Supporting Information

Olefin metathesis catalyzed by a Hoveyda-Grubbs-like complex chelated to bis(2-mercaptoimidazolyl) methane: a predictive DFT study

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Fig. S1 Alternative C=C coordination to the metal.

Fig. S2 Relative Gibbs free energies profiles (kcal/mol) of the initiation phase for precatalyst 1d. Energy differences are relative to complex 1a. Both paths via d, converged to the same MCB 6d.
The dissociative path reported in Figure 5 in the main manuscript corresponds to $\phi < 0$, which may be counterintuitive because the isopropoxy group hinders the styrene rotation in this direction. However, the energy barrier associated with this step is only 11.8 kcal/mol, which is calculated via $2d^\ddagger$ ($\phi = -69.6^\circ$, $d_{Ru-O} = 3.75 \text{ Å}$). A continued styrene rotation leads to the structure $3d'$ localized at 9.9 kcal/mol ($\phi = -113.5^\circ$, $d_{Ru-O} = 4.21 \text{ Å}$), followed by $3d$ ($\phi = 176.8^\circ$, $d_{Ru-O} = 4.66 \text{ Å}$). In the case of incomplete rotation of the styrene (these are not shown in Figure 5 and are denoted as $xd'$, $x = 3$ to 6), the isopropoxy group is located below the ruthenium atom (in standard orientation with NHC located above the ruthenium atom) in $4d$ and, based on linear transit calculations, we observed that the side- and bottom-bound mechanisms depend on the ethylene carbon that reacts first. In the case of $5d'^\ddagger_{cis}$, the isopropoxy group was spontaneously linked to ruthenium again ($\phi = 15.9^\circ$, $d_{Ru-O} = 2.48 \text{ Å}$). On the other hand, the analogous transition state $5d'^\ddagger_{trans}$ prevents the styrene back-rotation ($\phi = 167.9^\circ$, $d_{Ru-O} = 4.70 \text{ Å}$). The structural descriptors $d_1$, $d_2$, and $d_3$ are similar for both transition states, but the energy barrier from $4d$ to $5d'^\ddagger_{cis}$ is slightly lower (12.5 compared to 14.8 kcal/mol with $5d'^\ddagger_{trans}$, see Figure S2). On the other hand, $6d'^\ddagger_{cis}$ is highly stabilized by 14.1 kcal/mol compared to $1d$. Attempts to localize $7d'^\ddagger$ from $6d'^\ddagger_{cis}$ were unsuccessful, since the Ru-O bond dissociates during the linear-transit calculations. The high stabilization of $6d'^\ddagger_{cis}$ represents an important drawback from a practical point of view, since the course of the reaction may fall into a potential well: reversion via side $5d'^\ddagger_{cis}$ requires 24.9 kcal/mol, and progression to active catalyst $9d$ would require at least 31 kcal/mol. In contrast, even though MCB $6d_{trans}$ is moderately stabilized by 6.8 kcal/mol compared to $1d$, the 2,2'-cycloreversion is blocked by a large energy barrier of 41.7 kcal/mol, according to $7d^\ddagger$. Furthermore, we investigated an alternative pathway starting from the species $3d_r$, where the subscript “r” stands for rotated styrene at $\phi = -140.8^\circ$ and $d_{Ru-O} = 4.38 \text{ Å}$. Although $5d_r'^\ddagger_{trans}$ is 4.7 kcal/mol lower than the analogous $5d'^\ddagger_{cis}$ (details in Figure S2), the resulting MCB $6d_r$ is even more stabilized by 18.6 kcal/mol as compared to $1d$. Therefore, these results suggest that productive olefin metathesis is hindered by path $d$. 

S3
Table S1 Evolution of structural parameters as defined in Scheme 3 through the initiation phase for complex 1b-f. Torsional angle, $\phi$, in degrees and bond distances, $d_n$, in Å.

|   | $\xi$ | $\phi$ | $d_{Ru-O}$ | $d_1$ | $d_2$ | $d_3$ |
|---|-------|--------|-------------|-------|-------|-------|
| 1b |      | 10.9   | 2.375       |       |       |       |
| 2b‡ |      | 94.9   | 3.841       |       |       |       |
| 3b |      | 120.6  | 4.114       |       |       |       |
| 3c |      | -124.9 | 4.216       |       |       |       |
| 4bcis | | 126.1  | 4.227       | 2.213 | 2.924 | 1.399 |
| 4ctrans | | -119.9 | 4.231       | 2.197 | 3.150 | 1.394 |
| 5bcis | | -148.1 | 4.595       | 2.335 | 2.110 | 1.442 |
| 5ctrans | | 161.9  | 4.642       | 2.361 | 2.183 | 1.443 |
| 6cis | | -109.9 | 4.016       | 2.710 | 1.534 | 1.537 |
| 6trans | | 101.4  | 4.272       | 2.586 | 1.553 | 1.535 |
| 7cis | | -119.6 | 4.307       | 2.320 | 1.460 | 2.229 |
| 7trans | | 116.0  | 4.525       | 2.309 | 1.461 | 2.203 |
| 8cis | | -101.6 | 4.103       | 2.205 | 1.424 | 2.795 |
| 8trans | | 152.4  | 4.879       | 2.212 | 1.429 | 2.785 |
| 9c | | -     | 6.164       | 4.908 | 1.340 | 5.555 |
|   | ξ  | φ   | d_{Ru-O} | d_1  | d_2  | d_3  |
|---|----|-----|-----------|------|------|------|
| 1d| 12.7 | 2.425 |
| 2d‡ | -69.6 | 3.748 |
| 3d'| -113.5 | 4.213 |
| 3d | 176.8 | 4.659 |
| 4d | -99.2 | 4.083 | 2.170 | 3.002 | 1.426 |
| 5d\textsuperscript{trans} | 167.9 | 4.703 | 2.319 | 2.141 | 1.466 |
| 5d\textsuperscript{cis} | 15.9 | 2.484 | 2.354 | 2.151 | 1.435 |
| 6d\textsuperscript{trans} | 80.9 | 3.932 | 2.704 | 1.524 | 1.534 |
| 6d\textsuperscript{cis} | 32.7 | 2.422 | 2.661 | 1.565 | 1.532 |
| 7d‡ | 102.0 | 4.209 | 2.976 | 1.407 | 2.515 |
| 8d | 103.6 | 4.104 | 2.131 | 1.443 | 2.840 |
| 9d | - | 2.500 | 6.038 | 1.340 | 5.059 |

|   | 3d\textsubscript{r} | -140.8 | 4.378 |
|---|-----------------|-------|-------|
| 4d\textsubscript{r} | -147.5 | 4.459 | 2.226 | 3.620 | 1.419 |
| 5d\textsuperscript{trans} \textsubscript{cis} | -136.1 | 4.414 | 2.319 | 2.122 | 1.443 |
| 5d\textsuperscript{trans} \textsubscript{cis} | -138.5 | 4.440 | 2.308 | 2.142 | 1.456 |
| 6d\textsubscript{r} | -114.2 | 4.125 | 2.723 | 1.536 | 1.540 |

Subscript \( r \) stands for an alternative rotation of the styrene fragment.
Table S1  *Continued*…

| ξ  | φ  | $d_{Ru-O}$ | $d_1$ | $d_2$ | $d_3$ |
|----|----|------------|------|------|------|
| 1e | 2.7 | 2.302      |      |      |      |
| 2e | 69.7 | 3.688      |      |      |      |
| 3e' | 126.7 | 4.485      |      |      |      |
| 3e | -125.4 | 4.367      |      |      |      |
| 4e$_{cis}$ | -131.4 | 4.460 | 2.228 | 3.329 | 1.404 |
| 5e$_{cis}$ | -148.6 | 4.569 | 2.301 | 2.138 | 1.443 |
| 6e$_{cis}$ | -98.5 | 4.223 | 2.702 | 1.549 | 1.532 |
| 7e$_{cis}$ | -136.9 | 4.598 | 2.298 | 1.453 | 2.211 |
| 8e |      |      |      |      |      |
| 9e |      |      |      |      |      |

| ξ  | φ  | $d_{Ru-O}$ | $d_1$ | $d_2$ | $d_3$ |
|----|----|------------|------|------|------|
| 1f | -14.1 | 2.341      |      |      |      |
| 2f | -67.4 | 3.116      |      |      |      |
| 3f' | -118.0 | 4.130      |      |      |      |
| 3f | 121.8 | 4.142      |      |      |      |
| 4f$_{cis}$ | 144.2 | 4.494 | 3.360 | 3.785 | 1.337 |
| 4f$_{cis}$ | -159.3 | 4.573 | 2.147 | 2.973 | 1.438 |
| 5f$_{cis}$ | 177.9 | 4.742 | 2.260 | 1.930 | 1.491 |
| 6f$_{cis}$ | 112.9 | 4.258 | 2.683 | 1.548 | 1.530 |
| 7f$_{cis}$ | 87.7 | 4.032 | 2.276 | 1.476 | 1.994 |
| 8f | 102.0 | 4.173 | 2.142 | 1.442 | 2.820 |
| 9f |      |      |      |      |      |
**Pathways via 1e and 1f**

In the case of complex 1e, styrene rotation occurs via 2e (φ = 69.7°, d_{Ru-O} = 3.69 Å), which is characterized as a local minimum at an energy cost of 10.3 kcal/mol (see Fig. S3). During styrene rotation towards 3e, both thiones were bonded to Ru and both Ru-S bonds were kept until the MCB. Ethylene coordination releases 1.3 kcal/mol via 4e_{cis}, and the energy barrier calculated with 5e_{cis} to form the MCB is 17.2 kcal/mol. Even though 6e_{cis} is less stabilized than side-bound 6a-c, the product release is hampered by 31.7 kcal/mol at the 2,2-cycloreversion step, despite 7e is only 16.1 kcal/mol above the precatalyst 1e. Geometry optimizations of 7e resulted in the rupture of one Ru-S bond. We assumed the reaction from 6e_{cis} may proceed with only one Ru-S bond; but it would be probably reverted through the dissociative step before MCB formation. Additionally, considering the reaction mechanisms formulated by Houk et al. (J. Am. Chem. Soc. 2012, 134, 1464) for the Grubbs-carboxylate catalyst shown in Scheme 2c (analogous to nitrate), some intermediate species resulted in only one Ru-O bond, which suggests the chelating agent links the metal centre depending on the electronic environment.

![Figure S3](image.png)

**Fig. S3** Gibbs free energies profiles (kcal/mol) of the initiation phase for complexes 1e and 1f. Energy differences are relative to 1a.

In the case of 1f, the higher energy structure though the dissociative path is 3f' (φ = -118.0°, d_{Ru-O} = 4.13 Å) instead of 2f (φ = -67.4°, d_{Ru-O} = 3.12 Å), both are local minima, and the resulting energy barrier is therefore only 5.6 kcal/mol. Continued rotation is an exergonic process leading to intermediate 3f (φ = 121.8°, d_{Ru-O} = 4.14 Å), and releasing 4.9 kcal/mol. We additionally localized a transition state related to the η²-coordination of ethylene to form 4f_{cis}, which adds a second barrier of 8.2 kcal/mol via 4f as compared to 3f. The formation of 4f_{cis} releases 12.0 kcal/mol and the energy cost associated to the formation of a MCB is 21.5 by means of 5f_{cis}, yet the MCB 6f_{cis} is highly stabilized by 20.2 kcal/mol. Nonetheless, we observed that reversion of the reaction from the olefin coordination step towards 1f occurs at a lower energy cost. We conclude therefore that olefin metathesis across complex 1f is not viable since the reaction will be probably reverted before reaching the respective MCB.
Table S2 Strain ($\Delta E_{\text{strain}}$), interaction ($\Delta E_{\text{int}}$), and binding energies ($BE$) in kcal/mol for the active catalysts (fragment $f_i$) under study coordinated to ethylene ($f_2$). Electronic energies calculated at (PB-SC-PCM:toluene)M06-D3/LACV3P++//B3LYP-D3/LACVP**.

| Species | $\Delta E_{\text{str/i}}$ | $\Delta E_{\text{str/2}}$ | $\Delta E_{\text{strain}}$ | $\Delta E_{\text{int}}$ | $|BE|$ |
|---------|---------------------|---------------------|---------------------|---------------------|-------|
| 4a$_{\text{trans}}$ | 21.02 | 7.69 | 28.71 | -47.87 | 19.16 |
| 4a$_{\text{cis}}$ | 22.53 | 12.84 | 35.37 | -52.69 | 17.32 |
| 4b$_{\text{cis}}$ | 24.68 | 13.13 | 37.81 | -55.44 | 17.63 |
| 4c$_{\text{trans}}$ | 25.95 | 7.62 | 33.57 | -47.06 | 13.49 |
| 4c$_{\text{cis}}$ | 24.99 | 8.31 | 33.30 | -44.86 | 11.56 |
| 4d | 27.16 | 15.30 | 42.46 | -58.94 | 16.48 |
| 4d$_{\text{r}}$ | 20.38 | 12.20 | 32.58 | -55.61 | 23.03 |
| 4e$_{\text{cis}}$ | 14.41 | 9.68 | 24.08 | -42.75 | 18.67 |
| 4f$_{\text{cis}}$ | 20.73 | 19.55 | 40.28 | -63.29 | 23.01 |

* Strain is evaluated considering distortion of precatalyst 1.

Fig. S4 Coordination of the thione C=S bond to Ru followed by catalyst decomposition.
Fig. S5 3D representation of DFT-optimized geometries of a) active catalyst 9, and b) olefin coordination corresponding to the propagation phase. Gibbs energy comparisons are given in kcal/mol for each case. Structures to the left are the ones discussed in the main manuscript. Hydrogen atoms are hidden for the sake of clarity.
**Table S3** Total energy values (E) and Gibbs free energy values (G; as defined in the manuscript) for structures reported in Table S1 in the same order, along with Cartesian coordinates and its corresponding 3D view of optimized geometries. Species used for the analysis of stereoselectivity are also included consecutively.

| Species | gas-phase B3LYP-D3/LACVP** | solvated M06-D3/LACV3P++** | M06/B3LYP |
|---------|-----------------------------|-----------------------------|-----------|
|         | ZPE (kcal/mol)               | S (cal/mol)                 | H (kcal/mol) | E_{gas} (a.u.) | E_{solv} (kcal/mol) | G_{solv} (kcal/mol) |
| 1a      | 487.695                     | 282.000                     | 31.097      | -768.860014    | -1.7939            | -1737054.427         |
| 2a‡     | 487.414                     | 287.006                     | 31.334      | -768.834193    | -2.1463            | -1737040.113         |
| 3a'     | 486.715                     | 287.199                     | 31.122      | -768.827696    | -2.3037            | -1737037.163         |
| 3a      | 487.812                     | 284.998                     | 31.264      | -768.840739    | -2.2677            | -1737043.416         |
| 4a_{trans} | 522.232                 | 297.407                     | 33.437      | -847.425648    | -2.4487            | -1786323.645         |
| 5a_{trans} | 521.323                  | 296.682                     | 32.686      | -847.394068    | -2.0104            | -1786304.709         |
| 6a_{trans} | 523.543                  | 287.474                     | 32.021      | -847.421393    | -2.2068            | -1786317.752         |
| 7a‡     | 521.325                     | 294.878                     | 32.624      | -847.392770    | -2.3032            | -1786303.709         |
| 8a      | 521.412                     | 297.471                     | 33.085      | -847.417505    | -2.1249            | -1786319.278         |
| 9a      | 520.867                     | 302.795                     | 33.740      | -847.397570    | -2.2028            | -1786308.323         |
| 9a'     | 520.139                     | 306.563                     | 34.154      | -847.382516    | -1.9649            | -1786300.077         |
| 4a_{cis} | 522.167                   | 302.577                     | 33.581      | -847.422651    | -2.6113            | -1786323.265         |
| 5a_{cis} | 522.550                   | 295.490                     | 33.042      | -847.376893    | -2.1328            | -1786292.115         |
| 6a_{cis} | 524.358                   | 290.171                     | 32.745      | -847.456383    | -2.2213            | -1786338.988         |
| 7a‡     | 521.425                     | 299.061                     | 33.203      | -847.394757    | -1.7459            | -1786304.967         |
| 8a      | 521.936                     | 302.549                     | 33.546      | -847.409937    | -2.6022            | -1786315.535         |
| 1b      | 488.155                     | 282.289                     | 31.219      | -768.856583    | -2.9845            | -1737052.969         |
| 2b‡     | 487.753                     | 287.711                     | 31.426      | -768.831133    | -2.9158            | -1737038.742         |
| 3b'     | 487.647                     | 294.834                     | 32.047      | -768.833584    | -2.1687            | -1737041.142         |
| 3b      | 488.175                     | 289.539                     | 31.816      | -768.842569    | -1.3112            | -1737044.047         |
| 4b_{cis} | 522.267                   | 290.479                     | 32.900      | -847.421610    | -2.6124            | -1786318.585         |
| 5b_{cis} | 522.475                   | 282.350                     | 32.082      | -847.397051    | -1.8021            | -1786301.551         |
| 6b_{cis} | 524.728                   | 281.122                     | 31.883      | -847.445660    | -2.1124            | -1786329.944         |
| 7b‡     | 522.373                     | 291.782                     | 32.617      | -847.393338    | -1.6721            | -1786301.470         |
| 8b      | 522.206                     | 298.568                     | 33.375      | -847.415400    | -2.7399            | -1786317.814         |
| 9b      | 520.627                     | 304.415                     | 33.688      | -847.390989    | -1.8064            | -1786304.572         |
| Species | gas-phase B3LYP-D3/LACVP** | solvated M06-D3/LACV3P+++ | M06/B3LYP |
|---------|-----------------------------|-----------------------------|-----------|
|         | $ZPE$ (kcal/mol) | $S$ (cal/mol) | $H$ (kcal/mol) | $E_{\text{gas}}$ (a.u.) | $E_{\text{solv}}$ (kcal/mol) | $G_{\text{solv}}$ (kcal/mol) |
| 1c | 488.028 | 286.896 | 31.575 | -2768.856717 | -1.4085 | -1737052.622 |
| 2c | 486.760 | 293.093 | 31.627 | -2768.829413 | -1.7545 | -1737038.898 |
| 3c | 487.319 | 297.853 | 32.031 | -2768.834388 | -2.1130 | -1737042.835 |
| 3c | 487.743 | 293.362 | 31.883 | -2768.836708 | -2.1088 | -1737043.236 |
| 4c<sub>cis</sub> | 521.739 | 299.701 | 33.296 | -2847.409932 | -2.3820 | -1786314.909 |
| 4c<sub>trans</sub> | 521.517 | 299.322 | 33.228 | -2847.413130 | -2.3031 | -1786317.014 |
| 5c<sub>cis</sub> | 521.423 | 295.576 | 32.811 | -2847.391214 | -1.6913 | -1786302.044 |
| 5c<sub>trans</sub> | 521.150 | 298.190 | 32.836 | -2847.388470 | -1.4064 | -1786301.064 |
| 6c<sub>cis</sub> | 524.068 | 295.040 | 32.929 | -2847.456129 | -1.7160 | -1786339.881 |
| 6c<sub>trans</sub> | 523.624 | 293.043 | 32.554 | -2847.425150 | -2.0559 | -1786321.004 |
| 7c<sub>cis</sub> | 521.856 | 297.136 | 33.102 | -2847.395533 | -2.0368 | -1786304.841 |
| 7c<sub>trans</sub> | 521.394 | 294.436 | 32.725 | -2847.387992 | -1.9542 | -1786300.060 |
| 8c | 520.797 | 305.347 | 33.801 | -2847.390454 | -2.1005 | -1786304.526 |
| 1d | 488.680 | 281.213 | 31.303 | -2768.854235 | -3.3944 | -1737050.976 |
| 2d<sup>f</sup> | 487.822 | 284.083 | 31.328 | -2768.832857 | -3.2290 | -1737039.085 |
| 3d<sup>f</sup> | 487.989 | 287.611 | 31.700 | -2768.840018 | -3.6653 | -1737044.527 |
| 3d<sup>a</sup> | 488.447 | 289.990 | 31.805 | -2768.840223 | -3.1271 | -1737044.264 |
| 4d | 522.656 | 286.287 | 32.611 | -2847.416357 | -3.7022 | -1786316.030 |
| 5d<sub>trans</sub> | 522.755 | 290.966 | 32.649 | -2847.391720 | -3.0751 | -1786301.201 |
| 5d<sub>cis</sub> | 522.641 | 292.248 | 32.891 | -2847.394983 | -3.0954 | -1786303.523 |
| 6d<sub>trans</sub> | 524.123 | 291.023 | 33.423 | -2847.413783 | -1.8253 | -1786316.290 |
| 6d<sub>cis</sub> | 524.103 | 296.376 | 32.996 | -2847.434807 | -3.2793 | -1786328.361 |
| 7d<sup>f</sup> | 520.723 | 296.644 | 33.292 | -2847.352882 | -2.5899 | -1786279.426 |
| 8d | 522.619 | 297.369 | 33.218 | -2847.418198 | -2.8699 | -1786319.087 |
| 9d | 521.707 | 301.325 | 33.778 | -2847.379815 | -3.0672 | -1786296.730 |
| Species   | gas-phase B3LYP-D3/LACVP** | solvated M06-D3/LACV3P++** | M06//B3LYP |
|-----------|----------------------------|------------------------------|------------|
|           | ZPE (kcal/mol) | S (cal/mol) | H (kcal/mol) | \(\text{E}_{\text{gas}}\) (a.u.) | \(\text{E}_{\text{solv}}\) (kcal/mol) | \(G_{\text{solv}}\) (kcal/mol) |
| 3d\(_r\)  | 487.958         | 285.942   | 31.376     | -2768.849732      | -2.3530      | -1737049.168   |
| 4d\(_r\)  | 522.458         | 291.773   | 33.023     | -2847.427024      | -3.5521      | -1786323.995   |
| 5d\(_r\)  | 522.155         | 288.380   | 32.595     | -2847.382408      | -2.8461      | -1786295.011   |
| 5d\(_r\)  | 522.632         | 289.486   | 32.686     | -2847.391190      | -2.3054      | -1786299.743   |
| 6d\(_r\)  | 524.587         | 294.807   | 32.833     | -2847.444241      | -2.7323      | -1786332.945   |
| 1e        | 487.641         | 285.935   | 31.728     | -2768.846434      | -2.4436      | -1737047.152   |
| 2e        | 487.314         | 282.630   | 31.422     | -2768.829605      | -3.0231      | -1737036.819   |
| 3e        | 487.023         | 285.324   | 31.605     | -2768.835006      | -4.1103      | -1737047.540   |
| 4e        | 487.776         | 273.300   | 30.739     | -2768.837643      | -2.9506      | -1737039.229   |
| 5e\(_r\)  | 523.360         | 287.135   | 32.754     | -2847.410849      | -3.4955      | -1786311.772   |
| 5e\(_r\)  | 522.400         | 285.173   | 32.652     | -2847.384191      | -2.5603      | -1786294.586   |
| 6e\(_r\)  | 524.707         | 285.353   | 32.572     | -2847.387299      | -2.9052      | -1786326.083   |
| 7e\(_r\)  | 521.293         | 300.371   | 33.411     | -2847.374702      | -3.4864      | -1786294.437   |
| 8e        | 522.664         | 292.837   | 33.248     | -2847.406811      | -4.503       | -1786312.166   |
| 9e        | 520.921         | 294.807   | 32.833     | -2847.444241      | -2.7323      | -1786332.945   |
| 1f        | 487.899         | 274.076   | 30.636     | -2768.849583      | -1.8400      | -1737045.822   |
| 2f        | 486.362         | 280.737   | 31.157     | -2768.836631      | -2.0110      | -1737040.868   |
| 3f\(_r\)  | 487.135         | 292.714   | 31.977     | -2768.832700      | -1.8193      | -1737040.188   |
| 4f\(_r\)  | 487.678         | 289.331   | 31.909     | -2768.849084      | -3.5391      | -1737050.705   |
| 5f\(_r\)  | 521.079         | 308.440   | 34.197     | -2847.391269      | -2.7072      | -1786305.888   |
| 6f\(_r\)  | 522.421         | 299.102   | 33.510     | -2847.422623      | -1.8267      | -1786321.243   |
| 7f\(_r\)  | 521.798         | 290.501   | 32.593     | -2847.390721      | -1.2874      | -1786299.661   |
| 8f        | 524.850         | 289.066   | 32.647     | -2847.442797      | -1.8712      | -1786329.389   |
| 9f        | 520.529         | 303.017   | 33.767     | -2847.388166      | -1.1778      | -1786301.775   |
| 1g        | 487.305         | 279.773   | 31.451     | -2768.830174      | -3.4267      | -1737036.707   |
| 1h        | 487.657         | 281.702   | 31.475     | -2768.827055      | -2.8689      | -1737034.392   |
### Stereoselectivity

| Species | $E_{gas}$ (a.u.) | $E_{solv}$ (kcal/mol) | $G_{solv}$ (kcal/mol) |
|---------|------------------|------------------------|----------------------|
| 9a      | -2384.112912     | -2.1888                | -1495708.639         |
| 9a'     | -2384.106657     | -3.0125                | -1495703.660         |
| 10a$_{trans}$ | -2501.989940    | -1.8389                | -1569626.063         |
| 10a'$_{trans}$ | -2501.980252    | -1.8217                | -1569618.806         |
| 10a$_{cis}$  | -2501.981431    | -2.0743                | -1569620.375         |
| 10a'$_{cis}$ | -2501.969593    | -2.0500                | -1569614.318         |
| 11a'$_{path\,E}$ | -2501.950972    | -1.7915                | -1569599.755         |
| 12a$_{path\,E}$  | -2501.989299    | -1.7844                | -1569623.601         |
| 13a$_{path\,E}$  | -2501.948865    | -1.4108                | -1569600.229         |
| 14a$_{path\,E}$  | -2501.979440    | -2.3655                | -1569620.833         |
| 11a'$_{path\,E'}$ | -2501.948027    | -1.4327                | -1569598.963         |
| 12a$_{path\,E'}$  | -2501.994751    | -2.0553                | -1569626.261         |
| 13a'$_{path\,E'}$ | -2501.938013    | -1.6394                | -1569590.958         |
| 14a$_{path\,E'}$  | -2501.972613    | -2.1832                | -1569614.885         |
| 11a$_{path\,Z}$  | -2501.953562    | -1.5015                | -1569602.568         |
| 12a$_{path\,Z}$  | -2501.986201    | -2.1992                | -1569618.096         |
| 13a$_{path\,Z}$  | -2501.950525    | -1.4084                | -1569597.420         |
| 14a$_{path\,Z}$  | -2501.973315    | -1.9582                | -1569612.552         |
| 11a$_{path\,S}$  | -2501.972196    | -1.6555                | -1569600.203         |
| 12a$_{path\,S}$  | -2501.986320    | -1.8746                | -1569620.004         |
| 13a$_{path\,S}$  | -2501.948775    | -1.7070                | -1569596.996         |
| 14a$_{path\,S}$  | -2501.965091    | -3.1459                | -1569610.497         |

15a This structure corresponds to 9a generated with ethylene in the initiation phase, already reported above.
| Species | ZPE (kcal/mol) | S (cal/mol) | H (kcal/mol) | $E_{\text{gas}}$ (a.u.) | $E_{\text{solv}}$ (kcal/mol) | $G_{\text{solv}}$ (kcal/mol) |
|---------|----------------|-------------|--------------|--------------------------|-----------------------------|-----------------------------|
| 9e      | 397.292        | 246.258     | 26.452       | -2384.101623             | -4.3780                     | -1495701.665                |
| 9e'     | 396.961        | 243.902     | 26.033       | -2384.095200             | -4.8549                     | -1495698.159                |
| 10e     | 450.261        | 261.593     | 29.023       | -2501.959780             | -4.5137                     | -1569608.005                |
| 11e‡     | 449.794        | 263.665     | 28.890       | -2501.949723             | -3.9996                     | -1569602.398                |
| 12e     | 452.466        | 261.522     | 28.537       | -2501.997317             | -3.1968                     | -1569628.503                |
| 13e‡     | 450.476        | 262.486     | 28.699       | -2501.943445             | -1.3160                     | -1569594.932                |
| 14e     | 450.195        | 266.293     | 29.201       | -2501.975318             | -2.2508                     | -1569616.782                |

| Species |  |  |  |  |  |  |
|---------|  |  |  |  |  |  |
| ethene  | 32.065 | 52.323 | 2.501 | -78.539005 | 1.6695 | -49263.376 |
| styrene | 140.059 | 104.702 | 7.933 | -502.556887 | 1.6512 | -315241.046 |
| propene | 50.103 | 63.151 | 3.145 | -117.835434 | 2.0143 | -73906.479 |
| E 2-butene | 67.867 | 71.054 | 4.011 | -157.131053 | 2.3523 | -98548.261 |
| Z 2-butene | 67.970 | 71.837 | 4.017 | -157.129541 | 2.4379 | -98547.351 |
\[ 5a^+_{\text{cis}} (419.84i \text{ cm}^{-1}) \]

For the sake of clarity, the chemical structures and coordinates are not visible in this text format. However, they are present in the image. The coordinates and structures are essential for understanding the chemical compounds and their electronic states. If you need further assistance with interpreting the data, please let me know! 😊
RuC₃₈N₆H₄₆S₂O₉₄

§2b (5.05 cm⁻²)
| Atom  | X    | Y    | Z    |
|-------|------|------|------|
| H     | 4.92 | 5.60 | 1.36 |
| H     | 3.59 | 2.36 |      |
| N     | 4.00 | 1.42 | 1.37 |
| H     | 2.60 | 5.22 | 0.63 |
| H     | 1.18 | 4.36 | 1.24 |
| H     | 1.09 | 6.09 | 0.91 |
| H     | 2.54 | 3.86 |      |
| C     | 1.64 | 4.64 |      |
| N     | 0.24 | 4.48 |      |
| H     | 0.24 | 4.48 |      |
| C     | 0.24 | 4.48 |      |
| C     | 0.24 | 4.48 |      |
| C     | 0.24 | 4.48 |      |
| H     | 0.71 | 1.03 |      |
| H     | 1.09 | 1.21 |      |
| H     | 1.50 | 1.51 |      |
| H     | 1.53 | 1.24 |      |
| C     | 2.97 | 0.51 |      |
| H     | 0.54 | 1.75 |      |
| H     | 0.53 | 1.54 |      |
| H     | 0.93 | 0.93 |      |
| Ru    | 0.72 | 4.73 | 2.46 |
| H     | 3.49 | 3.16 | 1.84 |
| H     | 1.49 | 3.28 | 4.40 |
| H     | 0.23 | 3.74 | 5.31 |
| C     | 0.59 | 3.36 | 0.31 |
| H     | 3.96 | 4.50 | 1.55 |
| C     | 2.98 | 5.49 | 1.63 |
| H     | 1.43 | 4.10 | 0.02 |
| C     | 5.33 | 4.41 | 3.65 |
| H     | 2.49 | 3.66 | 2.91 |
| H     | 2.92 | 0.08 |      |
| C     | 1.16 | 4.09 | 0.69 |

**Image:**
- **1c:** A diagram showing a molecular structure with labeled atoms and bonds.
- **2c:** Another diagram showing a different molecular structure with labeled atoms and bonds.
| 8c from 6C\text{car} | 8c from 6C\text{trans} |
|---------------------|---------------------|
| \( \text{H} \) | \( \text{H} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{H} \) | \( \text{H} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{H} \) | \( \text{H} \) |
| \( \text{N} \) | \( \text{N} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{H} \) | \( \text{H} \) |
| \( \text{N} \) | \( \text{N} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{H} \) | \( \text{H} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{O} \) | \( \text{O} \) |
| \( \text{H} \) | \( \text{H} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{H} \) | \( \text{H} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{O} \) | \( \text{O} \) |
| \( \text{H} \) | \( \text{H} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{H} \) | \( \text{H} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{O} \) | \( \text{O} \) |
| \( \text{H} \) | \( \text{H} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{H} \) | \( \text{H} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{O} \) | \( \text{O} \) |
| \( \text{H} \) | \( \text{H} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{C} \) | \( \text{C} \) |
| \( \text{H} \) | \( \text{H} \) |
| \( \text{C} \) | \( \text{C} \) |
null
Stereoselectivity
RuC₃₃N₆H₄₄S₂
11a (230.64i cm⁻³)

path E

12a path E
