

Supporting Information

Sodiated Oppolzer Enolates: Solution Structures, Mechanism of Alkylation, and Origin of Stereoselectivity

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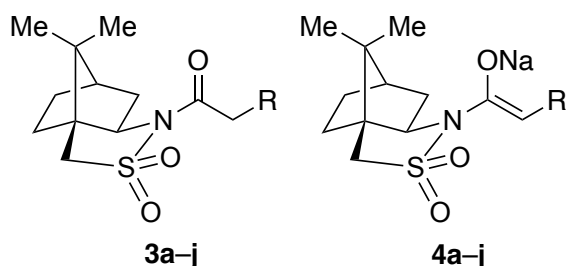
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Substrates and synthesis

Reagents and solvents. Toluene, hexanes, THF, MTBE, HMPA, and cyclopentane were distilled from blue or purple solutions containing sodium benzophenone ketyl. Methyl iodide and allyl bromide were distilled from 4Å molecular sieves.

Substrate synthesis. Substrates **3a–j** were prepared according to previously published literature procedures with identical characterization data.^{1,4}

Product synthesis. Products (2*R*)-*N*-[(2*R*)-2-Phenylpent-4-en-onyl]bornane-10,2-sultam (**14**) and (2*R*)-*N*-[(2*R*)-2-Phenylpropionyl]bornane-10,2-sultam (**15**) were synthesized according to the general procedure for in situ IR analysis described later in the ESI. The reaction vessel was taken off the IR probe and quenched with 5 mL 1M HCl and extracted 3 times with 10 mL Et₂O. The organic fractions were combined, washed with 30 mL saturated NaCl_(aq), dried over NaSO₄, and evaporated to yield a white solid. Both products were purified by recrystallization from hexanes. Characterization data are identical to those reported previously.^{4,25}



a: Me	e: CH ₂ Ph	h: <i>p</i> -Cl-C ₆ H ₄
b: Et	f: CH ₂ - <i>p</i> -F-C ₆ H ₄	i: <i>m</i> -F-C ₆ H ₄
c: <i>i</i> -Pr	g: Ph	j: <i>p</i> -F-C ₆ H ₄
d: cyclohexyl (Cy)		

Chart S1. *N*-acyl-camphorsultams and enolates studied in this work.

Structural Elucidation of Sodium Oppolzer Enolates

General procedure for sealed tube NMR spectroscopy

An NMR tube fitted with a double-septum under vacuum was flame-dried on a Schlenk line and allowed to cool to room temperature, backfilled with argon, and placed in a dry ice/acetone cooling bath. Individual stock solutions of the *N*-acyl sultams and NaHMDS were prepared at room temperature and 0 °C, respectively. The appropriate amounts of the *N*-acyl sultams, NaHMDS, solvent, and (when applicable) co-solvent were added sequentially via gastight syringe. The tube was flame-sealed under partial vacuum while cold to minimize evaporation. The tubes were mixed on a vortex mixer and stored at –80 °C.

Unless otherwise stated all tubes were sealed with a total enolate concentration of 0.10 M. Standard ^1H , ^{19}F , ^{13}C , and ^{31}P direct detection spectra were recorded on a 11.8 T spectrometer at 500.1, 470.6, 125.8, and 202.5 MHz, respectively. ^1H , ^{13}C , and ^{31}P resonances are referenced to their respective standards (Me_4Si and H_3PO_4 at 0.0 ppm). ^{19}F spectra are referenced to $\text{C}_6\text{H}_5\text{F}$ (–113.15 ppm).

For quantitated ^{19}F and ^{13}C spectra, the spin-lattice relaxation (T_1) was determined by standard inversion-recovery experiments on several samples. The relaxation delay (d_1) was set to seven times the average relaxation lifetime. Integration of the NMR signals was determined using the line-fitting method included in MNOVA (Mestrelab research S.L.).

THF-solvated enolate monomers (alkyl-amide-derived enolates)

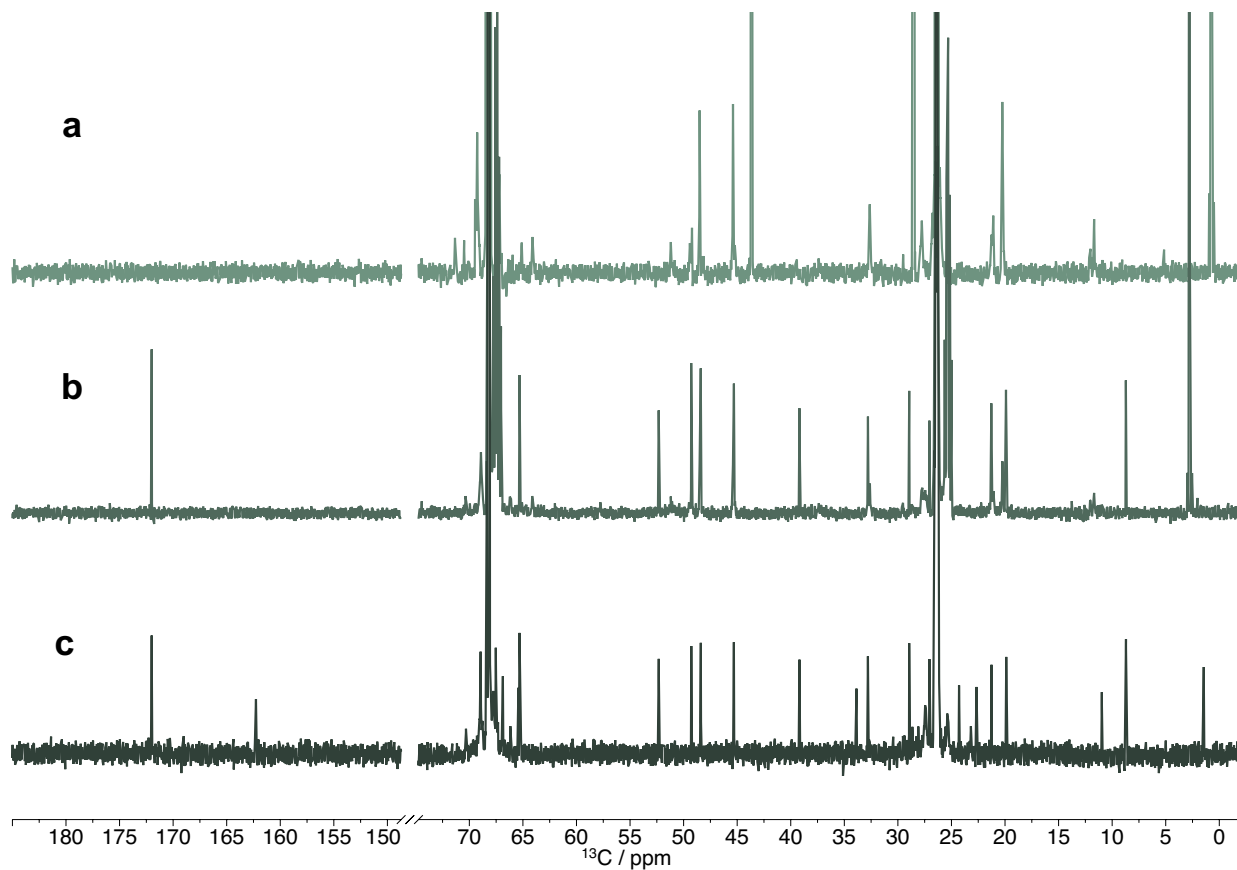
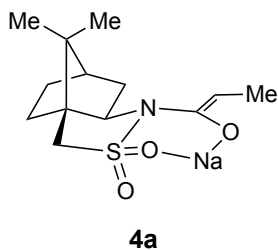
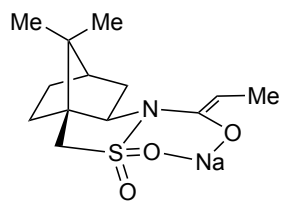


Figure S1. **a** | ^{13}C NMR spectrum of (S)-3a and 1.1 equiv NaPTA in THF at -80°C . **b** | ^{13}C NMR spectrum of (S)-3a and 1.1 equiv NaHMDS in THF at -80°C . **c** | ^{13}C NMR spectrum of (S)-3a in THF at -80°C . Full enolization of (S)-3a is seen in panel **a** (using NaPTA). Partial enolization at equilibrium can be seen in panel **b** (with NaHMDS). $K_{\text{eq}} = 1$



4a

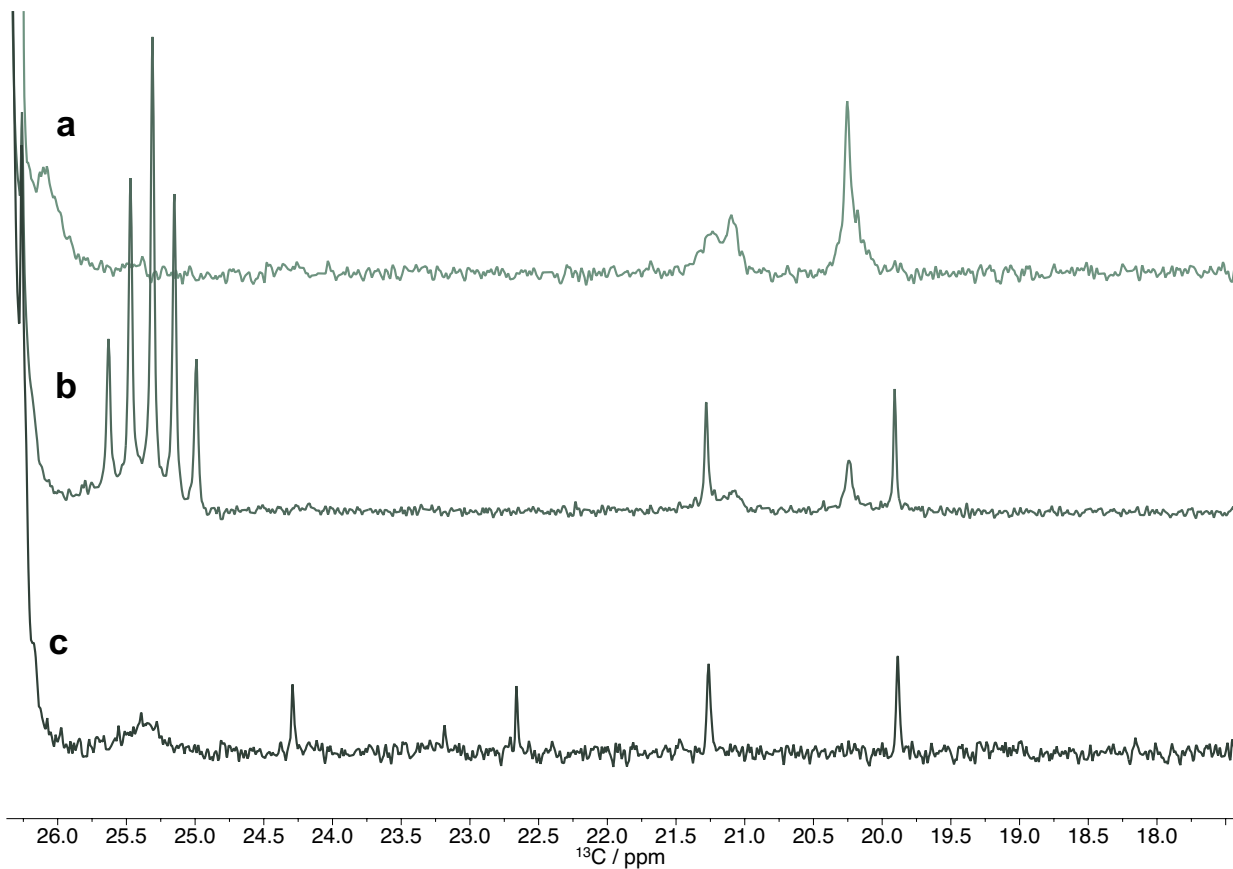


Figure S2. **a** | ^{13}C NMR spectrum of (*S*)-**3a** and 1.1 equiv NaPTA in THF at $-80\text{ }^\circ\text{C}$. **b** | ^{13}C NMR spectrum of (*S*)-**3a** and 1.1 equiv NaHMDS in THF at $-80\text{ }^\circ\text{C}$. **c** | ^{13}C NMR spectrum of (*S*)-**3a** in THF at $-80\text{ }^\circ\text{C}$. Spectra highlight the signals of the geminal di-methyl group. Full enolization of (*S*)-**3a** is seen in panel **a** (using NaPTA). Partial enolization at equilibrium can be seen in panel **b** (with NaHMDS). $K_{\text{eq}} = 1.02$

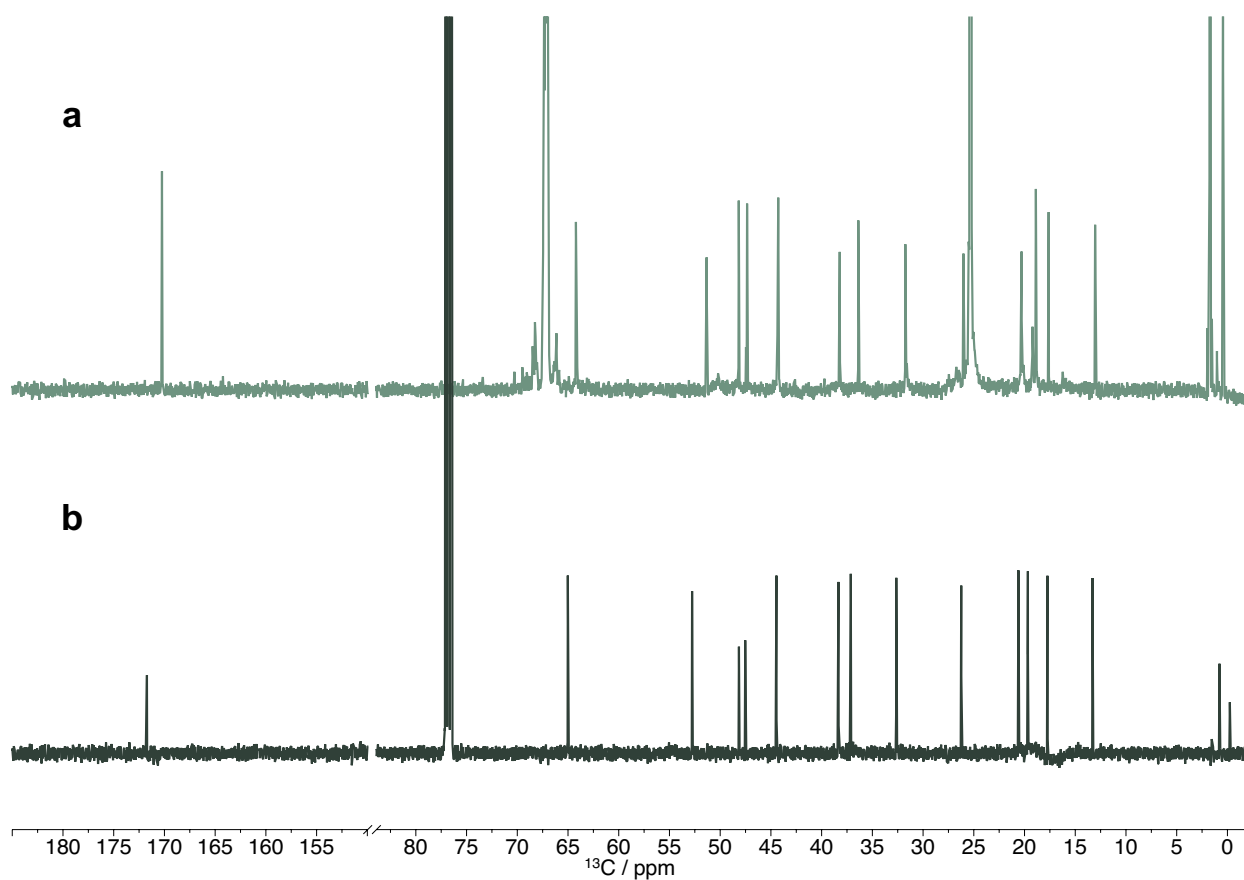
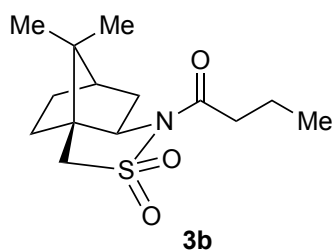


Figure S3. **a** | ¹³C NMR spectrum of (S)-3b and 1.1 equiv NaHMDS in THF at -80 °C. **b** | ¹³C NMR spectrum of (S)-3b in CDCl₃ at 25 °C. NaHMDS does not appear to visibly enolize the substrate.

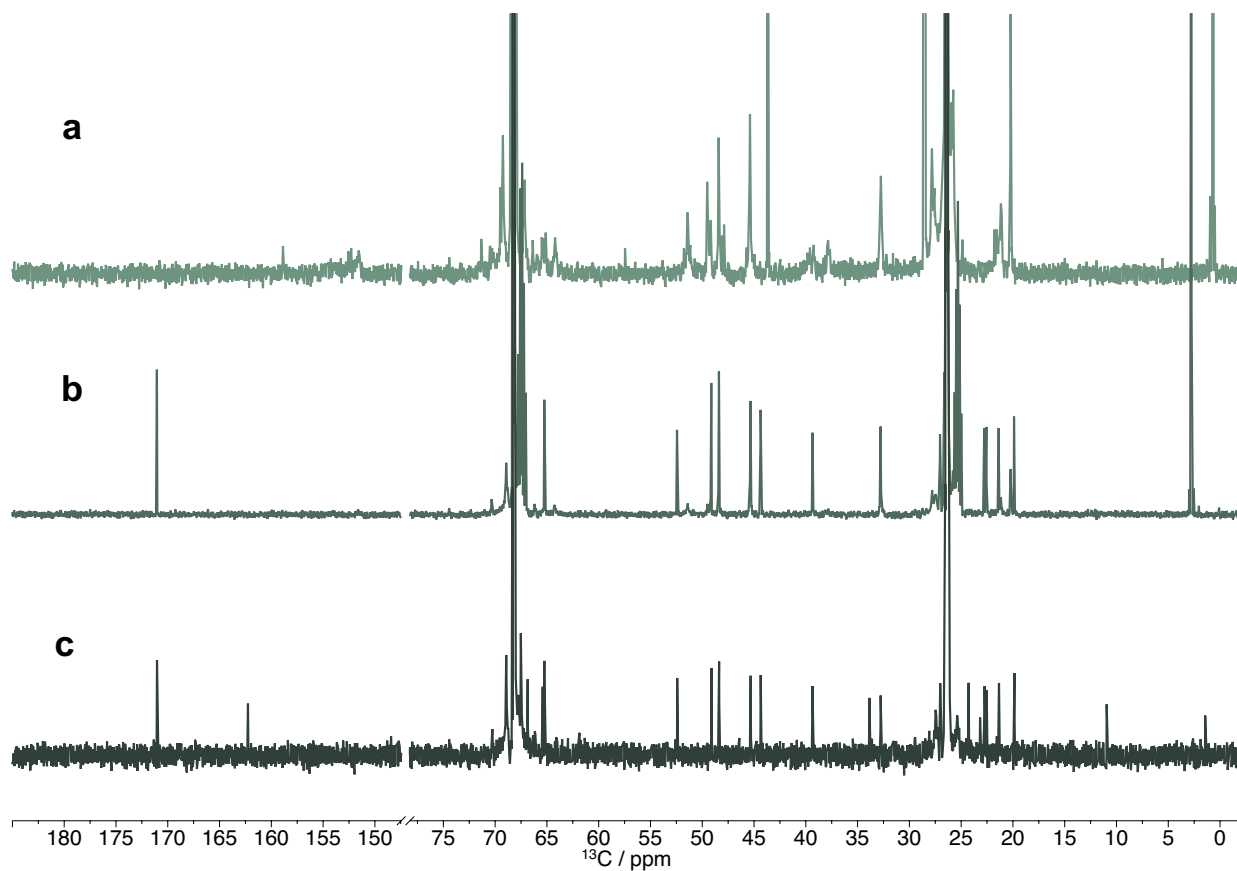
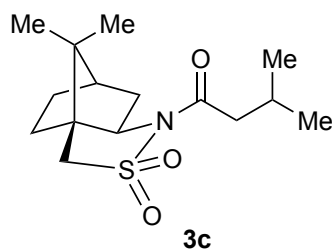


Figure S4. **a** | ^{13}C NMR spectrum of (*S*)-**3c** and 1.1 equiv NaPTA in THF at $-80\text{ }^\circ\text{C}$. **b** | ^{13}C NMR spectrum of (*S*)-**3c** and 1.1 equiv NaHMDS in THF at $-80\text{ }^\circ\text{C}$. **c** | ^{13}C NMR spectrum of (*S*)-**3c** in THF at $-80\text{ }^\circ\text{C}$. Full enolization of (*S*)-**3c** is seen in panel **a** (using NaPTA). Partial enolization at equilibrium can be seen in panel **b** (with NaHMDS). $K_{\text{eq}} = 0.96$

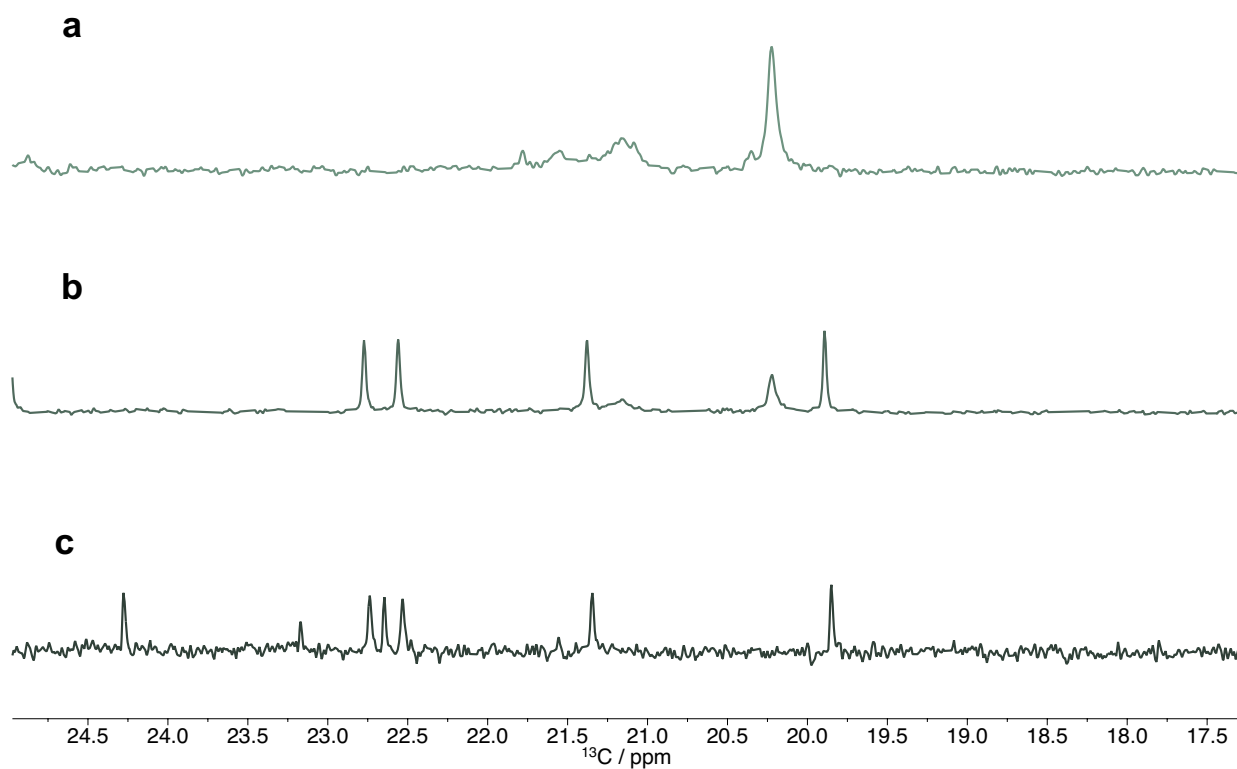
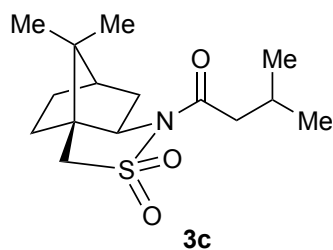


Figure S5. **a** | ^{13}C NMR spectrum of (*S*)-**3c** and 1.1 equiv NaPTA in THF at $-80\text{ }^\circ\text{C}$. **b** | ^{13}C NMR spectrum of (*S*)-**3c** and 1.1 equiv NaHMDS in THF at $-80\text{ }^\circ\text{C}$. **c** | ^{13}C NMR spectrum of (*S*)-**3c** in THF at $-80\text{ }^\circ\text{C}$. Spectra highlight the signals of the geminal di-methyl group. Full enolization of (*S*)-**3c** is seen in panel **a** (using NaPTA). Partial enolization at equilibrium can be seen in panel **b** (with NaHMDS). $K_{\text{eq}} = 0.96$

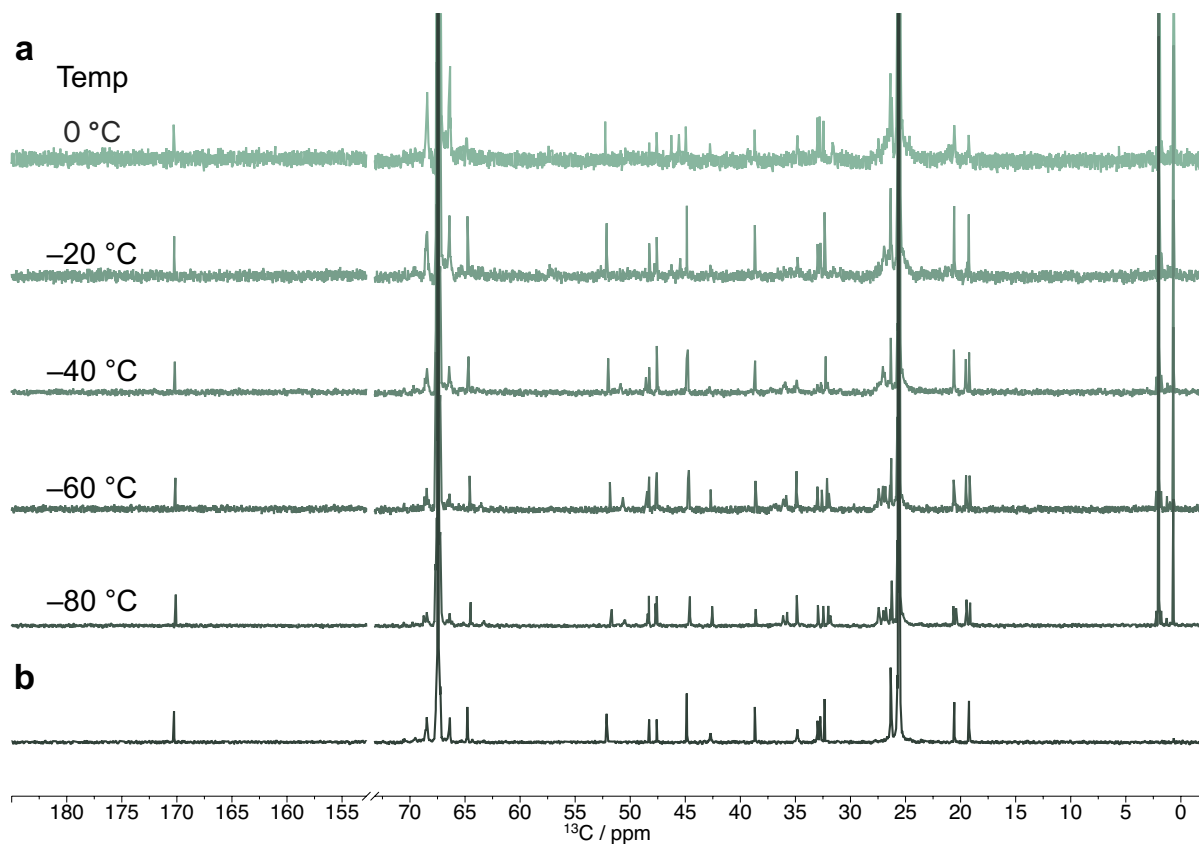
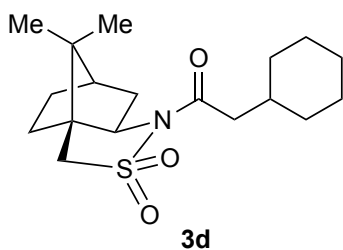
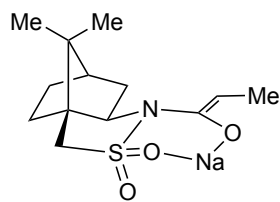


Figure S6. a | ¹³C NMR spectra of (*S*)-**3d** and 1.1 equiv NaHMDS in THF at various temperatures. The sealed NMR tube was held at each temperature for 40 min to allow for slow enolization. **b** | ¹³C NMR spectrum of (*S*)-**3d** without NaHMDS in THF at -80 °C. A new set of peaks appears suggesting partial enolization of (*S*)-**3d** at equilibrium. $K_{eq} = 0.40$



4a

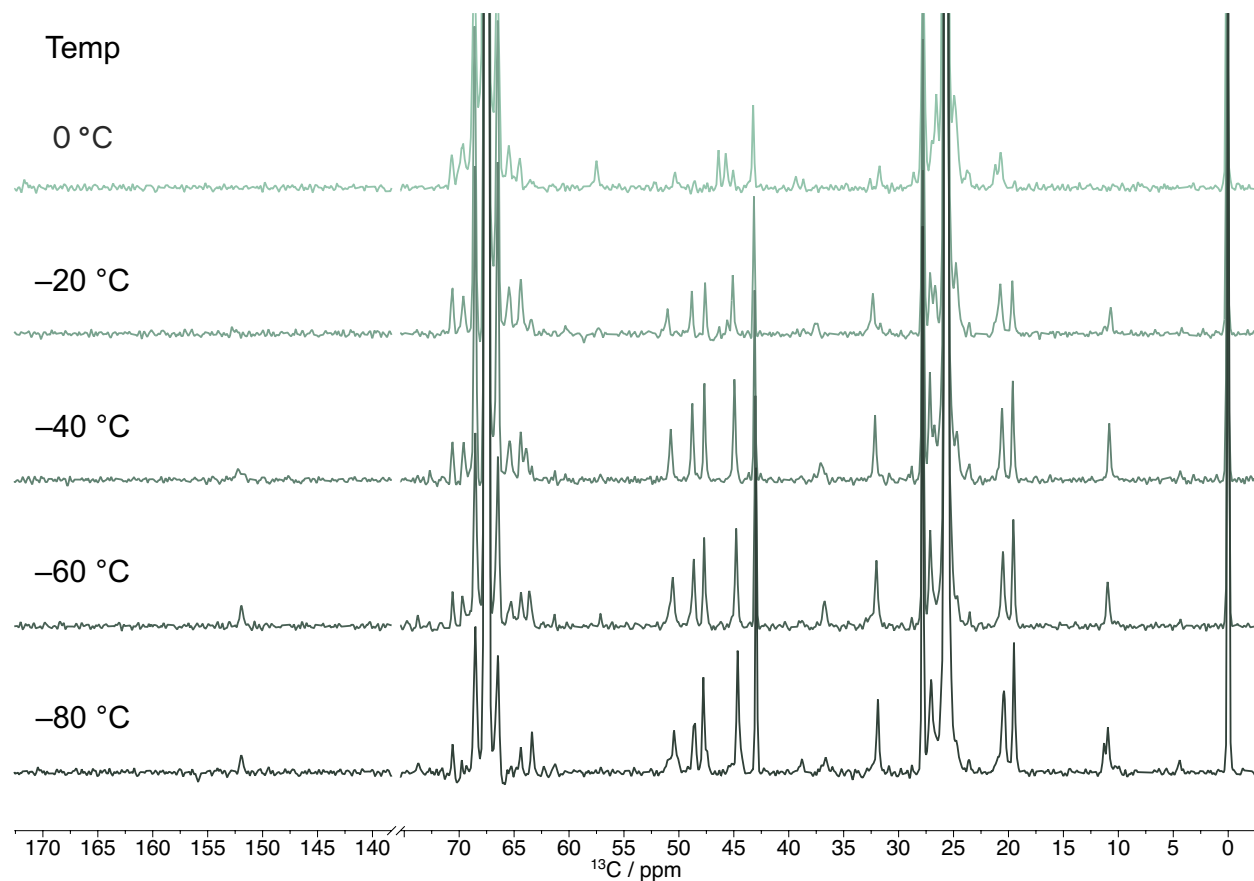
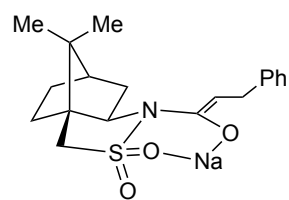
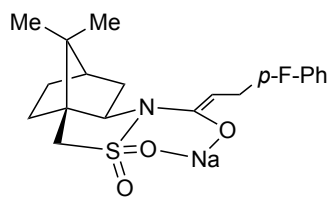


Figure S7. ^{13}C NMR spectra of (*S*)-**4a** generated from (*S*)-**3a** and 1.1 equiv NaPTA in THF at various temperatures. The sealed NMR tube was held at each temperature for 20 min to explore aggregate aging. No new resonances appear during the aging process suggesting no major changes in aggregate structure.



4e



4f

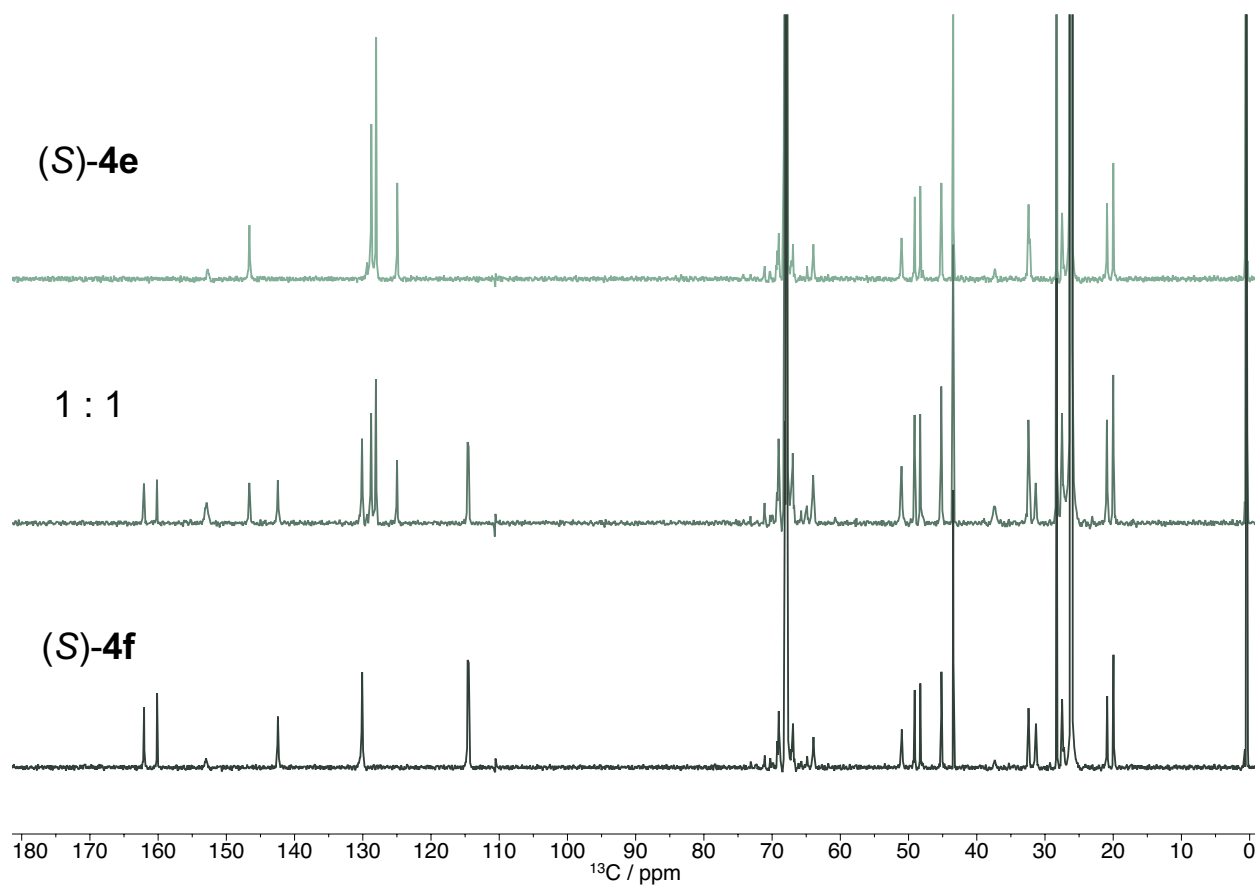


Figure S8. ^{13}C NMR spectra of mixtures of (S)-4e and (S)-4f in THF at $-80\text{ }^\circ\text{C}$. The sealed NMR tubes were not aged. No new resonances appear in the mixed tube consistent with a monomer model.

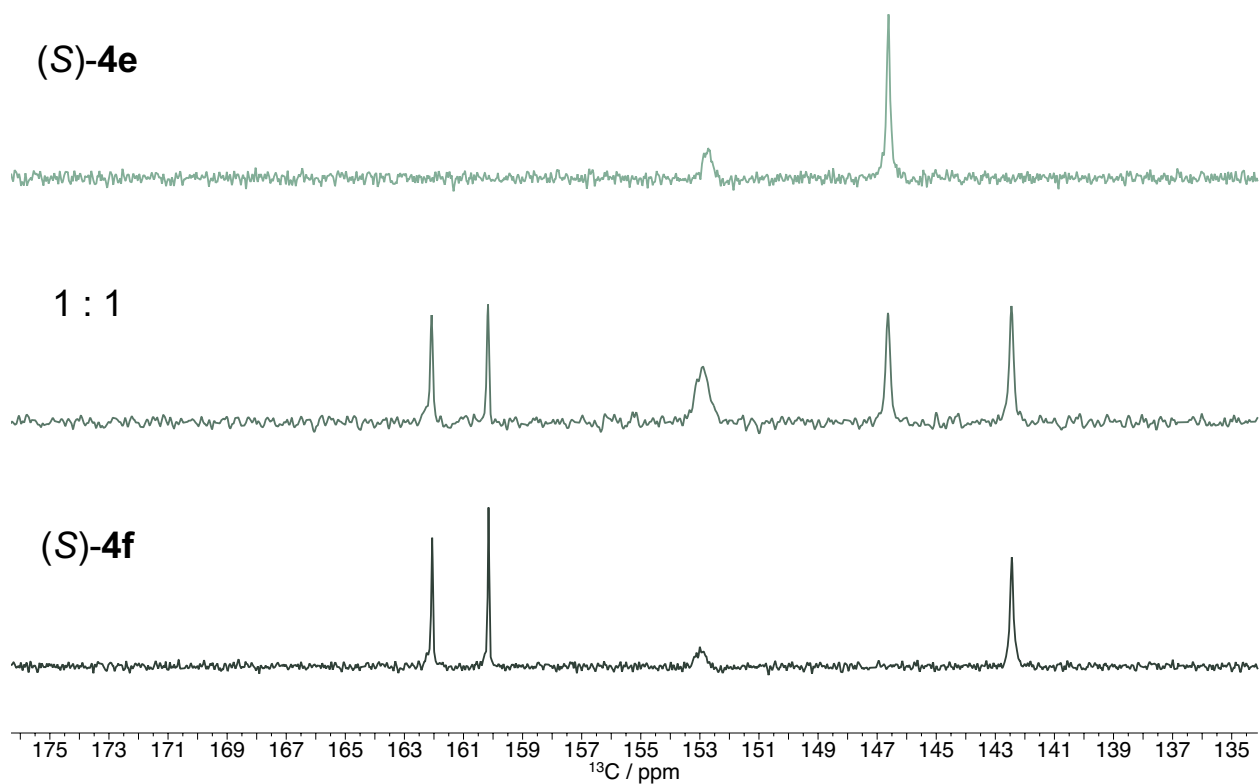
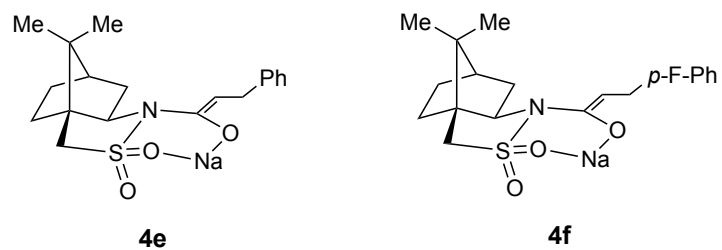


Figure S9. ^{13}C NMR spectra of mixtures of (S)-**4e** and (S)-**4f** in THF at $-80\text{ }^\circ\text{C}$ highlighting the downfield aromatic region. The sealed NMR tubes were not aged. No new resonances appear in the mixed tube consistent with a monomer model.

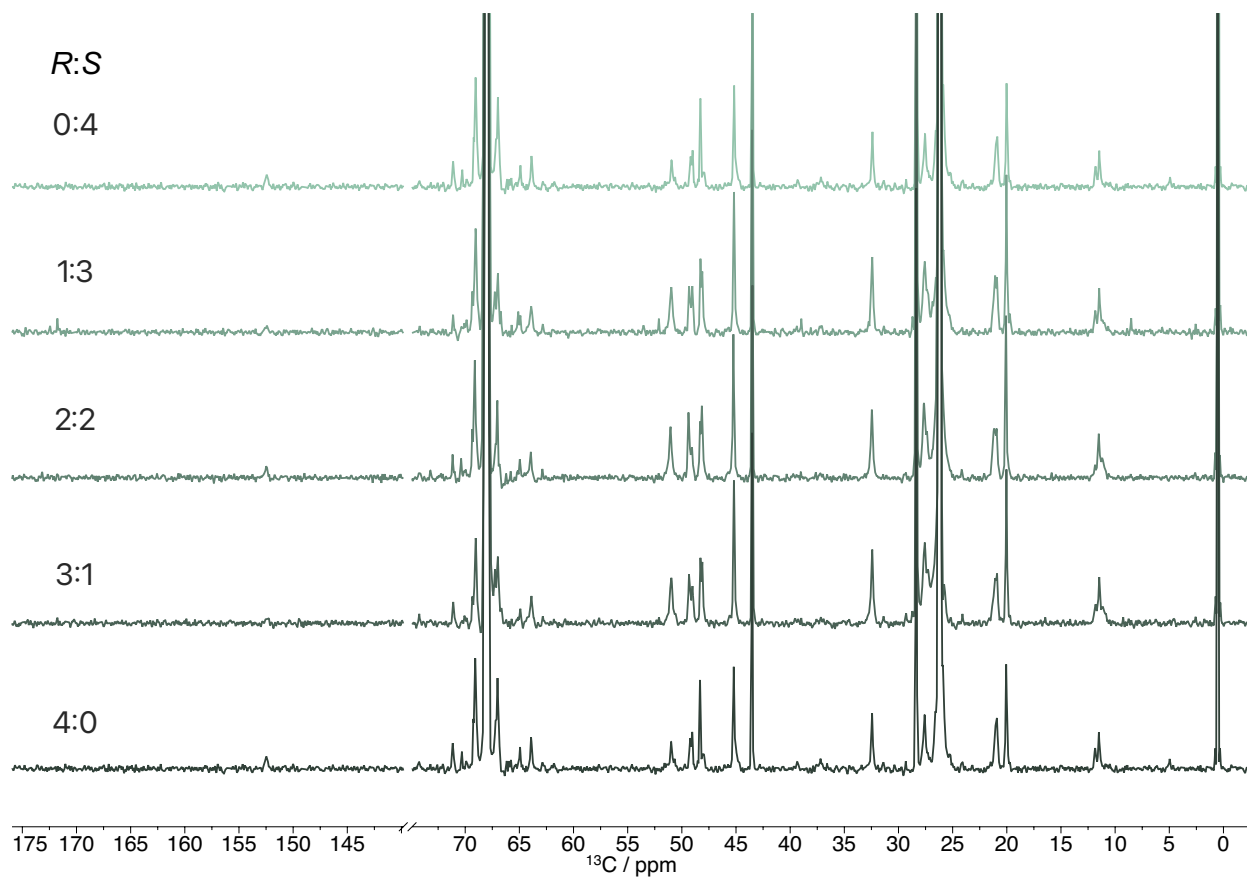
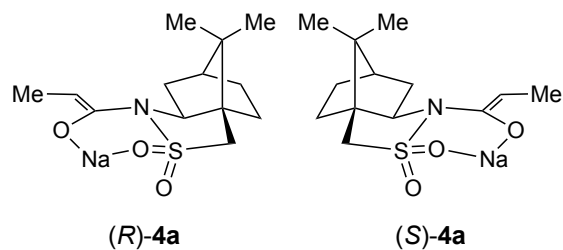


Figure S10. ^{13}C NMR spectra of mixtures of (*S*)-**4a** and (*R*)-**4a** in THF at $-80\text{ }^\circ\text{C}$. The sealed NMR tubes were not aged. No new resonances appear in the mixed tube consistent with a monomer model. *R*:*S* represents the total molar ratio of the two enantiomers.

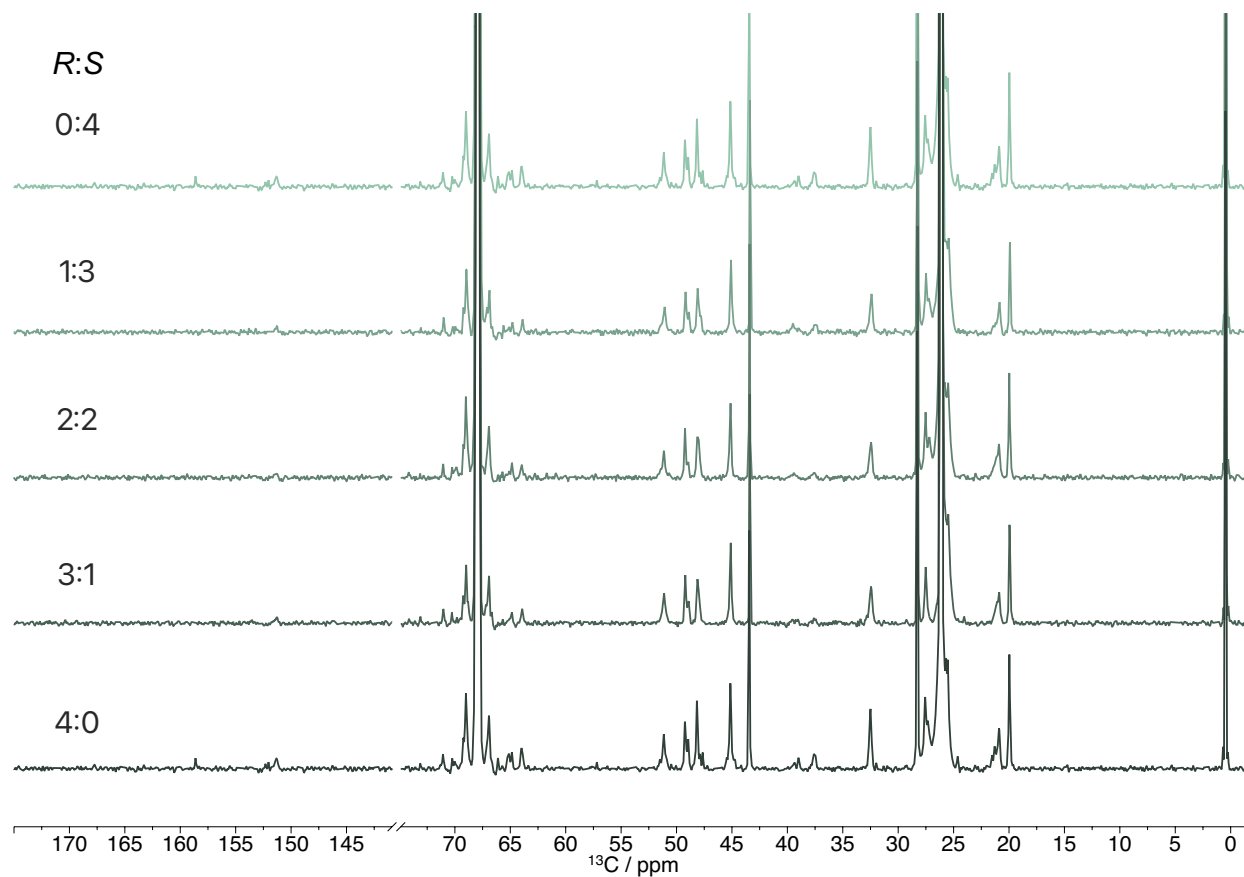
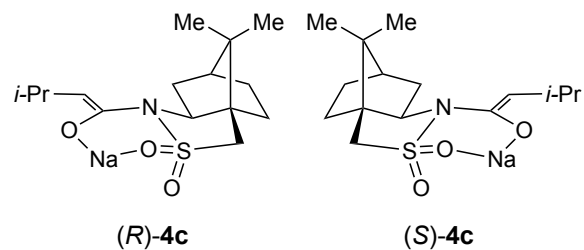


Figure S11. ^{13}C NMR spectra of mixtures of (*S*)-**4c** and (*R*)-**4c** in THF at $-80\text{ }^\circ\text{C}$. The sealed NMR tubes were not aged. No new resonances appear in the mixed tube consistent with a monomer model. *R:S* represents the total molar ratio of the two enantiomers.

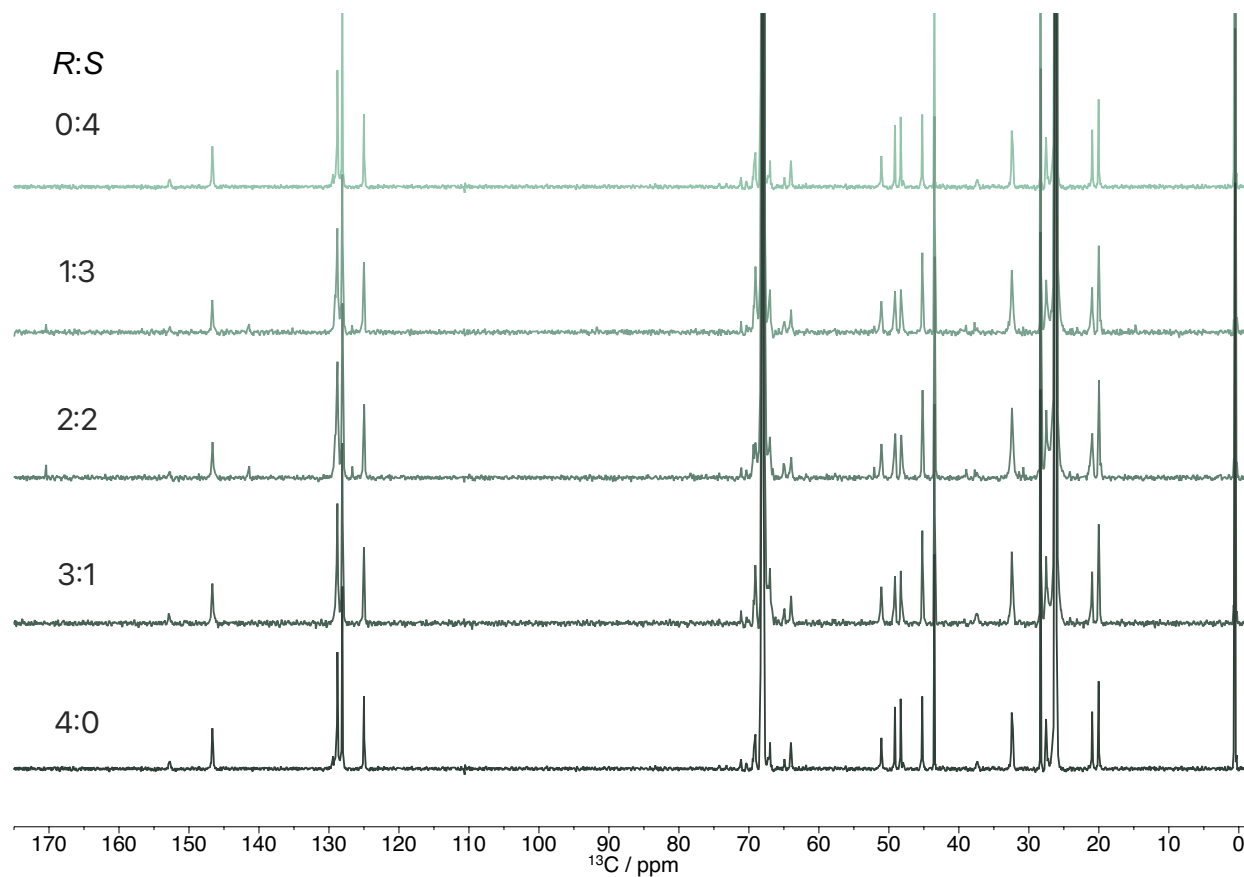
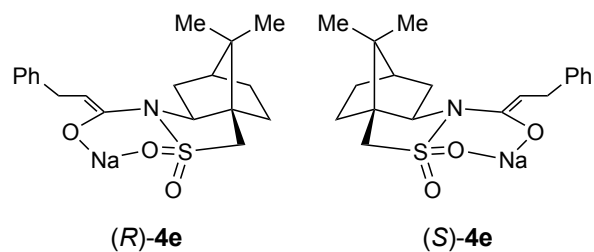


Figure S12. ^{13}C NMR spectra of mixtures of (*S*)-**4e** and (*R*)-**4e** in THF at $-80\text{ }^\circ\text{C}$. The sealed NMR tubes were not aged. No new resonances appear in the mixed tube consistent with a monomer model. *R:S* represents the total molar ratio of the two enantiomers.

THF-solvated enolate monomers (aryl-acetamide-derived enolates)

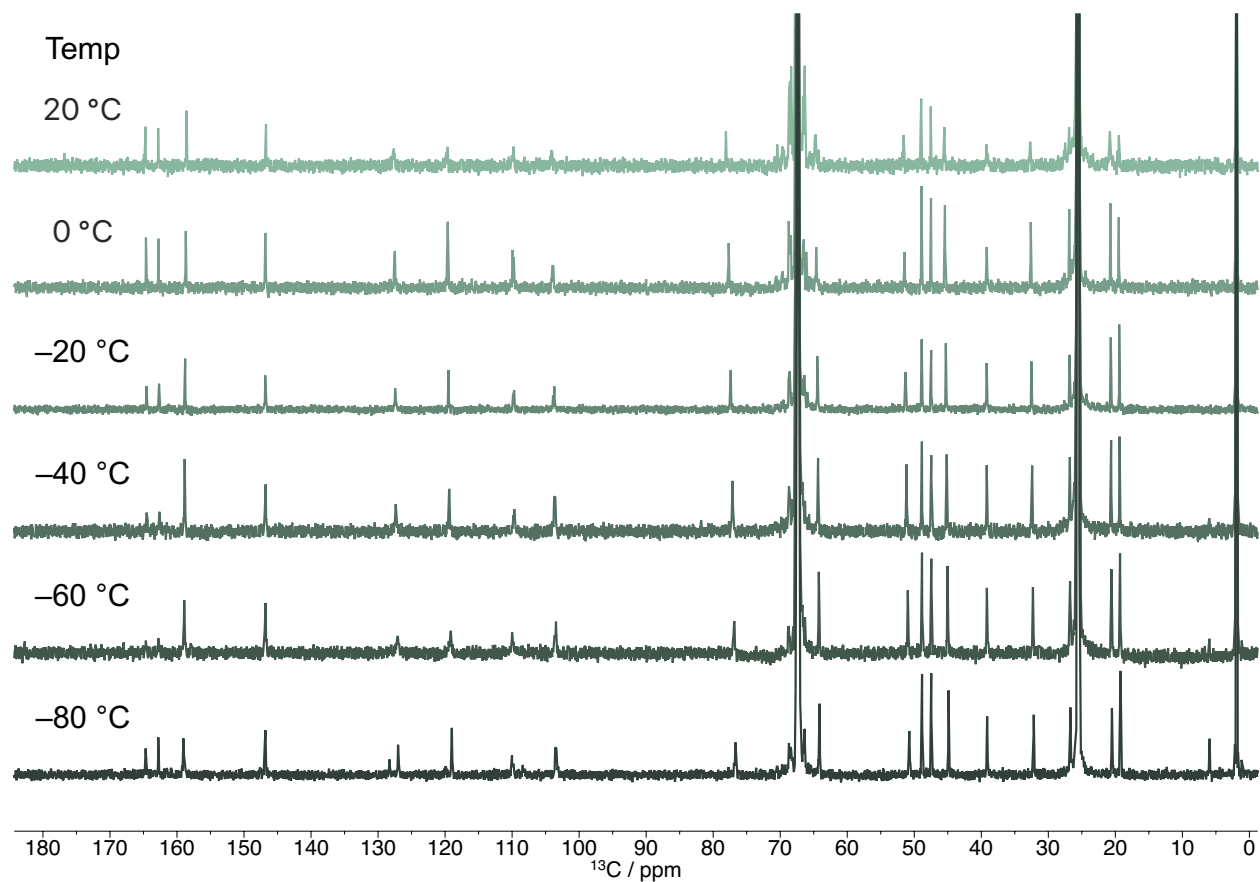
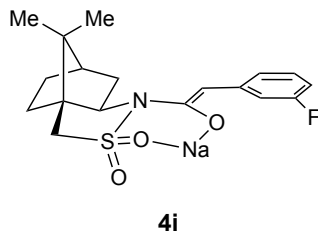
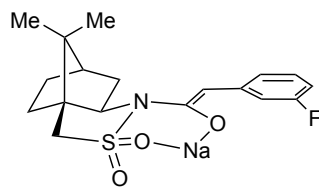


Figure S13. ¹³C NMR spectra of (*S*)-**4i** in THF at various temperatures. The sealed NMR tube was held at each temperature for 20 min to explore aggregate aging. No new resonances appear during the aging process suggesting no major changes in aggregate structure.



4i

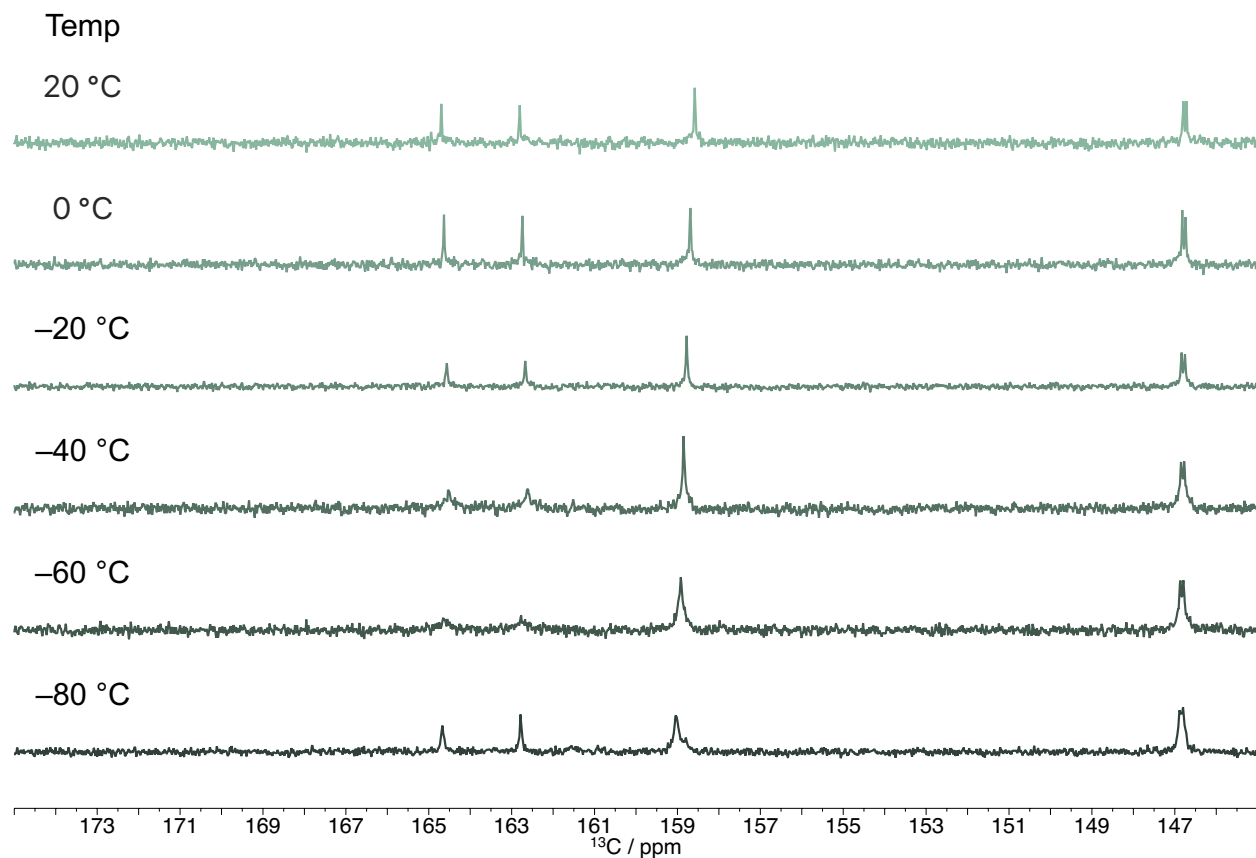


Figure S14. ¹³C NMR spectra of (S)-4i in THF at various temperatures highlighting the enolate and fluorinated carbons. The sealed NMR tube was held at each temperature for 20 min to explore aggregate aging. No new resonances appear during the aging process suggesting no major changes in aggregate structure.

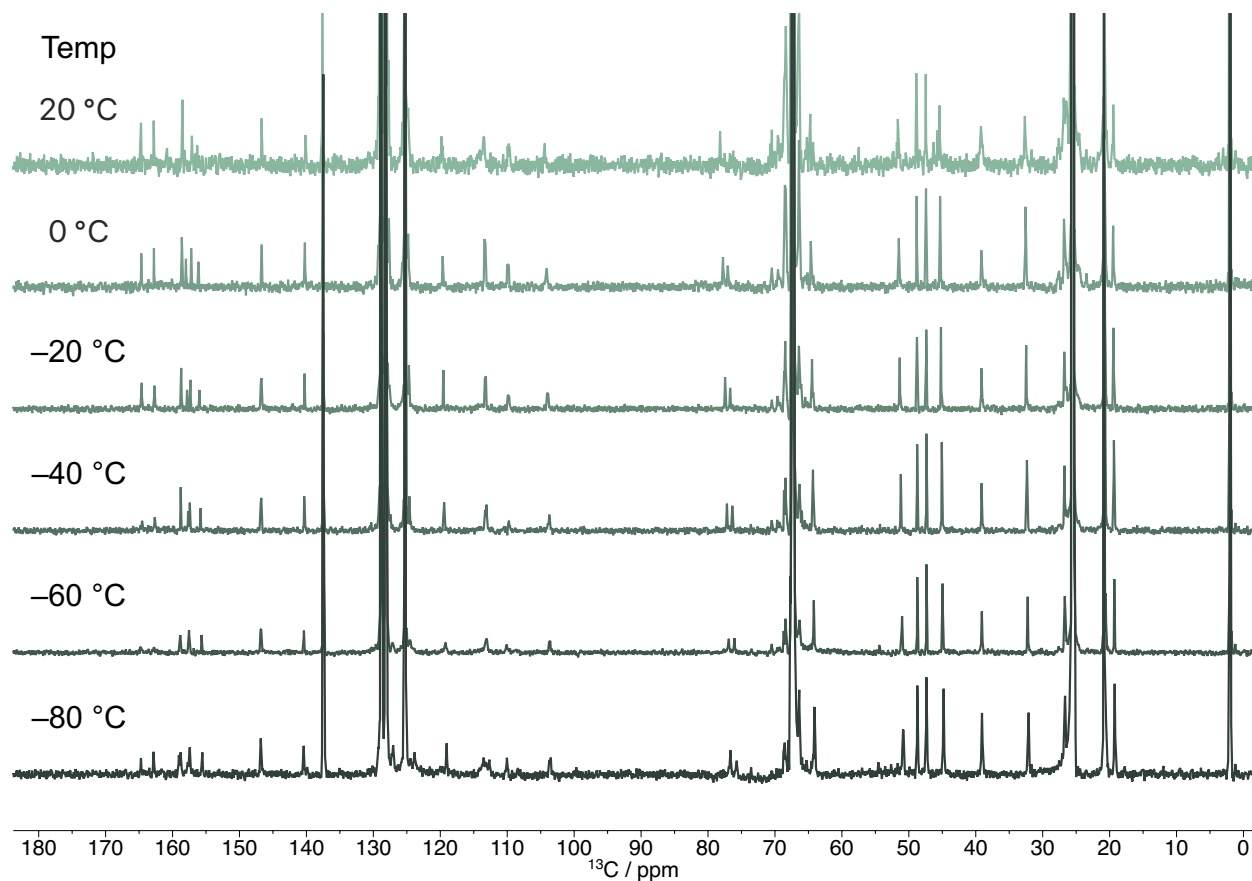
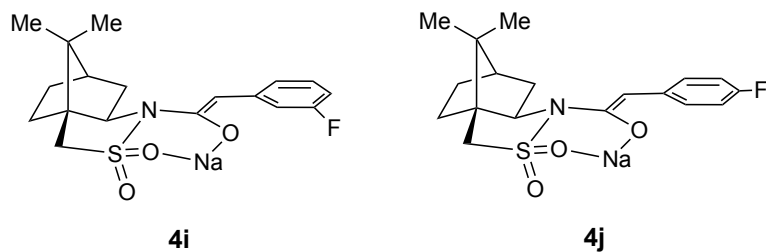


Figure S15. ¹³C NMR spectra of a 6:4 (**4i**:**4j**) mixture of (*S*)-**4i** and (*S*)-**4j** in 2:1 THF/toluene at various temperatures. The sealed NMR tube was held at each temperature for 20 min to explore aggregate aging. No new resonances appear during the aging process suggesting no major changes in aggregate structure.

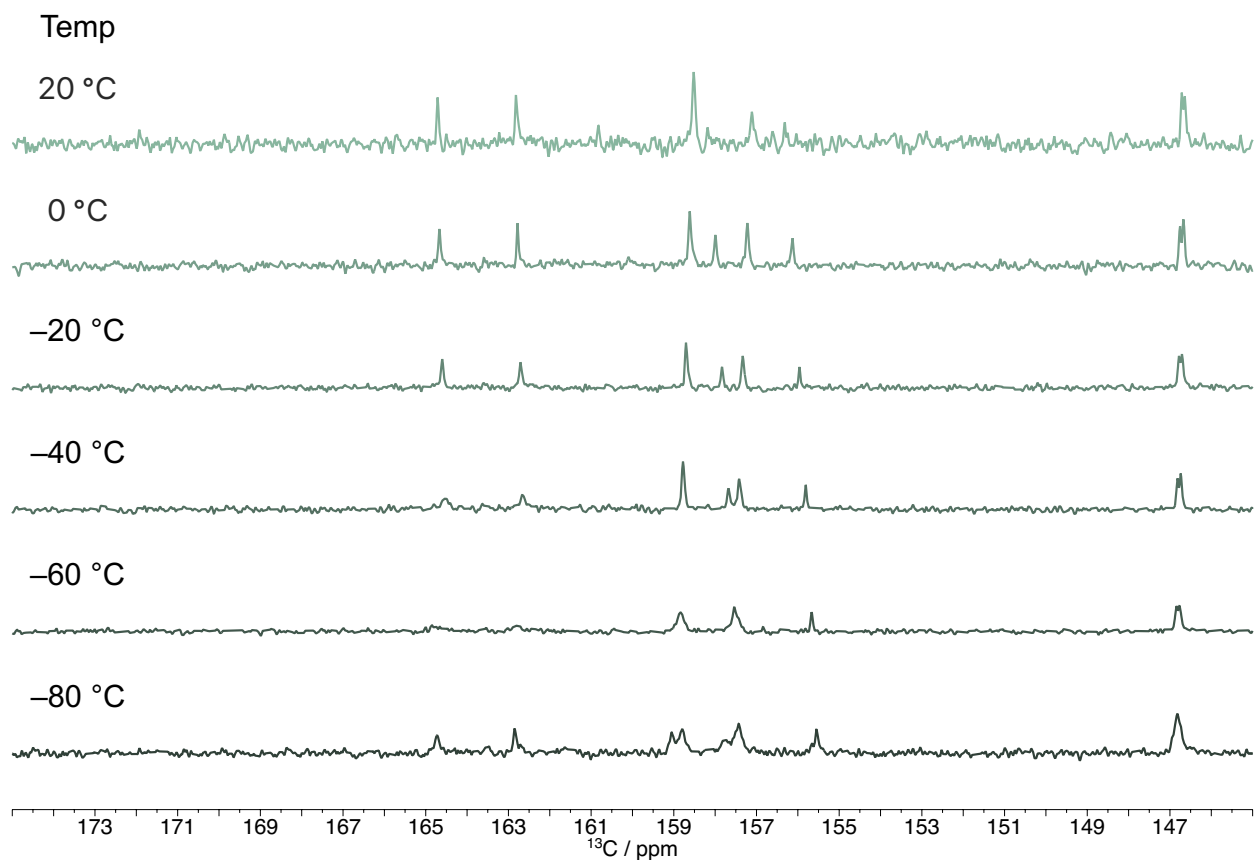
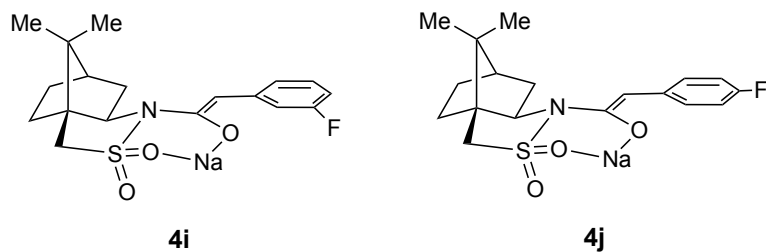


Figure S16. ^{13}C NMR spectra of a 6:4 (**4i**:**4j**) mixture of (*S*)-**4i** and (*S*)-**4j** in 2:1 THF/toluene at various temperatures highlighting the enolate and fluorinated carbons. The sealed NMR tube was held at each temperature for 20 min to explore aggregate aging. No new resonances appear during the aging process suggesting no major changes in aggregate structure.

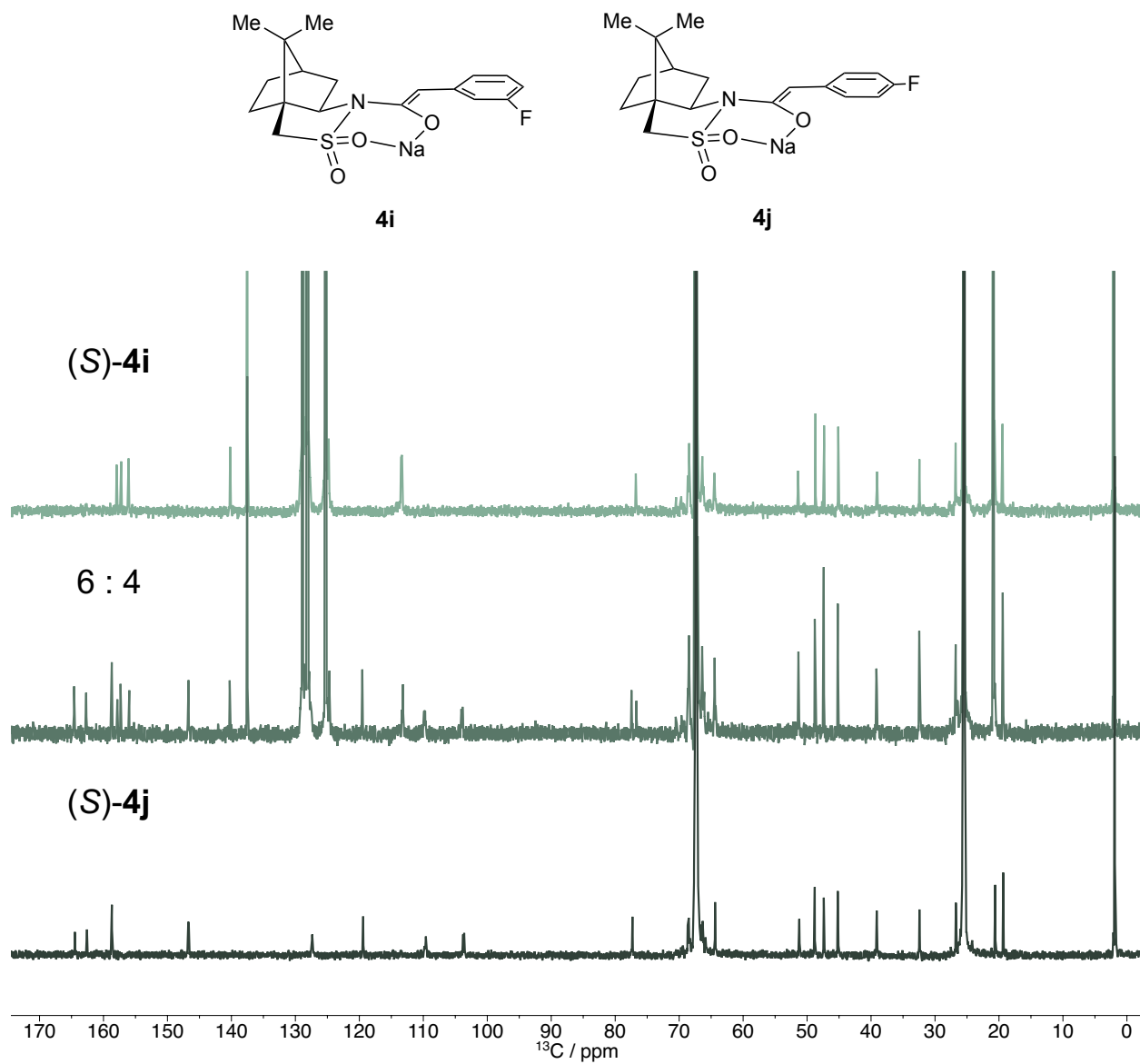
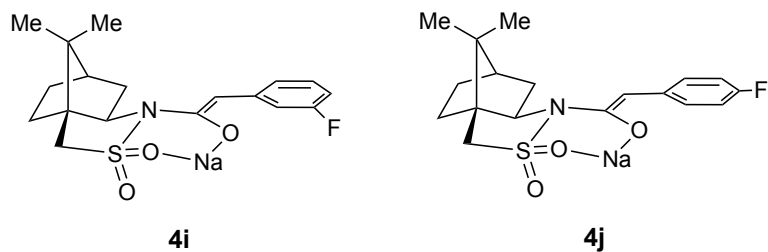


Figure S17. ^{13}C NMR spectra of **(S)-4i**, **(S)-4j**, and a 6:4 (**4i:4j**) mixture of the two in 2:1 THF/toluene at $-20\text{ }^\circ\text{C}$. The sealed NMR tubes were aged at $-20\text{ }^\circ\text{C}$ for 20 min. No new resonances appear in the mixed tube consistent with a monomer model.



(S)-4i



6 : 4



(S)-4j

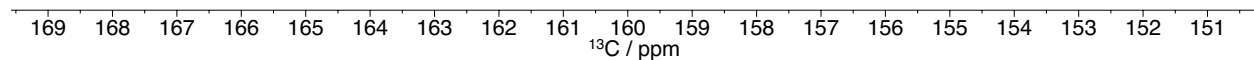


Figure S18. ^{13}C NMR spectra of (S)-4i, (S)-4j, and a 6:4 (4i:4j) mixture of the two in 2:1 THF/toluene at $-20\text{ }^\circ\text{C}$ highlighting the enolate and fluorinated carbons. The sealed NMR tubes were aged at $-20\text{ }^\circ\text{C}$ for 20 min. No new resonances appear in the mixed tube consistent with a monomer model.

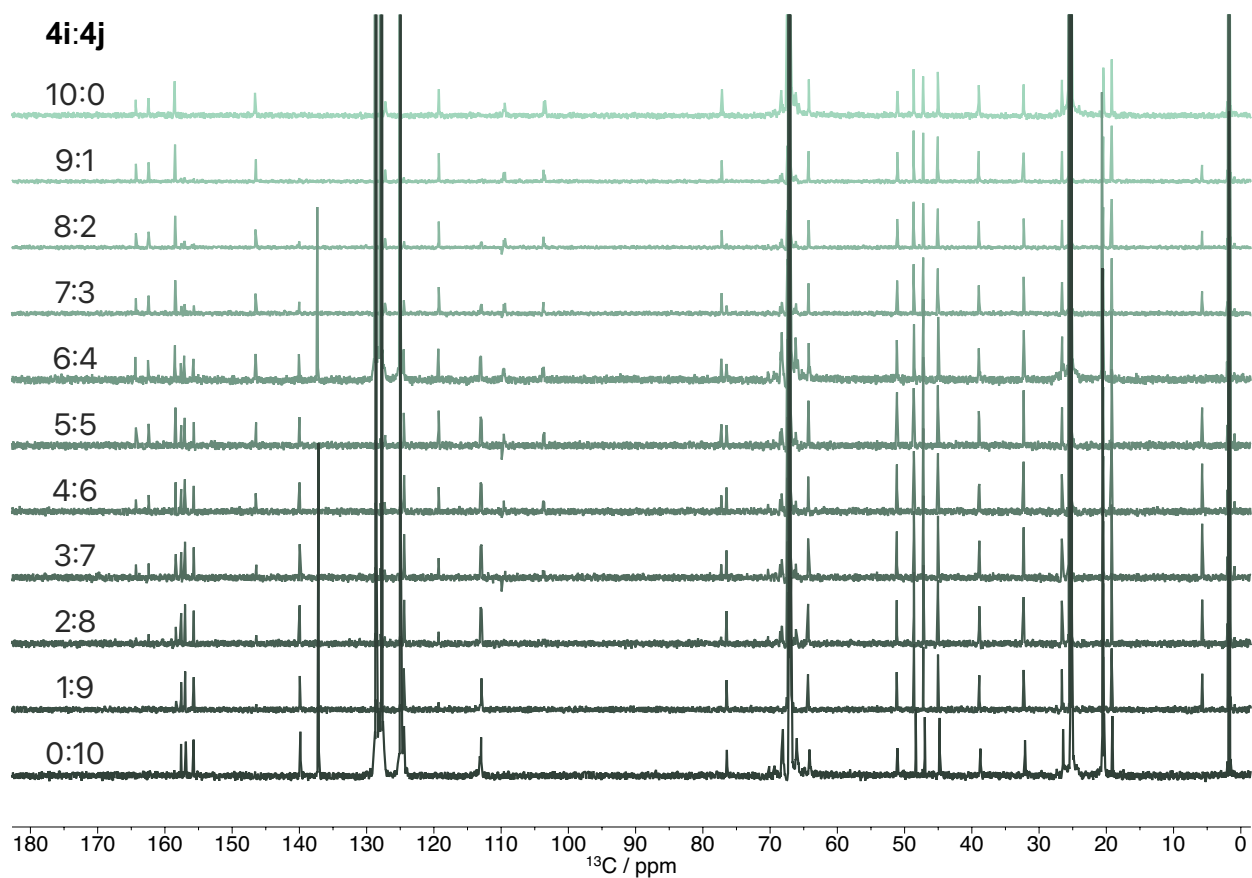
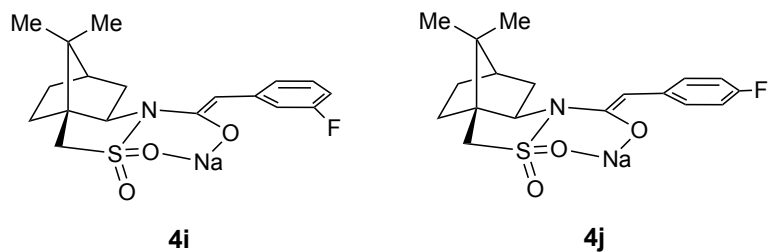


Figure S19. ^{13}C NMR spectra of mixtures of (*S*)-**4i** and (*S*)-**4j** in THF at $-20\text{ }^{\circ}\text{C}$. The sealed NMR tubes were aged at $-20\text{ }^{\circ}\text{C}$ for 20 min. No new resonances appear in the mixed tube consistent with a monomer model. **4i:4j** represents the molar ratio of the two enolates.

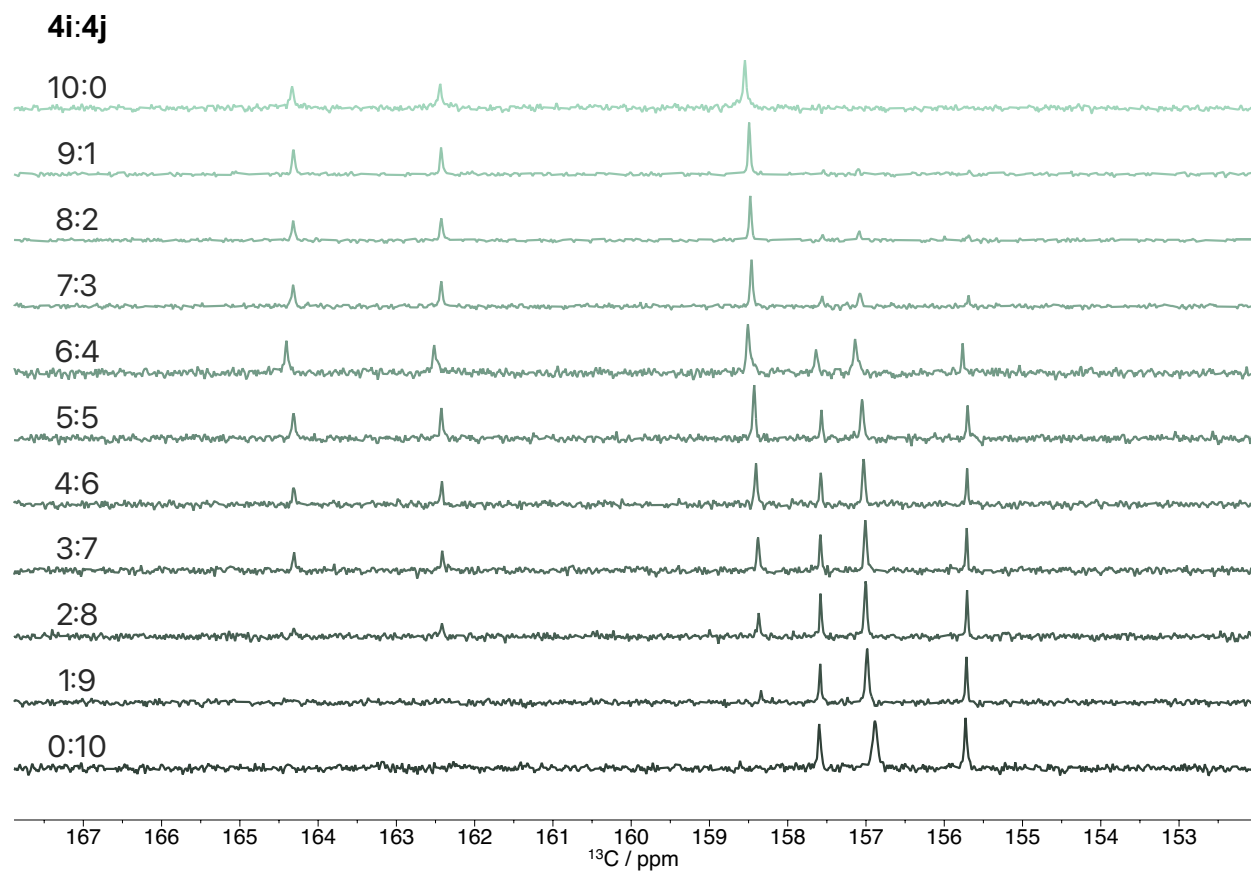
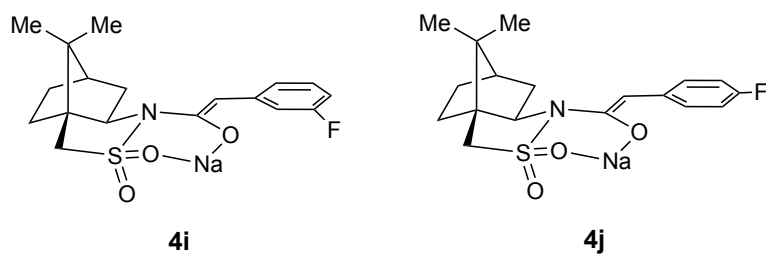


Figure S20. ^{13}C NMR spectra of mixtures of (*S*)-**4i** and (*S*)-**4j** in THF at $-20\text{ }^{\circ}\text{C}$ highlighting the enolate and fluorinated carbons. The sealed NMR tubes were aged at $-20\text{ }^{\circ}\text{C}$ for 20 min. No new resonances appear in the mixed tube consistent with a monomer model. **4i:4j** represents the molar ratio of the two enolates.

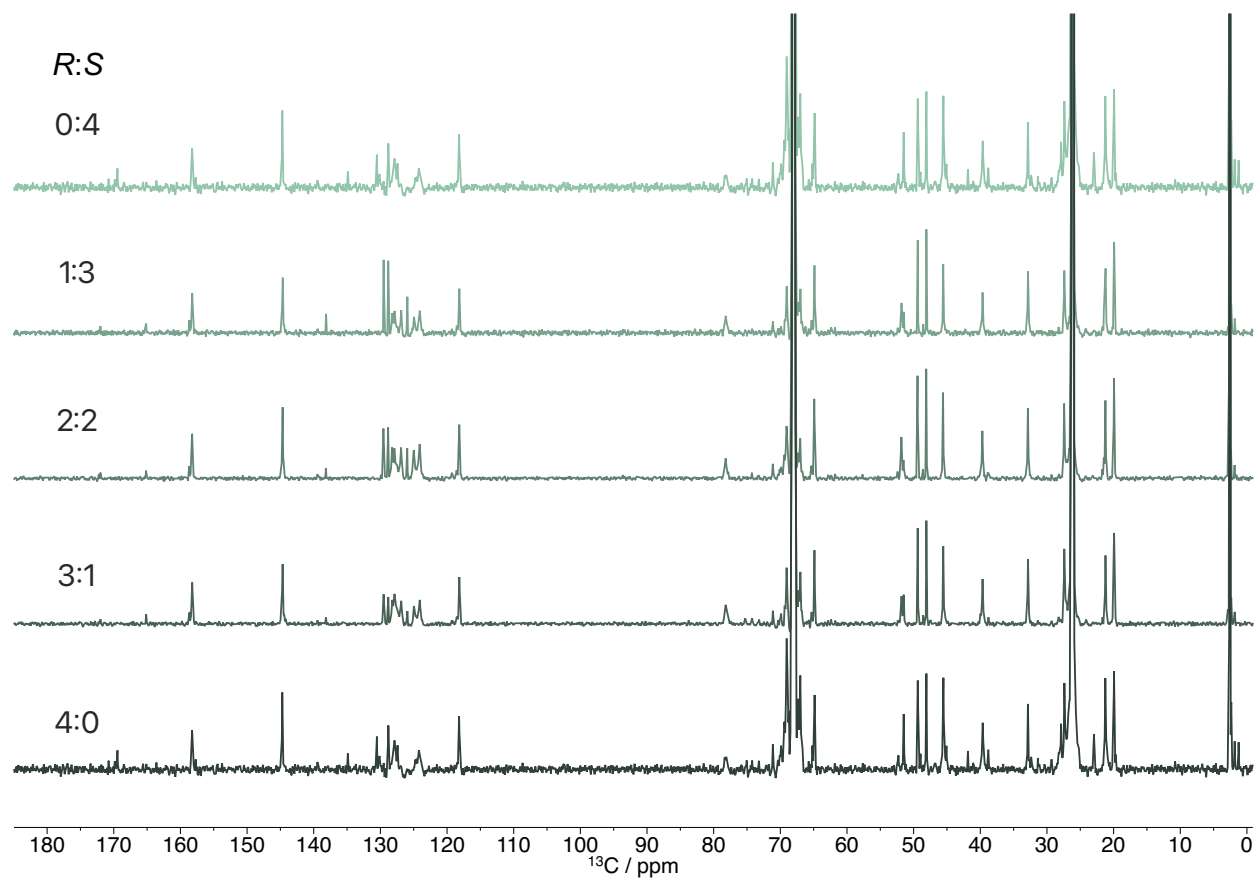
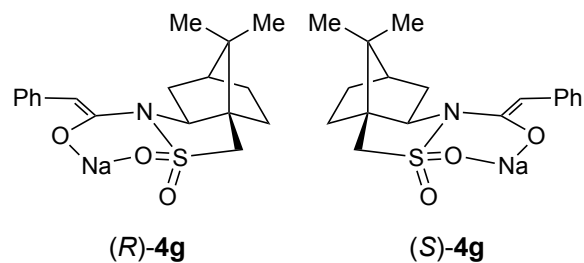
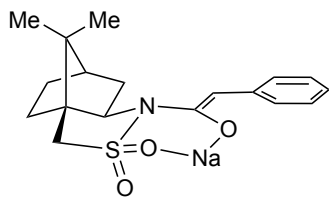
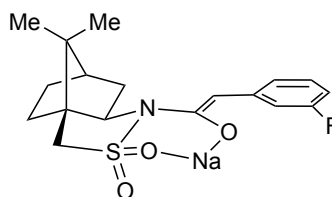


Figure S21. ^{13}C NMR spectra of mixtures of (*S*)-**4g** and (*R*)-**4g** in THF at $-80\text{ }^{\circ}\text{C}$. The sealed NMR tubes were not aged. No new resonances appear in the mixed tube consistent with a monomer model. *R:S* represents the total molar ratio of the two enantiomers.

TMEDA-solvated enolate dimers



4g



4i

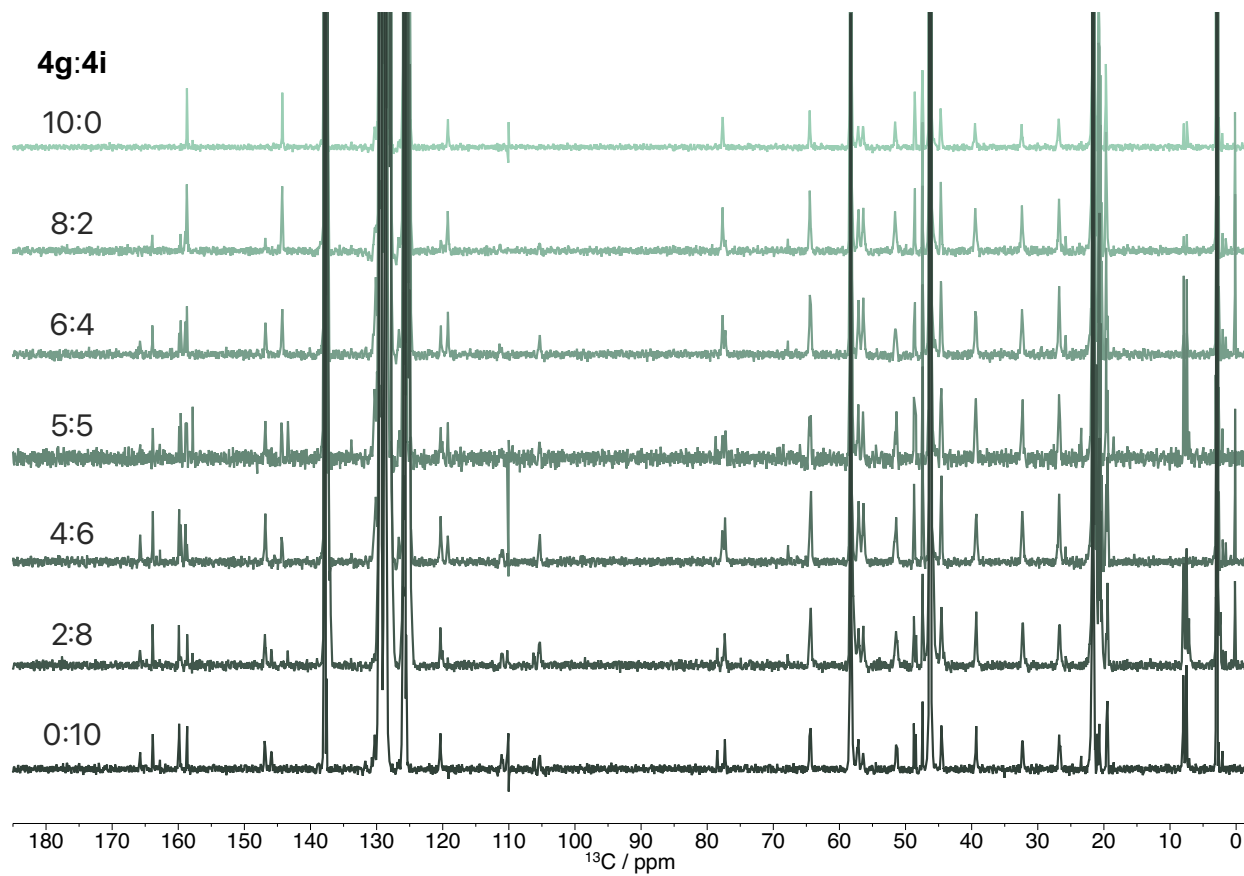


Figure S22. ¹³C NMR spectra of mixtures of (S)-4g and (S)-4i in 0.88 M TMEDA/toluene at -80 °C. The sealed NMR tubes were not aged. A new set of resonances appear in the mixed tube consistent with a dimer model.

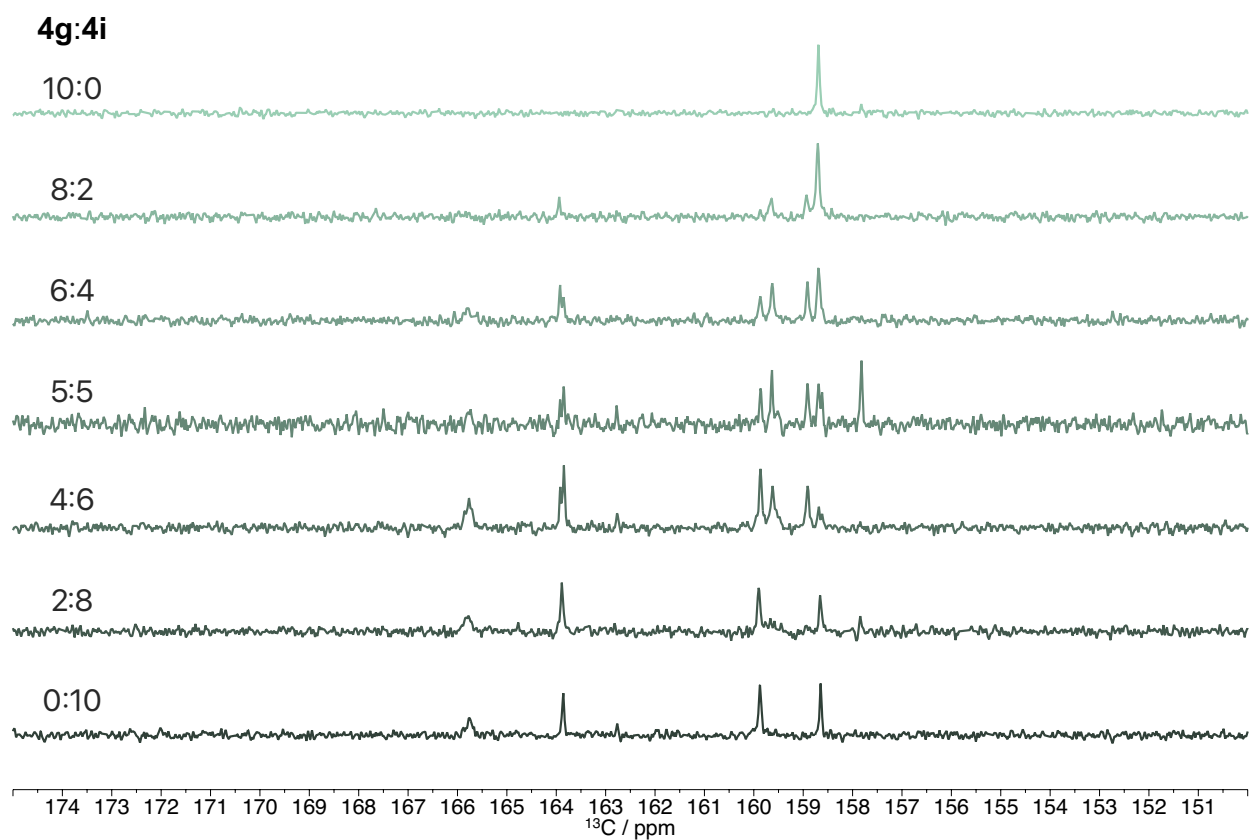
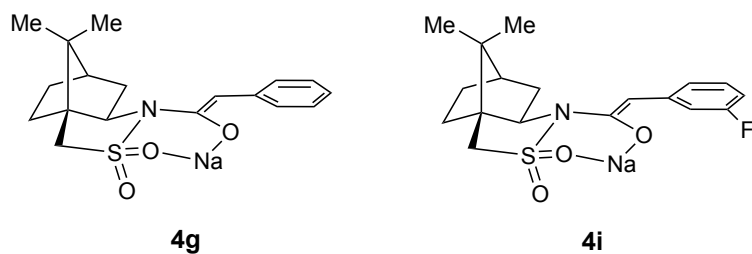


Figure S23. ^{13}C NMR spectra of mixtures of (*S*)-**4g** and (*S*)-**4i** in 0.88 M TMEDA/toluene at $-80\text{ }^\circ\text{C}$ highlighting the enolate and fluorinated carbons. The sealed NMR tubes were not aged. A new set of resonances appear in the mixed tube consistent with a dimer model.

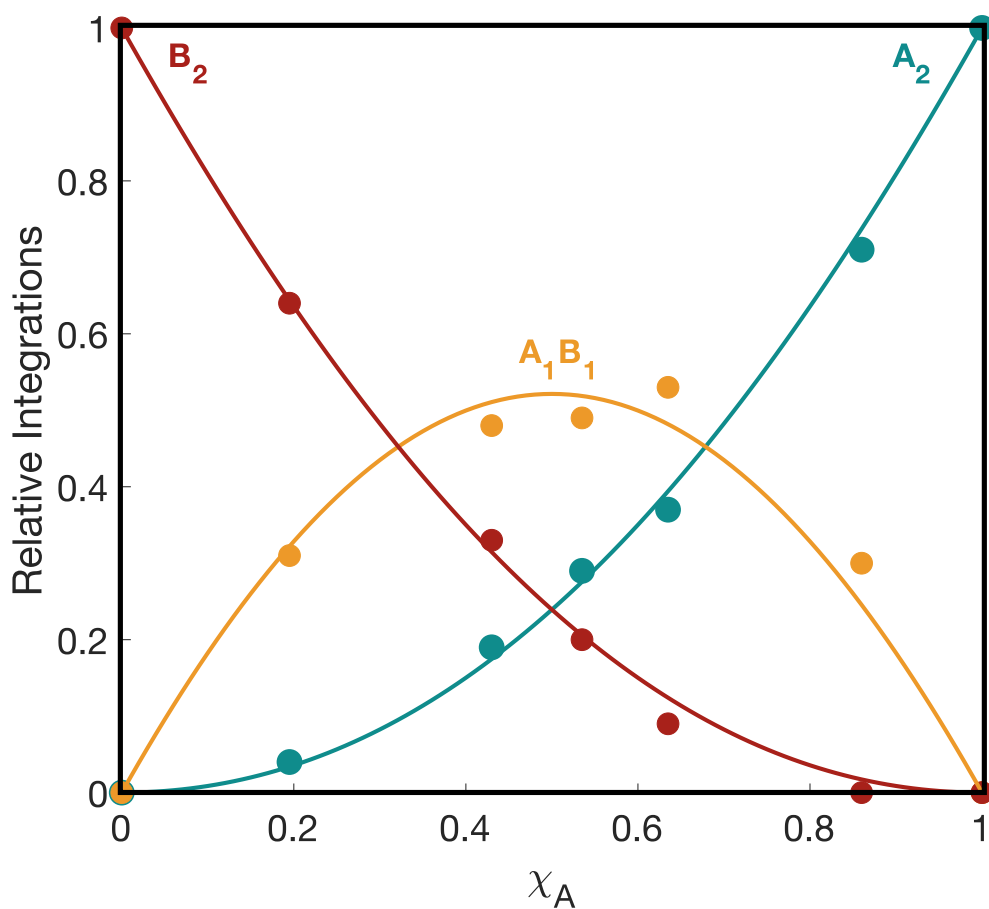
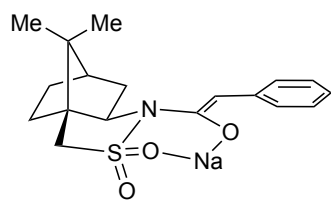
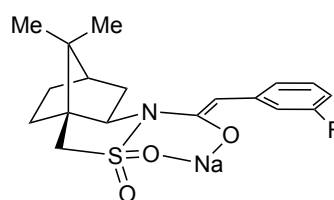


Figure S24. ^{13}C Job plot showing relative integrations of homodimers of **4g** (A_2 , red) and **4i** (B_2 , blue) and the heterodimer (A_1B_1 , orange) plotted against the measured mole fraction of **4g** (χ_A) for 0.20 M mixtures of sodium enolates **4g** and **4i** in 0.88 M TMEDA/toluene at -80°C monitored by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy (Figure S23). The curves result from a parametric fit to a dimer model.



4g



4i

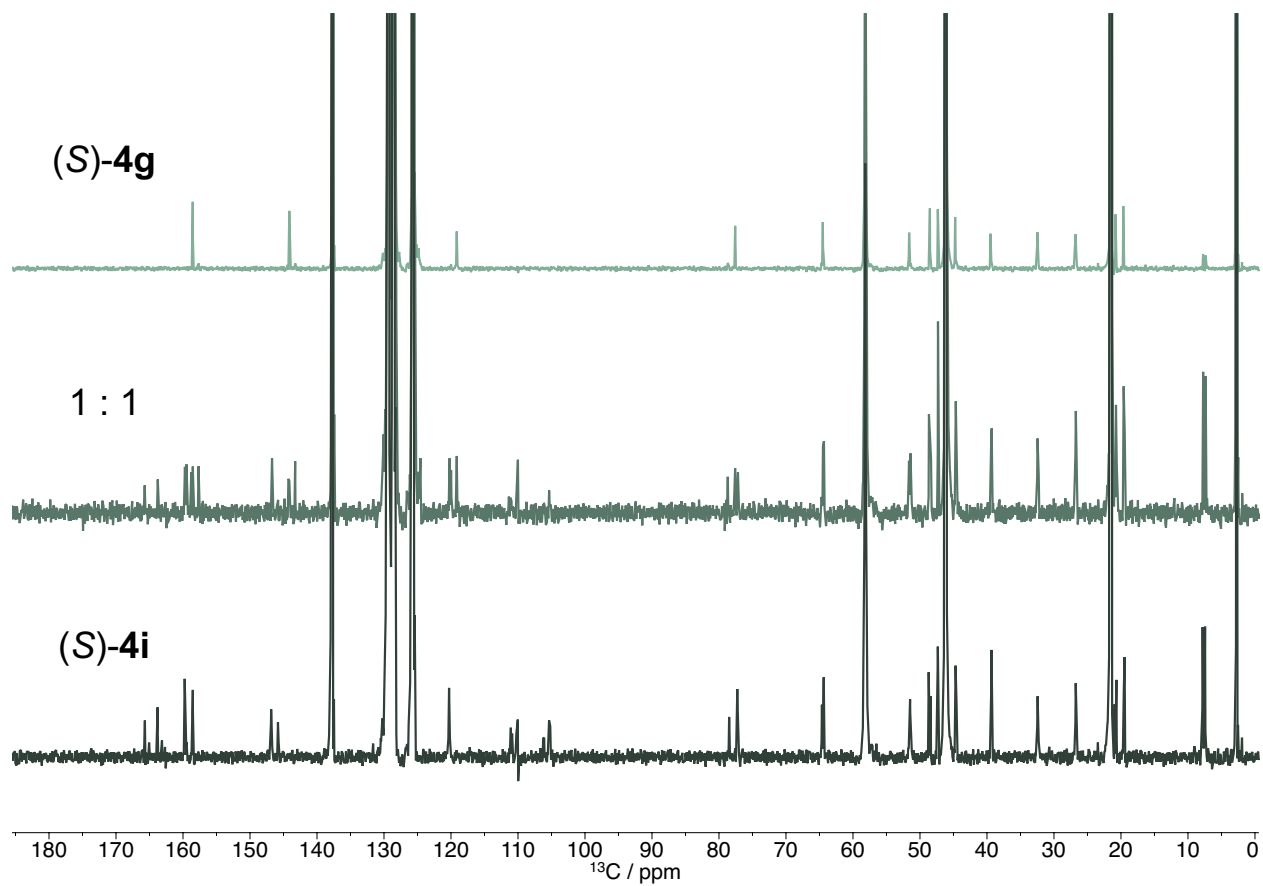


Figure S25. ^{13}C NMR spectra of mixtures of **(S)-4g** and **(S)-4i** in 0.88 M TMEDA/toluene at $-60\text{ }^\circ\text{C}$. The sealed NMR tubes were aged at $-60\text{ }^\circ\text{C}$ for 5 min before spectra collection. A new set of resonances appear in the mixed tube consistent with a dimer model.

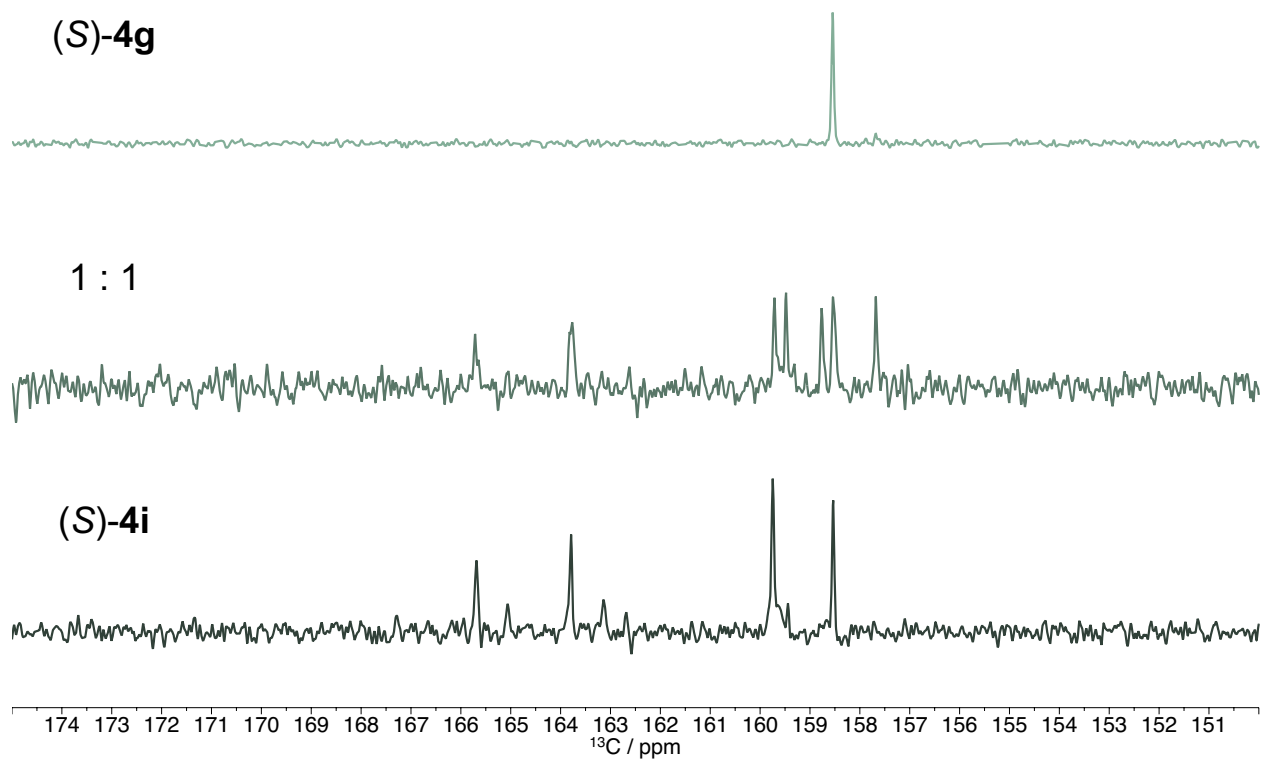
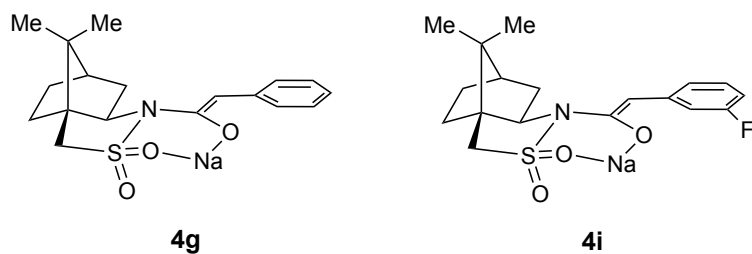


Figure S26. ¹³C NMR spectra of mixtures of (S)-**4g** and (S)-**4i** in 0.88 M TMEDA/toluene at $-60\text{ }^{\circ}\text{C}$ highlighting the enolate and fluorinated carbons. The sealed NMR tubes were aged at $-60\text{ }^{\circ}\text{C}$ for 5 min before spectra collection. A new set of resonances appear in the mixed tube consistent with a dimer model.

PMDTA-solvated enolate dimers

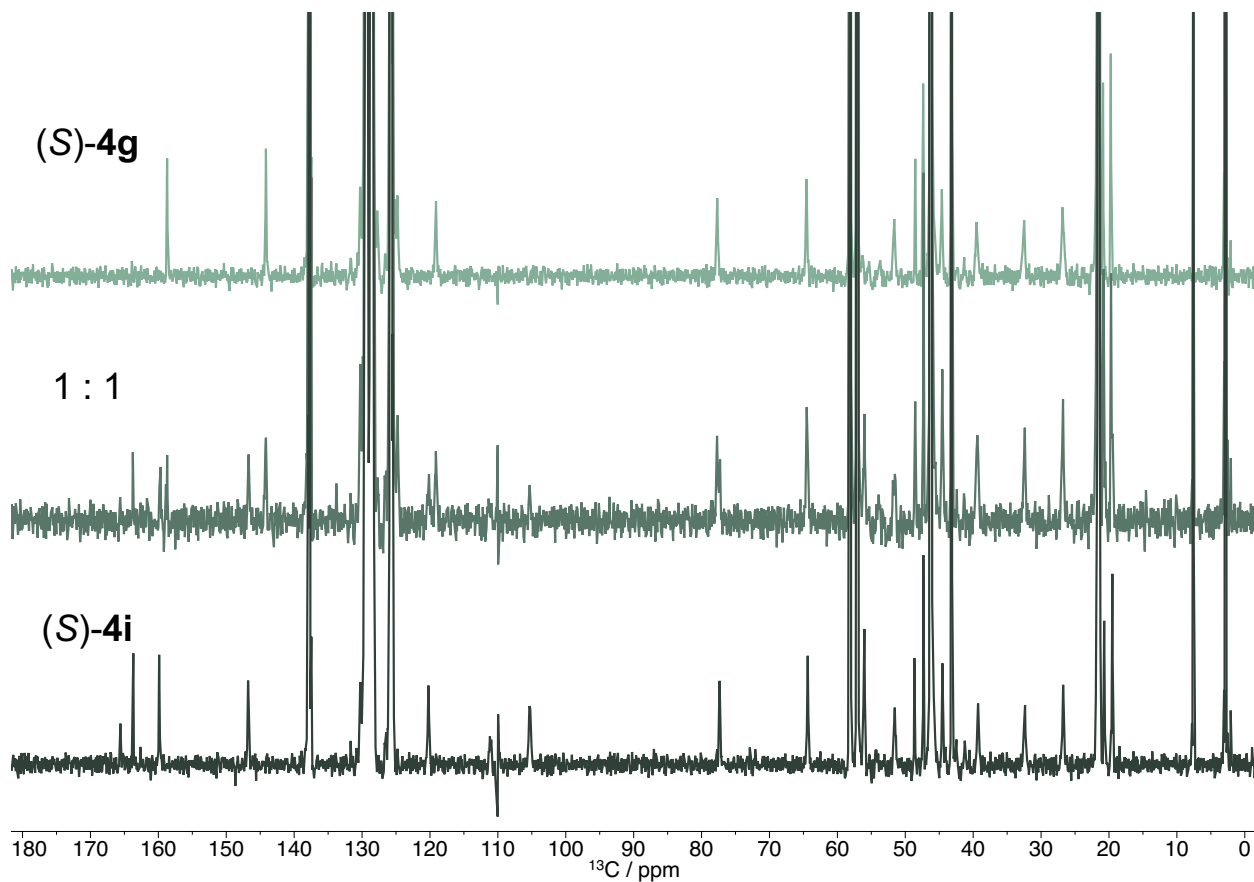
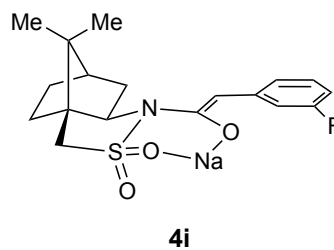
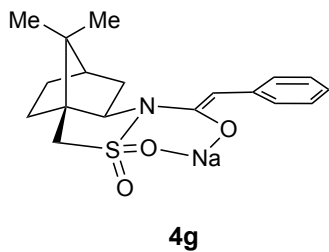
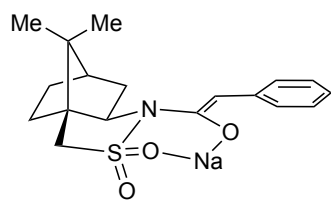
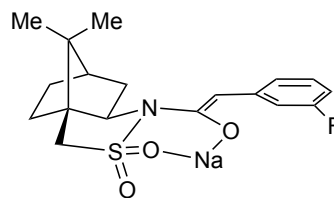


Figure S27. ¹³C NMR spectra of mixtures of (S)-4g and (S)-4i in 0.66 M PMDTA/toluene at -80 °C. The sealed NMR tubes were not aged. A new set of resonances appear in the mixed tube consistent with a dimer model.



4g



4i

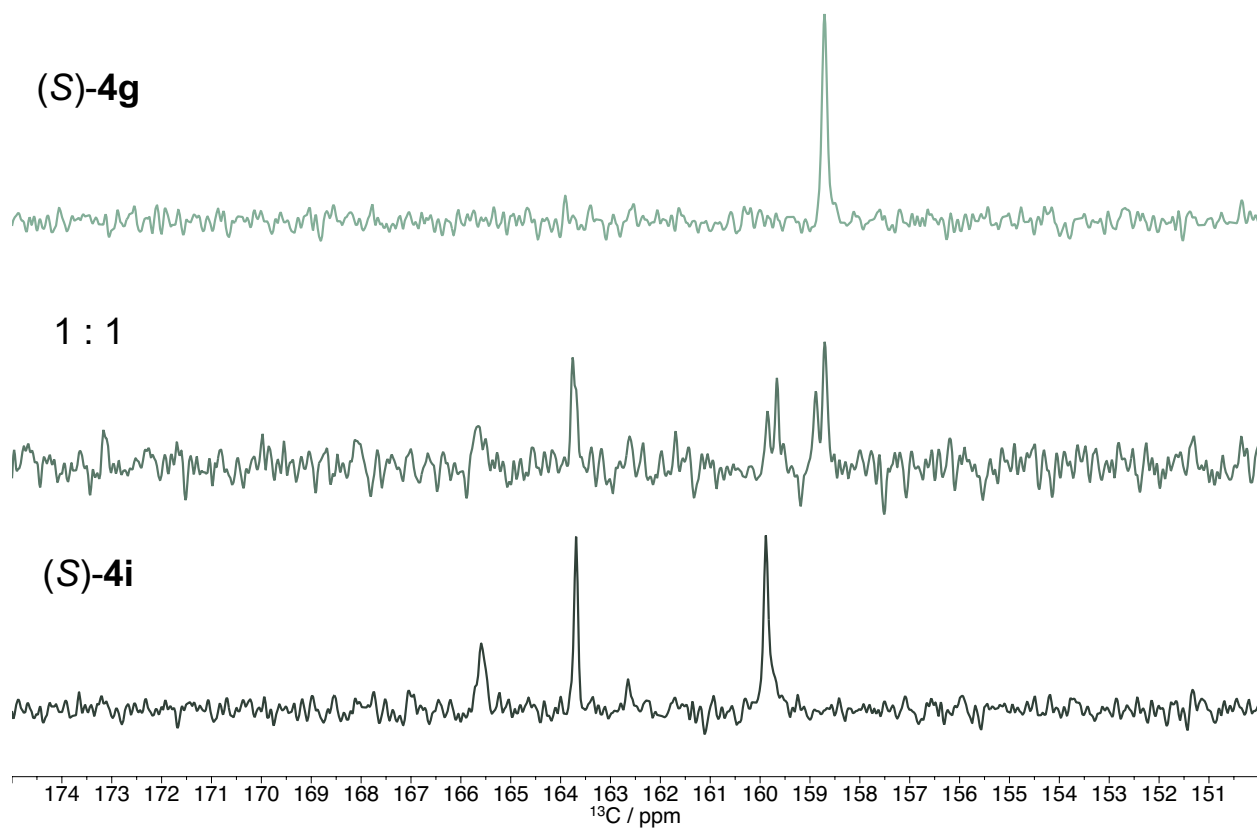


Figure S28. ¹³C NMR spectra of mixtures of (S)-4g and (S)-4i in 0.66 M PMDTA/toluene at -80 °C highlighting the enolate and fluorinated carbons. The sealed NMR tubes were not aged. A new set of resonances appear in the mixed tube consistent with a dimer model.

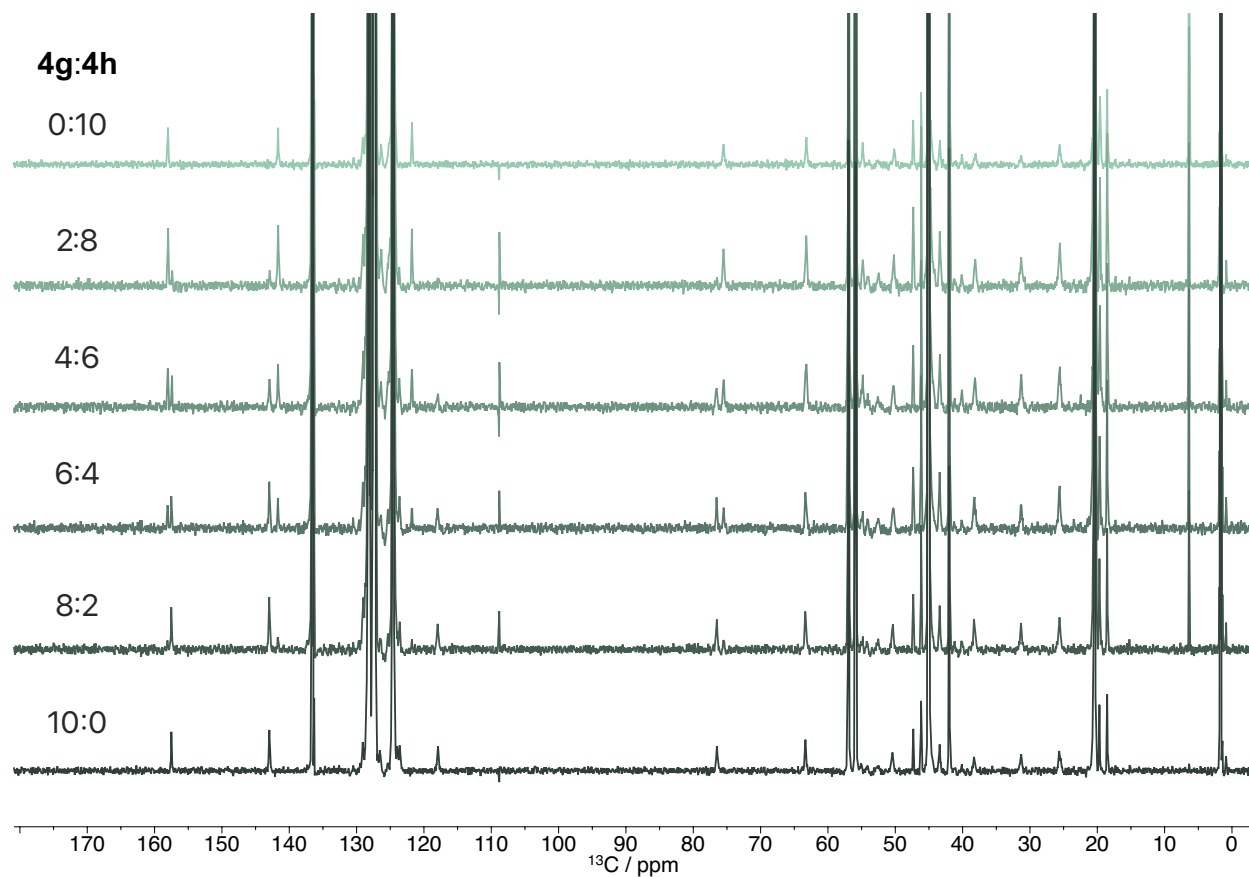
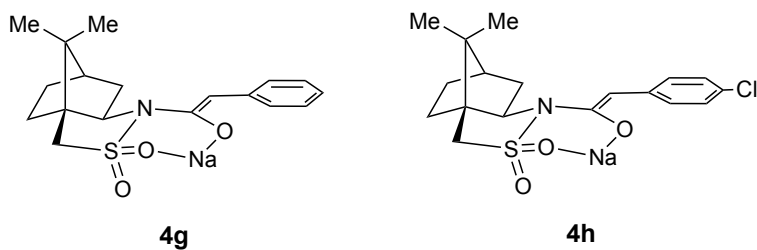


Figure S29. ^{13}C NMR spectra of mixtures of (*S*)-**4g** and (*S*)-**4h** in 0.66 M PMDTA/toluene at $-80\text{ }^\circ\text{C}$. The sealed NMR tubes were not aged. A new set of resonances appear in the mixed tube consistent with a dimer model. **4g:4h** represents the molar ratio of the two enolates.

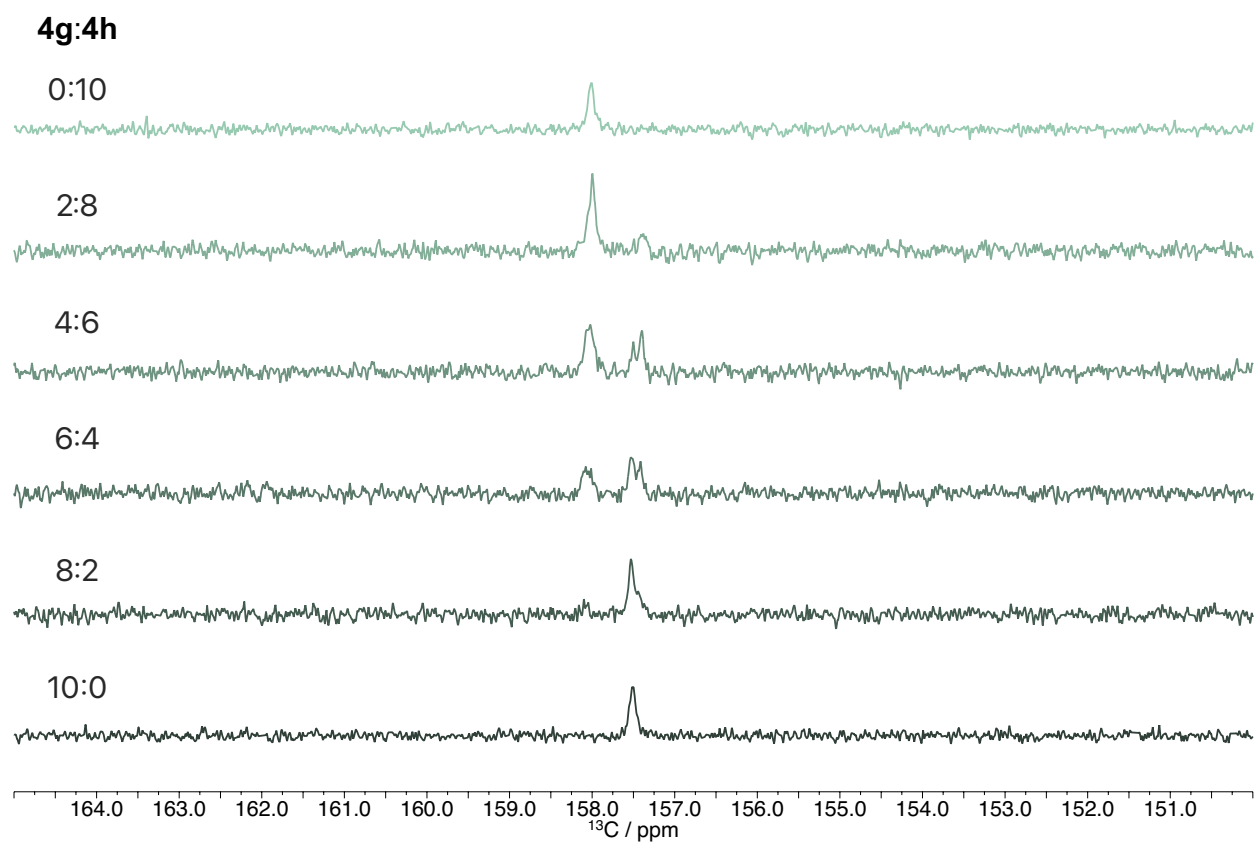
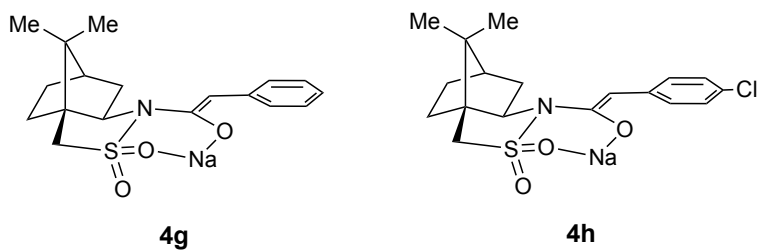


Figure S30. ^{13}C NMR spectra of mixtures of (*S*)-**4g** and (*S*)-**4h** in 0.66 M PMDTA/toluene at $-80\text{ }^{\circ}\text{C}$ highlighting the enolate carbons. The sealed NMR tubes were not aged. A new set of resonances appear in the mixed tube consistent with a dimer model. **4g:4h** represents the molar ratio of the two enolates.

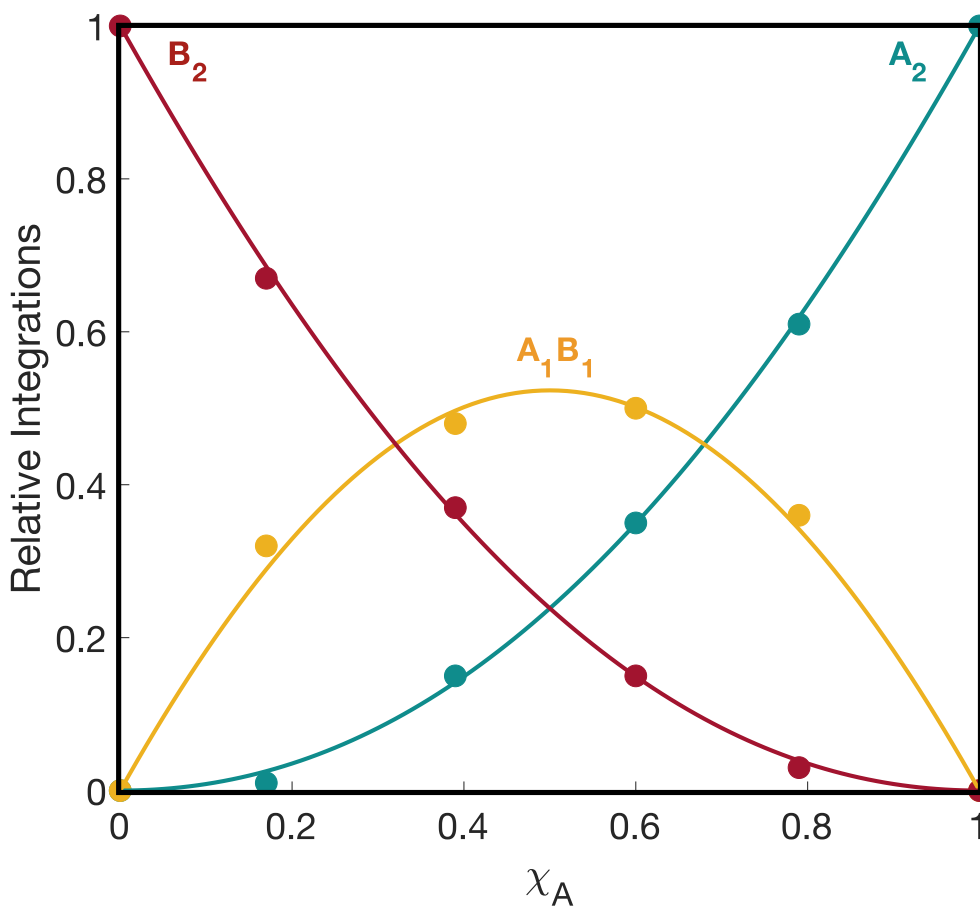


Figure S31. ^{13}C Job plot showing relative integrations of homodimers of **4g** (A_2 , red) and **4h** (B_2 , blue) and the heterodimer (A_1B_1 , orange) plotted against the measured mole fraction of **4g** (χ_A) for 0.20 M mixtures of sodium enolates **4g** and **4h** in 0.66 M PMDTA/toluene at $-80\text{ }^\circ\text{C}$ monitored by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy (Figure S30). The curves result from a parametric fit to a dimer model.

Rate Studies

General procedure for in situ IR analyses

IR spectra were recorded with an in situ IR spectrometer (ReactIR iC 10, Mettler Toledo AutoChem) fitted with a 30-bounce, silicon-tipped probe. The spectra were acquired at a gain of 1 and a resolution of 4 cm^{-1} . All tracked reactions were conducted under a positive pressure of argon from a Schlenk line. A representative reaction was carried out as follows:

The IR probe was inserted through a Teflon adapter and O-ring seal into an oven-dried, cylindrical flask fitted with a magnetic stir bar and a T-joint. The T-joint was fitted with a septum for injections and an argon line. After evacuation under full vacuum, heating, and flushing with argon, the flask was charged with the THF/cosolvent mixture of choice (toluene, 2,5-Me₂THF, toluene/cyclopentane) and cooled to $-78\text{ }^{\circ}\text{C}$ in a dry ice–acetone bath. A set of 256 baseline scans were collected and IR spectra were recorded every 15 seconds from 30 scans. The reaction vessel was charged to 0.025 M **3g** (1704 cm^{-1}). A 1.00 M stock solution of NaHMDS was injected (0.030 M, 1.2 equiv) through the septum, and enolization was tracked to completion (1616 cm^{-1}), typically ~ 10 min. Following full disappearance of **3g**, HMPA was added to the reaction as a 4.31 M (75 v/v%) stock solution in toluene to avoid freezing. For IR studies of the HMPA-free methylation this step was omitted. The reaction was left to stir for another 10 min. At this point, spectral collection was halted, and an additional 256 baseline scans were collected. The spectrometer was configured to collect spectra every 5 seconds from 16 scans. 1 set of scans was collected before addition of *neat* alkylating agent (methyl iodide or allyl bromide) through the septum. The reaction was tracked over 5 half-lives monitoring disappearance of the enolate (1616 cm^{-1}) and appearance of the adduct (1701 cm^{-1}).

HMPA-catalyzed allylation of enolate **4g** in THF

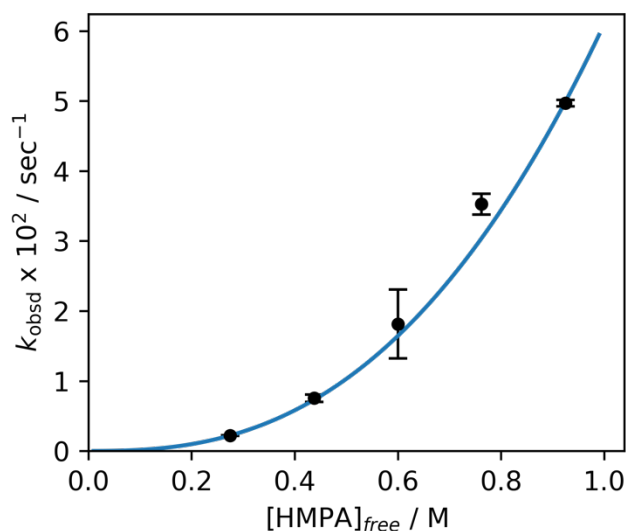


Figure S32. Plot of k_{obsd} against $[\text{HMPA}]_{\text{free}}$ for the allylation of enolate **4g** (0.025 M) with 0.275 M allyl bromide in 9.24 M THF/2,5-Me₂THF at -78 °C. The blue curve depicts an error-weighted least-squares fit to $f(x) = ax^b$ such that $a = 0.061 \pm 0.001$, $b = 2.56 \pm 0.01$.

Table S1. Average pseudo-first-order rate constants (k_{obsd}) at various free HMPA concentrations for the allylation of enolate **4g** (0.025 M) with 0.275 M allyl bromide in 9.24 M THF/2,5-Me₂THF at -78 °C.

[Free HMPA] / M	$k_{\text{obsd}} / \text{sec}^{-1}$	Standard deviation / sec^{-1}
0.275	0.00221135	0.00003754
0.438	0.0075508	0.00052481
0.6	0.0181295	0.00491934
0.762	0.035265	0.00148374
0.925	0.0496805	0.00045326

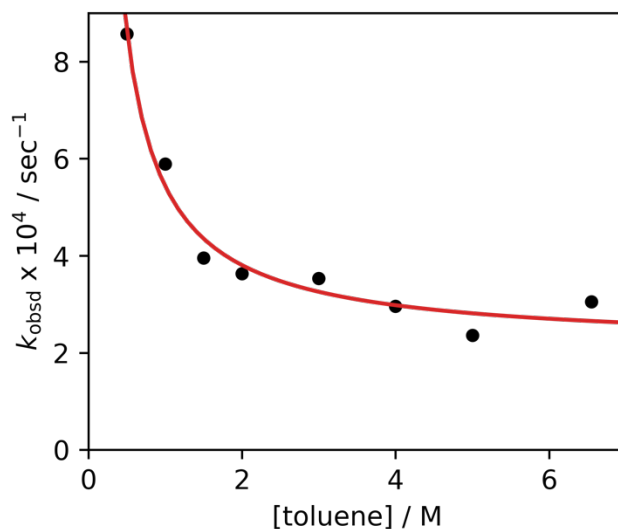


Figure S33. Plot of k_{obsd} against toluene concentration for the alkylation of 0.025 M **4g** at -78 °C with 0.275 M allyl bromide in 0.250 M *free* HMPA in 0.275 M THF using cyclopentane cosolvent. The curve depicts a least-squares fit to the function $f(x) = y_0 + ax^b$ such that $y_0 = 2.13 \times 10^{-4} \pm 0.58 \times 10^{-4}$, $a = 3.30 \times 10^{-4} \pm 0.79 \times 10^{-4}$, $b = -0.98 \pm 0.24$.

Table S2. Average pseudo-first-order rate constants (k_{obsd}) at various toluene concentrations for the alkylation of 0.025 M **4g** at -78 °C with 0.275 M allyl bromide in 0.250 M *free* HMPA in 0.275 M THF using cyclopentane cosolvent.

[toluene] / M	$k_{\text{obsd}} / \text{sec}^{-1}$
6.55	0.00030494
5	0.00021338
4	0.00029606
3	0.00035337
2	0.00036338
1.5	0.00039511
1	0.00058887
0.5	0.00073946

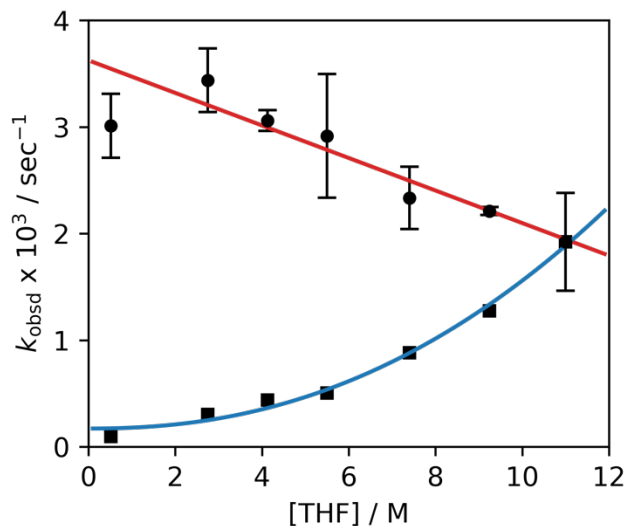


Figure S34. Plot of k_{obsd} against THF concentration for alkylation of 0.025 M **4g** with allyl bromide (0.275 M) in 0.250 M *free* HMPA at -78 °C in toluene (■) or 2,5-Me₂THF (●) cosolvent. The blue curve depicts a least-squares fit to the function $f(x) = y_0 + ax^b$ such that $y_0 = 1.71 \times 10^{-4} \pm 0.57 \times 10^{-4}$, $a = 8.16 \times 10^{-6} \pm 5.10 \times 10^{-6}$, $b = 2.2 \pm 0.2$. The red curve depicts an error-weighted least-squares fit to the function $f(x) = y_0 + ax$ such that $y_0 = 3.62 \times 10^{-3} \pm 0.14 \times 10^{-3}$, $a = -1.5 \times 10^{-4} \pm 0.17 \times 10^{-4}$.

Table S3. Average pseudo-first-order rate constants (k_{obsd}) at various THF concentrations for alkylation of 0.025 M **4g** with allyl bromide (0.275 M) in 0.250 M *free* HMPA at -78 °C in 2,5-Me₂THF or toluene cosolvent.

[THF] / M	k_{obsd} (2,5-Me ₂ THF) / sec ⁻¹	Standard deviation (2,5-Me ₂ THF) / sec ⁻¹	k_{obsd} (toluene) / sec ⁻¹
11	0.00192243	0.00045887	1.92243333
9.24	0.00221135	0.00003755	1.2744
7.4	0.00233345	0.00029239	0.88377
5.5	0.00291580	0.00057940	0.50462
4.125	0.00305995	0.00009694	0.43816
2.75	0.00343775	0.00029861	0.30494
0.52	0.00301025	0.00030017	0.098396

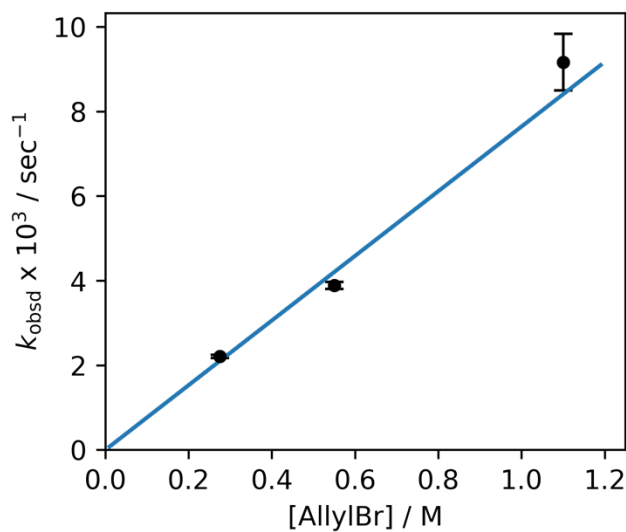


Figure S35. Plot of k_{obsd} against [allylbromide] for the alkylation of enolate **4g** (0.025 M) in 9.24 M THF/2,5-Me₂THF with 0.325 M HMPA at -78 °C. The blue curve depicts an error-weighted least-squares fit to $f(x) = ax$ such that $a = 7.6 \times 10^{-3} \pm 0.1 \times 10^{-3}$.

Table S4. Average pseudo-first-order rate constants (k_{obsd}) at various allyl bromide concentrations.

[AllylBromide] / M	k_{obsd} / sec ⁻¹	Standard deviation / sec ⁻¹
0.275	0.00221135	0.000037547
0.550	0.0038871	0.00008655
1.100	0.00916525	0.00067196

HMPA-free methylation of enolate **4g** in THF

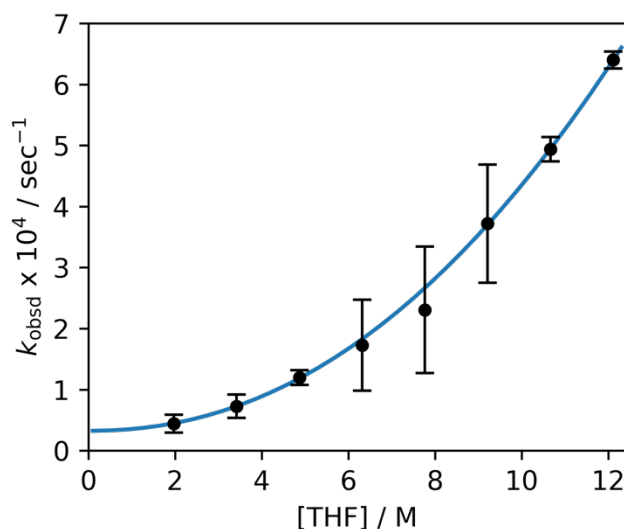


Figure S36. Plot of k_{obsd} against THF concentration for alkylation of 0.025 M **4g** with methyl iodide (0.275 M) at $-45\text{ }^{\circ}\text{C}$ in 2,5-Me₂THF cosolvent. The blue curve depicts an error-weighted least-squares fit to the function $f(x) = y_0 + ax^b$ such that $y_0 = 3.25 \times 10^{-5} \pm 1.76 \times 10^{-5}$, $a = 2.88 \times 10^{-6} \pm 1.88 \times 10^{-6}$, $b = 2.1 \pm 0.2$.

Table S5. Average pseudo-first-order rate constants (k_{obsd}) at various THF concentrations for alkylation of 0.025 M **4g** with methyl iodide (0.275 M) at $-45\text{ }^{\circ}\text{C}$ in 2,5-Me₂THF cosolvent.

[THF] / M	$k_{\text{obsd}} / \text{sec}^{-1}$	Standard deviation / sec^{-1}
12.11	0.00064005	0.000013789
10.66	0.00049399	0.000020032
9.21	0.0003719	0.000096852
7.765	0.00023054	0.000103619
6.32	0.00017296	0.000074529
4.87	0.00011978	0.000012304
3.42	0.00007265	0.000019225
1.97	0.00004413	0.000014592

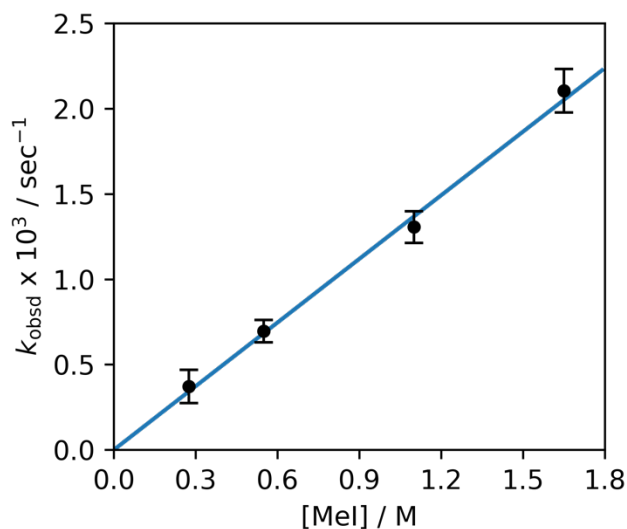


Figure S37. Plot of k_{obsd} against [methyl iodide] for the alkylation of enolate **4g** (0.025 M) in 9.21 M THF/2,5-Me₂THF at –45 °C. The blue curve depicts an error-weighted least-squares fit to $f(x) = ax^b$ such that $a = 1.24 \times 10^{-3} \pm 0.05 \times 10^{-3}$ and $b = 1.00 \pm 0.09$.

Table S6. Average pseudo-first-order rate constants (k_{obsd}) at various methyl iodide concentrations for the alkylation of enolate **4g** (0.025 M) in 9.21 M THF/2,5-Me₂THF at –45 °C.

[MeI] / M	$k_{\text{obsd}} / \text{sec}^{-1}$	Standard deviation / sec^{-1}
0.275	0.00037190	0.000096852
0.55	0.00069544	0.000065322
1.1	0.00130560	0.000093621
1.65	0.00210430	0.000127138

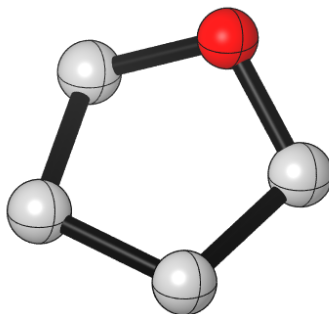
Computational Data

General computational methods

All DFT calculations were carried out using Gaussian 16.¹⁰ Prompted by a recent benchmarking of modern density functionals, all calculations were conducted at the M06-2X level of theory using Grimme's zero-dampened DFT-D3 dispersion corrections.^{11a-d} A pruned (99, 590) integration grid (equivalent to Gaussian's "UltraFine" option) was used for all calculations. Where appropriate solvation effects were accounted for by the Self Consistent Reaction Field method using the SMD model of Truhlar and coworkers.^{11e} Jensen's polarization-consistent segment-contracted basis set, pcseg-1, was used for geometry optimizations and the expanded pcseg-2 basis set for single-point energy calculations.^{11f} Basis set files were obtained from the Basis Set Exchange.^{11g} Ball-and-stick models were rendered using CYLview 1.0b.^{11h} A frequency calculation was conducted at all stationary points to ensure the existence of real minima. All reported geometries have exactly zero imaginary (negative) vibrational frequencies.

Solvent molecules

Table S7. Atomic coordinates and single point energies for THF



G = -232.197829

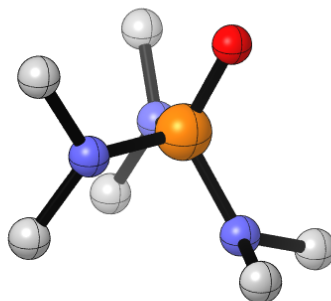
G_{SP} = -232.341142

13

THF_THF: optimized structure // E(RM062X) = -232.441249027 A.U. after 10 cycles

C	0.000193531183	-0.001120142042	-0.002218343448
O	-0.003348689250	0.001831686221	1.416587492296
C	1.365118788039	-0.001121684663	1.791131543289
C	2.047552984932	-0.981357489864	0.827081194122
H	3.066742585831	-0.664428870106	0.584974417430
H	2.103795309919	-1.980554397200	1.270795269330
H	1.783097557965	1.012859761982	1.678218028126
H	1.429104810742	-0.291947522954	2.843390856502
C	1.112187907216	-0.980272993237	-0.403542169761
H	1.618244867414	-0.661088421721	-1.319971282967
H	0.700282953596	-1.979292745326	-0.578797908991
H	-0.996733824418	-0.292894433246	-0.344172528780
H	0.219324265658	1.013088007676	-0.374971594194

Table S8. Atomic coordinates and single point energies for HMPA



G = -819.785578

G_{SP} = -820.128959

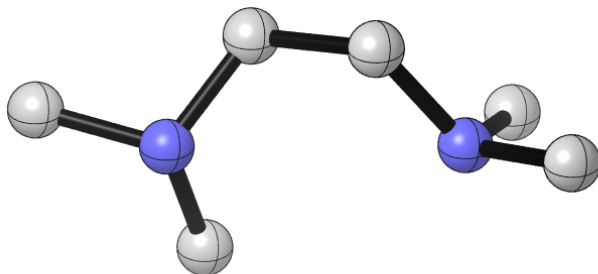
29

HMPA_thf: optimized structure // E(RM062X) = -820.361130487 A.U. after 11 cycles

P	-0.025567914380	-0.020486431481	0.008480120104
O	-0.026238823159	-0.039463510105	1.503272579432
N	1.552424137255	0.010560043168	-0.566672050650
N	-0.669150323789	-1.312082005521	-0.847342777849
N	-0.968902383748	1.252695981677	-0.552968110946
C	-2.115959063406	-1.508981163767	-0.824062535962
H	-2.410540575215	-2.081121762281	-1.712697954941
H	-2.435481950676	-2.067344008013	0.069468297027
H	-2.631888332646	-0.546015040917	-0.839171741873
C	0.059441314170	-2.577467181272	-0.849382434964
H	-0.230652172658	-3.152397040739	-1.737662183623
H	1.136425288508	-2.396917452461	-0.884319044270
H	-0.169309785010	-3.179885506485	0.043397468069
C	1.848724642941	0.037156427109	-1.990312825418
H	1.968232020531	1.064881402612	-2.368577312779
H	2.787521949607	-0.503371417081	-2.174718093747
H	1.053126086421	-0.457449335667	-2.554886583337
C	2.590838342963	0.602188325824	0.263889293610
H	2.321927790131	0.497196681207	1.317282354534
H	3.538278967611	0.075999022163	0.087018812595
H	2.742564642905	1.669373270030	0.035302746091
C	-1.145683415519	1.500930854431	-1.975580712475
H	-2.130727587935	1.958354379539	-2.141230837353
H	-0.381069831579	2.185996113872	-2.375485688864

H	-1.106570173942	0.561381974811	-2.534249620171
C	-1.069617185877	2.450429865001	0.268666840035
H	-2.047780462113	2.920130647876	0.101750075061
H	-0.985396990323	2.179781592731	1.323543724993
H	-0.287890695640	3.187074899832	0.021944367115

Table S9. Atomic coordinates and single point energies for TMEDA



G = -347.303443

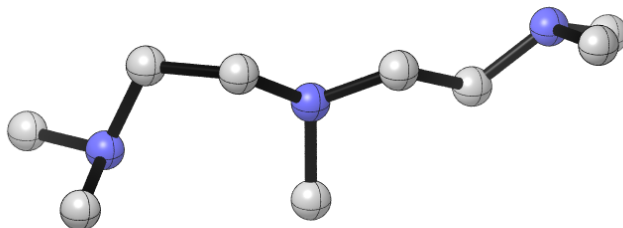
G_{SP} = -347.514523

24

TMEDA: optimized structure // E(RM062X) = -347.718043949 A.U. after 10 cycles

C	-0.013217225118	0.095125031841	-0.436366107906
H	0.263321978652	0.265919541559	0.623618828493
H	0.902567895402	0.253097852779	-1.019403875875
C	-1.004339679000	1.143353708496	-0.925866070166
H	-0.493853927271	2.130502770091	-0.903796116092
H	-1.232039484288	0.916089750163	-1.974878555560
N	-0.440101288674	-1.282952304075	-0.655658215173
N	-2.270858907432	1.214151863236	-0.206396971375
C	-3.195052821866	2.090446806160	-0.903726202065
H	-4.157924397869	2.104667509500	-0.380625825906
H	-2.821778927480	3.132026992774	-0.970300616115
H	-3.361720574371	1.720174816157	-1.921422789521
C	-2.096196331996	1.648972332024	1.167543056136
H	-1.612481494862	2.644515205694	1.235440014169
H	-3.074135887570	1.708559642438	1.658514164122
H	-1.484929261444	0.932342228458	1.726562707756
C	0.707025658180	-2.174624330587	-0.704405725177
H	1.286939483951	-2.173401783154	0.240105855939
H	0.366853396725	-3.199703249063	-0.891294290315
H	1.376960016835	-1.882670223618	-1.521000140905
C	-1.378871958061	-1.739450173676	0.359024713696
H	-1.709748738114	-2.756755656119	0.117660644619
H	-0.920169052304	-1.759078198208	1.369029717810
H	-2.251189488810	-1.081606853334	0.378225836429

Table S10. Atomic coordinates and single point energies for PMDTA



G = -520.365074

G_{SP} = -520.679589

35

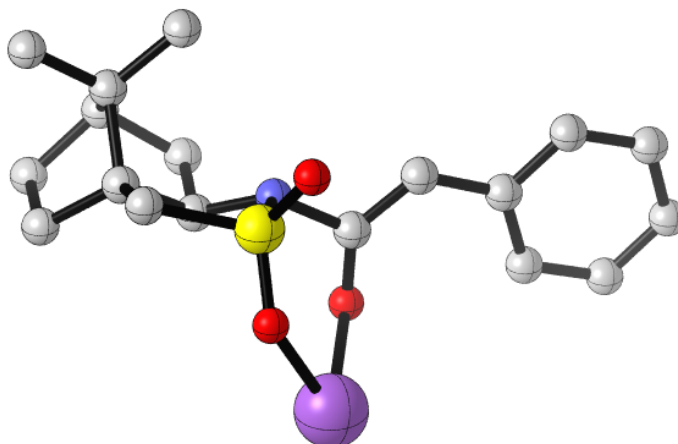
PMDTA: optimized structure // E(RM062X) = -520.982019496 A.U. after 10 cycles

C	-0.231120793835	0.215758318805	-0.436123939449
H	-0.140702893332	-0.251013320007	0.564495429766
H	0.792761129534	0.422000685317	-0.770388262511
C	-0.923153152423	1.570610004939	-0.354398258455
H	-0.266307809898	2.252966580183	0.227182351201
H	-0.986687385166	1.968557794805	-1.374735158737
N	-0.830333659925	-0.704619748151	-1.399554436295
N	-2.270612733652	1.571433697696	0.203866427938
C	-2.893872262324	2.868367876499	0.008791698346
H	-3.919715146640	2.847787064238	0.393618410959
H	-2.346689659760	3.682667503933	0.524562869282
H	-2.932112039709	3.104494782516	-1.060466855865
C	-2.279749629287	1.208087570502	1.609393529159
H	-1.657727842915	1.889790848693	2.224097127267
H	-3.307076946316	1.244664611497	1.989247600176
H	-1.908413960486	0.186826716383	1.748010536444
C	0.161314745301	-1.671599922836	-1.863442102606
H	1.031923822071	-1.117439813326	-2.236721387382
H	0.504678524580	-2.311566420373	-1.025310173887
C	-1.996183841558	-1.381038441560	-0.843173038114
H	-2.505809246880	-1.960631910812	-1.620472695091
H	-1.717713964318	-2.072916817454	-0.021851754339
H	-2.696338363783	-0.634633324771	-0.460901279541
C	-0.358982568488	-2.524342404646	-3.015988872472
H	-1.036713686822	-3.321477053876	-2.648112770356
H	-0.945976853949	-1.869018528234	-3.673043863907

N	0.724179980501	-3.100095623432	-3.804792030448
C	0.196147111742	-3.723667168945	-5.005875298811
H	-0.350502925192	-2.982012519227	-5.599014642778
H	1.021388043142	-4.110180925095	-5.614714563689
H	-0.491061704676	-4.563367433300	-4.781262834583
C	1.499048552345	-4.060185749693	-3.035820397597
H	0.873985214412	-4.889566606072	-2.647358116708
H	2.282222361489	-4.488977171544	-3.671035755031
H	1.988344380254	-3.570686965158	-2.187359558844

Unsolvated monomers

Table S11. Atomic coordinates and single point energies for unsolvated enolate **4g** with chelation to the *endo* sulfonyl oxygen.



G = -1539.107513

G_{SP} = -1539.754852

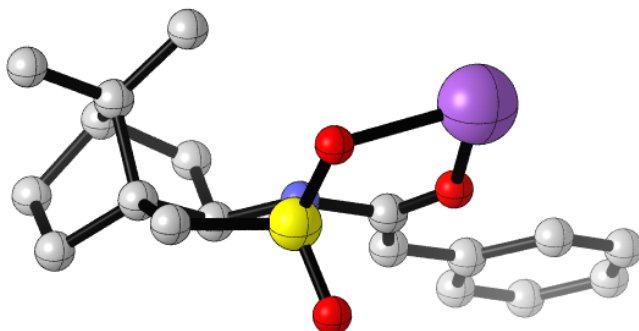
46

ES0_endo_thf: optimized structure // E(RM062X) = -1540.10263503 A.U. after 12 cycles

O	-0.188101495584	-1.116530551340	0.806152419149
C	-0.158579921251	-0.150238773631	1.631107683751
N	1.159465706637	0.140676471088	2.247622622814
S	2.144246287763	1.138810014081	1.323660111219
O	2.214464996668	0.644416406712	-0.084556890339
C	3.695210096921	0.700009596401	2.149003881406
C	3.351741486656	-0.476190338863	3.048370504283
C	1.960070032470	-1.027873019658	2.644960536901
C	1.458343861115	-1.728644207760	3.927750460664
C	2.680291748905	-1.619884711654	4.863404369308
C	3.800291172811	-2.504465671398	4.268182078951
C	4.293177342251	-1.692063458787	3.034198775259
H	4.202002129114	-2.245651958271	2.092943901285
H	5.339581877377	-1.385488582250	3.134844902537
H	3.417065480786	-3.492154677228	3.987917763318
H	4.609867580954	-2.664146913346	4.987917320152
C	3.195416869987	-0.187008368412	4.576390877181
C	2.213431324755	0.926678012315	4.949371483380
H	2.549969660357	1.890014460318	4.539669939098

H	1.194029415562	0.760145149220	4.598613973105
H	2.191383869771	1.031369232584	6.042091285584
C	4.526832390639	0.152882056692	5.251145092801
H	4.900531603829	1.119071924095	4.884438762070
H	4.376284961041	0.252429988555	6.333509568828
H	5.312312402247	-0.591143536665	5.093148905222
H	2.453594718076	-1.835138015423	5.913202452800
H	0.577035226963	-1.216945064925	4.328578951675
H	1.179423450135	-2.769230137122	3.733532253008
H	2.037934569751	-1.729586005162	1.803326422618
H	4.039129015106	1.589782383393	2.686681398036
H	4.396376483298	0.457054903827	1.344847007324
O	1.771523612355	2.544461231303	1.481263604429
C	-1.154739425075	0.689672226554	2.051691536740
H	-0.885286933518	1.449214619405	2.780794943675
C	-2.533588516074	0.665466445432	1.586622255085
C	-3.050976450001	-0.306992389187	0.704253681146
C	-3.422141327339	1.663224464360	2.040661187749
C	-4.383401506347	-0.268299924141	0.300837609544
H	-2.393598852596	-1.096736010489	0.353555537400
C	-4.749841998697	1.695071863133	1.634070795101
H	-3.050194971488	2.424894455699	2.725234121235
C	-5.244009195609	0.728727165454	0.756538414665
H	-4.755161016120	-1.034250172078	-0.378396291842
H	-5.405655353114	2.481231495852	2.004738067304
H	-6.283754982919	0.751476921376	0.437237838026
Na	0.852940753579	-0.820996072966	-1.067852373172

Table S12. Atomic coordinates and single point energies for unsolvated enolate **4g** with chelation to the *exo* sulfonyl oxygen.



G = -1539.110626

G_{SP} = -1539.757633

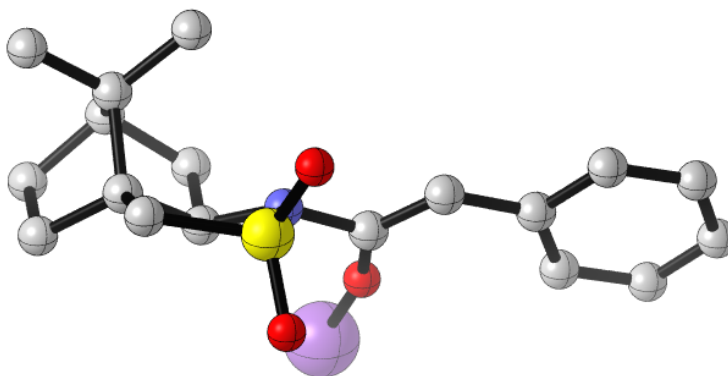
46

ES0_exo_thf: optimized structure // E(RM062X) = -1540.10624525 A.U. after 12 cycles

O	-0.001819327637	0.111920451153	-0.030185612003
C	0.002502704797	0.101084757315	1.239453501320
N	1.327652276837	0.080871373802	1.825806379933
S	2.455819184342	-0.873462488002	1.009348828198
O	1.974473146516	-2.238903023303	0.770367251761
C	3.697179196505	-0.864665988220	2.323718654811
C	3.137225473665	0.012860020444	3.424262767075
C	1.594923958281	0.094098458920	3.267180221988
C	1.239869405893	1.419451780708	3.989016319114
C	2.590409450653	1.848817775389	4.595425563252
C	2.959080144797	0.819817892798	5.687933796587
C	3.376089215742	-0.440304006153	4.874796535636
H	2.772870710103	-1.323691363853	5.110995459449
H	4.425690622885	-0.706533473828	5.037538998244
H	2.107818649654	0.622891835186	6.349292641884
H	3.781144944095	1.178112092814	6.316161523095
C	3.586005710752	1.508827024014	3.459619780366
C	3.370908497873	2.304434283641	2.169232037468
H	4.001266163774	1.905218955562	1.362708606189
H	2.339639608114	2.304369221394	1.811823190056
H	3.676416972427	3.345541730902	2.338366160917
C	5.059101722215	1.676186290988	3.840788921207

H	5.705565061525	1.272550327797	3.049247019909
H	5.293458454888	2.743764082946	3.938587270797
H	5.335660098674	1.189788737882	4.780017287423
H	2.606598659598	2.889066726073	4.937999431697
H	0.849720709529	2.154455429756	3.278660223172
H	0.475978790095	1.264160090745	4.758171296192
H	1.111114008894	-0.772718858303	3.740210930205
H	4.633994129634	-0.504881196608	1.885887517597
H	3.800528606548	-1.913900873317	2.618697250208
O	2.952783569059	-0.145468872976	-0.187784820428
C	-1.069022169986	0.130046169995	2.104117752946
H	-0.879577996577	0.075895113478	3.171759595506
C	-2.460081730548	0.266473395745	1.710709541363
C	-2.912885178294	0.334612856940	0.373689131603
C	-3.445217082514	0.340236353044	2.721794457403
C	-4.266882511835	0.476818119022	0.081978472370
H	-2.183747790491	0.269195801435	-0.426930217922
C	-4.793915987371	0.479138070294	2.421900027041
H	-3.131158590280	0.287667039326	3.764104837645
C	-5.221483000411	0.551240922024	1.095070779767
H	-4.580843350410	0.526136719164	-0.959974341901
H	-5.519584860322	0.532383169186	3.232184483617
H	-6.277415969945	0.660236895488	0.857283370941
Na	1.367083864053	0.558723100628	-1.603255647260

Table S13. Atomic coordinates and single point energies for unsolvated enolate **4g** with the enolate oriented *anti* to the sultam ring.



G = -1539.092397

G_{SP} = -1539.741632

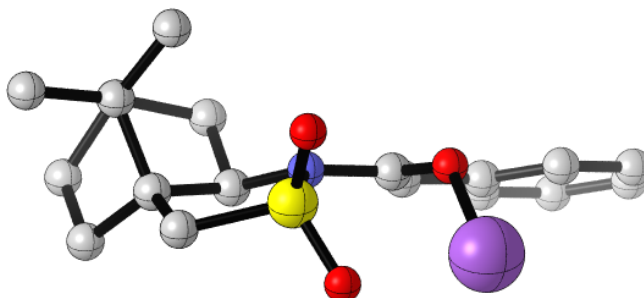
46

ES0_pendS_thf: optimized structure // E(RM062X) = -1540.08811398 A.U. after 13 cycles

O	-0.069035322330	1.937202605344	0.993238322165
C	0.014838190164	0.853388658275	1.649854513785
N	1.324285782011	0.576419434443	2.216855595760
S	1.452693919973	0.318506443783	3.886025765433
O	0.843247662365	1.425602938247	4.640274363315
C	3.259303340373	0.480507254652	3.937607807420
C	3.691707654707	0.831532116782	2.527342127497
C	2.462781906246	1.368253622043	1.753032236594
C	2.845947582117	1.131540040668	0.271511997071
C	4.288439426818	0.593034791640	0.372453956206
C	5.182302526967	1.751686962861	0.867480140167
C	4.784319184902	1.902360280967	2.365019722906
H	4.391909673063	2.896590986877	2.606814481910
H	5.628712601498	1.714318004690	3.036109930603
H	5.002179549568	2.668185820777	0.293664997555
H	6.244649710568	1.508728561979	0.760849084736
C	4.213176777097	-0.327172434113	1.616860336962
C	3.280842696139	-1.531874378186	1.457197672376
H	3.082383880912	-1.997728406452	2.432516093898
H	2.313842522822	-1.296293696806	1.009536210718
H	3.777182604271	-2.284959049411	0.830858135146

C	5.566684751702	-0.875947593641	2.076789864607
H	5.446978409905	-1.441045841020	3.011372399798
H	5.956066468750	-1.573397034153	1.324203473006
H	6.328292138907	-0.109712429997	2.245172253132
H	4.646059794085	0.113348065223	-0.545167403943
H	2.162527296242	0.415912850034	-0.196580107003
H	2.809626905126	2.060020497532	-0.312304726159
H	2.298362109447	2.433732229059	1.970349317288
H	3.661361794189	-0.467129564768	4.310324770512
H	3.456522568162	1.277308269843	4.661492567676
O	1.020013708686	-1.042454062520	4.224317726091
C	-0.949085142737	-0.103558039664	1.867172397990
H	-0.642383526588	-1.002633783985	2.395091595737
C	-2.342033448571	-0.017794242877	1.470469340579
C	-2.925221028835	1.086976774965	0.810087127416
C	-3.195266307691	-1.107794088959	1.758684425570
C	-4.274060031369	1.089627202428	0.464829350620
H	-2.303320926578	1.944727080151	0.577244731715
C	-4.538759071365	-1.099127612257	1.409029781035
H	-2.779646666732	-1.974373371340	2.271967398265
C	-5.095522484406	0.001916921966	0.755607284829
H	-4.690219794698	1.960406154193	-0.040472541364
H	-5.159705369981	-1.960504319130	1.650668242505
H	-6.148127656738	0.011122013041	0.481244544945
Na	0.295685973029	3.599576357167	-0.170335355094

Table S14. Atomic coordinates and single point energies for unsolvated enolate **4g** with the enolate oriented *syn* to the sultam ring.



G = -1539.109449

G_{SP} = -1539.756294

46

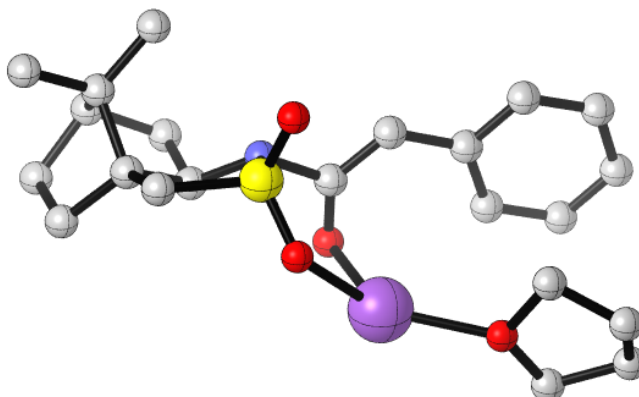
ES0_pendS_thf: optimized structure // E(RM062X) = -1540.10477389 A.U. after 13 cycles

O	-0.143335767427	1.420294805344	0.505311520738
C	-0.087493619983	0.563214988897	1.440338234170
N	1.237919056403	0.356730045411	1.979079424556
S	2.511351132574	0.723354638486	0.932383137470
O	2.265408593839	0.167939641409	-0.428536649333
C	3.742137879867	-0.301246393086	1.767730452662
C	3.122188647870	-0.704180709048	3.087199729193
C	1.578295638094	-0.711605090833	2.925209572972
C	1.074317306571	-0.512902219817	4.378524392320
C	2.374381945497	-0.602118549461	5.200880822460
C	2.910237078305	-2.046604797888	5.075510271877
C	3.478863268413	-2.099597816289	3.627462931453
H	3.023516311882	-2.884458152388	3.013749488237
H	4.562067583940	-2.259834396117	3.616747342352
H	2.110869358429	-2.779668856861	5.232772850960
H	3.688900725164	-2.253131755428	5.816919826003
C	3.367445610174	0.207621598767	4.332211599184
C	2.997511117100	1.684279832847	4.171502322840
H	3.708332210408	2.188622288868	3.504424909449
H	1.996604184716	1.855696962752	3.770022707710
H	3.062182315381	2.173960606023	5.152357451349

C	4.815619874628	0.164406058338	4.826457795338
H	5.490103649093	0.585855791319	4.068443704360
H	4.912672764623	0.783371548655	5.727388444605
H	5.173689913826	-0.838466177251	5.074659168868
H	2.265147229041	-0.253892179009	6.233568363498
H	0.578880373385	0.456817199462	4.487012877775
H	0.355436415020	-1.288721050551	4.662702518204
H	1.240626151029	-1.670596198313	2.507102268124
H	4.655147910746	0.297348701932	1.850671718857
H	3.908474001759	-1.151397121997	1.097731103696
O	2.854682682475	2.148036267737	0.962455423790
C	-1.115659751022	-0.171572849283	1.993661149036
H	-0.888455251504	-0.888711685091	2.775609278500
C	-2.512545684219	-0.067359307472	1.613727129870
C	-3.028758217428	0.867129442600	0.686595433698
C	-3.442464903399	-0.951700941432	2.208239121437
C	-4.386312943131	0.896735687636	0.377634265054
H	-2.348287427784	1.573910069129	0.223382512645
C	-4.794075744501	-0.915954514789	1.893328949448
H	-3.081120167199	-1.681880147432	2.932195630176
C	-5.283485973541	0.009412674737	0.969556021744
H	-4.748837366709	1.632853331304	-0.338958051235
H	-5.473833889899	-1.617645046200	2.374553163042
H	-6.342064745175	0.039593142553	0.720964219763
Na	0.668340759353	1.374523559101	-1.477204813708

THF-solvated monomers

Table S15. Atomic coordinates and single point energies for THF-solvated enolate **4g** with chelation to the *endo* sulfonyl oxygen.



G = -1771.322403

G_{SP} = -1772.105445

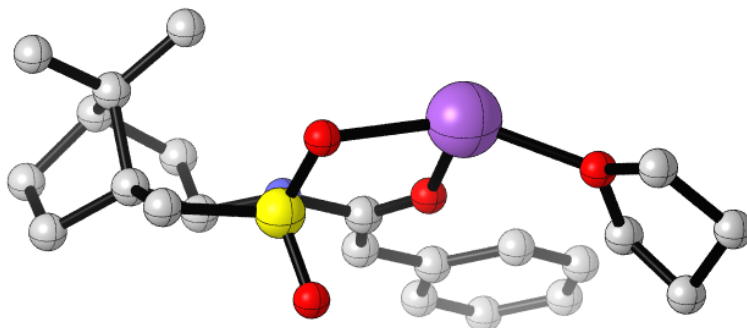
59

ETHF1_endo_thf: optimized structure // E(RM062X) = -1772.56774264 A.U. after 12 cycles

O	0.418079681613	-1.663188654702	0.838819723804
C	0.292788786107	-0.555488911019	1.439381653394
N	1.442861782521	-0.127889768046	2.267370708413
S	2.455657907902	0.934916858613	1.434517377727
O	2.579958907629	0.502669327741	0.012404937894
C	3.980184630273	0.514745957805	2.318767649951
C	3.587110338045	-0.556210719867	3.318691307970
C	2.257338674427	-1.202059613172	2.855741028421
C	1.667601509330	-1.788855657401	4.159338462142
C	2.793866465820	-1.529836316281	5.181668337483
C	3.990480342886	-2.425213855428	4.786580000087
C	4.562286547929	-1.729892931684	3.516352678769
H	4.568557491565	-2.382448530547	2.636361252216
H	5.586634288792	-1.373686730211	3.668292858303
H	3.666818092489	-3.452774318528	4.585930562616
H	4.738151518759	-2.471393475076	5.585207059829
C	3.289015999747	-0.114635126155	4.787070588561
C	2.244331687700	0.991704291541	4.953073796194
H	2.595338590768	1.924959596453	4.490403822300

H	1.272699018747	0.755559229109	4.516568211543
H	2.104011810928	1.193249444531	6.023295027280
C	4.542816575848	0.343587411761	5.536742313636
H	4.918078700173	1.284796835179	5.111482007453
H	4.291772841745	0.539971764082	6.586872412529
H	5.362358409457	-0.380046567135	5.522457415465
H	2.479254535325	-1.641105498386	6.225068749692
H	0.736791833509	-1.276386054924	4.424250640219
H	1.443522402987	-2.855468495178	4.055192987577
H	2.432845587483	-1.976743325827	2.099582668096
H	4.358929990343	1.439928809856	2.764790941516
H	4.673453669004	0.158845415111	1.550021888926
O	2.049509309830	2.326418573138	1.640140225209
C	-0.716402244706	0.375398541470	1.372028788449
H	-0.607587951358	1.271856797492	1.976950667664
C	-1.879282920806	0.290151956848	0.502768565433
C	-2.213311770445	-0.845566329348	-0.268374149360
C	-2.730771204488	1.412268927155	0.397457280234
C	-3.318618359949	-0.833537236059	-1.115948068890
H	-1.603887261129	-1.740856070183	-0.181160092415
C	-3.832992968381	1.414895047876	-0.447015236120
H	-2.503611933248	2.298557129486	0.989118498523
C	-4.133851006995	0.292335994027	-1.221302503666
H	-3.552426096850	-1.726236553256	-1.695509597001
H	-4.463008466142	2.301163169856	-0.503751486437
H	-4.996645799905	0.292106256236	-1.884396236398
Na	1.057526821043	-0.759994884676	-1.116699197678
O	-0.194079363194	-0.139505186395	-2.832871188434
C	-0.893402381409	-0.996399996901	-3.756937002144
C	-0.777597716833	1.176539859326	-2.846653130000
C	-1.963035958111	-0.126187459888	-4.415710115344
H	-0.160140040892	-1.369436469738	-4.482099822837
H	-1.314963529026	-1.846313529928	-3.207169540629
C	-1.419309212401	1.289696981446	-4.217191274549
H	-1.525545436742	1.248783959709	-2.045270423089
H	0.024526710989	1.898618361249	-2.664001069216
H	-2.920048298283	-0.235739589509	-3.892896510791
H	-2.112673594228	-0.389700696235	-5.467117502690
H	-2.196575324930	2.059203156805	-4.251366376523
H	-0.659210105578	1.523673323860	-4.973014514883

Table S16. Atomic coordinates and single point energies for THF-solvated enolate **4g** with chelation to the *exo* sulfonyl oxygen.



G = -1771.322186

G_{SP} = -1772.106579

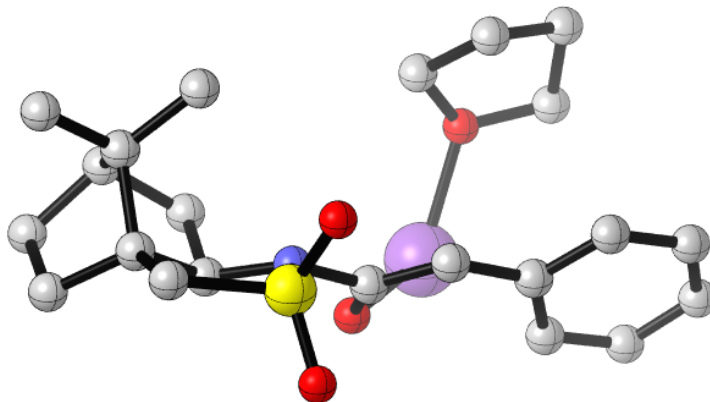
59

ETHF1_exo_thf: optimized structure // E(RM062X) = -1772.56774025 A.U. after 13 cycles

O	0.226050684058	0.456749886635	-0.093011559407
C	0.158277581971	0.159460605044	1.137740334673
N	1.440632803674	0.124787587363	1.809142450432
S	2.717593827634	-0.465623902391	0.874698258045
O	2.414112322157	-1.763972849386	0.259947985492
C	3.871586616182	-0.680113198117	2.250242844714
C	3.157315773837	-0.168828203402	3.484040881354
C	1.626223346286	-0.196645522669	3.226632880190
C	1.086372662164	0.864584277214	4.220064607142
C	2.344271656188	1.249387752802	5.023266706630
C	2.763590745007	0.015478552592	5.854145201204
C	3.364601901739	-0.950989428254	4.792216072235
H	2.852726513165	-1.918677873490	4.752943375601
H	4.426882448457	-1.148545578624	4.969827660150
H	1.903805959310	-0.422725942095	6.373401581296
H	3.503612380136	0.277938323925	6.617309137967
C	3.433459906203	1.304106267893	3.924463718803
C	3.203132704326	2.376767691000	2.856622164359
H	3.923453850252	2.260855171819	2.035205315694
H	2.203109306946	2.365042768474	2.419627248057
H	3.372169378881	3.365548878392	3.303399287787

C	4.854676866875	1.509157275795	4.455446447196
H	5.585553941085	1.387796709005	3.643909612152
H	4.959013360133	2.533411556158	4.835324502526
H	5.134225869017	0.827030218782	5.262847293696
H	2.225496179015	2.165075993190	5.612506616525
H	0.658999504184	1.716091098359	3.682154732191
H	0.301505908275	0.449707446252	4.861316025445
H	1.216679492769	-1.196086412883	3.433788293518
H	4.787025461664	-0.136713566102	1.995153724641
H	4.072250697734	-1.755766870342	2.283071002857
O	3.194001481380	0.591533613572	-0.053259064984
C	-0.961025135045	-0.108551539332	1.897185319353
H	-0.833125331986	-0.395924237825	2.936279598407
C	-2.329132198364	-0.019659576510	1.422244920836
C	-2.698262639318	0.365503784080	0.112738434310
C	-3.381407220409	-0.329937331454	2.314357107307
C	-4.036605438360	0.432112987485	-0.265291657668
H	-1.915304978439	0.608888803288	-0.597711163974
C	-4.713442133457	-0.263409130748	1.927804947612
H	-3.133591535165	-0.630185281451	3.332365662028
C	-5.058247003594	0.119403479798	0.630137372592
H	-4.283794641684	0.733987728544	-1.282693189722
H	-5.492034312179	-0.512551064772	2.647382100351
H	-6.101184188483	0.171619795274	0.325324273476
Na	1.614510818247	1.304351678240	-1.510765080115
O	0.570676914413	0.785908478689	-3.393296259053
C	-0.665254296757	0.057959564148	-3.219577496815
C	1.019748626261	0.687785601292	-4.759059375641
C	-0.757927181411	-0.846276736840	-4.436392164739
H	-0.613485639183	-0.467271985854	-2.261397505898
H	-1.494115348461	0.778855809378	-3.191336520463
C	-0.124521098648	0.028632030481	-5.517381517505
H	1.261200859402	1.693187074443	-5.118790870981
H	1.927310236012	0.070870673845	-4.782529539989
H	-1.788501650522	-1.138780534076	-4.658283664693
H	-0.163200738982	-1.754707446014	-4.279686057223
H	-0.841363138591	0.785038721575	-5.859918697639
H	0.227132800131	-0.533125029207	-6.387939397041

Table S17. Atomic coordinates and single point energies for THF-solvated enolate **4g** with the enolate oriented *anti* to the sultam ring.



G = -1771.311685

G_{SP} = -1772.096450

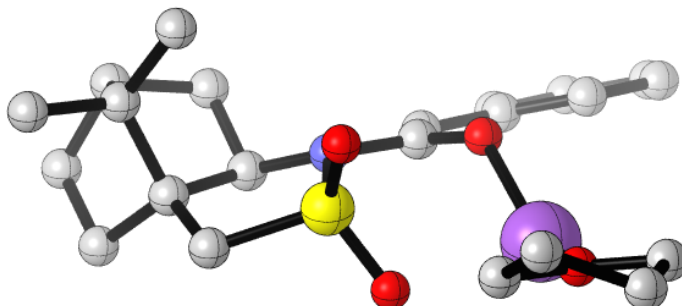
59

ETHF1_pendC_thf: optimized structure // E(RM062X) = -1772.56041661 A.U. after 13 cycles

O	0.535481016546	2.166230641710	0.510776190920
C	0.307160300085	1.008564671894	0.973024278860
N	1.421418762936	0.412790586359	1.668814302200
S	1.167593883148	-0.439204599213	3.112833690615
O	0.365839647167	0.347963118245	4.060888369483
C	2.906255624891	-0.422301093397	3.627586719167
C	3.675779090478	0.259002800091	2.515557820112
C	2.695893846433	1.135024450526	1.694498723305
C	3.401264454458	1.262541586780	0.322447406939
C	4.757766767305	0.574337262217	0.571336545373
C	5.545931920913	1.451679476155	1.570391368296
C	4.821298570401	1.200669058395	2.925094231362
H	4.427929998542	2.117554842856	3.377572091276
H	5.479284475554	0.727131438167	3.661411374910
H	5.519526073841	2.507027999761	1.275955534573
H	6.599197323292	1.156436389059	1.621209624058
C	4.354581522859	-0.645445653567	1.437480058380
C	3.437434652171	-1.649202266667	0.732702934097
H	3.077280997922	-2.404155302184	1.444859144248
H	2.557737181548	-1.201801250817	0.265534113958
H	4.011655656099	-2.176231958415	-0.041245321106

C	5.538233914928	-1.443258341568	1.990462676907
H	5.188520791172	-2.184734247400	2.722054707741
H	6.023067641515	-1.995406164785	1.175211274372
H	6.302921840618	-0.829915468031	2.474839581188
H	5.310046313116	0.336327259757	-0.344686577152
H	2.821565757641	0.760984133943	-0.458772300433
H	3.513278462153	2.311649575378	0.030511684148
H	2.552009210507	2.116915525693	2.162841127271
H	3.198174223432	-1.461459063927	3.811445125078
H	2.921103169541	0.140186553808	4.566508421380
O	0.706915776275	-1.802911835303	2.819019415972
C	-0.830097627969	0.229713790743	0.829087348007
H	-0.779807106179	-0.805400694219	1.156938953742
C	-2.047428281104	0.654865484502	0.179358348546
C	-2.381859199604	2.001904151996	-0.111700814172
C	-3.006047659198	-0.320176429953	-0.194964378818
C	-3.554903715858	2.331010702932	-0.790459561130
H	-1.744043243358	2.798823059880	0.269425424803
C	-4.174828680600	0.016271173966	-0.861415901818
H	-2.811511181383	-1.363415764715	0.052917884880
C	-4.455469728224	1.346162089470	-1.189996020949
H	-3.775430570021	3.379624860278	-0.987183834654
H	-4.878707258599	-0.769604702277	-1.132221149044
H	-5.368679657423	1.608238480303	-1.719209771376
Na	-0.096720703931	2.527406459531	-1.534755133212
O	-0.132787210198	0.672470205015	-2.717758518401
C	-1.371612051254	0.259672600922	-3.335544046765
C	0.642646778193	-0.477553568223	-2.331242202613
C	-1.291851078096	-1.258728455871	-3.449497255018
H	-2.199398444221	0.578249955327	-2.688824732958
H	-1.456344960106	0.760364736704	-4.306177194342
C	-0.344475020651	-1.630547441739	-2.308443788795
H	1.438585555006	-0.632246964303	-3.073282535973
H	1.088987467199	-0.273779869002	-1.351645241764
H	-0.855830650858	-1.547365910666	-4.413762878940
H	-2.277809788463	-1.726754514683	-3.364385250759
H	0.145792297687	-2.598634749296	-2.450376143688
H	-0.876589076977	-1.642058767583	-1.350226168727

Table S18. Atomic coordinates and single point energies for THF-solvated enolate **4g** with the enolate oriented *syn* to the sultam ring.



G = -1771.320716

G_{SP} = -1772.104908

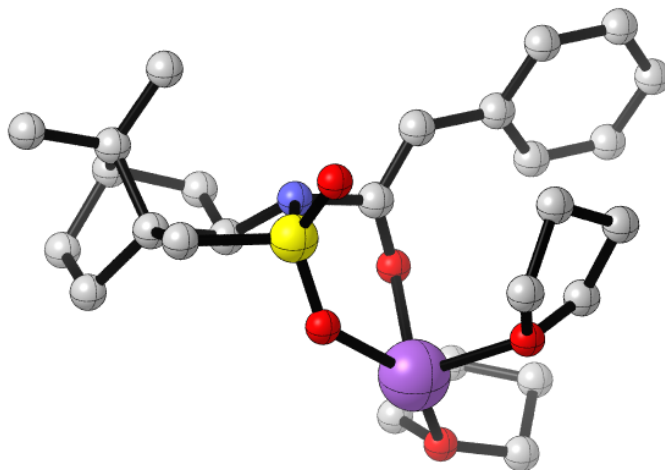
59

ETHF1_pendS_thf: optimized structure // E(RM062X) = -1772.56613503 A.U. after 13 cycles

O	-0.973841528668	0.292981432680	0.315904848884
C	-0.701489500735	-0.157303007287	1.469129090208
N	0.709115742737	-0.165313622582	1.788652941353
S	1.755200866666	-0.240077754946	0.464363619093
O	1.305253279990	-1.256063540486	-0.524562755500
C	3.168682468501	-0.892800795086	1.381027344600
C	2.817377017606	-0.750674936791	2.845041932342
C	1.272403807721	-0.799708112106	2.985612439431
C	1.020516292534	-0.058912616443	4.324781919259
C	2.447590884052	0.157087385002	4.864261629975
C	3.039662936651	-1.231728626264	5.195022822463
C	3.345689757986	-1.839140478576	3.795247481150
H	2.836455249682	-2.792806892545	3.618718878653
H	4.417475333648	-2.005463513194	3.644256202202
H	2.327088803737	-1.840707542432	5.762895556430
H	3.948204232947	-1.148312991432	5.800323545998
C	3.221970778302	0.564169756543	3.587035614805
C	2.739932774216	1.873412109932	2.956907266195
H	3.286876919842	2.078047296612	2.027784275928
H	1.674790146870	1.889962667429	2.717145528389
H	2.948724815954	2.697966164802	3.651665227715

C	4.734229276133	0.697039554335	3.783348331407
H	5.236810340559	0.800862716924	2.811789291330
H	4.949487282495	1.606397948356	4.358692016853
H	5.192669888352	-0.143848455329	4.310993579715
H	2.500333856129	0.873781613436	5.690871810648
H	0.493876961346	0.884466144687	4.151461779835
H	0.411104555223	-0.660723694799	5.007427545312
H	0.923712049860	-1.841401752368	3.027463007129
H	4.049298264999	-0.326835925200	1.060308439498
H	3.256721725189	-1.937880889880	1.065536376900
O	2.028207752005	1.088743799210	-0.095268536181
C	-1.569010279445	-0.623301442425	2.437310515669
H	-1.163484060187	-1.004554307987	3.368698943181
C	-3.014870687416	-0.643984809394	2.319498881877
C	-3.742876198050	-0.116725628534	1.227633769881
C	-3.771098998186	-1.223020522069	3.365571695149
C	-5.133662213184	-0.178360638585	1.195052205718
H	-3.197765901196	0.349109974922	0.413369866098
C	-5.157500748398	-1.281636880304	3.323780500104
H	-3.244151664488	-1.635253340783	4.225972101385
C	-5.857807662310	-0.760689988537	2.233995687161
H	-5.660719348241	0.241653747003	0.339113091477
H	-5.698353334056	-1.738308852497	4.151443135246
H	-6.944123217860	-0.805254170508	2.198651424520
Na	-0.519388013667	-0.470562483419	-1.654439328699
O	0.412345552222	0.184027593267	-3.547223881347
C	1.841572793737	0.394063986620	-3.537055475622
C	-0.155473132482	0.662190433968	-4.782475439512
C	2.107103024029	1.347128103262	-4.690980628506
H	2.121639540867	0.790472214706	-2.556069004770
H	2.335453911505	-0.574517747033	-3.691369157498
C	1.032966364243	0.928803249124	-5.693892109174
H	-0.840955475392	-0.100245303235	-5.165650146055
H	-0.719024256572	1.581089524017	-4.575383513573
H	3.126454327076	1.255583116319	-5.077654561243
H	1.947589632535	2.384374928574	-4.371443773659
H	1.332210891959	0.007938285226	-6.209541511963
H	0.814051236430	1.692149473608	-6.446444294228

Table S19. Atomic coordinates and single point energies for *bis*-THF-solvated enolate **4g** with chelation to the *endo* sulfonyl oxygen.



G = -2003.509475
 G_{SP} = -2004.447571

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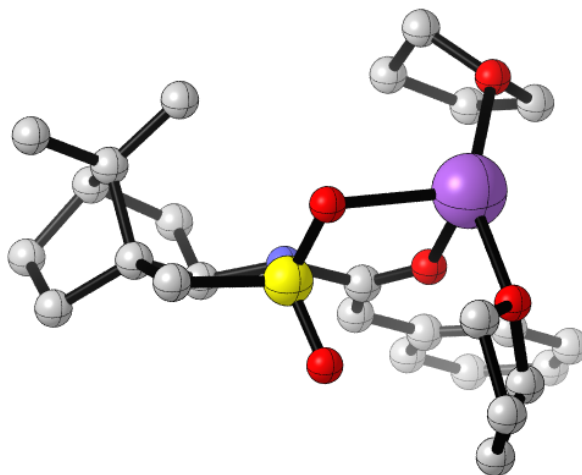
ETHF2_tet_endo_thf: optimized structure // E(RM062X) = -2005.02952347 A.U. after 13 cycles

O	1.026585752992	0.858983200558	-0.078046072922
C	0.679537596773	0.403848929685	1.056971708820
N	1.766988144737	0.274267827786	2.064091467750
S	2.116977414801	1.658068754277	2.936126525779
O	2.503037439400	2.776836326225	2.030530943451
C	3.650734472739	1.010925607857	3.654163384034
C	3.993772287628	-0.211191901892	2.812254183765
C	3.046095114686	-0.251909220952	1.581930270840
C	3.014349053392	-1.744281265727	1.187620206982
C	4.057647429268	-2.358178260453	2.142725664424
C	5.444157808151	-1.805194589421	1.738214500657
C	5.415038184311	-0.330620416249	2.239474391392
H	5.577714769511	0.397564735841	1.436831045807
H	6.175900564978	-0.140876505807	3.004098865775
H	5.599282437022	-1.872693434600	0.655600712271
H	6.254956879352	-2.370570027720	2.209175775817
C	3.772872118567	-1.612677383676	3.471013419486
C	2.378665368636	-1.867797409825	4.049757422724
H	2.161712265418	-1.168996679870	4.869955173906
H	1.567855272438	-1.769638715809	3.327395310171
H	2.347052120453	-2.879772375062	4.474177337228

C	4.779477467733	-1.908415964337	4.585930051616
H	4.600118255310	-1.254018658482	5.450209799847
H	4.652777550630	-2.940367146701	4.935893613858
H	5.825822386913	-1.789145704058	4.292341116181
H	4.017066853090	-3.451125096822	2.201300266890
H	2.011522083984	-2.159703934820	1.329842155639
H	3.279647467082	-1.885984817078	0.135069069506
H	3.427602193697	0.374072135689	0.761818716488
H	3.445119082650	0.786378552197	4.705561978253
H	4.376293718074	1.826297055792	3.582396314249
O	1.071725700326	1.949414264018	3.913180422546
C	-0.533533133946	0.004202922533	1.544701473257
H	-0.560781179313	-0.311426479554	2.584024073573
C	-1.790148605109	0.035641553922	0.814212470920
C	-1.864598482083	0.157768447106	-0.587045926949
C	-3.004067279390	-0.054361733330	1.521344745258
C	-3.092416092131	0.230519947963	-1.234520531627
H	-0.936084578157	0.195980987975	-1.150524456267
C	-4.228880532409	0.012064270576	0.869427313263
H	-2.973820648298	-0.164186125274	2.604677845374
C	-4.284281504629	0.167912632225	-0.514410121877
H	-3.119858078445	0.329211607815	-2.318882209219
H	-5.149181107596	-0.051948246190	1.446939162244
H	-5.242284783263	0.226745672575	-1.025562316578
Na	1.715271815856	2.988560354898	-0.067569939035
O	1.983997204215	2.787482589502	-2.291195264243
C	2.373312664937	1.468129503509	-2.691847388649
C	0.954091470120	3.189430636333	-3.190802315062
C	1.098598975805	0.789440706140	-3.215322104809
H	3.143369511561	1.556231849242	-3.471962707283
H	2.788861791737	0.966426722235	-1.814212339264
C	0.086867933672	1.945628247203	-3.356001428420
H	0.441489279886	4.051884959395	-2.753119480423
H	1.408763734814	3.497912605968	-4.145420090714
H	0.748534586250	0.043794902073	-2.496911720996
H	1.284561104011	0.291880913034	-4.172675945414
H	-0.658774948482	1.901987326939	-2.554875844749
H	-0.442990576691	1.937652057822	-4.313630002805
O	-0.125955050475	4.103238539058	0.549291699730
C	-0.479779982595	4.366763047205	1.918984548606
C	-1.239304298035	3.491474885061	-0.134032437289
C	-1.646912595326	3.437214470706	2.206667329501
H	0.401929051223	4.177990051159	2.538562234865
H	-0.769927276682	5.424330913149	2.008438033784

C	-2.387326126292	3.448181578294	0.868950183767
H	-1.474686375714	4.085681285438	-1.026150741496
H	-0.932012345498	2.480796192021	-0.431676631912
H	-2.259708581882	3.783458278457	3.045081482610
H	-1.273881704220	2.431616902432	2.439222442807
H	-3.003798447850	4.352504864250	0.782324731456
H	-3.030345290287	2.575043381943	0.714411065579

Table S20. Atomic coordinates and single point energies for *bis*-THF-solvated enolate **4g** with chelation to the *exo* sulfonyl oxygen.



G = -2003.532965

G_{SP} = -2004.452027

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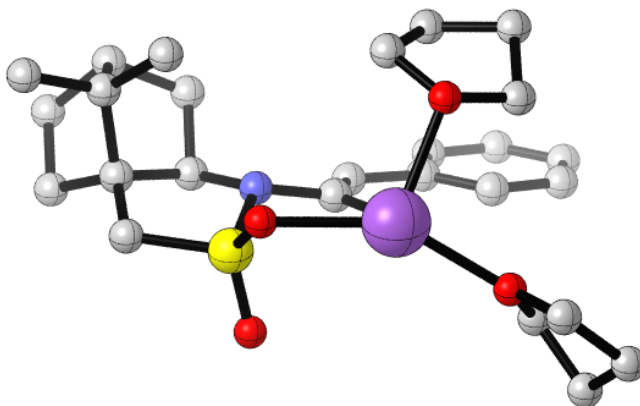
ETHF2_tet_exo_thf: optimized structure // E(RM062X) = -2005.03209592 A.U. after 13 cycles

O	0.205290515304	0.409388385468	-0.366200082345
C	0.211750533150	0.161706166288	0.873969213586
N	1.531217092369	0.201146877393	1.476607992527
S	2.773400040307	-0.351679268292	0.471037868556
O	2.453941559437	-1.635044657118	-0.171561680793
C	3.983393671734	-0.614426548799	1.790398967399
C	3.346170477616	-0.098871037307	3.063092249803
C	1.801221677786	-0.096919011024	2.884960898555
C	1.334293746983	0.988292915538	3.888389973237
C	2.633460442311	1.327057832615	4.644320249158
C	3.047662969327	0.069979943367	5.445438887528
C	3.597568004012	-0.895507381842	4.354361038567
H	3.075790663785	-1.858211701708	4.328836583510
H	4.664540272433	-1.102320096820	4.488086727160
H	2.191554742023	-0.356279179355	5.980652168134
H	3.812660997380	0.303329681289	6.193111943737
C	3.681446529766	1.360778797701	3.505240440715
C	3.442369978700	2.441707087497	2.449839932988
H	4.173895545321	2.348586899236	1.635520917389
H	2.448657681377	2.406305235717	2.002991978353
H	3.581827867360	3.430628431734	2.907195119783

C	5.125423408739	1.524537411740	3.986918618685
H	5.826325453722	1.342917805832	3.160459867120
H	5.282196927316	2.557025819312	4.324104477169
H	5.400520572146	0.862565625216	4.812502182573
H	2.566788083636	2.238695829489	5.247899555816
H	0.923623993863	1.852818823023	3.355879820655
H	0.555810945902	0.609261626624	4.558925028455
H	1.387730000768	-1.085267024744	3.132122723842
H	4.902960907773	-0.097820104807	1.496362677668
H	4.149618564745	-1.696392022240	1.802676644669
O	3.203936414014	0.737931986497	-0.436849501527
C	-0.857535107159	-0.095466889533	1.708538785602
H	-0.670780737935	-0.285065510154	2.760904963345
C	-2.247756443754	-0.108573444834	1.293022525379
C	-2.685473293752	0.022398964933	-0.045882262417
C	-3.251092346620	-0.264572233421	2.276881191250
C	-4.041174077448	0.008710107285	-0.362290274165
H	-1.941172607609	0.132118200639	-0.828488958037
C	-4.601140020141	-0.278946582625	1.951971950230
H	-2.950158419940	-0.372568995272	3.318864307540
C	-5.013726414473	-0.138761356350	0.625716877670
H	-4.341551657315	0.112027388634	-1.404393260808
H	-5.340195018190	-0.399212647631	2.742805142902
H	-6.070818228396	-0.148517346581	0.369099430034
Na	1.513917800835	1.295680606898	-1.883932768245
O	1.794057492383	-0.563554127841	-3.093163438807
C	0.862921839161	-1.639824636261	-2.844595276412
C	3.090055991485	-1.094647213552	-3.397923259638
C	1.668980627735	-2.928514323775	-2.976881239573
H	0.434384766992	-1.498486897124	-1.847302741464
H	0.071589491917	-1.571229853528	-3.602981483520
C	2.824338585404	-2.508586788098	-3.886647735872
H	3.553036606953	-0.444612332878	-4.147768022782
H	3.702580369133	-1.096195493254	-2.485806774240
H	1.069992307876	-3.747805946264	-3.386875277441
H	2.053025303556	-3.226416660878	-1.995738400922
H	2.505540321493	-2.491766095265	-4.936773231672
H	3.704250829285	-3.153872258271	-3.800216942338
O	0.628173952799	3.340410809674	-1.497960809636
C	1.104037396004	4.065159131019	-0.360825620384
C	-0.802441125897	3.269817489754	-1.382798633971
C	0.242098542606	3.560926663178	0.785797786092
H	2.174297700521	3.859931358853	-0.252749349403
H	0.962712454530	5.143923189823	-0.531767453932

C	-1.127584619947	3.352646511093	0.118754537234
H	-1.240166938413	4.107075371954	-1.943096520917
H	-1.124060905182	2.328771928645	-1.840329429756
H	0.211948524111	4.259473464536	1.628626666015
H	0.631588755376	2.600774776996	1.137419092626
H	-1.801008733232	4.192981907964	0.319028051808
H	-1.606658878254	2.436078156936	0.476250305385

Table S21. Atomic coordinates and single point energies for *bis*-THF-solvated enolate **4g** with the enolate oriented *anti* to the sultam ring. The coordinatively unsaturated sodium prefers to form a pseudo-contact with the *exo* sulfonyl oxygen.



G = -2003.534531

G_{SP} = -2004.455199

72

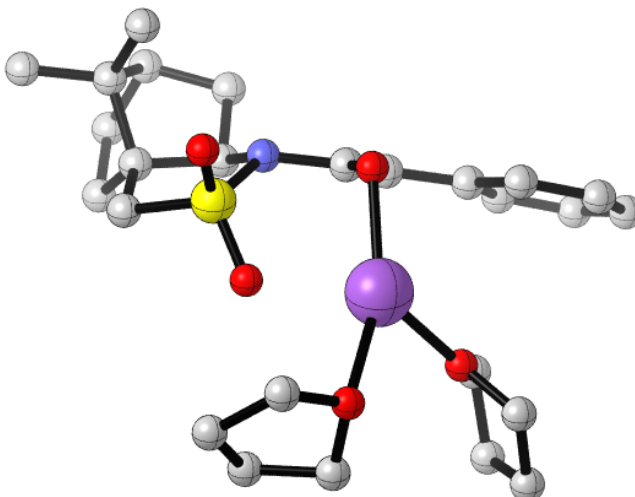
ETHF2_trig_pendC_thf: optimized structure // E(RM062X) = -2005.03240710 A.U. after 13 cycles

O	-0.000950955364	0.000465839279	-0.000889601929
C	0.000616743008	-0.011326894275	1.263895428295
N	1.323709112119	0.013696384219	1.857139561589
S	2.501759567971	-0.807265692134	0.961756604218
O	2.094729441214	-2.174068216769	0.610062028761
C	3.739595156270	-0.856030490778	2.279439136639
C	3.126535751984	-0.140348579868	3.465385137234
C	1.582284496088	-0.106638515294	3.295924949654
C	1.166100714702	1.115131015783	4.156806980062
C	2.490110055006	1.524962887056	4.830783029247
C	2.889297471794	0.392061456175	5.803597306858
C	3.368743427256	-0.747716781421	4.857820045359
H	2.801732198268	-1.676746808685	4.982133497283
H	4.426984410736	-0.986894102878	5.005490803400
H	2.039922439322	0.085460499234	6.424386166539
H	3.688605947117	0.708804694476	6.481647548752
C	3.511644913142	1.358015845799	3.679895861871
C	3.269606489876	2.282015192690	2.485109563369
H	3.884420597737	1.978194314092	1.626191491152
H	2.230691797699	2.304470801034	2.154077950443

H	3.565772285582	3.304271771123	2.755372538550
C	4.972128158458	1.542759027886	4.099170127205
H	5.642632072113	1.280078791759	3.269233632753
H	5.152994913749	2.597741751971	4.341039793658
H	5.266515267921	0.948694182651	4.968606286443
H	2.458808804802	2.518390648823	5.291158839928
H	0.751726811231	1.910454160866	3.529511265664
H	0.401339707959	0.842580230447	4.891798124319
H	1.130392052552	-1.037065920611	3.669406568532
H	4.650219741353	-0.390645799909	1.888470892391
H	3.913005224449	-1.921541739751	2.459963077307
O	2.955101817670	0.043769798293	-0.165746536126
C	-1.079058255613	0.000840534369	2.125962070057
H	-0.901561863914	-0.041048772865	3.195628606368
C	-2.460693279064	0.142992539525	1.711460402771
C	-2.884824569494	0.228610952293	0.364635938099
C	-3.468207559018	0.224944357388	2.700799117295
C	-4.229639854746	0.394705395144	0.043380132446
H	-2.137467838121	0.153071109640	-0.418288841811
C	-4.807160669276	0.386644774044	2.371091346167
H	-3.178606293935	0.161621081147	3.749632374926
C	-5.205403060382	0.476803832425	1.035507534835
H	-4.519259706029	0.456964732702	-1.005588033589
H	-5.549769609265	0.445099033542	3.165589820122
H	-6.254144541995	0.604347136136	0.776268856932
Na	1.306500723500	0.388066874658	-1.718931097588
O	-0.082241635922	-0.415601155016	-3.263370584367
C	-1.249377757497	-1.120954749939	-2.805628001435
C	0.001094592564	-0.477665450071	-4.699607590368
C	-1.576896156106	-2.084716896069	-3.931750594557
H	-1.005247192719	-1.588176236654	-1.847661465756
H	-2.067478082822	-0.401008546721	-2.652754629226
C	-1.244206004538	-1.232867423839	-5.156837092570
H	0.056799658420	0.542542724938	-5.095098292673
H	0.921985032402	-1.012207654139	-4.963640671394
H	-2.616871441089	-2.423254574156	-3.904353534304
H	-0.920432070308	-2.962226186595	-3.879579852569
H	-2.063453912089	-0.532454004503	-5.359867912299
H	-1.061304664865	-1.817777764812	-6.063171490554
O	0.577726837841	2.525717023519	-1.664679465998
C	0.783245221241	3.002996105648	-0.319475093915
C	-0.821406147500	2.567039028379	-1.989966560071
C	-0.606505888460	3.246747833226	0.258753763611
H	1.349700695415	2.245364007955	0.235484231718

H	1.375259053158	3.926691415006	-0.376548372999
C	-1.432068394267	3.539416354553	-0.994555552705
H	-0.914908007541	2.877511401263	-3.036032176825
H	-1.246580024772	1.560806515350	-1.869667197059
H	-0.614304807916	4.064884129977	0.986225479955
H	-0.978061281574	2.337650244664	0.746095023160
H	-1.277885692148	4.573519675395	-1.329122729572
H	-2.505116152999	3.373350293889	-0.852719504965

Table S22. Atomic coordinates and single point energies for *bis*-THF-solvated enolate **4g** with the enolate oriented *syn* to the sultam ring. The coordinatively unsaturated sodium prefers to form a pseudo-contact with the *endo* sulfonyl oxygen.



G = -2003.529967

G_{SP} = -2004.449152

72

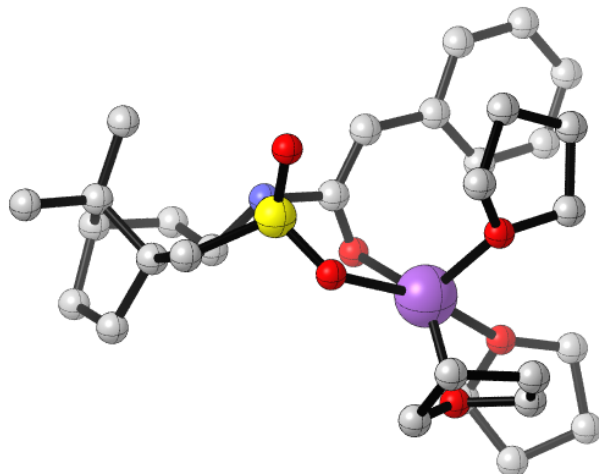
ETHF2_trig_pendS_thf: optimized structure // E(RM062X) = -2005.02707177 A.U. after 13 cycles

O	0.482126408245	1.827552231048	0.463747288891
C	0.204111934366	0.996349445662	1.377947783359
N	1.365298889296	0.364439447964	1.968251142641
S	2.636790854059	0.121752039268	0.866512598700
O	2.105962287573	-0.399864917285	-0.422733779940
C	3.406499421483	-1.244105094774	1.771881831735
C	2.695844047370	-1.318949940481	3.105355854791
C	1.269691591351	-0.737013264332	2.930773402716
C	0.881016491463	-0.318051603539	4.371115519724
C	2.061200349169	-0.851649694682	5.207934596896
C	2.010863385077	-2.395226191215	5.151446497413
C	2.493065744191	-2.720396049942	3.707944494805
H	1.760491141273	-3.292637472181	3.128043991888
H	3.429361441690	-3.288447566885	3.705007889216
H	0.997261487866	-2.765546795588	5.342574324131
H	2.667382409648	-2.847442761903	5.902080528497
C	3.280831779607	-0.518229244946	4.312612252125
C	3.501230387609	0.979282056462	4.085403793444
H	4.317417769285	1.143468475537	3.369759396066
H	2.624545572199	1.507747262912	3.706336946540

H	3.798913400956	1.442200618090	5.035725295824
C	4.608075416249	-1.089862180995	4.817933479718
H	5.387602750066	-0.973298146294	4.052520435421
H	4.935260916239	-0.529620895757	5.702986725950
H	4.564181134972	-2.147033282467	5.093557636578
H	2.100703500626	-0.442517107220	6.223239052204
H	0.778432251057	0.769496036671	4.439480666551
H	-0.071848272136	-0.763051877544	4.677330388471
H	0.592371776288	-1.505372789812	2.530160361907
H	4.477522173353	-1.024860967531	1.832496234931
H	3.238683290465	-2.131582193483	1.152704015372
O	3.533367813932	1.275262574886	0.781770644073
C	-1.040557482745	0.610352221456	1.840783875321
H	-1.106765270615	-0.145238731481	2.617363230966
C	-2.303045812786	1.118261180056	1.336501663733
C	-2.431748514643	2.156411752818	0.384956766700
C	-3.502104131947	0.524296257139	1.793848497452
C	-3.681736223324	2.541564067354	-0.092530341307
H	-1.536182068982	2.653837223482	0.027599588011
C	-4.744826554272	0.913672131823	1.312142745655
H	-3.441933773488	-0.272103735559	2.535787299443
C	-4.849600644891	1.923806598399	0.353494546007
H	-3.741734622818	3.343722204961	-0.827405266052
H	-5.641887775581	0.423119707446	1.687510751548
H	-5.821673000653	2.229545597157	-0.027508925470
Na	0.415793185628	0.765790466564	-1.471709676093
O	-1.567713712506	-0.046522758982	-2.085158238938
C	-2.560158007123	-0.800620148183	-1.386724043274
C	-2.118805113773	0.234877218644	-3.372943179565
C	-3.067102445749	-1.792968308452	-2.429658648655
H	-2.083285789000	-1.257632572601	-0.514795823473
H	-3.358465402089	-0.122712208095	-1.048857812078
C	-2.924787810577	-1.017642736122	-3.758376465746
H	-2.767342003338	1.119822095348	-3.295906440398
H	-1.285496566460	0.459027417444	-4.046901909809
H	-4.096081643667	-2.105103448856	-2.227444430784
H	-2.436539750082	-2.688925476414	-2.433812783212
H	-3.896514878272	-0.737713080249	-4.176613841708
H	-2.399082693973	-1.613348727941	-4.511466354942
O	1.245914069501	-0.090097408787	-3.387122367665
C	0.890015545194	-1.431541637006	-3.727153002795
C	2.673885614816	0.003648841657	-3.496563943166
C	1.966708285709	-2.278759029357	-3.063807067507
H	-0.121735518259	-1.611621194471	-3.352048500974

H	0.901690886385	-1.545255880851	-4.822736772385
C	3.225300710856	-1.404885389573	-3.208734342591
H	2.927864542765	0.339638874136	-4.510954141272
H	3.010853465594	0.757446999822	-2.778162108193
H	2.070196177945	-3.261681491337	-3.533853142809
H	1.721849850546	-2.417509849085	-2.005297746936
H	3.854178172839	-1.745572340743	-4.038052564295
H	3.826341391773	-1.417862900267	-2.295495045950

Table S23. Atomic coordinates and single point energies for *tris*-THF-solvated enolate **4g** with chelation to the *endo* sulfonyl oxygen.



G = -2235.736444

G_{SP} = -2236.791705

85

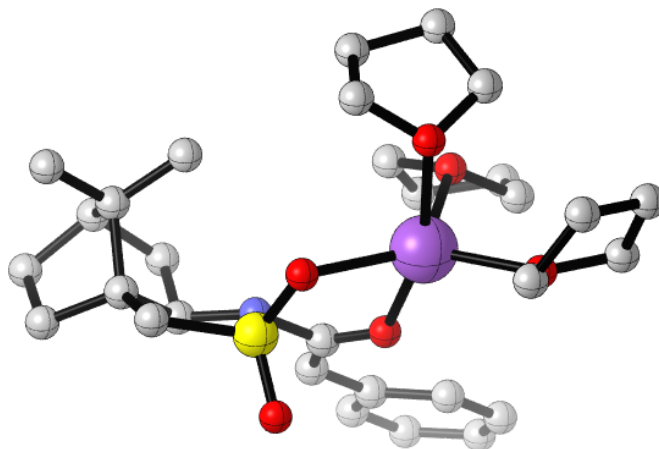
ETHF3_tbp_endo_thf: optimized structure // E(RM062X) = -2237.48738709 A.U. after 12 cycles

O	0.233879386728	-0.906556350947	0.726012612525
C	0.167042643705	-0.000290918828	1.599953525425
N	1.383422579354	0.192494382531	2.435592189980
S	2.404964680856	1.373756553880	1.805573543228
O	2.520677307661	1.221607519785	0.328277493205
C	3.927817539178	0.765462267791	2.577155509164
C	3.543602397491	-0.537098500104	3.255191579135
C	2.185078584330	-1.015572480977	2.683555294714
C	1.620333501382	-1.922028536569	3.801436022168
C	2.783165501774	-1.965422833545	4.814683277827
C	3.945999282833	-2.738233376008	4.150303404749
C	4.496260834757	-1.734170604398	3.094702554491
H	4.460256434137	-2.125546244231	2.071932620499
H	5.533104803567	-1.448055456989	3.300697579610
H	3.591805638039	-3.668409496926	3.691747761361
H	4.715805514329	-3.010032397331	4.880156586025
C	3.298651420741	-0.503713411935	4.797398583360
C	2.283646062731	0.532028741317	5.287241275476
H	2.635312319419	1.549925840262	5.065685714128
H	1.292042280451	0.426136095137	4.845190260636
H	2.188918776679	0.452659808226	6.378317734157

C	4.584391111233	-0.277417470267	5.596778057885
H	4.966183079694	0.737931261445	5.420454457857
H	4.371231990900	-0.362102859430	6.669966695088
H	5.387723898408	-0.981337967149	5.362470522923
H	2.498255595720	-2.350128019215	5.800057501354
H	0.710402482352	-1.486204110092	4.227381047151
H	1.367113541158	-2.917371754464	3.422222269255
H	2.318657990311	-1.562010641712	1.741803174214
H	4.278835927743	1.545590341697	3.260495024765
H	4.639299483409	0.641734042633	1.754779455146
O	2.025879715201	2.710813226106	2.274610032469
C	-0.842466747526	0.888757448318	1.889765911408
H	-0.686337503300	1.560589991000	2.729923502868
C	-2.099984479250	0.994107390463	1.169199621098
C	-2.413719233558	0.253883384504	0.006728247523
C	-3.080126314716	1.897508164145	1.639060460422
C	-3.638055453495	0.421883836269	-0.637622136972
H	-1.692804736149	-0.460399589074	-0.383908718800
C	-4.300620986665	2.052247266630	0.995115364263
H	-2.866304781610	2.482738152394	2.533327464568
C	-4.593088624273	1.315211875869	-0.154872497252
H	-3.850148660502	-0.164278124281	-1.531574152263
H	-5.030976621629	2.755697162381	1.392260710948
H	-5.548555796955	1.434525967144	-0.661359994447
O	2.324650259325	0.265863560391	-2.831856784240
C	3.615739247930	0.835280785365	-2.607404071137
C	1.743031188584	0.994471862931	-3.918908113975
C	3.376172928908	2.332643598606	-2.724180750396
H	3.957882792113	0.509293778837	-1.621720556360
H	4.312907759427	0.473291225781	-3.380078610219
C	2.334283088928	2.417079753292	-3.854057441136
H	2.006483344158	0.494398092563	-4.862799797461
H	0.655766391252	0.962255609019	-3.792550796170
H	4.292408120120	2.890514487267	-2.942592232500
H	2.956610999198	2.696816162336	-1.779372520185
H	2.802717126841	2.679794721763	-4.808668416670
H	1.563433830433	3.162700526460	-3.636022420143
Na	0.882028818476	0.323311796684	-1.059452695772
O	-0.377486152495	-0.965143073814	-2.459037737234
C	0.349977027506	-2.190974139373	-2.539298980746
C	-1.294039110374	-0.992344894976	-3.550131650105
C	0.654947382805	-2.356023914010	-4.026222059809
H	1.240830731538	-2.107547184542	-1.909499336558
H	-0.280574478261	-3.008431044606	-2.157783593213

C	-0.528851392080	-1.641706428678	-4.715490159256
H	-2.168702591509	-1.596245537022	-3.266071271548
H	-1.621703279480	0.032550995067	-3.747219031643
H	0.739645370863	-3.409580548668	-4.309959880243
H	1.600981825023	-1.857373911889	-4.261420306975
H	-1.172684718631	-2.337429924465	-5.262597683354
H	-0.175390750180	-0.887656036395	-5.425912894982
O	0.250183683852	2.408572163175	-1.564303133876
C	0.577045004908	3.611572361054	-0.867235796364
C	-0.983612221766	2.654453365381	-2.239625380805
C	-0.751694584864	4.075801070994	-0.284400978121
H	1.339135337495	3.373283202347	-0.121177334007
H	0.977862828735	4.345009212959	-1.587537813606
C	-1.779279609556	3.615621292035	-1.338561389344
H	-0.769965574037	3.105997191546	-3.221476431852
H	-1.477260393627	1.688973993272	-2.388175440436
H	-0.770157847913	5.156260558298	-0.111023890615
H	-0.928145959717	3.568993635525	0.671267162575
H	-2.170088737626	4.455673145105	-1.922317072390
H	-2.626888690257	3.106798034829	-0.869306765524

Table S24. Atomic coordinates and single point energies for *tris*-THF-solvated enolate **4g** with chelation to the *exo* sulfonyl oxygen.



G = -2235.738171

G_{SP} = -2236.794368

85

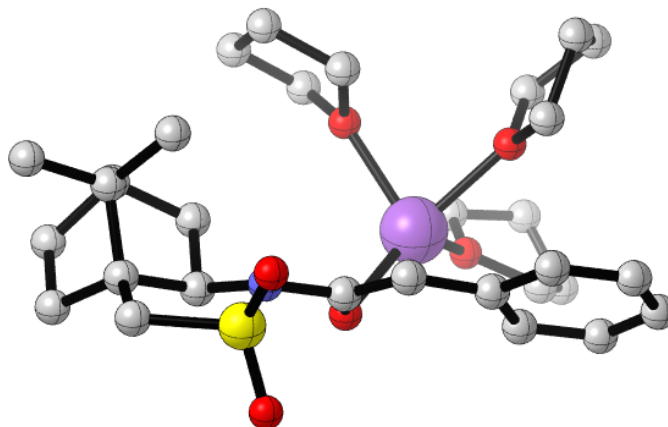
ETHF3_tbp_exo_thf: optimized structure // E(RM062X) = -2237.48984275 A.U. after 13 cycles

O	-0.436168685660	-0.199515180936	0.356045356009
C	-0.268201792213	0.138105988560	1.561245502590
N	1.114257046902	0.067295218894	2.007287534120
S	1.956937269764	-1.281800622365	1.423606000595
O	1.213060861838	-2.534043886378	1.604318283899
C	3.307854437962	-1.195717175390	2.626304205500
C	3.060562020277	0.046742677173	3.454986716397
C	1.555658994974	0.421559686490	3.358200458885
C	1.552149891213	1.940556141154	3.666365240229
C	3.016870246396	2.207503111898	4.066092503261
C	3.278387053326	1.459086647772	5.394048942065
C	3.358675473811	-0.034730146450	4.962007417459
H	2.626225892747	-0.669832932601	5.471901188966
H	4.349571358473	-0.463032148908	5.145371458534
H	2.471890733663	1.638701912138	6.113923682220
H	4.210866327725	1.788383325814	5.864056073055
C	3.804316278484	1.355554826191	3.040178621891
C	3.625227069648	1.783629217402	1.582515362367
H	4.097165998545	1.054561169345	0.908551535602
H	2.582408823227	1.880072467082	1.279352810273
H	4.123115828543	2.749981646611	1.423922933090

C	5.312078750471	1.293282078177	3.298717490312
H	5.778492027792	0.539966805770	2.648736745864
H	5.765916627891	2.261464724724	3.051773948095
H	5.579978815507	1.056495706745	4.331877323822
H	3.279066903585	3.270702645379	4.094156554548
H	1.248816809280	2.511815672393	2.782313880933
H	0.855434075262	2.186746072748	4.474637038825
H	0.973141472241	-0.147887976658	4.096612403464
H	4.246735737681	-1.189285364107	2.063117684410
H	3.226713196284	-2.121349936587	3.205000386307
O	2.451317694305	-1.000179656970	0.054539449176
C	-1.203258899962	0.590151307467	2.472982848254
H	-0.882117238943	0.839159846190	3.479705791421
C	-2.606583860394	0.803863521334	2.176854397083
C	-3.226367413821	0.457786089201	0.952592905689
C	-3.427795875388	1.407311543175	3.156918118234
C	-4.576546083596	0.718541287175	0.733362749111
H	-2.627501276899	-0.022095252792	0.184708731919
C	-4.774012083038	1.661302286345	2.930073628876
H	-2.984641924840	1.683022363787	4.113804571697
C	-5.365195123375	1.323299688610	1.711216205914
H	-5.020358113798	0.437387114335	-0.221163385121
H	-5.369045136252	2.130240281397	3.712520172624
H	-6.419353816262	1.522781753244	1.531180324788
O	2.680953158340	0.263755232397	-2.844078954947
C	3.864319768188	0.754530461549	-2.214031863609
C	2.284485626454	1.255719146063	-3.797149693786
C	3.555572923061	2.224618566968	-1.976253738967
H	4.024586431572	0.163655982495	-1.308254006739
H	4.722199343522	0.629333553823	-2.894626052055
C	2.784293502422	2.608921013845	-3.251021498912
H	2.744661629785	1.022524583832	-4.768905777160
H	1.195396492850	1.199820314091	-3.893851308339
H	4.453833806602	2.829525192654	-1.813911907084
H	2.911433301578	2.317650607784	-1.093683149108
H	3.443951831723	3.095782371279	-3.977618357418
H	1.950475208458	3.282066888791	-3.032943586830
Na	0.890639775494	-0.179492717352	-1.428985126545
O	0.184441724129	-1.233592953695	-3.301086217181
C	1.108152556110	-2.260933267483	-3.662544158825
C	-0.592577592667	-0.975375376795	-4.468042546152
C	1.577211186870	-1.885497186339	-5.066565099031
H	1.909419960711	-2.273016688968	-2.918132551078
H	0.586694296800	-3.230092842935	-3.653651616559

C	0.386092763625	-1.090360462455	-5.647102153498
H	-1.391381235649	-1.728131272017	-4.539409733889
H	-1.049282700942	0.012018688802	-4.356106400023
H	1.823525131787	-2.771282997167	-5.660215906616
H	2.471097690167	-1.257369722058	-4.999069334637
H	-0.082892041519	-1.603309317521	-6.492614372823
H	0.704565640546	-0.102272845170	-5.994379293691
O	0.244477801217	1.997388243816	-1.675147399833
C	0.353823019183	2.779310503350	-0.472414020344
C	-1.108157584785	2.025480534542	-2.155660882900
C	-1.064324745872	3.206905502564	-0.116138953538
H	0.813669325532	2.159669150892	0.306674763443
H	1.004718841186	3.640330806634	-0.683694495647
C	-1.748797528006	3.228465469894	-1.481733959500
H	-1.077367690005	2.097754187477	-3.248738903133
H	-1.613642203694	1.092775311305	-1.862480811204
H	-1.089279928343	4.170170395361	0.403111722921
H	-1.530443157732	2.449633764497	0.523096497060
H	-1.499099555848	4.146553300894	-2.029087961022
H	-2.838421820430	3.141952420143	-1.421892510845

Table S25. Atomic coordinates and single point energies for *tris*-THF-solvated enolate **4g** with the enolate oriented *anti* to the sultam ring.



G = -2235.730636

G_{SP} = -2236.789025

85

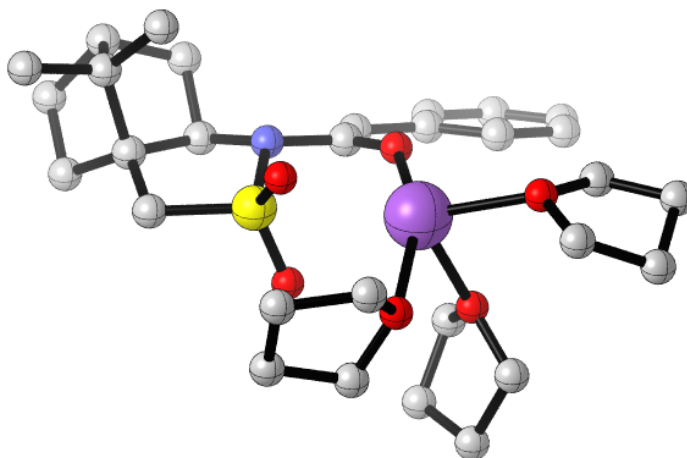
ETHF3_tet_pendC_thf: optimized structure // E(RM062X) = -2237.48216577 A.U. after 13 cycles

O	0.431457028863	1.451103796887	0.584457886962
C	0.307503370842	0.583685298481	1.494357700324
N	1.545225564475	0.194085872539	2.138963992098
S	1.619198968632	0.105389661101	3.829275579820
O	1.089517301110	1.327323909433	4.453532879934
C	3.431146425487	0.114949627226	3.920149109402
C	3.927615002506	0.144253912846	2.489753377450
C	2.802272625468	0.706460409121	1.587537720303
C	3.162220368772	0.155152792795	0.186825211960
C	4.511736830697	-0.549438068055	0.433795939197
C	5.553223487472	0.546520009413	0.752724228749
C	5.166011052507	1.006314785333	2.188843639763
H	4.919070103451	2.072175311079	2.245217167310
H	5.967171462118	0.816583537389	2.910952924122
H	5.501217146050	1.365910156063	0.026852913110
H	6.573956158351	0.150904136501	0.723025129064
C	4.291880779104	-1.217050413355	1.814671169384
C	3.198454020765	-2.289583802033	1.834316351020
H	2.937384425133	-2.554913795906	2.868155509801
H	2.273340998795	-1.992500314109	1.335215681450
H	3.580004779983	-3.198889307314	1.350684486720

C	5.547323151772	-1.857758445481	2.412265050573
H	5.345681983769	-2.203564730811	3.435501837954
H	5.828669260656	-2.739008081184	1.821531598154
H	6.414691882926	-1.192973083702	2.449517039589
H	4.815197405782	-1.229693018980	-0.371178690150
H	2.387059505001	-0.531628253237	-0.164804203570
H	3.240103516718	0.961869005884	-0.550200285236
H	2.791341789084	1.803563190445	1.596924570833
H	3.732031828573	-0.770765648910	4.489369763506
H	3.684848948308	1.020835591708	4.479741386568
O	1.066447892931	-1.174297472556	4.294394144240
C	-0.836198565080	-0.077633269810	1.917297756748
H	-0.712188725971	-0.880186570366	2.639925646433
C	-2.191737594831	0.240252206322	1.525255455566
C	-2.568421843535	1.312613148211	0.681335972930
C	-3.244968783790	-0.568987111451	2.019748343565
C	-3.900825111613	1.524700228205	0.332134226365
H	-1.808308938850	2.010186407613	0.336006454273
C	-4.568522760925	-0.347382575934	1.672814534013
H	-2.996641464718	-1.390620791973	2.691278939997
C	-4.914494164854	0.697362539710	0.810211764048
H	-4.149790666931	2.364063335025	-0.316416197878
H	-5.342903623449	-0.997542023056	2.077952518469
H	-5.952098600617	0.871008456031	0.533724245099
Na	-0.415273305071	0.736651980298	-1.333286618260
O	-1.088307903054	1.982570333452	-3.062942193432
C	-2.437305961446	2.473318209412	-3.018691359137
C	-0.608557974508	1.947001126693	-4.417487901673
C	-2.645885662449	3.172424927516	-4.353027062166
H	-3.122928532906	1.621917807943	-2.887707001359
H	-2.527504440250	3.140125678064	-2.154825859095
C	-1.806374211424	2.305717463026	-5.291798917356
H	0.200924633121	2.682214519400	-4.514415170676
H	-0.206382997280	0.947233395761	-4.620765045772
H	-2.243125242684	4.191761169624	-4.310654751459
H	-3.701139469465	3.226406896830	-4.636527439723
H	-1.505576154867	2.821973333236	-6.208423474155
H	-2.363546529876	1.403983016891	-5.575218887642
O	0.999522144004	-0.694317638779	-2.344753506077
C	0.959359689420	-1.999533509744	-1.763699792833
C	1.916778881252	-0.750771953080	-3.432108525678
C	2.371134717845	-2.588050018786	-1.948781755748
H	0.656940542310	-1.889749383619	-0.714630418770
H	0.200913366633	-2.603644120615	-2.284596174552

C	3.066779575247	-1.607151662613	-2.914267364976
H	1.427197560334	-1.220860026385	-4.300462245176
H	2.198581327075	0.274165631687	-3.689241893335
H	2.313962164334	-3.598603449980	-2.365197570169
H	2.906097104088	-2.651460438599	-0.995261566460
H	3.599971774743	-2.113138386226	-3.724854602671
H	3.783938026979	-0.977295272693	-2.376666977801
O	-1.936273831552	-0.772738606203	-1.971207989916
C	-2.655671641011	-1.725897019135	-1.170269272511
C	-2.031981828326	-1.108639663444	-3.360003031677
C	-2.984367587989	-2.877533764092	-2.110910429757
H	-2.022671821751	-2.014524555701	-0.323201790467
H	-3.562386880052	-1.240795141216	-0.784397695470
C	-3.136044136993	-2.153664967637	-3.448063758737
H	-2.252054557469	-0.195433622305	-3.922922109609
H	-1.063011391977	-1.506218460966	-3.697823644481
H	-3.882497174120	-3.420923114889	-1.802052868223
H	-2.149330430568	-3.588264728891	-2.155172309944
H	-4.116291737424	-1.663713376445	-3.503824216904
H	-3.025005615638	-2.807099559585	-4.318796991857

Table S26. Atomic coordinates and single point energies for *tris*-THF-solvated enolate **4g** with the enolate oriented *syn* to the sultam ring.



G = -2235.738691

G_{SP} = -2236.794903

85

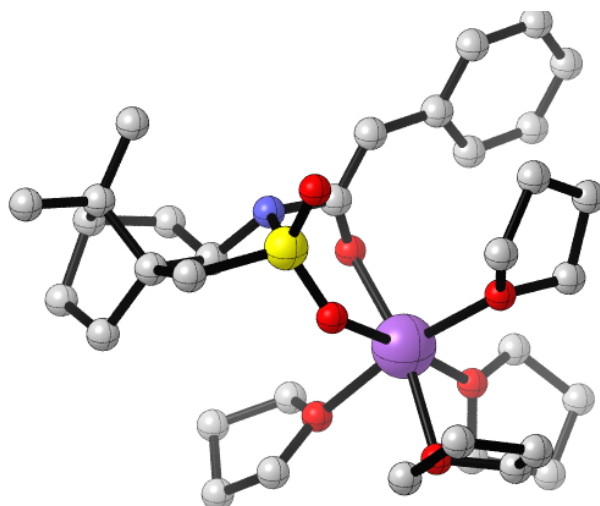
ETHF3_tet_pendS_thf: optimized structure // E(RM062X) = -2237.48785196 A.U. after 13 cycles

O	-0.583340588980	0.550249344811	0.193916933870
C	-0.410552904424	0.236769015715	1.402653697049
N	0.986464686329	0.176277420255	1.803123833528
S	1.983120111575	-0.473258346457	0.604819834358
O	1.418709483297	-1.727713212885	0.066601714744
C	3.385013938460	-0.830669505919	1.690920492959
C	2.985712788834	-0.329055831422	3.064171861430
C	1.437317895966	-0.238723997840	3.133122065161
C	1.196112885480	0.801313217783	4.256193456354
C	2.619903244508	1.067607730997	4.784340228718
C	3.110603338981	-0.228055153140	5.469188361117
C	3.399000715769	-1.183848184476	4.274713138977
H	2.815463508604	-2.110068733830	4.315175405434
H	4.456056558995	-1.464070393865	4.218182986414
H	2.349162078458	-0.630388934357	6.146811871196
H	4.012835045056	-0.051043816832	6.063805677542
C	3.457919835386	1.099826178401	3.482140383721
C	3.093048125616	2.233115046054	2.519936613970
H	3.596208833268	2.094020525899	1.552998214767
H	2.024336657063	2.322978731342	2.319444292067
H	3.447132192785	3.184445915097	2.938570049411

C	4.969809731721	1.181421692914	3.709123780950
H	5.504782445099	1.054889858525	2.757710934443
H	5.229139754661	2.174421351114	4.097693753028
H	5.357259921302	0.439320645013	4.412395488446
H	2.695602184087	1.961350841138	5.413038599403
H	0.724741678303	1.701944435974	3.850928099090
H	0.538279693370	0.404061219838	5.036486779173
H	1.004113021755	-1.219267155428	3.379946162213
H	4.264099238332	-0.337736010701	1.262440191949
H	3.506379400683	-1.917982024179	1.648406772234
O	2.323261449039	0.536441038770	-0.419042947166
C	-1.361283963506	-0.061835445898	2.360355139139
H	-1.039388017668	-0.327912504512	3.362594934011
C	-2.792578224468	-0.040200983550	2.127332752580
C	-3.396174830398	0.247520084266	0.879843659449
C	-3.664231644488	-0.341400245808	3.200120692921
C	-4.780778072210	0.231363217886	0.732672860277
H	-2.756752669938	0.476999924462	0.033293094721
C	-5.043798458214	-0.355958476760	3.042831364848
H	-3.234321401924	-0.569411652406	4.175449846849
C	-5.620847825919	-0.069122470382	1.804067004929
H	-5.209964303547	0.457729020448	-0.243110626442
H	-5.676751757278	-0.593887719167	3.896653667795
H	-6.701439766678	-0.079738087912	1.678854649101
Na	0.312595263301	0.182703079048	-1.781431666355
O	-0.882558510228	1.115894773215	-3.457100076318
C	-2.295630454937	1.150892321607	-3.189883043022
C	-0.642972923996	0.886912691086	-4.854324595224
C	-2.957866517779	1.290919198065	-4.553203075274
H	-2.578115474568	0.212480968012	-2.692621717339
H	-2.495604735544	1.990059919278	-2.515652777480
C	-1.994801680561	0.508700805684	-5.445897261170
H	-0.257323186323	1.815363475565	-5.298715598253
H	0.116524803282	0.103016795825	-4.948439858271
H	-2.986852315543	2.344832871058	-4.856892145106
H	-3.979845737976	0.899722443654	-4.562012707103
H	-2.070991489920	0.768925517664	-6.506250332208
H	-2.170478671469	-0.569140938728	-5.341065494465
O	1.684225302690	-0.823318152751	-3.281886113402
C	2.155875848424	-2.136187011923	-2.978046293220
C	2.789725119692	-0.121953112752	-3.845115512272
C	3.600455299236	-1.951448425603	-2.492464484511
H	1.487129854215	-2.554944002279	-2.220659531617
H	2.119077388297	-2.747581004849	-3.893495921033

C	3.998162614951	-0.551218762480	-3.010990096951
H	2.904950187773	-0.417728536349	-4.899928500330
H	2.570151532597	0.949565326218	-3.799610873790
H	4.249132022664	-2.741408832620	-2.884230229475
H	3.643941191332	-1.993778279078	-1.399355216749
H	4.913980312105	-0.564552019149	-3.610056448651
H	4.137051974524	0.139761461009	-2.174946173360
O	-1.043900748259	-1.596016010325	-1.994209275436
C	-1.505472824928	-2.370536900574	-0.889734988488
C	-1.193903560122	-2.403742883904	-3.155673641355
C	-0.924341430769	-3.753890980003	-1.154503342242
H	-1.149339392094	-1.891467184471	0.025849002951
H	-2.608249956697	-2.390418608225	-0.894270628965
C	-0.967470717599	-3.859584054392	-2.693227921489
H	-2.211602221337	-2.276247189230	-3.556931609285
H	-0.469663583261	-2.048618564235	-3.897102743532
H	-1.490578721930	-4.547735863559	-0.657096332855
H	0.107896435119	-3.781303345659	-0.787519622389
H	-1.788740894444	-4.500648737604	-3.030450600558
H	-0.038095508493	-4.274201253929	-3.096955830831

Table S27. Atomic coordinates and single point energies for *tetrakis*-THF-solvated enolate **4g** with chelation to the *endo* sulfonyl oxygen.



G = -2467.94456

G_{SP} = -2469.135377

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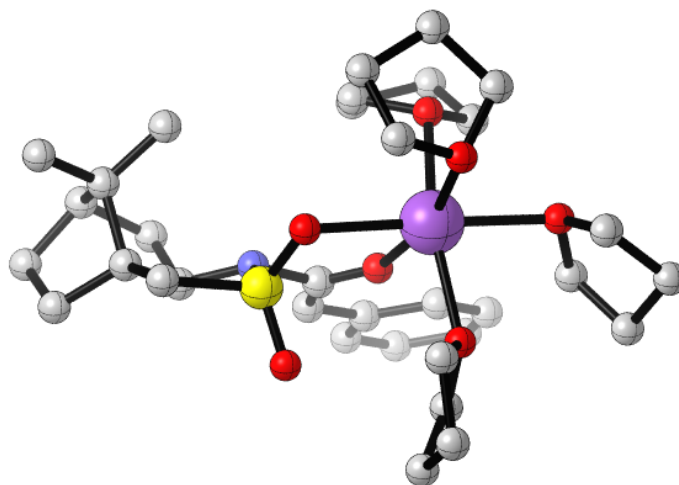
ETHF4_oh_endo_thf: optimized structure // E(RM062X) = -2469.94675555 A.U. after 12 cycles

O	0.025158219376	0.013839978795	-0.026181387332
C	0.026046225030	0.012001015300	1.231797959967
N	1.366273510551	-0.005564277713	1.876217891890
S	1.960614030073	1.505222311012	2.304854241610
O	1.929376366035	2.429988499973	1.140625648031
C	3.670422823495	0.959758433193	2.549636319623
C	3.732527314829	-0.425319838609	1.924785522669
C	2.438050868658	-0.659932634893	1.105926674826
C	2.327389102578	-2.198612378053	1.037402374705
C	3.624414068109	-2.663226988015	1.736041606791
C	4.809631570338	-2.282266688843	0.822408794417
C	4.894760777629	-0.733979164358	0.964138226189
H	4.760729968444	-0.208872933561	0.010292445389
H	5.854873488047	-0.412683267292	1.381667996048
H	4.635059083340	-2.600939174548	-0.211774185534
H	5.737253150403	-2.761201551742	1.153434167785
C	3.762966059501	-1.648045544310	2.898710927938
C	2.634457862146	-1.719309938417	3.931124596794
H	2.637216430629	-0.825479584971	4.571291340268

H	1.637443453361	-1.804714645421	3.497202552395
H	2.804319105700	-2.586028746646	4.583668992148
C	5.079064605028	-1.746033692090	3.675209332154
H	5.141048336459	-0.934586098026	4.413768993918
H	5.112520531336	-2.692617970950	4.229589432984
H	5.973863597521	-1.695907767150	3.048800966736
H	3.613221975207	-3.717405021707	2.033938439924
H	1.425748770204	-2.547583655460	1.552014751747
H	2.272170698628	-2.547893656079	0.000080081945
H	2.501053817002	-0.203678008844	0.108177783327
H	3.865693920932	0.973504958580	3.627079392167
H	4.293508395524	1.707111962143	2.048804448688
O	1.328263164620	1.996537342846	3.533772577340
C	-1.023633914659	0.024397197058	2.123616889817
H	-0.784003408475	0.009410177568	3.183852834589
C	-2.421039927015	0.097857790706	1.740927232687
C	-2.873878386283	0.042935542128	0.401942823800
C	-3.407120529581	0.239534285041	2.743704396200
C	-4.230387719870	0.135555048476	0.098944601721
H	-2.139175336015	-0.079894274594	-0.388492979544
C	-4.757039731989	0.334947496067	2.432337053553
H	-3.091914848027	0.282009396837	3.786299384974
C	-5.185290361889	0.286456822261	1.103344695337
H	-4.546012691302	0.085587291350	-0.943090036677
H	-5.484736659112	0.448543949043	3.234671942264
H	-6.242890981492	0.359940215895	0.858959695858
O	1.505439160269	4.021493201130	-1.694882270807
C	2.540388425726	4.677741900675	-0.969393886289
C	0.522289552375	5.011821896046	-2.002163507990
C	1.792687864854	5.605972676496	-0.023290365263
H	3.131647856840	3.910492942647	-0.462459678091
H	3.181171881041	5.240032497180	-1.669335767136
C	0.590025685310	6.056986352006	-0.872138313371
H	0.762529332288	5.463995931302	-2.976777736769
H	-0.442733209343	4.498805494265	-2.075421909084
H	2.409899012090	6.440750196026	0.324267376591
H	1.461769771757	5.024322746077	0.843363595161
H	0.746992047535	7.059073132195	-1.285830220362
H	-0.334585586447	6.076241715086	-0.286647126663
Na	0.564893255556	2.119177523750	-0.759438244185
O	-0.649742950386	1.976287660772	-2.691482114350
C	-0.025980497939	2.357427731901	-3.914665538704
C	-1.933620488993	1.493927645620	-3.068127831319
C	-1.127093998187	3.077388651600	-4.704977516319

H	0.850485470748	2.961419708269	-3.668398541193
H	0.301854136379	1.449845309871	-4.445477226523
C	-2.433612298891	2.503410165878	-4.106866241248
H	-1.826622682846	0.488925048198	-3.506199499677
H	-2.554812162573	1.420844994313	-2.171393092687
H	-1.035944016668	2.886137223667	-5.778859160682
H	-1.070821793892	4.160445015676	-4.553258935370
H	-3.072727996862	2.027362094093	-4.856898789132
H	-3.018508681230	3.291731500664	-3.620540072485
O	-0.845321243224	3.583691854533	0.381328897790
C	-0.803059367962	4.098647364258	1.711524016330
C	-2.187183584523	3.762551467971	-0.068738339609
C	-2.095702065516	3.608540378868	2.351152580938
H	0.104854206405	3.726942601379	2.190508203785
H	-0.775990224104	5.201177386887	1.670889309004
C	-3.086743981822	3.588338550150	1.169918395585
H	-2.291574744261	4.774112430894	-0.494513035819
H	-2.370957842640	3.028437134582	-0.859096699496
H	-2.419780652644	4.256859759082	3.171499974325
H	-1.946682278803	2.598024600205	2.745680068717
H	-3.814886802861	4.404020815949	1.232951889590
H	-3.640832703975	2.644749350195	1.134895996231
O	2.154119208474	1.088890526061	-2.004212269502
C	3.516607284810	1.488961881503	-2.156208838549
C	1.950381888894	-0.232811385357	-2.513031374036
C	4.203013764445	0.363620378561	-2.930665863372
H	3.544827836049	2.454286890986	-2.676487258115
H	3.953048986673	1.621650964071	-1.154582314498
C	3.339934745382	-0.849852981821	-2.579135813530
H	1.254866336824	-0.737552116698	-1.834629467262
H	1.500377310368	-0.168992173667	-3.515999028464
H	5.256329475629	0.248886062202	-2.654210577922
H	4.153201002041	0.559417260963	-4.009159351048
H	3.621423052648	-1.252284453628	-1.597664193772
H	3.406972140269	-1.658669937338	-3.313975150839

Table S28. Atomic coordinates and single point energies for *tetrakis*-THF-solvated enolate **4g** with chelation to the *exo* sulfonyl oxygen.



G = -2467.947533

G_{SP} = -2469.137891

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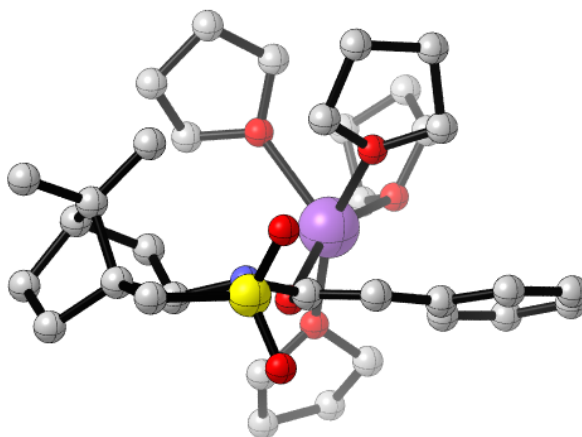
ETHF4_oh_exo_thf: optimized structure // E(RM062X) = -2469.95066693 A.U. after 14 cycles

O	-0.036051268223	0.097168752886	-0.054829989222
C	-0.022549744007	0.036220478748	1.204433626815
N	1.311693815694	0.011440410755	1.786667220808
S	2.422825122853	-0.906576370810	0.893198632107
O	1.930661326466	-2.270504027814	0.643272102758
C	3.695374096262	-0.962093596540	2.178706817738
C	3.103483744935	-0.271007402727	3.390793288364
C	1.562232599804	-0.171791321493	3.221460273061
C	1.190445999831	1.031802061170	4.126348068863
C	2.529737044401	1.373620097514	4.809231556568
C	2.889098708922	0.197990276636	5.745735223182
C	3.318956995481	-0.930997885359	4.763807026954
H	2.711792772330	-1.837724929410	4.859803972595
H	4.365549105476	-1.220850181474	4.903593635711
H	2.031892899953	-0.093122066413	6.363173858517
H	3.704078707708	0.463938171141	6.427121145390
C	3.543855133546	1.204219613445	3.652298190979
C	3.334831577422	2.171565378713	2.486024390772
H	3.890100711273	1.837197220077	1.597189936389
H	2.289460027038	2.284910796887	2.197767639444
H	3.724455961740	3.160365721547	2.762201471814

C	5.011304984675	1.319402902653	4.071676271718
H	5.667562765646	1.078317617434	3.223895550379
H	5.228806688728	2.353698528168	4.366805140657
H	5.290611934369	0.670241267539	4.905926562907
H	2.534757590781	2.353026067668	5.299762548741
H	0.798428951503	1.861023195272	3.529321796623
H	0.420218851841	0.758299095764	4.855192594398
H	1.075861510810	-1.097896447732	3.561269976525
H	4.587173531114	-0.473100318269	1.773789207289
H	3.891338681402	-2.027343940390	2.334573840899
O	2.890030093480	-0.149108983050	-0.288076427729
C	-1.093465202345	0.033304149405	2.079112120253
H	-0.908419811595	-0.061695166642	3.143946277532
C	-2.475206610211	0.222865276279	1.685443966774
C	-2.913118370026	0.389470140421	0.350083678088
C	-3.472271778035	0.263117215590	2.688804884420
C	-4.259091519152	0.590356485499	0.054395571992
H	-2.177314050655	0.351622112179	-0.446218061883
C	-4.812184917437	0.460257993957	2.384028404440
H	-3.172952687405	0.136876373982	3.729215831926
C	-5.223589495912	0.629337103628	1.060028198835
H	-4.557664013585	0.715572921509	-0.986218838430
H	-5.545270435887	0.483899729586	3.189145253782
H	-6.273107762152	0.784804328713	0.819858022486
O	2.835040129925	0.673760296649	-3.459981041021
C	4.169832025297	0.651772181956	-2.957588044161
C	2.648878314353	1.969524709360	-4.042761746900
C	4.321671602815	2.009835606085	-2.287509735366
H	4.260240136213	-0.199454297468	-2.278157169879
H	4.875667976235	0.534665459874	-3.796642544393
C	3.536774260543	2.936372239327	-3.234974035420
H	2.956604384859	1.928983427073	-5.098382082472
H	1.583403218230	2.204635898728	-3.976402083673
H	5.368070580383	2.307278803900	-2.162545906531
H	3.847973529424	1.968376864507	-1.299035885648
H	4.210539611390	3.488513050271	-3.899317870842
H	2.926824488152	3.657456365672	-2.683511864659
Na	1.183810716189	0.267437391940	-1.906585729483
O	-0.246172606615	0.498466798487	-3.718613769503
C	0.207524812009	-0.090023536678	-4.944034529267
C	-1.471395586653	-0.131707117634	-3.303673449622
C	-1.034233849851	-0.705889286797	-5.566349594687
H	0.664476989125	0.697710528493	-5.551083492972
H	0.963752567249	-0.854950411906	-4.718493201390

C	-1.747891489105	-1.233532900102	-4.323226447867
H	-1.346592856883	-0.512077260040	-2.281019733115
H	-2.263669368859	0.630368119722	-3.305626656020
H	-0.797707150595	-1.484170278938	-6.298686029811
H	-1.635529385570	0.068517185309	-6.059834886958
H	-1.276266716819	-2.169608549409	-4.002277671236
H	-2.818820219663	-1.409045481791	-4.464885891539
O	0.911779273821	2.545213623905	-1.621282159962
C	1.371914469670	2.892359916398	-0.304351892877
C	-0.484337900642	2.849638962421	-1.744450941620
C	0.144658798780	3.379640461780	0.463663975044
H	1.832150077229	2.006800471654	0.144007157202
H	2.129019037063	3.685357577143	-0.405466818185
C	-0.760080135730	3.881742905225	-0.663107339349
H	-0.666423903781	3.199497073640	-2.765724642584
H	-1.067671243155	1.936407497549	-1.562363837915
H	0.393728075675	4.151212232351	1.199715308531
H	-0.336837330351	2.541068972462	0.981809218263
H	-0.444863774725	4.878835925271	-0.997716070163
H	-1.817892909927	3.923051081146	-0.384031728912
O	0.790254156751	-1.953628590666	-2.305816448144
C	1.984163231552	-2.668654543993	-2.633335760176
C	-0.085043347416	-2.795971013397	-1.531342037189
C	1.565316606637	-4.129492403593	-2.639010719607
H	2.343865576327	-2.296824779837	-3.599447270712
H	2.747267505838	-2.479393313047	-1.863786285497
C	0.595624066178	-4.164121737688	-1.455095133712
H	-0.237581296047	-2.334098733576	-0.551464774512
H	-1.046268646132	-2.849842683292	-2.060184850507
H	2.413049953753	-4.813272450893	-2.528505075273
H	1.045733391531	-4.366647152225	-3.576819304566
H	1.153549272827	-4.248281195751	-0.517246034483
H	-0.125172480423	-4.986149877474	-1.511395924521

Table S29. Atomic coordinates and single point energies for *tetrakis*-THF-solvated enolate **4g** with the enolate oriented *anti* to the sultam ring.



G = -2467.932702

G_{SP} = -2469.126474

98

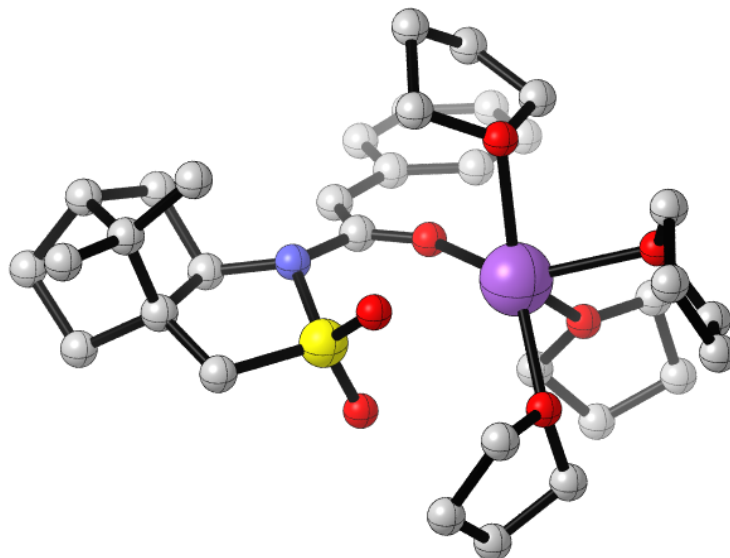
ETHF4_tbp_pendC_thf: optimized structure // E(RM062X) = -2469.93697613 A.U. after 14 cycles

O	0.194695919695	1.133496745171	0.151522296920
C	-0.084209055519	0.657281864688	1.284091575592
N	1.092604765090	0.253712346596	2.037962936882
S	1.046226574419	0.007808057331	3.713149106831
O	0.415673452319	1.131591574907	4.421723948868
C	2.838410709110	0.092422132942	3.967230061912
C	3.463764598169	0.251095905376	2.598835721246
C	2.392311843999	0.785602209649	1.607555964874
C	2.908373867819	0.288223556233	0.235074392213
C	4.296048967519	-0.280785503102	0.581469918309
C	5.184576910799	0.898053997870	1.044768408028
C	4.650874843284	1.220049384598	2.471087670031
H	4.323516230062	2.259364637324	2.583680345084
H	5.402427814196	1.025184944625	3.243660217187
H	5.088352476195	1.752609010230	0.365046773660
H	6.243765690020	0.620953677010	1.068080238504
C	4.014224685989	-1.034632940091	1.904305797667
C	3.014355504173	-2.185845100314	1.780520014331
H	2.821912536809	-2.631349389153	2.766355307574
H	2.050581035426	-1.885704143936	1.367781967141
H	3.441375460744	-2.974391530408	1.144691406494

C	5.264460156674	-1.597091919615	2.584491677307
H	5.034153928962	-1.909594480928	3.612536603786
H	5.606434113801	-2.488693244793	2.043338039435
H	6.102077209665	-0.895237846114	2.626720346360
H	4.745893980476	-0.884164759483	-0.215530640922
H	2.230224472386	-0.467481282250	-0.174187419924
H	2.954467684767	1.110889216140	-0.485435195332
H	2.354056640768	1.883181151967	1.634936733406
H	3.130976769937	-0.820002476064	4.497125380698
H	2.989489258803	0.962458915538	4.613758282231
O	0.517825469488	-1.335069131858	3.995274059490
C	-1.336176112185	0.436165885059	1.838001379705
H	-1.404269651632	-0.019284872492	2.822341881938
C	-2.585541459761	0.681997556545	1.161885690255
C	-2.721318078626	1.337737370584	-0.087850243692
C	-3.788159481712	0.224169006130	1.758569066120
C	-3.960277003218	1.457369237789	-0.712975391360
H	-1.841685720089	1.779938054579	-0.547656813409
C	-5.018451625859	0.352320956436	1.131228605191
H	-3.732257998898	-0.263827401088	2.731863158638
C	-5.121182089157	0.956480290908	-0.125524181906
H	-4.016721570794	1.959803028888	-1.678656744370
H	-5.911247920069	-0.028218397460	1.626188282993
H	-6.084175410344	1.050324585519	-0.622610571558
Na	-0.518659025044	0.237036037685	-1.788990185036
O	-0.397143366492	2.410063900497	-2.493932841443
C	-1.503210937831	3.214590187878	-2.891744271716
C	0.570031522900	3.316177790418	-1.959725529435
C	-0.855686988417	4.395584804301	-3.605916324282
H	-2.163401660406	2.600818496383	-3.510543954084
H	-2.053789747811	3.549028531785	-1.997199413013
C	0.456801338693	4.591631873921	-2.817067929016
H	0.333175279874	3.504042866079	-0.904679993519
H	1.546637734777	2.827752510905	-2.015349997421
H	-1.495384581191	5.283183123491	-3.602611060373
H	-0.646947228274	4.128864300100	-4.648208008845
H	0.418736047342	5.481002315734	-2.180290522944
H	1.312402058003	4.702289559891	-3.490132488212
O	0.914833222948	-1.281950423202	-2.811734051465
C	0.722238558243	-2.674816401371	-3.067948802576
C	2.288729441883	-1.020701930409	-3.092988111560
C	2.026769672880	-3.368096913523	-2.637156316655
H	-0.161355808646	-2.994090976425	-2.509269507882
H	0.538626776819	-2.819697052323	-4.143338830559

C	3.031154823793	-2.206719710601	-2.484484291524
H	2.435155705028	-0.974523274337	-4.184248378135
H	2.547336648308	-0.051293036499	-2.656268078934
H	2.346618137788	-4.092846450480	-3.392205524435
H	1.899827320259	-3.907312456376	-1.692348205070
H	3.985649972885	-2.395669436975	-2.985361154159
H	3.235342430598	-2.014470752308	-1.425582523616
O	-1.196218942384	-1.643316376534	-0.722585299937
C	-0.221300266013	-2.377202776389	0.017243099022
C	-2.447364058032	-2.237586608773	-0.392737686478
C	-0.711198065753	-3.839946567891	0.012073674443
H	0.746832562822	-2.222566928724	-0.472099348945
H	-0.177179401543	-1.975642119922	1.039604037702
C	-2.168423367174	-3.734436245151	-0.488790792639
H	-2.724712912292	-1.951723498358	0.632091792651
H	-3.203649271952	-1.859183476689	-1.088284822733
H	-0.657438937116	-4.264264457972	1.019684285835
H	-0.104929816201	-4.471193851932	-0.646922891014
H	-2.869666087445	-4.325756135088	0.107978243686
H	-2.247715199674	-4.064450096151	-1.531918762240
O	-1.823868247763	0.087907952875	-3.677455647243
C	-2.372683181696	-1.224599608260	-3.883486190632
C	-1.257476223322	0.566844951630	-4.901071836124
C	-1.975989187154	-1.645542607323	-5.304234464504
H	-1.946461337138	-1.881614486472	-3.115792546017
H	-3.460326793190	-1.183178285527	-3.746072059849
C	-0.834563944801	-0.685258359212	-5.648844387790
H	-2.020234336093	1.125892454148	-5.466252225173
H	-0.435543374458	1.242019097068	-4.642950523431
H	-2.813795303637	-1.492472163570	-5.994732902390
H	-1.687273595030	-2.700416965417	-5.356233433157
H	-0.724973188487	-0.516277840710	-6.724696371402
H	0.119765269479	-1.045287471850	-5.247145924525

Table S30. Atomic coordinates and single point energies for *tetrakis*-THF-solvated enolate **4g** with the enolate oriented *syn* to the sultam ring.



G = -2467.94169

G_{SP} = -2469.131767

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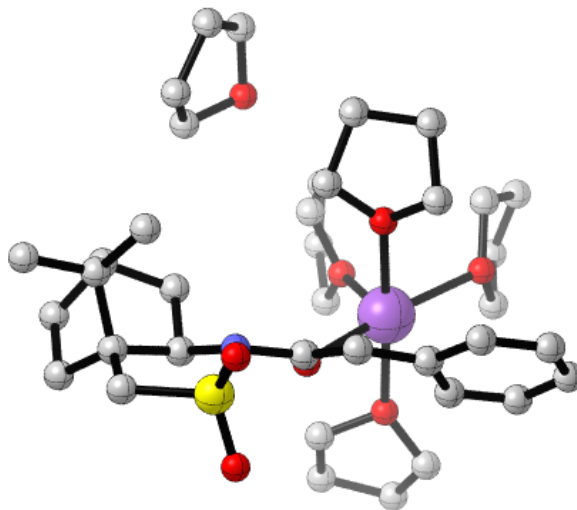
ETHF4_tbp_pendS_thf: optimized structure // E(RM062X) = -2469.94533870 A.U. after 14 cycles

O	-0.561366810003	0.027335497703	-0.001012480402
C	-0.442197035449	0.084994974415	1.248526720472
N	0.934051095312	0.147553790899	1.702357271300
S	1.998665977308	-0.704940281126	0.694971085450
O	1.551683487575	-2.089559763684	0.464649361926
C	3.380885858581	-0.718133747139	1.864344620128
C	2.901114444871	0.015999358040	3.100032543154
C	1.347370124883	0.044564518067	3.103392610387
C	1.025394225358	1.278538850493	3.986790266764
C	2.415638008580	1.708071288036	4.495539359499
C	2.931051463589	0.597846025611	5.439017630356
C	3.300859617566	-0.561845618413	4.468523798994
H	2.752046688544	-1.486867398457	4.676034064294
H	4.369098121928	-0.800076337263	4.500366999085
H	2.162160926391	0.303939876713	6.162425461483
H	3.803333513928	0.931428884433	6.010839631937
C	3.299900233540	1.519769991754	3.239053221043
C	2.920585522490	2.417199194854	2.058924758187
H	3.413093758120	2.075706656315	1.137326467294
H	1.848423097390	2.451843868914	1.861916284263
H	3.267526463808	3.439850984935	2.257973797430

C	4.797930074991	1.716644852488	3.484991620604
H	5.368761142790	1.452421353887	2.584025195989
H	4.998577781684	2.774462101295	3.697413672022
H	5.196267810232	1.130499244813	4.317656470762
H	2.431544535637	2.711016698928	4.935788731158
H	0.535845215270	2.060038377854	3.397714369954
H	0.352951957707	1.015178728453	4.810148839987
H	0.941455671292	-0.881193969846	3.537567730521
H	4.235059531780	-0.249758349968	1.364579357708
H	3.587822258774	-1.777776899652	2.043908486422
O	2.318778940398	0.087230910757	-0.509041628693
C	-1.443899426110	0.117480659014	2.205178604780
H	-1.175047382750	0.154337955377	3.256425084790
C	-2.860276555146	0.103804381193	1.897528248097
C	-3.399237388193	0.030326020137	0.588374467745
C	-3.791723672069	0.162288141332	2.961379306314
C	-4.775429174277	0.021874069491	0.378292074642
H	-2.714932765914	-0.020838928137	-0.254918450065
C	-5.162684043367	0.150643169963	2.740700126386
H	-3.415275084324	0.217810841879	3.982816700925
C	-5.673877694151	0.081422178098	1.443377743432
H	-5.152945690197	-0.033690072345	-0.642720971947
H	-5.840824261403	0.196908291898	3.591776471045
H	-6.747448404540	0.073555875286	1.268089945399
Na	0.360129119692	-0.089177629357	-2.030583048542
O	0.063642084557	2.201874234355	-1.914522331865
C	-1.371476104340	2.296450861024	-1.871741243243
C	0.630923036583	2.844519359465	-0.763183531037
C	-1.712180740125	2.972514228588	-0.546873078687
H	-1.697568802627	2.892366360875	-2.736201496115
H	-1.799578076454	1.288873012975	-1.955801225228
C	-0.450685007431	3.788972491186	-0.263110484272
H	0.873108152663	2.079006296796	-0.017619369609
H	1.551703918067	3.347207887023	-1.080827955014
H	-1.847443177417	2.214429698487	0.233200356591
H	-2.622092762758	3.578266179438	-0.612209345106
H	-0.329817537397	4.041836137511	0.795734218875
H	-0.448676616814	4.719265220586	-0.846397073685
O	1.763314081259	-1.621373891158	-3.011157429035
C	1.496092634970	-3.015156375185	-3.127283348298
C	3.182835400424	-1.509649767186	-2.967932238973
C	2.489888644617	-3.691283662183	-2.178023777472
H	0.444239335559	-3.176159752663	-2.877237885936
H	1.668398719254	-3.328115986122	-4.171220602344

C	3.649300585140	-2.673676930646	-2.086531222748
H	3.578706794849	-1.606393684047	-3.992796739823
H	3.431629220368	-0.524055835279	-2.568738658705
H	2.808523515309	-4.665483188622	-2.562056750730
H	2.035112403019	-3.831391794403	-1.193311044195
H	4.601959162813	-3.082205313703	-2.438718487643
H	3.782931615647	-2.340154840432	-1.052171560478
O	-1.358424015851	-1.594459322600	-2.192630575016
C	-1.404387959628	-2.568823274190	-1.149594384377
C	-2.614678337353	-1.684428155932	-2.846994684266
C	-2.102948503807	-3.784940658913	-1.781201758041
H	-0.379766966713	-2.738956958814	-0.803031705795
H	-1.984060952823	-2.162580211713	-0.308490368838
C	-2.851864381999	-3.188730406720	-2.996836260599
H	-3.390433796115	-1.225972680571	-2.211461559774
H	-2.551426528951	-1.129674255468	-3.787315050680
H	-2.782390983128	-4.259535157329	-1.066148799536
H	-1.376834514971	-4.541225159521	-2.099005745215
H	-3.917982770861	-3.436142021391	-3.005939211781
H	-2.415567311894	-3.546336478961	-3.936632325921
O	-0.340044559838	0.328272901116	-4.245957192958
C	-0.257874423212	-0.807372323849	-5.109439969970
C	0.357471617861	1.378782046120	-4.911137116354
C	1.087580433217	-0.690753535918	-5.854049698178
H	-0.343381231930	-1.699117763597	-4.482763716860
H	-1.101829955449	-0.778760136438	-5.815671459093
C	1.612064431132	0.697248098046	-5.443359959218
H	-0.262876090545	1.767359498504	-5.735916822680
H	0.535912610656	2.170918626790	-4.179978943781
H	0.934442108039	-0.754310314900	-6.936883297871
H	1.780172776767	-1.486137580941	-5.561989997089
H	2.072886181428	1.246596516172	-6.270618551790
H	2.348016240960	0.606197834056	-4.635297360785

Table S31. Atomic coordinates and single point energies for *penta*-THF-solvated enolate **4g** with the enolate oriented *anti* to the sultam ring. No stable minimum could be found for a hexa-coordinate sodium. The fifth THF is always ejected from from the primary solvation sphere.



G = -2700.129373

G_{SP} = -2701.462736

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ETHF5_oh_pendC_thf: optimized structure // E(RM062X) = -2702.38739140 A.U. after 14 cycles

O	-0.265669268218	0.233812601006	0.107554821463
C	-0.063386416844	0.197937950693	1.348555494831
N	1.338550601210	0.315389905935	1.739190434012
S	1.741512417191	1.365171536042	3.011997292356
O	1.112297069968	2.684825455530	2.844995896682
C	3.500256214398	1.498812259391	2.588065325931
C	3.701052704510	0.665450291333	1.339852706344
C	2.325770416375	0.438757405634	0.661271541633
C	2.548978861235	-0.849999203312	-0.163601676910
C	4.053900762237	-1.122521831942	0.025218620793
C	4.822885925174	0.010363411042	-0.692004076015
C	4.610014148492	1.239246513270	0.239515638341
H	4.124923208132	2.081528191114	-0.265975985133
H	5.553960253645	1.605953875922	0.656510504884
H	4.425943754103	0.180110683123	-1.699437158245
H	5.886105503563	-0.229520420755	-0.798590194277
C	4.264911397919	-0.779445417012	1.521543016210

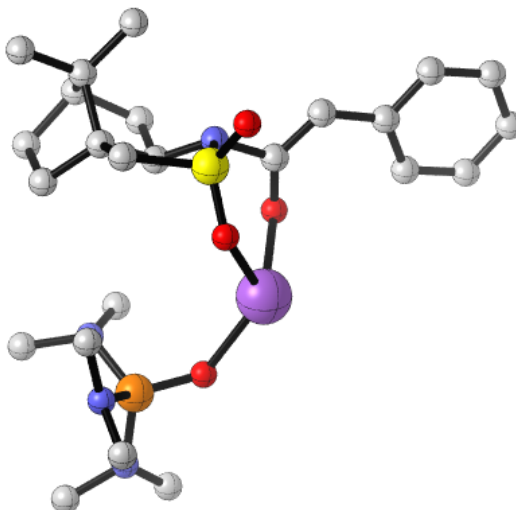
C	3.492662973002	-1.668710271747	2.499798276635
H	3.526202236792	-1.240630426360	3.511844482671
H	2.439706575059	-1.802634610702	2.243309577975
H	3.971221771927	-2.655852707105	2.547988730960
C	5.728372783480	-0.797165689039	1.969917307639
H	5.816514113473	-0.411085199514	2.994822847946
H	6.097603682276	-1.830848705739	1.980195368606
H	6.398573436186	-0.212276437792	1.333916649770
H	4.368532308850	-2.129604964096	-0.273244898823
H	1.928263928278	-1.658832924876	0.229688137171
H	2.276271636123	-0.703266424329	-1.214680176290
H	2.057936086723	1.283774196686	0.014052827380
H	4.070906368427	1.156199828700	3.457491610314
H	3.673485852253	2.567347507744	2.427499200369
O	1.550495995426	0.687754588726	4.301891028577
C	-0.975028700235	0.023177001284	2.380433185576
H	-0.587440213847	-0.141108607245	3.382810583931
C	-2.408238725342	0.021833305848	2.210202961450
C	-3.072798372590	0.477885488076	1.045370267146
C	-3.237762408604	-0.446090357144	3.259272028162
C	-4.457354562467	0.399007973961	0.919682586971
H	-2.488663792870	0.926138700629	0.243840943936
C	-4.617297356408	-0.514645645541	3.129714077515
H	-2.768891613009	-0.776758863146	4.186239737509
C	-5.247219265716	-0.110500133539	1.948797744789
H	-4.925740432571	0.753173994439	0.001129471145
H	-5.212434665806	-0.893431649662	3.959894994922
H	-6.327925613860	-0.175118030128	1.843749370901
Na	-1.843232071559	-1.049779972283	-0.904202453272
O	-2.248983824783	0.794932655085	-2.193586788585
C	-3.282379619050	1.736962772581	-2.461893418541
C	-1.031427489784	1.471108544735	-2.509584727693
C	-2.873497164112	2.386495083028	-3.787839210350
H	-4.234956554108	1.200534416188	-2.499045115047
H	-3.318743815299	2.477545071060	-1.647569818788
C	-1.334604771400	2.230285225521	-3.806550523662
H	-0.779399686471	2.153127788456	-1.685697087449
H	-0.242552423088	0.718125032247	-2.584092116340
H	-3.195625161547	3.430829376048	-3.839257876514
H	-3.329492244026	1.853283515457	-4.628765295647
H	-0.815531331219	3.193394089500	-3.830005589164
H	-1.011360481094	1.655582490980	-4.680977341270
O	1.619598443558	-5.095985987823	-1.526803063330
C	1.921522827673	-6.398045003115	-1.038379100383

C	2.750154579632	-4.298549804242	-1.206091418946
C	2.694249819967	-6.189739505865	0.277770522940
H	0.978509201233	-6.940730855568	-0.923306676891
H	2.542906488759	-6.928202631194	-1.776903103978
C	3.120965601581	-4.706292545643	0.220005339233
H	3.573049872428	-4.518198902985	-1.907451409013
H	2.466636178941	-3.247425992556	-1.315481233105
H	3.557139675400	-6.861081703574	0.333467600191
H	2.063258547514	-6.387277964331	1.149440983651
H	4.186544824289	-4.563387368949	0.427187977208
H	2.554652387829	-4.106988085226	0.944038039008
O	-1.353253988402	-2.771205955629	0.453597618062
C	-0.081700279516	-3.300691315478	0.808620477170
C	-2.237859279277	-3.237095669926	1.468296110452
C	-0.367718354189	-4.735800067237	1.280780155276
H	0.564133291614	-3.254128543008	-0.071996591847
H	0.344555789978	-2.683544034105	1.616724895078
C	-1.877154439283	-4.714069955362	1.620179014089
H	-2.033472017933	-2.684765334431	2.396932274639
H	-3.264506180377	-3.029965505881	1.148791356224
H	0.250777912864	-4.998468884812	2.145468353850
H	-0.151640295685	-5.449736430588	0.479283667346
H	-2.093638408619	-5.083734771742	2.627018902878
H	-2.443681935381	-5.321274963883	0.905431290899
O	-3.723154642333	-2.302080926386	-1.446291642524
C	-3.595566554968	-3.727260900517	-1.544764002836
C	-4.236745332196	-1.769482305626	-2.678440560994
C	-4.407035232824	-4.128260995702	-2.768725962419
H	-2.533208350094	-3.981662469783	-1.662532741842
H	-3.966194920013	-4.173083714300	-0.615875195685
C	-4.206325714689	-2.917915432691	-3.677663696111
H	-5.261689620219	-1.412610492577	-2.502526387210
H	-3.605518944279	-0.925908391634	-2.978896040665
H	-5.466812031358	-4.234778948449	-2.504629825269
H	-4.063564293017	-5.070626778085	-3.207399349999
H	-4.970848665029	-2.817097032404	-4.454448068111
H	-3.221579549351	-2.968339375578	-4.157055379566
O	-1.041354310449	-1.942804874098	-2.850938004799
C	-0.944535864717	-1.462275063497	-4.190812149201
C	-0.211287826211	-3.101567656926	-2.773323005426
C	-0.719338685055	-2.706944165910	-5.076731674263
H	-1.864490357635	-0.910139036450	-4.411317949434
H	-0.092341640989	-0.770812046440	-4.268648757723
C	-0.504419751122	-3.850097607786	-4.065364464706

H	0.845530669334	-2.794832597206	-2.723642256646
H	-0.466567621991	-3.647164632700	-1.862073043999
H	0.161378097760	-2.567092208123	-5.711898266699
H	-1.572159067326	-2.899744609275	-5.735198732054
H	0.308821176615	-4.526216793770	-4.344362136174
H	-1.418328505401	-4.445999389440	-3.946699403190

HMPA-solvated monomers

Table S32. Atomic coordinates and single point energies for HMPA-solvated enolate **4g** with chelation to the *endo* sulfonyl oxygen.



G = -2358.914288

G_{SP} = -2359.901354

75

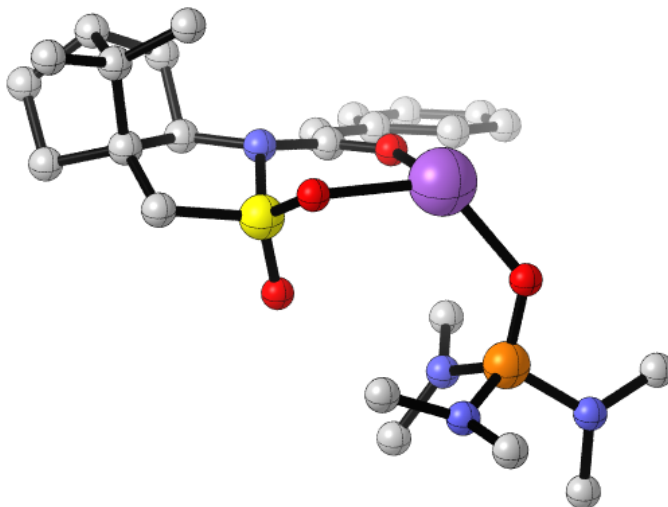
EHMPA1_endo_thf: optimized structure // E(RM062X) = -2360.49831418 A.U. after 12 cycles

O	-0.184645393671	-0.485822716618	0.153811545029
C	-0.130968590213	-0.243870821259	1.396295225687
N	1.227008193968	-0.208855765396	1.995269240761
S	1.952600212206	1.306121775706	1.959438469920
O	1.890320475167	1.875217624796	0.581747136898
C	3.639149968395	0.711582468024	2.250363734423
C	3.560767691094	-0.799162212982	2.095853004214
C	2.202885275106	-1.162407945587	1.446669748165
C	1.971558107384	-2.626328597403	1.881678781133
C	3.278606543942	-2.964516224566	2.631060614443
C	4.417419105334	-2.998050244170	1.588347837607
C	4.618826516512	-1.497246658357	1.222345046920
H	4.428021805336	-1.290389793641	0.163166940957
H	5.630570732258	-1.147881012616	1.456425528232
H	4.143817369115	-3.608550522701	0.719614633107
H	5.331062590491	-3.429891865123	2.010324882021
C	3.574305962948	-1.653677434207	3.403296558397
C	2.521843559011	-1.291374037916	4.454084469330

H	2.642338170388	-0.248219994770	4.779670739882
H	1.492628543531	-1.409202594065	4.112275606989
H	2.667999815512	-1.925464575441	5.338528358649
C	4.933566425211	-1.625495593688	4.107195792977
H	5.104272682424	-0.638299927688	4.558603804051
H	4.943662614881	-2.360380788124	4.922277247513
H	5.781534163445	-1.843274881279	3.451907073812
H	3.213295737880	-3.866949915154	3.248519638458
H	1.087771136589	-2.703586985982	2.523796867733
H	1.811049194785	-3.280374840826	1.017855155734
H	2.252041494206	-1.063053056500	0.353018853928
H	3.928599827221	1.045194345650	3.252408872100
H	4.260630914887	1.207843935677	1.498671094359
O	1.447376938851	2.165060204407	3.030735839708
C	-1.131278366299	0.008257567553	2.299779195269
H	-0.834541153473	0.179199930458	3.331168233285
O	1.926431343037	0.467038787366	-2.881207003544
P	3.374912745363	0.151131195379	-3.158092435888
N	3.583731578699	-0.036858829634	-4.799850474314
N	4.536754288072	1.277094831265	-2.756978307278
N	3.829999569058	-1.184160362996	-2.242893321182
C	4.891773398440	-0.215244095762	-5.413832421980
C	2.466217308307	-0.449515719223	-5.638410206632
C	4.864795994836	1.488018381637	-1.346718281504
C	4.587747107455	2.517150637743	-3.531246094049
C	5.173121788190	-1.728230508561	-2.422063893328
C	2.822895637613	-2.225306466737	-2.047268022339
H	5.074602101412	-1.268234131559	-5.674455764437
H	4.944045150298	0.379876041298	-6.336172499586
H	5.681493118920	0.125865037992	-4.738944682441
H	1.523639959021	-0.236387966724	-5.129931854466
H	2.493175022269	0.113770167649	-6.580498743393
H	2.516057789668	-1.522940391895	-5.874191591025
H	5.840335019011	1.985682193659	-1.290192224786
H	4.116237159277	2.119074533417	-0.843018785923
H	4.931772067457	0.530784610034	-0.824357912432
H	5.609851131119	2.912735886875	-3.498881200281
H	4.317046441745	2.329060874292	-4.573052295297
H	3.905881749776	3.275769477271	-3.119038809097
H	5.425492241338	-2.342034989147	-1.547393326885
H	5.245029573481	-2.365191391497	-3.317954947042
H	5.906000525670	-0.919176122695	-2.499339033290
H	3.114610651161	-2.830703732680	-1.179283164994
H	1.845942231643	-1.777563507595	-1.847382435706

H	2.742113158652	-2.891469105714	-2.921968205482
C	-2.547655676637	0.098460144925	1.984628864159
C	-3.452624111362	0.455143201282	3.007826551785
C	-3.088578382689	-0.153332189491	0.704808730812
C	-4.816738216292	0.561528863263	2.769462972358
H	-3.063463150584	0.653420489358	4.006075186897
C	-4.457595114332	-0.043901049600	0.473938674049
H	-2.417231459200	-0.443915721299	-0.097538984418
C	-5.334163611053	0.314200092926	1.496808867538
H	-5.483243819140	0.840735428816	3.584049210568
H	-4.844971675622	-0.245861086175	-0.523804711826
H	-6.402374782319	0.396858757726	1.308022518713
Na	0.723492710086	1.014005388280	-1.170720548612

Table S33. Atomic coordinates and single point energies for HMPA -solvated enolate **4g** with chelation to the *exo* sulfonyl oxygen.



G = -2358.91659

G_{SP} = -2359.902472

75

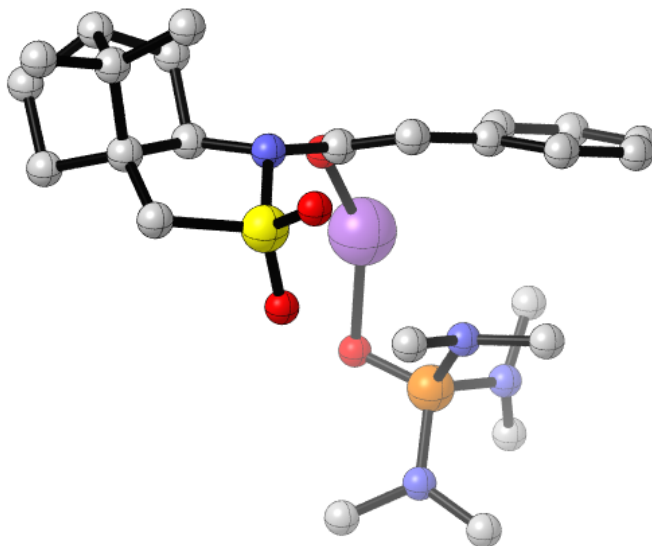
EHMPA1_exo_thf: optimized structure // E(RM062X) = -2360.49848286 A.U. after 12 cycles

O	0.010374211561	0.139364766805	0.055543563801
C	0.016970872797	0.130376912512	1.319664426938
N	1.348560871793	0.156191304240	1.907144924729
S	2.443820872547	-0.895620690421	1.172555060195
O	1.921623032812	-2.271237683494	1.111302295608
C	3.715109625318	-0.772916008378	2.453169751437
C	3.141391961130	0.134130519984	3.524131756988
C	1.600181671212	0.207962356507	3.350289917319
C	1.233190333382	1.553078482970	4.025548049637
C	2.577742295941	2.007215720898	4.627752563818
C	2.939158860476	1.016101382811	5.757526118344
C	3.366816029914	-0.269856994565	4.991171676911
H	2.762918075875	-1.145889786475	5.252012479456
H	4.415305778078	-0.527747094954	5.173429877686
H	2.082310112789	0.839125265171	6.417331412019
H	3.754483991171	1.397299476809	6.381161789356
C	3.585406397196	1.631501411034	3.513360818332
C	3.381844692793	2.378195156555	2.192731382135
H	4.011863847967	1.941616558568	1.404966263681
H	2.353206498313	2.372574345318	1.829418214902

H	3.697962510979	3.421952515060	2.320369267069
C	5.054251985190	1.815944240778	3.903552527453
H	5.708938164545	1.391267631523	3.129908439098
H	5.284110863020	2.886784328513	3.971930890943
H	5.324201165303	1.357673538286	4.858742037346
H	2.588391742880	3.058272774666	4.935825203536
H	0.845078257959	2.261885704467	3.287837074775
H	0.464140718846	1.419599058047	4.793625342697
H	1.115369865119	-0.646714501607	3.844566072608
H	4.622717814548	-0.391639756304	1.973998557836
H	3.874029405944	-1.801374699947	2.792244262952
O	2.924162145354	-0.335094347134	-0.112975423068
C	-1.053794572211	0.103568072642	2.187836137862
H	-0.862676946546	0.069039919318	3.255998268017
O	0.772139186271	-1.707171718351	-3.090342581667
P	0.868674702594	-3.193835615896	-2.836340921294
N	0.047010434848	-4.000687229563	-4.054528554579
N	2.377948746125	-3.902876670240	-2.863447858199
N	0.324889717770	-3.559599483859	-1.308798142135
C	-0.210224422660	-5.421214061342	-3.854312396928
C	-1.024691309843	-3.301416302821	-4.753737413211
C	3.326112146938	-3.505482361531	-1.822995138088
C	3.026090456860	-4.209082644218	-4.134258470613
C	0.651169704839	-4.772116477322	-0.575702927416
C	-0.782896376349	-2.808843948148	-0.728107885320
H	-1.089906916207	-5.595475678383	-3.213304731143
H	-0.391877645773	-5.893519361824	-4.827590897508
H	0.660459274518	-5.904404833929	-3.398411546853
H	-0.746122436960	-2.255995526488	-4.900425292053
H	-1.171683193033	-3.771368174775	-5.733923973281
H	-1.977219306189	-3.345349125649	-4.201595744805
H	3.991856588071	-4.350097996734	-1.602355722454
H	3.943306126425	-2.655617228182	-2.153027971616
H	2.799345952263	-3.222305421485	-0.906073517450
H	3.760755657296	-5.006447446924	-3.968599223149
H	2.289874982010	-4.553298313326	-4.863683623441
H	3.551739263852	-3.333149669940	-4.544370191120
H	0.978190765299	-4.497955963325	0.436824419474
H	-0.227418312367	-5.430312241806	-0.496075553969
H	1.456349537700	-5.320205010420	-1.070839451927
H	-0.522810652304	-2.506616184407	0.295013639400
H	-0.973635398827	-1.901688317045	-1.305450913903
H	-1.698098383161	-3.420827922576	-0.706787329693
C	-2.449959258463	0.122951647323	1.790689868271

C	-3.442066552047	0.105504457913	2.797952078168
C	-2.902673598453	0.149745005012	0.451455272368
C	-4.796663422020	0.111735031893	2.492757824459
H	-3.128539768321	0.084733614419	3.841572666767
C	-4.263228964496	0.157850467886	0.154684756906
H	-2.167394918376	0.164781645098	-0.346387046177
C	-5.224440489565	0.138198580792	1.164148334970
H	-5.527079436337	0.096862795918	3.300405139213
H	-4.576129089182	0.179345101022	-0.888546962320
H	-6.285113142346	0.143145629083	0.922561545266
Na	1.265938368842	-0.118403399194	-1.675304913205

Table S34. Atomic coordinates and single point energies for HMPA -solvated enolate **4g** with the enolate oriented *anti* to the sultam ring.



G = -2358.906155

G_{SP} = -2359.893385

75

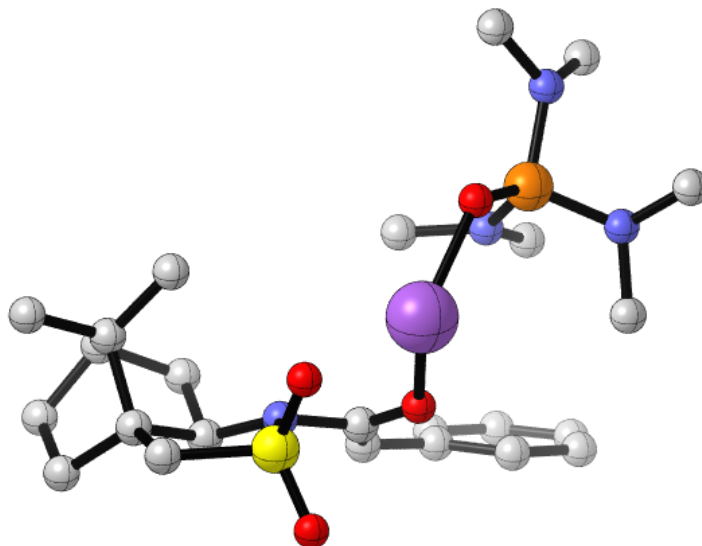
EHMPA1_pendC_thf: optimized structure // E(RM062X) = -2360.48950518 A.U. after 12 cycles

O	0.445468777383	-0.567320917949	-0.157658624521
C	0.389471674738	-0.166180359180	1.042869798470
N	1.663146159228	-0.150147928911	1.749871416186
S	2.219369182119	1.335548867567	2.337785404050
O	2.171010775497	2.371815950634	1.289647297444
C	3.936733200928	0.796297519385	2.568897386361
C	4.002343172633	-0.628896919456	2.054715941698
C	2.776266663942	-0.886108084074	1.144946787310
C	2.614912065670	-2.423842112869	1.184886974262
C	3.842608178911	-2.870557755007	2.005006090083
C	5.098584593236	-2.578163057678	1.152727316364
C	5.227382833466	-1.027579425407	1.213900130438
H	5.190782907749	-0.555600145446	0.225732470103
H	6.159508304201	-0.711215790176	1.693863319380
H	4.975069076992	-2.944006724138	0.127002000094
H	5.986881501141	-3.067551179608	1.565989495901
C	3.923785879811	-1.782476083156	3.105605318661
C	2.720820263606	-1.744694866616	4.052409352215
H	2.739240188773	-0.829164654957	4.660290162632
H	1.753210859842	-1.780259978452	3.549546966983

H	2.783464390807	-2.595688681476	4.743675339539
C	5.174059483759	-1.866822648468	3.985288699418
H	5.225874161780	-0.995959297847	4.653500106235
H	5.118577643209	-2.760142624425	4.620478932117
H	6.112689835399	-1.915391143926	3.426463142073
H	3.781837334333	-3.902105626581	2.369293472457
H	1.669534764630	-2.700035404819	1.663197134587
H	2.612515878446	-2.851387640195	0.177169075212
H	2.953321571821	-0.523714187072	0.124181793756
H	4.170406326191	0.903779041264	3.633187423694
H	4.538880524143	1.497571531438	1.982927401500
O	1.569018912324	1.653825352814	3.615212519541
C	-0.703174456792	0.255032604367	1.770463195078
H	-0.532884040146	0.558282991505	2.800442119594
O	0.350665588795	1.901109990513	-3.568646593235
P	-0.651088406572	2.994954189729	-3.278628796234
N	-0.006098582668	4.488142810112	-3.590275028688
N	-2.096833680264	2.961508465114	-4.111311796748
N	-1.136850592267	2.793729053601	-1.670260162003
C	-0.746954283382	5.691121119654	-3.232897359906
C	1.430465088419	4.667861641591	-3.752983644104
C	-2.908309911208	1.750992417541	-3.972183092925
C	-2.151748923467	3.515962057126	-5.463313370871
C	-2.379341007808	3.368470191682	-1.150676940238
C	-0.042242305882	2.940075834980	-0.694726983237
H	-0.429897324710	6.086403307075	-2.256269961711
H	-0.572593805179	6.463642519011	-3.993062063981
H	-1.820935137722	5.480737177313	-3.199970111736
H	1.890010397346	3.715405357111	-4.025850956667
H	1.615353063972	5.394684469679	-4.554256302390
H	1.894131469330	5.039675047419	-2.827507540781
H	-3.955521582043	1.997938556463	-4.183955906795
H	-2.585041042731	0.967563528672	-4.674591805458
H	-2.856191625103	1.361753477167	-2.950161662415
H	-3.198258292646	3.735710576123	-5.703423485636
H	-1.577167507469	4.443139170051	-5.519449752465
H	-1.761535899360	2.808812983044	-6.210474288784
H	-2.658035646780	2.814551835570	-0.245906386903
H	-2.252085702671	4.429047177187	-0.883914958566
H	-3.186608727560	3.282813113831	-1.881270491460
H	-0.299673181083	2.397194951128	0.222255661513
H	0.897040372197	2.532371136205	-1.084260713821
H	0.128831091490	3.997241799219	-0.437206952384
C	-2.038273745178	0.435243970344	1.234651740198

C	-2.971917977466	1.209260301635	1.963507499517
C	-2.498144397285	-0.132407332484	0.023250320589
C	-4.264433054207	1.422861284139	1.504282036964
H	-2.657674857483	1.649021974907	2.909584390582
C	-3.795300627349	0.091540278310	-0.435410002917
H	-1.845956363051	-0.813578235516	-0.517392528727
C	-4.688839873949	0.876123779883	0.290598625358
H	-4.949194023843	2.026981783987	2.097642633986
H	-4.117879663510	-0.376538636885	-1.364834636715
H	-5.700705999430	1.045228125289	-0.071101934641
Na	-0.125460318457	0.364086718693	-2.001081702574

Table S35. Atomic coordinates and single point energies for HMPA -solvated enolate **4g** with the enolate oriented *syn* to the sultam ring.



G = -2358.893361

G_{SP} = -2359.901934

75

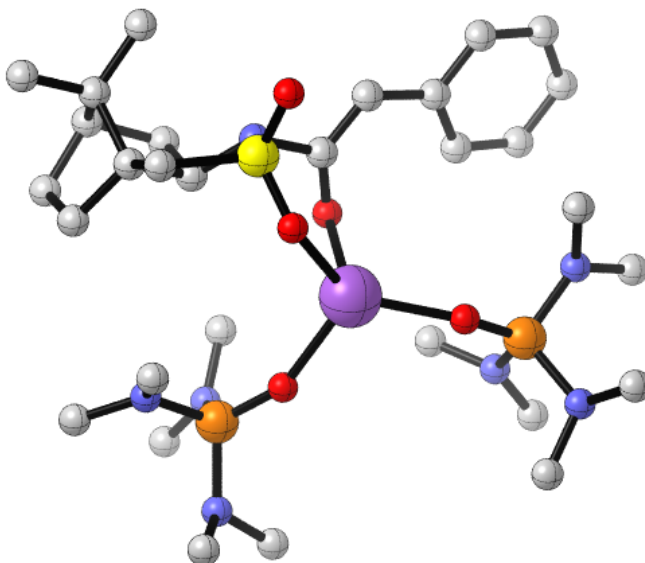
EHMPA1_pendS_thf: optimized structure // E(RM062X) = -2360.50071329 A.U. after 13 cycles

O	0.061895970812	0.460786565435	0.035246210959
C	0.044775659692	0.270894720099	1.288576593116
N	1.373073048086	0.153116420963	1.877435045938
S	2.496348211296	-0.677844827339	0.920076900936
O	2.019233437737	-1.975881197480	0.449947882415
C	3.709818526060	-0.919747174839	2.244963386614
C	3.155699718768	-0.218012013532	3.466610025511
C	1.617195947718	-0.073134307785	3.299396073942
C	1.281324716084	1.129575623981	4.220350964691
C	2.627591372135	1.421045365577	4.909367608876
C	2.950475613336	0.221187664576	5.828241245096
C	3.357209008910	-0.901633080422	4.830053118865
H	2.733912487673	-1.798545018343	4.916035986943
H	4.396533036189	-1.218546928370	4.967818369634
H	2.083406637610	-0.058867488498	6.436778512256
H	3.763448274604	0.452876712888	6.523932237118
C	3.637717336963	1.241726970658	3.749723683045
C	3.464435277015	2.239256011573	2.601370123916
H	4.112899803222	1.974814257920	1.755335841206
H	2.444245699450	2.299118141905	2.219662867433

H	3.765339301147	3.237914620982	2.944364212477
C	5.104960545862	1.313829603258	4.180680420896
H	5.767038040121	1.040074899319	3.348008442827
H	5.356480190436	2.344020065328	4.461707769076
H	5.357413983078	0.673351401126	5.029794150290
H	2.662330363924	2.391306110054	5.416371619867
H	0.918019161240	1.975275651238	3.628400168314
H	0.497336459064	0.879206665136	4.943011006147
H	1.099798599693	-0.989596152296	3.622233725605
H	4.664937427206	-0.525048716129	1.884402422603
H	3.777323494534	-2.005693144939	2.364944019774
O	3.047003019426	0.250656504902	-0.098170554661
C	-1.027996567513	0.240650632933	2.145681234913
H	-0.863437994064	0.104312481786	3.209160696010
O	0.914373471383	3.539816458293	-1.645958495675
P	-0.476446691209	4.120862895628	-1.575844904616
N	-0.386501394126	5.759087768353	-1.907800252487
N	-1.616013058459	3.580428063333	-2.666057103373
N	-1.187150988728	3.758044502362	-0.117572663928
C	-1.553970496498	6.589205601465	-1.666580307821
C	0.886945613193	6.454207660657	-1.810542358586
C	-2.051398221262	2.190760777572	-2.552751421220
C	-1.660705142290	4.092308173066	-4.027696308197
C	-2.607725624362	3.915882679288	0.166301581702
C	-0.362829840460	3.625410694913	1.075847742075
H	-1.581216373182	6.979497617221	-0.636292279101
H	-1.543895283977	7.443358524691	-2.356563811070
H	-2.470672869562	6.018987425331	-1.850337879742
H	1.699308901141	5.754404484985	-2.015480796169
H	0.915648807183	7.261085888427	-2.554365776045
H	1.038666234667	6.896545411388	-0.813192413795
H	-3.123058499791	2.120406357689	-2.781748972689
H	-1.505288435513	1.548382789962	-3.261679530001
H	-1.882427637008	1.818488665823	-1.537441242824
H	-2.690737196035	4.024288792512	-4.399869769621
H	-1.344486095206	5.137373171309	-4.051328059155
H	-1.010736546239	3.513085746708	-4.701321310645
H	-2.940705977595	3.083350562546	0.800579808777
H	-2.811001740857	4.860713591247	0.695457860366
H	-3.188513958343	3.895679703520	-0.759692143196
H	-0.728726433536	2.779337766111	1.671509873716
H	0.676097150453	3.434586484229	0.793449991009
H	-0.397628846838	4.540556936184	1.689063175809
C	-2.391921586739	0.511704013478	1.723448707778

C	-3.330361119804	0.996613832552	2.656966309116
C	-2.843107679145	0.316812042360	0.402266974466
C	-4.636747370627	1.294297963248	2.290238500094
H	-3.014471538042	1.149595207503	3.688635855510
C	-4.152523514065	0.615024017879	0.041663028542
H	-2.145799332230	-0.089364944268	-0.323936129744
C	-5.059574718978	1.114319828540	0.974222109545
H	-5.330958818868	1.673455729010	3.038170989999
H	-4.474889301408	0.442782390247	-0.984583346020
H	-6.081773647811	1.346752456275	0.684748785526
Na	1.519049371063	1.502161696782	-1.178630070490

Table S36. Atomic coordinates and single point energies for *bis*-HMPA -solvated enolate **4g** with chelation to the *endo* sulfonyl oxygen.



G = -3178.717517

G_{SP} = -3180.044957

104

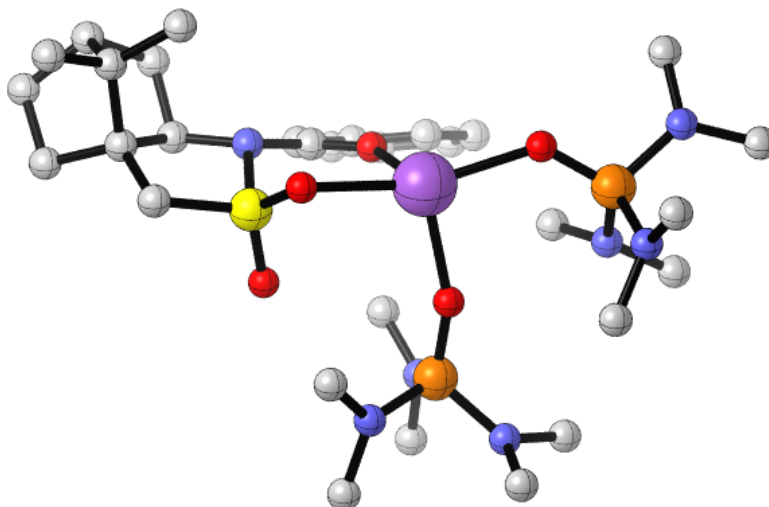
EHMPA2_endo_thf: optimized structure // E(RM062X) = -3180.89065262 A.U. after 12 cycles

O	0.021667586894	-0.037151294461	0.082896067353
C	0.058058811698	0.020209851214	1.346400580361
N	1.411239430186	-0.068209217614	1.953179486903
S	2.154923459265	1.407836533040	2.255447700837
O	2.044650208995	2.302199127899	1.071141783902
C	3.848243866720	0.758201819885	2.326353278947
C	3.744290805465	-0.694018739393	1.890565407991
C	2.367020248057	-0.909211970052	1.219663711620
C	2.114368701984	-2.424804478905	1.382124844467
C	3.436174785586	-2.918260242765	2.007614746153
C	4.539137724617	-2.763531785832	0.936957820862
C	4.766496062587	-1.224214476073	0.868114772128
H	4.556610604515	-0.814897889447	-0.126457387899
H	5.791178338733	-0.946353468074	1.140130007624
H	4.218786291661	-3.178089076108	-0.026257661421
H	5.454913718649	-3.289395332725	1.226949413673
C	3.780347341034	-1.785038447818	3.007635471966
C	2.766650095940	-1.615154711219	4.141645123423
H	2.947996628688	-0.675969223364	4.683651957157
H	1.727025223159	-1.605778254470	3.811315355779

H	2.895305260431	-2.433926647991	4.862009109473
C	5.159388014659	-1.914431873079	3.659487012572
H	5.378117268849	-1.020841196214	4.260534735641
H	5.167421422871	-2.774215081980	4.341622339849
H	5.979507403102	-2.046525604100	2.948287893646
H	3.373350302613	-3.922382769840	2.441225274297
H	1.251292880021	-2.603078070878	2.032481720428
H	1.908739183582	-2.905562093672	0.420001288724
H	2.395680810027	-0.605356852936	0.163558845530
H	4.203890930651	0.895547169472	3.352835444446
H	4.428339338333	1.386761548079	1.643568387869
O	1.703427133796	1.971890245645	3.529583443495
C	-0.955703441323	0.145335120917	2.264101876038
H	-0.674938125125	0.181042922025	3.313648816156
O	2.072795020941	1.412537873310	-2.427271734544
P	3.073498444784	0.549372287505	-3.141943924861
N	2.495452530190	-0.980753513519	-3.421492435645
N	3.510256299226	1.047408943245	-4.684283909311
N	4.478730560259	0.486698309875	-2.234029450664
C	2.996510233263	-1.892918918823	-4.439205587831
C	1.693471948352	-1.625278004436	-2.388444620725
C	4.439699312819	2.169435874933	-4.785771987470
C	2.434692828500	1.124107882623	-5.672561550928
C	5.584899078967	-0.352725325108	-2.666969989808
C	4.854080043108	1.599952473777	-1.371798215753
H	3.565409648776	-2.717341590755	-3.983193914616
H	2.150602579850	-2.326725350886	-4.990555569307
H	3.641760368394	-1.363522496150	-5.144042776029
H	1.264812405788	-0.887095490866	-1.702232218701
H	0.867169570360	-2.172425580116	-2.862297705771
H	2.296776402694	-2.345810896033	-1.813721539562
H	4.818713656690	2.214792795775	-5.813380106649
H	3.959278206025	3.132280111641	-4.550951174967
H	5.292052057215	2.024231951173	-4.117280256548
H	2.869666477331	1.076158312540	-6.678237899705
H	1.745867138934	0.282998300961	-5.550817090922
H	1.864474097788	2.061586061913	-5.580089291718
H	6.275353268273	0.175918409080	-3.343824514468
H	6.152463405554	-0.679928880186	-1.785983916749
H	5.209290540485	-1.245406903658	-3.176334812608
H	5.491691642873	2.334252195541	-1.889753835342
H	3.954804621612	2.101138091190	-1.002176104154
H	5.417623573429	1.207797838645	-0.514875299852
O	-0.981766973916	3.096020476984	-1.354118742835

P	-2.272600125172	3.055776282750	-2.125257673299
N	-3.544798922343	2.965304538527	-1.058378107454
N	-2.579540570645	4.378042670710	-3.115414314719
N	-2.319848468261	1.793363172933	-3.204703310073
C	-4.903350782471	2.811204370215	-1.544400758362
C	-3.416736880667	3.415838694471	0.319722599810
C	-1.607113431166	4.644938108948	-4.173151260128
C	-3.048148878288	5.600095171149	-2.467961382088
C	-3.110473931246	1.747240075324	-4.423417500170
C	-1.676699794430	0.531906003880	-2.860113635394
H	-5.487765726188	2.255982563446	-0.799940625860
H	-5.399892647385	3.779888750792	-1.720424009734
H	-4.912955228689	2.238398216093	-2.477798096767
H	-2.359407520342	3.464512747231	0.591791582325
H	-3.873480263883	4.408363203194	0.465510541263
H	-3.916129909449	2.696602684912	0.982669414443
H	-2.091821681760	5.217188244542	-4.973933225403
H	-0.749347956929	5.223899423347	-3.797314428471
H	-1.233325193377	3.706106307348	-4.592973764512
H	-3.472581699556	6.261548703055	-3.232638897401
H	-3.831738270894	5.372270048513	-1.740238450960
H	-2.233721372489	6.138248356684	-1.957885238942
H	-2.465031680556	1.499555597007	-5.279102593179
H	-3.892025254464	0.976027667107	-4.351340967866
H	-3.583866980979	2.714107163959	-4.608878903267
H	-0.924038568735	0.270262856697	-3.618325938884
H	-1.183289965259	0.595264726855	-1.885805486574
H	-2.420152428097	-0.277548605880	-2.813770452252
C	-2.371172732489	0.212753483746	1.939124666424
C	-3.305256539637	0.483934243225	2.962805193262
C	-2.885777304182	-0.022597662757	0.645892688210
C	-4.671603558139	0.513023246128	2.712411722533
H	-2.938623522165	0.669711178053	3.972072895214
C	-4.255550329583	0.001629157589	0.403208117544
H	-2.189758325545	-0.241881015551	-0.157130533857
C	-5.162642716339	0.269856527859	1.427630177313
H	-5.361606965909	0.724645983211	3.527983581118
H	-4.618151702029	-0.191601220751	-0.606359721273
H	-6.233123298418	0.287766783400	1.231912815553
Na	0.753412996371	1.922847444861	-0.782054844157

Table S37. Atomic coordinates and single point energies for *bis*-HMPA -solvated enolate **4g** with chelation to the *exo* sulfonyl oxygen.



G = -3178.716148

G_{SP} = -3180.041520

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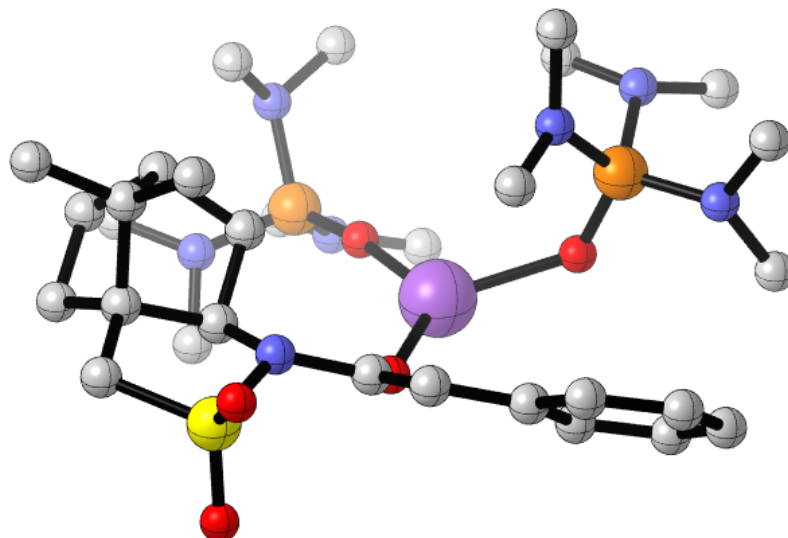
EHMPA2_exo_thf: optimized structure // E(RM062X) = -3180.88797286 A.U. after 13 cycles

O	0.195417805343	0.193400351435	0.124478397615
C	0.148971086001	0.139177772629	1.385012207681
N	1.455937654382	0.104436208455	2.027544741363
S	2.517724960231	-1.015791693259	1.333496595354
O	1.911361338934	-2.354174347570	1.272076216212
C	3.745527898139	-0.954662888746	2.662171662167
C	3.159669433384	-0.052269922847	3.731123673753
C	1.634777350854	0.101058762318	3.481403295311
C	1.294766900340	1.441934764281	4.177884614195
C	2.626486965219	1.816141352596	4.858905050271
C	2.883351703534	0.779088801205	5.976366405064
C	3.288731851609	-0.505172346218	5.195255686128
H	2.630720440421	-1.357020616611	5.399480404521
H	4.312715078925	-0.819295420473	5.423392728325
H	1.987012320283	0.626681846505	6.588136387537
H	3.683405315089	1.104052285293	6.649756415838
C	3.672084085002	1.422076149080	3.786245226157
C	3.572256959653	2.210299712044	2.477986019821
H	4.210073816994	1.755135200300	1.706951512215
H	2.562754466070	2.272992912765	2.069545717930

H	3.942403223943	3.230451975722	2.645308586304
C	5.125410534504	1.526871342781	4.256102412341
H	5.800173125199	1.095250113663	3.503836439265
H	5.399390356253	2.583434719886	4.369809009219
H	5.324225684952	1.029324291134	5.209169087985
H	2.670253596266	2.856974336333	5.197525185371
H	0.976664803997	2.187386355245	3.442569179048
H	0.482458334118	1.323810933762	4.902802802071
H	1.088533160969	-0.744113917664	3.926045027459
H	4.679539710158	-0.586963431197	2.225000286915
H	3.866582668889	-1.993503455188	2.984835051596
O	3.080702740792	-0.492762522371	0.068912062696
C	-0.960663059952	0.091778547925	2.204742738396
H	-0.819845740368	-0.019282028642	3.275585312187
O	1.049238294390	-2.412320329207	-2.048518389580
P	0.716626112788	-3.844946434861	-1.744540486152
N	-0.641475996940	-3.952219851885	-0.776858204008
N	0.277694802951	-4.846047889129	-3.013973650131
N	2.067337690172	-4.607106447484	-1.132941590652
C	-1.250229353406	-5.227629761336	-0.431227760592
C	-0.942107724660	-2.896528753796	0.185692856730
C	1.262381666916	-5.525238088591	-3.840760878782
C	-1.047765324733	-4.804076441502	-3.612187754392
C	2.050984527651	-5.996023244954	-0.716259852922
C	3.323938233643	-3.917513812120	-0.908409689087
H	-0.866151255154	-5.616659168477	0.525111967513
H	-2.335075712511	-5.087692751702	-0.328754785878
H	-1.073301099965	-5.971712382817	-1.212710657619
H	-0.467807114972	-1.959657108743	-0.114101712437
H	-2.031769625942	-2.750548345607	0.222598815186
H	-0.584625562792	-3.159840846777	1.191703369650
H	1.018999289023	-6.595136490645	-3.917641532679
H	1.275732715739	-5.105993931128	-4.857892363432
H	2.262034647830	-5.424048791460	-3.410683086620
H	-1.447621627855	-5.823936995079	-3.714802260821
H	-1.731467032265	-4.222369105638	-2.987642944932
H	-1.011072033880	-4.350504873158	-4.614733416230
H	2.913865767780	-6.527976358000	-1.144510190257
H	2.102941747392	-6.085409517584	0.379504635875
H	1.142873561434	-6.496932554838	-1.064660275953
H	4.114790737421	-4.351725534401	-1.541425282065
H	3.212036393017	-2.857205552793	-1.141666808115
H	3.624783253971	-4.006026380044	0.143945598227
O	0.608984282670	0.518765267974	-3.445435611958

P	-0.102476524747	-0.116232230745	-4.609441518352
N	-0.724616265036	1.095692971610	-5.584496763550
N	0.764806177109	-1.028376871381	-5.701408736686
N	-1.266443483700	-1.196903183889	-4.066722572798
C	-1.301861279822	0.857030591747	-6.898094677086
C	-1.145015511536	2.348923753650	-4.973429776031
C	1.147812102388	-2.398550591939	-5.375142462685
C	1.704856707996	-0.372826948117	-6.603598007804
C	-2.246576339331	-1.683148557232	-5.027990727893
C	-1.807803110169	-1.020767022121	-2.724017924748
H	-2.402001290487	0.866756872136	-6.866144024473
H	-0.974764944954	1.647169348447	-7.589275651953
H	-0.970223151071	-0.106127178850	-7.294855073910
H	-0.622921087835	2.490807828909	-4.024612788420
H	-0.891049722064	3.182559694754	-5.641761835886
H	-2.231240039190	2.368455999154	-4.794426231349
H	1.026440249150	-3.031449369633	-6.265661494907
H	2.200105209903	-2.444889177114	-5.055588367957
H	0.529742447469	-2.773577113143	-4.557029306139
H	1.741611252935	-0.925945534282	-7.551204592961
H	1.390796733330	0.653568864959	-6.808979067910
H	2.717976416112	-0.351728932465	-6.174895977684
H	-2.729100738068	-2.579898067287	-4.620420860114
H	-3.033283596079	-0.939058597478	-5.236715769804
H	-1.757221613447	-1.956452746505	-5.969254832026
H	-2.207598156176	-1.982367205131	-2.374089783740
H	-1.022070398067	-0.712501758004	-2.032220839330
H	-2.621718788448	-0.276247161513	-2.704531909838
C	-2.335045521892	0.134123086443	1.742364504370
C	-2.720082427469	0.359974234802	0.400386510524
C	-3.375720863158	-0.070920808311	2.677286792264
C	-4.062679751074	0.368726379342	0.031937871678
H	-1.945722653508	0.529339240537	-0.340873731717
C	-4.712270871434	-0.064440534280	2.299823715710
H	-3.114988522767	-0.245097301286	3.721170978699
C	-5.072865777994	0.153861776450	0.969072285016
H	-4.323965042174	0.549736993669	-1.010333506375
H	-5.481422798129	-0.231256765645	3.052676836629
H	-6.119038249181	0.159603492462	0.670823263107
Na	1.460191398371	-0.313619437391	-1.591538245560

Table S38. Atomic coordinates and single point energies for *bis*-HMPA -solvated enolate **4g** with the enolate oriented *anti* to the sultam ring.



G = -3178.707668

G_{SP} = -3180.037622

104

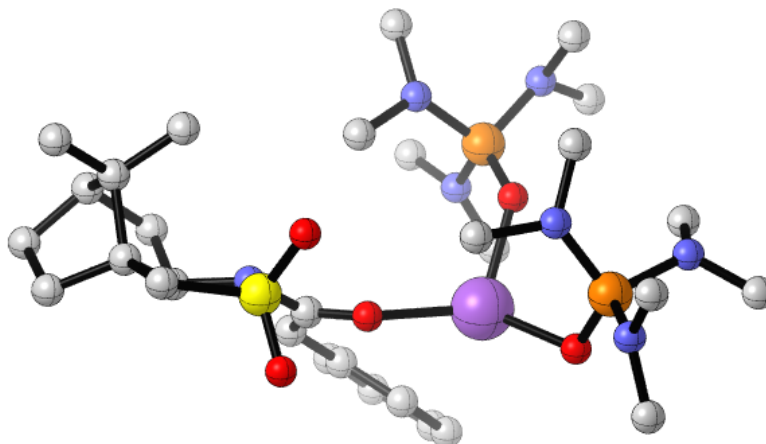
EHMPA2_pendC_thf: optimized structure // E(RM062X) = -3180.88322480 A.U. after 12 cycles

O	0.174978519416	0.323259113438	0.054495144904
C	0.256856318400	0.197118363160	1.310059405606
N	1.614470478753	0.216581008479	1.833005718867
S	2.007809914869	1.214283136858	3.136899591689
O	1.619224536659	2.610978399002	2.882647496737
C	3.803942965354	1.046473576228	2.938068411857
C	4.015077272868	0.153321291489	1.732152467265
C	2.722547161452	0.162046994256	0.878000629025
C	2.816137893828	-1.158709151389	0.074577967897
C	4.203712943019	-1.700930139688	0.475451099763
C	5.254343969364	-0.742340985028	-0.131297517196
C	5.152377575004	0.525188614320	0.766453051573
H	4.901546138476	1.431182666662	0.202832989291
H	6.083963939858	0.723301314337	1.306925809817
H	5.014419776321	-0.524139038967	-1.178014245462
H	6.261495638827	-1.173149693661	-0.104544509876
C	4.272526065448	-1.367250070312	1.986586677407
C	3.228713534601	-2.090520051834	2.841949935127
H	3.192053310810	-1.658886368117	3.851893290996
H	2.215380227902	-2.050437379918	2.438446859037

H	3.520020846291	-3.144293893105	2.946771990734
C	5.635706836763	-1.640317256187	2.627730670669
H	5.653857047871	-1.261413208372	3.659030685665
H	5.808838540318	-2.722994171228	2.677571054627
H	6.478966958429	-1.194568536971	2.092782832986
H	4.360759213859	-2.755822048183	0.221847439095
H	2.004298632718	-1.839716035582	0.355067034479
H	2.745518865673	-0.976739606728	-1.005009299044
H	2.689854227883	1.035607888311	0.212571156505
H	4.198490477659	0.642359376255	3.875908188765
H	4.172993825182	2.065944654280	2.788543052612
O	1.547213976755	0.612979786165	4.395961121966
C	-0.748783660413	-0.023888308151	2.230838590397
H	-0.453093603312	-0.214593037935	3.259214974573
O	1.662357694400	-1.011259888978	-3.266235479267
P	2.902541176454	-1.075454928593	-4.117142221698
N	4.103142477134	-0.107836848266	-3.487896848252
N	3.667212103208	-2.560938221473	-4.225701455283
N	2.509864478174	-0.618280443957	-5.669980041939
C	5.507622521152	-0.187751212870	-3.868425471305
C	3.710725927809	1.193748855719	-2.959152205755
C	3.081840515023	-3.563037269347	-5.112315700489
C	4.186464757573	-3.138524826586	-2.986910844974
C	3.535076139782	-0.507361524797	-6.695104587584
C	1.152177779790	-0.751331035656	-6.179152938123
H	5.772860093843	0.599243436683	-4.590381002864
H	6.132195522295	-0.052833107502	-2.974303534275
H	5.728664206066	-1.164216855398	-4.306593002014
H	2.683562791640	1.154517461821	-2.585117030273
H	4.375559756288	1.456406645699	-2.125563950153
H	3.783941755785	1.981081978221	-3.725057088655
H	3.854659635449	-4.294912954096	-5.375463581626
H	2.246027093836	-4.097807390445	-4.635404975409
H	2.724075170449	-3.097973412855	-6.035196429168
H	4.938568121251	-3.896491155331	-3.237063218927
H	4.663403629425	-2.364988485025	-2.377773782814
H	3.389865126843	-3.617743344865	-2.395454872057
H	3.611950580580	-1.423910573001	-7.301358362615
H	3.290777040226	0.328583140570	-7.362543167816
H	4.510771432144	-0.305113571454	-6.245970986479
H	1.045848693591	-1.642230180149	-6.818104237813
H	0.450277445757	-0.822806421841	-5.345204174591
H	0.900130401794	0.134529943201	-6.776022767056
O	-1.745092674891	-1.831484800796	-2.271255616098

P	-2.113159831611	-3.232780629139	-1.854626145703
N	-3.708846638422	-3.267025627770	-1.388261815272
N	-1.893986422051	-4.408203570200	-3.035122745552
N	-1.151574870861	-3.792335840400	-0.618192678462
C	-4.259841130237	-4.413435250140	-0.686355250133
C	-4.694856922510	-2.408850312276	-2.027570947801
C	-0.560404036061	-4.470400431864	-3.629869336925
C	-2.964527471842	-4.603051558185	-4.007662214953
C	-0.855989195984	-5.192997720590	-0.352125363880
C	-0.970484935046	-2.918711928856	0.537379511396
H	-4.983870568574	-4.063273027644	0.060618652005
H	-4.772426286541	-5.109547609447	-1.369577514190
H	-3.469050618077	-4.956149276772	-0.160867676595
H	-4.193086435615	-1.553003610684	-2.486055097098
H	-5.267235174515	-2.950618742585	-2.797738808950
H	-5.397966761821	-2.040539720077	-1.269585371665
H	-0.403354338709	-5.467790049116	-4.059308513766
H	-0.432821874732	-3.718966860406	-4.424920266090
H	0.202140296933	-4.300529035939	-2.862461272227
H	-2.766631411432	-5.529601991112	-4.559239551397
H	-3.926177891795	-4.712708740635	-3.498612507951
H	-3.032141813497	-3.776874729124	-4.733642659014
H	0.219817068069	-5.309182350025	-0.161444668092
H	-1.399659771384	-5.548499232868	0.536367530528
H	-1.133661187366	-5.810789977314	-1.208969293673
H	0.037654370127	-3.065171349462	0.947235746185
H	-1.080117612721	-1.870481134285	0.247561022538
H	-1.706393137926	-3.135328207545	1.328456595939
C	-2.159910476084	-0.118614769163	1.919886099189
C	-3.050735600318	-0.568897862553	2.922234581983
C	-2.722955036811	0.169636349345	0.654583378960
C	-4.404246594581	-0.752063710313	2.671869694848
H	-2.653443829443	-0.790394785972	3.912622943760
C	-4.080718954483	-0.012886586276	0.413017105554
H	-2.077310615522	0.531042238476	-0.138963667191
C	-4.936592215891	-0.482653282345	1.408968177444
H	-5.052147455617	-1.109631661256	3.471150546250
H	-4.475671030108	0.223413179400	-0.574015092557
H	-5.997107717956	-0.625712465066	1.211029268201
Na	0.069624442550	-0.676378919097	-1.850470620488

Table S39. Atomic coordinates and single point energies for *bis*- HMPA -solvated enolate **4g** with the enolate oriented *syn* to the sultam ring.



G = -3178.707433

G_{SP} = -3180.034985

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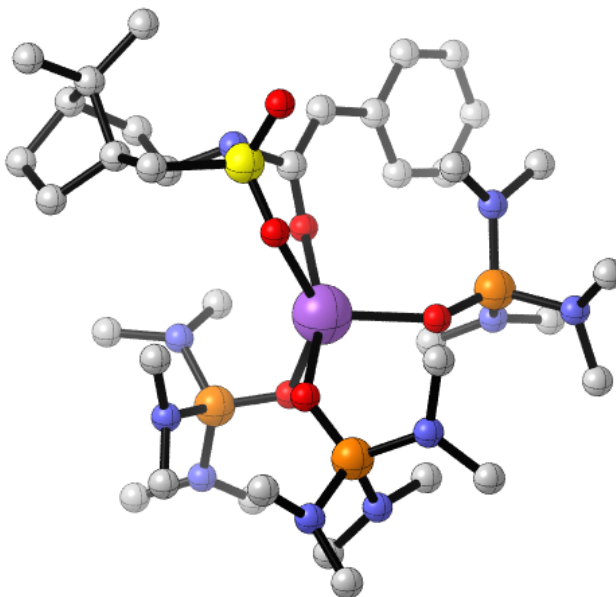
EHMPA2_pendS_thf: optimized structure // E(RM062X) = -3180.88110328 A.U. after 14 cycles

O	0.091440960338	-1.428052946954	0.521838545463
C	0.022268829309	-0.708708769173	1.558398824364
N	1.246707484595	-0.644337123979	2.308402082316
S	2.246177990486	-2.025872790668	2.137040086119
O	1.493734056972	-3.280834908391	2.265311355065
C	3.156268818271	-1.764683055997	3.686861958043
C	2.721736656667	-0.427150034217	4.238684279216
C	1.323190631319	-0.073689633458	3.654843606868
C	1.297885704096	1.476472481980	3.733408788436
C	2.579589597973	1.796103394467	4.524370076270
C	2.398901444212	1.232221915891	5.953713247210
C	2.563797182595	-0.304366781202	5.763382882277
H	1.699835398916	-0.877254800155	6.117371686951
H	3.448706444877	-0.689032556214	6.281720183779
H	1.415213166349	1.495138517856	6.359526685506
H	3.149918905247	1.631701811491	6.643310125027
C	3.601935097206	0.816446829856	3.900539203998
C	3.861367100683	1.036440533508	2.411019357432
H	4.576172819948	0.293225405999	2.032975107714
H	2.960853115579	0.955722889066	1.803146797514

H	4.302925151041	2.031056066376	2.257412506362
C	4.963101375055	0.804472184662	4.599415011073
H	5.559904157162	-0.052983064854	4.259413765510
H	5.518455610372	1.712670150930	4.331829171047
H	4.904977946811	0.762668005820	5.690632981002
H	2.863820121319	2.853821857733	4.494585603750
H	1.310804835441	1.914298227718	2.729522982018
H	0.400488868108	1.839703029348	4.245837960368
H	0.528178240486	-0.516446614955	4.272684838574
H	4.223210432712	-1.831939971866	3.450304218728
H	2.863228592800	-2.603720093775	4.325528712884
O	3.125794249862	-1.867509373549	0.972460068554
C	-1.059363138030	0.032915483719	2.009944159157
H	-0.935462073277	0.700737616502	2.855998923257
O	0.130884747827	0.055474794686	-2.756767214976
P	0.212902131995	1.554090971778	-2.601512185795
N	1.551791636412	2.022023633519	-1.746430791492
N	0.374760544522	2.411593779815	-4.034773769288
N	-1.158654922490	2.095231003234	-1.830109722810
C	2.228305165129	3.303732551442	-1.870883392219
C	1.866046790654	1.299170757489	-0.520072482911
C	-0.836808102510	2.717299064958	-4.788140056869
C	1.508273230376	2.056628366229	-4.884850144661
C	-1.216769005490	3.417295057764	-1.230843864458
C	-2.459896371904	1.493183684219	-2.089523054726
H	2.068325773718	3.918464158851	-0.972004504003
H	3.309071694869	3.140912202937	-1.984391492541
H	1.857946679397	3.848483726526	-2.742203344425
H	1.360323720650	0.328361483329	-0.493096455239
H	2.948880231473	1.125372819736	-0.466371973384
H	1.555561081943	1.879662312479	0.363600022526
H	-0.591168869026	3.466243866258	-5.550016564377
H	-1.254001420181	1.832741724804	-5.296808554411
H	-1.597889257649	3.143526698207	-4.128517815818
H	1.743240093029	2.904366993796	-5.540537542349
H	2.388409309934	1.843471667599	-4.269898777329
H	1.293643622408	1.176903562009	-5.512231336509
H	-1.632522551221	4.168104210426	-1.921953633573
H	-1.855180915071	3.374859484496	-0.338756654800
H	-0.219075264044	3.738195358623	-0.917636274073
H	-3.088497045350	2.151682229974	-2.709903321408
H	-2.336815930710	0.540955980752	-2.614742324552
H	-2.976574214859	1.311456492614	-1.139502508545
O	-0.681495425801	-3.326702114835	-2.835928352752

P	0.506062487542	-3.468127332117	-3.759849582241
N	0.988417093094	-5.060738698435	-3.786363432683
N	0.243232614794	-2.989492274769	-5.347252135230
N	1.814014939346	-2.568950673165	-3.290744236534
C	2.251154871619	-5.447809840805	-4.389687274113
C	0.037058332276	-6.141950069797	-3.585927826991
C	-0.311679729284	-1.647458292275	-5.524142970268
C	-0.320502055312	-3.966974599349	-6.272404051853
C	2.595463132188	-1.668591180306	-4.117248064733
C	2.155320126481	-2.524243434919	-1.872771724759
H	2.723603961848	-6.228590103548	-3.779243208343
H	2.117664024788	-5.841249607231	-5.410037565753
H	2.926910575468	-4.587796971613	-4.428691289582
H	-0.864671433996	-5.750229797355	-3.109184616395
H	-0.235818822210	-6.624815499778	-4.537561820214
H	0.478857568096	-6.900878142547	-2.926988794893
H	-0.009014107836	-1.258631629571	-6.505592582031
H	-1.412854028604	-1.660774219478	-5.479010542492
H	0.053859196019	-0.974841715862	-4.739540456443
H	-0.202532010671	-3.584808474593	-7.293386469640
H	0.215816033714	-4.917352649041	-6.202138402992
H	-1.393159726694	-4.145032439723	-6.093717920936
H	2.380781219728	-0.624979190474	-3.841887344537
H	3.666259249566	-1.864665905010	-3.961062900037
H	2.365468423224	-1.822195218174	-5.174261564434
H	1.990633335738	-1.521397260944	-1.454299065712
H	1.554133633013	-3.238779329235	-1.300252680559
H	3.212511281703	-2.784985177681	-1.729959092994
C	-2.360092240465	0.033200164130	1.370480117488
C	-3.260383615578	1.097569651279	1.614084498102
C	-2.838724761624	-1.017077405823	0.550581148239
C	-4.535206130768	1.122058888006	1.062607206900
H	-2.938338120565	1.917275914047	2.256392368782
C	-4.114878321795	-0.983753714717	-0.005774324711
H	-2.219517487371	-1.901805786089	0.420342760625
C	-4.975076642298	0.087006509286	0.234104318143
H	-5.193902037214	1.962302737400	1.278384992828
H	-4.446517407935	-1.820158416456	-0.620187949960
H	-5.972054216310	0.108200950734	-0.200400497069
Na	-0.672414655472	-1.557537609871	-1.496735448724

Table S40. Atomic coordinates and single point energies for *tris*-HMPA-solvated enolate **4g** with chelation to the *endo* sulfonyl oxygen.



G = -3998.514128

G_{SP} = -4000.176627

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EHMPA3_endo_thf: optimized structure // E(RM062X) = -4001.27429841 A.U. after 14 cycles

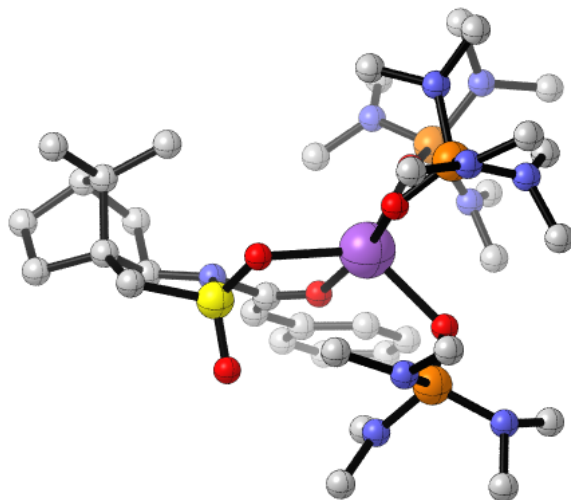
O	0.022575351626	-0.118367851572	0.209920624278
C	0.003683701470	-0.029705629129	1.462313468621
N	1.321898816587	-0.072114956083	2.157282888590
S	2.332584645364	1.238149396754	1.879108743481
O	2.374363076267	1.650422496660	0.455820458874
C	3.883890618075	0.370108155613	2.258016981980
C	3.487190365907	-1.058190860644	2.576603739142
C	2.078740636418	-1.323142167092	1.986404776818
C	1.553616733869	-2.499897025561	2.845523179244
C	2.761465628593	-2.835946176411	3.746604616147
C	3.866481787936	-3.428197855145	2.845751122123
C	4.381271234437	-2.195155666658	2.047261089387
H	4.262074183905	-2.313524097866	0.965633965660
H	5.440475896097	-1.992542816438	2.239302270469
H	3.469511311788	-4.213021871093	2.191224340887
H	4.667625015970	-3.879564733120	3.440719778479
C	3.325794415275	-1.435066539079	4.086160943608
C	2.376946860809	-0.558192419681	4.907386148652
H	2.715590703566	0.487240335380	4.907038092432
H	1.346760982367	-0.564311076283	4.549335339823

H	2.385535072004	-0.904739226945	5.949437686644
C	4.662544092678	-1.454207662231	4.833334838964
H	5.040437016435	-0.429841985920	4.956505364083
H	4.516569684415	-1.868715089518	5.839076732820
H	5.443775789942	-2.041264821330	4.342966275054
H	2.506738627732	-3.460950528137	4.609661823030
H	0.672860092215	-2.194395376951	3.420022106525
H	1.261086028708	-3.353789265001	2.223998117572
H	2.118033969355	-1.584125943676	0.917131605311
H	4.363567486321	0.900472188776	3.087542672407
H	4.493933717324	0.465259108863	1.353532519622
O	2.024932395352	2.308933461909	2.836809157731
C	-1.050448212006	0.058970356430	2.346310267161
H	-0.807544490551	0.173219221841	3.399554945143
O	-0.423234917390	2.481806783597	-2.033653423657
P	-1.889130729943	2.741611309314	-1.834364400718
N	-2.210896009448	2.934946604456	-0.215611599836
N	-2.531397299610	4.111049151116	-2.565220524308
N	-2.818861876668	1.539342240078	-2.519921769332
C	-3.567178845431	3.104329381800	0.267953210216
C	-1.162147868036	3.244097324779	0.742063963185
C	-2.591274555373	4.185073423652	-4.018325139835
C	-2.368957193648	5.413698437301	-1.935538803778
C	-4.209887210868	1.676077897068	-2.915742093915
C	-2.268506643464	0.207594102561	-2.728439949580
H	-3.691175691332	2.544964350326	1.205866298900
H	-3.808819040363	4.164325260928	0.455762751312
H	-4.286945759216	2.706418057645	-0.454373614621
H	-0.191458817965	2.934736484110	0.344647650146
H	-1.128509024672	4.321511964560	0.977887276980
H	-1.347923056794	2.688210040736	1.669859834069
H	-3.485973841417	4.745713526188	-4.322753762773
H	-1.708358199238	4.696157215227	-4.432705976457
H	-2.646261580986	3.182282221220	-4.452122670886
H	-3.245450259035	6.037560940747	-2.156210918696
H	-2.285220068421	5.307912803108	-0.850681888696
H	-1.474013596190	5.937291225053	-2.306714217047
H	-4.327467509329	1.402689573649	-3.975721351903
H	-4.855092783517	1.013082471882	-2.320620283939
H	-4.549070500400	2.706145304869	-2.783190192261
H	-2.269881621763	-0.035683102610	-3.802482516071
H	-1.239147668811	0.144735970700	-2.364096106300
H	-2.879677499078	-0.545977759713	-2.210033393090
O	2.818953896973	1.826105345828	-2.712671420232

P	2.622605743367	2.483934495320	-4.048159230066
N	4.117384911342	2.553189242708	-4.830789124476
N	1.670778491774	1.776996195922	-5.221350050515
N	1.936910183270	3.989456731413	-3.843905333820
C	4.218257371286	3.240816803319	-6.111281385717
C	5.278042155011	2.779842116539	-3.977686595202
C	0.221210054784	1.765648638628	-5.022471740007
C	2.141101835214	0.593597449158	-5.934564213562
C	1.481303783780	4.820620982318	-4.941794271865
C	1.785502510044	4.586485777994	-2.527359590122
H	4.270052533528	4.336030412270	-5.992797543784
H	5.132095045911	2.909983172337	-6.621164832930
H	3.362340402823	2.993634063335	-6.746468336159
H	5.176872875916	2.203009185996	-3.055160908548
H	6.179477533979	2.448612731080	-4.508652752212
H	5.401685272838	3.845654323202	-3.719966060898
H	-0.272764971134	1.832741002923	-6.002299719737
H	-0.085376858948	0.842099696054	-4.510966001884
H	-0.079089819035	2.608415000579	-4.395204845678
H	1.606243081288	0.529354588623	-6.891767971623
H	3.212021643293	0.667877085800	-6.139698968144
H	1.945175636093	-0.323147715234	-5.359180284803
H	0.440584414512	5.133947624660	-4.767342068608
H	2.095660005094	5.728771766042	-5.038052998010
H	1.516892745282	4.269391035961	-5.885487222382
H	0.725550093139	4.805422600268	-2.336648343591
H	2.126508609674	3.886476953801	-1.761460736097
H	2.368784322688	5.517298400578	-2.457029632142
O	0.951830634463	-0.703534403950	-2.911137631105
P	1.983166395816	-1.788592477667	-2.777250539985
N	1.962658977304	-2.726211125055	-4.169451883854
N	3.597733676961	-1.403697906688	-2.620322362407
N	1.697732955524	-2.655938688234	-1.368508100474
C	2.791674611863	-3.917984640892	-4.269706182466
C	0.741881334047	-2.790693485479	-4.960486189554
C	4.053416722705	-0.744854565234	-1.395878140988
C	4.398885338987	-1.020654059338	-3.778347494242
C	2.591769196198	-3.709249350142	-0.913541786329
C	0.306899907155	-2.875786026399	-0.986040624951
H	2.255603064655	-4.820264972446	-3.935153004442
H	3.089433641669	-4.066764443590	-5.316588311644
H	3.699564402380	-3.803609848304	-3.669554232241
H	0.177250764711	-1.862548885729	-4.842989379830
H	1.003879810129	-2.916583221440	-6.019781976121

H	0.104512747297	-3.638081094660	-4.660114500412
H	5.058335623414	-1.112222648806	-1.141795190497
H	4.077823008090	0.345117554405	-1.530833743515
H	3.378408134625	-0.978978206439	-0.567983175958
H	5.445169467908	-1.292930581358	-3.583054533433
H	4.063736453938	-1.552927765318	-4.671882047964
H	4.342650100917	0.062522934890	-3.959306392020
H	2.518329160925	-3.785041648064	0.181290613751
H	2.328036708712	-4.692313859693	-1.336524941832
H	3.628059435636	-3.477231718800	-1.177038225861
H	0.243175570538	-2.943361246909	0.108250840504
H	-0.298869471292	-2.022833825614	-1.295709716764
H	-0.087005990787	-3.809624517270	-1.421575163464
C	-2.452403733866	0.042406444176	1.977065597698
C	-2.906223728530	-0.218104185881	0.664500939445
C	-3.436670783047	0.278551605684	2.962192915497
C	-4.264970449673	-0.255762321388	0.372370500483
H	-2.164181653634	-0.389633831328	-0.109379024190
C	-4.793348076017	0.250851240197	2.659169995620
H	-3.117924854997	0.484410807723	3.984029407763
C	-5.223428897477	-0.019596273952	1.359291755786
H	-4.583569371728	-0.476338751690	-0.646593578934
H	-5.522325878379	0.439135109072	3.446218420377
H	-6.284815585965	-0.048570354644	1.121279314037
Na	1.137715864977	1.017544593815	-1.407203796453

Table S41. Atomic coordinates and single point energies for *tris*- HMPA -solvated enolate **4g** with chelation to the *exo* sulfonyl oxygen.



G = -3998.513921

G_{SP} = -4000.177839

133

EHMPA3_exo_thf: optimized structure // E(RM062X) = -4001.27436695 A.U. after 14 cycles

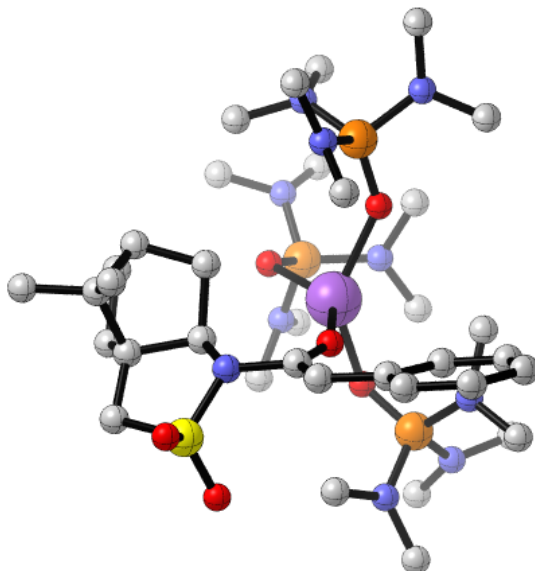
O	-0.052479639985	-0.337249732324	0.086257618715
C	-0.027819287680	-0.202408310024	1.336264275707
N	1.302773300225	-0.229316362415	1.910042862296
S	2.363754750494	-1.315313110489	1.173642157180
O	1.802715283804	-2.675911754012	1.102527975150
C	3.619984638319	-1.246731129224	2.477498768652
C	3.147088561856	-0.203541012767	3.467519859378
C	1.608319123933	-0.047635409000	3.327916871018
C	1.350322299381	1.380872257148	3.872728412914
C	2.736350941895	1.797243428040	4.402014027178
C	3.063958064606	0.892356936657	5.612046616385
C	3.394704078214	-0.481947070390	4.959786005370
H	2.751234541212	-1.293365758848	5.317326508534
H	4.432429665528	-0.782808012372	5.138559641165
H	2.213297498759	0.829611965207	6.300213372985
H	3.914869377151	1.277338789806	6.183759316505
C	3.685215049525	1.254549466644	3.305241493492
C	3.490524247401	1.892909088390	1.927168218062
H	4.111696462331	1.384037065272	1.177582041407
H	2.461813422577	1.867908654035	1.564275401148

H	3.818395959142	2.940527009473	1.969143034968
C	5.173402401622	1.380092637055	3.642222000704
H	5.777130568233	0.826643541191	2.909760198861
H	5.475243826728	2.433520729930	3.581447792628
H	5.439890194350	1.017302815225	4.638700659255
H	2.824142135220	2.869279419163	4.610123552326
H	0.995248539446	2.037558174161	3.071746393051
H	0.591661035824	1.380413062577	4.662657362304
H	1.087911535310	-0.812705382681	3.922665706119
H	4.575611881057	-1.016340002040	1.995508963286
H	3.647990878636	-2.256120129071	2.900155568251
O	2.881835594777	-0.753531411564	-0.088626131387
C	-1.079676214580	-0.003503921694	2.216616272741
H	-0.871094253021	0.048522394924	3.281006709307
O	0.665862874506	1.865333903097	-2.345779260387
P	-0.419984958961	2.896451970655	-2.259854455400
N	-0.311975206512	3.740204445441	-0.818299633116
N	-0.375267792712	4.136801862630	-3.380730974993
N	-1.919979126333	2.193943122519	-2.427657339683
C	-0.962995096438	5.016846559242	-0.571863656282
C	-0.110407254908	2.951269501919	0.392793647148
C	-1.191568989795	4.172244373770	-4.581369979922
C	0.784261138489	5.013249169750	-3.418497816454
C	-3.136010653539	2.968488285512	-2.244092621999
C	-2.107865639543	0.860427423912	-2.974304082892
H	-1.929249131999	4.888973055045	-0.058538874285
H	-0.317281820174	5.631441440928	0.070474890875
H	-1.127252499014	5.551616530992	-1.511312956088
H	0.443804273305	2.039675305918	0.153173360761
H	0.465520111117	3.547383838648	1.114003902965
H	-1.069437837465	2.666987124263	0.856165609193
H	-1.752771741659	5.117200271551	-4.635081093813
H	-0.564228401319	4.097701513111	-5.481561176607
H	-1.904188108930	3.343166862163	-4.590011697630
H	0.466182991930	6.046004706653	-3.619318424597
H	1.304175694505	4.994081618905	-2.455799303773
H	1.490711671041	4.707711000180	-4.208289151758
H	-3.765180200684	2.914047549223	-3.145524884072
H	-3.716070893706	2.589746190254	-1.390507891824
H	-2.904424727476	4.022782563775	-2.062856378660
H	-2.469973197668	0.903387965951	-4.016049650084
H	-1.175297703075	0.290844126824	-2.939397788718
H	-2.859168526860	0.322242877349	-2.380273126904
O	2.941055584082	-0.169966925539	-3.247584160472

P	3.015625985155	0.574414268893	-4.548136637315
N	4.168675696185	-0.177092749229	-5.517408852293
N	1.710391628469	0.623091602636	-5.583110729378
N	3.355222146956	2.191465988764	-4.277117853251
C	4.355748934431	0.107538143236	-6.929851131698
C	5.341886215579	-0.749485196296	-4.875063981452
C	0.679658178162	1.646357763688	-5.473973082212
C	1.220198931103	-0.632460102825	-6.145996577592
C	3.841408958622	3.007438662161	-5.375702532029
C	3.778462222394	2.621595085454	-2.953762216758
H	5.187962735092	0.808553370158	-7.101670925368
H	4.585728414511	-0.827042009703	-7.461619143286
H	3.443467130612	0.531543138922	-7.357481680653
H	5.106863674651	-1.006953449722	-3.839104069974
H	5.640217448051	-1.664641692785	-5.405355957820
H	6.196100748265	-0.052517466985	-4.888229860290
H	0.367984046688	1.946516869057	-6.484815595222
H	-0.198297961850	1.271086898515	-4.928333067713
H	1.070408405466	2.508870813771	-4.930543292354
H	0.665354381560	-0.409973799214	-7.066907800035
H	2.057664064278	-1.287501332091	-6.402394144551
H	0.557492428182	-1.156174991709	-5.439759559596
H	3.601100706615	4.060937170902	-5.178885551658
H	4.933216015959	2.926025251655	-5.509555870388
H	3.349832853560	2.720449412452	-6.311986480528
H	3.499921087410	3.674761312314	-2.817616703357
H	3.263575468449	2.027575658099	-2.196584525638
H	4.869057896046	2.531805627804	-2.816586514621
O	0.068000657385	-1.641188846423	-3.011437038458
P	0.466870229592	-3.091395427844	-2.998574005510
N	-0.267711693648	-3.848667526014	-4.317925340104
N	2.062726456605	-3.528128347552	-3.196404533478
N	0.071409393866	-3.779213721960	-1.535522884744
C	-0.160994088527	-5.299090263602	-4.409289261805
C	-1.589097372125	-3.354201376333	-4.689323515501
C	3.003451612857	-3.248483349554	-2.110254252143
C	2.696763322386	-3.450753593437	-4.507836085385
C	0.583981541934	-5.049106580054	-1.053468395349
C	-0.951420922658	-3.186915206806	-0.682287258517
H	-0.841599557081	-5.811523584070	-3.708418999277
H	-0.419467070229	-5.612780801595	-5.428424357295
H	0.865286207022	-5.618443721289	-4.202343484108
H	-1.603940925493	-2.263194929947	-4.630525364611
H	-1.805618875520	-3.659588360247	-5.720695816319

H	-2.382209955642	-3.757000218561	-4.036600903738
H	3.775282586691	-4.031453237783	-2.100682187184
H	3.474303020679	-2.265399737758	-2.251586513217
H	2.488788134257	-3.248159315025	-1.144943692056
H	3.493744138009	-4.205667663331	-4.558521790183
H	1.969124782983	-3.657686510811	-5.296904649833
H	3.139771482250	-2.457264667504	-4.672551778163
H	1.055228196200	-4.901821328312	-0.070161848123
H	-0.228980869932	-5.783094810131	-0.943973058670
H	1.329891706142	-5.453469945930	-1.743047364868
H	-0.548355601054	-3.060316947826	0.331100222210
H	-1.216319062742	-2.194843290667	-1.051825808394
H	-1.844957142417	-3.830095588609	-0.646860809633
C	-2.459344247568	0.178782655698	1.823887118475
C	-2.914690562799	0.170635645472	0.483121444557
C	-3.436836603170	0.388947231413	2.826254768455
C	-4.264325427217	0.342966814433	0.185835186450
H	-2.185732644058	0.018977953266	-0.308011276742
C	-4.778314231885	0.567590497389	2.517408216380
H	-3.120671563493	0.407338807484	3.869279187961
C	-5.211522174638	0.543010607232	1.189980083696
H	-4.585590749932	0.316328843335	-0.855505470339
H	-5.495900361121	0.724666667899	3.321712944874
H	-6.263351131563	0.674105039341	0.945321845855
Na	1.265473781949	-0.190014414455	-1.741946262110

Table S42. Atomic coordinates and single point energies for *tris*- HMPA -solvated enolate **4g** with the enolate oriented *anti* to the sultam ring.



G = -3998.511278

G_{SP} = -4000.177546

133

EHMPA3_exo_pendC: optimized structure // E(RM062X) = -4001.27398815 A.U. after 13 cycles

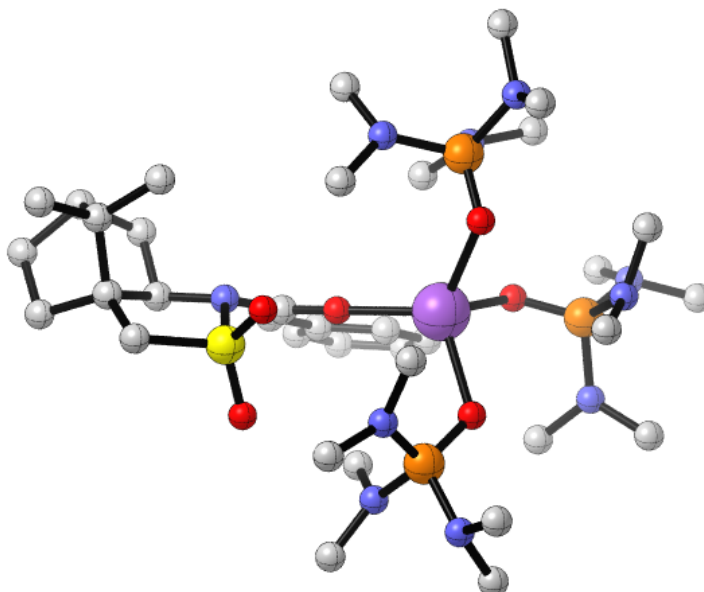
O	-0.014569265682	0.238981015980	0.117812874040
C	0.000174625569	0.139708515305	1.371884722478
N	1.329285453213	0.158838136476	1.971238721897
S	1.672814350745	1.145683320155	3.293573914968
O	1.241746675909	2.535422201642	3.066723716044
C	3.477834442450	1.043797313887	3.119917014418
C	3.744569122207	0.086159190030	1.977261588556
C	2.481612031519	0.027232584717	1.081466040152
C	2.596253519083	-1.352212977119	0.387359769160
C	3.988221710180	-1.834711230392	0.838275241158
C	5.024728259077	-0.889477535343	0.183597201546
C	4.902903573261	0.418009200560	1.021758653050
H	4.665399239249	1.296225906657	0.410880352945
H	5.821274671078	0.640776459617	1.575624931190
H	4.775411082423	-0.717683338837	-0.871180855905
H	6.038706324384	-1.301285821230	0.232760613591
C	4.020263713760	-1.411203596512	2.326888497787
C	2.967067552202	-2.095487663880	3.202487459724
H	2.964746736941	-1.659420386410	4.210716050613
H	1.948406233699	-2.021798946962	2.816537241103

H	3.223100168165	-3.158767822745	3.305703357019
C	5.373866848154	-1.624554554677	3.008675246950
H	5.392612731451	-1.124888748367	3.987310869439
H	5.530235956364	-2.695935574553	3.188508893111
H	6.226361568876	-1.259603123531	2.428818740918
H	4.174027369888	-2.898870172207	0.651755766024
H	1.791036111180	-2.018164990710	0.715674995649
H	2.550358467956	-1.269084940412	-0.702003394902
H	2.490526749783	0.852052953700	0.352142100836
H	3.878564040624	0.722381130845	4.086936603361
H	3.801027222677	2.067299708871	2.905152191442
O	1.212684071332	0.508881503123	4.535924087590
C	-1.062966420186	-0.033500370895	2.238766816518
H	-0.839597329909	-0.197195900343	3.290155915819
O	0.942099922516	2.337187822096	-2.291307486729
P	-0.253466339414	3.247947422125	-2.211193672438
N	-0.248037155443	4.139670233111	-0.810643088460
N	-0.352522753468	4.435163898717	-3.385913276048
N	-1.657409310123	2.352717701594	-2.314488186685
C	-0.926382925958	5.411846239958	-0.625483519879
C	0.139234539774	3.483868250441	0.435358894900
C	-1.155063264973	4.309730284754	-4.589140978966
C	0.702268414688	5.432070676936	-3.476130607645
C	-2.941282527304	2.940689755368	-1.976033364694
C	-1.730216498808	1.112806680669	-3.069483787791
H	-1.778242946516	5.305958908680	0.063138384108
H	-0.230031378246	6.144425595772	-0.192589877870
H	-1.291365085765	5.796451698780	-1.581286649106
H	0.707565903282	2.575975263411	0.220335704575
H	0.760715620550	4.163871212634	1.030417145447
H	-0.741144148926	3.202882883653	1.033966004039
H	-1.733901102036	5.230422063067	-4.751663076232
H	-0.522582024959	4.144300659112	-5.474997472377
H	-1.854375920327	3.474023796934	-4.501205466928
H	0.266581473159	6.419936947890	-3.682720093942
H	1.252304490438	5.490476673896	-2.531693812512
H	1.412367301030	5.194105146087	-4.284385466538
H	-3.447312079742	3.376996459667	-2.853320974554
H	-3.590868004964	2.165414799871	-1.552656580821
H	-2.817126603570	3.717281183719	-1.215922133213
H	-2.318433204392	1.238176753401	-3.994515954351
H	-0.728633148452	0.772337896397	-3.346629461680
H	-2.203520866182	0.329239340477	-2.461022432787
O	3.105655048487	-0.070949649831	-2.608343089214

P	3.209604577628	0.440644485814	-4.021266923124
N	4.097202196613	-0.647693708880	-4.932890200420
N	1.797676560367	0.609908817518	-4.889841307452
N	3.958436615192	1.928135283698	-4.011005486631
C	4.089348405759	-0.708697963722	-6.384417950422
C	5.288412956163	-1.226157782930	-4.328540990623
C	1.238487210891	1.897348404281	-5.269043385511
C	1.070829102787	-0.536216796954	-5.416733961171
C	4.402082934592	2.565769750270	-5.236433851392
C	3.938598340781	2.794282256052	-2.843170892329
H	5.026092421827	-0.310337482350	-6.804164657549
H	3.987311073787	-1.753649509957	-6.713853276821
H	3.254802020232	-0.133499855427	-6.793054084385
H	5.213275636963	-1.177339939211	-3.238918488217
H	5.380723613512	-2.280432574678	-4.625469633144
H	6.198334833384	-0.694850207026	-4.649913667812
H	1.402845844622	2.102118599983	-6.340042022512
H	0.156124745430	1.884242914768	-5.082792500051
H	1.664736291516	2.697849449436	-4.660197678529
H	1.055946140383	-0.512901652857	-6.517848907530
H	1.537869014144	-1.465308451996	-5.084720412308
H	0.038458937460	-0.536441828500	-5.044782282383
H	3.764598752586	3.424855313895	-5.498100431199
H	5.432819468052	2.928087979427	-5.118513730078
H	4.386643519666	1.859546225320	-6.072143066631
H	3.272559413999	3.655652176270	-3.000412422132
H	3.568854931914	2.237127652183	-1.980921192141
H	4.955716608789	3.158900295898	-2.639916525689
O	0.209586102852	-1.650793248923	-2.685896720405
P	0.493881637399	-3.126211149652	-2.660153860864
N	-0.494099625915	-3.865809085245	-3.799309293074
N	1.998870477974	-3.713993060126	-3.076837049610
N	0.312006068303	-3.695326743829	-1.097607996674
C	-0.507821637278	-5.315748313625	-3.932461324475
C	-1.769520401402	-3.238919534217	-4.122559374820
C	3.126320912089	-3.526689246143	-2.166097834644
C	2.421432644645	-3.840615373990	-4.467758476346
C	0.562316546608	-5.085272163658	-0.746565987068
C	-0.629287158542	-3.021228752412	-0.206093142784
H	-1.245787451195	-5.784054480829	-3.262021379398
H	-0.769158181801	-5.580500132343	-4.965762663509
H	0.481064202708	-5.729712892672	-3.713402148036
H	-1.679458021913	-2.154115235479	-4.030927366308
H	-2.038440048497	-3.489106245980	-5.157131414362

H	-2.578633589664	-3.588022250380	-3.461382310047
H	3.873680022050	-4.304107255099	-2.373353014556
H	3.584527246298	-2.534249386400	-2.299096483223
H	2.796857445187	-3.630442597176	-1.129539703106
H	3.008771643438	-4.762420335867	-4.581621405607
H	1.553325557584	-3.894977790977	-5.129060365242
H	3.048851664053	-2.986498219873	-4.766836045578
H	0.993832026894	-5.129331639801	0.263289850528
H	-0.363872979880	-5.680807584349	-0.746621599572
H	1.272948044047	-5.536231810118	-1.445148228371
H	-0.297766037514	-3.167050886441	0.831034030929
H	-0.646910831983	-1.947002455380	-0.413276879479
H	-1.646990141804	-3.434533997543	-0.298573348721
C	-2.451568373756	-0.070659368040	1.836700875000
C	-2.909986141088	0.162108898380	0.515940399716
C	-3.438425599972	-0.370860459344	2.806929388568
C	-4.263333687887	0.065211485543	0.201856703305
H	-2.181810946836	0.416683926064	-0.250486958587
C	-4.785333973225	-0.456671747616	2.483073333948
H	-3.122008218914	-0.543948756311	3.835308829597
C	-5.216286369513	-0.246650888357	1.171267462302
H	-4.581842028471	0.234917062781	-0.826813589054
H	-5.508286182996	-0.693808851353	3.262587753868
H	-6.270245751960	-0.322107895452	0.912573018757
Na	1.032060967555	0.180232196982	-1.781353946457

Table S43. Atomic coordinates and single point energies for *tris*-HMPA-solvated enolate **4g** with the enolate oriented *syn* to the sultam ring.



G = -3998.509562

G_{SP} = -4000.172949

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EHMPA3_exo_pendS: optimized structure // E(RM062X) = -4001.27137785 A.U. after 14 cycles

O	0.289936239702	-0.244711970052	-0.106249196559
C	0.056080467004	-0.248544822515	1.131955830558
N	1.211597116457	0.072851340884	1.955692704470
S	2.651565288338	-0.712959077636	1.476429065472
O	2.414639685814	-2.147758070405	1.247190163204
C	3.503559293351	-0.502971384253	3.067091090031
C	2.573740615404	0.293771533004	3.954210893355
C	1.129565428760	0.128037443239	3.418461810349
C	0.401543409040	1.375603065024	3.980547738856
C	1.477824530469	2.026163316271	4.873357542375
C	1.718756974316	1.079618753162	6.070505517146
C	2.505490677359	-0.105605050647	5.439423109331
H	1.998982408670	-1.069590855836	5.559906342192
H	3.508695398313	-0.207398338623	5.866798480762
H	0.771761193345	0.757662353728	6.518448240871
H	2.300057090035	1.569448606205	6.858864881381
C	2.766607383985	1.841573277652	4.033530626699
C	2.756886341210	2.581405653908	2.694704613881
H	3.590483633619	2.244681776083	2.062869449879
H	1.839505289091	2.439136297691	2.122358034939

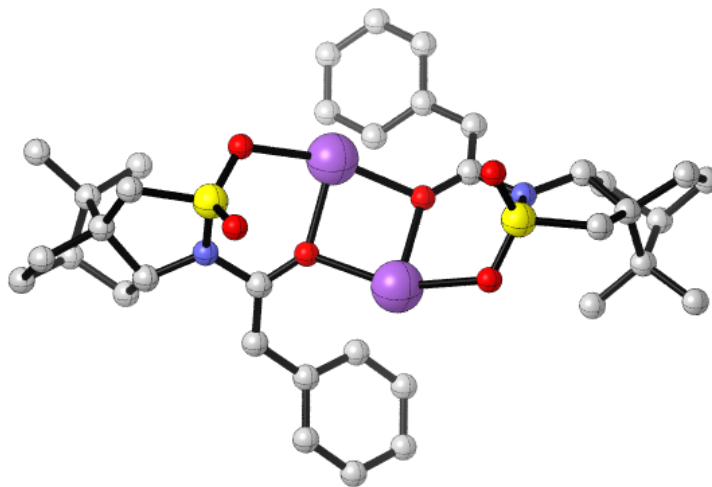
H	2.891359405614	3.656751937580	2.875304742141
C	4.054249378600	2.246071192874	4.755753987710
H	4.929506699757	1.976722625176	4.148610625269
H	4.074397905559	3.335371517076	4.888933345166
H	4.177840266557	1.789637210333	5.741692120239
H	1.247764554613	3.058504743379	5.159238264401
H	0.080147835665	2.031101684689	3.164686746047
H	-0.490476497712	1.099477601491	4.553129163190
H	0.695014569477	-0.807253689542	3.800432976731
H	4.461325151607	-0.016417387038	2.856662721116
H	3.673783309141	-1.519655261518	3.435180067480
O	3.353554599422	0.041660054868	0.431256383540
C	-1.134162020288	-0.499384759618	1.795400642972
H	-1.140380254893	-0.477957265437	2.879903489261
O	0.850683279371	-2.302749181498	-3.031102778856
P	1.875142715337	-3.151708525398	-2.320502197452
N	1.195691737079	-3.964714343949	-1.045499980494
N	2.544169282449	-4.419471104772	-3.207919781982
N	3.171068066409	-2.196823342344	-1.900887485012
C	1.854633120623	-5.029380439855	-0.307742943091
C	0.029278087779	-3.416107595808	-0.361385997380
C	3.507009038866	-4.066098519460	-4.244655197643
C	1.668101149474	-5.513340931155	-3.613629624490
C	4.267955501465	-2.729244742395	-1.116045723176
C	3.473396786775	-0.956543628553	-2.596923762363
H	2.228335735425	-4.659392692321	0.658546127891
H	1.133199745681	-5.837081647025	-0.116294243250
H	2.687153797204	-5.439864459970	-0.885978726976
H	-0.408851792034	-2.610862151385	-0.952712797095
H	-0.720441512575	-4.212162473730	-0.239198554555
H	0.307578441997	-3.012125965332	0.620147359932
H	4.083091782228	-4.959618334106	-4.514606833040
H	3.016059066145	-3.685212168265	-5.155424380561
H	4.205085667787	-3.308337585162	-3.878221581186
H	2.272962827479	-6.410987549736	-3.795397121309
H	0.946919303596	-5.734535853993	-2.822059919126
H	1.117601468210	-5.275458691676	-4.538035413539
H	5.060595941636	-3.159422244647	-1.753614695799
H	4.695941375654	-1.916161126283	-0.518200452547
H	3.908974567110	-3.490664810129	-0.420488746756
H	4.367385467550	-1.066736682575	-3.234262968585
H	2.636321632085	-0.661593835912	-3.236582522572
H	3.655456507293	-0.168185215730	-1.856319629738
O	-1.820935545345	-0.194716055061	-3.195476266011

P	-1.962239398894	-0.609402812601	-4.635814841072
N	-3.405092436117	0.025637998785	-5.232668083812
N	-0.863235154788	-0.083846129019	-5.770404540266
N	-1.879275082640	-2.268915863875	-4.753047457520
C	-3.838743494615	-0.381292836241	-6.562787036009
C	-4.508797618208	0.151899999032	-4.288122441006
C	0.493571373438	-0.630401585053	-5.747523368625
C	-0.906154808672	1.283064524823	-6.280945891832
C	-1.707398811275	-2.989807511553	-6.000280295716
C	-2.037040760971	-3.115777391311	-3.580770936522
H	-4.296394809976	-1.384741894529	-6.561655226930
H	-4.584911987967	0.334935750085	-6.928706317640
H	-2.992726305546	-0.378986976574	-7.257227071565
H	-4.132636672590	0.504696114344	-3.324385170632
H	-5.227016624325	0.884099603529	-4.678697203681
H	-5.039492061475	-0.804121569727	-4.138545001036
H	0.833009628166	-0.803843463341	-6.778700104512
H	1.173886139255	0.081805779530	-5.257691469672
H	0.522660423306	-1.570053522305	-5.187550081945
H	-0.460583657322	1.294106243981	-7.284850182345
H	-1.938335447722	1.633700390136	-6.354563997500
H	-0.335288020464	1.966467012383	-5.634103747065
H	-0.815374272015	-3.632672135520	-5.943971671968
H	-2.577064923051	-3.630982840856	-6.208199933648
H	-1.577178999059	-2.294648180582	-6.833830323514
H	-1.181033150912	-3.799168191068	-3.499890861932
H	-2.056804839506	-2.500237264373	-2.678376674244
H	-2.968141648737	-3.700047756775	-3.644080122615
O	0.903016930042	1.575068292954	-3.344709720943
P	0.321631503561	2.877494962316	-2.855962248116
N	0.539280269752	4.045120827674	-4.049018857352
N	-1.302798491975	3.002180329357	-2.532430049108
N	1.047499030191	3.301820691042	-1.413377238330
C	0.224606804202	5.428089351141	-3.711105878794
C	1.747186246830	3.922035332095	-4.858394653569
C	-1.839071214439	2.325623834727	-1.349452314816
C	-2.295880864722	3.183431600276	-3.584472509161
C	0.476342944572	4.253169917548	-0.474931862792
C	2.096862549117	2.465141059325	-0.837890412003
H	1.001442032412	5.885833531192	-3.075774753356
H	0.149053080193	6.011067741511	-4.637102769095
H	-0.736762781000	5.484989798107	-3.190906972660
H	1.913419925822	2.873276741735	-5.115483160631
H	1.613402817109	4.499401734180	-5.781389096159

H	2.638001427610	4.307366726648	-4.334229859761
H	-2.444011503565	3.026257731333	-0.756167678759
H	-2.457524009839	1.474967040285	-1.661169491028
H	-1.032092725099	1.933019761787	-0.718085556595
H	-3.143521113674	3.749918535375	-3.174918384679
H	-1.870406983279	3.747087998436	-4.418578115865
H	-2.663031241308	2.214667321081	-3.952561984166
H	0.092117693284	3.736012986604	0.419241868281
H	1.244030087796	4.970801435392	-0.152556807180
H	-0.348567003135	4.805956042743	-0.931912695149
H	1.696850052758	1.791709248104	-0.069076419156
H	2.554076195274	1.849400114192	-1.615005043976
H	2.870869777859	3.108844504721	-0.396348404471
C	-2.406969530890	-0.821166256502	1.180438280325
C	-2.633868248933	-0.919034261397	-0.210474778524
C	-3.520418548936	-1.072829246185	2.018276615373
C	-3.887228694229	-1.247203695956	-0.718611333016
H	-1.827710007972	-0.720898566702	-0.904385506914
C	-4.768202750088	-1.401842534493	1.505206280309
H	-3.387595975510	-1.007561269957	3.098268879406
C	-4.968659178223	-1.495206019382	0.126051494555
H	-4.005322654449	-1.304422966089	-1.800516375851
H	-5.594526149494	-1.588419356405	2.189900162268
H	-5.945338010531	-1.753512367682	-0.277678877378
Na	0.240644189903	-0.287200666909	-2.276049508162

Unsolvated dimers

Table S44. Atomic coordinates and single point energies for unsolvated dimer of enolate **4g** with double chelation to the *exo* sulfonyl oxygens.



G = -3078.26409

G_{SP} = -3079.552549

92

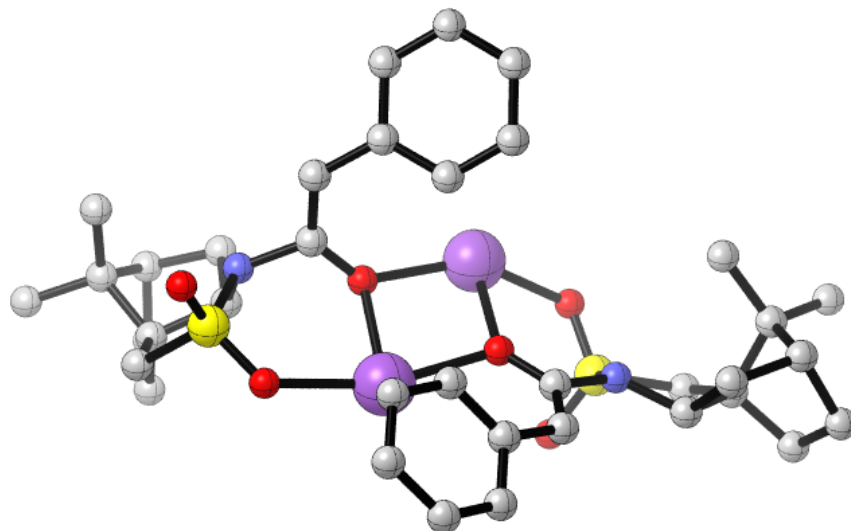
E2S0_exo-exo: optimized structure // E(RM062X) = -3080.26542481 A.U. after 13 cycles

O	0.128553233010	0.233798754983	0.170929268887
C	0.144447890976	0.262316627086	1.451226519228
N	1.440784083824	0.045827490654	2.014658486130
S	2.426424179950	-1.039026519773	1.163480286347
O	1.753910620901	-2.320075196061	0.918988117149
C	3.661329550939	-1.216697092995	2.472136732004
C	3.242232138982	-0.276549350939	3.584030676700
C	1.723766855956	0.018316640723	3.450596407045
C	1.563939856195	1.376520030439	4.180581528282
C	2.968841196925	1.610561556799	4.770245609518
C	3.206074039781	0.533476204612	5.853034128860
C	3.436520785563	-0.766895740390	5.029092821204
H	2.722426656920	-1.561802340740	5.270686974322
H	4.442165509953	-1.174579929024	5.175162894787
H	2.343733094691	0.451022857585	6.524165562749
H	4.077046656689	0.771649000941	6.472264572808
C	3.892937154667	1.143556340430	3.618881076786
C	3.773523910572	1.968575067700	2.334329475738

H	4.341929707446	1.497135508430	1.520965976545
H	2.749267126286	2.104614784478	1.982444113285
H	4.211770469681	2.960547996649	2.506768140750
C	5.379808644660	1.104900939577	3.981375071980
H	5.953873586484	0.615474846914	3.182633643650
H	5.760735734724	2.129798236849	4.074030533166
H	5.598085476972	0.585362090263	4.918208870735
H	3.133347303410	2.636349626864	5.117155561075
H	1.271339135384	2.162581060573	3.478195120178
H	0.795095511895	1.323950161150	4.958591166326
H	1.130373372988	-0.775800928800	3.926843174688
H	4.636805130575	-0.991064121901	2.029256276405
H	3.616165963817	-2.271872051669	2.760310646747
O	3.008521023331	-0.365156923652	-0.021395798183
C	-0.920534312749	0.468308541029	2.294552230838
H	-0.794611832144	0.309773214500	3.361832221787
O	-0.326820969008	0.646604557485	-2.678476863441
C	-0.481097379624	1.097438709119	-3.867246830887
C	0.235868569528	2.096336241066	-4.480419552602
H	0.105430413860	2.270780209843	-5.544671382761
N	-1.528000098214	0.450684540207	-4.595611408711
S	-1.723213146309	-1.200613523881	-4.266967552268
C	-2.811218934160	-1.531034415703	-5.672743140193
C	-3.049116723871	-0.196820338774	-6.350317422170
C	-3.103724668428	-0.189556812433	-7.887638320233
C	-3.659692499124	1.232187211630	-8.191773187802
C	-3.906891068563	1.831719555301	-6.788820583151
C	-2.532569701103	2.171503282598	-6.178885711464
H	-2.619963163757	2.700647340952	-5.225354435696
H	-1.927799571111	2.792159916430	-6.848380238197
C	-1.895969093763	0.772774567142	-5.975325275151
H	-1.028191571658	0.617277464293	-6.632845207421
H	-4.610268152324	2.671257911099	-6.779553450822
C	-4.338948719171	0.595323585025	-5.962784457547
C	-4.536526520677	0.867171460478	-4.468779427260
H	-5.438236517750	1.479388406487	-4.334934330097
H	-4.696882978617	-0.073936412500	-3.925178431120
H	-3.700490120462	1.382509232175	-3.992438177516
C	-5.619953851024	-0.078513680639	-6.461436034748
H	-5.777300576707	-1.031692366761	-5.938207014979
H	-6.482004613714	0.561954805902	-6.236105839647
H	-5.629896629508	-0.279885265446	-7.535946750823
H	-4.584709632297	1.181165442911	-8.775302663101
H	-2.949444740830	1.841174426719	-8.762325728109

H	-2.109724222324	-0.363388137418	-8.314160792638
H	-3.763496476453	-0.978951517477	-8.262365108451
H	-2.256745508213	-2.238636675727	-6.297512883321
H	-3.714108696697	-2.008031681656	-5.277938932495
O	-2.449572928286	-1.375471447738	-2.986852782242
O	-0.465919236341	-1.943715548812	-4.408918822614
C	1.252643323636	2.881529696176	-3.792299903181
C	2.319969404850	3.444825709451	-4.522065769223
C	1.224223867529	3.140636555214	-2.403057382235
C	3.318975146043	4.182350102083	-3.898004222630
H	2.362932159114	3.283670247553	-5.598694772607
C	2.233856532239	3.871998112441	-1.779975516791
H	0.374005062276	2.793214298801	-1.816939259028
C	3.295877691613	4.390617889450	-2.518367391369
H	4.130898145102	4.593752150894	-4.495440595864
H	2.176477183007	4.050817924720	-0.706991519740
H	4.083784763248	4.960023615426	-2.030754167422
C	-2.258676260727	0.795454638194	1.818927054787
C	-3.385604824900	0.438586768451	2.588160486083
C	-2.505087974713	1.487537487221	0.611351389900
C	-4.677714492637	0.715610399584	2.157904960624
H	-3.232912346754	-0.077408499105	3.535462298170
C	-3.802963325481	1.753902316147	0.178862345696
H	-1.660113465564	1.853048611133	0.028659680565
C	-4.901481131160	1.361721704748	0.941445151978
H	-5.521987783692	0.416274273854	2.776775971291
H	-3.952141239962	2.289974850472	-0.757586347012
H	-5.913773643433	1.569002058909	0.602202212683
Na	1.548996944550	0.583665774138	-1.490565944342
Na	-1.552338237336	-0.378042732564	-1.145900513854

Table S45. Atomic coordinates and single point energies for unsolvated dimer of enolate **4g** with chelation to one *exo* sulfonyl oxygen and one *endo* sulfonyl oxygen.



G = -3078.260215

G_{SP} = -3079.548789

92

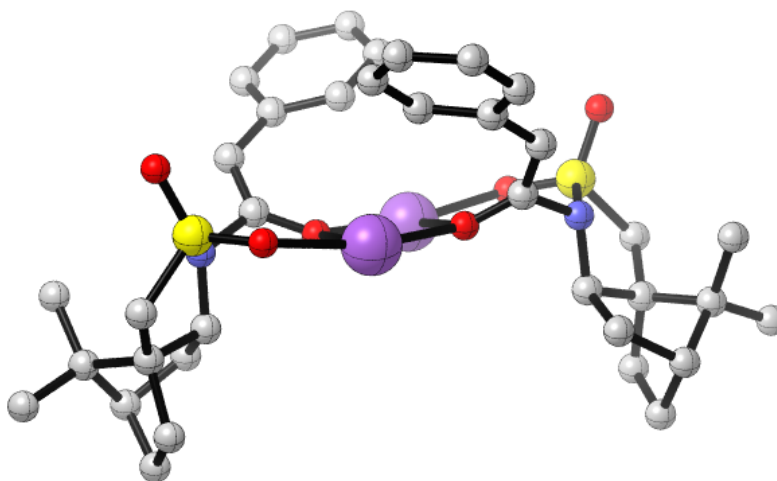
E2S0_exo-endo: optimized structure // E(RM062X) = -3080.26098795 A.U. after 12 cycles

O	0.187759084273	-0.018048988795	0.130660638179
C	0.312867071448	0.189073947444	1.389451122824
N	1.661951694252	0.000796895204	1.937338612002
S	2.630458645946	1.377331483851	1.815889055372
O	2.586553765152	1.917800489659	0.428929992670
C	4.206662060690	0.515448196876	2.039618735640
C	3.872882907718	-0.965227020077	1.952131835585
C	2.436050614089	-1.126385541178	1.392493448153
C	1.991771965154	-2.510186106441	1.917784935395
C	3.276275006007	-3.036277149934	2.591815623614
C	4.317125584091	-3.284911429599	1.475744422909
C	4.758333254547	-1.850635275872	1.058985246549
H	4.579272431538	-1.638485422928	-0.000927248855
H	5.821461367028	-1.674832566113	1.253633407537
H	3.877357569406	-3.842306324288	0.640983272476
H	5.166152633515	-3.870300401753	1.844046300109
C	3.830217911086	-1.769421422413	3.291550004234
C	2.921879850320	-1.200826871515	4.384582713885
H	3.268294612399	-0.204057123131	4.693229507950

H	1.875402074207	-1.106949398557	4.091727378952
H	2.978120219417	-1.849742769331	5.268501447269
C	5.215953222115	-1.947978875765	3.916932530777
H	5.600523041587	-0.979784429551	4.266827362101
H	5.142870312173	-2.604361116809	4.793304048978
H	5.959624228161	-2.378797194455	3.241210371855
H	3.110370665551	-3.898740946953	3.246449967375
H	1.161005659984	-2.408597299412	2.624269088300
H	1.659344753996	-3.160825352703	1.102369837386
H	2.429165745478	-1.085279372630	0.295374315155
H	4.610529618483	0.827504282879	3.008224472591
H	4.853177904142	0.874822868050	1.233317731266
O	2.324404469785	2.327190267805	2.885440030490
C	-0.631479720704	0.551858293703	2.305366840221
H	-0.337556896288	0.568424232900	3.351492748607
O	-0.827801165219	1.277799758639	-2.327585894625
C	-1.179858083213	1.919127161169	-3.381960176152
C	-0.849746906728	3.204709015541	-3.729922089842
H	-1.095251361422	3.564884133673	-4.724740230563
N	-2.002574970033	1.155612462886	-4.273282159772
S	-1.600589132504	-0.485978079765	-4.394370924358
C	-2.588722995826	-0.804821940970	-5.874506691134
C	-3.298370319321	0.494122135135	-6.198902251689
C	-3.426739277707	0.870707533612	-7.684733523431
C	-4.443863662879	2.048232730081	-7.640854100066
C	-4.810098060658	2.153774678483	-6.142917685557
C	-3.602833461834	2.772711180058	-5.411181536804
H	-3.815761464320	2.981786759938	-4.358490030264
H	-3.276164958860	3.709056214697	-5.875518775861
C	-2.523735464407	1.668168377860	-5.543124593919
H	-1.686737977293	1.984651041883	-6.182798329534
H	-5.754022721882	2.674560112236	-5.949658777638
C	-4.759477489091	0.677696424533	-5.677040510805
C	-4.963730999727	0.480601114435	-4.172646938200
H	-6.010826849092	0.698441823104	-3.924042287268
H	-4.772262366999	-0.564286997105	-3.892510503575
H	-4.326221790433	1.110173018905	-3.549590075799
C	-5.761270923385	-0.239448107229	-6.382868837557
H	-5.563938679996	-1.289008009113	-6.124885944895
H	-6.776765259680	-0.005717318016	-6.039056366932
H	-5.753376380852	-0.154854589252	-7.472777137123
H	-5.324749572204	1.835835935556	-8.255463330035
H	-4.009766984565	2.984533927913	-8.009207203325
H	-2.454279568708	1.157199849288	-8.099837563250

H	-3.799438420061	0.026672595446	-8.274313168283
H	-1.862947062351	-1.101073736933	-6.638671429405
H	-3.253971613299	-1.643469682549	-5.644094061530
O	-2.146167454132	-1.225009616336	-3.230710720971
O	-0.173762868236	-0.685017063275	-4.676470186257
C	-0.080679069440	4.101122772496	-2.873954481792
C	0.701016042441	5.119994850629	-3.456707969214
C	-0.083073697937	4.026366577166	-1.463971230742
C	1.463966129939	5.984059618081	-2.680700249495
H	0.710523516433	5.219863206070	-4.541593839585
C	0.691716581619	4.887629911203	-0.689584173174
H	-0.739375099282	3.311365857602	-0.970581902728
C	1.479461557622	5.867071131145	-1.290082734610
H	2.059991712753	6.754206938857	-3.167589019917
H	0.667562928826	4.793836528222	0.394965821172
H	2.085192062756	6.537400631778	-0.684682890075
C	-2.028175336069	0.831882295787	1.977359628370
C	-3.031554172784	0.617173117740	2.940757403515
C	-2.433833730777	1.338360802162	0.726088996836
C	-4.371224033072	0.857818878904	2.655734724576
H	-2.746719056265	0.247586917613	3.925062828157
C	-3.776829600853	1.576051893542	0.441594147844
H	-1.681308910996	1.593764728967	-0.018633383747
C	-4.757328425906	1.327426541561	1.400141537569
H	-5.122821346734	0.675114069168	3.421743502904
H	-4.052991159689	1.976590385953	-0.533108364877
H	-5.805982073494	1.512359428725	1.178382310472
Na	1.089896513372	1.533422906429	-1.227867005206
Na	-1.508291729294	-0.499019240788	-1.180536032302

Table S46. Atomic coordinates and single point energies for unsolvated dimer of enolate **4g** with double chelation to the *endo* sulfonyl oxygens.



G = -3078.252455

G_{SP} = -3079.542040

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E2S0_endo-endo: optimized structure // E(RM062X) = -3080.25493831 A.U. after 12 cycles

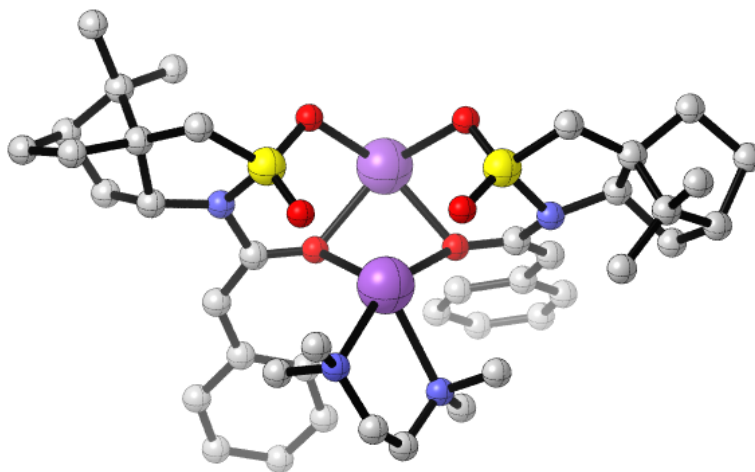
O	0.220369325246	-0.043760100994	0.107753487400
C	0.177515974529	0.034881457050	1.387675634054
N	1.475709704577	0.034965213448	2.075501891061
S	2.253650834420	1.530180315939	2.092681823830
O	2.379872303583	2.072258591667	0.710718169313
C	3.870402369164	0.879987409766	2.579818543797
C	3.775516713028	-0.624286096409	2.368798896161
C	2.464526739102	-0.947780222059	1.603705420894
C	2.156435275066	-2.408165395340	2.002144227399
C	3.406373817051	-2.796383571497	2.818797775603
C	4.608703984993	-2.822517015592	1.846479667735
C	4.892157969947	-1.316067037200	1.569815658980
H	4.830848237134	-1.056573419773	0.506958872941
H	5.882288368199	-1.012249985341	1.925060561670
H	4.365852046033	-3.374115496212	0.931155840590
H	5.477041559796	-3.313018944072	2.298342926938
C	3.672780539221	-1.515580740843	3.648669076510
C	2.553353135804	-1.154768401667	4.627944118311
H	2.717474383165	-0.153654036271	5.051421152794
H	1.555251501975	-1.163201379345	4.188205855013

H	2.569987927753	-1.864756967812	5.465322104093
C	4.974720428631	-1.543390528083	4.453340102383
H	5.174101325431	-0.552274221781	4.884171586315
H	4.876336621946	-2.247430175434	5.289262938971
H	5.852839756313	-1.839064407523	3.872854174370
H	3.285088999167	-3.715812946760	3.401614055478
H	1.236635903689	-2.464586085560	2.593902745200
H	2.026283589199	-3.045217883364	1.121220921434
H	2.604134534480	-0.846074360091	0.518559958402
H	4.037284331121	1.174220425876	3.621142431464
H	4.595286949130	1.380995903546	1.931198658071
O	1.645793418269	2.420976444196	3.080340281591
C	-0.904040785772	0.084669649463	2.216364269786
H	-0.718236738990	0.047377041376	3.286491255274
O	-0.240006506707	0.880556036331	-2.657056070293
C	-0.865151050024	1.511201342972	-3.583225078878
C	-1.086365611608	2.849353918131	-3.722408012889
H	-1.555409052402	3.187503903573	-4.642591974082
N	-1.393169410142	0.686661724110	-4.678530116673
S	-2.856063594766	-0.075432113874	-4.331828131887
C	-2.778169290762	-1.240341887981	-5.714216127831
C	-1.342942589028	-1.169366647479	-6.215538534387
C	-0.578157671011	-2.488458350739	-6.412989521113
C	0.678209208600	-2.023628762561	-7.207780726479
C	0.439390965731	-0.510188994490	-7.417819902140
C	0.673812824584	0.189752419373	-6.063145006804
H	0.625355200317	1.280949847551	-6.142731360932
H	1.644267965403	-0.070459778815	-5.628061886546
C	-0.493175584184	-0.350827160806	-5.207353041997
H	-0.131911980931	-0.985975148315	-4.386725692460
H	1.015774324338	-0.078894581157	-8.243350252735
C	-1.100158226256	-0.430880758830	-7.571516273878
C	-1.651740678277	0.993559788148	-7.666476633307
H	-1.397146926375	1.409354608916	-8.650271296269
H	-2.748582564937	0.989460249734	-7.592748197065
H	-1.275800085636	1.670293982418	-6.898133444326
C	-1.656182643686	-1.203045909289	-8.770661311359
H	-2.753727157550	-1.233743607909	-8.724519445533
H	-1.384178278321	-0.686559875714	-9.699837750952
H	-1.295263735602	-2.232388815442	-8.845982842128
H	0.760505952168	-2.551281290122	-8.163599592506
H	1.608242773658	-2.205152996578	-6.657202350685
H	-0.330222952988	-2.944882470432	-5.448129306143
H	-1.175003947478	-3.213980986040	-6.975352426710

H	-3.061491064530	-2.210831041452	-5.295812085333
H	-3.523558962328	-0.920394770082	-6.449630263078
O	-3.967396578013	0.871723876933	-4.411087540838
O	-2.752619189508	-0.860378341689	-3.069741386313
C	-0.647743534860	3.860827769463	-2.761259790989
C	-0.343422540320	5.161423317070	-3.204251162688
C	-0.527140791404	3.605819867612	-1.381259797863
C	0.093829875485	6.141557819373	-2.320175029541
H	-0.448224922921	5.395673309202	-4.262900766710
C	-0.086345940211	4.586926304902	-0.496303523672
H	-0.843321216339	2.639473621715	-0.992233726545
C	0.238429008142	5.859270168352	-0.961611780151
H	0.326884915219	7.136322533508	-2.695929748276
H	-0.010708250828	4.355041263651	0.564744231995
H	0.584345501229	6.626011988423	-0.272106213165
C	-2.293268674282	0.087013439923	1.759219777704
C	-3.299160614271	-0.460050018996	2.577487923109
C	-2.694321171036	0.634663883261	0.525006264043
C	-4.627096033168	-0.491112377013	2.166480534841
H	-3.023487795510	-0.871548868662	3.547680425760
C	-4.024211199044	0.600986037974	0.112354427574
H	-1.957774694717	1.148342686347	-0.090281673719
C	-4.998878962472	0.027185352431	0.925706486246
H	-5.380172275923	-0.926910065660	2.820713485098
H	-4.297856213152	1.039242967319	-0.845955488389
H	-6.037496835259	-0.001388276927	0.604107287479
Na	1.267990294408	1.465113844936	-1.159513119661
Na	-1.202644383825	-0.718287601196	-1.433195339679

TMEDA-solvated dimers

Table S47. Atomic coordinates and single point energies for TMEDA-solvated dimer of enolate **4g** with double chelation to the *exo* sulfonyl oxygens.



G = -3425.602853
GSP = -3427.092270

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E2TMEDA1_exo_exo: optimized structure // E(RM062X) = -3428.02829674 A.U. after 12 cycles

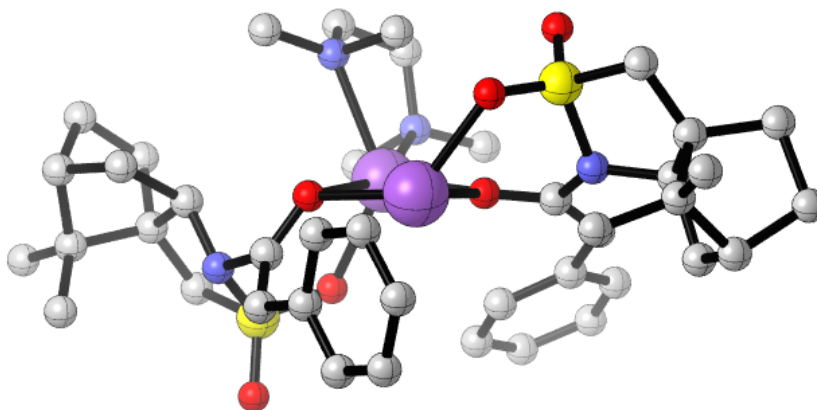
O	0.981450375177	0.064350736089	-0.097585345004
C	0.715848485127	0.261402714411	1.137304609332
N	1.819419372593	-0.027951863112	2.016685246508
S	2.943903987350	-1.113233681113	1.384935599563
O	2.301094540954	-2.321174384070	0.828473850871
C	3.729374025832	-1.508481740762	2.961767463788
C	3.140481402648	-0.549981999671	3.976154346230
C	1.744536399169	-0.080935187151	3.478174482279
C	1.558031735985	1.281568549338	4.196276089082
C	2.769307794677	1.329749303736	5.146427890002
C	2.589483620884	0.206916766248	6.194050359289
C	2.902569238732	-1.092118418463	5.395475270209
H	2.078342494317	-1.813522435916	5.406374061544
H	3.793128315429	-1.603589565240	5.775364464487
H	1.572197648452	0.206377443720	6.601647422829
H	3.275928726795	0.330348182193	7.037906734659

C	3.907796471822	0.782643220364	4.252031338431
C	4.216218233406	1.644666484724	3.025272268949
H	4.971735575202	1.157533612227	2.394913615510
H	3.349502478923	1.853426327142	2.394876101759
H	4.635435063002	2.602660233081	3.360445075120
C	5.233523958978	0.565389618991	4.985839374032
H	5.932575826185	0.001150486168	4.353341039747
H	5.697972117738	1.537129953789	5.195873192673
H	5.136204986155	0.033836503142	5.936320684770
H	2.948049349480	2.319889354982	5.579104739131
H	1.563649801006	2.104709249672	3.475497886963
H	0.607988010207	1.319654017748	4.739618936821
H	0.964686926435	-0.799819702179	3.770053585783
H	4.810874826485	-1.415986723425	2.818067027928
H	3.465230029192	-2.553489660569	3.154052252192
O	3.864965981149	-0.401456978788	0.474046998561
C	-0.456213754492	0.696779355173	1.706937962123
H	-0.507300934066	0.784694746398	2.787797479093
O	1.414016142015	-0.564934279566	-2.906646675736
C	1.657836735030	-0.633176132495	-4.158324177138
C	1.204185864076	0.193204144099	-5.157586704835
H	1.502539890827	-0.007774797347	-6.182122984049
N	2.508419590126	-1.744745582346	-4.514684186345
S	3.534625028394	-2.195779339784	-3.244026394338
C	4.729952890890	-3.089163324640	-4.264020195095
C	4.196693863893	-3.043181232939	-5.682274927160
C	5.209998435176	-2.814019803480	-6.816266711216
C	4.361435297824	-3.137753260467	-8.081430639577
C	2.999318790567	-3.587721816367	-7.502430958029
C	2.274792304969	-2.328148092069	-6.989298703277
H	1.259714671255	-2.543319843786	-6.639848133911
H	2.204625086271	-1.553951419638	-7.760616191242
C	3.176475463800	-1.875142115972	-5.812290706025
H	3.695870933272	-0.933072912471	-6.040886808597
H	2.398234332054	-4.190305079440	-8.191697284333
C	3.409188700897	-4.292898840229	-6.186944424591
C	2.238422127452	-4.727004958028	-5.305227996177
H	1.707618342365	-5.556955798938	-5.790220803070
H	2.602499454832	-5.093199761467	-4.335051910467
H	1.521047852399	-3.930649332097	-5.108920712177
C	4.300343800976	-5.522044361567	-6.382076544849
H	4.701425428953	-5.859318365417	-5.416301600098
H	3.701252811420	-6.345767574458	-6.790339193788
H	5.144147674468	-5.360801513208	-7.058226720233

H	4.824974953910	-3.928699138007	-8.679942101932
H	4.243705871346	-2.265294573808	-8.733999300875
H	5.587586532232	-1.786002943727	-6.803227038300
H	6.071210318930	-3.482731370593	-6.716727481259
H	5.670378483326	-2.544848596481	-4.133270847467
H	4.819552446459	-4.097698511483	-3.847476607176
O	2.817641859216	-3.074992110069	-2.304067513422
O	4.209487888950	-1.015511309939	-2.654409566476
C	0.337145020005	1.343413974675	-4.950779729022
C	-0.095563325360	2.072588676940	-6.080559584706
C	-0.101674463149	1.801988002990	-3.687062974059
C	-0.910979817748	3.190613816311	-5.961984030707
H	0.223497153695	1.744439643683	-7.069587923466
C	-0.914649697125	2.927781842866	-3.576965208015
H	0.202120625570	1.263924599141	-2.793688139469
C	-1.329306490699	3.632447201207	-4.705831912100
H	-1.222564720897	3.723258839404	-6.859229465493
H	-1.227857613292	3.255573518653	-2.586248705872
H	-1.965451326488	4.509633550910	-4.609671165046
C	-1.661504345279	1.053693022899	0.981173260526
C	-2.785409148330	1.489165427395	1.720249814045
C	-1.803677116501	0.991405013865	-0.423717989307
C	-3.974036075670	1.850538014272	1.101601662583
H	-2.708664042550	1.542578658138	2.806074483495
C	-2.998956529402	1.365698729818	-1.035941630785
H	-0.963599630028	0.650940110054	-1.024471547834
C	-4.093067380855	1.796489562946	-0.288463957080
H	-4.815330492653	2.180857587132	1.709044757643
H	-3.072495938007	1.323011533333	-2.122366272984
H	-5.020228990248	2.085272639855	-0.778544541491
C	-1.793798671845	-1.399760601394	-3.275577809647
H	-1.011975834376	-0.826215676904	-3.785888865913
H	-2.502177333352	-1.792088195657	-4.031359760832
C	-2.182284916106	-3.174147182868	-1.710617659349
H	-2.922418409973	-3.682512063979	-2.360917934594
H	-2.733654961041	-2.424970144637	-1.128162174628
C	-0.454213156573	-3.364011925437	-3.391626359698
H	0.142575306129	-4.089000944095	-2.823724068597
H	-1.132262719754	-3.921647136934	-4.068379128173
H	0.232965421139	-2.766969379673	-4.000169318624
N	-1.180961074530	-2.468933107603	-2.501540608593
Na	0.860703750536	-2.004133210990	-1.191398440549
Na	2.790656909657	0.390294471406	-1.417266824999
C	-1.570733500769	-4.217240553685	-0.785978378383

H	-2.375181808807	-4.629804922820	-0.145649071641
H	-1.177000229177	-5.054502273353	-1.375254680188
C	-0.951344627182	-2.694035058126	0.979247484572
H	-1.755266241958	-3.092376605083	1.628792666399
H	-0.113537788941	-2.377798874484	1.610174670826
H	-1.334321164228	-1.805906230634	0.459621570682
C	0.209481383780	-4.771346487358	0.717503467537
H	-0.463132110161	-5.314309920251	1.408926084664
H	0.603469006624	-5.486711294888	-0.013913421159
H	1.048769185615	-4.359668230137	1.286906900390
N	-0.476039315527	-3.690232082126	0.024539222438
H	-2.341545750684	-0.729528988558	-2.605972108203

Table S48. Atomic coordinates and single point energies for TMEDA-solvated dimer of enolate **4g** with chelation to one *exo* sulfonyl oxygen and one *endo* sulfonyl oxygen.



G = -3425.591574

G_{SP} = -3427.083436

116

E2TMEDA1_exo_endo: optimized structure // E(RM062X) = -3428.01877367 A.U. after 12 cycles

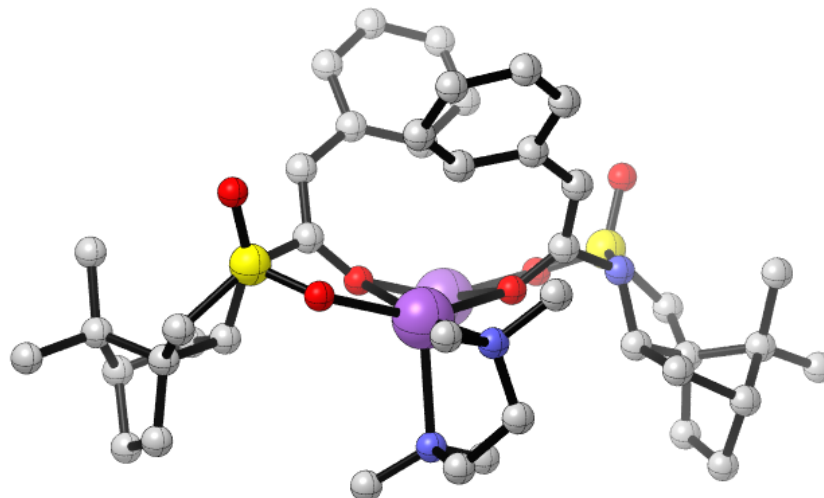
O	-0.190513440708	-0.834613225021	-0.112040502745
C	-0.190141886994	-0.087298565410	0.925598823397
N	1.053194364711	-0.077214039764	1.718312560455
S	2.195463643518	1.053039119428	1.213578277073
O	2.378518182735	0.981376784596	-0.259227966347
C	3.620595298898	0.252893092668	1.998157252732
C	3.113052336893	-1.095858293113	2.479074717700
C	1.734881967178	-1.375213832022	1.828732093118
C	1.060940048516	-2.359368996751	2.811685283057
C	2.188186960356	-2.638726887066	3.827481770121
C	3.295405945223	-3.421933475213	3.086256552498
C	3.957236073010	-2.346428660567	2.174619479736
H	3.904938652623	-2.605047113758	1.109326794645
H	5.012072508470	-2.188340195332	2.422684028479
H	2.874210415229	-4.253821427936	2.509632880683
H	4.021039421277	-3.849060234150	3.786201729958
C	2.830195586376	-1.240883271359	4.008409197079
C	1.897112599886	-0.188828235976	4.612712979401

H	2.341728365406	0.813241675686	4.529459745838
H	0.911249573770	-0.147595868692	4.147362114204
H	1.768236235469	-0.397020801682	5.683035569928
C	4.109793249178	-1.235100766019	4.848387380730
H	4.578280164642	-0.241589366625	4.816104179441
H	3.863506255876	-1.443943027834	5.897205829449
H	4.857409577539	-1.967379245295	4.531177652146
H	1.843488611794	-3.119826013730	4.749229847365
H	0.183820496326	-1.897971713833	3.277788498368
H	0.728537243473	-3.272524461398	2.307563131472
H	1.852620142918	-1.811149381522	0.827440463024
H	3.962235381277	0.913339208823	2.802128824564
H	4.384448174029	0.192400889702	1.216091386770
O	1.897599115379	2.376948099860	1.762058076370
C	-1.172601840912	0.728922477398	1.412382612454
H	-0.934774907223	1.361590974495	2.263751763773
O	0.077290376558	0.110814173800	-3.167893945440
C	-0.068346070635	0.605471638141	-4.339076634679
C	0.772136048818	1.439209791094	-5.031456856132
H	0.548481751755	1.657384702516	-6.072062080127
N	-1.312681477918	0.235936971192	-4.967829195361
S	-1.784558431589	-1.380690898098	-4.815723589064
C	-3.088885469096	-1.304591317676	-6.066884210123
C	-3.170865887132	0.145069922276	-6.498190078717
C	-3.463184263595	0.413992502884	-7.985145307020
C	-3.773472057027	1.938829724915	-7.993658210868
C	-3.663543079537	2.335952562852	-6.505113762551
C	-2.167384110232	2.324991695291	-6.129624770836
H	-1.988285794072	2.706765736302	-5.119966942098
H	-1.565315958576	2.923990696200	-6.820693808430
C	-1.804907585999	0.821165487493	-6.217789207126
H	-1.095838057633	0.612876179756	-7.031817194532
H	-4.171569079851	3.273175448474	-6.253778987278
C	-4.198601278612	1.077286611775	-5.777637931922
C	-4.107232605554	1.149482050981	-4.248658740879
H	-4.858310551189	1.863112624361	-3.884836772030
H	-4.339604725615	0.172562168707	-3.802692436467
H	-3.131538246668	1.468676566767	-3.874464393618
C	-5.650604981520	0.723068141878	-6.111093600472
H	-5.917151337879	-0.245341363050	-5.665697125033
H	-6.320955460187	1.475778274741	-5.677274920757
H	-5.863333874489	0.668465555179	-7.182116370579
H	-4.774524798048	2.139149698433	-8.389393689418
H	-3.062587959591	2.502916582424	-8.607766709640

H	-2.599553123793	0.147944645146	-8.604479638811
H	-4.312508066827	-0.181821285847	-8.334944480217
H	-2.753200362155	-1.969746631102	-6.869290423230
H	-4.000654800214	-1.700118855016	-5.607710262627
O	-2.370328697970	-1.608028276999	-3.472468910924
O	-0.725242037359	-2.310569972292	-5.226764772175
C	1.969718632065	2.055283719679	-4.477595530037
C	2.959140577813	2.552936297511	-5.350574635568
C	2.196218327923	2.211181095915	-3.094987079682
C	4.122811970635	3.142630016284	-4.870258723124
H	2.808562888659	2.458704015898	-6.425904979877
C	3.361770388548	2.803060875230	-2.617369875085
H	1.441885149380	1.882117911345	-2.386559502649
C	4.340188380510	3.266110624860	-3.496810143363
H	4.869027690842	3.506760983791	-5.574897628916
H	3.494538090137	2.894758701326	-1.540859198615
H	5.252582143948	3.724181186291	-3.120593236418
C	-2.482734650746	0.871260021743	0.769331719919
C	-3.091397573204	2.132549198496	0.638870437612
C	-3.186301985929	-0.243025240840	0.267334349713
C	-4.319616217526	2.278044242928	0.001492360976
H	-2.576760898527	3.008860367973	1.030508961785
C	-4.410053075226	-0.093663383860	-0.384693072904
H	-2.764327799979	-1.238789706919	0.408170565264
C	-4.981307631361	1.169892834809	-0.527416424661
H	-4.759817428414	3.269077232913	-0.093449548684
H	-4.924865467554	-0.973362906996	-0.768182310196
H	-5.936417036381	1.288279162618	-1.034448018801
N	1.761909088747	-3.091860137019	-1.552929569182
C	1.258807349573	-3.894860087068	-0.448263221998
H	2.002170742248	-3.925582007529	0.358198211208
H	1.045530181801	-4.935323120726	-0.759941632287
C	3.082796852552	-3.559056977257	-1.960913293607
H	3.727330759573	-3.551329082728	-1.071349460186
H	3.042675494278	-4.608193868747	-2.315865686115
C	0.807813832775	-3.127802551106	-2.659269993565
H	-0.185378505417	-2.845546532605	-2.289466913368
H	1.079408616638	-2.420638731400	-3.450267336754
H	0.731769392933	-4.137008947470	-3.107847228030
Na	1.582165049656	-0.631144010351	-1.687359429710
Na	-1.583316805376	-0.319271295542	-1.789617488200
H	0.341441080608	-3.436035294234	-0.061455912778
C	3.699231973640	-2.718235083663	-3.067953215774
H	4.730781410925	-3.082939496299	-3.241508492801

H	3.149621304089	-2.872616312842	-4.004166288248
N	3.701718480917	-1.282209418812	-2.790437025366
C	4.151479870486	-0.564660257111	-3.979104794503
H	4.194668032071	0.508435134850	-3.771117446624
H	5.154737490842	-0.902769846616	-4.302588892944
H	3.444470544300	-0.733037211575	-4.800155554766
C	4.555810150236	-0.959658043190	-1.652356733685
H	5.590993309750	-1.326905838286	-1.793179616203
H	4.579732898960	0.127656963019	-1.516448764562
H	4.151652785596	-1.404052594100	-0.733180682160

Table S49. Atomic coordinates and single point energies for TMEDA-solvated dimer of enolate **4g** with double chelation to the *endo* sulfonyl oxygens.



G = -3425.586377

G_{SP} = - 3427.076820

116

E2TMEDA1_endo_endo: optimized structure // E(RM062X) = -3428.01362289 A.U.
after 12 cycles

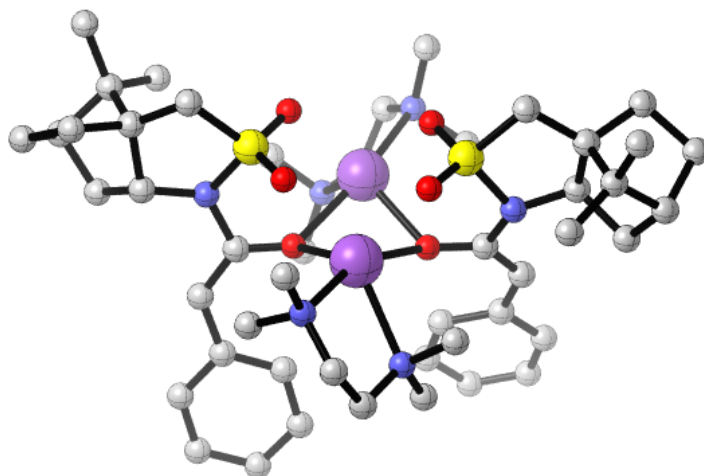
O	-0.049119285353	-0.018177847710	-0.023003734586
C	-0.022781957750	-0.001302560443	1.254966670309
N	1.323541366224	-0.005116828026	1.863633540682
S	2.027882220883	1.512093898242	2.025938372574
O	1.987690253541	2.247714947413	0.729530206772
C	3.714170552622	0.904325892868	2.280122075686
C	3.670344956478	-0.567154591402	1.895111314401
C	2.316233189193	-0.863893287383	1.200650551010
C	2.104672510193	-2.376004799448	1.432518966214
C	3.434367750412	-2.794674206688	2.093779268479
C	4.548488725829	-2.636729836861	1.032448047208
C	4.744707303886	-1.094849697369	0.930317245100
H	4.584808364733	-0.708307784184	-0.082652642844
H	5.747306053977	-0.786785949135	1.244474774338
H	4.248736303408	-3.080745414075	0.076000301678
H	5.472513483719	-3.134639094633	1.344026789973
C	3.714474415316	-1.612473400840	3.056043299129
C	2.666550309134	-1.431800708709	4.156761234433

H	2.824665154600	-0.481408278556	4.686159940901
H	1.636246961915	-1.438284616639	3.798486324906
H	2.782455645607	-2.235564236255	4.895681330219
C	5.079660757841	-1.670330193130	3.745931945880
H	5.277071418307	-0.726300368655	4.272786364881
H	5.079505098034	-2.469055930755	4.498291195758
H	5.915933665342	-1.855734239899	3.066327328620
H	3.402471701675	-3.783927823766	2.562689128368
H	1.240007924517	-2.553381022224	2.081328091280
H	1.931287080131	-2.907754512836	0.490026710892
H	2.361123520094	-0.619283295911	0.130599002820
H	3.965184808227	1.083921620106	3.330680945438
H	4.349963276205	1.518877257152	1.635750572488
O	1.480821027320	2.226134114878	3.180711633807
C	-1.044247597823	-0.012578143669	2.161122661177
H	-0.766610229500	-0.072699939221	3.210361127157
O	-1.196979817597	1.685632415900	-2.149798023298
C	-2.284670546363	2.319150883740	-2.380381469800
C	-2.933857970229	3.266409249220	-1.640111240647
H	-3.820725990971	3.702939885197	-2.092224420507
N	-2.949527206011	2.003682886454	-3.654890171728
S	-4.005080754300	0.697037561799	-3.592454383573
C	-4.085966376530	0.445852684557	-5.386166527228
C	-3.003582138497	1.341690529516	-5.966804614971
C	-2.070075183660	0.746314090680	-7.035003885108
C	-1.353557700995	2.010981814173	-7.593109511563
C	-1.998780762446	3.171507288041	-6.802822837653
C	-1.448347088892	3.111986645515	-5.362286168866
H	-1.760183823883	3.971166606554	-4.758935796284
H	-0.354106417439	3.071722528150	-5.343432762255
C	-2.073691058311	1.807481814363	-4.818565609438
H	-1.313380160654	1.049207175551	-4.588192478079
H	-1.886382638818	4.151688360707	-7.278738168494
C	-3.459125400614	2.684580675347	-6.625094943765
C	-4.328659198461	3.598658957653	-5.757524528733
H	-4.612849694324	4.482074480142	-6.344363443713
H	-5.258504661019	3.087428346310	-5.470027143005
H	-3.845667076835	3.935495337661	-4.839253322315
C	-4.217695420444	2.468935243543	-7.937445222180
H	-5.203026893018	2.026634701625	-7.734947987538
H	-4.390556704983	3.435900675597	-8.426688379427
H	-3.701463598349	1.822630170133	-8.652472636171
H	-1.520056774399	2.119295608800	-8.669942162383
H	-0.269453900921	1.977734677529	-7.435204573657

H	-1.375386454016	0.026456320055	-6.588449000281
H	-2.636111294981	0.218769633696	-7.809782920714
H	-3.909507170625	-0.623242087541	-5.540239178520
H	-5.100940162680	0.705267999411	-5.704883126498
O	-5.288006158142	1.090630079631	-3.003712797268
O	-3.344174060794	-0.483368577216	-2.976959834833
C	-2.515591167449	3.822320804321	-0.356460121440
C	-3.096443726771	5.037269775722	0.062517588904
C	-1.574373601121	3.232833803379	0.510598650470
C	-2.741671714162	5.638726394715	1.263041824159
H	-3.840216582825	5.509967015949	-0.577890516631
C	-1.217996036329	3.836780241349	1.714695597951
H	-1.162650056020	2.255579164712	0.276138874620
C	-1.791843374717	5.046897769839	2.096730293550
H	-3.211315793413	6.577628889339	1.551562241751
H	-0.490999708411	3.344785368768	2.360459116807
H	-1.512883348078	5.516016971059	3.037657889771
C	-2.466133310641	-0.098284363448	1.840480391446
C	-3.344409757790	-0.603944732028	2.818749706368
C	-3.026099841207	0.254695947123	0.596873698318
C	-4.694795736515	-0.797186229977	2.552947484851
H	-2.944672517543	-0.866883081215	3.797663629637
C	-4.379911390060	0.064492898139	0.331212250452
H	-2.404434809831	0.727371550319	-0.157724208222
C	-5.221651760944	-0.478001179684	1.300898356221
H	-5.341705526894	-1.202433557369	3.329377073579
H	-4.777072852709	0.352116492347	-0.642297988811
H	-6.277920628268	-0.631122516759	1.090337150362
C	0.168398782192	-1.474694068657	-4.526049921945
H	0.893633616955	-2.091701183387	-5.090135101995
H	-0.819026515180	-1.594137850632	-4.986148358474
C	1.385682309542	-1.620842868877	-2.469456171647
H	2.176847336351	-2.286069203874	-2.866749719236
H	1.696050229346	-0.582583059602	-2.641403744773
H	1.295561619337	-1.765687968653	-1.388300324830
C	-0.317781521554	-3.251714359023	-2.997322521598
H	-1.161889982180	-3.406622827605	-3.679849559543
H	0.491236426680	-3.929222605909	-3.333671102151
N	0.101372231095	-1.853593018055	-3.121040066491
Na	0.663566363352	1.853775127020	-1.049365185735
Na	-1.427278807507	-0.613153013026	-1.712435767269
H	0.471878483184	-0.424921614397	-4.611850718113
C	-0.717862483118	-3.647452332765	-1.583589531214
H	-0.912807030401	-4.737864274019	-1.570791139134

H	0.121226224934	-3.472858023713	-0.897873765548
C	-1.966590100683	-3.078629569413	0.375073024568
H	-2.026322739830	-4.147099822270	0.659471947824
H	-1.091170232927	-2.628104955482	0.859795533070
H	-2.863734458171	-2.569955052505	0.744792651904
C	-3.114636135172	-3.340625260175	-1.700956396340
H	-3.944207760385	-2.744116717864	-1.305904809159
H	-3.080116898655	-3.176190154416	-2.781941781347
H	-3.318823470336	-4.411289069865	-1.506167624445
N	-1.871842033076	-2.909608605503	-1.070676705622

Table S50. Atomic coordinates and single point energies for *bis*-TMEDA-solvated dimer of enolate **4g** with double chelation to the *exo* sulfonyl oxygens.



G = -3772.936020

G_{SP} = -3774.628955

140

E2TMEDA2_exo_exo: optimized structure // E(RM062X) = -3775.78741013 A.U. after 13 cycles

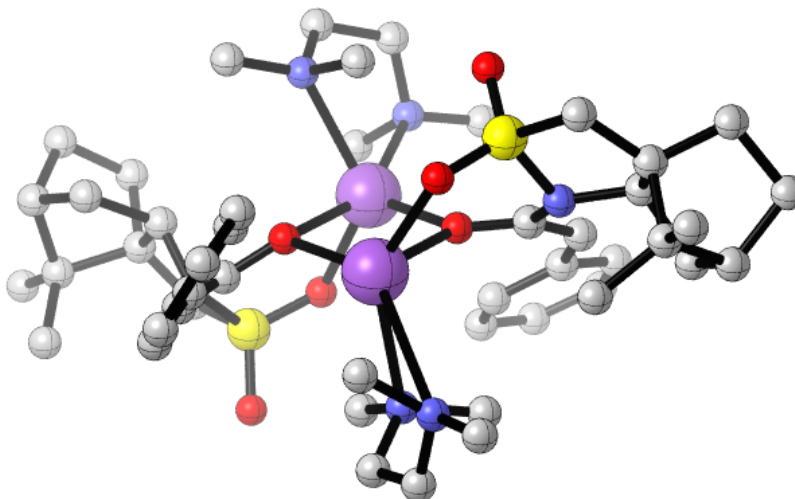
O	0.506980733597	-0.005825880448	-0.038114603798
C	0.219777088038	0.127173497763	1.194393790391
N	1.338424131118	-0.084295689159	2.081120887595
S	2.617993922001	-0.944835679481	1.386695581096
O	2.163230061158	-2.174298160979	0.705857205544
C	3.399073259386	-1.411664746268	2.948932243907
C	2.657550016080	-0.669484090895	4.040170904991
C	1.235943704431	-0.289192083493	3.527271271645
C	0.884170060692	0.961512019570	4.375776568821
C	2.030164104552	1.001017783715	5.402951836579
C	1.910247211982	-0.262196146022	6.289259809762
C	2.415036547647	-1.410125794689	5.365528586200
H	1.682877928683	-2.214986267296	5.238948460673
H	3.340085663883	-1.861247288532	5.739583786518
H	0.875041033413	-0.418649854397	6.613520068283
H	2.522479338450	-0.180046042445	7.193178875269
C	3.264930442141	0.684174508742	4.526662561232
C	3.541840428817	1.707945319299	3.425888511188

H	4.393366748397	1.388806458327	2.809784280483
H	2.696826022866	1.867679130466	2.756468852384
H	3.807656516587	2.670339106472	3.883603558945
C	4.565528721633	0.512223528825	5.315115714362
H	5.346438489327	0.077615613279	4.675947440957
H	4.924569432967	1.496113900702	5.642615116470
H	4.470065052860	-0.116457350498	6.204544659013
H	2.082243622466	1.938372126248	5.967157956702
H	0.855787506206	1.860580847846	3.751713891425
H	-0.094145503860	0.856882948804	4.856463153467
H	0.526521440020	-1.108022463655	3.717877172530
H	4.461643403483	-1.159486320904	2.869972003019
H	3.277468591416	-2.498095642326	3.005760138067
O	3.452079868483	-0.026964352614	0.590432351025
C	-0.992483340464	0.454037528240	1.761772124330
H	-1.060576444319	0.532349680225	2.842075145107
O	1.009763705300	-0.500283705184	-2.924883178285
C	1.256731071766	-0.610042422157	-4.168327201562
C	0.681873883349	0.069768870674	-5.219872781734
H	1.009749607649	-0.154417338397	-6.229856861437
N	2.264057305430	-1.595529760266	-4.479197711109
S	3.251024296072	-2.011786723562	-3.170597807119
C	4.580626499261	-2.732766289614	-4.161046780285
C	4.079907114825	-2.775160978405	-5.588952585801
C	5.090094367056	-2.466393882790	-6.706173128540
C	4.299274072816	-2.884465959367	-7.981187207945
C	2.983278655402	-3.474346964275	-7.419227201719
C	2.112531958657	-2.299406447185	-6.938288806258
H	1.128644218619	-2.628566439150	-6.588710969063
H	1.955884320478	-1.555453135937	-7.726390856070
C	2.948849287713	-1.718072498699	-5.767588437631
H	3.375324014008	-0.739826807749	-6.034476806674
H	2.466898070899	-4.150052454749	-8.109479749561
C	3.439490506511	-4.110068031166	-6.084814437782
C	2.302561746612	-4.649980350273	-5.217424042934
H	1.818520705827	-5.489397635701	-5.734572625669
H	2.693901509841	-5.030641127712	-4.264288491739
H	1.541520362281	-3.905831822005	-4.983450731850
C	4.456233122720	-5.242855172936	-6.245486040724
H	4.900604158835	-5.499402585765	-5.273914935965
H	3.944645944470	-6.140390339140	-6.615509810924
H	5.270803215842	-5.018240957385	-6.939353399488
H	4.853459142952	-3.623314560763	-8.569088550912
H	4.098690827807	-2.031996417034	-8.640227638569

H	5.371527999745	-1.407787154962	-6.701392516154
H	6.006822236532	-3.052179701049	-6.581267722787
H	5.429088282198	-2.055445914140	-4.020654021458
H	4.811764175958	-3.713197885525	-3.731846414279
O	2.562829018972	-3.012171411892	-2.335176192301
O	3.781895694082	-0.825541523427	-2.468492310637
C	-0.341605969722	1.089826617823	-5.091985875732
C	-0.863285361405	1.667239935874	-6.273241114212
C	-0.866815357828	1.560933712490	-3.865015128487
C	-1.853326669063	2.639128072498	-6.240965842489
H	-0.475377155082	1.330063911907	-7.234348058710
C	-1.865782284265	2.533325572954	-3.844862849937
H	-0.488873308148	1.146708310621	-2.932396712722
C	-2.370882055787	3.081779776711	-5.022149677306
H	-2.227405729329	3.053839213242	-7.175900259802
H	-2.259460549321	2.866494039889	-2.885030068947
H	-3.151276483410	3.838920871692	-4.991344340708
C	-2.217513091860	0.700118711242	1.024860807819
C	-3.374091038639	1.067989807607	1.751468672963
C	-2.351302862696	0.599885545134	-0.380586388253
C	-4.582677153086	1.334199487156	1.123618613396
H	-3.305371010098	1.148254989683	2.836238286627
C	-3.568955002540	0.875741418784	-1.001196690846
H	-1.486784776651	0.314253403661	-0.976599025944
C	-4.693240076718	1.245034059031	-0.265332107081
H	-5.446788700414	1.616937795505	1.723111725656
H	-3.637435703294	0.802708328554	-2.086203073324
H	-5.636577097758	1.458559166663	-0.763075762495
C	3.174695885743	2.101173166555	-3.791236461622
H	2.080158937342	2.173863622704	-3.748447440431
H	3.542805171191	2.814605403318	-4.554682327376
C	-2.115215377342	-1.750989546650	-3.233945054578
H	-1.427040204652	-1.081576689119	-3.761763911226
H	-2.788464879698	-2.228604484085	-3.972803425821
C	-2.230425004673	-3.560542678051	-1.667070553736
H	-2.926311426873	-4.148919515121	-2.298889003093
H	-2.847727086160	-2.887656417345	-1.057992969558
C	-0.548155968992	-3.532799816787	-3.401997414580
H	0.170129849745	-4.159100916092	-2.859192545873
H	-1.175486139571	-4.184621362293	-4.043034507889
H	0.019369276274	-2.854184750206	-4.048082985871
C	3.524124415742	3.721685938098	-2.039232310298
H	4.119456295569	3.889265369126	-1.133251764729
H	3.881128374082	4.450495291355	-2.793660217739

C	5.189642925983	2.062269531249	-2.500024722931
H	5.608523471396	2.205875303136	-1.497067490953
H	5.341502837220	1.018216821979	-2.791670483977
H	5.737791204680	2.717574715665	-3.204325341719
N	-1.349255447565	-2.734623866086	-2.483924148956
N	3.763657976299	2.350858423942	-2.480522952030
Na	0.645516944841	-2.007862473306	-1.200009483769
Na	2.239435054808	0.731620154980	-1.392244146716
C	-1.467631111967	-4.531245756032	-0.776802000693
H	-2.195941149274	-5.050456319354	-0.122774362600
H	-0.989676059103	-5.304019780685	-1.391355635033
C	-0.990551054960	-2.981951136411	1.009168700328
H	-1.705165436312	-3.499846545686	1.678826182790
H	-0.178363152073	-2.566056243245	1.615860554969
H	-1.511693181517	-2.144087438519	0.527966631622
C	0.426514800862	-4.877021749479	0.648920281473
H	-0.138865386696	-5.522722541551	1.348456034037
H	0.884852150398	-5.514614714140	-0.116203314123
H	1.224944366770	-4.368348227211	1.198410817872
N	-0.424128237523	-3.883099050901	0.012064498957
C	2.056554890975	4.007498323588	-1.754140059673
H	1.982066088988	5.029732340341	-1.330917695215
H	1.478888462574	4.008261734022	-2.687471392472
N	1.454571897828	3.023963045061	-0.861838181400
C	2.094095695233	3.010212078624	0.446852251505
H	2.099650365640	4.013937110872	0.917846317340
H	1.539597732339	2.325233205796	1.097520254165
H	3.126886141720	2.647424274799	0.379199554621
C	0.029965874325	3.274968071004	-0.705757710408
H	-0.417139615852	2.469352328627	-0.112958710460
H	-0.165659046378	4.242080896081	-0.202084021197
H	-0.448359228010	3.297048734361	-1.689563616611
H	3.429931834383	1.083917696352	-4.108602904225
H	-2.725576425951	-1.158942707738	-2.545399783057

Table S51. Atomic coordinates and single point energies for *bis*-TMEDA-solvated dimer of enolate **4g** with chelation to one *exo* sulfonyl oxygen and one *endo* sulfonyl oxygen



G = -3772.915012

G_{SP} = -3774.611249

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E2TMEDA2_exo_endo: optimized structure // E(RM062X) = -3775.76815616 A.U. after 13 cycles

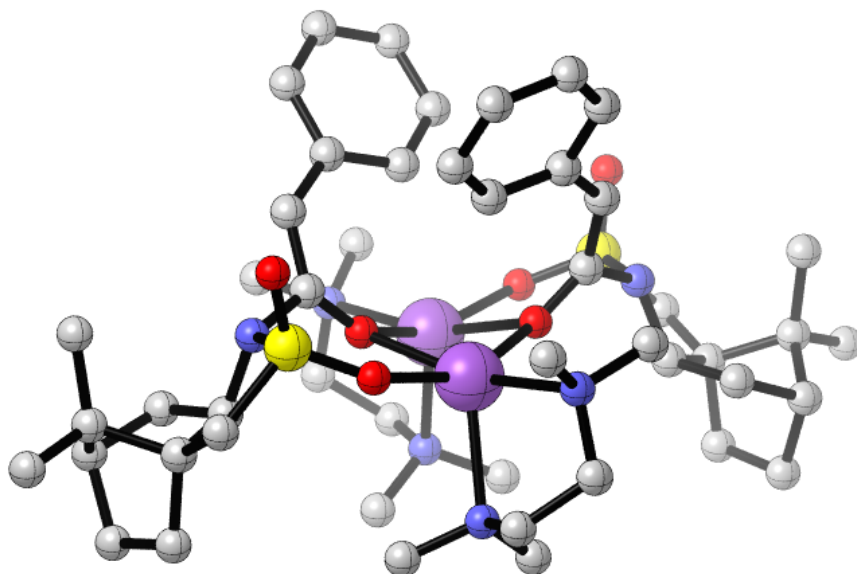
O	-0.046720552681	0.023248580552	-0.117216821107
C	-0.050167220934	0.031805861157	1.154411855770
N	1.255949547862	0.042332166587	1.844768666788
S	2.333363713222	1.281352501603	1.474468834041
O	2.574322932633	1.417289609969	0.015462691338
C	3.794078095949	0.471071056252	2.177632115198
C	3.379283199501	-0.967066007541	2.436976271209
C	2.006173657860	-1.226025351891	1.761709677675
C	1.410541277007	-2.387023142956	2.590285176045
C	2.574906705006	-2.758795030304	3.530215036445
C	3.709462576237	-3.344764207953	2.660077155595
C	4.292004603600	-2.098331636042	1.930752726216
H	4.242231596071	-2.185770629912	0.839005059473
H	5.338603893746	-1.917050757939	2.196897739455
H	3.323928418303	-4.094381882977	1.959161850657
H	4.471182587954	-3.838174042011	3.272788395252
C	3.135693370650	-1.371376776528	3.926200584322
C	2.153475165231	-0.490533003394	4.701236573323

H	2.549807726241	0.529552840597	4.804202581573
H	1.167200215082	-0.413280141751	4.241818630131
H	2.034601120247	-0.894157965371	5.715469423583
C	4.429217160466	-1.420648604133	4.743320925553
H	4.846528915179	-0.410128222295	4.854128072468
H	4.213577474934	-1.795191498682	5.752039628760
H	5.206248161011	-2.057912122457	4.312233418120
H	2.277117146311	-3.401137232446	4.365994656623
H	0.522936456841	-2.054638798686	3.137159304057
H	1.109333421729	-3.226590634158	1.955812530689
H	2.138993539155	-1.495250764229	0.702575379939
H	4.068783934304	1.025032201705	3.081217805191
H	4.575858063381	0.584691179424	1.420109880338
O	1.943571955805	2.505845584457	2.179946137387
C	-1.118997614936	-0.017694238181	2.010330212879
H	-0.926924071472	0.125652792570	3.070410962683
O	-0.048367383688	1.477407392902	-2.796778413254
C	-0.108753760099	2.055027323792	-3.933768266971
C	0.848256185486	2.824481382786	-4.555793310696
H	0.671016930609	3.154414047773	-5.574482986065
N	-1.371805435176	1.890564317217	-4.609726584724
S	-2.120016627704	0.383304340263	-4.410736626927
C	-3.350533713479	0.607610067026	-5.718248629699
C	-3.093702368411	1.974817575944	-6.318298680190
C	-3.168270068042	2.112473516098	-7.847624630698
C	-3.162711680050	3.658423264244	-8.036142332211
C	-3.173039895369	4.202531354148	-6.587791817532
C	-1.766288368376	3.988274622354	-5.999641146834
H	-1.662982986346	4.423141498301	-5.000204778497
H	-0.984114325616	4.419556485321	-6.633083828888
C	-1.660249779025	2.442710579308	-5.936317592548
H	-0.927262392601	2.055664260687	-6.659348407049
H	-3.533496063971	5.233170661287	-6.500555999910
C	-4.007750198119	3.140887977299	-5.833060614277
C	-4.063902247181	3.330171575224	-4.317850913819
H	-4.609663001363	4.254561816269	-4.089537776307
H	-4.612070891053	2.502320460695	-3.847145162429
H	-3.085207836244	3.381589599210	-3.839697380781
C	-5.452138939398	3.014168917758	-6.322985664673
H	-5.919776907314	2.112196108779	-5.904536855312
H	-6.034179019149	3.875038450225	-5.969924778852
H	-5.553012783565	2.971038338860	-7.411121098644
H	-4.039894600913	3.993850845476	-8.598984765082
H	-2.277121270112	4.005249041142	-8.580761819768

H	-2.318734284596	1.616719913221	-8.329927940843
H	-4.082915117511	1.654991056973	-8.239166105577
H	-3.166846745616	-0.215712302556	-6.415215607082
H	-4.337374755038	0.495426047868	-5.257430949075
O	-2.759483100685	0.311970561806	-3.078016967772
O	-1.231465766003	-0.726296463391	-4.780366590314
C	2.101997000675	3.251978835591	-3.958096198442
C	3.096481894811	3.817785897321	-4.786485353333
C	2.399275463495	3.159218899540	-2.582106192822
C	4.319761424295	4.234967140557	-4.277701900737
H	2.897046766004	3.916561783324	-5.853459388357
C	3.626430225282	3.577937691767	-2.075603201951
H	1.652809983507	2.773421026437	-1.896993919560
C	4.602952306554	4.111284343442	-2.915361396653
H	5.062943839509	4.658271398076	-4.951880368559
H	3.808403194923	3.474893380072	-1.007022776459
H	5.563055701503	4.433460536850	-2.517863436434
C	-2.497140980214	-0.249490777246	1.594513497417
C	-3.552503210132	0.081918095607	2.469604463751
C	-2.845041296368	-0.857645797404	0.367927997646
C	-4.877351162722	-0.174067324550	2.138432026422
H	-3.314637705445	0.542590119159	3.427997506910
C	-4.174928878493	-1.111077915703	0.041561646318
H	-2.055859664233	-1.173245109885	-0.312572239282
C	-5.201867954712	-0.770135263056	0.918938397682
H	-5.666303905874	0.096786623213	2.838390659295
H	-4.405641508416	-1.584773578497	-0.911389776197
H	-6.239932866633	-0.966695506089	0.659089107049
N	1.567800255086	-2.201706946073	-1.872065234245
C	1.053626417964	-3.136975712145	-0.884827294984
H	1.853157349026	-3.426765837545	-0.192943676383
H	0.659555234594	-4.057682659896	-1.356612269456
C	2.780896965290	-2.722807500977	-2.489760592911
H	3.493534748426	-2.947256091502	-1.684574255684
H	2.586720406217	-3.678314264871	-3.017179442046
C	0.528808366540	-1.916082724302	-2.855762072434
H	-0.360847181555	-1.534075319655	-2.340310360232
H	0.849926930036	-1.149270744790	-3.568134660330
H	0.238734088631	-2.814853650781	-3.432750622759
Na	1.550450648822	0.292813655679	-1.699072208844
Na	-1.669621053110	1.214473199173	-1.254953247376
H	0.249411169894	-2.655905425205	-0.313695096896
C	3.405055064193	-1.761143389494	-3.489960229853
H	4.383017722285	-2.179911962589	-3.799357204102

H	2.787194036694	-1.705182301185	-4.394253383365
N	3.568408035957	-0.397912076367	-2.984667114737
C	4.075122797807	0.449976667328	-4.058783545521
H	4.233132404891	1.466176653787	-3.685688150288
H	5.033292204158	0.067634051217	-4.460379588509
H	3.344631530033	0.486947969053	-4.875720020558
C	4.475231569539	-0.355106632940	-1.842501989685
H	5.456943890345	-0.811986646093	-2.075110926318
H	4.630239400288	0.688398400879	-1.545779191586
H	4.035226557452	-0.882778135617	-0.987090538840
C	-0.345346692853	3.297619700523	0.328142557831
H	0.368646511797	2.758526688768	-0.305007130818
H	0.108039611160	4.262693274878	0.622336025249
H	-0.516852156230	2.711469983745	1.237292637505
C	-1.397936735982	4.354646275607	-1.538369041371
H	-0.608442352608	3.927184329597	-2.169163777371
H	-2.320539412679	4.420803900835	-2.123989665605
H	-1.085492146956	5.372367951276	-1.234169987669
C	-2.587567709379	4.036784014690	0.553672716310
H	-2.770220997617	3.276501631103	1.325442641068
H	-2.162333415181	4.917732230858	1.073957301884
C	-3.897162059622	4.491155464818	-0.071495749496
H	-4.576285344934	4.763211287907	0.763993649399
H	-3.731962710267	5.409833720101	-0.649007651552
C	-5.742114252868	4.090266369609	-1.509420837856
H	-6.197205107765	3.388050432489	-2.216570199061
H	-6.486458534821	4.316151526373	-0.719027321033
H	-5.517243549372	5.021855692520	-2.041271845957
C	-4.820871513141	2.271392894134	-0.289697081942
H	-5.529546678494	2.404547053440	0.553678226446
H	-5.268783837437	1.572952842210	-1.005555412793
H	-3.909357086926	1.812532455909	0.111467589314
N	-4.522506046858	3.523852505717	-0.960492904236
N	-1.607521789819	3.485034990848	-0.383746019629

Table S52. Atomic coordinates and single point energies for *bis*-TMEDA-solvated dimer of enolate **4g** with double chelation to the *endo* sulfonyl oxygens.



G = -3772.919855

G_{SP} = -3774.612026

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E2TMEDA2_endo_endo: optimized structure // E(RM062X) = -3775.76965346 A.U.
after 12 cycles

O	-0.039295233703	0.083066253655	0.041465997525
C	-0.107412677745	-0.023412425653	1.309234109197
N	1.188080222414	-0.103942513274	2.019237861318
S	1.899233961401	1.384611953321	2.337692685540
O	1.919904371193	2.241313695346	1.123147431320
C	3.572180558189	0.740107431438	2.610828579364
C	3.511548591585	-0.724436661302	2.209969328146
C	2.206048464012	-0.972030432994	1.410495680498
C	1.942272638886	-2.482904599832	1.609302604586
C	3.196550209388	-2.944757752755	2.379924859376
C	4.401507465208	-2.821126248078	1.419764505979
C	4.643855799653	-1.285191410923	1.331885691002
H	4.573574767305	-0.902890326883	0.307769140297
H	5.627473937490	-1.001207967554	1.720653950749
H	4.175183023603	-3.261244580438	0.441658256849
H	5.281697414276	-3.341229333181	1.811975055634
C	3.430899334313	-1.773916767806	3.366131741580
C	2.303407846542	-1.566738273269	4.380616851542

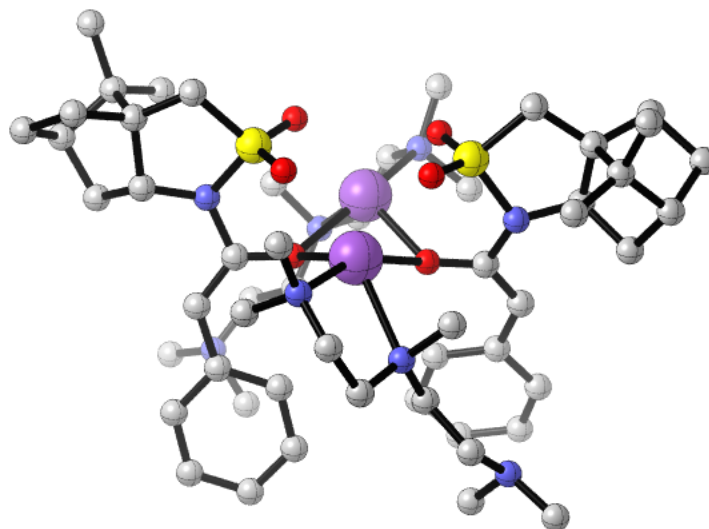
H	2.422855968247	-0.605509465964	4.900334860405
H	1.303450455887	-1.577726195248	3.944974236946
H	2.359496074499	-2.355323880900	5.142642352884
C	4.733144189856	-1.871791608168	4.165130338214
H	4.894797289851	-0.948447558130	4.738648941026
H	4.661278039894	-2.694322279644	4.887921910342
H	5.622387021578	-2.045252140706	3.553087057286
H	3.092476091029	-3.933115446428	2.840520090779
H	1.020412848059	-2.641994974994	2.178785210390
H	1.837975409426	-3.005085596364	0.652053848997
H	2.328936612469	-0.712050396600	0.350802242990
H	3.813685616416	0.904406817917	3.666484740074
H	4.228634063144	1.350273646028	1.982547786554
O	1.312079965414	1.990597321263	3.536891962942
C	-1.189121884578	-0.097511302573	2.144847417970
H	-0.972556195262	-0.242530764075	3.200171150047
O	-1.155292615494	1.866417520512	-2.042582732632
C	-2.257053199810	2.468712916248	-2.258520631340
C	-2.987894805974	3.311208925808	-1.464864279161
H	-3.879328484235	3.741899939849	-1.913751075263
N	-2.856986428249	2.254378318148	-3.593783425521
S	-3.776062551687	0.854164625172	-3.726175110988
C	-3.737177522087	0.773361881222	-5.537441711314
C	-2.750389356840	1.845439447290	-5.968824584131
C	-1.710022879583	1.485559923139	-7.043871935624
C	-1.136137693982	2.881027630500	-7.429756276506
C	-1.959109793841	3.864045378844	-6.566345771275
C	-1.466684414393	3.724672849841	-5.110838861451
H	-1.919402364879	4.466360990869	-4.444212799427
H	-0.378799630264	3.829755019959	-5.037799296563
C	-1.929777401542	2.298162912957	-4.733405013892
H	-1.081515623274	1.626450659491	-4.546776581187
H	-1.954833144991	4.894823240503	-6.936901311420
C	-3.349024579144	3.183030292330	-6.513885312032
C	-4.361800644240	3.882849157857	-5.603981839178
H	-4.715547304119	4.796473336725	-6.099810327997
H	-5.240403636718	3.243072135697	-5.439427482768
H	-3.968696112621	4.152329127452	-4.622818833601
C	-4.022073174073	3.014570068558	-7.878594669182
H	-4.934377020185	2.410287425062	-7.777818277575
H	-4.324204230004	3.996424105902	-8.264385526990
H	-3.389634475585	2.541682304408	-8.634795709799
H	-1.264033277916	3.082348217013	-8.498488579137
H	-0.065092525861	2.963143043090	-7.211279225970

H	-0.947127850229	0.809778618478	-6.642310071312
H	-2.176572453581	0.982485693761	-7.897414502581
H	-3.424780036402	-0.247301203442	-5.779555847143
H	-4.760430898090	0.940254655889	-5.890749140724
O	-5.122875140331	1.068566666593	-3.187458472829
O	-3.043800982193	-0.322673843554	-3.189183047091
C	-2.645501162922	3.766922129722	-0.121608476960
C	-3.309924560930	4.901369021258	0.388281438779
C	-1.680983303481	3.164986910236	0.711097119880
C	-3.012281301026	5.417339173135	1.643626884809
H	-4.070173038839	5.383546935101	-0.225596706130
C	-1.388558254628	3.677360993755	1.972569212520
H	-1.197233039150	2.247023214310	0.393231395631
C	-2.042836636470	4.813272216444	2.445450934277
H	-3.544134387903	6.297732885506	2.001069568210
H	-0.642575071945	3.175755452010	2.589755480919
H	-1.810560478214	5.214372146486	3.429663718750
C	-2.596187901366	-0.101656059846	1.758265241278
C	-3.545708549474	-0.552979554594	2.698029853955
C	-3.086189451506	0.300571087956	0.499634392288
C	-4.899234654939	-0.620945958137	2.391343387558
H	-3.201228544023	-0.860017535793	3.685138129348
C	-4.443774540385	0.240135215387	0.195133455368
H	-2.403901274006	0.725381563756	-0.229558953924
C	-5.360349601489	-0.230926252466	1.133198320105
H	-5.601619761360	-0.978945789220	3.142486940745
H	-4.783096278824	0.570557775778	-0.787056997647
H	-6.420089687884	-0.280949442535	0.892456332218
C	3.340958704363	3.422598671873	-1.740535572030
H	3.590604980698	3.436655678962	-0.671571767131
H	4.280185587116	3.597190568320	-2.301275995796
C	2.643839500770	1.885996954832	-3.479188206150
H	2.301139176208	0.861718216678	-3.659653409914
H	1.891123443236	2.565585395633	-3.891567805742
H	3.593225695095	2.036705187191	-4.027681597215
C	3.678449411223	1.069537175889	-1.486674742509
H	4.701203235889	1.119036597024	-1.908024427038
H	3.738492678441	1.199169079908	-0.399891874140
C	-0.168444469022	-1.109342127806	-4.736759700350
H	0.201011258944	-1.746171346425	-5.563789652163
H	-1.206608930334	-0.826836353281	-4.946373512855
C	1.278447961315	-2.097925428454	-3.113118973312
H	1.719826181190	-2.834421348243	-3.811455032779
H	1.873776262090	-1.180007098805	-3.159669669034

H	1.355787728177	-2.492796495688	-2.094997837824
C	-0.942209811449	-2.993011847690	-3.484166486844
H	-1.913561266991	-2.703308109459	-3.905796440520
H	-0.500926275151	-3.750277892633	-4.161577322563
N	-0.106170943895	-1.790040575784	-3.450042056975
N	2.804786027683	2.093209146319	-2.045034252665
Na	0.707704811564	2.128495947668	-0.836896414381
Na	-1.232055675216	-0.464755514826	-1.767299280939
H	0.443529846524	-0.199856706244	-4.703050382401
H	3.266173551441	0.075894045968	-1.700011292285
C	2.364167282897	4.547355943855	-2.046603196625
H	2.898336835908	5.513482253447	-1.972665024692
H	2.017651144737	4.466168859189	-3.083508012008
C	1.498510688976	5.164640718649	0.112437727737
H	1.746322511104	6.236067524222	-0.016196608192
H	0.631996519337	5.080864477410	0.777680582970
H	2.338730799672	4.657305850601	0.594945733509
C	0.070749334617	5.218204722807	-1.800023399614
H	0.329857263392	6.253885398177	-2.093799810611
H	-0.248525074562	4.664987879763	-2.690968575898
H	-0.771519322310	5.257724140273	-1.101269375175
N	1.193249335002	4.534867630226	-1.168071169187
C	-1.151805936186	-3.616253288384	-2.112828998082
H	-1.626604480784	-4.607415602179	-2.240651675350
H	-0.181824585922	-3.799064985939	-1.635835679375
C	-1.677118573019	-3.093726749814	0.172425971725
H	-1.851284826642	-4.165283044370	0.390403328225
H	-0.637411852241	-2.845729482943	0.415829758015
H	-2.331301664581	-2.498771767926	0.818426537249
C	-3.374444515115	-2.927653694817	-1.498163907667
H	-3.947049606955	-2.235265483479	-0.871153946497
H	-3.588883091650	-2.685450186705	-2.542938828464
H	-3.712564426655	-3.960790614637	-1.287897710290
N	-1.949898815685	-2.770918761855	-1.223135424522

PMDTA-solvated dimers

Table S53. Atomic coordinates and single point energies for *bis*-PMDTA-solvated dimer of enolate **4g** with double chelation to both sulfonyl oxygens and spirocyclic conformation (lowest energy *spiro*-isomer).



G = -4119.065139

G_{SP} = -4120.960284

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E2PMDTA2_exo_exo-ph-ph: optimized structure // E(RM062X) = -4122.32075582 A.U.
after 13 cycles

O	0.033301875522	0.001012685031	-0.022709311655
C	0.012785637471	0.046716443037	1.249495927047
N	1.324921942568	0.060421197919	1.852223293425
S	2.543355547848	-0.529302184800	0.834645459276
O	2.179773211980	-1.819669323815	0.214026542946
C	3.744854955503	-0.853743498203	2.147359436260
C	3.137521712002	-0.325620575369	3.430096767194
C	1.591364117419	-0.220935312889	3.264180455622
C	1.209040072288	0.897187406321	4.269703734676
C	2.528407145438	1.128828643146	5.028842971854
C	2.851974437956	-0.166430058917	5.812475752524
C	3.342875279235	-1.151859479516	4.710400805643
H	2.765813539201	-2.082312189084	4.676696482877
H	4.396232476428	-1.421065362678	4.840501289052
H	1.965253329074	-0.541448491767	6.336163402672

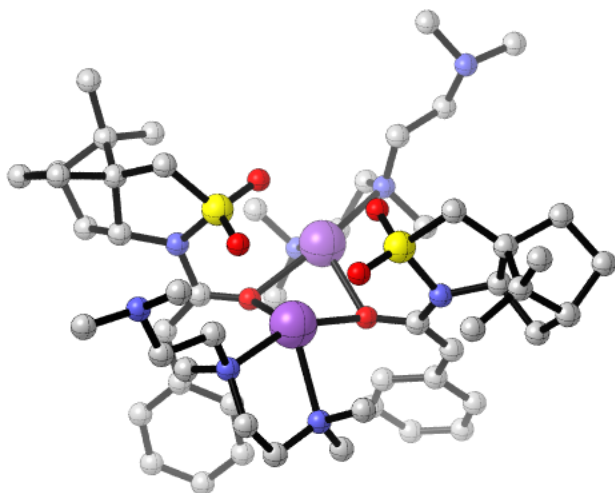
H	3.626063803289	0.002770629356	6.568002723500
C	3.572949353092	1.101698292638	3.887984794867
C	3.401156523762	2.200155660414	2.839764150328
H	4.128215864426	2.072288296760	2.025968476081
H	2.408442989823	2.220370239240	2.391660160608
H	3.592189979300	3.178066319127	3.301727185090
C	5.025372173018	1.162490416883	4.367373614998
H	5.710937816110	0.915920359114	3.544798577020
H	5.259634765256	2.184949687569	4.689598682964
H	5.248265825431	0.494029428660	5.203392769848
H	2.528058373626	2.034395519070	5.644974821145
H	0.867971435346	1.794697268944	3.743283193691
H	0.402527809315	0.576046328426	4.937196205313
H	1.109910411404	-1.173587545177	3.530751187737
H	4.682139036775	-0.368018064367	1.856630422582
H	3.871617292320	-1.940866972986	2.142969081854
O	2.978232097942	0.539273988489	-0.082174169832
C	-1.081874331035	0.101127300361	2.082840304819
H	-0.924470842097	0.173875350297	3.154004826928
O	-0.074425621982	-0.287821225019	-2.944247533585
C	-0.135723072616	-0.309789613563	-4.215775412864
C	-1.102379973344	0.233447242805	-5.031971517906
H	-1.024783468295	0.092502788823	-6.105086027482
N	0.956126122940	-1.020584443593	-4.838499011185
S	2.316509567806	-1.178558192329	-3.842397687491
C	3.484868792388	-1.541340200709	-5.174838454555
C	2.669602376104	-1.656979612798	-6.445724922789
C	3.265382127719	-1.063028760613	-7.732693136703
C	2.306679697182	-1.628149919066	-8.822712100954
C	1.352482395175	-2.552876640631	-8.028444612672
C	0.373509487011	-1.654759183187	-7.250186428845
H	-0.386657681614	-2.232930140770	-6.714616382758
H	-0.146232278625	-0.949022723100	-7.906649360401
C	1.310030016628	-0.919083622698	-6.255619359480
H	1.408830305303	0.144534334200	-6.518987086705
H	0.858307824731	-3.315047240075	-8.640455480709
C	2.266845716101	-3.093789446493	-6.903851137163
C	1.550109370899	-3.934541718659	-5.848247368288
H	1.181395328316	-4.860966185373	-6.308684462810
H	2.245069950451	-4.218933210271	-5.046138967010
H	0.707457940774	-3.422577694305	-5.385081922514
C	3.453878847470	-3.920065723749	-7.405121385345
H	4.177485448743	-4.082154691145	-6.594228338781
H	3.099828846363	-4.907793159002	-7.726328331448

H	3.986993568608	-3.470883256197	-8.247421110042
H	2.858517510207	-2.181846583767	-9.589236221969
H	1.750194779509	-0.834660132891	-9.334434405733
H	3.276090349822	0.031635325366	-7.694279606063
H	4.297241881949	-1.398415647539	-7.880128190252
H	4.173543808092	-0.690665364257	-5.177268799284
H	4.021297871729	-2.454382287651	-4.896358459515
O	2.126400079111	-2.318066939651	-2.927569983115
O	2.709108278852	0.103422106383	-3.222079121841
C	-2.246955228456	0.992893741771	-4.564752914254
C	-3.203250277389	1.417630212586	-5.516076304550
C	-2.477786673674	1.364871057208	-3.218625239871
C	-4.310261916655	2.174098191000	-5.158897061038
H	-3.058928630071	1.138886628709	-6.559711479346
C	-3.597798721051	2.119544014761	-2.870096823480
H	-1.773879758026	1.049327092829	-2.451120076438
C	-4.521191859500	2.535622874071	-3.826561499876
H	-5.019586777659	2.480313026095	-5.926704227957
H	-3.755974848688	2.379302593405	-1.823852106959
H	-5.390476222967	3.123516174318	-3.539820875638
C	-2.462180113306	0.073774119012	1.636604198062
C	-3.482649126256	0.222181809193	2.604345934335
C	-2.876766599909	-0.110996736324	0.295823944631
C	-4.827933303793	0.176749870758	2.267526174650
H	-3.195641844463	0.375880321793	3.644396022555
C	-4.231936631974	-0.147984585205	-0.032159747874
H	-2.125082755786	-0.217441394423	-0.483766698565
C	-5.219906360847	-0.009923692582	0.940191577804
H	-5.579191629390	0.294000250180	3.047462719360
H	-4.520555845956	-0.278108880572	-1.074702217315
H	-6.273113643910	-0.040407611207	0.669416060935
C	1.066255151722	2.819506771175	-4.052172234753
H	0.041830197527	2.633784503752	-3.703363427459
H	1.035171555547	3.622824280028	-4.814458242216
C	-2.775009022963	-2.212256872546	-2.811438410610
H	-2.289947108946	-1.400844788215	-3.366542207177
C	-2.235697418840	-4.073985446115	-1.341411535835
H	-2.877911390051	-4.816151528900	-1.853637387553
H	-2.865612331748	-3.560909039853	-0.602119975863
C	-0.874972076832	-3.635356364719	-3.302326185319
H	0.089441130753	-3.956704112397	-2.887347588044
H	-1.327469193331	-4.504612968121	-3.815067742645
H	-0.675553295313	-2.855909273307	-4.045808037173
C	1.554791811312	4.422658652827	-2.318785536727

H	2.337306254640	4.694855839487	-1.599375331798
H	1.516898107503	5.236089123451	-3.070168724262
C	3.327461374672	3.217581287680	-3.379408990416
H	3.980598472550	3.419216863442	-2.522164577825
H	3.610270931835	2.252103065920	-3.809669714212
N	-1.721576696763	-3.066215261157	-2.260741784438
N	1.942206641126	3.158314558315	-2.936356987280
Na	0.292589371027	-1.893911958033	-1.328635309043
Na	1.177992402742	1.168784478537	-1.651098182908
C	-1.119707746540	-4.847505791250	-0.652217433334
H	-1.575373229083	-5.517764428477	0.103297108026
H	-0.615341350714	-5.492937867184	-1.382288573144
C	-0.648175108823	-3.239347768222	1.081236910251
H	-1.092486399539	-3.904766832982	1.847508365060
H	0.158793331764	-2.661155262481	1.544287895955
H	-1.419535205255	-2.532872027194	0.747321969455
C	1.038656670666	-4.782391929601	0.375749075640
H	1.469382245784	-5.298386825883	-0.490471724928
H	1.800652281013	-4.119890740079	0.797307671701
N	-0.106587783698	-3.989293453025	-0.046324128631
C	0.208811614075	4.363104505114	-1.609179714686
H	0.071194903396	5.331413334118	-1.090465889588
H	-0.609088508403	4.269910893924	-2.336465651807
N	0.118031042914	3.232544160828	-0.693382875372
C	1.153559853531	3.255834050931	0.332626184503
H	1.244183918174	4.230017854382	0.848395011437
H	0.916336995969	2.487322525712	1.076392659596
H	2.133802549183	3.013223090163	-0.098449632480
C	-1.220258910417	3.072123051280	-0.122877022209
H	-1.236080731935	2.124586536175	0.428238695307
H	-1.919409298225	2.979578749404	-0.962204453077
H	1.431520112519	1.901384488017	-4.524992099993
H	-3.303218197430	-1.763746158872	-1.961918379412
C	-1.665906360245	4.188908410061	0.827390564151
H	-1.971003753966	5.091071038384	0.254854133715
H	-0.820728994139	4.482345516550	1.463415453037
N	-2.737676463923	3.756391004863	1.715667702674
C	-3.935904911755	3.400200436742	0.976053635600
C	-3.030512647627	4.784896610063	2.696984314154
H	-3.755127659901	2.510219291609	0.363098409110
H	-4.742058469541	3.160599773057	1.678710192695
H	-4.282798706718	4.224280164327	0.317424142245
H	-3.795898046645	4.423545293282	3.393559795020
H	-2.126529415112	5.017635910125	3.271658595708

H	-3.398061784945	5.722941064401	2.234389760526
H	3.488129549024	4.011180694484	-4.134570542728
C	-3.763491700553	-2.913280723469	-3.749681750868
H	-4.495034277498	-3.514741418578	-3.168416461267
H	-3.216282286294	-3.610598031548	-4.397195066331
N	-4.451129135253	-1.970693273541	-4.623438184916
C	-5.263828708833	-2.678752998119	-5.595399541944
C	-5.261352605176	-1.031888840945	-3.867250617734
H	-6.069037178207	-3.276596671810	-5.122919186497
H	-5.727755121872	-1.961014375266	-6.281860346405
H	-4.633575132600	-3.356556462045	-6.182739857038
H	-5.985091305332	-1.545323983305	-3.199543939549
H	-4.623090306298	-0.379281267251	-3.261290692043
H	-5.824995924135	-0.395219173366	-4.558607229669
H	0.761391318317	-5.542143434454	1.131913749461

Table S54. Atomic coordinates and single point energies for *bis*-PMDTA-solvated dimer of enolate **4g** with double chelation to both sulfonyl oxygens and spirocyclic conformation (higher energy *spiro*-isomer).



G = -4119.060957
 G_{SP} = -4120.960509

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E2P2_exo_exo_cm_cm_2: optimized structure // E(RM062X) = -4122.31546131 A.U.
 after 13 cycles

O	-0.057042263331	0.018259093068	0.005542275839
C	-0.049177017414	-0.003207851120	1.277807056988
N	1.272587313113	-0.022807339729	1.854526605283
S	2.491328015080	-0.491822391269	0.778812524549
O	2.152503216420	-1.729572614398	0.048053432449
C	3.714153533296	-0.895778976333	2.047074901584
C	3.128817282511	-0.445218238925	3.368132421243
C	1.577425976107	-0.371677419712	3.243700457693
C	1.193191883102	0.680099801898	4.318075657629
C	2.524643663076	0.904190477690	5.057686436578
C	2.900567924205	-0.421951841678	5.761823488417
C	3.387232713292	-1.333003193528	4.596319400971
H	2.833587245810	-2.275470971789	4.523684008061
H	4.449967511927	-1.581467677501	4.685213066030
H	2.037310867501	-0.848001917844	6.285881142912
H	3.689013527182	-0.273081092817	6.506728817328
C	3.538175949118	0.967875147051	3.890628405595
C	3.307171696364	2.118742668206	2.910933659913

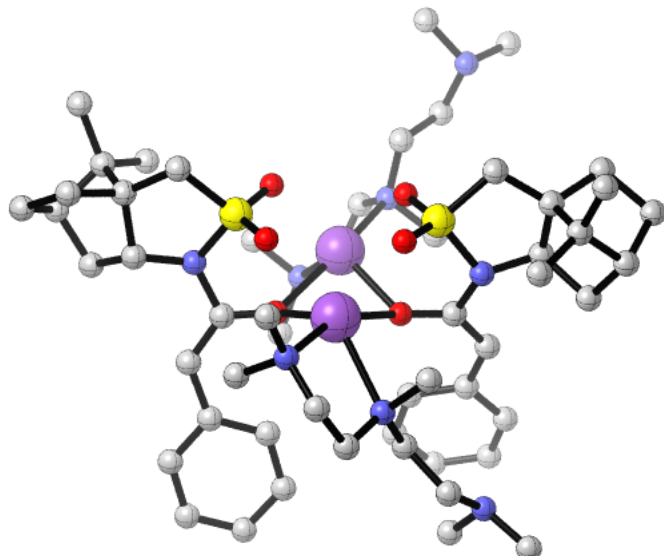
H	4.026890484109	2.068101463206	2.082821935347
H	2.308383404470	2.127547571070	2.474243199849
H	3.466682377769	3.073789401809	3.429419164200
C	5.000878600953	1.044988418392	4.334628462064
H	5.669772986691	0.861953646520	3.482410630349
H	5.216136678200	2.055248604373	4.705055183869
H	5.265071951558	0.339896607511	5.127440263681
H	2.517113004399	1.775322801834	5.721603375065
H	0.820367843211	1.596938571278	3.850422130706
H	0.411083911617	0.302624695773	4.985132080190
H	1.125949579145	-1.349350870255	3.468542458778
H	4.647793716135	-0.395628848733	1.769535107097
H	3.836948858040	-1.981649351017	1.978603433136
O	2.888467207060	0.664425515941	-0.043976566013
C	-1.124681554150	-0.003314028292	2.139190397110
H	-0.939522643737	-0.019303529272	3.208373647938
O	-0.180076137608	-0.199866989890	-2.964320210924
C	-0.207357344428	-0.172633246318	-4.236208534230
C	-1.137700401520	0.424937220240	-5.058439568653
H	-1.012398568602	0.348494496954	-6.133682262887
N	0.888218182009	-0.872999971929	-4.860113606158
S	2.202593461446	-1.158587449365	-3.833791242852
C	3.400918757018	-1.475636551078	-5.149265127456
C	2.617639434389	-1.518371984348	-6.443658905441
C	3.275439164943	-0.903333648332	-7.689618443630
C	2.328401441706	-1.387228082163	-8.827257861199
C	1.313775721983	-2.299247842132	-8.096137804121
C	0.349220610301	-1.391337504112	-7.311701259211
H	-0.447397243890	-1.959893518342	-6.821362232389
H	-0.122272518494	-0.640356395532	-7.954247638320
C	1.284315375963	-0.732691943164	-6.262922637629
H	1.433442895258	0.335073399231	-6.481712066391
H	0.807220135708	-3.017173954875	-8.750123738927
C	2.168395216044	-2.919517978176	-6.965552731149
C	1.380753754124	-3.767081553640	-5.966090485624
H	0.973441081647	-4.648347998022	-6.479750939537
H	2.039993022879	-4.127034315122	-5.164735615223
H	0.556046902683	-3.232883369121	-5.494030741259
C	3.333713860325	-3.779327165652	-7.460870547727
H	4.023722232151	-4.001244801473	-6.635135720647
H	2.947903816633	-4.738704485114	-7.828189030635
H	3.912034632098	-3.325012389103	-8.269974127396
H	2.879778044764	-1.935113377109	-9.598295823076
H	1.820705876580	-0.552774631410	-9.324550306552

H	3.330475743248	0.187635393202	-7.607142880057
H	4.297020996972	-1.275671791231	-7.819146838174
H	4.100039319200	-0.634598691565	-5.096690125758
H	3.918131793579	-2.407986896109	-4.900117269985
O	1.931774327629	-2.352553106440	-3.013596921905
O	2.622366399664	0.054973636616	-3.104481508560
C	-2.285535580529	1.183418050112	-4.599218426205
C	-3.164178486165	1.723104491138	-5.567809814119
C	-2.599525286119	1.435805650433	-3.242077991173
C	-4.288013675034	2.456108725589	-5.213612178060
H	-2.947781589193	1.551298383545	-6.622109296636
C	-3.734864253454	2.168075094545	-2.897671785571
H	-1.947595202690	1.041761677253	-2.465209696121
C	-4.589504946268	2.684750188299	-3.869545321433
H	-4.937251895206	2.851256492870	-5.993604322555
H	-3.955934236074	2.335212914017	-1.843801121333
H	-5.472298355046	3.253724660490	-3.586416354456
C	-2.516038275245	-0.005482962786	1.729534703245
C	-3.511401396624	0.013137873513	2.734696097770
C	-2.965335850813	-0.030697359740	0.387291672129
C	-4.864985248973	0.017977916362	2.428845387304
H	-3.198650028725	0.027477954922	3.778666081271
C	-4.327787344290	-0.019067783992	0.091631241233
H	-2.232371616688	-0.049218749022	-0.416592746866
C	-5.290373796630	0.005636229720	1.098964785764
H	-5.596179217040	0.034106297460	3.235774608036
H	-4.641876618397	-0.026994233517	-0.951791810819
H	-6.350086088850	0.015185161453	0.853737293012
C	1.095800984711	2.831451231973	-3.995932961095
H	0.086177303067	2.568157710196	-3.652285840529
H	0.993975973029	3.642173022092	-4.740689620540
C	-2.920482778156	-2.096781533712	-2.711125459860
H	-2.520919448559	-1.284279998597	-3.327568417893
H	-3.655643226961	-2.671663176405	-3.307970128411
C	-2.312982891643	-3.962986232254	-1.338104646773
H	-3.013726452259	-4.652238971926	-1.851315685841
H	-2.885124840959	-3.460265699878	-0.547128712979
C	-1.127187159326	-3.504373402574	-3.394467326480
H	-0.203692131112	-4.007657642823	-3.084234832480
H	-1.758869987948	-4.227227465244	-3.948991633646
H	-0.851966831354	-2.690054314655	-4.074082984768
C	1.528516040611	4.445977842047	-2.244564224672
H	2.288071836736	4.719318326101	-1.500814268303
H	1.488180095300	5.272621015658	-2.978785757708

C	3.369106744260	3.148070424162	-3.168454623316
H	3.906103228970	3.281801161464	-2.219865803536
H	3.600288780477	2.141152331850	-3.536775063616
N	-1.824317310156	-2.935201209129	-2.249070827484
N	1.940405320786	3.188940451314	-2.861078522406
Na	0.198573314004	-1.838625094756	-1.375752055441
Na	1.098806223585	1.199902009509	-1.613127929564
C	-1.194896253426	-4.797607905516	-0.725205413861
H	-1.654471018293	-5.475262759179	0.018851433171
H	-0.735785001799	-5.434032138189	-1.492658209659
C	-0.610902740054	-3.227989359843	1.023079509745
H	-1.112706695379	-3.858848150952	1.779722922526
H	0.243551390620	-2.726331404563	1.492076368722
H	-1.323713541901	-2.451767133553	0.713021187660
C	1.087612466235	-4.727654287180	0.118124495399
H	1.429564005003	-5.123268695379	-0.847603323541
H	1.844931056136	-4.015109127233	0.467044804497
N	-0.140730238958	-3.977178634081	-0.137395995321
C	0.158774198572	4.352284950070	-1.583214684077
H	-0.031991979683	5.307025332463	-1.052575607278
H	-0.623012337625	4.252874910400	-2.347834712541
N	0.037925059607	3.214891942816	-0.679486009836
C	0.973291638306	3.297772672910	0.434111006770
H	0.860299098880	4.242519074314	1.003080886883
H	0.782258282832	2.458423273235	1.112156052959
H	2.009868755388	3.217085544946	0.085710070423
C	-1.320957964833	3.107635328303	-0.169644213768
H	-1.409148643822	2.202296650495	0.440605865503
H	-1.600071789120	3.984526088972	0.447068482036
H	-2.022714907068	3.038336642855	-1.006529925774
H	1.519308006237	1.949265823691	-4.489997457290
H	-3.439545779836	-1.663733123556	-1.850495040522
C	3.849875058912	4.166324982224	-4.205205628692
H	3.854331467834	5.189965944088	-3.775140413600
H	3.148495330189	4.175221750403	-5.050039011247
C	6.195251046272	3.883107592106	-3.715568814065
H	6.003932869850	3.146298240619	-2.928866741668
H	7.167037432295	3.647544373022	-4.163810183530
H	6.263525340986	4.885840002590	-3.247302645950
C	5.504525615077	4.691671578154	-5.851205021389
H	6.468408746587	4.388846443086	-6.276166082221
H	4.742655009486	4.607965493729	-6.634583569516
H	5.577639818702	5.755794457186	-5.551247385745
N	5.163531389466	3.822290174507	-4.738477304588

C	0.970008578671	-5.853974448613	1.147882141120
H	0.398302572259	-6.708680353345	0.729019525846
H	0.408958717326	-5.486712825886	2.017419999661
C	2.125714386779	-7.216347649749	2.738932370261
H	1.593922929603	-8.143852847369	2.448054864341
H	3.112794914895	-7.494695292115	3.125662146508
H	1.562544553344	-6.737829663219	3.548250593790
C	3.068872171472	-6.894683670150	0.571265258542
H	2.560610964479	-7.766385669792	0.111685204454
H	3.283635670383	-6.164918165492	-0.215950190493
H	4.026593966364	-7.233869924900	0.981753302900
N	2.276061975692	-6.290271629250	1.629858291353

Table S55. Atomic coordinates and single point energies for *bis*-PMDTA-solvated dimer of enolate **4g** with double chelation to both sulfonyl oxygens and spirocyclic conformation (higher energy *spiro*-isomer).



G = -4119.062619

G_{SP} = -4120.960095

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E2PMDTA2_exo_exo: optimized structure // E(RM062X) = -4122.31796680 A.U. after 13 cycles

O	0.040273423700	0.015170137460	-0.062703238517
C	0.014575770436	0.042781638918	1.209534745068
N	1.323692965700	0.044531697075	1.819160579646
S	2.553945372497	-0.509136528315	0.796687709348
O	2.203752449610	-1.781000326737	0.132421964388
C	3.743800394422	-0.869714583144	2.109660499251
C	3.127262477659	-0.374369356561	3.400546832997
C	1.582040210438	-0.265987574995	3.226603112709
C	1.192297620436	0.829495898720	4.253980171444
C	2.504626505448	1.038049297525	5.031067407850
C	2.818390600527	-0.279086899878	5.782242616532
C	3.323432723360	-1.233995832125	4.659890690889
H	2.751234097763	-2.165872166108	4.594652781632
H	4.376716342594	-1.502367142746	4.792726068583
H	1.924441483321	-0.667916538655	6.283185045612
H	3.581937870107	-0.132079025416	6.553010098998
C	3.558254938744	1.040599282119	3.898343926406

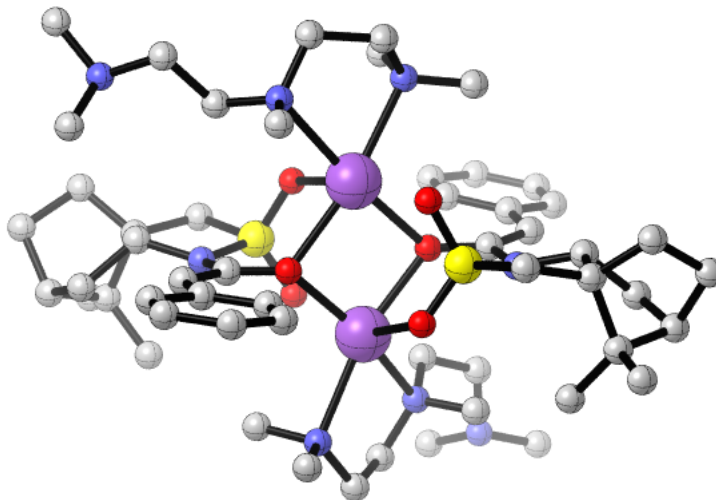
C	3.393798364629	2.164473156493	2.875677547102
H	4.140807551029	2.067153022191	2.075978708014
H	2.411180125959	2.184037545291	2.404933808775
H	3.561535672265	3.132448580181	3.366825822226
C	5.006534118720	1.090844156712	4.391372143171
H	5.700001743116	0.856141209013	3.571913760508
H	5.239381783003	2.107720556242	4.731973253476
H	5.221133343879	0.409019496490	5.218687628137
H	2.500136043286	1.926641013121	5.671464403137
H	0.860532944503	1.740922352677	3.745748964706
H	0.378152444179	0.495392646847	4.905568496029
H	1.099462543923	-1.224272283088	3.469425631857
H	4.683743281111	-0.378133301370	1.838782587017
H	3.867665192676	-1.957045446394	2.078898247125
O	2.992584983533	0.586590833363	-0.085917731246
C	-1.083862105050	0.086706243989	2.038808361544
H	-0.930824700744	0.143788540170	3.111447120805
O	-0.064602800579	-0.266252463703	-2.986770862564
C	-0.112468783728	-0.263493695952	-4.258502920394
C	-1.058093934769	0.313310242528	-5.077278670432
H	-0.949749188254	0.217896746786	-6.153061990325
N	0.975565235737	-0.977215529367	-4.884211327406
S	2.327582757131	-1.167583156943	-3.883426721279
C	3.499777614653	-1.522826370976	-5.214233367749
C	2.687989163168	-1.623035278449	-6.488474393501
C	3.294619165867	-1.027614360891	-7.769757040079
C	2.334423870919	-1.576255512158	-8.866792707376
C	1.367033237598	-2.494401349198	-8.081529498612
C	0.395515974225	-1.589430233591	-7.301508368049
H	-0.371752939720	-2.163524351822	-6.771934639156
H	-0.114081383772	-0.874612855174	-7.956087576912
C	1.336514262609	-0.870638139729	-6.299074377265
H	1.450392922166	0.193120684676	-6.555409921638
H	0.866075247576	-3.247317826387	-8.699423539274
C	2.270016207486	-3.052252170824	-6.956119526868
C	1.538038870896	-3.891052289998	-5.909182823420
H	1.160524163834	-4.809748090435	-6.377907442897
H	2.226149810530	-4.188978170677	-5.106363789608
H	0.699326350142	-3.372679468797	-5.445478162522
C	3.449606629097	-3.890282779343	-7.454956793807
H	4.158413483234	-4.077271035350	-6.636455167403
H	3.083513254328	-4.866740742940	-7.796564902845
H	4.003160791586	-3.437572617861	-8.282030479175
H	2.882844336784	-2.131533289451	-9.634648423858

H	1.788979650340	-0.773795482946	-9.376483280860
H	3.315537785499	0.066660928453	-7.724149220757
H	4.323733156634	-1.372025477779	-7.915275273572
H	4.192856407559	-0.675656512158	-5.207219397682
H	4.030845598904	-2.440865540293	-4.942093554450
O	2.119157164461	-2.321896572932	-2.991461708472
O	2.726331225288	0.100693487188	-3.239240669868
C	-2.200669573691	1.077075401841	-4.612241676220
C	-3.096559448130	1.597828725054	-5.575042409941
C	-2.490690587813	1.353764642998	-3.254595136874
C	-4.212849621172	2.339737748924	-5.214924008218
H	-2.899124394315	1.405472839284	-6.629520149499
C	-3.617781058046	2.095799460564	-2.904474132436
H	-1.826052584595	0.974773892757	-2.481059232100
C	-4.488893499952	2.595678893522	-3.870366922840
H	-4.875935252395	2.720361539022	-5.990460582405
H	-3.819957600675	2.282060790267	-1.849848895651
H	-5.365080377563	3.172220839760	-3.582142555639
C	-2.463165181321	0.068216986978	1.588212176792
C	-3.484594811365	0.215309091053	2.555909054806
C	-2.875565952874	-0.102715104405	0.245396249461
C	-4.829238724903	0.182232871667	2.215947522448
H	-3.198445795457	0.357663752477	3.597802707459
C	-4.230583890839	-0.124745159352	-0.085995581705
H	-2.121335122646	-0.208457814144	-0.532055609315
C	-5.219332735522	0.012021081006	0.885716120226
H	-5.581537858673	0.297631376515	2.995198235221
H	-4.518415448255	-0.241508405170	-1.130264640778
H	-6.272194260637	-0.007427980539	0.612433907869
C	1.103072665069	2.850069924238	-4.050664825051
H	0.076267792320	2.666710670638	-3.707214875974
H	1.079598649918	3.659794505077	-4.806389678160
C	-2.783454659034	-2.235014630313	-2.772940933933
H	-2.386003319583	-1.404195541588	-3.366250636286
H	-3.463977214203	-2.835888671104	-3.407789880249
C	-2.175504656041	-4.061052190946	-1.348756145646
H	-2.839440218986	-4.775077916276	-1.876803627699
H	-2.787753486798	-3.563677627811	-0.585083539989
C	-0.924631307023	-3.595990819294	-3.364303274891
H	-0.000141231217	-4.070001569541	-3.012332459112
H	-1.512701793532	-4.343770614624	-3.933712027924
H	-0.646759227458	-2.781781321395	-4.042051712717
C	1.597060817780	4.438413391708	-2.304825672961
H	2.376205365776	4.696411735386	-1.576686384695

H	1.574590109587	5.257402689038	-3.050787594182
C	3.364609785785	3.222737449570	-3.362728330449
H	4.013984065456	3.417248725510	-2.501045152854
H	3.642066730137	2.255649175622	-3.793122427806
N	-1.681751475197	-3.032387072023	-2.255480816841
N	1.976124597587	3.174360233293	-2.928204446622
Na	0.324445249972	-1.880289508342	-1.373714500569
Na	1.193469478653	1.187024743586	-1.675926766789
C	-1.058844664175	-4.857215275989	-0.686136700409
H	-1.526763765088	-5.530794559776	0.056478779907
H	-0.560559008920	-5.497269877692	-1.425866590291
C	-0.575412007078	-3.220919517862	1.031106572217
H	-1.116463135322	-3.831876167663	1.776802674607
H	0.251834724387	-2.704227678063	1.530974350274
H	-1.272086907771	-2.455709079133	0.661705044538
C	1.174224367364	-4.736357664998	0.264102120868
H	1.574493920114	-5.154677888352	-0.669440684455
H	1.904199482823	-4.009033801180	0.637903824603
N	-0.042588171178	-4.001931040532	-0.081155898582
C	0.244340724207	4.388204904788	-1.607197795512
H	0.112297399465	5.354851513391	-1.083624329037
H	-0.567886873558	4.308346211723	-2.342255447547
N	0.134358591371	3.252943657673	-0.699425944908
C	1.158594666552	3.264158604227	0.338538147150
H	1.251145937384	4.236516124984	0.857395469477
H	0.907278168224	2.495973626670	1.078369620494
H	2.141122123040	3.014150770248	-0.082183999709
C	-1.211347864039	3.099078235636	-0.144816060692
H	-1.236321368083	2.150587215524	0.404145931719
H	-1.903765353663	3.011467668900	-0.991143861980
H	1.465008081698	1.933756729231	-4.529819830869
H	-3.362407048232	-1.828412257389	-1.938952691683
C	1.005664821946	-5.834966486918	1.317473532845
H	0.506733073576	-6.725292157484	0.880411167242
H	0.355592405024	-5.463976750719	2.120891688481
C	2.065735004319	-7.109757200291	3.042178687242
H	1.602642419377	-8.066081960955	2.728020699760
H	3.023776675886	-7.335674760579	3.524421471729
H	1.410439672585	-6.639163276444	3.784021457601
C	3.190297207398	-6.793410357834	0.961790027907
H	2.764970461006	-7.697800171226	0.481530138203
H	3.443056943244	-6.072134685133	0.177910073204
H	4.120618772391	-7.078475999586	1.465819622037
N	2.278769696264	-6.202311212993	1.928037695708

C	-1.657792348103	4.214244486823	0.807696397555
H	-1.974287665107	5.113754829110	0.237254512043
H	-0.809592677855	4.514617657920	1.436243905290
N	-2.719223372808	3.775098232558	1.705515061107
C	-3.920952479736	3.415146098984	0.972905784873
C	-3.009773440596	4.801914056419	2.689315258830
H	-3.736469812441	2.531875719032	0.351086350544
H	-4.719662799180	3.162823588578	1.679648562635
H	-4.279310609320	4.241431496042	0.323313313650
H	-3.768793187050	4.436966299707	3.390965189292
H	-2.102943178031	5.038323045582	3.258009203351
H	-3.384615058177	5.738524379212	2.229710498340
H	3.536706997361	4.016270471308	-4.115386453380

Table S56. Atomic coordinates and single point energies for *bis*-PMDTA-solvated dimer of enolate **4g** with chelation to both sulfonyl oxygens and a C_2 symmetry axis (lowest energy isomer).



G = -4119.073339

G_{SP} = -4120.966678

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E2PMDTA2_exo_endo: optimized structure // E(RM062X) = -4122.32126843 A.U. after 13 cycles

O	0.089159954094	0.051283220899	0.031523622211
C	0.078849137454	0.027982709110	1.303498777247
N	1.395798726067	0.030719570552	1.888230097985
S	2.630092282567	-0.408837072042	0.818094926736
O	2.359449933226	-1.686547994772	0.120105604721
C	3.872751733294	-0.728829428156	2.092115486910
C	3.256356924784	-0.318414719873	3.412874983350
C	1.703195511754	-0.309787064576	3.278106856287
C	1.269050700906	0.723308271742	4.352464608054
C	2.584503680952	0.998571448805	5.102773599307
C	3.010651594372	-0.313217890890	5.804642759972
C	3.544388535027	-1.198797621382	4.639749683122
H	3.031828535663	-2.163761459856	4.562358433969
H	4.616250309105	-1.400791989155	4.735972477569
H	2.162401207325	-0.777269790670	6.320800613551
H	3.786734070568	-0.133603080422	6.555625492155
C	3.601926875158	1.108293974354	3.943052414193

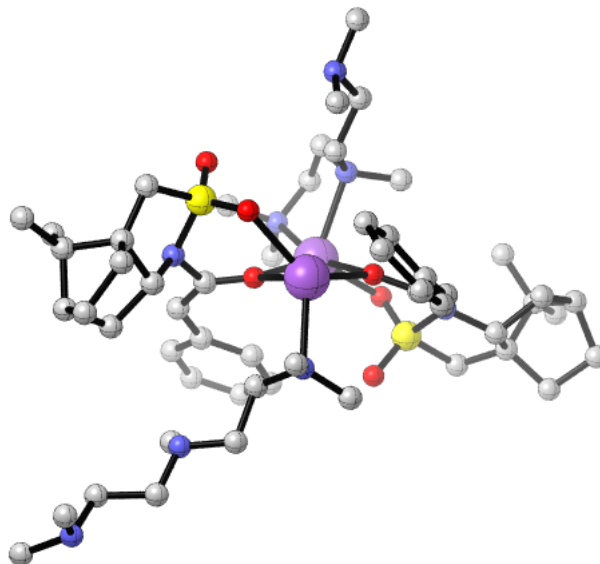
C	3.325676028893	2.246814218009	2.961520961280
H	4.051615357319	2.228131208695	2.137012115807
H	2.330375861331	2.206988157526	2.519508207896
H	3.438315956605	3.210006143047	3.477491018297
C	5.057186844525	1.246213001772	4.396586614984
H	5.739525065161	1.092255430416	3.549081182239
H	5.226924420761	2.264469609882	4.768777500941
H	5.345313079266	0.552141194052	5.190972314777
H	2.536305846225	1.866059688769	5.769679947406
H	0.865021927755	1.627119208472	3.885115636439
H	0.497078763275	0.312886298789	5.011761681415
H	1.289698724136	-1.305110133262	3.497466280804
H	4.769291286214	-0.163709885097	1.816545794576
H	4.072686471732	-1.802367731471	2.021050713943
O	2.971866430055	0.742871079071	-0.036526611570
C	-1.012739665811	0.037661851972	2.143635940118
H	-0.854450595329	0.057704986584	3.217208798126
O	1.502348214464	0.064808590449	-2.819269709477
C	1.533278768077	0.047174846331	-4.090718491937
C	2.635415413094	-0.106429019343	-4.903621629954
H	2.498731440124	-0.125571247352	-5.979099860576
N	0.244777497698	0.228099431648	-4.703876724467
S	-1.073274076494	0.188880364669	-3.642333943399
C	-2.334854401183	0.084240985504	-4.933907832912
C	-1.621600315492	0.227272697572	-6.260696128144
C	-2.094431811722	-0.660648259863	-7.423512130301
C	-1.357681535609	-0.020580377331	-8.637102847755
C	-0.639458742123	1.206183442985	-8.025912984413
C	0.564573267264	0.693910882492	-7.217012243881
H	1.162619554453	1.515927193155	-6.813757209197
H	1.227896401263	0.061485429797	-7.817462686485
C	-0.112978438032	-0.121522886737	-6.081447999179
H	0.044212605395	-1.200609255872	-6.224434442049
H	-0.379120254960	1.980412412676	-8.755710191267
C	-1.610654704501	1.647213551753	-6.906227940983
C	-1.078111636364	2.760288192555	-6.002782236195
H	-0.959050950626	3.681808894612	-6.588601700573
H	-1.793988612971	2.973195940830	-5.196773178515
H	-0.121056309376	2.523238868448	-5.536048219827
C	-2.985799795728	2.090932400663	-7.408979900653
H	-3.689810982970	2.182547717831	-6.570420375951
H	-2.902368662602	3.082040356677	-7.872723418788
H	-3.427825077568	1.416430552976	-8.147575078482
H	-2.063071789782	0.275332263196	-9.420588441325

H	-0.638433044602	-0.710300763548	-9.094182788180
H	-1.816168775854	-1.707422696351	-7.254795962317
H	-3.182968833988	-0.618057076817	-7.535382363829
H	-2.790605729566	-0.900636430228	-4.791957809149
H	-3.071779731605	0.868331742871	-4.730385649237
O	-1.126192189750	1.446083082700	-2.875404359714
O	-1.157795741640	-1.056254721863	-2.848433826661
C	3.998189955889	-0.247703419418	-4.424338302021
C	5.022441891587	-0.494891876454	-5.366903999579
C	4.387699350310	-0.153014631415	-3.066687585503
C	6.350207949221	-0.640980985776	-4.986159616208
H	4.756566703175	-0.572768973647	-6.421345765090
C	5.722182164999	-0.298117318384	-2.697049637811
H	3.635328430568	0.036787110229	-2.306397916506
C	6.716909646897	-0.544689160999	-3.642773276938
H	7.106814111869	-0.832241055499	-5.745836764568
H	5.986402186757	-0.215494954422	-1.642860757258
H	7.756186457055	-0.658190410679	-3.341767605039
C	-2.392011682030	0.024150202949	1.688795261052
C	-3.422596184967	0.222171832619	2.634980641452
C	-2.788503658663	-0.184421468822	0.346351643937
C	-4.762391171849	0.233277702997	2.268491074758
H	-3.151832175129	0.379717428688	3.679077729904
C	-4.134149768972	-0.172378336669	-0.010944886920
H	-2.029230495175	-0.337354466233	-0.416862258359
C	-5.134459233180	0.040262474916	0.936921672271
H	-5.524159988866	0.397405902327	3.029311585085
H	-4.401846535828	-0.332629504731	-1.055284263637
H	-6.182925242680	0.052074291567	0.646685773432
N	-0.436178456581	-3.479847507966	-0.422193983022
C	-0.466105914253	-3.323951311714	1.023898891334
H	0.543933738971	-3.092934016839	1.385163301434
H	-0.827188806903	-4.238354814034	1.535327760479
C	0.457552136704	-4.572361078947	-0.795904479201
H	1.432382381312	-4.373201074132	-0.329082309500
H	0.093009482017	-5.538014348757	-0.388934868974
C	-1.782235029697	-3.656125038347	-0.949028432173
H	-2.427213411843	-2.864489547226	-0.552402546548
H	-1.784846705344	-3.566071976364	-2.040379435903
H	-2.215469193700	-4.635968494779	-0.665592143087
Na	0.616948786595	-1.581369375305	-1.471484459929
Na	1.006726893239	1.620404381734	-1.323851953571
H	-1.125341564440	-2.490247124171	1.288669109192
C	0.626766723145	-4.720396103523	-2.303110566820

H	1.283501594606	-5.588457903618	-2.494795462688
H	-0.342180727187	-4.959099431233	-2.757412806158
N	1.143674902408	-3.505782174959	-2.928648823329
C	0.622198214263	-3.273755834095	-4.271478443554
H	1.065193526822	-2.336457867802	-4.627867266765
H	-0.460878164539	-3.105878978886	-4.197680095747
C	2.597328139103	-3.411911043621	-2.857782269579
H	3.112599330555	-4.241732721891	-3.375343201063
H	2.920290248909	-2.463682173918	-3.304576100269
H	2.920219715743	-3.410968530003	-1.809334119405
C	3.454264755117	3.649691394736	-2.418442090434
H	3.781126732657	2.735025955604	-2.927566597344
H	3.804616787469	4.520323145822	-3.005810681412
H	3.928773282252	3.682920292853	-1.431091371130
C	1.363813479761	3.512640867331	-3.573860296380
H	1.762448914948	2.632230468014	-4.094656152637
H	0.284189784847	3.371962967555	-3.455044719744
H	1.543400741832	4.404171949815	-4.207707008713
C	1.532358531368	4.808765170883	-1.545228042545
H	2.196461901342	4.959641078300	-0.685510504983
H	1.613553884953	5.720228745658	-2.170358852701
C	0.086922867503	4.683373443223	-1.064506742933
H	-0.163400010746	5.593837989218	-0.489707203278
H	-0.589038181684	4.652977181570	-1.928243034712
C	-1.519106749079	3.019936607655	-0.179117974533
H	-1.504332398917	1.930451272330	-0.048039799625
H	-2.002674703270	3.198573986140	-1.146355043541
C	0.575530758913	3.479499974441	0.981017355660
H	0.292207840630	4.337374084878	1.619955093872
H	0.353856028970	2.553080383017	1.525892394786
H	1.658791944276	3.519841234889	0.812388874991
N	-0.128986897548	3.467860535424	-0.290619061902
N	2.006681165267	3.632558637702	-2.271042179797
C	-2.337439481103	3.597524533675	0.970313560517
H	-3.351369297677	3.141014793981	0.930616052085
H	-1.894389071989	3.273709836356	1.922106877297
C	-3.173587392994	5.576129686177	-0.126687026436
H	-4.224509879179	5.222798792961	-0.114444946513
H	-3.179076664838	6.671820469825	-0.089315571547
H	-2.723690261158	5.274962392218	-1.078375598299
C	-2.959743880109	5.523221035741	2.247660332451
H	-2.339761680267	5.170720210266	3.080235200856
H	-2.967388130735	6.619256178034	2.264934197368
H	-3.995833360452	5.166707258838	2.413361653158

N	-2.406307981636	5.054217863931	0.989805641881
C	0.876031466584	-4.370125343616	-5.309646305564
H	0.222379568609	-5.227301289051	-5.104946866938
H	1.918630223423	-4.738604170441	-5.257894501320
C	0.156707563203	-4.923134824831	-7.553206121761
H	-0.090883770987	-4.493070669910	-8.530895885200
H	0.947901718502	-5.683203169483	-7.702454106210
H	-0.736377905362	-5.423389307755	-7.162969375335
C	1.694680024040	-3.132993003518	-7.204335255937
H	2.034120469167	-2.361476926300	-6.503427976366
H	2.552784519045	-3.799943162803	-7.420927194668
H	1.396364601030	-2.642253967933	-8.139221570404
N	0.566758668633	-3.863518103734	-6.647129075614

Table S57. Atomic coordinates and single point energies for *bis*-PMDTA-solvated dimer of enolate **4g** with chelation to one *exo* sulfonyl oxygen and one *endo* sulfonyl oxygen (higher energy *exo-endo* isomer). No stable minimum corresponding to a κ^2, κ^2 -isomer could be located.



G = -4119.003091

G_{SP} = -4120.936252

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E2PMDTA2_exo_endo-ph-ph: optimized structure // E(RM062X) = -4122.29388184

A.U. after 13 cycles

O	-0.045865946541	-0.096459163716	0.000670350085
C	-0.074422373364	-0.085503163236	1.275428009027
N	1.234411873356	-0.086115359911	1.941577536520
S	2.460302026862	0.673089992551	1.067470209631
O	2.849191184028	-0.096585733131	-0.145365855241
C	3.726867129769	0.314621926971	2.306019289194
C	3.226278393580	-0.934257834374	3.024641977958
C	1.831528108369	-1.333130312463	2.441907557388
C	1.122286548153	-2.050342540843	3.607818810902
C	2.272556030378	-2.201124343704	4.618974275070
C	3.341224977626	-3.129162422558	3.988385888862
C	4.064251883858	-2.218012399497	2.951316669119
H	4.069053639183	-2.634697956384	1.937359531913
H	5.107142888240	-2.028756220842	3.228555177867
H	2.869824657590	-3.999637361916	3.516608290582
H	4.040546106862	-3.514876136858	4.737538525309

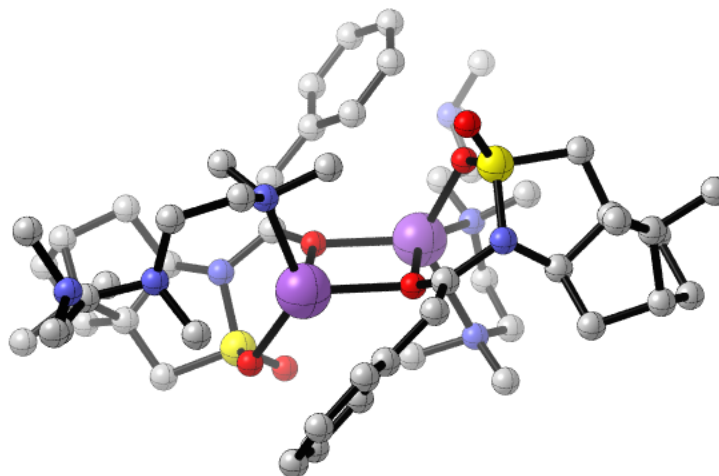
C	2.945403918510	-0.806791697816	4.554894762966
C	2.030640800183	0.357624626146	4.943031386131
H	2.596260703537	1.299101173908	4.964893158824
H	1.187806907179	0.503869826367	4.264335301022
H	1.642505341569	0.197898693164	5.957832895357
C	4.216388999454	-0.690732270103	5.399054997086
H	4.798539606155	0.194556262405	5.106905447155
H	3.946985733679	-0.564256970865	6.455166734609
H	4.875901959430	-1.560676265109	5.333116123486
H	1.946078819850	-2.517322182807	5.615793032762
H	0.304235712555	-1.446321731926	4.008293652901
H	0.695972208011	-3.007504100591	3.282657704991
H	1.985969847096	-2.025062247534	1.600300100408
H	3.789317687476	1.196835759182	2.950840006170
H	4.662482832557	0.183588889607	1.755380178896
O	2.160852794183	2.093905520422	0.907554442339
C	-1.157565143077	-0.050106434934	2.104304283526
H	-0.982809476260	0.117953575929	3.163139506033
O	-0.057857791564	-0.343525719711	-3.075578962935
C	-0.212063675687	-0.898494683427	-4.213298200280
C	0.655830499750	-1.713010322356	-4.900408628678
H	0.310479262240	-2.215221996282	-5.797868828358
N	-1.490497027942	-0.614371468363	-4.827395474913
S	-2.777193768079	-0.466996279765	-3.733005418474
C	-4.086462159998	-0.646810476421	-4.973384591465
C	-3.394687713180	-0.759870803736	-6.315301036496
C	-3.979118312212	-1.754236450393	-7.333642114862
C	-3.223768372895	-1.373224764765	-8.640293348180
C	-2.348909186599	-0.172488137068	-8.214259406202
C	-1.196767956539	-0.720729470896	-7.350276525245
H	-0.460362486242	0.044505942019	-7.088134091281
H	-0.656473109379	-1.529931564370	-7.852818165236
C	-1.931059421193	-1.224052505886	-6.080646022769
H	-1.884750978051	-2.320411436259	-5.989324779787
H	-2.014004341522	0.452353932802	-9.048928994484
C	-3.239933987981	0.540398847744	-7.167445672605
C	-2.566507139388	1.717634974750	-6.459807781591
H	-2.459141331310	2.551643022153	-7.165777675355
H	-3.185691041899	2.074056617042	-5.624870149305
H	-1.582764595691	1.482260245562	-6.053256288405
C	-4.570421838376	1.054759327049	-7.722620897726
H	-5.210689378788	1.426499431504	-6.911100162739
H	-4.385442093225	1.901712216525	-8.394776443740
H	-5.143269718042	0.311896319025	-8.283830621590

H	-3.919906298996	-1.101661952748	-9.440336062950
H	-2.610888757000	-2.197955591014	-9.020710893044
H	-3.801192956363	-2.789208517262	-7.021037956150
H	-5.062755283046	-1.631032393120	-7.433265146579
H	-4.620027473169	-1.557726822163	-4.684052742917
H	-4.746307465927	0.220416165497	-4.870018680567
O	-2.798867427152	0.886377609559	-3.146228395109
O	-2.840843346901	-1.594137109949	-2.792941551444
C	1.980381503907	-2.082859513319	-4.426931061951
C	2.536962292434	-3.321093948185	-4.808991338635
C	2.772123584078	-1.265161129135	-3.594152475498
C	3.784891809325	-3.730124258479	-4.358032027398
H	1.965255744521	-3.971852947763	-5.469779503148
C	4.013567050031	-1.686113619039	-3.124915373521
H	2.420533799083	-0.262310554369	-3.358664445082
C	4.528275906523	-2.926239542827	-3.494778116865
H	4.177450526973	-4.694474811213	-4.675167245325
H	4.585748165777	-1.028115974673	-2.472165502691
H	5.498884439431	-3.253423754683	-3.130668298645
C	-2.541594022497	-0.098092713978	1.653055900759
C	-3.559573106707	0.296652024826	2.543188878588
C	-2.942587337792	-0.529672940009	0.370680562064
C	-4.897789150248	0.281581921467	2.172520002604
H	-3.282712067427	0.626456063679	3.543882020507
C	-4.285135806646	-0.552334607515	0.007860292089
H	-2.203057051569	-0.882150662548	-0.343580091880
C	-5.273123350199	-0.139287682068	0.897787861464
H	-5.654951090037	0.601204339634	2.886129679621
H	-4.544425162529	-0.906644513155	-0.987628734126
H	-6.320955746299	-0.152047079100	0.607226390305
N	0.492847256969	-3.427452770342	-1.154610178725
C	-0.246171214742	-3.351004956917	0.106690510824
H	0.390839889454	-2.855681132929	0.850113998299
C	1.746892837101	-4.162976821544	-1.069516986960
H	2.328180161112	-3.810803949482	-0.206342023591
H	1.614843969701	-5.255684072616	-0.970361623490
C	-0.333080208218	-3.904184509234	-2.258527587222
H	-1.227200573052	-3.275554086607	-2.346466019995
H	0.233881483435	-3.826846689537	-3.193129156756
H	-0.641495499171	-4.958361882731	-2.127635345521
Na	1.222070905909	-1.165023033081	-1.434418707422
Na	-1.095113668643	1.066085000599	-1.574280840412
H	-1.102897429182	-2.688315444531	-0.063862238690
C	1.561885003462	2.519704907122	-2.384027398548

H	1.656325873907	1.466105125707	-2.678388480664
H	1.792704498111	2.588003939214	-1.313547223912
C	-0.269737232552	2.776289695926	-3.968913745551
H	0.035021952357	1.800371681618	-4.366294897397
H	-1.362918046801	2.827661891281	-4.028200175746
H	0.152535756976	3.577034391679	-4.604775507323
C	-0.238414212911	4.129568852183	-1.956263632598
H	0.415768984486	4.307006005316	-1.094211051224
H	-0.103594602580	4.990959727894	-2.637170108690
C	-1.695318880195	4.110994655070	-1.504005087207
H	-1.941290224206	5.105536021763	-1.077285936070
H	-2.350843468494	3.968256423071	-2.373963099424
C	-3.428248766176	2.998832317399	-0.286303371328
H	-3.645739229683	2.199788223955	0.430645201144
H	-3.964746435784	2.779062823888	-1.216799972605
C	-1.244534389259	3.201132383016	0.694197186317
H	-1.372904333437	4.211125456366	1.132894583899
H	-1.596454162529	2.458530908599	1.416925523237
H	-0.174292539643	3.016904771196	0.537461001934
N	-1.995897825762	3.050087172312	-0.547935976305
N	0.156748339715	2.871760228515	-2.579247262053
C	-0.692025536940	-4.681287419211	0.724387389628
H	0.091366539596	-5.434273180453	0.568366932428
H	-1.609636211620	-5.058944566013	0.230146554664
N	-0.876692353319	-4.545751957117	2.163947286599
C	-1.010964081232	-5.841124543729	2.809840206102
C	-1.983588405683	-3.655259004918	2.480767252167
H	-1.943463539872	-6.363695277958	2.515361731926
H	-0.178691083630	-6.468285190639	2.468145367130
H	-1.834977818921	-2.676540852746	2.013881673155
H	-2.958780490495	-4.059461427423	2.141829606011
H	-2.036475625885	-3.483871665184	3.561597642606
C	2.564972174318	3.380710702621	-3.153942955588
H	2.539059867314	3.126159530752	-4.235956316045
H	2.272039044260	4.437007157527	-3.064421245296
N	3.911934742746	3.255045056833	-2.620619570527
C	4.389696739335	1.884782404039	-2.648709768606
C	4.823978242723	4.139456624598	-3.312896616064
H	4.382747760890	1.450168275529	-3.670674187804
H	5.420123478978	1.856189144197	-2.274574693284
H	3.785295703056	1.253847107535	-1.986521008686
H	4.466979025447	5.173125752654	-3.237903585300
H	5.814437357705	4.090706048592	-2.846046888795
H	4.935347789857	3.889729124675	-4.388097041736

H	-3.807733645965	3.954357390323	0.126471057151
C	-0.962180010538	-5.741148430585	4.331853256890
H	-0.212805619059	-4.975531314689	4.623579266144
H	-1.932308714259	-5.400511689271	4.711690628790
N	-0.678147479725	-7.034799762414	4.936355468574
C	-1.188437603507	-7.126595241650	6.289687527154
C	0.736347969393	-7.350133897967	4.903721724571
H	-0.988067861088	-8.126527985227	6.690931614226
H	-2.273358327504	-6.976148800058	6.290083470070
H	-0.731664212543	-6.383980891028	6.974363335361
H	1.336619794096	-6.665437989921	5.536849888169
H	0.896766110649	-8.375466242003	5.255468608635
H	1.121704614824	-7.289124357477	3.880911770281
H	2.335035264330	-3.981765104546	-1.979101405092

Table S58. Atomic coordinates and single point energies for *bis*-PMDTA-solvated dimer of enolate **4g** with chelation to one *exo* sulfonyl oxygen and one *endo* sulfonyl oxygen (higher energy *exo-endo* isomer). No stable minimum corresponding to a κ^2, κ^2 -isomer could be located.



G = -4119.036572

G_{SP} = -4120.936922

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E2PMDTA2_exo_endo-ph-cm: optimized structure // E(RM062X) = -4122.29478039

A.U. after 13 cycles

O	0.048387599195	0.115427626811	-0.028420985698
C	0.046392134126	0.101428464897	1.242997612892
N	1.351831741823	0.091175904032	1.932504430167
S	2.451630879325	1.305433395863	1.551853362714
O	2.721670066072	1.405046886207	0.095333977079
C	3.887289000508	0.491684033712	2.300699435406
C	3.443196590154	-0.930217820507	2.597829385023
C	2.081757212878	-1.191320201079	1.898279410583
C	1.452308068157	-2.318896511090	2.748091921206
C	2.587387250530	-2.673796306293	3.729113362429
C	3.736167706329	-3.302622812682	2.908577018423
C	4.353634510204	-2.088498569938	2.153812834513
H	4.333475483138	-2.209755821884	1.064508656229
H	5.394608933601	-1.910297133258	2.443226610110
H	3.359399120201	-4.070782464042	2.223147132984
H	4.475378672458	-3.784093680136	3.557285654039

C	3.156432718223	-1.281054427128	4.093384084950
C	2.167740723819	-0.361684657008	4.813950524104
H	2.563978114114	0.662120413553	4.870002141949
H	1.186379761535	-0.305531576900	4.341118806554
H	2.037148549153	-0.714771836602	5.845429674956
C	4.427628267426	-1.321674252030	4.945507562467
H	4.850472738647	-0.312406300786	5.046224120002
H	4.181601057580	-1.672355929166	5.955870789496
H	5.210359405052	-1.974526193461	4.549616413628
H	2.259750531571	-3.284074343231	4.577681938507
H	0.554929103028	-1.960100168229	3.260765819823
H	1.156961312739	-3.174895336766	2.133355747920
H	2.232732407351	-1.495680606817	0.850220473829
H	4.160363907465	1.068233326018	3.190598106805
H	4.681998515913	0.566386947815	1.551916363362
O	2.064553385720	2.550784195058	2.221553413412
C	-1.023440160761	0.052441339769	2.097943470965
H	-0.831142369151	0.181400294075	3.159887643352
O	0.101747383396	1.496243881159	-2.724110364980
C	0.079392229140	2.037201662698	-3.880746729595
C	1.079721606225	2.732406806567	-4.520591288655
H	0.931216319968	3.025709976142	-5.555233570936
N	-1.186216331074	1.918997401265	-4.560197478708
S	-2.017550390632	0.460450786966	-4.348971955207
C	-3.247904055303	0.757524702822	-5.642289578364
C	-2.929761378358	2.116784877611	-6.230316986173
C	-3.037799237162	2.277102766684	-7.755163046703
C	-2.948291280665	3.821799660675	-7.928992503210
C	-2.882667935892	4.348105912939	-6.476006822301
C	-1.474651968196	4.042846774974	-5.932614600054
H	-1.313878676876	4.464167047117	-4.934999001424
H	-0.686351244758	4.428897987302	-6.587238097185
C	-1.462390361646	2.493182716538	-5.879636654242
H	-0.769536728710	2.065369925795	-6.619128747766
H	-3.177015603010	5.397596569027	-6.367729164746
C	-3.757488930795	3.330369699856	-5.705721728662
C	-3.753501223792	3.507770244735	-4.187629633869
H	-4.232609365064	4.462053492123	-3.931840800200
H	-4.336710660085	2.711246616302	-3.705690865518
H	-2.758134557682	3.492588642211	-3.744451598808
C	-5.221358796050	3.297444040845	-6.150095531420
H	-5.733388343988	2.427322821457	-5.716329621940
H	-5.735238450284	4.193846060058	-5.779695317918
H	-5.358978216026	3.261993413604	-7.234526264459

H	-3.821639684734	4.213806563305	-8.460469332617
H	-2.061369887537	4.123428729592	-8.497810516108
H	-2.231464159332	1.738592480269	-8.265027629924
H	-3.987593669999	1.877112817448	-8.125523507613
H	-3.111131730493	-0.065292386217	-6.350761918392
H	-4.234635886507	0.686686829934	-5.173532817660
O	-2.648141898368	0.424910618225	-3.010226911089
O	-1.197927625052	-0.699269005753	-4.724702229616
C	2.338622963366	3.136621470373	-3.915898397637
C	3.378867339171	3.606106244495	-4.747437448615
C	2.592594488795	3.117017090497	-2.529062538501
C	4.599609313766	4.013999535165	-4.227712290933
H	3.219490068431	3.632483831462	-5.825206386580
C	3.817705443855	3.528523034523	-2.010630111806
H	1.813548625014	2.796694301936	-1.845822645334
C	4.834286112073	3.978502736121	-2.850978433266
H	5.379858076028	4.357458793610	-4.905645782680
H	3.965327276494	3.487525987959	-0.932660777661
H	5.792198940617	4.296642021143	-2.444187092434
C	-2.405195186633	-0.147039781021	1.677572679006
C	-3.454505159951	0.193961836826	2.555979571451
C	-2.764258335293	-0.727459553159	0.440890833182
C	-4.784193509033	-0.025630389771	2.218306377314
H	-3.208456282045	0.635658417221	3.521161057557
C	-4.098848047586	-0.945215255756	0.108197354782
H	-1.981127947563	-1.050090818862	-0.243295842284
C	-5.119680430482	-0.594761148786	0.989071794861
H	-5.568028795637	0.253965004126	2.920566556649
H	-4.338304325419	-1.399052995341	-0.852190506510
H	-6.161413791679	-0.762875716947	0.723897931926
N	1.495363852703	-2.198864883853	-1.732247574759
C	0.919660826811	-3.065344835746	-0.716886672436
H	1.702332997790	-3.403967911007	-0.028558581556
H	0.444536392573	-3.961313590110	-1.161093851108
C	2.657740657458	-2.824765178906	-2.347087462445
H	3.347238611225	-3.111252795470	-1.541434764563
H	2.381877086646	-3.759105878433	-2.876082842109
C	0.475329906427	-1.860464551268	-2.718112458411
H	-0.378732906785	-1.395811116258	-2.210440642637
H	0.851328993245	-1.141516240021	-3.453323697461
H	0.113476150187	-2.749880863964	-3.268244018128
Na	1.664575725963	0.287602937506	-1.597847027714
Na	-1.536046579550	1.324876907349	-1.193344669506
H	0.166029226347	-2.506680481447	-0.147210948361

C	3.374945930378	-1.922001345366	-3.341527814156
H	4.300550308828	-2.446947293233	-3.642046634223
H	2.771380165085	-1.797886098270	-4.249881941086
N	3.661112004956	-0.585967604402	-2.817534612654
C	4.195389854557	0.291299597843	-3.865269551041
H	4.444380170059	1.251003510529	-3.397957831588
H	3.390646494712	0.493559480989	-4.585872359226
C	4.518752525580	-0.630985233658	-1.636834472839
H	5.436245141770	-1.230365989014	-1.783668455323
H	4.800721984114	0.391786548807	-1.360634207760
H	3.962581101896	-1.059388930815	-0.791768036410
C	-0.187652110129	3.364798242923	0.354868339614
H	0.494878626907	2.797452309625	-0.288659970289
H	0.311165458478	4.307861557406	0.646708538328
H	-0.371915119966	2.783351592526	1.264573928369
C	-1.216434792610	4.475146770926	-1.490477982653
H	-0.481681636617	3.998596413953	-2.153029424807
H	-2.148669750080	4.620075660912	-2.044497706195
H	-0.819088136392	5.463333050527	-1.187155600504
C	-2.383340291438	4.212032180654	0.619745111390
H	-2.567500070087	3.468541416231	1.407240605876
H	-1.905194553365	5.080481475264	1.115273621408
C	-3.702387889301	4.715602121794	0.052064854465
H	-4.306763962920	5.041532860466	0.916833739867
H	-3.521535129377	5.605170382023	-0.566498437024
C	-5.599122369964	4.299157385180	-1.423909715858
H	-5.840098288422	3.665862355349	-2.290048065408
H	-5.332022865652	5.284513287127	-1.827986197271
C	-4.684677028781	2.498132489498	-0.094091031608
H	-5.297085247911	2.620515345021	0.819809885237
H	-5.213363212171	1.821733476226	-0.777284201270
H	-3.747823035352	2.010260764227	0.203135847217
N	-4.412334027569	3.748752160156	-0.775829004477
N	-1.451436532661	3.611154829002	-0.337635708543
C	5.417483136142	-0.243815879903	-4.623469312767
H	5.088600948379	-0.948911221129	-5.396342083009
H	6.089176892605	-0.807744631332	-3.944508330337
C	6.866897069743	0.386984605263	-6.445887980131
H	6.170717360713	-0.040461040812	-7.175877442433
H	7.376820007501	1.235928458232	-6.916060300514
H	7.629737625406	-0.377968074614	-6.199105267405
C	7.041385676735	1.499819072280	-4.345092566306
H	6.501374052982	1.804872187587	-3.442307295922
H	7.875149264272	0.834104061952	-4.042731926892

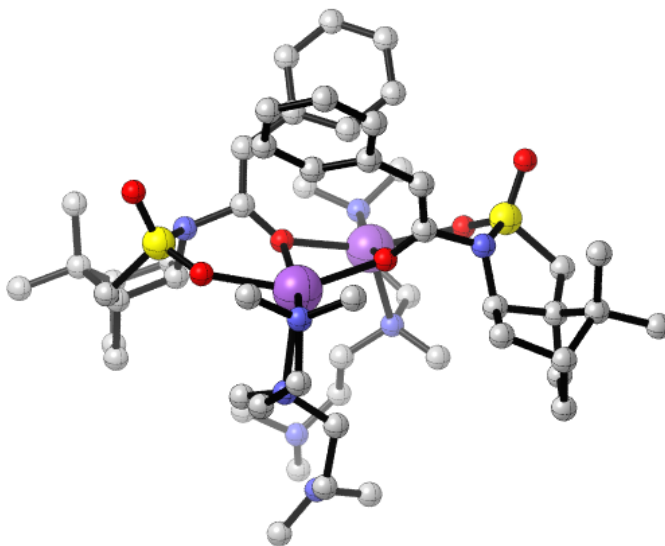
H	7.467832110454	2.400204066540	-4.803543167199
N	6.138007544843	0.845555443107	-5.276259958187
C	-6.883934103205	4.382717466893	-0.594504430771
H	-7.685520340004	4.783379697176	-1.252950482985
H	-7.192294095902	3.366703951435	-0.317285038998
C	-6.599526418998	6.572912201646	0.372756849879
H	-7.452401680383	7.006598168346	-0.187578446226
H	-6.502518986144	7.112613638562	1.321884259243
H	-5.685957247531	6.747038469560	-0.205456639585
C	-7.939340820224	4.937597366660	1.479366474785
H	-8.024147930101	3.872671063555	1.725039715414
H	-7.826774109272	5.497201052203	2.414878881946
H	-8.883118691211	5.258882067272	0.995315120285
N	-6.778883761298	5.156420170773	0.634496357596

Table S59. Atomic coordinates and single point energies for *bis*-PMDTA-solvated dimer of enolate **4g** with chelation to one *exo* sulfonyl oxygen and one *endo* sulfonyl oxygen (higher energy *exo-endo* isomer).

G =

G_{SP} =

Table S60. Atomic coordinates and single point energies for *bis*-PMDTA-solvated dimer of enolate **4g** with double chelation to the *endo* sulfonyl oxygens (lowest energy *endo-endo* isomer).



G = -4119.047381

G_{SP} = -4120.943269

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E2PMDTA2_endo_endo_Cm-Cm: optimized structure // E(RM062X) = -4122.30364231

A.U. after 12 cycles

O	-0.008647512353	-0.007749882845	-0.179944266041
C	0.063018605596	-0.024052899368	1.091274471611
N	1.430111652482	-0.055933773093	1.659747276014
S	2.140147486689	1.461772217509	1.797657434904
O	1.943984420752	2.263142984978	0.561840386485
C	3.856412520161	0.876790044987	1.837189050597
C	3.779293544591	-0.620288483079	1.599011399837
C	2.385929159418	-0.968098157202	1.014246178431
C	2.202381291875	-2.456401491269	1.397727214306
C	3.557322651867	-2.812069100652	2.047208297490
C	4.629795925297	-2.778536172189	0.936766870341
C	4.797016647916	-1.259498841125	0.636053065353
H	4.565779432160	-1.003719049713	-0.405037602750
H	5.814782976819	-0.910470183489	0.840124892650
H	4.308777165050	-3.347320975131	0.057671000308
H	5.571398413210	-3.220048271277	1.279802057551
C	3.882901342384	-1.537126559849	2.861332784326

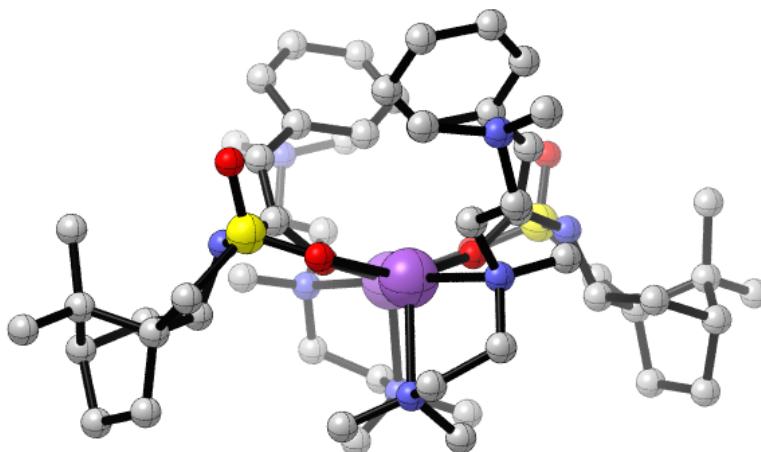
C	2.893489951363	-1.238754221902	3.990605782018
H	3.044404840924	-0.220943001676	4.377485055385
H	1.845910973092	-1.323504189786	3.698452317033
H	3.080749261992	-1.932463215893	4.820909196009
C	5.281548760677	-1.523907637680	3.484543580827
H	5.475673786035	-0.550490691760	3.955893491361
H	5.340243048127	-2.283639974129	4.274305299546
H	6.090611466972	-1.718904806774	2.775456082586
H	3.538970669665	-3.744643420377	2.621555620995
H	1.362168245261	-2.577008293631	2.090008480573
H	2.000843143260	-3.076794141078	0.516305996499
H	2.357332801582	-0.822250778475	-0.073583198174
H	4.269206538002	1.151748571998	2.813541314461
H	4.374606149329	1.430038782635	1.047420903879
O	1.727333048847	2.113718846557	3.044776329554
C	-0.918908176061	-0.028503618739	2.045892373843
H	-0.585413789626	-0.103921823384	3.077820980928
O	-1.375987515306	1.636839276115	-2.217477862511
C	-2.493004683381	2.232740819373	-2.358468377842
C	-3.128928492569	3.139468390674	-1.554383808100
H	-4.062891879211	3.547347234016	-1.932653200187
N	-3.228816155519	1.927137248006	-3.604361722506
S	-4.154338368804	0.525495290532	-3.543648422402
C	-4.304303864113	0.324637106125	-5.339952030570
C	-3.355125960913	1.347348423007	-5.943073935034
C	-2.425308962498	0.895560186575	-7.083006798084
C	-1.879226389474	2.250840327502	-7.621787445981
C	-2.610445031295	3.305961442054	-6.760966019054
C	-1.983725092197	3.268131580516	-5.351295315872
H	-2.367697645448	4.062193607572	-4.702060147935
H	-0.893126674193	3.363655984991	-5.386679720623
C	-2.416753582379	1.878531443057	-4.828971276068
H	-1.557288537360	1.212546814542	-4.675746618691
H	-2.634748968914	4.306299668854	-7.206613923316
C	-3.993835784911	2.649407754107	-6.528011743094
C	-4.910975448815	3.428303835973	-5.581947257666
H	-5.294907159072	4.313961991997	-6.105233576907
H	-5.780082350775	2.817798207540	-5.298259360791
H	-4.427009021293	3.753661507746	-4.660288075978
C	-4.793892701086	2.390503453324	-7.807479985505
H	-5.690667250699	1.797450354825	-7.579450987346
H	-5.134599272527	3.344803298382	-8.228626287767
H	-4.235023509884	1.865402895090	-8.586962485225
H	-2.104903758382	2.375820104571	-8.686042322882

H	-0.791686930431	2.332798474015	-7.510075923141
H	-1.632673655237	0.238594419824	-6.709424075038
H	-2.976220950966	0.340696789803	-7.849544262608
H	-4.033530493893	-0.715722905734	-5.545117392637
H	-5.356614556962	0.489825206786	-5.594051602800
O	-5.437766284215	0.786247340081	-2.884497115805
O	-3.371186459040	-0.617920483195	-3.005315491701
C	-2.631167886316	3.691529759471	-0.298745913165
C	-3.227290565631	4.870031593054	0.195401845549
C	-1.573600017148	3.146234563431	0.456872512632
C	-2.777105477674	5.482261787870	1.358671253465
H	-4.055856814256	5.310263828162	-0.358653106429
C	-1.126718002771	3.757019880501	1.625649841623
H	-1.132431989803	2.200261094578	0.160572028451
C	-1.716209003431	4.934707458802	2.081295604959
H	-3.260204281859	6.394352458273	1.705706549310
H	-0.310876565471	3.298080036960	2.184898728159
H	-1.363216545222	5.411693071661	2.993118474234
C	-2.360810565756	-0.046165041327	1.822027918133
C	-3.199644618760	-0.430851957454	2.888721511992
C	-2.989287376822	0.287173862692	0.606072688645
C	-4.580088235684	-0.495041053614	2.743638549968
H	-2.746572650595	-0.685798521775	3.846377412215
C	-4.373637826937	0.231992160390	0.463003819902
H	-2.391368496478	0.654529495003	-0.221592084223
C	-5.180067390285	-0.168089219408	1.526501028200
H	-5.194166319610	-0.799311592050	3.589835186558
H	-4.820806777637	0.507958892905	-0.492334605617
H	-6.261028208157	-0.214097504386	1.412664809191
C	3.124722257770	3.171183044260	-2.594650745716
H	3.499644705552	3.205660868928	-1.563184692056
H	4.000210504688	3.306626240693	-3.256802388688
C	2.192253549005	1.556038120778	-4.184705905680
H	1.454518844919	0.740860648183	-4.200116948722
H	1.701636451655	2.432330159841	-4.620418804639
C	3.286598585658	0.808194409117	-2.143369215493
H	4.308154892087	0.716184665647	-2.554516211736
H	3.362737636255	1.031206391601	-1.072791829242
C	-0.766757973548	-1.603498754337	-4.834220193288
H	-0.454454044639	-2.283240338170	-5.649365421349
H	-1.836269636765	-1.391440566607	-4.952876839542
C	0.876208706237	-2.334237697181	-3.192948019208
H	1.416176864053	-1.444873939965	-3.547751299757
H	0.987233099731	-2.358627248290	-2.099060265938

C	-1.371748366161	-3.344344422334	-3.302967703786
H	-2.400095270214	-3.067940523329	-3.571055392021
H	-1.074234916408	-4.163361242390	-3.983164788551
N	-0.547113963582	-2.149944089517	-3.504126279304
N	2.498534451784	1.858805913841	-2.780413189125
Na	0.604639930421	2.004079425339	-1.279071764769
Na	-1.412278493608	-0.670611523517	-1.791574984989
H	-0.217068473138	-0.660848607789	-4.937685806778
H	2.784982586840	-0.157512405167	-2.276853004567
C	2.151672225300	4.322778307170	-2.809184907693
H	2.718998163221	5.272067441385	-2.839630711298
H	1.667178196009	4.223659892126	-3.787208234193
C	1.579908202426	5.078123267571	-0.597239555427
H	0.818468302015	5.024819716724	0.188614112380
H	2.486417304738	4.601738000750	-0.213345978043
C	-0.088587689311	5.035913582890	-2.305256729057
H	0.132854452171	6.047462644516	-2.697458885278
H	-0.528651419157	4.431837773090	-3.107983858396
H	-0.829183326010	5.131785602059	-1.503849276447
N	1.105414314452	4.378494263169	-1.786203191496
C	-1.341325106664	-3.850814308798	-1.870414621248
H	-1.835449051757	-4.839971567266	-1.830246430961
H	-0.302561582564	-4.010708704548	-1.554769763193
C	-1.457575268967	-3.140097301091	0.417696330726
H	-1.600977651064	-4.187218507284	0.748479823818
H	-0.388996634782	-2.899149405370	0.451981031418
H	-1.979276974648	-2.480328577004	1.117827207171
C	-3.420338597906	-3.067464452902	-0.942282623968
H	-3.866531962462	-2.335296342719	-0.260152624415
H	-3.814676692863	-2.873203369538	-1.944508372533
N	-1.968040669045	-2.921016990023	-0.929852929756
C	1.531888424004	-3.567781951393	-3.819298733053
H	1.180190125755	-4.489046170774	-3.308079422197
H	1.218990811336	-3.648927035538	-4.870194017548
N	2.986075772077	-3.492488624976	-3.796650818212
C	3.564838699359	-4.635092035452	-4.478485680099
C	3.510533558960	-3.376182830504	-2.447801560715
H	4.656777383561	-4.541335365579	-4.499473726918
H	3.310044803105	-5.596309923092	-3.988981820092
H	3.202512854431	-4.672731958321	-5.512903645362
H	3.179244176616	-2.440163030700	-1.981421399119
H	3.199337293152	-4.223012617302	-1.801175373582
H	4.606699837784	-3.358647262887	-2.482877900302
C	3.395769097061	1.136521550968	-5.038568124223

H	3.272811492575	1.494255481448	-6.078843806422
H	4.303561018407	1.619822522244	-4.653615320581
N	3.580394787091	-0.311449578394	-5.002558032863
C	4.965208884154	-0.716042709652	-5.135903874458
C	2.757391606269	-0.966738416995	-6.001430702593
H	5.027146191608	-1.808001364520	-5.049735232714
H	5.410966336401	-0.418559186179	-6.105851049639
H	5.563853749299	-0.272715766379	-4.330545215994
H	1.715112982134	-0.642996891308	-5.900182576852
H	3.086796613300	-0.728396195420	-7.033685163241
H	2.798454281444	-2.051379611598	-5.850305136600
H	-3.725256578318	-4.082737015070	-0.622637793164
H	1.794663559279	6.142036924030	-0.816442853461

Table S61. Atomic coordinates and single point energies for *bis*-PMDTA-solvated dimer of enolate **4g** with double chelation to the *endo* sulfonyl oxygens (higher energy *endo-endo* isomer).



G = -4119.039375

G_{SP} = -4120.935082

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E2PMDTA2_endo_endo: optimized structure // E(RM062X) = -4122.29440001 A.U.
after 12 cycles

O	0.000000000000	0.000000000000	0.000000000000
C	0.000000000000	0.000000000000	1.274149160000
N	1.329953307796	0.000000000000	1.928315609370
S	2.057606358395	1.511218200007	2.023149273430
O	1.978507007166	2.239437169566	0.729854853432
C	3.752796142157	0.906954421149	2.238037692039
C	3.665658285972	-0.600825976052	2.093278018001
C	2.315612288251	-0.967625906029	1.421361686757
C	2.077016872101	-2.425752103621	1.886565059210
C	3.368115466520	-2.753979565589	2.664734684582
C	4.521990465851	-2.809361082834	1.638309465798
C	4.747215226523	-1.314732277726	1.262984513200
H	4.612017962051	-1.120708136183	0.193176110339
H	5.750199708139	-0.969574973066	1.534740355985
H	4.250813832511	-3.419008931783	0.768806057065
H	5.424783455719	-3.250472189816	2.073609857062
C	3.652091295638	-1.432658832096	3.417080188170

C	2.580833635928	-1.046490983436	4.439885590912
H	2.710258337872	-0.003879403400	4.762590356079
H	1.558840225369	-1.148105177843	4.071973685918
H	2.694054582553	-1.678579136515	5.330548437458
C	4.996983074775	-1.397709759630	4.148293928817
H	5.176558617351	-0.396151797692	4.563189428801
H	4.975135952329	-2.098874322072	4.992200311653
H	5.854494190597	-1.658670305299	3.522049890320
H	3.287507904699	-3.646226762053	3.295100489196
H	1.177619099967	-2.493515411157	2.508833478249
H	1.945347626000	-3.102066192784	1.036031373503
H	2.376472514327	-0.891668591094	0.327903529838
H	4.090163642137	1.241884640640	3.224752521331
H	4.343664867546	1.398869157783	1.458639298001
O	1.564604659805	2.242823773602	3.195464675051
C	-1.039783685282	-0.028678117155	2.162964695664
H	-0.773521614792	-0.099586152052	3.214610810259
O	-1.279876635669	1.542559736650	-2.199392681773
C	-2.354395797517	2.203398465550	-2.379528748908
C	-2.910054181784	3.214932591836	-1.645136781615
H	-3.803737142281	3.676235727571	-2.058050808436
N	-3.133623086478	1.862120411153	-3.592151975077
S	-4.103262259167	0.498292896036	-3.438182659695
C	-4.264689796518	0.166872562237	-5.213617590130
C	-3.362748588869	1.177300550886	-5.898188295899
C	-2.482619811810	0.693129017265	-7.064339165053
C	-2.001350605301	2.032471421477	-7.696563639199
C	-2.699247409650	3.109477243821	-6.836066662377
C	-1.990477415399	3.133984329913	-5.465648474180
H	-2.330479291584	3.957440164881	-4.827929507757
H	-0.905598317763	3.227532302070	-5.580598524654
C	-2.380347753158	1.766656179465	-4.852173389515
H	-1.506007305768	1.118493319999	-4.710183543439
H	-2.764223831486	4.091979581518	-7.316101891410
C	-4.054904647265	2.443467184021	-6.500592241322
C	-4.932573481293	3.249008846637	-5.539371326728
H	-5.384029546915	4.087146229533	-6.086504852830
H	-5.755794277565	2.630582018610	-5.154880098447
H	-4.396762703758	3.648394526899	-4.677171736426
C	-4.919080182877	2.117668785267	-7.721907323846
H	-5.809383035259	1.551285796635	-7.415189533251
H	-5.270751315779	3.049417640187	-8.182800160947
H	-4.404418423784	1.538998676080	-8.493868293987
H	-2.298386352980	2.105383673439	-8.748037203213

H	-0.911258082505	2.140105895546	-7.659897415687
H	-1.654670724456	0.074578229900	-6.700979796820
H	-3.058100446991	0.087801554653	-7.772399506374
H	-3.956756704140	-0.874699940877	-5.350992146217
H	-5.325711737868	0.273985622151	-5.463527864221
O	-5.382698802237	0.849669195856	-2.811916620977
O	-3.368065146748	-0.630283664381	-2.808829808041
C	-2.355763748372	3.828013114526	-0.437305783184
C	-2.714369465735	5.160598130598	-0.143793315355
C	-1.486808687029	3.189300777119	0.468073007155
C	-2.232940405149	5.815733827167	0.982628533098
H	-3.381881115483	5.685778008106	-0.826706185097
C	-1.027615843148	3.836552836217	1.614286420489
H	-1.191653911367	2.157193981057	0.304522289051
C	-1.391188653118	5.154145313389	1.877821009962
H	-2.518595482717	6.850283168565	1.165379481217
H	-0.366424972471	3.303359368927	2.296501352253
H	-1.020477046226	5.662537556500	2.765638278004
C	-2.465231549334	-0.111094671304	1.842337283897
C	-3.332565285895	-0.662178322673	2.809159600199
C	-3.050273957055	0.319139604651	0.635520747230
C	-4.698827970668	-0.779220204770	2.584617511512
H	-2.911974624412	-1.008094707078	3.753120096174
C	-4.424535406764	0.225899879586	0.421037201039
H	-2.436306707951	0.772725179256	-0.136859948019
C	-5.258348331261	-0.328716400776	1.388548396145
H	-5.331876118769	-1.225231962475	3.349870421772
H	-4.840153895697	0.581768799135	-0.520863927776
H	-6.329332055287	-0.409632871785	1.214176369226
C	3.329299277620	2.949666394699	-2.244289687571
H	3.530906997131	3.086715850771	-1.172953516230
H	4.303299490754	2.976533457178	-2.773043973098
C	2.437880040133	1.307225342697	-3.795042617240
H	2.059118285954	0.281286568599	-3.854998393644
H	1.673638235060	1.968428669747	-4.217356187340
H	3.349969615158	1.377697033222	-4.418773594558
C	3.533325462710	0.617142213136	-1.783919912345
H	4.530614852136	0.547427404287	-2.260616455639
H	3.667634858886	0.855785693577	-0.722837205117
C	-0.696468341538	-1.589472038470	-4.648432474643
H	-0.470031883100	-2.290495852034	-5.475427705968
H	-1.732643505957	-1.248641421249	-4.751622143038
C	0.858793940537	-2.616681309460	-3.151253221071
H	1.139553137336	-3.456126742142	-3.816112086633

H	1.517270330203	-1.770045272987	-3.372321746033
H	1.039944742067	-2.917836506781	-2.113898383745
C	-1.461125595538	-3.326676060432	-3.203813842065
H	-2.466314246289	-2.938741414689	-3.418930360782
H	-1.236286100915	-4.112325972074	-3.952976796612
N	-0.527008867045	-2.207075294185	-3.341248833401
N	2.698323334481	1.637579365702	-2.400098920433
Na	0.653013130922	1.936923073230	-1.138545577990
Na	-1.380094260021	-0.712032969395	-1.622707323987
H	-0.031754042618	-0.721809765694	-4.738212960254
H	3.043237366440	-0.360630500597	-1.862725179138
C	2.470336363017	4.097860640231	-2.752603200793
H	3.063042395580	5.026057475388	-2.694327016457
H	2.250191527920	3.949940524530	-3.816111451941
C	1.296748027948	4.987933641018	-0.794187539287
H	0.327296055083	4.915674297232	-0.287528400398
H	2.030588550283	4.489881129545	-0.149267913994
C	0.120676741091	4.666143602684	-2.903948393009
H	0.360790600168	5.588617611976	-3.463089790881
H	-0.111947578394	3.875215681530	-3.625871496947
H	-0.777170724230	4.847657058523	-2.303205518245
N	1.199781065835	4.214734375896	-2.034202472485
C	-1.448993567833	-3.953458288458	-1.818335944483
H	-2.092814711540	-4.847392058264	-1.839066221925
H	-0.441407313972	-4.316465336686	-1.584648515365
C	-1.062948176943	-3.151001048939	0.440637902796
H	-1.005775317481	-4.188225566554	0.817475043703
H	-0.045272079265	-2.796889191381	0.241324931796
H	-1.487858040265	-2.517519194323	1.226757162817
C	-3.300633681497	-3.013876730952	-0.518445764741
H	-3.513162709240	-2.195299926552	0.179377495433
H	-3.803278810278	-2.767968045902	-1.462745143752
N	-1.859169203386	-3.012370186034	-0.772701421728
C	-3.876572569252	-4.291272240320	0.102635966408
H	-4.016818917881	-5.083965361332	-0.662202891995
H	-3.171151262401	-4.681732816373	0.847940045782
C	-5.593285853062	-5.196985705625	1.504079513374
H	-6.501357826917	-4.956221552940	2.068842720759
H	-5.823710539011	-6.039692441315	0.821668311237
H	-4.827061619274	-5.529687616084	2.213687726932
C	-6.155374492063	-3.526169390594	-0.106256983535
H	-5.845730072589	-2.581130288820	-0.565670773327
H	-6.385542625075	-4.250201595723	-0.915298101212
H	-7.077059405422	-3.337874224602	0.456538189972

N	-5.129139961610	-4.018043562345	0.797092610285
C	1.615125475007	6.479651697551	-0.937018029443
H	2.695036026878	6.642455769546	-1.137923717603
H	1.060679200654	6.892883032227	-1.789989714804
C	1.878404768028	6.761492613146	1.448150748601
H	1.547843191772	7.360154381035	2.304743725374
H	1.634475875129	5.714291106149	1.659147403163
H	2.981198797552	6.855020780835	1.365716792232
C	1.389356416208	8.643462779092	0.061209656684
H	1.009662803825	9.187224056658	0.933861495221
H	2.455478843202	8.913634721651	-0.077793199142
H	0.832639229659	8.980117132952	-0.820925094931
N	1.195186714447	7.217962455783	0.249553577484

Table S62. Atomic coordinates and single point energies for *bis*-PMDTA-solvated dimer of enolate **4g** with double chelation to the *endo* sulfonyl oxygens (higher energy *endo-endo* isomer).

G =

G_{SP} =