

Table S1. Calculated activation energies ($\Delta E^\#/\text{kcal mol}^{-1}$), reaction energies ($\Delta E_r/\text{kcal mol}^{-1}$), activation Gibbs free energies ($\Delta G^\#/\text{kcal mol}^{-1}$), activation enthalpies ($\Delta H^\#/\text{kcal mol}^{-1}$), and activation entropies ($\Delta S^\#/\text{cal mol}^{-1}\text{K}^{-1}$) in gas phase at *meta* pathways of the 1,3-dipolar cycloaddition between **TVE (1)** and 3-oxo-1,2-pyrazolidinium ylides (**2a-e**) at the B3LYP/cc-pVDZ levels of theory.

Reaction	TSs	$\Delta E^\#$	ΔE_r	$\Delta G^\#$	$\Delta H^\#$	$\Delta S^\#$
1+2a→5a	TS3a	27.20	-11.14	34.07	26.98	-42.19
1+2a→6a	TS4a	15.86	-11.12	26.54	13.80	-40.84
1+2b→5b	TS3b	22.82	-10.53	29.08	16.93	-40.73
1+2b→6b	TS4b	14.32	-10.53	26.86	17.00	-47.37
1+2c→5c	TS3c	20.54	-11.46	33.49	20.75	-42.72
1+2c→6c	TS4c	13.99	-11.61	26.82	16.13	-47.03
1+2d→5d	TS3d	20.65	-11.38	33.41	20.90	-41.97
1+2d→6d	TS4d	14.19	-11.54	26.77	16.21	-45.34
1+2e→5e	TS3e	20.75	-11.16	33.63	21.00	-42.35
1+2e→6e	TS4e	14.80	-11.36	27.69	16.33	-48.83

Table S2. Calculated reaction Gibbs free energies (ΔG_r / kcal mol⁻¹), reaction enthalpies (ΔH_r / kcal mol⁻¹) and reaction entropies (ΔS_r / cal mol⁻¹K⁻¹) in gas phase at *ortho* and *meta* pathways of the 1,3-dipolar cycloaddition between TVE (**1**) and 3-oxo-1,2-pyrazolidinium ylides (**2a-2e**) at the B3LYP/cc-pVDZ level of theory.

Reaction	TSs	ΔG_r	ΔH_r	ΔS_r
1+2a→3a	TS1a	-2.45	-16.59	-47.43
1+2a→4a	TS2a	-2.75	-16.62	-46.56
1+2b→3b	TS1b	-2.08	-15.94	-41.06
1+2b→4b	TS2b	-2.11	-16.10	-42.06
1+2c→3c	TS1c	-2.69	-16.95	-47.83
1+2c→4c	TS2c	-2.57	-16.89	-48.06
1+2d→3d	TS1d	-2.77	-16.84	-47.20
1+2d→4d	TS2d	-2.60	-16.80	-47.50
1+2e→3e	TS1e	-2.49	-16.57	-47.23
1+2e→4e	TS2e	-2.06	-16.44	-48.27
1+2a→5a	TS3a	2.63	-11.38	-47.00
1+2a→6a	TS4a	2.51	-11.48	-46.97
1+2b→5b	TS3b	2.97	-10.76	-40.51
1+2b→6b	TS4b	2.05	-10.76	-40.41
1+2c→5c	TS3c	1.86	-11.69	-45.46
1+2c→6c	TS4c	2.01	-11.96	-46.86
1+2d→5d	TS3d	1.96	-11.60	-45.52
1+2d→6d	TS4d	1.86	-11.86	-46.04
1+2e→5e	TS3e	2.81	-11.42	-47.75
1+2e→6e	TS4e	2.11	-11.67	-46.23

Table S3. Calculated reaction Gibbs free energies (ΔG_r / kcal mol⁻¹), reaction enthalpies (ΔH_r / kcal mol⁻¹) and reaction entropies (ΔS_r / cal mol⁻¹K⁻¹) in gas phase for the elimination of ethanol from cycloadduct **4** at the B3LYP/cc-pVDZ level of theory.

Reaction	TSs	ΔG_r	ΔH_r	ΔS_r
4a → 7a	TS5a	-12.16	-13.08	-3.08
4b → 7b	TS5b	-10.83	-11.94	-3.25
4c → 7c	TS5c	-10.74	-11.46	-2.40
4d → 7d	TS5d	-10.75	-11.26	-1.69
4e → 7e	TS5e	-10.32	-10.80	-1.58

Table S4- Calculated activation energies ($\Delta E^{\#}_{Sol}$ / kcal mol⁻¹) and reaction energies ($\Delta E_{r Sol}$ / kcal mol⁻¹) in DMSO at *ortho* and *meta* pathways of the 1,3-dipolar cycloaddition between **TVE (1)** and 3-oxo-1,2-pyrazolidinium ylides (**2a-2e**) and the elimination of ethanol from cycloadduct **4** at the B3LYP/cc-pVDZ level of theory.

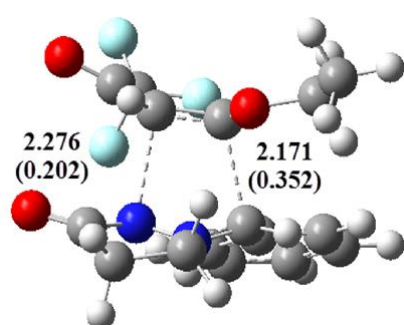
Reaction	TSs	$\Delta E^{\#}_{Sol}$	$\Delta E_{r Sol}$
1+2a→3a	TS1a	21.10	-12.66
1+2a→4a	TS2a	7.99	-11.62
1+2b→3b	TS1b	20.62	-14.17
1+2b→4b	TS2b	6.14	-13.50
1+2c→3c	TS1c	23.41	-12.56
1+2c→4c	TS2c	9.81	-11.49
1+2d→3d	TS1d	23.38	-12.48
1+2d→4d	TS2d	10.08	-11.36
1+2e→3e	TS1e	24.03	-11.77
1+2e→4e	TS2e	11.49	-10.76
1+2a→5a	TS3a	33.65	-17.16
1+2a→6a	TS4a	19.48	-18.81
1+2b→5b	TS3b	23.05	-16.44
1+2b→6b	TS4b	19.52	-18.33
1+2c→5c	TS3c	30.07	-14.48
1+2c→6c	TS4c	22.06	-16.25
1+2d→5d	TS3d	29.79	-14.86
1+2d→6d	TS4d	21.92	-16.52
1+2e→5e	TS3e	30.00	-14.61
1+2e→6e	TS4e	22.92	-16.14
4a→7a	TS5a	23.68	-7.94
4b→7b	TS5b	24.06	-6.46
4c→7c	TS5c	25.72	-6.68
4d→7d	TS5d	27.66	-6.71
4e→7e	TS5e	26.23	-5.79

Table S5. Calculated activation energies ($\Delta E^\ddagger$ /kcal mol⁻¹), activation Gibbs free energies ($\Delta G^\ddagger$ /kcal mol⁻¹), and reaction energies (ΔE_r /kcal mol⁻¹) at *ortho* pathway of the 1,3-dipolar cycloaddition between TVE (**1**) and 3-oxo-1,2-pyrazolidinium ylides **2a-2e** and the elimination of ethanol from cycloadduct **4** at the MPWB1K/cc-pVDZ level of theory.

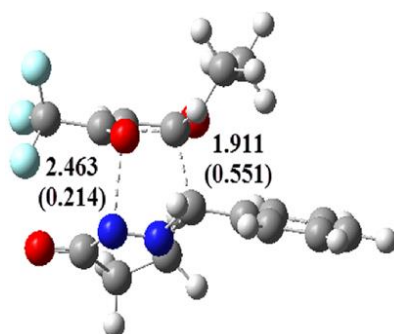
Reaction	TSs	$\Delta E^\ddagger$	$\Delta G^\ddagger$	ΔE_r
1+2a→3a	TS1a	13.27	28.47	-26.03
1+2a→4a	TS2a	2.88	19.18	-24.09
1+2b→3b	TS1b	12.48	31.53	-23.31
1+2b→4b	TS2b	1.59	17.96	-21.36
1+2c→3c	TS1c	12.45	28.81	-23.90
1+2c→4c	TS2c	1.66	17.18	-21.36
1+2d→3d	TS1d	12.61	28.35	-24.15
1+2d→4d	TS2d	1.86	17.37	-21.56
1+2e→3e	TS1e	12.83	28.98	-23.71
1+2e→4e	TS2e	2.33	16.20	-20.96
4a→7a	TS5a	24.57	41.29	-7.94
4b→7b	TS5b	24.22	42.09	-6.47
4c→7c	TS5c	24.67	40.24	-6.68
4d→7d	TS5d	26.77	43.13	-6.71
4e→7e	TS5e	24.96	43.15	-5.79

Table S6. Calculated activation energies ($\Delta E^\ddagger$ /kcal mol⁻¹) and reaction energies (ΔE_r /kcal mol⁻¹) of the 1,3-dipolar cycloaddition between 1-ethoxybut-3-en-2-one **1a** and 1-ethoxy-4,4,4-trifluorobut-1-ene **1b** with 3-oxo-1,2-pyrazolidinium ylide **2a** at the B3LYP/cc-pVDZ level of theory.

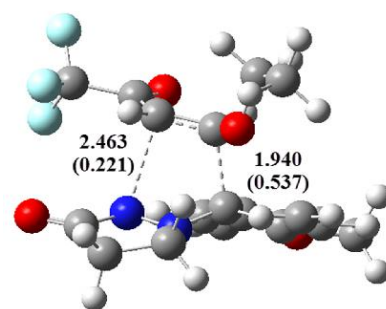
Reaction	TSs	$\Delta E^\ddagger$	ΔE_r
1a+2a→3aa	TS1aa	21.38	-21.03
1a+2a→4aa	TS2aa	17.81	-19.92
1a+2a→5aa	TS3aa	21.69	-16.37
1a+2a→6aa	TS4aa	22.08	-14.47
4aa→7aa	TS5aa	36.89	-3.71
1b+2a→3ba	TS1ba	23.63	-13.16
1b+2a→4ba	TS2ba	15.57	-12.25
1b+2a→5ba	TS3ba	29.85	-9.35
1b+2a→6ba	TS4ba	21.19	-2.18
4ba→7ba	TS5ba	37.26	-2.42



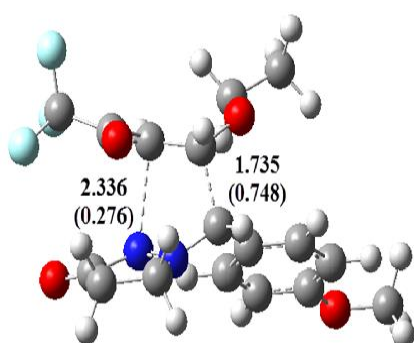
TS3a (GEDT=0.037)



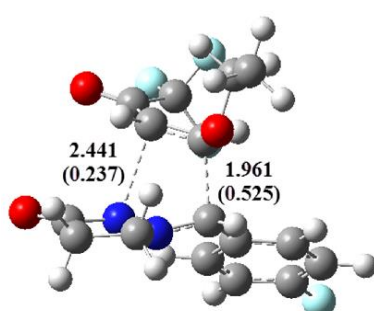
TS4a (GEDT=0.149)



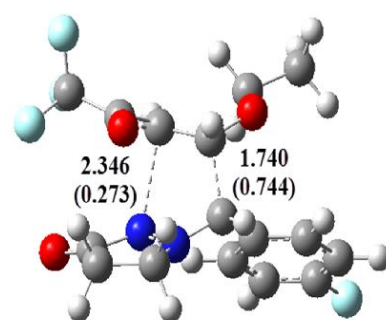
TS3b (GEDT=0.176)



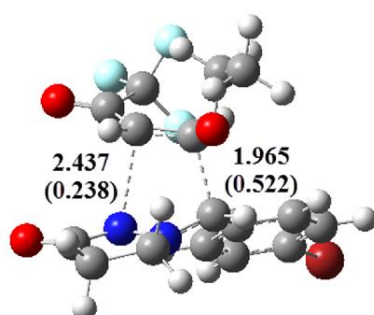
TS4b (GEDT=0.223)



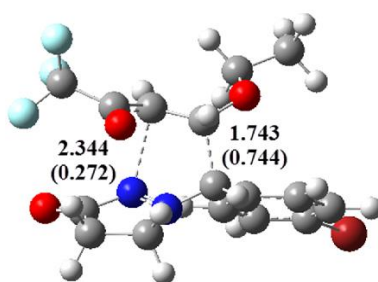
TS3c (GEDT=0.172)



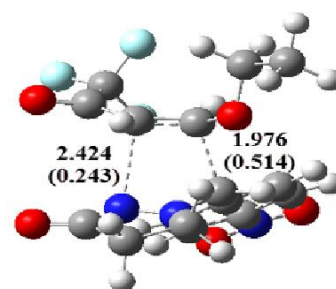
TS4c (GEDT=0.216)



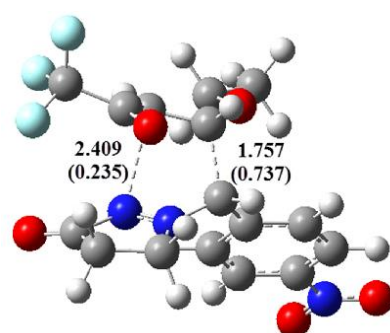
TS3d (GEDT=0.166)



TS4d (GEDT=0.211)



TS3e (GEDT=0.150)



TS4e (GEDT=0.211)

122 **Figure S1-** The geometrical optimized of transition states for *meta* pathways of the 13DC
123 reactions between TVE 1 and 3-oxo-1,2-pyrazolidinium ylides **2a-2e** at the B3LYP/cc-

124 pVDZ level of theory. Bond distances are given in Å, wiberg bond indices are given in
125 parenthesis and the natural charges (GEDT) of TSs are also given.