

# Supplementary Information

## The 1,3-Dipolar Cycloaddition of Nitrile Oxide to Vinylacetic Acid: Computational Study of Transition States Selectivity, Solvent Effects, and Bicyclo Formation

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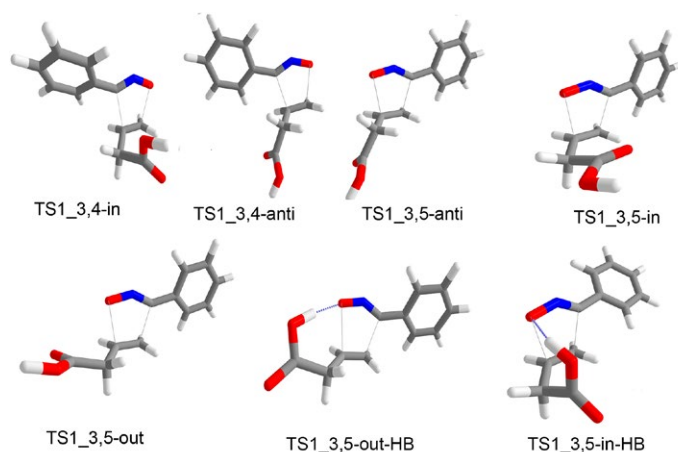


Figure S1. Transition structures found for the TS1.

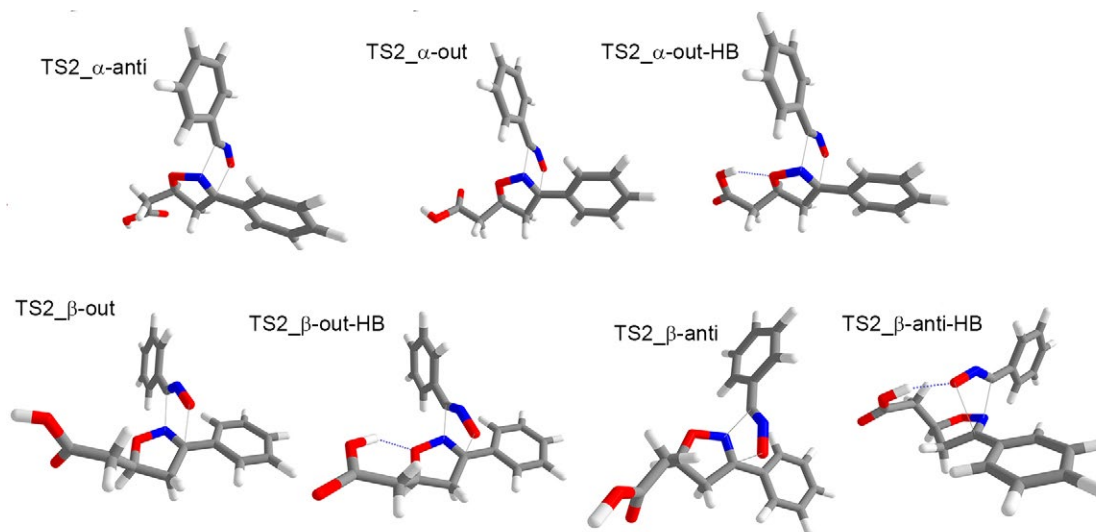
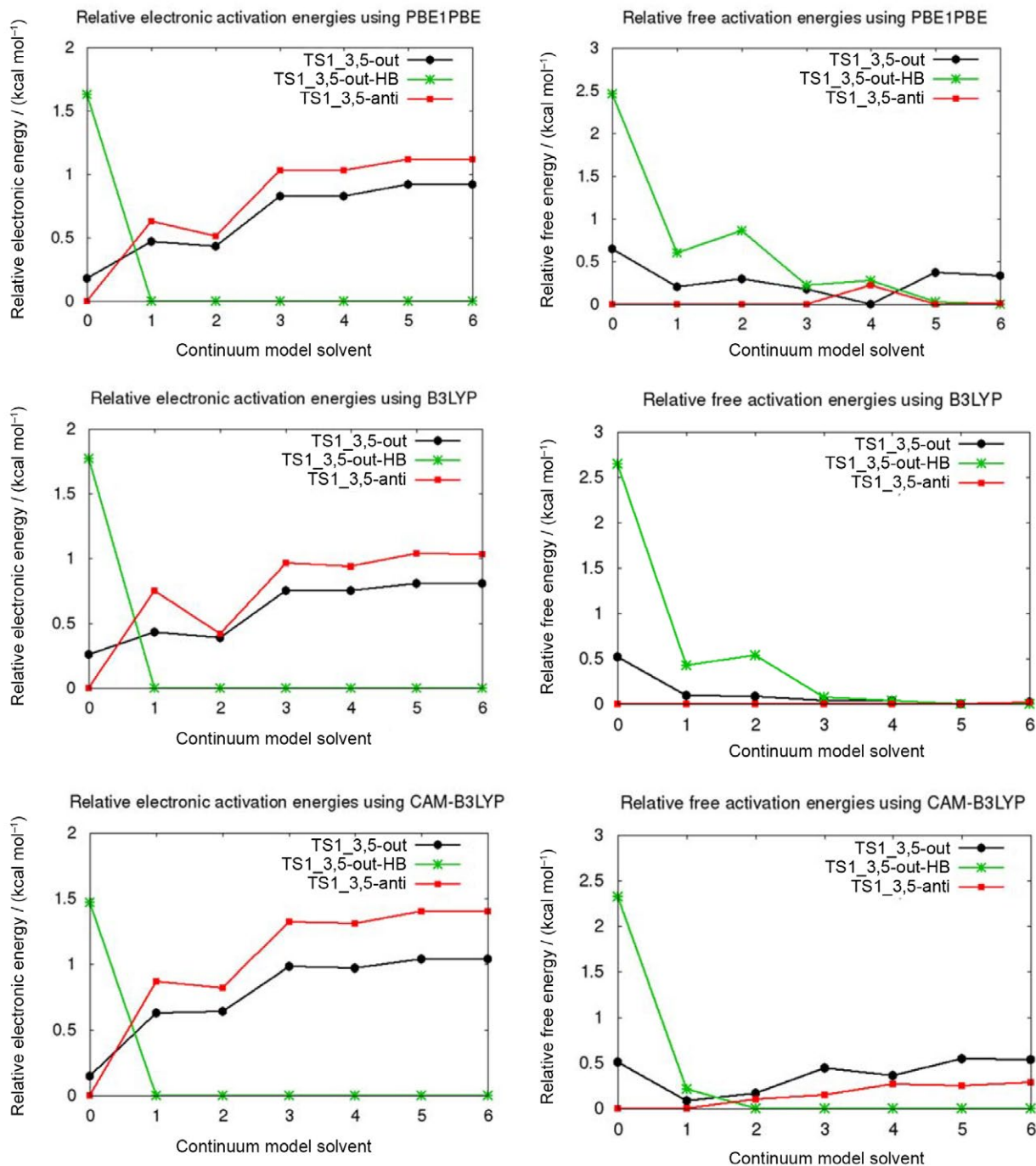


Figure S2. Transition structures found for the TS2.

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A clear visualization of the variation in energy involving the different functionals when solvent effects were included can be seen in Figure S3. This figure shows the relative activation electronic energies and activation free energies between structures obtained for the transition state, in relation to the structure with the lowest energy. For each one of the three functionals. The behavior of the electronic

energy graphs is very similar for the three functionals, and the relative energies are also very close. The structure containing a hydrogen bond (TS1\_3,5-out-HB) was largely stabilized by the inclusion of solvent effect, while the others were relatively destabilized. This destabilization increased with the dielectric constant of the medium. However, the free activation energy profile was quite different when

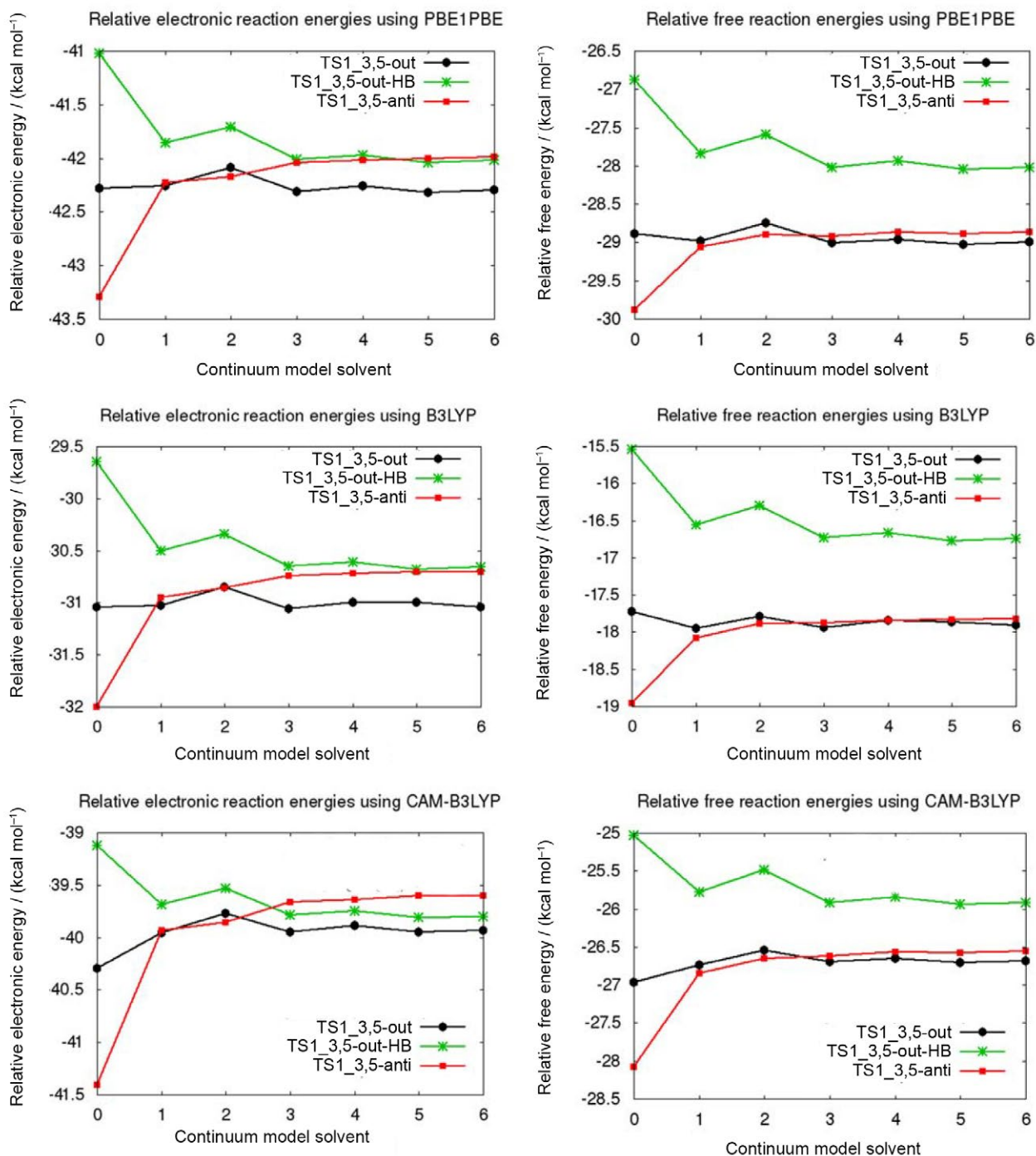


**Figure S3.** Activation electronic energy differences (left) and activation free energy differences (right) between transition structures obtained for TS1, at 298 K, in relation to the structure lower in energy in the gas phase (0) and with solvent effects: (1) CPCM/THF; (2) PCM/THF; (3) CPCM/ACN; (4) PCM/ACN; (5) CPCM/FORM; and (6) PCM/FORM. All energies in kcal mol<sup>-1</sup>. All optimized structures calculated with 6-311+G(2d,p) basis set.

CAM-B3LYP was used. For this functional, TS1\_3,5-out-HB presented a lower  $\Delta G^\ddagger$  when solvent effects were included. Whereas, TS1\_3,5-anti had a lower  $\Delta G^\ddagger$  when B3LYP and PBE1PBE were used.

The comparison between the reaction energies obtained from each functional can be seen in Figure S4. The behavior of the graphs of reaction free energies and reaction

electronic energies was similar for the three functionals. However, the B3LYP functional provided much higher reaction free energies, on the order of 10 kcal mol<sup>-1</sup>, i.e., a less exergonic reaction. In addition, the PBE1PBE and CAM-B3LYP functionals had closer results, but using PBE1PBE, the reaction was more exergonic by approximately 1-2 kcal mol<sup>-1</sup>.

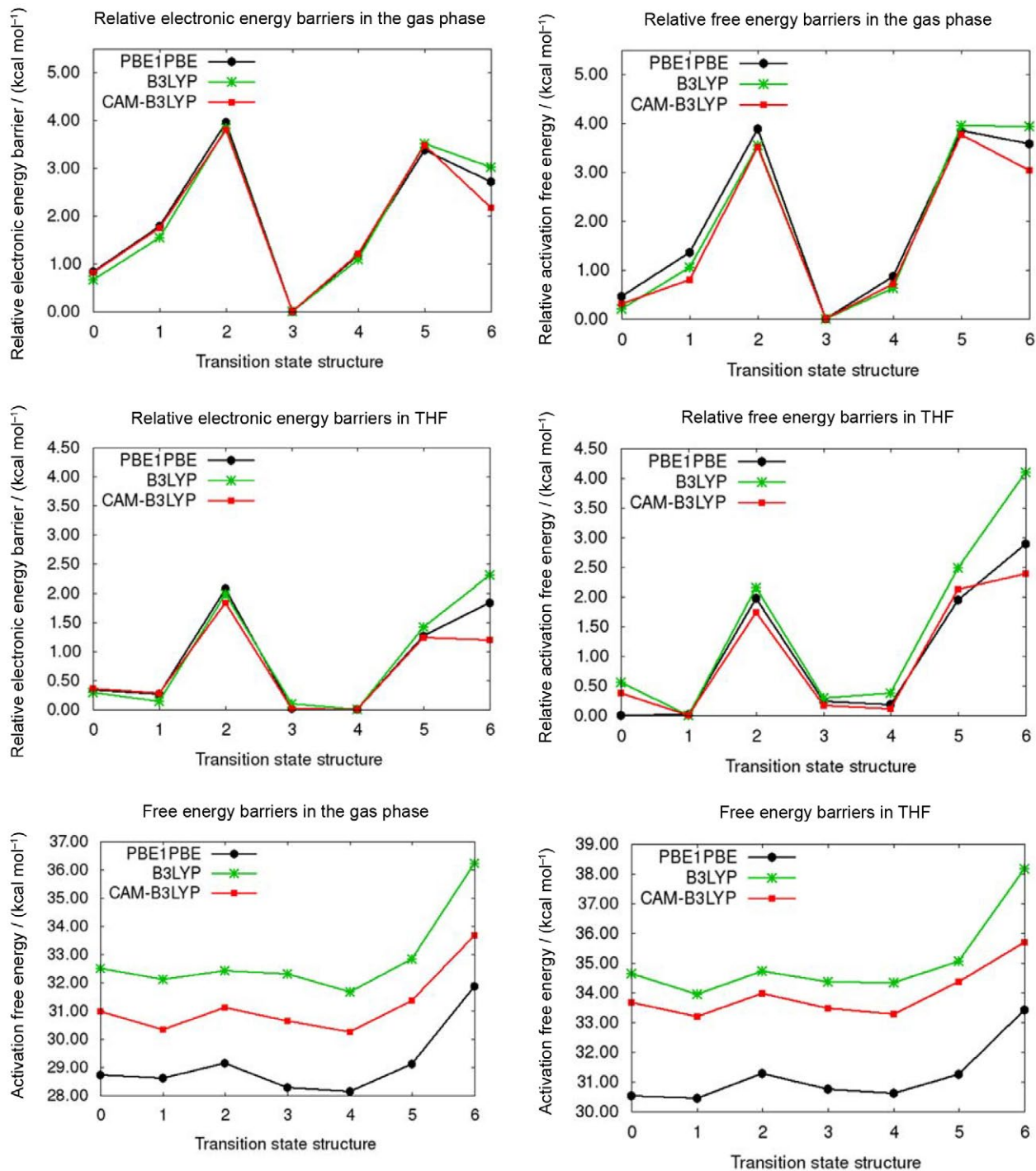


**Figure S4.** Reaction electronic energies (left) and reaction free energies (right) corresponding to structures of product1 with PBE1PBE, B3LYP and CAMB3LYP, in the gas phase (0) and with solvent effects: (1) CPCM/THF; (2) PCM/THF; (3) CPCM/ACN; (4) PCM/ACN; (5) CPCM/FORM; and (6) PCM/FORM. All energies in kcal mol<sup>-1</sup>. All optimized structures calculated with 6-311+G(2d,p) basis set.

In terms of electronic energy, in the gas phase, the TS2\_β-anti structure presented lower energy than other structures (Figure S5). When the 1,3-dipole approached the cycloadduct via the α face, the obtained electronic energy was slightly higher. When the solvent effect was included, the TS2\_β-out structure was stabilized and replaced by a slightly lower energy than that of TS2\_β-anti. This fact

again reflected the slight conformational preference for the *anti* position in the gas phase and for the out position when including the solvent effect.

Including solvent effects, α face attack began to have smaller  $\Delta G^\ddagger$ . In general, solvent effects were responsible for a decrease in energy differences between the lowest energy transition state structure and the other structures.

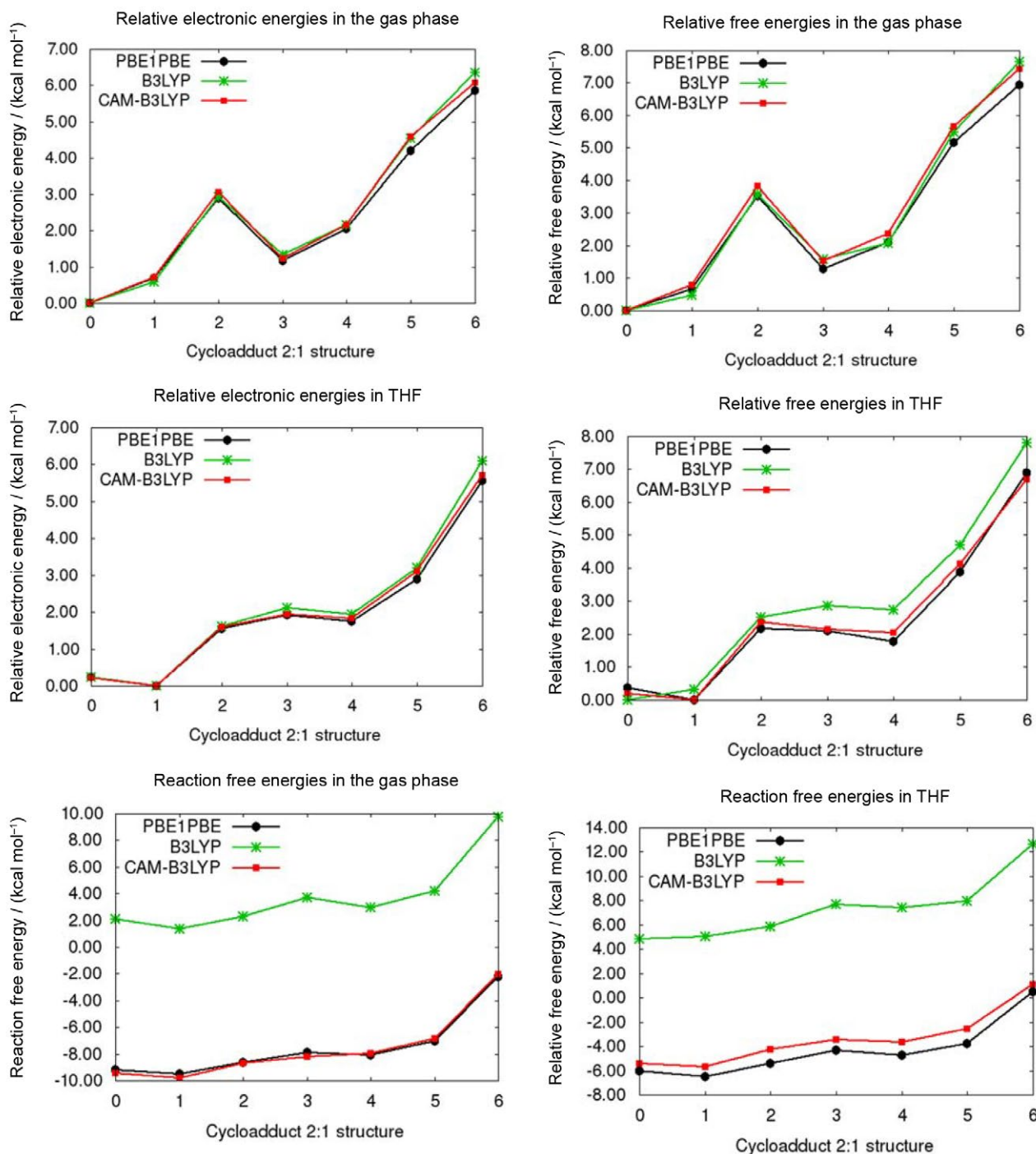


**Figure S5.** Energies for the transition states 2 related to the structure of lower energy, obtained with the three functionals, in the gas phase (on the left) and using CPCM and THF as solvent (on the right). Corresponding structures: 0 = TS2\_α-anti; 1 = TS2\_α-out; 2 = TS2\_α-out-HB; 3 = TS2\_β-anti; 4 = TS2\_β-out; 5 = TS2\_β-out-HB; 6 = TS2\_β-anti-HB.



Using THF as solvent, the four structures containing no hydrogen bonds presented energy differences less than 0.5 kcal mol<sup>-1</sup>. With the increment of the dielectric constant, the structures whose carboxyl group was in the out position were slightly stabilized, while the structures which presented a carboxylate group in the *anti* position were slightly destabilized.

Comparing the changes in reaction free energies and electronic free energies (Figure S6), the results were very similar between the three functionals, with a slightly larger difference in the PROD2\_trans-anti-HB structure containing a hydrogen bond. Thus, the relative energy differences between the seven calculated structures (see in Figure S2) were quite similar for the three functionals,



**Figure S6.** Energies found for bicyclo 2:1 in relation to the lowest energy structure, obtained in the gas phase (on the left) and using CPCM and THF as solvent (on the right). Corresponding structures: 0 = PROD2\_cis-anti; 1 = PROD2\_cis-out; 2 = PROD2\_cis-out-HB; 3 = PROD2\_trans-anti; 4 = PROD2\_trans-out; 5 = PROD2\_trans-out-HB; 6 = PROD2\_trans-anti-HB.

but the reaction free energies were very different. B3LYP provided much higher  $\Delta G_{\text{rxn}}$ , showing positive values for all structures. PBE1PBE and CAM-B3LYP provided similar values of reaction free energy, especially in the gas phase, where these values were practically the same. In terms of the stability of the structures (electronic energies) in the gas phase, the PROD2\_cis-anti structure

had a lower electronic energy than PROD2\_trans-anti by 1.17, 1.34 and 1.23 kcal mol<sup>-1</sup> (in PBE1PBE, B3LYP and CAM-B3LYP, respectively). When the solvent effect was included, the PROD2\_cis-out structure was favored over the PROD2\_trans-out structure by 1.76, 1.95 and 1.84 kcal mol<sup>-1</sup> (in PBE1PBE, B3LYP and CAM-B3LYP, respectively).

**Table S1.** Dipole moments (in D) of transition states and respective differences between dipole moment of transition state and sum of dipole moment of reactants and products (in parentheses), at 6-311+G(2d,p) level

	$\mu$ ( $\Delta\mu = \mu(\text{transition state}) - \mu(\text{reactants})$ ) / D			
	Gas phase	CPCM/THF	CPCM/ACN	CPCM/FORM
TS1_3,5-out				
PBE1PBE	4.3 (-1.9)	5.9 (-2.2)	6.3 (-2.1)	6.4 (-2.1)
B3LYP	4.3 (-1.9)	6.1 (-2.2)	6.5 (-2.1)	6.5 (-2.2)
CAM-B3LYP	4.6 (-2.0)	6.5 (-2.1)	6.8 (-2.2)	6.9 (-2.2)
TS1_3,5-out-HB				
PBE1PBE	9.0 (2.8)	11.2 (3.1)	11.6 (3.2)	11.6 (3.1)
B3LYP	9.0 (2.8)	11.2 (2.9)	11.6 (3.0)	11.7 (3.0)
CAM-B3LYP	9.4 (2.8)	11.7 (3.1)	12.1 (3.1)	12.2 (3.1)
TS1_3,5-anti				
PBE1PBE	3.9 (-2.3)	4.9 (-3.2)	5.1 (-3.3)	5.1 (-3.4)
B3LYP	3.7 (-2.3)	4.8 (-3.2)	5.1 (-3.3)	5.1 (-3.4)
CAM-B3LYP	4.0 (-2.6)	5.1 (-3.5)	5.3 (-3.7)	5.3 (-3.8)

$\mu$ : dipole moment; CPCM: conductor-like polarizable continuum model; THF: tetrahydrofuran; ACN: acetonitrile; FORM: formamide.

**Table S2.** Calculated activation barriers (kcal mol<sup>-1</sup>) of electronic energy, enthalpy and free energy, and activation entropies (cal mol<sup>-1</sup> K<sup>-1</sup>) obtained at 298 K in the gas phase, THF, acetonitrile and formamide, for both continuum models, CPCM and PCM

Transition state	Method	Solvent	CPCM Model / (kcal mol <sup>-1</sup> )				PCM Model / (kcal mol <sup>-1</sup> )			
			$\Delta E_e^\ddagger$	$\Delta H^\ddagger$	$\Delta G^\ddagger$	$\Delta S^\ddagger$ <sup>a</sup>	$\Delta E_e^\ddagger$	$\Delta H^\ddagger$	$\Delta G^\ddagger$	$\Delta S^\ddagger$ <sup>a</sup>
TS1_3,4-anti	PBE1PBE	gas phase	16.49	16.00	29.28	-44.54	-	-	-	-
		THF	18.13	17.81	29.89	-40.52	18.12	17.78	30.10	-41.35
		acetonitrile	18.34	18.03	30.18	-40.76	18.32	18.02	30.01	-40.23
		formamide	18.38	18.07	30.21	-40.74	18.37	18.07	30.13	-40.50
	B3LYP	gas phase	20.33	19.87	32.56	-42.56	-	-	-	-
		THF	21.69	21.31	33.73	-41.68	21.66	21.30	33.47	-40.84
		acetonitrile	21.91	21.53	34.08	-42.11	21.91	21.53	34.07	-42.09
		formamide	21.94	21.57	34.10	-42.06	21.94	21.57	34.10	-42.06
	CAM-B3LYP	gas phase	20.47	19.96	33.22	-44.49	-	-	-	-
		THF	22.15	21.80	34.08	-41.22	22.18	21.80	34.31	-41.98
		acetonitrile	22.35	22.02	33.90	-39.86	22.37	22.03	34.22	-40.90
		formamide	22.37	22.06	33.89	-39.68	22.37	22.06	33.73	-39.15
TS1_3,5-anti	PBE1PBE	gas phase	14.46	14.15	26.21	-40.47	-	-	-	-
		THF	15.95	15.68	27.47	-39.57	15.96	15.67	27.66	-40.23
		acetonitrile	16.19	15.93	27.59	-39.11	16.19	15.93	27.65	-39.32
		formamide	16.23	15.98	27.64	-39.11	16.23	15.98	27.66	-39.20
	B3LYP	gas phase	17.66	17.31	29.48	-40.83	-	-	-	-
		THF	19.25	18.93	30.96	-40.36	19.26	18.91	31.21	-41.27
		acetonitrile	19.50	19.19	31.14	-40.12	19.51	19.19	31.24	-40.46
		formamide	19.55	19.24	31.18	-40.08	19.55	19.24	31.22	-40.21
	CAM-B3LYP	gas phase	18.04	17.68	29.87	-40.89	-	-	-	-
		THF	19.93	19.61	31.65	-40.40	19.96	19.59	32.01	-41.66
		acetonitrile	20.22	19.92	31.77	-39.77	20.24	19.92	31.96	-40.41
		formamide	20.27	19.97	31.78	-39.64	20.28	19.97	31.86	-39.88
TS1_3,5-out	PBE1PBE	gas phase	14.63	14.26	26.86	-42.27	-	-	-	-
		THF	15.83	15.51	27.67	-40.83	15.88	15.53	27.96	-41.69
		acetonitrile	15.99	15.68	27.76	-40.55	15.99	15.69	27.43	-39.40
		formamide	16.03	15.71	28.00	-41.24	16.03	15.72	27.98	-41.14
	B3LYP	gas phase	17.93	17.53	30.00	-41.85	-	-	-	-
		THF	19.15	18.80	31.05	-41.11	19.23	18.84	31.30	-41.79
		acetonitrile	19.30	18.95	31.19	-41.06	19.32	18.97	31.29	-41.34
		formamide	19.32	18.98	31.18	-40.96	19.33	18.98	31.22	-41.05
	CAM-B3LYP	gas phase	18.19	17.78	30.38	-42.29	-	-	-	-
		THF	19.69	19.31	31.73	-41.65	19.77	19.36	32.08	-42.68
		acetonitrile	19.88	19.51	32.06	-42.11	19.90	19.52	32.05	-42.04
		formamide	19.91	19.54	32.08	-42.10	19.92	19.55	32.10	-42.13
TS1_3,5-out-HB	PBE1PBE	gas phase	16.09	15.58	28.66	-43.91	-	-	-	-
		THF	15.35	14.78	28.08	-44.61	15.45	14.85	28.52	-45.89
		acetonitrile	15.16	14.59	27.80	-44.34	15.16	14.60	27.70	-43.98
		formamide	15.11	14.55	27.67	-44.01	15.11	14.55	27.65	-43.95
	B3LYP	gas phase	19.44	18.88	32.13	-44.47	-	-	-	-
		THF	18.72	18.13	31.39	-44.49	18.83	18.21	31.75	-45.44
		acetonitrile	18.54	17.95	31.22	-44.54	18.57	17.97	31.28	-44.67
		formamide	18.51	17.91	31.18	-44.53	18.52	17.92	31.20	-44.56
	CAM-B3LYP	gas phase	19.52	18.96	32.19	-44.40	-	-	-	-
		THF	19.06	18.45	31.86	-45.01	19.13	18.51	31.91	-44.97
		acetonitrile	18.90	18.28	31.62	-44.74	18.93	18.30	31.69	-44.93
		formamide	18.87	18.25	31.53	-44.56	18.88	18.26	31.56	-44.65

<sup>a</sup>cal mol<sup>-1</sup> K<sup>-1</sup>.  $\Delta E_e^\ddagger$ ,  $\Delta H^\ddagger$ ,  $\Delta G^\ddagger$ ,  $\Delta S^\ddagger$ : electronic energy, enthalpy, free energy, and entropy of activation, respectively; THF: tetrahydrofuran.

**Table S3.** Calculated reaction energies (kcal mol<sup>-1</sup>) of zero point corrected electronic energy, enthalpy and free energy, and activation entropies (cal mol<sup>-1</sup> K<sup>-1</sup>) of the cycloaddition reaction of BNO and vinyl acetic acid, obtained at 298 K in gas phase, THF, acetonitrile and formamide, for both continuum models, CPCM and PCM

Product of the reaction	Method	Solvent	CPCM Model / (kcal mol <sup>-1</sup> )				PCM Model / (kcal mol <sup>-1</sup> )			
			$\Delta E_{\text{rxn}}^{\text{c}}$	$\Delta H_{\text{rxn}}$	$\Delta G_{\text{rxn}}$	$\Delta S_{\text{rxn}}^{\text{a}}$	$\Delta E_{\text{rxn}}^{\text{c}}$	$\Delta H_{\text{rxn}}$	$\Delta G_{\text{rxn}}$	$\Delta S_{\text{rxn}}^{\text{a}}$
PROD1_3,4-anti	PBE1PBE	gas phase	-40.17	-41.27	-26.59	-49.25	-	-	-	-
		THF	-39.12	-40.16	-25.79	-48.24	-39.05	-40.13	-25.54	-48.97
		acetonitrile	-38.93	-39.96	-25.66	-47.98	-38.91	-39.95	-25.59	-48.21
		formamide	-38.89	-39.92	-25.63	-47.95	-38.88	-39.92	-25.61	-48.02
	B3LYP	gas phase	-28.54	-29.61	-15.09	-48.74	-	-	-	-
		THF	-27.54	-28.57	-14.26	-48.00	-27.47	-28.53	-14.09	-48.46
		acetonitrile	-27.34	-28.37	-14.05	-48.07	-27.32	-28.36	-13.99	-48.22
		formamide	-27.31	-28.33	-14.00	-48.08	-27.30	-28.33	-13.99	-48.13
	CAM-B3LYP	gas phase	-38.02	-39.09	-24.47	-49.07	-	-	-	-
		THF	-36.59	-37.63	-23.23	-48.32	-36.56	-37.60	-23.24	-48.21
		acetonitrile	-36.34	-37.37	-23.00	-48.23	-36.33	-37.36	-22.96	-48.32
		formamide	-36.29	-37.32	-22.95	-48.24	-36.29	-37.32	-22.93	-48.30
PROD1_3,5-anti	PBE1PBE	gas phase	-43.29	-44.40	-29.88	-48.71	-	-	-	-
		THF	-42.23	-43.31	-29.06	-47.79	-42.17	-43.27	-28.90	-48.22
		acetonitrile	-42.04	-43.10	-28.92	-47.58	-42.02	-43.09	-28.87	-47.71
		formamide	-42.00	-43.06	-28.89	-47.55	-41.99	-43.06	-28.87	-47.60
	B3LYP	gas phase	-32.00	-33.07	-18.96	-47.33	-	-	-	-
		THF	-30.95	-31.98	-18.08	-46.66	-30.86	-31.92	-17.89	-47.08
		acetonitrile	-30.74	-31.77	-17.88	-46.63	-30.72	-31.76	-17.84	-46.70
		formamide	-30.70	-31.73	-17.83	-46.64	-30.70	-31.73	-17.82	-46.66
	CAM-B3LYP	gas phase	-41.41	-42.49	-28.08	-48.34	-	-	-	-
		THF	-39.93	-40.97	-26.85	-47.39	-39.86	-40.93	-26.65	-47.92
		acetonitrile	-39.66	-40.70	-26.62	-47.22	-39.64	-40.68	-26.57	-47.35
		formamide	-39.60	-40.64	-26.58	-47.20	-39.60	-40.64	-26.56	-47.24
PROD1_3,5-out	PBE1PBE	gas phase	-42.28	-43.40	-28.89	-48.68	-	-	-	-
		THF	-42.26	-43.35	-28.98	-48.23	-42.09	-43.19	-28.75	-48.44
		acetonitrile	-42.31	-43.39	-29.01	-48.24	-42.26	-43.34	-28.96	-48.27
		formamide	-42.32	-43.40	-29.03	-48.23	-42.30	-43.38	-29.00	-48.25
	B3LYP	gas phase	-31.04	-32.14	-17.73	-48.36	-	-	-	-
		THF	-31.03	-32.08	-17.95	-47.41	-30.85	-31.91	-17.79	-47.39
		acetonitrile	-31.06	-32.11	-17.94	-47.54	-31.00	-32.06	-17.84	-47.69
		formamide	-31.00	-32.06	-17.87	-47.59	-31.04	-32.10	-17.91	-47.61
	CAM-B3LYP	gas phase	-40.30	-41.39	-26.97	-48.41	-	-	-	-
		THF	-39.96	-41.02	-26.74	-47.92	-39.77	-40.85	-26.54	-48.00
		acetonitrile	-39.95	-41.01	-26.70	-48.00	-39.89	-40.96	-26.65	-47.99
		formamide	-39.95	-41.01	-26.71	-47.99	-39.93	-40.99	-26.69	-48.00
PROD1_3,5-out-HB	PBE1PBE	gas phase	-41.02	-42.33	-26.88	-51.85	-	-	-	-
		THF	-41.86	-43.17	-27.84	-51.42	-41.71	-43.04	-27.59	-51.86
		acetonitrile	-42.01	-43.32	-28.02	-51.33	-41.97	-43.28	-27.94	-51.49
		formamide	-42.04	-43.34	-28.05	-51.33	-42.02	-43.33	-28.02	-51.38
	B3LYP	gas phase	-29.65	-30.94	-15.54	-51.68	-	-	-	-
		THF	-30.50	-31.80	-16.56	-51.13	-30.34	-31.66	-16.30	-51.54
		acetonitrile	-30.65	-31.94	-16.73	-51.04	-30.61	-31.91	-16.67	-51.13
		formamide	-30.68	-31.97	-16.77	-51.02	-30.66	-31.96	-16.74	-51.06
	CAM-B3LYP	gas phase	-39.12	-40.42	-25.03	-51.63	-	-	-	-
		THF	-39.69	-40.98	-25.78	-51.01	-39.53	-40.84	-25.49	-51.52
		acetonitrile	-39.79	-41.08	-25.92	-50.87	-39.75	-41.04	-25.84	-51.02
		formamide	-39.81	-41.10	-25.94	-50.86	-39.80	-41.09	-25.92	-50.91

<sup>a</sup>cal mol<sup>-1</sup> K<sup>-1</sup>.  $\Delta E_{\text{rxn}}^{\text{c}}$ ,  $\Delta H_{\text{rxn}}$ ,  $\Delta G_{\text{rxn}}$ ,  $\Delta S_{\text{rxn}}^{\text{a}}$ : electronic energy, enthalpy, free energy, and entropy of reaction, respectively; THF: tetrahydrofuran.



**Table S4.** Calculated activation and reaction barriers (kcal mol<sup>-1</sup>) of electronic energy, enthalpy and free energy, and activation entropies (cal mol<sup>-1</sup> K<sup>-1</sup>) obtained at 298 K for the second cycloaddition, in the gas phase, THF, acetonitrile and formamide, using CPCMC as solvent model

Transition state/product of the reaction	Method	Solvent	Activation energy / (kcal mol <sup>-1</sup> )				Reaction energy / (kcal mol <sup>-1</sup> )				
			$\Delta E_s^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger a}$	$\Delta E_{rxn}^c$	$\Delta H_{rxn}$	$\Delta G_{rxn}$	$\Delta S_{rxn}^a$	
TS2_α-anti/ PROD2_cis-anti	B3LYP	gas phase	18.82	18.61	32.51	-46.64	-12.59	-13.46	2.12	-52.29	
		THF	21.20	21.07	34.51	-45.12	-9.10	-9.90	4.69	-48.94	
		acetonitrile	21.71	21.60	34.91	-44.68	-8.32	-9.11	5.63	-49.45	
		formamide	21.74	21.63	34.91	-44.57	-8.23	-9.02	5.75	-49.57	
	PBE1PBE	gas phase	15.45	15.32	28.73	-45.00	-23.48	-24.33	-9.18	-50.82	
		THF	17.66	17.62	30.43	-42.99	-20.25	-21.07	-6.12	-50.17	
		CAM-B3LYP	gas phase	17.69	17.53	30.96	-45.07	-23.62	-24.45	-9.46	-50.28
			THF	20.47	20.39	33.56	-44.20	-19.61	-20.41	-5.51	-50.01
TS2_α-out/ PROD2_cis-out	B3LYP	gas phase	19.71	19.48	32.35	-46.54	-12.00	-12.88	2.59	-51.90	
		THF	21.04	20.95	33.95	-43.62	-9.33	-10.17	5.01	-50.91	
		acetonitrile	21.32	21.27	34.06	-42.92	-8.72	-9.55	5.65	-51.00	
		formamide	21.31	21.26	34.02	-42.84	-8.68	-9.50	5.68	-50.95	
	PBE1PBE	gas phase	16.40	16.25	29.62	-44.86	-22.77	-23.61	-8.51	-50.68	
		THF	17.60	17.57	30.45	-43.22	-20.49	-21.30	-6.50	-49.66	
		CAM-B3LYP	gas phase	18.63	18.49	31.45	-43.48	-22.91	-23.74	-8.68	-50.54
			THF	20.39	20.33	33.19	-43.13	-19.82	-20.63	-5.71	-50.07
TS2_α-out-HB/ PROD2_cis-out-HB	B3LYP	gas phase	21.98	21.68	35.84	-47.51	-9.65	-10.66	5.69	-54.86	
		THF	22.89	22.70	36.11	-45.00	-7.71	-8.68	7.21	-53.33	
		acetonitrile	23.18	23.00	36.21	-44.33	-7.19	-8.15	7.61	-52.88	
		formamide	23.19	23.01	36.27	-44.49	-7.16	-8.12	7.62	-52.80	
	PBE1PBE	gas phase	18.56	18.32	32.16	-46.44	-20.59	-21.57	-5.64	-53.44	
		THF	19.39	19.25	32.41	-44.14	-18.93	-19.88	-4.32	-52.22	
		CAM-B3LYP	gas phase	20.69	20.41	34.15	-46.10	-20.56	-21.53	-5.65	-53.29
			THF	21.96	21.80	34.93	-44.04	-18.22	-19.19	-3.33	-53.21
TS2_β-out/ PROD2_trans-out	B3LYP	gas phase	19.24	18.97	32.92	-46.78	-10.44	-11.33	4.19	-52.08	
		THF	20.91	20.74	34.33	-45.62	-7.38	-8.26	7.43	-52.65	
		acetonitrile	21.31	21.15	34.68	-45.41	-6.70	-7.58	8.07	-52.51	
		formamide	21.31	20.57	34.67	-47.32	-6.64	-7.51	8.11	-52.44	
	PBE1PBE	gas phase	15.78	15.57	28.15	-42.20	-21.43	-22.30	-7.07	-51.12	
		THF	17.33	17.19	30.61	-45.03	-18.73	-19.55	-4.71	-49.79	
		CAM-B3LYP	gas phase	18.09	17.89	31.36	-45.20	-21.45	-22.32	-7.08	-51.13
			THF	20.11	19.99	33.29	-44.64	-17.98	-18.82	-3.65	-50.92
TS2_β-out-HB/ PROD2_trans-out-HB	B3LYP	gas phase	21.68	21.24	36.25	-50.37	-8.05	-9.14	7.60	-56.19	
		THF	22.33	21.94	36.45	-48.66	-6.15	-7.23	9.38	-55.72	
		acetonitrile	22.58	22.21	36.64	-48.45	-5.63	-6.71	9.83	-55.49	
		formamide	22.56	22.19	36.59	-48.32	-5.60	-6.67	9.84	-55.43	
	PBE1PBE	gas phase	17.98	17.61	32.12	-48.72	-19.28	-20.33	-4.03	-54.69	
		THF	18.58	18.24	32.38	-47.43	-17.60	-18.65	-2.63	-53.75	
		CAM-B3LYP	gas phase	20.37	19.98	34.41	-48.44	-19.05	-20.10	-3.81	-54.66
			THF	21.35	21.00	35.32	-48.07	-16.70	-17.76	-1.59	-54.25
TS2_β-anti/ PROD2_trans-anti	B3LYP	gas phase	18.15	17.87	32.30	-48.40	-11.24	-12.16	3.69	-53.18	
		THF	21.01	20.85	34.25	-44.94	-7.22	-8.10	7.54	-52.50	
		acetonitrile	21.67	21.51	34.93	-45.01	-6.37	-7.23	8.31	-52.16	
		formamide	21.72	21.57	35.00	-45.05	-6.27	-7.13	8.38	-52.05	
	PBE1PBE	gas phase	14.61	14.40	28.27	-46.52	-22.31	-23.17	-7.89	-51.27	
		THF	17.35	17.22	30.66	-45.09	-18.57	-19.42	-4.40	-50.41	
		CAM-B3LYP	gas phase	16.88	16.65	30.64	-46.97	-22.40	-23.27	-7.94	-51.45
			THF	20.13	20.01	33.35	-44.74	-17.88	-18.72	-3.56	-50.85
TS2_β-anti-HB/ PROD2_trans-anti-HB	B3LYP	gas phase	21.18	20.58	36.22	-52.48	-6.23	-7.41	9.77	-57.65	
		THF	23.22	22.68	38.05	-51.60	-3.24	-4.40	12.50	-56.72	
		acetonitrile	23.71	23.18	38.46	-51.27	-2.54	-3.70	13.10	-56.36	
		formamide	23.73	23.21	38.46	-51.18	-2.47	-3.63	13.14	-56.26	
	PBE1PBE	gas phase	17.33	16.83	31.85	-50.39	-17.63	-18.77	-2.24	-55.47	
		THF	19.13	18.69	33.41	-49.42	-14.96	-16.10	0.46	-55.58	
		CAM-B3LYP	gas phase	19.07	18.52	33.68	-50.87	-17.54	-18.70	-2.04	-55.89
			THF	21.31	20.84	35.58	-49.48	-14.13	-15.26	0.99	-54.54

<sup>a</sup>cal mol<sup>-1</sup> K<sup>-1</sup>.  $\Delta E_s^{\ddagger}$ ,  $\Delta H^{\ddagger}$ ,  $\Delta G^{\ddagger}$ ,  $\Delta S^{\ddagger}$ : electronic energy, enthalpy, free energy, and entropy of activation, respectively;  $\Delta E_{rxn}^c$ ,  $\Delta H_{rxn}$ ,  $\Delta G_{rxn}$ ,  $\Delta S_{rxn}^a$ : electronic energy, enthalpy, free energy, and entropy of reaction, respectively; THF: tetrahydrofuran.