Supporting information

Table S1. Bond lengths, angles and dihedral angles of the structures.

a) AM1 reproduction. The values in parenthesis are from Saripinar *et al*.

Bond lengths	**R1**	**R2**	**TS1**	**IN**	**TS2**	**P**
N1-C2	-	-	1.94 (1.92)	1.55 (1.54)	1.51 (1.50)	1.40 (1.40)
C2-C3	1.34 (1.34)	-	1.37 (1.37)	1.40 (1.40)	1.43 (1.43)	1.48 (1.48)
C4-C3	1.47 (1.46)	-	1.45 (1.45)	1.44 (1.44)	1.41 (1.41)	1.36 (1.36)
06-C2	1.18 (1.18)	-	1.20 (1.20)	1.24 (1.24)	1.24 (1.24)	1.24 (1.24)
O8-H10	-	-	2.48 (2.46)	2.19 (2.25)	1.40 (1.41)	0.97 (0.97)
H10-N1	-	0.99 (0.98)	1.01 (1.01)	1.03 (1.03)	1.22 (1.23)	2.53 (2.55)
08-C4	1.23 (1.24)	-	1.24 (1.24)	1.25 (1.25)	1.28 (1.28)	1.35 (1.35)
N1-C7	-	1.37 (1.36)	1.43 (1.43)	1.48 (1.48)	1.45 (1.45)	1.40 (1.40)

Angles	**R1**	**R2**	**TS1**	**IN**	**TS2**	**P**
O6-C2-C3	179.65 (179.00)	-	147.89 (146.59)	132.10 (131.59)	129.01 (129.14)	122.62 (122.65)
C3-C2-N1	-	-	108.11 (108.52)	115.40 (115.05)	115.32 (114.35)	116.79 (116.78)
C4-C3-C2	120.94 (121.12)	-	128.61 (128.60)	125.68 (125.20)	122.84 (122.03)	125.38 (125.34)
C5-C3-C2	120.62 (120.53)	-	114.68 (114.65)	116.26 (116.54)	117.42 (117.71)	114.81 (114.82)
O8-C4-C3	123.63 (123.66)	-	126.06 (125.98)	124.75 (124.56)	123.18 (123.20)	127.93 (127.86)
H10-N1-C2	-	-	101.90 (100.51)	107.64 (107.56)	104.07 (103.72)	-
H13-N1-C2	-	-	102.75 (99.92)	107.74 (108.20)	109.74 (110.09)	118.23 (118.38)

Dihedral angles	R1	R2	TS1	IN	TS2	P
C4-C3-C2-N1	-	-	-16.27 (-2.54)	-4.32 (-3.17)	2.11 (1.93)	-49.75 (-50.70)
H10-N1-C2-C3	-	-	62.85 (40.56)	42.31 (40.33)	-3.51 (-3.22)	-
C2-N1-H10-O8	-	-	-68.25 (-60.79)	-62.73 (-61.92)	5.45 (5.02)	-

b) HF/3-21G

Bond lengths	R1	R2	TS	P
N1-C2	-	-	2.07	1.39
C2-C3	1.32	-	1.35	1.46
C4-C3	1.47	-	1.44	1.33
06-C2	1.14	-	1.16	1.21
O8-H10	-	-	1.67	0.97
H10-N1	-	1.00	1.03	2.28
08-C4	1.21	-	1.23	1.34
N1-C7	-	1.35	1.40	1.39

Angles	R1	R2	TS	P
O6-C2-C3	179.64	-	151.42	123.32
C3-C2-N1	-	-	104.43	115.34
C4-C3-C2	117.93	-	130.69	124.96
C5-C3-C2	122.31	-	113.65	117.19
O8-C4-C3	124.67	-	129.22	128.73
H10-N1-C2	-	-	100.26	-
H13-N1-C2	-	-	101.47	118.99

Dihedral angles	R1	R2	TS	P
C4-C3-C2-N1	-	-	1.97	28.82
H10-N1-C2-C3	-	-	-1.04	-
C2-N1-H10-O8	-	-	-1.92	-

c) HF/6-31G**

Bond lengths	R1	R2	TS	IN	TS2	P
N1-C2	-	-	1.86	1.55	1.54	1.39
C2-C3	1.34	-	1.38	1.41	1.41	1.48
C4-C3	1.47	-	1.45	1.43	1.42	1.34
06-C2	1.13	-	1.16	1.19	1.19	1.19
O8-H10	-	-	1.78	1.49	1.42	0.95
H10-N1	-	0.99	1.02	1.08	1.11	2.30
08-C4	1.19	-	1.21	1.23	1.24	1.32
N1-C7	-	1.35	1.42	1.45	1.45	1.39

Angles	R1	R2	TS	IN	TS2	P
O6-C2-C3	179.20	-	143.61	133.79	133.27	122.79
C3-C2-N1	-	-	108.28	112.21	112.07	115.85
C4-C3-C2	116.88	-	127.99	112.94	122.34	125.67
C5C3-C2	119.93	-	114.09	118.20	118.63	117.08
O8-C4-C3	123.46	-	127.97	126.06	125.73	129.18
H10-N1-C2	-	-	105.08	105.02	104.40	-
H13-N1-C2	-	-	104.34	108.76	108.93	119.09

Dihedral angles	R1	R2	TS	IN	TS2	P
C4-C3-C2-N1	-	-	-0.35	1.77	2.65	34.62
H10-N1-C2-C3	-	-	18.96	-2.43	-3.78	-
C2-N1-H10-O8	-	-	-38.06	2.78	5.38	-

d) B3LYP/6-31+G**

Bond lengths	**R1**	**R2**	**TS**	**P**
N1-C2	-	-	1.98	1.42
C2-C3	1.34	-	1.39	1.48
C4-C3	1.49	-	1.45	1.36
06-C2	1.16	-	1.18	1.22
O8-H10	-	-	1.62	0.97
H10-N1	-	1.01	1.06	2.27
08-C4	1.22	-	1.24	1.34
N1-C7	-	1.36	1.41	1.40

Angles	**R1**	**R2**	**TS**	**P**
O6-C2-C3	0.05	-	143.96	123.32
C3-C2-N1	-	-	107.36	115.34
C4-C3-C2	118.78	-	128.14	124.96
C5-C3-C2	120.06	-	114.12	117.19
O8-C4-C3	124.99	-	127.77	128.73
H10-N1-C2	-	-	98.55	-
H13-N1-C2	-	-	103.05	118.99

Dihedral angles	**R1**	**R2**	**TS**	**P**
C4-C3-C2-N1	-	-	0.09	37.80
H10-N1-C2-C3	-	-	2.14	-
C2-N1-H10-O8	-	-	-7.63	-

Figure S1. Energetic profile obtained with the differents methods. The ZPEs have been included.

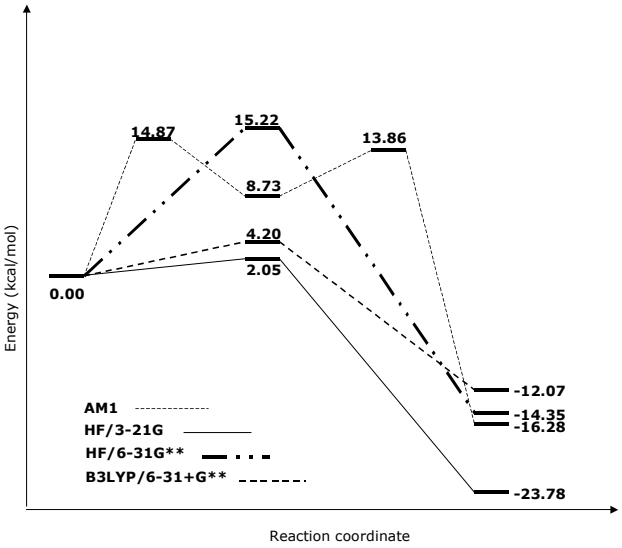
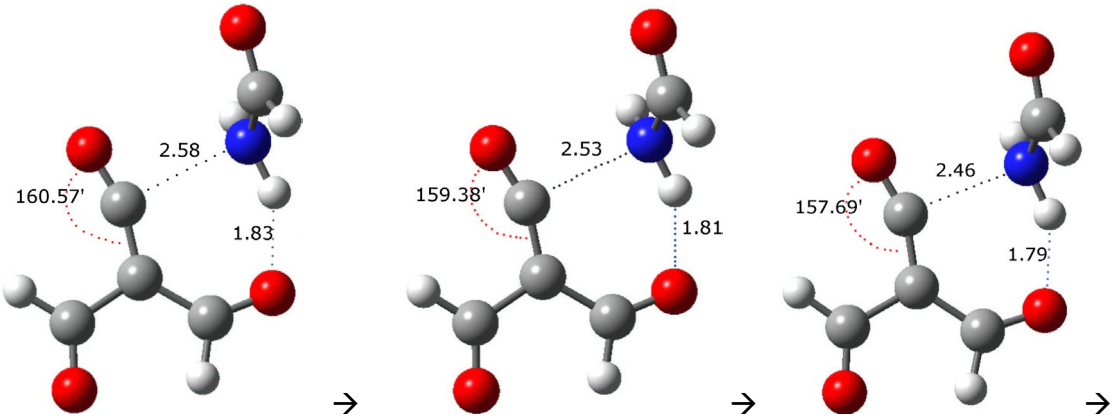
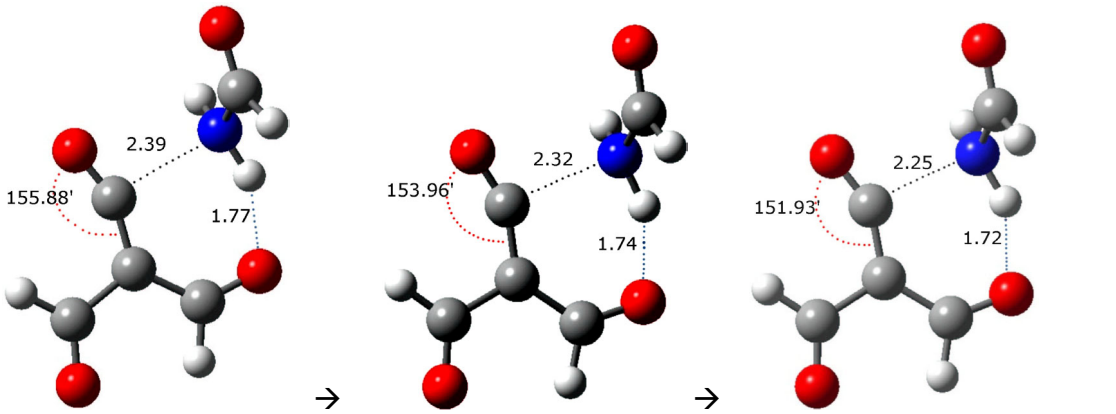


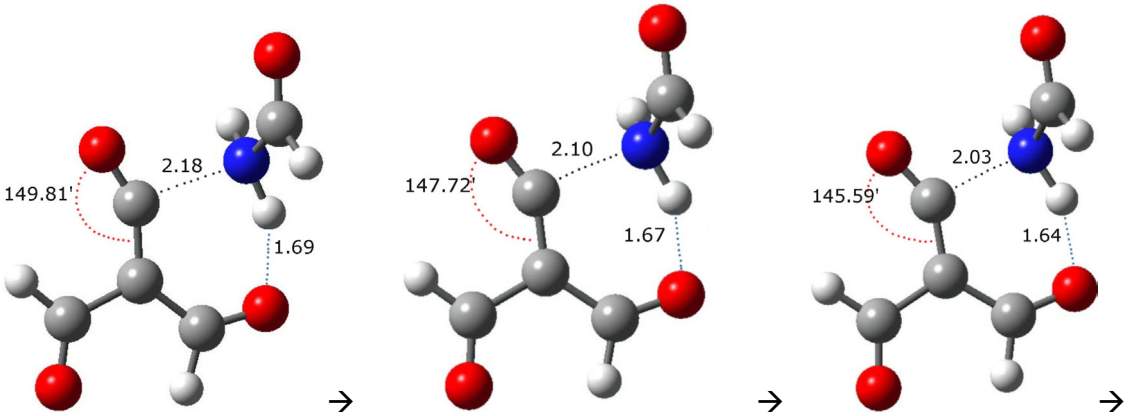
Figure S2. Reaction pathway, starting from reactants R1+R2. We can see how N1-C2 and H10-O8 distances and O6-C2-C3 angle are changing.



r.c.=-3.96 amu$^{1/2}$bohr → r.c.=-3.60 amu$^{1/2}$bohr → r.c.=-3.12 amu$^{1/2}$bohr →

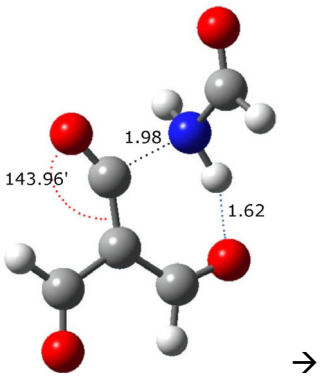


→ r.c.=-2.64 amu$^{1/2}$bohr → r.c.=-2.16 amu$^{1/2}$bohr → r.c.=-1.68 amu$^{1/2}$bohr →



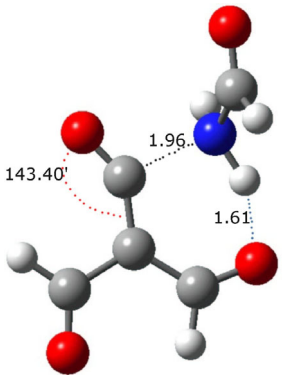
r.c.=-1.20 amu$^{1/2}$bohr → r.c.=-0.74 amu$^{1/2}$bohr → r.c.=-0.27 amu$^{1/2}$bohr →

A gradual approach of formamide nitrogen to the ketene carbon is observed; also we can see the reduction of the distance between O10 and H8. The angle O6-C2-C3 is getting shorter: from the initial 180º of R1 to 143.96º in TS. From this point we will arrive to P:

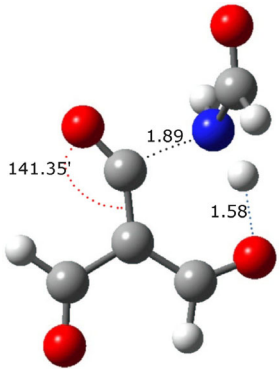


r.c.=0.00 amu$^{1/2}$bohr

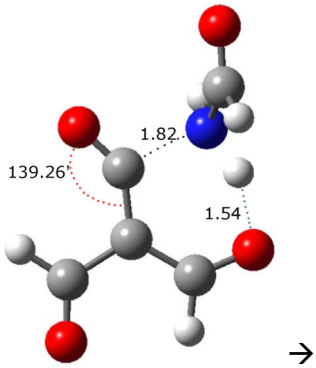
TS



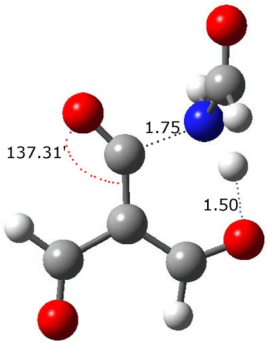
r.c.=0.04 amu$^{1/2}$bohr



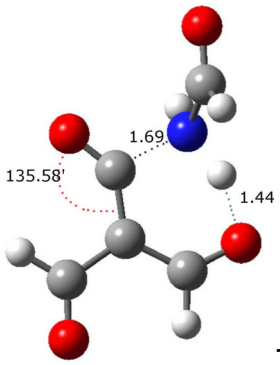
r.c.=0.49 amu$^{1/2}$bohr



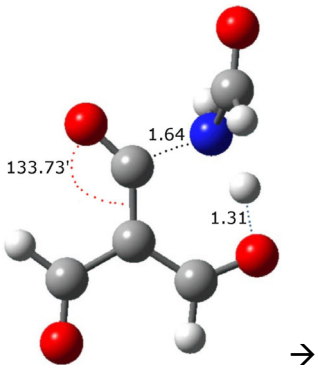
r.c.=0.97amu$^{1/2}$bohr



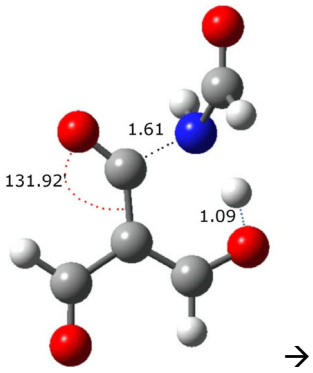
r.c.=1.45amu$^{1/2}$bohr



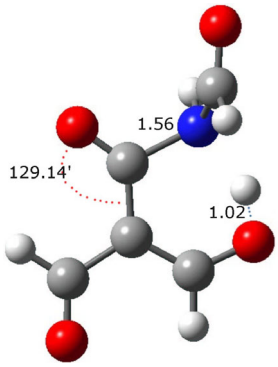
r.c.=1.93amu$^{1/2}$bohr



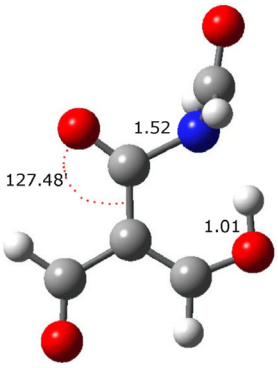
r.c.=2.41 amu$^{1/2}$bohr



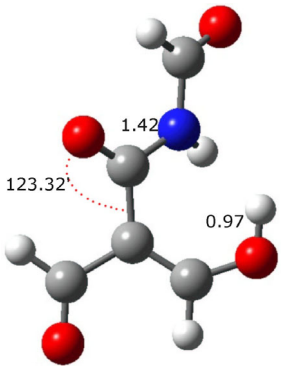
r.c.=2.89 amu$^{1/2}$bohr



r.c.=3.37 amu$^{1/2}$bohr



r.c.=3.97 amu$^{1/2}$bohr



P

The structure before P is the last point we got with IRC. From this structure only a rotation around the N1-C7 bond is needed to reach product P: the real reaction is completed and only a conformational arrangement remains to be done.

Table S2. Imaginary frequencies for the transtition structures(cm^{-1}).

	AM1	HF/3-21G	HF/ 6-31G(d,p)	B3LYP/ 6-31+G(d,p)
TS1	-444.25	-221.53	-322.37	-135.90
TS2	-1656.41	-	-262.06	-

Table S3. Energies and frequencies for the two studied solvatation models, with B3LYP/6-31+G(d,p) calculations. ZPE is included.

Onsager	Relative E (kcal/mol)	υ (cm^{-1})
R1+R2	0.00	-
TS	5.93	-141.12
P	-10.39	-

PCM	Relative E (kcal/mol)	υ (cm^{-1})
R1+R2	0.00	-
TS	5.72	-128.55
P	-11.59	-