

Mechanism of Pd-catalyzed Formation of Coumarin. A Theoretical Study.

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Supporting Information

XYZ coordinates for all stationary points in the Concerted Metalation-Deprotonation mechanism.

Structures were obtained from the RI-TPSS/def2-SVP (def2-TZVPP for Pd) level of theory. These structures include:

cNC - minima of bound Pd(OAc)₂ and phenylpropiolate with non-cleaved aryl C-H

c1TS - 1st transition state from the cleaving of the aryl C-H

cC - minima from cleaved aryl C-H

c2TS - 2nd transition state from concerted trans-protonation to ethynyl group and coumarin ring closure

cP - minima of coumarin product with still bound Pd(OAc)₂ catalyst

c3TS - 3rd transition state for removal of Pd(OAc)₂ catalyst from coumarin product

All structures that have trifluoroacetate will start with **f**.

After each label in bold, the absolute total energy (OK) is given (in hartrees), followed by the entropic contribution (in kJ/mol), followed by the imaginary frequency (a negative number) for only the transition state (in cm⁻¹).

XYZ coordinates follow on the next set of lines for each label.

cNC

-1081.30824970455 au, 483.55 kJ/mol

C 1.6731 -0.4620 -2.6606

C 1.4689 0.8969 -2.4600

C 0.2113 1.3440 -1.9790

C 0.6348 -1.3957 -2.4116

C -0.6078 -0.9690 -1.9586

C -0.8485 0.4095 -1.7141

O -0.0584 2.7082 -2.1507

C -0.6928 3.4100 -1.1580

O -1.0759 4.5412 -1.3214

C -0.8477 2.6606 0.0883

C -1.3004 2.2507 1.1864

H 2.6437 -0.8134 -3.0245

H 2.2359 1.6427 -2.6840

H 0.8154 -2.4611 -2.5836

H -1.4162 -1.6792 -1.7653
H -1.8701 0.7586 -1.5366
H -1.8018 2.1855 2.1419
Pd -0.0221 0.7453 0.4072
O 2.1031 0.6807 1.7712
O 1.2616 -0.7819 0.3262
C 2.1503 -0.4422 1.2413
C 3.1537 -1.5070 1.6069
H 4.0021 -1.0564 2.1428
H 3.4989 -2.0407 0.7065
H 2.6558 -2.2414 2.2647
O -0.9331 -0.4303 1.9536
O -2.8534 -0.0089 0.8267
C -2.1988 -0.6159 1.6881
C -2.8656 -1.6550 2.5921
H -2.1533 -2.4339 2.9033
H -3.2383 -1.1439 3.4976
H -3.7243 -2.0955 2.0631

fcNC

-1676.33833351352 au, 354.28 kJ/mol

C 1.8465 -0.1727 -2.4182
C 1.5655 1.1299 -2.0240
C 0.2137 1.5230 -1.8691
C 0.8094 -1.1071 -2.6664
C -0.5182 -0.7318 -2.5274
C -0.8492 0.5913 -2.1110
O -0.0156 2.8983 -1.7888
C -0.9876 3.4223 -0.9704
O -1.2934 4.5840 -1.0166
C -1.6089 2.4360 -0.0790
C -2.4486 1.7529 0.5504
H 2.8887 -0.4872 -2.5222
H 2.3505 1.8651 -1.8356
H 1.0639 -2.1285 -2.9621
H -1.3292 -1.4383 -2.7245
H -1.8748 0.9531 -2.2330
H -3.2880 1.3756 1.1203
Pd -0.6902 0.5549 0.1679
O 2.1127 0.5916 1.0694
O 0.6485 -0.9251 0.2149
C 1.7743 -0.5397 0.7628
C 2.7367 -1.7502 0.9195
F 3.8266 -1.4161 1.6197
F 3.1424 -2.1676 -0.3125
F 2.1357 -2.7884 1.5281

O -2.5212 -1.2228 1.4298
O -0.8769 0.1526 2.1720
C -1.7539 -0.8032 2.2896
C -1.7609 -1.4045 3.7252
F -2.5466 -2.4888 3.7768
F -0.5190 -1.7609 4.1043
F -2.2328 -0.4977 4.6103

c1TS

-1081.28408092116 au, 418.47 kJ/mol, -1432.14 cm⁻¹

C 0.7698 0.2153 -4.3213
C 0.7391 1.5476 -3.8956
C 0.5855 1.8436 -2.5319
C 0.6422 -0.8197 -3.3845
C 0.5042 -0.5174 -2.0206
C 0.4900 0.8177 -1.5752
O 0.5875 3.2133 -2.2423
C -0.0085 3.7436 -1.1433
O -0.0928 4.9417 -0.9949
C -0.5077 2.7842 -0.1577
C -1.2236 2.2294 0.7159
H 0.8903 -0.0105 -5.3857
H 0.8292 2.3808 -4.5989
H 0.6611 -1.8664 -3.7052
H 0.4377 -1.3303 -1.2900
H -1.3707 -0.7689 0.4201
H -2.0147 1.9951 1.4183
Pd 0.4300 0.9917 0.4144
O 0.6749 0.3124 2.4917
O 1.8229 -0.5096 0.7992
C 1.5336 -0.5260 2.0529
C 2.1845 -1.5294 2.9641
H 2.7345 -1.0046 3.7633
H 2.8666 -2.1788 2.3971
H 1.3981 -2.1388 3.4405
O -2.4250 -0.4898 1.1959
O -0.8744 -1.9031 0.9374
C -1.8727 -1.5503 1.6590
C -2.2936 -2.2518 2.9092
H -3.3701 -2.1153 3.0860
H -2.0334 -3.3187 2.8538
H -1.7383 -1.7952 3.7482

fc1TS

-1676.28981899956 au, 280.91 kJ/mol, -1259.84 cm⁻¹

C -0.3655 0.4705 -4.2440

C 0.4917 1.4833 -3.7921
C 0.8370 1.5856 -2.4314
C -0.8708 -0.4634 -3.3373
C -0.5596 -0.3445 -1.9526
C 0.3452 0.6623 -1.4937
O 1.7417 2.6052 -2.1448
C 1.7843 3.2572 -0.9368
O 2.5504 4.1693 -0.7568
C 0.8419 2.7448 0.0563
C -0.1463 2.5945 0.8163
H -0.6214 0.4106 -5.3059
H 0.9089 2.2232 -4.4822
H -1.5286 -1.2739 -3.6664
H -0.7388 -1.2051 -1.2941
H -2.0128 0.0338 -1.5542
H -1.0136 2.7151 1.4551
Pd 0.6473 0.6854 0.4515
O 0.9015 0.0139 2.5354
O 0.9148 -1.3613 0.7941
C 0.9824 -1.1495 2.0569
C 1.1131 -2.3632 2.9989
F 1.8168 -2.0379 4.0939
F 1.7217 -3.3881 2.3814
F -0.1175 -2.7629 3.3812
O -3.2170 -0.5226 -1.0200
O -2.3499 0.6156 0.7483
C -3.1567 -0.1492 0.2232
C -4.2248 -0.8546 1.1053
F -5.3417 -1.1589 0.4190
F -3.7022 -2.0065 1.5883
F -4.5673 -0.0818 2.1495

cC

-1081.33361204992 au, 484.86 kJ/mol

C 0.7091 0.1934 -4.2584
C 0.6910 1.5271 -3.8355
C 0.5437 1.8259 -2.4718
C 0.5722 -0.8396 -3.3206
C 0.4367 -0.5363 -1.9560
C 0.4389 0.8009 -1.5151
O 0.5572 3.1954 -2.1809
C -0.0279 3.7253 -1.0760
O -0.1024 4.9230 -0.9201
C -0.5318 2.7644 -0.0931
C -1.2643 2.2086 0.7696
H 0.8272 -0.0347 -5.3227

H 0.7869 2.3580 -4.5409
H 0.5830 -1.8866 -3.6407
H 0.3522 -1.3455 -1.2211
H -1.9927 -0.5831 -0.0240
H -2.0701 2.0293 1.4716
Pd 0.3729 0.9612 0.4760
O 0.5839 0.2353 2.5332
O 1.7625 -0.5483 0.8456
C 1.4585 -0.5898 2.0940
C 2.1030 -1.5994 3.0004
H 2.6079 -1.0815 3.8330
H 2.8210 -2.2153 2.4407
H 1.3163 -2.2434 3.4282
O -2.4031 -0.7656 0.8514
O -0.7493 -2.3092 0.8401
C -1.6732 -1.7667 1.4173
C -2.1131 -2.0583 2.8301
H -3.1890 -1.8709 2.9674
H -1.8571 -3.0966 3.0852
H -1.5502 -1.3767 3.4932

fcC

-1676.32791562323 au, 321.76 kJ/mol

C 1.0280 -0.2766 -4.3706
C 0.9573 1.0618 -3.9679
C 0.4252 1.3833 -2.7097
C 0.5226 -1.2870 -3.5404
C 0.0337 -0.9658 -2.2640
C 0.0443 0.3660 -1.8171
O 0.3240 2.7525 -2.4556
C -0.4266 3.2605 -1.4431
O -0.7730 4.4199 -1.4423
C -0.7410 2.3480 -0.3402
C -1.2432 1.9660 0.7549
H 1.4615 -0.5258 -5.3443
H 1.2986 1.8783 -4.6109
H 0.5369 -2.3332 -3.8623
H -0.2976 -1.7589 -1.5874
H -3.4639 -1.0214 -0.0282
H -1.8006 1.9897 1.6859
Pd 0.0908 0.5011 0.1784
O 0.7170 -0.0859 2.2098
O 1.3826 -1.1775 0.4018
C 1.4080 -0.9953 1.6583
C 2.3134 -1.8940 2.5268
F 3.1100 -1.1326 3.3020

F 3.0854 -2.6798 1.7623
F 1.5682 -2.6782 3.3297
O -3.5094 -1.2532 0.9249
O -1.4383 -2.0873 0.4905
C -2.3580 -1.8633 1.2422
C -2.3281 -2.2128 2.7499
F -3.4066 -2.9441 3.0908
F -1.2256 -2.9076 3.0365
F -2.3337 -1.0791 3.4816

c2TS

-1081.31794131192 au, 436.29 kJ/mol, -366.04 cm⁻¹

C 2.6782 2.2256 -2.6964
C 1.6267 2.8792 -2.0500
C 0.6973 2.1344 -1.3014
C 2.8018 0.8211 -2.6382
C 1.8684 0.0701 -1.9270
C 0.7923 0.7075 -1.2520
O -0.2750 2.8309 -0.6580
C -1.5544 2.2778 -0.3372
O -2.2915 2.9451 0.3389
C -1.7469 0.9290 -0.8733
C -1.0047 0.2084 -1.7319
H 3.4126 2.8148 -3.2557
H 1.5135 3.9664 -2.0848
H 3.6339 0.3215 -3.1444
H 1.9624 -1.0173 -1.8497
H -1.0666 -0.2512 -2.7214
Pd -0.3139 -0.3352 0.0492
H -3.0381 0.0406 -0.0134
O 0.7708 -0.2088 2.0220
O 1.2474 -1.7798 0.5439
C 1.4467 -1.2288 1.6872
C 2.5124 -1.7876 2.6034
H 3.4806 -1.3245 2.3410
H 2.6053 -2.8763 2.4687
H 2.2813 -1.5412 3.6506
O -3.6551 -0.5209 0.5844
O -1.7189 -1.5108 1.2315
C -2.9543 -1.3807 1.2959
C -3.7755 -2.2127 2.2460
H -3.9973 -1.6022 3.1396
H -4.7338 -2.4930 1.7815
H -3.2059 -3.1014 2.5513

fc2TS

-1676.31454606003 au, 301.27 kJ/mol, -317.01 cm⁻¹

C -2.4368 -0.0783 -4.1163

C -2.1275 1.1655 -3.5566

C -1.4090 1.2217 -2.3515

C -2.0633 -1.2749 -3.4738

C -1.3675 -1.2278 -2.2636

C -1.0232 0.0188 -1.6924

O -1.1001 2.4677 -1.8708

C -0.9121 2.7779 -0.5039

O -0.5856 3.8934 -0.2083

C -1.1544 1.6213 0.3792

C -1.6816 0.4383 0.1666

H -2.9815 -0.1175 -5.0650

H -2.4131 2.1039 -4.0400

H -2.3126 -2.2419 -3.9213

H -1.0668 -2.1513 -1.7576

H -0.6355 1.4285 2.3690

H -2.3915 -0.3102 0.5154

Pd 0.2933 0.1537 -0.2002

O 2.0414 0.2588 1.1589

O 2.0204 -1.0074 -0.6600

C 2.5906 -0.5912 0.4021

C 3.9634 -1.1799 0.7925

F 4.7479 -0.2340 1.3350

F 4.5893 -1.6987 -0.2761

F 3.7859 -2.1609 1.7010

O -0.1160 1.1527 3.1768

O -0.6161 -0.9533 2.4652

C -0.0397 -0.1715 3.2003

C 0.8954 -0.6896 4.3208

F 1.7813 -1.5543 3.7939

F 1.5662 0.2906 4.9403

F 0.1588 -1.3502 5.2407

cP

-1081.42457999764 au, 447.76 kJ/mol

C 1.5942 -0.0432 -4.1250

C 1.7837 0.9949 -3.2078

C 0.8631 1.1614 -2.1634

C 0.4931 -0.9167 -4.0116

C -0.4206 -0.7466 -2.9720

C -0.2513 0.2947 -2.0307

O 1.0838 2.1991 -1.2971

C 0.2285 2.5185 -0.2361

O 0.4757 3.4974 0.4230

C -0.9225 1.6029 -0.0307

C -1.1585 0.5231 -0.9215
H 2.3121 -0.1752 -4.9413
H 2.6296 1.6836 -3.2785
H 0.3563 -1.7242 -4.7373
H -1.2795 -1.4174 -2.8647
H -1.7071 1.9941 0.6228
H -2.1278 0.0127 -0.9044
Pd -0.2308 -0.1560 0.9180
O 1.7619 -0.2309 0.4010
O 0.9641 -1.5952 1.9199
C 1.9740 -1.1720 1.2574
C 3.3473 -1.7345 1.4652
H 4.0710 -1.2325 0.8070
H 3.3327 -2.8183 1.2603
H 3.6354 -1.5980 2.5212
O -1.3110 0.8268 3.3004
O -2.0821 -0.4276 1.6004
C -2.1987 0.1411 2.7949
C -3.5326 -0.1524 3.4612
H -3.6126 -1.2347 3.6612
H -3.6035 0.4087 4.4039
H -4.3626 0.1217 2.7885

fcP

-1676.40854981989 au, 317.21 kJ/mol

C 0.6942 -1.5708 -2.8390
C 1.3421 -0.4712 -2.2964
C 0.5735 0.6240 -1.8334
C -0.7209 -1.6037 -2.9889
C -1.4957 -0.5494 -2.5474
C -0.8733 0.5815 -1.9193
O 1.2509 1.7605 -1.4942
C 0.6048 2.7661 -0.7406
O 1.1878 3.7867 -0.5151
C -0.7918 2.4354 -0.3442
C -1.5864 1.5916 -1.1560
H 1.2857 -2.4333 -3.1594
H 2.4271 -0.4223 -2.1878
H -1.1954 -2.4831 -3.4333
H -2.5873 -0.5743 -2.6178
H -1.2479 3.1519 0.3425
H -2.6812 1.6272 -1.1477
Pd -0.6317 0.3273 0.2455
O 1.9243 -0.8718 0.6770
O -0.2052 -1.6347 0.5516
C 1.0826 -1.7645 0.6695

C 1.5152 -3.2563 0.6997
F 0.7051 -4.0156 1.4552
F 2.7690 -3.3897 1.1509
F 1.4761 -3.7442 -0.5736
O 0.2775 2.3377 2.3336
O -1.0321 0.4764 2.2021
C -0.4455 1.4741 2.8059
C -0.8137 1.4635 4.3210
F -0.1688 2.4372 4.9758
F -2.1438 1.6602 4.4751
F -0.4952 0.2835 4.8888

c3TS

-1081.40409117479 au, 459.10 kJ/mol, -235.04 cm⁻¹

C 1.6382 -0.0016 -3.8567
C 1.7264 1.1031 -3.0045
C 0.7777 1.2565 -1.9842
C 0.6101 -0.9544 -3.7029
C -0.3343 -0.7949 -2.6897
C -0.2692 0.3145 -1.8153
O 0.9108 2.3495 -1.1692
C 0.0049 2.6626 -0.1454
O 0.1490 3.7067 0.4416
C -1.0570 1.6618 0.1114
C -1.2024 0.5231 -0.7261
H 2.3811 -0.1257 -4.6517
H 2.5177 1.8507 -3.1043
H 0.5554 -1.8155 -4.3759
H -1.1362 -1.5271 -2.5489
H -1.8722 2.0157 0.7481
H -2.1228 -0.0674 -0.6786
Pd -0.2216 0.0108 1.1323
O 1.6856 -0.3730 0.3375
O 0.9405 -1.4066 2.1127
C 1.8906 -1.2372 1.2648
C 3.1766 -1.9993 1.3617
H 3.7667 -1.8666 0.4432
H 2.9618 -3.0665 1.5349
H 3.7522 -1.6263 2.2269
O -1.4056 0.7392 2.9555
O -2.4268 -0.7213 1.6355
C -2.3873 -0.0246 2.6970
C -3.5379 -0.1162 3.6878
H -3.5781 -1.1434 4.0881
H -3.4050 0.5998 4.5110
H -4.4888 0.0739 3.1635

fc3TS

-1676.40123597909 au, 343.80 kJ/mol, -18.08 cm⁻¹

C 0.9512 -1.1345 -2.6231

C 1.1301 0.1744 -2.2016

C 0.0745 0.8276 -1.5142

C -0.2616 -1.8354 -2.3767

C -1.3038 -1.2145 -1.7170

C -1.1715 0.1448 -1.2581

O 0.2016 2.1645 -1.3071

C -0.8939 2.9972 -0.9434

O -0.6695 4.1709 -0.7962

C -2.1882 2.3228 -0.8012

C -2.3241 0.9788 -0.9277

H 1.7657 -1.6446 -3.1446

H 2.0515 0.7306 -2.3855

H -0.3608 -2.8739 -2.7040

H -2.2527 -1.7304 -1.5395

H -3.0273 2.9766 -0.5534

H -3.2952 0.4939 -0.7840

Pd -0.1752 -0.1635 0.7380

O 2.7498 -0.1760 0.5042

O 1.0373 -1.6444 0.2341

C 2.2959 -1.2908 0.2998

C 3.2207 -2.5137 0.0391

F 4.5105 -2.1624 0.1085

F 2.9944 -3.0238 -1.2013

F 2.9946 -3.4952 0.9338

O -1.3438 1.1813 1.8357

O -0.0295 -0.2667 2.8455

C -0.8807 0.6710 2.9099

C -1.3458 1.2078 4.2761

F -0.6386 2.3072 4.5980

F -2.6487 1.5359 4.2258

F -1.1671 0.2846 5.2300