Table S1. Calculated activation energies (Δ*E* #/kcal mol-1), reaction energies (*∆Er*/kcal mol-1), activation Gibbs free energies (*∆G*#/kcal mol-1), activation enthalpies (ΔH#/kcal mol-1 ), and activation entropies (ΔS#/cal mol-1K-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* | *ΔE #* | *ΔEr* | *ΔG #* | *ΔH#* | *ΔS#* |
| 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 (Δ*Gr*/ kcal mol-1), reaction enthalpies (Δ*Hr*/ kcal mol-1) and reaction entropies (Δ*Sr*/ 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* | *ΔGr* | *ΔHr* | *ΔSr* |
| 1+2a→3a | **TS1a** | -2.45 | -16.59 | -47.43 |
| 1+2a→4*a* | **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 (Δ*Gr*/ kcal mol-1), reaction enthalpies (Δ*Hr*/ kcal mol-1) and reaction entropies (Δ*Sr*/ cal mol-1K-1) in gas phase for the elemination of ethanol from cycloadduct **4** at the B3LYP/cc-pVDZ level of theory.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Reaction | *TSs* | *ΔGr* | *ΔHr* | *ΔSr* |
| 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 (Δ*E* # ***Sol*** / kcal mol-1) and reaction energies (*∆Er* ***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 elemination of ethanol from cycloadduct **4** at the B3LYP/cc-pVDZ level of theory.

|  |  |  |  |
| --- | --- | --- | --- |
| Reaction | *TSs* | *ΔE #Sol* | *ΔEr 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 |
| 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 (Δ*E* #/kcal mol-1), activation Gibbs free energies (*∆G#/* kcal mol-1), and reaction energies (*∆Er*/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 elemination of ethanol from cycloadduct **4** at the MPWB1K/cc-pVDZ level of theory.

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

Table S6. Calculated activation energies (Δ*E* #/kcal mol-1)and reaction energies (*∆Er*/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 3-oxo-1,2-pyrazolidinium ylide **2a** at the B3LYP/cc-pVDZ level of theory.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| ***ΔEr*** | ***ΔE #*** | | ***TSs*** | | **Reaction** | |
| -21.03 | | 21.38 | | **TS1aa** | | **1a+2a→*3aa*** | |
| -19.92 | | 17.81 | | **TS2aa** | | **1a+2a→4*aa*** | |
| -16.37 | | 21.69 | | **TS3aa** | | **1a+2a→*5aa*** | |
| -14.47 | | 22.08 | | **TS4aa** | | **1a+2a→6*aa*** | |
| -3.71 | | 36.89 | | **TS5aa** | | **4aa→*7aa*** | |
| -13.16 | | 23.63 | | **TS1ba** | | **1b+2a→*3ba*** | |
| -12.25 | | 15.57 | | **TS2ba** | | **1b+2a→4*ba*** | |
| -9.35 | | 29.85 | | **TS3ba** | | **1b+2a→*5ba*** | |
| -2.18 | | 21.19 | | **TS4ba** | | **1b+2a→6*ba*** | |
| -2.42 | | 37.26 | | **TS5ba** | | **4ba→*7ba*** | |

|  |  |  |  |
| --- | --- | --- | --- |
|  |  |  |  |
| **TS3b (GEDT=0.176)** | **TS4a (GEDT=0.149)** | **TS3a (GEDT=0.037)** |
|  |  |  |
| **TS4c (GEDT=0.216)** | **TS3c (GEDT=0.172)** | **TS4b (GEDT=0.223)** |
|  |  |  |  |
|  | **TS3e (GEDT=0.150)** | **TS4d (GEDT=0.211)** | **TS3d (GEDT=0.166)** |
|  |  |  |  |
|  | **TS4e (GEDT=0.211)** |  |

**Figure S1**- The geometrical optimized of transition states for *meta* pathways of the 13DC reactions between **TVE** **1** and3-oxo-1,2-pyrazolidinium ylieds **2a-2e** at the B3LYP/cc-pVDZ level of theory. Bond distances are given in Å, wiberg bond indices are given in parenthesis and the natural charges (GEDT) of TSs are also given.