Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Theoretical study on the reaction of CO_2 and 2-aminobenzonitrile to form quinazoline-2,4(1*H*,3*H*)-dione in water without any catalyst

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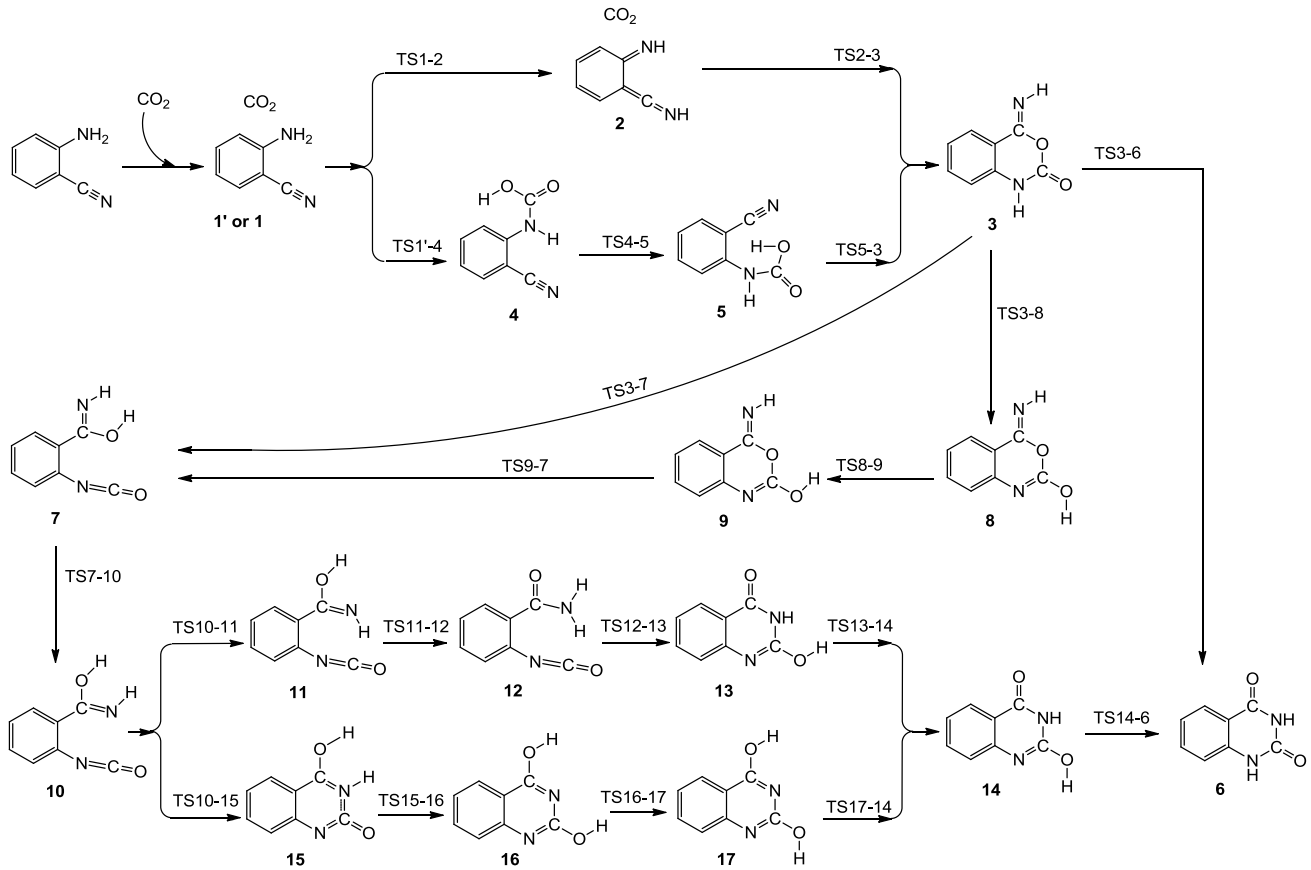


Scheme S1. The pathways of the non-catalytic reaction of CO_2 and 2-aminobenzonitrile.

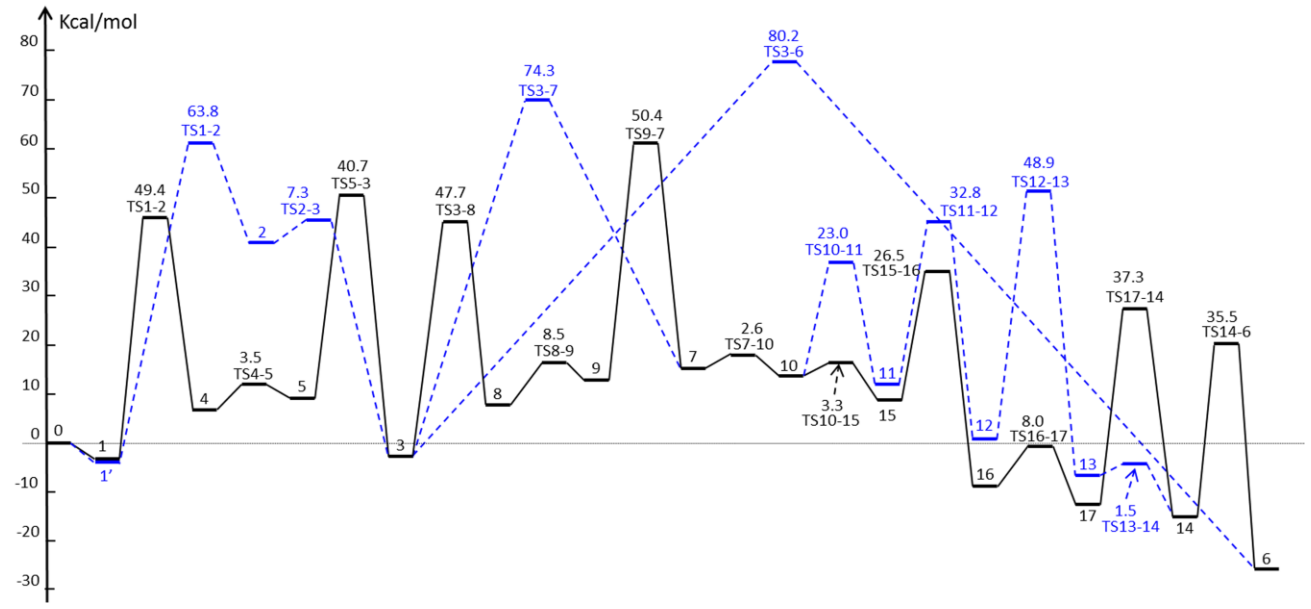


Figure S1. Potential energy curves of the pathways of the reaction of CO_2 and 2-aminobenzonitrile. Black solid line: the lowest energy path; Blue dashed line: less possible paths.

Exploring of the non-catalytic reaction pathways of CO_2 and 2-aminobenzonitrile

Multiple pathways of CO_2 and 2-aminobenzonitrile, displayed in SchemeS1, are to be discussed to illustrate how the most probable reaction pathway was discovered. A symbol is assigned underneath each structure as a notation of the species. Here, the numbers represent the reactants, product and intermediates of the reaction. TSn–m is used to denote the transition structures connecting the intermediates n and m. The potential energy curves are illustrated in Figure S1, in which the energy barriers are displayed above the corresponding transition states.

As shown in Scheme S1, there are two ways to convert 2-aminobenzonitrile to intermediate 3. The transition states of the process from intermediates 1 to 3 are shown in Figure S4. The first is through the intramolecular H transfer, converting 2-aminobenzonitrile to intermediate 2 which can be easily attacked by CO_2 to form intermediate 3. However, the barrier of the H transfer step is too high (63.8 kcal mol^{-1}). So the reaction prefers to form the carbamic acid (intermediate 4) by the CO_2 electrophilic attack on the amino group, and then followed by the isomerization of the carbamic acid (4→5) and the first intramolecular cyclization (5→3).

In the following process, intermediate 3 can be directly transformed into the target product quinazoline-2,4(1*H*,3*H*)-dione via transition state TS3-6 (see Figure S4). The calculated barrier for this step is 80.2 kcal mol^{-1}, which is too high to occur. There are two other pathways, both converting intermediate 3 to intermediate 7 (an isocyanate intermediate). One of them has higher energy barrier of 74.3 kcal mol^{-1}, in which intermediate 3 directly transforms to the isocyanate intermediate via a single H transfer step with transition state TS3-7 (see Figure S4). There are two H transfer steps in another pathway (3→8→9→7) with the corresponding energy barriers of 47.5 and 50.4 kcal mol^{-1} respectively, displayed as transition states TS3-8 and TS9-7 (see Figure S4). Between these two H transfer steps, there is an isomerization (8→9) as illustrated by the changes of the dihedral angle ∠N1C1O1H1, which are 0.00°, -92.08° and 180.0° in intermediates 8, TS8-9 and 9, respectively. Based on the view point of the energy barrier, it is evident that the transformation of intermediates 3 to 7 with two H transfer steps is favorable.

The following step is the isomerization of intermediate 7, with TS7-10 as the transition state. This process is well displayed by the changes of the dihedral angle ∠C1C2C3O1, which are -145.5°, -87.5° and 0.0° at intermediate 7, transition state TS7-10 and intermediate 10, respectively. There are two channels from intermediate 10 to intermediate 14, which are distinguished by how the N atom nucleophilicly attacks the isocyanate group. In one channel, the N atom is in the amide group (intermediate 12), while in the other channel the N atom is in the imino group (intermediate 10). The energy barrier of the attack of amide group is 48.94 kcal mol^{-1}, which is obviously higher than that of the attack of imino group (3.3 kcal mol^{-1}). The intermediate 15 can transform to a more stable intermediate 16 via transition state TS15-16. The rate-determining step in the imino group attack channel is the tautomerization of intermediate 17 to intermediate 14 with energy barrier of 37.3 kcal mol^{-1}, while that of the amide group attack step in the amide attack channel is 48.9 kcal mol^{-1}. Therefore, based on the view of the energy barrier, the imino group attack channel is favorable. After intermediate 14, the final product quinazoline-2,4(1*H*,3*H*)-dione (6) is formed. The transition state TS14-6 of this tautomerization is shown in Figure S4.

Based on the above discussions, the most probable mechanism for the reaction of CO_2 and 2-aminobenzonitrile without water and catalysts is extracted and drawn as Scheme 2 in the manuscript.

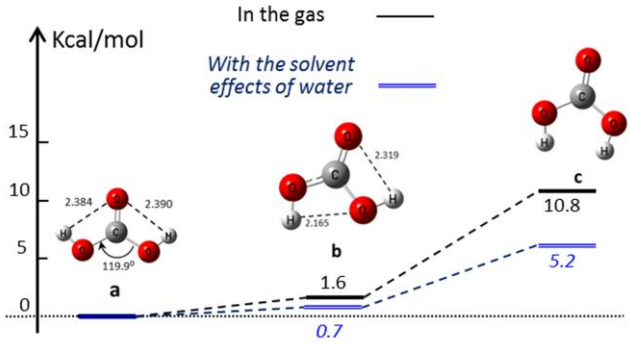


Figure S2. Stable structures and the corresponding potential energy curves of H_2CO_3. The bond distances (in angstroms) are labeled in the corresponding positions.

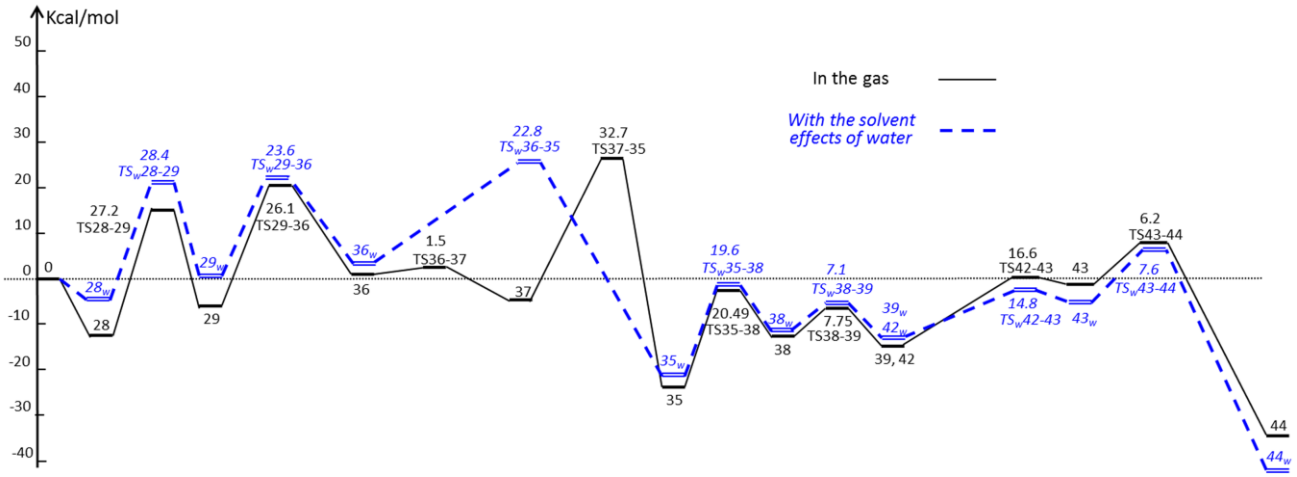
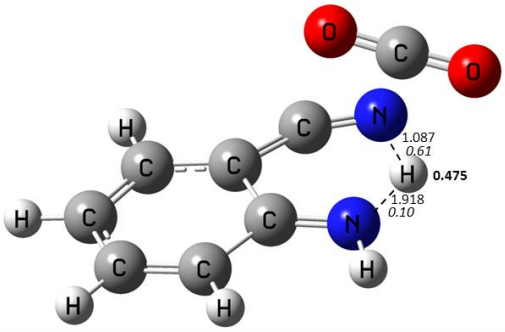
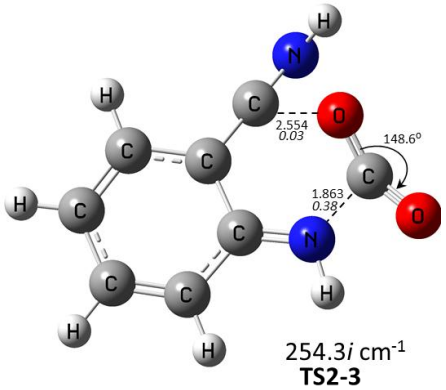


Figure S3. The potential energy curves of the proposed reaction mechanism of CO_2 and 2-aminobenzonitrile in water.

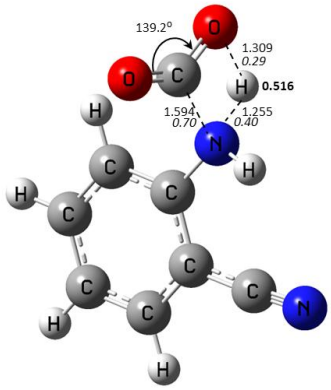
TS1-2			
C	-1.26522	0.87065	0.009624
N	-0.38642	1.610983	0.335438
C	-2.54522	0.64103	-0.40377
C	-3.27185	-0.57051	-0.55374
C	-3.17739	1.982787	-0.46126
C	-4.59868	-0.52656	-0.86341
H	-2.74353	-1.51582	-0.44895
C	-4.58289	1.925407	-0.82061
C	-5.2385	0.746077	-1.0109
H	-5.16615	-1.44223	-1.00804
H	-5.10356	2.874276	-0.94564
H	-6.2934	0.771772	-1.28504
N	-2.5046	3.059437	-0.14789
H	-3.10266	3.88171	-0.13182
H	-0.91167	2.470969	0.743464
O	-0.88409	2.367246	-2.70632
C	-0.44528	3.289078	-2.15072
O	0.021108	4.217757	-1.6326
TS2-3			
C	-0.20158200	0.637215	-0.00561
N	0.86313700	0.58698	0.532134
C	-1.49092300	0.666248	-0.42929
C	-2.23254300	-0.56212	-0.54795
C	-2.10457200	1.958731	-0.69385
C	-3.56415500	-0.52395	-0.81347
H	-1.71090900	-1.50465	-0.39215
C	-3.53440600	1.925111	-0.9097
C	-4.21361500	0.746844	-0.97175
H	-4.14156400	-1.44195	-0.88898
H	-4.04758200	2.874758	-1.05539
H	-5.28706300	0.76506	-1.16025
N	-1.38533900	3.054455	-0.732
H	-1.93469600	3.894635	-0.89945
O	0.75668000	2.240273	-1.7481
C	0.23117900	3.311887	-1.62163
O	0.25260200	4.48314	-1.82459
H	1.72810400	0.700617	-0.00071
TS1'-4			
C	-0.84761900	0.71428570	0.00000000
C	0.33929000	0.82976770	-0.72154300
C	0.59139300	1.99787270	-1.45778300
C	-0.33564800	3.04587570	-1.46223400
C	-1.51294300	2.92695470	-0.73465300
C	-1.76393800	1.76162170	-0.00763200
H	-1.05452800	-0.19701930	0.55934000
H	-0.12015500	3.94173870	-2.04062600
H	-2.23692000	3.73898570	-0.73729600
H	-2.68931700	1.66343370	0.55733300
C	1.81417900	2.09327370	-2.20876200
N	2.81170600	2.10521270	-2.79661300
N	1.30042900	-0.22176730	-0.68433900
H	1.97094100	-0.16844230	-1.45403700
H	1.75752700	-0.71385230	0.37540200
C	0.76048600	-1.70541730	-0.46314300
O	-0.01844700	-2.23540530	-1.18881200
O	1.39098000	-1.94644930	0.61897200



871.1*i* cm^{-1}
TS1-2



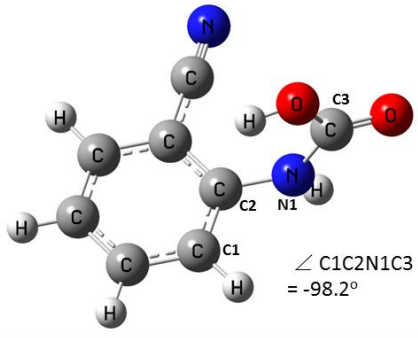
254.3*i* cm^{-1}
TS2-3



1583.2*i* cm^{-1}
TS1'-4

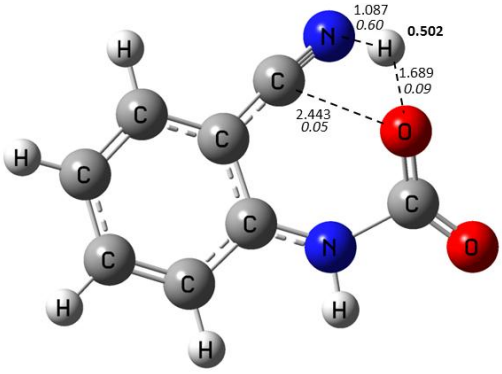
Figure S4. Optimized geometries of transition states in Scheme S1 and Scheme 2. The bond distances (in angstroms), bond orders (italic), angles (in degree) and atomic charges (bold) are labeled in the corresponding positions. For transition state, the imaginary vibrational frequency (cm^{-1}) is shown. (To be continued)

TS4-5			
C	-1.52102242	1.09001424	0.16869703
C	-1.29092242	2.46664624	0.22225903
C	-2.38008842	3.33399824	0.43767303
C	-3.67475142	2.82629024	0.60565003
C	-3.88745542	1.44894524	0.54978603
C	-2.81339742	0.58237924	0.32950303
H	-0.67411242	0.43070424	0.00103203
H	-4.49785342	3.51396124	0.77353003
H	-4.89011742	1.05224524	0.67735803
H	-2.98014642	-0.48980976	0.28529203
C	-2.15957842	4.76038724	0.48268603
N	-2.00449742	5.91007424	0.51812903
N	0.02679558	2.97530524	0.06289903
H	0.35192858	3.23986724	-0.85891697
H	-0.48839342	2.76036124	2.32639203
C	0.84313558	3.42452124	1.09440003
O	1.90805158	3.94950524	0.89635903
O	0.37282658	3.20117424	2.33965103



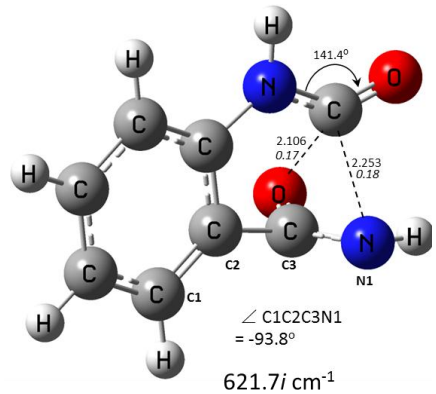
44.6*i* cm^{-1}
TS4-5

TS5-3			
C	-1.0475188	1.20301358	0.10087225
C	-0.8545468	2.61488858	0.13859525
C	-2.0411458	3.40110558	0.30396025
C	-3.3111418	2.81427258	0.56980125
C	-3.4389668	1.44822358	0.56897725
C	-2.2919168	0.65114658	0.30646625
H	-0.1825778	0.56482958	-0.05999175
H	-4.1654468	3.46377458	0.73590325
H	-4.4003798	0.98076058	0.75091125
H	-2.3940748	-0.43068542	0.28711425
C	-1.9061118	4.77213958	0.14948525
N	-1.7078958	5.92512158	-0.06029375
N	0.3789232	3.14891658	0.01718125
H	1.1197762	2.49887758	-0.22701775
H	-0.8772258	6.16919058	0.59548625
C	0.9883852	4.39748858	0.61588725
O	2.1684272	4.50851358	0.34134125
O	0.1850652	5.07601358	1.31008725



791.5*i* cm^{-1}
TS5-3

TS3-6			
C	-0.4292405	0.23135323	0.27752907
C	-1.6418355	-0.47066877	0.29896807
C	-2.8313945	0.23994223	0.31148807
C	-2.8081955	1.63773823	0.28805207
C	-1.6177325	2.35320123	0.25676507
C	-0.4203555	1.62787723	0.25699007
H	0.5094955	-0.31395477	0.27392307
H	-1.6556485	-1.55608877	0.30898607
H	-1.6125175	3.43969323	0.23458807
H	0.5242425	2.16321123	0.23780607
N	-4.0853275	2.24926023	0.28226707
H	-4.2042105	3.25059323	0.18843407
C	-4.2662865	-0.20086977	0.35693407
C	-5.2289145	1.53930223	0.24939607
O	-6.3779475	1.75366223	0.21939307
O	-4.8610435	-0.03415477	1.48337307
N	-4.8555545	-0.28696377	-0.83170293
H	-5.8472165	-0.50409977	-0.68178893



621.7*i* cm^{-1}
TS3-6

Figure S4. Optimized geometries of transition states in Scheme S1and Scheme 2. The bond distances (in angstroms), bond orders (italic), angles (in degree) and atomic charges (bold) are labeled in the corresponding positions. For transition state, the imaginary vibrational frequency (cm^{-1}) is shown. (Continued)

TS3-7			
C	-1.99047613	1.11428570	0
C	-1.36814413	2.29626570	-0.41582
C	-2.19254913	3.37188670	-0.758559
C	-3.57956613	3.32557270	-0.70502
C	-4.17683113	2.13491270	-0.285569
C	-3.38151513	1.03650370	0.066119
H	-1.35061613	0.27779470	0.265355
H	-4.16457913	4.19380470	-0.992243
H	-5.25952713	2.06493170	-0.235903
H	-3.85459513	0.11445770	0.392251
N	-1.52565113	4.61567770	-1.244244
C	0.14038187	2.41689470	-0.516011
N	0.83604087	1.41056670	-0.137284
O	0.57514987	3.57339770	-1.001645
C	-0.78703213	5.07716570	-0.26733
O	-0.37876513	5.71766570	0.589256
H	-0.63858913	4.17744070	-1.754298
H	1.82513187	1.63995570	-0.261602

TS3-8			
C	-2.17306692	0.25091496	0.01100365
H	-0.40394392	2.26553796	0.22225465
C	-0.18588892	1.17229796	-0.85285535
O	0.00713208	0.24417296	-1.77375435
H	0.10164808	-1.52413704	-3.29738535
C	-0.92803992	-0.81520304	-1.87879335
N	-0.74492992	-1.70358704	-2.75480135
C	-2.06111392	-0.78641704	-0.93374935
N	-1.18371792	1.22734996	0.01001765
O	0.57961108	2.16723296	-0.66320535
C	-3.02742392	-1.79815704	-0.98177435
H	-2.91364792	-2.58457504	-1.72208835
C	-4.09825192	-1.77667404	-0.09454335
C	-3.25019092	0.27376696	0.90445065
H	-3.32332192	1.08092796	1.62676365
C	-4.20348292	-0.73876404	0.84488265
H	-4.85049992	-2.55846804	-0.12848035
H	-5.04100892	-0.72150104	1.53691765

TS8-9			
C	-1.99047613	0.25714285	0
H	0.72818787	2.84956485	-1.37729
C	-0.07640113	1.22914385	-0.760542
O	0.13431487	0.28210485	-1.709918
H	0.31220187	-1.46059815	-3.272247
C	-0.74864913	-0.78561315	-1.862359
N	-0.54146713	-1.66376015	-2.749251
C	-1.88727813	-0.78380615	-0.933923
N	-1.03674813	1.28677185	0.066196
O	0.92856287	2.12710385	-0.766713
C	-2.84752413	-1.80103015	-0.982086
H	-2.73085113	-2.58970515	-1.719546
C	-3.91617913	-1.77603115	-0.092743
C	-3.07017413	0.27683385	0.893861
H	-3.13384713	1.08984385	1.610794
C	-4.02417513	-0.73466315	0.844058
H	-4.66704213	-2.56011215	-0.121421
H	-4.86070313	-0.71795915	1.537225

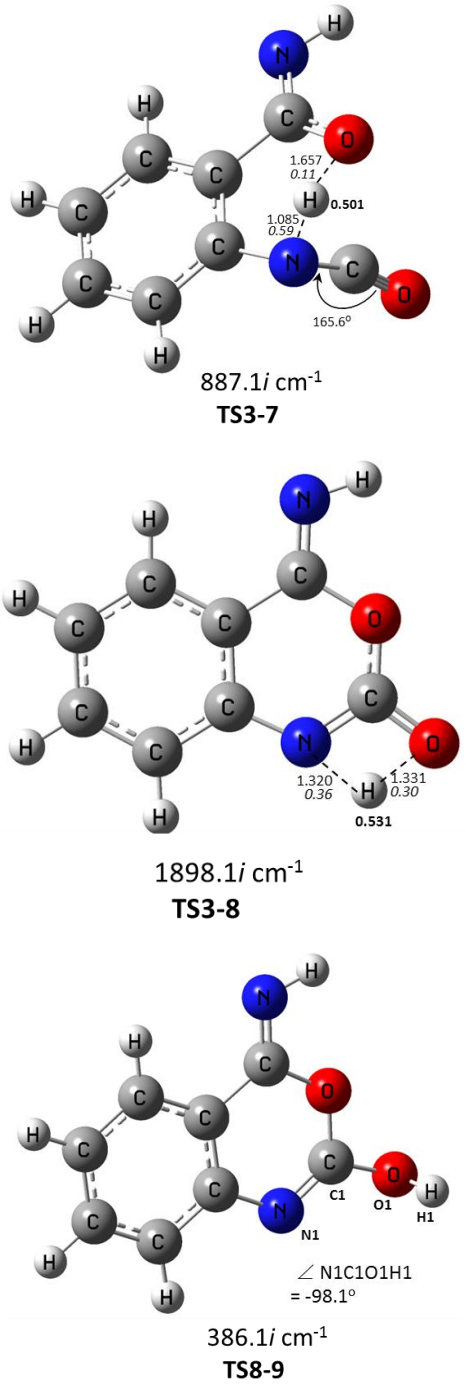
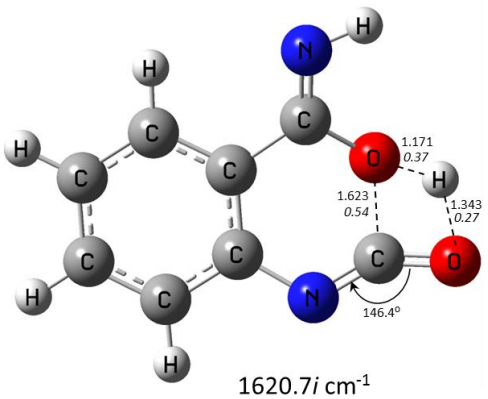
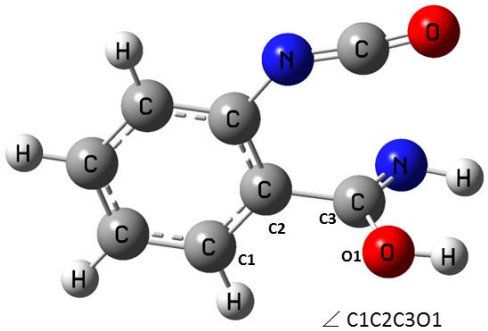


Figure S4. Optimized geometries of transition states in Scheme S1 and Scheme 2. The bond distances (in angstroms), bond orders (italic), angles (in degree) and atomic charges (bold) are labeled in the corresponding positions. For transition state, the imaginary vibrational frequency (cm^{-1}) is shown. (Continued)

TS9-7			
C	-1.54950587	0.6423242	-0.03849608
H	1.96991413	0.6466082	-0.15379008
C	0.57105613	1.5122722	-0.13077308
O	1.07739013	0.0091732	0.22848692
H	1.76575913	-2.2410328	-0.43201808
C	0.29193613	-1.0727458	-0.16893308
N	0.74623713	-2.2074978	-0.48172908
C	-1.14099987	-0.7079528	-0.08537208
N	-0.65496887	1.7263412	-0.16880608
O	1.72203413	1.9603872	-0.32748808
C	-2.09468387	-1.7315328	-0.03772808
H	-1.74543787	-2.7591758	-0.08200108
C	-3.44829687	-1.4267028	0.06948992
C	-2.91329787	0.9395982	0.06277792
H	-3.21008887	1.9836732	0.08398192
C	-3.85283887	-0.0864078	0.12363292
H	-4.18427087	-2.2236838	0.11283992
H	-4.90809187	0.1582972	0.20736492
TS7-10			
C	1.52438092	-0.88206237	-0.1613148
C	3.40304592	-0.16603837	-1.5237418
O	4.32839292	-1.63243937	1.2432002
H	4.86979192	-3.22006537	-0.6066258
C	3.51799092	-2.29098537	0.3721702
N	3.85595192	-3.08669237	-0.5534328
C	2.08651392	-1.92586537	0.5864672
N	2.27239392	-0.15478837	-1.0950688
O	4.46053192	-0.06050437	-2.0081648
C	1.30293592	-2.61411937	1.5088022
H	1.74991292	-3.42530237	2.0820132
C	-0.03646008	-2.27501337	1.6880772
C	0.18301392	-0.54077737	0.0178142
H	-0.23441008	0.27033563	-0.5749718
C	-0.59189308	-1.23755437	0.9402092
H	-0.64424708	-2.82098637	2.4069992
H	-1.63830108	-0.96782237	1.0737022
H	5.25229592	-1.84467437	1.0521582
TS10-11			
C	-2.39191597	-0.38255276	-0.05800121
C	-4.41365997	-1.75168876	-0.03084321
C	-3.05996197	2.06308524	0.10641479
C	-2.03267997	0.97619324	-0.01976221
N	-3.73423897	-0.75944576	-0.03586621
O	-5.18076497	-2.63655576	-0.02166721
C	-0.67252897	1.30643124	-0.08019321
H	-0.39496697	2.35664224	-0.06088421
C	0.31038003	0.32623124	-0.15615621
C	-1.40183997	-1.36941176	-0.14487121
H	-1.70276397	-2.41550976	-0.18027521
C	-0.05888797	-1.01824776	-0.18906821
H	1.36050803	0.60979924	-0.19342221
H	0.69879503	-1.79778476	-0.25470721
N	-4.22441097	1.93705324	0.48552479
O	-2.49669597	3.27199624	-0.24587721
H	-5.18183197	1.87874324	0.73953879
H	-3.19107297	3.93188324	-0.12501621

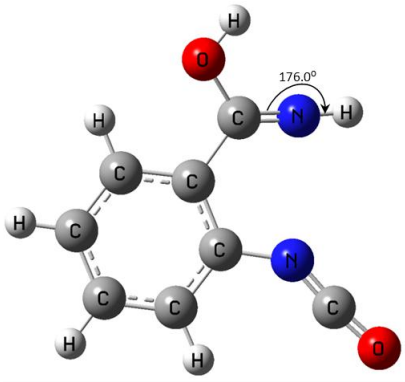


1620.7*i* cm^{-1}
TS9-7



∠ C1C2C3O1
= -87.5°

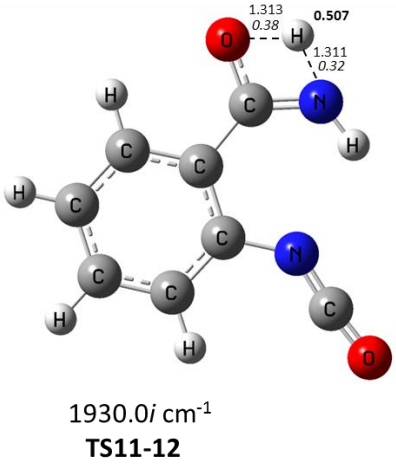
71.3*i* cm^{-1}
TS7-10

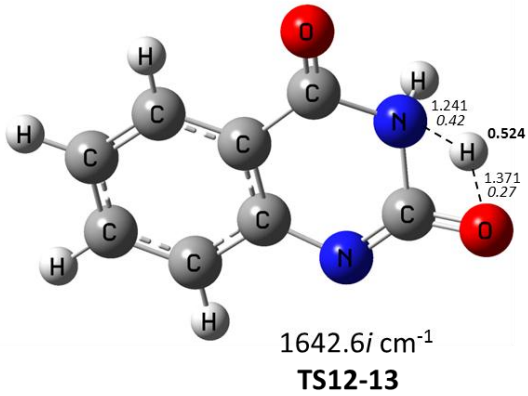


1036.2*i* cm^{-1}
TS10-11

Figure S4. Optimized geometries of transition states in Scheme S1 and Scheme 2. The bond distances (in angstroms), bond orders (italic), angles (in degree) and atomic charges (bold) are labeled in the corresponding positions. For transition state, the imaginary vibrational frequency (cm^{-1}) is shown. (Continued)

TS11-12			
C	-1.90715617	-0.10521163	0.0177925
H	-3.40247817	3.63543137	0.2479405
C	-3.87477417	-1.49266663	0.1304915
C	-2.49248417	2.36305837	0.1385475
C	-1.53044317	1.24695937	0.0300955
N	-3.26501917	-0.44498363	0.1118445
O	-4.56845617	-2.42791063	0.1586125
C	-0.17272217	1.57572437	-0.0641985
H	0.09326583	2.63058837	-0.0526575
C	0.79713983	0.58682237	-0.1687715
C	-0.93059517	-1.10135863	-0.0884665
H	-1.23332417	-2.14776863	-0.0977175
C	0.41217583	-0.75495063	-0.1812045
H	1.84862383	0.85709937	-0.2407605
H	1.16200283	-1.54030063	-0.2648985
N	-3.79522817	2.38226537	0.2465635
O	-2.09630717	3.59493837	0.1389675
H	-4.38138817	1.55865937	0.2733395
TS12-13			
C	-0.64063643	-0.55279076	0.04178927
H	2.93007557	-0.48191876	-0.35056673
C	1.48907557	0.22940224	-0.08761473
C	1.15332357	-2.29860876	-0.13619873
C	-0.26179243	-1.91457376	-0.07037473
N	0.24727557	0.52095224	-0.07032073
O	2.56076857	0.83669224	-0.40939073
C	-1.22730643	-2.93324276	-0.07204373
H	-0.88959443	-3.96393776	-0.17044773
C	-2.56934843	-2.62166476	0.06155727
C	-2.00671543	-0.26024776	0.17473127
H	-2.29789543	0.78562924	0.24551227
C	-2.94962043	-1.27752676	0.19080927
H	-3.31976743	-3.40943876	0.06722827
H	-4.00429043	-1.02511976	0.29692527
N	2.03255857	-1.15474276	0.18035227
O	1.62734057	-3.38365576	-0.32306573
H	2.29884057	-1.22819476	1.16696327
TS13-14			
C	-0.31085	0.080246	-0.00148
H	3.645842	-0.216	0.827974
C	1.957386	0.212765	0.01671
C	0.736806	2.330608	0.012227
C	-0.46058	1.479912	0.008611
N	0.933732	-0.55058	0.01276
O	3.211817	-0.31104	-0.02951
C	-1.7338	2.0662	0.003203
H	-1.80286	3.152683	0.009504
C	-2.8598	1.261185	-0.01089
C	-1.46357	-0.72416	-0.01686
H	-1.33673	-1.80482	-0.02451
C	-2.71769	-0.13697	-0.02126
H	-3.85291	1.706843	-0.01449
H	-3.6056	-0.76791	-0.03265
N	1.920248	1.586263	0.015289
O	0.7663	3.544617	0.005684
H	2.786954	2.106966	-0.05089





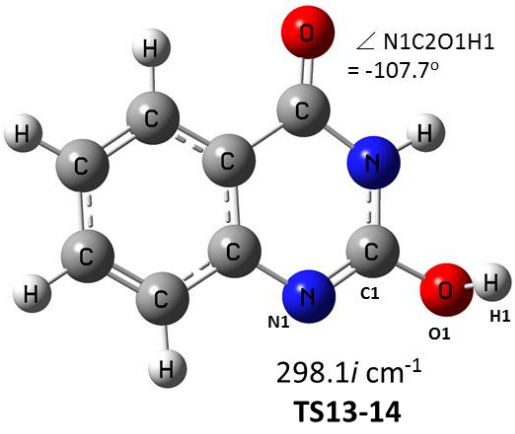
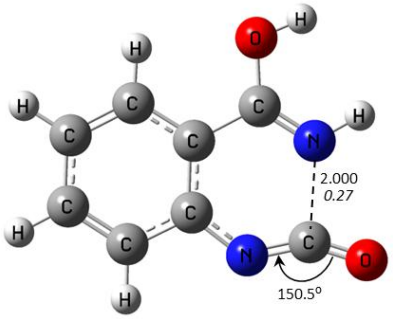
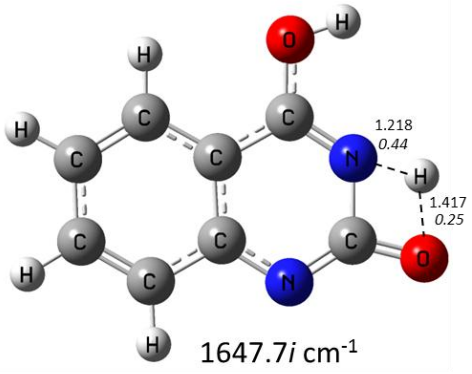


Figure S4. Optimized geometries of transition states in Scheme S1 and Scheme 2. The bond distances (in angstroms), bond orders (italic), angles (in degree) and atomic charges (bold) are labeled in the corresponding positions. For transition state, the imaginary vibrational frequency (cm^{-1}) is shown. (Continued)

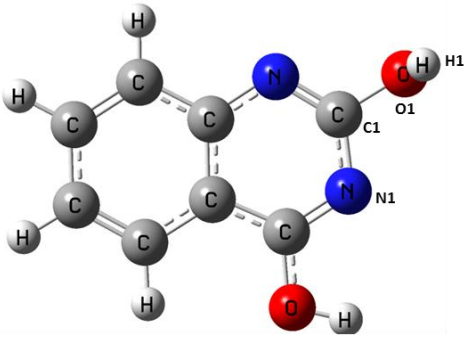
TS10-15			
C	-1.13896725	-0.63590138	0.00960659
C	-3.52346725	-0.80028838	0.00959659
O	-1.76592825	2.97734262	0.00958859
H	-4.04196725	1.83192362	0.00958159
C	-2.07379925	1.66476362	0.00959259
N	-3.25844125	1.18221162	0.00958859
C	-0.92621425	0.76333662	0.00960159
N	-2.36187025	-1.27369538	0.00960359
O	-4.68964125	-0.94947838	0.00959159
C	0.37926175	1.28206562	0.00960559
H	0.51321475	2.36097562	0.00960159
C	1.47722575	0.43958462	0.00961359
C	-0.00701025	-1.47332238	0.00961459
H	-0.17702325	-2.54769138	0.00961859
C	1.27350975	-0.94683538	0.00961859
H	2.48480175	0.84981062	0.00961659
H	2.12891075	-1.62134238	0.00962459
H	-2.57375525	3.50552262	0.00957959
TS15-16			
C	-0.89781495	0.78995092	0.06005183
C	-3.15489995	0.85535792	0.06006983
O	-1.99378395	4.27271792	0.06016083
H	-4.32117195	2.00624192	0.06011283
C	-2.01348695	2.94254092	0.06012183
N	-3.13184595	2.27050892	0.06011283
C	-0.78707895	2.21207692	0.06009083
N	-2.08435695	0.10630892	0.06004083
O	-4.40393995	0.59139892	0.06006983
C	0.47156205	2.85449992	0.06009783
H	0.51145905	3.94207592	0.06012683
C	1.62145405	2.10007192	0.06006783
C	0.31011205	0.04755292	0.06002283
H	0.23276305	-1.03751308	0.05999383
C	1.52869105	0.68815392	0.06003083
H	2.59653705	2.58263492	0.06007283
H	2.44257405	0.09482592	0.06000883
H	-2.89948095	4.61141192	0.06018083
TS16-17			
C	-1.53732622	0.5787023	-0.00742032
C	0.72407678	0.7488653	-0.02068232
O	-0.47558922	4.0350343	-0.00366232
H	2.29106278	0.0275283	-0.86401032
C	-0.42939522	2.6966193	-0.00608032
N	0.73736878	2.1089443	-0.01882332
C	-1.66635922	1.9856423	0.00365768
N	-0.31346022	-0.0363077	-0.02013132
O	1.95784078	0.1702223	0.02923368
C	-2.93784722	2.6016703	0.01946068
H	-3.00366722	3.6876783	0.02901168
C	-4.06579322	1.8133103	0.02235668
C	-2.71393822	-0.2093227	-0.00429032
H	-2.60667822	-1.2920067	-0.01164332
C	-3.94712922	0.4023033	0.00984368
H	-5.05359322	2.2705983	0.03498768
H	-4.84982922	-0.2074947	0.01260068
H	0.44022178	4.3495743	-0.00214432



274.1*i* cm^{-1}
TS10-15



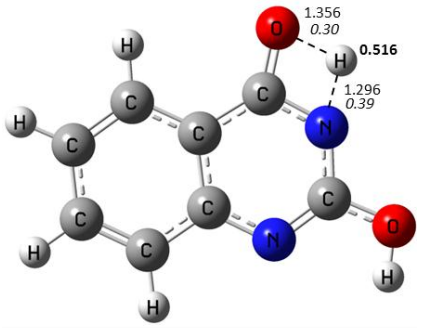
1647.7*i* cm^{-1}
TS15-16



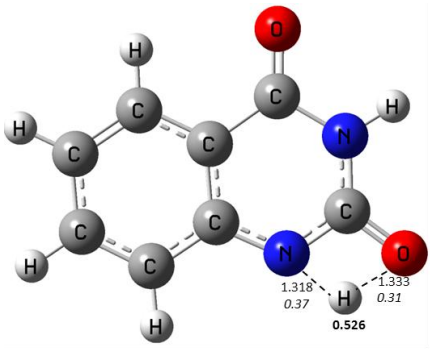
468.2*i* cm^{-1} ∠ N1C1O1H1 = -90.3°
TS16-17

Figure S4. Optimized geometries of transition states in Scheme S1 and Scheme 2. The bond distances (in angstroms), bond orders (italic), angles (in degree) and atomic charges (bold) are labeled in the corresponding positions. For transition state, the imaginary vibrational frequency (cm^{-1}) is shown. (Continued)

TS17-14			
C	-1.06227382	0.18163900	-0.000003
C	1.21851818	0.35389800	-0.000081
C	-0.01819782	2.33791200	0.000009
C	-1.23535782	1.59036900	0.000036
N	0.17358018	-0.42528300	-0.000063
O	2.44768718	-0.16890600	-0.000139
C	-2.51453982	2.17917000	0.000096
H	-2.59393582	3.26492500	0.000124
C	-3.62945782	1.36893900	0.000116
C	-2.22427282	-0.62283400	0.000019
H	-2.10276482	-1.70393500	-0.000011
C	-3.47276882	-0.03486900	0.000077
H	-4.62708082	1.80342600	0.000164
H	-4.35952182	-0.66789500	0.000093
N	1.16911218	1.70323300	-0.000045
O	0.24086418	3.58649900	0.000021
H	1.44802818	2.96860300	-0.000035
H	2.33735618	-1.13019600	-0.000159
TS14-6			
C	-0.99147483	0.583484	0.00485596
C	1.35500417	0.784022	0.00478096
C	0.09906417	2.845618	0.00486396
C	-1.10449683	1.989938	0.00488896
N	0.27095417	0.022051	0.00480096
O	2.38080617	0.022475	0.00473096
C	-2.36895283	2.59248	0.00494396
H	-2.41923183	3.680093	0.00496896
C	-3.51181983	1.809412	0.00496796
C	-2.15130983	-0.204957	0.00487896
H	-2.05463683	-1.288584	0.00485296
C	-3.39323883	0.410599	0.00493396
H	-4.49576283	2.273665	0.00501296
H	-4.29179983	-0.205243	0.00495096
N	1.31828817	2.132802	0.00480996
O	0.11126317	4.055884	0.00488596
H	2.17916917	2.66766	0.00478996
H	1.31667417	-0.780742	0.00475196



1855.4*i* cm^{-1}
TS17-14



1877.9*i* cm^{-1}
TS14-6

Figure S4. Optimized geometries of transition states in Scheme S1 and Scheme 2. The bond distances (in angstroms), bond orders (italic), angles (in degree) and atomic charges (bold) are labeled in the corresponding positions. For transition state, the imaginary vibrational frequency (cm^{-1}) is shown. (Finished)

TS18-19			
H	-1.06833289	1.10713104	-0.00488329
N	-0.47569489	0.91500704	0.78571371
H	-0.23936389	1.68065604	1.40437171
C	-0.40200089	-0.36707396	1.25177071
C	-0.91757389	-1.44280396	0.50204771
C	0.22640411	-0.66647596	2.48683671
C	-0.81563189	-2.74430396	0.96517671
C	0.31772911	-1.98816496	2.94062071
C	-0.19781789	-3.03233696	2.18925371
H	-1.22704589	-3.55389596	0.36297871
H	0.78747111	-2.16978596	3.90488871
H	-0.12829589	-4.05654196	2.54756971
C	0.73427011	0.46156604	3.24174971
N	0.81313311	1.67193604	3.32589571
H	-1.40046789	-1.23557396	-0.45257029
O	1.59782511	-0.00252796	4.66990371
H	2.47230311	-0.36193896	4.45607971
H	1.49309611	1.20774404	4.39516571
TS20-21			
C	-0.88987700	1.04380300	-0.039412
C	0.24372700	0.33327900	-0.435503
C	1.51653200	0.87863100	-0.213603
C	1.65267300	2.12967900	0.402518
C	0.52118200	2.82816700	0.799651
C	-0.74592900	2.28153300	0.576636
H	-1.87280300	0.60641800	-0.205716
H	2.64892800	2.53724600	0.560367
H	0.62443200	3.79914700	1.279618
H	-1.63416800	2.82987900	0.885815
C	2.67953700	0.14570900	-0.637555
N	3.58470800	-0.47674000	-1.003616
N	0.09190700	-0.92729800	-1.084076
H	-0.89065600	-1.03349400	-1.775751
C	-0.69963500	-2.12236300	-0.381827
O	-1.12273300	-1.69632500	0.839633
O	-1.98591400	-1.66373300	-1.450794
O	-0.28385600	-3.23929100	-0.616431
H	-1.23748100	-2.50221900	1.360135
H	0.96724200	-1.32735100	-1.424008
H	-2.17980300	-2.46375600	-1.955756
TS22-23			
C	-0.48971600	0.41882100	-0.026667
C	0.62922900	-0.31271300	-0.435689
C	1.91171200	0.19098500	-0.160387
C	2.07178300	1.41408100	0.504159
C	0.95310900	2.13095200	0.904715
C	-0.32395200	1.62766500	0.638243
H	-1.48205800	0.02022600	-0.231954
H	3.07598600	1.78602000	0.697083
H	1.07293200	3.08164400	1.42004
H	-1.20296800	2.18893700	0.951091
C	3.06184900	-0.56532400	-0.578562
N	3.95481800	-1.21128700	-0.934599
N	0.44622400	-1.54351900	-1.10713
H	-0.58555900	-1.73144300	-1.764019
C	-0.58906300	-2.72247900	-0.429127
O	-0.89184600	-2.38321200	0.851744
O	-1.51594900	-2.54195900	-1.338252
O	0.12098400	-3.90507400	-0.459567
H	-0.29398800	-2.85679300	1.444383
H	-0.19079900	-4.37757200	-1.242144
H	1.32058500	-1.95943100	-1.427851

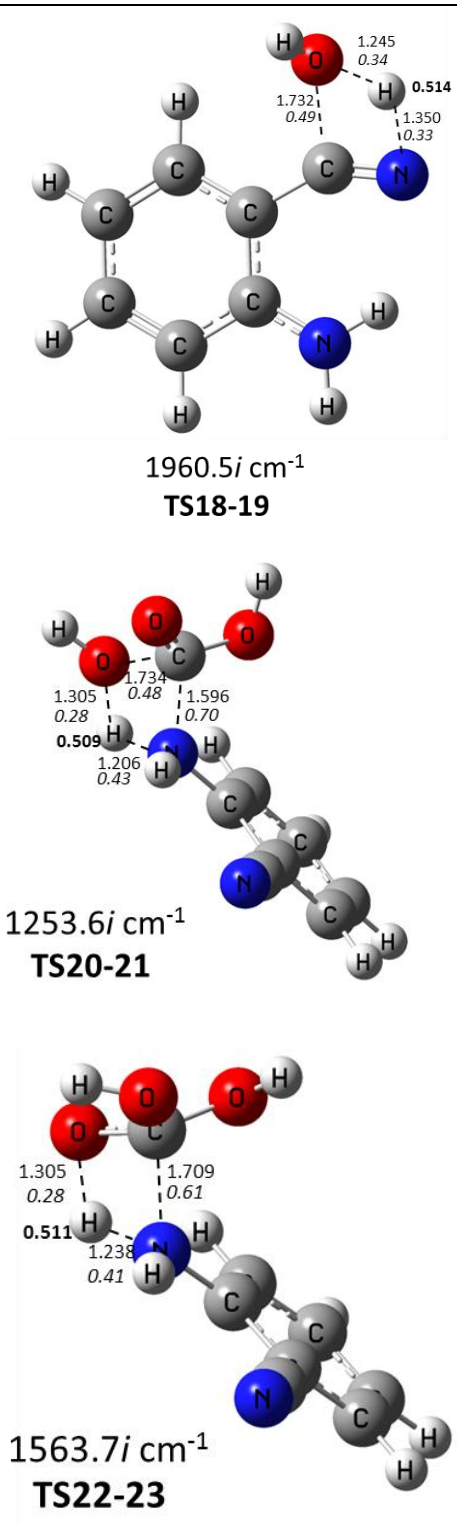
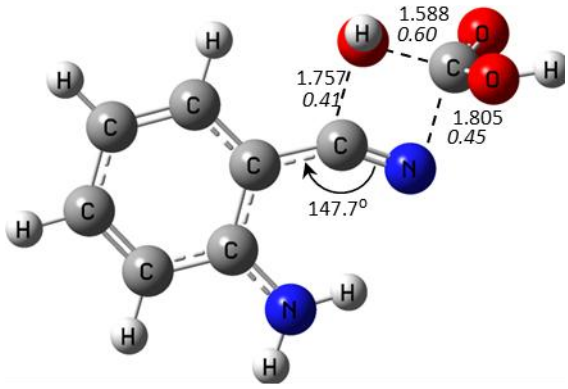


Figure S5. Optimized geometries of transition states in Scheme 3. The bond distances (in angstroms), bond orders (italic), angles (in degree) and atomic charges (bold) are labeled in the corresponding positions. For transition state, the imaginary vibrational frequency (cm^{-1}) is shown. (To be continued)

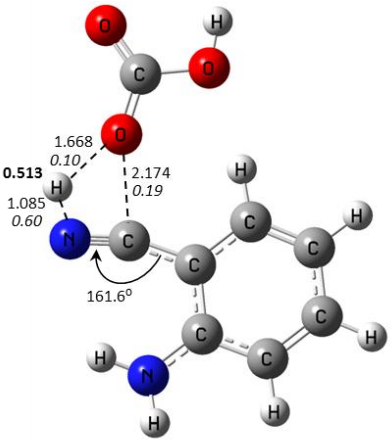
TS24-25			
H	-0.77334874	0.41782724	0.71359765
N	-0.18841274	0.23068624	1.51137065
H	0.03695026	1.00552524	2.12132965
C	-0.13607574	-1.04593476	1.99503065
C	-0.66173674	-2.12311576	1.25455865
C	0.47865826	-1.34119876	3.23778265
C	-0.58493374	-3.41963476	1.73455665
C	0.54240326	-2.65861576	3.71131765
C	0.01641926	-3.70232576	2.96838065
H	-1.00420474	-4.22997976	1.13905765
H	0.99676426	-2.84120076	4.68272765
H	0.06480126	-4.72262176	3.34066365
C	0.99963626	-0.21574976	3.97857565
N	1.09706226	0.98392324	4.07795365
H	-1.13343774	-1.92007276	0.29359865
O	1.90585026	-0.73765276	5.38988465
H	2.77796126	-1.09678976	5.15495465
C	2.06909826	0.82931124	5.59154465
O	1.55708226	1.30963624	6.55625065
O	3.34600426	1.05631624	5.15982865
H	3.63883526	1.85359824	5.62112565

TS26-27			
H	-1.16944600	0.00454300	-0.059921
N	-0.34922900	-0.13154000	0.507908
H	-0.02219700	0.66155800	1.03942
C	0.02968500	-1.40335600	0.827253
C	-0.56727200	-2.51777700	0.208535
C	1.06049400	-1.66529100	1.76744
C	-0.15115700	-3.80123100	0.518408
C	1.48005100	-2.97250600	2.078023
C	0.87154600	-4.04141100	1.449885
H	-0.63459200	-4.64186800	0.021729
H	2.27624300	-3.09887900	2.809825
H	1.18295400	-5.05738500	1.678306
C	1.64477700	-0.53549100	2.385635
N	1.87823700	0.58751700	2.686346
H	-1.35947900	-2.35411500	-0.520624
O	3.21681400	-0.99296500	3.815522
H	2.67613300	0.53447100	3.420364
C	4.04506500	-1.69895800	4.500898
O	4.88329500	-1.31155800	5.29333
O	3.90527600	-3.04948600	4.253588
H	4.56733500	-3.47572100	4.81204

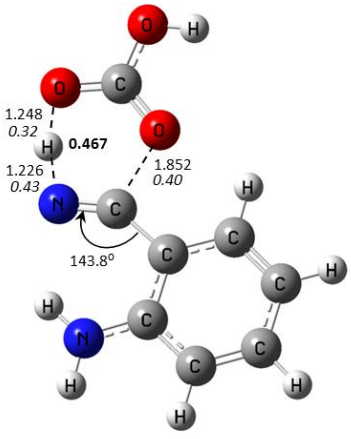
TS28-29			
H	-0.67338400	0.30711000	-0.062555
N	0.04911200	0.09355800	0.603221
H	0.52884500	0.84552300	1.07658
C	0.40141000	-1.20338600	0.819152
C	-0.26507700	-2.24118100	0.132909
C	1.43138500	-1.56587000	1.728844
C	0.07619700	-3.56477200	0.339679
C	1.76172000	-2.91569100	1.92311
C	1.09408000	-3.91552000	1.237086
H	-0.45810300	-4.34238200	-0.205243
H	2.55300000	-3.16046500	2.622679
H	1.35682000	-4.95854800	1.395745
C	2.08365400	-0.46595800	2.408172
N	2.10745600	0.72819100	2.515681
H	-1.05885800	-1.97932600	-0.566102
O	3.32953900	-1.29130700	3.50258
H	2.97595800	0.99446700	3.338993
C	4.00317300	-0.45839300	4.186369
O	3.88801800	0.79190100	4.16651
O	4.92996500	-0.95129300	5.013412
H	4.91235100	-1.91461600	4.929135



699.5*i* cm^{-1}
TS24-25



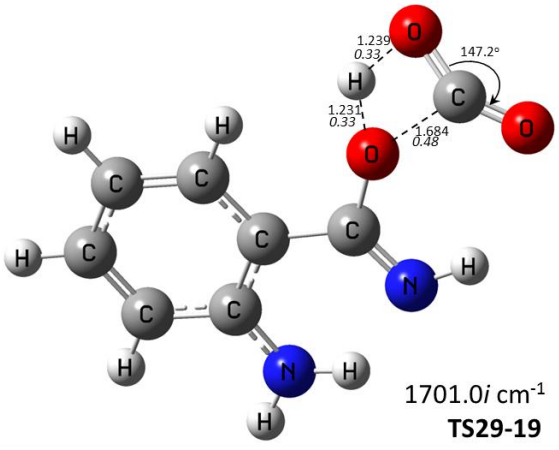
665.3*i* cm^{-1}
TS26-27

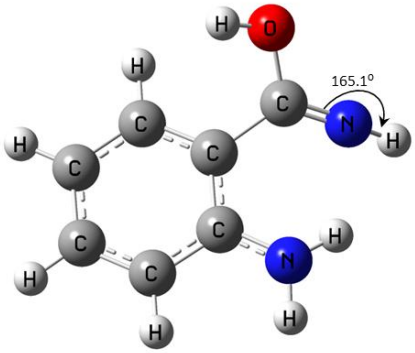


988.5*i* cm^{-1}
TS28-29

Figure S5. Optimized geometries of transition states in Scheme 3. The bond distances (in angstroms), bond orders (italic), angles (in degree) and atomic charges (bold) are labeled in the corresponding positions. For transition state, the imaginary vibrational frequency (cm^{-1}) is shown. (Finished)

TS29-19			
H	0.530048	0.486282	0.096595
N	1.384792	-0.0303	-0.02249
H	2.269623	0.446272	-0.14826
C	1.326114	-1.37596	-0.20056
C	0.074479	-2.03085	-0.12983
C	2.483361	-2.16886	-0.43766
C	-0.03466	-3.39641	-0.30275
C	2.335037	-3.55631	-0.61949
C	1.100909	-4.17844	-0.55691
H	-1.01678	-3.86467	-0.24461
H	3.213338	-4.15848	-0.84114
H	1.015792	-5.25198	-0.70684
C	3.817299	-1.55214	-0.50296
N	4.042367	-0.30038	-0.47588
H	-0.81379	-1.42983	0.064582
O	4.859837	-2.46458	-0.61444
H	5.039596	-0.09487	-0.53495
C	6.237956	-2.29655	0.339381
O	6.858165	-1.30516	0.32475
O	6.113401	-3.45424	0.800611
H	5.079026	-3.42813	0.11959
TS19-30			
H	-0.01533407	0.89711596	-0.07301321
N	-0.00742007	-0.09442804	0.11237879
H	-0.88243007	-0.57269604	-0.04729921
C	1.12590393	-0.77626604	-0.28336321
C	2.31611293	-0.06795204	-0.52813621
C	1.15058793	-2.18686404	-0.37715021
C	3.48549093	-0.72486104	-0.88165321
C	2.34442293	-2.82765304	-0.73647921
C	3.50950493	-2.11655204	-0.99745221
H	4.38720193	-0.14481704	-1.07526421
H	2.34647393	-3.91242604	-0.84859321
H	4.41903393	-2.63679204	-1.28941921
C	-0.08656507	-3.00507604	-0.14617321
N	-1.24506607	-2.69572104	-0.45240021
H	2.30669093	1.01842596	-0.43707621
O	0.15527593	-4.20217804	0.48505879
H	1.05015693	-4.20048604	0.84579379
H	-2.09410707	-2.51232604	-0.93375021
TS30-31			
H	-0.60469494	0.95031893	0.08537327
N	-0.03476594	0.18195693	0.41317527
H	0.87702006	0.17491693	-0.03017973
C	-0.70279094	-1.04444907	0.42012427
C	-2.10640594	-1.06051807	0.40811327
C	-0.00941094	-2.27331207	0.47045927
C	-2.81003294	-2.25599307	0.43984327
C	-0.74112594	-3.46719707	0.46203327
C	-2.12973494	-3.47511307	0.46218727
H	-3.89907194	-2.23663407	0.43303427
H	-0.20577194	-4.41553407	0.46021327
H	-2.67627194	-4.41547507	0.47068827
C	1.48079706	-2.32542507	0.54888827
N	2.24489806	-1.50762707	1.14375527
H	-2.64367594	-0.11268807	0.36759027
O	2.06704006	-3.36048407	-0.14713473
H	1.99369306	-4.18143807	0.35208327
H	1.69014706	-0.78758807	1.61062727





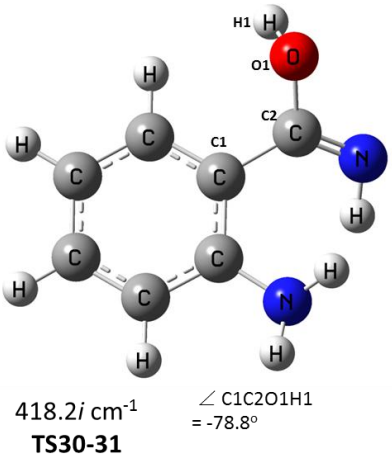


Figure S6. Optimized geometries of transition states in Scheme 4. The bond distances (in angstroms), bond orders (italic), angles (in degree) and atomic charges (bold) are labeled in the corresponding positions. For transition state, the imaginary vibrational frequency (cm^{-1}) is shown. (To be continued)

TS32-33			
H	-0.04849200	0.15431000	0.000894
N	-0.68627400	-0.81743800	0.473535
H	-1.60491700	-0.58271300	0.854495
C	-0.64098300	-2.15476500	-0.043374
C	0.59672300	-2.79132400	-0.137358
C	-1.80883600	-2.82283100	-0.442186
C	0.67584400	-4.08765600	-0.635385
C	-1.71541600	-4.13905400	-0.906637
C	-0.48057000	-4.76759400	-1.016468
H	1.64716000	-4.57345500	-0.710047
H	-2.62923700	-4.65929000	-1.185944
H	-0.41999100	-5.78746200	-1.391096
C	-3.14409500	-2.16454100	-0.399245
N	-3.44391300	-0.96578100	-0.705989
H	1.49669500	-2.27586600	0.194947
O	-4.11077500	-3.00955400	0.012622
H	-2.63799700	-0.46494100	-1.076738
C	0.46970200	-0.36928400	1.458794
O	0.71759400	-0.92125600	2.484408
O	0.90659200	0.61261300	0.768389
H	-4.94729800	-2.52404500	-0.04341

TS34-35			
H	0.02655063	0.70556434	0.34343222
N	0.68822163	0.69269834	1.10824522
H	0.34935263	1.22785334	1.89947722
C	1.16912363	-0.58402566	1.40503022
C	0.99651063	-1.61808466	0.47171322
C	1.86007263	-0.87097866	2.60143122
C	1.48044763	-2.89426266	0.71987322
C	2.31321263	-2.17445066	2.85052022
C	2.13816663	-3.18591866	1.91786322
H	1.33305763	-3.67414666	-0.02607578
H	2.82034963	-2.37265766	3.79228722
H	2.50741263	-4.18918566	2.11797822
C	2.15470863	0.17008934	3.61066422
N	2.34291263	1.42292434	3.36734122
H	0.46518163	-1.40633966	-0.45603878
O	2.24670963	-0.27955666	4.85198722
H	2.48631163	0.48857734	5.42516022
C	2.76514563	2.75029134	4.66765222
O	2.85567863	3.75541834	4.05720622
O	2.80603363	2.14832034	5.70776022
H	2.33260863	1.68866634	2.38680722

TS29-36			
H	0.105263	0.763158	0
N	0.932593	0.281883	-0.31768
H	1.821346	0.683359	-0.06164
C	0.856735	-1.08749	-0.39851
C	-0.41745	-1.68792	-0.46775
C	2.001552	-1.92367	-0.44747
C	-0.55999	-3.05671	-0.59791
C	1.823941	-3.31411	-0.57633
C	0.566667	-3.88663	-0.65876
H	-1.55957	-3.4865	-0.65677
H	2.70564	-3.94652	-0.61582
H	0.458036	-4.96338	-0.76692
C	3.360419	-1.34784	-0.37576
N	3.741654	-0.17941	-0.4144
H	-1.29766	-1.04625	-0.42915
O	4.304361	-2.3974	-0.10275
H	3.989262	0.715513	-0.77395
C	5.538213	-2.29604	-0.66708
O	5.824332	-1.68486	-1.64953
O	6.415733	-3.04126	0.022235
H	5.969174	-3.41577	0.792473

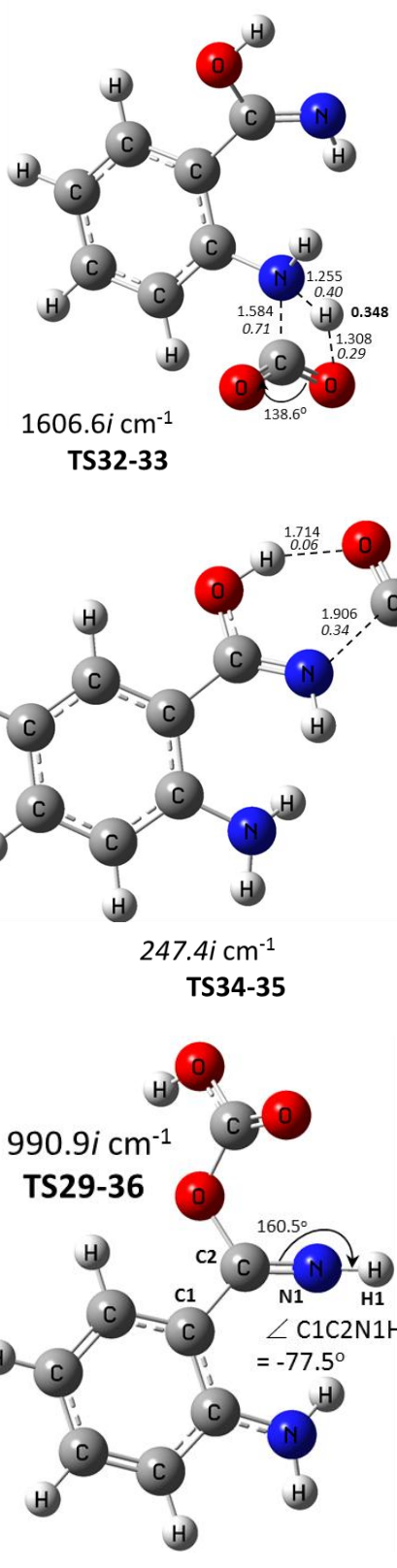


Figure S6. Optimized geometries of transition states in Scheme 4. The bond distances (in angstroms), bond orders (italic), angles (in degree) and atomic charges (bold) are labeled in the corresponding positions. For transition state, the imaginary vibrational frequency (cm^{-1}) is shown. (Continued)

TS36-37			
H	-0.23682	2.210526	0.0031
N	-1.02024	1.6614	0.330602
H	-1.89532	1.969564	-0.07658
C	-0.79199	0.285158	0.303806
C	0.525392	-0.19419	0.23961
C	-1.84464	-0.65135	0.379836
C	0.791085	-1.55628	0.24879
C	-1.55924	-2.02362	0.362238
C	-0.2516	-2.48444	0.30692
H	1.824352	-1.8982	0.201837
H	-2.39003	-2.72471	0.407514
H	-0.04439	-3.55209	0.307525
C	-3.25115	-0.20929	0.514274
N	-3.73622	0.804339	1.101238
H	1.344802	0.522098	0.179133
O	-4.11626	-1.07095	-0.12395
H	-3.00688	1.32644	1.585196
C	-5.45138	-0.97566	0.275623
O	-5.89143	-1.58223	1.194002
O	-6.16887	-0.21714	-0.54983
H	-5.57702	0.228936	-1.16857
TS37-35			
H	-0.44737	1.473684	0
N	0.215177	0.953195	-0.56024
H	1.169502	1.185483	-0.30699
C	-0.05778	-0.41513	-0.60888
C	-1.30382	-0.9	-0.18436
C	0.883555	-1.33813	-1.10958
C	-1.59591	-2.25598	-0.23957
C	0.587571	-2.70833	-1.12365
C	-0.64777	-3.1749	-0.69996
H	-2.57172	-2.60392	0.097209
H	1.350656	-3.39384	-1.48788
H	-0.87362	-4.23844	-0.72388
C	2.17706	-0.90932	-1.65637
N	2.541243	0.238528	-2.14756
H	-2.04137	-0.19694	0.20233
O	3.180566	-1.72644	-1.7512
H	1.924549	1.031189	-2.28861
C	4.164458	-0.49602	-2.40046
O	5.036461	-0.09162	-1.71056
O	4.27004	-0.77685	-3.70984
H	3.454605	-1.19329	-4.01347
TS35-38			
H	0.30131778	0.95414349	0.26852857
N	-0.41501322	0.25914049	0.39822357
H	-1.38126922	0.53776249	0.36042057
C	-0.11723022	-1.06957751	0.39439457
C	-1.20359222	-1.97988751	0.44073557
C	1.19799478	-1.61587451	0.37270157
C	-1.00686722	-3.34340651	0.46041457
C	1.36103378	-3.02126251	0.39688957
C	0.29050978	-3.88611251	0.43739457
H	-1.87318022	-4.00357151	0.49343457
H	2.38108378	-3.39958351	0.37805357
H	0.44395678	-4.96226851	0.45074557
C	2.44995678	-0.84331151	0.33600257
N	2.34389078	0.60628949	0.26407257
H	-2.21515822	-1.57501851	0.46155357
O	3.55303478	-1.34297451	0.38419157
H	2.86496478	-0.17454651	2.45631157
C	2.63623678	1.40902649	1.37227057
O	2.74102978	2.60261949	1.28799757
O	2.70551478	0.77345849	2.55749257
H	2.72503478	1.00756449	-0.58713043

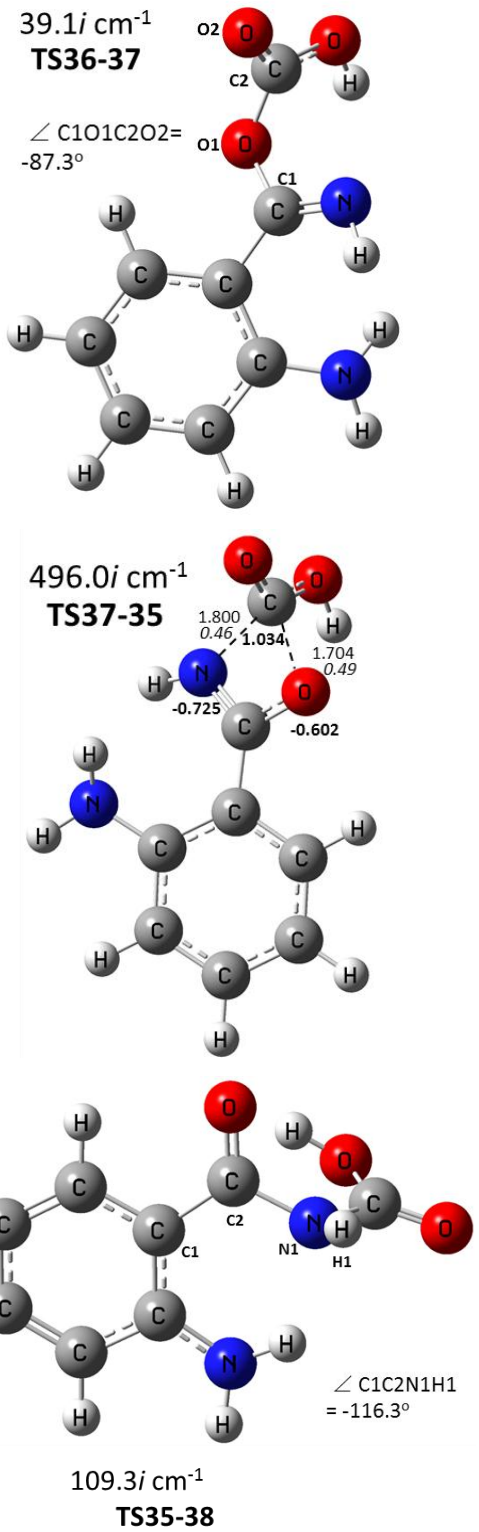
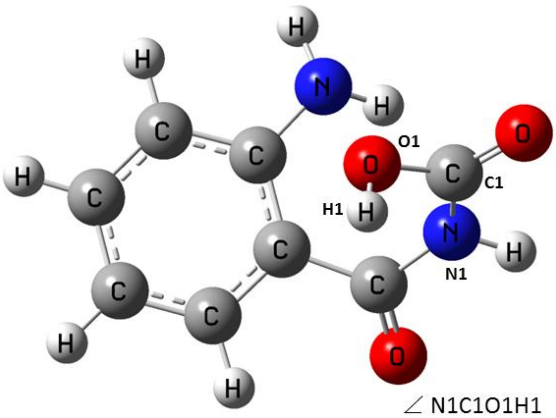


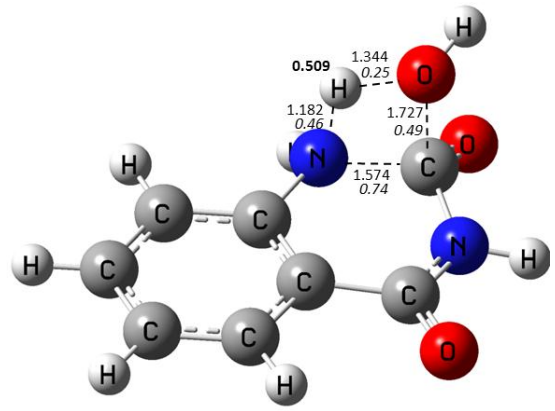
Figure S6. Optimized geometries of transition states in Scheme 4. The bond distances (in angstroms), bond orders (italic), angles (in degree) and atomic charges (bold) are labeled in the corresponding positions. For transition state, the imaginary vibrational frequency (cm^{-1}) is shown. (Continued)

TS38-39			
H	-0.37740877	0.83143406	-0.02895381
N	-1.05843377	0.27454106	0.46701319
H	-2.00203277	0.42323706	0.13995819
C	-0.73173977	-1.04857794	0.73135319
C	-1.75900277	-1.99211994	0.89498119
C	0.60057623	-1.48773094	0.87706919
C	-1.47395377	-3.31978694	1.18095319
C	0.87252823	-2.83832894	1.12322419
C	-0.15179977	-3.75928394	1.29231419
H	-2.29461077	-4.02511294	1.30705119
H	1.91596823	-3.14455494	1.18354019
H	0.07138523	-4.80307594	1.50108119
C	1.78256323	-0.59871894	0.70921419
N	1.73861723	0.71306406	1.22022419
H	-2.79379577	-1.66628994	0.78989019
O	2.77907523	-0.94171094	0.10867919
H	0.91897623	-0.06095494	3.72397619
C	1.08250423	1.24560106	2.32599519
O	1.15728023	2.41198106	2.59515919
O	0.35885823	0.34559606	3.05031219
H	2.46279623	1.31838006	0.84863119
TS39-41			
H	0.67527020	0.72808356	-0.10548854
N	1.34002320	0.28177556	0.52502346
H	1.27474320	0.56026456	1.67167346
C	1.52682620	-1.12433144	0.30275946
C	0.41740620	-1.94576144	0.11165046
C	2.81304220	-1.65851144	0.34504346
C	0.60259720	-3.31765144	-0.02716754
C	2.98538320	-3.03916844	0.21731146
C	1.88584920	-3.86831044	0.03507346
H	-0.26151280	-3.96309944	-0.17788054
H	4.00124020	-3.42861244	0.25178846
H	2.02309620	-4.94317144	-0.06654354
C	4.02423220	-0.78760844	0.43643646
N	3.78645320	0.56428156	0.41446346
H	-0.58249680	-1.51380644	0.08286346
O	5.15128220	-1.24098744	0.43437646
H	2.18842020	1.99463856	2.67231146
C	2.57381220	1.24784256	0.66833846
O	2.39596220	2.39616256	0.29555546
O	2.29872520	1.08559056	2.36576646
H	4.60465420	1.16199556	0.40169146
TS39-40			
H	-0.96084563	0.50465507	-0.24667488
N	-0.86015463	0.21000707	0.72856612
H	-1.72759163	-0.64565893	0.75454312
C	0.39065737	0.71444607	1.24119212
C	1.52481937	-0.05658093	1.42812512
C	0.36887237	2.08688607	1.52538212
C	2.67816237	0.56500807	1.91298412
C	1.52862337	2.69240007	2.00122212
C	2.68068937	1.93101307	2.19471912
H	3.57976637	-0.02476193	2.07202212
H	1.50333537	3.75906507	2.21726012
H	3.58578737	2.40393007	2.57160012
C	-0.87875863	2.92536507	1.34677912
N	-2.04133563	2.23095907	1.04182612
H	1.50602737	-1.12084593	1.20167812
O	-0.84748763	4.13484007	1.43585812
H	-2.42680863	-0.04522493	3.06216312
C	-2.09188063	0.83123207	1.41454812
O	-2.98800263	-0.00753093	0.92188712
O	-1.92682763	0.73807007	2.79953612
H	-2.89386463	2.76683607	1.16594212



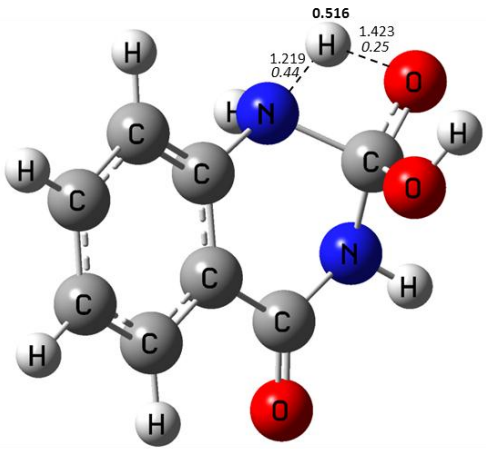
467.0i cm^{-1}

TS38-39



1200.8*i* cm^{-1}

TS39-41



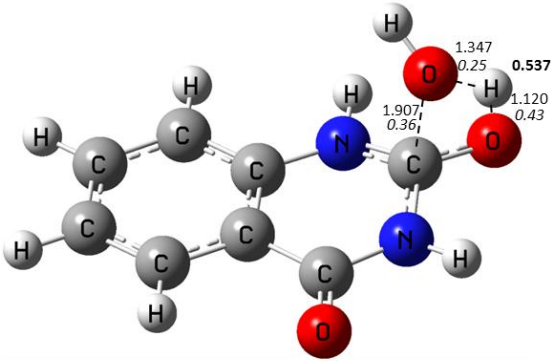
1564.3*i* cm^{-1}

TS39-40

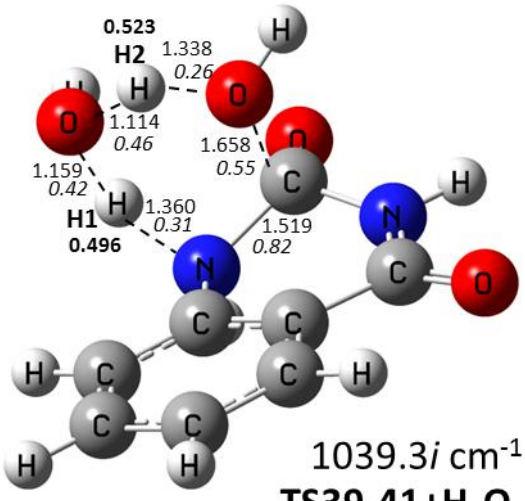
Figure S6. Optimized geometries of transition states in Scheme 4. The bond distances (in angstroms), bond orders (italic), angles (in degree) and atomic charges (bold) are labeled in the corresponding positions. For transition state, the imaginary vibrational frequency (cm^{-1}) is shown. (Continued)

TS40-41			
H	-1.05598900	0.69301100	0.026273
N	-0.84724100	1.67974800	0.093385
H	-3.29319900	1.92255000	1.118256
C	0.45651500	2.11069300	0.313189
C	1.52542800	1.20747500	0.326329
C	0.68950900	3.47820700	0.506368
C	2.81181300	1.68278200	0.54171
C	1.99087600	3.94068000	0.72252
C	3.05242800	3.04846000	0.743443
H	3.64308300	0.97926000	0.555385
H	2.13445100	5.01023700	0.866531
H	4.06647400	3.40466000	0.911696
C	-0.43881900	4.43343900	0.449992
N	-1.67615900	3.83585300	0.216789
H	1.34246900	0.14498400	0.170407
O	-0.33389400	5.63537300	0.55866
H	-2.03635800	1.59907100	2.642395
C	-1.92612300	2.48728900	0.315862
O	-3.12723300	2.03605000	0.016404
O	-2.47967000	2.28414700	2.129535
H	-2.49012500	4.43613700	0.287894

TS39-41+H_2O			
H	-0.95491	0.620941	-0.00528
N	-0.82165	0.290234	0.950812
H	-1.7661	0.772582	1.801777
C	-0.67454	-1.1445	1.007808
C	-1.80929	-1.95058	0.991288
C	0.598175	-1.71174	1.099317
C	-1.66746	-3.33498	1.062548
C	0.731007	-3.09783	1.176379
C	-0.39885	-3.90992	1.159598
H	-2.55396	-3.96713	1.051752
H	1.735668	-3.51204	1.241911
H	-0.29425	-4.99161	1.221583
C	1.828408	-0.85976	1.066719
N	1.585075	0.488305	1.096493
H	-2.79627	-1.49322	0.930576
O	2.946954	-1.32735	0.965946
H	0.754369	1.243594	3.531462
C	0.345273	1.102019	1.487107
O	0.227984	2.329499	1.354548
O	0.146244	0.652661	3.070337
H	2.382245	1.111893	1.058994
O	-2.16473	1.194862	2.804447
H	-1.1315	1.030495	3.186692
H	-2.24741	2.150131	2.674387



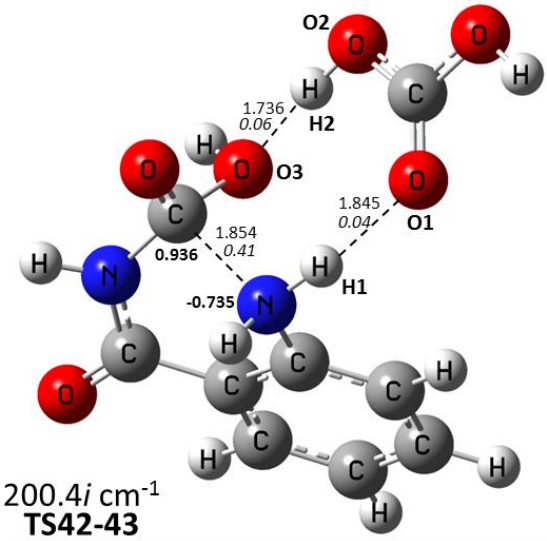
1220.9*i* cm^{-1}
TS40-41



1039.3*i* cm^{-1}
TS39-41+H_2O

Figure S6. Optimized geometries of transition states in Scheme 4. The bond distances (in angstroms), bond orders (italic), angles (in degree) and atomic charges (bold) are labeled in the corresponding positions. For transition state, the imaginary vibrational frequency (cm^{-1}) is shown. (Continued)

TS42-43			
H	-0.56164	-0.36986	0
N	-0.34463	-0.02574	0.93384
H	0.58562	0.414452	0.945755
C	-1.35789	0.831585	1.478605
C	-1.20261	2.213523	1.498927
C	-2.48764	0.231902	2.042935
C	-2.20212	3.004781	2.064229
C	-3.49287	1.033104	2.583402
C	-3.35024	2.418116	2.59775
H	-2.08332	4.086998	2.084133
H	-4.37457	0.545649	2.995876
H	-4.13089	3.041607	3.029764
C	-2.66493	-1.25719	2.065896
N	-1.52333	-2.01881	1.944831
H	-0.30162	2.658304	1.078655
O	-3.76254	-1.77128	2.166448
H	-0.14767	-1.38477	3.865888
C	-0.1503	-1.58395	1.920033
O	0.690606	-2.29103	1.395726
O	0.182239	-0.86964	3.118741
H	-1.65646	-3.00368	1.748877
H	1.884372	-0.53464	3.063058
C	3.028552	0.695334	2.206724
O	4.294245	1.117283	2.255568
O	2.209261	1.148223	1.423059
O	2.825298	-0.23643	3.102938
H	4.389503	1.793481	1.571955
TS43-44			
H	-0.97701	0.674704	-0.00578
N	-0.85415	0.344855	0.95555
H	-1.80227	0.58944	1.513577
C	-0.61671	-1.0904	0.99242
C	-1.70341	-1.95477	0.985217
C	0.69148	-1.56468	1.050178
C	-1.46668	-3.32884	1.019969
C	0.916104	-2.94012	1.084195
C	-0.1615	-3.82107	1.067924
H	-2.3098	-4.01748	1.016442
H	1.945853	-3.29071	1.123724
H	0.013623	-4.89482	1.097326
C	1.85521	-0.62733	1.061563
N	1.519096	0.705734	1.146505
H	-2.71602	-1.55445	0.96883
O	3.004837	-1.00206	0.961078
H	0.743407	1.026019	3.657777
C	0.251465	1.234905	1.525507
O	0.049875	2.433423	1.492986
O	0.050166	0.584907	3.150729
H	2.278021	1.377289	1.150993
H	-0.98264	0.938901	3.617882
C	-3.03252	1.194979	3.361911
O	-4.19629	1.563374	3.913565
O	-3.04223	0.80108	2.166045
O	-2.03457	1.279875	4.126245
H	-4.87414	1.474762	3.231082



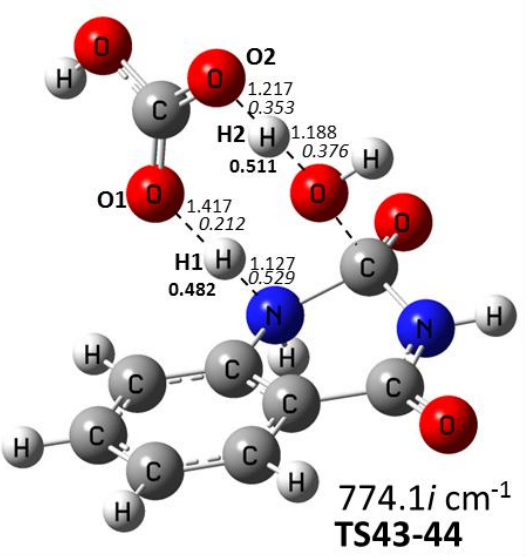


Figure S6. Optimized geometries of transition states in Scheme 4. The bond distances (in angstroms), bond orders (italic), angles (in degree) and atomic charges (bold) are labeled in the corresponding positions. For transition state, the imaginary vibrational frequency (cm^{-1}) is shown. (Finished)

Reference 18: Gaussian 09, Revision A.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.