Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Covalent Locking and Unlocking of an Atropisomeric Molecular Switch

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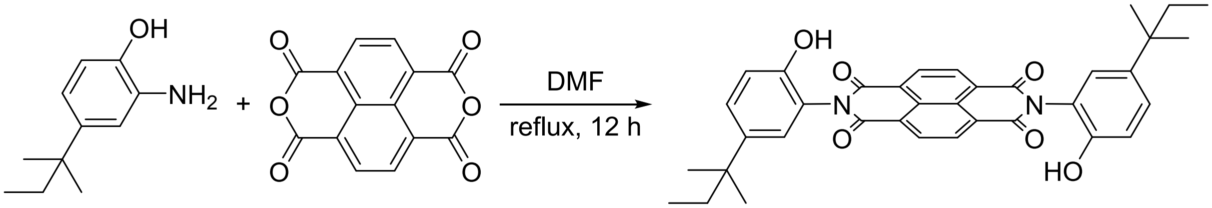
Contents

General.

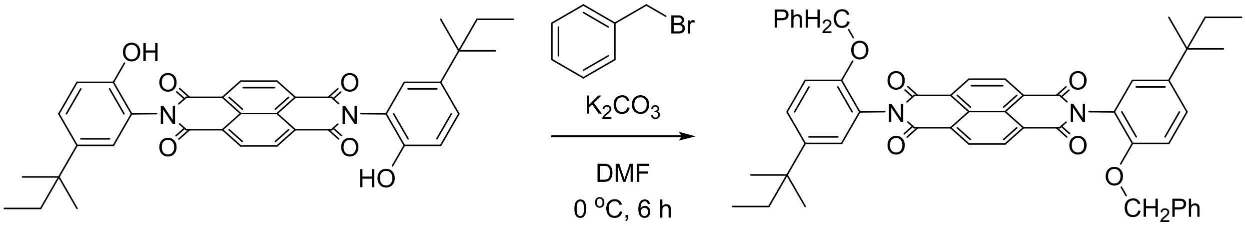
^1H NMR and ^{13}C NMR spectra were performed on a Varian: Mercury 300 MHz spectrometer, Varian: Mercury 400 MHz NMR spectrometer. All reagents were purchased from commercial suppliers and used as received.

Synthesis.



Scheme S1. Synthesis of *anti*-enriched Diol 1.

Diol **1** was prepared as previously reported.[1] To a solution of 2-amino-4-tertamylphenol (200 mg, 1.0822 mmol) in DMF (5 mL) 1,4,5,8-naphthalenetetracarboxylic anhydride (145.1 mg, 0.5411 mmol) was added and allowed to reflux for 12 hours. The crude mixture was then allowed to cool to room temperature and was then precipitated out of 1 N HCl, filtered, and concentrated *in vacuo* to give the title compound as a light brown solid (318 mg, 99 % yield). Pure Diol **1** was then crystalized to give *anti*-enriched Diol **1**. Heating a neat mixture of *syn/anti* Diol **1** up to 110 °C and allowing crystallization to occur gives a quantitative yield of *anti*-enriched Diol **1**.



Scheme S2. Synthesis of *anti*-enriched Diether 2.

Diether **1** was prepared as previously reported.[1] To a solution of *anti*-enriched Diol **1** (40 mg, 0.0.677 mmol) in dry DMF (5 mL) chilled in an ice water bath, benzyl bromide (40.3 µL, 0.339 mmol) and potassium carbonate (93.5 mg, 0.0677 mmol) was added and allowed to stir for 6 hours. The reaction mixture was then diluted with 1 N HCl and extracted with ethyl acetate, dried with $MgSO_4$, filtered, and concentrated *in vacuo*. The mixture of *syn/anti* Diether **2** was purified by flash chromatography on silica gel (33% ethyl acetate/ hexane) to give *anti*-enriched Diether **2** (41.2 mg, 79% yield). The ratio of *syn* to *anti* was 1:4 determined by NMR.

Rotational barrier studies.

The rotational barriers in this study were determined by measuring the kinetics of isomerization of an *anti*-enriched conformer following previously reported procedures and methodology.[1] The mixed solvent system 72:28 (v/v) benzene-d6: acetonitrile-d3 was chosen as both diol **1** and diether **2** were readily soluble in this solvent system over the entire range of *anti*/*syn* ratios. The change in the *anti*/*syn* ratio as measured by $ln\left(\frac{R- R_e}{R+1}\right)$, where R is the *anti*/*syn* ratio and R_e is the equilibrium ratio, plotted against time, and the slope is the observed rate of rotation. The rotational barrier is finally collected from Eyring equation as $\Delta G^{\ddagger}$.

Figure S1 shows the plot with data used to obtain the rotation barrier of diol-1 with and without DMSO (5, 10, 25, 50, and 200 eq.). The slope of the line in figure S1 is the rate of isomerization. The rate is then inserted into equation 1, to solve equations 2 and 3. Where k_{obs} is the slope of a line in Figure S1, $k_{reverse}$ and $k_{forward}$ are equal to the reverse and forward rates of rotation, k in equation 3 is a general rate constant ($k_{reverse}$), k_B is Boltzmann constant, h is planks constant, T is the temperature in kelvin, and R is the gas constant. Solving equation 3 twice (when k equals $k_{reverse}$ and again when k equals $k_{forward}$) and averaging the two will give the observed rotational barrier.

Equation 1.

$$k_{reverse} = \frac{k_{obs}}{(2+2/k_{obs})}$$

Equation 2.

$$k_{forward} = \frac{k_{reverse}}{k_{equilibrium}}$$

Equation 3.

$$\Delta G^{\neq} = ln\left(\frac{k}{K_B hT}\right)RT$$

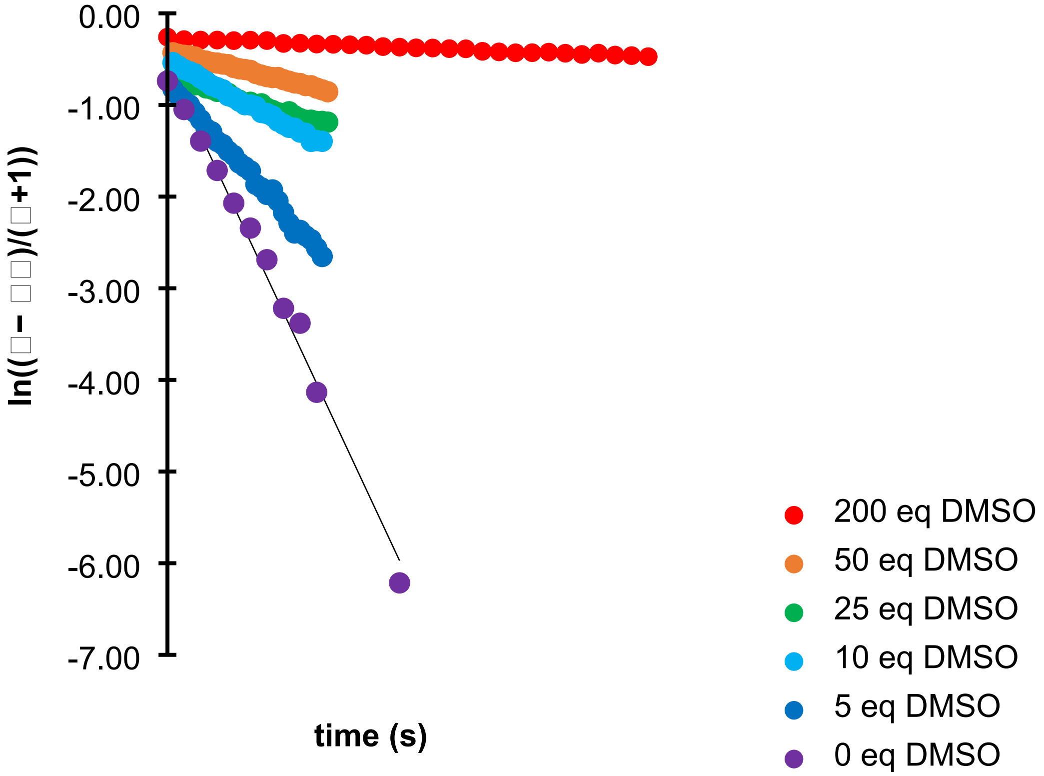


Figure S1. Isomerization of *anti*-enriched diol **1** in the presence of 0, 5, 10, 25, 50, and 200 equivalents of DMSO in 72:28 (v/v) benzene-d_6: acetonitrile-d_3 solution at 18.2 °C. R is the 1H NMR measured *anti*/*syn* ratio for diol **1** and Re is the *anti*/*syn* ratio at equilibrium.

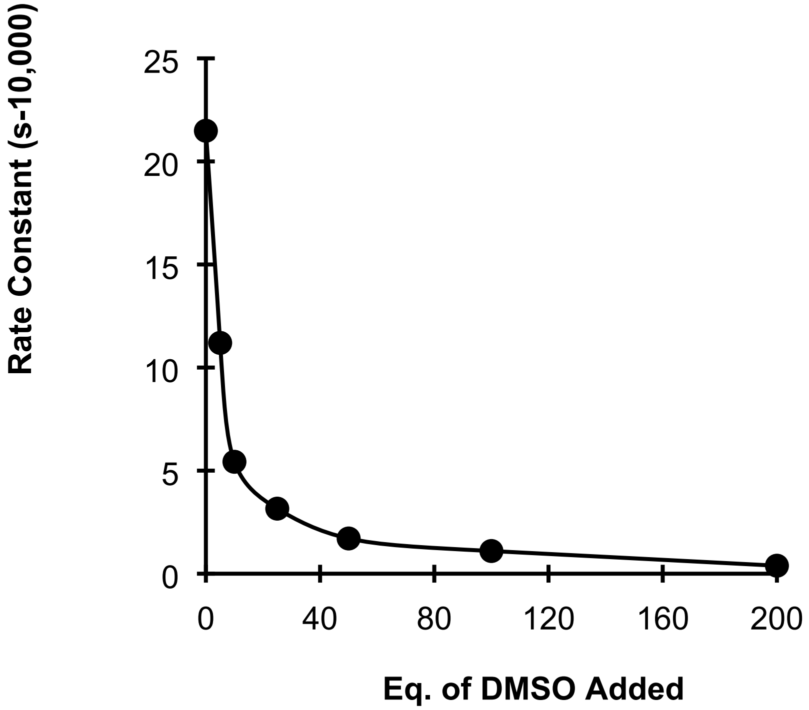


Figure S2. Isomerization rate of *anti*-enriched diol **1** in the presence of 0, 5, 10, 25, 50, and 200 equivalents of DMSO in 72:28 (v/v) benzene-d_6: acetonitrile-d_3 solution at 18.2 °C.

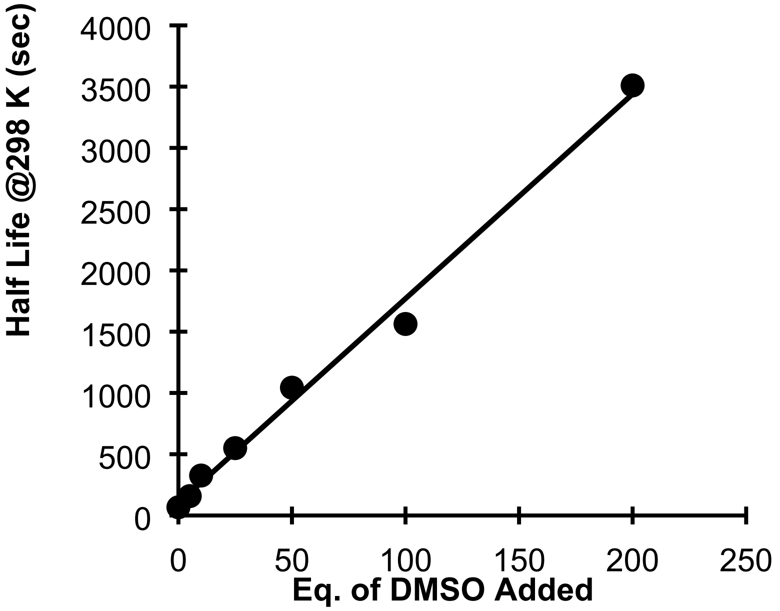


Figure S3. Half-lives of *anti*-enriched diol **1** in the presence of 0, 5, 10, 25, 50, and 200 equivalents of DMSO in 72:28 (v/v) benzene-d_6 : acetonitrile-d_3 solution at 18.2 °C.

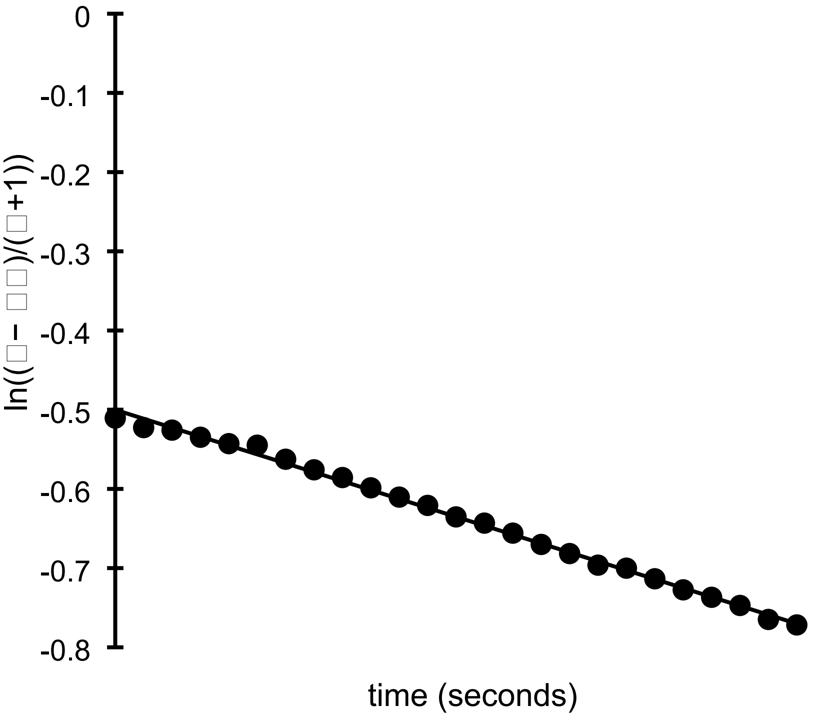


Figure S4. Isomerization of *anti*-enriched diether **2** in 72:28 (v/v) benzene-d_6: acetonitrile-d_3 solution at 70 °C. R is the 1H NMR measured *anti*/*syn* ratio for diether **1** and Re is the *anti*/*syn* ratio at equilibrium.

ON-OFF cycle of rotation for diol 1.

The reversibility of the braking effect was performed by adding and extracting 5 equivalents of DMSO in and out of a solution of *anti*-enrich diol **1**. Deuterated methylene chloride (CD_2Cl_2) was selected as the solvent for this study since DMSO partitioned into the aqueous layer upon extraction while diol **1** remained in the organic layer. Due to the rapid isomerization of diol **1** the experiment was performed at -10 ^{o}C and with the DMSO initially present. Differences between the "ON" states was considered to be due to error in measurement while adding DMSO to the sample.

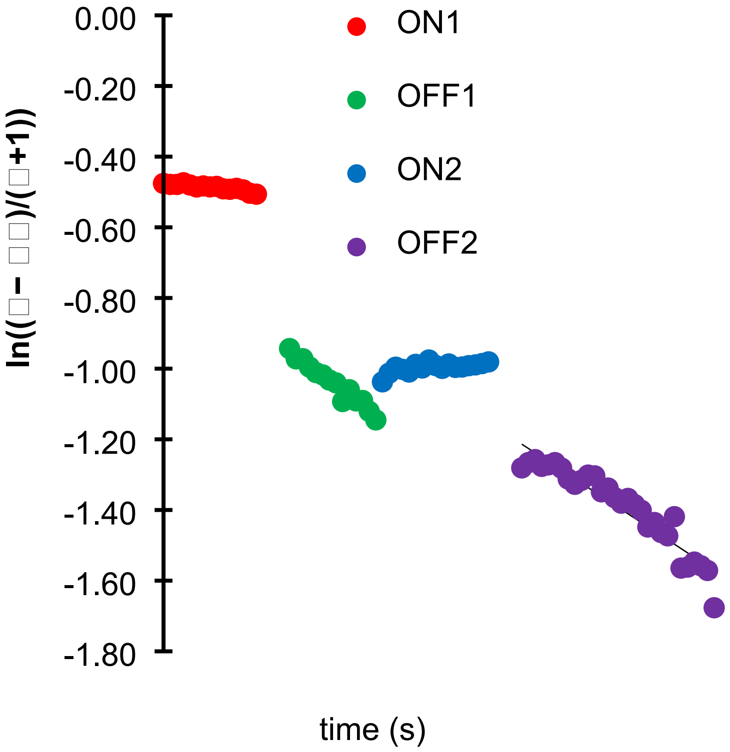


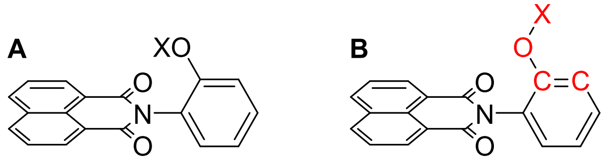
Figure S5. Measured rate constants for a single sample of diol **1** in CD_2Cl_2 at -10 ^oC in the presence (with) and absence (without) 5 equivalents of DMSO for two complete cycles.

Computational studies.

All calculations were performed with the Spartan 10 program package. Structures were optimized and single point energies were calculated using the B3LYP or M06-2X functional and 6-31G* basis set.

Because the barriers for the two rotors in **1** and **2** should be identical, a subset of the molecules including only one rotor were calculated (Scheme S3A). The ground states were calculated using the equilibrium geometry calculation function with the B3LYP functional and later reoptimized at the M06-2X functional. Transition states were found by constraining the dihedral angle about the C-N bond of the imide from -90 to 90^o in 181 steps to obtain a new structure for every degree. The transition states were verified by vibrational analysis. Because the imide has a C_4 symmetry and the phenyl ring only has C_2 there are two different dihedral angles which can be locked, the side with the alcohol (ether) or the side with a hydrogen substituent. Due to the alcohol or ether providing a major impact on the rotational barrier, the dihedral angle was always locked on their appropriate side.

In attempt to rule out the steric component of the “H” vs “CH_2Ph”, to extra rotational barriers were calculated of the phenol and methyl ether rotors where the “H” and “CH_3” were constrained at 0^o with the adjacent carbon on the rotor, to always face away from the carbonyl imide (Scheme S3B).



X = H,CH_3,$CH(CH_3)_2$,CH_2Ph

Scheme S3. A) Rotor (Phenyl ring) and stator (1,8-naphthalimide) used to compute the rotational barriers. B) The atoms used in the Dihedral angle which is locked in some computed rotational barriers.

Table S1. Rotational barriers in of selected rotors.[a]

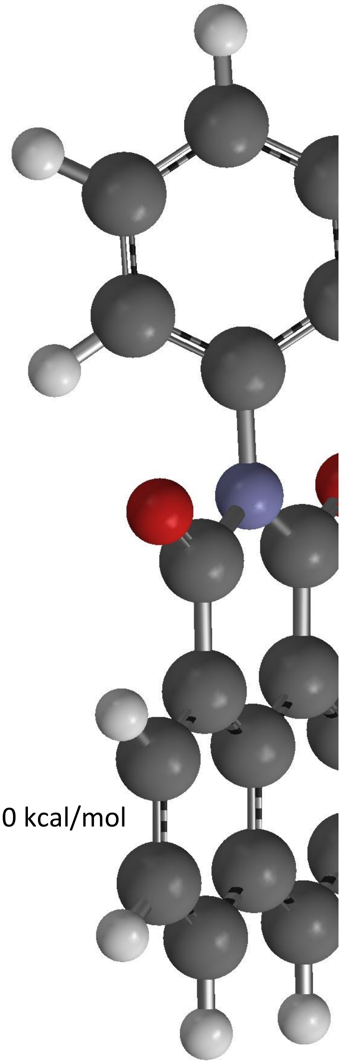
X	Ground state energy	Transition state energy	ΔG‡	Exp. ΔG‡	M062X ΔΔG‡[b]
OCH2Ph	-779915.82	-779888.31	27.51	27.50	0.01
OH	-610336.50	-610317.86	18.64	19.31[d]	0.67
OH[c]	-610333.43	-610307.06	26.37	NA	
Δ OH[e]	-3.07	-10.80	NA	NA	
OCH3	-634985.26	-634957.72	27.54	NA	
OCH3[c]	-634985.26	-634958.34	26.91	NA	
Δ OCH3[e]	0.00	0.62	NA	NA	

[a] all numbers are energy in kcal/mol. [b] difference between experimental and calculated values. [c] substituent off the oxygen atom is confined to have a dihedral angle of 0° so that the group faces away from the carbonyl imide. [d] estimated for a solvent with a beta parameter of zero (Y-intercept of Figure 3). [e] differences between the ground state and transition state energies when the substituent off of the oxygen in constrained or not.

Cartesian Coordinates of Rotors.

Table S2. Structures and Cartesian coordinates of ground and transition states of the phenol and anisole rotors optimized at the B3LYP/6-31G* level and recalculated for energy at the M062X/6-31G* level of theory. Energies listed under structures in kcal/mol.

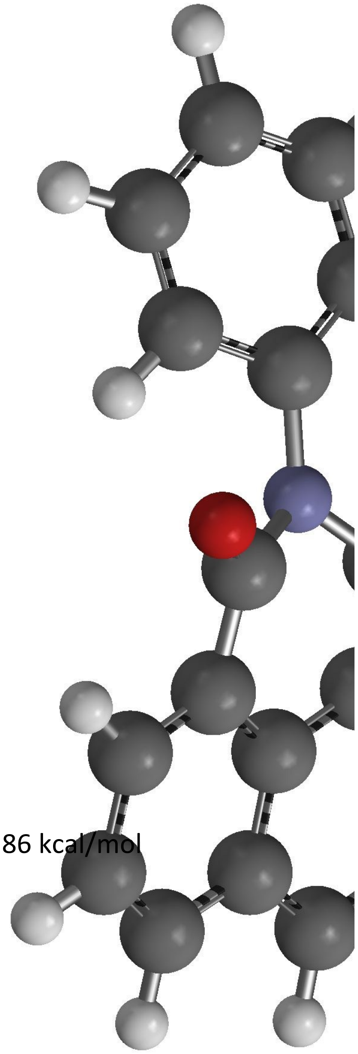
phenol rotor ground state



-610336.50 kcal/mol

	X	Y	Z
H	-1.6961599	-3.3658816	0.3757536
C	-2.1697054	-2.4164182	0.1500447
C	-1.4255424	-1.2558209	0.2717103
C	-4.1087553	-1.1488130	-0.5720921
C	-2.0247546	-0.0055660	-0.0125438
C	-3.5142167	-2.3590768	-0.2765184
C	-3.3840541	0.0643745	-0.4390786
C	-1.2864302	1.1797754	0.1988016
H	-4.0807101	-3.2806146	-0.3750620
H	-4.9763057	1.4123548	-1.0229216
H	-5.1446052	-1.110295	-0.8999487
C	-1.8738894	2.4140422	-0.0098754
H	-1.2997625	3.3127786	0.1904042
C	-3.2043143	2.4915192	-0.4763062
H	-3.6489603	3.4655023	-0.6589304
C	-3.9456136	1.3453692	-0.6833374
C	0.0163032	-1.3525322	0.6382146
C	0.0851311	1.083722	0.7525298
O	0.5645075	1.9642278	1.430969
O	0.4948389	-2.4234466	0.9778043
N	0.7964658	-0.1617643	0.5234938
C	2.1546621	-0.213106	0.0106405
C	4.8952253	-0.4799269	-0.7603961
C	2.7468824	-1.4611262	-0.2700008
C	2.9934887	0.9256209	-0.1470895
C	4.3388276	0.7653906	-0.5064626
C	4.0734824	-1.5978267	-0.6675546
H	4.9438433	1.6653391	-0.6114796
H	4.4597517	-2.591383	-0.8731095
H	5.9418784	-0.5668523	-1.0365420
H	2.1634845	-2.3574706	-0.1431713
O	2.486298	2.1921171	-0.0940112
H	3.19677	2.8080793	-0.3316613

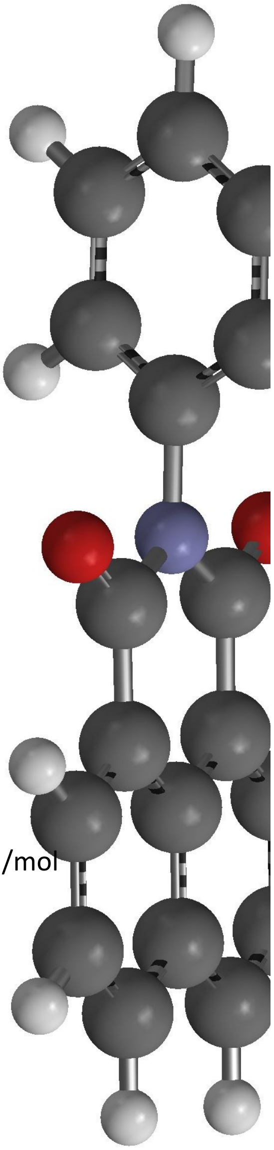
phenol rotor transition state



-610317.86 kcal/mol

	X	Y	Z
H	-1.5458862	-3.3240605	-0.0222982
C	-2.0905983	-2.3900398	-0.1039960
C	-1.4093651	-1.1967101	0.0663252
C	-4.1668492	-1.1930053	-0.4936452
C	-2.1077174	0.026864	-0.0241601
C	-3.4728041	-2.3821137	-0.3926288
C	-3.504974	0.0477396	-0.301321
C	-1.4113073	1.2260121	0.226966
H	-3.9901229	-3.3261702	-0.5353349
H	-5.2207462	1.3439184	-0.5656289
H	-5.2318874	-1.1949402	-0.7113950
C	-2.081428	2.4367821	0.2117670
H	-1.5355132	3.3478667	0.4329835
C	-3.4588152	2.4730892	-0.0943178
H	-3.9724163	3.4294548	-0.1239015
C	-4.156978	1.3078071	-0.3444097
C	0.0551716	-1.216806	0.3206554
C	0.0267859	1.170115	0.5746505
O	0.5706804	2.0769402	1.1690613
O	0.5793063	-2.2982519	0.5931955
N	0.7599359	-0.0146368	0.1252260
C	2.2338347	0.1338029	0.0500791
C	4.9440573	0.7236551	-0.6340144
C	3.2205973	-0.8958168	0.0206003
C	2.6556837	1.4091832	-0.4041546
C	3.9687123	1.7204907	-0.7100689
C	4.5576724	-0.5516313	-0.2782711
H	1.9278239	2.1964490	-0.5200674
H	4.2174483	2.7288161	-1.0264361
H	5.2697952	-1.3690236	-0.2305240
H	5.9842789	0.9364044	-0.8645719
O	3.0794475	-2.2003558	0.3160327
H	2.1321304	-2.3894253	0.5239398

phenol rotor (OH forced up) ground state



-610333.43 kcal/mol

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H	-1.5420549	-3.3534602	0.3026786
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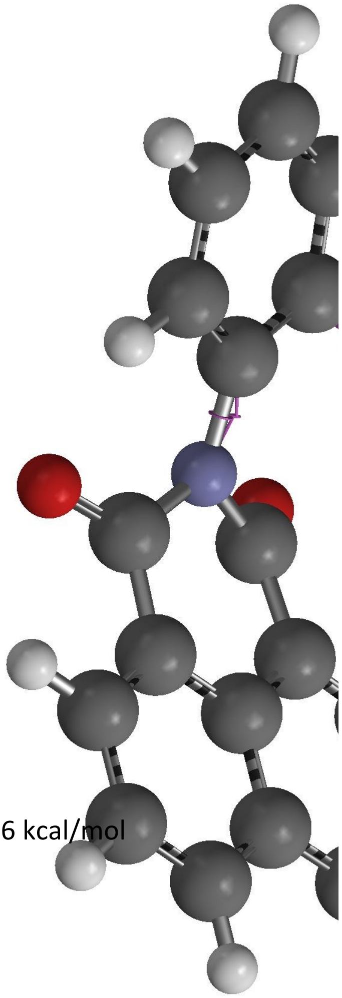
C	-1.3797049	-1.2539625	0.0507616
C	-4.1733878	-1.1960846	0.1902255
C	-2.0535562	-0.0141377	-0.0565900
C	-3.4989159	-2.3886317	0.2922495
C	-3.4703196	0.0236	0.0135988
C	-1.3289993	1.1884368	-0.2330357
H	-4.0476701	-3.3148670	0.4271227
H	-5.2069516	1.3107645	-0.0430185
H	-5.2586173	-1.1703466	0.2436411
C	-1.989066	2.3903576	-0.3376029
H	-1.4033937	3.2937573	-0.4732986
C	-3.3985	2.434596	-0.2680503
H	-3.9078412	3.3889772	-0.3509745
C	-4.1218828	1.2791628	-0.0965707
C	0.1041165	-1.3146973	-0.0158555
C	0.1546371	1.1693612	-0.3114873
O	0.8151407	2.1717415	-0.4680455
O	0.7193736	-2.3543559	0.0787745
N	0.7698016	-0.0919468	-0.2065112
C	2.2024363	-0.1134714	-0.2181383
C	4.9761292	-0.1233541	-0.2009606
C	2.9002348	-0.6446471	-1.2915401
C	2.8883615	0.4065314	0.8829283
C	4.2812026	0.4081744	0.8809955
C	4.2918239	-0.6564828	-1.2884661
H	4.8174757	0.8221092	1.7316762
H	4.8343177	-1.0746933	-2.1289802
H	6.0615618	-0.1197626	-0.1880556
H	2.337643	-1.0518909	-2.1253782
O	2.1431429	0.8884411	1.9090324
H	2.732561	1.2161625	2.6025668

phenol rotor (OH forced up) transition state



-610307.06 kcal/mol

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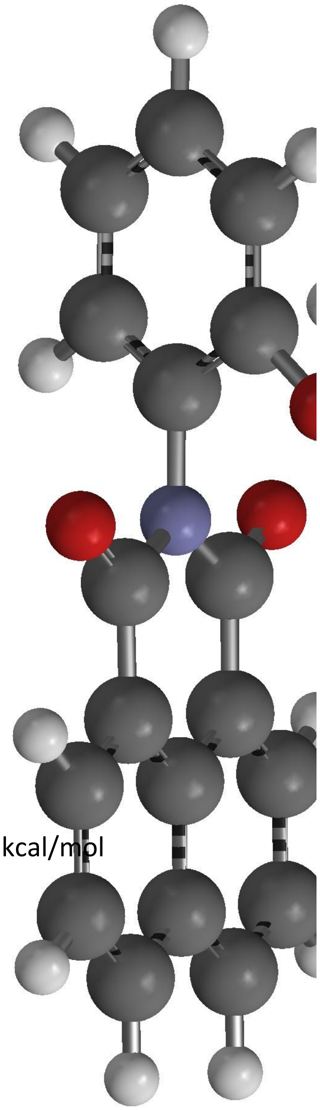
C	-1.4255424	-1.2558209	0.2717103
C	-4.1087553	-1.1488130	-0.5720921
C	-2.0247546	-0.0055660	-0.0125438
C	-3.5142167	-2.3590768	-0.2765184
C	-3.3840541	0.0643745	-0.4390786
C	-1.2864302	1.1797754	0.1988016
H	-4.0807101	-3.2806146	-0.3750620
H	-4.9763057	1.4123548	-1.0229216
H	-5.1446052	-1.110295	-0.8999487
C	-1.8738894	2.4140422	-0.0098754
H	-1.2997625	3.3127786	0.1904042
C	-3.2043143	2.4915192	-0.4763062
H	-3.6489603	3.4655023	-0.6589304
C	-3.9456136	1.3453692	-0.6833374
C	0.0163032	-1.3525322	0.6382146
C	0.0851311	1.083722	0.7525298
O	0.5645075	1.9642278	1.430969
O	0.4948389	-2.4234466	0.9778043
N	0.7964658	-0.1617643	0.5234938
C	2.1546621	-0.213106	0.0106405
C	4.8952253	-0.4799269	-0.7603961
C	2.7468824	-1.4611262	-0.2700008
C	2.9934887	0.9256209	-0.1470895
C	4.3388276	0.7653906	-0.5064626
C	4.0734824	-1.5978267	-0.6675546
H	4.9438433	1.6653391	-0.6114796
H	4.4597517	-2.591383	-0.8731095
H	5.9418784	-0.5668523	-1.0365420
H	2.1634845	-2.3574706	-0.1431713
O	2.486298	2.1921171	-0.0940112
H	3.19677	2.8080793	-0.3316613

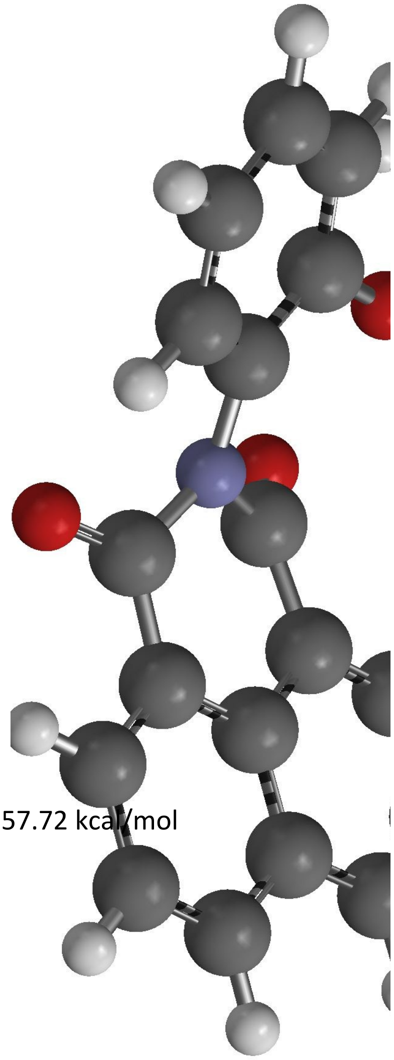
anisole rotor ground state



-634985.26 kcal/mol

	X	Y	Z
H	-1.4856721	-3.2565727	-0.1103277
C	-2.0894351	-2.3550676	-0.1009696
C	-1.4595772	-1.1436059	0.06363
C	-4.2391968	-1.2582360	-0.2337239
C	-2.2089441	0.0563638	0.0845623
C	-3.4919905	-2.4113062	-0.2515806
C	-3.619031	0.0065324	-0.0649279
C	-1.5656003	1.3051213	0.2552843
H	-3.9773855	-3.3728754	-0.381226
H	-5.4274219	1.1895241	-0.1521482
H	-5.319162	-1.2989908	-0.3484886
C	-2.2987476	2.468763	0.2759260
H	-1.7749489	3.4099123	0.4081833
C	-3.7022492	2.4257441	0.1277841
H	-4.2699017	3.3502476	0.1461759
C	-4.3471455	1.2240009	-0.0383640
C	0.0168813	-1.1133723	0.2276876
C	-0.0889408	1.3781672	0.4145846
O	0.4984053	2.4280643	0.5599418
O	0.6941638	-2.1169937	0.2269082
N	0.6013931	0.1545082	0.4004781
C	2.0302067	0.1943297	0.5075890
C	4.7922169	0.2204342	0.6877287
C	2.6400399	0.5451392	1.6987761
C	2.7970756	-0.1333118	-0.6201936
C	4.1874093	-0.1295467	-0.5188987
C	4.0297051	0.5648234	1.7960867
H	4.80262	-0.3920347	-1.3711185
H	4.5065135	0.8410125	2.7300620
H	5.8760253	0.2230758	0.7510933
H	2.0142183	0.804272	2.5465820
O	2.1022291	-0.4300492	-1.7432056
C	2.8317818	-0.8946796	-2.8575818
H	3.5164319	-0.1257772	-3.2347608
H	2.093333	-1.127482	-3.6241059
H	3.3987929	-1.7987985	-2.6081662

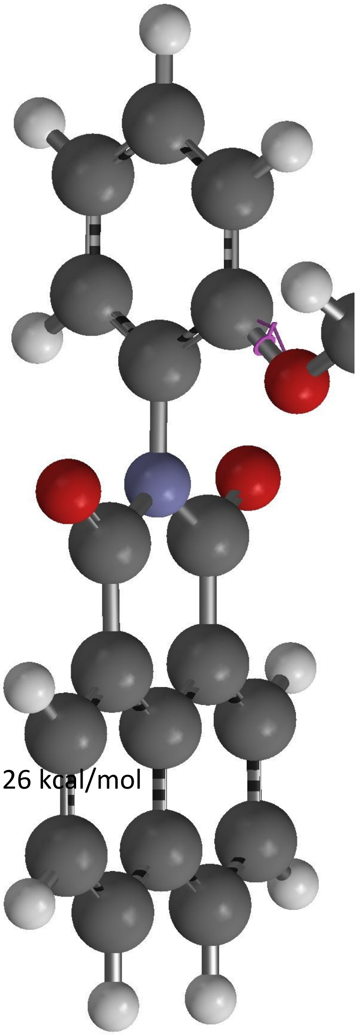
anisole rotor transition state



-634957.72 kcal/mol

	X	Y	Z
H	-2.2326478	-3.3041917	0.4552401
C	-2.5983478	-2.3147713	0.2027679
C	-1.7342743	-1.2384188	0.3041713
C	-4.3821295	-0.8632773	-0.5723325
C	-2.1935886	0.0624133	-0.013083
C	-3.9249814	-2.1226128	-0.2404160
C	-3.5324618	0.2683508	-0.458107
C	-1.3354475	1.1670145	0.1864892
H	-4.5874973	-2.9792492	-0.3231723
H	-4.9643549	1.7646985	-1.0923431
H	-5.4045056	-0.7220372	-0.9143673
C	-1.7863583	2.4521135	-0.0515503
H	-1.1239544	3.2891577	0.1428727
C	-3.0943373	2.6612639	-0.5411908
H	-3.4298211	3.6729616	-0.7498730
C	-3.9509236	1.5962847	-0.7364472
C	-0.310813	-1.4794036	0.6760999
C	0.0100764	0.9310558	0.7633217
O	0.5583369	1.7543230	1.4614125
O	0.0556291	-2.5846893	1.0424856
N	0.5908584	-0.3807043	0.5257810
C	1.9262928	-0.597186	-0.0057365
C	4.5963824	-1.2007945	-0.7980414
C	2.3369423	-1.9015802	-0.3338909
C	2.9056058	0.4306945	-0.1465072
C	4.2184662	0.1064949	-0.5132180
C	3.6353304	-2.2016672	-0.7387173
H	4.9457131	0.9036458	-0.6110821
H	3.8860577	-3.2312749	-0.9755824
H	5.6227261	-1.421001	-1.0766985
H	1.6394863	-2.7160178	-0.2304764
O	2.5021266	1.7260442	-0.0653700
C	3.4640854	2.761488	0.0223823
H	4.1813661	2.5774770	0.83187
H	2.8967842	3.6676475	0.2417742
H	4.0087865	2.8929175	-0.9228156

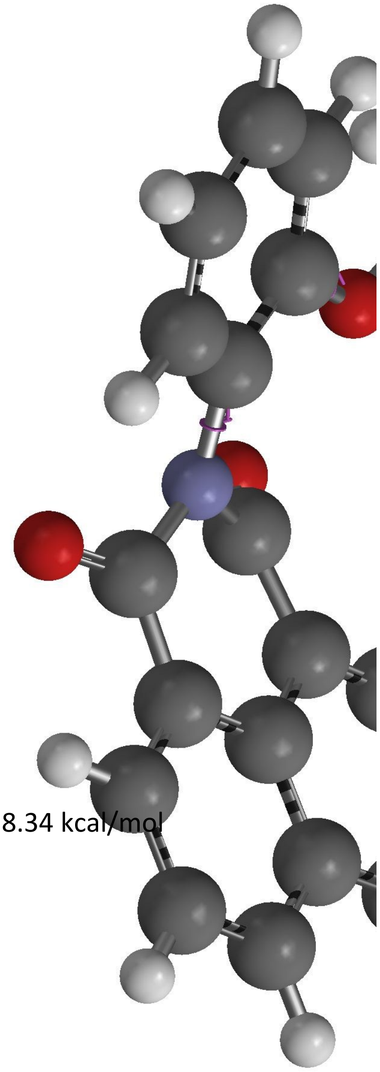
anisole rotor (OCH$_3$ forced up) ground state



-634985.26 kcal/mol

	X	Y	Z
H	-1.491883	-3.2518379	-0.0966966
C	-2.0939072	-2.3491332	-0.0918837
C	-1.4618334	-1.1381687	0.0676548
C	-4.2414194	-1.2487099	-0.2313120
C	-2.2088817	0.0633507	0.0825048
C	-3.4964535	-2.4033220	-0.2432807
C	-3.6189293	0.015623	-0.06789
C	-1.5632549	1.3116292	0.2478846
H	-3.9836366	-3.3645262	-0.3689160
H	-5.424892	1.2017787	-0.1624905
H	-5.3213724	-1.2878722	-0.3467803
C	-2.2941049	2.4768367	0.2622111
H	-1.7685293	3.4175669	0.3903406
C	-3.6975338	2.4359456	0.1129697
H	-4.2633543	3.361658	0.1262476
C	-4.3446513	1.2346859	-0.0478713
C	0.0146058	-1.110027	0.2324904
C	-0.086635	1.3824697	0.4084985
O	0.5027525	2.4318418	0.5493477
O	0.6902135	-2.114777	0.2354317
N	0.6012003	0.1573623	0.4013371
C	2.0299764	0.1950937	0.5099989
C	4.7917347	0.2187826	0.6934487
C	2.6389	0.5488812	1.7008808
C	2.7976704	-0.13706	-0.6158186
C	4.1878724	-0.1343248	-0.5128633
C	4.0284497	0.5673515	1.7998694
H	4.8038725	-0.4001328	-1.3635019
H	4.5044692	0.8458887	2.7335357
H	5.8754783	0.2204805	0.7579880
H	2.0123283	0.8113581	2.5471271
O	2.1038145	-0.4370771	-1.7385439
C	2.8346662	-0.9025402	-2.8517473
H	3.5193584	-0.1337086	-3.2289999
H	2.0970669	-1.13649	-3.6187435
H	3.4018322	-1.806164	-2.6008961

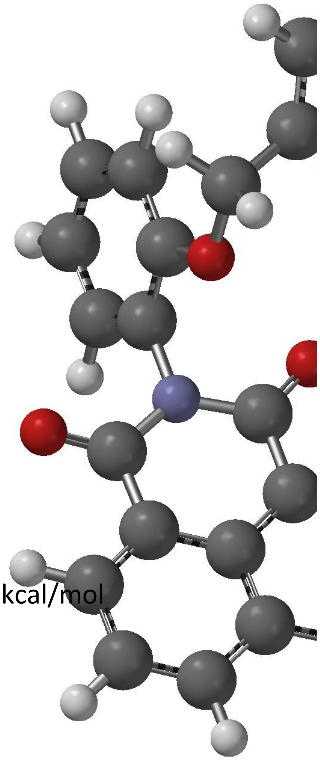
anisole rotor (OCH$_3$ forced up) transition state



-634958.34 kcal/mol

	X	Y	Z
H	-2.22627	-3.3242808	0.3413132
C	-2.5860212	-2.3264284	0.1143774
C	-1.7258991	-1.2545294	0.2779087
C	-4.3492095	-0.8481766	-0.6562014
C	-2.1768605	0.0567671	-0.0068749
C	-3.900147	-2.1188392	-0.3577723
C	-3.5037346	0.2783245	-0.4794146
C	-1.3238099	1.1533473	0.2500491
H	-4.5587494	-2.9722790	-0.4899190
H	-4.9195747	1.7968374	-1.0979658
H	-5.3624987	-0.6948151	-1.0194253
C	-1.7684087	2.4461101	0.0427107
H	-1.1102974	3.2758569	0.2793199
C	-3.0640373	2.6724717	-0.4710456
H	-3.3944494	3.6907524	-0.6542558
C	-3.9152409	1.6151937	-0.7232029
C	-0.3128804	-1.5093497	0.6791486
C	0.0088496	0.8979952	0.8476572
O	0.5460185	1.6989328	1.5791456
O	0.0421515	-2.6274116	1.0169621
N	0.5948306	-0.4086466	0.5904666
C	1.9272942	-0.6035239	0.0433229
C	4.5946768	-1.1531795	-0.7960303
C	2.3632914	-1.9011003	-0.2772021
C	2.8844841	0.4452659	-0.1109751
C	4.1965289	0.1463162	-0.5005310
C	3.6582072	-2.1743013	-0.7120633
H	4.9114473	0.9539472	-0.5990123
H	3.9272209	-3.1996495	-0.9480373
H	5.6195852	-1.3507943	-1.0967889
H	1.6870372	-2.7301771	-0.1519433
O	2.4614997	1.7317975	0.0100538
C	3.353617	2.7971366	-0.2596811
H	4.201577	2.8053257	0.4372488
H	2.7685043	3.7076938	-0.1178607
H	3.7310962	2.7585582	-1.2903105

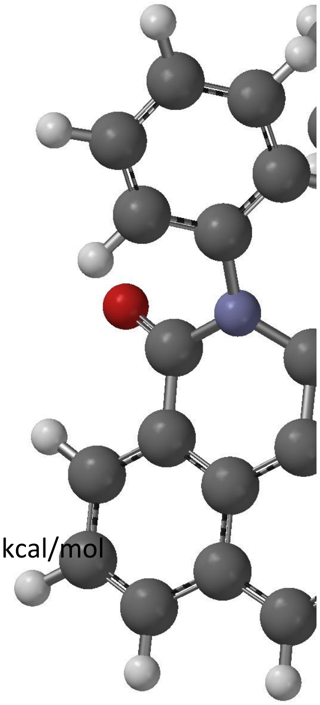
benzyl rotor ground state



-779915.82 kcal/mol

	X	Y	Z
H	4.002785306	-2.387715555	1.514220326
C	4.114480782	-1.372719356	1.147026204
C	3.061303342	-0.796767230	0.475092050
C	5.430441137	0.635867014	0.874517824
C	3.16344058	0.524751926	-0.019465550
C	5.309371734	-0.648372430	1.347659813
C	4.3616253	1.257687011	0.178763812
C	2.08110041	1.12280877	-0.707612430
H	6.133146901	-1.113284489	1.878909283
H	5.355744989	3.144614242	-0.178498927
H	6.349476493	1.195227024	1.028346937
C	2.185683462	2.408171733	-1.186262912
H	1.338196731	2.838324144	-1.709833002
C	3.376332898	3.141902396	-0.994570836
H	3.44689155	4.154444561	-1.377784996
C	4.438754831	2.580701661	-0.3279665
C	1.815272969	-1.581270053	0.276682627
C	0.819455309	0.369674549	-0.924542481
O	-0.133365218	0.849832560	-1.502039802
O	1.683511854	-2.710917364	0.693385699
N	0.783819174	-0.946459402	-0.439221895
C	-0.445622544	-1.667870821	-0.595126742
C	-2.827296878	-3.048698108	-0.855674489
C	-0.526338564	-2.742269004	-1.464215541
C	-1.55345677	-1.278802083	0.16884976
C	-2.756160255	-1.969737522	0.023612925
C	-1.721112861	-3.444341581	-1.5975299
H	-3.638640941	-1.662932034	0.572551334
H	-1.784910243	-4.286294875	-2.27796087
H	-3.768879098	-3.578750060	-0.959502133
H	0.357895685	-3.023187045	-2.027272452
O	-1.345573557	-0.233926412	1.011916286
C	-2.421319832	0.193053656	1.824623292
H	-1.961046733	0.875755686	2.544598272
H	-2.830937458	-0.657090879	2.387094948
C	-3.515198871	0.901903425	1.056315866
C	-5.544285155	2.253440388	-0.302639868
C	-3.261988645	1.460520093	-0.196115192
C	-4.786037857	1.016130544	1.621149973
C	-5.797200782	1.693974618	0.947378498
C	-4.278547498	2.132115895	-0.871075716
H	-2.27678999	1.353039398	-0.642916207
H	-4.986276956	0.569191646	2.593033701
H	-6.783305077	1.777562038	1.394010265
H	-4.07943899	2.558923229	-1.84943888
H	-6.33340847	2.776345565	-0.834348718

benzyl rotor transition state



-779888.31 kcal/mol

	X	Y	Z
H	4.217830192	-1.050854350	-1.441807341
C	4.638557662	-0.263528504	-0.825031386
C	3.806162297	0.445124569	0.009176169
C	6.540835831	1.033878068	-0.07413647
C	4.32104739	1.48597398	0.811432879
C	6.019927875	0.032350657	-0.858164372
C	5.701527187	1.800032557	0.775896820
C	3.435447573	2.256192417	1.593558859
H	6.670678612	-0.540398431	-1.510612717
H	7.224407257	3.120830096	1.564347489
H	7.603265163	1.260470322	-0.104681998
C	3.905391014	3.319886523	2.326310619
H	3.203369945	3.919977772	2.89574134
C	5.287181247	3.617529703	2.329321412
H	5.650192053	4.446159543	2.928447302
C	6.164956017	2.878916661	1.572801898
C	2.364524677	0.082357129	0.090019465
C	1.972915328	1.961371976	1.563874461
O	1.173802489	2.826052563	1.815663623
O	1.862284256	-0.674844896	-0.707856167
N	1.637384237	0.614646091	1.200018071
C	0.535949401	-0.188148518	1.703348541
C	-1.420616021	-2.022070311	2.626580444
C	0.699990736	-1.581528412	1.593583346
C	-0.602406417	0.259991706	2.402964409
C	-1.570487553	-0.662052825	2.820415283
C	-0.25550924	-2.484436560	2.024824156
H	-2.44702585	-0.277313797	3.330891532
H	-0.079603636	-3.546437541	1.891870552
H	-2.189403178	-2.710033467	2.962694832
H	1.59783294	-1.975486695	1.138966065
O	-0.7468744	1.566532370	2.742063506
C	-2.010386485	2.188451406	2.552313427
H	-1.801622241	3.245000702	2.741899753
H	-2.736592778	1.852400598	3.304475323
C	-2.557289546	1.994588502	1.160158063
C	-3.539670012	1.665181870	-1.431486893
C	-1.72613762	2.221928776	0.060429548
C	-3.873423319	1.590191615	0.954260455
C	-4.368275205	1.432679468	-0.339065902
C	-2.216028064	2.056041707	-1.229445784
H	-0.695970032	2.523472962	0.235910228
H	-4.515955887	1.395190777	1.810062742
H	-5.396597429	1.118881675	-0.490994977
H	-1.565310938	2.229664821	-2.081085496
H	-3.920275527	1.535184719	-2.43995311

References.

(1) Chong, Y. S.; Smith, M. D.; Shimizu, K. D. J. Am. Chem. Soc. 2001, 123 (30), 7463–7464.