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Supporting Information

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Supporting Information

Activation of C-H Bonds by Heteroatom Lewis Acid Complexation; An Experimental and computational Study of BF_3 Promoted ortho Lithiation of Aniline and Role of Fluorine-Lithium Interaction

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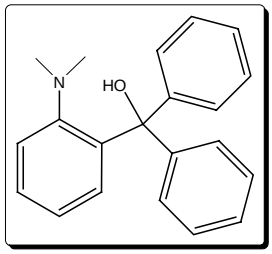
General Procedure for Lithiation-Substitution of N, N-Dimethylanilines

A. Into a flame dried two-necked round-bottomed flask equipped with a magnetic stir bar, septum cap and a bubbler, was placed a solution (0.3M) of the appropriate amine (1.0 mmol) in freshly distilled dry THF under an inert atmosphere of nitrogen. It was cooled to 0°C and $BF_3.OEt_2$ (1.1 equiv.) was added. The contents were stirred for 30 min, cooled to –78°C, stirred for 10 min and s-BuLi in pentane (2.2 equiv.) was added. The resulting pale yellow solution was stirred at –78°C for 1h before the addition of a solution of benzophenone (2.2 equiv.) in THF. The reaction mixture was stirred at –78°C for 30 min and then the temperature was allowed to rise to – 30°C slowly over a period of about 45 min. It was quenched with 10% HCl (5mL) and the contents were poured in diethyl ether. The organic layer was separated and extracted with 10% HCl (3x10mL). The combined aqueous layer was washed with ether, to remove non-basic impurities, basified with sodium carbonate and extracted with chloroform (3x10mL). The organic layer was washed with water, brine and dried over sodium sulphate. The solvent was removed in vacuo to afford the crude product, which was purified, by column chromatography or recrystallization.

B. Into a flame dried two-necked round-bottomed flask equipped with a magnetic stir bar, septum cap and a bubbler, was placed a solution (0.3M) of the appropriate amine (1.0 mmol) in freshly distilled dry THF under an inert atmosphere of nitrogen. It was cooled to –78°C, stirred for 10 min and *s*BuLi in pentane (1.1 equiv.) was added. The resulting pale yellow solution was stirred at –78°C for 1h and reacted with benzophenone (1.1 equiv.). Work up was carried out as in procedure A.

C. Into a flame dried two-necked round-bottomed flask equipped with a magnetic stir bar, septum cap and a bubbler, was taken a solution (0.3M) of *N, N*-dimethylaniline (1.0 mmol) and anisole (1.0 mmol) in dry THF and rest of the reaction was carried out as in general procedure A except that 1.1 equiv. of the sBuLi was used.

(2- Dimethylaminophenyl)-diphenylmethanol 13a [E=C(OH)Ph$_2$]



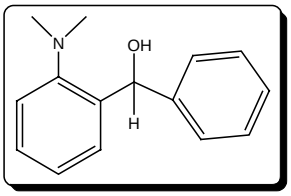
^{1}H NMR($CDCl_3$, 300MHz): δ 2.37 [s, 6H, N $(CH_3)_2$], 6.68-6.71 (dd, 1H, ArH), 7.00-7.06 (t, 1H, ArH), 7.20-7.37 (m, 12H, ArH).

^{13}C NMR ($CDCl_3$, 75MHz): δ 45.65, 83.02, 123.55, 125.21, 126.91, 128.32, 130.51, 143.03, 147.66, 152.07.

MS, m/z (relative intensity): 305 (M^++2, 4.2), 304 (M^++1, 25.1), 303 (M^+, 63.8), 226 (69.1), 210 (100), 194 (23.5), 167 (31.1), 120 (36.5), 105 (37.8), 91 (64), 77 (47.4).

Yield: 41% using *s*BuLi as base; 60% using *t*BuLi as base; 59% using Schlosser base. No product (**13a**) formation was observed when time of lithiation by sBuLi was extended to 6hrs in general procedure **A**.

(2-Dimethylaminophenyl)-phenylmethanol 13a [E=C(OH)Ph]



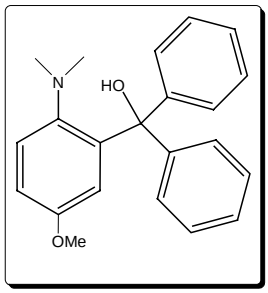
^{1}H NMR ($CDCl_3$, 300MHz): δ 2.57 [s, 6H, N $(C\underline{H}_3)_2$], 5.97 [s, 1H, CH(OH)Ph], 7.02-7.08 (dd, 1H, ArH), 7.09-7.13 (t, 1H, ArH), 7.23-7.41 (m, 7H, ArH), 7.46 (bs, 1H, OH, D_2O exchangeable)

^{13}C NMR ($CDCl_3$, 75MHz): δ 45.69, 83.05, 123.53, 125.27, 126.95, 127.73, 128.34, 130.56, 147.67, and 152.02.

MS, m/z (relative intensity): 228 (M^++1, 51.2), 227 (M^+100), 212 (72.7), 194 (90.7), 181 (9.3), 165 (15.4), 152 (12.2), 134 (25.3), 120 (25.7), 105 (27.8), 91 (36.3), 77 (34.7).

Yield: 51% by procedure A.

(2-Dimethylamino-5-methoxy-phenyl)-diphenylmethanol 13b[E=C(OH)Ph$_2$]



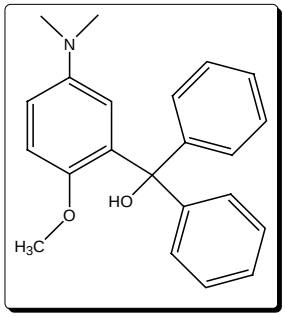
^{1}H NMR ($CDCl_3$, 300MHz)- δ 2.34 [s, 6H, N (C<u>H</u>$_3$)$_2$], 3.62 (S, 3H, OC<u>H</u>$_3$), 6.22-6.23 (d, 1H, Ar<u>H</u>), 6.78-6.82 (dd, 1H, Ar<u>H</u>), 7.20-7.31 (m,11H, Ar<u>H</u>), 9.8 (bs, 1H, O<u>H</u>, D_2O exchangeable).

^{13}C NMR ($CDCl_3$ 75MHz): δ 45.88, 55.26, 82.92, 112.75, 116.51, 124.41, 126.98, 127.71, 128.30, 144.44, 147.46, 156.40.

MS, m/ z (relative intensity): 335 (M^+ + 2, 3.8), 334 (M^+ +1,26.5), 333 (85.8); 319 (2.3); 300 (2.8); 256 (8.3); 241 (9.1); 224 (5.2); 213 (6.0); 183 (6.4); 165 (3.7); 151 (3.6); 136 (16.2); 106 (11.6); 105(100.0); 78 (11.4); 77 (34.7).

Yield- 40% by procedure A, mp 131.5-132.5^{0}C.

(5-Dimethylamino-2-methoxy-phenyl)-diphenylmethanol 14b[E=C(OH)Ph$_2$]



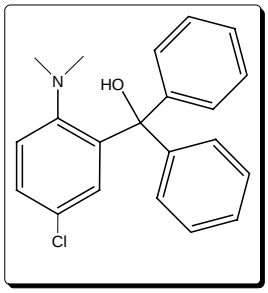
^{1}H NMR ($CDCl_3$, 300MHz): δ 2.66 [s, 6H, N (C<u>H</u>$_3$)$_2$], 3.53 (s, 3H, OC<u>H</u>$_3$), 6.01 (s, 1H, Ar<u>H</u>), 6.85-6.88 (d, 1H, Ar<u>H</u>), 7.21-7.31 (m, 11H, Ar<u>H</u>), 6.69 (bs, 1H, O<u>H</u>).

^{13}C NMR ($CDCl_3$, 75MHz): δ 41.25, 56.43, 82.30, 112.76, 113.77, 116.86, 126.95, 126.95, 127.58, 127.94, 136.38, 145.10, 146.82, 149.78.

MS m/z (relative intensity): 335 (M^+ +2, 2.9); 334 (M^+ +1, 19.1); 333 (60.9); 300 (15.6); 256 (64.8); 240 (60.3); 226 (19.2); 211 (9.0); 194 (8.0); 166 (20.3); 150 (32.2); 136 (37.0); 120 (28.8); 105 (84.4); 91 (44.7); 77 (100).

Yield- 24% by procedure A, mp 144-145^{0}C.

(5-Chloro-2-dimethylaminophenyl)-diphenylmethanol 13c[E=C(OH)Ph$_2$]

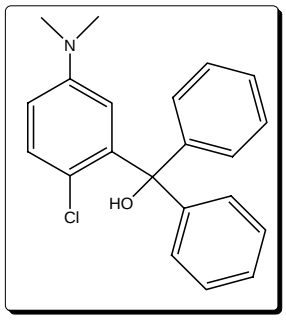


^{1}H NMR ($CDCl_3$, 300MHz): δ2.34 [s, 6H, N (C<u>H</u>$_3$)$_2$], 6.66-6.67 (d, 1H, Ar<u>H</u>), 7.22-7.32 (m, 12H, Ar<u>H</u>), 9.51 (bs, 1H, OH, D_2O exchangeable)

^{13}C NMR ($CDCl_3$, 75MHz): δ 45.7, 82.73, 125.18, 127.19, 127.84, 128.12, 128.43, 130.18, 145.25, 146.80, 150.70.

Yield: 30% by procedure A, mp 140-140.5^{0}C.

(2-Chloro-5-dimethylamino-phenyl)-diphenylmethanol 14c[E=C(OH)Ph$_2$]-



^{1}H NMR ($CDCl_3$, 300MHz): δ 2.34 [s, 3H, N (C<u>H</u>$_3$)$_2$], 4.46 (s, 1H, O<u>H</u>, D_2O exchangeable), 6.01-6.02 (d, 1H, Ar<u>H</u>), 6.52-6.56 (dd, 1H, Ar<u>H</u>), 7.16-7.19 (d, 1H, Ar<u>H</u>), 7.29 (s, 10H, Ar<u>H</u>).

^{13}C NMR ($CDCl_3$, 75MHz): δ 40.22, 82.82, 112.44, 116.46, 127.28, 127.86, 127.94, 131.53, 143.86, 145.84, 148.62.

Yield: 3% by procedure A, mp 129-130° C.

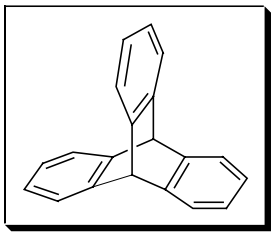
Reaction of BF_3 complex of N, N-Dimethylaniline with LTMP-

a) In the presence of thiophenol

A solution of N, N-dimethylaniline (0.47g, 0.5ml, 3.9mmol) in THF (15ml) was cooled to -78° under nitrogen atmosphere and BF_3. Et_2O (0.48g, 0.42ml, 3.9mmol) was added to it. The contents were stirred for 15 min and thiophenol (0.43g, 0.40ml, 3.9mmol) was added. A solution of LTMP [prepared by stirring a solution of TMP (1.2g, 1.4ml, 7.8mmol) and *n*BuLi (3.7mmol, 2.1M, 7.8mmol) in THF (3ml)] was transferred via a syringe and stirring was continued for 1h at –78°C.The reaction mixture was brought to room temperature over a period of 1h and poured into ether (50ml). The organic layer was washed with HCl (3×10ml, 5%), water, brine and dried. The solvent was evaporated in vacuo to give a liquid (0.27g, 38%), which was identified as diphenyl sulphide by comparision with an authentic sample. Its identity was confirmed by derivatizing it into its corresponding sulphoxide, mp 69-70°.

b) In the presence of anthracene

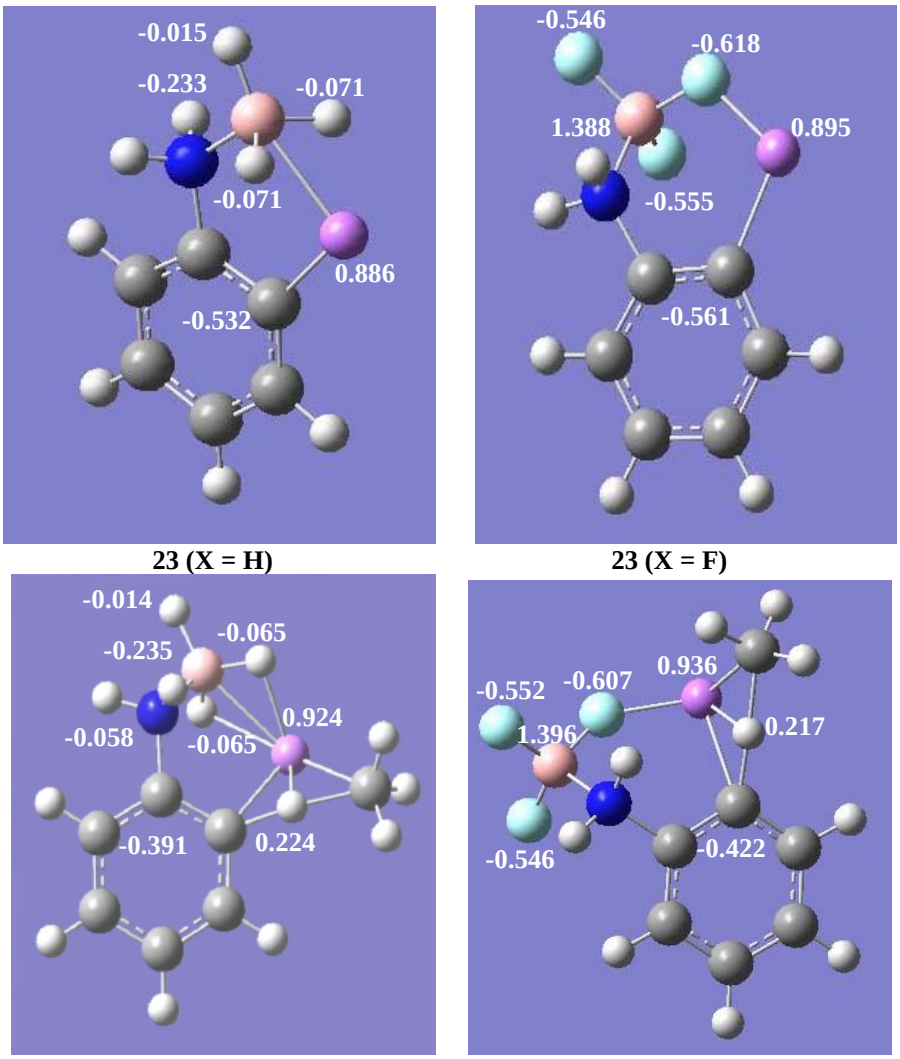
A solution of N, N-dimethylaniline (0.47g, 0.5ml, 3.9mmol) in THF (15ml) was cooled to -78°C under nitrogen atmosphere and BF_3. Et_2O (0.48g, 0.42ml, 3.9mmol) was added to it. The contents were stirred for 15 min and anthracene (0.7g, 3.9mmol) in THF (5ml) was added. A solution of LTMP [prepared by stirring a solution of TMP (1.2g, 1.4ml, 7.8mmol) and *n*BuLi (3.7mmol, 2.1M, 7.8mmol) in THF (3ml)] was transferred via a syringe and stirring was continued for 1h at –78°. The reaction mixture was brought to room temperature during a period of 1h and poured into ether (50ml). The organic layer was washed with HCl (3×10ml, 5%), water, brine and dried. The solvent was evaporated in vacuo and the residue thus obtained was dissolved in toluene (25ml) and maleic anhydride (0.49g, 5.0mmol) was added to it. The solution was heated under reflux for two hour. After removing the solvent under reduced pressure, the residue was made strongly basic with sodium hydroxide solution. The precipitate thus obtained was filtered, washed with water and recrystallized from methyl ethyl ketone to get pure triptycene.



^{1}H NMR ($CDCl_3$, 300MHz): δ 5.5 (s, 2H, -CH-), 7.02 (m, 6H, ArH), 7.36 (m, 6H, ArH).

Anal. Calcd. For $C_{20}H_{24}$: C, 94.48; H, 5.51. Found: C, 94.43; H, 5.49.

Yield: 11% (0.11g) and mp 252° C.



23 (X = H) **23 (X = F)**

22. TS (X = H) **22.TS (X = F)**

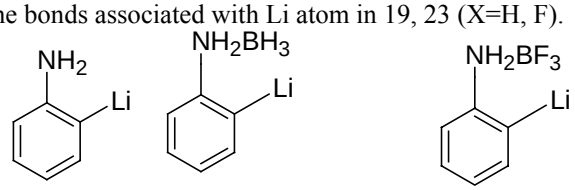
Figure. 1. 3D structures of lithiated intermediates **23** and the transition states **22** on the path of their formation. Color code for the atoms is: grey (C), white (H), blue (N), orange (B), purple (Li). The Li atom is directly bonded to B with a bond length of 2.21Å in **23**(X=H), and 2.27 Å in **22.TS (X=H)**. Li atom is bonded to F with a bond length of 1.80 Å in **23** (X=F) and 1.82 Å in **22.TS (X=F)**. The important partial atomic charges are also included in the figure.

Table 3. Absolute energy values of the species considered in this work calculated at B3LYP/6-31+G* level of quantum chemical calculations.

Structure	B3LYP (au)	ZPE (au)	B3LYP + ZPE[@]
16	-287.616113	0.117104	-287.501278
21 (X=H)	-314.270929	0.151260	-314.122603
21 (X=F)	-612.223748	0.133322	-612.093012
17.2Me_2O	-357.520231	0.197210	-357.326847
18	-335.049735	0.152878	-334.899823
18 (TS)	-335.009622	0.148697	-334.863810
19	-294.527426	0.107144	-294.422360
20	-40.520615	0.045015	-40.476466
22 (X=H)	-361.703812	0.187138	-361.520304
22 (X=F)	-659.655550	0.167953	-659.490855
22 (X=H) (TS)	-361.677617	0.183530	-361.497648
22 (X=F) (TS)	-659.634605	0.164698	-659.473102
23 (X=H)	-321.206685	0.141860	-321.067577
23.Me_2O (X=H)	-631.311257	0.304658	-631.012509
23 (X=F)	-619.160255	0.123050	-619.039592
23.Me_2O (X=F)	-929.270862	0.286463	-928.989956
24b	-733.686895	0.155497	-733.534415
24c	-754.127223	0.097613	-754.031504
25b	-733.669631	0.155239	-733.517404
25c	-754.125135	0.096243	-754.030759

[@] scaled by 0.9806

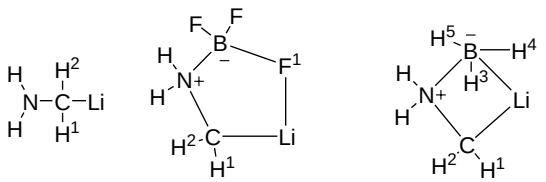
Table 4. The AIM parameters for the bonds associated with Li atom in 19, 23 (X=H, F).



19 **23** (X=H) **23** (X=F)

Structure	*Bond*	ρ	$\nabla^2\rho$	ε
19	C - Li	0.039	0.210	0.018
19	N - Li	0.029	0.187	0.136
23 (X=H)	C - Li	0.039	0.191	0.021
23 (X=H)	B – Li	0.021	0.110	2.743
23 (X=F)	C - Li	0.039	0.197	0.018
23 (X=F)	F – Li	0.036	0.294	0.023
23.2Me_2O (X=F)	C - Li	0.032	0.144	0.0223
23.2Me_2O (X=F)	Li - F	0.023	0.1735	0.056

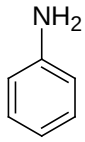
Table 5. Charge on atoms in molecules (**26**, **27**, **28, 23.**2Me_2O)obtained by their NBO Analysis.



26 **27** **28**

Molecule	N	C	H^1	H^2	Li	CH^1H^2	B	F^1	F^2/F^3	H^3	H^4
26	-0.942	-0.886	0.201	0.201	0.687	-0.484	-	-	-	-	-
27	-0.904	-0.931	0.213	0.205	0.891	-0.513	1.375	-0.624	-0.556	-	-
28	-0.834	-0.907	0.201	0.202	0.864	-0.504	-0.221	-		-0.072	-0.090
23.2Me_2O (X=F)	-	-0.501	-	-	0.821	-	-	-0.593	-	-	-

Listing of Optimized Geometeries and total energies (in GAUSSIAN archive format) for- Lithiated borane and trifluoroborane complexes-



16

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1\1\GINC-KASTURI\FOpt\RB3LYP\6-31+G(d)\C6H7N1\BHARATAM\15-Sep-2005\1\\
 # B3LYP/6-31+G* OPT=Z-MATRIX FREQ=NORAMAN\\aniline\\0,1\C\N,1,nc2\H,2,
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 cc6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\C,7,cc8,6,ccc8,5,dih8,0\C,8,cc9,7
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 Thermal correction to Enthalpy=                 0.123877
 Thermal correction to Gibbs Free Energy=        0.087911
 Sum of electronic and zero-point Energies=          -287.499026
 Sum of electronic and thermal Energies=             -287.493197
 Sum of electronic and thermal Enthalpies=           -287.492253
 Sum of electronic and thermal Free Energies=        -287.528219
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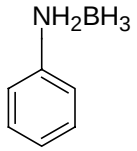

21(X=H)

```
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 cc6,1,ccc6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\C,7,cc8,6,ccc8,5,dih8,0\C,
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=120.27037738\dih7=-0.15586885\cc8=1.3979221\ccc8=119.72228996\dih8=-0
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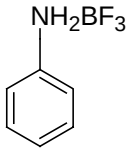
5139\hcc10=120.08005645\dih10=0.75788585\hc11=1.086548\hcc11=119.47802
061\dih11=180.13065579\hc12=1.08641788\hcc12=120.13820109\dih12=179.86
398441\hc13=1.08652493\hcc13=120.23706072\dih13=179.63850194\hc14=1.08
74616\hcc14=120.32963163\dih14=179.08794144\bn15=1.68186007\bnc15=116.
60594984\dih15=-94.19447327\hb16=1.21507052\hbn16=102.99332315\dih16=1
79.34002649\hb17=1.21073246\hbn17=105.01851998\dih17=298.85236926\hb18
=1.21024704\hbn18=104.89277712\dih18=59.71558309\\Version=SGI64-G98Rev
A.11\HF=-314.2709291\RMSD=2.977e-09\RMSF=3.121e-05\Dipole=0.882484,1.4
517048,-1.0962087\PG=C01 [X(C6H10B1N1)]\\@

Zero-point correction=	0.151260 (Hartree/Particle)
Thermal correction to Energy=	0.159017
Thermal correction to Enthalpy=	0.159961
Thermal correction to Gibbs Free Energy=	0.117711
Sum of electronic and zero-point Energies=	-314.119669
Sum of electronic and thermal Energies=	-314.111912
Sum of electronic and thermal Enthalpies=	-314.110968
Sum of electronic and thermal Free Energies=	-314.153218



21 (X=F)

1\1\GINC-SANJEEVINI\FOpt\RB3LYP\6-31+G(d)\C6H7B1F3N1\BHARATAM\22-Sep-2
005\1\\# B3LYP/6-31+G* OPT=Z-MATRIX FREQ=NORAMAN\\aniline-Bf3\\0,1\C\C
,1,cc2\C,2,cc3,1,ccc3\C,3,cc4,2,ccc4,1,dih4,0\C,4,cc5,3,ccc5,2,dih5,0\
C,1,cc6,2,ccc6,3,dih6,0\N,1,nc7,2,ncc7,3,dih7,0\H,2,hc8,1,hcc8,7,dih8,
0\H,3,hc9,2,hcc9,1,dih9,0\H,4,hc10,3,hcc10,2,dih10,0\H,5,hc11,4,hcc11,
3,dih11,0\H,6,hc12,1,hcc12,7,dih12,0\B,7,bn13,1,bnc13,2,dih13,0\F,13,f
b14,7,fbn14,1,dih14,0\F,13,fb15,7,fbn15,1,dih15,0\F,13,fb16,7,fbn16,1,
dih16,0\H,7,hn17,1,hnc17,2,dih17,0\H,7,hn18,1,hnc18,2,dih18,0\\cc2=1.3
9461995\cc3=1.39644968\ccc3=119.21096506\cc4=1.39762338\ccc4=120.31619
653\dih4=0.32281727\cc5=1.39728313\ccc5=119.8308485\dih5=0.19343131\cc

6=1.39425508\ccc6=121.10568133\dih6=-0.73001112\nc7=1.46008456\ncc7=11
9.37758393\dih7=181.43485776\hc8=1.08653734\hcc8=120.22645239\dih8=0.2
16254\hc9=1.08631648\hcc9=119.44499371\dih9=-180.02209336\hc10=1.08634
227\hcc10=120.09046953\dih10=-180.06904688\hc11=1.08631883\hcc11=120.2
58901\dih11=-180.50503492\hc12=1.08702347\hcc12=120.31774928\dih12=-0.
50187471\bn13=1.70313751\bnc13=117.52164216\dih13=84.87571951\fb14=1.3
8466187\fbn14=101.88207411\dih14=178.65330674\fb15=1.37461979\fbn15=10
5.18216566\dih15=59.38119604\fb16=1.37627394\fbn16=105.014178\dih16=-6
2.28005829\hn17=1.02237863\hnc17=110.43505032\dih17=206.25770233\hn18=
1.02258321\hnc18=110.57497911\dih18=-36.47961876\\Version=SGI64-G98Rev
A.11\HF=-612.2237478\RMSD=4.809e-09\RMSF=2.698e-05\Dipole=1.3366462,-2
.0300771,0.5814084\PG=C01 [X(C6H7B1F3N1)]\\@

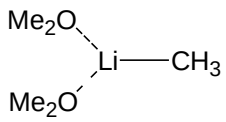
Methyl lithium (17)

1\1\GINC-SANJEEVINI\FOpt\RB3LYP\6-31+G(d)\C1H3Li1\BHARATAM\28-Sep-2005

\0\\# B3LYP/6-31+G* OPT FREQ=NORAMAN\\liMe\\0,1\C,0.0000026752,-0.0000
034496,-0.3917208512\Li,-0.0000111741,0.0000046054,1.593696495\H,1.020
2206592,-0.0000000878,-0.8102749844\H,-0.5100888353,-0.88354384,-0.810
2551202\H,-0.5101143527,0.8835508094,-0.8102342731\\Version=SGI64-G98R
evA.11\HF=-47.404986\RMSD=8.017e-09\RMSF=2.433e-05\Dipole=-0.0000212,0
.000034,2.1673535\PG=C01 [X(C1H3Li1)]\\@

```
Zero-point correction=                          0.033489 (Hartree/Particle)
Thermal correction to Energy=                   0.036990
Thermal correction to Enthalpy=                 0.037934
Thermal correction to Gibbs Free Energy=        0.011291
Sum of electronic and zero-point Energies=           -47.371497
Sum of electronic and thermal Energies=              -47.367996
Sum of electronic and thermal Enthalpies=            -47.367052
Sum of electronic and thermal Free Energies=         -47.393695
```

```
Zero-point correction=                          0.133322 (Hartree/Particle)
Thermal correction to Energy=                   0.143141
Thermal correction to Enthalpy=                 0.144086
Thermal correction to Gibbs Free Energy=        0.096011
Sum of electronic and zero-point Energies=          -612.090426
Sum of electronic and thermal Energies=             -612.080606
Sum of electronic and thermal Enthalpies=           -612.079662
Sum of electronic and thermal Free Energies=        -612.127737
```

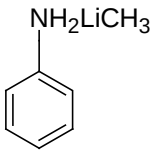


17.2Me2O

1\1\GINC-CHANDAN\FOpt\RB3LYP\6-31+G(d)\C5H15Li1O2\BHARATAM\02-Apr-2007
\0\\# OPT FREQ RB3LYP/6-31+G(D) GEOM=CONNECTIVITY\\liMe + 2 OMe2\\0,1\
C,0.1215275915,-0.2245955863,-2.7469781832\Li,0.0559808575,-0.11365493
71,-0.7066611688\H,1.1317399733,-0.0428471087,-3.163994458\H,-0.189508
376,-1.1943458473,-3.1829522869\H,-0.533869154,0.5267058904,-3.2318319
566\O,-1.2098710657,-1.1236068595,0.4102847147\O,1.1778603061,1.157777
0899,0.3006472142\C,1.7306023742,2.1605922487,-0.5607702331\H,1.240753
7001,2.0438963214,-1.5285870221\H,1.5414794356,3.160297767,-0.14583996
92\H,2.8117585479,2.0060290301,-0.676726667\C,1.7926326943,1.124767955
6,1.5814578504\H,1.3269269424,0.3151470181,2.1484208543\H,2.8702362245
,0.9284712082,1.4902585261\H,1.6423480213,2.0765905817,2.1107354541\C,
-1.9068311566,-2.1354336868,-0.3262700692\H,-2.9736089866,-1.883647644
1,-0.3990161138\H,-1.4630150734,-2.1528590651,-1.3227186971\H,-1.79039
12172,-3.1104527489,0.1669103537\C,-1.7299240533,-0.926485703,1.717925
2841\H,-1.6348327072,-1.843010558,2.317576721\H,-1.1521173467,-0.12431
58087,2.1828721102\H,-2.7878011802,-0.631127437,1.6752333325\\Version=
SGI64-G98RevA.11\HF=-357.520231\RMSD=4.570e-09\RMSF=3.138e-05\Dipole=-
0.1102727,0.2456896,2.939492\PG=C01 [X(C5H15Li1O2)]\\@

```
Zero-point correction=                          0.197210 (Hartree/Particle)
Thermal correction to Energy=                   0.211405
```

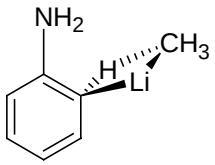
```
Thermal correction to Enthalpy=                  0.212350
Thermal correction to Gibbs Free Energy=         0.154674
Sum of electronic and zero-point Energies=           -357.323021
Sum of electronic and thermal Energies=              -357.308825
Sum of electronic and thermal Enthalpies=            -357.307881
Sum of electronic and thermal Free Energies=         -357.365556
```



18

```
1\1\GINC-SANJEEVINI\FOpt\RB3LYP\6-31+G(d)\C7H10Li1N1\BHARATAM\26-Sep-2
005\0\\# B3LYP/6-31+G* OPT FREQ=NORAMAN\\aniline-liMe LiMe attack\\0,1
\N,-0.0660960728,-0.7593617143,-1.5050429781\C,-0.069408074,-0.6505854
156,-0.0714345076\C,1.1368231276,-0.6910487336,0.6377586729\C,1.135939
1209,-0.5212646126,2.0240122078\C,-0.0616605484,-0.3073208794,2.711581
4357\C,-1.2628146412,-0.2628864207,1.9988388577\C,-1.271042835,-0.4317
693025,0.6124989403\H,2.0739867635,-0.8531146317,0.1089697628\H,2.0775
704015,-0.5568943914,2.5652212802\H,-0.0587470667,-0.1752590465,3.7896
191907\H,-2.201474232,-0.0959990414,2.5202916732\H,-2.2100458801,-0.39
1802691,0.064012733\H,0.6976649405,-1.3497203491,-1.8332433664\H,-0.93
20359176,-1.1722517485,-1.8503543489\Li,0.1452202491,1.0937941837,-2.4
284189149\C,0.3138913618,2.5423767387,-3.7941159258\H,0.4857643252,3.5
350625985,-3.3411018735\H,1.1523960103,2.3802650896,-4.4949960343\H,-0
.5884326519,2.6488554142,-4.4226995114\\Version=SGI64-G98RevA.11\HF=-3
35.0497351\RMSD=7.155e-09\RMSF=1.382e-05\Dipole=-0.288111,-2.4780518,2
.037664\PG=C01 [X(C7H10Li1N1)]\\@
```

```
Zero-point correction=                           0.152878 (Hartree/Particle)
Thermal correction to Energy=                    0.162727
Thermal correction to Enthalpy=                  0.163671
Thermal correction to Gibbs Free Energy=         0.115966
Sum of electronic and zero-point Energies=           -334.896857
Sum of electronic and thermal Energies=              -334.887008
Sum of electronic and thermal Enthalpies=            -334.886064
Sum of electronic and thermal Free Energies=         -334.933769
```

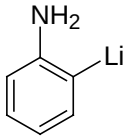


18. T.S.

```
1\1\GINC-BIONODE1\FTS\RB3LYP\6-31+G(d)\C7H10Li1N1\BHARATAM\20-Apr-2007
 \0\\# OPT=(TS,NOEIGENTEST,MODREDUNDANT) FREQ RB3LYP/6-31+G(D)\\TS for
 the lithiation in aniline\\0,1\C,0.474876458,-0.355331655,0.607560602\
 N,0.1607332177,-0.4483011117,2.046306488\H,0.5938013894,-1.2693459766,
 2.4671017398\H,0.5345179748,0.3602294501,2.5468550242\C,1.6586562155,-
 0.8983568477,0.09272702\C,1.9026178474,-0.8071043202,-1.2800259095\C,0
 .9723230665,-0.1702831981,-2.1102813707\C,-0.2033701695,0.3563070887,-
 1.5639825187\C,-0.4907050108,0.2763464689,-0.1911843408\Li,-1.75572226
 81,-0.1152263931,1.519324812\H,-0.9200810517,0.8390998638,-2.230008225
 2\H,1.1651446731,-0.0948907126,-3.1788171512\H,2.8161154907,-1.2246714
```

918,-1.6966922327\H,2.3819216356,-1.3857617157,0.7468286527\C,-2.85244
46054,1.5683386583,0.9545233579\H,-2.722801378,2.1355861869,1.89426317
49\H,-3.0100431895,2.3200152913,0.169344676\H,-3.8122631886,1.02039199
23,1.031197275\H,-1.6560008855,0.9636369043,0.3117861735\\Version=IA32
L-G03RevC.02\State=1-A\HF=-335.0096223\RMSD=9.803e-09\RMSF=1.563e-05\D
ipole=0.6377333,-1.1141028,1.1935919\PG=C01 [X(C7H10Li1N1)]\\@

Zero-point correction=	0.148697 (Hartree/Particle)
Thermal correction to Energy=	0.158519
Thermal correction to Enthalpy=	0.159463
Thermal correction to Gibbs Free Energy=	0.113566
Sum of electronic and zero-point Energies=	-334.860926
Sum of electronic and thermal Energies=	-334.851103
Sum of electronic and thermal Enthalpies=	-334.850159
Sum of electronic and thermal Free Energies=	-334.896057



19

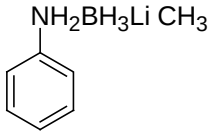
1\1\GINC-SANJEEVINI\FOpt\RB3LYP\6-31+G(d)\C6H6Li1N1\BHARATAM\26-May-20
07\0\\# OPT FREQ B3LYP/6-31+G(D) POP=NBO GEOM=CONNECTIVITY\\aniline-Li
\\0,1\C,-0.6929197206,0.3552725676,-0.0493538339\N,-1.9652853608,1.140
4562783,-0.0492148246\H,-2.2094769757,1.4278564223,-0.9980138098\H,-2.
7432490651,0.5626446531,0.2722715831\C,-0.5942262763,-0.8200201311,-0.
8082439006\C,0.6088259842,-1.527995867,-0.7847446601\C,1.6747085665,-1
.0487236372,-0.010305099\C,1.5311406632,0.1290951498,0.7315239414\C,0.
3385006548,0.8846352425,0.7446332378\Li,-0.9225912319,2.3162298188,1.1
895222416\H,2.3851537666,0.4671619811,1.320737885\H,2.6140995158,-1.59
97923001,0.0092337907\H,0.7147311075,-2.4430548191,-1.3633855919\H,-1.
4326663588,-1.1802792895,-1.4059649232\\Version=SGI64-G98RevA.11\HF=-2
94.5274263\RMSD=5.782e-09\RMSF=8.193e-06\Dipole=-0.0603967,-0.0982622,
1.9961369\PG=C01 [X(C6H6Li1N1)]\\@

Zero-point correction=	0.107144 (Hartree/Particle)
Thermal correction to Energy=	0.113825
Thermal correction to Enthalpy=	0.114769
Thermal correction to Gibbs Free Energy=	0.076625
Sum of electronic and zero-point Energies=	-294.420282
Sum of electronic and thermal Energies=	-294.413601
Sum of electronic and thermal Enthalpies=	-294.412657
Sum of electronic and thermal Free Energies=	-294.450802

Methane (20)

1\1\GINC-PHARMAINFO\FOpt\RB3LYP\6-31+G(d)\C1H4\BHARATAM\03-Apr-2007\0\
\# OPT FREQ B3LYP/6-31+G(D) GEOM=CONNECTIVITY\\methane\\0,1\C,0.,0.,0.
\H,0.0000000119,-0.0000000162,1.0942942981\H,1.0317105544,-0.000000066
2,-0.3647647772\H,-0.5158553452,-0.8934875117,-0.3647647737\H,-0.51585
52211,0.8934875942,-0.3647647472\\Version=Sun64-SVR4-Unix-G03RevB.05\S
tate=1-A1\HF=-40.5206149\RMSD=3.933e-09\RMSF=5.425e-05\Dipole=0.,0.,0.
\PG=TD [O(C1),4C3(H1)]\\@

```
Zero-point correction=                          0.045014 (Hartree/Particle)
Thermal correction to Energy=                   0.047879
Thermal correction to Enthalpy=                 0.048823
Thermal correction to Gibbs Free Energy=        0.027688
Sum of electronic and zero-point Energies=           -40.475601
Sum of electronic and thermal Energies=              -40.472736
Sum of electronic and thermal Enthalpies=            -40.471792
Sum of electronic and thermal Free Energies=         -40.492927
```



22 (X=H)

```
1\1\GINC-KASTURI\FOpt\RB3LYP\6-31+G(d)\C7H13B1Li1N1\BHARATAM\29-Sep-20
05\0\\# B3LYP/6-31+G* OPT FREQ=NORAMAN\\aniline-liMe-BH3-mu-2-LiMe att
ack\\0,1\C,-2.0089787279,-0.5459487135,-0.1110806864\C,-2.0467158486,-
0.6958734778,1.2777001951\C,-0.8777670583,-1.0034480095,1.9775268958\C
,0.3292192833,-1.164359752,1.2922486443\C,0.3509113459,-1.0142487886,-
0.0932358722\C,-0.8070543487,-0.7017179986,-0.8047883572\N,1.625037365
8,-1.1297494918,-0.8111612998\B,2.3428264438,0.2753134594,-1.276745082
6\H,3.3948195586,-0.0343448603,-1.7778088118\H,2.4817991095,0.92664257
01,-0.2584085694\H,1.582418452,0.7862310475,-2.0770031601\Li,1.1693514
892,2.3163945301,-0.8613634876\C,-0.0426574833,3.8787374212,-0.5504856
722\H,-0.7717702286,-0.5620532744,-1.8819272158\H,-2.9118881992,-0.292
5266627,-0.6584941324\H,-2.9823339941,-0.5637152252,1.8130765901\H,-0.
8987944451,-1.1140328348,3.0578204437\H,1.2431039291,-1.3914482661,1.8
370285519\H,2.2951891024,-1.6354878839,-0.2285594943\H,1.5009605961,-1
.7028759901,-1.6491284861\H,0.1557482289,4.4012728584,0.403140268\H,0.
0435172149,4.6488373949,-1.3388025149\H,-1.1119605462,3.5971525937,-0.
5222993786\\Version=SGI64-G98RevA.11\HF=-361.7038122\RMSD=6.709e-09\RM
SF=3.221e-05\Dipole=0.2404127,-3.9930749,0.3850802\PG=C01 [X(C7H13B1Li
1N1)]\\@
```

```
Zero-point correction=                          0.187138 (Hartree/Particle)
Thermal correction to Energy=                   0.199667
Thermal correction to Enthalpy=                 0.200611
Thermal correction to Gibbs Free Energy=        0.145835
Sum of electronic and zero-point Energies=          -361.516674
Sum of electronic and thermal Energies=             -361.504145
Sum of electronic and thermal Enthalpies=           -361.503201
Sum of electronic and thermal Free Energies=        -361.557977
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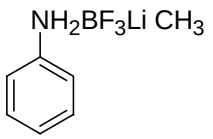
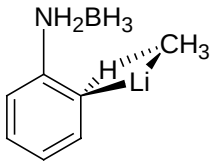


22 (X=F)

```
1\1\GINC-SANJEEVINI\FOpt\RB3LYP\6-31+G(d)\C7H10B1F3Li1N1\BHARATAM\28-S
ep-2005\0\\# B3LYP/6-31+G* OPT FREQ=NORAMAN\\aniline-liMe-BF3 -mu-2-Li
Me attack\\0,1\C,-2.7373439554,-0.7521880129,-1.5140395451\C,-2.768476
0256,-0.9849347507,-0.1369389169\C,-1.580216617,-1.188739036,0.5681599
923\C,-0.3712310319,-1.1582254897,-0.1235885055\C,-0.320304097,-0.9214
289405,-1.4961466847\C,-1.5154403766,-0.719593592,-2.1901547756\N,0.88
65044083,-1.3248705265,0.6234728819\B,1.6990115235,0.0458072026,1.0544
027101\F,0.7860998762,0.871046477,1.7190179028\F,2.0699584208,0.681259
```

7669,-0.133043823\F,2.7427335989,-0.3880173719,1.8240870681\Li,0.66337
78473,2.2605739307,0.1729902919\H,0.6331026596,-0.8716982009,-2.014759
7222\H,-1.4851510985,-0.5220107332,-3.2572921986\H,-3.6625283261,-0.58
45600578,-2.0573440106\H,-3.7150481713,-1.0000420719,0.3950369398\H,-1
.5999876222,-1.3509733852,1.6431824074\H,0.7125555174,-1.8464954556,1.
4871876474\H,1.5445494045,-1.8955335254,0.0843232524\C,-0.3448432551,3
.6971307989,-0.7937696671\H,-1.1169193088,4.1810596038,-0.1677910921\H
,0.3107487816,4.5141084895,-1.1467718066\H,-0.8740387658,3.3287555064,
-1.6927477327\\Version=SGI64-G98RevA.11\HF=-659.6555501\RMSD=5.839e-09
\RMSF=5.857e-05\Dipole=-0.438293,-4.1509915,0.2715385\PG=C01 [X(C7H10B
1F3Li1N1)]\\@

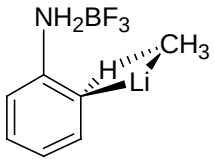
Zero-point correction=	0.167953 (Hartree/Particle)
Thermal correction to Energy=	0.182094
Thermal correction to Enthalpy=	0.183038
Thermal correction to Gibbs Free Energy=	0.124181
Sum of electronic and zero-point Energies=	-659.487598
Sum of electronic and thermal Energies=	-659.473456
Sum of electronic and thermal Enthalpies=	-659.472512
Sum of electronic and thermal Free Energies=	-659.531369



22.TS (X=H)

1\1\GINC-BIONODE1\FTS\RB3LYP\6-31+G(d)\C7H13B1Li1N1\BHARATAM\20-Apr-20
07\0\\# OPT=(TS,NOEIGENTEST,MODREDUNDANT) FREQ RB3LYP/6-31+G(D)\\TS fo
r the lithiation in aniline + BH3\\0,1\C,0.6871347681,-0.3434707233,0.
3055606682\N,0.6434842085,-0.6315748765,1.7653983812\H,1.3389867258,-1
.3508937751,1.9708054391\H,0.9530020109,0.1988020986,2.2776942923\C,1.
7596121398,-0.8727587087,-0.41704451\C,1.8334089821,-0.6400769546,-1.7
930981305\C,0.8366947942,0.1134537829,-2.4184097306\C,-0.2232624311,0.
6214769214,-1.6600023596\C,-0.336451359,0.4071633606,-0.2762869316\Li,
-2.1676865737,-0.0174708256,1.0060796786\H,-0.9957705758,1.2105479566,
-2.1557423147\H,0.8871969136,0.2989191312,-3.489031059\H,2.6621318342,
-1.047539262,-2.3661076918\H,2.5317429613,-1.4658959224,0.0734612565\C
,-2.606688861,1.9878770265,0.61703456\H,-2.4767275501,2.4916293659,1.5
88825778\H,-2.4585182897,2.7559616972,-0.1553774391\H,-3.6790801114,1.
7151964674,0.5443499401\H,-1.3550867341,1.1615855208,0.2200388402\B,-0
.7739078889,-1.1065263242,2.4402129779\H,-0.5053571075,-1.7165650263,3
.4439068078\H,-1.3885807229,-0.0896723824,2.7092502092\H,-1.3484178467
,-1.7979958649,1.6143119517\\Version=IA32L-G03RevC.02\State=1-A\HF=-36
1.6776165\RMSD=7.810e-09\RMSF=3.208e-06\Dipole=1.3031942,-0.86735,-0.0
62769\PG=C01 [X(C7H13B1Li1N1)]\\@

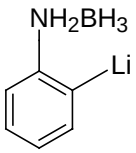
Zero-point correction=	0.183530 (Hartree/Particle)
Thermal correction to Energy=	0.194905
Thermal correction to Enthalpy=	0.195849
Thermal correction to Gibbs Free Energy=	0.146706
Sum of electronic and zero-point Energies=	-361.494087
Sum of electronic and thermal Energies=	-361.482712
Sum of electronic and thermal Enthalpies=	-361.481768
Sum of electronic and thermal Free Energies=	-361.530911



22.TS (X=F)

1\1\GINC-BIONODE2\FTS\RB3LYP\6-31+G(d)\C7H10B1F3Li1N1\BHARATAM\21-Apr-
2007\0\\# OPT=(TS,NOEIGENTEST,MODREDUNDANT) FREQ RB3LYP/6-31+G(D)\\TS
for the lithiation in aniline + BF3\\0,1\C,0.8056695155,0.2250484063,-
0.3336225413\N,0.6108083759,0.1696587058,1.1394316377\H,1.5120257814,0
.0443523345,1.6081522362\H,0.2503804304,1.0734750117,1.4623187048\C,1.
9494843055,-0.360893283,-0.8731001264\C,2.1226826383,-0.3218134542,-2.
2597092227\C,1.161849781,0.2985561294,-3.0642063197\C,0.0273075018,0.8
716061561,-2.4777334096\C,-0.1908939215,0.8417279119,-1.0909312124\Li,
-2.1514149641,0.4625592339,-0.1123735882\H,-0.7052634132,1.3640412047,
-3.118405708\H,1.301378727,0.33471287,-4.1423038777\H,3.0065643626,-0.
7710533712,-2.7042149172\H,2.6884809974,-0.8500217235,-0.240527581\C,-
2.2151624279,2.549605025,0.1198598529\H,-2.1165492063,2.6819210874,1.2
118397649\H,-1.8655185908,3.483933181,-0.3402346262\H,-3.3024755377,2.
513353292,-0.0900868681\H,-1.1323207814,1.6807114775,-0.5352758063\B,-
0.3765682419,-0.9994070731,1.7387887678\F,-0.4188201137,-0.7773506456,
3.0953905338\F,-1.6612221624,-0.7614179205,1.1449923455\F,0.1310534254
,-2.2119758772,1.3632340113\\Version=IA32L-G03RevC.02\State=1-A\HF=-65
9.634605\RMSD=5.690e-09\RMSF=1.200e-05\Dipole=0.744768,0.2193437,-0.83
51221\PG=C01 [X(C7H10B1F3Li1N1)]\\@

Zero-point correction=	0.164698 (Hartree/Particle)
Thermal correction to Energy=	0.178384
Thermal correction to Enthalpy=	0.179328
Thermal correction to Gibbs Free Energy=	0.123678
Sum of electronic and zero-point Energies=	-659.469907
Sum of electronic and thermal Energies=	-659.456221
Sum of electronic and thermal Enthalpies=	-659.455277
Sum of electronic and thermal Free Energies=	-659.510927

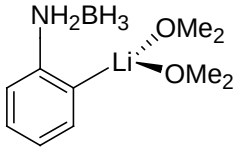


23 (X=H)

1\1\GINC-TULASI\FOpt\RB3LYP\6-31+G(d)\C6H9B1Li1N1\BHARATAM\22-Sep-2005
\0\\# B3LYP/6-31+G* OPT FREQ=NORAMAN GUESS=READ GEOM=CHECK\\aniline-Li
+ BH3\\0,1\C,-0.2716991327,-0.3306045196,-0.0111839997\C,0.7122055294
,-1.3270242348,-0.0706832121\C,2.052592045,-0.9418321924,-0.072328152\
C,2.3671526206,0.4214614183,-0.0146649408\C,1.3437444927,1.3728577834,
0.0433130544\C,-0.0349003892,1.0451269804,0.0481636403\H,0.4504334152,
-2.3856101283,-0.1151269548\H,2.8370989987,-1.6932116848,-0.1178107753
\H,3.4099271281,0.7349175634,-0.0153491737\H,1.6378900171,2.422840293,
0.0869774091\Li,-1.7655664807,2.0370383477,0.1187120956\N,-1.696958248
1,-0.8361686859,-0.0138720224\B,-2.9595581984,0.178586649,0.0503697277
\H,-3.9575996016,-0.498647316,0.033434264\H,-2.8769315013,0.81654063,1
.091929626\H,-2.9055101676,0.9090737663,-0.9305227306\H,-1.8067368392,
-1.4852487815,0.7692591416\H,-1.8299442732,-1.4114332405,-0.8493699157

\\Version=SGI64-G98RevA.11\HF=-321.2066853\RMSD=9.496e-09\RMSF=1.039e-05\Dipole=-0.4379085,-0.1021694,0.0022685\PG=C01 [X(C6H9B1Li1N1)]\\@

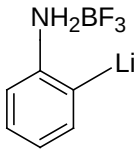
```
Zero-point correction=                          0.141860 (Hartree/Particle)
Thermal correction to Energy=                   0.150001
Thermal correction to Enthalpy=                 0.150946
Thermal correction to Gibbs Free Energy=        0.109485
Sum of electronic and zero-point Energies=          -321.064825
Sum of electronic and thermal Energies=             -321.056684
Sum of electronic and thermal Enthalpies=           -321.055740
Sum of electronic and thermal Free Energies=        -321.097200
```



23.2Me2O (X=H)

1\1\GINC-PHARMAINFO\FOpt\RB3LYP\6-31+G(d)\C10H21B1Li1N1O2\BHARATAM\11-Mar-2007\0\\# OPT FREQ B3LYP/6-31+G(D) GEOM=CONNECTIVITY\\lithiated aniline + BH3 --- with two methylethers\\0,1\C,-0.8894785169,-0.1826486551,1.9830635706\C,-0.8380611947,-0.467413349,3.3551699169\C,0.3690570365,-0.898243558,3.9068288836\C,1.4837706899,-1.0301631283,3.0699147022\C,1.370274689,-0.7306561256,1.7070397988\C,0.1740160681,-0.2886784239,1.0836678436\H,-1.7178257407,-0.3588364624,3.9928607579\H,0.4370105297,-1.1254567177,4.968223466\H,2.4340787428,-1.3650824119,3.4846005681\H,2.2705411554,-0.8492902175,1.0978859272\Li,-0.2340617393,0.1968912018,-0.8940531763\N,-2.2349016273,0.2750590502,1.4759260123\B,-2.4533329944,0.6754706377,-0.0825344525\H,-3.6190458141,1.0010619234,-0.1755820653\H,-1.7080843991,1.6008584796,-0.3429367285\H,-2.2193191875,-0.310750515,-0.7579517433\H,-2.5288755497,1.0831958372,2.0291484735\H,-2.9228902042,-0.4503764709,1.6907240265\O,0.0894748429,-1.1209133988,-2.4141995393\O,0.7980255251,1.7306962988,-1.7165268254\C,1.4518331233,-1.5281598822,-2.5232635149\H,1.6554381462,-1.9172499349,-3.5311871352\H,2.0650814078,-0.6440321409,-2.3390623382\H,1.6857675956,-2.3001941259,-1.7774538061\C,-0.82135171,-2.1912961479,-2.6556216533\H,-0.6653131018,-3.0038331694,-1.9325175855\H,-1.8284745976,-1.7887692623,-2.5374020486\H,-0.6911345791,-2.5792144496,-3.6759839678\C,0.3832518454,2.3001064654,-2.9535482224\H,0.0469458058,1.4768330059,-3.5875150466\H,-0.4438022137,3.0073399688,-2.798312412\H,1.2212419166,2.8210638858,-3.4387907924\C,1.2860172902,2.7024444925,-0.7914767861\H,1.5317360965,2.1666462589,0.1265725796\H,2.1800391716,3.1974080472,-1.1969634727\H,0.5140675325,3.4552249994,-0.5798432672\\Version=Sun64-SVR4-Unix-G03RevB.05\State=1-A\HF=-631.3112566\RMSD=3.591e-09\RMSF=6.079e-05\Dipole=0.26407,0.1238515,-1.1404981\PG=C01 [X(C10H21B1Li1N1O2)]\\@

```
Zero-point correction=                          0.304658 (Hartree/Particle)
Thermal correction to Energy=                   0.324975
Thermal correction to Enthalpy=                 0.325919
Thermal correction to Gibbs Free Energy=        0.253097
Sum of electronic and zero-point Energies=          -631.006598
Sum of electronic and thermal Energies=             -630.986281
Sum of electronic and thermal Enthalpies=           -630.985337
Sum of electronic and thermal Free Energies=        -631.058159
```



23 (X=F)

```
1\1\GINC-TULASI\FOpt\RB3LYP\6-31+G(d)\C6H6B1F3Li1N1\BHARATAM\20-Sep-20
 05\1\\# B3LYP/6-31+G* OPT=Z-MATRIX FREQ=NORAMAN\\aniline-Li + BF3\\0,1
 \C\N,1,nc2\H,2,hn3,1,hnc3\H,2,hn4,3,hnh4,1,dih4,0\C,1,cc5,2,ccn5,4,dih
 5,0\C,5,cc6,1,ccc6,2,dih6,0\C,6,cc7,5,ccc7,1,dih7,0\C,7,cc8,6,ccc8,5,d
 ih8,0\C,8,cc9,7,ccc9,6,dih9,0\Li,9,lic10,1,licc10,2,dih10,0\H,8,hc11,9
 ,hcc11,1,dih11,0\H,7,hc12,8,hcc12,9,dih12,0\H,6,hc13,7,hcc13,8,dih13,0
 \H,5,hc14,6,hcc14,7,dih14,0\B,2,bn15,1,bnc15,5,dih15,0\F,15,fb16,2,fbn
 16,1,dih16,0\F,15,fb17,2,fbn17,1,dih17,0\F,15,fb18,2,fbn18,1,dih18,0\\
 nc2=1.5064447\hn3=1.02411848\hnc3=108.88474437\hn4=1.02470272\hnh4=104
 .96653095\dih4=-116.13756473\cc5=1.39740191\ccn5=115.80561191\dih5=106
 .38996518\cc6=1.39654965\ccc6=118.3766516\dih6=182.35750475\cc7=1.3975
 6453\ccc7=119.04251579\dih7=0.29214384\cc8=1.4009678\ccc8=120.00488614
 \dih8=-0.71517701\cc9=1.4148139\ccc9=123.69360126\dih9=0.13567804\lic1
 0=2.00827873\licc10=114.98094729\dih10=-14.91803358\hc11=1.09114342\hc
 c11=119.09438801\dih11=180.30109227\hc12=1.08851703\hcc12=120.25274155
 \dih12=179.76743996\hc13=1.08691373\hcc13=120.89995825\dih13=179.34239
 754\hc14=1.09045967\hcc14=119.89795376\dih14=180.26937013\bn15=1.62723
 634\bnc15=121.51192251\dih15=-129.35045202\fb16=1.37850534\fbn16=105.2
 8515195\dih16=173.92054563\fb17=1.44952239\fbn17=106.74528884\dih17=29
 0.16055921\fb18=1.36748868\fbn18=109.36802847\dih18=49.70432821\\Versi
 on=SGI64-G98RevA.11\HF=-619.1602548\RMSD=6.404e-09\RMSF=4.487e-05\Dipo
 le=-0.6024997,0.9016362,-0.2816949\PG=C01 [X(C6H6B1F3Li1N1)]\\@
```

```
 Zero-point correction=                          0.123050 (Hartree/Particle)
 Thermal correction to Energy=                   0.133606
 Thermal correction to Enthalpy=                 0.134550
 Thermal correction to Gibbs Free Energy=        0.086225
 Sum of electronic and zero-point Energies=          -619.037205
 Sum of electronic and thermal Energies=             -619.026649
 Sum of electronic and thermal Enthalpies=           -619.025705
 Sum of electronic and thermal Free Energies=        -619.074030
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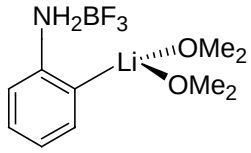

23.2Me_2O (X=F)

```
1\1\GINC-PHARMAINFO\FOpt\RB3LYP\6-31+G(d)\C10H18B1F3Li1N1O2\BHARATAM\1
 5-Mar-2007\0\\# OPT FREQ B3LYP/6-31+G* GEOM=CONNECTIVITY\\lithiated an
 iline + BF3 with two methyl ethers - B3lyp level optimization\\0,1\C,1
 8066241396,0.883322761,-0.4960574605\N,1.8585448042,0.9096821196,1.00
 67794906\H,2.8333524706,0.9686253694,1.3136284353\H,1.4198619371,1.777
 8436986,1.3267589384\C,3.0328347537,1.0276157136,-1.1518758314\C,3.038
 4413929,1.0571130078,-2.5486419456\C,1.8229190491,0.9486557636,-3.2305
 960441\C,0.6285826913,0.7953304209,-2.5118960345\C,0.5521359533,0.7473
 997538,-1.0980987463\Li,-1.0463503348,-0.0136230755,0.0213555921\H,-0.
 2912017722,0.7033961537,-3.0951947435\H,1.8100252611,0.9781658925,-4.3
 193668049\H,3.9755241733,1.1657991571,-3.0890047769\H,3.9714500814,1.1
 128246996,-0.6023761663\B,1.1860609482,-0.2861990249,1.8812434192\F,1.
```

5946046858,-0.0459709168,3.1855619767\F,-0.2270355695,-0.1345634019,1.
7758404506\F,1.6009465774,-1.49962776,1.3831690845\O,-1.590884295,-1.8
832008757,-0.4155648279\O,-2.8139791163,0.8551927866,0.3742312345\C,-0
.6233621174,-2.7106860298,-1.0693730131\H,-1.129244391,-3.5124675056,-
1.6254626532\H,-0.0687474822,-2.0689744639,-1.7549025608\H,0.069286763
2,-3.1425861729,-0.336033062\C,-2.3745034498,-2.6019711789,0.532895153
\H,-3.0735071077,-1.8901203941,0.9769196116\H,-2.9342713524,-3.4071967
156,0.0358928245\H,-1.7368551472,-3.0315299823,1.3175107577\C,-3.57258
09575,1.2187112613,-0.77713696\H,-3.238289312,2.1875855762,-1.17254347
21\H,-3.4090159503,0.4417210195,-1.526834003\H,-4.6421689504,1.2713920
229,-0.5300386056\C,-2.95660243,1.779407882,1.4506253244\H,-2.33438868
66,1.4148555256,2.2698126796\H,-2.6221767114,2.7820735176,1.1488082139
\H,-4.0053692943,1.8288094061,1.7751435688\\Version=Sun64-SVR4-Unix-G0
3RevB.05\State=1-A\HF=-929.2708622\RMSD=7.992e-09\RMSF=2.397e-06\Dipol
e=-1.6734464,0.5537833,-0.1796622\PG=C01 [X(C10H18B1F3Li1N1O2)]\\@

```
Zero-point correction=                          0.286463 (Hartree/Particle)
Thermal correction to Energy=                   0.309029
Thermal correction to Enthalpy=                 0.309973
Thermal correction to Gibbs Free Energy=        0.231307
Sum of electronic and zero-point Energies=          -928.984399
Sum of electronic and thermal Energies=             -928.961833
Sum of electronic and thermal Enthalpies=           -928.960889
Sum of electronic and thermal Free Energies=        -929.039555
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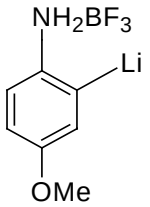

25b

1\1\GINC-SANJEEVINI\FOpt\RB3LYP\6-31+G(d)\C7H8B1F3Li1N1O1\BHARATAM\30-
Sep-2005\0\\# B3LYP/6-31+G* OPT FREQ=NORAMAN\\aniline-anisole-BF3- met
a-li\\0,1\C,-1.3872766019,-0.6887004674,0.1982312989\C,-1.4113159075,-
0.7451457545,1.5961906601\C,-0.151749608,-0.6244278262,2.1949974337\C,
1.0616823834,-0.4612658026,1.5290071404\C,1.0289570734,-0.4070632459,0
.1293820449\C,-0.1960836915,-0.5236572753,-0.5205711309\N,-0.241413844
7,-0.4523178216,-1.987478886\B,0.1237599827,0.9974212983,-2.7497044698
\F,-0.743304441,1.9335918363,-2.2338428736\F,-0.1129289894,0.697464928
8,-4.0871433442\F,1.4571359915,1.2440558503,-2.4786049646\H,-2.3207845
061,-0.765192096,-0.3646525005\Li,-2.1363029279,-0.8437314477,3.435163
017\O,-0.2341855037,-0.6834280501,3.6255742088\H,2.0144378467,-0.36527
90532,2.041096148\H,1.9428830635,-0.2493840333,-0.4342209111\H,0.38383
19506,-1.1491771664,-2.400747414\H,-1.1821468242,-0.6997659337,-2.3035
409196\C,0.9511714158,-0.5411908465,4.4010368467\H,0.6497093146,-0.605
2358702,5.4488643212\H,1.6611866254,-1.3461458791,4.1760035064\H,1.423
9389107,0.4306108065,4.2146644786\\Version=SGI64-G98RevA.11\HF=-733.66
96314\RMSD=3.417e-09\RMSF=1.840e-05\Dipole=-0.7405472,-2.0970447,3.943
1438\PG=C01 [X(C7H8B1F3Li1N1O1)]\\@

```
Zero-point correction=                          0.155239 (Hartree/Particle)
Thermal correction to Energy=                   0.168762
Thermal correction to Enthalpy=                 0.169706
Thermal correction to Gibbs Free Energy=        0.113710
Sum of electronic and zero-point Energies=          -733.514393
```

```
 Sum of electronic and thermal Energies=              -733.500869
 Sum of electronic and thermal Enthalpies=            -733.499925
 Sum of electronic and thermal Free Energies=         -733.555921
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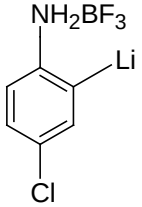
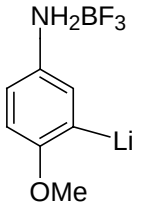


25c

```
1\1\GINC-BIOBOXSERV\FOpt\RB3LYP\6-31+G(d)\C6H5Cl1Li1N1\BHARATAM\27-Apr
 -2007\0\\# OPT FREQ RB3LYP/6-31+G(D) POP=NBO\\aniline-p-cl ortho-li\\0
 ,1\C,-1.4836180748,0.0000223332,-0.6426711305\C,-1.4836042616,0.000007
 8013,0.7586011325\C,-0.3244555942,-0.0000329485,1.552530022\C,0.891536
 3555,0.0000101522,0.839848164\C,0.9135125981,0.0000502086,-0.554907041
 7\C,-0.2606795645,0.0000359739,-1.3144646658\N,-2.7705751993,0.0000093
 121,1.513093051\Li,-1.5402647573,-0.000748661,3.0937133373\H,1.8431725
 292,-0.0000211492,1.3690373748\H,-0.2163019488,0.0000448563,-2.3988938
 692\H,-2.4127233326,0.0000491277,-1.2135147885\H,-3.3351691909,-0.8134
 720416,1.2642088573\H,-3.3346239771,0.8141382396,1.2650761892\Cl,2.467
 9010492,0.0000518024,-1.4113131774\\Version=IA32L-G03RevC.02\State=1-A
 \HF=-754.1272236\RMSD=3.047e-09\RMSF=4.401e-05\Dipole=-2.4659682,-0.00
 0525,1.6025087\PG=C01 [X(C6H5Cl1Li1N1)]\\@


 Zero-point correction=                           0.097613 (Hartree/Particle)
 Thermal correction to Energy=                    0.105481
 Thermal correction to Enthalpy=                  0.106425
 Thermal correction to Gibbs Free Energy=         0.064882
 Sum of electronic and zero-point Energies=           -754.029611
 Sum of electronic and thermal Energies=              -754.021743
 Sum of electronic and thermal Enthalpies=            -754.020798
 Sum of electronic and thermal Free Energies=         -754.062342
```



24b

```
1\1\GINC-SANJEEVINI\FOpt\RB3LYP\6-31+G(d)\C7H8B1F3Li1N1O1\BHARATAM\05-
 Dec-2005\0\\# B3LYP/6-31+G* OPT FREQ=NORAMAN\\aniline-anisole-BF3- ort
 ho-li\\0,1\C,-0.0740553776,-0.0183767677,-0.5189873954\C,-0.1093815206
 ,0.018208022,0.8816125759\C,1.1681321569,0.1004909585,1.4670076224\C,2
 .3633073561,0.1422332358,0.7303585822\C,2.3264581471,0.1019364724,-0.6
 707854805\C,1.08088367,0.0201137635,-1.2996040291\O,3.5215160856,0.222
 3438396,1.4615994213\C,4.7602789327,0.2678688059,0.7715044418\N,-1.370
 6264437,-0.1073016684,-1.3070938378\B,-2.8088021301,-0.1612610528,-0.5
 850100059\F,-2.8328923093,-1.2698196589,0.2924129398\F,-3.7463135511,-
 0.2371692692,-1.5835196597\F,-2.9490352301,0.9856474497,0.2300019434\L
 i,-1.9811682323,-0.0574947414,1.6339857624\H,1.2775713814,0.1359015931
 ,2.5510780825\H,3.2292226645,0.1323461598,-1.2702444728\H,1.0400373371
 ,-0.0118807739,-2.3896754189\H,-1.334555718,-0.9358862387,-1.908992372
 5\H,-1.4180882706,0.6856573689,-1.9544626391\H,5.5303684835,0.32903124
 48,1.5431148147\H,4.9193514081,-0.6382275729,0.1707165069\H,4.82629411
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04,1.1514350327,0.1217248202\\Version=SGI64-G98RevA.11\HF=-733.6868951
\RMSD=4.068e-09\RMSF=4.012e-06\Dipole=0.5248255,0.012867,-0.5145318\PG
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```
Zero-point correction=                          0.155497 (Hartree/Particle)
Thermal correction to Energy=                   0.168619
Thermal correction to Enthalpy=                 0.169563
Thermal correction to Gibbs Free Energy=        0.115603
Sum of electronic and zero-point Energies=          -733.531399
Sum of electronic and thermal Energies=             -733.518276
Sum of electronic and thermal Enthalpies=           -733.517332
Sum of electronic and thermal Free Energies=        -733.571292
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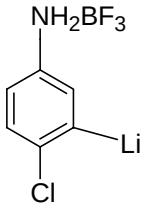

24c

1\1\GINC-BIOBOXSERV\FOpt\RB3LYP\6-31+G(d)\C6H5Cl1Li1N1\BHARATAM\27-Apr
-2007\0\\# OPT FREQ RB3LYP/6-31+G(D) POP=NBO\\aniline-cl meta-li\\0,1\
C,-1.2956246944,-0.0015384157,-0.1917808678\C,-1.2868817069,0.00087111
89,1.2045647351\C,-0.0658957616,0.0033194898,1.9053709051\C,1.14150052
94,0.0009059699,1.1808140786\C,1.194051416,-0.0046608021,-0.2254911284
\C,-0.0547731625,-0.0052252553,-0.8168549091\N,-0.0605883443,-0.054301
2263,3.3110983887\H,2.0723028125,-0.0007861614,1.7526952526\Li,2.15352
58311,-0.0204810669,-1.9434755409\H,-2.230836484,-0.0017886932,-0.7442
049758\H,-2.2293586186,-0.0079462696,1.7485528152\H,-0.8721220539,0.35
47212993,3.7601455992\H,0.7959010543,0.2780961946,3.7395146324\Cl,-0.0
803885596,-0.0083986599,-2.7025707238\\Version=IA32L-G03RevC.02\State=
1-A\HF=-754.1251348\RMSD=9.544e-09\RMSF=3.914e-05\Dipole=1.0573292,0.4
104224,-0.4588238\PG=C01 [X(C6H5Cl1Li1N1)]\\@

```
Zero-point correction=                          0.096243 (Hartree/Particle)
Thermal correction to Energy=                   0.104629
Thermal correction to Enthalpy=                 0.105573
Thermal correction to Gibbs Free Energy=        0.063335
Sum of electronic and zero-point Energies=          -754.028892
Sum of electronic and thermal Energies=             -754.020506
Sum of electronic and thermal Enthalpies=           -754.019562
Sum of electronic and thermal Free Energies=        -754.061800
```