Supporting Information

Table S1. NBO donor-acceptor interaction analysis for various **TSA** and **TSB** transition states.

TS	Donor	Acceptor	Bond Length/Å	Bond Angle	NBO e2pert/kJ/mol
N1-E1-TSA	C=O	N-H	2.06	119	7.2
	C=O	N-H	2.37	111	4.1
	C=O	N-H	2.17	127	6.23
	S	N-H	2.34	135	12.93
N1-E1-TSB	C=O	N-H	1.9	150	21.92
	C=O	N-H	1.76	166	37.61
	S	C+	3.2		1.84
N1-E2-TSA	C=O	Gua-α-C-H	2.34	130	2.51
	N=O	N-H	1.95	125	11.55
	S	N-H	2.31	153	19.79
N1-E2-TSB	C=O	N-H	1.85	151	6.71
	N=O	N-H	2.03	136	12.30
	S	C+	3.15		2.64
N1-E3-TSA	C=O	N-H	1.65	157	46.48
	C=O	Gua-α-C-H	2.34	131	2.55
	S	N-H	2.13	170	11.84
N1-E3-TSB	C=O	N-H	1.84	144	26.78
	C=O	N-H	1.75	158	37.07
	S	C+	3.15		5.31
N1-E4-TSA	C=O	N-H	1.62	163	52.59
	C=O	Gua-α-C-H	2.28	127	3.22
	S	N-H	2.23	170	9.79
N1-E4-TSB	C=O	N-H	1.90	139	19.08
	C=O	N-H	1.63	163	49.04
	S	C+	3.16		5.90
N1-E5-TSA	C=O	N-H	1.92	135	16.86
	C=O	N-H	2.30	116	6.78
	C=O	Gua-α-C-H	2.47	120	1.42
	S	N-H	2.34	135	13.39
	C=O	C=C	3.14		1.92
N1-E5-TSB	C=O	N-H	1.90	142	23.39
	C=O	N-H	1.75	155	37.66
	S	C+	3.12		6.44
	C=O	C=C	3.30		1.26
N1-E6-TSA	C=O	N-H	1.94	134	14.56
	C=O	N-H	2.29	118	5.65
	C=O	Gua-α-C-H	2.45	120	1.55
	S	N-H	2.43	131	10.21
	C=O	C=C	3.30		1.21
N1-E6-TSB	C=O	N-H	1.93	138	19.79
	C=O	N-H	1.69	156	44.89
	S	C+	3.11		6.95

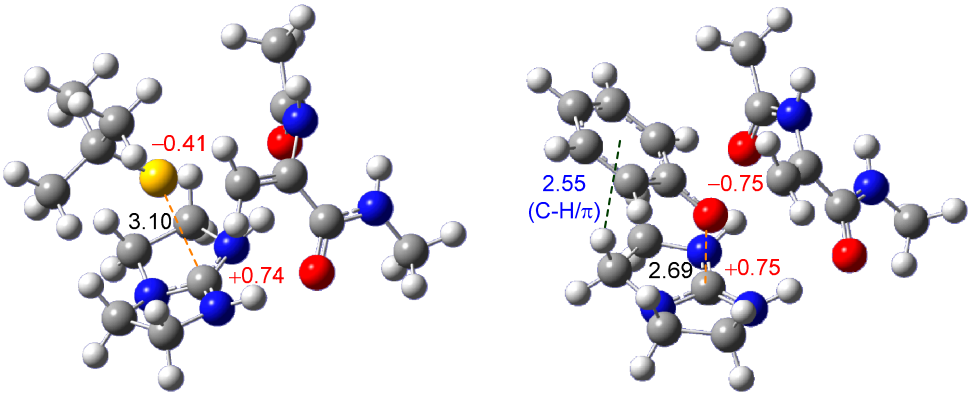
Table S1. *Cont.*

TS	Donor	Acceptor	Bond Length/Å	Bond Angle	NBO e2pert/kJ/mol
N2-E4-TSA	C=O	N-H	1.70	159	46.94
	C=O	Gua-α-C-H	2.26	134	3.60
	S	N-H	2.10	171	12.84
	N	C-H	2.76	160	2.80
N2-E4-TSB	C=O	N-H	1.90	140	20.88
	C=O	N-H	1.67	165	46.02
	S	C+	3.10		5.65
N3-E4-TSA	C=O	N-H	1.65	166	49.66
	C=O	Gua-α-C-H	2.33	127	2.43
	O	N-H	1.58	174	8.87
	C=O	C=C	3.02		2.26
N3-E4-TSB	C=O	N-H	1.89	145	20.79
	C=O	N-H	1.70	170	38.16
	O	C+	2.69		22.72
N4-E4-TSA	C=O	N-H	1.95	125	20.79
	C=O	N-H	1.72	157	36.94
	Se	N-H	2.71	119	4.73
N4-E4-TSB	C=O	N-H	1.92	139	19.00
	C=O	N-H	1.64	163	47.15
	Se	C+	3.10		8.28
N5-E4-TSA	C=O	N-H	1.88	149	30.38
	C=O	Gua-α-C-H	2.57	121	1.26
	O	C-H	2.29	136	8.41
N5-E4-TSB	C=O	N-H	1.94	139	18.87
	C=O	N-H	1.76	165	35.61
	O	C+	2.63		6.99
N6-E4-TSA	C=O	N-H	1.99	129	12.43
	C=O	Gua-α-C-H	2.17	130	6.23
	O	N-H	1.87	135	12.55
	O	N-H	2.13		12.22
	F	N-H	2.50	106	1.00
N6-E4-TSB	C=O	N-H	1.95	140	18.95
	C=O	N-H	1.70	165	42.80
	O	C+	2.61		11.42
	F	N-H	2.47	110	1.26
N7-E4-TSA	C=O	N-H	1.85	151	24.64
	C=O	Gua-α-C-H	2.28	133	2.01
	O=C=O	N-H	1.70	161	25.98
	O=C=O	N-H	2.43	109	1.38
	O=C=O	N-H	2.38	139	7.86

Table S1. *Cont.*

TS	Donor	Acceptor	Bond Length/Å	Bond Angle	NBO e2pert/kJ/mol
N7-E4-TSB	C=O	N-H	1.93	145	22.13
	C=O	N-H	1.69	170	47.99
	O=C=O	N-H	2.37	107	5.36
	O=C=O	C+	2.81		1.38
N8-E4-TSA	C=O	N-H	2.24	112	5.56
	C=O	Gua-α-C-H	2.34	119	2.43
	C≡N	N-H	2.08	132	7.07
	C≡N	N-H	2.17	126	8.79
N8-E4-TSB	C=O	N-H	1.69	167	41.09
	C=O	N-H	1.86	143	25.06
	C≡N	Gua-α-C-H	2.46	115	1.92
	C≡N	Gua-α-C-H	2.64	105	0.84
	N≡C	C+	2.94		2.59
	C≡N	C-H	2.91	118	1.63
TBD_N1-E4-TSA	C=O	N-H	1.73	145	35.48
	C=O	Gua-α-C-H	2.34	132	2.85
	S	N-H	2.34	148	8.33
TBD_N1-E4-TSB	C=O	N-H	2.03	132	11.55
	C=O	N-H	1.65	173	42.93
	S	C+	3.09		8.66

NBO e2pert is the donor and acceptor interaction energy of the NBO Lewis bonding molecular orbitals to the antibonding molecular orbitals; **Donor**: S = thiolate sulphur atom, O = anionic O atom, C=O = carbonyl O atom, O=C=O = carboxylate O atom, N=C = cyanide C atom, C=N = cyanide N atom, C=C is π donation from ethene or aromatic moiety, F= fluorine atom; **Acceptor**: N-H = guanidinium N-H hydrogen, Gua-α-C-H = C-H interaction of hydrogen on α carbon w.r.t to N of guanidine, C+ = central carbon atom in the guanidinium functional group, Ph-H = hydrogen on phenyl ring, C-H = hydrogen from methylene group; The interactions in black are between the catalyst with both electrophile and nucleophile while that in red are between the electrophile and nucleophile.



N2-E4-TSB **N3-E4-TSB**

Figure S1. Optimized (M06-2X/6−31G*) geometries of **N2-E4-TSB** and **N3-E4-TSB**. NBO atomic charges are in red. Interaction distances are in Å.

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