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Mechanistic Insights on *n*-BuLi Mediated Phospha-Brook Rearrangement

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Supporting Information

Content

^{31}P-NMR of Diethyl phosphite

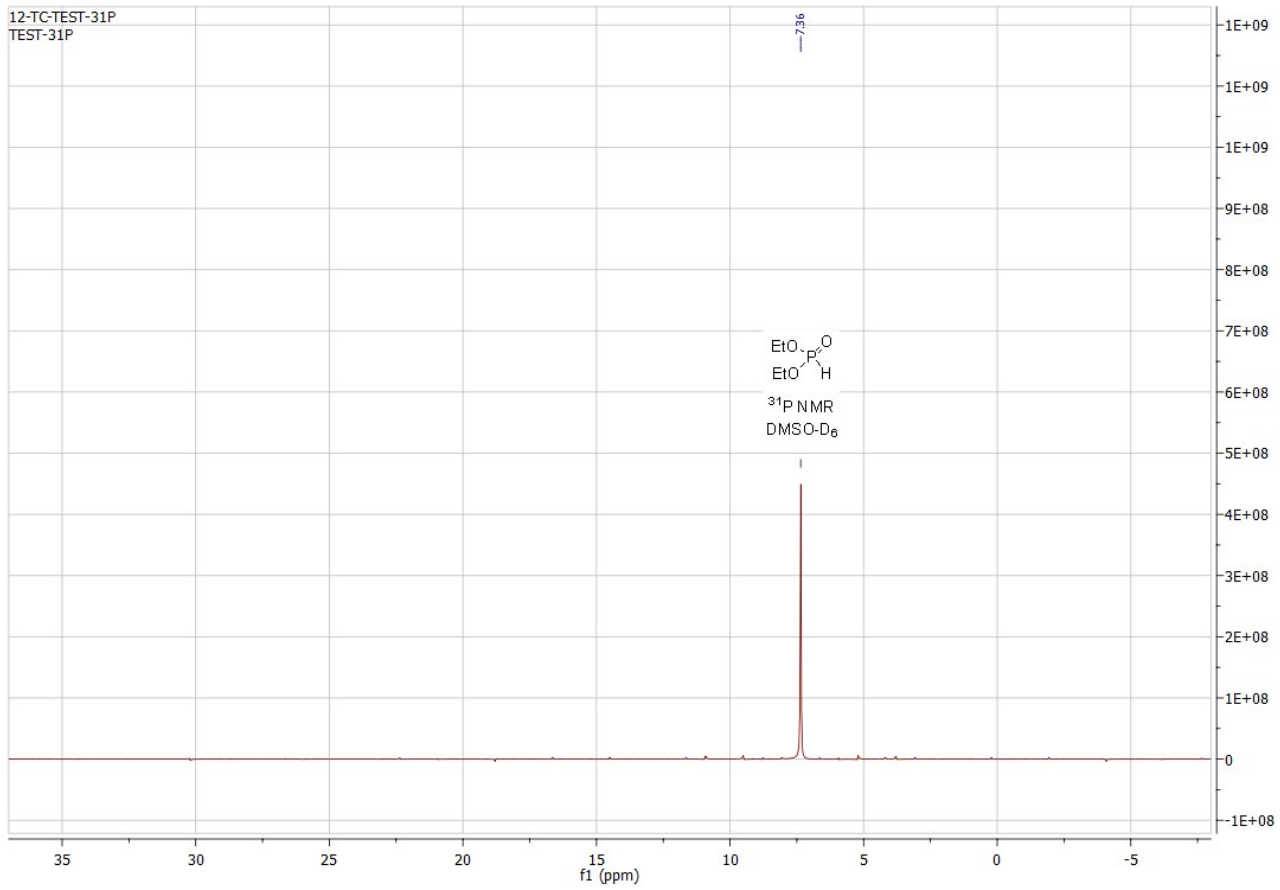
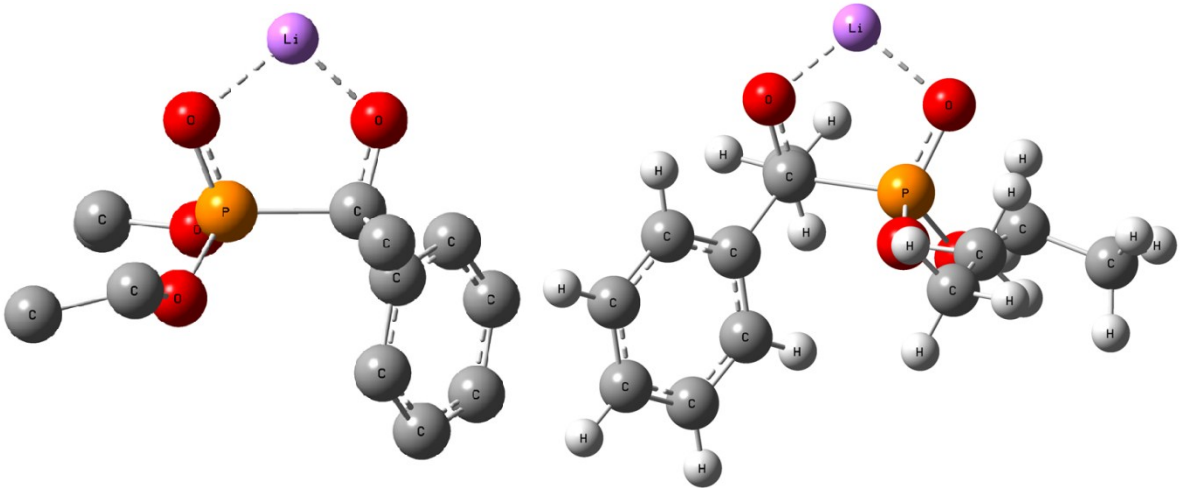


Figure *S1*: ^{31}P-NMR spectrum of diethyl phosphite in DMSO-D$_6$ solvent.

Predicted transition state of Intermediate I

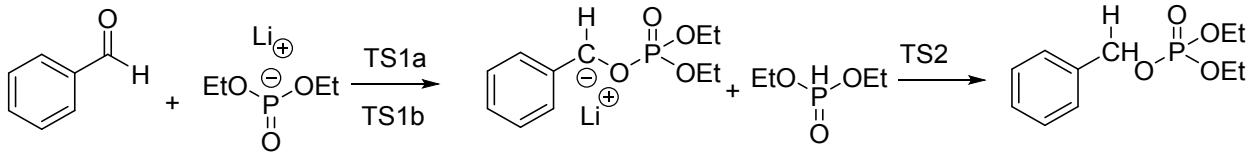


(a) (b)

Figure *S2*: Ball-stick representation of unoptimized transition state of proposed Int. I (a) without considering the hydrogen atoms; (b) with hydrogen atoms.

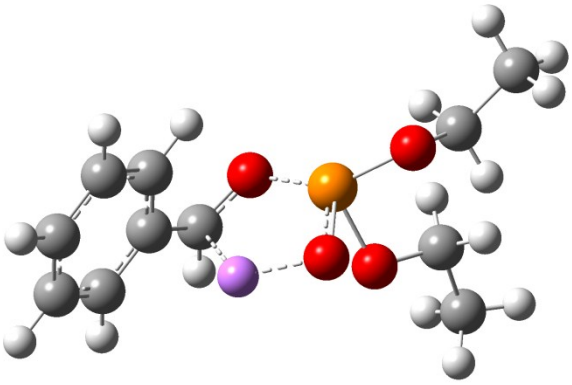
Geometry optimized structures and coordinates of transition states (TS1a, TS1b and TS-2) of the phospha-Brook rearrangement reactions involving benzaldehyde, p-methyl benzaldehyde, p-chloro benzaldehyde, acetophenone, p-methyl acetophenone and p-chloro acetophenone with diethyl phosphite

Benzaldehyde



Benzaldehyde Intermediate

TS1a (phospha-Brook rearrangement)



Atom	X	Y	Z
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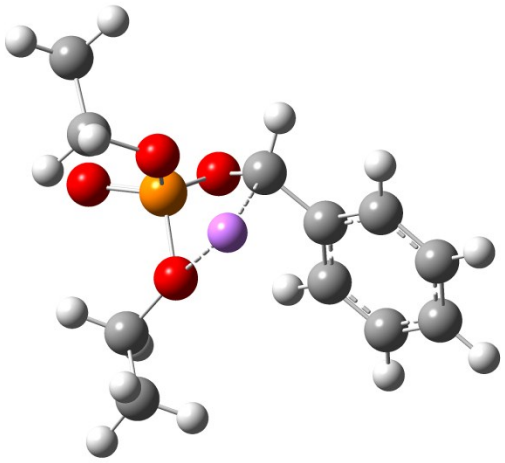
C	4.28849428	5.83642389	-0.34737896
C	4.43906467	6.78884017	0.71040266
C	3.37644870	7.73665854	0.87975303
C	2.25600227	7.71713089	0.04040379
H	1.27129069	6.77867065	-1.63825960
H	3.10221204	5.11439076	-1.97137865
H	5.07546818	5.10301600	-0.50606715
H	3.49246804	8.52271239	1.62046503
H	1.47741932	8.46181145	0.18647562
C	5.56508143	6.75460124	1.59018946
O	5.68464903	7.60431411	2.59092812
H	6.31037726	5.96258821	1.48304779
P	5.21654615	7.00284093	4.50791940
O	6.35468617	5.83272451	4.76715150
O	3.91658035	5.90580585	4.25397359
C	7.59018005	6.18673145	5.43575749
H	7.38066153	6.94524999	6.19638295
H	7.91500513	5.27308354	5.94235909
C	8.64102981	6.66602665	4.44615425
H	8.30899850	7.56998950	3.92807083
H	8.84557423	5.89706114	3.69536276
H	9.57474751	6.89165677	4.97233938
C	3.59733003	4.86753684	5.23836275
H	4.53916378	4.47890792	5.63086334
H	3.10397736	4.06779952	4.67614456
C	2.70382126	5.41394544	6.33749463
H	1.76679286	5.80183824	5.92640688
H	3.20589526	6.22107950	6.87553131
H	2.46259705	4.61470703	7.04678937
O	5.04361899	7.90073904	5.69768684
Li	3.38899005	6.08252586	2.47563126

TS1b (phospha-Brook rearrangement)



Atom	X	Y	Z
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C	-15.67004221	13.59433762	1.17621150
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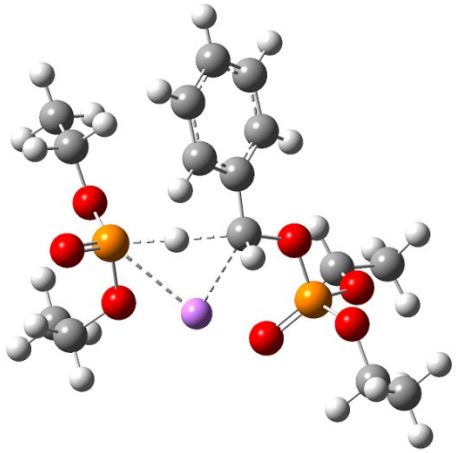
C	-13.33539934	12.99183001	1.34288294
C	-13.57335855	11.84555472	0.58302209
H	-15.04402436	10.68551638	-0.49056309
H	-16.89838140	12.26179469	0.02388867
H	-16.47744694	14.28366777	1.39652504
H	-12.32166501	13.22077902	1.66914154
H	-12.74935379	11.17907534	0.34306838
C	-14.10364961	15.03309166	2.54687929
O	-15.13028898	16.12132827	2.55651372
H	-13.10608678	15.45480873	2.40071744
P	-15.05334476	15.63884260	4.12067123
O	-13.65229020	15.21447081	5.08687644
O	-15.87034638	14.16860188	4.28787362
C	-13.50031558	15.75215337	6.42631502
H	-12.91128044	15.00807973	6.97599333
H	-14.48342864	15.84679349	6.89267152
C	-12.79032973	17.09504034	6.40076581
H	-13.39999214	17.82428717	5.86248502
H	-12.63321928	17.46033504	7.42172145
H	-11.81492382	17.01244709	5.91079980
C	-17.20558742	14.14037917	4.85362089
H	-17.90450960	14.50794918	4.09507888
H	-17.24391959	14.82129540	5.70667661
C	-17.53257107	12.71200653	5.24591605

H	-18.55029640	12.66004582	5.64555468
H	-17.47169103	12.04275886	4.38209149
H	-16.84857921	12.34900766	6.02096937
O	-15.73748347	16.67458107	4.96140534
Li	-14.03045466	13.43411344	4.30483762

TS2 (proton exchange process)



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C	-9.30013743	13.09158563	3.42501250
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H	-7.80967568	12.98274276	0.37256683
C	-10.52754543	12.51870824	3.09048678
H	-9.12756183	13.41975929	4.44707177
C	-10.78607217	12.10943001	1.78100165
H	-9.98033425	11.97191251	-0.21413594
H	-11.28589384	12.39913064	3.85969548
H	-11.74322189	11.66805983	1.51956330
O	-6.20414381	14.19349613	1.66814190
P	-4.75133464	14.77658728	1.78501572
O	-3.87785075	14.09973052	2.81639867
O	-4.15324589	14.71821633	0.30619177
O	-4.94120235	16.33941708	2.03500705
C	-3.73497496	13.44408928	-0.26551658
H	-4.61216499	12.79299605	-0.33542647
H	-3.00407768	12.98392420	0.40654349
C	-3.14178618	13.72310968	-1.63109584
H	-3.87922504	14.19563400	-2.28520572

H	-2.27273464	14.38159964	-1.54994513
H	-2.82223066	12.78305884	-2.09107396
C	-3.79155880	17.18910911	2.32471854
H	-3.25404347	16.76801134	3.17946689
H	-3.13050471	17.18231945	1.45231297
C	-4.30904027	18.58200052	2.61791011
H	-3.46741515	19.24675340	2.83558910
H	-4.97709197	18.57421468	3.48335601
H	-4.85444511	18.98272449	1.75953523
Li	-4.76826605	12.95405760	3.93421347
H	-7.09358758	14.69601681	3.50039649
P	-6.72668454	11.26783324	4.93083944
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C	-8.02212310	9.15952144	3.96654216
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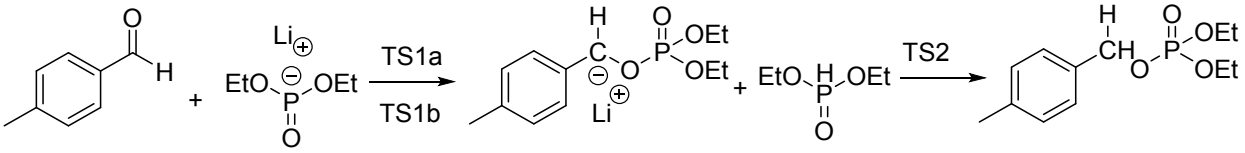
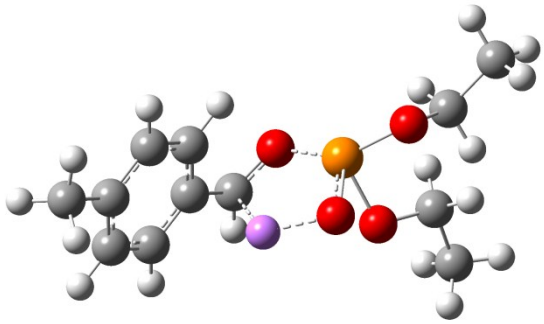
p-methyl benzaldehyde



TS1a



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C	3.96736873	5.46425480	-0.05666573
C	2.19925507	7.59567349	0.24008512
H	3.65999774	8.44608144	1.58710096
C	2.78387459	5.50273572	-0.77122687
H	4.64835995	4.62588018	-0.18442725
C	1.86276033	6.56929278	-0.64613037
H	1.52278634	8.44013100	0.35566218
H	2.55364407	4.68401512	-1.45027753
O	5.87742449	7.42696935	2.43744419
P	5.47903144	7.19588003	4.43415003
O	5.37753254	8.28769922	5.45920216
O	6.53184529	6.00343281	4.88989846
O	4.09832913	6.16964945	4.41948817
C	7.81297235	6.37246229	5.45236662
H	7.69352620	7.27737359	6.05677864
H	8.08304606	5.54901243	6.12042649
C	8.86233454	6.56231542	4.36774010
H	8.58186181	7.37336565	3.68983403
H	8.97801348	5.64857231	3.77750792
H	9.82946322	6.80688194	4.81994063

C	3.74033595	5.49502810	5.66416087
H	3.83668357	6.22096101	6.47671852
H	4.45588554	4.68575706	5.82865980
C	2.31915066	4.97776887	5.56014039
H	2.21622041	4.25268709	4.74427792
H	1.61119955	5.79762017	5.40248521
H	2.04108181	4.46670246	6.48753448
Li	3.34000137	6.07883506	2.71665970
H	6.17677339	5.57801891	1.53856716
C	0.58754514	6.59297659	-1.45237067
H	0.79127725	6.63735620	-2.52960992
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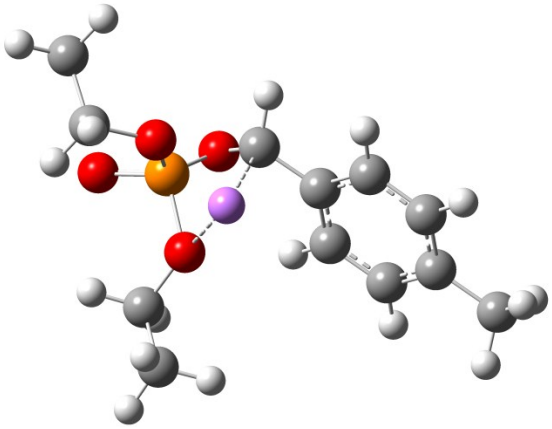
TS1b



Atom	X	Y	Z
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C	5.06250389	6.59795683	32.24303188
C	2.50313813	6.11701674	31.29087627
H	1.95070055	7.94737797	32.28225191
C	4.80092841	5.45823636	31.48071941
H	6.08061627	6.79694711	32.57539568
C	3.51735655	5.19495671	30.98696586
H	1.49844461	5.94443849	30.91097146
H	5.61410023	4.77428962	31.24881055
O	3.34595271	9.78269549	33.42370205
P	3.37713719	9.31815999	34.99353340
O	2.70248692	10.38106314	35.80807594
O	4.75212607	8.87715166	35.98767907
O	2.52003354	7.87102093	35.16933667

C	4.89836150	9.43317047	37.31992793
H	5.44706172	8.67775487	37.89536506
H	3.91054967	9.57494373	37.76375847
C	5.66067645	10.74689295	37.28371458
H	5.08999182	11.48962587	36.72145614
H	5.81395851	11.12482001	38.30066726
H	6.64050274	10.61751356	36.81310868
C	1.18607962	7.88099401	35.73807161
H	0.49506298	8.26506377	34.98048733
H	1.16783240	8.56516495	36.58912108
C	0.82168722	6.46302807	36.13534884
H	-0.19614677	6.43923578	36.53741559
H	0.86307087	5.79000483	35.27330343
H	1.49755586	6.08394374	36.90987827
Li	4.34020666	7.09605021	35.21381147
H	5.34907519	9.04852095	33.31303029
C	3.23727081	3.98523808	30.12689440
H	3.17492743	4.25570408	29.06540193
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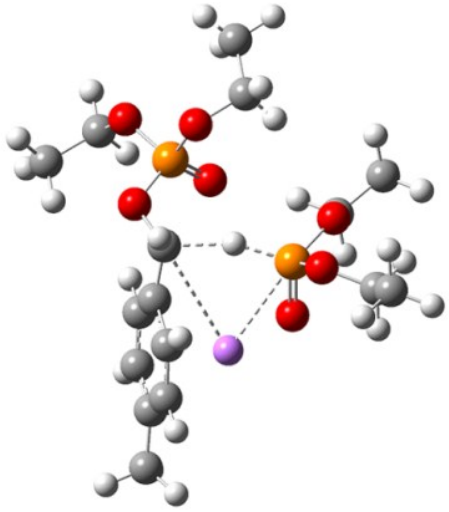
H	2.28501252	3.51497320	30.39347797

TS2



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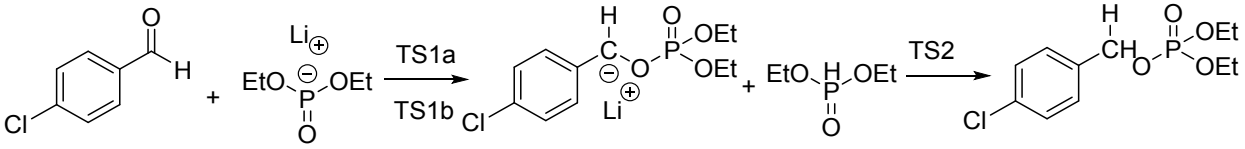
C	1.39481209	-9.96990411	0.75054310
C	0.57814760	-11.25139805	-1.57756226
H	2.41489137	-10.55619689	-2.44545013
C	0.19051969	-10.66945103	0.71500681

H	1.69714392	-9.48468958	1.67462848
C	-0.25790994	-11.33832917	-0.44567558
H	0.27630901	-11.75114077	-2.49566192
H	-0.41946551	-10.70580921	1.61491353
O	4.15559076	-8.93001991	-1.54666531
P	5.51394920	-9.66531164	-1.95352207
O	5.46668917	-11.15270517	-2.04673743
O	6.58237235	-9.06648546	-0.91805121
O	5.91435979	-8.91828038	-3.32270681
C	7.79502827	-9.79179966	-0.58507686
H	8.11147309	-9.36772633	0.37090454
H	7.54693055	-10.84515370	-0.43062838
C	8.87110978	-9.61432536	-1.64352913
H	9.79730205	-10.09486879	-1.31057483
H	9.07368650	-8.55354697	-1.81520605
H	8.57382192	-10.06787937	-2.59295643
C	5.35136213	-9.35416383	-4.58707995
H	6.14329028	-9.19156486	-5.32310645
H	5.14731716	-10.42825458	-4.53645953
C	4.10566511	-8.55770297	-4.93931890
H	3.72978028	-8.87159652	-5.91911630
H	3.31809957	-8.71062339	-4.19707807
H	4.33158296	-7.48859543	-4.98202886
Li	1.89632429	-12.25519707	0.13998960
H	3.69239355	-8.51250303	0.44622230
C	-1.59480236	-12.03937351	-0.49161705
H	-2.40525525	-11.34342377	-0.74507228
H	-1.60553669	-12.83327353	-1.24496078
H	-1.84886683	-12.48871018	0.47390436
P	4.57744569	-12.04770228	1.16724131
O	4.78019011	-11.68971551	2.73855101
O	5.96756586	-12.84994854	0.86846136
C	4.90523728	-12.73626343	3.73610120
H	5.78214062	-13.34598474	3.49656246
H	4.01613226	-13.37444770	3.69284978
C	5.04473653	-12.07613481	5.09437692
H	5.92954834	-11.43411184	5.12408411
H	5.14518307	-12.84008716	5.87216383
H	4.16666422	-11.46498753	5.32188860
C	6.06813272	-13.78361273	-0.24263720
H	5.24516211	-14.50144347	-0.17433286
H	5.97664623	-13.22005039	-1.17454486
C	7.41203645	-14.47969995	-0.13780802
H	7.50075444	-15.02449846	0.80691689
H	7.52381487	-15.19400954	-0.96009847
H	8.23218530	-13.75819857	-0.19818643
O	3.37624959	-12.96988989	0.92161273

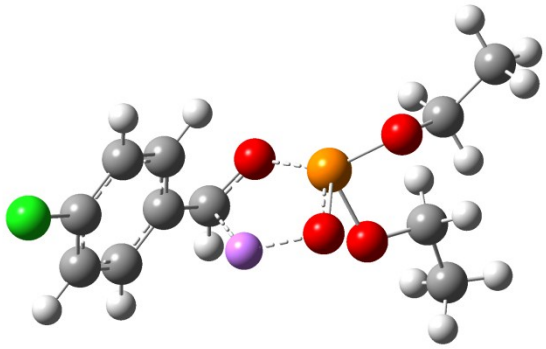
H	4.35170536	-10.67010695	0.48728896

p-Chloro-benzaldehyde



Intermediate

TS1a



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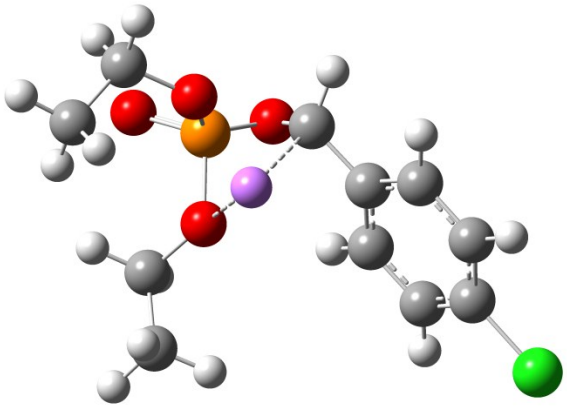
C	-42.27818752	37.13006220	2.20558022
C	-42.24037643	34.96801901	1.08453227
C	-40.90502283	37.24567531	2.01041567
H	-42.81625193	37.90022481	2.74630955
C	-40.86763413	35.08754703	0.90170206
H	-42.74606233	34.06869191	0.73893643
C	-40.19955505	36.22794718	1.36394260
H	-40.37660198	38.12219292	2.37138730
H	-40.31255143	34.29906785	0.40404970
Cl	-38.45953161	36.37989212	1.12260377
O	-45.13195094	36.86220263	2.41088770
P	-45.71525878	38.20117553	1.02709282
O	-47.30179436	37.87851489	0.95995634
O	-45.78322959	39.85131435	1.15592653
C	-48.14024803	38.43715239	-0.09041579
H	-48.10074617	39.52864159	-0.02650356
H	-47.73821181	38.12860940	-1.06138303

C	-49.54978688	37.91867886	0.11546728
H	-50.21024396	38.31860991	-0.66093486
H	-49.57434372	36.82671526	0.06209519
H	-49.93648686	38.22632479	1.09086015
C	-44.58442060	40.63393289	0.96518058
H	-44.63233480	41.43700456	1.70622825
H	-43.69739740	40.02711793	1.19005337
C	-44.51548733	41.19259362	-0.44703678
H	-45.40018623	41.79800938	-0.66492779
H	-44.45980852	40.38185412	-1.17759577
H	-43.62949401	41.82773179	-0.55626739
O	-44.99248162	37.81398861	-0.27691145
Li	-43.53883748	36.76373840	-0.24317213

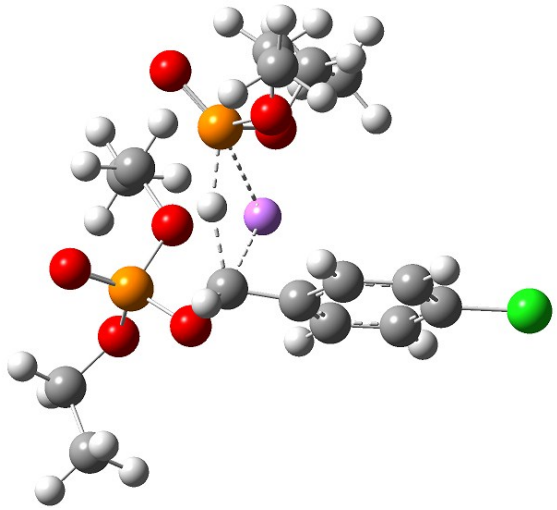
TS1b



Atom	X	Y	Z
C	4.99524629	27.65578116	1.99796537
H	5.85404888	28.22674410	1.63649154
C	4.84228130	26.35223831	1.32141179
C	3.58440630	25.76848934	1.08281971
C	5.98978475	25.62911676	0.93475589
C	3.47438907	24.51252080	0.49088856
H	2.69155435	26.32257941	1.34876255
C	5.89230400	24.36359106	0.35646673
H	6.97392769	26.07678896	1.06068527
C	4.62991956	23.81278337	0.14105508
H	2.49904991	24.07821207	0.29934204
H	6.78318236	23.82241122	0.05699477
Cl	4.49281656	22.21693449	-0.59658227
O	3.77646793	28.51574965	2.04928201

P	4.19395577	28.30623113	3.62531388
O	3.69042783	26.76324817	4.09841772
O	5.77705925	28.25588071	4.39073751
C	2.48435655	26.61304073	4.89102969
H	1.63273582	26.94098436	4.28750610
H	2.54654078	27.26606202	5.76528574
C	2.34840994	25.15322321	5.27932060
H	1.42943976	25.00649914	5.85539897
H	2.30190641	24.51438075	4.39231625
H	3.18955584	24.82810190	5.90149179
C	6.03489107	29.00447125	5.60392701
H	7.09339655	29.28311286	5.56094278
H	5.42627950	29.90946065	5.57932926
C	5.73989619	28.19333031	6.85628709
H	6.32755017	27.26700771	6.88198934
H	5.99672284	28.77078869	7.75093823
H	4.67705943	27.94157461	6.91239036
O	3.47036324	29.33804643	4.43574805
Li	5.60288130	26.33937185	3.93103689

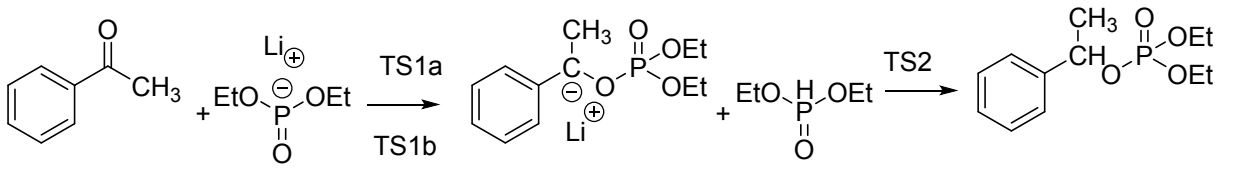
TS2



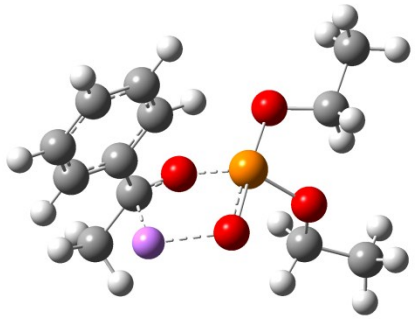
Atom	X	Y	Z
C	-5.69775966	14.28024881	3.22935054
H	-4.86145196	14.82264649	3.67303284
C	-6.89084797	14.22782020	4.07792370
C	-6.75289305	13.91668277	5.45569292
C	-8.20883662	14.31367022	3.56562629
C	-7.85747166	13.70539547	6.26690926
H	-5.75875284	13.83933314	5.88609262
C	-9.32601520	14.09940868	4.38274468

H	-8.36167344	14.61840635	2.53418556
C	-9.14598228	13.79274512	5.72532334
H	-7.72696702	13.47598343	7.31910213
H	-10.32626308	14.19373394	3.97304113
Cl	-10.54758881	13.52370198	6.76325196
O	-6.03045884	14.91769609	1.93689432
P	-5.44996442	14.26676437	0.60288393
O	-3.98583914	14.25061414	0.38434201
O	-6.32088576	14.97667729	-0.54102782
O	-6.14380506	12.77882685	0.67658971
C	-5.64660653	11.71228286	-0.20916362
H	-5.65188480	10.80990653	0.40406788
H	-4.61074604	11.94696487	-0.46174667
C	-6.53012319	11.58421641	-1.43447294
H	-6.16305320	10.76479591	-2.06101229
H	-7.56487019	11.36402078	-1.15482869
H	-6.51953599	12.50308042	-2.02577023
C	-5.79716402	16.13877985	-1.25095159
H	-6.29176509	16.11019015	-2.22428138
H	-4.72223857	16.00377668	-1.39836528
C	-6.10759056	17.42611707	-0.50817480
H	-7.18412801	17.53348777	-0.34938301
H	-5.75721706	18.28112145	-1.09569029
H	-5.60959132	17.45247115	0.46484492
Li	-6.86388174	12.45610091	2.51013122
P	-4.50490171	11.28823688	3.53125773
O	-4.37981533	11.12094162	5.15895002
O	-6.14941440	10.86499467	3.26607917
C	-3.61911371	10.04826187	5.76986630
H	-2.96535322	9.59698121	5.01843689
H	-4.32971859	9.28588621	6.11092696
C	-2.82470788	10.61050153	6.93471719
H	-2.10315127	11.35545869	6.58713362
H	-3.48550207	11.08394012	7.66680010
H	-2.27608526	9.80603009	7.43584418
C	-6.59075986	9.50294604	3.48390581
H	-6.65055144	9.33144869	4.56420018
H	-5.83851244	8.82841153	3.06334522
C	-7.94412248	9.29554190	2.82820741
H	-8.69282033	9.97766592	3.24494356
H	-7.88482848	9.45059792	1.74585109
H	-8.29057985	8.27195022	3.00236640
O	-3.60905518	10.35830703	2.76912630
H	-4.89853058	12.82332155	3.26118612

Acetophenone



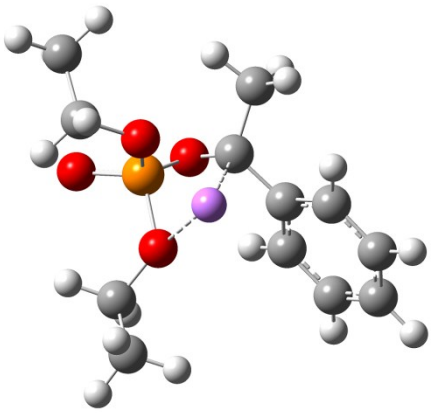
TS1a



Atom	X	Y	Z
C	-39.41238129	33.53734488	2.99323577
C	-39.02657483	33.48657053	4.34155165
C	-38.38880295	32.32612705	4.80038875
C	-38.13887814	31.24804223	3.95213259
C	-38.51483132	31.27504742	2.56315437
C	-39.17898878	32.47316313	2.12820427
H	-39.91169665	34.42375831	2.60934261
H	-38.07255149	32.25778513	5.83851615
H	-37.62270299	30.37254615	4.32903508
H	-39.49763646	32.56172094	1.09511081
C	-38.27427216	30.15188818	1.71159554
C	-38.75901657	30.04426861	0.29778904
H	-38.04375657	29.47939423	-0.30909818
H	-39.71321570	29.48007681	0.25666870
H	-38.92286874	31.00870394	-0.18827766
O	-37.84744949	29.00457153	2.24332020
P	-39.18401686	27.90587875	3.16507398
O	-39.65475437	26.36184971	2.78379350
O	-38.38390615	27.57501438	4.54341734
C	-40.58454308	26.16014671	1.69741159
H	-41.55524133	26.58330631	1.97815081
H	-40.22943081	26.68889352	0.80278205
C	-40.68962181	24.66873794	1.43858467
H	-41.39777342	24.47912829	0.62540836

H	-41.04167989	24.14555585	2.33210878
H	-39.71788765	24.25474787	1.15517128
C	-37.13681382	26.83702685	4.48162800
H	-37.33745989	25.83620832	4.08515512
H	-36.45029809	27.35377209	3.80266844
C	-36.56891063	26.76327457	5.88580782
H	-37.26754912	26.25957959	6.55970467
H	-36.36931619	27.76470135	6.27763214
H	-35.62911063	26.20193594	5.87790493
O	-40.39565993	28.77118679	3.51437158
Li	-40.34530972	30.56473565	3.62869678
H	-39.21113942	34.32305254	5.00676672

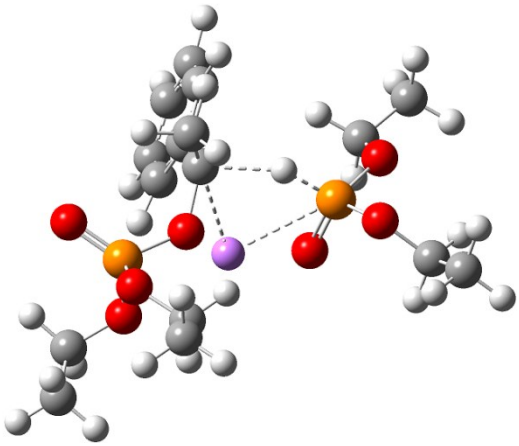
TS1b



Atom	X	Y	Z
C	-26.01775136	20.55721001	-0.00227511
C	-27.28013850	20.50170085	-0.59347800
C	-28.13586352	21.60134884	-0.47263910
C	-27.74732549	22.73371471	0.23919196
C	-26.47716711	22.81032994	0.84151996
C	-25.61857803	21.69668066	0.70123105
H	-25.33142656	19.72028920	-0.09961934
H	-29.11727750	21.57530491	-0.93883419
H	-28.41543791	23.58231165	0.33200505
H	-24.61211476	21.73147840	1.11639139
C	-26.06928750	23.96751798	1.68028341
C	-24.70564758	24.56494094	1.37999279
H	-24.43293730	25.31011215	2.13102383
H	-23.91832423	23.80413074	1.37206396
H	-24.70537611	25.05166150	0.39514064
O	-27.09159561	25.07380858	1.70102906
P	-27.08608116	24.60281209	3.26210198

O	-25.70799031	24.21127167	4.23705355
O	-27.88906620	23.12534784	3.41329494
C	-25.57944448	24.77677498	5.57017296
H	-24.98799831	24.04779094	6.13600658
H	-26.56976874	24.86540857	6.02163566
C	-24.88673299	26.12771994	5.52903398
H	-23.90454107	26.05039926	5.05187603
H	-24.74561507	26.51164428	6.54544097
H	-25.49997602	26.84043931	4.97278614
C	-29.24405715	23.07714217	3.92771766
H	-29.33761859	23.79862709	4.74207850
H	-29.92245905	23.38020886	3.12336863
C	-29.53869997	21.65961205	4.38051165
H	-28.87134486	21.35939049	5.19575973
H	-29.42603554	20.95080643	3.55419090
H	-30.56804132	21.59304267	4.74703728
O	-27.81891407	25.63109794	4.07004614
Li	-26.06788513	22.38979617	3.36669472
H	-27.59066119	19.61995460	-1.14558439

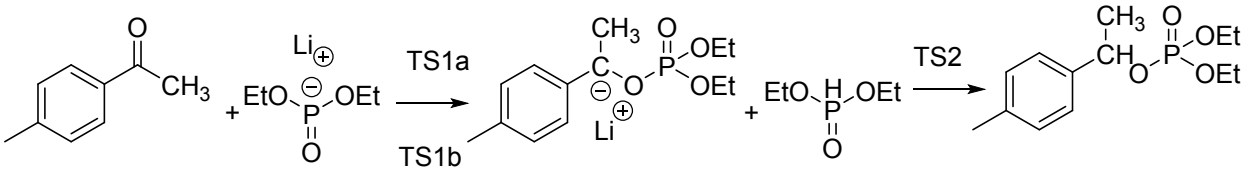
TS2



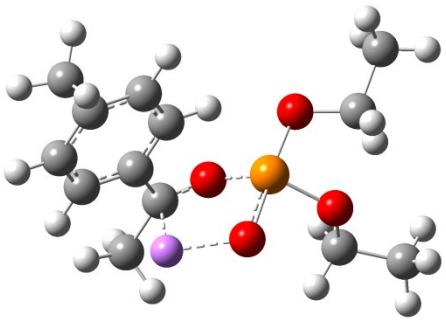
Atom	X	Y	Z
C	5.91593568	-10.64653189	-7.76053623
C	4.79438385	-11.49397242	-8.05105983
C	5.00616969	-12.84092014	-8.48551060
C	3.43491275	-11.14602547	-7.77458112
C	3.96206491	-13.74442827	-8.60250782
H	6.01386533	-13.16513550	-8.72849752
C	2.39551266	-12.07598813	-7.88985927
H	3.16671183	-10.10784051	-7.59154750
C	2.63877256	-13.38524572	-8.29261099
H	4.17867350	-14.75386229	-8.94501684

H	1.37746459	-11.74915032	-7.68964743
H	1.83020198	-14.10266947	-8.38595288
O	5.48281251	-9.33302887	-7.17795002
P	5.04012245	-8.01383137	-8.00398195
O	4.68574478	-8.13201686	-9.43312317
O	6.23131849	-6.95776704	-7.77130261
O	3.83629484	-7.55940379	-7.00625439
C	6.83883403	-6.74772945	-6.47070463
H	6.06885298	-6.40565488	-5.77034145
H	7.23836799	-7.70091679	-6.11140317
C	7.93554308	-5.71326466	-6.63209221
H	8.69162265	-6.05984930	-7.34154760
H	7.52806639	-4.76571570	-6.99505271
H	8.42041338	-5.53546168	-5.66707616
C	2.84497280	-6.59761483	-7.47258940
H	1.93882042	-6.83649306	-6.91081648
H	2.65704765	-6.78022728	-8.53402922
C	3.28842188	-5.16674752	-7.22017572
H	4.19122340	-4.92660845	-7.78821977
H	2.49666103	-4.47704938	-7.53058395
H	3.48760176	-5.00190185	-6.15707493
Li	4.39055874	-10.16999058	-5.77939811
C	7.11019448	-10.48774268	-8.65791099
H	6.90453446	-9.88336569	-9.55575518
H	7.95215528	-10.02622862	-8.12733623
H	7.44945923	-11.46966255	-9.00110656
P	6.42062980	-11.81088662	-4.77805079
O	6.37453449	-13.38275605	-4.37126462
O	7.74009353	-11.31818165	-3.99521182
C	5.18493128	-14.17073060	-4.65816428
H	4.33962241	-13.73988782	-4.11344707
H	4.96981211	-14.11738414	-5.73198113
C	5.45947442	-15.59704348	-4.22412178
H	4.58006156	-16.21811145	-4.42124054
H	5.68231176	-15.64287208	-3.15426047
H	6.30749970	-16.01463396	-4.77384278
C	7.80162224	-11.32167490	-2.53943198
H	7.63524981	-12.34391591	-2.18668842
H	7.00077762	-10.68232935	-2.15464920
C	9.16812549	-10.80934036	-2.13072000
H	9.32849429	-9.79204287	-2.49854533
H	9.24828065	-10.79898627	-1.03909952
H	9.95814759	-11.45147076	-2.52951028
O	5.13990301	-11.08803643	-4.36903741
H	6.59777448	-11.48820608	-6.21825432

4-methyl-acetophenone



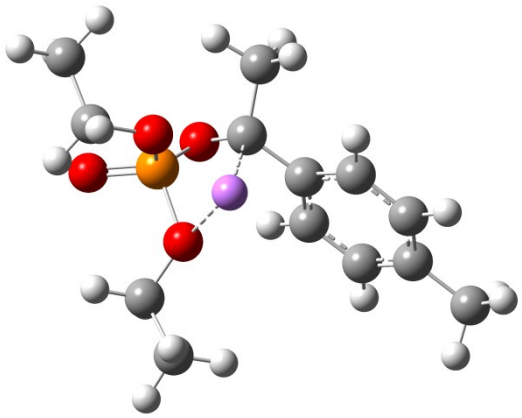
TS1a



Atom	X	Y	Z
P	7.69745640	-0.30492292	-3.07439375
O	6.79550008	-1.68121296	-3.29171780
O	8.26527703	-0.62888778	-1.58369148
C	5.94529057	-1.78230726	-4.45420631
H	6.49811289	-1.46377803	-5.34844356
H	5.09192322	-1.10713189	-4.32720277
C	5.49169057	-3.22436313	-4.58579346
H	6.34944774	-3.88936480	-4.72022150
H	4.83086665	-3.33151855	-5.45217373
H	4.94464652	-3.54103668	-3.69327379
C	9.21922438	-1.70663508	-1.40668589
H	10.08176980	-1.52841729	-2.05749264
H	8.74642006	-2.64982548	-1.69991155
C	9.62687316	-1.73284175	0.05377578
H	8.75650237	-1.89780280	0.69507867
H	10.34288178	-2.54279784	0.22606842
H	10.09736206	-0.78882218	0.34318942
O	6.79714508	0.92748825	-2.98016518

O	9.36006310	0.14761558	-3.98922349
C	9.35017680	1.23981291	-4.76017287
C	9.36354324	2.52774081	-4.14146426
C	9.63755810	2.67607053	-2.73840651
C	9.04742772	3.74709903	-4.82970916
C	9.59908638	3.91974343	-2.10927369
H	9.88826608	1.79140584	-2.16407106
C	9.02361877	4.97511354	-4.17630843
H	8.81342740	3.71846354	-5.88860965
C	9.29812931	5.10668204	-2.80136014
H	9.81813147	3.96845955	-1.04419642
H	8.77445397	5.86478837	-4.75186904
Li	7.37340873	2.63840049	-3.08265312
C	8.94824805	0.99939801	-6.18232075
H	7.86651239	0.75776770	-6.24940757
H	9.13872191	1.84910603	-6.84250663
H	9.48089126	0.13329323	-6.58850578
C	9.30955959	6.45191630	-2.11817149
H	10.29458621	6.93389755	-2.18276129
H	8.58831614	7.14015957	-2.57149877
H	9.06614229	6.36416267	-1.05435446

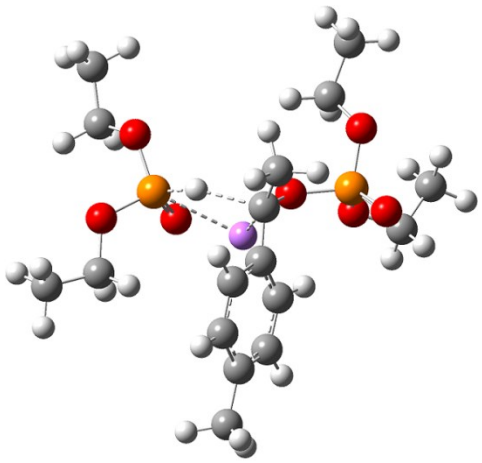
TS1b



Atom	X	Y	Z
P	-6.56340992	18.24062701	-0.61099129
O	-7.99750276	17.40539390	-0.28550182
O	-5.48927816	16.87480587	-0.55008910
C	-8.78283275	17.74027235	0.88672060
H	-8.12637266	17.78217572	1.75900388
H	-9.21178706	18.73630437	0.74027251
C	-9.87329524	16.69698924	1.04202871
H	-10.50316031	16.94269291	1.90291683

H	-10.50850511	16.66025905	0.15189207
H	-9.44808412	15.70130806	1.21061342
C	-4.60836737	16.68847949	0.59011412
H	-4.48816041	15.60340429	0.69101359
H	-5.09158940	17.08291720	1.48598746
C	-3.26830282	17.36579202	0.36154683
H	-2.79593979	17.00013647	-0.55573409
H	-3.40615985	18.44713684	0.28516308
H	-2.59360178	17.16245651	1.20050367
O	-6.19274571	19.03726192	0.60374681
O	-6.78543094	19.27065142	-1.85393674
C	-6.75380890	17.93638464	-2.55765950
C	-8.03877726	17.61064011	-3.23681713
C	-9.18895909	18.40743325	-3.07782853
C	-8.17052424	16.44030451	-4.01225117
C	-10.39669133	18.05310601	-3.66914256
H	-9.11272523	19.31756589	-2.49383732
C	-9.39278986	16.08471936	-4.59010547
H	-7.30327131	15.81075435	-4.20309735
C	-10.53033563	16.88213079	-4.43301145
H	-11.26034776	18.70152330	-3.53682828
H	-9.45261779	15.17887544	-5.18906508
Li	-7.12089519	16.00452012	-1.33927699
C	-5.50871061	17.86893550	-3.42515855
H	-5.41482044	16.90129891	-3.92921435
H	-5.53413350	18.64594196	-4.20109263
H	-4.60750162	18.01207196	-2.82432269
C	-11.84834126	16.51764964	-5.07437257
H	-11.79925488	15.53882244	-5.55952914
H	-12.65969868	16.48659715	-4.33835196
H	-12.13762151	17.25095077	-5.83666239

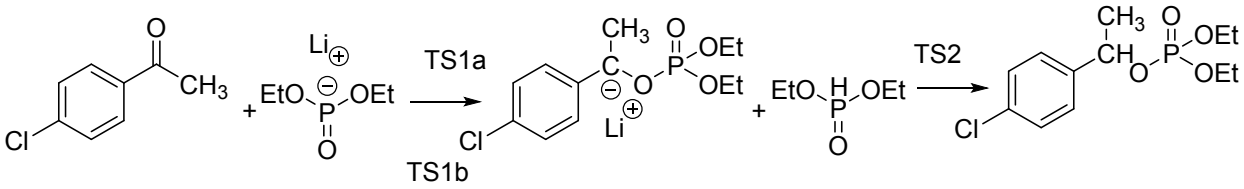
TS2



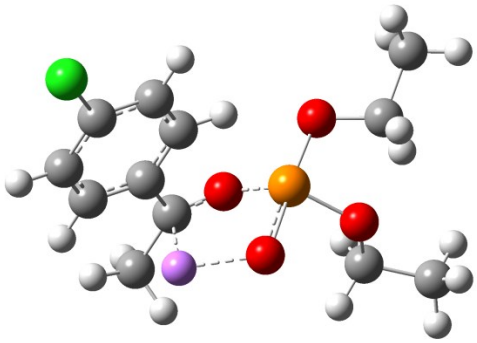
Atom	X	Y	Z
P	-2.77430650	-0.57454575	-0.32130475
O	-2.98306919	-0.62900382	1.29050247
O	-3.62732360	0.69086455	-0.83414779
C	-4.09318861	-1.39658540	1.83996239
H	-3.75340590	-1.70913412	2.83022599
H	-4.23936500	-2.28722145	1.22284889
C	-5.36084864	-0.56400201	1.93008886
H	-5.19910044	0.32767683	2.54307228
H	-5.69878970	-0.25163396	0.93831438
H	-6.15780535	-1.15638320	2.39150935
C	-3.39662483	2.03148915	-0.33137326
H	-2.35660265	2.30754856	-0.53076884
H	-3.55697351	2.03670929	0.75237502
C	-4.36188480	2.96492723	-1.03562875
H	-4.20951329	3.98949043	-0.68193676
H	-4.20058657	2.94379229	-2.11670935
H	-5.39801821	2.67930833	-0.83431541
O	-3.12227083	-1.80301900	-1.06466274
O	-1.23953118	-0.06305130	-0.30286586
C	-0.15301283	-0.46355486	-1.25800912
C	0.49617853	-1.67729831	-0.83537505
C	0.19723874	-2.37463650	0.37305510
C	1.63757231	-2.16266986	-1.54754081
C	0.99159979	-3.43413592	0.83190930
H	-0.72926766	-2.17354534	0.90757887
C	2.39931993	-3.21929419	-1.07933661
H	1.91509348	-1.69099369	-2.48579027
C	2.11057319	-3.88127362	0.13294991
H	0.69935193	-3.94105117	1.74986181
H	3.24984232	-3.55091034	-1.67288457
C	-0.53339990	-0.17543560	-2.68370868
H	0.31005085	-0.39619901	-3.34486092
H	-1.38893309	-0.77194037	-3.03794799
H	-0.77961497	0.88405075	-2.82531701
Li	0.03732280	-0.11861347	1.17403526
C	2.96495175	-5.02430583	0.62522399
H	3.98830930	-4.70297364	0.85921530
H	2.54662746	-5.46825448	1.53371677
H	3.04779730	-5.82195454	-0.12324736
P	1.95023777	1.59145626	0.11877191
O	1.76158308	3.16649987	-0.16626290
O	3.56897517	1.44979943	0.07965709
C	2.22161136	4.16292175	0.79266418
H	3.30828775	4.07634770	0.88676397
H	1.76662537	3.94882630	1.76485288

C	1.81550513	5.52864350	0.27651499
H	2.26592108	5.72398341	-0.70047233
H	2.15198183	6.30253908	0.97370145
H	0.72867928	5.60057938	0.17884949
C	4.19668529	0.21933080	0.53615835
H	3.96208459	0.07801864	1.59540472
H	3.78190899	-0.62593050	-0.02628138
C	5.68991058	0.34951642	0.30876136
H	5.91104523	0.49255374	-0.75252581
H	6.09592214	1.19873223	0.86577342
H	6.19558114	-0.55998125	0.64803726
O	1.37753226	1.12313624	1.45386875
H	1.17164153	0.83650468	-0.89976594

4-chloro, Acetophenone



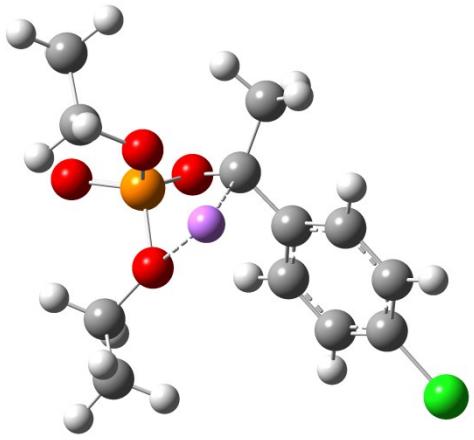
TS1a



Atom	X	Y	Z
C	8.91703940	-6.29920225	-1.53505220
C	7.53500015	-6.12285806	-1.56198876
C	6.89639545	-5.27580366	-0.65513428
C	7.66438340	-4.59938591	0.29421489

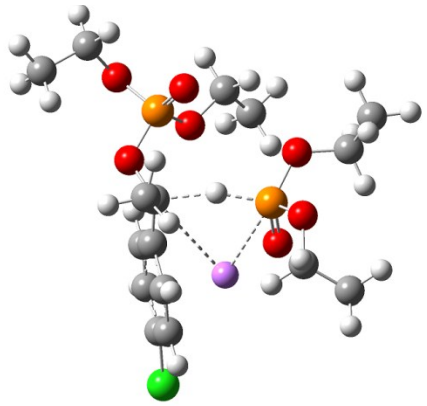
C	9.05596907	-4.76648195	0.35226234
C	9.66513347	-5.62131847	-0.57127053
H	9.39668735	-6.95359506	-2.25536663
H	5.82091222	-5.14101394	-0.69988531
H	7.16343712	-3.93337069	0.99131281
H	10.74359406	-5.72352392	-0.50712748
C	9.96878056	-4.05330696	1.36825921
C	9.78274285	-2.52204572	1.30227098
H	10.35630468	-2.04876690	2.10232868
H	8.73809642	-2.19618626	1.36156381
H	10.19708906	-2.19234445	0.34351481
O	11.26922037	-4.44724391	1.35825659
Cl	6.56931861	-6.98603728	-2.76376028
P	9.80322767	-4.73577701	3.06601959
O	8.16513436	-5.10288310	3.56643451
O	10.02146074	-6.38908264	2.90266681
C	7.44713995	-4.09529775	4.31030837
H	8.13024867	-3.65620848	5.04244466
H	7.12896900	-3.30385591	3.62055979
C	6.24475827	-4.72915015	4.98547995
H	6.55745440	-5.50009312	5.69782845
H	5.56754062	-5.17768187	4.25034562
H	5.68236700	-3.97031617	5.53845344
C	11.33293738	-7.00827622	2.68443361
H	11.10219398	-7.99694241	2.27436951
H	11.83704412	-6.39920971	1.93491975
C	12.11239060	-7.10777683	3.98268262
H	11.57602786	-7.70024670	4.73202244
H	13.07444463	-7.59440204	3.78933319
H	12.30040257	-6.11316401	4.39216599
O	10.50313052	-4.09080495	4.21273254
Li	8.24721346	-6.94059889	3.22529152

TS1b



Atom	X	Y	Z
C	1.19409460	-3.84077966	-2.51550848
C	-0.04960513	-3.85504915	-3.14120991
C	-0.92020554	-2.77104352	-3.01901340
C	-0.54726607	-1.67270774	-2.24998958
C	0.70140859	-1.61897839	-1.60078567
C	1.56304100	-2.72717152	-1.75783787
H	1.87412590	-4.67779938	-2.63094436
H	-1.88075435	-2.78777897	-3.52288321
H	-1.21892543	-0.82774547	-2.15354759
H	2.55602656	-2.71547062	-1.31467519
C	1.07489076	-0.48384154	-0.71760361
C	2.46571742	0.09226207	-0.91954061
H	3.24095590	-0.67883738	-0.86204112
H	2.54686195	0.57353782	-1.90328924
H	2.69234599	0.83714219	-0.15331180
O	0.06766822	0.63304809	-0.74048592
Cl	-0.52494258	-5.25391799	-4.10377675
P	-0.00211014	0.13569652	0.81546121
O	1.30120747	-0.34418549	1.86468924
O	-0.86536933	-1.31342998	0.89283662
C	1.37620554	0.17613581	3.21951842
H	1.85116112	-0.61596949	3.81019388
H	0.36572586	0.34922058	3.59484187
C	2.19288083	1.45574522	3.26831035
H	3.19750212	1.29538130	2.86425035
H	2.28981817	1.80345245	4.30270846
H	1.69583930	2.23702536	2.68821191
C	-2.24571731	-1.32112356	1.34096904
H	-2.34875048	-0.62562088	2.17657144
H	-2.87186133	-0.96121888	0.51801542
C	-2.61916370	-2.73980831	1.72651737
H	-2.00611893	-3.09596488	2.56162740
H	-2.49450581	-3.42371028	0.88115316
H	-3.66722454	-2.77565329	2.04016745
O	-0.72691467	1.18010001	1.60875641
Li	0.92120984	-2.11287824	0.97101042

TS2



Atom	X	Y	Z
P	-13.31999200	-18.48131700	17.34973800
O	-14.00716500	-19.69145400	16.53529700
O	-13.20934300	-17.34853900	16.20982000
C	-13.17268100	-20.50923000	15.67139500
H	-12.36561100	-20.93614300	16.27161300
H	-12.74206300	-19.86733900	14.89482300
C	-14.04739200	-21.58920800	15.06628400
H	-14.46699400	-22.22544100	15.85044200
H	-14.86839500	-21.15077300	14.49152800
H	-13.45243400	-22.21482400	14.39296000
C	-12.32102200	-16.21430200	16.38972500
H	-11.44809800	-16.53430400	16.96617800
H	-11.99268700	-15.94875900	15.38136500
C	-13.03957200	-15.05343300	17.05706600
H	-13.91781600	-14.75733000	16.47653500
H	-12.36575100	-14.19310300	17.12998400
H	-13.36846500	-15.32250400	18.06416800
O	-12.04920200	-18.79983500	18.04868100
O	-14.53826100	-17.95058200	18.24103500
C	-14.90224600	-18.70218000	19.43988700
C	-16.28452700	-19.04651800	19.44447000
C	-16.95058600	-19.51196300	20.62874200
C	-17.06080600	-19.12265700	18.23745200
C	-18.25231200	-20.01165100	20.60505700
H	-16.43917200	-19.46934400	21.58361600
C	-18.36291000	-19.61307400	18.21805500
H	-16.61003900	-18.78833500	17.31166000
C	-18.96655300	-20.07788200	19.40023500
H	-18.71578300	-20.35223700	21.52546800
H	-18.91346900	-19.64546600	17.28317000
Li	-16.98230000	-21.41024700	19.04229500
C	-14.20883900	-18.13819600	20.65621600
H	-14.35424800	-18.78319500	21.52981500
H	-13.13195800	-18.08829800	20.47346500
H	-14.55900100	-17.13001100	20.92666300
Cl	-20.61840000	-20.69462400	19.37473600

P	-14.15572200	-21.85507900	19.52807100
O	-13.55421600	-22.46516500	20.92525400
O	-13.01128300	-22.32710400	18.49323700
C	-14.39938100	-22.65242200	22.08457800
H	-13.79810500	-22.33718300	22.94210500
H	-15.27493100	-21.99436300	22.02781700
C	-14.82643300	-24.10450600	22.21646300
H	-15.44206900	-24.40131900	21.36368800
H	-13.95155000	-24.75956300	22.26330600
H	-15.40804900	-24.24252100	23.13450800
C	-12.63934700	-23.72762600	18.34792000
H	-12.75026600	-23.95992600	17.28492300
H	-13.33575200	-24.35911200	18.90702000
C	-11.21057900	-23.92876600	18.81749600
H	-11.12424600	-23.70663500	19.88385200
H	-10.90445000	-24.96686400	18.64829500
H	-10.52833300	-23.27293900	18.26961000
O	-15.52666600	-22.47672600	19.23209200
H	-14.27552000	-20.30341600	19.45031700

Intrinsic reaction coordinate (IRC) for the transition state TS1a

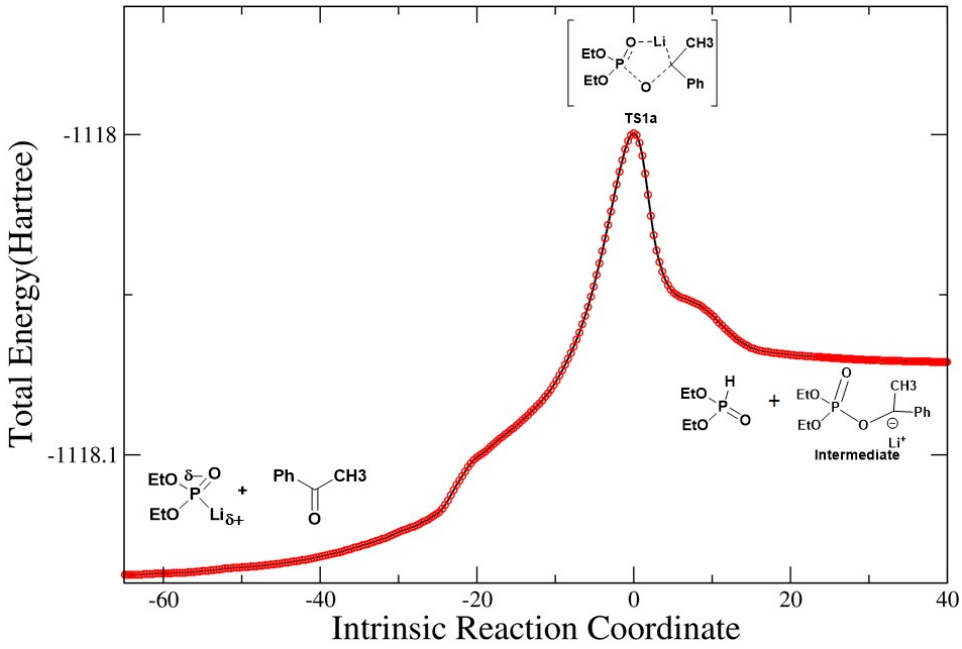
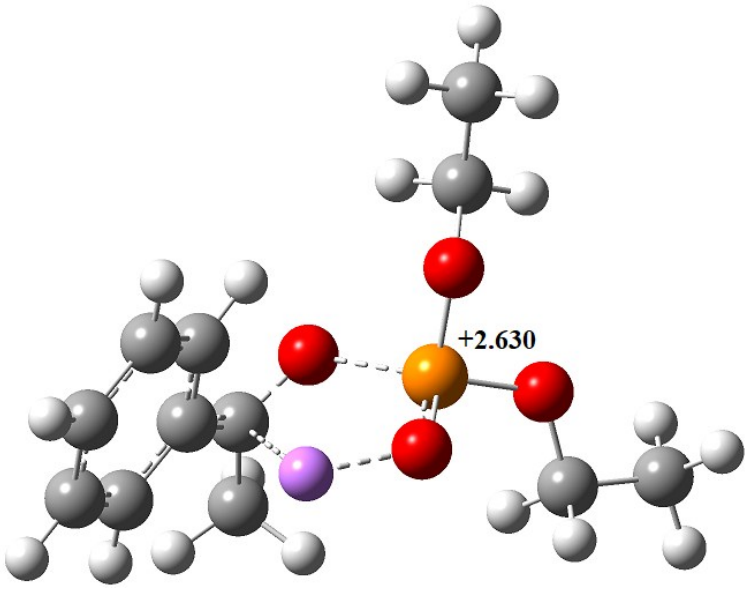


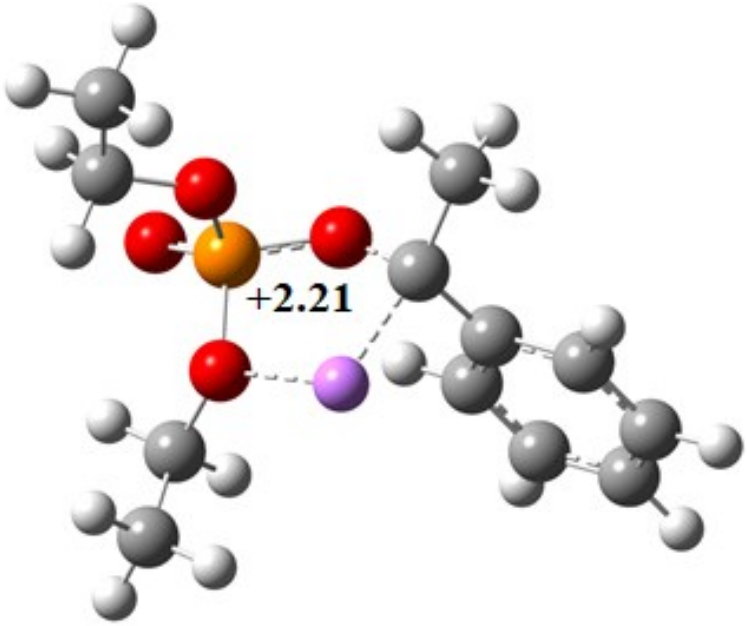
Figure *S4*. Intrinsic reaction coordinate (IRC) for the reaction of Li-diethyl phosphite with Acetophenone.

Optimized structures of Int. II and Int. III (*S5*)

Intermediate II



Intermediate III



In TS**1b**, Li^+ is found to be coordinating with four atoms (in between the two oxygens of OEt moieties, carbon and the phosphorous). Taking this structure as the reference, it has been found that the Li is not 4 coordinated in the **Int.III** but its coordination no 2 when it was optimized. Moreover, in both the intermediates (II and III), Li^+ is always forming a 5 membered ring which is quite surprising to us.

(The charge on P in **Int.II** and **Int.III** are 2.630 and 2.21 respectively having a difference of 0.4 (Mulliken charges). There is almost no interaction between P and Li in **Int.III** (bond length > 3.0 Å) which implies that phosphorus is coordinated by carbon of acetophenone moiety and oxygen of any one of the –OEt groups.

Table *S6*. Calculated rate coefficients using M06/6-31+G (d, p), B3LYP/6-31+G (d, p) level of theories

System	Activation Energy(E_a) (Kcal/mol)		Free Energy change($\Delta G^{\#}$) (Kcal/mol)		Rate Coefficients(s^{-1})		Reaction Time
	B3LYP	M06	B3LYP	M06	B3LYP	M06	
4-Methylbenzaldehyde	33.93	30.65	47.30	45.24	1.34×10^{-22}	4.24×10^{-21}	~ 4 h
Benzaldehyde	32.76	29.02	46.04	42.28	1.10×10^{-21}	6.33×10^{-19}	~ 4 h
4-Chlorobenzaldehyde	24.90	15.86	18.46	30.34	1.80×10^{-1}	3.53×10^{-10}	~ 15-20min
4-Methylacetophenone	23.79	18.41	37.28	32.39	2.90×10^{-15}	7.00×10^{-11}	~ 4 h
Acetophenone	22.43	16.9	35.39	30.75	6.98×10^{-14}	1.78×10^{-10}	~ 4 h
4-Chloroacetophenone	14.97	2.79	29.60	18.00	1.23×10^{-9}	3.96×10^{-1}	~ 15-20min

Table *S7*: Geometry optimized Energies (in Hartree) and imaginary frequency (in cm^{-1}) of all the transition states discussed in the text. All calculations have been performed at the B3LYP/6-31G (d, p) level of theory.

Entry	Substrate	TS1a	TS1b	TS2
1	Benzaldehyde	E= -1078.398150 υ (-ve)= -358.77	E= -1078.418000 υ (-ve)= -81.2687	E= -1804.449796 υ (-ve)= -797.7106
2	4-methylbenzaldehyde	E=-1117.691112 υ (-ve)= -368.73	E= -1117.711190 υ (-ve)= -80.5019	E= -1843.746427 υ (-ve)= -681.1619
3	4-chlorobenzaldehyde	E= -1538.022418 υ (-ve)= -335.38	E= -1538.022116 υ (-ve)= -90.3364	E= -2264.044965 υ (-ve)= -910.9808
4	Acetophenone	E= -1117.713609 υ (-ve)= -372.06	E= -1117.708768 υ (-ve)= -85.3057	E= -1843.735862 υ (-ve)= -456.1702
5	4-methylacetophenone	E= -1157.006057 υ (-ve)= -381.82	E= -1157.001760 υ (-ve)= -72.8092	E= -1883.027016 υ (-ve)= -426.6771
6	4-chloroacetophenone	E= -1577.325191 υ (-ve) = -171.81	E= -1577.313418 υ (-ve)= -84.7996	E= -2303.343281 υ (-ve)= -750.8079