Supplementary Material for Organic & Biomolecular Chemistry

Supporting Information

for

Regioselectivity in Lithiation of 1-Methylpyrazole: Experimental, Density Functional Theory and Multinuclear NMR Study

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Table 1. Absolute free energies and zero-point energies in solution (solution structures).

	Total free energy in solution[a]	**Zero-point energy**[a]	**BSSE**[b]	**# imag. freq.**
Compd.	hartree	hartree	hartree	
1	-265.539436	0.098762		0
MeLi	-47.425200	0.032588		0
2	-312.983939	0.133472		0
3-TS	-312.943751	0.128455		1
4-TS	-312.934768	0.129135		1
5-TS	-312.938150	0.128970		1
α-TS	-312.950025	0.128827		1
3-Li	-272.457296	0.086485		0
4-Li	-272.459504	0.087372		0
5-Li	-272.468058	0.087350		0
α-Li	-272.467237	0.086987		0
Methane	-40.525090	0.044709		0
α-Li·2THF	-737.439005	0.322849	0.003716	0
5-Li·3THF	-969.923743	0.441772	0.005484	0
THF	-232.474867	0.116471		0

[a] IEFPCM/B3LYP/6-31+G(d,p), solvent=THF, Radii=UAKS
[b] Counterpoise BSSE, calculated for gas phase (solution phase structures)

Solution structures
IEFPCM/B3LYP/6-31+G(d,p) (Solvent=THF, Radii=UAKS)
Gaussian 03: SGI64-G03RevB.02

(**1**)

Center Number	Atomic Number	Atomic Coordinates (Angstroms) X	Y	Z
1	1	-2.105005	0.275152	0.079390
2	6	-1.119729	-0.167701	0.041686
3	7	0.000289	0.600258	0.000836
4	7	1.127755	-0.145143	-0.042709
5	6	0.702176	-1.413925	-0.028755
6	6	-0.705827	-1.490511	0.024220
7	1	1.423085	-2.220589	-0.057168
8	1	-1.328875	-2.372638	0.046281
9	6	0.089058	2.051702	0.000183
10	1	0.653496	2.393572	0.871843
11	1	-0.920215	2.464478	0.038551
12	1	0.587140	2.396839	-0.909785

Methyllithium

Center Number	Atomic Number	Atomic Coordinates (Angstroms) X	Y	Z
1	1	-1.019238	0.000000	0.827160
2	6	0.000000	0.000000	0.401455

3	1	0.509619	0.882686	0.827160
4	3	0.000000	0.000000	-1.630071
5	1	0.509619	-0.882686	0.827160

(**2**)

Center Number	Atomic Number	Atomic Coordinates (Angstroms) X	Y	Z
1	3	-2.017214	0.738002	-0.038825
2	6	2.000595	-0.316774	0.061781
3	7	0.663920	-0.519139	-0.001563
4	7	-0.010212	0.655672	-0.075119
5	6	0.931227	1.610634	-0.047765
6	6	2.217679	1.053543	0.040749
7	1	0.641721	2.652606	-0.082314
8	1	3.165367	1.568218	0.089772
9	6	-0.043984	-1.791067	-0.099505
10	1	-1.036954	-1.679087	0.340131
11	1	0.516666	-2.551011	0.447761
12	1	-0.146750	-2.093636	-1.146156
13	1	2.688793	-1.148213	0.119396
14	6	-3.763414	-0.289235	0.117808
15	1	-4.629584	0.360642	0.340862
16	1	-4.024664	-0.828298	-0.811896
17	1	-3.751533	-1.053571	0.917289

(**3-TS**)

Center Number	Atomic Number	Atomic Coordinates (Angstroms) X	Y	Z
1	1	1.587131	2.432391	-0.000457
2	6	1.124712	1.454001	-0.000283
3	7	-0.226821	1.328381	0.000058
4	7	-0.574334	0.010906	-0.000151
5	6	0.562010	-0.729945	-0.000380
6	6	1.662138	0.175303	-0.000601
7	1	0.625137	-3.979100	0.006003
8	1	2.715246	-0.071726	-0.000942
9	6	-1.236104	2.371916	0.000872
10	1	-1.868078	2.291044	-0.888950
11	1	-0.738771	3.343354	-0.002343
12	1	-1.863656	2.294548	0.894064
13	3	-1.500236	-1.669907	-0.001076
14	1	-0.880784	-3.864624	-0.893615
15	1	-0.890529	-3.863521	0.888173
16	6	-0.354367	-3.482933	-0.000095
17	1	0.215468	-2.142962	-0.000178

(**4-TS**)

Center Number	Atomic Number	Atomic Coordinates (Angstroms) X	Y	Z
1	7	-0.054883	-0.005433	-0.162348
2	6	-0.206482	-0.064428	1.168165
3	7	1.287684	-0.009592	-0.343311
4	6	1.023673	-0.098670	1.887178
5	1	1.530606	0.954704	-2.193805
6	1	-1.214634	-0.086081	1.568425

7	6	1.951411	-0.069180	0.844529
8	6	1.840683	0.036787	-1.685817
9	1	1.499469	-0.825080	-2.266716
10	1	2.929839	0.014863	-1.616456
11	1	3.034652	-0.095563	0.854410
12	6	1.475857	-1.101526	4.570216
13	1	1.239327	-0.637351	3.147422
14	1	2.447151	-0.918674	5.064559
15	1	0.689527	-0.976514	5.336203
16	1	1.468809	-2.164782	4.297309
17	3	1.299081	0.858843	3.769229

(**5-TS**)

Center Number	Atomic Number	Atomic Coordinates (Angstroms) X	Y	Z
1	6	-0.096719	0.037455	0.105104
2	7	0.025343	0.020232	1.469154
3	7	1.306470	-0.018535	1.911146
4	6	2.043322	-0.021917	0.792688
5	6	1.227331	0.020583	-0.356405
6	1	3.123781	-0.046785	0.865276
7	1	1.553677	0.051440	-1.388140
8	6	-1.053951	0.038165	2.443332
9	1	-1.126413	-0.923237	2.962745
10	1	-1.990788	0.238840	1.921207
11	1	-0.876114	0.825517	3.180629
12	6	-2.525084	0.926513	-1.210854
13	1	-1.238862	0.493555	-0.477926
14	1	-2.484499	1.067623	-2.305185
15	1	-3.524829	0.518748	-0.972958
16	1	-2.500995	1.934007	-0.774731
17	3	-1.584049	-0.969410	-1.140462

(**α-TS**)

Center Number	Atomic Number	Atomic Coordinates (Angstroms) X	Y	Z
1	1	0.156287	0.311213	0.021550
2	6	0.134250	0.196810	1.095704
3	7	1.221590	-0.243714	1.767324
4	7	0.962065	-0.321433	3.101821
5	6	-0.317976	0.059056	3.256815
6	6	-0.885145	0.407973	2.022651
7	1	-0.762797	0.073765	4.242800
8	1	-1.887227	0.760487	1.826869
9	6	2.567848	-0.593897	1.320627
10	1	2.767966	-0.067602	0.382806
11	1	2.615888	-1.676470	1.135897
12	6	4.524199	0.535461	3.173301
13	1	4.974014	0.019957	4.044840
14	1	4.271203	1.558632	3.492493
15	1	5.331866	0.616897	2.435126
16	1	3.563030	-0.062830	2.264536
17	3	2.797010	-0.560205	3.753647

(**3-Li**)

Center	Atomic	Atomic Coordinates (Angstroms)

Number	Number	X	Y	Z
1	1	-2.160508	0.686525	0.094983
2	6	-1.235574	0.126118	0.052617
3	7	-0.035576	0.758431	-0.004014
4	7	0.999131	-0.143156	-0.049258
5	6	0.459058	-1.393213	-0.026105
6	6	-0.968083	-1.233295	0.039527
7	3	1.790937	-2.911300	-0.095671
8	1	-1.711721	-2.020833	0.070409
9	6	0.225350	2.183702	0.010396
10	1	0.749386	2.474624	0.927720
11	1	-0.722519	2.723723	-0.042940
12	1	0.843157	2.463060	-0.848866

(**4-Li**)

Center Number	Atomic Number	Atomic Coordinates (Angstroms) X	Y	Z
1	1	2.025519	0.195755	0.000000
2	6	0.998478	-0.153890	0.000000
3	7	-0.008604	0.775566	0.000000
4	7	-1.221241	0.176750	0.000000
5	6	-0.928455	-1.137062	0.000000
6	6	0.468906	-1.448973	0.000000
7	1	-1.764372	-1.831345	0.000000
8	3	1.391773	-3.234308	0.000000
9	6	0.093223	2.221324	0.000000
10	1	-0.385153	2.643075	-0.890187
11	1	1.149836	2.497761	0.000000
12	1	-0.385153	2.643075	0.890187

(**5-Li**)

Center Number	Atomic Number	Atomic Coordinates (Angstroms) X	Y	Z
1	3	-2.969214	-0.370469	0.035319
2	6	-0.947678	-0.415768	0.015348
3	7	-0.003295	0.583725	0.009115
4	7	1.297364	0.164859	-0.010627
5	6	1.201201	-1.170065	-0.016119
6	6	-0.148550	-1.580360	0.000240
7	1	2.104720	-1.769497	-0.027681
8	1	-0.507853	-2.602937	0.004105
9	6	-0.241854	2.014879	-0.006809
10	1	0.281901	2.500906	0.823070
11	1	-1.314108	2.189825	0.095095
12	1	0.105784	2.460915	-0.945920

(**α-Li**)

Center Number	Atomic Number	Atomic Coordinates (Angstroms) X	Y	Z
1	1	2.107761	-0.771387	0.000000
2	6	1.261812	-0.098857	0.000000
3	7	-0.001127	-0.582637	0.000000
4	7	-0.899498	0.444115	0.000000
5	6	-0.181291	1.576864	0.000000

6	6	1.195091	1.292550	0.000000
7	1	-0.680025	2.537279	0.000000
8	1	2.018968	1.991814	0.000000
9	6	-0.558827	-1.954126	0.000000
10	3	-2.369533	-0.915074	0.000000
11	1	-0.167220	-2.470710	0.886919
12	1	-0.167220	-2.470710	-0.886919

methane

Center Number	Atomic Number	Atomic Coordinates (Angstroms) X	Y	Z
1	1	0.630958	0.630958	0.630958
2	6	0.000000	0.000000	0.000000
3	1	-0.630958	-0.630958	0.630958
4	1	-0.630958	0.630958	-0.630958
5	1	0.630958	-0.630958	-0.630958

(5-Li·3thf)

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	7	-2.391336	-1.809711	0.703310
2	7	-3.026934	-3.006565	0.487086
3	1	-4.032621	-0.683230	1.385156
4	6	-2.242914	-3.612116	-0.413986
5	6	-1.136695	-2.802877	-0.750180
6	6	-1.231129	-1.602281	-0.007552
7	6	-2.994173	-0.901668	1.659315
8	1	-2.988985	-1.328524	2.669981
9	1	-0.357509	-3.053747	-1.460989
10	1	-2.514366	-4.597872	-0.777543
11	3	0.049186	0.086247	-0.042303
12	8	0.801085	0.673554	1.738221
13	6	2.008579	1.469241	1.864210
14	6	2.620500	1.112300	3.227271
15	6	2.034086	-0.281462	3.510757
16	6	0.635387	-0.158961	2.911967
17	8	-0.760854	1.736275	-0.865344
18	6	-1.861988	1.556215	-1.791220
19	6	-2.920139	2.565626	-1.352702
20	6	-2.054010	3.743685	-0.875367
21	6	-0.850529	3.039001	-0.234570
22	8	1.727710	-0.188529	-1.125445
23	6	2.474038	-1.423996	-0.975009
24	6	2.975318	-1.780539	-2.376040
25	6	3.134634	-0.395552	-3.024775
26	6	1.941058	0.366197	-2.446571
27	1	-2.419921	0.025543	1.660916
28	1	1.740461	2.527968	1.782703
29	1	2.664809	1.206136	1.027732
30	1	3.713803	1.123696	3.202643
31	1	2.293042	1.823159	3.994017
32	1	2.013179	-0.529356	4.575904

33	1	2.605328	-1.057633	2.988862
34	1	0.193938	-1.100926	2.579768
35	1	-0.054676	0.337483	3.608521
36	1	-2.171656	0.510844	-1.722688
37	1	-1.507330	1.766467	-2.809974
38	1	-3.513435	2.160216	-0.525342
39	1	-3.602521	2.835372	-2.163829
40	1	-1.734046	4.349620	-1.730468
41	1	-2.569314	4.401235	-0.169554
42	1	0.093118	3.570503	-0.396942
43	1	-0.986386	2.883418	0.841727
44	1	1.804308	-2.169737	-0.539157
45	1	3.307906	-1.241039	-0.284325
46	1	2.224238	-2.370233	-2.913706
47	1	3.905380	-2.355367	-2.349809
48	1	4.076327	0.069004	-2.710154
49	1	3.117235	-0.425206	-4.117936
50	1	2.109928	1.441212	-2.339684
51	1	1.034422	0.208913	-3.044447

(**α-Li·2THF**)

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	3	0.053922	0.558265	-0.294592
2	7	-2.320822	1.129512	0.172520
3	1	0.476119	-2.602502	-4.273235
4	8	1.441127	0.399356	1.127648
5	6	1.358359	-0.698124	2.075725
6	7	-1.841109	-0.136126	0.303718
7	6	-2.873715	-0.892061	0.702949
8	1	1.191040	-1.026208	-4.649630
9	1	-1.361044	2.954573	0.501469
10	6	-3.638215	1.169005	0.485803
11	6	-1.367491	2.170524	-0.271558
12	1	3.049934	-0.364284	3.401705
13	6	2.147528	-2.000109	-2.956260
14	1	1.985742	-2.902436	-2.355308
15	1	3.067078	-2.132409	-3.533648
16	6	1.694308	1.335134	3.290202
17	1	2.365696	1.933275	3.912971
18	6	1.888985	1.604689	1.799071
19	1	2.946906	1.769655	1.553978
20	1	0.662538	1.555434	3.586079
21	6	-0.034725	-1.012125	-2.851836
22	1	-0.707772	-1.720032	-2.355820
23	1	-0.633725	-0.220873	-3.312451
24	1	-1.783043	2.620919	-1.185883

25	1	1.895191	-1.554965	1.656125
26	6	2.192771	-0.764582	-2.059899
27	1	2.697366	0.074097	-2.559490
28	1	2.657982	-0.925847	-1.084662
29	1	0.301278	-0.962176	2.193940
30	1	1.293601	2.434957	1.410866
31	1	1.524993	-0.644813	4.260404
32	8	0.808420	-0.413573	-1.832196
33	6	1.970609	-0.175198	3.378924
34	6	0.918890	-1.704574	-3.833193
35	1	-2.736612	-1.951776	0.876733
36	1	-5.027179	-0.441412	1.137372
37	6	-4.041397	-0.117115	0.834754
38	1	-4.186156	2.099286	0.436897

(**THF**)

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	1	1.221737	1.137651	-1.092530
2	1	-0.096203	2.135239	-0.430286
3	1	-1.733760	-0.914532	0.300255
4	6	0.411022	-0.948165	0.717673
5	1	1.289543	-1.400556	0.242871
6	1	-0.075952	0.945919	1.672637
7	1	0.204371	-1.493436	1.643256
8	8	-0.649708	0.239190	-1.047284
9	6	0.633904	0.557609	0.932971
10	1	1.645212	0.803287	1.269947
11	6	0.324839	1.124507	-0.457164
12	6	-0.779792	-0.952172	-0.245477
13	1	-0.797117	-1.817771	-0.915892