Supporting information

Probing the gas phase structure of charge-tagged intermediates of a proline catalyzed aldol reaction – Vibrational spectroscopy distinguishes oxazolidinone from enamine species

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1 Mixing Tee Setup

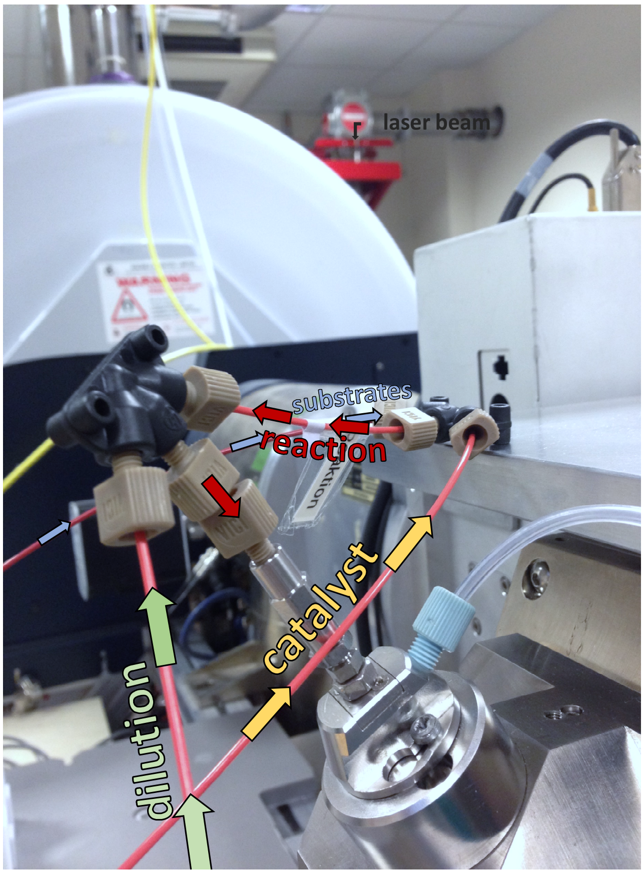


Fig. S1 – Continuous flow mixing tee setup for the ongoing detection of intermediates ^{1}**A**, ^{1}**B** and ^{1}**A**$_{(acetone)}$.

2 Mass Spectra

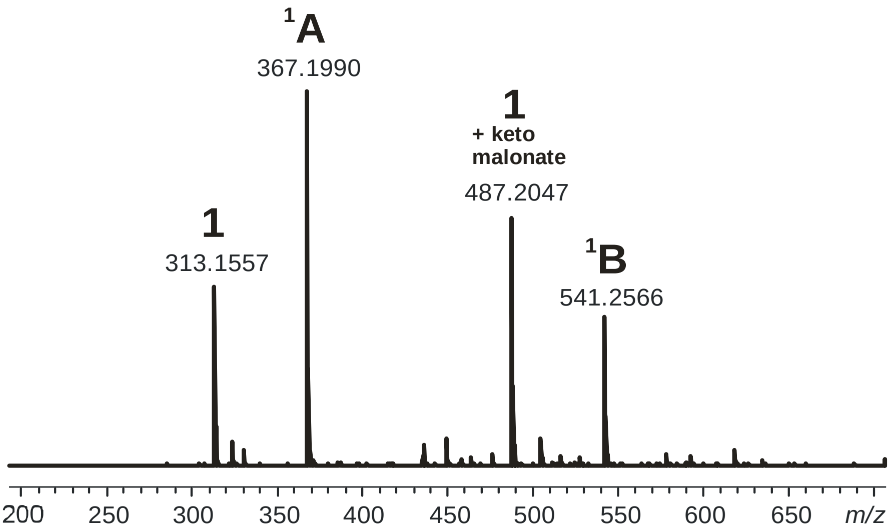


Fig. S2 – ESI(+) mass spectrum of acetonitrile solutions of diethyl ketomalonate and butyraldehyde [2 mM] as well as catalyst **1** [1 mM] recorded with the continuous-flow setup shown in Fig. S1.

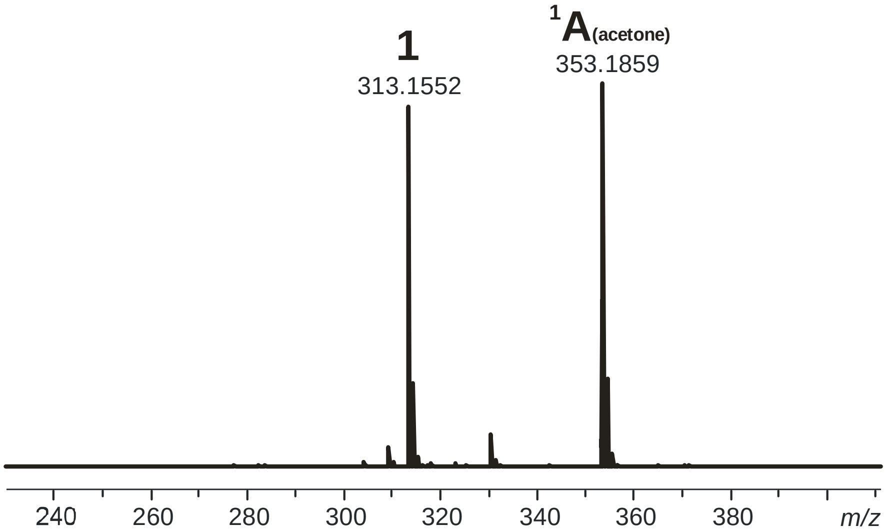


Fig. S3 – ESI(+) mass spectrum of acetonitrile solutions of acetone [10 % v/v] as well as catalyst **1** [1 mM] recorded with the continuous-flow setup shown in Fig. S1.

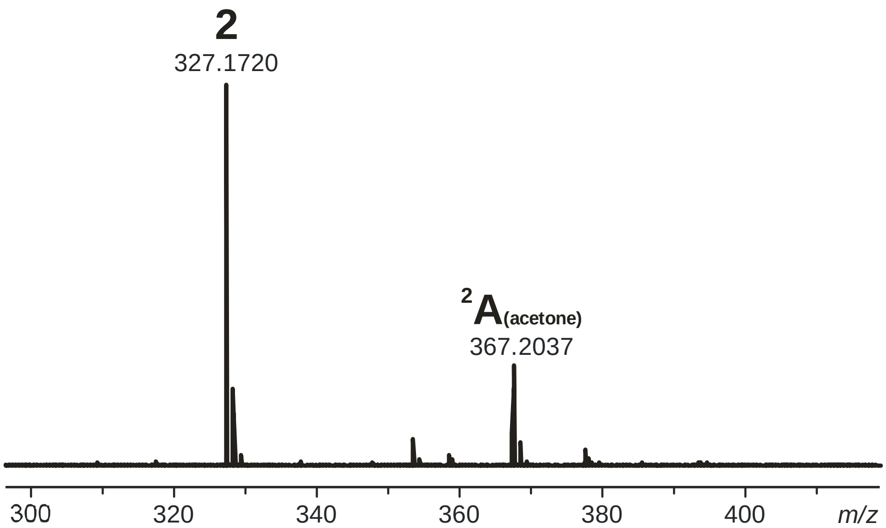


Fig. S4 – ESI(+) mass spectrum of catalyst **2** [1 mM] and acetone [50 % v/v] in acetonitrile.

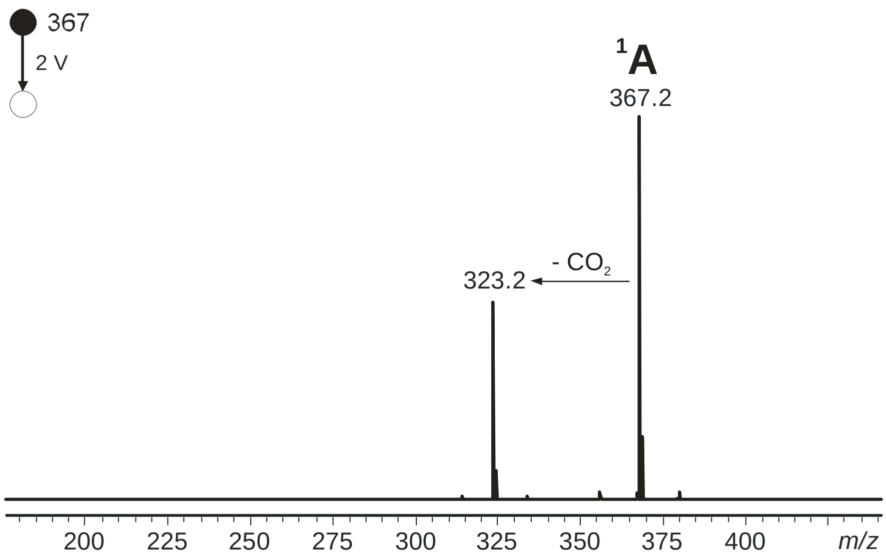


Fig. S5 – ESI(+) CID MS/MS spectrum of mass-selected ^{1}**A**.

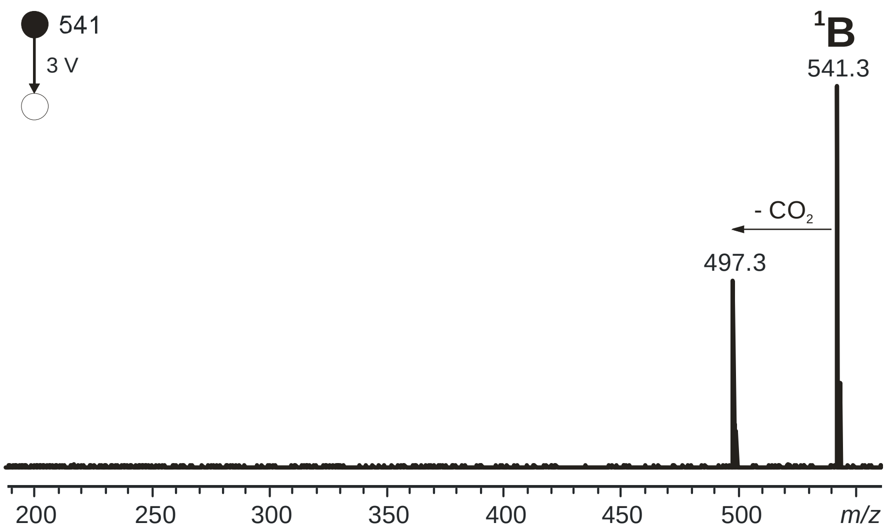


Fig. S6 – ESI(+) CID MS/MS spectrum of mass-selected ^{1}**B**.

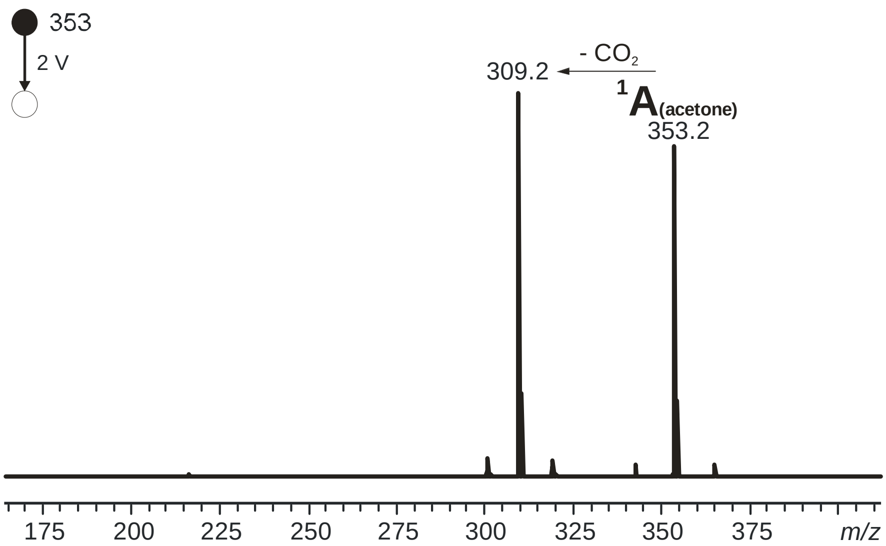


Fig. S7 – ESI(+) CID MS/MS spectrum of mass-selected ^{1}**A**$_{(acetone)}$.

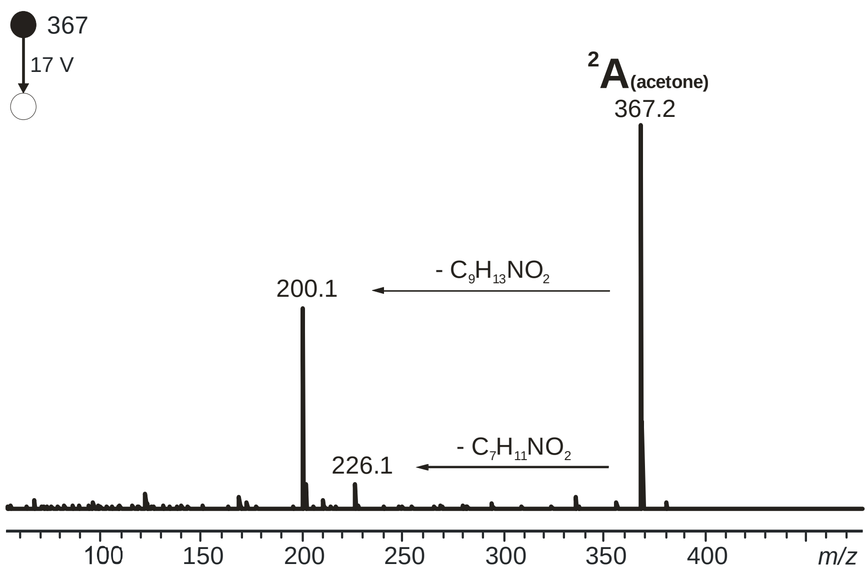


Fig. S8 – ESI(+) CID MS/MS spectrum of mass-selected ^{2}**A**$_{(acetone)}$.

3 Additional IRMPD spectra

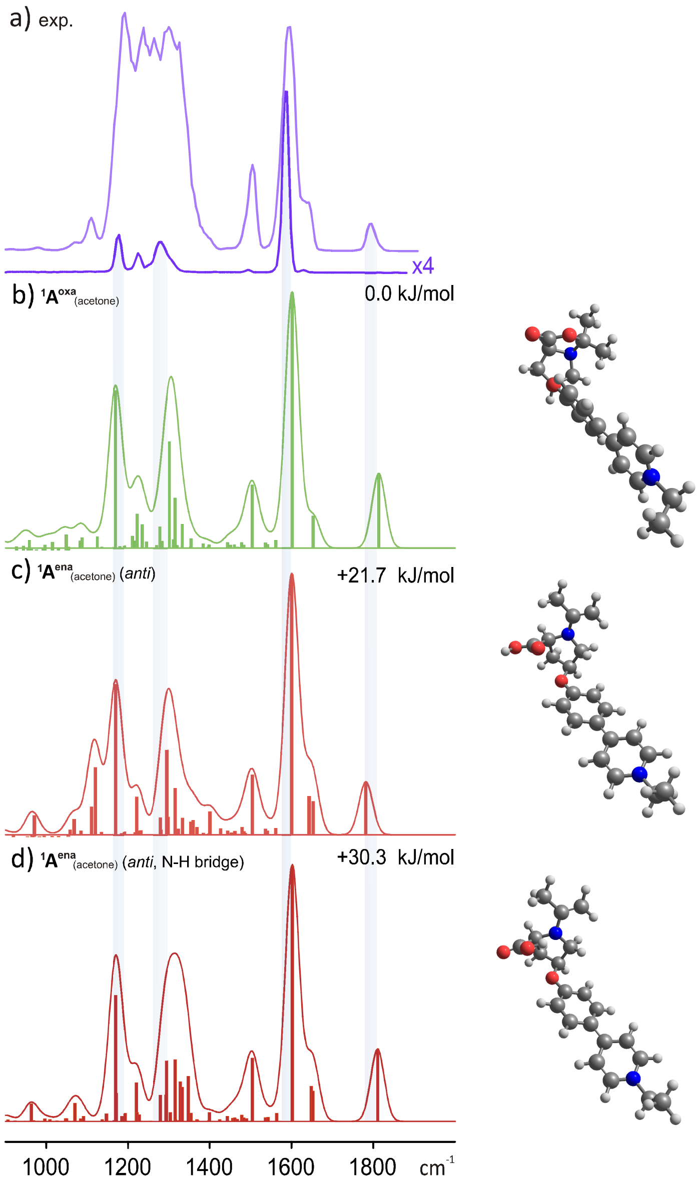


Fig. S9 – a: IRMPD spectra of $^{1}\mathbf{A}_{(\text{acetone})}$ (m/z = 353) with 3 dB (light purple) and 12 dB (deep purple) attenuation; b: Calculated* spectrum of $^{1}\mathbf{A}^{\mathbf{oxa}}_{(\text{acetone})}$; c: Calculated* spectrum of $^{1}\mathbf{A}^{\mathbf{ena}}_{(\text{acetone})}$ (*anti*); d: Calculated* spectrum of $^{1}\mathbf{A}^{\mathbf{ena}}_{(\text{acetone})}$ (*anti*, with N-H bridge); *B3LYP-D3/def2-TZVP (scaling: 0.979).

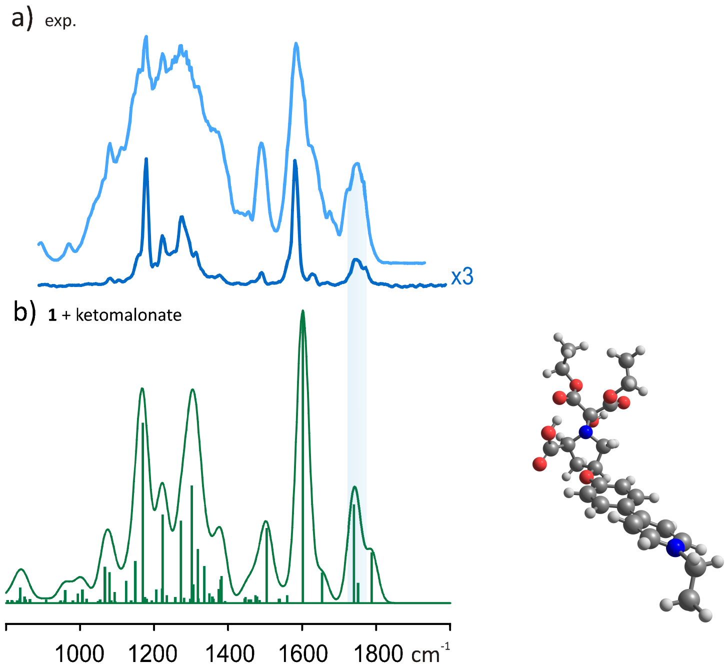


Fig. S10 – a: IRMPD spectra of the adduct of **1** and diethyl ketomalonate (*m/z* = 487) with 6 dB (light blue) and 15 dB (deep blue) attenuation; b: Calculated* spectrum of the amine derived from catalyst **1** and diethyl ketomalonate*)*; region of C=O stretching vibrations highlighted; *B3LYP-D3/def2-TZVP (scaling: 0.979).

4 Boltzmann-weighted calculated frequencies of ^{1}A^{oxa} (*exo*)

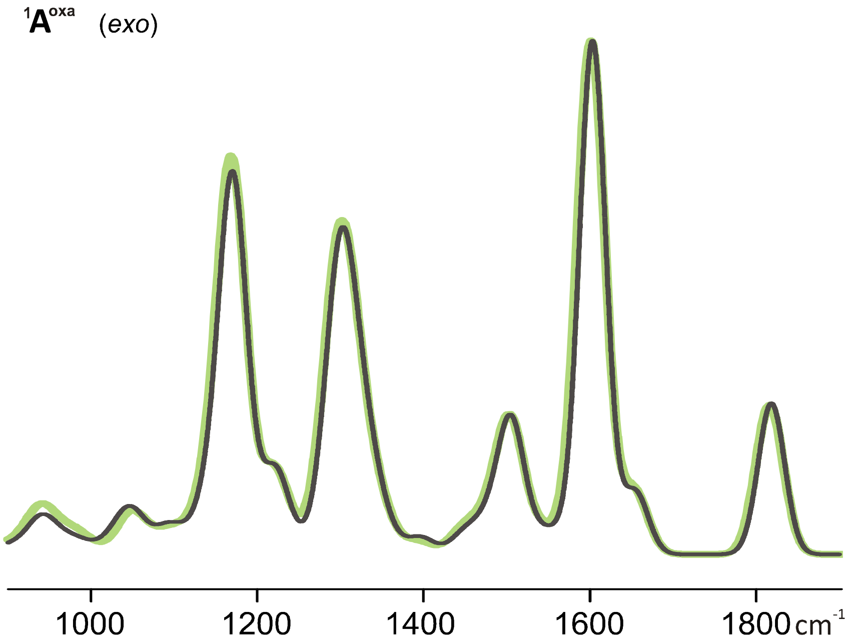
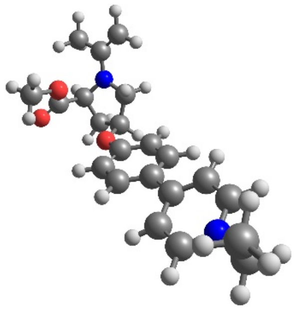


Fig. S11 – Calculated* spectra of **^{1}A^{oxa}** (*exo*); bright green line: Calculated* spectrum of the found minimum for **^{1}A^{oxa}** (*exo*)**; dark grey line: Boltzmann-weighted calculated* spectra of the 32 most stable rotamers observed during the Minima Hopping procedure; *B3LYP-D3/def2-TZVP (scaling: 0.979); **also shown in Fig. 4 b).

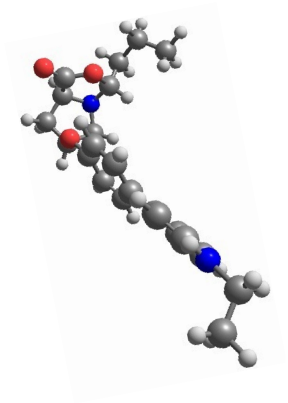
5 Optimized geometries of the presented structures

$^{2}A^{ena}_{(acetone)}$ (*anti*) – *anti* enamine derived from acetone and catalyst 2



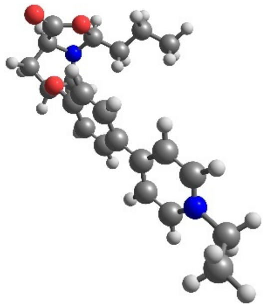
C	-4.66764	-0.19947	-0.59339
C	-3.96740	-0.37706	-1.94640
C	-2.61962	0.29500	-1.72737
C	-2.89959	1.40680	-0.70731
N	-4.22248	1.11654	-0.19316
C	-4.31377	-1.35661	0.35054
O	-4.63042	-2.49622	0.13060
O	-3.63192	-0.95448	1.43061
O	-1.75237	-0.72363	-1.17128
C	-0.45603	-0.48494	-0.98329
C	0.19847	0.70894	-1.32048
C	1.55357	0.83325	-1.09424
C	2.31155	-0.21140	-0.54047
C	1.63286	-1.40234	-0.20819
C	0.28290	-1.53556	-0.41371
C	3.73772	-0.07385	-0.32651
C	4.37406	1.18464	-0.25876
C	5.72374	1.28411	-0.06455
N	6.50089	0.18589	0.06706
C	5.93115	-1.03865	0.01437
C	4.58633	-1.19254	-0.17812
C	7.95065	0.32499	0.33902
C	8.23962	0.41097	1.82915
C	-4.74663	1.84462	0.86280
C	-4.10696	2.89100	1.40781
C	-6.10872	1.42323	1.33398
H	-5.74979	-0.23895	-0.71234
H	-4.52173	0.16815	-2.70938
H	-3.86965	-1.41604	-2.24972
H	-2.17161	0.65748	-2.65202
H	-2.87622	2.39900	-1.16979
H	-2.14533	1.39720	0.08833
H	-0.34198	1.53233	-1.76072
H	2.03329	1.75516	-1.39206
H	2.16464	-2.22362	0.25150
H	-0.23921	-2.44350	-0.14626
H	3.80662	2.09877	-0.33457
H	6.22929	2.23642	-0.00054
H	6.59964	-1.88062	0.11812
H	4.19795	-2.19646	-0.24623
H	8.29003	1.21607	-0.18631
H	8.44377	-0.53293	-0.11483
H	7.74910	1.27556	2.27737
H	9.31372	0.51164	1.98379
H	7.90374	-0.48681	2.34891
H	-3.12870	3.21608	1.08770
H	-4.58081	3.46105	2.19146
H	-6.83846	1.45699	0.52149
H	-6.44967	2.08819	2.12329
H	-6.10104	0.40592	1.73140
C	-3.29187	-1.98453	2.37331
H	-2.76925	-1.47986	3.18016
H	-2.65353	-2.73141	1.90262
H	-4.19254	-2.47183	2.74298

$^{1}A^{oxa}$ (*exo*) – *exo*-oxazolidinone derived from butyraldehyde and catalyst 1



C	-4.61055	-1.15871	-0.01542	H	-5.69959	-1.22728	-0.01368
C	-3.95242	-2.52568	-0.21736	H	-4.52266	-3.12353	-0.92797
C	-2.60615	-2.15887	-0.82398	H	-3.85759	-3.07666	0.71576
C	-2.96341	-0.97889	-1.72933	H	-2.11446	-2.98578	-1.33680
N	-4.09199	-0.29145	-1.08491	H	-3.26669	-1.36347	-2.70704
C	-4.16003	-0.47321	1.27765	H	-2.12925	-0.29611	-1.89015
O	-3.65232	0.73858	0.96435	H	-0.19688	-1.96173	-1.89738
O	-4.21492	-0.90382	2.39079	H	2.11368	-1.24414	-1.94158
O	-1.79925	-1.72734	0.29408	H	1.77537	0.12410	2.12866
C	-0.53226	-1.34164	0.14803	H	-0.56105	-0.61705	2.16047
C	0.22745	-1.49997	-1.01906	H	3.85856	-0.10050	2.20824
C	1.54167	-1.07872	-1.03916	H	6.19432	0.62963	2.07927
C	2.14961	-0.50036	0.08699	H	6.07232	0.79653	-2.05048
C	1.36405	-0.35075	1.24902	H	3.72079	0.10804	-2.09813
C	0.05218	-0.75150	1.28025	H	7.84768	1.69261	0.88246
C	3.53580	-0.07877	0.05929	H	7.79609	1.76182	-0.87274
C	4.28938	0.09879	1.23968	H	8.39938	-0.76716	0.77558
C	5.59636	0.49763	1.18958	H	9.58840	0.19464	-0.10706
N	6.21519	0.74079	0.01304	H	8.34806	-0.69685	-0.99290
C	5.53076	0.58025	-1.14138	H	-2.87367	1.39465	-0.81726
C	4.22227	0.18354	-1.14609	H	-5.88297	1.51332	-0.34746
C	7.65050	1.10805	-0.01446	H	-5.03385	2.16260	-1.73721
C	8.54486	-0.11915	-0.08924	H	-4.72621	3.12455	1.15395
C	-3.82209	0.99303	-0.46239	H	-5.65506	3.92437	-0.09362
C	-4.94994	1.98991	-0.66059	H	-2.60365	3.57903	-0.08730
C	-4.76512	3.31526	0.07967	H	-3.49624	5.07415	0.14039
C	-3.52692	4.10029	-0.34963	H	-3.52113	4.27243	-1.42912

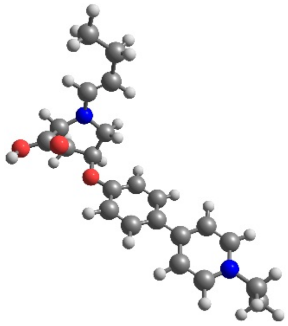
[1]A^{oxa} (*endo*) – *endo*-oxazolidinone derived from butyraldehyde and catalyst 1



H	8.03958	-1.39090	0.38876
C	8.16004	-0.36489	0.73777
H	9.22054	-0.11609	0.70298
H	7.83216	-0.31090	1.77635
H	7.50727	1.63554	0.20382
H	7.71170	0.56291	-1.17311
C	7.38475	0.60842	-0.13576
N	5.93172	0.31806	-0.12531
H	5.61109	1.54125	1.51271
H	6.08453	-0.95003	-1.75351
C	5.13649	0.85571	0.82608
C	5.40127	-0.54065	-1.02409
C	3.80454	0.55493	0.89687
C	4.07546	-0.87400	-0.99683
H	3.21721	1.04205	1.65920
H	3.71883	-1.58259	-1.72774
C	3.20790	-0.33542	-0.02236
C	1.79942	-0.67320	0.03422
H	1.65934	-1.35279	-2.01261
H	1.52220	-0.09114	2.10406
C	1.13301	-1.21064	-1.07907
C	1.04878	-0.47630	1.21204
C	-0.20897	-1.53025	-1.03797
C	-0.28198	-0.80522	1.27407
H	-0.68882	-1.92843	-1.91876
H	-0.85868	-0.66660	2.17799
C	-0.93068	-1.33594	0.14757

O	-2.21891	-1.63054	0.31543
H	-1.83993	1.44021	-0.64319
H	-2.40739	-0.16541	-1.87892
H	-2.70387	-2.81878	-1.32747
C	-1.26922	4.12132	-0.67019
C	-3.08798	-1.94818	-0.79523
H	-2.51645	3.30729	0.89101
C	-2.72334	2.05340	-0.84124
C	-3.31708	-0.72185	-1.67719
C	-2.53982	3.42494	-0.19408
H	-2.81220	2.16421	-1.92570
H	-3.71475	-1.05562	-2.63989
O	-3.76367	1.02123	1.08558
H	-4.41776	-2.73977	0.75064
C	-3.95229	1.33544	-0.33363
H	-3.40932	4.04842	-0.42015
C	-4.45919	-2.16230	-0.17020
N	-4.32485	0.09454	-0.98511
O	-4.46266	-0.60158	2.47337
C	-4.38919	-0.13938	1.37375
H	-5.10919	-2.67130	-0.88144
C	-4.93751	-0.72899	0.07063
H	-4.81309	2.01012	-0.36412
H	-6.02717	-0.65364	0.08479
H	-0.38345	3.52845	-0.42634
H	-1.15478	5.09874	-0.20021
H	-1.28014	4.27205	-1.75228

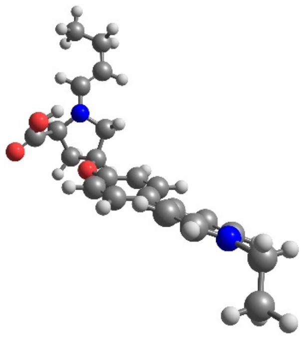
$^{1}A^{ena}$ (*E, anti*) – *anti*-enamine derived from butyraldehyde and catalyst 1



C	-0.39698	-1.70603	-0.66266
C	-1.70114	-1.31491	-0.83048
C	-2.35145	-0.50069	0.12014
C	-1.61674	-0.11239	1.25282
C	-0.30973	-0.50970	1.44205
C	0.31871	-1.31366	0.47990
H	0.11309	-2.29962	-1.40774
H	-2.21041	-1.60702	-1.73806
H	-2.08215	0.48398	2.02525
H	0.21432	-0.20191	2.33379
C	-3.72330	-0.07740	-0.06779
C	-4.26850	1.03876	0.60409
C	-4.60468	-0.75018	-0.94226
C	-5.56546	1.42048	0.40211
H	-3.66346	1.63673	1.26722
C	-5.89369	-0.32674	-1.10937
H	-4.28735	-1.62840	-1.48202
H	-5.99902	2.27722	0.89659
H	-6.58646	-0.83101	-1.76689
C	-7.79317	1.14746	-0.60119
H	-7.83670	2.22907	-0.48470
H	-8.08204	0.91473	-1.62474
C	-8.68786	0.44184	0.40544
H	-8.39991	0.68547	1.42856
H	-9.71968	0.76022	0.25779
H	-8.64508	-0.64069	0.28135
N	-6.37432	0.75038	-0.44907
O	1.56997	-1.76315	0.56310
C	2.47411	-1.26580	1.57632
C	3.79219	-1.99632	1.34653
C	2.80718	0.21603	1.35468
H	2.04485	-1.47172	2.55681
C	4.50629	-1.11247	0.31062
H	3.63987	-3.02323	1.02410
H	4.37137	-1.99792	2.26903
H	2.84602	0.76609	2.30181
H	2.04712	0.69672	0.72782
H	5.59008	-1.23088	0.37432
C	4.09526	-1.47503	-1.12032
O	3.34571	-0.84753	-1.81670
C	4.63885	1.35144	0.14735
H	5.55809	1.16855	-0.39433
C	4.14542	2.58839	0.25310
H	3.22245	2.74759	0.80062
C	4.77727	3.82190	-0.32682
H	4.04488	4.32031	-0.97281
H	4.97290	4.53456	0.48335
C	6.06326	3.59997	-1.11505
N	4.10077	0.20801	0.70957
O	4.69961	-2.61737	-1.51107
H	4.41806	-2.80747	-2.42011
H	5.89926	2.93791	-1.96805
H	6.84404	3.15964	-0.49109
H	6.44350	4.54695	-1.49913

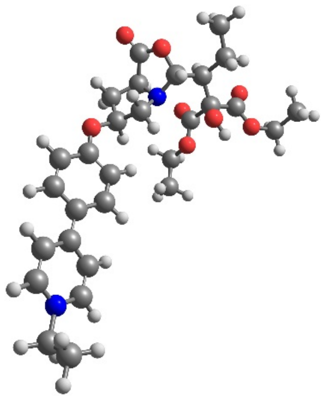
[1]A^{ena} (*E, anti*, with N-H bridge*) – *anti*-enamine with N-H bond derived from butyraldehyde and catalyst 1

*between the proton of the carboxylic acid function and the pyrrolidine nitrogen



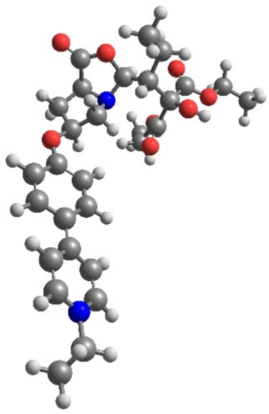
C	-0.51327	-1.57099	-0.44475
C	-1.82099	-1.19975	-0.63147
C	-2.44784	-0.26786	0.22135
C	-1.68150	0.27807	1.26345
C	-0.35909	-0.07038	1.45255
C	0.23673	-1.01078	0.60164
H	-0.03417	-2.29697	-1.08683
H	-2.37691	-1.66868	-1.43104
H	-2.10912	1.02161	1.92156
H	0.20172	0.38793	2.25235
C	-3.83290	0.11352	0.02548
C	-4.61068	0.68647	1.05431
C	-4.49299	-0.06446	-1.20963
C	-5.91541	1.03657	0.84147
H	-4.20172	0.83779	2.04094
C	-5.80023	0.30300	-1.37048
H	-3.97239	-0.46590	-2.06478
H	-6.53218	1.46620	1.61707
H	-6.32215	0.18580	-2.30883
C	-7.94182	1.17922	-0.54382
H	-8.16140	2.02674	0.10306
H	-8.06290	1.51031	-1.57391
C	-8.83650	-0.00939	-0.23052
H	-9.87844	0.27423	-0.37781
H	-8.61820	-0.85257	-0.88662
H	-8.71503	-0.33358	0.80348
N	-6.50826	0.85211	-0.35879
O	1.49150	-1.45178	0.70440
C	2.43208	-0.88159	1.63872
C	3.68070	-1.74261	1.52878
C	2.91755	0.48364	1.16486
H	1.99673	-0.86737	2.63741
C	4.32525	-1.23485	0.23220
H	3.46277	-2.80685	1.49921
H	4.33090	-1.53631	2.37880
H	3.37416	1.02222	2.00561
H	2.11578	1.10791	0.76706
H	5.41134	-1.32587	0.27104
C	3.86252	-2.06314	-0.98149
O	4.03942	-3.24570	-1.05215
C	4.85362	1.14301	-0.21644
H	5.65474	0.74816	-0.82793
C	4.80467	2.43997	0.08976
H	3.98221	2.81769	0.68802
C	5.80885	3.46727	-0.34973
H	5.28357	4.25217	-0.90638
H	6.20433	3.96853	0.54087
C	6.96859	2.94602	-1.19011
N	3.90778	0.17216	0.13861
O	3.25981	-1.35543	-1.94738
H	3.20804	-0.43699	-1.61464
H	7.64160	3.76108	-1.45625
H	6.61768	2.49076	-2.11856
H	7.55244	2.19957	-0.64745

$^{1}\mathbf{B}^{oxa}$ (*exo*) – *exo*-oxazolidinone derived from butyraldehyde, diethyl ketomalonate and catalyst 1



N	2.20340	-1.33499	-0.05615
C	2.53156	-2.51121	0.75988
C	1.19479	-3.12055	1.20156
C	0.17000	-2.07889	0.75494
C	0.81377	-1.44750	-0.47799
C	3.19932	-1.27540	-1.11099
C	4.34526	-0.29697	-0.81304
C	3.35761	-3.38170	-0.17809
O	3.70842	-2.62601	-1.24932
O	3.65856	-4.52952	-0.05281
C	5.16903	0.01230	-2.07195
C	3.72760	0.97974	-0.20861
O	2.73585	1.44251	-1.09684
N	-8.47390	1.15648	-0.30643
C	-8.28587	-0.09015	-0.79319
C	-7.08330	-0.72967	-0.67222
C	-5.98727	-0.10736	-0.03680
C	-6.22755	1.19403	0.45477
C	-7.44987	1.78914	0.30872
C	-4.70312	-0.76360	0.10380
C	-4.58439	-2.16551	0.01012
C	-3.36974	-2.78960	0.14509
C	-2.20506	-2.03554	0.36314
C	-2.29775	-0.63889	0.44719
C	-3.52889	-0.02735	0.32998
O	-1.07455	-2.73591	0.47685
C	-9.76590	1.85266	-0.51086
C	-9.77491	2.65451	-1.80262
C	5.92967	-1.17748	-2.65467
C	3.16142	0.68105	1.20331
O	3.74176	0.03585	2.03651
O	2.02461	1.36150	1.43269
C	0.20952	2.04173	2.81993
C	1.47860	1.22547	2.76021
C	4.81941	2.04152	0.05250
O	5.90660	1.79738	0.49361
O	4.35742	3.26929	-0.22832
C	6.18606	4.56459	-1.20990
C	5.27380	4.38018	-0.01749
H	3.16146	-2.22280	1.60479
H	1.15523	-3.31424	2.27021
H	1.00476	-4.06017	0.68266
H	0.00972	-1.33284	1.53547
H	0.42289	-0.46591	-0.74112
H	0.67111	-2.12531	-1.33253
H	2.72856	-1.01485	-2.05732
H	4.99128	-0.72908	-0.04790
H	5.89389	0.78602	-1.81953
H	4.50376	0.44015	-2.82657
H	2.56389	2.37119	-0.90203
H	-9.13388	-0.54323	-1.28525
H	-6.99015	-1.71543	-1.10011
H	-5.46160	1.73679	0.98616
H	-7.65944	2.77909	0.68645
H	-5.46270	-2.77972	-0.13067
H	-3.28352	-3.86602	0.09623
H	-1.41623	-0.03328	0.58464
H	-3.56334	1.05254	0.37153
H	-9.92590	2.49034	0.35699
H	-10.54316	1.09062	-0.50782
H	-8.99813	3.41976	-1.79758
H	-10.73922	3.14993	-1.91400
H	-9.62148	2.00978	-2.66854
H	5.26622	-1.95155	-3.03605
H	6.57166	-1.63868	-1.90202
H	6.56488	-0.84343	-3.47624
H	-0.23253	1.96530	3.81444
H	-0.52128	1.68567	2.09124
H	0.41274	3.09302	2.61438
H	2.21957	1.56674	3.48361
H	1.29632	0.16706	2.95608
H	5.60826	4.71249	-2.12290
H	6.83826	3.70156	-1.33685
H	6.81285	5.44449	-1.05475
H	5.83686	4.18856	0.89419
H	4.61965	5.23707	0.12951

^{1}B^{oxa} (*endo*) – *endo*-oxazolidinone derived from butyraldehyde, diethyl ketomalonate and catalyst 1



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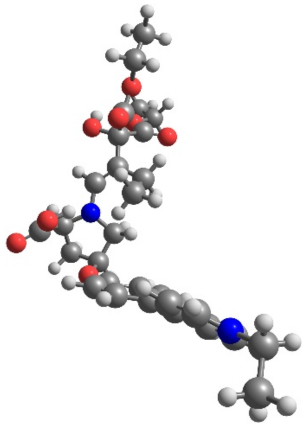
C	-2.54211	2.88100	0.95902
C	-1.19530	3.47453	1.38935
C	-0.20614	2.34832	1.07675
C	-0.91049	1.54173	-0.00765
C	-3.34258	1.22948	-0.40817
C	-3.09226	0.09876	-1.39590
C	-3.14592	3.50952	-0.30491
O	-3.55706	2.50193	-1.10943
O	-3.23588	4.66742	-0.58394
C	-4.01280	0.17257	-2.63221
C	-3.17879	-1.29849	-0.71989
O	-2.56870	-2.18357	-1.63209
N	8.04187	-1.57258	-0.55717
C	7.87597	-0.36141	-1.13415
C	6.74193	0.37505	-0.93408
C	5.69785	-0.10119	-0.11101
C	5.91485	-1.36850	0.47309
C	7.06801	-2.06481	0.24104
C	4.48500	0.65783	0.11172
C	4.43534	2.04596	-0.13234
C	3.28329	2.76406	0.06720
C	2.11346	2.12153	0.50457
C	2.13841	0.74132	0.75435
C	3.30933	0.03723	0.56536
O	1.04207	2.90791	0.64892
C	9.30850	-2.31896	-0.73779
C	10.33311	-1.95710	0.32563
C	-3.40389	0.96587	-3.78506
C	-2.39169	-1.33514	0.61848
O	-1.19626	-1.46716	0.68267
O	-3.20396	-1.22046	1.66608
C	-3.69590	-0.91208	3.97738
C	-2.58787	-1.07839	2.96670
C	-4.63857	-1.70578	-0.43307
O	-5.54442	-0.94760	-0.22114
O	-4.74759	-3.04042	-0.43428
C	-5.96274	-5.08966	-0.22616
C	-6.06240	-3.58703	-0.14245
H	-3.29861	2.91018	1.74632
H	-1.17947	3.75889	2.43846
H	-0.95865	4.35724	0.79611
H	-0.03165	1.72924	1.95875
H	-0.51706	0.54181	-0.14628
H	-0.83657	2.09257	-0.95575
H	-4.97591	0.59425	-2.34632
H	-4.20125	-0.84584	-2.97360
H	-2.83349	-3.08400	-1.40587
H	8.68146	-0.02137	-1.76829
H	6.65430	1.31755	-1.45103
H	5.18477	-1.80704	1.13499
H	7.25894	-3.03064	0.68520
H	5.32158	2.57739	-0.44970
H	3.25045	3.83082	-0.10452
H	1.25330	0.21070	1.06846
H	3.28498	-1.03042	0.73294
H	9.67313	-2.09080	-1.73787
H	9.06170	-3.37898	-0.71080
H	10.58160	-0.89597	0.28952
H	11.24696	-2.52633	0.15634
H	9.96543	-2.19333	1.32467
H	-3.21369	2.00038	-3.50324
H	-4.07942	0.97110	-4.64168
H	-2.46188	0.51600	-4.10780
H	-3.26944	-0.79259	4.97443
H	-4.35006	-1.78416	3.98732
H	-4.29840	-0.03206	3.75150
H	-1.93428	-0.20605	2.92412
H	-1.97654	-1.96023	3.15975
H	-6.93577	-5.53087	-0.00595
H	-5.24171	-5.47629	0.49495
H	-5.66344	-5.40781	-1.22539
H	-6.76733	-3.17654	-0.86485
H	-6.35554	-3.24339	0.84967
H	-4.25920	1.03678	0.14898
H	-2.06145	0.15666	-1.74724

$^{1}B^{ena}$ (*E*, *anti,* with N-H bridge*) – *anti*-enamine derived from butyraldehyde, diethyl ketomalonate and catalyst 1

*between the proton of the carboxylic acid function and the pyrrolidine nitrogen



N	-1.43413	2.19673	-0.00441	C	-6.26887	-1.19997	2.55798
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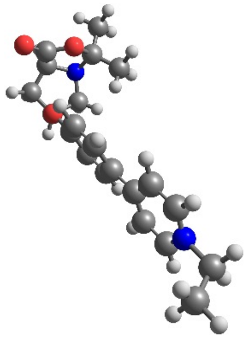
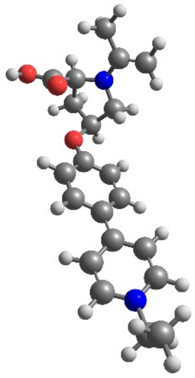
C	-0.87914	4.43742	0.56838	H	-1.62201	4.73119	1.30972
C	0.11169	3.47638	1.20610	H	-0.40887	5.32944	0.16390
C	-0.66457	2.16850	1.23859	H	0.48015	3.79364	2.18152
C	-2.50136	1.32105	-0.22243	H	-1.32159	2.14982	2.11645
C	-2.51636	0.00350	0.01064	H	-0.01582	1.29883	1.29448
C	-0.79558	3.73850	-1.86763	H	-1.63798	-1.85039	0.58916
O	-0.67111	4.80832	-2.39142	H	-1.03186	-0.50658	1.48153
O	-0.32159	2.60804	-2.41445	H	-5.61972	-0.05633	-0.54568
C	-1.33156	-0.81427	0.47621	H	6.92510	-2.55944	-1.81188
C	-3.82472	-0.73254	-0.23920	H	5.15075	-0.86790	-1.84202
O	-4.74463	0.09421	-0.92503	H	5.73294	-0.40821	2.40687
N	7.25282	-2.41240	0.22614	H	7.46207	-2.14069	2.26664
C	6.62118	-2.04635	-0.91135	H	4.37523	1.08306	-1.78204
C	5.64212	-1.09188	-0.90826	H	2.57650	2.74918	-1.72897
C	5.25574	-0.44891	0.28743	H	2.00157	2.00777	2.45548
C	5.94232	-0.85983	1.44987	H	3.76421	0.34485	2.41764
C	6.91548	-1.81884	1.39248	H	8.11426	-4.11290	-0.60540
C	4.21769	0.56286	0.31539	H	8.34077	-3.93858	1.12862
C	3.85509	1.26402	-0.85195	H	9.71206	-2.20496	-1.01409
C	2.86222	2.21217	-0.83529	H	10.48141	-3.49405	-0.08440
C	2.16969	2.48275	0.35375	H	9.93868	-2.02570	0.73277
C	2.51994	1.80768	1.52980	H	-0.42254	-1.10417	-1.46390
C	3.53325	0.87173	1.50232	H	0.66974	-1.40882	-0.10501
O	1.20620	3.40409	0.26195	H	0.28647	0.24302	-0.56605
C	8.35560	-3.40097	0.18208	H	-6.04237	-5.54541	-2.33927
C	9.70027	-2.73442	-0.06090	H	-6.85968	-4.04827	-1.87559
C	-0.12922	-0.76151	-0.47331	H	-6.02152	-5.01740	-0.65179
C	-3.62122	-1.96570	-1.15882	H	-3.82243	-4.51832	-1.76577
O	-2.68562	-2.13467	-1.89220	H	-4.65591	-3.55435	-2.98740
O	-4.68376	-2.76908	-1.07406	H	-8.16493	-0.89402	3.49256
C	-5.98661	-4.67345	-1.68601	H	-8.23738	-0.91431	1.72740
C	-4.71052	-3.91660	-1.96051	H	-7.59157	0.50254	2.57324
C	-4.38406	-1.23266	1.11001	H	-5.65605	-0.88176	3.40130
O	-3.78187	-1.95772	1.85654	H	-6.29721	-2.28935	2.55139
O	-5.61442	-0.76193	1.33650	H	-0.51738	1.88263	-1.79291
C	-7.64652	-0.58647	2.58330	H	-3.37820	1.78237	-0.65672

$^{1}A^{oxa}_{(acetone)}$ – oxazolidinone derived from acetone and catalyst 1



H	-9.30560	-0.25817	0.58484
C	-8.24574	-0.02746	0.69080
H	-7.92794	-0.33773	1.68666
H	-8.12311	1.05293	0.60831
H	-7.58443	-1.83408	-0.31447
H	-7.77893	-0.45504	-1.38608
C	-7.46093	-0.75504	-0.38906
N	-6.00847	-0.47760	-0.29405
H	-5.69147	-2.09871	0.95244
H	-6.15778	1.18430	-1.51812
C	-5.21554	-1.25304	0.47817
C	-5.47618	0.59287	-0.92464
C	-3.88387	-0.98319	0.63118
C	-4.15064	0.90616	-0.80447
H	-3.29816	-1.65906	1.23413
H	-3.79208	1.78597	-1.31522
C	-3.28520	0.12284	-0.01052
C	-1.87635	0.42965	0.13778
H	-1.73007	1.63896	-1.64738
H	-1.60587	-0.69247	1.97272
C	-1.20562	1.24592	-0.78762
C	-1.12855	-0.08320	1.21836
C	0.13840	1.53422	-0.66195
C	0.20389	0.20807	1.36661
H	0.62231	2.15402	-1.40091
H	0.77866	-0.17384	2.19888
C	0.85778	1.01921	0.42494
O	2.14836	1.24372	0.66377
H	1.75148	-1.36053	-1.00609
H	2.36686	0.45994	-1.86682
H	2.62927	2.84532	-0.58140
C	3.01932	1.86422	-0.30871
C	2.60932	-1.90807	-1.39322
C	3.26937	0.93444	-1.49561
H	2.47174	-2.96109	-1.15386
H	2.64767	-1.80631	-2.47776
H	3.68198	1.52912	-2.31602
O	3.72467	-1.50706	0.69240
H	4.33344	2.20057	1.40667
C	3.90375	-1.43067	-0.76836
C	4.38429	1.90519	0.36107
N	4.27053	-0.04210	-1.04641
O	4.42154	-0.32387	2.46980
C	4.34171	-0.46671	1.28536
H	5.03271	2.59836	-0.17420
C	4.87684	0.46560	0.19520
C	5.06632	-2.34885	-1.12266
H	5.96683	0.40861	0.19214
H	5.99104	-1.98922	-0.67227
H	5.20031	-2.36983	-2.20387
H	4.87607	-3.35949	-0.76268

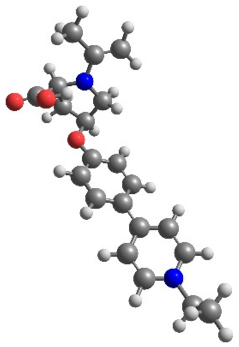
$^{1}A^{ena}_{(acetone)}$ (*anti*) – *anti* enamine derived from acetone and catalyst 1



C	-4.74900	-0.32216	-0.11551	H	-5.83787	-0.30094	-0.08098
C	-4.26250	-1.08310	-1.36018	H	-4.91013	-0.83592	-2.20053
C	-2.87651	-0.50129	-1.60202	H	-4.24076	-2.16290	-1.23731
C	-2.98337	0.94895	-1.12051	H	-2.55517	-0.59054	-2.63970
N	-4.18996	0.99015	-0.32000	H	-3.05264	1.64650	-1.96246
C	-4.27198	-0.99447	1.17563	H	-2.10480	1.23245	-0.53220
O	-3.40028	-0.59407	1.89707	H	-4.65215	-2.51022	2.23669
O	-4.97852	-2.12032	1.41018	H	-0.54238	0.38375	-2.38263
O	-1.97932	-1.27311	-0.77025	H	1.83259	0.75899	-2.13826
C	-0.67795	-0.98937	-0.71564	H	1.91706	-1.91423	1.23719
C	-0.01127	-0.11716	-1.58799	H	-0.48794	-2.28658	0.97506
C	1.34192	0.10089	-1.43477	H	3.56129	1.62018	-1.29621
C	2.08486	-0.54087	-0.43018	H	5.96906	1.95398	-0.98595
C	1.39659	-1.42557	0.42546	H	6.35429	-1.61936	1.05930
C	0.04756	-1.63996	0.29484	H	3.96901	-2.12343	0.80766
C	3.50320	-0.29533	-0.27105	H	8.04082	1.01859	-0.59459
C	4.13070	0.86102	-0.78339	H	8.19976	-0.49031	0.29171
C	5.47092	1.07083	-0.61391	H	7.38678	2.20663	1.53341
N	6.24710	0.18062	0.04371	H	8.96790	1.43618	1.69017
C	5.68611	-0.93969	0.55119	H	7.54848	0.68629	2.42595
C	4.35070	-1.19632	0.40982	H	-2.89728	3.34887	-0.23243
C	7.68228	0.46730	0.27299	H	-4.10345	4.11081	0.93024
C	7.90265	1.24630	1.55995	H	-6.62436	1.76961	0.66152
C	-4.50966	2.11572	0.42343	H	-5.93496	2.96256	1.76320
C	-3.78901	3.24625	0.36716	H	-5.64784	1.24694	2.03758
C	-5.74794	2.01414	1.26661				

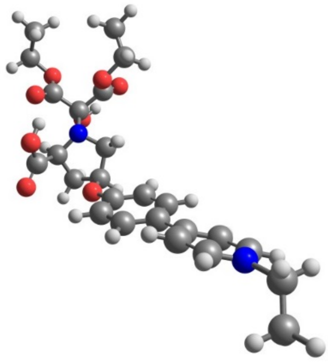
$^{1}A^{ena}_{(acetone)}$ (*anti*, with N-H bridge*) – *anti* enamine derived from acetone and catalyst 1

*between the proton of the carboxylic acid function and the pyrrolidine nitrogen



C	-4.71566	-0.45108	-0.19160	H	-5.80269	-0.41519	-0.19398
C	-4.18326	-0.80600	-1.58675	H	-4.82799	-0.37629	-2.35329
C	-2.83563	-0.10601	-1.62361	H	-4.11165	-1.87863	-1.74603
C	-3.11301	1.20488	-0.89984	H	-2.44222	0.02796	-2.63060
N	-4.11641	0.85849	0.10433	H	-3.50360	1.94261	-1.61190
C	-4.32380	-1.53028	0.83590	H	-2.22176	1.63203	-0.43755
O	-4.69402	-2.66479	0.73877	H	-3.36214	-0.16005	1.66353
O	-3.54510	-1.10292	1.84182	H	-0.48399	0.93958	-2.18708
O	-1.94348	-0.94425	-0.85919	H	1.90045	1.22201	-1.90414
C	-0.63937	-0.67810	-0.75778	H	1.93861	-1.94052	1.01930
C	0.03861	0.31039	-1.48307	H	-0.47568	-2.22419	0.71226
C	1.39810	0.47363	-1.30700	H	3.67560	1.88257	-0.97956
C	2.13058	-0.33362	-0.42234	H	6.10382	2.06941	-0.69941
C	1.42569	-1.31961	0.29816	H	6.38389	-1.78793	0.76311
C	0.07189	-1.48490	0.14434	H	3.97269	-2.15345	0.51214
C	3.56151	-0.16468	-0.26027	H	8.13489	1.02123	-0.51512
C	4.22421	1.03203	-0.60639	H	8.25829	-0.62803	0.07874
C	5.57689	1.16021	-0.45008	H	7.61301	1.82975	1.81710
N	6.32924	0.14910	0.03729	H	9.16036	0.98070	1.76566
C	5.73325	-1.01239	0.38653	H	7.73433	0.16769	2.41548
C	4.38442	-1.19159	0.24978	H	-3.65250	3.51592	0.01317
C	7.78353	0.33592	0.25420	H	-5.02178	3.93160	1.16746
C	8.08344	0.86041	1.64916	H	-6.81130	1.07261	0.99986
C	-4.82936	1.89055	0.73585	H	-6.35708	2.31298	2.16132
C	-4.47703	3.17723	0.62156	H	-5.69637	0.68184	2.30450
C	-5.98404	1.46241	1.59701				

Amine derived from diethyl ketomalonate and catalyst 1

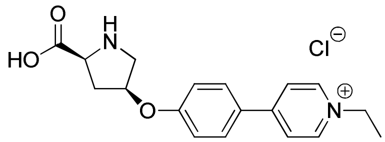


C	2.70900	-2.14142	0.26851
C	1.92577	-2.70105	1.45624
C	0.79243	-1.69903	1.59603
C	1.46801	-0.36262	1.30190
N	2.59210	-0.66808	0.39415
C	2.14359	-2.67849	-1.06625
O	1.68179	-3.78442	-1.15612
O	2.21303	-1.85358	-2.10829
O	-0.16107	-2.03265	0.56476
C	-1.35439	-1.45472	0.48672
C	-1.86921	-0.52730	1.40494
C	-3.14313	-0.02782	1.22743
C	-3.94059	-0.40280	0.13311
C	-3.39333	-1.32340	-0.78671
C	-2.13731	-1.84423	-0.61426
C	-5.27366	0.13083	-0.04598
C	-6.00571	0.71226	1.01292
C	-7.26651	1.20162	0.81558
N	-7.86058	1.15472	-0.39805
C	-7.19546	0.60584	-1.43955
C	-5.93324	0.10218	-1.29518
C	-9.25367	1.62724	-0.56915
C	-10.25973	0.50904	-0.34697
C	3.80296	0.02537	0.72844
C	4.80085	-0.04431	-0.45811
O	5.98286	0.41936	-0.09358
C	7.02487	0.48425	-1.11144
C	3.52678	1.53843	0.93910
O	3.81766	2.09132	1.96954
O	4.51121	-0.42586	-1.56566
O	2.98848	2.10150	-0.12815
C	2.78370	3.54498	-0.09047
C	4.05352	4.27720	-0.46195
C	6.91257	1.75944	-1.91656
O	4.39771	-0.47789	1.90055
H	3.75448	-2.44608	0.30943
H	2.54225	-2.66626	2.35373
H	1.57176	-3.71336	1.28505
H	0.29873	-1.72945	2.56692
H	1.82642	0.05593	2.24660
H	0.78360	0.35108	0.84181
H	2.77502	-1.08480	-1.88009
H	-1.28142	-0.19561	2.24697
H	-3.50513	0.69990	1.94045
H	-3.97703	-1.66657	-1.62925
H	-1.72108	-2.56501	-1.30440
H	-5.59711	0.75812	2.01011
H	-7.84831	1.63784	1.61414
H	-7.71421	0.60148	-2.38691
H	-5.44393	-0.29211	-2.17169
H	-9.33024	2.03954	-1.57400
H	-9.40274	2.44434	0.13452
H	-10.11129	-0.30292	-1.05955
H	-11.26904	0.89792	-0.48062
H	-10.18178	0.10323	0.66212
H	6.94475	-0.40045	-1.73988
H	7.94825	0.44387	-0.53892
H	2.43554	3.81664	0.90454
H	1.99127	3.71232	-0.81618
H	4.83757	4.09663	0.27255
H	3.85708	5.35020	-0.49218
H	4.40588	3.96604	-1.44531
H	5.98294	1.78228	-2.48438
H	7.74304	1.81518	-2.62219
H	6.95842	2.63360	-1.26649
H	4.64378	0.27863	2.45622

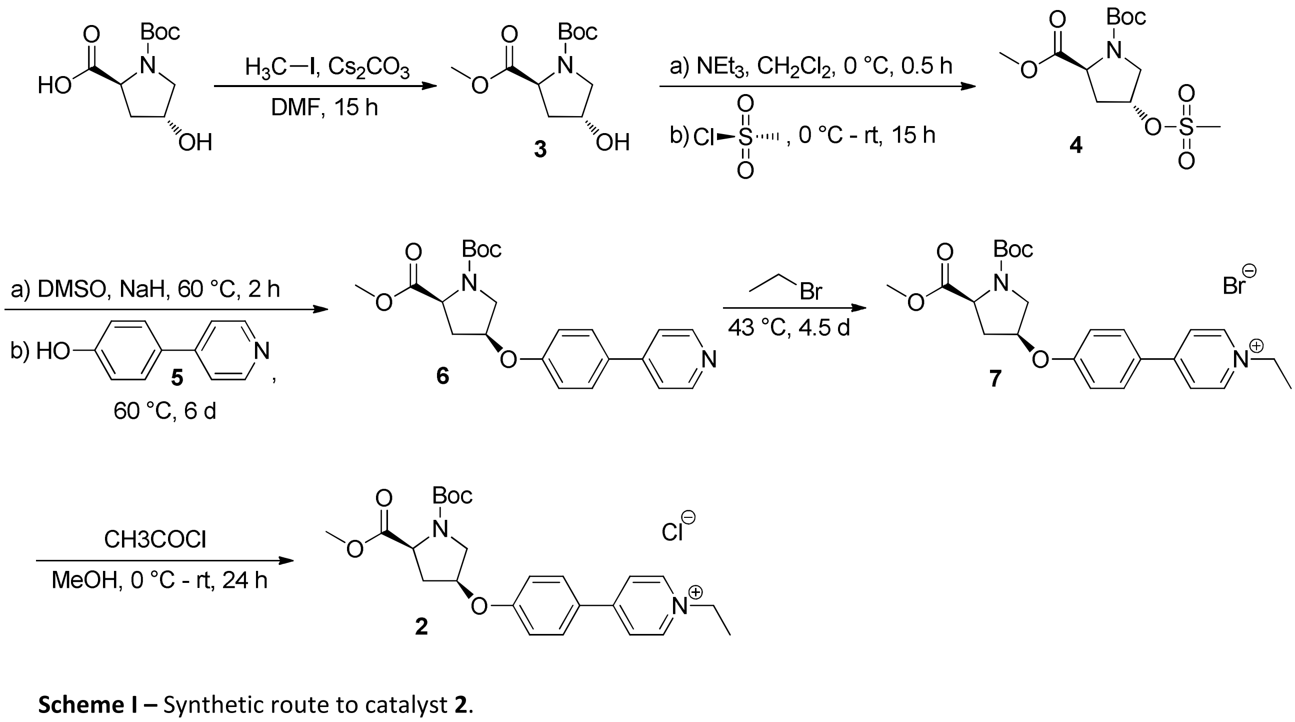
6 Syntheses

Commercially purchased chemicals were used as received without further purification. Reactions under inert gas atmosphere were performed using dry argon, standard Schlenk techniques and oven-dried glassware. For thin-layer chromatography silica gel plates from Merck were used and spots were visualized under UV light (254/366 nm). Column chromatography was performed on silica gel from Merck (pore size 60 Å, 40-63 µm). ^{1}H NMR spectra were recorded at 400 MHz and 500 MHz and ^{13}C NMR spectra were recorded at 100 MHz and 125 MHz. Chemical shifts are reported relative to the solvent residual peak (^{1}H) or the solvent peak (^{13}C) respectively.[1] The abbreviation "s" indicades singlet, "d" doublet, "pd" pseudo-doublet, "t" triplet, "q" quartet and "m" multiplet.

Catalyst 1

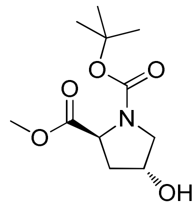


Preparation of the charge-tagged catalyst **1** has been described previously.[2]



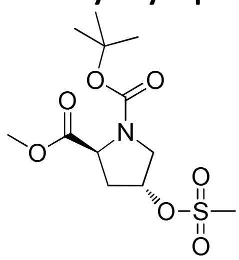
Scheme I – Synthetic route to catalyst **2**.

(4*R*)-*N*-(*tert*-Butoxycarbonyl)-4-hydroxy-L-proline methyl ester (3)



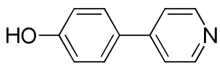
Compound **3** was prepared according to a literature protocol.[3]
Yield = 95 %; **^{1}H-NMR** (500 MHz, DMSO-d_6) δ [ppm]: 5.09 (d, 1H, J = 3.7 Hz), 4.25 (s, 1H), 4.23-4.18 (m, 1H), 3.65/3.62 (s, 3H), 3.43-3.35 (m, 1H), 3.29-3.23 (m, 1H), 2.15-2.07 (m, 1H), 1.93-1.84 (m, 1H), 1.39/1.32 (s, 9H); **^{13}C-{^{1}H}-NMR** (125 MHz, DMSO-d_6) δ [ppm]: 173.3/172.9, 153.7/153.0, 79.0/78.9, 68.5/67.8, 57.7/57.4, 54.7/54.4, 51.8/51.7, 38.7, 28.1/27.8. **HR-ESI-MS(+)** [*m/z*]: 268.1160 $[M+Na]^+$, calc. for $C_{11}H_{19}NO_5Na^+$: 268.1155.

(4*R*)-*N*-*tert*-Butoxycarbonyl-4-methylsulfonyloxy-L-proline methyl ester (4)



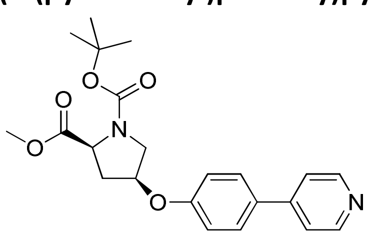
Compound **4** was prepared according to a literature protocol.[2] The spectroscopic data are in agreement with those previously published.[4]

4-(Pyridine-4'-yl)phenol (5)



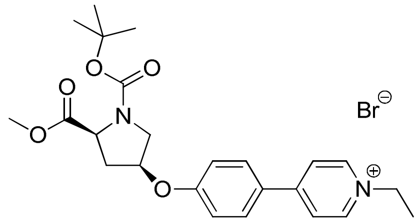
Compound **5** was prepared according to a literature protocol and the spectroscopic data are in agreement with those published.[5]

(2*S*,4*S*)-1-*tert*-Butyl-2-methyl 4-(4-(pyridin-4´-yl)phenoxy)pyrrolidine-1,2-dicarboxylate (6)



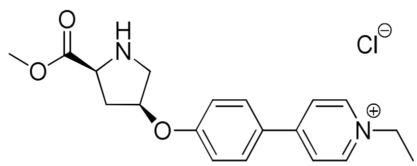
Compound **6** was prepared according to a reported procedure which was slightly modified:[2] 4-(Pyridine-4'-yl)phenol (**5**, 0.34 g, 2.00 mmol) and NaH (60% dispersion in mineral oil, 0.12 g, 3.00 mmol) were dissolved in dry DMSO (20 mL) under inert gas atmosphere. The suspension was heated to 60 °C and stirred for 2.0 h. (4*R*)-*N*-*tert*-Butoxycarbonyl-4-methylsulfonyloxy-L-proline methyl ester (**4**, 0.65 g, 2.00 mmol) was added and the mixture was stirred for 6 d at 60 °C. The reaction was quenched by the addition of H_2O (30 mL) and the aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL) and with Et_2O (2 × 25 mL). The combined organic extracts were dried with $MgSO_4$ and the solvents were removed *in vacuo*. Remaining DMSO was removed by vacuum distillation. The crude product was purified by column chromatography on silica gel using cyclohexane/ethyl acetate (1:2) with 5% triethylamine as eluent (R_f = 0.50). Compound **6** was obtained as yellowish solid.
Yield = 51 %; **^{1}H-NMR** (500 MHz, Methanol-d_4) δ [ppm]: 8.55-8.49 (m, 2H), 7.72 (pd, 2H, *J* = 8.7 Hz), 7.69-7.64 (m, 2H), 7.02-6.97 (m, 2H), 5.14-5.06 (m, 1H), 4.54-4.45 (m, 1H), 3.83-3.75 (m, 1H), 3.73/3,71 (s, 3H) 3.69-3.60 (m, 1H), 2.65-2.50 (m, 1H), 2.48-2.40 (m, 1H), 1.51-1.40 (m, 9H); **^{13}C-{^{1}H}-NMR** (125 MHz, Methanol-d_4) δ [ppm]: 174.1/173.9, 159.3, 156.1/155.9, 150.4, 150.1, 131.6, 129.5, 122.5, 117.4/117.3, 81.7, 77.0/76.1, 59.3/58.9, 53.4, 52.9/52.8/52.7, 36.9/36.2, 28.7/28.5; **HR-ESI-MS(+)** [*m/z*]: 399.1900 $[M+H]^+$, calc. for $C_{22}H_{26}N_2O_5H^+$: 399.1914.

4-(4-(((3S,5S)-1-(*tert*-Butoxycarbonyl)-5-(methoxycarbonyl)pyrrolidin-3-yl)oxy)phenyl)-1-ethylpyridinium bromide (7)



Compound **7** was prepared according to a reported procedure.[2]
(2*S*,4*S*)-1-*tert*-Butyl-2-methyl 4-(4-(pyridin-4´-yl)phenoxy)pyrrolidine-1,2-dicarboxylate (**6**, 0.20 g, 0.50 mmol) was dissolved in bromoethane (99 %, 17 mL, 225.50 mmol) and stirred for 4.5 d at 43 °C. Excessive bromoethane was removed *in vacuo*. Compound **7** was obtained as brownish-yellow, highly viscous oil.
Yield = quant.; **^{1}H-NMR** (400 MHz, Methanol-d_4) δ [ppm]: 8.91 (pd, 2H, *J* = 6.8 Hz), 8.37-8.32 (m, 2H), 8.05-7.99 (m, 2H), 7.11 (pd, 2H, *J* = 8.9 Hz), 5.23-5.17 (m, 1H), 4.64 (q, 2H, *J* = 7.3 Hz), 4.55-4.49 (m, 1H), 3.88-3.77 (m, 1H), 3.73/3.71 (s, 3H), 3.69-3.61 (m, 1H), 2.72-2.56 (m, 1H), 2.48-2.41 (m, 1H), 1.67 (t, 3H, *J* = 7.3 Hz), 1.50-1.40 (m, 9H); **^{13}C-{^{1}H}-NMR** (100 MHz, Methanol-d_4) δ [ppm]: 174.0/173.8, 161.8, 156.9, 156.0/155.8, 145.2, 131.2, 127.7, 124.9, 117.8, 81.8, 77.4, 76.5, 59.2/58.9, 57.2, 53.4/52.8/52.8, 36.9, 36.2, 28.7/28.5, 16.7; **HR-ESI-MS(+)** [*m/z*]: 427.2198 $[M]^+$, calc. for $C_{24}H_{31}N_2O_5^+$: 427.2227.

1-Ethyl-4-(4-(((3*S*,5*S*)-5-(methoxycarbonyl)pyrrolidin-3-yl)oxy)phenyl)pyridinium chloride (2)



Compound **2** was prepared according to a literature protocol.[6]

4-(4-(((3*S*,5*S*)-1-(*tert*-Butoxycarbonyl)-5-(methoxycarbonyl)pyrrolidin-3-yl)oxy)phenyl)-1-ethylpyridinium bromide (**7**, 0.13 g, 0.26 mmol) was dissolved in MeOH (18 mL) and cooled to 0 °C with an ice bath. After dropwise addition of acetyl chloride (98 %, 1.0 mL, 13.73 mmol) the solution was stirred for 24 h without further cooling. The solvent was removed *in vacuo*. Compound **2** was obtained as brown, highly viscous oil.

Yield = quant.; **^{1}H-NMR** (500 MHz, Methanol-d_4) δ [ppm]: 8.90 (pd, 2H, J = 6.3 Hz), 8.35 (pd, 2H, J = 6.3 Hz), 8.05 (pd, 2H, J = 8.4 Hz), 7.20-7.15 (m, 2H), 5.42-5.36 (m, 1H), 4.78-4.71 (m, 1H), 4.63 (q, 2H, J = 7.3 Hz), 3.83 (s, 3H), 3.76-3.70 (m, 2H), 2.82-2.73 (m, 1H), 2.72-2.65 (m, 1H), 1.67 (t, 3H, J = 7.3 Hz); **^{13}C-{^{1}H}-NMR** (125 MHz, Methanol-d_4) δ [ppm]: 170.1, 160.6, 156.5, 145.3, 131.3, 128.3, 125.1, 117.9, 76.6, 59.8, 57.3, 54.3, 52.5, 35.6, 16.8; **ESI-MS(+)** [*m/z*]: 327.1711 $[M]^+$, calc. for $C_{19}H_{22}N_2O_3^+$: 327.1703.

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