Supporting Information:

Exploring the Redox Decomposition of Ethylene Carbonate−Propylene Carbonate in Li-Ion Batteries

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Marcus electron transfer theory[1]Marcus' theory of electron transfer describes the rates of electron transfer between weakly coupled donor and acceptor states. It provides a parabolic model to calculate the activation energy of an electron-transfer reaction. The reactant and product energy surfaces were simplified representation of two parabolas. Then, the reorganization energy and change in Gibbs free energy can be obtained for the activation energy. The activation energy can be substituted into the Arrhenius or Eyring equation to calculate a rate constant for an electron-transfer reaction.

Adiabatic (E_{ad}) and vertical (E_{vert}) oxidation potentials

To calculate electrochemical stability of the representative complexes versus Li/Li^+, the energy cycle shown in Fig. S1 is used. The absolute oxidation potential and vertical oxidation potential of a complex M relative to an electron at rest in vacuum is given by equations (1)-(3).[2-4]

$$E_{ad}(M) = \left[\Delta G_e + \Delta G_s^{\circ}(M^+) - \Delta G_s^{\circ}(M)\right]/F - 1.4 \quad (1)$$

$$E_{vert}(M) = \left[\Delta G_e + \Delta G_s^{\circ}(M^+)_v - \Delta G_s^{\circ}(M)_v\right]/F - 1.4 \quad (2)$$

$$\lambda = E_{vert} - E_{ad} \quad (3)$$

Where E_{ad} and E_{vert} are the adiabatic oxidation and the neutral vertical oxidation respectively; λ is reorganization energy; ΔG_e is the free energies of the electron attachment; $\Delta G(M^+)$ and $\Delta G(M)$ are the free energies of the oxidized solvent-phase, and neutral solvent-phase complexes; and F is the Faraday constant (F=23.061 Kcal $mol^{-1}V^{-1}$); Subscript of "s" and "v" denote the adiabatic oxidation and the vertical

oxidation respectively. In the former, the optimized or relaxed geometry is required during calculation, while the complex geometry does not change during electron transfer in the latter. The Li /Li^+ oxidation potential is 1.4 V In this work, we used a value of 1.4 V for to convert from the absolute scale to Li^+/Li.

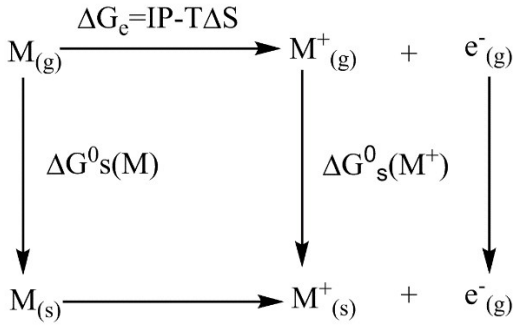

Fig. S1 Free-energy cycle for the redox reaction ($M \rightarrow M^+ + e^-$), where M (g) denotes molecule M in gas-phase, $M_{(S)}$ denotes the solvated molecule, and IP denotes ionization potential.

Table S1 The dielectric constants and dipole moments of EC, PC anf FEC.

	EC	PC	FEC
Dielectric Constant[5, 6]	89	65	78.4
Dipole Moment (Debye)	5.64[7], 4.81[5]	5.36[5]	4.97[7]

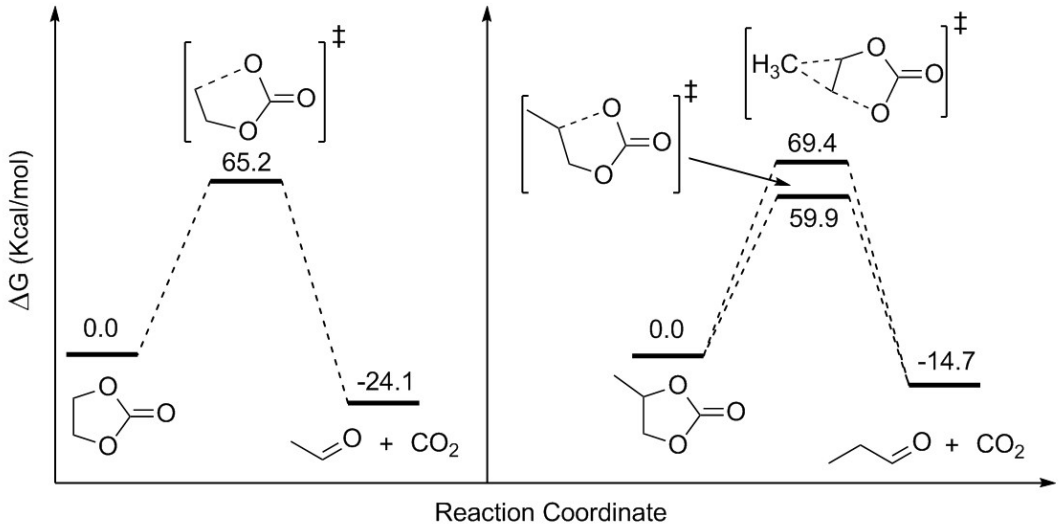

Fig. S2 Calculated free energy profile ΔG of **EC** (left) and **PC** (right) decomposition.

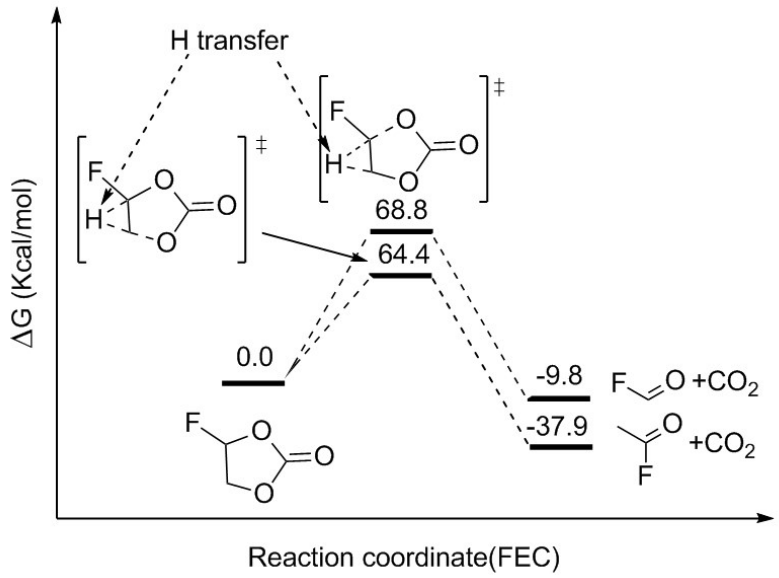

Fig. S3 Calculated free energy profile ΔG of **FEC** decomposition.

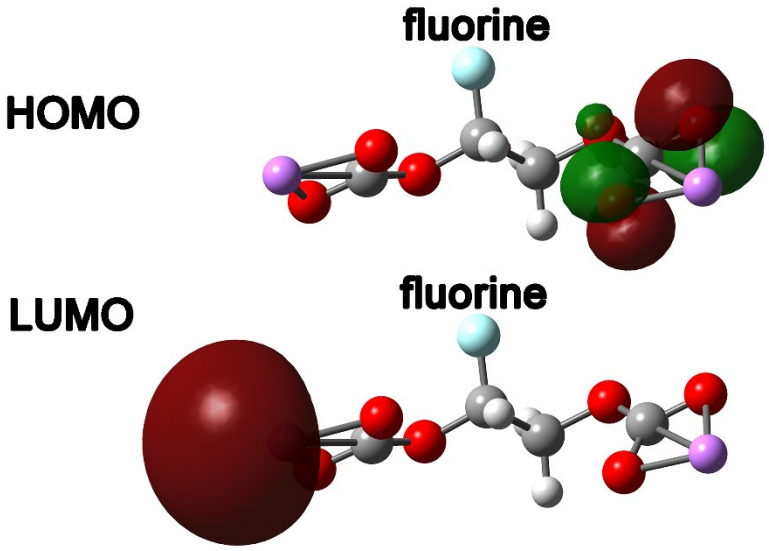

Fig. S4 3D plots of the HOMO and LUMO orbitals of **Product-F1**.

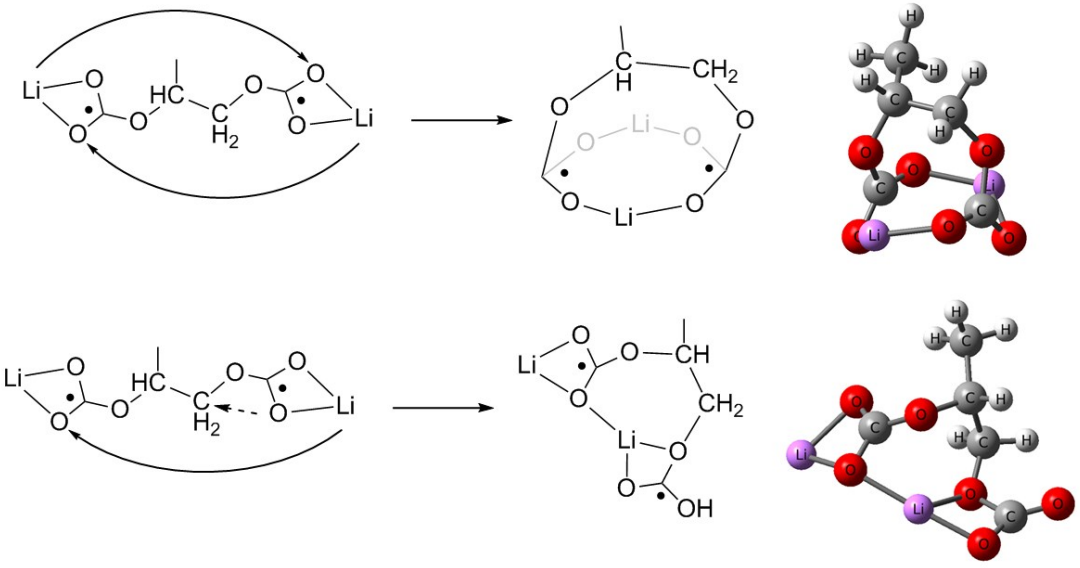

Fig. S5 Ring formation of **Product-P1**.

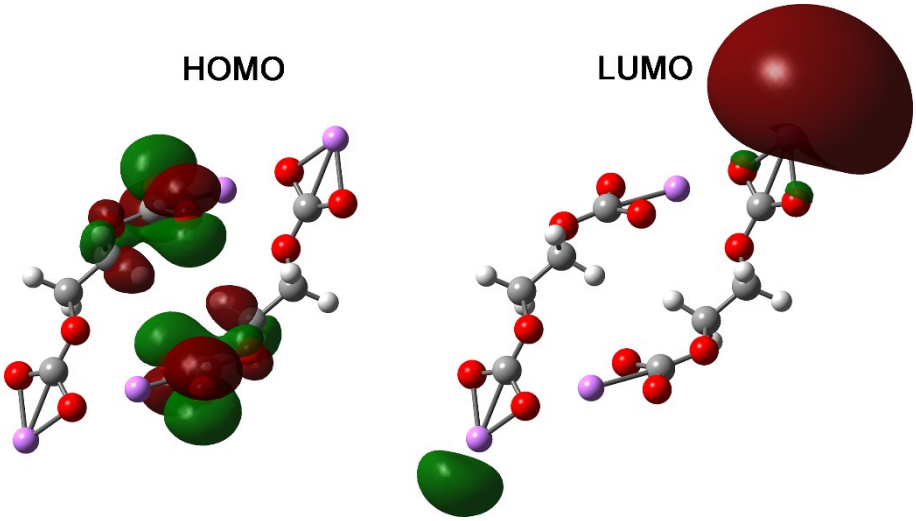

Fig. S6 3D plots of the HOMO and LUMO orbitals of the lithium alkylcarbonate complexes (dimer **Product-E1** complex).

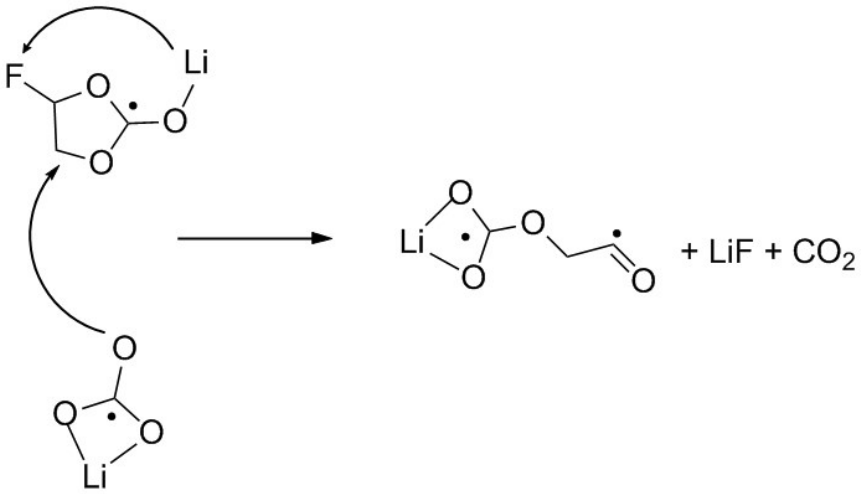

Fig. S7 The reaction between FEC and $LiCO_3^-$ anion to produce inorganic LiF and less-reduced organic intermidate.

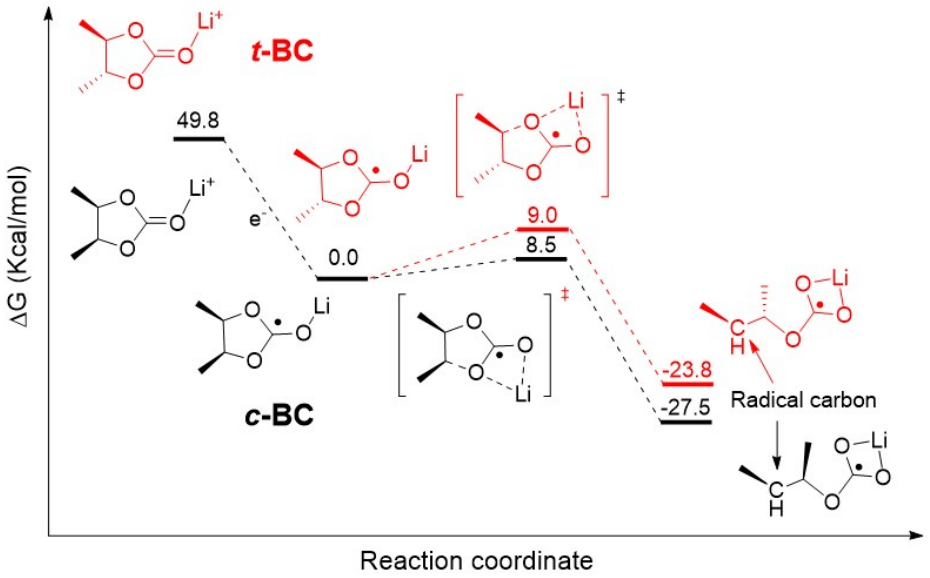

Fig. S8 Calculated possible pathways of *trans*-2,3-butylene carbonate (*t*-BC) and *cis*-2,3-butylene carbonate (*c*-BC) decomposition assisted by Li ions. The hydration energy of the solvated electron in water was -1.63 eV.

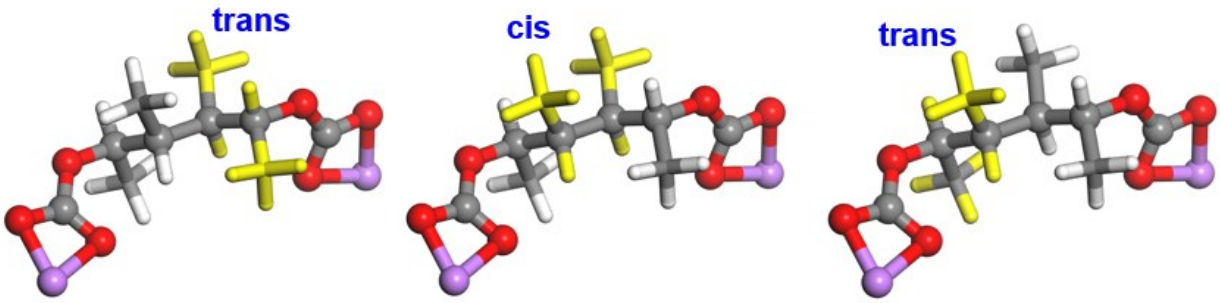

Fig. S9 Geometrical structure of dimerized *trans*-2,3-butylene carbonate (*trans*-BC).

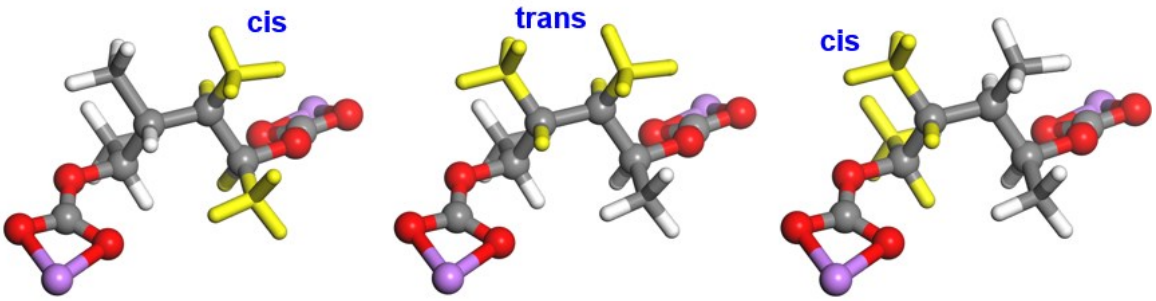

Fig. S10 Geometrical structure of dimerized *cis*-2,3-butylene carbonate (*cis*-BC).

TS-E1

imaginary frequency :-734.48 cm^{-1}

C	1.64927400	-0.52113700	0.00029100
C	1.44783700	0.96440300	-0.00026000
C	-0.65610400	-0.24789600	-0.00001800
H	2.15581100	-0.89262800	-0.89350700
H	2.15493500	-0.89202300	0.89483600
H	1.69012800	1.50379000	0.90992000
H	1.68964900	1.50302300	-0.91102600
O	-0.26495000	1.01207600	0.00016600
O	0.31422800	-1.15860800	-0.00021100
O	-1.85174900	-0.57144200	-0.00004600
Li	-2.63893500	1.11646900	0.00014300

Int-E2

C	1.55273000	-0.27237700	-0.51160800
C	2.18162500	0.51004900	0.58283000
C	-0.78770700	-0.14575900	-0.02082500
H	1.32849400	0.35696400	-1.37572300
H	2.17850800	-1.11339800	-0.81983200
H	2.82067400	0.02397400	1.31317900
H	1.86677200	1.53052500	0.76910000

O	-0.73768200	1.08575900	-0.35438600
O	0.31126700	-0.92256800	-0.08401300
O	-1.85617900	-0.70312900	0.37615300
Li	-2.53786300	0.98998800	0.10295400

TS-E2

imaginary frequency :-163.09 cm^{-1}

C	-1.99262200	-0.11045500	0.62681300
C	-2.37993500	0.36610200	-0.58179200
C	0.90840700	-0.15030600	-0.01137600
H	-1.44297800	0.51535800	1.31917700
H	-2.34364900	-1.06919500	0.99424900
H	-2.98267500	-0.22806500	-1.26294700
H	-2.04152900	1.33648100	-0.93111600
O	0.74149500	1.10064800	0.19202900
O	-0.08473500	-1.01226400	-0.02982500
O	2.07216800	-0.65376200	-0.20462200
Li	2.58810500	1.11213500	0.00603600

TS-P1

imaginary frequency :-705.67 cm^{-1}

C	1.29854800	-0.10690700	0.46323600
O	-0.24085800	-0.88529200	0.09389100
C	-1.08556800	0.10706000	-0.04708900
C	0.91356700	1.26521600	-0.00995400
H	1.31899100	-0.22944000	1.54458500
H	1.28913700	1.47343300	-1.01726500
H	1.21995700	2.06785100	0.66682600
O	-0.54612600	1.33317100	-0.06223000
O	-2.31368500	-0.04004000	-0.12711600
C	2.33879700	-0.88597500	-0.28426000
H	2.17818800	-0.82566800	-1.36570400
H	3.34679400	-0.50043200	-0.06882500
H	2.32202600	-1.93985100	0.00928000
Li	-2.55393600	-1.86165600	0.08771500

Int-P2

C	1.22547300	-0.53142700	0.22315400
O	-0.22315800	-0.76823000	0.17950000
C	-1.14751000	0.37552900	-0.10111800

C	1.58365500	0.48753700	1.24733100
H	1.59954700	-1.51230700	0.54791900
H	1.83150500	1.50254800	0.96145700
H	1.41495500	0.27366000	2.29879600
O	-0.67017700	1.46686000	-0.31163800
O	-2.32591900	-0.09201200	-0.05243100
C	1.76146200	-0.22850000	-1.17365000
H	1.37907900	0.73123400	-1.52734700
H	2.85653000	-0.18988400	-1.15134800
H	1.45981900	-1.01184000	-1.87764600
Li	-1.77529400	-1.75506500	0.35013800

TS-P2

imaginary frequency :-236.40 cm^{-1}

C	-1.70887400	0.52389600	-0.19995600
O	0.44517200	0.69049400	-0.41494000
C	1.22177100	-0.34085100	0.11665800
C	-1.65997000	0.70369800	1.15524500
H	-1.84133600	1.40642600	-0.82325300
H	-1.54066500	-0.14156600	1.82499500
H	-1.64839100	1.69857900	1.59084700
O	0.75391600	-1.30761600	0.68719500

O	2.45463500	-0.02063500	-0.13570400
C	-1.91399900	-0.80111300	-0.86955800
H	-1.48176700	-1.60646200	-0.27307200
H	-2.98986500	-0.98207200	-1.00505100
H	-1.44940800	-0.80953600	-1.85981700
Li	2.02936100	1.67430100	-0.58713200

TS-P1-1

imaginary frequency :-749.69 cm^{-1}

C	-1.31371200	-0.04355400	-0.45130900
O	-0.11698900	-0.92612100	-0.46867000
C	0.97309300	-0.28341900	-0.05493400
C	-0.80786800	1.35548400	-0.23959900
H	-1.74761000	-0.17353500	-1.44711100
H	-1.17576600	1.89385600	0.62840500
H	-0.66216700	1.97482900	-1.11942400
O	0.81491400	0.99428700	0.22863500
O	2.07053200	-0.85291100	0.03132100
C	-2.25815500	-0.55532200	0.62613600
H	-1.81859500	-0.42108400	1.62040400

H	-3.20537900	-0.00602000	0.58730100
H	-2.46750500	-1.61869700	0.47943800
Li	3.12307400	0.59649100	0.54631100

Int-P3

C	1.76527800	-0.54020200	-0.19917100
O	-1.41411000	-1.40782200	-0.26839800
C	-1.47002200	-0.20721700	-0.13919500
C	0.80713200	-0.36270300	0.92402600
H	1.52854500	-1.30386200	-0.93562100
H	1.27039900	0.15077800	1.77411700
H	0.39553300	-1.32012000	1.25052500
O	-0.32708100	0.47581100	0.55222000
O	-2.29976000	0.69836600	-0.45451700
C	2.83128300	0.45657500	-0.50982100
H	3.20299000	0.95109400	0.39739100
H	3.68471000	-0.00719400	-1.01946900
H	2.46995800	1.25528600	-1.18287200
Li	-1.27551800	2.02148400	0.20881600

TS-P3

imaginary frequency :-156.59 cm^{-1}

C	1.87884800	-0.41315900	-0.25018400
O	-1.33107200	-1.38326900	-0.44090900
C	-1.51541500	-0.23022500	-0.10414300
C	1.29989700	-0.66971800	0.94950400
H	1.55318000	-1.00477300	-1.10432100
H	1.59296500	-0.12727000	1.84493700
H	0.61781500	-1.50169000	1.06553800
O	-0.59400500	0.53079300	0.58725400
O	-2.54017000	0.55533200	-0.28424000
C	2.89199300	0.65580500	-0.50723500
H	3.14812500	1.20535200	0.40463100
H	3.81581700	0.22934400	-0.92266700
H	2.52523100	1.37406500	-1.25448200
Li	-1.62103200	2.04863800	0.18062600

TS-F1

imaginary frequency :-743.30 cm^{-1}

C	1.11690500	1.12106500	0.23108100
C	1.34276300	-0.33755400	0.41813900
C	-0.98720700	0.19530800	-0.02203200

H	1.23691900	1.67596700	1.16502000
H	1.74905800	1.54358900	-0.55360500
H	1.72733300	-0.72745800	1.35445800
O	-0.31900000	-0.83541800	0.45353400
O	-0.27027000	1.30816500	-0.21433600
O	-2.19388600	0.16082900	-0.29039500
F	1.86546900	-0.97009400	-0.64810600
Li	-2.69068400	-1.56759100	0.17117800

Int-F2

C	-0.98938400	-0.23425700	0.92914500
C	-1.79235600	0.58763300	0.00348200
C	1.21196900	-0.15114400	0.00330900
H	-0.60993900	0.38788700	1.74240000
H	-1.59171400	-1.05366700	1.32831200
H	-1.47401800	1.54583500	-0.39187300
O	1.21492500	1.09498100	0.28428200
O	0.13816800	-0.91506000	0.29208400
O	2.19354900	-0.73124100	-0.54843700
F	-2.66776400	-0.06619900	-0.78594500
Li	2.91034600	0.97096600	-0.48146200

TS-F3

imaginary frequency :-151.19 cm^{-1}

C	-1.39837700	0.00460900	1.07005500
C	-1.89800600	0.49250900	-0.08363300
C	1.34495400	-0.16835100	-0.01272000
H	-0.71248800	0.61574200	1.63826200
H	-1.79200400	-0.90565600	1.50605000
H	-1.55965800	1.39833700	-0.57400100
O	1.20941100	1.09984600	0.11930300
O	0.36087500	-1.01304500	0.20018100
O	2.46260100	-0.69094800	-0.35906200
F	-2.83220700	-0.16464600	-0.77592500
Li	2.99983100	1.07799100	-0.37085600

TS-F2

imaginary frequency :-740.97 cm^{-1}

C	0.93534700	1.27581700	0.27066800
C	1.34290200	-0.15904300	0.37661400
C	-0.93261300	-0.23130000	0.05901200
H	0.84983600	1.82927200	1.20029900
H	1.35323500	1.82920700	-0.56249500

H	1.94077000	-0.41962100	1.25349000
O	0.14234300	-0.93930300	0.46956400
O	-0.69920200	1.03267900	-0.19696500
O	-2.04475700	-0.76153600	-0.00913700
F	2.01950000	-0.55927300	-0.74610000
Li	-3.19341000	0.60901100	-0.50728400

Int-F3

C	-1.67751600	0.89326800	-0.84741900
C	-1.36754600	-0.39786100	-0.18928800
C	1.01876900	-0.11946700	-0.08480600
H	-1.74263100	0.93105200	-1.92896100
H	-1.70555500	1.80488700	-0.26707000
H	-1.99245500	-1.21289400	-0.57291800
O	-0.04816700	-0.89844200	-0.42119000
O	0.85397700	1.05315900	0.37338700
O	2.15698600	-0.64350500	-0.25596000
F	-1.58317800	-0.30883300	1.16855000
Li	2.71487700	0.97037200	0.47039400

TS-F4

imaginary frequency :-287.77 cm^{-1}

C	1.90704300	-0.13972900	1.11166300
C	1.76117900	-0.28884000	-0.23336000
C	-1.13301500	-0.18599200	0.03756600
H	2.11925100	-1.01100400	1.71877900
H	1.68753700	0.80689900	1.58833700
H	2.03075900	-1.18334200	-0.78193100
O	-0.17934200	-1.07984700	-0.15081700
O	-0.90752400	0.98663900	0.49039200
O	-2.31482800	-0.57424900	-0.27346100
F	1.59444400	0.77020000	-1.02246800
Li	-2.72841200	1.16089200	0.21763200

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