*SUPPLEMENTARY INFORMATION***Beyond the Corey Reaction: One-Step Diolefination of Cyclic Ketones**

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Table 1s. The XYZ-coordinates of computed species:**TS1** (B3PW91/ 6-311+G(d), HF= -941.51391)

C	2.701490	1.462035	0.076425
C	3.722614	0.486330	-0.513136
C	3.579688	-0.977085	-0.094427
C	2.194875	-1.608247	-0.284499
C	1.147094	-1.096627	0.707990
C	0.457700	0.260854	0.427269
C	1.275713	1.234861	-0.444750
H	3.014253	2.479100	-0.187881
H	2.708507	1.425065	1.172370
H	0.717371	2.176756	-0.444484
H	1.342580	0.901960	-1.487806
H	3.666536	0.551867	-1.609292
H	4.734120	0.820411	-0.249340
H	4.319658	-1.565802	-0.651391
H	3.856276	-1.078317	0.964045
H	0.370643	-1.851990	0.870122
H	1.621231	-0.967686	1.688280
H	1.857464	-1.475863	-1.321830
H	2.300928	-2.691663	-0.149447
O	-0.099429	0.781430	1.459958
S	-2.466551	-0.137894	-0.329342
O	-3.608872	-0.562046	-1.165086
C	-2.576296	1.574819	0.142642
C	-2.456563	-0.982667	1.239226
C	-0.841706	-0.278729	-0.907857
H	-2.518584	2.164676	-0.772639
H	-2.303948	-2.042902	1.036997
H	-3.538153	1.726492	0.632761
H	-3.429841	-0.824431	1.704313
H	-1.711933	1.743974	0.806722
H	-1.625832	-0.536216	1.807008
H	-0.785980	0.362695	-1.790518
H	-0.691718	-1.320161	-1.200777

TS2 (B3PW91/ 6-311+G(d), HF= -1059.4120818)

C	3.595138	-.059775	-.941209
C	1.652608	-1.491661	.826700
C	2.789374	-2.284244	.153934
C	3.969008	-1.442153	-.374661
C	.321507	1.389214	-.374785
C	3.755997	1.084096	.076951
C	2.794698	2.268287	-.064628
C	1.381697	2.079180	.516051
H	2.365039	-2.866082	-.675033
H	2.034482	-.559176	1.242263
H	1.271186	-2.039852	1.692468
H	-.501788	2.098760	-.507989
H	.714886	1.205562	-1.382824
H	1.003455	3.077040	.762973
H	1.433656	1.564073	1.480469
H	2.728450	2.576143	-1.118007
H	3.246952	3.121635	.456155
H	3.664895	.690988	1.096489
H	4.787348	1.454571	.013763
H	2.572778	-.081828	-1.325305
H	4.497523	-2.031314	-1.133070
H	4.697785	-1.294882	.433039
H	3.189398	-3.030513	.850242
C	.471177	-1.208540	-.118372
H	-.219773	-2.058430	-.054183
H	.810491	-1.183168	-1.161463
H	4.219470	.163515	-1.814205
C	-.308544	.086487	.204067
O	-.742273	.182831	1.415067
S	-3.260847	-.112707	-.334467
O	-4.471080	-.252366	-1.168675
C	-3.275199	1.386599	.624368
C	-3.149783	-1.383142	.906750
C	-1.688215	-.122216	-1.071932
H	-3.272061	2.220247	-.078150
H	-3.065321	-2.337307	.386068
H	-4.190516	1.393231	1.216675
H	-4.065971	-1.352581	1.496892
H	-2.357010	1.340975	1.234998
H	-2.244913	-1.134326	1.486774
H	-1.689496	.688246	-1.804466
H	-1.607335	-1.078706	-1.593627

TS3 (B3PW91/ 6-311+G(d), HF= -1138.0302252)

C	4.683114	-1.159785	-0.273653
C	1.338519	-1.498623	0.449016
C	2.338934	-2.344696	-0.340074
C	3.781859	-2.318907	0.184767
C	-0.231251	1.145510	-0.459200
C	3.101987	2.461657	0.057529
C	1.648348	2.901986	-0.149414
C	0.625378	1.958870	0.523677
C	4.373439	0.244686	0.273825
C	3.469737	1.117962	-0.600267
H	2.339661	-2.023019	-1.391197
H	1.742579	-0.496082	0.577938
H	1.227805	-1.895334	1.464000
H	-1.024774	1.805632	-0.828234
H	0.354410	0.878003	-1.348113
H	-0.047423	2.529549	1.170147
H	1.143246	1.286979	1.212724
H	1.438094	2.986160	-1.224324
H	1.537380	3.917464	0.248967
H	3.279295	2.393710	1.139182
H	3.779834	3.247264	-0.298483
H	2.559810	0.566924	-0.851074
H	3.965840	1.298214	-1.562584
H	5.316186	0.785183	0.430382
H	3.927931	0.152800	1.273429
H	4.696701	-1.129699	-1.372306
H	5.706766	-1.424094	0.018666
H	4.275165	-3.246812	-0.130928
H	3.772062	-2.354618	1.283153
H	1.983427	-3.383744	-0.356111
C	-0.038988	-1.418547	-0.222314
H	-0.629644	-2.301197	0.051391
H	0.088332	-1.451249	-1.313293
C	-0.841290	-0.152149	0.160112
O	-1.217221	-0.064159	1.386264
S	-3.828892	-0.163185	-0.280331
O	-5.081243	-0.224545	-1.060821
C	-3.647117	1.408890	0.538716
C	-3.806927	-1.320139	1.070007
C	-2.295697	-0.436839	-1.043248
H	-3.553000	2.171527	-0.234295
H	-3.866115	-2.319531	0.637912
H	-4.548927	1.577912	1.127642
H	-4.677632	-1.123862	1.695994
H	-2.739364	1.312833	1.153085

TS4 (MP2/cc-pVDZ, MP2= - 863.1251262)

C	3.136888	-.776797	.080857
C	3.206026	.595604	-.602956
C	1.879416	1.367189	-.557335
C	1.206241	1.328466	.824474
C	.403787	.062778	1.100521
C	.627031	-1.161244	.453684
C	1.881238	-1.579821	-.295479
H	1.977123	1.467726	1.608272
H	.524235	2.193109	.930505
H	2.063411	2.415178	-.857497
H	1.181259	.946491	-1.305275
H	3.995518	1.200979	-.119201
H	3.511517	.466653	-1.658322
H	4.041214	-1.353512	-.186352
H	3.157432	-.655674	1.179381
H	2.060206	-2.649173	-.081956
H	1.729751	-1.521830	-1.393343
H	.032283	-1.996780	.847822
C	-.870626	.202142	1.714658
H	-1.336975	-.675147	2.186619
H	-1.156658	1.163269	2.168102
S	-2.138039	-.127249	-.167141
O	-3.511565	-.655728	.179196
C	-2.176531	1.527221	-.875550
C	-1.134707	-1.010571	-1.164206
H	-2.787600	1.514607	-1.790679
H	-2.621903	2.186704	-.115083
H	-1.138410	1.826809	-1.087411
H	-1.376873	-2.071394	-1.256689
H	-.506966	-.506012	-1.900220

TS5 (MP2/cc-pVDZ, MP2= -863.1947528)

C -1.832911 -1.784393 -.240245
 C -2.514182 -.674259 -1.055683
 C -3.216648 -.406822 -.218817
 C -2.256372 1.319588 .609643
 C -.811981 1.184646 .173163
 C -.108953 -.072431 .618030
 C -1.009758 -1.266198 .950128
 H -2.567175 2.372685 .499850
 H -2.333312 1.075988 1.683688
 H -3.790085 1.046554 -.913316
 H -3.958413 -.063683 .453593
 H -1.765367 -.181707 -1.701444
 H -3.252765 -1.134258 -1.737521
 H -2.596756 -2.488841 .140144
 H -1.173199 -2.361787 -.913952
 H -.378519 -2.088008 1.335794
 H -1.692506 -.995393 1.778759
 H .529433 -.464283 -.489835
 C -.219149 2.126713 -.599251
 H .782473 1.977023 -1.011399
 H -.745065 3.049938 -.864518
 S 2.639068 -.675474 -.001152
 O 1.543605 -.829684 -1.140946
 C 3.406310 .937203 -.315587
 C 1.059798 .075397 1.432155
 H 3.851565 .923429 -1.321870
 H 2.666555 1.747108 -.234446
 H 4.197707 1.070411 .441713
 H 1.237060 -.646352 2.242231
 H 1.437521 1.087713 1.637301

TS5_Li (MP2/cc-pVDZ, MP2= -870.51832)

C -1.7459599 0.5011153 -1.651836
 C -1.1368196 -0.8461356 -2.0868392
 C 0.0436919 -0.7272012 -3.0659856
 C 1.2480659 0.0919105 -2.5283389
 C 1.3985985 0.0347105 -1.0205676
 C 0.3852897 0.8361739 -0.2219323
 C -0.7453693 1.4991543 -1.0199466
 H 2.1709552 -0.2926982 -2.9919050
 H 1.1610826 1.1434735 -2.8478322
 H 0.3828951 -1.7517536 -3.2974186
 H -0.3145493 -0.2900614 -4.0144781
 H -0.7331630 -1.4166484 -1.2184124
 H -1.9218939 -1.4713697 -2.5558643
 H -2.2328118 0.9638207 -2.5279652
 H -2.5976215 0.3486478 -0.9442643
 H -1.2993180 2.1879842 -0.3590731
 H -0.3124059 2.1308637 -1.8128369
 H -0.2532605 -0.1380532 0.3760741
 C 2.3700545 -0.7125357 -0.4456141
 H 2.4968554 -0.7773886 0.6393878
 H 3.0935176 -1.2560347 -1.0603529
 S -0.4965069 0.1684452 2.5499193
 O -0.9233758 -0.7570637 1.2757750
 C 0.8534816 -0.7906439 3.2682215
 C 0.7626062 1.4624691 0.9951397
 H 0.4460744 -1.6620966 3.8010665
 H 1.5447723 -1.1082517 2.4751548
 H 1.3674272 -0.1226893 3.9798122
 H 0.2839108 2.4009684 1.2984748
 H 1.7671010 1.2977097 1.4075595
 Li -2.2311903 -1.3732295 0.1606942

TS4_Li (MP2/cc-pVDZ, MP2= -870.4592798)

C -0.8287779 -0.0129666 -3.2829739
 C 0.3883905 0.9192294 -3.3471845
 C 1.2193004 0.9318109 -2.0558922
 C 1.4775798 -0.4738915 -1.4892255
 C 0.3284160 -1.0430550 -0.6707815
 C -1.0163456 -0.6654797 -0.8222307
 C -1.6222426 0.1113806 -1.9701621
 H 1.7016864 -1.1722068 -2.3177904
 H 2.3840316 -0.4767984 -0.8565935
 H 2.1830442 1.4337164 -2.2515242
 H 0.7033301 1.5419675 -1.2891050
 H 1.0323014 0.6113414 -4.1904577
 H 0.0550281 1.9496473 -3.5668200
 H -1.4992877 0.2095930 -4.1308733
 H -0.5170732 -1.0659814 -3.4076537
 H -2.6490850 -0.2669728 -2.1164991
 H -1.7375774 1.1827736 -1.7102425
 H -1.7233949 -1.2660459 -0.2325034
 C 0.6159797 -1.8170235 0.4764244
 H -0.1662797 -2.4467895 0.9195754
 H 1.6491814 -2.1039076 0.7164702
 S 0.0662699 -0.0009005 1.9505709
 O -0.2212156 -0.2423636 3.4778037
 C 1.5053499 1.0705789 1.8126856
 C -1.1665911 0.8701589 1.1972540
 H 1.2911741 2.0342542 2.2984035
 H 2.3261795 0.5447635 2.3227191
 H 1.7269115 1.1998969 0.7428433
 H -2.1752195 0.4459183 1.2404678
 H -0.9437762 1.7208408 0.5497769
 Li -1.5575427 0.9605998 3.8689326

Figure 1s. The MP2/cc-pVDZ optimized geometries of the transition structures for the [2,3]-sigmatropic rearrangement of ylide and the elimination of sulfenic acid from sulfoxid with Li-ion present.

^{13}C NMR spectra

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16b

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