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Electronic Supplementary Information

Accelerating Role of Deaggregation Agents in Lithium-Catalysed Hydrosilylation of Carbonyl Compounds

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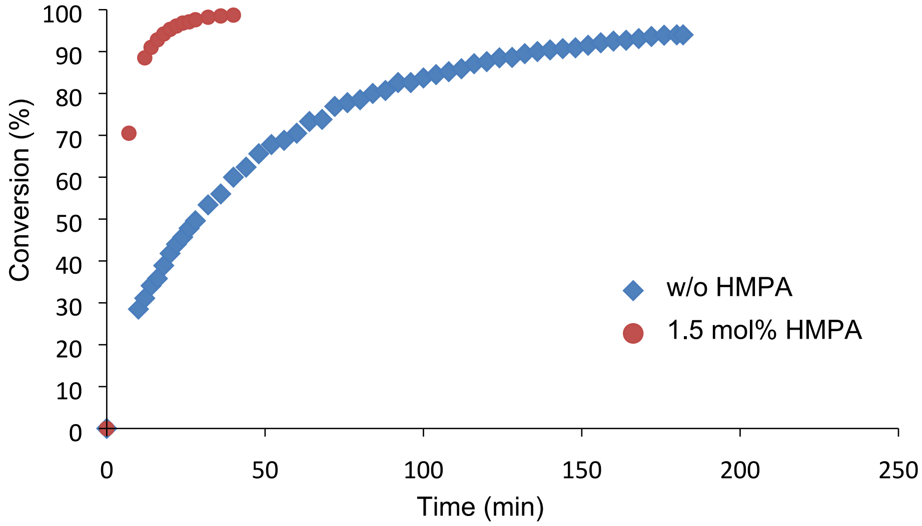


Figure S1. Kinetic profile of the transformation of acetophenone into the corresponding silylether via hydrosilylation catalysed by 0.25 mol% LDA (blue diamonds) or by 0.25 mol% LDA and 1.5 mol% HMPA (red circles).

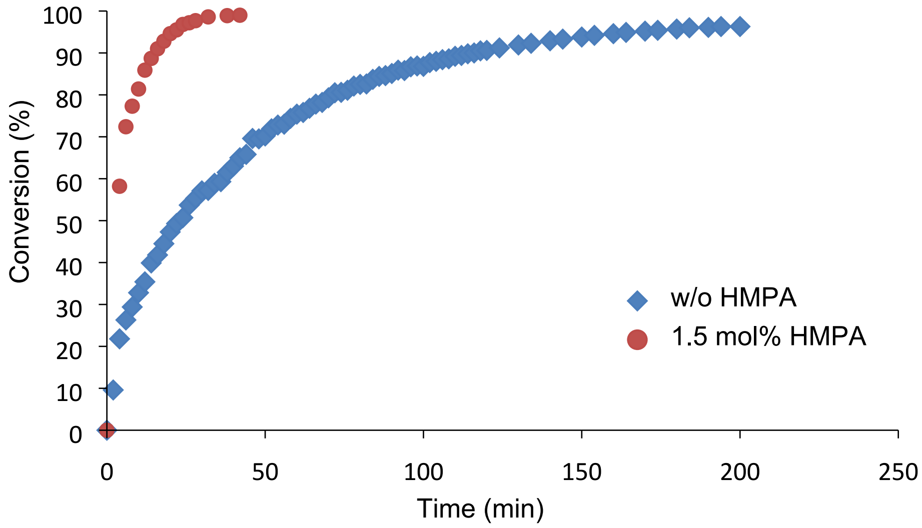


Figure S2. Kinetic profile of the transformation of acetophenone into the corresponding silylether via hydrosilylation catalysed by 0.25 mol% LiHMDS (blue diamonds) or by 0.25 mol% LiHMDS and 1.5 mol% HMPA (red circles).

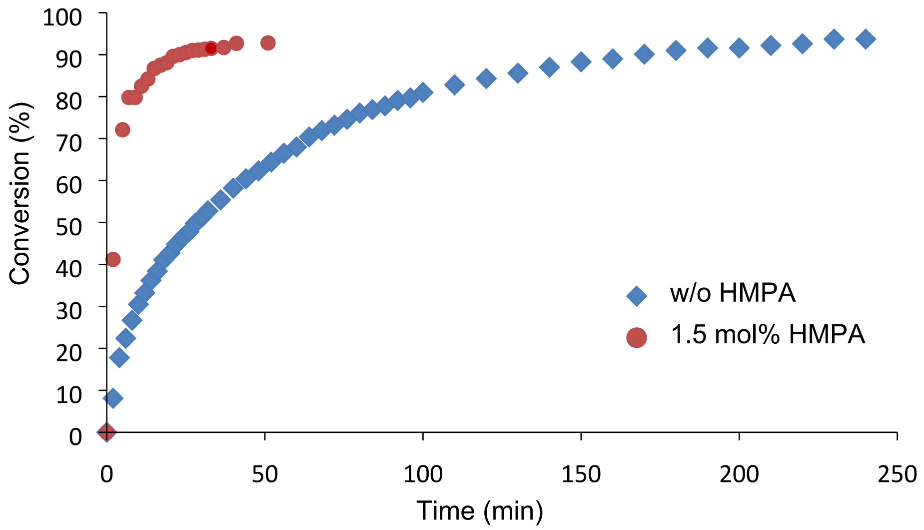


Figure S3. Kinetic profile of the transformation of acetophenone into the corresponding silylether via hydrosilylation catalysed by 0.25 mol% LiTMP (blue diamonds) or by 0.25 mol% LiTMP and 1.5 mol% HMPA (red circles).

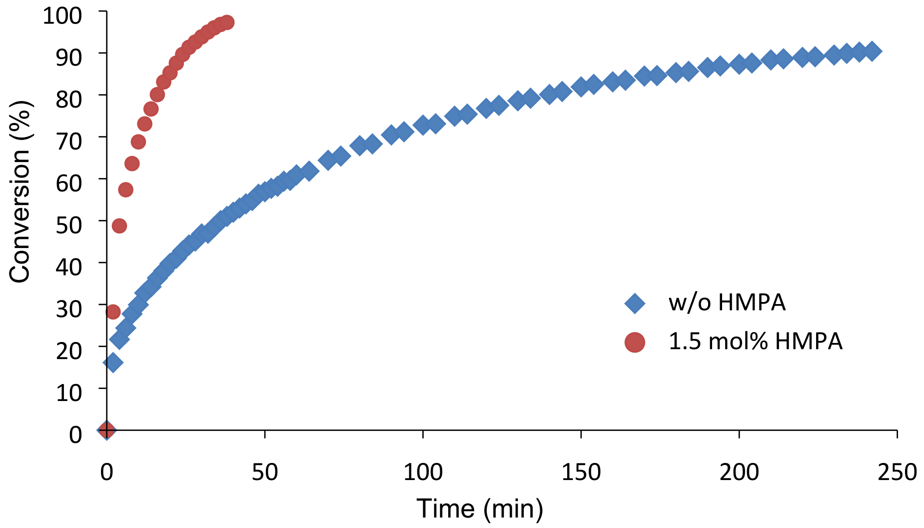


Figure S4. Kinetic profile of the transformation of acetophenone into the corresponding silylether via hydrosilylation catalysed by 0.25 mol% LiAQ (blue diamonds) or by 0.25 mol% LiAQ and 1.5 mol% HMPA (red circles).

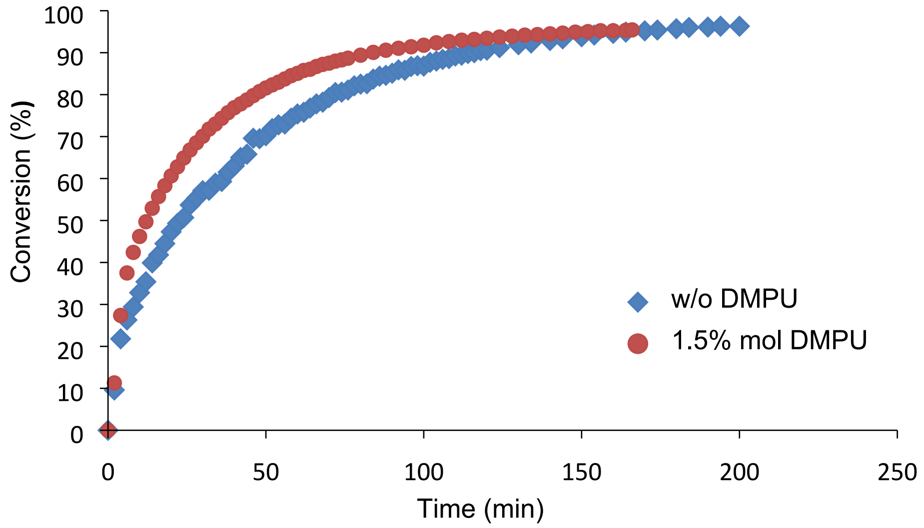


Figure S5. Kinetic profile of the transformation of acetophenone into the corresponding silylether via hydrosilylation catalysed by 0.25 mol% LiHMDS (blue diamonds) or by 0.25 mol% LiHMDS and 1.5 mol% DMPU (red circles).

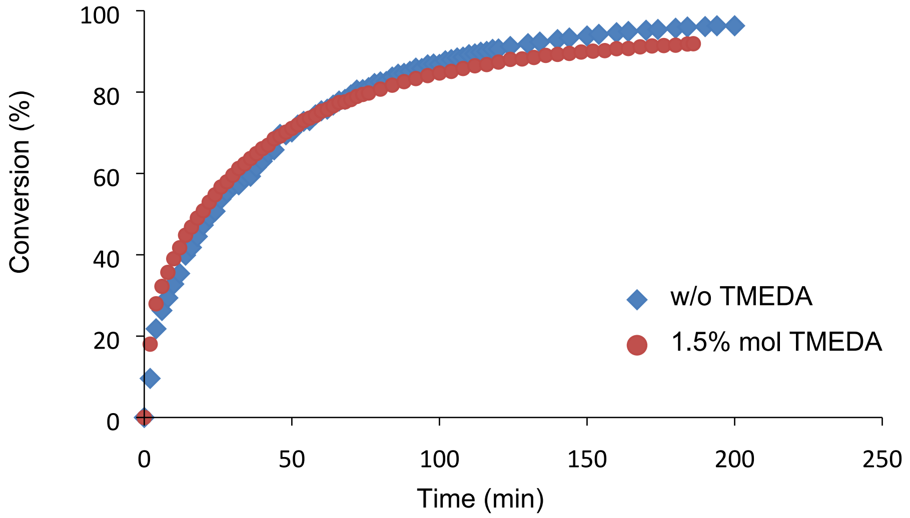


Figure S6. Kinetic profile of the transformation of acetophenone into the corresponding silylether via hydrosilylation catalysed by 0.25 mol% LiHMDS (blue diamonds) or by 0.25 mol% LiHMDS and 1.5 mol% TMEDA (red circles).

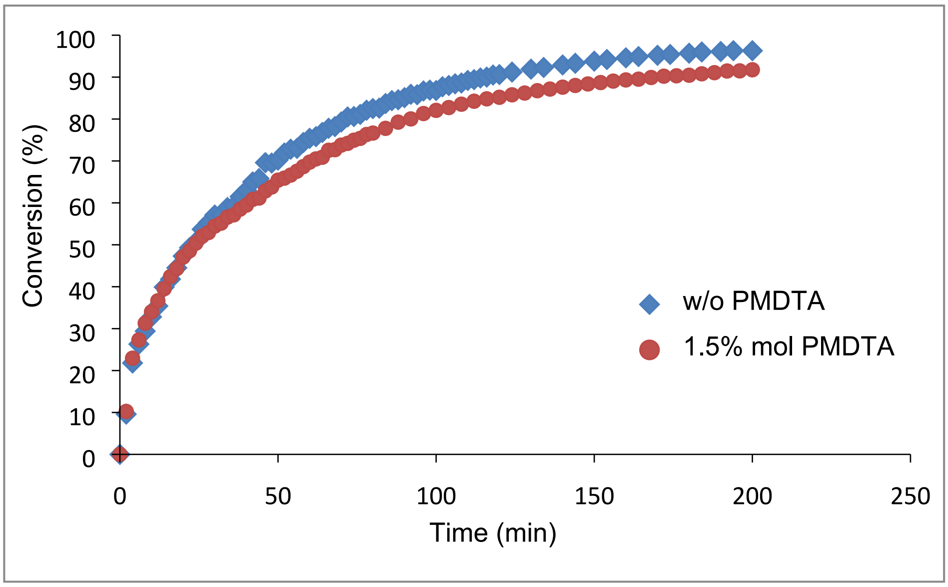


Figure S7. Kinetic profile of the transformation of acetophenone into the corresponding silylether via hydrosilylation catalysed by 0.25 mol% LiHMDS and 1.5 mol% PMDTA.

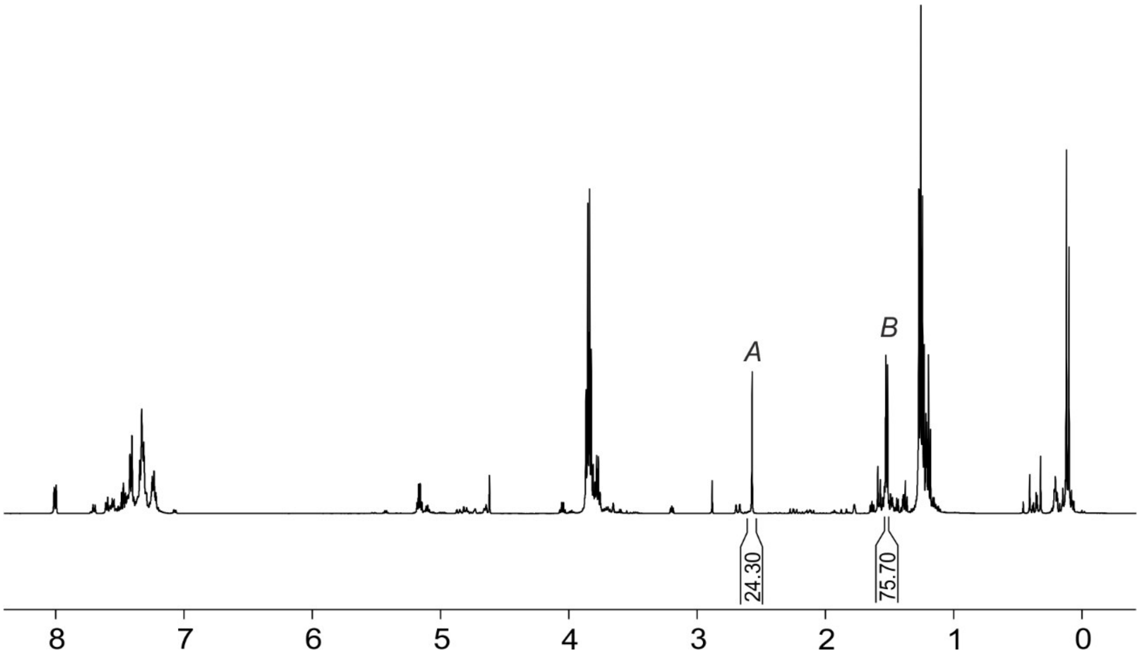


Figure S8. ^{1}H NMR (500.13 MHz, THF-d_8) spectrum of a typical catalytic reaction crude at 76 % conversion. Signals A and B correspond to the methyl moiety of acetophenone and hydrosilylated product, respectively.

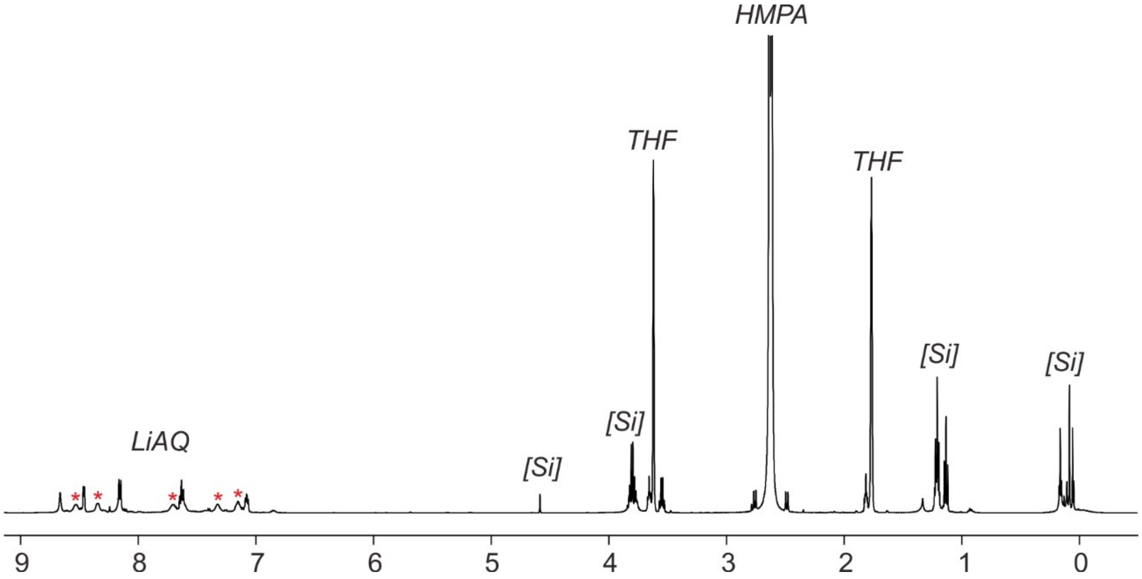


Figure S9. ^{1}H NMR (500.13 MHz, THF-d_8) spectrum at 294 K of the stoichiometric experiment containing LiAQ (0.012 mmol), $(EtO)_2MeSiH$ (0.024 mmol) and HMPA (0.096 mmol).

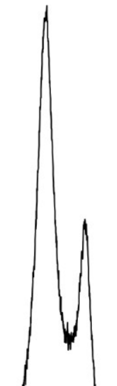


Figure S10. ^{7}Li NMR (194.37 MHz, THF-d_8) spectrum at 294 K of the stoichiometric experiment containing LiAQ (0.012 mmol), $(EtO)_2MeSiH$ (0.024 mmol) and HMPA (0.096 mmol).

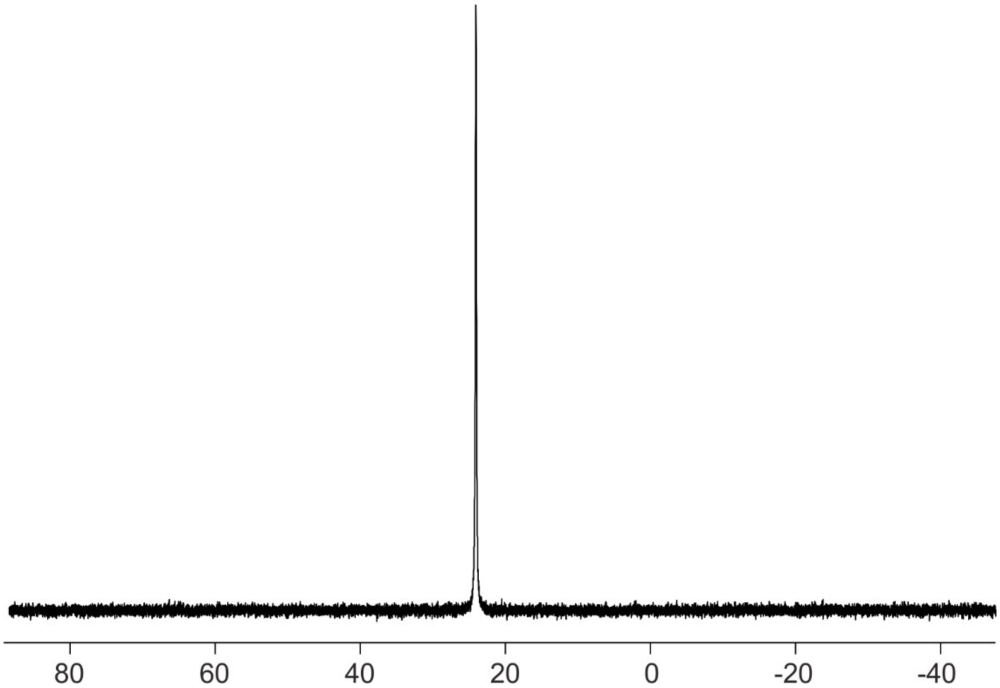
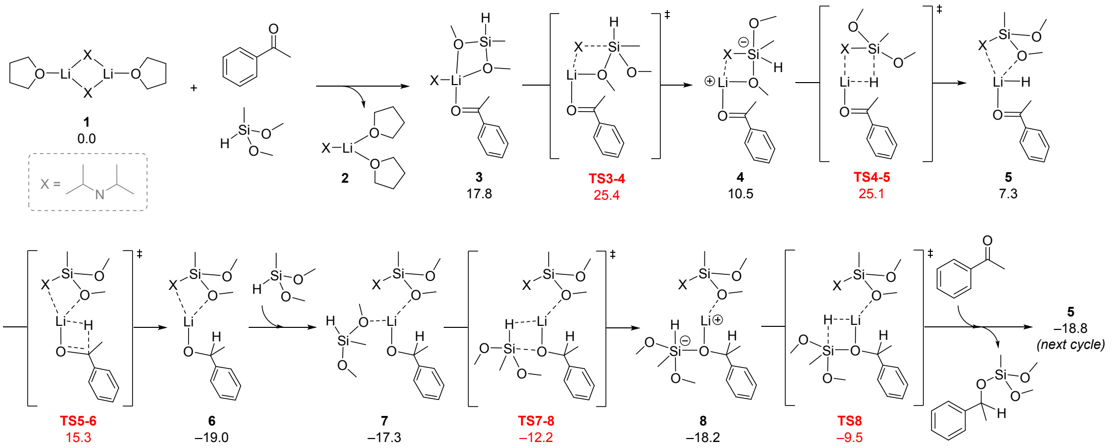


Figure S11. ^{31}P NMR (202.46 MHz, THF-d_8) spectrum at 294 K of the stoichiometric experiment containing LiAQ (0.012 mmol), $(EtO)_2MeSiH$ (0.024 mmol) and HMPA (0.096 mmol).

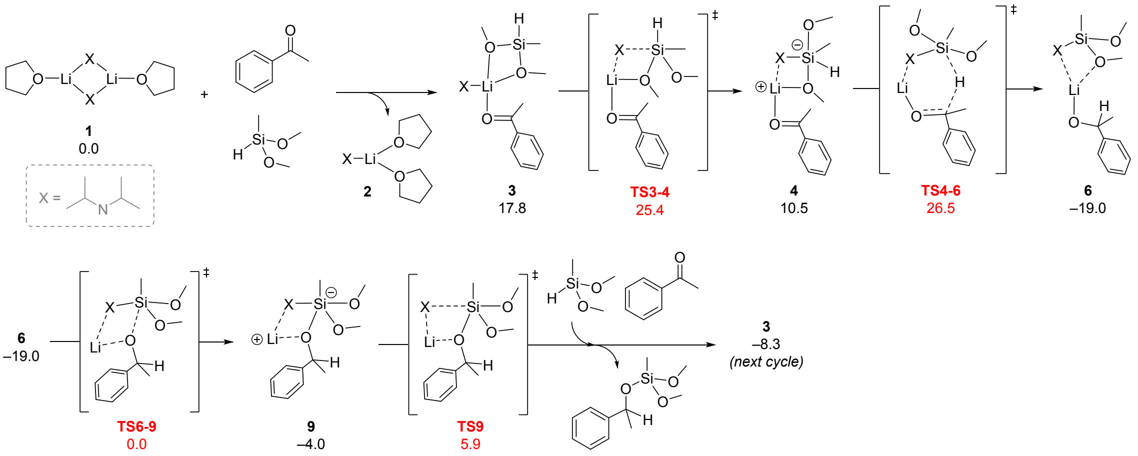
Table S1. Hydrosilylations performed in THF at 294 K using LiHMDS and TMEDA at different concentrations.

mol % TMEDA	0	0.125	3.75	100
Conversion after 20'	51.1	52.8	56.0	60.1

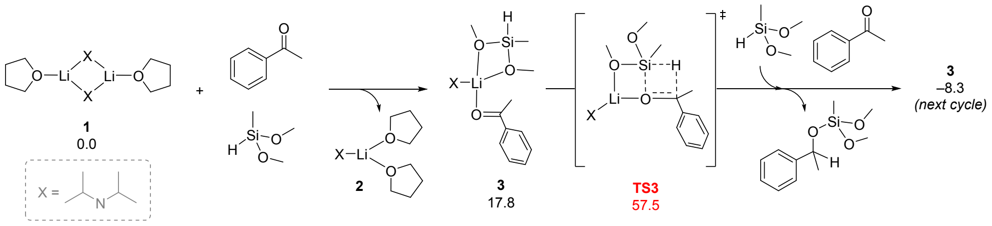
1. Computed reaction mechanisms. Mechanism **A** (Scheme S1) is discussed in the main text. Mechanism **B** (Scheme S2) proceeds through a similar pentacoordinated hydridosilicate using **3** as active species (in the absence of hydride **5**). Mechanism **C** (Scheme S3) involves a high-energy transition state where **3** is acting as Lewis acid.



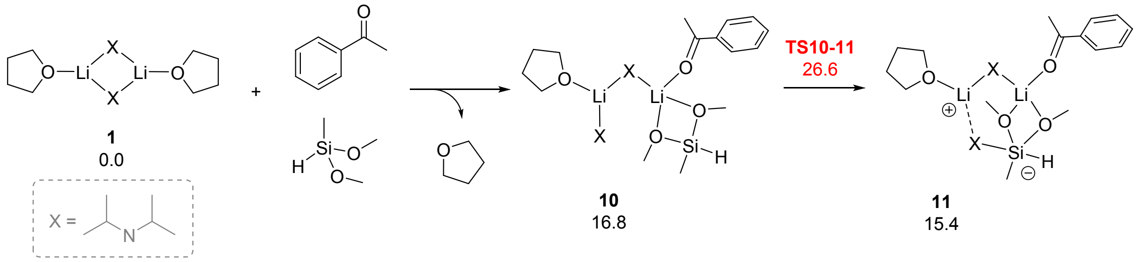
Scheme S1. Reaction mechanism (**A**) for the hydrosilylation of acetophenone via hydride **5**. Gibbs energies in THF in kcal mol^{-1}.



Scheme S2. Reaction mechanism (**B**) for the hydrosilylation of acetophenone via species **3**. Gibbs energies in THF in kcal mol^{-1}.



Scheme S3. Reaction mechanism (**C**) for the hydrosilylation of acetophenone via species **3**. Gibbs energies in THF in kcal mol^{-1}.



Scheme S4. Activation step via Li dimer **10**. Gibbs energies in THF in kcal mol^{-1}.

2. Cited Literature.

1. A. Raya-Barón, P. Oña-Burgos, A. Rodríguez-Diéguez and I. Fernández, *Organometallics*, 2018, **37**, 2682.