Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Stereospecific Synthesis of a Twinned Alanine Ester

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Table of Contents

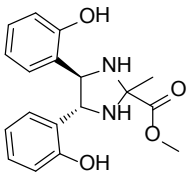
General Information

Commercially available compounds were used without further purification or drying. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 400 spectrometer or a Bruker Advance III spectrometer operating at 400 MHz. High resolution mass spectra (HRMS) were obtained on an ABI/Sciex QStar Mass Spectrometer (ESI) at Advanced Instrumentation for Molecular Structure (AIMS) at the University of Toronto and on a ThermoFinnigan LCQ™ Classic, Quadrupole Ion-Trap Mass Spectrometer at Seoul National University. HPLC analysis was performed on a Hewlett-Packard 1100 Series HPLC, UV detection monitored at 254.4 nm using a Chiralpak® IA column (25cm). Optical rotation was obtained at 589 nm using a Rudolph Autopol IV polarimeter at the University of Toronto and on a JASCO P-1030 automatic polarimeter at Seoul National University. Melting points were recorded using an Electrothermal IA 9100 digital melting point apparatus. Reactions were monitored using ^{1}H NMR spectroscopy. Chromatography was performed on Silicycle 230-400 mesh silica gel and thin-layer chromatography (TLC) was performed on EMD Silica Gel 60 F_{254} plates. Visualization of the developed plates was performed under UV light (254 nm). All calculations were performed using Spartan '08 for Windows from Wavefunction Inc.

Preparation of 5-membered imidazolidine intermediate (1)

After adding methyl pyruvate (407 µL, 4.51 mmol) to (*R,R*)-1,2-bis(2-hydroxylphenyl)-1,2-diaminoethane (1.0 g, 4.1 mmol) in $CHCl_3$, the reaction mixture was stirred at 50 °C for 1 h until starting material was all removed. The solvent was removed *in vacuo* and 2 mL of diethyl ether was added to afford a desired product and 5 mL of *n*-hexane was added to reduce the loss of isolated yield. The solid was filtered, washed with 10 mL of *n*-hexane, and dried in vacuum. The desired product was obtained as light yellow solid (1.25 g, 93% yield).

(*R,R*)- **1**



Light yellow solid (93% yield), mp 137-138 °C

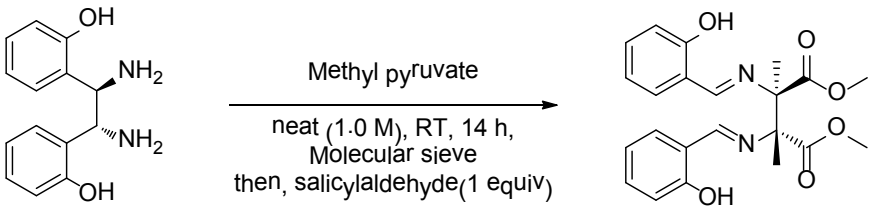
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.74 (s, 2H), 7.23 – 7.08 (m, 2H), 6.92 – 6.80 (m, 2H), 6.61 (td, *J* = 7.4, 1.1 Hz, 1H), 6.56 (td, *J* = 7.5, 1.1 Hz, 1H), 6.33 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.20 (dd, *J* = 7.6, 1.5 Hz, 1H), 4.64 (d, *J* = 9.7 Hz, 1H), 4.36 (d, *J* = 9.8 Hz, 1H), 3.91 (s, 3H), 1.79 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 174.4, 157.5, 157.3, 130.0, 129.7, 129.5, 129.3, 119.5, 119.4, 119.1, 118.9, 117.2, 117.0, 76.4, 67.4, 66.1, 53.6, 27.3.

$[\alpha]_D^{24}$ +6.51 (c = 1.0, $CHCl_3$)

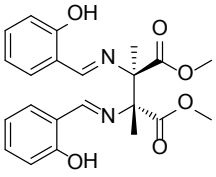
HRMS (ESI) calculated for $C_{18}H_{21}N_2O_4$ $[M+H]^+$: 329.1501, Found: 329.1494

Preparation of chiral diimine containing vicinal quaternary carbon centers (3)



After adding methyl pyruvate (2.05 mL, 1.0 M) with activated molecular sieve (3 Å) to *(R,R)*-1,2-bis(2-hydroxylphenyl)-1,2-diaminoethane (0.5 g, 2.05 mmol) in $CHCl_3$, the mixture was stirred at room temperature for 14 h until 5-membered ring was all removed. Salicylaldehyde (218 μL, 2.05 mmol) was added to the reaction mixture and the mixture was stirred at room temperature for 1 h. The reaction mixture was purified using short column chromatography eluting with hexane / ethyl acetate (20 %) to remove excess methyl pyruvate and salicylaldehyde. Recrystallization of obtained crude product in diethyl ether / *n*-hexane gave the desired product as a yellow monoclinic crystal (60% yield).

(*R,R*)- **3**



Yellow monoclinic crystal (60% yield), mp 115-116 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 12.98 (s, 1H); 8.39 (s, 1H; 7.34 (t, *J* = 7.8 Hz, 1H); 7.28 (d, *J* = 7.6 Hz, 1H); 6.98 (d, *J* = 8.4 Hz, 1H); 6.89 (t, *J* = 7.5 Hz, 1H); 3.76 (s, 3H); 1.70 (s, 3H).

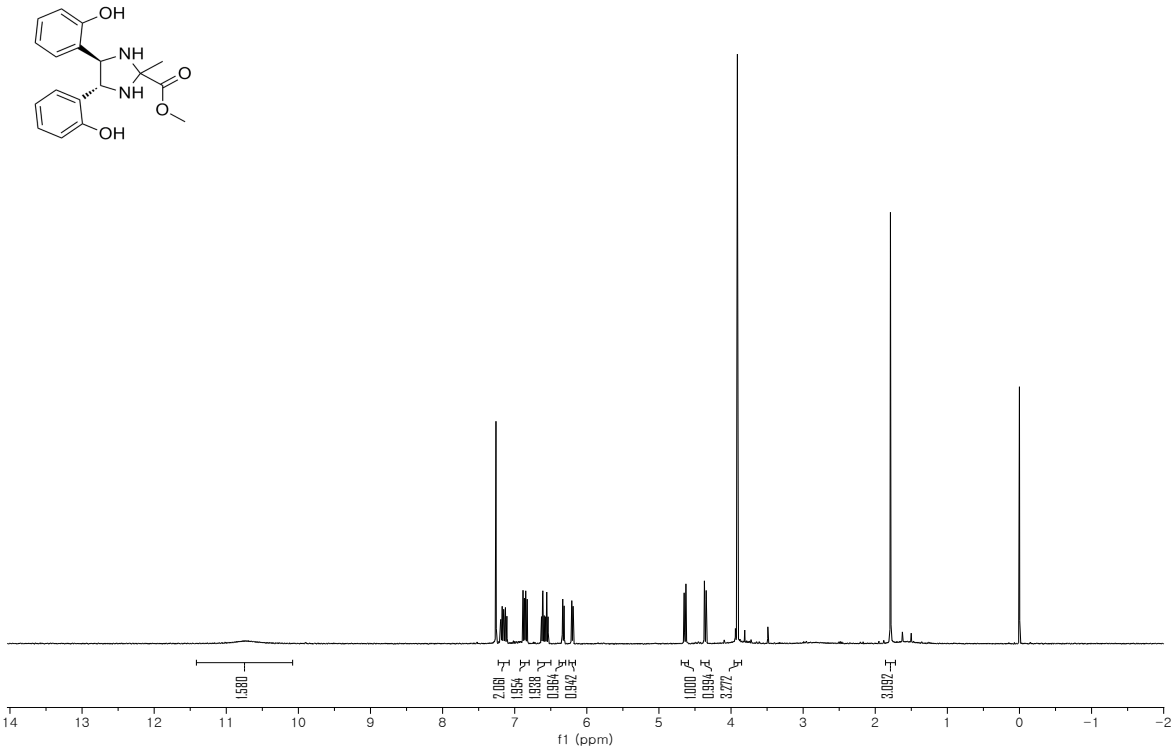
^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 172.0, 165.2, 161.1, 133.2, 132.4, 119.0, 118.9, 117.5, 73.6, 53.0, 19.3.

The enantiopurity was confirmed by HPLC analysis (Chiralpak® IA column, *n*-Hexane : *i*-PrOH = 90:10, 1.0 ml/min); *Rac*-**3** t_R= 8.96 min, t_R = 16.34 min, (*R,R*)-**3** t_R= 16.32 min, (*S,S*)-**3** t_R= 8.98 min

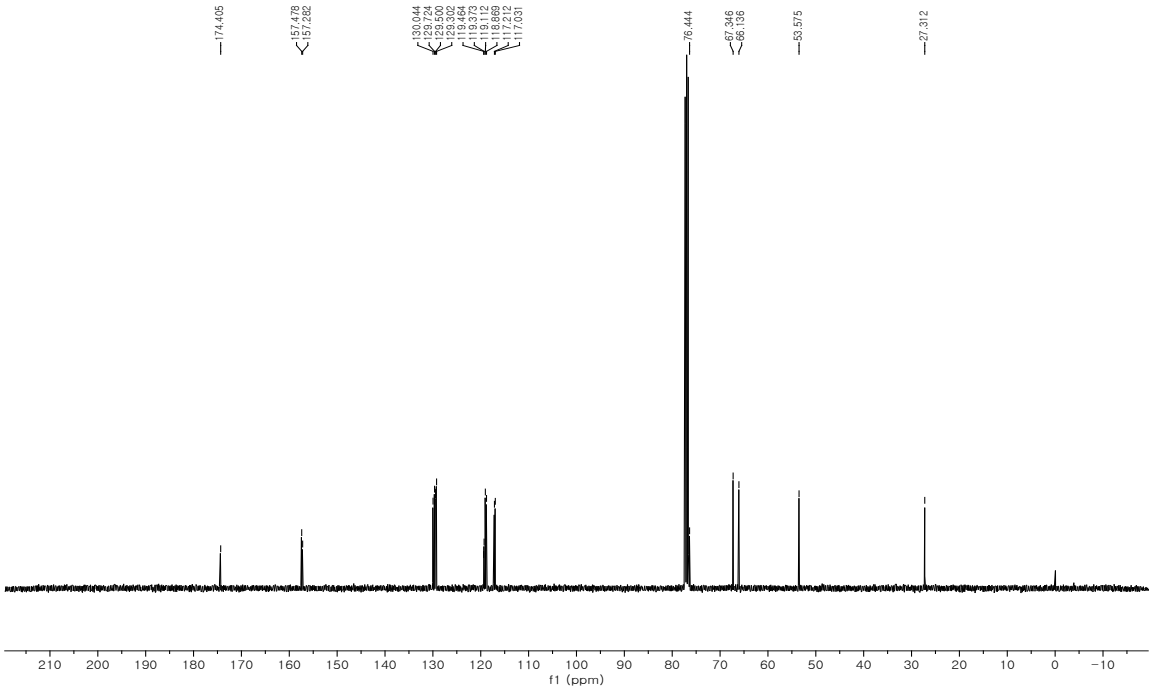
$[\alpha]_D^{27}$ +175.95 (c = 1.0, $CHCl_3$)

HRMS (ESI) calculated for $C_{22}H_{25}N_2O_6$ $[M+H]^+$: 413.1713, Found: 413.1707.

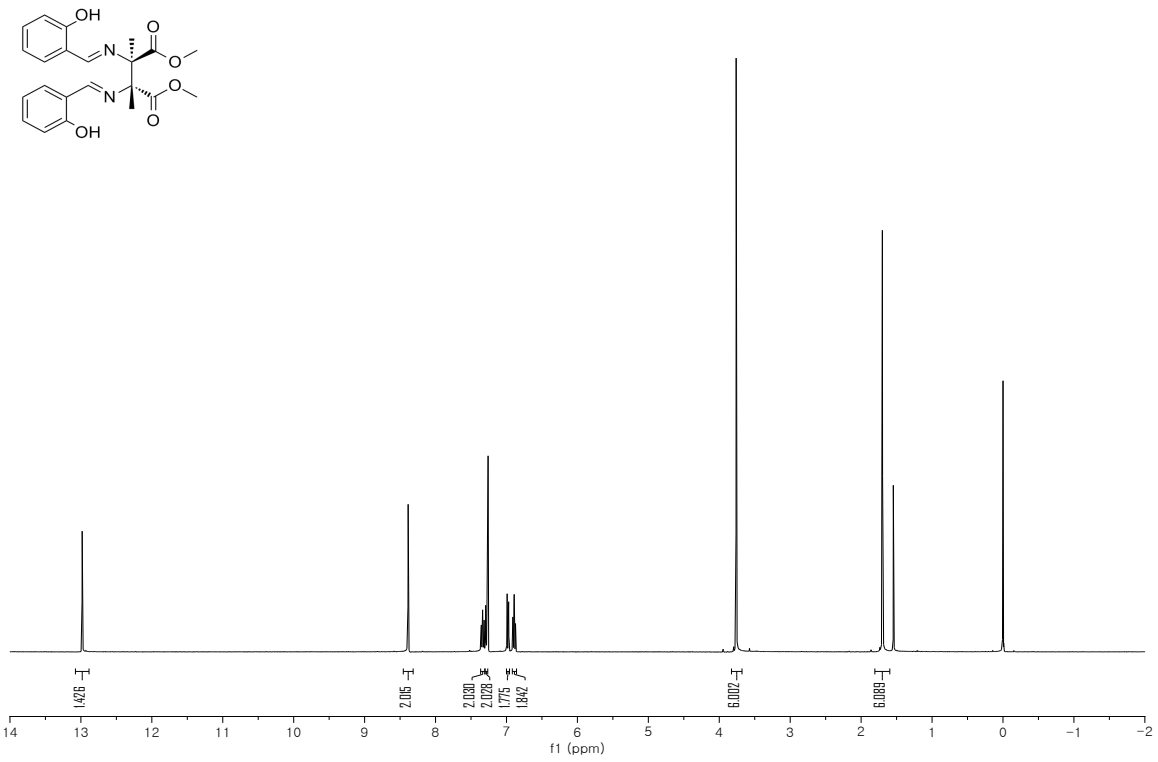
NMR spectra



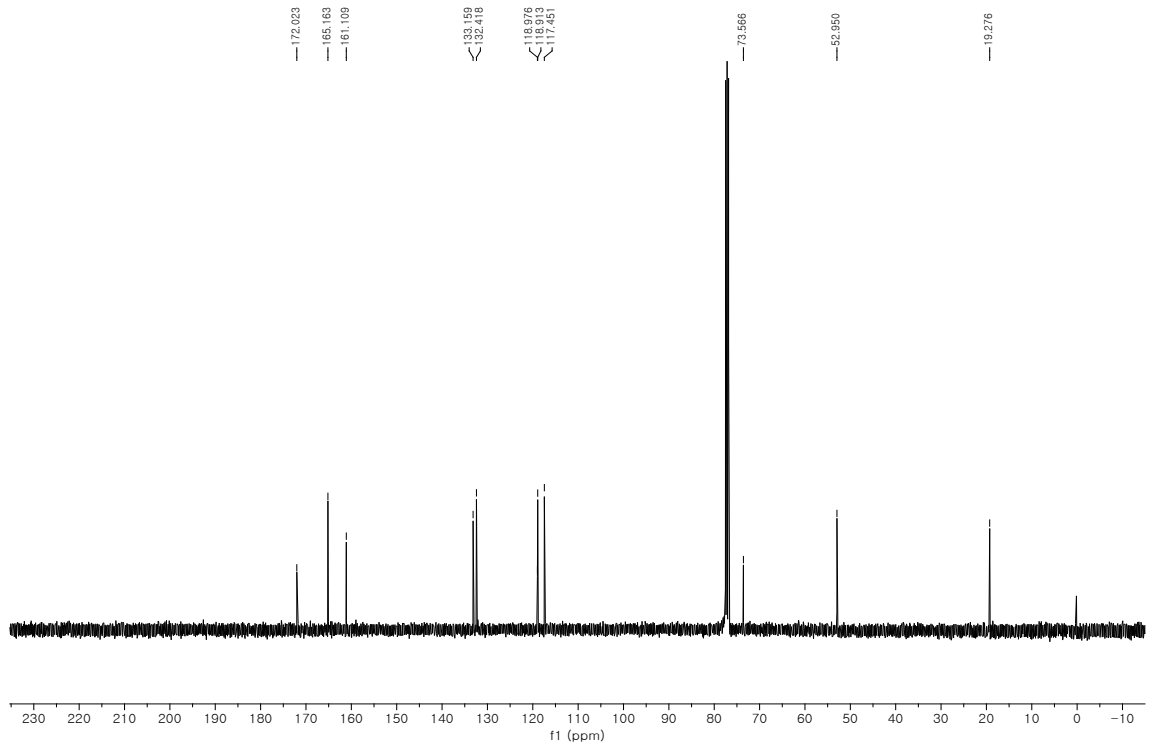
Compound **1** (400 MHz, $CDCl_3$)



Compound **1** (100 MHz, $CDCl_3$)



Compound **3** (400 MHz, $CDCl_3$)

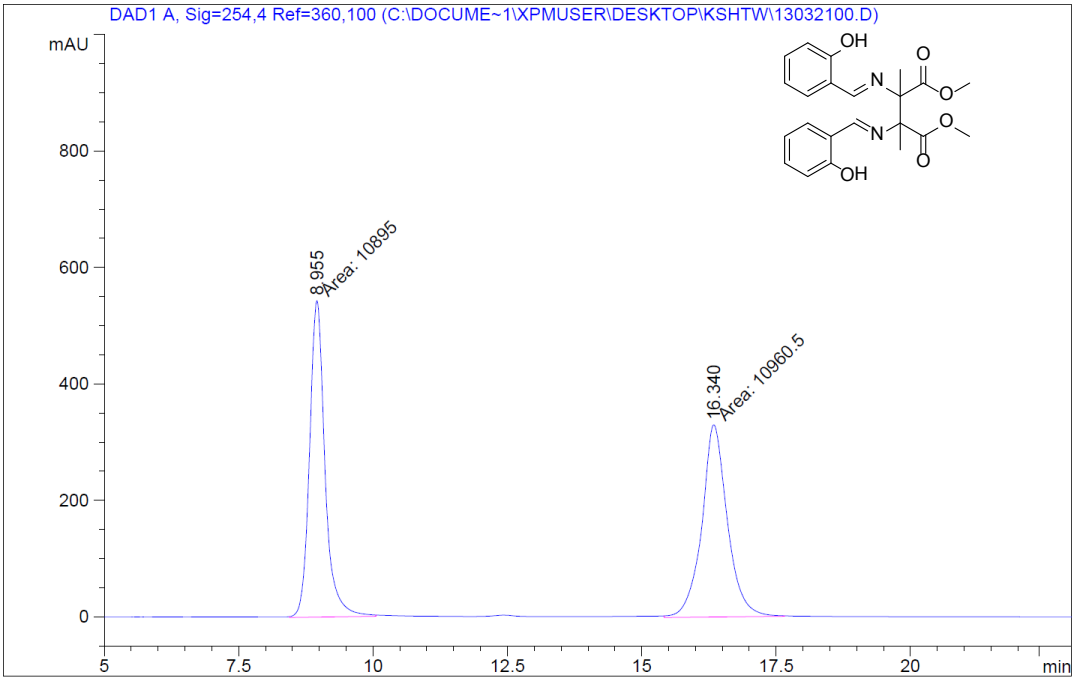


Compound **3** (100 MHz, $CDCl_3$)

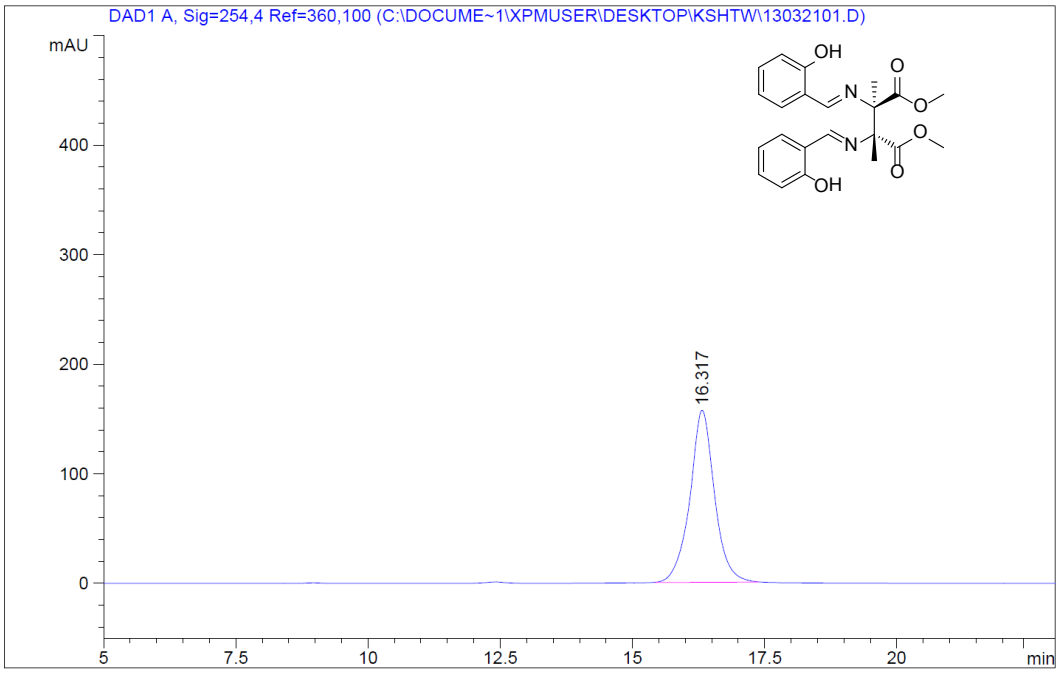
HPLC result

Chiralpak® IA column, *n*-Hexane : *i*-PrOH = 90:10, Flow rate = 1.0 ml/min

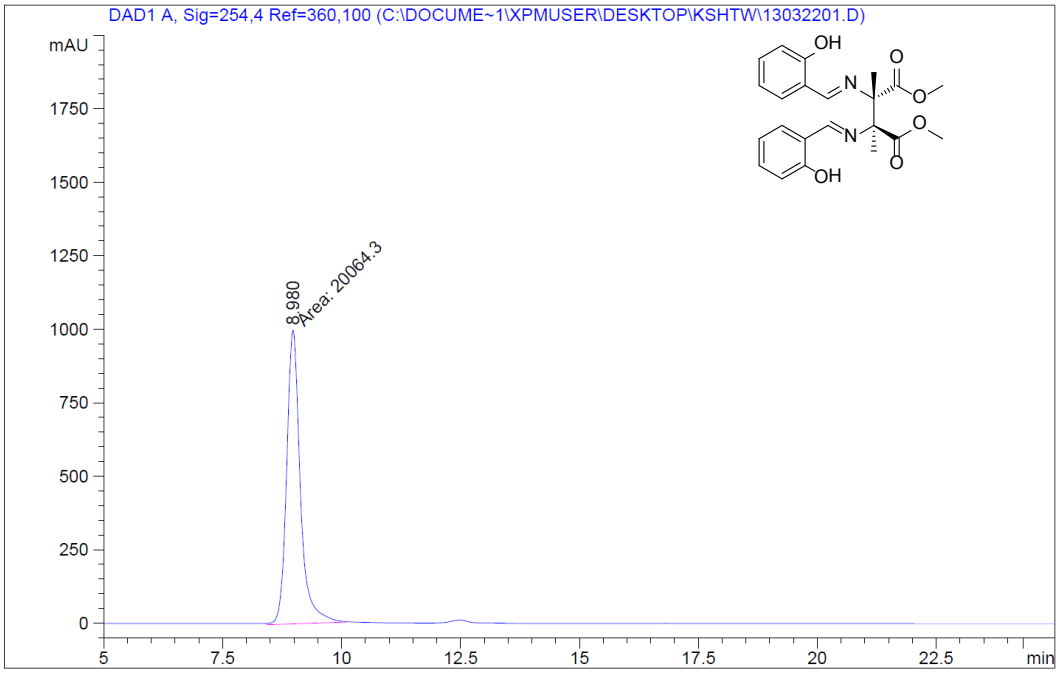
***Rac*-3**



(*R*,*R*)-3



(*S*,*S*)-3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20
22.5
min
OH
N
O
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O
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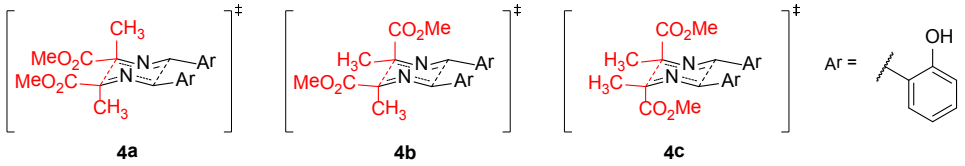
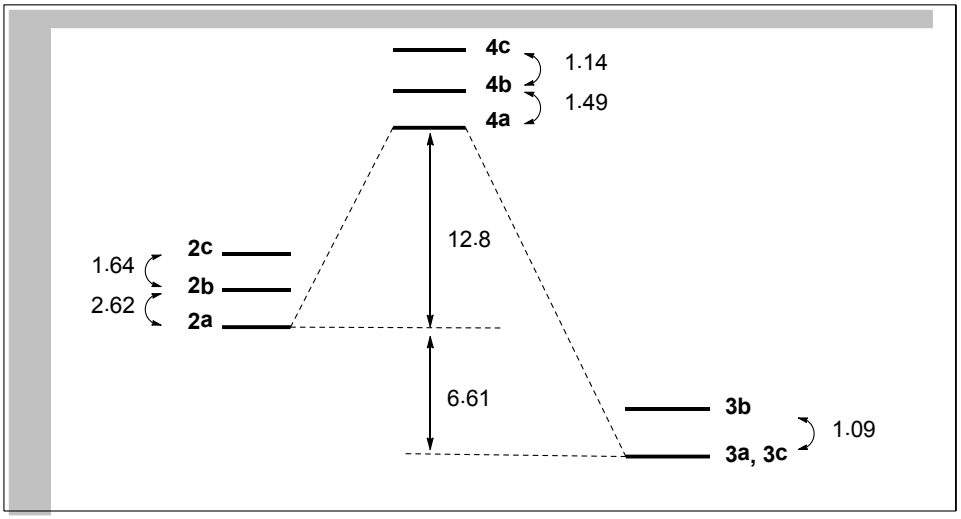
Calculation result

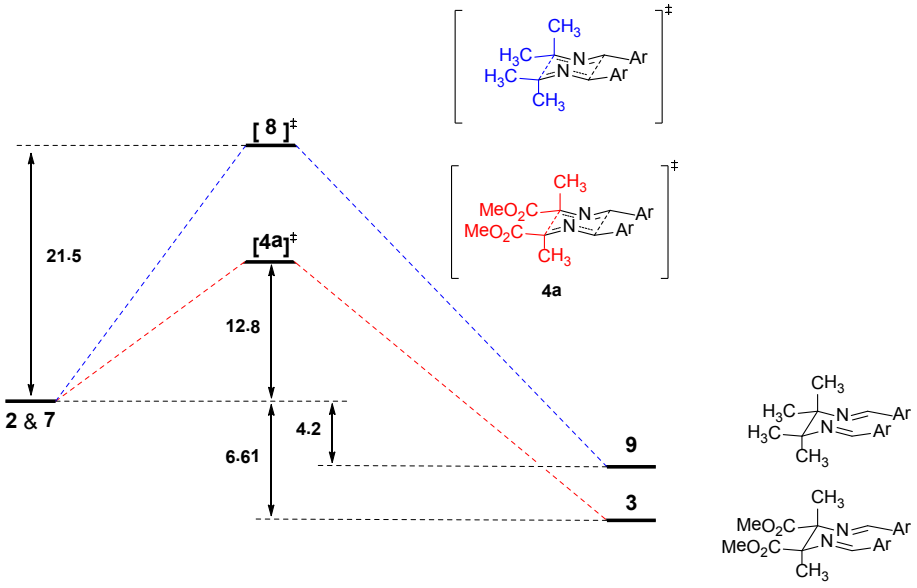




Enthalpy values in kcal/mol.

Molecules	Energy (hartree)	E+ZPVE (hartree)	$\Delta H_{298.15K}$ (hartree)	Imaginary frequency (cm^{-1})
2a	-1413.627618	-1413.194171	-1413.164382	
2b	-1413.624778	-1413.190705	-1413.160212	
2c	-1413.621111	-1413.187197	-1413.157592	
3a, 3c	-1413.638968	-1413.204239	-1413.174917	
3b	-1413.636684	-1413.203042	-1413.173175	
4a	-1413.605623	-1413.173733	-1413.144003	*i* 265.644
4b	-1413.603385	-1413.171061	-1413.141625	*i* 277.903
4c	-1413.601180	-1413.169660	-1413.139813	*i* 277.864

B3LYP/6-31G (d) level

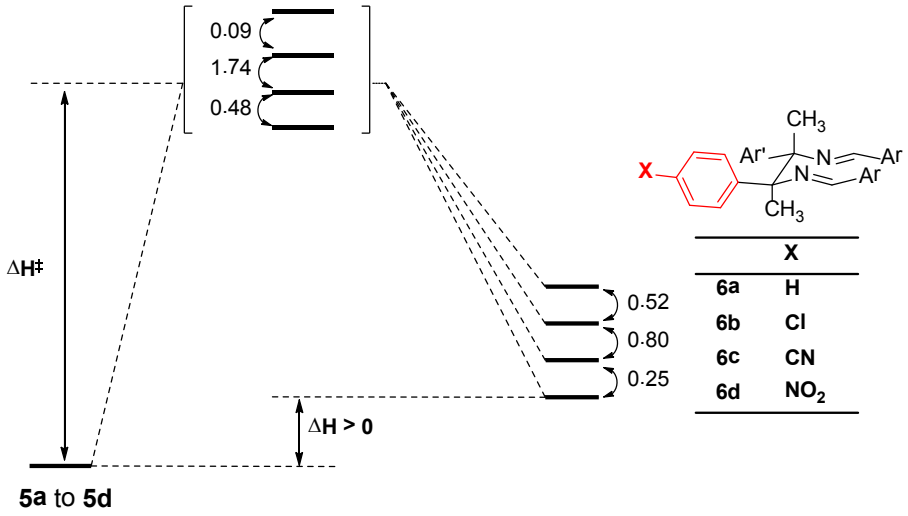


Enthalpy values in kcal/mol.

Molecules	Energy (hartree)	E+ZPVE (hartree)	$\Delta H_{298.15K}$ (hartree)	Imaginary frequency (cm^{-1})
2	-1413.627618	-1413.194171	-1413.164382	
3	-1413.638968	-1413.204239	-1413.174917	
4a	-1413.605623	-1413.173733	-1413.144003	*i* 265.644
7	-1036.526725	-1036.122058	-1036.097803	
8	-1036.488949	-1036.087035	-1036.063595	*i* 254.482
9	-1036.532881	-1036.127726	-1036.104496	

B3LYP/6-31G (d) level

The effect of para-substituents on acetophenone



Enthalpy values in kcal/mol.

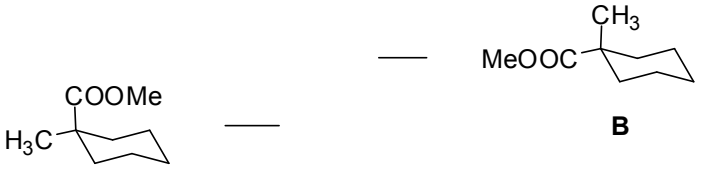
Molecules		Energy (hartree)	E+ZPVE (hartree)	$\Delta H_{298.15K}$ (hartree)	$\Delta H^{\ddagger}$ (kcal/mol) / ΔH (kcal/mol)
	5a	-1419.999729	-1419.488580	-1419.458128	16.1
H	**TS-a**	-1419.969228	-1419.461794	-1419.432493	
	6a	-1419.990193	-1419.479841	-1419.450020	5.09
	5b	-2339.191082	-2338.699175	-2338.666259	16.0
Cl	**TS-b**	-2339.161835	-2338.673315	-2338.640794	
	6b	-2339.182350	-2338.69132	-2338.658987	4.56
	5c	-1604.483396	-1603.975129	-1603.940979	14.2
CN	**TS-c**	-1604.457011	-1603.951937	-1603.918286	
	6c	-1604.475962	-1603.968511	-1603.934976	3.77
	5d	-1828.999027	-1828.482670	-1828.447075	13.8
NO_2	**TS-d**	-1828.973518	-1828.460264	-1828.425153	
	6d	-1828.992002	-1828.476485	-1828.441466	3.52

B3LYP/6-31G (d) level

Additional comment about calculation.

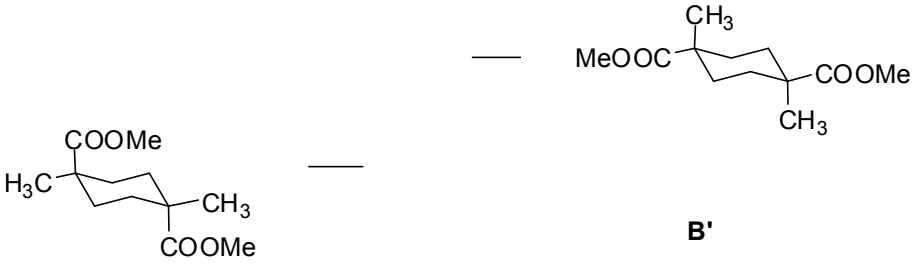
Organic chemistry textbooks shows that the 1,3-diaxial strain is greater for methane than for esters. Thus it should be better to have the ester in the axial position than have the methyl in the axial. However, we need to be careful when extending this to systems with many substituents.

Molecular mechanics computation shows that **A** is more stable than **B** as expected from the individual 1,3-diaxial strain.



A **B**

Furthermore, computation shows that **A'** is more stable than **B'** as expected.



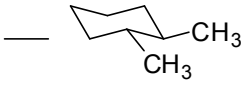
A' **B'**

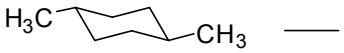
However, when we bring the substituents closer together the trend is reversed! Here it is better to have the carboxylates together in the equatorial positions (**B''**) than to have the methyls together in the equatorial positions (**A''**).

A'' **B''**

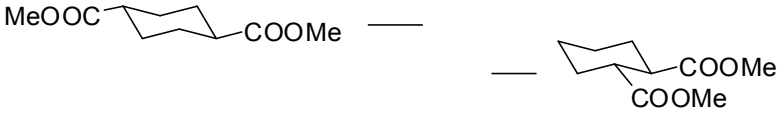
Further analysis below shows that in 1,2-disubstituted cyclohexanes, it is better to have carboxylates together than to have methyls together.

Computation shows that 1,2-dimethyl cyclohexane is less stable than 1,4-dimethyl cyclohexane due apparently to greater steric effect (gauche interaction) when the two methyl groups are closer.

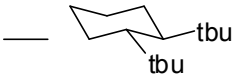


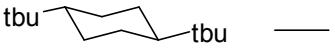


The gap is reduced significantly for the dicarboxylates. Indeed, the 1,2-disubstituted carboxylate is more stable than the 1,4-disubstituted one. Thus there appears to be even energetically favorable interactions between the two carboxylates.



The energy gap increases in case of the t-butyl substituent as shown below.





Atom coordinates

Atom coordinates of **2***			
c	X	Y	Z
N	-0.24177	-1.35358	-0.48556
C	1.042863	1.316444	-1.47721
C	0.466833	0.648199	0.766609
N	0.241774	1.353577	-0.48556
C	-0.46683	-0.6482	0.766609
C	-1.04286	-1.31644	-1.47721
H	1.495352	0.293007	0.884003
H	-1.49535	-0.29301	0.884003
C	-2.35601	-0.59046	-1.61161
H	-3.0866	-1.21471	-2.13051
H	-2.19377	0.313962	-2.21322
H	-2.76315	-0.27786	-0.64934
C	2.356012	0.590463	-1.61161
H	3.086596	1.21471	-2.13051
H	2.193766	-0.31396	-2.21322
H	2.763146	0.277862	-0.64934
C	0.522307	2.067422	-2.69777
O	-0.65084	2.265437	-2.93179
O	1.526077	2.47701	-3.49421
C	1.123997	3.201433	-4.67159
H	0.561345	4.095556	-4.39263
H	0.500102	2.5706	-5.30993
H	2.050579	3.468551	-5.17923
C	-0.52231	-2.06742	-2.69777
O	0.65084	-2.26544	-2.93179
O	-1.52608	-2.47701	-3.49421
C	-1.124	-3.20143	-4.67159
H	-0.5001	-2.5706	-5.30993
H	-2.05058	-3.46855	-5.17923
H	-0.56135	-4.09556	-4.39263
C	0.103507	1.557714	1.926088
C	-0.61968	3.117447	4.144251
C	0.904175	1.592081	3.072466

C	-1.06853	2.347265	1.892026
C	-1.42318	3.11517	3.007061
C	0.55469	2.362295	4.180722
H	1.808681	0.988828	3.097002
H	-2.32931	3.710581	2.95029
H	1.189486	2.368815	5.061779
H	-0.90638	3.722104	5.000882
C	-0.10351	-1.55771	1.926088
C	0.619679	-3.11745	4.144251
C	-0.90418	-1.59208	3.072466
C	1.068531	-2.34727	1.892026
C	1.423176	-3.11517	3.007061
C	-0.55469	-2.3623	4.180722
H	-1.80868	-0.98883	3.097002
H	2.329313	-3.71058	2.95029
H	-1.18949	-2.36882	5.061779
H	0.906379	-3.7221	5.000882
O	-1.89766	2.377882	0.809834
H	-1.356	2.127723	0.022888
O	1.897664	-2.37788	0.809834
H	1.355997	-2.12772	0.022888

*Calculation was performed using (*S,S*)-*hpen*.

Atom coordinates of **3**			
Atom	X	Y	Z
N	0.286684	1.442507	0.313175
C	-0.88507	-1.3394	-0.82129
C	-0.58063	-0.57537	1.441142
N	-0.28668	-1.44251	0.313175
C	0.580634	0.575371	1.441142
C	0.885065	1.339397	-0.82129
C	0.529141	2.196396	-1.9406
C	-0.1365	3.802427	-4.13545
C	1.192229	2.044803	-3.17386
C	-0.48895	3.184317	-1.81951
C	-0.80854	3.978239	-2.93291
C	0.870953	2.834086	-4.26722
H	1.967406	1.285705	-3.25614

H	-1.58744	4.725739	-2.82053
H	1.390372	2.704634	-5.21163
H	-0.39694	4.427812	-4.98562
C	-0.52914	-2.1964	-1.9406
C	0.136502	-3.80243	-4.13545
C	0.488952	-3.18432	-1.81951
C	-1.19223	-2.0448	-3.17386
C	-0.87095	-2.83409	-4.26722
C	0.808541	-3.97824	-2.93291
H	-1.96741	-1.28571	-3.25614
H	-1.39037	-2.70463	-5.21163
H	1.587439	-4.72574	-2.82053
H	0.396938	-4.42781	-4.98562
O	-1.16331	3.387697	-0.67807
H	-0.78057	2.777447	0.016835
O	1.163313	-3.3877	-0.67807
H	0.780574	-2.77745	0.016835
C	1.988374	-0.04773	1.428281
H	2.73928	0.744324	1.338706
H	2.102857	-0.74298	0.594875
H	2.18371	-0.6031	2.344317
C	-1.98837	0.047729	1.428281
H	-2.10286	0.742983	0.594875
H	-2.18371	0.603098	2.344317
H	-2.73928	-0.74432	1.338706
C	0.37402	1.469844	2.691243
C	-0.37402	-1.46984	2.691243
O	0.347911	-2.43967	2.733637
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O	1.087963	1.033561	3.748568
O	-1.08796	-1.03356	3.748568
C	-0.90462	-1.78801	4.959772
H	-1.21891	-2.82431	4.81351
H	-1.53045	-1.29744	5.705619
H	0.145974	-1.7729	5.260462
C	0.904616	1.788008	4.959772
H	1.218909	2.824311	4.81351
H	1.530449	1.297439	5.705619

H	-0.14597	1.772903	5.260462
H	-1.68325	-0.61169	-1.00325
H	1.683253	0.61169	-1.00325

Atom coordinates of **4a***

Atom	X	Y	Z
N	-0.62714	-1.29552	-0.39519
C	1.147043	0.7949	-1.48369
C	0.796956	0.769905	0.848834
N	0.627143	1.295518	-0.39519
C	-0.79696	-0.76991	0.848834
C	-1.14704	-0.7949	-1.48369
H	1.583618	0.036324	1.028889
H	-1.58362	-0.03632	1.028889
C	-2.20101	0.279044	-1.54794
H	-2.17527	0.799833	-2.5047
H	-2.07608	1.018572	-0.75465
H	-3.19647	-0.17493	-1.44105
C	2.201012	-0.27904	-1.54794
H	2.17527	-0.79983	-2.5047
H	2.076082	-1.01857	-0.75465
H	3.196466	0.174933	-1.44105
C	0.75335	1.545782	-2.72753
O	-0.04067	2.464158	-2.76179
O	1.394854	1.074632	-3.82067
C	1.087992	1.75887	-5.04679
H	1.339989	2.819275	-4.96521
H	0.024232	1.663908	-5.27974
H	1.69705	1.275648	-5.81116
C	-0.75335	-1.54578	-2.72753
O	0.040672	-2.46416	-2.76179
O	-1.39485	-1.07463	-3.82067
C	-1.08799	-1.75887	-5.04679
H	-0.02423	-1.66391	-5.27974
H	-1.69705	-1.27565	-5.81116
H	-1.33999	-2.81928	-4.96521
C	0.429363	1.602886	1.991292

C	-0.29161	3.105111	4.254108
C	0.952852	1.300902	3.263516
C	-0.47271	2.697907	1.870531
C	-0.82658	3.429534	3.01129
C	0.6087	2.04135	4.387175
H	1.642879	0.466186	3.352799
H	-1.51621	4.258946	2.88956
H	1.031816	1.793406	5.355685
H	-0.57163	3.692636	5.124592
C	-0.42936	-1.60289	1.991292
C	0.291613	-3.10511	4.254108
C	-0.95285	-1.3009	3.263516
C	0.472708	-2.69791	1.870531
C	0.826581	-3.42953	3.01129
C	-0.6087	-2.04135	4.387175
H	-1.64288	-0.46619	3.352799
H	1.516207	-4.25895	2.88956
H	-1.03182	-1.79341	5.355685
H	0.571629	-3.69264	5.124592
O	-1.02621	3.064014	0.692748
H	-0.5298	2.605479	-0.0358
O	1.026213	-3.06401	0.692748
H	0.529801	-2.60548	-0.0358

*Calculation was performed using *(S,S)-hpen*.

Atom coordinates of **4b**			
Atom	X	Y	Z
N	-0.73	0.788997	0.907515
C	0.815364	-0.82615	-0.7373
C	-1.47276	-1.51492	-0.87642
N	-0.22163	-1.70125	-0.53943
C	-1.6524	0.034982	1.438761
C	0.603008	0.522134	0.991217
H	0.689228	-0.01462	-1.44604
H	0.962662	-0.22868	1.696164
C	1.537798	1.604867	0.699715
C	3.429887	3.611424	0.157
C	1.160996	2.768298	-0.03172

C	2.870572	1.492812	1.145549
C	3.812059	2.479624	0.888753
C	2.124081	3.753865	-0.29711
H	3.153416	0.605246	1.705603
H	4.830881	2.370578	1.247522
H	1.810445	4.628554	-0.85816
H	4.156257	4.391863	-0.05502
C	2.172384	-1.34265	-0.56169
C	4.824519	-2.20979	-0.22047
C	3.244847	-0.66264	-1.17031
C	2.461761	-2.48825	0.229386
C	3.787174	-2.90348	0.397781
C	4.558396	-1.08911	-1.01491
H	3.023508	0.214345	-1.77229
H	3.975718	-3.78175	1.007444
H	5.367477	-0.55255	-1.50093
H	5.84783	-2.55145	-0.08776
C	-3.05205	0.515654	1.168266
O	-3.33556	1.516768	0.542609
O	-3.98008	-0.31403	1.702009
C	-5.34611	0.068028	1.467249
H	-5.55951	0.067821	0.395378
H	-5.5389	1.065033	1.870803
H	-5.95032	-0.68044	1.980221
C	-1.40743	-1.08258	2.422312
H	-0.55659	-1.70476	2.130997
H	-2.28776	-1.71649	2.52916
H	-1.18151	-0.65814	3.411472
O	-0.08409	2.981662	-0.494
H	-0.67878	2.267982	-0.15339
O	1.48467	-3.1979	0.845378
H	0.62822	-2.90042	0.439392
C	-2.45701	-2.62167	-0.58482
H	-3.32555	-2.25443	-0.03022
H	-1.96516	-3.40963	-0.00991
H	-2.8377	-3.05371	-1.51874
C	-1.94184	-0.36268	-1.72256
O	-1.23269	0.495778	-2.21215

O	-3.28065	-0.40207	-1.8941
C	-3.83105	0.707943	-2.63188
H	-3.63489	1.638182	-2.09579
H	-4.9019	0.511666	-2.69026
H	-3.39179	0.755623	-3.63107

Atom coordinates of **4c***

Atom	X	Y	Z
N	-0.71292	-1.16717	0.890635
C	-1.90642	0.711928	-1.1781
C	0.464873	0.478675	-0.98034
N	-0.71307	1.166901	-0.89012
C	0.464968	-0.47883	0.980837
C	-1.90628	-0.71225	1.178497
H	0.48667	-0.47052	-1.50756
H	0.486684	0.47033	1.508124
C	1.700372	1.260405	-0.98848
C	4.128858	2.675382	-1.08166
C	2.870936	0.668796	-1.50305
C	1.775974	2.596517	-0.50444
C	2.995302	3.285681	-0.55609
C	4.073443	1.360367	-1.56025
H	2.814753	-0.35414	-1.86582
H	3.018164	4.305437	-0.18451
H	4.958845	0.88388	-1.96971
H	5.062911	3.229961	-1.12236
C	1.700587	-1.26036	0.988755
C	4.129504	-2.67479	1.080963
C	2.871127	-0.66855	1.503151
C	1.7764	-2.59641	0.504498
C	2.995957	-3.2853	0.555615
C	4.073833	-1.35984	1.559883
H	2.81475	0.354332	1.866154
H	3.019023	-4.30501	0.18376
H	4.959209	-0.88319	1.969202
H	5.06374	-3.22915	1.121235
O	0.712104	3.245028	0.012893

H	-0.08172	2.672251	-0.13487
O	0.712505	-3.24512	-0.01252
H	-0.08131	-2.67239	0.135149
C	-3.07272	-1.6576	1.016096
H	-3.42727	-2.00427	1.994897
H	-2.75602	-2.52414	0.431282
H	-3.92513	-1.17781	0.525732
C	-3.07293	1.657187	-1.01584
H	-3.92533	1.177273	-0.52575
H	-3.42729	2.003933	-1.99461
H	-2.75656	2.523599	-0.43087
C	-2.14519	0.5796	1.906678
O	-3.44249	0.687206	2.281359
C	-3.76348	1.864755	3.042144
H	-3.58152	2.765239	2.449619
H	-3.15596	1.909017	3.949756
H	-4.82134	1.771809	3.288891
O	-1.31284	1.427805	2.171074
C	-2.14517	-0.5799	-1.90639
O	-1.31274	-1.4283	-2.17013
O	-3.44239	-0.68725	-2.28197
C	-3.76312	-1.86452	-3.04329
H	-3.58415	-2.76512	-2.44991
H	-3.1532	-1.91001	-3.94922
H	-4.82022	-1.77009	-3.29293

*Calculation was performed using (*S,S*)-*hpen*.

Atom coordinates of **5a**			
Atom	X	Y	Z
N	-0.27169	-1.36129	0.14372
C	0.487411	0.62356	-1.09985
C	1.164592	1.453148	1.060243
N	0.271692	1.36129	0.14372
C	-1.16459	-1.45315	1.060243
C	-0.48741	-0.62356	-1.09985
H	1.503932	0.227466	-1.18968
H	-1.50393	-0.22747	-1.18968
C	-0.20317	-1.54253	-2.28003

C	0.364944	-3.13429	-4.52546
C	0.895899	-2.43134	-2.26942
C	-1.01054	-1.49472	-3.42166
C	-0.73881	-2.279	-4.54194
C	1.174904	-3.21448	-3.39533
H	-1.85912	-0.81472	-3.43372
H	-1.379	-2.21904	-5.41718
H	2.027467	-3.88571	-3.3538
H	0.59152	-3.75092	-5.3916
C	0.203173	1.542531	-2.28003
C	-0.36494	3.134287	-4.52546
C	1.010536	1.494723	-3.42166
C	-0.8959	2.43134	-2.26942
C	-1.1749	3.214483	-3.39533
C	0.738805	2.278997	-4.54194
H	1.859115	0.814719	-3.43372
H	-2.02747	3.885714	-3.3538
H	1.379002	2.21904	-5.41718
H	-0.59152	3.750921	-5.3916
C	-2.54254	-0.81784	0.976784
H	-3.15978	-1.07192	1.839104
H	-3.06403	-1.17581	0.081989
H	-2.47461	0.272314	0.899839
O	1.716923	-2.55545	-1.18632
H	1.215661	-2.17971	-0.41822
O	-1.71692	2.555454	-1.18632
H	-1.21566	2.17971	-0.41822
C	2.542544	0.817836	0.976784
H	2.474605	-0.27231	0.899839
H	3.064026	1.175805	0.081989
H	3.159784	1.071921	1.839104
C	-0.81832	-2.2557	2.270507
C	-0.10683	-3.7527	4.542481
C	0.050344	-3.35553	2.161345
C	-1.32403	-1.92135	3.536702
C	-0.96274	-2.65774	4.664929
C	0.395898	-4.10035	3.285817
H	0.438687	-3.62869	1.185392

H	-1.98032	-1.06407	3.652328
H	-1.35195	-2.37472	5.63911
H	1.056379	-4.9569	3.180938
H	0.164754	-4.33453	5.419229
C	0.818323	2.255704	2.270507
C	0.106832	3.752704	4.542481
C	-0.05034	3.355528	2.161345
C	1.324028	1.92135	3.536702
C	0.962736	2.65774	4.664929
C	-0.3959	4.100349	3.285817
H	-0.43869	3.628685	1.185392
H	1.980322	1.064066	3.652328
H	1.351951	2.374724	5.63911
H	-1.05638	4.956899	3.180938
H	-0.16475	4.334533	5.419229

Atom coordinates of **TS-a**

Atom	X	Y	Z
N	-0.02642	-1.40097	0.621237
C	-1.25056	1.044813	-0.96086
C	1.100548	0.76202	-1.02838
N	-0.02538	1.402803	-0.62472
C	1.099184	-0.76117	1.027624
C	-1.25123	-1.04329	0.959103
H	-1.43796	0.259848	-1.69596
H	-1.43757	-0.25931	1.695569
C	-2.41252	-1.77844	0.50447
C	-4.71146	-3.16108	-0.33953
C	-2.31816	-2.8234	-0.45971
C	-3.68674	-1.45837	1.019909
C	-4.82597	-2.1368	0.610409
C	-3.4713	-3.50058	-0.87221
H	-3.76243	-0.66143	1.755485
H	-5.79566	-1.8751	1.022684
H	-3.36601	-4.29113	-1.60863
H	-5.59742	-3.69933	-0.66623
C	-2.41157	1.780219	-0.50595

C	-4.71042	3.161266	0.340993
C	-3.68633	1.45858	-1.01916
C	-2.31665	2.826271	0.457136
C	-3.46967	3.502651	0.871165
C	-4.8255	2.136193	-0.60812
H	-3.76263	0.660841	-1.75383
H	-3.36386	4.293978	1.606795
H	-5.79565	1.873023	-1.0184
H	-5.59639	3.698705	0.669034
C	1.046773	0.330972	2.070037
H	1.902663	1.003467	1.992847
H	1.053173	-0.10545	3.079342
H	0.153455	0.949469	1.973089
O	-1.13383	-3.16947	-1.00689
H	-0.44214	-2.62593	-0.53591
O	-1.13157	3.173771	1.00208
H	-0.44046	2.631875	0.528017
C	1.052567	-0.3326	-2.06859
H	1.893948	-1.02089	-1.96717
H	1.092456	0.099314	-3.07912
H	0.145991	-0.93473	-1.9921
C	2.370009	1.479218	-0.81089
C	4.810984	2.87486	-0.4266
C	3.596978	0.961603	-1.28089
C	2.410624	2.725772	-0.14313
C	3.607964	3.405614	0.049591
C	4.793793	1.651768	-1.09541
H	3.625129	0.010446	-1.79839
H	1.48922	3.178215	0.20006
H	3.599171	4.363675	0.562567
H	5.718103	1.223688	-1.47482
H	5.744913	3.411613	-0.28307
C	2.368427	-1.47925	0.811635
C	4.807471	-2.87911	0.429331
C	2.406792	-2.72971	0.150536
C	3.597145	-0.95969	1.2755
C	4.792757	-1.65198	1.091236
C	3.603165	-3.4115	-0.04137

H	1.484095	-3.18388	-0.18706
H	3.627953	-0.00503	1.786725
H	5.718077	-1.22247	1.466238
H	3.592492	-4.37242	-0.5491
H	5.740504	-3.41748	0.286801

Atom coordinates of **6a**

Atom	X	Y	Z
N	1.37913	-0.10669	-0.32641
C	-2.53948	0.601366	-0.57742
C	-0.66728	0.453836	0.922866
N	-1.37913	0.106694	-0.32641
C	0.667283	-0.45384	0.922866
C	2.539483	-0.60137	-0.57742
H	-3.0579	1.254985	0.137267
H	3.057896	-1.25499	0.137267
C	3.255815	-0.31566	-1.81165
C	4.686178	0.220582	-4.15851
C	2.697294	0.526662	-2.81253
C	4.530766	-0.87317	-2.02294
C	5.248103	-0.61538	-3.18163
C	3.429541	0.785761	-3.98151
H	4.94894	-1.51638	-1.2512
H	6.230193	-1.05329	-3.33082
H	2.985137	1.4307	-4.73295
H	5.238836	0.430292	-5.07092
C	-3.25582	0.315655	-1.81165
C	-4.68618	-0.22058	-4.15851
C	-4.53077	0.873166	-2.02294
C	-2.69729	-0.52666	-2.81253
C	-3.42954	-0.78576	-3.98151
C	-5.2481	0.615379	-3.18163
H	-4.94894	1.516377	-1.2512
H	-2.98514	-1.4307	-4.73295
H	-6.23019	1.053294	-3.33082
H	-5.23884	-0.43029	-5.07092
C	0.297922	-1.95176	0.829053

H	-0.22071	-2.1495	-0.11119
H	-0.34713	-2.27513	1.647363
H	1.208003	-2.55896	0.853837
O	1.485592	1.087112	-2.67335
H	1.110918	0.762388	-1.80581
O	-1.48559	-1.08711	-2.67335
H	-1.11092	-0.76239	-1.80581
C	-0.29792	1.951764	0.829053
H	0.220712	2.149503	-0.11119
H	0.347125	2.275126	1.647363
H	-1.208	2.558964	0.853837
C	-1.53393	0.171662	2.168239
C	-3.11811	-0.35576	4.456566
C	-2.495	-0.85441	2.171244
C	-1.38881	0.922981	3.344567
C	-2.17048	0.666465	4.472409
C	-3.27426	-1.11738	3.298186
H	-2.651	-1.44938	1.277789
H	-0.6577	1.721446	3.395009
H	-2.03414	1.272231	5.3646
H	-4.00984	-1.91702	3.264027
H	-3.7293	-0.55438	5.332954
C	1.533926	-0.17166	2.168239
C	3.118113	0.355759	4.456566
C	2.494999	0.854412	2.171244
C	1.388805	-0.92298	3.344567
C	2.170481	-0.66647	4.472409
C	3.274256	1.117381	3.298186
H	2.651	1.449376	1.277789
H	0.657695	-1.72145	3.395009
H	2.034142	-1.27223	5.3646
H	4.009835	1.917023	3.264027
H	3.729304	0.554384	5.332954

Atom coordinates of **5b**

Atom	X	Y	Z
N	-0.30662	-1.35338	-0.55302

C	0.501264	0.611473	-1.79808
C	1.213454	1.444908	0.349546
N	0.306618	1.353377	-0.55302
C	-1.21345	-1.44491	0.349546
C	-0.50126	-0.61147	-1.79808
H	1.508477	0.193468	-1.89144
H	-1.50848	-0.19347	-1.89144
C	-0.23368	-1.5397	-2.97508
C	0.30629	-3.15035	-5.21333
C	0.851491	-2.44499	-2.96219
C	-1.04222	-1.48432	-4.11559
C	-0.78402	-2.27805	-5.23228
C	1.116893	-3.23785	-4.08418
H	-1.88035	-0.79156	-4.12978
H	-1.42439	-2.21245	-6.10692
H	1.959087	-3.92187	-4.04097
H	0.521767	-3.77447	-6.07683
C	0.233681	1.539698	-2.97508
C	-0.30629	3.150345	-5.21333
C	1.042224	1.484319	-4.11559
C	-0.85149	2.44499	-2.96219
C	-1.11689	3.237846	-4.08418
C	0.784017	2.278051	-5.23228
H	1.880354	0.791555	-4.12978
H	-1.95909	3.921871	-4.04097
H	1.424385	2.212448	-6.10692
H	-0.52177	3.774473	-6.07683
C	-2.58381	-0.79594	0.253511
H	-3.21597	-1.04717	1.105708
H	-3.09768	-1.14357	-0.64952
H	-2.50327	0.293816	0.183208
O	1.673139	-2.57586	-1.87916
H	1.179729	-2.18908	-1.11297
O	-1.67314	2.575859	-1.87916
H	-1.17973	2.18908	-1.11297
C	2.583813	0.795944	0.253511
H	2.503269	-0.29382	0.183208
H	3.097678	1.143566	-0.64952

H	3.215968	1.047168	1.105708
C	-0.88924	-2.26338	1.554815
C	-0.21269	-3.78366	3.805889
C	-0.00927	-3.35447	1.44912
C	-1.42367	-1.95886	2.816167
C	-1.0839	-2.70502	3.943509
C	0.325969	-4.11802	2.562446
H	0.403486	-3.61301	0.479545
H	-2.09245	-1.11277	2.938589
H	-1.49004	-2.45249	4.917074
H	0.99473	-4.96704	2.469427
C	0.889241	2.263379	1.554815
C	0.212685	3.783655	3.805889
C	0.00927	3.354473	1.44912
C	1.423666	1.95886	2.816167
C	1.083898	2.705016	3.943509
C	-0.32597	4.118019	2.562446
H	-0.40349	3.613012	0.479545
H	2.092445	1.11277	2.938589
H	1.490038	2.452491	4.917074
H	-0.99473	4.967044	2.469427
Cl	0.212471	-4.73964	5.217265
Cl	-0.212471	4.739639	5.217265

Atom coordinates of **TS-b**

Atom	X	Y	Z
N	-0.77891	-1.41597	0.595073
C	-1.99567	1.072644	-0.95112
C	0.354254	0.782778	-1.01157
N	-0.77126	1.42326	-0.60451
C	0.344316	-0.78201	1.020237
C	-2.00113	-1.06721	0.950389
H	-2.1797	0.29293	-1.69268
H	-2.17984	-0.29572	1.702071
C	-3.16539	-1.78749	0.484082
C	-5.46927	-3.15038	-0.37468
C	-3.07621	-2.81637	-0.4981

C	-4.4374	-1.47172	1.008702
C	-5.57889	-2.14086	0.59201
C	-4.23227	-3.48429	-0.91748
H	-4.50845	-0.68653	1.757197
H	-6.54681	-1.88416	1.011281
H	-4.13166	-4.26313	-1.66687
H	-6.3575	-3.68149	-0.7065
C	-3.15851	1.799904	-0.4918
C	-5.46197	3.166674	0.363378
C	-4.43234	1.475808	-1.00723
C	-3.06766	2.841569	0.47652
C	-4.22304	3.510915	0.895084
C	-5.5734	2.146488	-0.59194
H	-4.50554	0.682418	-1.74675
H	-4.1203	4.299264	1.634169
H	-6.54271	1.882557	-1.00346
H	-6.35007	3.698708	0.694072
C	0.265899	0.276821	2.093059
H	1.178664	0.868961	2.159075
H	0.104017	-0.19218	3.074827
H	-0.55543	0.97426	1.916419
O	-1.895	-3.15605	-1.05573
H	-1.20004	-2.61818	-0.58395
O	-1.883	3.192255	1.019461
H	-1.1914	2.661413	0.535263
C	0.308248	-0.29851	-2.06551
H	1.150384	-0.98693	-1.97152
H	0.345828	0.143975	-3.07127
H	-0.59686	-0.90261	-1.99513
C	1.62372	1.492684	-0.78038
C	4.058082	2.863953	-0.36844
C	2.836554	1.030623	-1.33632
C	1.684818	2.679566	-0.01352
C	2.879818	3.354695	0.199083
C	4.039252	1.705898	-1.14077
H	2.853574	0.133729	-1.9435
H	0.779309	3.093412	0.410249
H	2.897397	4.264572	0.789927

H	4.955598	1.330345	-1.58386
C	1.613401	-1.49432	0.793861
C	4.037277	-2.8811	0.375052
C	1.643218	-2.76193	0.166083
C	2.853025	-0.9572	1.204686
C	4.050533	-1.63861	1.003513
C	2.83283	-3.44769	-0.04634
H	0.715055	-3.23368	-0.13013
H	2.898793	0.010169	1.688695
H	4.988751	-1.20315	1.330372
H	2.825673	-4.4224	-0.5228
Cl	5.547002	-3.74385	0.116843
Cl	5.572756	3.718236	-0.11168

Atom coordinates of **6b**

Atom	X	Y	Z
N	-0.15794	-1.37038	-1.01532
C	0.714157	2.499275	-1.28424
C	0.479534	0.649186	0.23375
N	0.157937	1.370378	-1.01532
C	-0.47953	-0.64919	0.23375
C	-0.71416	-2.49928	-1.28424
H	1.408058	2.985203	-0.58479
H	-1.40806	-2.9852	-0.58479
C	-0.44744	-3.22325	-2.51715
C	0.052192	-4.67107	-4.86086
C	0.443953	-2.7088	-3.49926
C	-1.07299	-4.46367	-2.7461
C	-0.83355	-5.18892	-3.90334
C	0.684312	-3.44947	-4.66667
H	-1.75444	-4.8479	-1.98967
H	-1.32331	-6.14386	-4.06655
H	1.368064	-3.03953	-5.40321
H	0.247946	-5.23104	-5.77184
C	0.447439	3.223254	-2.51715
C	-0.05219	4.671065	-4.86086
C	1.072993	4.463669	-2.7461

C	-0.44395	2.708803	-3.49926
C	-0.68431	3.449465	-4.66667
C	0.833554	5.188915	-3.90334
H	1.754443	4.847901	-1.98967
H	-1.36806	3.03953	-5.40321
H	1.323312	6.143863	-4.06655
H	-0.24795	5.231044	-5.77184
C	-1.9627	-0.22101	0.148781
H	-2.14148	0.315988	-0.78471
H	-2.26068	0.426321	0.975445
H	-2.60548	-1.10634	0.165222
O	1.069158	-1.53103	-3.34299
H	0.747955	-1.14136	-2.48179
O	-1.06916	1.531029	-3.34299
H	-0.74796	1.141358	-2.48179
C	1.962701	0.221014	0.148781
H	2.141479	-0.31599	-0.78471
H	2.260678	-0.42632	0.975445
H	2.605479	1.106335	0.165222
C	0.229152	1.529567	1.475001
C	-0.23449	3.139565	3.740089
C	-0.73906	2.547994	1.464335
C	0.950138	1.343685	2.664375
C	0.730394	2.137647	3.790622
C	-0.97654	3.349316	2.580264
H	-1.31443	2.73771	0.565094
H	1.702624	0.567001	2.733474
H	1.305864	1.977532	4.696424
H	-1.72594	4.133246	2.545438
C	-0.22915	-1.52957	1.475001
C	0.234485	-3.13957	3.740089
C	0.739062	-2.54799	1.464335
C	-0.95014	-1.34369	2.664375
C	-0.73039	-2.13765	3.790622
C	0.976542	-3.34932	2.580264
H	1.314428	-2.73771	0.565094
H	-1.70262	-0.567	2.733474
H	-1.30586	-1.97753	4.696424

H	1.725944	-4.13325	2.545438
Cl	0.516476	-4.15465	5.149117
Cl	-0.516476	4.15465	5.149117

Atom coordinates of **5c**

Atom	X	Y	Z
N	-0.31413	-1.34868	-0.42021
C	0.503368	0.609365	-1.66818
C	1.229232	1.446506	0.472091
N	0.314126	1.34868	-0.42021
C	-1.22923	-1.44651	0.472091
C	-0.50337	-0.60937	-1.66818
H	1.509099	0.18894	-1.76428
H	-1.5091	-0.18894	-1.76428
C	-0.23483	-1.54173	-2.84129
C	0.307951	-3.15637	-5.07498
C	0.853164	-2.44324	-2.82693
C	-1.04521	-1.49155	-3.98098
C	-0.78519	-2.2875	-5.0954
C	1.120095	-3.23842	-3.94661
H	-1.88556	-0.80156	-3.99631
H	-1.42646	-2.22657	-5.96961
H	1.964501	-3.91955	-3.90257
H	0.524416	-3.78215	-5.9369
C	0.234827	1.541732	-2.84129
C	-0.30795	3.156366	-5.07498
C	1.045214	1.49155	-3.98098
C	-0.85316	2.443238	-2.82693
C	-1.1201	3.238422	-3.94661
C	0.785192	2.287502	-5.0954
H	1.885556	0.801563	-3.99631
H	-1.9645	3.919548	-3.90257
H	1.426458	2.226574	-5.96961
H	-0.52442	3.782154	-5.9369
C	-2.60625	-0.81473	0.36612
H	-3.24177	-1.07506	1.21321
H	-3.10847	-1.16686	-0.54158

H	-2.53871	0.27624	0.298499
O	1.677802	-2.56825	-1.74449
H	1.186162	-2.18388	-0.97798
O	-1.6778	2.568249	-1.74449
H	-1.18616	2.183883	-0.97798
C	2.606251	0.814727	0.36612
H	2.538705	-0.27624	0.298499
H	3.108474	1.166857	-0.54158
H	3.241768	1.075061	1.21321
C	-0.90082	-2.25673	1.684233
C	-0.21628	-3.76509	3.957154
C	-0.02464	-3.35171	1.5807
C	-1.43063	-1.93502	2.944107
C	-1.08776	-2.67104	4.073538
C	0.311257	-4.10353	2.698689
H	0.381577	-3.61681	0.610385
H	-2.09754	-1.08638	3.05674
H	-1.49041	-2.40494	5.045399
H	0.977613	-4.95515	2.607249
C	0.90082	2.25673	1.684233
C	0.216275	3.765093	3.957154
C	0.024636	3.351712	1.5807
C	1.43063	1.935017	2.944107
C	1.087755	2.671037	4.073538
C	-0.31126	4.103525	2.698689
H	-0.38158	3.616811	0.610385
H	2.097535	1.086377	3.05674
H	1.490412	2.40494	5.045399
H	-0.97761	4.955145	2.607249
C	0.132551	-4.53353	5.116161
N	0.416921	-5.15453	6.057791
C	-0.13255	4.533534	5.116161
N	-0.41692	5.154526	6.057791

Atom coordinates of **TS-c**

Atom	X	Y	Z
N	-0.62954	-1.41546	0.625111

C	-1.84013	1.063296	-0.98755
C	0.50798	0.78607	-1.03493
N	-0.62085	1.419743	-0.62708
C	0.498502	-0.78694	1.044244
C	-1.84773	-1.05722	0.987027
H	-2.01083	0.27575	-1.72397
H	-2.01599	-0.27256	1.727278
C	-3.01945	-1.77061	0.536976
C	-5.34027	-3.12475	-0.28487
C	-2.94684	-2.8118	-0.43432
C	-4.28502	-1.43684	1.068837
C	-5.43426	-2.10156	0.670297
C	-4.11185	-3.47572	-0.83521
H	-4.34278	-0.64211	1.808303
H	-6.39671	-1.8329	1.094304
H	-4.0247	-4.26497	-1.57517
H	-6.23557	-3.65319	-0.60129
C	-3.0112	1.781655	-0.54343
C	-5.33244	3.138669	0.273376
C	-4.27703	1.444679	-1.07287
C	-2.93874	2.829014	0.421081
C	-4.10366	3.494128	0.819991
C	-5.42635	2.110623	-0.67661
H	-4.33515	0.646192	-1.80824
H	-4.01613	4.288065	1.55488
H	-6.38897	1.838997	-1.09832
H	-6.2279	3.667922	0.587986
C	0.429846	0.289294	2.099364
H	1.346805	0.875183	2.157321
H	0.261878	-0.1612	3.088567
H	-0.38593	0.990402	1.9102
O	-1.77387	-3.16618	-0.99768
H	-1.07049	-2.63298	-0.53484
O	-1.76444	3.188545	0.9782
H	-1.06242	2.660832	0.507506
C	0.458478	-0.30494	-2.07718
H	1.337272	-0.94982	-2.03434
H	0.410214	0.130544	-3.0858

H	-0.41098	-0.95169	-1.9482
C	1.772739	1.491811	-0.78758
C	4.214586	2.873457	-0.33549
C	2.997606	1.021948	-1.31566
C	1.81838	2.687615	-0.02914
C	3.006809	3.360486	0.199844
C	4.1926	1.697278	-1.10042
H	3.025155	0.120327	-1.91472
H	0.90328	3.104785	0.368686
H	3.009212	4.276595	0.781878
H	5.115442	1.313928	-1.52375
C	1.762548	-1.49527	0.799493
C	4.196056	-2.88803	0.339662
C	1.785882	-2.74857	0.138807
C	3.005947	-0.97114	1.223032
C	4.196999	-1.65092	1.00246
C	2.970106	-3.4292	-0.09125
H	0.855222	-3.20719	-0.16781
H	3.053615	-0.0176	1.733038
H	5.1354	-1.22414	1.34176
H	2.955162	-4.39167	-0.59261
C	5.442865	3.571857	-0.10773
N	6.440668	4.14055	0.081837
C	5.420752	-3.59198	0.109402
N	6.415435	-4.16553	-0.08198

Atom coordinates of **6c**

Atom	X	Y	Z
N	-0.1502	-1.37227	-0.88358
C	0.708837	2.499647	-1.15814
C	0.479073	0.65138	0.361643
N	0.150204	1.372273	-0.88358
C	-0.47907	-0.65138	0.361643
C	-0.70884	-2.49965	-1.15814
H	1.410541	2.983315	-0.4648
H	-1.41054	-2.98332	-0.4648
C	-0.43673	-3.22373	-2.38833

C	0.071757	-4.67357	-4.72834
C	0.460134	-2.71125	-3.36672
C	-1.06398	-4.46353	-2.61961
C	-0.81995	-5.18946	-3.7749
C	0.705019	-3.45302	-4.53232
H	-1.7501	-4.84618	-1.86665
H	-1.31047	-6.14354	-3.9402
H	1.392922	-3.04502	-5.26598
H	0.27108	-5.2346	-5.6378
C	0.436728	3.22373	-2.38833
C	-0.07176	4.67357	-4.72834
C	1.06398	4.46353	-2.61961
C	-0.46013	2.711249	-3.36672
C	-0.70502	3.453024	-4.53232
C	0.81995	5.189457	-3.7749
H	1.750104	4.846182	-1.86665
H	-1.39292	3.045016	-5.26598
H	1.310467	6.143543	-3.9402
H	-0.27108	5.234598	-5.6378
C	-1.96365	-0.2282	0.275329
H	-2.1426	0.305075	-0.65996
H	-2.26661	0.420331	1.099252
H	-2.6037	-1.11542	0.292982
O	1.086148	-1.53391	-3.20912
H	0.761875	-1.14203	-2.35124
O	-1.08615	1.533906	-3.20912
H	-0.76188	1.142027	-2.35124
C	1.963646	0.228202	0.275329
H	2.1426	-0.30508	-0.65996
H	2.266609	-0.42033	1.099252
H	2.603697	1.115424	0.292982
C	0.225872	1.527015	1.605694
C	-0.2459	3.136145	3.888137
C	-0.74995	2.54005	1.596486
C	0.954104	1.34147	2.792174
C	0.730774	2.13002	3.91731
C	-0.98909	3.333014	2.713978
H	-1.3254	2.726279	0.696994

H	1.713499	0.57133	2.853378
H	1.312044	1.969465	4.819729
H	-1.7463	4.109945	2.680107
C	-0.22587	-1.52702	1.605694
C	0.2459	-3.13615	3.888137
C	0.749945	-2.54005	1.596486
C	-0.9541	-1.34147	2.792174
C	-0.73077	-2.13002	3.91731
C	0.98909	-3.33301	2.713978
H	1.325401	-2.72628	0.696994
H	-1.7135	-0.57133	2.853378
H	-1.31204	-1.96947	4.819729
H	1.746304	-4.10995	2.680107
C	-0.4815	3.953531	5.04211
N	-0.67434	4.615134	5.979297
C	0.481503	-3.95353	5.04211
N	0.674335	-4.61513	5.979297

Atom coordinates of **5d**

Atom	X	Y	Z
N	-0.3316	-1.34315	-0.78916
C	0.510742	0.602736	-2.03818
C	1.252784	1.438526	0.096773
N	0.331603	1.343149	-0.78916
C	-1.25278	-1.43853	0.096773
C	-0.51074	-0.60274	-2.03818
H	1.511287	0.170505	-2.13552
H	-1.51129	-0.17051	-2.13552
C	-0.25217	-1.54048	-3.20922
C	0.272006	-3.16687	-5.43841
C	0.827435	-2.4519	-3.19364
C	-1.06405	-1.48618	-4.34775
C	-0.8131	-2.28794	-5.45997
C	1.085257	-3.25293	-4.31113
H	-1.89818	-0.78871	-4.36386
H	-1.45514	-2.22386	-6.33336
H	1.923246	-3.94185	-4.26616

H	0.481214	-3.79743	-6.29861
C	0.252171	1.540481	-3.20922
C	-0.27201	3.166874	-5.43841
C	1.06405	1.48618	-4.34775
C	-0.82744	2.451899	-3.19364
C	-1.08526	3.252929	-4.31113
C	0.813098	2.287941	-5.45997
H	1.898179	0.788709	-4.36386
H	-1.92325	3.941845	-4.26616
H	1.455144	2.223858	-6.33336
H	-0.48121	3.797434	-6.29861
C	-2.62742	-0.80315	-0.01622
H	-3.26978	-1.06636	0.82479
H	-3.12357	-1.14857	-0.92971
H	-2.55617	0.288094	-0.0769
O	1.652991	-2.5814	-2.11218
H	1.166378	-2.19295	-1.34523
O	-1.65299	2.581395	-2.11218
H	-1.16638	2.192954	-1.34523
C	2.627424	0.80315	-0.01622
H	2.556165	-0.28809	-0.0769
H	3.123573	1.148571	-0.92971
H	3.269779	1.066362	0.82479
C	-0.93178	-2.24904	1.311675
C	-0.26889	-3.73978	3.565295
C	-0.05969	-3.34827	1.210986
C	-1.46601	-1.92096	2.568807
C	-1.132	-2.65613	3.702456
C	0.271141	-4.10039	2.331602
H	0.34795	-3.61675	0.242407
H	-2.12965	-1.06937	2.676605
H	-1.52577	-2.40449	4.679459
H	0.932052	-4.95598	2.266308
C	0.931784	2.249037	1.311675
C	0.268893	3.739778	3.565295
C	0.059692	3.34827	1.210986
C	1.46601	1.920964	2.568807
C	1.131996	2.656133	3.702456

C	-0.27114	4.100389	2.331602
H	-0.34795	3.616748	0.242407
H	2.129647	1.069365	2.676605
H	1.525767	2.404492	4.679459
H	-0.93205	4.955983	2.266308
N	-0.08362	4.527371	4.758787
O	0.41707	4.191603	5.831411
O	-0.85913	5.470715	4.610018
N	0.083622	-4.52737	4.758787
O	0.859131	-5.47072	4.610018
O	-0.41707	-4.1916	5.831411

Atom coordinates of **TS-d**

Atom	X	Y	Z
N	-1.01273	-1.41124	0.612526
C	-2.22207	1.071428	-1.00548
C	0.121088	0.757896	-1.00204
N	-1.01278	1.411245	-0.61242
C	0.121126	-0.75779	1.002003
C	-2.22203	-1.07167	1.005741
H	-2.38284	0.286207	-1.74738
H	-2.38285	-0.2866	1.747794
C	-3.40073	-1.78274	0.56921
C	-5.73305	-3.128	-0.22847
C	-3.34083	-2.82342	-0.40288
C	-4.6591	-1.44333	1.114026
C	-5.81446	-2.1035	0.727121
C	-4.51232	-3.48409	-0.79145
H	-4.70603	-0.64638	1.851957
H	-6.77199	-1.83095	1.159531
H	-4.43581	-4.27403	-1.5318
H	-6.6335	-3.65326	-0.53544
C	-3.40083	1.782356	-0.56887
C	-5.73322	3.127498	0.228797
C	-4.65923	1.44265	-1.11343
C	-3.34094	2.823201	0.403053
C	-4.51247	3.483849	0.791559

C	-5.81463	2.10277	-0.72655
H	-4.70615	0.64544	-1.85107
H	-4.43596	4.274018	1.531659
H	-6.77217	1.830004	-1.15879
H	-6.63371	3.65271	0.535744
C	0.05723	0.301794	2.076082
H	0.961667	0.908385	2.116083
H	-0.07242	-0.16731	3.062012
H	-0.77773	0.987009	1.91846
O	-2.17517	-3.18095	-0.97716
H	-1.46641	-2.64737	-0.52347
O	-2.17529	3.180887	0.977276
H	-1.46649	2.647155	0.523835
C	0.056903	-0.30138	-2.07639
H	0.962048	-0.90681	-2.1183
H	-0.07492	0.168066	-3.06188
H	-0.77703	-0.98766	-1.91778
C	1.383148	1.478313	-0.76834
C	3.786675	2.870901	-0.33517
C	2.619238	0.983903	-1.24732
C	1.408947	2.70862	-0.06507
C	2.590662	3.397105	0.157186
C	3.809579	1.670985	-1.0407
H	2.661752	0.050461	-1.79333
H	0.483717	3.142974	0.287905
H	2.600914	4.339803	0.690437
H	4.751619	1.288805	-1.41447
C	1.38318	-1.47819	0.768239
C	3.786817	-2.87058	0.33496
C	1.409474	-2.70694	0.062288
C	2.618814	-0.98533	1.249972
C	3.809169	-1.67251	1.04362
C	2.591302	-3.39504	-0.16048
H	0.484586	-3.14033	-0.2927
H	2.660866	-0.05318	1.798238
H	4.750812	-1.29161	1.419674
H	2.602006	-4.33623	-0.69643
N	5.03866	3.598634	-0.11198

O	6.073491	3.113817	-0.57258
O	4.982105	4.651785	0.525385
N	5.0388	-3.59828	0.111623
O	6.071759	-3.12034	0.583855
O	4.984054	-4.64451	-0.53755

Atom coordinates of **6d**

Atom	X	Y	Z
N	-0.17508	-1.36795	-1.24222
C	0.760067	2.480471	-1.52363
C	0.49178	0.642104	0.002491
N	0.175084	1.367953	-1.24222
C	-0.49178	-0.6421	0.002491
C	-0.76007	-2.48047	-1.52363
H	1.477798	2.949014	-0.83634
H	-1.4778	-2.94901	-0.83634
C	-0.49804	-3.20743	-2.75401
C	-0.00976	-4.66315	-5.09467
C	0.415761	-2.71352	-3.72639
C	-1.15258	-4.43193	-2.99189
C	-0.91852	-5.16055	-4.14741
C	0.650146	-3.4579	-4.89234
H	-1.8517	-4.80048	-2.24385
H	-1.42965	-6.10287	-4.3177
H	1.351379	-3.06402	-5.62108
H	0.181755	-5.22667	-6.00425
C	0.498042	3.207425	-2.75401
C	0.009761	4.663146	-5.09467
C	1.152582	4.431931	-2.99189
C	-0.41576	2.713522	-3.72639
C	-0.65015	3.457904	-4.89234
C	0.918515	5.160549	-4.14741
H	1.851697	4.800477	-2.24385
H	-1.35138	3.064018	-5.62108
H	1.429651	6.102867	-4.3177
H	-0.18176	5.226671	-6.00425
C	-1.96801	-0.18948	-0.08329

H	-2.13575	0.346852	-1.01882
H	-2.25801	0.465624	0.740174
H	-2.62589	-1.06347	-0.06482
O	1.067838	-1.55113	-3.56267
H	0.747772	-1.15387	-2.7061
O	-1.06784	1.551127	-3.56267
H	-0.74777	1.153869	-2.7061
C	1.968009	0.189475	-0.08329
H	2.135749	-0.34685	-1.01882
H	2.25801	-0.46562	0.740174
H	2.625891	1.063468	-0.06482
C	0.25653	1.523523	1.246126
C	-0.16971	3.132437	3.499778
C	-0.6948	2.560825	1.232172
C	0.97953	1.319228	2.433884
C	0.777633	2.115334	3.558487
C	-0.91458	3.364388	2.346935
H	-1.26491	2.758126	0.331941
H	1.717745	0.529169	2.496608
H	1.341484	1.958514	4.47001
H	-1.64464	4.164571	2.332478
C	-0.25653	-1.52352	1.246126
C	0.169711	-3.13244	3.499778
C	0.6948	-2.56083	1.232172
C	-0.97953	-1.31923	2.433884
C	-0.77763	-2.11533	3.558487
C	0.914578	-3.36439	2.346935
H	1.264914	-2.75813	0.331941
H	-1.71775	-0.52917	2.496608
H	-1.34148	-1.95851	4.47001
H	1.644643	-4.16457	2.332478
N	-0.38919	3.980967	4.681309
O	0.287386	3.750348	5.683025
O	-1.23729	4.86887	4.59597
N	0.389187	-3.98097	4.681309
O	1.237293	-4.86887	4.59597
O	-0.28739	-3.75035	5.683025

Atom coordinates of **7***			
Atom	X	Y	Z
N	-0.50548	-1.27888	-1.50608
C	1.470752	1.241299	-2.34271
C	0.551784	0.567221	-0.2268
N	0.505483	1.278877	-1.50608
C	-0.55178	-0.56722	-0.2268
C	-1.47075	-1.2413	-2.34271
H	1.516751	0.081962	-0.05318
H	-1.51675	-0.08196	-0.05318
C	-2.77351	-0.48099	-2.16613
H	-2.62061	0.524734	-1.76471
H	-3.43253	-1.01633	-1.47012
H	-3.30156	-0.39796	-3.1201
C	2.77351	0.480985	-2.16613
H	2.620608	-0.52473	-1.76471
H	3.432532	1.016334	-1.47012
H	3.301556	0.397964	-3.1201
C	0.286788	1.556457	0.898906
C	-0.29446	3.279511	3.039777
C	1.021667	1.500874	2.087322
C	-0.74201	2.519022	0.785488
C	-1.02979	3.367852	1.859669
C	0.741806	2.350974	3.157181
H	1.816934	0.764679	2.177032
H	-1.82664	4.095663	1.739773
H	1.323804	2.285041	4.071819
H	-0.52523	3.947445	3.865804
C	-0.28679	-1.55646	0.898906
C	0.294459	-3.27951	3.039777
C	-1.02167	-1.50087	2.087322
C	0.74201	-2.51902	0.785488
C	1.029793	-3.36785	1.859669
C	-0.74181	-2.35097	3.157181
H	-1.81693	-0.76468	2.177032
H	1.826641	-4.09566	1.739773
H	-1.3238	-2.28504	4.071819

H	0.525231	-3.94745	3.865804
O	-1.48497	2.646391	-0.353
H	-0.93232	2.262641	-1.08262
O	1.484965	-2.64639	-0.353
H	0.932316	-2.26264	-1.08262
C	1.339302	2.035688	-3.61813
H	1.39107	1.371	-4.49051
H	2.171847	2.745088	-3.71416
H	0.395933	2.585534	-3.63993
C	-1.3393	-2.03569	-3.61813
H	-2.17185	-2.74509	-3.71416
H	-0.39593	-2.58553	-3.63993
H	-1.39107	-1.371	-4.49051

*Calculation was performed using (*S,S*)-*hpen*.

Atom coordinates of **8***			
Atom	X	Y	Z
N	-0.70081	-1.29009	-1.44072
C	1.08517	0.677193	-2.5515
C	0.906887	0.800369	-0.20441
N	0.700811	1.290092	-1.44072
C	-0.90689	-0.80037	-0.20441
C	-1.08517	-0.67719	-2.5515
H	1.607742	-0.01802	-0.03783
H	-1.60774	0.018016	-0.03783
C	-2.0801	0.461633	-2.57605
H	-2.08051	0.951918	-3.55397
H	-1.88699	1.218571	-1.81342
H	-3.09406	0.066797	-2.40912
C	2.080102	-0.46163	-2.57605
H	2.080505	-0.95192	-3.55397
H	1.886992	-1.21857	-1.81342
H	3.094055	-0.0668	-2.40912
C	0.579084	1.611113	0.958855
C	-0.05955	3.097405	3.260306
C	1.057617	1.231654	2.228722
C	-0.236	2.774919	0.865867
C	-0.54999	3.499732	2.020491

C	0.752453	1.962975	3.37061
H	1.677253	0.34164	2.301557
H	-1.17265	4.38303	1.916273
H	1.136624	1.650762	4.337029
H	-0.30727	3.677585	4.145528
C	-0.57908	-1.61111	0.958855
C	0.059545	-3.09741	3.260306
C	-1.05762	-1.23165	2.228722
C	0.236003	-2.77492	0.865867
C	0.549987	-3.49973	2.020491
C	-0.75245	-1.96298	3.37061
H	-1.67725	-0.34164	2.301557
H	1.172651	-4.38303	1.916273
H	-1.13662	-1.65076	4.337029
H	0.307269	-3.67759	4.145528
O	-0.72994	3.205509	-0.31813
H	-0.27925	2.662089	-1.023
O	0.729939	-3.20551	-0.31813
H	0.279253	-2.66209	-1.023
C	0.930516	1.460986	-3.83038
H	0.717831	0.814351	-4.68871
H	1.870768	1.984527	-4.06172
H	0.145122	2.214809	-3.73762
C	-0.93052	-1.46099	-3.83038
H	-1.87077	-1.98453	-4.06172
H	-0.14512	-2.21481	-3.73762
H	-0.71783	-0.81435	-4.68871

*Calculation was performed using (*S,S)-hpen.*

Atom coordinates of **9***			
Atom	X	Y	Z
N	1.427965	-0.22249	-1.33761
C	-0.60199	0.530116	-2.51561
C	-1.42284	0.946618	-0.27489
N	-1.42797	0.222485	-1.33761
C	1.422841	-0.94662	-0.27489
C	0.601988	-0.53012	-2.51561
H	-0.81534	1.853899	-0.1897

H	0.81534	-1.8539	-0.1897
C	0.071299	-1.97772	-2.54022
H	-0.39316	-2.19726	-3.50524
H	-0.67103	-2.17027	-1.76199
H	0.901752	-2.6812	-2.41224
C	-0.0713	1.977722	-2.54022
H	0.393158	2.197259	-3.50524
H	0.671034	2.170267	-1.76199
H	-0.90175	2.681204	-2.41224
C	-2.22477	0.609743	0.894508
C	-3.73003	-0.00668	3.173969
C	-2.18126	1.435755	2.032798
C	-3.04787	-0.54941	0.915709
C	-3.79532	-0.84321	2.065927
C	-2.92305	1.140484	3.16739
H	-1.5454	2.318421	2.00929
H	-4.41767	-1.73252	2.06112
H	-2.87802	1.786909	4.038336
H	-4.3159	-0.24857	4.057142
C	2.224766	-0.60974	0.894508
C	3.730028	0.006679	3.173969
C	2.18126	-1.43576	2.032798
C	3.047874	0.549406	0.915709
C	3.795324	0.84321	2.065927
C	2.923051	-1.14048	3.16739
H	1.545401	-2.31842	2.00929
H	4.417671	1.732516	2.06112
H	2.87802	-1.78691	4.038336
H	4.315901	0.248566	4.057142
O	-3.12997	-1.37779	-0.13988
H	-2.55613	-0.97945	-0.85914
O	3.129974	1.377791	-0.13988
H	2.55613	0.979454	-0.85914
C	-1.53402	0.336421	-3.7302
H	-1.00238	0.475084	-4.67635
H	-2.33624	1.081064	-3.68675
H	-2.00279	-0.65071	-3.72841
C	1.53402	-0.33642	-3.7302

H	2.336243	-1.08106	-3.68675
H	2.00279	0.65071	-3.72841
H	1.002381	-0.47508	-4.67635

*Calculation was performed using *(S,S)-hpen*

Crystal structure and data

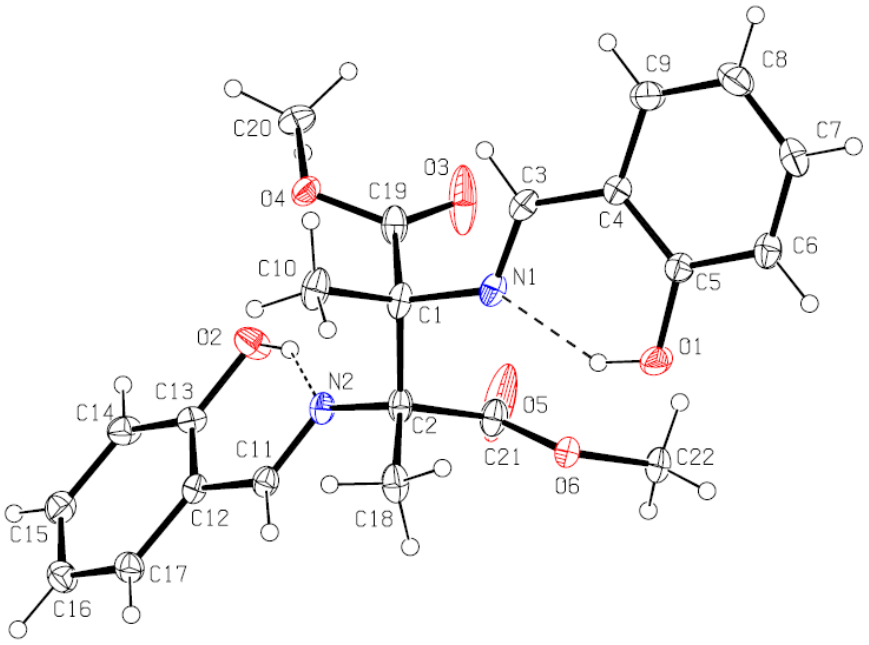

Figure S1. Crystal structure of diimine 3

Table S1. Crystal data and structure refinement for d12336.

Identification code	d12336	
Empirical formula	C22 H24 N2 O6	
Formula weight	412.43	
Temperature	147(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 6.9679(3) Å	a= 90°.
	b = 19.0540(9) Å	b= 93.428(2)°.
	c = 7.6683(4) Å	g = 90°.
Volume	1016.27(8) Å^3	
Z	2	
Density (calculated)	1.348 Mg/m^3	
Absorption coefficient	0.819 mm^{-1}	
F(000)	436	
Crystal size	0.28 x 0.15 x 0.12 mm^3	
Theta range for data collection	4.64 to 66.31°.	

Index ranges	-8<=h<=7, -22<=k<=21, -9<=l<=9
Reflections collected	12698
Independent reflections	3412 [R(int) = 0.0305]
Completeness to theta = 66.31°	97.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.6930
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3412 / 1 / 283
Goodness-of-fit on F^2	1.067
Final R indices [I>2sigma(I)]	R1 = 0.0305, wR2 = 0.0761
R indices (all data)	R1 = 0.0306, wR2 = 0.0763
Absolute structure parameter	0.16(14)
Largest diff. peak and hole	0.175 and -0.217 e.$Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for d12336. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4456(2)	3221(1)	5202(2)	38(1)
O(2)	6771(2)	6630(1)	10659(2)	37(1)
O(3)	3030(3)	5554(1)	7322(3)	78(1)
O(4)	4970(2)	6389(1)	6500(2)	31(1)
O(5)	5173(3)	4783(1)	10189(3)	90(1)
O(6)	5861(2)	3857(1)	8609(1)	26(1)
N(1)	5003(2)	4582(1)	5374(2)	27(1)
N(2)	7816(2)	5568(1)	8809(2)	26(1)
C(1)	5994(3)	5204(1)	6119(2)	29(1)
C(2)	7246(2)	4944(1)	7780(2)	27(1)
C(3)	3520(2)	4655(1)	4325(2)	29(1)
C(4)	2443(2)	4058(1)	3611(2)	26(1)
C(5)	2954(2)	3367(1)	4058(2)	27(1)
C(6)	1909(3)	2804(1)	3314(2)	34(1)
C(7)	364(2)	2932(1)	2158(2)	36(1)
C(8)	-206(3)	3611(1)	1750(2)	43(1)
C(9)	831(3)	4167(1)	2467(2)	37(1)
C(10)	7250(3)	5531(1)	4761(2)	38(1)
C(11)	9532(2)	5640(1)	9476(2)	26(1)
C(12)	10041(2)	6224(1)	10648(2)	24(1)
C(13)	8639(2)	6690(1)	11209(2)	27(1)
C(14)	9173(3)	7231(1)	12369(2)	32(1)
C(15)	11075(3)	7311(1)	12937(2)	33(1)
C(16)	12483(2)	6854(1)	12409(2)	33(1)
C(17)	11965(2)	6313(1)	11279(2)	30(1)
C(18)	8899(2)	4481(1)	7228(2)	34(1)
C(19)	4482(3)	5728(1)	6719(2)	32(1)
C(20)	3600(3)	6904(1)	7062(2)	36(1)
C(21)	5945(2)	4536(1)	8996(2)	32(1)
C(22)	4659(2)	3434(1)	9666(2)	34(1)

Table S3. Bond lengths [Å] and angles [°] for d12336.

O(1)-C(5)	1.354(2)
O(1)-H(1O)	0.86(4)
O(2)-C(13)	1.349(2)
O(2)-H(2O)	0.86(3)
O(3)-C(19)	1.184(2)
O(4)-C(19)	1.318(2)
O(4)-C(20)	1.453(2)
O(5)-C(21)	1.186(2)
O(6)-C(21)	1.327(2)
O(6)-C(22)	1.4450(19)
N(1)-C(3)	1.278(2)
N(1)-C(1)	1.470(2)
N(2)-C(11)	1.280(2)
N(2)-C(2)	1.467(2)
C(1)-C(10)	1.533(2)
C(1)-C(19)	1.542(2)
C(1)-C(2)	1.579(2)
C(2)-C(18)	1.532(2)
C(2)-C(21)	1.549(2)
C(3)-C(4)	1.453(2)
C(3)-H(3A)	0.9500
C(4)-C(9)	1.399(2)
C(4)-C(5)	1.401(2)
C(5)-C(6)	1.398(2)
C(6)-C(7)	1.375(3)
C(6)-H(6A)	0.9500
C(7)-C(8)	1.384(3)
C(7)-H(7A)	0.9500
C(8)-C(9)	1.379(3)
C(8)-H(8A)	0.9500
C(9)-H(9A)	0.9500
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800

C(11)-C(12)	1.461(2)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.407(2)
C(12)-C(17)	1.408(2)
C(13)-C(14)	1.398(2)
C(14)-C(15)	1.379(2)
C(14)-H(14A)	0.9500
C(15)-C(16)	1.389(3)
C(15)-H(15A)	0.9500
C(16)-C(17)	1.382(2)
C(16)-H(16A)	0.9500
C(17)-H(17A)	0.9500
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800

C(5)-O(1)-H(1O)	109(2)
C(13)-O(2)-H(2O)	106.0(15)
C(19)-O(4)-C(20)	115.38(13)
C(21)-O(6)-C(22)	115.92(12)
C(3)-N(1)-C(1)	119.96(14)
C(11)-N(2)-C(2)	121.19(14)
N(1)-C(1)-C(10)	109.79(13)
N(1)-C(1)-C(19)	108.96(13)
C(10)-C(1)-C(19)	111.52(14)
N(1)-C(1)-C(2)	106.61(12)
C(10)-C(1)-C(2)	111.38(14)
C(19)-C(1)-C(2)	108.43(12)
N(2)-C(2)-C(18)	115.59(13)
N(2)-C(2)-C(21)	103.43(12)

C(18)-C(2)-C(21)	110.69(13)
N(2)-C(2)-C(1)	107.43(12)
C(18)-C(2)-C(1)	110.23(13)
C(21)-C(2)-C(1)	109.13(13)
N(1)-C(3)-C(4)	122.07(14)
N(1)-C(3)-H(3A)	119.0
C(4)-C(3)-H(3A)	119.0
C(9)-C(4)-C(5)	118.44(15)
C(9)-C(4)-C(3)	119.79(15)
C(5)-C(4)-C(3)	121.76(14)
O(1)-C(5)-C(6)	118.04(15)
O(1)-C(5)-C(4)	121.78(14)
C(6)-C(5)-C(4)	120.18(14)
C(7)-C(6)-C(5)	119.70(17)
C(7)-C(6)-H(6A)	120.1
C(5)-C(6)-H(6A)	120.1
C(6)-C(7)-C(8)	120.97(17)
C(6)-C(7)-H(7A)	119.5
C(8)-C(7)-H(7A)	119.5
C(9)-C(8)-C(7)	119.50(16)
C(9)-C(8)-H(8A)	120.3
C(7)-C(8)-H(8A)	120.3
C(8)-C(9)-C(4)	121.14(17)
C(8)-C(9)-H(9A)	119.4
C(4)-C(9)-H(9A)	119.4
C(1)-C(10)-H(10A)	109.5
C(1)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(1)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
N(2)-C(11)-C(12)	120.94(14)
N(2)-C(11)-H(11A)	119.5
C(12)-C(11)-H(11A)	119.5
C(13)-C(12)-C(17)	118.91(14)
C(13)-C(12)-C(11)	121.44(14)

C(17)-C(12)-C(11)	119.63(14)
O(2)-C(13)-C(14)	118.44(14)
O(2)-C(13)-C(12)	121.74(14)
C(14)-C(13)-C(12)	119.82(14)
C(15)-C(14)-C(13)	119.74(15)
C(15)-C(14)-H(14A)	120.1
C(13)-C(14)-H(14A)	120.1
C(14)-C(15)-C(16)	121.45(16)
C(14)-C(15)-H(15A)	119.3
C(16)-C(15)-H(15A)	119.3
C(17)-C(16)-C(15)	119.20(16)
C(17)-C(16)-H(16A)	120.4
C(15)-C(16)-H(16A)	120.4
C(16)-C(17)-C(12)	120.88(16)
C(16)-C(17)-H(17A)	119.6
C(12)-C(17)-H(17A)	119.6
C(2)-C(18)-H(18A)	109.5
C(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
O(3)-C(19)-O(4)	123.32(17)
O(3)-C(19)-C(1)	123.42(16)
O(4)-C(19)-C(1)	113.26(13)
O(4)-C(20)-H(20A)	109.5
O(4)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
O(4)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
O(5)-C(21)-O(6)	122.90(16)
O(5)-C(21)-C(2)	125.02(15)
O(6)-C(21)-C(2)	112.00(13)
O(6)-C(22)-H(22A)	109.5
O(6)-C(22)-H(22B)	109.5

H(22A)-C(22)-H(22B)	109.5
O(6)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for d12336. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	46(1)	23(1)	43(1)	0(1)	-17(1)	-1(1)
O(2)	29(1)	38(1)	43(1)	-15(1)	-3(1)	5(1)
O(3)	74(1)	42(1)	128(2)	-39(1)	76(1)	-28(1)
O(4)	30(1)	22(1)	40(1)	5(1)	6(1)	3(1)
O(5)	147(2)	37(1)	97(1)	-25(1)	98(1)	-31(1)
O(6)	29(1)	22(1)	28(1)	1(1)	4(1)	-4(1)
N(1)	38(1)	21(1)	22(1)	-2(1)	6(1)	-4(1)
N(2)	30(1)	22(1)	27(1)	-3(1)	5(1)	-4(1)
C(1)	38(1)	22(1)	27(1)	-3(1)	10(1)	-8(1)
C(2)	31(1)	22(1)	30(1)	-6(1)	10(1)	-6(1)
C(3)	37(1)	22(1)	29(1)	2(1)	7(1)	2(1)
C(4)	30(1)	25(1)	22(1)	-1(1)	4(1)	0(1)
C(5)	31(1)	27(1)	24(1)	0(1)	1(1)	-1(1)
C(6)	40(1)	28(1)	32(1)	-3(1)	3(1)	-8(1)
C(7)	33(1)	46(1)	30(1)	-5(1)	4(1)	-14(1)
C(8)	30(1)	59(1)	39(1)	4(1)	-5(1)	-5(1)
C(9)	34(1)	39(1)	37(1)	5(1)	-1(1)	5(1)
C(10)	49(1)	30(1)	37(1)	-2(1)	20(1)	-8(1)
C(11)	28(1)	24(1)	27(1)	0(1)	8(1)	-1(1)
C(12)	28(1)	21(1)	25(1)	2(1)	5(1)	-3(1)
C(13)	28(1)	27(1)	27(1)	2(1)	0(1)	3(1)
C(14)	37(1)	29(1)	30(1)	-4(1)	-3(1)	6(1)
C(15)	42(1)	28(1)	28(1)	-2(1)	-4(1)	-3(1)
C(16)	30(1)	39(1)	29(1)	1(1)	-2(1)	-6(1)
C(17)	26(1)	34(1)	30(1)	2(1)	6(1)	-1(1)
C(18)	33(1)	28(1)	41(1)	-11(1)	15(1)	-7(1)
C(19)	39(1)	27(1)	30(1)	-8(1)	10(1)	-10(1)
C(20)	39(1)	32(1)	38(1)	2(1)	4(1)	11(1)
C(21)	38(1)	25(1)	32(1)	-5(1)	12(1)	-5(1)
C(22)	35(1)	29(1)	37(1)	5(1)	8(1)	-8(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for d12336.

	x	y	z	U(eq)
H(3A)	3110	5115	4003	35
H(6A)	2265	2335	3607	40
H(7A)	-322	2548	1631	44
H(8A)	-1303	3693	981	51
H(9A)	443	4633	2180	44
H(10A)	6428	5754	3838	57
H(10B)	8029	5165	4251	57
H(10C)	8098	5885	5327	57
H(11A)	10489	5308	9206	31
H(14A)	8228	7543	12765	39
H(15A)	11431	7686	13706	40
H(16A)	13786	6914	12820	40
H(17A)	12919	5996	10923	36
H(18A)	9485	4239	8254	50
H(18B)	9868	4773	6703	50
H(18C)	8403	4133	6372	50
H(20A)	3930	7368	6614	54
H(20B)	3643	6917	8341	54
H(20C)	2303	6774	6609	54
H(22A)	4701	2945	9281	50
H(22B)	3333	3606	9541	50
H(22C)	5130	3466	10894	50
H(1O)	5060(50)	3600(20)	5470(40)	100(12)
H(2O)	6700(30)	6265(13)	10000(30)	50(6)

Table S6. Torsion angles [°] for d12336.

C(3)-N(1)-C(1)-C(10)	-78.11(19)
C(3)-N(1)-C(1)-C(19)	44.29(18)
C(3)-N(1)-C(1)-C(2)	161.11(13)
C(11)-N(2)-C(2)-C(18)	-13.0(2)
C(11)-N(2)-C(2)-C(21)	108.15(16)
C(11)-N(2)-C(2)-C(1)	-136.51(14)
N(1)-C(1)-C(2)-N(2)	-164.66(12)
C(10)-C(1)-C(2)-N(2)	75.59(16)
C(19)-C(1)-C(2)-N(2)	-47.48(15)
N(1)-C(1)-C(2)-C(18)	68.61(15)
C(10)-C(1)-C(2)-C(18)	-51.14(17)
C(19)-C(1)-C(2)-C(18)	-174.22(12)
N(1)-C(1)-C(2)-C(21)	-53.15(15)
C(10)-C(1)-C(2)-C(21)	-172.90(13)
C(19)-C(1)-C(2)-C(21)	64.03(15)
C(1)-N(1)-C(3)-C(4)	-177.38(13)
N(1)-C(3)-C(4)-C(9)	-179.96(15)
N(1)-C(3)-C(4)-C(5)	1.1(2)
C(9)-C(4)-C(5)-O(1)	-177.71(14)
C(3)-C(4)-C(5)-O(1)	1.2(2)
C(9)-C(4)-C(5)-C(6)	2.5(2)
C(3)-C(4)-C(5)-C(6)	-178.57(15)
O(1)-C(5)-C(6)-C(7)	179.45(16)
C(4)-C(5)-C(6)-C(7)	-0.8(2)
C(5)-C(6)-C(7)-C(8)	-1.7(3)
C(6)-C(7)-C(8)-C(9)	2.2(3)
C(7)-C(8)-C(9)-C(4)	-0.4(3)
C(5)-C(4)-C(9)-C(8)	-1.9(2)
C(3)-C(4)-C(9)-C(8)	179.12(16)
C(2)-N(2)-C(11)-C(12)	-173.55(13)
N(2)-C(11)-C(12)-C(13)	5.8(2)
N(2)-C(11)-C(12)-C(17)	-176.20(14)
C(17)-C(12)-C(13)-O(2)	-179.66(15)
C(11)-C(12)-C(13)-O(2)	-1.6(2)

C(17)-C(12)-C(13)-C(14)	0.2(2)
C(11)-C(12)-C(13)-C(14)	178.23(15)
O(2)-C(13)-C(14)-C(15)	-179.21(15)
C(12)-C(13)-C(14)-C(15)	1.0(2)
C(13)-C(14)-C(15)-C(16)	-1.3(3)
C(14)-C(15)-C(16)-C(17)	0.5(3)
C(15)-C(16)-C(17)-C(12)	0.6(2)
C(13)-C(12)-C(17)-C(16)	-1.0(2)
C(11)-C(12)-C(17)-C(16)	-179.07(14)
C(20)-O(4)-C(19)-O(3)	0.4(3)
C(20)-O(4)-C(19)-C(1)	-179.43(14)
N(1)-C(1)-C(19)-O(3)	35.3(2)
C(10)-C(1)-C(19)-O(3)	156.6(2)
C(2)-C(1)-C(19)-O(3)	-80.4(2)
N(1)-C(1)-C(19)-O(4)	-144.94(13)
C(10)-C(1)-C(19)-O(4)	-23.6(2)
C(2)-C(1)-C(19)-O(4)	99.40(15)
C(22)-O(6)-C(21)-O(5)	3.8(3)
C(22)-O(6)-C(21)-C(2)	-179.33(13)
N(2)-C(2)-C(21)-O(5)	20.0(3)
C(18)-C(2)-C(21)-O(5)	144.4(2)
C(1)-C(2)-C(21)-O(5)	-94.2(3)
N(2)-C(2)-C(21)-O(6)	-156.76(13)
C(18)-C(2)-C(21)-O(6)	-32.37(19)
C(1)-C(2)-C(21)-O(6)	89.11(16)

Symmetry transformations used to generate equivalent atoms:

Table S7. Hydrogen bonds for d12336 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1O)...N(1)	0.86(4)	1.87(4)	2.6232(17)	146(3)
O(1)-H(1O)...O(6)	0.86(4)	2.48(3)	2.9914(17)	119(3)
O(2)-H(2O)...N(2)	0.86(3)	1.82(3)	2.6006(18)	151(2)

Symmetry transformations used to generate equivalent atoms: