

Supporting Information

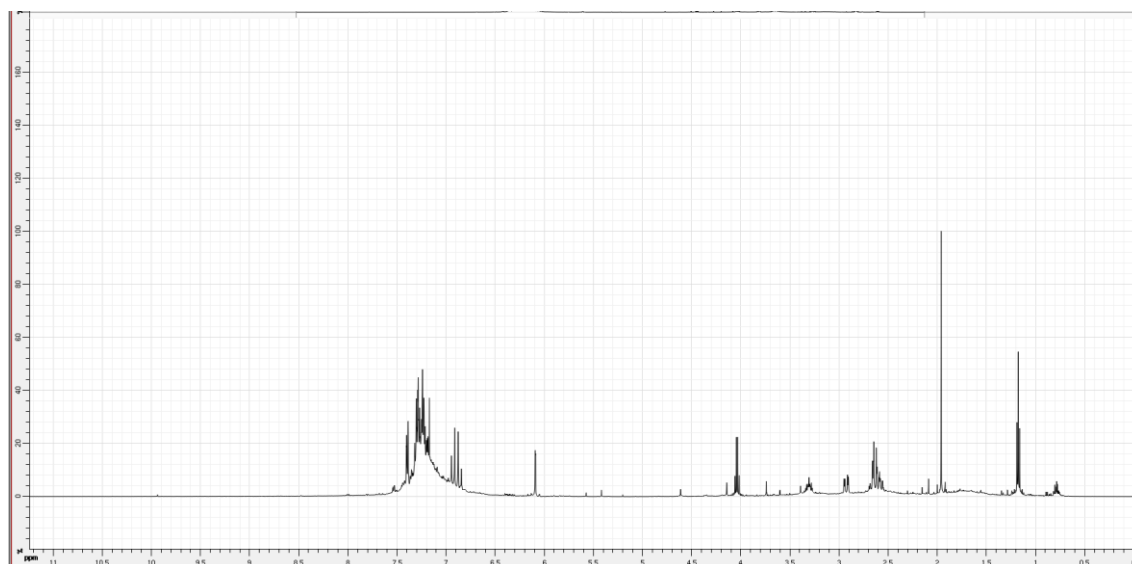
Mechanism and Free Energy Profile of Base-Catalyzed Knoevenagel Condensation Reaction

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and Josefredo R. Pliego Jr.*

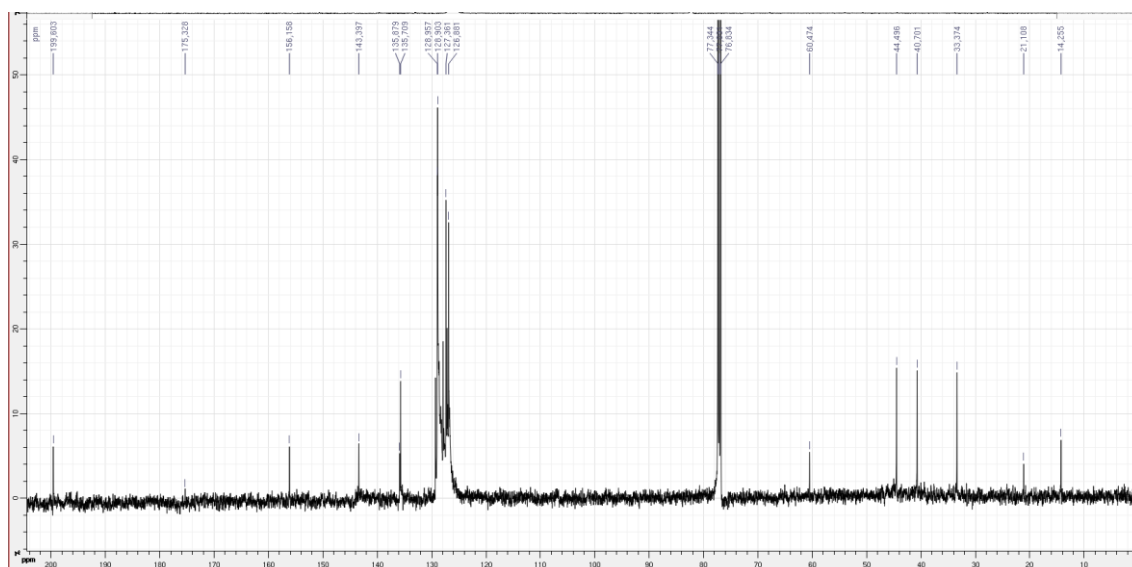
NMR Spectra

Apolar fraction (reaction using 100 mol% NaOH)

NMR ^1H

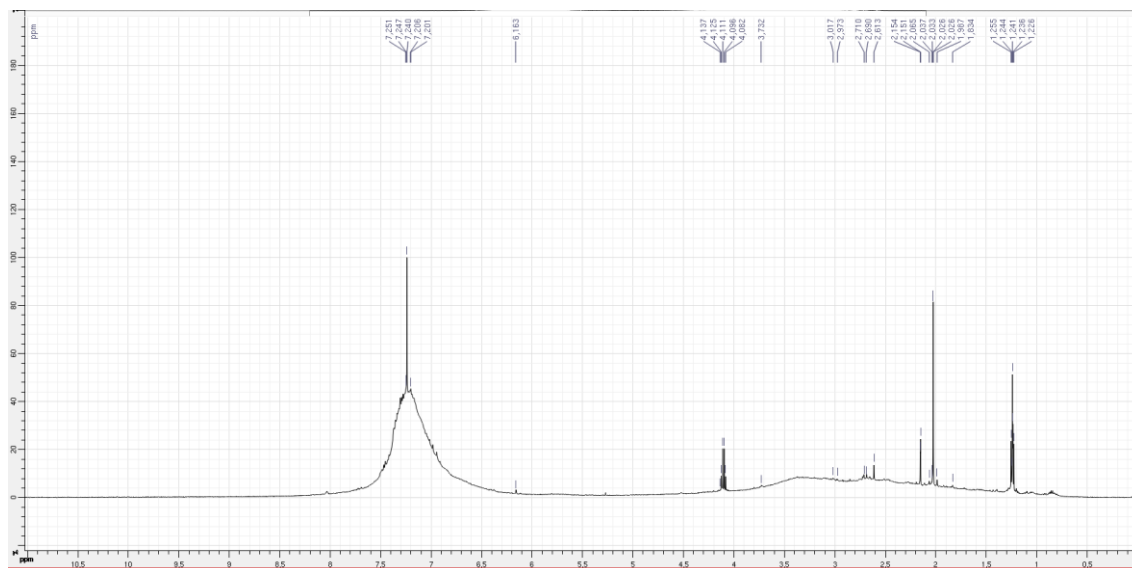


NMR ^{13}C

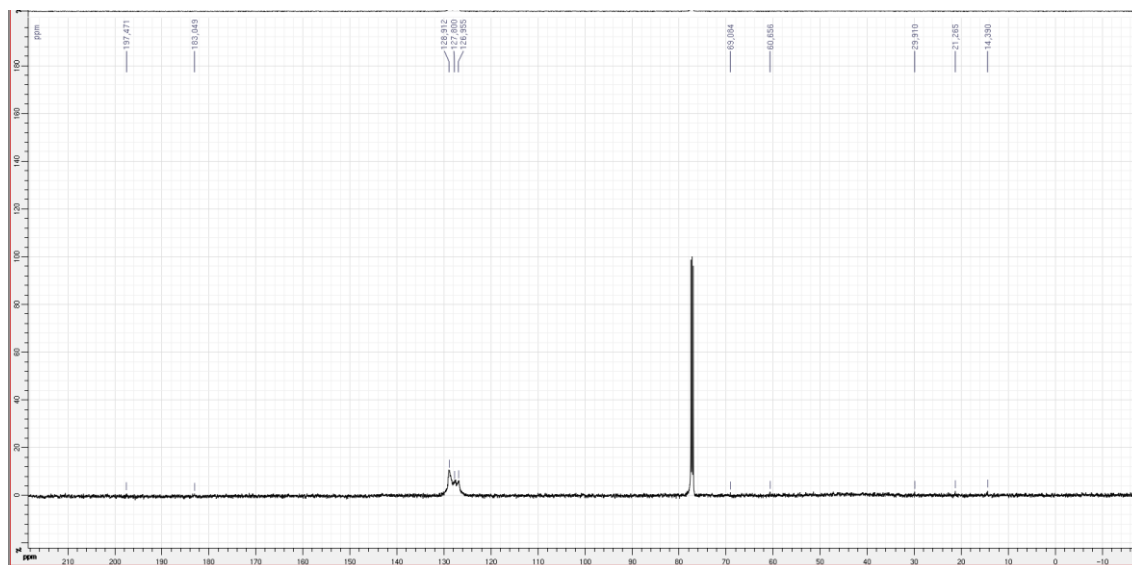


Polar Fraction (reaction using 100 mol% NaOH)

NMR ^1H



NMR ^{13}C



Optimized Structures with the GAMESS program at PCM/X3LYP/6-31(+)G(d) level.

MS1

E = -691.0935292286

C	6.0	1.8598214854	-0.7664089358	2.4894293669
C	6.0	1.8419277237	-0.6741233617	0.9915349703
O	8.0	2.7455698738	-0.1383446852	0.3577828990
C	6.0	0.6413293921	-1.2800164821	0.2567310913
C	6.0	0.9410818481	-2.7549189904	-0.0681867140
C	6.0	0.2511852924	-0.4733293766	-1.0211177966
C	6.0	-0.1217218531	-3.5417865972	-0.7904553516
O	8.0	2.0045443863	-3.2581737463	0.2645001836
C	6.0	-0.2101123228	0.9403930492	-0.6774232942
O	8.0	1.3025511389	-0.5247735749	-1.9773839168
C	6.0	-1.4544255108	1.1137544709	-0.0548472746
C	6.0	-1.9120601505	2.3863985836	0.2824406866
C	6.0	-1.1316380428	3.5090508386	-0.0043608760
C	6.0	0.1028111612	3.3462690594	-0.6324918653
C	6.0	0.5614684214	2.0693985222	-0.9674681649
H	1.0	1.0754244020	-0.1151823055	2.8971082920
H	1.0	2.8294061282	-0.4569446962	2.8830103030
H	1.0	1.6263844052	-1.7869266516	2.8121221124
H	1.0	-0.2249235294	-1.2835943571	0.9307639160
H	1.0	-0.5913981975	-0.9917990151	-1.4873335091
H	1.0	-0.1539186678	-3.2343262393	-1.8426880432
H	1.0	-1.1134768282	-3.3588080892	-0.3646355437
H	1.0	0.1151179220	-4.6060166521	-0.7438539925
H	1.0	2.1215291350	-0.2729326367	-1.5065591900
H	1.0	-2.0783082846	0.2489137558	0.1611800145
H	1.0	-2.8802132889	2.5008935526	0.7615955796
H	1.0	-1.4867679618	4.5022282204	0.2547979368
H	1.0	0.7142422438	4.2129965711	-0.8670921794
H	1.0	1.5195906787	1.9595787693	-1.4648306399

MS1a

E=- -690.5996947809

C	6.0	1.2345950113	-2.6762627589	1.2393829523
C	6.0	0.0202421360	-1.8097410696	1.0095860703
O	8.0	-0.8332508113	-2.1539974481	0.1807288024
C	6.0	-0.1194999396	-0.4920820562	1.6997615018
C	6.0	-0.1482704986	-0.4101826328	3.1889637961
C	6.0	1.1918143665	0.5947961330	1.2294011744
C	6.0	0.7817102085	-1.2458777722	4.0290017827
O	8.0	-0.8948167742	0.4184862103	3.7289693995
O	8.0	2.3735883335	0.2496355162	1.6980155821
C	6.0	1.0685284762	0.7357563374	-0.2913197805
C	6.0	1.8880258698	-0.0030968855	-1.1522043565
C	6.0	1.8005853740	0.1577707711	-2.5362650244
C	6.0	0.8952967720	1.0709886336	-3.0825774623
C	6.0	0.0754546364	1.8173642211	-2.2326578397
C	6.0	0.1641617458	1.6479011050	-0.8498537714

H	1.0	2.1153107649	-2.0455561038	1.4009982456
H	1.0	1.3718600863	-3.3401242142	0.3822964555
H	1.0	1.0983753328	-3.2992728195	2.1304036303
H	1.0	-1.0196460266	-0.0045818368	1.3211490952
H	1.0	0.7489778613	1.5094477138	1.6815520922
H	1.0	0.7667741392	-0.8907433631	5.0617632736
H	1.0	1.7918969743	-1.1795701171	3.6117335288
H	1.0	0.4760108258	-2.2980275059	4.0141938740
H	1.0	2.6053468019	-0.6964183296	-0.7238994568
H	1.0	2.4461420083	-0.4245298337	-3.1892700604
H	1.0	0.8329800388	1.2032703658	-4.1593793566
H	1.0	-0.6264726784	2.5377873319	-2.6451895264
H	1.0	-0.4701150351	2.2415944079	-0.1936626216

MS1b

E= -690.6095231519

C	6.0	-0.2333340278	-3.4821985126	-0.1487934355
C	6.0	-0.3437099729	-1.9891287839	-0.4594643008
O	8.0	-1.5197555043	-1.5680316759	-0.6507831436
C	6.0	0.7846364026	-1.1181024608	-0.5817278660
C	6.0	2.1583193413	-1.4401467522	-0.3563510430
C	6.0	0.5183228328	0.2896359901	-1.0658596061
C	6.0	2.6129301522	-2.7229196741	0.3379046290
O	8.0	3.1017678798	-0.6525966067	-0.6828326865
O	8.0	0.1337990855	0.2705904793	-2.4700188626
C	6.0	-0.4525032321	1.1030502560	-0.2135426999
C	6.0	-1.4747747698	1.8823792500	-0.7656636323
C	6.0	-2.2795408374	2.6913808510	0.0416411852
C	6.0	-2.0724327862	2.7422474850	1.4202670018
C	6.0	-1.0476986503	1.9761073203	1.9824617249
C	6.0	-0.2470897749	1.1710308543	1.1728544563
H	1.0	0.5917475425	-3.9751444697	-0.6667857556
H	1.0	-1.1720550856	-3.9511048292	-0.4536873624
H	1.0	-0.1058227026	-3.6598044958	0.9258037288
H	1.0	1.4825697381	0.8049013834	-1.0148797410
H	1.0	3.6033298201	-2.5376558783	0.7606643914
H	1.0	2.7097162431	-3.5479780232	-0.3777440970
H	1.0	1.9440390904	-3.0482000131	1.1360089648
H	1.0	0.2699647648	1.1614272075	-2.8314786787
H	1.0	-1.6566493441	1.8530476805	-1.8351802117
H	1.0	-3.0719794491	3.2815922228	-0.4118876476
H	1.0	-2.6980383233	3.3706981999	2.0483444576
H	1.0	-0.8709298913	2.0058166809	3.0548344635
H	1.0	0.5456384585	0.5756003147	1.6189397670

TS2

E= -690.5996351886

C	6.0	0.0925381957	2.2143980764	1.9613151375
C	6.0	0.0073586180	2.1939735422	0.4544867415
O	8.0	-0.9103731487	2.8010881913	-0.1167471833
C	6.0	0.9553572927	1.3737057862	-0.3512747264
C	6.0	2.4263060484	1.5838140591	-0.2658935982

C	6.0	3.1019210834	1.8417483598	1.0561093306
O	8.0	3.1084319487	1.4590264680	-1.2942313396
H	1.0	0.3901578499	1.2255892613	2.3262489197
H	1.0	-0.8732263318	2.5168173644	2.3735338256
H	1.0	0.8463908996	2.9357971856	2.2952637552
H	1.0	0.6633044851	1.4388266672	-1.4003917320
H	1.0	4.1834649759	1.7409817338	0.9415489833
H	1.0	2.7244937704	1.1278616131	1.7955738538
H	1.0	2.8796638326	2.8527728142	1.4158275203
C	6.0	0.7516586053	-0.3655836147	0.0425400982
O	8.0	1.1448438347	-0.6885129722	1.2528110044
C	6.0	-0.7012309993	-0.6751660873	-0.3258312624
C	6.0	-1.6940124706	-0.7481811269	0.6580562234
C	6.0	-3.0085888985	-1.0772772356	0.3225664031
C	6.0	-3.3502682929	-1.3407534692	-1.0062321477
C	6.0	-2.3668610153	-1.2715572298	-1.9963667167
C	6.0	-1.0549146908	-0.9398435717	-1.6549476617
H	1.0	1.3942191166	-0.7337643322	-0.7863016202
H	1.0	-1.4166208610	-0.5629607611	1.6913988525
H	1.0	-3.7669982971	-1.1338153955	1.0995158528
H	1.0	-4.3717005347	-1.6038485406	-1.2676181662
H	1.0	-2.6204502515	-1.4829979717	-3.0320604101
H	1.0	-0.2901447648	-0.8974108142	-2.4285849374

TS4

E= -690.5686907474

C	6.0	1.4916436656	-2.6086204633	-1.4963592213
C	6.0	0.7534978108	-1.9663835995	-0.3387221097
O	8.0	-0.4765920356	-2.0293123081	-0.2953362102
C	6.0	1.5381856718	-1.2155987382	0.6884107094
C	6.0	2.5249669759	-1.9255175178	1.5037112706
C	6.0	1.3296302965	0.1220353903	0.9749979678
C	6.0	2.6808430059	-3.4334983885	1.3726821300
O	8.0	3.2230777896	-1.3468031739	2.3574022964
O	8.0	2.9860360374	1.4226637901	-0.0033070926
C	6.0	0.2554095035	1.0072375851	0.4934454199
C	6.0	-0.3116351954	1.9082926032	1.4113279442
C	6.0	-1.3410470704	2.7691591817	1.0318654888
C	6.0	-1.8076920175	2.7634438765	-0.2831914487
C	6.0	-1.2376192031	1.8891535460	-1.2137052579
C	6.0	-0.2214924220	1.0183097284	-0.8296548806
H	1.0	2.5186246401	-2.8850313533	-1.2516821194
H	1.0	1.5464663659	-1.8612739795	-2.3001955760
H	1.0	0.9426368412	-3.4739204565	-1.8770967983
H	1.0	1.8525606348	0.4810676309	1.8512575669
H	1.0	2.8689644245	-3.8495692023	2.3657928884
H	1.0	3.5557036237	-3.6620979641	0.7516620888
H	1.0	1.8127849796	-3.9336150599	0.9357005279
H	1.0	2.3793751263	1.9401880289	-0.5561021485
H	1.0	0.0566994837	1.9257824321	2.4337155279
H	1.0	-1.7697738322	3.4505576102	1.7612498884
H	1.0	-2.6019896509	3.4396790170	-0.5858393053
H	1.0	-1.5833014297	1.8895704101	-2.2435940266
H	1.0	0.2225889799	0.3619623743	-1.5699785203

P1

E= -614.6803638143

C	6.0	-0.0983067490	-1.4258408044	-2.8397808621
C	6.0	-0.6566805553	-1.3667667143	-1.4347531768
O	8.0	-1.7764390373	-1.8263619862	-1.1865219406
C	6.0	0.1367031336	-0.7661746751	-0.3357528304
C	6.0	-0.5889643279	-0.7505161729	0.9922182829
C	6.0	1.4033191614	-0.3261006974	-0.5348346054
C	6.0	-0.3559849982	-1.9228308545	1.9055867495
O	8.0	-1.3434417507	0.1710560489	1.2747707524
C	6.0	2.3743097936	0.2553843063	0.3901596507
C	6.0	3.0698180590	1.2816086832	2.4832455084
C	6.0	2.0678434055	0.7597788875	1.6704839405
C	6.0	4.3952162558	1.3142600271	2.0405918209
C	6.0	4.7144761991	0.8314984557	0.7699307133
C	6.0	3.7134618999	0.3167610053	-0.0475238024
H	1.0	0.8179553243	-2.0249647963	-2.8723400578
H	1.0	0.1456668500	-0.4245983623	-3.2096768748
H	1.0	-0.8434302722	-1.8801108388	-3.4943787235
H	1.0	1.7949923543	-0.4388923158	-1.5428832133
H	1.0	-0.9157954469	-1.8079552134	2.8358934758
H	1.0	0.7147093111	-2.0235034804	2.1192113413
H	1.0	-0.6659494719	-2.8425890765	1.3952455122
H	1.0	2.8139734881	1.6723701519	3.4633841694
H	1.0	1.0450924930	0.7782223280	2.0269974435
H	1.0	5.1724314816	1.7230222440	2.6793835035
H	1.0	5.7400974568	0.8612288020	0.4149343576
H	1.0	3.9640059424	-0.0544739516	-1.0375501349

Acetylacetone

E= -345.6677172742

C	6.0	-0.1317585181	0.6716519974	-2.7770771816
C	6.0	0.0286545030	0.3704006289	-1.3121010696
O	8.0	0.9901153596	-0.2375737710	-0.8624999016
C	6.0	-1.0923576085	0.8434881952	-0.3813542351
C	6.0	-2.1836603969	-0.2316740280	-0.3130672362
C	6.0	-2.0725555782	-1.2412760136	0.7961015139
O	8.0	-3.0817425799	-0.2538038436	-1.1427193995
H	1.0	-1.1320373548	0.3801229291	-3.1166696938
H	1.0	0.6329249538	0.1590658369	-3.3630384347
H	1.0	-0.0479974557	1.7546573584	-2.9324169837
H	1.0	-1.5422592666	1.7602425977	-0.7706973758
H	1.0	-0.6671590862	1.0191346240	0.6091770238
H	1.0	-2.8112186217	-2.0347439288	0.6726707408
H	1.0	-2.2304203301	-0.7375538072	1.7578522427
H	1.0	-1.0610830197	-1.6628877755	0.8241799905

Benzaldehyde

E= -345.4307686563

C	6.0	-0.2892051211	-1.2816896587	1.0900993987
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C	6.0	0.1201866799	-1.0955652149	-0.2248808159
C	6.0	0.1566502534	0.1998768931	-0.7681393517
C	6.0	-0.2223961209	1.2999311939	0.0158788449
C	6.0	-0.6309261336	1.1105766763	1.3341954633
C	6.0	-0.6629206814	-0.1792687247	1.8692668681
C	6.0	0.5929225874	0.4374330251	-2.1506878208
O	8.0	0.9617005882	-0.4292522729	-2.9379769037
H	1.0	-0.3181561034	-2.2807984738	1.5139315397
H	1.0	0.4147999233	-1.9377566288	-0.8429327908
H	1.0	-0.1931926597	2.2990758250	-0.4115900688
H	1.0	-0.9226129528	1.9612317146	1.9422423036
H	1.0	-0.9800707749	-0.3284861485	2.8973230149
H	1.0	0.5775145156	1.4958867943	-2.4726786817

TS2N

E= -691.0493644937

C	6.0	5.9570075632	-2.0663139202	0.0038715613
C	6.0	6.0673998058	-1.4516953229	-1.2494479745
C	6.0	5.7066805432	-1.3038086798	1.1492472157
C	6.0	5.9269192656	-0.0750369073	-1.3644417155
C	6.0	5.5620165410	0.0739564542	1.0432371433
C	6.0	5.6721627285	0.6995103023	-0.2148505399
C	6.0	5.5406604395	2.1328938467	-0.2844753981
O	8.0	5.9278146674	2.7647150519	-1.3605513561
H	1.0	6.0669139187	-3.1432634507	0.0872191939
H	1.0	6.2622165325	-2.0513901543	-2.1327143472
H	1.0	5.6261187747	-1.7849548314	2.1184864898
H	1.0	6.0084698528	0.4110030856	-2.3305383823
H	1.0	5.3736118891	0.6742670741	1.9287838589
H	1.0	5.4580501674	2.7174469126	0.6272902587
C	6.0	2.4659105245	2.4184240785	2.1093534374
C	6.0	3.1927391881	3.2141674861	1.0370383356
O	8.0	3.8173844618	4.2443524582	1.3509344108
C	6.0	3.0942190019	2.6792559329	-0.3088062713
C	6.0	3.2160417853	3.4481977038	-1.5056984247
O	8.0	4.0221963425	4.4159351655	-1.6385142687
C	6.0	2.3716235656	3.0585796133	-2.7004632105
H	1.0	1.3850831936	2.5859012724	2.0223837187
H	1.0	2.7924008957	2.7340603941	3.1024411940
H	1.0	2.6312853766	1.3420947578	1.9874244395
H	1.0	2.4830876063	1.7848964501	-0.3928712716
H	1.0	5.4735618063	3.6699760490	-1.3991598109
H	1.0	2.9540538179	3.1586398768	-3.6213322485
H	1.0	1.5208444382	3.7488983191	-2.7699936453
H	1.0	1.9736153063	2.0440409817	-2.6201123925