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Supplementary material

SUPPLEMENTARY MATERIAL TO

A theoretical study on the regio- and stereoselectivity of [3+2] cycloddition of 2-(trifluoroacetyl)vinyl ethyl ether to 2-arylidene-5-oxopyrazolidin-2-ium-1-ides

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TABLE S-I. Calculated activation energies ($\Delta E^{\neq}$ / kcal mol^{-1}), reaction energies (ΔE_{r} / kcal mol^{-1}), activation Gibbs energies ($\Delta G^{\neq}$ / kcal** mol^{-1}), activation enthalpies ($\Delta H^{\neq}$ / kcal mol^{-1}) and activation entropies ($\Delta S^{\neq}$ / cal mol^{-1} K^{-1}) in the gas phase for the *meta* pathways of the 1,3-dipolar cycloaddition between TVE (**1**) and the 5-oxopyrazolidin-2-ium-1-ides **2a–e** at the B3LYP/cc-pVDZ level of theory

Reaction	TSs	$\Delta E^{\neq}$	ΔE_{r}	$\Delta G^{\neq}$	$\Delta H^{\neq}$	$\Delta S^{\neq}$
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 S-II. Calculated reaction Gibbs energies (ΔG_{r} / kcal mol^{-1}), reaction enthalpies (ΔH_{r} / / kcal mol^{-1}) and reaction entropies (ΔS_{r} / cal mol^{-1} K^{-1}) in the gas phase for *ortho* and *meta* pathways of the 1,3-dipolar cycloaddition between TVE (**1**) and 5-oxopyrazolidin-2-ium-1-ides **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

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** 1 kcal = 4184 J

TABLE S-II. Continued

Reaction	TSs	ΔG_r	ΔH_r	ΔS_r
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 S-III. Calculated reaction Gibbs energies (ΔG_r / kcal mol^{-1}), reaction enthalpies (ΔH_r / kcal mol^{-1}) and reaction entropies (ΔS_r / cal mol^{-1} K^{-1}) in the gas phase for the elimination of ethanol from the cycloadducts **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 S-IV. Calculated activation energies ($\Delta E^{\neq}_\mathrm{Sol}$ / kcal mol^{-1}) and reaction energies ($\Delta E_\mathrm{r,Sol}$ / kcal mol^{-1}) in DMSO for the *ortho* and *meta* pathways of the 1,3-dipolar cycloaddition between TVE (**1**) and 5-oxopyrazolidin-2-ium-1-ides **2a–2e** and the elimination of ethanol from the cycloadducts **4** at the B3LYP/cc-pVDZ level of theory

Reaction	TSs	$\Delta E^{\neq}_\mathrm{Sol}$	$\Delta E_\mathrm{r,Sol}$
1+2a→3a	**TS1a**	21.10	–12.66
1+2a→4*a*	**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

TABLE S-IV. Continued

Reaction	TSs	$\Delta E^{\neq}_{\text{Sol}}$	$\Delta E_{\text{r,Sol}}$
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 S-V. Calculated activation energies ($\Delta E^{\neq}$ / kcal mol^{-1}), activation Gibbs energies ($\Delta G^{\neq}$ / kcal mol^{-1}) and reaction energies (ΔE_{r} / kcal mol^{-1}) for the *ortho* pathway of the 1,3-dipolar cycloaddition between TVE (**1**) and the 5-oxopyrazolidin-2-ium-1-ides **2a**–**2e**, and the elimination of ethanol from the cycloadducts **4** at the MPWB1K/cc-pVDZ level of theory

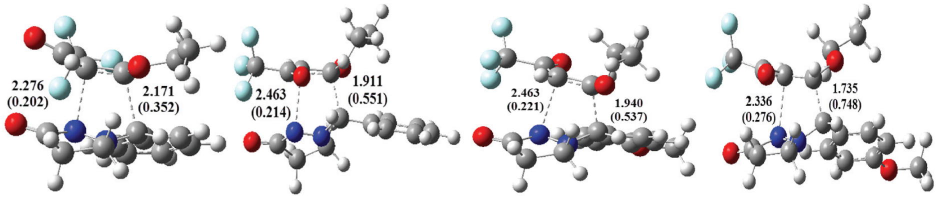
Reaction	TSs	$\Delta E^{\neq}$	$\Delta G^{\neq}$	ΔE_{r}
1+2a→3a	**TS1a**	13.27	28.47	–26.03
1+2a→4a	**TS2a**	2.88	19.18	–24.09
1+2b→3b	**TS1b**	12.48	31.53	–23.31
1+2b→4b	**TS2b**	1.59	17.96	–21.36
1+2c→3c	**TS1c**	12.45	28.81	–23.90
1+2c→4c	**TS2c**	1.66	17.18	–21.36
1+2d→3d	**TS1d**	12.61	28.35	–24.15
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 S-VI. Calculated activation energies ($\Delta E^{\neq}$ / 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-triflourobut-1-ene **1b** with 5-oxopyrazolidin-2-ium-1-ide **2a** at the B3LYP/cc-pVDZ level of theory

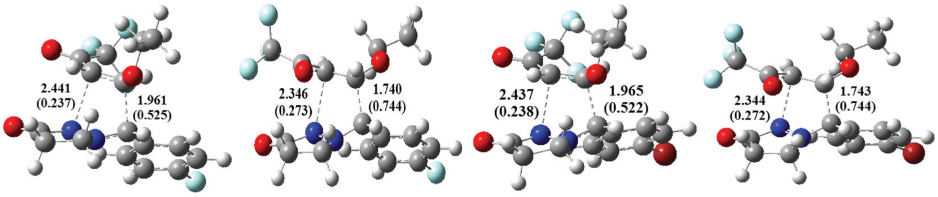
Reaction	TSs	$\Delta E^{\neq}$	ΔE_{r}
1a+2a→3aa	**TS1aa**	21.38	–21.03
1a+2a→4aa	**TS2aa**	17.81	–19.92
1a+2a→5aa	**TS3aa**	21.69	–16.37
1a+2a→6aa	**TS4aa**	22.08	–14.47
4aa→7aa	**TS5aa**	36.89	–3.71
1b+2a→3ba	**TS1ba**	23.63	–13.16
1b+2a→4ba	**TS2ba**	15.57	–12.25
1b+2a→5ba	**TS3ba**	29.85	–9.35

TABLE S-VI. Continued

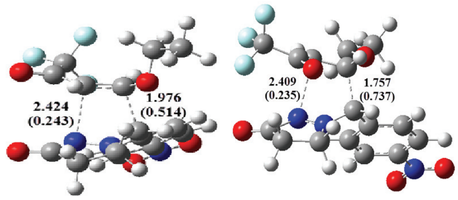
Reaction	TSs	$\Delta E^{\#}$	ΔE_r
1b+2a→6ba	**TS4ba**	21.19	–2.18
4ba→7ba	**TS5ba**	37.26	–2.42



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)

Fig. S-1. The geometrical optimized of transition states for the *meta* pathways of the 13DC reactions between TVE (**1**) and 5-oxopyrazolidin-2-ium-1-ides **2a–e** at the B3LYP/cc-pVDZ level of theory. Bond distances are given in Å, Wiberg bond indices are given in parentheses and the natural charges (*GEDT,* in e) of the TSs are given.