*Supporting Information*

# Breaking Down The Reactivity of $\lambda^3$-Iodanes: The Impact of Structure and Bonding on Competing Reactions Mechanisms

Halua Pinto de Magalhães[†], Hans Peter Lüthi[*†], Patrick Bultinck[‡]

[†] *Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir-Prelog-Weg 2, 8093 Zürich*

[‡] *Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281, B-9000 Gent, Belgium*

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[*]To whom correspondence should be addressed

# 1 Domain Averaged Fermi Hole Analysis

## 1.1 Model Systems

| | | $IH_3$ | | $IH_3]^\dagger$ | | $IF_3$ | | $IF_3]^\dagger$ | |
|---|---|---|---|---|---|---|---|---|---|
| $\Omega$ | $\varphi_i^\Omega$ | canon. | local. | canon. | local. | canon. | local. | canon. | local. |
| | s | 1.96 | 1.96 | 1.95 | 1.95 | 1.90 | 1.90 | 1.90 | 1.90 |
| | $p_z$ | 1.90 | 1.90 | 1.93 | 1.93 | 1.89 | 1.89 | 1.89 | 1.89 |
| I | 2cb | 1.05 | 1.04 | 1.13 | 1.12 | 0.53 | 0.49 | 0.53 | 0.49 |
| | 3cb | 1.06 | 1.06 | 1.13 | 1.12 | 0.49 | 0.31 | 0.49 | 0.31 |
| | $3cb^{nb}$ | 0.24 | 0.25 | 0.20 | 0.21 | 0.09 | 0.31 | 0.09 | 0.31 |
| | core | | | | | 2.00 | 2.00 | 2.00 | 2.00 |
| | $s/p_x$ | | | | | 2.00 | 2.00 | 2.00 | 2.00 |
| X | $p_y$ | | | | | 1.92 | 1.92 | 1.90 | 1.90 |
| | $p_z$ | | | | | 1.96 | 1.96 | 1.96 | 1.96 |
| | $3cb^{nb}$ | 1.27 | 1.27 | 1.15 | 1.15 | 1.67 | 1.67 | 1.67 | 1.67 |
| | core | | | | | 2.00 | 2.00 | 2.00 | 2.00 |
| | $p_x$ | | | | | 2.00 | 2.00 | 2.00 | 2.00 |
| $L^{3c}$ | py | | | | | 1.92 | 1.92 | 1.90 | 1.90 |
| | $p_z$ | | | | | 1.96 | 1.96 | 1.96 | 1.96 |
| | 3cb | 1.27 | 1.27 | 1.15 | 1.15 | 1.67 | 1.67 | 1.67 | 1.67 |
| | core | | | | | 2.00 | 2.00 | 2.00 | 2.00 |
| | s | | | | | 1.99 | 1.99 | 2.00 | 2.00 |
| $L^{2c}$ | $p_y$ | | | | | 1.93 | 1.93 | 1.90 | 1.90 |
| | $p_z$ | | | | | 1.96 | 1.96 | 1.96 | 1.96 |
| | 2cb | 1.02 | 1.02 | 1.15 | 1.15 | 1.57 | 1.57 | 1.67 | 1.67 |
| $\sum$ | 3cb | 2.33 | 2.33 | 2.28 | 2.27 | 2.16 | 1.98 | 2.18 | 2.03 |
| | $3cb^{nb}$ | 1.51 | 1.52 | 1.35 | 1.36 | 1.76 | 1.98 | 1.73 | 2.02 |

Table 1: DAFH analysis of the model systems (equilibrium and transition state geometries): occupation numbers $G_{ii}^\Omega$ of the different domains before (canonical) and after localization. The domains are labeled as follows: iodine $\Omega_I$, substituent $\Omega_X$, 3-center ligand ipso-atom $\Omega_{L^{3c}}$, 2-center ligand ipso-atom $\Omega_{L^{2c}}$. In addition, we summed up the associated broken valence pairs $\sum G_{ii}^\Omega$.

| | | $IH_3$ | $IH_3]^\dagger$ | $IF_3$ | $IF_3]^\dagger$ |
|---|---|---|---|---|---|
| $k_{\Omega_I\Omega_{3cb}\Omega'_{3cb}}$ | | -0.089 | - | -0.045 | - |
| | s | 0.20 | 0.44 | 0.10 | 0.09 |
| $3cb^{nb}$ | p | 0.25 | 0.30 | 0.85 | 0.93 |
| | $p_y$ | 0.00 | - | 0.68 | - |
| 3cb | s | 0.00 | 0.01 | 0.10 | 0.09 |
| | p | 1.00 | 1.22 | 0.85 | 0.93 |
| 2cb | s | 0.54 | 0.01 | 0.35 | 0.09 |
| | p | 0.94 | 1.22 | 0.71 | 0.68 |
| $lp_s$ | s | 1.73 | 1.85 | 1.77 | 1.87 |
| | p | 0.38 | 0.00 | 0.32 | 0.00 |

Table 2: 3-center index, and basis function components of the localized valence DNOs (the lone pair that resemble very much iodine $p_z$-orbitals is not considered) belonging to iodine domain $\Omega_I$ of the model compounds (equilibrium and transition state geometries).

## 1.2 Togni Reagents: 3,3-dimethyl-1-(trifluoromethyl)-1$\lambda^3$,2-benziodoxol (DMTB) & 3-oxo-1-(trifluoromethyl)-1,2-benziodoxole (OTB)

| | | DMTB | | DMTB-H$^+$ | | OTB | | OTB-H$^+$ | |
|---|---|---|---|---|---|---|---|---|---|
| $\Omega$ | $\varphi_i^\Omega$ | canon. | local. | canon. | local. | canon. | local. | canon. | local. |
| I | s | 1.94 | 1.94 | 1.96 | 1.96 | 1.95 | 1.95 | 1.96 | 1.96 |
| | $p_z$ | 1.87 | 1.87 | 1.89 | 1.89 | 1.87 | 1.87 | 1.88 | 1.88 |
| | 2cb | 1.12 | 1.10 | 1.21 | 1.17 | 1.13 | 1.12 | 1.15 | 1.11 |
| | 3cb | 0.80 | 0.79 | 0.97 | 1.00 | 0.84 | 0.84 | 0.96 | 1.00 |
| | 3cb$^{nb}$ | 0.14 | 0.16 | 0.08 | 0.08 | 0.13 | 0.14 | 0.08 | 0.09 |
| O | core | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| | s/$p_x$ | 1.97 | 1.97 | 1.95 | 1.95 | 1.97 | 1.97 | 1.98 | 1.98 |
| | $p_y$ | 1.43 | 1.45 | 1.49 | 1.52 | 1.53 | 1.55 | 1.58 | 1.58 |
| | $p_z$ | 1.87 | 1.87 | 1.61 | 1.59 | 1.75 | 1.75 | 1.64 | 1.64 |
| | 3cb$^{nb}$ | 1.62 | 1.60 | 1.85 | 1.85 | 1.67 | 1.65 | 1.76 | 1.76 |
| L$^{3c}$ | core | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| | $p_x$ | 0.36 | 0.32 | 0.36 | 0.33 | 0.37 | 0.33 | 0.36 | 0.33 |
| | py | 0.31 | 0.33 | 0.31 | 0.33 | 0.31 | 0.33 | 0.31 | 0.33 |
| | $p_z$ | 0.31 | 0.33 | 0.31 | 0.33 | 0.31 | 0.33 | 0.31 | 0.33 |
| | 3cb | 1.24 | 1.23 | 0.99 | 0.98 | 1.19 | 1.18 | 1.00 | 0.99 |
| L$^{2c}$ | core | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| | s | 1.30 | 1.07 | 1.30 | 1.14 | 1.30 | 1.11 | 1.30 | 1.08 |
| | $p_y$ | 0.96 | 1.10 | 0.99 | 1.11 | 0.98 | 1.12 | 0.98 | 1.15 |
| | $p_z$ | 1.03 | 1.03 | 1.08 | 1.08 | 1.03 | 1.03 | 1.03 | 1.03 |
| | 2cb | 0.83 | 0.90 | 0.74 | 0.78 | 0.81 | 0.87 | 0.79 | 0.84 |
| $\sum$ | 3cb | 2.04 | 2.03 | 1.97 | 1.98 | 2.03 | 2.02 | 1.97 | 1.99 |
| | 3cb$^{nb}$ | 1.76 | 1.76 | 1.93 | 1.93 | 1.80 | 1.79 | 1.85 | 1.85 |

Table 3: DAFH analysis of the Togni reagents: occupation numbers $G_{ii}^\Omega$ of the different domains before (canonical) and after localization. The domains are labeled as follows: iodine $\Omega_{\mathrm{I}}$, oxygen $\Omega_{\mathrm{O}}$, 3-center ligand ipso-atom $\Omega_{\mathrm{L}^{3c}}$, 2-center ligand ipso-atom $\Omega_{\mathrm{L}^{2c}}$. In addition, we summed up the associated broken valence pairs $\sum G_{ii}^\Omega$.

### 1.2.1 Domain Natural Orbitals

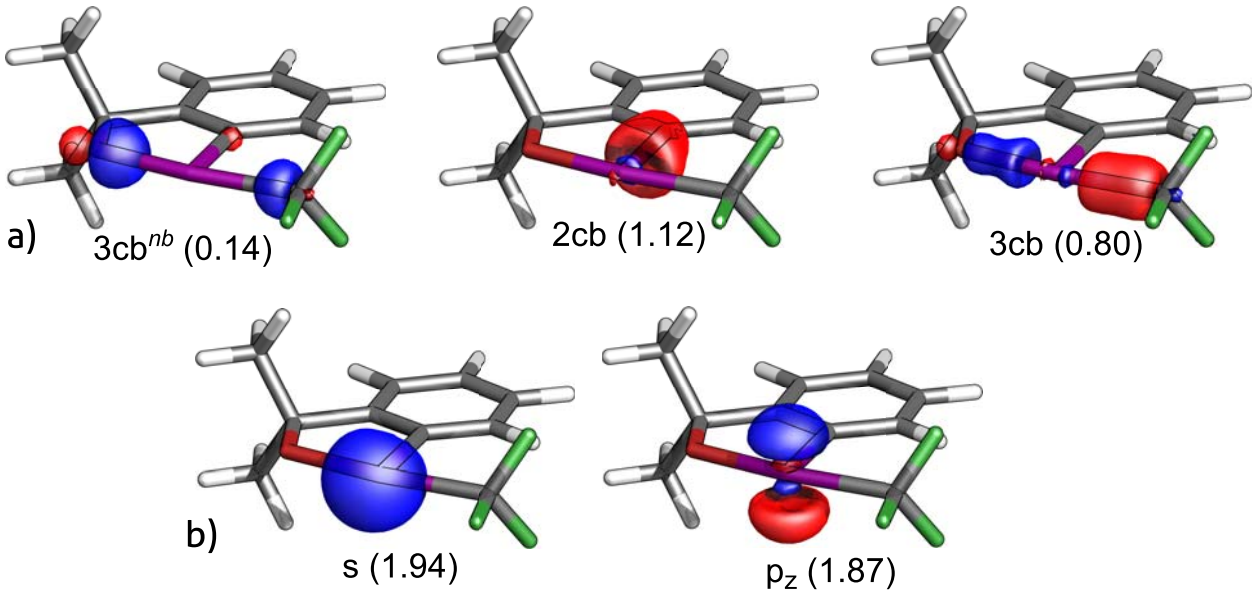


Figure 1: Canonical domain natural orbitals (DNOs) associated with the iodine domain $\Omega_{\mathrm{I}}$ of unprotonated DMTB: a) broken valence orbitals: 3-center bonding (3cb), 3-center non-bonding (3cb$^{nb}$) and 2-center bonding (2cb) orbital, b) s- and $p_z$-lone pair orbitals. The occupation numbers of the DNOs are given in parentheses.

## 1.3 Diaryliodane Series

| | X | Ph | | Ph[1] | | Me | | $N_3$ | | $NH_2$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\Omega$ | $\varphi_i^\Omega$ | canon. | local. | canon. | local. | canon. | local. | canon. | local. | canon. | local. |
| | s | 1.95 | 1.95 | 1.95 | 1.95 | 1.96 | 1.96 | 1.95 | 1.95 | 1.95 | 1.95 |
| | $p_z$ | 1.86 | 1.86 | 1.86 | 1.86 | 1.87 | 1.87 | 1.87 | 1.87 | 1.87 | 1.87 |
| I | 2cb | 1.09 | 1.08 | 1.09 | 1.08 | 1.08 | 1.07 | 1.11 | 1.10 | 1.11 | 1.10 |
| | 3cb | 0.99 | 0.99 | 0.99 | 0.99 | 1.02 | 1.02 | 0.94 | 0.94 | 0.92 | 0.92 |
| | $3cb^{nb}$ | 0.21 | 0.21 | 0.21 | 0.21 | 0.21 | 0.22 | 0.13 | 0.14 | 0.17 | 0.19 |
| | core | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| | $s/p_x$ | 0.93 | 0.92 | 0.93 | 0.92 | 0.99 | 0.99 | 1.92 | 1.92 | 1.89 | 1.89 |
| X | $p_y$ | 0.87 | 0.89 | 0.87 | 0.92 | 0.92 | 0.97 | 0.71 | 0.71 | 1.26 | 1.31 |
| | $p_z$ | 0.89 | 0.92 | 0.90 | 0.90 | 0.92 | 0.98 | 1.36 | 1.36 | 1.31 | 1.30 |
| | $3cb^{nb}$ | 1.39 | 1.36 | 1.39 | 1.35 | 1.34 | 1.22 | 1.27 | 1.27 | 1.53 | 1.49 |
| | core | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| | $p_x$ | 0.93 | 0.93 | 0.93 | 0.92 | 0.92 | 0.90 | 0.90 | 0.96 | 0.94 | 0.94 |
| $C^{3c}$ | py | 0.86 | 0.91 | 0.87 | 0.92 | 0.85 | 0.90 | 0.89 | 0.96 | 0.86 | 0.91 |
| | $p_z$ | 0.92 | 0.91 | 0.90 | 0.90 | 0.92 | 0.92 | 0.99 | 0.99 | 0.92 | 0.91 |
| | 3cb | 1.38 | 1.34 | 1.39 | 1.35 | 1.39 | 1.36 | 1.31 | 1.18 | 1.37 | 1.32 |
| | core | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| | s | 1.30 | 1.06 | 1.29 | 1.06 | 1.29 | 1.05 | 1.30 | 1.11 | 1.30 | 1.08 |
| $C^{2c}$ | $p_y$ | 0.98 | 1.06 | 0.94 | 1.06 | 0.97 | 0.97 | 0.97 | 1.09 | 0.96 | 1.11 |
| | $p_z$ | 0.94 | 0.98 | 0.98 | 0.98 | 0.94 | 0.99 | 1.02 | 1.02 | 1.01 | 1.01 |
| | 2cb | 0.85 | 0.97 | 0.85 | 0.97 | 0.86 | 1.05 | 0.81 | 0.88 | 0.82 | 0.90 |
| $\sum$ | 3cb | 2.37 | 2.33 | 2.38 | 2.34 | 2.41 | 2.38 | 2.26 | 2.12 | 2.29 | 2.24 |
| | $3cb^{nb}$ | 1.60 | 1.57 | 1.60 | 1.56 | 1.55 | 1.44 | 1.40 | 1.41 | 1.70 | 1.68 |

Table 4: DAFH analysis of the diaryliodane series (I): occupation numbers $G_{ii}^\Omega$ of the different domains before (canonical) and after localization. The domains are labeled as follows: iodine $\Omega_I$, substituent $\Omega_X$, 3-center carbon ipso-atom $\Omega_{C^{3c}}$, 2-center carbon ipso-atom $\Omega_{C^{2c}}$. In addition, we summed up the associated broken valence pairs $\sum G_{ii}^\Omega$.

[1] same as Ph but without methoxy group on the phenyl ring (= triphenyl-iodane)

| | X | OH | | F | | $PMe_2$ | | $PH_2$ | | SPh | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\Omega$ | $\varphi_i^\Omega$ | canon. | local. | canon. | local. | canon. | local. | canon. | local. | canon. | local. |
| | s | 1.94 | 1.94 | 1.94 | 1.94 | 1.96 | 1.96 | 1.96 | 1.96 | 1.95 | 1.95 |
| | $p_z$ | 1.87 | 1.87 | 1.86 | 1.86 | 1.87 | 1.87 | 1.88 | 1.88 | 1.87 | 1.87 |
| I | 2cb | 1.09 | 1.08 | 1.10 | 1.08 | 1.16 | 1.07 | 1.14 | 1.09 | 1.09 | 1.09 |
| | 3cb | 0.87 | 0.86 | 0.84 | 0.85 | 1.05 | 1.14 | 1.07 | 1.11 | 1.01 | 1.00 |
| | $3cb^{nb}$ | 0.14 | 0.16 | 0.11 | 0.12 | 0.22 | 0.22 | 0.20 | 0.21 | 0.17 | 0.18 |
| | core | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| | $s/p_x$ | 1.98 | 1.98 | 2.00 | 2.00 | 1.87 | 1.87 | 1.89 | 1.89 | 1.97 | 1.97 |
| X | $p_y$ | 1.53 | 1.55 | 1.96 | 1.96 | 0.53 | 0.58 | 0.56 | 0.59 | 0.93 | 0.93 |
| | $p_z$ | 1.88 | 1.88 | 1.92 | 1.92 | 0.62 | 0.58 | 0.60 | 0.58 | 1.84 | 1.84 |
| | $3cb^{nb}$ | 1.67 | 1.65 | 1.76 | 1.76 | 1.08 | 1.07 | 1.14 | 1.13 | 1.44 | 1.44 |
| | core | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| | $p_x$ | 0.92 | 0.93 | 0.91 | 0.94 | 0.91 | 0.91 | 0.91 | 0.92 | 0.90 | 0.95 |
| $C^{3c}$ | py | 0.88 | 0.93 | 0.88 | 0.95 | 0.86 | 0.90 | 0.87 | 0.92 | 0.89 | 0.95 |
| | $p_z$ | 0.97 | 0.97 | 0.98 | 0.98 | 0.94 | 0.93 | 0.95 | 0.95 | 0.98 | 0.98 |
| | 3cb | 1.35 | 1.29 | 1.33 | 1.23 | 1.37 | 1.33 | 1.35 | 1.30 | 1.32 | 1.20 |
| | core | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| | s | 1.30 | 1.06 | 1.30 | 1.08 | 1.29 | 1.04 | 1.29 | 1.07 | 1.30 | 1.09 |
| $C^{2c}$ | $p_y$ | 0.94 | 1.08 | 0.97 | 1.12 | 0.97 | 1.05 | 0.99 | 0.99 | 0.96 | 1.07 |
| | $p_z$ | 1.01 | 1.01 | 1.02 | 1.02 | 0.93 | 0.97 | 0.95 | 1.07 | 1.01 | 1.01 |
| | 2cb | 0.82 | 0.92 | 0.82 | 0.89 | 0.86 | 0.99 | 0.84 | 0.93 | 0.83 | 0.92 |
| | 3cb | 2.22 | 2.15 | 2.17 | 2.08 | 2.43 | 2.47 | 2.42 | 2.41 | 2.33 | 2.21 |
| $\sum$ | $3cb^{nb}$ | 1.81 | 1.81 | 1.88 | 1.89 | 1.29 | 1.29 | 1.34 | 1.34 | 1.60 | 1.61 |

Table 5: DAFH analysis of the diaryliodane series (II): occupation numbers $G_{ii}^\Omega$ of the different domains before (canonical) and after localization. The domains are labeled as follows: iodine $\Omega_I$, substituent $\Omega_X$, 3-center carbon ipso-atom $\Omega_{C^{3c}}$, 2-center carbon ipso-atom $\Omega_{C^{2c}}$. In addition, we summed up the associated broken valence pairs $\sum G_{ii}^\Omega$.

| | X | SH | | Cl | | Br | |
|---|---|---|---|---|---|---|---|
| $\Omega$ | $\varphi_i^\Omega$ | canon. | local. | canon. | local. | canon. | local. |
| | s | 1.96 | 1.96 | 1.95 | 1.95 | 1.96 | 1.96 |
| | $p_z$ | 1.88 | 1.88 | 1.87 | 1.87 | 1.88 | 1.88 |
| I | 2cb | 1.12 | 1.11 | 1.12 | 1.11 | 1.14 | 1.13 |
| | 3cb | 1.01 | 1.00 | 0.96 | 0.95 | 0.99 | 0.99 |
| | $3cb^{nb}$ | 0.17 | 0.18 | 0.13 | 0.14 | 0.13 | 0.14 |
| | core | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| | $s/p_x$ | 1.98 | 1.98 | 2.00 | 2.00 | 2.00 | 2.00 |
| X | $p_y$ | 1.00 | 1.00 | 1.96 | 1.96 | 1.91 | 1.91 |
| | $p_z$ | 1.84 | 1.84 | 1.92 | 1.92 | 1.96 | 1.96 |
| | $3cb^{nb}$ | 1.49 | 1.49 | 1.69 | 1.69 | 1.67 | 1.67 |
| | core | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| | $p_x$ | 0.90 | 0.94 | 0.90 | 0.97 | 0.89 | 0.97 |
| $C^{3c}$ | py | 0.88 | 0.94 | 0.89 | 0.96 | 0.90 | 0.97 |
| | $p_z$ | 0.97 | 0.97 | 1.00 | 0.99 | 1.00 | 1.00 |
| | 3cb | 1.33 | 1.24 | 1.31 | 1.17 | 1.31 | 1.15 |
| | core | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| | s | 1.30 | 1.08 | 1.30 | 1.12 | 1.31 | 1.09 |
| $C^{2c}$ | $p_y$ | 1.01 | 1.01 | 0.97 | 1.02 | 0.97 | 1.12 |
| | $p_z$ | 0.96 | 1.11 | 1.02 | 1.09 | 1.03 | 1.03 |
| | 2cb | 0.82 | 0.89 | 0.81 | 0.87 | 0.80 | 0.86 |
| | 3cb | 2.34 | 2.24 | 2.27 | 2.13 | 2.30 | 2.14 |
| $\sum$ | $3cb^{nb}$ | 1.65 | 1.66 | 1.82 | 1.83 | 1.80 | 1.81 |

Table 6: DAFH analysis of the diaryliodane series (III): occupation numbers $G_{ii}^\Omega$ of the different domains before (canonical) and after localization. The domains are labeled as follows: iodine $\Omega_I$, substituent $\Omega_X$, 3-center carbon ipso-atom $\Omega_{C^{3c}}$, 2-center carbon ipso-atom $\Omega_{C^{2c}}$. In addition, we summed up the associated broken valence pairs $\sum G_{ii}^\Omega$.

| | X | Ph | Ph[2] | Me | $N_3$ | $NH_2$ | OH | F |
|---|---|---|---|---|---|---|---|---|
| $k_{\Omega_I\Omega_{3cb}\Omega'_{3cb}}$ | | -0.071 | -0.071 | -0.074 | -0.051 | -0.096 | -0.072 | -0.051 |
| $3cb^{nb}$ | s | 0.31 | 0.31 | 0.24 | 0.35 | 0.29 | 0.15 | 0.25 |
| | p | 0.23 | 0.20 | 0.34 | 0.32 | 0.34 | 0.43 | 0.41 |
| | $p_y$ | 0.03 | 0.00 | 0.10 | 0.24 | 0.32 | 0.33 | 0.32 |
| 3cb | s | 0.01 | 0.00 | 0.05 | 0.22 | 0.13 | 0.21 | 0.24 |
| | p | 1.06 | 0.99 | 1.20 | 1.35 | 1.29 | 1.35 | 1.37 |
| 2cb | s | 0.62 | 0.62 | 0.61 | 0.55 | 0.57 | 0.56 | 0.58 |
| | p | 0.97 | 0.93 | 1.18 | 1.28 | 1.24 | 1.25 | 1.25 |
| $lp_s$ | s | 2.04 | 2.04 | 2.03 | 2.04 | 2.03 | 2.05 | 2.05 |
| | p | 0.36 | 0.35 | 0.47 | 0.50 | 0.44 | 0.42 | 0.43 |

Table 7: 3-center index, and basis function components of the localized valence DNOs (the lone pair that resemble very much iodine $p_z$-orbitals is not considered) belonging to iodine domain $\Omega_I$ of the diaryliodane systems (I).

| | X | $PMe_2$ | $PH_2$ | SPh | SH | Cl | Br |
|---|---|---|---|---|---|---|---|
| $k_{\Omega_I\Omega_{3cb}\Omega'_{3cb}}$ | | -0.074 | -0.091 | -0.086 | -0.103 | -0.079 | -0.088 |
| $3cb^{nb}$ | s | 0.22 | 0.27 | 0.29 | 0.26 | 0.24 | 0.28 |
| | p | 0.36 | 0.27 | 0.39 | 0.32 | 0.30 | 0.30 |
| | $p_y$ | 0.11 | 0.07 | 0.16 | 0.21 | 0.23 | 0.20 |
| 3cb | s | 0.06 | 0.11 | 0.20 | 0.23 | 0.26 | 0.27 |
| | p | 1.07 | 1.16 | 1.26 | 1.29 | 1.31 | 1.21 |
| 2cb | s | 0.54 | 0.55 | 0.52 | 0.50 | 0.51 | 0.50 |
| | p | 1.07 | 1.18 | 1.26 | 1.25 | 1.25 | 1.19 |
| $lp_s$ | s | 2.03 | 2.03 | 2.04 | 2.04 | 2.04 | 2.04 |
| | p | 0.39 | 0.40 | 0.52 | 0.38 | 0.44 | 0.47 |

Table 8: 3-center index, and basis function components of the localized valence DNOs (the lone pair that resemble very much iodine $p_z$-orbitals is not considered) belonging to iodine domain $\Omega_I$ of the diaryliodane systems (II).

[2] same as Ph but without methoxy group on the phenyl ring (= triphenyl-iodane)

# 2 Structures

## 2.1 Model Systems

### 2.1.1 $IH_3$

| 4 | equilibrium structure | | |
|---|---|---|---|
| I | 0.000000 | 0.000000 | 0.038871 |
| H | 0.000000 | 0.000000 | -1.594248 |
| H | 0.000000 | 1.832169 | -0.232955 |
| H | 0.000000 | -1.832169 | -0.232955 |

| 4 | isomerization TS | | |
|---|---|---|---|
| I | 0.000000 | 0.000000 | 0.000000 |
| H | 0.000000 | 1.912563 | 0.000000 |
| H | 1.656328 | -0.956281 | 0.000000 |
| H | -1.656328 | -0.956281 | 0.000000 |

### 2.1.2 $IF_3$

| 4 | equilibrium structure | | |
|---|---|---|---|
| I | 0.000000 | 0.000000 | 0.254125 |
| F | 0.000000 | 0.000000 | -1.638655 |
| F | 0.000000 | 1.960994 | 0.071071 |
| F | 0.000000 | -1.960994 | 0.071071 |

| 4 | isomerization TS | | |
|---|---|---|---|
| I | 0.000000 | 0.000000 | 0.000000 |
| F | 0.000000 | 1.982525 | 0.000000 |
| F | 1.716917 | -0.991263 | 0.000000 |
| F | -1.716917 | -0.991263 | 0.000000 |

## 2.2 Togni Reagents

### 2.2.1 DMTB

| 25 | | DMTB | |
|---|---|---|---|
| I | 0.729271 | -0.938597 | -0.000403 |
| C | -0.522652 | 0.814505 | -0.000319 |
| C | -0.036524 | 2.111493 | -0.000470 |
| C | -0.956787 | 3.152707 | -0.000237 |
| C | -2.319336 | 2.875483 | 0.000168 |
| C | -2.765401 | 1.562518 | 0.000317 |
| C | -1.865305 | 0.492283 | 0.000059 |
| H | 1.018314 | 2.329266 | -0.000781 |
| H | -0.603146 | 4.174346 | -0.000375 |
| H | -3.035900 | 3.685459 | 0.000372 |
| H | -3.827790 | 1.361006 | 0.000654 |
| C | -2.326111 | -0.972919 | 0.000429 |
| C | 2.665544 | 0.301349 | 0.000055 |
| F | 3.655684 | -0.619663 | 0.000082 |
| F | 2.848500 | 1.082579 | -1.085155 |
| F | 2.848184 | 1.082337 | 1.085479 |
| O | -1.205717 | -1.821053 | -0.001292 |
| C | -3.152595 | -1.259423 | 1.266927 |
| C | -3.155790 | -1.259336 | -1.263964 |
| H | -3.435638 | -2.311645 | 1.271103 |
| H | -2.557962 | -1.060562 | 2.158174 |
| H | -4.059779 | -0.655527 | 1.311735 |
| H | -3.438451 | -2.311660 | -1.267661 |
| H | -4.063346 | -0.655827 | -1.306284 |
| H | -2.563514 | -1.060051 | -2.156676 |

| 26 | | DMTB-H$^{]+}$ | |
|---|---|---|---|
| I | 0.849131 | -0.856654 | -0.254396 |
| C | -0.574950 | 0.780844 | -0.147166 |
| C | -0.070615 | 2.064251 | -0.267452 |
| C | -0.961185 | 3.126575 | -0.171199 |
| C | -2.310137 | 2.876332 | 0.030621 |
| C | -2.775104 | 1.572724 | 0.117784 |
| C | -1.919800 | 0.469435 | 0.025712 |
| H | 0.973768 | 2.263740 | -0.441383 |
| H | -0.590199 | 4.137422 | -0.261430 |
| H | -3.008705 | 3.697148 | 0.107658 |
| H | -3.832214 | 1.402348 | 0.256737 |
| C | -2.475829 | -0.948319 | 0.143905 |
| C | -2.535702 | -1.383889 | 1.611416 |
| C | -3.827468 | -1.117927 | -0.547741 |
| H | -1.560176 | -1.311347 | 2.091228 |
| H | -2.887098 | -2.414356 | 1.687054 |
| H | -3.230655 | -0.754341 | 2.164898 |
| H | -3.782921 | -0.781202 | -1.581383 |
| H | -4.106615 | -2.172126 | -0.536779 |
| H | -4.615899 | -0.575846 | -0.029943 |
| O | -1.514139 | -1.777028 | -0.576668 |
| C | 2.735588 | 0.278991 | 0.235596 |
| F | 2.584583 | 0.955657 | 1.357328 |
| F | 3.067984 | 1.096451 | -0.748009 |
| F | 3.654419 | -0.660608 | 0.378634 |
| H | -1.721777 | -2.710132 | -0.440775 |

### 2.2.2 OTB

| 25 | | OTB | |
|---|---|---|---|
| I | 0.679116 | -0.918519 | 0.000022 |
| C | -0.811220 | 0.630703 | -0.000002 |
| C | -0.537735 | 1.986243 | 0.000007 |
| C | -1.627251 | 2.854017 | -0.000015 |
| C | -2.929308 | 2.360867 | -0.000043 |
| C | -3.159410 | 0.993163 | -0.000046 |
| C | -2.087188 | 0.100801 | -0.000024 |
| H | 0.464993 | 2.380471 | 0.000029 |
| H | -1.447320 | 3.920457 | -0.000010 |
| H | -3.763878 | 3.048485 | -0.000060 |
| H | -4.157987 | 0.578593 | -0.000062 |
| C | -2.314728 | -1.394372 | -0.000010 |
| O | -3.435138 | -1.857425 | -0.000032 |
| C | 2.425471 | 0.541218 | -0.000004 |
| F | 3.527958 | -0.229822 | 0.000117 |
| F | 2.474193 | 1.331215 | -1.084703 |
| F | 2.474073 | 1.331389 | 1.084574 |
| O | -1.205709 | -2.089748 | 0.000014 |

| 26 | | OTB-H$^{]+}$ | |
|---|---|---|---|
| I | -0.741872 | -0.894261 | 0.000045 |
| C | 0.788822 | 0.627347 | -0.000027 |
| C | 0.470880 | 1.968538 | -0.000040 |
| C | 1.523017 | 2.886964 | -0.000084 |
| C | 2.844157 | 2.459949 | -0.000114 |
| C | 3.136111 | 1.104313 | -0.000104 |
| C | 2.104695 | 0.160079 | -0.000063 |
| H | -0.543689 | 2.330815 | -0.000016 |
| H | 1.289992 | 3.942835 | -0.000094 |
| H | 3.647034 | 3.182997 | -0.000148 |
| H | 4.159510 | 0.758809 | -0.000131 |
| C | 2.366872 | -1.287973 | -0.000060 |
| O | 3.638561 | -1.634529 | -0.000056 |
| O | 1.453383 | -2.109297 | -0.000009 |
| C | -2.533350 | 0.483695 | 0.000048 |
| F | -2.542744 | 1.240776 | 1.082919 |
| F | -2.542573 | 1.241000 | -1.082666 |
| F | -3.569725 | -0.335554 | -0.000118 |
| H | 3.718969 | -2.602499 | -0.000030 |

## 2.3 Diaryliodane Series

### 2.3.1 $X = Ph$

| 38 | equilibrium structure | | |
|---|---|---|---|
| I | 0.546441 | -0.838197 | 0.035035 |
| C | 0.640748 | 1.320623 | -0.005908 |
| C | 1.461081 | 1.938564 | -0.934231 |
| C | 1.512439 | 3.329529 | -0.960989 |
| C | 0.762932 | 4.076304 | -0.059459 |
| C | -0.048712 | 3.434112 | 0.868596 |
| C | -0.121233 | 2.044177 | 0.895377 |
| H | 2.061153 | 1.356082 | -1.617650 |
| H | 2.140445 | 3.823885 | -1.689877 |
| H | 0.811198 | 5.156531 | -0.080139 |
| H | -0.628989 | 4.010065 | 1.576865 |
| H | -0.771253 | 1.543338 | 1.597569 |
| C | -1.753159 | -0.590630 | 0.094702 |
| C | -2.486570 | 0.109862 | -0.852754 |
| C | -3.881367 | 0.080831 | -0.859771 |
| C | -4.559108 | -0.668704 | 0.101961 |
| C | -3.832432 | -1.382294 | 1.056753 |
| C | -2.445254 | -1.340088 | 1.044722 |
| H | -1.983300 | 0.703206 | -1.608099 |
| H | -4.420258 | 0.638037 | -1.611781 |
| H | -4.373268 | -1.957292 | 1.796572 |
| H | -1.903853 | -1.905390 | 1.796739 |
| O | -5.917001 | -0.765666 | 0.190964 |
| C | -6.709424 | -0.062461 | -0.749004 |
| H | -7.743065 | -0.278176 | -0.491670 |
| H | -6.515951 | -0.399310 | -1.771072 |
| H | -6.541765 | 1.016418 | -0.689294 |
| C | 2.873727 | -0.784459 | -0.011390 |
| C | 3.653507 | -0.072275 | 0.896098 |
| C | 5.035242 | -0.239829 | 0.925053 |
| C | 5.649601 | -1.124549 | 0.043127 |
| C | 4.878084 | -1.841421 | -0.863358 |
| C | 3.494067 | -1.671127 | -0.885100 |
| H | 3.192370 | 0.624728 | 1.587024 |
| H | 5.632832 | 0.317143 | 1.636134 |
| H | 6.723601 | -1.254066 | 0.064495 |
| H | 5.350517 | -2.529759 | -1.553128 |
| H | 2.904425 | -2.241341 | -1.596525 |

| 38 | reductive elimination TS | | |
|---|---|---|---|
| I | 0.114397 | -0.503261 | 0.060979 |
| C | 1.562555 | 1.269836 | -0.010424 |
| C | 1.784685 | 1.868963 | -1.238551 |
| C | 2.395585 | 3.119509 | -1.258548 |
| C | 2.744120 | 3.759278 | -0.074299 |
| C | 2.474407 | 3.144001 | 1.142849 |
| C | 1.864302 | 1.893592 | 1.187981 |
| H | 1.512475 | 1.378014 | -2.161018 |
| H | 2.592322 | 3.591509 | -2.212256 |
| H | 3.212374 | 4.733175 | -0.099632 |
| H | 2.732056 | 3.635342 | 2.071942 |
| H | 1.651981 | 1.422835 | 2.136298 |
| C | -2.147942 | -0.361923 | 0.134881 |
| C | -2.889795 | -0.315736 | -1.038604 |
| C | -4.280446 | -0.224606 | -1.010911 |
| C | -4.939906 | -0.170562 | 0.217362 |
| C | -4.200358 | -0.207636 | 1.404142 |
| C | -2.819828 | -0.298315 | 1.357651 |
| H | -2.393122 | -0.355668 | -2.001198 |
| H | -4.830804 | -0.197323 | -1.939509 |
| H | -4.731727 | -0.164163 | 2.345345 |
| H | -2.265675 | -0.325225 | 2.288587 |
| O | -6.289084 | -0.080711 | 0.363873 |
| C | -7.099204 | -0.038977 | -0.799342 |
| H | -8.124897 | 0.029134 | -0.447452 |
| H | -6.983495 | -0.944557 | -1.400265 |
| H | -6.870690 | 0.834502 | -1.415331 |
| C | 2.655075 | -0.986441 | -0.033049 |
| C | 3.337913 | -1.256762 | 1.141868 |
| C | 4.585347 | -1.879072 | 1.096208 |
| C | 5.145603 | -2.227176 | -0.128405 |
| C | 4.456433 | -1.953940 | -1.305262 |
| C | 3.209116 | -1.331573 | -1.255474 |
| H | 2.918111 | -0.988176 | 2.105909 |
| H | 5.117146 | -2.090300 | 2.016068 |
| H | 6.114583 | -2.707012 | -0.165484 |
| H | 4.887023 | -2.224351 | -2.261849 |
| H | 2.686020 | -1.123978 | -2.183451 |

| 38 | isomerization TS | | |
|---|---|---|---|
| I | 0.719951 | 0.036567 | 0.020184 |
| C | 0.367295 | 2.339921 | -0.038302 |
| C | 0.344836 | 3.046742 | 1.151736 |
| C | 0.168641 | 4.428662 | 1.112648 |
| C | 0.029551 | 5.078655 | -0.109130 |
| C | 0.066764 | 4.353677 | -1.295618 |
| C | 0.242378 | 2.971534 | -1.263656 |
| H | 0.458313 | 2.540609 | 2.102437 |
| H | 0.142856 | 4.994164 | 2.035313 |
| H | -0.103752 | 6.151732 | -0.136864 |
| H | -0.038256 | 4.861097 | -2.246047 |
| H | 0.275954 | 2.406649 | -2.186968 |
| C | -1.505462 | -0.590841 | 0.132237 |
| C | -2.193470 | -0.869781 | -1.032761 |
| C | -3.523988 | -1.285420 | -0.975991 |
| C | -4.148596 | -1.427107 | 0.263600 |
| C | -3.437359 | -1.155616 | 1.437539 |
| C | -2.116115 | -0.744387 | 1.370312 |
| H | -1.715193 | -0.765742 | -1.999031 |
| H | -4.052808 | -1.494174 | -1.893743 |
| H | -3.940548 | -1.275869 | 2.387357 |
| H | -1.573864 | -0.541384 | 2.285506 |
| O | -5.437072 | -1.825323 | 0.433725 |
| C | -6.215906 | -2.123128 | -0.714027 |
| H | -5.785737 | -2.949201 | -1.285820 |
| H | -6.321434 | -1.250209 | -1.363123 |
| H | -7.194632 | -2.414854 | -0.343572 |
| C | 2.808489 | -1.242154 | -0.024708 |
| C | 3.485333 | -1.535552 | 1.157515 |
| C | 4.682362 | -2.248470 | 1.136889 |
| C | 5.211747 | -2.677290 | -0.076638 |
| C | 4.544636 | -2.392334 | -1.264293 |
| C | 3.349234 | -1.677080 | -1.233124 |
| H | 3.085105 | -1.208770 | 2.113070 |
| H | 5.201628 | -2.470165 | 2.061691 |
| H | 6.140834 | -3.232021 | -0.096709 |
| H | 4.956451 | -2.726390 | -2.209223 |
| H | 2.842050 | -1.461099 | -2.169176 |

### 2.3.2 Triphenyliodane

| 34 | equilibrium structure | | |
|---|---|---|---|
| I | 0.000002 | 0.851469 | -0.000013 |
| C | -0.000003 | -1.308262 | -0.000007 |
| C | 0.797869 | -1.979774 | 0.910632 |
| C | 0.787875 | -3.371831 | 0.910062 |
| C | -0.000010 | -4.067028 | 0.000004 |
| C | -0.787892 | -3.371834 | -0.910060 |
| C | -0.797878 | -1.979776 | -0.910640 |
| H | 1.427158 | -1.438153 | 1.601428 |
| H | 1.397927 | -3.907643 | 1.624726 |
| H | -0.000013 | -5.148494 | 0.000008 |
| H | -1.397946 | -3.907648 | -1.624720 |
| C | -2.992037 | 1.558422 | -0.854095 |
| C | -4.381237 | 1.670030 | -0.805775 |
| C | -5.104073 | 0.924431 | 0.117504 |
| C | -4.435816 | 0.070031 | 0.989938 |
| C | -3.048974 | -0.038637 | 0.935449 |
| C | -2.318548 | 0.702432 | 0.010554 |
| H | -4.895442 | 2.334839 | -1.488626 |
| H | -6.181992 | 1.008029 | 0.159018 |
| H | -4.995232 | -0.509241 | 1.714075 |
| H | -2.545818 | -0.711638 | 1.620577 |
| C | 2.318551 | 0.702424 | -0.010556 |
| C | 3.048990 | -0.038632 | -0.935450 |
| C | 4.435832 | 0.070037 | -0.989921 |
| C | 5.104078 | 0.924427 | -0.117468 |
| C | 4.381230 | 1.670015 | 0.805811 |
| C | 2.992030 | 1.558404 | 0.854113 |
| H | 2.545844 | -0.711625 | -1.620592 |
| H | 4.995258 | -0.509225 | -1.714058 |
| H | 6.181997 | 1.008027 | -0.158967 |
| H | 4.895425 | 2.334815 | 1.488677 |
| H | 2.440839 | 2.149479 | 1.579106 |
| H | -1.427165 | -1.438158 | -1.601441 |
| H | -2.440856 | 2.149506 | -1.579089 |

| 34 | reductive elimination TS | | |
|---|---|---|---|
| I | -0.498319 | -0.508381 | -0.000054 |
| C | 0.940818 | 1.271369 | 0.000012 |
| C | 1.200020 | 1.882640 | -1.214375 |
| C | 1.806075 | 3.135750 | -1.201395 |
| C | 2.112830 | 3.764321 | 0.000095 |
| C | 1.806152 | 3.135633 | 1.201545 |
| C | 1.200098 | 1.882523 | 1.214441 |
| H | 0.959189 | 1.400749 | -2.150099 |
| H | 2.031361 | 3.618421 | -2.143296 |
| H | 2.577374 | 4.740283 | 0.000127 |
| H | 2.031506 | 3.618210 | 2.143477 |
| H | 0.959339 | 1.400534 | 2.150134 |
| C | 2.041763 | -0.979971 | -0.000036 |
| C | 2.660320 | -1.284404 | 1.201501 |
| C | 3.911630 | -1.900638 | 1.203191 |
| C | 4.538338 | -2.207614 | 0.000030 |
| C | 3.911868 | -1.900279 | -1.203164 |
| C | 2.660558 | -1.284046 | -1.201540 |
| H | 2.186672 | -1.049112 | 2.149011 |
| H | 4.394114 | -2.139482 | 2.143182 |
| H | 5.510434 | -2.682451 | 0.000055 |
| H | 4.394544 | -2.138836 | -2.143131 |
| H | 2.187107 | -1.048459 | -2.149074 |
| C | -2.779996 | -0.378539 | -0.000017 |
| C | -3.478273 | -0.331749 | -1.203756 |
| C | -4.868134 | -0.252237 | -1.204590 |
| C | -5.562778 | -0.212402 | 0.000045 |
| C | -4.868074 | -0.252109 | 1.204649 |
| C | -3.478213 | -0.331627 | 1.203753 |
| H | -2.946162 | -0.361918 | -2.147494 |
| H | -5.407910 | -0.221207 | -2.142590 |
| H | -6.642839 | -0.149578 | 0.000069 |
| H | -5.407802 | -0.220976 | 2.142673 |
| H | -2.946054 | -0.361703 | 2.147467 |

| 34 | isomerization TS | | |
|---|---|---|---|
| I | 0.279840 | 0.000000 | -0.000005 |
| C | -1.321688 | -1.700363 | -0.000129 |
| C | -1.760749 | -2.209821 | 1.209371 |
| C | -2.690974 | -3.247644 | 1.205482 |
| C | -3.154554 | -3.763155 | -0.000287 |
| C | -2.690985 | -3.247450 | -1.205978 |
| C | -1.760760 | -2.209625 | -1.209707 |
| H | -1.396460 | -1.810462 | 2.147703 |
| H | -3.049683 | -3.651978 | 2.143350 |
| H | -3.874156 | -4.570722 | -0.000349 |
| H | -3.049701 | -3.651632 | -2.143908 |
| H | -1.396480 | -1.810115 | -2.147978 |
| C | 2.711095 | 0.000000 | -0.000047 |
| C | 3.421416 | 0.000086 | -1.199609 |
| C | 4.814482 | 0.000087 | -1.204850 |
| C | 5.511185 | 0.000002 | -0.000099 |
| C | 4.814526 | -0.000084 | 1.204677 |
| C | 3.421460 | -0.000085 | 1.199488 |
| H | 2.893014 | 0.000154 | -2.148671 |
| H | 5.356744 | 0.000154 | -2.142846 |
| H | 6.593431 | 0.000003 | -0.000119 |
| H | 5.356823 | -0.000151 | 2.142654 |
| H | 2.893094 | -0.000154 | 2.148569 |
| C | -1.321691 | 1.700362 | 0.000175 |
| C | -1.760727 | 2.209617 | 1.209769 |
| C | -2.690953 | 3.247441 | 1.206074 |
| C | -3.154558 | 3.763153 | 0.000400 |
| C | -2.691013 | 3.247650 | -1.205386 |
| C | -1.760787 | 2.209826 | -1.209308 |
| H | -1.396420 | 1.810102 | 2.148027 |
| H | -3.049642 | 3.651618 | 2.144017 |
| H | -3.874160 | 4.570720 | 0.000487 |
| H | -3.049749 | 3.651989 | -2.143242 |
| H | -1.396526 | 1.810473 | -2.147653 |

### 2.3.3 $X = Me$

| 31 | equilibrium structure | | |
|---|---|---|---|
| I | 1.212229 | -1.350215 | -0.090718 |
| C | 1.796577 | 0.717775 | 0.075772 |
| C | 1.311895 | 1.467001 | 1.135049 |
| C | 1.708551 | 2.795501 | 1.255368 |
| C | 2.564856 | 3.360291 | 0.316794 |
| C | 3.031596 | 2.595165 | -0.745145 |
| C | 2.652505 | 1.260969 | -0.868394 |
| H | 0.625969 | 1.033907 | 1.848292 |
| H | 1.344409 | 3.385886 | 2.085458 |
| H | 2.865505 | 4.394799 | 0.411606 |
| H | 3.688912 | 3.032100 | -1.484944 |
| H | 3.021660 | 0.666080 | -1.690544 |
| C | -0.982742 | -0.560456 | 0.044574 |
| C | -1.512484 | 0.458791 | -0.734282 |
| C | -2.877297 | 0.750964 | -0.723728 |
| C | -3.734404 | 0.004101 | 0.083994 |
| C | -3.215792 | -1.026463 | 0.869785 |
| C | -1.855154 | -1.299813 | 0.841440 |
| H | -0.868126 | 1.057285 | -1.368994 |
| H | -3.254392 | 1.551203 | -1.343488 |
| H | -3.893725 | -1.594383 | 1.493212 |
| H | -1.478322 | -2.109211 | 1.459933 |
| O | -5.082331 | 0.203140 | 0.173708 |
| C | -5.667068 | 1.229220 | -0.606871 |
| H | -5.519215 | 1.055699 | -1.676420 |
| H | -5.266356 | 2.212618 | -0.345275 |
| H | -6.730956 | 1.206911 | -0.385280 |
| C | 3.506618 | -1.798247 | -0.139553 |
| H | 3.556713 | -2.881150 | -0.027876 |
| H | 3.956931 | -1.499659 | -1.082938 |
| H | 3.995553 | -1.304631 | 0.696820 |

| 31 | reductive elimination TS | | |
|---|---|---|---|
| I | 0.690205 | -0.889773 | -0.079171 |
| C | 2.692347 | 0.305887 | -0.011937 |
| C | 3.217861 | 0.619740 | 1.227594 |
| C | 4.256386 | 1.547263 | 1.291119 |
| C | 4.733770 | 2.151979 | 0.133851 |
| C | 4.169628 | 1.831599 | -1.095785 |
| C | 3.130506 | 0.906230 | -1.177699 |
| H | 2.843898 | 0.155658 | 2.129394 |
| H | 4.686130 | 1.794828 | 2.253127 |
| H | 5.537047 | 2.873462 | 0.190560 |
| H | 4.531640 | 2.301637 | -2.001044 |
| H | 2.689743 | 0.663391 | -2.134373 |
| C | -1.523338 | -0.298079 | 0.082218 |
| C | -2.256041 | 0.037252 | -1.050243 |
| C | -3.601135 | 0.395091 | -0.966954 |
| C | -4.225733 | 0.425866 | 0.280102 |
| C | -3.497044 | 0.100724 | 1.428837 |
| C | -2.162109 | -0.251942 | 1.324253 |
| H | -1.787252 | 0.020625 | -2.028021 |
| H | -4.143261 | 0.644406 | -1.867068 |
| H | -4.000647 | 0.132431 | 2.385875 |
| H | -1.616065 | -0.499257 | 2.227807 |
| O | -5.530684 | 0.758444 | 0.480861 |
| C | -6.326259 | 1.098316 | -0.641890 |
| H | -6.395637 | 0.268503 | -1.350040 |
| H | -5.936680 | 1.979906 | -1.157542 |
| H | -7.315993 | 1.319989 | -0.251855 |
| C | 2.875162 | -2.351939 | -0.334976 |
| H | 2.366173 | -3.302823 | -0.436999 |
| H | 3.397925 | -2.032797 | -1.226650 |
| H | 3.449036 | -2.253706 | 0.576821 |

| 31 | isomerization TS | | |
|---|---|---|---|
| I | -0.738388 | 0.850472 | -0.081353 |
| C | -2.870627 | -0.348570 | 0.003317 |
| C | -3.438503 | -0.867478 | -1.160323 |
| C | -4.656975 | -1.542110 | -1.126034 |
| C | -5.323244 | -1.705842 | 0.084831 |
| C | -4.769384 | -1.195402 | 1.255191 |
| C | -3.550090 | -0.522861 | 1.209141 |
| H | -2.932421 | -0.749401 | -2.114413 |
| H | -5.087265 | -1.939441 | -2.037735 |
| H | -6.269898 | -2.229547 | 0.116519 |
| H | -5.287426 | -1.322864 | 2.198381 |
| H | -3.132442 | -0.132469 | 2.132911 |
| C | 1.465847 | 0.224418 | 0.090790 |
| C | 2.143893 | -0.189433 | -1.039419 |
| C | 3.467164 | -0.620415 | -0.939787 |
| C | 4.092270 | -0.644660 | 0.307218 |
| C | 3.387509 | -0.242412 | 1.446859 |
| C | 2.073495 | 0.183622 | 1.339255 |
| H | 1.663615 | -0.180331 | -2.009726 |
| H | 3.989176 | -0.932826 | -1.831563 |
| H | 3.889007 | -0.275292 | 2.404497 |
| H | 1.535837 | 0.485044 | 2.229164 |
| O | 5.373531 | -1.045540 | 0.517336 |
| C | 6.144453 | -1.476669 | -0.593027 |
| H | 6.263678 | -0.679200 | -1.330810 |
| H | 7.118791 | -1.744490 | -0.194163 |
| H | 5.698893 | -2.351100 | -1.073808 |
| C | -0.057088 | 3.136822 | -0.386222 |
| H | -0.990294 | 3.674193 | -0.506716 |
| H | 0.477853 | 3.399453 | 0.517747 |
| H | 0.556912 | 3.133512 | -1.277988 |

### 2.3.4 $X = \mathrm{N_3}$

| 30 | equilibrium structure | | |
|---|---|---|---|
| I | 0.865001 | -1.039077 | -0.282398 |
| C | 1.460699 | 1.042835 | -0.057241 |
| C | 0.661220 | 1.905150 | 0.671108 |
| C | 1.074213 | 3.228656 | 0.803102 |
| C | 2.253814 | 3.659914 | 0.209017 |
| C | 3.032636 | 2.767155 | -0.517329 |
| C | 2.643194 | 1.437354 | -0.655047 |
| H | -0.260378 | 1.575429 | 1.125203 |
| H | 0.467655 | 3.915707 | 1.377458 |
| H | 2.567687 | 4.689163 | 0.316108 |
| H | 3.953091 | 3.096121 | -0.980026 |
| H | 3.252957 | 0.721251 | -1.186798 |
| C | -1.250270 | -0.539078 | -0.008648 |
| C | -2.003938 | -0.052807 | -1.067814 |
| C | -3.372492 | 0.158946 | -0.925639 |
| C | -3.994424 | -0.130223 | 0.290831 |
| C | -3.236069 | -0.629892 | 1.354432 |
| C | -1.875159 | -0.834609 | 1.202862 |
| H | -1.537678 | 0.170298 | -2.018738 |
| H | -3.937144 | 0.539806 | -1.762815 |
| H | -3.735186 | -0.853025 | 2.287126 |
| H | -1.304167 | -1.227021 | 2.034550 |
| O | -5.317581 | 0.034456 | 0.534824 |
| C | -6.150876 | 0.527249 | -0.504751 |
| H | -6.149605 | -0.142944 | -1.367544 |
| H | -5.845043 | 1.527506 | -0.820479 |
| H | -7.152285 | 0.573019 | -0.086852 |
| N | 3.210875 | -1.547656 | -0.657306 |
| N | 3.856254 | -1.666540 | 0.355769 |
| N | 4.492925 | -1.790633 | 1.301824 |

| 30 | reductive elimination TS | | |
|---|---|---|---|
| I | -0.638630 | -1.282509 | -0.271032 |
| C | -1.969594 | 0.701512 | -0.184724 |
| C | -2.055685 | 1.404133 | -1.372350 |
| C | -2.322712 | 2.766849 | -1.289534 |
| C | -2.478152 | 3.390661 | -0.054486 |
| C | -2.374277 | 2.643564 | 1.110594 |
| C | -2.106004 | 1.274426 | 1.062345 |
| H | -1.960413 | 0.913031 | -2.328334 |
| H | -2.416833 | 3.335763 | -2.205223 |
| H | -2.682152 | 4.450839 | -0.003890 |
| H | -2.500048 | 3.113639 | 2.077021 |
| H | -2.048527 | 0.693794 | 1.970809 |
| C | 1.394396 | -0.633519 | -0.186442 |
| C | 2.090598 | -0.366157 | -1.365955 |
| C | 3.402728 | 0.063833 | -1.307666 |
| C | 4.035758 | 0.237591 | -0.071545 |
| C | 3.335465 | -0.026547 | 1.106653 |
| C | 2.014871 | -0.460069 | 1.042917 |
| H | 1.614557 | -0.495303 | -2.327710 |
| H | 3.960829 | 0.273245 | -2.209369 |
| H | 3.800639 | 0.099306 | 2.072038 |
| H | 1.481808 | -0.662158 | 1.961339 |
| O | 5.320429 | 0.662211 | -0.122819 |
| C | 6.024826 | 0.870458 | 1.093772 |
| H | 7.016726 | 1.208367 | 0.808630 |
| H | 6.109595 | -0.054902 | 1.668208 |
| H | 5.543546 | 1.636891 | 1.705517 |
| N | -3.300391 | -1.101894 | -0.356739 |
| N | -3.852285 | -1.113493 | 0.709153 |
| N | -4.360049 | -1.075700 | 1.741409 |

| 30 | isomerization TS | | |
|---|---|---|---|
| I | 1.081913 | -0.680825 | -0.298411 |
| C | 1.462839 | 1.469856 | -0.047118 |
| C | 1.339840 | 2.315002 | -1.139814 |
| C | 1.625336 | 3.667189 | -0.976334 |
| C | 2.038958 | 4.149967 | 0.260659 |
| C | 2.171620 | 3.284573 | 1.340297 |
| C | 1.886822 | 1.929975 | 1.190339 |
| H | 1.028350 | 1.937221 | -2.103800 |
| H | 1.529259 | 4.339190 | -1.818554 |
| H | 2.264710 | 5.200628 | 0.380981 |
| H | 2.500633 | 3.657774 | 2.300752 |
| H | 1.998752 | 1.254444 | 2.027151 |
| C | -1.062698 | -0.419792 | 0.007703 |
| C | -1.896170 | -0.330785 | -1.093701 |
| C | -3.272803 | -0.219740 | -0.913861 |
| C | -3.803499 | -0.209209 | 0.377097 |
| C | -2.949082 | -0.316157 | 1.481240 |
| C | -1.583127 | -0.428318 | 1.298493 |
| H | -1.494172 | -0.347416 | -2.097465 |
| H | -3.911764 | -0.148041 | -1.780382 |
| H | -3.380381 | -0.315576 | 2.472396 |
| H | -0.934196 | -0.521494 | 2.158273 |
| O | -5.122422 | -0.106485 | 0.663397 |
| C | -6.052879 | -0.006218 | -0.406376 |
| H | -6.020299 | -0.891181 | -1.045905 |
| H | -7.032049 | 0.066194 | 0.057546 |
| H | -5.870989 | 0.886782 | -1.008759 |
| N | 2.566297 | -2.642840 | -0.802894 |
| N | 3.029951 | -3.220404 | 0.143432 |
| N | 3.479348 | -3.779749 | 1.044408 |

### 2.3.5 $X = \mathrm{NH_2}$

| 30 | equilibrium structure | | |
|---|---|---|---|
| I | 1.071093 | -1.322131 | -0.020507 |
| C | 1.936521 | 0.681048 | -0.06367 |
| C | 1.121997 | 1.764461 | -0.34427 |
| C | 1.691784 | 3.035262 | -0.362453 |
| C | 3.04509 | 3.204554 | -0.098367 |
| C | 3.837529 | 2.096883 | 0.176364 |
| C | 3.288993 | 0.816632 | 0.191569 |
| H | 0.069093 | 1.639545 | -0.540311 |
| H | 1.066533 | 3.889465 | -0.585311 |
| H | 3.480041 | 4.194836 | -0.110781 |
| H | 4.893241 | 2.218613 | 0.37944 |
| H | 3.885353 | -0.068947 | 0.365548 |
| C | -1.013047 | -0.42442 | 0.097253 |
| C | -1.845709 | -0.478277 | -1.012191 |
| C | -3.192924 | -0.119866 | -0.930817 |
| C | -3.718003 | 0.297465 | 0.290584 |
| C | -2.890328 | 0.348865 | 1.417058 |
| C | -1.557531 | -0.01276 | 1.316286 |
| H | -1.457563 | -0.802601 | -1.971356 |
| H | -3.810921 | -0.171875 | -1.814731 |
| H | -3.317349 | 0.670224 | 2.357584 |
| H | -0.938035 | 0.031502 | 2.204572 |
| O | -5.01282 | 0.669069 | 0.489302 |
| C | -5.905658 | 0.632889 | -0.610904 |
| H | -6.006646 | -0.378849 | -1.01246 |
| H | -5.585337 | 1.306815 | -1.409843 |
| H | -6.867232 | 0.963496 | -0.22778 |
| N | 3.221123 | -2.07062 | -0.068009 |
| H | 3.221625 | -2.840192 | 0.597924 |
| H | 3.361703 | -2.493729 | -0.982659 |

| 30 | reductive elimination TS | | |
|---|---|---|---|
| I | 1.017068 | -1.440702 | -0.068303 |
| C | 2.145676 | 0.537555 | -0.024288 |
| C | 2.296318 | 1.156736 | 1.212828 |
| C | 2.569303 | 2.519645 | 1.248996 |
| C | 2.664191 | 3.264365 | 0.078259 |
| C | 2.474102 | 2.627778 | -1.143674 |
| C | 2.199888 | 1.266332 | -1.208853 |
| H | 2.224214 | 0.591746 | 2.130415 |
| H | 2.701077 | 2.998843 | 2.210805 |
| H | 2.870666 | 4.324440 | 0.117951 |
| H | 2.531515 | 3.191995 | -2.065900 |
| H | 2.054239 | 0.785674 | -2.165034 |
| C | -1.016827 | -0.677520 | 0.077083 |
| C | -1.621288 | -0.519551 | 1.325488 |
| C | -2.918155 | -0.047248 | 1.423694 |
| C | -3.636310 | 0.280088 | 0.269637 |
| C | -3.037616 | 0.129014 | -0.980793 |
| C | -1.731275 | -0.347797 | -1.066666 |
| H | -1.082160 | -0.768443 | 2.230047 |
| H | -3.397588 | 0.077016 | 2.384876 |
| H | -3.569709 | 0.376091 | -1.886772 |
| H | -1.281739 | -0.459520 | -2.044652 |
| O | -4.902190 | 0.733277 | 0.468459 |
| C | -5.684359 | 1.087103 | -0.660806 |
| H | -6.642324 | 1.417716 | -0.269275 |
| H | -5.841231 | 0.231532 | -1.322549 |
| H | -5.224994 | 1.901993 | -1.225893 |
| N | 3.399523 | -1.278140 | -0.163421 |
| H | 4.005057 | -1.483397 | 0.628650 |
| H | 3.947362 | -1.406705 | -1.011775 |

| 30 | isomerization TS | | |
|---|---|---|---|
| I | 1.208820 | -1.293429 | -0.044325 |
| C | 1.823874 | 0.872114 | -0.016857 |
| C | 2.022931 | 1.537350 | -1.218054 |
| C | 2.473406 | 2.854991 | -1.204584 |
| C | 2.732896 | 3.491338 | 0.004173 |
| C | 2.545496 | 2.810313 | 1.202093 |
| C | 2.095905 | 1.492470 | 1.194037 |
| H | 1.829130 | 1.043565 | -2.161548 |
| H | 2.624214 | 3.380453 | -2.138707 |
| H | 3.085554 | 4.513844 | 0.012586 |
| H | 2.752041 | 3.301323 | 2.144233 |
| H | 1.958612 | 0.964144 | 2.128630 |
| C | -0.892830 | -0.532509 | 0.095667 |
| C | -1.620441 | -0.289877 | -1.056269 |
| C | -2.953852 | 0.110959 | -0.978241 |
| C | -3.559359 | 0.253432 | 0.269935 |
| C | -2.825051 | -0.010282 | 1.430145 |
| C | -1.501118 | -0.407233 | 1.340880 |
| H | -1.164526 | -0.402610 | -2.031633 |
| H | -3.501035 | 0.303180 | -1.888657 |
| H | -3.313503 | 0.099042 | 2.388723 |
| H | -0.948473 | -0.614212 | 2.248260 |
| O | -4.850858 | 0.634916 | 0.460656 |
| C | -5.653729 | 0.910034 | -0.675583 |
| H | -5.757259 | 0.029719 | -1.315056 |
| H | -6.630423 | 1.190411 | -0.291076 |
| H | -5.246490 | 1.737197 | -1.262640 |
| N | 2.264655 | -3.287238 | -0.159510 |
| H | 2.490538 | -3.788449 | -1.013386 |
| H | 2.579650 | -3.833152 | 0.636789 |

### 2.3.6 $X =$ OH

| 29 | equilibrium structure | | |
|---|---|---|---|
| I | 1.073332 | -1.324220 | -0.035427 |
| C | 1.888689 | 0.693956 | 0.028400 |
| C | 1.099691 | 1.761070 | 0.421711 |
| C | 1.669272 | 3.032064 | 0.445896 |
| C | 2.994763 | 3.217074 | 0.072811 |
| C | 3.760752 | 2.126485 | -0.321340 |
| C | 3.212654 | 0.846646 | -0.343267 |
| H | 0.067240 | 1.624392 | 0.702551 |
| H | 1.066895 | 3.874158 | 0.759406 |
| H | 3.428989 | 4.207517 | 0.090677 |
| H | 4.792691 | 2.263126 | -0.616040 |
| H | 3.786260 | -0.025443 | -0.626154 |
| C | -0.993436 | -0.526668 | 0.079451 |
| C | -1.672579 | -0.123574 | -1.063663 |
| C | -3.015838 | 0.244438 | -1.013437 |
| C | -3.697223 | 0.200679 | 0.203378 |
| C | -3.024414 | -0.211444 | 1.357027 |
| C | -1.688574 | -0.572091 | 1.289631 |
| H | -1.162334 | -0.087588 | -2.018468 |
| H | -3.514541 | 0.554309 | -1.919362 |
| H | -3.569040 | -0.243473 | 2.290748 |
| H | -1.187735 | -0.892601 | 2.195162 |
| O | -5.005296 | 0.532953 | 0.366855 |
| C | -5.749648 | 0.950454 | -0.766379 |
| H | -5.792431 | 0.167367 | -1.527435 |
| H | -5.332659 | 1.859788 | -1.206557 |
| H | -6.753756 | 1.155050 | -0.405553 |
| O | 3.137782 | -2.031141 | -0.222008 |
| H | 3.519285 | -2.121953 | 0.658587 |

| 29 | reductive elimination TS | | |
|---|---|---|---|
| I | 0.934165 | -1.422584 | -0.074966 |
| C | 2.212128 | 0.455472 | -0.023104 |
| C | 2.456587 | 1.043918 | 1.211223 |
| C | 2.847959 | 2.376820 | 1.239047 |
| C | 2.978003 | 3.113253 | 0.065245 |
| C | 2.706257 | 2.501174 | -1.151952 |
| C | 2.307769 | 1.168526 | -1.211452 |
| H | 2.378044 | 0.472526 | 2.122962 |
| H | 3.054404 | 2.837958 | 2.196256 |
| H | 3.280429 | 4.150200 | 0.100799 |
| H | 2.792252 | 3.059907 | -2.075048 |
| H | 2.089482 | 0.705273 | -2.162093 |
| C | -1.076930 | -0.651365 | 0.075449 |
| C | -1.663212 | -0.465109 | 1.328590 |
| C | -2.948764 | 0.034711 | 1.430069 |
| C | -3.670606 | 0.360879 | 0.277297 |
| C | -3.086878 | 0.179889 | -0.976757 |
| C | -1.791681 | -0.323384 | -1.068492 |
| H | -1.119061 | -0.712195 | 2.230055 |
| H | -3.416732 | 0.182147 | 2.393438 |
| H | -1.351208 | -0.457416 | -2.047310 |
| H | -3.622291 | 0.424848 | -1.881178 |
| O | -4.922701 | 0.843215 | 0.480883 |
| C | -5.708741 | 1.201855 | -0.645363 |
| H | -5.892915 | 0.341770 | -1.293779 |
| H | -5.235606 | 1.998427 | -1.224673 |
| H | -6.653917 | 1.560099 | -0.247567 |
| O | 3.305488 | -1.317620 | -0.047740 |
| H | 3.752713 | -1.351176 | -0.902604 |

| 29 | isomerization TS | | |
|---|---|---|---|
| I | 1.144450 | -1.300014 | -0.038233 |
| C | 1.893002 | 0.797907 | -0.018900 |
| C | 2.165414 | 1.418195 | 1.191772 |
| C | 2.686074 | 2.709228 | 1.192475 |
| C | 2.940989 | 3.359722 | -0.009936 |
| C | 2.679216 | 2.720636 | -1.216658 |
| C | 2.157415 | 1.429720 | -1.225342 |
| H | 1.974696 | 0.911071 | 2.128266 |
| H | 2.895028 | 3.202661 | 2.132567 |
| H | 3.348755 | 4.361458 | -0.006307 |
| H | 2.883549 | 3.222489 | -2.153296 |
| H | 1.961967 | 0.930766 | -2.165223 |
| C | -0.921660 | -0.509754 | 0.099365 |
| C | -1.647987 | -0.283115 | -1.056907 |
| C | -2.970464 | 0.150378 | -0.981646 |
| C | -3.564601 | 0.342006 | 0.265970 |
| C | -2.829437 | 0.094104 | 1.429854 |
| C | -1.516367 | -0.335823 | 1.345400 |
| H | -1.199762 | -0.436693 | -2.029744 |
| H | -3.519233 | 0.328516 | -1.893793 |
| H | -3.309679 | 0.240975 | 2.387386 |
| H | -0.961869 | -0.531728 | 2.253678 |
| O | -4.843781 | 0.757754 | 0.453031 |
| C | -5.651322 | 1.014952 | -0.685458 |
| H | -5.778413 | 0.117384 | -1.295588 |
| H | -5.231579 | 1.814900 | -1.300373 |
| H | -6.618090 | 1.327536 | -0.301193 |
| O | 2.100535 | -3.301219 | -0.243181 |
| H | 2.323102 | -3.689801 | 0.611247 |

### 2.3.7 $X = \mathrm{PMe_2}$

| 36 | equilibrium structure | | |
|---|---|---|---|
| I | 0.748265 | -1.077458 | -0.073989 |
| C | 1.072045 | 1.047212 | 0.035638 |
| C | 1.415486 | 1.741664 | -1.115101 |
| C | 1.646348 | 3.112690 | -1.030920 |
| C | 1.538569 | 3.767583 | 0.190093 |
| C | 1.195128 | 3.054589 | 1.333320 |
| C | 0.957226 | 1.685234 | 1.262223 |
| H | 1.494308 | 1.234769 | -2.065669 |
| H | 1.905761 | 3.664685 | -1.924319 |
| H | 1.720157 | 4.831892 | 0.250821 |
| H | 1.108414 | 3.561056 | 2.285237 |
| H | 0.673705 | 1.135494 | 2.148025 |
| C | -1.540994 | -0.568740 | 0.001968 |
| C | -2.160534 | 0.620936 | -0.342800 |
| C | -3.552929 | 0.739722 | -0.327602 |
| C | -4.334707 | -0.354377 | 0.038329 |
| C | -3.716629 | -1.558422 | 0.384167 |
| C | -2.333798 | -1.655215 | 0.361297 |
| H | -1.576931 | 1.487853 | -0.628087 |
| H | -4.007158 | 1.681115 | -0.600038 |
| H | -4.337558 | -2.397763 | 0.667925 |
| H | -1.875913 | -2.602596 | 0.633227 |
| O | -5.698610 | -0.348984 | 0.090728 |
| C | -6.382899 | 0.843451 | -0.247489 |
| H | -6.184803 | 1.142060 | -1.280602 |
| H | -6.112826 | 1.665572 | 0.421082 |
| H | -7.441650 | 0.624852 | -0.135524 |
| P | 3.490335 | -1.530840 | -0.016406 |
| C | 4.228548 | -0.515871 | -1.397796 |
| C | 4.051447 | -0.505620 | 1.437903 |
| H | 5.316108 | -0.615437 | -1.371592 |
| H | 3.883710 | -0.899508 | -2.357972 |
| H | 3.982599 | 0.544644 | -1.329496 |
| H | 5.141255 | -0.536224 | 1.503146 |
| H | 3.651206 | -0.930238 | 2.358416 |
| H | 3.741597 | 0.538510 | 1.367742 |

| 36 | reductive elimination TS | | |
|---|---|---|---|
| I | -0.322004 | -0.659197 | -0.015632 |
| C | -1.900424 | 0.940391 | 0.009405 |
| C | -2.299036 | 1.455514 | 1.235742 |
| C | -3.055219 | 2.624471 | 1.259768 |
| C | -3.381836 | 3.278551 | 0.076987 |
| C | -2.950089 | 2.760129 | -1.139351 |
| C | -2.194029 | 1.592242 | -1.181304 |
| H | -2.033756 | 0.962003 | 2.159737 |
| H | -3.381579 | 3.023547 | 2.211329 |
| H | -3.962827 | 4.189959 | 0.103213 |
| H | -3.195383 | 3.264877 | -2.064702 |
| H | -1.849619 | 1.201923 | -2.128330 |
| C | 1.973469 | -0.325122 | 0.101958 |
| C | 2.716565 | -0.138629 | -1.054587 |
| C | 4.092883 | 0.081224 | -0.997598 |
| C | 4.729065 | 0.126871 | 0.243164 |
| C | 3.982720 | -0.047707 | 1.413283 |
| C | 2.616809 | -0.264920 | 1.338056 |
| H | 2.237206 | -0.168671 | -2.026644 |
| H | 4.649119 | 0.213610 | -1.913769 |
| H | 4.496803 | -0.008094 | 2.364427 |
| H | 2.055991 | -0.395109 | 2.256576 |
| O | 6.062417 | 0.336549 | 0.418470 |
| C | 6.877828 | 0.527413 | -0.725254 |
| H | 6.571899 | 1.409856 | -1.293267 |
| H | 6.860311 | -0.347009 | -1.381036 |
| H | 7.887649 | 0.674473 | -0.351923 |
| P | -3.029668 | -2.132909 | -0.184684 |
| C | -3.957317 | -1.601511 | 1.335476 |
| C | -4.077278 | -1.306379 | -1.479173 |
| H | -4.949788 | -2.059834 | 1.330566 |
| H | -3.432783 | -1.952410 | 2.224025 |
| H | -4.084198 | -0.519111 | 1.402685 |
| H | -5.065740 | -1.773580 | -1.489482 |
| H | -3.628982 | -1.456916 | -2.461115 |
| H | -4.207112 | -0.236032 | -1.310698 |

| 36 | isomerization TS | | |
|---|---|---|---|
| I | -0.964583 | 0.051777 | 0.027896 |
| C | -3.167628 | -0.571977 | -0.009401 |
| C | -3.796760 | -0.866532 | -1.217268 |
| C | -5.133590 | -1.253888 | -1.240555 |
| C | -5.850068 | -1.350356 | -0.051758 |
| C | -5.228005 | -1.059134 | 1.158222 |
| C | -3.891002 | -0.672329 | 1.177334 |
| H | -3.247306 | -0.796864 | -2.149324 |
| H | -5.615821 | -1.481086 | -2.183165 |
| H | -6.888911 | -1.652494 | -0.068120 |
| H | -5.783769 | -1.134254 | 2.084577 |
| H | -3.415855 | -0.449435 | 2.125999 |
| C | 1.535945 | -0.166138 | 0.126962 |
| C | 2.230369 | -0.504319 | -1.021448 |
| C | 3.550805 | -0.963192 | -0.961221 |
| C | 4.172563 | -1.105090 | 0.277339 |
| C | 3.465104 | -0.796705 | 1.441996 |
| C | 2.155366 | -0.341695 | 1.361258 |
| H | 1.762108 | -0.423702 | -1.996495 |
| H | 4.067847 | -1.211234 | -1.876690 |
| H | 3.956809 | -0.927920 | 2.397131 |
| H | 1.625083 | -0.125427 | 2.282274 |
| O | 5.453764 | -1.543048 | 0.456236 |
| C | 6.213076 | -1.891025 | -0.686907 |
| H | 6.345804 | -1.037208 | -1.357351 |
| H | 5.752038 | -2.713011 | -1.241445 |
| H | 7.184466 | -2.209488 | -0.317793 |
| P | 0.054839 | 2.738498 | -0.125030 |
| C | 1.265702 | 2.970711 | 1.245845 |
| C | 1.184572 | 2.759866 | -1.581508 |
| H | 1.528639 | 4.034200 | 1.243174 |
| H | 0.789980 | 2.751158 | 2.200230 |
| H | 2.168344 | 2.374945 | 1.138244 |
| H | 1.484417 | 3.803540 | -1.723876 |
| H | 2.073478 | 2.146829 | -1.451053 |
| H | 0.644152 | 2.445022 | -2.472606 |

### 2.3.8 $X = PH_2$

| 30 | equilibrium structure | | |
|---|---|---|---|
| I | 1.093185 | -1.157541 | -0.062157 |
| C | 1.502337 | 0.957107 | 0.087051 |
| C | 2.293213 | 1.561604 | -0.873636 |
| C | 2.545902 | 2.926305 | -0.765555 |
| C | 2.024141 | 3.653997 | 0.297543 |
| C | 1.236809 | 3.022072 | 1.253103 |
| C | 0.961548 | 1.661549 | 1.149085 |
| H | 2.716639 | 0.989051 | -1.685201 |
| H | 3.152831 | 3.414769 | -1.515844 |
| H | 2.230939 | 4.712109 | 0.381404 |
| H | 0.832293 | 3.583057 | 2.084713 |
| H | 0.330371 | 1.173583 | 1.876743 |
| C | -1.136404 | -0.574628 | 0.050767 |
| C | -1.753778 | 0.224188 | -0.899431 |
| C | -3.133223 | 0.429356 | -0.879530 |
| C | -3.906776 | -0.182404 | 0.107489 |
| C | -3.290983 | -0.994370 | 1.062478 |
| C | -1.917722 | -1.188753 | 1.026301 |
| H | -1.172753 | 0.709984 | -1.674708 |
| H | -3.586643 | 1.058100 | -1.631337 |
| H | -3.905888 | -1.460979 | 1.820316 |
| H | -1.462179 | -1.828746 | 1.774098 |
| O | -5.258034 | -0.051382 | 0.220594 |
| C | -5.944223 | 0.748126 | -0.727292 |
| H | -5.605620 | 1.787210 | -0.696864 |
| H | -5.823189 | 0.359907 | -1.742055 |
| H | -6.994277 | 0.706063 | -0.450943 |
| P | 3.871596 | -1.688856 | -0.121181 |
| H | 4.192996 | -0.933075 | -1.284257 |
| H | 4.260932 | -0.642381 | 0.760968 |

| 30 | reductive elimination TS | | |
|---|---|---|---|
| I | -0.571119 | -0.798884 | -0.009208 |
| C | -2.472139 | 0.565718 | -0.007554 |
| C | -2.882367 | 1.075272 | 1.210330 |
| C | -3.824768 | 2.102519 | 1.211420 |
| C | -4.313667 | 2.611303 | 0.013980 |
| C | -3.861457 | 2.093281 | -1.194755 |
| C | -2.922436 | 1.064367 | -1.216149 |
| H | -2.498474 | 0.684672 | 2.141784 |
| H | -4.169533 | 2.502407 | 2.156097 |
| H | -5.040986 | 3.411281 | 0.022061 |
| H | -4.237499 | 2.484594 | -2.131040 |
| H | -2.577180 | 0.657718 | -2.155568 |
| C | 1.638293 | -0.276546 | 0.103632 |
| C | 2.363275 | -0.030595 | -1.054509 |
| C | 3.719197 | 0.286752 | -0.997679 |
| C | 4.354216 | 0.368320 | 0.242358 |
| C | 3.624860 | 0.133538 | 1.413189 |
| C | 2.278697 | -0.179868 | 1.339977 |
| H | 1.883810 | -0.089378 | -2.024440 |
| H | 4.261891 | 0.465363 | -1.913823 |
| H | 4.136903 | 0.202707 | 2.363466 |
| H | 1.729706 | -0.357187 | 2.257022 |
| O | 5.668308 | 0.668499 | 0.415628 |
| C | 6.468075 | 0.919525 | -0.728859 |
| H | 6.102629 | 1.782646 | -1.290841 |
| H | 6.507211 | 0.048935 | -1.388382 |
| H | 7.466053 | 1.131379 | -0.355359 |
| P | -3.168421 | -2.323489 | -0.253457 |
| H | -2.481345 | -3.479063 | 0.226359 |
| H | -3.652667 | -2.002377 | 1.045224 |

| 30 | isomerization TS | | |
|---|---|---|---|
| I | -0.819472 | 0.875488 | -0.006433 |
| C | -2.330684 | -0.905101 | -0.019651 |
| C | -2.715513 | -1.452755 | -1.232082 |
| C | -3.610473 | -2.520801 | -1.235533 |
| C | -4.099892 | -3.023090 | -0.034296 |
| C | -3.699516 | -2.462991 | 1.174341 |
| C | -2.805440 | -1.394270 | 1.185847 |
| H | -2.335123 | -1.060453 | -2.166804 |
| H | -3.924412 | -2.957001 | -2.175169 |
| H | -4.794546 | -3.852196 | -0.040051 |
| H | -4.082488 | -2.854408 | 2.108063 |
| H | -2.495090 | -0.956333 | 2.126141 |
| C | 1.349810 | 0.208015 | 0.114558 |
| C | 2.056794 | -0.036286 | -1.049241 |
| C | 3.386158 | -0.450085 | -0.985013 |
| C | 3.996481 | -0.618157 | 0.259083 |
| C | 3.270968 | -0.372109 | 1.430485 |
| C | 1.950971 | 0.038278 | 1.357320 |
| H | 1.591516 | 0.093731 | -2.018104 |
| H | 3.927500 | -0.634003 | -1.900631 |
| H | 3.764542 | -0.507567 | 2.383122 |
| H | 1.399916 | 0.227459 | 2.269611 |
| O | 5.282274 | -1.014493 | 0.435615 |
| C | 6.081683 | -1.274569 | -0.708461 |
| H | 6.188516 | -0.383206 | -1.331301 |
| H | 5.667499 | -2.088857 | -1.307952 |
| H | 7.056983 | -1.567327 | -0.330301 |
| P | -1.744491 | 3.720995 | -0.139375 |
| H | -0.851729 | 4.045398 | 0.923340 |
| H | -0.759982 | 3.978440 | -1.137440 |

### 2.3.9 $X =$ SPh

| 39 | equilibrium structure | | |
|---|---|---|---|
| I | -0.446113 | 0.078092 | -0.203932 |
| C | 0.253478 | 2.118993 | -0.047817 |
| C | 1.371839 | 2.507665 | -0.765665 |
| C | 1.797811 | 3.828692 | -0.662779 |
| C | 1.112921 | 4.726249 | 0.148125 |
| C | -0.006569 | 4.307974 | 0.857187 |
| C | -0.452334 | 2.992315 | 0.760543 |
| H | 1.911616 | 1.808210 | -1.386143 |
| H | 2.664764 | 4.150776 | -1.223666 |
| H | 1.449548 | 5.751146 | 0.223924 |
| H | -0.543535 | 5.002199 | 1.489185 |
| H | -1.340106 | 2.666272 | 1.283105 |
| C | 1.657137 | -0.638488 | -0.145979 |
| C | 2.394574 | -0.612188 | 1.028070 |
| C | 3.673493 | -1.162113 | 1.074977 |
| C | 4.213548 | -1.754955 | -0.067872 |
| C | 3.465053 | -1.790997 | -1.247589 |
| C | 2.195079 | -1.237693 | -1.282934 |
| H | 1.988719 | -0.160333 | 1.924185 |
| H | 4.229759 | -1.126762 | 1.999404 |
| H | 3.897876 | -2.256724 | -2.122225 |
| H | 1.628258 | -1.278016 | -2.204702 |
| O | 5.446040 | -2.321529 | -0.131378 |
| C | 6.256587 | -2.327708 | 1.033713 |
| H | 5.781704 | -2.880599 | 1.847874 |
| H | 6.482807 | -1.312347 | 1.368631 |
| H | 7.179690 | -2.826380 | 0.752277 |
| S | -3.043543 | 1.114573 | -0.235705 |
| C | -3.698720 | -0.515615 | -0.005021 |
| C | -4.201665 | -0.922699 | 1.239750 |
| C | -4.723700 | -2.196639 | 1.414992 |
| C | -4.746776 | -3.101786 | 0.357227 |
| C | -4.245763 | -2.715898 | -0.880219 |
| C | -3.729193 | -1.437580 | -1.061805 |
| H | -4.184229 | -0.222418 | 2.063457 |
| H | -5.113404 | -2.485600 | 2.382737 |
| H | -5.153162 | -4.094480 | 0.496876 |
| H | -4.263367 | -3.408143 | -1.712311 |
| H | -3.365364 | -1.131792 | -2.033355 |

| 39 | reductive elimination TS | | |
|---|---|---|---|
| I | -0.143152 | -0.489586 | -0.989227 |
| C | 0.910354 | 1.464927 | -0.162314 |
| C | 1.285136 | 1.422496 | 1.167465 |
| C | 1.392622 | 2.634239 | 1.848042 |
| C | 1.101374 | 3.836823 | 1.215345 |
| C | 0.695098 | 3.830802 | -0.115830 |
| C | 0.576891 | 2.637118 | -0.820329 |
| H | 1.525424 | 0.492275 | 1.659818 |
| H | 1.706065 | 2.622547 | 2.883939 |
| H | 1.183083 | 4.769986 | 1.754788 |
| H | 0.467437 | 4.759990 | -0.622187 |
| H | 0.273089 | 2.637186 | -1.856263 |
| C | -2.176043 | -0.546954 | -0.241357 |
| C | -3.219350 | -0.056125 | -1.014096 |
| C | -4.526051 | -0.086610 | -0.533939 |
| C | -4.783789 | -0.603674 | 0.736585 |
| C | -3.726713 | -1.087567 | 1.516262 |
| C | -2.432286 | -1.059047 | 1.030887 |
| H | -3.030991 | 0.349580 | -1.998931 |
| H | -5.324211 | 0.292725 | -1.153890 |
| H | -3.946203 | -1.482730 | 2.498373 |
| H | -1.625555 | -1.439140 | 1.643183 |
| O | -6.014706 | -0.679611 | 1.300263 |
| C | -7.137897 | -0.220534 | 0.561041 |
| H | -7.261855 | -0.785072 | -0.366504 |
| H | -7.056207 | 0.844848 | 0.330962 |
| H | -8.001593 | -0.384535 | 1.199020 |
| S | 2.720003 | 0.168737 | -1.615491 |
| C | 3.557895 | -0.684614 | -0.324694 |
| C | 3.362235 | -2.057726 | -0.100016 |
| C | 4.048060 | -2.720796 | 0.908193 |
| C | 4.939183 | -2.030927 | 1.726683 |
| C | 5.138236 | -0.668782 | 1.521537 |
| C | 4.458337 | -0.001479 | 0.510342 |
| H | 2.679833 | -2.602753 | -0.738670 |
| H | 3.888485 | -3.782096 | 1.053549 |
| H | 5.473252 | -2.549519 | 2.511858 |
| H | 5.830699 | -0.122189 | 2.149898 |
| H | 4.624134 | 1.054655 | 0.347007 |

| 39 | isomerization TS | | |
|---|---|---|---|
| I | -0.314194 | 0.402866 | -0.757058 |
| C | 0.299319 | 2.334980 | 0.151713 |
| C | 0.932881 | 3.285893 | -0.632705 |
| C | 1.276008 | 4.507040 | -0.059094 |
| C | 0.972393 | 4.762787 | 1.273758 |
| C | 0.322264 | 3.801820 | 2.039856 |
| C | -0.024321 | 2.575994 | 1.477480 |
| H | 1.160561 | 3.089857 | -1.671636 |
| H | 1.775751 | 5.257403 | -0.657176 |
| H | 1.236992 | 5.714639 | 1.713583 |
| H | 0.078965 | 4.003277 | 3.074587 |
| H | -0.538790 | 1.830646 | 2.068941 |
| C | 1.648860 | -0.523207 | -0.375918 |
| C | 1.843103 | -1.237113 | 0.793052 |
| C | 3.062515 | -1.869703 | 1.024270 |
| C | 4.076526 | -1.787367 | 0.068523 |
| C | 3.859868 | -1.075047 | -1.116736 |
| C | 2.646866 | -0.448903 | -1.341942 |
| H | 1.058261 | -1.313074 | 1.533550 |
| H | 3.203979 | -2.420567 | 1.941334 |
| H | 4.655361 | -1.030783 | -1.847438 |
| H | 2.487327 | 0.090830 | -2.265497 |
| O | 5.296515 | -2.363826 | 0.192398 |
| C | 5.585107 | -3.116031 | 1.362594 |
| H | 4.910314 | -3.969183 | 1.463699 |
| H | 5.525139 | -2.495361 | 2.259674 |
| H | 6.602838 | -3.475314 | 1.241609 |
| S | -2.770015 | -0.484918 | -1.890565 |
| C | -3.551067 | -1.111357 | -0.431514 |
| C | -4.191884 | -0.255369 | 0.476888 |
| C | -4.808811 | -0.754700 | 1.617613 |
| C | -4.804339 | -2.119739 | 1.883858 |
| C | -4.174507 | -2.980728 | 0.989754 |
| C | -3.556425 | -2.486290 | -0.150989 |
| H | -4.213286 | 0.806095 | 0.270000 |
| H | -5.300229 | -0.071647 | 2.299282 |
| H | -5.287963 | -2.507432 | 2.770373 |
| H | -4.166301 | -4.046752 | 1.179860 |
| H | -3.074680 | -3.162985 | -0.843567 |

### 2.3.10 $X =$ SH

| 29 | equilibrium structure | | |
|---|---|---|---|
| I | 0.970659 | -1.118001 | 0.005280 |
| C | 1.642780 | 0.963555 | -0.063478 |
| C | 0.783014 | 1.931917 | -0.551034 |
| C | 1.230748 | 3.250222 | -0.591267 |
| C | 2.505140 | 3.574774 | -0.142961 |
| C | 3.343681 | 2.577813 | 0.340422 |
| C | 2.918512 | 1.252025 | 0.378399 |
| H | -0.211874 | 1.685468 | -0.887399 |
| H | 0.574337 | 4.018274 | -0.977637 |
| H | 2.844608 | 4.601118 | -0.174235 |
| H | 4.338181 | 2.821254 | 0.689232 |
| H | 3.577197 | 0.459680 | 0.708745 |
| C | -1.154042 | -0.433995 | 0.115385 |
| C | -1.984684 | -0.638484 | -0.975729 |
| C | -3.350844 | -0.365153 | -0.896456 |
| C | -3.887293 | 0.114249 | 0.297560 |
| C | -3.051174 | 0.312885 | 1.402588 |
| C | -1.699032 | 0.034750 | 1.311317 |
| H | -1.583349 | -1.014150 | -1.909098 |
| H | -3.975009 | -0.530428 | -1.761550 |
| H | -3.487620 | 0.679474 | 2.321606 |
| H | -1.070800 | 0.189029 | 2.179491 |
| O | -5.198270 | 0.412519 | 0.488850 |
| C | -6.105526 | 0.219933 | -0.585399 |
| H | -6.139199 | -0.827035 | -0.896696 |
| H | -5.846921 | 0.844937 | -1.443801 |
| H | -7.081088 | 0.513864 | -0.208733 |
| S | 3.580801 | -2.028271 | -0.044214 |
| H | 3.762305 | -1.802198 | -1.359220 |

| 29 | reductive elimination TS | | |
|---|---|---|---|
| I | 0.773306 | -1.269811 | -0.036115 |
| C | 2.119428 | 0.677715 | -0.019842 |
| C | 2.254146 | 1.284216 | 1.217327 |
| C | 2.517883 | 2.651377 | 1.246927 |
| C | 2.609259 | 3.387242 | 0.071627 |
| C | 2.431453 | 2.746323 | -1.150160 |
| C | 2.168961 | 1.381699 | -1.211659 |
| H | 2.186825 | 0.719179 | 2.134433 |
| H | 2.647480 | 3.134862 | 2.206471 |
| H | 2.810766 | 4.448396 | 0.106562 |
| H | 2.498593 | 3.304586 | -2.074867 |
| H | 2.048988 | 0.887577 | -2.163572 |
| C | -1.296745 | -0.630278 | 0.093222 |
| C | -2.011186 | -0.351426 | -1.063612 |
| C | -3.335056 | 0.072888 | -0.990542 |
| C | -3.945291 | 0.223501 | 0.255497 |
| C | -3.220510 | -0.052984 | 1.420129 |
| C | -1.905800 | -0.473728 | 1.338917 |
| H | -1.549453 | -0.464289 | -2.035223 |
| H | -3.872675 | 0.280480 | -1.902953 |
| H | -3.710243 | 0.069380 | 2.376172 |
| H | -1.358798 | -0.683604 | 2.248028 |
| O | -5.225991 | 0.629142 | 0.439794 |
| C | -6.020175 | 0.928820 | -0.698847 |
| H | -6.138950 | 0.054395 | -1.343035 |
| H | -5.592897 | 1.751330 | -1.277298 |
| H | -6.991490 | 1.226419 | -0.314556 |
| S | 3.732595 | -1.384198 | -0.232374 |
| H | 3.924854 | -1.386875 | 1.099671 |

| 29 | isomerization TS | | |
|---|---|---|---|
| I | 1.101228 | -0.944439 | 0.002126 |
| C | 1.711011 | 1.199595 | -0.028647 |
| C | 1.998298 | 1.834148 | 1.169810 |
| C | 2.427912 | 3.158287 | 1.143607 |
| C | 2.575193 | 3.821013 | -0.069872 |
| C | 2.296495 | 3.163909 | -1.263225 |
| C | 1.865844 | 1.840056 | -1.248198 |
| H | 1.893267 | 1.315613 | 2.113197 |
| H | 2.651269 | 3.666905 | 2.072045 |
| H | 2.913433 | 4.848083 | -0.085838 |
| H | 2.417313 | 3.676868 | -2.208158 |
| H | 1.657203 | 1.326160 | -2.176760 |
| C | -1.044756 | -0.405827 | 0.116239 |
| C | -1.790457 | -0.323862 | -1.045836 |
| C | -3.154032 | -0.044258 | -0.979053 |
| C | -3.761484 | 0.140150 | 0.263764 |
| C | -2.998443 | 0.038854 | 1.432642 |
| C | -1.645087 | -0.240102 | 1.359875 |
| H | -1.329228 | -0.473829 | -2.012810 |
| H | -3.723354 | 0.021094 | -1.893582 |
| H | -3.489680 | 0.177402 | 2.385708 |
| H | -1.068193 | -0.325539 | 2.270859 |
| O | -5.077239 | 0.413678 | 0.442271 |
| C | -5.916992 | 0.516766 | -0.698432 |
| H | -5.942185 | -0.419689 | -1.260657 |
| H | -5.597423 | 1.328194 | -1.356709 |
| H | -6.910805 | 0.733748 | -0.317780 |
| S | 2.554097 | -3.366740 | -0.044263 |
| H | 2.534621 | -3.453697 | -1.388227 |

### 2.3.11 $X = \mathrm{Cl}$

| 28 | equilibrium structure | | |
|---|---|---|---|
| I | 0.935976 | -1.112425 | -0.002689 |
| C | 1.662892 | 0.939356 | -0.061236 |
| C | 0.808055 | 1.938274 | -0.492641 |
| C | 1.286707 | 3.245694 | -0.517971 |
| C | 2.585971 | 3.526550 | -0.113978 |
| C | 3.417388 | 2.497991 | 0.311612 |
| C | 2.962678 | 1.181705 | 0.338743 |
| H | -0.204023 | 1.724848 | -0.799027 |
| H | 0.635100 | 4.038960 | -0.858506 |
| H | 2.950436 | 4.544487 | -0.135030 |
| H | 4.431257 | 2.708237 | 0.623809 |
| H | 3.610090 | 0.367236 | 0.631457 |
| C | -1.147555 | -0.464303 | 0.119275 |
| C | -1.964765 | -0.594958 | -0.994089 |
| C | -3.324929 | -0.300222 | -0.914555 |
| C | -3.867540 | 0.127018 | 0.297273 |
| C | -3.041855 | 0.252091 | 1.421415 |
| C | -1.695132 | -0.047290 | 1.333466 |
| H | -1.556271 | -0.927196 | -1.939673 |
| H | -3.940744 | -0.408307 | -1.794191 |
| H | -3.482577 | 0.578941 | 2.352954 |
| H | -1.073408 | 0.047287 | 2.213815 |
| O | -5.172197 | 0.439713 | 0.488033 |
| C | -6.072225 | 0.322489 | -0.604897 |
| H | -6.123015 | -0.705856 | -0.970194 |
| H | -5.790989 | 0.986860 | -1.425377 |
| H | -7.045137 | 0.616333 | -0.222023 |
| Cl | 3.511883 | -1.992787 | -0.127898 |

| 28 | reductive elimination TS | | |
|---|---|---|---|
| I | 0.749685 | -1.321441 | -0.026057 |
| C | 2.158518 | 0.670556 | -0.020040 |
| C | 2.304509 | 1.257832 | 1.218122 |
| C | 2.510502 | 2.636294 | 1.242955 |
| C | 2.552587 | 3.374303 | 0.065808 |
| C | 2.391014 | 2.730025 | -1.155211 |
| C | 2.182955 | 1.353078 | -1.217154 |
| H | 2.295034 | 0.678028 | 2.127188 |
| H | 2.642869 | 3.122901 | 2.200345 |
| H | 2.713358 | 4.442488 | 0.099579 |
| H | 2.430301 | 3.289941 | -2.080352 |
| H | 2.082239 | 0.845171 | -2.162975 |
| C | -1.272499 | -0.646776 | 0.097827 |
| C | -1.871280 | -0.456314 | 1.344252 |
| C | -3.177247 | -0.010503 | 1.421271 |
| C | -3.902867 | 0.255765 | 0.254534 |
| C | -3.300875 | 0.069901 | -0.990958 |
| C | -1.985901 | -0.378973 | -1.062758 |
| H | -1.322876 | -0.658803 | 2.253383 |
| H | -3.659542 | 0.139066 | 2.377003 |
| H | -1.529799 | -0.519925 | -2.032593 |
| H | -3.838501 | 0.268670 | -1.905116 |
| O | -5.174095 | 0.686548 | 0.436084 |
| C | -5.970460 | 0.975584 | -0.704717 |
| H | -6.107183 | 0.089595 | -1.328993 |
| H | -5.532789 | 1.778608 | -1.302204 |
| H | -6.934144 | 1.297168 | -0.320908 |
| Cl | 3.688633 | -1.247856 | -0.176211 |

| 28 | isomerization TS | | |
|---|---|---|---|
| I | 1.064142 | -0.940980 | -0.007526 |
| C | 1.743635 | 1.141901 | -0.024787 |
| C | 2.018364 | 1.771800 | 1.180110 |
| C | 2.491899 | 3.080246 | 1.159424 |
| C | 2.694614 | 3.731214 | -0.052402 |
| C | 2.428303 | 3.078109 | -1.250556 |
| C | 1.953094 | 1.770018 | -1.243644 |
| H | 1.872256 | 1.260513 | 2.121304 |
| H | 2.707158 | 3.585077 | 2.091510 |
| H | 3.067475 | 4.746203 | -0.063083 |
| H | 2.594220 | 3.581025 | -2.193712 |
| H | 1.756020 | 1.257281 | -2.174701 |
| C | -1.038896 | -0.390628 | 0.111261 |
| C | -1.778985 | -0.275007 | -1.053008 |
| C | -3.137221 | 0.023301 | -0.983646 |
| C | -3.746301 | 0.192537 | 0.261136 |
| C | -2.988556 | 0.057027 | 1.430535 |
| C | -1.640034 | -0.240117 | 1.357666 |
| H | -1.316665 | -0.415665 | -2.020192 |
| H | -3.702444 | 0.113489 | -1.898350 |
| H | -3.480911 | 0.182201 | 2.384626 |
| H | -1.067696 | -0.354548 | 2.267679 |
| O | -5.056355 | 0.480783 | 0.440594 |
| C | -5.894369 | 0.613696 | -0.699813 |
| H | -5.929061 | -0.312626 | -1.277601 |
| H | -5.564470 | 1.433222 | -1.342422 |
| H | -6.885617 | 0.835035 | -0.315529 |
| Cl | 2.433399 | -3.365302 | -0.109356 |

### 2.3.12 $X =$ Br

| 28 | equilibrium structure | | |
|---|---|---|---|
| I | 0.678301 | -0.833517 | 0.021625 |
| C | 1.135095 | 1.290701 | -0.061928 |
| C | 0.208574 | 2.147557 | -0.629294 |
| C | 0.513341 | 3.505412 | -0.673518 |
| C | 1.714218 | 3.973334 | -0.154225 |
| C | 2.621822 | 3.083847 | 0.407532 |
| C | 2.341379 | 1.720567 | 0.455404 |
| H | -0.728568 | 1.787649 | -1.024812 |
| H | -0.194260 | 4.190562 | -1.120286 |
| H | 1.943671 | 5.029446 | -0.191401 |
| H | 3.559846 | 3.440699 | 0.810301 |
| H | 3.057415 | 1.014728 | 0.851713 |
| C | -1.474918 | -0.438306 | 0.131072 |
| C | -2.271164 | -0.739491 | -0.963239 |
| C | -3.656654 | -0.601949 | -0.889167 |
| C | -4.242848 | -0.160201 | 0.296694 |
| C | -3.435012 | 0.136019 | 1.401874 |
| C | -2.062640 | -0.008679 | 1.321081 |
| H | -1.828410 | -1.084326 | -1.888683 |
| H | -4.257239 | -0.841363 | -1.753183 |
| H | -3.909103 | 0.471104 | 2.313901 |
| H | -1.454156 | 0.217389 | 2.186561 |
| O | -5.574526 | 0.010509 | 0.479484 |
| C | -6.458125 | -0.286789 | -0.592619 |
| H | -6.387325 | -1.336414 | -0.887063 |
| H | -6.261410 | 0.348726 | -1.459297 |
| H | -7.457667 | -0.084873 | -0.218955 |
| Br | 3.513287 | -1.451232 | -0.082822 |

| 28 | reductive elimination TS | | |
|---|---|---|---|
| I | 0.433715 | -1.135518 | 0.007191 |
| C | 1.752049 | 0.946637 | 0.003914 |
| C | 1.841268 | 1.555493 | 1.236447 |
| C | 1.959667 | 2.944761 | 1.246306 |
| C | 1.969065 | 3.669264 | 0.060132 |
| C | 1.861428 | 3.002390 | -1.154682 |
| C | 1.741256 | 1.614149 | -1.201280 |
| H | 1.855363 | 0.988032 | 2.153289 |
| H | 2.049632 | 3.450337 | 2.198768 |
| H | 2.061071 | 4.745884 | 0.082234 |
| H | 1.874986 | 3.552938 | -2.086154 |
| H | 1.680340 | 1.090764 | -2.142110 |
| C | -1.639759 | -0.618150 | 0.107204 |
| C | -2.265208 | -0.478969 | 1.347219 |
| C | -3.602783 | -0.136749 | 1.409760 |
| C | -4.333307 | 0.076963 | 0.235133 |
| C | -3.704302 | -0.056669 | -1.003794 |
| C | -2.357624 | -0.401801 | -1.061294 |
| H | -1.713446 | -0.641379 | 2.262361 |
| H | -4.106578 | -0.029007 | 2.360033 |
| H | -4.245106 | 0.103000 | -1.923740 |
| H | -1.880612 | -0.503572 | -2.025998 |
| O | -5.635974 | 0.406803 | 0.403136 |
| C | -6.439747 | 0.638344 | -0.745617 |
| H | -6.499964 | -0.252411 | -1.375203 |
| H | -6.059847 | 1.476282 | -1.334610 |
| H | -7.429846 | 0.881546 | -0.371516 |
| Br | 3.537797 | -0.984810 | -0.122292 |

| 28 | isomerization TS | | |
|---|---|---|---|
| I | 0.936154 | -0.347668 | 0.014697 |
| C | 1.046819 | 1.841799 | -0.018421 |
| C | 1.120651 | 2.531839 | 1.182168 |
| C | 1.229598 | 3.919000 | 1.150169 |
| C | 1.274849 | 4.588730 | -0.067532 |
| C | 1.214233 | 3.877345 | -1.260501 |
| C | 1.103710 | 2.489915 | -1.243090 |
| H | 1.096380 | 2.008833 | 2.127910 |
| H | 1.284821 | 4.471661 | 2.078306 |
| H | 1.364548 | 5.666181 | -0.086722 |
| H | 1.258064 | 4.397498 | -2.207850 |
| H | 1.066554 | 1.934616 | -2.169848 |
| C | -1.238686 | -0.388097 | 0.119711 |
| C | -1.975166 | -0.453054 | -1.050470 |
| C | -3.364149 | -0.524266 | -0.989704 |
| C | -4.003190 | -0.540668 | 0.251668 |
| C | -3.243230 | -0.490392 | 1.426414 |
| C | -1.863741 | -0.420257 | 1.362840 |
| H | -1.486567 | -0.450495 | -2.014906 |
| H | -3.928493 | -0.571243 | -1.908135 |
| H | -3.756635 | -0.514127 | 2.377306 |
| H | -1.286543 | -0.393680 | 2.276523 |
| O | -5.343559 | -0.609372 | 0.422231 |
| C | -6.180893 | -0.680878 | -0.724573 |
| H | -7.197733 | -0.730620 | -0.346804 |
| H | -6.071093 | 0.206247 | -1.352434 |
| H | -5.969978 | -1.575251 | -1.314966 |
| Br | 3.029547 | -2.447267 | -0.069921 |