Supplementary Material

Diastereoselective deacylative aldol reaction of 3-acetyl-3-fluorooxindoles with aldehydes

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2. COMPUTATIONAL DETAILS

All of the calculations were performed using the Gaussian09 program.\(^1\) Computations were done using B3LYP functional\(^2\) in conjunction with Grimme's dispersion correction.\(^3\) Standard basis sets def2SVP was employed.\(^4\) The nature of stationary points was defined on the basis of calculations of normal vibrational frequencies (force constant Hessian matrix). The optimizations were carried out using the Berly analytical gradient optimization method.\(^5\) Minimum energy pathways for the reactions studied were found by gradient descent of transition states in the forward and backward direction of the transition vector (IRC analysis),\(^6\) using using the Hratchian-Schlegel algorithm.\(^7\) Analytical second derivatives of the energy were calculated to classify the nature of every stationary point, to determine the harmonic vibrational frequencies, and to provide zero-point vibrational energy corrections. The thermal and entropic contributions to the free energies were also obtained from the vibrational frequency calculations, using the unscaled frequencies. Correction to free energy was made by substracing \(S_{\text{trans}}\) contribution and considering a 1M concentration.\(^8\) Structural representations were generated using CYLView.\(^9\)

### Energies

| EN | -1282.122492 | -1282.187897 |
| BA | -345.627457  | -345.657969  |
| SC | -1395.305108 | 0.0          | -1395.374081 | 0.0          |
| (R,R)-TS | -1395.302850 | 1.4          | -1395.367677 | 4.0          | -354.0 |
| (R,S)-TS | -1395.302850 | 1.4          | -1395.367677 | 4.0          | -354.4 |
| (R,R)-PR | -1395.308442 | -2.1         | -1395.373290 | 0.5          |
| (R,S)-PR | -1395.305077 | 0.0          | -1395.368071 | 3.8          |

### Cartesian Coordinates

\(^1\) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian, Inc., Wallingford CT.: 2009.

\(^2\) (a) Becke, A. D. J. Chem. Phys. 1993, 98, 5648-5652. (b) Lee, C.; Yang, W.; Parr, R. G. Phys. Rev. B 1988, 37, 785-789.

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\(^5\) (a) Schlegel, H. B. J. Comput. Chem. 1982, 3, 214218. (b) Schlegel, H. B. In Modern Electronic Structure Theory; Yarkony, D. R., Ed.; World Scientific Publishing: Singapore, 1994.

\(^6\) (a) Fukui, K. Acc. Chem. Res. 1981, 14, 363-368. (b) Fukui, K. J. Phys. Chem. 1970, 74, 4161-4163.

\(^7\) Hratchian, H. P.; Schlegel, H. B. J. Phys. Chem. A 2002, 106, 165-169.

\(^8\) Tanaka, R.; Yamashita, M.; Chung, L. W.; Morokuma, K.; Nozaki, K. Organometallics 2011, 30, 6742-6750

\(^9\) C. Y. Legault, Université de Sherbrooke, 2009, http://www.cylview.org.
### Cartesian Coordinates

**PR-RR**

| Element | X            | Y            | Z            |
|---------|--------------|--------------|--------------|
| C       | -0.9945226627 | -1.0646935582 | -1.7651170980 |
| C       | -0.4629806304  | -0.0846136213  | -2.8144174404  |
| C       | -1.6384676673  | -0.2204012837  | -0.5556020680  |
| O       | -2.6640186296  | 0.5210173672   | -0.9815750774  |
| O       | -1.1317416439  | 0.7049631507   | -3.4801977512  |
| Li      | -2.8423684964  | 1.2621860034   | -2.6329402931  |
| O       | -4.4275879131  | 0.7323606103   | -3.6582813448  |
| C       | -4.5217653978  | -0.6738627016  | -3.9287544150  |
| C       | -5.6182144057  | 1.0780479864   | -2.9425792926  |
| C       | -5.2343828282  | -1.2920976435  | -2.7081138547  |
| O       | -3.5025187910  | -1.0509849129  | -4.0759808225  |
| H       | -5.1041454924  | -0.8205755894  | -4.8559703029  |
| C       | -5.8044306614  | -0.6925491471  | -1.9472775479  |
| H       | -6.4657739256  | 1.1482042412   | -3.6504993609  |
| H       | -5.4591713312  | 2.0638849720   | -2.4848992778  |
| H       | -6.0220236091  | -1.9909573593  | -3.0259024739  |
| H       | -4.5156479790  | -1.8370294197  | -2.0847696734  |
| H       | -6.8548488961  | -0.1946040624  | -1.6475699522  |
| H       | -5.1905348434  | 0.1257912264   | -1.0575535003  |
| O       | -2.9300406294  | 3.1910889082   | -2.4386257453  |
| C       | -2.1613152885  | 4.1344804661   | -3.2045741090  |
| C       | -3.2074957836  | 3.7039762105   | -1.118869565   |
| C       | -2.1546576111  | 5.4220855648   | -2.3806430057  |
| H       | -2.6259208352  | 4.2505974135   | -4.1958349869  |
| H       | -1.1433257897  | 3.7303357831   | -3.343434669   |
| C       | -2.2634509307  | 4.8893112695   | -0.9459975960  |
| H       | -3.0449030833  | 2.8769703427   | -0.4139726458  |
| H       | -4.2646958868  | 4.0221327223   | -1.0746662464  |
| H       | -1.2538281513  | 6.0271600610   | -2.5569502975  |
| H       | -3.0339520056  | 6.0389691564   | -2.6265849459  |
| H       | -1.2812595100  | 4.5464915452   | -0.5849152277  |
| H       | -2.6482914687  | 5.6328560177   | -0.2335230535  |
| F       | -2.0198050609  | -1.8428554835  | -2.2943689493  |
| N       | 0.8996450652   | -0.1711500019  | -2.8146162511  |
| C       | 1.7741927190   | 0.7231271282   | -3.5390900387  |
| H       | 2.3914730837   | 1.3066622943   | -2.8377534406  |
| H       | 1.1491767920   | 1.4059040548   | -4.1271040936  |
| H       | 2.4349501477   | 0.1593956800   | -4.2153423422  |
| C       | 0.2224389391   | -1.8498233430  | -1.3932402633  |
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PR-RS

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| C     | -0.8631678145 | -0.5647992426 | -1.0381180451 |
| H     | -0.5209503823 | 0.4272273818  | -2.1568208880 |
| C     | -0.9528294337 | 0.2706612429  | 0.3343675400  |
| O     | -1.9319941375 | 1.1820743074  | 0.2732745455  |
| O     | -1.2304360741 | 1.3494436969  | -2.5504216989 |
| Li    | -2.6273690365 | 1.9242922478  | -1.2147718809 |
| O     | -4.3906311535 | 1.2525444992  | -1.7202032018 |
| C     | -4.5355863174 | 0.4262466552  | -2.8913758954 |
| C     | -5.0582299212 | 0.6521234144  | -0.5892617863 |
| C     | -5.6078051915 | -0.6001816080 | -2.5336260333 |
| H     | -3.5687953292 | -0.0572921550 | -3.1018637492 |
| H     | -4.8060161966 | 1.0706094931  | -3.7419838087 |
| C     | -5.3888728400 | -0.7720835711 | -1.0252084471 |
| H     | -5.9703508868 | 1.2335042869  | -0.3673515332 |
| H     | -4.3677322304 | 0.7043965893  | 0.2648313083  |
| H     | -6.6133379946 | -0.1952353039 | -2.7332018904 |
| H     | -5.4965020966 | -1.5349595968 | -3.1017827200 |
| H     | -6.2633374571 | -1.1812536354 | -0.4992108161 |
|   |   |   |   |   |
|---|---|---|---|---|
| H | -4.5264722262 | -1.4294944582 | -0.8407575464 |
| O | -2.7357665437 | 3.8556537025 | -1.538464789 |
| C | -1.5267616601 | 4.4859089336 | -1.9732654152 |
| C | -3.7649850830 | 4.3316942087 | -2.4105711418 |
| C | -1.6113683178 | 4.5198396864 | -3.5103819568 |
| H | -0.6836543698 | 3.8989306132 | -1.5860249944 |
| H | -1.4790279114 | 5.5056086863 | -1.5499824177 |
| C | -3.1225998772 | 4.329339485 | -3.8036344219 |
| H | -4.0582682611 | 5.3531537607 | -2.1048905910 |
| H | -4.6241882202 | 3.6576835797 | -2.3065317953 |
| H | -1.2209863599 | 5.4669508739 | -3.9095718352 |
| H | -1.0275856921 | 3.6969178508 | -3.9426701776 |
| H | -3.5379271796 | 5.118745239 | -4.4461819824 |
| C | -3.2999497885 | 3.3635810223 | -4.2991386652 |
| F | -2.1175627898 | -1.1244534790 | -1.2783786975 |
| N | 0.7403321382 | 0.1445308531 | -2.5993952050 |
| C | 1.4514262002 | 0.9149410014 | -3.5957395697 |
| H | 2.4106592336 | 1.7252410699 | -3.1934121596 |
| H | 0.8280128139 | 1.7740068628 | -3.8715868345 |
| H | 1.6483966494 | 0.3063962229 | -4.4925337966 |
| C | 0.2520459141 | -1.5601726115 | -1.1283251341 |
| C | 0.4726756556 | -2.7709005324 | -0.4845485395 |
| H | -0.2740440490 | -3.1790771530 | 0.1971969558 |
| C | 1.2149315875 | -1.0507290175 | -2.0194171362 |
| C | 1.6743380423 | -3.4569253738 | -0.7288350990 |
| C | 1.8620472626 | -4.4119443242 | -0.2336982612 |
| C | 2.6340071263 | -2.9234426225 | -1.5949013409 |
| H | 3.5678940566 | -3.4638062295 | -1.7663072968 |
| C | 2.4177785893 | -1.7049977688 | -2.2604146681 |
| H | 3.1628169669 | -1.2991075065 | -2.9459737914 |
| H | 0.0830753904 | 0.6950265304 | 0.4278809123 |
| C | -1.0961433220 | -0.7413153524 | 1.4738608579 |
| C | 0.0038581617 | -1.1183458613 | 2.2539488209 |
| C | -2.3436409642 | -1.3207291429 | 1.7456738565 |
| C | -0.1291338998 | -2.0653342698 | 3.2751019619 |
| H | 0.9800688190 | -0.6685848347 | 2.0520110584 |
| C | -2.4812557485 | -2.2744232609 | 2.7568423194 |
| H | -3.2043331108 | -1.0138633945 | 1.1518772469 |
| C | -1.3728354597 | -2.6523310390 | 3.5253254745 |
| H | 0.7401655135 | -2.3454502223 | 3.8757753557 |
| H | -3.4585118720 | -2.7245235487 | 2.9515997175 |
| H | -1.4814017511 | -3.3948321075 | 4.3200093928 |
| Symbol | x    | y    | z    |
|--------|------|------|------|
| C      | 0.3566839368 | -1.2116721677 | 0.7703238795 |
| C      | 0.0682404808 | -0.0645223318  | 1.4551590526 |
| C      | -2.2321020488 | 1.325088984   | -1.1543247905 |
| O      | -2.8824948585 | 1.6801732191  | -0.1778198525 |
| H      | -1.1292852866 | 1.2380016071  | -1.0735957914 |
| O      | -0.2312225919 | 1.1692217090  | 1.3270314730  |
| Li     | -1.9649880156 | 1.7887150453  | 1.5701576876  |
| O      | -2.9130424861 | 0.5429958182  | 2.7135970819  |
| C      | -2.3006218063 | 0.2123097855  | 3.9747768385  |
| C      | -3.5699921116 | -0.6143531105 | 2.1486756882  |
| C      | -2.2535576489 | -1.3109737143 | 1.2475261276  |
| C      | -1.3086727208 | 0.6849071429  | 4.0094386398  |
| C      | -2.9188166768 | 0.6245305796  | 4.7922099520  |
| C      | -3.5213061122 | -1.6863850121 | 3.2371564516  |
| H      | -4.5929754641 | -0.3279458607 | 1.8610929096  |
| H      | -3.0197636056 | -0.9219193232 | 1.2475261276  |
| H      | -2.2406997849 | -1.7031243889 | 5.0413858077  |
| H      | -1.3595138411 | -1.6783022202 | 3.4910300455  |
| H      | -4.4071728045 | -1.6179087098 | 3.8889820567  |
| H      | -3.4840960820 | -2.7011242928 | 2.8158045461  |
| O      | -2.4326972109 | 3.5575480852  | 2.2087665411  |
| C      | -3.7662857477 | 3.6975743506  | 2.7145848451  |
| C      | -2.2364402971 | 4.6503564338  | 1.3029476661  |
| C      | -4.6010281881 | 4.1033462869  | 1.4943278461  |
| H      | -4.0528749566 | 2.7371892510  | 3.1610263565  |
| C      | -3.7780399446 | 4.4824685418  | 3.4928965452  |
| C      | -3.5857937566 | 4.8414702327  | 0.5842163460  |
| H      | -1.9582526242 | 5.5495332824  | 1.8809001204  |
| H      | -1.4030246846 | 4.3910299264  | 0.6356081369  |
| H      | -5.4588173380 | 4.7300252835  | 1.7764608919  |
| H      | -4.9833837764 | 3.2061511160  | 0.9876942339  |
| H      | -3.8226116971 | 5.9087183679  | 0.4690669154  |
| H      | -3.5632188421 | 4.3887983355  | -0.4161960716 |
| F      | -1.2626387489 | -1.1958404688 | -0.2547456835 |
| N      | 0.9509536633  | -0.5302068343 | 2.4608346537  |
| C      | 1.6082376442  | 0.3278533934  | 3.4121001154  |
| H      | 2.7061316563  | 0.2434219313  | 3.3443004781  |
| H      | 1.3158761083  | 1.3614999007  | 3.1860216327  |
| H      | 1.3074844140  | 0.0897976699  | 4.4468647893  |
| C      | 0.2108634153  | -2.3779876686 | 1.396816735   |
| C      | 0.1179256244  | -3.7623828811 | 1.1058015996  |
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| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| C    | -0.5147691425 | -4.1432033719 | 0.3001713172 |
| C    | 1.0458212533  | -1.9085601240 | 2.4134426264 |
| C    | 0.8431090218  | -6.4008212880 | 1.9188200810 |
| H    | 0.7726251961  | -5.7167494005 | 1.74091280165 |
| C    | 1.6610114608  | -4.1655175487 | 2.9605379327 |
| H    | 2.2173517671  | -4.8730227465 | 3.5802290657 |
| C    | 1.7690467925  | -2.7892279697 | 3.2158993303 |
| H    | 2.3990474000  | -2.4178190474 | 4.0274386387 |
| C    | -2.8223386651 | 0.9888990584  | -2.454604671 |
| C    | -1.9827043098 | 0.5555999674  | -3.4942401484 |
| C    | -4.2109497227 | 1.0818498545  | -2.6619762116 |
| C    | -2.5255406566 | 0.2187605292  | -4.7345927016 |
| H    | -0.9062937140 | 0.4801756731  | -3.3200107085 |
| C    | -4.7493249543 | 0.7476696469  | -3.901200889 |
| H    | -4.8457578312 | 1.4169766758  | -1.8395311273 |
| C    | -3.9066195472 | 0.3162133818  | -1.4830938355 |
| H    | -1.8760724675 | -0.1202761422 | -5.544260233 |
| H    | -5.8261462923 | 0.8190123345  | -4.0689748128 |
| H    | -4.3326691573 | 0.0531466640  | -5.907377992 |

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| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| C    | 0.5173291099 | -1.4958086930 | -0.1733188616 |
| C    | 0.2108481885 | -0.4858764854 | -1.1848834204 |
| C    | 0.1884729440 | -0.3532975081 | 1.4830938355 |
| O    | -1.0220643317 | 0.0448600580 | 1.4200208542 |
| O    | -0.8930238900 | 0.0140332028 | -1.4647843174 |
| Li   | -2.1990884087 | 0.2289799989 | -0.0280369512 |
| O    | -3.5551402432 | -1.1575668716 | 0.0077315353 |
| C    | -3.5094209409 | -2.2045818767 | -0.9855293735 |
| C    | -3.7856740914 | -1.7145418185 | 1.3173865348 |
| C    | -3.9125616765 | -3.4856658340 | -0.2548149868 |
| H    | -2.4813504123 | -2.2628812471 | -1.3738264045 |
| H    | -4.1894820864 | -1.9397907162 | -1.8099372716 |
| C    | -3.4580978766 | -3.1969819540 | 1.1810426691 |
| H    | -4.8426804199 | -1.5549425500 | 1.5969111170 |
| H    | -3.133373616 | -1.835718709 | 2.0246784137 |
| H    | -5.0052431327 | -3.6249911312 | -0.2898632863 |
| H    | -3.4413083682 | -4.3780737134 | -0.6912208850 |
| H    | -3.9682321348 | -3.8142136282 | 1.9344985618 |
| H    | -2.3724205483 | -3.3469674092 | 1.2745736060 |
| O    | -2.8677322676 | 2.0469345627 | -0.1519340746 |
| C     | -2.7533143549  | 2.7399839639 | -1.3993992972 |
| C     | -2.5864432829  | 2.9577883521 | 0.9285779839  |
| C     | -1.6422837636  | 3.7556610900 | -1.1621343443 |
| H     | -3.7113173674  | 3.2360293387 | -1.6440037268 |
| H     | -2.5214088403  | 1.9968701316 | -2.1740334261 |
| C     | -1.8950948398  | 4.1837635434 | 0.2948859632  |
| H     | -1.9486325593  | 2.4149452291 | 1.6405698404  |
| H     | -3.5296749510  | 3.2320516684 | 1.4295845597  |
| H     | -0.6646393320  | 3.2603818771 | -1.2644906825 |
| H     | -1.6749302910  | 4.5969050116 | -1.8690430608 |
| H     | -0.9673294031  | 4.4506735684 | 0.8207256440  |
| H     | -2.5597347368  | 5.0599051540 | 0.3279614318  |
| F     | -0.4102201202  | -2.4719793907 | 0.0718857134 |
| N     | 1.4275247926   | -0.0476720913 | -1.6808372485 |
| C     | 1.5913299846   | 1.1063454304 | -2.5319459282 |
| H     | 2.0939233098   | 0.8336584335 | -3.4733915529 |
| H     | 2.1807827623   | 1.8854904302 | -2.0227926471 |
| H     | 0.5932591576   | 1.5016265356 | -2.7582160263 |
| C     | 1.9267506616   | -1.8203526384 | -0.3112282908 |
| C     | 2.7702478545   | -2.7542129204 | 0.2894204172 |
| H     | 2.3642074303   | -3.5176835610 | 0.9568717200 |
| C     | 2.4691357423   | -0.8374754252 | -1.1805664305 |
| C     | 4.1468408826   | -2.6896220759 | 0.0253454747 |
| C     | 4.8192809485   | -3.417551288 | 0.4852953019 |
| H     | 4.6706279443   | -1.6986298967 | -0.8158628017 |
| C     | 5.7468510797   | -1.6585131942 | -0.9995539981 |
| C     | 3.8339515004   | -0.7543124153 | -1.4325330185 |
| H     | 4.2438711903   | 0.0166092433 | -2.0871440202 |
| H     | 0.4217433425   | -1.2447465006 | 2.1078256004 |
| C     | 1.3089074638   | 0.6398556395 | 1.4502388984 |
| C     | 1.1051015058   | 1.9048094290 | 0.8797330613 |
| C     | 2.5814346158   | 0.3162525635 | 1.9425301102 |
| C     | 2.1515279803   | 2.8227233284 | 0.7868372046 |
| H     | 0.1150105652   | 2.1443170766 | 0.4960978587 |
| C     | 3.6311096969   | 1.2341765797 | 1.8569252513 |
| H     | 2.7500244813   | -0.6667229619 | 2.3874801527 |
| C     | 3.4214080559   | 2.4885177478 | 1.2745955241 |
| H     | 1.9785569322   | 3.8017277779 | 0.3321986663 |
| H     | 4.6190275218   | 0.9671346718 | 2.2401359263 |
| H     | 4.2432703877   | 3.2052616450 | 1.2037533023 |

TS-RS
C  -4.4323380840  1.5850731320  -1.3818044241
H  -5.4764401289  1.3617183404  -1.6129939077
C  -0.607366324  2.8963833023  -1.0574595512
H  -4.8176807588  3.6838844954  -1.0353115882
C  -2.7250205072  3.2213031356  -0.7653238167
H  -2.4368106405  4.2455045316  -0.5221557103
C  -2.1292710741 -1.4394656989  0.9913990040
C  -3.3345357884 -0.8416644021  1.3881640636
C  -2.1347179987 -2.7792998629  0.5735388406
C  -4.5275854573 -1.5685055690  1.3684982483
H  -3.333300570  0.2019040460  1.7122313235
C  -3.3273205778 -3.5029963056  0.5426139840
H  -1.1893342639 -3.2353198773  0.2761380654
C  -4.5279755470 -2.8997814142  0.9404463588
H  -5.4602709883 -1.0933412174  1.6824729355
H  -3.3250179983 -4.5448563204  0.2116181865
H  -5.4606260659 -3.4691270710  0.9202306748