Carbon dioxide-based facile synthesis of cyclic carbamates from amino alcohols

Teemu Niemi,[a] Israel Fernández,*[b] Bethany Steadman,[a] Jere K. Mannisto,[a] and Timo Repo*[a]*

[a]Synthesis and Analysis, Department of Chemistry, University of Helsinki, P.O Box 55, 00014 Helsinki (Finland)

[b] Departamento de Quimica Orgánica I and Centro de Innovación en Química Avanzada (ORFEO-CINQA), Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Ciudad Universitaria, 28040 Madrid (Spain)

Electronic supporting information

1. General procedures and methods

All solvents employed were purchased at HPLC-grade and used as received. Aminoalcohols, bases, and other reagents were purchased at the highest commercially available purity levels and used as received, or synthesized in accordance to protocols previously reported in literature[S1,S2]. Deuterated solvents were purchased at the highest purity level and used without further purification. CO_2 was purchased at the 4.5 grade and used as received.

Analytical thin-layer chromatography was performed on silica gel 60 precoated plates (0.20 mm thickness), visualising the reaction progress with UV light at 254 nm. Quantitative flash column chromatography was carried out using silica gel (VWR Silica Gel 40-63 μm). The eluent used is quoted in volume ratios (v1:v2).

All nuclear magnetic resonance (NMR) experiments (^{1}H, ^{13}C,) were performed on a Varian Unity Inova 500 (^{1}H-frequency 500 MHz) spectrometer operating with the frequency, deuterated solvent, and at the temperature indicated in parentheses. All chemical shift values (δ) are reported in parts per million (ppm) downfield in relation to tetramethylsilane using the residual undeuterated solvent signal as a secondary internal standard ($CDCl_3$; δ_H = 7.26 ppm and δ_C = 77.16 ppm, d_6-DMSO; δ_H = 2.50 ppm and δ_C = 39.52 ppm). All coupling constants (*J*) are quoted to the nearest 0.1 Hz with the involved nuclei subscripted, and the resonances are noted as follows: ^{1}H: δ chemical shift in ppm (number of protons, multiplicity, *J* value(s), assignment); ^{13}C: δ chemical shift in ppm (assignment). Splitting patterns are denoted as s (singlet), d (doublet), t (triplet), m (multiplet), br. (broad resonance), app. (apparent). All ^{13}C spectra were proton-decoupled. When available, a previously reported spectrum is cited for comparison.

Gas chromatographic analyses were carried out either on a Bruker Scion 456-GC equipped with a BR-5MS column, or an Agilent 6890N GC fitted with a DB-1ms column. Both gas chromatographs were equipped with a single quadrupole mass spectrometer, operated using electron ionization (EI). For previously unreported compounds, the full EI-MS is given, and it's most intensive peaks annotated as: m/z (intensity).

Enantiomeric excess (ee) was measured using an Agilent 1200 series HPLC equipped with a Daicel CHIRALCEL OD-H 250 x 4.6 mm column. The HPLC was operated at 35 °C, using an isocratic eluent of 1:1 n-hexane:i-PrOH with a flow rate of 0.2 mL/min. Detection was achieved with UV detection at 245nm.

For both GC and HPLC, all samples were prepared using VWR 13 mm syringe filters with 0.2 μm PTFE membranes in order to protect the columns from solid particles.

Melting points (m.p.) of products were measured with a Buchi B-545 melting point apparatus and are noted as follows: m.p.: measured melting point (literature melting point, if available).

[S1] A. S. Chakraborti, S. Rudrawar, A. Kondaskar, *Eur. J. Org. Chem.* **2004**, 3597.
[S2] M. I. N. C. Harris, A. C. H. Braga, *J. Braz. Chem. Soc.* **2004**, *15*, 971.

2. Reaction optimization studies

Reactions conducted at 1 barg CO_2 pressure were performed in thick wall two-necked needle-valved 100 ml Schlenk vessels equipped with Glindemann PTFE sealing rings to assure minimal fluctuations of pressure in the vessel during the reaction. When higher pressures were required, a 1200 mL stainless steel autoclave was employed.

In a typical optimization reaction, 2-(phenylamino)ethan-1-ol (0.5 mmol, 68.6 mg, 62.7 μL) **1a**, TsCl (1.1 equiv., 52.4 mg), and a base (3 equiv.) were added to a 20 mL test tube containing a magnetic stirring bar and 5 mL of solvent at 0 °C. Up to 14 of these test tubes were then sealed with PTFE septa and placed in a 1200 mL stainless steel autoclave, which was then sealed, pressurized with CO_2 to desired pressure, and placed in an oil bath for heating at required temperature.

Upon reaching desired reaction time, the autoclave was cooled to room temperature and depressurized. To each test tube, an internal standard was added (mesitylene, 0.25mmol, 30.0 mg, 34.8 μL), the reaction was diluted to 20.0 mL volume with EtOAc, and an aliquot was taken for GC/MS analysis. The yield and selectivity could then be determined using the multiple point calibration curves provided in the figures and tables below. All reactions were repeated at least three times to ensure accuracy of the results.

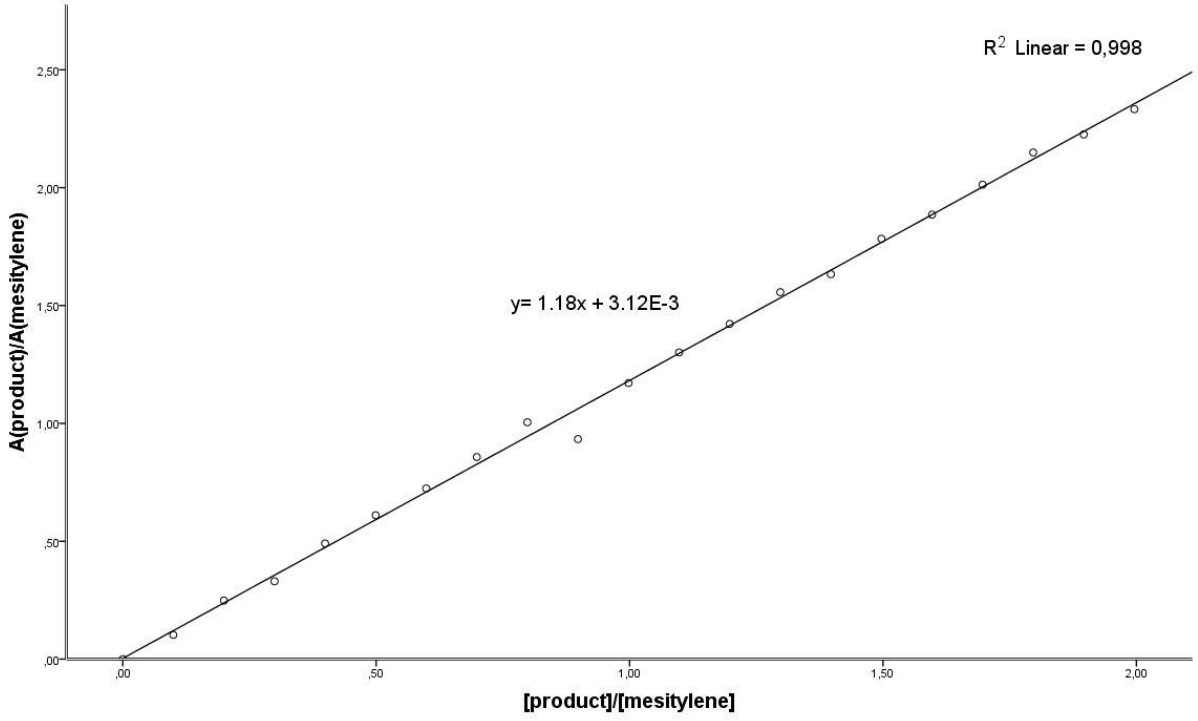


Figure S1. GC-calibration curve for oxazolidinone/mesitylene standard ratio.

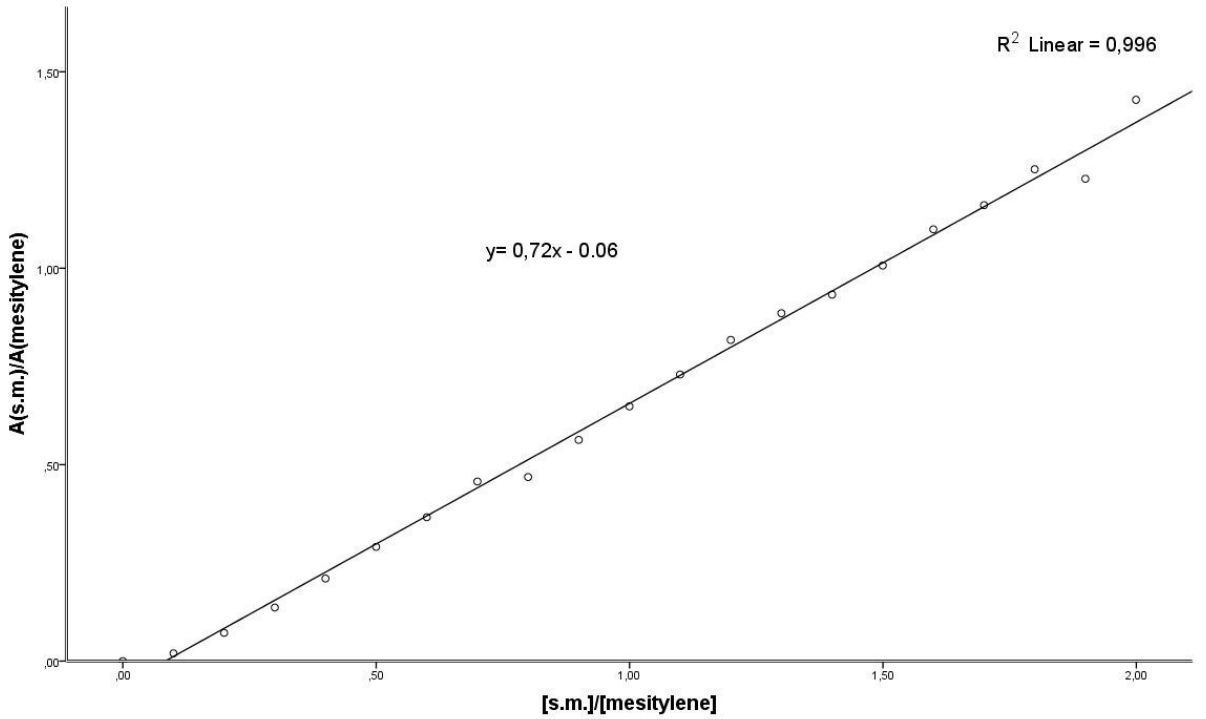


Figure S2. GC-calibration curve for aminoalcohol/mesitylene standard ratio.

Table S1. Values for the calibration curves illustrated above.

[mesitylene]	[product]	[s.m.]	A(mesitylene)	A(product)	A(s.m.)
0,01500465	0	0,03	7108	0	5992
0,01500465	0,001497425	0,0285	6801	265	4165
0,01500465	0,00299485	0,027	6981	869	4134
0,01500465	0,004492275	0,0255	6891	1463	3629
0,01500465	0,0059897	0,024	6373	2168	3525
0,01500465	0,007487125	0,0225	6443	2742	3240
0,01500465	0,00898455	0,021	6438	3355	2771
0,01500465	0,010481975	0,0195	9322	6106	4358
0,01500465	0,0119794	0,018	9701	6917	4149
0,01500465	0,013476825	0,0165	10120	5272	7968
0,01500465	0,01497425	0,015	10170	7024	3049
0,01500465	0,016471675	0,0135	9012	7580	2129
0,01500465	0,0179691	0,012	9179	8688	1457
0,01500465	0,019466525	0,0105	9168	9202	1330
0,01500465	0,02096395	0,009	8853	11280	1128
0,01500465	0,022461375	0,0075	9375	9896	614
0,01500465	0,0239588	0,006	8800	12860	369
0,01500465	0,025456225	0,0045	8482	11350	0
0,01500465	0,02695365	0,003	9021	13790	0
0,01500465	0,028451075	0,0015	9449	14520	0
0,01500465	0,0299485	0	9189	14060	0

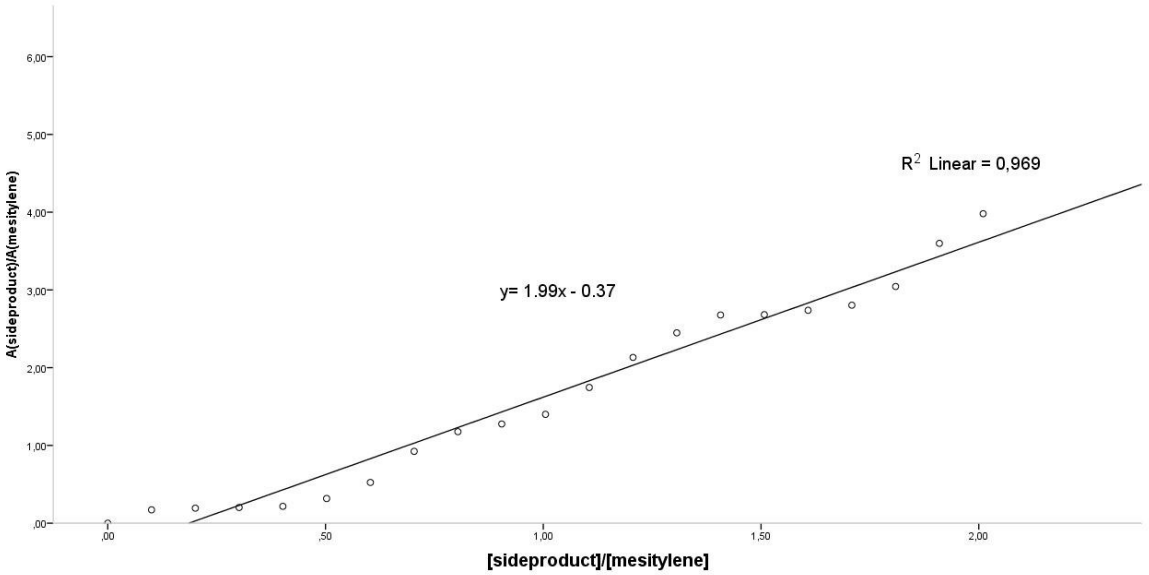


Figure S3. GC-calibration curve for the N-tosylated sideproduct/mesitylene standard ratio.

Table S2. Values for the calibration curve illustrated above.

Ratio of A	0,000	0,172	0,194	0,202	0,216	0,317	0,524	0,924	1,177	1,276	1,400	1,746	2,132	2,448	2,677	2,682	2,738	2,804	3,044	3,599	3,981
Ratio of c	0,000	0,100	0,201	0,301	0,402	0,502	0,603	0,703	0,804	0,904	1,005	1,105	1,206	1,306	1,407	1,507	1,608	1,708	1,809	1,909	2,010

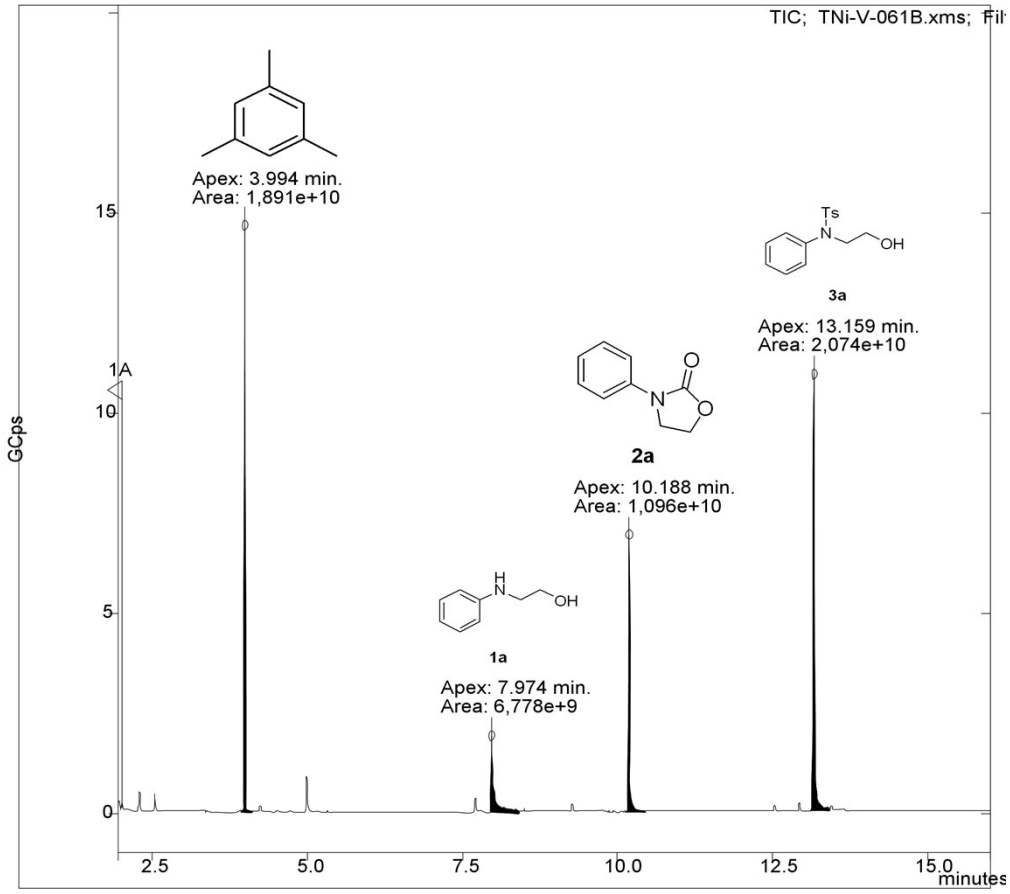
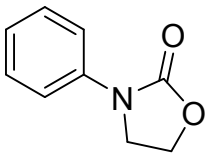


Figure S4. An exemplary chromatogram from optimization studies.

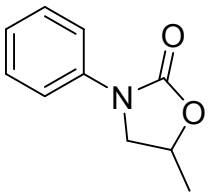
3. Substrate scope and spectroscopic data

General procedure: In a typical reaction, aminoalcohol **1** (0.5 mmol), TsCl (1.1 equiv., 52.4 mg), and Cs_2CO_3 (3 equiv., 489 mg)) were added to a 20 mL glass vial containing a magnetic stirring bar and 5 mL of acetone at 0 °C. Up to five of these vials were then sealed with PTFE septa and placed in a 1200 mL stainless steel autoclave, which was then sealed, pressurized with CO_2 to 5 bars, and stirred at room temperature for 20 hours. The autoclave was then depressurized, and a small aliquot was taken from each vial for GC/MS analysis. Next, the solvent was evaporated, the residue dissolved in 20 mL saturated aqueous NH_4Cl solution and extracted with 3 x 20 mL EtOAc. The organic phase was dried with $MgSO_4$ and evaporated, followed by isolation of the pure product **2** by flash column chromatography. Each reaction was repeated at least twice to ensure the accuracy of the results.



3-Phenyloxazolidin-2-one (2a): 2-(phenylamino)ethan-1-ol **1a** (0.5 mmol, 68.6 mg, 62.7 µL) was subjected to the general procedure described above. After purification by flash column chromatography (n-hexane:EtOAc; 1:1), 38.3 mg of **2a** (47% isolated yield) was obtained as a white solid. The spectroscopic data was consistent with previous reports.[S3]

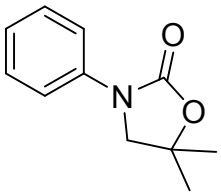
^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): δ 7.53 (2H, d, $^3J_{HH}$=7.5 Hz, 2 x Ar***H***), 7.35 (2H, m, 2 x Ar***H***), 7.13 (1H, dd, $^3J_{HH}$=7.5 Hz, Ar***H***), 4.47 (2H, app. t, $^3J_{HH}$= 7.8 Hz, C***H***$_2$), 4.09(2H, app. t, $^3J_{HH}$= 7.6 Hz, C***H***$_2$N); **^{13}C NMR** (125.8 MHz, $CDCl_3$, 27 °C): δ 155.5 (**C**=O), 138.5 (Ar**C**N), 129.3 (2 x Ar**C**H), 124.3 (Ar**C**H), 118.5 (2 x Ar**C**H), 61.5 (**C**H_2), 45.4 (**C**H_2). **m.p.**: 120 °C (118-119 °C)[S4]



5-methyl-3-phenyloxazolidin-2-one (2b): 1-(phenylamino)propan-2-ol **1b** (0.5 mmol, 75.6 mg) was subjected to the general procedure described above. After purification by flash column chromatography (n-hexane:EtOAc; 1:1), 73.6 mg of **2b** (83% isolated yield) was obtained as a white solid. The spectroscopic data was consistent with previous reports.[S5]

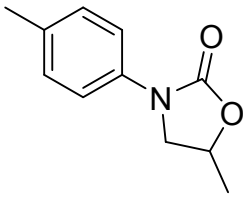
^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): δ 7.52 (2H, d, $^3J_{HH}$=7.8 Hz, 2 x Ar***H***), 7.36 (2H, m, 2 x Ar***H***), 7.12 (1H, t, $^3J_{HH}$=7.4 Hz, Ar***H***), 4.76 (1H, m, C***H***), 4.09 (1H, t, $^3J_{HH}$= 8.5 Hz, C***H***$_2$), 3.61 (1H, t, $^3J_{HH}$= 8.7 Hz, C***H***$_2$), 1.51 (3H, d, $^3J_{HH}$= 6.3 Hz, C***H***$_3$); **^{13}C NMR** (125.8 MHz, $CDCl_3$, 27 °C): δ 155.0 (**C**=O), 138.5 (Ar**C**N), 129.1 (2 x Ar**C**H), 124.0 (Ar**C**H), 118.3 (2 x Ar**C**H), 69.6 (**C**H), 51.9 (**C**H_2), 20.8 (**C**H_3). **m.p.**: 80 °C (78-80 °C)[S6]

[S3] C. J. Dinsmore, S. P. Mercer *Org. Lett.* **2004**, 6, 2885-2888.
[S4] R. Gupta, M. Yadav, R. Gaur, G. Arora, R. K. Sharma, *Green Chem.* **2017**, 19, 3801-3812.
[S5] B. Wang, Z. Luo, E. H. M. Elageed, S. Wu, Y. Zhang, X. Wu, F. Xia, G. Zhang, G. Gao, *ChemCatChem* **2016**, *8*, 830.
[S6] C. Beattie, M. North, *RSC Adv.* **2014**, 4, 31345-31352.



5,5-dimethyl-3-phenyloxazolidin-2-one (2c): 2-methyl-1-(phenylamino)propan-2-ol **1c** (0.5 mmol, 82.6 mg) was subjected to the general procedure described above. After purification by flash column chromatography (n-hexane:EtOAc; 2:1), 9.6 mg of **2c** (10% isolated yield) was obtained as a white solid. The spectroscopic data was consistent with previous reports.[S7]

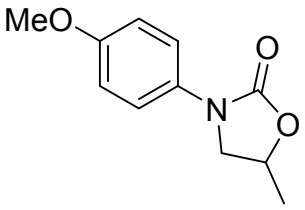
^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): δ 7.52 (2H, m, 2 x Ar***H***), 7.36 (2H, t, $^3J_{HH}$=7.8 Hz, 2 x Ar***H***), 7.16 (1H, m, Ar***H***), 3.74 (2H, s, C***H*****$_2$**), 1.53 (6H, s, 2 x C***H*****$_3$**); **^{13}C NMR** (125.8 MHz, $CDCl_3$, 27 °C): δ 154.6 (**C**=O), 138.7 (Ar**C**N), 129.4 (2 x Ar**C**H), 124.0 (Ar**C**H), 118.3 (2 x Ar**C**H), 77.0 (**C**), 57.2 (**C**H_2), 27.7 (2 x **C**H_3). **m.p.**: 97 °C (98-99.5 °C)[S8]



5-methyl-3-(4-methyl)oxazolidin-2-one (2d): 1-(p-tolylamino)propan-2-ol **1d** (0.5 mmol, 82.6 mg) was subjected to the general procedure described above. After purification by flash column chromatography (n-hexane:EtOAc; 2:1), 81.3 mg of **2d** (85% isolated yield) was obtained as a white solid. The spectroscopic data was consistent with previous reports.[S9]

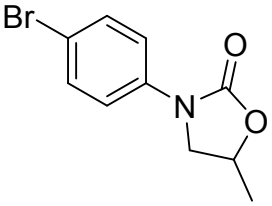
^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): δ 7.40 (2H, d, $^3J_{HH}$=8.6 Hz, 2 x Ar***H***), 7.17 (2H, m, 2 x Ar***H***), 4.77 (1H, m, C***H***), 4.08 (1H, t, $^3J_{HH}$=8.4 Hz, C***H*****$_2$**), 3.59 (1H, t, $^3J_{HH}$=8.5 Hz, C***H*****$_2$**), 2.32 (3H, s, Ar-C***H*****$_3$**), 1.52 (3H, d, $^3J_{HH}$=6.3 Hz, C***H3***); **^{13}C NMR** (125.8 MHz, $CDCl_3$, 27 °C): δ 155.2 (**C**=O), 136.1 (Ar**C**N), 133.8 (Ar**C**Me), 129.8 (2 x Ar**C**H), 118.5 (2 x Ar**C**H), 69.7 (**C**H), 52.3 (**C**H_2), 21.0 (2 x **C**H_3). **m.p.**: 66 °C (66 °C)[S9]

[S7] W. Mahy, P. K. Plucinski, C. G. Frost, *Org. Lett.* **2014**, *16*, 5020.
[S8] L. A. Carpino, K. N. Parameswaran, R. K. Kirkley, J. W. Spiewak, E. Schmitz, *J. Org. Chem.* **1970**, 35, 3291-3295.
[S9] M. Fujiwara, A. Baba, H. Matsuda, *J. Heterocycl. Chem.* **1988**, 25, 1351-1357.



3-(4-methoxyphenyl)-5-methyloxazolidin-2-one (2e): 1-((4-methoxyphenyl)amino)propan-2-ol **1e** (0.5 mmol, 90.62 mg) was subjected to the general procedure described above. After purification by flash column chromatography (n-hexane:EtOAc; 1:1), 51.8 mg of **2e** (50% isolated yield) was obtained as a white solid. The spectroscopic data was consistent with previous reports.[S9]

^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): δ 7.48 (2H, d, $^3J_{HH}$=8.3 Hz, 2 x Ar***H***), 6.96 (2H, d, $^3J_{HH}$=8.6 Hz, 2 x Ar***H***), 4.76 (1H, m, C***H***), 4.10 (1H, m, C$\boldsymbol{H}_2$), 3.80 (3H, s, OC$\boldsymbol{H}_3$) 3.57 (1H, t, $^3J_{HH}$=8.1 Hz, C$\boldsymbol{H}_2$), 1.51 (3H, d, $^3J_{HH}$=6.3 Hz, C$\boldsymbol{H}_3$); **^{13}C NMR** (125.8 MHz, $CDCl_3$, 27 °C): δ 156.5 (**C**=O), 148.9 (Ar**C**), 131.8 (Ar**C**), 120.4 (2 x Ar**C**H), 114.5 (2 x Ar**C**H), 69.7 (**C**H), 55.7 (**C**H_3) 52.6 (**C**H_2), 20.9 (**C**H_3). **m.p.**: 87 °C (88 °C)[S9]

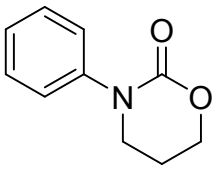


3-(4-bromophenyl)-5-methyloxazolidin-2-one (2f): 1-((4-bromophenyl)amino)propan-2-ol **1f** (0.5mmol, 86.0 mg) was subjected to the general procedure described above. After purification by flash column chromatography (n-hexane:EtOAc; 1:1), 57.6 mg of **2f** (45% isolated yield) was obtained as a white solid. The spectroscopic data was consistent with previous reports[S10].

^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): δ 7.448 (4H, m, 4 x Ar***H***), 4.79 (1H, m, C***H***), 4.08 (1H, t, $^3J_{HH}$= 8.4 Hz, C$\boldsymbol{H}_2$), 3.59 (1H, t, $^3J_{HH}$=8.6 Hz, C$\boldsymbol{H}_2$), 1.53 (3H, d, $^3J_{HH}$=6.2 Hz, C$\boldsymbol{H}_3$); **^{13}C NMR** (125.8 MHz, $CDCl_3$, 27 °C): δ 154.9 (**C**=O), 137.8 (Ar**C**), 132.2 (2 x Ar**C**H), 119.9 (2 x Ar**C**H), 116.9 (Ar**C**), 69.8 (**C**H), 52.0 (**C**H_2), 20.9 (**C**H_3). **m.p.**: 85 °C.

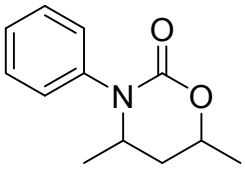
[S9] M. Fujiwara, A. Baba, H. Matsuda, *J. Heterocycl. Chem.* **1988**, 25, 1351-1357.

[S10] P. Wang, J. Qin, D. Yuan, Y. Wang, Y. Yao, *ChemCatChem* **2015**, 7, 1145-1151.



3-phenyl-1,3-oxazinan-2-one (4a): 3-(phenylamino)propan-1-ol **1g** (0.5 mmol, 75.6 mg, 70.0 µL) was subjected to the general procedure described above. After purification by flash column chromatography (n-hexane:EtOAc; 1:1), 40.8 mg of **4a** (46% isolated yield) was obtained as a white solid. The spectroscopic data was consistent with previous reports.[S11]

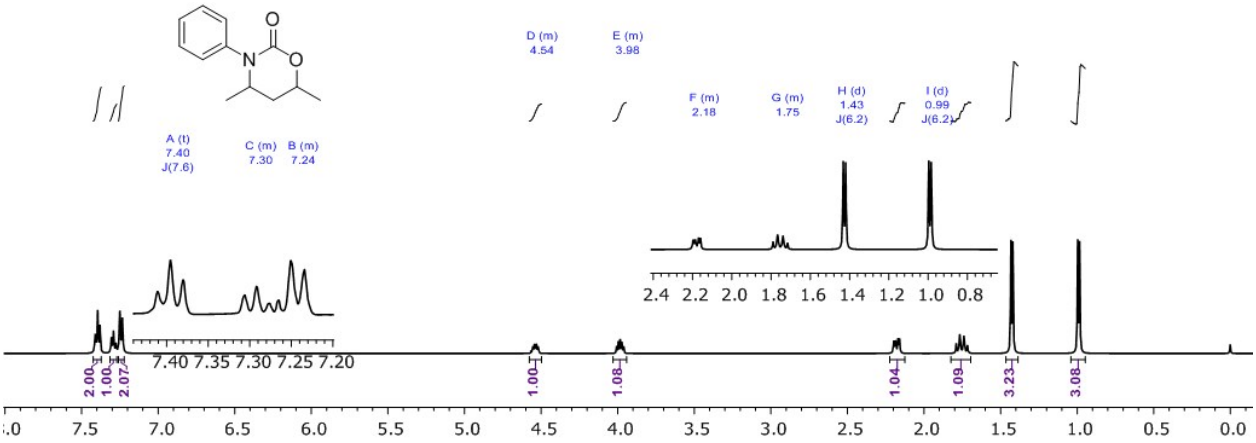
^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): δ 7.41 (2H, t, $^3J_{HH}$= 7.9 Hz, 2 x Ar***H***), 7.34 (2H, d, $^3J_{HH}$= 7.5 Hz, 2 x Ar***H***), 7.28 (1H, m, Ar***H***), 4.43 (2H, t, $^3J_{HH}$= 5.4 Hz, C***H***$_2$), 3.74 (2H, app. t, $^3J_{HH}$= 6.1 Hz, C***H***$_2$), 2.22 (2H, m, C***H***$_2$); **^{13}C NMR** (125.8 MHz, $CDCl_3$, 27 °C): δ 152.9 (**C**=O), 143.1 (Ar**C**N), 129.3 (2 x Ar**C**H), 126.9 (Ar**C**H), 126.0 (2 x Ar**C**H), 67.1 (**C**H_2), 48.9 (**C**H_2), 22.7 (**C**H_2). **m.p.**: 98 °C (99 °C)[S11]

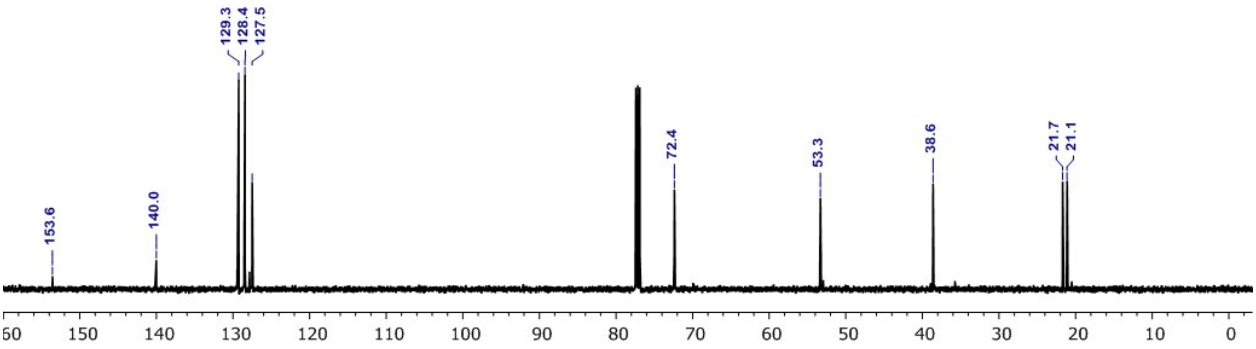


4,6-dimethyl-3-phenyl-1,3-oxazinan-2-one (4b): 4-(phenylamino)pentan-2-ol **1h** (0.5 mmol, 89.6 mg) was subjected to the general procedure described above. After purification by flash column chromatography (gradient, n-hexane:EtOAc 1:1 to 100% EtOAc), 58.5 mg of **4b** (57% isolated yield) was obtained as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): δ 7.40 (2H, t, $^3J_{HH}$= 7.6 Hz, 2 x Ar***H***), 7.30 (1H, m, Ar***H***), 7.24 (2H, m, 2 x Ar***H***), 4.54 (1H, m, C***H***), 3.98 (1H, m, C***H***), 2.18 (1H, m, C***H***$_2$), 1.75 (1H, m, C***H***$_2$), 1.43 (3H, d, $^3J_{HH}$ = 6.2 Hz, C***H***$_3$) 0.99 (3H, d, $^3J_{HH}$ = 6.2 Hz, C***H***$_3$); **^{13}C NMR** (125.8 MHz, $CDCl_3$, 27 °C): δ 153.6 (**C**=O), 140.3 (Ar**C**N), 129.3 (2 x Ar**C**H), 128.4 (2 x Ar**C**H), 127.5 (Ar**C**H), 72.4 (**C**H), 53.3 (**C**H), 38.6 (**C**H_2), 21.7 (**C**H_3), 21.1 (**C**H_3). **EI-MS**: 205.1 (20), 146.1 (27), 119.1 (70), 104.0 (100), 77.1 (75).**m. p.**: 93 °C.

[S11] M. Fujiwara, A. Baba, H. Matsuda, *J. Heterocycl. Chem.* **1989**, 26, 1659.





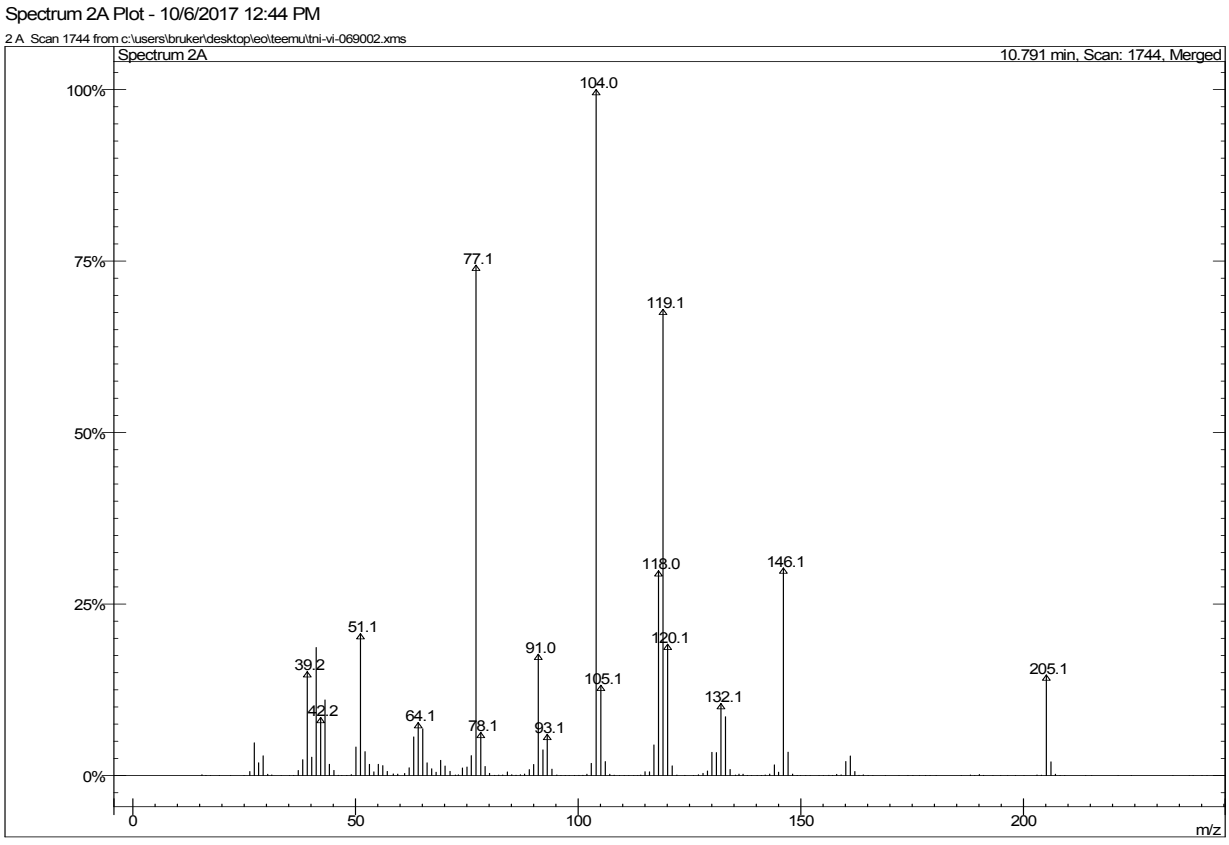
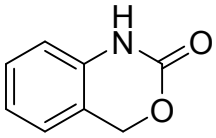
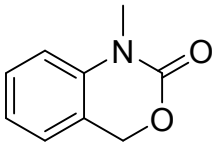


Figure S5. 1H NMR, 13C NMR, and EI-MS spectra of product **4b**.



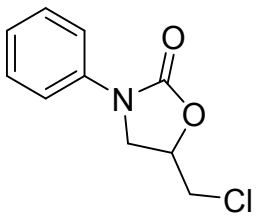
1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (5a): (2-aminophenyl)methanol (0.5 mmol, 61.6 mg) was subjected to the general procedure described above. After purification by flash column chromatography (n-hexane:EtOAc; 1:2), 48.5 mg of **5a** (65% isolated yield) was obtained as a white solid. The spectroscopic data was consistent with previous reports. [S12]

^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): δ 9.05 (1H, s, N***H***), 7.27 (1H, t, $^3J_{HH}$= 7.6 Hz, Ar***H***), 7.11 (1H, m, Ar***H***), 7.07 (1H, m, Ar***H***), 6.90 (1H, d, $^3J_{HH}$= 8.0 Hz, Ar***H***), 5.33 (2H, s, CH_2); **^{13}C NMR** (125.8 MHz, $CDCl_3$, 27 °C): δ 154.1 (**C**=O), 135.8 (Ar**C**), 129.4 (Ar**C**N), 124.4 (Ar**C**H), 123.5 (Ar**C**H), 118.0 (Ar**C**H), 114.6 (Ar**C**H), 68.9 (**C**H_2). **m. p.**: 116 °C (119 °C)[S12]



1-methyl-1,4-dihydro-2H-benzo[d][1,3]oxazin-2-one (5b): (2-(methylamino)phenyl)methanol (0.5 mmol, 68.6 mg) was subjected to the general procedure described above. After purification by flash column chromatography (n-hexane:EtOAc; 1:1), 65.3 mg of **5b** (80% isolated yield) was obtained as a yellow oil. The spectroscopic data was consistent with previous reports.[S12]

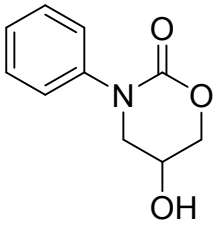
^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): δ 7.45 (1H, m, Ar***H***), 7.21 (1H, m, Ar***H***), 7.00 (1H, m, Ar***H***), 6.81 (1H, m, Ar***H***), 5.08 (2H, s, CH_2), 3.27 (3H, m, CH_3); **^{13}C NMR** (125.8 MHz, $CDCl_3$, 27 °C): δ 154.0 (**C**=O), 138.5 (Ar**C**), 129.3 (Ar**C**N), 124.4 (Ar**C**H), 123.1 (Ar**C**H), 120.7 (Ar**C**H), 112.9 (Ar**C**H), 67.5 (**C**H_2), 31.6 (**C**H_3).



5-(chloromethyl)-3-phenyloxazolidin-2-one (2g): 1-chloro-3-(phenylamino)propan-2-ol **1i** (0.5 mmol, 92.8 mg) was subjected to the general procedure described above. After purification by flash column chromatography (n-hexane:EtOAc; 3:1), 43.4 mg of **2g** (41% isolated yield) was obtained as a white solid. The spectroscopic data was consistent with previous reports.[S13]

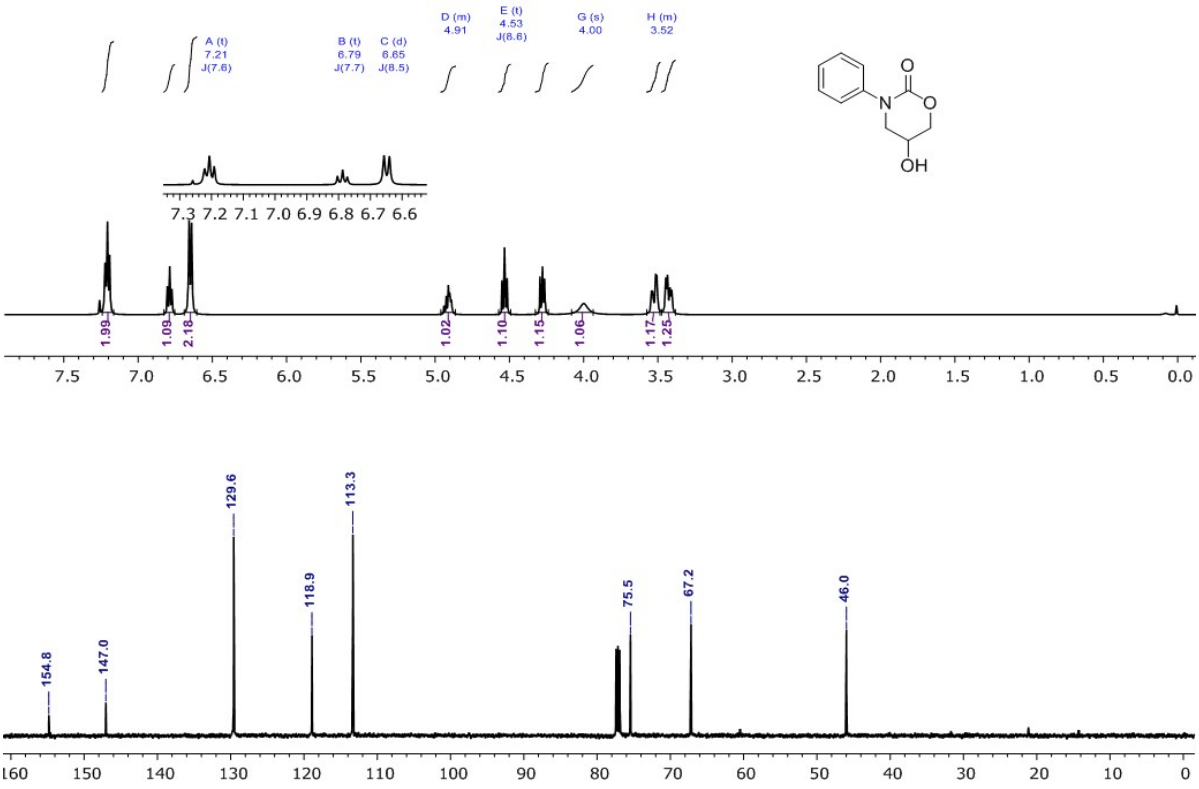
^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): δ 7.55 (2H, d, $^3J_{HH}$ = 8.6 Hz, 2 x Ar***H***), 7.39 (2H, m, 2 x Ar***H***), 7.16 (1H, t, $^3J_{HH}$ = 7.4 Hz, Ar***H***), 4.87 (1H, m, C***H***), 4.17 (1H, t, $^3J_{HH}$ = 9.0 Hz, CH_2), 3.96 (1H, dd, $^3J_{HH}$ = 9.2, 5.7 Hz, CH_2), 3.77 (2H, m, CH_2); **^{13}C NMR** (125.8 MHz, $CDCl_3$, 27 °C): δ 154.1 (**C**=O), 138.0 (Ar**C**N), 129.4 (2 x Ar**C**H), 124.6 (Ar**C**H), 118.6 (2 x Ar**C**H), 71.1 (**C**H), 48.4 (**C**H_2), 44.7 (**C**H_2). **m.p.**: 99 °C (98-100 °C)[S14]

[S12] Y. Zhao, B. Huang, C. Yang, Q. Chen, W. Xia, *Org. Lett.* **2016**, 18, 5572-5575.
[S13] W. Paisuwan, T. Chantra, P. Rashatasakhon, M. Sukwattanasinitt, A. Ajavakom, *Tetrahedron* **2017**, *73*, 3363.
[S14] A. Baba, I. Shibata, K. Masuda, H. Matsuda, *Synthesis* **1985**, 1144-1155.



5-hydroxy-3-phenyl-1,3-oxazinan-2-one (4c): 1-chloro-3-(phenylamino)propan-2-ol **1i** (0.5 mmol, 92.8 mg) was subjected to the general procedure described above. After purification by flash column chromatography (n-hexane:EtOAc; 3:1), 48.3 mg of **4c** (50% isolated yield) was obtained as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): δ 7.21 (2H, t, $^3J_{HH}$ = 7.6 Hz, 2 x Ar***H***), 6.79 (1H, t, $^3J_{HH}$ = 7.7 Hz, Ar***H***), 6.65 (2H, d, $^3J_{HH}$ = 8.5 Hz, 2 x Ar***H***), 4.91 (1H, m, C***H***), 4.53 (1H, t, $^3J_{HH}$ = 8.6 Hz, C***H$_2$***), 4.28 (1H, m, C***H***$_2$), 4.00 (1H, br. s, O***H***), 3.52 (1H, m, C***H$_2$***), 3.43 (1H, m, C***H***$_2$); **^{13}C NMR** (125.8 MHz, $CDCl_3$, 27 °C): δ 154.8 (**C**=O), 147.0 (Ar**C**N), 129.6 (2 x Ar**C**H), 118.9 (Ar**C**H), 113.3 (2 x Ar**C**H), 75.5 (**C**H), 67.2 (**C**H_2), 46.0 (**C**H_2). **EI-MS:** 193.1 (8), 106.0 (100), 77.1 (28), 51.1 (10%). **m.p.**: 114 °C.



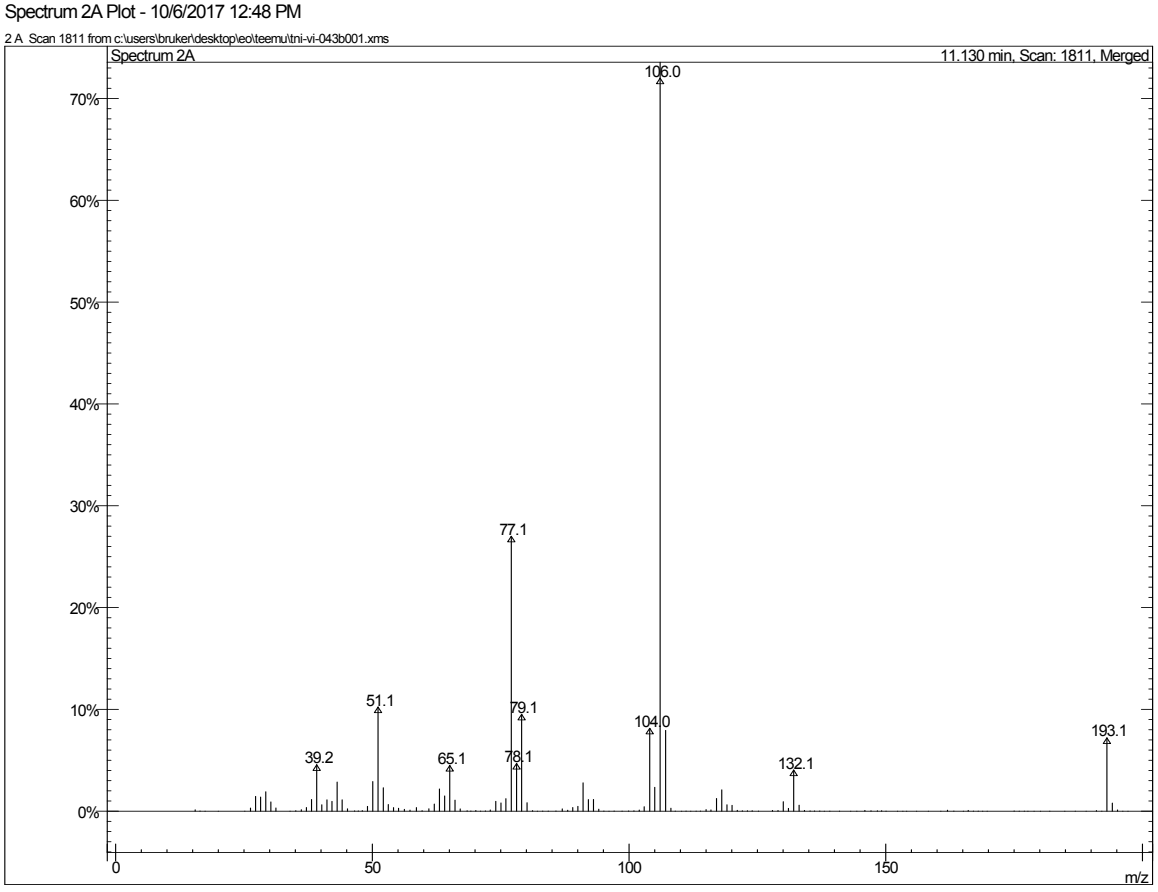
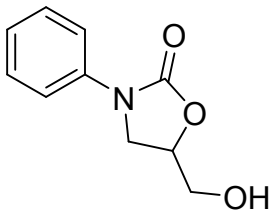
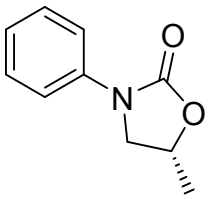


Figure S5. 1H NMR, 13C NMR, and EI-MS spectra of product **4c**.



5-(hydroxymethyl)-3-phenyloxazolidin-2-one (2h): 3-(phenylamino)propane-1,2-diol **1j** (0.5 mmol, 83.6 mg) was subjected to the general procedure described above. After purification by flash column chromatography (n-hexane:EtOAc; 1:1), 82.1 mg of **2h** (85% isolated yield) was obtained as a white solid. The spectroscopic data was consistent with previous reports.[S15]

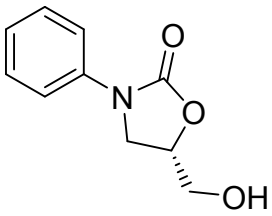
^{1}H NMR (500 MHz, DMSO, 27 °C): δ 7.58 (2H, d, $^3J_{HH}$ = 8.7 Hz, 2 x Ar***H***), 7.38 (2H, m, 2 x Ar***H***), 7.11 (1H, t, $^3J_{HH}$ = 7.3 Hz, Ar***H***), 4.69 (1H, m, C***H***), 4.09 (1H, app. t, $^3J_{HH}$ = 9.0 Hz, C***H*****$_2$**), 3.83 (1H, m, C***H***$_2$), 3.68 (1H, m, C***H***$_2$), 3.57 (1H, m, C***H***$_2$); **^{13}C NMR** (125.8 MHz, DMSO, 27 °C): δ 154.4 (**C**=O), 138.6 (Ar**C**N), 128.8 (2 x Ar**C**H), 123.2 (Ar**C**H), 117.7 (2 x Ar**C**H), 73.1 (**C**H), 61.6 (**C**H$_2$), 45.9 (**C**H$_2$). **m.p.**: 117 °C (118-121 °C)[S16]



(R)-5-methyl-3-phenyloxazolidin-2-one (2i): (R)-1-(phenylamino)propan-2-ol **1k** (0.5 mmol, 75.6 mg) was subjected to the general procedure described above. After purification by flash column chromatography (n-hexane:EtOAc; 1:1), 73.6 mg of **2i** (83% isolated yield) was obtained as a white solid. The spectroscopic data was consistent with previous reports.[S5]

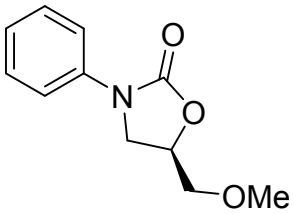
^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): δ 7.52 (2H, d, $^3J_{HH}$=7.8 Hz, 2 x Ar***H***), 7.36 (2H, m, 2 x Ar***H***), 7.12 (1H, t, $^3J_{HH}$=7.4 Hz, Ar***H***), 4.76 (1H, m, C***H***), 4.09 (1H, t, $^3J_{HH}$= 8.5 Hz, C***H*****$_2$**), 3.61 (1H, t, $^3J_{HH}$= 8.7 Hz, C***H*****$_2$**), 1.51 (3H, d, $^3J_{HH}$= 6.3 Hz, C***H***$_3$); **^{13}C NMR** (125.8 MHz, $CDCl_3$, 27 °C): δ 155.0 (**C**=O), 138.5 (Ar**C**N), 129.1 (2 x Ar**C**H), 124.0 (Ar**C**H), 118.3 (2 x Ar**C**H), 69.6 (**C**H), 51.9 (**C**H$_2$), 20.8 (**C**H$_3$). **ee (**HPLC): >99 %. **m.p.**: 80 °C (78-80 °C)[S6]

[S15] W. A. Gregory, D. R. Brittelli, C. L. J. Wang, M. A. Wuonola, R. J. McRipley, D. C. Eustice, V. S. Eberly, A. M. Slee, M. Forbes, P. T. Bartholomew, J. Med. Chem 1989, 32, 1673.
[S16] W. Tam, J. Org. Chem. 1986, 51, 2977-2981.



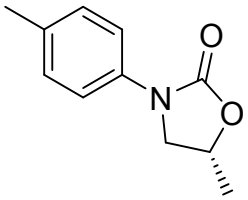
(S)-5-(hydroxymethyl)-3-phenyloxazolidin-2-one (2j): (R)-3-(phenylamino)propane-1,2-diol **1l** (0.5 mmol, 83.6 mg) was subjected to the general procedure described above. After purification by flash column chromatography (n-hexane:EtOAc; 1:1), 82.1 mg of **2j** (85% isolated yield) was obtained as a white solid. The spectroscopic data was consistent with previous reports.[S15]

^{1}H NMR (500 MHz, DMSO, 27 °C): δ 7.58 (2H, d, $^3J_{HH}$ = 8.7 Hz, 2 x Ar***H***), 7.38 (2H, m, 2 x Ar***H***), 7.11 (1H, t, $^3J_{HH}$ = 7.3 Hz, Ar***H***), 4.69 (1H, m, C***H***), 4.09 (1H, app. t, $^3J_{HH}$ = 9.0 Hz, C***H*****$_2$**), 3.83 (1H, m, C***H***$_2$), 3.68 (1H, m, C***H***$_2$), 3.57 (1H, m, C***H***$_2$); **^{13}C NMR** (125.8 MHz, DMSO, 27 °C): δ 154.4 (**C**=O), 138.6 (Ar**C**N), 128.8 (2 x Ar**C**H), 123.2 (Ar**C**H), 117.7 (2 x Ar**C**H), 73.1 (**C**H), 61.6 (**C**H$_2$), 45.9 (**C**H$_2$). **ee** (HPLC): 90 %. **m.p.**: 117 °C (118-121 °C)[S16]



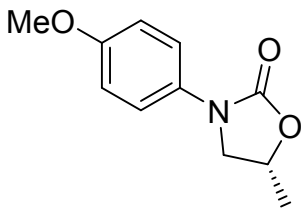
(R)-5-(methoxymethyl)-3-phenyloxazolidin-2-one (2k): (S)-1-methoxy-3-(phenylamino)propan-2-ol **1m** (0.5mmol, 90.6 mg) was subjected to the general procedure described above. After purification by flash column chromatography (n-hexane:EtOAc; 3:1), 49.7 mg of **2k** (48% isolated yield) was obtained as a yellow oil. The spectroscopic data was consistent with previous reports.[S10]

^{1}H NMR (500 MHz, CDl$_3$, 27 °C): δ 7.55 (2H, d, $^3J_{HH}$ = 8.7 Hz, 2 x Ar***H***), 7.37 (2H, t, $^3J_{HH}$ = 8.0 Hz 2 x Ar***H***), 7.13 (1H, t, $^3J_{HH}$ = 7.4 Hz, Ar***H***), 4.74 (1H, m, C***H***), 4.05 (1H, t, $^3J_{HH}$ = 8.8 Hz, C***H*****$_2$**), 3.91 (1H, app. t, $^3J_{HH}$ = 8.7 Hz, C***H*****$_2$**), 3.64 (2H, d, $^3J_{HH}$ = 4.6 Hz, C***H*****$_2$**), 3.43 (3H, s, C***H***$_3$); **^{13}C NMR** (125.8 MHz, CDCl$_3$, 27 °C): δ 154.8 (**C**=O), 138.5 (Ar**C**N), 129.3 (2 x Ar**C**H), 124.2 (Ar**C**H), 118.4 (2 x Ar**C**H), 72.8 (**C**H), 71.4 (**C**H$_2$), 59.9 (**C**H$_3$), 47.3 (**C**H$_2$). **ee** (HPLC): >99%.



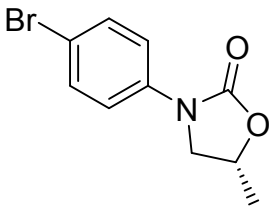
(R)-5-methyl-3-(4-methyl)oxazolidin-2-one (2l): 1-(p-tolylamino)propan-2-ol **1n** (0.5 mmol, 82.6 mg) was subjected to the general procedure described above. After purification by flash column chromatography (n-hexane:EtOAc; 2:1), 81.3 mg of **2l** (85% isolated yield) was obtained as a white solid. The spectroscopic data was consistent with previous reports.[S9]

^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): δ 7.40 (2H, d, $^3J_{HH}$=8.6 Hz, 2 x Ar***H***), 7.17 (2H, m, 2 x Ar***H***), 4.77 (1H, m, C***H***), 4.08 (1H, t, $^3J_{HH}$=8.4 Hz, C$\boldsymbol{H_2}$), 3.59 (1H, t, $^3J_{HH}$=8.5 Hz, C$\boldsymbol{H_2}$), 2.32 (3H, s, Ar-C$\boldsymbol{H_3}$), 1.52 (3H, d, $^3J_{HH}$=6.3 Hz, C***H3***); **^{13}C NMR** (125.8 MHz, $CDCl_3$, 27 °C): δ 155.2 (**C**=O), 136.1 (Ar**C**N), 133.8 (Ar**C**Me), 129.8 (2 x Ar**C**H), 118.5 (2 x Ar**C**H), 69.7 (**C**H), 52.3 (**C**H_2), 21.0 (2 x **C**H_3). **m.p.**: 66 °C (66 °C)[S9]



3-(4-methoxyphenyl)-5-methyloxazolidin-2-one (2m): 1-((4-methoxyphenyl)amino)propan-2-ol **1o** (0.5 mmol, 90.62 mg) was subjected to the general procedure described above. After purification by flash column chromatography (n-hexane:EtOAc; 1:1), 51.8 mg of **2m** (50% isolated yield) was obtained as a white solid. The spectroscopic data was consistent with previous reports.[S9]

^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): δ 7.48 (2H, d, $^3J_{HH}$=8.3 Hz, 2 x Ar***H***), 6.96 (2H, d, $^3J_{HH}$=8.6 Hz, 2 x Ar***H***), 4.76 (1H, m, C***H***), 4.10 (1H, m, C$\boldsymbol{H_2}$), 3.80 (3H, s, OC$\boldsymbol{H_3}$) 3.57 (1H, t, $^3J_{HH}$=8.1 Hz, C$\boldsymbol{H_2}$), 1.51 (3H, d, $^3J_{HH}$=6.3 Hz, C$\boldsymbol{H_3}$); **^{13}C NMR** (125.8 MHz, $CDCl_3$, 27 °C): δ 156.5 (**C**=O), 148.9 (Ar**C**), 131.8 (Ar**C**), 120.4 (2 x Ar**C**H), 114.5 (2 x Ar**C**H), 69.7 (**C**H), 55.7 (**C**H_3) 52.6 (**C**H_2), 20.9 (**C**H_3). **m.p.**: 87 °C (88 °C)[S9]



3-(4-bromophenyl)-5-methyloxazolidin-2-one (2n): 1-((4-bromophenyl)amino)propan-2-ol **1p** (0.5mmol, 86.0 mg) was subjected to the general procedure described above. After purification by flash column chromatography (n-hexane:EtOAc; 1:1), 56.3 mg of **2n** (44% isolated yield) was obtained as a white solid. The spectroscopic data was consistent with previous reports.[S10]

^{1}H NMR (500 MHz, $CDCl_3$, 27 °C): δ 7.448 (4H, m, 4 x Ar***H***), 4.79 (1H, m, C***H***), 4.08 (1H, t, $^3J_{HH}$= 8.4 Hz, C$\boldsymbol{H_2}$), 3.59 (1H, t, $^3J_{HH}$=8.6 Hz, C$\boldsymbol{H_2}$), 1.53 (3H, d, $^3J_{HH}$=6.2 Hz, C$\boldsymbol{H_3}$); **^{13}C NMR** (125.8 MHz, $CDCl_3$, 27 °C): δ 154.9 (**C**=O), 137.8 (Ar**C**), 132.2 (2 x Ar**C**H), 119.9 (2 x Ar**C**H), 116.9 (Ar**C**), 69.8 (**C**H), 52.0 (**C**H_2), 20.9 (**C**H_3). **m.p.**: 85 °C.

4. Computational details

All the calculations reported in this paper were obtained with the GAUSSIAN 09 suite of programs.[S17] Geometry optimizations were carried at the dispersion corrected metahybrid functional M06-2X[S18] using the standard double-z quality plus polarization and diffuse functions 6-31+G(d) for all atoms. Reactants and products were characterized by frequency calculations,[S19] and have positive definite Hessian matrices. Transition structures (TS's) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.[S20]S14 Solvent effects (solvent=acetone) were taken into account during the optimizations using the Polarizable Continuum Model (PCM).[S21] Single point calculations on the PCM-M06-2X/6-31+G(d) optimized geometries were performed to estimate the change in the Gibbs energies at the M06-2X level using the triple-z quality plus polarization def2-TZVPP[S22] basis set for all atoms. This level is denoted PCM(acetone)-M06-2X/def2-TZVPP//PCM(acetone)-M06-2X/6-31+G(d).

[S17] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[S18] Y. Zhao, D. G. Truhlar, *Acc. Chem. Res*. **2008**, *41*, 157

[S19] J. W. McIver, A. K. Komornicki, *J. Am. Chem. Soc.* **1972**, *94*, 2625.

[S20] C. González, H. B. Schlegel, *J. Phys. Chem*. **1990**, *94*, 5523.

[S21] a) S. Miertuš, E. Scrocco, J. Tomasi, *Chem. Phys*. **1981**, *55*, 117; b) J. L. Pascual-Ahuir, E. Silla, I. Tuñón, *J. Comp. Chem*. **1994**, *15*, 1127; c) V. Barone, M. Cossi, *J. Phys. Chem. A*, **1998**, *102*, 1995.

[S22] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

Cartesian coordinates (in Å) and free energies (in a. u.) of all the stationary points discussed in the text. All calculations have been performed at the PCM(acetone)-M06-2X/def2-TZVPP//PCM(acetone)-M06-2X/6-31+G(d) level.

1a: G= -441.283688

H	-1.192240000	1.441860000	0.901980000
O	-2.916020000	0.692500000	-0.992420000
N	-0.901710000	0.480550000	1.043810000
C	-2.469090000	-0.591630000	-0.572270000
C	-2.006520000	-0.451080000	0.870060000
H	-1.641740000	-0.935670000	-1.206610000
H	-3.282700000	-1.326570000	-0.627510000
H	-1.733320000	-1.431210000	1.272170000
H	-2.840050000	-0.080890000	1.475250000
H	-3.131760000	0.660740000	-1.935270000
C	0.352500000	0.215680000	0.492930000
C	1.225520000	1.286580000	0.225280000
C	0.808260000	-1.090400000	0.247610000
C	2.508490000	1.057430000	-0.257250000
C	2.098110000	-1.307790000	-0.236830000
C	2.960340000	-0.243540000	-0.493410000
H	0.885260000	2.303910000	0.406350000
H	0.163900000	-1.943150000	0.435660000
H	3.159920000	1.904660000	-0.454700000
H	2.425860000	-2.328250000	-0.417260000
H	3.961340000	-0.420770000	-0.874030000

TS1: G= -629.864113

H	-1.158710000	0.259170000	1.190750000
O	-1.637840000	2.571480000	0.677550000
N	-0.920890000	-0.076830000	0.255200000
C	-1.403710000	2.167050000	-0.664940000
C	-1.718300000	0.685380000	-0.728090000
H	-0.358960000	2.349400000	-0.947230000
H	-2.056020000	2.705320000	-1.362790000
H	-1.530050000	0.280150000	-1.723950000
H	-2.769780000	0.508270000	-0.486940000
H	-1.354020000	3.489740000	0.792200000
C	0.507530000	-0.009320000	0.087630000
C	1.311590000	0.394970000	1.151700000
C	1.081040000	-0.403380000	-1.122790000
C	2.698090000	0.409470000	1.003440000
C	2.466320000	-0.377820000	-1.264780000
C	3.278820000	0.027610000	-0.204750000
H	0.854080000	0.700970000	2.089430000
H	0.453800000	-0.736720000	-1.944790000
H	3.321170000	0.724600000	1.834890000
H	2.911170000	-0.684280000	-2.206770000
H	4.358030000	0.043240000	-0.320870000
C	-1.419760000	-1.914170000	0.283970000
O	-1.928230000	-2.133720000	-0.774830000
O	-1.063210000	-2.310360000	1.353690000

INT1: G= -629.862772

H	-1.193960000	0.336250000	1.119680000
O	-1.556860000	2.542620000	0.528190000
N	-0.946930000	-0.099060000	0.224750000
C	-1.297980000	2.112070000	-0.800860000
C	-1.667740000	0.643920000	-0.847610000
H	-0.240510000	2.253350000	-1.056230000
H	-1.912000000	2.656620000	-1.526910000
H	-1.418530000	0.188680000	-1.806550000
H	-2.735290000	0.505750000	-0.660420000
H	-1.255510000	3.455850000	0.639560000
C	0.505730000	-0.067060000	0.095460000
C	1.265310000	0.568990000	1.071060000
C	1.101530000	-0.689520000	-0.999280000
C	2.654450000	0.582920000	0.947590000
C	2.489440000	-0.666650000	-1.113520000
C	3.266610000	-0.031910000	-0.143370000
H	0.778070000	1.053670000	1.913000000
H	0.491170000	-1.193460000	-1.743400000
H	3.253590000	1.077930000	1.705390000
H	2.963570000	-1.151170000	-1.961190000
H	4.347900000	-0.018380000	-0.238180000
C	-1.456330000	-1.693000000	0.361490000
O	-1.816480000	-2.120220000	-0.716900000
O	-1.328690000	-2.051160000	1.515750000

TS1′: G= -1489.955298

C	0.683770000	1.927850000	-0.127000000
H	-0.074680000	2.647930000	0.194470000
H	0.573100000	1.788840000	-1.203580000
C	2.077830000	2.457690000	0.214950000
H	2.843320000	1.772850000	-0.157220000
H	2.195310000	2.542970000	1.303090000
O	2.299050000	3.697030000	-0.426720000
H	1.820550000	4.393760000	0.046520000
N	0.396170000	0.635370000	0.542940000
H	0.401530000	0.768850000	1.558680000
C	1.313680000	-0.441580000	0.237790000
C	1.687600000	-0.701760000	-1.080330000
C	1.767470000	-1.245280000	1.281810000
C	2.533850000	-1.776870000	-1.343540000
C	2.612960000	-2.316880000	1.007230000
C	2.998500000	-2.584370000	-0.305750000
H	1.325270000	-0.085200000	-1.895860000
H	1.458780000	-1.036560000	2.303260000
H	2.828960000	-1.981050000	-2.367980000
H	2.967430000	-2.940900000	1.821460000
H	3.658720000	-3.418790000	-0.520540000
S	-1.547010000	-0.073200000	0.066680000
O	-1.329170000	0.145500000	-1.348850000
O	-1.338500000	-1.314040000	0.781300000

Cl	-3.995010000	-0.701040000	-0.409290000
C	-2.306510000	1.261720000	1.017100000
H	-1.537870000	1.803070000	1.566370000
H	-2.818640000	1.895510000	0.294280000
H	-3.013580000	0.778900000	1.688160000

INT1': G= -1029.575032

C	-0.889690000	1.603880000	-0.162170000
H	-1.940140000	1.769040000	0.084300000
H	-0.789960000	1.550420000	-1.246490000
C	-0.010150000	2.715940000	0.417970000
H	1.033760000	2.558850000	0.137330000
H	-0.076240000	2.728540000	1.513380000
O	-0.402630000	3.947350000	-0.142720000
H	-1.196540000	4.272830000	0.307130000
N	-0.499750000	0.265840000	0.411150000
H	-0.654840000	0.304050000	1.428110000
C	0.899150000	-0.113660000	0.191600000
C	1.413990000	-0.120790000	-1.101350000
C	1.662480000	-0.473570000	1.296010000
C	2.744990000	-0.484820000	-1.280060000
C	2.994230000	-0.832800000	1.100930000
C	3.534160000	-0.836800000	-0.183610000
H	0.801260000	0.140250000	-1.959050000
H	1.233670000	-0.469200000	2.294970000
H	3.163160000	-0.495710000	-2.280990000
H	3.603680000	-1.107220000	1.955210000
H	4.571880000	-1.116760000	-0.333740000
S	-1.684150000	-1.114680000	-0.216640000
O	-2.491110000	-0.442220000	-1.207070000
O	-0.795140000	-2.199520000	-0.548700000
C	-2.593960000	-1.455640000	1.267750000
H	-1.895330000	-1.812910000	2.026110000
H	-3.131600000	-0.556970000	1.571700000
H	-3.298150000	-2.246650000	0.995640000

INT2: G= -629.425796

O	3.006510000	-0.990860000	-1.072500000
N	0.607750000	0.091900000	0.478690000
C	1.941270000	-1.760550000	-0.541380000
C	1.345000000	-1.148140000	0.721800000
H	2.320070000	-2.764100000	-0.306070000
H	1.145730000	-1.869830000	-1.294590000
H	0.661980000	-1.875640000	1.168540000
H	2.140710000	-0.948820000	1.446100000
H	2.982660000	-0.113150000	-0.615130000
C	-0.779340000	0.008460000	0.202460000
C	-1.637480000	-0.671960000	1.074710000
C	-1.314070000	0.573280000	-0.962960000
C	-2.996430000	-0.792230000	0.784880000
C	-2.674080000	0.466630000	-1.241650000
C	-3.523700000	-0.220870000	-0.372370000
H	-1.240370000	-1.099900000	1.991400000
H	-0.651560000	1.101810000	-1.641400000

H	-3.645080000	-1.325360000	1.474700000
H	-3.070310000	0.911770000	-2.150340000
H	-4.582880000	-0.309820000	-0.595440000
C	1.305070000	1.325670000	0.374370000
O	2.573190000	1.235390000	0.364530000
O	0.631210000	2.376460000	0.324510000

TS2: G= -1678.111692

O	-1.266200000	-1.556860000	0.717740000
N	1.559240000	-1.100070000	-0.121720000
C	-0.198860000	-1.288470000	1.628310000
C	1.123290000	-1.810320000	1.078450000
H	-0.426070000	-1.772780000	2.585370000
H	-0.116090000	-0.204130000	1.784550000
H	1.887490000	-1.688190000	1.849460000
H	1.039080000	-2.879360000	0.857760000
H	-0.803020000	-1.887640000	-0.212060000
C	2.488540000	-0.033970000	0.009840000
C	3.721920000	-0.245590000	0.633640000
C	2.168310000	1.244620000	-0.459170000
C	4.621530000	0.808530000	0.791250000
C	3.076820000	2.290590000	-0.316600000
C	4.305430000	2.079530000	0.312880000
H	3.980750000	-1.240880000	0.986240000
H	1.203600000	1.402970000	-0.931030000
H	5.576750000	0.630120000	1.277090000
H	2.818290000	3.278490000	-0.687800000
H	5.009740000	2.898030000	0.429110000
C	0.975390000	-1.390910000	-1.367970000
O	-0.059620000	-2.160850000	-1.321720000
O	1.483100000	-0.933840000	-2.401700000
S	-2.415540000	0.110460000	0.068530000
C	-3.078290000	0.099300000	1.749670000
H	-2.775460000	1.043500000	2.201470000
H	-4.160150000	0.048490000	1.640350000
H	-2.679960000	-0.767370000	2.270000000
O	-3.049320000	-0.778600000	-0.882460000
O	-1.194310000	0.859670000	-0.156440000
Cl	-3.844390000	1.947990000	-0.370600000

INT3: G= -1217.337661

C	-0.034040000	0.054440000	0.673790000
C	-0.962190000	-0.206790000	-0.506600000
O	0.007560000	2.629350000	0.085950000
C	1.123270000	2.090820000	-0.119900000
N	1.199580000	0.699010000	0.254220000
H	0.203910000	-0.890850000	1.168940000
H	-1.336240000	0.741410000	-0.900320000
H	-0.467760000	-0.764340000	-1.304830000
O	2.147590000	2.609740000	-0.618940000
H	-0.552280000	0.698060000	1.388720000
C	2.364400000	-0.081500000	0.113540000
C	3.641390000	0.448580000	0.373840000
C	2.275790000	-1.438260000	-0.240690000

C	4.775920000	-0.349250000	0.264750000
C	3.417790000	-2.233410000	-0.336710000
C	4.678810000	-1.696370000	-0.091400000
H	3.730690000	1.489200000	0.657240000
H	1.309580000	-1.886230000	-0.451520000
H	5.749090000	0.087890000	0.473440000
H	3.312260000	-3.278670000	-0.614870000
H	5.568870000	-2.313590000	-0.169390000
O	-2.062200000	-1.054320000	-0.074100000
S	-3.498610000	-0.390090000	0.177240000
C	-4.143660000	-0.195320000	-1.465190000
H	-3.485270000	0.468510000	-2.027190000
H	-4.200620000	-1.181650000	-1.925860000
H	-5.135800000	0.248120000	-1.366770000
O	-4.258450000	-1.409440000	0.880770000
O	-3.327080000	0.921270000	0.784380000

TS3: G= -1217.308856

C	-0.126000000	0.249200000	0.022920000
C	-1.143190000	1.260740000	-0.465070000
O	0.189640000	2.719240000	-0.071260000
C	1.335120000	2.150030000	-0.151430000
N	1.217080000	0.751860000	-0.234210000
H	-0.274050000	-0.689450000	-0.510840000
H	-1.780190000	1.791970000	0.223660000
H	-1.107170000	1.589210000	-1.493940000
O	2.443500000	2.704970000	-0.198090000
H	-0.279160000	0.061050000	1.096500000
C	2.310730000	-0.140340000	-0.105270000
C	3.348410000	0.095690000	0.804100000
C	2.336560000	-1.303810000	-0.883570000
C	4.396490000	-0.815790000	0.920310000
C	3.378460000	-2.219260000	-0.751490000
C	4.416220000	-1.978300000	0.148880000
H	3.331630000	0.996470000	1.407250000
H	1.542390000	-1.484960000	-1.602810000
H	5.196790000	-0.619790000	1.628550000
H	3.382320000	-3.117220000	-1.362710000
H	5.230980000	-2.689210000	0.248900000
O	-2.486410000	0.082310000	-0.914020000
S	-3.275440000	-0.574130000	0.226940000
C	-4.891590000	-0.792070000	-0.484080000
H	-5.287030000	0.188740000	-0.749340000
H	-4.798980000	-1.426700000	-1.366060000
H	-5.518940000	-1.271360000	0.269390000
O	-2.741460000	-1.906750000	0.547550000
O	-3.395070000	0.344960000	1.371850000

2a: G= -553.461030

C	-1.501350000	-1.450660000	-0.075350000
C	-2.929500000	-0.964280000	-0.316500000
O	-2.914230000	0.400020000	0.136290000
C	-1.641760000	0.859180000	0.160020000
N	-0.781280000	-0.181130000	-0.092400000

H	-1.148250000	-2.114900000	-0.866630000
H	-3.678810000	-1.506060000	0.257570000
H	-3.189020000	-0.967660000	-1.377800000
O	-1.379670000	2.020800000	0.385370000
H	-1.392270000	-1.947140000	0.895870000
C	0.627620000	-0.100370000	-0.047820000
C	1.297850000	1.104380000	-0.303140000
C	1.367310000	-1.258960000	0.218740000
C	2.689090000	1.138720000	-0.270420000
C	2.760130000	-1.208350000	0.242820000
C	3.430370000	-0.011250000	0.003350000
H	0.733970000	2.001010000	-0.524770000
H	0.866910000	-2.202160000	0.410310000
H	3.196350000	2.078380000	-0.469240000
H	3.317720000	-2.116080000	0.453840000
H	4.515080000	0.025430000	0.024100000