

# Theoretical Study of the Thermal Decomposition of 5-Methyl-2-Furanylmethyl Radical

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### Spin contamination and diagnostic T1

|                       | R <sub>1</sub> | R <sub>2</sub> | R <sub>3</sub> | R <sub>4</sub> | R <sub>5</sub> | R <sub>6</sub> |
|-----------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| $\langle s^2 \rangle$ | 1.07           | 1.15           | 0.97           | 1.05           | 0.96           | 0.88           |
| T <sub>1diag</sub>    | 0.030          | 0.033          | 0.028          | 0.028          | 0.023          | 0.025          |

|                       | R <sub>7</sub> | R <sub>8</sub> | R <sub>9</sub> | R <sub>10</sub> | TS <sub>R1-R2</sub> | TS <sub>R1-M8+H</sub> |
|-----------------------|----------------|----------------|----------------|-----------------|---------------------|-----------------------|
| $\langle s^2 \rangle$ | 0.87           | 0.78           | 0.86           | 0.77            | 1.26                | 1.37                  |
| T <sub>1diag</sub>    | 0.021          | 0.019          | 0.024          | 0.017           | 0.052               | 0.039                 |

|                       | TS <sub>R31-R16</sub> | TS <sub>R16-C5H7+CO</sub> | TS <sub>R6-R7</sub> | TS <sub>R12-M2</sub> | TS <sub>R12-M3</sub> | TS <sub>R12-R15</sub> |
|-----------------------|-----------------------|---------------------------|---------------------|----------------------|----------------------|-----------------------|
| $\langle s^2 \rangle$ | 1.23                  | 1.27                      | 0.96                | 1.37                 | 1.2                  | 1.14                  |
| T <sub>1diag</sub>    | 0.035                 | 0.038                     | 0.026               | 0.043                | 0.039                | 0.037                 |

|                       | TS <sub>R15-C5H7+CO</sub> | TS <sub>R7-c-C5H7+CO</sub> |
|-----------------------|---------------------------|----------------------------|
| $\langle s^2 \rangle$ | 1.23                      | 0.96                       |
| T <sub>1diag</sub>    | 0.035                     | 0.026                      |

|                       | TS <sub>R2-R3</sub> | TS <sub>R3-R31</sub> | TS <sub>R3-R5</sub> | TS <sub>R5-R12</sub> | TS <sub>R5-R6</sub> | TS <sub>R5-M9</sub> |
|-----------------------|---------------------|----------------------|---------------------|----------------------|---------------------|---------------------|
| $\langle s^2 \rangle$ | 0.90                | 1.22                 | 1.48                | 1.08                 | 0.81                | 0.79                |
| T <sub>1diag</sub>    | 0.028               | 0.033                | 0.04                | 0.032                | 0.020               | 0.02                |

### Geometries obtained at the B3LYP/CBSB7 level of theory

**R1**

|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | -1.04496  | 0.005233  | -7.6e-005 |
| 2  | C | -0.598785 | 1.30441   | -0.000208 |
| 3  | C | 0.808829  | 1.26277   | 0.000218  |
| 4  | C | 1.18203   | -0.095457 | -4.7e-005 |
| 5  | O | 0.01723   | -0.853711 | -0.000207 |
| 6  | H | -1.22714  | 2.18157   | -0.000295 |
| 7  | H | 1.49401   | 2.09535   | 0.000252  |
| 8  | C | -2.39637  | -0.605289 | 0.000176  |
| 9  | H | -2.54398  | -1.23804  | -0.881416 |
| 10 | H | -2.5442   | -1.23689  | 0.882578  |
| 11 | H | -3.16151  | 0.172185  | -0.000434 |
| 12 | C | 2.39616   | -0.734033 | 6.5e-005  |
| 13 | H | 3.30971   | -0.157425 | 0.000262  |
| 14 | H | 2.4539    | -1.81285  | -6.2e-005 |

**R2**

|    |   |          |           |           |
|----|---|----------|-----------|-----------|
| 1  | C | 1.19056  | -0.216631 | -2.1e-005 |
| 2  | C | 0.468081 | 1.05299   | 3.4e-005  |
| 3  | C | -0.93446 | 1.18353   | 2.6e-005  |
| 4  | C | -1.8541  | 0.206535  | -3.8e-005 |
| 5  | O | 0.612977 | -1.29543  | 6.3e-005  |
| 6  | H | 1.05057  | 1.96837   | 0.000104  |
| 7  | H | -1.32637 | 2.19973   | -8.5e-005 |
| 8  | C | 2.71015  | -0.132094 | -6.7e-005 |
| 9  | H | 3.12548  | -1.13877  | -0.000501 |
| 10 | H | 3.06847  | 0.409959  | -0.880999 |
| 11 | H | 3.0684   | 0.408989  | 0.881521  |
| 12 | C | -2.81956 | -0.657062 | -2.7e-005 |
| 13 | H | -3.22721 | -1.05413  | 0.92679   |
| 14 | H | -3.22717 | -1.05433  | -0.926772 |

**R3**

|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | 1.49093   | 0.020757  | -0.000217 |
| 2  | C | 0.437479  | -0.998001 | 0.265898  |
| 3  | C | -0.901663 | -0.875221 | 0.193526  |
| 4  | C | -1.68143  | 0.287771  | -0.199971 |
| 5  | O | 2.57591   | -0.348116 | -0.475651 |
| 6  | H | 0.855797  | -1.97697  | 0.478082  |
| 7  | H | -1.48937  | -1.76378  | 0.41541   |
| 8  | C | 1.30604   | 1.39848   | 0.363713  |
| 9  | H | 0.455091  | 1.74406   | 0.935825  |
| 10 | H | 2.10175   | 2.09239   | 0.122441  |
| 11 | C | -3.01944  | 0.313353  | -0.168794 |
| 12 | H | -3.57858  | 1.18671   | -0.481876 |
| 13 | H | -3.59475  | -0.542142 | 0.171026  |
| 14 | H | -1.14867  | 1.16181   | -0.560624 |

**R4**

|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | -1.10665  | 0.033577  | 0.005117  |
| 2  | C | -0.356509 | 1.28327   | 0.001409  |
| 3  | C | 1.04148   | 1.30174   | 0.074266  |
| 4  | C | 1.79273   | 0.149661  | -0.003953 |
| 5  | O | -2.31953  | -0.000205 | -0.150485 |
| 6  | H | -0.933663 | 2.19904   | -0.05062  |
| 7  | H | 1.54943   | 2.25785   | 0.158878  |
| 8  | C | -0.299743 | -1.23066  | 0.296036  |
| 9  | H | -0.281271 | -1.33202  | 1.38912   |
| 10 | H | -0.84921  | -2.08813  | -0.094986 |
| 11 | C | 1.14568   | -1.1831   | -0.228402 |
| 12 | H | 1.74158   | -1.98171  | 0.223357  |
| 13 | H | 1.15199   | -1.38768  | -1.31057  |
| 14 | H | 2.8755    | 0.207299  | 0.021857  |

**R5**

|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | 1.50229   | 0.329424  | -0.056995 |
| 2  | C | 0.630021  | -0.762665 | -0.53568  |
| 3  | C | -0.836132 | -0.743275 | -0.401598 |
| 4  | C | -1.57729  | 0.344358  | 0.049778  |
| 5  | O | 1.82556   | 1.47434   | -0.179269 |
| 6  | H | 1.01819   | -1.33665  | -1.37484  |
| 7  | H | -1.35953  | -1.66178  | -0.656462 |
| 8  | C | 1.59344   | -0.892148 | 0.747681  |
| 9  | H | 2.44746   | -1.5537   | 0.644862  |
| 10 | H | 1.11816   | -0.889815 | 1.7242    |
| 11 | C | -2.94337  | 0.341221  | 0.234358  |
| 12 | H | -3.46732  | 1.22454   | 0.575363  |
| 13 | H | -3.5355   | -0.545837 | 0.037137  |
| 14 | H | -1.03971  | 1.26705   | 0.258639  |

**R6**

|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | -1.12467  | 0.047057  | -0.001177 |
| 2  | C | -0.309065 | 1.27916   | 0.008066  |
| 3  | C | 1.02977   | 1.26386   | 0.031756  |
| 4  | C | 1.85656   | 0.009515  | 0.005096  |
| 5  | O | -2.33257  | 0.077607  | -0.12214  |
| 6  | H | -0.867957 | 2.20882   | -0.003359 |
| 7  | H | 1.57516   | 2.20377   | 0.063401  |
| 8  | C | -0.378031 | -1.27396  | 0.207698  |
| 9  | H | -0.478088 | -1.49097  | 1.28934   |
| 10 | H | -0.935486 | -2.06462  | -0.300288 |
| 11 | C | 1.05174   | -1.22749  | -0.205539 |
| 12 | H | 1.54818   | -2.13424  | -0.529034 |
| 13 | H | 2.62964   | 0.105769  | -0.769211 |
| 14 | H | 2.43124   | -0.038234 | 0.950868  |

**R7**

|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | 1.35076   | -1.27637  | -0.664419 |
| 2  | C | 0.417067  | -1.56604  | 0.250402  |
| 3  | C | -0.869565 | -0.990635 | 0.358745  |
| 4  | C | -1.39445  | 0.069172  | -0.557121 |
| 5  | O | 2.17709   | -1.04366  | -1.45216  |
| 6  | H | 0.734708  | -2.32853  | 0.956522  |
| 7  | H | -1.47611  | -1.30518  | 1.19796   |
| 8  | C | -0.708149 | 1.90386   | 1.06202   |
| 9  | H | -0.247232 | 1.20218   | 1.74899   |
| 10 | H | -0.676556 | 2.95316   | 1.33222   |
| 11 | C | -1.28412  | 1.50085   | -0.065448 |
| 12 | H | -1.73266  | 2.24134   | -0.726057 |
| 13 | H | -0.898015 | 0.00762   | -1.53658  |
| 14 | H | -2.45497  | -0.126584 | -0.769076 |

**R8**

|    |   |          |           |           |
|----|---|----------|-----------|-----------|
| 1  | C | -1.40257 | -0.449627 | 0.244254  |
| 2  | C | 1.3533   | -1.50666  | 0.489698  |
| 3  | C | 1.67214  | -0.540497 | -0.374268 |
| 4  | C | 1.42337  | 0.89682   | -0.202666 |
| 5  | O | -2.15447 | -1.04502  | -0.444901 |
| 6  | H | 1.5857   | -2.54439  | 0.278815  |
| 7  | H | 2.2214   | -0.809017 | -1.27577  |
| 8  | C | -1.1311  | 1.049     | 0.221126  |
| 9  | H | -1.74982 | 1.48879   | -0.574466 |
| 10 | H | -1.53374 | 1.42097   | 1.17287   |
| 11 | C | 0.28532  | 1.54207   | 0.077609  |
| 12 | H | 0.347267 | 2.62476   | 0.158618  |
| 13 | H | 0.865833 | -1.2946   | 1.43279   |
| 14 | H | 2.29634  | 1.5271    | -0.368164 |

**R9**

|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | -1.64752  | -0.311716 | 0.013724  |
| 2  | C | -1.34882  | 0.971501  | -0.044732 |
| 3  | C | -0.020093 | 1.5675    | -0.205379 |
| 4  | C | 1.18397   | 1.03901   | 0.057233  |
| 5  | O | -1.94529  | -1.4343   | 0.050687  |
| 6  | H | -2.21667  | 1.6228    | -0.022158 |
| 7  | H | -0.052945 | 2.58273   | -0.588875 |
| 8  | C | 1.8518    | -1.3008   | -0.472821 |
| 9  | H | 1.08845   | -1.77007  | -1.08159  |
| 10 | H | 2.88008   | -1.37797  | -0.804403 |
| 11 | C | 1.46955   | -0.341421 | 0.612648  |
| 12 | H | 0.592933  | -0.709996 | 1.15694   |
| 13 | H | 2.28197   | -0.262738 | 1.34328   |
| 14 | H | 2.05516   | 1.64514   | -0.172726 |

**R10**

|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | 1.69057   | 0.494054  | -0.034573 |
| 2  | C | 0.367247  | 0.357056  | 0.743153  |
| 3  | C | -0.67023  | 1.27483   | 0.125199  |
| 4  | C | -1.63561  | 0.586341  | -0.479211 |
| 5  | O | 2.25428   | -0.334542 | -0.657858 |
| 6  | H | 0.609453  | 0.648528  | 1.7709    |
| 7  | H | -0.579393 | 2.3533    | 0.153109  |
| 8  | C | -0.284375 | -1.0513   | 0.648063  |
| 9  | H | 0.443492  | -1.81024  | 0.360705  |
| 10 | H | -0.683886 | -1.32194  | 1.628     |
| 11 | C | -1.43948  | -0.906676 | -0.375461 |
| 12 | H | -1.17916  | -1.3281   | -1.35394  |
| 13 | H | -2.34611  | -1.42413  | -0.046975 |
| 14 | H | -2.46736  | 1.03309   | -1.01196  |

**TSR1\_R2**

|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | -1.06682  | -0.108438 | 0.001175  |
| 2  | C | -0.556623 | 1.21589   | 0.05991   |
| 3  | C | 0.830635  | 1.25572   | -0.07823  |
| 4  | C | 1.51578   | 0.074142  | -0.076369 |
| 5  | O | -0.234061 | -1.04314  | -0.138126 |
| 6  | H | -1.18285  | 2.09461   | 0.116688  |
| 7  | H | 1.36123   | 2.17418   | -0.31028  |
| 8  | C | -2.53694  | -0.429372 | 0.075249  |
| 9  | H | -2.82959  | -1.00585  | -0.806096 |
| 10 | H | -2.73404  | -1.05353  | 0.951231  |
| 11 | H | -3.14871  | 0.471872  | 0.136064  |
| 12 | C | 2.55318   | -0.711941 | 0.115019  |
| 13 | H | 2.6334    | -1.67352  | -0.379461 |
| 14 | H | 3.33772   | -0.438707 | 0.816333  |

**TSR1\_M1+H**

|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | -1.05151  | -0.034198 | -0.105763 |
| 2  | C | -0.581518 | 1.30796   | -0.013901 |
| 3  | C | 0.792915  | 1.25676   | 0.057744  |
| 4  | C | 1.16984   | -0.119729 | 0.011594  |
| 5  | O | 0.030525  | -0.867227 | -0.086555 |
| 6  | H | -1.20809  | 2.17654   | -0.004733 |
| 7  | H | 1.47832   | 2.07616   | 0.133806  |
| 8  | C | -2.31914  | -0.536019 | -0.185711 |
| 9  | H | -2.4876   | -1.58922  | -0.294413 |
| 10 | H | -3.07406  | -0.963724 | 2.0934    |
| 11 | H | -3.15727  | 0.130978  | -0.237939 |
| 12 | C | 2.39449   | -0.709667 | 0.048465  |
| 13 | H | 3.27871   | -0.107155 | 0.125256  |
| 14 | H | 2.4953    | -1.77639  | 0.002505  |

**TSR2\_R3**

|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | -1.40153  | 0.06692   | 0.021471  |
| 2  | C | -0.55329  | -1.14617  | 0.12244   |
| 3  | C | 0.79362   | -1.11006  | 0.039556  |
| 4  | C | 1.52513   | 0.123512  | -0.093582 |
| 5  | O | -2.59746  | -0.019787 | -0.197693 |
| 6  | H | -1.09053  | -2.08615  | 0.176892  |
| 7  | H | 1.36075   | -2.04125  | 0.036896  |
| 8  | C | -0.704608 | 1.3916    | 0.152682  |
| 9  | H | -1.09453  | 2.1632    | -0.508491 |
| 10 | H | -0.61003  | 1.72914   | 1.18574   |
| 11 | H | 0.547165  | 1.08246   | -0.130478 |
| 12 | C | 2.82328   | 0.392137  | -0.081063 |
| 13 | H | 3.20675   | 1.39908   | -0.207563 |
| 14 | H | 3.56451   | -0.395837 | 0.059523  |

**TSR3\_R4**

|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | -1.13872  | 0.035663  | 0.089502  |
| 2  | C | -0.273548 | 1.25847   | 0.104372  |
| 3  | C | 1.07867   | 1.24065   | 0.083631  |
| 4  | C | 1.83481   | 0.009905  | 0.009855  |
| 5  | O | -2.23606  | 0.072654  | -0.451436 |
| 6  | H | -0.814974 | 2.19837   | 0.099825  |
| 7  | H | 1.62272   | 2.17834   | 0.164598  |
| 8  | C | -0.625804 | -1.19246  | 0.713393  |
| 9  | H | -0.06273  | -1.13628  | 1.63597   |
| 10 | H | -1.17568  | -2.10433  | 0.511565  |
| 11 | C | 1.3133    | -1.11245  | -0.581245 |
| 12 | H | 1.81256   | -2.07019  | -0.485103 |
| 13 | H | 0.60785   | -1.03138  | -1.39791  |
| 14 | H | 2.76649   | -0.054433 | 0.565491  |

**TSR3\_R5**

|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | 1.49092   | 0.239945  | 0.013063  |
| 2  | C | 0.530682  | -0.635591 | -0.691962 |
| 3  | C | -0.874399 | -0.593541 | -0.608161 |
| 4  | C | -1.61155  | 0.377109  | 0.118239  |
| 5  | O | 2.22866   | 1.13694   | -0.298887 |
| 6  | H | 0.987547  | -1.2852   | -1.43264  |
| 7  | H | -1.43125  | -1.37305  | -1.12058  |
| 8  | C | 1.40879   | -0.776226 | 1.04161   |
| 9  | H | 2.26024   | -1.42113  | 1.23535   |
| 10 | H | 0.563503  | -0.822707 | 1.71177   |
| 11 | C | -2.9626   | 0.368923  | 0.259596  |
| 12 | H | -3.47841  | 1.1463    | 0.808666  |
| 13 | H | -3.57126  | -0.413037 | -0.182251 |
| 14 | H | -1.05074  | 1.18961   | 0.576502  |

**TSR4\_R6**

|    |   |          |           |           |
|----|---|----------|-----------|-----------|
| 1  | C | 1.10729  | 0.057319  | 8.7e-005  |
| 2  | C | 0.325923 | 1.28461   | -0.03921  |
| 3  | C | -1.04231 | 1.29529   | -0.056835 |
| 4  | C | -1.81107 | 0.089564  | 0.021204  |
| 5  | O | 2.32482  | 0.046834  | 0.095837  |
| 6  | H | 0.896253 | 2.20588   | -0.04005  |
| 7  | H | -1.57991 | 2.23649   | -0.087307 |
| 8  | C | 0.362506 | -1.28857  | -0.12097  |
| 9  | H | 0.614967 | -1.6874   | -1.11829  |
| 10 | H | 0.822926 | -1.98719  | 0.586054  |
| 11 | C | -1.12596 | -1.21581  | 0.024383  |
| 12 | H | -1.73492 | -2.10968  | -0.020898 |
| 13 | H | -1.6377  | -0.474634 | 1.10793   |
| 14 | H | -2.87853 | 0.107404  | -0.166086 |

**TSR4\_M2+H**

|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | 1.11501   | -0.003204 | -0.004684 |
| 2  | C | 0.413889  | 1.28895   | 0.009262  |
| 3  | C | -0.935274 | 1.35783   | -0.014489 |
| 4  | C | -1.77689  | 0.175591  | -0.064034 |
| 5  | O | 2.32457   | -0.09122  | 0.101419  |
| 6  | H | 1.03586   | 2.17427   | 0.071906  |
| 7  | H | -1.42333  | 2.32715   | 0.017196  |
| 8  | C | 0.249917  | -1.25311  | -0.182839 |
| 9  | H | 0.501608  | -1.66417  | -1.17183  |
| 10 | H | 0.593325  | -2.01015  | 0.528903  |
| 11 | C | -1.2337   | -1.05678  | -0.108338 |
| 12 | H | -1.86518  | -1.93562  | -0.182026 |
| 13 | H | -1.58348  | -1.52085  | 2.16596   |
| 14 | H | -2.85305  | 0.303485  | -0.05073  |

**TSR4\_R9**

|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | -1.36745  | 0.228221  | -0.042549 |
| 2  | C | -0.550635 | 1.29083   | -0.066867 |
| 3  | C | 0.88716   | 1.35627   | 0.114892  |
| 4  | C | 1.77416   | 0.351985  | 0.042408  |
| 5  | O | -2.39593  | -0.348947 | -0.057987 |
| 6  | H | -1.0846   | 2.21262   | -0.287525 |
| 7  | H | 1.26704   | 2.35753   | 0.294231  |
| 8  | C | 0.079826  | -1.46356  | 0.305926  |
| 9  | H | -0.045718 | -1.35601  | 1.37893   |
| 10 | H | -0.52847  | -2.22181  | -0.172061 |
| 11 | C | 1.3798    | -1.06411  | -0.29236  |
| 12 | H | 2.15687   | -1.75467  | 0.076767  |
| 13 | H | 1.35802   | -1.20786  | -1.38184  |
| 14 | H | 2.82716   | 0.563974  | 0.186701  |

**TSR6\_R7**

|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | 1.25418   | -0.233653 | 0.068838  |
| 2  | C | 0.340931  | -1.32028  | 0.166103  |
| 3  | C | -1.01715  | -1.26115  | 0.126552  |
| 4  | C | -1.77919  | -0.022354 | -0.272455 |
| 5  | O | 2.30126   | 0.062645  | -0.400942 |
| 6  | H | 0.836076  | -2.25468  | 0.41941   |
| 7  | H | -1.58977  | -2.14368  | 0.39068   |
| 8  | C | -0.008351 | 1.47462   | 0.644929  |
| 9  | H | -0.138104 | 1.06379   | 1.63999   |
| 10 | H | 0.677952  | 2.30797   | 0.553779  |
| 11 | C | -0.877754 | 1.17402   | -0.355077 |
| 12 | H | -0.805532 | 1.70261   | -1.30023  |
| 13 | H | -2.28633  | -0.191657 | -1.22996  |
| 14 | H | -2.5803   | 0.147301  | 0.460524  |

**TSR6\_M2+H**

|    |   |           |          |           |
|----|---|-----------|----------|-----------|
| 1  | C | -1.13082  | 0.034887 | 0.011924  |
| 2  | C | -0.346961 | 1.2795   | -0.003321 |
| 3  | C | 0.998667  | 1.26415  | -0.067922 |
| 4  | C | 1.7692    | 0.021542 | -0.122834 |
| 5  | O | -2.34745  | 0.028912 | -0.001048 |
| 6  | H | -0.912478 | 2.20395  | 0.009485  |
| 7  | H | 1.54944   | 2.19903  | -0.093305 |
| 8  | C | -0.342148 | -1.27669 | 0.062776  |
| 9  | H | -0.545792 | -1.71859 | 1.05084   |
| 10 | H | -0.794437 | -1.97584 | -0.648986 |
| 11 | C | 1.13538   | -1.17525 | -0.133333 |
| 12 | H | 1.70078   | -2.09504 | -0.240364 |
| 13 | H | 2.82998   | 0.082711 | -0.333215 |
| 14 | H | 2.4522    | 0.183638 | 1.78019   |

**TSR6\_M3+H**

|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | -1.10464  | 0.054851  | -0.033677 |
| 2  | C | -0.29501  | 1.28943   | 0.048285  |
| 3  | C | 1.04282   | 1.26463   | 0.047786  |
| 4  | C | 1.83377   | -0.002859 | -0.034384 |
| 5  | O | -2.32021  | 0.078666  | -0.116974 |
| 6  | H | -0.852982 | 2.21807   | 0.093208  |
| 7  | H | 1.60658   | 2.1916    | 0.103943  |
| 8  | C | -0.341805 | -1.22528  | -0.031855 |
| 9  | H | -0.666721 | -1.53121  | 1.94044   |
| 10 | H | -0.932584 | -2.12498  | -0.160274 |
| 11 | C | 1.00614   | -1.24244  | -0.124053 |
| 12 | H | 1.53406   | -2.18621  | -0.223324 |
| 13 | H | 2.52383   | 0.046765  | -0.889982 |
| 14 | H | 2.50181   | -0.073316 | 0.839169  |

**TSR5\_R8**

|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | 1.67975   | 0.306445  | -0.142089 |
| 2  | C | 0.529189  | -1.04895  | -0.386221 |
| 3  | C | -0.809629 | -0.691039 | -0.539586 |
| 4  | C | -1.5613   | 0.163485  | 0.317768  |
| 5  | O | 1.85643   | 1.45879   | -0.361744 |
| 6  | H | 0.943998  | -1.81838  | -1.02464  |
| 7  | H | -1.31041  | -1.05124  | -1.43425  |
| 8  | C | 1.39784   | -0.697854 | 0.851227  |
| 9  | H | 2.18194   | -1.43962  | 0.990225  |
| 10 | H | 0.922351  | -0.409954 | 1.79328   |
| 11 | C | -2.85743  | 0.501279  | 0.117048  |
| 12 | H | -3.38702  | 1.14692   | 0.805919  |
| 13 | H | -3.41063  | 0.133263  | -0.740707 |
| 14 | H | -1.06223  | 0.568526  | 1.19524   |

**TSR7\_C5H7+CO**

|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | 2.62777   | -0.166998 | -0.477337 |
| 2  | C | 0.922727  | 1.44811   | -0.149275 |
| 3  | C | -0.24841  | 1.17692   | 0.372198  |
| 4  | C | -0.734049 | -0.141852 | 0.918824  |
| 5  | O | 2.42035   | -1.19863  | -0.047518 |
| 6  | H | 1.39612   | 2.3262    | -0.560407 |
| 7  | H | -0.975744 | 1.99676   | 0.429632  |
| 8  | C | -2.4677   | -0.286361 | -0.92752  |
| 9  | H | -2.03962  | 0.540751  | -1.48359  |
| 10 | H | -3.34009  | -0.76528  | -1.35698  |
| 11 | C | -1.94755  | -0.708775 | 0.220388  |
| 12 | H | -2.40952  | -1.55217  | 0.729915  |
| 13 | H | 0.072816  | -0.879966 | 0.897997  |
| 14 | H | -0.983453 | -0.003483 | 1.9799    |

**TSR8\_C5H7+CO**

|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | 1.85931   | 0.788061  | 0.01028   |
| 2  | C | -1.7863   | 1.39758   | 0.07054   |
| 3  | C | -2.13144  | 0.128523  | -0.204581 |
| 4  | C | -1.25523  | -1.01045  | -0.415917 |
| 5  | O | 2.69792   | 0.364429  | -0.65666  |
| 6  | H | -2.54712  | 2.15902   | 0.197279  |
| 7  | H | -3.19113  | -0.086625 | -0.329738 |
| 8  | C | 0.723031  | -0.418137 | 1.00897   |
| 9  | H | 1.53227   | -0.901931 | 1.54943   |
| 10 | H | 0.161331  | 0.293562  | 1.60241   |
| 11 | C | -0.00871  | -1.24427  | 0.092261  |
| 12 | H | 0.490109  | -2.15102  | -0.238633 |
| 13 | H | -0.755904 | 1.72458   | 0.134702  |
| 14 | H | -1.67683  | -1.8009   | -1.03148  |

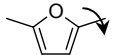
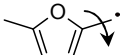
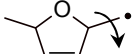
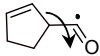
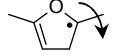
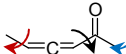
**TSR9\_R10**

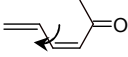
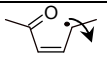
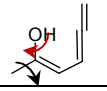
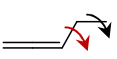
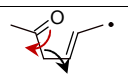
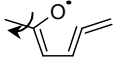
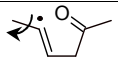
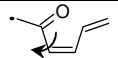
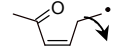
|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | 1.79053   | 0.09065   | 0.053807  |
| 2  | C | 0.601934  | 0.221197  | 0.686729  |
| 3  | C | -0.352089 | 1.28261   | 0.213605  |
| 4  | C | -1.5262   | 0.926122  | -0.299571 |
| 5  | O | 2.69943   | -0.298301 | -0.569628 |
| 6  | H | 0.703289  | 0.071353  | 1.76122   |
| 7  | H | -0.064003 | 2.32474   | 0.304659  |
| 8  | C | -0.898964 | -1.38669  | 0.333425  |
| 9  | H | -0.342682 | -2.14132  | -0.209915 |
| 10 | H | -1.13257  | -1.64921  | 1.35986   |
| 11 | C | -1.893    | -0.535833 | -0.410129 |
| 12 | H | -1.94739  | -0.810738 | -1.47138  |
| 13 | H | -2.90994  | -0.674117 | -0.017318 |
| 14 | H | -2.2354   | 1.67735   | -0.637295 |

**TSR10\_C5H7+CO**

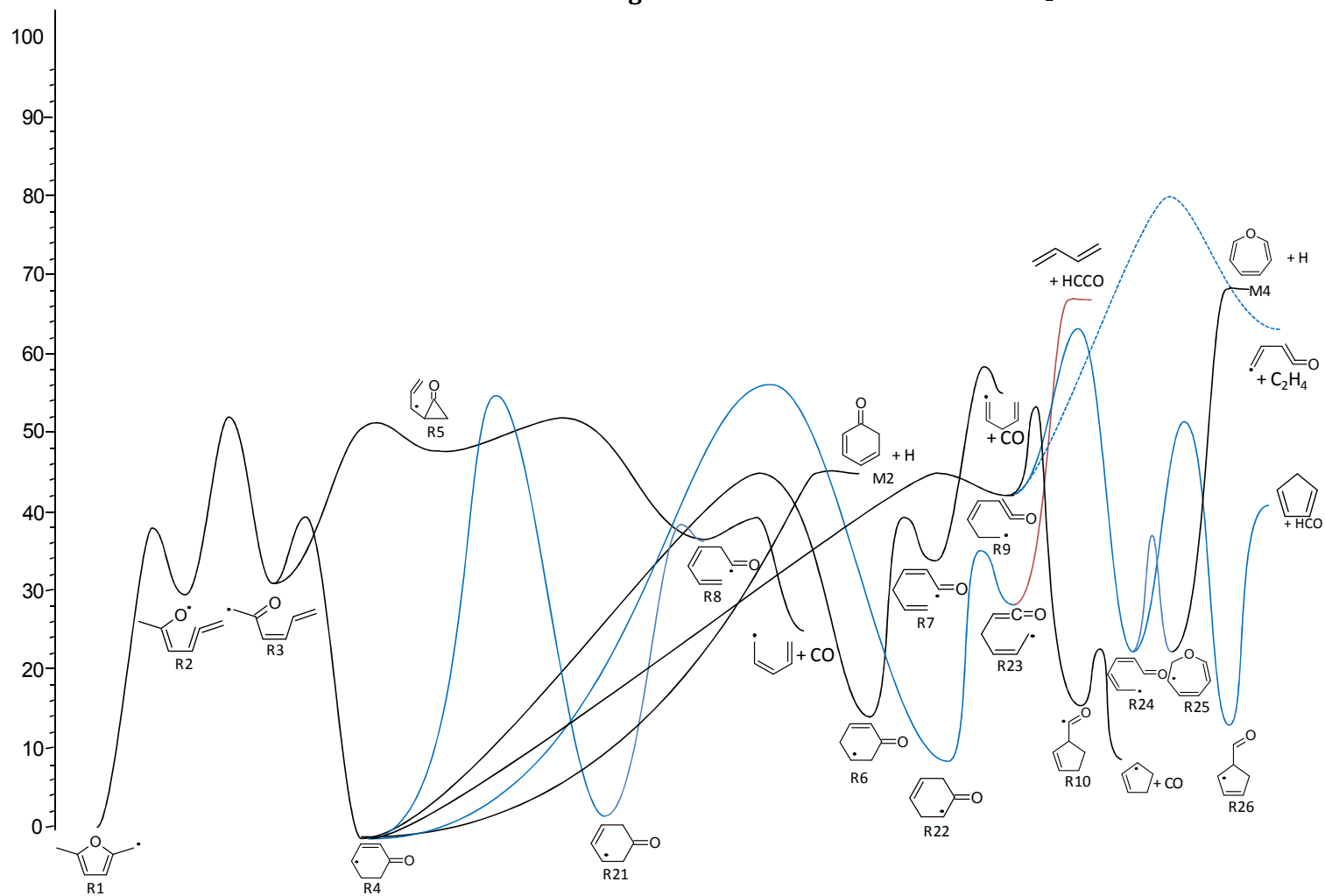
|    |   |           |           |           |
|----|---|-----------|-----------|-----------|
| 1  | C | 1.75347   | -0.472237 | -0.465798 |
| 2  | C | 0.225098  | -0.237771 | 0.751714  |
| 3  | C | -0.275938 | 1.10344   | 0.512119  |
| 4  | C | -1.39688  | 1.075     | -0.240577 |
| 5  | O | 2.67642   | 0.204459  | -0.319822 |
| 6  | H | 0.797767  | -0.456007 | 1.64921   |
| 7  | H | 0.227833  | 2.00002   | 0.851398  |
| 8  | C | -0.863471 | -1.2003   | 0.308916  |
| 9  | H | -0.462748 | -2.0736   | -0.209319 |
| 10 | H | -1.40774  | -1.56075  | 1.18877   |
| 11 | C | -1.79848  | -0.338527 | -0.581679 |
| 12 | H | -1.63252  | -0.536491 | -1.64842  |
| 13 | H | -2.85905  | -0.533565 | -0.393799 |
| 14 | H | -1.93777  | 1.94708   | -0.587427 |

Internal rotation database for DMF schemes established with relaxed scans at the B3LYP/6-31+G(d,p) level of theory.

| Species                                                                             | Rotation characteristics |             |          |
|-------------------------------------------------------------------------------------|--------------------------|-------------|----------|
|                                                                                     | V<br>(kcal/mol)          | #<br>minima | symmetry |
|    | 1.25                     | 3           | 3        |
|    | 19                       | 2           | 2        |
|    | 2.96                     | 1           | 1        |
|    | 0.96                     | 2           | 2        |
|    | 1.41                     | 2           | 1        |
|    | 4.42                     | 3           | 3        |
|                                                                                     | 3.1                      | 1           | 1        |
|    | 3.05                     | 2           | 1        |
|   | 1.4                      | 3           | 3        |
|  | 3.93                     | 2           | 1        |
|  | 6.3                      | 1           | 1        |
|                                                                                     | 0.73                     | 3           | 3        |
|                                                                                     | 1.2                      | 3           | 3        |
|  | 7.04                     | 1           | 1        |
|                                                                                     | 1.5                      | 3           | 3        |
|                                                                                     | 0.71                     | 3           | 3        |
|  | 2.77                     | 1           | 1        |
|                                                                                     | 2.32                     | 2           | 1        |

|                                                                                   |      |   |   |
|-----------------------------------------------------------------------------------|------|---|---|
|  | 3.16 | 1 | 1 |
|                                                                                   | 3.17 | 2 | 1 |
|  | 10   | 1 | 1 |
|  | 0.36 | 3 | 3 |
|  | 2.42 | 3 | 3 |
|                                                                                   | 8.77 | 1 | 1 |
|  | 3.09 | 3 | 3 |
|                                                                                   | 1.66 | 3 | 1 |
|  | 5.09 | 1 | 1 |
|                                                                                   | 2.17 | 1 | 1 |
|  | 0.2  | 3 | 3 |
|  | 0.27 | 3 | 3 |
|  | 6.18 | 1 | 1 |
|  | 0.47 | 2 | 2 |

Full potential energy diagram of the decomposition of R<sub>4</sub> computed at the CBS-QB3 level of theory at 0K.  
Potential energies are relative to the first reactant R<sub>1</sub>.



**Table 5.** High pressure limit rate constants calculated at the CBS-QB3 level of theory, for reactions not retained in the final scheme (figure 4), fitted with a modified Arrhenius form:  $k = AT^n \exp\left(-\frac{E}{RT}\right)$  between 500 and 2000K.

| Reaction                                                           | A (s <sup>-1</sup> )  | n      | E (kcal mol <sup>-1</sup> ) |
|--------------------------------------------------------------------|-----------------------|--------|-----------------------------|
| R <sub>1</sub> → R <sub>13</sub>                                   | 2.40×10 <sup>6</sup>  | 2.182  | 59237                       |
| R <sub>1</sub> → R <sub>11</sub>                                   | 3.84×10 <sup>12</sup> | 0.143  | 57693                       |
| R <sub>11</sub> → R <sub>12</sub>                                  | 5.18×10 <sup>14</sup> | -0.164 | 37812                       |
| R <sub>2</sub> → CH <sub>2</sub> CCHCHCO+CH <sub>3</sub>           | 1.14×10 <sup>14</sup> | -0.085 | 58229                       |
| R <sub>2</sub> → R <sub>14</sub>                                   | 2.79×10 <sup>11</sup> | -0.036 | 30202                       |
| R <sub>2</sub> → R <sub>15</sub>                                   | 1.98×10 <sup>10</sup> | 0.504  | 31411                       |
| R <sub>2</sub> → R <sub>16</sub>                                   | 1.00×10 <sup>5</sup>  | 2.436  | 51463                       |
| R <sub>3</sub> → CH <sub>2</sub> CO+nC <sub>4</sub> H <sub>5</sub> | 6.47×10 <sup>13</sup> | 0.230  | 47044                       |
| R <sub>13</sub> → R <sub>3</sub>                                   | 1.13×10 <sup>11</sup> | 0.555  | 15525                       |
| R <sub>14</sub> → R <sub>17</sub>                                  | 5.40×10 <sup>11</sup> | 0.540  | 31950                       |
| R <sub>18</sub> → R <sub>3</sub>                                   | 5.39×10 <sup>12</sup> | 0.245  | 32341                       |
| R <sub>18</sub> → R <sub>19</sub>                                  | 3.35×10 <sup>13</sup> | 0.137  | 51924                       |
| R <sub>18</sub> → C <sub>6</sub> H <sub>6</sub> O +H               | 2.32×10 <sup>11</sup> | 0.892  | 46563                       |
| R <sub>4</sub> → R <sub>21</sub>                                   | 2.10×10 <sup>06</sup> | 2.010  | 46978                       |
| R <sub>4</sub> → R <sub>22</sub>                                   | 1.73×10 <sup>06</sup> | 2.040  | 54292                       |
| R <sub>21</sub> → R <sub>8</sub>                                   | 3.77×10 <sup>13</sup> | 0.138  | 37532                       |

|                                                             |                       |       |       |
|-------------------------------------------------------------|-----------------------|-------|-------|
| $R_{22} \rightarrow R_{23}$                                 | $3.60 \times 10^{12}$ | 0.315 | 35896 |
| $R_{23} \rightarrow 1,3\text{-C}_4\text{H}_6 + \text{CHCO}$ | $8.71 \times 10^{11}$ | 1.094 | 38406 |
| $R_9 \rightarrow R_{24}$                                    | $7.64 \times 10^{04}$ | 1.800 | 15858 |
| $R_{24} \rightarrow R_{26}$                                 | $3.54 \times 10^{11}$ | 0.273 | 32088 |
| $R_{26} \rightarrow \text{C}_5\text{H}_6 + \text{CHO}$      | $1.41 \times 10^{13}$ | 0.303 | 30470 |
| $R_{25} \rightarrow \text{M}_4 + \text{H}$                  | $3.32 \times 10^{11}$ | 1.041 | 54362 |

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