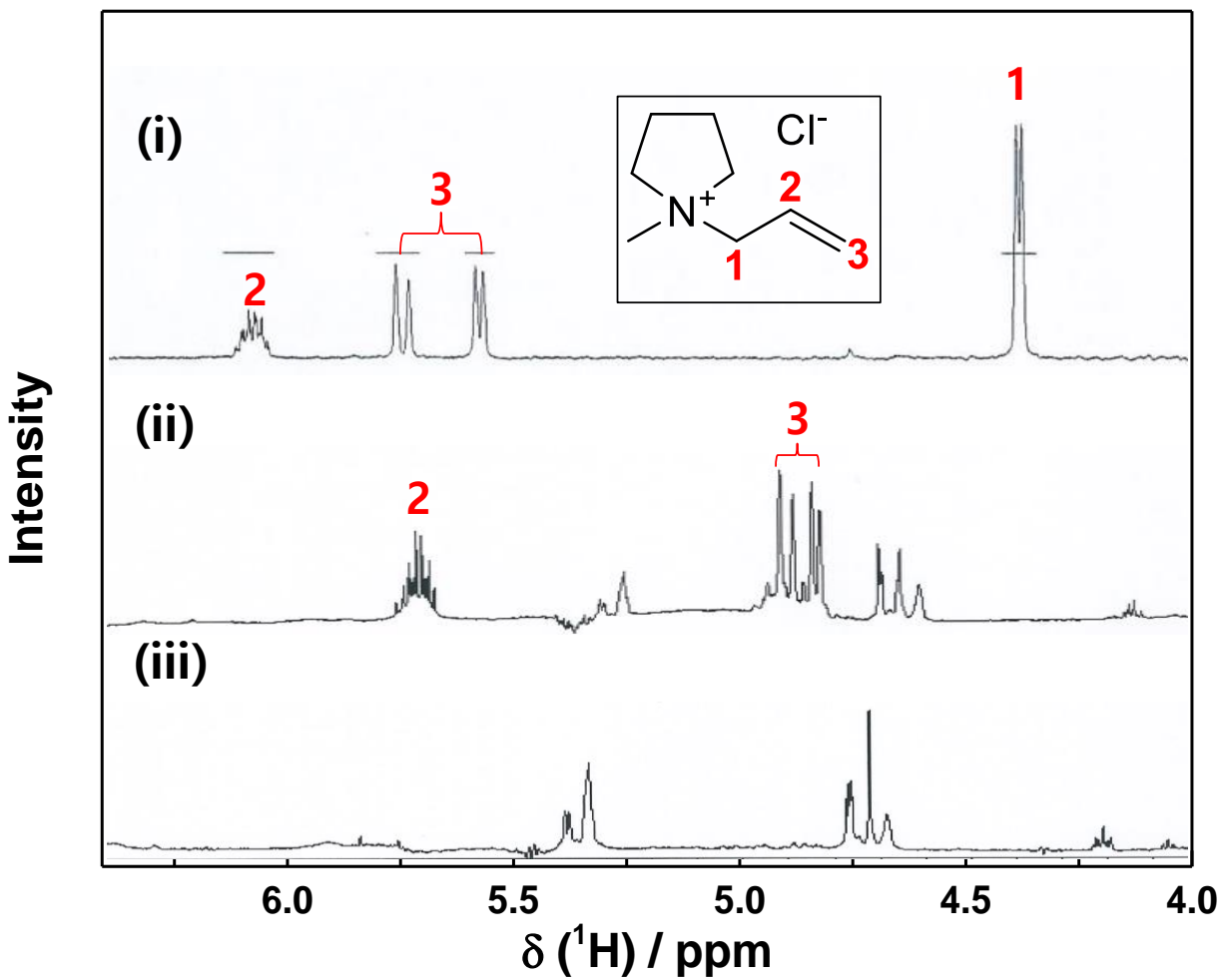


Fig. S10. ^1H NMR spectra (600 MHz, THF- d_8 , 25 °C) of (i) AMPyrrCl, (ii) 2:1 molar ratio of EtMgCl-AMPyrrCl, and (iii) EtMgCl in THF.

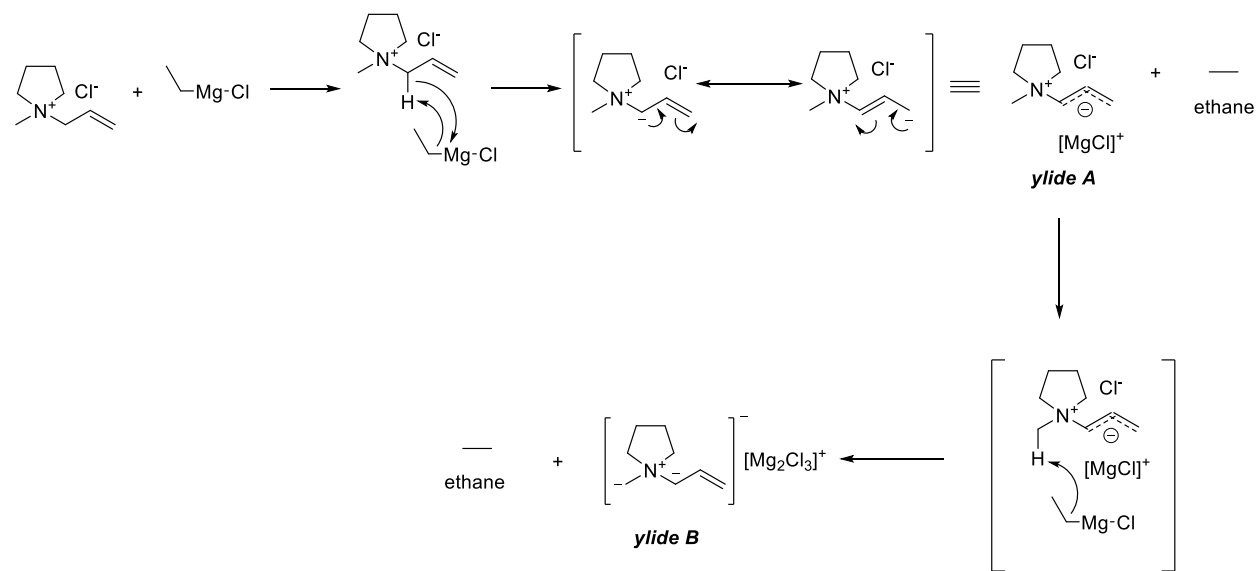


Fig. S11. Proposed reaction mechanism between AMPyrrCl and EtMgCl in THF.