Supplementary Material (ESI) for Green Chemistry

Electronic Supplementary Information for

Atom Economic Synthesis of Amides via Transition Metal Catalyzed Rearrangement of Oxaziridines

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Experimental Details

1. Synthesis of imines.

Imines were synthesised from the corresponding aldehydes and amines either on basic alumina according to the procedure of Texier-Boullet[1] or in aqueous medium as reported by Tashiro and coworkers.[2]

2. Sodium tungstate-catalyzed oxidation of imines to oxaziridines.

Except for a lowered catalyst loading (2 mol% instead of 10 mol%), the procedure was the same as described by Rao and coworkers.[3] To the imine (1 mmol) was added $Na_2WO_4 \cdot 2H_2O$ (0.02 mmol) and acetonitrile (5 ml), followed by dropwise addition of H_2O_2 (5 ml, 30% in H_2O). The mixture was stirred at room temperature for 10 hr. The mixture was then reduced in volume *in vacuo*, cooled to 4^{o}C and quenched with Na_2SO_3. Extraction with chloroform followed by drying with $MgSO_4$ and removal of solvent *in vacuo* yielded the corresponding oxaziridines, which were then used for the metal-catalyzed isomerization to amides without further purification.

3. Metal catalyzed rearrangement of oxaziridines to amides.

A mixture of oxaziridine (0.25 mmol), 1,3,5-trimethoxybenzene (10.0 mg) and metal complex in 5 ml solvent was heated at reflux for 12 hr. Standard Schlenk techniques were applied in the case of Pd, Rh and Ir compounds to exclude air. Yields were determined by the ^{1}H NMR peak integrations of the resulting amides with respect to the internal standard 1,3,5-trimethoxybenzene. The identity of the amides was confirmed by comparison of the ^{1}H NMR data to published spectra.[4]

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[1] F. Texier-boullet, *Synthesis*, 1985, 679.
[2] A. Simion, C. Simion, T. Kanda, S. Nagashima, Y. Mitoma, T. Yamada, K. Mimura and M. Tashiro, *J. Chem. Soc.-Perkin Trans. 1*, 2001, 2071.
[3] M. Shailaja, A. Manjula and B. V. Rao, *Synlett*, 2005, 1176.
[4] a) W.-J. Yoo and C.-J. Li, *J. Am. Chem. Soc.*, 2006, **128**, 13064 b) Y. J. Kang, H. A. Chung, J. J. Kim and Y. J. Yoon, *Synthesis*, 2002, 733; J. H. Rigby and S. Laurent, *J. Org. Chem.*, 1998, **63**, 6742.

Computational Details

References for the theoretical methods

B3PW91 hybrid functional:

[1] A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

[2] J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244.

sddall basis set:

[3] D. Andrae, U. Haussermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta*, 1990, **77**, 123.

[4] A. W. Ehlers, M. Bohme, S. Dapprich, A. Gobbi, A. Hollwarth, V. Jonas, K. F. Kohler, R. Stegmann, A. Veldkamp and G. Frenking, *Chem. Phys. Lett*., 1993, **208**, 111.

[5] A. Bergner, M. Dolg, W. Kuchle, H. Stoll and H. Preuss, *Mol. Phys*., 1993, **30**, 1431.

[6] A. Hollwarth, H. Bohme, S. Dapprich, A. W. Ehlers, A. Gobbi, V. Jonas, K. F. Kohler, R. Stegmann, A. Veldkamp and G. Frenking, *Chem. Phys. Lett*., 1993, **203**, 237.

6-31g(d,p) basis set:

[7] P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.

Geometries and energies

Optimized geometries and absolute potential (E), enthalpy (H) and Gibbs free (G) energies in hartrees. The **S**, **C** and **P** labels stand for the substrate, catalyst and product respectively.

S E=-248.334240946 H=-248.222619 G=-248.271154

N	-0.132023	-0.530816	0.549628
O	1.153537	0.011908	0.037447
C	-0.068925	0.396973	-0.534001
H	-0.358591	1.432307	-0.320141
C	-0.403811	0.073273	1.848673
H	-0.127257	1.134610	1.902463
H	-1.475850	-0.039241	2.044722
H	0.146292	-0.478861	2.614787
C	-0.380136	-0.098242	-1.914887
H	0.174726	0.482592	-2.658543
H	-0.097541	-1.149273	-1.999385
H	-1.448687	0.006288	-2.129582

C E=-437.673655382 H=-437.472172 G=-437.539042

Rh	-0.168212	-0.403368	0.603061
Cl	0.036312	0.236707	2.801233
C	1.207633	0.947606	-0.116939
C	2.046634	0.358749	-1.229205

C	-1.717203	0.313882	-1.850449
C	1.255262	-0.639681	-2.092811
C	-1.147210	-0.923401	-1.184922
C	0.192617	-1.351094	-1.269986
H	1.778194	1.318646	0.735257
H	2.891673	-0.157108	-0.760409
H	0.787369	-0.134073	-2.943922
H	-1.857633	0.148405	-2.928821
H	-1.890464	-1.680524	-0.917975
H	2.481467	1.160918	-1.844840
H	-2.716277	0.479434	-1.433457
H	1.940245	-1.378159	-2.521662
H	0.392574	-2.401191	-1.046674
C	-0.117961	1.469788	-0.262374
H	-0.436241	2.179835	0.501100
C	-0.853327	1.562226	-1.593942
H	-1.489458	2.452810	-1.592166
H	-0.127905	1.710112	-2.401348

I1 E=-686.052301803 H=-685.735915 G=-685.825785

Rh	0.270431	-0.105320	0.034271
Cl	2.372726	-0.140553	-1.070194
N	-0.542568	-0.490267	-1.897893
O	-1.878948	-0.001642	-2.292980
C	-0.341065	-1.856992	-2.390740
H	-0.768598	-1.981908	-3.390437
H	0.738042	-2.028295	-2.400251
H	-0.816294	-2.551177	-1.695879
C	-0.711781	0.517555	-2.901737
H	-0.557841	0.170476	-3.926817
C	-0.324385	1.934302	-2.626974
H	-0.492809	2.179110	-1.576164
H	0.735936	2.074806	-2.853775
H	-0.916768	2.603144	-3.259868
C	1.119377	0.921634	1.688989
C	0.137786	1.948356	2.209848
C	-1.107981	-1.671484	2.178783
C	-1.324909	1.477939	2.109267
C	-1.466678	-0.844038	0.962753
C	-1.542960	0.565402	0.910049
H	2.056874	1.327014	1.310257
H	0.264742	2.855736	1.608574
H	-1.630622	0.963964	3.026961
H	-1.969738	-1.767894	2.857153
H	-2.048938	-1.384973	0.214096
H	0.387720	2.232192	3.243625
H	-0.880637	-2.685560	1.830115
H	-1.982337	2.349895	2.023715
H	-2.153744	0.979773	0.108238
C	1.098483	-0.451009	1.973623
H	2.015966	-1.002216	1.771986

C	0.116217	-1.114258	2.925653
H	0.623228	-1.926340	3.457411
H	-0.192978	-0.398376	3.694154

I2 E=-686.028817121 H=-685.714325 G=-685.802862

Rh	0.287523	0.003020	-0.163766
Cl	2.285515	-0.708008	0.825549
N	0.032931	0.111049	3.138792
O	-0.519266	0.597791	1.831538
C	0.257497	1.265887	3.993748
H	-0.540305	2.018074	3.934289
H	0.330941	0.884146	5.017850
H	1.215301	1.713102	3.721829
C	-1.316906	-0.135149	2.761006
H	-2.088653	0.492809	3.217290
C	-1.704593	-1.537800	2.416508
H	-0.865825	-2.039596	1.928635
H	-1.964739	-2.078746	3.332463
H	-2.576671	-1.548079	1.756448
C	0.679567	-1.165368	-1.848360
C	-0.599849	-1.727955	-2.427269
C	-0.438989	2.084552	-2.177998
C	-1.785505	-0.757124	-2.287679
C	-1.066003	1.371442	-0.998431
C	-1.658213	0.090847	-1.030155
H	1.406514	-1.913663	-1.534086
H	-0.826106	-2.650869	-1.881307
H	-1.863525	-0.108315	-3.166630
H	-1.212660	2.505260	-2.838484
H	-1.377809	2.033747	-0.187879
H	-0.451040	-2.023627	-3.477284
H	0.122770	2.938143	-1.782586
H	-2.721947	-1.324440	-2.252976
H	-2.385434	-0.130224	-0.248838
C	1.178009	0.141657	-2.059283
H	2.241321	0.283160	-1.871004
C	0.520736	1.174767	-2.964726
H	1.298197	1.784392	-3.436785
H	-0.003517	0.670731	-3.783821

TS1 E=-686.007212333 H=-685.693341 G=-685.781599

Rh	0.295691	-0.231895	0.053471
Cl	2.522132	-0.555421	-0.667178
N	-0.313234	0.847772	-2.132446
O	-0.265664	-0.989818	-1.838017
C	0.881543	1.279804	-2.818044
H	1.485292	0.450309	-3.202950
H	0.524020	1.877316	-3.674938
H	1.497925	1.893885	-2.163155
C	-0.959506	-0.248380	-2.792066
H	-0.573379	-0.456091	-3.801737

C	-2.467076	-0.290322	-2.759575
H	-2.853780	-0.057491	-1.766284
H	-2.879472	0.426952	-3.477292
H	-2.807102	-1.290570	-3.045991
C	1.044542	0.961698	1.629288
C	0.090117	2.084121	1.966336
C	-1.358604	-1.464059	2.209722
C	-1.380207	1.656383	1.838013
C	-1.587708	-0.744976	0.896867
C	-1.565621	0.645479	0.718722
H	2.038672	1.278937	1.317988
H	0.286982	2.906296	1.269312
H	-1.749745	1.240715	2.780493
H	-2.272944	-1.446166	2.822228
H	-2.093327	-1.340525	0.136786
H	0.300882	2.479022	2.971825
H	-1.168424	-2.517682	1.977482
H	-2.002123	2.534287	1.632828
H	-2.014990	1.044825	-0.186745
C	0.925707	-0.378222	2.060378
H	1.838598	-0.970965	2.014959
C	-0.158385	-0.900236	2.993523
H	0.265277	-1.690112	3.622241
H	-0.475562	-0.109116	3.681057

I3 E=-686.039670368 H=-685.723855 G=-685.811809

Rh	0.299059	-0.315395	-0.041847
Cl	2.424899	-0.155819	-0.985135
N	-0.603965	0.789068	-1.541481
O	-0.392588	-1.439074	-1.511255
C	0.127234	1.924381	-2.072542
H	1.104645	1.688833	-2.507231
H	-0.513317	2.344483	-2.865468
H	0.246051	2.703573	-1.315188
C	-0.554439	-0.389718	-2.429143
H	0.317768	-0.334399	-3.107356
C	-1.830259	-0.534507	-3.242791
H	-2.702597	-0.545821	-2.583734
H	-1.936766	0.280860	-3.966697
H	-1.789650	-1.480994	-3.792215
C	0.620753	1.468299	1.277569
C	-0.720639	2.111571	1.531482
C	-0.401890	-1.609643	2.503704
C	-1.862530	1.106688	1.763149
C	-1.164831	-1.321113	1.228087
C	-1.756997	-0.119173	0.879631
H	1.330265	2.070554	0.712096
H	-0.966688	2.725025	0.659488
H	-1.906545	0.804298	2.813369
H	-1.105397	-1.934421	3.284866
H	-1.418679	-2.187690	0.619007

H	-0.643162	2.805283	2.381818
H	0.247901	-2.472478	2.316346
H	-2.815390	1.603296	1.553455
H	-2.385669	-0.126505	-0.004636
C	1.139871	0.351843	1.911567
H	2.202722	0.164933	1.766368
C	0.458623	-0.434806	3.020474
H	1.233296	-0.839189	3.679680
H	-0.140634	0.238227	3.639714

TS2 E=-686.014326758 H=-685.701543 G=-685.786469

Rh	-0.281147	-0.072629	-0.163199
Cl	-2.539604	-0.664261	0.351802
N	1.113145	0.200777	-1.763516
O	-0.919318	1.112108	-1.661465
C	1.902425	-0.947226	-2.167670
H	1.356473	-1.908583	-2.167555
H	2.255952	-0.773141	-3.194410
H	2.793763	-1.047906	-1.545422
C	-0.196499	0.198832	-2.370965
H	-0.652051	-0.867760	-2.107552
C	-0.305405	0.307897	-3.890613
H	0.156596	1.249746	-4.199388
H	0.186016	-0.526557	-4.395674
H	-1.362322	0.320010	-4.163095
C	1.221973	-1.318113	0.932881
C	2.444712	-0.472313	1.219500
C	-0.757348	0.920153	2.639759
C	2.125409	1.010564	1.479475
C	-0.399010	1.479562	1.283936
C	0.896430	1.492136	0.730801
H	1.384702	-2.175846	0.280350
H	3.119472	-0.540937	0.363470
H	1.987996	1.194287	2.550463
H	-0.459634	1.641192	3.416022
H	-1.132979	2.154170	0.845651
H	2.991742	-0.903574	2.070586
H	-1.844843	0.836875	2.680016
H	2.981759	1.619306	1.174180
H	1.066053	2.144465	-0.120410
C	0.065578	-1.317728	1.693266
H	-0.629220	-2.140856	1.558187
C	-0.137698	-0.463437	2.931051
H	-0.797167	-1.002301	3.617187
H	0.821705	-0.356088	3.448520

I4 E=-686.085010525 H=-685.770357 G=-685.861502

Rh	-0.410115	-0.312401	-0.098526
Cl	-2.453321	-0.421626	1.109204
N	0.595843	-0.222094	-1.928859
O	-1.366401	0.673716	-1.683191

C	1.700027	-0.831181	-2.622258
H	1.824299	-1.871038	-2.301030
H	1.536017	-0.839802	-3.705613
H	2.643534	-0.304523	-2.430785
C	-0.413994	0.387913	-2.502274
H	-0.922320	-1.648866	-0.616948
C	-0.549541	0.737518	-3.954870
H	0.379330	1.136303	-4.371046
H	-0.833071	-0.147811	-4.534606
H	-1.342234	1.480174	-4.057669
C	1.288130	-1.318131	0.797814
C	2.546419	-0.483039	0.705574
C	-0.199311	1.213282	2.669577
C	2.361461	1.026036	0.972190
C	-0.067057	1.702564	1.247725
C	1.049709	1.594013	0.478107
H	1.343139	-2.277740	0.284301
H	2.975481	-0.622599	-0.289751
H	2.456311	1.231464	2.042458
H	0.275763	1.934592	3.350879
H	-0.904451	2.279768	0.860825
H	3.289286	-0.893515	1.406842
H	-1.263539	1.203511	2.909824
H	3.184774	1.565658	0.491334
H	1.053950	2.080579	-0.494360
C	0.303818	-1.184223	1.777410
H	-0.360730	-2.030389	1.925084
C	0.372334	-0.198293	2.936574
H	-0.181267	-0.631093	3.774889
H	1.415686	-0.132831	3.266701

TS3 E=-686.051105867 H=-685.739899 G=-685.832406

Rh	-0.256097	-0.080920	-0.037498
Cl	-2.568070	-0.717826	0.313863
N	0.534697	-0.521460	-2.080319
O	-0.817914	1.144169	-1.668633
C	1.412720	-1.388753	-2.827022
H	1.327757	-2.410521	-2.446588
H	1.154893	-1.409096	-3.892520
H	2.460577	-1.079054	-2.727154
C	-0.110041	0.537627	-2.542837
H	-0.459692	-1.214440	-1.149039
C	-0.059655	1.025885	-3.959113
H	0.967482	1.237523	-4.272336
H	-0.472687	0.276149	-4.642234
H	-0.654028	1.936921	-4.035091
C	1.163587	-1.323735	0.984648
C	2.458791	-0.554728	1.148244
C	-0.635237	1.028867	2.771074
C	2.248199	0.930653	1.488414
C	-0.261132	1.555223	1.405420

C	1.011713	1.504435	0.811399
H	1.247171	-2.230177	0.383899
H	3.002341	-0.623015	0.199096
H	2.181723	1.074904	2.571574
H	-0.340725	1.740797	3.557091
H	-0.969033	2.267489	0.982364
H	3.092890	-1.052038	1.898916
H	-1.726713	0.961212	2.798365
H	3.129269	1.496777	1.168019
H	1.194922	2.203531	-0.003244
C	0.036875	-1.224781	1.805110
H	-0.694728	-2.024122	1.732820
C	-0.051317	-0.364431	3.054801
H	-0.686087	-0.878743	3.783104
H	0.939624	-0.290379	3.515187

I5 E=-686.156066230 H=-685.838468 G=-685.933205

Rh	0.167128	-0.046394	0.286313
Cl	2.254935	-0.200098	-0.898511
N	0.303402	0.043986	-3.259139
O	-1.092379	-0.038170	-1.469816
C	0.595234	0.105374	-4.675530
H	0.244321	-0.785594	-5.209279
H	0.154484	0.990672	-5.146875
H	1.678219	0.164784	-4.793012
C	-0.907854	0.022057	-2.711758
H	1.087338	-0.017820	-2.590529
C	-2.111051	0.080260	-3.617945
H	-2.134054	1.027103	-4.167942
H	-2.088583	-0.727983	-4.355789
H	-3.013281	-0.004154	-3.013861
C	1.191948	0.781213	1.913192
C	0.337573	1.824905	2.600593
C	-1.185121	-1.671390	2.397804
C	-1.159417	1.469059	2.580217
C	-1.549491	-0.730265	1.269135
C	-1.520799	0.680146	1.330392
H	2.136640	1.155407	1.519614
H	0.486903	2.769535	2.065585
H	-1.436991	0.899003	3.473274
H	-2.001082	-1.734682	3.134137
H	-2.177747	-1.170059	0.493501
H	0.689663	1.996882	3.629530
H	-1.083845	-2.673987	1.967276
H	-1.754726	2.387840	2.615286
H	-2.120455	1.211790	0.591748
C	1.094342	-0.615865	2.092531
H	1.966701	-1.202571	1.807626
C	0.139834	-1.280739	3.075606
H	0.616005	-2.174743	3.491962
H	-0.040118	-0.613107	3.925439

P E=-248.434069086 H=-248.320779 G=-248.372866

N	-0.663982	-0.067659	-0.652655
O	-0.904854	0.031503	1.590340
C	0.076125	0.032743	-1.890026
H	0.395970	1.058694	-2.121679
H	0.964548	-0.604911	-1.868985
H	-0.554572	-0.316425	-2.711139
C	-0.162249	-0.004994	0.619650
H	-1.671014	-0.000302	-0.686905
C	1.348542	-0.008030	0.748749
H	1.779106	-0.932762	0.349243
H	1.803315	0.828672	0.207948
H	1.594834	0.070306	1.807138