

Supplementary Information for:

Alane-centered Ring Expansion of *N*-Heterocyclic Carbenes

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Figure S1: ¹H NMR spectrum (500.1 MHz, C₆D₆, 298K) of compound **6**, [HC{C(Me)NDipp}₂AlCH₂N(Ph)(CH)₂N(Ph)].

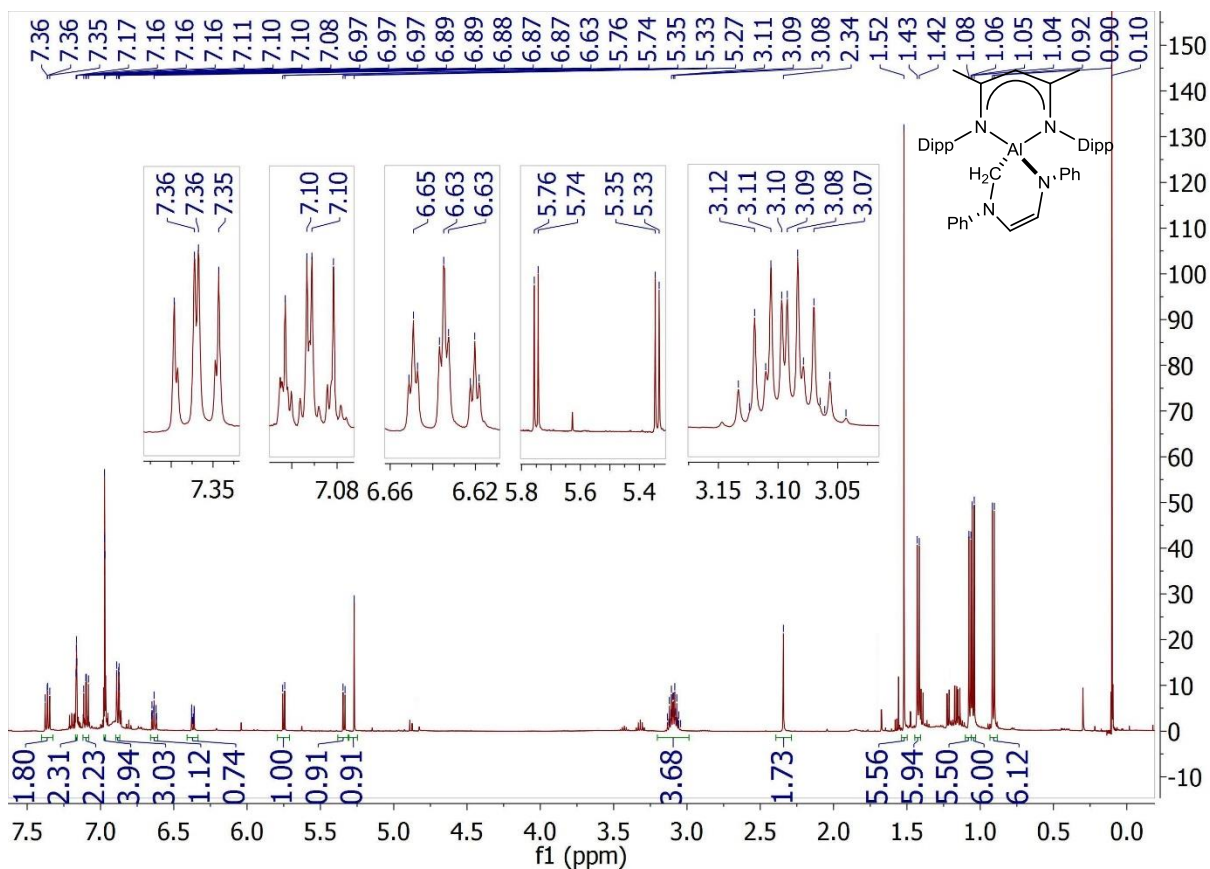


Figure S2: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125.8 MHz, 298K) of compound **6**, $[\text{HC}\{\text{C}(\text{Me})\text{NDipp}\}_2\text{AlCH}_2\text{N}(\text{Ph})(\text{CH})_2\text{N}(\text{Ph})]$.

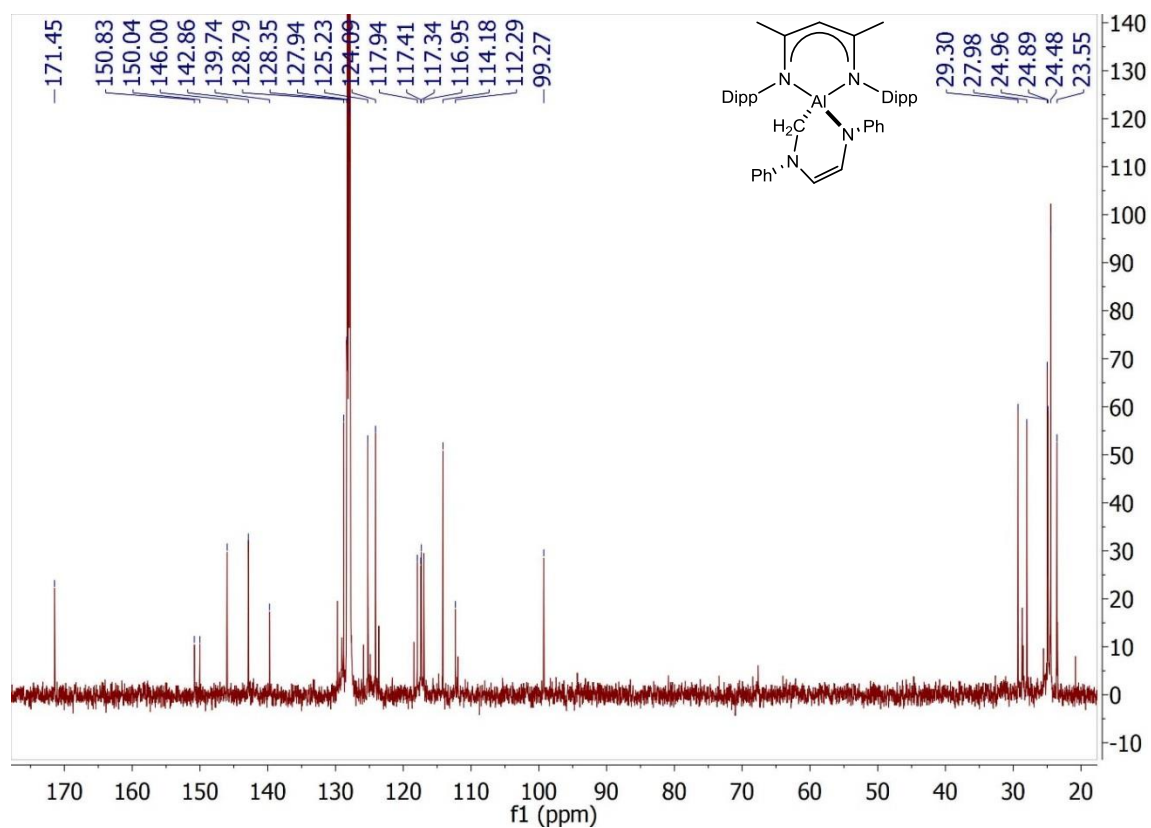


Figure S3: ^1H NMR spectrum (500 MHz, 298K) of compound **7**, $[\text{HC}\{\text{C}(\text{Me})\text{NMes}\}_2\text{AlCH}_2\text{N}(\text{Mes})(\text{CH})_2\text{N}(\text{Mes})]$.

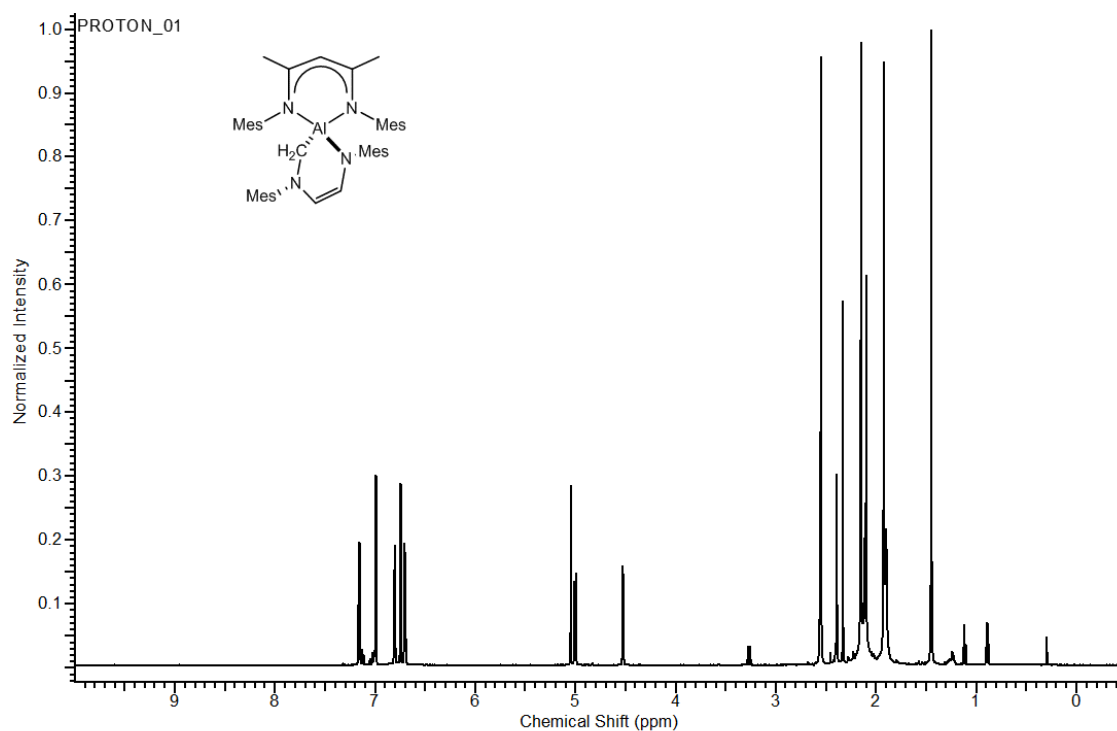


Figure S4: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (128.5 MHz, 298K) of compound **7**, $[\text{HC}\{\text{C}(\text{Me})\text{NMe}\}_2\text{AlCH}_2\text{N}(\text{Me})(\text{CH})_2\text{N}(\text{Me})]$.

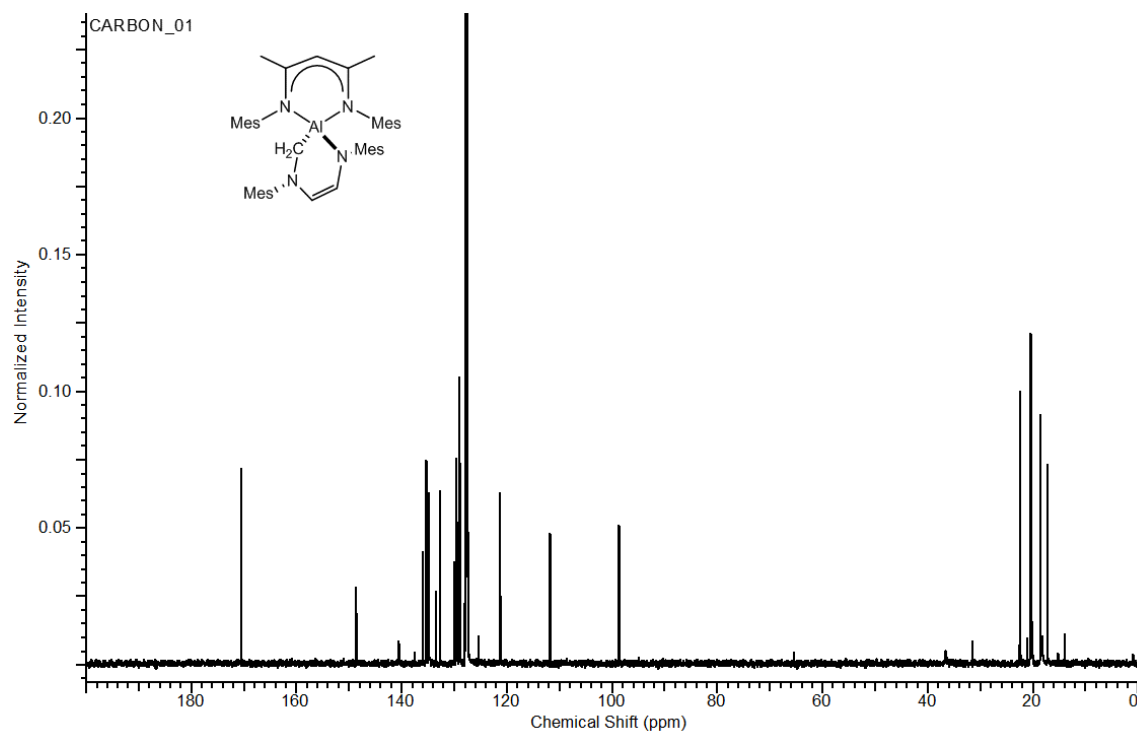


Figure S5: ^1H NMR spectrum (500.1 MHz, 298K) of compound **8**, $[\text{HC}\{\text{C}(\text{Me})\text{NMe}\}_2\text{AlCH}_2\text{N}(\text{Ph})(\text{CH})_2\text{N}(\text{Ph})]$.

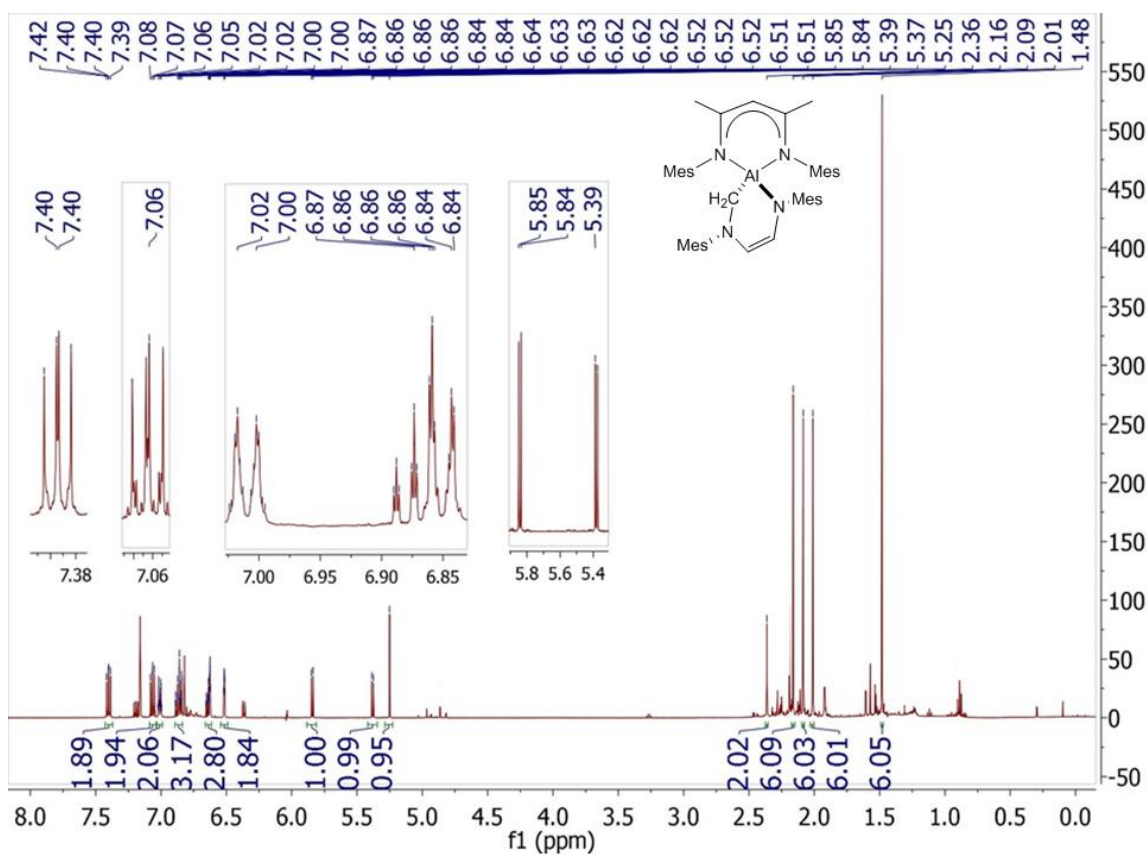


Figure S6: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (128.5 MHz, 298K) of compound **8**, $[\text{HC}\{\text{C}(\text{Me})\text{NMes}\}_2\text{AlCH}_2\text{N}(\text{Ph})(\text{CH})_2\text{N}(\text{Ph})]$.

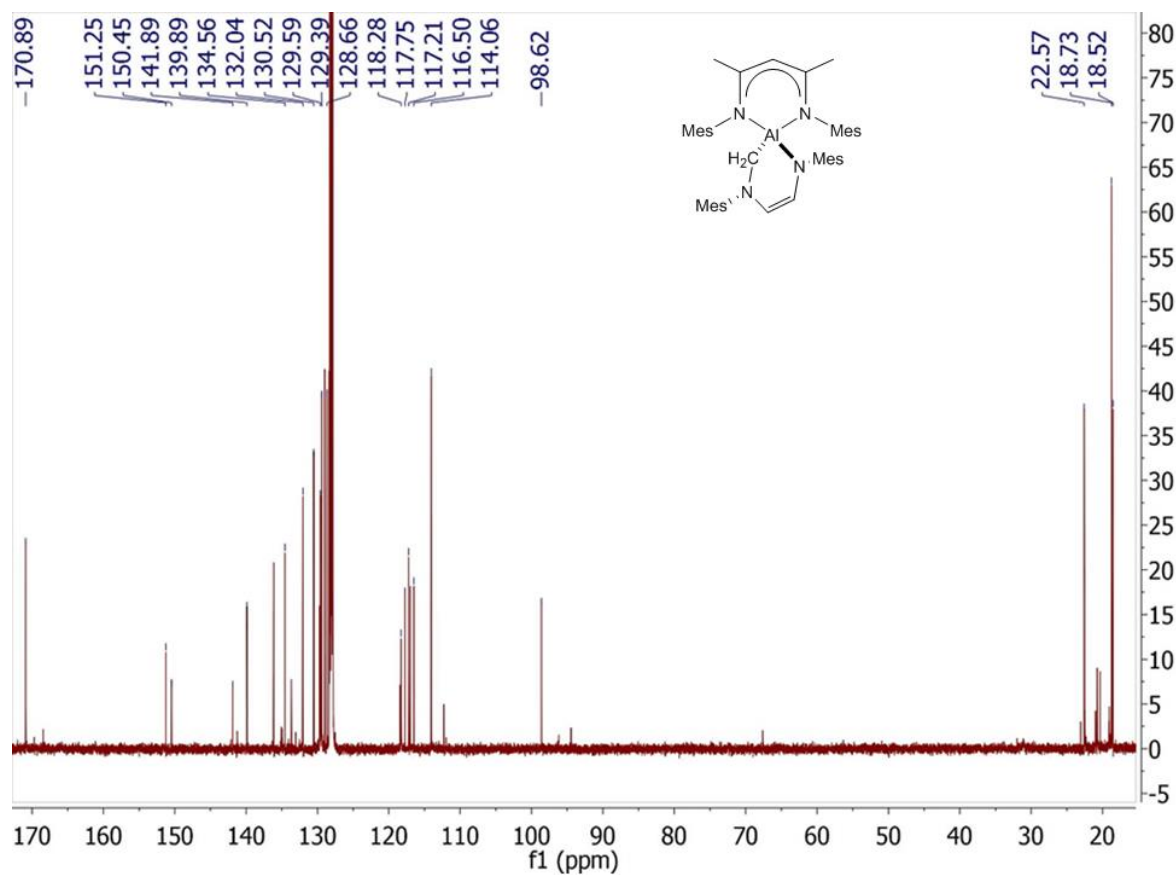


Table S1: Single crystal X-ray diffraction analysis of compounds **6** and **7**.

Compound	6	7
Empirical formula	C ₄₄ H ₅₅ AlN ₄	C ₉₇ H ₁₁₉ Al ₂ N ₈
Formula weight	666.90	1450.95
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2/ <i>n</i>
<i>a</i> /Å	10.11890(9)	21.1542(2)
<i>b</i> /Å	21.49866(17)	15.35141(13)
<i>c</i> /Å	18.65685(19)	26.8601(3)
β /°	103.9254(10)	102.8102(10)
<i>U</i> /Å ³	3939.38(6)	8505.59(14)
<i>Z</i>	4	4
ρ_{calc} /cm ³	1.124	1.133
μ /mm ⁻¹	0.701	0.702
<i>F</i> (000)	1440.0	3132.0
Crystal size/mm ³	0.4349 × 0.1849 × 0.1571	0.2000 × 0.0750 × 0.0500
2 θ range for data collection/°	8.226 to 143.834	8.328 to 143.918
Index ranges	-10 ≤ <i>h</i> ≤ 12, -25 ≤ <i>k</i> ≤ 26, -20 ≤ <i>l</i> ≤ 22	-25 ≤ <i>h</i> ≤ 26, -11 ≤ <i>k</i> ≤ 18, -33 ≤ <i>l</i> ≤ 32
Reflections collected	26825	73011
Independent reflections, <i>R</i> _{int}	7666, 0.0358	16537, 0.0414
Data/restraints/parameters	7666/0/452	16537/0/911
Goodness-of-fit on <i>F</i> ²	1.021	1.038
Final <i>R</i> 1, <i>wR</i> 2[<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0478, 0.1300	0.0459, 0.1215
Final <i>R</i> 1, <i>wR</i> 2[all data]	0.0524, 0.1354	0.0569, 0.1287
Largest diff. peak/hole / e Å ⁻³	0.31/-0.32	0.40/-0.35