Carbon–chalcogen bond formation initiated by [Al(NON\text{Dipp})E]⁻ anions containing Al–E (E = S, Se) multiple bonds

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Cartesian coordinates and computed energies
**General Experimental Procedures**

All manipulations were performed under dry nitrogen using standard Schlenk-line techniques, or in a conventional nitrogen-filled glovebox. Solvents were dried over appropriate drying agents and degassed prior to use. NMR spectra were recorded using a Jeol JNM-ECZ500S 500 MHz spectrometer equipped with a ROYAL digital auto tune probe S, operating at 500.1 (\(^1)\text{H}\)), 125.7 (\(^{13})\text{C}\{\(^1)\text{H}\}\)) and 95.4 (\(^{77})\text{Se}\)) MHz. Spectra were recorded at 298 K (unless stated otherwise) and proton and carbon chemical shifts were referenced internally to residual solvent resonances. Coupling constants are quoted in Hz. K[Al(NONDipp)] (K[A]), K[Al(NONDipp)(S\(_4\))] (K[B]), and [K(Et\(_2\)O)][Al(NONDipp)(Se)] ([K(Et\(_2\)O)][VI]),\(^3\) were prepared according to the literature procedures. All other chemicals were purchased from Sigma-Aldrich and used without further purification.

**Synthesis of K[Al(NONDipp)(S)] (K[1-S])**

A THF solution of triphenylphosphine (371 mg, 1.42 mmol) was added to a yellow solution of K[Al(NONDipp)(S\(_4\))] (K[B]) (355 mg, 0.52 mmol) in THF. The mixture was stirred for 18 hours to give a pale-yellow solution. The volatiles were removed in vacuo and the product extracted with hexane. Large colourless crystals were grown from a hexane solution via slow evaporation at room temperature. Yield 187 mg, 66 %.

\(^1)\text{H} \text{NMR (C}_6\text{D}_6\): } \delta \text{ 7.11 – 7.00 (m, 12H*, C}_6\text{H}_3 \text{ and C}_6\text{H}_5\), 3.96 (sept, } J = 6.9, \text{ 4H, CHMe}_2\), 1.42 (d, } J = 6.9, \text{ 12H, CHMe}_2\), 1.38 (br d, 12H, CHMe\(_2\)), 0.34 (s, 12H, SiMe\(_2\)).

\(^{13})\text{C} \{\(^1)\text{H}\} \text{ NMR (C}_6\text{D}_6\): } \delta \text{ 147.1, 144.1, 123.7 (C}_6\text{H}_3\), 28.2 (CHMe\(_2\)), 26.0, 24.2 (CHMe\(_2\)), 2.1 (SiMe\(_2\)).

* overlap with aromatic resonance from residual Ph\(_3\)P=S. Elemental analysis was not obtained for this compound due to persistent contamination with residual Ph\(_3\)P=S.
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$^{1}$H NMR spectrum (500 MHz, C$_6$D$_6$) of K[Al(NON$^{3}$Dipp)(S)] K[1-S]

* = Ph$_3$PS
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* = Ph$_3$PS
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Synthesis of [K(2.2.2-crypt)][Al(NON\textsuperscript{Dipp})(S)] ([K(2.2.2-crypt)][1-S])

A solution of K[1-S] was prepared by adding 246 mg of triphenylphosphine (0.94 mmol) to a THF solution of K[B] (212 mg, 0.31 mmol) and stirring for 2 hours. The volatiles were removed \textit{in vacuo} and the residue dissolved in toluene. A solution of [2.2.2]cryptand (118 mg, 0.31 mmol) in toluene was added at \(-30^\circ\text{C}\) to give a white suspension. The suspension was washed three times with cold toluene (\(-30^\circ\text{C}\)) and recrystallised from THF at \(-30^\circ\text{C}\) to yield large colourless plate-like crystals. Yield 25 mg, 8 %.

Anal. Calc'd for C\textsubscript{46}H\textsubscript{82}AlKN\textsubscript{4}O\textsubscript{7}Si\textsubscript{2} (957.48): C, 57.70; H, 8.63; N, 5.85 %. Found: C, 57.37; H, 8.27; N, 5.63 %.

\textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}, 343 K): δ 7.13 (d, J = 7.6, 4H, C\textsubscript{6}H\textsubscript{3}), 7.01 (t, J = 7.6, 2H, C\textsubscript{6}H\textsubscript{3}), 4.27 (sept, J = 6.8, 4H, CHMe\textsubscript{2}), 3.23 (s, 12H, crypt-C\textsubscript{2}H), 3.17 (t, 12H, J = 4.7, crypt-CH\textsubscript{2}), 2.19 (t, J = 4.7, 12H, crypt-CH\textsubscript{2}), 1.67 (d, J = 6.8, 12H, CHMe\textsubscript{2}), 1.50 (d, J = 6.8, 12H, CHMe\textsubscript{2}), 0.49 (s, 12H, SiMe\textsubscript{2}).

\textsuperscript{13}C{\textsuperscript{1}H} NMR (C\textsubscript{6}D\textsubscript{6}, 343 K) δ 146.7, 145.5, 123.0, 122.3 (C\textsubscript{6}H\textsubscript{3}), 70.8, 68.3, 55.3 (crypt-CH\textsubscript{2}), 28.5 (CHMe\textsubscript{2}), 26.2, 24.7 (CHMe\textsubscript{2}), 2.8 (SiMe\textsubscript{2}).
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$^1$H NMR spectrum (500 MHz, C$_6$D$_6$, 343 K) of [K(2.2.2-crypt)][Al(NON$^{Dipp}$)(S)] [K(2.2.2-crypt)][1-S]
**Figure S6**

$^{13}$C($^1$H) NMR spectrum (125 MHz, C₆D₆, 343 K) of [K(2.2.2-crypt)][Al(NONDipp)(S)] [K(2.2.2-crypt)][1-S]
Figure S7  ORTEP (displacement ellipsoids 30 %) of the asymmetric unit of \([\text{K(2.2.2-crypt)}][\text{Al(NON}^{\text{Dpp}})](\text{S})\) [\text{K(2.2.2-crypt)}][1-S]
Synthesis of \([\text{K(Et}_2\text{O})_2][\text{Al(NON}^{\text{Dipp}}\text{(SC}^\text{O})\text{O})]\) ([\text{K(Et}_2\text{O})][2-S])

A solution of \(\text{K[1-S]}\) (187 mg, 0.32 mmol) was prepared in toluene-\(d_8\) and added to an NMR tube fitted with a Teflon tap. The toluene solution was degassed and one atmosphere of \(^{13}\text{CO}_2\) gas was added. Reaction progress was monitored by \(^{13}\text{C}[^{1}\text{H}]\) NMR spectroscopy and shown to be complete after 2 days at room temperature. The solvent was removed \textit{in vacuo} and the white solid dissolved in diethyl ether. Crystals were grown at \(-30 \degree \text{C}\) from a diethyl ether solution. Yield 52 mg, 26%.

\(^1\text{H NMR (C}_6\text{D}_6): \delta 7.12 (dd, J = 7.6, 1.8, 2H, C_6H_3), 7.08 (dd, J = 7.6, 1.8, 2H, C_6H_3), 7.00 (t, J = 7.6, 2H, C_6H_3), 4.05 (br sept, J = 6.8, 4H, CHMe_2), 3.26 (q, J = 7.1, 2H*, OCH_2CH_3), 1.39 (d, J = 6.8, 6H, CHMe_2), 1.33 (d, J = 6.8, 6H, CHMe_2), 1.23 (br d, 6H, CHMe_2), 1.19 (br d, 6H, CHMe_2), 1.12 (t, J = 7.1, 3H*, OCH_2CH_3), 0.50 (s, 6H, SiMe_2), 0.39 (s, 6H, SiMe_2).

\(^{13}\text{C}[^{1}\text{H}] (\text{C}_6\text{D}_6): \delta 180.1 (S^{13}\text{CO}_2), 147.6, 146.9, 144.1, 124.8, 123.9, 123.5 (C_6H_3), 65.9, (OCH_2CH_3), 31.9 (OCH_2CH_3), 28.0, 27.8 (CHMe_2), 25.7, 25.5, 25.3, 25.0 (CHMe_2), 2.7, 2.0 (SiMe_2). * Sample exposed to vacuum prior to NMR analysis resulting in loss of Et_2O, as determined by smaller integrals of the peaks in the \(^1\text{H NMR spectrum relative to expected value from X-ray diffraction data. Despite repeated attempts we were unable to obtain accurate elemental analysis for [K(Et}_2\text{O)][2-S].}
Figure S8

$^1$H NMR spectrum (500 MHz, C$_6$D$_6$) of [K(Et$_2$O)$_2$][Al(NON$_{Dipp}$)$_{(13C(O))}$][K(Et$_2$O)][2-S]
$^{13}$C($^1$H) NMR spectrum (125 MHz, C$_6$D$_6$) of [K(Et$_2$O)$_2$][Al(NON$^{Dipp}$)(S$_{13}$C(O)O)] [K(Et$_2$O)][2-S]
Figure S10  ORTEP (displacement ellipsoids 30 %) of the asymmetric unit of [K(Et₂O)₂][Al(NON₆ip)(SC(O)O)] [K(Et₂O)][2-S]
Synthesis of [K(THF)$_3$][Al(NON$_{Dipp}$)(SeC(O)O)] ([K(THF)][2-Se])

A solution of K[VI] (150 mg, 0.23 mmol) was prepared in a 50:1 mixture of THF:C$_6$D$_6$ and added to an NMR tube fitted with a Teflon tap. The THF/C$_6$D$_6$ solution was degassed and one atmosphere of $^{13}$CO$_2$ gas was added. Reaction progress was monitored by $^{13}$C{'H} NMR spectroscopy and shown to be complete within 15 minutes at room temperature. The solvent was removed *in vacuo* and the white solid dissolved in THF. Crystals were grown at –30 °C from a THF solution. Yield 50 mg, 31 %.

Anal. Calc’d for C$_{33}$H$_{54}$AlKN$_2$O$_4$SeSi$_2$ corresponding to loss of 2 × THF, 744.03: C, 53.27; H, 7.32; N, 3.77 %. Found: C, 53.67; H, 7.34; N, 3.85 %.

$^1$H NMR (500 MHz, THF-$D_8$) : δ 6.97 − 6.91 (m, 4H, C$_6$H$_3$), 6.84 (t, J = 7.6, 2H, C$_6$H$_3$), 3.98 (sept, J = 6.8, 2H, CHMe$_2$), 3.90 (sept, J = 6.8, 2H, CHMe$_2$), 3.63 − 3.60 (m, 4H, THF-CH$_2$), 1.79 − 1.76 (m, 4H, THF-CH$_2$), 1.22 (d, J = 6.8, 6H, CHMe$_2$), 1.19 (d, J = 6.8, 6H, CHMe$_2$), 1.17 (d, J = 6.8, 6H, HCM$e$$_2$), 1.16 (d, J = 6.8, 6H, HCM$e$$_2$), 0.12 (s, 6H, SiMe$_2$), 0.08 (s, 6H, SiMe$_2$)

$^{13}$C{'H} (THF-$D_8$): δ 166.0 (J$_{Se-C}$ = 128.1, Se$^{13}$CO$_2$), 147.5, 147.2, 145.0, 123.9, 123.8, 123.0 (C$_6$H$_3$), 28.4, 28.3 (CHMe$_2$), 26.6, 26.4, 26.2, 26.1 (CHMe$_2$), 2.9, 2.8 (SiMe$_2$). $^{77}$Se NMR (THF-$d_8$): δ 150 (d, J = 128, SeCO$_2$).
Figure S11  $^1$H NMR spectrum (500 MHz, THF-$d_8$) of [K(THF)$_3$][Al(NON$_{Dipp}$)(Se$_{13}$C(O)O)] [K(THF)][2-Se]
$^{13}\text{C}^{(1)}\text{H}$ NMR spectrum (125 MHz, THF-$d_8$) of $[\text{K(THF)}_3][\text{Al(NON}^{\text{Dipp}})(\text{Se}^{13}\text{C(O))})][\text{K(THF)}][2\text{-Se}]$
Figure S13  Expansion of $^{13}\text{C}({}^1\text{H}) [\text{Se}^{13}\text{C}(\text{O})\text{O}]$ resonance from \([\text{K(THF)}_3][\text{Al(NON}^{\text{Dipp}})(\text{Se}^{13}\text{C}(\text{O})\text{O})][\text{K(THF)}][2-\text{Se}]\) showing $^{1}J_{\text{SeC}}$ coupling
Figure S14  $^{77}$Se NMR spectrum (95 MHz, THF-$d_8$) of [K(THF)$_3$][Al(NON$_{Dipp}$)(Se$_{13}$C(O))][K(THF)][2-Se]
Figure S15  ORTEP (displacement ellipsoids 30%) of the asymmetric unit of [K(THF)][Al(NON\textsuperscript{Dpp})(SeC(O)O)] [K(Et\textsubscript{2}O)][2-Se]
Synthesis of $\text{K[Al(NON}^\text{Dipp})(\text{SC(O)}\text{Ph}_2)]([[\text{K}[3-S]])}$

A solution of $\text{K[1-S]}$ (50 mg, 0.09 mmol) in Et$_2$O was added to a stirred solution of benzophenone (16 mg, 0.09 mmol) in Et$_2$O to give a colourless solution. Crystals were obtained via slow evaporation of the diethyl ether solution at room temperature. Yield 60 mg, 91 %.

Anal. Calc'd for $\text{C}_{41}\text{H}_{56}\text{AlKN}_2\text{O}_2\text{Si}_2$ (763.21): C, 64.52; H, 7.40; N, 3.67 %. Found: C, 63.92; H, 7.39; N, 3.14 %.

$^1\text{H}$ and $^{13}\text{C}[^1\text{H}]$ NMR spectra recorded in THF-$D_8$ indicated rapid decomposition with release of benzophenone. See Figs. S16 and S17 for representative spectra.
Figure S16  
$^1$H NMR spectrum (500 MHz, THF-$d_8$) of $\text{K}[\text{Al(NON}^{\text{Dipp}}\text{)(SC(O)}\text{Ph}_2)]\text{K}[3-\text{S}]$  

\* = $\text{Ph}_2\text{CO}$
Figure S1

$^{13}$C{H} NMR spectrum (125 MHz, THF-d$_8$) of K[Al(NON$_2$Dipp)$_2$(SC(O)Ph)$_2$]K$_3$.
Figure S18: ORTEP (displacement ellipsoids 30%) of the asymmetric unit of K[Al(NONDipp)(SC(O)Ph2)] K[3-S]
Synthesis of $\text{K[Al(NON_Dipp)(SeC(O)Ph_2)] [{K[3-Se]}]}$

A solution of K[VI] (133 mg, 0.22 mmol) in THF was added to a stirred solution of benzophenone (39 mg, 0.22 mmol) in THF to give a colourless solution. Crystals were obtained by storage of the solution at –30 °C for 18 hours. Yield 152 mg, 88 %.

Anal. Calc’d for $\text{C}_{41}\text{H}_{56}\text{AlKN}_2\text{O}_2\text{SeSi}_2$ corresponding to loss of $3 \times \text{THF}$, (810.11): C, 60.79; H, 6.97; N, 3.46 %. Found: C, 60.05; H, 6.99; N, 3.18 %.

$^1\text{H}$ and $^{13}\text{C}[^1\text{H}]$ and $^{77}\text{Se}$ NMR spectra recorded in THF-$D_8$ indicated rapid decomposition with release of benzophenone. See Figs. S19 - S21 for representative spectra.
\( ^1 \text{H NMR spectrum (500 MHz, THF-d}_8 \text{) of } [\text{K(THF)}_3][\text{Al(NON}^{\text{Dipp}}\text{(SeC(O)Ph}_2\text{)}][\text{K(THF)}][\text{3-Se}] \)
Figure S20  $^{13}$C($^1$H) NMR spectrum (125 MHz, THF-$d_8$) of $[\text{K(THF)}_3][\text{Al(NON}^{\text{Dipp}}\text{)(SeC(O)Ph}_2\text{)}][\text{K(THF)}][\text{3-Se}]$
Figure S21  $^{77}$Se NMR spectrum (95 MHz, THF-$d_8$) of [K(THF)$_3$][Al(NON$^{\text{Dipp}}$)(SeC(O)Ph$_2$)] [K(THF)][3-Se]
Figure S22  ORTEP (displacement ellipsoids 30 %) of the asymmetric unit of [K(THF)$_3$][Al(NON(Dipp)(SeC(0)Ph$_2$)][K(THF)][3-Se]
Synthesis of K[Al(NON\text{Dipp})(\text{OC(Ph)}\text{S})] ([K]\text{[4-S]})

A solution of benzaldehyde (34 mg, 0.32 mmol) in C\text{6}D\text{6} was added to K[Al(NON\text{Dipp})(\text{S})] (96 mg, 0.16 mmol) in an NMR tube fitted with a Teflon tap. The reaction was instantaneous, and the solvent was removed \textit{in vacuo} and replaced with toluene. Slow evaporation at room temperature yielded colourless crystals. Yield 47 mg, 36 %.

\begin{array}{l}
\text{\textsuperscript{1}H NMR (500 MHz, C\text{6}D\text{6}): } \delta 7.64 (d, J = 8.3, 4H, C\text{6}H\text{5}), 7.20 – 7.08 (m, 9H, C\text{6}H\text{5}, C\text{6}H\text{3}), 6.77 (d, J = 7.6, 2H, C\text{6}H\text{3}), 6.52 (t, J = 7.6, 1H, C\text{6}H\text{3}), 6.38 (s, 2H, PhCHO), 4.52 (sept, J = 6.8, 2H, CHMe\text{2}), 4.31 (sept, J = 6.8 Hz, 2H, CHMe\text{2}), 1.36 – 1.31 (m, 18H, CHMe\text{2})\text{†}, 1.29 (d, J = 6.8, 6H, CHMe\text{2}), 0.63 (s, 6H, SiMe\text{2}), 0.58 (s, 6H, SiMe\text{2}). \text{* overlapping with solvent peak; † overlapping doublets from isopropyl substituents.}
\end{array}

\begin{array}{l}
\text{\textsuperscript{13}C\{\textsuperscript{1}H\} NMR (126 MHz, C\text{6}D\text{6}): } \delta 149.4, 149.3, 147.5, 146.0, 145.0, 127.4, 126.5, 123.8, 123.7, 123.0, 122.1 (C\text{6}H\text{5}, C\text{6}H\text{3}), 84.8 (PhCHO), 27.9, 27.8 (CHMe\text{2}), 27.2, 26.2, 25.6, 24.7 (CHMe\text{2}), 3.6, 2.7 (SiMe\text{2}).
\end{array}

Despite repeated attempts we were unable to obtain accurate elemental analysis for K[4-S].
Figure S23  \(^1\)H NMR spectrum (500 MHz, C\(_6\)D\(_6\)) of K[Al(NON\(^{dipp}\})(\{OC(H)Ph\}_2S)] K[4-S]
Figure S24  $^{13}$C($^1$H) NMR spectrum (125 MHz, C$_6$D$_6$) of K[Al(NON$^{Dipp}$)(OC(H)Ph)$_2$S] K[4-S]
Figure S25  ORTEP (displacement ellipsoids 30 %) of the asymmetric unit of K[Al(NON^{Dipp})(OC(H)Ph)_2S)] K[4-S]
Synthesis of K[Al(NONDipp)(OC(H)Ph)2Se)] ([K][4-Se])

The reaction was performed as outlined for [K][4-S], using 16 mg of benzaldehyde (0.15 mmol) and 47 mg of K[Al(NONDipp)(Se)] (0.07 mmol). Slow evaporation from a toluene solution at room temperature yielded colourless crystals. Yield 35 mg, 56%.

Anal. Calc’d for C42H58AlKN2O3SeSi2 (840.13): C, 60.04; H, 6.96; N, 3.33 %. Found: C, 59.12; H, 6.79; N, 3.25 %.

1H NMR (500 MHz, C6D6): δ 7.61 (d, J = 8.4, 2H, C6H5), 7.16 – 7.08 (m, 7H, C6H5, C6H3), 7.00 (t, J = 7.6, 2H, C6H3), 6.93 (s, 2H, PhCHO), 6.81 (d, J = 7.6, 2H, C6H3), 6.56 (t, J = 7.6, 1H, C6H3), 4.50 (sept, J = 7.2, 4H, CHMe2), 4.24 (sept, J = 6.8, 4H, CHMe2), 1.38 (d, J = 6.8, 6H, CHMe2), 1.35 (d, J = 6.8, 6H, CHMe2), 1.30 (d, J = 6.8, 6H, CHMe2), 1.25 (d, J = 6.8, 6H, CHMe2), 0.61 (s, 6H, SiMe2), 0.56 (s, 6H, SiMe2).

13C{1H} NMR (126 MHz, C6D6): δ 149.4, 149.1, 147.4, 146.3, 146.0, 144.6, 127.1, 126.0, 123.8, 123.7, 123.1, 122.3 (C6H5, C6H3), 83.2 (PhCHO), 27.9, 27.8 (CHMe2), 27.2, 26.2, 25.7, 24.7 (CHMe2), 3.5, 2.7 (SiMe2).
Figure S26  
$^1$H NMR spectrum (500 MHz, C$_6$D$_6$) of K[Al(NON$^{\text{Dipp}}$)((OC(H)Ph)$_2$Se)] K[4-Se]
Figure S27  Expansion of $^1$H OC(H)Ph resonance from K[Al(NONDipp)(OC(H)Ph)Se)] K[4-Se] showing $^2J_{SeH}$ coupling
$^{13}$C($^1$H) NMR spectrum (125 MHz, C$_6$D$_6$) of K[Al(NON$^{Dipp}$)((OC(H)Ph)$_2$Se)] K[4-Se]
Figure S29  

$^{77}\text{Se}$ NMR spectrum (95 MHz, C$_6$D$_6$) of K[Al(NON$^\text{Dipp}$)$_2$]$_2$[OC(Ph)$_2$Se] K[4-Se]
Figure S30  ORTEP (displacement ellipsoids 30%) of the asymmetric unit of K[Al(NON\text{Dipp})_{2}((OC(H)Ph)_{2}Se)] K[4-Se]
Comparison of bond lengths in thio- and selenocarbonate ligands from \([\text{K(Et}_2\text{O)}][2-\text{S}]\) and \([\text{K(THF)}][2-\text{Se}]\) with examples of \([\text{SC(O)}\text{O}]^2-\) and \([\text{SeC(O)}\text{O}]^2-\) ligands from uranium compounds, \([[(\text{AdArO})_3\text{N}]_2\text{U}\mu-\eta^1:\chi^2-\text{EC(O)}\text{O}}\) (where \([(\text{AdArO})_3\text{N}]^3-\) is the trianion of tris(2-hydroxy-3-adamantyl-5-methylbenzyl)amine).\(^{[54]}\)

**Figure S31**

\(\text{[K(Et}_2\text{O)}][2-\text{S}]\)

\(\begin{align*}
a &= 1.317(4) \ \text{Å} & 1.290(4) \ \text{Å} \\
b &= 1.229(4) \ \text{Å} & 1.236(4) \ \text{Å} \\
c &= 1.766(3) \ \text{Å} & 1.783(3) \ \text{Å}
\end{align*}\)

\(\text{[K(THF)}][2-\text{Se}]\)

\(\begin{align*}
a &= 1.318(3) \ \text{Å} \\
b &= 1.227(3) \ \text{Å} \\
c &= 1.929(2) \ \text{Å}
\end{align*}\)

\(\begin{align*}
a &= 1.283(5) \ \text{Å} \\
b &= 1.262(5) \ \text{Å} \\
c &= 1.742(5) \ \text{Å}
\end{align*}\)

\(\begin{align*}
a &= 1.285(8) \ \text{Å} \\
b &= 1.252(8) \ \text{Å} \\
c &= 1.925(7) \ \text{Å}
\end{align*}\)
Crystallographic Details

Crystals were covered in inert oil and suitable single crystals were selected under a microscope and mounted on an Agilent SuperNova diffractometer fitted with an EOS S2 detector. Data were collected at 120 K (unless indicated otherwise) using focused microsource Cu Kα radiation at 1.54184 Å. Intensities were corrected for Lorentz and polarisation effects and for absorption using multi-scan methods. Space groups were determined from systematic absences and checked for higher symmetry. All structures were solved using direct methods with SHELXS, refined on F² using all data by full matrix least-squares procedures with SHELXL-97 within the WinGX program. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions or manually assigned from residual electron density where appropriate, unless otherwise stated. The functions minimized were $\Sigma w(F_2-F_2c)$, with $w = [a2(F_2o) + aP2 + bP]^{-1}$, where $P = [max(Fo)^2 + 2F_2c]/3$. The isotropic displacement parameters are 1.2 or 1.5 times the isotropic equivalent of their carrier atoms.

Additional Details:

$[K(\text{Al(NON}_3\text{pp})(S))]_4 \{K[1-S]\}_2$: Several poorly defined solvent molecules are present in the unit cell, with electron density patterns indicative of linear and cyclic arrangements of carbon atoms. From the experimental procedure, the crystals have been exposed to both hexane and toluene and the formula was therefore approximated as containing 3 x hexane and 3 x toluene. This solvents were treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.

$[K(2.2.2\text{-crypt})][\text{Al(NON}_3\text{pp})(S)] [K(2.2.2\text{-crypt})][1-S]$: Data was collected at 150 K. The THF solvate is poorly defined. The oxygen atoms was modelled over two positions with each atom isotropic.

$[K(\text{Et}_2\text{O})][\text{Al(NON}_3\text{pp})(\text{SC(O)}\text{O}) ] [K(\text{Et}_2\text{O})][2-S]$: Data was collected at 150 K. The ether molecules are highly disordered. A model was used that treated two separate molecules as disorder over two positions and a third ether molecule as disordered over three positions. Several SIMU and DELU restraints and EADP/EXYZ commands were used to obtain satisfactory models.

$[K(\text{THF})][\text{Al(NON}_3\text{pp})(\text{SeC(O)}\text{Ph}_2)][K(\text{THF})][3-Se]$: Two of the coordinated THF molecules are disordered and were modelled with two positions for the affected methylene groups (three on one molecule and one on the second molecule).

$K[\text{Al(NON}_3\text{pp})(\text{OC(H)}\text{Ph}_2)] [K[4-S]$ and $K[\text{Al(NON}_3\text{pp})(\text{OC(H)}\text{Ph}_2)] [K[4-Se]$: Each crystal structure contains a poorly resolved, rotationally disordered toluene solvate. They were modelled over 2 positions with fixed geometry for the aromatic ring (AFIX66) and all carbon atoms refined isotropically. The maximum residual electron density is located in this region and may correspond to a third (not modelled) orientation of the molecule.
| Table S1 | Crystal structure and refinement data for [K\{Al(NON\textsuperscript{2.2.2-crypt})\}4 [K\{1-S\}]4, [K\{2.2.2-crypt\}] [Al(NON\textsuperscript{2.2.2-crypt})\}4 [K\{1-S\}]4, [K\{Et\textsubscript{2}O\}] [Al(NON\textsuperscript{2.2.2-crypt})\} [K\{THF\}] [2-Se] | | | |
| Empirical formula | C\textsubscript{53}H\textsubscript{355}Al\textsubscript{4}K\textsubscript{4}N\textsubscript{6}O\textsubscript{8}S\textsubscript{8}Si\textsubscript{8} | C\textsubscript{52}H\textsubscript{35}AlKN\textsubscript{4}O\textsubscript{8}S\textsubscript{8}Si\textsubscript{8} | C\textsubscript{61}H\textsubscript{35}Al\textsubscript{2}K\textsubscript{2}N\textsubscript{6}O\textsubscript{8}S\textsubscript{8}Si\textsubscript{8} | C\textsubscript{60}H\textsubscript{35}Al\textsubscript{2}K\textsubscript{2}N\textsubscript{6}O\textsubscript{8}S\textsubscript{8}Si\textsubscript{8} |
| CCDC Number | 2038726 | 2038727 | 2038728 | 2038729 |
| Mass (g/mol) | 1029.57 | 1029.57 | 1546.48 | 1776.42 |
| T [K] | 120.0(1) | 150.0(2) | 150.0(1) | 120.0(1) |
| Crystal size [mm] | 0.28 x 0.21 x 0.12 | 0.15 x 0.12 x 0.11 | 0.34 x 0.25 x 0.17 | 0.22 x 0.09 x 0.07 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | P\textsubscript{2}/c (No.14) | P\textsubscript{1} (No.2) | P\textsubscript{2} (No.4) | P\textsubscript{2}/n (alternative No.14) |
| a [Å] | 25.01159(15) | 10.0626(4) | 12.27766(9) | 15.4374(2) |
| b [Å] | 19.41543(12) | 17.1004(6) | 24.87997(17) | 13.47603(18) |
| c [Å] | 33.7313(2) | 17.2361(6) | 14.90060(11) | 22.5971(3) |
| \(\alpha\) [°] | 90 | 88.851(3) | 90 | 90 |
| \(\beta\) [°] | 100.8841(6) | 83.037(3) | 94.3187(6) | 93.2318(13) |
| \(\gamma\) [°] | 90 | 84.293(3) | 90 | 90 |
| V [Å\textsuperscript{3}] | 16085.64(18) | 2929.34(17) | 4538.73 | 4693.51(12) |
| Z | 2 | 2 | 2 | 2 |
| D\textsubscript{calc} [mg m\textsuperscript{-3}] | 1.181 | 1.167 | 1.132 | 1.257 |
| Absorption coefficient [mm\textsuperscript{-1}] | 2.647 | 2.062 | 2.447 | 2.894 |
| \(\delta\) range for data collection [°] | 3.489 to 73.471 | 3.649 to 73.337 | 3.553 to 73.5958 | 3.8207 to 73.4183 |
| Reflections collected | 116133 | 40119 | 63075 | 36167 |
| Independent reflections | 32116 [R\textsubscript{int} 0.031] | 11663 [R\textsubscript{int} 0.049] | 17697 [R\textsubscript{int} 0.049] | 9384 [R\textsubscript{int} 0.035] |
| Reflections with \(I > 2\sigma(I)\) | 26321 | 8652 | 17308 | 8048 |
| Data/restraints/parameters | 32116 / 0 / 1345 | 11663 / 0 / 616 | 17697 / 19 / 944 | 9384 / 0 / 499 |
| Final R indices \([I > 2\sigma(I)]\) | \(R_1 = 0.039, wR_2 = 0.112\) | \(R_1 = 0.061, wR_2 = 0.138\) | \(R_1 = 0.036, wR_2 = 0.096\) | \(R_1 = 0.035, wR_2 = 0.087\) |
| Final R indices \([I > 2\sigma(I)]\) \textsuperscript{a} | \(R_1 = 0.049, wR_2 = 0.106\) | \(R_1 = 0.088, wR_2 = 0.151\) | \(R_1 = 0.037, wR_2 = 0.097\) | \(R_1 = 0.044, wR_2 = 0.092\) |
| GOOF on F\textsuperscript{2} | 1.024 | 1.083 | 1.022 | 1.006 |
| Largest diff. peak/hole [eÅ\textsuperscript{3}] | 0.36 and −0.37 | 0.57 and −0.34 | 0.66 and −0.29 | 0.57 and −0.64 |
Table S2 Crystal structure and refinement data for [K(Al(NON^dipp)(SeC(O)Ph_2)] [K][3-Se], [K(THF)]_3[Al(NON^dipp)(SeC(O)Ph_2)] [K][3-Se], K[Al(NON^dipp)((OC(H)Ph)_2)S] [K][4-Se] and K[Al(NON^dipp)((OC(H)Ph)_2)S] [K][4-Se]

|                          | [K][3-Se]               | [K][3-Se]               | [K][4-Se]               | [K][4-Se]               |
|--------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| **Empirical formula**    | C_{2}H_{2}AlKN_{2}O_{3}Si_{2} | C_{2}H_{2}AlKN_{2}O_{3}Si_{2} | C_{2}H_{2}AlKN_{2}O_{3}Si_{2} | C_{2}H_{2}AlKN_{2}O_{3}SeSi_{2} |
| **CCDC Number**          | 2097188                 | 2097189                 | 2097190                 | 2097191                 |
| **M**                    | 837.31                  | 1026.41                 | 885.35                  | 932.25                  |
| **T [K]**                | 122(2)                  | 120.0(1)                | 120.0(1)                | 120.0(1)                |
| **Crystal size [mm]**    | 0.18 x 0.13 x 0.05      | 0.14 x 0.08 x 0.06      | 0.34 x 0.25 x 0.17      | 0.45 x 0.31 x 0.11      |
| **Space group**          | Monoclinic              | Monoclinic              | Monoclinic              | Monoclinic              |
| **CCDC Number**          | P2_1/c (No.14)          | P2_1/n (alternative No.14) | P2_1/n (alternative No.14) | P2_1/n (alternative No.14) |
| **a [Å]**                | 15.4597(16)             | 9.75833(9)              | 14.78551(10)            | 14.84213(8)             |
| **b [Å]**                | 12.38750(13)            | 31.8983(3)              | 13.04163(7)             | 13.02613(7)             |
| **c [Å]**                | 24.7548(3)              | 17.54162(15)            | 25.96015(16)            | 26.00620(15)            |
| **α [°]**                | 90                      | 90                      | 90                      | 90                      |
| **β [°]**                | 90.4615(10)             | 92.6949(8)              | 104.1317(6)             | 103.7250(5)             |
| **γ [°]**                | 90                      | 90                      | 90                      | 90                      |
| **V [Å^3]**              | 4740.57(9)              | 5454.21(8)              | 4854.33(5)              | 4884.35(4)              |
| **Z**                    | 4                       | 4                       | 4                       | 4                       |
| **D_{calc} [mg m^{-3}]** | 1.173                   | 1.25                    | 1.211                   | 1.268                   |
| **Absorption coefficient [mm^{-1}]** | 2.351               | 2.548                    | 2.327                   | 2.765                   |
| **θ range for data collection [°]** | 3.568 to 73.5249     | 3.7476 to 73.5402       | 3.3899 to 73.4985       | 3.3929 to 73.5902       |
| **Reflections collected** | 36321                   | 40652                   | 66239                   | 62964                   |
| **Independent reflections** | 9498 [R_{int} 0.026] | 10877 [R_{int} 0.027] | 9751 [R_{int} 0.028] | 9821 [R_{int} 0.030] |
| **Reflections with \( l > 2σ(l) \)** | 8559                   | 9743                    | 8999                    | 9387                    |
| **Data/restraints/parameters** | 9498 / 0 / 510          | 10877 / 0 / 632           | 9751 / 0 / 514          | 9821 / 0 / 514          |
| **Final R indices \( l > 2σ(l) \)** | \( R_1 = 0.031, \ W_{R1} = 0.078 \) | \( R_1 = 0.031, \ W_{R1} = 0.076 \) | \( R_1 = 0.048, \ W_{R1} = 0.131 \) | \( R_1 = 0.044, \ W_{R1} = 0.113 \) |
| **Final R indices \( l > 2σ(l) \)** | \( R_1 = 0.036, \ W_{R1} = 0.081 \) | \( R_1 = 0.036, \ W_{R1} = 0.079 \) | \( R_1 = 0.051, \ W_{R1} = 0.134 \) | \( R_1 = 0.045, \ W_{R1} = 0.114 \) |
| **GOOF on \( F^2 \)**   | 1.027                   | 1.023                   | 1.057                   | 1.025                   |
| **Largest diff. peak/hole \[e.Å^{-3}\]** | 0.33 and –0.34          | 0.91 and –0.47          | 1.52 and –0.76          | 2.14 and –0.79          |
Computational Methods

DFT calculations were run with Gaussian 16 (A.03). The Al, Si, and S centres were described with the Stuttgart RECPs and associated basis sets, and 6-31G** basis sets were used for all other atoms (BS1). A polarization function was also added to Al ($\zeta_d = 0.190$) and Si ($\zeta_d = 0.284$) and S ($\zeta_d = 0.503$). Initial BP86 optimizations were performed using the ‘grid = ultrafine’ option, with all stationary points being fully characterized via analytical frequency calculations as either minima (all positive eigenvalues). The Quantum Theory of Atoms in Molecules (QTAIM, AIMALL program) and Natural Bonding Orbital (NBO3) analyses were performed on the BP86-optimized geometries of the [Al(NON(Dipp))(E)]$^-$ anions. All energies were recomputed with a larger basis set featuring 6-311++G** on all atoms. Corrections for the effect of toluene ($\epsilon = 2.2706$) solvent were run using the polarizable continuum model and BS1. Single-point dispersion corrections to the BP86 results employed Grimme’s D3 parameter set with Becke-Johnson damping as implemented in Gaussian.
Figure S32 Frontier orbitals (LUMO, HOMO, HOMO–1) for the anions [Al(NON$^{Dipp}$)(E)]$^-$ (E = O, S, Se, Te).
Table S3  Molecular Orbital Coefficients for HOMO / HOMO–1 of $\text{K}[\text{Al}(\text{NON}^{\text{Dipp}})\text{E}]$ (E = O, S, Se, Te)

| Complex                     | Atom | Atomic Orbital | HOMO-1   | HOMO   |
|-----------------------------|------|----------------|----------|--------|
| $\text{K}[\text{Al}(\text{NON}^{\text{Dipp}})\text{(O)}]$ | O    | 2$p_x$         | -0.32153 | 0.43893|
|                             |      | 2$p_y$         | 0.35718  | 0.33719|
|                             |      | 2$p_z$         | -0.24282 | 0.04177|
|                             |      | 3$p_x$         | -0.23005 | 0.31385|
|                             |      | 3$p_y$         | 0.26297  | 0.24063|
|                             |      | 3$p_z$         | -0.16609 | 0.02241|
|                             | Al   | 4$p_x$         | -0.12337 | 0.10408|
|                             |      | 4$p_y$         | 0.00758  | 0.01487|
|                             |      | 4$p_z$         | -0.09904 | 0.03581|
| $\text{K}[\text{Al}(\text{NON}^{\text{Dipp}})\text{(S)}]$ | S    | 3$p_x$         | 0.48992  | 0.33318|
|                             |      | 3$p_y$         | -0.25812 | 0.48481|
|                             |      | 4$p_x$         | 0.29209  | 0.20249|
|                             |      | 4$p_y$         | -0.15919 | 0.29243|
|                             | Al   | 3$p_y$         | 0.06323  | -0.07262|
|                             |      | 4$p_x$         | 0.02145  | 0.00201|
| $\text{K}[\text{Al}(\text{NON}^{\text{Dipp}})\text{(Se)}]$ | Se   | 3$p_x$         | 0.46389  | 0.29125|
|                             |      | 3$p_y$         | -0.19724 | 0.42146|
|                             |      | 3$p_z$         | 0.20287  | -0.19510|
|                             |      | 4$p_x$         | -0.33246 | -0.20979|
|                             |      | 4$p_y$         | -0.14881 | -0.29935|
|                             |      | 4$p_z$         | -0.13505 | 0.14318|
|                             | Al   | 3$p_x$         | 0.07791  | 0.02196|
|                             |      | 3$p_y$         | -0.06168 | 0.07524|
|                             |      | 4$p_z$         | 0.07005  | 0.00638|
| $\text{K}[\text{Al}(\text{NON}^{\text{Dipp}})\text{(Te)}]$ | Te   | 3$p_x$         | -0.05363 | 0.45839|
|                             |      | 3$p_y$         | 0.43911  | 0.05422|
|                             |      | 4$p_x$         | -0.05107 | 0.45873|
|                             |      | 4$p_y$         | 0.44517  | 0.05602|
|                             |      | 5$p_x$         | -0.01903 | 0.11185|
|                             |      | 5$p_y$         | 0.10200  | 0.00560|
|                             | Al   | 4$p_x$         | 0.02520  | -0.07428|
|                             |      | 4$p_y$         | -0.15097 | 0.00216|

NOTE: NBO Molecular Orbital Coefficients greater than ±0.07 are emphasised (in bold font).
| Complex (Species)                     | Atom Pair | WBI $^a$ |
|--------------------------------------|-----------|----------|
| K[Al(NON$_{Dipp}$)(O)]               | Al–O      | 0.906    |
|                                      |           | (1.112)  |
| K[Al(NON$_{Dipp}$)(S)] (I$_K$)       | Al–S      | 1.145    |
|                                      |           | (1.297)  |
| C (K[3-S])                           | Al–S      | 0.5350   |
| H$_{cis}$ (K[4-S])                   | Al–S      | 0.059    |
| K[Al(NON$_{Dipp}$)(Se)]              | Al–Se     | 1.236    |
|                                      |           | (1.377)  |
| K[Al(NON$_{Dipp}$)(Te)]              | Al–Te     | 1.441    |
|                                      |           | (1.534)  |

$^a$ value in parentheses corresponds to the WBI for the anion calculated without the potassium counter-ion.
Table S5  
Relative energies (kcal mol\(^{-1}\)) for computed structures. Data in **bold** are those used in the manuscript. Values are quoted relative to A (K[1-S]).

| Ph\(_2\)CO | \(\Delta E_{\text{BSI}}\) | \(\Delta H_{\text{BSI}}\) | \(\Delta G_{\text{BSI}}\) | \(\Delta G_{\text{BSI}/\text{Et}_2\text{O}}\) | \(\Delta E_{6-311++G\ast\ast}\) | \(\Delta G_{\text{Et}_2\text{O}}\) |
|------------|----------------|----------------|----------------|----------------|----------------|----------------|
| A          | 0.0            | 0.0            | 0.0            | 0.0            | 0.0            | 0.0            |
| TS(A-B)    | 5.5            | 5.9            | 21.1           | 27.6           | 4.6            | 9.5            | **8.6**       |
| B          | 4.9            | 5.8            | 20.9           | 26.7           | 1.1            | 9.0            | **5.3**       |
| TS(B-C)    | 6.0            | 6.4            | 23.2           | 29.0           | 2.3            | 10.6           | **6.9**       |
| C          | -13.9          | -13.2          | 4.1            | 11.3           | -15.7          | -10.0          | **-11.9**     |
| TS(C-D)    | 17.9           | 18.9           | 52.4           | 61.4           | 1.0            | 25.4           | **8.5**       |
| D          | -3.1           | -1.5           | 32.9           | 43.4           | -17.9          | 3.7            | **-11.1**     |

| PhHCO      | \(\Delta E_{\text{BSI}}\) | \(\Delta H_{\text{BSI}}\) | \(\Delta G_{\text{BSI}}\) | \(\Delta G_{\text{BSI}/\text{C}_6\text{H}_6}\) | \(\Delta G_{\text{BSI}/\text{C}_6\text{H}_6+\text{D3BJ}}\) | \(\Delta E_{6-311++G\ast\ast}\) | \(\Delta G_{\text{C}_6\text{H}_6}\) |
|------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| A          | 0.0            | 0.0            | 0.0            | 0.0            | 0.0            | 0.0            | 0.0            |
| TS(A-E)    | -0.5           | 0.1            | 13.9           | 18.5           | 4.9            | 2.9            | **8.3**       |
| E          | -23.6          | -22.2          | -7.5           | -2.5           | -18.5          | -19.4          | **-14.2**     |
| TS(E-F)    | -21.4          | -19.2          | 10.4           | 17.1           | -13.1          | -13.9          | **-5.6**      |
| F          | -21.8          | -19.1          | 10.2           | 17.0           | -15.3          | -13.5          | **-7.0**      |
| TS(F-H)\(_{cis}\) | -17.9       | -15.7          | 15.2           | 21.4           | -10.4          | -10.1          | **-2.6**      |
| INT(F-H)\(_{cis}\) | -39.5      | -36.4          | -6.7           | 0.1            | -31.6          | -32.3          | **-24.4**     |
| \(H_{cis}\) | -41.9          | -38.8          | -8.5           | -1.9           | -34.3          | -34.9          | **-27.3**     |
| TS(H)\(_{cis-trans}\) | -19.0      | -16.8          | 12.9           | 18.4           | -10.8          | -12.2          | **-3.9**      |
| \(H_{trans}\) | -32.9          | -29.7          | 0.0            | 5.9            | -28.1          | -26.1          | **-21.3**     |
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Cartesian Coordinates and Computed Energies
(in Hartrees)

\[ \text{SCF (BP86) Energy} = -1299.8528777 \]
Enthalpy OK = -1299.185961
Enthalpy 298K = -1299.140204
Free Energy 298K = -1299.263213
Lowest Frequency = 14.5811 \text{ cm}^{-1}
Second Frequency = 24.2796 \text{ cm}^{-1}

\[
\begin{array}{cccc}
1 & S & 0.00003 & 0.00005 \to 2.94856 \\
2 & Si & -1.40323 & -0.65265 \to 1.97693 \\
3 & Si & 1.40332 & 0.65241 \to 1.97713 \\
4 & Al & 0.00000 & 0.00007 \to -0.84114 \\
5 & O & -0.00012 & 0.00012 \to 2.68067 \\
6 & N & -1.50819 & -0.12728 \to 0.29097 \\
7 & C & 1.50816 & 0.12723 \to 2.9105 \\
8 & C & -2.81119 & 0.15250 \to -0.25548 \\
9 & C & -3.31997 & 1.49109 \to -0.23352 \\
10 & C & -4.59928 & 1.75700 \to -0.75542 \\
11 & H & -4.97858 & 2.78574 \to -0.73999 \\
12 & C & -5.39234 & 0.73991 \to -1.29981 \\
13 & H & -6.38745 & 0.96498 \to -1.71004 \\
14 & C & -4.88982 & -0.56407 \to -1.33879 \\
15 & H & -5.49381 & -1.36237 \to -1.78631 \\
16 & C & -3.61276 & -0.88086 \to -0.83235 \\
17 & C & -2.46981 & 2.65003 \to 0.28528 \\
18 & H & -1.66125 & 2.20194 \to 0.88879 \\
19 & C & -3.24533 & 3.62950 \to 1.19063 \\
20 & H & -3.74261 & 3.10628 \to 2.02589 \\
21 & C & -2.55804 & 4.38179 \to 1.61792 \\
22 & H & -4.02314 & 4.18165 \to 0.63210 \\
23 & C & -1.81058 & 3.40088 \to -0.89664 \\
24 & H & -2.58140 & 3.87440 \to -1.53225 \\
25 & H & -1.13313 & 4.19580 \to -0.53265 \\
26 & H & -1.23282 & 2.71215 \to -1.53950 \\
27 & C & -3.11421 & -2.31964 \to -0.96436 \\
28 & H & -2.13967 & -2.37037 \to -0.45059 \\
29 & C & -4.06577 & -3.33225 \to -0.28870 \\
30 & H & -5.94998 & -3.36173 \to -0.79136 \\
31 & C & -6.64332 & -4.35255 \to -0.33475 \\
32 & H & -4.24608 & -3.08267 \to 0.77200 \\
33 & C & -2.87385 & -2.68889 \to -2.44622 \\
34 & H & -2.14113 & -1.99754 \to -2.89835 \\
35 & H & -2.48341 & -3.72034 \to -2.52894 \\
36 & C & -3.81446 & -2.63670 \to -0.32576 \\
37 & H & -2.88980 & -0.04093 \to 2.98622 \\
38 & H & -2.93976 & 1.06002 \to 2.99138 \\
39 & C & -3.83772 & -0.42153 \to 2.75115 \\
40 & H & -2.80255 & -0.38787 \to 4.03045 \\
41 & C & -1.25267 & -2.53594 \to 2.21004 \\
42 & H & -1.03238 & -2.76638 \to 3.26732 \\
43 & H & -2.18203 & -0.35944 \to 1.93003 \\
44 & C & -0.43377 & -2.94610 \to 1.59541 \\
45 & C & 1.25340 & 2.53569 \to 2.21076 \\
46 & H & 1.03316 & 2.76587 \to 3.26811 \\
47 & H & 2.18291 & 3.05901 \to 1.93092 \\
48 & H & 0.43463 & 2.94624 \to 1.59625 \\
49 & C & 2.88961 & 0.03991 \to 2.98635 \\
50 & C & 2.93728 & -1.06106 \to 2.99138 \\
51 & H & 3.83770 & 0.42013 \to 2.57130 \\
52 & H & 2.80254 & 0.38677 \to 4.03062 \\
53 & H & 2.81119 & -0.15234 \to -0.25546 \\
54 & C & 3.61270 & 0.88102 \to -0.83241 \\
55 & C & 4.88881 & 0.56424 \to -1.33899 \\
\end{array}
\]

HPCO
SCF (BP86) Energy = -345.568700604
Enthalpy OK = -345.455589
Enthalpy 298K = -345.454644
Free Energy 298K = -345.492725
Lowest Frequency = 122.5891 \text{ cm}^{-1}
Second Frequency = 208.5129 \text{ cm}^{-1}
SCF (BP86-D3BJ) Energy = -345.590746037
SCF (C6H6) Energy = -345.571192783
SCF (Et2O) Energy = -345.572491016
SCF (BS2) Energy = -345.622106507

O & -2.86337 & -0.39887 & -0.00011 \\
& -1.99941 & 0.47368 & 0.00006 \\
& -2.72637 & 1.56455 & 0.00011 \\
& -0.53708 & 0.21716 & 0.00006 \\
& -0.04798 & -1.10752 & 0.00006 \\
& 0.36461 & 1.30093 & 0.00002 \\
& 1.33077 & -1.34072 & 0.00001 \\
& 1.74661 & 1.06581 & 0.00004 \\
& 2.22796 & -0.25467 & -0.00004 \\
& -0.77386 & -1.92703 & 0.00010 \\
& -0.02654 & 2.32586 & 0.00003 \\
& 1.71498 & -2.36060 & 0.00000 \\
& 2.44861 & 1.90589 & -0.00009 \\
& 3.30734 & -0.44032 & -0.00008 \\

PhCO
SCF (BP86) Energy = -576.623309768
Enthalpy OK = -576.426282
Enthalpy 298K = -576.425337
Free Energy 298K = -576.4765233
Lowest Frequency = 42.1740 \text{ cm}^{-1}
Second Frequency = 64.3121 \text{ cm}^{-1}
SCF (BP86-D3BJ) Energy = -576.670272545
SCF (C6H6) Energy = -576.626243352
SCF (Et2O) Energy = -576.627839186
SCF (BS2) Energy = -576.769376491

S51
SCF (BP86) Energy = -1328.1790741
Enthalpy 0K = -1327.463513
Enthalpy 298K = -1327.590388
SCF (C6H6) Energy = -1905.09957584
Enthalpy 0K = -1904.79360898
Enthalpy 298K = -1904.80538885
SCF (Et2O) Energy = -1904.81240690
SCF (BS2) Energy = -3676.6061997

TS (A-B)
SCF (BP86) Energy = -1904.79360898
Enthalpy 0K = -1903.879397
Enthalpy 298K = -1903.878452
Free Energy 298K = -1904.031997
Lowest Frequency = -56.8502 cm⁻¹
Second Frequency = -6.3777 cm⁻¹
SCF (BP86-D3BJ) Energy = -1905.09957584
SCF (C6H6) Energy = -1904.80538885
SCF (Et2O) Energy = -1904.81240690
SCF (BS2) Energy = -3676.6061997

S52
SCF (BP86) Energy = -1904.79464076
Enthalpy OK = -1903.879574
Enthalpy 298K = -1903.878630
Free Energy 298K = -1904.032337
Lowest Frequency = 13.4380 cm⁻¹
Second Frequency = 20.1737 cm⁻¹
SCF (BP86-D3BJ) Energy = -1905.104756
SCF (C6H6) Energy = -1904.8159614
SCF (Et2O) Energy = -1904.8159614
SCF (BS2) Energy = -3676.6073232

B
| C   | H   | C   | C   | H   | 3.30869 | 1.04628 | 0.47421 |
|-----|-----|-----|-----|-----|---------|---------|---------|
| H   | 3.32144 |       |     |     |         |         |         |
| H   | 2.10263 | 5.37063 | -0.37535 |     |         |         |         |
| C   | 2.83217 | 6.13805 | -0.35202 |     |         |         |         |
| K   | -2.96322 | 2.19767 | -1.43504 |     |         |         |         |

| SCF (BP86) Energy = -1904.8246111 |
| Enthalpy 0K = -1903.908867 |
| SCF (BP86) Energy = -1905.1368109 |
| SCF (C6H6) Energy = -1904.8357157 |
| SCF (Et2O) Energy = -1904.84230352 |
| SCF (BS2) Energy = -3676.63711201 |

| S   | -0.14699 | 1.35051 | -1.67692 |
| Si  | -1.40595 | -2.96711 | 1.01006 |
| Si  | 1.35357 | -3.24277 | -0.37150 |
| Al  | 0.05253 | -0.32936 | -0.05091 |
| C   | -0.09084 | -3.79310 | 0.34565 |
| O   | 0.28841 | 1.19976 | 0.93964 |
| N   | -1.53815 | -1.36035 | 0.21676 |
| O   | 1.50898 | -1.50729 | -0.02051 |
| C   | -2.81290 | -0.93586 | -0.25344 |
| C   | -3.82660 | -0.45467 | 0.65335 |
| C   | -5.00663 | -0.05289 | 0.15492 |
| Al  | 0.09530 | 0.28342 | 0.86334 |
| C   | -5.38779 | -0.09576 | -1.21405 |
| C   | -6.37910 | 0.19659 | -1.57844 |
| O   | -4.40790 | -0.56534 | -2.10328 |
| C   | -6.44494 | -0.63726 | -3.17112 |
| C   | -3.13813 | 0.09122 | -1.65918 |
| C   | -3.60279 | -0.38600 | 2.16592 |
| C   | -2.54146 | -0.62724 | 2.34250 |
| C   | -3.86641 | 1.02207 | 2.74361 |
| C   | -3.23907 | 1.78920 | 2.26021 |
| C   | -3.63415 | 1.04094 | 3.82268 |
| C   | -4.92527 | 1.32016 | 2.63392 |
| C   | -4.74757 | -1.41876 | 2.91326 |
| C   | -5.55342 | -1.19582 | 2.77817 |
| C   | -4.26839 | -1.39726 | 3.99687 |
| C   | -4.30700 | -2.44549 | 2.55440 |
| C   | -2.17775 | 1.58545 | -2.69002 |
| C   | -1.19031 | 1.66078 | 2.20360 |
| C   | -2.01823 | -0.72577 | -3.96122 |
| C   | -2.95619 | -0.66722 | -4.54402 |
| C   | -1.25706 | -1.17312 | -4.62403 |
| C   | -1.68846 | 0.30002 | -3.72354 |
| C   | -2.62331 | -3.01751 | -3.07147 |
| C   | -2.69331 | -3.66817 | -2.18631 |
| C   | -1.90344 | -3.47218 | -3.77385 |
| C   | -3.61380 | -3.00276 | -3.56119 |
| C   | -1.10353 | -2.87002 | 2.88352 |
| C   | -0.69811 | 3.38376 | 3.22974 |
| C   | -2.03286 | -2.67535 | 3.44355 |
| C   | -0.37599 | -2.80506 | 3.14505 |
| C   | -2.93457 | -4.04370 | 0.66453 |
| C   | -2.74343 | -4.68054 | -0.21441 |
| C   | -3.84914 | -3.45999 | 0.47450 |
| C   | -3.12470 | -4.71188 | 1.52201 |
| C   | -3.76284 | 4.23393 | 0.36726 |
| C   | -3.76284 | -4.20089 | 1.46789 |
| C   | 3.76245 | -3.84857 | 0.03276 |
| C   | 2.70377 | 5.28867 | 0.0569 | 2.11754 | 3.70360 | 2.20751 |

| C   | SCF (BP86) Energy = -1904.8246111 |
| Enthalpy 0K = -1903.908867 |
| SCF (BP86) Energy = -1905.1368109 |
| SCF (C6H6) Energy = -1904.8357157 |
| SCF (Et2O) Energy = -1904.84230352 |
| SCF (BS2) Energy = -3676.63711201 |
SCF (Et2O) Energy =

SCF (C6H6) Energy =

2481.80984268

2481.41657199

2481.40943262

SCF (HS2) Energy = -4253.35006683
SCF (BP86) Energy = -2481.43056624
Enthalpy OK = -2480.315649
| H   | 5.76068 | -0.78403 | -0.32352 | SCF (C6H6) Energy = -1673.7595657 |
| H   | -6.73812 | -1.23048 | -0.53824 | SCF (Et2O) Energy = -1673.76580584 |
| C   | -5.19029 | 0.15009 | -1.20067 | SCF (BS2) Energy = -3445.50925524 |
| H   | -5.73411 | 0.43602 | -2.10852 |
| C   | -3.95719 | 0.77724 | -0.91997 |
| C   | -3.16098 | -0.95136 | 2.48195 |
| H   | -2.13923 | -0.53734 | 2.48192 |
| C   | -3.05479 | -2.48783 | 2.61147 |
| H   | -4.35581 | -2.96584 | 3.48713 |
| H   | -2.52134 | -2.75721 | 3.53844 |
| H   | -2.48234 | -2.92691 | 1.77658 |
| C   | -3.91757 | -0.39222 | 3.70093 |
| H   | -3.99230 | 0.70654 | 3.69007 |
| C   | -3.39519 | -0.68341 | 4.63765 |
| H   | -4.94531 | -0.79560 | 3.76178 |
| C   | -3.45421 | 1.83547 | -1.89733 |
| H   | -2.64566 | 2.37333 | -1.37918 |
| C   | -2.85013 | 1.18016 | -3.15803 |
| H   | -1.99618 | 0.55605 | -2.89223 |
| H   | -2.48814 | 1.94531 | -3.86759 |
| H   | -3.60687 | 0.57199 | -3.68989 |
| C   | -4.53466 | 2.86567 | -2.28952 |
| H   | -5.32985 | 2.42120 | -2.91511 |
| H   | -4.07596 | 3.68000 | -2.87589 |
| C   | -5.01436 | 3.14442 | -1.40406 |
| H   | 0.97703 | -1.69110 | 1.43053 |
| C   | 0.44343 | -2.17547 | 2.80617 |
| H   | 0.86611 | -1.21869 | 3.77404 |
| C   | -0.12671 | -0.16229 | 3.50179 |
| C   | -0.30394 | -1.61057 | 5.06589 |
| H   | -0.56163 | -0.84571 | 5.80676 |
| H   | -0.35486 | -2.97043 | 5.40940 |
| C   | -0.00864 | -3.93449 | 4.44720 |
| H   | -0.04011 | -4.99989 | 4.70024 |
| C   | 0.39304 | -3.54122 | 3.16205 |
| H   | 0.68167 | -3.30614 | 2.43580 |
| C   | 0.33950 | -1.80772 | -1.51673 |
| C   | -0.49507 | -2.52562 | -2.61566 |
| C   | -0.89700 | -3.88060 | -2.54348 |
| C   | -0.60448 | -4.48468 | -1.67681 |
| C   | -1.66139 | -4.46012 | -3.57472 |
| H   | -1.95681 | -5.51276 | -3.50180 |
| C   | -2.02155 | -3.70215 | -4.70172 |
| H   | -2.60900 | -4.15429 | -5.50761 |
| H   | -1.59710 | -2.36460 | -4.79494 |
| C   | 1.84902 | -1.77002 | -5.67957 |
| H   | 0.84118 | -1.78530 | -3.76283 |
| H   | -0.50383 | -0.74833 | -3.83340 |
| C   | 2.47094 | -2.10464 | 1.35576 |
| C   | 3.44559 | -1.14300 | 1.68279 |
| C   | 2.89341 | -3.42252 | 1.09934 |
| C   | 4.80035 | -1.49422 | 1.77851 |
| C   | 4.24815 | -3.77636 | 1.19236 |
| C   | 5.20926 | -2.81505 | 1.54354 |
| C   | 3.13658 | -0.10920 | 1.83506 |
| C   | 2.16055 | -4.17528 | 0.78628 |
| C   | 5.53767 | -0.72343 | 2.02774 |

**TS (A-E)**

SCF (BP66) Energy = -1673.74863875

Enthalpy OK = -1672.917974

Enthalpy 298K = -1672.917029

Free Energy 298K = -1673.060994

Lowest Frequency = -84.5337 cm⁻¹

Second Frequency = 9.1472 cm⁻¹

SCF (BP66-D3BJ) Energy = -1674.01484000

| S58 |
SCF (C6H6) Energy =

Lowest Frequency = 9.6952

Enthalpy 298K =

\[
\begin{align*}
\text{H} & \quad 1.08616 & 4.46711 & 0.95908 \\
\text{C} & \quad 0.1891 & 4.84023 & -0.58120 \\
\text{C} & \quad 1.08616 & 4.6711 & -1.08663 \\
\text{C} & \quad 1.1458 & 2.50235 & 0.43391 \\
\text{K} & \quad -2.92911 & 1.88467 & -0.57022 \\
\end{align*}
\]

SCF (BP86) Energy = -1673.78543001

Enthalpy OK = -1672.953567

Enthalpy 298K = -1672.952622

Free Energy 298K = -1673.095059

Lowest Frequency = 9.6952 cm⁻¹

Second Frequency = 29.9610 cm⁻¹

SCF (BP86-D3BJ) Energy =

1674.05523107

SCF (C6H6) Energy = -1673.79583529

SCF (Et2O) Energy = -1673.80176615

SCF (BS2) Energy = -3445.54474318

S = 0.38602 1.44383 -0.83550
Si = -0.07140 -3.04454 0.89326
Si = 2.50707 -2.15458 -0.50506
Al = 0.24784 -0.04170 -0.12599
O = 1.45668 -3.23590 0.20304
O = -0.20674 1.46791 0.82246
N = 0.81937 -1.57438 0.18795
N = 2.05580 -0.51054 -0.08911
C = 2.21954 -1.52478 -0.08188
C = 3.16803 -1.22182 0.95876
C = 4.54877 -1.10894 0.64892
H = 5.25185 -0.89418 1.45711
C = 5.01853 -1.28310 -0.65911
H = -6.08962 -1.20714 -0.87848
C = -4.10285 -1.60764 -1.67190
C = -4.47045 -1.78581 -2.68942
C = -2.72291 -1.75221 -1.41370
C = -2.74006 -1.02020 2.41306
C = -1.64655 -1.14506 2.44404
C = -3.04749 0.40620 2.92015
C = -2.48762 1.15707 2.33731
C = -2.73705 0.51615 3.97394
SCF (BP86) Energy = -2019.37934393
Enthalpy OK = -2018.430865
Enthalpy 298K = -2018.429921
Free Energy 298K = -2018.586463
Lowest Frequency = 13.1562 cm⁻¹
Second Frequency = 18.5187 cm⁻¹
SCF (BP86-D3BJ) Energy = -
SCF (C6H6) Energy = -2019.38938201
SCF (Et2O) Energy = -2019.39509552
SCF (BS2) Energy = -3791.22740967
SCF (B3LYP) Energy = -2019.38325836
Enthalpy OK = -2018.434691
Enthalpy 298K = -2018.437346
Free Energy 298K = -2018.589415
Lowest Frequency = 13.5058 cm⁻¹
Second Frequency = 23.3818 cm⁻¹
SCF (B3LYP-D3BJ) Energy = -

H

S

H

C

H

H

H

H

H

H

H

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H
H  3.37683  -0.11803  -2.76132
H  3.54700  1.50300  -3.49096
C  0.50489  2.15856  -4.41359
H  0.85866  1.86123  -5.41574
H  0.91752  3.15879  -4.19508
H  -0.59191  2.24156  -4.41459
C  -1.26583  -2.94140  -3.83344
H  -1.39975  -2.80641  -4.92040
H  -2.12423  -3.52481  -3.76131
H  -0.34600  -3.52486  -3.67313
C  -2.40013  -0.10391  -3.86074
H  -2.47146  0.88667  -3.38200
H  -3.41064  -0.53997  -3.89942
H  -2.06299  0.04437  -4.90180
C  -2.04100  -2.15688  -0.43159
C  -3.40838  -1.79647  -0.14781
C  -4.18497  -2.58993  0.72327
H  -5.22237  -2.29632  0.92072
C  -3.68047  -3.75619  1.31333
H  -4.30703  -4.36874  1.97135
C  -2.37418  -4.14969  0.99563
H  -1.98363  -5.08769  1.40667
C  -1.54970  -3.39697  0.13656
C  -4.10575  -0.62072  -0.83127
H  -3.32704  -0.03128  -1.34223
C  -4.85242  0.31533  0.14263
H  -5.67572  -0.20396  0.66526
H  -5.30099  1.15834  -0.40980
H  -4.17929  0.74227  0.90297
C  -5.10450  -1.15617  -1.88789
H  -4.62639  -1.86206  -2.58678
H  -5.53789  -0.32723  -2.47447
H  -5.92679  -1.69375  -1.39885
C  -0.17149  -3.96965  -0.19004
H  0.39995  -3.18504  -0.71330
C  0.60692  -4.40865  1.07152
H  0.62823  -3.62976  1.85316
H  1.65436  -4.65173  0.81352
H  0.17039  -5.31767  1.52094
C  -0.30161  -5.18884  -1.13592
H  -0.84578  -6.01140  -0.63772
H  -0.69693  -5.56822  -2.41162
H  -0.84537  -4.93893  -2.05837
C  0.17906  0.82614  2.28354
H  0.95005  1.50833  1.87805
H  -0.78152  1.64121  3.14932
C  -2.16529  1.66397  2.88999
C  -2.53711  1.14813  1.99618
C  -3.05089  2.38056  3.71804
H  -4.12297  2.38970  3.48925
C  -2.55711  3.10320  4.81216
H  -3.23922  3.66786  5.45657
C  -1.17151  3.11036  5.06431
H  -0.77346  3.68236  5.90963
H  -0.29534  2.38465  4.24845
H  0.77735  2.36367  4.46598
H  2.27155  -1.61787  0.76377
H  1.63743  -1.83025  1.64045
C  3.67693  -1.99535  0.81500
C  4.20194  -2.50025  2.03185
H  3.56020  -2.51697  2.91920
C  5.53241  -2.92399  2.09874
H  5.93926  -3.30197  3.04196
C  6.35059  -2.85466  0.95503
H  7.39292  -3.18603  1.00943
C  5.83573  -2.35850  -0.25761
H  6.34560  -2.31062  -1.11486
C  4.50813  -1.92592  -0.33093

\[
\text{SCF (BP86) Energy} = -2019.3689229
\]

\[
\text{Enthalpy 298K} = -2018.420171
\]

\[
\text{Free Energy 298K} = -2018.419227
\]

\[
\text{Lowest Frequency} = -21.8753 \text{ cm}^{-1}
\]

\[
\text{Second Frequency} = -21.8753 \text{ cm}^{-1}
\]

\[
\text{SCF (BP86-D3BJ) Energy} = -2019.6890943
\]

\[
\text{SCF (C6H6) Energy} = -2019.38019437
\]

\[
\text{SCF (Et2O) Energy} = -2019.38676972
\]

\[
\text{SCF (BS2) Energy} = -3791.21753970
\]

\[
\text{SCF (BP86) Energy} = -2019.3689229
\]

\[
\text{Enthalpy 298K} = -2018.420171
\]

\[
\text{Free Energy 298K} = -2018.419227
\]

\[
\text{Lowest Frequency} = -21.8753 \text{ cm}^{-1}
\]

\[
\text{Second Frequency} = -21.8753 \text{ cm}^{-1}
\]

\[
\text{SCF (BP86-D3BJ) Energy} = -2019.6890943
\]

\[
\text{SCF (C6H6) Energy} = -2019.38019437
\]

\[
\text{SCF (Et2O) Energy} = -2019.38676972
\]

\[
\text{SCF (BS2) Energy} = -3791.21753970
\]
