Supporting Information

Solvation Effects on the Structure and Stability of Alkali Metal Carbenoids

Katharina Dilchert, Michelle Schmidt, Angela Großjohann, Kai-Stephan Feichtner, Robert E. Mulvey,* and Viktoria H. Gessner*

anie_202011278_sm_miscellaneous_information.pdf
Index

1. Experimental Details 2
   1.1 General methods 2
   1.2 Synthesis of the chiral carbenoids 3

2. NMR spectra 5
   2.1 NMR spectra of the isolated compounds 5
   2.2 VT $^{31}$P($^1$H) NMR spectroscopy 13

3. DOSY NMR spectroscopy 17
   3.1 General procedure 17
   3.2 DOSY NMR data of rac-1-Li 18
   3.3 DOSY NMR Data of rac-1-Na 22
   3.4 DOSY NMR data of rac-1-K 26

4. Determination of ee 30

5. Crystal Structure Determination 31
   5.1 General information 31
   5.2 Further Details to the Crystal Structures 33

6. Computational Details 52
   6.1 General 52
   6.2 Structures of the energy-optimized compounds 53
   6.3 Energies of the optimized compounds 56
   6.4 Coordinates 59
      6.4.1 Coordinates of the monomeric structures of 1-Li 59
      6.4.2 Coordinates of the dimeric structures of 1-Li 74
      6.4.3 Coordinates of the monomeric structures of 1-Na 93
      6.4.4 Coordinates of the dimeric structures of 1-Na 108
      6.4.5 Coordinates of the monomeric structures of 1-K 118
      6.4.6 Coordinates of the dimeric structures of 1-K 132

7. References 141
1. Experimental Details

1.1 General methods

All experiments were carried out under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Involved solvents were dried using an MBraun SPS-800 (THF, toluene, Et₂O, DCM, pentane, hexane) or dried in accordance with standard procedures. H₂O is distilled water. ¹H, ¹³C{¹H}, ³¹P{¹H} NMR spectra were recorded on Avance-400 or AVIII-400 spectrometers at 25 °C if not stated otherwise. All values of the chemical shift are in ppm regarding the δ-scale. All spin-spin coupling constants (J) are printed in Hertz (Hz). To display multiplicities and signal forms correctly the following abbreviations were used: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Signal assignment was supported by DEPT, APT, HSQC and HMBC experiments and by literature studies on similar compounds.

Elemental analyses were performed on an Elementar vario MICRO-cube elemental analyzer.

For column chromatography silica gel 60M purchased from Machery-Nagel was used. The solvent mixtures are given as volume fractions (v/v). Pre-coated TLC sheets (ALUGRAM ALOX N/UV 254) with fluorescence indicator purchased from Machery-Nagel were used. The detection was done by means of UV light (λ = 254 nm).

For automated Column Chromatography a Reveleris X2 Flash Instrument by Büchi was used. Solid loaders with a screw cap and Flash cartridges (FlashPure Silica) by Büchi were used. The detection was done by means of integrated UV detection (λ₁ = 254 nm, λ₂ = 265 nm, λ₃ = 280 nm) and ELSD.

For the determination of the ee an analytical Knauer Azura HPLC system equipped with a Dr. Maisch Reprosil Chiral-NR 8µm, 250•4.6 mm was used. A mixture of hexane and isopropanol (85:15) were used with a flow rate of 1.5 mL/min.

All other reagents were purchased from Sigma-Aldrich, ABCR, Rockwood Lithium or Acros Organics and used without further purification.

¹H₂ was synthesized according to literature.[¹]
1.2 Synthesis of the chiral carbenoids

Synthesis of R-1

901 mg (2.337 mmol) of R-2 were dissolved in 50 mL THF and cooled to –80 °C. 1.64 mL (1.71 M in Hex, 2.805 mmol) tBuLi were added dropwise. The yellow solution was stirred between −80 °C and −30 °C for 1 h. 719.24 mg of hexachloroethane were dissolved in 50 mL THF. The yellow reaction mixture was transferred to hexachloroethane via temperature gradient and warmed to RT slowly overnight. 25 mL of H2O were added, and the phases were separated. The aqueous phase was extracted with 25 mL of Et2O three times. The combined organic phases were dried over Na2SO4. After filtration the solvent was removed in vacuo. The crude product was purified by column chromatography (THF/Hex 1:2.5, r = 0.4). The product was obtained as a white solid in 54 % yield (525 mg, 1.25 mmol). The same procedure was also used for racemic mixtures of the sulfoximine. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of hexane from a solution of the rac-1 at RT.

1H NMR (400.33 MHz, CDCl3): δH = 2.77 + 2.88 (s + s, 3H; NCH3), 5.71 + 5.78 (d + d, 1H, JCP = 4.49 Hz + 4.81 Hz; CHCl), 7.29-7.35 (m, 4H; CHPh,ortho/meta), 7.37-7.51 (m, 5H, CH), 7.73-7.93 (m, 6H; CHPh,ortho/meta/para), 13C(1H) NMR (100.67 Hz, CDCl3): δC = 29.6 (s, NCH3), 31.0 (s, NCH3), 69.2 (s, CCl) 75.9 (s, CCl), 128.5 (s, PCPh,para) 128.5 (s, PCPh,para), 128.6 (bs, PCPh, ortho), 129.0 (s, SPh, meta), 129.2 (s, SPh, meta), 130.3 (s, PCPh, ipso), 130.6 (s, PCPh,para), 130.9 (s, SPh, ortho), 131.6 (s, PCPh,para), 132.1 (s, PCPh, ortho/meta), 132.2 (s, PCPh, ortho/meta), 132.2 (s, PCPh, ortho/meta), 132.3 (s, PCPh, ortho/meta), 132.4 (s, PCPh, ortho/meta), 132.5 (s, PCPh, ortho/meta), 133.5 (s, SPh, para), 134.0 (s, SPh, para), 135.6 (s, PCPh, ipso), 139.0 (s, PCPh,ipso), 31P(1H) NMR (162.1 MHz, CDCl3): δP = 45.1 (s), 46.5 (s). Anal. Calcd. for C26H19ClNOPS: C, 57.21; H, 4.56; N, 3.34; S, 15.27. Found: C, 57.32; H, 4.55; N, 3.28; S, 15.30.

Preparation of R-1-Li-2THF

12.4 mg (0.0295 mmol) of R-1 were dissolved in 1 mL of THF and cooled to 0 °C. 0.02 mL (0.0295 mmol, 1.6M in Et2O) MeLi were added slowly. The resulting yellow solution was stirred for 1 h at 0 °C. The solvent was removed, and the product was obtained as a yellow solid in 93 % yield. R-1 is coordinated by two THF molecules. (15.6 mg, 0.0274 mmol). NMR spectroscopic characterization was performed at −30 °C. Single crystals suitable for X-ray diffraction analysis were obtained from a concentrated THF solution at −30 °C.

1H NMR (400.33 MHz, d8-THF): δH = 2.91 (s, 3H; NCH3), 7.13-7.19(m, 3H; SCHPh,meta,para + PCHPh,meta,para), 7.27-7.29 (m, 6H; SCHPh,meta,para + PCHPh,meta,para), 7.70-7.75 (m, 2H; PCHPh,ortho), 8.11-8.13 (m, 4H; PCHPh,ortho + SCHPh,ortho), 13C(1H) NMR (100.67 MHz, d8-THF): δC = 29.8 (s, NCH3), 49.2 (d, 1JCp = 83.1 Hz; CCI), 127.8 – 128.1 (d + d, 1JCp = 11.9 Hz; PCPh,meta); 128.0 (s, SPh,meta); 129.0 (SPh,ortho); 130.0 (d, 1JCp = 2.5 Hz; CPh,para); 130.2 (d, 1JCp = 4.4 Hz; CPh,para); 130.2 (s, 2JCp = 10.3 Hz; SPh,para); 133.1 (d, 2JCp = 9.8 Hz; CPh,ortho); 133.2 (d, 2JCp = 10.1 Hz; CPh,ortho); 139.1 + 140.7 (d + d, 1JCp = 88.8 Hz + 96.2 Hz; CPh,ipso); 145.8 (s, SPh,ipso), 31P(1H) NMR (162.1 MHz, d8-THF): δP = 42.2 (s). Anal. Calcd. for C26H14ClN2LiO3PS2: C 58.99, H 6.01, N 2.46, S 11.25. Found: C 58.76, H 5.81, N 2.74, S 11.64.
Preparation of \(R\)-1-Na-THF

13.4 mg (0.0319 mmol) of \(R\)-1 were dissolved in 1 mL of THF and cooled to 0 °C. Subsequently, the solution was added to 2.3 mg (0.1821 mmol) of NaH. The reaction solution was stirred for 1 h at 0 °C and subsequently filtered through a cannula. The solvent was removed in vacuo. The product was obtained as a pale-yellow solid in 92 % yield (15.1 mg, 0.0294 mmol). Suitable crystals for X-ray diffraction analysis were obtained by slow diffusion of pentane into a solution of 1eq. of \(18\)-C-6 and \(rac\)-1-\(Na\)-THF in THF at -30 °C.

\(^1\)H NMR (400.3 MHz, \(d_8\)-THF): \(\delta_H = 2.84\) (s, 3H; NCH\(_3\)), 7.13-7.31 (m, 9H; SCH\(_{Ph,meta,para}\) + PCH\(_{Ph,meta,para}\)), 7.85-7.89 (m, 2H; PCH\(_{Ph,ortho}\)), 7.98-8.10 (m, 4H; PCH\(_{Ph,ortho} + \) SCH\(_{Ph,ortho}\))

\(^{13}\)C\(^{(1)}\)H\) NMR (100.7 MHz, \(d_8\)-THF): \(\delta_C = 30.2\) (NCH\(_3\)), 50.4 (d, \(^1\)J\(_{CP} = 88.5\) Hz; CCl), 127.7 + 127.9 (d + d, \(^3\)J\(_{CP} = 12.1\) Hz; PCH\(_{Ph,meta}\)), 128.1 (SC\(_{Ph,meta}\)), 128.4 (SC\(_{Ph,ortho}\)), 129.8 (SC\(_{Ph,para}\)), 130.0 (d, \(^4\)J\(_{CP} = 2.2\) Hz; PCH\(_{Ph,para}\)), 130.2 (d, \(^4\)J\(_{CP} = 2.9\) Hz; PCH\(_{Ph,para}\)), 133.3 (d, \(^2\)J\(_{CP} = 10.3\) Hz; PCH\(_{Ph,ortho}\)), 139.2 + 140.5 (d + d, \(^1\)J\(_{CP} = 87.9\) Hz + 95.6 Hz; PCH\(_{Ph,ipso}\)), 147.3 (s, SC\(_{Ph,ipso}\))

\(^{31}\)P\(^{(1)}\)H\) NMR (162.1 MHz, \(d_8\)-THF): \(\delta_P = 43.1\). \(^7\)Li NMR (155.6 MHz, THF): 0.53. Anal. Calcd. for C\(_{20}\)H\(_{28}\)CI\(_2\)N\(_2\)O\(_2\)S\(_2\): C, 52.45; H, 3.96; N, 3.06; S, 14.00. Found: C, 52.4, H, 4.36, N, 3.05, S, 13.78.

Preparation of \(R\)-1-K

22.2 mg (0.0528 mmol) of \(R\)-1 were dissolved in 1 mL of THF and cooled to 0 °C. Subsequently, the solution was added to 6.4 mg (0.16 mmol) KH and stirred at 0 °C for 1 h. The reaction solution was filtered through a cannula, and the solvent was removed in vacuo. The product was obtained as a yellow solid in 88 % yield (21.3 mg, 0.046 mmol). Crystals suitable for X-ray diffraction analysis were obtained from a saturated solution of \(rac\)-1-K and 2 eq. of 15-C-5 in THF at -30 °C.

\(^1\)H NMR (400.3 MHz, \(d_8\)-THF): \(\delta_H = 2.68\) (s, 3H; NCH\(_3\)), 7.13-7.31 (m, 9H; SCH\(_{Ph,meta,para}\) + PCH\(_{Ph,meta,para}\)), 7.85-7.89 (m, 2H; PCH\(_{Ph,ortho}\)), 7.98-8.00 (m, 2H; SCH\(_{Ph,ortho}\)), 8.05-8.10 (m, 2H; PCH\(_{Ph,ortho}\))

\(^{13}\)C\(^{(1)}\)H\) NMR (100.7 MHz, \(d_8\)-THF): \(\delta_C = 29.6\) (s, NCH\(_3\)), 49.8 (d, \(^1\)J\(_{CP} = 86.3\) Hz; CCl), 127.6 + 127.7 (d + d, \(^3\)J\(_{CP} = 13.9\) Hz; PCH\(_{Ph,meta}\)), 128.2 (SC\(_{Ph,meta}\)), 128.5 (s, SC\(_{Ph,meta}\)), 129.9 (dd, \(^4\)J\(_{CP} = 4.13\) Hz; PCH\(_{Ph,para} + \) SC\(_{Ph,para}\)), 133.1 + 133.2 (d + d, \(^2\)J\(_{CP} = 10.2\) Hz + 9.7 Hz; PCH\(_{Ph,ortho}\)), 139.5 (d, \(^1\)J\(_{CP} = 85.9\) Hz; PCH\(_{Ph,ipso}\)), 140.4 (d, \(^1\)J\(_{CP} = 90.0\) Hz; PCH\(_{Ph,ipso}\)), 146.5 (s, SC\(_{Ph,ipso}\))

\(^{31}\)P\(^{(1)}\)H\) NMR (162.1 MHz, \(d_8\)-THF): \(\delta_P = 44.1\) (s). Anal. Calcd. for C\(_{20}\)H\(_{18}\)CIKNOPS\(_2\): C, 52.45; H, 3.96; N, 3.06; S, 14.00. Found: C, 52.4, H, 4.36, N, 3.05, S, 13.78.
2. NMR spectra

2.1 NMR spectra of the isolated compounds

**Figure S1.** $^1$H NMR spectrum of R-1 in CDCl$_3$ recorded at room temperature.

**Figure S2.** $^{13}$C($^1$H)($^{31}$P) NMR spectrum of R-1 in CDCl$_3$ recorded at room temperature.
Figure S3. $^{31}\text{P}^{1}\text{H}$ NMR spectrum of R-1 in CDCls recorded at room temperature.

Figure S4. $^1\text{H}$ NMR spectrum of R-1-Li 2THF in d8-THF recorded at 243 K.
Figure S5. $^{13}$C{H} NMR spectrum of R-1-Li\textsubscript{2}THF in d$_8$-THF recorded at 243 K.

Figure S6. $^7$Li NMR spectrum of R-1-Li\textsubscript{2}THF in THF recorded at RT.
Figure S7. $^{31}$P($^1$H) NMR spectra of $\text{R-1-Li-2THF}$ in THF recorded at RT (top) and in toluene recorded at 263K (bottom).
**Figure S8.** $^1$H NMR spectrum of R-1-Na·1THF in d$_8$-THF recorded at room temperature.

**Figure S9.** $^{13}$C($^1$H) NMR spectrum of R-1-Na·1THF in d$_8$-THF recorded at room temperature.
Supporting Information

Figure S10. $^{31}$P($^1$H) NMR spectra of R-1-Na•THF in d$_8$-THF recorded at room temperature (top) and in d$_8$-toluene at room temperature (bottom).
**Figure S11.** $^1$H NMR spectra of $R$-1-K in d$_8$-THF recorded at room temperature.

**Figure S12.** $^{13}$C($^1$H) NMR spectrum of $R$-1-K in d$_8$-THF recorded at room temperature.
Figure S13. $^{31}\text{P}[^1\text{H}]$ NMR spectra of R-1-K in d$_8$-THF recorded at room temperature (top) and in d$_8$-toluene at room temperature (bottom).
2.2 VT $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy

The carbenoids were prepared according to the synthesis stated above. A J. Young NMR tube was set under vacuum and flushed with Ar three times and cooled to $-40 \ ^\circ\text{C}$. The deuterated solvent ($d_8$-THF or $d_8$-Tol) was cooled to $-40 \ ^\circ\text{C}$. 0.6 mL of cooled deuterated solvent was added to the Schlenk flask which was also cooled to $-40 \ ^\circ\text{C}$ and the carbenoids were dissolved and subsequently, transferred via a syringe to the J. Young NMR tube. The NMR tube was cooled while transporting to the NMR instrument.

**NMR instrument:** The NMR instrument is cooled to $-30 \ ^\circ\text{C}$ prior to the injection of the sample to prevent sample decomposition. The VT NMR studies are performed in automation starting at $-30 \ ^\circ\text{C}$ and incrementing the temperature by 10 °C steps with a start delay of 3515 sec. until a temperature of 50 °C is reached.

![Figure S14. VT $^{31}\text{P}\{^1\text{H}\}$ NMR Spectra of rac-1-Li in $d_8$-THF.](image)
Figure S15. VT $^{31}\text{P}^\text{(1H)}$ NMR Spectra of rac-$\text{1-Li}$ in $\text{d}_8$-Tol.

Figure S16. VT $^{31}\text{P}^\text{(1H)}$ NMR Spectra of rac-$\text{1-Na}$ in $\text{d}_8$-THF.
Figure S17. VT $^{31}$P($^1$H) NMR Spectra of rac-1-Na in d8-Tol.

Figure S18. VT $^{31}$P($^1$H) NMR Spectra of rac-1-K in d8-THF.
Figure S19. VT $^{31}$P($^1$H) NMR Spectra of rac-1-K in d$_8$-Tol.
3. **DOSY NMR spectroscopy**

3.1 **General procedure**

General procedure of the sample preparation for DOSY NMR spectroscopic measurements.

DOSY measurements were recorded on an AV 400 MHz spectrometer operating at 400.13 MHz. A double stimulated echo sequence (dstebpg3s) was used and the pulse gradients (g) were incremented from 2 to 95% of the maximum gradient strength in a linear ramp. The Stejskal-Tanner diffusion delay (d20) was set to 0.2 s and the eddy-current delay (d21) to 5 ms. After Fourier transformation and baseline correction, the diffusion dimension was processed with the Topspin 3.6.1 software (BrukerBiospin). Diffusion coefficients were calculated by exponential fits with the T1/T2 software of Topspin. Tetramethylsilane and adamantane have been used as references in DOSY measurements in THF and toluene, respectively. The molecular masses were calculated by the ECC-MW estimation software by Stalke et al. [143]

All carbenoids were prepared according to the synthetic procedure stated above with 0.075 mmol of the protonated precursor. The corresponding metal base was added to a THF solution of the protonated precursor. After stirring for 1h at that temperature, the solvent was removed in vacuo. The obtained solid was subsequently dissolved in 0.6 mL of cooled deuterated solvent and transferred via a syringe into a J. Young NMR tube with the corresponding internal standard and used for DOSY NMR spectroscopy measurements. The THF used for synthesis could not be removed completely in vacuo and residual THF was still present during the DOSY measurements (see above).

**Measurements in d₈-toluene:**

4 mg (0.03 mmol) adamantane were added to a J. Young NMR tube and the NMR tube was evaporated and flushed with Ar three times. 0.6 mL cooled (−40 °C) d₈-Tol was added to the cooled (−40 °C) Schlenk flask containing the respective carbenoid. The carbenoid was prepared as stated above, dissolved in d₈-Tol and subsequently transferred to the J. Young NMR tube via a syringe under Ar. The J. Young NMR tube was cooled to −40 °C and the sample was kept at that temperature while transferring it to the NMR instrument.

**Measurements in d₈-THF:**

A J. Young NMR tube was evaporated and flushed with Ar three times. 0.6 mL d₈-THF cooled to −40 °C were added to the cooled (−40 °C) Schlenk flask containing the carbenoid. The J. Young NMR tube is placed in a cooling bath at −40 °C and the d₈-THF solution of the carbenoid (prepared as stated above) is transferred to the J. Young NMR tube. Then, 4 µL TMS (0.03 mmol) were added to the J. Young tube under Ar. The sample was kept at −40 °C while transferring it to the NMR instrument.

**NMR instrument:**

The NMR instrument is cooled to −30 °C prior to the injection of the sample to prevent sample decomposition. The DOSY NMR spectra are recorded at -30 °C, -10 °C and 27 °C, respectively. The instrument is warmed up to the respective temperature manually.
3.2 DOSY NMR data of rac-1-Li

Figure S20. $^1$H DOSY NMR spectrum for rac-1-Li in $d_8$-THF at 27 °C.

Table S1. $^1$H DOSY NMR data for rac-1-Li at 27 °C in $d_8$-THF.

| Solvent | Int. reference | $D_{\text{ref}}$ [m$^2$s$^{-1}$] | log$_{D_{\text{ref}}}$ | $\Theta$ | log$_{D_{\text{Carb}}}$ | MW$_{\text{DOSY}}$ [g/mol] | MW$_{\text{calc}}$ [g/mol] | Species | Error [%] |
|---------|----------------|---------------------------------|-----------------------|---------|------------------------|----------------------------|-----------------------------|---------|-----------|
| THF     | TMS            | 2.21E-9                         | -9.05                 | 464     | 497.96                 | -6.8                       |                             | Monomer | +1THF     |

Figure S21. $^1$H DOSY NMR spectrum for rac-1-Li in $d_8$-THF at –10 °C.

Table S2. $^1$H DOSY NMR data for rac-1-Li at –10 °C in $d_8$-THF.

| Solvent | Int. reference | $D_{\text{ref}}$ [m$^2$s$^{-1}$] | log$_{D_{\text{ref}}}$ | $\Theta$ | log$_{D_{\text{Carb}}}$ | MW$_{\text{DOSY}}$ [g/mol] | MW$_{\text{calc}}$ [g/mol] | Species | Error [%] |
|---------|----------------|---------------------------------|-----------------------|---------|------------------------|----------------------------|-----------------------------|---------|-----------|
| THF     | TMS            | 1.28E-9                         | -8.89                 | -9.33   | 554                    | 570.07                     | -2.8                        | Monomer | + 2 THF   |
**Figure S22.** $^1$H DOSY NMR spectrum for rac-1-Li in d$_8$-THF at −10 °C.

**Table S3.** $^1$H DOSY NMR data for rac-1-Li at −30 °C in d$_8$-THF.

| Solvent | Int. reference | $D_{\text{ref}}$ [m$^2$s$^{-1}$] | log $D_{\text{ref}}$ | $\phi$ | log $D_{\text{carb}}$ | MW$_{\text{DOSY}}$ [g/mol] | MW$_{\text{calc}}$ [g/mol] | Species            | Error [%] |
|---------|----------------|-------------------------------|---------------------|--------|----------------------|---------------------------|--------------------------|--------------------|-----------|
| THF     | TMS            | 8.75E-10                      | -9.06               | -9.51  | 600                  | 570.07                    | 642.17                   | Monomer + 2 THF    | + 5.3    |
|         |                |                               |                     |        |                      |                           |                          | Monomer + 3 THF    | + 6.6    |

**Figure S23.** $^1$H DOSY NMR spectrum for rac-1-Li in d$_8$-Tol at 27 °C.
Table S4. $^1$H DOSY NMR data for rac-1-Li at 27 °C in d$_8$-Tol.

| Solvent | Int. reference | ØD$_{ref}$ $[^{m^2s^{-1}}]$ | ØlogD$_{re}$ | ØlogD$_{Carb}$ | MW$_{DOSY}$ [g/mol] | MW$_{calc}$ [g/mol] | Species | Error [%] |
|---------|----------------|-----------------------------|-------------|-----------------|----------------------|---------------------|---------|-----------|
| Tol     | Adam           | 1.69E-9                    | -8.77       | -9.25           | 904                  | 851.71              | Dimer   | +6.1      |
|         |                |                             |             |                 | 923.81              |                     | Dimer   | -2.1      |

Figure S24. $^1$H DOSY NMR spectrum for rac-1-Li in d$_8$-Tol at –10 °C.

Table S5. $^1$H DOSY NMR data for rac-1-Li at –10 °C in d$_8$-Tol.

| Solvent | Int. reference | ØD$_{ref}$ $[^{m^2s^{-1}}]$ | ØlogD$_{re}$ | ØlogD$_{Carb}$ | MW$_{DOSY}$ [g/mol] | MW$_{calc}$ [g/mol] | Species | Error [%] |
|---------|----------------|-----------------------------|-------------|-----------------|----------------------|---------------------|---------|-----------|
| Tol     | Adam           | 8.62E-10                   | -9.06       | -9.58           | 1051                 | 995.92              | Dimer   | +5.5      |
|         |                |                             |             |                 | 1068.03              |                     | Dimer   | -1.6      |
Figure S25. $^1$H DOSY NMR spectrum for rac-1-Li in d$_8$-Tol at –30 °C.

Table S6. $^1$H DOSY NMR data for rac-1-Li at –30 °C in d$_8$-Tol.

| Solvent | Int. reference | $\bar{\Omega}_{\text{ref}}$ [m$^2$s$^{-1}$] | $\bar{\Omega}_{\text{logD}}$ | $\bar{\Omega}_{\text{logDCarb}}$ | $\text{MW}_{\text{DOSY}}$ [g/mol] | $\text{MW}_{\text{calc}}$ [g/mol] | Species | Error [%] |
|---------|----------------|----------------------------------|----------------|-------------------------------|-------------------------------|-------------------------------|---------|----------|
| Tol     | Adam 5.36E-10   | -9.27                            | -9.78            | 1025                          | 995.92                        | 1068.03                      | Dimer + 2 THF | 2.9      |
|         |                 |                                  |                  |                               |                               |                               | Dimer + 2 THF | -4.0     |
3.3 DOSY NMR Data of rac-1-Na

Figure S26. $^1$H DOSY NMR spectrum for rac-1-Na in $d_8$-THF at 27 °C.

Table S7. $^1$H DOSY NMR data for rac-1-Na at 27 °C in $d_8$-THF.

| Solvent | Int. reference | $D_{\text{ref}}$ [m$^2$s$^{-1}$] | log$D_{\text{ref}}$ | $\varnothing$ | MW$_{\text{DOSY}}$ [g/mol] | MW$_{\text{calc}}$ [g/mol] | Species | Error [%] |
|---------|---------------|-------------------------------|------------------|-----------|----------------|----------------|---------|---------|
| THF     | TMS           | 2.33E-9                       | -8.63            | -9.03     | 471            | 441.90         | Monomer + 0 THF | 6.6     |
|         |               |                               |                  |           |                | 514.01         | Monomer + 1 THF | -8.3    |

Figure S27. $^1$H DOSY NMR spectrum for rac-1-Na in $d_8$-THF at −10 °C.
Table S8. $^1$H DOSY NMR data for rac-1-Na at $-10$ °C in d$_8$-THF.

| Solvent | Int. reference | $D_{\text{ref}}$ [m$^2$s$^{-1}$] | $\log D_{\text{ref}}$ | $\Theta$ | $\log D_{\text{Carb}}$ | $\text{MW}_{\text{DOSY}}$ [g/mol] | $\text{MW}_{\text{calc}}$ [g/mol] | Species | Error [%] |
|---------|----------------|-------------------------------|---------------------|-------|------------------------|-------------------------------|---------------------------|---------|-----------|
| THF     | TMS            | 1.44E-9                      | -8.84               | -9.30 | -8.84                  | 595                           | 586.12                    | Monomer + 2THF             | +1.5     |

Table S9. $^1$H DOSY NMR data for rac-1-Na at $-30$ °C in d$_8$-THF.

| Solvent | Int. reference | $D_{\text{ref}}$ [m$^2$s$^{-1}$] | $\log D_{\text{ref}}$ | $\Theta$ | $\log D_{\text{Carb}}$ | $\text{MW}_{\text{DOSY}}$ [g/mol] | $\text{MW}_{\text{calc}}$ [g/mol] | Species | Error [%] |
|---------|----------------|-------------------------------|---------------------|-------|------------------------|-------------------------------|---------------------------|---------|-----------|
| THF     | TMS            | 1.01E-9                      | -8.99               | -9.41 | -8.99                  | 683                           | 658.23                    | Monomer + 3THF             | +3.8     |
Table S10. $^1$H DOSY NMR data for rac-1-Na at 27 °C in $d_8$-Tol.

| Solvent | Int. reference | $\Delta D_{\text{ref}}$ [m$^2$s$^{-1}$] | $\Delta \log D_{\text{ref}}$ | $\Delta \log D_{\text{Carb}}$ | MW$_{\text{DOSY}}$ [g/mol] | MW$_{\text{calc}}$ [g/mol] | Species | Error [%] |
|---------|----------------|--------------------------------|-----------------------------|-------------------------------|-----------------------------|-----------------------------|---------|-----------|
| Tol     | Adam           | 1.80E-9                          | -8.75                       | -9.33                         | 1330                        | 1316.46                    | Dimer   | +1.0      |
|         |                |                                 |                             |                               |                             | 1325.70                    | Trimer  | -0.3      |

Table S11. $^1$H DOSY NMR data for rac-1-Na at −10 °C in $d_8$-Tol.

| Solvent | Int. reference | $\Delta D_{\text{ref}}$ [m$^2$s$^{-1}$] | $\Delta \log D_{\text{ref}}$ | $\Delta \log D_{\text{Carb}}$ | MW$_{\text{DOSY}}$ [g/mol] | MW$_{\text{calc}}$ [g/mol] | Species | Error [%] |
|---------|----------------|--------------------------------|-----------------------------|-------------------------------|-----------------------------|-----------------------------|---------|-----------|
| Tol     | Adam           | 9.14E-10                         | -9.04                       | -9.62                         | 1312                        | 1316.46                    | Dimer   | -0.3      |
|         |                |                                 |                             |                               |                             | 1325.70                    | Trimer  | -1.0      |
**Figure S31.** $^1$H DOSY NMR spectrum for rac-1-Na in d$_8$-Tol at –30 °C.

**Table S12.** $^1$H DOSY NMR data for rac-1-Na at –30 °C in d$_8$-Tol.

| Solvent | Int. reference | $\Omega_{D,ref}$ [m$^2$s$^{-1}$] | $\Omega_{logD}$ | $\Omega_{logD_Carb}$ | MW$_{DOSY}$ [g/mol] | MW$_{calc}$ [g/mol] | Species | Error [%] |
|---------|----------------|---------------------------------|-----------------|-----------------------|---------------------|---------------------|---------|-----------|
| Tol     | Adam           | 9.53E-10                        | -9.26           | -9.81                 | 1195                | 1172.24             | Dimer   | +1.9      |
3.4 DOSY NMR data of rac-1-K

Figure S32. ¹H DOSY NMR spectrum for rac-1-K in d₈-THF at 27 °C.

Table S13. ¹H DOSY NMR data for rac-1-K at 27 °C in d₈-THF.

| Solvent | Int. reference | Dₚₒₑᵣ [m²s⁻¹] | logDₚₒₑᵣ | Ø logDₑᵣₑᵣ | MWₑᵣₒᵣ [g/mol] | MWₑᵣₑᵣ [g/mol] | Species | Error [%] |
|---------|----------------|----------------|-----------|-------------|-----------------|----------------|---------|----------|
| THF     | TMS            | 2.17E-9        | -8.66     | -9.083      | 521             | 530.12         | Monomer + 1THF | -1.7     |

Figure S33. ¹H DOSY NMR spectrum for rac-1-K in d₈-THF at −10 °C.
Table S14. $^1$H DOSY NMR data for rac-1-K at $-10$ °C in d$_8$-THF.

| Solvent | Int. reference | $D_{ref}$ [m$^2$s$^{-1}$] | $\log D_{ref}$ | $\Phi$ | $\log D_{Carb}$ | MW$_{DOSY}$ [g/mol] | MW$_{calc}$ [g/mol] | Species | Error [%] |
|---------|----------------|---------------------------|----------------|------|-----------------|----------------|----------------|---------|----------|
| THF     | TMS            | 1.24E-9                   | -8.91          | -9.34| 555             | 530.12         | 602.23         | Monomer | +4.7     |
|         |                |                           |                |      |                 |                |                | +1THF   |         |
|         |                |                           |                |      |                 |                |                | Monomer | -7.8     |
|         |                |                           |                |      |                 |                |                | +2THF   |          |

Figure S34. $^1$H DOSY NMR spectrum for rac-1-K in d$_8$-THF at $-30$ °C.

Table S15. $^1$H DOSY NMR data for rac-1-K at $-30$ °C in d$_8$-THF.

| Solvent | Int. reference | $D_{ref}$ [m$^2$s$^{-1}$] | $\log D_{ref}$ | $\Phi$ | $\log D_{Carb}$ | MW$_{DOSY}$ [g/mol] | MW$_{calc}$ [g/mol] | Species | Error [%] |
|---------|----------------|---------------------------|----------------|------|-----------------|----------------|----------------|---------|----------|
| THF     | TMS            | 9.16E-10                  | -9.04          | -9.51| 633             | 602.23         | 674.33         | Monomer | +5.1     |
|         |                |                           |                |      |                 |                |                | +2THF   |          |
|         |                |                           |                |      |                 |                |                | Monomer | -6.1     |
|         |                |                           |                |      |                 |                |                | +3THF   |          |
Figure S35. $^1$H DOSY NMR spectrum for rac-1-K in d$_8$-Tol at 27 °C.

Table S16. $^1$H DOSY NMR data for rac-1-K at 27 °C in d$_8$-Tol.

| Solvent | Int. reference | ØD$_{ref}$ [m$^2$s$^{-1}$] | ØlogD$_{ref}$ | ØlogD$_{Carb}$ | MW$_{DOSY}$ [g/mol] | MW$_{calc}$ [g/mol] | Species | Error [%] |
|---------|----------------|-----------------------------|---------------|-----------------|---------------------|-------------------|---------|-----------|
| Tol     | Adam           | 1.71E-9                     | -8.77         | -9.31           | 1135                | 1132.35           | Dimer + | +0.2      |
|         |                |                             |               |                 |                     |                   | 3THF    |           |

Figure S36. $^1$H DOSY NMR spectrum for rac-1-K in d$_8$-Tol at –10 °C.

Table S17. $^1$H DOSY NMR data for rac-1-K at –10 °C in d$_8$-Tol.

| Solvent | Int. reference | ØD$_{ref}$ [m$^2$s$^{-1}$] | ØlogD$_{ref}$ | ØlogD$_{Carb}$ | MW$_{DOSY}$ [g/mol] | MW$_{calc}$ [g/mol] | Species | Error [%] |
|---------|----------------|-----------------------------|---------------|-----------------|---------------------|-------------------|---------|-----------|
| Tol     | Adam           | 9.51E-9                     | -9.02         | -9.53           | 1012                | 1060.24           | Dimer + | -4.5      |
|         |                |                             |               |                 |                     |                   | 2THF    |            |
Figure S37. $^1$H DOSY NMR spectrum for rac-1-K in d$_8$-Tol at −30 °C.

Table S18. $^1$H DOSY NMR data for rac-1-K at −30 °C in d$_8$-Tol.

| Solvent | Int. reference | ØD$_{ref}$ | ØlogD$_{ref}$ | ØlogD$_{Carb}$ | MW$_{DOSY}$ | MW$_{calc}$ | Species | Error |
|---------|----------------|------------|---------------|----------------|-------------|-------------|---------|-------|
| Tol     | Adam 4.70E-10  | -9.33      | -9.89         |                | 1252        | 1251.46     | Dimer   | 0.0   |
|         |                |            |               |                |             |             | 6THF    |       |
4. Determination of ee

| Retention Time | Area [mAU.s] | Height [mAU] | Area [%] | WOS [min] | PDA Peak Purity | Compound Name | PDA Best Match Name |
|----------------|--------------|--------------|----------|-----------|-----------------|---------------|---------------------|
| 1              | 14.223       | 4963.300     | 1317.071 | 100.0     | 0.50            | 901           |                     |
| Total          | 4363.300     | 1317.071     | 100.0    |           |                 |               |                     |

**Figure S38.** HPLC chromatogram of $R\text{-}2$ in hexane:isopropanol (85:15).

| Retention Time | Area [mAU.s] | Height [mAU] | Area [%] | WOS [min] | PDA Peak Purity | Compound Name | PDA Best Match Name |
|----------------|--------------|--------------|----------|-----------|-----------------|---------------|---------------------|
| 1              | 14.237       | 25766.386    | 831.276  | 90.0      | 0.52            | 925           |                     |
| 2              | 15.467       | 25803.460    | 743.596  | 95.0      | 0.55            | 907           |                     |
| Total          | 51569.775    | 15753.732    | 96.0     |           |                 |               |                     |

**Figure S39.** HPLC chromatogram of $rac\text{-}2$ in hexane:isopropanol (85:15).
5. Crystal Structure Determination

5.1 General information

Data collection of all compounds was conducted with an Oxford Synergy. The structures were solved using direct methods, refined with the Shelx software package and expanded using Fourier techniques. The crystals of all compounds were mounted in an inert oil (perfluoropolyalkylether). Crystal structure determinations were affected at 100 K. Crystallographic data (including structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2022984-2022987. Copies of the data can be obtained free of charge on application to Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; [fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk].

The structure of rac-1-Na(18crown6) has been solved using the DELU and SIMU commands to prevent distortion of an ellipsoid due to residue electron density from a minor disorder.

The structure of rac-1-K(18crown6) contained a twin with the occupancy 0.59:0.41 and was solved with the TWIN and BASF commands (Twin law: $-1 0 0 0 1 0 0 0 -1$)

Table S19. Data collection and structure refinement details for compound S,S-1-H and rac-1-Li.

| Parameter                        | S,S-1-H       | rac-1-Li       |
|----------------------------------|---------------|----------------|
| CCDC No.                         | CCDC-2022984  | CCDC-2022985   |
| Emperical formula                | $C_{20}H_{19}ClNOPS_2$ | $C_{32}H_{42}ClLiNO_4PS_2$ |
| Formula weight                   | 419.90 g/mol  | 642.14 g/mol   |
| Temperature                      | 100(2) K      | 100(2) K       |
| Wavelength                       | 0.71073 Å     | 1.54184 Å      |
| Crystal system                   | Monoclinic    | Monoclinic     |
| Space group                      | $P2_1$        | $P2_1/c$       |
| Unit cell dimensions             | a = 9.3549(5) Å | a = 8.9364(4) Å |
|                                  | b = 9.4299(5) Å | b = 19.994(3) Å |
|                                  | c = 10.8508(6) Å | c = 18.1879(14) Å |
|                                  | $\alpha$ = 90° | $\alpha$ = 90° |
|                                  | $\beta$ = 92.165(2)° | $\beta$ = 97.652(6)° |
|                                  | $\gamma$ = 90° | $\gamma$ = 90° |
| Volume                           | 956.53(9) Å$^3$ | 3220.8(5) Å$^3$ |
| Formula unit per cell            | 2             | 4              |
| Density (calculated)             | 1.458 Mg/m$^3$ | 1.324 Mg/m$^3$ |
| Absorption coefficient           | 0.511 mm$^{-1}$ | 3.025 mm$^{-1}$ |
| F(000)                           | 436           | 1360           |
| Crystal size                     | 0.30 x 0.25 x 0.24 mm$^3$ | 0.409 x 0.164 x 0.116 mm$^3$ |
| $\Theta$ range for data collection | 1.878 to 26.395° | 3.301 to 72.483° |
Table S20. Data collection and structure refinement details for compound rac-1-Na(18crown6) and rac-1-K(18crown6).

| Parameter                              | rac-1-Na(18crown6)                  | rac-1-K(18crown6)                  |
|----------------------------------------|-------------------------------------|------------------------------------|
| CCDC No.                               | CCDC-2022986                        | CCDC-2022987                       |
| Empirical formula                      | C_{60}H_{116}Cl_{11}N_{13}Na_{12}O_{18}P_{2}S_{4} | C_{40}H_{56}ClKNO_{11}PS_{2}      |
| Formula weight                         | 1700.80 g/mol                       | 898.51 g/mol                       |
| Temperature                            | 100(2) K                            | 100(2) K                           |
| Wavelength                             | 1.54184 Å                           | 1.54184 Å                          |
| Crystal system                         | Triclinic                           | Triclinic                          |
| Space group                            | P̅1                                 | P̅1                                |
| Unit cell dimensions                   | a = 9.2135(3) Å                     | a = 9.1916(3) Å                    |
|                                        | b = 20.4163(6) Å                    | b = 20.6188(8) Å                   |
|                                        | c = 23.8781(8) Å                    | c = 23.3493(5) Å                   |
|                                        | α = 75.754(3)°                      | α = 89.975(2)°                     |
|                                        | β = 80.345(3)°                      | β = 84.739(2)°                     |
|                                        | γ = 87.399(3)°                      | γ = 89.983(3)°                     |
| Volume                                 | 4291.7(2) Å                         | 4406.5(2) Å                        |
| Formula unit per cell                  | 2                                   | 4                                  |
| Density (calculated)                   | 1.316 Mg/m³                         | 1.354 Mg/m³                        |
| Absorption coefficient                 | 2.586 mm⁻¹                          | 3.323 mm⁻¹                         |
| F(000)                                 | 1808                                | 1904                               |
| Crystal size                           | 0.129 x 0.059 x 0.059 mm⁻³          | 0.295 x 0.036 x 0.017 mm⁻³         |
| Θ range for data collection            | 3.290 to 67.080°                    | 2.865 to 67.499°                   |
| Index ranges                           | -11 ≤ h ≤ 11, -24 ≤ k ≤ 20, -28 ≤ l ≤ 28 | -10 ≤ h ≤ 11, -24 ≤ k ≤ 24, -26 ≤ l ≤ 27 |
| Reflections collected                  | 29548                               | 79386                              |
| Independent reflections                | 15283 [R(int) = 0.0564]             | 15421 [R(int) = 0.1498]            |
Supporting Information

| Refinement method                     | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
|---------------------------------------|------------------------------------|------------------------------------|
| Data / restraints / parameters        | 15283 / 7 / 997                    | 15421 / 0 / 1049                   |
| Goodness-of-fit on $F^2$              | 1.024                              | 1.040                              |
| Final $R$ indices [$I>2\sigma(I)$]    | $R_1 = 0.0519$, $wR_2 = 0.1281$    | $R_1 = 0.0799$, $wR_2 = 0.2051$    |
| $R$ indices (all data)                | $R_1 = 0.0798$, $wR_2 = 0.1432$    | $R_1 = 0.0855$, $wR_2 = 0.2103$    |
| Largest diff. peak and hole           | 1.573 and -0.597 e.Å$^3$           | 1.422 and -1.312 e.Å$^3$           |

5.2 Further Details to the Crystal Structures

Crystal Structure Determination of (S,S)-1-H

![ORTEP of compound S,S-1-H](image)

Figure S40. ORTEP of compound S,S-1-H. Ellipsoids are drawn at the 50% probability level.

Table S21. Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for S,S-1-H. U(eq) is defined as one third of the trace of the orthogonalized $U^i_j$ tensor.

|       | x     | y     | z     | U(eq) |
|-------|-------|-------|-------|-------|
| Cl(1) | 8242(1)| 11120(1)| 5139(1)| 18(1) |
| S(1)  | 8418(1)| 9172(1)| 1977(1)| 18(1) |
| S(2)  | 6077(1)| 8978(1)| 4718(1)| 13(1) |
| P(1)  | 7297(1)| 10780(1)| 2499(1)| 11(1) |
| O(1)  | 5467(2)| 9451(2)| 5862(1)| 17(1) |
| N(1)  | 7085(2)| 7745(2)| 4670(2)| 17(1) |
| C(1)  | 6767(2)| 10695(2)| 4130(2)| 12(1) |
| C(2)  | 5613(2)| 11039(2)| 1649(2)| 13(1) |
| C(3)  | 4751(2)| 12213(2)| 1895(2)| 16(1) |
Table S22. Anisotropic displacement parameters (Å² x 10³) for S,S-1-H. The anisotropic displacement factor exponent takes the form: -2p²[ h² a*²U₁₁ + ... + 2 h k a* b* U₁₂ ]

|     | U₁¹ | U₂² | U₃³ | U₂³ | U₁³ | U₁² |
|-----|-----|-----|-----|-----|-----|-----|
| Cl(1) | 18(1) | 22(1) | 15(1) | 0(1) | -4(1) | -5(1) |
| S(1) | 16(1) | 17(1) | 20(1) | -4(1) | 3(1) | 3(1) |
| S(2) | 11(1) | 14(1) | 14(1) | 2(1) | -1(1) | -1(1) |
| P(1) | 11(1) | 13(1) | 11(1) | -1(1) | 1(1) | 0(1) |
| O(1) | 18(1) | 20(1) | 13(1) | 1(1) | 2(1) | -1(1) |
| N(1) | 15(1) | 17(1) | 20(1) | 0(1) | -3(1) | 1(1) |
| C(1) | 11(1) | 14(1) | 11(1) | -1(1) | -1(1) | -2(1) |
| C(2) | 13(1) | 16(1) | 11(1) | 2(1) | 0(1) | -2(1) |
| C(3) | 17(1) | 16(1) | 15(1) | -1(1) | 0(1) | -2(1) |
| C(4) | 17(1) | 16(1) | 23(1) | 4(1) | 1(1) | 1(1) |
| C(5) | 18(1) | 23(1) | 20(1) | 7(1) | -6(1) | -3(1) |
| C(6) | 24(1) | 21(1) | 16(1) | 0(1) | -3(1) | -6(1) |
| C(7) | 18(1) | 17(1) | 14(1) | 0(1) | 1(1) | -2(1) |
| C(8) | 11(1) | 16(1) | 15(1) | 2(1) | -2(1) | -2(1) |
| C(9) | 14(1) | 19(1) | 16(1) | 0(1) | 0(1) | 0(1) |
| C(10) | 18(1) | 17(1) | 23(1) | -1(1) | -5(1) | 0(1) |
| C(11) | 16(1) | 20(1) | 28(1) | 9(1) | -7(1) | -5(1) |
| C(12) | 14(1) | 30(1) | 20(1) | 9(1) | 1(1) | -2(1) |
| C(13) | 14(1) | 21(1) | 16(1) | 2(1) | 1(1) | 1(1) |
| C(14) | 12(1) | 16(1) | 16(1) | 4(1) | -1(1) | -4(1) |
| C(15) | 17(1) | 16(1) | 20(1) | 2(1) | 1(1) | -1(1) |
| C(16) | 25(1) | 20(1) | 20(1) | -1(1) | -2(1) | -6(1) |
| C(17) | 19(1) | 25(1) | 19(1) | 5(1) | -5(1) | -8(1) |
| C(18) | 13(1) | 22(1) | 24(1) | 6(1) | -1(1) | -1(1) |
| C(19) | 16(1) | 16(1) | 18(1) | 2(1) | 1(1) | -2(1) |
| C(20) | 14(1) | 23(1) | 31(1) | 3(1) | -7(1) | 4(1) |
Crystal Structure Determination of rac-1-Li

Figure S41. ORTEP of compound rac-1-Li. Ellipsoids are drawn at the 50% probability level.

Table S23. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å² x 10^3) for rac-1-Li. U(eq) is defined as one third of the trace of the orthogonized U^ij tensor.

|      | x    | y    | z    | U(eq) |
|------|------|------|------|-------|
| Li(1) | 3025(3) | 5815(1) | 2182(1) | 24(1) |
| Cl(1) | 7063(1) | 6836(1) | 4726(1) | 23(1) |
| S(1)  | 5020(1) | 6278(1) | 3538(1) | 18(1) |
| S(2)  | 4178(1) | 8238(1) | 4248(1) | 25(1) |
| P(1)  | 5592(1) | 7799(1) | 3658(1) | 18(1) |
| N(1)  | 5930(1) | 5632(1) | 3632(1) | 22(1) |
| O(1)  | 4221(1) | 6458(1) | 2803(1) | 21(1) |
| O(2)  | 4174(1) | 5459(1) | 1439(1) | 26(1) |
| O(3)  | 2257(1) | 5067(1) | 2676(1) | 25(1) |
| O(4)  | 1346(1) | 6334(1) | 1695(1) | 28(1) |
| C(1)  | 6080(2) | 6955(1) | 3822(1) | 19(1) |
| C(2)  | 7437(2) | 8218(1) | 3797(1) | 21(1) |
| C(3)  | 8700(2) | 7909(1) | 3563(1) | 25(1) |
Table S24. Anisotropic displacement parameters (Å² x 10³) for rac-1-Li. The anisotropic displacement factor exponent takes the form: -2p²\[ h^2 a^*2 U_{11} + ... + 2 h k a^* b^* U_{12} \]

|       | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U¹³  | U¹₂  |
|-------|------|------|------|------|------|------|
| Li(1) | 23(1)| 24(1)| 23(1)| 1(1) | 1(1) | -1(1)|
| Cl(1) | 21(1)| 29(1)| 17(1)| 2(1) | -2(1)| -1(1)|
| S(1)  | 16(1)| 20(1)| 17(1)| 1(1) | 1(1) | -1(1)|
| S(2)  | 22(1)| 28(1)| 25(1)| -6(1)| 6(1) | 1(1) |
| P(1)  | 15(1)| 20(1)| 17(1)| -1(1)| 1(1) | -1(1)|
| N(1)  | 19(1)| 23(1)| 25(1)| 1(1) | 4(1) | 1(1)|
|   | O(1) | O(2) | O(3) | O(4) | C(1) | C(2) | C(3) | C(4) | C(5) | C(6) | C(7) | C(8) | C(9) | C(10) | C(11) | C(12) | C(13) | C(14) | C(15) | C(16) | C(17) | C(18) | C(19) | C(20) | C(21) | C(22) | C(23) | C(24) | C(25) | C(26) | C(27) | C(28) | C(29) | C(30) | C(31) | C(32) |
|---|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
|   | 21   | 28   | 22   | 29   | 18   | 18   | 22   | 22   | 24   | 31   | 24   | 24   | 24   | 25   | 28   | 27   | 20   | 21   | 17   | 21   | 20   | 20   | 20   | 28   | 29   | 22   | 30   | 22   | 22   | 31   | 37   | 29   | 29   | 29   | 42   | 42   |      |
|   | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  |      |
|   | 24   | 26   | 24   | 26   | 18   | 16   | 20   | 31   | 36   | 24   | 26   | 23   | 36   | 30   | 23   | 29   | 22   | 25   | 17   | 25   | 23   | 29   | 29   | 29   | 29   | 30   | 30   | 29   | 26   | 34   | 25   | 25   | 36   |      |
|   | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  |      |
|   | 18   | 23   | 24   | 26   | 25   | 16   | 20   | 31   | 36   | 31   | 26   | 23   | 36   | 30   | 23   | 29   | 22   | 25   | 17   | 25   | 23   | 29   | 29   | 29   | 29   | 30   | 30   | 29   | 26   | 34   | 25   | 25   | 36   |      |
|   | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  | (1)  |      |
|   | 1   | 2    | 4    | -1   | 1    | 1    | 2    | 2    | 11   | 3    | 2    | 0    | 0    | 2    | 7    | 8    | 2    | 3    | 0    | 0    | 0    | 4    | 0    | 0    | 2    | 8    | 8    | 0    | 0    | 2    | 2    | 4    | 1    | 1    | 1    | 1    | 1    |      |
|   | 0   | 5    | 9    | -4   | -1   | -3   | 0    | 0    | -5   | -8   | -4   | 1    | 0    | 0    | -3   | -2   | 2    | 5    | -3   | -1   | -2   | 5    | -1   | 1    | -2   | -6   | -8   | -1   | -6   | -6   | -5   | -5   | -5   | -5   | -5   | -5   | -5   |      |
|   | -3  | 1    | 0    | 5    | 0    | 0    | -1   | -4   | -11  | -8   | 0    | 0    | 0    | 1    | 5    | 2    | 1    | 2    | 0    | 0    | 0    | 2    | 0    | 0    | 2    | -3   | -2   | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    |      |
Crystal Structure Determination of rac-1-Na

Figure S42. ORTEP of compound rac-1-Na. Ellipsoids are drawn at the 50% probability level.

Table S25. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\AA^2 \times 10^3$) for rac-1-Na. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|      | x    | y    | z    | U(eq) |
|------|------|------|------|-------|
| Cl(1)| 5297(1) | 1768(1) | 3051(1) | 27(1) |
| S(1) | 6898(1) | 1295(1) | 2077(1) | 24(1) |
| P(1) | 5741(1) | 281(1) | 3199(1) | 21(1) |
| O(1) | 7227(2) | 655(1) | 1907(1) | 29(1) |
| N(1) | 6416(3) | 1916(1) | 1645(1) | 29(1) |
| C(1) | 5677(3) | 1081(1) | 2711(1) | 23(1) |
| Cl(2) | 3175(1) | 5885(1) | 1360(1) | 30(1) |
| O(2) | 3626(3) | 6907(1) | 2613(1) | 33(1) |
| S(2) | 7494(1) | -31(1) | 3571(1) | 33(1) |
| P(2) | 3322(1) | 5396(1) | 2621(1) | 25(1) |
| N(2) | 3799(3) | 7396(1) | 1468(1) | 35(1) |
| C(2) | 4145(3) | 312(1) | 3762(1) | 23(1) |
| S(3) | 3242(1) | 6876(1) | 2032(1) | 30(1) |
| C(3) | 4340(3) | 413(2) | 4297(1) | 26(1) |
|   |   |   |   |   |
|---|---|---|---|---|
| S(4) | 1287(1) | 5249(1) | 3047(1) | 34(1) |
| C(4) | 3134(4) | 479(2) | 4716(1) | 27(1) |
| C(5) | 1711(4) | 436(2) | 4605(1) | 29(1) |
| C(6) | 1502(4) | 329(2) | 4077(2) | 31(1) |
| C(7) | 2714(3) | 270(2) | 3656(1) | 26(1) |
| C(8) | 5213(4) | -332(2) | 2825(1) | 28(1) |
| C(9) | 5733(4) | -993(2) | 2961(2) | 39(1) |
| C(10) | 5214(5) | -1474(2) | 2716(2) | 52(1) |
| C(11) | 4209(5) | -1306(2) | 2339(2) | 54(1) |
| C(12) | 3724(4) | -646(2) | 2192(2) | 48(1) |
| C(13) | 4231(4) | -163(2) | 2432(2) | 35(1) |
| C(14) | 8590(3) | 1584(2) | 2198(1) | 26(1) |
| C(15) | 9674(4) | 1104(2) | 2333(2) | 34(1) |
| C(16) | 11020(4) | 1309(2) | 2417(2) | 39(1) |
| C(17) | 11269(4) | 1983(2) | 2373(2) | 40(1) |
| C(18) | 10172(4) | 2459(2) | 2255(2) | 35(1) |
| C(19) | 8816(3) | 2257(2) | 2171(1) | 29(1) |
| C(20) | 4964(4) | 1873(2) | 1482(2) | 34(1) |
| C(21) | 3724(4) | 6062(2) | 1986(1) | 28(1) |
| C(22) | 4017(3) | 4643(2) | 2373(1) | 23(1) |
| C(23) | 5285(3) | 4670(2) | 1958(1) | 28(1) |
| C(24) | 5833(4) | 4091(2) | 1789(1) | 30(1) |
| C(25) | 5127(4) | 3476(2) | 2039(1) | 30(1) |
| C(26) | 3870(4) | 3449(2) | 2456(1) | 29(1) |
| C(27) | 3306(3) | 4029(2) | 2620(1) | 25(1) |
| C(28) | 4620(3) | 5446(2) | 3112(1) | 26(1) |
| C(29) | 6042(4) | 5693(2) | 2904(2) | 33(1) |
| C(30) | 7044(4) | 5657(2) | 3283(2) | 41(1) |
| C(31) | 6599(5) | 5393(2) | 3877(2) | 47(1) |
| C(32) | 5182(5) | 5158(2) | 4090(2) | 51(1) |
| C(33) | 4200(4) | 5176(2) | 3707(2) | 39(1) |
| C(34) | 1292(4) | 7024(2) | 2051(2) | 33(1) |
| C(35) | 674(4) | 7154(2) | 1545(2) | 37(1) |
| C(36) | -848(4) | 7273(2) | 1583(2) | 39(1) |
| C(37) | -1694(4) | 7264(2) | 2120(2) | 40(1) |
| C(38) | -1059(4) | 7132(2) | 2617(2) | 41(1) |
| C(39) | 443(4) | 7005(2) | 2585(2) | 37(1) |
| C(40) | 5368(4) | 7393(2) | 1235(2) | 41(1) |
| Na1 | 9081(1) | 2667(1) | 4848(1) | 28(1) |
| O11 | 10339(3) | 3581(1) | 5159(1) | 34(1) |
| C11 | 9450(4) | 4011(2) | 5459(2) | 43(1) |
| Atom | u1  | u2  | u3   | u4  | u5  |
|------|-----|-----|------|-----|-----|
| O21  | 7260(3) | 3377(1) | 5628(1) | 39(1) |
| C21  | 8315(4) | 3579(2) | 5915(2) | 45(1) |
| O31  | 5284(3) | 2539(1) | 5321(1) | 40(1) |
| C31  | 6072(4) | 3029(2) | 6053(2) | 45(1) |
| O41  | 7332(2) | 1781(1) | 4727(1) | 27(1) |
| C41  | 4874(5) | 2921(2) | 5748(2) | 48(1) |
| O51  | 10201(2) | 1923(1) | 5645(1) | 39(1) |
| C51  | 5533(4) | 1843(2) | 5555(2) | 37(1) |
| O61  | 11677(2) | 3028(1) | 4275(1) | 32(1) |
| C61  | 5989(4) | 1508(2) | 5067(2) | 31(1) |
| O71  | 7883(4) | 1406(2) | 4304(1) | 33(1) |
| C71  | 4874(5) | 2921(2) | 5748(2) | 48(1) |
| O81  | 8176(2) | 3351(1) | 4064(1) | 33(1) |
| C81  | 9102(4) | 1783(2) | 3873(2) | 32(1) |
| C91  | 11518(4) | 2160(2) | 3804(2) | 37(1) |
| C101 | 12463(4) | 2459(2) | 4132(2) | 34(1) |
| C111 | 12505(4) | 3403(2) | 4533(2) | 38(1) |
| C121 | 11505(4) | 3921(2) | 4747(2) | 37(1) |
| C131 | 10811(5) | 2026(2) | 6080(2) | 45(1) |
| C141 | 9953(5) | 1633(2) | 6660(2) | 46(1) |
| C151 | 9144(4) | 1100(2) | 6482(2) | 35(1) |
| C161 | 9603(4) | 1252(2) | 5821(2) | 36(1) |
| C171 | 6664(4) | 3390(2) | 3988(2) | 45(1) |
| C181 | 6688(6) | 3587(3) | 3335(2) | 66(1) |
| C191 | 8180(5) | 3904(2) | 3085(2) | 50(1) |
| C201 | 8914(4) | 3870(2) | 3610(2) | 48(1) |
| Na12 | 0 | 10000 | 0 | 37(1) |
| O12  | -2102(3) | 9835(1) | 934(1) | 46(1) |
| C12  | -3541(5) | 10087(3) | 871(2) | 58(1) |
| O22  | 281(4) | 9020(1) | 1022(1) | 50(1) |
| C22  | -2099(6) | 9289(2) | 1431(2) | 56(1) |
| O32  | 2662(3) | 9340(2) | 98(1) | 51(1) |
| C32  | -589(6) | 9146(2) | 1534(2) | 57(1) |
| O42  | -845(3) | 9107(2) | -314(1) | 52(1) |
| C42  | 1768(6) | 8863(2) | 1091(2) | 62(1) |
| C52  | 2580(6) | 8726(2) | 535(2) | 63(1) |
| C62  | 3417(5) | 9253(3) | -446(2) | 59(1) |
| C72  | -2056(6) | 8706(3) | 37(2) | 70(2) |
| C82  | -2223(5) | 8133(2) | -243(2) | 52(1) |
| C92  | -1433(5) | 8377(2) | -860(2) | 48(1) |
| C102 | -757(7) | 9025(3) | -879(2) | 68(2) |
Table S26. Anisotropic displacement parameters (Å$^2 \times 10^3$) for rac-1-Na. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^2 U_{11} + \ldots + 2hk a^* b^* U_{12}]$

|       | U$^{11}$ | U$^{22}$ | U$^{33}$ | U$^{23}$ | U$^{13}$ | U$^{12}$ |
|-------|----------|----------|----------|----------|----------|----------|
| Cl(1) | 29(1)    | 21(1)    | 29(1)    | -10(1)   | 4(1)     | -1(1)    |
| S(1)  | 21(1)    | 26(1)    | 23(1)    | -8(1)    | 2(1)     | -3(1)    |
| P(1)  | 20(1)    | 22(1)    | 21(1)    | -7(1)    | 2(1)     | -2(1)    |
| O(1)  | 30(1)    | 30(1)    | 28(1)    | -14(1)   | 6(1)     | -4(1)    |
| N(1)  | 24(1)    | 34(1)    | 26(1)    | -5(1)    | -1(1)    | -6(1)    |
| C(1)  | 25(2)    | 19(1)    | 26(2)    | -10(1)   | 1(1)     | 0(1)     |
| Cl(2) | 29(1)    | 32(1)    | 32(1)    | -10(1)   | -8(1)    | 0(1)     |
| O(2)  | 42(1)    | 24(1)    | 38(1)    | -16(1)   | -5(1)    | -2(1)    |
| S(2)  | 24(1)    | 42(1)    | 29(1)    | -8(1)    | -3(1)    | 7(1)     |
| P(2)  | 20(1)    | 21(1)    | 32(1)    | -7(1)    | 0(1)     | -3(1)    |
| N(2)  | 25(1)    | 32(2)    | 47(2)    | -3(1)    | -9(1)    | 1(1)     |
| C(2)  | 25(2)    | 16(1)    | 25(1)    | -5(1)    | 2(1)     | -3(1)    |
| S(3)  | 30(1)    | 23(1)    | 38(1)    | -10(1)   | -8(1)    | -1(1)    |
| C(3)  | 24(2)    | 26(2)    | 30(2)    | -11(1)   | -2(1)    | -4(1)    |
| S(4)  | 23(1)    | 31(1)    | 47(1)    | -13(1)   | 6(1)     | -5(1)    |
| C(4)  | 31(2)    | 29(2)    | 23(1)    | -12(1)   | 3(1)     | -4(1)    |
| C(5)  | 28(2)    | 24(2)    | 32(2)    | -12(1)   | 9(1)     | -4(1)    |
| C(6)  | 23(2)    | 31(2)    | 39(2)    | -14(1)   | 1(1)     | -3(1)    |
| C(7)  | 25(2)    | 28(2)    | 27(2)    | -12(1)   | -1(1)    | -1(1)    |
| C(8)  | 28(2)    | 25(2)    | 29(2)    | -11(1)   | 8(1)     | -6(1)    |
| C(9)  | 49(2) | 26(2) | 34(2) | -8(1) | 19(2) | -5(2) |
|-------|-------|-------|-------|-------|-------|-------|
| C(10) | 71(3) | 26(2) | 49(2) | -18(2) | 33(2) | -13(2) |
| C(11) | 64(3) | 50(2) | 53(2) | -38(2) | 23(2) | -30(2) |
| C(12) | 42(2) | 66(3) | 45(2) | -35(2) | 10(2) | -23(2) |
| C(13) | 29(2) | 44(2) | 33(2) | -21(2) | 8(1) | -12(1) |
| C(14) | 19(2) | 30(2) | 24(2) | -5(1) | 6(1) | -5(1) |
| C(15) | 27(2) | 36(2) | 36(2) | -8(1) | 4(1) | 0(1) |
| C(16) | 24(2) | 55(2) | 35(2) | -11(2) | -1(1) | 5(2) |
| C(17) | 26(2) | 61(2) | 34(2) | -18(2) | 3(1) | -11(2) |
| C(18) | 31(2) | 42(2) | 31(2) | -12(1) | 3(1) | -16(2) |
| C(19) | 23(2) | 32(2) | 29(2) | -10(1) | 3(1) | -4(1) |
| C(20) | 28(2) | 41(2) | 32(2) | -6(1) | -3(1) | -2(1) |
| C(21) | 29(2) | 29(2) | 29(2) | -9(1) | -6(1) | -2(1) |
| C(22) | 18(1) | 25(2) | 26(1) | -7(1) | -6(1) | -1(1) |
| C(23) | 24(2) | 33(2) | 28(2) | -7(1) | -6(1) | -5(1) |
| C(24) | 26(2) | 36(2) | 31(2) | -13(1) | -6(1) | 3(1) |
| C(25) | 29(2) | 34(2) | 35(2) | -17(1) | -14(1) | 5(1) |
| C(26) | 31(2) | 29(2) | 31(2) | -9(1) | -10(1) | -7(1) |
| C(27) | 21(2) | 29(2) | 26(2) | -7(1) | -6(1) | -3(1) |
| C(28) | 26(2) | 27(2) | 30(2) | -13(1) | -4(1) | -1(1) |
| C(29) | 29(2) | 31(2) | 41(2) | -14(1) | -4(1) | 1(1) |
| C(30) | 36(2) | 37(2) | 57(2) | -20(2) | -13(2) | 0(2) |
| C(31) | 59(3) | 46(2) | 50(2) | -23(2) | -30(2) | 3(2) |
| C(32) | 65(3) | 57(3) | 37(2) | -17(2) | -18(2) | -6(2) |
| C(33) | 43(2) | 41(2) | 34(2) | -12(2) | -5(2) | -9(2) |
| C(34) | 30(2) | 27(2) | 43(2) | -10(1) | -5(2) | 4(1) |
| C(35) | 32(2) | 36(2) | 41(2) | -11(2) | -4(2) | 0(1) |
| C(36) | 30(2) | 42(2) | 50(2) | -17(2) | -10(2) | -1(2) |
| C(37) | 27(2) | 40(2) | 56(2) | -23(2) | -3(2) | 0(1) |
| C(38) | 36(2) | 42(2) | 47(2) | -18(2) | 2(2) | -1(2) |
| C(39) | 38(2) | 38(2) | 38(2) | -10(2) | -9(2) | 4(2) |
| C(40) | 29(2) | 33(2) | 53(2) | -1(2) | -2(2) | -2(1) |
| Na11  | 30(1) | 27(1) | 30(1) | -8(1) | -11(1) | 0(1) |
| O11   | 30(1) | 34(1) | 41(1) | -20(1) | 1(1) | -3(1) |
| C11   | 35(2) | 40(2) | 62(2) | -34(2) | 2(2) | -3(2) |
| O21   | 35(1) | 44(1) | 40(1) | -20(1) | -1(1) | -7(1) |
| C21   | 41(2) | 56(2) | 45(2) | -29(2) | -2(2) | 0(2) |
| O31   | 45(2) | 39(1) | 39(1) | -17(1) | -2(1) | -1(1) |
| C31   | 45(2) | 57(2) | 36(2) | -22(2) | 4(2) | -6(2) |
| O41   | 23(1) | 28(1) | 30(1) | -13(1) | 2(1) | -7(1) |
| C41   | 45(2) | 55(2) | 49(2) | -30(2) | 5(2) | -8(2) |
|       | 20(1) | 33(1) | 34(1) | -14(1) | 3(1)  | -3(1) |
|-------|-------|-------|-------|--------|-------|-------|
| O51   | 29(2) | 41(2) | 36(2) | -9(2)  | 7(1)  | -5(1) |
| C51   | 22(1) | 35(1) | 41(1) | -18(1) | -4(1) | -1(1) |
| O61   | 24(2) | 30(2) | 39(2) | -9(1)  | 3(1)  | -10(1)|
| C61   | 47(2) | 33(1) | 39(1) | -6(1)  | -17(1)| 1(1)  |
| O71   | 29(2) | 31(2) | 33(2) | -17(1)| 0(1)  | -5(1) |
| C71   | 22(1) | 37(1) | 33(1) | 7(1)   | -7(1)| -5(1) |
| C81   | 30(2) | 39(2) | 32(2) | -18(1)| -1(1)| -4(1) |
| C91   | 29(2) | 39(2) | 43(2) | -19(2)| 11(2)| -9(1) |
| C101  | 22(2) | 37(2) | 45(2) | -17(2)| 5(1) | -1(1) |
| C111  | 24(2) | 45(2) | 50(2) | -24(2)| -5(2)| -7(1) |
| C121  | 27(2) | 35(2) | 52(2) | -19(2)| -1(2)| -12(1)|
| C131  | 47(2) | 40(2) | 50(2) | -9(2) | -19(2)| 4(2)  |
| C141  | 59(3) | 41(2) | 39(2) | -10(2)| -13(2)| -2(2) |
| C151  | 32(2) | 34(2) | 39(2) | -9(2) | -3(1)| 3(1)  |
| C161  | 37(2) | 31(2) | 40(2) | -10(2)| -9(2)| 6(1)  |
| C171  | 24(2) | 51(2) | 50(2) | 10(2) | -11(2)| -5(2) |
| C181  | 62(3) | 79(3) | 58(3) | -4(2) | -37(2)| -1(3) |
| C191  | 70(3) | 42(2) | 30(2) | -1(2) | 1(2)  | 12(2) |
| C201  | 28(2) | 44(2) | 57(2) | 13(2)| 0(2) | -4(2) |
| Na12  | 41(1) | 42(1) | 33(1) | -18(1)| 0(1) | -7(1) |
| O12   | 53(2) | 45(2) | 37(1) | -17(1)| 12(1)| -12(1)|
| C12   | 33(2) | 85(3) | 66(3) | -46(3)| 10(2)| -8(2) |
| O22   | 82(2) | 39(2) | 34(1) | -12(1)| -20(1)| 2(1)  |
| C22   | 90(4) | 41(2) | 33(2) | -14(2)| 16(2)| -26(2)|
| O32   | 50(2) | 52(2) | 58(2) | -26(1)| -16(1)| 16(1) |
| C32   | 107(4) | 35(2) | 27(2) | -5(2) | -9(2)| -16(2)|
| O42   | 52(2) | 72(2) | 38(1) | -31(1)| 8(1) | -26(1)|
| C42   | 94(4) | 44(2) | 60(3) | -11(2)| -48(3)| 14(2) |
| C52   | 73(3) | 48(3) | 73(3) | -15(2)| -33(3)| 23(2) |
| C62   | 44(2) | 74(3) | 69(3) | -41(3)| -6(2)| 17(2) |
| C72   | 73(3) | 91(4) | 50(3) | -37(3)| 18(2)| -41(3)|
| C82   | 55(3) | 54(2) | 47(2) | -16(2)| 4(2) | -15(2)|
| C92   | 51(2) | 50(2) | 44(2) | -19(2)| 0(2) | -11(2)|
| C102  | 95(4) | 63(3) | 43(2) | -22(2)| 18(2)| -35(3)|
| Na13  | 26(1) | 34(1) | 42(1) | -6(1) | -5(1)| -7(1) |
| O13   | 22(1) | 35(1) | 30(1) | -13(1)| -5(1)| -1(1) |
| C13   | 25(2) | 46(2) | 34(2) | -18(2)| -2(1)| -4(1) |
| O23   | 19(1) | 44(1) | 28(1) | -11(1)| -4(1)| -1(1) |
| C23   | 30(2) | 34(2) | 32(2) | -11(1)| 1(1) | 0(1)  |
| O33   | 20(1) | 37(1) | 24(1) | -5(1) | -3(1)| -1(1) |
|   | C33 | 23(2) | 39(2) | 32(2) | -9(1) | -1(1) | 5(1) |
|---|-----|-------|-------|-------|-------|-------|------|
| C43 | O43 | 28(1) | 36(1) | 61(2) | 1(1)  | -19(1) | -6(1) |
| C53 | C43 | 23(2) | 41(2) | 35(2) | -8(1) | -11(1) | 2(1) |
| C63 | C53 | 29(2) | 34(2) | 32(2) | -5(1) | -12(1) | 1(1) |
| C73 | C63 | 22(2) | 50(2) | 23(2) | -7(1) | -1(1)  | -6(1) |
| C83 | C73 | 31(2) | 39(2) | 38(2) | 4(2)  | -8(2)  | -5(1) |
| C93 | C83 | 37(2) | 40(2) | 53(2) | -3(2) | -12(2) | -6(2) |
| C103 | C93 | 35(2) | 44(2) | 64(3) | 10(2) | -19(2) | -15(2) |
|     |     | 26(2) | 43(2) | 43(2) | -3(2) | -12(2) | -3(2) |
Crystal Structure Determination of rac-1-K

**Figure S43.** ORTEP of compound rac-1-K. Ellipsoids are drawn at the 50% probability level.

**Table S27.** Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for rac-1-K U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

|     | x     | y     | z     | U(eq) |
|-----|-------|-------|-------|-------|
| K(1)| 611(1)| 2885(1)| 5268(1)| 23(1) |
| K(2)| 844(1)| 2086(1)| 240(1) | 26(1) |
| Cl(1)| 5143(1)| 3909(1)| 1892(1)| 29(1) |
| Cl(2)| 4361(2)| -1071(1)| 2976(1)| 33(1) |
| S(1)| 3370(2)| 4472(1)| 2859(1)| 29(1) |
| Atomic Symbol | Value 1 (Standard Deviation) | Value 2 (Standard Deviation) | Value 3 (Standard Deviation) | Value 4 (Standard Deviation) |
|---------------|------------------------------|------------------------------|------------------------------|------------------------------|
| S(2)          | 2343(2)                      | 5332(1)                      | 1408(1)                      | 38(1)                        |
| S(3)          | 6150(2)                      | -379(1)                      | 2092(1)                      | 31(1)                        |
| S(4)          | 6968(2)                      | 15(1)                        | 3768(1)                      | 36(1)                        |
| P(1)          | 4159(1)                      | 5281(1)                      | 1794(1)                      | 23(1)                        |
| P(2)          | 5394(1)                      | 220(1)                       | 3279(1)                      | 24(1)                        |
| O(1)          | 2901(5)                      | 5113(2)                      | 3072(2)                      | 42(1)                        |
| O(2)          | 6544(5)                      | 290(2)                       | 1925(2)                      | 42(1)                        |
| O(3)          | -1213(6)                     | 3280(3)                      | 6248(3)                      | 68(2)                        |
| O(4)          | 1613(6)                      | 3800(4)                      | 6123(2)                      | 63(2)                        |
| O(5)          | 2488(5)                      | 3998(2)                      | 4935(2)                      | 42(1)                        |
| O(6)          | -402(4)                      | 4046(2)                      | 4615(2)                      | 36(1)                        |
| O(7)          | -2420(5)                     | 3151(2)                      | 5156(3)                      | 50(1)                        |
| O(8)          | -1317(5)                     | 1859(2)                      | 5720(2)                      | 36(1)                        |
| O(9)          | 1523(5)                      | 2086(2)                      | 6121(2)                      | 39(1)                        |
| O(10)         | 3516(4)                      | 2348(2)                      | 5138(2)                      | 35(1)                        |
| O(11)         | 1994(4)                      | 2592(2)                      | 4149(2)                      | 32(1)                        |
| O(12)         | -222(4)                      | 1780(2)                      | 4577(2)                      | 32(1)                        |
| O(13)         | 613(6)                       | 1464(3)                      | 1431(2)                      | 61(2)                        |
| O(14)         | 3140(6)                      | 1213(3)                      | 641(2)                       | 57(1)                        |
| O(15)         | 1944(5)                      | 1046(3)                      | -433(2)                      | 47(1)                        |
| O(16)         | -1043(5)                     | 991(3)                       | -94(2)                       | 45(1)                        |
| O(17)         | -1938(5)                     | 1777(2)                      | 843(2)                       | 44(1)                        |
| O(18)         | -365(5)                      | 3139(2)                      | 901(2)                       | 41(1)                        |
| O(19)         | 2635(5)                      | 3160(3)                      | 515(2)                       | 43(1)                        |
| O(20)         | 3745(5)                      | 2341(2)                      | -343(2)                      | 40(1)                        |
| O(21)         | 1229(5)                      | 2683(2)                      | -936(2)                      | 38(1)                        |
| O(22)         | -1430(4)                     | 2885(2)                      | -207(2)                      | 36(1)                        |
| N(1)          | 4016(5)                      | 3978(3)                      | 3251(2)                      | 34(1)                        |
| N(2)          | 5509(5)                      | -837(3)                      | 1667(2)                      | 42(1)                        |
| C(1)          | 4483(6)                      | 4627(3)                      | 2249(2)                      | 27(1)                        |
| C(2)          | 5475(7)                      | 4109(4)                      | 3425(3)                      | 46(2)                        |
| C(3)          | 1754(6)                      | 4051(3)                      | 2703(2)                      | 30(1)                        |
| C(4)          | 540(7)                       | 4423(4)                      | 2598(3)                      | 37(1)                        |
| C(5)          | -758(7)                      | 4101(4)                      | 2493(3)                      | 44(2)                        |
| C(6)          | -821(7)                      | 3447(4)                      | 2486(3)                      | 45(2)                        |
| C(7)          | 395(8)                       | 3081(4)                      | 2586(3)                      | 46(2)                        |
| C(8)          | 1684(6)                      | 3385(3)                      | 2701(3)                      | 35(1)                        |
| C(9)          | 4458(6)                      | 6029(3)                      | 2189(2)                      | 26(1)                        |
| C(10)         | 3709(7)                      | 6584(3)                      | 2082(3)                      | 37(1)                        |
| C(11)         | 4059(9)                      | 7175(3)                      | 2345(3)                      | 46(2)                        |
|   |     |     |     |     |
|---|-----|-----|-----|-----|
|C(12)| 5121(9)| 7190(3)| 2712(3)| 47(2) |
|C(13)| 5875(8)| 6633(3)| 2836(3)| 43(2) |
|C(14)| 5534(6)| 6058(3)| 2578(3)| 36(1) |
|C(15)| 5763(5)| 5272(3)| 1263(2)| 25(1) |
|C(16)| 5583(7)| 5363(3)| 689(2)| 35(1) |
|C(17)| 6802(8)| 5369(3)| 280(3)| 47(2) |
|C(18)| 8152(7)| 5283(3)| 456(3)| 44(2) |
|C(19)| 8349(7)| 5185(3)| 1029(4)| 49(2) |
|C(20)| 7143(6)| 5182(3)| 1442(3)| 35(1) |
|C(21)| 5052(6)| -305(3)| 2714(2)| 32(1) |
|C(22)| 3991(7)| -737(4)| 1540(3)| 47(2) |
|C(23)| 7800(6)| -814(3)| 2205(2)| 34(1) |
|C(24)| 7856(7)| -1482(4)| 2171(3)| 41(2) |
|C(25)| 10410(7)| -1438(4)| 2315(3)| 48(2) |
|C(26)| 10308(7)| -789(4)| 2367(3)| 48(2) |
|C(27)| 8999(7)| -463(4)| 2313(3)| 38(1) |
|C(29)| 3621(5)| 242(3)| 3707(2)| 25(1) |
|C(30)| 3539(6)| 308(3)| 4297(2)| 30(1) |
|C(31)| 2149(7)| 352(3)| 4606(3)| 40(2) |
|C(32)| 900(6)| 317(3)| 4325(3)| 37(1) |
|C(33)| 994(6)| 248(3)| 3738(3)| 40(2) |
|C(34)| 2341(6)| 209(3)| 3425(3)| 33(1) |
|C(35)| 5545(6)| 1051(3)| 3009(2)| 26(1) |
|C(36)| 4554(6)| 1313(3)| 2660(2)| 31(1) |
|C(37)| 4615(7)| 1962(3)| 2504(3)| 37(1) |
|C(38)| 5653(7)| 2365(3)| 2693(3)| 36(1) |
|C(39)| 6663(7)| 2111(4)| 3043(3)| 39(1) |
|C(40)| 6609(6)| 1466(3)| 3193(3)| 32(1) |
|C(43)| -2547(9)| 3569(4)| 6134(4)| 66(3) |
|C(44)| -3218(7)| 3149(4)| 5717(4)| 56(2) |
|C(45)| -2815(8)| 3666(4)| 4790(4)| 56(2) |
|C(46)| -1565(9)| 3783(4)| 4339(3)| 53(2) |
|C(47)| 844(8)| 4194(3)| 4230(3)| 40(2) |
|C(48)| 1966(7)| 4479(3)| 4568(3)| 38(1) |
|C(49)| 3226(8)| 4234(4)| 5389(4)| 54(2) |
|C(50)| 2233(9)| 4396(4)| 5912(4)| 61(2) |
|C(51)| 18(7)| 1921(3)| 3980(3)| 38(1) |
|C(52)| -1688(7)| 1585(3)| 4760(3)| 42(2) |
|C(53)| -1701(7)| 1344(3)| 5361(3)| 39(2) |
|       | $U_{11}$   | $U_{22}$   | $U_{33}$   | $U_{12}$   | $U_{13}$   | $U_{23}$   |
|-------|------------|------------|------------|------------|------------|------------|
| K(1)  | 23(1)      | 20(1)      | 24(1)      | 1(1)       | 4(1)       | 5(1)       |
| K(2)  | 26(1)      | 24(1)      | 26(1)      | -4(1)      | 3(1)       | -1(1)      |
| Cl(1) | 31(1)      | 24(1)      | 31(1)      | 0(1)       | 1(1)       | 2(1)       |
| Cl(2) | 35(1)      | 27(1)      | 37(1)      | -3(1)      | 5(1)       | -2(1)      |

**Table S28.** Anisotropic displacement parameters (Å$^2 \times 10^3$) for rac-1-K. The anisotropic displacement factor exponent takes the form: 

$$-2\pi^2 \left[ a^2 U_{11} + 2 a b U_{12} + b^2 U_{22} + \cdots \right]$$
|      | S(1)  | S(2)  | S(3)  | S(4)  | P(1)  | P(2)  | O(1)  | O(2)  | O(3)  | O(4)  | O(5)  | O(6)  | O(7)  | O(8)  | O(9)  | O(10) | O(11) | O(12) | O(13) | O(14) | O(15) | O(16) | O(17) | O(18) | O(19) | O(20) | O(21) | O(22) | N(1)  | N(2)  | C(1)  | C(2)  | C(3)  | C(4)  | C(5)  | C(6)  | C(7)  | C(8)  | C(9)  | C(10) |
|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
|   | C(11) | C(12) | C(13) | C(14) | C(15) | C(16) | C(17) | C(18) | C(19) | C(20) | C(21) | C(22) | C(23) | C(24) | C(25) | C(26) | C(27) | C(28) | C(29) | C(30) | C(31) | C(32) | C(33) | C(34) | C(35) | C(36) | C(37) | C(38) | C(39) | C(40) | C(41) | C(42) | C(43) | C(44) | C(45) | C(46) | C(47) | C(48) | C(49) | C(50) | C(51) | C(52) |
|---|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
|   | 66(4)| 21(3)| 48(4)| 3(3) | 5(3) | 22(3)| 44(4)| 39(4)| 45(4)| -7(3)| 10(3)| -5(3)| 44(4)| 39(4)| 45(4)| -7(3)| 1(3) | -1(3)| 28(3)| 35(3)| 45(3)| -9(3)| -4(2)| 2(2)| 21(2)| 21(3)| 33(3)| -3(2)| 1(2) | -5(2)| 38(3)| 41(4)| 24(3)| -1(2)| 7(2) | -12(3)| 61(4)| 40(4)| 35(3)| -4(3)| 20(3)| -17(3)| 47(4)| 27(3)| 52(4)| -9(3)| 31(3)| -5(3)| 27(3)| 26(3)| 91(6)| 3(3) | 9(3) | 3(2)| 25(3)| 28(3)| 51(4)| 4(3) | 2(2) | 0(2)| 30(3)| 34(3)| 30(3)| -2(2)| 6(2) | -3(2)| 37(3)| 71(5)| 34(3)| -2(3)| -3(2)| 1(3)| 27(3)| 49(4)| 22(3)| -6(2)| 7(2) | 4(2)| 30(3)| 56(4)| 37(3)| -14(3)| 0(2) | -2(3)| 58(4)| 52(4)| 37(3)| -15(3)| 0(3) | 14(3)| 33(3)| 80(6)| 31(3)| -12(3)| 1(2) | 19(3)| 33(3)| 81(6)| 29(3)| -2(3)| 0(2) | -3(3)| 33(3)| 49(4)| 30(3)| -1(3)| 10(2)| 3(3)| 23(2)| 17(3)| 34(3)| 2(2) | 5(2) | 5(2) | 35(3)| 25(3)| 30(3)| -2(2)| -3(2)| -5(2)| 47(4)| 31(3)| 38(3)| -2(3)| 21(3) | -8(3)| 29(3)| 25(3)| 55(4)| 4(3) | 16(3) | -3(2)| 23(3)| 28(3)| 67(4)| 8(3) | 4(3) | 1(2)| 26(3)| 33(3)| 38(3)| 0(3) | 1(2) | 1(2)| 22(2)| 30(3)| 26(3)| 2(2) | 2(2) | 1(2)| 29(3)| 31(3)| 33(3)| 3(2) | -1(2) | 1(2)| 34(3)| 41(4)| 34(3)| 2(3) | -1(2) | 6(3)| 45(3)| 29(3)| 32(3)| 8(2) | 9(3) | 0(3)| 34(3)| 44(4)| 39(3)| 1(3) | 2(2) | -10(3)| 27(3)| 35(3)| 35(3)| 2(2) | -2(2) | -6(2)| 56(5)| 36(4)| 94(6)| -10(4)| 51(5) | 1(3)| 27(3)| 43(4)| 94(6)| 17(4) | 12(3) | 6(3)| 37(3)| 33(4)| 101(6)| 18(4) | -27(4) | -1(3)| 69(5)| 38(4)| 58(4) | 0(3) | -34(4) | 6(3)| 50(4)| 35(3)| 32(3)| 6(3) | 13(3) | 11(3)| 34(3)| 30(3)| 48(4) | 3(3) | 14(3) | 7(2)| 34(3)| 52(5)| 76(5) | 11(4) | -16(3) | -7(3)| 51(4)| 62(5)| 73(5) | -31(4) | -25(4) | 11(4)| 41(3)| 45(4)| 30(3)| -4(3) | -12(2) | 9(3)| 24(3)| 37(4)| 67(4) | -11(3) | -6(3) | -4(3)|
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| C(53) | 28(3) | 26(3) | 61(4) | -4(3) | 13(3) | -3(2) |
| C(54) | 46(3) | 30(3) | 39(3) | 8(3) | 18(3) | 8(3) |
| C(55) | 49(4) | 29(3) | 38(3) | 7(3) | 14(3) | 14(3) |
| C(56) | 37(3) | 53(4) | 43(4) | -1(3) | -13(3) | 4(3) |
| C(57) | 32(3) | 33(3) | 59(4) | -1(3) | -12(3) | 7(3) |
| C(58) | 27(3) | 42(4) | 44(3) | -9(3) | 4(2) | 4(3) |
| C(59) | 32(3) | 31(3) | 37(3) | -2(2) | 9(2) | 2(2) |
| C(60) | 49(3) | 27(3) | 25(3) | -1(2) | 3(2) | 6(3) |
| C(61) | 49(4) | 70(5) | 42(4) | 3(4) | -7(3) | 2(4) |
| C(62) | 51(4) | 63(5) | 60(5) | 23(4) | -19(3) | -8(4) |
| C(63) | 51(4) | 57(5) | 37(4) | 1(3) | 10(3) | -21(3) |
| C(64) | 63(5) | 53(5) | 42(4) | -10(3) | 20(3) | -13(4) |
| C(65) | 35(3) | 41(4) | 73(5) | 5(4) | 12(3) | -8(3) |
| C(66) | 26(3) | 41(4) | 53(4) | -3(3) | -1(3) | 0(3) |
| C(67) | 39(3) | 50(4) | 26(3) | -8(3) | 1(2) | 10(3) |
| C(68) | 33(3) | 51(4) | 28(3) | -9(3) | 6(2) | -3(3) |
| C(69) | 37(3) | 52(4) | 44(4) | -4(3) | -4(3) | 12(3) |
| C(70) | 57(4) | 40(4) | 59(5) | 7(3) | -4(3) | 15(3) |
| C(71) | 39(3) | 39(4) | 35(3) | -11(3) | -4(2) | -4(3) |
| C(72) | 38(3) | 45(4) | 33(3) | -18(3) | 0(2) | -5(3) |
| C(73) | 31(3) | 30(3) | 64(4) | -11(3) | -3(3) | -1(2) |
| C(74) | 27(3) | 29(3) | 56(4) | -1(3) | -1(3) | 0(2) |
| C(75) | 54(4) | 37(4) | 46(4) | 8(3) | -19(3) | -1(3) |
| C(76) | 58(4) | 28(3) | 40(3) | 1(3) | -10(3) | 2(3) |
| C(77) | 51(4) | 39(4) | 35(3) | 2(3) | 8(3) | -13(3) |
| C(78) | 46(4) | 41(4) | 44(4) | -9(3) | 16(3) | -4(3) |
| C(79) | 33(3) | 38(4) | 69(5) | -9(3) | -5(3) | 0(3) |
| C(80) | 25(3) | 63(5) | 64(4) | -18(4) | -7(3) | 2(3) |
| C(41A) | 86(18) | 29(12) | 52(10) | 0(8) | -6(10) | 4(10) |
| C(42A) | 110(20) | 45(12) | 38(10) | 0(9) | 33(11) | 0(12) |
| C(41B) | 26(5) | 37(10) | 31(6) | -15(5) | -1(4) | 1(5) |
| C(42B) | 25(6) | 46(9) | 29(6) | 9(5) | 6(4) | -4(5) |
6. Computational Details

6.1 General

All calculations were performed without symmetry restrictions. Starting coordinates for the corresponding structures were obtained from the crystal structure analyses or modelled with GaussView 6.0.16. The geometry optimization was performed with the Gaussian 16 (Revision C.01) program package. The geometry optimization was performed using Density-Functional Theory (DFT) with the PBE0 functional and the MWB10 basis set and the corresponding Stuttgart-Dresden ECP for Potassium and the def2svp basis set for all other atoms including Grimme’s D3 dispersion correction with Becke-Johnson damping. Solvent corrections were included by using the polarizable continuum model (PCM) for THF. Harmonic vibrational frequency analysis was performed on the same levels of theory to determine the nature of the structure. The vibrational frequency analysis showed no imaginary frequencies for all calculated structures. Coordinates of all energy-optimized structures are provided as cartesian coordinates in Angstrom in the Tables below.

Single point energies were obtained with the PBE0 functional and the MWB10 basis set and the corresponding Stuttgart-Dresden ECP for Potassium and the def2tzvp basis set for all other atoms with Grimme’s D3 dispersion correction with Becke-Johnson damping. Solvent corrections were included by using the polarizable continuum model (PCM) for THF and toluene, which are also the solvents used in experiments.

The energies were corrected by conversion from the standard state (1 atm) to the solution state as follows:

\[ \Delta G_M^0 = \Delta G_{gas}^0 + RT \ln \left( \frac{K_M^0}{K_{gas}^0} \right) \]

with \( R = 8.31447 \text{ J K}^{-1} \text{ mol}^{-1} \), \( T = \) temperature in K = 298.15 K, \( c_{gas} = p/RT = 0.0408 \text{ mol/L (ideal gas)} \),

in THF: \( c_M(\text{monomer}) = 0.05 \text{ mol/l, } c_M(\text{dimer}) = 0.025 \text{ mol/l, } c_M(\text{THF}) = 12 \text{ mol/l, } \)
in toluene: \( c_M(\text{monomer}) = 0.05 \text{ mol/l, } c_M(\text{dimer}) = 0.025 \text{ mol/l, } c_M(\text{THF}) = 0.05 \text{ mol/l.} \)

| THF | toluene |
|-----|---------|
| monomer(THF)_3 + 2 THF → monomer(THF)_5 | −28.18 | monomer(THF)_3 + 2 THF → monomer(THF)_5 | −1.01 |
| monomer(THF)_3 + THF → monomer(THF)_4 | −14.09 | monomer(THF)_3 + THF → monomer(THF)_4 | −0.50 |
| monomer(THF)_3 → monomer(THF)_3 + THF | 14.09 | monomer(THF)_3 → monomer(THF)_3 + THF | 0.50 |
| monomer(THF)_3 → monomer(THF) + 2 THF | 28.18 | monomer(THF)_3 → monomer(THF) + 2 THF | 1.01 |
| 2 monomer(THF)_3 → dimer(THF)_2 + 4 THF | 54.14 | 2 monomer(THF)_3 → dimer(THF)_2 + 4 THF | −0.21 |
| 2 monomer(THF)_3 → dimer(THF)_4 + 2 THF | 25.96 | 2 monomer(THF)_3 → dimer(THF)_4 + 2 THF | −1.21 |
| 2 monomer(THF)_3 → dimer + 6 THF | 82.32 | 2 monomer(THF)_3 → dimer + 6 THF | 0.80 |
6.2 Structures of the energy-optimized compounds

Structures of monomeric 1-Li

Figure S44. Li monomers.
Structures of dimeric 1-Li

Figure S45. Li dimers (Part I).
Figure S46. Li dimers (Part II).
### 6.3 Energies of the optimized compounds

Table S30. SCF energies and enthalpy/free energy corrections in Hartree for all calculated monomers and dimers.

| Structure                  | Corr(G)    | Corr(H)    | E_{SCF}(THF)     | E_{SCF}(toluene)  |
|----------------------------|------------|------------|-------------------|-------------------|
| κO-Li(THF)$_3$             | 0.611318   | 0.740854   | -3204.14980656   | -3204.14139252    |
| κN-Li(THF)$_3$             | 0.612755   | 0.741198   | -3204.13862831   | -3204.12969871    |
| κO,κN-Li(THF)$_3$          | 0.499075   | 0.614954   | -2971.84616503   | -2971.83624384    |
| κO,κCl-Li(THF)$_3$         | 0.498669   | 0.615170   | -2971.84374276   | -2971.83278651    |
| κO-Li(THF)$_2$             | 0.499311   | 0.614947   | -2971.85127750   | -2971.83885075    |
| κN,κS-Li(THF)$_2$          | 0.498936   | 0.615071   | -2971.85326828   | -2971.84694075    |
| κO,κS-Li(THF)$_2$          | 0.498165   | 0.614769   | -2971.84916164   | -2971.84301703    |
| κO,κN-Li(THF)              | 0.389890   | 0.489412   | -2739.54907333   | -2739.53598398    |
| κO,κS,κCl-Li(THF)          | 0.388617   | 0.488997   | -2739.55158286   | -2739.54181955    |
| κN,κS,κCl-Li(THF)          | 0.390717   | 0.489058   | -2739.55833053   | -2739.54956014    |
| κN,κS-Li(THF)              | 0.390951   | 0.488434   | -2739.55620864   | -2739.54573801    |
| κO,κN,κS-Li(THF)           | 0.386978   | 0.489206   | -2739.55054668   | -2739.54303523    |
| κO,κS-Li(THF)              | 0.386894   | 0.488934   | -2739.55316844   | -2739.54272824    |
| κO,κS-Li$_2$(THF)$_2$       | 0.799234   | 0.981443   | -5479.14610678   | -5479.13728744    |
| κN,κS-Li$_2$(THF)$_2$       | 0.805385   | 0.981212   | -5479.14937283   | -5479.13867604    |
| κO,κN,κCl-Li$_2$(THF)$_2$  | 0.808277   | 0.982759   | -5479.15020428   | -5479.13550119    |
| κO,κN-Li$_2$(THF)$_4$       | 1.026769   | 1.233798   | -5943.74225062   | -5943.73226938    |
| κO,κN,κS,κCl-Li$_2$        | 0.585839   | 0.730979   | -5014.57443118   | -5014.56302866    |
| κN,κS,κCl-Li$_2$           | 0.588293   | 0.730560   | -5014.55088939   | -5014.53312623    |
| κO,κS,κCl-Li$_2$           | 0.582736   | 0.729228   | -5014.54493149   | -5014.52972574    |
| κO,κN-Li$_2$               | 0.584598   | 0.730825   | -5014.54769161   | -5014.52064536    |
| κO,κS-Li$_2$               | 0.582668   | 0.728486   | -5014.54537659   | -5014.52072488    |
| κS,κCl-Li$_2$              | 0.588351   | 0.730557   | -5014.55089132   | -5014.53314863    |
| κO,κN,κCl-Li$_2$           | 0.585758   | 0.730791   | -5014.55606304   | -5014.54056817    |
| κO-Na(THF)$_3$             | 0.605654   | 0.739556   | -3358.82170887   | -3358.81141961    |
| κS-Na(THF)$_5$             | 0.826338   | 0.991020   | -3823.38603574   | -3823.37738340    |
| κO-Na(THF)$_4$             | 0.716097   | 0.864732   | -3591.10906578   | -3591.09872543    |
| κS,κCl-Na(THF)$_4$         | 0.714107   | 0.864689   | -3591.10150089   | -3591.09358604    |
| κO,κN-Na(THF)$_3$          | 0.606526   | 0.739755   | -3358.81612601   | -3358.80652647    |
| κN-Na(THF)$_3$             | 0.605838   | 0.739727   | -3358.81680171   | -3358.80579866    |
| κS,κCl-Na(THF)$_3$         | 0.602772   | 0.739384   | -3358.81120355   | -3358.80343449    |
| κO-Na(THF)$_2$             | 0.494900   | 0.613818   | -3126.52827985   | -3126.51409305    |
| κS,κCl-Na(THF)$_2$         | 0.494753   | 0.613917   | -3126.52185991   | -3126.50839103    |
| κO,κS-Na(THF)$_2$          | 0.494581   | 0.613737   | -3126.52723608   | -3126.51962030    |
| κO,κN-Na(THF)              | 0.383998   | 0.488412   | -2894.22919197   | -2894.21429946    |
| κS,κCl-Na$_3$(THF)$_2$     | 0.801258   | 0.979786   | -5788.49203279   | -5788.47734246    |
| κN,κS,κCl-Na$_2$(THF)$_2$  | 0.800781   | 0.980535   | -5788.48094950   | -5788.49508176    |
| κO,κN,κS-Na$_3$(THF)$_2$   | 0.797536   | 0.979414   | -5788.51446562   | -5788.50544530    |
| κO,κS,κCl-Na$_2$(THF)$_2$  | 0.797808   | 0.979125   | -5788.50372250   | -5788.49038243    |
Table S31. Gibbs free energies $\Delta G_M$ (kJ/mol), enthalpies $\Delta H$ (kJ/mol) and entropies $\Delta S_M$ (JK$^{-1}$mol$^{-1}$) relative to $\kappa O$-$\text{M}(\text{THF})_3$ (M=Li,Na,K), respectively. $\Delta G_M$ and $\Delta S_M$ are the solution state correct energy and entropy.

| Structure                  | THF | Toluol |
|----------------------------|-----|--------|
|                            | $\Delta G_M$ | $\Delta H$ | $\Delta S_M$ | $\Delta G_M$ | $\Delta H$ | $\Delta S_M$ |
| $\kappa O$-$\text{Li}(\text{THF})_3$ | 33.1 | 30.3 | -9.6 | 34.5 | 28.5 | -20.1 |
| $\kappa N$-$\text{Li}(\text{THF})_3$ | 44.1 | 75.9 | 106.8 | 34.5 | 76.8 | 141.9 |
| $\kappa O$-$\kappa N$-$\text{Li}(\text{THF})_3$ | 49.9 | 82.9 | 110.5 | 43.0 | 86.4 | 145.6 |
| $\kappa O$-$\text{Li}(\text{THF})_2$ | 31.3 | 62.5 | 104.6 | 28.2 | 69.9 | 139.8 |
| $\kappa N$-$\kappa S$-$\text{Li}(\text{THF})_2$ | 25.1 | 57.6 | 109.0 | 6.0 | 49.0 | 144.2 |
| $\kappa O$-$\kappa S$-$\text{Li}(\text{THF})_2$ | 33.8 | 67.6 | 113.2 | 14.3 | 58.5 | 148.3 |
| $\kappa O$-$\kappa N$-$\text{Li}(\text{THF})$ | 79.0 | 135.6 | 189.8 | 64.1 | 144.8 | 270.5 |
| $\kappa O$-$\kappa S$-$\kappa \text{Cl}$-$\text{Li}(\text{THF})$ | 69.1 | 127.9 | 197.3 | 46.0 | -31.5 | -260.1 |
| $\kappa N$-$\kappa S$-$\kappa \text{Cl}$-$\text{Li}(\text{THF})$ | 56.9 | 111.5 | 183.3 | 31.2 | -50.5 | -274.1 |
| $\kappa N$-$\kappa S$-$\text{Li}(\text{THF})$ | 63.1 | 114.3 | 171.8 | 41.9 | -43.3 | -285.6 |
| $\kappa O$-$\kappa S$-$\kappa S$-$\text{Li}(\text{THF})$ | 67.5 | 131.2 | 193.5 | 50.7 | -28.0 | -263.9 |
| $\kappa O$-$\kappa S$-$\text{Li}(\text{THF})_2$ | 60.4 | 123.6 | 213.6 | 38.6 | -34.2 | -243.9 |
| $\kappa O$-$\kappa S$-$\text{Li}_2(\text{THF})_2$ | 81.0 | 152.2 | 238.8 | 6.8 | 132.3 | 420.9 |
| $\kappa N$-$\kappa S$-$\text{Li}_2(\text{THF})_2$ | 88.5 | 143.0 | 182.6 | 19.3 | 128.0 | 364.7 |
| $\kappa O$-$\kappa N$-$\kappa \text{Cl}$-$\text{Li}_2(\text{THF})_2$ | 94.0 | 144.9 | 170.7 | 51.4 | 31.3 | -67.4 |
| $\kappa O$-$\kappa N$-$\text{Li}_2(\text{THF})_4$ | 30.0 | 31.0 | 3.2 | -14.5 | 13.6 | 94.3 |
| $\kappa O$-$\kappa N$-$\kappa \text{Cl}$-$\text{Li}_2$ | 104.8 | 214.0 | 366.4 | 10.8 | 201.5 | 202.3 |
| $\kappa N$-$\kappa S$-$\kappa \text{Cl}$-$\text{Li}_2$ | 173.0 | 274.7 | 341.1 | 95.7 | 278.9 | 279.7 |
| $\kappa O$-$\kappa S$-$\kappa \text{Cl}$-$\text{Li}_2$ | 174.1 | 286.9 | 387.3 | 90.1 | 284.3 | 285.1 |
| $\kappa O$-$\kappa M$-$\text{Li}_2$ | 171.7 | 283.8 | 376.0 | 118.8 | 312.4 | 313.2 |
| $\kappa O$-$\kappa S$-$\text{Li}_2$ | 172.7 | 283.8 | 372.4 | 97.0 | 289.5 | 290.3 |
| $\kappa S$-$\kappa \text{Cl}$-$\text{Li}_2$ | 173.2 | 274.7 | 340.6 | 95.8 | 278.8 | 279.7 |
| Bond Type | Energy (kcal/mol) |
|-----------|------------------|
| $\kappa O, \kappa S, \kappa O$-Li$_2$ | 152.8 | 261.8 | 365.5 | 69.6 | 260.0 | 260.8 |
| $\kappa O$-Na(THF)$_3$ | $-$14.6 | 261.8 | 365.5 | 69.6 | 260.0 | 260.8 |
| $\kappa S$-Na(THF)$_5$ | 13.4 | 15.2 | 365.5 | 69.6 | 260.0 | 260.8 |
| $\kappa O$-Na(THF)$_4$ | 8.6 | 80.2 | 15.9 | 21.6 | 140.7 |
| $\kappa S$-Na(THF)$_4$ | 20.0 | 23.9 | 13.4 | 20.5 | 23.9 |
| $\kappa O$-Na(THF)$_3$ | 13.4 | 13.3 | 15.2 | 15.2 | 0.1 |
| $\kappa S$-Na(THF)$_3$ | 23.1 | 27.1 | 13.3 | 15.2 | 0.1 |
| $\kappa O$-Na(THF)$_2$ | 21.2 | 49.5 | 95.1 | 59.8 | 140.7 |
| $\kappa S$-Na(THF)$_2$ | 37.7 | 66.7 | 97.3 | 75.0 | 142.8 |
| $\kappa O$-Na(THF)$_2$ | 23.1 | 52.1 | 97.2 | 45.0 | 142.8 |
| $\kappa O$-Na(THF) | 56.8 | 114.8 | 194.4 | 126.9 | 287.2 |
| $\kappa S$-Na(THF)$_2$ | 110.5 | 149.0 | 129.4 | 134.7 | 311.6 |
| $\kappa O$-Na(THF)$_3$ | 138.3 | 180.1 | 140.2 | 90.1 | 322.4 |
| $\kappa O$-Na(THF)$_4$ | 41.8 | 89.2 | 158.9 | 60.0 | 341.1 |
| $\kappa S$-Na(THF)$_4$ | 70.7 | 116.6 | 154.0 | 98.8 | 336.2 |
| $\kappa O$-Na(THF)$_5$ | 6.2 | 9.4 | 10.6 | 10.9 | 101.6 |
| $\kappa S$-Na(THF)$_5$ | $-$28.8 | $-$55.8 | $-$90.6 | $-$66.2 | $-$136.2 |
| $\kappa O$-K(THF)$_3$ | 0.5 | 5.0 | 14.9 | 5.7 | 14.9 |
| $\kappa O$-K(THF)$_4$ | 13.2 | 11.2 | 6.7 | 9.1 | 6.7 |
| $\kappa O$-K(THF)$_5$ | 4.2 | 2.5 | 5.9 | 8.6 | 5.9 |
| $\kappa O$-K(THF)$_6$ | 21.8 | 47.5 | 86.1 | 54.5 | 131.6 |
| $\kappa O$-K(THF)$_7$ | 15.4 | 38.7 | 78.3 | 44.2 | 123.9 |
| $\kappa O$-K(THF)$_8$ | 32.9 | 58.6 | 86.0 | 67.4 | 131.5 |
| $\kappa O$-K(THF)$_9$ | 18.5 | 43.7 | 84.6 | 35.2 | 130.2 |
| $\kappa O$-K(THF)$_10$ | 52.1 | 100.9 | 163.8 | 109.6 | 256.7 |
| $\kappa O$-K(THF)$_11$ | 16.1 | 66.5 | 169.1 | 31.9 | 351.3 |
| $\kappa O$-K(THF)$_12$ | 44.0 | 87.8 | 147.0 | 61.3 | 329.2 |
| $\kappa O$-K(THF)$_13$ | 68.1 | 118.0 | 167.6 | 98.7 | 349.8 |
| $\kappa O$-K(THF)$_14$ | 9.6 | 5.7 | 51.2 | 41.6 | 39.9 |
6.4 Coordinates

6.4.1 Coordinates of the monomeric structures of 1-Li

κO-Li(THF)_3

E = -3204.14980656

Li 2.311501 0.881552 -0.058066
O 0.598002 0.161150 0.234416
O 2.545079 2.293360 1.243068
O 3.798702 -0.327115 0.027859
O 2.317650 1.726652 -1.785287
S 0.215719 -1.110369 0.954055
C 1.453183 3.214598 1.336212
C 3.002354 1.924570 2.547068
C 4.512301 -0.675742 -1.161407
C 4.110369 -1.232665 1.090690
C 2.787309 3.051537 -1.995738
C 1.302175 1.412646 -2.748936
N 0.725359 -1.389494 2.382955
C -1.478976 -1.158993 0.800520
C 0.972891 -2.436505 0.030056
H 0.654179 2.884636 0.654423
H 1.801085 4.213653 1.016490
C 1.036127 3.204695 2.793115
C 2.357421 2.918476 3.497710
H 4.102209 1.949877 2.555731
H 2.674379 0.892488 2.762949
H 5.020362 0.219535 -1.550618
H 3.787496 -1.018945 -1.918339
C 5.466341 -1.788942 -0.75522
C 4.722185 -2.439237 0.406015
H 3.183220 -1.448596 1.643312
H 4.830901 -0.750038 1.776115
H 3.627849 3.046465 -2.715150
H 3.153186 3.437148 -1.033814
C 1.585397 3.783840 -2.559282
C 0.991732 2.720257 -3.480345
C 0.435082 1.004536 -2.208211
H 1.678911 0.633139 -3.431599
C 0.065057 -0.732938 3.489040
Cl -2.156707 -2.696707 1.334819
P -2.260832 -0.346310 -0.560390
C 1.237611 -2.233758 -1.323785
C 1.182279 -3.677164 0.632207
H 0.319609 2.387954 2.971290
H 0.563283 4.146212 3.103928
H 2.963715 3.835579 3.567810
H 2.236555 2.511569 4.511474
H 6.425126 -1.369641 -0.410918
H 5.676543 -2.479541 -1.584206
H 3.927510 -3.102820 0.032731
H 5.372113 -3.020948 1.074449
H 1.852114 4.714210 -3.079934
H 0.882302 4.029089 -1.747201
H 1.491020 2.746440 -4.461097
H -0.085560 2.850616 -3.652001
H -1.004305 -0.527065 3.296940
H 0.545206 0.224950 3.761852
H 0.123463 -1.383383 4.375754
S -1.813923 -0.818767 -2.442951
Supporting Information

\[ \kappa N-Li(THF)_3 \]

\[ E = -3204.13862831 \]

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| O    | 1.885583 | 1.907612 | 1.894087 |
| O    | 3.947915 | -0.251153 | 0.532550 |
| O    | 3.111294 | 2.319444 | -0.820445 |
| S    | 0.296341 | -1.094494 | 0.244675 |
| O    | 0.545092 | 2.378231 | 1.732331 |
| C    | 0.998632 | 1.468357 | 3.239899 |
| O    | 4.881907 | -0.457615 | -0.528472 |
| C    | 4.417989 | -0.840346 | 1.744793 |
| O    | 3.063539 | 3.077265 | -0.406414 |
| C    | 3.001527 | 2.358695 | -2.234075 |
| C    | -1.381731 | -1.103979 | 0.485770 |
| C    | 0.794855 | -2.709861 | -0.379321 |
| C    | 0.168605 | 2.007821 | 0.766870 |
| C    | 0.546519 | 3.484093 | 1.713662 |
| C    | -0.216518 | 1.839301 | 2.927786 |
| C    | 0.855056 | 1.882235 | 4.012065 |
| H    | 3.024785 | 1.926888 | 3.619322 |
| H    | 2.212470 | 0.374155 | 3.230822 |
| H    | 0.504952 | 0.501632 | -1.039295 |
| H    | 4.444116 | -1.168574 | -1.251619 |
| C    | 6.129220 | -1.024485 | 0.131094 |
| C    | 5.542583 | -1.770761 | 1.324697 |
| H    | 3.570410 | -1.344335 | 2.232031 |
| C    | 4.785038 | -0.045319 | 2.417861 |
| H    | 4.046161 | 4.147124 | -0.598005 |
| H    | 2.866301 | 3.690514 | 0.672221 |
| C    | 1.972922 | 4.313386 | -1.270760 |
| C    | 1.923471 | 3.404614 | -2.515989 |
\( \kappa O, \kappa N - Li(THF)_3 \)

\[ E = -2971.84616503 \]

Li -2.409307 1.054184 -0.609377
O -0.847967 0.308114 0.474695
O -2.160148 2.924890 -0.555529
O -4.000417 0.193637 -0.016215
S -0.588937 -0.681153 -0.631807
C -2.609623 3.923958 -1.471945
C -1.607116 3.525230 0.625320
C -4.238041 -0.015977 1.380748
C -4.705427 -0.771608 -0.802668
N -1.308783 -0.339799 -1.973812
C 1.084987 -0.866171 -0.733322
C -1.382164 -2.197807 -1.28528
H -3.594600 3.628475 -1.863878
H -1.901285 3.981698 -2.317252
C -2.630530 5.215959 -0.673907
C -1.469531 4.999016 -0.673907
H -0.656907 3.024729 0.856948
H -2.306002 3.362715 1.464256
H -4.495497 0.948468 1.844367
H -3.307705 -0.388927 1.840177
C -5.355928 -1.043020 1.452016
C -5.125606 -1.849982 0.178666
H -4.027484 -1.127644 -1.592522
H -5.576640 -0.294251 -1.271482
C -0.592034 0.489029 -2.929998
Cl 1.544388 -2.236856 -1.760394
P 2.088836 -0.453696 0.7272
C -1.428695 -2.480466 1.237044
C -1.830926 -3.110693 -1.081079
H -3.578954 5.309894 -0.121206
H -2.516778 6.104967 -1.309534
H -0.509577 5.184856 -0.215530
H -1.511237 5.637691 1.183597
H -6.339333 -0.547216 1.423332
H -5.306584 -1.648345 2.367797
H -4.305739 -2.569059 0.323750
H -6.013345 -2.403268 -0.157749
H 0.431452 0.123338 -3.122611
H -0.513564 1.551802 -2.630554
H -1.140894 0.459311 -3.883044
S 1.826063 -1.324234 2.422890
C 3.790997 -0.730895 0.029965
C 1.995472 1.374455 0.781817
H -1.027074 -1.757629 1.949727
C -1.964500 -3.697212 1.652840
C -2.361920 -4.325835 -0.651458
C -1.773352 -2.847576 -2.137970
C 4.168753 -0.283816 -1.242882
C 4.731101 -1.353005 0.851995
C 2.129223 1.984485 2.029715
C 1.876490 2.163792 -0.367769
H -2.013726 -3.929912 2.719890
H -2.430978 -4.617427 0.711843
H -2.725666 -5.048260 -1.385688
H 3.432990 0.188872 -1.896487
C 5.478747 -0.455939 -1.680882
C 6.043434 -1.524681 0.410465
H 4.413132 -1.699205 1.839661
H 2.204413 1.350579 2.917652
C 2.155982 3.375949 2.128965
C 1.915708 3.552303 -0.267423
H 1.734854 1.681321 -1.336910
H -2.849802 -5.570297 1.043826
H 5.768044 -0.108254 -2.675556
Supporting Information

\[ \kappa_0, \kappa C/Li(THF)_3 \]

\[ E = -2971.84374276 \]

\[
\begin{align*}
\text{Li} & : 1.763449 0.732799 \\
\text{O} & : 3.155749 1.090779 \\
\text{Cl} & : 3.833560 0.303040 \\
\text{C} & : 3.929856 1.943632 \\
\text{P} & : 4.517380 0.816507 \\
\text{Cl} & : 4.633864 -0.357881 \\
\text{H} & : 4.603160 0.692988 \\
\text{H} & : 4.644197 1.054118 \\
\text{H} & : 4.625621 1.698816 \\
\text{C} & : 4.873960 0.44044 \\
\text{C} & : 4.766724 -1.429699 \\
\text{H} & : 4.880056 -0.336081 \\
\text{H} & : 4.626611 -2.188826 \\
\text{C} & : 4.635648 0.633736 -1.298775 \\
\text{P} & : 4.38035 0.189699 -0.692988 \\
\text{H} & : 4.506372 0.317504 0.544198 \\
\text{H} & : 4.562562 1.883091 1.698816 \\
\text{C} & : 4.867837 1.237396 0.440444 \\
\text{C} & : 4.746672 1.222743 -1.429699 \\
\text{H} & : 4.858085 -0.124859 -1.336081 \\
\text{H} & : 4.362266 1.689565 -2.188826 \\
\text{C} & : 4.565564 0.633736 -1.298775 \\
\text{C} & : 4.390973 -1.692419 0.854417 \\
\text{H} & : 4.204445 2.647891 1.572032 \\
\text{H} & : 4.104239 3.943819 2.790411 \\
\text{H} & : 4.024550 5.501291 1.229638 \\
\text{H} & : 3.163908 4.656529 0.150135 \\
\text{H} & : 3.872259 1.642091 0.229565 \\
\text{H} & : 3.822998 0.220457 0.463047 \\
\text{H} & : 3.606842 2.150894 -1.922297 \\
\text{H} & : 3.899191 0.374303 -1.958485 \\
\text{S} & : 1.745525 -2.988033 -1.440074 \\
\text{C} & : 2.453113 0.054483 -1.831918 \\
\text{C} & : 2.980531 -1.072076 0.743962 \\
\text{H} & : 2.904482 -2.810420 -1.085096 \\
\text{C} & : 2.879518 -3.432825 -1.273097 \\
\text{C} & : 2.430508 -2.432867 0.291998 \\
\text{H} & : 3.568498 -0.996449 1.675779 \\
\text{C} & : 2.820144 1.334352 -1.394916 \\
\text{C} & : 2.579912 -0.285066 -3.178428 \\
\text{C} & : 4.137500 -1.853233 0.682246 \\
\text{C} & : 2.797829 -0.184336 1.807867 \\
\text{H} & : 2.681530 -4.110536 -2.106918 \\
\text{C} & : 4.176889 -3.296186 -0.774151 \\
\text{H} & : 5.444396 -2.333582 0.687361 \\
\text{H} & : 2.728223 1.600068 -0.344242 \\
\text{C} & : 3.303887 2.267372 -2.312308 \\
\text{C} & : 3.062967 0.651822 -4.092771
\end{align*}
\]

\[ 6.418789 -1.075585 -0.854361 \]

\[ 6.774638 -2.013184 1.059122 \]

\[ 2.257314 3.848101 3.109232 \]

\[ 2.059335 4.161440 0.980855 \]

\[ 1.825830 4.163467 -1.169054 \]

\[ 7.446329 -1.210299 -1.201193 \]

\[ 2.085245 5.251154 1.058586 \]
Supporting Information

\[ 2.99097 \text{-} 1.294753 \text{-} 3.491122 \\
4.257350 \text{-} 2.562645 \text{-} 0.140873 \\
5.114346 \text{-} 1.732834 \text{-} 1.669949 \\
3.775014 \text{-} 0.065878 \text{-} 2.793523 \\
1.870820 \text{-} 0.388199 \text{-} 1.862702 \\
-4.994991 \text{-} 3.868368 \text{-} 1.218135 \\
3.592210 \text{-} 3.264255 \text{-} 1.969623 \\
3.423004 \text{-} 1.927813 \text{-} 3.662044 \\
3.625672 \text{-} 0.626435 \text{-} 3.624263 \\
3.803115 \text{-} 2.660624 \text{-} 4.378071 \\
5.701525 \text{-} 0.744840 \text{-} 3.499267 \\
-0.468413 \text{-} 2.690276 \text{-} 2.936794 \\
-1.275971 \text{-} 3.341854 \text{-} 3.547391 \\
0.300155 \text{-} 0.381521 \text{-} 3.363871 \\
-0.892915 \text{-} 3.351217 \text{-} 3.772507 \\
-0.300155 \text{-} 0.381521 \text{-} 3.363871 \\
H \text{-} 1.202802 \text{-} 2.008234 \text{-} 3.078064 \\
H \text{-} 0.045481 \text{-} 0.949682 \text{-} 3.785394 \\
\]

**κO-Li(THF)₂**

\[ E = -2971.85127750 \]

\[ O \text{ 0.742740 0.128423 0.777312} \]
\[ O \text{ 2.098612 2.715756 -0.097633} \]
\[ O \text{ 3.817967 0.444926 1.165445} \]
\[ S \text{ 0.374432 -1.332132 0.868066} \]
\[ C \text{ 2.403851 4.090284 0.139986} \]
\[ C \text{ 1.636945 2.521153 -1.441065} \]
\[ C \text{ 4.661131 0.625591 0.023888} \]
\[ C \text{ 0.300155 -0.381521 3.363871} \]
\[ C \text{-0.892915 -2.102483 3.772507} \]
\[ C \text{-1.441221 0.219962 1.741565} \]

\[ E = -2971.85127750 \]

\[ O \text{ 0.742740 0.128423 0.777312} \]
\[ O \text{ 2.098612 2.715756 -0.097633} \]
\[ O \text{ 3.817967 0.444926 1.165445} \]
\[ S \text{ 0.374432 -1.332132 0.868066} \]
\[ C \text{ 2.403851 4.090284 0.139986} \]
\[ C \text{ 1.636945 2.521153 -1.441065} \]
\[ C \text{ 4.661131 0.625591 0.023888} \]
\[ C \text{ 0.300155 -0.381521 3.363871} \]
\[ C \text{-0.892915 -2.102483 3.772507} \]
\[ C \text{-1.441221 0.219962 1.741565} \]

\[ κO-Li(THF)₂ \]

\[ E = -2971.85127750 \]
$\kappa N, \kappa S$-Li(THF)$_2$

$E = -2971.8532682$

Cl $0.714492 -0.243982 -2.276262$
S $0.052810 -1.973623 1.410860$
O $-2.486229 -2.456635 -1.174136$
C $0.758105 0.447578 -0.655495$
P $1.320538 -0.623566 0.624610$
C $-2.486089 -2.017942 -2.538123$
C $-1.923308 -3.761626 -1.11645$
C $2.055031 0.410803 1.935999$
C $2.753519 -1.471796 -0.130579$
C $-0.397539 2.904083 -1.315638$
H $-3.511153 -2.081125 -2.940499$
H $-2.165462 -0.966262 -2.531594$
C $-1.515989 -2.939852 -3.289577$
C $-0.842792 -3.740631 -2.173757$
H $-1.544114 -3.917687 -0.092134$
H $-2.699634 -4.519019 -1.330764$
C $2.655341 1.634997 1.621394$
C $2.074998 -0.58985 3.250564$
C $3.733895 -0.724849 -0.795843$
C $2.889659 -2.855529 -0.157979$
C $0.110310 4.069338 -0.743816$
C $-0.743753 2.843996 -2.665949$
H $-0.793171 -2.370259 -3.889850$
H $-2.064267 -3.609376 -3.969565$
H $0.033743 -3.200292 -1.783341$
\begin{align*}
\kappa O, \kappa S - \text{Li(THF)}_2 \\
E &= -2971.84916164
\end{align*}
| Atom | x           | y           | z           |
|------|-------------|-------------|-------------|
| C    | -0.676324   | -3.605675   | -2.899454   |
| C    | 0.387760    | -3.912438   | -1.846105   |
| H    | 0.075965    | -3.952785   | -0.591596   |
| H    | -0.907797   | -3.912438   | -1.846105   |
| C    | 2.202100    | 2.620319    | 1.011901    |
| C    | 2.438068    | 1.104664    | 2.885548    |
| C    | 3.675957    | 0.182844    | -1.120142   |
| C    | 3.347127    | -1.982626   | -0.089827   |
| C    | -1.168660   | 3.382715    | -1.835914   |
| C    | -2.661639   | 1.626466    | -2.615391   |
| H    | 0.075965    | -3.952785   | -0.591596   |
| H    | -0.907797   | -3.912438   | -1.846105   |
| C    | 2.202100    | 2.620319    | 1.011901    |
| C    | 2.438068    | 1.104664    | 2.885548    |
| C    | 3.675957    | 0.182844    | -1.120142   |
| C    | 3.347127    | -1.982626   | -0.089827   |
| C    | -1.168660   | 3.382715    | -1.835914   |
| C    | -2.661639   | 1.626466    | -2.615391   |
| H    | 0.075965    | -3.952785   | -0.591596   |
| H    | -0.907797   | -3.912438   | -1.846105   |
| C    | 2.202100    | 2.620319    | 1.011901    |
| C    | 2.438068    | 1.104664    | 2.885548    |
| C    | 3.675957    | 0.182844    | -1.120142   |
| C    | 3.347127    | -1.982626   | -0.089827   |
| C    | -1.168660   | 3.382715    | -1.835914   |
| C    | -2.661639   | 1.626466    | -2.615391   |
| H    | 0.075965    | -3.952785   | -0.591596   |
| H    | -0.907797   | -3.912438   | -1.846105   |
| C    | 2.202100    | 2.620319    | 1.011901    |
| C    | 2.438068    | 1.104664    | 2.885548    |
| C    | 3.675957    | 0.182844    | -1.120142   |
| C    | 3.347127    | -1.982626   | -0.089827   |
| C    | -1.168660   | 3.382715    | -1.835914   |
| C    | -2.661639   | 1.626466    | -2.615391   |
| H    | 0.075965    | -3.952785   | -0.591596   |
| H    | -0.907797   | -3.912438   | -1.846105   |
| C    | 2.202100    | 2.620319    | 1.011901    |
| C    | 2.438068    | 1.104664    | 2.885548    |
| C    | 3.675957    | 0.182844    | -1.120142   |
| C    | 3.347127    | -1.982626   | -0.089827   |
| C    | -1.168660   | 3.382715    | -1.835914   |
| C    | -2.661639   | 1.626466    | -2.615391   |
| H    | 0.075965    | -3.952785   | -0.591596   |
| H    | -0.907797   | -3.912438   | -1.846105   |
| C    | 2.202100    | 2.620319    | 1.011901    |
| C    | 2.438068    | 1.104664    | 2.885548    |
| C    | 3.675957    | 0.182844    | -1.120142   |
| C    | 3.347127    | -1.982626   | -0.089827   |
| C    | -1.168660   | 3.382715    | -1.835914   |
| C    | -2.661639   | 1.626466    | -2.615391   |
| H    | 0.075965    | -3.952785   | -0.591596   |
| H    | -0.907797   | -3.912438   | -1.846105   |
| C    | 2.202100    | 2.620319    | 1.011901    |
| C    | 2.438068    | 1.104664    | 2.885548    |
| C    | 3.675957    | 0.182844    | -1.120142   |
| C    | 3.347127    | -1.982626   | -0.089827   |
| C    | -1.168660   | 3.382715    | -1.835914   |
| C    | -2.661639   | 1.626466    | -2.615391   |
| H    | 0.075965    | -3.952785   | -0.591596   |
| H    | -0.907797   | -3.912438   | -1.846105   |
| C    | 2.202100    | 2.620319    | 1.011901    |
| C    | 2.438068    | 1.104664    | 2.885548    |
| H    | -0.501178   | 1.102006    | 0.554339    |
| O    | -1.686955   | -1.892688   | 1.980612    |
| C    | -1.224854   | 1.922721    | -2.397287   |
| C    | -2.123268   | 3.340087    | -1.549575   |
| C    | -0.561577   | 3.298170    | -1.549575   |
| C    | -0.501178   | 1.102006    | 0.554339    |
| O    | -1.686955   | -1.892688   | 1.980612    |
| C    | -1.224854   | 1.922721    | -2.397287   |
| C    | -2.123268   | 3.340087    | -1.549575   |
| C    | -0.561577   | 3.298170    | -1.549575   |
| C    | -0.501178   | 1.102006    | 0.554339    |
| O    | -1.686955   | -1.892688   | 1.980612    |
| C    | -1.224854   | 1.922721    | -2.397287   |
| C    | -2.123268   | 3.340087    | -1.549575   |
| C    | -0.561577   | 3.298170    | -1.549575   |

κOκN-Li(THF)
\[
\begin{array}{l}
E = -2739.54907333 \\
\text{Li} 2.318590 \ 1.644395 \ -1.029824 \\
\text{O} 0.956659 \ 1.39231 \ 0.426642 \\
\text{O} 3.912270 \ 0.834214 \ -0.379088 \\
\text{S} -0.184321 \ 1.589944 \ -0.515395 \\
\text{C} 5.147449 \ 0.561381 \ -1.037224 \\
\text{C} 3.955022 \ 0.385790 \ 0.986279 \\
\text{N} 0.476467 \ 1.976479 \ -1.885710 \\
\text{C} -1.217051 \ 0.248218 \ -0.511091 \\
\text{C} -1.117439 \ 2.980983 \ 0.119144 \\
\text{H} 5.381555 \ 1.401844 \ -1.707433 \\
\text{H} 5.045116 \ -0.354957 \ -1.646196 \\
\text{C} 6.152089 \ 0.367876 \ 0.082849 \\
\text{C} 5.294113 \ -0.317917 \ 1.141049 \\
\text{H} 3.088663 \ -0.264473 \ 1.170733 \\
\text{H} 3.875624 \ 1.268596 \ 0.426642 \\
\text{C} -0.289943 \ 1.844209 \ -3.106254 \\
\text{C} -1.996161 \ -1.042170 \ 0.670643 \\
\text{C} -1.887374 \ 2.791874 \ 1.267464 \\
\text{C} -1.009068 \ 4.223125 \ -0.499463 \\
\text{H} 6.511655 \ 1.344103 \ 0.445694 \\
\text{H} 7.024004 \ -0.223847 \ -0.228762 \\
\text{H} 5.189371 \ -1.389247 \ 0.911725 \\
\text{H} 5.696837 \ -0.227080 \ 2.159207 \\
\text{H} -1.103670 \ 2.587937 \ -3.200303 \\
\text{H} -0.745107 \ 0.842271 \ -3.216953 \\
\text{H} 0.391230 \ 1.996159 \ -3.956248 \\
\text{C} -1.320503 \ -0.721030 \ 2.606929 \\
\text{C} -2.113133 \ -2.349887 \ 0.028076 \\
\text{C} 0.666766 \ -1.741824 \ 0.366023 \\
\text{C} -1.951755 \ 1.798051 \ 1.726277 \\
\text{C} -2.560097 \ 3.847671 \ 1.805824 \\
\text{C} -1.694413 \ 5.308661 \ 0.046323 \\
\text{H} -0.390419 \ 4.325388 \ -1.393685 \\
\text{C} -2.063395 \ -2.713998 \ -1.323335 \\
\text{C} -2.988070 \ -3.006037 \ 0.893394 \\
\text{C} 1.289040 \ -2.469973 \ 1.833593 \\
\text{C} 1.281937 \ -1.633898 \ -0.885931 \\
\text{H} -3.165735 \ 3.757777 \ 2.706899 \\
\text{C} -2.465588 \ 5.138702 \ 1.195918 \\
\text{H} -1.624536 \ 6.290109 \ -0.428194 \\
\text{H} -1.387304 \ -2.189754 \ -2.002685 \\
\text{C} -2.882577 \ -3.733816 \ -1.798654 \\
\text{C} -3.809767 \ -4.026749 \ 0.413710 \\
\text{H} -3.011405 \ -2.701108 \ 1.943574 \\
\text{H} 0.807117 \ -2.524562 \ 2.363523 \\
\text{C} 2.508058 \ -3.103184 \ 1.144955 \\
\text{C} 2.505575 \ -2.258654 \ -1.117760 \\
\text{H} 0.801156 \ -1.041585 \ -1.668148 \\
\text{H} -3.001632 \ 5.990652 \ 1.620990 \\
\text{H} -2.842827 \ -4.015508 \ -2.853649 \\
\text{C} -3.756902 \ -4.391970 \ -0.930276 \\
\text{H} -4.494651 \ -4.537665 \ 1.094848 \\
\text{H} 2.988071 \ -3.674653 \ 1.942995 \\
\text{C} 3.115399 \ -3.002790 \ -0.107286 \\
\text{H} 2.985056 \ -2.165495 \ -2.095316 \\
\text{H} -4.400252 \ -5.191430 \ -1.306077 \\
\text{H} 4.070181 \ -3.500357 \ -0.294537 \\
\kappa_{O,S,Cl}\cdot Li(THF)
\end{array}

\[ E = -2739.55158286 \]

| Element | Coordinates |
|---------|-------------|
| C       | -0.176335, -0.365862, 0.932914 |
| Cl      | -1.807319, -0.411863, 1.627372 |
| S       | 0.376102, -1.968441, 0.650273 |
| P       | 0.079935, 0.834852, -0.342257 |
| S       | -0.348511, 0.387553, -2.265878 |
| N       | 0.352351, -2.691909, 2.010128 |
| C       | 0.644272, -4.111721, 1.962273 |
| H       | 1.690240, -4.336822, 1.670192 |
| H       | 0.496883, -4.525497, 2.971045 |
| H       | -0.014421, -4.673551, 1.274769 |
| C       | 2.045098, -1.749244, 0.029287 |
| C       | 3.034480, -1.428466, 0.957490 |
| C       | 2.343472, -1.261825, 0.517423 |
| H       | 0.328094, -2.678193, -0.492012 |
| C       | 1.690240, -4.336822, 1.670192 |
| O       | 0.496883, -4.525497, 2.971045 |
| H       | 0.496883, -4.525497, 2.971045 |
| Li      | 1.419673, -1.779552, -1.713285 |

\[ \kappa N, \kappa S, \kappa Cl - Li(THF) \]
\[ E = -2739.55833053 \]

\[
\begin{align*}
\text{C} & : -0.136017 -0.323295 0.926378 \\
\text{Cl} & : -1.678349 -0.376873 1.795746 \\
\text{S} & : 0.518948 -1.909638 0.838663 \\
\text{P} & : -0.039458 0.839505 -0.395810 \\
\text{S} & : -0.631349 0.333299 -2.260926 \\
\text{Cl} & : 2.238075 -1.680193 0.399818 \\
\text{C} & : 3.192070 -1.714505 1.414790 \\
\text{S} & : 0.518948 -1.909638 0.838663 \\
\text{P} & : -0.039458 0.839505 -0.395810 \\
\text{S} & : -0.631349 0.333299 -2.260926 \\
\text{Cl} & : 2.238075 -1.680193 0.399818 \\
\text{C} & : 3.192070 -1.714505 1.414790 \\
\text{S} & : 0.518948 -1.909638 0.838663 \\
\text{P} & : -0.039458 0.839505 -0.395810 \\
\text{S} & : -0.631349 0.333299 -2.260926 \\
\text{Cl} & : 2.238075 -1.680193 0.399818 \\
\text{C} & : 3.192070 -1.714505 1.414790 \\
\text{S} & : 0.518948 -1.909638 0.838663 \\
\text{P} & : -0.039458 0.839505 -0.395810 \\
\text{S} & : -0.631349 0.333299 -2.260926 \\
\text{Cl} & : 2.238075 -1.680193 0.399818 \\
\text{C} & : 3.192070 -1.714505 1.414790 \\
\text{S} & : 0.518948 -1.909638 0.838663 \\
\text{P} & : -0.039458 0.839505 -0.395810 \\
\text{S} & : -0.631349 0.333299 -2.260926 \\
\text{Cl} & : 2.238075 -1.680193 0.399818 \\
\text{C} & : 3.192070 -1.714505 1.414790 \\
\text{S} & : 0.518948 -1.909638 0.838663 \\
\text{P} & : -0.039458 0.839505 -0.395810 \\
\text{S} & : -0.631349 0.333299 -2.260926 \\
\text{Cl} & : 2.238075 -1.680193 0.399818 \\
\text{C} & : 3.192070 -1.714505 1.414790 \\
\text{S} & : 0.518948 -1.909638 0.838663 \\
\text{P} & : -0.039458 0.839505 -0.395810 \\
\text{S} & : -0.631349 0.333299 -2.260926 \\
\text{Cl} & : 2.238075 -1.680193 0.399818 \\
\end{align*}
\]

\[ \kappa N, \kappa S-Li(THF) \]
E = -2739.55620864
S -0.391256 -2.376835 -1.304385
C -0.577785 0.783527 -0.563470
P -1.239252 -0.831813 -0.330033
C -1.305754 -1.149778 1.464294
C -2.991110 -0.667520 -0.821507
C 1.076268 2.862418 0.282561
C -1.780362 -0.157112 3.692113
C -0.936726 -2.397660 1.149779
C -3.680541 0.530156 -0.596728
C -3.660671 -1.766896 -1.363629
C 0.900115 3.358759 1.572985
C 1.290611 3.710017 -0.804210
H -2.048134 0.825153 1.935000
C -1.881528 -0.418799 3.692113
C -1.038501 -2.654961 3.331646
H -0.563683 -3.157075 1.273378
H -3.144639 1.393449 -0.195529
H 0.749803 2.658901 2.396955
C 0.927940 4.736817 1.775226
C 1.314248 5.598663 0.695923
H 1.480756 5.675856 -1.430528
H -1.589246 -1.869290 5.267379
H -6.768816 -0.410336 -1.683735
H 1.152548 6.678759 0.858937
S 0.995692 1.086222 0.031306
O 1.143869 0.482040 1.377085
N 2.042820 0.697912 -1.067335
C 3.426255 1.043190 -0.781434
H 4.038314 0.785673 -1.658253
H 3.572629 2.122550 -0.590114
H 3.841052 0.496817 0.085045
Li 1.678668 -1.104526 -1.899148
O 3.075605 -2.212017 -1.142934
C 4.383376 -2.543502 -1.606441
C 2.958027 -2.451602 0.265936
C 5.050357 -3.274712 -0.452176
H 4.296889 -3.152552 -2.519307
H 4.923352 -1.613733 -1.859854
C 4.384370 -2.623283 0.754924
H 2.423493 -1.604111 0.720989
H 2.358653 -3.364551 0.423404
H 6.144268 -3.170961 -0.464434
H 4.809581 -4.349125 -0.487995
H 4.840272 -1.641960 0.963107
H 4.445049 -3.227090 1.670902
Cl -0.851989 1.429762 -2.186993

κO,κN,κS-Li(THF)
\[ E = -2739.55054668 \]

|   |   |   |   |   |
|---|---|---|---|---|
| S | -1.185196 | -1.539479 | -2.073358 |
| C | -0.592307 | 1.051860 | -0.164519 |
| P | -1.521730 | -0.432768 | -0.422448 |
| C | -1.339086 | -1.458015 | 1.076581 |
| C | -3.253112 | 0.138362 | -0.388740 |
| C | 1.891418 | 2.098589 | 0.531490 |
| C | -0.963787 | -0.884809 | 2.295326 |
| C | -1.620625 | -2.825167 | 1.005295 |
| C | -3.751215 | 0.763161 | 0.761348 |
| C | -4.075441 | -0.034928 | 1.502266 |
| C | 3.220324 | 2.387195 | 0.219172 |
| C | 1.235662 | 2.728607 | 1.588140 |
| H | -0.716315 | 0.178169 | 2.327483 |
| C | -0.877379 | -1.677287 | 3.437970 |
| C | -1.536019 | -3.613564 | 2.151590 |
| H | -1.888190 | -3.264640 | 0.040896 |
| C | -3.107179 | 0.902057 | 1.632937 |
| C | -5.069456 | 1.208554 | 1.689624 |
| C | -5.395971 | 0.412977 | -1.467455 |
| H | -3.668314 | -0.526212 | -2.390004 |
| H | 3.698617 | 1.880055 | 0.621650 |
| H | 3.906890 | 3.322015 | -0.990259 |
| C | 1.930544 | 3.666825 | 2.347631 |
| H | 0.190695 | 2.484120 | 1.790084 |
| H | -0.574897 | -1.228447 | 4.387172 |
| C | -1.165596 | -3.040822 | 3.368810 |
| H | -1.755778 | -4.682258 | 2.092332 |
| C | -5.457633 | 1.694739 | 1.689624 |
| C | -5.893010 | 1.033980 | -0.322858 |
| H | -6.038474 | 0.275382 | -2.340360 |
| H | 4.948281 | 3.556490 | 0.759196 |
| C | 3.262831 | 3.959828 | 2.051595 |
| H | 1.428816 | 4.172559 | 3.175537 |
| H | -1.094500 | -3.60921 | 4.265773 |
| H | -6.927854 | 1.383869 | -0.296249 |
| H | 3.803129 | 4.695908 | 2.651394 |
| S | 1.084441 | 0.823137 | -0.422628 |
| O | 1.380007 | -0.525932 | 0.145098 |
| N | 1.684396 | 0.798802 | -1.868237 |
| C | 1.522917 | 1.917709 | -2.773483 |
| H | 0.501946 | 1.995335 | -3.184562 |
| H | 1.771149 | 2.892300 | -2.312962 |
| H | 2.213224 | 1.772976 | -3.618303 |
| Li | 1.348252 | -1.251179 | -1.954384 |
| O | 2.829328 | -2.448865 | -1.669778 |
| C | 4.067651 | -1.768411 | -1.442498 |
| C | 2.602051 | -3.423601 | -0.640809 |
| C | 4.370470 | -1.987691 | 0.026825 |
| H | 4.848486 | -2.205524 | -2.090727 |
| H | 3.926299 | -0.711589 | -1.714467 |
| C | 3.849080 | -3.406344 | 0.233399 |
| H | 1.705479 | -3.124788 | -0.072950 |
| H | 2.413380 | -4.01069 | -1.110461 |
| H | 3.787839 | -1.274517 | 0.629036 |
| H | 5.437418 | -1.872542 | 0.263883 |
| H | 3.622192 | -3.640865 | 1.282728 |
| H | 4.585687 | -4.141969 | -0.127133 |
| Cl | -1.216864 | 2.550032 | -0.867278 |

\( \kappa O, \kappa S-Li(THF) \)
6.4.2 Coordinates of the dimeric structures of 1-Li

\( \kappa O, \kappa S-Li_2(THF)_2 \)

\[ E = -5479.14610678 \]

Cl: -3.881936 1.720549 -1.969288
Cl: 3.881650 -1.720805 1.969188
S: -0.942092 1.079989 1.388326
S: 0.942126 -1.079824 -1.388499
O: 0.081845 2.493836 1.966786
O: -0.081620 2.493970 -1.966937
C: -3.307647 0.548813 -0.814909
C: 3.307619 -0.548892 0.814858
P: -2.88523 0.976033 0.826525
P: 2.88541 -0.975957 -0.826628
C: 0.268267 -2.162981 3.347234
C: 0.672659 -3.759718 1.664891
C: -0.268588 2.162981 -3.347289
C: -0.672074 3.760001 -1.664975
S: 0.942126 1.079824 -1.388499
S: -0.942092 -1.079989 1.388326
O: 0.081620 -2.493970 1.966937
O: -0.081845 -2.493836 -1.966786
C: -3.307647 -0.548813 0.814909
C: 3.307619 0.548892 -0.814858
P: 2.88523 0.976033 -0.826525
P: -2.88541 -0.975957 0.826628
C: 0.268267 2.162981 -3.347234
C: 0.672659 3.759718 -1.664891
C: -0.268588 -2.162981 3.347289
C: -0.672074 -3.760001 1.664975
H: 0.642957 -1.659239 3.699048
H: 1.116389 -1.462802 3.434845
C: 0.532392 -3.493964 4.023858
C: 1.334098 -4.228948 2.953918
H: 1.389319 3.632985 0.838693
H: 0.124952 4.445968 1.333406
C: 4.284093 1.988802 1.647125
C: 0.642519 1.659256 -3.699435
C: -1.116703 1.462744 -3.434845
C: -0.533056 3.493964 -4.023858
C: -1.334216 4.228948 -2.953918
C: -1.388238 3.633544 -0.838693
H: 0.125825 4.446233 -1.333406
C: -4.945865 -0.765804 1.590339
C: -3.236393 -0.378557 3.258336
C: -5.068632 2.726352 0.912030
C: -2.939539 3.681167 1.558060
C: 4.945998 0.765837 -1.590222
C: 3.236493 0.378928 -3.258263
C: 5.086064 -2.726334 -0.912197
C: 2.939985 -3.681042 -1.558342
C: -4.555145 -3.062034 -0.800664
C: -5.149447 1.651387 -2.690255
H: 1.073382 -3.383770 4.974295
H: -0.416653 4.016372 4.227418
H: 2.382541 -3.897658 2.976596
H: 1.319765 -5.322439 3.060794
C: 4.555271 3.061883 -0.800895
C: 5.149413 1.651107 2.690441
H: -1.074528 3.383557 -4.974096
H: 0.415881 4.016271 -4.228065
H: -2.382660 3.897698 -2.975771
H: -1.314170 5.322496 -3.060761
H: -5.335525 -0.600745 0.583338
C: -5.618333 -1.604591 2.477303
C: -3.912495 -1.216200 4.143258
H: -2.297920 0.101573 3.546595
H: -5.658516 1.877416 0.559639
Supporting Information

\[ \kappa N, \kappa S-Li_2(THF)_2 \]
E = -5479.14937283

Cl -2.350006 -0.655674 2.040689
Cl 2.350152 0.655766 -2.040698
S -0.908357 -0.876635 -1.515934
S 0.908327 0.876611 1.515873
O -0.466811 2.603675 -1.952099
O 0.466803 -2.603661 1.952031
C -3.305662 -0.280646 0.598348
C 3.305729 0.280633 -0.598328
P -2.773935 -1.199576 -0.802527
P 2.773939 1.199542 0.802549
C -1.532182 2.525843 -2.903255
C 1.532148 -2.525772 2.903217
C -0.363952 -3.733905 -2.210765
C 0.363925 3.733915 2.210792
H -2.469672 2.317261 -2.365356
H -1.334132 1.684301 -3.589112
C -1.514116 3.858785 -3.631051
C 1.514085 -3.858684 3.631069
H 1.415312 3.426067 2.122602
H 0.167583 4.509633 1.450079
C 5.366489 1.150996 1.822391
C 3.602803 0.731609 3.430166
C 3.871793 3.328966 -0.661774
C 2.121144 3.910566 0.909174
H -1.932275 3.790055 -4.644962
H -2.096676 4.609611 -3.072889
H 0.515284 3.638572 -4.367805
H 0.178104 5.276484 -3.753432
C 1.932209 -3.789901 4.644991
H 2.096682 -4.609521 3.072959
H -0.515347 -3.638478 4.367729
H -0.178111 -5.276416 3.753453
H -5.678401 -1.339615 -0.792958
C -6.312732 -1.044539 -2.835894
C -4.556517 -0.621505 -4.442423
H -2.537554 -0.613447 -3.643640
H -4.484777 -2.565521 1.146329
C -3.998273 -4.672102 1.010478
C -2.261172 -5.253958 -0.566175
H -1.375420 -3.596174 -1.644124
H 5.678412 1.339546 0.793097
C 6.312646 1.044560 2.836078
C 4.556354 0.621594 4.442539
H 2.537431 0.613508 3.643661
H 4.484841 2.565466 -1.146247
C 3.998384 4.672059 -1.010388
| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| C    | 2.261259 | 5.253940 | 0.566231 |
| H    | 1.375432  | 3.596162  | 1.644130  |
| C    | -7.37379  | -1.164280 | -2.602722 |
| C    | -5.909393 | -0.777571 | -4.146697 |
| C    | -4.238479 | -0.412564 | -5.466585 |
| C    | -4.726424 | -4.968342 | -1.769147 |
| C    | -3.195856 | -5.635180 | 0.396519  |
| H    | -1.629650 | -6.004880 | -1.046803 |
| C    | 7.373304  | 1.164293  | 2.602722  |
| C    | 5.909244  | 0.777646  | 4.146697  |
| C    | 4.238265  | 0.412701  | 5.466695  |
| H    | 4.238479  | 0.412564  | 5.466585  |
| C    | 4.726562  | 4.968342  | -1.769047 |
| H    | 4.726424  | 4.968342  | -1.769147 |
| C    | 3.195978  | 5.635150  | -0.396434 |
| H    | 1.629745  | 6.004873  | 1.046850  |
| Li   | 0.593480  | -1.414846 | 0.433001  |
| O    | 4.443645  | 1.621411  | -0.796605 |
| O    | 4.443642  | 1.621544  | 0.796555  |
| C    | 5.965791  | 1.949619  | 1.655916  |
| C    | 4.763698  | 2.444000  | 4.134771  |
| H    | -2.882730 | 2.049384  | 3.121128  |
| C    | -6.749705 | 2.281925  | 2.758623  |
| H    | -6.404431 | 1.760143  | 0.674643  |
| C    | -6.149834 | 2.525580  | 3.995625  |
| H    | -4.296838 | 2.641933  | 5.102355  |
| H    | -7.834544 | 2.353969  | 2.651877  |
| C    | 4.583659  | 1.864138  | 1.811615  |
| C    | -3.969167 | 2.113221  | 3.038579  |
| C    | -5.965791 | 1.949619  | 1.655916  |
| C    | -4.763698 | 2.444000  | 4.134771  |
| C    | 4.443642  | 1.621544  | 0.796555  |
| C    | 5.965791  | 1.949619  | 1.655916  |
| C    | 4.763698  | 2.444000  | 4.134771  |
| C    | 2.261259  | 5.253940  | 0.566231  |

\( \kappa O, \kappa N, \kappa Cl-L_2(THF)_2 \)

\[ E = -5479.15020428 \]

Cl 1.444965 1.365199 -2.156734
Cl 1.591586 -1.537747 2.103500
Supporting Information

\[ \kappa_O \kappa_N\text{-Li}_2(\text{THF})_4 \]

\[ E = -5943.74225062 \]

C -3.756808 0.073296 -0.577335
S -2.182556 0.668452 -0.402962
P -5.087192 0.117379 0.577651
O -1.396811 0.119752 -1.558497
S -4.722508 0.865530 2.375659
Li 0.161823 1.349813 1.594188
Li -0.161771 -1.349956 -1.593967
O 1.396837 -0.119870 1.558640
S 2.182622 -0.668510 0.403079
P 5.087106 -0.117341 -0.577776
S 4.722210 -0.865646 -2.375676
Cl 4.224556 0.352679 2.223259
Cl -4.224426 -0.352511 -2.223313
C 6.446837 -1.047377 0.208020
C 6.152363 -2.098751 1.081851
C 7.774417 -0.794888 -0.154096
C 7.179704 -2.890383 1.591156
H 5.114154 -2.290380 1.364090
C 8.799850 -1.585400 0.360823
H 8.006589 0.020731 -0.843978
C 8.503741 -2.633766 1.233438
H 6.944694 -3.710196 2.274228
H 9.835792 -1.383126 0.078287
H 9.308934 -3.252853 1.636487
C 5.700548 1.606168 -0.689217
C 5.457207 2.343056 -1.852397
C 6.341949 2.219025 0.395878
C 5.831867 3.683336 -2.375676
Cl 4.224426 -0.352511 -2.223313
C 6.446792 1.047527 -0.208242
C 6.152180 2.098927 1.081851
C 7.774421 0.795080 -0.153724
C 7.179432 2.890632 -1.591366
H 5.113934 2.290521 -1.364121
C 8.799764 1.585666 -0.361262
H 8.006702 -0.020560 -0.843542
C 8.503517 2.634061 -1.233795
H 6.944312 3.710466 -2.274375
H 9.835792 1.585666 -0.361262
H 8.006702 -0.020560 -0.843542
C 8.503517 2.634061 -1.233795
H 6.944312 3.710466 -2.274375
H 9.835792 1.585666 -0.361262
H 8.006702 -0.020560 -0.843542
C 8.503517 2.634061 -1.233795
H 6.944312 3.710466 -2.274375
H 9.835792 1.585666 -0.361262
H 8.006702 -0.020560 -0.843542
C 8.503517 2.634061 -1.233795
H 6.944312 3.710466 -2.274375
H 9.835792 1.585666 -0.361262
H 8.006702 -0.020560 -0.843542
C 8.503517 2.634061 -1.233795
H 6.944312 3.710466 -2.274375
H 9.835792 1.585666 -0.361262
H 8.006702 -0.020560 -0.843542
C 8.503517 2.634061 -1.233795
H 6.944312 3.710466 -2.274375
H 9.835792 1.585666 -0.361262
H 8.006702 -0.020560 -0.843542
C 8.503517 2.634061 -1.233795
H 6.944312 3.710466 -2.274375
H 9.835792 1.585666 -0.361262
H 8.006702 -0.020560 -0.843542
C 8.503517 2.634061 -1.233795
H 6.944312 3.710466 -2.274375
H 9.835792 1.585666 -0.361262
H 8.006702 -0.020560 -0.843542
C 8.503517 2.634061 -1.233795
H 6.944312 3.710466 -2.274375
H 9.835792 1.585666 -0.361262
H 8.006702 -0.020560 -0.843542
\[ k_{O,S,Cl-Li} \]

\[ E = -2.171063 -2.262695 -0.534921 \]
\[ O -3.356053 -1.987812 -2.827968 \]
\[ C -2.202394 -3.718242 -0.597977 \]
\[ H -1.390037 -4.110623 0.032363 \]
\[ H -3.147976 -4.151741 -0.220464 \]
\[ H -2.044796 -4.101554 -1.620889 \]
\[ N -2.170989 2.262628 0.535035 \]
\[ O -3.356164 1.987804 2.828003 \]
\[ C -2.202264 3.718176 0.598071 \]
\[ H -1.389826 4.110515 -0.032192 \]
\[ H -3.147794 4.151706 -0.220460 \]
\[ H -2.044752 4.101498 1.620992 \]
\[ Li -0.605600 1.372502 0.209895 \]
\[ Li -0.605525 1.372384 -0.209676 \]
\[ \kappa_{O,S,Cl-Li} \]

\[ E = -5014.54493149 \]
\[ Cl 1.687089 -0.684620 -2.542398 \]
\[ Cl -1.665168 0.756919 2.499473 \]
\[ S 0.918041 -1.339170 1.094720 \]
\[ S -0.942025 1.343624 1.094720 \]
\[ C 2.798511 -0.180265 1.267644 \]
\[ C -2.784192 0.212346 1.248644 \]
\[ P 2.700037 -1.234419 0.135051 \]
\[ P -2.718119 1.241390 -0.173915 \]
\[ C 4.024791 -0.727692 1.272984 \]
\[ C 3.159032 -2.88702 0.467337 \]
\[ C -4.053725 0.696391 -1.280902 \]
\[ C -3.186833 2.901794 0.403039 \]
\[ C 2.798511 -0.180265 1.267644 \]
\[ C -2.784192 0.212346 1.248644 \]
\[ H 3.186833 2.901794 0.403039 \]
\[ C 4.527012 1.912659 -0.587815 \]
\[ C -4.497341 -1.920312 0.656879 \]
\[ C 5.392484 -0.826829 0.859320 \]
\[ C 3.719177 -0.243945 2.545611 \]
\[ C 3.997408 -3.031571 -1.578988 \]
\[ C 2.704083 -4.019136 0.218635 \]
\[ C -5.381661 0.778079 -0.843221 \]
\[ C -3.763404 0.199156 -2.551849 \]
\[ C -4.016711 3.056241 1.519562 \]
\[ C -2.748587 4.024184 -0.306507 \]
\[ C 4.881040 2.569659 0.585410 \]
\[ C 5.467287 1.622333 -1.576364 \]
\[ C -4.875682 -2.603915 -0.493358 \]
\[ C -5.412999 -1.623405 1.666320 \]
\[ H 5.599004 -1.199830 -0.138354 \]
\[ C 6.380282 -0.435715 1.718699 \]
\[ C 4.746200 0.151244 3.401403 \]
\[ H 2.673478 -0.184735 2.856583 \]
\[ H 4.327924 -2.141224 -2.119367 \]
\[ C 4.383193 -4.304260 -1.994720 \]
\[ C 3.097832 -5.288648 -0.199092 \]
\[ H 2.031541 -3.894422 1.071175 \]
\[ H -5.609203 1.161169 0.153479 \]
\[ H -6.411565 0.355630 -1.676877 \]
\[ H -4.799074 -0.227433 -3.817333 \]
\[ H -2.722689 0.154090 -2.881518 \]
\[ H -4.333923 2.172592 2.078616 \]
\[ C -4.410966 4.332289 1.916461 \]
\[ C -3.150594 5.297085 0.092700 \]
\[ H -2.082389 3.891071 -1.162744 \]
\[ H 4.115903 2.774498 1.334434 \]
\[ C 6.216530 2.920679 0.783788 \]
| Atom | X  | Y  | Z  |
|------|----|----|----|
| C    | 6.796660 | 1.973487 | -1.366825 |
| H    | 5.149755 | 1.111832 | -2.488321 |
| H    | -4.129715 | -2.812063 | -1.260597 |
| C    | -6.211358 | -2.976155 | -0.646714 |
| C    | -6.742967 | -1.995595 | 1.501571 |
| H    | 5.045970 | 0.532951 | 4.396393 |
| C    | 5.031799 | -4.16085 | -2.866681 |
| C    | 3.937589 | -5.431885 | -1.304194 |
| H    | 2.742484 | -6.170769 | 0.335853 |
| H    | -7.446011 | 0.412622 | -1.331706 |
| C    | -6.120718 | -0.149822 | 2.945253 |
| H    | -4.570907 | -0.619791 | -4.375420 |
| H    | -6.525788 | -3.500439 | -1.551974 |
| C    | 3.981978 | 5.451781 | 1.202533 |
| H    | 2.808128 | 6.172945 | -0.463214 |
| H    | 6.511636 | 3.423718 | 1.707409 |
| H    | 4.241044 | -6.428594 | -1.633493 |
| Li   | 0.477521 | 1.169935 | 0.949891 |

$kO_{\kappa N}LI_2$

| Atom | X  | Y  | Z  |
|------|----|----|----|
| C    | -3.854938 | -0.821620 | -0.620586 |
| S    | -2.269042 | -0.244514 | -0.428446 |
| P    | -5.109875 | -0.460811 | 0.586464 |
| O    | -1.561936 | -0.532465 | -1.724170 |
| S    | -4.646061 | -0.849735 | 2.473458 |
| Li   | -0.347295 | 0.402468 | 1.901249 |
| Li   | 0.281922 | -0.587365 | -2.047543 |
| O    | 1.489172 | 0.558365 | 1.581917 |
| S    | 2.232941 | 0.188999 | 0.327189 |
| C    | 3.791700 | 0.845508 | 0.494722 |
| P    | 5.088713 | 0.422085 | -0.644679 |
| S    | 4.653803 | 0.606654 | -2.568729 |
Supporting Information

\[ \kappa O, \kappa S-Li_2 \]

\[ E = -5014.54537659 \]

| Atom | \( x \) | \( y \) | \( z \) |
|------|-------|-------|-------|
| Cl   | -2.415761 | -0.624826 | 2.788636 |
| Cl   | 2.417420  | 0.628673  | -2.787575 |
| S    | -0.835572  | -1.514350  | -0.947656 |
| S    | 0.835353  | 1.513656  | 0.949596 |
| C    | -2.893837  | -0.140338  | 1.180542 |
| C    | 2.893696  | 0.141751  | -1.179689 |
| P    | -2.678780  | 1.283943  | 0.122553 |
| P    | -2.678780  | 1.283943  | 0.122553 |
| C    | -3.894783  | -0.853518  | 1.412671 |
| C    | -3.237762  | -2.891176  | -0.531425 |
| C    | 3.894195  | 0.853697  | 1.419800 |
| C    | 3.238316  | 2.891620  | -0.531425 |
| C    | -4.539348  | 2.079559  | 0.513492 |
| C    | 4.539343  | -2.079872  | -0.518634 |
| C    | -5.236016  | -0.679430  | -1.053073 |
| C    | -3.509223  | -0.731018  | -2.748296 |
| C    | -4.303112  | -2.953538  | 1.443091 |
| C    | -2.643811  | -4.069797  | 0.076309 |
| C    | 5.235191  | 0.675816  | 1.055532 |
| C    | 3.508412  | 0.730650  | 2.750676 |
| C    | 4.304702  | 2.954720  | -1.437734 |
| C    | 2.643700  | 0.409842  | -0.072093 |
| C    | -4.927943  | 2.651306  | -0.692921 |
| C    | -5.434038  | 1.938664  | 1.575211 |
| C    | 4.929747  | -2.653406  | 0.686339 |
| C    | 5.432290  | -1.937980  | -1.581708 |
| C    | -5.536265  | -0.756448  | -0.006549 |
| C    | -6.183087  | -0.377500  | -2.027199 |
| C    | -4.459402  | -0.420185  | -3.719930 |
| H    | -2.459757  | -0.878275  | -3.015930 |
| H    | -4.750182  | -2.031682  | 1.820875 |
| C    | -4.771188  | -4.190304  | 1.878007 |
| C    | -3.117202  | -5.305577  | 0.515301 |
| H    | -1.804978  | -4.007351  | -0.621779 |
| H    | 5.535617  | 0.751843  | 0.008980 |
| C    | 6.181812  | 0.373077  | 2.029870 |
| C    | 4.458123  | 0.419033  | 3.722502 |
| H    | 2.459139  | 0.879506  | 3.018193 |
| H    | 4.752287  | 2.033187  | -1.815688 |
| C    | 4.773155  | 4.191828  | -1.872041 |
| C    | 3.117467  | 5.305983  | -0.509684 |
| H    | 1.804092  | 4.006801  | 0.625010 |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| H       | -4.201243 | 2.736155  | -1.501613 |
| C       | -6.248740 | 3.074805  | -0.845629 |
| H       | -4.204389 | 2.739053  | 1.496143  |
| C       | 6.250609  | -3.077755 | 0.836198  |
| C       | 6.748278  | -2.359430 | -1.421178 |
| H       | 5.091658  | -1.490286 | -2.518820 |
| C       | 6.248740  | 3.074805  | 0.845629  |
| C       | 6.749948  | 2.359286  | 1.411853  |
| H       | 5.094802  | 1.492330  | 2.513472  |
| C       | 4.204389  | -2.739053 | 1.496143  |
| C       | 6.250609  | -3.077755 | 0.836198  |
| C       | 6.748278  | -2.359430 | -1.421178 |
| H       | 5.091658  | -1.490286 | -2.518820 |
| C       | 6.248740  | 3.074805  | 0.845629  |
| C       | 6.749948  | 2.359286  | 1.411853  |
| H       | 5.094802  | 1.492330  | 2.513472  |
| C       | 4.204389  | -2.739053 | 1.496143  |
| C       | 6.250609  | -3.077755 | 0.836198  |
| C       | 6.748278  | -2.359430 | -1.421178 |
| H       | 5.091658  | -1.490286 | -2.518820 |
| C       | 6.248740  | 3.074805  | 0.845629  |
| C       | 6.749948  | 2.359286  | 1.411853  |
| H       | 5.094802  | 1.492330  | 2.513472  |
| C       | 4.204389  | -2.739053 | 1.496143  |

**KL, KCl-Li**

\[
E = -5014.5509132
\]

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| Cl      | 1.731505  | 0.594659  | 2.590935  |
| Cl      | -1.731199 | -0.595370 | -2.590556 |
| S       | 1.248339  | 0.745082  | -1.321327 |
| S       | -1.248215 | -0.744801 | 1.321575  |
| C       | 2.981476  | 0.173306  | 1.399790  |
| C       | -2.981325 | -0.173705 | -1.399690 |

**KS, KCl-Li**

\[
E = -5014.5509132
\]

| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| Cl      | 1.731505  | 0.594659  | 2.590935  |
| Cl      | -1.731199 | -0.595370 | -2.590556 |
| S       | 1.248339  | 0.745082  | -1.321327 |
| S       | -1.248215 | -0.744801 | 1.321575  |
| C       | 2.981476  | 0.173306  | 1.399790  |
| C       | -2.981325 | -0.173705 | -1.399690 |
| P       | 2.820599  | 1.101346  | -0.082125 |
| P       | -2.820522 | -1.101295 | 0.082511  |
| C       | 4.375656  | 0.977812  | -1.016824 |
| C       | 2.745051  | 2.837385  | 0.480308  |
| Atom  | X     | Y     | Z     |
|-------|-------|-------|-------|
| Cl    | -1.921525 | -0.070102 | 2.546259 |
| S     | 5.353018    | -0.011028   | -0.829781  |
| S     | -5.352780    | 0.010706    | 0.830311   |
| C     | 2.120394    | -0.023350   | -0.779888  |
| C     | -2.120193   | 0.023676    | 0.779668   |
| P     | 3.631420    | 0.781147    | -0.265743  |
| P     | -3.631171   | -0.781218   | 0.265980   |
| C     | 3.542412    | 0.974258    | 1.555745   |
| C     | 3.395005    | 2.473000    | -0.915005  |
| C     | -3.542616   | -0.974627   | -1.555492  |
| C     | -3.394248   | -2.472915   | 0.915412   |
| C     | 2.666591    | -2.892400   | -0.494323  |
| C     | -2.666913   | 2.892459    | 0.494016   |
| C     | 2.697387    | 1.923756    | 2.146450   |
| C     | 4.347943    | 0.170621    | 2.365587   |
| C     | 2.116888    | 3.040224    | -0.992621  |
| C     | 4.514785    | 3.211612    | -1.303014  |
| C     | -2.697896   | -1.924364   | -2.146259  |
| C     | -4.348237   | -0.171010   | -2.365268  |
| C     | -2.115979   | -3.039790   | 0.992971   |
| C     | -4.513815   | -3.211817   | 1.303505   |
| C     | 2.391347    | -3.769220   | -1.542870  |
| C     | 3.828787    | -3.011937   | 0.268621   |
| C     | -2.391624   | 3.769389    | 1.542451   |
| C     | -3.829272   | 3.011739    | -0.268721  |
| H     | 2.090995    | 2.588866    | 1.527302   |
| C     | 2.626074    | 2.025961    | 3.536443   |
| C     | 4.269833    | 0.270976    | 3.753484   |
| H     | 5.049648    | -0.519769   | 1.890119   |
| H     | 1.245270    | 2.454515    | -0.690837  |
| C     | 1.969070    | 4.348575    | -1.447854  |
| C     | 4.360171    | 4.520492    | -1.757757  |
| H     | 5.501272    | 2.742201    | -1.254430  |
| H     | -2.091434   | -2.589442   | -1.527138  |
| C     | -2.627017   | -2.026881   | -3.536245  |
| C     | -4.270541   | -0.271665   | -3.753167  |
| H     | -5.049696   | 0.519596    | -1.889756  |
| H     | -1.244556   | -2.453825   | 0.691132   |
| C     | -1.967789   | -4.348107   | 1.448193   |

\( \kappa O, \kappa N, \kappa Cl-Li_2 \)

\[ E = -5014.55606304 \]
C -4.358825 -4.520646 1.758247
H -5.500423 -2.742654 1.254972
H 1.470230 -3.651057 -2.114165
C 3.300271 -4.786808 -1.827247
C 4.723969 -4.037192 -0.019096
H 4.023956 -2.314681 1.083814
H 1.965535 2.786907 3.989628
C 3.402049 1.190769 4.341938
H 4.896901 -0.368601 4.379031
H 0.970996 4.786915 -1.508284
C 3.088639 5.089803 -1.829522
H 5.237245 5.096637 -2.061982
H -1.966734 -2.770198 -3.989470
C -3.403098 1.191736 -4.341685
H -4.897681 0.367897 -4.378657
H -0.969591 -4.786876 1.508549
C -3.087136 -5.086629 1.829923
H -5.235723 -5.097020 2.062552
H 3.086246 -5.481013 -2.645435
C 4.462423 -4.920931 -1.067422
H 5.633993 -4.142323 0.575324
H -3.096662 4.810861 2.645083
C -4.463023 4.920669 1.067350
H -5.634754 4.141765 -0.575149
H 3.343249 1.271397 5.429790
H 2.968521 6.114517 2.189648
H -3.344626 -1.272601 -5.429538
H -2.966736 -6.114314 2.190034
H 5.170826 -5.721634 -1.292611
H -5.171327 5.721255 1.292636
S 1.568633 -1.517724 -0.182616
O 0.346688 -1.881671 -0.987886
S -1.568715 1.518024 0.182025
O -0.346564 1.882332 0.986816
N -1.440155 1.294088 -1.349189
C -1.354759 2.425625 -2.258138
H -2.132727 2.337656 -3.034258
H -1.484264 3.405395 -1.769616
H -0.373932 2.432965 2.760699
N 1.439590 -1.294204 1.348620
C 1.354440 -2.425672 2.257461
H 1.481471 -3.405525 1.768453
H 2.133956 -2.339123 3.032204
H 0.374532 -2.431649 2.761816
Li 0.612825 0.448864 1.786211
Li -0.613464 -0.448874 -1.786650
6.4.3 Coordinates of the monomeric structures of 1-Na

κO-Na(THF)₃

E = -3358.82170887

O  0.556258  0.193141  0.155741
O  2.683118  2.571931  1.493066
O  4.128284 -0.481801 -0.171687
S  1.662285  3.556623  1.643864
C  3.020284  2.000525  2.760203
C  4.823006 -1.023535 -1.293784
C  2.094572  3.607461 -2.332028
C  0.865302 -2.896308 -2.181737
N  0.873730 -1.366206  2.273852
C  1.007850 -2.385528 -0.102286
H  0.928119  3.437180  0.832067
H  2.109340  4.564429  1.565388
H  1.728700  3.317622  3.021763
C  2.292350  2.838447  3.800997
H  4.114907  2.013024  2.878593
H  2.682092  0.949075  2.777107
H  5.425431 -0.228726 -1.761226
H  4.084887 -1.382126 -2.032479
C  5.657163 -2.171950 -0.747591
C  4.804287 -2.643461  0.424987
H  3.298882 -1.418233  1.474262
H  4.990959 -0.866396  1.671730
H  2.005654  3.857205 -3.141787
H  2.480129  4.036235 -1.394116
C  0.887087  4.050899 -2.681350
C  0.228595  2.901201 -3.571796
H  0.312551  2.522676  2.970852
H  0.601424  4.215236  3.445393
H  2.910834  3.695990  4.109706
H  2.039017  2.260910  4.701034
H  6.633544 -1.805317 -0.391966
H  5.840185 -2.951577 -1.500414
H  3.968879 -3.263954  0.066967
H  5.364666 -3.219345  1.174784
H  0.856277  5.032379 -3.175136
H  0.067092  4.096611 -1.771703
H  0.620829  3.031434 -4.592855
H  -0.863665  2.807911 -3.638405
H  -0.837781 -0.967671  3.488967
H  0.347482  0.361032  3.438663
H  0.722927 -1.124813  4.327032
S -1.959883 -0.974783 -2.385718
C -4.072200 -0.842017 -0.051512
C -2.257188  1.346282 -0.272346
H  1.071408 -1.144263 -1.859347
C  1.761753 -3.165016 -2.247007
\[ \kappa S-Na(THF)_5 \]

\[
E = -3823.38603574
\]

\[
\begin{align*}
\text{Cl} & : 2.361663 1.063208 -2.373846 \\
\text{S} & : -0.170011 0.605228 1.406888 \\
\text{C} & : 2.208608 0.251013 -0.834168 \\
\text{P} & : 1.620813 1.040505 0.616610 \\
\text{C} & : 2.900560 0.875695 1.921060 \\
\text{C} & : 1.681377 2.828184 0.196723 \\
\text{C} & : 4.321484 -1.628995 -0.933969 \\
\text{C} & : 4.251554 0.144990 1.564499 \\
\text{C} & : 2.540930 0.600815 1.270812 \\
\text{C} & : 2.872111 3.423221 -2.39243 \\
\text{C} & : 0.537070 3.611483 0.352187 \\
\text{C} & : 5.053701 -2.071558 0.165662 \\
\text{C} & : 4.949757 -1.328861 -2.145158 \\
\text{H} & : 4.530880 0.794077 0.508706 \\
\text{C} & : 5.233590 0.745393 2.550655 \\
\text{C} & : 3.524608 0.789851 4.255900 \\
\text{H} & : 1.480135 0.891953 3.532541 \\
\text{H} & : 3.772432 2.820142 -0.369901 \\
\text{C} & : 2.909509 4.786566 -0.518128 \\
\text{C} & : 0.574563 4.976666 0.66885 \\
\text{H} & : -0.377008 3.127804 0.708281 \\
\text{C} & : 4.524439 -2.300300 1.091830 \\
\text{C} & : 6.438705 -2.193836 0.058692 \\
\text{C} & : 6.334653 -1.447390 -2.240269 \\
\text{H} & : 4.352218 -1.001440 -2.998205 \\
\text{H} & : 6.286026 0.686684 2.262430 \\
\text{C} & : 4.872214 0.739397 3.898096 \\
\text{C} & : 3.236488 0.773859 5.309990 \\
\text{C} & : 3.841782 5.244453 -0.857282 \\
\text{C} & : 1.760163 5.565735 -0.368335 \\
\text{H} & : -0.326458 5.582872 0.190584 \\
\end{align*}
\]
Supporting Information

\( \text{K}_2\text{O-Na(THF)}_4 \)

\[
E = -3591.10906578
\]

H -0.260299 2.336012 -3.890481 
H -2.010722 2.037820 -4.026921 
H 0.246583 0.065868 -4.428354 
H -1.405951 0.010589 -5.083068 
O -3.796890 1.703899 -0.207974 
C -4.465396 2.086954 -1.395973 
C -3.796768 2.825571 0.650800 
C -4.161890 3.581471 -1.598781 
H -1.405951 0.010589 -5.083068 
H -5.552902 1.922471 -1.281399 
C -3.520449 4.011055 -0.267081 
H -4.099309 1.437368 -2.203267 
H -5.552902 1.922471 -1.281399 

O 0.003687 0.168436 0.129064
O -2.581856 -0.848872 2.023296
O -3.420934 1.801500 0.003838
O -1.729642 -1.806483 -1.777028
S 0.683766 1.463123 0.477030
C -1.965059 -2.036010 2.503300
C -2.564832 0.169059 3.024854
C -2.869735 3.123536 0.045300
C -4.733591 1.797350 0.550371
C -2.118892 -3.145878 1.505179
C -0.517409 -1.786451 -2.538650
N 0.236220 2.282537 1.709976
C 2.347123 1.089258 0.503261
C 0.297042 2.577431 -0.862231
H -1.349790 -2.466946 1.697735
H -2.741745 -2.773587 2.780096
C -1.152621 -1.608002 3.719198
C -2.018024 -0.491023 4.284579
C -3.586303 0.559992 3.159278
C -1.921510 0.994738 2.675836
H -2.504883 3.392680 -0.957914
H -2.006314 3.117767 0.730537
C -3.990694 4.028437 0.536864
C -4.827748 3.068604 1.374285
H -4.868425 0.874955 1.132196
H -5.481241 1.796353 -0.265234
H -2.920032 -3.454705 -2.203934
H -2.526303 -3.196314 -0.484560
C -0.863600 -3.973462 -1.706453
C -0.203704 -3.239171 -2.867612
H 0.276467 -1.322402 -1.932735
H -0.669011 -1.167720 -3.437907
C 0.749797 1.885417 3.004196
Cl 3.346162 2.529901 0.736941
P 3.030660 -0.160483 -0.542757
C -0.697777 2.035464 -2.092936
C 0.431865 3.954610 -0.688360
H -0.179793 -1.210082 3.384514
H -0.967133 -2.430062 4.417288
H -2.836653 -0.914716 4.887638
H -1.460975 0.213261 4.918209
Supporting Information

O  -2.908743 -1.795161  1.324029
C  1.455159  0.101357  0.886099
P  1.283694  -0.881324  -0.555229
C  -3.397992  -1.852959  2.649723
C  -2.149061  -2.974832  1.113684
C  2.804914  -0.645515  -1.536287
C  1.403553  -2.605955   0.043285
H  -4.270922   -2.533586  2.699031
H  -3.726815   -0.843670  2.933084
C  -2.233166  -2.400581  3.464798
C  -1.510541  -3.322196  2.466846
C  -2.816505   -0.555229  0.555229
C  1.455159   -0.101357   -0.886099
C  2.149061  -2.974832   1.113684
C  3.397992  -1.852959  -2.649723
C  4.709687  -2.005564   -0.250633
C  4.912449   0.624504   1.734357
C  4.035741  -1.847575  -0.246719
C  5.157399  -1.067758   -1.898916
C  3.928909   0.336868  -3.434279
C  1.825441  -0.609986  -2.978984
C  2.415342  -2.058407   1.859592
C  2.167320  -4.210055   1.684370
C  1.032259  -4.968500  -0.310190
C  0.389811  -3.411131   -1.676088
C  4.224888   2.588320  -1.034457
C  6.094305   1.836143  -0.207423
C  5.871818   0.457471   1.768527
C  3.840593   0.160687   2.479323
C  6.090697  -1.541931  -1.587400
C  5.121995   0.270559  -3.043252
C  3.899501   0.961267  -4.330496
H  2.425649  -4.427352   2.637010
C  1.664954  -5.249854   0.902192
H  0.636121  -5.781759  -0.923113
H  6.721240  -2.305650  -0.962951
C  6.674063   1.061433   0.795101
H  6.327938  -0.146735   2.556531
H  6.029826  -0.122053  -3.632371
H  1.762820  -6.284506  1.239939
H  7.757866   0.924692   0.821601
S  2.140883   1.669293   0.736627
Na  -2.426053   0.153028   0.168048
N  1.775748   2.395519   2.056486
O  1.888336   2.344095  -0.570116
C  2.341000   3.720048   2.196716
H  2.071076   4.411960   1.375155
H  1.957851   4.161231   3.129659
H  3.448745   3.723826   2.269985
O  -4.573578   0.834878   1.035850
C  -4.963769   2.203378   1.000160
C  -5.685588  -0.002303   0.710260
C  -6.231717   2.236651   0.167017
H  -5.155749   2.565740   0.207954
H  -4.132808   2.781338   0.573413
\[ \kappa O, \kappa N-Na(THF)_3 \]

\[ E = -3358.81612601 \]

O - 1.542569 2.232693 - 2.281515
O - 4.301498 - 0.229438 - 0.733299
O - 3.156829 2.703886 0.855542
S - 0.271316 - 0.964881 - 0.073907
C - 0.142091 2.358945 - 2.028773
C - 1.766311 1.697177 - 3.585884
C - 5.360656 - 0.411822 0.206429
C - 4.555477 - 0.965151 - 1.930057
C - 2.394533 3.898363 0.735535
C - 3.271729 2.358945 2.236950
C 1.377723 - 1.118947 - 0.422990
C - 0.885734 - 2.522250 0.586883
H 0.071800 1.964678 - 1.023805
H 0.135518 3.429125 - 2.052542
C 0.548053 1.570592 - 3.128483
C - 0.420656 1.750630 - 4.292540
H - 2.548412 2.290656 - 4.084426
H - 2.122223 0.656025 - 3.491402
H - 5.702096 0.573528 0.559926
H - 4.970387 - 0.972061 1.074887
C - 6.438054 - 1.195392 - 0.530754
C - 5.619470 - 1.980105 - 1.551319
H - 3.606603 - 1.409349 - 2.266794
H - 4.918682 - 0.276752 - 2.714790
H - 3.053552 4.783013 0.827408
Supporting Information

\[ \text{H} -1.938760 \quad 3.910157 \quad -0.264968 \\
\text{C} -1.407741 \quad 3.824141 \quad 1.883982 \\
\text{C} -2.291975 \quad 3.261765 \quad 2.995621 \\
\text{H} -3.024833 \quad 1.289850 \quad 2.340854 \\
\text{H} -4.313195 \quad 2.501569 \quad 2.570431 \\
\text{Cl} 1.702604 \quad -2.499932 \quad -1.485481 \\
P 2.706337 \quad -0.685481 \quad 0.656021 \\
\text{C} -0.038706 \quad -3.387092 \quad 1.275961 \\
\text{C} -2.256395 \quad -2.767938 \quad 0.492994 \\
\text{H} 0.608260 \quad 0.512941 \quad 2.830674 \\
\text{H} 1.561277 \quad 1.939333 \quad -3.343202 \\
\text{H} -0.274059 \quad 2.732997 \quad -4.769775 \\
\text{H} -0.323331 \quad 0.977708 \quad -5.067763 \\
\text{H} -7.128862 \quad -0.508607 \quad -1.044949 \\
\text{H} -7.030820 \quad -1.830675 \quad 0.141885 \\
\text{H} -5.156761 \quad -2.863679 \quad -1.082223 \\
\text{H} -6.205148 \quad -2.323319 \quad -2.415255 \\
\text{H} -0.958484 \quad 4.795442 \quad 2.134138 \\
\text{H} -0.595232 \quad 3.124182 \quad 1.633785 \\
\text{H} -2.832969 \quad 4.076185 \quad 3.501251 \\
\text{H} -1.726430 \quad 2.714699 \quad 3.762385 \\
\text{S} 3.134626 \quad -1.839535 \quad 2.224863 \\
\text{C} 4.142040 \quad -0.573403 \quad -0.477975 \\
\text{C} 2.474795 \quad 1.058078 \quad 1.177241 \\
\text{H} 1.030243 \quad -3.162953 \quad 1.358429 \\
\text{H} -2.895433 \quad -2.059350 \quad -0.037247 \\
\text{C} 3.981464 \quad -0.181280 \quad -1.812640 \\
\text{C} 5.422643 \quad -0.812440 \quad 0.025636 \\
\text{C} 2.485844 \quad 1.387971 \quad 2.532732 \\
\text{C} 2.386763 \quad 2.074004 \quad 0.219064 \\
\text{H} 0.077532 \quad -5.219967 \quad 2.403038 \\
\text{C} -1.944965 \quad -4.793009 \quad 1.773462 \\
\text{H} -3.856574 \quad -4.111528 \quad 1.024083 \\
\text{H} 2.976709 \quad -0.023178 \quad -2.210186 \\
\text{C} 5.098322 \quad -0.019063 \quad -2.629083 \\
\text{C} 6.538469 \quad -0.647488 \quad -0.794112 \\
\text{H} 5.527555 \quad -1.136492 \quad 1.064697 \\
\text{H} 2.592870 \quad 0.585148 \quad 3.267162 \\
\text{C} 2.372707 \quad 2.720527 \quad 2.930351 \\
\text{C} 2.281660 \quad 3.403389 \quad 0.616230 \\
\text{H} 2.408502 \quad 1.822950 \quad -0.841928 \\
\text{H} -2.360658 \quad -5.690309 \quad 2.238172 \\
\text{H} 4.967995 \quad 0.281301 \quad -3.671619 \\
\text{C} 6.377980 \quad -0.248296 \quad -2.120702 \\
\text{H} 7.537958 \quad -0.835241 \quad -0.394443 \\
\text{H} 2.374129 \quad 2.970682 \quad 3.994026 \\
\text{C} 2.268004 \quad 3.728908 \quad 1.974297 \\
\text{H} 2.211776 \quad 4.190909 \quad -0.138200 \\
\text{H} 7.252316 \quad -0.122238 \quad -2.764036 \\
\text{H} 2.182255 \quad 4.772875 \quad 2.285494 \\
\text{N} -0.588934 \quad 0.178775 \quad 0.937730 \\
\text{C} -0.459811 \quad -0.077466 \quad 2.360132 \\
\text{H} 0.469099 \quad -0.601138 \quad 2.646311 \\
\text{H} -0.448230 \quad 0.890599 \quad 2.880762 \\
\text{H} -1.306345 \quad -0.666574 \quad 2.762663 \\
\text{O} -1.050466 \quad -0.756064 \quad -1.329448 \\
\text{Na} -2.394721 \quad 1.009747 \quad -0.516536
| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| O       | -3.58153 | -2.59981 | 0.539881 |
| O       | -2.599524  | 0.966938  | -0.642634 |
| O       | 2.991560  | -0.217246  | 2.771552  |
| S       | 0.094940  | -0.520340  | -0.970295 |
| C       | 4.190998  | -3.839882  | 0.083535  |
| C       | 3.455685  | -2.788386  | -1.878395 |
| C       | 4.470284  | 2.225610   | -0.170876 |
| C       | 3.711718  | 1.027918   | -2.042949 |
| C       | 3.772181  | 0.732098   | 3.473851  |
| C       | 1.756867  | -0.347999  | 3.474366  |
| C       | -1.583466 | -0.849425  | -0.893308 |
| C       | 0.370390  | 1.238787   | -0.799328 |
| H       | 3.937525  | -3.757148  | 1.152161  |
| H       | 5.266159  | -4.087724  | 0.003568  |
| C       | 3.3400040 | -4.840457  | -0.675946 |
| C       | 3.439125  | -4.297924  | -2.098403 |
| H       | 4.125378  | -2.265844  | -2.580315 |
| H       | 2.452796  | -2.338261  | -1.961230 |
| H       | 5.375160  | 2.063964   | 0.436160  |
| H       | 3.690681  | 2.683192   | 0.469969  |
| C       | 4.722408  | 3.065151   | -1.413980 |
| C       | 3.683867  | 2.507024   | -2.380456 |
| H       | 2.756917  | 0.514032   | -2.233061 |
| H       | 4.511163  | 0.501737   | -2.595964 |
| H       | 4.582088  | 1.071824   | 2.812401  |
| H       | 4.224676  | 0.264811   | 4.369791  |
| C       | 2.778792  | 1.816912   | 3.860030  |
| C       | 1.492360  | 1.018938   | 4.128249  |
| H       | 1.853482  | -1.143626  | 4.234226  |
| H       | 0.984471  | -0.636519  | 2.746659  |
| Cl      | -2.413093 | -0.772040  | -2.456732 |
| P       | -2.586971 | -0.262867  | 0.441861  |
| C       | 0.789177  | 1.807504   | 0.401291  |
| C       | 0.016201  | 2.035226   | -1.891437 |
| H       | 2.299647  | -4.799853  | -0.317772 |
| C       | 3.700253  | -5.873562  | -0.572764 |
| H       | 4.377775  | -4.633342  | -2.566997 |
| H       | 2.608700  | -4.614621  | -2.744562 |
| H       | 5.740277  | 2.890344   | -1.797809 |
| H       | 4.611495  | 4.141679   | -1.222255 |
| H       | 2.689717  | 2.923243   | -2.158843 |
| H       | 3.912765  | 2.704135   | -3.437037 |
| H       | 2.643169  | 2.509195   | 3.015130  |
| H       | 3.112127  | 2.407482   | 4.724688  |
| H       | 0.607320  | 1.504227   | 3.692645  |
| H       | 1.305605  | 0.906002   | 5.205561  |
| S       | -1.720924 | -0.141862  | 2.218520 |
| C       | -3.309503 | 1.352123   | -0.039126 |
| C       | -4.016134 | -1.395569  | 0.495367  |
| H       | 1.029208  | 1.153501   | 1.238349  |
| C       | 0.867594  | 3.196447   | 0.502454  |
| C       | 0.082899  | 3.420827   | -1.772842 |
| H       | -0.312576 | 1.563209   | -2.818819 |
| C       | -4.354519 | 1.439762   | -0.968771 |
| C       | -2.732493 | 2.523804   | 0.460160  |
| C       | -5.167758 | -1.014194  | 1.193928  |
| C       | -3.933368 | -2.671843  | -0.066175 |
| H       | 1.195238  | 3.652810   | 1.439860  |
| C       | 0.512072  | 4.003194   | -0.578461 |
| H       | -0.199853 | 4.050091   | -2.619690 |
Supporting Information

$\kappa S, \kappa Cl - Na(THF)_3$

$E = -3358.81120355$

Cl -0.349078 0.298503 -1.823836
S -0.773358 0.359534 2.131482
O -3.423767 1.757857 -0.893308
C 0.917361 0.005358 -0.644473
P 0.737259 0.833033 0.886151
C -4.397759 1.576728 -1.904884
C -2.711775 2.934546 -1.243612
C 2.344461 0.683493 1.736988
C 0.607675 2.602195 0.436556
H -5.229277 2.294235 -1.753418
H -4.800284 0.560333 -1.817298
C -3.652111 1.871266 -3.203024
C -2.604199 2.917692 -2.774961
H -1.743816 2.914092 -0.727858
H -3.276111 3.818818 -0.894057
C 3.493748 -1.079672 -0.848180
C 3.456253 1.381829 1.251649
C 2.468070 -0.126104 2.867211
C 1.136422 3.071501 -0.771620
C -0.014981 3.493613 1.315698
H -3.161320 0.966449 -3.568158
H -4.322406 2.228803 -3.997151
H -1.594653 2.623478 -3.093812
H -2.809676 3.911794 -3.196580
C 4.421028 -1.662454 0.007533
C 3.890447 -0.217471 -1.870311
H 3.365597 2.011193 0.364406
C 4.684089 1.269211 1.896994
C 3.701324 -0.243118 3.505430
H 1.588663 -0.657625 3.237535
H 1.610449 2.364668 -1.456722
C 1.030020 4.421938 -1.099786
C -0.109082 4.844965 0.989311
H -0.44271 3.107799 2.243836
Supporting Information

\[
\begin{align*}
\text{H} & : 4.067613 -2.325435 0.798290 \\
C & : 5.773592 -1.354980 -0.147065 \\
C & : 5.240150 0.086472 -2.016221 \\
H & : 3.135111 0.215542 -2.531015 \\
H & : 5.549654 1.813385 1.512972 \\
C & : 4.808515 0.454251 3.022591 \\
H & : 3.759613 -0.811195 4.837236 \\
H & : 1.431402 4.782285 -2.049949 \\
C & : 0.407931 5.309369 -0.220810 \\
H & : -0.597897 5.537319 1.678814 \\
H & : 6.509885 -1.794946 0.529824 \\
C & : 6.182351 -0.480357 -1.151822 \\
H & : 5.562554 0.768949 -2.806353 \\
H & : 5.774149 0.362414 3.525973 \\
H & : 0.322494 6.367006 -0.481939 \\
H & : 7.241289 -0.236198 -1.265893 \\
S & : 1.743124 -1.496366 -0.707541 \\
\text{Na} & : -2.500101 -0.187119 -0.003932 \\
N & : 1.290103 -2.155283 -2.031516 \\
O & : 1.678075 -2.246434 0.879052 \\
C & : 2.014177 -3.341673 -2.430777 \\
H & : 1.909845 -4.189135 -1.725131 \\
H & : 1.612595 -3.680951 -3.397952 \\
H & : 3.101282 -3.173003 -2.574254 \\
O & : -4.675108 -0.568603 0.669828 \\
C & : -5.162774 -1.881026 0.917578 \\
C & : -5.155997 0.326076 1.675621 \\
C & : -5.356301 -1.933573 2.420458 \\
H & : -6.122339 -2.036303 0.388043 \\
H & : -4.421573 -2.589826 0.523039 \\
C & : -5.905839 -0.535609 2.693019 \\
H & : -4.289005 0.837973 2.125682 \\
H & : -5.797428 1.093124 1.212303 \\
H & : -4.383054 -2.075461 2.918196 \\
H & : -6.029607 -2.740134 2.743121 \\
H & : -5.747052 -0.196072 3.725981 \\
H & : -6.988964 -0.511624 2.495506 \\
O & : -2.130733 -2.428891 -0.260422 \\
C & : -1.545516 -3.218318 0.780116 \\
C & : -1.951813 -3.062366 -1.529352 \\
C & : -0.856339 -4.380327 0.081169 \\
H & : -0.842341 -2.591587 1.347918 \\
H & : -2.352304 -3.557987 1.455349 \\
C & : -1.661725 -4.517001 -1.206228 \\
H & : -2.868790 -2.912197 -2.121144 \\
H & : -1.092685 -2.597664 -2.042218 \\
H & : -0.843137 -5.293009 0.693876 \\
H & : 0.180144 -4.091303 -0.142742 \\
H & : -2.597108 -5.073162 -1.027713 \\
H & : -1.111121 -5.022448 -2.012777 \\
\end{align*}
\]

$\kappa\text{O-}\text{Na(THF)}$_2

\[
E = -3126.52827985
\]

\[
\begin{align*}
\text{O} & : -0.729526 0.076672 -0.716263 \\
\text{O} & : -1.954229 3.041072 0.132853 \\
\text{O} & : -3.995902 0.341754 -1.199551 \\
\text{S} & : -0.355390 -1.375008 -0.832878 \\
C & : -2.080259 4.460016 0.157780 \\
C & : -1.554111 2.548769 1.417433 \\
C & : -4.691660 0.478269 0.036966 \\
C & : -4.151990 -0.985250 -1.717606
\end{align*}
\]
Na -2.091046 1.552489 -1.568205

\( \kappa S, \kappa Cl{-}Na(THF)_2 \)

\[ E = -3126.52185991 \]

\[
\begin{align*}
Q & 0.133909 3.404879 -1.152821 \\
O & 3.907815 1.838707 0.342756 \\
S & 0.654852 1.552489 -1.568205 \\
C & -0.648474 3.158319 -2.323226 \\
C & -0.682452 3.927526 -0.103556 \\
C & 5.152890 2.229819 -0.222467 \\
C & 4.126481 0.889341 1.394912 \\
C & -0.34580 2.098321 -1.733772 -0.464038 \\
H & -0.419601 2.145609 -2.690497 \\
H & -0.365017 3.887331 -1.152821 \\
C & -2.096463 3.337190 -1.896152 \\
C & -1.973582 4.362670 -0.774910 \\
H & -0.141943 4.752273 0.385863 \\
H & -0.861424 3.135027 0.644272 \\
H & 5.534534 3.135358 1.283816 \\
C & 6.068558 1.044378 0.009687 \\
C & 5.625573 0.592449 1.398501 \\
H & 3.523095 1.177681 \\
H & 3.777428 1.314978 2.349402 \\
Cl & 0.519500 0.662225 1.249903 \\
P & -1.750875 -1.244692 0.670352 \\
C & 1.934777 -2.522472 0.673936 \\
C & 3.332623 -1.634954 -1.106396 \\
H & -2.496850 2.389910 -1.505433 \\
H & -2.743911 3.660488 -2.722939 \\
H & -1.871281 5.378233 -1.189633 \\
H & -2.824568 4.362303 -0.083977 \\
H & 7.134039 1.307457 -0.046636 \\
H & 5.865043 0.261475 -0.737160 \\
H & 6.138223 1.185629 2.171499 \\
H & 5.832872 -0.468766 1.593906 \\
S & -1.571510 -3.055276 1.480931 \\
C & -2.432779 -0.062737 1.900684 \\
C & -3.025457 -1.228722 -0.640557 \\
H & 0.948834 -2.602962 1.146995 \\
C & 3.038595 -3.196644 1.192356 \\
C & 4.425466 -2.330924 -0.590425 \\
H & 3.429919 -1.005706 -1.992674 \\
H & -2.981133 1.155084 1.482600 \\
H & -2.381685 -0.368655 3.260701 \\
H & -4.149781 -2.043639 -0.482580 \\
H & -2.936411 -0.374983 -1.743181 \\
H & 2.925484 -3.803567 2.093835 \\
C & 4.281521 -3.103228 0.562483 \\
H & 5.395861 -2.265458 -1.088471 \\
H & -3.032363 1.392571 0.417922 \\
C & -3.468026 2.060791 2.421868 \\
C & -2.865727 0.541179 4.200751 \\
H & -1.963247 -1.332561 3.563771 \\
H & -4.195199 -2.727677 0.369013 \\
C & -5.188310 -1.988770 -1.411242 \\
C & -3.975180 -0.322067 -2.670181 \\
H & -2.033911 0.223145 -1.873960 \\
H & 5.142328 -3.637673 0.971448
\end{align*}
\]
\( \kappa_{O,S}\text{Na(THF)}_2 \)

\[ E = -3126.52723608 \]

\begin{align*}
\text{Cl} & : 1.664747 -0.274585 -1.952130 \\
\text{S} & : 0.189335 -1.762467 1.644784 \\
\text{O} & : -0.836189 -3.639971 -1.507270 \\
\text{C} & : 0.821114 0.533172 -0.621995 \\
\text{P} & : 1.123599 -0.103990 0.993591 \\
\text{C} & : -0.315106 -3.246446 -2.783143 \\
\text{C} & : 0.120728 4.472387 -0.842810 \\
\text{H} & : 0.907842 1.267557 2.813107 \\
\text{H} & : 2.934042 -0.387358 0.993408 \\
\text{H} & : -0.599320 2.144030 -2.376359 \\
\text{H} & : -0.940995 3.676803 -3.582699 \\
\text{H} & : -0.369932 -2.148454 -2.841941 \\
\text{C} & : 1.127434 -3.752488 -2.836569 \\
\text{C} & : 1.451342 -4.013957 -1.368389 \\
\text{H} & : -0.011157 4.327381 0.240967 \\
\text{H} & : -0.085413 5.353011 -1.086865 \\
\text{C} & : 1.214954 2.580241 1.807817 \\
\text{C} & : 0.497685 0.992866 3.468335 \\
\text{C} & : 3.797180 0.588925 0.479534 \\
\text{C} & : 3.458954 -1.557536 1.543133 \\
\text{C} & : -0.230818 3.437709 -2.006804 \\
\text{C} & : -0.831701 1.804023 -3.705694 \\
\text{H} & : 1.802118 3.019232 -3.299931 \\
\text{H} & : 1.192450 -4.686916 -3.415814 \\
\text{H} & : 1.736718 -3.078426 -0.865178 \\
\text{H} & : 2.249840 -4.754706 -1.219646 \\
\text{H} & : 1.508466 2.786941 0.776621 \\
\text{C} & : 1.114627 3.609097 2.739776 \\
\text{C} & : 0.396580 2.026872 4.417712 \\
\text{H} & : 0.247523 -0.036279 3.757400 \\
\text{H} & : 3.386455 1.495871 0.030781 \\
\text{C} & : 5.174297 0.391733 0.523447 \\
\text{C} & : 4.839942 -1.752139 1.585316 \\
\text{H} & : 2.768286 -2.311028 1.931450 \\
\text{H} & : -0.072625 3.668423 -0.951419 \\
\text{C} & : -0.088445 4.408045 -2.994459 \\
\text{C} & : -0.679767 2.782206 -4.688823 \\
\text{H} & : -1.131507 0.784473 -3.951954 \\
\text{H} & : 1.348677 4.634511 2.443128 \\
\text{C} & : 0.705565 3.334595 4.046844 \\
\text{H} & : 0.071794 1.807855 5.437872 \\
\text{H} & : 5.844227 1.153814 0.118168 \\
\text{C} & : 5.698105 -0.778503 1.077666
\end{align*}
Supporting Information

κO,κN-Na(THF)

E = -2894.229197

O -0.797856 1.388843 -0.274606
O -4.113224 0.901925 0.273409
S 0.413914 1.567674 0.579262
C -5.393689 0.437191 0.682015
C -3.865415 0.545797 -1.094749
N -0.057946 2.015937 2.002279
C 1.361404 0.158486 0.505597
C 1.371924 2.866926 -0.172135
H -5.839506 1.182932 1.357694
H -5.286489 -0.514663 1.235071
C -6.169880 0.233648 -0.606302
C -5.071999 -0.270079 0.153742
H -2.915019 -0.004313 -0.156134
H -3.763327 1.475225 -1.680330
C 0.824529 1.813212 3.131668
Cl 0.305742 0.393107 0.933489
P 0.962310 -1.109417 -0.650796
C 1.991951 2.642374 -1.397959
C 1.437246 4.130679 0.448825
H -6.574286 1.194381 -0.963763
H -7.007475 -0.468766 -0.492113
H -4.889752 -1.341646 -1.366049
H -5.301298 -0.131854 -2.603133
H 1.704310 2.485323 3.136646
H 1.205016 0.776511 3.196271
H 0.255823 2.015800 4.051443
S 1.102143 -0.807372 -2.613910
C 2.061777 -2.476529 -0.116363
C -0.701423 -1.727008 -0.191114
H 1.923936 1.648125 -1.856195
6.4.4 Coordinates of the dimeric structures of 1-Na

$xS, \kappa Cl-Na_2(THF)_2$

E = -5788.49203279

Cl 1.476145 1.515779 1.699285
Cl -1.483862 -1.405375 -1.770364
S 1.346507 0.974221 -1.888525
S -1.224298 -0.976798 1.818187
C 3.475709 -2.168549 1.699761
C 2.589557 -2.918383 2.475411
C 2.432961 -4.276524 2.206188
C 3.163157 -4.876419 1.179250
C 4.061645 -4.121904 0.425194
C 4.225452 -2.762022 0.684280
O 0.770085 -3.548715 -0.706280
C -3.648613 2.174500 -1.632098
C -2.863168 2.963044 -2.473493
C -2.744883 4.326557 -2.212619
C -3.415894 4.893235 -1.128348
C -4.220240 4.099803 -0.310256
C -4.344524 2.734401 -0.569041
O -0.769125 3.577669 0.467190
C 2.569203 0.369816 0.894019
C -2.594327 -0.332168 -0.888842
P 2.987262 0.962526 -0.718991
P -2.918621 -0.968396 0.729050
H 2.038665 -2.427330 3.279685
H 1.735666 -4.868999 2.803202
H 3.033589 -5.940612 0.968294
H 4.643901 -4.592080 -0.370762
Supporting Information

\[ \kappa N, \kappa S, \kappa Cl - \text{Na}_2(\text{THF})_2 \]

\[ E = -5788.48094950 \]

Cl -1.675277 1.505043 -1.918606
Cl 1.676549 -1.502744 1.920478
S -1.430462 0.161517 1.637814
S 1.430158 -0.160042 -1.635880
O -0.909680 -3.620635 0.583844
O 0.909487 3.620390 -0.581749
C -3.091662 0.785157 -1.119493
C 3.093221 -0.784639 1.120068
P -2.971820 0.979869 0.617143
P 2.971582 -0.979727 -0.616449
C -2.045555 -3.601239 1.430299
C 0.012383 -4.529962 1.161497
C 2.043521 3.600562 -1.430676
C -0.012677 4.531743 -1.156040
C -4.550803 0.482625 1.373262
C -2.902620 2.798523 0.829334
C 4.550475 -0.484621 -1.374176
C 2.900202 -2.798408 -0.827904
C -5.246100 -0.964239 -1.522090
H -2.658300 -4.507669 1.253736
H -2.641849 -2.715100 1.171868
C -1.459838 -3.583369 2.834917
C -0.168516 -4.408698 2.683667
H 1.016999 -4.261398 0.811277
H -0.216631 -5.553061 0.809775
C 5.248720 0.964209 1.519359
H 2.658016 4.505804 -1.254087
H 2.639021 2.713100 -1.174983
C 1.454671 3.585636 -2.833991
C 0.165220 4.413100 -2.678782
| X  | Y  | Z  |
|----|----|----|
| H  | -1.016929 | 4.263566 | -0.804460 |
| C  | 0.218028  | 5.553963  | -0.802874 |
| C  | -5.746429 | 1.058184  | 0.926409 |
| C  | -4.563509 | -0.423222 | 2.434866 |
| C  | -3.563309 | 3.634803  | -0.078609 |
| C  | -2.215979 | 3.350896  | 1.913885 |
| C  | 5.745974  | -1.060580 | -0.927491 |
| C  | 4.563122  | 0.419926  | -2.436886 |
| C  | 3.561511  | -3.635019 | 0.079294 |
| C  | 2.211337  | -3.350501 | -1.911185 |
| C  | -5.568147 | -1.889241 | -0.533992 |
| C  | -6.230410 | -0.305387 | -2.255688 |
| H  | -1.229823 | -2.544169 | 3.115519 |
| H  | -2.150153 | -3.992426 | 3.586527 |
| H  | 0.688380  | -3.900049 | 3.146515 |
| C  | -0.255738 | -5.401191 | 3.149364 |
| C  | 5.569654  | 1.888246  | 0.529980 |
| C  | 6.233837  | 0.305911  | 2.252357 |
| H  | 1.222193  | 2.547213  | -3.115447 |
| H  | 2.144047  | 3.994413  | -3.586612 |
| H  | -0.693466 | 3.907004  | -3.141104 |
| H  | 0.253572  | 5.406345  | -3.142665 |
| H  | -5.734715 | 1.760382  | 0.091162 |
| C  | -6.947483 | 0.718262  | 1.537991 |
| C  | -5.771982 | -0.764561 | 3.040854 |
| H  | -3.615945 | -0.843769 | 2.782238 |
| H  | -4.061617 | 3.189286  | -0.943490 |
| C  | -3.541446 | 5.014887  | 0.107513 |
| C  | -2.193103 | 4.733600  | 2.092004 |
| H  | -1.692925 | 2.686105  | 2.607371 |
| H  | 5.734305  | -1.761723 | -0.091362 |
| C  | 6.946685  | -0.722322 | -1.540338 |
| C  | 5.771422  | 0.759571  | -3.044173 |
| H  | 3.615635  | 0.840825  | -2.784055 |
| H  | 4.061521  | -3.189706 | 0.943296 |
| C  | 3.538091  | -5.015135 | -0.106355 |
| C  | 2.186831  | -4.733250 | -2.088773 |
| H  | 1.687877  | -2.685452 | -2.604127 |
| H  | -4.765524 | -2.388155 | 0.011668 |
| C  | -6.909759 | -2.149929 | -0.263877 |
| C  | -7.568122 | -0.563907 | -1.970446 |
| H  | -5.930212 | 0.386632  | -3.044806 |
| H  | 4.766402  | 2.386784  | -0.015110 |
| C  | 6.910961  | 2.148463  | 0.257936 |
| C  | 7.571233  | 0.563393  | 1.965210 |
| H  | 5.934505  | -0.385315 | 3.042498 |
| H  | -7.880105 | 1.161510  | 1.182674 |
| C  | -6.961699 | -0.193714 | 2.594817 |
| H  | -5.780388 | -1.474443 | 3.871384 |
| H  | -4.051074 | 5.665892  | -0.606875 |
| C  | -2.858423 | 5.565643  | 1.192845 |
| H  | -1.649946 | 5.160891  | 2.938138 |
| H  | 7.879385  | -1.165849 | -1.185142 |
| C  | 6.961016  | 0.188352  | -2.598290 |
| H  | 5.779781  | 1.468432  | -3.875575 |
| H  | 4.048242  | -5.666383 | 0.607438 |
| C  | 2.852820  | -5.565614 | -1.190416 |
| H  | 1.641888  | -5.160300 | -2.933879 |
| H  | -7.176825 | -2.869694 | 0.512738 |
| C  | -7.906245 | -1.485828 | -0.977707 |
| H  | -8.353020 | -0.053673 | -2.533931 |
| H  | 7.177172  | 2.867443  | -0.519700 |
Supporting Information

\[ \text{Na}_2(\text{THF})_2 \]

\[ E = -5788.51446562 \]

\[ \kappa \text{O}, \kappa \text{N}, \kappa \text{S} - \text{Na}_2(\text{THF})_2 \]

\[ \text{Cl} - 4.372690 0.861597 -1.960439 \]
\[ \text{Cl} 4.373044 -0.861747 1.960266 \]
\[ \text{S} -1.448361 1.712795 0.985619 \]
\[ \text{S} 1.448430 -1.713059 -0.984561 \]
\[ \text{O} 0.408950 -2.674913 2.673636 \]
\[ \text{O} -0.409639 2.675426 -2.677266 \]
\[ \text{C} -3.561432 -0.057573 -0.706918 \]
\[ \text{C} 3.562058 0.057768 0.706760 \]
\[ \text{P} -3.199908 0.744015 0.810877 \]
\[ \text{P} 3.199949 -0.744172 -0.810747 \]
\[ \text{C} 1.420419 -2.505071 3.679834 \]
\[ \text{C} 0.641757 -3.876664 1.954264 \]
\[ \text{C} -1.420377 2.505424 -3.679433 \]
\[ \text{C} -0.643462 3.876826 -1.952902 \]
\[ \text{C} -3.371785 -0.479588 2.158986 \]
\[ \text{C} -4.597591 1.899482 1.062116 \]
\[ \text{C} 3.371172 0.479289 -2.159073 \]
\[ \text{C} 4.597665 -1.889512 -1.062400 \]
\[ \text{C} -3.393235 -2.678475 -1.724452 \]
\[ \text{H} 0.951080 -2.526497 4.677556 \]
\[ \text{H} 1.880377 -1.516106 3.521075 \]
\[ \text{C} 2.420222 -3.644131 3.478985 \]
\[ \text{C} 2.139422 -4.090231 2.046980 \]
\[ \text{H} 0.276971 -3.732327 0.926300 \]
\[ \text{H} 0.082070 -4.712806 2.415793 \]
\[ \text{C} 3.393212 2.678619 1.724269 \]
\[ \text{H} -0.950383 2.527154 -4.676838 \]
\[ \text{H} -1.880123 1.516268 -3.521127 \]
\[ \text{C} -2.420688 3.644104 -3.479025 \]
\[ \text{C} -2.141132 4.089842 -2.046662 \]
\[ \text{H} -0.279422 3.732260 -0.924706 \]
\[ \text{H} -0.083754 4.713349 -2.413711 \]
\[ \text{C} -4.157232 -1.623538 1.984993 \]
\[ \text{C} -2.725821 -0.256201 3.378545 \]
Supporting Information

\[ \kappa O, \kappa S, \kappa Cl - Na_2(THF)_2 \]

\[ E = -5788.50372250 \]

Cl 1.847915 1.787980 1.844655
Cl -1.848076 -1.783312 -1.844643
S 1.135029 0.360063 -1.738790
S -1.135021 -0.366148 1.738730
O 0.709298 -4.028987 -0.486474
O -0.709234 4.029531 0.486951
C 2.978155 0.803508 0.925072
C -2.978194 -0.803508 -0.925072
P 2.824415 0.979404 -0.814328
P -2.824417 -0.979473 0.814307
C 1.729277 -4.277107 -1.439539
C -0.376186 -4.876353 -0.835430
C -1.729541 4.277152 1.439540
C 0.375961 -4.876364 0.835769
C 4.275908 0.150392 -1.540341
C 3.051808 2.767877 -1.101746
C -4.275877 -0.150340 1.540341
C -3.051885 -2.767905 1.101882
C 5.059250 -1.008983 1.442779
H 2.228860 -5.238838 -1.212765
H 2.473409 -3.472394 -1.359895
C 0.984588 -4.341213 -2.766452
C -0.367738 -4.963613 -2.370914
H -1.293876 -4.440970 -0.418388
H -0.233924 -5.871188 -0.378843
C -5.059067 1.008998 -1.443027
H -2.229215 5.238638 1.211981
H -2.473497 3.472252 1.360172
C -0.985327 4.342219 2.766705
C 0.367413 4.963816 2.371221
H 1.293806 4.441210 0.418824
H 0.223391 5.871092 0.379039
C 5.561429 0.626281 -1.255065
C 4.110945 -0.957988 -2.372434
C 3.851745 3.525525 -0.236873
C 2.433323 3.380546 -2.195530
C -5.561412 -0.626127 1.254855
C -4.110892 0.958012 2.372366
C -3.851861 -3.525606 0.237093
C -2.433471 -3.380475 2.195761
C 5.589629 -2.124099 0.803866
C 5.874651 -0.986193 2.098009
H 0.844007 -3.323352 -3.161914
H 1.524492 -4.923829 -3.525918
H -1.209317 -4.407823 -2.807160
H -0.452760 -6.007730 -2.704295
C -5.589392 2.124201 -0.804219
C -5.874511 0.086210 -2.098206
H -0.845262 3.324690 3.163195
H 1.525378 4.925725 3.525382
H 1.208592 4.407471 2.807535
H 0.453129 6.007894 2.704536
H 5.695130 1.487600 -0.598213
C 6.673036 -0.009129 -1.798958
C 5.227807 -1.588150 -2.907152
H 3.100350 -1.307460 -2.596563
H 4.304010 -3.044076 -0.633160
C 4.033600 -4.886460 0.473418
C 2.620169 -4.742185 2.428611
H -1.792628 -2.782315 2.848760
H 4.917012 -2.820381 -0.302430
C 6.973086 -2.304990 1.798677
C 7.252832 -0.273845 2.085731
H 5.642137 0.773894 2.596635
H -4.916747 2.820381 -0.302430
C -6.972836 2.304990 -0.799653
C -7.252680 0.273955 -2.085977
H -5.421278 -0.773952 -2.596741
H 7.674455 0.361364 -1.569976
C 6.507547 -1.124263 -2.621913
H 5.095539 -2.469250 -3.553247
H 4.650123 5.476997 0.208419
H 3.419895 5.495422 -1.568956
H 2.131637 5.217758 -3.281976
H -7.674442 -0.361065 1.569610
C -6.507503 1.124461 2.621661
H -5.095468 2.469336 3.553116
H -4.650346 -5.477087 -0.207977
C -3.420151 -5.495370 1.569422
H -2.131922 -5.217567 3.282444
H 7.404131 -3.168627 0.287970
C 7.802240 -1.381916 1.433675
H 7.904360 0.446295 2.586236
H -7.403838 3.168897 -0.288465
C -7.802035 1.382114 -1.434026
H -7.904242 -0.446186 -2.586437
H 7.382370 -1.626363 -3.042140
H 3.559424 6.564145 -1.748508
H -7.382322 1.626620 3.041826
H -3.559752 -6.564063 1.749099
H 8.885501 -1.523934 1.422190
H -8.885287 1.524201 -1.422576
Supporting Information

\[ \kappa O, \kappa N - Na_2(THF)_4 \]

\[ E = -6253.09435252 \]

\[
\begin{align*}
C & & \quad 3.828451 & 0.031806 & -0.572054 \\
S & & \quad 3.209951 & -0.383168 & 1.499382 \\
P & & \quad 5.214687 & -0.020145 & 0.518591 \\
O & & \quad 1.490068 & -0.383168 & 1.500382 \\
S & & \quad 4.862434 & 0.349086 & 2.432822 \\
C & & \quad 3.828281 & -0.031806 & 0.572054 \\
P & & \quad 5.214774 & -0.020291 & 0.518595 \\
S & & \quad 4.862434 & 0.349086 & 2.432822 \\
Cl & & \quad 4.253746 & -0.237755 & 2.275619 \\
C & & \quad 6.436133 & 1.179192 & 0.121794 \\
C & & \quad 6.014747 & 2.270300 & 0.887388 \\
C & & \quad 7.782181 & 1.067313 & -0.245739 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.436133 & 1.179192 & 0.121794 \\
C & & \quad 6.014747 & 2.270300 & 0.887388 \\
C & & \quad 7.782181 & 1.067313 & -0.245739 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.436133 & 1.179192 & 0.121794 \\
C & & \quad 6.014747 & 2.270300 & 0.887388 \\
C & & \quad 7.782181 & 1.067313 & -0.245739 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.436133 & 1.179192 & 0.121794 \\
C & & \quad 6.014747 & 2.270300 & 0.887388 \\
C & & \quad 7.782181 & 1.067313 & -0.245739 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.436133 & 1.179192 & 0.121794 \\
C & & \quad 6.014747 & 2.270300 & 0.887388 \\
C & & \quad 7.782181 & 1.067313 & -0.245739 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.436133 & 1.179192 & 0.121794 \\
C & & \quad 6.014747 & 2.270300 & 0.887388 \\
C & & \quad 7.782181 & 1.067313 & -0.245739 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.436133 & 1.179192 & 0.121794 \\
C & & \quad 6.014747 & 2.270300 & 0.887388 \\
C & & \quad 7.782181 & 1.067313 & -0.245739 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.436133 & 1.179192 & 0.121794 \\
C & & \quad 6.014747 & 2.270300 & 0.887388 \\
C & & \quad 7.782181 & 1.067313 & -0.245739 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.436133 & 1.179192 & 0.121794 \\
C & & \quad 6.014747 & 2.270300 & 0.887388 \\
C & & \quad 7.782181 & 1.067313 & -0.245739 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.436133 & 1.179192 & 0.121794 \\
C & & \quad 6.014747 & 2.270300 & 0.887388 \\
C & & \quad 7.782181 & 1.067313 & -0.245739 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.436133 & 1.179192 & 0.121794 \\
C & & \quad 6.014747 & 2.270300 & 0.887388 \\
C & & \quad 7.782181 & 1.067313 & -0.245739 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.436133 & 1.179192 & 0.121794 \\
C & & \quad 6.014747 & 2.270300 & 0.887388 \\
C & & \quad 7.782181 & 1.067313 & -0.245739 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.436133 & 1.179192 & 0.121794 \\
C & & \quad 6.014747 & 2.270300 & 0.887388 \\
C & & \quad 7.782181 & 1.067313 & -0.245739 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.932821 & 2.270300 & 0.887388 \\
C & & \quad 6.436133 & 1.179192 & 0.121794
6.4.5 Coordinates of the monomeric structures of 1-K

κO-K(THF)$_3$

E = $-3224.9355907$

O 0.494338 0.319543 0.099420
O 2.409912 2.806809 1.456226
O 4.487364 -0.412954 -0.174579
O 1.117257 3.228826 -2.162012
S 0.448202 -1.073668 0.653949
C 1.097242 3.322053 1.680835
C 2.802790 2.006892 2.563599
C 5.144671 -1.233466 -1.130358
C 4.558905 -1.012964 1.122866
C 0.953746 4.612354 -1.877065
C -0.095638 2.685002 -2.692288
N 1.159516 -1.429963 1.979543
C -1.202560 -1.498353 0.651394
C 1.334493 -2.096260 -0.517886
H 0.403587 2.920607 0.924350
| Atom | X  | Y  | Z  |
|------|----|----|----|
| H    | 1.134643 | 4.419685 | 1.574666 |
| C    | 0.701438  | 2.897061  | 3.094570  |
| C    | 2.045344  | 2.584222  | 3.743870  |
| H    | 3.897624  | 2.062380  | 2.660847  |
| H    | 2.516381  | 0.951729  | 2.391467  |
| H    | 5.641563  | -0.585519 | -1.869716 |
| C    | 4.404867  | -1.861833 | -1.659622 |
| C    | 6.107937  | -2.089346 | -0.327845 |
| H    | 3.538500  | -1.147044 | 1.518696  |
| H    | 5.112428  | -0.329258 | 1.791142  |
| H    | 1.463701  | 5.216666  | -2.650876 |
| H    | 1.425519  | 4.836103  | -0.907253 |
| C    | -0.545520 | 4.856876  | -1.892997 |
| C    | -0.993110 | 3.879050  | -2.972765 |
| H    | -0.545697 | 2.004028  | -1.949725 |
| H    | 0.137128  | 2.096863  | -3.594150 |
| C    | 0.491711  | -1.132542 | 3.225684  |
| Cl   | -1.467634 | -3.197288 | 1.050386  |
| P    | -2.334662 | -0.746883 | -0.474421 |
| C    | 1.315093  | -1.725268 | -1.863496 |
| C    | 1.901160  | -3.033907 | -0.112737 |
| H    | 0.085475  | 1.986802  | 3.053218  |
| H    | 0.125662  | 3.697771  | 3.622608  |
| C    | 2.535956  | 3.504687  | 4.099218  |
| H    | 1.970629  | 1.860324  | 4.589888  |
| H    | 7.025917  | -1.522841 | -0.101281 |
| H    | 6.395532  | -3.012294 | -0.851407 |
| C    | 4.579115  | -3.151877 | 0.774442  |
| H    | 5.913255  | -2.966445 | 1.812231  |
| H    | -0.806025 | 5.903699  | -2.104061 |
| H    | -0.990318 | 4.577759  | -0.923930 |
| H    | -0.789525 | 4.293602  | -3.973433 |
| H    | -2.059575 | 3.622473  | -2.921240 |
| H    | -0.609481 | 1.209582  | 3.158340  |
| H    | 0.731453  | -0.124947 | 3.613180  |
| H    | 0.825859  | 1.853512  | 3.988553  |
| S    | -2.077692 | -0.852634 | -2.449331 |
| C    | -3.934633 | -1.508585 | 0.005719  |
| C    | -2.579283 | 0.988838  | 0.061363  |
| H    | 0.809885  | -0.805140 | -2.162459 |
| C    | 1.899884  | -2.565427 | -2.809132 |
| C    | 2.481596  | -4.138262 | -1.067188 |
| H    | 1.886519  | -3.560323 | 0.947105  |
| C    | -4.357366 | -1.465346 | 1.340294  |
| C    | -4.744288 | -2.105817 | -0.959335 |
| C    | -3.186349 | 1.883314  | -0.824774 |
| C    | -2.276291 | 1.401107  | 1.361721  |
| H    | 1.889163  | -2.281589 | -3.864196 |
| C    | 2.483803  | -3.770289 | -2.413245 |
| H    | 2.933605  | -5.083337 | -0.756634 |
| H    | -3.719568 | -1.004352 | 2.098177  |
| C    | -5.584048 | -2.015724 | 1.699762  |
| C    | -5.972913 | -2.659565 | -0.593636 |
| H    | -4.393813 | -2.124085 | -1.995385 |
| H    | -3.404972 | 1.548439  | -1.842590 |
| C    | -3.494943 | 3.178114  | -0.411670 |
| C    | -2.579717 | 2.698920  | 1.770348  |
| H    | -1.794564 | 0.694935  | 2.041275  |
| H    | 2.937962  | -4.427612 | -3.158473 |
| H    | -5.911048 | -1.980329 | 2.741852  |
| C    | -6.394012 | -2.614346 | 0.731376  |
H -6.603363 -3.127870 -1.356307
H -3.973915 3.871494 -1.107463
C -3.190463 3.589020 0.886635
H -2.337588 3.017748 2.786710
H -7.356738 -3.046326 1.015878
H -3.429953 4.604923 1.210392
K 2.702213 1.480021 -0.881829

\( \kappa O-K(THF)_{4} \)

\[ E = -3457.231249 \]

O 0.054487 -0.830675 1.163115
O 2.020833 2.043168 2.445604
O 3.569331 -0.931539 0.927114
O 1.970800 3.445681 -0.839793
S -0.726821 2.107770 1.015878
C 0.788176 2.230440 3.117470
C 2.918897 1.401241 3.342473
C 4.585456 -1.351510 0.018141
C 3.215138 -1.996189 1.802806
C 2.252492 4.443019 0.127630
C 1.007856 3.947497 -1.762484
N -0.929796 -3.009261 2.281013
C -2.155249 -1.612663 0.267464
C 0.207689 -3.190704 -0.030102
H 0.002596 2.382354 2.364448
H 0.830628 3.133003 3.760083
C 0.617426 0.965023 3.939549
C 2.053798 0.679404 4.392883
C 3.576045 2.153349 3.815747
C 3.544390 0.720132 2.746753
H 5.413362 -0.623358 0.039236
H 4.165637 -1.355151 -1.002422
C 5.008994 -2.743117 0.469938
C 3.737185 -3.257273 1.135173
H 2.124553 -1.986924 1.941100
H 3.695209 -1.843364 2.784874
H 3.034491 5.134435 -0.243994
H 2.614598 3.938744 1.034489
C 0.928723 5.160839 0.313094
C 0.394111 5.200760 -1.119079
H 0.269442 3.149127 -1.943210
H 1.496689 4.182291 -2.724661
C -1.874132 -2.575179 3.284256
Cl -3.193714 -2.938468 -0.231381
P -2.255265 -0.045345 -0.518829
C 0.748237 -2.631002 -1.187877
C 0.343551 -4.548766 0.247746
H 0.246156 0.165195 3.281610
H -0.085589 1.088830 4.775345
H 2.243217 1.090144 5.395932
H 2.266016 -0.398313 4.433650
H 5.827650 -2.679704 1.204973
H 5.352734 -3.369502 -0.366616
H 3.020681 -3.607349 0.377503
H 3.910157 -4.076947 1.846833
H 1.033364 6.156507 0.767091
H 0.272776 4.556155 0.958409
H 0.742513 6.109430 -1.632961
H -0.704414 5.198710 -1.16571
H -2.870555 -2.337148 2.863828
H -1.536323 -1.691258 3.859125
| Atom | X    | Y    | Z    |
|------|------|------|------|
| H    | -2.014143 | -3.392667 | 4.007743 |
| S    | -0.964445  | 0.514770  | -1.957818 |
| C    | -3.962709  | 0.003256  | -1.180313 |
| H    | 0.570098   | -1.576150 | -1.415350 |
| C    | -2.324801  | 1.260684  | 0.767763  |
| O    | 1.059410   | -5.353731 | -0.638044 |
| H    | -0.106858  | -4.941401 | 1.159836  |
| C    | -5.050466  | 0.092234  | -0.300342 |
| C    | -4.185071  | 0.044214  | -2.555467 |
| H    | 1.892970   | -3.012652 | -2.971656 |
| C    | 1.623970   | -4.02974  | -1.788932 |
| C    | 1.177185   | -6.418984 | 0.425772  |
| H    | -4.880052  | -0.151720 | -1.109410 |
| C    | -6.349930  | -0.080842 | -0.798896 |
| C    | -5.488720  | 0.051089  | -3.052455 |
| H    | -3.323716  | 0.102627  | -2.26269 |
| C    | -1.941388  | 2.835157  | -0.652202 |
| C    | -2.370459  | 3.616201  | 1.323496  |
| H    | -2.797533  | 1.966032  | 3.033411  |
| H    | -2.727273  | -0.099853 | 2.382472  |
| H    | 2.186053   | -5.436864 | -2.478113 |
| H    | -7.196252  | 0.127727  | -0.109410 |
| C    | -6.570895  | -0.010422 | -2.176224 |
| H    | -5.658057  | 0.107174  | -4.130521 |
| C    | -2.276010  | 4.660842  | 1.017221  |
| C    | -2.675551  | 3.300927  | 2.648826  |
| H    | -3.026174  | 1.712758  | 4.071434  |
| H    | -7.591942  | -0.001380 | -2.565583 |
| H    | -2.813906  | 4.098190  | 3.383038  |
| C    | 1.685884   | 0.846629  | -0.025288 |
| C    | 2.955649   | 0.351186  | -2.439720 |
| C    | 3.904276   | 1.378693  | -2.731517 |
| C    | 2.284235   | -0.035546 | -3.628570 |
| C    | 3.738612   | 1.713659  | -4.214889 |
| H    | 3.675198   | 2.244409  | -2.088610 |
| H    | 4.920693   | 1.023130  | -2.491504 |
| C    | 2.337125   | 1.191569  | -4.518342 |
| H    | 2.825782   | -0.890438 | -4.105115 |
| H    | 1.263093   | -0.347934 | -3.638747 |
| H    | 4.482125   | 1.173044  | -4.821480 |
| H    | 3.859674   | 2.787430  | -4.416746 |
| H    | 2.172622   | 0.963326  | -5.580850 |
| H    | 1.570640   | 1.915970  | -4.198736 |

$k\text{Ph}_x\kappa S-K(\text{THF})_3$

$E = -3224.93366894$

| Atom | X    | Y    | Z    |
|------|------|------|------|
| K    | -1.588434 | -0.061148 | 0.317991 |
| Cl   | 0.521440  | -0.825218 | -2.003475 |
| S    | 1.057144  | 0.999996  | 1.769935 |
| C    | 0.449683  | -2.972894 | 0.665417 |
| C    | -0.566847 | -3.574061 | -0.080284 |
| C    | -1.789907 | -3.843346 | 0.533232 |
| C    | -1.989231 | -3.520052 | 1.877441 |
| C    | -0.961122 | -2.928403 | 2.615123 |
| C    | 0.264734  | -2.647509 | 2.010916 |
| O    | -2.936257 | 0.509655  | 2.634382 |
| C    | 1.798550  | -0.917121 | -0.780128 |
| P    | 2.150553  | 0.532249  | 0.147352 |
H -5.170034 3.483722 -2.175120  
H -4.020831 4.448670 0.320654  
H -3.704867 5.150514 -1.273331  
S 1.988849 -2.484925 -0.101670  
O 2.973575 -2.300501 0.996729  
N 2.155377 -3.579425 -1.175543  
C 3.218579 -3.824399 -2.137693  
H 4.230369 -3.482456 -1.699912  
H 3.128965 -4.151444 -2.920150  
H 3.176315 -2.395682 -2.639568  
κN-K(THF)_3  

E = -3224.93163716  
O 1.502702 -4.048887 -0.704662  
O 4.350580 -0.122348 -1.678606  
O 4.511083 -0.630188 1.879782  
S 0.267545 -0.123928 0.039798  
C 1.061469 -5.192430 0.005248  
C 0.526832 -3.801525 -1.705849  
C 4.019204 0.319380 -3.049275  
C 5.799106 1.659769 0.996729  
C 3.709319 2.788956 0.039798  
C -1.395095 -0.473323 -0.212925  
C 0.536150 1.642721 0.037211  
H 1.536133 -5.183242 0.997584  
H 1.388673 -6.108022 -0.522797  
H 0.666924 -4.506675 -2.548845  
H 0.655040 -2.769969 -2.059149  
H 4.869332 1.643989 -0.734547  
H 3.146435 1.793711 -0.607636  
C 3.683551 1.957466 -2.561453  
C 3.105722 0.839392 -3.420797  
C 3.529654 -1.302446 -3.162733  
H 4.937276 -0.323253 -3.659697  
H 5.974148 -0.037466 0.571672  
H 6.576091 -0.710233 2.108616  
C 5.782687 1.330890 2.292946  
C 4.295558 1.588065 2.533288  
H 3.83864 -0.128313 3.832334  
H 2.709755 0.052177 2.568942  
Cl -1.849847 -0.602965 -1.924232  
P -2.638710 0.311401 0.776808  
C 0.825557 2.334359 1.210510  
C 0.366702 2.312435 -1.177113  
H -0.834830 -4.814904 1.043366  
H -0.927107 -6.077536 -0.195465  
H -1.601060 -4.327084 -1.696071  
H -1.108882 -3.087514 -0.518542  
H 4.596358 2.369098 -3.022288  
H 2.982795 2.785044 -2.385249  
H 2.077555 0.612588 -3.100513  
H 3.109254 1.057446 -4.498079  
H 6.254656 2.087312 1.649594  
H 6.326640 1.325403 3.250003  
H 3.812411 2.002698 1.635357  
H 4.102597 2.276263 3.368910  
S -2.197768 0.528507 2.691835  
C -3.077729 1.922396 0.018385
Supporting Information

\[ \begin{align*}
\text{H:} & \quad 0.918007 \quad 1.770244 \quad 2.138411 \\
\text{C:} & \quad 0.980582 \quad 3.719422 \quad 1.158608 \\
\text{C:} & \quad 0.507176 \quad 3.696546 \quad -1.212801 \\
\text{H:} & \quad 0.120946 \quad 1.749410 \quad -2.079018 \\
\text{C:} & \quad 3.779491 \quad 1.992071 \quad -1.193464 \\
\text{C:} & \quad 2.614031 \quad 3.099696 \quad 0.613049 \\
\text{C:} & \quad 0.980582 \quad 3.719422 \quad -1.158608 \\
\text{H:} & \quad 0.120946 \quad 1.749410 \quad -2.079018 \\
\text{C:} & \quad 3.779491 \quad 1.992071 \quad -1.193464 \\
\text{D:} & \quad 6.528842 \quad -0.967875 \quad 0.747910 \\
\text{C:} & \quad 0.380900 \quad -1.827239 \quad 1.982121 \\
\text{H:} & \quad 0.680250 \quad -1.818678 \quad 2.283655 \\
\text{H:} & \quad 0.538618 \quad -2.690434 \quad 1.310447 \\
\text{H:} & \quad 0.977067 \quad -2.003772 \quad 2.891930 \\
\text{O:} & \quad 0.993843 \quad -0.617141 \quad 0.947628 \\
\text{K:} & \quad 3.132652 \quad -1.955784 \quad -0.042393 \\
\end{align*} \]

\[ \begin{align*}
\kappa_O \kappa_S \text{K(THF)}_3 \\
E = -3224.934281 \\
\end{align*} \]
\( \kappa O, \kappa N-K(THF)_2 \)

\[ E = -2992.64304011 \]

\[
\begin{align*}
O & \ -0.759698 \ 0.136482 \ -0.079947 \\
O & \ -2.083466 \ 3.354930 \ -0.408902 \\
O & \ -4.475404 \ -0.143911 \ -0.352061 \\
S & \ -0.304535 \ -1.086692 \ -0.817843 \\
C & \ -2.308340 \ 4.740161 \ -0.606985 \\
C & \ -1.723328 \ 3.103444 \ 0.953696 \\
C & \ -4.143481 \ -0.187776 \ 1.037640 \\
N & \ -5.098640 \ -1.360503 \ -0.749060 \\
N & \ -8.05075 \ -1.300813 \ -2.274757 \\
C & \ 1.386547 \ -1.104425 \ -0.667080 \\
C & \ -1.023004 \ -2.476025 \ 0.044682 \\
H & \ -3.121404 \ 4.865448 \ -1.339331 \\
H & \ -1.398522 \ 5.219383 \ -1.018023 \\
C & \ -2.632840 \ 5.292484 \ 0.769764 \\
C & \ -1.697465 \ 4.462584 \ 1.642884 \\
H & \ -0.758285 \ 2.577041 \ 0.984609 \\
H & \ -2.484794 \ 2.438511 \ 1.397195 \\
H & \ -4.491115 \ 0.740541 \ 1.519072 \\
H & \ -3.045694 \ -0.241089 \ 1.037640 \\
C & \ -4.817625 \ -1.434015 \ 1.590845 \\
C & \ -4.826267 \ -2.349106 \ 0.371987 \\
H & \ -4.679749 \ -1.678342 \ -1.71421 \\
H & \ -6.183909 \ -1.194509 \ -0.884217 \\
C & \ -0.033906 \ -0.701348 \ -3.345262 \\
Cl & \ 2.120693 \ -2.599784 \ -1.238561 \\
P & \ 2.169879 \ -0.231293 \ 0.650934 \\
C & \ -1.190775 \ -2.365792 \ 1.425773 \\
C & \ -1.298051 \ -3.665048 \ -0.628489 \\
H & \ -3.868623 \ 5.088689 \ 1.022593 \\
H & \ -2.465548 \ 6.376134 \ 0.848353 \\
H & \ -0.680768 \ 4.883027 \ 1.615859 \\
H & \ -2.010791 \ 4.406097 \ 2.694836 \\
H & \ -5.847021 \ -1.208433 \ 1.913167 \\
H & \ -4.275170 \ -1.857515 \ 2.447648 \\
H & \ -3.837866 \ -2.813738 \ 0.240023 \\
H & \ -5.577691 \ -3.149479 \ 0.425350 \\
H & \ 1.052715 \ -0.872599 \ -3.244038 \\
H & \ -0.174868 \ 0.394173 \ -3.455281 \\
H & \ -0.352475 \ -1.153077 \ -4.297171 \\
S & \ 1.815362 \ -0.686434 \ 2.557000 \\
C & \ 3.94962 \ -0.435067 \ 0.252326 \\
C & \ 1.900590 \ 1.557076 \ 0.341721 \\
C & \ -0.924177 \ -1.433432 \ 1.928288 \\
C & \ -1.669403 \ -3.463912 \ 2.136564 \\
C & \ -1.778286 \ -4.756602 \ 0.093655 \\
H & \ -1.145938 \ -3.706629 \ -1.707584 \\
C & \ 4.423620 \ -0.106673 \ -1.024106 \\
C & \ 4.837413 \ -0.891893 \ 1.225616 \\
C & \ 2.077473 \ 2.455465 \ 1.397252 \\
C & \ 1.587581 \ 2.039493 \ -0.932605 \\
H & \ -1.808199 \ -3.388791 \ 3.217630 \\
C & \ -1.966638 \ -4.655884 \ 1.472842 \\
H & \ -2.006918 \ -5.691061 \ -0.424177 \\
H & \ 3.726933 \ 0.243546 \ -1.789406 \\
C & \ 5.778250 \ -0.233795 \ -1.317374 \\
C & \ 6.194888 \ -1.021086 \ 0.928710 \\
H & \ 4.443754 \ -1.139920 \ 2.215639 \\
H & \ 2.299763 \ 2.061253 \ 2.392541 \\
\end{align*}
\]
C 1.954465 3.826742 1.177770
C 1.447061 3.409312 -1.145426
H 1.438048 1.328134 -1.747388
H 2.343854 -5.513242 2.035354
H 6.145059 0.023286 -2.314113
C 6.666271 -0.691749 -0.340855
H 6.886499 -1.380839 1.694535
H 2.098761 4.52387 5 2.006917
C 1.636812 4.305928 -0.093336
H 1.188260 3.780734 -2.140273
H 7.729437 -0.791625 -0.573397
H 1.529789 5.380243 -0.263238
K -2.611705 1.131295 -1.830769

**KO-K(THF)_{2}**

E = -2992.64651467
O -0.759516 -0.125480 -0.699322
O -2.191738 3.019263 0.467396
S -0.244620 -1.530655 -0.783004
C -2.462083 4.386559 0.751585
C -1.710496 2.354205 1.635620
C -4.248259 0.252568 0.003947
C -4.018012 -1.145786 -1.821617
N -0.508504 -2.386668 -2.043210
C -1.132002 -2.442806 0.467880
H -3.465116 4.647245 0.375813
H -1.725273 5.020148 0.223425
C -2.331680 4.537239 2.261215
C -1.302704 3.461320 2.589502
O -0.885884 1.682326 1.356381
H -2.522947 1.742189 2.070203
H -4.648510 1.243455 0.264563
H -3.297844 0.104602 0.548218
C -5.195807 -0.902872 0.260684
C -4.624169 -1.967678 -0.674511
H -2.988203 -1.474415 -2.043126
H -4.613623 -1.206606 -2.747005
C 0.282957 -2.084703 -3.215081
Cl 2.184569 -2.966370 -1.450186
P 2.004709 -0.028666 0.536227
C -1.521732 -1.753332 1.616144
C -1.377956 -3.804618 0.320466
H -3.290558 4.310308 2.754469
H -2.028546 5.550434 2.560655
H -0.286081 3.814608 2.353771
H -1.313478 3.141437 3.640570
H -6.220693 -0.623275 -0.031962
H -5.211065 -1.218077 1.313923
H -3.838414 -2.539219 -0.159727
H -5.81438 -2.682890 -1.025302
H 1.369599 -2.057679 -3.007450
H 0.018059 -1.121580 -3.695047
H 0.109631 -2.871818 -3.964640
S 1.424455 0.304206 2.414612
C 3.828014 -0.221007 0.449866
C 1.716719 1.457475 -0.509806
H -1.275225 -0.695760 1.718995
C -2.203722 -2.440438 2.617707
C -2.061028 -4.483498 1.329435
Supporting Information

\[ E = -2992.63903055 \]

O -1.588665 3.277379 -0.410908
O 3.528624 3.073284 0.399639
S 1.233739 -0.823885 -0.953860
C -2.592879 3.712112 -1.318459
C -2.151359 3.069139 0.887532
C 4.633001 3.447420 -0.414084
C 3.854245 1.910333 1.167512
C 0.017390 -0.567501 0.188261
C 2.612817 -1.720003 -0.210261
H -2.419485 3.229258 -2.292767
H -2.522492 4.806953 -1.463398
C -3.913498 3.325281 -0.672282
C -3.593849 3.546599 0.803194
H -1.558983 3.623289 1.633694
H -2.087903 1.996762 1.133066
H 5.144788 4.323598 0.026587
H 4.262021 3.738919 -1.410154
C 5.550496 2.236670 -0.443976
C 5.340709 1.669153 0.955201
H 3.252650 1.064361 0.796898
H 3.589648 2.087984 2.221945
Cl 0.433094 0.517384 1.509155
P -1.369719 -1.655614 0.244094
C 2.344780 -2.766035 0.670946
C 3.919834 -1.391722 -0.566935
H -4.141115 2.272951 -0.870092
H -4.756056 3.937832 -1.034857
H -3.666512 4.616015 1.057981
H -4.255108 2.991384 1.482624
H 6.594837 2.496975 -0.666448
H 5.206221 1.518896 -1.205647
H 5.937793 2.233784 1.689233
H  5.606254  0.606473  1.044323
S -1.144337 -3.619620  0.520000
C -2.355845 -0.999383  1.647786
C -2.421612 -1.311174 -1.212886
H  1.305864 -3.019969  0.912907
C  3.410500 -3.478749  1.217906
C  4.978963 -2.114646 -0.019166
H  4.090942 -0.568069 -1.261563
C  3.519636 -0.247561  1.464372
C  1.942174 -1.315837  2.948723
C  3.260603 -2.306708 -1.715396
C -2.421369 -0.039835 -1.795730
H  3.211928 -4.295590  1.916057
C  4.724960 -3.153880  0.876760
H  6.006963 -1.863054 -0.291754
H  3.865454  0.191300  2.562626
C -2.665525 -0.862682  4.047029
H -1.052407 -1.933731  3.091869
H  3.261458  0.229305 -2.874326
H -1.753009  0.728914 -1.398383
H  5.556071 -3.715939  1.310092
H -5.172150  0.764411  2.413367
C -3.825358 -0.106556  3.859142
H -2.329385 -1.108546  5.057305
H  4.749940 -2.819167 -3.193626
C -4.101049 -0.766902 -3.377258
H  3.256244  1.220751 -3.343222
H  4.399659  0.239723  4.721897
H -4.754093 -0.554045 -4.227246
N  0.514976 -1.699558 -1.998551
C  1.249055 -2.628889 -2.818395
H  1.942422 -3.277817 -2.248196
H  0.523600 -3.295259 -3.310040
H  1.837190 -2.143999 -3.621333
O  1.881049  0.466378 -1.362038
K  1.049577  2.879412 -0.720083

\kappa O_{\kappa S-K(THF)}

E = -2992.64457655

Cl 2.530646 0.091045 1.164802
S  0.007944 1.771712 -1.767765
O  0.648841 4.085757  1.479877
C  1.018098 -0.442587  0.439937
P  0.715058 -0.030817 -1.240502
C  1.563781  3.481459  2.401185
C  1.353646  4.568067  0.342062
O -0.310166 -1.359824 -1.971487
C  2.354809 -0.293327 -2.022110
C  0.173322 -2.037033  2.561390
H  1.453749  3.959193  3.388973
H  1.308522  2.413094  2.499535
C  2.956068  3.667569  1.808600
C  2.654368  3.788946  0.319639
H  0.736449  4.394952 -0.553186
H  1.535459  5.655765  0.441286
C -0.135135 -2.688072 -1.569896
C -1.225788 -1.055288 -2.978744
C  3.118145 -1.422279 -1.698016
Supporting Information

$E = -2760.34854473$

O 0.729144 1.373703 0.021389
O 4.108743 0.63811 0.075590
S -0.579650 1.546145 -0.667590
C 5.368056 -0.020289 0.079001
C 3.585983 0.723572 1.403048
N -0.339862 1.961107 -2.149606

$kO,kN-K(THF)$

$E = -2760.34854473$

O 0.729144 1.373703 0.021389
O 4.108743 0.63811 0.075590
S -0.579650 1.546145 -0.667590
C 5.368056 -0.020289 0.079001
C 3.585983 0.723572 1.403048
N -0.339862 1.961107 -2.149606
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -1.523389 | 0.144821 | -0.419858 |
| C    | -1.418275  | 2.876213 | 0.206455  |
| H    | 6.074943   | 0.544213 | -0.550978 |
| H    | 5.255475  | -1.030869 | -0.355053 |
| C    | 5.796171   | -0.096485 | 1.537073  |
| C    | 4.449377   | -0.200855 | 2.243941  |
| H    | 2.521696   | 0.449994 | 1.386320  |
| C    | 3.664898   | 1.768827 | 1.756496  |
| C    | -1.377950  | 1.692633 | -3.120529 |
| Cl   | -3.261747  | 0.378924 | -0.53772  |
| P    | -0.903003  | -1.119386 | 0.630712  |
| C    | -1.825288  | 2.659651 | 1.523549  |
| C    | -1.594600  | 4.104269 | -0.422423 |
| H    | 6.314816   | 0.829124 | 1.835140  |
| H    | 6.469610   | -0.941869 | 1.737680  |
| C    | 4.067152   | -1.232226 | 2.191595 |
| H    | 4.481273   | 0.095837 | 3.301658  |
| H    | -2.255786  | 2.363270 | -3.036296 |
| H    | -1.759142  | 0.654267 | -3.066610 |
| H    | -0.957465  | 1.838196 | -4.127583 |
| C    | -0.662174  | -0.845165 | 2.591408 |
| C    | -2.053696  | -2.513113 | 0.313017 |
| C    | 0.654764   | -1.691107 | -0.159494 |
| H    | -1.675869  | 1.676708 | 1.985986  |
| C    | -2.420381  | 3.707273 | 2.220370  |
| C    | -2.196581  | 5.146446 | 0.284341  |
| H    | -1.254791  | 4.226463 | -1.453569 |
| C    | -2.420896  | -2.840931 | -0.99397 |
| C    | -2.535409  | -3.274321 | 1.378164 |
| C    | 1.643108   | -2.291630 | 0.623664 |
| C    | 0.828413   | -1.601251 | -1.545172 |
| H    | -2.744741  | 3.556725 | 3.252845  |
| C    | -2.066481  | 4.947440 | 1.602261  |
| H    | -2.345086  | 6.116290 | -0.196462 |
| H    | -2.056900  | -2.234507 | -1.830591 |
| C    | -3.258890  | -3.926755 | -1.235803 |
| C    | -3.377049  | -3.461019 | 1.137798  |
| H    | -2.239877  | -2.996288 | 2.393908  |
| H    | 1.496771   | -2.342594 | 1.706349  |
| C    | 2.798106   | -2.796402 | 0.027026  |
| C    | 1.986631   | -2.102192 | -2.138587 |
| H    | 0.059474   | -1.109328 | -2.145918 |
| H    | -3.078501  | 5.764016 | 2.154057  |
| H    | -3.545129  | -4.177983 | -2.260023 |
| C    | -3.738063  | -4.689023 | -0.167803 |
| H    | -3.752255  | -4.952510 | 1.976341  |
| H    | 3.567973   | -3.265267 | 0.644836  |
| C    | 2.973457   | -2.701936 | -1.353183 |
| H    | 2.117511   | -2.028340 | -3.221726 |
| H    | -4.397787  | -5.539602 | -0.356576 |
| H    | 3.879544   | -3.097244 | -1.819110 |
| K    | 2.537361   | 1.526619 | -1.939397 |
6.4.6 Coordinates of the dimeric structures of 1-K

κOκNκS-K2(THF)2

E = –5520.75133972

Cl 4.814649 0.902496 1.696501
Cl -4.814297 -0.902754 -1.696605
S 1.700897 1.489447 -1.399194
S -1.700539 -1.489138 1.398843
O -1.356179 3.608766 2.260178
O -1.355486 -3.608698 -2.260305
P 3.395930 0.494614 -0.978041
P -3.395788 -0.494578 0.977961
C 3.731955 -0.005653 0.668843
C -3.732035 0.005807 -0.668842
P 3.395960 0.494614 -0.978041
P -3.395788 -0.494578 0.977961
C 3.731955 -0.005653 0.668843
C -3.732035 0.005807 -0.668842

H 2.095165 -3.572791 -4.195814
H -2.653151 -2.247422 -3.127921
C -3.607359 -4.161695 -2.708180
C -3.336991 -4.282646 -1.213441
H -1.378656 -4.064520 -0.249305
H -1.514485 -5.471269 -1.351604
C -3.643328 2.532714 -1.931746
H 2.095512 3.572650 4.195817
H 2.653486 2.247256 3.127944
C 3.608051 4.161426 2.708487
C 3.337953 4.282532 1.213712
H 1.379749 4.064766 0.249228
H 1.515939 5.471399 1.351673
C 4.293212 -2.077400 -1.680921
C -2.899686 -0.970945 -3.192122
C 6.140812 0.959497 -1.303193
C 4.686254 2.772922 -1.977672
H -4.293637 2.077134 1.681247
H -2.899526 0.970879 3.319176
C -6.140582 -0.960087 1.303012
H -4.685614 -2.773066 1.977807
C 3.485798 -3.742231 1.257508
C 4.560620 -2.397774 2.975844
H -4.568079 -3.680169 -2.937577
H -3.596939 -5.155593 -3.184319
H -3.634843 -3.359270 -0.699357
H -3.854629 -5.125189 -0.733095
C -3.487020 3.742402 -1.257423
C -4.561224 2.397657 -2.975920
H 4.568663 3.679741 2.938005
H 3.597700 5.155290 3.184699
H 3.635768 3.358110 0.699610
H 3.855788 5.125041 0.733518
H 4.775734 -2.078141 -0.700926
H 4.408511 -3.179281 -2.526135
H 3.018078 -2.074690 -4.163777
H 2.302610 -0.103070 -3.613546
H 6.275497 -0.038914 -0.880738
\begin{align*}
C & : 7.248919 \ 1.705089 \ -1.693408 \\
C & : 5.800005 \ 3.519244 \ -2.366604 \\
H & : -2.302163 \ 0.103134 \ 3.613309 \\
H & : -6.275486 \ 0.038228 \ 0.701336 \\
C & : -3.018074 \ 2.074500 \ 4.163883 \\
H & : 2.752481 \ -3.811309 \ 0.452573 \\
C & : 4.277113 \ -4.830578 \ 1.623033 \\
C & : 5.348451 \ -3.490612 \ 3.329397 \\
H & : 4.654092 \ -1.444236 \ 3.499233 \\
C & : -2.753798 \ 3.816098 \ -0.452420 \\
C & : -4.278679 \ 4.830492 \ -1.622966 \\
C & : -5.349401 \ 3.490239 \ -3.329491 \\
H & : -4.654317 \ 1.444111 \ -3.499233 \\
H & : 4.994228 \ -4.044715 \ 2.208773 \\
C & : 3.769094 \ -3.182011 \ -3.766627 \\
H & : 2.518614 \ -2.069797 \ 5.135747 \\
H & : 8.251243 \ -1.286617 \ 1.581988 \\
C & : 7.079988 \ -2.987630 \ 2.222753 \\
H & : 5.664203 \ 4.520627 \ -2.779832 \\
H & : -4.995108 \ 4.044715 \ 2.208773 \\
C & : -3.769464 \ 3.181656 \ -3.766987 \\
H & : 2.518441 \ 2.069636 \ 5.135747 \\
H & : -8.251243 \ 1.286617 \ 1.581988 \\
C & : -7.079304 \ -2.987630 \ 2.222753 \\
H & : -5.663171 \ -4.520886 \ 2.780195 \\
H & : 4.163057 \ -5.782969 \ 1.099803 \\
C & : 5.209249 \ -4.704585 \ -2.653426 \\
H & : 6.072814 \ -3.395709 \ 4.141678 \\
H & : -4.165000 \ 5.782998 \ -1.099681 \\
C & : -5.210680 \ 4.704228 \ -2.653448 \\
H & : -6.073658 \ 3.395125 \ -4.141842 \\
H & : 3.855292 \ -4.049432 \ -4.254249 \\
C & : 7.952294 \ 3.570720 \ -2.526655 \\
H & : -3.855792 \ 4.048979 \ 4.425897 \\
H & : -7.951480 \ -3.571561 \ 2.526806 \\
H & : 5.828402 \ -5.559179 \ 2.936142 \\
H & : -5.830102 \ 5.558622 \ -2.936179 \\
S & : 2.684116 \ -1.099144 \ 1.423266 \\
O & : 1.790501 \ -1.615483 \ 0.339347 \\
S & : -2.684445 \ 1.099581 \ -1.423217 \\
O & : -1.791014 \ 1.616190 \ -0.339274 \\
N & : -2.077832 \ 0.431552 \ -2.681009 \\
C & : -1.417627 \ 1.269773 \ -3.665856 \\
H & : -1.312643 \ 0.691833 \ -4.597035 \\
H & : -1.981165 \ 2.188215 \ -3.916862 \\
H & : 0.403007 \ 1.579463 \ -3.353631 \\
N & : 2.077744 \ -0.430939 \ 2.681080 \\
C & : 1.417420 \ -1.268994 \ 3.666020 \\
H & : 1.980882 \ -2.187394 \ 3.917207 \\
H & : 1.312433 \ -0.690851 \ 4.597096 \\
H & : 0.402796 \ -1.578627 \ 3.353791 \\
K & : 0.134877 \ 1.330551 \ 1.463047 \\
K & : -0.134853 \ -1.330011 \ -1.463522
\end{align*}

$\kappa N, \kappa S, \kappa Cl-K_2(THF)_2$
\( E = -5520.74331077 \)

| Element | Charge | X      | Y       | Z      |
|---------|--------|--------|---------|--------|
| Cl      | -1     | 2.414896 | 0.976694 | 1.653604 |
| Cl      | -1     | -2.409098 | -0.976869 | -1.650284 |
| S       | -2     | 1.503008  | 0.059922  | -2.104532 |
| S       | -2     | 1.508530  | 0.056649  | 2.112121  |
| O       | -2     | 0.419798  | -3.986256 | 1.018115  |
| O       | -2     | -0.420991 | 3.990233  | 1.025463  |
| C       | 0      | 3.422650  | 0.127455  | 0.489302  |
| P       | -3     | 3.182790  | 0.562813  | -1.186840 |
| C       | 3      | 3.185790  | -0.563743 | 1.187849  |
| C       | 3      | 1.119018  | -3.847829 | -2.245636 |
| C       | 3      | 0.899170  | -4.451821 | -1.290454 |
| C       | 3      | 1.151514  | -4.221862 | -2.798315 |
| C       | 3      | 1.598943  | -3.889022 | 0.654719  |
| C       | 3      | -0.986348 | -5.518361 | -1.019009 |
| C       | 3      | -5.627750 | 1.101632  | -1.743918 |
| C       | 3      | -1.560668 | 4.815261  | 2.562093  |
| C       | 3      | -1.932330 | 3.121317  | 2.103826  |
| C       | 3      | -0.055605 | 3.386311  | 3.231183  |
| C       | 3      | 1.151058  | 4.219445  | 2.795848  |
| C       | 3      | 1.597795  | 3.888892  | 0.661965  |
| C       | 3      | 0.988857  | 5.519023  | 1.028415  |
| C       | 3      | 5.937590  | 0.403546  | -1.625989 |
| C       | 3      | 4.544658  | -0.542493 | -3.365873 |
| C       | 3      | 4.086450  | 3.071795  | -0.296971 |
| C       | 3      | 2.524284  | 3.119107  | -2.144825 |
| C       | 3      | -5.941816 | -0.402041 | 1.617925  |
| C       | 3      | -4.553850 | 0.541623  | 3.363034  |
| C       | 3      | -4.089473 | -3.071110 | 0.293863  |
| C       | 3      | -2.533526 | -3.121275 | 2.146886  |
| C       | 3      | 6.813794  | -1.509696 | 1.121071  |
| C       | 3      | 5.649795  | -0.435246 | 2.966474  |
| C       | 3      | -0.127419 | -2.314154 | -3.081562 |
| C       | 3      | 0.337707  | -3.549549 | -4.276866 |
| C       | 3      | -2.107519 | -3.710652 | -2.969611 |
| C       | 3      | -1.176585 | -5.180279 | -3.328668 |
| C       | 3      | -6.808276 | 1.512486  | -1.130477 |
| C       | 3      | -5.639459 | 0.435795  | -2.971516 |
| C       | 3      | 0.127722  | 2.310286  | 3.081632  |
| C       | 3      | -0.336953 | 3.540437  | 4.282565  |
| C       | 3      | 2.107601  | 3.709035  | 2.976565  |
| C       | 3      | 1.174547  | 5.176701  | 3.338352  |
| C       | 3      | 6.036587  | 0.884159  | -0.650534 |
| C       | 3      | 7.073931  | 0.078622  | -2.360571 |
| C       | 3      | 5.686318  | -0.865010 | -4.099238 |
| C       | 3      | 3.545811  | -0.783866 | -3.739038 |
| C       | 3      | 4.635094  | 2.505876  | 0.459620  |
| C       | 3      | 4.194563  | 4.459259  | -0.356844 |
| C       | 3      | 2.632232  | 4.508929  | -2.198894 |
| H       | 1      | 1.872518  | 2.579902  | -2.838263 |
\( \kappa \text{Ph}, \kappa \text{S}, \kappa \text{Cl} - \text{K}_2(\text{THF})_2 \)

\[
E = -5520.73154420
\]

\[
\begin{align*}
\kappa & = -0.815455 \quad 1.892088 \quad 0.327708 \\
\kappa & = 0.851963 \quad -1.927614 \quad -0.271178
\end{align*}
\]

Supporting Information
Supporting Information

\[ \kappa_{O,N,S-K_2(THF)}^4 \]

\[ \text{E} = -5985.32646643 \]

Cl 4.659622 2.154968 1.219149  
Cl -4.437387 -2.154364 -1.237084  
S 1.595233 0.955574 1.362393  
H -7.528748 0.957194 0.502555  
H -7.361123 0.458550 2.201285  
H -6.685894 2.013432 1.653479

\[ \kappa_{O,N,S-K_2(THF)}^4 \]
C 3.732211 0.794329 0.631158
C -3.719310 -0.795011 -0.641623
P 3.422034 0.538008 -1.074891
P -3.422295 -0.538086 1.066616
C -2.045688 -4.593427 -1.535261
C -1.773248 -4.747737 0.782454
C 2.051963 4.587860 1.531306
C 1.754542 4.754095 -0.782882
C 3.968193 -1.145579 -1.544593
C 4.668869 1.584572 -1.912763
C -3.981747 1.141581 1.534202
C -4.668945 -1.592037 1.895775
C 3.949465 -0.801695 2.921897
H -1.435008 -5.102739 -2.300169
H -2.447237 -3.662746 -1.969703
C -3.153449 -5.482890 -0.982057
C -3.232160 -5.031925 0.472544
H -1.633567 -3.985963 1.565244
H -1.242250 -5.694543 1.091975
C -3.934362 0.810594 -2.927286
H 1.457316 5.096800 2.308926
H 2.450281 3.649558 1.952394
C 3.160819 5.469785 0.969315
C 3.215553 5.021627 -0.486951
H 1.599842 3.993837 2.921897
H 1.230829 5.681458 -1.087601
C 4.878225 -1.839559 -0.742544
C 3.562909 -1.688861 -2.767200
C 6.030326 1.410151 -1.632585
C 4.270347 2.523161 -2.864318
C -4.889595 1.830771 0.725506
C -3.590300 1.685593 2.760934
C -6.029595 -1.424090 1.607770
C -4.271585 -2.529520 2.848888
C 4.232162 -2.162176 2.812682
C 4.590551 -0.007141 3.874914
H -4.099451 -5.355823 -1.527657
H -2.866360 -6.545411 -1.040990
H -3.818413 -4.104847 0.550476
H -3.676232 -5.779394 1.145620
C -4.214362 2.171523 -2.817098
C -4.576105 0.018291 -3.881790
H 4.111539 5.332949 1.504205
H 2.883152 6.534487 1.034155
H 3.794928 4.088396 -0.572404
H 3.665173 5.765436 -1.163050
H 5.181134 -1.410082 0.215516
C 5.388057 -3.064576 -1.168625
C 4.080540 -2.909926 -3.193295
H 2.836981 -1.145387 -3.77905
H 6.347113 0.673240 -0.890916
C 6.979998 2.181823 -2.294987
C 5.224921 3.296204 -3.526364
H 3.204075 2.634280 -3.079230
H -5.181675 1.400821 -0.236678
H -5.411374 3.051546 1.149272
C -4.120025 2.902200 3.184751
H -2.865474 1.146276 3.376589
H -6.345735 -0.687852 0.865173
C -6.979334 -2.201399 2.263438
C -5.226174 -3.308261 3.504186
H -3.206186 -2.635178 3.070643
C 1.726542 -5.286723 -1.768015
C 2.061980 -4.487059 0.306832
C 2.787677 -6.228268 -1.180089
H 0.713584 -5.715165 -1.649047
H 1.884008 -5.045973 -2.829140
C 3.076570 -5.624050 0.207970
H 2.407459 -3.601825 0.856185
H 1.119696 -4.840816 0.768711
H 3.694614 -6.238272 -1.800551
H 2.416343 -7.261512 -1.121981
H 4.099929 -5.225055 0.252323
H 2.961717 -6.349733 1.025620
7. References

[1] K.-S. Feichtner, S. Englert, V. H. Gessner, Chem Eur. J. 2016, 22, 506-510.
[2] a) G. M. Sheldrick, Acta Cryst. 2008, A64, 112; b) A. Thorn, B. Dittrich, G. M. Sheldrick, Acta Cryst. 2012, A68, 448; c) G. M. Sheldrick, Acta Cryst. 2008, A64, 112; d) G. M. Sheldrick, Acta Cryst. 2015, C71, 3.
[3] R. Dennington, T. A. Keith, J. M. Millam, GaussView, Semichem Inc. Shawnee Mission KS, 2016.
[4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji et al., Gaussian 16 Revision C.01, 2016.
[5] a) W. Kohn, L. J. Sham, Phys. Rev. 1965, 140, A1133-A1138; b) P. Hohenberg, W. Kohn, Phys. Rev. 1964, 136, B864-B871; c) J. Reinhold, Cryst. Res. Technol. 1990, 25, 624; d) R. G. Parr, W. Yang, Density-Functional Theory of Atoms and Molecules (International Series of Monographs on Chemistry), Oxford University Press, USA, 1994.
[6] C. Adamo, V. Barone, J. Chem. Phys. 1999, 110, 6158.
[7] A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss Mol. Phys. 1993, 80, 1431.
[8] A. Schäfer, H. Horn, R. Ahlrichs, J. Chem. Phys. 1992, 97, 2571.
[9] a) S. Grimme, S. Ehrlich, L. Goerigk, J. Comput. Chem. 2011, 32, 1456; b) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104.
[10] P. Deglmann, F. Furch, R. Ahlrichs, Chem. Phys. Lett. 2002, 362, 511.
[11] A. Schäfer, C. Huber, R. Ahlrichs, J. Chem. Phys. 1994, 100, 5829.