

# Localized Orbital Corrections for the Calculation of Barrier Heights in Density Functional Theory: Supporting Information

Michelle Lynn Hall, Dahlia A. Goldfeld, Arteum D. Bochevarov, and Richard A. Friesner

## Contents

- I. Literature references for dataset, p.S1
- II. Images of all transition states, p. S2
- III. Assignment of all B3LYP-LOC parameters, p. S6
- IV. Tests for over-fitting, p. S11
- V. Complete suite of B3LYP-LOC parameters p. S12
- VI. Enthalpy of reaction as computed by B3LYP and B3LYP-LOC, p. S14
- VII. Barrier height as computed by B3LYP and B3LYP-LOC, p. S17

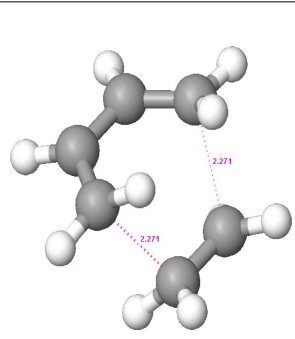
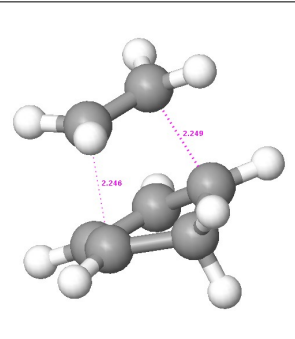
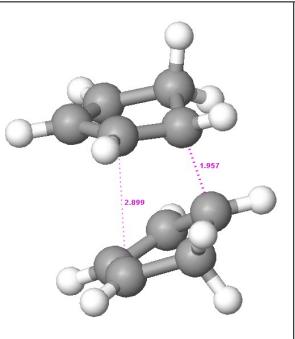
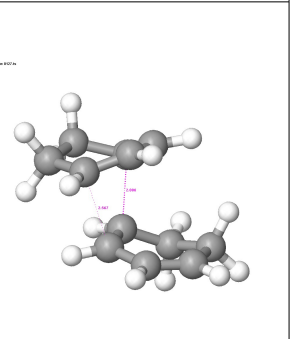
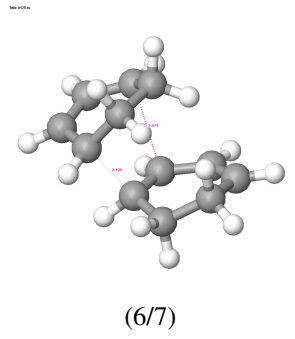
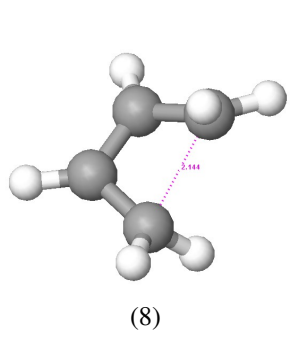
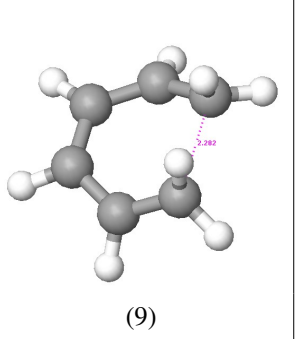
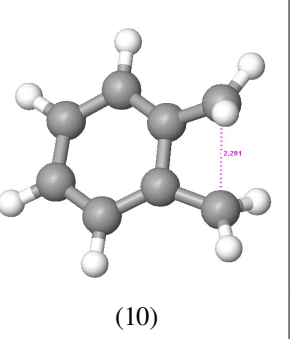
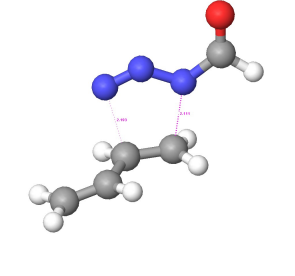
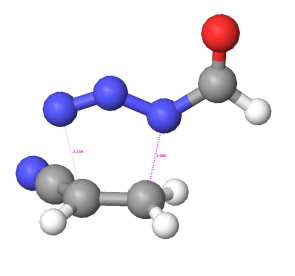
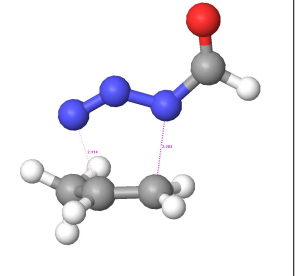
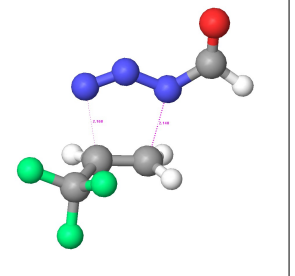
## I. Literature references for dataset

**Table S1:** List of literature references for dataset

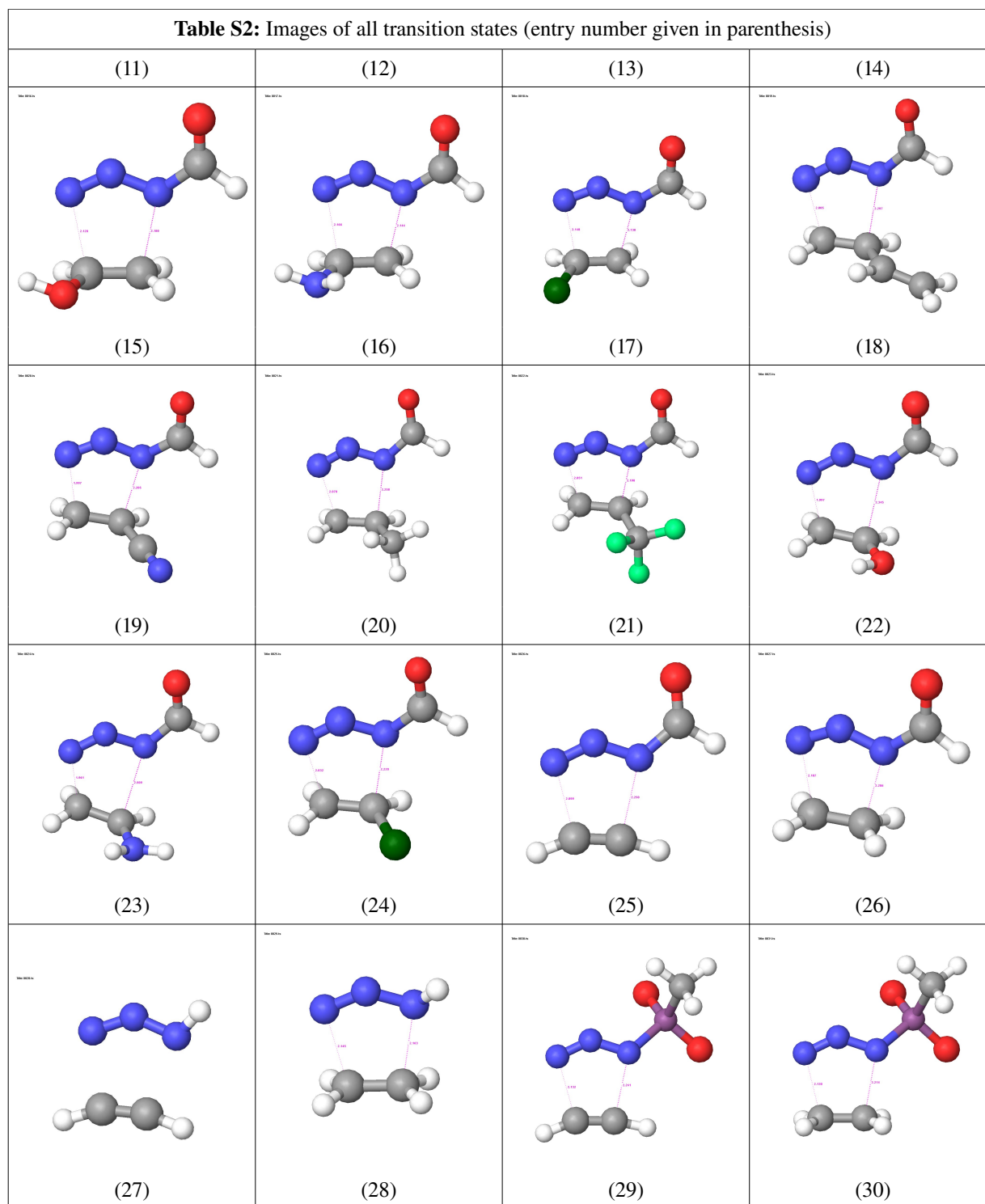
| <i>entry</i> | $\Delta H_{rx}$ | $\Delta H^\ddagger$ | <i>entry</i> | $\Delta H_{rx}$ | $\Delta H^\ddagger$ | <i>entry</i> | $\Delta H_{rx}$ | $\Delta H^\ddagger$ | <i>entry</i> | $\Delta H_{rx}$ | $\Delta H^\ddagger$ | <i>entry</i> | $\Delta H_{rx}$ | $\Delta H^\ddagger$ | <i>entry</i> | $\Delta H_{rx}$ | $\Delta H^\ddagger$ |
|--------------|-----------------|---------------------|--------------|-----------------|---------------------|--------------|-----------------|---------------------|--------------|-----------------|---------------------|--------------|-----------------|---------------------|--------------|-----------------|---------------------|
|              | <i>n</i>        |                     |              | <i>n</i>        |                     |              | <i>n</i>        |                     |              | <i>n</i>        |                     |              | <i>n</i>        |                     |              | <i>n</i>        |                     |
| 1            | I               | II                  | 19           | II              | II                  | 37           | V               | V                   | 55           | VI              | VI                  | 73           | VII             | VII                 | 91           | VIII            | VIII                |
| 2            | I               | II                  | 20           | II              | II                  | 38           | V               | V                   | 56           | VI              | VI                  | 74           | VII             | VII                 | 92           | VIII            | VIII                |
| 3            | I               | II                  | 21           | II              | II                  | 39           | V               | V                   | 57           | VI              | VI                  | 75           | VII             | VII                 | 93           | VIII            | VIII                |
| 4            | III             | III                 | 22           | II              | II                  | 40           | V               | V                   | 58           | VI              | VI                  | 76           | VII             | VII                 | 94           | VIII            | VIII                |
| 5            | III             | III                 | 23           | II              | II                  | 41           | V               | V                   | 59           | VI              | VI                  | 77           | VII             | VII                 | 95           | VIII            | VIII                |
| 6            | III             | III                 | 24           | II              | II                  | 42           | V               | V                   | 60           | VI              | VI                  | 78           | VII             | VII                 | 96           | VIII            | VIII                |
| 7            | III             | III                 | 25           | II              | II                  | 43           | VI              | VI                  | 61           | VI              | VI                  | 79           | VII             | VII                 | 97           | VIII            | VIII                |
| 8            | I               | II                  | 26           | II              | II                  | 44           | VI              | VI                  | 62           | VI              | VI                  | 80           | VII             | VII                 | 98           | VIII            | VIII                |
| 9            | I               | II                  | 27           | II              | II                  | 45           | VI              | VI                  | 63           | VI              | VI                  | 81           | VII             | VII                 | 99           | VIII            | VIII                |
| 10           | I               | II                  | 28           | II              | II                  | 46           | VI              | VI                  | 64           | VI              | VI                  | 82           | VII             | VII                 | 100          | VIII            | VIII                |
| 11           | II              | II                  | 29           | II              | II                  | 47           | VI              | VI                  | 65           | VI              | VI                  | 83           | VII             | VII                 | 101          | I               | II                  |
| 12           | II              | II                  | 30           | II              | II                  | 48           | VI              | VI                  | 66           | VI              | VI                  | 84           | VII             | VII                 | 102          | I               | II                  |
| 13           | II              | II                  | 31           | II              | II                  | 49           | VI              | VI                  | 67           | VI              | VI                  | 85           | VII             | VII                 | 103          | I               | II                  |
| 14           | II              | II                  | 32           | II              | II                  | 50           | VI              | VI                  | 68           | VI              | VI                  | 86           | VII             | VII                 | 104          | I               | II                  |
| 15           | II              | II                  | 33           | II              | II                  | 51           | VI              | VI                  | 69           | VI              | VI                  | 87           | VIII            | VIII                | 105          | I               | II                  |
| 16           | II              | II                  | 34           | II              | II                  | 52           | VI              | VI                  | 70           | VI              | VI                  | 88           | VIII            | VIII                |              |                 |                     |
| 17           | II              | II                  | 35           | IV              | IV                  | 53           | VI              | VI                  | 71           | VII             | VII                 | 89           | VIII            | VIII                |              |                 |                     |
| 18           | II              | II                  | 36           | IV              | IV                  | 54           | VI              | VI                  | 72           | VII             | VII                 | 90           | VIII            | VIII                |              |                 |                     |

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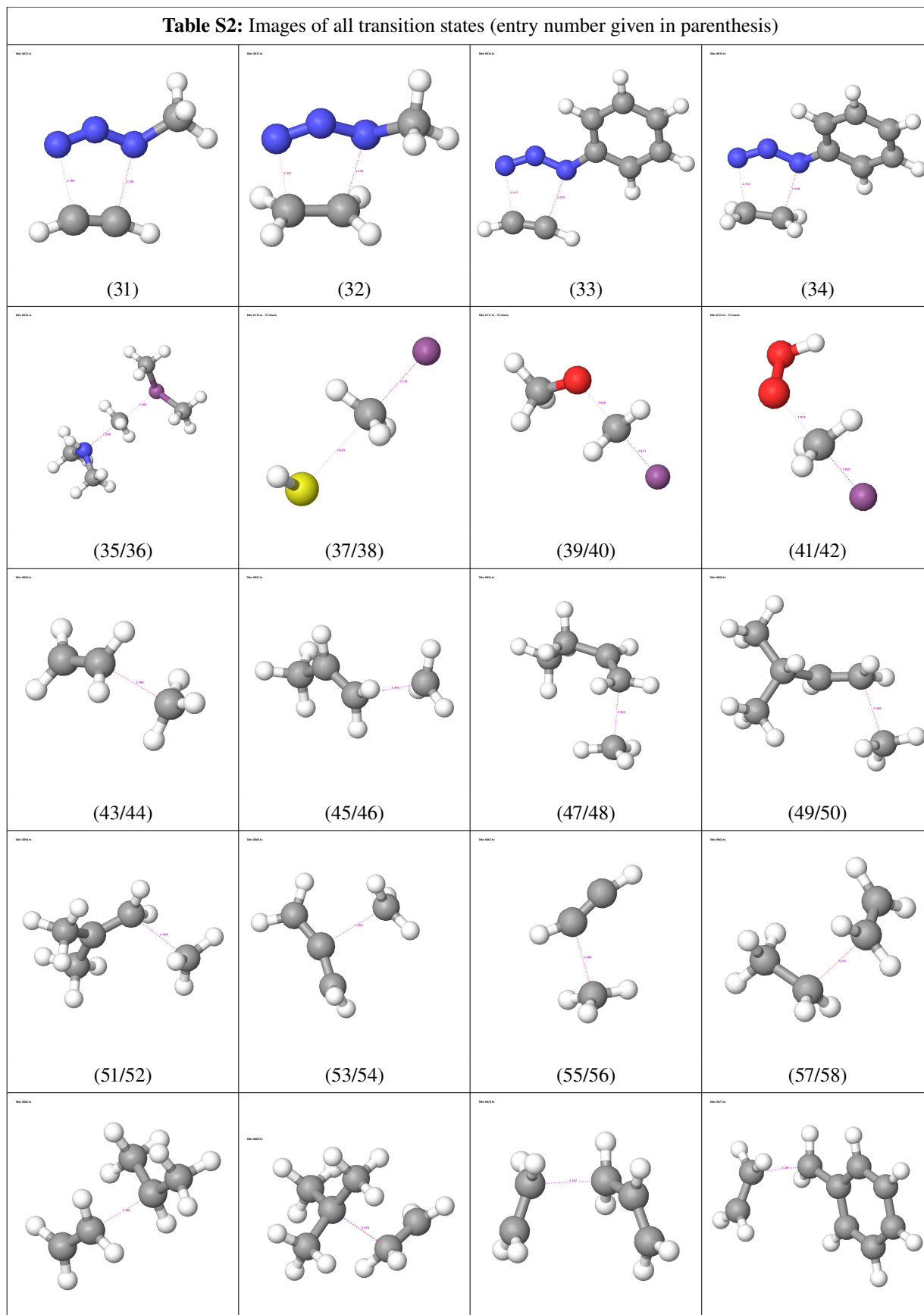
## II. Images of all transition states

| Table S2: Images of all transition states (entry number given in parenthesis)       |   |  |   |
|---|---|--|---|
|   |   |   |   |
| (1)   | (2)   | (3)  | (4/5)   |
|  |  |  |  |
| (6/7)   | (8)   | (9)  | (10)  |
|  |  |  |  |

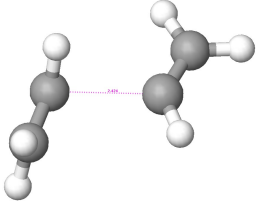
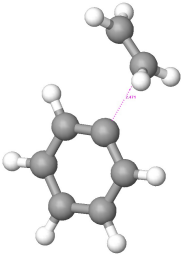
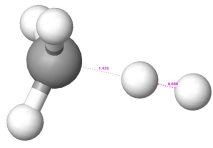
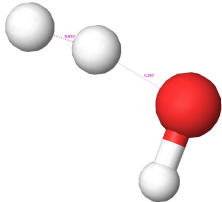
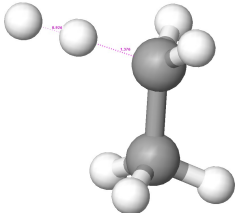
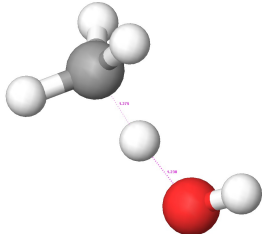
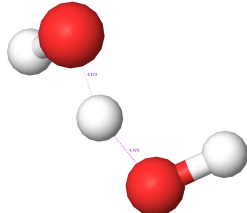
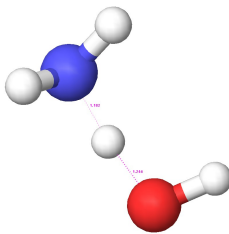
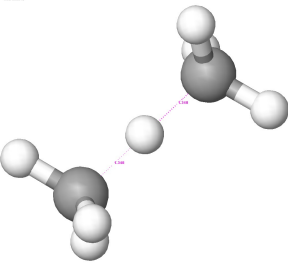
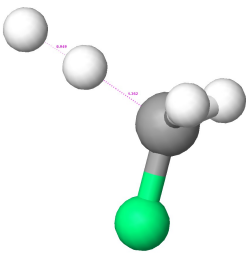
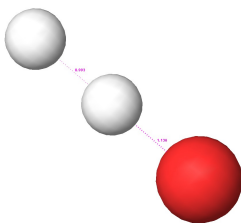
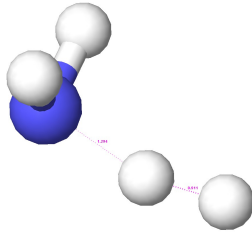
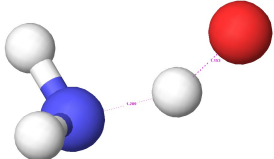
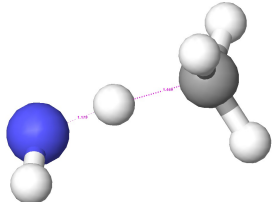
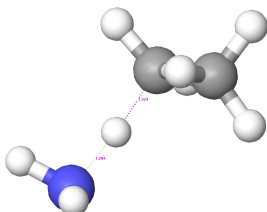
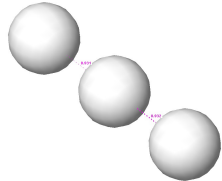
**Table S2:** Images of all transition states (entry number given in parenthesis)



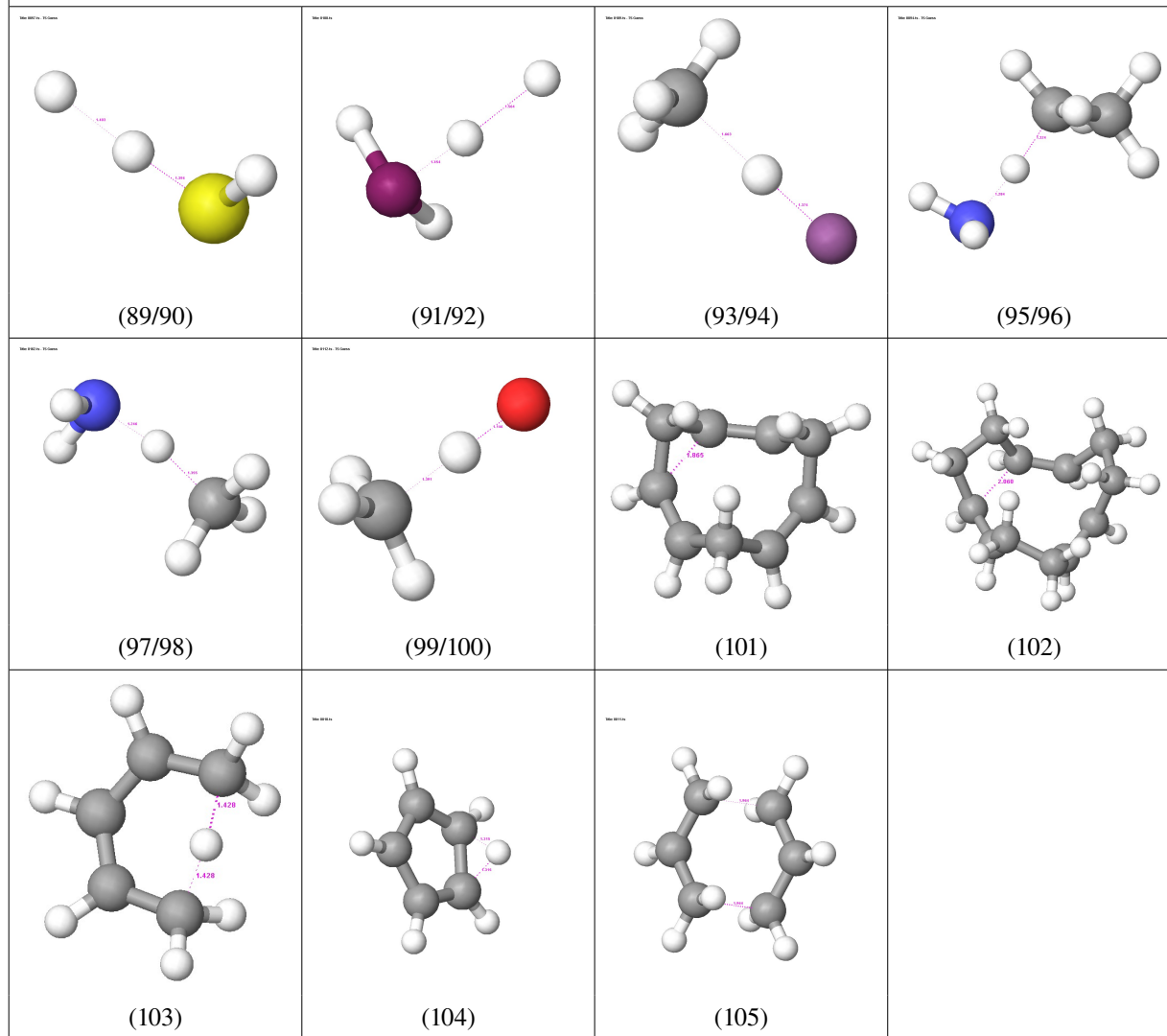
**Table S2:** Images of all transition states (entry number given in parenthesis)



**Table S2:** Images of all transition states (entry number given in parenthesis)

| (59/60)  | (61/62)  | (63/64)   | (65/66)  |
|--|--|---|--|
|  <p>(67/68)</p> |  <p>(69/70)</p> |  <p>(71/72)</p>   |  <p>(73/74)</p> |
|  <p>(75/76)</p> |  <p>(77)</p>    |  <p>(78)</p>      |  <p>(79)</p>    |
|  <p>(80)</p>   |  <p>(81)</p>   |  <p>(82)</p>     |  <p>(83)</p>   |
|  <p>(84)</p>  |  <p>(85)</p>  |  <p>(86/87)</p> |  <p>(88)</p>  |

**Table S2:** Images of all transition states (entry number given in parenthesis)



### III. Assignment of all B3LYP-LOC parameters

**Table S3:** B3LYP-LOC Parameter Assignments

|      | parameters exclusive to transition states |                  |                |                      |               |               |               |                | global parameters     |               |                |                |                  |              |              |                |              |             |              |             |             |             |             |            |               |              |           |             |           |           |           |                      |
|------|---|------------------|----------------|----------------------|---------------|---------------|---------------|----------------|-----------------------|---------------|----------------|----------------|------------------|--------------|--------------|----------------|--------------|-------------|--------------|-------------|-------------|-------------|-------------|------------|---------------|--------------|-----------|-------------|-----------|-----------|-----------|----------------------|
|      | <i>N/P_sp1.5</i>                          | <i>N/P_sp2.5</i> | <i>O_sp2.5</i> | <i>MSBC/LSBC_0.5</i> | <i>AA_1.5</i> | <i>AA_2.5</i> | <i>HH_0.5</i> | <i>H_dival</i> | <i>ion correction</i> | <i>N/P_sp</i> | <i>N/P_sp2</i> | <i>N/P_sp3</i> | <i>N/P_quart</i> | <i>O_sp2</i> | <i>O_sp3</i> | <i>OCT_EXP</i> | <i>NPOLH</i> | <i>POLH</i> | <i>NPOLF</i> | <i>POLF</i> | <i>SSBC</i> | <i>MSBC</i> | <i>LSBC</i> | <i>DBC</i> | <i>TBNPOL</i> | <i>TBPOL</i> | <i>CT</i> | <i>ESBC</i> | <i>RH</i> | <i>RA</i> | <i>RT</i> | <i>H2 correction</i> |
| 1-r  |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              |                | 10           |             |              |             |             | 1           |             | 3          |               |              |           |             |           |           |           |                      |
| 1-ts |   |                  |                | 2                    | 4             |               |               |                |                       |               |                |                |                  |              |              |                | 10           |             |              |             |             |             |             |            |               |              |           | 6           |           |           |           |                      |
| 1-p  |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              |                | 10           |             |              |             |             | 5           |             | 1          |               |              |           | 8           |           |           |           |                      |
| 2-r  |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              |                | 10           |             |              |             |             | 3           |             | 3          |               |              |           | 2           |           |           |           |                      |
| 2-ts |   |                  |                | 2                    | 4             |               |               |                |                       |               |                |                |                  |              |              |                | 10           |             |              |             |             | 2           |             |            |               |              |           | 6           |           |           |           |                      |
| 2-p  |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              |                | 10           |             |              |             |             | 7           |             | 1          |               |              |           | 12          |           |           |           |                      |

**Table S3: B3LYP-LOC Parameter Assignments**

|           | parameters exclusive to transition states |                  |                |                      |               |               |               |                | global parameters     |               |                |                |                  |              |              |                |              |             |              |             |             |             |             |            |               |              |           |             |           |           |           |                      |
|-----------|---|------------------|----------------|----------------------|---------------|---------------|---------------|----------------|-----------------------|---------------|----------------|----------------|------------------|--------------|--------------|----------------|--------------|-------------|--------------|-------------|-------------|-------------|-------------|------------|---------------|--------------|-----------|-------------|-----------|-----------|-----------|----------------------|
|           | <i>N/P_sp1.5</i>                          | <i>N/P_sp2.5</i> | <i>O_sp2.5</i> | <i>MSBC/LSBC_0.5</i> | <i>AA_1.5</i> | <i>AA_2.5</i> | <i>HH_0.5</i> | <i>H_dival</i> | <i>ion correction</i> | <i>N/P_sp</i> | <i>N/P_sp2</i> | <i>N/P_sp3</i> | <i>N/P_quart</i> | <i>O_sp2</i> | <i>O_sp3</i> | <i>OCT_EXP</i> | <i>NPOLH</i> | <i>POLH</i> | <i>NPOLF</i> | <i>POLF</i> | <i>SSBC</i> | <i>MSBC</i> | <i>LSBC</i> | <i>DBC</i> | <i>TBNPOL</i> | <i>TBPOL</i> | <i>CT</i> | <i>ESBC</i> | <i>RH</i> | <i>RA</i> | <i>RT</i> | <i>H2 correction</i> |
| 3-r       |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 12             |              |             |              |             | 6           |             | 4           |            |               |              |           | 4           |           |           |           |                      |
| 3-ts      |   |                  |                | 2                    | 4             |               |               |                |                       |               |                |                |                  |              |              | 12             |              |             |              |             | 5           |             | 1           |            |               |              |           | 15          |           |           |           |                      |
| 3-p       |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 12             |              |             |              |             | 10          |             | 2           |            |               |              |           | 18          |           |           |           |                      |
| 4-t/5-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 16             |              |             |              |             | 8           |             | 4           |            |               |              |           | 8           |           |           |           |                      |
| 4-ts/5-ts |   |                  |                | 2                    | 4             |               |               |                |                       |               |                |                |                  |              |              | 16             |              |             |              |             | 7           |             | 1           |            |               |              |           | 26          |           |           |           |                      |
| 4-p/5-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 16             |              |             |              |             | 1           |             | 2           |            |               |              |           | 32          |           |           |           |                      |
| 6-t/7-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 16             |              |             |              |             | 8           |             | 4           |            |               |              |           | 8           |           |           |           |                      |
| 6-ts/7-ts |   |                  |                | 2                    | 4             |               |               |                |                       |               |                |                |                  |              |              | 16             |              |             |              |             | 7           |             | 1           |            |               |              |           | 26          |           |           |           |                      |
| 6-p/7-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 16             |              |             |              |             | 1           |             | 2           |            |               |              |           | 32          |           |           |           |                      |
| 8-r       |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 6              |              |             |              |             | 3           |             | 1           |            |               |              |           |             |           |           |           |                      |
| 8-ts      |   |                  |                | 1                    | 3             |               |               |                |                       |               |                |                |                  |              |              | 6              |              |             |              |             |             |             |             |            |               |              |           |             |           |           |           |                      |
| 8-p       |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 6              |              |             |              |             | 1           |             | 2           |            |               |              |           |             |           |           |           |                      |
| 9-r       |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 8              |              |             |              |             | 2           |             | 3           |            |               |              |           |             |           |           |           |                      |
| 9-ts      |   |                  |                | 1                    | 5             |               |               |                |                       |               |                |                |                  |              |              | 8              |              |             |              |             |             |             |             |            |               |              |           | 6           |           |           |           |                      |
| 9-p       |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 8              |              |             |              |             | 4           |             | 2           |            |               |              |           | 4           |           |           |           |                      |
| 10-r      |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 8              |              |             |              |             | 4           |             | 4           |            |               |              |           | 4           |           |           |           |                      |
| 10-ts     |   |                  |                | 1                    | 7             |               |               |                |                       |               |                |                |                  |              |              | 8              |              |             |              |             | 1           |             | 0           |            |               |              |           | 9           |           |           |           |                      |
| 10-p      |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 8              |              |             |              |             | 3           | 3           | 3           |            |               |              |           |             |           |           |           |                      |
| 11-r      |   |                  |                |                      |               |               |               |                |                       | 1             | 1              |                | 1                |              | 1            | 7              |              |             |              |             | 1           | 2           | 3           |            | 1             | 1            |           |             |           |           |           |                      |
| 11-ts     | 2   | 1                | 1              |                      | 3             | 1             |               |                |                       |               |                |                |                  |              | 7            |                |              |             |              |             | 2           |             | 1           |            |               | 1            | 10        |             |           |           |           |                      |
| 11-p      |   |                  |                |                      |               |               |               |                |                       | 2             | 1              |                | 1                |              | 7            |                |              |             |              | 3           | 3           | 3           |             |            |               |              |           | 14          |           |           |           |                      |
| 12-r      |   |                  |                |                      |               |               |               |                |                       | 2             | 1              |                | 1                |              | 4            |                |              |             |              | 1           | 2           | 2           |             | 2          | 1             |              |           |             |           |           |           |                      |
| 12-ts     | 2   | 1                | 1              |                      | 3             | 1             |               |                |                       | 1             |                |                |                  |              | 4            |                |              |             |              |             | 2           |             |             |            | 1             | 1            | 10        |             |           |           |           |                      |
| 12-p      |   |                  |                |                      |               |               |               |                |                       | 1             | 2              | 1              |                  | 1            | 4            |                |              |             |              | 3           | 3           | 2           |             | 1          |               |              | 14        |             |           |           |           |                      |
| 13-r      |   |                  |                |                      |               |               |               |                |                       | 1             | 1              |                | 1                |              | 7            |                |              |             |              | 1           | 2           | 2           |             | 1          | 1             |              |           |             |           |           |           |                      |
| 13-ts     | 2   | 1                | 1              |                      | 3             | 1             |               |                |                       |               |                |                |                  |              | 7            |                |              |             |              |             | 2           |             |             |            |               | 1            | 10        |             |           |           |           |                      |
| 13-p      |   |                  |                |                      |               |               |               |                |                       | 2             | 1              |                | 1                |              | 7            |                |              |             |              | 3           | 3           | 2           |             |            |               |              | 14        |             |           |           |           |                      |
| 14-r      |   |                  |                |                      |               |               |               |                |                       | 1             | 1              |                | 1                |              | 4            |                |              |             | 3            | 1           | 2           |             | 2           |            | 1             | 1            |           |             |           |           |           |                      |
| 14-ts     | 2   | 1                | 1              |                      | 3             | 1             |               |                |                       |               |                |                |                  |              | 4            |                |              |             | 3            |             | 2           |             |             |            |               | 1            | 10        |             |           |           |           |                      |
| 14-p      |   |                  |                |                      |               |               |               |                |                       | 2             | 1              |                | 1                |              | 4            |                |              |             | 3            | 3           | 3           |             | 2           |            |               |              | 14        |             |           |           |           |                      |
| 15-r      |   |                  |                |                      |               |               |               |                |                       | 1             | 1              |                | 1                |              | 2            | 4              | 1            |             |              | 2           | 1           | 2           |             | 1          | 1             |              |           |             |           |           |           |                      |
| 15-ts     | 2   | 1                | 1              |                      | 3             | 1             |               |                |                       |               |                |                |                  | 1            | 4            | 1              |              |             |              | 1           | 1           |             |             |            |               | 1            | 10        |             |           |           |           |                      |
| 15-p      |   |                  |                |                      |               |               |               |                |                       | 2             | 1              |                | 1                | 1            | 4            | 1              |              |             |              | 4           | 2           | 2           |             |            |               |              | 14        |             |           |           |           |                      |
| 16-r      |   |                  |                |                      |               |               |               |                |                       | 1             | 1              | 1              | 1                |              | 6            |                |              |             |              | 2           | 1           | 2           |             | 1          | 1             |              |           |             |           |           |           |                      |
| 16-ts     | 2   | 1                | 1              |                      | 3             | 1             |               |                |                       |               |                | 1              |                  |              | 6            |                |              |             |              | 1           | 1           |             |             |            |               | 1            | 10        |             |           |           |           |                      |
| 16-p      |   |                  |                |                      |               |               |               |                |                       | 2             | 2              |                | 1                |              | 6            |                |              |             |              | 4           | 2           | 2           |             |            |               |              | 14        |             |           |           |           |                      |
| 17-r      |   |                  |                |                      |               |               |               |                |                       | 1             | 1              |                | 1                |              | 4            |                |              |             |              | 1           | 2           | 2           |             | 1          | 1             |              |           |             |           |           |           |                      |
| 17-ts     | 2   | 1                | 1              |                      | 3             | 1             |               |                |                       |               |                |                |                  |              | 4            |                |              |             |              |             | 2           |             |             |            |               | 1            | 10        |             |           |           |           |                      |

**Table S3: B3LYP-LOC Parameter Assignments**

|       | parameters exclusive to transition states |                  |                |                      |               |               |               |                | global parameters     |               |                |                |                  |              |              |                |              |             |              |             |             |             |             |            |               |              |           |             |           |           |           |                      |  |  |
|-------|---|------------------|----------------|----------------------|---------------|---------------|---------------|----------------|-----------------------|---------------|----------------|----------------|------------------|--------------|--------------|----------------|--------------|-------------|--------------|-------------|-------------|-------------|-------------|------------|---------------|--------------|-----------|-------------|-----------|-----------|-----------|----------------------|--|--|
|       | <i>N/P_sp1.5</i>                          | <i>N/P_sp2.5</i> | <i>O_sp2.5</i> | <i>MSBC/LSBC_0.5</i> | <i>AA_1.5</i> | <i>AA_2.5</i> | <i>HH_0.5</i> | <i>H_dival</i> | <i>ion correction</i> | <i>N/P_sp</i> | <i>N/P_sp2</i> | <i>N/P_sp3</i> | <i>N/P_quart</i> | <i>O_sp2</i> | <i>O_sp3</i> | <i>OCT_EXP</i> | <i>NPOLH</i> | <i>POLH</i> | <i>NPOLF</i> | <i>POLF</i> | <i>SSBC</i> | <i>MSBC</i> | <i>LSBC</i> | <i>DBC</i> | <i>TBNPOL</i> | <i>TBPOL</i> | <i>CT</i> | <i>ESBC</i> | <i>RH</i> | <i>RA</i> | <i>RT</i> | <i>H2 correction</i> |  |  |
| 17-p  |   |                  |                |                      |               |               |               |                |                       |               | 2              | 1              |                  | 1            |              |                | 4            |             |              |             | 3           | 3           |             | 2          |               |              |           |             |           |           | 14        |                      |  |  |
| 18-r  |   |                  |                |                      |               |               |               |                |                       | 1             | 1              |                | 1                |              | 1            |                | 7            |             |              |             | 1           | 2           |             | 3          |               | 1            | 1         |             |           |           |           |                      |  |  |
| 18-ts | 2   | 1                | 1              |                      | 3             | 1             |               |                |                       |               |                |                |                  |              |              |                | 7            |             |              |             |             | 2           |             | 1          |               |              | 1         | 10          |           |           |           |                      |  |  |
| 18-p  |   |                  |                |                      |               |               |               |                |                       |               | 2              | 1              |                  | 1            |              |                | 7            |             |              |             | 3           | 3           |             | 3          |               |              |           |             |           |           |           | 14                   |  |  |
| 19-r  |   |                  |                |                      |               |               |               |                |                       | 2             | 1              |                | 1                |              | 1            |                | 4            |             |              |             | 1           | 2           |             | 2          |               | 2            | 1         |             |           |           |           |                      |  |  |
| 19-ts | 2   | 1                | 1              |                      | 3             | 1             |               |                |                       | 1             |                |                |                  |              |              |                | 4            |             |              |             |             | 2           |             |            |               | 1            | 1         | 10          |           |           |           |                      |  |  |
| 19-p  |   |                  |                |                      |               |               |               |                |                       | 1             | 2              | 1              |                  | 1            |              |                | 4            |             |              |             | 3           | 3           |             | 2          |               | 1            |           |             |           |           |           | 14                   |  |  |
| 20-r  |   |                  |                |                      |               |               |               |                |                       | 1             | 1              |                | 1                |              | 1            |                | 7            |             |              |             | 1           | 2           |             | 2          |               | 1            | 1         |             |           |           |           |                      |  |  |
| 20-ts | 2   | 1                | 1              |                      | 3             | 1             |               |                |                       |               |                |                |                  |              |              |                | 7            |             |              |             |             | 2           |             |            |               |              | 1         | 10          |           |           |           |                      |  |  |
| 20-p  |   |                  |                |                      |               |               |               |                |                       |               | 2              | 1              |                  | 1            |              |                | 7            |             |              |             | 3           | 3           |             | 2          |               |              |           |             |           |           |           | 14                   |  |  |
| 21-r  |   |                  |                |                      |               |               |               |                |                       | 1             | 1              |                | 1                |              | 1            |                | 4            |             |              |             | 3           | 1           | 2           | 2          |               | 1            | 1         |             |           |           |           |                      |  |  |
| 21-ts | 2   | 1                | 1              |                      | 3             | 1             |               |                |                       |               |                |                |                  |              |              |                | 4            |             |              |             | 3           |             |             |            |               |              | 1         | 10          |           |           |           |                      |  |  |
| 21-p  |   |                  |                |                      |               |               |               |                |                       |               | 2              | 1              |                  | 1            |              |                | 4            |             |              |             | 3           | 3           | 3           | 2          |               |              |           |             |           |           |           | 14                   |  |  |
| 22-r  |   |                  |                |                      |               |               |               |                |                       | 1             | 1              |                | 1                |              | 2            |                | 4            | 1           |              |             | 2           | 1           |             | 2          |               | 1            | 1         |             |           |           |           |                      |  |  |
| 22-ts | 2   | 1                | 1              |                      | 3             | 1             |               |                |                       |               |                |                |                  | 1            |              |                | 4            | 1           |              |             | 1           | 1           |             |            |               |              | 1         | 10          |           |           |           |                      |  |  |
| 22-p  |   |                  |                |                      |               |               |               |                |                       |               | 2              | 1              |                  | 1            | 1            |                | 4            | 1           |              |             | 4           | 2           |             | 2          |               |              |           |             |           |           |           | 14                   |  |  |
| 23-r  |   |                  |                |                      |               |               |               |                |                       | 1             | 1              | 1              | 1                |              | 1            |                | 6            |             |              |             | 2           | 1           |             | 2          |               | 1            | 1         |             |           |           |           |                      |  |  |
| 23-ts | 2   | 1                | 1              |                      | 3             | 1             |               |                |                       |               |                | 1              |                  |              |              |                | 6            |             |              |             | 1           | 1           |             |            |               |              | 1         | 10          |           |           |           |                      |  |  |
| 23-p  |   |                  |                |                      |               |               |               |                |                       |               | 2              | 2              |                  | 1            |              |                | 6            |             |              |             | 4           | 2           |             | 2          |               |              |           |             |           |           |           | 14                   |  |  |
| 24-r  |   |                  |                |                      |               |               |               |                |                       | 1             | 1              |                | 1                |              | 1            |                | 4            |             |              |             | 1           | 2           |             | 2          |               | 1            | 1         |             |           |           |           |                      |  |  |
| 24-ts | 2   | 1                | 1              |                      | 3             | 1             |               |                |                       |               |                |                |                  |              |              |                | 4            |             |              |             |             | 2           |             |            |               |              | 1         | 10          |           |           |           |                      |  |  |
| 24-p  |   |                  |                |                      |               |               |               |                |                       |               | 2              | 1              |                  | 1            |              |                | 4            |             |              |             | 3           | 3           |             | 2          |               |              |           |             |           |           |           | 14                   |  |  |
| 25-r  |   |                  |                |                      |               |               |               |                |                       | 1             | 1              |                | 1                |              | 1            |                | 3            |             |              |             | 1           | 1           |             | 1          | 1             | 1            | 1         |             |           |           |           |                      |  |  |
| 25-ts | 2   | 1                | 1              |                      | 2             | 2             |               |                |                       |               |                |                |                  |              |              |                | 3            |             |              |             |             | 1           |             |            |               |              | 1         | 5           |           |           |           |                      |  |  |
| 25-p  |   |                  |                |                      |               |               |               |                |                       |               | 2              | 1              |                  | 1            |              |                | 3            |             |              |             | 3           | 1           |             | 3          |               |              |           |             |           |           |           | 6                    |  |  |
| 26-r  |   |                  |                |                      |               |               |               |                |                       | 1             | 1              |                | 1                |              | 1            |                | 5            |             |              |             | 1           | 1           |             | 2          |               | 1            | 1         |             |           |           |           |                      |  |  |
| 26-ts | 2   | 1                | 1              |                      | 3             | 1             |               |                |                       |               |                |                |                  |              |              |                | 5            |             |              |             |             | 1           |             |            |               |              | 1         | 7           |           |           |           |                      |  |  |
| 26-p  |   |                  |                |                      |               |               |               |                |                       |               | 2              | 1              |                  | 1            |              |                | 5            |             |              |             | 3           | 2           |             | 2          |               |              |           |             |           |           |           | 10                   |  |  |
| 27-r  |   |                  |                |                      |               |               |               |                |                       |               | 2              |                | 1                |              |              |                | 3            |             |              |             |             |             |             | 2          | 1             | 1            |           |             |           |           |           |                      |  |  |
| 27-ts | 1   | 1                |                |                      | 1             | 1             |               |                |                       |               | 1              |                |                  |              |              |                | 3            |             |              |             |             |             |             | 1          |               |              | 1         | 1           |           |           |           |                      |  |  |
| 27-p  |   |                  |                |                      |               |               |               |                |                       |               | 2              | 1              |                  |              |              |                | 3            |             |              |             | 2           | 1           |             | 2          |               |              |           |             |           |           |           | 2                    |  |  |
| 28-r  |   |                  |                |                      |               |               |               |                |                       |               | 2              |                | 1                |              |              |                | 5            |             |              |             |             |             |             | 3          |               | 1            |           |             |           |           |           |                      |  |  |
| 28-ts | 1   | 1                |                |                      | 2             |               |               |                |                       |               | 1              |                |                  |              |              |                | 5            |             |              |             |             |             |             | 1          |               |              | 1         | 3           |           |           |           |                      |  |  |
| 28-p  |   |                  |                |                      |               |               |               |                |                       |               | 2              | 1              |                  |              |              |                | 5            |             |              |             | 2           | 2           |             | 1          |               |              |           |             |           |           |           | 6                    |  |  |
| 29-r  |   |                  |                |                      |               |               |               |                |                       |               | 2              |                | 1                |              | 2            | 1              | 5            |             |              |             |             |             | 4           | 2          | 1             |              | 3         | 2           |           |           |           |                      |  |  |
| 29-ts | 1   | 1                |                |                      | 1             | 1             |               |                |                       |               | 1              |                |                  |              | 2            | 1              | 5            |             |              |             |             |             | 4           | 1          |               |              | 3         | 6           |           |           |           |                      |  |  |
| 29-p  |   |                  |                |                      |               |               |               |                |                       |               | 2              | 1              |                  |              | 2            | 1              | 5            |             |              |             | 2           | 1           | 4           | 2          |               |              | 2         | 8           |           |           |           |                      |  |  |
| 30-r  |   |                  |                |                      |               |               |               |                |                       |               | 2              |                | 1                |              | 2            | 1              | 7            |             |              |             |             |             | 4           | 3          |               |              | 3         | 2           |           |           |           |                      |  |  |
| 30-ts | 1   | 1                |                |                      | 2             |               |               |                |                       |               | 1              |                |                  |              | 2            | 1              | 7            |             |              |             |             |             | 4           | 1          |               |              | 3         | 8           |           |           |           |                      |  |  |
| 30-p  |   |                  |                |                      |               |               |               |                |                       |               | 2              | 1              |                  |              | 2            | 1              | 7            |             |              |             | 2           | 2           | 4           | 1          |               |              | 2         | 12          |           |           |           |                      |  |  |



**Table S3: B3LYP-LOC Parameter Assignments**

|             | parameters exclusive to transition states |                  |                |                      |               |               |               |                | global parameters     |               |                |                |                  |              |              |                |              |             |              |             |             |             |             |            |               |              |           |             |           |           |           |                      |  |
|-------------|---|------------------|----------------|----------------------|---------------|---------------|---------------|----------------|-----------------------|---------------|----------------|----------------|------------------|--------------|--------------|----------------|--------------|-------------|--------------|-------------|-------------|-------------|-------------|------------|---------------|--------------|-----------|-------------|-----------|-----------|-----------|----------------------|--|
|             | <i>N/P_sp1.5</i>                          | <i>N/P_sp2.5</i> | <i>O_sp2.5</i> | <i>MSBC/LSBC_0.5</i> | <i>AA_1.5</i> | <i>AA_2.5</i> | <i>HH_0.5</i> | <i>H_dival</i> | <i>ion correction</i> | <i>N/P_sp</i> | <i>N/P_sp2</i> | <i>N/P_sp3</i> | <i>N/P_quart</i> | <i>O_sp2</i> | <i>O_sp3</i> | <i>OCT_EXP</i> | <i>NPOLH</i> | <i>POLH</i> | <i>NPOLF</i> | <i>POLF</i> | <i>SSBC</i> | <i>MSBC</i> | <i>LSBC</i> | <i>DBC</i> | <i>TBNPOL</i> | <i>TBPOL</i> | <i>CT</i> | <i>ESBC</i> | <i>RH</i> | <i>RA</i> | <i>RT</i> | <i>H2 correction</i> |  |
| 31-r        |   |                  |                |                      |               |               |               |                |                       | 2             |                | 1              |                  |              |              | 5              |              |             |              |             | 1           |             |             | 2          | 1             |              | 1         |             |           |           |           |                      |  |
| 31-ts       | 1   | 1                |                |                      | 1             | 1             |               |                |                       | 1             |                |                |                  |              |              | 5              |              |             |              |             | 1           |             |             | 1          |               |              | 1         | 4           |           |           |           |                      |  |
| 31-p        |   |                  |                |                      |               |               |               |                |                       | 2             | 1              |                |                  |              |              | 5              |              |             |              |             | 3           | 1           |             | 2          |               |              |           | 6           |           |           |           |                      |  |
| 32-r        |   |                  |                |                      |               |               |               |                |                       | 2             |                | 1              |                  |              |              | 7              |              |             |              |             | 1           |             |             | 3          |               |              | 1         |             |           |           |           |                      |  |
| 32-ts       | 1   | 1                |                |                      | 2             |               |               |                |                       | 1             |                |                |                  |              |              | 7              |              |             |              |             | 1           |             |             | 1          |               |              | 1         | 6           |           |           |           |                      |  |
| 32-p        |   |                  |                |                      |               |               |               |                |                       | 2             | 1              |                |                  |              |              | 7              |              |             |              |             | 3           | 2           |             | 1          |               |              |           | 10          |           |           |           |                      |  |
| 33-r        |   |                  |                |                      |               |               |               |                |                       | 2             |                | 1              |                  |              |              | 7              |              |             |              |             | 4           |             |             | 5          | 1             |              | 1         | 2           |           |           |           |                      |  |
| 33-ts       | 1   | 1                |                |                      | 1             | 1             |               |                |                       | 1             |                |                |                  |              |              | 7              |              |             |              |             | 4           |             |             | 4          |               |              | 1         | 6           |           |           |           |                      |  |
| 33-p        |   |                  |                |                      |               |               |               |                |                       | 2             | 1              |                |                  |              |              | 7              |              |             |              |             | 6           | 1           |             | 5          |               |              |           | 8           |           |           |           |                      |  |
| 34-r        |   |                  |                |                      |               |               |               |                |                       | 2             |                | 1              |                  |              |              | 9              |              |             |              |             | 4           |             |             | 6          |               |              | 1         | 2           |           |           |           |                      |  |
| 34-ts       | 1   | 1                |                |                      | 2             |               |               |                |                       | 1             |                |                |                  |              |              | 9              |              |             |              |             | 4           |             |             | 4          |               |              | 1         | 8           |           |           |           |                      |  |
| 34-p        |   |                  |                |                      |               |               |               |                |                       | 2             | 1              |                |                  |              |              | 9              |              |             |              |             | 6           | 2           |             | 4          |               |              |           | 12          |           |           |           |                      |  |
| 35-r/36-p   |   |                  |                |                      |               |               |               | 3.69           |                       |               |                | 1              |                  |              |              | 16             |              |             |              |             | 2           |             | 3           |            |               |              |           | 8           |           |           |           |                      |  |
| 35-ts       |   |                  |                | 1                    |               |               |               | 1.85           |                       |               |                |                |                  |              | 1            | 16             |              |             |              |             | 2           |             | 2           |            |               |              |           | 11          |           |           |           |                      |  |
| 36-ts       |   |                  |                | 1                    |               |               |               | 1.85           |                       |               |                |                |                  |              | 1            | 16             |              |             |              |             | 2           |             | 2           |            |               |              |           | 11          |           |           |           |                      |  |
| 35-p/36-r   |   |                  |                |                      |               |               |               | 0              |                       |               |                |                |                  |              | 16           |                |              |             |              |             | 3           |             | 2           |            |               |              |           | 8           |           |           |           |                      |  |
| 37-r/38-p   |   |                  |                |                      |               |               |               | 0.69           |                       |               |                |                |                  |              |              | 3              |              |             |              |             |             |             | 1           |            |               |              |           |             |           |           |           |                      |  |
| 37-ts       |   |                  |                | 2                    |               |               |               | -1.04          |                       |               |                |                |                  |              | 1            | 3              |              |             |              |             |             |             |             |            |               |              |           | 1           |           |           |           |                      |  |
| 38-ts       |   |                  |                | 2                    |               |               |               | -1.04          |                       |               |                |                |                  |              | 1            | 3              |              |             |              |             |             |             |             |            |               |              |           | 1           |           |           |           |                      |  |
| 37-p/38-r   |   |                  |                |                      |               |               |               | 1.38           |                       |               |                |                |                  |              |              | 3              |              |             |              |             |             |             |             | 1          |               |              |           |             |           |           |           |                      |  |
| 39-r/40-p   |   |                  |                |                      |               |               |               | 0.23           |                       |               |                |                |                  |              | 1            | 6              |              |             |              |             | 1           | 1           |             |            |               |              |           |             |           |           |           |                      |  |
| 39-ts       |   |                  |                |                      |               |               |               | -1.38          |                       |               |                |                |                  |              | 1            | 1              | 6            |             |              |             |             | 1           |             |            |               |              |           |             | 1.5       |           |           |                      |  |
| 40-ts       |   |                  |                |                      |               |               |               | -1.38          |                       |               |                |                |                  |              | 1            | 1              | 6            |             |              |             |             | 1           |             |            |               |              |           |             | 1.5       |           |           |                      |  |
| 39-p/40-r   |   |                  |                |                      |               |               |               | 2.54           |                       |               |                |                |                  |              | 1            | 6              |              |             |              |             |             | 2           |             |            |               |              |           | 2           |           |           |           |                      |  |
| 41-r/42-p   |   |                  |                |                      |               |               |               | 0.23           |                       |               |                |                |                  |              | 2            | 3              | 1            |             |              |             | 1           |             | 1           |            |               |              |           |             |           |           |           |                      |  |
| 41-ts       |   |                  |                |                      |               |               |               | -1.38          |                       |               |                |                |                  |              | 2            | 1              | 3            | 1           |              |             |             | 1           |             |            |               |              |           |             | 1.5       |           |           |                      |  |
| 42-ts       |   |                  |                |                      |               |               |               | -1.38          |                       |               |                |                |                  |              | 2            | 1              | 3            | 1           |              |             |             | 1           |             |            |               |              |           |             | 1.5       |           |           |                      |  |
| 41-p/42-r   |   |                  |                |                      |               |               |               | 2.54           |                       |               |                |                |                  |              | 2            | 3              | 1            |             |              |             |             | 1           | 1           |            |               |              |           | 2           |           |           |           |                      |  |
| 43-r/44-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 7              |              |             |              |             |             |             |             | 1          |               |              |           |             | 3         |           |           |                      |  |
| 43-ts/44-ts |   |                  |                | 1                    | 1             |               |               |                |                       |               |                |                |                  |              |              | 7              |              |             |              |             |             |             |             |            |               |              |           | 1           | 5         | 0         |           |                      |  |
| 43-p/44-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 7              |              |             |              |             |             | 2           |             |            |               |              |           | 2           | 2         | 1         |           |                      |  |
| 45-r/46-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 9              |              |             |              |             |             | 1           |             | 1          |               |              |           |             | 3         |           |           |                      |  |
| 45-ts/46-ts |   |                  |                | 1                    | 1             |               |               |                |                       |               |                |                |                  |              |              | 9              |              |             |              |             |             | 1           |             |            |               |              |           | 2.5         | 4         | 1         |           |                      |  |
| 45-p/46-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 9              |              |             |              |             |             | 3           |             |            |               |              |           | 4           | 1         | 2         |           |                      |  |
| 47-r/48-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 11             |              |             |              |             |             | 2           |             | 1          |               |              |           | 2           | 3         |           |           |                      |  |
| 47-ts/48-ts |   |                  |                | 1                    | 1             |               |               |                |                       |               |                |                |                  |              |              | 11             |              |             |              |             |             | 2           |             |            |               |              |           | 4.5         | 4         | 1         |           |                      |  |
| 47-p/48-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 11             |              |             |              |             |             | 4           |             |            |               |              |           | 6           | 1         | 2         |           |                      |  |
| 49-r/50-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 13             |              |             |              |             |             | 3           |             | 1          |               |              |           | 6           | 3         |           |           |                      |  |
| 49-ts/50-ts |   |                  |                | 1                    | 1             |               |               |                |                       |               |                |                |                  |              |              | 13             |              |             |              |             |             | 3           |             |            |               |              |           | 8.5         | 4         | 1         |           |                      |  |
| 49-p/50-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 13             |              |             |              |             |             | 5           |             |            |               |              |           | 10          | 1         | 2         |           |                      |  |

**Table S3: B3LYP-LOC Parameter Assignments**

|             | parameters exclusive to transition states |                  |                |                      |               |               |               |                | global parameters     |               |                |                |                  |              |              |                |              |             |              |             |             |             |             |            |               |              |           |             |           |           |           |                      |  |
|-------------|---|------------------|----------------|----------------------|---------------|---------------|---------------|----------------|-----------------------|---------------|----------------|----------------|------------------|--------------|--------------|----------------|--------------|-------------|--------------|-------------|-------------|-------------|-------------|------------|---------------|--------------|-----------|-------------|-----------|-----------|-----------|----------------------|--|
|             | <i>N/P_sp1.5</i>                          | <i>N/P_sp2.5</i> | <i>O_sp2.5</i> | <i>MSBC/LSBC_0.5</i> | <i>AA_1.5</i> | <i>AA_2.5</i> | <i>HH_0.5</i> | <i>H_dival</i> | <i>ion correction</i> | <i>N/P_sp</i> | <i>N/P_sp2</i> | <i>N/P_sp3</i> | <i>N/P_quart</i> | <i>O_sp2</i> | <i>O_sp3</i> | <i>OCT_EXP</i> | <i>NPOLH</i> | <i>POLH</i> | <i>NPOLF</i> | <i>POLF</i> | <i>SSBC</i> | <i>MSBC</i> | <i>LSBC</i> | <i>DBC</i> | <i>TBNPOL</i> | <i>TBPOL</i> | <i>CT</i> | <i>ESBC</i> | <i>RH</i> | <i>RA</i> | <i>RT</i> | <i>H2 correction</i> |  |
| 51-r/52-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 11             |              |             |              |             |             | 2           |             | 1          |               |              |           | 2           | 3         |           |           |                      |  |
| 51-ts/52-ts |   |                  |                | 1                    | 1             |               |               |                |                       |               |                |                |                  |              |              | 11             |              |             |              |             |             | 2           |             |            |               |              |           | 6           | 3         | 2         |           |                      |  |
| 51-p/52-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 11             |              |             |              |             |             | 4           |             |            |               |              |           | 8           |           | 3         |           |                      |  |
| 53-r/54-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 7              |              |             |              |             |             |             |             |            |               |              |           |             |           | 3         |           |                      |  |
| 53-ts/54-ts |   |                  |                | 1                    | 1             |               |               |                |                       |               |                |                |                  |              |              | 7              |              |             |              |             |             |             |             |            | 1             |              |           | 1           | 5         |           |           |                      |  |
| 53-p/54-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 7              |              |             |              |             |             | 2           |             | 0.4        |               |              |           | 2           | 2         | 1         |           |                      |  |
| 55-r/56-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 5              |              |             |              |             |             |             |             |            | 1             |              |           |             | 3         |           |           |                      |  |
| 55-ts/56-ts |   |                  |                | 1                    |               | 1             |               |                |                       |               |                |                |                  |              |              | 5              |              |             |              |             |             |             |             |            |               |              |           |             | 4         |           |           |                      |  |
| 55-p/56-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 5              |              |             |              |             |             | 1           |             | 1          |               |              |           |             | 1         | 1         |           |                      |  |
| 57-r/58-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 9              |              |             |              |             |             |             | 1           |            | 1             |              |           |             |           | 2         | 1         |                      |  |
| 57-ts/58-ts |   |                  |                | 1                    | 1             |               |               |                |                       |               |                |                |                  |              |              | 9              |              |             |              |             |             | 1           |             |            |               |              |           | 2.5         | 4         | 1         |           |                      |  |
| 57-p/58-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 9              |              |             |              |             |             | 3           |             |            |               |              |           | 4           | 2         | 1         |           |                      |  |
| 59-r/60-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 11             |              |             |              |             |             |             | 2           |            | 1             |              |           | 2           | 1         | 2         |           |                      |  |
| 59-ts/60-ts |   |                  |                | 1                    | 1             |               |               |                |                       |               |                |                |                  |              |              | 11             |              |             |              |             |             |             | 2           |            |               |              |           | 6           | 3         | 2         |           |                      |  |
| 59-p/60-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 11             |              |             |              |             |             | 4           |             |            |               |              |           | 8           | 2         | 1         |           |                      |  |
| 61-r/62-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 13             |              |             |              |             |             |             | 3           |            | 1             |              |           | 6           |           | 3         |           |                      |  |
| 61-ts/62-ts |   |                  |                | 1                    | 1             |               |               |                |                       |               |                |                |                  |              |              | 13             |              |             |              |             |             |             | 3           |            |               |              |           | 11.5        | 2         | 3         |           |                      |  |
| 61-p/62-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 13             |              |             |              |             |             |             | 5           |            |               |              |           | 14          | 2         | 1         |           |                      |  |
| 63-r/64-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 9              |              |             |              |             |             |             | 1           |            | 2             |              |           |             | 2         | 1         |           |                      |  |
| 63-ts/64-ts |   |                  |                | 1                    | 1             |               |               |                |                       |               |                |                |                  |              |              | 9              |              |             |              |             |             |             | 1           |            | 1             |              |           | 2.5         | 4         | 1         |           |                      |  |
| 63-p/64-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 9              |              |             |              |             |             |             | 3           |            | 1             |              |           | 4           | 2         | 1         |           |                      |  |
| 65-r/66-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 11             |              |             |              |             |             | 3           | 1           |            | 4             |              |           | 2           | 2         | 1         |           |                      |  |
| 65-ts/66-ts |   |                  |                | 1                    | 1             |               |               |                |                       |               |                |                |                  |              |              | 11             |              |             |              |             |             | 3           | 1           |            | 3             |              |           | 4           | 4         | 1         |           |                      |  |
| 65-p/66-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 11             |              |             |              |             |             | 3           | 3           |            | 3             |              |           | 6           | 2         | 1         |           |                      |  |
| 67-r/68-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 7              |              |             |              |             |             |             |             |            | 2             |              |           |             | 1         | 1         |           |                      |  |
| 67-ts/68-ts |   |                  |                | 1                    | 1             |               |               |                |                       |               |                |                |                  |              |              | 7              |              |             |              |             |             |             |             |            | 1             |              |           | 1           | 3         | 1         |           |                      |  |
| 67-p/68-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 7              |              |             |              |             |             |             | 2           |            | 1             |              |           | 2           | 2         | 1         |           |                      |  |
| 69-r/70-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 9              |              |             |              |             |             | 3           |             |            | 4             |              |           |             |           | 2         |           |                      |  |
| 69-ts/70-ts |   |                  |                | 1                    | 1             |               |               |                |                       |               |                |                |                  |              |              | 9              |              |             |              |             |             | 3           |             |            | 3             |              |           | 2.5         | 2         | 2         |           |                      |  |
| 69-p/70-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 9              |              |             |              |             |             | 3           | 2           |            | 3             |              |           | 4           | 2         | 1         |           |                      |  |
| 71-r/72-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 4              |              |             |              |             |             |             |             |            |               |              |           |             |           |           |           |                      |  |
| 71-ts/72-ts |   |                  |                |                      |               |               | 1             |                |                       |               |                |                |                  |              |              | 3              |              |             |              |             |             |             |             |            |               |              |           |             | 3         |           |           |                      |  |
| 71-p/72-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 3              |              |             |              |             |             |             |             |            |               |              |           |             | 3         |           |           | 1                    |  |
| 73-r/74-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  | 1            |              |                | 2            |             |              |             |             |             |             |            |               |              |           |             |           |           |           |                      |  |
| 73-ts/74-ts |   |                  | 1              |                      |               |               | 1             | 1              |                       |               |                |                |                  |              |              |                | 1            |             |              |             |             |             |             |            |               |              |           |             | 1         |           |           |                      |  |
| 73-p/74-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                | 1                |              |              |                | 1            |             |              |             |             |             |             |            |               |              |           |             | 1         |           |           | 1                    |  |
| 75-r/76-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 5              |              |             |              |             |             |             | 1           |            |               |              |           |             | 2         | 1         |           | 1                    |  |
| 75-ts/76-ts |   |                  |                |                      |               |               | 1             |                |                       |               |                |                |                  |              |              | 5              |              |             |              |             |             |             | 1           |            |               |              |           |             | 2         | 1         |           |                      |  |

**Table S3: B3LYP-LOC Parameter Assignments**

|             | parameters exclusive to transition states |                  |                |                      |               |               |               |                | global parameters     |               |                |                |                  |              |              |                |              |             |              |             |             |             |             |            |               |              |           |             |           |           |           |                      |
|-------------|---|------------------|----------------|----------------------|---------------|---------------|---------------|----------------|-----------------------|---------------|----------------|----------------|------------------|--------------|--------------|----------------|--------------|-------------|--------------|-------------|-------------|-------------|-------------|------------|---------------|--------------|-----------|-------------|-----------|-----------|-----------|----------------------|
|             | <i>N/P_sp1.5</i>                          | <i>N/P_sp2.5</i> | <i>O_sp2.5</i> | <i>MSBC/LSBC_0.5</i> | <i>AA_1.5</i> | <i>AA_2.5</i> | <i>HH_0.5</i> | <i>H_dival</i> | <i>ion correction</i> | <i>N/P_sp</i> | <i>N/P_sp2</i> | <i>N/P_sp3</i> | <i>N/P_quart</i> | <i>O_sp2</i> | <i>O_sp3</i> | <i>OCT_EXP</i> | <i>NPOLH</i> | <i>POLH</i> | <i>NPOLF</i> | <i>POLF</i> | <i>SSBC</i> | <i>MSBC</i> | <i>LSBC</i> | <i>DBC</i> | <i>TBNPOL</i> | <i>TBPOL</i> | <i>CT</i> | <i>ESBC</i> | <i>RH</i> | <i>RA</i> | <i>RT</i> | <i>H2 correction</i> |
| 75-p/76-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              | 6              |              |             |              |             |             | 1           |             |            |               |              |           |             |           |           |           |                      |
| 77-r        |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  | 1            |              |                | 4            | 1           |              |             |             |             |             |            |               |              |           |             |           | 1         |           |                      |
| 77-ts       |   |                  | 1              |                      |               |               |               | 1              |                       |               |                |                |                  |              |              |                | 3            | 1           |              |             |             |             |             |            |               |              |           |             |           | 4         |           |                      |
| 77-p        |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              | 1            |                | 3            | 2           |              |             |             |             |             |            |               |              |           |             |           | 3         |           |                      |
| 78-r/78-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  | 1            | 1            |                |              | 3           |              |             |             |             |             |            |               |              |           |             | 1         |           |           |                      |
| 78-ts       |   |                  | 2              |                      |               |               |               | 1              |                       |               |                |                |                  |              |              |                |              | 2           |              |             |             |             |             |            |               |              |           |             | 2         |           |           |                      |
| 79-r        |   |                  |                |                      |               |               |               |                |                       |               |                | 1              |                  | 1            |              |                | 3            | 1           |              |             |             |             |             |            |               |              |           |             | 1         |           |           |                      |
| 79-ts       |   | 1                | 1              |                      |               |               |               | 1              |                       |               |                |                |                  |              |              |                | 2            | 1           |              |             |             |             |             |            |               |              |           |             | 3         |           |           |                      |
| 79-p        |   |                  |                |                      |               |               |               |                |                       |               | 1              |                |                  |              | 1            |                | 2            | 2           |              |             |             |             |             |            |               |              |           |             | 2         |           |           |                      |
| 80-r/80-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              |                | 7            |             |              |             |             |             |             |            |               |              |           |             | 3         |           |           |                      |
| 80-ts       |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              |                | 6            |             |              |             |             |             |             |            |               |              |           |             | 6         |           |           |                      |
| 81-r        |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              |                | 3            |             |              |             | 1           |             |             |            |               |              |           |             |           |           |           |                      |
| 81-ts       |   |                  |                |                      |               |               |               | 1              |                       |               |                |                |                  |              |              |                | 2            |             |              |             | 1           |             |             |            |               |              |           |             | 2         | 1         |           |                      |
| 81-p        |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              |                | 2            |             |              |             | 1           |             |             |            |               |              |           |             | 2         | 1         | 1         |                      |
| 82-r        |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              |                |              |             |              |             |             |             |             |            |               |              |           |             |           |           | 1         |                      |
| 82-ts       |   |                  |                |                      |               |               |               | 1              | 1                     |               |                |                |                  |              |              |                |              |             |              |             |             |             |             |            |               |              |           |             |           |           |           |                      |
| 82-p        |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  | 1            |              |                |              | 1           |              |             |             |             |             |            |               |              |           |             | 1         |           |           |                      |
| 83-r        |   |                  |                |                      |               |               |               |                |                       |               |                | 1              |                  |              |              |                | 3            |             |              |             |             |             |             |            |               |              |           |             |           |           |           |                      |
| 83-ts       |   | 1                |                |                      |               |               |               | 1              | 1                     |               |                |                |                  |              |              |                | 2            |             |              |             |             |             |             |            |               |              |           |             | 2         |           |           |                      |
| 83-p        |   |                  |                |                      |               |               |               |                |                       |               | 1              |                |                  |              |              |                | 2            |             |              |             |             |             |             |            |               |              |           |             | 2         |           | 1         |                      |
| 84-r        |   |                  |                |                      |               |               |               |                |                       |               |                | 1              |                  |              |              |                | 3            |             |              |             |             |             |             |            |               |              |           |             |           |           |           |                      |
| 84-ts       |   | 1                |                |                      |               |               |               | 1              |                       |               |                |                |                  |              |              |                | 2            |             |              |             |             |             |             |            |               |              |           |             | 2         |           |           |                      |
| 84-p        |   |                  |                |                      |               |               |               |                |                       |               | 1              |                |                  | 1            |              |                | 2            | 1           |              |             |             |             |             |            |               |              |           |             | 3         |           |           |                      |
| 85-r        |   |                  |                |                      |               |               |               |                |                       |               |                | 1              |                  |              |              |                | 5            |             |              |             |             |             |             |            |               |              |           |             | 2         |           |           |                      |
| 85-ts       | 1   |                  |                |                      |               |               |               | 1              |                       |               |                |                |                  |              |              |                | 4            |             |              |             |             |             |             |            |               |              |           |             | 4         |           |           |                      |
| 85-p        |   |                  |                |                      |               |               |               |                |                       |               | 1              |                |                  |              |              |                | 5            |             |              |             |             |             |             |            |               |              |           |             | 5         |           |           |                      |
| 86-r/87-p   |   |                  |                |                      |               |               |               |                |                       |               | 1              |                |                  |              |              |                | 8            |             |              |             |             |             | 1           |            |               |              |           |             | 2         |           |           |                      |
| 86-ts/87-ts |   | 1                |                |                      |               |               |               | 1              |                       |               |                |                |                  |              |              |                | 7            |             |              |             |             |             | 1           |            |               |              |           |             | 4         | 1         |           |                      |
| 86-p/87-r   |   |                  |                |                      |               |               |               |                |                       |               |                | 1              |                  |              |              |                | 8            |             |              |             |             |             | 1           |            |               |              |           |             | 2         | 1         |           |                      |
| 88-r/88-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              |                |              |             |              |             |             |             |             |            |               |              |           |             |           |           | 1         |                      |
| 88-ts       |   |                  |                |                      |               |               |               | 2              | 1                     |               |                |                |                  |              |              |                |              |             |              |             |             |             |             |            |               |              |           |             |           |           |           |                      |
| 89-r/90-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              |                |              |             |              |             |             |             |             |            |               |              |           |             |           |           |           |                      |
| 89-ts/90-ts |   |                  |                |                      |               |               |               | 1              | 1                     |               |                |                |                  |              |              |                |              |             |              |             |             |             |             |            |               |              |           |             | 1         |           |           |                      |
| 89-p/90-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              |                |              |             |              |             |             |             |             |            |               |              |           | 1           |           | 1         |           |                      |
| 91-r/92-p   |   |                  |                |                      |               |               |               |                |                       |               |                | 1              |                  |              |              |                | 3            |             |              |             |             |             |             |            |               |              |           |             |           |           |           |                      |
| 91-ts/92-ts |   |                  |                |                      |               |               |               | 1              | 1                     |               |                |                |                  |              |              |                | 2            |             |              |             |             |             |             |            |               |              |           |             | 2         |           |           |                      |
| 91-p/92-r   |   |                  |                |                      |               |               |               |                |                       |               | 1              |                |                  |              |              |                | 2            |             |              |             |             |             |             |            |               |              |           |             | 2         |           | 1         |                      |
| 93-r/94-p   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              |                | 3            | 1           |              |             |             |             |             |            |               |              |           |             | 3         |           |           |                      |
| 93-ts/94-ts |   |                  |                |                      |               |               |               | 1              |                       |               |                |                |                  |              |              |                | 3            |             |              |             |             |             |             |            |               |              |           |             | 3         |           |           |                      |
| 93-p/94-r   |   |                  |                |                      |               |               |               |                |                       |               |                |                |                  |              |              |                | 4            |             |              |             |             |             |             |            |               |              |           |             |           |           |           |                      |

| Table S3: B3LYP-LOC Parameter Assignments |                  |                  |                |                      |               |               |               |                   |                       |               |                |                |                  |              |              |                |              |             |              |             |             |             |             |            |               |              |           |             |           |           |           |                      |
|---|------------------|------------------|----------------|----------------------|---------------|---------------|---------------|-------------------|-----------------------|---------------|----------------|----------------|------------------|--------------|--------------|----------------|--------------|-------------|--------------|-------------|-------------|-------------|-------------|------------|---------------|--------------|-----------|-------------|-----------|-----------|-----------|----------------------|
| parameters exclusive to transition states |                  |                  |                |                      |               |               |               | global parameters |                       |               |                |                |                  |              |              |                |              |             |              |             |             |             |             |            |               |              |           |             |           |           |           |                      |
|   | <i>N/P_sp1.5</i> | <i>N/P_sp2.5</i> | <i>O_sp2.5</i> | <i>MSBC/LSBC_0.5</i> | <i>AA_1.5</i> | <i>AA_2.5</i> | <i>HH_0.5</i> | <i>H_dival</i>    | <i>ion correction</i> | <i>N/P_sp</i> | <i>N/P_sp2</i> | <i>N/P_sp3</i> | <i>N/P_quart</i> | <i>O_sp2</i> | <i>O_sp3</i> | <i>OCT_EXP</i> | <i>NPOLH</i> | <i>POLH</i> | <i>NPOLF</i> | <i>POLF</i> | <i>SSBC</i> | <i>MSBC</i> | <i>LSBC</i> | <i>DBC</i> | <i>TBNPOL</i> | <i>TBPOL</i> | <i>CT</i> | <i>ESBC</i> | <i>RH</i> | <i>RA</i> | <i>RT</i> | <i>H2 correction</i> |
| 95-r/96-p                                 |                  |                  |                |                      |               |               |               |                   |                       | 1             |                |                |                  |              |              |                | 7            |             |              |             |             | 1           |             |            |               |              |           |             | 4         | 1         |           |                      |
| 95-ts/96-ts                               | 1                |                  |                |                      |               |               |               | 1                 |                       |               |                |                |                  |              |              |                | 6            |             |              |             |             | 1           |             |            |               |              |           |             | 3         | 1         |           |                      |
| 95-p/96-r                                 |                  |                  |                |                      |               |               |               |                   |                       |               | 1              |                |                  |              |              |                | 7            |             |              |             |             | 1           |             |            |               |              |           |             | 2         |           |           |                      |
| 97-r/98-p                                 |                  |                  |                |                      |               |               |               |                   |                       |               | 1              |                |                  |              |              |                | 6            |             |              |             |             |             |             |            |               |              |           |             | 2         |           |           |                      |
| 97-ts/98-ts                               |                  | 1                |                |                      |               |               |               | 1                 |                       |               |                |                |                  |              |              |                | 5            |             |              |             |             |             |             |            |               |              |           |             | 5         |           |           |                      |
| 97-p/98-r                                 |                  |                  |                |                      |               |               |               |                   |                       |               |                | 1              |                  |              |              |                | 6            |             |              |             |             |             |             |            |               |              |           |             | 3         |           |           |                      |
| 99-r/100-p                                |                  |                  |                |                      |               |               |               |                   |                       |               |                |                |                  |              |              |                | 4            |             |              |             |             |             |             |            |               |              |           |             |           |           |           |                      |
| 99-ts/100-ts                              |                  |                  |                |                      |               |               |               | 1                 |                       |               |                |                |                  |              |              |                | 3            |             |              |             |             |             |             |            |               |              |           |             | 3         |           |           |                      |
| 99-p/100-r                                |                  |                  |                |                      |               |               |               |                   |                       |               |                |                |                  | 1            |              |                | 3            | 1           |              |             |             |             |             |            |               |              |           |             | 4         |           |           |                      |
| 101-r                                     |                  |                  |                |                      |               |               |               |                   |                       |               |                |                |                  |              |              |                | 12           |             |              |             | 9           | 3           |             |            |               |              |           |             | 12        |           |           |                      |
| 101-ts                                    |                  |                  |                | 1.5                  | 3             |               |               |                   |                       |               |                |                |                  |              |              |                | 12           |             |              |             | 3           | 3           |             |            |               |              |           | 9           |           |           |           |                      |
| 101-p                                     |                  |                  |                |                      |               |               |               |                   |                       |               |                |                |                  |              |              |                | 12           |             |              |             |             | 6           |             | 3          |               |              |           | 6           |           |           |           |                      |
| 102-r                                     |                  |                  |                |                      |               |               |               |                   |                       |               |                |                |                  |              |              |                | 18           |             |              |             |             | 1           | 5           |            |               |              |           | 12          |           |           |           |                      |
| 102-ts                                    |                  |                  |                | 3                    | 3             |               |               |                   |                       |               |                |                |                  |              |              |                | 18           |             |              |             |             | 9           |             |            |               |              |           | 15          |           |           |           |                      |
| 102-p                                     |                  |                  |                |                      |               |               |               |                   |                       |               |                |                |                  |              |              |                | 18           |             |              |             |             | 9           |             | 3          |               |              |           | 12          |           |           |           |                      |
| 103-r/103-p                               |                  |                  |                |                      |               |               |               |                   |                       |               |                |                |                  |              |              |                | 8            |             |              |             |             | 2           |             | 2          |               |              |           |             |           |           |           |                      |
| 103-ts                                    |                  |                  |                |                      | 4             |               |               |                   |                       |               |                |                |                  |              |              |                | 7            |             |              |             |             |             |             |            |               |              |           | 3           |           |           |           |                      |
| 104-r/104-p                               |                  |                  |                |                      |               |               |               |                   |                       |               |                |                |                  |              |              |                | 6            |             |              |             |             | 3           |             | 2          |               |              |           | 2           |           |           |           |                      |
| 104-ts                                    |                  |                  |                |                      | 4             |               |               |                   |                       |               |                |                |                  |              |              |                | 5            |             |              |             |             | 1           |             |            |               |              |           | 6           |           |           |           |                      |
| 105-r/105-p                               |                  |                  |                |                      |               |               |               |                   |                       |               |                |                |                  |              |              |                | 10           |             |              |             |             | 3           |             | 2          |               |              |           | 4           |           |           |           |                      |
| 105-ts                                    |                  |                  |                | 2                    | 4             |               |               |                   |                       |               |                |                |                  |              |              |                | 10           |             |              |             |             |             |             |            |               |              |           | 6           |           |           |           |                      |

#### IV. Tests for over-fitting

To test for over-fitting, the dataset was divided into two roughly equivalent subsets, “A” and “B”. Subset A consisted of entries 1, 6-8, 15-21, 26, 28, 30-33, 35-38, 43-46, 51-54, 59-62, 67-85, and 102-104. Subset B consisted of all reactions excluded from subset A. These were both used as training sets and test sets to obtain the results shown in Table S4.

| Table S4: mean unsigned error (MUE) in kcal/mole as a function of training and test set |     |              |      |      |
|---|-----|--------------|------|------|
|   |     | training set |      |      |
|   |     | A            | B    | A+B  |
| test set  | A   | 1.07         | 1.30 |      |
|   | B   | 1.26         | 1.07 |      |
|   | A+B | 1.16         | 1.21 | 1.12 |

## V. Complete suite of B3LYP-LOC parameters

All values are in kcal/mol unless otherwise specified.

### global parameters

#### a. atomic corrections

|   |                             |  | <i>aug-cc-pVTZ</i> | <i>6-311++G(3df,3pd)</i> |
|---|-----------------------------|--|--------------------|--------------------------|
| 1 | Be_ <i>sp</i>               | <i>sp</i> hybridized Be  | 7.21               | 7.29                     |
| 2 | N/P_ <i>sp</i> <sup>2</sup> | <i>sp</i> <sup>2</sup> hybridized N or P   | 4.01               | 4.49                     |
| 3 | N/P_ <i>sp</i> <sup>3</sup> | <i>sp</i> <sup>3</sup> hybridized N or P   | 3.10               | 3.71                     |
| 4 | N/P_ <i>quart</i>           | quaternary hybridized N or P   | 8.58               | 6.70                     |
| 5 | O_ <i>sp</i> <sup>2</sup>   | <i>sp</i> <sup>2</sup> hybridized O  | 0.42               | 1.33                     |
| 6 | O_ <i>sp</i> <sup>3</sup>   | <i>sp</i> <sup>3</sup> hybridized O  | 0.58               | 1.78                     |
| 7 | OCT_EXP                     | Defined previously for Cl, P, or S atoms that have a valence shell expansion beyond the usual octet. Also applied to any transition state in which an atom (other than hydrogen) experiences an increase in coordination number beyond its octet. This includes the pseudo-penta coordinate transition state of S <sub>N</sub> 2 reactions, for example. | 3.54               | 4.92                     |

#### b. bond corrections

|    |        |  | <i>aug-cc-pVTZ</i> | <i>6-311++G(3df,3pd)</i> |
|----|--------|--|--------------------|--------------------------|
| 8  | NPOLH  | All A-H bonds other than those assigned to POLH (F-H, O-H, Cl-H) and IPOLH (S-H)   | 0.28               | 0.24                     |
| 9  | POLH   | F-H, O-H, Cl-H   | -0.81              | -1.05                    |
| 10 | NPOLF  | F attached to any double bonded group such as C=O, C=C   | -0.27              | 0.82                     |
| 11 | POLF   | Li-F, B-F, C-F, O-F, Cl-F, S-F   | -1.86              | -0.91                    |
| 12 | SSBC   | Li-Li, B-Cl, C-N, C-O, any single bond in a three-membered-ring, any single bond in a valence bond representation of an aromatic ring  | -1.81              | -1.36                    |
| 13 | MSBC   | C-C, C-Cl, N-N, O-O, N-O, F-F, O-Cl, Na <sub>2</sub>   | -2.52              | -1.90                    |
| 14 | LSBC   | Si-C, S-C, S-O, S-N, any pair of second row atoms other than NaCl  | -4.21              | -2.57                    |
| 15 | DBC    | All double bonds   | -1.34              | -1.00                    |
| 16 | TBNPOL | Nonpolar triple bonds: C≡C, N≡N, P≡P,  | -1.82              | -1.03                    |
| 17 | TBPOL  | Polar triple bonds: C≡N  | 0.91               | 1.56                     |
| 18 | CT     | Na-Cl, Al-F, Si-F, P-F, any valence bond formally charged localized pair including those where the + and - formal charges are separated by multiple atoms (Li-F and other short bond ionics count as normal single bonds.) | -6.44              | -4.52                    |

#### c. bond environmental correction term

|    |      |  | <i>aug-cc-pVTZ</i> | <i>6-311++G(3df,3pd)</i> |
|----|------|--|--------------------|--------------------------|
| 19 | ESBC | Applied for every bond A-B (of order 0.5, 1, or 1.5; where neither A nor B are fluorine or hydrogen, and the bond is not part of a three- or four-membered ring) with neighboring single bond A'-A (where neither A nor A' are fluorine or hydrogen). Likewise, 1/2 ESBC is applied for every neighboring bond A'-A (where neither A nor A' are fluorine or hydrogen) with bond order 0.5 or 1.5 with the same restrictions on A-B stated above. | -0.51              | -0.50                    |

#### d. radical environmental correction parameters

|    |    |  | <i>aug-cc-pVTZ</i> | <i>6-311++G(3df,3pd)</i> |
|----|----|--|--------------------|--------------------------|
| 20 | RH | Applied if the atom on which the localized singly occupied | 0.34               | 0.54                     |

|    |    |  |       |       |
|----|----|--|-------|-------|
|    |    | orbital is localized is bonded to a hydrogen. Applied additively for each radical and each bonded hydrogen.  |       |       |
| 21 | RA | Applied if the atom on which the localized singly occupied orbital is localized is bonded to another atom other than hydrogen. Applied additively for each radical and each bonded atom. | 1.71  | 1.60  |
| 22 | RT | Applied if the radical resides on an atom that is part of a triple bond.   | -2.43 | -2.33 |

**transition state parameters**

*aug-cc-pVTZ & 6-311++G(3df,3pd)*

|    |                       |   |  |       |
|----|-----------------------|---|--|-------|
| 23 | N/P_sp <sup>1.5</sup> | Applied for every N or P atom with hybridization that can be considered partially sp and partially sp <sup>2</sup>  |  | 4.47  |
| 24 | N/P_sp <sup>2.5</sup> | Applied for every N or P atom with hybridization that can be considered partially sp <sup>2</sup> and partially sp <sup>3</sup>   |  | 4.03  |
| 25 | O_sp <sup>2.5</sup>   | Applied for every O with hybridization that can be considered partially sp <sup>2</sup> and partially sp <sup>3</sup>   |  | 2.02  |
| 26 | MSBC/LSBC_0.5         | Applied for every bond of approximate order 0.5 between any atom pairs falling within the description of MSBC and LSBC. Specifically, C•••C, C•••Cl, N•••N, O•••O, N•••O, F•••F, O•••Cl, Na•••Na, Si•••C, S•••C, S•••O, S•••N, any pair of second row atoms other than NaCl |  | -1.82 |
| 27 | AA_1.5                | Applied for every bond with approximate bond order 1.5  |  | -0.36 |
| 28 | AA_2.5                | Applied for every bond with approximate bond order 2.5  |  | -0.91 |
| 29 | HH_0.5                | Applied for every hydrogen-hydrogen bond with approximate bond order 0.5  |  | 0.55  |
| 30 | H_dival               | Applied for every transition state in which a hydrogen atom is partially bonded to two atoms, at least one of which is neither carbon nor hydrogen  |  | 3.76  |

**ionization potential/cation parameters**

|   |              |   |  |                          |
|---|--------------|---|--|--------------------------|
| <b>a. intrinsic correction for the removal of e- from the following atomic orbital:</b> |              |   |  | <i>6-311++G(3df,3pd)</i> |
| 31  | IP_U2p_A     | Unpaired 2p in free atom  |  | -10.15                   |
| 32  | IP_P2p_A     | Paired 2p in free atom  |  | -5.77                    |
| 33  | IP_U3p_A/M   | Unpaired 3p or hybrid 3p in free atom or molecule                             |  | -0.46                    |
| 34  | IP_P3p_A/M   | Paired 3p or hybrid 3p in free atom or molecule                               |  | -0.46                    |
| 35  | IP_U2p_M     | Unpaired 2p hybridized in molecule  |  | -2.54                    |
| 36  | IP_P2p_M     | Paired 2p hybridized in molecule  |  | -4.61                    |
| <b>b. intrinsic correction for the removal of e- from the following bond:</b>           |              |   |  | <i>6-311++G(3df,3pd)</i> |
| 37  | IP_B_A1-H_P  | A-H bond (polar and single), where A is a first row atom                      |  | -0.69                    |
| 38  | IP_B_A2-H    | A-H bond (single), where A is a second row atom                               |  | 0.92                     |
| 39  | IP_B_A-B     | A-B bond (single), where A and B are first or second row atoms but not H or F |  | 2.08                     |
| 40  | IP_B_A-F     | A-F bond (single), where A is a first or second row atom                      |  | -0.69                    |
| 41  | IP_B_M_short | Short multiple bond such as C≡C, C=C, C≡N, C=N, C=O, N≡N                      |  | 2.31                     |
| 42  | IP_B_M_long  | Long multiple bond such as P≡P, C=S, Si≡Si, C-C in aromatic rings             |  | 4.38                     |
| <b>c. correction for the delocalization of positive charge</b>                          |              |   |  | <i>6-311++G(3df,3pd)</i> |
| 43  | IP_D_SB_A-H  | In a single bond through neighboring e- density from A-H bonds                |  | 0.23                     |
| 44  | IP_D_SB_A-F  | In a single bond through neighboring e- density from A-F bonds                |  | 2.31                     |

|    |             |  |      |
|----|-------------|--|------|
| 45 | IP_D_SB_A-B | In a single bond through neighboring e- density from A-B bonds | 2.54 |
| 46 | IP_D_A_A-H  | On an atom through neighboring e- density from A-H bonds       | 0.46 |
| 47 | IP_D_A_A-B  | On an atom through neighboring e- density from A-B bonds       | 2.08 |

*electron affinity/anion parameters*

*a. intrinsic correction for the addition of an e- to the following atomic orbital* *aug-cc-pVTZ*

|    |           |                                |       |
|----|-----------|--------------------------------|-------|
| 48 | EA_AO_U2p | Unpaired 2p orbital in an atom | -2.54 |
| 49 | EA_AO_E2p | Empty 2p orbital in an atom    | -4.61 |
| 50 | EA_AO_U3p | Unpaired 3p orbital in an atom | -1.38 |
| 51 | EA_AO_E3p | Empty 3p orbital in an atom    | -2.08 |

*b. intrinsic correction for the addition of an e- to the following molecular orbital* *aug-cc-pVTZ*

|    |             |   |       |
|----|-------------|---|-------|
| 52 | EA_A1_close | Closed first shell atom   | -6.69 |
| 53 | EA_Ep       | Empty p or p-hybridized shell in an atom  | -1.15 |
| 54 | EA_R1_noMB  | First row atom with localized radical that is not a member of a multiple bond         | -0.23 |
| 55 | EA_R2_noMB  | Second row atom with localized radical that is not a member of a multiple bond        | -0.69 |
| 56 | EA_R_MB     | First and second row atom with a localized radical AND is a member of a multiple bond | -1.38 |

*c. negative charge delocalization* *aug-cc-pVTZ*

|    |          |  |       |
|----|----------|--|-------|
| 57 | EA_RD(-) | Resonance delocalization of negative charge in anion | -2.31 |
|----|----------|--|-------|

*parameters shared among ionization potential/cations and electron affinity/anions*

*a. correction for interacting unpaired parallel spins from* *aug-cc-pVTZ & 6-311++G(3df,3pd)*

|    |          |   |       |
|----|----------|---|-------|
| 58 | SS_2p    | 2p and hybridized orbitals on atom in cation or neutral         | -2.77 |
| 59 | SS_3p    | 3p and hybridized orbitals on atom in cation, neutral, or anion | -1.61 |
| 60 | SS_2p(-) | 2p and 2p hybridized orbitals on atom in anion                  | -1.61 |

## VI. Enthalpy of reaction as computed by B3LYP and B3LYP-LOC

**Table S5:** Enthalpies of reaction ( $\Delta H_{\text{rxn}}$ ) in kcal/mol

| <i>entry</i> | <i>reference</i> | <i>B3LYP</i> | <i>B3LYP error</i> | <i>B3LYP-LOC</i> | <i>B3LYP-LOC error</i> |
|--------------|------------------|--------------|--------------------|------------------|------------------------|
| 1            | -39.6            | -30.1        | -9.5               | -40.8            | 1.2                    |
| 2            | -23.2            | -13.3        | -9.9               | -25.0            | 1.8                    |
| 3            | -19.7            | -4.4         | -15.3              | -18.2            | -1.5                   |
| 4            | -30.4            | -11.7        | -18.7              | -30.6            | 0.2                    |
| 5            | 30.4             | 11.7         | 18.7               | 30.6             | -0.2                   |
| 6            | -29.7            | -10.3        | -19.4              | -29.2            | -0.5                   |
| 7            | 29.7             | 10.3         | 19.4               | 29.2             | 0.5                    |

**Table S5:** Enthalpies of reaction ( $\Delta H_{\text{rxn}}$ ) in kcal/mol

| <i>entry</i> | <i>reference</i> | <i>B3LYP</i> | <i>B3LYP error</i> | <i>B3LYP-LOC</i> | <i>B3LYP-LOC error</i> |
|--------------|------------------|--------------|--------------------|------------------|------------------------|
| 8            | -10.6            | -15.7        | 5.1                | -12.4            | 1.8                    |
| 9            | -15.3            | -10.2        | -5.1               | -15.6            | 0.3                    |
| 10           | -10.5            | -11.1        | 0.6                | -10.4            | -0.1                   |
| 11           | -18.3            | -7.0         | -11.3              | -16.4            | -1.9                   |
| 12           | -15.2            | -5.7         | -9.5               | -15.1            | -0.1                   |
| 13           | -23.2            | -13.8        | -9.4               | -23.2            | 0.0                    |
| 14           | -21.0            | -10.6        | -10.4              | -20.0            | -1.0                   |
| 15           | -20.0            | -11.8        | -8.2               | -21.2            | 1.2                    |
| 16           | -17.4            | -10.7        | -6.7               | -20.1            | 2.7                    |
| 17           | -20.8            | -11.4        | -9.4               | -20.8            | 0.0                    |
| 18           | -19.7            | -8.0         | -11.7              | -17.4            | -2.3                   |
| 19           | -15.6            | -5.8         | -9.8               | -15.2            | -0.4                   |
| 20           | -23.7            | -13.6        | -10.1              | -23.0            | -0.7                   |
| 21           | -22.5            | -10.9        | -11.6              | -20.3            | -2.2                   |
| 22           | -23.8            | -11.9        | -11.9              | -21.3            | -2.5                   |
| 23           | -19.9            | -8.6         | -11.3              | -18.0            | -1.9                   |
| 24           | -23.8            | -14.1        | -9.7               | -23.5            | -0.3                   |
| 25           | -57.7            | -51.3        | -6.4               | -54.5            | -3.3                   |
| 26           | -22.0            | -15.7        | -6.3               | -23.1            | 1.1                    |
| 27           | -63.7            | -58.3        | -5.4               | -62.4            | -1.4                   |
| 28           | -21.5            | -14.5        | -7.0               | -22.8            | 1.3                    |
| 29           | -60.7            | -53.4        | -7.3               | -59.5            | -1.2                   |
| 30           | -24.9            | -16.1        | -8.8               | -26.4            | 1.5                    |
| 31           | -69.0            | -62.4        | -6.6               | -68.5            | -0.5                   |
| 32           | -25.6            | -17.0        | -8.6               | -27.3            | 1.7                    |
| 33           | -66.0            | -58.4        | -7.6               | -64.5            | -1.5                   |
| 34           | -24.1            | -15.5        | -8.6               | -25.8            | 1.7                    |
| 35           | -14.1            | -11.0        | -3.1               | -16.5            | 2.4                    |
| 36           | 14.1             | 11.0         | 3.1                | 16.5             | -2.4                   |
| 37           | -20.4            | -22.1        | 1.7                | -23.1            | 2.7                    |
| 38           | 20.4             | 22.1         | -1.7               | 23.1             | -2.7                   |
| 39           | -16.0            | -15.1        | -0.9               | -13.8            | -2.2                   |
| 40           | 16.0             | 15.1         | 0.9                | 13.8             | 2.2                    |
| 41           | -12.7            | -12.4        | -0.3               | -11.1            | -1.6                   |
| 42           | 12.7             | 12.4         | 0.3                | 11.1             | 1.6                    |



**Table S5:** Enthalpies of reaction ( $\Delta H_{\text{rxn}}$ ) in kcal/mol

| <i>entry</i> | <i>reference</i> | <i>B3LYP</i> | <i>B3LYP error</i> | <i>B3LYP-LOC</i> | <i>B3LYP-LOC error</i> |
|--------------|------------------|--------------|--------------------|------------------|------------------------|
| 43           | -23.2            | -21.4        | -1.8               | -24.7            | 1.5                    |
| 44           | 23.2             | 21.4         | 1.8                | 24.7             | -1.5                   |
| 45           | -23.4            | -20.4        | -3.0               | -23.6            | 0.2                    |
| 46           | 23.4             | 20.4         | 3.0                | 23.6             | -0.2                   |
| 47           | -23.0            | -20.4        | -2.6               | -23.6            | 0.6                    |
| 48           | 23.0             | 20.4         | 2.6                | 23.6             | -0.6                   |
| 49           | -23.1            | -19.6        | -3.5               | -22.8            | -0.3                   |
| 50           | 23.1             | 19.6         | 3.5                | 22.8             | 0.3                    |
| 51           | -22.9            | -19.2        | -3.7               | -22.4            | -0.5                   |
| 52           | 22.9             | 19.2         | 3.7                | 22.4             | 0.5                    |
| 53           | -48.1            | -42.5        | -5.6               | -46.5            | -1.6                   |
| 54           | 48.1             | 42.5         | 5.6                | 46.5             | 1.6                    |
| 55           | -26.2            | -25.3        | -0.9               | -25.9            | -0.3                   |
| 56           | 26.2             | 25.3         | 0.9                | 25.9             | 0.3                    |
| 57           | -22.2            | -18.1        | -4.1               | -23.5            | 1.3                    |
| 58           | 22.2             | 18.1         | 4.1                | 23.5             | -1.3                   |
| 59           | -21.5            | -15.1        | -6.4               | -22.5            | 1.0                    |
| 60           | 21.5             | 15.1         | 6.4                | 22.5             | -1.0                   |
| 61           | -20.7            | -11.4        | -9.3               | -20.9            | 0.2                    |
| 62           | 20.7             | 11.4         | 9.3                | 20.9             | -0.2                   |
| 63           | -7.5             | -3.2         | -4.3               | -8.6             | 1.1                    |
| 64           | 7.5              | 3.2          | 4.3                | 8.6              | -1.1                   |
| 65           | -11.3            | -5.3         | -6.0               | -10.7            | -0.6                   |
| 66           | 11.3             | 5.3          | 6.0                | 10.7             | 0.6                    |
| 67           | -33.2            | -31.4        | -1.8               | -35.2            | 2.0                    |
| 68           | 33.2             | 31.4         | 1.8                | 35.2             | -2.0                   |
| 69           | -39.0            | -32.2        | -6.8               | -38.1            | -0.9                   |
| 70           | 39.0             | 32.2         | 6.8                | 38.1             | 0.9                    |
| 71           | 0.8              | -0.2         | 1.0                | 1.5              | -0.7                   |
| 72           | -0.8             | 0.2          | -1.0               | -1.5             | 0.7                    |
| 73           | 15.0             | 13.1         | 1.9                | 14.3             | 0.8                    |
| 74           | -15.0            | -13.1        | -1.9               | -14.3            | -0.8                   |
| 75           | 2.6              | 4.9          | -2.3               | 2.2              | 0.4                    |
| 76           | -2.6             | -4.9         | 2.3                | -2.2             | -0.4                   |
| 77           | -14.3            | -13.3        | -1.0               | -12.8            | -1.5                   |

**Table S5:** Enthalpies of reaction ( $\Delta H_{\text{rxn}}$ ) in kcal/mol

| <i>entry</i> | <i>reference</i> | <i>B3LYP</i> | <i>B3LYP error</i> | <i>B3LYP-LOC</i> | <i>B3LYP-LOC error</i> |
|--------------|------------------|--------------|--------------------|------------------|------------------------|
| 78           | n/a              | n/a          | n/a                | n/a              | n/a                    |
| 79           | -11.0            | -11.4        | 0.4                | -10.1            | -0.9                   |
| 80           | n/a              | n/a          | n/a                | n/a              | n/a                    |
| 81           | -2.2             | -4.5         | 2.3                | -1.8             | -0.4                   |
| 82           | 2.5              | 0.4          | 2.1                | 0.6              | 1.9                    |
| 83           | 4.5              | 1.6          | 2.9                | 4.0              | 0.5                    |
| 84           | 6.5              | 2.2          | 4.3                | 4.8              | 1.7                    |
| 85           | 12.9             | 9.1          | 3.8                | 12.1             | 0.8                    |
| 86           | -7.0             | -6.6         | -0.4               | -6.3             | -0.7                   |
| 87           | 7.0              | 6.6          | 0.4                | 6.3              | 0.7                    |
| 88           | n/a              | n/a          | n/a                | n/a              | n/a                    |
| 89           | -13.8            | -13.7        | -0.1               | -12.9            | -0.9                   |
| 90           | 13.8             | 13.7         | 0.1                | 12.9             | 0.9                    |
| 91           | -20.1            | -22.2        | 2.1                | -19.8            | -0.3                   |
| 92           | 20.1             | 22.2         | -2.1               | 19.8             | 0.3                    |
| 93           | -6.2             | -2.1         | -4.1               | -2.4             | -3.8                   |
| 94           | 6.2              | 2.1          | 4.1                | 2.4              | 3.8                    |
| 95           | -10.8            | -4.6         | -6.2               | -8.6             | -2.2                   |
| 96           | 10.8             | 4.6          | 6.2                | 8.6              | 2.2                    |
| 97           | -3.3             | -2.0         | -1.3               | -2.8             | -0.5                   |
| 98           | 3.3              | 2.0          | 1.3                | 2.8              | 0.5                    |
| 99           | 5.6              | 0.3          | 5.3                | 2.1              | 3.5                    |
| 100          | -5.6             | -0.3         | -5.3               | -2.1             | -3.5                   |
| 101          | n/a              | n/a          | n/a                | n/a              | n/a                    |
| 102          | n/a              | n/a          | n/a                | n/a              | n/a                    |
| 103          | n/a              | n/a          | n/a                | n/a              | n/a                    |
| 104          | n/a              | n/a          | n/a                | n/a              | n/a                    |
| 105          | n/a              | n/a          | n/a                | n/a              | n/a                    |

calculated using Hess's Law from G2 or expt. enthalpies of reaction given in Kang, J. K.; Musgrave, C. B. *JChemPhys* 2001, 115, 11040

Zhao, Y.; Gonzalez-Garcia, N.; Truhlar, D. G. *J. Phys. Chem. A* 2005, 109, 2012-2018

Kang, J. K.; Musgrave, C. B. *JChemPhys* 2001, 115, 11040

## VII. Barrier height ( $\Delta H^\ddagger$ ) as computed by B3LYP and B3LYP-LOC

*Table S6: Barrier height ( $\Delta H^\ddagger$ ) in kcal/mole*

| <i>entry</i> | <i>reference</i> | <i>B3LYP</i> | <i>B3LYP error</i> | <i>B3LYP-LOC</i> | <i>B3LYP-LOC error</i> |
|--------------|------------------|--------------|--------------------|------------------|------------------------|
| 1            | 25.0             | 26.9         | -1.9               | 22.3             | 2.7                    |
| 2            | 21.6             | 23.7         | -2.1               | 20.1             | 1.5                    |
| 3            | 15.9             | 23.8         | -7.9               | 16.6             | -0.7                   |
| 4            | 21.8             | 32.1         | -10.3              | 21.3             | 0.5                    |
| 5            | 52.2             | 43.8         | 8.4                | 51.9             | 0.3                    |
| 6            | 23.4             | 33.6         | -10.2              | 22.8             | 0.6                    |
| 7            | 53.1             | 43.9         | 9.2                | 52.0             | 1.1                    |
| 8            | 31.9             | 31.3         | 0.6                | 34.7             | -2.8                   |
| 9            | 30.2             | 30.3         | -0.1               | 29.0             | 1.2                    |
| 10           | 28.1             | 26.9         | 1.2                | 27.9             | 0.2                    |
| 11           | 20.5             | 26.2         | -5.7               | 22.0             | -1.5                   |
| 12           | 20.3             | 24.7         | -4.4               | 20.5             | -0.2                   |
| 13           | 19.4             | 23.8         | -4.4               | 19.6             | -0.2                   |
| 14           | 19.3             | 24.8         | -5.5               | 20.6             | -1.3                   |
| 15           | 21.8             | 26.0         | -4.2               | 21.8             | 0.0                    |
| 16           | 20.9             | 25.5         | -4.6               | 21.3             | -0.4                   |
| 17           | 21.4             | 26.1         | -4.7               | 21.9             | -0.5                   |
| 18           | 19.6             | 24.9         | -5.3               | 20.7             | -1.1                   |
| 19           | 20.8             | 25.9         | -5.1               | 21.7             | -0.9                   |
| 20           | 19.1             | 22.9         | -3.8               | 18.7             | 0.4                    |
| 21           | 18.7             | 25.1         | -6.4               | 20.9             | -2.2                   |
| 22           | 19.9             | 22.1         | -2.2               | 17.9             | 2.0                    |
| 23           | 16.8             | 17.5         | -0.7               | 13.3             | 3.5                    |
| 24           | 20.7             | 25.3         | -4.6               | 21.1             | -0.4                   |
| 25           | 20.1             | 22.0         | -1.9               | 20.6             | -0.5                   |
| 26           | 19.3             | 20.9         | -1.6               | 18.3             | 1.0                    |
| 27           | 19.0             | 21.6         | -2.6               | 18.9             | 0.1                    |
| 28           | 19.0             | 21.5         | -2.5               | 17.6             | 1.4                    |
| 29           | 17.3             | 20.6         | -3.3               | 16.4             | 0.9                    |
| 30           | 16.4             | 19.7         | -3.3               | 14.3             | 2.1                    |
| 31           | 17.3             | 20.7         | -3.4               | 16.5             | 0.8                    |
| 32           | 16.9             | 21.7         | -4.8               | 16.3             | 0.6                    |
| 33           | 17.3             | 20.7         | -3.4               | 16.5             | 0.8                    |

**Table S6:** Barrier height ( $\Delta H^\ddagger$ ) in kcal/mole

| <i>entry</i> | <i>reference</i> | <i>B3LYP</i> | <i>B3LYP error</i> | <i>B3LYP-LOC</i> | <i>B3LYP-LOC error</i> |
|--------------|------------------|--------------|--------------------|------------------|------------------------|
| 34           | 16.7             | 20.3         | -3.6               | 14.9             | 1.8                    |
| 35           | 7.9              | 8.3          | -0.4               | 7.2              | 0.7                    |
| 36           | 22.0             | 19.3         | 2.7                | 23.7             | -1.7                   |
| 37           | -1.3             | -5.1         | 3.8                | -4.9             | 3.6                    |
| 38           | 19.0             | 17.0         | 2.0                | 18.2             | 0.8                    |
| 39           | -3.4             | -3.8         | 0.4                | -0.8             | -2.6                   |
| 40           | 12.6             | 11.3         | 1.3                | 13.0             | -0.4                   |
| 41           | -4.6             | -5.2         | 0.6                | -2.2             | -2.4                   |
| 42           | 8.0              | 7.2          | 0.8                | 8.9              | -0.9                   |
| 43           | 6.1              | 6.2          | -0.1               | 5.1              | 1.0                    |
| 44           | 29.3             | 27.6         | 1.7                | 29.8             | -0.5                   |
| 45           | 5.8              | 7.3          | -1.5               | 6.5              | -0.7                   |
| 46           | 29.3             | 27.6         | 1.7                | 30.1             | -0.8                   |
| 47           | 5.8              | 7.5          | -1.7               | 6.7              | -0.9                   |
| 48           | 28.8             | 27.9         | 0.9                | 30.4             | -1.5                   |
| 49           | 5.7              | 7.6          | -1.9               | 6.8              | -1.1                   |
| 50           | 28.8             | 27.2         | 1.6                | 29.7             | -0.8                   |
| 51           | 5.4              | 7.1          | -1.7               | 6.6              | -1.2                   |
| 52           | 28.4             | 26.3         | 2.1                | 29.0             | -0.7                   |
| 53           | 8.2              | 11.0         | -2.8               | 8.9              | -0.7                   |
| 54           | 56.3             | 53.5         | 2.8                | 55.4             | 0.9                    |
| 55           | 7.5              | 8.2          | -0.7               | 7.3              | 0.2                    |
| 56           | 33.7             | 33.5         | 0.2                | 33.2             | 0.4                    |
| 57           | 5.4              | 6.8          | -1.4               | 5.0              | 0.5                    |
| 58           | 27.6             | 24.9         | 2.7                | 28.4             | -0.8                   |
| 59           | 4.1              | 7.4          | -3.3               | 4.8              | -0.7                   |
| 60           | 25.7             | 22.5         | 3.2                | 27.3             | -1.7                   |
| 61           | 2.5              | 7.6          | -5.1               | 4.2              | -1.7                   |
| 62           | 23.2             | 19.0         | 4.2                | 25.2             | -1.9                   |
| 63           | 12.0             | 14.3         | -2.3               | 12.5             | -0.4                   |
| 64           | 19.6             | 17.5         | 2.1                | 21.0             | -1.5                   |
| 65           | 9.7              | 11.8         | -2.1               | 10.2             | -0.5                   |
| 66           | 21.1             | 17.1         | 4.0                | 20.9             | 0.3                    |
| 67           | 2.0              | 3.1          | -1.1               | 2.0              | 0.0                    |
| 68           | 35.3             | 34.6         | 0.7                | 37.3             | -2.0                   |

**Table S6:** Barrier height ( $\Delta H^\ddagger$ ) in kcal/mole

| entry | reference | B3LYP | B3LYP error | B3LYP-LOC | B3LYP-LOC error |
|-------|-----------|-------|-------------|-----------|-----------------|
| 69    | -0.5      | 2.0   | -2.5        | 0.2       | -0.6            |
| 70    | 38.6      | 34.1  | 4.5         | 38.1      | 0.5             |
| 71    | 10.9      | 8.7   | 2.2         | 10.7      | 0.2             |
| 72    | 10.8      | 8.9   | 1.9         | 9.2       | 1.6             |
| 73    | 18.5      | 12.0  | 6.5         | 18.3      | 0.2             |
| 74    | 3.9       | -1.1  | 5.0         | 4.1       | -0.2            |
| 75    | 11.5      | 10.3  | 1.2         | 10.6      | 0.9             |
| 76    | 7.3       | 5.5   | 1.8         | 8.5       | -1.2            |
| 77    | 4.7       | -2.0  | 6.7         | 4.3       | 0.4             |
| 78    | 8.6       | 0.4   | 8.2         | 7.2       | 1.4             |
| 79    | 1.4       | -4.8  | 6.2         | 1.9       | -0.5            |
| 80    | 14.8      | 14.1  | 0.7         | 15.5      | -0.7            |
| 81    | 9.0       | 6.3   | 2.7         | 9.3       | -0.3            |
| 82    | 8.8       | 3.2   | 5.6         | 7.3       | 1.5             |
| 83    | 11.4      | 7.5   | 3.9         | 13.7      | -2.3            |
| 84    | 8.1       | 1.1   | 7.0         | 6.8       | 1.3             |
| 85    | 18.7      | 14.1  | 4.6         | 20.2      | -1.5            |
| 86    | 10.4      | 7.0   | 3.4         | 13.0      | -2.6            |
| 87    | 17.4      | 13.6  | 3.8         | 19.3      | -1.9            |
| 88    | 9.6       | 3.8   | 5.8         | 8.4       | 1.2             |
| 89    | 3.5       | 0.8   | 2.7         | 5.7       | -2.2            |
| 90    | 17.3      | 14.5  | 2.8         | 18.6      | -1.3            |
| 91    | 3.1       | 0.8   | 2.3         | 3.0       | 0.1             |
| 92    | 23.2      | 22.8  | 0.4         | 22.6      | 0.6             |
| 93    | n/a       | n/a   | n/a         | n/a       | n/a             |
| 94    | n/a       | n/a   | n/a         | n/a       | n/a             |
| 95    | 7.5       | 6.3   | 1.2         | 9.4       | -1.9            |
| 96    | 18.3      | 10.9  | 7.4         | 18.1      | 0.2             |
| 97    | 14.5      | 9.8   | 4.7         | 14.7      | -0.2            |
| 98    | 17.8      | 11.8  | 6.0         | 17.5      | 0.3             |
| 99    | 13.7      | 3.1   | 10.6        | 8.3       | 5.4             |
| 100   | 8.1       | 2.8   | 5.3         | 6.2       | 1.9             |
| 101   | 24.3      | 20.2  | 4.1         | 25.5      | -1.2            |
| 102   | 51.6      | 46.6  | 5.0         | 50.0      | 1.6             |
| 103   | 36.8      | 35.8  | 1.0         | 37.5      | -0.7            |

**Table S6:** Barrier height ( $\Delta H^\ddagger$ ) in kcal/mole

| <i>entry</i> | <i>reference</i> | <i>B3LYP</i> | <i>B3LYP error</i> | <i>B3LYP-LOC</i> | <i>B3LYP-LOC error</i> |
|--------------|------------------|--------------|--------------------|------------------|------------------------|
| 104          | 23.7             | 24.9         | -1.2               | 26.1             | -2.4                   |
| 105          | 34.5             | 34.4         | 0.1                | 35.1             | -0.6                   |

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