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### Selective [3+1] Fragmentations of $P_4$ by “P” Transfer from a Lewis Acid Stabilized $[RP_4]^-$ Butterfly Anion

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#### DOI

[10.1002/anie.201607234](https://doi.org/10.1002/anie.201607234)

[10.1002/ange.201607234](https://doi.org/10.1002/ange.201607234)

#### Publication date

2017

#### Document Version

Other version

#### Published in

Angewandte Chemie, International Edition

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#### Citation for published version (APA):

Borger, J. E., Ehlers, A. W., Lutz, M., Slootweg, J. C., & Lammertsma, K. (2017). Selective [3+1] Fragmentations of  $P_4$  by “P” Transfer from a Lewis Acid Stabilized  $[RP_4]^-$  Butterfly Anion. *Angewandte Chemie, International Edition*, 56(1), 285-290.

<https://doi.org/10.1002/anie.201607234>, <https://doi.org/10.1002/ange.201607234>

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Supporting Information

**Selective [3+1] Fragmentations of P<sub>4</sub> by “P” Transfer from a Lewis Acid Stabilized [RP<sub>4</sub>]<sup>-</sup> Butterfly Anion**

*Jaap E. Borger, Andreas W. Ehlers, Martin Lutz, J. Chris Sloatweg, and Koop Lammertsma\**

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## Supporting Information

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## 1. Experimental Details

All manipulations regarding the preparation of air-sensitive compounds were carried out under an atmosphere of dry nitrogen, using standard Schlenk and drybox techniques. Solvents were purified, dried and degassed according to standard procedures.

$^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker Avance 400 and internally referenced to the residual solvent resonances (THF- $d_8$ :  $^1\text{H}$   $\delta$  3.58, 1.72 ppm,  $^{13}\text{C}\{^1\text{H}\}$   $\delta$  67.2, 25.3 ppm;  $\text{C}_6\text{D}_6$ :  $^1\text{H}$   $\delta$  7.16 ppm,  $^{13}\text{C}\{^1\text{H}\}$   $\delta$  128.1 ppm;  $\text{CD}_2\text{Cl}_2$ :  $^1\text{H}$   $\delta$  5.32,  $^{13}\text{C}\{^1\text{H}\}$   $\delta$  53.8; DMSO- $d_6$ :  $^1\text{H}$   $\delta$  2.50,  $^{13}\text{C}\{^1\text{H}\}$   $\delta$  39.5).  $^{31}\text{P}\{^1\text{H}\}$ ,  $^{31}\text{P}$ ,  $^{11}\text{B}\{^1\text{H}\}$ ,  $^{11}\text{B}$  and  $^7\text{Li}$  NMR spectra were recorded on a Bruker Avance 400 and externally referenced (85%  $\text{H}_3\text{PO}_4$ ,  $\text{BF}_3\cdot\text{OEt}_2$  and  $\text{LiCl}$ , respectively). Chemical shifts are reported in ppm. Melting points were measured on samples in sealed capillaries and are uncorrected. ESI Mass spectra were recorded on a Bruker Daltonics micrOTOF spectrometer in negative or positive (capillary potential of 4500 V) ion mode and the IR spectrum was recorded on a Shimadzu FTIR-8400S spectrophotometer.

Phenyl isocyanate (PhNCO) and 1,3-cyclohexadiene (1,3-CHD) were purchased from commercial resources and distilled prior to use and stored over molecular sieves (4 Å).  $[\text{Li}(\text{THF})_{2,2}][\text{Mes}^*\text{P}_4\cdot\text{BPh}_3]$ ,<sup>[S1]</sup>  $[\text{IDippH}][\text{Cl}]$ <sup>[S2]</sup> and  $[\text{Me}_3\text{NH}][\text{BPh}_4]$ <sup>[S1,S3]</sup> were prepared according to previously published procedures.

### Protonation of $[\text{Li}(\text{THF})_{2,2}][\text{Mes}^*\text{P}_4\cdot\text{BPh}_3]$ using $[\text{Me}_3\text{NH}][\text{BPh}_4]$

$[\text{Li}(\text{THF})_{2,2}][\text{Mes}^*\text{P}_4\cdot\text{BPh}_3]$  (0.015 g, 0.019 mmol, 1.0 equiv.) and  $[\text{Me}_3\text{NH}][\text{BPh}_4]$  (0.007 g, 0.019 mmol, 1.0 equiv.) were loaded in an NMR tube and THF- $d_8$  (0.6 mL) was added to give a crème colored mixture which was directly analyzed using  $^{31}\text{P}\{^1\text{H}\}$ ,  $^{31}\text{P}$  and  $^{11}\text{B}\{^1\text{H}\}$  NMR spectroscopy.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum revealed full conversion of the starting material and the formation of two new bicyclic tetraphosphabutane species (Figure S1). The  $^{31}\text{P}\{^1\text{H}\}$  resonances of the two products were simulated<sup>[S4]</sup> as  $\text{AMX}_2$  spin systems (inset; inverted), consistent with those expected for the neutral *exo,endo* and *exo,exo* isomers of  $\text{Mes}^*\text{P}_4\text{H}$  (1:0.7 ratio respectively). The former being easily distinguished from the latter by the smaller  $^2J_{\text{P,P}}$  coupling constant (19.1 Hz vs. 303.9 Hz). The  $^{31}\text{P}$  NMR spectrum (Figure S2) showed additional splitting of nearly all signals into doublets (*exo,endo*- $\text{Mes}^*\text{P}_4\text{H}$ :  $^1J_{\text{P,H}} = 147.8$  Hz,  $^2J_{\text{P,H}}$  = not resolved,  $^3J_{\text{P,H}} = 17.2$  Hz; *exo,exo*- $\text{Mes}^*\text{P}_4\text{H}$ :  $^1J_{\text{P,H}} = 133.9$  Hz,  $^2J_{\text{P,H}} = 11.7$  Hz,  $^3J_{\text{P,H}} = 111.1$  Hz). The  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum showed two signals at 34.4 ppm and -6.5 ppm corresponding to  $\text{BPh}_3$  (the signal is observed at 56.3 ppm in Tol- $d_8$ <sup>[S1]</sup>) and  $[\text{Li}][\text{BPh}_4]$  respectively,<sup>[S5]</sup> confirming both neutral  $\text{P}_4$  derivatives to be devoid of Lewis acid.

In addition to the two tetraphosphanes, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum revealed the presence of  $\text{Mes}^*\text{PH}_2$  by a sharp singlet signal at -132.2 ppm. Within 2 h, this primary phosphane was the only observable product suggesting complete decomposition of  $\text{Mes}^*\text{P}_4\text{H}$  toward  $\text{Mes}^*\text{PH}_2$  and other undetected P-containing species.

***Exo,endo-Mes\*P<sub>4</sub>H:***

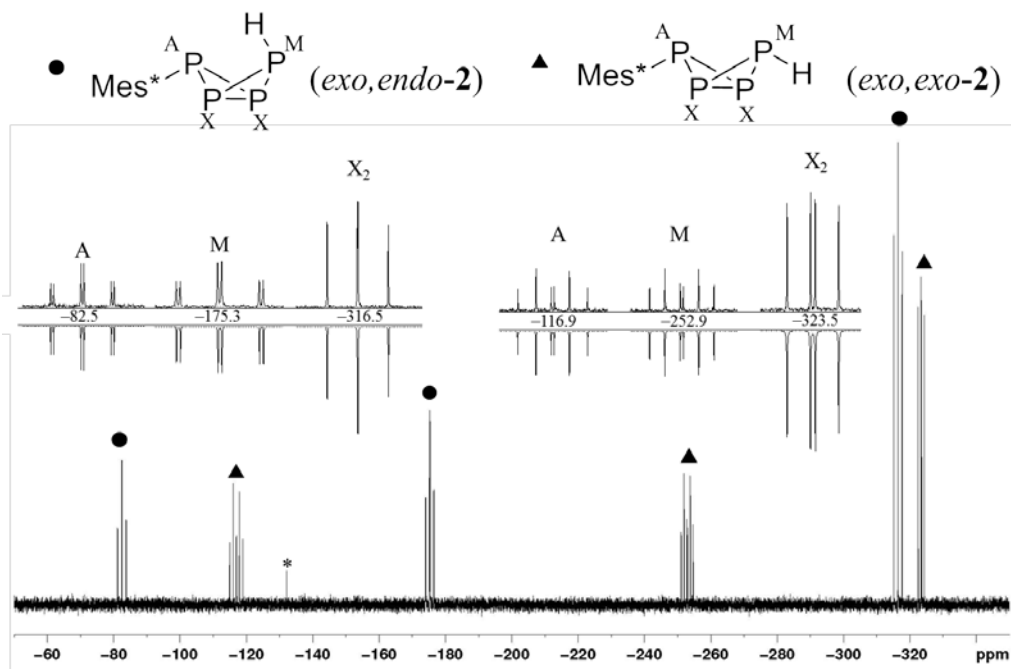
<sup>31</sup>P{<sup>1</sup>H} NMR (162.0 MHz, THF-*d*<sub>8</sub>, 291 K): AMX<sub>2</sub> spin system, δ<sub>PA</sub> -82.5, δ<sub>PM</sub> -175.3, δ<sub>PX</sub> -316.5 ppm, <sup>1</sup>J<sub>PA,PX</sub> = -202.7, <sup>1</sup>J<sub>PM,PX</sub> = -198.5, <sup>2</sup>J<sub>PA,PM</sub> = 19.1 Hz.

<sup>1</sup>H NMR (400.1 MHz, THF-*d*<sub>8</sub>, 291 K): δ 7.22 (d, <sup>4</sup>J<sub>H,P</sub> = 1.2 Hz, 1H; *m*-C<sub>6</sub>H<sub>2</sub>), 1.71 (s, 18H; *o*-C(CH<sub>3</sub>)<sub>3</sub>), 1.27 (s, 9H; *p*-C(CH<sub>3</sub>)<sub>3</sub>), -1.34 (dd, <sup>1</sup>J<sub>H,P</sub> = 147.5 Hz, <sup>3</sup>J<sub>H,P</sub> = 17.3 Hz, 1H; Mes\*P<sub>4</sub>H).

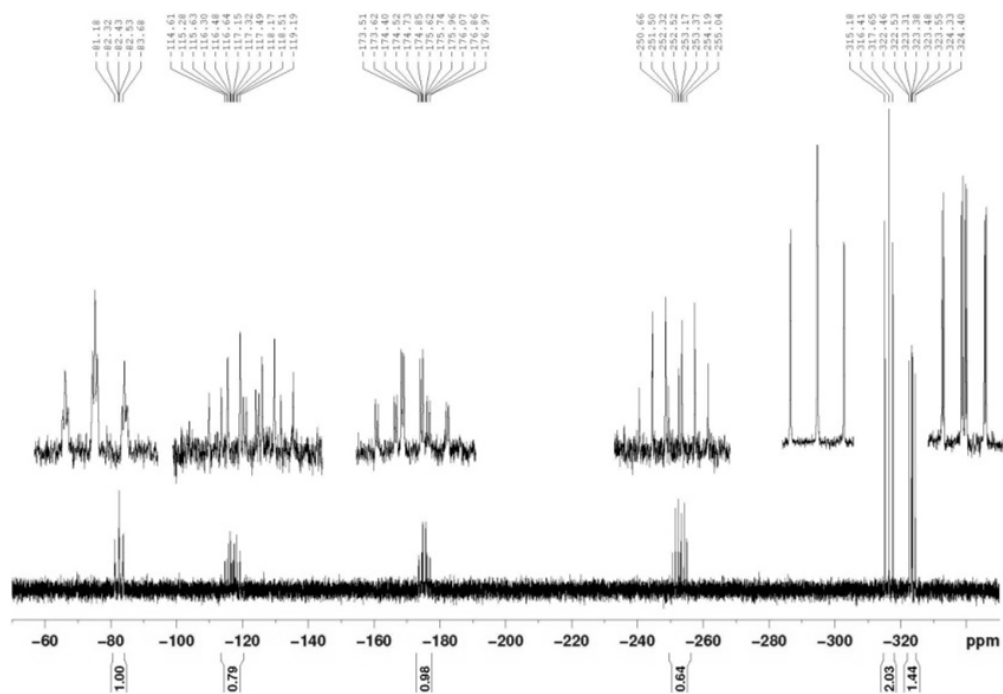
***Exo,exo-Mes\*P<sub>4</sub>H:***

<sup>31</sup>P{<sup>1</sup>H} NMR (162.0 MHz, THF-*d*<sub>8</sub>, 291 K): AMX<sub>2</sub> spin system, δ<sub>PA</sub> -116.9, δ<sub>PM</sub> -252.9, δ<sub>PX</sub> -323.5 ppm, <sup>1</sup>J<sub>PA,PX</sub> = -165.5, <sup>1</sup>J<sub>PM,PX</sub> = -137.0, <sup>2</sup>J<sub>PA,PM</sub> = 303.9 Hz.

<sup>1</sup>H NMR (400.1 MHz, THF-*d*<sub>8</sub>, 291 K): δ 7.23 (d, <sup>4</sup>J<sub>H,P</sub> = 1.2 Hz, 1H; *m*-C<sub>6</sub>H<sub>2</sub>), 1.68 (s, 18H; *o*-C(CH<sub>3</sub>)<sub>3</sub>), 1.27 (s, 9H; *p*-C(CH<sub>3</sub>)<sub>3</sub>), 0.65 (ddt, <sup>1</sup>J<sub>H,P</sub> = 133.2 Hz, <sup>2</sup>J<sub>H,P</sub> = 11.3 Hz, <sup>3</sup>J<sub>H,P</sub> = 109.0 Hz, 1H; Mes\*P<sub>4</sub>H).



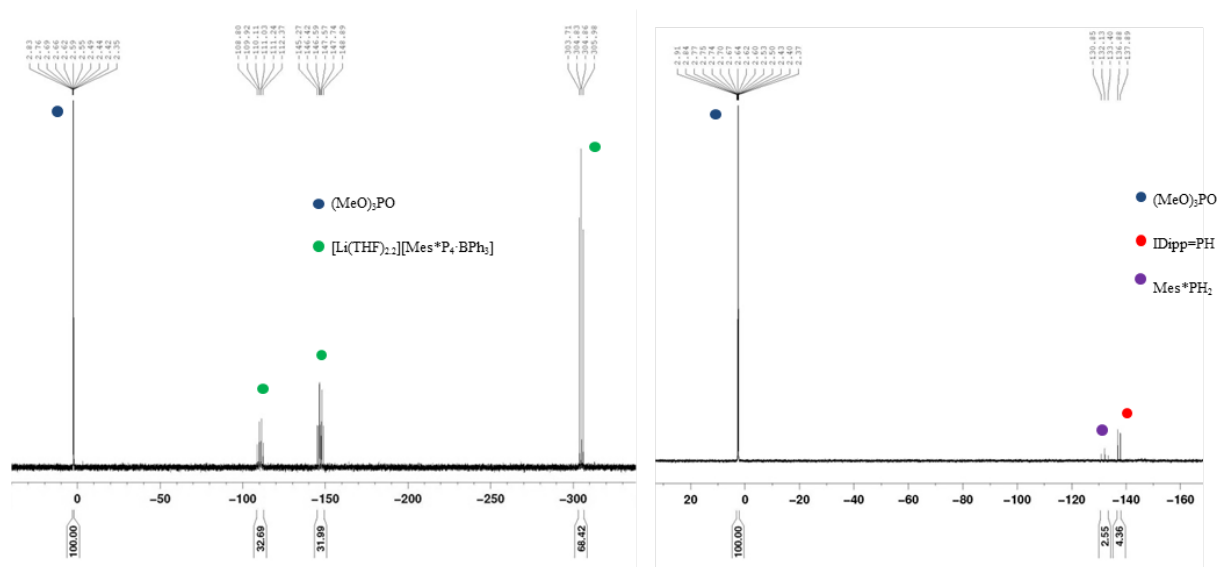
**Figure S1.** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (162.0 MHz, THF-*d*<sub>8</sub>, 291 K) recorded directly after mixing [Li(THF)<sub>2,2</sub>][Mes\*P<sub>4</sub>·BPh<sub>3</sub>] and [Me<sub>3</sub>NH][BPh<sub>4</sub>]: expansion (inset) shows the experimental (top) and simulated<sup>[S4]</sup> (inverted) spectrum. The resonance signal corresponding to Mes\*PH<sub>2</sub> is marked with an asterisk (\*).



**Figure S2.**  $^{31}\text{P}$  NMR spectrum (162.0 MHz,  $\text{THF-}d_6$ , 291 K) recorded directly after mixing  $[\text{Li}(\text{THF})_{2,2}][\text{Mes}^*\text{P}_4\cdot\text{BPh}_3]$  and  $[\text{Me}_3\text{NH}][\text{BPh}_4]$ .

## Fragmentation of $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\text{BPh}_3]$ using $[\text{IDippH}][\text{Cl}]$

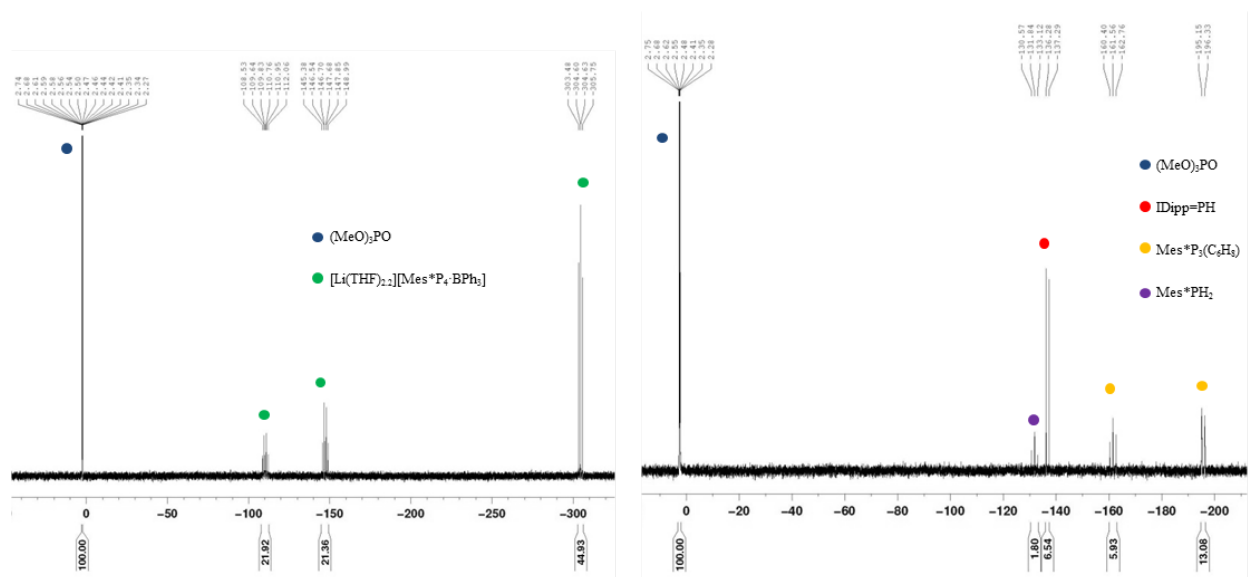
$[\text{IDippH}][\text{Cl}]$  (0.012 g, 0.028 mmol, 1.1 equiv.) was added to a solution of  $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\text{BPh}_3]$  (0.020 g, 0.026 mmol, 1.0 equiv.) in  $\text{THF-}d_8$  (0.6 mL), in an NMR tube containing  $(\text{MeO})_3\text{PO}$  in a sealed capillary as an internal standard, at room temperature. The orange suspension was left for 2.5 h at room temperature and analyzed using  $^{31}\text{P}$  NMR spectroscopy, showing ca. 13% conversion toward  $\text{IDipp}=\text{PH}$  and ca. 8% to  $\text{Mes}^*\text{PH}_2$  (see Figure S3). The recorded  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum showed signals at 2.6 and  $-7.4$  ppm, corresponding to the adducts  $[\text{IDippH}][\text{BPh}_3\text{Cl}]$  and  $\text{IDipp-BPh}_3$ , respectively. These species were independently confirmed by analysis of the reaction solutions obtained after stirring a stoichiometric mixture of either  $[\text{IDippH}][\text{Cl}]$  or  $\text{IDipp}$  with  $\text{BPh}_3$  in  $\text{THF-}d_8$ , revealing one signal at 3.2 ppm in case of the former and  $-7.2$  ppm in case of the latter, in the  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum.



**Figure S3.**  $^{31}\text{P}$  NMR spectra (ppm scale) of  $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\text{BPh}_3]$  in  $\text{THF-}d_8$  prior to the addition of  $[\text{IDippH}][\text{Cl}]$  (left) and 2.5 h thereafter (right).

### Fragmentation in the presence of 1,3-CHD:

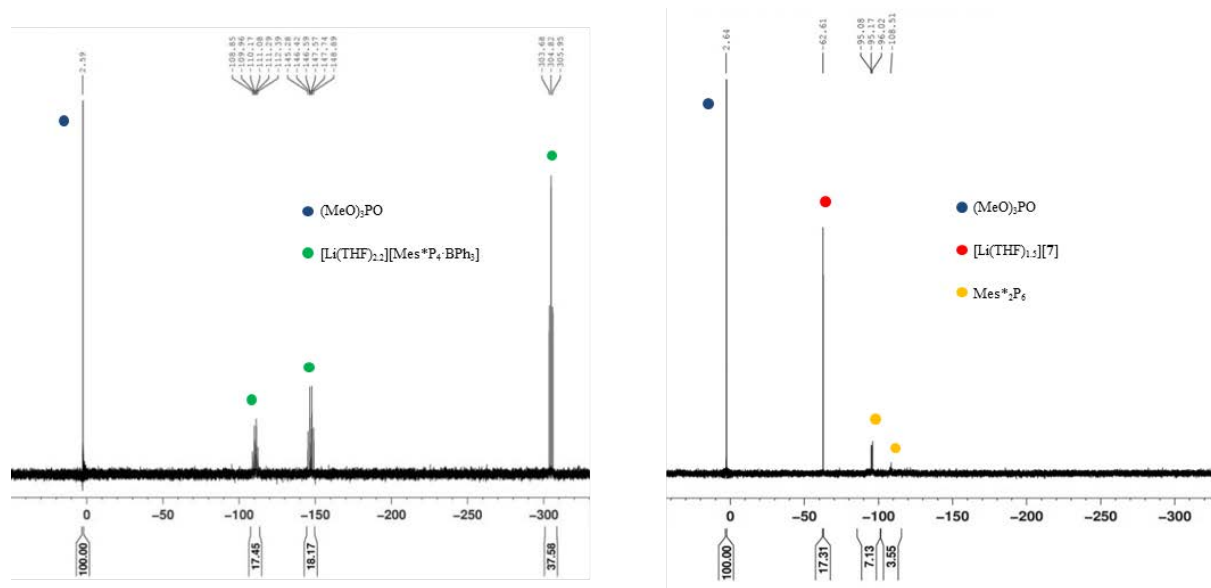
$[\text{IDippH}][\text{Cl}]$  (0.012 g, 0.028 mmol, 1.1 equiv.) was added to a solution of  $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\text{BPh}_3]$  (0.020 g, 0.026 mmol, 1.0 equiv.) and 1,3-CHD (0.12 mL, 1.3 mmol, 50 equiv.) in  $\text{THF-}d_8$  (0.6 mL), in an NMR tube containing  $(\text{MeO})_3\text{PO}$  in a sealed capillary as an internal standard, at room temperature. The orange suspension was left for 2.5 h at room temperature and analyzed using  $^{31}\text{P}$  NMR spectroscopy, showing ca. 30% conversion toward  $\text{IDipp}=\text{PH}$ , ca. 27% conversion to  $\text{Mes}^*\text{P}_3(\text{C}_6\text{H}_8)$  and ca. 8% to  $\text{Mes}^*\text{PH}_2$  (see Figure S4). The recorded  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum showed signals at 2.6 and  $-7.4$  ppm, corresponding to the adducts  $[\text{IDippH}][\text{BPh}_3\text{Cl}]$  and  $\text{IDipp-BPh}_3$ , respectively.



**Figure S4.**  $^{31}\text{P}$  NMR spectra (ppm scale) of  $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\cdot\text{BPh}_3]$  in  $\text{THF}-d_8$  prior to the addition of  $[\text{IDippH}][\text{Cl}]$  (left) and 2.5 h thereafter (right).

## Fragmentation of $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\cdot\text{BPh}_3]$ using PhNCO

An excess of PhNCO (0.041 mL, 0.38 mmol, 20 equiv.) was added to a solution of  $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\cdot\text{BPh}_3]$  (0.015 g, 0.019 mmol, 1.0 equiv.) in THF- $d_8$  (0.6 mL), in an NMR tube containing  $(\text{MeO})_2\text{PO}$  in a sealed capillary as an internal standard, at room temperature. The clear brown solution was quickly analyzed using  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy, showing ca. 100% conversion toward  $[\text{Li}(\text{THF})_{1.5}][7]$  and ca. 19% conversion to  $\text{Mes}^*_2\text{P}_6$  (see Figure S5). The  $^{11}\text{B}$  NMR spectrum revealed a signal at 57.9 ppm corresponding to  $\text{BPh}_3$ .



**Figure S5.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra (ppm scale) of  $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\cdot\text{BPh}_3]$  in THF- $d_8$  prior to the addition of excess PhNCO (left) and directly thereafter (right).

### Isolation of $\text{Mes}^*_2\text{P}_6$ and $[\text{Li}(\text{THF})_{1.5}][7]$ :

An excess of PhNCO (0.62 mL, 5.66 mmol, 20 equiv.) was added to a solution of  $[\text{Li}(\text{THF})_{2.2}][\text{Mes}^*\text{P}_4\cdot\text{BPh}_3]$  (0.220 g, 0.283 mmol, 1.0 equiv.) in THF (10 mL) at room temperature. Within one minute the clear solution colored red and then brown with the precipitation of a white solid. After standing for 16 h the solid was collected by filtration and subsequently washed with THF (2 x 10 mL). Drying *in vacuo* yielded spiro-phosphoranide  $[\text{Li}(\text{THF})_{1.5}][7]$  as analytically pure white powder in 80% yield (0.140 g, 0.225 mmol). The filtrate and the THF washings were combined and evaporated to dryness to give an oily red residue which was washed with acetone (2 x 10 mL), cold DCM (1 mL, 0 °C) and *n*-pentane (5 mL) to give  $\text{Mes}^*_2\text{P}_6$  as a white powder in 18% yield (0.017 g, 0.025 mmol).

### Characterization of spiro-phosphoranide [Li(THF)<sub>1.5</sub>][7]:

Crystals suitable for X-ray diffraction were obtained directly from the reaction solution upon standing overnight without stirring.

**Mp. (nitrogen, sealed capillary):** 149 °C.

**<sup>1</sup>H NMR (400.1 MHz, DMSO-*d*<sub>6</sub>, 294 K):** δ 7.46 (d, <sup>3</sup>J<sub>H,H</sub> = 7.9 Hz, 4H; *o*-C<sub>6</sub>H<sub>5</sub>), 7.42 (d, <sup>3</sup>J<sub>H,H</sub> = 7.9 Hz, 4H; *o*-C<sub>6</sub>H<sub>5</sub>), 7.34 (t, <sup>3</sup>J<sub>H,H</sub> = 7.3 Hz, 2H; *p*-C<sub>6</sub>H<sub>5</sub>), 7.22 (br. t, <sup>3</sup>J<sub>H,H</sub> = 7.3 Hz, 8H; *m*-C<sub>6</sub>H<sub>5</sub>), 6.96 (t, <sup>3</sup>J<sub>H,H</sub> = 7.3 Hz, 2H; *p*-C<sub>6</sub>H<sub>5</sub>).

**<sup>7</sup>Li (155.5 MHz, DMSO-*d*<sub>6</sub>, 294 K):** δ -1.1 (s).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, DMSO-*d*<sub>6</sub>, 294 K):** δ 175.8 (d, <sup>1</sup>J<sub>C,P</sub> = 23.8 Hz; P-C(O)), 153.1 (d, <sup>2</sup>J<sub>C,P</sub> = 7.1 Hz; PN-C(O)), 142.6 (d, <sup>2</sup>J<sub>C,P</sub> = 4.3 Hz; *ipso*-PN-C<sub>6</sub>H<sub>5</sub>), 136.2 (s; *ipso*-PC(O)N-C<sub>6</sub>H<sub>5</sub>), 128.6 (s; *m*-PC(O)N-C<sub>6</sub>H<sub>5</sub>), 128.3 (*o*-PC(O)N-C<sub>6</sub>H<sub>5</sub>), 127.8 (*m*-PN-C<sub>6</sub>H<sub>5</sub>), 127.2 (*p*-PC(O)N-C<sub>6</sub>H<sub>5</sub>), 124.0 (d, <sup>3</sup>J<sub>C,P</sub> = 4.5 Hz; *o*-PN-C<sub>6</sub>H<sub>5</sub>), 122.2 (s; *p*-PN-C<sub>6</sub>H<sub>5</sub>).

**<sup>31</sup>P{<sup>1</sup>H} NMR (162.0 MHz, DMSO-*d*<sub>6</sub>, 293 K):** δ -67.1 (s).

**HR-MS (ESI):** 269.0499 [M - 2 PhNCO]<sup>-</sup>. Calcd.: for C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>P 269.0485.

**IR (cm<sup>-1</sup>):** 2976 (w), 2876 (w), 1706 (m), 1678 (m), 1642 (s), 1595 (m), 1488 (s), 1378 (s), 1322 (m), 1166 (m), 1048 (m), 891 (m), 833 (m), 761 (s), 690 (s), 647 (m), 569 (m).

*Comment on the solubility and stability of [Li(THF)<sub>1.5</sub>][7]:*

The product was found to be insoluble in THF but soluble and moderately stable in DMSO-*d*<sub>6</sub>, showing only trace impurities in the recorded <sup>1</sup>H NMR spectrum after standing for 24 h in.

### Characterization of Mes\*<sub>2</sub>P<sub>6</sub>:<sup>[S6]</sup>

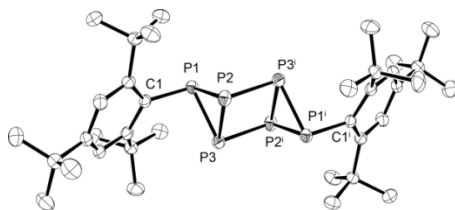
The obtained multinuclear NMR data were found to be in full agreement with the previously reported data for Mes\*<sub>2</sub>P<sub>6</sub> by Schulz et al.<sup>[S6]</sup>

**<sup>1</sup>H NMR (400.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 294 K):** δ 7.00 (s, 4H; *m*-C<sub>6</sub>H<sub>2</sub>), 1.63 (s, 36H; *o*-C(CH<sub>3</sub>)<sub>3</sub>), 1.14 (s, 18H; *p*-C(CH<sub>3</sub>)<sub>3</sub>).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 294 K):** δ 158.0 (s; *o*-C<sub>6</sub>H<sub>2</sub>), 149.3 (s; *p*-C<sub>6</sub>H<sub>2</sub>), 123.2 (s; *m*-C<sub>6</sub>H<sub>2</sub>), 40.2 (s; *o*-C(CH<sub>3</sub>)<sub>3</sub>), 34.8 (s; *o*-C(CH<sub>3</sub>)<sub>3</sub>), 34.6 (s; *p*-C(CH<sub>3</sub>)<sub>3</sub>), 31.1 (s; *p*-C(CH<sub>3</sub>)<sub>3</sub>), not observed (*ipso*-C<sub>6</sub>H<sub>2</sub>).

**<sup>31</sup>P{<sup>1</sup>H} NMR (162.0 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 293 K):** δ -96.1 (m, 4P; Mes\*P<sub>2</sub>(P<sub>4</sub>)), -107.2 (m, 2P; Mes\*P<sub>2</sub>(P<sub>4</sub>)).

Crystals suitable for X-ray diffraction were grown by layering a THF solution of Mes\*<sub>2</sub>P<sub>6</sub> with *n*-pentane.



**Figure S6.** Molecular structure of Mes\*<sub>2</sub>P<sub>6</sub> in the crystal (ellipsoids are set at 50% probability; H-atoms omitted).

### Isolation of Mes\*P<sub>3</sub>(C<sub>6</sub>H<sub>8</sub>):

PhNCO (0.112 mL, 1.03 mmol, 4.0 equiv.) was added to a solution of [Li(THF)<sub>2.2</sub>][Mes\*P<sub>4</sub>BPh<sub>3</sub>] (0.200 g, 0.257 mmol, 1.0 equiv.) and 1,3-CHD (1.22 mL, 12.9 mmol, 50 equiv.) in THF (10 mL) at room temperature. Within one minute the clear solution colored red and then brown with the precipitation of a white solid.\* The mixture was stirred for 15 min. after which the volatiles were removed *in vacuo*. The product was extracted into *n*-pentane (20 mL), evaporated to dryness and washed with acetonitrile (2 x 5 mL) at 0 °C to give Mes\*P<sub>3</sub>(C<sub>6</sub>H<sub>8</sub>) as a pale yellow powder in 69% yield (0.074 g, 0.177 mmol). Crystals suitable for X-ray diffraction were grown from a saturated *n*-hexane solution at +6 °C.

\*Though not required to obtain pure Mes\*P<sub>3</sub>(C<sub>6</sub>H<sub>8</sub>), the white solid can be collected by filtration giving pure [Li(THF)<sub>1.5</sub>][7] after washing with THF in quantitative yield.

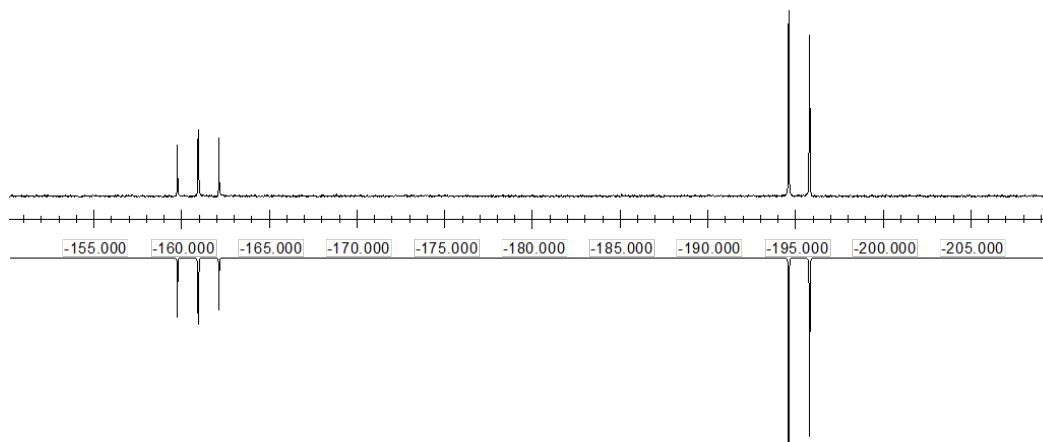
**Mp. (nitrogen, sealed capillary):** 129–144 °C (trajectory).

**<sup>1</sup>H NMR (400.1 MHz, C<sub>6</sub>D<sub>6</sub>, 291 K):** δ 7.30 (d, <sup>4</sup>J<sub>H,P</sub> = 2.0 Hz, 2H; C<sub>6</sub>H<sub>2</sub>), 5.53-5.50 (m, 2H; C(H)=C(H)), 2.81-2.75 (m, 2H; C(H)-C(H)=C(H)), 1.82 (s, 18H; *o*-C(CH<sub>3</sub>)<sub>3</sub>), 1.21 (s, 9H; *p*-C(CH<sub>3</sub>)<sub>3</sub>), 0.89-0.80 (m, 4H; C(H)<sub>2</sub>-C(H)).

**<sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>, 291 K):** δ 158.3 (s; *o*-C<sub>6</sub>H<sub>2</sub>), 148.2 (s; *p*-C<sub>6</sub>H<sub>2</sub>), 123.2 (s; *m*-C<sub>6</sub>H<sub>2</sub>), 121.5 (d, <sup>3</sup>J<sub>C,P</sub> = 11.3 Hz; C(H)=C(H)), 40.0 (s; *o*-C(CH<sub>3</sub>)<sub>3</sub>), 34.9 (d, <sup>4</sup>J<sub>C,P</sub> = 9.0 Hz; *o*-C(CH<sub>3</sub>)<sub>3</sub>), 34.4 (s; *p*-C(CH<sub>3</sub>)<sub>3</sub>), 31.3 (s; *p*-C(CH<sub>3</sub>)<sub>3</sub>), 26.7 (td, <sup>1</sup>J<sub>C,P</sub> = 20.4 Hz, <sup>2</sup>J<sub>C,P</sub> = 13.8 Hz; C(H)-C(H)=C(H)), 23.0 (m; C(H)<sub>2</sub>-C(H)), not observed (*ipso*-C<sub>6</sub>H<sub>2</sub>).

**<sup>31</sup>P{<sup>1</sup>H} NMR (162.0 MHz, C<sub>6</sub>D<sub>6</sub>, 291 K):** δ -160.9 (1P; Mes\*P), -195.2 (2P; P<sub>2</sub>(C<sub>6</sub>H<sub>8</sub>)); AB<sub>2</sub> second order spin-system: <sup>1</sup>J<sub>P<sub>A</sub>,P<sub>B</sub></sub> = 192.0 Hz (Figure S7).<sup>[S4]</sup>

**HR-MS (ESI):** 441.2012 [M + Na]<sup>+</sup>. Calcd.: for C<sub>24</sub>H<sub>37</sub>NaP<sub>3</sub> 441.2000.

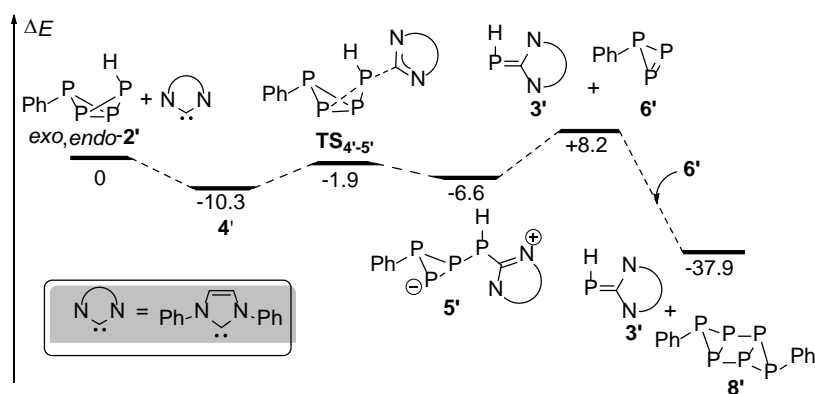


**Figure S7.** Experimental (top) and simulated (inverted) <sup>31</sup>P{<sup>1</sup>H} NMR spectra (ppm scale) of Mes\*P<sub>3</sub>C<sub>6</sub>H<sub>8</sub>.

## 2. Computational Details

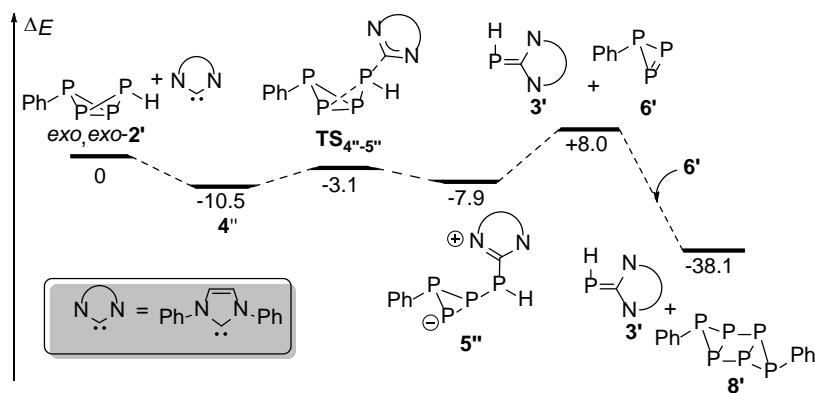
Density functional calculations were performed at the  $\omega$ B97X-D<sup>[S7]</sup> level of theory using Gaussian09, revision D.01.<sup>[S8]</sup> Geometry optimizations were performed using the 6-31G(d) basis set<sup>[S9,S10]</sup> and uncorrected energies were obtained from single point calculations using the 6-311+G(2d,p) basis set.<sup>[S10,S11,S12]</sup> The nature of each stationary point was confirmed by frequency calculations.

### Calculated minimum energy reaction pathway for the fragmentation of *exo,endo-2'* using IPh (NHC<sup>Ph</sup>)



**Scheme S1.** Relative  $\omega$ B97X-D/6-311+G(2d,p)//6-31G(d) energies (in kcal mol<sup>-1</sup>) for the computed fragmentation pathway leading from *exo,endo-2'* to 3' and 8'. NHC = *N*-heterocyclic carbene.

### Calculated minimum energy reaction pathway for the fragmentation of *exo,exo-2'* using IPh (NHC<sup>Ph</sup>)



**Scheme S2.** Relative  $\omega$ B97X-D/6-311+G(2d,p)//6-31G(d) energies (in kcal mol<sup>-1</sup>) for the computed fragmentation pathway leading from *exo,exo-2'* to 3' and 8'. NHC = *N*-heterocyclic carbene.

**Optimized geometries (Cartesian coordinates) and uncorrected energies (in a.u.)**

**IPh:**

E = -688.218086101

C	0.000036000	0.340490000	-0.091191000
C	0.673457000	-1.770164000	0.534193000
C	-0.673520000	-1.770109000	0.534367000
H	1.373936000	-2.540778000	0.813925000
H	-1.374192000	-2.540811000	0.813332000
N	1.060505000	-0.487865000	0.152216000
N	-1.060475000	-0.487922000	0.151684000
C	2.410998000	-0.063807000	0.014792000
C	3.405335000	-0.976440000	-0.330025000
C	2.731357000	1.276140000	0.228135000
C	4.724995000	-0.548733000	-0.444343000
H	3.152627000	-2.012200000	-0.533938000
C	4.049413000	1.694839000	0.098902000
H	1.936226000	1.968175000	0.479779000
C	5.052656000	0.785766000	-0.230510000
H	5.495327000	-1.264286000	-0.715312000
H	4.293687000	2.739771000	0.264535000
H	6.081944000	1.117491000	-0.325771000
C	-2.410924000	-0.063790000	0.014373000
C	-2.731385000	1.276039000	0.228473000
C	-3.405236000	-0.976262000	-0.330853000
C	-4.049491000	1.694655000	0.099638000
H	-1.936156000	1.967894000	0.480344000
C	-4.724969000	-0.548619000	-0.444786000
H	-3.152615000	-2.011908000	-0.535502000
C	-5.052730000	0.785725000	-0.230113000
H	-4.293678000	2.739515000	0.265931000
H	-5.495205000	-1.264177000	-0.716008000
H	-6.082059000	1.117443000	-0.324921000

*exo,endo-2'*:

E = -1597.68320194

P	-1.561812000	-1.095181000	-0.599801000
P	-1.563545000	1.101210000	-0.588227000
P	-3.378814000	-0.001756000	0.055957000
P	-0.503992000	-0.004656000	1.031830000
C	1.232837000	-0.001239000	0.407097000
C	1.918830000	-1.206054000	0.215459000
C	1.915538000	1.205154000	0.213823000
C	3.253931000	-1.203473000	-0.176222000
C	3.250682000	1.205567000	-0.177830000
C	3.921380000	0.001822000	-0.374671000
H	3.771719000	-2.145770000	-0.327794000
H	3.766015000	2.149012000	-0.330614000
H	-3.149637000	-0.009153000	1.463023000
H	1.403141000	2.151809000	0.365426000
H	1.408825000	-2.153821000	0.368276000
H	4.963200000	0.003015000	-0.680647000

*exo,exo-2'*:

E = -1597.68286819

P	-1.529007000	-1.027237000	-0.708765000
P	-1.557386000	1.142380000	-0.493549000
P	-3.304562000	-0.047177000	0.221134000
P	-0.514485000	-0.091574000	1.044613000
C	1.218757000	-0.025226000	0.412762000
C	1.934410000	-1.214358000	0.230703000
C	1.870864000	1.195409000	0.207137000
C	3.266730000	-1.182972000	-0.168242000
C	3.204044000	1.224465000	-0.191252000
C	3.903491000	0.036395000	-0.381416000
H	3.805913000	-2.114100000	-0.314278000
H	3.695523000	2.178855000	-0.354305000
H	-4.037324000	0.067912000	-0.994583000
H	1.337244000	2.130895000	0.353195000
H	1.447302000	-2.172362000	0.393976000
H	4.943179000	0.060642000	-0.693631000

4':

E = -2285.91762683

P	-1.042116000	-0.891341000	-0.938179000
P	-1.568266000	-2.842545000	-0.028272000
P	0.458434000	-1.958829000	0.265269000
P	-2.309155000	-0.949363000	0.877486000
C	-4.010218000	-0.721579000	0.200790000
C	-4.855810000	0.083918000	0.972188000
C	-4.498221000	-1.258961000	-0.995563000
C	-6.157729000	0.350626000	0.559403000
C	-5.800342000	-0.994814000	-1.407071000
C	-6.631881000	-0.189356000	-0.632188000
H	-6.801630000	0.977128000	1.169703000
H	-6.168168000	-1.420998000	-2.335787000
H	0.261966000	-1.310458000	1.513511000
H	-3.862826000	-1.889115000	-1.613244000
H	-4.489147000	0.506986000	1.904817000
H	-7.648338000	0.013660000	-0.956216000
C	2.343268000	0.752734000	0.264893000
N	1.674027000	1.823911000	-0.259038000
N	3.559059000	0.858149000	-0.349937000
C	2.438579000	2.556628000	-1.161919000
C	3.637821000	1.944285000	-1.217201000
H	2.072567000	3.443790000	-1.654269000
H	4.516796000	2.164082000	-1.802315000
C	4.638474000	-0.037622000	-0.105252000
C	5.940487000	0.453094000	-0.031031000
C	4.386612000	-1.397199000	0.060189000
C	6.995435000	-0.424326000	0.199609000
H	6.126174000	1.518443000	-0.128522000
C	5.446180000	-2.263082000	0.303940000
H	3.367806000	-1.761825000	-0.008419000
C	6.752304000	-1.783425000	0.370276000
H	8.008172000	-0.037470000	0.260412000
H	5.247989000	-3.322459000	0.434790000
H	7.575442000	-2.466390000	0.556348000
C	0.341963000	2.159467000	0.109113000

C	-0.559185000	2.603803000	-0.856910000
C	-0.053469000	2.033615000	1.438231000
C	-1.862745000	2.920317000	-0.488246000
H	-0.253381000	2.664380000	-1.896979000
C	-1.359096000	2.349002000	1.795975000
H	0.663566000	1.673566000	2.167287000
C	-2.266853000	2.793957000	0.837859000
H	-2.568443000	3.249380000	-1.244357000
H	-1.668474000	2.237764000	2.830552000
H	-3.288580000	3.029786000	1.118442000

**4<sup>o</sup>:**

E = -2285.91535138

P	-0.913529000	-0.923332000	-0.558464000
P	-1.571563000	-2.778681000	0.420281000
P	0.241882000	-1.681161000	1.163653000
P	-2.503525000	-0.832380000	0.981637000
C	-4.028086000	-0.733337000	-0.050334000
C	-4.995067000	0.166786000	0.411041000
C	-4.279287000	-1.446707000	-1.227858000
C	-6.184268000	0.354941000	-0.286868000
C	-5.468825000	-1.260408000	-1.923856000
C	-6.422935000	-0.359156000	-1.456648000
H	-6.924210000	1.057979000	0.084232000
H	-5.651131000	-1.820976000	-2.836009000
H	1.159737000	-2.434401000	0.377800000
H	-3.546067000	-2.153956000	-1.607774000
H	-4.814220000	0.724842000	1.326730000
H	-7.351402000	-0.217505000	-2.001832000
C	2.386905000	0.786566000	0.276609000
N	1.628641000	1.789465000	-0.258080000
N	3.492759000	0.810518000	-0.527367000
C	2.234097000	2.403534000	-1.350390000
C	3.417541000	1.783163000	-1.521204000
H	1.788458000	3.228922000	-1.882543000
H	4.182713000	1.929249000	-2.266507000
C	4.602980000	-0.059653000	-0.338986000

C	5.884030000	0.342863000	-0.711709000
C	4.403177000	-1.316477000	0.229040000
C	6.959511000	-0.521993000	-0.531925000
H	6.051097000	1.335345000	-1.117874000
C	5.484912000	-2.166997000	0.416567000
H	3.401706000	-1.603204000	0.525091000
C	6.766162000	-1.778517000	0.031681000
H	7.955114000	-0.201422000	-0.823555000
H	5.322672000	-3.143491000	0.862578000
H	7.607369000	-2.449495000	0.174807000
C	0.358581000	2.163183000	0.263651000
C	-0.656954000	2.576433000	-0.596680000
C	0.135822000	2.095243000	1.637171000
C	-1.897801000	2.932451000	-0.076368000
H	-0.492887000	2.583925000	-1.669819000
C	-1.108111000	2.446958000	2.145811000
H	0.935436000	1.749903000	2.282235000
C	-2.126074000	2.871526000	1.294754000
H	-2.691052000	3.240272000	-0.750433000
H	-1.283568000	2.381231000	3.214801000
H	-3.096396000	3.143798000	1.698576000

**TS<sub>4-5</sub>:**

E = -2285.9043779

P	-0.530693000	-1.183481000	-0.490460000
P	-0.955240000	-2.550210000	1.179805000
P	1.097257000	-0.770079000	0.938087000
P	-2.089761000	-0.676239000	1.017743000
C	-3.653567000	-1.049830000	0.090249000
C	-4.610011000	-0.028704000	0.048719000
C	-3.936748000	-2.258066000	-0.553914000
C	-5.817224000	-0.204977000	-0.621829000
C	-5.140357000	-2.434547000	-1.229274000
C	-6.083670000	-1.410157000	-1.265578000
H	-6.552123000	0.595509000	-0.638357000
H	-5.345202000	-3.379475000	-1.725078000
H	0.402423000	0.070528000	1.835692000

H	-3.207968000	-3.064439000	-0.511399000
H	-4.406258000	0.912705000	0.554616000
H	-7.025680000	-1.553362000	-1.787616000
C	1.933612000	0.873297000	0.121168000
N	1.317570000	1.981528000	-0.354069000
N	3.135403000	0.854037000	-0.504407000
C	2.116124000	2.638678000	-1.272783000
C	3.263056000	1.929536000	-1.367138000
H	1.799435000	3.553442000	-1.747624000
H	4.164498000	2.100565000	-1.933245000
C	-0.001072000	2.415914000	0.007374000
C	-0.998708000	2.413542000	-0.960551000
C	-0.251432000	2.833381000	1.308498000
C	-2.274798000	2.842885000	-0.614248000
H	-0.784142000	2.044635000	-1.958382000
C	-1.531508000	3.257642000	1.645313000
H	0.546532000	2.817755000	2.043740000
C	-2.539137000	3.266346000	0.685388000
H	-3.066554000	2.822485000	-1.355515000
H	-1.741584000	3.574198000	2.661465000
H	-3.539131000	3.592441000	0.954238000
C	4.145206000	-0.143736000	-0.322873000
C	4.579003000	-0.460668000	0.959603000
C	4.683011000	-0.769887000	-1.442087000
C	5.563044000	-1.428864000	1.119952000
H	4.143800000	0.041293000	1.816894000
C	5.677284000	-1.727225000	-1.270993000
H	4.307157000	-0.529227000	-2.431838000
C	6.116096000	-2.058226000	0.007785000
H	5.898545000	-1.689066000	2.118434000
H	6.097700000	-2.223943000	-2.139314000
H	6.885079000	-2.812874000	0.138314000

**TS<sub>4<sup>+</sup>,5<sup>+</sup></sub>:**

E = -2285.90586027

P	-0.727500000	-0.928663000	-0.580885000
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P	-0.953772000	-2.590878000	0.853435000
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P	0.825958000	-0.688658000	0.938670000
P	-2.187575000	-0.786358000	1.090637000
C	-3.748223000	-1.062955000	0.126564000
C	-4.663167000	-0.003028000	0.124020000
C	-4.076972000	-2.231360000	-0.567425000
C	-5.870007000	-0.100908000	-0.561647000
C	-5.283343000	-2.330057000	-1.255031000
C	-6.182946000	-1.267207000	-1.254763000
H	-6.569386000	0.730928000	-0.552028000
H	-5.523643000	-3.245504000	-1.788811000
H	1.768620000	-1.599205000	0.407373000
H	-3.379314000	-3.065186000	-0.563041000
H	-4.423787000	0.909351000	0.666461000
H	-7.126789000	-1.350231000	-1.786366000
C	1.989697000	0.813483000	0.055525000
N	1.474067000	2.018678000	-0.271257000
N	3.259584000	0.846717000	-0.412975000
C	2.398228000	2.791080000	-0.955478000
C	3.527153000	2.054650000	-1.043670000
H	2.167549000	3.789966000	-1.289568000
H	4.494837000	2.278046000	-1.463622000
C	0.137827000	2.444250000	0.039023000
C	-0.786784000	2.586307000	-0.989280000
C	-0.204056000	2.691068000	1.363152000
C	-2.083896000	2.981115000	-0.680152000
H	-0.501324000	2.353081000	-2.010027000
C	-1.503041000	3.084826000	1.661417000
H	0.535221000	2.554078000	2.145129000
C	-2.439889000	3.231280000	0.642523000
H	-2.821046000	3.071353000	-1.470954000
H	-1.784892000	3.262590000	2.693641000
H	-3.456332000	3.529057000	0.880600000
C	4.206542000	-0.214713000	-0.277379000
C	4.406006000	-0.801271000	0.968325000
C	4.921245000	-0.636870000	-1.393969000
C	5.327703000	-1.835001000	1.090672000
H	3.843247000	-0.450258000	1.827531000

C	5.853578000	-1.659774000	-1.256552000
H	4.732761000	-0.184000000	-2.362499000
C	6.055104000	-2.261330000	-0.017380000
H	5.479193000	-2.303448000	2.057526000
H	6.410961000	-1.996553000	-2.124627000
H	6.777355000	-3.064978000	0.084067000

5':

E = -2285.91175449

P	0.193055000	-1.459443000	-0.113988000
P	0.776280000	-3.210003000	-1.108142000
P	-1.259600000	0.012586000	-1.489148000
P	1.998147000	-1.402174000	-1.382206000
C	3.359851000	-1.394139000	-0.112188000
C	4.418308000	-0.509936000	-0.352723000
C	3.397004000	-2.179859000	1.042914000
C	5.475967000	-0.395015000	0.547227000
C	4.450261000	-2.065396000	1.945095000
C	5.490367000	-1.170051000	1.703630000
H	6.290348000	0.295071000	0.342046000
H	4.462416000	-2.681800000	2.840101000
H	-0.234590000	0.902990000	-1.881799000
H	2.595924000	-2.892253000	1.226946000
H	4.413144000	0.092566000	-1.259624000
H	6.311609000	-1.084340000	2.409672000
C	-1.716567000	1.044159000	-0.078598000
N	-1.067344000	2.097207000	0.480362000
N	-2.823622000	0.855390000	0.683910000
C	-1.783969000	2.580406000	1.562988000
C	-2.879275000	1.801913000	1.692603000
H	-1.427548000	3.417567000	2.140581000
H	-3.682436000	1.809448000	2.411211000
C	-3.815687000	-0.157676000	0.474235000
C	-5.100923000	0.227606000	0.107421000
C	-3.481924000	-1.495076000	0.659496000
C	-6.071821000	-0.750413000	-0.077167000
H	-5.326760000	1.278323000	-0.046226000

C	-4.457886000	-2.465095000	0.457999000
H	-2.472904000	-1.767853000	0.955325000
C	-5.749945000	-2.094478000	0.094921000
H	-7.077454000	-0.462177000	-0.365949000
H	-4.204852000	-3.511711000	0.589552000
H	-6.508294000	-2.855800000	-0.057958000
C	0.191150000	2.643870000	0.056272000
C	0.198128000	3.846942000	-0.641484000
C	1.370733000	1.981459000	0.380359000
C	1.416355000	4.397699000	-1.024810000
H	-0.740646000	4.334052000	-0.886670000
C	2.582528000	2.539312000	-0.012848000
H	1.339234000	1.036288000	0.913214000
C	2.605424000	3.743717000	-0.711256000
H	1.434623000	5.334226000	-1.572849000
H	3.504039000	2.019201000	0.226678000
H	3.554188000	4.173845000	-1.016414000

5”:

E = -2285.91346587

P	0.245242000	-1.370226000	-0.130355000
P	0.933515000	-3.010511000	-1.253872000
P	-1.223243000	-0.002659000	-1.508855000
P	2.068532000	-1.128580000	-1.353587000
C	3.413665000	-1.180718000	-0.068270000
C	4.484580000	-0.303807000	-0.274143000
C	3.432569000	-1.998112000	1.065373000
C	5.536356000	-0.226137000	0.636036000
C	4.476688000	-1.917391000	1.981741000
C	5.530198000	-1.029114000	1.773199000
H	6.360699000	0.459271000	0.455856000
H	4.473122000	-2.557541000	2.860126000
H	-2.343461000	-0.864230000	-1.452014000
H	2.626487000	-2.711911000	1.219752000
H	4.489004000	0.330870000	-1.158387000
H	6.345998000	-0.972287000	2.488566000
C	-1.809518000	1.009558000	-0.128838000

N	-1.081298000	2.014385000	0.416435000
N	-2.945804000	0.940518000	0.611136000
C	-1.761178000	2.577610000	1.481729000
C	-2.929346000	1.912002000	1.601490000
H	-1.341498000	3.396448000	2.042851000
H	-3.745850000	2.015821000	2.297288000
C	-3.988419000	-0.032187000	0.469146000
C	-5.239126000	0.374366000	0.019603000
C	-3.730890000	-1.357432000	0.807847000
C	-6.255066000	-0.569869000	-0.094282000
H	-5.406384000	1.413501000	-0.246303000
C	-4.749725000	-2.293988000	0.677984000
H	-2.741329000	-1.644372000	1.152113000
C	-6.009518000	-1.900974000	0.230655000
H	-7.234920000	-0.264983000	-0.447332000
H	-4.556687000	-3.332404000	0.925690000
H	-6.801107000	-2.636971000	0.132172000
C	0.253303000	2.373029000	0.022798000
C	0.462637000	3.045100000	-1.174881000
C	1.307463000	2.017767000	0.857420000
C	1.765366000	3.363602000	-1.543522000
H	-0.379244000	3.294616000	-1.812149000
C	2.603434000	2.352572000	0.485001000
H	1.114001000	1.454626000	1.764436000
C	2.830311000	3.021290000	-0.714977000
H	1.946140000	3.873007000	-2.484192000
H	3.435364000	2.055747000	1.113929000
H	3.845999000	3.263102000	-1.012000000

**3':**

E = -1030.19541279

C	0.001716000	-0.204665000	-0.037281000
C	-0.678701000	1.972465000	-0.133462000
C	0.663111000	1.977971000	-0.132607000
H	-1.397288000	2.775232000	-0.161879000
H	1.373702000	2.786628000	-0.185612000
N	-1.089329000	0.640908000	-0.069191000

N	1.085128000	0.651605000	-0.080011000
H	-1.302965000	-2.120083000	0.032337000
P	0.106646000	-1.957402000	0.039875000
C	-2.460620000	0.262709000	-0.007979000
C	-3.291672000	0.547127000	-1.087202000
C	-2.968084000	-0.337338000	1.142346000
C	-4.646096000	0.234926000	-1.011253000
H	-2.871622000	1.002011000	-1.979012000
C	-4.318600000	-0.658139000	1.205401000
H	-2.298182000	-0.557380000	1.967008000
C	-5.159544000	-0.368762000	0.132321000
H	-5.297298000	0.457671000	-1.850790000
H	-4.717236000	-1.129370000	2.098288000
H	-6.215272000	-0.615499000	0.188825000
C	2.456615000	0.272487000	-0.037299000
C	3.275555000	0.814033000	0.950867000
C	2.977939000	-0.595704000	-0.993745000
C	4.628347000	0.490473000	0.976371000
H	2.848142000	1.475230000	1.698769000
C	4.327166000	-0.926428000	-0.949714000
H	2.325166000	-1.010732000	-1.753447000
C	5.155059000	-0.383123000	0.029722000
H	5.267349000	0.912375000	1.745968000
H	4.732973000	-1.608969000	-1.689805000
H	6.209090000	-0.641860000	0.056733000

**6':**

E = -1255.69276001

P	-2.309804000	-0.362757000	1.010464000
P	-2.312926000	-0.389118000	-0.996738000
P	-1.009917000	1.111192000	-0.014624000
C	0.668888000	0.335626000	-0.005571000
C	1.730876000	1.248734000	-0.003188000
C	0.960034000	-1.032058000	-0.002376000
C	3.049904000	0.807405000	0.002751000
C	2.279878000	-1.473721000	0.003028000
C	3.327000000	-0.556660000	0.005922000

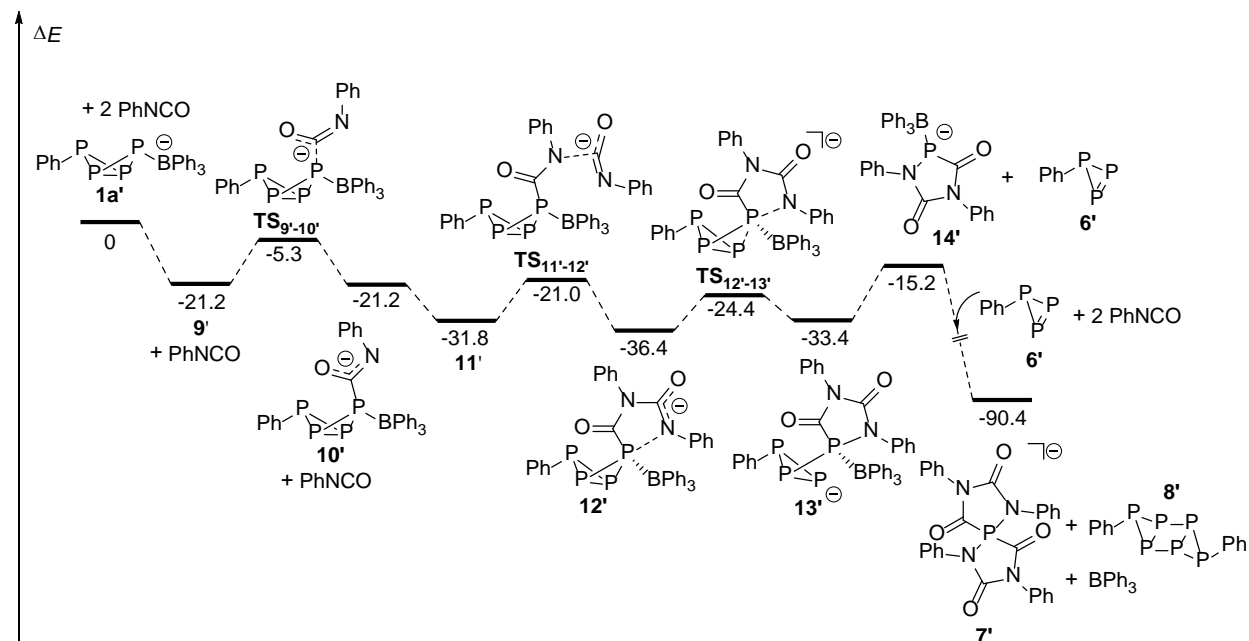
H	3.860555000	1.529860000	0.004746000
H	2.489093000	-2.539397000	0.005168000
H	0.161125000	-1.768260000	-0.004140000
H	1.523782000	2.316590000	-0.006099000
H	4.355692000	-0.904514000	0.010398000

**8':**

E = -2511.45902234

P	-0.509851000	1.003685000	-1.125093000
P	0.509851000	-1.003685000	-1.125093000
P	0.509837000	-1.003692000	1.125022000
P	-0.509837000	1.003692000	1.125022000
P	1.104311000	2.025105000	-0.000052000
P	-1.104311000	-2.025105000	-0.000052000
C	-0.411425000	-3.737500000	-0.000009000
C	-0.206717000	-4.417199000	1.205968000
C	-0.206531000	-4.417230000	-1.205933000
C	0.206531000	-5.745641000	1.204385000
H	-0.362083000	-3.905608000	2.151961000
C	0.206717000	-5.745675000	-1.204248000
H	-0.361747000	-3.905666000	-2.151965000
C	0.414677000	-6.411875000	0.000093000
H	0.368532000	-6.258783000	2.147543000
H	0.368864000	-6.258841000	-2.147367000
H	0.739704000	-7.448003000	0.000132000
C	0.411425000	3.737500000	-0.000009000
C	0.206717000	4.417199000	1.205968000
C	0.206531000	4.417230000	-1.205933000
C	-0.206531000	5.745641000	1.204385000
H	0.362083000	3.905608000	2.151961000
C	-0.206717000	5.745675000	-1.204248000
H	0.361747000	3.905666000	-2.151965000
C	-0.414677000	6.411875000	0.000093000
H	-0.368532000	6.258783000	2.147543000
H	-0.368864000	6.258841000	-2.147367000
H	-0.739704000	7.448003000	0.000132000

## Calculated minimum energy reaction pathway for the fragmentation of 1a' using PhNCO



**Scheme S3.** Relative  $\omega$ B97X-D/6-311+G(2d,p)//6-31G(d) energies (in kcal mol<sup>-1</sup>) for the computed fragmentation pathway leading from 1a' to 7', 8' and BPh<sub>3</sub>. A Li<sup>+</sup> counter cation was included in all anionic species but is not shown.

### Optimized geometries (Cartesian coordinates) and uncorrected energies (in a.u.)

#### PhNCO:

E = -399.703737546

C	0.853686000	-1.290537000	-0.000030000
C	-0.090604000	-0.264583000	-0.000096000
C	0.322618000	1.070387000	-0.000118000
C	1.679795000	1.369027000	0.000005000
C	2.627107000	0.348355000	0.000090000
C	2.208647000	-0.979603000	0.000061000
H	0.513109000	-2.320454000	-0.000035000
H	-0.418096000	1.864569000	-0.000225000
H	1.996643000	2.407554000	0.000025000
H	3.686043000	0.586526000	0.000218000
H	2.940790000	-1.781129000	0.000104000
N	-1.444932000	-0.614230000	-0.000133000
C	-2.526681000	-0.080795000	0.000068000

O -3.631421000 0.313630000 0.000121000

**BPh<sub>3</sub>:**

E = -719.761820912

B -0.003002000 -0.001125000 0.000212000

C 0.973861000 -1.228024000 -0.000521000

C 0.641630000 -2.431150000 0.647674000

C 2.220134000 -1.168356000 -0.649162000

C 1.513219000 -3.514940000 0.660755000

H -0.313990000 -2.512419000 1.159073000

C 3.085956000 -2.256317000 -0.663293000

H 2.509046000 -0.253674000 -1.160256000

C 2.735704000 -3.430440000 -0.001232000

H 1.238258000 -4.427761000 1.181572000

H 4.036995000 -2.187520000 -1.183622000

H 3.414877000 -4.278539000 -0.001228000

C -1.554029000 -0.231377000 0.000640000

C -2.427077000 0.663751000 0.644035000

C -2.128823000 -1.341686000 -0.643146000

C -3.802131000 0.456240000 0.656951000

H -2.016453000 1.532709000 1.151720000

C -3.504815000 -1.542398000 -0.657378000

H -1.482931000 -2.053953000 -1.149941000

C -4.343835000 -0.645461000 -0.000762000

H -4.453004000 1.156127000 1.173115000

H -3.923796000 -2.400642000 -1.174857000

H -5.418590000 -0.804838000 -0.001462000

C 0.573906000 1.457314000 0.001191000

C -0.096594000 2.510592000 -0.645689000

C 1.784396000 1.764279000 0.647952000

C 0.419829000 3.801772000 -0.659543000

H -1.035112000 2.308927000 -1.155419000

C 2.294239000 3.057969000 0.661290000

H 2.329118000 0.973698000 1.157289000

C 1.614594000 4.078334000 0.000530000

H -0.111027000 4.594533000 -1.178904000

H 3.224658000 3.270404000 1.180040000

H 2.015977000 5.087950000 0.000071000

**6'**:

E = -1255.69276001

P -2.309804000 -0.362757000 1.010464000

P -2.312926000 -0.389118000 -0.996738000

P -1.009917000 1.111192000 -0.014624000

C 0.668888000 0.335626000 -0.005571000

C 1.730876000 1.248734000 -0.003188000

C 0.960034000 -1.032058000 -0.002376000

C 3.049904000 0.807405000 0.002751000

C 2.279878000 -1.473721000 0.003028000

C 3.327000000 -0.556660000 0.005922000

H 3.860555000 1.529860000 0.004746000

H 2.489093000 -2.539397000 0.005168000

H 0.161125000 -1.768260000 -0.004140000

H 1.523782000 2.316590000 -0.006099000

H 4.355692000 -0.904514000 0.010398000

Li[1a']:

E = -2324.44060227

P 1.573662000 0.186425000 0.778547000

P 1.581949000 -0.586950000 -1.265334000

P -0.071268000 0.709746000 -0.611086000

P 2.794961000 1.227925000 -0.776305000

C -2.356233000 1.334642000 0.650802000

C -3.179801000 2.160370000 -0.141530000

C -1.781467000 1.945007000 1.788541000

C -3.367517000 3.518756000 0.137862000

C -1.961884000 3.299456000 2.082276000

C -2.742744000 4.103494000 1.243842000

C -2.735662000 -0.654523000 -1.142057000

C -3.932267000 -1.328310000 -0.846367000

C -2.457010000 -0.442689000 -2.498776000

C -4.804120000 -1.756347000 -1.841774000

C -3.320484000 -0.868576000 -3.507690000

C -4.501502000 -1.526153000 -3.182205000

C	-1.599622000	-1.253751000	1.223245000
C	-0.843923000	-2.402343000	0.934944000
C	-2.195784000	-1.200369000	2.490890000
C	-0.663202000	-3.420265000	1.864617000
C	-2.029063000	-2.217072000	3.430366000
C	-1.253162000	-3.328958000	3.123429000
B	-1.834730000	-0.124976000	0.096097000
C	4.449949000	0.451908000	-0.485681000
C	5.085421000	0.558651000	0.756541000
C	5.129556000	-0.171885000	-1.538379000
C	6.362771000	0.039623000	0.945272000
C	6.405630000	-0.692726000	-1.348309000
C	7.024639000	-0.588483000	-0.105776000
H	6.839947000	0.123907000	1.917184000
H	6.915410000	-1.182470000	-2.172780000
H	-1.137361000	1.349620000	2.430452000
H	-1.536713000	0.063289000	-2.788475000
H	-3.065928000	-0.689821000	-4.549301000
H	-1.484648000	3.731582000	2.957314000
H	-5.177578000	-1.862157000	-3.963587000
H	-2.878789000	5.158549000	1.460470000
H	-3.995621000	4.122738000	-0.511066000
H	-5.720105000	-2.276265000	-1.572944000
H	-4.178838000	-1.528952000	0.194215000
H	-3.647208000	1.732495000	-1.024092000
H	-0.398189000	-2.510743000	-0.052417000
H	-2.823429000	-0.351179000	2.753680000
H	-2.510609000	-2.139488000	4.401884000
H	-1.115680000	-4.121643000	3.853677000
H	-0.065784000	-4.290103000	1.604644000
H	4.577652000	1.042536000	1.587089000
H	4.655122000	-0.260581000	-2.512446000
H	8.019314000	-0.997864000	0.043308000
Li	-0.893993000	3.032497000	-0.209706000

Li[9']:

E = -2724.17809876

P	0.655727000	-0.427202000	0.460495000
P	0.222350000	-1.770173000	-1.212158000
P	-0.984714000	0.059978000	-0.952011000
P	1.892713000	-0.302790000	-1.390090000
C	-2.846861000	1.459736000	0.431773000
C	-3.611763000	2.308289000	-0.394244000
C	-2.011519000	2.104631000	1.370946000
C	-3.525975000	3.703084000	-0.316631000
C	-1.925080000	3.494590000	1.466580000
C	-2.673875000	4.305703000	0.610791000
C	-3.920627000	-0.654359000	-0.863079000
C	-5.198905000	-0.841720000	-0.309843000
C	-3.796348000	-0.887281000	-2.238180000
C	-6.288915000	-1.228901000	-1.081198000
C	-4.880074000	-1.279804000	-3.024403000
C	-6.133446000	-1.450122000	-2.448494000
C	-2.594240000	-1.112860000	1.416675000
C	-2.265017000	-2.467772000	1.240290000
C	-2.868623000	-0.707627000	2.730443000
C	-2.175107000	-3.354964000	2.306204000
C	-2.788988000	-1.587908000	3.809362000
C	-2.431773000	-2.915200000	3.603258000
B	-2.736239000	-0.150992000	0.125537000
C	3.371656000	-1.340293000	-0.991500000
C	3.562557000	-2.072173000	0.185003000
C	4.390463000	-1.340521000	-1.951572000
C	4.742265000	-2.779385000	0.395327000
C	5.568251000	-2.051596000	-1.745182000
C	5.748089000	-2.770519000	-0.566978000
H	4.874599000	-3.339227000	1.316694000
H	6.344521000	-2.044389000	-2.504854000
H	-1.389450000	1.495701000	2.021830000
H	-2.827350000	-0.768745000	-2.721380000
H	-4.739509000	-1.456292000	-4.087807000
H	-1.258351000	3.945906000	2.196150000
H	-6.980474000	-1.758111000	-3.055586000
H	-2.596132000	5.386850000	0.669064000

H	-4.125596000	4.318378000	-0.981856000
H	-7.261342000	-1.365948000	-0.614962000
H	-5.336863000	-0.687325000	0.758620000
H	-4.271660000	1.859752000	-1.131750000
H	-2.097254000	-2.843622000	0.232409000
H	-3.174046000	0.318033000	2.924308000
H	-3.013286000	-1.233679000	4.812587000
H	-2.366952000	-3.605107000	4.440290000
H	-1.914911000	-4.394436000	2.124461000
H	2.789708000	-2.093661000	0.948534000
H	4.261622000	-0.774176000	-2.871393000
H	6.667619000	-3.324246000	-0.400666000
Li	-1.211612000	2.673674000	-0.923933000
O	0.529373000	3.593728000	-0.958850000
C	1.518077000	3.195928000	-0.421261000
N	2.486456000	2.902076000	0.184783000
C	3.617762000	2.135500000	0.473153000
C	3.696496000	1.485676000	1.702988000
C	4.637701000	2.025129000	-0.469808000
C	4.807558000	0.698184000	1.978692000
H	2.886798000	1.585499000	2.417493000
C	5.743229000	1.235448000	-0.176542000
H	4.547446000	2.534936000	-1.422919000
C	5.829993000	0.570674000	1.042540000
H	4.867600000	0.174385000	2.927028000
H	6.530438000	1.125224000	-0.914764000
H	6.685778000	-0.060742000	1.255702000

Li[TS<sub>9-10</sub>]:

E = -2724.15276292

P	-1.694964000	-1.634815000	-0.979287000
P	-1.688701000	-0.401641000	0.853795000
P	-0.013493000	-0.279112000	-0.554914000
P	-2.852491000	0.269409000	-0.927895000
B	1.595688000	-1.315947000	0.186352000
C	0.756023000	2.019633000	-1.238860000
O	1.731590000	1.730485000	-1.899663000

N	-0.041551000	2.747327000	-0.675123000
C	-4.553655000	-0.330422000	-0.513201000
C	-5.600203000	0.469514000	-0.985851000
C	-4.868252000	-1.484553000	0.214762000
C	-6.927217000	0.130185000	-0.737764000
H	-5.374446000	1.369288000	-1.553805000
C	-6.194100000	-1.824561000	0.461148000
H	-4.079634000	-2.128592000	0.596203000
C	-7.226608000	-1.018855000	-0.013104000
H	-7.725740000	0.764494000	-1.111377000
H	-6.421054000	-2.723996000	1.026047000
H	-8.260927000	-1.286385000	0.181878000
C	0.114929000	4.082009000	-0.254641000
C	1.372632000	4.678949000	-0.130052000
C	-1.035637000	4.793681000	0.083766000
C	1.468731000	5.988646000	0.326915000
H	2.267045000	4.116069000	-0.380712000
C	-0.928189000	6.105330000	0.530849000
H	-1.999262000	4.304489000	-0.011092000
C	0.321827000	6.706792000	0.656142000
H	2.446967000	6.449903000	0.425242000
H	-1.826872000	6.657559000	0.788721000
H	0.402875000	7.729171000	1.012056000
C	2.553697000	-0.115699000	0.802854000
C	3.949919000	-0.092663000	0.610428000
C	2.019624000	0.984767000	1.501621000
C	4.751525000	0.969362000	1.041729000
H	4.432393000	-0.934565000	0.114397000
C	2.806166000	2.043568000	1.943783000
H	0.951383000	1.022430000	1.698616000
C	4.178902000	2.049415000	1.702623000
H	5.823973000	0.939060000	0.868024000
H	2.340811000	2.876870000	2.462500000
H	4.793089000	2.880840000	2.035331000
C	1.101112000	-2.386075000	1.290909000
C	0.540008000	-3.610672000	0.891135000
C	1.163536000	-2.142956000	2.669896000

C	0.058363000	-4.536088000	1.811171000
H	0.482809000	-3.847129000	-0.169772000
C	0.687322000	-3.063684000	3.600934000
H	1.598544000	-1.214303000	3.031450000
C	0.130389000	-4.265148000	3.175095000
H	-0.373041000	-5.470578000	1.462157000
H	0.756544000	-2.842362000	4.662841000
H	-0.241337000	-4.985338000	3.898723000
C	2.341473000	-2.021640000	-1.093063000
C	3.320250000	-3.005367000	-0.851348000
C	2.165331000	-1.649854000	-2.439217000
C	4.087090000	-3.555028000	-1.871364000
H	3.471072000	-3.348149000	0.169519000
C	2.939092000	-2.187336000	-3.474582000
H	1.380546000	-0.939696000	-2.707715000
C	3.909100000	-3.139381000	-3.191796000
H	4.829765000	-4.313231000	-1.638424000
H	2.760095000	-1.874019000	-4.499566000
H	4.509162000	-3.567540000	-3.989133000
Li	2.946874000	0.337158000	-1.460558000

Li[10<sup>3</sup>]:

E = -2724.17806291

P	2.357382000	0.418495000	-1.026760000
P	2.158125000	0.048504000	1.176020000
P	0.404141000	0.110313000	-0.108034000
P	2.797043000	-1.602758000	-0.186586000
C	-2.233049000	0.920017000	-0.938034000
C	-3.376373000	0.326955000	-0.377055000
C	-2.129953000	0.867535000	-2.341848000
C	-4.371224000	-0.266623000	-1.161054000
C	-3.120401000	0.297099000	-3.142512000
C	-4.254553000	-0.274491000	-2.553740000
C	-1.486038000	1.741027000	1.556953000
C	-1.927414000	2.988440000	2.023776000
C	-1.511806000	0.678373000	2.475246000
C	-2.376878000	3.169091000	3.329367000

C	-1.951680000	0.851722000	3.785535000
C	-2.388715000	2.099716000	4.219484000
C	-0.413508000	2.955905000	-0.599058000
C	0.777182000	3.469171000	-0.056861000
C	-1.034624000	3.734824000	-1.584564000
C	1.342309000	4.658891000	-0.502337000
C	-0.485887000	4.935544000	-2.032267000
C	0.713024000	5.397240000	-1.501792000
B	-1.073352000	1.602974000	-0.004815000
C	4.629077000	-1.443261000	0.004541000
C	5.444434000	-1.182614000	-1.102940000
C	5.229500000	-1.687413000	1.245213000
C	6.828552000	-1.145576000	-0.966484000
C	6.613709000	-1.648580000	1.379296000
C	7.415388000	-1.374980000	0.274579000
H	7.448557000	-0.933942000	-1.832475000
H	7.066065000	-1.830344000	2.349475000
H	-1.244062000	1.274048000	-2.821485000
H	-1.193500000	-0.314309000	2.160997000
H	-1.948160000	0.007303000	4.470447000
H	-3.003833000	0.287502000	-4.222393000
H	-2.731263000	2.238492000	5.241296000
H	-5.032507000	-0.715855000	-3.170022000
H	-5.233330000	-0.722950000	-0.683960000
H	-2.712366000	4.150929000	3.653310000
H	-1.916822000	3.841431000	1.350051000
H	-3.487615000	0.320153000	0.702831000
H	1.264866000	2.938722000	0.759518000
H	-1.981016000	3.410505000	-2.008905000
H	-1.000980000	5.511455000	-2.796686000
H	1.148251000	6.328407000	-1.853351000
H	2.268832000	5.015812000	-0.061118000
H	4.998461000	-1.003656000	-2.077888000
H	4.614513000	-1.905280000	2.114847000
H	8.495437000	-1.342054000	0.381055000
C	-0.396620000	-1.532123000	-0.505993000
O	-0.549588000	-1.768792000	-1.741432000

N	-0.962906000	-2.035024000	0.551773000
C	-2.006885000	-2.959777000	0.386397000
C	-3.093458000	-2.837040000	1.269773000
C	-2.071791000	-3.949025000	-0.614604000
C	-4.216230000	-3.641379000	1.138374000
H	-3.035182000	-2.080791000	2.046794000
C	-3.207260000	-4.753744000	-0.737729000
H	-1.225724000	-4.093110000	-1.277066000
C	-4.286074000	-4.599702000	0.126235000
H	-5.044318000	-3.521226000	1.831214000
H	-3.234173000	-5.516171000	-1.511460000
H	-5.165498000	-5.227890000	0.024049000
Li	-2.425908000	-1.708730000	-1.823647000

Li[11\*]:

E = -3123.89878575

P	2.266460000	-0.949133000	1.139080000
P	1.866720000	-0.403833000	-0.997926000
P	0.284434000	-0.273690000	0.502351000
P	3.065059000	0.955217000	0.304028000
C	4.771652000	0.388400000	-0.136800000
C	5.142747000	-0.894203000	-0.559973000
C	5.762484000	1.371214000	-0.024671000
C	6.470481000	-1.181532000	-0.858542000
C	7.090747000	1.082571000	-0.322332000
C	7.446931000	-0.196128000	-0.739442000
H	6.741889000	-2.181343000	-1.184200000
H	7.846433000	1.856664000	-0.228204000
H	4.400892000	-1.682460000	-0.661716000
H	5.491876000	2.373482000	0.299689000
H	8.483002000	-0.424770000	-0.970759000
C	-0.072414000	1.491361000	1.027513000
O	-0.645051000	1.595092000	2.159892000
N	0.224378000	2.401646000	0.144916000
C	0.027063000	3.749324000	0.473504000
C	0.387316000	4.306147000	1.718423000
C	-0.535766000	4.601094000	-0.489894000

C	0.138091000	5.650832000	1.994387000
H	0.884600000	3.679834000	2.453067000
C	-0.781563000	5.938621000	-0.205806000
H	-0.783391000	4.189549000	-1.463644000
C	-0.459947000	6.471627000	1.041454000
H	0.434100000	6.060137000	2.956603000
H	-1.227593000	6.572181000	-0.966899000
H	-0.652822000	7.517127000	1.259048000
C	-3.008504000	2.537077000	-0.144851000
O	-3.177937000	3.072549000	0.914344000
N	-2.879811000	2.075084000	-1.214883000
C	-2.487904000	1.276038000	-2.285385000
C	-3.448916000	0.517648000	-2.948867000
C	-1.150175000	1.267699000	-2.681927000
C	-3.061909000	-0.251286000	-4.039979000
H	-4.471517000	0.516831000	-2.589401000
C	-0.782909000	0.496111000	-3.778815000
H	-0.419360000	1.830955000	-2.108392000
C	-1.735230000	-0.253880000	-4.464641000
H	-3.801839000	-0.853725000	-4.557007000
H	0.257602000	0.471704000	-4.086919000
H	-1.440279000	-0.854437000	-5.319604000
B	-1.068386000	-1.932195000	0.583949000
C	-0.364268000	-2.818991000	-0.574381000
C	-0.970495000	-2.509394000	2.092494000
C	-2.579381000	-1.425566000	0.298659000
C	0.585942000	-3.811156000	-0.289667000
C	-0.605684000	-2.549911000	-1.932542000
C	-1.332186000	-3.850180000	2.300213000
C	-0.672276000	-1.754433000	3.234602000
C	-3.160066000	-0.379098000	1.032334000
C	-3.434139000	-2.147227000	-0.546508000
C	1.251831000	-4.502295000	-1.299734000
H	0.814475000	-4.043802000	0.747151000
C	0.050737000	-3.234436000	-2.949370000
H	-1.317542000	-1.773530000	-2.198986000
C	-1.369742000	-4.415026000	3.570806000

H	-1.594697000	-4.467279000	1.443482000
C	-0.704467000	-2.310405000	4.511980000
H	-0.427479000	-0.697885000	3.137232000
C	-4.506831000	-0.049243000	0.907922000
H	-2.543793000	0.175860000	1.737020000
C	-4.785570000	-1.832322000	-0.673435000
H	-3.040653000	-2.987941000	-1.110717000
C	0.985713000	-4.217883000	-2.635427000
H	1.983018000	-5.263380000	-1.040496000
H	-0.163381000	-2.994461000	-3.987874000
C	-1.047810000	-3.646509000	4.686480000
H	-1.649650000	-5.458456000	3.690821000
H	-0.459869000	-1.693748000	5.373256000
C	-5.328553000	-0.773302000	0.046510000
H	-4.920467000	0.767185000	1.495393000
H	-5.416434000	-2.422959000	-1.333058000
H	1.504233000	-4.754627000	-3.425303000
H	-1.070503000	-4.084689000	5.680447000
H	-6.383168000	-0.527540000	-0.045450000
Li	-1.711365000	3.120568000	2.214280000

Li[TS<sub>11'-12'</sub>]:

E = -3123.88159176

P	-0.888746000	-1.998396000	-1.476012000
P	-1.510338000	-1.021175000	0.430010000
P	0.467824000	-0.652556000	-0.428471000
P	-2.258494000	-0.230201000	-1.513835000
B	2.127249000	-1.543165000	0.475328000
C	0.757892000	0.998943000	-1.338145000
O	1.000012000	0.896667000	-2.531299000
N	0.852451000	2.044279000	-0.498512000
C	-0.501168000	2.140360000	1.058973000
O	0.213159000	1.923480000	2.015580000
N	-1.546943000	2.417687000	0.485177000
C	1.415653000	3.278049000	-0.904566000
C	1.471555000	4.296418000	0.064613000
C	2.014473000	3.521616000	-2.152264000

C	2.113043000	5.502983000	-0.191629000
H	0.987963000	4.157656000	1.028861000
C	2.653080000	4.732956000	-2.394903000
H	1.969615000	2.762510000	-2.919442000
C	2.715045000	5.728891000	-1.424452000
H	2.130495000	6.269655000	0.577355000
H	3.108885000	4.896831000	-3.367359000
H	3.214924000	6.670250000	-1.629621000
C	-2.855965000	2.340445000	0.990287000
C	-3.161612000	1.746481000	2.219791000
C	-3.882715000	2.830564000	0.180379000
C	-4.488420000	1.651058000	2.627843000
H	-2.365225000	1.357746000	2.847697000
C	-5.204223000	2.738725000	0.601711000
H	-3.624445000	3.271480000	-0.776430000
C	-5.512954000	2.147222000	1.824818000
H	-4.719440000	1.183874000	3.580408000
H	-5.996301000	3.119953000	-0.035372000
H	-6.546082000	2.069248000	2.149108000
C	-3.890134000	-1.094744000	-1.499359000
C	-4.252098000	-1.992030000	-2.509930000
C	-4.830007000	-0.757651000	-0.517512000
C	-5.523593000	-2.557169000	-2.525865000
H	-3.539200000	-2.256221000	-3.286836000
C	-6.101002000	-1.321839000	-0.539396000
H	-4.570378000	-0.054113000	0.268944000
C	-6.449539000	-2.223365000	-1.541292000
H	-5.790849000	-3.259961000	-3.309249000
H	-6.818486000	-1.053507000	0.230276000
H	-7.441016000	-2.665932000	-1.555981000
C	1.399193000	-2.438889000	1.613972000
C	0.723743000	-1.855876000	2.703036000
C	1.331170000	-3.836647000	1.517001000
C	0.058169000	-2.618403000	3.657880000
H	0.688677000	-0.771398000	2.797217000
C	0.662606000	-4.610185000	2.463153000
H	1.808070000	-4.333969000	0.677692000

C	0.029935000	-4.005342000	3.543813000
H	-0.448368000	-2.127514000	4.484570000
H	0.631700000	-5.690424000	2.349449000
H	-0.492252000	-4.606570000	4.282711000
C	3.040202000	-0.281120000	0.975381000
C	3.638794000	0.565473000	0.017611000
C	3.285600000	0.035381000	2.322279000
C	4.367763000	1.698622000	0.374209000
H	3.498946000	0.350890000	-1.038861000
C	4.027494000	1.161835000	2.696346000
H	2.881734000	-0.602847000	3.100832000
C	4.554408000	2.011861000	1.724201000
H	4.764771000	2.350322000	-0.397831000
H	4.183227000	1.377163000	3.749377000
H	5.108377000	2.900610000	2.009823000
C	2.946233000	-2.347166000	-0.667283000
C	3.965437000	-3.210726000	-0.229607000
C	2.813562000	-2.183771000	-2.052139000
C	4.785098000	-3.894723000	-1.119980000
H	4.118112000	-3.351984000	0.838530000
C	3.633333000	-2.861348000	-2.954314000
H	2.073735000	-1.495898000	-2.457364000
C	4.618039000	-3.726108000	-2.492817000
H	5.557107000	-4.560170000	-0.742678000
H	3.496784000	-2.707895000	-4.021253000
H	5.254226000	-4.260237000	-3.192887000
Li	2.010771000	1.883860000	1.231440000

Li[12\*]:

E = -3123.90608572

P	2.002123000	0.593095000	-1.628913000
P	2.383356000	0.059134000	0.532565000
P	0.328542000	0.064207000	-0.193975000
P	2.740565000	-1.428448000	-1.089132000
C	4.572698000	-1.246016000	-1.257752000
C	5.282890000	-0.041770000	-1.190548000
C	5.280290000	-2.434254000	-1.468264000

C	6.666461000	-0.031080000	-1.327644000
C	6.665533000	-2.422841000	-1.608013000
C	7.360929000	-1.220415000	-1.536962000
H	7.203264000	0.911407000	-1.273568000
H	7.198540000	-3.354550000	-1.772994000
H	4.759269000	0.899252000	-1.037878000
H	4.743133000	-3.377999000	-1.526495000
H	8.441313000	-1.207525000	-1.647279000
C	-0.530115000	-1.336655000	-1.153160000
O	-0.363487000	-1.547467000	-2.325739000
N	-1.538661000	-1.949666000	-0.403599000
C	-2.627841000	-2.609978000	-1.059797000
C	-3.329223000	-1.925210000	-2.050782000
C	-2.976557000	-3.909749000	-0.709344000
C	-4.392458000	-2.551679000	-2.689961000
H	-3.032656000	-0.919282000	-2.335033000
C	-4.049543000	-4.523508000	-1.347260000
H	-2.419767000	-4.428022000	0.062482000
C	-4.757225000	-3.848494000	-2.337641000
H	-4.935225000	-2.021432000	-3.466173000
H	-4.326267000	-5.536658000	-1.072575000
H	-5.590747000	-4.333381000	-2.836645000
C	-1.473181000	-1.827708000	0.986121000
O	-2.329560000	-2.335717000	1.736501000
N	-0.480840000	-1.024786000	1.386336000
C	0.114455000	-1.232306000	2.649536000
C	0.160115000	-0.208591000	3.600676000
C	0.710552000	-2.465252000	2.951308000
C	0.779948000	-0.414025000	4.833340000
H	-0.278831000	0.755155000	3.366151000
C	1.318445000	-2.666212000	4.181258000
H	0.694432000	-3.253874000	2.205465000
C	1.356910000	-1.642073000	5.128763000
H	0.813017000	0.395028000	5.556678000
H	1.776908000	-3.625791000	4.399835000
H	1.841671000	-1.802598000	6.086380000
B	-0.876366000	1.798427000	-0.082566000

C	0.212604000	2.941456000	0.301304000
C	-1.610123000	2.070833000	-1.513462000
C	-2.060017000	1.527352000	1.024660000
C	0.473459000	4.005617000	-0.575247000
C	0.962628000	2.923012000	1.490514000
C	-2.626917000	3.045594000	-1.497690000
C	-1.336703000	1.487262000	-2.756144000
C	-3.181854000	0.747160000	0.673620000
C	-2.096585000	2.097979000	2.306944000
C	1.407306000	4.995636000	-0.279563000
H	-0.063130000	4.060890000	-1.517334000
C	1.896913000	3.906678000	1.800576000
H	0.837774000	2.103107000	2.194107000
C	-3.328861000	3.410024000	-2.639866000
H	-2.870638000	3.539634000	-0.559223000
C	-2.046043000	1.832727000	-3.908414000
H	-0.558236000	0.740073000	-2.854082000
C	-4.241659000	0.508862000	1.547944000
H	-3.232376000	0.314678000	-0.320580000
C	-3.145234000	1.865213000	3.204150000
H	-1.290699000	2.757841000	2.614413000
C	2.121732000	4.954283000	0.912935000
H	1.579850000	5.799707000	-0.989915000
H	2.455946000	3.846202000	2.730521000
C	-3.045903000	2.794988000	-3.857697000
H	-4.100549000	4.172975000	-2.579634000
H	-1.804099000	1.344318000	-4.848481000
C	-4.224413000	1.059722000	2.834602000
H	-5.071167000	-0.115314000	1.229919000
H	-3.125636000	2.328230000	4.186751000
H	2.852571000	5.723727000	1.145279000
H	-3.594972000	3.068228000	-4.754515000
H	-5.045419000	0.883872000	3.523233000
Li	-2.397940000	-0.597575000	2.684111000

Li[TS<sub>12'-13'</sub>]:

E = -3123.88698772

P	2.419396000	0.416492000	-2.289133000
P	2.471323000	0.563149000	-0.100867000
P	0.323640000	0.135625000	-0.114701000
P	3.029422000	-1.333052000	-1.126555000
B	-1.253442000	1.522388000	-0.549088000
C	-0.226395000	-1.513581000	-0.827944000
O	-0.136883000	-1.949780000	-1.940742000
N	-1.000679000	-2.134052000	0.169954000
C	-0.957790000	-1.574344000	1.450000000
O	-1.709898000	-2.003201000	2.342627000
N	-0.122627000	-0.526540000	1.517102000
C	-1.901405000	-3.204130000	-0.128513000
C	-2.835992000	-3.042301000	-1.153125000
C	-1.872898000	-4.375508000	0.628169000
C	-3.754541000	-4.057450000	-1.407460000
H	-2.820542000	-2.144517000	-1.760751000
C	-2.802175000	-5.377529000	0.372474000
H	-1.133862000	-4.489732000	1.412560000
C	-3.745018000	-5.219828000	-0.641555000
H	-4.473167000	-3.937721000	-2.211825000
H	-2.781977000	-6.288559000	0.961847000
H	-4.464319000	-6.007563000	-0.841726000
C	0.290015000	0.051116000	2.754010000
C	0.551184000	1.418501000	2.825392000
C	0.491322000	-0.755767000	3.876178000
C	0.991266000	1.978426000	4.020215000
H	0.412061000	2.056868000	1.960547000
C	0.920578000	-0.183103000	5.066547000
H	0.311921000	-1.822529000	3.820023000
C	1.171464000	1.184596000	5.146744000
H	1.188580000	3.044924000	4.056346000
H	1.070806000	-0.817075000	5.935031000
H	1.513804000	1.624109000	6.078231000
C	4.864799000	-1.224076000	-0.858804000
C	5.688917000	-0.224398000	-1.382728000
C	5.444260000	-2.247921000	-0.100446000
C	7.059581000	-0.242583000	-1.141351000

H	5.246008000	0.566758000	-1.983727000
C	6.814464000	-2.267316000	0.139953000
H	4.814680000	-3.037273000	0.304700000
C	7.625499000	-1.261788000	-0.379753000
H	7.689249000	0.541284000	-1.553069000
H	7.249534000	-3.067888000	0.731755000
H	8.696096000	-1.275253000	-0.195649000
C	-1.564046000	1.659935000	-2.134925000
C	-2.448492000	2.701962000	-2.471244000
C	-1.142481000	0.832787000	-3.181733000
C	-2.899724000	2.899574000	-3.770494000
H	-2.789015000	3.381911000	-1.692791000
C	-1.585885000	1.027268000	-4.490886000
H	-0.427353000	0.039702000	-2.999377000
C	-2.469784000	2.055504000	-4.792328000
H	-3.580946000	3.718178000	-3.988191000
H	-1.224251000	0.368809000	-5.276118000
H	-2.812621000	2.207495000	-5.812211000
C	-2.565248000	0.882270000	0.228396000
C	-2.793452000	0.993776000	1.615238000
C	-3.599691000	0.271683000	-0.507191000
C	-3.990095000	0.596368000	2.217230000
H	-2.023098000	1.416006000	2.251930000
C	-4.798411000	-0.150972000	0.076949000
H	-3.476905000	0.162029000	-1.580775000
C	-5.013238000	0.031354000	1.447565000
H	-4.123289000	0.730394000	3.286554000
H	-5.573343000	-0.593966000	-0.542290000
H	-5.957599000	-0.252064000	1.903854000
C	-0.729856000	2.940391000	0.040799000
C	-1.457488000	3.744734000	0.929027000
C	0.489503000	3.465374000	-0.421958000
C	-0.972429000	4.970987000	1.382260000
H	-2.434923000	3.422748000	1.277099000
C	0.991101000	4.679043000	0.033702000
H	1.058474000	2.915404000	-1.167632000
C	0.264830000	5.435160000	0.950930000

H	-1.567912000	5.564256000	2.071279000
H	1.946216000	5.039289000	-0.337733000
H	0.652938000	6.383880000	1.310841000
Li	-3.376947000	-1.645446000	1.438353000

Li[13\*]:

E = -3123.90126941

P	1.200850000	-1.369321000	-0.896280000
P	2.499309000	-1.636396000	0.852258000
P	1.244284000	-3.318974000	0.093146000
C	-1.858662000	-0.809737000	-1.071053000
C	-2.360607000	-1.174294000	1.228515000
P	-0.427575000	-0.038275000	-0.154996000
O	-1.970078000	-0.888160000	-2.267751000
O	-3.021886000	-1.559069000	2.158109000
N	-2.739100000	-1.308831000	-0.126982000
N	-1.131026000	-0.531642000	1.331873000
C	-3.928868000	-2.011793000	-0.496717000
C	-4.825806000	-1.421456000	-1.381542000
C	-4.164537000	-3.282690000	0.019546000
C	-5.971956000	-2.116359000	-1.752558000
H	-4.621177000	-0.435519000	-1.784076000
C	-5.320894000	-3.961453000	-0.345537000
H	-3.455505000	-3.725084000	0.709535000
C	-6.224178000	-3.382753000	-1.232952000
H	-6.671030000	-1.661994000	-2.447663000
H	-5.511953000	-4.948485000	0.063755000
H	-7.124211000	-3.918176000	-1.519549000
C	-0.594277000	-0.290196000	2.644446000
C	-0.815670000	0.930003000	3.275146000
C	0.126598000	-1.299001000	3.275895000
C	-0.261657000	1.156845000	4.531028000
H	-1.414628000	1.689020000	2.788730000
C	0.669277000	-1.067817000	4.534716000
H	0.251390000	-2.254983000	2.776671000
C	0.485406000	0.163726000	5.158096000
H	-0.422257000	2.114135000	5.016814000

H	1.237050000	-1.851559000	5.026356000
H	0.917561000	0.345304000	6.137693000
B	-0.054188000	2.015595000	-0.594317000
C	1.524505000	2.197574000	-0.273382000
C	-0.458914000	2.076898000	-2.162246000
C	-1.054838000	2.786074000	0.412275000
C	2.406054000	2.760855000	-1.207127000
C	2.069327000	1.862842000	0.978068000
C	-1.517765000	2.876814000	-2.615392000
C	0.253768000	1.368863000	-3.144826000
C	-2.427053000	2.486577000	0.470317000
C	-0.595688000	3.790743000	1.274105000
C	3.754254000	2.971626000	-0.916162000
H	2.027962000	3.050486000	-2.183422000
C	3.413878000	2.057435000	1.278351000
H	1.424645000	1.442743000	1.748445000
C	-1.852008000	2.961474000	-3.964898000
H	-2.088716000	3.462189000	-1.900962000
C	-0.075656000	1.437514000	-4.493493000
H	1.098514000	0.749652000	-2.850287000
C	-3.289009000	3.124730000	1.355637000
H	-2.839820000	1.730718000	-0.197187000
C	-1.449582000	4.446411000	2.159372000
H	0.457039000	4.057994000	1.262616000
C	4.266456000	2.614559000	0.327504000
H	4.403508000	3.419422000	-1.664415000
H	3.793729000	1.773631000	2.255961000
C	-1.135979000	2.236339000	-4.910863000
H	-2.674548000	3.599887000	-4.276635000
H	0.496099000	0.865405000	-5.219321000
C	-2.798523000	4.108459000	2.212212000
H	-4.340420000	2.852506000	1.381658000
H	-1.057022000	5.218136000	2.816250000
H	5.317086000	2.771636000	0.555747000
H	-1.397108000	2.296804000	-5.963802000
H	-3.464130000	4.608651000	2.909868000
C	4.104993000	-1.770756000	-0.096354000

C	4.918249000	-2.910786000	0.028136000
C	4.528803000	-0.734949000	-0.943248000
C	6.107245000	-3.024164000	-0.694994000
H	4.610406000	-3.717835000	0.691230000
C	5.721600000	-0.846704000	-1.654384000
H	3.920130000	0.159587000	-1.047851000
C	6.508488000	-1.991610000	-1.540640000
H	6.720509000	-3.914218000	-0.588405000
H	6.031742000	-0.034604000	-2.305037000
H	7.433717000	-2.076905000	-2.101996000
Li	3.075098000	-3.253316000	-1.559375000

Li[14\*]:

E = -1868.17947674

C	1.393442000	0.888566000	-1.234428000
C	1.665296000	-1.376450000	-0.610084000
P	-0.298399000	0.229423000	-1.508052000
O	1.789054000	2.015566000	-1.402496000
O	2.265562000	-2.406742000	-0.213163000
N	2.262824000	-0.160575000	-0.786072000
N	0.358610000	-1.355058000	-0.950788000
C	3.622386000	0.088881000	-0.430044000
C	4.472831000	0.679140000	-1.359845000
C	4.075454000	-0.231531000	0.846917000
C	5.791196000	0.944602000	-1.006308000
H	4.097068000	0.940260000	-2.342287000
C	5.398944000	0.025085000	1.186443000
H	3.390559000	-0.673416000	1.561677000
C	6.258312000	0.613854000	0.262683000
H	6.454875000	1.411152000	-1.727544000
H	5.756084000	-0.226741000	2.180474000
H	7.289701000	0.819493000	0.532452000
C	-0.330143000	-2.589232000	-0.855891000
C	-0.265881000	-3.500382000	-1.915111000
C	-0.918950000	-2.963759000	0.356787000
C	-0.744666000	-4.799993000	-1.744761000
H	0.192457000	-3.188162000	-2.848118000

C	-1.397191000	-4.264439000	0.520469000
H	-0.966318000	-2.235576000	1.161405000
C	-1.296329000	-5.188737000	-0.522100000
H	-0.682422000	-5.509716000	-2.563626000
H	-1.849072000	-4.552032000	1.464503000
H	-1.663736000	-6.201367000	-0.389030000
B	-1.372727000	1.004080000	0.104025000
C	-0.720816000	0.471712000	1.500614000
C	-1.248846000	2.597513000	-0.181583000
C	-2.907769000	0.492145000	-0.085717000
C	0.609686000	0.736045000	1.875577000
C	-1.467536000	-0.297300000	2.409880000
C	-0.672021000	3.506147000	0.714906000
C	-1.771768000	3.134953000	-1.371013000
C	-3.922034000	1.199822000	0.582846000
C	-3.317009000	-0.639207000	-0.801406000
C	1.165226000	0.245772000	3.055057000
H	1.228612000	1.366570000	1.242345000
C	-0.923301000	-0.800176000	3.592277000
H	-2.510342000	-0.508657000	2.186522000
C	-0.606743000	4.870487000	0.440435000
H	-0.274918000	3.146146000	1.659918000
C	-1.702822000	4.492883000	-1.661378000
H	-2.264176000	2.471193000	-2.080193000
C	-5.252102000	0.795057000	0.554430000
H	-3.653314000	2.095981000	1.138055000
C	-4.647341000	-1.056187000	-0.846336000
H	-2.587478000	-1.218318000	-1.365902000
C	0.404086000	-0.539842000	3.917848000
H	2.193993000	0.492625000	3.306810000
H	-1.544709000	-1.387131000	4.264925000
C	-1.115154000	5.370099000	-0.753478000
H	-0.156695000	5.545486000	1.164256000
H	-2.115203000	4.869669000	-2.594014000
C	-5.623240000	-0.341577000	-0.162091000
H	-6.004412000	1.371593000	1.086908000
H	-4.919348000	-1.937654000	-1.422463000

H	0.833255000	-0.921093000	4.840661000
H	-1.059765000	6.433167000	-0.972260000
H	-6.662363000	-0.658184000	-0.193480000
Li	1.333054000	-3.950637000	0.079457000

Li[7\*]:

E = -1947.87146257

C	0.549833000	-1.583212000	-0.058907000
C	2.363265000	-0.060242000	-0.527482000
O	0.060355000	-2.571253000	0.435788000
O	3.298433000	0.582785000	0.004713000
N	1.867321000	-1.212150000	0.135193000
N	1.650999000	0.245281000	-1.602875000
C	2.707482000	-1.934071000	1.041939000
C	2.312415000	-2.130728000	2.361519000
C	3.922678000	-2.434428000	0.585142000
C	3.140362000	-2.839174000	3.225178000
H	1.358281000	-1.744356000	2.703311000
C	4.752247000	-3.129363000	1.457419000
H	4.213082000	-2.275325000	-0.448429000
C	4.361351000	-3.336450000	2.777303000
H	2.830048000	-3.000251000	4.252921000
H	5.701400000	-3.517292000	1.100812000
H	5.005550000	-3.888008000	3.455131000
C	1.945421000	1.390758000	-2.360200000
C	0.891756000	2.039614000	-3.029555000
C	3.241710000	1.928248000	-2.499617000
C	1.116706000	3.186041000	-3.777426000
H	-0.107450000	1.624175000	-2.964307000
C	3.453222000	3.084321000	-3.252420000
H	4.081054000	1.429369000	-2.031109000
C	2.397482000	3.726028000	-3.887898000
H	0.280010000	3.662953000	-4.279597000
H	4.463364000	3.472812000	-3.347563000
H	2.568496000	4.626372000	-4.469282000
P	-0.487026000	-0.369772000	-1.113068000
C	-0.422928000	1.022265000	0.185451000

N	-2.067338000	-0.803308000	-0.343276000
O	0.457471000	1.870910000	0.344569000
N	-1.521123000	0.972689000	0.978457000
C	-2.520321000	-0.015693000	0.666671000
C	-2.967533000	-1.680709000	-1.022918000
C	-1.726364000	1.903673000	2.047361000
O	-3.584116000	-0.038067000	1.240041000
C	-2.593483000	-3.001132000	-1.259602000
C	-4.186961000	-1.201867000	-1.505806000
C	-0.832676000	1.924291000	3.113249000
C	-2.808781000	2.775126000	2.004862000
C	-3.435939000	-3.836581000	-1.988800000
H	-1.657444000	-3.364821000	-0.850575000
C	-5.028273000	-2.046733000	-2.217716000
H	-4.474750000	-0.174022000	-1.313265000
C	-1.017458000	2.841782000	4.141598000
H	-0.002710000	1.225164000	3.132594000
C	-2.992459000	3.682737000	3.042165000
H	-3.505038000	2.729699000	1.175359000
C	-4.653343000	-3.365299000	-2.467763000
H	-3.139110000	-4.864911000	-2.172044000
H	-5.977105000	-1.669601000	-2.587676000
C	-2.096524000	3.721263000	4.107045000
H	-0.320435000	2.863022000	4.973493000
H	-3.838577000	4.362131000	3.016749000
H	-5.309298000	-4.020605000	-3.032857000
H	-2.241422000	4.434666000	4.912515000
Li	2.257990000	2.226678000	-0.102763000

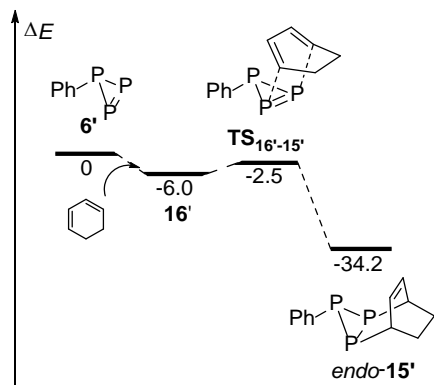
**8':**

E = -2511.45902234

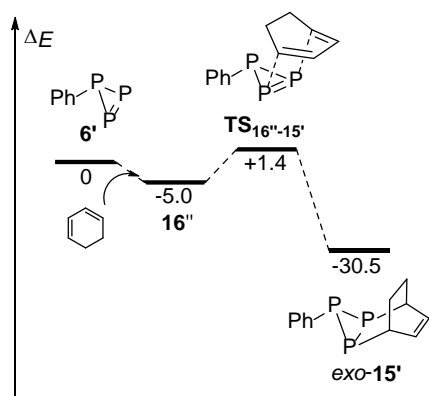
P	-0.509851000	1.003685000	-1.125093000
P	0.509851000	-1.003685000	-1.125093000
P	0.509837000	-1.003692000	1.125022000
P	-0.509837000	1.003692000	1.125022000
P	1.104311000	2.025105000	-0.000052000
P	-1.104311000	-2.025105000	-0.000052000

C	-0.411425000	-3.737500000	-0.000009000
C	-0.206717000	-4.417199000	1.205968000
C	-0.206531000	-4.417230000	-1.205933000
C	0.206531000	-5.745641000	1.204385000
H	-0.362083000	-3.905608000	2.151961000
C	0.206717000	-5.745675000	-1.204248000
H	-0.361747000	-3.905666000	-2.151965000
C	0.414677000	-6.411875000	0.000093000
H	0.368532000	-6.258783000	2.147543000
H	0.368864000	-6.258841000	-2.147367000
H	0.739704000	-7.448003000	0.000132000
C	0.411425000	3.737500000	-0.000009000
C	0.206717000	4.417199000	1.205968000
C	0.206531000	4.417230000	-1.205933000
C	-0.206531000	5.745641000	1.204385000
H	0.362083000	3.905608000	2.151961000
C	-0.206717000	5.745675000	-1.204248000
H	0.361747000	3.905666000	-2.151965000
C	-0.414677000	6.411875000	0.000093000
H	-0.368532000	6.258783000	2.147543000
H	-0.368864000	6.258841000	-2.147367000
H	-0.739704000	7.448003000	0.000132000

## Calculated minimum energy reaction pathway for the Diels-Alder reaction of **6'** with 1,3-CHD



**Scheme S4.** Relative  $\omega$ B97X-D/6-311+G(2d,p)//6-31G(d) energies (in kcal mol<sup>-1</sup>) for the computed Diels-Alder reaction leading from **6'** to *endo*-**15'**.



**Scheme S5.** Relative  $\omega$ B97X-D/6-311+G(2d,p)//6-31G(d) energies (in kcal mol<sup>-1</sup>) for the computed Diels-Alder reaction leading from **6'** to *exo*-**15'**.

### Optimized geometries (Cartesian coordinates) and uncorrected energies (in a.u.)

#### 1,3-CHD:

E = -233.404661857

C	-0.303155000	0.704456000	-1.191086000
C	-0.049312000	1.420877000	0.112316000
C	0.049312000	0.732441000	1.255873000
C	-0.049312000	-0.732441000	1.255873000
C	0.049312000	-1.420877000	0.112316000
C	0.303155000	-0.704456000	-1.191086000

H	-1.392287000	0.637250000	-1.343689000
H	-0.008857000	2.507140000	0.112175000
H	0.184641000	1.245432000	2.204256000
H	-0.184641000	-1.245432000	2.204256000
H	0.008857000	-2.507140000	0.112175000
H	-0.090483000	-1.280055000	-2.035362000
H	0.090483000	1.280055000	-2.035362000
H	1.392287000	-0.637250000	-1.343689000

**6':**

E = -1255.69276001

P	-2.309804000	-0.362757000	1.010464000
P	-2.312926000	-0.389118000	-0.996738000
P	-1.009917000	1.111192000	-0.014624000
C	0.668888000	0.335626000	-0.005571000
C	1.730876000	1.248734000	-0.003188000
C	0.960034000	-1.032058000	-0.002376000
C	3.049904000	0.807405000	0.002751000
C	2.279878000	-1.473721000	0.003028000
C	3.327000000	-0.556660000	0.005922000
H	3.860555000	1.529860000	0.004746000
H	2.489093000	-2.539397000	0.005168000
H	0.161125000	-1.768260000	-0.004140000
H	1.523782000	2.316590000	-0.006099000
H	4.355692000	-0.904514000	0.010398000

**16':**

E = -1489.10702713

P	0.408644000	-0.854059000	-1.107530000
P	0.339987000	-1.291149000	0.855828000
P	-0.570580000	0.618833000	0.222626000
C	-2.380816000	0.262932000	0.067236000
C	-3.209532000	1.389128000	0.144758000
C	-2.972182000	-0.991805000	-0.108241000
C	-4.591822000	1.266426000	0.045140000
C	-4.354705000	-1.115837000	-0.204256000
C	-5.168064000	0.011726000	-0.129907000

H	-5.218405000	2.151606000	0.103979000
H	-4.798301000	-2.098010000	-0.339396000
C	3.507433000	-0.127688000	1.367997000
H	3.597419000	-0.555856000	2.362901000
C	3.358408000	1.065952000	-1.204714000
H	3.228299000	1.481765000	-2.200353000
C	2.903932000	1.059115000	1.188737000
C	2.725047000	1.608639000	-0.153341000
H	2.052826000	2.451397000	-0.283851000
H	2.498029000	1.606048000	2.034848000
C	4.036053000	-0.920207000	0.199757000
C	4.369317000	-0.036006000	-1.009339000
H	3.275784000	-1.662783000	-0.087363000
H	4.920060000	-1.494052000	0.497533000
H	4.451011000	-0.652300000	-1.910255000
H	5.355137000	0.433676000	-0.866442000
H	-2.767451000	2.373339000	0.284036000
H	-2.357154000	-1.884935000	-0.173396000
H	-6.246436000	-0.088509000	-0.209066000

**TS<sub>16'-15'</sub>:**

E = -1489.1014183

P	0.594601000	-0.946636000	-1.017438000
P	0.601869000	-0.900794000	1.021621000
P	-0.453348000	0.719080000	-0.033356000
C	-2.242828000	0.248480000	-0.011253000
C	-3.133952000	1.328366000	-0.012439000
C	-2.764181000	-1.049333000	0.005500000
C	-4.509669000	1.119225000	0.003591000
C	-4.139296000	-1.258812000	0.021410000
C	-5.015946000	-0.176719000	0.020753000
H	-5.186034000	1.969123000	0.002829000
H	-4.528182000	-2.273015000	0.034579000
C	2.975402000	0.444739000	1.406194000
H	2.886606000	0.464860000	2.489099000
C	3.025081000	0.368889000	-1.404749000
H	2.973123000	0.330449000	-2.489569000

C	2.611616000	1.536093000	0.679901000
C	2.643826000	1.498889000	-0.751433000
H	2.217369000	2.328888000	-1.306010000
H	2.154192000	2.389122000	1.171146000
C	3.829184000	-0.654840000	0.819586000
C	3.815482000	-0.728101000	-0.730617000
H	3.546079000	-1.618355000	1.254435000
H	4.854337000	-0.467113000	1.165054000
H	3.454631000	-1.703986000	-1.070949000
H	4.844079000	-0.651170000	-1.105824000
H	-2.746377000	2.344745000	-0.026048000
H	-2.096015000	-1.905606000	0.006370000
H	-6.088962000	-0.343951000	0.033817000

*endo-15'*:

E = -1489.15190831

P	-0.667041000	-1.096898000	-0.634131000
P	-0.668037000	1.102050000	-0.626135000
P	0.335321000	-0.002851000	1.016960000
C	2.061097000	-0.000575000	0.344766000
C	2.750348000	-1.204029000	0.161654000
C	2.748289000	1.203727000	0.159795000
C	4.092647000	-1.202864000	-0.204809000
C	4.090627000	1.204170000	-0.206670000
C	4.766325000	0.001088000	-0.389540000
H	4.610976000	-2.146274000	-0.349133000
H	4.607422000	2.148196000	-0.352459000
C	-2.436190000	1.351039000	0.080905000
H	-2.572786000	2.432590000	0.162571000
C	-2.435117000	-1.352437000	0.070673000
H	-2.570916000	-2.434672000	0.144307000
C	-2.639464000	0.664183000	1.389330000
C	-2.638969000	-0.675571000	1.384200000
H	-2.717609000	-1.260179000	2.295606000
H	-2.718624000	1.241769000	2.305151000
C	-3.411654000	0.777090000	-0.978220000
C	-3.410742000	-0.771376000	-0.984387000

H	-3.157438000	1.172495000	-1.968040000
H	-4.414970000	1.145919000	-0.741797000
H	-3.155415000	-1.158549000	-1.977183000
H	-4.413753000	-1.143304000	-0.751568000
H	2.233031000	-2.150074000	0.297659000
H	2.229435000	2.149126000	0.294299000
H	5.813837000	0.001753000	-0.676012000

**16'':**

E = -1489.10530744

P	0.253742000	-1.349892000	-1.046590000
P	0.317503000	-1.241150000	0.959498000
P	-0.501155000	0.512267000	-0.113820000
C	-2.337908000	0.298939000	-0.033444000
C	-3.074270000	1.489493000	-0.070448000
C	-3.027965000	-0.913122000	0.061450000
C	-4.464230000	1.469589000	-0.013326000
C	-4.418190000	-0.933724000	0.119787000
C	-5.139590000	0.256202000	0.082798000
H	-5.019134000	2.402699000	-0.043418000
H	-4.938456000	-1.884094000	0.194971000
C	3.374291000	0.507436000	1.461704000
C	3.689021000	0.160004000	-1.343530000
C	3.429218000	1.752524000	0.612445000
C	3.121886000	1.472959000	-0.866571000
C	3.654185000	-0.695211000	0.938614000
C	3.932804000	-0.844725000	-0.490528000
H	-2.554831000	2.442363000	-0.145400000
H	-2.484763000	-1.853512000	0.090329000
H	-6.224421000	0.237597000	0.129399000
H	3.858301000	0.030114000	-2.409369000
H	4.309616000	-1.797521000	-0.851943000
H	3.676840000	-1.580105000	1.569405000
H	3.183356000	0.615857000	2.526225000
H	2.736375000	2.508966000	0.994997000
H	4.438539000	2.182214000	0.710726000
H	3.498636000	2.295461000	-1.484053000

H 2.033090000 1.459398000 -1.021905000

**TS<sub>16''-15'</sub>:**

E = -1489.09521651

P 0.616581000 -0.918428000 -1.027146000

P 0.616563000 -0.918158000 1.027344000

P -0.450302000 0.727271000 -0.000127000

C -2.241145000 0.273881000 -0.000064000

C -3.137593000 1.349968000 -0.000140000

C -2.754329000 -1.027032000 0.000055000

C -4.511552000 1.132661000 -0.000095000

C -4.128543000 -1.245082000 0.000099000

C -5.010024000 -0.167271000 0.000026000

H -5.193782000 1.977868000 -0.000151000

H -4.512624000 -2.261181000 0.000193000

C 3.048218000 0.157340000 1.398775000

H 2.994096000 0.108528000 2.483055000

C 3.048280000 0.157037000 -1.398756000

H 2.994191000 0.107985000 -2.483027000

C 2.819147000 1.514311000 0.775698000

C 2.819183000 1.514142000 -0.775981000

H 3.629502000 2.159389000 -1.139451000

H 1.894654000 1.954673000 1.159685000

C 3.674705000 -0.847187000 0.709770000

C 3.674731000 -0.847343000 -0.709508000

H -2.754370000 2.368154000 -0.000236000

H -2.079656000 -1.878888000 0.000114000

H -6.082279000 -0.340095000 0.000064000

H 4.018530000 -1.731805000 -1.238318000

H 4.018483000 -1.731532000 1.238787000

H 3.629449000 2.159637000 1.139066000

H 1.894710000 1.954425000 -1.160105000

**exo-15'**:

E = -1489.14597723

P -0.668109000 -1.041373000 -0.788122000

P -0.680419000 1.149983000 -0.628014000

P	0.316263000	-0.059532000	0.952351000
C	2.062380000	-0.016440000	0.355425000
C	2.771922000	-1.211328000	0.193409000
C	2.732092000	1.197671000	0.173604000
C	4.120579000	-1.191768000	-0.147003000
C	4.081552000	1.215466000	-0.166164000
C	4.778808000	0.021716000	-0.326979000
H	4.655955000	-2.127905000	-0.275337000
H	4.586825000	2.165997000	-0.309719000
C	-2.464882000	1.341236000	0.045118000
H	-2.625823000	2.419511000	0.130797000
C	-2.451654000	-1.345347000	-0.153765000
H	-2.603024000	-2.425753000	-0.229410000
C	-2.735899000	0.663778000	1.408570000
C	-2.727197000	-0.878591000	1.294747000
H	-3.705871000	-1.277369000	1.582300000
H	-2.007997000	1.006898000	2.149635000
C	-3.373901000	0.733618000	-0.989312000
C	-3.366787000	-0.600217000	-1.087997000
H	2.265287000	-2.163866000	0.325094000
H	2.195435000	2.135545000	0.288262000
H	5.831443000	0.036784000	-0.593492000
H	-3.985388000	1.366731000	-1.624967000
H	-3.972358000	-1.139555000	-1.809989000
H	-3.719651000	1.005056000	1.748514000
H	-1.992941000	-1.317003000	1.977172000

### 3. X-ray Structure Determinations

#### X-ray crystal structure determination of Li[7]

$C_{36}H_{36}LiN_4O_6P$ , Fw = 658.60, colourless block,  $0.36 \times 0.33 \times 0.22$  mm<sup>3</sup>, orthorhombic, P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (no. 19), a = 18.7146(8), b = 18.2933(10), c = 9.9827(6) Å, V = 3319.0(3) Å<sup>3</sup>, Z = 4, D<sub>x</sub> = 1.318 g/cm<sup>3</sup>, μ = 0.14 mm<sup>-1</sup>. 67455 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin θ/λ)<sub>max</sub> = 0.65 Å<sup>-1</sup>. The Eval15 software<sup>[S13]</sup> was used for the integration of the intensities. A model for large mosaicity [1.6 °] appeared to be necessary for the prediction of the reflection profiles. Multiscan absorption correction and scaling was performed with SADABS<sup>[S14]</sup> (correction range 0.62-0.75). 7612 Reflections were unique (R<sub>int</sub> = 0.046), of which 6609 were observed [I > 2σ(I)]. The structure was solved with Patterson superposition methods using SHELXT.<sup>[S15]</sup> Least-squares refinement was performed with SHELXL-2014<sup>[S16]</sup> against F<sup>2</sup> of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. The monophosphorus anion was refined with whole molecule disorder resulting in a ratio of 0.740(4):0.260(4) between the two disorder components. One of the THF molecules showed ring puckering disorder. Hydrogen atoms were introduced in calculated positions and refined with a riding model. 601 Parameters were refined with 489 restraints (displacement parameters, distances, angles, and planarity of the phenyl rings and in the disordered moieties). R1/wR2 [I > 2σ(I)]: 0.0775 / 0.2017. R1/wR2 [all refl.]: 0.0877 / 0.2090. S = 1.070. Flack parameter<sup>[S17]</sup> x = 0.09(3). Residual electron density between -0.39 and 0.58 e/Å<sup>3</sup>. Geometry calculations and checking for higher symmetry were performed with the PLATON program.<sup>[S18]</sup>

#### X-ray crystal structure determination of 15

$C_{24}H_{37}P_3$ , Fw = 418.44, colourless plate,  $0.27 \times 0.23 \times 0.07$  mm<sup>3</sup>, monoclinic, P2/c (no. 13), a = 20.4101(9), b = 6.2198(3), c = 19.0401(10) Å, β = 97.006(2) °, V = 2399.01(19) Å<sup>3</sup>, Z = 4, D<sub>x</sub> = 1.159 g/cm<sup>3</sup>, μ = 0.26 mm<sup>-1</sup>. The crystal appeared to be cracked into two fragments related by a 3.9 ° rotation about an arbitrary vector. Consequently two orientation matrices were used for the integration with Eval15.<sup>[S13]</sup> 120873 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin θ/λ)<sub>max</sub> = 0.65 Å<sup>-1</sup>. Multiscan absorption correction and scaling was performed with TWINABS<sup>[S14]</sup> (correction range 0.68-0.75). 6016 Reflections were unique (R<sub>int</sub> = 0.034), of which 5363 were observed [I > 2σ(I)]. The structure was solved with Patterson superposition methods using SHELXT.<sup>[S15]</sup> Least-squares refinement was performed with SHELXL-2014<sup>[S16]</sup> against F<sup>2</sup> of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. The t-butyl group was refined with a disorder model. Slight whole molecule disorder was present but has been ignored in the refinement. Hydrogen atoms were introduced in calculated positions and refined with a riding model. 285 Parameters were refined with 187 restraints (distances, angles and displacement parameters in the disordered t-butyl moiety). R1/wR2 [I > 2σ(I)]: 0.0398 / 0.1043. R1/wR2 [all refl.]: 0.0450 / 0.1079. S = 1.026. Residual electron density between -0.21 and 1.18 e/Å<sup>3</sup>. Batch scale factor for the second crystal fragment BASF = 0.0537(10). Geometry calculations and checking

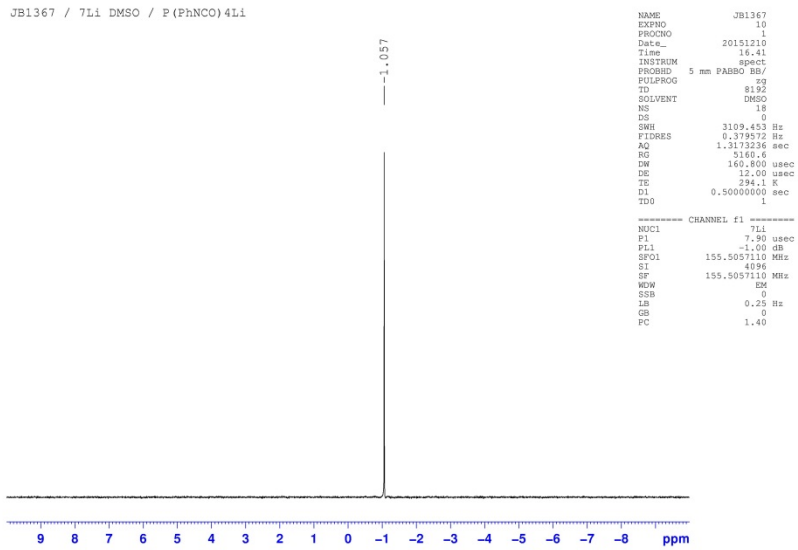
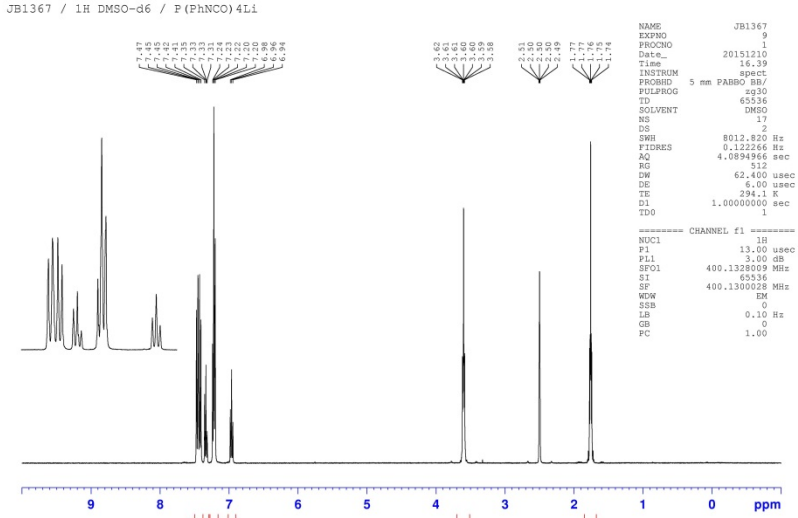
for higher symmetry were performed with the PLATON program.<sup>[S18]</sup>

### **X-ray crystal structure determination of 8**

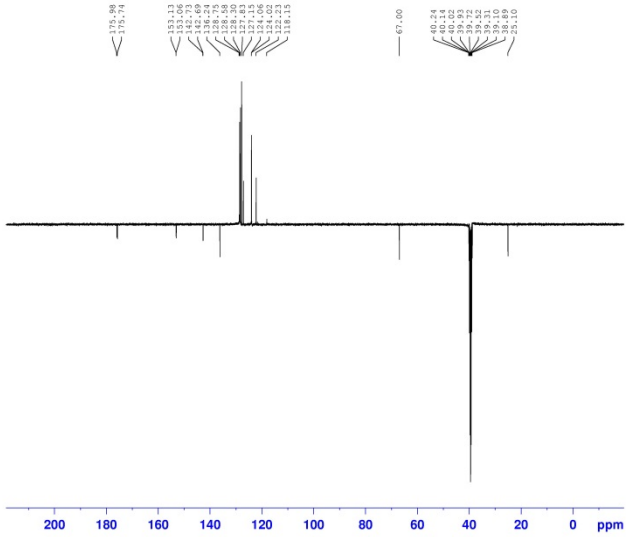
$C_{36}H_{58}P_6$ , Fw = 676.64, yellow block,  $0.57 \times 0.24 \times 0.14 \text{ mm}^3$ , triclinic,  $P\bar{1}$  (no. 2),  $a = 6.1532(3)$ ,  $b = 9.7600(8)$ ,  $c = 16.4721(11) \text{ \AA}$ ,  $\alpha = 93.816(3)$ ,  $\beta = 91.486(4)$ ,  $\gamma = 103.156(3)^\circ$ ,  $V = 960.29(11) \text{ \AA}^3$ ,  $Z = 1$ ,  $D_x = 1.170 \text{ g/cm}^3$ ,  $\mu = 0.30 \text{ mm}^{-1}$ . The crystal was twinned with a twofold rotation about  $uvw = [1,0,0]$  as twin operation. Additional crystal fragments were present. In total four orientation matrices were therefore used for the integration with Eval15.<sup>[S13]</sup> 50104 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator ( $\lambda = 0.71073 \text{ \AA}$ ) at a temperature of 150(2) K up to a resolution of  $(\sin \theta/\lambda)_{\max} = 0.65 \text{ \AA}^{-1}$ . Multiscan absorption correction and scaling was performed with TWINABS<sup>[S14]</sup> (correction range 0.52-0.75). 4510 Reflections were unique ( $R_{\text{int}} = 0.052$ ), of which 3749 were observed [ $I > 2\sigma(I)$ ]. The structure was solved with Patterson superposition methods using SHELXT.<sup>[S15]</sup> Least-squares refinement was performed with SHELXL-2014<sup>[S16]</sup> against  $F^2$  of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were located in difference Fourier maps and refined with a riding model. 202 Parameters were refined with no restraints. R1/wR2 [ $I > 2\sigma(I)$ ]: 0.0740 / 0.2146. R1/wR2 [all refl.]: 0.0862 / 0.2226. S = 1.141. Residual electron density between -0.67 and 1.06  $e/\text{\AA}^3$ . Batch scale factors for the other crystal fragments BASF = 0.326(5), 0.188(6), 0.076(5). Geometry calculations and checking for higher symmetry were performed with the PLATON program.<sup>[S18]</sup>

CCDC 1491988-1491990 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

# 5. NMR Spectra



Spiro-Phosphoramide 13C APT



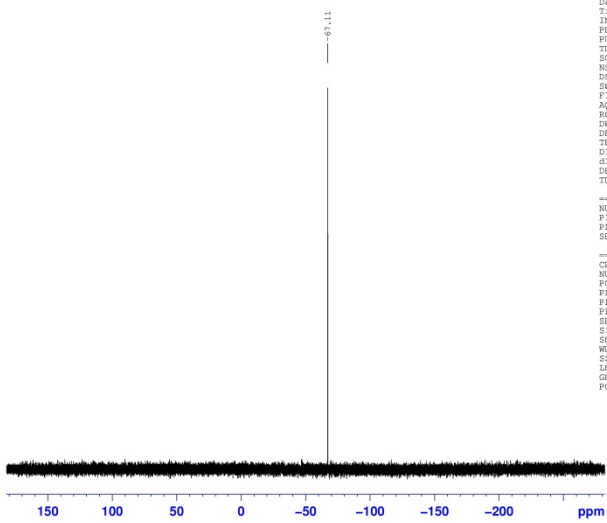
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EXPNO         12
PROCNO        1
Date_         20151212
Time          3.03
INSTRUM       spect
PROBHD        5 mm PABBO BB/
PULPROG       smod
TD             65536
SOLVENT       DMSO
NS            10240
DS             4
SWE           23980.814 Hz
FIDRES        0.365918 Hz
AQ            1.3664756 sec
RG            16384
DW            20.850 usec
DE            6.00 usec
TE            294.1 K
CNS12         145.0000000
CNST11        1.0000000
D1            2.00000000 sec
d20           0.00689655 sec
DELTA         0.00001120 sec
TD0           1

===== CHANNEL f1 =====
NUC1          13C
P1            8.80 usec
P2            17.60 usec
PL1           -1.00 dB
SFO1          100.6282898 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         80.00 usec
PL2           3.00 dB
PL12          18.00 dB
SFO2          400.1316005 MHz
SI            28768
SF            100.6181880 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
    
```

JBI1367 / 31P{1H} DMSO-d6 / P(PhNCO)4Li



```

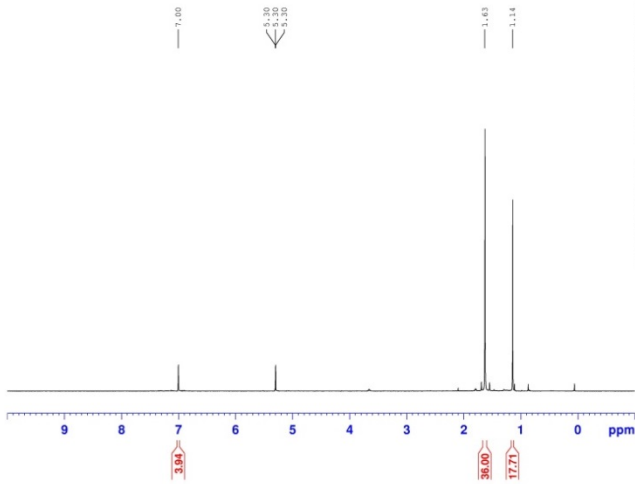
NAME          JBI1367
EXPNO         8
PROCNO        1
Date_         20151210
Time          16.35
INSTRUM       spect
PROBHD        5 mm PABBO BB/
PULPROG       zgpg30
TD             65536
SOLVENT       DMSO
NS            65
DS             4
SWE           75187.869 Hz
FIDRES        1.147577 Hz
AQ            0.4358644 sec
RG            7296.2
DW            6.650 usec
DE            6.00 usec
TE            294.1 K
CNS12         2.000000000
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0           1

===== CHANNEL f1 =====
NUC1          31P
P1            6.25 usec
P11           -1.00 dB
SFO1          161.9674942 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         80.00 usec
PL2           3.00 dB
PL12          18.00 dB
SFO2          400.1316005 MHz
SI            65536
SF            161.9755930 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
    
```

# Mes\*<sub>2</sub>P<sub>6</sub> (8):

JB1367 / 1H CD2Cl2 / Mes\*2P6



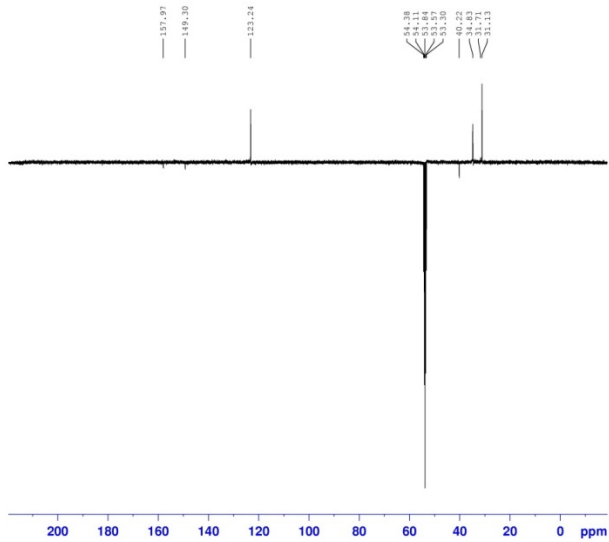
```

NAME          JB1367
EXPNO         6
PROCNO        1
Date_         20151210
Time          14.18
INSTRUM       spect
PROBHD        5 mm PABBO BB
PULPROG       zgpg30
TD            65536
SOLVENT       CD2Cl2
NS            17
DS            2
SWH           8012.820 Hz
FIDRES       0.222266 Hz
AQ           4.0894965 sec
RG           812.7
DM           62.400 usec
DE           6.00 usec
TE           294.1 K
D1           1.00000000 sec
TD0          1
  
```

```

===== CHANNEL f1 =====
NUC1          1H
P1            13.00 usec
PL1           3.00 dB
SFO1         400.1328009 MHz
SI           65536
SF           400.1300229 MHz
WVW          EM
SSB           0
LB           0.10 Hz
GB           0
PC           1.00
  
```

Mes\*2P6 13C APT



```

NAME          JB1367
EXPNO         16
PROCNO        1
Date_         20151212
Time          21.05
INSTRUM       spect
PROBHD        5 mm PABBO BB/
PULPROG       jmod
TD            65536
SOLVENT       CD2Cl2
NS            10240
DS            4
SWH           23960.814 Hz
FIDRES       0.365910 Hz
AQ           1.3664756 sec
RG           16384
DM           20.850 usec
DE           6.00 usec
TE           294.1 K
CNST2        145.0000000
CNST11        1.0000000
D1            2.0000000 sec
d20           0.00689655 sec
DELTA        0.00001120 sec
TD0          1
  
```

```

===== CHANNEL f1 =====
NUC1          13C
P1            8.80 usec
p2           17.60 usec
PL1           1.00 dB
SFO1         100.6228298 MHz

===== CHANNEL f2 =====
CPDPRG2      waltz16
NUC2          1H
PCPD2        80.00 usec
PL2           3.00 dB
PL12         18.00 dB
SFO2         400.1316005 MHz
SI           32768
SF           100.6127249 MHz
WVW          DM
SSB           0
LB           1.00 Hz
GB           0
PC           1.40
  
```





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