SUPPORTING INFORMATION

Lithium Hexamethyldisilazide Mediated Enolization of Acylated Oxazolidinones: Solvent, Cosolvent, and Isotope Effects on Competing Monomer- and Dimer-Based Pathways

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Chart 1. Substrates and intermediates. S-11

I. NMR spectroscopic studies

Figure 1. Plot of [**2**]/[**1**]$^{1/2}$ vs [THF]$_{total}$ for 0.10 M LiHMDS in hexane at –80 °C. S-12

Figure 2. Plot of [**2**]/[**1**]$^{1/2}$ vs [THF]$_{total}$ for 0.10 M LiHMDS in toluene at –80 °C. S-12

Figure 3. ^{1}H NMR spectrum of oxazolidinone **9** in $CDCl_3$. S-13

Figure 4. ^{13}C NMR spectrum of oxazolidinone **9** in $CDCl_3$. S-14

Figure 5. ^{1}H NMR spectrum of oxazolidinone **9**-d_2 in $CDCl_3$. S-15

Figure 6. ^{13}C NMR spectrum of oxazolidinone **9**-d_2 in $CDCl_3$. S-16

II. Mechanistic models

i. LiHMDS mechanistic model: Derivations and equations S-17

ii. Discussion of alternative models S-20

iii. Toluene-mediated rate suppression: Explicit molecular stabilization S-21

iv. Simulation of the LiHMDS mechanistic model using *Mathematica* S-22

v. Fitting in *IgorPro* S-26

vi. Alternative simulation strategy S-27

Chart 2. Transition structures and activation energies. S-32

III. Rate studies

Figure 7. Lithiation of oxazolidinone **9** with equimolar LiHMDS in neat THF at –78 °C showing the loss of **9**. S-34

Figure 8. Lithiation of 0.0050 M oxazolidinone **9** with 0.10 M LiHMDS in neat THF at –78 °C showing the loss of **9** (pseudo-first-order conditions). S-34

Table 1. k_{obsd} for the enolization of oxazolidinone **9** with 0.10 M LiHMDS at various concentrations of **9** in neat THF at –78 ºC. S-35

Table 2. k_{obsd} for the enolization of oxazolidinone **9** with 0.10 M LiHMDS at various concentrations of **9** and 1.0 M THF–hexane at –78 ºC. S-35

Figure 9. Plot of k_{obsd} vs [THF] for the enolization of 0.0050 M oxazolidinone **9** with 0.10 M LiHMDS at various concentrations of THF in hexane at –78 ºC. S-36

Figure 10. Plot of k_{obsd} vs [THF] for the enolization of 0.0050 M oxazolidinone **9** with 0.10 M LiHMDS at various concentrations of THF in toluene at –78 ºC. S-38

Figure 11. Plot of k_{obsd} vs [THF] for the enolization of 0.0050 M oxazolidinone **9** with 0.10 M LiHMDS at various concentrations of THF in toluene at –50 ºC. S-39

Figure 12. Plot of k_{obsd} vs [THF] for the enolization of 0.0050 M oxazolidinone **9** with 0.05 M LiHMDS at various concentrations of THF in toluene at –50 ºC. S-40

Figure 13. Plot of k_{obsd} vs [THF] for the enolization of 0.0050 M oxazolidinone **9** with 0.10 M LiHMDS at various concentrations of THF in cyclopentane at –78 ºC. S-41

Figure 14. Plot of k_{obsd} vs [toluene] for the enolization of 0.0050 M oxazolidinone **9** with 0.10 M LiHMDS at various concentrations of toluene in 3.1 M THF–hexane at –78 ºC. S-42

Figure 15. Lithiation of oxazolidinone **9**-d_2 with equimolar LiHMDS in neat THF at –78 °C showing the loss of **9**-d_2. S-43

Figure 16. Lithiation of 0.0050 M oxazolidinone **9**-d_2 with 0.10 M LiHMDS in neat THF at –78 °C showing the loss of **9**-d_2 (pseudo-first-order conditions). S-43

Figure 17. Plot of k_{obsd} vs [THF] for the enolization of 0.0050 M oxazolidinone **9**-d_2 with 0.10 M LiHMDS at various concentrations of THF in hexane at –78 ºC. S-44

Figure 18. Plot of k_{obsd} vs [THF] for the enolization of 0.0050 M oxazolidinone **9**-d_2 with 0.10 M LiHMDS at various concentrations of THF in hexane at –50 ºC. S-45

Figure 19. Plot of initial rates vs [THF] for the enolization of 0.0050 M oxazolidinone **9**-d_2 with 0.10 M LiHMDS at various concentrations of THF in toluene at –78 ºC. S-46

Figure 20. Plot of k_{obsd} vs [THF] for the enolization of 0.0050 M oxazolidinone **9**-d_2 with 0.10 M LiHMDS at various concentrations of THF in toluene at –50 ºC. S-47

Figure 21. Plot of k_{obsd} vs [LiHMDS] for the enolization of 0.0050 M oxazolidinone **9** at various concentrations of LiHMDS and 1.0 M THF–hexane at –78 ºC. S-48

Figure 22. Plot of k_{obsd} vs [LiHMDS] for the enolization of 0.0050 M oxazolidinone **9** at various concentrations of LiHMDS and 1.0 M THF–toluene at –78 ºC. S-49

Figure 23. Plot of k_{obsd} vs [LiHMDS] for the enolization of 0.0050 M oxazolidinone **9** at various concentrations of LiHMDS and 7.1 M THF–hexane at –78 ºC. S-50

Figure 24. Plot of k_{obsd} vs [LiHMDS] for the enolization of 0.0050 M oxazolidinone **9** at various concentrations of LiHMDS and 7.1 M THF–toluene at –78 ºC. S-51

Figure 25. Plot of k_{obsd} vs [LiHMDS] for the enolization of 0.0050 M oxazolidinone **9** at various concentrations of LiHMDS in neat THF at –78 ºC. S-52

Figure 26. Plot of k_{obsd} vs [LiHMDS] for the enolization of 0.0050 M oxazolidinone **9**-d_2 at various concentrations of LiHMDS and 1.0 M THF–toluene at –50 ºC. S-53

Figure 27. Plot of k_{obsd} vs [LiHMDS] for the enolization of 0.0050 M oxazolidinone **9**-d_2 at various concentrations of LiHMDS and 3.1 M THF–hexane at –78 ºC. S-54

Figure 28. Plot of k_{obsd} vs [LiHMDS] for the enolization of 0.0050 M oxazolidinone **9**-d_2 at various concentrations of LiHMDS in neat THF at –78 ºC. S-55

Figure 29. Plot of k_H/k_D vs [THF] for the enolization of 0.0050 M oxazolidinones **9**-d_2 and **9** with 0.10 M LiHMDS at various concentrations of THF in hexane at –78 ºC. S-56

Figure 30. Plot of k_H/k_D vs [THF] for the enolization of 0.0050 M oxazolidinones **9**-d_2 and **9** with 0.10 M LiHMDS at various S-57

concentrations of THF in toluene at –50 ºC.

Figure 31. Biphasic decay for the enolization of a 1:1 mixture of oxazolidinones **9**-d_2 and **9** (total concentration = 0.0050 M) with 0.10 M LiHMDS in neat THF at –78 ºC. S-58

Figure 32. Biphasic decay for the enolization of a 1:1 mixture of oxazolidinones **9**-d_2 and **9** (total concentration = 0.0050 M) with 0.10 M LiHMDS in 3.1 M THF–hexane at –78 ºC. S-58

Figure 33. Contributions of $\mathbf{[A_2S_3]^‡}$, $[AS]^‡$, $[A_2S_8]^‡$, and $[AS_8]^‡$ for the enolization of oxazolidinone **9** in THF–hexane at –78 °C from Figure 9. S-59

Figure 34. Contributions of $\mathbf{[A_2S_3]^‡}$, $[AS]^‡$, $[A_2S_8]^‡$, and $[AS_8]^‡$ for the enolization of oxazolidinone **9** in THF–toluene at –78 °C from Figure 10. S-60

Figure 35. Contributions of $\mathbf{[A_2S_3]^‡}$, $[AS]^‡$, $[A_2S_8]^‡$, and $[AS_8]^‡$ for the enolization of oxazolidinone **9**-d_2 in THF–hexane at –78 °C from Figure 17. S-61

Figure 36. Predicted LiHMDS order vs THF concentration for **9** and **9**-d_2. S-62

IV. Ground state computations

Table 3. Geometric coordinates and thermally corrected MP2 energies for tetrahydrofuran (THF). S-63

Table 4. Geometric coordinates and thermally corrected MP2 energies for LiHMDS disolvated cyclic dimer **1** with two THF. S-64

Table 5. Geometric coordinates and thermally corrected MP2 energies for LiHMDS trisolvated monomer **2** with three THF. S-66

Table 6. Geometric coordinates and thermally corrected MP2 energies for oxazolidinone **9**. S-68

Table 7. Geometric coordinates and thermally corrected MP2 energies for η^2-coordinated oxazolidinone **16** with one Li^+ and two THF. S-69

Table 8. Geometric coordinates and thermally corrected MP2 energies for η^2-coordinated oxazolidinone **17** with one Li^+ and three THF. S-71

V. Transition state computations

Table 9. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by AS (**11**; S-73

anti to benzyl group).

Table 10. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by AS (**11**; *syn* to benzyl group). S-75

Table 11. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by A_2S_3 (**12**; *anti* to benzyl group). S-77

Table 12. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by A_2S_3 (**12**; *syn* to benzyl group). S-79

Table 13. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by AS_3 (**13**; *anti* to benzyl group). S-81

Table 14. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by AS_3 (**13**; *syn* to benzyl group). S-83

Table 15. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by A_2S_2 (**15**; *anti* to benzyl group). S-85

Table 16. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by A_2S_2 (**15**; *syn* to benzyl group). S-87

Table 17. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by A_2S_4 (**18**; *anti* to benzyl group). S-89

Table 18. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by A_2S_4 (**18**; *syn* to benzyl group). S-91

Table 19. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by AS_2 (**19**; *anti* to benzyl group). S-93

Table 20. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by AS_2 (**19**; *syn* to benzyl group). S-95

VI. Intrinsic reaction coordinate (IRC) computations

Table 21. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by AS (**11**; *anti* to benzyl group). S-97

Table 22. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by AS (**11**; *anti* to benzyl group). S-99

Table 23. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by AS (**11**; *syn* to benzyl group). S-101

Table 24. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by AS (**11**; *syn* to benzyl group). S-103

Table 25. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by A_2S_3 (**12**; *anti* to benzyl group). S-105

Table 26. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by A_2S_3 (**12**; *anti* to benzyl group). S-107

Table 27. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by A_2S_3 (**12**; *syn* to benzyl group). S-109

Table 28. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by A_2S_3 (**12**; *syn* to benzyl group). S-111

Table 29. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by AS_3 (**13**; *anti* to benzyl group). S-113

Table 30. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by AS_3 (**13**; *anti* to benzyl group). S-115

Table 31. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by AS_3 (**13**; *syn* to benzyl group). S-117

Table 32. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by AS_3 (**13**; *syn* to benzyl group). S-119

Table 33. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by S-121

A_2S_2 (**15**; *anti* to benzyl group).

Table 34. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by A_2S_2 (**15**; *anti* to benzyl group). S-123

Table 35. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by A_2S_2 (**15**; *syn* to benzyl group). S-125

Table 36. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by A_2S_2 (**15**; *syn* to benzyl group). S-127

Table 37. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by A_2S_4 (**18**; *anti* to benzyl group). S-129

Table 38. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by A_2S_4 (**18**; *anti* to benzyl group). S-131

Table 39. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by A_2S_4 (**18**; *syn* to benzyl group). S-133

Table 40. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by A_2S_4 (**18**; *syn* to benzyl group). S-135

Table 41. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by AS_2 (**19**; *anti* to benzyl group). S-137

Table 42. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by AS_2 (**19**; *anti* to benzyl group). S-139

Table 43. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by AS_2 (**19**; *syn* to benzyl group). S-141

Table 44. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by AS_2 (**19**; *syn* to benzyl group). S-143

VII. Appendix A Revisiting the LiHMDS-mediated enolization of 2-methylcyclohexanone

Figure 37. Lithiation of 0.0050 M 2-methylcyclohexanone **3** with 0.10 M LiHMDS and 9.0 M THF–hexane at –78 °C showing the loss of **3** (pseudo-first-order conditions). S-146

Figure 38. Plot of k_{obsd} vs [THF] for the enolization of 0.0050 M 2-methylcyclohexanone **3** with 0.10 M LiHMDS at various concentrations of THF in hexane at –78 ºC. S-147

Figure 39. Plot of k_{obsd} vs [THF] for the enolization of 0.0050 M 2-methylcyclohexanone **3** with 0.10 M LiHMDS at various concentrations of THF in toluene at –78 ºC. S-148

Figure 40. Plot of k_{obsd} vs [LiHMDS] for the enolization of 0.0050 M 2-methylcyclohexanone **3** at various concentrations of LiHMDS and 2.0 M THF–hexane at –78 ºC. S-149

Figure 41. Plot of k_{obsd} vs [LiHMDS] for the enolization of 0.0050 M 2-methylcyclohexanone **3** at various concentrations of LiHMDS in neat THF at –78 ºC. S-150

Chart 3. Substrates, transition structures and activation energies. S-151

Table 45. Geometric coordinates and thermally corrected MP2 energies for 2-methylcyclohexanone **3** (Me = equatorial). S-152

Table 46. Geometric coordinates and thermally corrected MP2 energies for 2-methylcyclohexanone **3** (Me = axial). S-153

Table 47. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of 2-methylcyclohexanone **3** by AS_2 (**20**; Me = syn–equatorial). S-154

Table 48. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of 2-methylcyclohexanone **3** by AS_2 (**20**; Me = syn–axial). S-156

Table 49. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of 2-methylcyclohexanone **3** by AS_2 (**20**; Me = anti–equatorial). S-158

Table 50. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of 2-methylcyclohexanone **3** by AS_2 (**20**; Me = anti–axial). S-160

Table 51. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of 2-methylcyclohexanone **3** by AS_2 (**20**; Me = *syn*–equatorial). S-162

Table 52. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of 2- S-164

methylcyclohexanone **13** by AS_2 (**20**; Me = *syn*–equatorial).

Table 53. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of 2-methylcyclohexanone **3** by AS_2 (**20**; Me = *syn*–axial). S-166

Table 54. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of 2-methylcyclohexanone **3** by AS_2 (**20**; Me = *syn*–axial). S-168

Table 55. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of 2-methylcyclohexanone **3** by AS_2 (**20**; Me = *anti*–equatorial). S-170

Table 56. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of 2-methylcyclohexanone **3** by AS_2 (**20**; Me = *anti*–equatorial). S-172

Table 57. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of 2-methylcyclohexanone **3** by AS_2 (**20**; Me = *anti*–axial). S-174

Table 58. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of 2-methylcyclohexanone **3** by AS_2 (**20**; Me = *anti*–axial). S-176

VIII. Appendix B Computational studies of lithium hexamethyldisilazide solution structures

Chart 4. LiHMDS solution structures S-178

Table 59. Geometric coordinates and thermally corrected MP2 energies for LiHMDS unsolvated cyclic dimer **21**. S-179

Table 60. Geometric coordinates and thermally corrected MP2 energies for LiHMDS monosolvated cyclic dimer **22** with two THF. S-181

Table 61. Geometric coordinates and thermally corrected MP2 energies for LiHMDS monosolvated monomer **23** with one THF. S-183

Table 62. Geometric coordinates and thermally corrected MP2 energies for LiHMDS disolvated monomer **24** with two THF. S-184

Table 63. Geometric coordinates and thermally corrected MP2 energies for LiHMDS triple ion **25**. S-185

Table 64. Geometric coordinates and thermally corrected MP2 energies for hexamethyldisilazide anion **26**. S-186

Table 65. Geometric coordinates and thermally corrected MP2 energies for LiHMDS triple ion **27**. S-187

Table 66. Geometric coordinates and thermally corrected MP2 energies for hexamethyldisilazide anion **28**. S-189

Table 67. Geometric coordinates and thermally corrected MP2 energies for LiHMDS monosolvated open dimer **29** with one THF on a terminal Li. S-191

Table 68. Geometric coordinates and thermally corrected MP2 energies for LiHMDS disolvated open dimer **30** with two THF on a terminal Li. S-193

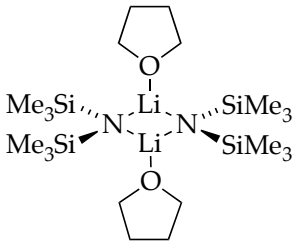
Table 69. Geometric coordinates and thermally corrected MP2 energies for LiHMDS trisolvated open dimer **31** with two THF on a terminal Li and one THF on the internal Li. S-195

IX. References S-197

X. Full reference 33 (Gaussian) S-197

Chart 1. Substrates and intermediates.

THF



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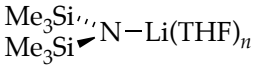

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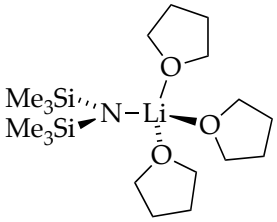

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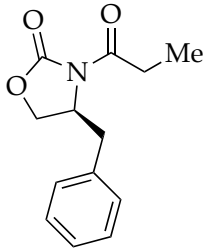

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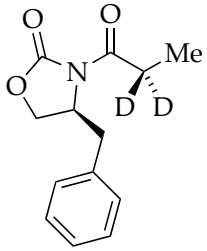

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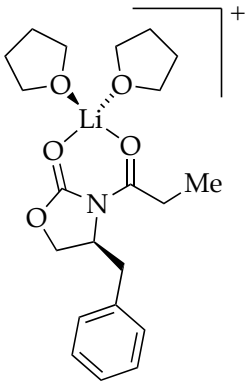

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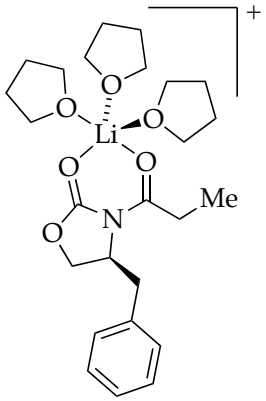


17

I. NMR spectroscopic studies

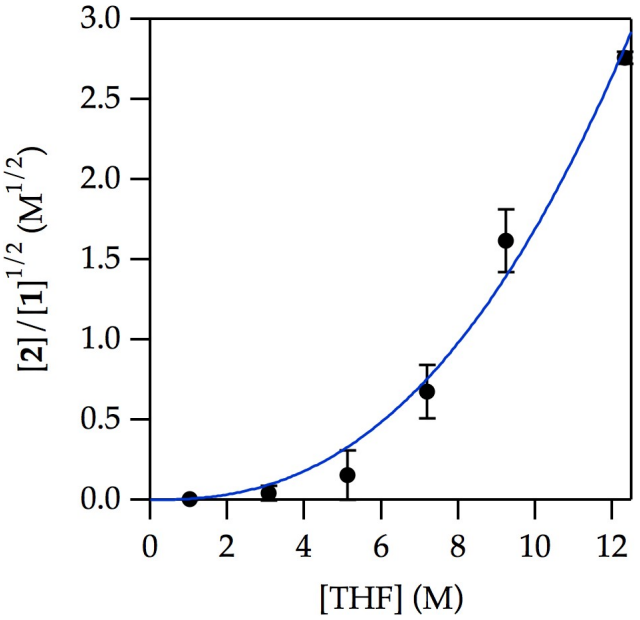


Figure 1. Plot of $[\mathbf{2}]/[\mathbf{1}]^{1/2}$ vs $[\mathrm{THF}]_{total}$ 0.10 M LiHMDS in hexane at –80 °C. The data are fit by nonlinear least-squares methods to the function $[\mathbf{2}]/[\mathbf{1}]^{1/2} = K_{eq}[\mathrm{THF}]^{(n-1)}$ ($K_{eq} = (6.0 \pm 3.9) \times 10^{-3}$, $n = 3.4 \pm 0.3$).

The THF dependence on the $[\mathbf{2}]/[\mathbf{1}]^{1/2}$ ratio has been studied in depth previously (pentane at –80 °C; $K_{eq} = (4.2 \pm 0.8) \times 10^{-3}$; $n = 3.6 \pm 0.2$).[S1]

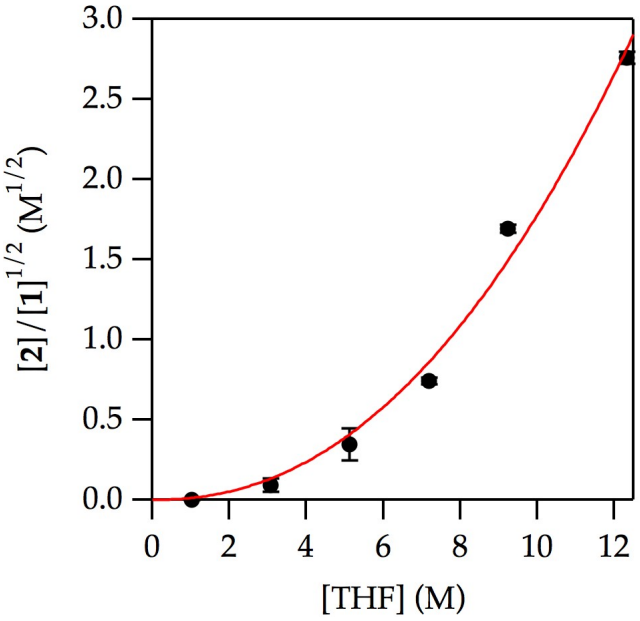


Figure 2. Plot of $[\mathbf{2}]/[\mathbf{1}]^{1/2}$ vs $[\mathrm{THF}]_{total}$ for 0.10 M LiHMDS in toluene at –80 °C. The data are fit by nonlinear least-squares methods to the function $[\mathbf{2}]/[\mathbf{1}]^{1/2} = K_{eq}[\mathrm{THF}]^{(n-1)}$ ($K_{eq} = (1.1 \pm 0.5) \times 10^{-2}$, $n = 3.2 \pm 0.2$).

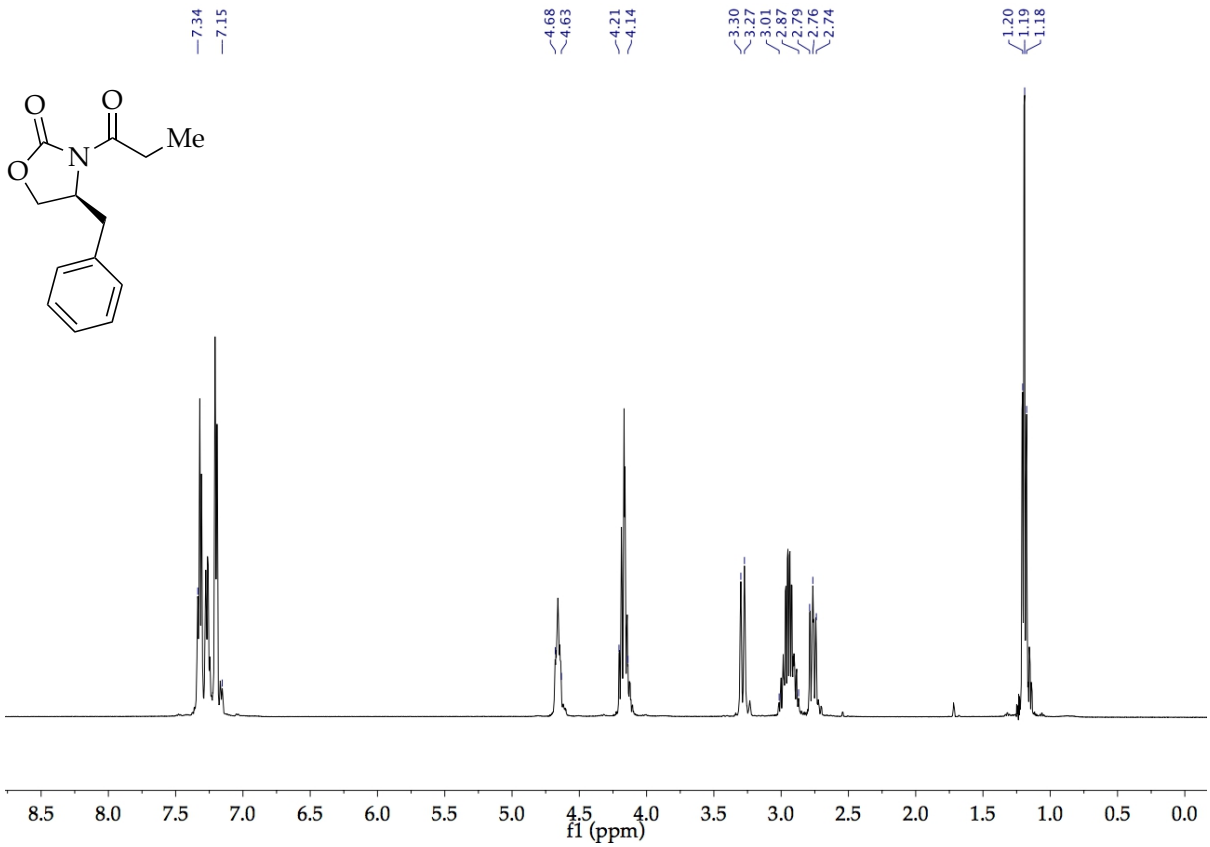


Figure 3. ^{1}H NMR spectrum of oxazolidinone **9** in $CDCl_3$.

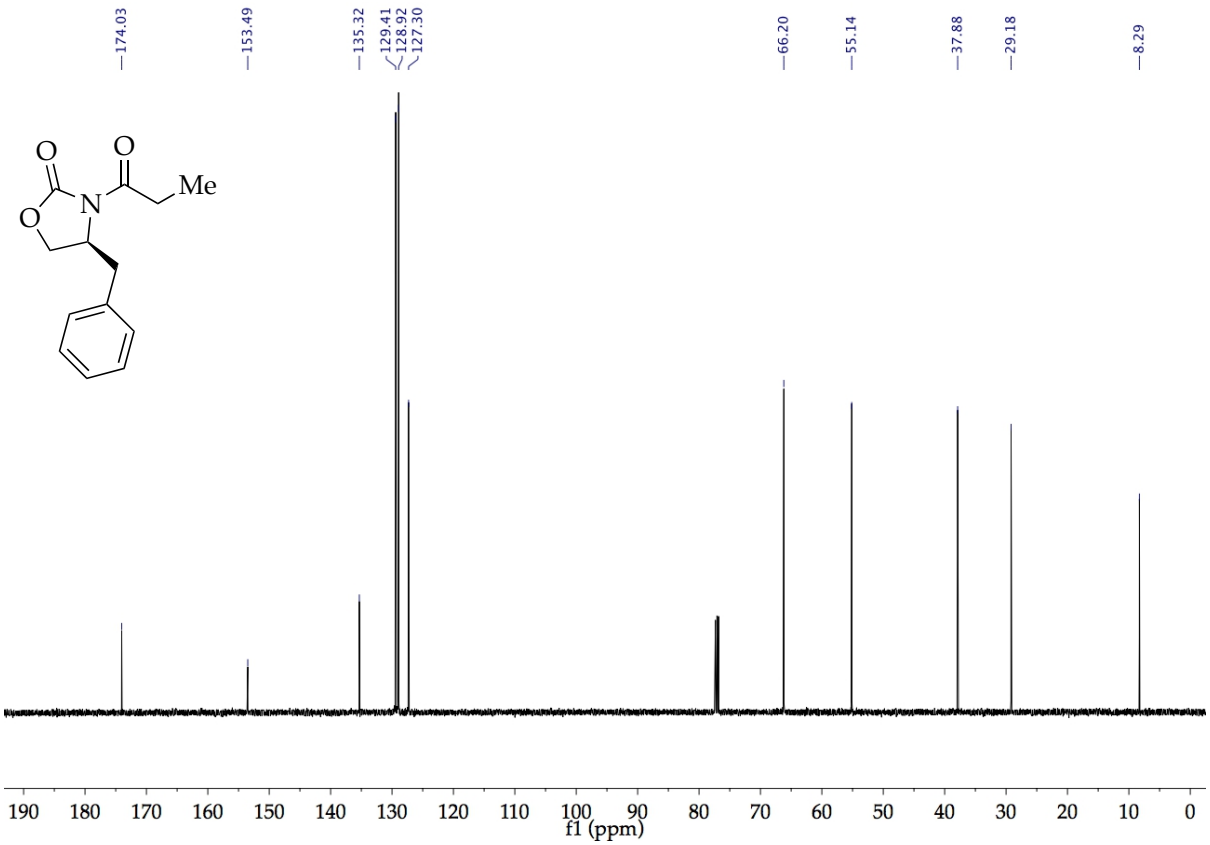


Figure 4. ^{13}C NMR spectrum of oxazolidinone **9** in $CDCl_3$.

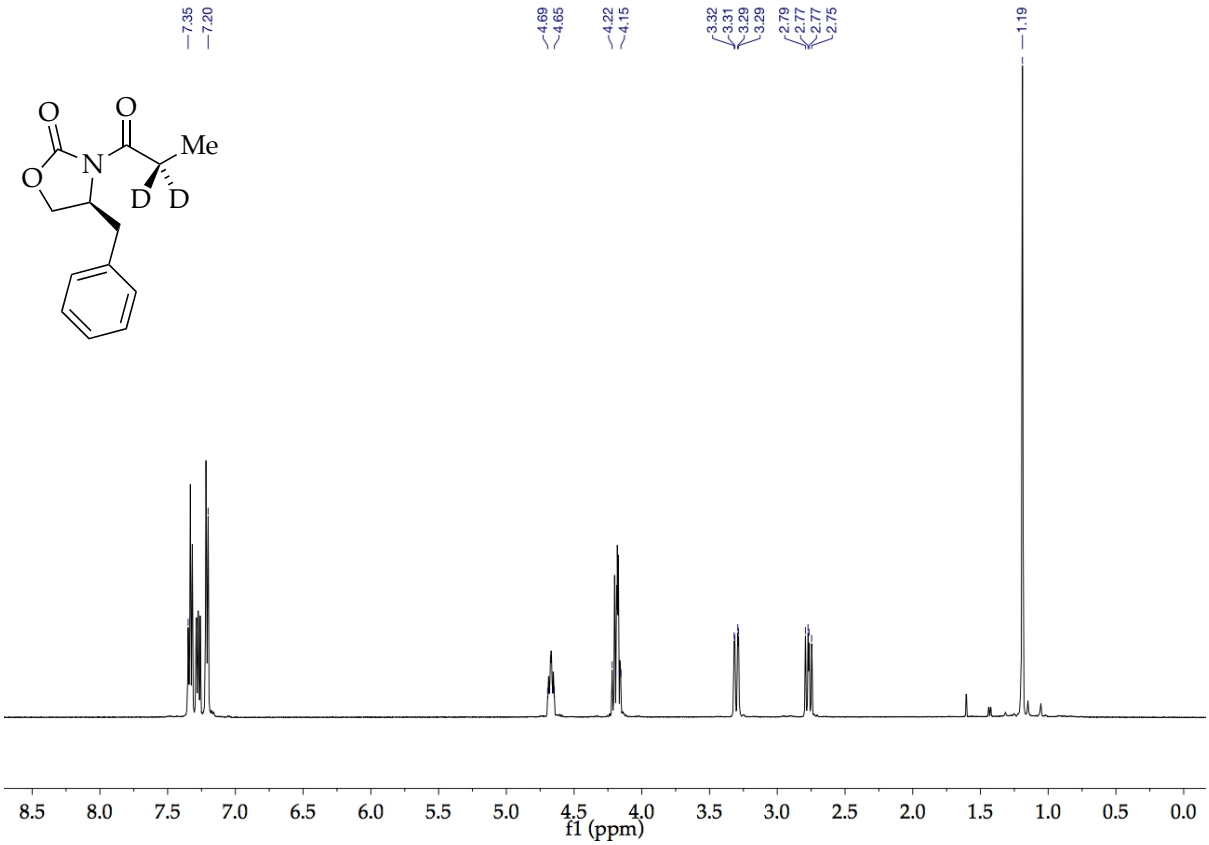


Figure 5. ^{1}H NMR spectrum of oxazolidinone **9**-d_2 in $CDCl_3$.

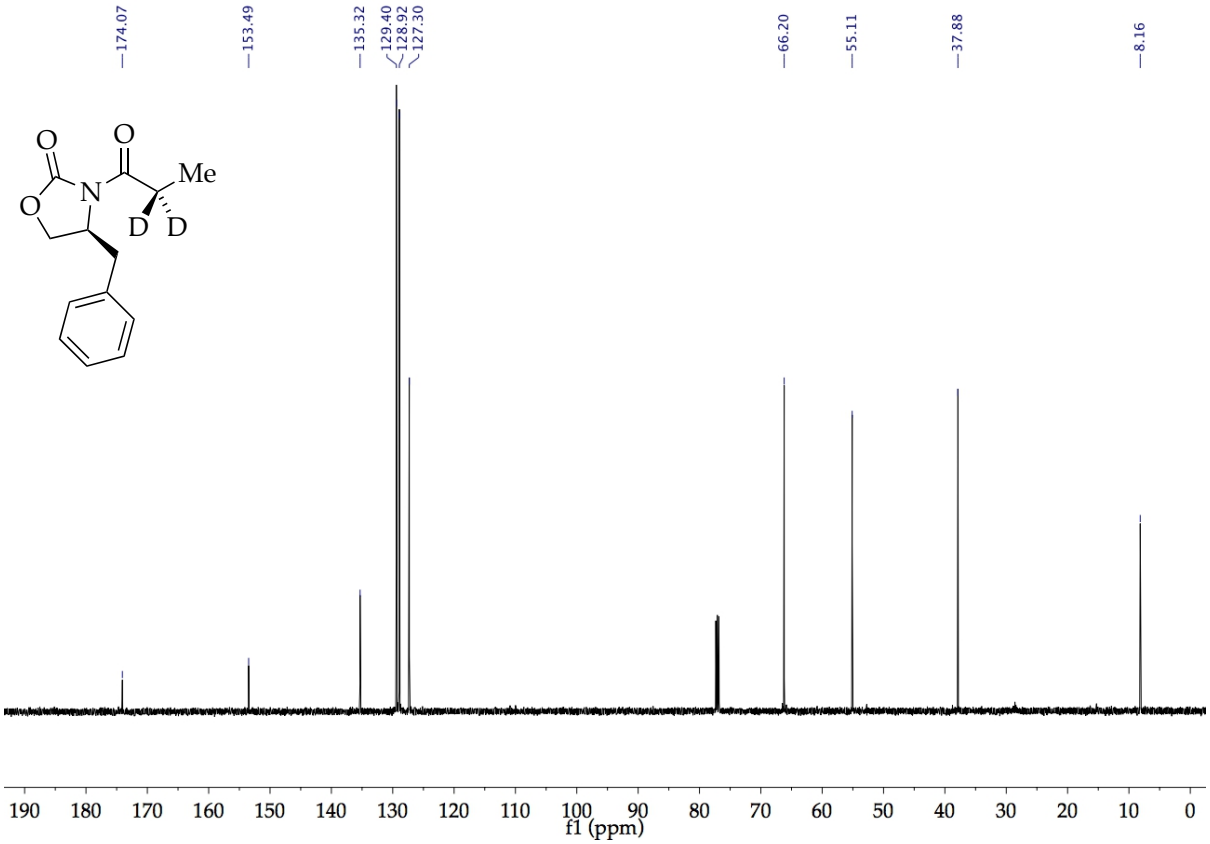
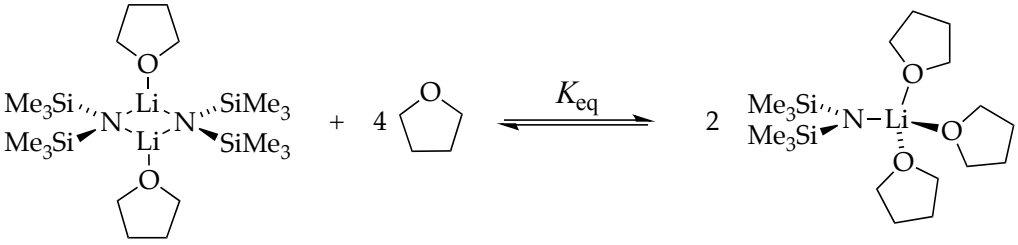


Figure 6. ^{13}C NMR spectrum of oxazolidinone **9**-d_2 in $CDCl_3$.

II. Mechanistic models

i. LiHMDS mechanistic model: Derivations and equations

To simplify mechanistic discussions, we introduce the following shorthand: A = a LiHMDS subunit, and S = THF. For example, A_2S_2 corresponds to disolvated LiHMDS dimer **1**, and AS_3 corresponds to trisolvated LiHMDS monomer **2**.



1 **2** (1)

Given $K_{eq} = [AS_3]^2 / \{[A_2S_2][S]^4\}$ and $2[A_2S_2] + [AS_3] = [A]_0$, one can solve for $[A_2S_2]$ as a function of [S]:

$$K_{eq} = \frac{[AS_3]^2}{[A_2S_2][S]^4} = \frac{([A]_0 - 2[A_2S_2])^2}{[A_2S_2][S]^4} \quad (2)$$

Rearranging,

$$4[A_2S_2]^2 - \left(4[A]_0 + K_{eq}[S]^4\right)[A_2S_2] + [A]_0^2 = 0 \quad (3)$$

Applying the quadratic equation to $[A_2S_2]$ gives:

$$[A_2S_2] = \frac{\left(4[A]_0 + K_{eq}[S]^4\right) - \sqrt{\left(4[A]_0 + K_{eq}[S]^4\right)^2 - 16[A]_0^2}}{8} = \frac{4[A]_0 + K_{eq}[S]^4 - \sqrt{K_{eq}}[S]^2\sqrt{K_{eq}[S]^4 + 8[A]_0}}{8} \quad (4)$$

In the case that many distinct aggregates can react at equilibrium and are exclusively non-observable, the following general formula applies:

$$[A_aS_s] \propto [A_2S_2]^{\frac{a}{2}}[S]^{s-a} \quad (5)$$

To prove the formula $\left[\mathrm{A}_a\mathrm{S}_s\right] \propto \left[\mathrm{A}_2\mathrm{S}_2\right]^{\frac{a}{2}}\left[\mathrm{S}\right]^{s-a}$ for non-observable species, suppose that $m\mathrm{X} + n\mathrm{Y} \underset{}{\overset{K}{\rightleftharpoons}} \mathrm{X}_m\mathrm{Y}_n$. Alternatively stated:

$$\begin{aligned} K &= \frac{\left[\mathrm{X}_m\mathrm{Y}_n\right]}{\left[\mathrm{X}\right]^m\left[\mathrm{Y}\right]^n} \\ &= \frac{\left[\mathrm{X}_m\mathrm{Y}_n\right]}{\left(\left[\mathrm{X}\right]_0 - m\left[\mathrm{X}_m\mathrm{Y}_n\right]\right)^m\left(\left[\mathrm{Y}\right]_0 - n\left[\mathrm{X}_m\mathrm{Y}_n\right]\right)^n} \\ &\approx \frac{\left[\mathrm{X}_m\mathrm{Y}_n\right]}{\left(\left[\mathrm{X}\right]_0\right)^m\left(\left[\mathrm{Y}\right]_0\right)^n} \end{aligned} \tag{6}$$

where $[\mathrm{X}_m\mathrm{Y}_n] << [\mathrm{X}]_0, [\mathrm{Y}]_0$ is invoked in the last step. Rearranging gives the generic form:

$$\left[\mathrm{X}_m\mathrm{Y}_n\right] \propto \left[\mathrm{X}\right]^m\left[\mathrm{Y}\right]^n \tag{7}$$

Assuming the activated complex $\mathrm{A}_a\mathrm{S}_s$•substrate reacts as the rate-limiting step—tantamount to enforcing that all preceding species are at equilibrium—we can write:

$$\begin{aligned} -\frac{\mathrm{d}\left[\mathrm{substrate}\right]}{\mathrm{d}t} &= k'\left[\mathrm{A}_a\mathrm{S}_s \bullet \mathrm{substrate}\right] \\ &= k\left(\left[\mathrm{A}_2\mathrm{S}_2\right]^{\frac{a}{2}}\left[\mathrm{S}\right]^{s-a}\left[\mathrm{substrate}\right]\right) \end{aligned} \tag{8}$$

Therefore, the most general expression that describes reaction out of multiple aggregates is:

$$\begin{aligned} -\frac{\mathrm{d}\left[\mathrm{substrate}\right]}{\mathrm{d}t} &= \left[\mathrm{substrate}\right]\sum_i k_i\left(\left[\mathrm{A}_2\mathrm{S}_2\right]^{\frac{a_i}{2}}\left[\mathrm{S}\right]^{s_i-a_i}\right) \\ &= \left[\mathrm{substrate}\right]\sum_i k_i\left(\left(\frac{4\left[\mathrm{A}\right]_0 + K_{\mathrm{eq}}\left[\mathrm{S}\right]^4 - \sqrt{K_{\mathrm{eq}}}\left[\mathrm{S}\right]^2\sqrt{K_{\mathrm{eq}}\left[\mathrm{S}\right]^4 + 8\left[\mathrm{A}\right]_0}}{8}\right)^{\frac{a_i}{2}}\left[\mathrm{S}\right]^{s_i-a_i}\right) \end{aligned} \tag{9}$$

where i indexes the individual reacting aggregate and k_i is the corresponding rate constant.

To account for the role of cosolvent we assume generically:

$$k_{\mathrm{obsd}} \propto f\left(\left[\mathrm{cosolvent}\right]\right) \propto f\left(12.3 - \left[\mathrm{S}\right]\right) \tag{10}$$

This term accounts for the deviation in THF-concentration dependencies observed when simply varying cosolvent. We hasten to add that f([cosolvent]) is necessarily a function of cosolvent and THF concentrations and settled upon the following form to empirically

describe, without attribution, the role of toluene-mediated rate suppression (*m* is different from the one in eq 6–7):

$$f([\mathrm{S}]) = \begin{cases} 1 \text{ for hexane} \\ \dfrac{a'[\text{toluene}]^m}{1 + b'[\text{toluene}]^m} + c \text{ for toluene} \end{cases} = \begin{cases} 1 \text{ for hexane} \\ \dfrac{a(12.3 - [\mathrm{S}])^m}{1 + b(12.3 - [\mathrm{S}])^m} + c \text{ for toluene} \end{cases} \tag{11}$$

By including constraints applied by the dependencies on THF and LiHMDS concentration, cosolvent choice, and influence of isotopic substitution, the subset of mechanisms required to *fit all data* reduces to four (eqs 12–15) that are described by eq 16. This is true for *all* fits on plots of k_{obsd} vs [S] for the enolization of oxazolidinones **9** and **9**-d_2.

$$A_2S_2 + S \rightleftharpoons A_2S_3 + \mathbf{9} \xrightarrow{k_8} [A_2S_3\bullet\mathbf{9}]^{\ddagger} \tag{12}$$

$$A_2S_2 + 6S \rightleftharpoons A_2S_8 + \mathbf{9} \xrightarrow{k_9} [A_2S_8\bullet\mathbf{9}]^{\ddagger} \tag{13}$$

$$\tfrac{1}{2}\, A_2S_2 \rightleftharpoons AS + \mathbf{9} \xrightarrow{k_{10}} [AS\bullet\mathbf{9}]^{\ddagger} \tag{14}$$

$$\tfrac{1}{2}\, A_2S_2 + 7S \rightleftharpoons AS_8 + \mathbf{9} \xrightarrow{k_{11}} [AS_8\bullet\mathbf{9}]^{\ddagger} \tag{15}$$

$$k_{obsd} = f([\mathrm{S}])\left\{\left(k_8[\mathrm{S}] + k_9[\mathrm{S}]^6\right)\left(\frac{4[\mathrm{A}]_0 + K_{eq}[\mathrm{S}]^4 - \sqrt{K_{eq}}[\mathrm{S}]^2\sqrt{8[\mathrm{A}]_0 + K_{eq}[\mathrm{S}]^4}}{8}\right) + \left(k_{10} + k_{11}[\mathrm{S}]^7\right)\left(\frac{4[\mathrm{A}]_0 + K_{eq}[\mathrm{S}]^4 - \sqrt{K_{eq}}[\mathrm{S}]^2\sqrt{8[\mathrm{A}]_0 + K_{eq}[\mathrm{S}]^4}}{8}\right)^{\frac{1}{2}}\right\} \tag{16}$$

$$\text{where } f([\mathrm{S}]) = \begin{cases} 1 \text{ for hexane} \\ \dfrac{a(12.3 - [\mathrm{S}])^m}{1 + b(12.3 - [\mathrm{S}])^m} + c \text{ for toluene} \end{cases}$$

Eq 16 is the general equation used for the unweighted least-squares fits on all the plots of k_{obsd} vs [S] for the enolization of oxazolidinones **9** and **9**-d_2.

ii. Discussion of alternative models

We entertained a variety of models to account for the simultaneously shifting LiHMDS orders, isotope effects, and cosolvent dependencies and summarize salient features in this section.

Model	THF dependence **9**	THF dependence **9**-d_2	Isotope Effect	LiHMDS order	Central flaw(s)
$[AS_2]^‡$	✓	✖	✖	✖	Inadequately describes LiHMDS orders at all THF concentrations
$[A_2S_3]^‡$	✓	✖	✖	✖	Does not accommodate rising rates at high THF for **9**-d_2
$[A_2S_3]^‡$, $[AS_n]^‡$	✓	✓	✖	✖	Does not account for drifting isotope effect at low THF
$[AS]^‡$, $[A_2S_3]^‡$, $[AS_n]^‡$	✓	✓	✓	✖	Does not adequately describe LiHMDS dimeric reactivity for **9**-d_2 in neat THF

iii. Toluene-mediated rate suppression: Explicit molecular stabilization

Although the model described above (section i) ascribes no molecular role for the influence of toluene as a cosolvent, to account for explicit stabilization of LiHMDS by toluene involves the following equilibria:

$$A_2S_2 + 4\ S \overset{K_{eq}}{\rightleftharpoons} 2\ AS_3$$

$$A_2S_2 + a\ Tol \overset{K_{Tol}{}^1}{\rightleftharpoons} A_2S_2Tol_a$$

$$AS_3 + b\ Tol \overset{K_{Tol}{}^2}{\rightleftharpoons} AS_3Tol_b$$

One can construct scenarios whereby A_2S_2 alone, not $A_2S_2Tol_a$, sources the reactive forms of LiHMDS while retaining a monomer/dimer ratio consistent with experiment. Although this scheme can successfully replicate the observed toluene suppression, the sigmoidal shape of the toluene suppression function is (in this model) inconsistent with the inverse-first-order dependence of k_{obsd} vs toluene at a fixed THF concentration. The only variations of explicit toluene coordination models that were consistent with all experiments entailed mechanism-dependent sensitivities to toluene. This was implemented by allowing reactivity out of both A_2S_2 and $A_2S_2Tol_a$. We elected to abandon these models due to the adequate description by an arbitrary toluene suppression function.

iv. Simulation of the LiHMDS mechanistic model using *Mathematica*

To construct a generic model for observable differentially solvated dimer and monomer sharing common subunits, consider the following equilibrium:

$$A_2S_n + m\ S \overset{K_{eq}}{\rightleftharpoons} 2\ AS_{(n+m)/2}$$

for which $K_{eq}=[AS_{(n+m)/2}]^2/\{[A_2S_n][S]^m\}$. Within this section, we cordon off *Mathematica* input into boxed tables for which the top line illustrates syntax and the bottom line contains an example of directly executable code. Optional parameters are demarcated by italics. To solve for $[A_2S_n]$ and $[AS_{(n+m)/2}]$ we execute the following expression in *Mathematica*:

Solve[{«equilibrium constant definition(s)», «mass balance expression(s)»}, {«list of components to solve for»}]
Solve[{keq == a^2/(a2*s^m), a0 == 2 a2 + a}, {a2, a}]

```
Solve[{keq == a^2/(a2*s^m), a0 == 2 a2 + a}, {a2, a}]
{{a2 -> 1/8 (4 a0 + keq s^m + Sqrt[keq] s^(m/2) Sqrt[8 a0 + keq s^m]), a -> 1/4 (-keq s^m - Sqrt[keq] s^(m/2) Sqrt[8 a0 + keq s^m])},
 {a2 -> 1/8 (4 a0 + keq s^m - Sqrt[keq] s^(m/2) Sqrt[8 a0 + keq s^m]), a -> 1/4 (-keq s^m + Sqrt[keq] s^(m/2) Sqrt[8 a0 + keq s^m])}}
```

We accept the second root corresponding to the physically realistic circumstance where all concentrations are positive. Given the verifiable assumption that all reactivity proceeds through rate-limiting proton transfer, we can construct a function that describes reactivity out of any number of differentially aggregated and solvated forms. For sake of example we consider the following mechanistic scenario:

$$A_2S_n + x\ S \rightleftharpoons A_2S_{n+x} + \textbf{substrate} \xrightarrow{k_a} [A_2S_{n+x}\bullet\textbf{substrate}]^{\ddagger}$$

$$1/2\ A_2S_n + y\ S \rightleftharpoons AS_{n/2+y} + \textbf{substrate} \xrightarrow{k_b} [AS_{n/2+y}\bullet\textbf{substrate}]^{\ddagger}$$

This scenario translates into the following *Mathematica* input:

«rate expression»/.«physically realistic solution affiliated with ground state»
(ka*s^x*a2+kb*s^y*a2^(1/2))/.{a2->1/8 (4 a0+keq s^m-Sqrt[keq] s^(m/2) Sqrt[8 a0+keq s^m]),a->1/4 (-keq s^m+Sqrt[keq] s^(m/2) Sqrt[8 a0+keq s^m])}

The expression above can be used directly to simulate the kinetic behavior affiliated with this highly generalized mechanism. As written, these inputs must be nested within a Manipulate command that assigns values for the remaining variables. For this system, an appropriate form is:

Manipulate[{«list of expression(s) to manipulate»}, «list of parameters to float according to the form {{«parameter»,«initial value»,"«parameter identifier»"},«low limit»,«high limit»}»]

(1) Solvent dependence:

Plot[«rate expression»,{s,«low limit»,«high limit»},*PlotRange->{«low limit»,«high limit»}*]
Plot[(ka*s^x*a2+kb*s^y*a2^(1/2))/.{a2->1/8 (4 a0+keq s^m-Sqrt[keq] s^(m/2) Sqrt[8 a0+keq s^m]),a->1/4 (-keq s^m+Sqrt[keq] s^(m/2) Sqrt[8 a0+keq s^m])},{s,0,1}]

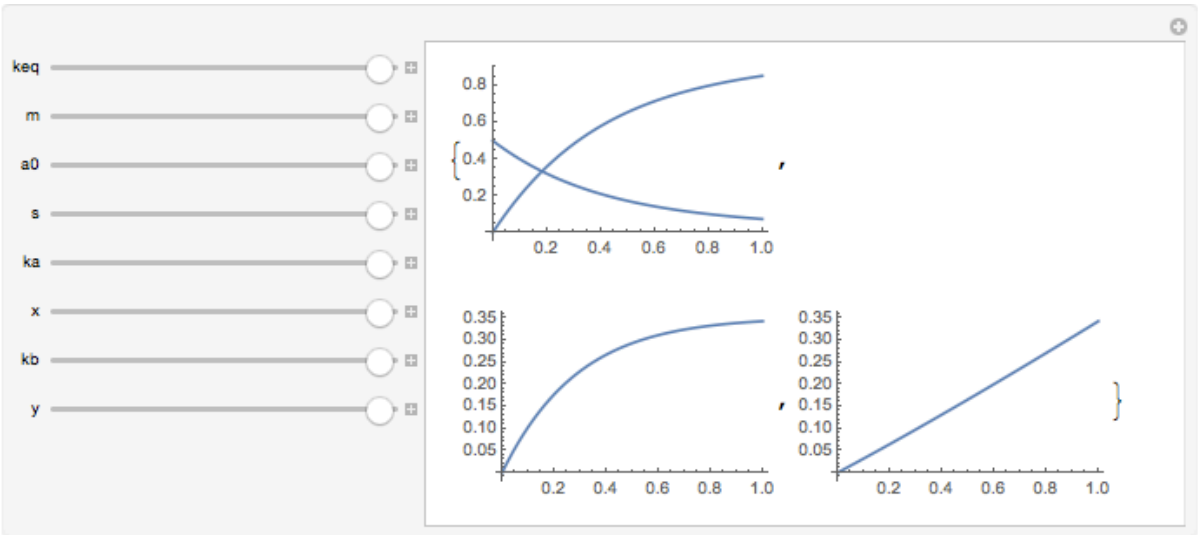
(2) Aggregating component dependence:

Plot[«rate expression»,{a0,«low limit»,«high limit»},*PlotRange->{«low limit»,«high limit»}, AxesLabel->{"«independent variable label»","«dependent variable label»"}*]
Plot[(ka*s^x*a2+kb*s^y*a2^(1/2))/.{a2->1/8 (4 a0+keq s^m-Sqrt[keq] s^(m/2) Sqrt[8 a0+keq s^m]),a->1/4 (-keq s^m+Sqrt[keq] s^(m/2) Sqrt[8 a0+keq s^m])},{a0,0,1}]

Nesting these within a Manipulate command gives the following:

```
Manipulate[{Plot[{a2,a}/.{a2->1/8 (4 a0+keq s^m-Sqrt[keq] s^(m/2) Sqrt[8 a0+keq s^m]),a->1/4 (-keq s^m+Sqrt[keq] s^(m/2) Sqrt[8 a0+keq s^m])},{s,0,1}],Plot[(ka*s^x*a2+kb*s^y*a2^(1/2))/.{a2->1/8 (4 a0+keq s^m-Sqrt[keq] s^(m/2) Sqrt[8 a0+keq s^m]),a->1/4 (-keq s^m+Sqrt[keq] s^(m/2) Sqrt[8 a0+keq s^m])},{s,0,1}],Plot[(ka*s^x*a2+kb*s^y*a2^(1/2))/.{a2->1/8 (4 a0+keq s^m-Sqrt[keq] s^(m/2) Sqrt[8 a0+keq s^m]),a->1/4 (-keq s^m+Sqrt[keq] s^(m/2) Sqrt[8 a0+keq s^m])},{a0,0,1}]},{{keq,10,"keq"},0,10},{{m,2,"m"},0,2},{{a0,1,"a0"},0,1},{{s,1,"s"},0,1},{{ka,1,"ka"},0,1},{{x,1,"x"},0,1},{{kb,1,"kb"},0,1},{{y,1,"y"},0,1}]
```

Executing the above code affords the following *Mathematica* output:



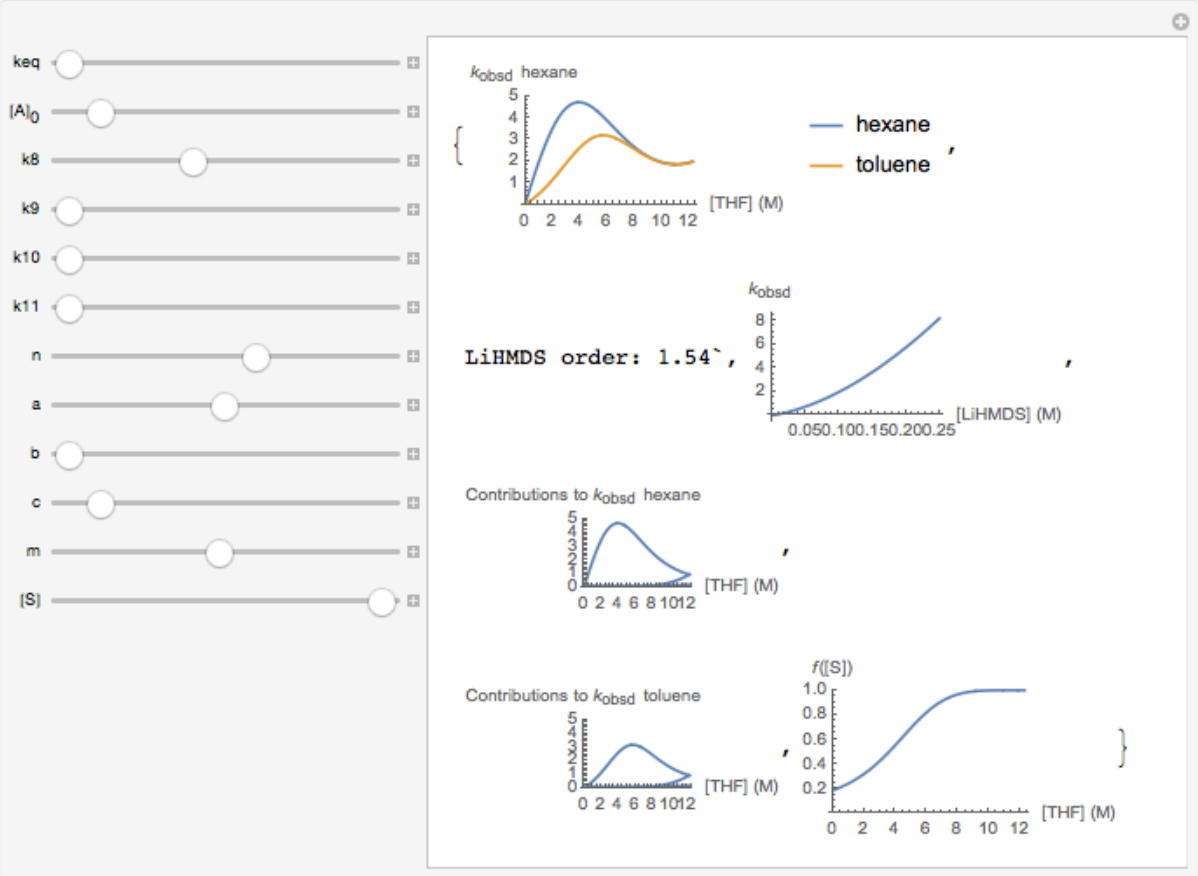
To extract a simulated order in a particular component, the FindFit function is applied to arrayed data according to the assumed power function $y = ax^b$.

FindFit[Table[{«component to vary»,«function to fit»},{«component to vary»,«increment»,«final value»,«increment»}],«v1»*«v2»^«v3»,{«v1»,«v3»},«v2»]
Solvent order, for example:

```
FindFit[Table[{s,(ka*s^x*a2+kb*s^y*a2^(1/2))/.{a2->1/8 (4 a0+keq s^m-Sqrt[keq] s^(m/2) Sqrt[8 a0+keq s^m]),a->1/4 (-keq s^m+Sqrt[keq] s^(m/2) Sqrt[8 a0+keq s^m])}},{s,0.005,1,0.005}],a*d^b,{a,b},d]
```

We construct the final mechanistic model in *Mathematica* using eq 16 and the rate data (*vide infra*) with the following input:

```
Manipulate[{Plot[{(k8*s*a2s2+k9*s^n*a2s2+k10*a2s2^0.5+k11*s^(n+1)*a2s2^0.5)/.a2s2->1/8 (4 a0+keq s^4-Sqrt[keq] s^2 Sqrt[8 a0+keq s^4]),(a (12.3-s)^m/(1+b*(12.3-s)^m)+c) (k8*s*a2s2+k9*s^n*a2s2+k10*a2s2^0.5+k11*s^(n+1)*a2s2^0.5)/.a2s2->1/8 (4 a0+keq s^4-Sqrt[keq] s^2 Sqrt[8 a0+keq s^4])},{s,0,12.3},PlotRange->{0,5},AxesLabel->{"[THF] (M)","\!\(\*SubscriptBox[StyleBox[\"k\",\nFontSlant->\"Italic\"], \(obsd\)]\) hexane"},PlotLegends->{"hexane","toluene"}],StringForm["LiHMDS order: ``",Round[bb/.FindFit[Table[
{a0,(k8*s*a2s2+k9*s^n*a2s2+k10*a2s2^0.5+k11*s^(n+1)*a2s2^0.5)/.a2s2->1/8 (4 a0+keq s^4-Sqrt[keq] s^2 Sqrt[8 a0+keq
s^4])},{a0,0.0005,0.25,0.0005}],aa*x^bb,{aa,bb},x],0.01]],Plot[(a (12.3-s)^m/(1+b*(12.3-s)^m)+c) (k8*s*a2s2+k9*s^n*a2s2+k10*a2s2^0.5+k11*s^(n+1)*a2s2^0.5)/.a2s2->1/8 (4 a0+keq s^4-Sqrt[keq] s^2 Sqrt[8 a0+keq s^4]),{a0,0,0.25},AxesLabel->{"[LiHMDS] (M)","\!\(\*SubscriptBox[StyleBox[\"k\",\nFontSlant->\"Italic\"], \(obsd\)]\)"}],Plot[{k8*s*a2s2,k9*s^n*a2s2,k10*a2s2^0.5,k11*s^(n+1)*a2s2^0.5}/.a2s2->1/8 (4 a0+keq s^4-Sqrt[keq] s^2 Sqrt[8 a0+keq s^4]),{s,0,12.3},PlotRange->{0,5},AxesLabel->{"[THF] (M)","Contributions to \!\(\*SubscriptBox[StyleBox[\"k\",\nFontSlant->\"Italic\"], \(obsd\)]\) hexane"}],Plot[(a (12.3-s)^m/(1+b*(12.3-s)^m)+c)
{k8*s*a2s2,k9*s^n*a2s2,k10*a2s2^0.5,k11*s^(n+1)*a2s2^0.5}/.a2s2->1/8 (4 a0+keq s^4-Sqrt[keq] s^2 Sqrt[8 a0+keq s^4]),{s,0,12.3},PlotRange->{0,5},AxesLabel->{"[THF] (M)","Contributions to \!\(\*SubscriptBox[StyleBox[\"k\",\nFontSlant->\"Italic\"], \(obsd\)]\) toluene"}],Plot[(a (12.3-s)^m/(1+b*(12.3-s)^m)+c),{s,0,12.3},PlotRange->{0,1},AxesLabel->{"[THF] (M)","\!\(\*StyleBox[\"f\",\nFontSlant->\"Italic\"]\)\!\(\*StyleBox[\"(\",\nFontSlant->\"Italic\"]\)[S])"}]},{{keq,0.00022,"keq"},0,1},{{a0,0.1,"[A\!\(\*SubscriptBox[\(]\), \(0\)]\)"},0,1},{{k8,39.6,"k8"},0,100},{{k9,2.5*10^-5,"k9"},0,100},{{k10,0.2,"k10"},0,100},{{k11,5*10^-7,"k11"},0,100},{{n,6,"n"},0,10},{{a,-0.0000319,"a"},-1,1},{{b,0.0000336,"b"},0,1},{{c,1,"c"},0,10},{{m,4.81,"m"},0,10},{{s,12.3,"[S]"},0,12.3}]
```

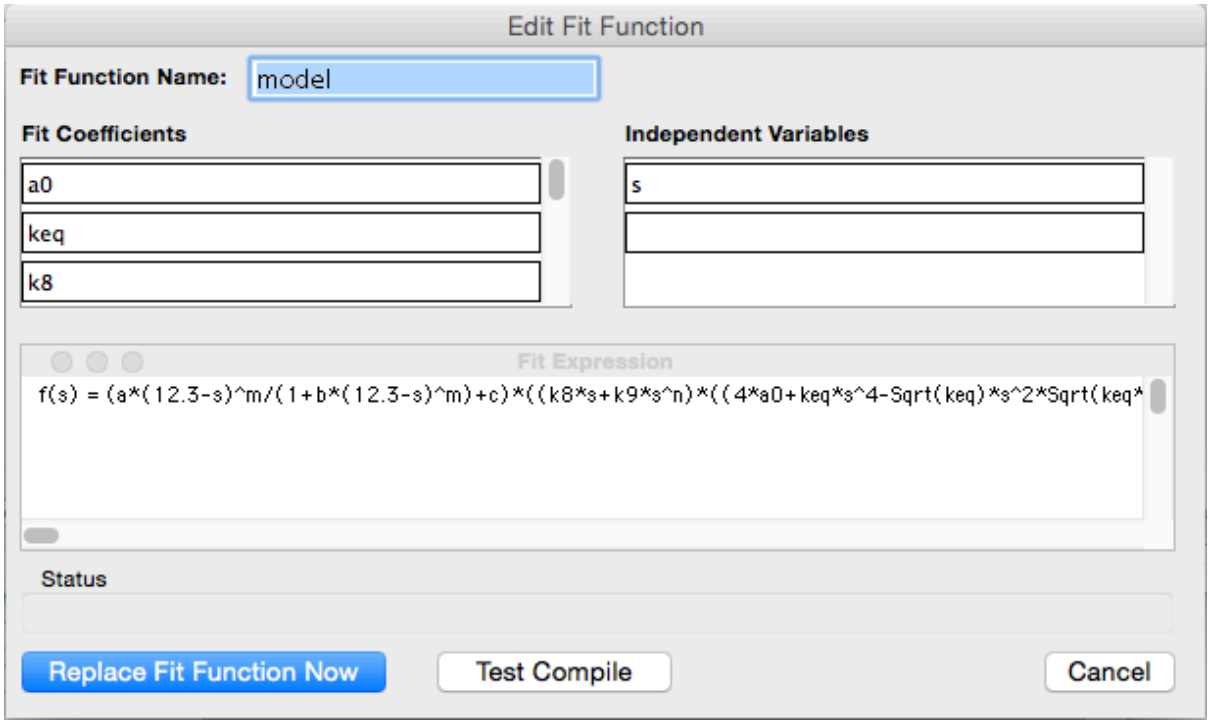


Note that the complexity in this system originates not from the ground state variation but instead in the number of transition states. One can similarly construct more elaborate schemes wherein multiple ground states are accessible.

v. Fitting in *IgorPro*

We illustrate eq 16 —ready to paste into *IgorPro*—for rate data analysis using unweighted least-squares fits:

```
f(s) = (a*(12.3-s)^m/(1+b*(12.3-s)^m)+c)*((k8*s+k9*s^n)*((4*a0+keq*s^4-
Sqrt(keq)*s^2*Sqrt(keq*s^4+8*a0))/8)+(k10+k11*s^(n+1))*((4*a0+keq*s^4-
Sqrt(keq)*s^2*Sqrt(keq*s^4+8*a0))/8)^0.5)
```



vi. Alternative Simulation Strategy

Although the description considered above is correct, it cannot readily extend to pairwise equilibrating systems of higher aggregates (*i.e.* pentamer/trimer). To appreciate where the problem lies consider the following equilibrium:

$$\mathrm{A}_m\mathrm{S}_n + (my/x–n)\ \mathrm{S} \underset{}{\overset{K_{\mathrm{eq}}}{\rightleftharpoons}} m/x\ \mathrm{A}_x\mathrm{S}_y$$

Converting this expression to an equilibrium constant definition (and accounting for the mass balance $[\mathrm{A}]_0 = m[\mathrm{A}_m\mathrm{S}_n] + x[\mathrm{A}_x\mathrm{S}_y]$) follows:

$$K_{\mathrm{eq}} = \frac{\left[\mathrm{A}_x\mathrm{S}_y\right]^{\frac{m}{x}}}{\left[\mathrm{A}_m\mathrm{S}_n\right]\left[\mathrm{S}\right]^{\frac{my}{x}-n}} = \frac{\left[\mathrm{A}_x\mathrm{S}_y\right]^{\frac{m}{x}}}{\left(\frac{\left[\mathrm{A}\right]_0}{m} - \frac{x\left[\mathrm{A}_x\mathrm{S}_y\right]}{m}\right)\left[\mathrm{S}\right]^{\frac{my}{x}-n}}$$

Rearranging the expression above gives:

$$\frac{\left[\mathrm{A}_x\mathrm{S}_y\right]^{\frac{m}{x}}}{K_{\mathrm{eq}}\left[\mathrm{S}\right]^{\frac{my}{x}-n}} + \frac{x\left[\mathrm{A}_x\mathrm{S}_y\right]}{m} - \frac{\left[\mathrm{A}\right]_0}{m} = 0$$

Extracting the roots affiliated with this equation is impossible for $m/x \geq 5$; selecting appropriate closed-form roots that are analytically tractable for other cases is often prohibitive. An alternative strategy is to differentiate the expression above with respect to $[\mathrm{A}]_0$:

$$\frac{m\left[\mathrm{A}_x\mathrm{S}_y\right]^{\frac{m}{x}-1}}{xK_{\mathrm{eq}}\left[\mathrm{S}\right]^{\frac{my}{x}-n}}\frac{\mathrm{d}\left[\mathrm{A}_x\mathrm{S}_y\right]}{\mathrm{d}\left[\mathrm{A}\right]_0} + \frac{x}{m}\frac{\mathrm{d}\left[\mathrm{A}_x\mathrm{S}_y\right]}{\mathrm{d}\left[\mathrm{A}\right]_0} - \frac{1}{m} = 0$$

Continue by isolating $\mathrm{d}[\mathrm{A}_x\mathrm{S}_y]/\mathrm{d}[\mathrm{A}]_0$:

$$\frac{\mathrm{d}\left[\mathrm{A}_x\mathrm{S}_y\right]}{\mathrm{d}\left[\mathrm{A}\right]_0} = \frac{1}{\frac{m^2\left[\mathrm{A}_x\mathrm{S}_y\right]^{\frac{m}{x}-1}}{xK_{\mathrm{eq}}\left[\mathrm{S}\right]^{\frac{my}{x}-n}} + x}$$

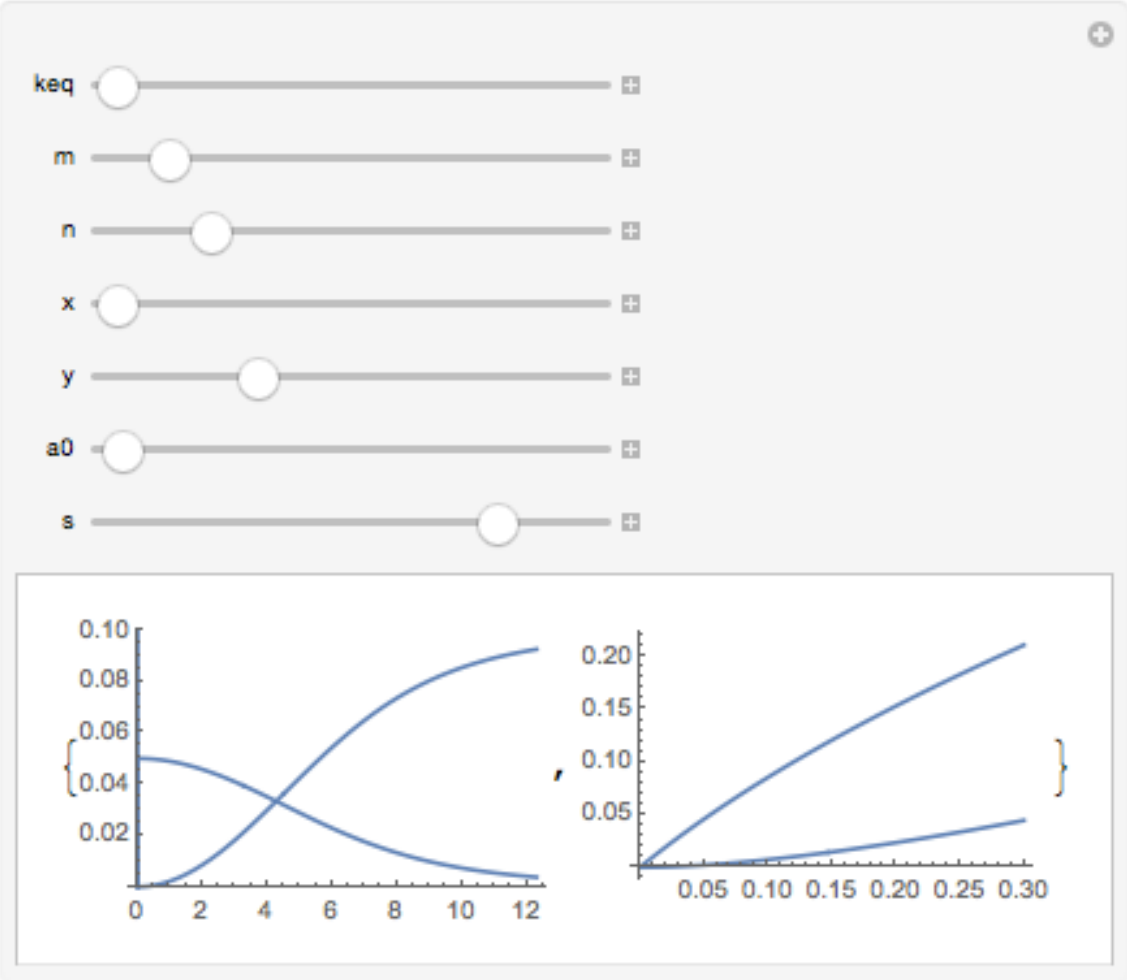
The differential equation above describing $[A_xS_y]$ is well suited for numerical solution (with the trivial boundary condition $[A_xS_y](0) = 0$) that can be implemented either with NDSolveValue or with an explicit finite-difference sum.

Using NDSolveValue to generate the ordered set $\{[A_mS_n],[A_xS_y]\}$ requires the following code:

```
NDSolveValue[{y'[v]==1/(m^2*y[v]^(m/x-1)/(x*keq*s^(m*y/x-n))+x),y[0]==0},{a0/m-x*y[a0]/m,y[a0]},{v,0,10},MaxSteps->1000]
```

A visually tractable output of $[A_mS_n]$ and $[A_xS_y]$ vs $[A]_0$ and $[S]$ can be achieved with the following code:

```
Manipulate[{Plot[NDSolveValue[{z'[v]==1/(m^2*z[v]^(m/x-1)/(x*keq*s^(m*y/x-n))+x),z[0]==0},{a0/m-x*z[a0]/m,z[a0]},{v,0,10},MaxSteps->5000],{s,0,12.3},PlotRange->{0,a0}],Plot[NDSolveValue[{z'[v]==1/(m^2*z[v]^(m/x-1)/(x*keq*s^(m*y/x-n))+x),z[0]==0},{a0/m-x*z[a0]/m,z[a0]},{v,0,10},MaxSteps->5000],{a0,0,0.3}]},{{keq,0.0001,"keq"},0.0001,10},{{m,2,"m"},1,10},{{n,2,"n"},0,10},{{x,1,"x"},1,10},{{y,3,"y"},0,10},{{a0,0.1,"a0"},0,10},{{s,10,"s"},0,12.3}]
```



One may achieve a similar outcome employing (sometimes at greater computational cost) finite-difference summation:

```
t=0;Do[t=t+i*1/(m^2*t^(m/x-1)/(x*keq*s^(m*y/x-n))+x),a0/i];t//N
```

The above expression approximates the value of $[A_xS_y]$ by executing the discrete sum shown below (i is the increment step size and x is the index of summation):

$$\left[\mathrm{A}_x\mathrm{S}_y\right]_z = \sum_{z=1}^{[\mathrm{A}]_0/i} \frac{i}{\dfrac{m^2\left[\mathrm{A}_x\mathrm{S}_y\right]_{z-1}^{\frac{m}{x}-1}}{xK_{\mathrm{eq}}\left[\mathrm{S}\right]^{\frac{my}{x}-1}} + x}$$

Casting the above into executable *Mathematica* code entails the following:

```
Manipulate[{Plot[{a0/m-x/m(t=0;Do[t=t+i*1/(m^2*t^(m/x-1)/(x*keq*s^(m*y/x-
n))+x),a0/i];t//N),t=0;Do[t=t+i*1/(m^2*t^(m/x-1)/(x*keq*s^(m*y/x-
n))+x),a0/i];t//N},{s,0,12.3},PlotRange->{0,a0}],Plot[{a0/m-
x/m(t=0;Do[t=t+i*1/(m^2*t^(m/x-1)/(x*keq*s^(m*y/x-
n))+x),a0/i];t//N),t=0;Do[t=t+i*1/(m^2*t^(m/x-1)/(x*keq*s^(m*y/x-
n))+x),a0/i];t//N},{a0,0,0.3}]},{{keq,0.0001,"keq"},0.0001,10},{{m,2,"m"},1,10},{{n,2,"n"
},0,10},{{x,1,"x"},1,10},{{y,3,"y"},0,10},{{a0,0.1,"a0"},0,10},{{s,10,"s"},0,12.3},{{i,0.001
,"i"},0,0.1}]
```

One can implement the above sum in *Microsoft Excel* according to the following VBA macro:

```
Sub SolveSystem()
'
' SolveSystem Macro
Range("F1").Select
   ActiveCell.FormulaR1C1 = "=R[5]C[2]/R[3]C[2]"
   Range("F2").Select
   ActiveCell.FormulaR1C1 = _
      "=R[4]C[2]/(RC[2]^2*R[-1]C^(RC[2]/R[2]C[2]-1)/(R[2]C[2]*R[-1]C[2]*RC[-
4]^(RC[2]*R[3]C[2]/R[2]C[2]-R[1]C[2]))+R[2]C[2])+R[-1]C"
   Range("F3").Select

   Dim i
   Range("J6").Select
   ActiveCell.FormulaR1C1 = "=ROUNDDOWN(R[-4]C[-9]/RC[-2],0)"
   Dim j

   j = ActiveCell.Value - 2

   For i = 1 To j
   Range("F2").Select
```

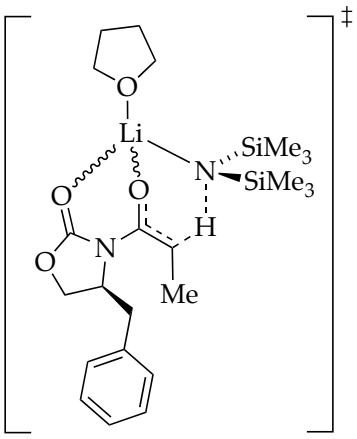
```
    Application.CutCopyMode = False
    Selection.Copy
    Range("F1").Select
    Selection.PasteSpecial Paste:=xlValues, Operation:=xlNone, SkipBlanks:= _
        False, Transpose:=False
    Range("D5").Select
    Next i

    Range("F2").Select
    Application.CutCopyMode = False
    Selection.Copy
    Range("E2").Select
    Selection.PasteSpecial Paste:=xlValues, Operation:=xlNone, SkipBlanks:= _
        False, Transpose:=False
    Range("D2").Select
    Application.CutCopyMode = False
    ActiveCell.FormulaR1C1 = "=RC[-3]/RC[4]-R[2]C[4]*RC[1]/RC[4]"
    Range("F1:F2").Select
    Range("F2").Activate
    ActiveCell.FormulaR1C1 = ""
    Range("F1").Select
    ActiveCell.FormulaR1C1 = ""
    Range("J6").Select
    ActiveCell.FormulaR1C1 = ""
    Range("E3").Select
End Sub

Sub CreateSheet()
'
' CreateSheet Macro
'
    Range("A1").Select
    Application.CutCopyMode = False
    ActiveCell.FormulaR1C1 = "[A]0"
    Range("B1").Select
    ActiveCell.FormulaR1C1 = "[S]"
    Range("D1").Select
    ActiveCell.FormulaR1C1 = "[AmSn]"
    Range("E1").Select
    ActiveCell.FormulaR1C1 = "[AxSy]"
    Range("G1").Select
    ActiveCell.FormulaR1C1 = "Keq"
    Range("A2").Select
    ActiveCell.FormulaR1C1 = "0.1"
    Range("B2").Select
    ActiveCell.FormulaR1C1 = "2"
    Range("G2").Select
    ActiveCell.FormulaR1C1 = "m"
    Range("G3").Select
```

```
    ActiveCell.FormulaR1C1 = "n"
    Range("G4").Select
    ActiveCell.FormulaR1C1 = "x"
    Range("G5").Select
    ActiveCell.FormulaR1C1 = "y"
    Range("G6").Select
    ActiveCell.FormulaR1C1 = "increment"
    Range("H1").Select
    ActiveCell.FormulaR1C1 = "0.0001"
    Range("H2").Select
    ActiveCell.FormulaR1C1 = "2"
    Range("H3").Select
    ActiveCell.FormulaR1C1 = "2"
    Range("H4").Select
    ActiveCell.FormulaR1C1 = "1"
    Range("H5").Select
    ActiveCell.FormulaR1C1 = "3"
    Range("H6").Select
    ActiveCell.FormulaR1C1 = "0.001"
    Range("A1").Select
End Sub
```

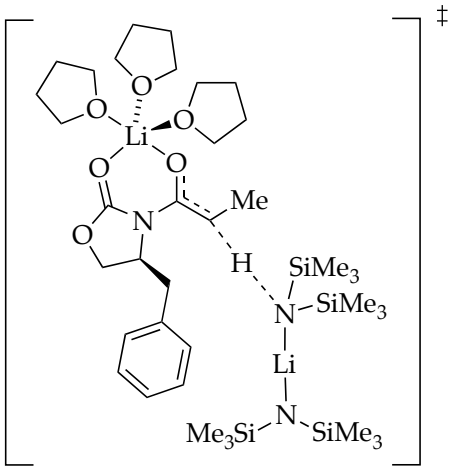
Chart 2. Transition structures and activation energies.



11

[AS•**9**]‡

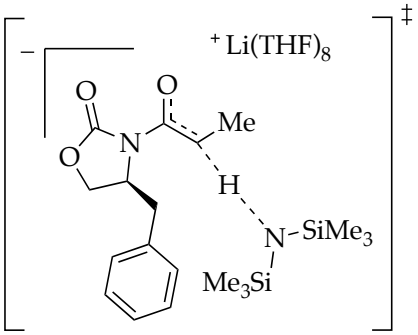
$\Delta G^{‡}_{anti}$ = 16.9 kcal/mol
$\Delta G^{‡}_{syn}$ = 19.4 kcal/mol



12

[A_2S_3•**9**]‡

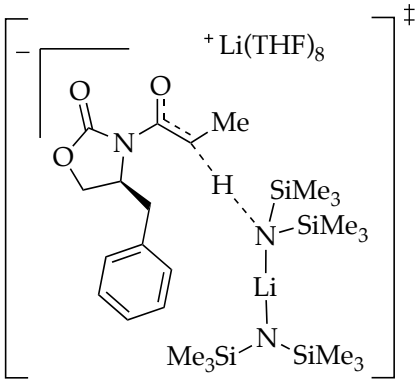
$\Delta G^{‡}_{anti}$ = 17.2 kcal/mol
$\Delta G^{‡}_{syn}$ = 22.8 kcal/mol



13

[AS_8•**9**]‡

$\Delta G^{‡}_{anti}$ = Not determined [a]
$\Delta G^{‡}_{syn}$ = Not determined [a]



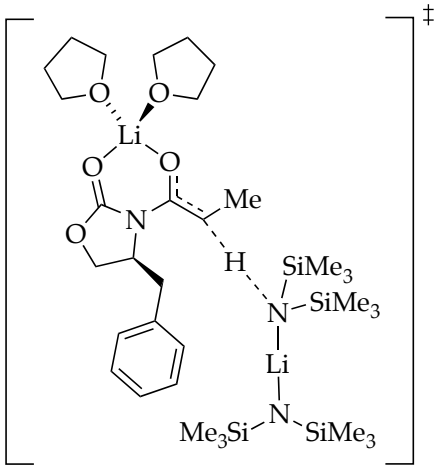
14

[A_2S_8•**9**]‡

$\Delta G^{‡}_{anti}$ = Not determined [a]
$\Delta G^{‡}_{syn}$ = Not determined [a]

[a] The anionic fragment of the transition structures was studied using $^{+}Li(THF)_{3–4}$. Transition (and ground state) structures containing $^{+}Li(THF)_{n\geq5}$ do not converge; these have a bias towards tetrahedral Li. However, there is precedence for hypersolvated ^{+}Li in the literature, including crystallographic and rate data.[S2] Our data strongly supports octasolvated transition structures **13** and **14** (*vide infra*).

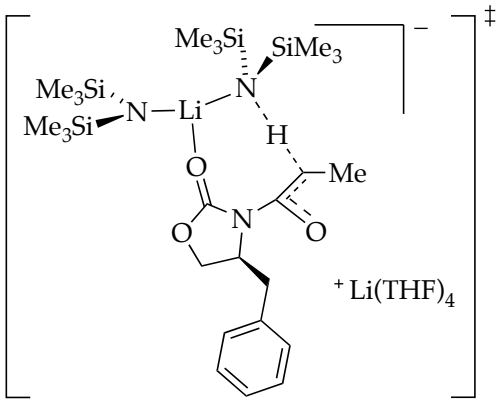
Other potential transition structures and activation energies:



15

$[A_2S_2•\mathbf{9}]^‡$

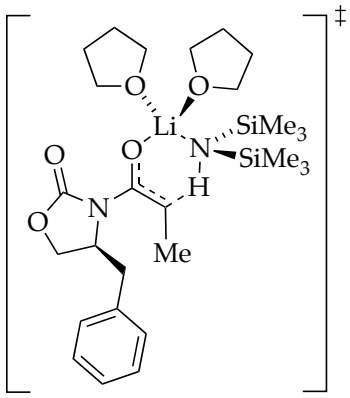
$\Delta G^‡_{anti}$ = 21.9 kcal/mol
$\Delta G^‡_{syn}$ = 26.8 kcal/mol



18

$[A_2S_4•\mathbf{9}]^‡$

$\Delta G^‡_{anti}$ = 32.5 kcal/mol
$\Delta G^‡_{syn}$ = 29.4 kcal/mol



19

$[AS_2•\mathbf{9}]^‡$

$\Delta G^‡_{anti}$ = 17.9 kcal/mol
$\Delta G^‡_{syn}$ = 18.3 kcal/mol

III. Rate studies

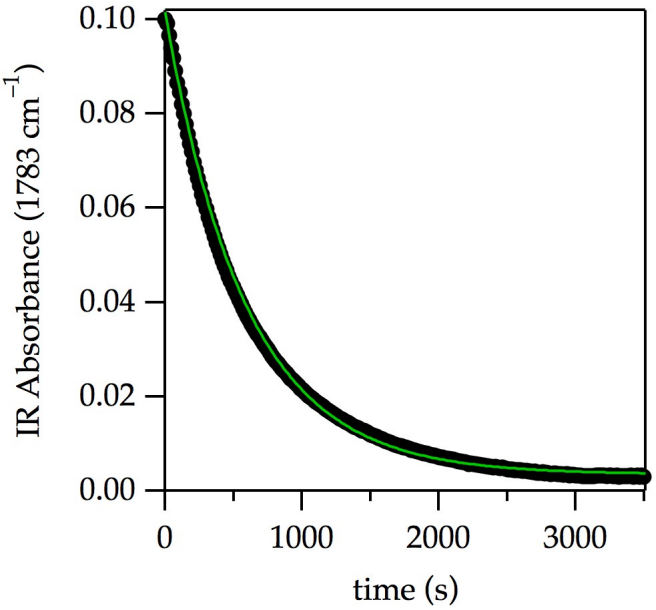


Figure 7. Lithiation of oxazolidinone **9** with equimolar LiHMDS in neat THF at –78 °C showing the loss of **9**. The decay was fit to the first-order function $f(t) = a + be^{-kt}$ [$a = (3.48 \pm 0.09) \times 10^{-3}$; $b = (9.81 \pm 0.02) \times 10^{-2}$; $k = (1.699 \pm 0.008) \times 10^{-3}$ s^{-1}]. The origin of the fit to the first-order function in the stoichiometric enolization stems from a non-linear relation between IR absorbance and [**9**] at > 0.015 M of **9** (deviation from Beer's law).

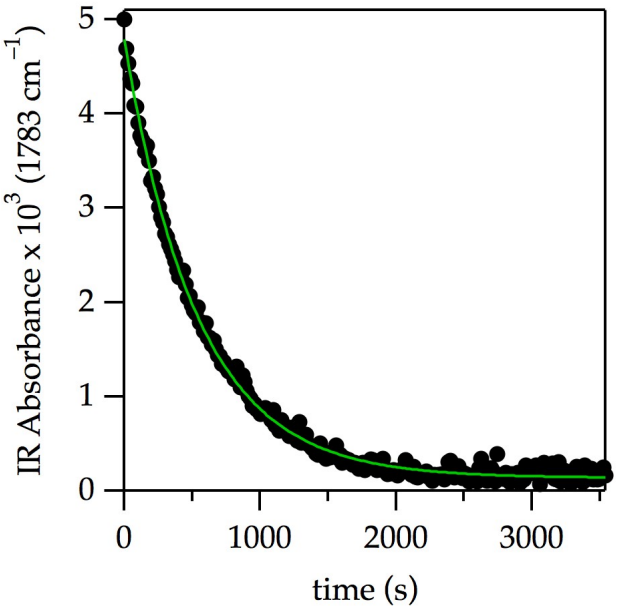


Figure 8. Lithiation of 0.0050 M oxazolidinone **9** with 0.10 M LiHMDS in neat THF at –78 °C showing the loss of **9** (pseudo-first-order conditions). The decay was fit to $f(t) = a + be^{-kt}$ [$a = (1.37 \pm 0.06) \times 10^{-4}$; $b = (4.65 \pm 0.02) \times 10^{-3}$; $k = 1.85 \pm 0.02) \times 10^{-3}$ s^{-1}].

Table 1. k_{obsd} for the enolization of oxazolidinone **9** with 0.10 M LiHMDS at various concentrations of **9** in neat THF at –78 ºC.

[**9**] (M)	$k_{obsd} \times 10^3$ (s^{-1}) [a]
0.001	1.86 ± 0.09
0.002	1.70 ± 0.03
0.003	2.10 ± 0.03
0.004	1.65 ± 0.01
0.005	1.85 ± 0.02
0.010	1.52 ± 0.02

[a] Average = 1.8 ± 0.1

Table 2. k_{obsd} for the enolization of oxazolidinone **9** with 0.10 M LiHMDS at various concentrations of **9** and 1.0 M THF–hexane at –78 ºC.

[**9**] (M)	$k_{obsd} \times 10^3$ (s^{-1}) [a]
0.002	2.26 ± 0.09
0.003	2.1 ± 0.1
0.004	1.72 ± 0.05
0.005	1.75 ± 0.05
0.006	1.81 ± 0.03

[a] Average = 1.9 ± 0.2

* For individual runs, the error represents the error of the fit. For replicated runs, the error represents the standard deviation. This is true for *every single kinetic run.* *

Solvent orders

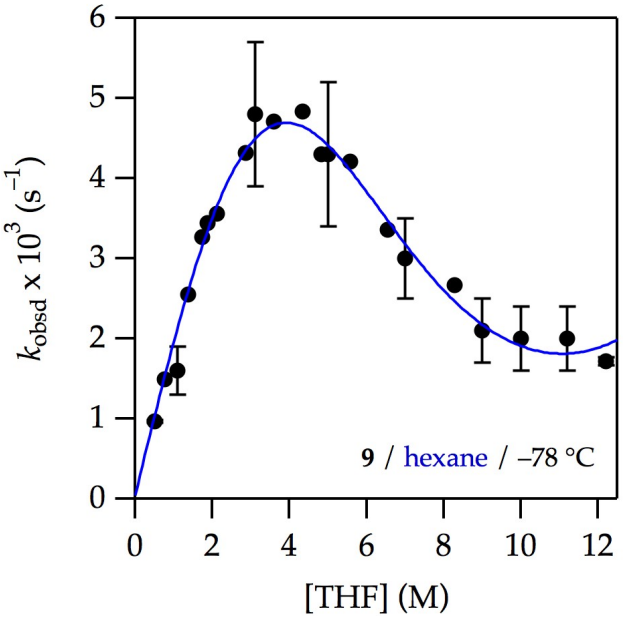


Figure 9. Plot of k_{obsd} vs [THF] for the enolization of 0.0050 M oxazolidinone **9** with 0.10 M LiHMDS at various concentrations of THF in hexane at –78 ºC. The curve depicts the result of an unweighted least-squares fit to eq 16 ($[A]_0$ is set at 0.10; $K_{eq} = (2.3 \pm 0.2) \times 10^{-4}$; $k_8 = (3.9 \pm 0.1) \times 10^{-2}$; $k_9 = (2 \pm 10) \times 10^{-8}$; k_{10} is set to 2.0×10^{-4}; $k_{11} = (5 \pm 4) \times 10^{-10}$).

[THF] (M)	$k_{obsd}^1 \times 10^3$ (s^{-1})	$k_{obsd}^2 \times 10^3$ (s^{-1})	$k_{obsd}^3 \times 10^3$ (s^{-1})	$k_{obsd}^4 \times 10^3$ (s^{-1})	$k_{obsd}^{avg} \times 10^3$ (s^{-1})
0.50		0.95 ± 0.02		0.99 ± 0.01	0.97 ± 0.02
0.76		1.49 ± 0.03			
1.1	1.85 ± 0.07			1.40 ± 0.09	1.6 ± 0.3
1.4		2.55 ± 0.04			
1.7		3.27 ± 0.06			
1.9		3.44 ± 0.07			
2.1			3.56 ± 0.05		
2.9			4.32 ± 0.06		
3.1	5.5 ± 0.1			4.2 ± 0.2	4.8 ± 0.9
3.6			4.71 ± 0.07		
4.3			4.83 ± 0.08		
4.8			4.30 ± 0.07		
5.0	4.90 ± 0.06			3.61 ± 0.03	4.3 ± 0.9
5.6			4.21 ± 0.06		
6.5			3.36 ± 0.04		
7.0	3.36 ± 0.04			2.63 ± 0.04	3.0 ± 0.5
8.3			2.67 ± 0.04		

Figure 9. continued.

9.0	2.33 ± 0.03	1.81 ± 0.02	2.1 ± 0.4
10.0	2.31 ± 0.04	1.70 ± 0.01	2.0 ± 0.4
11.2	2.28 ± 0.02	1.68 ± 0.02	2.0 ± 0.4
12.2	1.68 ± 0.01	1.76 ± 0.01	1.72 ± 0.05

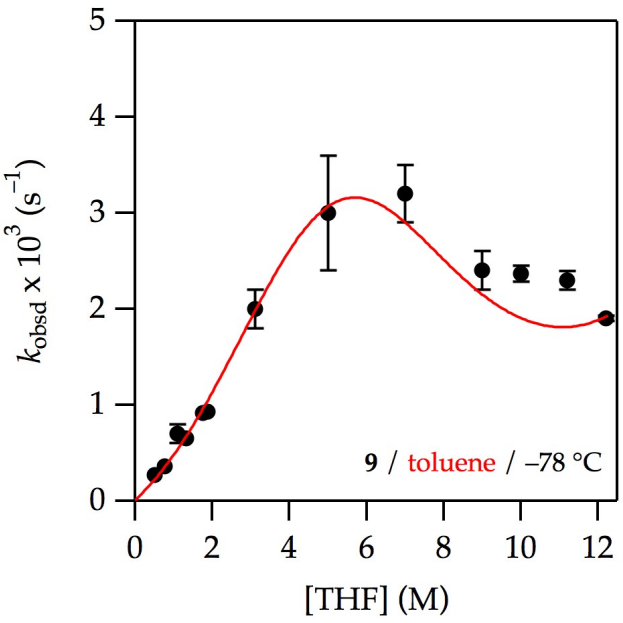


Figure 10. Plot of k_{obsd} vs [THF] for the enolization of 0.0050 M oxazolidinone **9** with 0.10 M LiHMDS at various concentrations of THF in toluene at –78 ºC. The curve depicts the result of an unweighted least-squares fit to eq 16 (All parameters carried over from the fit from Figure 9; additionally, $a = -3.19 \times 10^{-5} \pm 0$; $b = 3.36 \times 10^{-5} \pm 0$, c is set at 1.0, $m = 4.81 \pm 0$).

[THF] (M)	$k_{obsd}^{1} \times 10^3$ (s^{-1})	$k_{obsd}^{2} \times 10^3$ (s^{-1})	$k_{obsd}^{3} \times 10^3$ (s^{-1})	$k_{obsd}^{avg} \times 10^3$ (s^{-1})
0.51		0.271 ± 0.002		
0.76		0.363 ± 0.002		
1.1	0.59 ± 0.01	0.537 ± 0.008	0.731 ± 0.004	0.6 ± 0.1
1.4		0.655 ± 0.008		
1.7		0.92 ± 0.01		
1.9		0.93 ± 0.01		
3.1	1.85 ± 0.02		2.15 ± 0.02	2.0 ± 0.2
5.0	2.59 ± 0.05		3.51 ± 0.03	3.0 ± 0.6
7.0	3.00 ± 0.04		3.39 ± 0.03	3.2 ± 0.3
9.0	2.28 ± 0.03		2.59 ± 0.02	2.4 ± 0.2
10.0	2.43 ± 0.03		2.32 ± 0.02	2.37 ± 0.08
11.2	2.40 ± 0.02		2.24 ± 0.03	2.3 ± 0.1
12.2	1.92 ± 0.01		1.88 ± 0.03	1.90 ± 0.03

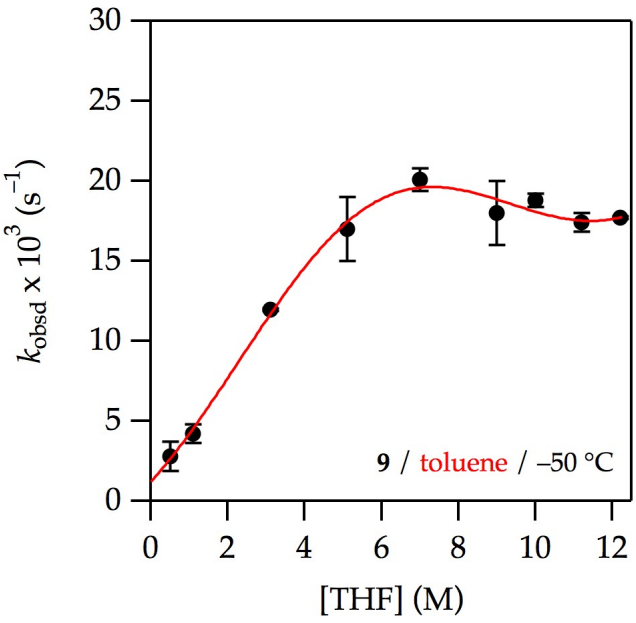


Figure 11. Plot of k_{obsd} vs [THF] for the enolization of 0.0050 M oxazolidinone **9** with 0.10 M LiHMDS at various concentrations of THF in toluene at –50 ºC. The curve depicts the result of an unweighted least-squares fit to eq 16 ($[A]_0$ is set at 0.10; $K_{eq} = (1.0) \times 10^{-4}$; $k_8 = (2.5) \times 10^{-1}$; $k_9 = (7.8) \times 10^{-8}$; $k_{10} = (2.7) \times 10^{-2}$; $k_{11} = (2.8) \times 10^{-9}$; $a = (–9.7) \times 10^{-3}$; $b = (1.1) \times 10^{-2}$; $c = (0.83)$; $m = 2.2$).

[THF] (M)	$k_{obsd}^{1} \times 10^3$ (s^{-1})	$k_{obsd}^{2} \times 10^3$ (s^{-1})	$k_{obsd}^{avg} \times 10^3$ (s^{-1})
0.50	2.12 ± 0.03	3.40 ± 0.05	2.8 ± 0.9
1.1	3.78 ± 0.06	4.62 ± 0.06	4.2 ± 0.6
3.1	12.0 ± 0.5	11.9 ± 0.3	11.97 ± 0.07
5.1	16.3 ± 0.8	18.7 ± 0.5	17 ± 2
7.0	21 ± 1	19.6 ± 0.6	20.1 ± 0.7
9.0	16.8 ± 0.9	19.9 ± 0.7	18 ± 2
10.0	19 ± 1	18.6 ± 0.3	18.8 ± 0.4
11.2	17.0 ± 0.8	17.8 ± 0.5	17.4 ± 0.6
12.2	17.0 ± 0.5	18 ± 1	17.7 ± 0.09

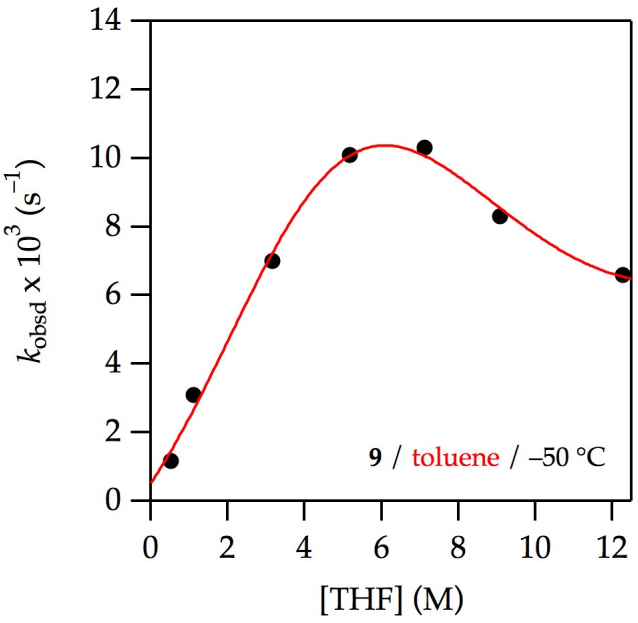


Figure 12. Plot of k_{obsd} vs [THF] for the enolization of 0.0050 M oxazolidinone **9** with 0.050 M LiHMDS at various concentrations of THF in toluene at –50 ºC. The curve depicts the result of an unweighted least-squares fit to eq 16 ($[A]_0$ is set at 0.05; K_{eq} is set at 1.0×10^{-4} ; $k_8 = (2.7) \times 10^{-1}$; $k_9 = (7.9) \times 10^{-7}$; $k_{10} = (1.4) \times 10^{-2}$; $k_{11} = (0.0)$; $a = (-1.9) \times 10^{-3}$; $b = (2.0) \times 10^{-3}$; c is set at 1 ; m is set to 3).

[THF] (M)	$k_{obsd} \times 10^3$ (s^{-1})
0.52	1.17 ± 0.02
1.1	3.10 ± 0.09
326	7.0 ± 0.3
5.2	10.1 ± 0.4
7.1	10.3 ± 0.2
9.1	8.3 ± 0.2
12.3	6.6 ± 0.1

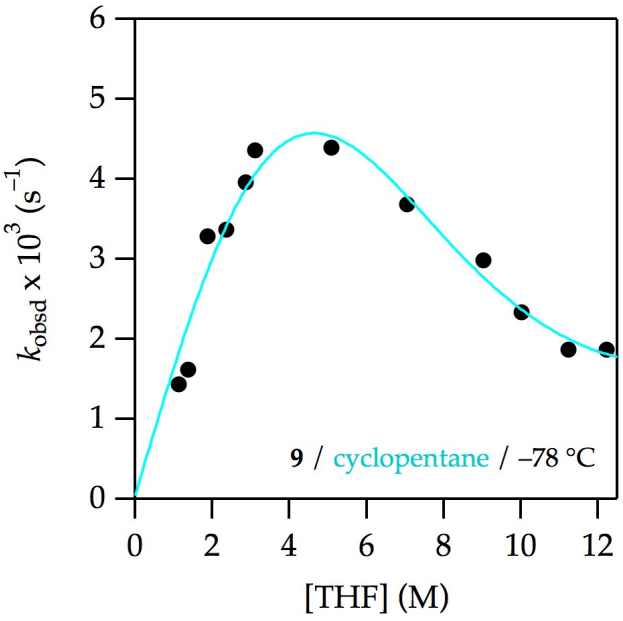


Figure 13. Plot of k_{obsd} vs [THF] for the enolization of 0.0050 M oxazolidinone **9** with 0.10 M LiHMDS at various concentrations of THF in cyclopentane at –78 ºC. The curve depicts the result of an unweighted least-squares fit to eq 16 ($[A]_0$ is set at 0.10; $K_{eq} = (1.2 \pm 0.3) \times 10^{-4}$; $k_8 = (3.3 \pm 0.2) \times 10^{-2}$; $k_9 = (2.9) \times 10^{-8}$; k_{10} is set at 2.0×10^{-4}; $k_{11} = (6.0) \times 10^{-11}$.

[THF] (M)	$k_{obsd}{}^1 \times 10^3$ (s^{-1})	$k_{obsd}{}^2 \times 10^3$ (s^{-1})
1.1	1.43 ± 0.02	
1.4		1.62 ± 0.03
1.9		3.28 ± 0.04
2.4		3.37 ± 0.05
2.9		3.96 ± 0.06
3.1	4.36 ± 0.04	
5.1	4.39 ± 0.09	
7.0	3.68 ± 0.06	
9.0	2.98 ± 0.05	
10.0		2.33 ± 0.03
11.2		1.87 ± 0.03
12.2	1.87 ± 0.02	

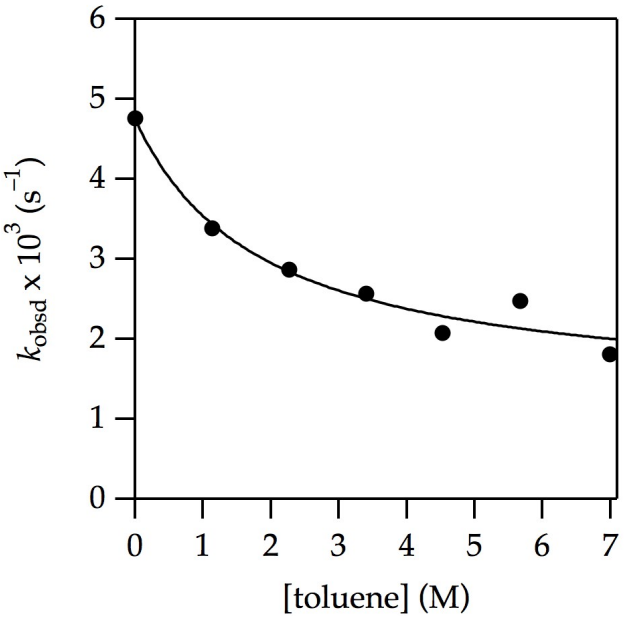


Figure 14. Plot of k_{obsd} vs [toluene] for the enolization of 0.0050 M oxazolidinone **9** with 0.10 M LiHMDS at various concentrations of toluene in 3.1 M THF–hexane at –78 ºC. The curve depicts the result of an unweighted least-squares fit to $f(x) = (a + bx)/(1 + cx)$, ($a = (4.7 \pm 0.2) \times 10^{-3}$, $b = (7 \pm 5) \times 10^{-4}$, $c = 0.5 \pm 0.2$).

[toluene] (M)	$k_{obsd} \times 10^3$ (s^{-1})
0	4.8 ± 0.1
1.1	3.39 ± 0.05
2.3	2.87 ± 0.04
3.4	2.57 ± 0.03
4.5	2.08 ± 0.03
5.7	2.48 ± 0.03
7.0	1.81 ± 0.02

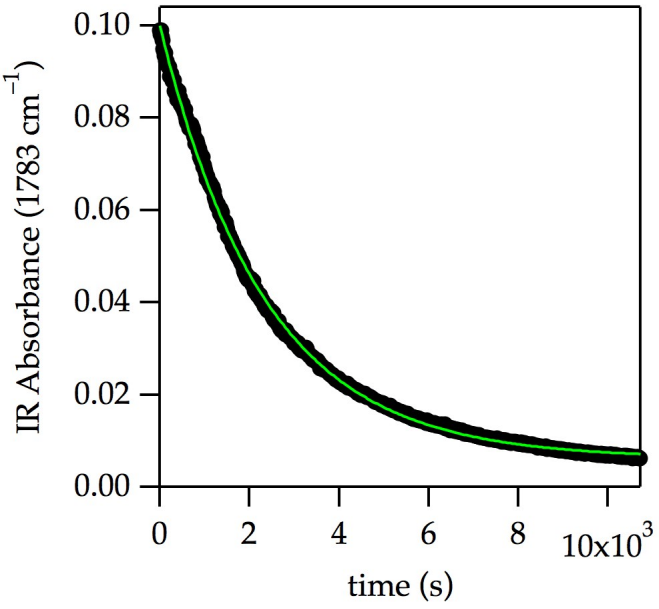


Figure 15. Lithiation of oxazolidinone **9**-d_2 with equimolar LiHMDS in neat THF at –78 °C showing the loss of **9**-d_2. The decay was fit to the first-order function $f(t) = a + be^{-kt}$ [$a = (6.17 \pm 0.06) \times 10^{-3}$; $b = (9.44 \pm 0.01) \times 10^{-2}$; $k = (4.27 \pm 0.01) \times 10^{-4}$ s^{-1}]. The origin of the fit to the first-order function in the stoichiometric enolization stems from a non-linear relation between IR absorbance and [**9**] at > 0.015 M of **9** (deviation from Beer's law).

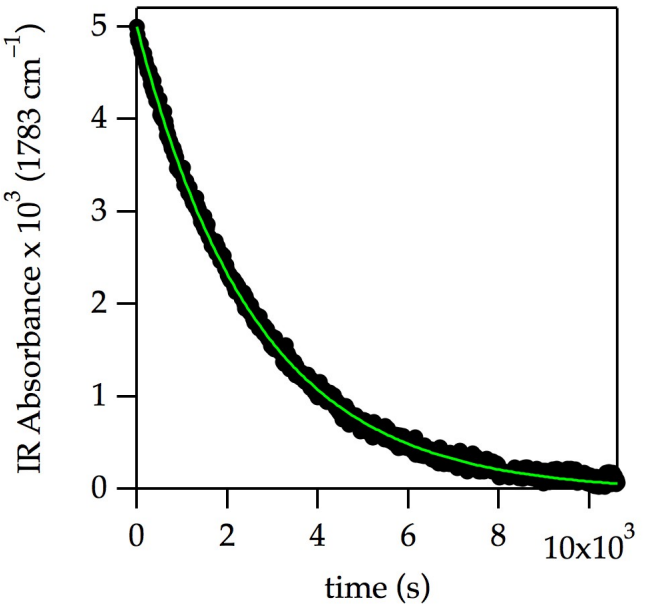


Figure 16. Lithiation of 0.0050 M oxazolidinone **9**-d_2 with 0.10 M LiHMDS in neat THF at –78 °C showing the loss of **9**-d_2 (pseudo-first-order conditions). The decay was fit to $f(t) = a + be^{-kt}$ [$a = (-3.7 \pm 0.6) \times 10^{-5}$; $b = (5.03 \pm 0.06) \times 10^{-3}$; $k = (2.55 \pm 0.01) \times 10^{-4}$ s^{-1}].

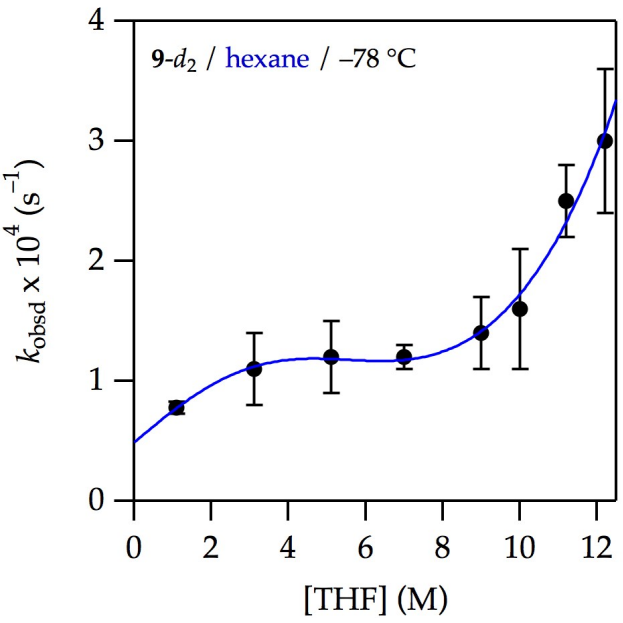


Figure 17. Plot of k_{obsd} vs [THF] for the enolization of 0.0050 M oxazolidinone **9**-d_2 with 0.10 M LiHMDS at various concentrations of THF in hexane at –78 ºC. The curve depicts the result of an unweighted least-squares fit to eq 16 ($[A]_0$ is set at 0.10; $K_{eq} = (1.1 \pm 1) \times 10^{-4}$; $k_8 = (5 \pm 4) \times 10^{-4}$; $k_9 = (8) \times 10^{-9}$; $k_{10} = (2 \pm 1) \times 10^{-4}$; $k_{11} = (7 \pm 3) \times 10^{-11}$).

[THF] (M)	$k_{obsd}^1 \times 10^4$ (s^{-1})	$k_{obsd}^2 \times 10^4$ (s^{-1})	$k_{obsd}^{avg} \times 10^4$ (s^{-1})
1.1	0.750 ± 0.003	0.817 ± 0.003	0.78 ± 0.05
3.1	0.911 ± 0.009	1.30 ± 0.01	1.1 ± 0.3
5.1	0.934 ± 0.005	1.37 ± 0.01	1.2 ± 0.3
7.0	1.132 ± 0.007	1.267 ± 0.006	1.2 ± 0.1
9.0	1.182 ± 0.004	1.578 ± 0.009	1.4 ± 0.3
10.0	1.22 ± 0.01	1.90 ± 0.02	1.6 ± 0.5
11.2	2.27 ± 0.01	2.695 ± 0.009	2.5 ± 0.3
12.2	2.55 ± 0.01	3.44 ± 0.02	3.0 ± 0.6

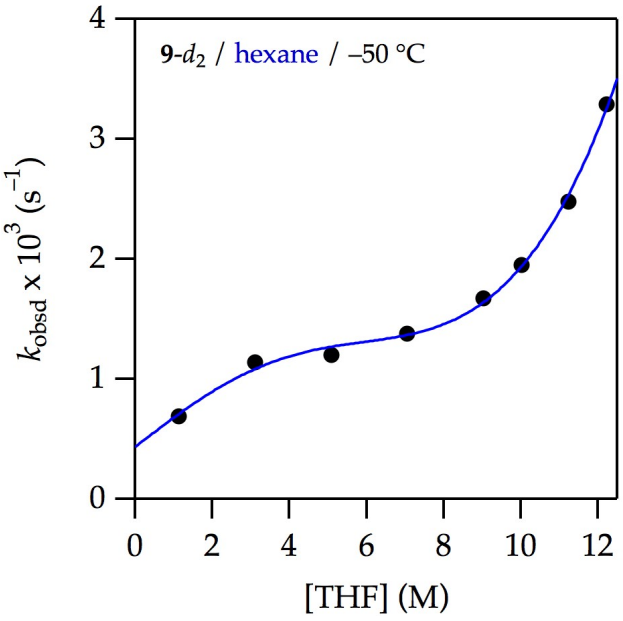


Figure 18. Plot of k_{obsd} vs [THF] for the enolization of 0.0050 M oxazolidinone **9**-d_2 with 0.10 M LiHMDS at various concentrations of THF in hexane at –50 ºC. The curve depicts the result of an unweighted least-square fit to eq 16 ($[A]_0$ is set at 0.10; $K_{eq} = (5 \pm 4) \times 10^{-5}$; $k_8 = (5 \pm 2) \times 10^{-3}$; $k_9 = (5 \pm 5) \times 10^{-8}$; $k_{10} = (1.9 \pm 0.6) \times 10^{-3}$; $k_{11} = (4 \pm 1) \times 10^{-10}$).

[THF] (M)	$k_{obsd} \times 10^3$ (s^{-1})
1.1	0.69 ± 0.03 [a]
3.1	1.14 ± 0.04 [a]
5.1	1.20 ± 0.08 [a]
7.0	1.38 ± 0.02
9.0	1.67 ± 0.09
10.0	1.95 ± 0.02
11.2	2.48 ± 0.04
12.2	3.29 ± 0.07

[a] A reaction burst was observed by IR during the first 2–5 minutes of monitoring. After excluding the burst data points from the plot, the decays afforded unweighted least-squares fits to the first-order function $f(t) = a + be^{-kt}$. Extended ^{6}Li NMR and IR studies at different **9**-d_2 and THF concentrations were performed, but the origin of the burst is still unknown. However, the k_{obsd} were reproducible regardless of the presence, absence, or extent of the reaction burst.

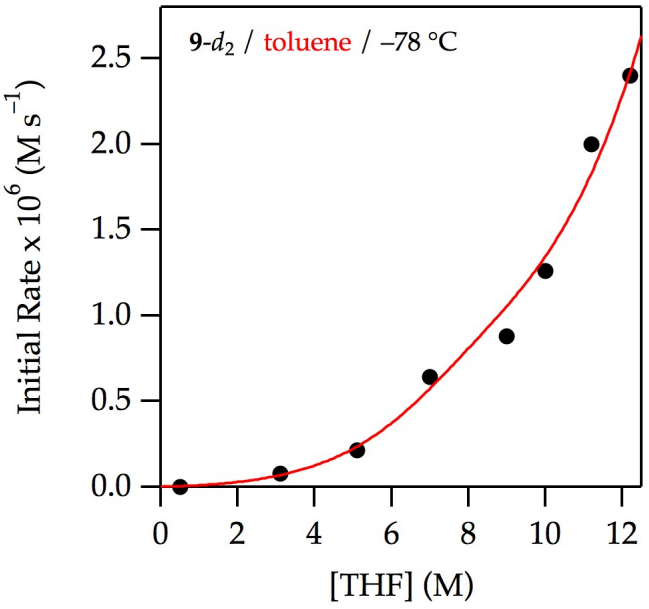


Figure 19. Plot of initial rates vs [THF] for the enolization of 0.0050 M oxazolidinone **9**-d_2 with 0.10 M LiHMDS at various concentrations of THF in toluene at –78 ºC. The curve depicts the result of an unweighted least-squares fit to eq 16 (All parameters carried over from the fit from Figure 17; additionally, $a = (–2) \times 10^{–4}$; $b = (1) \times 10^{–4}$, $c = 1.57 \pm 0.07$, $m = (5.0)$).

[THF] (M)	Initial Rate × 10^6 (M s^{-1})
0.50	[a]
3.1	0.076 ± 0.002
5.1	0.215 ± 0.005
7.0	0.64 ± 0.06
9.0	0.88 ± 0.06
10.0	1.26 ± 0.08
11.2	2.0 ± 0.4
12.2	2.4 ± 0.1

[a] No reaction was observed after 2.5 hours of monitoring by IR.

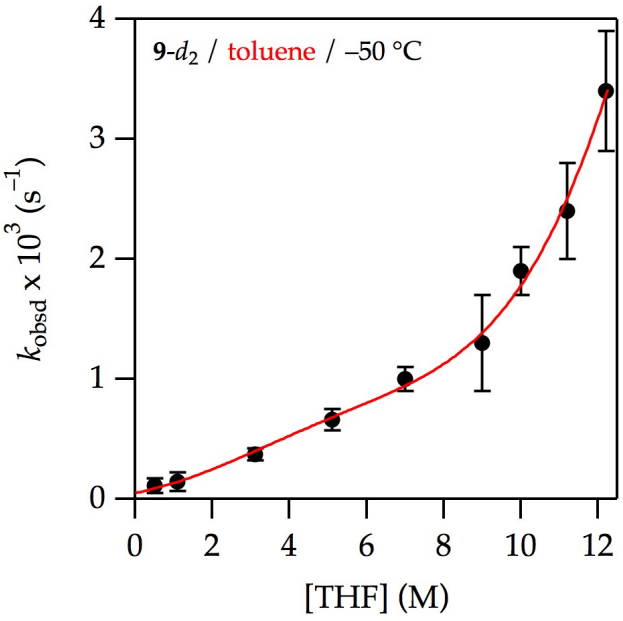


Figure 20. Plot of k_{obsd} vs [THF] for the enolization of 0.0050 M oxazolidinone **9**-d_2 with 0.10 M LiHMDS at various concentrations of THF in toluene at –50 ºC. The curve depicts the result of an unweighted least-squares fit to eq 16 (All parameters carried over from the fit from Figure 18; additionally, a = (–4) × 10^{-2}; b = (9) × 10^{-3}, c = (1.04), m = 1.3).

[THF] (M)	$k_{obsd}^{1} \times 10^3$ (s^{-1})	$k_{obsd}^{2} \times 10^3$ (s^{-1})	$k_{obsd}^{avg} \times 10^3$ (s^{-1})
0.50	0.153 ± 0.001	0.0642 ± 0.0005	0.11 ± 0.06
1.1	0.139 ± 0.002	0.1500 ± 0.0005	0.145 ± 0.08
3.1	0.331 ± 0.002	0.407 ± 0.001	0.37 ± 0.05
5.1	0.602 ± 0.007	0.724 ± 0.006	0.66 ± 0.09
7.0	0.866 ± 0.004	1.05 ± 0.01	1.0 ± 0.1
9.0	1.04 ± 0.01	1.64 ± 0.02	1.3 ± 0.4
10.0	1.72 ± 0.02	2.02 ± 0.03	1.9 ± 0.2
11.2	2.14 ± 0.02	2.66 ± 0.03	2.4 ± 0.4
12.2	3.71 ± 0.05	3.06 ± 0.03	3.4 ± 0.5

LiHMDS orders

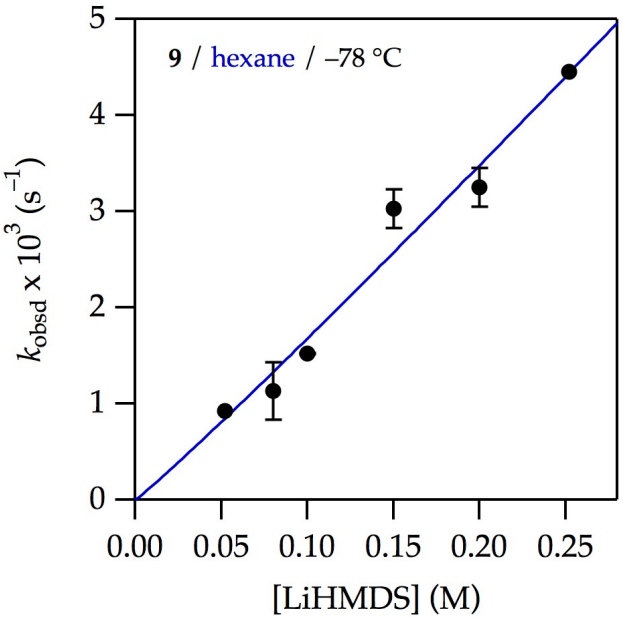


Figure 21. Plot of k_{obsd} vs [LiHMDS] for the enolization of 0.0050 M oxazolidinone **9** at various concentrations of LiHMDS and 1.0 M THF–hexane at –78 ºC. The curve depicts the result of an unweighted least–squares fit to $k_{obsd} = k[\text{LiHMDS}]^n$ ($k = (1.9 \pm 0.4) \times 10^{-2}$ s^{-1}; $n = 1.1 \pm 0.1$).

[LiHMDS] (M)	$k_{obsd}^1 \times 10^3$ (s^{-1})	$k_{obsd}^2 \times 10^3$ (s^{-1})	$k_{obsd}^{avg} \times 10^3$ (s^{-1})
0.052		0.93 ± 0.02	
0.080	0.92 ± 0.04	1.34 ± 0.05	1.1 ± 0.3
0.10	1.51 ± 0.04	1.52 ± 0.05	1.52 ± 0.01
0.16	3.20 ± 0.09	2.86 ± 0.09	3.0 ± 0.2
0.21	3.4 ± 0.1	3.1 ± 0.1	3.2 ± 0.2
0.25	4.5 ± 0.2		

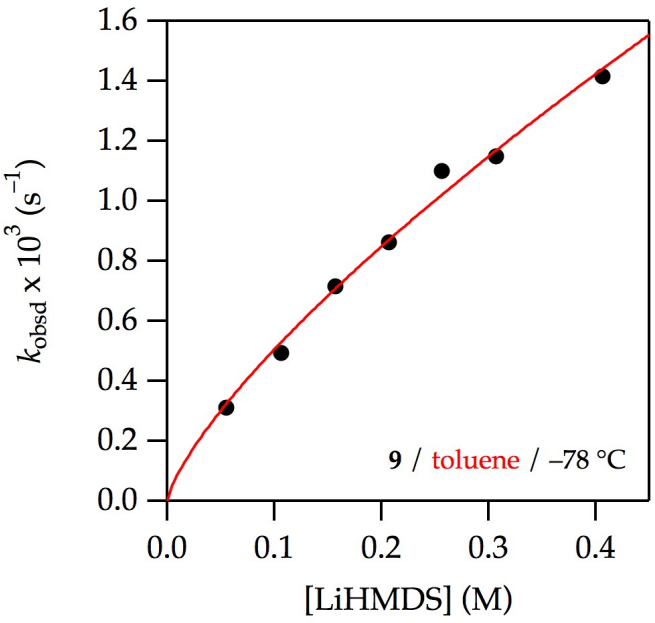


Figure 22. Plot of k_{obsd} vs [LiHMDS] for the enolization of 0.0050 M oxazolidinone **9** at various concentrations of LiHMDS and 1.0 M THF–toluene at –78 ºC. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k[\text{LiHMDS}]^n$ ($k = (2.8 \pm 0.2) \times 10^{-3}$ s^{-1}; $n = 0.75 \pm 0.04$).

[LiHMDS] (M)	$k_{obsd} \times 10^3$ (s^{-1})
0.055	0.311 ± 0.002
0.11	0.494 ± 0.006
0.16	0.717 ± 0.006
0.21	0.863 ± 0.008
0.26	1.10 ± 0.01
0.31	1.15 ± 0.01
0.41	1.42 ± 0.03

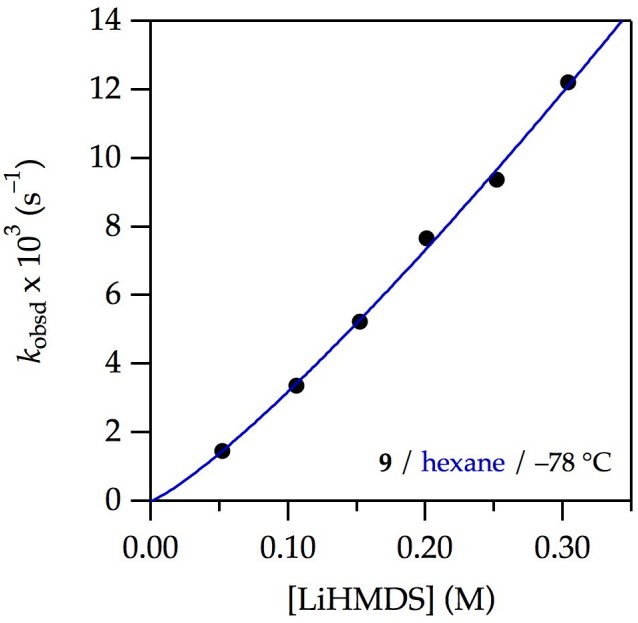


Figure 23. Plot of k_{obsd} vs [LiHMDS] for the enolization of 0.0050 M oxazolidinone **9** at various concentrations of LiHMDS and 7.1 M THF–hexane at –78 ºC. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k[\text{LiHMDS}]^n$ ($k = (5.1 \pm 0.3) \times 10^{-2}$ s^{-1}; $n = 1.20 \pm 0.04$).

[LiHMDS] (M)	$k_{obsd} \times 10^3$ (s^{-1})
0.052	1.46 ± 0.01
0.11	3.36 ± 0.04
0.15	5.24 ± 0.07
0.20	7.7 ± 0.1
0.25	9.4 ± 0.1
0.30	12.2 ± 0.3

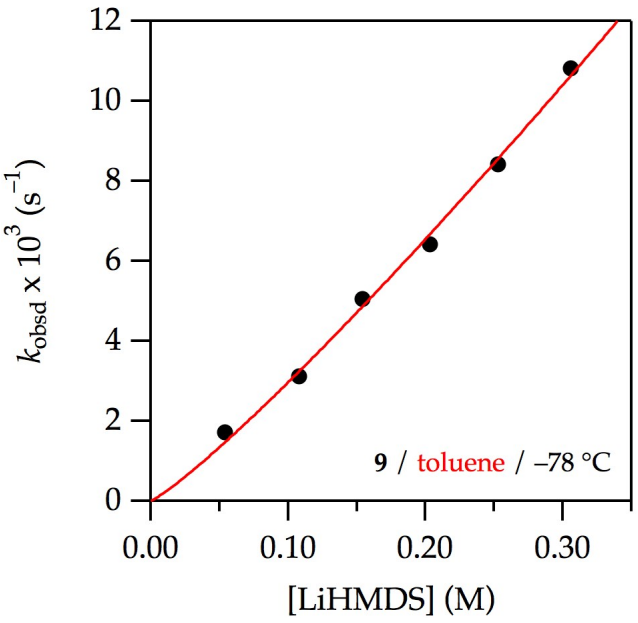


Figure 24. Plot of k_{obsd} vs [LiHMDS] for the enolization of 0.0050 M oxazolidinone **9** at various concentrations of LiHMDS and 7.1 M THF–toluene at –78 ºC. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k[\text{LiHMDS}]^n$ ($k = (4.1 \pm 0.3) \times 10^{-2}$ s^{-1}; $n = 1.14 \pm 0.05$).

[LiHMDS] (M)	$k_{obsd} \times 10^3$ (s^{-1})
0.054	1.72 ± 0.02
0.11	3.12 ± 0.04
0.15	5.05 ± 0.08
0.20	6.4 ± 0.1
0.25	8.4 ± 0.2
0.31	10.8 ± 0.4

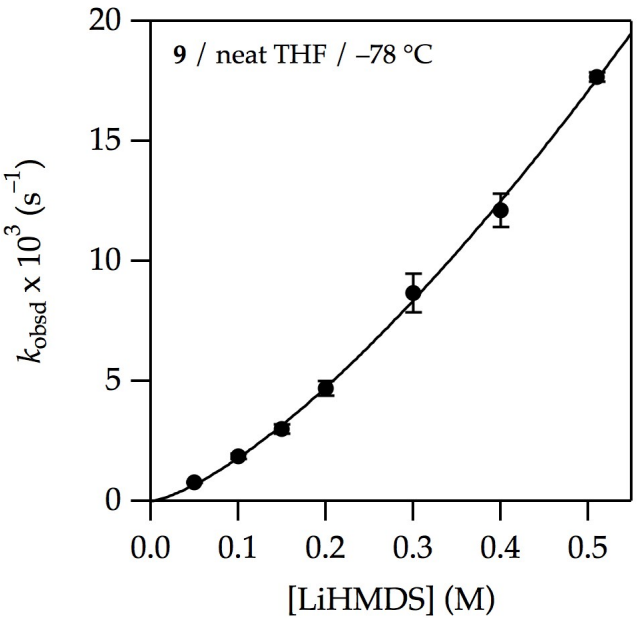


Figure 25. Plot of k_{obsd} vs [LiHMDS] for the enolization of 0.0050 M oxazolidinone **9** at various concentrations of LiHMDS in neat THF at –78 ºC. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k[\text{LiHMDS}]^n$ ($k = (4.5 \pm 0.1) \times 10^{-2}$ s^{-1}; $n = 1.40 \pm 0.03$).

[LiHMDS] (M)	$k_{obsd}^1 \times 10^3$ (s^{-1})	$k_{obsd}^2 \times 10^3$ (s^{-1})	$k_{obsd}^{avg} \times 10^3$ (s^{-1})
0.050	0.75 ± 0.01	0.798 ± 0.004	0.78 ± 0.03
0.10	1.80 ± 0.02	1.949 ± 0.009	1.9 ± 0.1
0.15	2.82 ± 0.05	3.17 ± 0.03	3.0 ± 0.2
0.20	4.48 ± 0.06	4.91 ± 0.07	4.7 ± 0.3
0.30	8.1 ± 0.2	9.3 ± 0.1	8.7 ± 0.8
0.40	11.6 ± 0.4	12.6 ± 0.4	12.1 ± 0.7
0.51	18 ± 1	17.5 ± 0.3	17.7 ± 2

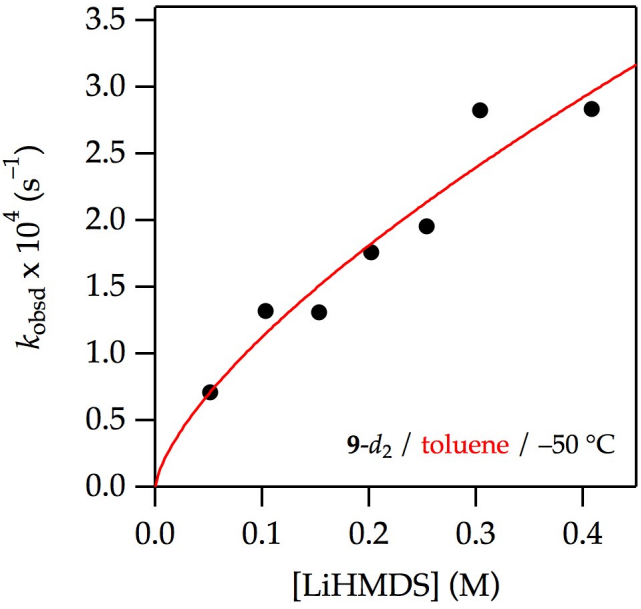


Figure 26. Plot of k_{obsd} vs [LiHMDS] for the enolization of 0.0050 M oxazolidinone **9**-d_2 at various concentrations of LiHMDS and 1.0 M THF–toluene at –50 ºC. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k[\text{LiHMDS}]^n$ ($k = (5.5 \pm 0.8) \times 10^{-4}$ s^{-1}; $n = 0.7 \pm 0.1$).

[LiHMDS] (M)	$k_{obsd} \times 10^4$ (s^{-1})
0.051	0.708 ± 0.003
0.10	1.32 ± 0.01
0.15	1.31 ± 0.01
0.20	1.76 ± 0.02
0.25	1.957 ± 0.009
0.30	2.82 ± 0.02
0.41	2.83 ± 0.03

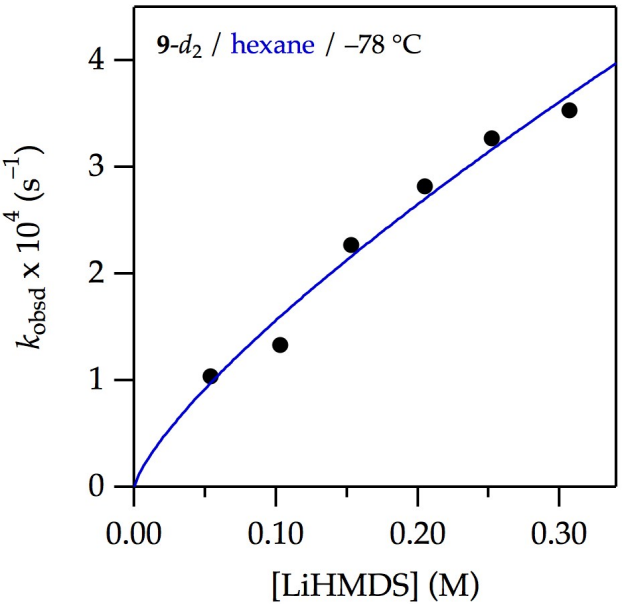


Figure 27. Plot of k_{obsd} vs [LiHMDS] for the enolization of 0.0050 M oxazolidinone **9**-d_2 at various concentrations of LiHMDS and 3.1 M THF–hexane at –78 ºC. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k[\text{LiHMDS}]^n$ ($k = (9 \pm 1) \times 10^{-4}$ s^{-1}; $n = 0.76 \pm 0.08$).

[LiHMDS] (M)	$k_{obsd} \times 10^4$ (s^{-1})
0.054	1.036 ± 0.006
0.10	1.333 ± 0.008
0.15	2.27 ± 0.01
0.20	2.82 ± 0.01
0.25	3.27 ± 0.03
0.31	3.53 ± 0.02

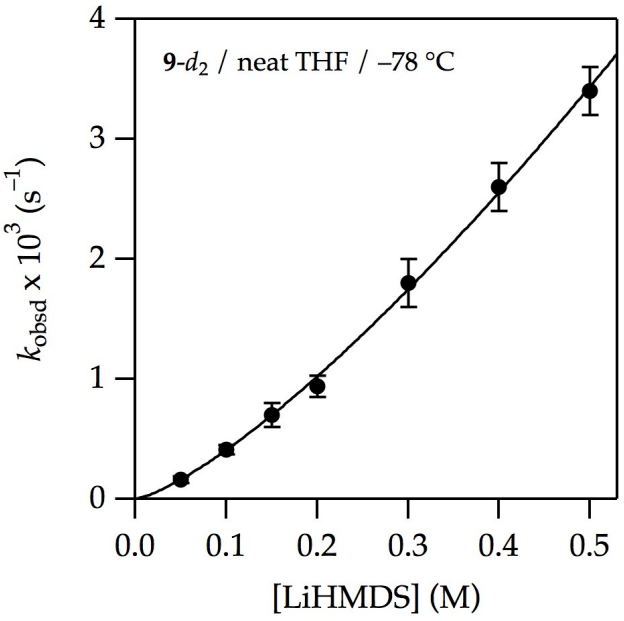


Figure 28. Plot of k_{obsd} vs [LiHMDS] for the enolization of 0.0050 M oxazolidinone **9**-d_2 at various concentrations of LiHMDS in neat THF at –78 ºC. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k[\text{LiHMDS}]^n$ (k = (8.6 ± 0.3) × 10^{-3} s^{-1}; n = 1.32 ± 0.03).

[LiHMDS] (M)	$k_{obsd}^1 \times 10^3$ (s^{-1})	$k_{obsd}^2 \times 10^3$ (s^{-1})	$k_{obsd}^{avg} \times 10^3$ (s^{-1})
0.050	0.139 ± 0.001	0.1812 ± 0.0008	0.16 ± 0.03
0.10	0.385 ± 0.005	0.440 ± 0.02	0.41 ± 0.04
0.15	0.605 ± 0.006	0.748 ± 0.004	0.7 ± 0.1
0.20	0.873 ± 0.008	0.998 ± 0.006	0.94 ± 0.09
0.30	1.66 ± 0.02	1.95 ± 0.01	1.8 ± 0.2
0.40	2.48 ± 0.04	2.78 ± 0.03	2.6 ± 0.2
0.50	3.26 ± 0.06	3.50 ± 0.06	3.4 ± 0.2

Isotope effects

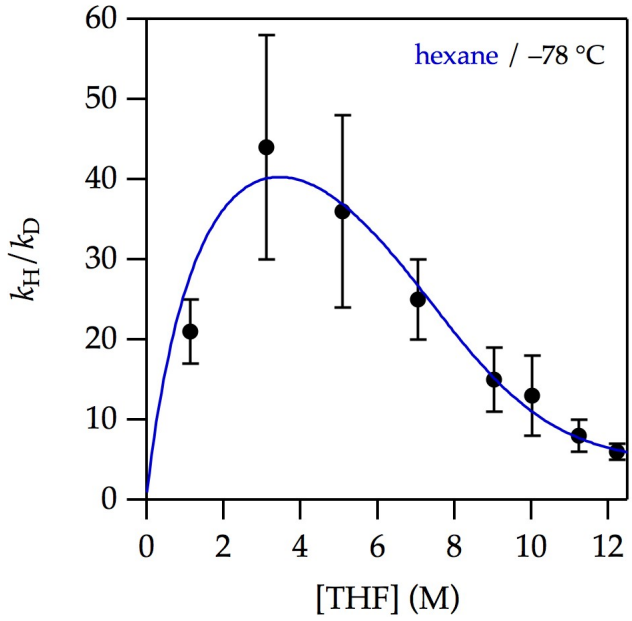


Figure 29. Plot of k_H/k_D vs [THF] for the enolization of 0.0050 M oxazolidinones **9**-d_2 and **9** with 0.10 M LiHMDS at various concentrations of THF in hexane at –78 ºC. The curve depicts the result of an unweighted least-squares fit to $f(x)$ = (eq^H 16)/(eq^D 16) using the values derived from the least-squares fits to eq 16 on Figures 9 and 17 (contributions to k_H and k_D, respectively).

[THF] (M)	k_H/k_D
1.1	21 ± 4
3.1	44 ± 14
5.1	36 ± 12
7.1	25 ± 5
9.0	15 ± 4
10.0	13 ± 5
11.2	8 ± 2
12.2	6 ± 1

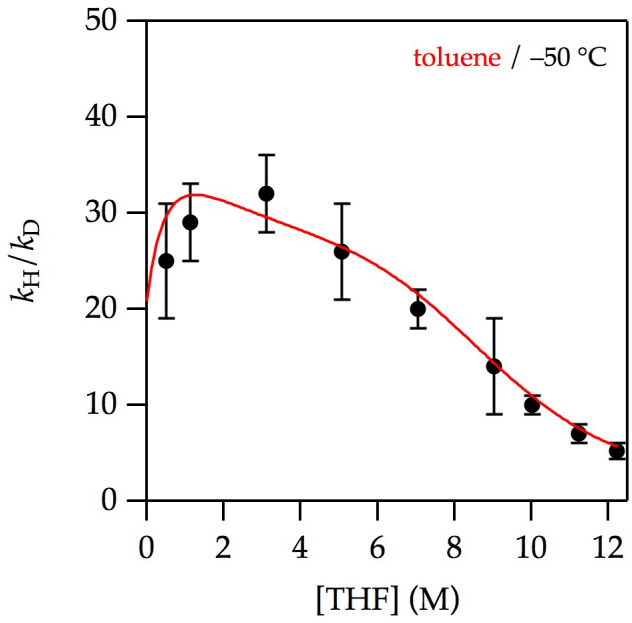


Figure 30. Plot of k_H/k_D vs [THF] for the enolization of 0.0050 M oxazolidinones **9**-d_2 and **9** with 0.10 M LiHMDS at various concentrations of THF in toluene at –50 °C. The curve depicts the result of an unweighted least-squares fit to $f(x)$ = (eq^H 16)/(eq^D 16) using the values derived from the least-squares fits to eq 16 on Figures 11 and 20 (contributions to k_H and k_D, respectively).

[THF] (M)	k_H/k_D
0.50	25 ± 6
1.1	29 ± 4
3.1	32 ± 4
5.1	26 ± 5
7.1	20 ± 2
9.0	14 ± 5
10.0	10 ± 1
11.2	7 ± 1
12.2	5.2 ± 0.8

Probing for isotope effects using biphasic kinetics

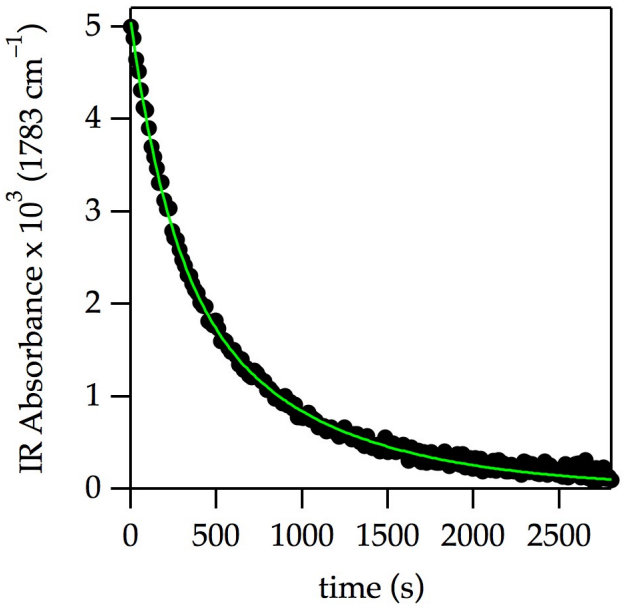


Figure 31. Biphasic decay for the enolization of a 1:1 mixture of oxazolidinones **9**-d_2 and **9** (total concentration = 0.0050 M) with 0.10 M LiHMDS in neat THF at –78 ºC. The decay was fit to $f(t) = a[(\exp(-k_H t) + (\exp(-k_D t)]$, $a = (2.52 \pm 0.01) \times 10^{-3}$, $k_H = (4.24 \pm 0.09) \times 10^{-3}$ s^{-1}, $k_D = (1.1149 \pm 0.008) \times 10^{-3}$ s^{-1}; $\boldsymbol{k_H/k_D = 3.8}$.

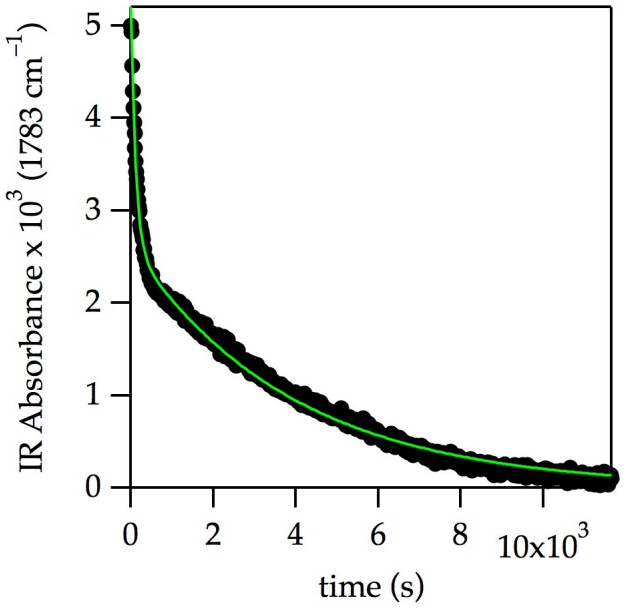


Figure 32. Biphasic decay for the enolization of a 1:1 mixture of oxazolidinones **9**-d_2 and **9** (total concentration = 0.0050 M) with 0.10 M LiHMDS in 3.1 M THF–hexane at –78 ºC. The decay was fit to $f(t) = a[(\exp(-k_H t) + (\exp(-k_D t)]$, $a = (2.617 \pm 0.009) \times 10^{-3}$, $k_H = (8.5 \pm 0.2) \times 10^{-3}$ s^{-1}, $k_D = (2.55 \pm 0.01) \times 10^{-4}$ s^{-1}; $\boldsymbol{k_H/k_D = 33}$.

Contributions of individual enolization pathways to k_{obsd}

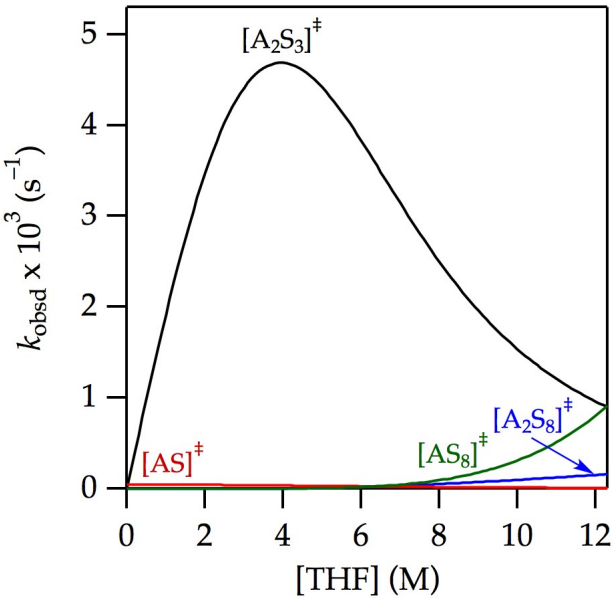


Figure 33. Contributions of **$[A_2S_3]^‡$**, $[AS]^‡$, $[A_2S_8]^‡$, and $[AS_8]^‡$ for the enolization of oxazolidinone **9** in THF–hexane at –78 °C from Figure 9 (see caption).

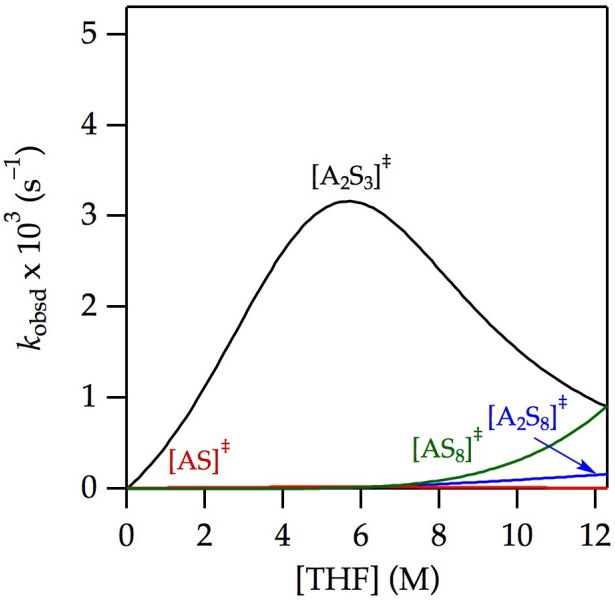


Figure 34. Contributions of **$[A_2S_3]^‡$**, $[AS]^‡$, $[A_2S_8]^‡$, and $[AS_8]^‡$ for the enolization of oxazolidinone **9** in THF–toluene at –78 °C from Figure 10 (see caption).

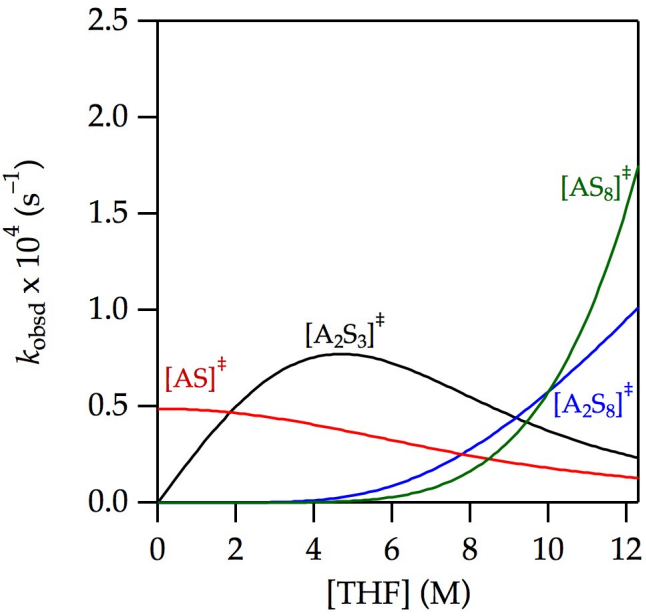


Figure 35. Contributions of **[A_2S_3]‡**, [AS]‡, [A_2S_8]‡, and [AS_8]‡ for the enolization of oxazolidinone **9**-d_2 in THF–hexane at –78 °C from Figure 17 (see caption).

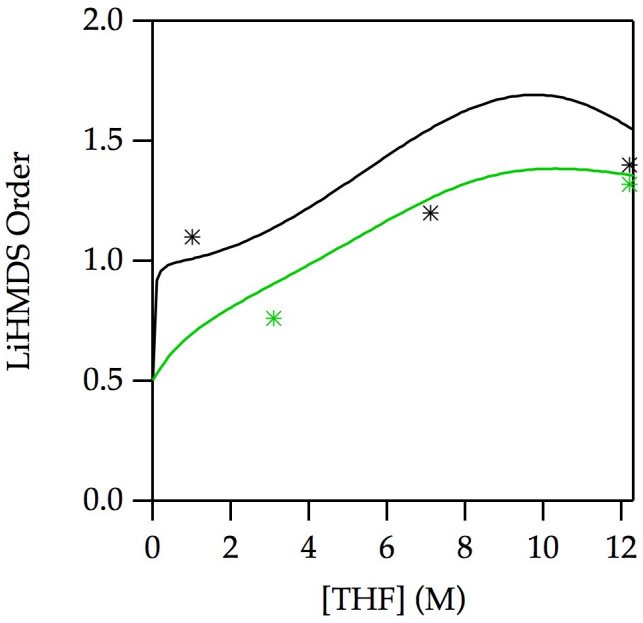
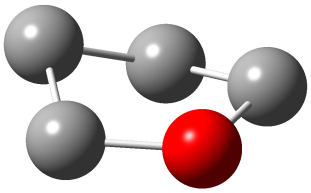


Figure 36. Predicted LiHMDS order vs THF concentration for **9** (black trace overlaid on observed orders) and **9**-d_2 (green trace overlaid on observed orders). All parameters were carried over from the fits in Figures 9 and 17.

IV. Ground state computations

Geometries are optimized at the B3LYP level of theory using the 6–31G(d) basis set. Energies are defined as follows: G is the sum of electronic and thermal free energies calculated at the B3LYP level of theory (T = 195 K). G_{MP2} is derived from an MP2 SP calculation corresponding to the DFT-optimized geometry and includes a thermal correction from the DFT calculation.

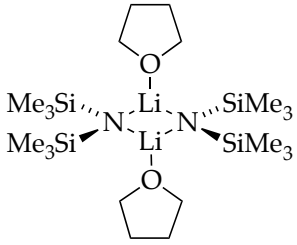
Table 3. Geometric coordinates and thermally corrected MP2 energies for tetrahydrofuran (THF).



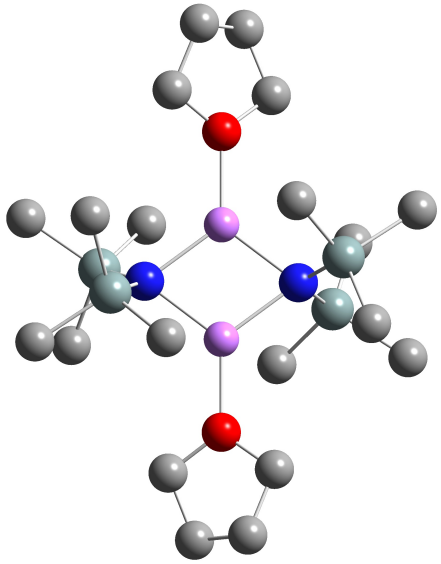
G = –232.349382 Hartree
G_{MP2} = –145312.2903 kcal/mol

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
O	-1.16595900	-0.81799300	-0.14189700
C	-2.33079700	0.00578200	-0.26371900
C	-1.89345100	1.43342400	0.08935700
C	-0.42612000	1.42734800	-0.36432500
H	-0.36194300	1.58113000	-1.44827300
H	0.18639000	2.19179800	0.12390500
H	-2.50141700	2.19800900	-0.40425600
H	-1.95597500	1.59676500	1.17200000
H	-2.70953200	-0.04841600	-1.29615400
H	-3.10975000	-0.38360000	0.40254800
H	0.36109400	-0.05099500	1.03924900
H	0.78781100	-0.39627200	-0.65128200

Table 4. Geometric coordinates and thermally corrected MP2 energies for disolvated LiHMDS cyclic dimer **1** with two THF.



1



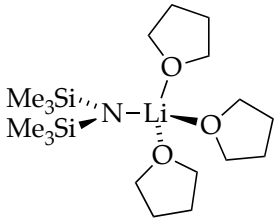
G = –2226.149254 Hartree
G_{MP2} = –1393218.9313 kcal/mol

Atom	X	Y	Z
Si	0.00000000	0.00000000	0.00000000
C	1.51908600	0.51158200	1.03413900
H	2.19652000	1.15427700	0.45864100
H	1.22382900	1.06550800	1.93497200
H	2.09074500	-0.36593200	1.36423800
C	-1.04282100	1.58316400	-0.23666300
H	-0.50565200	2.37344700	-0.77341900
H	-1.96430100	1.37896600	-0.79712200
H	-1.33721100	1.99539700	0.73753000
N	0.40080300	-0.84309100	-1.45584100
Si	0.80185500	0.00018500	-2.91153200
C	-0.71728500	0.51284200	-3.94505100
H	-1.28920100	-0.36445700	-4.27529200
H	-1.39442400	1.15537300	-3.36903400
H	-0.42229200	1.06707800	-4.84577300
C	1.87169300	-1.09153500	-4.05950000
H	2.02482500	-0.58080200	-5.01916800
H	2.86245100	-1.27918500	-3.62755200
H	1.42040600	-2.06505400	-4.28433300
C	1.84567400	1.58265200	-2.67462100
H	1.30935700	2.37285300	-2.13689500
H	2.76756400	1.37770000	-2.11511500
H	2.13938200	1.99536200	-3.64882100
C	-1.07070900	-1.09126500	1.14762400
H	-2.06231000	-1.27658100	0.71663400
H	-0.62098000	-2.06587700	1.37092500
H	-1.22178400	-0.58134900	2.10806500
N	0.40012500	-4.11064100	-1.45580400

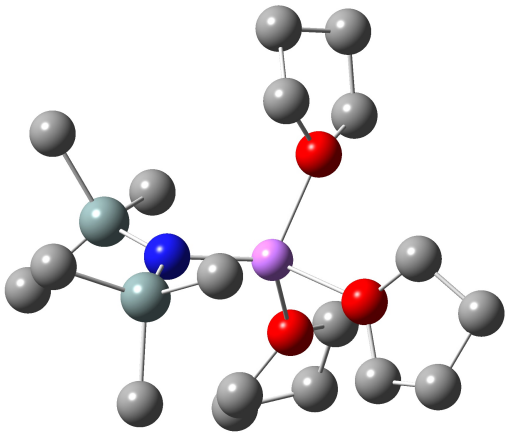
Atom	X	Y	Z
Si	0.80082200	-4.95388000	-0.00000100
C	-0.71843500	-5.46564900	1.03378500
H	-1.39617100	-6.10758200	0.45779600
H	-0.42352400	-6.02035600	1.93424600
H	-1.28966100	-4.58806500	1.36445200
C	1.87129700	-3.86268600	1.14792000
H	2.02352600	-4.37337700	2.10775900
H	2.86240300	-3.67612900	0.71632200
H	1.42086500	-2.88870100	1.37242700
C	1.84395700	-6.53682000	-0.23678900
H	1.30713400	-7.32708500	-0.77391000
H	2.76555100	-6.33226000	-0.79693000
H	2.13817600	-6.94924200	0.73737700
Si	-0.00059400	-4.95361600	-2.91174600
C	1.51884500	-5.46526000	-3.94534300
H	2.09033400	-4.58760100	-4.27536800
H	2.19625600	-6.10753300	-3.36934900
H	1.22424200	-6.01951700	-4.84617800
C	-1.07094900	-3.86211800	-4.05945100
H	-1.22102800	-4.37128000	-5.02043900
H	-2.06294200	-3.67787600	-3.62890600
H	-0.62174900	-2.88699300	-4.28152800
C	-1.04361400	-6.53669200	-2.67545000
H	-0.50664800	-7.32700200	-2.13852900
H	-1.96536300	-6.33260200	-2.11539800
H	-1.33753400	-6.94886100	-3.64981700
C	-3.63055200	-1.38521600	-1.92875900
O	-2.80106800	-2.47679200	-1.45597200

C	-3.63074700	-3.56809600	-0.98287000	C	4.43175800	-3.56930300	-1.92829900
C	-5.04550500	-2.99566600	-0.88980500	C	5.84647300	-2.99687300	-2.02169400
C	-5.04529100	-1.95753800	-2.02234200	C	5.84626600	-1.95819600	-0.88965300
H	-5.19793500	-2.44798500	-2.99090600	C	4.43151200	-1.38594000	-0.98347400
H	-5.81277000	-1.18678300	-1.90591900	H	4.37282600	-0.56640500	-1.71007300
H	-5.81296900	-3.76639400	-1.00650700	H	4.02762500	-1.03992500	-0.02929000
H	-5.19850400	-2.50522000	0.07870200	H	6.61371700	-1.18747500	-1.00649200
H	-3.57194800	-4.38826100	-1.70874600	H	5.99896900	-2.44816700	0.07914200
H	-3.22712200	-3.91336100	-0.02829800	H	5.99942600	-2.50688800	-2.99044300
Li	-0.81840100	-2.47659200	-1.45558400	H	6.61396800	-3.76751700	-1.90463800
H	-3.57189500	-0.56533700	-1.20253400	H	4.37298000	-4.38904800	-1.20194100
H	-3.22666100	-1.03960000	-2.88308900	H	4.02810200	-3.91512100	-2.88265700
O	3.60202700	-2.47774900	-1.45581200	Li	1.61940100	-2.47717100	-1.45556500

Table 5. Geometric coordinates and thermally corrected MP2 energies for trisolvated LiHMDS monomer **2** with three THF.



2; $n = 3$

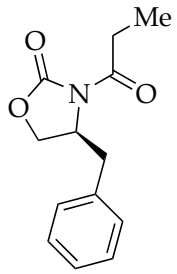


G = –1577.764650 Hartree
G_{MP2} = –987233.8981 kcal/mol

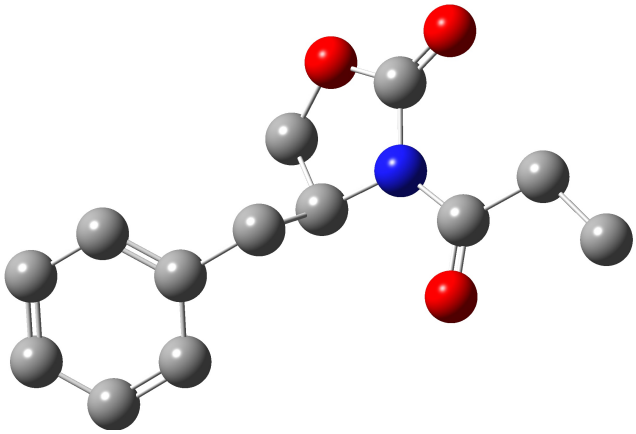
Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	0.71192800	-5.88098900	-0.09236400
O	-0.43585800	-1.22673000	-0.62237600	C	-1.17881900	-0.93520900	-1.83342900
Li	-0.83529800	-3.10801800	0.13855900	C	-1.61825800	0.51915800	-1.68865400
O	-0.28837500	-3.46519600	2.09725800	C	-0.42428600	1.13638800	-0.94160200
C	-0.93554900	-4.55316100	2.79826500	H	0.38227700	1.37380000	-1.64533600
C	-1.02061000	-4.09342600	4.25143700	H	-0.67662400	2.05170500	-0.39793200
C	0.28658700	-3.29832500	4.40425600	H	-1.81488300	0.99600500	-2.65363800
C	0.42887900	-2.62978100	3.02901400	H	-2.52935300	0.58180300	-1.08324900
H	1.47025300	-2.54259900	2.69899700	H	-0.51212600	-1.06545700	-2.69813500
H	-0.02702700	-1.63205000	3.01589900	H	-1.99156600	-1.66312600	-1.88579200
H	1.12566800	-3.97949100	4.58901100	H	-0.48889000	0.08213200	0.97812400
H	0.26007200	-2.56875300	5.21914400	H	1.08446300	-0.04615500	0.15385000
H	-1.10067100	-4.92983700	4.95227600	Si	-3.93462300	-2.90180500	0.51334700
H	-1.88976700	-3.44144000	4.39452600	C	-5.15976300	-1.98562300	-0.63602000
H	-1.89392500	-4.72634200	2.30626800	H	-5.69477600	-2.67938100	-1.29517400
H	-0.31647700	-5.45698000	2.70379600	H	-5.91337000	-1.42827600	-0.06289300
O	0.97496000	-3.88601900	-0.57470900	H	-4.63852800	-1.26538700	-1.28134900
C	1.52106800	-5.14571600	-0.12419000	C	-3.25960000	-1.53493100	1.67319600
C	2.62897900	-5.50636700	-1.11928000	H	-4.07495200	-1.06020200	2.23451200
C	3.09432400	-4.12343900	-1.60133100	H	-2.54420500	-1.93830800	2.40012500
C	1.77541900	-3.35142100	-1.64948000	H	-2.74558000	-0.74550100	1.11045300
H	1.25086600	-3.51585700	-2.60006000	C	-5.02115100	-4.00364200	1.64203500
H	1.87869800	-2.27632400	-1.48708800	H	-5.51192000	-4.80322800	1.07292500
H	3.59978600	-4.14976600	-2.57138200	H	-4.42683100	-4.48842300	2.42852000
H	3.77822700	-3.67210800	-0.87221300	H	-5.81057500	-3.42268900	2.13809300
H	2.21792100	-6.08159300	-1.95673200	N	-2.66541300	-3.71303700	-0.28549200
H	3.42603900	-6.09871700	-0.65993700	Si	-2.83472300	-5.09585800	-1.27235500
H	1.91259200	-5.00871400	0.89148600	C	-2.52510000	-6.73154700	-0.32326700

H	-1.53928200	-6.73809100	0.16279700
H	-3.27336000	-6.86743400	0.46853300
H	-2.57431300	-7.61171000	-0.97864600
C	-1.57360000	-5.08797400	-2.70879600
H	-1.63682900	-6.00442600	-3.31018800
H	-1.75151500	-4.23813600	-3.38122200
H	-0.54708100	-5.00169700	-2.33396500
C	-4.53353500	-5.33026500	-2.12049700
H	-5.35468400	-5.41780500	-1.39776500
H	-4.77078400	-4.48980600	-2.78482900
H	-4.53907400	-6.24341400	-2.73098700

Table 6. Geometric coordinates and thermally corrected MP2 energies for oxazolidinone **9**.



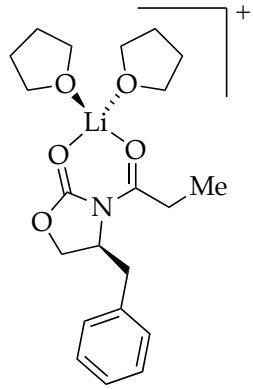
9



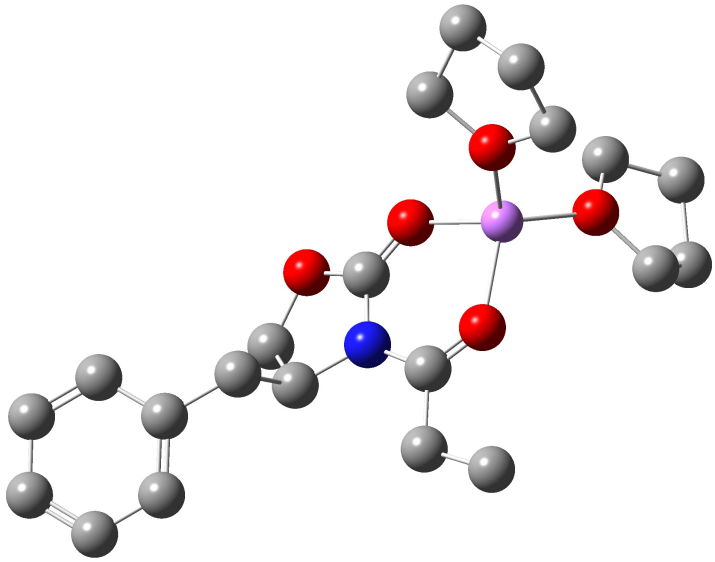
G = –784.641923 Hartree
G_{MP2} = –490848.9278 kcal/mol

Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	O	-2.95252800	1.75737500	-0.83937600
C	0.22120100	1.44648600	0.46900700	H	0.18536600	-0.72041500	0.79903300
H	0.14249800	1.54832100	1.55678600	C	0.82368100	-0.39161900	-1.24838400
H	1.16844100	1.87015500	0.13291600	H	0.41679100	-1.33532200	-1.62456300
O	-0.85067100	2.19977300	-0.13629800	H	0.67080000	0.36840900	-2.02462500
C	-1.87660300	1.36923500	-0.46061200	C	2.29789400	-0.54394600	-0.94110200
N	-1.44100300	0.04725100	-0.28452800	C	2.75986400	-1.67228900	-0.24664000
C	-2.18988400	-1.13563100	-0.39887900	C	4.11088200	-1.81286300	0.06854700
O	-1.61791700	-2.20225100	-0.24014900	C	5.02564600	-0.82606300	-0.30741900
C	-3.67253200	-1.01905900	-0.69927200	C	4.58010000	0.29829300	-1.00265200
C	-4.35552700	-2.38569700	-0.73198300	C	3.22590300	0.43641400	-1.31570400
H	-4.25847700	-2.90163200	0.22781800	H	2.88758700	1.30955500	-1.86996800
H	-5.42069200	-2.26466100	-0.95392200	H	5.28537900	1.06721400	-1.30679400
H	-3.91341700	-3.03135300	-1.49617700	H	6.07905600	-0.93689400	-0.06497200
H	-3.79300000	-0.48447300	-1.64844700	H	4.45131300	-2.69601000	0.60272900
H	-4.13226600	-0.35686000	0.04372100	H	2.05321300	-2.44908600	0.03813000

Table 7. Geometric coordinates and thermally corrected MP2 energies for η^2-coordinated oxazolidinone **4** with one Li^+ and two THF.



4

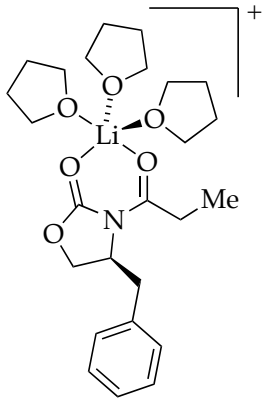


G = –1256.798527 Hartree
G_{MP2} = –786126.7701 kcal/mol

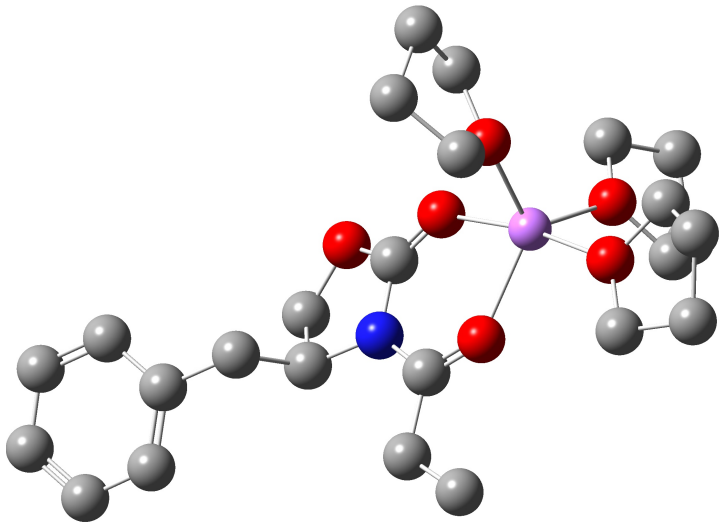
Atom	X	Y	Z	Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000	C	-3.27252100	-1.61663000	2.32408500
O	-1.40523400	0.01443600	-1.34749300	C	-2.43247900	-1.82356700	3.58439800
C	-2.55989300	-0.33331500	-1.19216100	H	-2.02678600	-0.87612700	3.94968400
N	-3.17836500	-0.75983500	-0.00339700	H	-3.05350200	-2.25837500	4.37247600
C	-4.64678600	-0.84096900	-0.21256700	H	-1.59366400	-2.49853500	3.39594400
C	-4.67769400	-0.99053600	-1.74124300	H	-3.69391400	-2.57191200	1.97926500
H	-4.65267100	-2.03338500	-2.06953400	H	-4.13440100	-0.97251900	2.53694300
H	-5.51334000	-0.47216700	-2.20913200	O	1.47037600	-1.20008300	-0.35144300
O	-3.45035400	-0.35514700	-2.18542900	C	2.08811100	-1.31739200	-1.66566900
H	-5.04846800	-1.73175600	0.27330600	C	3.01593000	-2.53308700	-1.58370000
C	-5.37785200	0.42743300	0.28620100	C	2.34584800	-3.39202600	-0.49930900
H	-5.14283700	0.57845900	1.34645800	C	1.84762600	-2.33056700	0.47742300
H	-4.97413800	1.29400200	-0.25157100	H	2.63852800	-2.01307500	1.16879000
C	-6.87740200	0.33645000	0.08694500	H	0.96855300	-2.62573400	1.05630100
C	-7.65460300	-0.49321400	0.90841900	H	3.03056900	-4.10310900	-0.02929200
C	-9.03088500	-0.60143800	0.71279400	H	1.50254100	-3.95374400	-0.91745700
C	-9.65166000	0.12196000	-0.30835900	H	4.01910400	-2.23030100	-1.26416700
C	-8.89033300	0.95583400	-1.12748200	H	3.10835600	-3.04622700	-2.54453600
C	-7.51178900	1.06137200	-0.93039200	H	1.28823200	-1.45588300	-2.40200800
H	-6.92831200	1.72768200	-1.56253100	H	2.61263900	-0.38262600	-1.88404600
H	-9.36752300	1.53020900	-1.91619000	O	0.57232900	1.80433100	0.37000500
H	-10.7241710	0.04116700	-0.45846800	C	1.67248800	2.13140300	1.26439800
H	-9.61979400	-1.24355900	1.36140600	C	1.79716300	3.65662500	1.23057100
H	-7.18508500	-1.04907100	1.71830600	C	1.26835100	4.00057600	-0.17095300
C	-2.47947700	-1.02041700	1.17632300	C	0.13117200	2.99526000	-0.33433200
O	-1.27272700	-0.81161900	1.26029600	H	-0.07612600	2.71468900	-1.37016700

H	-0.79587800	3.35503100	0.13036500	H	1.16389500	4.11127800	2.00046300
H	2.04144700	3.83038900	-0.92885400	H	1.43763700	1.73407800	2.25646200
H	0.92562600	5.03495900	-0.26021700	H	2.57453200	1.63582300	0.88751200
H	2.82458300	3.99064800	1.39791700				

Table 8. Geometric coordinates and thermally corrected MP2 energies for η^2-coordinated oxazolidinone **5** with one Li^+ and three THF.



5



G = –1489.147616 Hartree
G_{MP2} = –931447.2779 kcal/mol

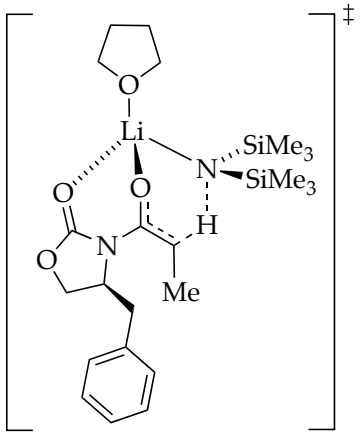
Atom	X	Y	Z	Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000	O	-1.41496800	-0.60722300	-1.40294400
O	-1.72267500	0.99903200	0.77793400	C	-3.34492000	-1.10617900	-2.75423300
C	-2.85756200	1.02942900	0.35790900	C	-2.43285900	-1.96420200	-3.63013300
N	-3.40128700	0.28896800	-0.70852100	H	-1.99930800	-2.79060700	-3.06017300
C	-4.87600300	0.44332000	-0.71985500	H	-3.00767200	-2.38415500	-4.46038500
C	-4.99656700	1.77355800	0.03915200	H	-1.61241300	-1.37296400	-4.04500100
H	-4.97129300	2.64389400	-0.62325000	H	-3.78949400	-0.29267100	-3.34507300
H	-5.87220800	1.82395700	0.68489300	H	-4.19015100	-1.69863400	-2.38347900
O	-3.81526200	1.81232600	0.87760700	O	1.48617000	-1.05802100	-0.97476500
H	-5.23967200	0.54476500	-1.74395600	C	2.83040800	-1.05616900	-0.43893400
C	-5.59232100	-0.72647500	-0.00386300	C	3.51853900	-2.27226100	-1.05697800
H	-5.28581900	-1.66940000	-0.47185800	C	2.85832000	-2.33292500	-2.44283200
H	-5.24194300	-0.76283500	1.03488200	C	1.41567900	-1.92412500	-2.13291000
C	-7.10053900	-0.58553600	-0.04614100	H	0.79275200	-2.79129400	-1.88001400
C	-7.80385000	-0.83169900	-1.23435300	H	0.93036800	-1.37718600	-2.94566100
C	-9.18862800	-0.67778500	-1.28778500	H	2.92013500	-3.31937500	-2.91082200
C	-9.89251000	-0.27608000	-0.14997900	H	3.32679800	-1.60883000	-3.11928000
C	-9.20508400	-0.03442700	1.03953700	H	3.29080700	-3.17765700	-0.48199100
C	-7.81799800	-0.18855800	1.08985100	H	4.60572100	-2.16215900	-1.09918600
H	-7.29155900	-0.01427000	2.02606000	H	3.32861100	-0.12230600	-0.73008600
H	-9.74655900	0.26774100	1.93132700	H	2.75366300	-1.08593600	0.65059200
H	-10.9715550	-0.15992800	-0.18980200	O	0.26893700	-1.00604300	1.73006100
H	-9.71918700	-0.87846500	-2.21415400	C	0.25416400	-2.45159700	1.78418300
H	-7.26802900	-1.16094300	-2.12308200	C	-0.33776500	-2.80243400	3.14810500
C	-2.62246200	-0.48040200	-1.57299800	C	0.17900100	-1.64865500	4.02154000

C	0.10261900	-0.45644600	3.06392100
H	0.89069400	0.28468200	3.22920700
H	-0.86807900	0.04852700	3.10509100
H	1.21534200	-1.83505700	4.32493900
H	-0.41407300	-1.49225400	4.92669800
H	-0.02205500	-3.78815000	3.50095600
H	-1.43319000	-2.79042700	3.10412200
H	-0.33234900	-2.81771600	0.93667200
H	1.28236500	-2.82347900	1.68387100
O	0.96779900	1.75680600	-0.20720600
C	0.95049300	2.86173100	0.73506300
C	1.60625200	4.04119500	0.01159800
C	1.28645900	3.74031300	-1.46076500
C	1.41487000	2.21854600	-1.50345300
H	2.45681900	1.90770900	-1.65410800
H	0.79452500	1.74009100	-2.26664100
H	1.96338200	4.23714400	-2.16136400
H	0.26150600	4.04582300	-1.70227900
H	2.68997500	4.04012400	0.17386500
H	1.21579200	5.00453100	0.35095000
H	-0.09203700	3.06440900	1.00111600
H	1.48995800	2.55234200	1.63563200

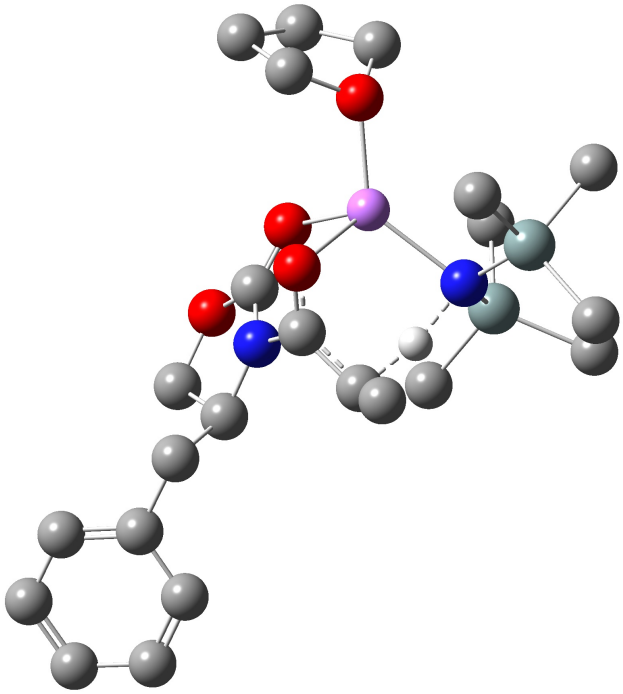
V. Transition state computations

Geometries are optimized at the B3LYP level of theory using the 6–31G(d) basis set. Energies are defined as follows: G is the sum of electronic and thermal free energies calculated at the B3LYP level of theory (T = 195 K). G_{MP2} is derived from an MP2 SP calculation corresponding to the DFT-optimized geometry and includes a thermal correction from the DFT calculation. $\Delta G^{\ddagger}_{MP2}$ is the difference between G_{MP2} of the transition structure, and G_{MP2} of LiHMDS disolvated dimer **1**, oxazolidinone **9**, and THF, based on the corresponding stoichiometries ($G_{MP2}^{TS} - G_{MP2}^{GS}$).

Table 9. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by AS (**11**; *anti* to benzyl group).



11 *anti*

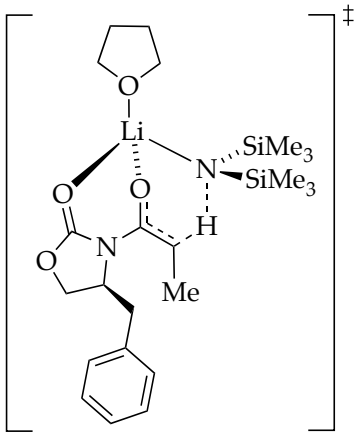


G = –1897.687682 Hartree
G_{MP2} = –1187441.5039 kcal/mol
$\Delta G^{\ddagger}_{MP2}$ = 16.9 kcal/mol

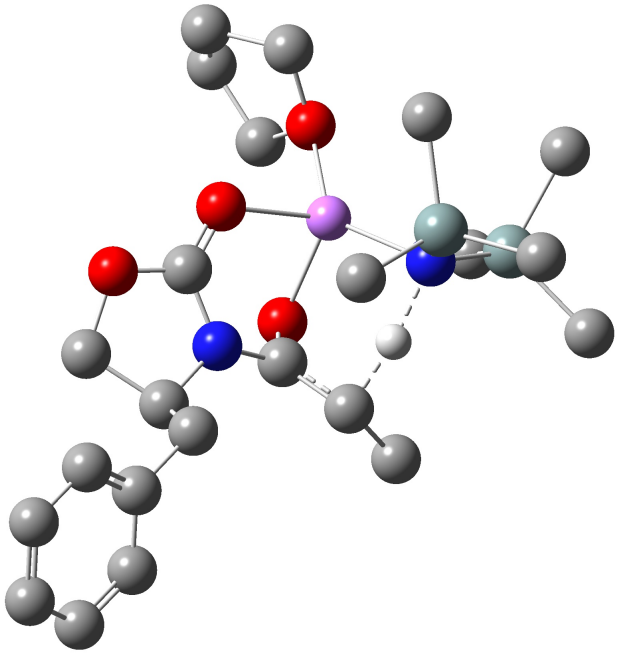
Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.29881700	1.11619200	1.02241700
H	0.84115800	0.76967400	1.90198100
H	0.83951000	1.95256200	0.56597700
O	-0.99430600	1.59447500	1.45277800
C	-1.93517500	1.19417700	0.56828600
N	-1.36989400	0.37022600	-0.37710200
C	-2.18481900	-0.22912900	-1.40826000
O	-3.02157000	0.51685200	-1.95200100
Li	-4.43791800	0.47730100	-0.50627100
N	-4.59329600	-1.58013100	-0.11393900
Si	-5.98038800	-2.12034200	-1.03738500
C	-6.18861500	-1.08915400	-2.62088400
H	-5.30550400	-1.11219200	-3.26730900
H	-7.03703400	-1.47414100	-3.20193700
H	-6.40098300	-0.03912800	-2.38685700
C	-7.62370200	-1.90930400	-0.09138600
H	-8.46766500	-2.20906000	-0.72660000
H	-7.67586400	-2.51029900	0.82379100
H	-7.78656200	-0.86186700	0.19304700
C	-5.87551100	-3.94550600	-1.56867600
H	-4.97779900	-4.14036800	-2.16772200
H	-5.84997100	-4.62237300	-0.70713200
H	-6.74421600	-4.22178100	-2.18075300

Si	-4.41073200	-2.02364800	1.56507600
C	-5.31975200	-0.81289600	2.71912500
H	-4.92653600	0.20459100	2.59591200
H	-6.39698600	-0.78757300	2.51442800
H	-5.19141600	-1.08920700	3.77402200
C	-2.58155500	-1.99729300	2.10322700
H	-2.50163000	-2.40557100	3.11886000
H	-1.95293800	-2.61796300	1.45346900
H	-2.15750400	-0.98745000	2.13456400
C	-5.00317900	-3.78165400	2.00751400
H	-6.07284700	-3.93474200	1.82536600
H	-4.45983600	-4.54312700	1.43430200
H	-4.82246000	-3.98093200	3.07217100
O	-5.80286300	1.87580200	-0.74919500
C	-6.54926800	2.43138100	0.34740900
C	-5.78515900	3.70293600	0.73674500
C	-5.13443300	4.16068000	-0.59724200
C	-5.40132500	2.99263600	-1.57129000
H	-4.52759600	2.67126400	-2.14031600
H	-6.21976400	3.22629100	-2.26550300
H	-4.06213600	4.32544600	-0.46581400
H	-5.57275400	5.08995700	-0.97395900
H	-5.01184500	3.46144500	1.46997900
H	-6.44632900	4.45991200	1.16915900
H	-7.57030300	2.65716100	0.00654700
H	-6.59609800	1.67337500	1.13222000
C	-2.17312300	-1.65762800	-1.51363000
C	-2.45530200	-2.29452800	-2.86810900
H	-1.55201500	-2.35401400	-3.49063700
H	-2.83706100	-3.31391000	-2.74682700
H	-3.20138400	-1.71768400	-3.41945400
H	-1.37521500	-2.14868600	-0.95343600
O	-3.11098600	1.50709900	0.68061200
H	0.00068800	-0.97795200	0.49816800
C	0.97441200	-0.02924000	-1.18973000
H	0.61434100	-0.77302300	-1.91001500
H	0.94037600	0.94468700	-1.69206300
C	2.39083800	-0.35710900	-0.76170400
C	2.73774900	-1.66388400	-0.38704900
C	4.03206300	-1.96721400	0.03400100
C	5.00550700	-0.96675900	0.08471500
C	4.67550000	0.33555000	-0.29090300
C	3.37773400	0.63590900	-0.70993500
H	3.13194800	1.65151000	-1.01272100
H	5.42799300	1.11910300	-0.26304000
H	6.01520500	-1.20312900	0.40897000
H	4.28242300	-2.98619200	0.31672300
H	1.98976600	-2.45268900	-0.43491300
H	-3.31904000	-1.76022300	-0.79962200

Table 10. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by AS (**11**; *syn* to benzyl group).



11 *syn*

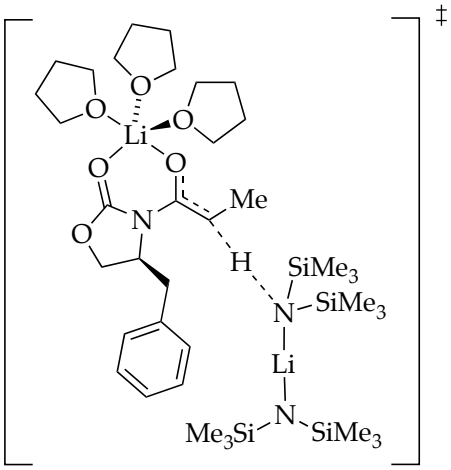


G = –1897.684384 Hartree
G_{MP2} = –1187439.0021 kcal/mol
$\Delta G^{\ddagger}_{MP2}$ = 19.4 kcal/mol

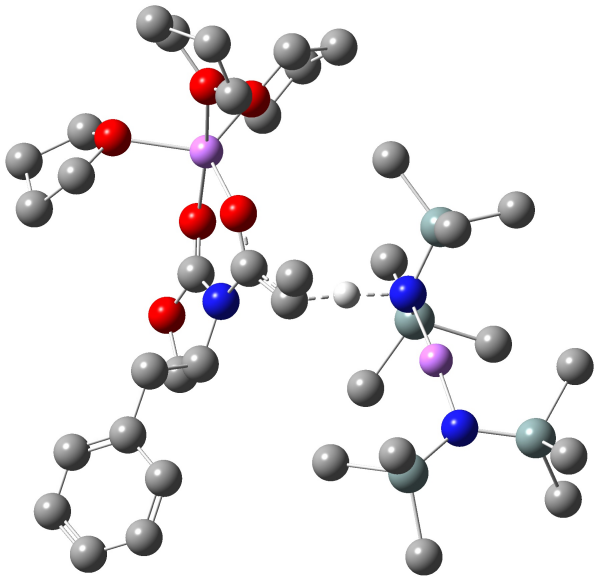
Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	-0.28405000	1.39621700	0.59493600
H	-0.36221000	2.16792100	-0.17787200
H	-1.16662100	1.42538800	1.23401600
O	0.87143200	1.69123600	1.41382200
C	1.91175600	0.94691200	0.97388500
N	1.47093100	0.00582900	0.07369100
C	2.41138200	-0.61036800	-0.84187600
O	3.34442600	0.11470500	-1.23787700
Li	4.52800800	0.00335000	0.41122700
O	5.89509900	1.42198100	0.46103400
C	5.78227400	2.42040600	-0.58999600
C	6.20699300	3.74703600	0.04614100
C	5.83308600	3.53796800	1.52211000
C	6.17805000	2.06450100	1.72736100
H	5.57371300	1.57655300	2.49585400
H	7.24088500	1.92200900	1.96269200
H	4.75932700	3.69356500	1.67209800
H	6.37918700	4.19512600	2.20558300
H	5.70167400	4.60334300	-0.41035700
H	7.28817400	3.89703300	-0.05728600
H	6.41852800	2.10811700	-1.42282500
H	4.74122800	2.43719000	-0.92894800
N	4.62063600	-2.07338700	0.68563100
Si	4.24586800	-2.62453200	2.29898700
C	2.40054400	-2.37411700	2.68620400
H	1.75311800	-2.90338900	1.97793700
H	2.17544900	-2.75837300	3.68936800
H	2.12808600	-1.31311700	2.67403300
C	5.18755900	-1.65030500	3.63742900
H	4.92296500	-2.00589400	4.64206200
H	6.27427500	-1.74081800	3.53074400
H	4.93498200	-0.58259900	3.59345200
C	4.57950000	-4.47649900	2.60615800
H	4.01869400	-5.10358700	1.90186000
H	5.63907700	-4.74054200	2.50846300
H	4.26565600	-4.75813500	3.61993300
Si	6.08479000	-2.58871000	-0.12594400
C	7.61123700	-2.61247400	1.01716900
H	7.79010700	-1.62754800	1.46617900
H	7.52691300	-3.33813100	1.83471400
H	8.50705100	-2.87616300	0.43927300
C	6.53205500	-1.38182200	-1.52686000
H	7.33474000	-1.80027300	-2.14775600
H	5.68229000	-1.15577700	-2.17948400
H	6.89566700	-0.43169100	-1.11657500
C	5.95847700	-4.32703300	-0.89114800
H	5.73965300	-5.08779900	-0.13300300

H	5.17202900	-4.38345000	-1.65233100
H	6.90425000	-4.60494300	-1.37491200
C	2.37255400	-2.03283500	-0.99214800
C	2.81197700	-2.64000000	-2.31840900
H	3.71644300	-2.15605500	-2.69438200
H	3.02489300	-3.70716000	-2.19829900
H	2.03639000	-2.54429700	-3.09055300
H	1.49495700	-2.51208000	-0.55806500
O	3.05252800	1.09605800	1.38637300
H	-0.31496000	-0.04792900	-1.04626400
C	-0.66591600	-1.14508300	0.79850700
H	-0.28889300	-2.09814900	0.41413200
H	-0.34239700	-1.07842700	1.84310600
C	-2.17739100	-1.11283400	0.70671400
C	-2.82805600	-1.48129400	-0.48056500
C	-4.21826300	-1.43427000	-0.57966200
C	-4.98539000	-1.01927000	0.51142900
C	-4.35227000	-0.65570100	1.70008700
C	-2.95966300	-0.70246200	1.79456600
H	-2.47405100	-0.43006300	2.72927000
H	-4.94045700	-0.34018000	2.55770300
H	-6.06882500	-0.98617100	0.43643000
H	-4.70351900	-1.72828600	-1.50657100
H	-2.24100300	-1.82047800	-1.33187800
H	3.41410900	-2.19262300	-0.14461800

Table 11. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by A_2S_3 (**12**; *anti* to benzyl group).



12 *anti*

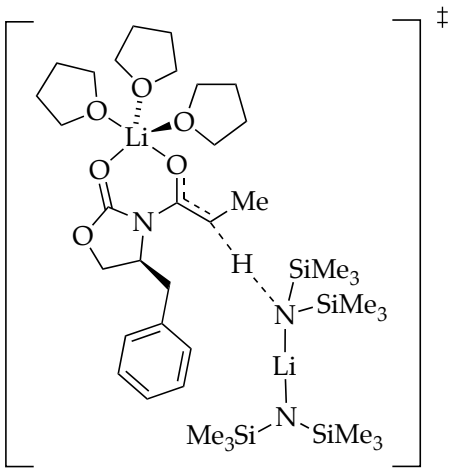


G = –3243.102080 Hartree
G_{MP2} = –2029362.9359 kcal/mol
$\Delta G^{\ddagger}_{MP2}$ = 17.2 kcal/mol

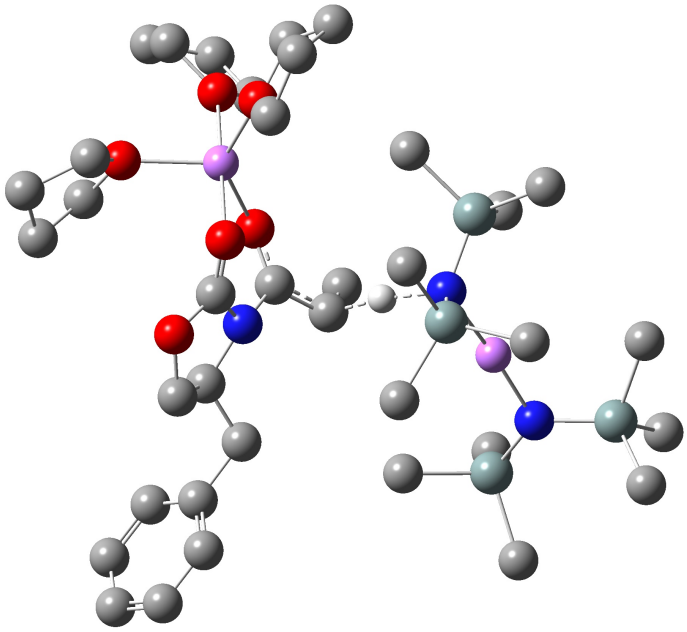
Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000
O	-0.46480000	1.15885800	-1.68544700
C	-1.34156200	2.00702500	-1.68657100
N	-2.48591400	2.06953400	-0.92050800
C	-3.15550700	3.37313300	-1.11056000
C	-2.53525400	3.79734400	-2.44974300
H	-3.14909300	3.49365200	-3.30350700
H	-2.32197200	4.86489000	-2.51061600
O	-1.28289100	3.07883300	-2.51577400
H	-4.23265500	3.24211200	-1.21852300
C	-2.86093200	4.34360200	0.05691800
H	-3.19109000	3.86048300	0.98408100
H	-1.77447400	4.47927500	0.13452800
C	-3.54396000	5.68503300	-0.10824500
C	-4.93180400	5.80224400	0.06180300
C	-5.56817000	7.03084400	-0.11280700
C	-4.82789300	8.16424600	-0.45745100
C	-3.44687500	8.06115400	-0.62515900
C	-2.81205500	6.82925100	-0.45222000
H	-1.73277500	6.75859400	-0.57333300
H	-2.86096100	8.93840200	-0.88657300
H	-5.32463200	9.12147800	-0.58999700
H	-6.64357200	7.10225000	0.02517000
H	-5.52091100	4.93065200	0.33935500
C	-2.75658500	1.15305400	0.16291500
O	-1.79915200	0.48739000	0.60926600
C	-4.11884200	1.03607700	0.58889900
C	-4.32820000	0.67028700	2.05615800
H	-4.00258600	1.47021500	2.73612500
H	-5.38884600	0.48671200	2.25701000
H	-3.77521800	-0.23361900	2.32542100
H	-4.75211900	1.86386900	0.27038300
O	0.43780800	-0.96092500	1.86328600
C	1.77029400	-1.18825700	2.35450400
C	1.67814700	-0.99706800	3.86708900
C	0.29030600	-1.58629300	4.16408800
C	-0.52274500	-1.17055200	2.92945600
H	-1.06519700	-0.23297000	3.07830400
H	-1.23993500	-1.93273200	2.61113000
H	-0.14950300	-1.21435200	5.09414800
H	0.35262400	-2.67845600	4.23656200
H	1.70605100	0.07037800	4.11720200
H	2.48754600	-1.49646300	4.40844100
H	2.08606100	-2.21327300	2.10659300
H	2.42819400	-0.48030900	1.84717800
O	1.65263700	1.29090400	0.31451200

C	1.34033400	2.50383800	1.03270800
C	1.78004200	3.64881600	0.11954400
C	3.00637700	3.03758500	-0.57639200
C	2.57302100	1.58023800	-0.76687600
H	3.40318000	0.86885300	-0.70939200
H	2.03882200	1.43821400	-1.71124400
H	3.88550700	3.10036600	0.07585000
H	3.25205200	3.52410100	-1.52473900
H	2.00576800	4.56483500	0.67382600
H	1.00016400	3.87232700	-0.61749200
H	0.26980300	2.49659800	1.25757100
H	1.89665900	2.51192200	1.98055000
O	0.56102900	-1.59626400	-1.12573200
C	0.60728400	-1.58407600	-2.57458600
C	0.95093600	-3.01545200	-2.98803400
C	0.28946400	-3.83450500	-1.86987100
C	0.54484500	-2.96017700	-0.64141800
H	1.52007400	-3.18089800	-0.18733900
H	-0.22852700	-3.04108300	0.12478900
H	0.70611500	-4.84028900	-1.76048800
H	-0.78710800	-3.92943400	-2.05239100
H	2.03685800	-3.16935400	-2.98439400
H	0.57610000	-3.26044800	-3.98615700
H	-0.37201700	-1.27406200	-2.95423700
H	1.34918700	-0.84374100	-2.88526500
Si	-10.2697720	-0.77470000	-0.04338500
C	-11.5942400	-0.96071300	1.32006200
H	-12.1180110	-0.01608900	1.51532900
H	-12.3541540	-1.70381300	1.04321200
H	-11.1413200	-1.28409400	2.26590200
C	-9.58165700	-2.53640600	-0.32649400
H	-10.3793630	-3.22097000	-0.64359300
H	-8.81138400	-2.56360100	-1.10937300
H	-9.14293300	-2.95116300	0.59042100
C	-11.2052850	-0.32901100	-1.64704600
H	-11.6801950	0.65676100	-1.57170100
H	-10.5185480	-0.29234600	-2.50326900
H	-11.9913050	-1.05937100	-1.88240600
N	-8.99177500	0.29978400	0.33316100
Li	-7.30248800	-0.40284500	-0.06581500
N	-5.48674800	-1.01999900	-0.70766500
Si	-5.42212500	-0.80568800	-2.44530700
C	-6.79701100	-1.72140600	-3.38109300
H	-6.74825600	-2.80817800	-3.25990100
H	-7.79087500	-1.39533600	-3.05032300
H	-6.72510800	-1.50415400	-4.45529600
C	-3.75354400	-1.33245400	-3.20146700
H	-2.91951700	-0.81039300	-2.71494800
H	-3.57836100	-2.40999500	-3.09177900
H	-3.71446900	-1.10214800	-4.27414400
C	-5.65660700	1.03406900	-2.85792100
H	-4.78929100	1.62406000	-2.54471700
H	-5.77662100	1.17079900	-3.93998800
H	-6.54678300	1.45284100	-2.37235200
Si	-5.13235800	-2.55289200	0.06998600
C	-3.26344600	-2.80414700	0.32959500
H	-2.76608600	-2.99035900	-0.63086400
H	-2.79300400	-1.91985200	0.77238700
H	-3.06904700	-3.66838100	0.97909700
C	-5.73960800	-4.07549600	-0.89353300
H	-6.82458500	-4.06145500	-1.04511000
H	-5.26419100	-4.17105400	-1.87684000
H	-5.49940700	-4.98476200	-0.32653400
C	-5.97333600	-2.63187600	1.77309000
H	-5.80697400	-3.61735300	2.22751100
H	-5.58719500	-1.88009400	2.46930100
H	-7.05996600	-2.49184600	1.70481000
Si	-9.16294500	1.85353500	1.01628300
C	-10.6192820	2.88624200	0.33630000
H	-10.5380040	3.02015200	-0.74989000
H	-11.5862670	2.40622100	0.53343600
H	-10.6515460	3.88402800	0.79453000
C	-7.60314500	2.91516900	0.68217700
H	-7.73451600	3.93237700	1.07568500
H	-6.71590000	2.48940500	1.16899800
H	-7.40036500	2.99368500	-0.39433700
C	-9.35419500	1.84621500	2.91644400
H	-10.2697720	1.32464100	3.22136200
H	-8.51258000	1.32396800	3.39087300
H	-9.39577200	2.86138600	3.33450600
H	-4.70567200	0.00032500	-0.11412700

Table 12. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by A_2S_3 (**12**; *syn* to benzyl group).



12 *syn*

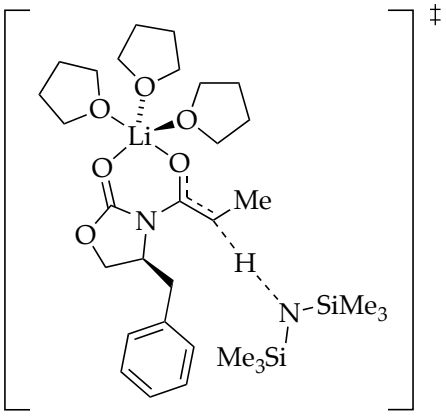


G = –3243.092711 Hartree
G_{MP2} = –2029357.3127 kcal/mol
$\Delta G^{\ddagger}_{MP2}$ = 22.8 kcal/mol

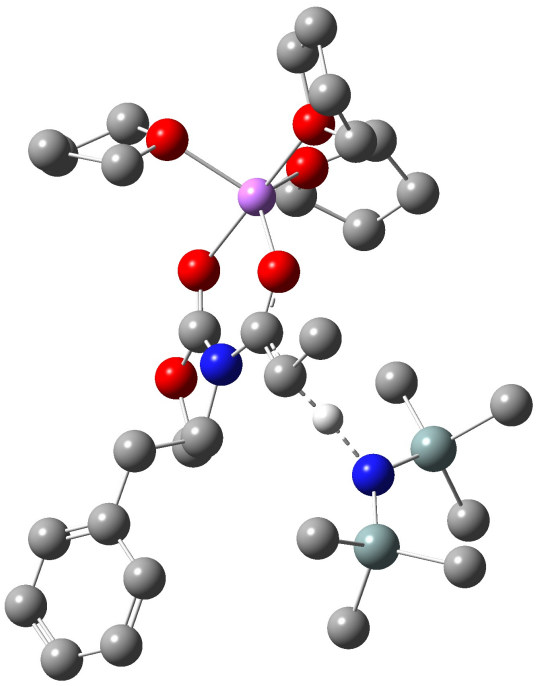
Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000
O	0.65381800	1.09390800	-1.71419500
C	1.28029100	2.12343100	-1.52539000
N	2.36331100	2.32425400	-0.69372500
C	2.64445200	1.33634400	0.34787800
O	1.67206800	0.70405000	0.80738500
C	4.01561100	1.12360800	0.69259600
C	4.28252100	0.63474500	2.11374200
H	4.01945600	1.38895600	2.86795300
H	5.34349400	0.39964500	2.24445800
H	3.70988800	-0.26949900	2.33790100
H	4.67264200	1.93252000	0.38096800
C	2.58619900	3.79035600	-0.54403700
C	1.94218100	4.27611000	-1.84894900
H	2.66962200	4.31376900	-2.66737300
H	1.44203400	5.23970700	-1.75852400
O	0.95417700	3.27539900	-2.16472000
H	1.98950800	4.13780900	0.31306200
C	4.02701300	4.29835900	-0.36978700
H	4.65949400	3.87518900	-1.15622600
H	4.42613800	3.95059000	0.58657700
C	4.07456200	5.81536300	-0.41292500
C	3.63416500	6.57391000	0.68192500
C	3.65461400	7.96782300	0.64125300
C	4.12132700	8.62883500	-0.49710200
C	4.57092400	7.88634800	-1.58937500
C	4.54667400	6.49088900	-1.54608900
H	4.91532300	5.91982800	-2.39524300
H	4.94889900	8.39123700	-2.47427800
H	4.14375300	9.71469600	-0.52753200
H	3.31595700	8.53801000	1.50225200
H	3.28774400	6.06818500	1.58111800
O	-0.52690800	-0.99045000	1.83712500
C	-1.86529800	-1.15678500	2.32343400
C	-1.78312000	-0.78140600	3.80148900
C	-0.42702000	-1.39127500	4.20147800
C	0.40300100	-1.30667100	2.90239900
H	1.15100500	-0.51279300	2.91060000
H	0.90423800	-2.25380300	2.67108200
H	0.04925200	-0.86034400	5.03069900
H	-0.55729800	-2.43460700	4.50928000
H	-1.76473500	0.30950000	3.90791800
H	-2.62033500	-1.16966500	4.38964000
H	-2.18676500	-2.20342200	2.19977700
H	-2.50753100	-0.51165500	1.72162300
O	-1.66614600	1.25249800	0.17707300

C	-1.54455700	2.42875300	1.00532500
C	-2.01710400	3.59352800	0.13479600
C	-3.10963500	2.92494300	-0.71417000
C	-2.51890800	1.53282300	-0.96162400
H	-3.27661000	0.74524000	-1.02432800
H	-1.89715700	1.50673300	-1.86198100
H	-4.04497900	2.85481400	-0.14638400
H	-3.31816300	3.45752200	-1.64650200
H	-2.38186400	4.43921400	0.72547900
H	-1.20215000	3.94353200	-0.50842200
H	-0.50286800	2.50178300	1.33026400
H	-2.18107100	2.30919700	1.89338800
O	-0.53459800	-1.58654500	-1.15632800
C	-0.51469000	-1.59074400	-2.60646100
C	-1.01748200	-2.97410300	-3.01974300
C	-0.50904800	-3.85251900	-1.86709100
C	-0.70076600	-2.93511100	-0.65839600
H	-1.71036900	-3.02999900	-0.23720000
H	0.02969700	-3.09811200	0.13627000
H	-1.05285600	-4.79650500	-1.76511900
H	0.55346400	-4.08399900	-2.00345200
H	-2.11345200	-2.99226300	-3.06035500
H	-0.63622500	-3.27889000	-3.99883300
H	0.51122400	-1.41176800	-2.94410700
H	-1.14246100	-0.76798500	-2.95704700
Si	10.0982280	-0.83593100	-0.09929800
C	11.4112710	-1.17089300	1.24743300
H	11.9488290	-0.25612600	1.52827700
H	12.1608440	-1.89826900	0.90766200
H	10.9491750	-1.57038600	2.15920700
C	9.37206400	-2.55014900	-0.53889200
H	10.1530900	-3.21822800	-0.92538400
H	8.59439400	-2.49014600	-1.31284500
H	8.93286300	-3.03866800	0.34061500
C	11.0575620	-0.27582200	-1.65317600
H	11.5575750	0.68654800	-1.48865900
H	10.3784140	-0.14596100	-2.50642800
H	11.8256850	-1.00378900	-1.94782500
N	8.84627500	0.23543800	0.36334400
Li	7.13754500	-0.35328100	-0.12505800
N	5.30380500	-0.84380600	-0.80897100
Si	5.26001400	-0.45034800	-2.51499600
C	6.66549500	-1.25905400	-3.50462700
H	6.60936800	-2.35277100	-3.50547700
H	7.64854300	-0.97854300	-3.10616000
H	6.63140800	-0.92538800	-4.55041300
C	3.61512000	-0.91089500	-3.35880600
H	2.76678700	-0.43357300	-2.85260200
H	3.44108100	-1.99422100	-3.35322100
H	3.60654700	-0.58434600	-4.40701600
C	5.47678200	1.42514300	-2.72901700
H	4.60560200	1.96670600	-2.34516100
H	5.58918000	1.68050100	-3.79030400
H	6.36720800	1.79521500	-2.20489500
Si	4.89484500	-2.43187800	-0.19344800
C	3.02365300	-2.61989400	0.09952900
H	2.47639000	-2.59349700	-0.85090700
H	2.63077100	-1.80858300	0.72161800
H	2.79821100	-3.57502500	0.59328100
C	5.40443900	-3.86716300	-1.33310600
H	6.48789400	-3.89398800	-1.49496300
H	4.91980700	-3.82135500	-2.31560400
H	5.11906100	-4.82209300	-0.87199700
C	5.76380000	-2.73967900	1.46936200
H	5.53258900	-3.74825100	1.83683500
H	5.45433900	-2.03039100	2.24463500
H	6.85555900	-2.67473300	1.38135100
Si	9.06598000	1.70530600	1.20466300
C	10.5478080	2.76018200	0.61956400
H	10.4599930	3.01123900	-0.44515700
H	11.5011910	2.23311000	0.75199300
H	10.6154010	3.70245100	1.18002300
C	7.53611800	2.83772300	1.00621000
H	7.69529700	3.80689500	1.49730800
H	6.64257000	2.38835100	1.45857000
H	7.31990000	3.03456500	-0.05231200
C	9.28095700	1.48162400	3.08959500
H	10.1726580	0.88470800	3.31767900
H	8.42014400	0.95146400	3.51891000
H	9.37888800	2.44086300	3.61620900
H	4.51588000	0.15657300	-0.09784500

Table 13. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by AS_3 (**13**; *anti* to benzyl group).



13 *anti*

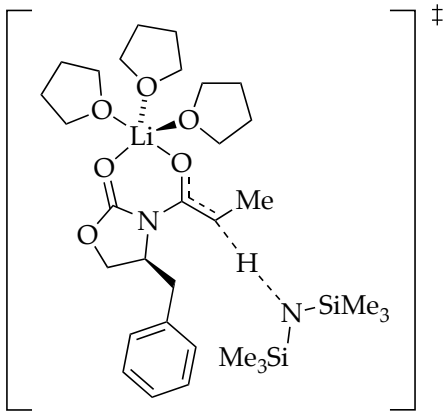


G = –2362.388426 Hartree
G_{MP2} = –1478074.6254 kcal/mol
$\Delta G^{‡}_{MP2}$ = 8.3 kcal/mol

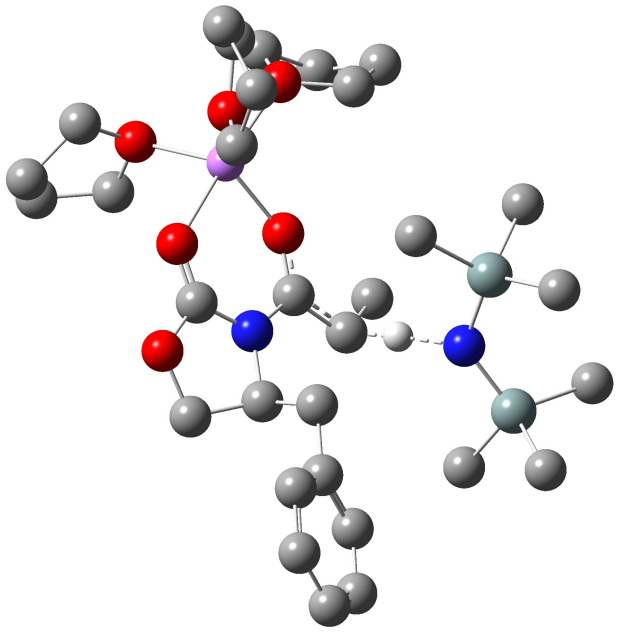
Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000
O	1.25802800	1.28801500	1.06155900
C	2.47883200	1.26897100	1.00599300
N	3.29314200	0.71750100	0.03758600
C	4.69670500	1.13351700	0.25859300
C	4.62330600	1.50303800	1.74494800
H	4.85827200	0.65402700	2.39343800
H	5.23733200	2.36190900	2.01502000
O	3.23394800	1.86269700	1.95559200
H	5.35711500	0.27665400	0.10068400
C	5.07326500	2.33699100	-0.64066800
H	4.98689500	2.02681800	-1.68827800
H	4.32849400	3.12787200	-0.48449400
C	6.45968100	2.88442300	-0.36734700
C	7.60426000	2.14310300	-0.69590900
C	8.87878900	2.64109700	-0.42558100
C	9.03219400	3.89259500	0.17549000
C	7.90233200	4.64199400	0.50348200
C	6.62752900	4.13878200	0.23461500
H	5.75090100	4.73181400	0.48780000
H	8.00994000	5.61902600	0.96739200
H	10.0255360	4.28051000	0.38426700
H	9.75167400	2.04893500	-0.68610400
H	7.50063600	1.16950800	-1.16699700
C	2.83813700	-0.21477700	-0.94246400
O	1.63680300	-0.54968700	-0.92185900
C	3.84312100	-0.78913500	-1.80685900
C	3.30235300	-1.63800700	-2.94971700
H	2.63081000	-1.08217400	-3.61842100
H	4.13269300	-2.02438400	-3.54852300
H	2.74924600	-2.50156700	-2.56522300
H	4.57986200	-0.05277300	-2.13766700
O	-0.83162400	-0.75982400	1.74791500
C	-1.35952100	-2.09097000	1.87362800
C	-0.46497700	-2.78326700	2.91521000
C	0.10021900	-1.60518900	3.75700400
C	-0.50016200	-0.35443400	3.08902000
H	0.18257400	0.49071400	3.01029800
H	-1.42190400	-0.03633800	3.59961000
H	1.19189800	-1.58750600	3.70221100
H	-0.18242700	-1.66778100	4.81226500
H	0.34876400	-3.32413000	2.42460400
H	-1.03059400	-3.50090400	3.51722300
H	-2.40187700	-2.03003200	2.22292900
H	-1.34064500	-2.53874100	0.88054300
O	-1.21740400	-1.29017800	-1.22165000

C	-0.70373000	-2.24219500	-2.17133900
C	-1.43054100	-1.90190700	-3.46921800
C	-2.84681800	-1.56624300	-2.96232000
C	-2.60082200	-1.02291400	-1.53527600
H	-3.24379500	-1.51723300	-0.79514900
H	-2.73755800	0.05724300	-1.45179700
H	-3.46360600	-2.47093100	-2.92827500
H	-3.36332600	-0.84034100	-3.59736200
H	-1.41849600	-2.72219200	-4.19331000
H	-0.96449300	-1.02665900	-3.93614700
H	0.37683700	-2.11022100	-2.19643400
H	-0.94331800	-3.26523400	-1.84037400
O	-1.07467600	1.67654000	-0.64523100
C	-0.42441000	2.41920900	-1.70255400
C	-0.78666000	3.88781600	-1.46845600
C	-0.92720200	3.93942900	0.06078800
C	-1.57008300	2.58619500	0.36549600
H	-2.66487100	2.62945800	0.28666900
H	-1.29885800	2.18527500	1.34422100
H	-1.53218300	4.78019500	0.41328700
H	0.05860900	3.99879900	0.53409700
H	-1.74109300	4.13111700	-1.95036200
H	-0.02635400	4.57109300	-1.85844400
H	0.65725200	2.25335500	-1.63001500
H	-0.77557000	2.02629100	-2.66180900
N	5.60579300	-2.31703800	-0.31380200
Si	7.14658000	-2.47892500	-1.04782300
C	7.65479400	-4.27006500	-1.47540600
H	7.70976700	-4.90379500	-0.58116700
H	6.93032400	-4.73177100	-2.15812200
H	8.63918700	-4.30458800	-1.96167200
C	8.56865000	-1.77518800	0.01771100
H	8.38978000	-0.72664200	0.28922700
H	8.67339000	-2.33533700	0.95528200
H	9.53417500	-1.82514100	-0.50431400
C	7.21758200	-1.54005900	-2.71123400
H	6.96511600	-0.47554800	-2.62205600
H	8.22635600	-1.59751800	-3.14056000
H	6.52670900	-1.97559000	-3.44376600
Si	4.92902500	-3.34819200	0.87304300
C	3.45842100	-2.50422800	1.75903000
H	3.77432300	-1.60672300	2.30765800
H	2.67074400	-2.21050100	1.05449700
H	3.01161800	-3.19335800	2.48868000
C	6.13782300	-3.84332200	2.26602900
H	6.98529800	-4.42743100	1.88586600
H	6.55118300	-2.95849300	2.76629500
H	5.63730400	-4.45431800	3.02945500
C	4.21199100	-4.97600900	0.17667600
H	3.73718400	-5.58670800	0.95693600
H	3.45603100	-4.77378800	-0.59358300
H	4.99423400	-5.58604900	-0.29142700
H	4.60281500	-1.53174100	-1.08283900

Table 14. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by AS_3 (**13**; *syn* to benzyl group).



13 *syn*

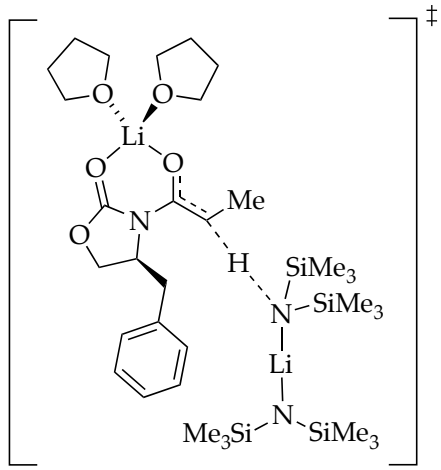


G = –2362.386558 Hartree
G_{MP2} = –1478075.0490 kcal/mol
$\Delta G^{\ddagger}_{MP2}$ = 7.8 kcal/mol

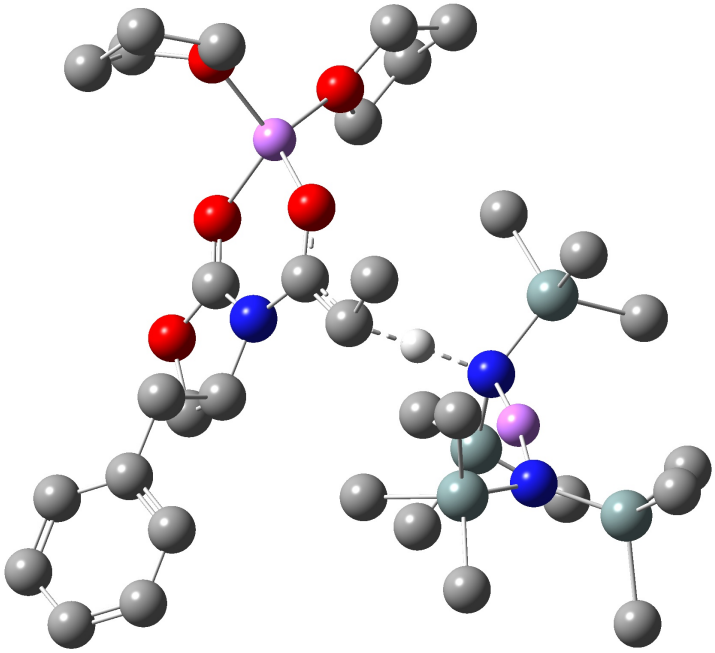
Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000
O	-0.46218200	-0.20010800	1.99557900
C	0.39046000	-0.88991100	2.94589100
C	-0.09705200	-0.46270400	4.33398300
C	-1.57797100	-0.14462600	4.07795700
C	-1.51977100	0.49268000	2.69022300
H	-1.27725200	1.56082700	2.74778300
H	-2.43882000	0.37833300	2.10885100
H	-2.01661800	0.52099900	4.82749500
H	-2.17019000	-1.06738700	4.05156400
H	0.43370500	0.43689600	4.66611500
H	0.05657800	-1.24232700	5.08598200
H	0.28003000	-1.96722300	2.78147700
H	1.42770000	-0.60694500	2.74860300
O	-1.50966000	-0.81236200	-1.17439400
C	-2.26572400	-1.85803400	-0.51899300
C	-2.00531700	-3.12504600	-1.33169400
C	-1.86102400	-2.56095200	-2.75414600
C	-1.12925800	-1.23811400	-2.50499300
H	-1.40415300	-0.44799500	-3.21128800
H	-0.04112700	-1.36256500	-2.52540000
H	-2.84775500	-2.37827600	-3.19601900
H	-1.30625600	-3.22063700	-3.42792400
H	-2.81203000	-3.85832000	-1.23740800
H	-1.06891000	-3.58787400	-1.00490200
H	-1.91880200	-1.91568100	0.51539300
H	-3.32941000	-1.58145900	-0.52882300
O	-0.83287900	1.96812200	-0.00244000
C	0.06565000	3.04733900	0.36373100
C	-0.22539000	4.21184800	-0.60290000
C	-1.00379500	3.53358200	-1.74358200
C	-1.76285500	2.44617600	-0.98738200
H	-2.06497700	1.58736700	-1.58898600
H	-2.65360100	2.86038300	-0.48832500
H	-0.31497800	3.07763500	-2.46324700
H	-1.66517800	4.22021600	-2.28136100
H	0.69235300	4.70080200	-0.94101500
H	-0.84913600	4.97166600	-0.11822100
H	-0.11307600	3.32099700	1.41046200
H	1.08277700	2.66485000	0.26416100
O	1.64054500	0.53825300	-0.89426300
C	2.76618300	0.07257500	-1.15646000
N	3.04035700	-1.27678400	-0.76606900
C	2.07582700	-2.12863000	-0.25985100
O	2.58222000	-3.37929000	-0.15083500
C	3.88056800	-3.42150900	-0.78376300
C	4.35316900	-1.96063000	-0.78365400
H	4.88722700	-1.73051000	-1.70715400

C	5.21948200	-1.58270900	0.44144800
H	5.44195300	-0.50686800	0.39559000
H	4.62034100	-1.75242200	1.34499800
C	6.49672600	-2.39376600	0.51842300
C	7.56735300	-2.13528100	-0.35101900
C	8.73478300	-2.89726900	-0.29618100
C	8.85588400	-3.93322600	0.63253600
C	7.80258600	-4.19759000	1.50833800
C	6.63488300	-3.43401100	1.44865600
H	5.82273400	-3.63898000	2.14351600
H	7.88929800	-4.99454100	2.24248700
H	9.76716400	-4.52350200	0.67822200
H	9.55446200	-2.67392800	-0.97392500
H	7.49455800	-1.31705600	-1.06233400
H	3.75356300	-3.82109900	-1.79609800
H	4.52144600	-4.08502400	-0.20395400
O	0.92313300	-1.88724700	0.05922100
C	3.83006900	0.82194400	-1.78530100
C	3.35590800	2.04275100	-2.57015100
H	2.79882400	2.72705200	-1.92370600
H	4.21921600	2.58885600	-2.96159000
H	2.70592200	1.77737600	-3.41503500
H	4.50969700	0.19084100	-2.36344000
N	5.61971900	1.93305600	0.02854700
Si	7.10809200	2.33086500	-0.72072600
C	7.23840500	1.52070900	-2.44831200
H	7.09510300	0.43253300	-2.41826200
H	6.49854900	1.92680400	-3.14909900
H	8.23061700	1.70496600	-2.88035800
C	8.64340600	1.73633200	0.24524000
H	8.70757000	2.21858600	1.22817000
H	8.61465200	0.65323900	0.41772100
H	9.57276500	1.96464100	-0.29452700
C	7.37273700	4.19903100	-1.02658700
H	7.42019700	4.76007700	-0.08422100
H	8.30684100	4.39546000	-1.57022000
H	6.54876400	4.62219500	-1.61522500
Si	4.92806100	2.64693400	1.41934600
C	3.97187500	4.26460700	1.06051300
H	4.64527900	5.03557900	0.66565600
H	3.19179600	4.10345700	0.30453400
H	3.48908400	4.67290700	1.95915700
C	6.17133200	3.07477100	2.80429700
H	6.73552700	2.18967700	3.12303000
H	6.90070800	3.82833600	2.48143900
H	5.65640000	3.47709600	3.68739000
C	3.65230300	1.46953000	2.22502800
H	3.14749000	1.95905000	3.06904400
H	2.88107700	1.16199000	1.50786000
H	4.13844200	0.56336200	2.60862800
H	4.60558900	1.28656300	-0.89060900

Table 15. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by A_2S_2 (**15**; *anti* to benzyl group).



15 *anti*

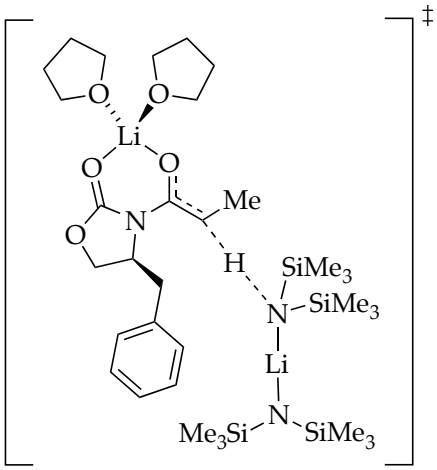


G = –3010.761089 Hartree
G_{MP2} = –1884045.9289 kcal/mol
$\Delta G^{‡}_{MP2}$ = 21.9 kcal/mol

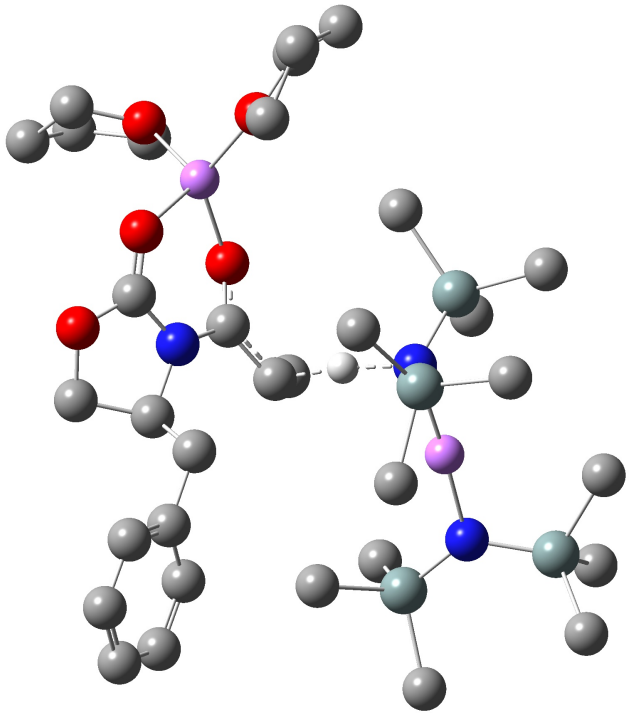
Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000
N	1.73742200	-0.41488200	-0.95080500
Li	7.24889100	0.46682900	0.38315100
O	5.43997100	0.78326700	0.78652400
C	4.57298100	1.51352900	0.25691600
N	5.00551900	2.42378100	-0.77110000
C	4.23934700	3.59468900	-1.25280100
C	5.03851400	3.92914400	-2.51701500
H	4.65432600	3.41304100	-3.40201200
H	5.11682000	4.99798100	-2.71453400
O	6.36465700	3.42134700	-2.24058700
C	6.28431300	2.46508200	-1.29342700
O	7.26472600	1.78997900	-1.00516800
H	3.22237700	3.30265100	-1.51169200
C	4.22812600	4.73569500	-0.20657100
H	3.81565700	4.33535000	0.72613300
H	5.26704500	5.02388500	-0.00111800
C	3.43105600	5.94145700	-0.65858800
C	2.02943300	5.93030000	-0.60132800
C	1.29102600	7.02738500	-1.04475900
C	1.94150100	8.15518600	-1.55063600
C	3.33529700	8.18164100	-1.60476300
C	4.07266500	7.08197600	-1.16080000
H	5.16013200	7.11680000	-1.19059800
H	3.85107600	9.05888300	-1.98624900
H	1.36516600	9.01024000	-1.89316800
H	0.20633300	7.00160500	-0.98803300
H	1.50863600	5.06685200	-0.19296300
C	3.17186000	1.44656500	0.55303800
C	2.83885000	0.97403500	1.96683500
H	3.08829900	1.72801100	2.72604900
H	1.76915600	0.76069600	2.06416700
H	3.38930000	0.06279000	2.21388200
H	2.61134900	2.33638700	0.26798400
O	8.33156000	0.89759400	1.97531200
C	7.68717900	0.95645100	3.27779500
C	8.32816100	2.13855400	4.02174600
C	8.90277200	2.99488700	2.88060200
C	9.33960500	1.92765900	1.88058100
H	10.3181810	1.50330300	2.14459800
H	9.36627100	2.26724700	0.84178400
H	9.72775200	3.63922600	3.19842300
H	8.12285700	3.62683000	2.44015400
H	9.13509600	1.79078300	4.67650600

H	7.60422400	2.67686700	4.63987000
H	6.61625200	1.09397600	3.10270200
H	7.84341900	-0.00035300	3.78690000
O	7.90835900	-1.20955500	-0.35350600
C	7.98817500	-2.44680800	0.39678600
C	8.02223800	-3.56949100	-0.64603200
C	8.62824800	-2.86662700	-1.87154200
C	8.00422500	-1.47635900	-1.77250100
H	6.99755800	-1.45504800	-2.20869100
H	8.60244200	-0.67932900	-2.22059000
H	8.39014700	-3.36524700	-2.81559100
H	9.71913400	-2.80367200	-1.78229600
H	7.00537200	-3.90997800	-0.86898700
H	8.60484100	-4.43135200	-0.30810100
H	8.90185800	-2.41657200	1.00195500
H	7.12121000	-2.50596700	1.06179500
Si	2.24221200	-2.03836000	-0.52065600
C	1.59952200	-2.47508400	1.21375200
H	0.50438700	-2.43501200	1.27384200
H	1.89659700	-3.49799800	1.47972800
H	1.99540400	-1.80733200	1.98637400
C	4.13762800	-2.21641100	-0.48384600
H	4.42127300	-3.22026700	-0.13907500
H	4.56006000	-2.07732000	-1.48794400
H	4.60364700	-1.47905000	0.17849500
C	1.61310200	-3.39629900	-1.69166100
H	0.52464900	-3.37123700	-1.81215000
H	2.06335500	-3.32960700	-2.68899600
H	1.87653400	-4.38001500	-1.28093600
Si	1.55568600	0.19109100	-2.58263700
C	0.42840900	-0.83842300	-3.71156600
H	0.83344400	-1.82838300	-3.94190000
H	-0.56694900	-0.98043600	-3.27420300
H	0.29145900	-0.30801300	-4.66355000
C	3.22447100	0.35313600	-3.49121000
H	3.10809000	0.86637200	-4.45487800
H	3.96171900	0.90671200	-2.89740400
H	3.65462300	-0.63511300	-3.69857900
C	0.73188900	1.90279800	-2.50088200
H	-0.28620400	1.82060900	-2.09794800
H	1.26167900	2.61961800	-1.86319700
H	0.65096400	2.34566500	-3.50202600
N	-1.61509000	0.60155900	0.73467900
Si	-1.69320900	2.00374400	1.70469900
C	-0.38650100	3.28997000	1.15127600
H	-0.55123200	3.57832000	0.10498800
H	-0.43640400	4.19879000	1.76575900
H	0.63392700	2.89422000	1.23589200
C	-1.33243300	1.66633200	3.54996000
H	-1.34702500	2.58391600	4.15391500
H	-2.07571700	0.97833300	3.97218300
H	-0.34831600	1.19693200	3.68220500
C	-3.35307100	2.94973500	1.65853500
H	-3.60285600	3.27050300	0.63933800
H	-4.18751000	2.33669100	2.02166000
H	-3.31110500	3.84819900	2.28890800
Si	-2.90633700	-0.46141300	0.37811900
C	-3.89731100	-1.06003900	1.89632500
H	-3.23964600	-1.55661700	2.62136800
H	-4.38409900	-0.22572600	2.41733900
H	-4.68384100	-1.77342400	1.61551400
C	-2.22398600	-2.05073900	-0.44280900
H	-3.04460900	-2.70032000	-0.77443500
H	-1.61363200	-1.83464700	-1.33122700
H	-1.60862900	-2.63847600	0.25113300
C	-4.17781200	0.23978600	-0.86110700
H	-4.68097700	1.12862700	-0.46188100
H	-3.68708500	0.53801000	-1.79704900
H	-4.95449800	-0.49533000	-1.11229400
H	2.56446700	0.50835800	-0.25779000

Table 16. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by A_2S_2 (**15**; *syn* to benzyl group).



15 *syn*

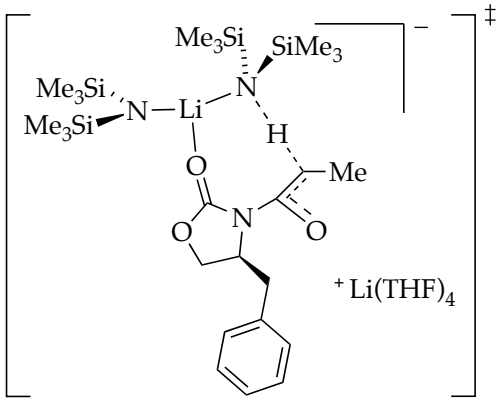


G = –3010.752696 Hartree
G_{MP2} = –1884041.0875 kcal/mol
$\Delta G^{‡}_{MP2}$ = 26.8 kcal/mol

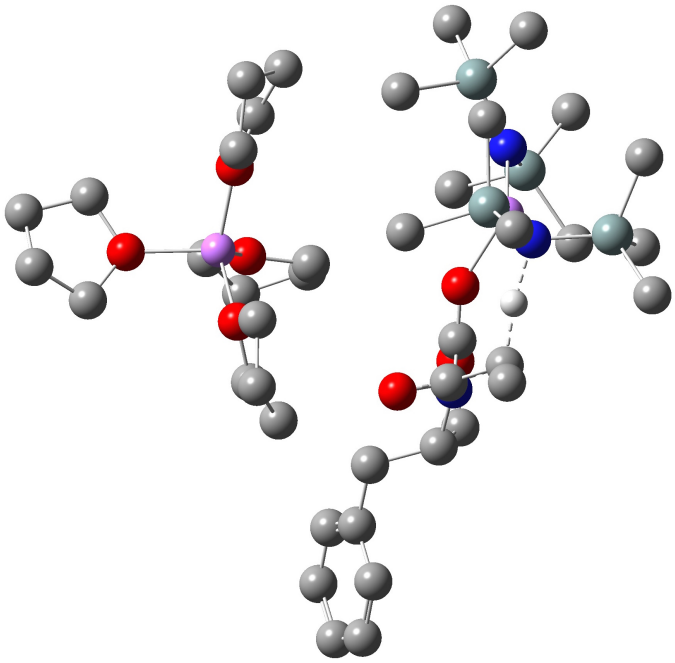
Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000
O	1.72962400	0.28774200	0.71001200
C	2.61029700	1.11740400	0.39176800
N	2.15500100	2.35390400	-0.19993800
C	0.83036400	2.59690200	-0.51231200
O	0.60821900	3.92456200	-0.60418700
C	1.76567100	4.63124300	-0.10068700
H	1.89705500	5.53585400	-0.69374900
H	1.57383400	4.89822600	0.94397200
C	2.91447500	3.62499800	-0.25599900
C	3.68616300	3.80322300	-1.58084900
H	2.96620200	3.77232400	-2.40792300
H	4.35161100	2.94623500	-1.71138800
C	4.47350400	5.09734800	-1.61945200
C	5.63633400	5.24798800	-0.84856700
C	6.35020600	6.44610900	-0.86395700
C	5.91442100	7.51466900	-1.65094400
C	4.76281000	7.37561100	-2.42583300
C	4.04934300	6.17509500	-2.40844300
H	3.16023000	6.06843800	-3.02693300
H	4.42069900	8.19757800	-3.04911000
H	6.47355400	8.44622800	-1.66512600
H	7.25257200	6.54031000	-0.26611400
H	5.99920500	4.42052100	-0.24255000
H	3.60013900	3.67697200	0.59153800
O	-0.07425100	1.79590800	-0.70825100
C	4.01743200	0.91279200	0.56957000
C	4.39786300	0.21627300	1.87886600
H	4.27890500	0.87682300	2.74852300
H	5.44408600	-0.10499100	1.85925000
H	3.77597000	-0.66698000	2.04329400
H	4.62267800	1.79986100	0.38054600
O	-1.22935700	-0.27811400	1.52344200
C	-0.67851900	-0.62306400	2.82507600
C	-1.51214200	0.14712900	3.85902700
C	-2.07419000	1.31955900	3.03857700
C	-2.31559500	0.66260600	1.68182900
H	-3.27000400	0.11870200	1.66099800
H	-2.27834200	1.35464300	0.83656100
H	-2.98427700	1.75014800	3.46647500
H	-1.32823800	2.11730200	2.94326500
H	-2.33018400	-0.47628300	4.23751300
H	-0.91194800	0.46897500	4.71477100
H	0.37397800	-0.32467700	2.82234000

H	-0.73975100	-1.70891600	2.94976300
O	-0.56451300	-1.20585200	-1.41476900
C	-0.95093400	-2.58820900	-1.21913000
C	-1.07904500	-3.18429200	-2.62358700
C	-1.47091900	-1.95912800	-3.46499500
C	-0.64000100	-0.85230600	-2.81726400
H	0.37705600	-0.81476200	-3.22664400
H	-1.08505000	0.14327200	-2.88766700
H	-1.24986800	-2.07715100	-4.52976300
H	-2.54129200	-1.74653700	-3.35941200
H	-0.11470800	-3.58372300	-2.95754500
H	-1.81447100	-3.99288700	-2.66635400
H	-1.90434300	-2.60457300	-0.67733000
H	-0.18410700	-3.07408000	-0.60964600
Li	7.03338400	-0.63657200	-0.38103400
N	5.18580600	-0.92838200	-1.17290100
Si	4.69412000	-2.56635400	-0.77556000
C	5.51750100	-3.12202300	0.84658800
H	6.61163000	-3.03800400	0.81263300
H	5.28491600	-4.17820200	1.03623900
H	5.17458900	-2.55102100	1.71541600
C	2.81325100	-2.71906200	-0.53930000
H	2.54141600	-3.74021100	-0.23935300
H	2.28470400	-2.48891700	-1.47361900
H	2.44837300	-2.02140800	0.22143700
C	5.17104300	-3.87287300	-2.07086900
H	6.23709400	-3.84514100	-2.32084400
H	4.60584100	-3.77099700	-3.00389100
H	4.95400600	-4.87036400	-1.66610600
Si	5.24628600	-0.21872400	-2.77151300
C	5.94538300	-1.32102500	-4.15066000
H	5.26762900	-2.13096300	-4.43861000
H	6.90511600	-1.77299700	-3.87587300
H	6.11828700	-0.70374300	-5.04252300
C	3.52227800	0.32843200	-3.37660400
H	3.58439500	0.89275500	-4.31607300
H	2.99445300	0.95025600	-2.64504100
H	2.89631700	-0.55405100	-3.56579200
C	6.41101400	1.28407900	-2.70423900
H	7.45671600	0.95654600	-2.63141400
H	6.23510300	1.94181700	-1.84548200
H	6.32732400	1.89461400	-3.61267700
N	8.72204500	-0.25140100	0.33952400
Si	8.93559400	0.98105000	1.49988100
C	7.74664300	2.44399400	1.15941200
H	7.94118000	2.86630600	0.16494400
H	7.87007700	3.24628400	1.89925600
H	6.69588800	2.12723600	1.19279500
C	8.56205900	0.41140400	3.28493600
H	8.65695800	1.22841600	4.01335800
H	9.25197900	-0.38609800	3.58874000
H	7.54512200	0.00586800	3.37100100
C	10.6745910	1.77002100	1.56089000
H	10.9394540	2.23282800	0.60204200
H	11.4527370	1.03213500	1.79382100
H	10.7252030	2.55080800	2.33179200
Si	9.91532200	-1.32993300	-0.23791900
C	10.8365680	-2.30811400	1.11943300
H	10.1343480	-2.87963900	1.73991200
H	11.3923010	-1.63975400	1.78985100
H	11.5586410	-3.01733200	0.69277400
C	9.09766900	-2.64849700	-1.35985700
H	9.85329900	-3.32826000	-1.77485400
H	8.57707700	-2.19351300	-2.21441400
H	8.37403400	-3.26937900	-0.81527800
C	11.2640970	-0.52426200	-1.32354000
H	11.8428420	0.22037300	-0.76407000
H	10.8206530	-0.01046800	-2.18659700
H	11.9715780	-1.27099400	-1.70913400
H	4.49504100	0.00419000	-0.36988100

Table 17. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by A_2S_4 (**18**; *anti* to benzyl group).



18 *anti*

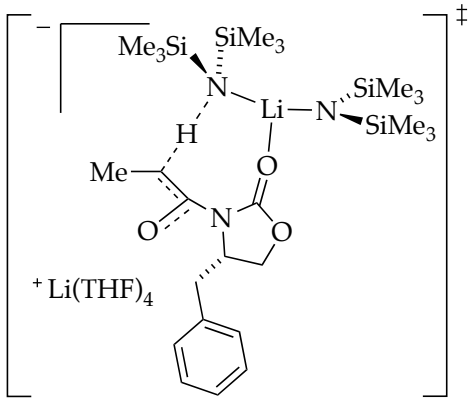


G = –-3475.417695 Hartree
G_{MP2} = –2174659.9067kcal/mol
$\Delta G^{\ddagger}_{MP2}$ = 32.5 kcal/mol

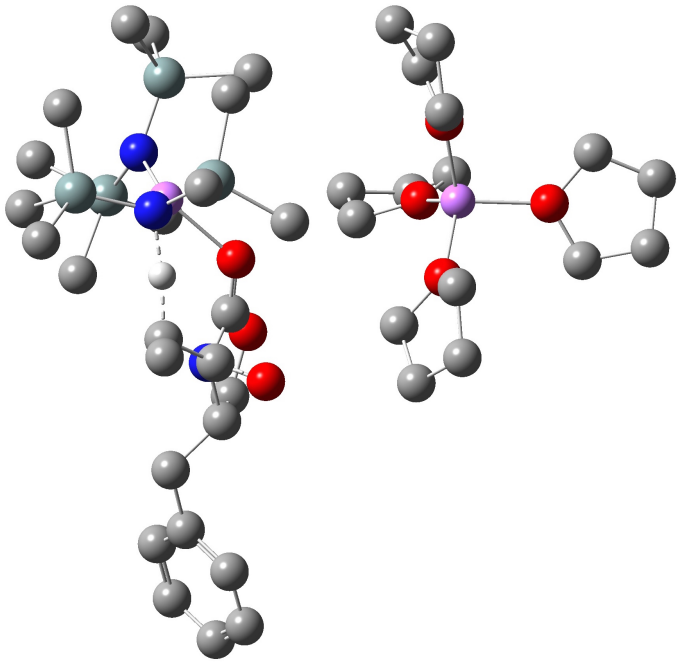
Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	-6.41333600	-3.18195900	-4.77628000
N	-0.60905100	-1.29390600	0.32680500	C	-4.83796600	-2.01674600	-2.39961500
C	-1.27908800	-1.80641700	-0.73487700	H	-5.02889600	-1.25218400	-3.16518900
O	-1.73889300	-2.92974600	-0.86418000	H	-3.99576100	-1.66695800	-1.79260500
Li	-3.10797300	-4.28798600	-0.47178700	H	-5.72380300	-2.06503400	-1.75601000
N	-3.98212000	-4.90338500	-2.14276200	C	-3.15731100	-3.28002100	-4.57685100
Si	-3.85134000	-6.55911300	-2.50018900	H	-2.86562200	-4.17360400	-5.14422900
C	-2.06313500	-7.18892800	-2.15663700	H	-2.25346400	-2.87623600	-4.10259800
H	-1.38286800	-6.74233200	-2.89599200	H	-3.51627600	-2.53295400	-5.29852500
H	-1.97666900	-8.28201300	-2.23422700	N	-2.93342200	-4.57954300	1.73701100
H	-1.71077200	-6.89387200	-1.15985800	Si	-4.54474200	-4.18835600	2.30151600
C	-5.03919500	-7.64942900	-1.47746300	C	-5.37586500	-3.01754800	1.06574900
H	-4.87868200	-8.72408700	-1.64175900	H	-5.52984100	-3.50270000	0.09438000
H	-6.07539100	-7.42240300	-1.76053700	H	-4.78250100	-2.11039800	0.89322300
H	-4.95117300	-7.45827300	-0.40194000	H	-6.36032400	-2.69825100	1.43213300
C	-4.14773500	-7.11689200	-4.30975200	C	-5.68840100	-5.69715800	2.49005100
H	-3.53434600	-6.55525800	-5.02555800	H	-5.34957300	-6.38823800	3.27171700
H	-5.19495000	-6.99905100	-4.61127300	H	-5.77239200	-6.26274900	1.55515500
H	-3.89563800	-8.18060200	-4.42400600	H	-6.69826700	-5.36522200	2.76564400
Si	-4.47343700	-3.69130700	-3.24344000	C	-4.57526500	-3.29959000	3.98976700
C	-6.08517000	-4.06456200	-4.20972300	H	-4.12375500	-3.90578100	4.78448000
H	-6.89811700	-4.33721700	-3.52413800	H	-5.61163600	-3.08894400	4.28564100
H	-5.96904700	-4.88673100	-4.92525400	H	-4.04394600	-2.34089300	3.96075000

Si	-2.08722500	-5.99291400	2.29765400
C	-2.00903900	-6.19756400	4.19641000
H	-3.01309100	-6.29911800	4.62751900
H	-1.52047800	-5.35688300	4.69924800
H	-1.45478600	-7.10973700	4.45717200
C	-2.77710500	-7.66095100	1.69320400
H	-2.86577100	-7.71404800	0.60464300
H	-3.76771200	-7.87246200	2.11018800
H	-2.11061300	-8.47398000	2.01657900
C	-0.28332100	-5.93243700	1.67964900
H	0.29278500	-6.75326100	2.13031900
H	0.21525300	-4.98731800	1.92138300
H	-0.24152000	-6.05629900	0.59028300
O	-1.34959400	-0.87368000	-1.72961400
C	-0.88546100	0.38645200	-1.20200300
H	-0.34647900	0.91151300	-1.99151100
H	-1.75723600	0.97516000	-0.89813900
C	-0.25897900	-2.08937400	1.52086800
O	0.92447600	-2.43597700	1.62530100
C	-1.34790900	-2.37200000	2.40647800
C	-0.92651700	-2.68455800	3.84023500
H	-0.19610900	-3.49862100	3.86575400
H	-1.78817700	-2.98564200	4.44094000
H	-0.46078100	-1.81744800	4.32944600
H	-2.13134700	-1.61184800	2.33567200
C	1.51010800	-0.08802700	-0.33321700
H	2.00020800	-0.58768200	0.50672400
H	1.63469300	-0.73808900	-1.20861100
C	2.12727600	1.26862800	-0.59446700
C	2.41195000	2.13707300	0.47052500
C	2.95587300	3.40045000	0.24044800
C	3.22938900	3.81971500	-1.06368200
C	2.95634600	2.96559300	-2.13237000
C	2.40987800	1.70209200	-1.89696500
H	2.20841200	1.03897000	-2.73594200
H	3.16973500	3.27993900	-3.15067800
H	3.65494800	4.80311900	-1.24396200
H	3.17061600	4.05659500	1.07990700
H	2.21160000	1.81543300	1.49065600
H	-0.14498900	0.69864100	0.83069300
H	-2.06132000	-3.45212600	1.97967200
C	1.07645200	-4.38156200	-1.82891400
O	2.34915300	-5.09488000	-1.98326200
Li	3.26021600	-6.18243700	-0.64211800
O	3.74425300	-5.23986500	1.02229500
C	3.87819500	-3.78592900	1.07063200
C	3.89051600	-3.40542800	2.55685900
C	4.30613200	-4.71204500	3.25133700
C	3.63164300	-5.75817900	2.36993500
H	4.11827700	-6.73809000	2.38762200
H	2.57160600	-5.87529700	2.62261100
H	5.39533700	-4.84159100	3.23224800
H	3.97266600	-4.76916800	4.29159800
H	4.57614800	-2.57777800	2.76182900
H	2.88386900	-3.10371000	2.85753500
H	3.03444200	-3.33613400	0.54501400
H	4.81499400	-3.53279100	0.55953200
O	2.39660600	-7.95397700	-0.47173300
C	2.48736600	-8.85622000	0.65730400
C	1.75168700	-10.1259550	0.23086400
C	0.65541300	-9.56302900	-0.68607000
C	1.38108300	-8.42629000	-1.40509600
H	1.89222300	-8.77559800	-2.31148300
H	0.72806000	-7.59142200	-1.66230500
H	0.25421100	-10.3020510	-1.38485500
H	-0.17856200	-9.16811700	-0.09716900
H	2.42216200	-10.7898760	-0.32819200
H	1.35691200	-10.6822090	1.08581100
H	2.00632800	-8.38593800	1.52296200
H	3.54778500	-9.01478500	0.88080300
O	5.04610300	-6.62479700	-1.44953600
C	6.31172400	-6.18546600	-0.90719500
C	7.21788500	-7.41194200	-0.97862300
C	6.75771200	-8.06018000	-2.29455500
C	5.24753500	-7.78461000	-2.29729100
H	4.85418400	-7.56164600	-3.29447600
H	4.66909200	-8.60991000	-1.86958800
H	7.24006300	-7.56898100	-3.14704900
H	6.98298800	-9.12877900	-2.35214800
H	8.28034400	-7.15226500	-0.97395300
H	7.02362700	-8.07803400	-0.12965200
H	6.11954800	-5.81577700	0.10191200
H	6.70296000	-5.36315700	-1.52251500
C	2.91689500	-4.79954300	-3.27864800
C	2.30322300	-3.46395900	-3.68345500
C	0.87517200	-3.59691700	-3.13142500
H	0.24523900	-4.16298500	-3.82510200
H	0.38318800	-2.63704100	-2.96135900
H	2.33428700	-3.29899700	-4.76457600
H	2.83833700	-2.64005200	-3.19503200
H	2.63895900	-5.59319100	-3.98712400
H	4.00408600	-4.78864400	-3.16752300
H	1.16521500	-3.73865600	-0.94877400
H	0.28525700	-5.11216900	-1.65083000

Table 18. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by A_2S_4 (**18**; *syn* to benzyl group).



18 *syn*

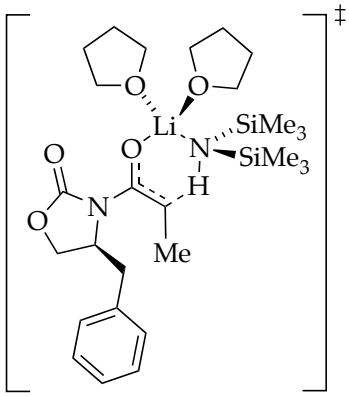


G = –3475.421789 Hartree
G_{MP2} = –2174662.9919 kcal/mol
$\Delta G^{\ddagger}_{MP2}$ = 29.4 kcal/mol

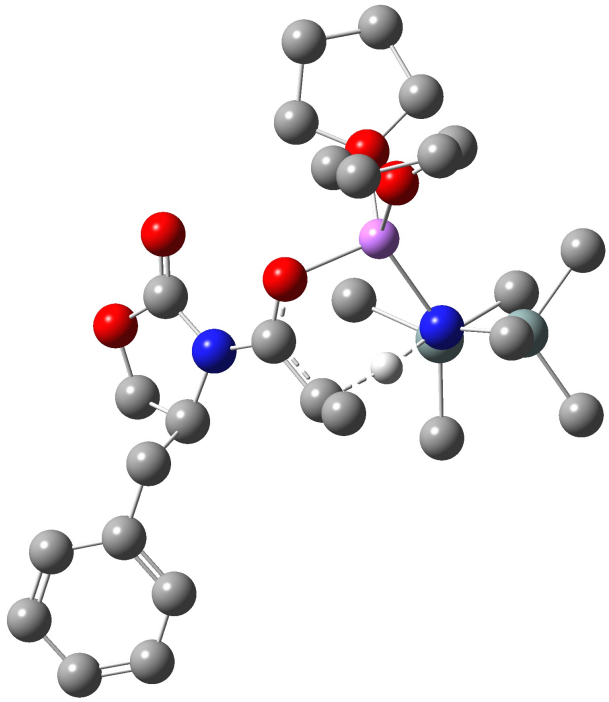
Atom	X	Y	Z
Si	0.00000000	0.00000000	0.00000000
N	-1.13020900	1.20943400	-0.38586300
Li	-1.02504000	1.92730500	-2.23181000
O	-0.12524500	3.76661500	-2.20148400
C	-0.67483700	4.85370700	-2.08219300
N	-1.54804300	5.45417900	-2.94127100
C	-1.44774000	5.14614200	-4.40688700
O	-0.61759900	5.81017000	-5.03020600
C	-2.30415000	4.10924100	-4.88443300
C	-2.47763100	4.09609100	-6.40080600
H	-1.50385700	4.07933300	-6.90091400
H	-3.03730700	3.21607200	-6.72552700
H	-3.00726900	4.98750500	-6.76486400
H	-3.23573800	4.05338900	-4.31344300
C	-1.73531400	6.86001300	-2.55362900
C	-1.32560300	6.79199500	-1.07486200
O	-0.44215000	5.65330000	-1.00024800
H	-0.78575200	7.67234700	-0.72346000
H	-2.18357500	6.60257500	-0.42095900
C	-3.16696200	7.36176400	-2.79757500
H	-3.39217700	7.23755100	-3.86372400
H	-3.86259500	6.71834200	-2.24669300
C	-3.34419800	8.81148100	-2.39390600
C	-2.83833500	9.84206200	-3.20047400
C	-2.97073100	11.1778260	-2.82191400
C	-3.61436000	11.5077760	-1.62683400
C	-4.12589200	10.4929570	-0.81756300
C	-3.99089500	9.15658400	-1.19981600
H	-4.40386000	8.37221000	-0.56936400
H	-4.63641800	10.7392970	0.10978400
H	-3.72234100	12.5484950	-1.33324800
H	-2.57778700	11.9622160	-3.46371900
H	-2.34639200	9.59349900	-4.13871600
H	-1.03147400	7.48105800	-3.12411500
N	-1.43654100	1.52659800	-4.30071500
Si	-2.84303300	0.47808600	-4.38177000
C	-3.94496700	0.75220900	-2.86699800
H	-3.40396900	0.55256200	-1.93459600
H	-4.31896600	1.78291900	-2.82320200
H	-4.81905200	0.08875900	-2.90405100
C	-2.41438300	-1.37632000	-4.43963100
H	-1.85647800	-1.65434000	-5.34231800
H	-1.82769500	-1.69094300	-3.57037600
H	-3.34216600	-1.96397800	-4.43973400
C	-3.96402200	0.77423600	-5.89764500
H	-3.42018000	0.70850200	-6.84729700

H	-4.75704800	0.01462500	-5.91868900
H	-4.45602800	1.75308500	-5.86106700
Si	-0.01029300	1.20018400	-5.24462200
C	-0.33645400	0.79739300	-7.08076100
H	-0.92692600	-0.11858100	-7.20476000
H	-0.87762000	1.60784200	-7.58288800
H	0.61024200	0.64850400	-7.61768200
C	1.04219000	-0.24353600	-4.57775400
H	1.32374400	-0.08746100	-3.52938500
H	0.51749500	-1.20338100	-4.63213700
H	1.96687300	-0.34200200	-5.16476700
C	1.15783700	2.70577300	-5.23133700
H	2.02585500	2.49697800	-5.87363400
H	0.67838200	3.61999100	-5.59733500
H	1.51780600	2.90953300	-4.21535600
Si	-2.08120800	2.09108800	0.71995600
C	-3.17460200	1.04413700	1.88963600
H	-3.80563300	0.35394700	1.31511200
H	-2.58303000	0.44246100	2.58959500
H	-3.84008800	1.68316200	2.48666500
C	-3.33925000	3.23746600	-0.15922700
H	-3.78964900	3.92940100	0.56620700
H	-2.89418200	3.84595900	-0.95643900
H	-4.15499600	2.66119200	-0.61035300
C	-1.08605700	3.26746300	1.86450600
H	-0.32999900	2.72173100	2.44393000
H	-0.56604600	4.02754600	1.26730100
H	-1.73499000	3.79016400	2.58125100
C	1.79344900	0.55045200	-0.43492000
H	2.10297300	1.36104100	0.23847200
H	2.51953100	-0.26892200	-0.33666200
H	1.85187900	0.93672600	-1.46184000
C	-0.27168900	-1.62354100	-0.96210800
H	0.46255900	-2.39307900	-0.68671600
H	-1.27143500	-2.02709900	-0.75798700
H	-0.19719200	-1.46830300	-2.04454800
C	0.12457100	-0.53641600	1.83430400
H	0.30903000	0.30981300	2.50829300
H	-0.79156200	-1.03292300	2.17569400
H	0.95039500	-1.24891000	1.96795300
H	-1.80385400	2.87939700	-4.55015900
C	2.66995200	4.49835700	-0.15159100
O	4.06650100	4.54749000	-0.59314000
Li	4.76397100	4.43060500	-2.41568200
O	3.81014000	5.53395500	-3.72830700
C	2.54320600	6.19823500	-3.48086900
C	2.37981000	7.23918300	-4.60704500
C	3.47076500	6.85704100	-5.64241500
C	3.95405800	5.48554200	-5.16231500
H	5.00495200	5.27497000	-5.37955300
H	3.32774600	4.67760300	-5.56090300
H	4.29622700	7.57706600	-5.62510200
H	3.08378500	6.81459200	-6.66421600
H	2.52975300	8.25929000	-4.24072900
H	1.37331200	7.16334500	-5.02287600
H	1.74278700	5.45389600	-3.51759100
H	2.60151700	6.62395200	-2.47683500
O	5.12849500	2.56552300	-2.90521400
C	5.16075600	2.03441900	-4.25524100
C	5.56249400	0.56697600	-4.11018100
C	4.93728300	0.19913000	-2.75611800
C	5.14358800	1.47540900	-1.94115000
H	6.11852900	1.48317200	-1.43531800
H	4.35367800	1.65338500	-1.20857300
H	5.40503300	-0.67059500	-2.28609300
H	3.86895800	-0.00973700	-2.86956200
H	6.65403500	0.46727300	-4.07434500
H	5.18979000	-0.04574500	-4.93571700
H	4.16343400	2.13827800	-4.69645000
H	5.87288800	2.63021100	-4.83568400
O	6.56994200	5.27885000	-2.37246800
C	6.75570300	6.71265800	-2.43440200
C	8.18787200	6.91308600	-2.92691800
C	8.90709800	5.70904000	-2.29781700
C	7.85098300	4.60472700	-2.40622100
H	7.88608800	3.88449600	-1.58342400
H	7.92888600	4.05741100	-3.35317900
H	9.14296800	5.91345700	-1.24709300
H	9.83787800	5.44465300	-2.80751200
H	8.60555800	7.87573600	-2.61878400
H	8.22856300	6.85784200	-4.02106500
H	5.98618800	7.11581100	-3.09647500
H	6.61412600	7.13263400	-1.42913500
C	4.94475100	4.59839100	0.55620200
C	4.04508600	4.91458300	1.75058700
C	2.73277800	4.22568600	1.34854000
H	2.78995200	3.14870200	1.54028700
H	1.85330400	4.60965300	1.87054800
H	4.46131500	4.54465900	2.69227800
H	3.90025500	5.99768800	1.84386900
H	5.43050300	3.61966900	0.67155200
H	5.71539300	5.35123900	0.36528500
H	2.20852700	5.46732500	-0.36631000
H	2.14887400	3.73000200	-0.72448300

Table 19. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by AS_2 (**19**; *anti* to benzyl group).



19 *anti*

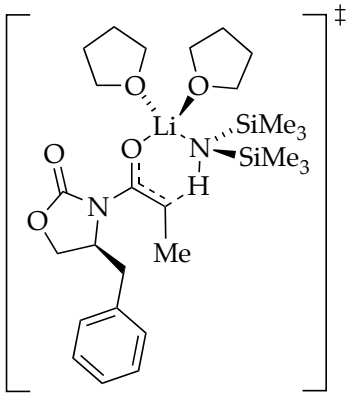


G = –2130.026547 Hartree
G_{MP2} = –1332752.7681 kcal/mol
$\Delta G^{\ddagger}_{MP2}$ = 17.9 kcal/mol

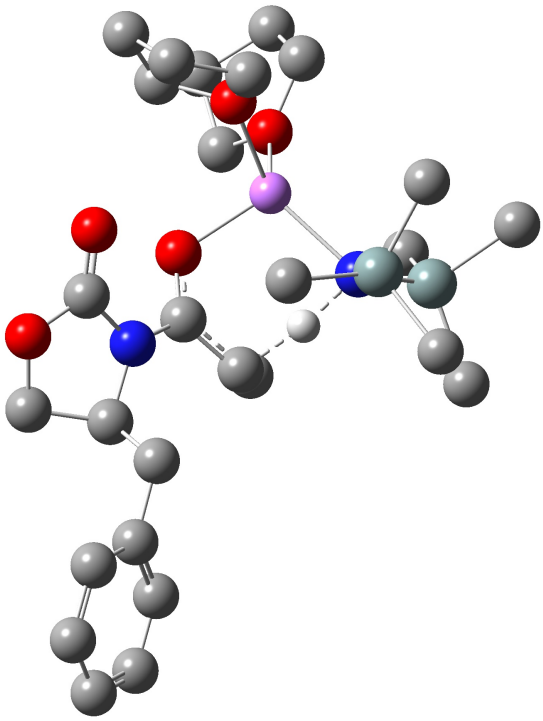
Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.49804400	-0.89705200	-1.14047600
H	0.29879400	-0.45680500	-2.12441500
H	1.55722100	-1.14744400	-1.06280300
O	-0.26786300	-2.10283100	-1.00825300
C	-1.43581000	-1.83830200	-0.34375200
N	-1.36306100	-0.53063500	0.16743500
C	-2.38943700	0.10099700	0.92434900
O	-3.45153700	-0.53645300	1.12450800
Li	-5.07016700	0.31384900	0.46011900
O	-6.37656400	-0.27831500	1.99842700
C	-5.95812100	-1.41355500	2.78131900
C	-6.42722700	-1.08778000	4.20513100
C	-7.68362600	-0.20142300	3.98205400
C	-7.69790900	0.04222000	2.45689700
H	-7.90608400	1.07476300	2.17241100
H	-8.42451900	-0.61761500	1.95894200
H	-7.60082800	0.74157500	4.52940300
H	-8.60415500	-0.69413100	4.30952900
H	-5.65216000	-0.52937200	4.73861600
H	-6.64332000	-1.99252400	4.78115500
H	-6.45532500	-2.31768500	2.39674400
H	-4.88088700	-1.51133800	2.65461900
O	-5.87837900	-0.81431800	-1.00389600
C	-5.35120500	-2.12877300	-1.31438600
C	-6.58251000	-3.02561900	-1.37603700
C	-7.61343600	-2.09371200	-2.03545600
C	-7.24576100	-0.71558900	-1.45795700
H	-7.86722400	-0.45333200	-0.59410100
H	-7.31976400	0.09035600	-2.19630300
H	-8.65036400	-2.36903600	-1.82045300
H	-7.48473500	-2.09969800	-3.12376700
H	-6.90129700	-3.30442100	-0.36427700
H	-6.40683000	-3.94378000	-1.94444800
H	-4.84138600	-2.08886000	-2.28713600
H	-4.61607600	-2.37991600	-0.55040800
N	-4.49373600	2.33475700	-0.04357400
Si	-5.58245300	3.47458600	0.72064200
C	-5.71865800	3.19557500	2.59744900
H	-4.85578700	3.59610100	3.13865500
H	-6.61011300	3.71269800	2.97682400
H	-5.80690000	2.13512900	2.85475100
C	-7.36247300	3.30837700	0.05200200
H	-8.04997800	3.94487600	0.62504100
H	-7.44101400	3.60466800	-0.99892700
H	-7.73130600	2.27695500	0.12567100
C	-5.09063800	5.30337400	0.51165400
H	-4.07734300	5.48648000	0.89022900

H	-5.11611600	5.63451700	-0.53327500
H	-5.77508500	5.95075000	1.07568900
Si	-3.98227100	2.59506100	-1.70423400
C	-5.37203100	3.18038200	-2.86631900
H	-6.21916900	2.48369600	-2.86882500
H	-5.75910400	4.17330400	-2.61130300
H	-4.98835400	3.23545200	-3.89363100
C	-3.31696300	0.99744900	-2.48286700
H	-2.99069900	1.19042200	-3.51319300
H	-2.46110400	0.58754400	-1.93660400
H	-4.09156900	0.22439700	-2.51164300
C	-2.57719600	3.87535500	-1.82097700
H	-2.89838300	4.87052600	-1.49316200
H	-1.72700500	3.58423800	-1.19148900
H	-2.21019200	3.96710500	-2.85176400
C	-2.23394400	1.47566500	1.31740600
C	-2.59020600	1.80604400	2.76674300
H	-1.81795700	1.46928500	3.47517600
H	-2.70102700	2.88739800	2.90072600
H	-3.53227600	1.33645400	3.06006700
H	-1.29643100	1.94357700	1.01715400
O	-2.30992700	-2.66013800	-0.24914400
H	-0.03085400	1.04142600	-0.32488100
C	0.83633100	-0.12707600	1.29660500
H	0.28326900	0.36795500	2.10246700
H	0.90467200	-1.18964100	1.55957100
C	2.21998300	0.47228800	1.16563700
C	2.39475200	1.86453300	1.15773600
C	3.66232000	2.42674400	1.01043600
C	4.78261900	1.60418700	0.87021900
C	4.62469400	0.21824900	0.88190700
C	3.35316700	-0.34062100	1.02819400
H	3.23998300	-1.42257800	1.04741800
H	5.49060200	-0.43085300	0.78137200
H	5.77107400	2.04141400	0.75826200
H	3.77636900	3.50759000	1.01063100
H	1.53002200	2.51403500	1.27851000
H	-3.35338300	2.02296100	0.60026900

Table 20. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of oxazolidinone **9** by AS_2 (**19**; *syn* to benzyl group).



19 *syn*



G = –2130.024138 Hartree
G_{MP2} = –1332752.3836 kcal/mol
$\Delta G^{\ddagger}_{MP2}$ = 18.3 kcal/mol

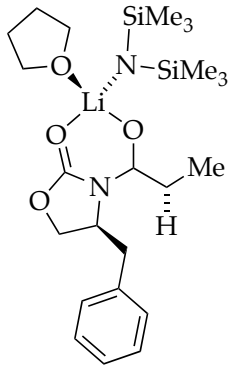
Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.53618300	-1.43549700	-0.09834400
H	0.45897600	-1.83675800	-1.11566400
H	1.56076000	-1.54468800	0.25952800
O	-0.32913000	-2.19264400	0.76663200
C	-1.53173900	-1.55029200	0.88066300
N	-1.41442000	-0.28375200	0.29440300
C	-2.51586300	0.48519300	-0.17591100
O	-3.63216400	-0.07923800	-0.26697800
C	-2.32865700	1.88380700	-0.44322800
C	-2.89445600	2.39264400	-1.76896200
H	-3.87309500	1.94868500	-1.96847800
H	-3.01875500	3.48036400	-1.75658700
H	-2.24220300	2.15029300	-2.62099600
H	-1.32398400	2.26120000	-0.24880700
O	-2.47452800	-2.04927600	1.44184800
H	0.07859300	0.52237200	-0.95601800
C	0.69732200	0.82274900	1.11086700
H	0.12419700	1.74205400	1.27097600
H	0.64741200	0.25313000	2.04647600
C	2.13526700	1.15784600	0.77427600
C	2.43077100	2.13131900	-0.19215100
C	3.75094400	2.43070300	-0.52694200
C	4.80311100	1.76105900	0.10235000
C	4.52428100	0.79441500	1.06867800
C	3.20057100	0.49683400	1.40009400
H	2.99107800	-0.24979900	2.16317900
H	5.33583400	0.27337400	1.56976200
H	5.83221800	1.99597800	-0.15552300
H	3.95892800	3.19136300	-1.27486300
H	1.61809400	2.66695100	-0.67891700
Li	-5.10650000	0.77792100	0.71254400
O	-5.79154100	-0.80494400	1.90508400
C	-5.71901100	-2.05687800	1.16097600
C	-5.77317200	-3.17979500	2.20187600
C	-5.20911800	-2.49710400	3.45625500
C	-5.77404900	-1.08500200	3.32201200
H	-5.16681400	-0.32229500	3.81080300
H	-6.80034700	-1.02176100	3.71307600
H	-4.11681800	-2.47296800	3.40828500
H	-5.51470700	-2.98145400	4.38919000
H	-5.18672200	-4.04880400	1.89057300
H	-6.80627600	-3.50698700	2.37372100
H	-6.55974900	-2.08472900	0.45997300
H	-4.77810900	-2.05026300	0.61018800
O	-6.68128600	0.58637100	-0.54709800
C	-6.51917100	0.22063700	-1.93415900
C	-7.73617300	-0.64339400	-2.25813400

C	-8.83212800	0.03129800	-1.41585800
C	-8.06880900	0.47411500	-0.15816800
H	-8.12818500	-0.26181800	0.65060400
H	-8.40660700	1.44268500	0.22610800
H	-9.66834900	-0.63366800	-1.18033900
H	-9.23419600	0.90149000	-1.94709800
H	-7.57128900	-1.67511200	-1.92575400
H	-7.96583800	-0.66239900	-3.32779100
H	-6.50258400	1.13293300	-2.54612300
H	-5.55722300	-0.28737300	-2.02405500
N	-4.32585500	2.72920200	1.28850800
Si	-3.82994700	2.66942900	2.96935400
C	-2.69823000	1.17011400	3.25461600
H	-1.70726200	1.34515300	2.82109700
H	-2.55397900	1.00890400	4.33089400
H	-3.07847800	0.23719800	2.82490300
C	-5.30166500	2.52218500	4.17421700
H	-4.95824100	2.17846500	5.15925900
H	-5.80048200	3.48579300	4.32274600
H	-6.06265600	1.81611100	3.82277900
C	-2.82510000	4.17810700	3.55775800
H	-1.94589700	4.34846200	2.92420200
H	-3.41542700	5.10208800	3.55710900
H	-2.46729200	4.02177900	4.58422400
Si	-5.13382500	4.16860900	0.68690600
C	-6.42778700	4.87062200	1.89776200
H	-7.16668200	4.11529800	2.19143400
H	-5.98273700	5.27075300	2.81583200
H	-6.97198200	5.69422100	1.41666900
C	-6.10213600	3.86110600	-0.92037500
H	-6.64307000	4.77521800	-1.19800900
H	-5.45584600	3.59361100	-1.76197700
H	-6.83438900	3.05753700	-0.79587900
C	-3.91935600	5.59083900	0.32097300
H	-3.42147800	5.94473600	1.23096100
H	-3.13383400	5.28941500	-0.38250700
H	-4.44538600	6.44706600	-0.12162100
H	-3.25859100	2.38849200	0.50453800

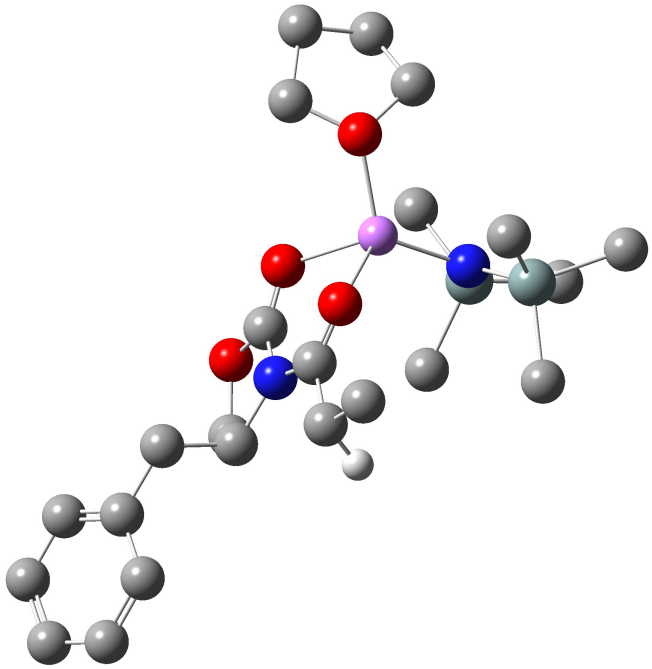
VI. Intrinsic reaction coordinate (IRC) computations

Geometries are optimized at the B3LYP level of theory using the 6–31G(d) basis set. Energies are defined as follows: G is the sum of electronic and thermal free energies calculated at the B3LYP level of theory (T = 195 K). G_{MP2} is derived from an MP2 SP calculation corresponding to the DFT-optimized geometry and includes a thermal correction from the DFT calculation. ΔG^1_{MP2} is the difference between G_{MP2} of the IRC-derived reactants (R) or products (P), and G_{MP2} of LiHMDS disolvated dimer **1**, oxazolidinone **9**, and THF, based on the corresponding stoichiometries ($G_{MP2}^{IRC} - G_{MP2}^{GS}$). ΔG^2_{MP2} is the difference between G_{MP2} of the corresponding transition structure, and G_{MP2} of the IRC-derived reactants or products ($G_{MP2}^{TS} - G_{MP2}^{IRC}$).

Table 21. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by AS (**11**; *anti* to benzyl group).



IRC-R **11** *anti*



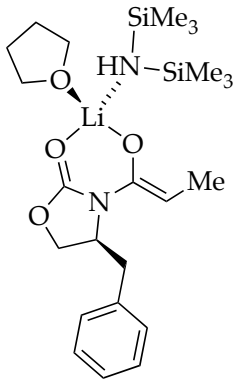
G = –1897.708171 Hartree
G_{MP2} = –1187452.3792 kcal/mol
ΔG^1_{MP2} = 6.0 kcal/mol
ΔG^2_{MP2} = 10.9 kcal/mol

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	-0.13669600	0.45892000	1.45833300
H	-0.47448900	-0.34407400	2.11982100
H	0.76661800	0.92137400	1.85487900
O	-1.17438200	1.46474800	1.41176300
C	-1.98172100	1.22904600	0.35865900
N	-1.37673300	0.26385000	-0.46634900
C	-2.00698400	-0.28077400	-1.59389000
O	-3.11230800	0.09811200	-1.94536600
Li	-4.62461400	0.74959300	-0.67436600

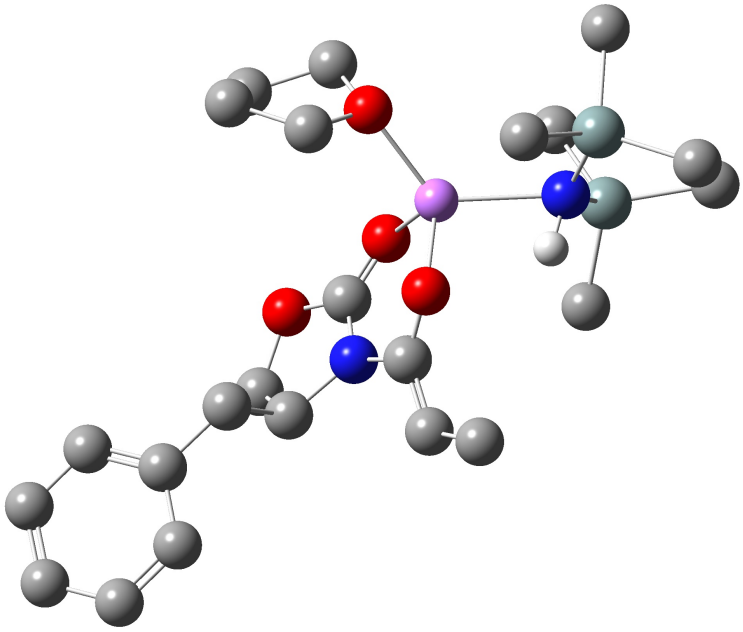
Atom	X	Y	Z
N	-5.46701900	-0.68704700	0.33831600
Si	-6.00528500	-1.96423700	-0.65219400
C	-6.19322900	-1.38048700	-2.46435100
H	-5.26339900	-0.96424400	-2.87038900
H	-6.49542100	-2.21285600	-3.11422800
H	-6.96582300	-0.60489000	-2.55123100
C	-7.71016800	-2.71041200	-0.21550900
H	-8.02144200	-3.44226200	-0.97343200
H	-7.70883700	-3.22045300	0.75443100
H	-8.48239400	-1.93142200	-0.17262800

C	-4.80165000	-3.45722000	-0.71055900
H	-3.80315900	-3.14707800	-1.05013800
H	-4.67811000	-3.90252600	0.28558000
H	-5.14848300	-4.25144100	-1.38576400
Si	-5.40806700	-0.57687400	2.03578400
C	-5.71824700	1.21841700	2.61535500
H	-5.02265300	1.92022100	2.13695100
H	-6.73943500	1.53694000	2.36661600
H	-5.59801500	1.32485700	3.70183900
C	-3.70226800	-1.05433000	2.78370000
H	-3.73473100	-1.09215800	3.88110100
H	-3.37768400	-2.04036800	2.42619400
H	-2.92879800	-0.32273300	2.51357700
C	-6.66165200	-1.64728200	3.00340800
H	-7.69370900	-1.43992300	2.69608300
H	-6.48721200	-2.72111100	2.85890000
H	-6.58964300	-1.44713300	4.08108900
O	-5.70678200	2.21509900	-1.41519000
C	-7.10125000	2.24164900	-1.03368600
C	-7.29194300	3.60988800	-0.38661000
C	-6.39685600	4.50061500	-1.26635800
C	-5.23327600	3.56332300	-1.63852800
H	-4.35563900	3.71160900	-1.00212700
H	-4.92955800	3.66327500	-2.68682700
H	-6.05135300	5.40302100	-0.75319400
H	-6.94058900	4.81428300	-2.16491500
H	-6.92621800	3.58804800	0.64596800
H	-8.33807200	3.93092600	-0.37655200
H	-7.72437600	2.12982700	-1.93252600
H	-7.26130000	1.38832800	-0.37144900
C	-1.26740800	-1.39806400	-2.31092000
C	-1.97561900	-1.84229100	-3.59080100
H	-2.05366700	-1.01740800	-4.30506700
H	-1.41402200	-2.65544000	-4.06111300
H	-2.98644700	-2.19537600	-3.37544600
H	-0.23773200	-1.08790300	-2.52478100
O	-3.03736900	1.79540400	0.19266200
H	0.22402100	-1.06714700	-0.05418900
C	1.04833600	0.82048800	-0.79108800
H	0.92974700	0.60950800	-1.86003400
H	0.82268300	1.88504900	-0.65583400
C	2.46914500	0.52531000	-0.35703000
C	3.08765400	-0.68096300	-0.71751400
C	4.38763100	-0.96928800	-0.30383000
C	5.09345200	-0.05180400	0.47793500
C	4.49185900	1.15374600	0.83932500
C	3.18917100	1.43841200	0.42434500
H	2.73186200	2.38645000	0.69952800
H	5.03589400	1.87685800	1.44069000
H	6.10738800	-0.27413900	0.79829000
H	4.85159100	-1.90725300	-0.59629400
H	2.55188000	-1.39759400	-1.33731300
H	-1.19164900	-2.23884300	-1.60588400

Table 22. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by AS (**11**; *anti* to benzyl group).



IRC-P **11** *anti*

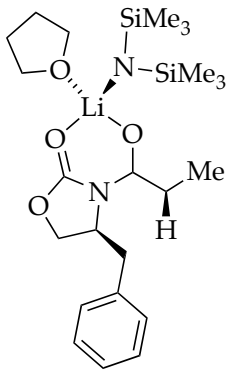


G = –1897.729360 Hartree
G_{MP2} = –1187463.5281 kcal/mol
ΔG^{1}_{MP2} = –5.1 kcal/mol
ΔG^{2}_{MP2} = 22.0 kcal/mol

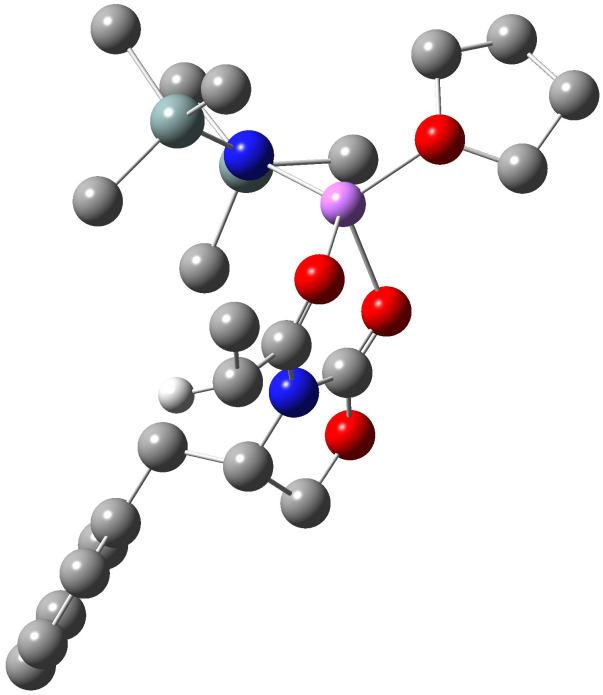
Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.18381300	0.61096900	1.39948400
H	0.22458200	-0.15466200	2.18204300
H	1.05712600	1.26001200	1.48284500
O	-0.99980600	1.40765900	1.60754900
C	-1.97081200	0.96700200	0.75665300
N	-1.45961900	0.08365400	-0.13455800
C	-2.21155000	-0.46279400	-1.28843000
O	-3.17404700	0.28043000	-1.72016400
Li	-4.23247300	1.39319000	-0.71678500
N	-6.04520200	0.13541400	-0.76946800
Si	-7.16174100	0.65917900	-2.04850200
C	-6.13477400	1.37090300	-3.46389100
H	-5.29679100	0.71022000	-3.71496400
H	-6.74484200	1.50628800	-4.36551900
H	-5.71507000	2.34401000	-3.18829500
C	-8.30886200	1.98554500	-1.34114300
H	-8.98142600	2.36122700	-2.12225000
H	-8.93716900	1.61011100	-0.52506800
H	-7.73487600	2.83803600	-0.95925500
C	-8.19605100	-0.77709600	-2.72697500
H	-7.55283300	-1.57899300	-3.11028900
H	-8.85118800	-1.21338600	-1.96502600
H	-8.83006300	-0.44052700	-3.55743800
Si	-6.46036100	-0.39576700	0.87906100
C	-6.50996600	1.10985500	2.02033100
H	-5.51510800	1.56433700	2.09330700
H	-7.20977800	1.87159400	1.65607900
H	-6.82544200	0.82941700	3.03322500
C	-5.11720400	-1.59911200	1.43555300
H	-5.30229400	-1.93801900	2.46250100
H	-5.07842900	-2.48819200	0.79465800
H	-4.13136900	-1.12363800	1.41176800
C	-8.13933600	-1.27401500	0.96332900
H	-8.97075500	-0.63357900	0.64595800
H	-8.15499700	-2.17507400	0.33906500
H	-8.34660100	-1.58418600	1.99574000
O	-4.25223600	3.33114200	-1.19924600
C	-4.21913000	4.30255200	-0.13423700
C	-2.78125200	4.81141500	-0.11961500
C	-2.44746600	4.85694900	-1.62191500
C	-3.26935200	3.69289000	-2.20912600
H	-2.67700300	2.79527700	-2.40640300
H	-3.79647000	3.97496800	-3.12706600
H	-1.37783600	4.74600700	-1.82309300
H	-2.76868300	5.81111900	-2.05451600

H	-2.14457400	4.09094500	0.40392100
H	-2.68140800	5.78449100	0.37101600
H	-4.93378000	5.10929700	-0.35361800
H	-4.52021700	3.79364100	0.78383900
C	-1.77586300	-1.65654300	-1.77017100
C	-2.37758300	-2.30782400	-2.98238100
H	-1.61097500	-2.60790400	-3.71216900
H	-2.94482700	-3.21936500	-2.73631900
H	-3.06380300	-1.61784600	-3.48289700
H	-0.98863100	-2.18949700	-1.24526100
O	-3.12496200	1.38432400	0.87445300
H	0.32501500	-1.04291500	-0.00582800
C	0.72241100	0.76535100	-1.13340200
H	0.31835400	0.38563200	-2.07836300
H	0.45418700	1.82715600	-1.06415500
C	2.22481900	0.59775800	-1.09254700
C	2.81579000	-0.60530000	-1.50845900
C	4.19752400	-0.78277500	-1.44818700
C	5.01719000	0.24317700	-0.97138800
C	4.44415800	1.44648100	-0.55945300
C	3.05958900	1.61941400	-0.62011400
H	2.62159900	2.56554800	-0.30816000
H	5.07342200	2.25408600	-0.19444900
H	6.09432800	0.10659700	-0.92742600
H	4.63602200	-1.72037600	-1.77990700
H	2.18518500	-1.40396900	-1.89361200
H	-5.29531100	-0.43999300	-1.16900900

Table 23. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by AS (**11**; *syn* to benzyl group).



IRC-R **11** *syn*

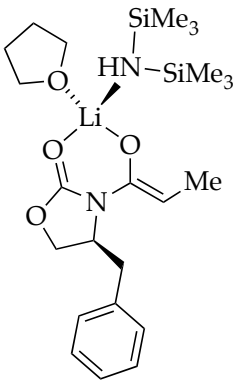


G = –1897.708597 Hartree
G_{MP2} = –1187453.4782 kcal/mol
ΔG^1_{MP2} = 4.9 kcal/mol
ΔG^2_{MP2} = 14.5 kcal/mol

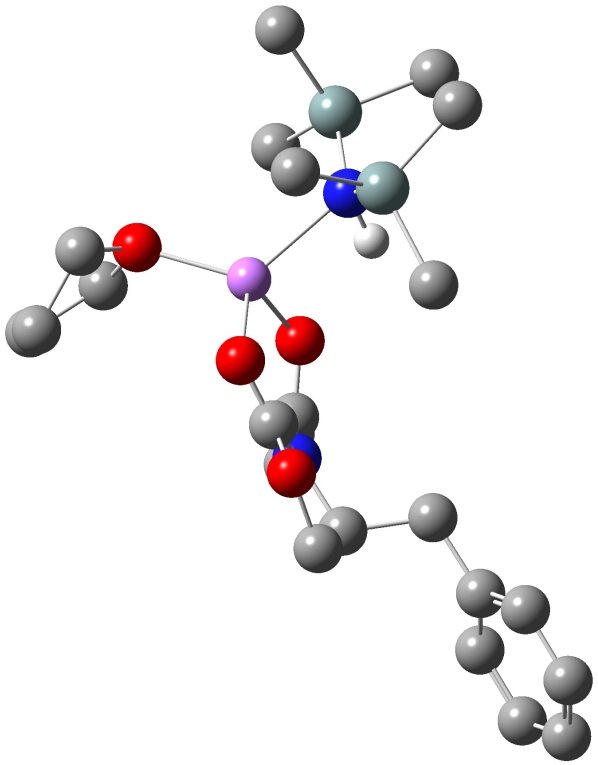
Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	-0.10520200	-0.38236000	-1.48647700
H	-0.34977300	-1.43959500	-1.63119100
H	-0.80909000	0.23809300	-2.04045900
O	1.21601800	-0.14940100	-2.02004800
C	2.12346000	-0.13931400	-1.02507200
N	1.44840700	-0.20212900	0.20529900
C	2.11089900	-0.39987900	1.42383600
O	3.32945900	-0.37745300	1.49316600
Li	4.53987700	0.74962300	0.22464700
O	6.26756400	-0.16306200	0.03605300
C	6.51233000	-1.30440100	-0.81804600
C	7.96867500	-1.18043900	-1.29343700
C	8.24684700	0.32471700	-1.14287400
C	7.45287100	0.66335300	0.11565600
H	7.11134500	1.69857400	0.18343200
H	8.01036300	0.40240800	1.02605500
H	7.84784600	0.87901500	-1.99964900
H	9.31151400	0.55790200	-1.04499300
H	8.10150600	-1.54444100	-2.31666000
H	8.63617700	-1.75658000	-0.64198200
H	6.32678500	-2.21896600	-0.24429400
H	5.79940000	-1.26016900	-1.64827500
N	4.45289000	2.69287000	0.43479700
Si	4.22088400	3.56002500	-1.01134400
C	5.14232200	2.72152300	-2.46113300
H	4.84791300	1.67043200	-2.57357000
H	4.93625200	3.22424800	-3.41548600
H	6.22856900	2.75284100	-2.30284700
C	4.81424800	5.37696000	-1.02638400
H	4.73334200	5.79856900	-2.03752100
H	4.22133000	6.01415500	-0.35886400
H	5.86189700	5.46387700	-0.71342800
C	2.38610100	3.65292500	-1.57539600
H	1.99683400	2.65660400	-1.82543000
H	1.75483300	4.07506900	-0.78173100
H	2.25974700	4.28025800	-2.46830400
Si	4.40817600	3.20462500	2.05712300
C	5.21587500	4.89198300	2.44663600
H	6.25492100	4.92663900	2.09560200
H	4.68666400	5.72935700	1.97706400
H	5.22676800	5.07559800	3.52974100
C	5.32051500	1.95931400	3.18621700
H	5.22615500	2.23929500	4.24428400

H	4.93581700	0.93750700	3.07842900
H	6.39314200	1.93252100	2.95267800
C	2.63006700	3.33845500	2.77367700
H	2.03386100	4.06945100	2.21137700
H	2.10255100	2.37549500	2.71493100
H	2.62511200	3.64949200	3.82729900
C	1.23255300	-0.69303600	2.62936000
C	2.04445200	-0.91972700	3.90419700
H	2.64352800	-0.03871400	4.14750200
H	1.36976100	-1.12506400	4.74113600
H	2.72690500	-1.76656200	3.79231200
H	0.61440000	-1.57229000	2.39840700
O	3.31664600	-0.09498200	-1.22020300
H	-0.57236200	-0.69716900	0.61591900
C	-0.43056400	1.45702400	0.29337800
H	-0.15677500	1.70386900	1.32575400
H	0.15329500	2.12828900	-0.34563500
C	-1.91394400	1.67195400	0.07520300
C	-2.85478500	1.14468500	0.97234500
C	-4.22184600	1.32063000	0.76056400
C	-4.67175500	2.03167000	-0.35440900
C	-3.74660800	2.56775300	-1.25048500
C	-2.37829400	2.38800500	-1.03638000
H	-1.66140700	2.82255000	-1.72948800
H	-4.08693900	3.13187800	-2.11453000
H	-5.73648000	2.17278100	-0.51825600
H	-4.93572700	0.90972300	1.46940700
H	-2.51494900	0.60380800	1.85385500
H	0.53234100	0.14057600	2.76644500

Table 24. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by AS (**11**; *syn* to benzyl group).



IRC-P **11** *syn*

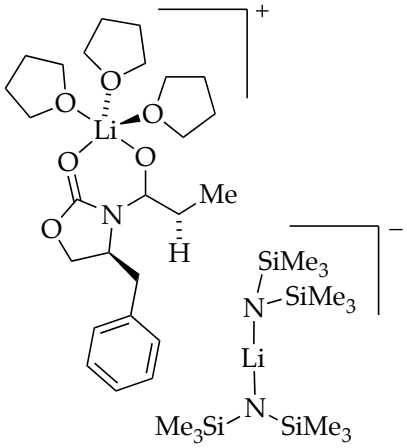


G = –1897.728975 Hartree
G_{MP2} = –1187463.4144 kcal/mol
ΔG^{1}_{MP2} = –5.0 kcal/mol
ΔG^{2}_{MP2} = 24.4 kcal/mol

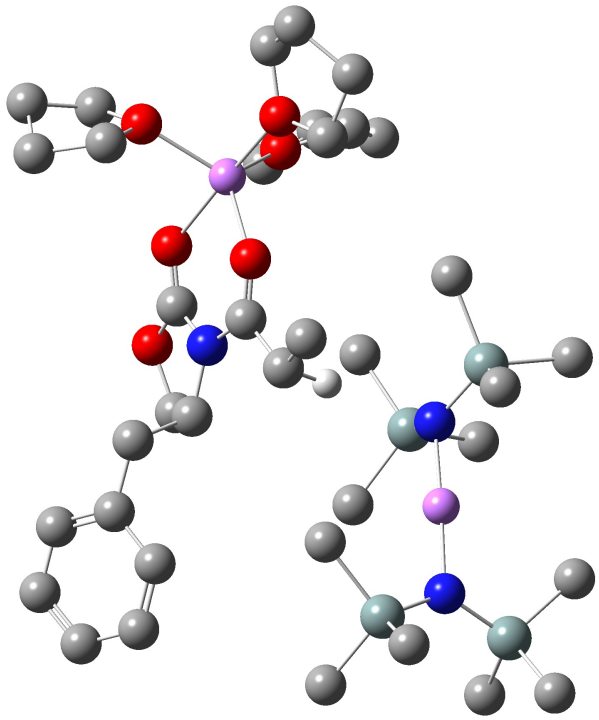
Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.15001500	-0.07805300	-1.52923500
H	0.46367900	0.87800500	-1.96288100
H	0.82758800	-0.86574400	-1.86259400
O	-1.17427300	-0.38032600	-2.01213300
C	-2.07417800	-0.04732600	-1.04397500
N	-1.43904300	0.27113300	0.10929200
C	-2.13292200	0.52530800	1.39238500
O	-3.27062800	-0.06974700	1.52973400
Li	-4.51927600	-0.20913000	0.18620900
O	-5.77854800	1.31094600	-0.08097700
C	-5.45698800	2.47564700	0.72898900
C	-5.21213600	3.64128200	-0.25399400
C	-5.16291600	2.95573800	-1.63354100
C	-6.07015500	1.74780800	-1.42145000
H	-5.86514800	0.90992900	-2.09160100
H	-7.13396200	2.01842200	-1.49634500
H	-4.15033600	2.60956700	-1.86272500
H	-5.50250600	3.60550900	-2.44604000
H	-4.29062700	4.18274600	-0.02273300
H	-6.03879300	4.35898500	-0.21219500
H	-6.29620300	2.67579400	1.40494600
H	-4.57962500	2.21090000	1.32338200
N	-5.16927200	-2.25374300	0.74138300
Si	-4.95808200	-3.40613800	-0.59857900
C	-3.10490100	-3.65579500	-0.87723300
H	-2.59088100	-3.93406000	0.05134300
H	-2.93895300	-4.46595600	-1.59838200
H	-2.63071100	-2.75523100	-1.27932600
C	-5.76235900	-2.70016900	-2.15519000
H	-5.69586200	-3.40630100	-2.99232300
H	-6.82352000	-2.47389100	-1.99675900
H	-5.25616300	-1.77561800	-2.45691900
C	-5.71831700	-5.10622600	-0.23474900
H	-5.25667400	-5.57368900	0.64309000
H	-6.79975200	-5.06678100	-0.06082500
H	-5.55319200	-5.77574700	-1.08893700
Si	-6.53883200	-2.18283200	1.87650400
C	-8.15113500	-2.25521800	0.89059200
H	-8.20614300	-1.43667300	0.16318700
H	-8.28123800	-3.19800200	0.34748200
H	-9.00753800	-2.15078900	1.56856800
C	-6.44630400	-0.55597300	2.82824000
H	-7.08206500	-0.58733000	3.72168500

H	-5.41867500	-0.33915300	3.14126200
H	-6.78152400	0.27810500	2.20250700
C	-6.48567000	-3.61001800	3.12258700
H	-6.55456700	-4.58925200	2.63609500
H	-5.55344300	-3.59102000	3.70097500
H	-7.31515200	-3.53453700	3.83752100
C	-1.47756700	1.32703600	2.27280400
C	-1.99922600	1.61859600	3.65065400
H	-2.92048500	1.05771800	3.83379200
H	-1.27734400	1.34388500	4.43487300
H	-2.22363900	2.68633400	3.79814100
H	-0.54365900	1.79434400	1.97379600
O	-3.28145200	-0.06695700	-1.29473200
H	0.57778800	0.83817800	0.39698000
C	0.39676500	-1.29254800	0.75046700
H	0.01843000	-1.19314600	1.77395100
H	-0.12503300	-2.13975500	0.28877700
C	1.89054300	-1.52961000	0.75933700
C	2.72379200	-0.76887700	1.59406200
C	4.10542100	-0.95695500	1.59071500
C	4.68127100	-1.91372400	0.75124000
C	3.86486200	-2.68072300	-0.08024800
C	2.48149700	-2.48808300	-0.07480500
H	1.85007700	-3.09900000	-0.71669600
H	4.30229500	-3.43329200	-0.73118700
H	5.75760800	-2.06336600	0.75042500
H	4.73298900	-0.36112000	2.24844900
H	2.28080800	-0.03104200	2.25995800
H	-4.28915700	-2.09684800	1.24474100

Table 25. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by A_2S_3 (**12**; *anti* to benzyl group).



IRC-R **12** *anti*

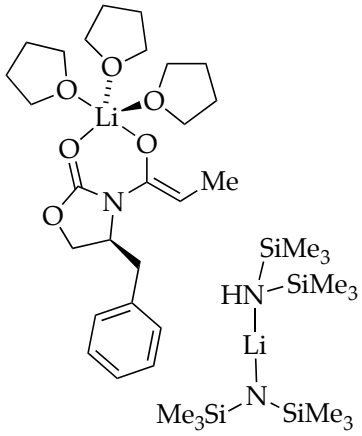


G = –3243.117653 Hartree
G_{MP2} = –2029371.1331 kcal/mol
ΔG^1_{MP2} = 9.0 kcal/mol
ΔG^2_{MP2} = 8.2 kcal/mol

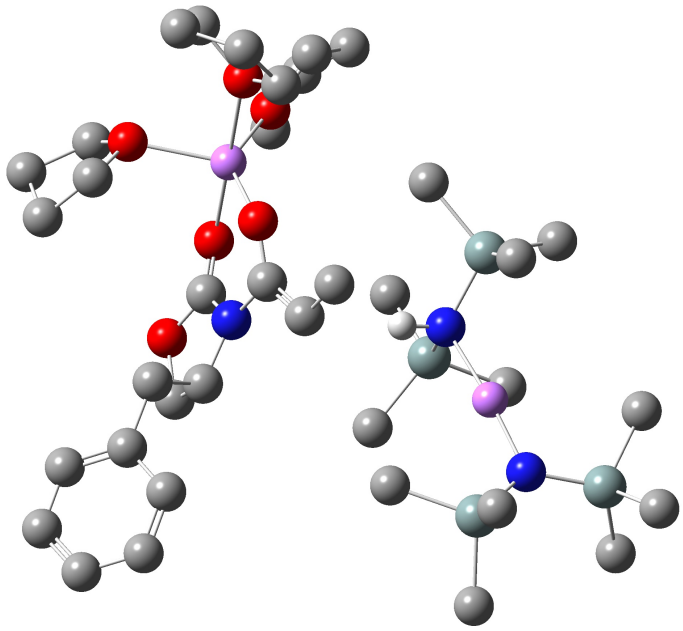
Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000
O	0.73592300	1.60203600	1.16542500
C	1.88370100	1.99421100	1.23225700
N	2.93088000	1.74762900	0.33513900
C	4.09028400	2.60999000	0.67291000
C	3.77359300	2.89649100	2.14632500
H	4.21657300	2.15781200	2.81847000
H	4.04219800	3.90439200	2.45975000
O	2.32819300	2.77278600	2.22952400
H	5.01933300	2.04709800	0.58215100
C	4.12344100	3.88493000	-0.20364600
H	4.20117500	3.58220100	-1.25470100
H	3.16232100	4.40283100	-0.09308600
C	5.26144100	4.81667600	0.16297800
C	6.58554500	4.48830200	-0.16228400
C	7.63803700	5.32618300	0.20594200
C	7.38059200	6.51036600	0.90057400
C	6.06671700	6.85269900	1.22169100
C	5.01524400	6.00956600	0.85577600
H	3.99194000	6.28723400	1.10157900
H	5.85700400	7.77607500	1.75497800
H	8.20024400	7.16358700	1.18667700
H	8.65602600	5.04812400	-0.05139800
H	6.80090800	3.57583500	-0.71234900
C	2.84268600	0.81525000	-0.70443200
O	1.78360900	0.23589400	-0.93667700
C	4.11294300	0.51294900	-1.45854100
C	3.86252400	-0.15143200	-2.81321000
H	3.25378900	0.48484800	-3.46524400
H	4.82038000	-0.33151800	-3.30854100
H	3.35201700	-1.10974500	-2.69658700
H	4.71741000	1.41488800	-1.58484500
O	-0.57971400	-1.46901800	-1.37942300
C	-1.94996600	-1.87762000	-1.55777400
C	-2.00997800	-2.48970000	-2.95590200
C	-0.63500700	-3.16899200	-3.05065000
C	0.27472800	-2.17913000	-2.31333800
H	0.71881600	-1.44324300	-2.99147000
H	1.08052700	-2.66217400	-1.75377200
H	-0.30691300	-3.34591000	-4.07897900
H	-0.65374100	-4.13522700	-2.53325200
H	-2.10420300	-1.70238100	-3.71351500

H	-2.84737500	-3.18324200	-3.07787900
H	-2.21196300	-2.62128800	-0.79064500
H	-2.57671100	-0.99464200	-1.41759500
O	-1.63773300	1.14702600	-0.49317400
C	-1.48761300	1.94760900	-1.68833300
C	-1.91181600	3.36329600	-1.29513100
C	-2.98200700	3.08960100	-0.22672500
C	-2.40138700	1.87435300	0.50051400
H	-3.16385100	1.19958800	0.90198400
H	-1.72147800	2.16923600	1.30661800
H	-3.93879900	2.83827400	-0.69921800
H	-3.14777300	3.93608700	0.44582700
H	-2.28451500	3.94029800	-2.14644700
H	-1.06647100	3.90579200	-0.85651600
H	-0.44792000	1.87361300	-2.02021400
H	-2.13575600	1.53410700	-2.47255900
O	-0.19513900	-1.18930100	1.61830300
C	-0.17341600	-0.74944800	2.99857500
C	-0.43405700	-2.00573500	3.82619000
C	0.27875300	-3.07847400	2.98939900
C	-0.02184900	-2.62942700	1.55698800
H	-0.95376100	-3.06868500	1.18093900
H	0.78561800	-2.85403700	0.85614000
H	-0.07574800	-4.09397800	3.18857100
H	1.35746200	-3.05078900	3.17868500
H	-1.50950300	-2.21235800	3.88627100
H	-0.04400900	-1.92180100	4.84469200
H	0.81036000	-0.32094900	3.22193800
H	-0.93092700	0.02986500	3.11484800
Si	10.8333310	-1.43342900	0.16794000
C	12.3130400	-1.83141200	-0.97218100
H	12.8063460	-0.91806500	-1.32916200
H	13.0717290	-2.42966200	-0.44979300
H	11.9921740	-2.39676100	-1.85601800
C	10.2162340	-3.11354900	0.83723000
H	11.0031580	-3.64221700	1.39137300
H	9.36261800	-2.99847500	1.52003400
H	9.89395200	-3.76906900	0.01702400
C	11.5668360	-0.50366100	1.66851500
H	11.9837940	0.46683400	1.36962800
H	10.7936360	-0.30448900	2.42235200
H	12.3690630	-1.07329600	2.15710600
N	9.53899800	-0.61222800	-0.58056400
Li	7.85114200	-1.25254800	-0.00708100
N	6.17283400	-1.81623300	0.78463700
Si	5.98109100	-1.27979700	2.38870700
C	6.65947700	-2.43704400	3.74495300
H	6.13640100	-3.40122200	3.75539200
H	7.72367700	-2.64893300	3.58297800
H	6.55794700	-1.99371200	4.74499300
C	4.15070600	-0.97070400	2.89581100
H	3.62881500	-0.33969300	2.16428100
H	3.60200500	-1.92050300	2.94513500
H	4.06960300	-0.49342400	3.88242900
C	6.89169200	0.38117700	2.63962100
H	6.56187900	1.15353000	1.93134100
H	6.74949500	0.77503100	3.65522200
H	7.97240500	0.26517600	2.48568200
Si	5.59604200	-3.23621900	0.03448300
C	3.68068400	-3.32930700	-0.10131800
H	3.22874800	-3.45545100	0.89169000
H	3.26080500	-2.41463900	-0.53926800
H	3.36413500	-4.18082400	-0.71952500
C	6.09807300	-4.87508400	0.87233500
H	7.18833000	-4.94873300	0.96827400
H	5.67720100	-4.96019400	1.88230700
H	5.75419200	-5.74557000	0.29722400
C	6.26176000	-3.32920300	-1.75165200
H	5.91809300	-4.23754900	-2.26388000
H	5.94203800	-2.46957300	-2.35509300
H	7.36016400	-3.34653200	-1.76941700
Si	9.54035600	0.71315500	-1.63578500
C	10.2862900	2.32445300	-0.91732900
H	9.78194700	2.60738300	0.01641200
H	11.3504000	2.19809900	-0.67938500
H	10.2057130	3.16650000	-1.61972300
C	7.72753100	1.15872500	-2.08289500
H	7.66546000	2.06191500	-2.70518800
H	7.24459200	0.34140900	-2.63544300
H	7.14163800	1.33325400	-1.16945700
C	10.4079170	0.44119600	-3.31492700
H	11.4821460	0.25807000	-3.19065500
H	9.98923400	-0.43152200	-3.83234600
H	10.2947770	1.31049600	-3.97734800
H	4.70575200	-0.15712700	-0.80631200

Table 26. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by A_2S_3 (**12**; *anti* to benzyl group).



IRC-P **12** *anti*

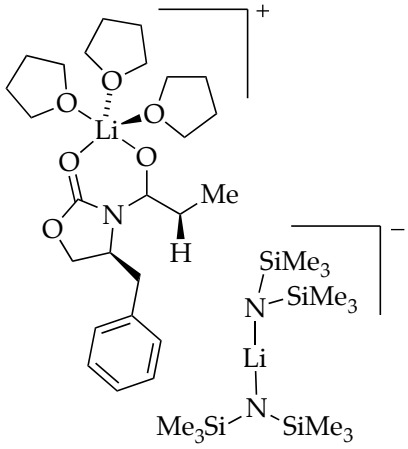


G = –3243.124524 Hartree
G_{MP2} = –2029374.8489 kcal/mol
ΔG^1_{MP2} = 5.3 kcal/mol
ΔG^2_{MP2} = 11.9 kcal/mol

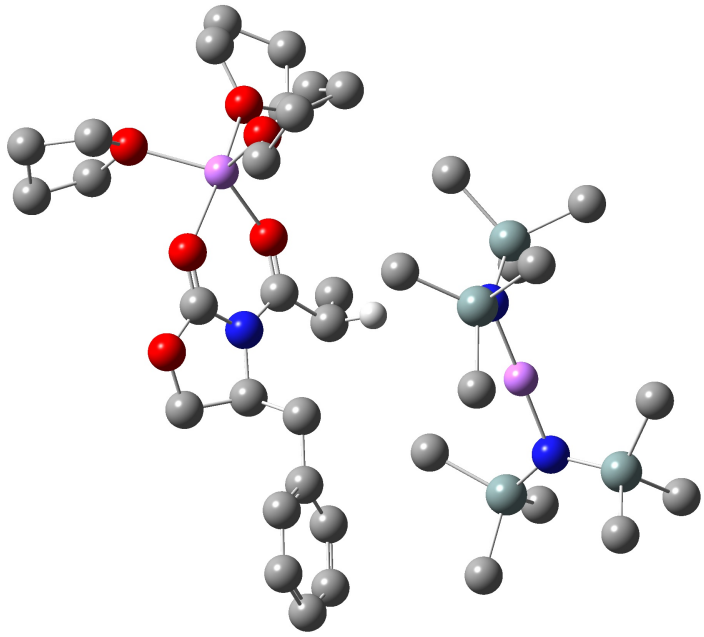
Atom	X	Y	Z	Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000	H	-5.75518400	7.67225300	0.46987800
O	-0.64002200	0.92965900	-1.75740200	H	-4.73953500	5.43930800	0.75602500
C	-1.35561200	1.92183700	-1.67911800	C	-2.48508600	1.48510400	0.50705400
N	-2.29804600	2.23919800	-0.74840000	O	-1.49674400	0.76256100	0.87890700
C	-2.80837800	3.60126800	-0.96719300	C	-3.67915600	1.66821200	1.15246100
C	-2.35585600	3.83567400	-2.41866000	C	-3.90631500	1.14894200	2.54936400
H	-3.14549600	3.59917300	-3.14003800	H	-3.42509700	1.77429600	3.31945900
H	-1.99091800	4.84750500	-2.60236500	H	-4.97536700	1.12294600	2.79385000
O	-1.26746600	2.91238800	-2.61817300	H	-3.50881400	0.13591400	2.68338900
H	-3.89939500	3.61439000	-0.90667400	H	-4.41145400	2.35822100	0.74782200
C	-2.23440400	4.61552400	0.04923700	O	0.69686700	-0.98616700	1.86933800
H	-2.43408100	4.21734900	1.05004200	C	2.04705400	-1.05382900	2.33255400
H	-1.14494600	4.66005200	-0.07370000	C	2.02684400	-0.31053500	3.66859300
C	-2.83734700	5.99510200	-0.10177700	C	0.66674900	-0.73834500	4.25830900
C	-4.15807400	6.24084000	0.30494300	C	-0.17987800	-1.09611000	3.01201900
C	-4.73191300	7.50177400	0.14608000	H	-1.00722500	-0.41289200	2.82116300
C	-3.99386600	8.54325000	-0.42181200	H	-0.56491400	-2.12362300	3.07287700
C	-2.67902500	8.31393900	-0.82713900	H	0.20561800	0.05481700	4.85380300
C	-2.10827900	7.04911000	-0.66815600	H	0.78615800	-1.61105300	4.90948400
H	-1.07835200	6.88091100	-0.97680800	H	2.04595800	0.76972100	3.48741200
H	-2.09404300	9.11892500	-1.26447300	H	2.87423300	-0.56437900	4.31335800
H	-4.44033400	9.52645200	-0.54325600	H	2.35209300	-2.10505100	2.46935700

H	2.67465600	-0.59166400	1.56885100
O	1.78649800	1.15657000	-0.01075000
C	1.63288400	2.43637600	0.64224200
C	1.96665300	3.48208600	-0.42197900
C	3.05252900	2.76124800	-1.23613500
C	2.54321600	1.31555300	-1.23494600
H	3.34849200	0.57322500	-1.24192200
H	1.86793200	1.12583700	-2.07518700
H	4.02137900	2.83273800	-0.72747700
H	3.17008400	3.15848700	-2.24864400
H	2.30350900	4.42936800	0.01032200
H	1.09325200	3.67871000	-1.05412300
H	0.61141700	2.48983800	1.02766400
H	2.33486200	2.49291400	1.48666400
O	0.38363800	-1.76041800	-1.03431100
C	0.36186100	-1.88056300	-2.47539600
C	0.81124100	-3.31136500	-2.77625200
C	0.26976700	-4.07272900	-1.55748700
C	0.49959800	-3.06620800	-0.42771800
H	1.50435400	-3.16773600	0.00237300
H	-0.23127800	-3.13603100	0.38058400
H	0.77490800	-5.02662600	-1.37723600
H	-0.80137100	-4.27403100	-1.67959500
H	1.90582700	-3.37374800	-2.80912900
H	0.42173500	-3.68039200	-3.72994000
H	-0.65666900	-1.69016100	-2.83150900
H	1.01836000	-1.11332700	-2.89260000
Si	-10.4344760	-0.41576300	-0.09245300
C	-11.8191850	-0.47685200	1.21746600
H	-12.3042980	0.50033200	1.33746600
H	-12.6005550	-1.19839700	0.94400900
H	-11.4244010	-0.76727700	2.19909100
C	-9.79046500	-2.21145700	-0.25400400
H	-10.5952720	-2.90077600	-0.54051700
H	-9.00936000	-2.30199200	-1.02222300
H	-9.37436000	-2.57423900	0.69566700
C	-11.2847280	-0.01828700	-1.75439800
H	-11.7224060	0.98759900	-1.74348100
H	-10.5665010	-0.04705500	-2.58470600
H	-12.0901040	-0.72811300	-1.98645500
N	-9.12861900	0.62183000	0.28090100
Li	-7.44460100	-0.08420800	-0.00742200
N	-5.57365900	-0.75838400	-0.59684500
Si	-5.45487400	-0.57132600	-2.37707000
C	-6.87027400	-1.49056500	-3.22072200
H	-6.83424100	-2.57295200	-3.06234300
H	-7.84853500	-1.13268800	-2.87857300
H	-6.82190300	-1.31540700	-4.30314500
C	-3.79599300	-1.18720600	-3.04642700
H	-2.95597000	-0.68220200	-2.55466500
H	-3.67125000	-2.26709600	-2.90087500
H	-3.71993100	-0.99121300	-4.12368100
C	-5.62471500	1.27547800	-2.72995400
H	-4.83889100	1.84385000	-2.22062100
H	-5.53927800	1.47280600	-3.80577700
H	-6.59445800	1.66535900	-2.39780200
Si	-5.21249900	-2.26215200	0.31948300
C	-3.34921600	-2.46099300	0.55323000
H	-2.86321700	-2.73732500	-0.39028500
H	-2.87844700	-1.53352900	0.90039700
H	-3.13346500	-3.25076300	1.28472400
C	-5.90503400	-3.76429500	-0.59198700
H	-6.98617700	-3.69061800	-0.75227800
H	-5.42564300	-3.92859500	-1.56382800
H	-5.72581900	-4.66186100	0.01362900
C	-6.06416800	-2.11011800	1.99996100
H	-5.86538900	-2.99699900	2.61515700
H	-5.70433800	-1.23823600	2.55811900
H	-7.15455500	-2.02280600	1.90667400
Si	-9.19067700	2.22173200	0.87778900
C	-10.3242680	3.39976100	-0.10729100
H	-10.0352480	3.43547400	-1.16540900
H	-11.3726240	3.07675500	-0.06819500
H	-10.2839360	4.42475600	0.28520900
C	-7.44002100	2.99297400	0.80461900
H	-7.44364300	4.02042100	1.19238400
H	-6.72255200	2.42454600	1.41263400
H	-7.05675100	3.03272100	-0.22420100
C	-9.72471300	2.35754700	2.70446700
H	-10.7466970	1.98869600	2.85451500
H	-9.06721800	1.75989600	3.34942900
H	-9.69082100	3.39478300	3.06457200
H	-4.99856800	-0.01073400	-0.16721600

Table 27. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by A_2S_3 (**12**; *syn* to benzyl group).



IRC-R **12** *syn*

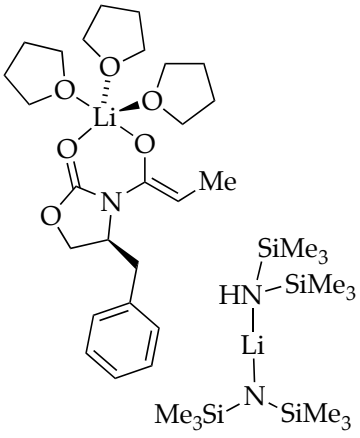


G = –3243.112057 Hartree
G_{MP2} = –2029366.9139 kcal/mol
ΔG^1_{MP2} = 13.2 kcal/mol
ΔG^2_{MP2} = 9.6 kcal/mol

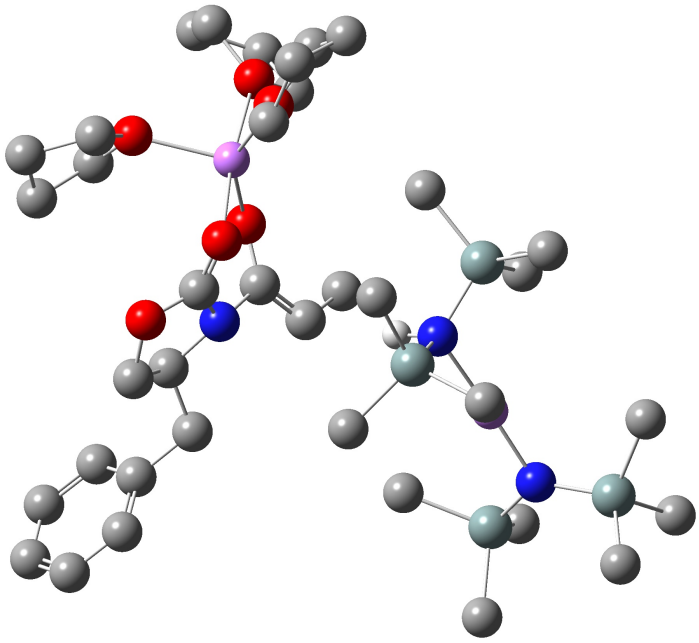
Atom	X	Y	Z	Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000	C	-5.81116700	4.07859300	0.88060100
O	-0.55730000	1.97951600	0.58296100	C	-6.87604100	4.12035300	-0.03121800
C	-1.54883100	2.60832300	0.27618700	C	-7.82096100	5.14505800	0.02362600
N	-2.70504000	2.14487200	-0.36472600	C	-7.71351500	6.14731200	0.99030800
C	-2.79157600	0.85743900	-0.91792200	C	-6.66139500	6.11462500	1.90599200
O	-1.81154000	0.11687900	-0.91277900	C	-5.71895300	5.08588600	1.85092700
C	-4.10677900	0.43017600	-1.51861700	H	-4.91611500	5.05212400	2.58498200
C	-3.91261200	-0.40676500	-2.78981400	H	-6.57882800	6.88157700	2.67143600
H	-3.36743400	0.15372300	-3.55818300	H	-8.45375200	6.94117500	1.03715000
H	-4.89084100	-0.67579800	-3.19474900	H	-8.64917200	5.14636300	-0.67910400
H	-3.36238100	-1.32525900	-2.57658900	H	-6.98639700	3.33430600	-0.77435200
H	-4.75291100	1.28448400	-1.72803300	O	0.50697500	-1.71833500	-1.06195500
C	-3.75398500	3.19684400	-0.32474900	C	1.84154900	-2.25977000	-1.12287100
C	-2.86613100	4.43320800	-0.11539300	C	1.89349500	-3.05863800	-2.42316500
H	-3.31550200	5.17864400	0.53934600	C	0.47146800	-3.63733900	-2.48116300
H	-2.56449200	4.90045400	-1.05825700	C	-0.37824700	-2.49294300	-1.91516900
O	-1.67631200	3.92225000	0.53173000	H	-0.75160700	-1.82904700	-2.70154900
H	-4.26329200	3.25503000	-1.28810700	H	-1.22763900	-2.83734400	-1.32032100
C	-4.77692400	2.97295800	0.81030700	H	0.15942700	-3.92446300	-3.48942800
H	-4.23294700	2.90180600	1.75974500	H	0.39744500	-4.52459400	-1.84183100
H	-5.26442500	2.00497600	0.65700400	H	2.07462500	-2.39125200	-3.27442200

H	2.67493400	-3.82444100	-2.41688200
H	2.01083900	-2.91361000	-0.25438500
H	2.53693300	-1.42008400	-1.07231700
O	1.82942300	0.87487200	-0.51031300
C	1.84973900	1.64251800	-1.73603900
C	2.59948800	2.94012400	-1.41566700
C	3.52888500	2.50511000	-0.27168500
C	2.63831100	1.52811300	0.49500500
H	3.19125000	0.75328500	1.03382400
H	1.97593600	2.05188300	1.19388900
H	4.41321000	1.99171500	-0.66709200
H	3.86735600	3.33901500	0.35004300
H	3.13406400	3.33705100	-2.28354100
H	1.90104500	3.70729700	-1.06344300
H	0.81720000	1.80942800	-2.05978700
H	2.36398700	1.05049100	-2.50359000
O	0.05499400	-0.76640500	1.84222000
C	-0.17446200	-0.02251100	3.06333800
C	0.08080600	-1.01994900	4.19020900
C	-0.45915900	-2.32186300	3.57826700
C	-0.06009900	-2.19051300	2.10396400
H	0.91569700	-2.64771600	1.90195500
H	-0.79841300	-2.61474600	1.41879100
H	-0.04449400	-3.22288300	4.03959300
H	-1.54884000	-2.36019100	3.67677300
H	1.15512600	-1.10221700	4.39506600
H	-0.42511300	-0.73914100	5.11846500
H	-1.21041800	0.33629000	3.07439900
H	0.50101900	0.83646200	3.06180700
Si	-10.8402940	-1.12304900	0.39074300
C	-12.2852270	-1.88408800	-0.60162900
H	-12.7827070	-1.13530400	-1.23159600
H	-13.0491280	-2.31122600	0.06214600
H	-11.9315250	-2.68418900	-1.26389100
C	-10.2304940	-2.50247700	1.56555000
H	-11.0420150	-2.86453000	2.21076300
H	-9.42321000	-2.15857100	2.22687000
H	-9.84872800	-3.36565600	1.00371900
C	-11.6250140	0.20870800	1.51478200
H	-12.0600560	1.02579600	0.92497400
H	-10.8720470	0.65410100	2.17799600
H	-12.4235490	-0.20465000	2.14599300
N	-9.53289200	-0.56038400	-0.54955100
Li	-7.87621600	-1.16274400	0.15594200
N	-6.18491800	-1.73840000	0.91283400
Si	-5.87970600	-1.09971700	2.46171400
C	-6.09447500	-2.30531100	3.92783600
H	-5.36524100	-3.12516400	3.89456700
H	-7.09272800	-2.75977300	3.92164400
H	-5.96894600	-1.79159000	4.89078000
C	-4.08916300	-0.42850000	2.67327200
H	-3.86174800	0.36776800	1.95294500
H	-3.36194000	-1.23306200	2.50431400
H	-3.92159900	-0.02476500	3.68171700
C	-7.03943900	0.36951000	2.82921500
H	-7.01162400	1.13893100	2.04690800
H	-6.77938300	0.85599500	3.77897800
H	-8.08359700	0.04096500	2.91043100
Si	-5.67555100	-3.22929000	0.25658800
C	-3.76525900	-3.42831100	0.17685200
H	-3.33987200	-3.51934700	1.18589800
H	-3.29884300	-2.55549600	-0.29814600
H	-3.47252300	-4.32489300	-0.38679100
C	-6.30157500	-4.78301100	1.17057600
H	-7.39707500	-4.77779000	1.23433700
H	-5.91934700	-4.83892200	2.19699900
H	-6.00290600	-5.70523200	0.65369000
C	-6.31374500	-3.40262800	-1.53309600
H	-6.03507300	-4.37134400	-1.96868300
H	-5.92005600	-2.61865400	-2.19192400
H	-7.40973800	-3.33517000	-1.57058900
Si	-9.53200000	0.42960000	-1.92564100
C	-10.3137470	2.16173500	-1.68600500
H	-9.84131300	2.69258500	-0.84895900
H	-11.3843690	2.08985600	-1.45514400
H	-10.2148510	2.78534900	-2.58588100
C	-7.72410400	0.77299800	-2.46806900
H	-7.67367600	1.46536200	-3.31926800
H	-7.22201700	-0.15721600	-2.76544500
H	-7.14838700	1.20988700	-1.64014100
C	-10.3731010	-0.31056900	-3.47271500
H	-11.4434490	-0.48198200	-3.30536500
H	-9.92757600	-1.27995900	-3.73080000
H	-10.2759630	0.34657300	-4.34807400
H	-4.63291600	-0.17026100	-0.75336000

Table 28. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by A_2S_3 (**12**; *syn* to benzyl group).



IRC-P **12** *syn*

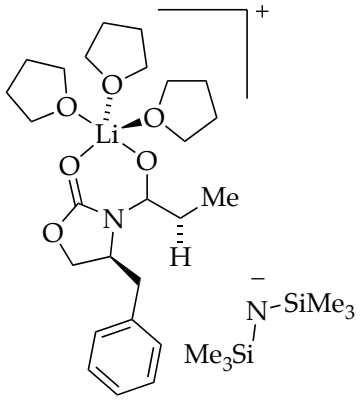


G = –3243.120202 Hartree
G_{MP2} = –2029372.3182 kcal/mol
ΔG^1_{MP2} = 7.8 kcal/mol
ΔG^2_{MP2} = 15.0 kcal/mol

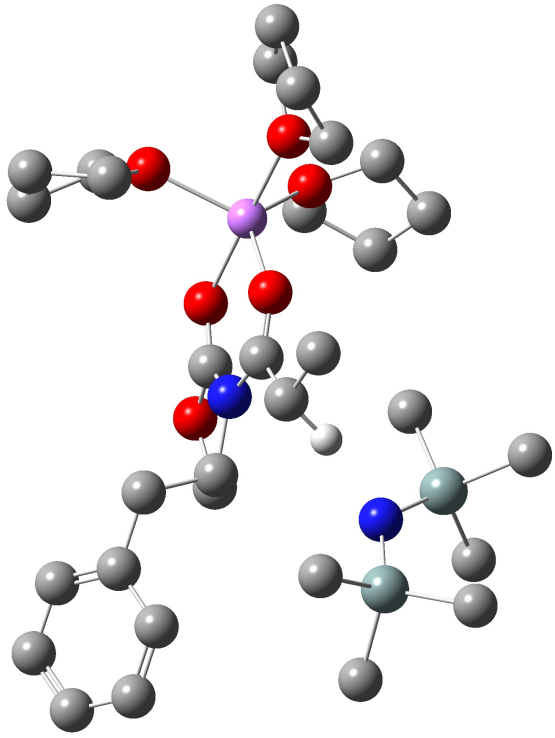
Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000
O	0.85530800	0.90489300	-1.78611000
C	1.21526900	2.06192500	-1.60829900
N	2.03989400	2.55535300	-0.63690100
C	2.21830200	1.76132000	0.60967300
O	1.18404700	1.11174400	1.00412400
C	3.43913700	1.84384400	1.21313600
C	3.67900100	1.26254400	2.58367100
H	3.05876100	1.74468700	3.35519700
H	4.72442000	1.39067200	2.88738000
H	3.44844700	0.18960000	2.63771100
H	4.21735600	2.44692900	0.76003900
C	1.92245400	4.03011700	-0.61175200
C	1.44280100	4.28337800	-2.04777700
H	2.28602100	4.44753100	-2.72953600
H	0.73662900	5.10905300	-2.14007500
O	0.77777900	3.06414900	-2.42804300
H	1.13327000	4.30727800	0.10451100
C	3.19936100	4.80417800	-0.25177400
H	4.00268600	4.50687900	-0.93620500
H	3.50655700	4.50600800	0.75448800
C	2.98307600	6.30373200	-0.31071200
C	2.28026700	6.96175200	0.71001100
C	2.05578600	8.33710000	0.65418100
C	2.53472800	9.08260300	-0.42550100
C	3.24116700	8.44254500	-1.44418500
C	3.46180300	7.06489300	-1.38537500
H	4.02523200	6.57632900	-2.17739600
H	3.62761600	9.01502000	-2.28333800
H	2.36543800	10.1551570	-0.46739300
H	1.51438500	8.82868800	1.45833400
H	1.91745500	6.39148300	1.56274700
O	-0.66735300	-1.08435800	1.80105500
C	-2.02838000	-1.21591400	2.22327300
C	-2.07780100	-0.51359600	3.57950400
C	-0.72985600	-0.92941300	4.19726200
C	0.18954500	-1.10987800	2.96846800
H	0.90730700	-0.30038900	2.83211600
H	0.72398000	-2.06861900	2.99900100
H	-0.33943200	-0.18460300	4.89676900
H	-0.83775000	-1.87265300	4.74458400
H	-2.11596300	0.57153100	3.43276500
H	-2.93988300	-0.81011900	4.18548200
H	-2.29578600	-2.28115900	2.32220200

H	-2.65219400	-0.76033500	1.45172500
O	-1.84344700	0.96886000	-0.20612200
C	-1.98993600	2.18058800	0.57071700
C	-2.41977600	3.25535200	-0.42779500
C	-3.26672300	2.44248100	-1.41940000
C	-2.49136900	1.12289300	-1.49171900
H	-3.13261300	0.25155300	-1.66138600
H	-1.71337300	1.15207300	-2.26175500
H	-4.27430000	2.28007300	-1.01802300
H	-3.36413300	2.91987500	-2.39890400
H	-2.96923600	4.07479800	0.04554500
H	-1.54501300	3.67209400	-0.93890200
H	-1.03180000	2.36801800	1.06162200
H	-2.76224300	2.01974200	1.33664100
O	-0.20804100	-1.77671500	-1.09339400
C	-0.15384500	-1.86658300	-2.53651600
C	-0.62318300	-3.28119400	-2.88071800
C	-0.13435500	-4.07882000	-1.66302000
C	-0.38109500	-3.09102800	-0.52085500
H	-1.40382600	-3.17681100	-0.13147300
H	0.31554200	-3.19641900	0.31335700
H	-0.66283900	-5.02620400	-1.51904100
H	0.93622700	-4.29750600	-1.75585500
H	-1.71734800	-3.32075900	-2.94779700
H	-0.21255500	-3.63817200	-3.83013400
H	0.87670500	-1.68959700	-2.86248800
H	-0.78291000	-1.07684100	-2.95294300
Si	10.4325400	-0.12965900	-0.11892700
C	11.7347600	-0.29591800	1.26527200
H	12.2170000	0.66596400	1.48196200
H	12.5274350	-1.00410800	0.98929100
H	11.2801470	-0.64997700	2.19896100
C	9.81705200	-1.90423100	-0.48024700
H	10.6480970	-2.57212700	-0.74139400
H	9.11508900	-1.92399300	-1.32552800
H	9.31077100	-2.34045400	0.39145900
C	11.3823060	0.41271600	-1.68356800
H	11.8232660	1.40932300	-1.55668000
H	10.7135250	0.46453600	-2.55303700
H	12.1969990	-0.28100000	-1.93147500
N	9.10208000	0.87163800	0.26211500
Li	7.38914000	0.28526500	-0.10996400
N	5.51353800	-0.34214700	-0.74520200
Si	5.40650300	-0.04467700	-2.51362200
C	6.96021100	-0.71753300	-3.34721200
H	7.04728900	-1.80598900	-3.26270700
H	7.87174400	-0.27441500	-2.92772100
H	6.94213600	-0.47265300	-4.41691900
C	3.86631100	-0.82461700	-3.28438300
H	2.95452500	-0.43133000	-2.81940100
H	3.85844400	-1.91661500	-3.18366500
H	3.82049200	-0.59539300	-4.35687900
C	5.32312600	1.82789200	-2.73581600
H	4.45774700	2.24594500	-2.20821100
H	5.22345800	2.08277000	-3.79823700
H	6.22516400	2.32545000	-2.35992700
Si	5.20818700	-1.91449000	0.06811400
C	3.35411100	-2.18176600	0.30281800
H	2.84188600	-2.31500600	-0.65685800
H	2.88898000	-1.32285000	0.80050000
H	3.16552400	-3.07372600	0.91466000
C	5.95202900	-3.32171500	-0.94705300
H	7.03287800	-3.20464800	-1.08185100
H	5.49313700	-3.42114200	-1.93718100
H	5.79168100	-4.26972000	-0.41795400
C	6.05551900	-1.84835300	1.75684000
H	5.89739200	-2.78686700	2.30361300
H	5.65392700	-1.03810200	2.37666300
H	7.14078000	-1.70229100	1.67766700
Si	9.09647000	2.43347500	0.95256700
C	10.1701320	3.72038100	0.04051600
H	9.89301600	3.78766200	-1.01925500
H	11.2344540	3.45488900	0.08064300
H	10.0663170	4.72198600	0.47894200
C	7.30570200	3.11347400	0.91018700
H	7.24933600	4.11262100	1.36130500
H	6.61093000	2.47520600	1.47552700
H	6.92405800	3.20389500	-0.11661300
C	9.61665600	2.49752600	2.78701500
H	10.6553230	2.17271500	2.92398600
H	8.98775400	1.83572300	3.39676100
H	9.53003600	3.51220900	3.19869600
H	4.90945600	0.35083700	-0.27382300

Table 29. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by AS_3 (**13**; *anti* to benzyl group).



IRC-R **13** *anti*



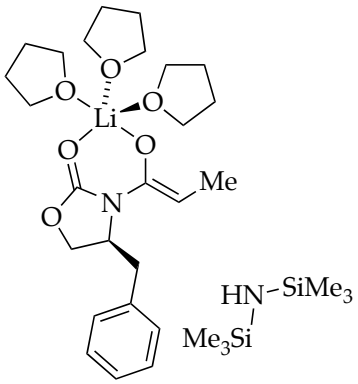
G = –2362.387265 Hartree
G_{MP2} = –1478075.1807 kcal/mol
ΔG^1_{MP2} = 7.8 kcal/mol
ΔG^2_{MP2} = 0.6 kcal/mol

Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000
O	1.36421700	1.02373800	1.15073000
C	2.57702100	1.03222300	1.01482800
N	3.32127600	0.62062000	-0.08772400
C	4.74534100	1.02087300	0.08164300
C	4.77736400	1.20559300	1.60272300
H	5.08276500	0.29343100	2.12040800
H	5.38494300	2.04858900	1.92913500
O	3.39680000	1.49019900	1.96967700
H	5.39343800	0.18042000	-0.20865300
C	5.03412600	2.33117600	-0.69274300
H	4.96456100	2.12381200	-1.76715600
H	4.23884900	3.05187600	-0.46092700
C	6.37812000	2.95554000	-0.37181100
C	7.57628000	2.31289400	-0.71508700
C	8.80773800	2.89161000	-0.40781600
C	8.86322600	4.12573200	0.24385300
C	7.67834300	4.77648200	0.58803200
C	6.44685600	4.19240700	0.28368200
H	5.52654100	4.70727200	0.55251100
H	7.70924600	5.73836300	1.09327900
H	9.82333500	4.57602300	0.48108500
H	9.72335000	2.37317200	-0.67823600
H	7.55019700	1.35294100	-1.22140300

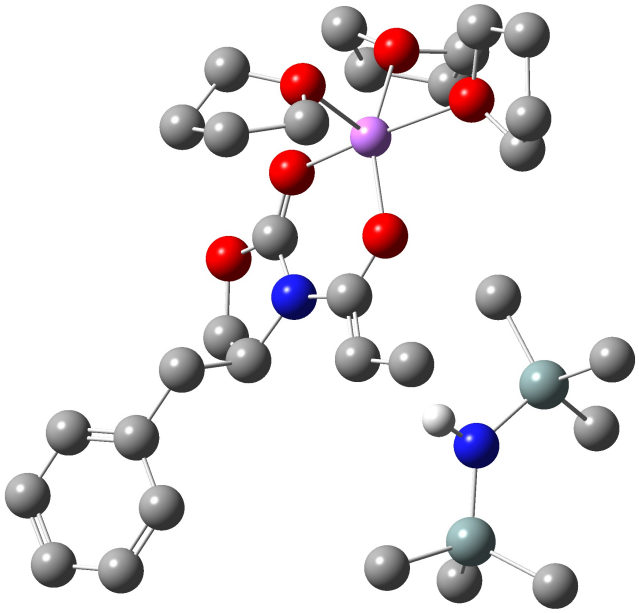
Atom	X	Y	Z
C	2.78276000	-0.13848100	-1.13526700
O	1.57827100	-0.41400700	-1.14722700
C	3.74849200	-0.62997100	-2.16293000
C	3.09197900	-1.41090400	-3.29777500
H	2.35328900	-0.81309400	-3.84458600
H	3.86096100	-1.73559800	-4.00519000
H	2.59053900	-2.30640900	-2.91771100
H	4.32674800	0.21571300	-2.55421900
O	-0.69910600	-1.07945000	1.60197100
C	-1.02289400	-2.47977600	1.53941100
C	-0.08700200	-3.17287500	2.54917200
C	0.37944400	-2.01934200	3.47941800
C	-0.42478900	-0.80709400	2.98878100
H	0.11508000	0.13841100	3.03294300
H	-1.37968600	-0.71275100	3.52783700
H	1.45042600	-1.84210400	3.35003700
H	0.19567300	-2.22666300	4.53782300
H	0.77009500	-3.62520000	2.04406600
H	-0.61154400	-3.96397600	3.09344200
H	-2.07887700	-2.61335700	1.81822100
H	-0.88766600	-2.79611300	0.50488700
O	-1.28768300	-1.04366000	-1.34746000
C	-0.94839400	-1.92208400	-2.43104200
C	-1.89137000	-1.49889800	-3.55782000

C	-3.19089200	-1.13947400	-2.79760000
C	-2.71983000	-0.91119600	-1.33812300
H	-3.15041300	-1.66044800	-0.65958900
H	-2.93998100	0.08348300	-0.94684200
H	-3.91612300	-1.95792500	-2.84441300
H	-3.67507500	-0.25222600	-3.21599300
H	-2.03792800	-2.28469200	-4.30471100
H	-1.48409000	-0.61975800	-4.06870700
H	0.11245700	-1.78435400	-2.63580000
H	-1.12884100	-2.96772200	-2.13362600
O	-1.07051900	1.73414900	-0.38126500
C	-0.81593500	2.35497200	-1.66300400
C	-1.10349400	3.84639700	-1.47304900
C	-0.75459500	4.05326700	0.00890900
C	-1.24862700	2.74919800	0.63552000
H	-2.31526300	2.80250100	0.89158200
H	-0.67998800	2.44557800	1.51642900
H	-1.22889400	4.93594300	0.44790100
H	0.32973800	4.14775700	0.13831300
H	-2.16463100	4.05910100	-1.64853500
H	-0.51588900	4.47307500	-2.15034400
H	0.23139200	2.17427600	-1.93594100
H	-1.45523500	1.87525400	-2.40996500
N	5.97177700	-2.04219200	-0.50467200
Si	7.40431300	-2.08557400	-1.41127400
C	7.96613100	-3.80821400	-2.03181400
H	8.19856600	-4.48037600	-1.19548100
H	7.18424100	-4.29253100	-2.63051200
H	8.86807700	-3.73908700	-2.65556200
C	8.93719800	-1.39089800	-0.49246000
H	8.75606500	-0.39026400	-0.07960800
H	9.19933300	-2.03907900	0.35405300
H	9.81934500	-1.33043300	-1.14526000
C	7.24225100	-1.05119600	-3.02016500
H	6.94149300	-0.00927400	-2.84495200
H	8.19198900	-1.02379600	-3.57074600
H	6.49222500	-1.49339300	-3.68977200
Si	5.40646400	-3.15975300	0.63246400
C	3.74907100	-2.58779000	1.42667000
H	3.85716600	-1.65698900	2.00019100
H	2.96901300	-2.42886900	0.66954500
H	3.38093800	-3.35433000	2.12250500
C	6.56302900	-3.46895900	2.12770100
H	7.51489100	-3.91020600	1.80440400
H	6.80472900	-2.53121800	2.64533500
H	6.11838500	-4.15227000	2.86445000
C	4.98437800	-4.89804500	-0.05405400
H	4.56976900	-5.55715400	0.72157500
H	4.24579100	-4.83196000	-0.86426800
H	5.87112100	-5.39302900	-0.46808100
H	4.51143200	-1.26200500	-1.62454300

Table 30. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by AS_3 (**13**; *anti* to benzyl group).



IRC-P **13** *anti*

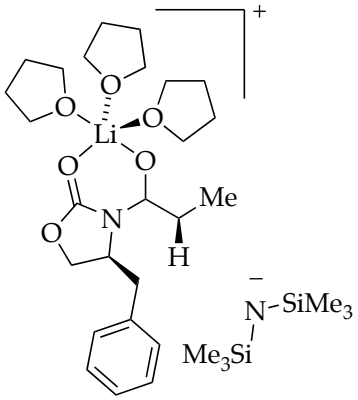


G = –2362.419779 Hartree
G_{MP2} = –1478092.9451 kcal/mol
ΔG^1_{MP2} = –10.0 kcal/mol
ΔG^2_{MP2} = 18.3 kcal/mol

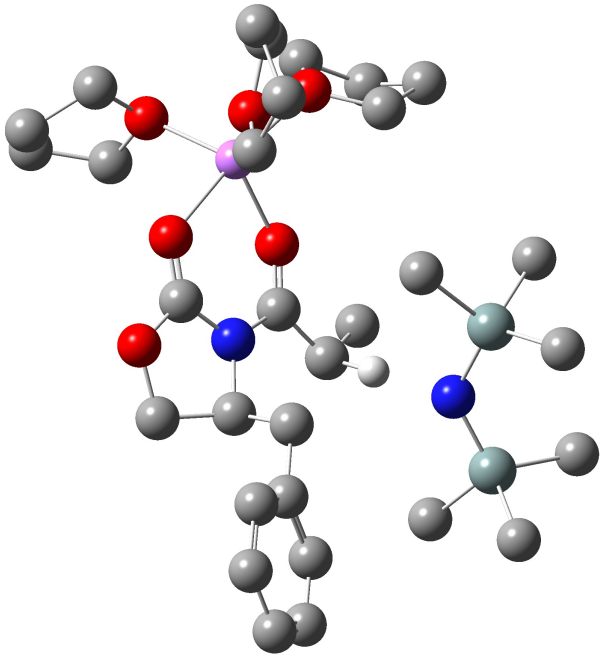
Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000
O	-1.18329100	-1.04680400	1.26869300
C	-2.40652900	-1.05874400	1.18313600
N	-3.22792200	-0.59188000	0.20047400
C	-4.59593500	-1.07648700	0.42233300
C	-4.53943600	-1.35132600	1.92918100
H	-4.82805600	-0.47453600	2.51998100
H	-5.12939900	-2.21413400	2.24193500
O	-3.14847100	-1.63611800	2.17659800
H	-5.31285800	-0.28518800	0.19245000
C	-4.90046100	-2.34346000	-0.41861500
H	-4.66418800	-2.11134500	-1.46197800
H	-4.21060900	-3.13530700	-0.10004900
C	-6.33130200	-2.81732200	-0.28825600
C	-7.36952300	-2.14332700	-0.94981000
C	-8.69457800	-2.55584600	-0.81143400
C	-9.00765800	-3.65555400	-0.00905400
C	-7.98554500	-4.33940800	0.64950300
C	-6.66025600	-3.92191800	0.50933500
H	-5.86788700	-4.46869600	1.01653600
H	-8.21678100	-5.20139400	1.26996700
H	-10.0396080	-3.97911200	0.09694900
H	-9.48270500	-2.02077100	-1.33469600
H	-7.13687700	-1.29276400	-1.58678300
C	-2.78644200	0.21304700	-0.94850100
O	-1.55731700	0.57606700	-0.92059600
C	-3.72340500	0.50944900	-1.90284200
C	-3.38291700	1.30153300	-3.13648300
H	-2.29928300	1.42995900	-3.21991700
H	-3.73051400	0.80064200	-4.05211100
H	-3.83115600	2.30795900	-3.14221700
H	-4.73179600	0.12112600	-1.82403500
O	1.36343900	0.31976300	1.74375800
C	1.53857300	1.64482100	2.26189900
C	0.67221800	1.70884500	3.53498900
C	0.52176200	0.21895900	3.95144400
C	1.34231000	-0.53774500	2.89315600
H	0.89688400	-1.48462000	2.58996600
H	2.37613300	-0.70829700	3.23306000
H	-0.52419000	-0.09262100	3.89973400
H	0.88724100	0.02391200	4.96459400
H	-0.30425200	2.14918200	3.31489300
H	1.14634000	2.31835200	4.31084700
H	2.60236600	1.80188400	2.50185700
H	1.24698600	2.34001200	1.47409200
O	1.24585600	1.48081500	-0.91656200

C	0.73296500	2.47527400	-1.81938700
C	1.51658900	2.25069000	-3.11018900
C	2.92202500	1.91743400	-2.57371300
C	2.63676600	1.24235600	-1.21191400
H	3.25732100	1.65917100	-0.40895400
H	2.77708100	0.15846800	-1.22984800
H	3.50235000	2.83631700	-2.43305700
H	3.49233900	1.26895500	-3.24587500
H	1.50701300	3.12065000	-3.77428100
H	1.09554400	1.39868900	-3.65565200
H	-0.34095700	2.30219000	-1.88799100
H	0.92288500	3.48150400	-1.41272300
O	0.81939700	-1.60376300	-1.07981100
C	0.41171200	-1.57961900	-2.47283400
C	-0.08012400	-2.99831800	-2.81236100
C	-0.36729400	-3.60480300	-1.42877700
C	0.71067000	-2.94543900	-0.57201800
H	1.67739500	-3.46067500	-0.67877100
H	0.45313500	-2.87554800	0.48632400
H	-0.31258300	-4.69789200	-1.41598900
H	-1.35879800	-3.30243800	-1.07401000
H	0.70438400	-3.57064000	-3.32120900
H	-0.95870900	-2.98242200	-3.46374400
H	-0.37537700	-0.82582600	-2.55699000
H	1.26971900	-1.27915400	-3.08608900
N	-5.06808000	3.27245700	-0.20128200
Si	-6.75906200	3.56390800	-0.54339700
C	-7.02004400	5.10749600	-1.61491300
H	-6.62915600	6.01079800	-1.13038200
H	-6.51113800	5.00772300	-2.58120800
H	-8.08568900	5.28005100	-1.81395900
C	-7.77076000	3.77758100	1.04480500
H	-7.67038200	2.90079100	1.69572500
H	-7.45046500	4.65391500	1.61970700
H	-8.83686700	3.90588600	0.81677300
C	-7.42084400	2.05677500	-1.48212300
H	-7.38267800	1.15027100	-0.86563600
H	-8.46698800	2.20978400	-1.77501600
H	-6.84415400	1.86861000	-2.39549700
Si	-3.80178300	4.29006700	0.45518100
C	-2.58987100	3.21840200	1.43404600
H	-3.09366500	2.71461300	2.26819700
H	-2.13735700	2.45039700	0.79385300
H	-1.77859100	3.82977600	1.85127800
C	-4.56289300	5.59484200	1.59842900
H	-5.28355400	6.23857100	1.07994700
H	-5.07669300	5.13464600	2.45019300
H	-3.77723600	6.24798800	1.99884500
C	-2.83543200	5.17958200	-0.91293700
H	-2.03514800	5.80982300	-0.50331100
H	-2.37414600	4.45514500	-1.59530400
H	-3.49429500	5.82194600	-1.50968500
H	-4.69935300	2.42090600	-0.63706400

Table 31. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by AS_3 (**13**; *syn* to benzyl group).



IRC-R **13** *syn*

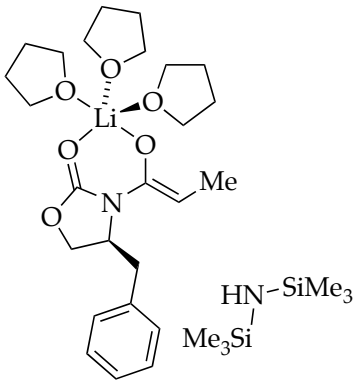


G = –2362.383476 Hartree
G_{MP2} = –1478074.0715 kcal/mol
ΔG^1_{MP2} = 8.9 kcal/mol
ΔG^2_{MP2} = –1.0 kcal/mol

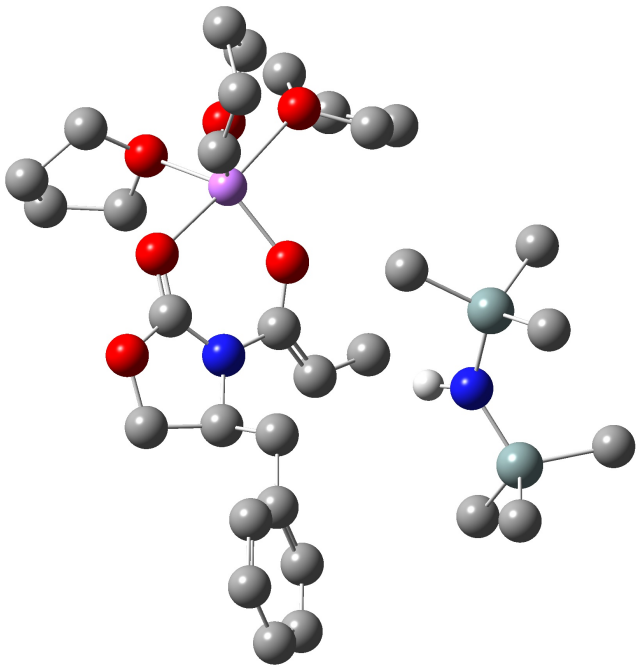
Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000
O	-0.36898600	-0.20904400	2.01466600
C	0.50027000	-0.91794500	2.93692400
C	0.02948900	-0.52496600	4.33979700
C	-1.46043200	-0.22788500	4.11313300
C	-1.43647700	0.43953100	2.73843500
H	-1.22137300	1.51215200	2.81594800
H	-2.36034900	0.31326200	2.16687700
H	-1.89869000	0.41450600	4.88279000
H	-2.03695900	-1.16022100	4.07749300
H	0.55132500	0.37696700	4.67940000
H	0.20825800	-1.31572900	5.07427200
H	0.39079000	-1.99192300	2.75008500
H	1.53303900	-0.62387400	2.73239400
O	-1.57550600	-0.74273200	-1.09149600
C	-2.37016700	-1.72649600	-0.38574000
C	-2.26895900	-3.00787800	-1.21119100
C	-2.16395100	-2.45350700	-2.64050400
C	-1.30434000	-1.20225800	-2.43777600
H	-1.54335800	-0.39112700	-3.13296400
H	-0.23457000	-1.42698400	-2.51411500
H	-3.15584600	-2.18264100	-3.02109300
H	-1.71187600	-3.15689900	-3.34599500
H	-3.12808500	-3.66953300	-1.06551000
H	-1.35799300	-3.55299700	-0.94320000
H	-1.96256200	-1.81769400	0.62382900
H	-3.40530300	-1.36306200	-0.32653400
O	-0.64599000	1.98792700	0.06779500
C	0.30548300	2.95234800	0.59307300
C	0.03248600	4.27107500	-0.14011900
C	-0.59690500	3.79220200	-1.45762200
C	-1.41945600	2.59456500	-0.98638200
H	-1.59340200	1.83496100	-1.75164200
H	-2.39248000	2.91283600	-0.58336800
H	0.18016300	3.46601700	-2.15785900
H	-1.20767700	4.55568800	-1.94936400
H	0.94618300	4.85525200	-0.27975600
H	-0.68118400	4.88710400	0.41981600
H	0.16512700	3.02634200	1.67637100
H	1.31124200	2.57449900	0.39341500
O	1.62485600	0.45515100	-1.05248400
C	2.74174800	-0.03045600	-1.26205900
N	3.01258000	-1.34978800	-0.83440800
C	2.03430100	-2.18866200	-0.31009800
O	2.52944400	-3.43571800	-0.18540500
C	3.83636000	-3.49765900	-0.80689300

C	4.32633900	-2.04260800	-0.80993200
H	4.88461100	-1.82573800	-1.72195700
C	5.16056700	-1.65629300	0.43419200
H	5.41571000	-0.58485800	0.37567000
H	4.53023600	-1.79500600	1.32167000
C	6.41440100	-2.49621900	0.56507400
C	7.52971400	-2.25026200	-0.24967300
C	8.67827600	-3.03546900	-0.14593600
C	8.73501600	-4.08139200	0.77780300
C	7.63667700	-4.33248200	1.60077200
C	6.48790500	-3.54587100	1.49245500
H	5.64099800	-3.73857700	2.14858900
H	7.67397900	-5.13581300	2.33216500
H	9.63205600	-4.68903300	0.86196800
H	9.53427000	-2.82101900	-0.78020200
H	7.50652100	-1.42096100	-0.95087500
H	3.71109000	-3.90374100	-1.81649400
H	4.46187900	-4.16348000	-0.21403100
O	0.88884200	-1.91884000	0.00391100
C	3.84135100	0.70918400	-1.92339900
C	3.36298100	1.93386800	-2.70305400
H	2.86116000	2.64457100	-2.04095100
H	4.22658500	2.44177900	-3.14160600
H	2.66812600	1.67044600	-3.50978500
H	4.43227600	0.04067000	-2.55902200
N	5.81567300	1.73487000	0.11020700
Si	7.26910800	2.12493100	-0.67529500
C	7.35852200	1.32099600	-2.41574700
H	7.19402500	0.23483100	-2.39476500
H	6.61033300	1.74794400	-3.09672200
H	8.34313600	1.48955800	-2.87167600
C	8.84507700	1.53603200	0.23572300
H	8.93958700	2.03092900	1.21072400
H	8.82185500	0.45553500	0.42576200
H	9.75741600	1.75669800	-0.33583200
C	7.54939200	3.99103300	-1.00640500
H	7.62266800	4.55707200	-0.06836400
H	8.47318300	4.17538100	-1.57201300
H	6.71691100	4.42006200	-1.57930400
Si	5.09803300	2.46806200	1.45501700
C	4.15027700	4.09045500	1.06198900
H	4.83734500	4.85811200	0.68411500
H	3.39409400	3.92892400	0.28110100
H	3.64080100	4.50528900	1.94335700
C	6.27584700	2.91708800	2.89506900
H	6.82785900	2.03544000	3.24455600
H	7.01966700	3.66269200	2.58537700
H	5.73279500	3.33370800	3.75476000
C	3.77631700	1.32129300	2.25194400
H	3.24820600	1.83501500	3.06724800
H	3.02329400	1.00063200	1.51901200
H	4.23986300	0.41959100	2.67284000
H	4.56889600	1.06410600	-1.10929300

Table 32. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by AS_3 (**13**; *syn* to benzyl group).



IRC-P **13** *syn*

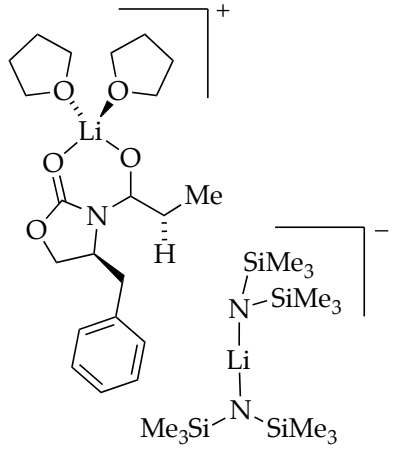


G = –2362.417970 Hartree
G_{MP2} = –1478092.0999 kcal/mol
ΔG^1_{MP2} = –9.1 kcal/mol
ΔG^2_{MP2} = 17.1 kcal/mol

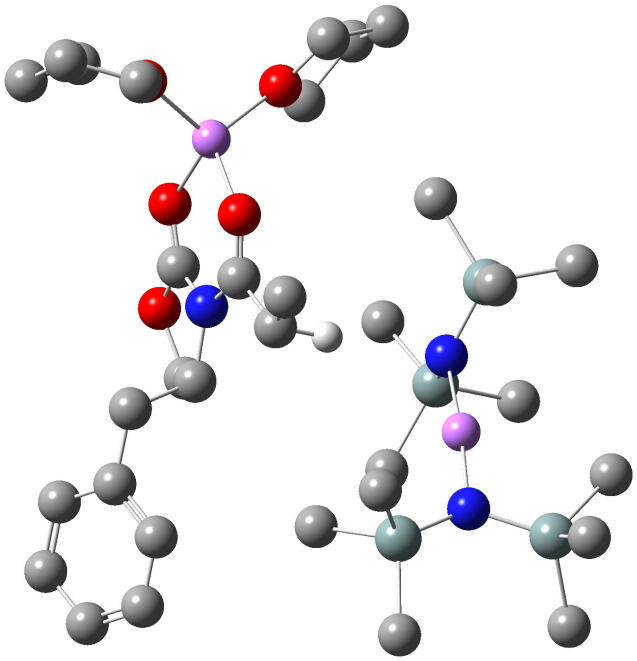
Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000
O	0.55158300	-0.04103800	2.00019600
C	-0.25830000	0.63831000	2.99147600
C	0.16706900	0.07010600	4.35387500
C	1.58580700	-0.45040500	4.07396700
C	1.44153300	-0.96912300	2.64442900
H	1.00553600	-1.97658400	2.62444000
H	2.37480600	-0.98765700	2.07623600
H	1.91055300	-1.22540600	4.77522700
H	2.31207200	0.37061800	4.10974100
H	-0.48784400	-0.75867100	4.64703300
H	0.13001500	0.82281300	5.14719000
H	-0.06124800	1.71088200	2.90306100
H	-1.31328600	0.45829100	2.76506400
O	1.64824400	0.74166500	-1.10894800
C	2.45550300	1.69065700	-0.37391000
C	2.30552000	3.02287200	-1.10787000
C	2.12307100	2.56341600	-2.56306200
C	1.27954800	1.29662700	-2.39347900
H	1.46845400	0.53807800	-3.16001800
H	0.20749500	1.52172600	-2.37782400
H	3.09327100	2.32382200	-3.01522600
H	1.63011700	3.30871900	-3.19467500
H	3.16915400	3.68009900	-0.96597300
H	1.40742600	3.53810800	-0.75405400
H	2.08899500	1.71168900	0.65477300
H	3.49761200	1.34001700	-0.37973000
O	0.81477800	-2.09564500	-0.21659800
C	-0.19014200	-3.13489700	-0.23862900
C	0.03632400	-3.94680400	-1.53738800
C	1.12755200	-3.14866800	-2.27912700
C	1.85743300	-2.46508900	-1.12393900
H	2.38689800	-1.54988800	-1.39276600
H	2.55895300	-3.16149000	-0.63393100
H	0.67403400	-2.39086700	-2.92704800
H	1.78267700	-3.77955400	-2.88868100
H	-0.88066000	-4.04123100	-2.12600600
H	0.38857000	-4.95841000	-1.30669000
H	-0.07685800	-3.76467900	0.65453800
H	-1.15456100	-2.62700700	-0.21142300
O	-1.68564400	-0.41457600	-0.68893200
C	-2.63103100	0.27482000	-1.21412400
N	-2.77763700	1.64781500	-0.68849600
C	-1.78344600	2.32000500	-0.04659400
O	-2.21287500	3.57011900	0.30969600
C	-3.47586800	3.82007800	-0.33137900

C	-4.02359300	2.42344800	-0.66802100
H	-4.48814900	2.42779000	-1.65675100
C	-5.02897600	1.88244500	0.37533400
H	-5.20738500	0.82530000	0.15308400
H	-4.55560400	1.92793800	1.36379100
C	-6.33250900	2.65075100	0.38749500
C	-7.25029400	2.52090900	-0.66686700
C	-8.44302600	3.24419600	-0.67420000
C	-8.74273500	4.11492900	0.37610400
C	-7.84196200	4.25265500	1.43232300
C	-6.64875800	3.52692500	1.43474200
H	-5.95724900	3.63250900	2.26810800
H	-8.06752000	4.92228700	2.25832400
H	-9.67302800	4.67654000	0.37256800
H	-9.14136400	3.12358400	-1.49832500
H	-7.03142400	1.83955600	-1.48613400
H	-3.29674300	4.42135200	-1.23059700
H	-4.10989200	4.38168200	0.35681100
O	-0.63851100	1.97041300	0.21892800
C	-3.50950200	-0.11025700	-2.18805600
C	-3.39029100	-1.44263600	-2.87780700
H	-2.71456300	-2.09802400	-2.31980400
H	-4.35500200	-1.95981500	-2.97502700
H	-2.98457800	-1.35002400	-3.89872100
H	-4.21234700	0.60708500	-2.60014500
N	-5.84025300	-2.02753600	-0.05233500
Si	-7.43810000	-2.23141200	-0.74504700
C	-7.41979200	-1.48278500	-2.48405200
H	-7.05504000	-0.44864300	-2.47882200
H	-6.77553400	-2.05475500	-3.16179200
H	-8.42932600	-1.47521100	-2.91348200
C	-8.76536500	-1.35614000	0.28480900
H	-8.79844300	-1.73907400	1.31167100
H	-8.57427100	-0.27785200	0.34086400
H	-9.76299500	-1.49767800	-0.15124000
C	-7.91173600	-4.06301000	-0.88359700
H	-7.93937300	-4.56020600	0.09358300
H	-8.90659900	-4.17735700	-1.33320000
H	-7.19684300	-4.60829900	-1.51136000
Si	-5.05708700	-2.77363000	1.32734300
C	-4.16645400	-4.38018900	0.85138900
H	-4.86823600	-5.11753800	0.44298400
H	-3.40424300	-4.19321800	0.08497800
H	-3.66624700	-4.83806500	1.71481800
C	-6.35216600	-3.18060100	2.64925300
H	-6.86816800	-2.27786000	2.99633900
H	-7.11381200	-3.88318500	2.29086900
H	-5.87068100	-3.64301700	3.52031300
C	-3.78456300	-1.57118200	2.04134500
H	-3.21560100	-2.04506500	2.85248000
H	-3.06997000	-1.24143400	1.27618100
H	-4.27597600	-0.68136300	2.45373300
H	-5.19534300	-1.49745800	-0.64279100

Table 33. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by A_2S_2 (**15**; *anti* to benzyl group).



IRC-R **15** *anti*

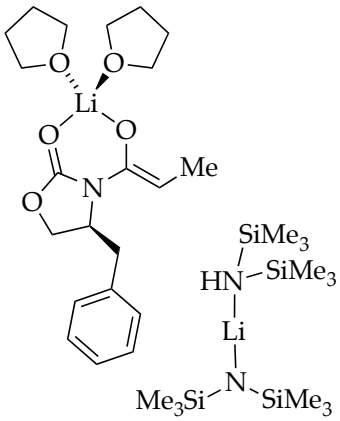


G = –3010.771137 Hartree
G_{MP2} = –1884051.1328 kcal/mol
ΔG^1_{MP2} = 16.7 kcal/mol
ΔG^2_{MP2} = 5.2 kcal/mol

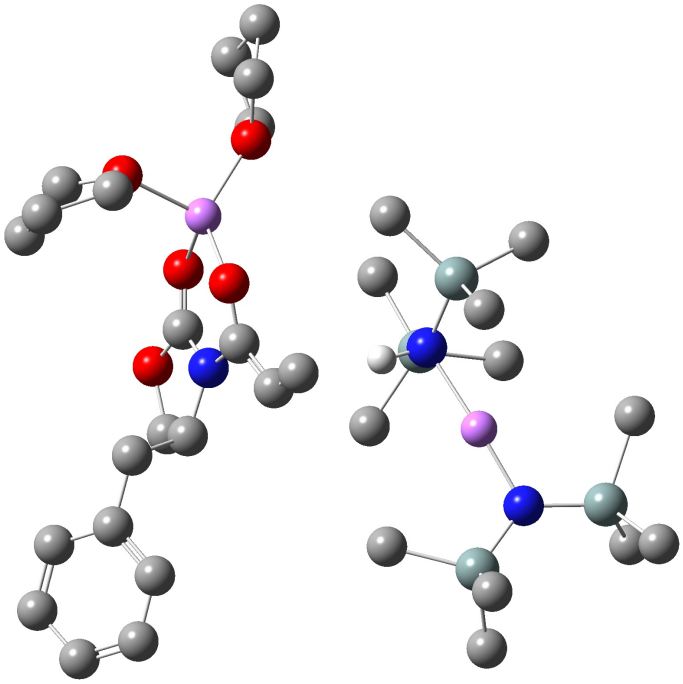
Atom	X	Y	Z	Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000	C	3.31620600	8.14795600	-1.76963000
N	1.65516100	-0.59550700	-0.82779000	C	4.11208700	7.12197500	-1.25596600
Li	7.62921500	0.55245300	0.38634000	H	5.19479400	7.18287100	-1.34960000
O	5.86420300	0.94038200	1.05731900	H	3.78174800	8.99491300	-2.26637900
C	4.97688200	1.68682600	0.64351700	H	1.30687700	8.88341500	-2.03681800
N	5.23146900	2.56430400	-0.42118600	H	0.26328300	6.94361300	-0.87694600
C	4.32468700	3.62118200	-0.93950600	H	1.66496600	5.13943600	0.03724100
C	4.91976600	3.80368500	-2.34072000	C	3.57786600	1.64538300	1.18936800
H	4.46176800	3.14232000	-3.08007000	C	3.50801900	1.09384600	2.61571700
H	4.90261300	4.83533000	-2.68920600	H	4.06881200	1.72125500	3.31783800
O	6.31008400	3.40644000	-2.18916500	H	2.46450500	1.06706000	2.94137800
C	6.43281300	2.59102900	-1.13791200	H	3.90935700	0.07945800	2.66628100
O	7.47019200	1.99709200	-0.89440500	H	3.10524800	2.62925100	1.13596900
H	3.30386300	3.24486400	-1.00317900	O	8.91780800	0.85141000	1.81386600
C	4.39832800	4.89944600	-0.07117000	C	8.54223900	0.87005100	3.21851900
H	4.09803400	4.64164700	0.95125900	C	9.57251500	1.76465400	3.92057200
H	5.44616200	5.22185200	-0.02210900	C	10.0760300	2.66402100	2.77950500
C	3.53388000	6.02341400	-0.60566800	C	10.0710880	1.69831900	1.59765000
C	2.13839800	5.97434700	-0.47467600	H	10.9750750	1.07534300	1.57997200
C	1.34243700	6.99768700	-0.98901200	H	9.95040600	2.17971000	0.62341600
C	1.92859400	8.08619600	-1.63896700	H	11.0652380	3.08983400	2.97024800

H	9.37626300	3.48827300	2.59877100
H	10.3961800	1.16262700	4.32028100
H	9.13348900	2.32597700	4.74997100
H	7.52470100	1.26861600	3.28419800
H	8.54082900	-0.15915400	3.59029900
O	7.94536100	-1.08385300	-0.58385300
C	7.93964300	-2.39896700	0.03529300
C	7.77504700	-3.40375700	-1.11049800
C	8.33051700	-2.63406400	-2.31969800
C	7.86267800	-1.21154900	-2.02584000
H	6.82344400	-1.05474500	-2.34073200
H	8.48992300	-0.43057500	-2.46276600
H	7.95321000	-3.00714100	-3.27611400
H	9.42571900	-2.67932600	-2.34076800
H	6.71511700	-3.63381700	-1.25919000
H	8.30346800	-4.34137000	-0.91578900
H	8.89229400	-2.52184200	0.56338800
H	7.11734200	-2.43957800	0.75549300
Si	2.16439300	-2.08679500	-0.16237400
C	1.46503400	-2.28674500	1.59991000
H	0.36708000	-2.28172500	1.60672400
H	1.78540700	-3.23571400	2.05002100
H	1.79463800	-1.47887700	2.26555400
C	4.06969200	-2.25515500	0.01009800
H	4.33986300	-3.21900300	0.46400100
H	4.55215300	-2.20090100	-0.97506100
H	4.49777200	-1.45845200	0.63136900
C	1.62889700	-3.64015700	-1.13282500
H	0.54407200	-3.64690200	-1.29364200
H	2.10464900	-3.68868200	-2.12075600
H	1.89220300	-4.56130500	-0.59554600
Si	1.82076300	-0.02907200	-2.42722600
C	0.95512800	-1.06354200	-3.77547500
H	1.36333000	-2.07937300	-3.83916800
H	-0.11770300	-1.15958300	-3.56539700
H	1.05751000	-0.60152200	-4.76691300
C	3.64643500	0.11147400	-3.01967000
H	3.72725300	0.61031200	-3.99557100
H	4.26398400	0.66547900	-2.29981400
H	4.09730800	-0.88394300	-3.12713800
C	1.06611400	1.71902600	-2.58099300
H	-0.01625000	1.69338700	-2.39733100
H	1.48234700	2.42720600	-1.85210000
H	1.21459500	2.14129600	-3.58388700
N	-1.56854200	0.71981600	0.77452300
Si	-1.49540000	2.10942800	1.74707600
C	-0.11580300	3.28454900	1.11738900
H	-0.36294000	3.65886400	0.11565600
H	0.02763700	4.14642000	1.78356300
H	0.84121200	2.75040100	1.04308600
C	-1.05374800	1.75191300	3.57334000
H	-0.96386500	2.66868400	4.17247500
H	-1.82112400	1.12258900	4.04172700
H	-0.10349600	1.20566100	3.65246400
C	-3.07657600	3.18107900	1.79472200
H	-3.35799500	3.51815500	0.78928400
H	-3.93066200	2.62528200	2.20240000
H	-2.94007100	4.07370000	2.42040100
Si	-2.91995900	-0.26553100	0.43428100
C	-3.85514000	-0.89654300	1.97657700
H	-3.18232000	-1.45167800	2.64290200
H	-4.27659900	-0.06660000	2.55901100
H	-4.68585700	-1.56358000	1.70907100
C	-2.34893600	-1.82982000	-0.50697300
H	-3.20757000	-2.45232400	-0.79145400
H	-1.81144500	-1.58161600	-1.43309000
H	-1.68493100	-2.45664500	0.10355200
C	-4.23209100	0.55607800	-0.68499400
H	-4.66732800	1.44344600	-0.20881300
H	-3.78693800	0.88154000	-1.63443800
H	-5.05608500	-0.13082400	-0.92170600
H	2.99720600	0.98831000	0.50353800

Table 34. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by A_2S_2 (**15**; *anti* to benzyl group).



IRC-P **15** *anti*

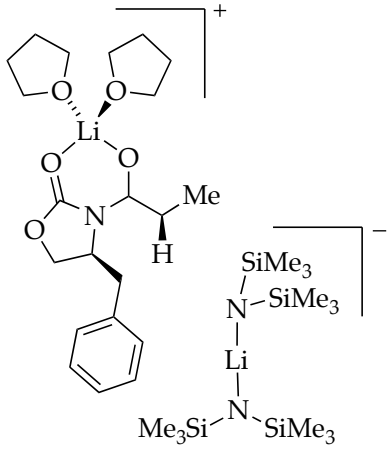


G = –3010.784471 Hartree
G_{MP2} = –1884059.0792 kcal/mol
ΔG^1_{MP2} = 8.8 kcal/mol
ΔG^2_{MP2} = 13.2 kcal/mol

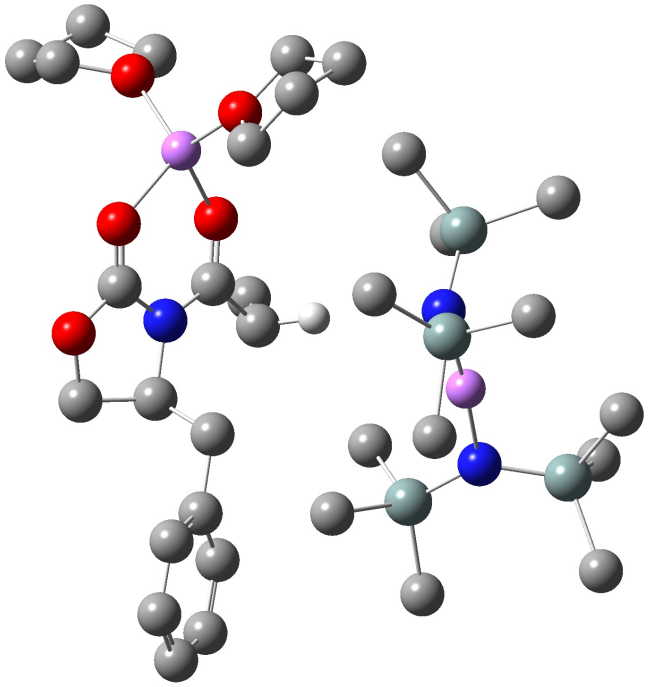
Atom	X	Y	Z	Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000	C	5.85691300	6.85051400	-0.97920400
N	1.86945100	-0.79655700	-0.39581900	H	6.88181100	6.58610600	-1.23204200
Li	7.14664900	-0.36818700	0.07137600	H	6.04478800	8.86030200	-1.73068200
O	5.84154800	0.53270600	0.99232600	H	3.70959100	9.48733800	-1.14228100
C	4.99435500	1.40170300	0.57918600	H	2.22678200	7.81679600	-0.04583500
N	5.32642100	2.07464800	-0.69830100	H	3.06434700	5.54843400	0.45353300
C	4.90000200	3.44511700	-1.03267000	C	3.83489700	1.79616900	1.18954700
C	5.38786800	3.54105900	-2.48623000	C	3.48614100	1.36307200	2.58859900
H	4.60414300	3.28059700	-3.20549400	H	3.68177500	2.15411100	3.33039900
H	5.80621700	4.51573100	-2.74177800	H	2.42248900	1.10792500	2.69337500
O	6.43539000	2.55514500	-2.58136300	H	4.07631200	0.49071000	2.88426000
C	6.28527200	1.65825000	-1.57084400	H	3.21691200	2.56424400	0.73917400
O	6.98034600	0.64078900	-1.55460600	O	8.90899500	-0.04058400	1.00775300
H	3.81156600	3.52521500	-0.99422800	C	8.77594500	0.43181400	2.37942700
C	5.52830200	4.49588100	-0.08816700	C	9.68157600	1.66790800	2.50072200
H	5.28736900	4.19553500	0.93723500	C	9.84104600	2.12319900	1.04049000
H	6.61979400	4.45136400	-0.19461500	C	9.85258900	0.78959700	0.29778500
C	5.03228000	5.89844200	-0.36517900	H	10.8471100	0.32154300	0.32960400
C	3.71939800	6.26804200	-0.03338800	H	9.51727800	0.85289100	-0.74048500
C	3.24582600	7.54954100	-0.31245600	H	10.7471400	2.71177700	0.86757600
C	4.07833700	8.48814400	-0.92699400	H	8.97635700	2.71880800	0.72642600
C	5.38686500	8.13581400	-1.25779000	H	10.6567500	1.39619300	2.92123600

H	9.24213000	2.43650500	3.14292300
H	7.71850100	0.66477300	2.53140500
H	9.07312900	-0.37798400	3.05463400
O	7.29077800	-2.26713400	-0.49495200
C	7.89962400	-3.25958900	0.36776000
C	8.51281800	-4.31829300	-0.56154400
C	8.71406900	-3.54145000	-1.87303600
C	7.49122100	-2.62774300	-1.88012200
H	6.59993000	-3.15448400	-2.24752200
H	7.61186600	-1.70155500	-2.44516200
H	8.76284900	-4.18792300	-2.75439400
H	9.63332700	-2.94527700	-1.83262400
H	7.81196900	-5.14661900	-0.71664600
H	9.44040800	-4.73513800	-0.15848500
H	8.65693100	-2.74894000	0.97194100
H	7.12874500	-3.66550300	1.03069100
Si	2.09820700	-2.22908100	0.67139700
C	1.13727600	-1.90514300	2.26693600
H	0.06439000	-1.75715100	2.08814400
H	1.23447500	-2.76001900	2.94825900
H	1.51398600	-1.02276900	2.79696500
C	3.92534700	-2.48066700	1.06529600
H	4.04654300	-3.22738300	1.86128000
H	4.48251300	-2.82983300	0.18814500
H	4.40186600	-1.54894600	1.39264000
C	1.39234200	-3.76940800	-0.16367700
H	0.32777300	-3.66131500	-0.39843000
H	1.92066300	-4.03615300	-1.08621000
H	1.48893400	-4.62106000	0.52183200
Si	2.09170900	-0.78838600	-2.17702000
C	0.64368400	-1.66768700	-3.00784100
H	0.58550000	-2.73155700	-2.75691600
H	-0.31534600	-1.20642200	-2.74304300
H	0.74906800	-1.59291600	-4.09776700
C	3.72257900	-1.59344000	-2.69600400
H	3.84462800	-1.54782800	-3.78577500
H	4.57942800	-1.08216600	-2.24194700
H	3.76948700	-2.64940500	-2.40417900
C	2.09602200	1.02456400	-2.70467400
H	1.13994000	1.51392400	-2.48390500
H	2.88764300	1.57894600	-2.18865200
H	2.27112700	1.11214000	-3.78417900
N	-1.66752800	0.78660300	0.11701400
Si	-1.67914200	2.43711200	0.55837600
C	0.11442400	3.10716200	0.54003300
H	0.56172700	3.03810800	-0.46110100
H	0.14445300	4.16323500	0.83977400
H	0.76140400	2.55873400	1.23880000
C	-2.33274100	2.77308900	2.31882800
H	-2.27718000	3.83824100	2.58129200
H	-3.37920300	2.46146500	2.42226200
H	-1.75402700	2.21499400	3.06646800
C	-2.67292600	3.57156100	-0.61134800
H	-2.31074000	3.49228100	-1.64432000
H	-3.73761400	3.30472100	-0.61969600
H	-2.60279900	4.62598400	-0.31201800
Si	-3.00384500	-0.22002500	-0.23428900
C	-4.46494200	-0.08283600	0.98470000
H	-4.14117900	-0.26697700	2.01668500
H	-4.92098000	0.91523300	0.95949500
H	-5.25469300	-0.80799300	0.74703300
C	-2.44973500	-2.05136800	-0.18413200
H	-3.27501600	-2.72694500	-0.44404100
H	-1.63934700	-2.25368500	-0.89878400
H	-2.09756000	-2.33783800	0.81603100
C	-3.73621500	0.04932400	-1.97666900
H	-4.10651600	1.07509900	-2.09584200
H	-2.97930900	-0.11175800	-2.75597000
H	-4.57328800	-0.63163300	-2.18174800
H	2.45373900	-0.03605900	-0.00759400

Table 35. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by A_2S_2 (**15**; *syn* to benzyl group).



IRC-R **15** *syn*

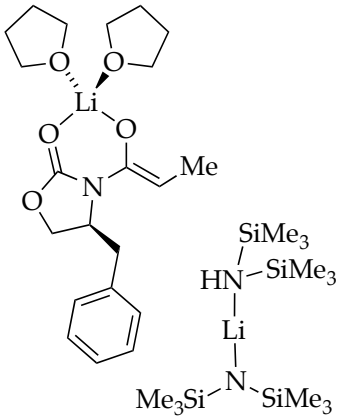


G = –3010.766719 Hartree
G_{MP2} = –1884047.9349 kcal/mol
ΔG^1_{MP2} = 19.9 kcal/mol
ΔG^2_{MP2} = 6.8 kcal/mol

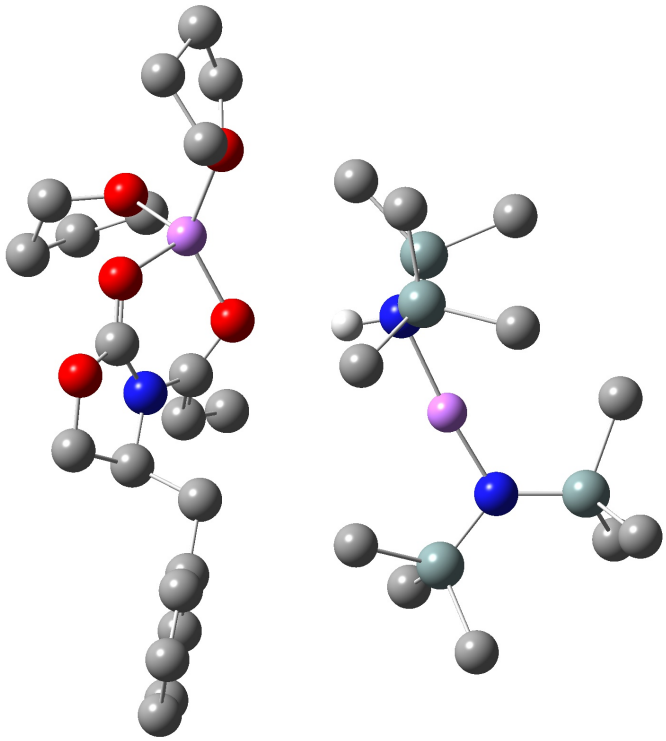
Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000
O	1.78440900	0.20074000	0.70643500
C	2.58526900	1.13438400	0.67641500
N	2.14607200	2.42137000	0.31814500
C	0.81499500	2.71267400	-0.00290800
O	0.65615900	4.03783300	-0.10689000
C	1.85995300	4.71318500	0.33527100
H	2.01374600	5.58241100	-0.30259100
H	1.70420600	5.03278200	1.37013100
C	2.96539600	3.65614900	0.19758900
C	3.72163600	3.72589700	-1.14766200
H	2.99136300	3.63564300	-1.96119800
H	4.38408300	2.85723700	-1.22262700
C	4.51345700	5.00981000	-1.29313300
C	5.72212500	5.18319500	-0.60279300
C	6.43938300	6.37407200	-0.71713000
C	5.96065900	7.40938500	-1.52314900
C	4.76316500	7.24518800	-2.21998000
C	4.04606200	6.05261400	-2.10477700
H	3.12376100	5.92333600	-2.66815100
H	4.38972900	8.03969700	-2.86040400
H	6.52343500	8.33415000	-1.61532900
H	7.37898400	6.48672400	-0.18356600
H	6.12142200	4.37704400	0.00893500
H	3.66439600	3.72538900	1.03205000
O	-0.10824000	1.93697000	-0.17864100
C	4.02644500	0.93590600	1.04945800
C	4.15644000	0.26967300	2.43148000
H	3.73907700	0.90034800	3.22547500
H	5.21331200	0.10158500	2.65196000
H	3.64353700	-0.69472500	2.44457600
H	4.59167500	1.86787100	1.02706600
O	-1.11069600	-0.74996300	1.41576500
C	-0.55676300	-1.64004600	2.42475900
C	-1.43587000	-1.46662200	3.67039000
C	-2.03330800	-0.06341100	3.47359900
C	-2.23450700	-0.02076700	1.96109400
H	-3.16602700	-0.52007400	1.66287100
H	-2.21623000	0.98424500	1.53088800
H	-2.96446500	0.09024100	4.02643200
H	-1.31863700	0.70821500	3.78307700
H	-2.23267600	-2.21859900	3.68734100

H	-0.86197900	-1.56455000	4.59598800
H	0.48141500	-1.33873400	2.59689000
H	-0.56645300	-2.66005200	2.02898200
O	-0.35015400	-0.83472600	-1.69893700
C	-0.35177600	-2.27241000	-1.90915800
C	-0.13592400	-2.46801500	-3.41059000
C	-0.77066700	-1.19938600	-4.00175400
C	-0.37735200	-0.13967500	-2.97348800
H	0.62278600	0.26234000	-3.17230700
H	-1.08950200	0.68590300	-2.88965100
H	-0.40180700	-0.96050300	-5.00323200
H	-1.86111300	-1.30084900	-4.05298900
H	0.93494200	-2.50093400	-3.63924500
H	-0.59157600	-3.39209400	-3.77756600
H	-1.32213400	-2.66434600	-1.58018100
H	0.44250600	-2.70913000	-1.29777500
Li	7.47058600	-0.72067100	-0.47993800
N	5.74601700	-1.22811700	-1.21907900
Si	5.24652900	-2.76938400	-0.66959700
C	5.92194700	-3.08575400	1.08537200
H	7.01683800	-3.00565000	1.11906500
H	5.65983700	-4.09164100	1.43920100
H	5.52566000	-2.36688800	1.81333800
C	3.34095200	-2.97619300	-0.55644100
H	3.06627100	-3.94154600	-0.10951800
H	2.89434600	-2.93582100	-1.55942000
H	2.88615000	-2.17733800	0.04256100
C	5.83591400	-4.24358500	-1.72911000
H	6.92660500	-4.23393900	-1.84611200
H	5.40297200	-4.22326600	-2.73683900
H	5.55966100	-5.20243800	-1.26968400
Si	5.44490800	-0.47388000	-2.71684200
C	5.83140900	-1.51119400	-4.27177500
H	5.17616100	-2.38740300	-4.35535600
H	6.86357500	-1.88182900	-4.24643900
H	5.71182500	-0.92108900	-5.19065500
C	3.61553500	0.07580100	-2.95786200
H	3.46508400	0.56881700	-3.92818100
H	3.28682800	0.77302800	-2.17556300
H	2.94849500	-0.79491900	-2.91366400
C	6.49776900	1.10973600	-2.87650200
H	7.56943300	0.87185700	-2.91063700
H	6.35658300	1.79400900	-2.02919300
H	6.26032700	1.66406100	-3.79407600
N	9.07984500	-0.16026200	0.36227300
Si	9.02096800	0.98772200	1.60885400
C	7.76143700	2.36943700	1.17320900
H	8.12788900	2.94848800	0.31585700
H	7.59043100	3.06083100	2.01004600
H	6.79531900	1.93421000	0.88395500
C	8.43754100	0.26212800	3.28017400
H	8.31483000	1.02693200	4.05960400
H	9.16191300	-0.47521600	3.64927800
H	7.48057100	-0.26624100	3.17141100
C	10.6469090	1.91450200	1.99502000
H	11.0198300	2.45384100	1.11547500
H	11.4394220	1.22699400	2.31695800
H	10.5045540	2.64803100	2.80039700
Si	10.4025530	-1.06733500	-0.21800500
C	11.2611760	-2.15261900	1.10041700
H	10.5447080	-2.84101000	1.56720300
H	11.6946120	-1.54263700	1.90410200
H	12.0736050	-2.75615000	0.67322800
C	9.79280300	-2.27318100	-1.57149200
H	10.6230510	-2.86784000	-1.97494000
H	9.33714600	-1.74068000	-2.41805400
H	9.04748500	-2.98209600	-1.18560700
C	11.7837020	-0.03177300	-1.03537500
H	12.2603370	0.64451000	-0.31514500
H	11.3799120	0.58815900	-1.84634800
H	12.5714280	-0.66791500	-1.46152400
H	4.47253800	0.26925400	0.28413600

Table 36. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by A_2S_2 (**15**; *syn* to benzyl group).



IRC-P **15** *syn*

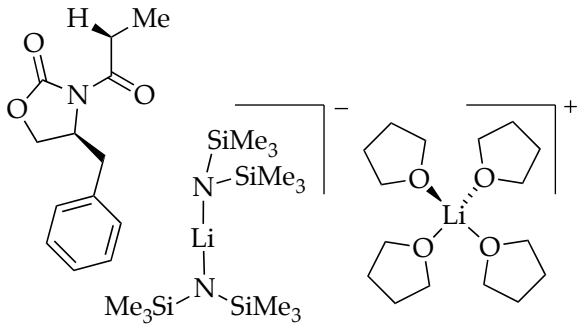


G = –3010.784346 Hartree
G_{MP2} = –1884061.9729 kcal/mol
ΔG^1_{MP2} = 5.9 kcal/mol
ΔG^2_{MP2} = 20.9 kcal/mol

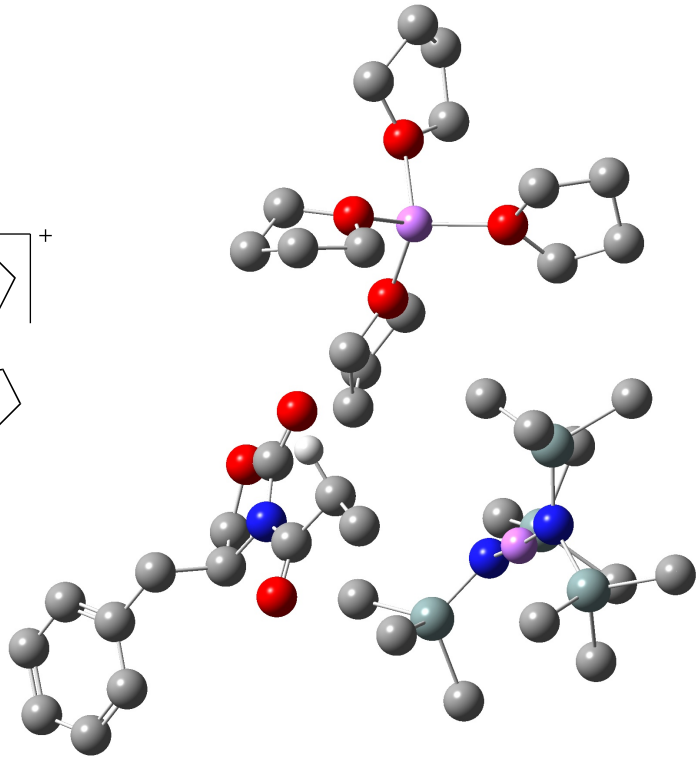
Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000
O	1.75225200	0.54109100	0.41333000
C	1.85299800	1.70406400	0.98743900
N	1.20676800	2.82615900	0.27135700
C	0.06414600	2.70551500	-0.44357700
O	-0.26457600	3.88192900	-1.03720400
C	0.59060700	4.91524500	-0.50602900
H	0.86153000	5.59078300	-1.31841700
H	0.02599700	5.46887600	0.25223300
C	1.79369900	4.16343200	0.09384600
C	3.04163500	4.14058000	-0.81571200
H	2.75300700	3.74115100	-1.79539000
H	3.75879400	3.43923100	-0.37699800
C	3.66957600	5.50922400	-0.96811800
C	4.40972500	6.07399000	0.08190500
C	4.96654500	7.34688000	-0.03834600
C	4.79380700	8.08045200	-1.21450000
C	4.06498200	7.52947200	-2.26862600
C	3.50814200	6.25475200	-2.14366800
H	2.95287000	5.82613800	-2.97557800
H	3.93296800	8.08792000	-3.19171300
H	5.23102100	9.07063500	-1.31022300
H	5.54282100	7.76323100	0.78369100
H	4.56243600	5.50307600	0.99517700
H	2.06293200	4.59188500	1.06215700
O	-0.65883600	1.71541800	-0.58628800
C	2.47180200	2.03076900	2.15175500
C	3.23218500	1.04933200	2.99620000
H	2.84911100	1.00652800	4.02676300
H	4.30015300	1.30173900	3.07497000
H	3.15993300	0.04274300	2.57330600
H	2.42974300	3.05820700	2.50068500
O	-1.06429400	-0.45209700	1.67566700
C	-0.30422900	-0.86593100	2.84496000
C	-0.86072400	-0.06493200	4.03338100
C	-1.54840600	1.12776400	3.34893000
C	-2.09211900	0.48076300	2.07894600
H	-3.02464100	-0.06837000	2.27549300
H	-2.24549200	1.17171400	1.24780300
H	-2.33139300	1.58526000	3.96133200
H	-0.80888200	1.89371900	3.09041500
H	-1.59365000	-0.65851300	4.59210200

H	-0.07191400	0.23713800	4.72777500
H	0.74449500	-0.63462200	2.64200000
H	-0.41819500	-1.94818900	2.97156300
O	-0.72912600	-1.26398400	-1.37633200
C	-1.46803000	-2.45442300	-0.99567700
C	-2.59505700	-2.61497700	-2.02872500
C	-2.73842100	-1.19621900	-2.60417400
C	-1.29422300	-0.70606400	-2.58786600
H	-0.73087100	-1.08366600	-3.45216200
H	-1.18608400	0.37742800	-2.52395700
H	-3.17761900	-1.18080400	-3.60618300
H	-3.35531500	-0.57047000	-1.94879400
H	-2.29773400	-3.31516700	-2.81764200
H	-3.51692600	-2.99253500	-1.57667600
H	-1.84480900	-2.28966800	0.01808300
H	-0.77951800	-3.30532500	-0.98269300
Li	5.99328200	-0.62680000	-0.16755200
N	4.09171900	-1.33277900	-0.63021800
Si	3.92768400	-2.88103000	0.26218700
C	4.84012600	-2.70105600	1.90716400
H	5.90800200	-2.48829800	1.77086300
H	4.76567900	-3.62631100	2.49287400
H	4.41980000	-1.89236900	2.51675700
C	2.10558700	-3.25207800	0.60118300
H	1.99313800	-4.14936300	1.22267400
H	1.55558100	-3.41508100	-0.33219800
H	1.63387100	-2.41364600	1.12500700
C	4.68639500	-4.30028500	-0.72480300
H	5.75175400	-4.14517800	-0.92384200
H	4.18024200	-4.47084500	-1.68158800
H	4.59764800	-5.22585500	-0.14162800
Si	3.89382000	-1.14297000	-2.40467800
C	5.47663900	-1.70625500	-3.26786300
H	5.67371100	-2.77490500	-3.12932800
H	6.35744500	-1.15515900	-2.91446700
H	5.39429100	-1.52611200	-4.34750400
C	2.42310800	-2.12373600	-3.08235800
H	2.27957700	-1.90030000	-4.14755000
H	1.49950200	-1.86189200	-2.55336900
H	2.56756700	-3.20710900	-2.99528400
C	3.61112500	0.69661300	-2.70491800
H	4.49045700	1.28968900	-2.42540400
H	2.76505200	1.04972100	-2.10472600
H	3.39762500	0.89717400	-3.76205100
N	7.75088200	-0.15586400	0.19282100
Si	7.84256400	1.41737000	0.85522800
C	6.22462100	2.35434900	0.44424700
H	6.10739400	2.46995000	-0.64214600
H	6.23237700	3.36347600	0.87730900
H	5.32489200	1.85426700	0.83211100
C	7.99628300	1.45221300	2.75725500
H	7.98573200	2.47651000	3.15397700
H	8.92869900	0.97884000	3.08929300
H	7.16999500	0.90344300	3.22867200
C	9.25271700	2.51321600	0.18403800
H	9.19674600	2.60986000	-0.90738100
H	10.2394070	2.09761100	0.42515300
H	9.21137200	3.52402200	0.61152300
Si	9.06364500	-1.19878500	-0.14533400
C	10.3160310	-1.38722200	1.28326000
H	9.82370600	-1.74717400	2.19564600
H	10.7991320	-0.43270900	1.52906700
H	11.1121000	-2.10014800	1.03004000
C	8.42915600	-2.96225000	-0.51714300
H	9.25915500	-3.64390200	-0.74386500
H	7.75991500	-2.97191200	-1.38816100
H	7.88365600	-3.38656600	0.33611600
C	10.0719970	-0.69033100	-1.68423500
H	10.5369770	0.29423400	-1.55247100
H	9.42724100	-0.62764500	-2.57094300
H	10.8731710	-1.40829800	-1.90614400
H	3.44818300	-0.65070200	-0.18828500

Table 37. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by A_2S_4 (**18**; *anti* to benzyl group).



IRC-R **18** *anti*

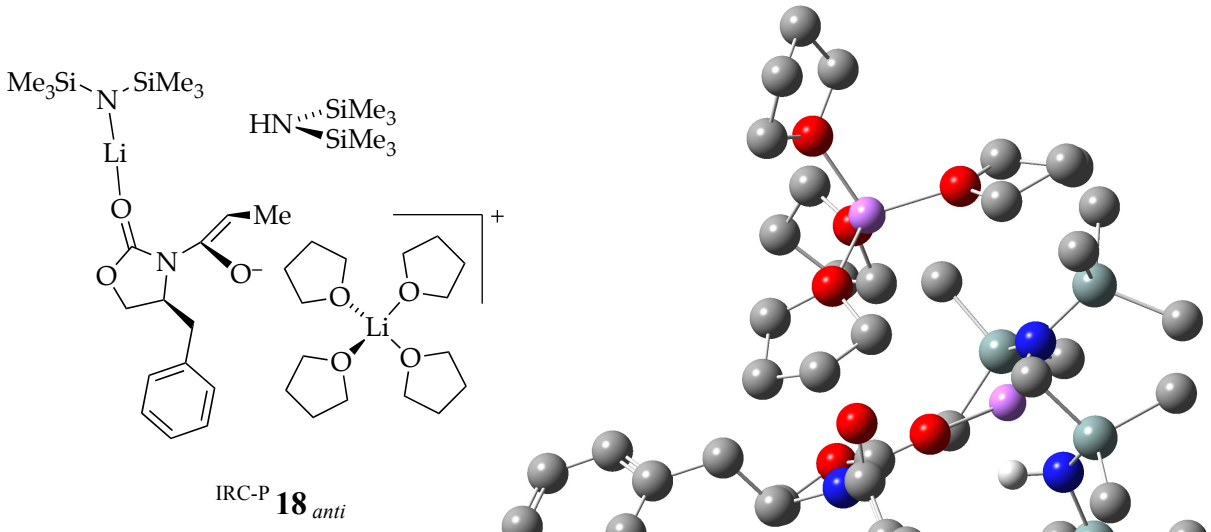


G = –3475.456938 Hartree
G_{MP2} = –2174679.6090 kcal/mol
ΔG^1_{MP2} = 12.8 kcal/mol
ΔG^2_{MP2} = 19.7 kcal/mol

Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	-0.59194100	5.02811800	4.29425400
N	1.01456700	0.38115700	-0.99757400	C	0.56662600	3.67951900	1.59535700
C	2.27754400	-0.06705900	-0.62417500	H	-0.42884500	3.26577600	1.80830100
O	3.30702700	-0.05471600	-1.26554400	H	1.11645600	2.94269000	0.99278400
Li	3.24513800	5.12991200	0.97777900	H	0.41457200	4.56106500	0.95876700
N	3.08594800	4.61646400	2.82764800	C	1.40038300	2.52659100	4.28580700
Si	4.27817800	5.26721300	3.85350000	H	1.85949700	2.68161600	5.27016700
C	5.99518700	5.14647600	3.01438000	H	1.92305600	1.68150000	3.81895400
H	6.26339300	4.09619400	2.83338200	H	0.35773400	2.22378500	4.45534200
H	6.78579700	5.59621200	3.63000700	N	3.60753200	5.64554400	-0.82415600
H	6.00043900	5.65868400	2.04271700	Si	2.60179600	6.91503400	-1.36560400
C	4.04035900	7.11436100	4.27041900	C	1.61334400	7.63409600	0.10073200
H	4.84266600	7.50574000	4.91084700	H	2.28043500	8.01766400	0.88423200
H	3.08821100	7.28083800	4.78965900	H	0.95635300	6.88739200	0.56688800
H	4.01834900	7.72158700	3.35592500	H	0.97360300	8.46612500	-0.22217500
C	4.46994000	4.37918800	5.53954300	C	3.53522500	8.39367000	-2.13997900
H	4.64130400	3.30247800	5.40934400	H	4.08821900	8.10076800	-3.04248400
H	3.56808000	4.48849500	6.15546100	H	4.26330300	8.80992300	-1.43187900
H	5.31097800	4.78546400	6.11755700	H	2.84976600	9.20274900	-2.42610600
Si	1.50660000	4.10834300	3.20801600	C	1.31116100	6.36274700	-2.66137400
C	0.42895500	5.39456000	4.12021900	H	1.79987300	5.96251900	-3.55896900
H	0.35572500	6.32660300	3.54594100	H	0.65802400	7.18684200	-2.97872600
H	0.85686400	5.65031200	5.09866800	H	0.67111600	5.56794400	-2.25576300

Si	4.92702800	4.93661500	-1.60987900
C	4.69377200	4.54774200	-3.46982300
H	4.54866100	5.46618200	-4.05295400
H	3.81229200	3.91681100	-3.63935300
H	5.56452200	4.02714800	-3.89281800
C	6.54473800	5.96147200	-1.52975900
H	6.84172600	6.14719600	-0.48854000
H	6.41263600	6.94159500	-2.00425000
H	7.37899700	5.45863900	-2.04163600
C	5.35645900	3.25869300	-0.78715700
H	6.31969100	2.86625900	-1.14377700
H	4.58728800	2.50429000	-0.99925800
H	5.42247700	3.36206800	0.30453200
O	2.20490300	-0.57945000	0.62977700
C	0.90559900	-0.28677200	1.20664800
H	0.59244600	-1.15601800	1.78636900
H	1.01264800	0.57968200	1.86387500
C	0.63625500	1.07813900	-2.16816300
O	-0.54688800	1.31497400	-2.33267600
C	1.72217100	1.50260700	-3.13489900
C	1.15317000	2.26826000	-4.32886200
H	0.42817200	1.66293300	-4.88131900
H	1.96397700	2.54845500	-5.00876200
H	0.64794900	3.18208100	-4.00505900
H	2.45411500	2.11100000	-2.58997900
C	-0.83989900	-1.21156300	-0.46341600
H	-1.25766000	-0.96339400	-1.44360600
H	-0.17507000	-2.07479900	-0.59417600
C	-1.95104800	-1.54605500	0.50874200
C	-3.07688000	-0.71396300	0.60469100
C	-4.09548000	-0.99394500	1.51447800
C	-4.00773900	-2.11461000	2.34416400
C	-2.89663100	-2.95302900	2.25477900
C	-1.87675000	-2.66820200	1.34379200
H	-1.01812700	-3.33305600	1.27173000
H	-2.82239100	-3.83104500	2.89111100
H	-4.80264400	-2.33382600	3.05181800
H	-4.96062600	-0.33895800	1.57334800
H	-3.15589600	0.15473400	-0.04539300
H	-0.65267300	0.85499700	0.18389300
H	2.27552700	0.61049300	-3.45018700
C	5.44830900	0.23247800	1.73466800
O	6.86342600	0.43350500	2.03819300
Li	8.23686900	0.29273300	0.66756000
O	7.55086900	-0.82190800	-0.80052900
C	7.11785300	-2.18430500	-0.55424100
C	5.84298400	-2.36560400	-1.37372800
C	6.11287100	-1.46916200	-2.59158600
C	6.84742200	-0.28437700	-1.96438800
H	7.59197700	0.17134500	-2.62373700
H	6.15089600	0.48401800	-1.61914600
H	6.75005700	-1.98233900	-3.32171700
H	5.19286700	-1.15272500	-3.08792200
H	5.66667800	-3.41299200	-1.63673600
H	4.97335000	-1.98677800	-0.82909100
H	6.97474300	-2.30301900	0.52403800
H	7.91131000	-2.86932200	-0.88213400
O	8.97112000	2.03846300	0.13940700
C	9.71320600	2.32087800	-1.06540400
C	10.6197790	3.49134700	-0.69730400
C	9.70247900	4.32026600	0.21827900
C	8.85695800	3.25581600	0.93613400
H	9.23840400	3.02267000	1.93636700
H	7.80341600	3.53035600	1.01184000
H	10.2573190	4.94514900	0.92359600
H	9.06038500	4.97610700	-0.37656700
H	11.5006930	3.13164300	-0.15176000
H	10.9638180	4.04716200	-1.57425700
H	9.01635400	2.59254600	-1.86941800
H	10.2459080	1.40789100	-1.34796300
O	9.84500900	-0.70188000	1.35822200
C	10.5181840	-1.74674400	0.61669000
C	12.0097190	-1.46319600	0.78153700
C	12.0642690	-0.89555500	2.20848400
C	10.7694280	-0.07995800	2.28692200
H	10.3154730	-0.08352000	3.28251300
H	10.9181880	0.95871300	1.96980000
H	12.0517900	-1.70906300	2.94260400
H	12.9508120	-0.28395200	2.39794200
H	12.6237490	-2.35839900	0.64836500
H	12.3388440	-0.71164200	0.05426200
H	10.1631150	-1.70234800	-0.41568100
H	10.2446020	-2.72001900	1.04528000
C	7.02074100	0.80747400	3.42990100
C	5.68421100	0.48808900	4.09667600
C	4.68872000	0.74561000	2.95506400
H	4.46647600	1.81453100	2.86108100
H	3.74189300	0.21681100	3.08846900
H	5.50093800	1.11377200	4.97426800
H	5.65512400	-0.56282200	4.40961600
H	7.24754500	1.87950500	3.48434000
H	7.86409800	0.24116800	3.83867000
H	5.28531700	-0.84007600	1.57601300
H	5.21379300	0.76881700	0.81393100

Table 38. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by A_2S_4 (**18**; *anti* to benzyl group).



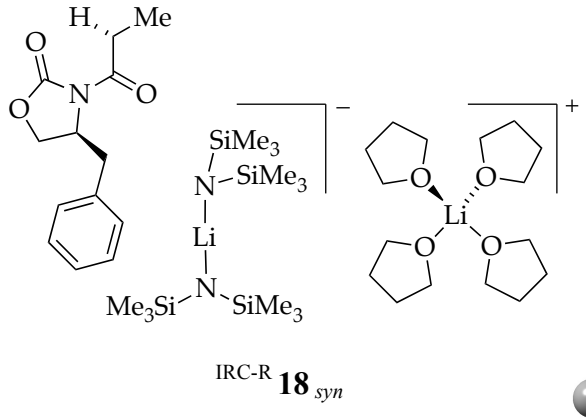
IRC-P **18** *anti*

G = –3475.452650 Hartree
G_{MP2} = –2174678.2852 kcal/mol
ΔG^1_{MP2} = 14.2 kcal/mol
ΔG^2_{MP2} = 18.4 kcal/mol

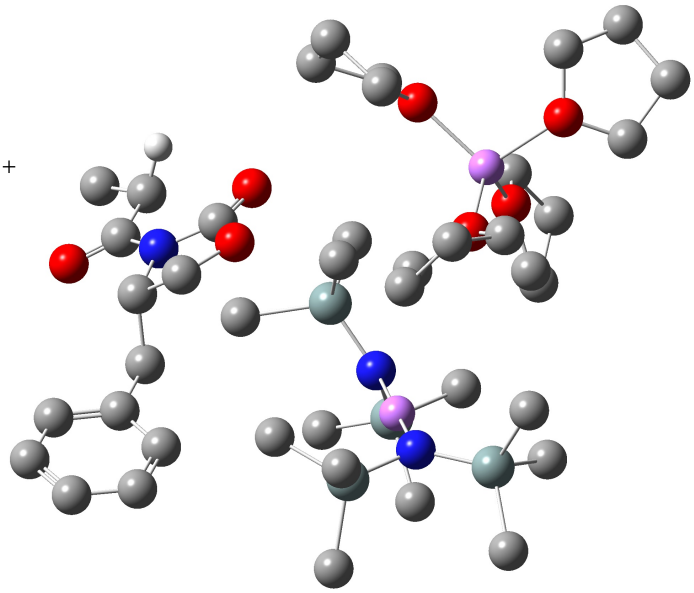
Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	-7.14842500	-3.09768300	-4.78478000
N	-0.65633400	-1.19712700	0.52716400	C	-4.85787400	-1.78490600	-3.00934500
C	-1.56782000	-1.66581300	-0.33476400	H	-5.11038300	-1.13909100	-3.86138200
O	-2.22544900	-2.70920200	-0.26277700	H	-3.83845000	-1.53019500	-2.69633400
Li	-3.68904900	-3.83379000	-0.72543000	H	-5.53596700	-1.51802500	-2.18911000
N	-4.52716400	-4.65748500	-2.23386900	C	-4.00951600	-3.80812600	-5.10528100
Si	-4.76487100	-6.34270300	-2.17662600	H	-4.08703100	-4.82094700	-5.51912500
C	-3.24009300	-7.20719300	-1.39802500	H	-2.94596500	-3.61293600	-4.91146700
H	-2.36837400	-7.07371800	-2.05342100	H	-4.33795200	-3.10596800	-5.88381900
H	-3.39998200	-8.28567400	-1.26287600	N	-3.81243400	-4.03329400	1.86218200
H	-2.98891300	-6.78264100	-0.41822200	Si	-5.24140700	-3.07310200	2.28092000
C	-6.26860300	-6.86000600	-1.11796000	C	-5.81508500	-2.14788600	0.73771300
H	-6.37888400	-7.95044000	-1.04037800	H	-6.11324500	-2.83854500	-0.06077600
H	-7.19505500	-6.46252700	-1.55203900	H	-5.02938700	-1.49409600	0.33874000
H	-6.19247100	-6.45850000	-0.09905200	H	-6.68032500	-1.51148500	0.96337600
C	-4.98352100	-7.23960600	-3.85257000	C	-6.63094000	-4.20715500	2.87622900
H	-4.10650600	-7.10425500	-4.49830100	H	-6.38964200	-4.71510200	3.81724800
H	-5.85725900	-6.87931800	-4.40853400	H	-6.87486600	-4.97218800	2.13031500
H	-5.11789000	-8.31918300	-3.69905400	H	-7.53827000	-3.61512600	3.05032200
Si	-5.03187700	-3.62010400	-3.49837900	C	-4.84093000	-1.79657700	3.62443600
C	-6.86488900	-3.82188300	-4.00887000	H	-4.60599500	-2.27479600	4.58252300
H	-7.52719100	-3.66041100	-3.14822700	H	-5.68267100	-1.11175200	3.78965200
H	-7.08137300	-4.82329300	-4.40169200	H	-3.96968300	-1.19339200	3.34028600

Si	-3.14368700	-5.39553400	2.77640000
C	-2.97100500	-5.01454400	4.62729900
H	-3.93848700	-4.80236100	5.09864200
H	-2.32324400	-4.14519900	4.78923500
H	-2.52826800	-5.86511900	5.16234300
C	-4.23622800	-6.92860100	2.59522400
H	-4.39369400	-7.19238600	1.54405900
H	-5.22182100	-6.79210200	3.05321500
H	-3.76390900	-7.78717400	3.09098800
C	-1.42003100	-5.75401400	2.08411100
H	-0.87800500	-6.42239300	2.76758100
H	-0.82335300	-4.84201400	1.95587500
H	-1.47931500	-6.24958700	1.10798000
O	-1.72679800	-0.81422900	-1.39131200
C	-0.99955300	0.40034000	-1.10367100
H	-0.52607000	0.74309800	-2.02527200
H	-1.71581600	1.15464000	-0.76142600
C	-0.05643500	-2.00602700	1.65163000
O	0.74188100	-2.93112100	1.28365600
C	-0.43741200	-1.55825800	2.88156100
C	0.10508600	-2.12283600	4.16346500
H	0.67709700	-3.03597400	3.96666100
H	-0.69015600	-2.37680100	4.87994500
H	0.77599200	-1.42146400	4.68784900
H	-1.13134900	-0.72387300	2.93789800
C	1.43161000	-0.28672400	-0.51429200
H	1.96667700	-0.81105100	0.28335200
H	1.36641100	-0.98393900	-1.35875400
C	2.16665500	0.97098000	-0.92157000
C	2.65979400	1.85254600	0.05297800
C	3.31340900	3.02992300	-0.30895600
C	3.48958700	3.34894100	-1.65762900
C	3.00926300	2.48037100	-2.63777300
C	2.35394100	1.30290300	-2.27014600
H	1.99077500	0.62678500	-3.04159900
H	3.14529700	2.71608100	-3.69013200
H	4.00040800	4.26533200	-1.94078300
H	3.68970600	3.69718500	0.46222700
H	2.53473000	1.60780400	1.10586900
H	0.04968100	0.76295600	0.78292900
H	-3.03980600	-3.41629000	1.59071400
C	0.23621800	-4.68705800	-1.58507500
O	1.41619500	-5.51972200	-1.86786300
Li	2.44400900	-6.43339900	-0.50249000
O	3.18064100	-5.30355800	0.91648900
C	3.64672900	-3.96520300	0.57649900
C	3.92238000	-3.24501700	1.91330900
C	3.75055900	-4.34993800	2.97406200
C	2.74232100	-5.27145200	2.29946500
H	2.75552000	-6.30144700	2.66605500
H	1.73379200	-4.84951500	2.34159000
H	4.69336400	-4.88108200	3.15402000
H	3.38419200	-3.96113800	3.92851800
H	4.91437700	-2.78419200	1.94203500
H	3.16193600	-2.47602500	2.06135900
H	2.86389000	-3.45429300	0.01296900
H	4.54092500	-4.09252800	-0.04274700
O	1.44898100	-8.06947600	0.04026600
C	1.44538300	-8.68963600	1.34885600
C	0.59804000	-9.95240400	1.20071300
C	-0.44330800	-9.51174900	0.16082500
C	0.37981900	-8.62688500	-0.77611500
H	0.84061400	-9.20749800	-1.58556800
H	-0.18989200	-7.80347700	-1.20941300
H	-0.90921700	-10.3483830	-0.36706900
H	-1.23830100	-8.92622800	0.63321400
H	1.20542000	-10.7804740	0.81586800
H	0.15477400	-10.2677420	2.14960700
H	1.00101300	-7.99192000	2.06847300
H	2.48445800	-8.88311500	1.63371700
O	4.09788700	-7.14818800	-1.40505600
C	5.43011800	-6.91859500	-0.88600000
C	6.11229400	-8.28436300	-0.91127200
C	5.50381400	-8.91387200	-2.17434800
C	4.05952100	-8.40222800	-2.13215800
H	3.63679700	-8.21562500	-3.12445100
H	3.39621600	-9.08382100	-1.58813100
H	6.01753500	-8.54321700	-3.06867100
H	5.55625200	-10.0063200	-2.18371800
H	7.20281400	-8.20800300	-0.94797000
H	5.83957200	-8.86435400	-0.02152400
H	5.32140500	-6.48335700	0.10924400
H	5.94681800	-6.20162200	-1.53830600
C	1.81223400	-5.34264800	-3.24155600
C	1.32606900	-3.94456700	-3.60852600
C	-0.01888700	-3.87750100	-2.86644300
H	-0.80982700	-4.34228400	-3.46418600
H	-0.33788700	-2.85580700	-2.64867000
H	1.22974600	-3.80227000	-4.68920100
H	2.02550900	-3.19273400	-3.22283100
H	1.32632200	-6.10633900	-3.86708100
H	2.89602100	-5.47885900	-3.29230500
H	0.46714800	-4.07255000	-0.70979800
H	-0.59909000	-5.35034700	-1.34443600

Table 39. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by A_2S_4 (**18**; *syn* to benzyl group).



IRC-R **18** *syn*

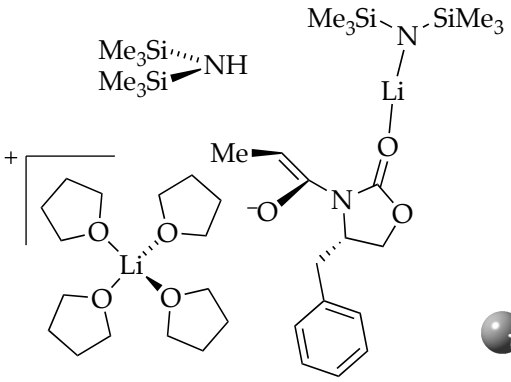


G = –3475.458828 Hartree
G_{MP2} = –2174682.6982 kcal/mol
ΔG^1_{MP2} = 9.7 kcal/mol
ΔG^2_{MP2} = 19.7 kcal/mol

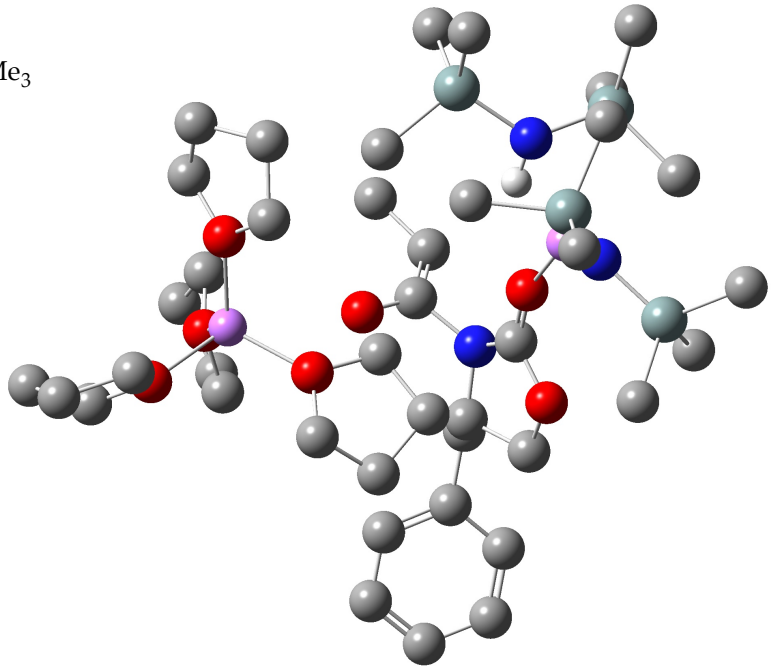
Atom	X	Y	Z
Si	0.00000000	0.00000000	0.00000000
N	-1.00510000	-0.21604800	1.35820700
Li	-0.27936900	0.08668900	3.11569400
O	-2.49454300	-6.00777800	4.36615500
C	-3.63743600	-5.84740700	3.99661500
N	-4.71698700	-5.32876400	4.70536200
C	-4.77497000	-4.94872600	6.06430800
O	-5.83961000	-4.55088900	6.50181100
C	-3.51389700	-5.05864000	6.89820100
C	-3.74763500	-4.61974000	8.34344200
H	-4.52111400	-5.22593100	8.82406300
H	-2.82044600	-4.72030100	8.91661700
H	-4.06827400	-3.57557300	8.39000500
H	-2.73204800	-4.45625200	6.42082900
C	-5.89504700	-5.15798400	3.83620100
C	-5.49505500	-6.06202900	2.65900400
O	-4.05479400	-6.17613400	2.74794500
H	-5.91851800	-7.06868300	2.73678700
H	-5.74350200	-5.63610500	1.68655000
C	-6.12312300	-3.68036100	3.44782000
H	-6.19677600	-3.10336200	4.37457800
H	-5.24597600	-3.31234300	2.90296800
C	-7.37658300	-3.50137100	2.61719300
C	-8.64165000	-3.60798900	3.21496500
C	-9.80335100	-3.47140600	2.45592600
C	-9.71956600	-3.22394600	1.08334700
C	-8.46781300	-3.11021500	0.47852100
C	-7.30536500	-3.24944300	1.24072700
H	-6.33315100	-3.13766600	0.76568800
H	-8.39203800	-2.90463800	-0.58592600
H	-10.6246600	-3.11192300	0.49250800
H	-10.7747370	-3.55025100	2.93708900
H	-8.71342800	-3.78511000	4.28626400
H	-6.77660600	-5.53854700	4.35520500
N	0.41752100	0.22825600	4.89856100
Si	0.89710400	1.83398400	5.24533200
C	0.37206500	2.99023200	3.82096200
H	0.80258400	2.68436200	2.85844900
H	-0.71968100	3.00808200	3.70145200
H	0.69746100	4.02265700	4.00548100
C	2.78899200	2.04784000	5.43021800
H	3.18113100	1.42729300	6.24659700
H	3.31555600	1.75456600	4.51251100
H	3.06219100	3.08929800	5.64719600
C	0.14203300	2.58762900	6.83122200
H	0.43879300	2.03449600	7.73193100
H	0.46240600	3.62930800	6.96802200
H	-0.95443900	2.58075400	6.79027900
Si	0.16138700	-1.02336100	6.01904200
C	-1.39170000	-0.83722500	7.11671000
H	-1.33685800	0.06187500	7.74210100
H	-2.29536000	-0.74851000	6.50002900

H	-1.52591800	-1.69819000	7.78708400
C	1.60963800	-1.31858900	7.24169700
H	2.55680700	-1.50041900	6.71535900
H	1.76892000	-0.44400600	7.88551200
H	1.42306300	-2.17707200	7.90210000
C	-0.08274800	-2.69306600	5.11291700
H	-0.28477400	-3.50473500	5.82661200
H	-0.93223300	-2.64957300	4.41926400
H	0.80257900	-2.97162200	4.52640500
Si	-2.70964500	-0.21523200	1.41547700
C	-3.52585600	1.46422200	1.01958400
H	-3.14582300	2.24816500	1.68753000
H	-3.31422700	1.78393200	-0.00780900
H	-4.61742000	1.42760500	1.13778000
C	-3.30313700	-0.67675700	3.17248600
H	-4.39747400	-0.62220700	3.24855700
H	-2.99975400	-1.69756900	3.44242300
H	-2.89358600	-0.00517700	3.93919700
C	-3.56055400	-1.48172400	0.25305300
H	-3.28941600	-1.31680400	-0.79782300
H	-3.27266100	-2.51071800	0.50738500
H	-4.65498400	-1.41043500	0.32273500
C	1.65331100	0.81899700	0.49496800
H	2.11955700	0.31935700	1.35430000
H	2.37951000	0.80560600	-0.32893200
H	1.49775900	1.86737900	0.77832400
C	-0.70710300	1.08644000	-1.40372600
H	0.01544200	1.19741000	-2.22364300
H	-1.62409600	0.66045500	-1.83133400
H	-0.95317100	2.09165400	-1.03996500
C	0.49338300	-1.64453000	-0.86028600
H	0.99668200	-2.32433000	-0.15994800
H	-0.39361700	-2.16458200	-1.24635200
H	1.17171900	-1.47388100	-1.70761200
H	-3.14703800	-6.09074800	6.84465700
C	-0.52411300	-4.44607000	1.53669300
O	0.81855200	-4.95644400	1.25101900
Li	2.19460000	-5.28167800	2.58189300
O	1.54677800	-6.50409500	3.99030500
C	0.53498500	-7.51324700	3.71604600
C	0.23749600	-8.16720100	5.06352600
C	0.42636700	-6.98959000	6.03171900
C	1.61553200	-6.24891800	5.41982700
H	2.57419100	-6.63552900	5.78999600
H	1.57757200	-5.16883600	5.57589300
H	0.62031700	-7.30084700	7.06239100
H	-0.46304200	-6.35307000	6.01668100
H	0.95575100	-8.96833700	5.27657100
H	-0.77145400	-8.58668500	5.09663000
H	-0.35612500	-7.02155400	3.31599600
H	0.94499000	-8.20065000	2.96946600
O	3.07499300	-3.63761700	3.17657900
C	3.90092800	-3.44275200	4.35038000
C	4.66292200	-2.14456600	4.09919900
C	3.63175400	-1.31971800	3.31339600
C	2.93867200	-2.37577300	2.44995400
H	3.42046700	-2.50273000	1.47331800
H	1.87527200	-2.18119600	2.29744600
H	4.08966500	-0.53447500	2.70581000
H	2.90758900	-0.84730500	3.98609300
H	5.55785600	-2.33604700	3.49386200
H	4.97538500	-1.66205000	5.02958800
H	3.25323700	-3.35813100	5.23088300
H	4.54162100	-4.32443300	4.45911900
O	3.64227300	-6.33693700	1.67328100
C	4.09430300	-7.63510500	2.12096700
C	5.61795500	-7.54356500	2.13156800
C	5.88343700	-6.64961000	0.90948000
C	4.71005900	-5.66203500	0.95561200
H	4.34065200	-5.38323400	-0.03620200
H	4.95432200	-4.74969400	1.50923600
H	5.85029800	-7.24489600	-0.00996800
H	6.85154500	-6.14240900	0.94662200
H	6.09934800	-8.52338300	2.06308800
H	5.96367700	-7.05540000	3.05042900
H	3.64151100	-7.81837200	3.09774300
H	3.74548700	-8.40126100	1.41452300
C	0.82377400	-5.53324400	-0.07129400
C	-0.58146400	-6.10036400	-0.23928600
C	-1.44147000	-5.01658900	0.43667800
H	-1.69830000	-4.23369700	-0.28292900
H	-2.36953800	-5.41544100	0.85336900
H	-0.84637600	-6.26408400	-1.28830800
H	-0.66773700	-7.05672000	0.29015100
H	1.02846500	-4.74753600	-0.81040700
H	1.62547200	-6.27554900	-0.09756700
H	-0.79163100	-4.79684700	2.53638200
H	-0.49756100	-3.35264700	1.53182600

Table 40. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by A_2S_4 (**18**; *syn* to benzyl group).



IRC-P **18** *syn*



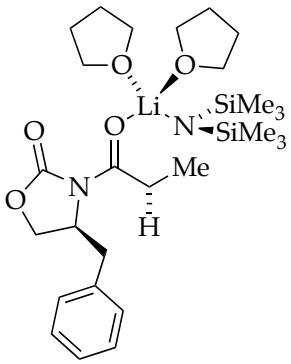
G = –3475.454804 Hartree
G_{MP2} = –2174679.0976 kcal/mol
ΔG^1_{MP2} = 13.3 kcal/mol
ΔG^2_{MP2} = 16.1 kcal/mol

Atom	X	Y	Z
Si	0.00000000	0.00000000	0.00000000
N	-0.19047900	1.69220000	-0.02060600
Li	-0.95474800	2.54136200	1.51564200
O	-2.33874400	3.76336200	1.98390700
C	-3.14830000	4.66598000	1.75852400
N	-4.08695000	5.16732800	2.58272000
C	-4.65740800	4.36167500	3.72457200
O	-5.53207300	3.50449200	3.36528200
C	-4.17731400	4.72970300	4.94544800
C	-4.66077800	4.12508800	6.23321500
H	-5.25684400	3.22682700	6.03863200
H	-3.83317800	3.83806600	6.89803800
H	-5.29373200	4.81623800	6.81467100
H	-3.45014000	5.53482000	4.99057100
C	-4.99536900	6.04115400	1.83157200
C	-4.12765100	6.36959700	0.60651100
O	-3.16694700	5.29333900	0.54605800
H	-4.67336000	6.39513200	-0.33766600
H	-3.57955300	7.31033900	0.73377900
C	-5.44608400	7.26525000	2.64347100
H	-5.86878700	6.89812600	3.58582700
H	-4.56093000	7.85684300	2.90643600
C	-6.45365800	8.11554000	1.89895100

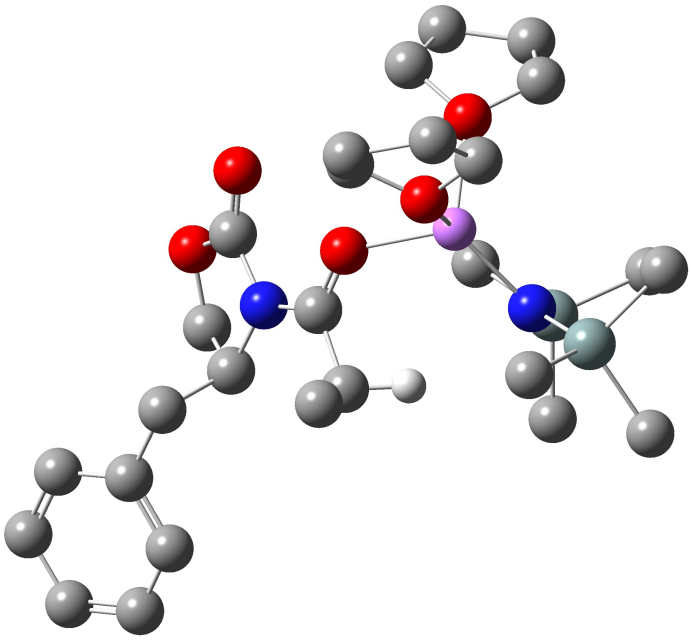
Atom	X	Y	Z
C	-7.79087200	7.70394500	1.79175200
C	-8.72024700	8.46196200	1.07995900
C	-8.32912000	9.65161900	0.46120800
C	-7.00419800	10.0764050	0.56419900
C	-6.07701600	9.31360300	1.27742600
H	-5.04858700	9.65833300	1.36129900
H	-6.69058100	11.0045780	0.09348900
H	-9.05303000	10.2451970	-0.09069100
H	-9.75268200	8.12787600	1.01363800
H	-8.10506200	6.78386200	2.28061300
H	-5.87963400	5.45533700	1.54304200
N	-0.82063300	2.32291600	4.06075100
Si	0.65306500	3.21925900	4.47307600
C	1.19849600	4.20142100	2.95569900
H	1.47445300	3.54143900	2.12407500
H	0.40669800	4.87373700	2.60293500
H	2.07341700	4.82238700	3.18661600
C	2.02361400	2.01174700	4.95879100
H	1.80608200	1.47381500	5.88887200
H	2.20395200	1.27052700	4.17196800
H	2.96006200	2.56231000	5.11404100
C	0.35198800	4.43939700	5.89201900
H	0.09249000	3.92574500	6.82488100

H	1.24369100	5.05013600	6.08378700
H	-0.47282000	5.12245200	5.65373900
Si	-1.50451700	0.95288000	4.95251100
C	-1.60710200	1.26982900	6.82145400
H	-0.61781000	1.42703000	7.26839800
H	-2.21702100	2.15285600	7.04382000
H	-2.06239400	0.41295900	7.33562600
C	-0.46831000	-0.60813300	4.69628700
H	-0.33879500	-0.84269600	3.63492200
H	0.52968000	-0.52085600	5.13906800
H	-0.96051800	-1.46612200	5.17372600
C	-3.25842500	0.66361700	4.30396700
H	-3.78982500	-0.03103800	4.96919800
H	-3.84241100	1.58986000	4.24531800
H	-3.24408100	0.22147700	3.30092100
Si	0.32328300	2.73610300	-1.27686900
C	2.15329500	2.51522900	-1.79049000
H	2.81832000	2.66267500	-0.92939800
H	2.35595000	1.51296200	-2.18867900
H	2.44618500	3.23972600	-2.56263200
C	0.17064400	4.56905100	-0.77093900
H	0.44368200	5.21782600	-1.61433500
H	-0.85050500	4.83260700	-0.47150200
H	0.84059800	4.82080000	0.06052600
C	-0.70297600	2.57862500	-2.88435900
H	-0.63125500	1.57313500	-3.31657000
H	-1.76480300	2.77590400	-2.68426800
H	-0.37246400	3.29288400	-3.65090700
C	-1.54145700	-0.84471800	0.77048900
H	-2.40710300	-0.70047900	0.10920300
H	-1.39753200	-1.92548400	0.90580000
H	-1.79443500	-0.41777500	1.74874700
C	1.50273600	-0.58061300	1.02743200
H	1.57348800	-1.67489200	1.09648200
H	2.43403500	-0.21620600	0.57485800
H	1.46580300	-0.18300900	2.04980600
C	0.18221000	-0.86844800	-1.69528300
H	-0.69489200	-0.69847400	-2.33251400
H	1.06169700	-0.52022600	-2.24999300
H	0.28947900	-1.95396100	-1.56359700
H	-1.57819300	2.97580700	3.83153400
C	-4.96739000	1.57030600	0.57514600
O	-6.14819200	0.73279600	0.31653300
Li	-7.21580800	-0.06696500	1.71675700
O	-8.01848900	1.17878500	2.99626500
C	-8.44642200	2.48066800	2.50220800
C	-8.67300100	3.36840400	3.74114700
C	-8.61562600	2.37775300	4.91832300
C	-7.64036500	1.33242700	4.39086900
H	-7.73470300	0.34841400	4.85885000
H	-6.61129500	1.70037100	4.43901500
H	-9.59679100	1.92577000	5.11011900
H	-8.26132900	2.84482500	5.84161400
H	-9.61972600	3.91549200	3.69320400
H	-7.84136700	4.07135400	3.82005100
H	-7.66103300	2.88981400	1.86268100
H	-9.35641900	2.31137100	1.91581400
O	-6.22700900	-1.63510200	2.43539900
C	-6.31990100	-2.18087100	3.77251900
C	-5.48112100	-3.45799400	3.75132500
C	-4.36328600	-3.08332200	2.76601000
C	-5.10459000	-2.23756900	1.72930600
H	-5.50988000	-2.85129200	0.91498800
H	-4.49246200	-1.44197400	1.30202000
H	-3.87468700	-3.95152300	2.31518900
H	-3.59462500	-2.48452600	3.26493300
H	-6.07141800	-4.29874900	3.36748900
H	-5.11018100	-3.72761800	4.74432800
H	-5.91757000	-1.44858800	4.48286700
H	-7.37823600	-2.34920000	3.99587700
O	-8.83013600	-0.86050800	0.81170100
C	-10.1811370	-0.62989700	1.27839100
C	-10.8390690	-2.00761900	1.29919100
C	-10.1834080	-2.68427600	0.08494200
C	-8.74984800	-2.14392900	0.14193400
H	-8.30426100	-1.99308700	-0.84638500
H	-8.08898900	-2.78856200	0.73215500
H	-10.6777500	-2.36564700	-0.83977900
H	-10.2164850	-3.77672600	0.12593700
H	-11.9291870	-1.95315800	1.22778900
H	-10.5829270	-2.54009200	2.22291600
H	-10.1099380	-0.14311000	2.25296500
H	-10.6897560	0.04453000	0.57610600
C	-6.53045500	0.84949600	-1.06833300
C	-6.00471700	2.21313500	-1.50455900
C	-4.66785900	2.28736400	-0.74936000
H	-3.88505000	1.75960600	-1.30406500
H	-4.31799000	3.30947600	-0.58986800
H	-5.89172000	2.29309600	-2.58993500
H	-6.68889700	3.00270900	-1.17049200
H	-6.06163800	0.04058300	-1.64789500
H	-7.61717100	0.73951300	-1.11994400
H	-5.21663700	2.24482100	1.40068600
H	-4.14696200	0.91741000	0.88509100

Table 41. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by AS_2 (**19**; *anti* to benzyl group).



IRC-R **19** *anti*

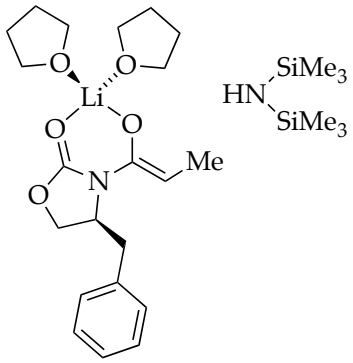


G = –2130.046596 Hartree
G_{MP2} = –1332765.2539 kcal/mol
ΔG^1_{MP2} = 5.4 kcal/mol
ΔG^2_{MP2} = 12.5 kcal/mol

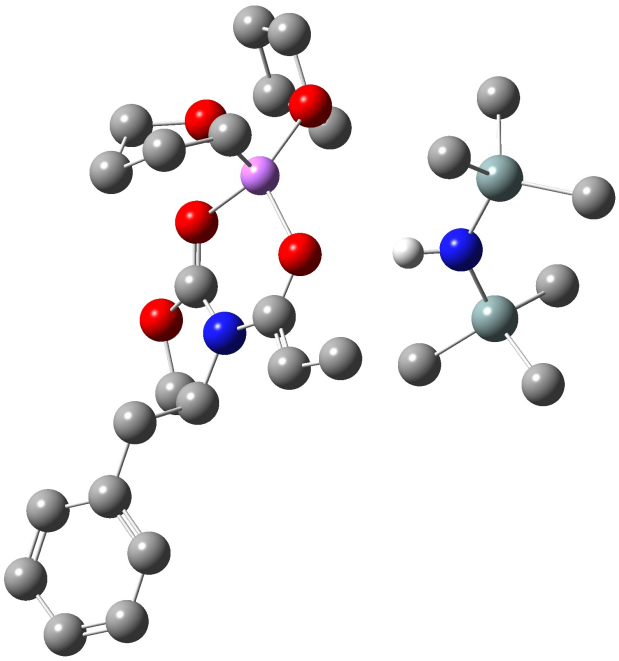
Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.49864000	-0.68350800	-1.28178500
H	0.22265300	-0.12104300	-2.18003600
H	1.57264100	-0.87135000	-1.28092100
O	-0.18293200	-1.94991700	-1.30383200
C	-1.33160800	-1.87546900	-0.58010700
N	-1.32318100	-0.64061200	0.12559900
C	-2.43429100	-0.13844500	0.80292200
O	-3.50538800	-0.73582400	0.77053400
Li	-5.36131600	0.04385400	0.60479800
O	-6.10050100	-0.90737200	2.33187100
C	-5.56033800	-2.18364500	2.70658900
C	-6.26492300	-2.51887700	4.02455000
C	-7.66847600	-1.88366600	3.84512300
C	-7.51217100	-0.98086700	2.59812000
H	-7.86787000	0.04017000	2.74109500
H	-8.01869900	-1.41500100	1.72483300
H	-7.95808400	-1.30487100	4.72651500
H	-8.44082200	-2.64148200	3.68147700
H	-5.73576200	-2.05179500	4.86128800
H	-6.30475400	-3.59629300	4.21121300
H	-5.79238600	-2.92522000	1.92749300
H	-4.47793300	-2.07601800	2.77577800
O	-6.22075300	-1.26689400	-0.69966500
C	-5.70421500	-2.53185800	-1.14916900
C	-5.87564000	-2.52127200	-2.68080800
C	-6.97150600	-1.44792000	-2.93366400
C	-7.36041900	-0.97711700	-1.52141500
H	-8.23149000	-1.53452400	-1.14302300
H	-7.55627600	0.09337600	-1.43767500
H	-7.83481700	-1.84593400	-3.47555300
H	-6.56876200	-0.61429800	-3.51546700
H	-6.16281800	-3.50869500	-3.05479900
H	-4.93885400	-2.24265400	-3.17120400
H	-4.66994700	-2.60312700	-0.81093200
H	-6.29454700	-3.34195500	-0.69353200
N	-5.42409900	1.99004300	0.20169700
Si	-6.40379300	2.92576700	1.24671200
C	-6.02789200	2.54223500	3.08112300
H	-5.04386700	2.94220700	3.36034000
H	-6.76732700	3.00204500	3.75054400
H	-6.00907300	1.46524500	3.28468200
C	-8.27615200	2.60892200	0.98751400
H	-8.89780900	3.14251000	1.71940000
H	-8.58193100	2.94673300	-0.01142400
H	-8.52877000	1.54219500	1.05261200

C	-6.21839800	4.82489800	1.10996300
H	-5.19099800	5.14735800	1.32010000
H	-6.48320900	5.19965600	0.11323700
H	-6.87551000	5.32857100	1.83187400
Si	-4.88676100	2.49747000	-1.33757600
C	-6.27961400	2.96544900	-2.56448900
H	-6.95815200	2.12072700	-2.74446000
H	-6.89137800	3.79080500	-2.17847100
H	-5.88004900	3.28092700	-3.53785400
C	-3.88092700	1.12499100	-2.21760600
H	-3.70307200	1.39098000	-3.26803900
H	-2.89626400	0.98150900	-1.75290800
H	-4.39556900	0.15794700	-2.19759400
C	-3.69019800	3.99348800	-1.32949700
H	-4.17258600	4.91051800	-0.97293900
H	-2.82726900	3.80750300	-0.67503600
H	-3.30073100	4.19586000	-2.33684700
C	-2.30609300	1.15711300	1.57565600
C	-2.48208700	0.91823100	3.08736300
H	-1.68978800	0.28066300	3.49839600
H	-2.45735800	1.87549900	3.61634700
H	-3.44764600	0.44758600	3.28837900
H	-1.36625500	1.67866400	1.38199600
O	-2.15349600	-2.74854700	-0.55795600
H	-0.10993400	1.07320500	-0.16369600
C	0.89677400	-0.26650800	1.23161500
H	0.36683800	0.08503700	2.12454700
H	1.01856800	-1.35082800	1.34225100
C	2.24912500	0.40756800	1.12877400
C	2.36800800	1.79457700	1.30211100
C	3.60562500	2.42632800	1.18514100
C	4.74921500	1.67891500	0.89405200
C	4.64606900	0.29817400	0.72430600
C	3.40458500	-0.33070400	0.84089600
H	3.33429300	-1.40961000	0.71973700
H	5.53124900	-0.29288200	0.50551000
H	5.71429100	2.16999900	0.80571500
H	3.67805100	3.50126800	1.32643200
H	1.48582500	2.38556800	1.54106500
H	-3.13751100	1.78188900	1.21374400

Table 42. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by AS_2 (**19**; *anti* to benzyl group).



IRC-P **19** *anti*

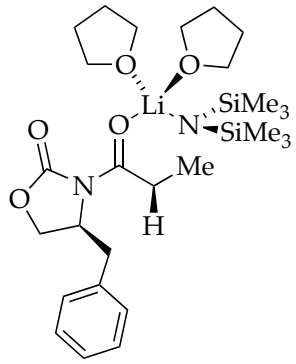


G = –2130.078903 Hartree
G_{MP2} = –1332778.4466 kcal/mol
ΔG^1_{MP2} = –7.8 kcal/mol
ΔG^2_{MP2} = 25.7 kcal/mol

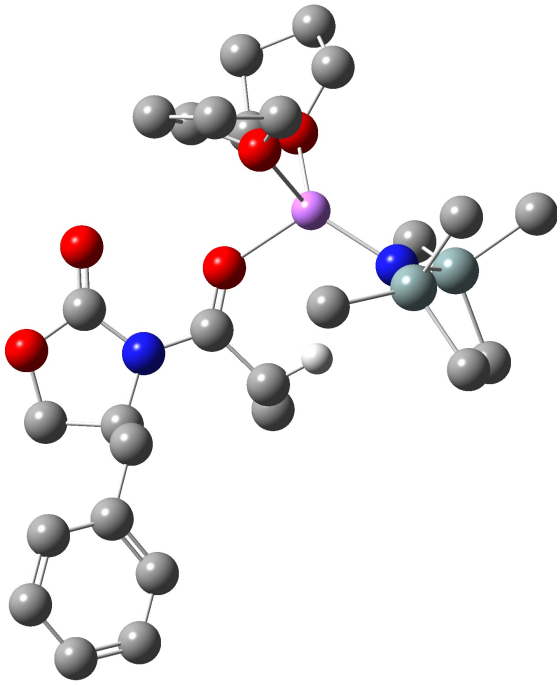
Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	-0.18354400	0.38146600	-1.47252200
H	0.21577300	-0.38028500	-2.15143200
H	-1.21458900	0.61309600	-1.74310700
O	0.60479700	1.58149200	-1.61530000
C	1.55945900	1.58299300	-0.64183200
N	1.32682000	0.58147300	0.24922400
C	2.24946800	0.15350500	1.31695300
O	3.44455700	0.64070400	1.23766700
Li	3.96362700	2.23355900	0.49976600
O	4.01942400	3.73215700	1.83551200
C	2.94403900	4.69436800	1.78307500
C	2.06151100	4.36325300	2.98373100
C	3.10663100	3.96387400	4.03855800
C	4.18246400	3.25382400	3.20238600
H	4.04651300	2.16879200	3.17731600
H	5.20096400	3.48537300	3.53116700
H	2.70063100	3.31456900	4.81934500
H	3.51752000	4.85747900	4.52278700
H	1.41049800	3.51395600	2.74752400
H	1.43473900	5.20535500	3.29301700
H	3.36096900	5.70905400	1.85940900
H	2.44949900	4.57862900	0.81581700
O	5.56483800	2.45961700	-0.64512700
C	5.49779000	1.87042100	-1.95677300
C	5.16950100	3.04484300	-2.88397200
C	5.85590700	4.25370000	-2.19211200
C	6.25540200	3.71291900	-0.79929500
H	5.95368800	4.34661600	0.03666000
H	7.33656300	3.52930900	-0.73683600
H	5.16907000	5.10098400	-2.11118900
H	6.73769200	4.59572800	-2.74263500
H	4.08629100	3.18855500	-2.91878300
H	5.52943200	2.87955100	-3.90393500
H	6.46881700	1.41359500	-2.19376700
H	4.73468000	1.09126000	-1.92494800
N	5.66842100	-1.50490000	0.76677700
Si	7.18530400	-1.04921400	1.50138300
C	6.82841000	-0.04519200	3.06741100
H	6.31048100	-0.65307300	3.81851200
H	7.75280500	0.33604600	3.51981500
H	6.18666600	0.81404200	2.84003200
C	8.23684400	0.02991800	0.34678600
H	9.17764500	0.34227500	0.81878100
H	8.48852400	-0.50212100	-0.57906700
H	7.67797000	0.93287600	0.07257900

C	8.19743100	-2.58291000	1.96701200
H	7.66133200	-3.21194500	2.68717700
H	8.44185400	-3.20535700	1.09810700
H	9.14735600	-2.28435400	2.42844000
Si	5.16180700	-2.91544500	-0.12977700
C	6.42170400	-3.35395100	-1.47928500
H	6.52912200	-2.53353000	-2.19904500
H	7.41590600	-3.56271300	-1.06607500
H	6.10688100	-4.24716800	-2.03403400
C	3.49577800	-2.52621000	-0.94071800
H	3.10582200	-3.39966900	-1.47845300
H	2.75829500	-2.23566500	-0.18259500
H	3.58352600	-1.70198100	-1.65924300
C	4.93888700	-4.43890000	0.97924200
H	5.87824400	-4.72800700	1.46570600
H	4.20710900	-4.23585600	1.77058200
H	4.58318400	-5.30586600	0.40699700
C	1.77155900	-0.72808500	2.23850800
C	2.62196900	-1.27146000	3.35170500
H	2.22335000	-1.01096000	4.34457200
H	2.69095200	-2.36949500	3.32424200
H	3.63902200	-0.87678400	3.28488000
H	0.74406800	-1.06885400	2.19138800
O	2.44325700	2.44090700	-0.66026300
H	0.04401700	-1.08337100	0.13064100
C	-1.08764100	0.61283300	0.91967000
H	-0.73965400	0.52934400	1.95396100
H	-1.16233900	1.68371600	0.69244600
C	-2.43916300	-0.04838800	0.75695300
C	-2.67054100	-1.33359400	1.27122000
C	-3.90504200	-1.96029500	1.10489600
C	-4.93547900	-1.31120000	0.42048300
C	-4.72144500	-0.03195300	-0.09279500
C	-3.48294900	0.59142900	0.07504800
H	-3.32758000	1.59402800	-0.31822200
H	-5.51832100	0.48485600	-0.62123600
H	-5.89854900	-1.79810100	0.29312800
H	-4.06473600	-2.95438700	1.51427500
H	-1.87849500	-1.84416600	1.81528500
H	4.91537100	-0.82480900	0.92765400

Table 43. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of oxazolidinone **9** by AS_2 (**19**; *syn* to benzyl group).



IRC-R **19** *syn*

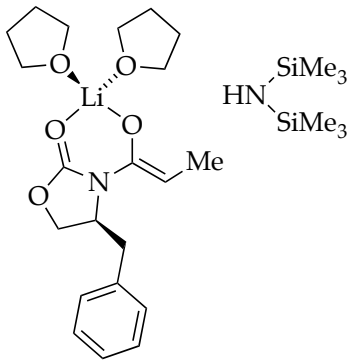


G = –2130.046360 Hartree
G_{MP2} = –1332764.5193 kcal/mol
ΔG^1_{MP2} = 6.2 kcal/mol
ΔG^2_{MP2} = 12.1 kcal/mol

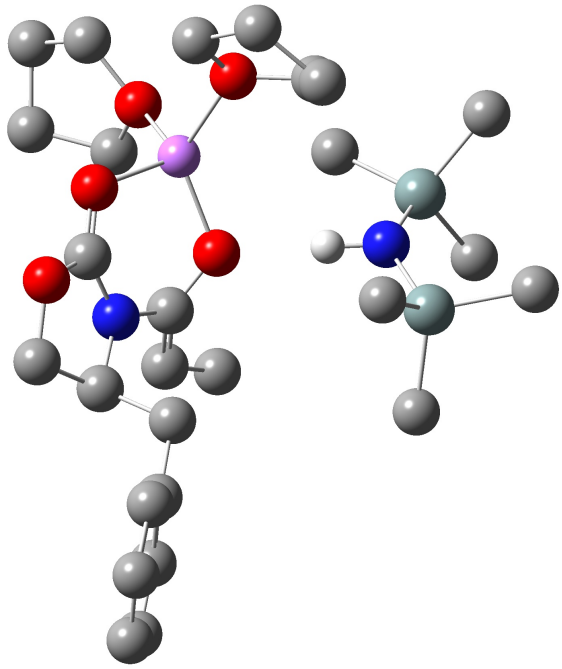
Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.71764600	-1.27008100	-0.47525300
H	0.74534400	-1.34597900	-1.56793100
H	1.72693800	-1.37144900	-0.07556700
O	-0.08628700	-2.34611800	0.04170800
C	-1.36222400	-1.91829600	0.24899900
N	-1.38181300	-0.51185900	0.07372400
C	-2.54875000	0.25920000	0.04478700
O	-3.64292200	-0.25744500	0.23721400
C	-2.41312700	1.72323900	-0.31843900
C	-2.41648800	1.91766500	-1.84841300
H	-3.32999000	1.50428700	-2.28609400
H	-2.38856600	2.98614300	-2.08254300
H	-1.55801400	1.44007400	-2.33639700
H	-1.51143500	2.16624600	0.11537700
O	-2.26362600	-2.65856500	0.53249700
H	0.07790700	0.79257200	-0.74595400
C	0.49970300	0.50232100	1.37676600
H	-0.20532200	1.25441200	1.74951700
H	0.46334800	-0.33694700	2.08177000
C	1.89905700	1.07774800	1.31562300
C	2.12238400	2.35132800	0.77155900
C	3.41113300	2.87745900	0.68874000
C	4.50147600	2.13710000	1.15158200
C	4.29307600	0.87153000	1.70015600
C	3.00108800	0.34776300	1.78055900
H	2.84483600	-0.63355000	2.22367600
H	5.13391900	0.29215100	2.07174500
H	5.50536400	2.54811200	1.09106200
H	3.56337800	3.86850300	0.26992500
H	1.27839100	2.94330800	0.42255800
Li	-5.36849600	0.49131800	1.06075300
O	-5.36509800	-0.81960100	2.73604800
C	-5.04551200	-2.20488400	2.51385000
C	-4.43132700	-2.70456200	3.83787200
C	-4.88140700	-1.64948700	4.88520800
C	-5.82525300	-0.73420800	4.09023700
H	-5.79200100	0.31379300	4.38732500
H	-6.86675500	-1.08907000	4.14709100
H	-4.02347900	-1.07696900	5.25055000
H	-5.37915700	-2.09411400	5.75243000
H	-3.34096200	-2.74885000	3.76624500
H	-4.78492200	-3.71093500	4.08247400
H	-5.97135000	-2.75206000	2.27891700
H	-4.36595000	-2.25407700	1.66480700
O	-6.66085300	-0.74563100	0.08848100

C	-6.38442200	-1.59514000	-1.04464800
C	-7.51598400	-2.62313300	-1.06182500
C	-8.69917400	-1.79755900	-0.53136500
C	-8.02834200	-0.90721300	0.52069500
H	-8.02237300	-1.37807500	1.51206700
H	-8.48401900	0.08382700	0.60739400
H	-9.50257400	-2.40855600	-0.10909600
H	-9.12530100	-1.18521900	-1.33446700
H	-7.28994600	-3.45240900	-0.38090200
H	-7.69013500	-3.03880600	-2.05889700
H	-6.38546500	-0.98101500	-1.95496800
H	-5.38902900	-2.02300900	-0.90592400
N	-5.46081300	2.47162600	1.16834900
Si	-4.96663600	3.14553900	2.65749200
C	-3.50850300	2.13912100	3.39001600
H	-2.59206200	2.32464700	2.81186500
H	-3.29679500	2.42733000	4.42819800
H	-3.69500200	1.05896200	3.36992500
C	-6.34151000	3.19947100	3.98977700
H	-5.96130200	3.51254600	4.97186100
H	-7.11960100	3.91613400	3.69640000
H	-6.84179900	2.23116900	4.11688600
C	-4.30736300	4.94180200	2.60141600
H	-3.49969500	5.05822800	1.86772400
H	-5.09308700	5.66068900	2.33781200
H	-3.91053400	5.23952300	3.58173400
Si	-6.32818400	3.29285800	-0.05431700
C	-8.04929200	3.93180300	0.48326100
H	-8.67523200	3.10942700	0.85493400
H	-7.96930600	4.66640800	1.29492900
H	-8.58811200	4.41311900	-0.34423500
C	-6.65884500	2.16228800	-1.56052100
H	-7.15447100	2.72287100	-2.36386800
H	-5.72573100	1.75409900	-1.97183100
H	-7.29839600	1.31201900	-1.30054900
C	-5.42687300	4.80646800	-0.80634400
H	-5.26994700	5.60690500	-0.07456100
H	-4.43882900	4.52643600	-1.19644200
H	-6.00029800	5.23064300	-1.64183400
H	-3.28960300	2.21783700	0.12134400

Table 44. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of oxazolidinone **9** by AS_2 (**19**; *syn* to benzyl group).



IRC-P **19** *syn*



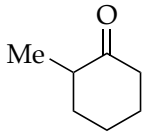
G = –2130.080845 Hartree
G_{MP2} = –1332780.3457 kcal/mol
ΔG^1_{MP2} = –9.7 kcal/mol
ΔG^2_{MP2} = 28.0 kcal/mol

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.50120600	-1.25259900	0.74268600
H	0.82417800	-2.03955500	0.05216500
H	1.30245200	-1.04597300	1.45423000
O	-0.64509300	-1.73406500	1.47168500
C	-1.76830600	-1.20477900	0.91107300
N	-1.44426400	-0.25826600	-0.00353800
C	-2.43601500	0.60711200	-0.67614900
O	-3.48249600	0.89452900	0.03054900
C	-2.11251300	1.00289300	-1.93573300
C	-2.95464800	1.93771000	-2.75669800
H	-3.81905200	2.28298400	-2.18320800
H	-2.39429500	2.82833800	-3.07811400
H	-3.33008000	1.46147000	-3.67564300
H	-1.20484600	0.61416200	-2.38913900
O	-2.88158300	-1.60835000	1.24968900
H	0.38751300	0.01647500	-1.02186300
C	0.34659700	1.33753300	0.69391600
H	-0.25217600	2.11586500	0.20786300
H	0.02287500	1.28507900	1.74047200
C	1.81888500	1.67390400	0.61026700
C	2.37514000	2.13091000	-0.59444100
C	3.73684600	2.41461400	-0.69287100
C	4.57044400	2.24764600	0.41571100
C	4.03046100	1.79911300	1.62125300
C	2.66618400	1.51528900	1.71507800
H	2.25039200	1.17895200	2.66267600
H	4.66864800	1.67403100	2.49218500
H	5.63112400	2.47175700	0.34089400
H	4.14690100	2.77257400	-1.63370700
H	1.72993400	2.27546600	-1.45866300
Li	-4.40814000	-0.45361100	0.89706100
O	-5.32699900	-0.27203600	2.65138300
C	-5.01976700	-1.20096100	3.72242500
C	-5.03100100	-0.38179300	5.02672500
C	-4.91053500	1.06983700	4.53091500
C	-5.67248800	1.01336700	3.21012900
H	-5.38791300	1.77948900	2.48494500
H	-6.75957000	1.05837700	3.37352200
H	-3.86328400	1.33246000	4.34494800
H	-5.32956600	1.79895400	5.23113300
H	-4.22028200	-0.67222200	5.70128400
H	-5.97686200	-0.52195000	5.56231600
H	-5.77116700	-1.99917300	3.72459000

H	-4.04275900	-1.63680700	3.49774200
O	-5.68656600	-1.39945700	-0.29690700
C	-5.45211000	-1.35696600	-1.72571600
C	-5.37152300	-2.81932300	-2.15809600
C	-6.39284600	-3.48091300	-1.21923300
C	-6.19060500	-2.70012300	0.08579800
H	-5.44419300	-3.17835300	0.73189700
H	-7.11498400	-2.56183500	0.65583700
H	-6.23190000	-4.55518200	-1.08848200
H	-7.41002400	-3.33499400	-1.60135900
H	-4.36621400	-3.21499400	-1.97202600
H	-5.60489400	-2.95770600	-3.21814300
H	-6.29409900	-0.84003200	-2.20465100
H	-4.53933800	-0.78239100	-1.89618900
N	-4.93137600	3.52545000	0.39474700
Si	-3.74391300	4.63678300	1.03834800
C	-2.73631300	3.73177000	2.36381600
H	-2.43100300	2.74831800	1.98655200
H	-1.83397400	4.28703700	2.64876400
H	-3.33058900	3.57013700	3.27152000
C	-4.60287600	6.13888100	1.81079300
H	-3.85664500	6.82852300	2.22517600
H	-5.19428100	6.70371200	1.08032100
H	-5.27206800	5.84633000	2.62843600
C	-2.54582300	5.24989100	-0.29808700
H	-2.02790400	4.40706600	-0.77237800
H	-3.07886500	5.79290300	-1.08792500
H	-1.78347400	5.92312100	0.11525800
Si	-6.53446600	3.75409200	-0.26420100
C	-7.78884200	4.15703800	1.10082300
H	-7.84059900	3.34821500	1.84002400
H	-7.52254700	5.07624700	1.63588100
H	-8.79607600	4.29714700	0.68767700
C	-7.04801300	2.14451500	-1.11839400
H	-8.07989800	2.21016900	-1.48588000
H	-6.40043300	1.93337600	-1.97759200
H	-6.98628200	1.28437200	-0.44114200
C	-6.59729500	5.16058700	-1.53754000
H	-6.29696900	6.12203900	-1.10299200
H	-5.92549200	4.95701000	-2.38014800
H	-7.61030200	5.28820500	-1.94081600
H	-4.50439300	2.61847000	0.16153900

VII. Appendix A

Revisiting the LiHMDS-mediated enolization of 2-methylcyclohexanone



3

i. Rate studies

By including constraints applied by the dependencies on THF concentration, and cosolvent choice, the subset of mechanisms required to *fit all data* reduces to one (eq 17) that is described by eq 18. This is true for *all* fits on plots of k_{obsd} vs [S] (S = THF) for the enolization of 2-methylcyclohexanone **3**.

$$\tfrac{1}{2}\,A_2S_2 + S \rightleftharpoons AS_2 + \mathbf{3} \xrightarrow{k} [AS_2\bullet\mathbf{3}]^{\ddagger} \tag{17}$$

$$k_{obsd} = f\left([S]\right)\left\{\left(k[S]\right)\left(\frac{4[A]_0 + K_{eq}[S]^4 - \sqrt{K_{eq}}[S]^2\sqrt{8[A]_0 + K_{eq}[S]^4}}{8}\right)^{\frac{1}{2}} + \right. \tag{18}$$

$$\text{where } f\left([S]\right) = \begin{cases} 1 \text{ for hexane} \\ \dfrac{a\left(12.3 - [S]\right)^m}{1 + b\left(12.3 - [S]\right)^m} + c \text{ for toluene} \end{cases}$$

Eq 18 is the general equation used for the unweighted least-squares fits on all the plots of k_{obsd} vs [S] for the enolization of 2-methylcyclohexanone **3**.

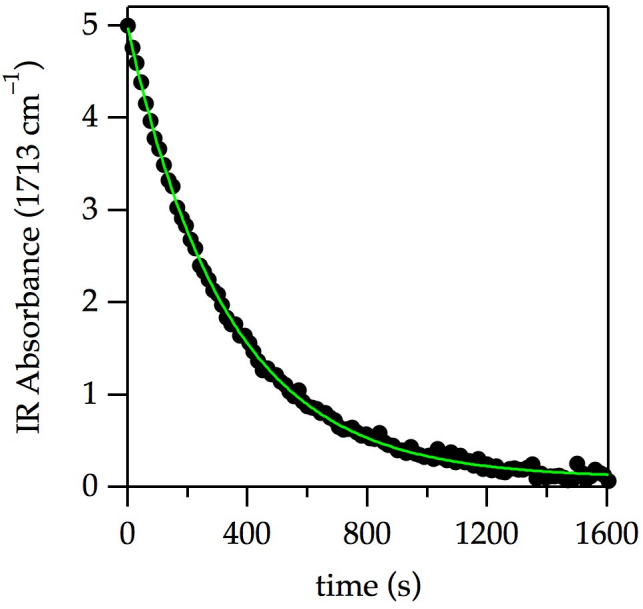


Figure 37. Lithiation of 0.0050 M 2-methylcyclohexanone **3** with 0.10 M LiHMDS and 9.0 M THF–hexane at –78 °C showing the loss of **3** (pseudo-first-order conditions). The decay was fit to $f(t) = a + be^{-kt}$ [$a = (9.5 \pm 0.8) \times 10^{-5}$; $b = (4.88 \pm 0.02) \times 10^{-3}$; $k = (3.02 \pm 0.02) \times 10^{-3}$ s^{-1}].

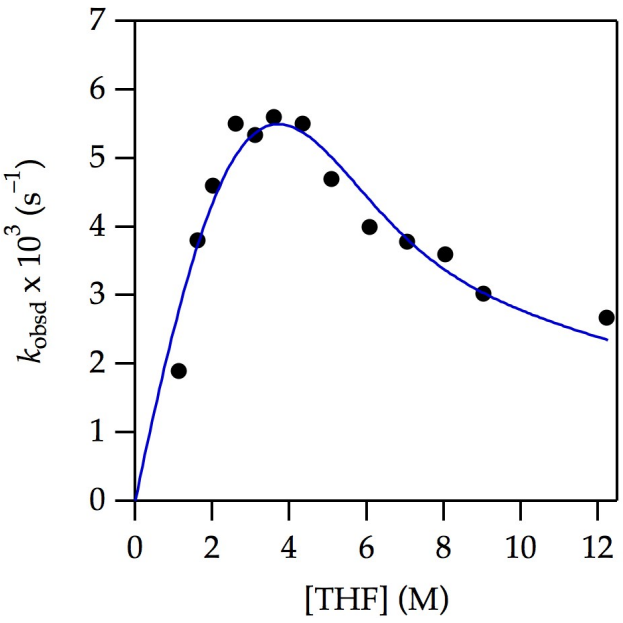


Figure 38. Plot of k_{obsd} vs [THF] for the enolization of 0.0050 M 2-methylcyclohexanone **3** with 0.10 M LiHMDS at various concentrations of THF in hexane at –78 °C. The curve depicts the result of an unweighted least-squares fit to eq 18 ($[A]_0$ is set at 0.10; $K_{eq} = (1.7 \pm 0.3) \times 10^{-2}$; $k = (2.4 \pm 0.1) \times 10^{-2}$).

[THF] (M)	$k_{obsd}{}^1 \times 10^3$ (s^{-1})	$k_{obsd}{}^2 \times 10^3$ (s^{-1})
1.1	1.90 ± 0.01	
1.6		3.8 ± 0.1
2.0	4.6 ± 0.2	
2.6		5.5 ± 0.2
3.1	5.34 ± 0.08	
3.6		5.6 ± 0.2
4.3		5.5 ± 0.2
5.1	4.7 ± 0.1	
6.1		4.0 ± 0.1
7.0	3.78 ± 0.05	
8.0		3.6 ± 0.1
9.0	3.02 ± 0.02	
12.2	2.67 ± 0.02	

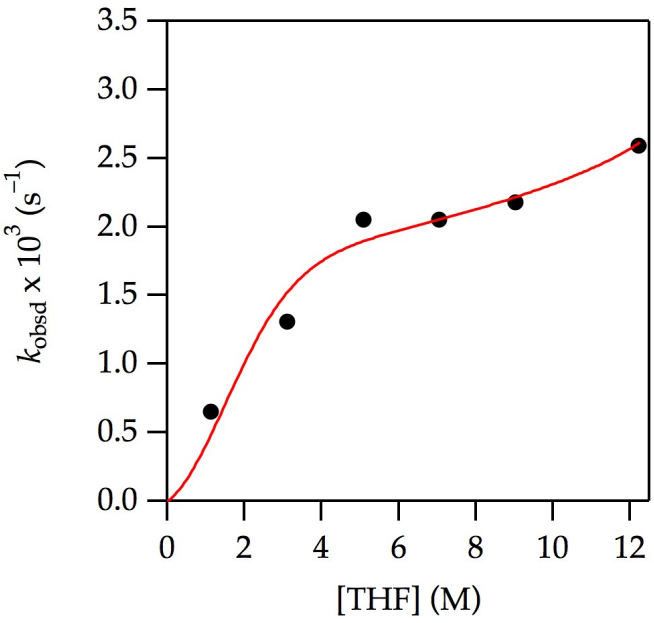


Figure 39. Plot of k_{obsd} vs [THF] for the enolization of 0.0050 M 2-methylcyclohexanone **3** with 0.10 M LiHMDS at various concentrations of THF in toluene at –78 °C. The curve depicts the result of an unweighted least-squares fit to eq 18 (All parameters carried over from the fit from Figure 38; additionally, $a = (-8 \pm 7) \times 10^{-2}$; $b = (8 \pm 6) \times 10^{-2}$, $c = (5.58 \pm 0.5) \times 10^{-1}$, $m = 1.0 \pm 0.8$).

[THF] (M)	$k_{obsd} \times 10^3$ (s^{-1})
1.1	0.65 ± 0.02
3.1	1.31 ± 0.03
5.1	2.05 ± 0.06
7.0	2.05 ± 0.07
9.0	2.18 ± 0.09
12.2	2.59 ± 0.05

Enolization of **3** in THF/toluene was previously studied, and the data was fitted to the equation $f(x) = (a + bx)/(1 + cx)$.[S3] Our values are equal to the ones previously determined within experimental error. Data from ref S3 was succesfully fitted using eq 18 with the same parameters presented above (see figure caption).

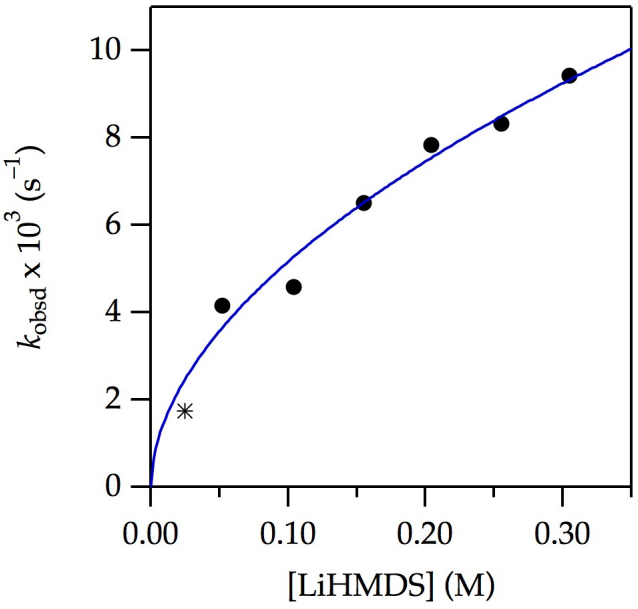


Figure 40. Plot of k_{obsd} vs [LiHMDS] for the enolization of 0.0050 M 2-methylcyclohexanone **3** at various concentrations of LiHMDS and 2.0 M THF–hexane at –78 ºC. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k[\text{LiHMDS}]^n$ ($k = (1.7 \pm 0.2) \times 10^{-2}$ s^{-1}; $n = 0.53 \pm 0.06$). The * denotes a measured point that was not included in the fit.

[LiHMDS] (M)	$k_{obsd} \times 10^3$ (s^{-1})
0.026	1.7 ± 0.5 *
0.052	4.16 ± 0.07
0.10	4.6 ± 0.2
0.15	6.5 ± 0.2
0.20	7.8 ± 0.4
0.25	8.3 ± 0.3
0.30	9.4 ± 0.9

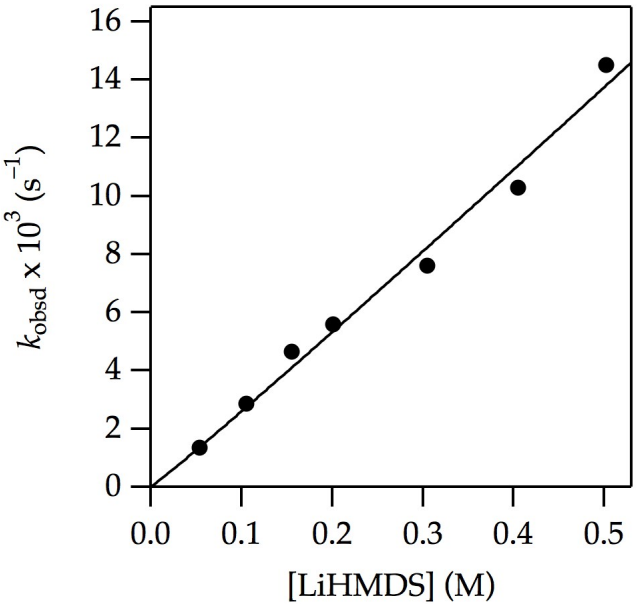
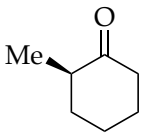


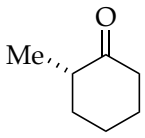
Figure 41. Plot of k_{obsd} vs [LiHMDS] for the enolization of 0.0050 M 2-methylcyclohexanone **3** at various concentrations of LiHMDS in neat THF at –78 ºC. The curve depicts the result of an unweighted least-squares fit to $k_{obsd} = k[\text{LiHMDS}]^n$ ($k = (2.8 \pm 0.2) \times 10^{-2}$ s^{-1}; $n = 1.03 \pm 0.08$).

[LiHMDS] (M)	$k_{obsd} \times 10^3$ (s^{-1})
0.055	1.35 ± 0.01
0.10	2.86 ± 0.04
0.15	4.66 ± 0.09
0.20	5.6 ± 0.1
0.30	7.6 ± 0.2
0.40	10.3 ± 0.5
0.50	14.5 ± 0.8

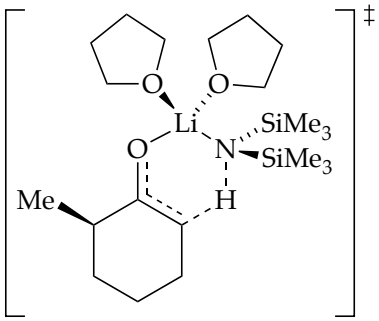
Chart 3. Substrates, transition structures and activation energies.



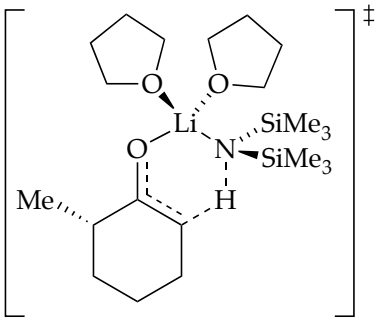
3$_{ax}$



3$_{eq}$



20$_{ax}$



20$_{eq}$

[AS$_2$•**3**$_{ax}$]‡

$\Delta G^{‡}_{anti}$ = 10.9 kcal/mol
$\Delta G^{‡}_{syn}$ = 10.5 kcal/mol

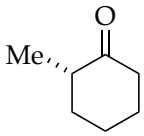
[AS$_2$•**3**$_{eq}$]‡

$\Delta G^{‡}_{anti}$ = 10.4 kcal/mol
$\Delta G^{‡}_{syn}$ = 12.9 kcal/mol

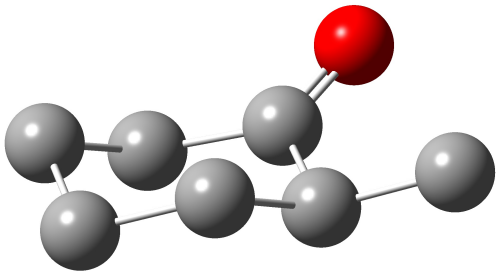
ii. Ground state computations

Geometries are optimized at the B3LYP level of theory using the 6–31G(d) basis set. Energies are defined as follows: G is the sum of electronic and thermal free energies calculated at the B3LYP level of theory (T = 195 K). G_{MP2} is derived from an MP2 SP calculation corresponding to the DFT-optimized geometry and includes a thermal correction from the DFT calculation.

Table 45. Geometric coordinates and thermally corrected MP2 energies for 2-methylcyclohexanone **3** (Me = equatorial).



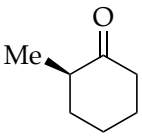
3$_{eq}$



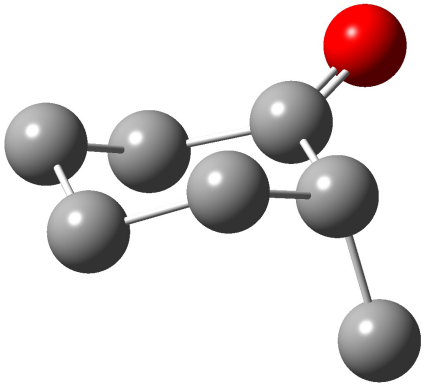
G = –349.045936 Hartree
G_{MP2} = –218287.3206 kcal/mol

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.39136500	1.44764600	-0.31053300
O	-0.39614100	2.25470000	-0.76883500
C	1.84362500	1.80837500	-0.02027700
C	2.81630100	0.80949800	-0.68143200
C	2.46529500	-0.63789700	-0.31149000
C	1.00932900	-0.96615800	-0.67003900
H	0.76444900	-1.99583800	-0.38042500
H	0.87989900	-0.91085200	-1.76094400
H	2.61937600	-0.78761000	0.76733000
H	3.14296400	-1.33269500	-0.82302000
H	3.84621000	1.04678300	-0.38874100
H	2.76523100	0.92863800	-1.77265600
H	1.98931300	1.77999600	1.07039500
H	2.01861100	2.83515600	-0.35454400
H	0.12181400	-0.11711600	1.09031900
C	-1.45037500	-0.29965400	-0.37819600
H	-1.71631800	-1.32594000	-0.10094200
H	-2.13864900	0.38660300	0.12313400
H	-1.60346600	-0.18331900	-1.45639800

Table 46. Geometric coordinates and thermally corrected MP2 energies for 2-methylcyclohexanone **3** (Me = axial).



3$_{ax}$



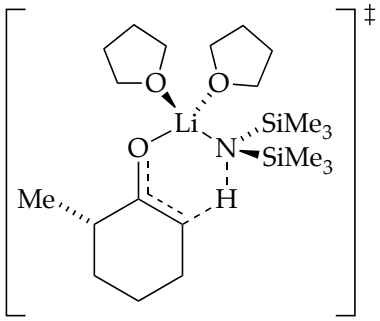
G = –349.042286 Hartree
G_{MP2} = –218285.1432 kcal/mol
ΔG_{MP2} = 2.2 kcal/mol (equatorial – axial)

Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.12637700	-1.50939100	0.23265500
O	1.08478200	-2.13946400	-0.17478000
C	-1.00023900	-2.17155500	1.01855600
C	-2.39204400	-1.75963400	0.49726700
C	-2.53055500	-0.23311800	0.42006700
C	-1.42906500	0.37524600	-0.46142500
H	-1.52279600	1.46860100	-0.49548600
H	-1.56969600	0.01947600	-1.49182900
H	-2.48593900	0.19223500	1.43226300
H	-3.51485600	0.03534500	0.01685500
H	-3.16931400	-2.18876200	1.14099000
H	-2.54295300	-2.18852000	-0.50341700
H	-0.90662300	-1.85906800	2.06992500
H	-0.84892600	-3.25449300	0.98505400
C	0.43634500	0.76516700	1.26802900
H	1.45575900	0.48786200	1.55696600
H	0.41993500	1.84471100	1.07852600
H	-0.22078800	0.56880200	2.12219400
H	0.71357600	0.24072900	-0.79595600

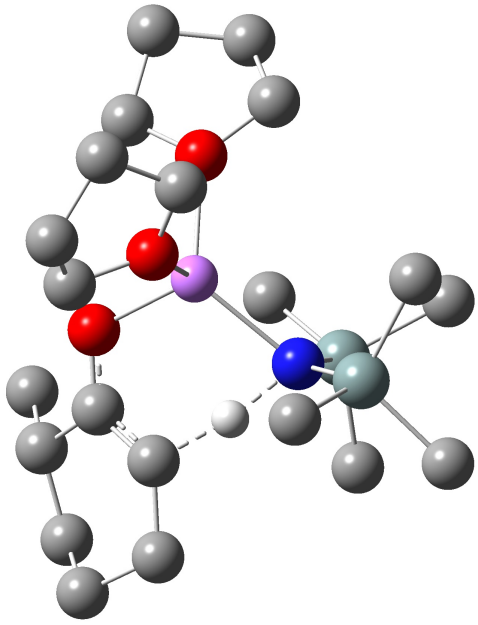
iii. Transition state computations

Geometries are optimized at the B3LYP level of theory using the 6–31G(d) basis set. Energies are defined as follows: G is the sum of electronic and thermal free energies calculated at the B3LYP level of theory (T = 195 K). G_{MP2} is derived from an MP2 SP calculation corresponding to the DFT-optimized geometry and includes a thermal correction from the DFT calculation. $\Delta G^{\ddagger}_{MP2}$ is the difference between G_{MP2} of the transition structure, and G_{MP2} of LiHMDS disolvated dimer **1**, 2-methylcyclohexanone **3**, and THF, based on the corresponding stoichiometries ($G_{MP2}^{TS} - G_{MP2}^{GS}$).

Table 47. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of 2-methylcyclohexanone **3** by AS_2 (**20**; Me = *syn*–equatorial).



20 *syn*–eq

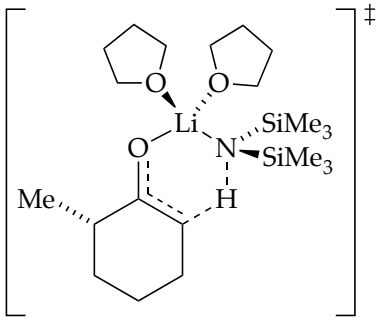


G = –1694.441767 Hartree
G_{MP2} = –1060196.2183 kcal/mol
$\Delta G^{\ddagger}_{MP2}$ = 12.9 kcal/mol

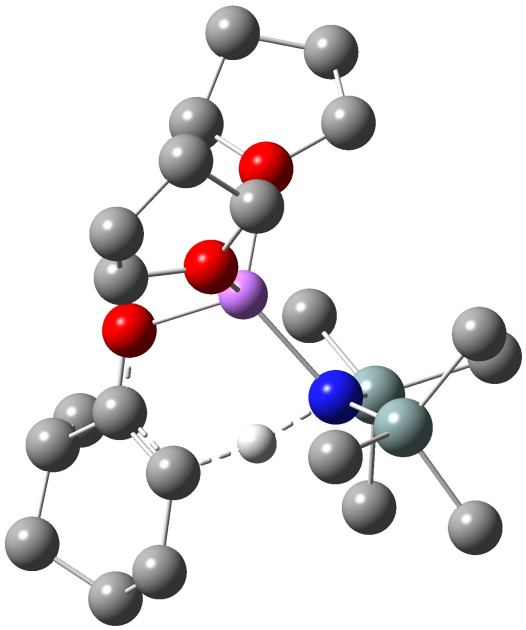
Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	5.60373800	-1.17672800	-3.79451300
C	0.93806800	0.81258000	-0.90576500	H	4.09564100	-0.34794700	-2.07388400
O	2.15595600	0.90678400	-0.56603700	H	3.14623200	0.09418800	-3.50606900
Li	3.07763100	2.47674200	-1.22115700	O	4.58967400	2.93840600	0.05324300
O	4.26394600	1.62766800	-2.67523400	C	4.91795100	1.96525200	1.07666000
C	4.11007300	0.22440900	-3.00686300	C	5.99255500	2.62480700	1.94514900
C	5.30917000	-0.12757700	-3.89243900	C	5.64508900	4.11641300	1.81671000
C	6.38137800	0.85519500	-3.39709700	C	5.19799100	4.21178800	0.35737800
C	5.54875800	2.10710700	-3.11733100	H	6.05353700	4.36767900	-0.31467300
H	5.41279400	2.71113400	-4.02461000	H	4.45911800	4.99429700	0.16865500
H	5.95907200	2.74261600	-2.32825000	H	6.48565000	4.77985900	2.04087100
H	7.17844700	1.03424300	-4.12502200	H	4.81698300	4.37498300	2.48642200
H	6.84010300	0.48643100	-2.47169400	H	6.99215500	2.42981600	1.53840100
H	5.07917200	0.06263600	-4.94736600	H	5.97131200	2.26320200	2.97740500

H	4.00677500	1.74135000	1.64105500
H	5.25290200	1.04946800	0.58151600
N	1.59133200	3.93288600	-1.73047700
Si	1.85159300	4.68503000	-3.28541700
C	1.98123300	3.37731100	-4.65965000
H	1.03160400	2.85265300	-4.81767200
H	2.25003200	3.86018500	-5.60818100
H	2.74833100	2.62926300	-4.43173100
C	3.47817200	5.67779200	-3.32644200
H	3.66062900	6.09887200	-4.32407500
H	3.46388500	6.51165100	-2.61517700
H	4.33876500	5.04454000	-3.07412800
C	0.46345000	5.86915700	-3.83888800
H	-0.50180600	5.34978000	-3.88764900
H	0.33944200	6.72869100	-3.16966500
H	0.67407100	6.26465700	-4.84142800
Si	0.96002900	4.83477800	-0.37432500
C	1.61533200	6.62214500	-0.25455200
H	2.70989400	6.65471600	-0.18282100
H	1.32567600	7.24186200	-1.11075900
H	1.21551800	7.10497500	0.64710400
C	1.43118700	4.00608700	1.26958600
H	0.89944100	4.47625700	2.10691600
H	1.18808600	2.93930600	1.27142500
H	2.50550200	4.09041800	1.46886900
C	-0.93969900	4.93673100	-0.40756000
H	-1.30109900	5.43804500	-1.31316800
H	-1.38782500	3.93543700	-0.38783000
H	-1.32864100	5.48966300	0.45750500
C	0.45541800	1.45060500	-2.09668700
C	-1.01034800	1.32888100	-2.52705200
C	-1.75530500	0.18516400	-1.82463400
C	-1.48758900	0.22808100	-0.31726600
H	-2.08766500	-0.52557800	0.21016900
H	-1.80146300	1.20544700	0.07998300
H	-1.41703600	-0.78289500	-2.22352200
H	-2.83300400	0.25006000	-2.02496200
H	-1.07061900	1.19785000	-3.61531800
H	-1.54621700	2.26735800	-2.31439100
H	1.17039800	1.34171600	-2.91607200
H	0.23380100	-1.04260400	-0.27981200
C	0.30927400	0.14452500	1.49492900
H	0.03480800	1.14063800	1.86123900
H	-0.26108000	-0.59021000	2.07577100
H	1.37387700	-0.00748300	1.68876800
H	0.87935600	2.75967100	-1.87351200

Table 48. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of 2-methylcyclohexanone **3** by AS_2 (**20**; Me = *syn*–axial).



20 *syn*–ax

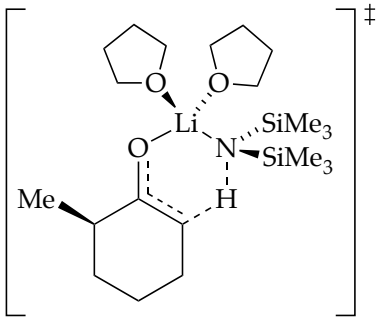


G = –1694.440903 Hartree
G_{MP2} = –1060196.4011 kcal/mol
$\Delta G^{\ddagger}_{MP2}$ = 10.5 kcal/mol

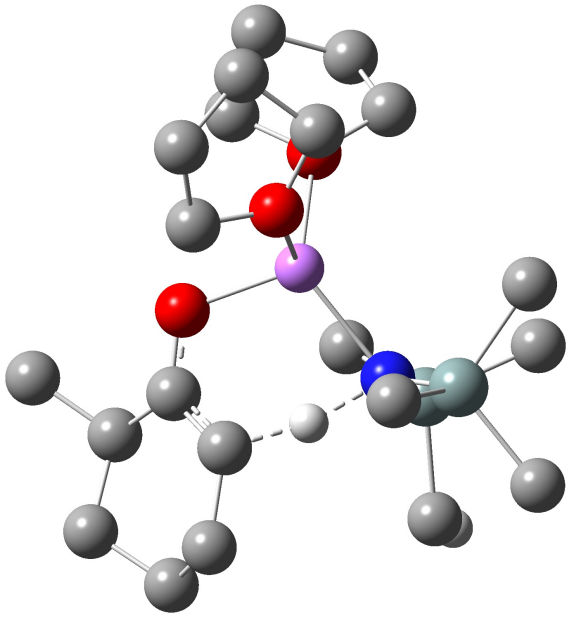
Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000
O	0.90479300	-1.46509800	-0.89058800
C	2.10316200	-1.64841200	-0.51587400
C	3.05774900	-2.32124200	-1.51320200
C	4.38061200	-2.76497100	-0.85445500
C	4.95042300	-1.68600600	0.07202100
C	3.98340100	-1.43520600	1.23584800
H	4.34048600	-0.58937600	1.84115300
H	4.01193600	-2.31241500	1.90272300
C	2.55748800	-1.17065400	0.75724100
H	1.80436800	-1.32815600	1.53430900
H	5.11030800	-0.75611800	-0.49101500
H	5.93273800	-1.99052200	0.45494500
H	5.10431100	-3.03803600	-1.63394400
H	4.20570500	-3.67445900	-0.26164100
C	3.28800400	-1.45611400	-2.76643300
H	2.33414200	-1.17909000	-3.22373900
H	3.87386600	-2.01285300	-3.50782800
H	3.83349400	-0.53505400	-2.53236500
H	2.51233400	-3.21549400	-1.84766400
O	-1.16637600	-1.04645600	1.34309700
C	-1.10344400	-2.49417900	1.37235000
C	-2.27939600	-2.94017900	2.24436400
C	-3.30784600	-1.82617000	1.99559700
C	-2.41227900	-0.58892300	1.90646800
H	-2.21641200	-0.16013100	2.89815700
H	-2.81000500	0.19499500	1.25627100
H	-4.06025500	-1.74304800	2.78562200
H	-3.82839400	-1.99172500	1.04462400
H	-1.98932200	-2.95961500	3.30150000
H	-2.64388900	-3.93582800	1.97426000
H	-1.18230400	-2.86498200	0.34491700
H	-0.12747300	-2.78482200	1.76922400
O	-1.52012900	0.63335400	-1.18277700
C	-1.75783200	-0.10466900	-2.40614300
C	-2.92348800	0.61045200	-3.08937800
C	-2.68660500	2.07143700	-2.67442800
C	-2.17165300	1.92206100	-1.23948200
H	-2.99531000	1.92832000	-0.51299700
H	-1.44744400	2.68850500	-0.95059100
H	-3.58638100	2.69123900	-2.73111900
H	-1.91973400	2.52760600	-3.31075900
H	-3.88183200	0.24984300	-2.69637000
H	-2.92418600	0.46436300	-4.17361200
H	-0.84730700	-0.07702700	-3.01505200
H	-1.96432500	-1.14356000	-2.13769200
N	1.49824300	1.36989400	0.70247300
Si	1.27894700	1.89683000	2.35430900
C	1.11892600	0.41355700	3.53392200
H	2.05710200	-0.14737200	3.61790400

H	0.86064000	0.76827600	4.54031000
H	0.33765800	-0.28199700	3.20920800
C	-0.31354600	2.92356500	2.56307600
H	-0.47749500	3.18892400	3.61595100
H	-0.27810500	3.85768700	1.99101600
H	-1.19513100	2.36386600	2.22395700
C	2.71622500	2.93693500	3.05131000
H	3.65998300	2.37883500	3.00747500
H	2.86679100	3.87893600	2.51170400
H	2.53309800	3.18931900	4.10417800
Si	2.10893700	2.45589900	-0.52230100
C	1.51440100	4.26033900	-0.34622500
H	0.42035000	4.33839100	-0.37896500
H	1.84905500	4.73862200	0.58117000
H	1.90759600	4.85754900	-1.17989400
C	1.54187700	1.91824600	-2.25627100
H	2.13475700	2.41902100	-3.03249600
H	1.63870800	0.83864700	-2.40261600
H	0.49100300	2.18053400	-2.42618800
C	4.01053800	2.50481600	-0.53936500
H	4.40726500	2.89538700	0.40535400
H	4.43324000	1.50240800	-0.67933400
H	4.39076200	3.14164000	-1.34868800
H	2.20289500	0.17199900	0.67554100

Table 49. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of 2-methylcyclohexanone **3** by AS_2 (**20**; Me = *anti*–equatorial).



20 *anti*–eq



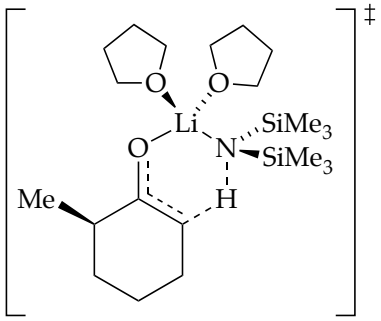
G = –1694.445211 Hartree
G_{MP2} = –1060198.6806 kcal/mol
$\Delta G^{‡}_{MP2}$ = 10.4 kcal/mol

Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000
O	0.64266600	1.81268300	0.20085300
C	1.86985300	1.98339200	-0.06966600
C	2.52275700	1.18328100	-1.06204800
C	3.96855900	1.45438400	-1.46925900
C	4.77196000	2.12337200	-0.34684300
C	4.01858500	3.34472700	0.18717500
H	4.62043900	3.88478700	0.93020700
H	3.84266200	4.04919800	-0.64036800
C	2.66835900	2.95475800	0.81361100
C	1.83061800	4.18563400	1.18857000
H	2.38866100	4.83254300	1.87576900
H	1.58442100	4.77678500	0.29765300
H	0.89291700	3.89205700	1.66577700
H	2.87944400	2.40373000	1.74503000
H	4.93689600	1.40980100	0.47351400
H	5.76478800	2.41403800	-0.71344900
H	4.45729100	0.51584800	-1.76802100
H	4.00548800	2.10623300	-2.35722100
H	1.86297000	0.97446100	-1.90883800
O	-1.24810500	0.20888300	-1.61889700
C	-1.22347000	1.43089100	-2.40267000
C	-2.58390800	1.51194400	-3.11387500
C	-3.48014700	0.61033500	-2.24884200
C	-2.49657900	-0.47564300	-1.81773200

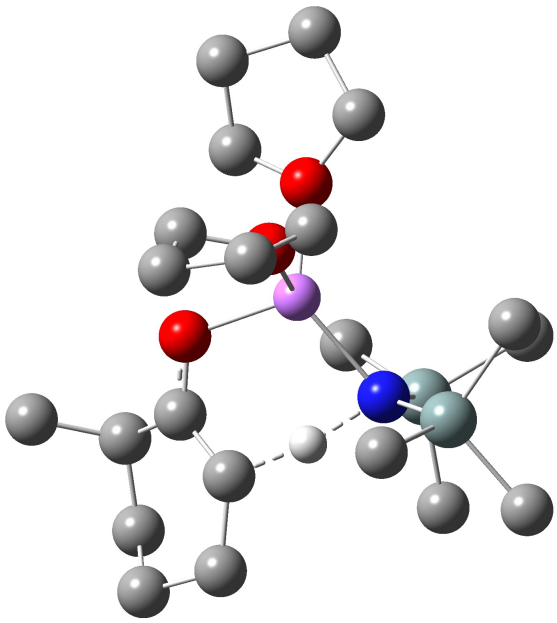
Atom	X	Y	Z
H	-2.37805600	-1.24172500	-2.59726100
H	-2.75569000	-0.96482100	-0.87588300
H	-4.34342200	0.21094200	-2.78981800
H	-3.84728100	1.15771200	-1.37238600
H	-2.51311400	1.10818000	-4.13035500
H	-2.95058000	2.54000600	-3.18748600
H	-1.04677200	2.25643900	-1.70894100
H	-0.38382800	1.38017500	-3.10313600
O	-1.48188600	-0.20788300	1.39275100
C	-1.99354100	1.04391000	1.91958200
C	-3.04065000	0.65433400	2.96482400
C	-2.50082900	-0.68979600	3.47791500
C	-1.94151400	-1.31472100	2.19883600
H	-2.71776200	-1.85981700	1.64409200
H	-1.09705300	-1.98633000	2.37052900
H	-3.26456800	-1.31507500	3.94971600
H	-1.69605600	-0.52588800	4.20369600
H	-4.02307600	0.51716100	2.49708400
H	-3.14267800	1.40818700	3.75106300
H	-1.15623700	1.60033100	2.35243600
H	-2.39629400	1.62383200	1.08471800
N	1.72364300	-1.27120400	-0.10145900
Si	1.61829200	-2.42072700	-1.41266000
C	1.44039200	-1.53677500	-3.08616900
H	2.32019900	-0.93101100	-3.33241400

H	1.31930200	-2.27927900	-3.88564800
H	0.56118500	-0.88364800	-3.10092900
C	0.09319400	-3.55065100	-1.23871300
H	0.00173800	-4.22785500	-2.09831700
H	0.14354200	-4.16971200	-0.33563700
H	-0.83138600	-2.96174000	-1.18375100
C	3.13187000	-3.56572200	-1.59691100
H	4.05449400	-2.98723400	-1.72974100
H	3.27837900	-4.22517200	-0.73315800
H	3.01670200	-4.20827300	-2.47990600
Si	2.35973000	-1.72951300	1.45863400
C	1.74940000	-3.43373200	2.05947200
H	0.65484200	-3.49566400	2.09790400
H	2.09770200	-4.25114500	1.41751200
H	2.12577600	-3.63340700	3.07152600
C	1.83618900	-0.48210100	2.79585500
H	2.15876700	-0.82646100	3.78707600
H	2.28015300	0.50553700	2.63107000
H	0.74923500	-0.34683100	2.82124700
C	4.26125100	-1.78977600	1.50106200
H	4.66087500	-2.56690500	0.83948000
H	4.69493100	-0.83417600	1.18152000
H	4.62817200	-1.99634900	2.51518600
H	2.29478100	-0.07180400	-0.51887000

Table 50. Geometric coordinates and thermally corrected MP2 energies for the transition state leading to enolization of 2-methylcyclohexanone **3** by AS_2 (**20**; Me = *anti*–axial).



20 *anti*–ax



G = –1694.441989 Hartree
G_{MP2} = –1060195.9740 kcal/mol
$\Delta G^{‡}_{MP2}$ = 10.9 kcal/mol

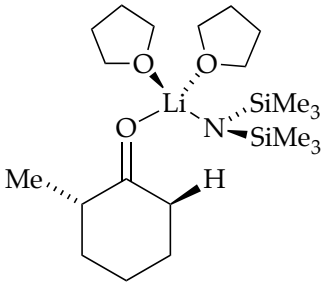
Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.83992700	-1.02571200	0.76468800
O	2.06839400	-1.11452500	0.45591100
Li	2.77525600	-2.92482300	0.39105400
O	4.35807200	-2.75481200	1.82728000
C	4.74375200	-1.39950300	2.12111300
C	4.87099700	-1.36064400	3.64849200
C	5.30301500	-2.80681500	4.01351100
C	5.15635000	-3.58428200	2.68596800
H	4.64597500	-4.54241500	2.78708100
H	6.13715700	-3.75242800	2.21591400
H	4.65695400	-3.22620300	4.78960700
H	6.33266400	-2.85099900	4.38141500
H	3.90218800	-1.12352100	4.09840200
H	5.58915300	-0.60574500	3.98247600
H	5.71037500	-1.18618300	1.63715000
H	3.97192700	-0.75292300	1.70433300
O	3.96265400	-2.89692100	-1.24261100
C	4.15329300	-1.66641200	-1.97670400
C	5.66736100	-1.51931100	-2.09400800
C	6.10493000	-2.97960500	-2.29937100
C	5.10653100	-3.76069800	-1.42724800
H	5.51279100	-3.98678500	-0.43537600
H	4.77559400	-4.69558900	-1.89227300
H	7.14315700	-3.16639000	-2.00933700
H	5.99607300	-3.26094600	-3.35289300
H	6.08254300	-1.11683900	-1.16225500
H	5.96632200	-0.86109300	-2.91544800
H	3.68557100	-1.76053700	-2.96710600
H	3.64543600	-0.87993100	-1.41674500
C	-1.51503000	-0.17638200	0.22668800
C	-1.84536300	-0.44825000	1.69914700
C	-1.20945900	-1.77059900	2.15142700
C	0.25653000	-1.91185300	1.72524300
H	0.94831600	-2.11777800	2.54558500
H	-1.29200300	-1.86637700	3.24169400
H	-1.80275900	-2.60067600	1.73700800
H	-1.46939100	0.37646700	2.32054000
H	-2.93302200	-0.47849900	1.84412700
H	-2.04378600	0.71518900	-0.13591800
H	-1.87976600	-1.01959100	-0.37727000
C	0.48845600	1.41686200	0.37083400
H	1.56470800	1.50780400	0.19830000
H	-0.02670400	2.16806100	-0.23925100
H	0.29353100	1.64844600	1.42453600
H	0.22584000	-0.14393800	-1.06548900
H	0.53535900	-3.10042300	1.10964700
N	1.12671500	-4.25508200	0.55746700
Si	1.37571300	-5.47145200	1.78052500
C	1.63641400	-4.65494500	3.48143500

H	0.70377700	-4.21683300	3.85670300
H	1.96394900	-5.40220500	4.21600600
H	2.38616800	-3.85637600	3.45547900
C	2.91127700	-6.54384200	1.41433800
H	3.16537900	-7.18541600	2.26887500
H	2.73818800	-7.20031100	0.55365900
H	3.79389400	-5.93584500	1.17936200
C	-0.06470900	-6.69355700	2.02745800
H	-0.99450400	-6.17015100	2.28113600
H	-0.26010400	-7.30206300	1.13646400
H	0.15965700	-7.38502800	2.85064700
Si	0.36497600	-4.64335600	-0.96736400
C	1.07930500	-6.21301000	-1.77852000
H	2.16736500	-6.14017900	-1.90004800
H	0.87287100	-7.11970600	-1.19716400
H	0.64432800	-6.36053600	-2.77584800
C	0.60558700	-3.24015100	-2.22427200
H	0.11766100	-3.49520400	-3.17397900
H	0.17326600	-2.29497400	-1.87738900
H	1.66787800	-3.06777200	-2.42532500
C	-1.51755900	-4.88989200	-0.81657300
H	-1.77853600	-5.74098400	-0.17758600
H	-1.99669900	-3.99999000	-0.38863700
H	-1.97016600	-5.06396900	-1.80185100

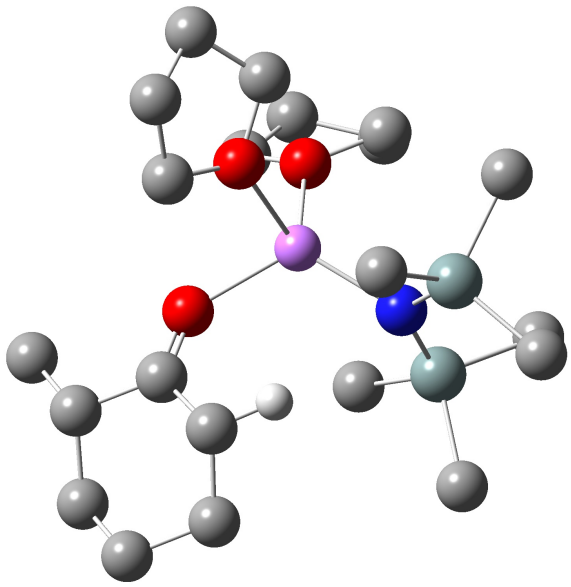
iv. Intrinsic reaction coordinate (IRC) computations

Geometries are optimized at the B3LYP level of theory using the 6–31G(d) basis set. Energies are defined as follows: G is the sum of electronic and thermal free energies calculated at the B3LYP level of theory (T = 195 K). G_{MP2} is derived from an MP2 SP calculation corresponding to the DFT-optimized geometry and includes a thermal correction from the DFT calculation. ΔG^1_{MP2} is the difference between G_{MP2} of the IRC-derived reactants or products, and G_{MP2} of LiHMDS disolvated dimer **1**, 2-methylcyclohexanone **3**, and THF, based on the corresponding stoichiometries ($G_{MP2}^{IRC} - G_{MP2}^{GS}$). ΔG^2_{MP2} is the difference between G_{MP2} of the corresponding transition structure, and G_{MP2} of the IRC-derived reactants or products ($G_{MP2}^{TS} - G_{MP2}^{IRC}$).

Table 51. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of 2-methylcyclohexanone **3** by AS_2 (**20**; Me = *syn*–equatorial).



IRC-R **20** *syn*–eq

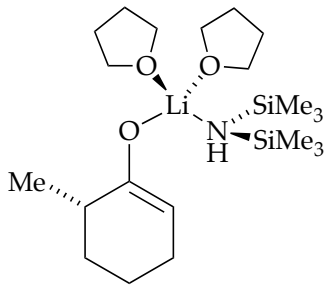


G = –1694.465280 Hartree
G_{MP2} = –1060211.3288 kcal/mol
ΔG^1_{MP2} = –2.3 kcal/mol
ΔG^2_{MP2} = 15.1 kcal/mol

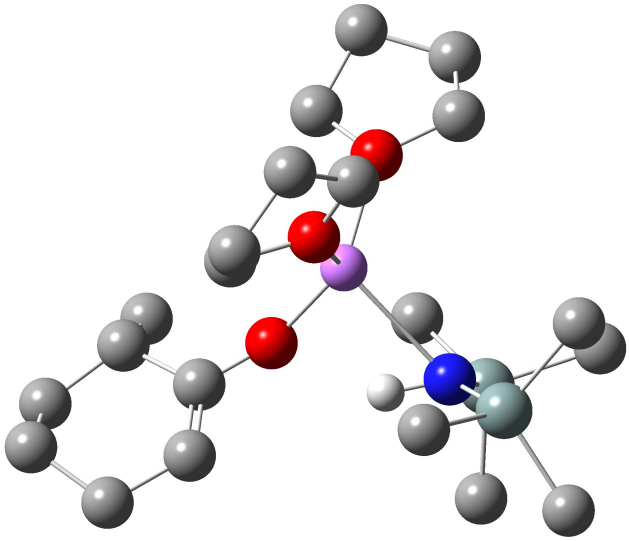
Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	-6.03361400	4.40783400	-2.32711100
C	-1.43216000	-0.38467000	-0.35944400	H	-4.77860100	4.45220000	-1.07316300
O	-2.39333700	0.16475800	0.17268300	H	-4.61462000	3.04575600	-3.79552200
Li	-4.41663800	-0.07857800	-0.10611700	H	-3.42471500	4.16801500	-3.11056100
O	-4.53311400	1.64769100	-1.28755300	H	-2.66980600	2.52667800	-1.49302900
C	-3.50257900	2.20372200	-2.13024100	H	-3.14798500	1.41991200	-2.80688100
C	-4.14776400	3.38475000	-2.86365800	O	-5.28457200	0.82189900	1.51887500
C	-5.22358300	3.83635100	-1.86411700	C	-4.55982700	1.43989500	2.60687800
C	-5.69910500	2.49864400	-1.29701600	C	-5.49192000	1.39394200	3.82958300
H	-6.46731400	2.04163600	-1.93422300	C	-6.46067800	0.25150000	3.47890400
H	-6.07436800	2.55466300	-0.27291200	C	-6.59512500	0.41196800	1.96722200

H	-7.32591200	1.19492500	1.71469500
H	-6.84732800	-0.50078300	1.42500900
H	-7.42088200	0.32768600	3.99809600
H	-6.01734700	-0.72157700	3.71668700
H	-6.04026300	2.33780200	3.93165600
H	-4.94301200	1.22421800	4.76064900
H	-3.63970700	0.86732200	2.76227800
H	-4.28757400	2.46112700	2.31726100
N	-5.14732600	-1.85084500	-0.59293800
Si	-6.15095100	-1.90614000	-1.97380200
C	-5.36168500	-0.98196400	-3.44953300
H	-4.42235700	-1.46132300	-3.75592300
H	-6.02534200	-0.96721300	-4.32424900
H	-5.13320300	0.05653000	-3.18280300
C	-7.85287500	-1.07139300	-1.69387400
H	-8.46831500	-1.06858100	-2.60381300
H	-8.41928000	-1.59824500	-0.91460400
H	-7.74568200	-0.02835800	-1.36547000
C	-6.56413700	-3.64574700	-2.65307200
H	-5.65869500	-4.18699400	-2.95442100
H	-7.08846100	-4.26893100	-1.91744400
H	-7.21224500	-3.57174000	-3.53688600
Si	-4.95075900	-3.10164500	0.54888600
C	-6.55947500	-3.65711600	1.43023400
H	-7.02849300	-2.83531600	1.98769900
H	-7.30327700	-4.02153500	0.70978400
H	-6.37108400	-4.47065800	2.14407500
C	-3.76964500	-2.57229200	1.96133000
H	-3.71331500	-3.35231200	2.73203400
H	-2.74909100	-2.39873700	1.59727200
H	-4.09907400	-1.64758500	2.45111000
C	-4.18438100	-4.72245800	-0.12294900
H	-4.85222600	-5.22656000	-0.83105100
H	-3.23852800	-4.53623900	-0.64817400
H	-3.97600400	-5.42912600	0.69217700
C	-1.60218900	-1.46295000	-1.40972100
C	-0.71902000	-2.69555100	-1.11528200
C	0.73796800	-2.30475900	-0.84136000
C	0.82926100	-1.27682700	0.29312100
H	1.87172000	-0.98471100	0.47025700
H	0.46776600	-1.72667800	1.22901100
H	1.18781100	-1.88474900	-1.75316800
H	1.32504800	-3.19532200	-0.58554600
H	-0.78549600	-3.39313700	-1.95786500
H	-1.12710300	-3.22305600	-0.24368800
H	-1.29412000	-1.02677500	-2.37343100
H	0.41642600	0.44012700	-0.92247700
C	0.07900000	1.03139100	1.12585800
H	-0.33356000	0.62695700	2.05637300
H	1.12183000	1.31289600	1.30878600
H	-0.48546700	1.93576000	0.88093200
H	-2.66352800	-1.72815100	-1.47453500

Table 52. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of 2–methylcyclohexanone **3** from disolvated LiHMDS monomer **7** (Me = *syn*–equatorial).



IRC-P **20** *syn*–eq

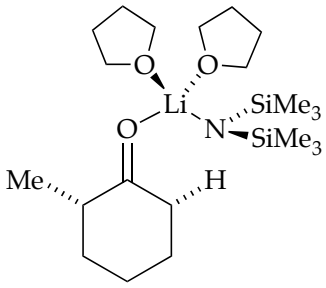


G = –1694.468361 Hartree
G_{MP2} = –1060209.5732 kcal/mol
ΔG^{1}_{MP2} = –0.5 kcal/mol
ΔG^{2}_{MP2} = 13.4 kcal/mol

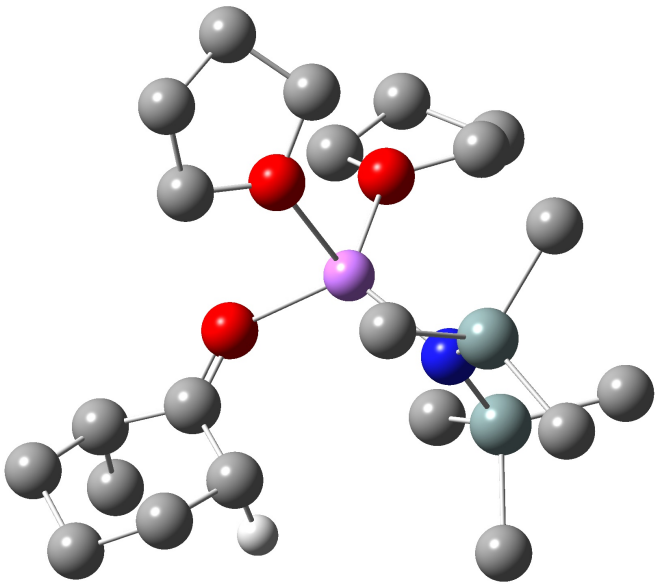
Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000
C	0.96997100	-0.56964400	1.04766700
O	2.18954300	-0.05803500	1.02680000
Li	3.34647200	1.13232000	1.66434800
O	2.62803900	2.01719300	3.30877000
C	1.21036000	1.85392600	3.56734200
C	1.03685500	2.29852000	5.01579400
C	2.02857400	3.47145800	5.10504900
C	3.18196400	3.01038300	4.19807400
H	3.98916800	2.53586200	4.76863300
H	3.60793200	3.82577500	3.60259100
H	2.36326800	3.68146800	6.12520600
H	1.57023200	4.38454600	4.70783600
H	1.32701900	1.49131000	5.69840000
H	0.00749100	2.58879000	5.24644900
H	0.64485800	2.50214300	2.88294800
H	0.95331200	0.81347100	3.35737700
O	4.20123500	2.67873000	0.72742100
C	3.50168100	3.28938900	-0.38575700
C	4.43114800	4.38927300	-0.90658100
C	5.82123200	3.83391200	-0.55751700
C	5.56276000	3.15477000	0.78825300
H	5.65393100	3.86553400	1.62120600
H	6.21296100	2.29816500	0.98490600
H	6.59382900	4.60591900	-0.49456200
H	6.13653200	3.09501600	-1.30306800
H	4.25105100	5.33130700	-0.37523400
H	4.29579400	4.57305500	-1.97629800
H	3.31557100	2.51632500	-1.13916500
H	2.54029400	3.66321500	-0.02182900
N	4.83175800	-0.82895000	1.88852700
Si	5.36114700	-1.10572400	3.54802300
C	3.85366600	-1.02062600	4.68300200
H	3.13508200	-1.81560000	4.45194600
H	4.15344000	-1.13667100	5.73223300
H	3.33120400	-0.06413700	4.57823300
C	6.60234200	0.23987300	4.04415000
H	6.94205400	0.10686200	5.07917400
H	7.49144300	0.22689500	3.40281400
H	6.15381300	1.23843300	3.96633200
C	6.19755000	-2.78989100	3.80319700
H	5.51366600	-3.61213700	3.56104300
H	7.09624900	-2.91482000	3.18753700
H	6.50241300	-2.91138300	4.85082900
Si	5.66550600	-1.31638300	0.40670200
C	7.51218600	-0.90792900	0.54894400
H	7.68254900	0.16217200	0.71999000
H	8.00792800	-1.45625100	1.35848000

H	8.02516900	-1.17578100	-0.38349700
C	4.91373700	-0.37677100	-1.04794100
H	5.21352600	-0.81402000	-2.00826300
H	3.82109900	-0.40747900	-0.97106600
H	5.21643000	0.67678700	-1.04573600
C	5.47155600	-3.17109800	0.07121600
H	5.89944200	-3.78146400	0.87478400
H	4.41109500	-3.43716700	-0.01755700
H	5.96424900	-3.45998800	-0.86627800
C	0.55547500	-1.50948000	1.93962200
C	-0.84012600	-2.08067400	2.01106500
C	-1.85336500	-1.17927000	1.29410500
C	-1.31854500	-0.79139900	-0.08575300
H	-2.06188300	-0.20721900	-0.64674200
H	-1.14462700	-1.70945900	-0.66761100
H	-2.01840300	-0.26902800	1.88937200
H	-2.82571800	-1.68247700	1.20430100
H	-1.14360700	-2.21561000	3.06066000
H	-0.88775800	-3.09187500	1.56660800
H	1.29229300	-1.89473100	2.64531800
H	-0.23882900	1.03032100	0.32097200
C	0.65366500	0.10123300	-1.38665600
H	0.92711300	-0.89433900	-1.75907000
H	-0.03739200	0.55142300	-2.11133400
H	1.56421700	0.70439900	-1.35032000
H	3.81170800	-0.94053000	1.75075500

Table 53. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of 2-methylcyclohexanone **3** from disolvated LiHMDS monomer **7** (Me = *syn*–axial; H = axial).



IRC-R **20** *syn*–ax

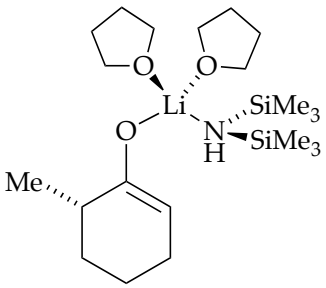


G = –1694.461163 Hartree
G_{MP2} = –1060208.3888 kcal/mol
ΔG^{1}_{MP2} = –1.5 kcal/mol
ΔG^{2}_{MP2} = 12.0 kcal/mol

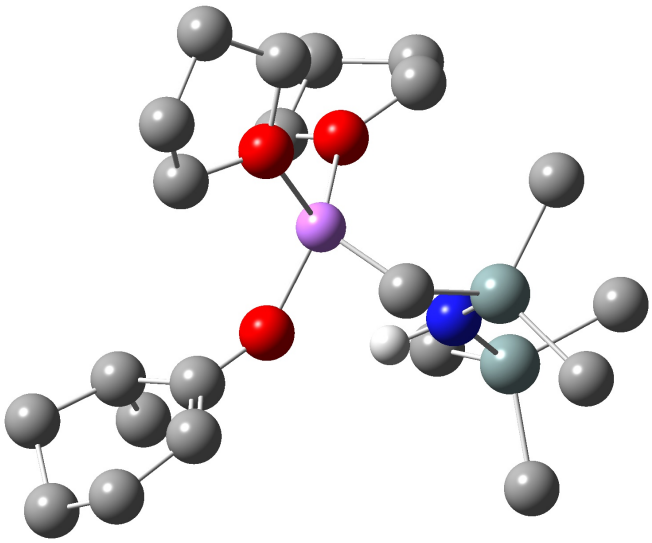
Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000
O	1.92754700	0.07700000	0.70241300
C	2.90348000	-0.64346500	0.50354500
C	4.25068400	-0.30718500	1.13333700
C	5.38650100	-0.42487600	0.08554300
C	5.34949000	-1.74260700	-0.70319300
C	3.98591000	-1.94047700	-1.37825500
H	3.94840400	-2.89742600	-1.91067700
H	3.83491100	-1.15785500	-2.13532400
C	2.83091000	-1.88656700	-0.35479500
H	1.84048500	-1.94416700	-0.81855000
H	5.55565600	-2.59005000	-0.03538200
H	6.14802700	-1.74160500	-1.45516300
H	6.35235800	-0.30138000	0.59192900
H	5.29863400	0.41141100	-0.62253900
C	4.49142500	-1.19910600	2.37220100
H	3.67571400	-1.09475600	3.09552100
H	5.42260000	-0.89857700	2.86542800
H	4.57789700	-2.25899500	2.11292100
H	4.18038400	0.73088100	1.47845100
O	0.28605800	1.68727400	-1.20841300
C	1.52574700	2.15939500	-1.77746600
C	1.17149700	3.41258800	-2.58748400
C	-0.07529300	3.93157400	-1.85521500
C	-0.77523100	2.62648800	-1.47744300
H	-1.38934000	2.24585300	-2.30405000
H	-1.39112700	2.69156000	-0.57806300
H	-0.70202300	4.58170800	-2.47305100
H	0.21179400	4.48707100	-0.95419300
H	0.91968000	3.14256700	-3.61947300
H	1.99260500	4.13521400	-2.61688900
H	2.21718900	2.38493400	-0.95673800
H	1.95384800	1.36011600	-2.39079700
O	-1.10657400	1.02987800	1.39241900
C	-0.56756100	1.66741000	2.57223600
C	-1.75577300	1.88671000	3.51918600
C	-2.73289200	0.78117100	3.08666900
C	-2.51267400	0.74503100	1.57620500
H	-3.10441000	1.52105300	1.06903200
H	-2.71244500	-0.21781400	1.10324400
H	-3.77207100	0.99393200	3.35516400
H	-2.45230600	-0.17905000	3.53360000
H	-2.20299400	2.87424200	3.35407600
H	-1.46429300	1.82143500	4.57175200
H	0.18522600	0.99963900	3.00582400
H	-0.07453200	2.59865400	2.27348500
N	-0.77427000	-1.71262200	-0.61077300
Si	-1.42805700	-1.72727300	-2.18833400

C	-0.21949400	-0.95371600	-3.45228300
H	0.70969600	-1.53666400	-3.50878100
H	-0.64917100	-0.91915500	-4.46228300
H	0.04745300	0.06990400	-3.16472100
C	-3.04683700	-0.71293400	-2.32387000
H	-3.42852100	-0.66317200	-3.35270500
H	-3.83374000	-1.15760300	-1.70048500
H	-2.90388800	0.31870100	-1.97433800
C	-1.85262700	-3.44405000	-2.91869200
H	-0.96066000	-4.07708400	-3.00530000
H	-2.58408700	-3.99092800	-2.31048600
H	-2.27974800	-3.33938300	-3.92529900
Si	-0.95586500	-2.93788500	0.56014400
C	-2.76801800	-3.36586600	1.01534100
H	-3.30625500	-2.49516600	1.41350400
H	-3.32945200	-3.71548900	0.13941200
H	-2.82098000	-4.15799600	1.77480100
C	-0.14221100	-2.43099100	2.21910300
H	-0.33453600	-3.18439800	2.99420100
H	0.94635600	-2.32574100	2.12860500
H	-0.53071900	-1.47233600	2.58429200
C	-0.15083700	-4.61856900	0.12223300
H	-0.62563000	-5.07721700	-0.75314900
H	0.91652000	-4.50668000	-0.10998100
H	-0.23470000	-5.33168000	0.95381300
H	2.91721600	-2.75123900	0.32099600

Table 54. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of 2–methylcyclohexanone **3** from disolvated LiHMDS monomer **7** (Me = *syn*–axial).



IRC-P **20** *syn*–ax

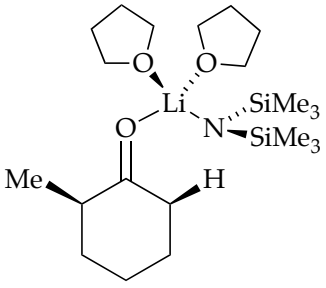


G = –1694.467838 Hartree
G_{MP2} = –1060209.1329 kcal/mol
ΔG^{1}_{MP2} = –2.2 kcal/mol
ΔG^{2}_{MP2} = 12.7 kcal/mol

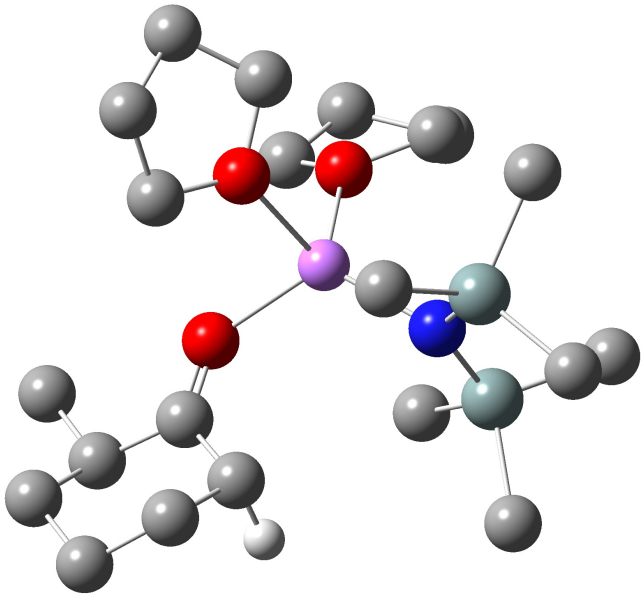
Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000
O	-1.20755100	-1.20675300	-0.49094800
C	-2.44757400	-1.66127200	-0.40143300
C	-3.43724400	-1.03670500	-1.39238500
C	-4.90388200	-1.35480300	-1.03633300
C	-5.09123600	-2.82973000	-0.66502800
C	-4.25028800	-3.17604300	0.57106500
H	-4.21269100	-4.26982100	0.69245600
H	-4.77320100	-2.80698200	1.47263900
C	-2.85230200	-2.61095500	0.48292400
H	-2.10499100	-3.02055100	1.16352200
H	-4.77923100	-3.46180400	-1.50748500
H	-6.15213600	-3.04842000	-0.48327200
H	-5.56107400	-1.07598500	-1.87234000
H	-5.21113400	-0.73742500	-0.17923200
C	-3.09090200	-1.42846900	-2.84130500
H	-2.04276300	-1.20042000	-3.05771600
H	-3.71924100	-0.88431300	-3.55880200
H	-3.23918500	-2.50181900	-3.00948500
H	-3.29508700	0.05385400	-1.31797100
O	-0.62690700	1.00206500	1.61973900
C	-2.02799900	0.85609200	1.96482500
C	-2.13534000	1.45018300	3.36525800
C	-1.15882500	2.63546200	3.27884600
C	-0.04658000	2.09423700	2.36422800
H	0.80056000	1.69683400	2.93598300
H	0.32934100	2.84544300	1.66046100
H	-0.77503400	2.95453900	4.25235400
H	-1.65148300	3.49730600	2.81400900
H	-1.79917800	0.72293100	4.11342300
H	-3.15615900	1.75310400	3.61671900
H	-2.63574200	1.42181800	1.24466300
H	-2.28171800	-0.20198500	1.87773200
O	0.83587200	1.45567000	-1.07650700
C	0.11813900	1.99659500	-2.21407400
C	1.03425400	3.07077900	-2.80554600
C	2.43169500	2.53331400	-2.45794900
C	2.20259600	1.92168300	-1.07470100
H	2.32008800	2.67045200	-0.27941800
H	2.85194200	1.07026900	-0.85347800
H	3.20472200	3.30736500	-2.44896700
H	2.73264900	1.75903400	-3.17293700
H	0.86309200	4.03686200	-2.31602000
H	0.87746700	3.20313700	-3.87994400
H	-0.07089300	1.18139300	-2.92101700
H	-0.84131000	2.38318100	-1.85897600
N	1.43878800	-1.98112800	0.30405600
Si	2.01347100	-2.17906200	1.95963200

C	0.54354900	-1.98104400	3.12969400
H	-0.22220100	-2.74307200	2.94367900
H	0.86402700	-2.07689000	4.17481700
H	0.07144000	-1.00119100	3.00349100
C	3.30408500	-0.84422500	2.34644000
H	3.67448600	-0.93506900	3.37548700
H	4.17113000	-0.90923000	1.67865500
H	2.87513600	0.15972500	2.23452600
C	2.80905300	-3.87078700	2.28609000
H	2.09399800	-4.68426100	2.11493800
H	3.68202600	-4.05838400	1.64976400
H	3.14592900	-3.94050300	3.32862300
Si	2.20710600	-2.57882000	-1.17182000
C	4.06409800	-2.19847900	-1.12254300
H	4.25609500	-1.12416700	-1.01130300
H	4.58176200	-2.71438900	-0.30548600
H	4.53651300	-2.52094800	-2.05907000
C	1.41805800	-1.71537100	-2.65459700
H	1.67398100	-2.21554100	-3.59662600
H	0.32861100	-1.72139500	-2.53534000
H	1.73779300	-0.66944900	-2.72761900
C	1.96483100	-4.44626100	-1.38374500
H	2.41481800	-5.01514700	-0.56206400
H	0.89644900	-4.69337500	-1.41135100
H	2.41089700	-4.80361600	-2.32096700
H	0.41093600	-2.07098100	0.20706700

Table 55. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of 2-methylcyclohexanone **3** from disolvated LiHMDS monomer **7** (Me = *anti*–equatorial; H = axial).



IRC-R **20** *anti*–eq

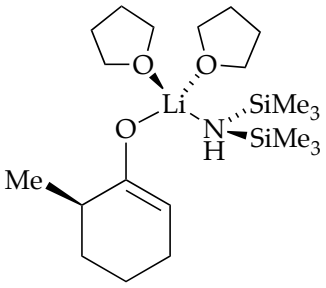


G = –1694.46459 Hartree
G_{MP2} = –1060210.7786 kcal/mol
ΔG^{1}_{MP2} = –1.7 kcal/mol
ΔG^{2}_{MP2} = 12.1 kcal/mol

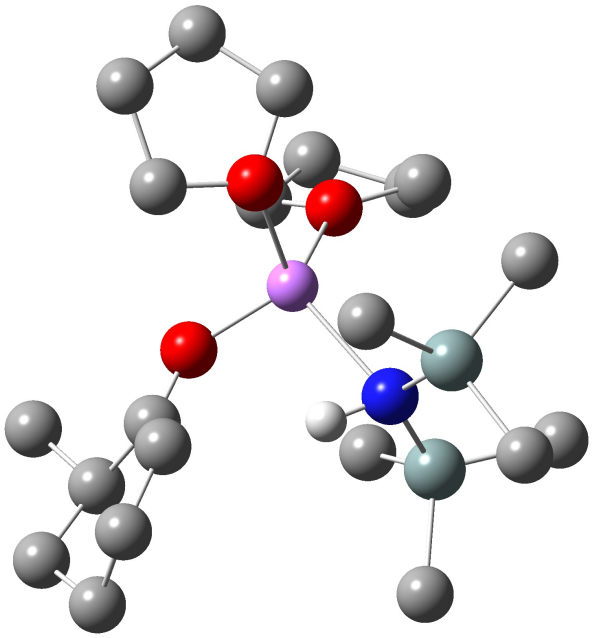
Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000
O	-1.87795200	-0.29428900	-0.78840100
C	-2.64207200	-1.25466800	-0.73992900
C	-2.30650700	-2.51971500	0.01997300
C	-3.43780000	-2.89671300	1.00132600
C	-4.79807900	-2.94921900	0.29423500
C	-5.10372700	-1.62731500	-0.42215500
H	-6.06210500	-1.68625700	-0.95255300
H	-5.20877100	-0.82217900	0.32009400
C	-3.99877200	-1.22792400	-1.43617000
C	-4.28941400	0.09870900	-2.13747700
H	-5.25275100	0.05021600	-2.65689200
H	-4.33103200	0.92339100	-1.41755500
H	-3.51396800	0.33984200	-2.87015100
H	-3.95291200	-2.03226200	-2.18924800
H	-4.79838900	-3.77005300	-0.43754400
H	-5.59302000	-3.17364700	1.01612100
H	-3.20252700	-3.85923800	1.46916000
H	-3.47498800	-2.15675200	1.81335600
H	-1.33497100	-2.39835900	0.51023700
O	-0.71392100	1.36591900	1.40690800
C	-2.01856600	1.38120800	2.02361500
C	-1.98736800	2.51665100	3.05320200
C	-0.95110200	3.47577000	2.44725400
C	0.06223100	2.49792700	1.85325800
H	0.78446400	2.16049600	2.60819700
H	0.60628800	2.88360800	0.98854700
H	-0.50255400	4.15056600	3.18250400
H	-1.40695200	4.08420700	1.65680500
H	-1.63668400	2.14332800	4.02222500
H	-2.97081400	2.97312800	3.20079000
H	-2.76707800	1.55914100	1.24185200
H	-2.20242200	0.40024800	2.47310900
O	0.82936200	1.45863400	-1.18164800
C	0.15997500	2.11328100	-2.28277000
C	1.26838500	2.66971300	-3.18884700
C	2.45979200	1.75365500	-2.86259300
C	2.26268700	1.50791400	-1.36886700
H	2.67413500	2.33510100	-0.77211300
H	2.66635300	0.56490100	-0.99672300
H	3.42836700	2.20925500	-3.08972600
H	2.38617100	0.81017600	-3.41466900
H	1.50234000	3.70622000	-2.91833900
H	0.98593700	2.65432600	-4.24578800
H	-0.45712800	1.36724900	-2.79518900
H	-0.49880500	2.89164400	-1.88237100
N	1.17662400	-1.54025800	0.38705100
Si	1.84422900	-1.60927400	1.95760300

C	0.51218200	-1.31571900	3.29782500
H	-0.26097700	-2.09482600	3.25839700
H	0.93940900	-1.32572000	4.30939800
H	0.01691600	-0.34872200	3.15151500
C	3.17902700	-0.26781500	2.25422600
H	3.55471100	-0.27191200	3.28652800
H	4.03900600	-0.42389800	1.58967400
H	2.79144500	0.73937600	2.04801400
C	2.67761700	-3.25765800	2.45467500
H	1.96525500	-4.09175800	2.43460900
H	3.51087800	-3.52267400	1.79169500
H	3.08073600	-3.19386800	3.47444700
Si	1.61624300	-2.52918700	-0.93034700
C	3.46814600	-2.45599800	-1.41865800
H	3.77421600	-1.44372400	-1.71543500
H	4.11469600	-2.75399200	-0.58335200
H	3.69292900	-3.12501500	-2.26059400
C	0.67242600	-2.02654700	-2.52061800
H	1.04504400	-2.58993100	-3.38625300
H	-0.40343600	-2.22742200	-2.44118500
H	0.78681900	-0.95892500	-2.74632500
C	1.23538800	-4.39399200	-0.72344500
H	1.83931600	-4.84702800	0.07149600
H	0.18191800	-4.56386100	-0.46468400
H	1.44145400	-4.94841100	-1.64939300
H	-2.19978000	-3.32647500	-0.72096200

Table 56. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of 2–methylcyclohexanone **3** from disolvated LiHMDS monomer **7** (Me = *anti*–equatorial).



IRC-P **20** *anti*–eq



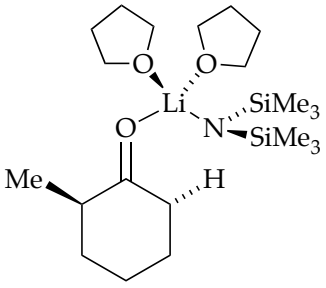
G = –1694.46681 Hartree
G_{MP2} = –1060211.3462 kcal/mol
ΔG^{1}_{MP2} = –2.3 kcal/mol
ΔG^{2}_{MP2} = 12.7 kcal/mol

Atom	X	Y	Z
Li	0.00000000	0.00000000	0.00000000
O	1.20444400	-1.27003500	-0.47180900
C	2.48053600	-1.39562000	-0.18218500
C	3.06832800	-0.91362300	0.95726200
C	4.53896500	-1.01771900	1.28712900
C	5.37619500	-1.30925200	0.03596400
C	4.74525100	-2.45864900	-0.75286400
H	5.37513300	-2.74281500	-1.60770900
H	4.69028800	-3.34474500	-0.10164200
C	3.32850600	-2.11511800	-1.24711800
C	2.61458900	-3.37075200	-1.77060300
H	3.19885600	-3.84748800	-2.56834100
H	2.48448300	-4.10608900	-0.96569300
H	1.62440900	-3.12194900	-2.15939800
H	3.42352400	-1.41927600	-2.09863200
H	5.41538900	-0.41065200	-0.59785200
H	6.41200800	-1.55029700	0.31097300
H	4.89523000	-0.08941600	1.76084400
H	4.73239500	-1.81194600	2.03210900
H	2.41684000	-0.49724300	1.72701900
O	-0.91078700	-0.64787100	1.71698900
C	-0.35094200	-1.88948900	2.24156800
C	-1.54102100	-2.70313600	2.77910800
C	-2.75388900	-2.05847700	2.08654300

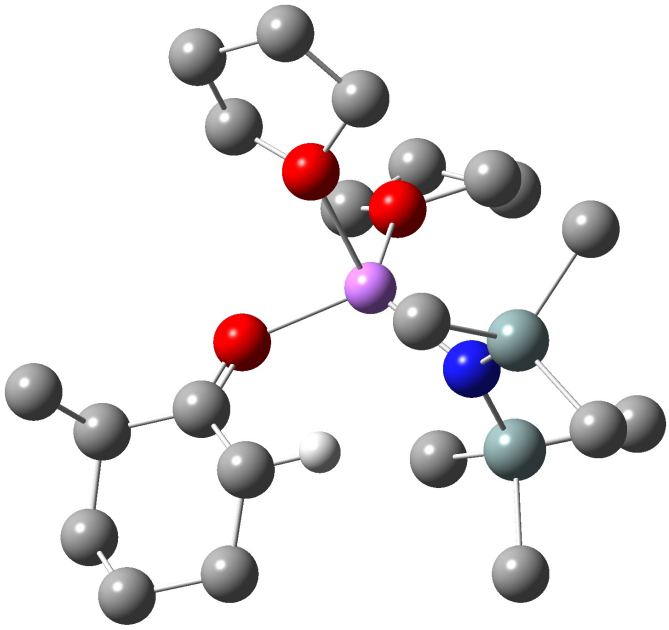
Atom	X	Y	Z
C	-2.31779100	-0.59764600	1.99777300
H	-2.48948400	-0.07142000	2.94886500
H	-2.79435500	-0.03768700	1.18966100
H	-3.68922800	-2.19057100	2.63934700
H	-2.88834100	-2.47043000	1.07945400
H	-1.62701900	-2.59454200	3.86643800
H	-1.44167700	-3.76992200	2.55837200
H	0.17493800	-2.36192000	1.40962900
H	0.37525300	-1.63968300	3.02122500
O	-1.60625500	-0.01377900	-1.22994000
C	-1.65808700	-1.21121000	-2.05606000
C	-2.70600300	-0.92933000	-3.13930100
C	-2.68947600	0.60471000	-3.23744700
C	-2.45664200	1.00817900	-1.78178800
H	-3.40257300	1.03701600	-1.22112200
H	-1.95084200	1.97003300	-1.66064800
H	-3.61412600	1.02318000	-3.64631000
H	-1.85540000	0.94060200	-3.86363100
H	-3.69603600	-1.27810100	-2.82237800
H	-2.46346300	-1.42238200	-4.08509600
H	-0.65462400	-1.37730600	-2.45583300
H	-1.91672200	-2.05887300	-1.41450100
N	1.26875100	1.90981700	0.17913800
Si	0.87319400	2.90411500	1.59894700

C	1.03285600	1.83120100	3.14375100
H	2.05919300	1.47149800	3.28210800
H	0.76171200	2.40773100	4.03728300
H	0.37281500	0.96015700	3.08254100
C	-0.90844800	3.52608200	1.44335000
H	-1.19103600	4.11360600	2.32599200
H	-1.04831600	4.16658900	0.56544500
H	-1.61248900	2.68873000	1.36404300
C	2.01912400	4.40234700	1.81337400
H	3.06459800	4.08829300	1.91912900
H	1.96806900	5.10568500	0.97449900
H	1.74991800	4.95762800	2.72130300
Si	1.74848300	2.54622900	-1.41644900
C	0.73673000	4.09688500	-1.82205900
H	-0.34127500	3.89494700	-1.82167300
H	0.92104300	4.92870400	-1.13382500
H	1.00037100	4.44399400	-2.82928600
C	1.41839000	1.25511700	-2.75401100
H	2.02622700	1.45119100	-3.64615900
H	1.64110800	0.24734500	-2.38683100
H	0.36566200	1.26410300	-3.06004700
C	3.59265500	2.97218500	-1.42058700
H	3.83569200	3.75221500	-0.68981100
H	4.19103300	2.08687100	-1.17271700
H	3.91731300	3.32525500	-2.40762600
H	1.94551100	1.17341300	0.43586400

Table 57. Geometric coordinates and thermally corrected MP2 energies for IRC-derived reactants leading to enolization of 2-methylcyclohexanone **3** from disolvated LiHMDS monomer **7** (Me = *anti*–axial; H = equatorial).



IRC-R **20** *anti*–ax

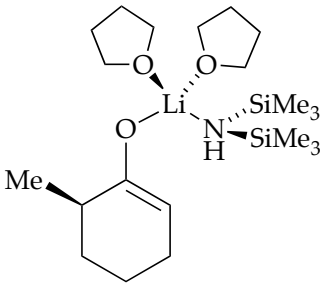


G = –1694.460816 Hartree
G_{MP2} = –1060208.0737 kcal/mol
ΔG^{1}_{MP2} = –1.2 kcal/mol
ΔG^{2}_{MP2} = 12.1 kcal/mol

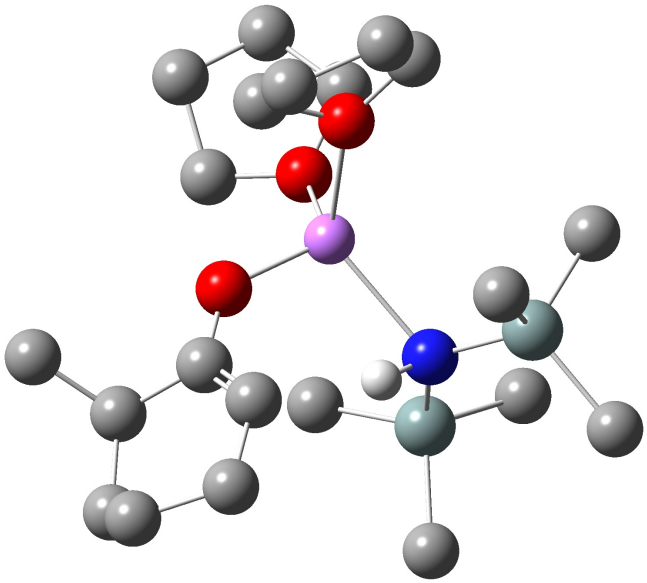
Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	-8.12516900	0.60098600	2.66698200
C	-1.36936400	-0.43030200	-0.51379000	H	-6.85817900	-0.63988600	2.72384700
O	-2.38149100	0.15911300	-0.13795200	H	-6.49716600	2.39179300	3.03456100
Li	-4.33777100	-0.06958600	-0.67900600	H	-5.85639300	1.13322000	4.10354900
O	-4.29632700	1.74262500	-1.84975900	H	-4.15836700	0.49876000	2.50534500
C	-3.68990300	2.88242800	-1.22417900	H	-4.32636600	2.20279400	2.02610000
C	-3.62311000	3.94783600	-2.32849100	C	0.86856200	-1.22778700	0.36734000
C	-4.82157500	3.58656500	-3.24883400	C	0.89576400	-2.29819900	-0.73375400
C	-5.36774700	2.27545400	-2.64510200	C	-0.52594300	-2.75199400	-1.08785400
H	-5.63810000	1.52011900	-3.38207400	C	-1.42270200	-1.56756300	-1.50925800
H	-6.23677200	2.46906300	-1.99864000	H	-1.06122600	-1.16853700	-2.47034100
H	-4.49034100	3.43511700	-4.28001400	H	-0.51040100	-3.49291400	-1.89502000
H	-5.58892300	4.36639600	-3.26009900	H	-0.97821000	-3.24961900	-0.21956700
H	-2.67927200	3.87071900	-2.87689600	H	1.39571000	-1.90849300	-1.63119200
H	-3.68976000	4.96137500	-1.92137500	H	1.49210000	-3.15473600	-0.39651900
H	-4.32238500	3.21394200	-0.38687200	H	1.88427400	-0.88693400	0.60574000
H	-2.72323200	2.56658800	-0.83130600	H	0.46792100	-1.67814500	1.28605700
O	-5.36254400	0.83750000	0.85797600	C	0.67870100	0.91244300	-1.04723300
C	-4.86427800	1.25671600	2.14832200	H	0.04988200	1.77866700	-1.28088600
C	-6.09158800	1.37339000	3.06237500	H	1.63063000	1.28326100	-0.65109900
C	-7.08108200	0.38839300	2.41814000	H	0.88858100	0.38576600	-1.98360000
C	-6.78353400	0.57456200	0.93178100	H	-0.18083300	0.60110200	0.89867200
H	-7.32828300	1.43745800	0.52211500	H	-2.46947400	-1.86263300	-1.64655800
H	-6.98255900	-0.30274400	0.31246600	N	-5.00272000	-1.83245400	-1.28675400

Si	-5.65166200	-1.88420300	-2.86548800
C	-4.46214900	-1.05805400	-4.11851300
H	-3.59846300	-1.71290600	-4.29652000
H	-4.93977700	-0.87964900	-5.09143800
H	-4.06844900	-0.10138800	-3.75366600
C	-7.33977800	-0.98598400	-2.99635300
H	-7.69977400	-0.91151700	-4.03166100
H	-8.09777600	-1.53838100	-2.42506600
H	-7.30833000	0.02972600	-2.58140400
C	-5.98520000	-3.61483400	-3.60779000
H	-5.06540600	-4.20740800	-3.68396400
H	-6.70165400	-4.19461700	-3.01219200
H	-6.40277300	-3.52253700	-4.61965100
Si	-5.08118900	-3.08288500	-0.12811700
C	-6.85469800	-3.56535800	0.41139100
H	-7.39111900	-2.71115900	0.84640300
H	-7.44898500	-3.91497900	-0.44276000
H	-6.85315200	-4.36897100	1.16040200
C	-4.18848100	-2.57492500	1.48713400
H	-4.23672600	-3.37904100	2.23303700
H	-3.12810700	-2.34952400	1.31443500
H	-4.64025000	-1.68196500	1.93533100
C	-4.24606500	-4.72803700	-0.63614700
H	-4.76042100	-5.20604700	-1.47793500
H	-3.20286500	-4.57054000	-0.94083600
H	-4.24157900	-5.44461500	0.19665500

Table 58. Geometric coordinates and thermally corrected MP2 energies for IRC-derived products leading to enolization of 2–methylcyclohexanone **3** from disolvated LiHMDS monomer **7** (Me = *anti*–axial).



IRC-P **20** *anti*–ax



G = –1694.464806 Hartree
G_{MP2} = –1060209.5662 kcal/mol
ΔG^{1}_{MP2} = –2.7 kcal/mol
ΔG^{2}_{MP2} = 13.6 kcal/mol

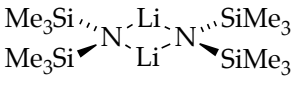
Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	-7.43750200	1.50466600	-1.68510200
C	-0.81282600	0.95228800	0.88772000	H	-6.51308600	1.95237600	-3.12571400
O	-2.06206500	1.13225800	0.50892400	H	-5.64944000	-0.00526100	-0.92807900
Li	-3.13746600	2.59013300	0.42289800	H	-5.59561100	-0.26440300	-2.68302900
O	-4.63279700	2.21344100	1.89385200	H	-3.79123000	1.37250800	-2.94261400
C	-4.58406300	0.81978000	2.27274000	H	-3.32183500	0.63192500	-1.37992300
C	-4.58864600	0.85339500	3.80218500	C	1.51495400	0.08364500	0.27190800
C	-5.45747900	2.09592100	4.13200700	C	1.82406800	0.08785600	1.77279600
C	-5.57625300	2.83654700	2.77781600	C	1.18269200	1.30896700	2.44575100
H	-5.32836900	3.89861900	2.83193800	C	-0.24290800	1.52695400	1.98879200
H	-6.58870000	2.73462600	2.35917300	H	-0.88306600	2.12983500	2.63388900
H	-4.98373400	2.72325800	4.89232000	H	1.21681500	1.18241100	3.53893700
H	-6.44657300	1.81537700	4.50744200	H	1.81110000	2.19560800	2.24177900
H	-3.56654800	0.98646300	4.16923500	H	1.42966200	-0.82932000	2.23091700
H	-4.98581600	-0.06867600	4.23716200	H	2.90937600	0.08166600	1.94134600
H	-5.48078200	0.31198900	1.88223500	H	2.03150100	-0.74687600	-0.22984800
H	-3.68349800	0.41032100	1.81123000	H	1.91232900	1.00929800	-0.17038800
O	-4.31550100	2.41389100	-1.21314300	C	-0.53924000	-1.43811300	0.12792700
C	-4.11477400	1.15882600	-1.91414700	H	-1.62084500	-1.45229700	-0.03799600
C	-5.48327700	0.48575900	-1.89422600	H	-0.06619800	-2.10453800	-0.60494600
C	-6.42795500	1.68736400	-2.06558500	H	-0.34873200	-1.84653700	1.12768300
C	-5.70545100	2.80076200	-1.28796900	H	-0.18278500	0.31248300	-1.03921700
H	-6.07736900	2.89479500	-0.26221100	H	-1.12345300	3.58916100	1.00956500
H	-5.77804000	3.77720300	-1.78035900	N	-1.69333200	4.34363100	0.59631900

Si	-2.16668300	5.51386000	1.84678000
C	-2.27349000	4.59346100	3.49409400
H	-1.27844300	4.29539700	3.84417600
H	-2.71720500	5.23319800	4.26747100
H	-2.87868700	3.68514000	3.41072600
C	-3.85218700	6.25071600	1.39680000
H	-4.21679200	6.90632000	2.19780200
H	-3.80302800	6.84960100	0.48079700
H	-4.60362400	5.46825200	1.23708600
C	-0.93403500	6.93849800	2.06785100
H	0.05925100	6.56350800	2.34206900
H	-0.81991000	7.54858100	1.16465700
H	-1.26673700	7.60714700	2.87254700
Si	-0.96879300	4.79317800	-0.97286300
C	-1.84867100	6.32176000	-1.66163300
H	-2.92205400	6.14181700	-1.79395400
H	-1.72998900	7.21344200	-1.03616100
H	-1.43440200	6.56165700	-2.64910700
C	-1.17232700	3.38656800	-2.21028300
H	-0.58008500	3.57876200	-3.11398900
H	-0.85154300	2.42964800	-1.78603500
H	-2.22189400	3.28052700	-2.50269400
C	0.87870900	5.15194500	-0.76349700
H	1.06411000	6.00625300	-0.10266400
H	1.39348400	4.28317200	-0.33486000
H	1.34981900	5.36960400	-1.73051600

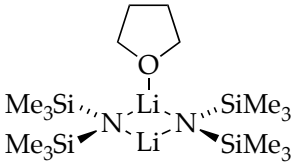
VIII. Appendix B

Computational studies of lithium hexamethyldisilazide (LiHMDS) solution structures

Chart 4. LiHMDS solution structures



21



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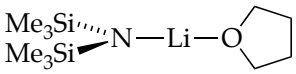

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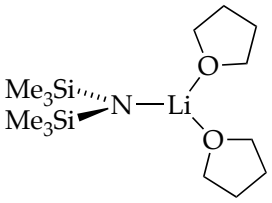

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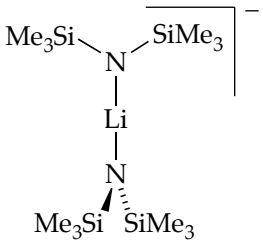

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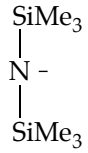

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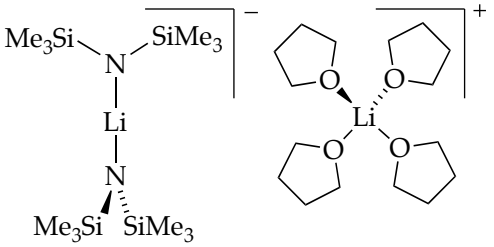
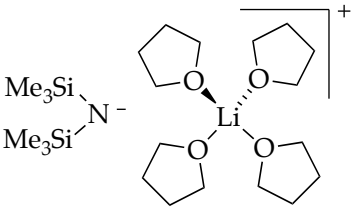
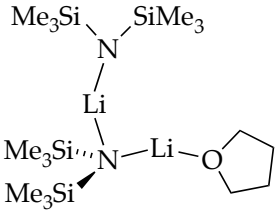


27



28



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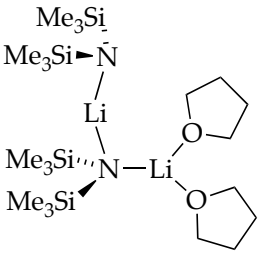

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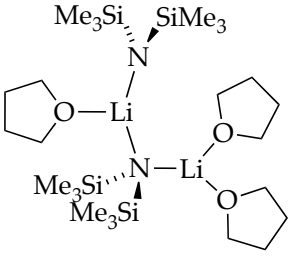
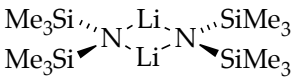


31

LiHMDS ground state computations

Geometries are optimized at the B3LYP level of theory using the 6–31G(d) basis set. Energies are defined as follows: G is the sum of electronic and thermal free energies calculated at the B3LYP level of theory (T = 195 K). G_{MP2} is derived from an MP2 SP calculation corresponding to the DFT-optimized geometry and includes a thermal correction from the DFT calculation.

Table 59. Geometric coordinates and thermally corrected MP2 energies for unsolvated LiHMDS cyclic dimer **21**.



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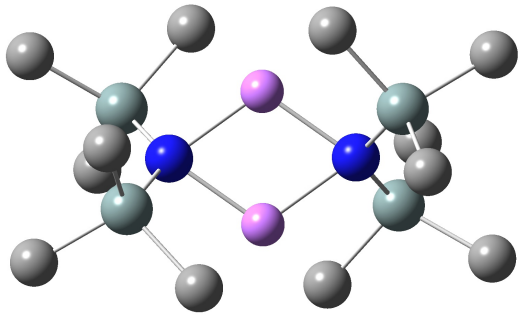
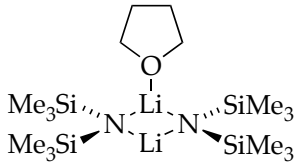


G = –1761.437553 Hartree
G_{MP2} = –1102571.6121 kcal/mol

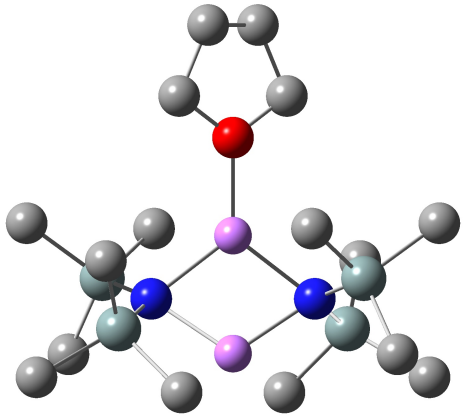
Atom	X	Y	Z
Si	0.00000000	0.00000000	0.00000000
C	-0.37990700	1.52130000	-1.07162800
H	-1.06360700	1.26136600	-1.88924000
H	-0.84946900	2.32540100	-0.49054400
H	0.53168600	1.93075700	-1.52561200
C	-1.59194200	-0.47794700	0.92187100
H	-2.39340100	-0.77576500	0.23538200
H	-1.41989400	-1.31613600	1.60883700
H	-1.96959100	0.36442500	1.51566700
N	0.77488500	-1.28419600	-0.84968600
Si	0.00000100	-2.56839300	-1.69937200
C	-0.37991000	-4.08969200	-0.62774400
H	0.53168100	-4.49914800	-0.17375400
H	-1.06361400	-3.82975800	0.18986400
H	-0.84946800	-4.89379400	-1.20882900
C	1.22317600	-3.15333300	-3.06637900
H	0.79801800	-4.01110100	-3.60162600
H	1.40467300	-2.38676300	-3.83821700
H	2.19599900	-3.49486900	-2.68065800
C	-1.59193800	-2.09044700	-2.62124900
H	-2.39340000	-1.79263200	-1.93476200
H	-1.41988900	-1.25225600	-3.30821200
H	-1.96958300	-2.93281900	-3.21504800
Li	2.38749200	-1.28418700	0.30114600
N	4.00009700	-1.28419700	-0.84968600
Si	4.77497900	0.00000200	-1.69937200
C	5.15487700	1.52130400	-0.62774300
H	5.83856600	1.26137100	0.18987700
H	5.62444700	2.32540200	-1.20882400
H	4.24327900	1.93076500	-0.17377100
C	3.55180800	0.58493200	-3.06638500
H	3.97696300	1.44270100	-3.60163300
H	3.37031800	-0.18164200	-3.83822100
H	2.57898200	0.92646300	-2.68066800
C	6.36692500	-0.47793900	-2.62123700
H	7.16838600	-0.77574600	-1.93474500
H	6.19488500	-1.31613500	-3.30819700
H	6.74456800	0.36443100	-3.21503900
Si	4.77497700	-2.56839600	0.00000000
C	5.15487700	-4.08969800	-1.07162800
H	4.24328100	-4.49915800	-1.52560300
H	5.83856900	-3.82976500	-1.88924700
H	5.62444600	-4.89379600	-0.49054700
C	3.55180400	-3.15332800	1.36701100

H	3.97696100	-4.01109300	1.90226200
H	3.37030600	-2.38675300	2.13884400
H	2.57898100	-3.49486400	0.98129000
C	6.36692200	-2.09045500	0.92187000
H	7.16838400	-1.79264900	0.23537900
H	6.19488000	-1.25225900	1.60882900
H	6.74456300	-2.93282600	1.51567200
Li	2.38749100	-1.28420500	-2.00051800
C	1.22317200	0.58493700	1.36701000
H	1.40467100	-0.18163600	2.13884400
H	2.19599300	0.92647700	0.98129100
H	0.79801100	1.44270100	1.90226100

Table 60. Geometric coordinates and thermally corrected MP2 energies for monosolvated LiHMDS cyclic dimer **22** with one THF.



22

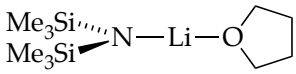


G = –1993.794164 Hartree
G_{MP2} = –1247895.0782 kcal/mol

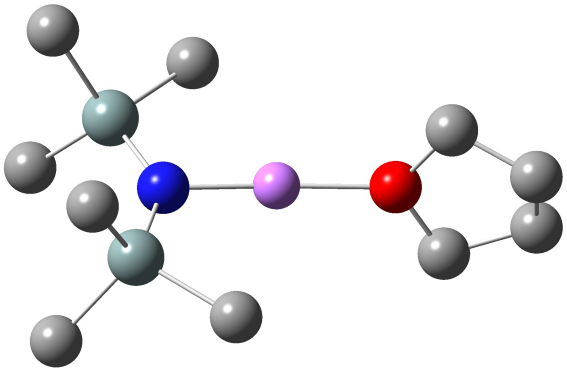
Atom	X	Y	Z
Si	0.00000000	0.00000000	0.00000000
C	-0.25517600	1.35053700	1.31594900
H	-1.00113900	2.07950400	0.97407100
H	-0.61226900	0.93601400	2.26752700
H	0.67280300	1.89854200	1.52133400
C	-1.63649400	-0.96616300	-0.11391000
H	-2.46653300	-0.35202900	-0.48194500
H	-1.54986600	-1.83475000	-0.77813100
H	-1.92377400	-1.33862400	0.87810500
N	0.64853400	0.59804900	-1.48532200
Si	-0.32786900	1.00462700	-2.85396900
C	-0.99968000	-0.50812200	-3.79654100
H	-0.18747200	-1.16644400	-4.13177000
H	-1.67029600	-1.10913300	-3.17118000
H	-1.56471500	-0.20548800	-4.68801400
C	0.70477100	1.99682400	-4.11559100
H	0.08707000	2.26730600	-4.98165500
H	1.09161800	2.93099500	-3.68759900
H	1.55998600	1.42592100	-4.49755200
C	-1.83185400	2.10478700	-2.44464100
H	-2.55596700	1.59537600	-1.79781600
H	-1.53154800	3.02688400	-1.93041900
H	-2.36351300	2.39601900	-3.36002700
Li	2.27691800	-0.49466200	-1.50111000
N	3.90530600	0.59803300	-1.51696800
Si	4.88171300	1.00461300	-0.14832300
C	5.55351800	-0.50813600	0.79425300
H	6.22412900	-1.10915300	0.16889300
H	6.11855700	-0.20550200	1.68572300
H	4.74130700	-1.16645100	1.12948800
C	3.84908000	1.99681800	1.11329800
H	4.46678200	2.26729600	1.97936300
H	3.46224100	2.93099000	0.68530300
H	2.99385900	1.42592300	1.49525800
C	6.38570100	2.10476800	-0.55765500
H	7.10981000	1.59535500	-1.20448100
H	6.08539600	3.02686500	-1.07187700
H	6.91736300	2.39600000	0.35772800
Si	4.55382900	-0.00002700	-3.00229200
C	4.80901100	1.35050800	-4.31824300
H	3.88103600	1.89852100	-4.52362700
H	5.55497900	2.07947000	-3.97636400
H	5.16609900	0.93598400	-5.26982100
C	3.30075300	-1.26857300	-3.72049400
H	3.65365300	-1.63915000	-4.69116200
H	3.20340600	-2.15968900	-3.07830800
H	2.29514900	-0.86262900	-3.89676300
C	6.19032000	-0.96619700	-2.88838800
H	7.02036300	-0.35206800	-2.52035400
H	6.10368900	-1.83478500	-2.22416700
H	6.47759600	-1.33865900	-3.88040400
Li	2.27692600	1.85694100	-1.50117100
O	2.27694000	3.81006300	-1.50115800
C	3.34939400	4.63995900	-2.01887000
C	2.77262000	6.05405500	-2.08824000
C	1.78127500	6.05405200	-0.91405900
C	1.20449100	4.63996000	-0.98343600
H	0.35597200	4.57946800	-1.67506200
H	0.90035500	4.23569600	-0.01462700
H	1.00689800	6.82171500	-0.99999700

H	2.31053300	6.20705100	0.03367800
H	2.24336400	6.20706000	-3.03597600
H	3.54700100	6.82171300	-2.00229800
H	4.19791200	4.57946100	-1.32724400
H	3.65353200	4.23570300	-2.98768100
C	1.25306900	-1.26855000	0.71821000
H	1.35041800	-2.15967100	0.07602900
H	2.25867300	-0.86261100	0.89449000
H	0.90015900	-1.63912400	1.68887600

Table 61. Geometric coordinates and thermally corrected MP2 energies for monosolvated LiHMDS monomer **23** with one THF.



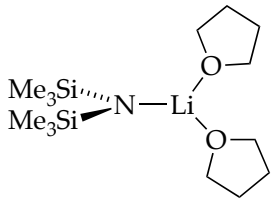
23



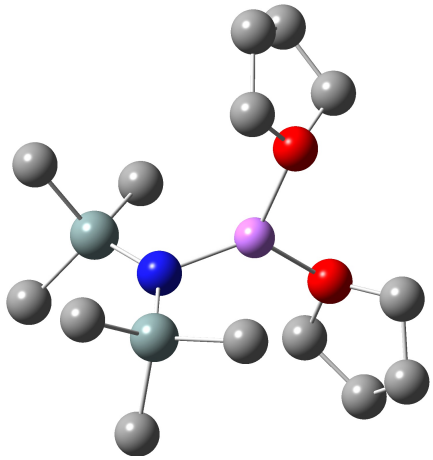
G = –1113.064315 Hartree
G_{MP2} = –696591.7714 kcal/mol

Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	6.93354700	-2.82443600	-0.28744300
O	0.86217600	-0.29801300	1.13351500	C	4.01738900	-2.86644900	1.15101400
Li	2.75311700	-0.24012800	1.09994200	H	4.45609900	-3.87240000	1.14779100
N	4.56487400	0.00242700	1.17638400	H	3.35582700	-2.81549600	2.02937500
Si	5.04586300	1.63511200	1.20998000	H	3.39170900	-2.79534200	0.24775500
C	5.89667300	2.17556300	2.82778900	C	6.41273800	-1.82955200	2.75058200
H	6.83770800	1.63227500	2.98089800	H	7.23650100	-1.10900800	2.83243200
H	6.13094700	3.24845600	2.83134000	H	5.80828800	-1.73340700	3.66144800
H	5.25987200	1.96904100	3.69751200	H	6.85415600	-2.83504000	2.74521900
C	3.46885600	2.71635600	1.05201100	C	0.07664700	-0.39885700	2.35277000
H	3.70281400	3.78852500	1.06859400	C	-1.27972000	0.21174900	2.00598500
H	2.93922300	2.52073700	0.10764300	C	-1.42886500	-0.15868200	0.52144600
H	2.76770100	2.53227400	1.88018700	H	-1.76251600	-1.19723500	0.41720400
C	6.19571600	2.15819100	-0.21724000	H	-2.13574700	0.48140700	-0.01353100
H	7.15044300	1.61850200	-0.17633100	H	-2.08400900	-0.18417200	2.63217000
H	5.74213500	1.93905800	-1.19211100	H	-1.25204600	1.30011700	2.13042400
H	6.42361900	3.23203300	-0.18735500	H	-0.00749400	-1.45802000	2.62360600
Si	5.36546800	-1.49939700	1.19310600	H	0.61373700	0.13086300	3.14449800
C	6.49327200	-1.81867900	-0.30912900	H	0.20662800	1.02597600	-0.32564100
H	5.93756100	-1.71603700	-1.24985000	H	0.25288300	-0.69051300	-0.80941500
H	7.31967200	-1.09757100	-0.34242900				

Table 62. Geometric coordinates and thermally corrected MP2 energies for disolvated LiHMDS monomer **24** with two THF.



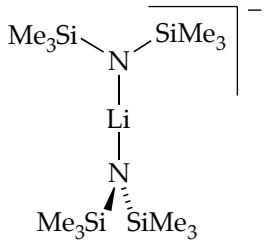
24



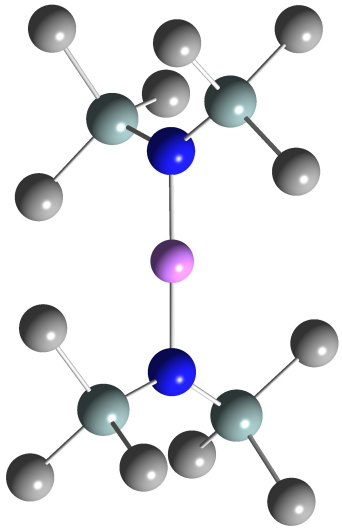
G = –1345.423107 Hartree
G_{MP2} = –841918.0493 kcal/mol

Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	C	4.03546000	2.38879800	2.78711700
O	1.13948600	0.39530900	0.79147300	H	3.44264100	1.55633300	3.19025700
C	1.55033600	-0.71368300	1.64565800	H	4.53555800	2.87294800	3.63586800
C	0.64868600	-1.90180500	1.27056200	H	3.33205500	3.12470900	2.36947700
C	0.11694500	-1.51671400	-0.12086200	C	6.34699000	3.31904200	1.03116500
H	0.84302100	-1.77650500	-0.89919200	H	6.86598000	3.73126900	1.90705600
H	-0.83632000	-1.99489000	-0.36514200	H	7.10866400	3.07068300	0.28124200
H	1.19723300	-2.84776100	1.26945700	H	5.72797400	4.12173300	0.60723700
H	-0.18091400	-1.99621500	1.98034500	C	6.46763600	0.58436300	2.37644200
H	2.60995100	-0.89180300	1.44254800	H	5.93574300	-0.31407400	2.71445500
H	1.43507400	-0.40659100	2.68998800	H	7.28117800	0.25167200	1.71873200
Li	2.59641900	1.51701600	0.12811500	H	6.92903400	1.05012100	3.25747700
O	1.78934500	3.15365600	-0.56807800	Si	4.96170300	0.17618900	-1.16027000
C	0.81176900	3.95495600	0.12191500	C	6.46888400	0.85728000	-2.11400700
C	1.53977800	5.25962700	0.43304000	H	6.28146900	1.87461700	-2.48087600
C	2.38262900	5.46505700	-0.83998500	H	7.35879600	0.90315700	-1.47274900
C	2.68162800	4.02921800	-1.31675200	H	6.72125100	0.23159400	-2.98052400
H	3.69820200	3.69483900	-1.09636800	C	3.53939600	0.06189000	-2.44135500
H	2.48554300	3.89496600	-2.38597400	H	3.80654100	-0.58595900	-3.28617200
H	3.29827600	6.03162500	-0.64988500	H	2.62298700	-0.35518300	-1.99780800
H	1.80480300	6.00890200	-1.59518400	H	3.28738800	1.04793300	-2.85567500
H	2.18423400	5.12772600	1.30904000	C	5.39596000	-1.62907200	-0.70956000
H	0.85480300	6.08933500	0.63181800	H	6.22638300	-1.66827200	0.00657000
H	-0.05556500	4.12343700	-0.53306200	H	4.54388100	-2.14111700	-0.24207300
H	0.48827800	3.39186000	1.00122900	H	5.69082500	-2.21538500	-1.59032900
N	4.44528100	1.12343900	0.15474600	H	-0.92435200	0.29296700	0.51800000
Si	5.29304900	1.78661600	1.47184500	H	0.05733700	0.53526500	-0.95165200

Table 63. Geometric coordinates and thermally corrected MP2 energies for LiHMDS triple ion **25**.



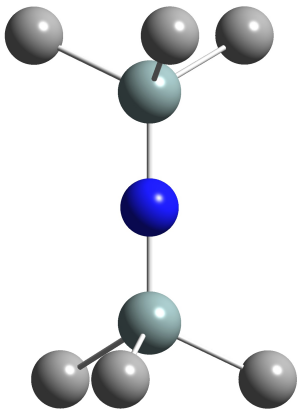
25

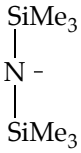


G = –1753.909684 Hartree
G_{MP2} = –1097873.2698 kcal/mol

Atom	X	Y	Z
Si	0.00000000	0.00000000	0.00000000
C	-0.55663200	1.72995100	-0.60633400
H	-1.35453100	1.64874300	-1.35576800
H	-0.93055000	2.35948500	0.21375900
H	0.27898000	2.26145100	-1.08056400
C	1.33808700	0.32630500	1.32444700
H	0.99302200	1.03786900	2.08733600
H	1.61749500	-0.60234000	1.83936600
H	2.25480900	0.73869800	0.88127500
C	-1.50873800	-0.70551100	0.94957100
H	-2.37139400	-0.84738300	0.28482700
H	-1.27427600	-1.68215900	1.39200100
H	-1.82671200	-0.03697400	1.76196800
N	0.61658800	-0.99876300	-1.22653400
Li	2.52766400	-1.07010800	-1.29407400
N	4.44122200	-1.01104800	-1.31176200
Si	5.17798600	-2.19526900	-0.34567200
C	3.84360400	-3.24110700	0.53676300
H	3.20538500	-2.61783100	1.17682300
H	3.18684300	-3.74587700	-0.18505200
H	4.29061900	-4.01798300	1.17229100
C	6.30885000	-1.51502600	1.04432400
H	7.16134200	-0.95898600	0.63147400
H	5.75426400	-0.82407700	1.69214700
H	6.71457500	-2.31644800	1.67789000
C	6.25784300	-3.45366300	-1.30519800
H	7.09116300	-2.95746100	-1.81872100
H	6.68326300	-4.22095300	-0.64276500
H	5.66340600	-3.96614100	-2.07287800
Si	5.10275600	0.26343000	-2.21649900
C	6.61989300	-0.20171200	-3.29208000
H	7.47153700	-0.51083200	-2.67135300
H	6.38524900	-1.03870800	-3.96201300
H	6.95443300	0.64150100	-3.91279400
C	5.67938100	1.75814500	-1.16577000
H	4.84950900	2.15686300	-0.56751700
H	6.47210400	1.46736700	-0.46411100
H	6.06806100	2.57801900	-1.78664500
C	3.79928500	0.95808800	-3.42842100
H	4.17511000	1.83420900	-3.97477400
H	3.51010100	0.20237900	-4.17066300
H	2.88320700	1.26529300	-2.90563200
Si	-0.18436600	-1.89688500	-2.42236300
C	-1.08396400	-3.45436800	-1.76427000
H	-0.37587500	-4.11702400	-1.24945300
H	-1.86271000	-3.18705800	-1.03856800
H	-1.56094300	-4.03333300	-2.56785600
C	1.06669800	-2.54129100	-3.71610500
H	0.57493900	-3.14908600	-4.48821200
H	1.57956700	-1.71290600	-4.22225600
H	1.83981100	-3.16803800	-3.25042400
C	-1.50627500	-0.92518000	-3.41389400
H	-2.31558700	-0.57175000	-2.76079800
H	-1.06339900	-0.04082000	-3.88986600
H	-1.96409700	-1.53731000	-4.20379000

Table 64. Geometric coordinates and thermally corrected MP2 energies for hexamethyldisilazide anion **26**.



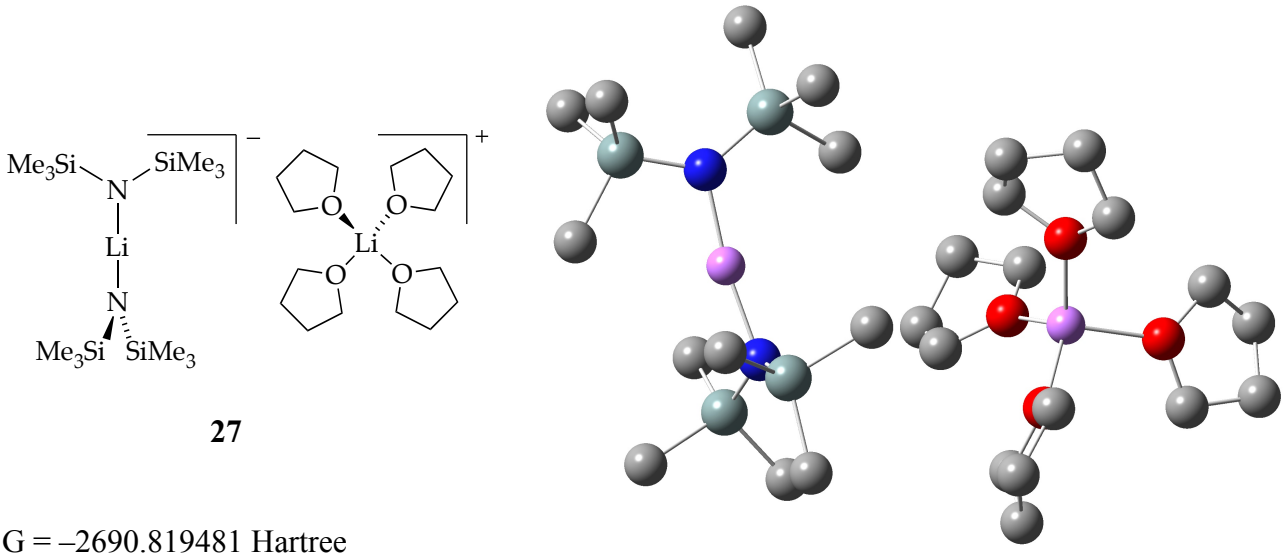


26

G = –873.149540 Hartree
G_{MP2} = –546558.8948 kcal/mol

Atom	X	Y	Z
Si	0.00000000	0.00000000	0.00000000
N	1.64477400	-0.00015700	0.00058400
Si	3.28965200	-0.00008500	0.00102600
C	4.09120700	-1.26762300	-1.20735500
H	3.77556600	-2.29100000	-0.96289800
H	3.77503300	-1.07147400	-2.24097100
H	5.19107100	-1.24224000	-1.18311200
C	4.09137500	-0.41279900	1.70246200
H	3.77552400	0.31162700	2.46532100
H	3.77482000	-1.40556800	2.05017300
H	5.19134500	-0.40516100	1.66891100
C	4.09316700	1.67935100	-0.49316200
H	5.19316200	1.64396700	-0.48194900
H	3.77937300	1.97745900	-1.50273100
H	3.77853700	2.47875700	0.19132800
C	-0.80378500	1.34947500	-1.11438800
H	-0.49257300	2.35345300	-0.79552300
H	-0.48728600	1.23033900	-2.15940800
H	-1.90352800	1.31743800	-1.09223000
C	-0.80229100	0.29108200	1.72678000
H	-0.48487300	-0.48333300	2.43826200
H	-0.48860700	1.25836700	2.14257600
H	-1.90234900	0.28305200	1.69272200
C	-0.80101900	-1.64191700	-0.60990800
H	-0.48494800	-2.48422600	0.02037300
H	-1.90096500	-1.61057500	-0.59903500
H	-0.48355700	-1.87078800	-1.63623000

Table 65. Geometric coordinates and thermally corrected MP2 energies for LiHMDS triple ion **27**.



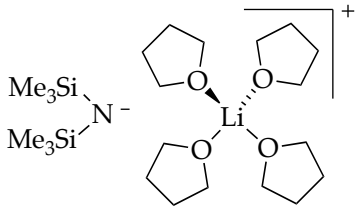
27

G = –2690.819481 Hartree
G_{MP2} = –1683826.9398 kcal/mol

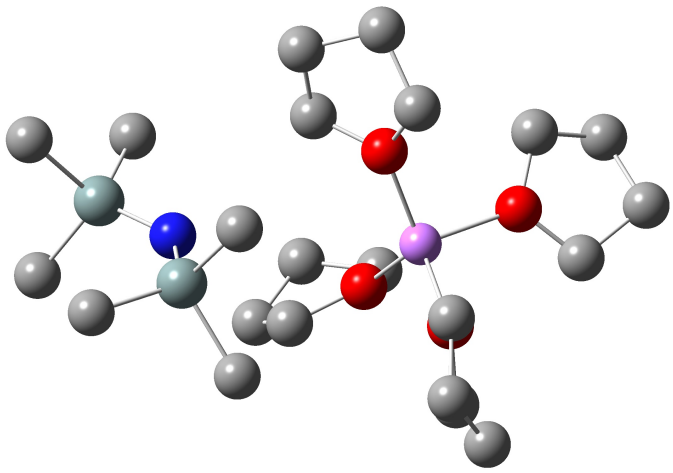
Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	H	0.64437200	5.12883400	1.02627300
O	1.37997600	0.47627000	-0.01574000	H	2.29909100	5.10335700	1.69519800
Li	1.94294200	1.97516600	1.10997100	O	3.85597500	1.63690800	1.53594900
O	0.92733300	1.97183000	2.77525500	C	4.44008400	0.36718900	1.91479800
C	1.03944000	0.88738600	3.72781100	C	5.53678200	0.70358200	2.92513300
C	-0.20516600	0.97896000	4.60865100	C	6.01167400	2.07916300	2.43180000
C	-0.47468100	2.49130500	4.63045600	C	4.70051800	2.72752300	1.98392500
C	-0.10176500	2.91594400	3.20977200	H	4.81283700	3.43139300	1.15529200
H	0.32340800	3.92087500	3.15787700	H	4.19696400	3.23698900	2.81553300
H	-0.94981300	2.85602100	2.52035900	H	6.69426900	1.96624500	1.58174700
H	0.17005300	2.98849400	5.36505100	H	6.52227800	2.66327100	3.20248700
H	-1.51310300	2.73679400	4.86653400	H	6.33056600	-0.04839000	2.94462400
H	-0.03936700	0.55582400	5.60386600	H	5.11693700	0.78243900	3.93472500
H	-1.04172800	0.45086500	4.14108700	H	3.64640500	-0.26753200	2.31810200
H	1.11079300	-0.05022600	3.16683200	H	4.85185700	-0.11087700	1.01673800
H	1.96150200	1.02362000	4.31025100	C	2.07638700	-0.06644100	-1.16519000
O	1.93843600	3.71986900	0.20251900	C	1.12191700	-1.08545700	-1.79446100
C	1.70683200	5.03247500	0.77793500	C	-0.25564000	-0.52665900	-1.40743900
C	2.11943900	6.02387800	-0.30632600	H	-0.54335700	0.29685500	-2.07066500
C	1.69918900	5.28226100	-1.58491700	H	-1.05414500	-1.27213800	-1.42924300
C	2.01275500	3.82207600	-1.24600000	H	1.26736900	-1.17385100	-2.87492700
H	3.02717500	3.53558300	-1.55122000	H	1.27213000	-2.07656600	-1.35068800
H	1.29383500	3.11971200	-1.67556300	H	2.30102000	0.75703000	-1.85458600
H	2.23445500	5.62211100	-2.47616500	H	3.02034500	-0.50405600	-0.82498000
H	0.62655200	5.41067600	-1.75789900	H	-0.08529900	-0.79144700	0.75408500
H	3.20348800	6.18886000	-0.28725300	H	-0.64118800	0.83519600	0.28290100
H	1.62119300	6.99029200	-0.19157000	Si	-3.00586500	4.66188100	-0.34591100

C	-4.40587800	4.66969500	-1.63950900
H	-5.12403200	5.47301000	-1.43192300
H	-4.03073700	4.81324300	-2.66213400
H	-4.96325100	3.72385000	-1.62103000
C	-1.78385300	3.30880500	-0.94682600
H	-1.46932000	3.46494100	-1.98873900
H	-0.88490300	3.28506700	-0.31517500
H	-2.25868900	2.32012800	-0.89001200
C	-2.07831500	6.32349500	-0.58620900
H	-2.72582500	7.17794600	-0.35246000
H	-1.19832600	6.40274500	0.06641700
H	-1.74124400	6.44896800	-1.62482200
N	-3.53062600	4.33268400	1.23456700
Li	-4.66306300	2.77046500	1.37720600
N	-5.58371900	1.11182300	1.26877600
Si	-4.69656100	-0.32896200	1.32389500
C	-3.10911500	-0.07947100	2.37150000
H	-2.53258400	0.78266800	2.00759400
H	-3.37492500	0.11961200	3.41803500
H	-2.45455200	-0.96267400	2.35036400
C	-4.07561500	-0.92579600	-0.38841000
H	-4.92034900	-1.15746500	-1.04933400
H	-3.48822200	-0.14240300	-0.88660800
H	-3.45274000	-1.82981900	-0.31834800
C	-5.57642300	-1.83923000	2.09682300
H	-6.46230300	-2.12990200	1.51769600
H	-4.91435200	-2.71503300	2.14206400
H	-5.91307400	-1.62180100	3.11809700
Si	-7.25355300	1.34934100	1.00837600
C	-8.37404600	0.68852400	2.40696300
H	-8.28554900	-0.39949200	2.51598300
H	-8.09886300	1.13559500	3.37106900
H	-9.43252200	0.91806900	2.22314600
C	-7.91763600	0.58134200	-0.61136900
H	-7.36444400	0.96112400	-1.48009900
H	-7.81114700	-0.51178300	-0.61030700
H	-8.98135900	0.80627300	-0.76812700
C	-7.61667700	3.22202700	0.89782100
H	-8.68675300	3.40909700	0.73761100
H	-7.33567500	3.74564500	1.82246300
H	-7.07538600	3.69808100	0.06950100
Si	-3.79835400	5.38258900	2.54890100
C	-2.21860300	6.20471500	3.26147100
H	-1.49172700	5.45759800	3.60659800
H	-1.71898100	6.83042100	2.51059700
H	-2.45543700	6.84940700	4.11869900
C	-4.55953900	4.40153900	4.00183700
H	-4.72412100	5.04219000	4.87823500
H	-5.53208900	3.96311500	3.73888700
H	-3.90888400	3.57375200	4.31642100
C	-4.99186400	6.83181100	2.19888000
H	-4.59864500	7.49708600	1.41875100
H	-5.96432100	6.46232600	1.84974500
H	-5.16962000	7.44467300	3.09304700

Table 66. Geometric coordinates and thermally corrected MP2 energies for hexamethyldisilazide anion **28**.



28

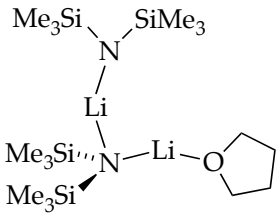


G = –1810.084892 Hartree
G_{MP2} = –1132530.3599 kcal/mol

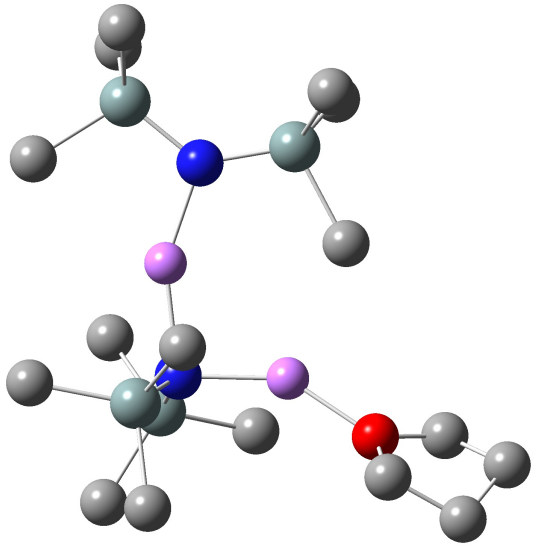
Atom	X	Y	Z	Atom	X	Y	Z
C	0.00000000	0.00000000	0.00000000	O	-3.81979900	0.57800700	-1.55618600
O	-1.16658100	0.89605500	-0.07324700	C	-4.15116100	-0.52919200	-0.68657300
Li	-1.97155800	1.35927300	-1.77366100	C	-5.52430200	-1.01849400	-1.14941900
O	-1.27640500	0.51711900	-3.39043200	C	-6.17232900	0.28100300	-1.65306000
C	-1.79223100	-0.69835100	-3.95808800	C	-4.98531800	0.99799100	-2.30064600
C	-0.55870400	-1.48480300	-4.38847100	H	-5.04585900	2.08862700	-2.24920600
C	0.35932100	-0.36702800	-4.91150600	H	-4.85594200	0.70012100	-3.34958500
C	0.02491100	0.82862800	-4.00501900	H	-6.56061500	0.86614900	-0.81132600
H	-0.08531900	1.76055000	-4.56922800	H	-6.99282500	0.11260600	-2.35640400
H	0.75817200	0.97413800	-3.19979900	H	-6.08765000	-1.50105900	-0.34566200
H	0.12656500	-0.14604500	-5.95991000	H	-5.41987900	-1.73715800	-1.97064700
H	1.41862700	-0.62827100	-4.84805100	H	-3.36040400	-1.27966400	-0.77083100
H	-0.78537200	-2.24678600	-5.14083800	H	-4.17971000	-0.16826300	0.34910400
H	-0.10706100	-1.97819300	-3.52097700	C	-1.52319100	1.35105400	1.24664300
H	-2.39971900	-1.19243700	-3.19452300	C	-0.89920200	0.33906500	2.20539200
H	-2.43560500	-0.46283900	-4.82050000	C	0.40609800	-0.01405800	1.47485800
O	-2.28500500	3.28687300	-2.10905600	H	1.16833800	0.75087900	1.65579500
C	-2.47102100	3.87052800	-3.42080100	H	0.81942800	-0.98041900	1.77782400
C	-2.80018600	5.33937700	-3.16285800	H	-0.74103300	0.75645200	3.20463500
C	-1.94017900	5.63876800	-1.92461900	H	-1.54386700	-0.54370200	2.30101700
C	-2.03143500	4.33236400	-1.13072600	H	-1.10835100	2.35461100	1.40955800
H	-2.86942000	4.33897200	-0.42236200	H	-2.61584400	1.40689700	1.30395800
H	-1.10927800	4.08960200	-0.59792900	H	-0.33498500	-0.98741500	-0.34217900
H	-2.29609300	6.49784300	-1.34859400	H	0.78926200	0.39371000	-0.65679200
H	-0.90341800	5.82741300	-2.22019000	Si	2.59692500	2.99647400	-1.48378800
H	-3.86634300	5.46077400	-2.93544500	N	2.49902100	1.33484700	-1.70158700
H	-2.55825800	5.97572400	-4.01902200	Si	3.63090600	0.10339700	-1.89909400
H	-1.54244500	3.76218900	-3.99297600	C	5.04747000	0.04251500	-0.60872800
H	-3.26828200	3.31645200	-3.92498400	H	5.67498200	0.94150600	-0.66069900

H	4.64814200	-0.01543500	0.41260200
H	5.70402900	-0.82604100	-0.75857600
C	4.51802800	0.08461000	-3.60088300
H	3.79908600	0.03554000	-4.43055500
H	5.10567200	1.00128200	-3.74306900
H	5.20447800	-0.76708600	-3.70696900
C	2.80196900	-1.62448100	-1.76878000
H	3.52452100	-2.43170900	-1.94911700
H	2.37012500	-1.79211600	-0.77265900
H	1.99122400	-1.74294700	-2.50081400
C	1.56610900	3.97325900	-2.78324100
H	1.94067800	3.79661100	-3.79999600
H	0.51505800	3.65466000	-2.76192100
H	1.59512800	5.05759700	-2.60256700
C	4.33335300	3.80129600	-1.55558800
H	4.99180900	3.40281600	-0.77341400
H	4.81941800	3.60547200	-2.52027400
H	4.28662500	4.89146600	-1.42417000
C	1.85486000	3.56990300	0.19565900
H	2.45063400	3.19390600	1.03809000
H	1.80287100	4.66377300	0.29099000
H	0.83731000	3.17215200	0.31822700

Table 67. Geometric coordinates and thermally corrected MP2 energies for LiHMDS monosolvated open dimer **29** with one THF on a terminal Li.



29

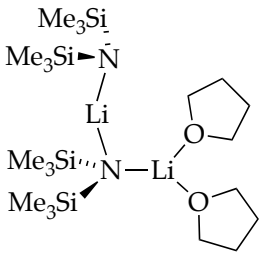


G = –1993.785221 Hartree
G_{MP2} = –1247884.1735 kcal/mol

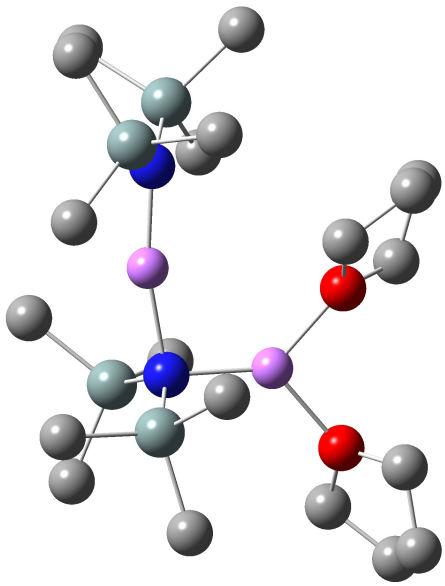
Atom	X	Y	Z
Si	0.00000000	0.00000000	0.00000000
C	0.66106100	0.90627100	1.54111100
H	1.75629100	0.97004200	1.52124900
H	0.27471700	1.93175600	1.61515100
H	0.38754600	0.37529200	2.46180900
C	0.40712800	1.10150400	-1.50135500
H	1.49058400	1.17842400	-1.65418800
H	-0.01826800	0.68438200	-2.42298200
H	0.01921400	2.12219100	-1.38196400
N	0.43851000	-1.63009500	-0.14038000
Si	1.97220500	-2.36447600	-0.31478900
C	2.98047300	-1.76328700	-1.81723400
H	2.40695800	-1.86698000	-2.74703200
H	3.25591400	-0.70526100	-1.72158400
H	3.91122800	-2.33440700	-1.93300900
C	1.70959100	-4.24263300	-0.57036500
H	2.66814800	-4.77002200	-0.65850400
H	1.17326200	-4.70564300	0.27083600
H	1.14637200	-4.45180700	-1.49099800
C	3.10794700	-2.18846000	1.20640100
H	3.33530500	-1.13554000	1.41626400
H	2.63340800	-2.60253600	2.10538900
H	4.06392200	-2.70978000	1.06380300
Li	-0.90750300	-2.92627700	-0.09896100
N	-2.80667100	-3.55959200	-0.02177100
Si	-3.01476400	-4.21907200	1.56723200
C	-3.91133600	-2.91775500	2.65007500
H	-4.92448100	-2.70303000	2.28012000
H	-4.02056700	-3.27617400	3.68134300
H	-3.35873800	-1.96802300	2.71308500
C	-1.34040800	-4.54965300	2.40852400
H	-1.47591600	-4.87660000	3.44769600
H	-0.78178900	-5.33988600	1.88995900
H	-0.70133000	-3.65597300	2.43456000
C	-4.03799800	-5.81500400	1.68997800
H	-5.06696100	-5.67039200	1.33988400
H	-3.59941800	-6.62935800	1.10056600
H	-4.08890300	-6.15719200	2.73157300
Si	-3.13026500	-4.33393200	-1.53950300
C	-2.04265600	-5.85803100	-1.86976600
H	-0.97391400	-5.60943600	-1.85595000
H	-2.20473800	-6.63801900	-1.11516800
H	-2.26366000	-6.29962100	-2.85006500
C	-2.77576400	-3.06704300	-2.91879600
H	-2.90929100	-3.51155400	-3.91310100
H	-3.44917000	-2.19878400	-2.86466300
H	-1.74859300	-2.68188400	-2.86790900
C	-4.93790300	-4.89716800	-1.76006700
H	-5.18767100	-5.73253400	-1.09622500
H	-5.65013300	-4.08872700	-1.54658600
H	-5.11993400	-5.23108700	-2.78982100
Li	-3.66102900	-1.82664200	0.08479800
O	-5.28972900	-0.83984900	-0.10400800
C	-6.18918600	-0.85005200	-1.24623900
C	-7.37811700	0.01343400	-0.82966300
C	-6.71446900	1.05284400	0.08716700

C	-5.66893600	0.21606300	0.82426200
H	-6.07944700	-0.25498900	1.72486800
H	-4.76649000	0.77248900	1.08999200
H	-7.41611500	1.53379300	0.77431300
H	-6.23001100	1.83491800	-0.50841500
H	-8.10768900	-0.58380300	-0.27072600
H	-7.88735400	0.45784600	-1.68935300
H	-5.66084300	-0.42577400	-2.10892500
H	-6.44748700	-1.88952600	-1.46180300
C	-1.92279400	0.09613600	0.15622700
H	-2.38260300	-0.30770700	-0.75884100
H	-2.25267500	-0.46924500	1.04253100
H	-2.28361500	1.12577600	0.27348600

Table 68. Geometric coordinates and thermally corrected MP2 energies for LiHMDS disolvated open dimer **30** with two THF on a terminal Li.



30

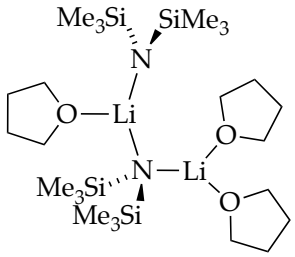


G = –2226.138035 Hartree
G_{MP2} = –1393208.2729 kcal/mol

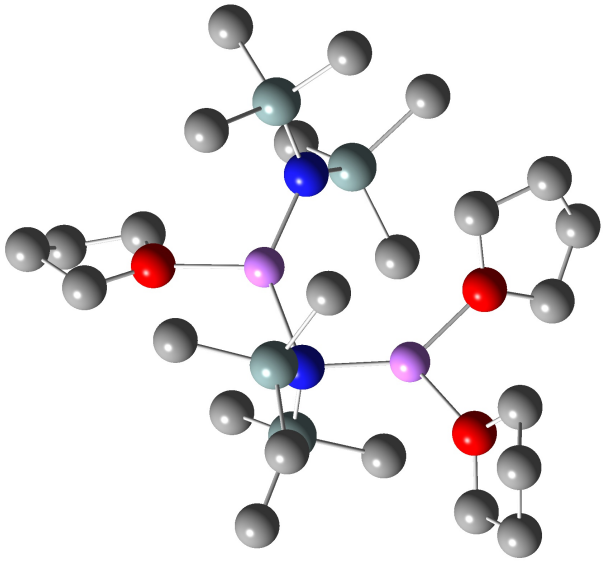
Atom	X	Y	Z	Atom	X	Y	Z
Si	0.00000000	0.00000000	0.00000000	H	-5.94372500	-0.82636100	1.40438000
C	1.24886300	-0.89821600	1.12752600	H	-5.02582000	-1.67573400	2.64482200
H	2.18358200	-1.12575400	0.60204500	H	-4.21375700	-0.48722100	1.62797500
H	1.50263200	-0.29435200	2.00937400	C	-2.96770800	-3.53542800	1.02001500
H	0.83583000	-1.85066100	1.48450700	H	-3.10330000	-3.90480500	2.04500300
C	0.82400600	1.66014100	-0.47825400	H	-2.71773900	-4.39919200	0.39010800
H	1.72511700	1.50023900	-1.08428500	H	-2.08814600	-2.87757700	1.03241200
H	0.14899100	2.29213400	-1.07106500	C	-5.94588800	-3.95383200	0.54702600
H	1.12595200	2.23598400	0.40687800	H	-6.92619100	-3.53091400	0.29498700
N	-0.56988100	-0.91111200	-1.32932000	H	-5.79086700	-4.83004300	-0.09342300
Si	0.36546800	-1.38177100	-2.68663300	H	-6.00159200	-4.31452900	1.58239400
C	0.30963400	-0.10410200	-4.10923200	Si	-4.78128100	-2.76556200	-2.67386200
H	-0.71916900	0.07634900	-4.44976300	C	-4.04243400	-4.49926200	-2.92287800
H	0.72133900	0.86146900	-3.78743600	H	-2.94732800	-4.48784400	-2.87196200
H	0.88888600	-0.43530600	-4.98145400	H	-4.39967000	-5.19925300	-2.15729300
C	-0.29622300	-3.01605100	-3.41908800	H	-4.32146300	-4.91468500	-3.89995600
H	0.29620400	-3.33283700	-4.28753700	C	-4.22745600	-1.67325300	-4.13673500
H	-0.24719900	-3.82345200	-2.67606100	H	-4.45610100	-2.15623500	-5.09523100
H	-1.33757600	-2.93883400	-3.75779500	H	-4.74626700	-0.70326500	-4.13728500
C	2.21775600	-1.69540500	-2.34882500	H	-3.15031000	-1.46615400	-4.12643900
H	2.73203200	-0.79846300	-1.98121700	C	-6.67058200	-2.94382000	-2.88109800
H	2.35899600	-2.48411800	-1.59957400	H	-7.10524900	-3.64308700	-2.15806200
H	2.73224500	-2.01284600	-3.26568600	H	-7.17154500	-1.97594200	-2.74890500
Li	-2.31439100	-1.62675500	-1.23422900	H	-6.92073500	-3.31077700	-3.88519300
N	-4.30300500	-1.99270300	-1.19515100	Li	-4.99081100	-0.14328000	-1.20702200
Si	-4.54390500	-2.67462400	0.38375600	O	-6.86091400	0.50409100	-1.28275300
C	-4.96848100	-1.28349000	1.62133000	C	-7.31336400	1.23153700	-2.45364400

C	-8.79949100	0.90361100	-2.58859200
C	-9.22308200	0.73814700	-1.12111700
C	-8.00264000	0.04952200	-0.50681000
H	-8.06181600	-1.04107600	-0.59127200
H	-7.83182500	0.31716600	0.53924200
H	-10.1350490	0.14714200	-0.99893700
H	-9.38763900	1.71751100	-0.65704100
H	-8.93503200	-0.03617100	-3.13556100
H	-9.35183300	1.68829500	-3.11352300
H	-7.14795700	2.30340700	-2.28796600
H	-6.71056700	0.90936600	-3.30713400
O	-4.03523100	1.50249100	-1.61010100
C	-2.95179200	1.65565500	-2.58428500
C	-2.59900900	3.14314800	-2.57077300
C	-2.95253900	3.55699400	-1.13371500
C	-4.20877900	2.73069800	-0.86236200
H	-5.11279000	3.24038400	-1.22201600
H	-4.34541700	2.47118800	0.19169600
H	-3.13202600	4.63066900	-1.02371600
H	-2.15125600	3.26906800	-0.44546600
H	-3.21192600	3.69768100	-3.29161900
H	-1.54727800	3.31146600	-2.81787900
H	-2.11740900	1.02110000	-2.26689500
H	-3.32239200	1.30603500	-3.55169400
C	-1.45987300	0.45531300	1.14999900
H	-2.28622100	0.91603700	0.59269300
H	-1.85796100	-0.43069600	1.66103200
H	-1.15054700	1.16196200	1.93120000

Table 69. Geometric coordinates and thermally corrected MP2 energies for LiHMDS disolvated open dimer **31** with two THF on a terminal Li and one THF on the internal Li.



31



G = –2458.473474 Hartree
G_{MP2} = –1538521.6974 kcal/mol

Atom	X	Y	Z	Atom	X	Y	Z
Si	0.00000000	0.00000000	0.00000000	C	4.35137600	-2.94213700	-1.54028600
C	-1.63136800	-0.33690200	-0.94436300	H	5.37233700	-2.66551800	-1.24744300
H	-2.50975200	-0.19759200	-0.30242700	H	4.42898200	-3.40947100	-2.53073200
H	-1.73594300	0.34892400	-1.79634300	H	3.77284300	-2.01843800	-1.67335400
H	-1.67610300	-1.35708100	-1.34487000	C	1.85441800	-4.56662100	-1.19950500
C	-0.03957400	1.89599400	0.28454500	H	2.06895900	-4.96351500	-2.20075400
H	-0.89588500	2.18863600	0.90600700	H	1.27261600	-5.31873700	-0.65697300
H	0.86132100	2.26588800	0.78967200	H	1.21327300	-3.68692000	-1.33333200
H	-0.13248800	2.43727600	-0.66679000	C	4.50200100	-5.75491400	-0.34693300
N	0.27087500	-0.93814700	1.40197600	H	5.53758000	-5.60922000	-0.01792500
Si	-0.51565500	-0.66494800	2.89773900	H	4.06054500	-6.52482500	0.29839000
C	0.16586200	0.81145300	3.91079000	H	4.53452600	-6.16256500	-1.36571100
H	1.22150400	0.66589800	4.17641300	Si	3.73618900	-3.97399900	2.78287300
H	0.09128400	1.75679400	3.35898500	C	2.48032300	-5.15698400	3.58423800
H	-0.39010800	0.93496400	4.85001700	H	1.52616800	-4.66063100	3.79214000
C	-0.32778400	-2.17021000	4.05938900	H	2.27818600	-6.02391000	2.94323000
H	-0.82692100	-1.98414500	5.01945200	H	2.86635800	-5.53517300	4.53995400
H	-0.77265500	-3.07140600	3.62067500	C	3.89327100	-2.49239600	3.97949500
H	0.72344900	-2.39310000	4.28403600	H	4.06313200	-2.83610200	5.00800200
C	-2.40161700	-0.35365900	2.78876800	H	4.73654900	-1.83469000	3.72413400
H	-2.63458300	0.55210400	2.21433300	H	2.98732000	-1.87461800	3.98439500
H	-2.92272400	-1.18839500	2.30158000	C	5.40516900	-4.89549000	2.91278800
H	-2.84210100	-0.22866800	3.78717500	H	5.39377800	-5.86270400	2.39856900
Li	1.22248000	-2.67233700	1.33220300	H	6.23443900	-4.30907000	2.49979200
N	3.30585400	-3.37412600	1.22066700	H	5.63633900	-5.09085100	3.96864700
Si	3.48698200	-4.14075800	-0.31716000	Li	4.49319000	-1.77744800	1.00218600

O	4.31789400	0.15100600	1.10078500
C	3.46728100	0.84998400	2.06393600
C	3.69271300	2.33966300	1.79913500
C	4.04773600	2.36419200	0.30425300
C	4.87473200	1.08864500	0.15140700
H	5.93114300	1.26054400	0.39819500
H	4.81409100	0.64103800	-0.84495500
H	4.60406900	3.25759000	0.00489400
H	3.13944900	2.30237700	-0.30345900
H	4.52912900	2.72077600	2.39775600
H	2.80679900	2.93378900	2.03881200
H	2.43588600	0.52888800	1.89090200
H	3.77439300	0.53836900	3.06634600
O	6.55665100	-1.78605400	1.10163300
C	7.23826300	-0.96997500	2.07719000
C	8.44478000	-1.79978300	2.50280400
C	8.86337000	-2.44418000	1.17045300
C	7.52400300	-2.64211000	0.43709800
H	7.15279300	-3.66787900	0.50626800
H	7.58118700	-2.35977100	-0.61920300
H	9.40199200	-3.38658400	1.30259800
H	9.51251600	-1.76453100	0.60740400
H	8.13962300	-2.56304000	3.22689400
H	9.23572000	-1.19303100	2.95353200
H	7.54735200	-0.02178400	1.61467300
H	6.53249000	-0.75521000	2.88179200
O	-0.30785100	-4.17892000	1.19676000
C	-1.41854900	-3.79408100	0.34614300
C	-2.29415700	-5.04093500	0.20188500
C	-2.02908500	-5.77660200	1.52270300
C	-0.54339500	-5.49291900	1.74401400
H	0.08660400	-6.22219900	1.21532200
H	-0.25369300	-5.48362700	2.79615200
H	-2.24814600	-6.84793700	1.47879000
H	-2.62514700	-5.33843400	2.33189500
H	-1.96150200	-5.65118300	-0.64635000
H	-3.34781700	-4.79029700	0.04669000
H	-1.94395500	-2.96352800	0.82477300
H	-1.01458000	-3.44178900	-0.60585000
C	1.37616700	-0.30483900	-1.29049400
H	2.36812000	-0.14939800	-0.84904600
H	1.34848600	-1.33219400	-1.67628300
H	1.27863200	0.36635600	-2.15399700

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[S2] (a) $^{+}Li(THF)_5$: Olmstead, M. M.; Power, P. P.; Sigel, G. *Inorg. Chem.* **1986**, *25*, 1027. (b) $^{+}Li(THF)_5$: Zhang, X.-Q.; Lin, M.-S.; Hu, B.; Chen, W.-Q.; Zheng, L.-N.; Wu, J.; Chen, Y.-M.; Zhou, F.-Y.; Li, Y.-H.; Li, W.; *Polyhedron* **2012**, *33*, 273. (c) $^{+}Li(THF)_6$: Schenk, C.; Schnepf, A. *Angew. Chem., Int. Ed. Engl.* **2007**, *46*, 5314. (d) $^{+}Li(THF)_6$: Schenk, C.; Henke, F.; Santiso-Quinones, G.; Krossing, I.; Schnepf, A. *Dalton Trans.* **2008**, 4436. (e) $^{+}Li(THF)_{10}$: Depue, J. S.; Collum, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 5524.

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