Chapter 2

Lewis Base-Activated Lithiation and Sodiation of Trifluoromethylbenzene: Structural, Spectroscopic and Theoretical Insights

Supporting Information

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Additional Crystal Information

Table S1 Selected crystallographic data and refinement parameters for compounds **3**-**5**.

Compound	**3**	**4**	**5**
Formula	$C_{26}H_{40}F_6Li_2N_4$	$C_{26}H_{40}F_6N_4Na_2$	$C_{32}H_{54}F_6N_6Na_2$
M_r (g mol^{-1})	536.50	568.60	682.79
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/m	P21/m
Temperature (K)	150(2)	123(2)	123(2)
a/ Å	14.9318(7)	12.4249(6)	9.3966(2)
b/ Å	12.8892(7)	14.6166(5)	13.8611(3)
c/ Å	16.7268(9)	17.6830(8)	14.2631(3)
β (º)	116.089(7)	110.919(5)	94.259(2)
V/Å^3	2891.2(3)	2999.7(2)	1852.60(7)
Z	4	4	2
Measured reflections	9846	12224	18861
Unique reflections	3119	3945	4871
R_{int}	0.0248	0.0179	0.0258
Observed rflns [$I > 2\sigma(I)$]	2229	3339	3827
μ (mm^{-1})	0.099	0.126	0.114
No. of parameters	177	201	237
2ϑmax (°)	57.00	58.98	59.00
R [on *F*, obs rflns only]	0.0408	0.0335	0.0416
wR [on F^2, all data]	0.1220	0.0890	0.1125
GoF	1.063	1.030	1.045
Largest diff. peak/hole/e Å^{-3}	0.279/–0.200	0.338/-0.273	0.363/-0.252

NMR Spectra

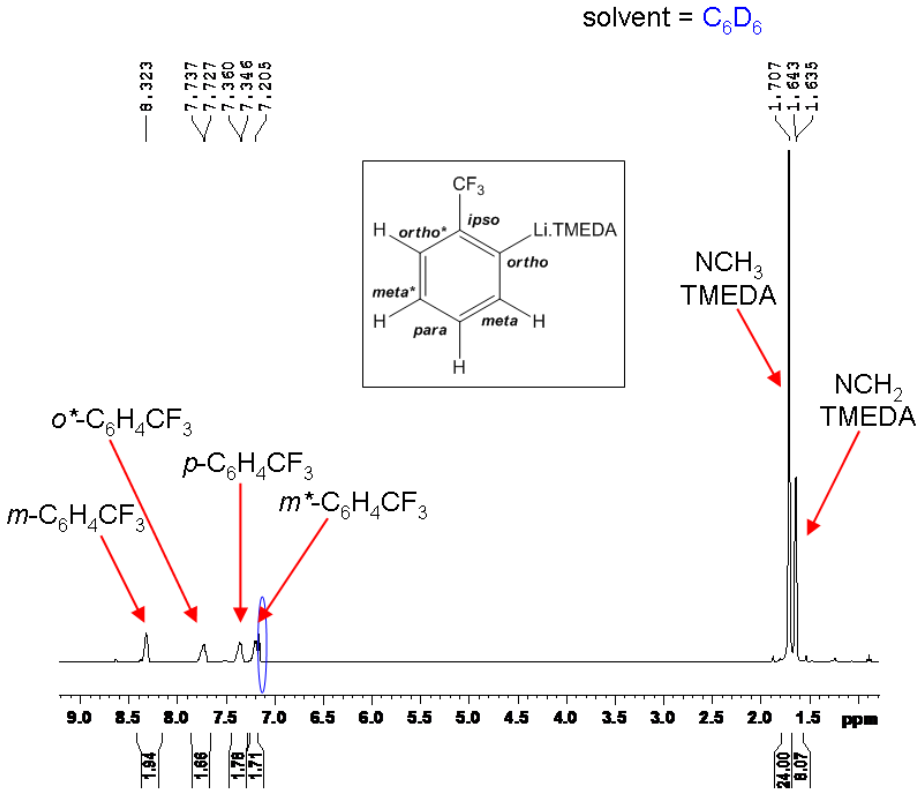


Figure S1 ^{1}H NMR spectrum of [(TMEDA)·Li(C_6H_4-CF_3)]$_2$ (**3**).

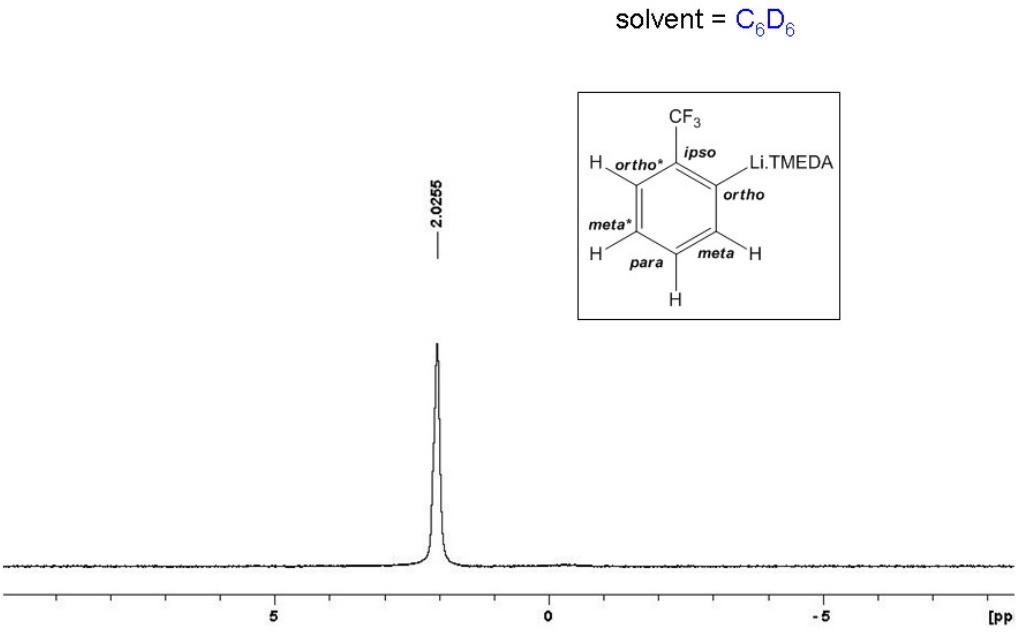


Figure S2 ^{7}Li NMR spectrum of [(TMEDA)·Li(C_6H_4-CF_3)]$_2$ (**3**).

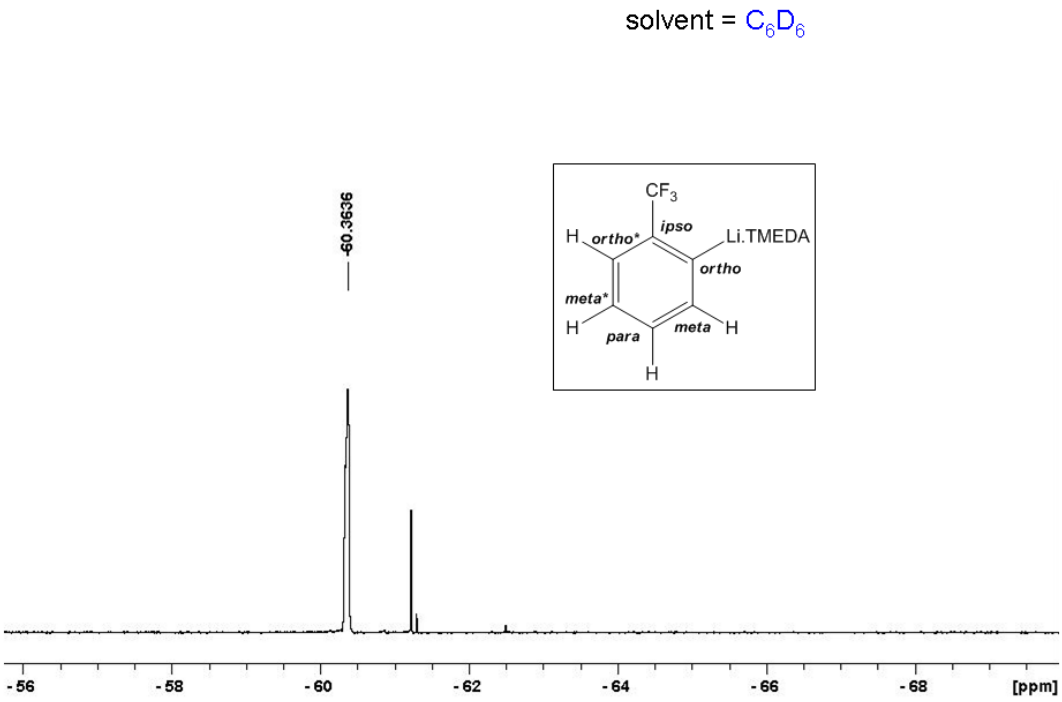


Figure S2 ^{19}F NMR spectrum of [(TMEDA)·Li(C_6H_4-CF_3)]$_2$ (**3**).

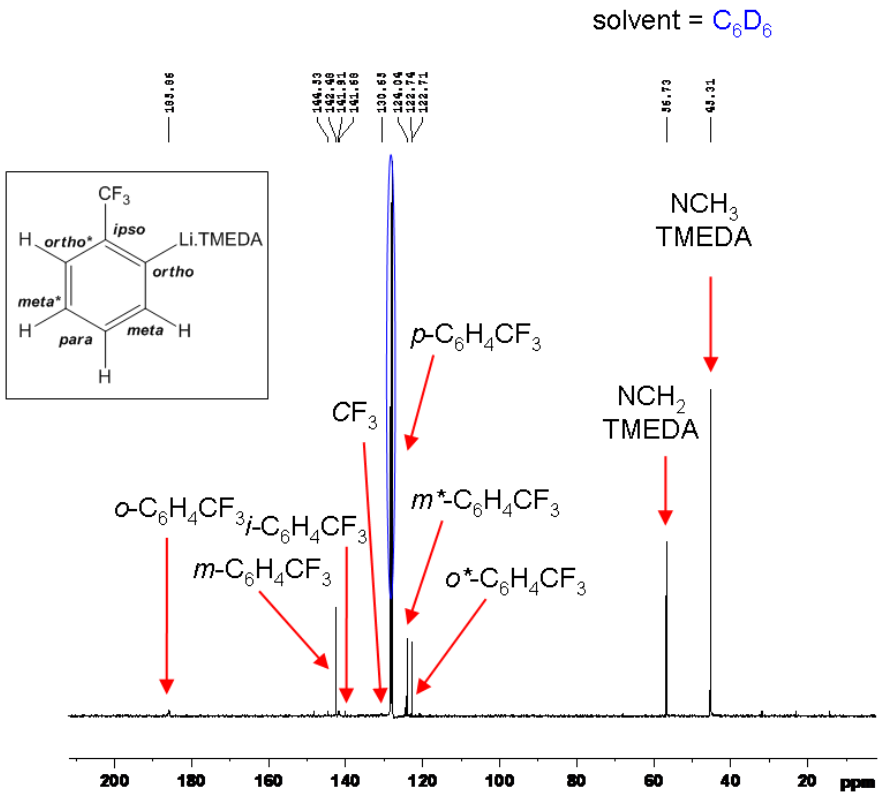


Figure S3 ^{13}C NMR spectrum of [(TMEDA)·Li(C_6H_4-CF_3)]$_2$ (**3**).

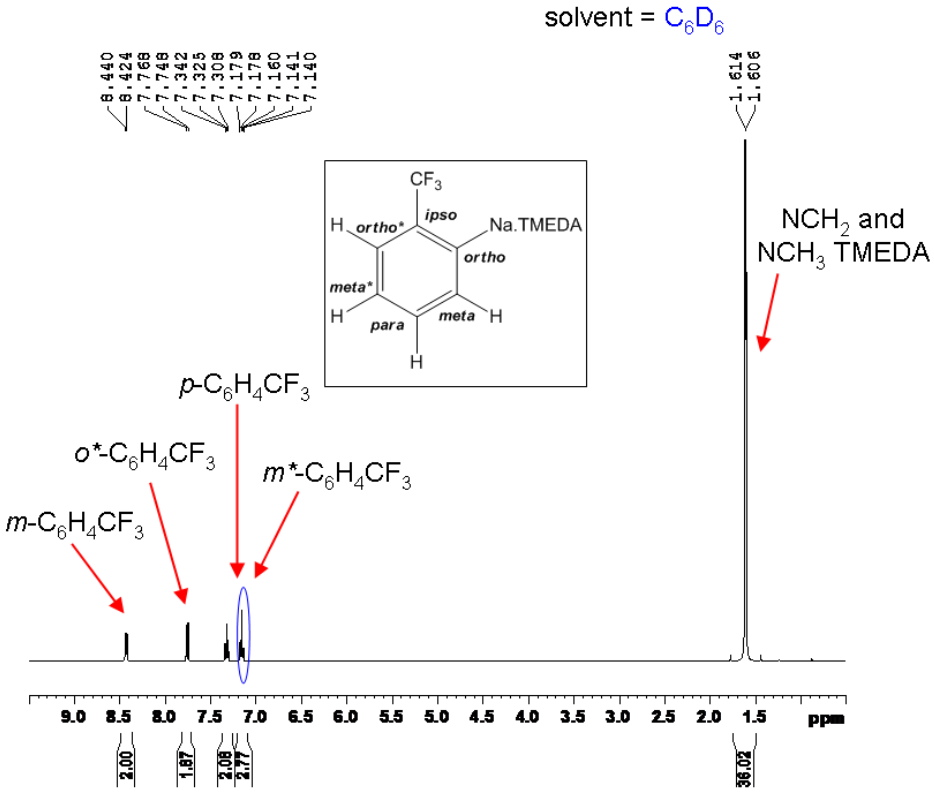


Figure S4 ^{1}H NMR spectrum of [(TMEDA)·Na(C_6H_4-CF_3)]$_2$ (**4**).

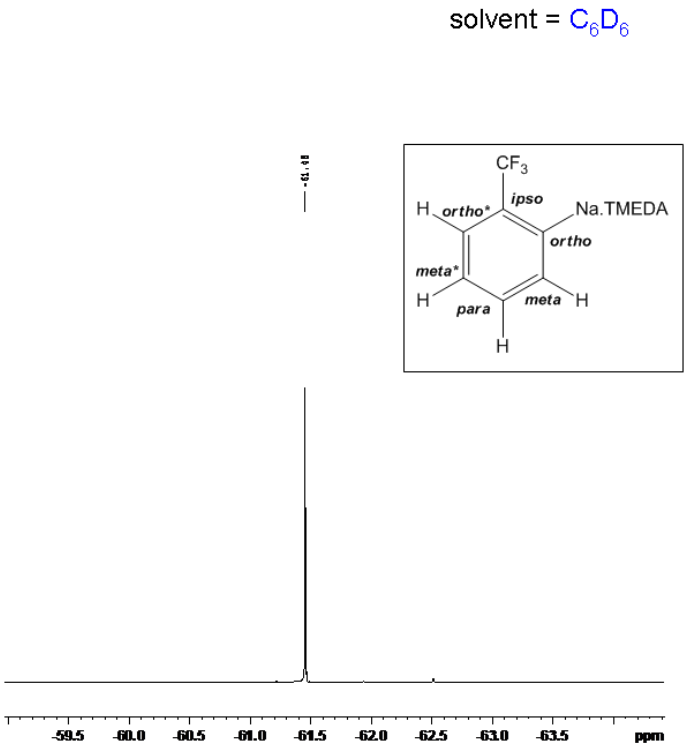


Figure S5 ^{19}F NMR spectrum of [(TMEDA)·Na(C_6H_4-CF_3)]$_2$ (**4**).

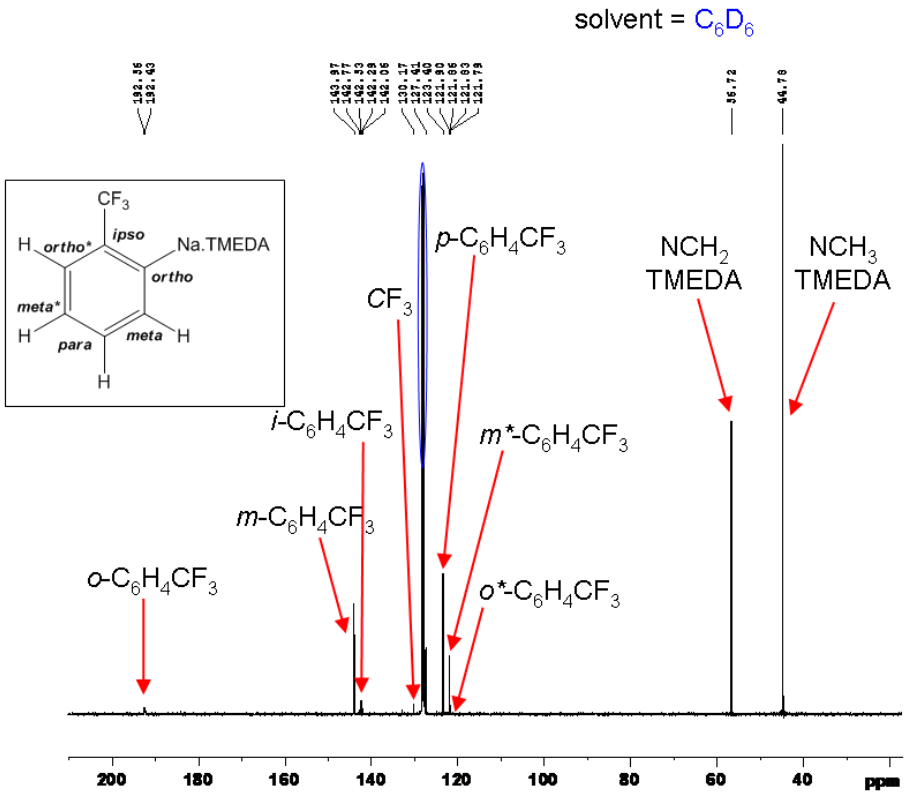


Figure S6 ^{13}C NMR spectrum of [(TMEDA)·Na(C_6H_4-CF_3)]$_2$ (**4**).

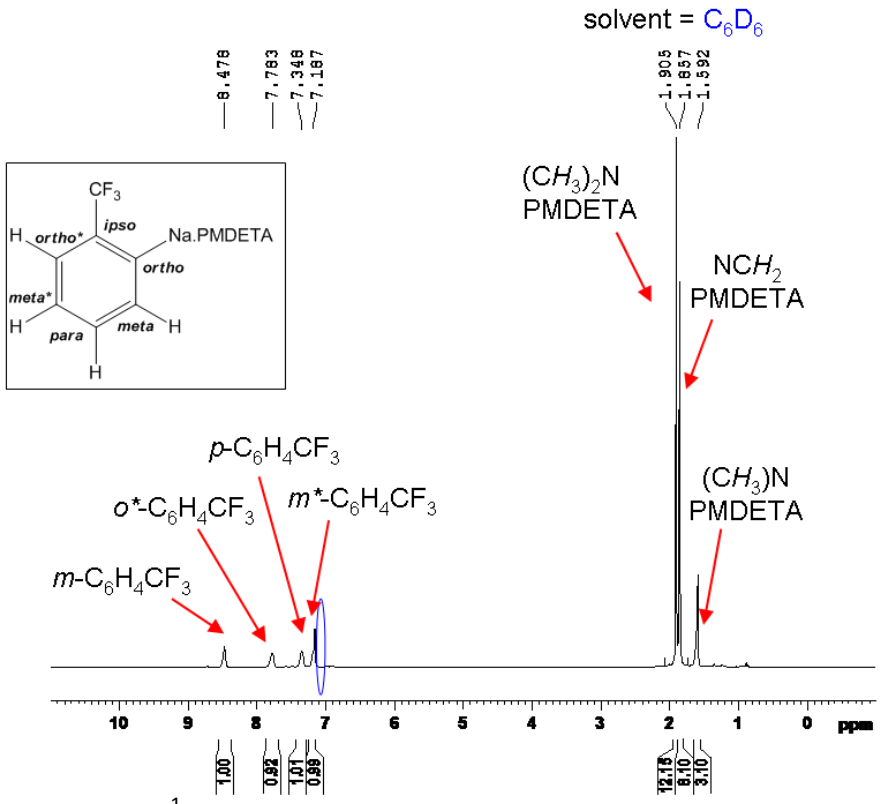


Figure S7 ^{1}H NMR spectrum of [(PMDETA)·Na(C_6H_4-CF_3)]$_2$ (**5**).

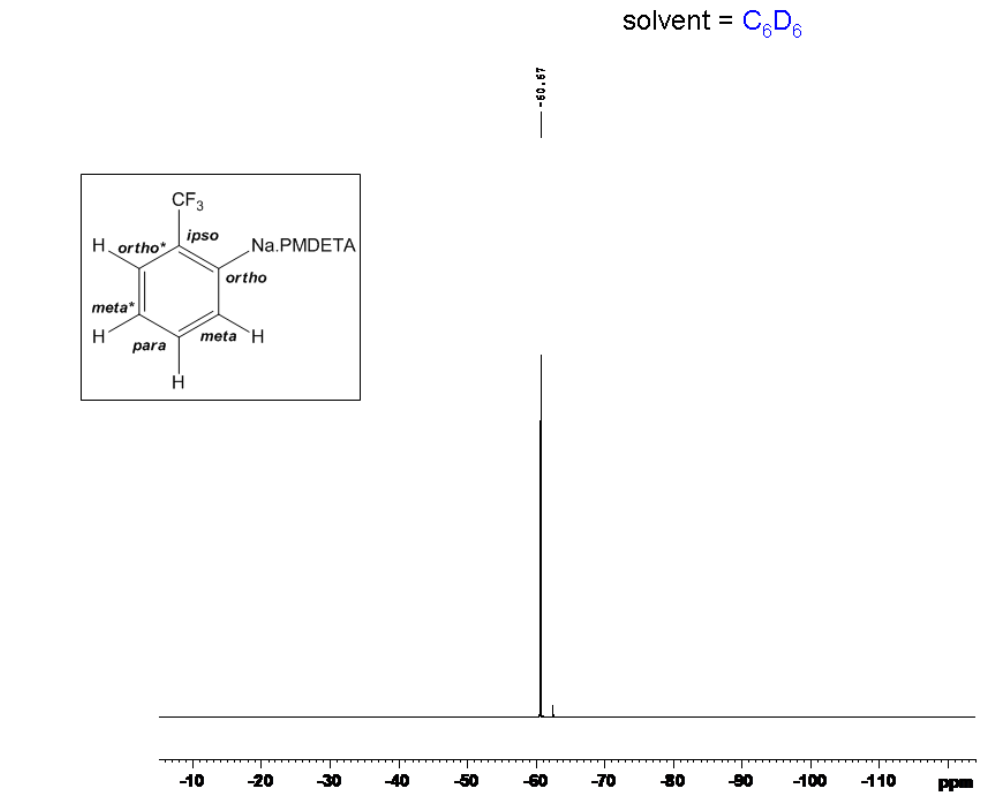


Figure S8 ^{19}F NMR spectrum of [(PMDETA)·Na(C_6H_4-CF_3)]$_2$ (**5**).

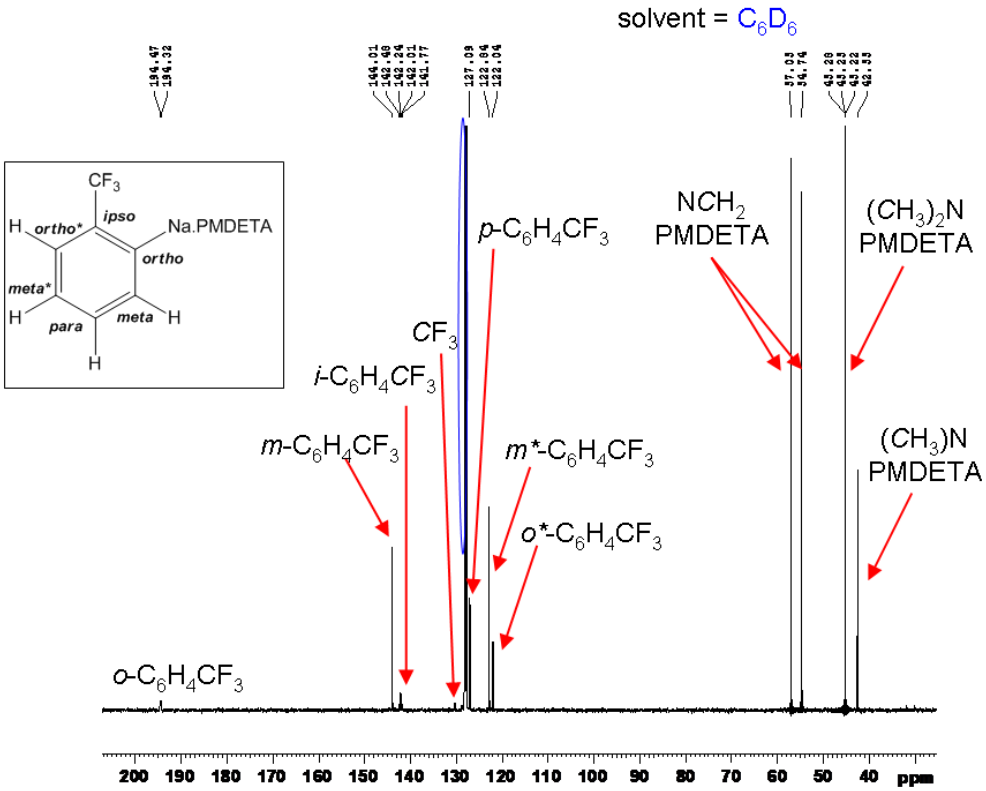


Figure S9 ^{13}C NMR spectrum of [(PMDETA)·Na(C_6H_4-CF_3)]$_2$ (**5**).

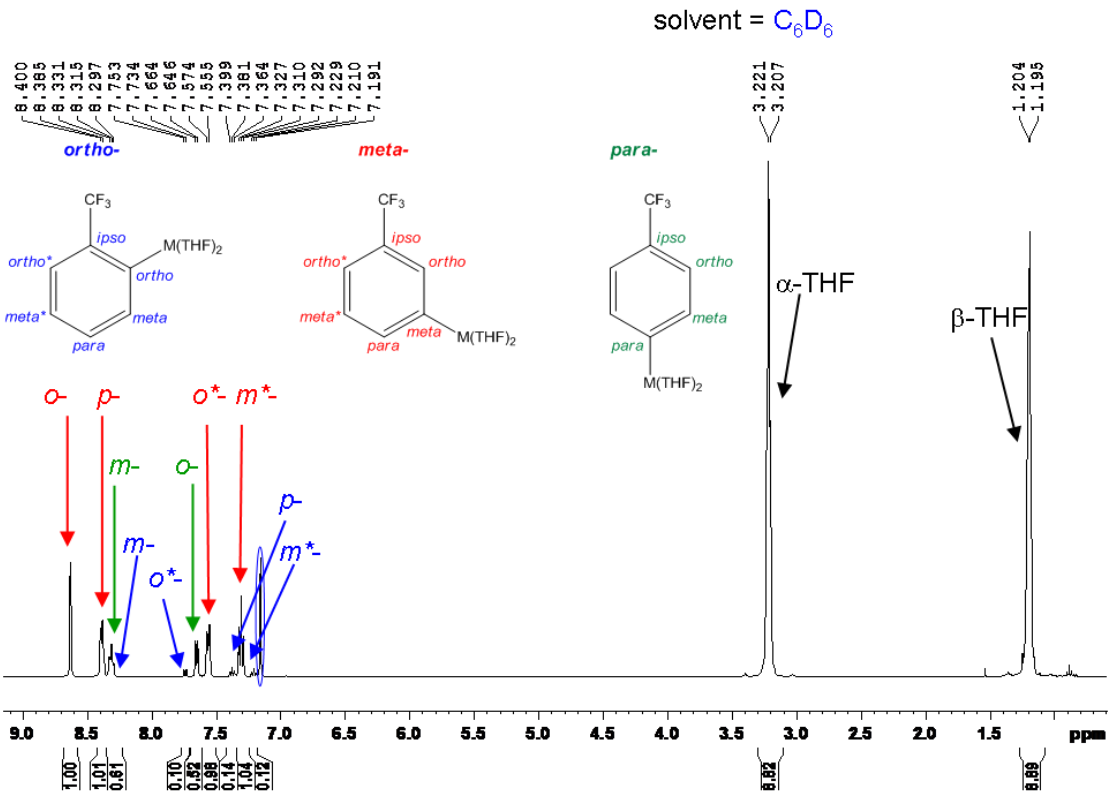


Figure S10 ^{1}H NMR spectrum of $[(THF)_2{\cdot}Li(C_6H_4\text{-}CF_3)]_2$ (**6**).

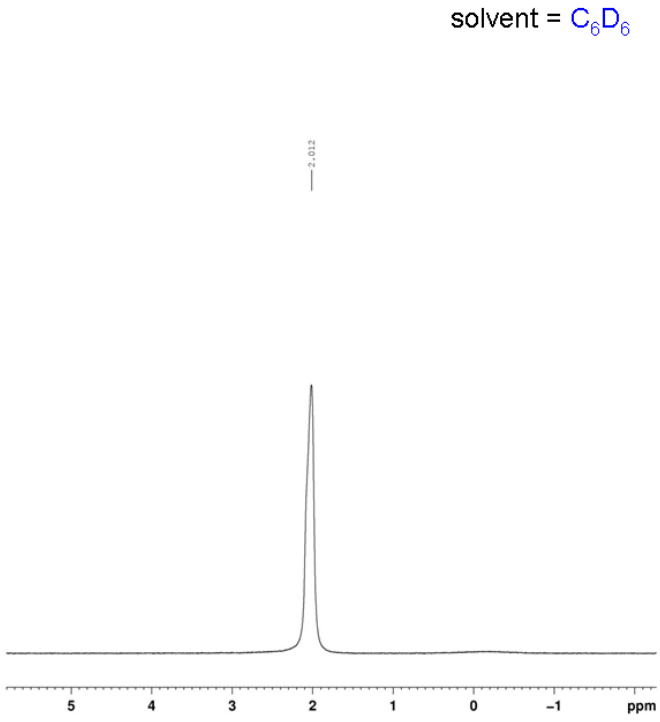


Figure S11 ^{7}Li NMR spectrum of $[(THF)_2{\cdot}Li(C_6H_4\text{-}CF_3)]_2$ (**6**).

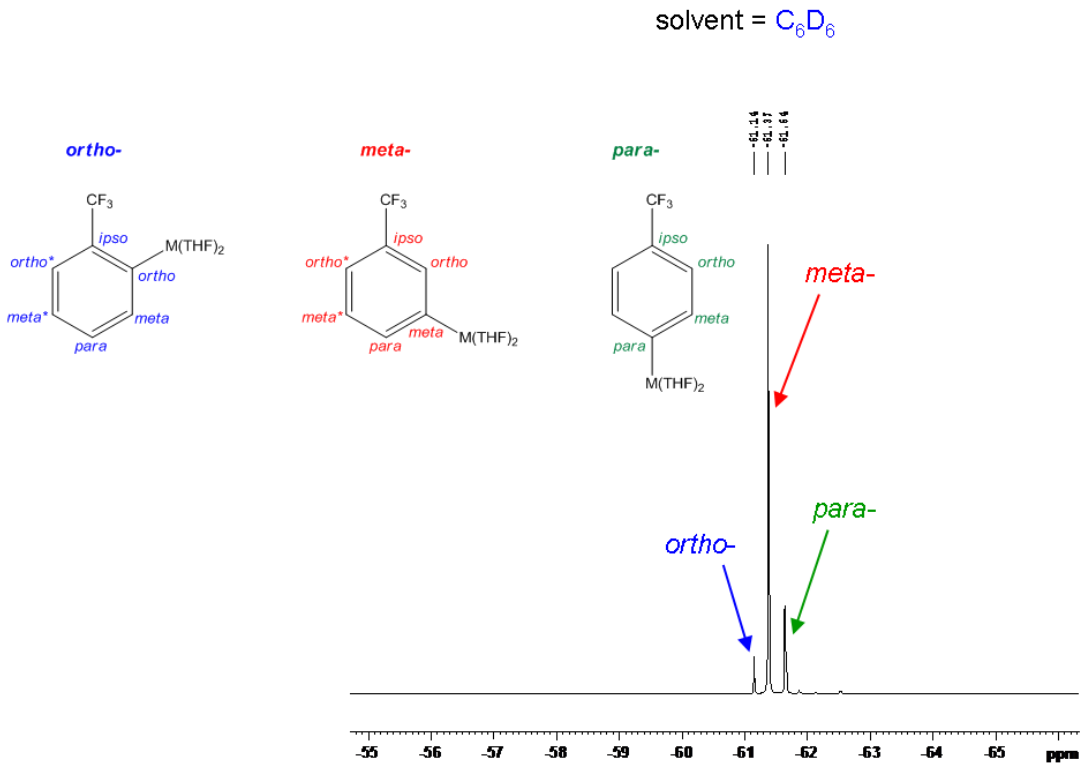


Figure S12 ^{19}F NMR spectrum of $[(THF)_2{\cdot}Li(C_6H_4\text{-}CF_3)]_2$ (**6**).

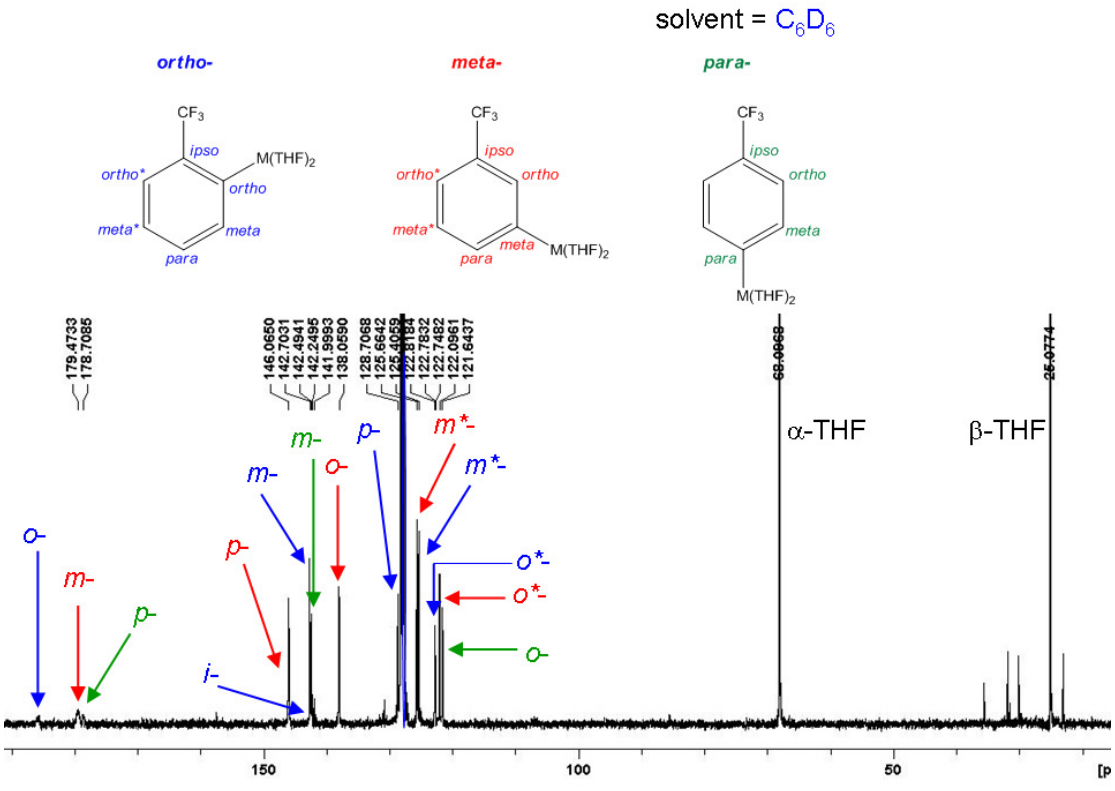


Figure S13 ^{13}C NMR spectrum of $[(THF)_2{\cdot}Li(C_6H_4\text{-}CF_3)]_2$ (**6**).

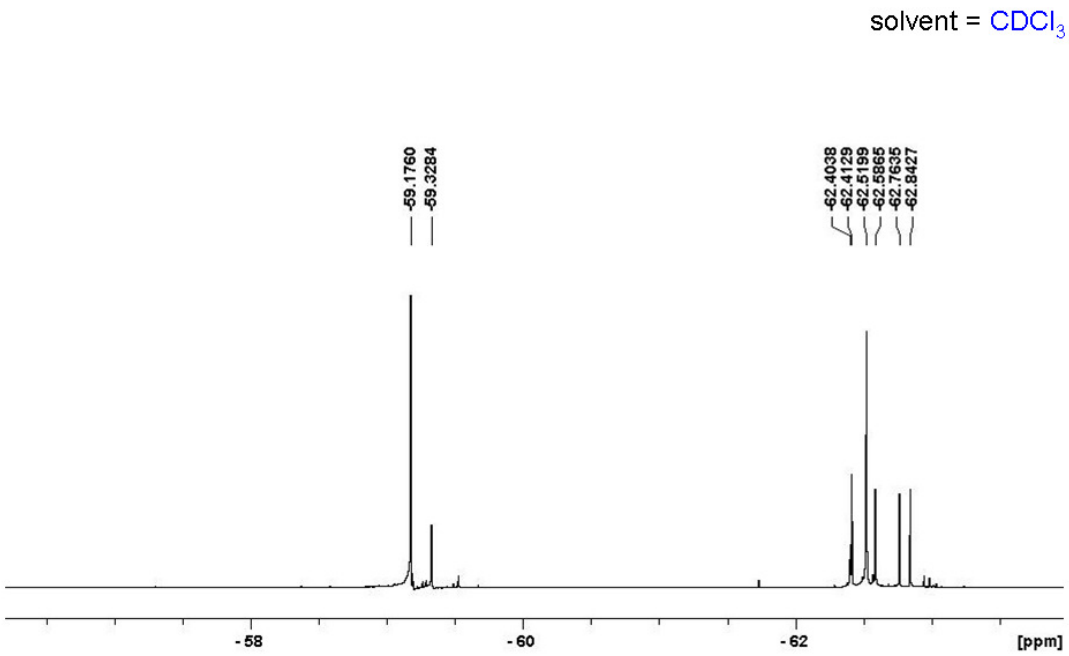
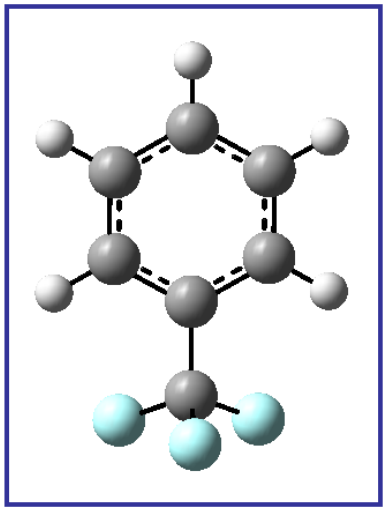


Figure S14 ^{19}F NMR spectrum of the iodine quenched reaction of ^{t}BuLi, **2** and PMDETA, showing the complex mixture of products obtained.

DFT Calculations

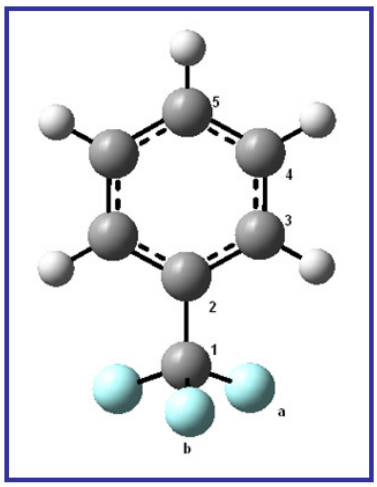
Model 2_{calc}: $PhCF_3$



E = -569.342866 a.u.

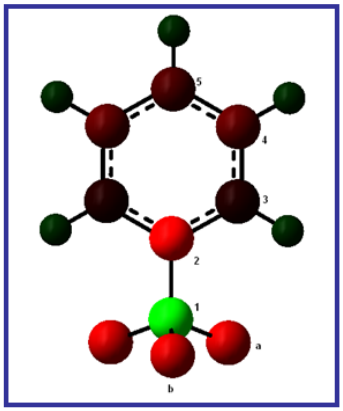
Principal Bond Lengths (Å) and Angles (˚)

C1-C2	1.504
C2-C3	1.395
C3-C4	1.392
C4-C5	1.393
C1-F_a	1.351
C1-F_b	1.355
F_a-C1-C2	112.1
F_b-C1-C2	111.7
C1-C2-C3	119.8
C2-C3-C4	119.7
C3-C4-C5	120.1
C4-C5-C4'	120.0



Charge Distribution

C1	+0.72
C2	-0.28
C3	-0.03
C4	-0.10
C5	-0.08
F_a	-0.21
F_b	-0.21

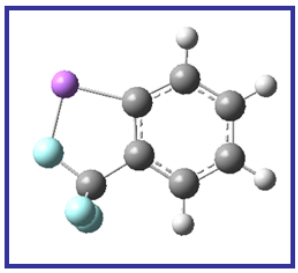


Model [Li(C_6H_4-CF_3)]

Model [*ortho*-Li(C_6H_4-CF_3)]

Principal Bond Lengths (Å)

C-Li	1.970
Li-F	1.874
C-F	1.427, 1.347, 1.342

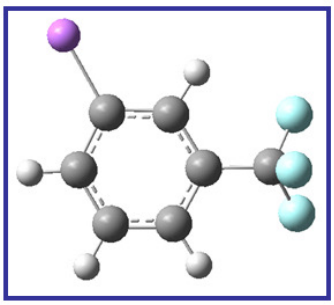


E = -576.272105 a.u.

Model [*meta*-Li(C_6H_4-CF_3)]

Principal Bond Lengths (Å)

C-Li	1.963
Li-F	1.874, 5.475
C-F	1.360, 1.354, 1.356

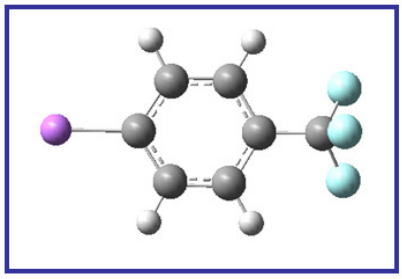


E = -576.251040 a.u.

Model [*para*-Li(C_6H_4-CF_3)]

Principal Bond Lengths (Å)

C-Li	1.965
Li-F	6.920
C-F	1.355, 1.359, 1.355



E = -576.250500 a.u.

Model [Li(C_6H_4-CF_3)]: Total Energies/a.u. and Relative Energies/kcal mol^{-1}

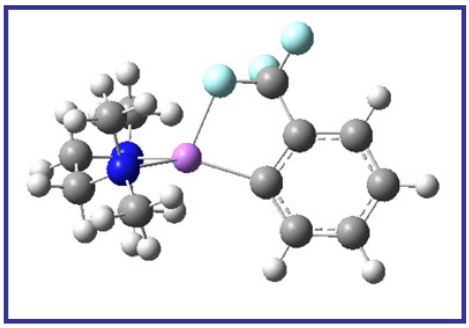
ortho	-576.272105	0.00
meta	-576.251040	+13.22
para	-576.250500	+13.56

Model [(TMEDA)·Li(C_6H_4-CF_3)]

Model [(TMEDA)·*ortho*-Li(C_6H_4-CF_3)]

Principal Bond Lengths (Å)

C-Li	2.054
Li-F	2.050
C-F	1.400, 1.363, 1.347
Li-N	2.127, 2.124

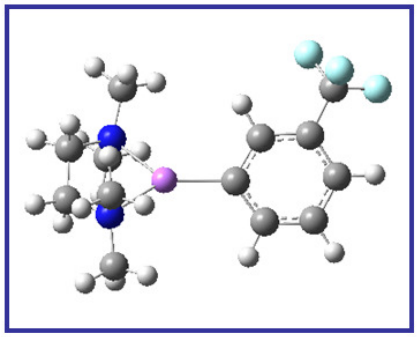


E = -923.940621 a.u.

Model [(TMEDA)·*meta*-Li(C_6H_4-CF_3)]

Principal Bond Lengths (Å)

C-Li	2.026
Li-F	5.505
C-F	1.359, 1.362, 1.356
Li-N	2.112, 2.109

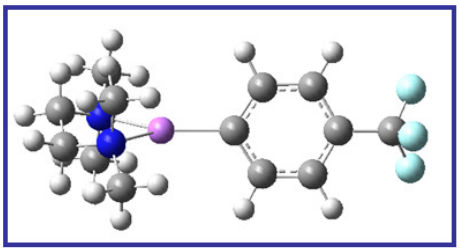


E = -923.924710 a.u.

Model [(TMEDA)·*para*-Li(C_6H_4-CF_3)]

Principal Bond Lengths (Å)

C-Li	2.030
Li-F	6.995
C-F	1.400, 1.363, 1.347
Li-N	2.113, 2.110



E = -923.923866 a.u.

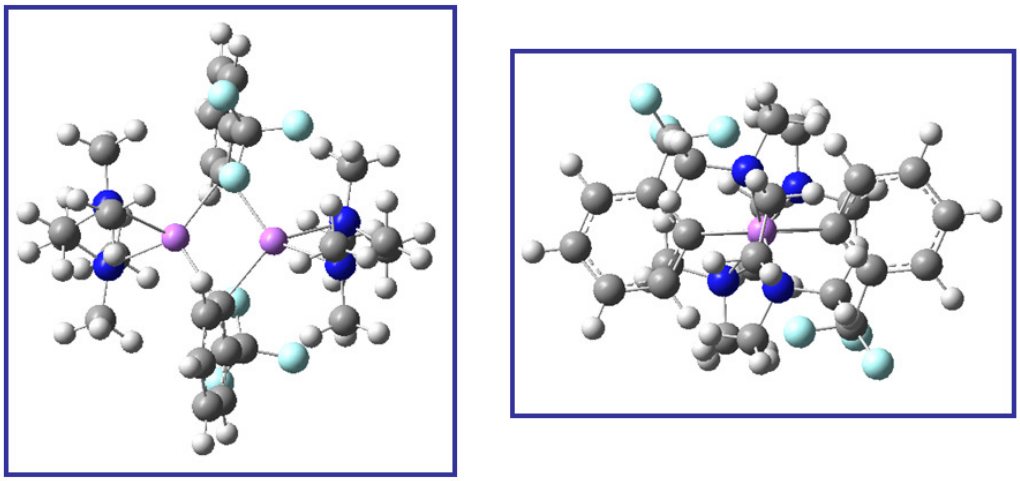
Model [(TMEDA)·Li(C_6H_4-CF_3)]: Total Energies/a.u. and Relative Energies/kcal mol^{-1}

ortho	-923.940621	0.00
meta	-923.924710	+9.98
para	-923.923866	+10.51

Model 3_{calc}: $[(TMEDA)\cdot Li(C_6H_4\text{-}CF_3)]_2$

Model 3_{calc}-*ortho*: $[(TMEDA)\cdot$*ortho*$\text{-}Li(C_6H_4\text{-}CF_3)]_2$

Optimised Geometry

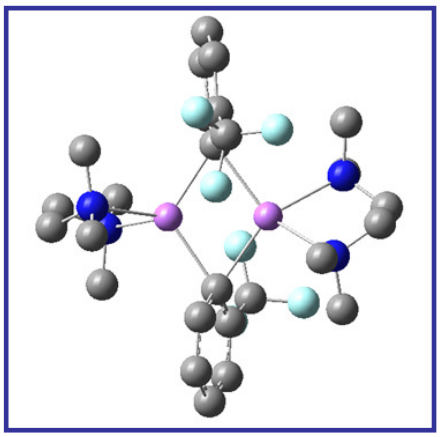


E = -1847.895997 a.u.

Principal Bond Lengths (Å) and Angles (º)

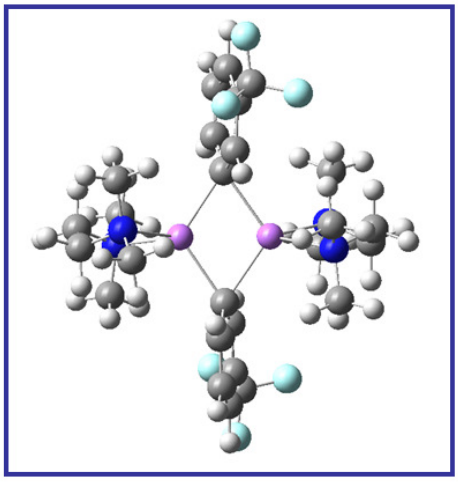
Li-C	2.234, 2.292
Li-N	2.365, 2.333
Li…C	2.957, 3.250, 3.162, 3.276
Li…F	2.897, 3.123

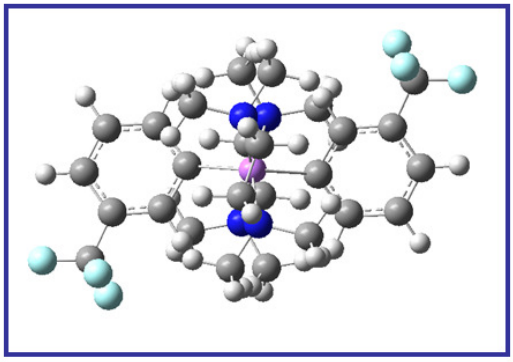
C-Li-C	112.4, 108.1
Li-C-Li	69.7, 69.7
N-Li-N	81.1, 79.3



Model 3_{calc}-*meta*: [(TMEDA)·*meta*-Li(C_6H_4-CF_3)]$_2$

Optimised Geometry



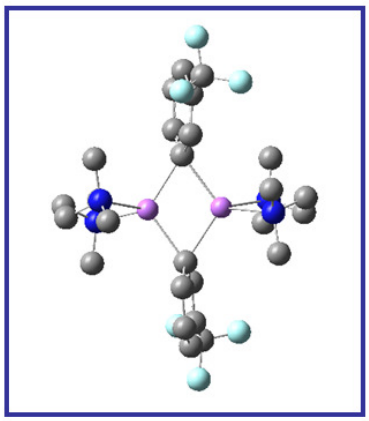


E = -1847.884089 a.u.

Principal Bond Lengths (Å) and Angles (º)

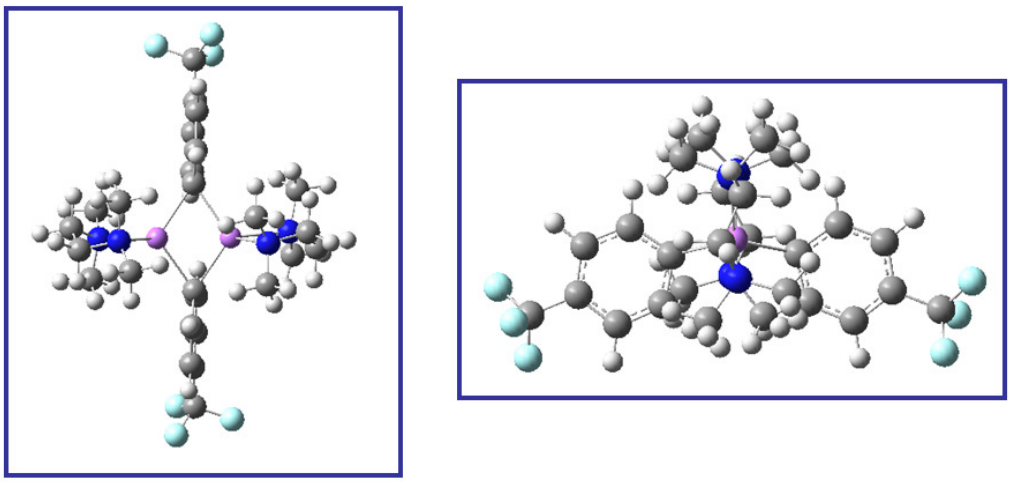
Li-C	2.223, 2.248
Li-N	2.281, 2.102
Li…C	2.946, 3.312, 3.145, 3.132
Li…F	5.223, 5.470

C-Li-C	112.0, 110.2
Li-C-Li	68.9, 68.9
N-Li-N	83.5, 82.8



Model 3_{calc}-*para*: [(TMEDA)·*para*-Li(C_6H_4-CF_3)]$_2$

Optimised Geometry

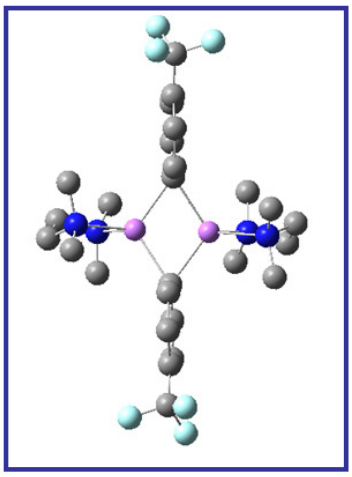


E = -1847.879143 a.u.

Principal Bond Lengths (Å) and Angles (º)

Li-C	2.236, 2.241
Li-N	2.256, 2.240
Li…C	3.011, 3.290, 3.047, 3.215
Li…F	6.711, 6.711

C-Li-C	108.3, 108.3
Li-C-Li	67.5, 67.5
N-Li-N	84.0, 84.0



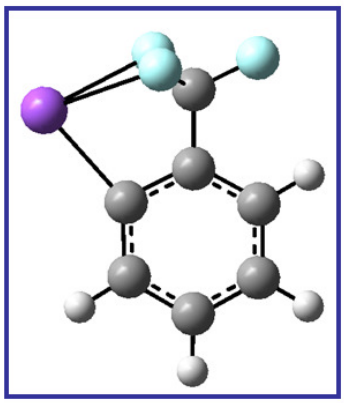
Model 3_{calc} [(TMEDA)·Li(C_6H_4-CF_3)]$_2$: Total Energies/a.u. and Relative Energies/kcal mol^{-1}

ortho	-1847.895997	+0.00
meta	-1847.884089	+7.48
para	-1847.879143	+10.58

Model [Na(C_6H_4-CF_3)]

Model [*ortho*-Na(C_6H_4-CF_3)]

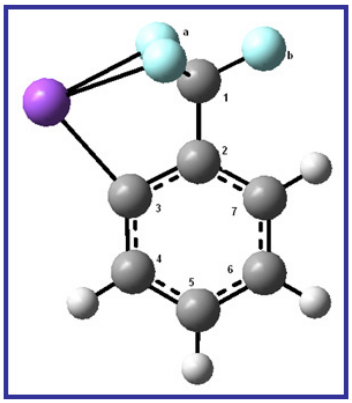
Optimised Geometry



E = -731.036758 a.u.

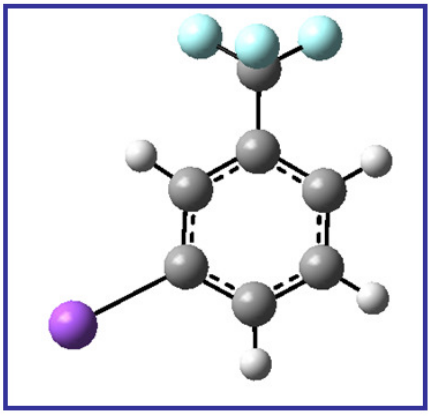
Principal Bond Lengths (Å) and Angles (º)

C1-C2	1.494	F_a-C1-C2	112.5
C2-C3	1.412	F_b-C1-C2	116.1
C3-C4	1.405	Na-F_a-C1	87.1
C4-C5	1.397	C3-Na-F_a	73.5
C5-C6	1.395	Na-C3-C2	105.1
C6-C7	1.390	Na-C3-C4	140.9
C2-C7	1.400		
Na-C3	2.330		
Na-F_a	2.542		
C1-F_a	1.389		
C1-F_b	1.336		



Model [*meta*-Na(C_6H_4-CF_3)]

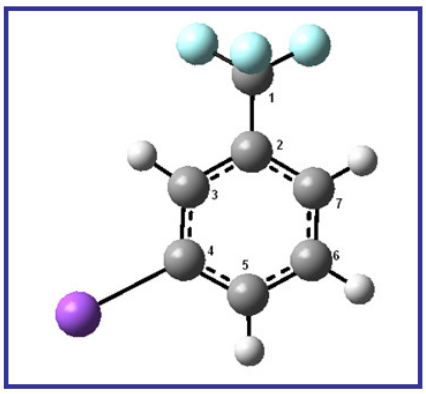
Optimised Geometry



E = -731.021843 a.u.

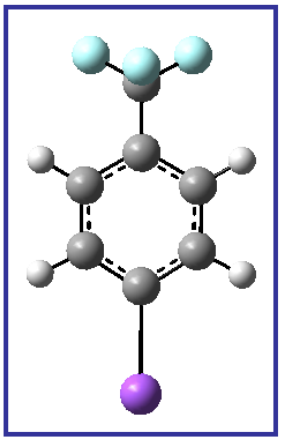
Principal Bond Lengths (Å) and Angles (º)

C1-C2	1.499
C2-C3	1.400
C3-C4	1.407
C4-C5	1.409
C5-C6	1.397
C6-C7	1.391
C2-C7	1.394
Na-C4	2.306
C1-F	1.360, 1.355, 1.356
F-C1-C2	112.2, 112.8, 112.5
Na-C4-C3	120.6
Na-C4-C5	124.2



Model [*para*-Na(C_6H_4-CF_3)]

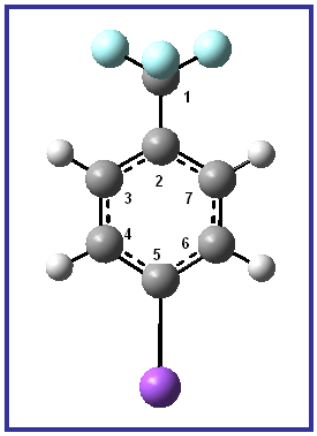
Optimised Geometry



E = -731.021385 a.u.

Principal Bond Lengths (Å) and Angles (º)

C1-C2	1.497
C2-C3	1.395
C3-C4	1.395
C4-C5	1.409
C5-C6	1.409
C6-C7	1.395
C2-C7	1.395
Na-C5	2.306
C1-F	1.360, 1.355, 1.355
F-C1-C2	112.3, 112.5, 112.5
Na-C5-C6	122.5
Na-C5-C4	122.5



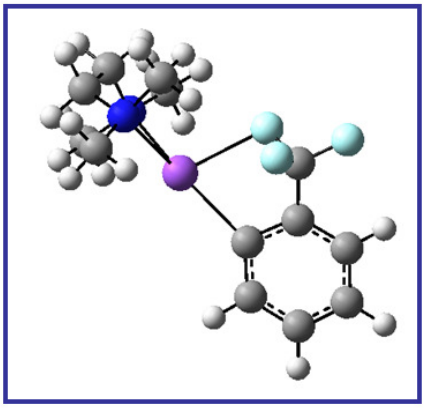
Model [Na(C_6H_4-CF_3)]: Total Energies/a.u. and Relative Energies/kcal mol^{-1}

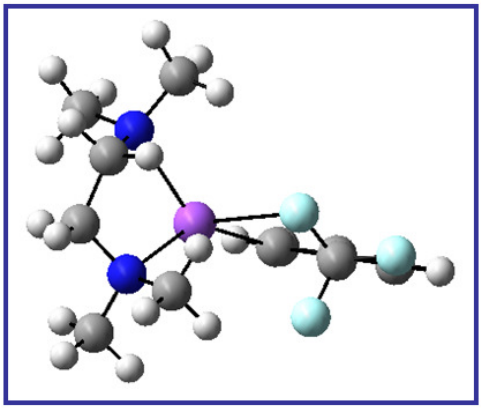
ortho	-731.036758	0.00
meta	-731.021843	+9.36
para	-731.021385	+9.65

Model [(TMEDA)·Na(C_6H_4-CF_3)]

Model [(TMEDA)·*ortho*-Na(C_6H_4-CF_3)]

Optimised Geometry

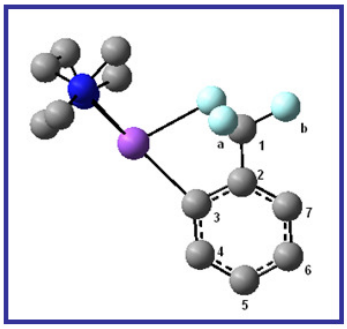




E = -1078.694247 a.u.

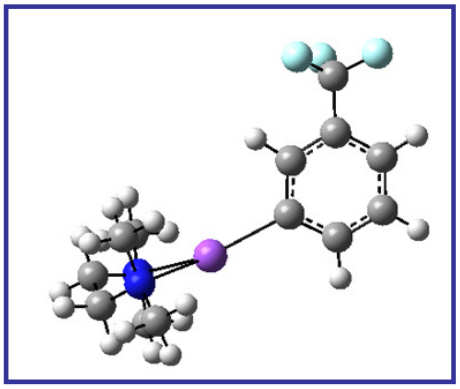
Principal Bond Lengths (Å) and Angles (º)

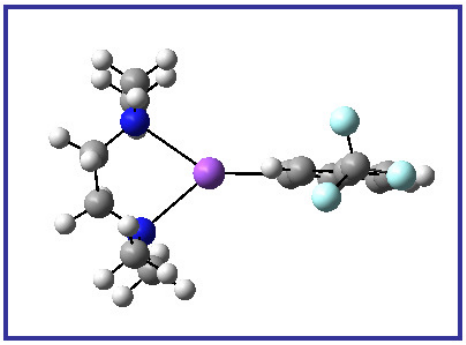
C1-C2	1.497	F_a-C1-C2	112.7, 113.3
C2-C3	1.413	F_b-C1-C2	115.2
C3-C4	1.410	Na-F_a-C1	103.9, 71.2
C4-C5	1.396	C3-Na-F_a	72.7, 64.0
C5-C6	1.395	Na-C3-C2	110.1
C6-C7	1.390	Na-C3-C4	136.1
C2-C7	1.402	N-Na-N	75.8
Na-C3	2.313		
Na-F_b	2.427, 3.229		
C1-F_a	1.394, 1.370		
C1-F_b	1.346		
N-Na	2.496, 2.495		



Model [(TMEDA)·*meta*-Na(C_6H_4-CF_3)]

Optimised Geometry

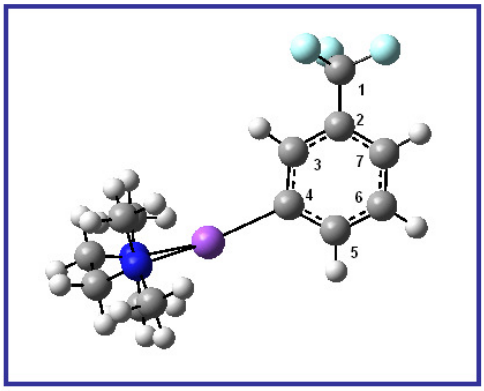




E = -1078.678250 a.u.

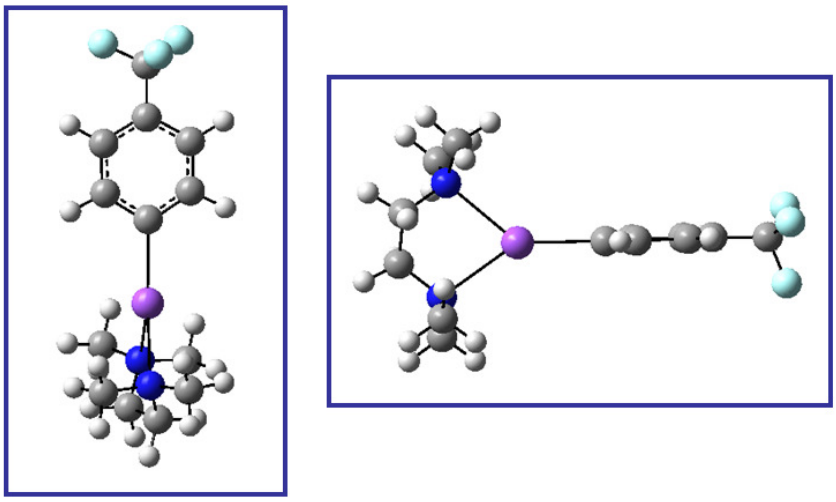
Principal Bond Lengths (Å) and Angles (º)

C1-C2	1.497
C2-C3	1.402
C3-C4	1.410
C4-C5	1.414
C5-C6	1.397
C6-C7	1.392
C2-C7	1.394
Na-C4	2.364
Na-F	5.837, 6.059, 6.956
C1-F	1.355, 1.360, 1.362
N-Na	2.507, 2.499
F-C1-C2	112.5, 112.4, 113.3
Na-C4-C3	119.5
Na-C4-C5	126.7
N-Na-N	75.2



Model [(TMEDA)·*para*-Na(C_6H_4-CF_3)]

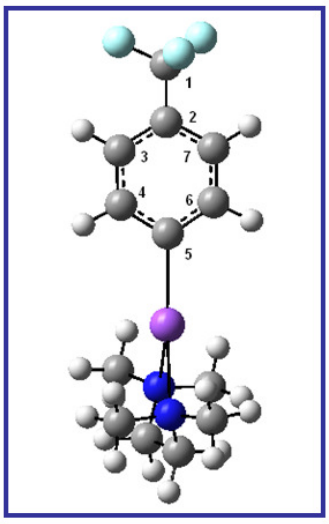
Optimised Geometry



E = -1078.677687 a.u.

Principal Bond Lengths (Å) and Angles (º)

C1-C2	1.495
C2-C3	1.395
C3-C4	1.396
C4-C5	1.413
C5-C6	1.414
C6-C7	1.394
C2-C7	1.396
Na-C4	2.368
Na-F	7.378, 7.341, 7.378
C1-F	1.355, 1.362, 1.358
N-Na	2.505, 2.504
F-C1-C2	112.6, 112.9, 112.6
Na-C4-C3	122.3
Na-C4-C5	123.9
N-Na-N	75.2



Model [(TMEDA)·Na(C_6H_4-CF_3)]: Total Energies/a.u. and Relative Energies/kcal mol^{-1}

ortho	-1078.694247	0.00
meta	-1078.678250	+10.04
para	-1078.677687	+10.39

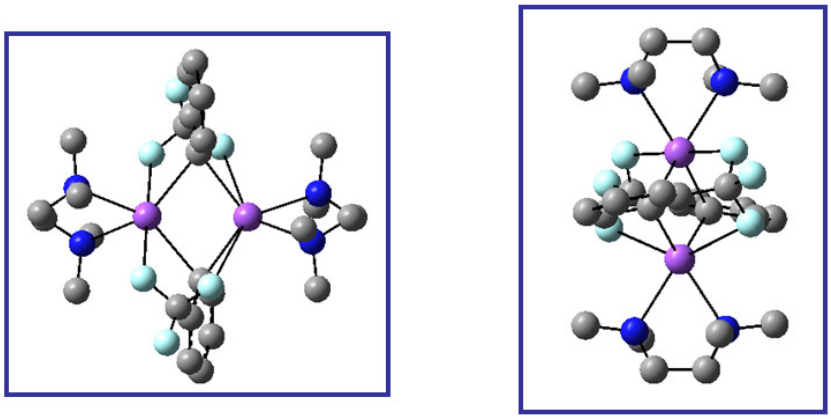
TMEDA + [Na(C_6H_4-CF_3)] = [(TMEDA)·Na(C_6H_4-CF_3)]

ortho ΔE = -23.52 kcal mol-1
meta ΔE = -22.84 kcal mol-1
para ΔE = -22.78 kcal mol-1

Model 4_{calc}: $[(TMEDA)\cdot Na(C_6H_4\text{-}CF_3)]_2$

Model 4_{calc}-*ortho* $[(TMEDA)\cdot$*ortho*$\text{-}Na(C_6H_4\text{-}CF_3)]_2$

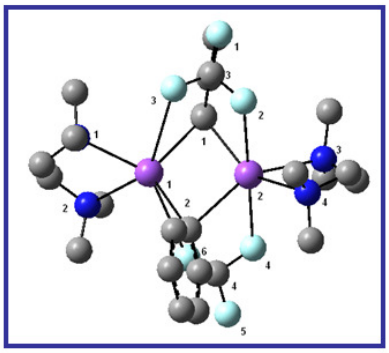
Optimised Geometry (initial geometry taken from the lithium dimer)



E = -2157.429869 a.u.

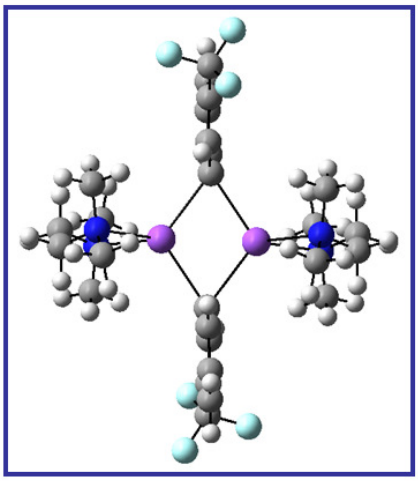
Principal Bond Lengths (Å) and Angles (º)

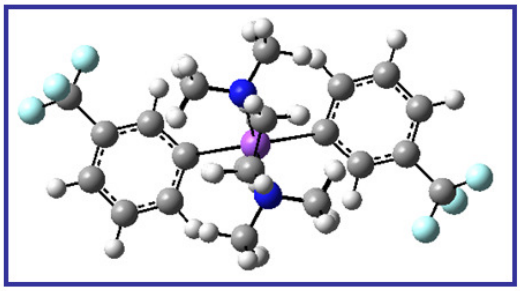
Na1-N1	2.580	N1-Na1-N2	73.3
Na1-N2	2.580	N3-Na2-N4	73.1
Na1-C1	2.563	Na1-C1-Na2	72.5
Na1-C2	2.563	Na1-C2-Na2	72.5
Na1-F3	3.174	C1-Na1-C2	110.3
Na1-F6	3.174	C1-Na2-C2	104.5
Na2-N3	2..578	Na2-N4	2.578
Na2-C1	2.660	Na2-C2	2.660
Na2-F2	2.519	Na2-F4	2.519
C3-F1	1.348	C3-F2	1.383
C3-F3	1.368	C4-F4	1.383
C4-F5	1.348	C4-F6	1.368



Model 4_{calc}-*meta* [(TMEDA)·*meta*-Na(C_6H_4-CF_3)]$_2$

Optimised Geometry (C_i symmetry)

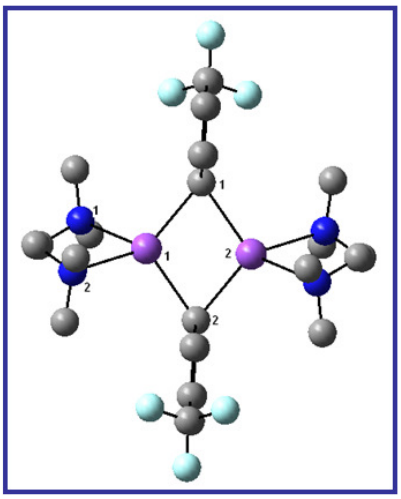




E = -2157.405212 a.u.

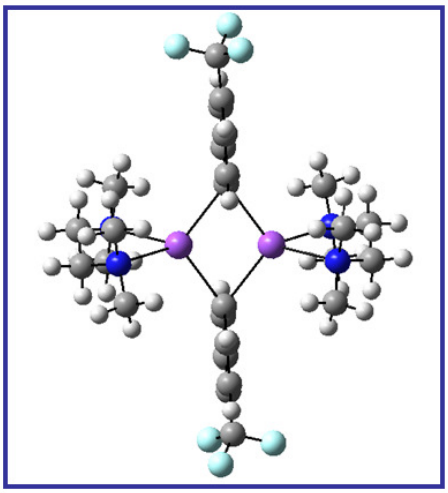
Principal Bond Lengths (Å) and Angles (º)

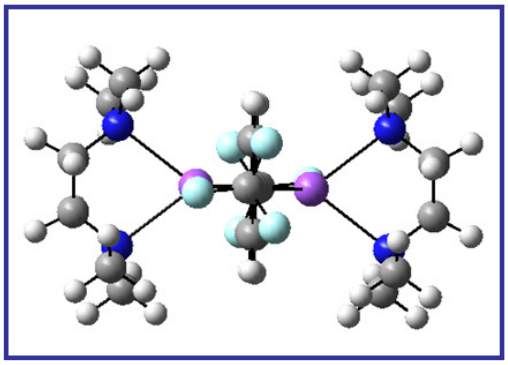
Na1-N1	2.536
Na1-N2	2.541
Na1-C1	2.546
Na1-C2	2.554
Na2-C1	2.554
Na2-C2	2.546
C-F	1.350 1.364 1.364
Na···F	5.326 5.288
N1-Na1-N2	75.3
Na-C-Na	72.5
C-Na-C	107.5



Model 4_{calc}-*para* [(TMEDA)·*para*-Na(C_6H_4-CF_3)]$_2$

Optimised Geometry (C_i symmetry)

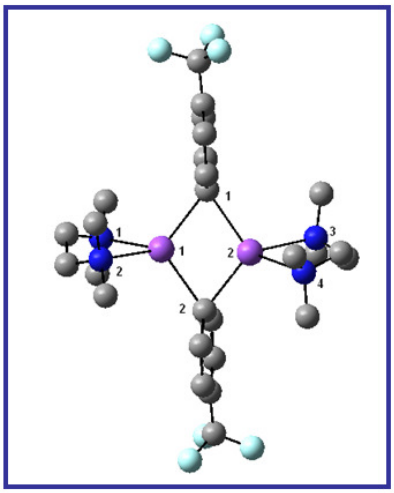




E = -2157.399255 a.u.

Principal Bond Lengths (Å) and Angles (º)

Na1-N1	2.532	N-Na-N	75.3
Na1-N2	2.531	N-Na-N	75.3
Na1-C1	2.561	Na-C-Na	70.2
Na1-C2	2.567	C-Na-C	109.8
Na2-N3	2.531		
Na2-N4	2.532		
Na2-C1	2.567		
Na2-C2	2.561		
C-F	1.361	1.356	1.354
Na...F	6.844		



Model 4_{calc} $[(TMEDA)Na(C_6H_4\text{-}CF_3)]_2$: Total Energies/a.u. and Relative Energies/kcal mol^{-1}

ortho	-2157.429869	+0.00
meta	-2157.405212	+15.47
para	-2157.399255	+19.21

Model 4_{calc} $[(TMEDA)Na(C_6H_4\text{-}CF_3)]_2$: Dimerisation Energies

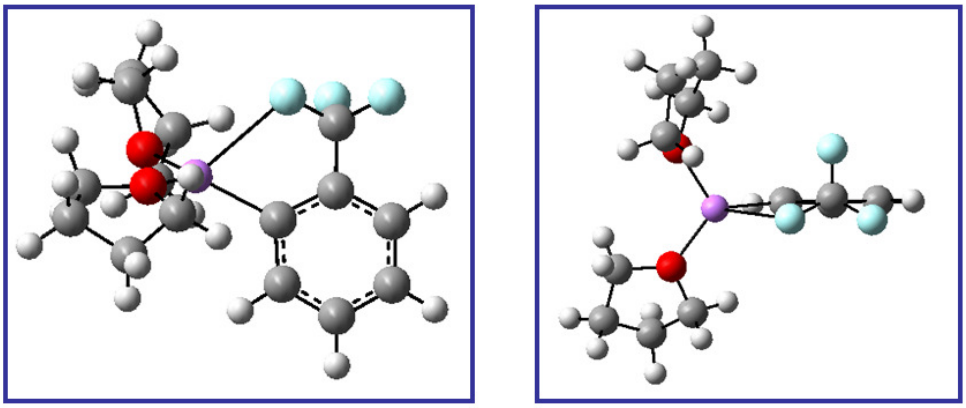
Defined as energy/kcal mol^{-1} of the reaction
$[(TMEDA)\cdot Na(C_6H_4\text{-}CF_3)] = ½\ [(TMEDA)\cdot Na(C_6H_4\text{-}CF_3)]_2$

ortho	-12.98
meta	-15.28
para	-13.80

Model $[(THF)_2 \cdot Li(C_6H_4\text{-}CF_3)]$

Model $[(THF)_2 \cdot \textit{ortho}\text{-}Li(C_6H_4\text{-}CF_3)]$

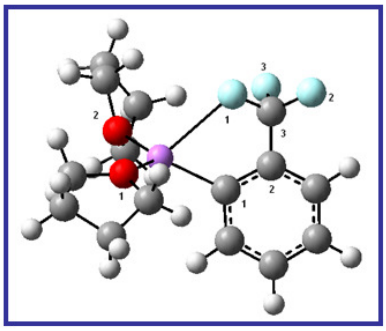
Optimised Geometry



E = -1041.123943 a.u.

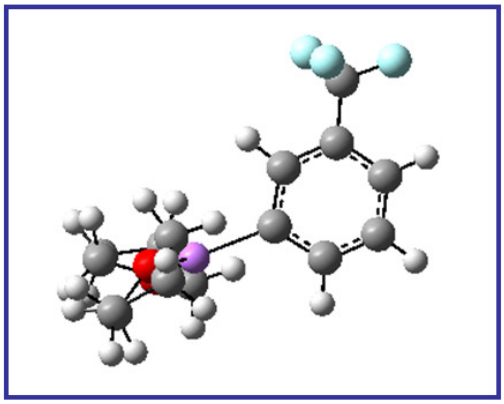
Principal Bond Lengths (Å) and Angles (º)

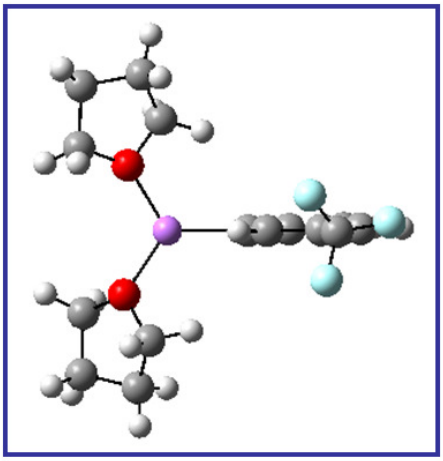
Li-O1	1.942	O1-Li-C1	123.2
Li-O2	1.965	O2-Li-C1	121.1
Li-F1	2.121	O1-Li-O2	111.5
Li-C1	2.072	Li-C1-C2	125.8
C1-C2	1.412	Li-F1-C3	109.0
C2-C3	1.497	C1-C2-C3	117.7
C3-F1	1.389	C2-C3-F1	112.3
C3-F2	1.349	C2-C3-F2	114.9
C3-F3	1.368	C2-C3-F3	113.6



Model [$(THF)_2$·*meta*-Li(C_6H_4-CF_3)]

Optimised Geometry

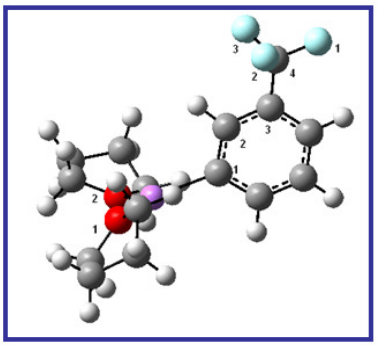




E = -1041.109013 a.u.

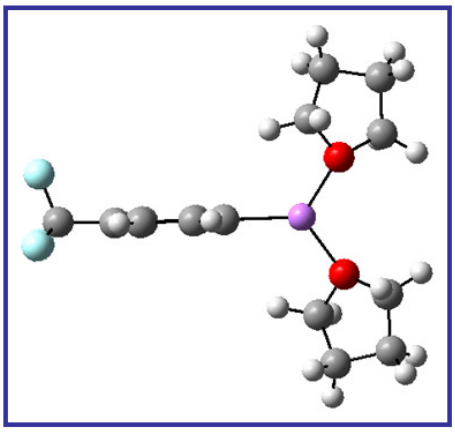
Principal Bond Lengths (Å) and Angles (º)

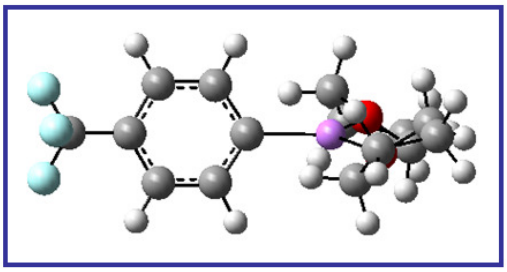
Li-O1	1.937	O1-Li-C1	122.7
Li-O2	1.940	O2-Li-C1	122.2
Li-C1	2.053	O1-Li-O2	115.0
C1-C2	1.411	Li-C1-C2	120.3
C2-C3	1.402	C1-C2-C3	123.8
C3-C4	1.497	C2-C3-C4	119.1
C4-F1	1.355	C3-C4-F1	113.3
C4-F2	1.362	C3-C4-F2	112.3
C4-F3	1.360	C3-C4-F3	112.4



Model [(THF)$_2$·*para*-Li(C$_6$H$_4$-CF$_3$)]

Optimised Geometry

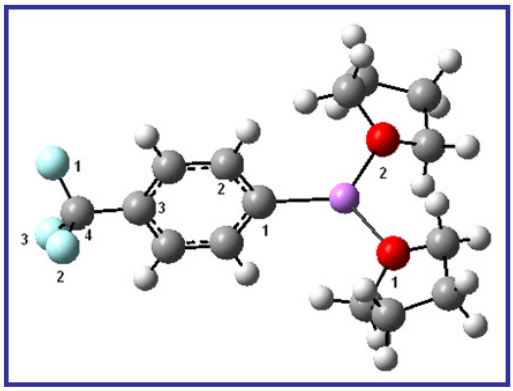




E = -1041.108373 a.u.

Principal Bond Lengths (Å) and Angles (º)

Li-O1	1.940
Li-O2	1.939
Li-C1	2.052
C1-C2	1.416
C3-C4	1.495
C4-F1	1.356
C4-F2	1.362
C4-F3	1.356
O1-Li-C1	122.7
O2-Li-C1	122.8
O1-Li-O2	114.5
Li-C1-C2	123.4
C3-C4-F1	112.7
C3-C4-F2	112.5
C3-C4-F3	112.7



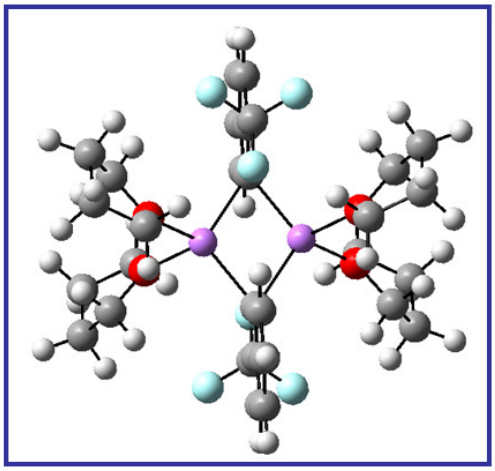
Model [(THF)$_2$·Li(C$_6$H$_4$-CF$_3$)]: Total Energies/a.u. and Relative Energies/kcal mol^{-1}

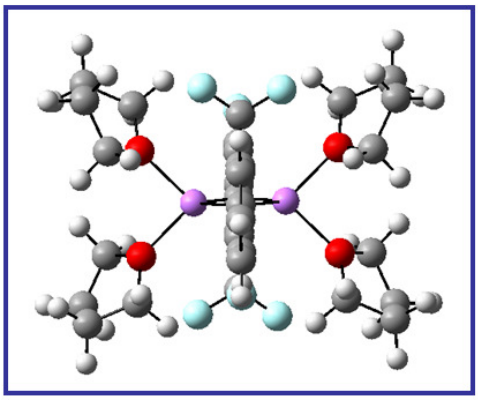
ortho	-1041.123943	0.00
meta	-1041.109013	+9.37
para	-1041.108373	+9.76

Model 6_{calc}: $[(THF)_2 \cdot Li(C_6H_4\text{-}CF_3)]_2$

Model 6_{calc} -*ortho* $[(THF)_2 \cdot$*ortho*$\text{-}Li(C_6H_4\text{-}CF_3)]_2$

Optimised Geometry

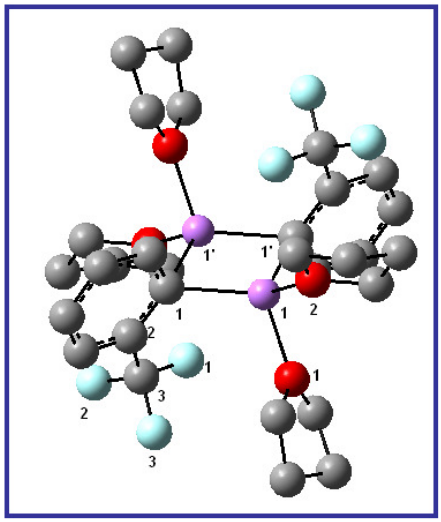




E = -2082.264388 a.u.

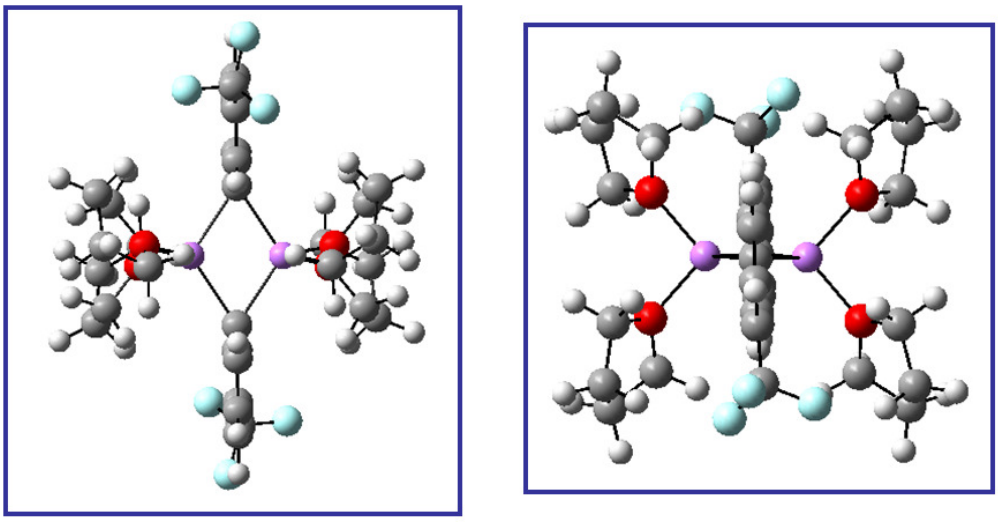
Principal Bond Lengths (Å) and Angles (º)

Li-O1	2.044	O1-Li-C1	112.0
Li-O2	2.051	O2-Li-C1	114.6
Li1...F1	2.995	O1-Li-O2	89.9
Li1...F1	3.001	Li1-C1-Li1'	67.7
Li1-C1	2.254	C1-Li1-C1'	112.3
Li1'-C1	2.262	C1-C2-C3	120.6
C1-C2	1.410	C2-C3-F1	114.7
C2-C3	1.504	C2-C3-F2	112.6
C3-F1	1.352	C2-C3-F3	112.4
C3-F2	1.369		
C3-F3	1.370		



Model 6_{calc}-*meta* $[(THF)_2 \cdot$*meta*$-Li(C_6H_4-CF_3)]_2$

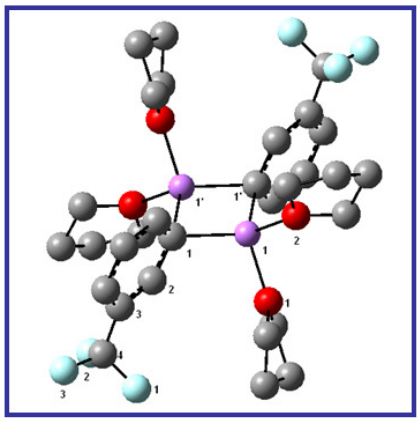
Optimised Geometry



E = -2082.253831 a.u.

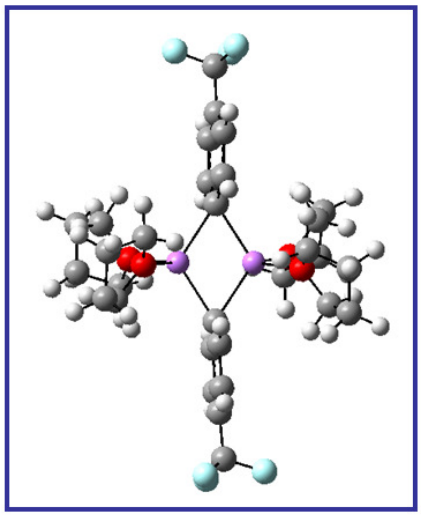
Principal Bond Lengths (Å) and Angles (º)

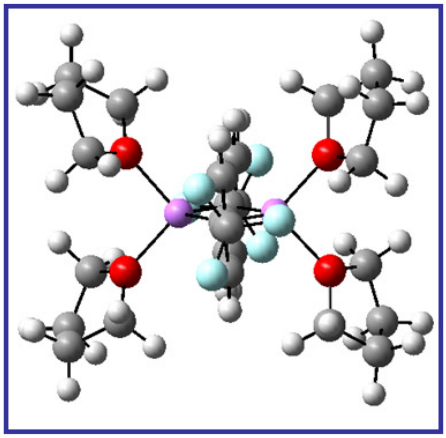
Li1-O1	2.013	O1-Li1-C1	107.5
Li1-O2	2.007	O2-Li1-C1	114.7
Li1-C1	2.239	O1-Li1-O2	98.5
Li1'-C1	2.232	Li1-C1-Li1'	67.0
C1-C2	1.411	C1-Li1-C1'	113.0
C2-C3	1.402	C1-C2-C3	124.0
C3-C4	1.496	C2-C3-C4	119.3
C4-F1	1.366	C3-C4-F1	112.2
C4-F2	1.362	C3-C4-F2	112.6
C4-F3	1.351	C3-C4-F3	113.5



Model 6_{calc}-*para* $[(THF)_2 \cdot$*para*-$Li(C_6H_4\text{-}CF_3)]_2$

Optimised Geometry

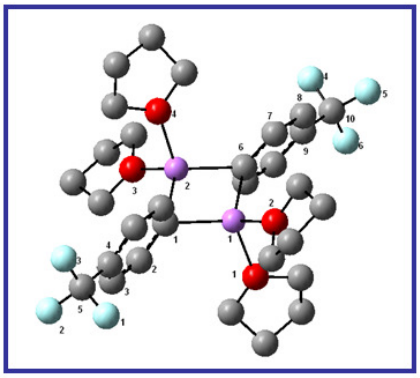




E = -2082.246466 a.u.

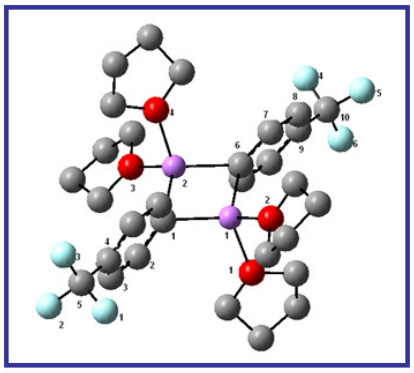
Principal Bond Lengths (Å)

Li1-O1	2.018	Li2-O3	2.016
Li1-O2	2.010	Li2-O4	2.017
Li1-C1	2.236	Li2-C1	2.228
Li1-C6	2.233	Li2-C6	2.234
C1-C2	1.414	C6-C7	1.414
C2-C3	1.397	C7-C8	1.397
C3-C4	1.395	C8-C9	1.394
C4-C5	1.496	C9-C10	1.496
C5-F1	1.361	C10-F4	1.361
C5-F2	1.354	C10-F5	1.354
C5-F3	1.356	C10-F6	1.356



Principal Bond Angles (º)

O1-Li1-C1	115.8	O3-Li2-C6	109.3
O2-Li1-C1	107.4	O4-Li2-C6	112.9
O1-Li1-O2	95.8	O3-Li2-O4	97.1
Li1-C1-Li2	66.2	Li1-C1-Li2	66.2
C1-Li1-C6	113.6	C1-Li2-C6	113.9
C1-C2-C3	124.3	C6-C7-C8	124.3
C2-C3-C4	119.5	C7-C8-C9	119.5
C3-C4-C5	120.6	C8-C9-C10	120.7
C4-C5-F1	112.2	C9-C10-F4	112.3
C4-C5-F2	112.7	C9-C10-F5	112.7
C4-C5-F3	112.5	C9-C10-F6	112.5



Model 6_{calc} $[(THF)_2{\cdot}Li(C_6H_4\text{-}CF_3)]_2$: Total Energies/a.u. and Relative Energies/kcal mol^{-1}

ortho	-2082.264388	+0.00
meta	-2082.253831	+6.62
para	-2082.246466	+11.25

Model 6_{calc} $[(THF)_2{\cdot}Li(C_6H_4\text{-}CF_3)]_2$: Dimerisation Energies

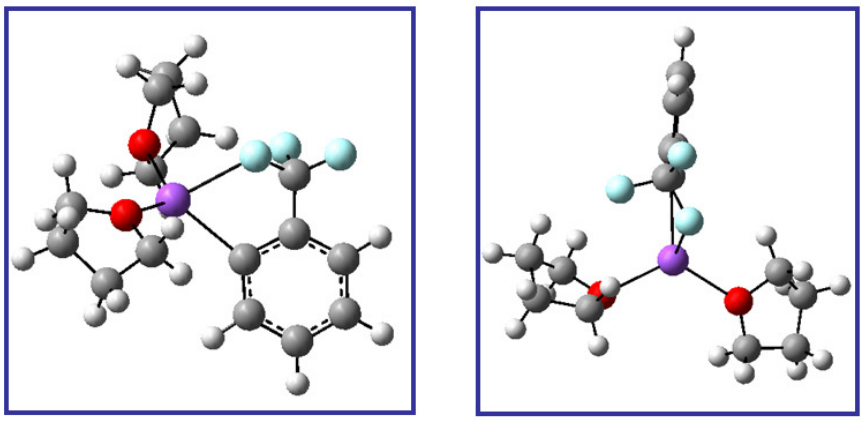
Defined as energy/kcal mol^{-1} of the reaction
$[(THF)_2{\cdot}Li(C_6H_4\text{-}CF_3)] = ½\ [(THF)_2{\cdot}Li(C_6H_4\text{-}CF_3)]_2$

ortho	-5.18
meta	-11.23
para	-9.32

Model [$(THF)_2$·$Na(C_6H_4$-$CF_3)$]

Model [$(THF)_2$·*ortho*-$Na(C_6H_4$-$CF_3)$]

Optimised Geometry

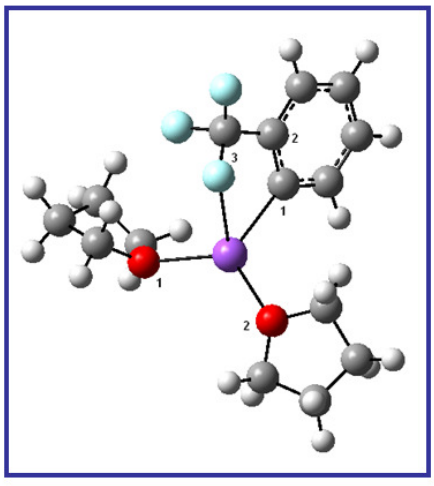


E = -1195.877768 a.u.

Principal Bond Lengths (Å) and Angles (º)

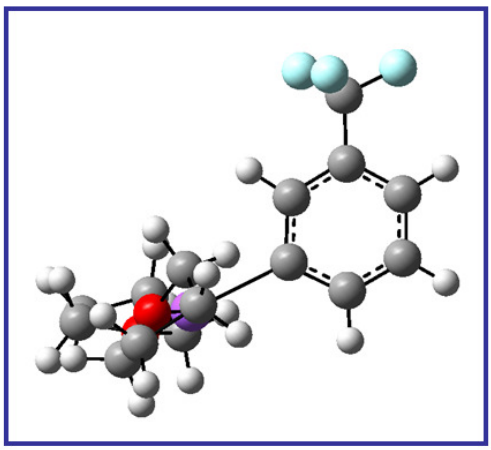
Na-O1	2.312		
Na-O2	2.296		
Na-C1	2.410		
Na-F	2.418	3.456	
C1-C2	1.413		
C2-C3	1.499		
C3-F	1.387	1.372	1.349

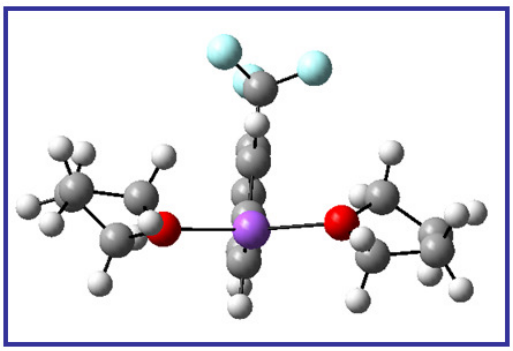
O1-Na-C1	116.1		
O1-Na-C1	118.5		
O1-Na-O2	123.7		
Na-C1-C2	111.6		
C1-C2-C3	117.9		
C2-C3-F	113.1	113.3	114.8
C1-Na-F	71.9		



Model [$(THF)_2$·*meta*-Li(C_6H_4-CF_3)]

Optimised Geometry

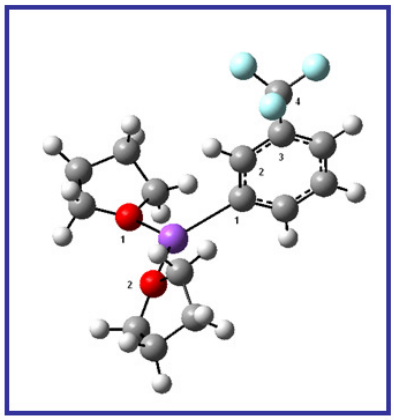




E = -1195.863030 a.u.

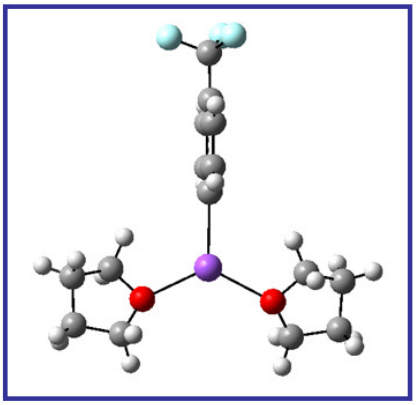
Principal Bond Lengths (Å) and Angles (º)

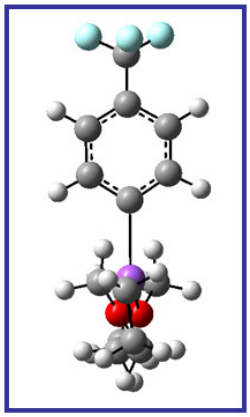
Na-O1	2.303		
Na-O2	2.302		
Na-C1	2.386		
C1-C2	1.411		
C2-C3	1.403		
C3-C4	1.497		
C4-F	1.355	1.362	1.360
O1-Na-C1	115.7		
O1-Na-C1	115.3		
O1-Na-O2	127.9		
Na-C1-C2	118.8		
C1-C2-C3	123.7		
C2-C3-C4	119.2		
C3-C4-F	113.3	112.3	112.5



Model [(THF)$_2$·*para*-Li(C$_6$H$_4$-CF$_3$)]

Optimised Geometry

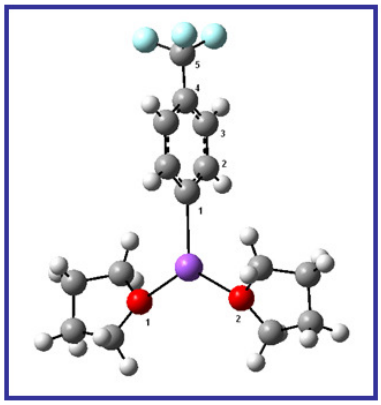




E = -1195.862355 a.u.

Principal Bond Lengths (Å) and Angles (º)

Na-O1	2.302
Na-O2	2.302
Na-C1	2.387
C1-C2	1.414
C2-C3	1.396
C3-C4	1.395
C4-C5	1.495
C5-F	1.356 1.362 1.357
O1-Na-C1	116.4
O1-Na-C1	116.6
O1-Na-O2	126.9
Na-C1-C2	123.9
C1-C2-C3	124.0
C2-C3-C4	119.6
C3-C4-C5	120.1
C4-C5-F	112.6 112.6 112.8



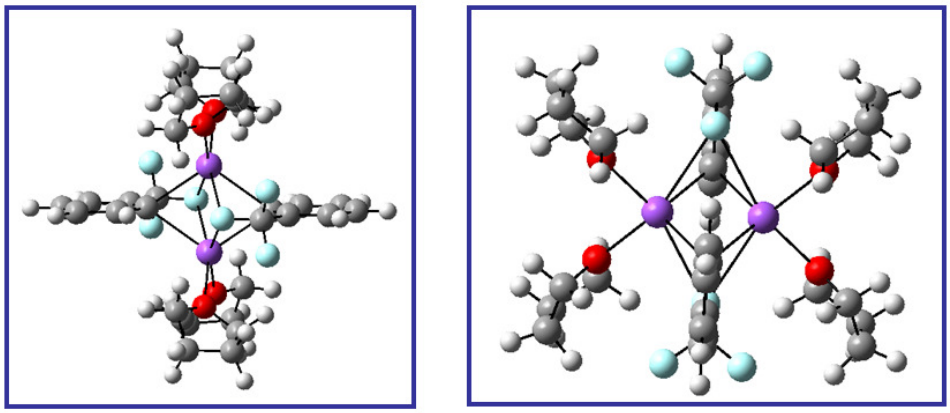
Model [(THF)$_2$·Na(C$_6$H$_4$-CF$_3$)]: Total Energies/a.u. and Relative Energies/kcal mol^{-1}

ortho	-1195.877768	+0.00
meta	-1195.863030	+9.25
para	-1195.862355	+9.67

Model 7_{calc}: $[(THF)_2 \cdot Na(C_6H_4\text{-}CF_3)]_2$

Model 7_{calc}-*ortho* $[(THF)_2 \cdot$*ortho*$\text{-}Na(C_6H_4\text{-}CF_3)]_2$

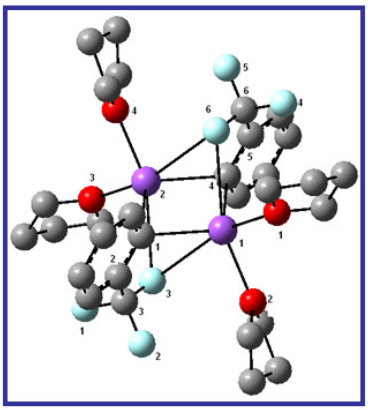
Optimised Geometry



E = -2391.788701 a.u.

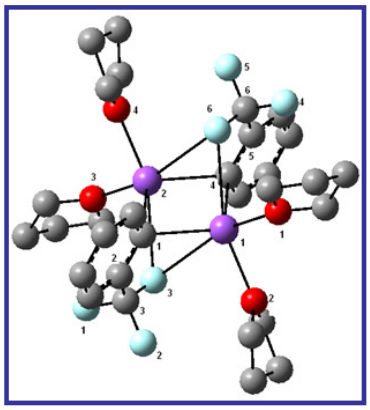
Principal Bond Lengths (Å)

Na1-O1	2.346	Na2-O3	2.347
Na1-O2	2.343	Na2-O4	2.343
Na1-C1	2.583	Na2-C1	2.589
Na1-C4	2.587	Na2-C4	2.582
Na1-F3	2.990	Na2-F6	2.988
Na1-F6	2.977	Na2-F3	2.977
C1-C2	1.410	C4-C5	1.410
C2-C3	1.503	C5-C6	1.503
C3-F1	1.368	C6-F4	1.368
C3-F2	1.368	C6-F5	1.368
C3-F3	1.359	C6-F6	1.359



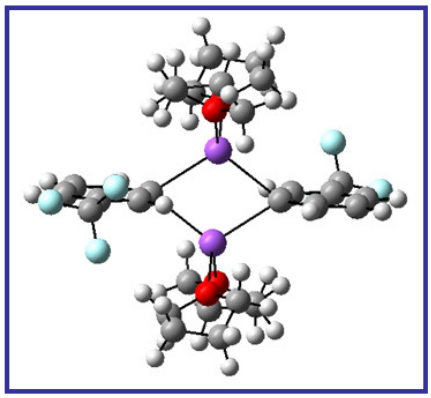
Principal Bond Angles (º)

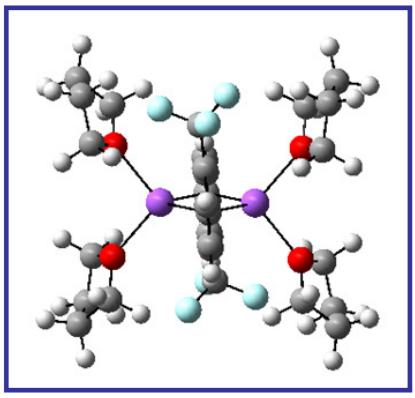
O1-Na1-C1	115.1	O3-Na2-C6	115.4
O2-Na1-C1	110.7	O4-Na2-C6	110.9
O1-Na1-O2	92.3	O3-Na2-O4	92.4
Na1-C1-Na2	69.1	Na1-C1-Na2	69.1
C1-Na1-C4	110.9	C1-Na2-C4	110.9
C1-C2-C3	119.9	C4-C5-C6	119.9
C2-C3-F1	112.9	C5-C6-F4	112.9
C2-C3-F2	112.9	C5-C6-F5	112.9
C2-C3-F3	114.3	C5-C6-F6	114.2



Model 7_{calc}-*meta* $[(THF)_2 \cdot$*meta*-$Na(C_6H_4\text{-}CF_3)]_2$

Optimised Geometry

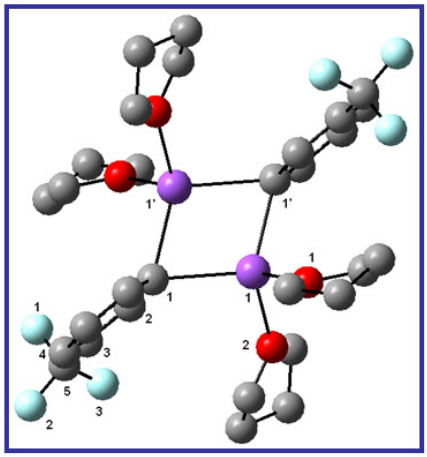




E = -2391.771428 a.u.

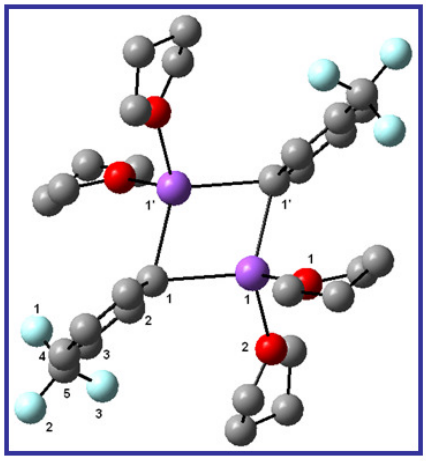
Principal Bond Lengths (Å)

Na1-O1	2.340
Na1-O2	2.340
Na1-C1	2.566
Na1'-C1	2.569
C1-C2	1.411
C2-C3	1.404
C3-C4	1.495
C4-F1	1.368
C4-F2	1.351
C4-F3	1.363



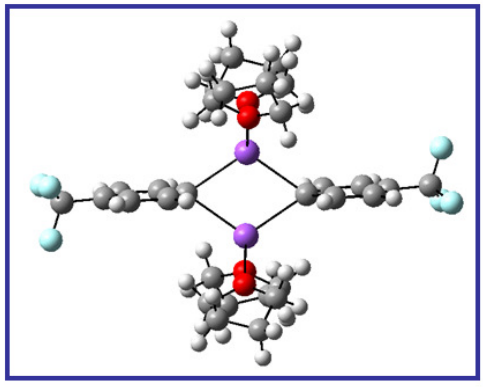
Principal Bond Angles (º)

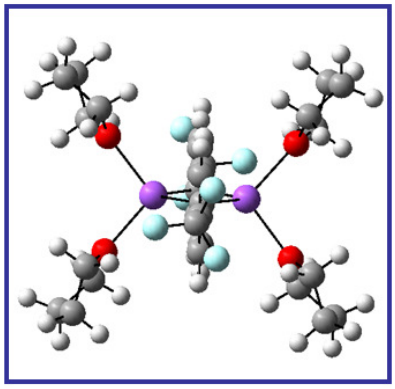
O1-Na1-C1	116.8
O2-Na1-C1	102.7
O1-Na1-O2	103.2
Na1-C1-Na1'	70.7
C1-Na1-C1'	109.3
C1-C2-C3	124.0
C2-C3-C4	119.1
C3-C4-F1	112.2
C3-C4-F2	113.7
C3-C4-F3	112.6



Model 7_{calc}-*para* $[(THF)_2 \cdot$*para*$-Na(C_6H_4-CF_3)]_2$

Optimised Geometry

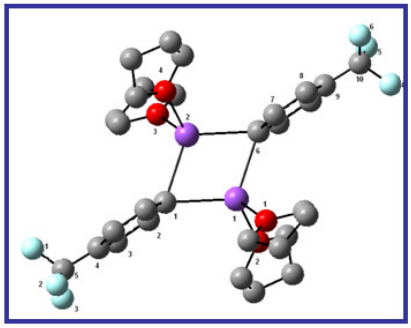




E = -2391.764198 a.u.

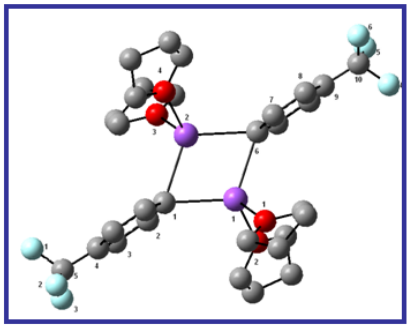
Principal Bond Lengths (Å)

Na1-O1	2.340	Na2-O3	2.339
Na1-O2	2.341	Na2-O4	2.342
Na1-C1	2.565	Na2-C1	2.566
Na1-C6	2.578	Na2-C6	2.579
C1-C2	1.417	C6-C7	1.417
C2-C3	1.397	C7-C8	1.397
C3-C4	1.395	C8-C9	1.396
C4-C5	1.496	C9-C10	1.496
C5-F1	1.362	C10-F4	1.362
C5-F2	1.355	C10-F5	1.354
C5-F3	1.356	C10-F6	1.356



Principal Bond Angles (º)

O1-Na1-C1	115.2	O3-Na2-C6	115.9
O2-Na1-C1	108.0	O4-Na2-C6	107.5
O1-Na1-O2	101.3	O3-Na2-O4	101.5
Na1-C1-Na2	69.5	Na1-C1-Na2	69.5
C1-Na1-C6	110.5	C1-Na2-C6	110.5
C1-C2-C3	124.3	C6-C7-C8	124.3
C2-C3-C4	119.5	C7-C8-C9	119.5
C3-C4-C5	120.1	C8-C9-C10	120.1
C4-C5-F1	112.3	C9-C10-F4	112.3
C4-C5-F2	112.7	C9-C10-F5	112.7
C4-C5-F3	112.6	C9-C10-F6	112.6



Model 7_{calc} $[(THF)_2{\cdot}Na(C_6H_4\text{-}CF_3)]_2$: Total Energies/a.u. and Relative Energies/kcal mol^{-1}

ortho	-2391.788701	+0.00
meta	-2391.771428	+10.84
para	-2391.764198	+15.44

Model 7_{calc} $[(THF)_2{\cdot}Na(C_6H_4\text{-}CF_3)]_2$: Dimerisation Energies

Defined as energy/kcal mol^{-1} of the reaction
$[(THF)_2{\cdot}Na(C_6H_4\text{-}CF_3)] = ½\ [(THF)_2{\cdot}Na(C_6H_4\text{-}CF_3)]_2$

ortho	-10.41
meta	-14.23
para	-12.39