Supporting Information for: Rationalizing Ring-Size Selectivity in
Intramolecular Pd-Catalyzed Allylations of Resonance-Stabilized
Carbanions

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Note: all energies determined at BP86/LACVP**

TS geometries optimized in solvent model CH₂Cl₂

Cartesian coordinates (A) and solution phase energies (Hartree)

Table 1, entries 1-12 S2-S11

Table 1, entry 1: amide anti_endo

am_H_a_n_TS.s25.xyz		-1492.0670182 a. u.	
H	-0.77253	-0.13274	1.05115
P	-0.01332	-0.27642	2.24979
P	3.19118	0.32320	0.29320
H	2.60740	-0.40984	-0.78303
H	-0.12521	-1.69421	2.36969
H	-1.04727	0.06914	3.17085
H	4.51013	-0.21899	0.21150
H	3.43765	1.54697	-0.39919
Pd	2.20040	0.59091	2.40663
C	2.37655	1.18719	5.18882
C	2.92820	1.86085	4.08438
C	4.03320	1.32776	3.34951
C	4.46898	1.75374	6.45805
H	1.54554	1.62570	5.75275
H	2.61658	0.14756	5.42370
H	4.60786	2.03130	2.73355
C	5.18271	0.48886	6.30583
O	5.49104	-0.23110	7.30064
C	3.99208	2.25739	7.69791
O	3.90724	1.65478	8.81167
H	3.62792	3.31229	7.65556
N	5.63423	0.09315	5.03057
C	6.51417	-1.09472	5.04256
H	7.25018	-1.00398	5.85530
H	5.95064	-2.03975	5.18983
H	7.04422	-1.14508	4.07682
C	4.76061	0.06961	3.80217
H	4.03004	-0.75892	3.93714
H	5.42909	-0.24106	2.98337
H	4.57890	2.50026	5.67316
H	2.61059	2.89499	3.89704
Na	5.12981	-0.21221	9.58146

Table 1, entry 2: amide anti_exo

am_H_a_x_TS_24.s31.xyz		-1492.0873315 a. u.	
H	-0.15273	-0.12603	0.19132
P	-0.00352	-0.09393	1.60757
P	3.76124	0.03699	1.08471
H	3.44925	-0.01449	-0.30463
H	-1.00808	-1.04591	1.94420
H	-0.74607	1.08986	1.88081
H	4.93019	-0.78041	1.03944
H	4.41760	1.30233	1.08447
Pd	2.05071	-0.33576	2.69219
C	1.00138	-0.78208	4.50850

C	2.36931	-0.69174	4.92404
C	3.31677	-1.73068	4.84921
C	2.76604	-3.20055	6.83192
H	0.31872	0.01256	4.83507
H	0.53022	-1.76682	4.37860
H	4.34119	-1.49102	5.16624
C	3.79857	-4.09526	6.31004
O	4.55828	-4.81514	7.02554
C	2.72344	-2.71235	8.15647
O	3.60748	-2.84643	9.06523
H	1.80635	-2.13033	8.41575
N	3.91646	-4.09585	4.93406
C	4.71515	-5.08982	4.21885
H	4.07741	-5.71049	3.56038
H	5.49480	-4.59987	3.60496
H	5.20376	-5.73676	4.96262
C	3.17403	-3.08201	4.17503
H	2.11292	-3.37076	4.03306
H	3.62639	-3.03708	3.16595
H	1.83452	-3.09977	6.26966
H	2.71272	0.23622	5.40034
Na	5.00106	-4.71320	9.29826

Table 1, entry 3: amide syn_exo

am_H_s_x_TS_2.s17.xyz	-1492.0923526 a. u.		
H	-0.06624	0.02995	0.08395
P	-0.09403	-0.19446	1.49124
P	1.86954	0.26475	4.70893
H	2.59425	-0.33145	5.78701
H	-1.12967	-1.17376	1.51178
H	-0.87761	0.93894	1.85882
H	0.64569	0.46387	5.41185
H	2.38629	1.58659	4.85640
Pd	1.89740	-0.78524	2.57965
C	2.58181	-2.05646	0.98145
C	3.38486	-2.40475	2.11322
C	4.50608	-1.63089	2.48588
C	6.51216	-2.79689	1.72546
H	1.84965	-2.78021	0.60398
H	2.98979	-1.36694	0.22711
H	4.75154	-0.74949	1.87813
C	7.25884	-1.77302	2.46320
O	8.35797	-1.26403	2.09202
C	6.65058	-3.02829	0.33687
O	7.29669	-2.31959	-0.50069
H	6.11058	-3.92400	-0.05339
C	5.23440	-1.73527	3.81238

H	4.80176	-1.01909	4.53730
H	5.11658	-2.74672	4.25502
H	6.04021	-3.60118	2.29988
H	3.15405	-3.31740	2.67952
Na	9.10968	-0.89259	-0.06852
N	6.64176	-1.36375	3.62656
C	7.32125	-0.55101	4.63290
H	7.33103	-1.06836	5.61098
H	8.35751	-0.38705	4.30084
H	6.82591	0.43228	4.75147

Table 1, entry 4: CH2 anti_endo

CH2_H_a_n_TS_1.s33.xyz	-1436.7251744	a. u.
H	-0.49362	0.68386
P	0.07448	-0.01645
P	3.56632	-0.07771
H	3.94181	-1.04364
H	0.49601	-1.16914
H	-1.14151	-0.56474
H	3.79516	-0.87915
H	4.79155	0.64988
Pd	1.56890	1.15420
C	-0.18733	3.06933
C	1.11590	3.25019
C	2.28774	2.78509
C	-0.24091	4.76366
H	-1.05242	3.40558
H	-0.40749	2.35204
H	3.24348	3.18015
C	0.40632	3.90017
O	-0.22724	3.21693
C	-1.63092	5.11172
O	-2.52584	4.60644
H	-1.93581	5.90878
C	1.91640	3.70244
C	2.27505	2.45692
H	1.56265	1.64780
H	3.27411	2.09688
H	0.39417	5.42106
H	1.23445	3.89753
Na	-2.37528	3.18892
H	2.43312	4.60247
H	2.27504	3.49681

Table 1, entry 5: CH2 anti_exo

CH2_H_a_x_TS_1.s21.xyz	-1436.7226069	a. u.
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H	-0.47006	-0.00577	0.30646
P	-0.09701	0.06669	1.68239
P	3.64791	0.04616	0.72707
H	3.28276	-0.52012	-0.53088
H	-0.91019	-1.00870	2.15010
H	-0.97180	1.12870	2.05920
H	4.90500	-0.62163	0.84655
H	4.15965	1.27773	0.21815
Pd	2.09109	0.14473	2.52182
C	1.37150	0.32517	4.53803
C	2.78690	0.43978	4.66449
C	3.68593	-0.65250	4.88871
C	3.69698	-1.08123	7.06850
H	0.76195	1.22835	4.66966
H	0.86767	-0.61111	4.81673
H	4.75078	-0.38795	4.82212
C	4.68081	-2.11680	6.78541
O	5.78737	-2.23784	7.36732
C	3.92780	0.03624	7.94200
O	5.03746	0.39939	8.41583
H	3.02874	0.65218	8.18242
C	4.33579	-2.96547	5.56447
C	3.38790	-2.12983	4.66745
H	2.32983	-2.35171	4.89057
H	3.54284	-2.37794	3.59977
H	2.64182	-1.34125	6.92950
H	3.22453	1.44366	4.74848
Na	6.96863	-0.88269	8.89426
H	5.28466	-3.20975	5.05214
H	3.88354	-3.92747	5.87220

Table 1, entry 6: CH₂ syn_exo

CH ₂ _H_s_x_TS_1.s11.xyz	-1436.7245689 a. u.		
H	-0.09421	0.05865	-0.00956
P	-0.01706	-0.02336	1.41279
P	2.25073	-0.00122	4.50868
H	3.61831	-0.39164	4.63594
H	-0.15848	-1.43963	1.51702
H	-1.37795	0.31314	1.68470
H	1.68537	-1.25839	4.87934
H	2.13253	0.61460	5.79182
Pd	1.67158	1.17190	2.52635
C	1.94419	2.71726	1.04782
C	2.98130	2.91044	2.01126
C	2.82896	3.77324	3.14326
C	3.75843	5.74735	2.63499
H	2.19121	2.30593	0.06144

H	1.05897	3.36981	1.07381
H	1.81792	4.17756	3.30672
C	3.39675	6.16652	3.98080
O	2.74620	7.20212	4.26424
C	3.29286	6.39340	1.43887
O	2.36149	7.23908	1.36190
H	3.79881	6.08470	0.49379
C	3.72545	5.13117	5.05208
C	3.72853	3.73978	4.36930
H	3.35460	2.97476	5.07474
H	4.74860	3.43123	4.07617
H	4.69220	5.18351	2.52240
H	3.98864	2.52330	1.80152
Na	1.49818	8.73620	2.97553
H	2.95461	5.20802	5.84008
H	4.69652	5.36158	5.53046

Table 1, entry 7: CH2 anti_endo (high energy enolate)

CH2_H_a_n_hi_TS.s89.xyz	-	-1436.7218318	a. u.
H	0.21594	-1.26919	0.95701
P	-0.03071	0.03494	1.48559
P	3.50064	0.05363	3.09580
H	3.64289	-1.31836	2.72790
H	-1.18201	-0.31618	2.25854
H	-0.74585	0.54374	0.35681
H	3.78396	-0.09194	4.48706
H	4.79610	0.48493	2.68950
Pd	1.65118	1.37706	2.51662
C	-0.04692	3.39873	3.29255
C	1.17073	3.53579	2.56506
C	2.44401	3.32117	3.19484
C	-0.12279	5.13875	4.80209
H	-1.00001	3.54956	2.77291
H	-0.09735	2.78751	4.19461
H	3.32800	3.59885	2.60419
C	1.18655	5.67396	4.47206
O	1.36263	6.57919	3.61449
C	-1.36746	5.75605	4.43452
O	-1.53537	6.69775	3.61476
H	-2.27228	5.32828	4.93093
C	2.41116	5.01845	5.10173
C	2.57270	3.50806	4.69620
H	1.82038	2.91451	5.24257
H	3.56079	3.16932	5.05029
H	-0.17897	4.47686	5.67572
H	1.12720	3.94466	1.54865
Na	-0.01153	8.06167	2.42745

H	3.29538	5.59419	4.77655
H	2.34560	5.07173	6.20627

Table 1, entry 8: CH2 anti_exo (high energy enolate)

CH2_H_a_x_hi_TS.xyz	-1436.7210422 a. u.		
H	0.00000	0.00000	0.00000
P	0.00000	0.00000	1.42660
P	3.84378	0.00000	1.31452
H	3.80256	-0.25236	-0.08891
H	-0.97709	-1.02658	1.60328
H	-0.87528	1.11241	1.60634
H	5.00690	-0.78321	1.58722
H	4.50850	1.26192	1.24301
Pd	1.94558	-0.10454	2.73037
C	1.02771	-0.12280	4.72086
C	2.44051	-0.05663	4.89874
C	3.31839	-1.19955	4.93834
C	3.96720	-1.69084	6.98228
H	0.42667	0.77760	4.89916
H	0.48622	-1.07079	4.83252
H	4.36064	-0.99739	4.67227
C	2.61909	-2.19443	7.21214
O	1.85450	-1.81051	8.12730
C	4.55723	-0.59332	7.69676
O	3.95682	0.20673	8.46149
H	5.64662	-0.43149	7.51672
C	2.12538	-3.11541	6.09885
C	2.81562	-2.64252	4.78548
H	2.11898	-2.71269	3.93030
H	3.67798	-3.28874	4.55167
H	4.68464	-2.38336	6.52525
H	2.90151	0.92421	5.08036
Na	2.00127	-0.12475	9.76812
H	2.37099	-4.16942	6.33347
H	1.02435	-3.04551	6.05767

Table 1, entry 9: CH2 syn_exo (high energy enolate)

CH2_H_s_x_h_TS.s50.xyz	-1436.7225217 a. u.		
H	-0.61965	-0.95861	2.03154
P	-0.00533	0.14882	1.37254
P	3.77199	0.21900	1.94521
H	3.97936	-0.49989	0.72959
H	-1.20602	0.85355	1.05697
H	0.16992	-0.47579	0.10144
H	4.21190	-0.81206	2.83029
H	5.00170	0.94543	1.91425

Pd	1.72540	1.28887	2.48056
C	0.46712	2.69832	3.54419
C	1.80401	3.13039	3.76757
C	2.64550	2.63731	4.82848
C	2.31147	3.73239	6.65687
H	-0.17849	3.28356	2.87764
H	-0.05817	2.11715	4.31548
H	2.31755	1.72072	5.32973
C	3.45563	4.57730	6.32088
O	3.41818	5.81471	6.13144
C	0.96177	4.21617	6.75948
O	0.53201	5.29907	6.28369
H	0.23857	3.54195	7.27792
C	4.67082	3.73715	5.96088
C	4.16197	2.89596	4.75111
H	4.70253	1.93503	4.69507
H	4.36995	3.45285	3.82026
H	2.53378	2.84662	7.26451
H	2.18937	3.97552	3.17911
Na	1.63829	7.38644	6.02596
H	4.94613	3.08373	6.80926
H	5.53755	4.36556	5.69931

Table 1, entry 10: ester anti_endo

O_H_a_n_TS_2.s42.xyz	-1472.6381050 a. u.		
H	-1.44748	0.49273	1.34915
P	-0.14717	-0.07333	1.50484
P	1.86121	0.01855	4.77093
H	3.18623	-0.05162	5.29381
H	0.09027	-0.35737	0.12731
H	-0.56857	-1.38291	1.88227
H	1.51040	-1.34875	4.96639
H	1.22685	0.54828	5.93373
Pd	1.55596	1.08671	2.70927
C	1.80094	3.52986	1.09469
C	2.74835	2.56882	1.52901
C	3.19690	2.47161	2.89864
C	3.07509	5.48469	1.03356
H	1.48592	3.54057	0.04502
H	1.10448	4.00594	1.79201
H	4.13249	1.91748	3.05559
C	2.90962	5.63373	2.46127
O	2.07866	6.35601	3.04465
C	2.43769	6.34856	0.07479
O	1.59976	7.25565	0.32102
H	2.71935	6.16292	-0.98860
C	3.01585	3.65189	3.82925

H	1.96728	3.95245	3.99734
H	3.49429	3.48943	4.80636
H	3.94673	4.92825	0.67967
H	3.30774	2.02570	0.75566
Na	1.09441	8.40808	2.38135
O	3.73225	4.79619	3.20705

Table 1, entry 11: ester anti_exo

O_H_a_x_TS_2.s9.xyz	-1472.6477735 a. u.		
H	0.00784	0.14998	0.02692
P	-0.00145	-0.03088	1.44096
P	3.81009	0.00583	1.32459
H	3.68570	-0.14101	-0.08827
H	-0.95847	-1.08530	1.50182
H	-0.87404	1.04385	1.77836
H	5.00102	-0.76539	1.47696
H	4.42565	1.29287	1.32264
Pd	1.92283	-0.30275	2.74117
C	0.75766	-0.65577	4.51553
C	2.11462	-0.64170	4.96808
C	2.98020	-1.76686	4.97802
C	2.52526	-3.05506	6.85973
H	0.11682	0.19377	4.78196
H	0.22651	-1.61000	4.39171
H	4.03233	-1.57760	5.23061
C	3.46833	-4.01980	6.32243
O	4.31105	-4.69139	6.94261
C	2.67777	-2.48327	8.16002
O	3.68491	-2.59337	8.91506
H	1.82225	-1.86009	8.51080
C	2.73126	-3.08347	4.26843
H	1.66082	-3.34738	4.20356
H	3.14993	-3.07846	3.24754
H	1.51350	-3.03454	6.44508
H	2.50765	0.27260	5.43170
Na	5.20350	-4.41232	9.13405
O	3.45602	-4.14847	4.95036

Table 1, entry 12: ester syn_exo_endo

O_H_s_x_TS.s15.xyz	-1472.6503383 a.u.		
H	0.59984	0.65184	0.19198
P	0.11159	-0.02599	1.34752
P	2.48339	0.04972	4.31219
H	3.65799	-0.29483	5.04937
H	-0.97658	-0.70068	0.72175
H	-0.63090	1.05240	1.91103
H	1.62594	0.23868	5.43546

H	2.80959	1.42186	4.09939
Pd	1.64820	-1.32394	2.56375
C	1.28469	-3.10328	1.41027
C	2.07500	-3.53966	2.51894
C	3.49529	-3.51953	2.47379
C	4.29162	-5.61122	2.09167
H	0.22479	-3.38160	1.36667
H	1.77038	-2.95593	0.43420
H	3.96553	-3.07022	1.58764
C	5.61996	-5.06429	2.32970
O	6.66771	-5.30541	1.70718
C	3.93676	-6.21797	0.84561
O	4.60964	-6.17699	-0.22180
H	2.95181	-6.73963	0.82913
C	4.37482	-3.58988	3.70324
H	4.59197	-2.58801	4.11143
H	3.92724	-4.20857	4.50244
H	3.69928	-5.91171	2.96241
H	1.58718	-4.00984	3.38359
Na	6.95603	-6.02471	-0.56815
O	5.68160	-4.11794	3.32941

Text discussion: amide syn_endo

am_H_s_n_TS_1.s23.xyz -1492.0613933

H	0.06404	0.05200	-0.09035
P	0.00339	0.07841	1.33432
P	3.88741	-0.09493	1.56037
H	3.91566	-0.55958	0.21124
H	-0.71936	-1.14051	1.50339
H	-1.11475	0.95953	1.44360
H	4.77172	-1.06724	2.11772
H	4.83522	0.96130	1.41691
Pd	1.92520	0.45374	2.70142
C	0.66553	1.39426	5.64746
C	1.50665	1.63866	4.55543
C	2.84141	1.05767	4.52478
C	2.07433	2.97507	6.96183
H	-0.28189	1.93161	5.77771
H	0.82549	0.52422	6.29701
H	2.94478	0.11476	5.09236
C	3.25715	2.18105	7.29392
O	3.46265	1.72515	8.45817
C	1.09826	3.38760	7.91591
O	0.96456	3.00811	9.11693
H	0.35317	4.11924	7.51961

N	4.22756	1.94625	6.31400
C	5.39019	1.13956	6.72229
H	5.65138	1.37474	7.76380
H	5.18435	0.05143	6.66002
H	6.24068	1.38183	6.06410
C	3.97941	2.01610	4.84239
H	4.93572	1.75827	4.35898
H	3.73105	3.05179	4.54554
H	2.08925	3.57131	6.04703
H	1.37648	2.61985	4.06982
Na	2.50920	1.90140	10.52889