## Supplementary Information

# Selective aromatic halogenation by a manganese compound I model: A mimic of chloroperoxidase

Lina Zhang,[a#] Steiny Russelisaac Premakumari,[b#] Maggie Ng,[b] Jisheng Zhang,[c] Yong-Min Lee,*[a] Shunichi Fukuzumi,*[a] Kyung-Bin Cho,*[b] and Wonwoo Nam*[a,d,e]

[a.] *Department of Chemistry and Nano Science, Ewha Womans University, Seoul 03760, Korea. Email: yomlee@ewha.ac.kr, fukuzumi@chem.eng.osaka-u.ac.jp, wwnam@ewha.ac.kr*
[b.] *Department of Chemistry and Research Institute for Materials and Energy Sciences, Jeonbuk National University, Jeonju 54896, Korea. Email: workforkyung@jbnu.ac.kr*
[c.] *Institute of Green Chemistry and Chemical Technology, School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, P. R. China.*
[d.] *Graduate Program in Innovative Biomaterials Convergence, Ewha Womans University, Seoul 03760, Korea.*
[e.] *College of Chemistry and Chemical Engineering, Henan Key Laboratory of Function-Oriented Porous Materials, Luoyang Normal University, Luoyang 471934, P. R. China*
[#] These authors contributed equally to this work.

**Table of Contents**

**Electrophilic ($C_1$-HAT) and nucleophilic ($C_1$- and $C_2$-hydroxylation) reaction of $[Mn^{IV}OH(Por^{+\bullet})Cl]^+$ or $[Mn^{IV}OH(Por^{+\bullet})OTf]^+$, naphthalene and chloride**

**Table S1** Relative energies (in kcal $mol^{-1}$) of the electrophilic ($C_1$-HAT) and nucleophilic ($C_1$ and $C_2$ hydroxylation) reaction of $[Mn^{IV}(OH)(Por^{+\bullet})Cl]^+$, naphthalene and chlorine.

| $[Mn^{IV}(OH)(Por^{+\bullet})Cl]^+$ | ΔDef2-SVP | ΔΔDef2-TZVPP | $\Delta E^a$ | $\Delta Z_0$ | $\Delta E_{thermal}{}^b$ | $-T\Delta S^b$ | ΔDisp | ΔCplx$^c$ | $\Delta G^d$ |
|---|---|---|---|---|---|---|---|---|---|
| **Separated (3 components)** | 30.83 | -21.02 | **9.81** | -2.30 | -1.01 | -14.99 | +10.61 | +3.78 | **5.89** |
| **Electrophilic ($C_1$-HAT)** | | | | | | | | | |
| **$^5$[Reactant Complex]** | 0.04 | -0.08 | **-0.05** | -0.03 | +0.00 | -0.08 | -0.11 | +0.00 | **-0.27** |
| **$^5$[Transition State]** | 9.09 | +1.38 | **10.46** | -2.66 | -0.53 | +2.04 | +0.65 | +0.00 | **9.97** |
| **$^5$[Product Complex]** | -48.84 | +0.61 | **-48.24** | +0.04 | +0.42 | -1.13 | -3.89 | +0.00 | **-52.80** |
| **Nucleophilic ($C_1$-hydroxylation)** | | | | | | | | | |
| **$^5$[Reactant Complex]** | 1.21 | -1.05 | **0.16** | -0.14 | +0.06 | -0.61 | +1.50 | +0.00 | **1.58** |
| **$^5$[Transition State]** | 10.40 | -0.49 | **9.91** | -0.97 | -0.37 | +0.72 | -0.13 | +0.00 | **8.43** |
| **$^5$[Product Complex]** | -34.45 | +4.01 | **-30.44** | +2.19 | -0.64 | +1.89 | -6.51 | +0.00 | **-35.39** |
| **Nucleophilic ($C_2$-hydroxylation)** | | | | | | | | | |
| **$^5$[Reactant Complex]** | **0.00** | **+0.00** | **0.00** | **+0.00** | **+0.00** | **+0.00** | **+0.00** | **+0.00** | **0.00** |
| **$^5$[Transition State]** | 7.67 | +0.01 | **7.68** | -0.87 | -0.49 | +0.00 | -1.17 | +0.00 | **5.15** |
| **$^5$[Product Complex]** | -34.11 | +3.94 | **-30.18** | +2.14 | -0.64 | +0.00 | -6.20 | +0.00 | **-34.88** |

[a] Def2-TZVPP electronic energy = sum of the two previous columns. [b] $T$ = 298.15 K. [c] Complexation energy due to change of standard states of the solvent. [d] Gibb's free energy = sum of the previous six columns.

**Table S2** Mulliken spin density distribution of the electrophilic ($C_1$-HAT) and nucleophilic ($C_1$ and $C_2$ hydroxylation) reaction of $[Mn^{IV}(OH)(Por^{+\bullet})Cl]^+$, naphthalene and chlorine.

| $[Mn^{IV}(OH)(Por^{+\bullet})Cl]^+$ | Mn | OH | $Cl_{axial}$ | Porphine | Naphthalene | Cl |
|---|---|---|---|---|---|---|
| **Separated (3 components)** | 3.06 | 0.10 | 0.04 | 0.80 | 0.00 | 0.00 |
| **Electrophilic ($C_1$-HAT)** | | | | | | |
| **$^5$[Reactant Complex]** | 3.15 | 0.04 | 0.01 | -0.20 | 0.56 | 0.44 |
| **$^5$[Transition State]** | 3.59 | -0.08 | -0.04 | -0.20 | 0.62 | 0.04 |
| **$^5$[Product Complex]** | 3.97 | 0.02 | 0.15 | -0.14 | 0.00 | 0.00 |
| **Nucleophilic ($C_1$-hydroxylation)** | | | | | | |
| **$^5$[Reactant Complex]** | 3.17 | 0.06 | -0.01 | -0.22 | 1.01 | -0.01 |
| **$^5$[Transition State]** | 3.50 | -0.10 | 0.04 | -0.22 | 0.77 | 0.01 |
| **$^5$[Product Complex]** | 3.96 | 0.01 | 0.16 | -0.13 | 0.00 | -0.00 |
| **Nucleophilic ($C_2$-hydroxylation)** | | | | | | |
| **$^5$[Reactant Complex]** | 3.17 | 0.05 | -0.01 | -0.21 | 0.48 | 0.52 |
| **$^5$[Transition State]** | 3.54 | -0.12 | 0.05 | -0.22 | 0.64 | 0.12 |
| **$^5$[Product Complex]** | 3.96 | 0.01 | 0.16 | -0.13 | 0.00 | 0.00 |

**Table S3** Selected DFT optimized geometries (in Å) of the electrophilic ($C_1$-HAT) and nucleophilic ($C_1$ and $C_2$ hydroxylation) reaction of $[Mn^{IV}(OH)(Por^{+\bullet})Cl]^+$, naphthalene and chlorine.

| $[Mn^{IV}(OH)(Por^{+\bullet})Cl]^+$ | Mn-O | Mn-Cl | HO-$H_{Naphthalene}$ | Mn-$N_{eq}$ (average) | C-Cl |
|---|---|---|---|---|---|
| **Separated (3 components)** | 1.80 | 2.29 | ∞ | 2.04 | ∞ |
| **Electrophilic ($C_1$-HAT)** | | | | | |
| **$^5$[Reactant Complex]** | 1.83 | 2.30 | 2.32 | 2.03 | 2.58 |
| **$^5$[Transition State]** | 1.95 | 2.38 | 1.57 | 2.04 | 1.86 |
| **$^5$[Product Complex]** | 2.45 | 2.42 | 0.97 | 2.05 | 1.76 |
| **Nucleophilic ($C_1$-hydroxylation)** | | | | | |
| **$^5$[Reactant Complex]** | 1.83 | 2.31 | 3.34 | 2.04 | 2.15 |
| **$^5$[Transition State]** | 1.91 | 2.36 | 2.80 | 2.04 | 2.15 |
| **$^5$[Product Complex]** | 2.53 | 2.41 | 2.42 | 2.04 | 2.15 |
| **Nucleophilic ($C_2$-hydroxylation)** | | | | | |
| **$^5$[Reactant Complex]** | 1.83 | 2.30 | 4.50 | 2.03 | 2.59 |
| **$^5$[Transition State]** | 1.92 | 2.37 | 2.35 | 2.04 | 1.95 |
| **$^5$[Product Complex]** | 2.53 | 2.41 | 1.43 | 2.04 | 1.85 |

**Table S4** Relative energies (in kcal $mol^{-1}$) of the electrophilic ($C_1$-HAT) and nucleophilic ($C_1$ and $C_2$ hydroxylation) reaction of $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$, naphthalene and chlorine.

| $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$ | ΔDef2-SVP | ΔΔDef2-TZVPP | $\Delta E^a$ | $\Delta Z_0$ | $\Delta E_{thermal}{}^b$ | $-T\Delta S^b$ | ΔDisp | ΔCplx$^c$ | $\Delta G^d$ |
|---|---|---|---|---|---|---|---|---|---|
| **Separated (3 components)** | 33.65 | -20.64 | **13.01** | -1.14 | -0.76 | -16.24 | +10.38 | +3.79 | **9.04** |
| **$^5$[3 + Naphthalene] + $Cl^-$-(1)** | 31.58 | -19.08 | **12.49** | -0.91 | -0.44 | -9.28 | +2.65 | +1.89 | **6.40** |
| **$^5$[3 + Naphthalene] + $Cl^-$-(2)** | 30.87 | -17.52 | **13.35** | -0.94 | +0.11 | -6.89 | +0.85 | +1.89 | **8.38** |
| **Electrophilic ($C_1$-HAT)** | | | | | | | | | |
| **$^5$[Reactant Complex]** | **0.00** | **+0.00** | **0.00** | **+0.00** | **+0.00** | **+0.00** | **+0.00** | **+0.00** | **0.00** |
| **$^5$[Transition State]** | 6.26 | +0.81 | **7.06** | -1.92 | -0.36 | +0.69 | +1.11 | +0.00 | **6.58** |
| **$^5$[Product Complex]** | -55.36 | +1.20 | **-54.16** | +0.20 | +0.33 | -2.25 | -1.92 | +0.00 | **-57.80** |
| **$^3$[Reactant Complex]** | -0.06 | +0.14 | **0.08** | -0.09 | +0.04 | -0.28 | -0.93 | +0.00 | **-1.18** |
| **$^3$[Transition State]** | 21.69 | +2.41 | **24.10** | -5.11 | -0.08 | +0.79 | +1.11 | +0.00 | **20.81** |
| **$^3$[Product Complex]** | -42.10 | +6.23 | **-35.87** | +1.67 | -0.51 | +1.70 | +0.14 | +0.00 | **-32.86** |
| **Nucleophilic ($C_1$-hydroxylation)** | | | | | | | | | |
| **$^5$[Reactant Complex]** | 0.80 | -0.57 | **0.23** | -0.13 | +0.06 | -0.58 | +0.34 | +0.00 | **-0.09** |
| **$^5$[Transition State]** | 8.24 | -1.17 | **7.07** | -1.18 | -0.20 | -0.36 | +0.51 | +0.00 | **5.84** |
| **$^5$[Intermediate Complex]** | -39.23 | +4.45 | **-34.78** | +2.18 | -0.57 | +1.41 | -6.83 | +0.00 | **-38.60** |
| **Nucleophilic ($C_2$-hydroxylation)** | | | | | | | | | |
| **$^5$[Reactant Complex]** | -0.06 | +0.15 | **0.09** | -0.07 | +0.04 | -0.17 | -0.45 | +0.00 | **-0.56** |
| **$^5$[Transition State]** | 5.08 | -0.70 | **4.38** | -1.13 | -0.34 | +0.55 | -0.60 | +0.00 | **2.85** |
| **$^5$[Intermediate Complex]** | -39.03 | +4.41 | **-34.62** | 2.16 | -0.61 | +0.96 | -5.75 | +0.00 | **-37.85** |

[a] Def2-TZVPP electronic energy = sum of the two previous columns. [b] $T$ = 298.15 K. [c] Complexation energy due to change of standard states of the solvent. [d] Gibb's free energy = sum of the previous six columns.

**Table S5** Mulliken spin density distribution of the electrophilic ($C_1$-HAT) and nucleophilic ($C_1$ and $C_2$ hydroxylation) reaction of $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$, naphthalene and chlorine.

| $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$ | Mn | OH | $OTf_{axial}$ | Porphine | Naphthalene | Cl |
|---|---|---|---|---|---|---|
| **Separated (3 components)** | 3.09 | 0.06 | 0.02 | 0.83 | 0.00 | 0.00 |
| **$^5$[3 + Naphthalene] + $Cl^-$-(1)** | 3.05 | 0.09 | 0.02 | 0.82 | 0.02 | 0.00 |
| **$^5$[3 + Naphthalene] + $Cl^-$-(2)** | 3.09 | 0.06 | 0.02 | 0.58 | 0.25 | 0.00 |
| **Electrophilic ($C_1$-HAT)** | | | | | | |
| **$^5$[Reactant Complex]** | 3.11 | 0.04 | 0.01 | -0.16 | 0.56 | 0.44 |
| **$^5$[Transition State]** | 3.55 | -0.09 | 0.02 | -0.22 | 0.68 | 0.06 |
| **$^5$[Product Complex]** | 4.06 | 0.03 | 0.05 | -0.13 | 0.00 | 0.00 |
| **$^3$[Reactant Complex]** | 3.10 | 0.04 | 0.01 | -0.16 | -0.56 | -0.44 |
| **$^3$[Transition State]** | 3.90 | -0.23 | 0.04 | -0.29 | -1.24 | -0.17 |
| **$^3$[Product Complex]** | 2.05 | -0.01 | 0.02 | -0.06 | 0.00 | 0.00 |
| **Nucleophilic ($C_1$-hydroxylation)** | | | | | | |
| **$^5$[Reactant Complex]** | 3.10 | 0.04 | 0.01 | -0.16 | 1.00 | 0.44 |
| **$^5$[Transition State]** | 3.40 | -0.08 | 0.02 | -0.20 | 0.86 | 0.21 |
| **$^5$[Intermediate Complex]** | 4.06 | 0.01 | 0.05 | -0.13 | 0.01 | 0.00 |
| **Nucleophilic ($C_2$-hydroxylation)** | | | | | | |
| **$^5$[Reactant Complex]** | 3.11 | 0.04 | 0.01 | -0.16 | 0.47 | 0.52 |
| **$^5$[Transition State]** | 3.47 | -0.09 | 0.02 | -0.22 | 0.69 | 0.13 |
| **$^5$[Intermediate Complex]** | 4.05 | 0.02 | 0.06 | -0.14 | 0.00 | 0.00 |

**Table S6** Selected DFT optimized geometries (in Å) of the electrophilic ($C_1$-HAT) and nucleophilic ($C_1$ and $C_2$ hydroxylation) reaction of $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$, naphthalene and chlorine.

| $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$ | Mn-O | Mn-OTf | HO-(H,[a] C[b])$_{Naphthalene}$ | Mn-$N_{eq}$ (average) | C-Cl |
|---|---|---|---|---|---|
| **Separated (3 components)** | 1.79 | 1.97 | ∞ | 2.03 | ∞ |
| **$^5$[3 + Naphthalene] + $Cl^-$-(1)** | 1.79 | 2.01 | 3.72 | 2.02 | ∞ |
| **$^5$[3 + Naphthalene] + $Cl^-$-(2)** | 1.79 | 1.97 | 3.86 | 2.03 | ∞ |
| **Electrophilic ($C_1$-HAT)** | | | | | |
| **$^5$[Reactant Complex]** | 1.79 | 2.00 | 2.39 | 2.02 | 2.58 |
| **$^5$[Transition State]** | 1.89 | 2.18 | 1.75 | 2.04 | 1.88 |
| **$^5$[Product Complex]** | 2.32 | 2.11 | 0.97 | 2.04 | 1.77 |
| **$^3$[Reactant Complex]** | 1.79 | 1.80 | 2.38 | 2.02 | 2.58 |
| **$^3$[Transition State]** | 2.07 | 2.07 | 1.24 | 2.04 | 1.87 |
| **$^3$[Product Complex]** | 2.03 | 2.04 | 0.98 | 2.03 | 1.77 |
| **Nucleophilic ($C_1$-hydroxylation)** | | | | | |
| **$^5$[Reactant Complex]** | 1.79 | 2.00 | 3.28 | 2.02 | 2.57 |
| **$^5$[Transition State]** | 1.85 | 2.07 | 2.00 | 2.03 | 2.79 |
| **$^5$[Intermediate Complex]** | 2.39 | 2.16 | 1.44 | 2.03 | 2.76 |
| **Nucleophilic ($C_2$-hydroxylation)** | | | | | |
| **$^5$[Reactant Complex]** | 1.80 | 2.00 | 3.42 | 2.02 | 3.42 |
| **$^5$[Transition State]** | 1.85 | 2.08 | 1.97 | 2.04 | 1.97 |
| **$^5$[Intermediate Complex]** | 2.40 | 2.16 | 1.40 | 2.03 | 1.40 |

[a] OH-$H_{Naphthalene}$ distance for the electrophilic reaction. [b] OH-$C_{Naphthalene}$ distance for the nucleophilic reaction.

## Electrophilic ($C_1$-HAT) and nucleophilic ($C_1$- and $C_2$-hydroxylation) reaction of $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$ and naphthalene in absence of chloride

**Table S7** Relative Energies (in kcal $mol^{-1}$) of the electrophilic ($C_1$-HAT) and nucleophilic ($C_1$ and $C_2$ hydroxylation) reaction of $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$ and naphthalene.

| $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$ | ΔDef2-SVP | ΔΔDef2-TZVPP | $\Delta E^a$ | $\Delta Z_0$ | $\Delta E_{thermal}{}^b$ | $-T\Delta S^b$ | ΔDisp | ΔCplx$^c$ | $\Delta G^d$ |
|---|---|---|---|---|---|---|---|---|---|
| **Separated RC (2 components)** | 2.60 | -1.87 | **0.73** | -0.26 | -0.88 | -8.89 | +12.21 | +1.89 | **4.80** |
| **Electrophilic ($C_1$-HAT)** | | | | | | | | | |
| **$^5$[Reactant Complex]-1** | +0.53 | -0.32 | **0.20** | -0.02 | +0.03 | -1.93 | +2.20 | +1.89 | **2.37** |
| **$^5$[Reactant Complex]-2** | -0.18 | +1.24 | **1.07** | -0.05 | -0.01 | +0.46 | +1.22 | +0.00 | **2.68** |
| **$^5$[Transition State]** | +32.16 | +4.81 | **36.97** | -3.43 | -0.39 | +1.85 | +0.29 | +0.00 | **35.30** |
| **$^5$[Product Complex]** | +29.20 | +4.66 | **33.86** | -0.41 | +0.10 | -0.24 | +2.20 | +0.00 | **35.50** |
| **Nucleophilic ($C_1$-hydroxylation) α-electron transfer** | | | | | | | | | |
| **$^5$[Reactant Complex]** | 0.51 | -0.35 | **0.17** | +0.05 | +0.01 | -1.65 | +2.97 | +0.00 | **1.55** |
| **$^5$[Transition State]** | 10.22 | +0.94 | **11.16** | -1.72 | +0.08 | +0.37 | -1.83 | +0.00 | **8.05** |
| **$^5$[Intermediate Complex]** | -16.76 | +4.03 | **-12.73** | +1.67 | -0.15 | +0.46 | -2.02 | +0.00 | **-12.78** |
| **Nucleophilic ($C_1$-hydroxylation) β-electron transfer** | | | | | | | | | |
| **$^5$[Reactant Complex]** | +0.53 | -0.32 | **0.20** | +0.01 | +6.46 | -1.93 | +3.01 | +0.00 | **7.75** |
| **$^5$[Transition State]** | +11.18 | +3.42 | **14.59** | +0.16 | -7.94 | +2.32 | -0.59 | +0.00 | **8.55** |
| **$^5$[Intermediate Complex]** | -16.75 | +4.05 | **-12.69** | +1.65 | -1.62 | -0.01 | -2.10 | +0.00 | **-14.77** |
| **Nucleophilic ($C_2$-hydroxylation) α-electron transfer** | | | | | | | | | |
| **$^5$[Reactant Complex]** | **0.00** | **+0.00** | **0.00** | **+0.00** | **+0.00** | **+0.00** | **+0.00** | **+0.00** | **0.00** |
| **$^5$[Transition State]** | 12.40 | +0.71 | **13.11** | -1.80 | +0.08 | -0.02 | -0.61 | +0.00 | **10.75** |
| **$^5$[Intermediate Complex]** | -11.77 | +3.19 | **-8.58** | +1.20 | -0.14 | +0.85 | -0.75 | +0.00 | **-7.41** |
| **Nucleophilic ($C_2$-hydroxylation) β-electron transfer** | | | | | | | | | |
| **$^5$[Reactant Complex]** | 1.14 | -0.36 | **0.78** | -0.01 | +0.12 | -2.52 | +6.84 | +0.00 | **5.21** |
| **$^5$[Transition State]** | 14.20 | +3.21 | **17.41** | +0.26 | -0.54 | +2.36 | +1.00 | +0.00 | **20.49** |
| **$^5$[Intermediate Complex]** | -12.10 | +3.47 | **-8.62** | +1.26 | -0.17 | +1.12 | -0.61 | +0.00 | **-7.01** |

[a] Def2-TZVPP electronic energy = sum of the two previous columns. [b] $T$ = 298.15 K. [c] Complexation energy due to change of standard states of the solvent. [d] Gibb's free energy = sum of the previous six columns.

**Table S8** Mulliken spin density distribution of the electrophilic ($C_1$-HAT) and nucleophilic ($C_1$ and $C_2$ hydroxylation) reaction of $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$ and naphthalene.

| $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$ | Mn | OH | $OTf_{axial}$ | Porphine | Naphthalene |
|---|---|---|---|---|---|
| **Separated RC (2 components)** | 3.09 | 0.06 | 0.02 | 0.83 | 0.00 |
| **Electrophilic ($C_1$-HAT)** | | | | | |
| **$^5$[Reactant Complex]-1** | 3.05 | 0.09 | 0.02 | 0.82 | 0.02 |
| **$^5$[Reactant Complex]-2** | 3.09 | 0.07 | 0.03 | 0.55 | 0.27 |
| **$^5$[Transition State]** | 3.04 | 0.06 | 0.02 | 0.00 | 0.88 |
| **$^5$[Product Complex]** | 3.02 | 0.02 | 0.02 | -0.01 | 0.95 |
| **Nucleophilic ($C_1$) α-transfer** | | | | | |
| **$^5$[Reactant Complex]** | 3.05 | 0.10 | 0.03 | 0.79 | 0.02 |
| **$^5$[Transition State]** | 3.87 | -0.23 | 0.06 | 0.82 | -0.51 |
| **$^5$[Intermediate Complex]** | 4.05 | 0.01 | 0.07 | -0.13 | 0.00 |
| **Nucleophilic ($C_1$) β-transfer** | | | | | |
| **$^5$[Reactant Complex]** | 3.05 | 0.09 | 0.02 | 0.82 | 0.02 |
| **$^5$[Transition State]** | 3.31 | 0.00 | 0.03 | -0.11 | 0.77 |
| **$^5$[Intermediate Complex]** | 4.06 | 0.00 | 0.06 | -0.13 | 0.01 |
| **Nucleophilic ($C_2$) α-transfer** | | | | | |
| **$^5$[Reactant Complex]** | 3.06 | 0.08 | 0.02 | 0.74 | 0.09 |
| **$^5$[Transition State]** | 3.88 | -0.23 | 0.05 | 0.83 | -0.54 |
| **$^5$[Intermediate Complex]** | 4.05 | 0.00 | 0.06 | -0.13 | 0.01 |
| **Nucleophilic ($C_2$) β-transfer** | | | | | |
| **$^5$[Reactant Complex]** | 3.07 | 0.08 | 0.03 | 0.81 | 0.01 |
| **$^5$[Transition State]** | 3.33 | 0.01 | 0.03 | -0.12 | 0.75 |
| **$^5$[Intermediate Complex]** | 4.05 | 0.01 | 0.07 | -0.13 | 0.00 |

**Table S9** Selected DFT optimized geometries (in Å) of the electrophilic ($C_1$-HAT) and nucleophilic ($C_1$ and $C_2$ hydroxylation) reaction of $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$ and naphthalene.

| $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$ | Mn-O | Mn-OTf | HO-$H_{Naphthalene}$ | Mn-$N_{eq}$ (average) |
|---|---|---|---|---|
| **Separated RC (2 components)** | 1.79 | 1.97 | 3.72 | 2.03 |
| **Electrophilic ($C_1$-HAT)** | | | | |
| **$^5$[Reactant Complex]-1** | 1.79 | 2.01 | 3.72 | 2.02 |
| **$^5$[Reactant Complex]-2** | 1.79 | 1.97 | 2.50 | 2.03 |
| **$^5$[Transition State]** | 1.95 | 1.89 | 1.12 | 1.99 |
| **$^5$[Product Complex]** | 2.04 | 1.86 | 1.00 | 1.99 |
| **Nucleophilic ($C_1$) α-transfer** | | | | |
| **$^5$[Reactant Complex]** | 1.77 | 1.98 | 4.11 | 2.03 |
| **$^5$[Transition State]** | 2.03 | 2.15 | 2.11 | 2.04 |
| **$^5$[Intermediate Complex]** | 2.50 | 2.13 | 1.41 | 2.03 |
| **Nucleophilic ($C_1$) β-transfer** | | | | |
| **$^5$[Reactant Complex]** | 1.77 | 1.98 | 4.14 | 2.03 |
| **$^5$[Transition State]** | 1.92 | 1.96 | 1.92 | 2.02 |
| **$^5$[Intermediate Complex]** | 2.5 | 2.13 | 1.41 | 2.03 |
| **Nucleophilic ($C_2$) α-transfer** | | | | |
| **$^5$[Reactant Complex]** | 1.77 | 1.98 | 3.33 | 2.03 |
| **$^5$[Transition State]** | 2.06 | 2.15 | 2.03 | 2.04 |
| **$^5$[Intermediate Complex]** | 2.49 | 2.13 | 1.41 | 2.04 |
| **Nucleophilic ($C_2$) β-transfer** | | | | |
| **$^5$[Reactant Complex]** | 1.79 | 1.97 | 2.50 | 2.03 |
| **$^5$[Transition State]** | 1.95 | 1.89 | 1.12 | 2.01 |
| **$^5$[Intermediate Complex]** | 2.04 | 1.86 | 1.00 | 2.03 |

**Electrophilic ($C_1$- and $C_2$-HAT) and nucleophilic ($C_1$- and $C_2$-hydroxylation) reaction of $[Mn^{IV}(OH)(TDCPP^{+\bullet})OTf]^+$, naphthalene and chloride with $[OTf]^-$ hydrogen bonded to $Mn^{IV}(OH)$ (large model).**

**Table S10** Relative Energies (in kcal $mol^{-1}$) of the electrophilic ($C_1$- and $C_2$-HAT) and nucleophilic ($C_1$ and $C_2$ hydroxylation) reaction of $[Mn^{IV}(OH)(TDCPP^{+\bullet})OTf]^+$, naphthalene and chlorine with $[OTf]^-$ hydrogen bonded to $Mn^{IV}(OH)$.

| $[Mn^{IV}(OH)(TDCPP^{+\bullet})OTf]^+$ | ΔDef2-SVP | ΔΔDef2-TZVPP | $\Delta E^a$ | $\Delta Z_0$ | $\Delta E_{thermal}{}^b$ | $-T\Delta S^b$ | ΔDisp | ΔCplx$^c$ | $\Delta G^d$ |
|---|---|---|---|---|---|---|---|---|---|
| **Separated (4 components)** | 47.46 | -30.79 | **16.67** | -2.20 | -0.95 | -30.61 | +22.45 | +5.68 | **11.04** |
| **{$^5$3 + $[OTf]^-$} + Naphthalene + $Cl^-$** | 27.38 | -20.83 | **6.55** | -1.58 | -0.70 | -18.36 | +12.93 | +3.79 | **2.62** |
| **{$^5$3 + $[OTf]^-$ + Naphthalene } + $Cl^-$** | 23.20 | -15.49 | **7.71** | -1.30 | +0.25 | -9.33 | +4.75 | +1.89 | **3.97** |
| **Electrophilic ($C_1$-HAT)** | | | | | | | | | |
| **$^5$[Reactant Complex]** | **0.00** | **+0.00** | **0.00** | **+0.00** | **+0.00** | **+0.00** | **+0.00** | **+0.00** | **0.00** |
| **$^5$[Transition State]** | 8.05 | +1.16 | **9.21** | -1.79 | -0.35 | +1.66 | -2.71 | +0.00 | **6.01** |
| **$^5$[Product Complex]** | -57.63 | +1.17 | **-56.46** | +0.27 | +0.39 | -2.09 | -0.68 | +0.00 | **-58.57** |
| **Electrophilic ($C_2$-HAT)** | | | | | | | | | |
| **$^5$[Reactant Complex]** | 0.35 | +0.99 | **1.33** | -0.07 | -0.04 | +0.42 | -1.40 | +0.00 | **0.25** |
| **$^5$[Transition State]** | 27.77 | +1.29 | **29.06** | -5.56 | +0.35 | -1.20 | -5.74 | +0.00 | **16.92** |
| **$^5$[Product Complex]** | -58.57 | +1.11 | **-57.46** | +0.31 | +0.32 | -1.40 | -1.21 | +0.00 | **-59.44** |
| **Nucleophilic ($C_1$-hydroxylation)** | | | | | | | | | |
| **$^5$[Reactant Complex]** | 1.79 | +0.72 | **2.51** | -0.04 | -0.04 | +0.45 | -0.74 | +0.00 | **2.14** |
| **$^5$[Transition State]** | 11.71 | +1.11 | **12.83** | -0.91 | -0.22 | +2.08 | -7.17 | +0.00 | **6.62** |
| **$^5$[Intermediate Complex]** | -38.49 | +5.84 | **-32.65** | +2.12 | -0.57 | +2.59 | -13.07 | +0.00 | **-41.58** |
| **Nucleophilic ($C_2$-hydroxylation)** | | | | | | | | | |
| **$^5$[Reactant Complex]** | 3.43 | -1.38 | **2.05** | -0.20 | +0.04 | +0.29 | -1.50 | +0.00 | **0.67** |
| **$^5$[Transition State]** | 7.74 | +2.07 | **9.81** | -0.94 | -0.46 | +3.69 | -5.66 | +0.00 | **6.43** |
| **$^5$[Intermediate Complex]** | -38.05 | +6.95 | **-31.10** | +2.20 | -0.70 | +3.26 | -12.80 | +0.00 | **-39.15** |

[a] Def2-TZVPP electronic energy = sum of the two previous columns. [b] $T$ = 298.15 K. [c] Complexation energy due to change of standard states of the solvent. [d] Gibb's free energy = sum of the previous six columns.

**Table S11** Mulliken spin density distribution of the electrophilic ($C_1$- and $C_2$-HAT) and nucleophilic ($C_1$ and $C_2$ hydroxylation) reaction of $[Mn^{IV}(OH)(TDCPP^{+\bullet})OTf]^+$, naphthalene and chlorine with $[OTf]^-$ hydrogen bonded to $Mn^{IV}(OH)$.

| $[Mn^{IV}(OH)(TDCPP^{+\bullet})OTf]^+$ | Mn | OH | $OTf_{axial}$ | $OTf_{H\text{-}bond}$ | TDCPP | Naphthalene | Cl |
|---|---|---|---|---|---|---|---|
| **Separated (4 components)** | 2.97 | 0.15 | 0.02 | 0.00 | 0.84 | 0.00 | 0.00 |
| **$\{^5$3 + $[OTf]^-\}$ + Naphthalene + $Cl^-$** | 2.97 | 0.15 | 0.02 | 0.01 | 0.85 | 0.00 | 0.00 |
| **$\{^5$3 + $[OTf]^-$ + Naphthalene $\}$ + $Cl^-$** | 3.05 | 0.07 | 0.03 | 0.01 | 0.85 | 0.00 | 0.00 |
| **Electrophilic ($C_1$-HAT)** | | | | | | | |
| **$^5$[Reactant Complex]** | 3.04 | 0.11 | 0.01 | 0.00 | -0.16 | 0.48 | 0.52 |
| **$^5$[Transition State]** | 3.60 | -0.08 | 0.02 | 0.01 | -0.21 | 0.62 | 0.05 |
| **$^5$[Product Complex]** | 4.04 | 0.04 | 0.05 | 0.00 | -0.13 | 0.00 | 0.00 |
| **Electrophilic ($C_2$-HAT)** | | | | | | | |
| **$^5$[Reactant Complex]** | 3.05 | 0.11 | 0.00 | 0.00 | -0.16 | 0.48 | 0.52 |
| **$^5$[Transition State]** | 3.93 | -0.30 | 0.03 | 0.00 | -0.16 | 0.04 | 0.46 |
| **$^5$[Product Complex]** | 4.04 | 0.03 | 0.04 | 0.00 | -0.11 | 0.00 | 0.00 |
| **Nucleophilic ($C_1$-hydroxylation)** | | | | | | | |
| **$^5$[Reactant Complex]** | 3.04 | 0.09 | 0.00 | 0.01 | -0.14 | 0.57 | 0.43 |
| **$^5$[Transition State]** | 3.60 | -0.17 | 0.02 | 0.00 | -0.21 | 0.41 | 0.34 |
| **$^5$[Intermediate Complex]** | 4.05 | 0.03 | 0.05 | 0.00 | -0.14 | 0.01 | 0.00 |
| **Nucleophilic ($C_2$-hydroxylation)** | | | | | | | |
| **$^5$[Reactant Complex]** | 3.05 | 0.09 | 0.00 | 0.01 | -0.15 | 0.60 | 0.40 |
| **$^5$[Transition State]** | 3.47 | -0.09 | 0.02 | 0.00 | -0.20 | 0.65 | 0.15 |
| **$^5$[Intermediate Complex]** | 4.05 | 0.01 | 0.04 | 0.00 | -0.12 | 0.01 | 0.00 |

**Table S12** Selected DFT optimized geometries (in Å) of the electrophilic ($C_1$- and $C_2$-HAT) and nucleophilic ($C_1$ and $C_2$ hydroxylation) reaction of $[Mn^{IV}(OH)(TDCPP^{+\bullet})OTf]^+$, naphthalene and chlorine with $[OTf]^-$ hydrogen bonded to $Mn^{IV}(OH)$.

| $[Mn^{IV}(OH)(TDCPP^{+\bullet})OTf]^+$ | Mn-O | Mn-$OTf_{axial}$ | HO-$H_{Naphthalene}$ | Mn-$N_{eq}$ (average) | OH-$OTf_{H\text{-}bond}$ | C-Cl |
|---|---|---|---|---|---|---|
| **Separated (4 components)** | 1.74 | 2.01 | ∞ | 2.03 | ∞ | ∞ |
| **$\{^5$3 + $[OTf]^-\}$ + Naphthalene + $Cl^-$** | 1.74 | 2.01 | ∞ | 2.01 | 1.55 | ∞ |
| **$\{^5$3 + $[OTf]^-$ + Naphthalene $\}$ + $Cl^-$** | 1.79 | 1.97 | 2.68 | 2.01 | 1.60 | ∞ |
| **Electrophilic ($C_1$-HAT)** | | | | | | |
| **$^5$[Reactant Complex]** | 1.76 | 2.05 | 2.66 | 2.01 | 1.66 | 2.56 |
| **$^5$[Transition State]** | 1.88 | 2.17 | 1.78 | 2.03 | 1.80 | 1.88 |
| **$^5$[Product Complex]** | 2.25 | 2.21 | 0.97 | 2.03 | 1.66 | 1.76 |
| **Electrophilic ($C_2$-HAT)** | | | | | | |
| **$^5$[Reactant Complex]** | 1.75 | 2.06 | 2.51 | 2.01 | 1.66 | 2.95 |
| **$^5$[Transition State]** | 2.11 | 2.20 | 1.16 | 2.02 | 1.68 | 2.95 |
| **$^5$[Product Complex]** | 2.25 | 2.22 | 0.97 | 2.03 | 1.69 | 1.76 |
| **Nucleophilic ($C_1$-hydroxylation)** | | | | | | |
| **$^5$[Reactant Complex]** | 1.75 | 2.06 | 3.46 | 2.02 | 1.66 | 2.57 |
| **$^5$[Transition State]** | 1.88 | 2.16 | 2.39 | 2.03 | 1.79 | 2.84 |
| **$^5$[Intermediate Complex]** | 2.35 | 2.18 | 1.43 | 2.04 | 1.67 | 2.77 |
| **Nucleophilic ($C_2$-hydroxylation)** | | | | | | |
| **$^5$[Reactant Complex]** | 1.75 | 2.06 | 3.42 | 2.02 | 1.67 | 2.56 |
| **$^5$[Transition State]** | 1.84 | 2.16 | 2.60 | 2.03 | 1.80 | 1.99 |
| **$^5$[Intermediate Complex]** | 2.37 | 2.21 | 1.43 | 2.03 | 1.60 | 1.86 |

## Electrophilic ($C_1$-HAT) reaction of $Mn^{IV}$-oxo species [$Mn^{IV}$(O)($Por^{+\bullet}$)OTf], naphthalene and chloride

**Table S13** Relative energies (in kcal $mol^{-1}$) of the electrophilic ($C_1$-HAT) reaction of [$Mn^{IV}$(O)($Por^{+\bullet}$)OTf], naphthalene and chlorine.

| [$Mn^{IV}$(O)($Por^{+\bullet}$)OTf] | ΔDef2-SVP | ΔΔDef2-TZVPP | $\Delta E^a$ | $\Delta ZPE$ | $\Delta E_{thermal}{}^b$ | $-T\Delta S^b$ | ΔDisp | ΔCplx[c] | $\Delta G^d$ |
|---|---|---|---|---|---|---|---|---|---|
| **$^5$[3 + Naphthalene ] + $Cl^-$** | 16.77 | -18.60 | **-1.83** | -2.14 | -2.01 | +4.94 | +14.28 | +1.89 | **15.14** |
| **$^5$[Reactant Complex]** | **0.00** | **+0.00** | **0.00** | **+0.00** | **+0.00** | **+0.00** | **+0.00** | **+0.00** | **0.00** |
| **$^5$[Transition State]** | 12.83 | +1.11 | **13.94** | -4.27 | -0.52 | +1.39 | -0.59 | +0.00 | **9.96** |
| **$^5$[Product Complex]** | -43.55 | -1.50 | **-45.05** | -0.76 | +0.24 | -1.46 | +1.40 | +0.00 | **-45.63** |

[a] Def2-TZVPP electronic energy = sum of the two previous columns. [b] $T$ = 298.15 K. [c] Complexation energy due to change of standard states of the solvent. [d] Gibb's free energy = sum of the previous six columns.

**Table S14** Mulliken spin density distribution of the electrophilic ($C_1$-HAT) reaction of [$Mn^{IV}$(O)($Por^{+\bullet}$)OTf], naphthalene and chlorine.

| [$Mn^{IV}$(O)($Por^{+\bullet}$)OTf] | Mn | O | $OTf_{axial}$ | Porphine | Naphthalene | Cl |
|---|---|---|---|---|---|---|
| **$^5$[3 + Naphthalene ] + $Cl^-$** | 2.56 | 0.57 | 0.01 | 0.78 | 0.00 | 0.00 |
| **$^5$[Reactant Complex]** | 2.65 | 0.48 | 0.00 | -0.14 | 0.00 | 0.43 |
| **$^5$[Transition State]** | 3.16 | 0.22 | 0.01 | -0.16 | 0.77 | 0.05 |
| **$^5$[Product Complex]** | 3.93 | 0.18 | 0.01 | -0.13 | 0.01 | 0.00 |

**Table S15** Selected DFT optimized geometries (in Å) of the electrophilic ($C_1$-HAT) reaction of [$Mn^{IV}$(O)($Por^{+\bullet}$)OTf], naphthalene and chlorine.

| [$Mn^{IV}$(O)($Por^{+\bullet}$)OTf] | Mn-O | Mn-OTf | $O\text{-}H_{Naphthalene}$ | $Mn\text{-}N_{eq}$ (average) | C-Cl |
|---|---|---|---|---|---|
| **$^5$[3 + Naphthalene ] + $Cl^-$** | 1.64 | 2.14 | ∞ | 2.05 | ∞ |
| **$^5$[Reactant Complex]** | 1.65 | 2.21 | 2.22 | 2.04 | 2.60 |
| **$^5$[Transition State]** | 1.71 | 2.26 | 1.31 | 2.05 | 1.86 |
| **$^5$[Product Complex]** | 1.98 | 2.51 | 0.97 | 2.05 | 1.76 |

**Electrophilic ($C_1$- and $C_2$-HAT) and nucleophilic ($C_1$- and $C_2$-hydroxylation) reaction of $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$ or $[Mn^{IV}(OH)(TDCPP^{+\bullet})OTf]^+$, naphthalene, chloride and/or $[OTf]^-$ hydrogen bonded to $Mn^{IV}(OH)$ in other combinations than above.**

**Table S16** Relative energies (in kcal $mol^{-1}$) of the electrophilic ($C_1$-HAT) and nucleophilic ($C_2$-hydroxylation) reaction of $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$, naphthalene and chlorine with $[OTf]^-$ hydrogen bonded to $Mn^{IV}(OH)$.

| $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$ | ΔDef2-SVP | ΔΔDef2-TZVPP | $\Delta E^a$ | $\Delta ZPE$ | $\Delta E_{thermal}{}^b$ | $-T\Delta S^b$ | ΔDisp | ΔCplx[c] | $\Delta G^d$ |
|---|---|---|---|---|---|---|---|---|---|
| **Separated (4 components)** | 50.21 | -31.39 | **18.82** | -2.11 | -2.93 | -27.99 | +18.96 | +5.68 | **12.74** |
| **{$^5$3 + Naphthalene + $[OTf]^-$} + $Cl^-$** | 24.46 | -16.48 | **7.98** | -1.06 | -0.17 | -7.51 | +2.18 | +1.89 | **3.65** |
| **Electrophilic ($C_1$-HAT)** | | | | | | | | | |
| **$^5$[Reactant Complex]** | 3.07 | -1.45 | **1.62** | -0.22 | +0.08 | -0.21 | -0.98 | +0.00 | **0.28** |
| **$^5$[Transition State]** | 10.48 | +0.08 | **10.56** | -2.34 | -0.40 | +2.57 | -1.87 | +0.00 | **8.52** |
| **$^5$[Product Complex]** | -54.83 | +0.51 | **-54.32** | +0.15 | +0.32 | -1.30 | -1.68 | +0.00 | **-56.83** |
| **Nucleophilic ($C_2$-hydroxylation)** | | | | | | | | | |
| **$^5$[Reactant Complex]** | **0.00** | **+0.00** | **0.00** | **+0.00** | **+0.00** | **+0.00** | **+0.00** | **+0.00** | **0.00** |
| **$^5$[Transition State]** | 8.98 | -0.43 | **8.55** | -1.25 | -0.39 | +2.50 | -3.74 | +0.00 | **5.67** |
| **$^5$[Intermediate Complex]** | -35.34 | 3.39 | **-31.94** | +1.70 | -0.52 | +1.77 | -8.99 | +0.00 | **-37.98** |

[a] Def2-TZVPP electronic energy = sum of the two previous columns. [b] $T$ = 298.15 K. [c] Complexation energy due to change of standard states of the solvent. [d] Gibb's free energy = sum of the previous six columns.

**Table S17** Mulliken spin density distribution of the electrophilic ($C_1$-HAT) and nucleophilic ($C_2$-hydroxylation) reaction of $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$, naphthalene and chlorine with $[OTf]^-$ hydrogen bonded to $Mn^{IV}(OH)$.

| $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$ | Mn | OH | $OTf_{axial}$ | $OTf_{H\text{-}bond}$ | Porphine | Naphthalene | Cl |
|---|---|---|---|---|---|---|---|
| **Separated (4 components)** | 3.09 | 0.06 | 0.02 | 0.00 | 0.83 | 0.00 | 0.00 |
| **{$^5$3 + Naphthalene + $[OTf]^-$} + $Cl^-$** | 3.02 | 0.13 | 0.02 | 0.01 | 0.81 | 0.02 | 0.00 |
| **Electrophilic ($C_1$-HAT)** | | | | | | | |
| **$^5$[Reactant Complex]** | 3.06 | 0.09 | 0.01 | 0.00 | -0.16 | 0.57 | 0.43 |
| **$^5$[Transition State]** | 3.58 | -0.09 | 0.02 | 0.00 | -0.22 | 0.66 | 0.05 |
| **$^5$[Product Complex]** | 4.06 | 0.03 | 0.04 | 0.00 | -0.13 | 0.00 | 0.00 |
| **Nucleophilic ($C_2$-hydroxylation)** | | | | | | | |
| **$^5$[Reactant Complex]** | 3.06 | 0.09 | 0.01 | 0.00 | -0.17 | 0.60 | 0.40 |
| **$^5$[Transition State]** | 3.49 | -0.10 | 0.02 | 0.00 | -0.21 | 0.67 | 0.13 |
| **$^5$[Intermediate Complex]** | 4.06 | 0.02 | 0.04 | 0.00 | -0.13 | 0.01 | 0.00 |

**Table S18** Selected DFT optimized geometries (in Å) of the electrophilic ($C_1$-HAT) and nucleophilic ($C_2$-hydroxylation) reaction of $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$, naphthalene and chlorine with $[OTf]^-$ hydrogen bonded to $Mn^{IV}(OH)$.

| $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$ | Mn-O | $Mn_1$-$OTf_{axial}$ | HO-$H_{Naphthalene}$ | Mn-$N_{eq}$ (average) | OH-$OTf_{H\text{-}bond}$ | C-Cl |
|---|---|---|---|---|---|---|
| **Separated (4 components)** | 1.79 | 1.90 | ∞ | 2.03 | ∞ | ∞ |
| **{$^5$3 + Naphthalene + $[OTf]^-$} + $Cl^-$** | 1.75 | 2.01 | 2.66 | 2.03 | 1.60 | ∞ |
| **Electrophilic ($C_1$-HAT)** | | | | | | |
| **$^5$[Reactant Complex]** | 1.76 | 2.05 | 2.46 | 2.02 | 1.68 | 2.57 |
| **$^5$[Transition State]** | 1.87 | 2.16 | 1.69 | 2.03 | 1.77 | 1.87 |
| **$^5$[Product Complex]** | 2.25 | 2.22 | 0.97 | 2.04 | 1.69 | 1.76 |
| **Nucleophilic ($C_2$-hydroxylation)** | | | | | | |
| **$^5$[Reactant Complex]** | 1.76 | 2.05 | 4.92 | 2.02 | 1.66 | 2.60 |
| **$^5$[Transition State]** | 1.84 | 2.14 | 2.50 | 2.03 | 1.78 | 1.96 |
| **$^5$[Intermediate Complex]** | 2.34 | 2.20 | 1.43 | 2.03 | 1.65 | 1.86 |

**Table S19** Relative energies (in kcal $mol^{-1}$) of the electrophilic ($C_1$-HAT) and nucleophilic ($C_2$-hydroxylation) reaction of $[Mn^{IV}(OH)(TDCPP^{+\bullet})OTf]^+$, naphthalene and chlorine.

| $[Mn^{IV}(OH)(TDCPP^{+\bullet})OTf]^+$ | ΔDef2-SVP | ΔΔDef2-TZVPP | $\Delta E^a$ | $\Delta ZPE$ | $\Delta E_{thermal}{}^b$ | $-T\Delta S^b$ | ΔDisp | ΔCplx$^c$ | $\Delta G^d$ |
|---|---|---|---|---|---|---|---|---|---|
| **Separated (3 components)** | 34.55 | -20.42 | **14.13** | -1.44 | -0.61 | -17.56 | +11.57 | +3.79 | **9.89** |
| **$^5$[3 + Naphthalene] + $Cl^-$** | 31.68 | -17.00 | **14.68** | -0.87 | +0.19 | -8.36 | +5.34 | +1.89 | **12.86** |
| **Electrophilic ($C_1$-HAT)** | | | | | | | | | |
| **$^5$[Reactant Complex]** | **0.00** | **+0.00** | **0.00** | **+0.00** | **+0.00** | **+0.00** | **+0.00** | **+0.00** | **0.00** |
| **$^5$[Transition State]** | 5.74 | +1.48 | **7.23** | -1.94 | -0.32 | +1.32 | -0.21 | +0.00 | **6.08** |
| **$^5$[Product Complex]** | -54.76 | +0.67 | **-54.09** | -0.01 | +0.54 | -1.89 | -3.83 | +0.00 | **-59.28** |
| **Nucleophilic ($C_2$-hydroxylation)** | | | | | | | | | |
| **$^5$[Reactant Complex]** | 0.84 | -0.69 | **0.15** | +0.02 | +0.00 | -0.57 | +0.42 | +0.00 | **0.03** |
| **$^5$[Transition State]** | 3.92 | +0.66 | **4.58** | -1.07 | -0.35 | +1.74 | -2.11 | +0.00 | **2.79** |
| **$^5$[Intermediate Complex]** | -40.38 | +4.55 | **-35.83** | +2.15 | -0.53 | +0.68 | -7.01 | +0.00 | **-40.53** |

[a] Def2-TZVPP electronic energy = sum of the two previous columns. [b] $T$ = 298.15 K. [c] Complexation energy due to change of standard states of the solvent. [d] Gibb's free energy = sum of the previous six columns.

**Table S20** Mulliken spin density distribution of the electrophilic ($C_1$-HAT) and nucleophilic ($C_2$-hydroxylation) reaction of $[Mn^{IV}(OH)(TDCPP^{+\bullet})OTf]^+$, naphthalene and chlorine.

| $[Mn^{IV}(OH)(TDCPP^{+\bullet})OTf]^+$ | Mn | OH | $OTf_{axial}$ | TDCPP | Naphthalene | Cl |
|---|---|---|---|---|---|---|
| **Separated (3 components)** | 2.97 | 0.15 | 0.02 | 0.84 | 0.00 | 0.00 |
| **$^5$[3 + Naphthalene] + $Cl^-$** | 3.05 | 0.07 | 0.03 | 0.85 | 0.00 | 0.00 |
| **Electrophilic ($C_1$-HAT)** | | | | | | |
| **$^5$[Reactant Complex]** | 3.07 | 0.04 | 0.01 | -0.12 | 0.57 | 0.43 |
| **$^5$[Transition State]** | 3.55 | -0.09 | 0.02 | -0.20 | 0.65 | 0.06 |
| **$^5$[Product Complex]** | 4.04 | 0.02 | 0.05 | -0.11 | 0.00 | 0.00 |
| **Nucleophilic ($C_2$-hydroxylation)** | | | | | | |
| **$^5$[Reactant Complex]** | 3.07 | 0.04 | 0.04 | -0.13 | 0.56 | 0.44 |
| **$^5$[Transition State]** | 3.44 | -0.09 | 0.02 | -0.20 | 0.69 | 0.14 |
| **$^5$[Intermediate Complex]** | 4.04 | 0.01 | 0.05 | -0.12 | 0.01 | 0.00 |

**Table S21** Selected DFT optimized geometries (in Å) of the electrophilic ($C_1$-HAT) and nucleophilic ($C_2$-hydroxylation) reaction of $[Mn^{IV}(OH)(TDCPP^{+\bullet})OTf]^+$, naphthalene and chlorine.

| $[Mn^{IV}(OH)(TDCPP^{+\bullet})OTf]^+$ | Mn-O | Mn-OTf | HO-$H_{Naphthalene}$ | Mn-$N_{eq}$ (average) | C-Cl |
|---|---|---|---|---|---|
| **Separated (3 components)** | 1.74 | 2.01 | ∞ | 2.03 | ∞ |
| **$^5$[3 + Naphthalene] + $Cl^-$** | 1.79 | 1.97 | 2.68 | 2.01 | ∞ |
| **Electrophilic ($C_1$-HAT)** | | | | | |
| **$^5$[Reactant Complex]** | 1.80 | 2.04 | 1.91 | 2.02 | 2.57 |
| **$^5$[Transition State]** | 1.89 | 2.11 | 1.76 | 2.02 | 1.88 |
| **$^5$[Product Complex]** | 2.08 | 2.14 | 1.00 | 2.03 | 1.75 |
| **Nucleophilic ($C_2$-hydroxylation)** | | | | | |
| **$^5$[Reactant Complex]** | 1.80 | 2.00 | 4.57 | 2.01 | 2.56 |
| **$^5$[Transition State]** | 1.85 | 2.07 | 2.59 | 2.03 | 1.96 |
| **$^5$[Intermediate Complex]** | 2.39 | 2.15 | 1.44 | 2.03 | 1.85 |

**Possible reaction step after the initial nucleophilic ($C_2$-hydroxylation) reaction**

**Table S22** Relative energies (in kcal $mol^{-1}$) of the electrophilic ($C_1$-HAT) reaction of $[Mn^{IV}(OH)(TDCPP^{+\bullet})OTf]^+$ and 1-chloro-1,2-dihydronaphthalen-2-ol (naphthalene-OH) with $[OTf]^-$ hydrogen bonded to $Mn^{IV}(OH)$.

| $[Mn^{IV}(OH)(TDCPP^{+\bullet})OTf]^+$ | ΔDef2-SVP | ΔΔDef2-TZVPP | $\Delta E^a$ | $\Delta Z_0$ | $\Delta E_{thermal}{}^b$ | $-T\Delta S^b$ | ΔDisp | ΔCplx$^c$ | $\Delta G^d$ |
|---|---|---|---|---|---|---|---|---|---|
| **$^5$[Intermediate-1 Complex]** | **0.00** | **+0.00** | **0.00** | **+0.00** | **+0.00** | **+0.00** | **+0.00** | **+0.00** | **0.00** |
| **$^5$[Transition State]** | 12.04 | +1.59 | **13.62** | -3.59 | +0.03 | +0.71 | -6.94 | +0.00 | **3.83** |
| **$^5$[Intermediate-2 Complex]** | -35.58 | -2.13 | **-37.71** | -0.81 | +1.02 | -4.00 | +3.22 | +0.00 | **-38.28** |

[a] Def2-TZVPP electronic energy = sum of the two previous columns. [b] $T$ = 298.15 K. [c] Complexation energy due to change of standard states of the solvent. [d] Gibb's free energy = sum of the previous six columns.

**Table S23** Mulliken spin density distribution of the electrophilic ($C_1$-HAT) reaction of $[Mn^{IV}(OH)(TDCPP^{+\bullet})OTf]^+$ and 1-chloro-1,2-dihydronaphthalen-2-ol (naphthalene-OH) with $[OTf]^-$ hydrogen bonded to $Mn^{IV}(OH)$.

| $[Mn^{IV}(OH)(TDCPP^{+\bullet})OTf]^+$ | Mn | OH | $OTf_{axial}$ | $OTf_{H\text{-}bond}$ | TDCPP | NaphthaleneOH | Cl |
|---|---|---|---|---|---|---|---|
| **$^5$[Intermediate-1 Complex]** | 3.00 | 0.12 | 0.02 | 0.00 | 0.85 | 0.00 | 0.00 |
| **$^5$[Transition State]** | 3.78 | -0.21 | 0.04 | 0.00 | 0.85 | -0.42 | -0.03 |
| **$^5$[Intermediate-2 Complex]** | 4.04 | 0.02 | 0.05 | 0.00 | -0.11 | 0.00 | 0.00 |

**Table S24** Selected DFT optimized geometries (in Å) of the electrophilic ($C_1$-HAT) reaction of $[Mn^{IV}(OH)(TDCPP^{+\bullet})OTf]^+$ and 1-chloro-1,2-dihydronaphthalen-2-ol (naphthalene-OH) with $[OTf]^-$ hydrogen bonded to $Mn^{IV}(OH)$.

| $[Mn^{IV}(OH)(TDCPP^{+\bullet})OTf]^+$ | Mn-O | $Mn\text{-}OTf_{axial}$ | $HO\text{-}H_{Naphthalene}$ | $Mn\text{-}N_{eq}$ (average) | $OH\text{-}OTf_{H\text{-}bond}$ |
|---|---|---|---|---|---|
| **$^5$[Intermediate-1 Complex]** | 1.76 | 2.00 | 2.78 | 2.02 | 1.68 |
| **$^5$[Transition State]** | 2.00 | 2.16 | 1.47 | 2.03 | 1.92 |
| **$^5$[Intermediate-2 Complex]** | 2.30 | 2.19 | 0.97 | 2.03 | 1.77 |

**Ionization and Electron Affinities**

**Table S25** Ionisation energies of naphthalene and $Cl^-$, both separate and complexed (in kcal $mol^{-1}$).

| Compound (unionized)[a] | ΔDef2-SVP | ΔΔDef2-TZVPP | $\Delta E^b$ | $\Delta Z_0$ | $\Delta E_{thermal}{}^c$ | $-T\Delta S^c$ | ΔDisp | $\Delta G^d$ |
|---|---|---|---|---|---|---|---|---|
| **Naphthalene** | 142.41 | +0.55 | **142.96** | -0.25 | +0.15 | -0.68 | +0.00 | **142.18** |
| **$Cl^-$ (anion)** | 121.15 | +20.29 | **141.44** | +0.00 | +0.00 | -0.41 | +0.00 | **141.03** |
| **[$Cl^-$ + Naphthalene] (in complex)** | 107.12 | +14.50 | **121.62** | +0.01 | -0.06 | +0.23 | -1.27 | **120.54** |

[a] Ionization energies are expresses as the energy of the structurally optimized ionized compound minus the unionized compound. [b] Def2-TZVPP electronic energy = sum of the two previous columns. [c] $T$ = 298.15 K. [d] Gibb's free energy = sum of the previous five columns.

**Table S26** Mulliken spin density distribution of the ionised compounds.

| Compound | Naphthalene | Cl |
|---|---|---|
| **Naphthalene$^{+\bullet}$** | 1.00 | — |
| **Cl$^\bullet$** | — | 1.00 |
| **[Cl + Naphthalene]$^\bullet$** | 0.44 | 0.56 |

**Table S27** Electron Affinity of $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$ (in kcal $mol^{-1}$) .

| Compound (unreduced)[a] | ΔDef2-SVP | ΔΔDef2-TZVPP | $\Delta E^b$ | $\Delta Z_0$ | $\Delta E_{thermal}{}^c$ | $-T\Delta S^c$ | ΔDisp | $\Delta G^d$ |
|---|---|---|---|---|---|---|---|---|
| **$^5[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$** | -136.36 | +2.08 | **-134.28** | +0.35 | +0.01 | +7.59 | -0.53 | **-126.85** |

[a] Electron affinity is expresses as the energy of the structurally optimized reduced compound minus the unreduced compound. [b] Def2-TZVPP electronic energy = sum of the two previous columns. [c] $T$ = 298.15 K. [d] Gibb's free energy = sum of the previous five columns.

**Table S28** Mulliken spin density distribution of the unreduced $[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$ and reduced catalyst (**2OH-OTf**).

| Compound | Mn | OH | $OTf_{axial}$ | Porphine |
|---|---|---|---|---|
| **$^5[Mn^{IV}(OH)(Por^{+\bullet})OTf]^+$** | 3.06 | 0.08 | 0.03 | 0.83 |
| **$^4[Mn^{IV}(OH)(Por)OTf]$** | 3.10 | 0.05 | 0.01 | -0.17 |

**Table S29** One-electron oxidation potentials of substrates, second-order rate constants ($k_2$), and log($k_2$) values for the aromatic ring activation of various substrates by **3**/$Cl^-$ in $CH_2Cl_2/CH_3CN$ (*v/v* 20:1) at –10 °C.

| substrate | $E_{ox}$ *vs.* SCE, V | $k_2$, $M^{-1}$ $s^{-1}$ | log($k_2$) |
|---|---|---|---|
| 1-Me-naphthalene | 1.57 | $1.4(1) \times 10^2$ | 2.1 |
| naphthalene | 1.76 | 2.0(2) | 0.30 |
| 1-Br-naphthalene | 1.81 | $8.3(6) \times 10^{-1}$ | –0.081 |
| 1-$NO_2$-naphthalene | 2.10 | $6.5(5) \times 10^{-3}$ | –2.2 |
| anisole | 1.76 | 2.3(2) | 0.36 |
| toluene | 2.10 | $2.5(2) \times 10^{-2}$ | –1.6 |
| benzene | 2.23 | $4.7(4) \times 10^{-3}$ | –2.3 |

**Table S30** One-electron oxidation potentials of substrates, second-order rate constants ($k_2$), and log($k_2$) values for the OAT reaction of various substrates by **3**/$Cl^-$ in $CH_2Cl_2/CH_3CN$ (*v/v* 20:1) at –40 °C.

| substrate | $E_{ox}$ *vs*. SCE, V | $k_2$, $M^{-1}$ $s^{-1}$ | log($k_2$) |
|---|---|---|---|
| 4-CN-thioanisole | 1.67 | $6.8(5) \times 10^{-2}$ | 2.83 |
| 4-CHO-thioanisole | 1.67 | $1.9(1) \times 10^{-2}$ | 2.27 |
| 4-$NO_2$-thioanisole | 1.73 | 82(6) | 1.91 |

**Table S31** One-electron oxidation potentials of substrates, second-order rate constants ($k_2$), and log($k_2$) values for the oxidation reaction of styrene derivatives by **3**/$Cl^-$ in $CH_2Cl_2/CH_3CN$ (*v/v* 20:1) at –10 °C.

| substrate | $E_{ox}$ *vs*. SCE, V | $k_2$, $M^{-1}$ $s^{-1}$ | log($k_2$) |
|---|---|---|---|
| 4-Me-styrene | 1.80 | 1.9(2) | 0.28 |
| styrene | 1.86 | $4.7(4) \times 10^{-1}$ | –0.33 |
| 4-Cl-styrene | 1.93 | $2.4(2) \times 10^{-1}$ | –0.62 |
| 3-Cl-styrene | 2.04 | $6.8(5) \times 10^{-2}$ | –1.17 |
| 4-$NO_2$-styrene | 2.38 | $2.5(2) \times 10^{-3}$ | –2.60 |

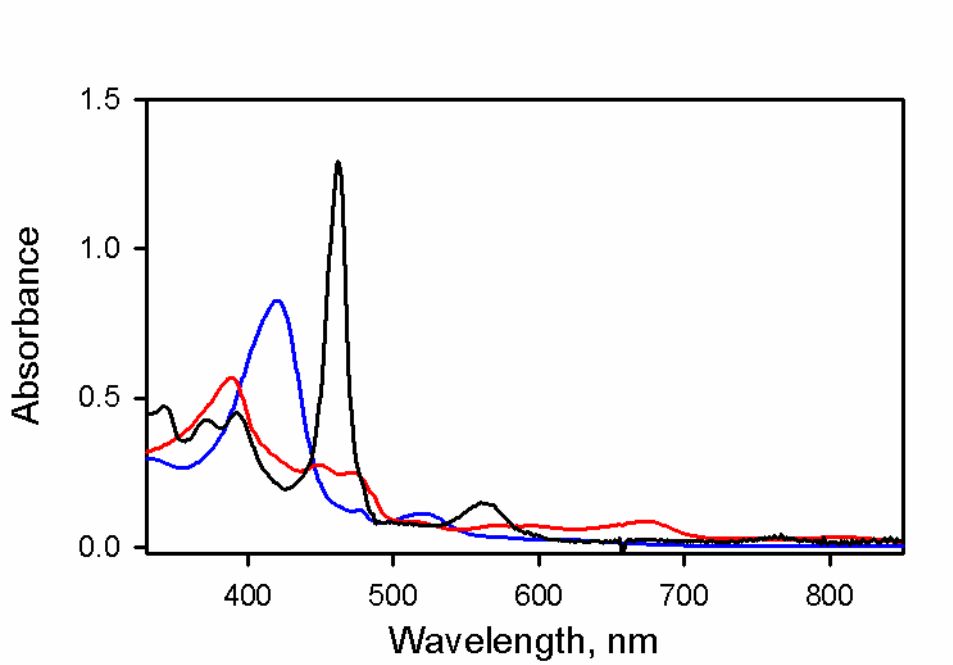


**Fig. S1** UV-vis spectra of **1**/$Cl^-$ (0.10 mM; black line), **2**/$Cl^-$ (0.10 mM; blue line) and **3**/$Cl^-$ (0.10 mM; red line) in $CH_2Cl_2$ at –10 °C.

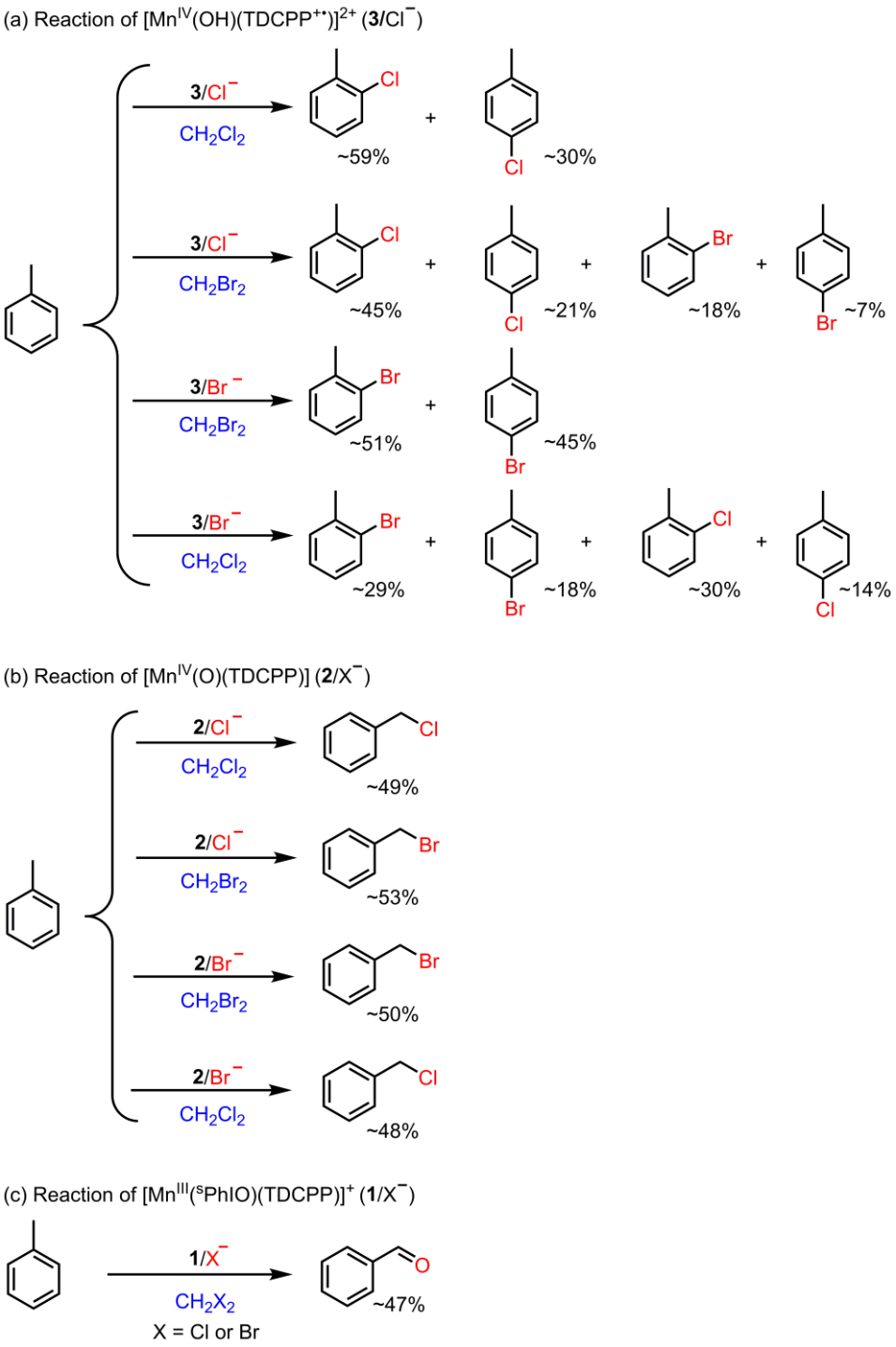


**Fig. S2** Products produced in the oxidation of toluene by $[Mn^{IV}(OH)(TDCPP^{+\bullet})]^{2+}$, $[Mn^{IV}(O)(TDCPP)]$ and $[Mn^{III}(^{s}PhIO)(TDCPP)]^{+}$ with different conter anion in different solvent system at –10 $^{o}$C.

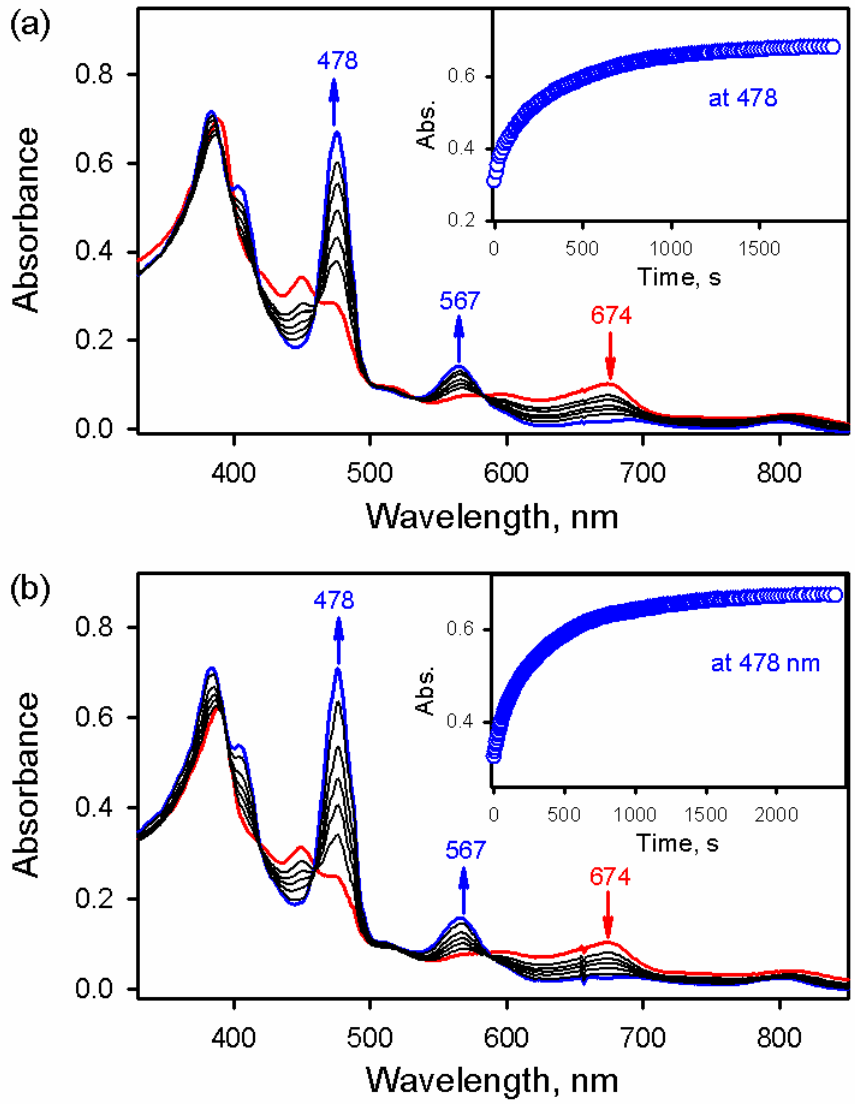


**Fig. S3** UV-vis spectral changes observed in the reaction of **3**/$Cl^-$ (0.10 mM; red line) with (a) naphthalene (2.0 mM) and (b) benzene (0.60 M) in $CH_2Cl_2/CH_3CN$ (*v/v* 20:1) at –10 °C.

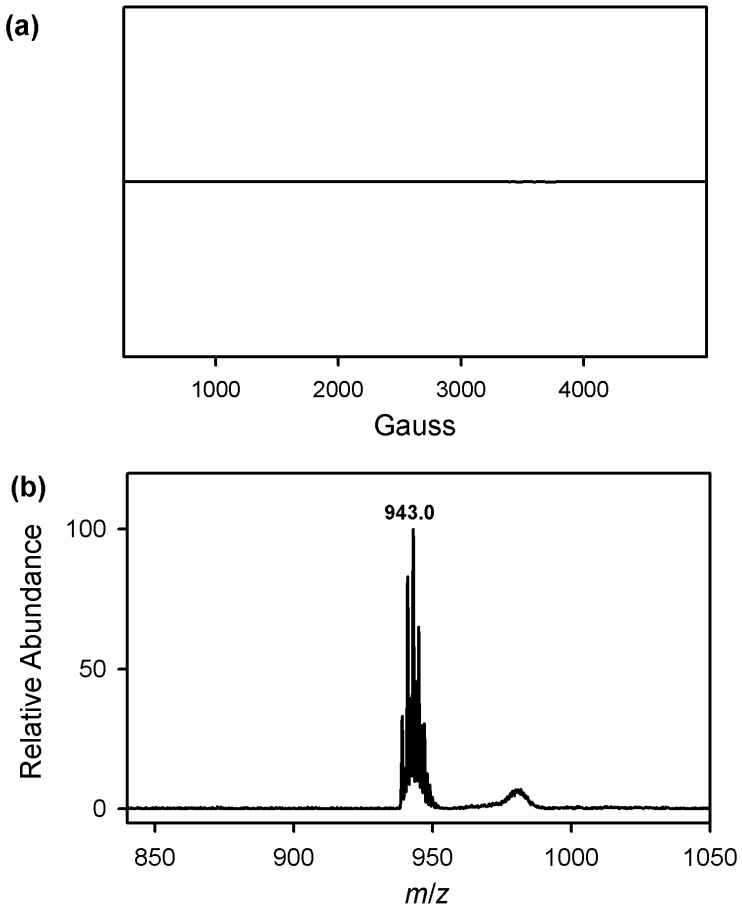


**Fig. S4** (a) X-band CW-EPR spectrum of the complete reaction solution obtained in the oxidation of naphthalene (5.0 mM) by **3**/$Cl^-$ (0.50 mM) in $CH_2Cl_2/CH_3CN$ (*v/v* 20:1) at –10 °C. Spectrum was recorded at 5 K. A silent EPR indicates that Mn(III) complex is the final product. (b) ESI-MS spectrum of the complete reaction solution obtained in the oxidation of naphthalene (0.30 mM) by **3**/$Cl^-$ (0.030 mM) in $CH_2Cl_2/CH_3CN$ (*v/v* 20:1) at –40 °C. The peak at *m/z* = 943.0 corresponds to $[Mn^{III}(TDCPP)]^+$ (*calcd. m/z* = 943.2).

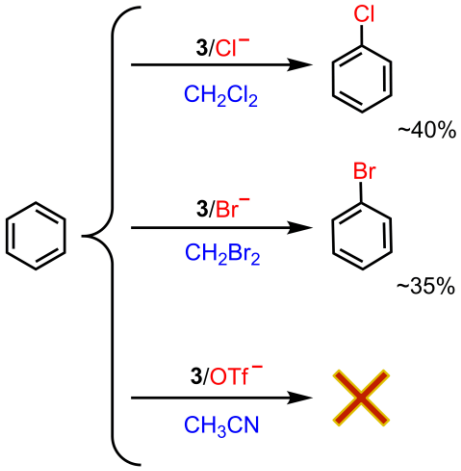


**Fig. S5** Products obtained in the oxidation of benzene by **3**/$X^-$ in different solvent system at –10 °C.

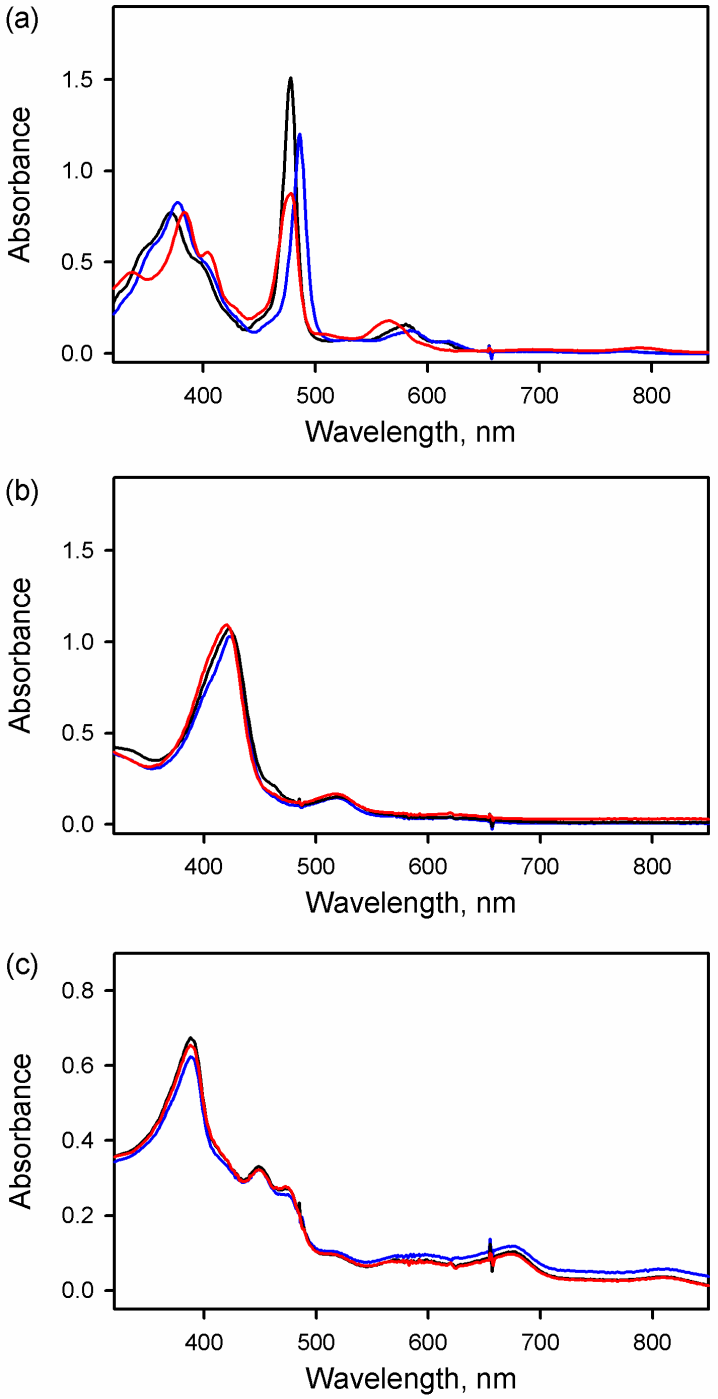


**Fig. S6** (a) UV-vis spectra of $Mn^{III}$(TDCPP)(Cl) (0.10 mM; black line), $Mn^{III}$(TDCPP)(Br) (0.10 mM; blue line) and $Mn^{III}$(TDCPP)(OTf) (0.10 mM; red line) in $CH_2Cl_2$ at –10 °C. (b) UV-vis spectra of **2**/$Cl^-$, **2**/$Br^-$ and **2**/$OTf^-$ generated by using corresponding starting compound in $CH_2Cl_2$ at –10 °C. (c) UV-vis spectra of **3**/$Cl^-$, **3**/$Br^-$ and **3**/$OTf^-$ generated by using corresponding starting compound in $CH_2Cl_2$ at –10 °C.

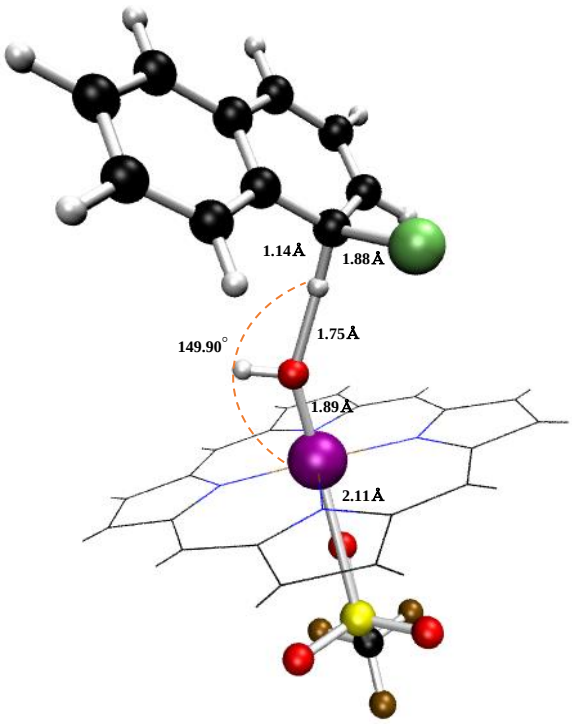


**Fig. S7** Schematic representation of the transition state structure of C-H activation alongside with chlorine addition with important bond length and bond angles.

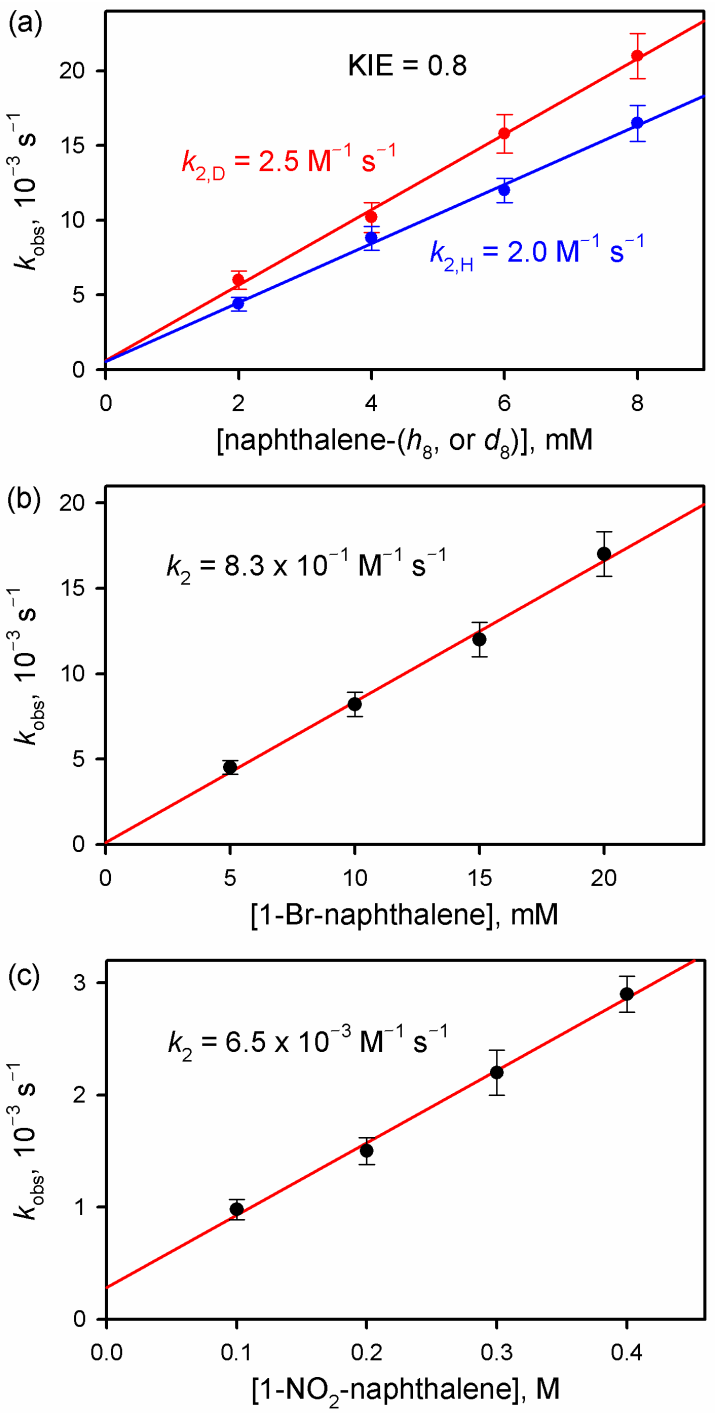


**Fig. S8** Plots of the first-order rate constants ($k_{obs}$) against concentrations of (a) naphthalene (blue circles) and naphthalene-$d_8$ (red circles), (b) 1-Br-naphthalene, and (c) 1-$NO_2$-naphthalene for the aromatic halogenation by **3**/$Cl^-$ in $CH_2Cl_2$/$CH_3CN$ (v/v 20:1) at –10 °C to determine the second-order rate constants ($k_2$).

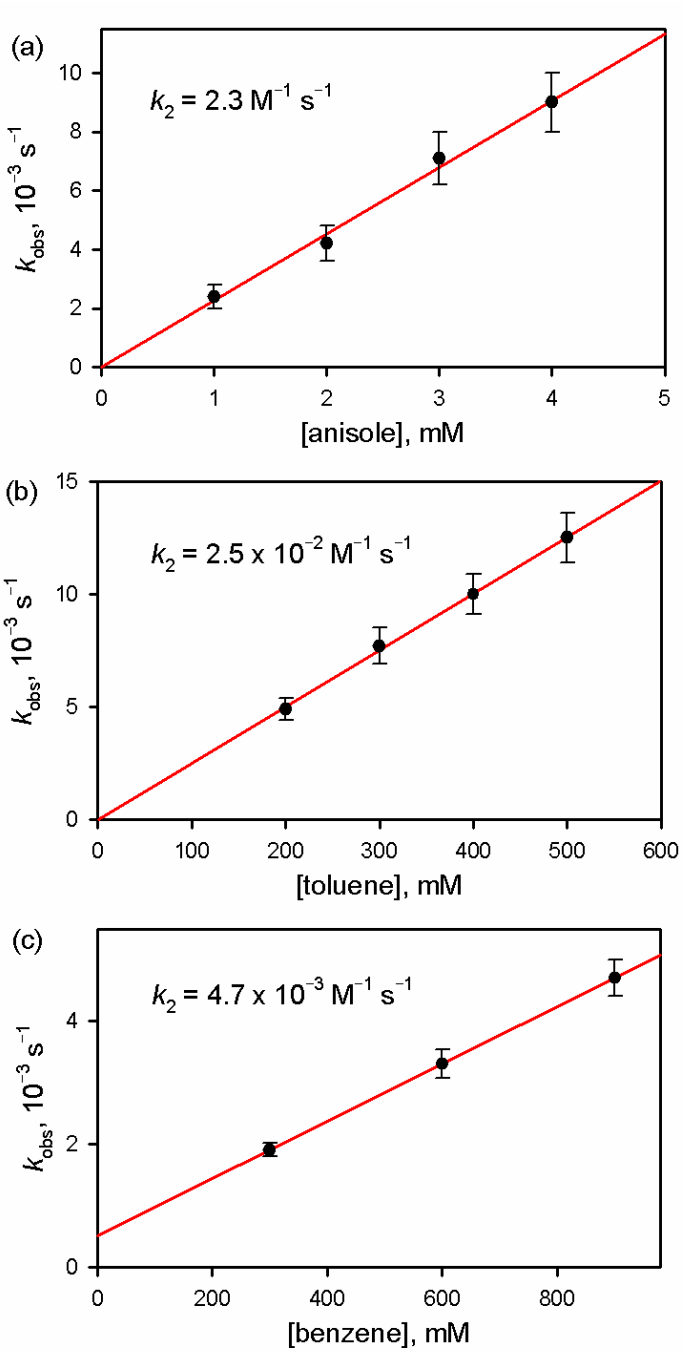


**Fig. S9** Plots of the first-order rate constants ($k_{obs}$) against concentrations of (a) anisole, (b) toluene, and (c) benzene for the oxidation of aromatic substrates by **3**/$Cl^-$ in $CH_2Cl_2/CH_3CN$ (v/v 20:1) at –10 °C to determine the second-order rate constants ($k_2$).

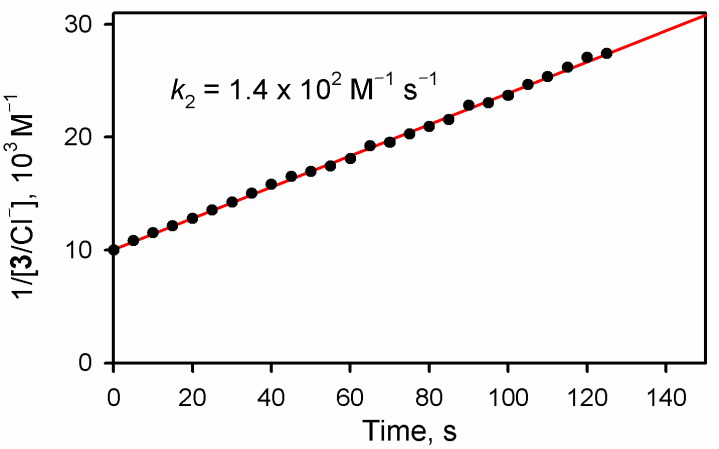


**Fig. S10** Second-order plot of 1/[**3**/$Cl^-$] against time for the oxidation of 1-Me-naphthalene (0.10 mM) by **3**/$Cl^-$ (0.10 mM) in $CH_2Cl_2$/$CH_3CN$ (*v*/*v* 20:1) at –10 °C.

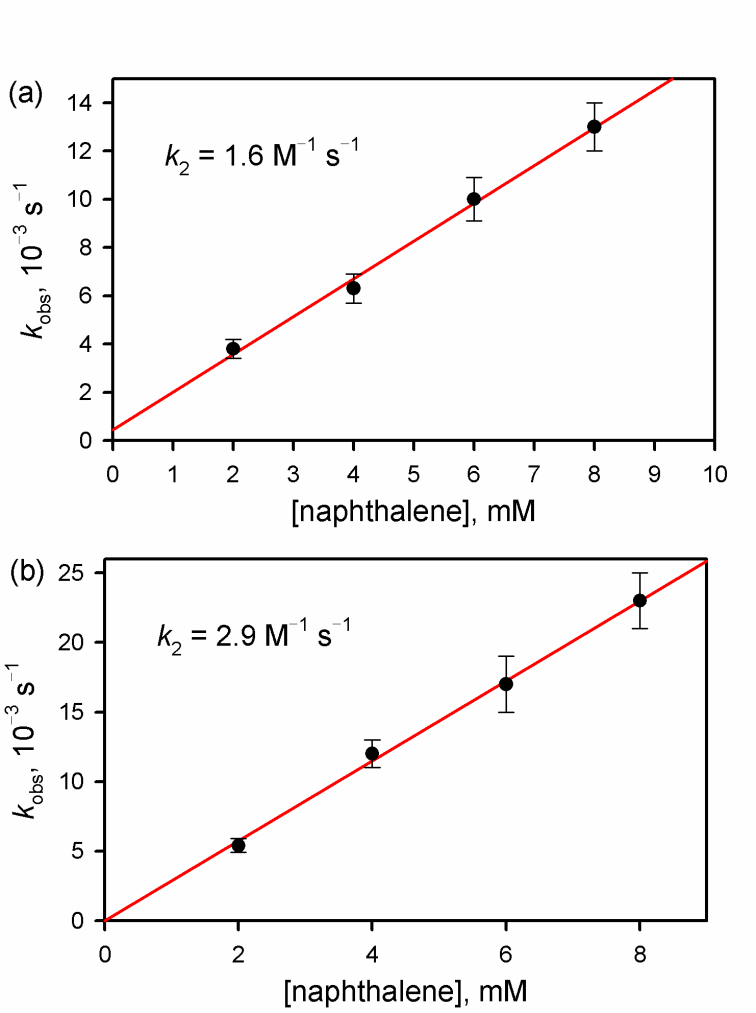


**Fig. S11** Plots of the first-order rate constants ($k_{obs}$) against concentrations of naphthalene for the oxidation of naphthalene by (a) **3**/$Br^-$ and (b) **3**/$OTf^-$ in $CH_2Cl_2$/$CH_3CN$ (*v*/*v* 20:1) at –10 °C to determine the second-order rate constants ($k_2$).

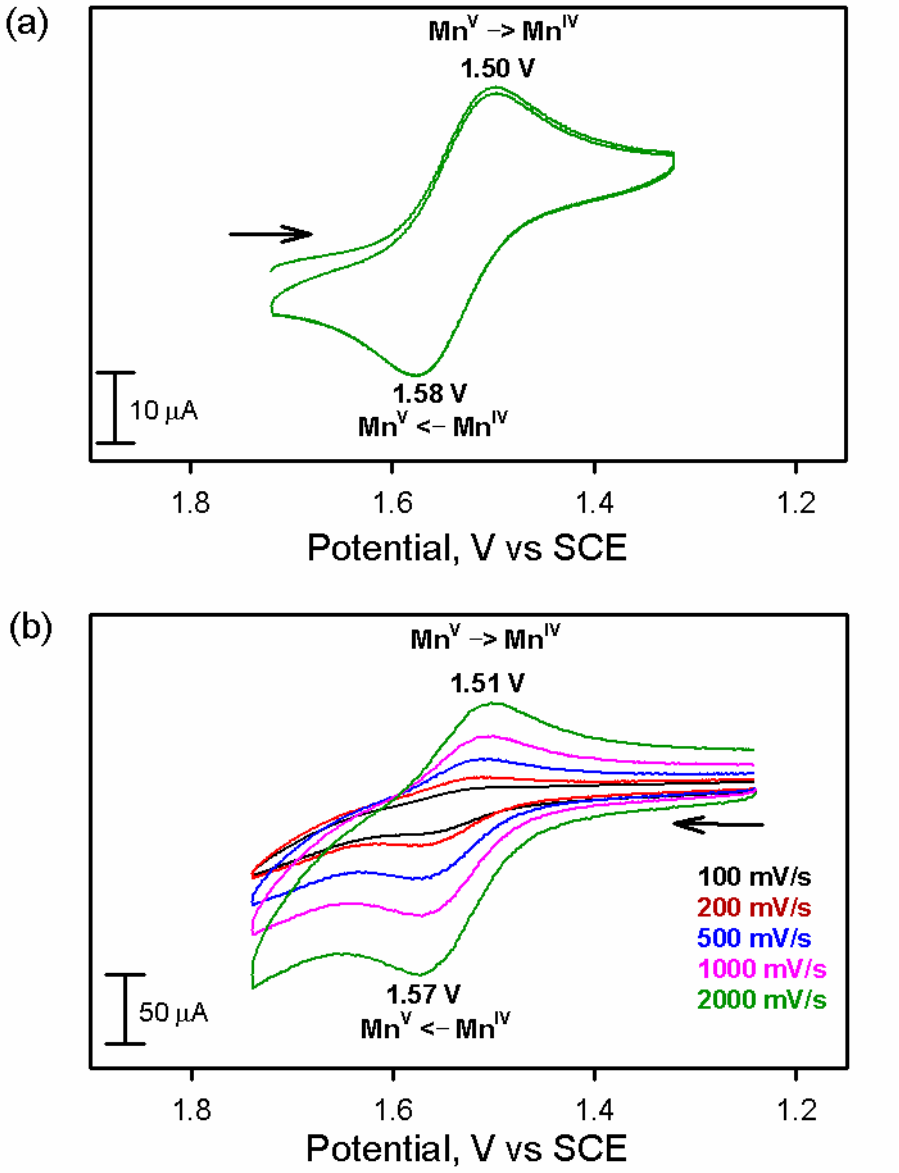


**Fig. S12** Cyclic voltammograms of (a) $[Mn^{IV}(OH)(TDCPP^{+\bullet})]^{2+}$ (**3**/$Cl^{-}$; 0.50 mM) and (b) $[Mn^{IV}(O)(TDCPP)]$ (**2**/$Cl^{-}$; 0.50 mM) in the presence of *n*-$Bu_4NPF_6$ (0.10 M) as a supporting electrolyte in $CH_3CN/CH_2Cl_2$/TFE (v/v/v 1:1:0.01) at –40 °C. A Pt electrode was used as a working electrode. The scan rate used in Fig. S12a was 100 mV/s. The one-electron reduction potential ($E_{red}$) of **3**/$Cl^{-}$ was determined to be 1.54 V vs SCE.

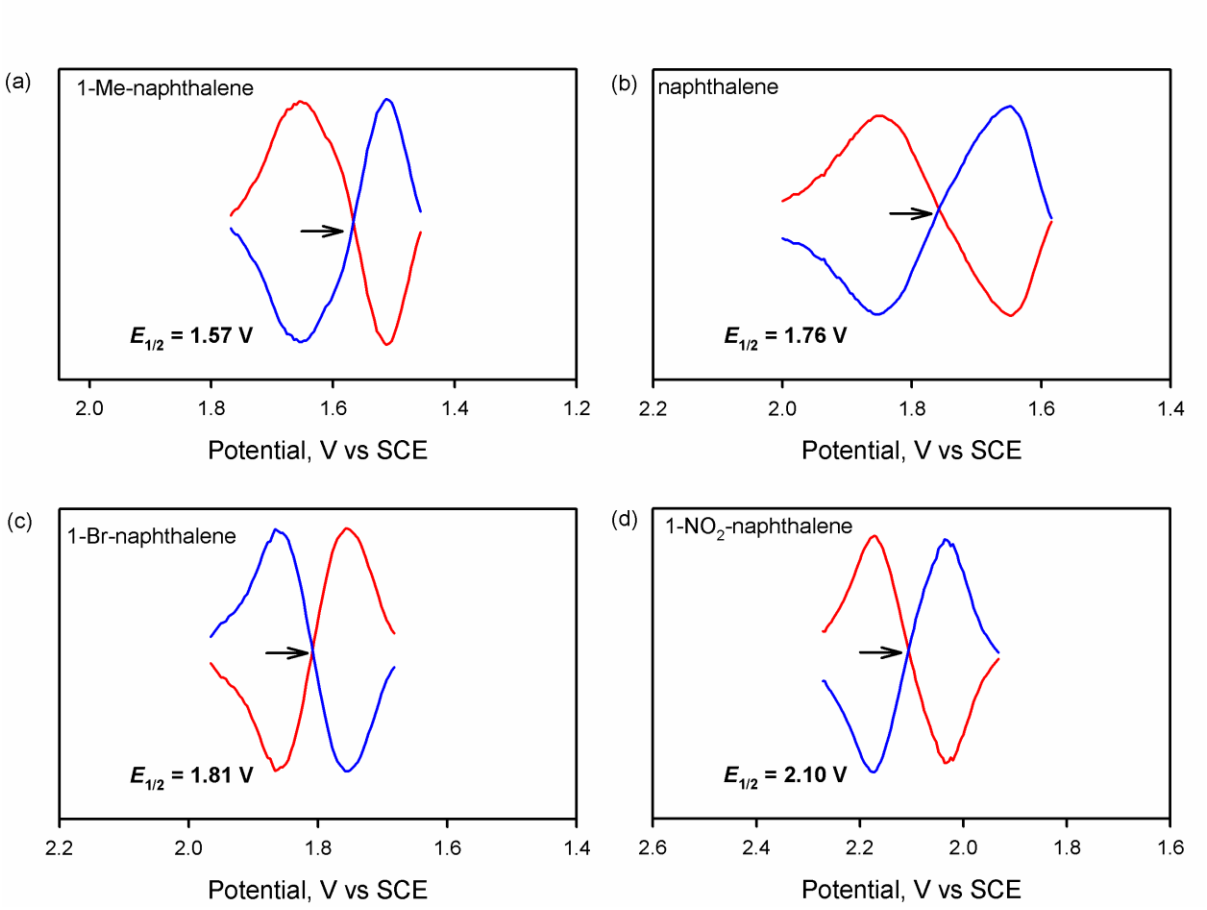


**Fig. S13** SHACV voltammograms of (a) 1-Me-naphthalene (2.0 mM), (b) naphthalene (2.0 mM), (c) 1-Br-naphthalene (2.0 mM), and (d) 1-$NO_2$-naphthalene (2.0 mM) in the presence of *n*-$Bu_4NPF_6$ (0.10 M) as a supporting electrolyte in $CH_3CN/CH_2Cl_2$ (*v/v* 1:1) at 25 $^oC$.

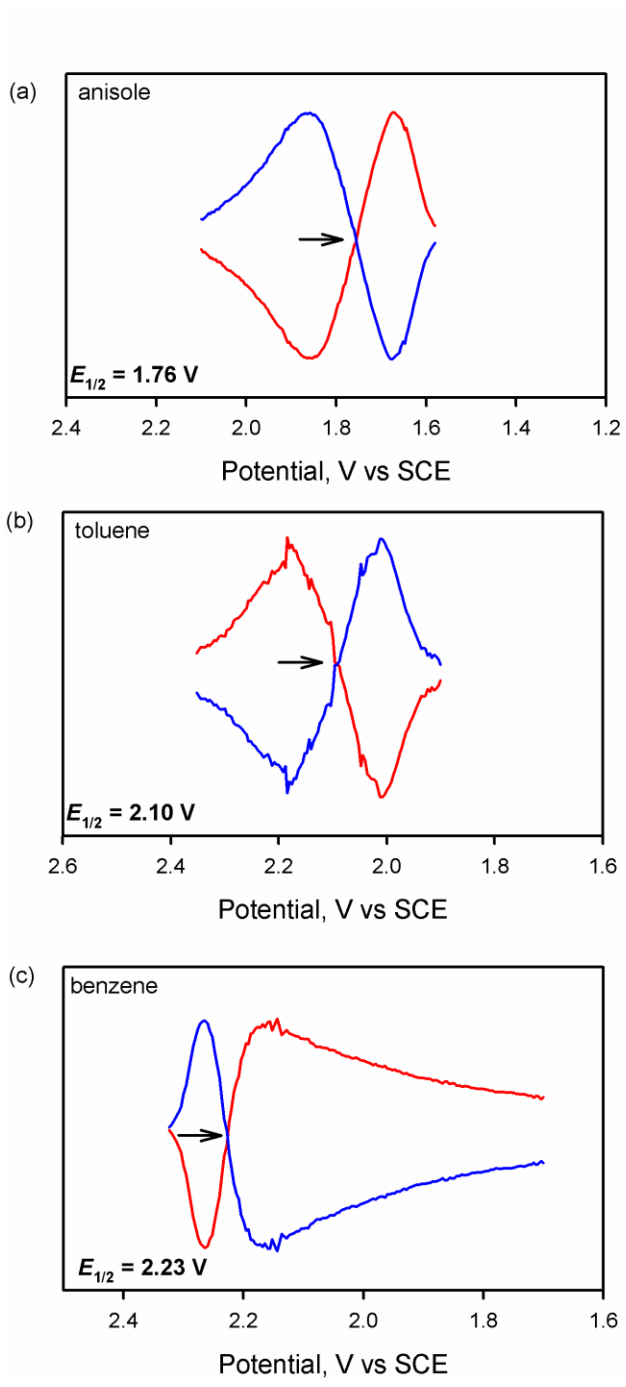


**Fig. S14** SHACV voltammograms of (a) anisole (2.0 mM), (b) toluene (2.0 mM) and (c) benzene (2.0 mM) in the presence of *n*-$Bu_4NPF_6$ (0.10 M) as a supporting electrolyte in $CH_3CN/CH_2Cl_2$ (*v/v* 1:1) at 25 °C.

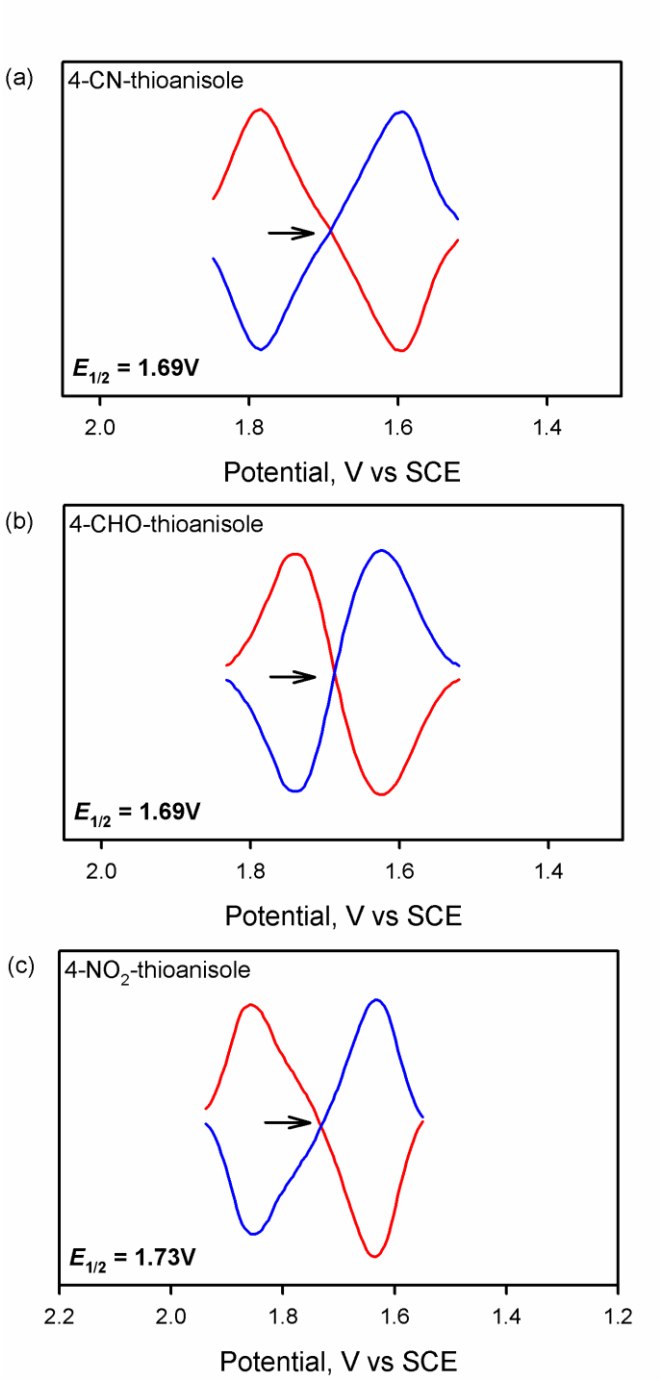


**Fig. S15** SHACV voltammograms of (a) 4-CN-thioanisole (2.0 mM), (b) 4-CHO-thioanisole (2.0 mM) and (c) 4-$NO_2$-thioanisole (2.0 mM) in the presence of *n*-$Bu_4NPF_6$ (0.10 M) as a supporting electrolyte in $CH_3CN/CH_2Cl_2$ (*v/v* 1:1) at 25 °C.

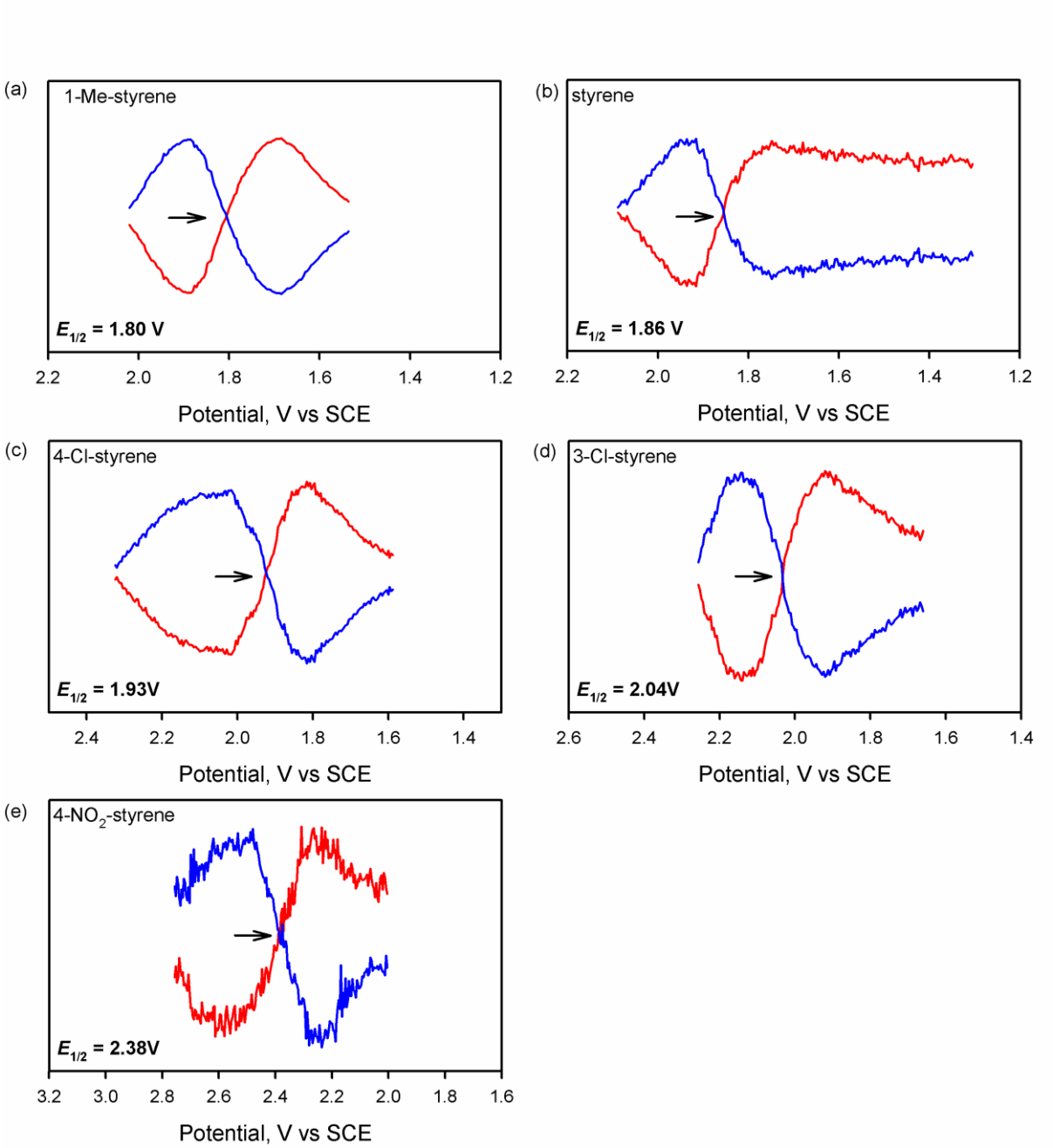


**Fig. S16** SHACV voltammograms of (a) 1-Me-styrene (2.0 mM), (b) styrene (2.0 mM), (c) 4-Cl-styrene (2.0 mM), (d) 3-Cl-styrene (2.0 mM), and (e) 4-$NO_2$-styrene (2.0 mM) in the presence of *n*-$Bu_4NPF_6$ (0.10 M) as a supporting electrolyte in $CH_3CN/CH_2Cl_2$ (*v/v* 1:1) at 25 $^oC$.

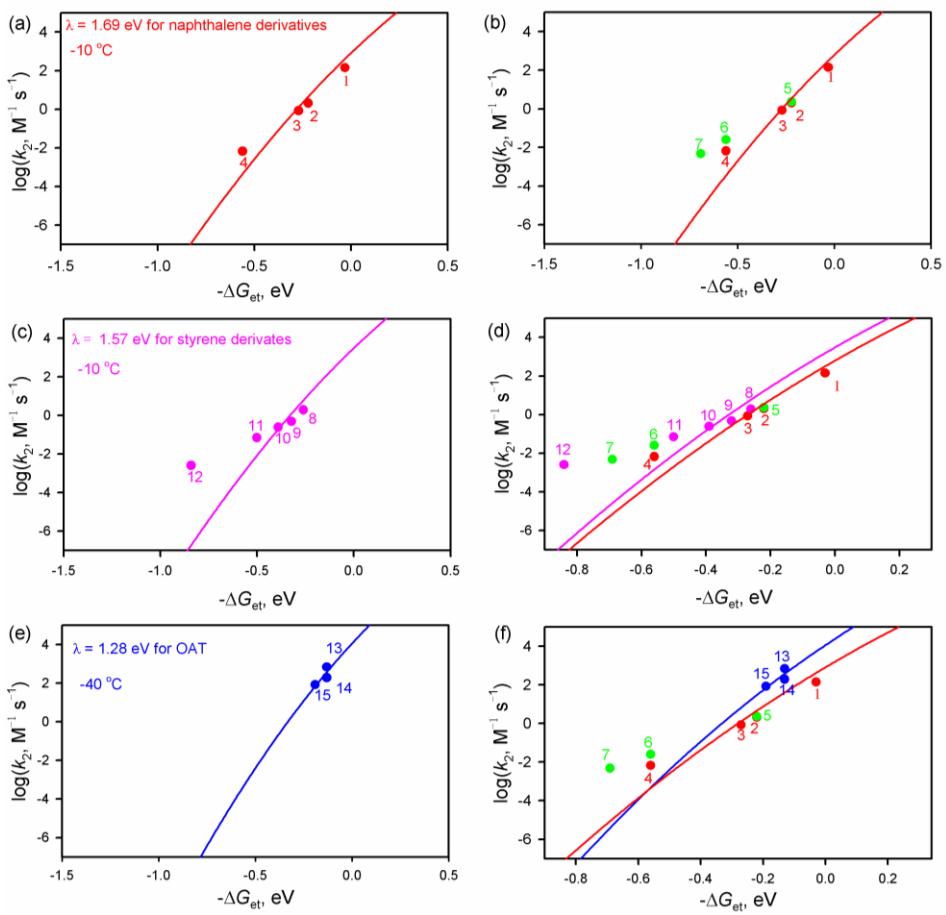


**Fig. S17** Plots of log $k_2$ for oxidation of different substrates [ (1) 1-Me-naphthalene, (2) naphthalene, (3) 1-Br-naphthalene, (4) 1-$NO_2$-naphthalene, (5) anisole, (6) toluene, (7) benzene, (8) 4-Me-styrene, (9) styrene, (10) 4-Cl-styrene, (11) 3-Cl-styrene, and (12) 4-$NO_2$-naphthalene] at −10 °C and [(13) 4-CN-thioanisole, (14) 4-CHO-thioanisole, and (15) 4-$NO_2$-thioanisole] at −40 °C *vs*. the driving force of electron transfer [$-\Delta G_{et} = -e(E_{ox} - E_{red})$].

## DFT calculated cartesian coordinates

Optimized geometries of the species in all the reactions of naphthalene by **3** at the B3LYP/Def2-SVP level. The coordinate format is in xyz-format. Charge/multiplicity is in parenthesis.

**$[Mn^{IV}OH(Por^{\bullet+})Cl]^+$ electrophilic reaction at $C_1$**

66
RC (0/5)
O -0.28567 -0.81680 0.01206
N 0.36522 1.57334 1.24674
N 0.15034 -0.89150 2.71756
N 2.11072 0.28484 -0.63316
N 1.95783 -2.15757 0.88344
C 0.60570 2.64798 0.42854
C 0.24588 -2.11606 3.33875
C -0.51603 1.99257 2.21146
C -0.68839 -0.11733 3.48630
C 2.11331 1.54254 -1.18349
C 1.78384 -3.21026 1.74653
C 2.91074 -0.50092 -1.42721
C 2.76940 -2.59965 -0.13068
C -0.14136 3.79092 0.89897
C -0.57293 -2.11929 4.52478
C -0.83925 3.38441 1.99969
C -1.15472 -0.88587 4.61295
C 2.94068 1.55156 -2.36524
C 2.51931 -4.35617 1.26593
C 3.43090 0.28690 -2.51835
C 3.12455 -3.97997 0.10141
H -0.12566 4.77268 0.42844
H -0.67931 -2.96929 5.19691
H -1.51529 3.96258 2.62760
H -1.83592 -0.51010 5.37474
H 3.10750 2.42545 -2.99262
H 2.55116 -5.32221 1.76724
H 4.08951 -0.09685 -3.29578
H 3.76215 -4.57061 -0.55444
C 1.42311 2.64772 -0.69709
C 1.00173 -3.19777 2.89713
C 3.21170 -1.84174 -1.21069
C -1.01632 1.21451 3.25088
H -1.70332 1.69216 3.95058
H 0.96705 -4.11095 3.49254
H 3.86327 -2.33270 -1.93469
H 1.51841 3.58290 -1.25006
Mn 1.13882 -0.29999 1.04288
Cl 2.93686 0.34435 2.32726
H -0.90531 -1.33146 0.55431
C -4.43046 -0.36366 -4.35936
C -3.45389 -1.27077 -4.74413
C -2.32186 -1.47362 -3.93661
C -2.15881 -0.75200 -2.73796
C -3.17808 0.15939 -2.30444
C -4.32311 0.36873 -3.13863
H -1.34715 -0.98759 -2.04671
H -1.55569 -2.19142 -4.23511
Cl -0.40274 0.74342 -3.89417
H -3.56299 -1.82882 -5.67648
H -5.30885 -0.20401 -4.99036
C -3.07687 0.85121 -1.07459
C -4.07271 1.73593 -0.68525
C -5.32318 1.28168 -2.71606
C -5.19777 1.95468 -1.51064
H -2.20003 0.67145 -0.44743
H -3.98671 2.26821 0.26505
H -5.97389 2.65570 -1.19425
H -6.19712 1.44438 -3.35216

66
TS (0/5)
O -0.18963 0.90678 0.43632
N 1.31671 2.79414 1.89487
N 0.42686 0.33535 3.11410
N 2.46858 1.29096 -0.28075
N 1.63960 -1.17229 0.98024
C 1.80198 3.84261 1.15640
C 0.13955 -0.93046 3.56812
C 0.68887 3.32877 2.98991
C -0.05517 1.21826 4.05167
C 2.80137 2.55202 -0.70598
C 1.16208 -2.22309 1.72040
C 2.95668 0.40949 -1.21185
C 2.23728 -1.70281 -0.13444
C 1.47671 5.08808 1.81362
C -0.56256 -0.84271 4.82541
C 0.78659 4.77023 2.94820
C -0.68412 0.48557 5.12365
C 3.52147 2.46640 -1.95488
C 1.47592 -3.46645 1.05419
C 3.61645 1.13996 -2.26911
C 2.14003 -3.14424 -0.09477
H 1.74742 6.07359 1.43770
H -0.91082 -1.70044 5.39880
H 0.37223 5.43980 3.70040
H -1.15232 0.94451 5.99311
H 3.90065 3.32332 -2.50958
H 1.21080 -4.45314 1.43099
H 4.09174 0.68056 -3.13451
H 2.53545 -3.81123 -0.85938
C 2.49688 3.74112 -0.04660
C 0.47153 -2.12157 2.92634
C 2.85005 -0.97907 -1.15514
C 0.05293 2.60613 3.99736
H -0.39208 3.17369 4.81592
H 0.16362 -3.05108 3.40729
H 3.28836 -1.54751 -1.97677
H 2.82473 4.67044 -0.51456
Mn 1.47778 0.81146 1.43480
Cl 3.53289 0.70514 2.62730
H -0.91202 0.62891 1.02432
C -3.02256 -0.50784 -3.33300
C -1.68937 -0.24469 -3.67258
C -0.97402 0.74518 -3.02277
C -1.53439 1.47584 -1.88683
C -2.98725 1.26909 -1.61227
C -3.69099 0.24443 -2.31661
H -0.93165 1.16755 -0.92667
H 0.05834 0.96301 -3.30490
Cl -1.06401 3.27050 -1.96817
H -1.21239 -0.81704 -4.47179
H -3.57997 -1.28247 -3.86494
C -3.65816 2.00216 -0.62174
C -4.99592 1.74711 -0.32672
C -5.05336 0.00235 -1.99857
C -5.69742 0.74253 -1.01978
H -3.11949 2.78681 -0.08681
H -5.50125 2.33078 0.44649
H -6.74631 0.54680 -0.78495
H -5.58765 -0.78260 -2.54003

66
PC (0/5)
O -0.89344 -0.56823 -0.23803
N 0.76077 1.60036 1.18929
N 0.14052 -0.81724 2.63560
N 2.02563 0.04332 -0.87253
N 1.40257 -2.37569 0.57235
C 1.15659 2.63235 0.37437
C -0.04671 -2.06272 3.18325
C 0.09837 2.16420 2.25194
C -0.43378 0.08615 3.49561
C 2.25100 1.29227 -1.39951
C 1.04605 -3.40562 1.40961
C 2.56778 -0.86323 -1.75126
C 2.03434 -2.94239 -0.50847
C 0.72474 3.89011 0.93731
C -0.76770 -1.94293 4.42900
C 0.06788 3.60017 2.09958
C -1.00973 -0.61204 4.62119
C 2.95141 1.17042 -2.65616
C 1.45725 -4.66429 0.83442
C 3.14552 -0.16486 -2.87517
C 2.06724 -4.37763 -0.35454
H 0.90479 4.86440 0.48555
H -1.05009 -2.78145 5.06382
H -0.40209 4.28719 2.80173
H -1.53113 -0.13080 5.44732
H 3.24954 2.00982 -3.28258
H 1.29050 -5.63801 1.29266
H 3.63697 -0.64814 -3.71833
H 2.50642 -5.06747 -1.07369
C 1.85353 2.49882 -0.82535
C 0.37538 -3.26822 2.62415
C 2.57295 -2.24840 -1.59107
C -0.46061 1.46934 3.32343
H -0.95668 2.05883 4.09603
H 0.15552 -4.18125 3.17962
H 3.04584 -2.83943 -2.37695
H 2.09802 3.41435 -1.36581
Mn 1.23012 -0.37359 0.96653
Cl 3.34130 -0.21962 2.14198
H -1.07217 -1.51223 -0.36552
C -2.79150 -1.01179 -3.30917
C -1.58651 -0.47481 -3.71028
C -1.26372 0.87214 -3.40534
C -2.16211 1.65186 -2.70359
C -3.42479 1.14330 -2.26669
C -3.73246 -0.22618 -2.58559
H -0.78714 -0.22624 -1.14045
H -0.30967 1.29558 -3.72279
Cl -1.72418 3.31358 -2.34501
H -0.86659 -1.07977 -4.26593
H -3.04116 -2.04951 -3.54314
C -4.37833 1.91106 -1.54174
C -5.57917 1.35607 -1.14993
C -4.98226 -0.76260 -2.16331
C -5.88594 0.00764 -1.46256
H -4.14507 2.94835 -1.29907
H -6.30027 1.96006 -0.59393
H -6.84090 -0.41853 -1.14577
H -5.21248 -1.80296 -2.40723

**$[Mn^{IV}OH(Por^{\bullet+})Cl]^+$ nucleophilic reaction at $C_1$**

58
RC (1/5)
N 2.16591 0.28378 -1.71088
N 0.56342 2.35830 -0.53280
N 2.25245 -1.10290 0.80411
N 0.58698 0.93606 1.97012
C 2.97673 -0.76809 -2.08595
C -0.20160 3.22623 0.18662
C 2.05638 1.09242 -2.80778
C 0.65896 2.88443 -1.80136
C 3.03089 -1.96554 0.09137
C -0.19226 2.00475 2.35275
C 2.15150 -1.62825 2.07191
C 0.71022 0.13682 3.06815
C 3.36684 -0.61838 -3.46235
C -0.60244 4.34157 -0.63454
C 2.79351 0.53972 -3.91174
C -0.06639 4.12861 -1.87290
C 3.44742 -3.06854 0.92072
C -0.56840 1.86627 3.73653
C 2.89859 -2.85896 2.15408
C -0.00645 0.70224 4.18206
H 4.00274 -1.31611 -4.00395
H -1.21641 5.17271 -0.29289
H 2.86022 0.99222 -4.89929
H -0.14667 4.74740 -2.76461
H 4.07661 -3.89144 0.58696
H -1.18342 2.57742 4.28475
H 2.98226 -3.47275 3.04893
H -0.06239 0.25589 5.17308
C 3.37579 -1.81186 -1.25982
C -0.55983 3.06558 1.53473
C 1.43812 -1.06285 3.12132
C 1.34689 2.30339 -2.85787
H 1.34378 2.83509 -3.81069
H -1.18221 3.84458 1.97765
H 1.44593 -1.59445 4.07422
H 4.01696 -2.57762 -1.69901
C -5.93711 -0.17270 -1.50890
C -6.20628 -1.44697 -1.05259
C -5.18081 -2.24506 -0.46863
C -3.85544 -1.70053 -0.36161
C -3.61047 -0.38108 -0.84179
C -4.62737 0.36480 -1.40250
H -6.43141 -3.97783 -0.06903
H -6.73342 0.42868 -1.95501
H -7.21470 -1.86219 -1.13393
C -5.42245 -3.56395 0.01269
C -2.82673 -2.49652 0.22126
H -2.59831 0.02357 -0.75501
H -4.42818 1.37567 -1.76786
C -3.09572 -3.77111 0.67729
C -4.40517 -4.30967 0.57252
H -1.82131 -2.07287 0.29625
H -2.29933 -4.37333 1.12240
H -4.60445 -5.32041 0.93784
O -0.13700 -0.29672 -0.30259
H -0.10989 -0.65824 -1.20404
Mn 1.37529 0.60904 0.12891
Cl 3.24941 1.75544 0.72955

58
TS (1/5)
N 1.75347 -0.19466 -1.75101
N 0.33894 2.08768 -0.81795
N 1.76915 -1.28330 0.90898
N 0.30767 0.98328 1.83315
C 2.36776 -1.39908 -2.02365
C -0.45278 3.03726 -0.21188
C 1.79794 0.54561 -2.91277
C 0.55549 2.51398 -2.10827
C 2.37312 -2.33392 0.26149
C -0.46509 2.09584 2.06982
C 1.78864 -1.57811 2.25165
C 0.52763 0.38337 3.05312
C 2.77874 -1.42748 -3.40381
C -0.75347 4.08624 -1.15424
C 2.44116 -0.22057 -3.94859
C -0.11708 3.77128 -2.32084
C 2.77165 -3.33104 1.22405
C -0.76213 2.18736 3.47706
C 2.42301 -2.85643 2.45702
C -0.13553 1.13672 4.08701
H 3.27997 -2.26928 -3.87861
H -1.36692 4.95721 -0.92969
H 2.59956 0.13229 -4.96625
H -0.10500 4.32465 -3.25835
H 3.26938 -4.26601 0.97224
H -1.36263 2.97457 3.92980
H 2.56608 -3.32381 3.42985
H -0.12202 0.87601 5.14395
C 2.62754 -2.40936 -1.10495
C -0.85308 3.03580 1.11893
C 1.22994 -0.79918 3.26044
C 1.25784 1.81563 -3.08397
H 1.35486 2.27791 -4.06685
H -1.47107 3.86785 1.45827
H 1.31767 -1.16124 4.28542
H 3.12463 -3.30705 -1.47439
C -5.65090 0.07951 -0.25785
C -5.23080 -1.00342 -1.02322
C -3.98485 -1.62577 -0.76500
C -3.15790 -1.11819 0.28745
C -3.60715 -0.02861 1.05324
C -4.84232 0.56387 0.78453
H -4.18637 -3.15397 -2.29894
H -6.61444 0.55079 -0.46300
H -5.86311 -1.39070 -1.82558
C -3.55158 -2.76821 -1.49761
C -1.87082 -1.73485 0.52785
H -2.98032 0.35602 1.86033
H -5.18085 1.40845 1.38843
C -1.52573 -2.93171 -0.17869
C -2.34448 -3.41442 -1.19031
H -1.37368 -1.52654 1.47459
H -0.59453 -3.44144 0.07369
H -2.05638 -4.31035 -1.74374
O -0.61140 -0.44943 -0.33899
H -0.70055 -0.61063 -1.29460
Mn 1.07773 0.42331 0.04910
Cl 3.02607 1.45332 0.50728

58
PC (1/5)
N 1.94417 0.02325 -1.80161
N 0.33457 2.07417 -0.59272
N 1.94646 -1.43443 0.67401
N 0.28377 0.58631 1.86377
C 2.72037 -1.04042 -2.19849
C -0.42526 2.94557 0.15091
C 1.83364 0.85651 -2.89016
C 0.44534 2.62227 -1.84895
C 2.71977 -2.29776 -0.06592
C -0.45156 1.67736 2.27709
C 1.82317 -1.99084 1.92510
C 0.41038 -0.23858 2.96093
C 3.09943 -0.87987 -3.58155
C -0.81095 4.07440 -0.66181
C 2.54940 0.29499 -4.01029
C -0.27319 3.87311 -1.90147
C 3.09041 -3.43565 0.74085
C -0.82434 1.51773 3.66051
C 2.53439 -3.24602 1.97440
C -0.29251 0.33141 4.08333
H 3.70949 -1.58666 -4.14184
H -1.41989 4.90756 -0.31434
H 2.61420 0.75385 -4.99565
H -0.34812 4.50663 -2.78390
H 3.69817 -4.26933 0.39256
H -1.41739 2.23348 4.22765
H 2.59113 -3.89104 2.84984
H -0.35871 -0.12691 5.06886
C 3.08707 -2.12011 -1.39780
C -0.78851 2.77209 1.48520
C 1.11215 -1.44179 2.99174
C 1.13921 2.06387 -2.92022
H 1.14034 2.61848 -3.85974
H -1.38607 3.55915 1.94740
H 1.11461 -1.99504 3.93205
H 3.70875 -2.89255 -1.85282
C -5.85937 0.06520 -1.09522
C -5.71767 -1.10290 -0.36884
C -4.41822 -1.56441 -0.01285
C -3.26524 -0.80052 -0.38913
C -3.42831 0.37004 -1.12347
C -4.71464 0.79185 -1.47834
H -5.13229 -3.37710 0.90928
H -6.85092 0.42327 -1.37742
H -6.59055 -1.68524 -0.06633
C -4.24141 -2.80039 0.64370
C -1.91060 -1.25956 0.07883
H -2.55197 0.94505 -1.42470
H -4.83197 1.70563 -2.06566
C -1.84167 -2.65082 0.59398
C -2.97060 -3.35021 0.93020
H -1.75778 -0.69007 1.03573
H -0.84309 -3.05896 0.77220
H -2.90119 -4.33701 1.38999
O -0.83314 -0.86640 -0.72891
H -0.83153 -1.36504 -1.56114
Mn 1.31530 0.42215 0.09954
Cl 3.26923 1.57766 0.82152

**$[Mn^{IV}OH(Por^{\bullet+})Cl]^+$ nucleophilic reaction at $C_2$**

58
RC (1/5)
N -1.76694 2.11844 0.63721
N -1.74084 0.54232 -1.77270
N -1.85272 -0.29268 2.19742
N -1.90194 -1.86777 -0.20648
C -1.78900 2.69734 1.88515
C -1.75230 -0.35518 -2.80007
C -1.69729 3.14198 -0.26029
C -1.67075 1.79052 -2.34802
C -1.87574 0.60726 3.22725
C -1.89680 -2.44262 -1.45573
C -1.94159 -1.54214 2.77465
C -1.97147 -2.89409 0.68885
C -1.74004 4.13302 1.76225
C -1.68710 0.33093 -4.06449
C -1.68145 4.40986 0.42575
C -1.63560 1.66793 -3.78293
C -1.96050 -0.07875 4.48792
C -1.97196 -3.87776 -1.33685
C -2.00093 -1.41709 4.20631
C -2.01897 -4.15899 -0.00079
H -1.74765 4.82645 2.60102
H -1.68359 -0.15994 -5.03581
H -1.63131 5.37911 -0.06665
H -1.58118 2.50651 -4.47451
H -1.98865 0.41240 5.45870
H -1.98462 -4.56820 -2.17801
H -2.06994 -2.25479 4.89765
H -2.07850 -5.12908 0.48887
C -1.83995 2.00338 3.08737
C -1.82545 -1.74953 -2.65857
C -1.99088 -2.74778 2.08323
C -1.64853 2.99540 -1.65510
H -1.59252 3.91035 -2.24711
H -1.82810 -2.34031 -3.57596
H -2.05693 -3.66066 2.67735

H -1.85758 2.59274 4.00546
C 7.44964 -2.87589 -1.77724
C 6.14133 -3.20949 -1.49239
C 5.16216 -2.19960 -1.26723
C 5.55896 -0.82011 -1.34148
C 6.91761 -0.51092 -1.63776
C 7.84154 -1.51352 -1.85061
H 3.50398 -3.55980 -0.91481
H 8.19075 -3.66091 -1.94779
H 5.83791 -4.25862 -1.43548
C 3.80346 -2.50938 -0.97083
C 4.58009 0.19041 -1.11609
H 7.21804 0.53909 -1.69401
H 8.88080 -1.26201 -2.07699
C 3.27206 -0.14374 -0.83117
C 2.88019 -1.50636 -0.75804
H 4.88463 1.23930 -1.17308
H 2.52106 0.63073 -0.65769
H 1.83815 -1.74236 -0.53040
O 0.01577 0.06800 0.20115
H 0.38918 -0.10578 1.08112
Mn -1.79333 0.12494 0.21292
Cl -4.07159 0.21164 0.16557

58
TS (1/5)
N -1.03070 1.97851 0.80188
N -1.34872 0.78450 -1.79033
N -1.06696 -0.60466 1.98938
N -1.45725 -1.79896 -0.59090
C -1.00380 2.37690 2.11767
C -1.67911 0.06324 -2.91565
C -0.89199 3.11491 0.03772
C -1.18215 2.09027 -2.18921
C -1.05631 0.14110 3.14986
C -1.76410 -2.17237 -1.87861
C -1.03662 -1.93104 2.36953
C -1.36104 -2.95397 0.14686
C -0.85029 3.80895 2.18621
C -1.70896 0.93961 -4.05880
C -0.76441 4.26296 0.90104
C -1.38560 2.19030 -3.61222
C -0.99783 -0.73928 4.28741
C -1.86464 -3.60868 -1.95406
C -0.96852 -2.01776 3.80518
C -1.59987 -4.09329 -0.70425
H -0.80038 4.37910 3.11233
H -1.94016 0.62066 -5.07376
H -0.63839 5.28578 0.54994
H -1.30517 3.11427 -4.18240
H -0.97301 -0.40478 5.32315
H -2.09685 -4.16301 -2.86186
H -0.92371 -2.95166 4.36296
H -1.57865 -5.12858 -0.36811
C -1.04583 1.52963 3.21974
C -1.89245 -1.31082 -2.96341
C -1.13515 -3.02557 1.51861
C -0.93290 3.17300 -1.35047
H -0.82117 4.15303 -1.81585
H -2.13890 -1.75009 -3.93070
H -1.09424 -4.01733 1.97049
H -1.02294 1.98528 4.21026
C 6.58864 0.07773 0.53607
C 5.73616 -1.03131 0.50678
C 4.48920 -0.95714 -0.12999
C 4.09716 0.28126 -0.75308
C 4.98949 1.39399 -0.71357
C 6.21517 1.29050 -0.07584
H 3.91926 -3.02992 0.24743
H 7.55640 -0.00024 1.03661
H 6.04184 -1.96653 0.98171
C 3.59144 -2.08561 -0.19450
C 2.85034 0.35522 -1.39571
H 4.68919 2.32900 -1.19230
H 6.89329 2.14569 -0.04750
C 1.94145 -0.75465 -1.38308
C 2.37480 -2.00108 -0.80946
H 2.54674 1.27861 -1.89297
H 1.13992 -0.76713 -2.12082
H 1.71620 -2.86864 -0.87098
O 0.66035 -0.01498 -0.07868
H 1.08296 -0.15609 0.78704
Mn -1.27402 0.09725 0.11061
Cl -3.50904 0.25595 0.31521

58
PC (1/5)
N -1.01252 1.85267 0.87433
N -0.82297 0.43814 -1.62057
N -1.74849 -0.58748 2.20335
N -1.62855 -1.98711 -0.30260
C -1.11890 2.34598 2.15311
C -0.85582 -0.38808 -2.72583
C -0.64788 2.90868 0.07432
C -0.52406 1.70270 -2.08609
C -1.75954 0.24572 3.29715
C -1.50889 -2.48374 -1.57831
C -2.09709 -1.83759 2.65798
C -1.98625 -3.04480 0.49940
C -0.80620 3.75518 2.16093
C -0.52968 0.36825 -3.90826
C -0.51537 4.10428 0.87258
C -0.32473 1.66123 -3.51284
C -2.11459 -0.50313 4.47845
C -1.79539 -3.89871 -1.58137
C -2.32372 -1.79393 4.08249
C -2.09040 -4.24643 -0.29371
H -0.81126 4.38515 3.04909
H -0.47286 -0.04843 -4.91266
H -0.23194 5.08062 0.48241
H -0.06547 2.52257 -4.12652
H -2.18944 -0.08094 5.47936
H -1.76753 -4.53373 -2.46550
H -2.60563 -2.65190 4.69086
H -2.35521 -5.22655 0.09998
C -1.46871 1.60828 3.28174
C -1.15886 -1.74699 -2.70909
C -2.21039 -2.98303 1.87285
C -0.42654 2.84899 -1.30128
H -0.16249 3.77956 -1.80585
H -1.12654 -2.27825 -3.66143
H -2.49405 -3.90867 2.37581
H -1.51646 2.14086 4.23272
C 6.86961 0.54955 -1.41214
C 6.06292 -0.57551 -1.55313
C 4.73766 -0.56041 -1.08949
C 4.24066 0.65775 -0.46862
C 5.10579 1.79571 -0.33250
C 6.39704 1.73879 -0.79963
H 4.30269 -2.63306 -1.61223
H 7.89797 0.51609 -1.78008
H 6.45880 -1.47807 -2.02235
C 3.88521 -1.71957 -1.18355
C 2.95005 0.67907 0.02583
H 4.71456 2.69924 0.13945
H 7.06076 2.59982 -0.70634
C 2.00979 -0.43189 -0.21207
C 2.60750 -1.69292 -0.73129
H 2.56173 1.55610 0.55185
H 1.47857 -0.02067 -1.12360
H 1.95057 -2.56293 -0.79350
O 0.98961 -0.57166 0.73921
H 1.33714 -0.96820 1.55321
Mn -1.52136 -0.02572 0.25445
Cl -3.80662 0.48306 -0.19005

**[Mn$^{IV}$OH(Por$^{+\bullet}$)OTf]$^{+}$ electrophilic reaction at $C_1$**

66
RC (0/5)
O -1.21823 -0.60657 -0.23640
N 0.05205 1.49078 1.03304
N -0.05489 -1.12248 2.17338
N 1.02358 0.37776 -1.40871
N 1.00122 -2.22727 -0.23522
C 0.27154 2.66691 0.35574
C 0.17228 -2.40288 2.62816
C -0.61367 1.81401 2.19316
C -0.67635 -0.43799 3.19360
C 1.13712 1.70619 -1.74242
C 1.06024 -3.36262 0.53731
C 1.35501 -0.34626 -2.53002
C 1.31808 -2.59704 -1.52015
C -0.24086 3.77015 1.12912
C -0.32737 -2.52828 3.97306
C -0.80654 3.24111 2.25488
C -0.87214 -1.32122 4.31365
C 1.56737 1.82364 -3.11353
C 1.44635 -4.48328 -0.28460
C 1.68157 0.55540 -3.60642
C 1.58481 -4.01393 -1.56048
H -0.18493 4.81389 0.82455
H -0.27417 -3.43933 4.56688
H -1.30169 3.76078 3.07352
H -1.34743 -1.03261 5.24973
H 1.73625 2.76879 -3.62670
H 1.57340 -5.50082 0.08141
H 1.97381 0.23971 -4.60645
H 1.86148 -4.56333 -2.45885
C 0.81905 2.78005 -0.91771
C 0.71846 -3.44401 1.88363
C 1.45654 -1.73174 -2.60161
C -0.98108 0.91951 3.19202
H -1.48484 1.32392 4.07073
H 0.82188 -4.41297 2.37346
H 1.73109 -2.16754 -3.56298
H 0.94463 3.78369 -1.32551
Mn 0.45838 -0.37684 0.37214
H -1.68351 -1.25384 0.31996
C -6.12485 -0.22418 -3.84208
C -5.22422 -1.12235 -4.39639
C -3.96950 -1.32334 -3.79696
C -3.60703 -0.60813 -2.63916
C -4.54034 0.29388 -2.02896
C -5.81295 0.50078 -2.65251
H -2.68747 -0.84682 -2.10285
H -3.26177 -2.03387 -4.22765
Cl -2.06872 0.90440 -4.04989
H -5.48911 -1.67502 -5.30021
H -7.09964 -0.06620 -4.31123
C -4.23383 0.97951 -0.83019
C -5.15282 1.85464 -0.26873
C -6.73075 1.40413 -2.05760
C -6.40435 2.07041 -0.88679
H -3.26100 0.80666 -0.36319
H -4.90786 2.38191 0.65636
H -7.11858 2.76401 -0.43674
H -7.70164 1.56482 -2.53320
O 2.35225 -0.20315 0.98875
S 3.05944 0.73391 1.97830
O 2.45622 0.74838 3.31440
O 3.45154 2.01149 1.37651
C 4.65185 -0.23004 2.17134
F 5.44952 0.41405 3.02287
F 4.40406 -1.44736 2.65222
F 5.27646 -0.34597 1.00139

66
TS (0/5)
O -2.26226 3.21314 1.66622
N -0.65100 5.11674 3.02967
N -1.17124 2.52084 4.15301
N 0.22562 3.87585 0.58836
N -0.20341 1.27445 1.74950
C -0.37644 6.25568 2.31131
C -1.28901 1.20475 4.54265
C -1.16357 5.52183 4.23857
C -1.57881 3.29088 5.21914
C 0.39638 5.18816 0.22044
C -0.48264 0.13515 2.46355
C 0.60475 3.10723 -0.48619
C 0.22363 0.87304 0.50729
C -0.70396 7.41702 3.10183
C -1.79584 1.14556 5.89047
C -1.19352 6.96298 4.29358
C -1.97816 2.43459 6.30707
C 0.90129 5.25097 -1.12914
C -0.20349 -1.02584 1.65236
C 1.02878 3.96319 -1.56745
C 0.23074 -0.56895 0.44048
H -0.57377 8.44580 2.76985
H -1.98157 0.22349 6.43902
H -1.54802 7.54064 5.14573
H -2.34308 2.79050 7.26920
H 1.12614 6.17374 -1.66155
H -0.33275 -2.05529 1.98276
H 1.38197 3.60721 -2.53396
H 0.53431 -1.14459 -0.43252
C 0.12233 6.29859 1.01358
C -0.97303 0.09327 3.76614
C 0.60214 1.71543 -0.53475
C -1.59032 4.68196 5.26252
H -1.95648 5.15099 6.17669
H -1.13307 -0.88971 4.21112
H 0.92917 1.24676 -1.46394
H 0.30060 7.28223 0.57731
Mn -0.50051 3.19794 2.35927
H -2.85898 2.83073 2.33231
C -6.50644 2.53993 -1.41442
C -5.28373 2.38384 -2.08518
C -4.14250 3.01666 -1.63457
C -4.13597 3.83316 -0.41403
C -5.45044 3.99331 0.28054
C -6.60861 3.33638 -0.23170
H -3.35971 3.45632 0.32445
H -3.19807 2.91237 -2.17317
Cl -3.37280 5.50453 -0.81949
H -5.23794 1.76415 -2.98371
H -7.40468 2.04971 -1.79736
C -5.55104 4.73921 1.46262
C -6.77116 4.86095 2.12680
C -7.84171 3.47790 0.45742
C -7.92279 4.23226 1.61783
H -4.65942 5.23086 1.85726
H -6.83156 5.44690 3.04698
H -8.87666 4.33350 2.14060
H -8.72730 2.97416 0.06182
O 1.48186 3.08412 3.08601
S 2.37872 4.05692 3.83355
O 1.93942 4.33728 5.20765
O 2.83507 5.19222 3.01974
C 3.89818 2.98402 4.03675
F 4.84178 3.66562 4.69039
F 3.61034 1.88362 4.73411
F 4.38382 2.62092 2.84843

66
PC (0/5)
O -1.44229 0.83195 0.02228
N 0.97010 1.88182 1.56101
N -0.00827 -0.76000 2.13940
N 1.33660 1.14131 -1.19657
N 0.41596 -1.51804 -0.60675
C 1.42536 3.08987 1.08736
C -0.42243 -2.06991 2.22618
C 0.71705 2.05105 2.90211
C -0.10829 -0.22787 3.40430
C 1.75296 2.44967 -1.28162
C -0.07108 -2.71662 -0.13933
C 1.48144 0.59643 -2.45201
C 0.67980 -1.69080 -1.94554
C 1.46477 4.04924 2.16355
C -0.80808 -2.36749 3.58370
C 1.02759 3.40582 3.28718
C -0.61301 -1.22769 4.31269
C 2.15999 2.74236 -2.63403
C -0.11717 -3.67433 -1.21701
C 1.99394 1.59500 -3.35794
C 0.34931 -3.03957 -2.33495
H 1.78857 5.08351 2.05814
H -1.17687 -3.33391 3.92395
H 0.91768 3.80246 4.29526
H -0.78933 -1.06487 5.37478
H 2.52896 3.70919 -2.97283
H -0.46227 -4.70225 -1.11659
H 2.19766 1.42504 -4.41401
H 0.46432 -3.43841 -3.34165
C 1.79000 3.36141 -0.22897
C -0.46049 -2.98089 1.17260
C 1.17896 -0.71612 -2.80748
C 0.22188 1.07657 3.76491
H 0.08049 1.35790 4.80936
H -0.82024 -3.98670 1.39426
H 1.34150 -1.00323 -3.84726
H 2.14062 4.36981 -0.45317
Mn 0.73998 0.16961 0.48780
H -2.09397 0.33063 0.53565
C -6.13779 -2.36085 -1.98731
C -4.85195 -2.85629 -2.00689
C -3.76434 -2.01678 -2.35349
C -3.99975 -0.69672 -2.67150
C -5.30982 -0.12863 -2.66730
C -6.39955 -1.00007 -2.31269
H -1.72781 0.73397 -0.90366
H -2.74643 -2.40947 -2.36844
Cl -2.61880 0.31775 -3.10241
H -4.65618 -3.90124 -1.75612
H -6.97679 -3.00813 -1.72039
C -5.59133 1.22877 -2.98858
C -6.88598 1.70525 -2.96157
C -7.72134 -0.47002 -2.29694
C -7.96194 0.85033 -2.61317
H -4.76716 1.89059 -3.25735
H -7.08433 2.75047 -3.21082
H -8.98188 1.24187 -2.59630
H -8.54640 -1.13446 -2.02739
O 2.76507 -0.51680 0.91895
S 3.88910 0.08848 1.72960
O 3.63545 0.11267 3.17855
O 4.47666 1.29592 1.12864
C 5.20453 -1.22275 1.51234
F 6.31088 -0.86914 2.17220
F 4.78653 -2.39790 1.98945
F 5.51368 -1.37548 0.22224

66
RC (0/3)
O -0.99751 -0.96128 -0.55488
N -0.23178 1.31007 0.81185
N -0.06192 -1.28382 1.98637
N 1.18714 0.36385 -1.47147
N 1.42416 -2.21216 -0.25934
C -0.10626 2.50894 0.14998
C 0.31409 -2.50708 2.49518
C -1.07686 1.52527 1.87613
C -0.91057 -0.70924 2.90497
C 1.13595 1.69278 -1.81465
C 1.58214 -3.31771 0.54224
C 1.73659 -0.30601 -2.53965
C 1.93466 -2.53271 -1.49462
C -0.86892 3.51982 0.83866
C -0.32175 -2.70955 3.77185
C -1.48644 2.90722 1.89253
C -1.09742 -1.60976 4.01326
C 1.68487 1.87066 -3.13596
C 2.23164 -4.36468 -0.20722
C 2.03672 0.63254 -3.59276
C 2.42857 -3.88740 -1.47275
H -0.93140 4.56154 0.52850
H -0.19343 -3.59699 4.38948
H -2.15180 3.34373 2.63557
H -1.72713 -1.40173 4.87674
H 1.76439 2.82956 -3.64510
H 2.48152 -5.34548 0.19417
H 2.47914 0.36289 -4.55036
H 2.88598 -4.39036 -2.32328
C 0.56710 2.70621 -1.05042
C 1.10737 -3.44701 1.84409
C 2.05205 -1.66072 -2.57342
C -1.42492 0.58190 2.83697
H -2.09123 0.90197 3.63895
H 1.30954 -4.38361 2.36502
H 2.49050 -2.05237 -3.49208
H 0.58419 3.71674 -1.45968
Mn 0.53648 -0.46920 0.24416
H -1.36184 -1.74756 -0.11457
C -5.99195 -0.04382 -3.94388
C -4.99791 -0.59995 -4.73611
C -3.71777 -0.82891 -4.20423
C -3.42530 -0.48491 -2.87004
C -4.45133 0.05345 -2.02476
C -5.75046 0.29309 -2.57783
H -2.47420 -0.76893 -2.41707
H -2.93637 -1.27247 -4.82384
Cl -2.10967 1.57581 -3.69223
H -5.20895 -0.86082 -5.77529
H -6.98680 0.13662 -4.35971
C -4.21026 0.35018 -0.66289
C -5.21962 0.88013 0.12835
C -6.76157 0.83881 -1.74593
C -6.49886 1.12855 -0.41607
H -3.21571 0.15690 -0.25365
H -5.02449 1.10805 1.17891
H -7.28480 1.54835 0.21626
H -7.75312 1.02389 -2.16693
O 2.29395 0.00127 1.07520
S 2.72404 1.01605 2.14386
O 1.96711 0.91667 3.39543
O 2.98821 2.34845 1.59354
C 4.40830 0.29961 2.53378
F 4.98872 1.04072 3.47727
F 4.29038 -0.94967 2.98123
F 5.18227 0.29966 1.45056

66
TS (0/3)
O-2.262263.213141.66622
N-0.651005.116743.02967
N-1.171242.520844.15301
N0.225623.875850.58836
N-0.203411.274451.74950
C-0.376446.255682.31131
C-1.289011.204754.54265
C-1.163575.521834.23857
C-1.578813.290885.21914
C0.396385.188160.22044
C-0.482640.135152.46355
C0.604753.10723-0.48619
C0.223630.873040.50729
C-0.703967.417023.10183
C-1.795841.145565.89047
C-1.193526.962984.29358
C-1.978162.434596.30707
C0.901295.25097-1.12914
C-0.20349-1.025841.65236
C1.028783.96319-1.56745
C0.23074-0.568950.44048
H-0.573778.445802.76985
H-1.981570.223496.43902
H-1.548027.540645.14573
H-2.343082.790507.26920
H1.126146.17374-1.66155
H-0.33275-2.055291.98276
H1.381973.60721-2.53396
H0.53431-1.14459-0.43252
C0.122336.298591.01358
C-0.973030.093273.76614
C0.602141.71543-0.53475
C-1.590324.681965.26252
H-1.956485.150996.17669
H-1.13307-0.889714.21112
H0.929171.24676-1.46394
H0.300607.282230.57731
Mn-0.500513.197942.35927
H-2.858982.830732.33231
C-6.506442.53993-1.41442
C-5.283732.38384-2.08518
C-4.142503.01666-1.63457
C-4.135973.83316-0.41403
C-5.450443.993310.28054
C-6.608613.33638-0.23170
H-3.359713.456320.32445
H-3.198072.91237-2.17317
Cl-3.372805.50453-0.81949

H-5.237941.76415-2.98371
H-7.404682.04971-1.79736
C-5.551044.739211.46262
C-6.771164.860952.12680
C-7.841713.477900.45742
C-7.922794.232261.61783
H-4.659425.230861.85726
H-6.831565.446903.04698
H-8.876664.333502.14060
H-8.727302.974160.06182
O1.481863.084123.08601
S2.378724.056923.83355
O1.939424.337285.20765
O2.835075.192223.01974
C3.898182.984024.03675
F4.841783.665624.69039
F3.610341.883624.73411
F4.383822.620922.84843

66
PC (0/3)
O -1.36508 -0.11892 0.50608
N 0.49969 1.70442 1.60170
N 0.38977 -1.02258 2.50213
N 0.78869 0.80902 -1.09879
N 0.69473 -1.92445 -0.19938
C 0.57044 2.93604 0.99442
C 0.40558 -2.37391 2.74866
C 0.30500 1.94268 2.94207
C 0.22757 -0.40711 3.71837
C 0.84520 2.16107 -1.33841
C 0.67524 -3.15508 0.41445
C 0.93067 0.19177 -2.31850
C 0.84796 -2.16274 -1.54428
C 0.42306 3.98022 1.97916
C 0.24354 -2.61951 4.16310
C 0.25525 3.36365 3.18737
C 0.12809 -1.39822 4.76448
C 1.01909 2.40510 -2.75075
C 0.80625 -4.20001 -0.57282
C 1.07206 1.18294 -3.35927
C 0.91109 -3.58432 -1.78888
H 0.44311 5.04677 1.75973
H 0.22063 -3.60663 4.62270
H 0.11014 3.81926 4.16586
H -0.00787 -1.17322 5.82137
H 1.09073 3.39214 -3.20543
H 0.81637 -5.26610 -0.35021
H 1.19720 0.95759 -4.41743
H 1.02729 -4.04049 -2.77103
C 0.73860 3.15763 -0.37069
C 0.54234 -3.37226 1.78506
C 0.95040 -1.18562 -2.53437
C 0.17366 0.96917 3.92941
H 0.03111 1.31319 4.95522
H 0.53985 -4.40727 2.13105
H 1.07377 -1.52808 -3.56328
H 0.78832 4.19396 -0.70879
Mn 0.66285 -0.10535 0.71165
H -1.68873 -1.02297 0.35688
C -5.22973 -2.16855 -3.67711
C -3.86267 -2.25038 -3.52382
C -3.12910 -1.14556 -3.02473
C -3.79341 0.01409 -2.68860
C -5.20752 0.15625 -2.82469
C -5.93156 -0.97790 -3.33671
H -1.68955 0.40725 -0.25263
H -2.04625 -1.21001 -2.90577
Cl -2.84714 1.37594 -2.07499
H -3.32834 -3.16619 -3.78609
H -5.79572 -3.01972 -4.06346
C -5.92713 1.33687 -2.48795
C -7.29607 1.39749 -2.64960
C -7.34380 -0.87511 -3.48876
C -8.01271 0.28334 -3.15454
H -5.38129 2.19701 -2.09848
H -7.83300 2.31191 -2.38607
H -9.09660 0.34637 -3.27723
H -7.89025 -1.73807 -3.87799
O 2.57646 -0.19722 0.87473
S 3.61016 0.74757 1.51749
O 3.50164 0.82943 2.97564
O 3.81988 1.98226 0.75820
C 5.12999 -0.29489 1.19344
F 6.19759 0.34248 1.67296
F 5.02668 -1.47606 1.79869
F 5.29659 -0.49003 -0.11277

**[Mn$^{IV}$OH(Por$^{\bullet+}$)OTf]$^+$ nucleophilic reaction at $C_1$**

66
RC (0/5)
O 0.20911 0.22051 -1.16707
N -0.99515 0.76596 1.25083
N -2.17846 -0.99023 -0.65847
N 1.45118 -0.68763 1.06033
N 0.23628 -2.49783 -0.78430
C -0.29794 1.42735 2.23392
C -2.65218 -2.05619 -1.39084
C -2.16054 1.46656 1.04336
C -3.19855 -0.06914 -0.58180
C 1.80842 0.15801 2.08209
C -0.55501 -3.34697 -1.52015
C 2.57463 -1.40392 0.72011
C 1.52555 -2.96361 -0.87889
C -1.06479 2.56133 2.68639
C -4.01076 -1.79428 -1.79154
C -2.20538 2.59886 1.93470
C -4.33955 -0.55639 -1.31277
C 3.19887 -0.04050 2.40766
C 0.25972 -4.39739 -2.08037
C 3.67831 -0.99077 1.55149
C 1.54917 -4.14721 -1.70294
H -0.74529 3.24754 3.46894
H -4.62105 -2.47683 -2.38071
H -3.02395 3.31532 1.98028
H -5.28043 -0.01834 -1.41581
H 3.73283 0.50367 3.18481
H -0.11989 -5.20764 -2.70077
H 4.68496 -1.40068 1.48741
H 2.44698 -4.71676 -1.93764
C 0.98947 1.12167 2.66125
C -1.91346 -3.17353 -1.76870
C 2.62705 -2.43907 -0.20841
C -3.17934 1.10153 0.16995
H -4.06037 1.74296 0.12590
H -2.41929 -3.93264 -2.36664
H 3.59161 -2.92178 -0.37017
H 1.41625 1.73532 3.45514
Mn -0.35477 -0.82238 0.17818
H -0.35517 0.08884 -1.94744
C 3.30759 3.98514 -4.17450
C 3.28427 2.63069 -3.87312
C 2.40957 2.14459 -2.88782
C 1.56557 3.02529 -2.18386
C 1.54501 4.42190 -2.50884
C 2.44471 4.90940 -3.51126
H 0.80708 2.60725 -1.52205
H 2.36380 1.08067 -2.65003
Cl 3.09705 2.91599 -0.12321
H 3.94361 1.94087 -4.40413
H 3.98917 4.36373 -4.94085
C 0.66562 5.32615 -1.87031
C 0.67675 6.67317 -2.20241
C 2.43762 6.29223 -3.82824
C 1.56868 7.15849 -3.18402
H -0.01721 4.95068 -1.10426
H -0.00616 7.36397 -1.70233
H 1.57054 8.22152 -3.43611
H 3.12511 6.66532 -4.59167
O -0.92144 -2.06096 1.64724
S -1.90790 -1.93499 2.81574
O -3.24979 -1.49942 2.41649
O -1.30713 -1.33225 4.00912
C -2.08595 -3.75380 3.21825
F -2.93545 -3.89389 4.23577
F -2.56270 -4.41880 2.16671
F -0.91151 -4.27696 3.56418

66
TS (0/5)
O 0.66763 1.14917 -1.42809
N -0.99829 1.10260 1.16926
N -1.84128 -0.41934 -1.12246
N 1.48788 -0.33385 1.20603
N 0.61456 -1.90909 -1.03646
C -0.42441 1.72806 2.25179
C -2.09039 -1.27390 -2.17296
C -2.21640 1.70792 0.96252
C -2.94919 0.38799 -0.99820
C 1.71028 0.47825 2.29609
C 0.03162 -2.54654 -2.10724
C 2.59994 -1.13633 1.07838
C 1.85366 -2.48095 -0.86201
C -1.30920 2.75370 2.74586
C -3.38707 -0.98744 -2.73466
C -2.41743 2.74278 1.94596
C -3.91707 0.04293 -2.00944
C 3.00537 0.19018 2.85984
C 0.92800 -3.55363 -2.61994
C 3.55670 -0.80732 2.10528
C 2.05680 -3.51162 -1.85052
H -1.09476 3.39692 3.59785
H -3.82545 -1.51709 -3.57899
H -3.30211 3.37469 2.00572
H -4.88113 0.53343 -2.13435
H 3.42764 0.69519 3.72711
H 0.70897 -4.20233 -3.46665
H 4.52464 -1.29133 2.22520
H 2.95657 -4.11917 -1.93368
C 0.82912 1.43919 2.78551
C -1.22606 -2.26358 -2.63568
C 2.78071 -2.12751 0.11640
C -3.12633 1.38279 -0.03999
H -4.05900 1.94773 -0.07171
H -1.55794 -2.86113 -3.48590
H 3.72221 -2.67821 0.13640
H 1.14777 2.01407 3.65609
Mn -0.21992 -0.44865 0.10830
H 0.16211 1.27405 -2.24638
C 1.99481 2.85475 -4.15896
C 2.64086 1.71997 -3.82778
C 2.87301 1.36393 -2.39522
C 1.84370 1.97743 -1.43529
C 1.47642 3.40324 -1.78781
C 1.49018 3.79081 -3.14855
H 2.23536 1.91896 -0.41207
H 2.90148 0.27959 -2.23649
Cl 4.56242 1.94067 -1.89820
H 3.04889 1.05737 -4.59467
H 1.85940 3.12238 -5.21078
C 1.02815 4.29865 -0.81335
C 0.59464 5.58024 -1.17210
C 1.04152 5.07612 -3.49823
C 0.59874 5.96606 -2.51697
H 1.01608 3.99132 0.23585
H 0.25077 6.27488 -0.40206
H 0.25720 6.96426 -2.80168
H 1.05040 5.37820 -4.54891
O -1.08536 -1.95005 1.40162
S -2.00705 -1.85527 2.59925
O -3.35753 -1.37158 2.27513
O -1.36399 -1.30695 3.80283
C -2.24262 -3.67018 2.98312
F -3.04996 -3.80782 4.03799
F -2.79123 -4.30626 1.94539
F -1.07415 -4.25022 3.26673

**[Mn$^{IV}$OH(Por$^{\bullet+}$)OTf]$^+$ nucleophilic reaction at $C_2$**

66
RC (0/5)
N -0.10375 -0.44475 1.72476
N -0.04187 1.92764 0.15217
N -0.99182 -1.92512 -0.54589
N -0.98585 0.45433 -2.10551
C 0.01686 -1.70739 2.25868
C 0.08719 2.91685 -0.79437
C 0.19045 0.44648 2.72988
C 0.22683 2.50036 1.37088
C -0.77372 -2.98502 0.30350
C -0.72440 1.64261 -2.74593
C -1.63246 -2.42390 -1.65761
C -1.61031 -0.36632 -3.01520
C 0.38991 -1.60752 3.64723
C 0.45466 4.15383 -0.14958
C 0.47391 -0.27623 3.94426
C 0.51943 3.90091 1.19103
C -1.26939 -4.19430 -0.30245
C -1.19199 1.56597 -4.10760
C -1.82276 -3.84381 -1.50255
C -1.76102 0.33320 -4.26684
H 0.54720 -2.46004 4.30591
H 0.62067 5.09491 -0.67137
H 0.72648 0.19156 4.89438
H 0.76438 4.58726 1.99971
H -1.21782 -5.17983 0.15745
H -1.10850 2.37252 -4.83426
H -2.30688 -4.48419 -2.23809
H -2.22934 -0.08769 -5.15511
C -0.25967 -2.89727 1.59374
C -0.19047 2.78270 -2.15128
C -1.95782 -1.69670 -2.79880
C 0.29935 1.82501 2.58478
H 0.53982 2.40884 3.47375
H -0.04927 3.66048 -2.78313
H -2.45200 -2.22837 -3.61280
H -0.13909 -3.82632 2.15220
C 6.11901 -2.98575 1.25462
C 6.96844 -2.00135 0.77406
C 6.44532 -0.84118 0.14760
C 5.02545 -0.69872 0.02591
C 4.17987 -1.72043 0.51797
C 4.71974 -2.84645 1.12319
H 8.37279 0.06442 -0.29212
H 6.53221 -3.87570 1.73527
H 8.05178 -2.11095 0.86920
C 7.28955 0.18022 -0.38357
C 4.49666 0.48063 -0.59572
H 3.09881 -1.59964 0.41448
H 4.05969 -3.63039 1.50204
C 5.36892 1.44851 -1.13064
C 6.76099 1.29661 -1.01532
H 4.95105 2.32225 -1.63383
H 7.42640 2.05963 -1.42458
O 1.22018 -0.33376 -0.68551
H 1.24514 -0.99732 -1.39530
Mn -0.48228 -0.00677 -0.20680
Cl 3.95414 2.06752 1.36740
H 3.42367 0.53083 -0.78770
O -2.38872 0.40964 0.23418
S -3.30726 0.04774 1.40971
O -3.17580 0.96894 2.54204
O -3.37960 -1.39017 1.68603
C -4.94599 0.47522 0.61348
F -5.92815 0.23045 1.48053
F -4.98314 1.76210 0.27431
F -5.14133 -0.26528 -0.47666

66
TS (0/5)
N -0.03923 -0.62342 1.50207
N -0.31002 1.96390 0.27939
N -0.73915 -1.86512 -0.99036
N -1.11231 0.72096 -2.18808
C 0.07802 -1.93571 1.89449
C -0.52281 3.10173 -0.46265
C 0.33808 0.14808 2.57564
C 0.08188 2.37232 1.53177
C -0.55969 -3.00512 -0.23804
C -1.19502 2.03258 -2.58757
C -1.13722 -2.27412 -2.24481
C -1.42808 -0.04927 -3.28035
C 0.51808 -1.99357 3.26645
C -0.25650 4.26455 0.34809
C 0.68025 -0.70434 3.68739
C 0.11934 3.81308 1.58159
C -0.83915 -4.16446 -1.04599
C -1.59443 2.09263 -3.97343
C -1.19565 -3.71294 -2.28582
C -1.73833 0.80409 -4.40237
H 0.68098 -2.91488 3.82330
H -0.35163 5.29244 0.00187
H 1.00353 -0.34460 4.66283
H 0.39635 4.39250 2.46079
H -0.77215 -5.19200 -0.69232
H -1.74012 3.01488 -4.53361
H -1.48235 -4.29248 -3.16185
H -2.02751 0.44509 -5.38880
C -0.17400 -3.04732 1.09793
C -0.93282 3.14398 -1.79206
C -1.45129 -1.44040 -3.31367
C 0.39154 1.53743 2.60125
H 0.69698 2.01108 3.53505
H -1.05247 4.12728 -2.24875
H -1.73917 -1.91634 -4.25192
H -0.05668 -4.03056 1.55510
C 5.54824 -2.16471 2.26763
C 5.48693 -2.34009 0.89006
C 4.94400 -1.33338 0.05579
C 4.47516 -0.12602 0.64831
C 4.53923 0.03077 2.03798
C 5.06608 -0.97892 2.84625
H 5.19504 -2.44667 -1.80403
H 5.96655 -2.95081 2.90071
H 5.84931 -3.26574 0.43537
C 4.81135 -1.52390 -1.36198
C 3.97129 0.97201 -0.22496
H 4.18107 0.95952 2.48930
H 5.10601 -0.84332 3.92955
C 3.66800 0.59711 -1.61782
C 4.15902 -0.58378 -2.16223
H 3.17133 1.33787 -2.24396
H 4.01253 -0.78795 -3.22559
O 1.27128 0.03804 -0.88988
H 1.47972 -0.84390 -1.24189
Mn -0.50072 0.04994 -0.36326
Cl 5.38794 2.31160 -0.36746
H 3.18703 1.57303 0.24213
O -2.51690 0.11124 0.13781
S -3.29186 -0.18033 1.41691
O -3.03780 0.78171 2.49703
O -3.34030 -1.60592 1.76662
C -5.01847 0.22154 0.81861
F -5.88807 0.02850 1.81211
F -5.09717 1.49322 0.42526
F -5.35866 -0.56457 -0.20336

66
PC (0/5)
N -0.56917 -0.47449 1.85806
N -0.37445 1.97235 0.35723
N -0.73306 -1.96303 -0.59087
N -0.60181 0.49155 -2.09013
C -0.67809 -1.73521 2.39836
C -0.36400 3.03519 -0.51889
C -0.42015 0.39632 2.91270
C -0.27251 2.50329 1.62320
C -0.83714 -3.01719 0.28875
C -0.54495 1.75641 -2.62983
C -0.79695 -2.49777 -1.85815
C -0.67261 -0.38707 -3.14713
C -0.60177 -1.65571 3.83587
C -0.23860 4.26913 0.21619
C -0.43768 -0.33676 4.15409
C -0.17733 3.93953 1.54121
C -0.95793 -4.25195 -0.44541
C -0.58152 1.67256 -4.06892
C -0.92946 -3.93102 -1.77389
C -0.65660 0.34561 -4.38918
H -0.66231 -2.51161 4.50619
H -0.20231 5.25807 -0.23800
H -0.33745 0.11471 5.13986
H -0.08242 4.60234 2.39981
H -1.05112 -5.23589 0.01158
H -0.54879 2.53014 -4.73905
H -0.99672 -4.59698 -2.63272
H -0.70105 -0.11109 -5.37667
C -0.81398 -2.91894 1.67780
C -0.44462 2.94314 -1.90648
C -0.75946 -1.77405 -3.04781
C -0.27807 1.77778 2.81192
H -0.18019 2.33992 3.74163
H -0.41556 3.87481 -2.47311

H -0.81582 -2.33931 -3.97915
H -0.89839 -3.84555 2.24713
C 6.82655 -2.41099 0.26778
C 6.13851 -2.03951 -0.88985
C 5.14647 -1.04577 -0.84591
C 4.86107 -0.41292 0.38758
C 5.55147 -0.79432 1.54210
C 6.53001 -1.79244 1.48736
H 4.71529 -1.07957 -3.00043
H 7.59387 -3.18747 0.21943
H 6.36233 -2.52924 -1.84133
C 4.37963 -0.67502 -2.04103
C 3.85596 0.70379 0.40977
H 5.32663 -0.30019 2.49122
H 7.06274 -2.08411 2.39555
C 2.75586 0.58859 -0.65602
C 3.28191 0.10117 -1.98047
H 2.27484 1.56991 -0.75823
H 2.70234 0.33287 -2.87722
O 1.71705 -0.28523 -0.17311
H 1.96531 -1.20879 -0.33668
Mn -0.65956 0.01570 -0.11334
Cl 4.73897 2.30586 0.12817
H 3.39035 0.81292 1.39633
O -2.81321 0.20338 -0.11727
S -3.84296 0.11516 0.98962
O -3.74272 1.19358 1.98445
O -4.05935 -1.24985 1.49208
C -5.39846 0.50996 0.02979
F -6.45344 0.48318 0.84815
F -5.32053 1.72426 -0.51954
F -5.59490 -0.38371 -0.94229

**[Mn$^{IV}$OH(Por$^{+\bullet}$)OTf]$^{+}$ without Cl$^{-}$, electrophilic reaction at C$_1$**

65
RC (1/5)
O -1.79670 -0.56863 0.44566
N -0.53446 1.67602 1.42036
N -0.17780 -0.89016 2.63047
N 0.06753 0.54678 -1.13998
N 0.51850 -2.00614 0.08955
C -0.60465 2.82142 0.68745
C 0.22178 -2.14468 3.06063
C -0.96319 1.99730 2.69644
C -0.59371 -0.21264 3.74030
C -0.04819 1.87111 -1.52629
C 0.78598 -3.10392 0.84998
C 0.30388 -0.16942 -2.27180
C 0.68351 -2.38687 -1.22768
C -1.06234 3.91351 1.50947
C 0.03431 -2.24458 4.48614
C -1.29971 3.39944 2.75194
C -0.48571 -1.05186 4.90440
C 0.12635 1.97020 -2.95688
C 1.14452 -4.21796 0.00770
C 0.33183 0.70253 -3.42024
C 1.06768 -3.77695 -1.28284
H -1.19138 4.93639 1.16085
H 0.26792 -3.12805 5.07748
H -1.65792 3.91236 3.64267
H -0.76075 -0.74766 5.91247
H 0.08440 2.90104 -3.51943
H 1.40970 -5.20824 0.37315
H 0.49992 0.37157 -4.44321
H 1.26431 -4.32631 -2.20171
C -0.33394 2.92964 -0.68899
C 0.68213 -3.16614 2.25014
C 0.55493 -1.55570 -2.32607
C -1.00941 1.13019 3.76919
H -1.34881 1.52726 4.72663
H 0.94960 -4.10853 2.72970
H 0.72349 -1.99121 -3.31125
H -0.40424 3.92263 -1.13440
Mn -0.07460 -0.18085 0.74408
H -2.15272 -1.18137 1.11173
C -3.72477 -1.66008 -5.32823
C -3.08117 -2.79328 -4.85569
C -2.62046 -2.84533 -3.52171
C -2.80759 -1.76270 -2.67125
C -3.46557 -0.58640 -3.12835
C -3.93375 -0.53305 -4.48475
H -2.46265 -1.79635 -1.63548
H -2.11802 -3.74403 -3.15655
H -2.93034 -3.65043 -5.51591
H -4.08210 -1.62055 -6.36057
C -3.67155 0.53612 -2.28001
C -4.31554 1.66902 -2.75488
C -4.59201 0.64226 -4.93813
C -4.77912 1.72175 -4.08876
H -3.30853 0.48545 -1.25028
H -4.46786 2.52659 -2.09524
H -5.28720 2.61858 -4.45089
H -4.95073 0.68400 -5.96984
O 1.84654 0.17054 0.98522
S 2.61986 1.28979 1.71901
O 2.29240 1.37029 3.14428
O 2.69076 2.52585 0.93768
C 4.32919 0.52988 1.63158
F 5.19229 1.35167 2.22224
F 4.34407 -0.64215 2.25989
F 4.69313 0.35244 0.36547

65
TS (1/5)
O -1.09055 -0.03351 0.77072
N 0.32295 1.79577 2.24851
N 0.37531 -0.93143 2.93804
N 1.09063 1.14666 -0.39406
N 1.21446 -1.57539 0.30744
C 0.06338 3.02350 1.67357
C 0.26203 -2.30314 3.03495
C 0.18362 1.95356 3.61358
C 0.25565 -0.42911 4.21653
C 0.74623 2.46116 -0.62147
C 0.98997 -2.86070 0.74874
C 1.75974 0.70558 -1.51522
C 1.86725 -1.67385 -0.90186
C -0.25306 3.97433 2.70477
C 0.02517 -2.66763 4.40708
C -0.14513 3.32275 3.90354
C 0.05394 -1.51334 5.14089
C 1.17769 2.84624 -1.93908
C 1.49286 -3.79526 -0.22401
C 1.83521 1.77363 -2.47679
C 2.06422 -3.06163 -1.22795
H -0.50155 5.01885 2.52456
H -0.11191 -3.68899 4.75824
H -0.30181 3.71998 4.90492
H -0.07131 -1.39192 6.21551
H 1.02135 3.83146 -2.37504
H 1.43689 -4.87794 -0.12474
H 2.31255 1.69253 -3.45192
H 2.55835 -3.41898 -2.12984
C 0.20673 3.32701 0.32390
C 0.48938 -3.20680 2.00143
C 2.17207 -0.60409 -1.73858
C 0.20926 0.92250 4.54593
H 0.08619 1.18508 5.59709
H 0.37660 -4.26829 2.22481
H 2.68288 -0.82301 -2.67676
H -0.01300 4.34759 0.00885
Mn 0.79055 0.11995 1.28023
H -1.67815 -0.22449 1.52282
C -2.78701 -2.49741 -3.60210
C -2.47745 -3.26437 -2.48897
C -2.28600 -2.63834 -1.23247
C -2.21974 -1.26153 -1.20545
C -2.61381 -0.42094 -2.27564
C -2.88056 -1.07796 -3.53307
H -1.47995 -0.61946 -0.11350
H -2.14390 -3.24033 -0.33081
H -2.41457 -4.35232 -2.56519
H -3.00406 -2.98884 -4.55400
C -2.72629 0.98923 -2.18947
C -3.09714 1.72947 -3.30117
C -3.22299 -0.28045 -4.65661
C -3.34073 1.09415 -4.53954
H -2.53300 1.47859 -1.23302
H -3.19098 2.81494 -3.22304
H -3.61320 1.69396 -5.41070
H -3.37839 -0.76888 -5.62192
O 2.61753 0.21625 1.76471
S 3.55131 1.42427 2.11284
O 3.58603 1.67190 3.55110
O 3.40755 2.54448 1.18659
C 5.17256 0.58891 1.67395
F 6.15840 1.45494 1.87981
F 5.36087 -0.48194 2.43435
F 5.16377 0.22866 0.39526

65
PC (1/5)
O -1.79900 -0.22615 0.03948
N -0.44178 1.67718 1.52598
N -0.49540 -0.98933 2.39349
N 0.53308 0.84331 -0.98713
N 0.55912 -1.81402 -0.09994
C -0.64064 2.86492 0.84970
C -0.63275 -2.35142 2.57481
C -0.68419 1.93300 2.86234
C -0.69823 -0.40282 3.62643
C 0.22649 2.14319 -1.33388
C 0.27460 -3.06680 0.40192
C 1.31054 0.33054 -2.00592
C 1.32947 -2.00144 -1.22923
C -1.02587 3.88676 1.78406
C -0.97686 -2.62043 3.94541
C -1.01772 3.32031 3.03032
C -0.98343 -1.41990 4.60201
C 0.78592 2.43743 -2.62542
C 0.84903 -4.06813 -0.45668
C 1.48744 1.33178 -3.02259
C 1.53063 -3.40880 -1.44429
H -1.24830 4.91713 1.51201
H -1.15581 -3.61426 4.35214
H -1.24732 3.78728 3.98650
H -1.18470 -1.22611 5.65420
H 0.67850 3.39060 -3.14017
H 0.76408 -5.14119 -0.29395
H 2.05811 1.18628 -3.93815
H 2.10388 -3.83141 -2.26765
C -0.38587 3.07335 -0.50162
C -0.33818 -3.32419 1.62480
C 1.72948 -0.99218 -2.10034
C -0.74864 0.96808 3.86083
H -0.94746 1.30307 4.87928
H -0.48670 -4.36750 1.90538
H 2.32766 -1.27549 -2.96703
H -0.56725 4.07101 -0.90274
Mn 0.11652 -0.05483 0.73003
H -2.45069 -0.52579 0.69714
C -3.91699 -2.34810 -4.73979
C -3.03425 -3.15010 -4.04711
C -2.41679 -2.67852 -2.84644
C -2.75524 -1.42220 -2.45404
C -3.63779 -0.52789 -3.08107
C -4.24553 -1.03482 -4.29277
H -1.97744 -0.72908 -0.79880
H -1.71623 -3.31113 -2.29580
H -2.79493 -4.15462 -4.40536
H -4.38372 -2.71712 -5.65649
C -3.96116 0.78197 -2.62687
C -4.84810 1.56377 -3.33728
C -5.15426 -0.19040 -4.99061
C -5.44835 1.07514 -4.52635
H -3.49797 1.15418 -1.71105
H -5.09226 2.56802 -2.98293
H -6.14877 1.70859 -5.07573
H -5.61804 -0.56588 -5.90664
O 1.86457 0.05946 1.35883
S 2.78358 1.30321 1.67596
O 2.66720 1.69525 3.07529
O 2.74554 2.31251 0.62324
C 4.42089 0.40045 1.49460
F 5.39745 1.27189 1.71189
F 4.49989 -0.58472 2.37746
F 4.52935 -0.08967 0.26644

**[Mn$^{IV}$OH(Por$^{+\bullet}$)OTf]$^{+}$ without Cl$^{-}$, nucleophilic α-electron transfer reaction at C$_1$**

65
RC(1/5)
N 0.77548 -0.46747 -1.49295
N -0.75237 1.66036 -0.34289
N 1.08551 -1.63823 1.10141
N -0.39713 0.52875 2.25821
C 1.55669 -1.51434 -1.85412
C -1.27694 2.70401 0.41030
C 0.37270 0.14853 -2.66977
C -0.87170 2.02584 -1.64473
C 1.88682 -2.51494 0.38668
C -1.01528 1.67019 2.64479
C 1.06243 -2.08882 2.37926
C -0.25318 -0.25014 3.39608
C 1.69088 -1.57455 -3.29074
C -1.74129 3.74570 -0.47695
C 0.94439 -0.55239 -3.79793
C -1.50389 3.31787 -1.75078
C 2.38447 -3.54239 1.27496
C -1.27884 1.64678 4.06513
C 1.86124 -3.28564 2.50799
C -0.82110 0.44865 4.52875
H 2.27905 -2.31773 -3.82553
H -2.19885 4.67653 -0.14686
H 0.79473 -0.27133 -4.83879
H -1.71701 3.82623 -2.68912
H 3.04006 -4.35612 0.97051
H -1.76049 2.45106 4.61786
H 2.00107 -3.83896 3.43463
H -0.83827 0.06216 5.54614
C 2.12591 -2.45681 -0.96745
C -1.39217 2.72459 1.78178
C 0.39894 -1.46120 3.45919
C -0.39721 1.28494 -2.75158
H -0.61753 1.67921 -3.74416
H -1.84392 3.60566 2.23912
H 0.45036 -1.95835 4.42874
H 2.76791 -3.22367 -1.40257
C -4.36564 0.45349 -1.82983
C -4.31895 -0.65711 -2.64802
C -4.39822 -1.97137 -2.10370
C -4.52905 -2.12743 -0.68159
C -4.57457 -0.96103 0.13673
C -4.49185 0.30066 -0.42301
H -4.25443 -3.01583 -4.00418
H -4.31006 1.45585 -2.26065
H -4.22341 -0.54137 -3.73099
C -4.35375 -3.13571 -2.92200
C -4.61197 -3.44000 -0.13728
H -4.68074 -1.07984 1.21839
H -4.53849 1.18682 0.21486
C -4.56663 -4.54857 -0.95860
C -4.43603 -4.39505 -2.36298
H -4.71304 -3.55663 0.94507
H -4.63220 -5.55124 -0.52900
H -4.40188 -5.28095 -3.00190
O -1.33756 -0.97560 0.16942
H -2.15839 -0.45651 0.06226
Mn 0.12949 -0.00636 0.37630
O 3.85479 0.45288 -0.52569
S 2.90530 1.52130 -0.20683
O 2.43121 2.39128 -1.28615
O 1.76769 1.04249 0.72112
C 3.78442 2.64541 1.00510
F 4.83525 3.19036 0.39857
F 4.20105 1.95252 2.06018
F 2.96635 3.61205 1.41125

65
TS(1/5)
N 2.05517 -0.31278 -1.59071
N 0.46431 1.99781 -0.93732
N 1.73004 -1.29813 1.10669
N 0.18683 1.04757 1.77713
C 2.75319 -1.47066 -1.72503
C -0.29327 3.03863 -0.42781
C 2.09839 0.31567 -2.82070
C 0.74349 2.32054 -2.22897
C 2.49881 -2.32851 0.60263
C -0.53389 2.19107 1.90542
C 1.51890 -1.58056 2.41919
C 0.17208 0.43266 3.01395
C 3.26141 -1.60021 -3.06847
C -0.49896 4.03326 -1.45220
C 2.85537 -0.48747 -3.75016
C 0.14761 3.58766 -2.57123
C 2.76259 -3.29227 1.64398
C -1.02670 2.32848 3.25475
C 2.15444 -2.82526 2.77586
C -0.58535 1.23489 3.94559
H 3.85505 -2.43777 -3.42987
H -1.06167 4.95499 -1.31624
H 3.04454 -0.22108 -4.78847
H 0.22470 4.06685 -3.54538
H 3.34601 -4.20187 1.51368
H -1.62826 3.16096 3.61488
H 2.13349 -3.27225 3.76799
H -0.74948 0.98133 4.99139
C 2.96489 -2.41711 -0.69925
C -0.76093 3.12804 0.87271
C 0.78518 -0.77280 3.31609
C 1.50552 1.53072 -3.11753
H 1.63577 1.91567 -4.13015
H -1.35120 4.00936 1.12933
H 0.69474 -1.13383 4.34195
H 3.56088 -3.29446 -0.95599
C -5.59210 -0.16445 0.79944
C -5.39767 -0.61096 -0.49792
C -4.20812 -1.29847 -0.85413
C -3.20577 -1.51787 0.14550
C -3.43169 -1.05837 1.46099
C -4.60674 -0.39187 1.78409
H -4.76353 -1.63454 -2.92962
H -6.51198 0.36186 1.06418
H -6.16187 -0.44346 -1.26098
C -3.99363 -1.80104 -2.17191
C -1.98842 -2.19372 -0.22560
H -2.66816 -1.22920 2.22354
H -4.77059 -0.04153 2.80575
C -1.84932 -2.72429 -1.52978
C -2.83749 -2.50560 -2.49680
H -1.32175 -2.53538 0.56491
H -0.94912 -3.28899 -1.77905
H -2.70487 -2.89755 -3.50735
O -0.61115 -0.61760 -0.47760
H -1.09860 -0.11757 -1.15449
Mn 1.08512 0.34651 0.08308
O 4.97225 0.23797 0.14714
S 4.22567 1.50440 0.10968
O 4.25653 2.27394 -1.14292
O 2.84217 1.41001 0.72818
C 5.07801 2.59877 1.36376
F 6.33995 2.81048 0.98803
F 5.08187 2.01983 2.56526
F 4.45761 3.77554 1.45802

65
PC(1/5)
N 1.01575 -0.48900 -1.78696
N -0.21923 1.99177 -1.04332
N 0.39508 -1.57099 0.79965
N -0.76245 0.93764 1.57296
C 1.52711 -1.75385 -1.97317
C -0.83536 3.10060 -0.50575
C 1.20869 0.19094 -2.96877
C 0.15772 2.33395 -2.32345
C 1.02103 -2.67769 0.26480
C -1.31003 2.18990 1.74504
C 0.08692 -1.88895 2.10718
C -0.93173 0.26724 2.76394
C 2.05617 -1.87330 -3.30839
C -0.86116 4.16305 -1.47947
C 1.86062 -0.66872 -3.92399
C -0.24499 3.68913 -2.60361
C 1.07837 -3.72725 1.24960
C -1.84181 2.30909 3.07959
C 0.50344 -3.23861 2.38981
C -1.60496 1.11999 3.71122
H 2.51831 -2.77305 -3.71129
H -1.29633 5.14640 -1.30880
H 2.12776 -0.37480 -4.93774
H -0.07013 4.20243 -3.54778
H 1.51552 -4.70982 1.07952
H -2.33128 3.19907 3.47183
H 0.37027 -3.73762 3.34835
H -1.86099 0.83092 4.72927
C 1.53330 -2.77449 -1.02599
C -1.34902 3.19798 0.78479
C -0.53254 -1.04221 3.02203
C 0.82025 1.50317 -3.22302
H 1.04886 1.91208 -4.20808
H -1.81248 4.14354 1.06942
H -0.72205 -1.43670 4.02119
H 1.99116 -3.72193 -1.31327
C -6.58853 -1.61577 1.00565
C -6.28941 -2.59127 0.07193
C -5.01381 -2.60104 -0.56114
C -4.03747 -1.61246 -0.20887
C -4.35867 -0.63690 0.72847
C -5.62657 -0.63749 1.32333
H -5.48362 -4.26473 -1.84722
H -7.56526 -1.59739 1.49196
H -7.02097 -3.35690 -0.19442
C -4.71938 -3.52839 -1.58140
C -2.66670 -1.69856 -0.82680
H -3.62539 0.12722 0.98850
H -5.87226 0.14004 2.05042
C -2.54304 -2.59758 -2.00498
C -3.50534 -3.52168 -2.30912
H -2.06639 -2.26786 -0.07010
H -1.60773 -2.54090 -2.56859
H -3.36154 -4.23262 -3.12385
O -1.99664 -0.46791 -0.95217
H -2.42639 0.09163 -1.61891
Mn 0.22590 0.26268 -0.07065
O 4.01965 -0.51915 0.15612
S 3.50215 0.85650 0.15553
O 3.75099 1.67697 -1.03799
O 2.08500 0.97325 0.68868
C 4.44021 1.71641 1.52545
F 5.74434 1.71836 1.24323
F 4.25787 1.08744 2.68800
F 4.03147 2.97971 1.65546

**[Mn$^{IV}$OH(Por$^{+\bullet}$)OTf]$^{+}$ without Cl$^{-}$, nucleophilic β-electron transfer reaction at C$_1$**

65
RC(1/5)
N 0.68877 -0.47820 -1.61873
N -0.74716 1.68272 -0.41802
N 1.20041 -1.57183 0.97579
N -0.19321 0.62691 2.17764
C 1.45043 -1.52936 -2.00748
C -1.20075 2.75469 0.34119
C 0.18348 0.09402 -2.77821
C -0.97692 2.00369 -1.71647
C 1.95778 -2.46115 0.22941
C -0.77055 1.78483 2.57767
C 1.26679 -1.99072 2.26252
C 0.02666 -0.12449 3.32216
C 1.46712 -1.63744 -3.44758
C -1.73408 3.76974 -0.53882
C 0.66837 -0.64107 -3.92548
C -1.61055 3.29621 -1.81239
C 2.52289 -3.46313 1.10704
C -0.92960 1.80076 4.01365
C 2.08115 -3.17994 2.36577
C -0.45182 0.60930 4.47415
H 2.01846 -2.39294 -4.00391

H -2.15697 4.71486 -0.20311
H 0.43068 -0.39788 -4.95945
H -1.90146 3.77387 -2.74594
H 3.16230 -4.28036 0.77846
H -1.36173 2.62462 4.57832
H 2.28690 -3.70967 3.29388
H -0.39880 0.24942 5.50005
C 2.09780 -2.43865 -1.13948
C -1.20377 2.81894 1.71604
C 0.67696 -1.33710 3.36980
C -0.59850 1.22368 -2.83390
H -0.90615 1.58167 -3.81713
H -1.61140 3.71745 2.18083
H 0.79389 -1.81104 4.34526
H 2.71427 -3.21181 -1.59959
C -4.49043 0.41084 -1.43151
C -4.51420 -0.70560 -2.24263
C -4.53732 -2.01600 -1.68388
C -4.53644 -2.16178 -0.25466
C -4.51166 -0.98963 0.55602
C -4.48604 0.26815 -0.01784
H -4.56489 -3.07433 -3.58200
H -4.47851 1.41016 -1.87282
H -4.51860 -0.59762 -3.33062
C -4.56374 -3.18637 -2.49440
C -4.56337 -3.47060 0.30430
H -4.51612 -1.10082 1.64370
H -4.47722 1.15894 0.61526
C -4.58925 -4.58522 -0.50959
C -4.58902 -4.44177 -1.92116
H -4.56443 -3.57933 1.39223
H -4.61090 -5.58486 -0.06856
H -4.61007 -5.33235 -2.55416
O -1.29017 -0.93407 0.21622
H -2.11859 -0.41609 0.20582
Mn 0.18829 0.03780 0.27899
O 3.83412 0.51951 -0.94403
S 2.89243 1.57488 -0.56477
O 2.30930 2.41283 -1.61576
O 1.84919 1.09138 0.46581
C 3.84646 2.74127 0.54619
F 4.82214 3.30402 -0.16123
F 4.37638 2.07700 1.56836
F 3.04182 3.69235 1.01198

65
TS(1/5)
N 1.80761 -0.20176 -1.72093
N 0.28415 2.02211 -0.84563
N 1.80132 -1.25673 0.93261
N 0.32832 1.00367 1.82581
C 2.35273 -1.43893 -1.99813
C -0.56814 2.93978 -0.26791
C 1.84666 0.52426 -2.89255
C 0.53922 2.46375 -2.12649
C 2.36479 -2.33855 0.29668
C -0.52871 2.05878 2.03654
C 1.89644 -1.49259 2.28546
C 0.60885 0.46084 3.05982
C 2.74028 -1.49041 -3.38302
C -0.87755 3.97251 -1.22286
C 2.45052 -0.27054 -3.92887
C -0.17554 3.69140 -2.36172
C 2.80322 -3.29824 1.27727
C -0.80912 2.17628 3.44502
C 2.53632 -2.76404 2.50732
C -0.08798 1.20258 4.07952
H 3.19659 -2.35494 -3.86224
H -1.53397 4.81789 -1.02338
H 2.60895 0.06896 -4.95102
H -0.14611 4.25135 -3.29489
H 3.27985 -4.24787 1.03990
H -1.46083 2.93029 3.88327
H 2.73588 -3.19006 3.48914
H -0.03592 0.98399 5.14480
C 2.58013 -2.45135 -1.07353
C -0.98334 2.94084 1.05930
C 1.37210 -0.68042 3.28659
C 1.29618 1.78782 -3.07751
H 1.40444 2.24852 -4.05986
H -1.65331 3.74117 1.37547
H 1.51189 -0.99827 4.32037
H 3.03720 -3.37188 -1.43819
C -5.59856 0.14322 -0.14439
C -5.21135 -0.88799 -0.99429
C -3.97112 -1.54597 -0.80574
C -3.11454 -1.12842 0.26341
C -3.53137 -0.09418 1.11587
C -4.76292 0.53534 0.91413
H -4.23872 -2.96032 -2.43275
H -6.55730 0.64345 -0.29548
H -5.86483 -1.20776 -1.80920
C -3.57825 -2.64261 -1.62238
C -1.82917 -1.78237 0.43029
H -2.88659 0.21957 1.93900
H -5.07631 1.33716 1.58601
C -1.52509 -2.93578 -0.37498
C -2.37542 -3.33261 -1.39237
H -1.33499 -1.68758 1.39755
H -0.59536 -3.47386 -0.18359
H -2.11891 -4.19224 -2.01421
O -0.56802 -0.54110 -0.32737
H -0.91398 -0.30341 -1.20694
Mn 1.06512 0.39774 0.04832
O 4.71094 -0.04057 0.07985
S 4.15222 1.30957 -0.00970
O 4.37010 2.08640 -1.23065
O 2.69276 1.40372 0.49533
C 4.96427 2.28498 1.36832
F 6.27541 2.32919 1.14623
F 4.74193 1.69685 2.54076
F 4.48724 3.52536 1.40396

65
PC(1/5)
N 1.00943 -0.45019 -1.82065
N -0.26504 2.01000 -1.07720
N 0.45582 -1.52211 0.78592
N -0.74094 0.96828 1.55734
C 1.54157 -1.70654 -2.00544
C -0.89704 3.10965 -0.53914
C 1.16885 0.22326 -3.01106
C 0.08390 2.34921 -2.36604
C 1.09342 -2.62103 0.24885
C -1.31346 2.20968 1.72752
C 0.17923 -1.83400 2.10195
C -0.87325 0.30618 2.75765
C 2.05035 -1.82700 -3.34848
C -0.96176 4.16273 -1.52119
C 1.82137 -0.63157 -3.97027
C -0.35294 3.69278 -2.65098
C 1.19037 -3.66022 1.24152
C -1.82380 2.33001 3.07028
C 0.62806 -3.17247 2.38839
C -1.54836 1.15295 3.70887
H 2.52309 -2.72101 -3.75187
H -1.41565 5.13780 -1.35181
H 2.06570 -0.34104 -4.99074
H -0.20441 4.20162 -3.60203
H 1.64342 -4.63560 1.07172
H -2.32648 3.21246 3.46286
H 0.52330 -3.66521 3.35366
H -1.77939 0.86832 4.73414
C 1.58403 -2.71884 -1.05032
C -1.39168 3.20735 0.75879
C -0.44063 -0.99167 3.02057
C 0.74926 1.52501 -3.26956
H 0.95301 1.93016 -4.26160
H -1.87144 4.14496 1.04275
H -0.60290 -1.38033 4.02678
H 2.05510 -3.65963 -1.33817
C -6.50128 -1.63899 1.19175
C -6.21698 -2.63908 0.27964
C -4.96200 -2.65035 -0.39349
C -3.99011 -1.63752 -0.10299
C -4.29628 -0.63783 0.81375
C -5.54482 -0.63754 1.44804
H -5.44621 -4.35953 -1.61268
H -7.46237 -1.61920 1.70823
H -6.94507 -3.42292 0.06086
C -4.68586 -3.60380 -1.39467
C -2.63793 -1.72501 -0.76012
H -3.56649 0.14383 1.02703
H -5.77932 0.15897 2.15804
C -2.53899 -2.65417 -1.91695
C -3.49672 -3.60049 -2.16236
H -2.00977 -2.26928 -0.00739
H -1.62309 -2.60087 -2.51193
H -3.36855 -4.33282 -2.96058
O -1.98403 -0.49210 -0.93574
H -2.43847 0.04764 -1.60228
Mn 0.23334 0.29966 -0.09746
O 4.04798 -0.39498 0.06527
S 3.49823 0.96810 0.06639
O 3.70514 1.78685 -1.13628
O 2.08884 1.05476 0.62536
C 4.44101 1.85854 1.41339
F 5.73917 1.88980 1.10652
F 4.29565 1.23268 2.58280
F 4.00469 3.11255 1.54383

**[$Mn^{IV}OH(Por^{+\bullet})OTf]^+$ without $Cl^-$, nucleophilic α-electron transfer reaction at $C_2$**

65
RC(1/5)
N 0.42166 1.89077 -0.21665
N -1.27528 0.83004 -2.27563
N 0.73618 -0.73907 0.86203
N -1.00996 -1.78983 -1.14796
C 1.15375 2.23134 0.87160
C -2.16201 0.16202 -3.10418
C 0.26154 3.04617 -0.96536
C -1.22951 2.11419 -2.71187
C 1.38414 -0.02614 1.86217
C -1.87707 -2.10204 -2.14439
C 0.80473 -2.05021 1.21744
C -0.63273 -2.98978 -0.56401
C 1.47524 3.63962 0.84326
C -2.68888 1.08305 -4.08576
C 0.93474 4.14229 -0.30353
C -2.10051 2.29114 -3.84983
C 1.87348 -0.94428 2.86334
C -2.09118 -3.52824 -2.19887
C 1.52550 -2.20012 2.45514
C -1.30899 -4.08065 -1.22735
H 2.04858 4.15748 1.60965
H -3.40915 0.81654 -4.85705
H 0.96225 5.16424 -0.67732
H -2.23943 3.23017 -4.38209
H 2.42050 -0.64674 3.75552
H -2.75376 -4.02666 -2.90374
H 1.71937 -3.15228 2.94508
H -1.19735 -5.12960 -0.95901
C 1.57775 1.33792 1.88052
C -2.45880 -1.18185 -3.04242
C 0.21017 -3.12160 0.51622
C -0.48086 3.15554 -2.12062
H -0.53099 4.13501 -2.59797
H -3.16738 -1.57794 -3.77078
H 0.39893 -4.12748 0.89272
H 2.12293 1.76090 2.72444
C 5.64921 0.47173 2.65933
C 5.53657 -0.80281 2.13599
C 5.11691 -1.00511 0.79038
C 4.80904 0.14035 -0.01941
C 4.93146 1.43884 0.54975
C 5.34390 1.60102 1.86072
H 5.22901 -3.17453 0.83930
H 5.97689 0.61216 3.69214
H 5.77383 -1.67507 2.75070
C 4.99204 -2.30414 0.22180
C 4.39224 -0.06207 -1.36682
H 4.70229 2.31040 -0.06883
H 5.43998 2.60418 2.28309
C 4.27935 -1.33880 -1.88888
C 4.58040 -2.46893 -1.08688
H 4.17008 0.81022 -1.98727
H 3.96361 -1.47981 -2.92533
H 4.49088 -3.47162 -1.51130
O 1.13985 -0.22435 -1.80675
H 1.96949 -0.42942 -1.33519
Mn -0.23980 0.04165 -0.72420
O -1.77364 0.45643 0.44964
S -2.92401 -0.41253 1.00166
O -3.96058 -0.67358 0.00066
O -2.45098 -1.52079 1.83505
C -3.65952 0.83733 2.18572
F -4.07102 1.91467 1.52446
F -2.75682 1.19906 3.09293
F -4.69853 0.28169 2.80313

65
TS(1/5)
N -1.10982 2.15933 0.30370
N -1.46551 0.76390 -2.20240
N -1.13967 -0.36034 1.70300
N -1.55978 -1.75144 -0.78898
C -0.95751 2.64567 1.56264
C -1.69589 -0.06679 -3.28134
C -1.08044 3.24944 -0.54441
C -1.40676 2.02954 -2.69576
C -1.00229 0.47974 2.79448
C -1.75675 -2.23247 -2.04570
C -1.19572 -1.62692 2.19705
C -1.53106 -2.84644 0.04981
C -0.83078 4.08289 1.53682
C -1.77403 0.71688 -4.49026
C -0.90439 4.45856 0.22499
C -1.59132 2.02238 -4.12556
C -0.95950 -0.30245 4.00502
C -1.86461 -3.67097 -2.02257
C -1.07611 -1.61285 3.63276
C -1.72014 -4.05337 -0.71815
H -0.70188 4.71153 2.41592
H -1.94843 0.30874 -5.48422
H -0.84975 5.46035 -0.19722
H -1.58610 2.90841 -4.75770
H -0.85471 0.11103 5.00650
H -2.02836 -4.29624 -2.89828
H -1.08908 -2.49837 4.26544
H -1.74268 -5.05818 -0.30029
C -0.91841 1.86090 2.73559
C -1.83203 -1.44562 -3.21458
C -1.36293 -2.79519 1.42429
C -1.21393 3.19545 -1.92261
H -1.17929 4.14239 -2.46376
H -2.00882 -1.97421 -4.15277
H -1.37345 -3.74333 1.96413
H -0.80842 2.39409 3.68125
C 6.41388 -0.54912 1.26262
C 5.60092 -1.49348 0.64523
C 4.50813 -1.09227 -0.15069
C 4.24460 0.31381 -0.31217
C 5.09831 1.25803 0.32913
C 6.16232 0.83262 1.10291
H 3.88133 -3.10532 -0.70667
H 7.25693 -0.87722 1.87523
H 5.80484 -2.55967 0.77163
C 3.65472 -2.04149 -0.81498
C 3.15702 0.71691 -1.11790
H 4.89672 2.32435 0.20013
H 6.81157 1.56204 1.59213
C 2.28810 -0.23649 -1.70627
C 2.59461 -1.63625 -1.57678
H 2.96372 1.78086 -1.27085
H 1.61793 0.08611 -2.50217
H 1.96095 -2.36492 -2.08577
O 0.73077 0.03712 -0.43394
H 1.15614 -0.20981 0.40560
Mn -1.31118 0.20141 -0.24564
O -3.43904 0.46621 -0.08063
S -4.63113 -0.23395 0.54015
O -5.77100 -0.33261 -0.37772
O -4.28155 -1.42685 1.32699
C -5.16083 1.02791 1.81593
F -5.47982 2.18378 1.23275
F -4.17196 1.25357 2.68968
F -6.22221 0.58082 2.48745

**[$Mn^{IV}OH(Por^{+\bullet})OTf]^+$ without $Cl^-$, nucleophilic β-electron transfer reaction at $C_2$**

65
RC(1/5)
N -1.13916 2.49844 0.97897
N -0.50400 1.31145 -1.55821
N -0.91655 -0.07374 2.22148
N -0.36798 -1.27023 -0.31915
C -1.48450 2.87605 2.23277
C -0.28978 0.54965 -2.69734
C -1.08067 3.65709 0.21920
C -0.56143 2.60361 -1.96390
C -1.34692 0.65663 3.32390
C -0.13390 -1.66273 -1.59598
C -0.75737 -1.35415 2.64818
C -0.21532 -2.40026 0.47272
C -1.66776 4.30750 2.29951
C -0.21881 1.41932 -3.85007
C -1.40664 4.79383 1.05270
C -0.37785 2.69474 -3.39291
C -1.43786 -0.21707 4.47010
C 0.15521 -3.07533 -1.64813
C -1.06226 -1.46096 4.05263
C 0.11407 -3.53201 -0.36367
H -1.95336 4.85242 3.19714
H -0.05906 1.07767 -4.87106
H -1.43802 5.82436 0.70396
H -0.38150 3.62469 -3.95814
H -1.74793 0.10167 5.46358
H 0.36743 -3.62870 -2.56080
H -1.00283 -2.38233 4.62856
H 0.27899 -4.54273 0.00469
C -1.61781 2.00595 3.33883
C -0.13140 -0.81659 -2.72808
C -0.38580 -2.44945 1.83617
C -0.80515 3.71798 -1.12775
H -0.80375 4.70103 -1.60034
H 0.04072 -1.28607 -3.69720
H -0.25638 -3.41320 2.33001
H -1.93603 2.44783 4.28385
C 8.78172 -2.05197 -1.69672
C 7.78808 -2.73106 -1.02155
C 6.52963 -2.11599 -0.76255
C 6.30822 -0.77077 -1.21711
C 7.35519 -0.09874 -1.91102
C 8.56318 -0.72326 -2.14570
H 5.65303 -3.81108 0.27749
H 9.74287 -2.53558 -1.88859
H 7.95498 -3.75468 -0.67485
C 5.48280 -2.78753 -0.06797
C 5.04977 -0.15597 -0.95710
H 7.18554 0.92502 -2.25605
H 9.35817 -0.19602 -2.67912
C 4.05468 -0.83311 -0.28111
C 4.27539 -2.16208 0.16753
H 4.88394 0.86821 -1.30316
H 3.09443 -0.34758 -0.08741
H 3.48118 -2.68926 0.70242
O 1.05652 0.90408 0.58193
H 1.32552 0.78067 1.50856
Mn -0.68737 0.62582 0.33824
O -2.62087 0.44295 0.04724
S -3.50427 -0.76639 -0.34188
O -3.36322 -1.13071 -1.75285
O -3.48763 -1.82494 0.66998
C -5.17477 0.06664 -0.18975
F -5.25659 1.09113 -1.03211
F -5.35942 0.50322 1.05206
F -6.12033 -0.81982 -0.48624

65
TS(1/5)
N -0.95902 2.12668 0.58992
N -1.28932 0.85970 -1.94980
N -1.13408 -0.40345 1.86428
N -1.57143 -1.65712 -0.65700
C -0.98079 2.57595 1.89006
C -1.68911 0.12870 -3.04687
C -0.68305 3.21515 -0.20731
C -0.99306 2.12684 -2.39951
C -1.16525 0.38421 2.99788
C -1.90230 -2.05885 -1.93313
C -1.10962 -1.71640 2.29018
C -1.45521 -2.79888 0.10454
O -3.43904 0.46621 -0.08063
S -4.63113 -0.23395 0.54015
O -5.77100 -0.33261 -0.37772
O -4.28155 -1.42685 1.32699
C -5.16083 1.02791 1.81593
F -5.47982 2.18378 1.23275
F -4.17196 1.25357 2.68968
F -6.22221 0.58082 2.48745

C -0.72814 3.99446 1.91262
C -1.63825 0.95963 -4.22199
C -0.52020 4.38463 0.61920
C -1.18556 2.18774 -3.82560
C -1.14523 -0.45725 4.16480
C -2.02136 -3.49293 -1.96832
C -1.08410 -1.75173 3.72803
C -1.72189 -3.95179 -0.71517
H -0.69637 4.60018 2.81673
H -1.90462 0.62719 -5.22388
H -0.29508 5.38015 0.24024
H -1.01608 3.07536 -4.43284
H -1.16058 -0.08873 5.18914
H -2.28274 -4.06760 -2.85524
H -1.05238 -2.66463 4.32033
H -1.69864 -4.98009 -0.35849
C -1.12603 1.77415 3.01793
C -2.00535 -1.22657 -3.04259
C -1.20508 -2.83623 1.47266
C -0.66287 3.21666 -1.59809
H -0.45049 4.16237 -2.09804
H -2.28769 -1.68295 -3.99193
H -1.16250 -3.81506 1.95153
H -1.13575 2.26599 3.99114
C 6.56076 -0.15242 0.64530
C 5.66800 -1.22371 0.51325
C 4.44025 -1.05170 -0.13733
C 4.10914 0.24804 -0.66728
C 5.04145 1.32073 -0.52308
C 6.24807 1.11916 0.12604
H 3.78213 -3.12329 0.06911
H 7.51411 -0.30817 1.15527
H 5.93005 -2.20372 0.91848
C 3.50050 -2.13611 -0.30551
C 2.88512 0.42206 -1.32589
H 4.78600 2.30084 -0.93233
H 6.95810 1.94114 0.23477
C 1.93197 -0.65371 -1.42778
C 2.30383 -1.95787 -0.93595
H 2.62560 1.39269 -1.75341
H 1.18687 -0.59076 -2.22151
H 1.61393 -2.79072 -1.07879
O 0.64780 0.01137 -0.18167
H 1.05422 -0.06496 0.70156
Mn -1.25621 0.23577 -0.03087
O -3.17990 0.58014 0.11381
S -4.40020 -0.35807 0.28160
O -4.90301 -0.85428 -0.99976
O -4.25947 -1.29295 1.39923
C -5.63620 0.92980 0.85071
F -5.79641 1.86398 -0.08128
F -5.21929 1.50172 1.97693
F -6.80362 0.33168 1.07316

65
PC(1/5)
N 0.01072 1.89570 0.84990
N 0.06731 0.43583 -1.62444
N -0.65517 -0.51769 2.25598
N -0.69910 -1.95376 -0.22947
C -0.02899 2.41290 2.12497
C -0.03476 -0.40705 -2.71422
C 0.35755 2.93316 0.01483
C 0.36651 1.68807 -2.12457
C -0.61891 0.33763 3.33530
C -0.65653 -2.47266 -1.50390
C -0.99206 -1.75865 2.74923
C -1.01479 -2.99866 0.61004
C 0.29820 3.81668 2.09142
C 0.24288 0.32613 -3.92189
C 0.53766 4.13897 0.78496
C 0.49157 1.62077 -3.55767
C -0.92701 -0.38815 4.54193
C -0.95480 -3.88213 -1.46606
C -1.15667 -1.68571 4.17924
C -1.17479 -4.20803 -0.15708
H 0.33802 4.46283 2.96689
H 0.23836 -0.10596 -4.92128
H 0.81397 5.10489 0.36510
H 0.73239 2.46853 -4.19709
H -0.96169 0.05335 5.53662
H -0.98670 -4.53059 -2.34011
H -1.41921 -2.52999 4.81464
H -1.42487 -5.17952 0.26624
C -0.32807 1.69838 3.28232
C -0.35723 -1.75977 -2.66235
C -1.15468 -2.91571 1.99219
C 0.51824 2.84614 -1.36679
H 0.77427 3.76300 -1.89949
H -0.38351 -2.30495 -3.60671
H -1.41776 -3.83049 2.52488
H -0.33038 2.24839 4.22433
C 7.88547 0.05253 -1.51930
C 7.00465 -1.02331 -1.58961
C 5.68239 -0.88661 -1.14039
C 5.26611 0.40396 -0.61032
C 6.20687 1.48801 -0.54486
C 7.49311 1.31087 -0.99472
H 5.11066 -2.95892 -1.51679
H 8.91079 -0.07613 -1.87463
H 7.34156 -1.98046 -1.99170
C 4.75394 -1.99066 -1.15949
C 3.97797 0.54820 -0.13441
H 5.87766 2.44753 -0.14103
H 8.21393 2.12905 -0.95509
C 2.96482 -0.51219 -0.30656
C 3.47873 -1.84654 -0.72486
H 3.64498 1.48379 0.32447
H 2.46067 -0.13409 -1.24327
H 2.76507 -2.67296 -0.73200
O 1.94264 -0.51833 0.65865
H 2.26131 -0.88873 1.49701
Mn -0.44979 -0.00659 0.30027
O -2.49859 0.51075 0.02571
S -3.71199 -0.32583 -0.33988
O -3.72351 -0.76211 -1.74322
O -4.07577 -1.31570 0.68377
C -5.05054 0.97566 -0.23747
F -4.81396 1.96381 -1.10219
F -5.11346 1.49073 0.99174
F -6.23188 0.42855 -0.53002

**[Mn$^{IV}$OH(TDCPP$^{+\bullet}$)OTf]$^{+}$ with H bonding to OTf, electrophilic reaction at $C_1$**

114
RC (-1/5)
O -0.99513 -0.04074 -0.30594
N 0.88206 1.90104 -0.23367
N 0.36235 0.29024 2.05262
N 1.23235 -0.45173 -1.80757
N 0.69349 -2.04812 0.47730
C 1.36866 2.50111 -1.36970
C 0.38450 -0.62283 3.07962
C 0.48677 2.90442 0.61689
C 0.03360 1.50727 2.60004
C 1.64671 0.46630 -2.73939
C 0.66100 -2.65291 1.71145
C 1.12611 -1.66065 -2.45076
C 0.67631 -3.05222 -0.46382
C 1.29291 3.93437 -1.22231
C 0.06977 0.04526 4.31894
C 0.71990 4.18293 -0.00982
C -0.18135 1.35095 4.01825
C 1.83125 -0.19135 -4.01173
C 0.63245 -4.08416 1.54233
C 1.48271 -1.49821 -3.84006
C 0.61076 -4.32948 0.20092
H 1.61999 4.65670 -1.96596
H 0.02476 -0.43535 5.29287
H 0.49755 5.14819 0.43809
H -0.45997 2.15102 4.69939
H 2.16304 0.29656 -4.92477
H 0.60526 -4.80734 2.35348
H 1.48463 -2.29273 -4.58197
H 0.57586 -5.29304 -0.30105
C 1.77473 1.84754 -2.54037
C 0.58111 -2.00313 2.95014
C 0.83288 -2.88986 -1.84589
C 0.03521 2.73930 1.93342
C -0.37238 3.95922 2.70194
C 0.64597 -2.83994 4.19230
C 0.77390 -4.10809 -2.71542
C 2.29034 2.67417 -3.67876
Mn 0.71128 -0.07554 0.10775
H -1.56488 -0.71588 0.16147
C -4.79022 4.10148 -4.41299
C -4.06536 5.22098 -4.03629
C -3.22406 5.17471 -2.90332
C -3.11829 4.01113 -2.15487
C -3.84990 2.85656 -2.51503
C -4.69856 2.89798 -3.66775
H -2.47964 3.97920 -1.26960
H -2.65377 6.06104 -2.61535
Cl -5.46225 2.05605 0.11837
H -4.14248 6.14304 -4.61746
H -5.43930 4.13266 -5.29200
C -3.77380 1.64012 -1.75555
C -4.47200 0.49045 -2.17833
C -5.41402 1.71999 -4.04174
C -5.29658 0.54448 -3.31532
H -3.02861 1.54897 -0.96432
H -4.36551 -0.44216 -1.61847
H -5.84237 -0.34843 -3.62812
H -6.05651 1.75735 -4.92566
O 2.71686 -0.13499 0.51792
S 3.69711 0.72343 1.31422
O 3.51835 0.64030 2.76803
O 3.93681 2.05000 0.73446
C 5.26363 -0.23877 0.96501
F 6.28707 0.34441 1.59265
F 5.15732 -1.49444 1.40070
F 5.52301 -0.25966 -0.34285
O -2.69145 -1.68086 0.91249
S -3.62246 -2.74022 0.41817
O -4.13111 -2.52157 -0.95536
O -3.22349 -4.12038 0.74222
C -5.13328 -2.45256 1.48425
C -0.50828 -3.29969 4.85834
C -0.43804 -4.07776 6.01739
C 0.81002 -4.41908 6.53866
C 1.97848 -3.99168 5.90743
C 1.88581 -3.21468 4.74984
Cl -2.08778 -2.90448 4.22328
H -1.35921 -4.40991 6.49739
H 0.87282 -5.02660 7.44418
H 2.96075 -4.25403 6.30187
Cl 3.37027 -2.70247 3.97796
F -6.09123 -3.33503 1.17604
F -4.84121 -2.59589 2.78311
F -5.62204 -1.22369 1.29972
C -1.71190 4.39520 2.72364
C -2.11312 5.52808 3.43719
C -1.16376 6.25711 4.15381
C 0.17414 5.86046 4.15925
C 0.55320 4.72468 3.43919
Cl -2.92924 3.50256 1.83555
H -3.16174 5.82757 3.42486
H -1.46918 7.14346 4.71429
H 0.92617 6.42108 4.71551
Cl 2.23747 4.25021 3.46631
C 3.67199 2.87144 -3.87492
C 4.17160 3.63990 -4.92985
C 3.28107 4.23142 -5.82632
C 1.90517 4.05452 -5.67534
C 1.42846 3.28214 -4.61315
Cl 4.81295 2.13163 -2.77453
H 5.24916 3.76663 -5.03970
H 3.66323 4.83394 -6.65329
H 1.19881 4.50624 -6.37264
Cl -0.30200 3.06474 -4.45876
C 1.92867 -4.83725 -3.06047
C 1.87796 -5.96726 -3.88043
C 0.64534 -6.39450 -4.37662
C -0.52415 -5.70506 -4.05438
C -0.45024 -4.57757 -3.23168
Cl 3.48730 -4.32709 -2.44514
H 2.79815 -6.50072 -4.12108
H 0.59592 -7.27658 -5.01891
H -1.49352 -6.03270 -4.43175
Cl -1.92761 -3.74163 -2.81711

114
TS (-1/5)
O -2.43998 3.01783 2.11630
N -0.39384 4.92149 2.15441
N -0.86771 3.31599 4.48109
N -0.11858 2.53937 0.56930
N -0.64560 0.94724 2.88892
C -0.02647 5.51058 0.96849
C -0.90196 2.39572 5.50015
C -0.67817 5.93703 3.03555
C -1.04558 4.55207 5.05249
C 0.23233 3.45759 -0.38967
C -0.74672 0.34952 4.12374
C -0.14246 1.31073 -0.04269
C -0.60751 -0.06611 1.95813
C -0.08037 6.94582 1.10701
C -1.09986 3.07563 6.75805
C -0.50182 7.20912 2.37720
C -1.20943 4.40474 6.47950
C 0.45550 2.78110 -1.64625
C -0.78325 -1.08282 3.96422
C 0.20594 1.45790 -1.43638
C -0.71503 -1.33875 2.62728
H 0.16283 7.65910 0.32346
H -1.15851 2.58998 7.72876
H -0.66341 8.18042 2.83784
H -1.36732 5.22196 7.17871
H 0.75238 3.26481 -2.57333
H -0.86576 -1.79957 4.77722
H 0.26399 0.64537 -2.15612
H -0.72281 -2.30627 2.13199
C 0.30978 4.84656 -0.21965
C -0.81948 1.00446 5.36016
C -0.38793 0.08057 0.58276
C -1.00628 5.78678 4.39094
C -1.27100 7.02180 5.19819
C -0.82326 0.16557 6.60271
C -0.33470 -1.15618 -0.26182
C 0.74615 5.67213 -1.39253
Mn -0.60487 2.93174 2.50649
H -2.92990 2.22227 2.43842
C -5.24451 6.77549 -1.70762
C -4.71691 7.88129 -1.06095
C -4.23354 7.75561 0.25445
C -4.29047 6.52849 0.91357
C -4.82908 5.39793 0.28347
C -5.31098 5.51555 -1.05602
H -3.93067 6.44731 1.94052
H -3.81193 8.62408 0.76614
Cl -5.75289 4.25270 2.63918
H -4.67134 8.84633 -1.57116
H -5.61440 6.85671 -2.73294
C -4.89373 4.07458 0.98080
C -5.52341 2.97543 0.23516
C -5.85803 4.37327 -1.71584
C -5.94868 3.13232 -1.06881
H -3.85932 3.73870 1.32491
H -5.60685 2.00577 0.73219
H -6.37411 2.27693 -1.59915
H -6.22243 4.48391 -2.74014
O 1.53502 2.82212 2.87891
S 2.56845 3.59375 3.66914
O 2.33155 3.62223 5.12022
O 2.99283 4.85207 3.03706
C 4.04388 2.45956 3.46683
F 5.09784 2.96902 4.11218
F 3.78909 1.24826 3.96932
F 4.36638 2.32242 2.17812
O -4.07825 0.93669 2.97362
S -4.95549 -0.20694 2.60267
O -5.50007 -0.15058 1.22448
O -4.48198 -1.53041 3.04772
C -6.48282 0.08251 3.64904
C -2.01530 -0.22643 7.24359
C -2.01558 -1.00538 8.40409
C -0.80032 -1.41443 8.95363
C 0.40428 -1.05192 8.35002
C 0.38090 -0.27292 7.19031
Cl -3.55410 0.26010 6.57257
H -2.96439 -1.28476 8.86344
H -0.79178 -2.02327 9.86042
H 1.36132 -1.36608 8.76794
Cl 1.90812 0.16229 6.45507
F -7.35283 -0.92238 3.48368
F -6.17808 0.15281 4.95101
F -7.09631 1.22017 3.30581
C -2.58368 7.46751 5.45068
C -2.85345 8.61415 6.20170
C -1.79099 9.34956 6.72820
C -0.47471 8.94204 6.50959
C -0.22949 7.79158 5.75489
Cl -3.93803 6.55797 4.81339
H -3.88730 8.91908 6.36733
H -1.99093 10.24757 7.31690
H 0.36457 9.50468 6.91987
Cl 1.43156 7.30066 5.51194
C 2.09417 6.04556 -1.56651
C 2.51994 6.81405 -2.65331
C 1.58732 7.22863 -3.60464
C 0.24317 6.87753 -3.47469
C -0.15901 6.10823 -2.37970
Cl 3.28543 5.53433 -0.39314
H 3.57399 7.07842 -2.74487
H 1.91146 7.82974 -4.45705
H -0.49569 7.19249 -4.21235
Cl -1.85024 5.67682 -2.24853
C 0.88023 -1.81722 -0.53053
C 0.94508 -2.96249 -1.32797
C -0.22952 -3.47634 -1.87956
C -1.45527 -2.85699 -1.63370
C -1.49649 -1.71237 -0.83233
Cl 2.36929 -1.19814 0.15348
H 1.90872 -3.44007 -1.50841
H -0.18894 -4.37108 -2.50474
H -2.38074 -3.25247 -2.05387
Cl -3.04594 -0.97075 -0.51240

114
PC (-1/5)
O -1.29053 -0.04061 -0.40116
N 0.97277 1.90194 -0.25341
N 0.49993 0.28243 2.06893
N 1.27330 -0.46768 -1.84767
N 0.75072 -2.08310 0.46799
C 1.37883 2.50120 -1.42328
C 0.40752 -0.64729 3.07823
C 0.71319 2.91202 0.64255
C 0.27601 1.51340 2.63915
C 1.59488 0.45870 -2.80919
C 0.62918 -2.68987 1.69689
C 1.22050 -1.69075 -2.47133
C 0.79647 -3.08864 -0.47012
C 1.37106 3.93434 -1.25853
C 0.12664 0.02120 4.32576
C 0.93998 4.18861 0.01030
C 0.02372 1.35301 4.05089
C 1.76224 -0.20373 -4.08093
C 0.60090 -4.12182 1.52696
C 1.51322 -1.52893 -3.87572
C 0.68642 -4.36738 0.18793
H 1.65025 4.65429 -2.02378
H 0.00717 -0.47183 5.28721
H 0.80424 5.15633 0.48667
H -0.18971 2.16209 4.74489
H 2.02123 0.28882 -5.01483
H 0.51033 -4.84598 2.33262
H 1.53510 -2.33228 -4.60778
H 0.68571 -5.33160 -0.31407
C 1.69222 1.84562 -2.62229
C 0.49992 -2.03874 2.93242
C 0.97931 -2.92506 -1.85069
C 0.33820 2.75178 1.98431
C 0.01778 3.98279 2.77586
C 0.42034 -2.88365 4.16827
C 0.94900 -4.14815 -2.71510
C 2.11625 2.67940 -3.79261
Mn 0.90039 -0.09339 0.11296
H -1.94691 -0.64801 0.03490
C -4.23125 3.71907 -4.45938
C -4.69062 5.01274 -4.32760
C -5.26937 5.44034 -3.10613
C -5.37933 4.56987 -2.04102
C -4.91661 3.22816 -2.14526
C -4.32654 2.79049 -3.38323
H -5.82439 4.90097 -1.10191
H -5.63067 6.46706 -3.00804
Cl -5.71031 2.74364 0.45349
H -4.60933 5.71192 -5.16356
H -3.78107 3.38521 -5.39788
C -5.00116 2.27197 -1.08612
C -4.54504 0.97882 -1.22930
C -3.85694 1.45174 -3.50683
C -3.96436 0.56758 -2.45534
H -1.71813 0.82708 -0.42818
H -4.62358 0.26779 -0.40712
H -3.61554 -0.46353 -2.53372
H -3.40849 1.13675 -4.45237
O 3.07491 -0.16805 0.49399
S 4.08176 0.66014 1.25330
O 4.09610 0.40543 2.70235
O 4.16322 2.06462 0.82143
C 5.67872 -0.09455 0.63676
F 6.72236 0.51199 1.21154
F 5.73724 -1.39672 0.92894
F 5.79045 0.04531 -0.68807
O -3.09932 -1.59291 0.77499
S -3.81304 -2.75748 0.15915
O -4.22635 -2.54790 -1.24482
O -3.23907 -4.07471 0.48066
C -5.42829 -2.74014 1.10493
C -0.80897 -3.32670 4.69607
C -0.88253 -4.11403 5.84850
C 0.29391 -4.47819 6.50441
C 1.53280 -4.06135 6.01606
C 1.58269 -3.27450 4.86243
Cl -2.29727 -2.88822 3.89063
H -1.85681 -4.43405 6.21958
H 0.24481 -5.09352 7.40553
H 2.45973 -4.33872 6.51919
Cl 3.14888 -2.76295 4.27295
F -6.22512 -3.72760 0.68326
F -5.21575 -2.90538 2.41501
F -6.07654 -1.58086 0.93171
C -1.28931 4.50791 2.80934
C -1.61380 5.65445 3.53908
C -0.61548 6.30776 4.26269
C 0.69259 5.82204 4.25850
C 0.99369 4.67367 3.52128
Cl -2.56676 3.70798 1.91608
H -2.64011 6.02319 3.53518
H -0.85958 7.20463 4.83633
H 1.48172 6.32334 4.81996
Cl 2.64174 4.08764 3.53247
C 3.47716 2.91649 -4.07112
C 3.89057 3.68986 -5.15915
C 2.93092 4.24824 -6.00432
C 1.57188 4.03702 -5.76767
C 1.18311 3.26080 -4.67315
Cl 4.70139 2.22561 -3.02887
H 4.95539 3.84729 -5.33420
H 3.24534 4.85400 -6.85706
H 0.81230 4.46637 -6.42183
Cl -0.52898 3.00862 -4.39970
C 2.11857 -4.85996 -3.04517
C 2.09479 -5.99508 -3.85946
C 0.87454 -6.44460 -4.36622
C -0.30911 -5.77136 -4.06125
C -0.26179 -4.63862 -3.24392
Cl 3.66210 -4.31848 -2.41886
H 3.02597 -6.51468 -4.08794
H 0.84585 -7.33084 -5.00406
H -1.26876 -6.11573 -4.44843

Cl -1.76016 -3.82269 -2.85792

**[$Mn^{IV}$OH(TDCPP$^{\bullet-}$)OTf]$^{+}$ with H bonding to OTf, electrophilic reaction at $C_2$**

114
RC (-1/5)
O -0.82816 -0.14655 -0.21191
N 0.70134 2.06188 -0.11386
N 0.07348 0.59525 2.23054
N 1.67235 -0.32591 -1.34157
N 0.98183 -1.80130 0.96747
C 0.82106 2.54457 -1.39400
C -0.37242 -0.30003 3.17218
C 0.37132 3.12467 0.69040
C -0.12201 1.85366 2.74362
C 1.74913 0.50544 -2.43229
C 0.36055 -2.37816 2.05140
C 2.31120 -1.49829 -1.67899
C 1.62916 -2.80725 0.29011
C 0.53697 3.95980 -1.40065
C -0.85606 0.41957 4.32595
C 0.29749 4.32436 -0.10949
C -0.67459 1.74772 4.07307
C 2.47203 -0.15792 -3.48940
C 0.61133 -3.79822 2.04556
C 2.84793 -1.37873 -3.01227
C 1.41559 -4.05825 0.97468
H 0.54800 4.59528 -2.28244
H -1.26365 -0.03903 5.22341
H 0.06228 5.31480 0.27192
H -0.91636 2.58920 4.71754
H 2.68508 0.27225 -4.46472
H 0.23684 -4.50206 2.78459
H 3.41869 -2.14847 -3.52541
H 1.81709 -5.01793 0.65901
C 1.27780 1.82348 -2.50487
C -0.30118 -1.69649 3.08116
C 2.32620 -2.67511 -0.91959
C 0.04719 3.06159 2.05179
C -0.22900 4.33942 2.78660
C -0.90864 -2.50453 4.18614
C 3.02477 -3.88416 -1.46915
C 1.31037 2.50361 -3.83929
Mn 0.79223 0.12125 0.40384
H -0.97572 -0.96414 -0.76717
C -8.07902 0.83857 -0.39815
C -8.46558 0.49549 -1.68440
C -7.49951 0.11172 -2.64076
C -6.15257 0.08538 -2.30733
C -5.73304 0.44492 -1.00551
C -6.71003 0.81526 -0.02721
H -5.39598 -0.21610 -3.03552
H -7.81739 -0.16734 -3.64835
Cl -3.51486 2.74624 -1.39373
H -9.52282 0.51535 -1.96000
H -8.82651 1.12499 0.34637
C -4.34675 0.43872 -0.63489
C -3.96809 0.71457 0.69349
C -6.27571 1.12534 1.29801
C -4.93552 1.06380 1.65125
H -3.61939 0.04423 -1.34390
H -2.91109 0.64377 0.95479
H -4.62791 1.28891 2.67435
H -7.02681 1.40276 2.04270
O 2.67581 0.38105 1.19694
S 3.77197 1.42776 1.34707
O 4.10944 1.67096 2.75432
O 3.64927 2.58464 0.45371
C 5.25206 0.49537 0.68411
F 6.30376 1.31722 0.63833
F 5.55603 -0.53331 1.47640
F 5.01833 0.04082 -0.54792
O -1.51543 -2.26805 -1.64897
S -2.36300 -2.31511 -2.87802
O -2.97673 -1.01980 -3.25181
O -1.79999 -3.10195 -3.98901
C -3.81652 -3.34746 -2.30482
C -2.25454 -2.91742 4.13470
C -2.84173 -3.67096 5.15430
C -2.07620 -4.02966 6.26449
C -0.73918 -3.64065 6.35738
C -0.17364 -2.88776 5.32518
Cl -3.23632 -2.48080 2.75235
H -3.88745 -3.96884 5.07064
H -2.52658 -4.61869 7.06644
H -0.13144 -3.91413 7.22056
Cl 1.50456 -2.40976 5.46788
F -4.72693 -3.45497 -3.27935
F -3.41918 -4.57770 -1.96599
F -4.41042 -2.79323 -1.24059
C -1.50591 4.93556 2.80313
C -1.76523 6.12245 3.49374
C -0.73191 6.74467 4.19518
C 0.54705 6.18738 4.20853
C 0.78369 4.99962 3.51116
Cl -2.81716 4.18170 1.92522
H -2.76975 6.54663 3.47582
H -0.92580 7.67281 4.73745
H 1.36345 6.66209 4.75394
Cl 2.38979 4.31291 3.55037
C 2.36861 3.34054 -4.24366
C 2.38218 3.97372 -5.48934
C 1.31857 3.77143 -6.36963
C 0.25611 2.93941 -6.01470
C 0.26276 2.31458 -4.76472
Cl 3.72790 3.59574 -3.17064
H 3.22292 4.61399 -5.75854
H 1.32054 4.26362 -7.34473
H -0.57717 2.76747 -6.69696
Cl -1.06674 1.25653 -4.35161
C 4.30235 -4.26745 -1.01296
C 4.96756 -5.39239 -1.50750
C 4.35228 -6.17445 -2.48500
C 3.08520 -5.83712 -2.96058
C 2.43649 -4.70725 -2.45352
Cl 5.10306 -3.31586 0.21702
H 5.95681 -5.64394 -1.12360
H 4.86416 -7.05571 -2.87798
H 2.58991 -6.44195 -3.72107
Cl 0.84720 -4.32163 -3.06526

114
TS (-1/5)
O -0.89901 -1.40491 -0.80326
N 0.84636 0.93008 -0.63866
N 0.18612 -0.52382 1.73258
N 1.88589 -1.47035 -1.81645
N 1.19679 -2.93171 0.52963
C 1.06413 1.41665 -1.90431
C -0.19736 -1.40881 2.71186
C 0.45875 1.99443 0.13922
C -0.09179 0.73801 2.19868
C 2.02448 -0.63502 -2.90017
C 0.63967 -3.49012 1.65739
C 2.50701 -2.65621 -2.14259
C 1.83971 -3.94386 -0.14290
C 0.77833 2.83144 -1.93227
C -0.74532 -0.67950 3.83009
C 0.43665 3.19412 -0.66356
C -0.65981 0.64760 3.52200
C 2.75731 -1.31412 -3.94033
C 0.92742 -4.90341 1.68539
C 3.07766 -2.55061 -3.46257
C 1.68296 -5.17994 0.58344
H 0.85303 3.46789 -2.81025
H -1.13029 -1.12774 4.74269
H 0.16817 4.18376 -0.30260
H -0.97005 1.49400 4.12967
H 3.01128 -0.88671 -4.90702
H 0.60340 -5.59314 2.46071
H 3.63743 -3.33489 -3.96576
H 2.08971 -6.14072 0.27808
C 1.58328 0.69322 -2.98786
C -0.03086 -2.80135 2.67810
C 2.51138 -3.82479 -1.36945
C 0.06352 1.93508 1.48273
C -0.25109 3.21747 2.19165
C -0.55036 -3.59738 3.83622
C 3.21818 -5.03522 -1.90220
C 1.70462 1.38089 -4.31414
Mn 1.02910 -0.99769 -0.05088
H -1.05893 -2.13686 -1.46546
C -7.45866 -0.18278 -0.23876
C -8.23971 -0.19756 -1.38264
C -7.64685 -0.40647 -2.64775
C -6.27601 -0.58879 -2.75978
C -5.45644 -0.56554 -1.60908
C -6.05393 -0.37282 -0.32117
H -5.81331 -0.74819 -3.73631
H -8.27312 -0.42384 -3.54290
Cl -3.16707 1.62222 -2.20542
H -9.31991 -0.05202 -1.30817
H -7.91673 -0.03156 0.74197
C -4.03068 -0.74526 -1.69629
C -3.30016 -0.78696 -0.50978
C -5.22940 -0.40479 0.84208
C -3.85670 -0.62786 0.75724
H -3.57758 -1.02980 -2.64955
H -1.97070 -1.00848 -0.61144
H -3.24391 -0.66966 1.65921
H -5.69355 -0.25902 1.82157
O 2.99963 -0.62503 0.85617
S 4.07583 0.42757 0.95915
O 4.47835 0.70577 2.34645
O 3.90128 1.58137 0.06445
C 5.54612 -0.47594 0.23676
F 6.60255 0.34191 0.18087
F 5.87476 -1.53112 0.98819
F 5.28174 -0.90230 -1.00221
O -1.57510 -3.37429 -2.47775
S -2.17635 -3.40084 -3.84441
O -2.69489 -2.09533 -4.31706
O -1.42579 -4.18941 -4.83603
C -3.73059 -4.40733 -3.56720
C -1.84969 -4.14116 3.83269
C -2.35031 -4.88451 4.90458
C -1.54128 -5.10104 6.02072
C -0.24647 -4.58256 6.06646
C 0.23194 -3.84249 4.98214
Cl -2.88394 -3.88974 2.44196
H -3.36322 -5.28565 4.85626
H -1.92362 -5.68083 6.86369
H 0.39562 -4.74620 6.93261
Cl 1.86050 -3.20570 5.06500
F -4.40450 -4.55023 -4.71331
F -3.43341 -5.62447 -3.10207
F -4.53841 -3.80842 -2.68212
C -1.52658 3.81344 2.14319
C -1.81686 5.00609 2.81131
C -0.81629 5.63327 3.55478
C 0.46070 5.07597 3.63248
C 0.72834 3.88249 2.95677
Cl -2.79641 3.04999 1.21251
H -2.81899 5.43091 2.74363
H -1.03435 6.56597 4.07977
H 1.25092 5.55563 4.21114
Cl 2.33289 3.19634 3.07339
C 2.79619 2.20656 -4.64774
C 2.89327 2.84905 -5.88505
C 1.88255 2.66809 -6.82980
C 0.79035 1.84740 -6.54642
C 0.71320 1.21311 -5.30343
Cl 4.09123 2.43636 -3.49342
H 3.75714 3.47986 -6.09738
H 1.94992 3.16757 -7.79885
H -0.00200 1.69089 -7.27932
Cl -0.65112 0.16639 -4.98596
C 4.51112 -5.38368 -1.46242
C 5.18155 -6.51452 -1.93574
C 4.55651 -7.33445 -2.87581
C 3.27731 -7.02676 -3.33968
C 2.62433 -5.88997 -2.85423
Cl 5.32395 -4.37409 -0.28636
H 6.18226 -6.74101 -1.56619
H 5.07218 -8.22109 -3.25134
H 2.77807 -7.65853 -4.07528
Cl 1.02862 -5.52408 -3.46422

114
PC (-1/5)
O -1.00662 0.28179 -1.18038
N 0.98464 2.32911 -0.31610
N -0.24314 0.75642 1.74222
N 1.93570 -0.06898 -1.58897
N 0.67902 -1.64462 0.45285
C 1.56319 2.90380 -1.42222
C -0.83975 -0.15854 2.57790
C 0.60716 3.35747 0.51525
C -0.48731 2.00040 2.27356
C 2.35303 0.83649 -2.53466
C -0.03864 -2.22693 1.47233
C 2.36644 -1.30648 -2.00426
C 1.28435 -2.66672 -0.24131
C 1.52280 4.34062 -1.29752
C -1.50637 0.53425 3.65412
C 0.95265 4.62018 -0.09092
C -1.27753 1.86674 3.47344
C 3.06882 0.14662 -3.58145
C 0.10768 -3.66049 1.40806
C 3.09312 -1.17417 -3.24429
C 0.93210 -3.93137 0.35587
H 1.90454 5.04398 -2.03333
H -2.06878 0.05703 4.45272
H 0.77059 5.59713 0.34975
H -1.62061 2.69185 4.09262
H 3.50610 0.61870 -4.45760
H -0.35828 -4.36842 2.08879
H 3.54876 -1.99432 -3.79335
H 1.26833 -4.90395 0.00556
C 2.16499 2.22530 -2.49172
C -0.76474 -1.55432 2.46572
C 2.09634 -2.53043 -1.37656
C -0.06360 3.22639 1.73900
C -0.34428 4.46789 2.53001
C -1.44851 -2.37846 3.51456
C 2.66977 -3.77415 -1.98614
C 2.66561 3.03823 -3.64700
Mn 0.85443 0.34396 0.08019
H -1.53077 -0.55097 -1.30579
C -8.06577 -0.28290 1.88425
C -8.37576 -1.60481 1.63584
C -7.68119 -2.32846 0.63127
C -6.69161 -1.71985 -0.11365
C -6.35377 -0.35480 0.11695
C -7.04961 0.37727 1.13710
H -6.14155 -2.26529 -0.88394
H -7.93346 -3.37661 0.45074
Cl -3.78227 2.41832 -1.32077
H -9.15781 -2.10142 2.21594
H -8.59678 0.27503 2.66042
C -5.33833 0.29366 -0.64261
C -5.03439 1.60952 -0.37857
C -6.69273 1.73676 1.36670
C -5.70193 2.35022 0.62955
H -4.81503 -0.26861 -1.41693
H -1.67312 0.97324 -1.03993
H -5.42368 3.38854 0.81506
H -7.21528 2.29833 2.14568
O 2.68327 0.37876 1.33737
S 3.85485 1.24813 1.71207
O 4.12392 1.26382 3.15847
O 3.92228 2.53672 1.00532
C 5.28374 0.27441 0.99712
F 6.43423 0.92267 1.20942
F 5.37319 -0.93146 1.56748
F 5.13577 0.10801 -0.32121
O -2.58501 -1.87050 -1.41376
S -3.19050 -2.54745 -2.60013
O -4.59433 -2.16158 -2.87155
O -2.31795 -2.63591 -3.78494
C -3.33772 -4.31530 -1.99901
C -2.77082 -2.83706 3.35519
C -3.41630 -3.60223 4.33056
C -2.73537 -3.92876 5.50375
C -1.42304 -3.49749 5.70240
C -0.79853 -2.73325 4.71353
Cl -3.64208 -2.44753 1.89015
H -4.44146 -3.93413 4.16255
H -3.23199 -4.52642 6.27135
H -0.87942 -3.74718 6.61420
Cl 0.84890 -2.20732 4.98928
F -3.75110 -5.11116 -2.99150
F -2.16353 -4.77325 -1.55591
F -4.22311 -4.40380 -0.99855
C -1.47585 5.27295 2.29543
C -1.73931 6.42660 3.03817
C -0.85457 6.80260 4.04964
C 0.28060 6.03597 4.31602
C 0.52274 4.88566 3.56040
Cl -2.59638 4.82518 1.02644
H -2.62955 7.01728 2.81940
H -1.05149 7.70297 4.63579
H 0.98039 6.32034 5.10264
Cl 1.95402 3.94324 3.91343
C 3.99720 3.49185 -3.73043
C 4.45946 4.25026 -4.80949
C 3.58115 4.57348 -5.84431
C 2.25423 4.14374 -5.80409
C 1.81471 3.38685 -4.71509
Cl 5.12383 3.10322 -2.44938
H 5.49886 4.57967 -4.82933
H 3.93457 5.16577 -6.69124
H 1.55794 4.38765 -6.60718
Cl 0.14562 2.85723 -4.69492
C 3.92060 -4.28461 -1.58874
C 4.46654 -5.44050 -2.15328
C 3.75425 -6.11712 -3.14442
C 2.51025 -5.64649 -3.56693
C 1.98281 -4.48860 -2.98839
Cl 4.83258 -3.45459 -0.34626
H 5.43905 -5.79863 -1.81369
H 4.17316 -7.02141 -3.59157
H 1.94358 -6.16762 -4.33949
Cl 0.42024 -3.91637 -3.52155

**[$Mn^{IV}$OH(TDCPP$^{\bullet-}$)OTf]$^{+}$ with H bonding to OTf, nucleophilic reaction at $C_1$**

114
RC (-1/5)
N -0.37592 -0.46301 2.13344
N -0.49309 2.03262 0.77487
N -1.33781 -1.77622 -0.21850
N -1.50778 0.71795 -1.55397
C -0.17178 -1.75925 2.54091
C -0.44307 3.10049 -0.08761
C -0.07638 0.34682 3.19998
C -0.18616 2.51145 2.02555
C -1.00575 -2.89524 0.51101
C -1.35119 1.97428 -2.08860
C -1.98281 -2.21346 -1.35233
C -2.16766 -0.04038 -2.49409
C 0.26742 -1.76645 3.91578
C -0.07495 4.29009 0.64117
C 0.30081 -0.46804 4.33061
C 0.05164 3.93276 1.94980
C -1.44610 -4.07360 -0.19213
C -1.93056 2.00948 -3.40946
C -2.06947 -3.65177 -1.32940
C -2.45957 0.77604 -3.64691
H 0.50213 -2.65753 4.49240
H 0.04586 5.27789 0.20383
H 0.57854 -0.08661 5.30996
H 0.30619 4.56848 2.79400
H -1.30940 -5.09470 0.15457
H -1.94835 2.87982 -4.06039
H -2.53253 -4.26056 -2.10178
H -2.98644 0.43550 -4.53457
C -0.42844 -2.91108 1.78682
C -0.80296 3.08869 -1.44094
C -2.43230 -1.41262 -2.41065
C -0.02992 1.74771 3.18850
C 0.27859 2.44927 4.47710
C -0.67041 4.35864 -2.22587
C -3.16048 -2.07470 -3.54351
C -0.11587 -4.23963 2.40373
C 7.60954 -0.34641 2.69338
C 7.79239 -0.17066 1.33059
C 6.67819 -0.03059 0.46468
C 5.35843 -0.06307 1.01979
C 5.19946 -0.24920 2.41235
C 6.30686 -0.38904 3.23648
H 7.84147 0.13671 -1.36515
H 8.47525 -0.45513 3.35112
H 8.79985 -0.14372 0.90721
C 6.83082 0.11823 -0.94840
C 4.23587 0.09278 0.14100
H 4.19175 -0.27012 2.83329
H 6.17192 -0.53085 4.31142
C 4.43263 0.19093 -1.24978
C 5.73149 0.21665 -1.78582
H 3.55971 0.22374 -1.90115
H 5.86895 0.29822 -2.86564
O 0.80118 -0.08684 -0.27351
H 0.95714 -0.70012 -1.04783
Mn -0.85759 0.12044 0.25755
Cl 3.77213 2.61862 0.24850
H 3.22385 -0.05044 0.52137
O -2.80077 0.28349 0.91648
S -3.78286 1.26870 1.53525
O -3.39290 2.67900 1.43251
O -4.30951 0.78830 2.81785
C -5.22917 1.11002 0.35924
F -6.15660 2.01693 0.67673
F -4.84533 1.32228 -0.90046
F -5.77860 -0.10210 0.44679
C -4.54371 -2.33786 -3.47356
C -5.24278 -2.95248 -4.51567
C -4.55662 -3.32610 -5.67116
C -3.18647 -3.09031 -5.78250
C -2.50675 -2.47397 -4.72801
Cl -5.43615 -1.88722 -2.03892
H -6.31348 -3.13182 -4.41233
H -5.09404 -3.80721 -6.49134
H -2.63564 -3.38118 -6.67764
Cl -0.78871 -2.21081 -4.90043
C -1.02881 -4.91199 3.23898
C -0.73288 -6.14645 3.82260
C 0.50576 -6.73916 3.57253
C 1.43740 -6.10985 2.74589
C 1.12011 -4.87563 2.17208
Cl -2.59216 -4.19205 3.56280
H -1.47066 -6.63072 4.46324
H 0.74602 -7.70384 4.02498
H 2.40627 -6.56594 2.53932
Cl 2.28847 -4.11271 1.11891
C 1.58996 2.82106 4.83498
C 1.87925 3.46507 6.04092
C 0.84129 3.75242 6.92806
C -0.47184 3.39926 6.61564
C -0.73800 2.75502 5.40439
Cl 2.90822 2.48118 3.73659
H 2.91024 3.73411 6.27328
H 1.05826 4.25601 7.87272
H -1.29228 3.61672 7.30041
Cl -2.38934 2.31456 5.03853
C 0.49066 4.63671 -2.97452
C 0.63609 5.81329 -3.71442
C -0.39960 6.74801 -3.72120
C -1.57014 6.51022 -2.99988
C -1.69340 5.32700 -2.26683
Cl 1.80313 3.48066 -2.99018
H 1.55464 5.98554 -4.27642
H -0.29459 7.67052 -4.29647
H -2.38875 7.23073 -3.00050
Cl -3.17762 5.05194 -1.38198
O 1.50154 -1.52063 -2.38102
S 2.35128 -2.75036 -2.47962
O 1.60254 -4.00105 -2.69306
C 3.21407 -2.47494 -4.12009
O 3.46255 -2.81271 -1.50918
F 4.06807 -3.47392 -4.36765

F 2.33335 -2.42208 -5.12587
F 3.90757 -1.32780 -4.11906

114
TS(-1/5)
N 0.02899 -0.74133 1.47514
N -0.20637 1.77692 0.13814
N -0.79388 -2.07863 -0.93033
N -1.04743 0.43270 -2.25690
C 0.24774 -2.03352 1.88844
C -0.33757 2.87587 -0.67607
C 0.31582 0.07441 2.54169
C 0.01755 2.25061 1.41022
C -0.52487 -3.18844 -0.15974
C -0.98007 1.71098 -2.76115
C -1.38192 -2.53075 -2.09009
C -1.56792 -0.36260 -3.25159
C 0.69596 -2.03144 3.26045
C -0.17567 4.07895 0.10360
C 0.72202 -0.73085 3.66896
C 0.02506 3.69313 1.39423
C -0.94234 -4.37383 -0.86470
C -1.43789 1.71192 -4.13024
C -1.48659 -3.96689 -2.04665
C -1.82743 0.43940 -4.42267
H 0.94617 -2.91737 3.83842
H -0.23065 5.09089 -0.28937
H 1.00337 -0.34311 4.64488
H 0.17205 4.32763 2.26438
H -0.84006 -5.38990 -0.49253
H -1.47759 2.58535 -4.77584
H -1.90793 -4.58527 -2.83500
H -2.24140 0.06685 -5.35602
C -0.00481 -3.19201 1.14107
C -0.64488 2.86765 -2.04361
C -1.78981 -1.74351 -3.17555
C 0.26299 1.47630 2.55105
C 0.48617 2.17953 3.85630
C -0.71560 4.18464 -2.75696
C -2.50026 -2.41549 -4.31406
C 0.23541 -4.51587 1.80062
C 5.94768 -2.29471 1.44493
C 6.06083 -2.04646 0.08028
C 5.25944 -1.07078 -0.54220
C 4.32224 -0.33376 0.25287
C 4.22317 -0.60688 1.64208
C 5.02551 -1.57248 2.22957
H 6.01968 -1.41956 -2.55473
H 6.57557 -3.05779 1.91145
H 6.77045 -2.61566 -0.52466
C 5.34931 -0.80153 -1.95561
C 3.50786 0.64585 -0.37653
H 3.51024 -0.03992 2.24298
H 4.94298 -1.77614 3.29957
C 3.71241 0.98263 -1.75586
C 4.60145 0.17190 -2.54524
H 2.93886 1.56218 -2.25448
H 4.66780 0.35596 -3.61827
O 1.37709 -0.28941 -0.92937
H 1.58260 -1.01305 -1.57758
Mn -0.42580 -0.16441 -0.42200
Cl 4.91132 2.91013 -1.35196
H 2.84507 1.26565 0.22206
O -2.49756 -0.09506 0.19869
S -3.51351 0.75463 0.92811
O -3.20308 2.19093 0.97090
O -4.00303 0.12992 2.16572
C -4.97574 0.65211 -0.23553
F -5.95030 1.45962 0.19435
F -4.63279 1.02884 -1.46999
F -5.45801 -0.59279 -0.28741
C -3.88725 -2.66438 -4.25596
C -4.58040 -3.28694 -5.29701
C -3.88537 -3.67988 -6.44101
C -2.51326 -3.45229 -6.54274
C -1.83976 -2.82792 -5.48867
Cl -4.79204 -2.18085 -2.83918
H -5.65354 -3.45640 -5.20271
H -4.41804 -4.16761 -7.26037
H -1.95618 -3.75441 -7.43026
Cl -0.12244 -2.56391 -5.65140
C -0.72319 -5.10942 2.64552
C -0.50219 -6.33666 3.27553
C 0.70541 -7.00376 3.06435
C 1.67908 -6.45534 2.22893
C 1.43652 -5.22685 1.60781
Cl -2.25181 -4.29984 2.91989
H -1.27361 -6.75787 3.92109
H 0.88740 -7.96335 3.55338
H 2.62387 -6.97030 2.05102
Cl 2.65641 -4.57295 0.54066
C 1.71815 2.76931 4.20190
C 1.92165 3.42128 5.42071
C 0.87234 3.49828 6.33678
C -0.36632 2.93074 6.03766
C -0.54648 2.28301 4.81268
Cl 3.06484 2.70156 3.08162
H 2.89535 3.86008 5.64096
H 1.02163 4.00615 7.29212
H -1.19634 2.98605 6.74287
Cl -2.11230 1.58978 4.46331
C 0.43893 4.83590 -3.23576
C 0.38082 6.05609 -3.91468
C -0.85696 6.66402 -4.12413
C -2.02512 6.06329 -3.65396
C -1.94366 4.84241 -2.97960
Cl 2.01741 4.12939 -2.95909
H 1.30269 6.51859 -4.26898
H -0.91145 7.61761 -4.65385
H -2.99861 6.53201 -3.80174
Cl -3.42927 4.12955 -2.38877
O 2.14191 -2.11465 -2.87529
S 2.83024 -3.42227 -3.07510
O 1.93088 -4.56258 -3.33654
C 3.69972 -3.19498 -4.72450
O 3.95429 -3.69078 -2.15315
F 4.31335 -4.33221 -5.07569
F 2.83965 -2.87405 -5.69928
F 4.62944 -2.22975 -4.67124

114
PC(-1/5)
N 0.02899 -0.74133 1.47514
N -0.20637 1.77692 0.13814
N -0.79388 -2.07863 -0.93033
N -1.04743 0.43270 -2.25690
C 0.24774 -2.03352 1.88844
C -0.33757 2.87587 -0.67607
C 0.31582 0.07441 2.54169
C 0.01755 2.25061 1.41022
C -0.52487 -3.18844 -0.15974
C -0.98007 1.71098 -2.76115
C -1.38192 -2.53075 -2.09009
C -1.56792 -0.36260 -3.25159
C 0.69596 -2.03144 3.26045
C -0.17567 4.07895 0.10360
C 0.72202 -0.73085 3.66896
C 0.02506 3.69313 1.39423
C -0.94234 -4.37383 -0.86470
C -1.43789 1.71192 -4.13024
C -1.48659 -3.96689 -2.04665
C -1.82743 0.43940 -4.42267
H 0.94617 -2.91737 3.83842
H -0.23065 5.09089 -0.28937
H 1.00337 -0.34311 4.64488
H 0.17205 4.32763 2.26438
H -0.84006 -5.38990 -0.49253
H -1.47759 2.58535 -4.77584
H -1.90793 -4.58527 -2.83500
H -2.24140 0.06685 -5.35602
C -0.00481 -3.19201 1.14107
C -0.64488 2.86765 -2.04361
C -1.78981 -1.74351 -3.17555
C 0.26299 1.47630 2.55105
C 0.48617 2.17953 3.85630
C -0.71560 4.18464 -2.75696
C -2.50026 -2.41549 -4.31406
C 0.23541 -4.51587 1.80062
C 5.94768 -2.29471 1.44493
C 6.06083 -2.04646 0.08028
C 5.25944 -1.07078 -0.54220
C 4.32224 -0.33376 0.25287
C 4.22317 -0.60688 1.64208
C 5.02551 -1.57248 2.22957
H 6.01968 -1.41956 -2.55473
H 6.57557 -3.05779 1.91145
H 6.77045 -2.61566 -0.52466
C 5.34931 -0.80153 -1.95561
C 3.50786 0.64585 -0.37653
H 3.51024 -0.03992 2.24298
H 4.94298 -1.77614 3.29957
C 3.71241 0.98263 -1.75586
C 4.60145 0.17190 -2.54524
H 2.93886 1.56218 -2.25448
H 4.66780 0.35596 -3.61827
O 1.37709 -0.28941 -0.92937
H 1.58260 -1.01305 -1.57758
Mn -0.42580 -0.16441 -0.42200
Cl 4.91132 2.91013 -1.35196
H 2.84507 1.26565 0.22206
O -2.49756 -0.09506 0.19869
S -3.51351 0.75463 0.92811
O -3.20308 2.19093 0.97090
O -4.00303 0.12992 2.16572
C -4.97574 0.65211 -0.23553
F -5.95030 1.45962 0.19435
F -4.63279 1.02884 -1.46999
F -5.45801 -0.59279 -0.28741
C -3.88725 -2.66438 -4.25596
C -4.58040 -3.28694 -5.29701
C -3.88537 -3.67988 -6.44101
C -2.51326 -3.45229 -6.54274
C -1.83976 -2.82792 -5.48867
Cl -4.79204 -2.18085 -2.83918
H -5.65354 -3.45640 -5.20271
H -4.41804 -4.16761 -7.26037
H -1.95618 -3.75441 -7.43026
Cl -0.12244 -2.56391 -5.65140
C -0.72319 -5.10942 2.64552
C -0.50219 -6.33666 3.27553
C 0.70541 -7.00376 3.06435
C 1.67908 -6.45534 2.22893
C 1.43652 -5.22685 1.60781
Cl -2.25181 -4.29984 2.91989
H -1.27361 -6.75787 3.92109
H 0.88740 -7.96335 3.55338
H 2.62387 -6.97030 2.05102
Cl 2.65641 -4.57295 0.54066
C 1.71815 2.76931 4.20190
C 1.92165 3.42128 5.42071
C 0.87234 3.49828 6.33678
C -0.36632 2.93074 6.03766
C -0.54648 2.28301 4.81268
Cl 3.06484 2.70156 3.08162
H 2.89535 3.86008 5.64096
H 1.02163 4.00615 7.29212
H -1.19634 2.98605 6.74287
Cl -2.11230 1.58978 4.46331
C 0.43893 4.83590 -3.23576
C 0.38082 6.05609 -3.91468
C -0.85696 6.66402 -4.12413
C -2.02512 6.06329 -3.65396
C -1.94366 4.84241 -2.97960
Cl 2.01741 4.12939 -2.95909
H 1.30269 6.51859 -4.26898
H -0.91145 7.61761 -4.65385
H -2.99861 6.53201 -3.80174
Cl -3.42927 4.12955 -2.38877
O 2.14191 -2.11465 -2.87529
S 2.83024 -3.42227 -3.07510
O 1.93088 -4.56258 -3.33654
C 3.69972 -3.19498 -4.72450
O 3.95429 -3.69078 -2.15315
F 4.31335 -4.33221 -5.07569
F 2.83965 -2.87405 -5.69928
F 4.62944 -2.22975 -4.67124

**[Mn$^{IV}$OH(TDCPP$^{\bullet-}$)OTf]$^{+}$ with H bonding to OTf, nucleophilic reaction at $C_2$**

114
RC (-1/5)
N -0.31118 -0.38006 2.11878
N -0.50678 2.11218 0.76139
N -1.09565 -1.73252 -0.27660
N -1.34245 0.75578 -1.61555
C -0.06759 -1.66582 2.53733
C -0.48303 3.18583 -0.09459
C -0.09734 0.44129 3.19733
C -0.28976 2.60230 2.02679
C -0.75454 -2.83641 0.47250
C -1.22328 2.01946 -2.14167
C -1.66300 -2.19826 -1.44057
C -1.90728 -0.03447 -2.58978
C 0.31337 -1.65410 3.92954
C -0.22530 4.39221 0.65401
C 0.27168 -0.35584 4.34326
C -0.13933 4.03604 1.96643
C -1.10678 -4.03273 -0.24937
C -1.73235 2.02760 -3.49188
C -1.68650 -3.63882 -1.41904
C -2.18125 0.76842 -3.75696
H 0.56400 -2.53402 4.51644
H -0.14740 5.38863 0.22659
H 0.49125 0.03748 5.33261
H 0.03305 4.68207 2.82344
H -0.94379 -5.04678 0.10646
H -1.76247 2.89781 -4.14266
H -2.08118 -4.26750 -2.21310
H -2.64137 0.40265 -4.67131
C -0.24369 -2.82817 1.77632
C -0.76988 3.15881 -1.46539
C -2.10163 -1.41906 -2.51944
C -0.13360 1.84265 3.19235
C 0.05798 2.55368 4.49830
C -0.65405 4.43681 -2.23904
C -2.73605 -2.11521 -3.68738
C 0.07241 -4.14307 2.42105
C 6.66258 -2.22298 2.04906
C 6.71955 -1.72997 0.75486
C 5.86058 -0.67973 0.34464
C 4.93813 -0.12926 1.28960
C 4.89576 -0.65151 2.60199
C 5.74403 -1.68399 2.97617
H 6.55387 -0.61841 -1.71363
H 7.32692 -3.03503 2.35407
H 7.42276 -2.15253 0.03272
C 5.86480 -0.17635 -0.99004
C 4.07919 0.94101 0.87239
H 4.19171 -0.22376 3.31977
H 5.70316 -2.08228 3.99278
C 4.09986 1.38870 -0.46374
C 5.00020 0.83538 -1.38428
H 3.40189 2.16797 -0.77223
H 5.00613 1.18676 -2.41746
O 0.94689 0.08481 -0.24435
H 1.18371 -0.56807 -0.96342
Mn -0.73971 0.18449 0.22160
Cl 5.31970 3.02842 1.68444
H 3.28050 1.26736 1.53622
O -2.71951 0.24099 0.79989
S -3.78289 1.17444 1.36055
O -3.44972 2.60178 1.29781
O -4.37089 0.65587 2.60104
C -5.14373 0.97060 0.09255
F -6.12293 1.84028 0.35406
F -4.68867 1.20599 -1.13925
F -5.65209 -0.26154 0.13860
C -4.10517 -2.45072 -3.68762
C -4.71711 -3.09794 -4.76417
C -3.95438 -3.43110 -5.88352
C -2.59462 -3.12316 -5.92516
C -2.00268 -2.47541 -4.83708
Cl -5.09082 -2.05194 -2.29936
H -5.78069 -3.33390 -4.71561
H -4.42352 -3.93725 -6.73011
H -1.98476 -3.38185 -6.79143
Cl -0.29451 -2.12114 -4.91978
C -0.86903 -4.83310 3.20930
C -0.57406 -6.05320 3.82274
C 0.69296 -6.61319 3.65198
C 1.65355 -5.96567 2.87415
C 1.33673 -4.74624 2.26906
Cl -2.46776 -4.15440 3.43469
H -1.33449 -6.55186 4.42469
H 0.93278 -7.56638 4.12840
H 2.64507 -6.39617 2.72932
Cl 2.54212 -3.96182 1.27612
C 1.31074 3.04173 4.92007
C 1.48243 3.69089 6.14598
C 0.38411 3.86615 6.98802
C -0.87481 3.39790 6.61064
C -1.02402 2.75086 5.38131
Cl 2.71545 2.85731 3.88924
H 2.47196 4.05189 6.42868
H 0.51057 4.37273 7.94740
H -1.74247 3.52833 7.25831
Cl -2.61076 2.16976 4.93329
C 0.53038 4.77067 -2.92503
C 0.66748 5.96001 -3.64498
C -0.40379 6.85251 -3.69624
C -1.59938 6.55892 -3.03966
C -1.71229 5.36353 -2.32481
Cl 1.88624 3.66134 -2.90086
H 1.60554 6.17496 -4.15781
H -0.30681 7.78514 -4.25631
H -2.44563 7.24576 -3.07653
Cl -3.22729 5.01871 -1.52093
O 1.81528 -1.44934 -2.22882
S 2.70364 -2.64896 -2.31930
O 2.00332 -3.91538 -2.60050
C 3.63843 -2.31222 -3.90800
O 3.77242 -2.70829 -1.30252
F 4.48838 -3.31355 -4.16596
F 2.80495 -2.19906 -4.94950
F 4.34906 -1.17930 -3.82527

114
TS (-1/5)
N -0.01156 -0.71067 1.67941
N -0.25961 1.80117 0.34575
N -0.79525 -2.05227 -0.72683
N -1.09743 0.45289 -2.04418
C 0.22925 -1.99835 2.09353
C -0.31508 2.89125 -0.48747
C 0.20346 0.10651 2.76142
C -0.05997 2.28003 1.61859
C -0.47331 -3.16025 0.02558
C -1.03106 1.72870 -2.54953
C -1.36190 -2.51278 -1.89400
C -1.64547 -0.33960 -3.02513
C 0.62369 -1.99144 3.48222
C -0.11502 4.09663 0.28080
C 0.58658 -0.69423 3.90034
C 0.01105 3.72100 1.58461
C -0.83177 -4.35276 -0.69951
C -1.54893 1.74008 -3.89720
C -1.39476 -3.95300 -1.87513
C -1.95523 0.47029 -4.17911
H 0.88061 -2.87275 4.06430
H -0.10249 5.10416 -0.12724
H 0.81463 -0.30506 4.88948
H 0.15576 4.36057 2.45152
H -0.68124 -5.36879 -0.34392
H -1.61438 2.61798 -4.53489
H -1.78527 -4.57820 -2.67388
H -2.40963 0.10377 -5.09594
C 0.03137 -3.15847 1.33255
C -0.62374 2.87525 -1.85486
C -1.81577 -1.72866 -2.96388
C 0.12707 1.50742 2.77259
C 0.26183 2.20453 4.09418
C -0.59789 4.17547 -2.60038
C -2.48460 -2.41914 -4.11635
C 0.30142 -4.47922 1.98689
C 6.24582 -2.49747 1.89338
C 6.19280 -2.20480 0.53575
C 5.40867 -1.12817 0.05859
C 4.68288 -0.33757 0.99311
C 4.74302 -0.64918 2.35810
C 5.51397 -1.72198 2.80868
H 5.84063 -1.47435 -2.04854
H 6.85025 -3.33568 2.24858
H 6.74216 -2.81688 -0.18358
C 5.28080 -0.85762 -1.34533
C 3.90966 0.83243 0.50393
H 4.18703 -0.03616 3.07150
H 5.54819 -1.95725 3.87518
C 3.66206 0.89444 -0.94132
C 4.40164 0.11417 -1.82007
H 2.99375 1.67155 -1.30726
H 4.26482 0.23423 -2.89560
O 1.31116 -0.20305 -0.72496
H 1.52453 -0.94752 -1.34286
Mn -0.45334 -0.13493 -0.21630
Cl 5.01880 2.44916 0.87053
H 3.04243 1.08375 1.11847
O -2.51545 -0.09284 0.41427
S -3.58057 0.81462 0.99025
O -3.23308 2.24200 1.02053
O -4.22176 0.24665 2.18522
C -4.91487 0.71332 -0.31955
F -5.87007 1.61064 -0.05597
F -4.42029 0.97277 -1.53280
F -5.47489 -0.49877 -0.33502
C -3.84668 -2.78046 -4.06089
C -4.49502 -3.42357 -5.11834
C -3.77879 -3.72478 -6.27679
C -2.42933 -3.38720 -6.37606
C -1.80068 -2.74424 -5.30572
Cl -4.77929 -2.41601 -2.62706
H -5.55074 -3.68040 -5.02498
H -4.27651 -4.22768 -7.10886
H -1.85529 -3.61860 -7.27395
Cl -0.10769 -2.34933 -5.46704
C -0.65523 -5.11090 2.80612
C -0.40730 -6.33452 3.43307
C 0.82611 -6.95983 3.24420
C 1.79842 -6.37390 2.43311
C 1.52858 -5.14963 1.81476
Cl -2.21610 -4.35513 3.05205
H -1.17819 -6.78554 4.05881
H 1.02927 -7.91624 3.73110
H 2.76306 -6.85641 2.27150
Cl 2.74543 -4.45147 0.77323
C 1.46828 2.78253 4.53586
C 1.58386 3.42131 5.77335
C 0.47085 3.49489 6.61096
C -0.74471 2.93585 6.21607
C -0.83703 2.30109 4.97464
Cl 2.88885 2.72076 3.51243
H 2.54093 3.85270 6.06873
H 0.55168 3.99241 7.57992
H -1.62371 2.98641 6.85961
Cl -2.37389 1.61159 4.50847
C 0.56420 4.62055 -3.26054
C 0.61304 5.83132 -3.95603
C -0.52695 6.63390 -4.00763
C -1.70294 6.23010 -3.37470
C -1.72707 5.01518 -2.68470
Cl 2.01078 3.63221 -3.23331
H 1.53747 6.13245 -4.44992
H -0.49923 7.58229 -4.54863
H -2.60216 6.84599 -3.41072
Cl -3.22016 4.53443 -1.90999
O 2.08343 -2.10560 -2.60773
S 2.85468 -3.35027 -2.88275
O 2.03251 -4.52084 -3.24470
C 3.74161 -2.94875 -4.48834
O 3.97662 -3.61799 -1.95739
F 4.45712 -4.00452 -4.89489
F 2.88413 -2.63168 -5.46574
F 4.58771 -1.91561 -4.34071

114
PC (-1/5)
N -0.09646 -0.40703 2.15082
N -0.24253 2.12310 0.82340
N -0.90251 -1.72170 -0.27216
N -1.08032 0.81643 -1.58895
C 0.03721 -1.70773 2.57770
C -0.29759 3.23118 0.00696
C 0.12163 0.39617 3.24491
C -0.03339 2.58666 2.10490
C -0.64962 -2.84236 0.48525
C -1.01547 2.10168 -2.07469
C -1.41547 -2.15960 -1.47041
C -1.59916 0.03551 -2.59714
C 0.37786 -1.72219 3.97949
C -0.06477 4.41951 0.78881
C 0.41271 -0.42344 4.39567
C 0.07152 4.02393 2.08675
C -0.99816 -4.02217 -0.26734
C -1.49299 2.12854 -3.43575
C -1.48604 -3.59978 -1.46836
C -1.87401 0.85771 -3.75023
H 0.55390 -2.61650 4.57184
H -0.03587 5.43215 0.39452
H 0.62923 -0.04853 5.39285
H 0.24023 4.64970 2.95945
H -0.88543 -5.04448 0.08427
H -1.54570 3.01430 -4.06367
H -1.84669 -4.20959 -2.29283
H -2.29352 0.50137 -4.68751
C -0.19362 -2.85879 1.81077
C -0.61282 3.23873 -1.35943
C -1.78906 -1.35285 -2.55558
C 0.11009 1.79958 3.25610
C 0.22904 2.48456 4.58539
C -0.59669 4.55188 -2.08395
C -2.40666 -2.01768 -3.74977
C -0.00981 -4.18745 2.47907
C 6.77898 -1.39806 1.51946
C 6.39097 -1.09970 0.21165
C 5.25672 -0.31013 -0.03758
C 4.51966 0.19572 1.05719
C 4.90701 -0.11663 2.36466
C 6.03217 -0.91352 2.59970
H 5.44430 -0.34940 -2.22302
H 7.66168 -2.01751 1.69782
H 6.95872 -1.49803 -0.63307
C 4.79586 -0.03689 -1.40109
C 3.37145 1.12048 0.77865
H 4.32958 0.27793 3.20475
H 6.32747 -1.15258 3.62433
C 2.64265 0.87879 -0.55395
C 3.59816 0.51538 -1.66046
H 2.11943 1.81037 -0.81212
H 3.25227 0.64643 -2.68854
O 1.64072 -0.13120 -0.36890
H 1.86276 -0.95745 -0.87863
Mn -0.61274 0.20242 0.28641
Cl 4.02751 2.85988 0.73843
H 2.64626 1.12798 1.59899
O -2.72406 0.30252 0.91561
S -3.78440 1.25110 1.41613
O -3.40010 2.67041 1.40193
O -4.48484 0.75545 2.61136
C -5.06841 1.12495 0.06096
F -6.05900 1.99390 0.28853
F -4.53429 1.40348 -1.13225
F -5.59401 -0.10312 0.01441
C -3.78422 -2.31424 -3.79105
C -4.38303 -2.93276 -4.89151
C -3.59858 -3.27250 -5.99407
C -2.23115 -2.99681 -5.99741
C -1.65357 -2.37730 -4.88552
Cl -4.79714 -1.89493 -2.42753
H -5.45343 -3.14075 -4.87543
H -4.05741 -3.75675 -6.85892
H -1.60579 -3.25793 -6.85182
Cl 0.06320 -2.05297 -4.92156
C -1.06604 -4.83029 3.15427
C -0.90300 -6.06459 3.78810
C 0.34575 -6.68720 3.75669
C 1.41941 -6.08539 3.09963
C 1.23300 -4.85039 2.47218
Cl -2.64201 -4.06840 3.21323
H -1.74980 -6.52484 4.29834
H 0.48292 -7.65243 4.24921
H 2.39920 -6.56318 3.06639
Cl 2.58771 -4.12187 1.64226
C 1.44951 2.97249 5.09088
C 1.54825 3.59726 6.33696
C 0.40181 3.74831 7.11720
C -0.82951 3.28018 6.65765
C -0.90387 2.65756 5.40894
Cl 2.90848 2.81347 4.13586
H 2.51747 3.95774 6.68325
H 0.46878 4.23545 8.09247
H -1.73391 3.39202 7.25671
Cl -2.46029 2.07953 4.86077
C 0.55366 5.01160 -2.75493
C 0.58661 6.23182 -3.43489
C -0.55729 7.02999 -3.45920
C -1.72185 6.61223 -2.81452
C -1.73080 5.38780 -2.14103
Cl 2.00687 4.03339 -2.75776
H 1.50256 6.54382 -3.93777
H -0.54155 7.98569 -3.98768
H -2.62435 7.22422 -2.82884
Cl -3.20876 4.88974 -1.35066
O 2.02866 -2.28503 -1.90719
S 2.97575 -3.43974 -1.97568
O 2.31614 -4.75599 -2.06437
C 3.74547 -3.24980 -3.67607
O 4.13666 -3.34882 -1.06885
F 4.72414 -4.14949 -3.83758
F 2.84173 -3.44660 -4.64266
F 4.27434 -2.03093 -3.85109

**[$Mn^{IV}O(Por^{+\bullet})OTf$] electrophilic reaction at $C_1$**

65
RC (1/5)
O -1.27720 0.12778 -0.01856
N 0.23384 1.55195 1.73417
N -0.15126 -1.29062 1.99627
N 1.00832 1.19585 -1.01940
N 0.64167 -1.64971 -0.75318
C 0.46696 2.86502 1.41794
C -0.25973 -2.65475 1.93172
C -0.18317 1.52461 3.03983
C -0.51016 -0.92149 3.26535
C 1.13705 2.55804 -0.94932
C 0.42286 -2.96418 -0.43255
C 1.34167 0.82903 -2.29692
C 1.02766 -1.61899 -2.06703
C 0.20025 3.69939 2.56875
C -0.69762 -3.17129 3.21074
C -0.20434 2.86846 3.57387
C -0.85517 -2.09595 4.03700
C 1.57542 3.07421 -2.22828
C 0.68897 -3.79864 -1.58470
C 1.70150 2.00220 -3.06399
C 1.06115 -2.96394 -2.59853
H 0.31476 4.78235 2.58809
H -0.85687 -4.22603 3.43097
H -0.49133 3.12544 4.59264
H -1.17020 -2.08127 5.07953
H 1.76094 4.12623 -2.44075
H 0.59684 -4.88384 -1.59742
H 2.01274 1.98783 -4.10765
H 1.33753 -3.21829 -3.62075
C 0.88870 3.34038 0.17752
C 0.00757 -3.43943 0.81051
C 1.35204 -0.47369 -2.79190
C -0.53328 0.38241 3.75676
H -0.84334 0.51956 4.79414
H -0.12297 -4.51811 0.91389
H 1.63783 -0.60865 -3.83625
H 1.03511 4.41748 0.07944
Mn 0.29423 -0.03547 0.44766
C -6.29717 -0.60015 -3.03221
C -5.71311 -1.84090 -2.82569
C -4.42971 -1.93186 -2.25814
C -3.72002 -0.76855 -1.90103
C -4.32748 0.51940 -2.06799
C -5.62798 0.60553 -2.66090
H -2.77823 -0.82116 -1.34799
H -3.97123 -2.90814 -2.09056
Cl -2.28121 -1.08995 -4.03672
H -6.24855 -2.75067 -3.10578
H -7.29301 -0.53059 -3.47839
C -3.66813 1.70050 -1.65282
C -4.27142 2.93694 -1.83683
C -6.21696 1.88339 -2.83902
C -5.54725 3.02870 -2.43610
H -2.68471 1.60377 -1.18385
H -3.75855 3.84687 -1.51566
H -6.01009 4.00847 -2.57758
H -7.20863 1.95322 -3.29367
O 2.41291 -0.31983 1.01550
S 3.32374 0.23782 2.07289
O 2.95417 -0.10872 3.45640
O 3.76555 1.62354 1.83595
C 4.86269 -0.77817 1.75827
F 5.82787 -0.42901 2.61710
F 4.61718 -2.08315 1.91658
F 5.32076 -0.58596 0.51690

65
TS(1/5)
O -2.19612 3.34786 1.36769
N -0.94186 4.78622 3.38665
N -1.45453 1.96194 3.63978
N 0.31516 4.33566 0.83207
N -0.17969 1.50314 1.09140
C -0.62654 6.08577 3.08216
C -1.60881 0.60133 3.57656
C -1.57388 4.80294 4.60352
C -2.01531 2.37351 4.82027
C 0.45257 5.69726 0.88462
C -0.51616 0.20763 1.38416
C 0.87047 3.92271 -0.35038
C 0.44341 1.48888 -0.12877
C -1.06511 6.95583 4.15009
C -2.28625 0.13218 4.76578
C -1.65167 6.16091 5.09300
C -2.53824 1.23075 5.53657
C 1.12881 6.16589 -0.30560
C -0.07823 -0.66349 0.31510
C 1.38915 5.06547 -1.07069
C 0.51727 0.13102 -0.62262
H -0.93063 8.03655 4.16255
H -2.52725 -0.91005 4.97060
H -2.10021 6.45207 6.04177
H -3.02991 1.28043 6.50715
H 1.36941 7.20793 -0.51172
H -0.21489 -1.74397 0.30092
H 1.88814 5.01367 -2.03744
H 0.97182 -0.16025 -1.56857
C 0.01780 6.51747 1.92448
C -1.17684 -0.21970 2.53566
C 0.93747 2.60543 -0.80227
C -2.07445 3.68961 5.27579
H -2.55315 3.86291 6.24108
H -1.37345 -1.28911 2.62988
H 1.41302 2.43413 -1.76955
H 0.20086 7.58879 1.82575
Mn -0.70046 3.16609 2.16961
C -6.71215 2.50011 0.61498
C -5.85330 1.48241 0.18815
C -4.60364 1.77166 -0.34380
C -4.08894 3.12846 -0.35637
C -5.04953 4.21661 -0.04746
C -6.33323 3.87626 0.48721
H -3.16803 3.19024 0.50877
H -3.94578 0.97033 -0.68760
Cl -3.04305 3.45631 -1.85788
H -6.17390 0.43940 0.26141
H -7.69790 2.25938 1.02019
C -4.70439 5.57364 -0.18108
C -5.58854 6.58275 0.19133
C -7.21541 4.92427 0.86167
C -6.85282 6.25474 0.71695
H -3.72504 5.82807 -0.59089
H -5.29822 7.63013 0.07635
H -7.54663 7.04706 1.00973
H -8.19640 4.66166 1.26767
O 1.31121 2.82879 3.15225
S 2.12300 3.55913 4.18297
O 1.58337 3.49555 5.55327
O 2.65156 4.86354 3.74532
C 3.64293 2.47003 4.25755
F 4.51942 2.95886 5.14317
F 3.32464 1.22582 4.63137
F 4.24760 2.40640 3.06619

65
PC(1/5)
O -0.53314 1.65325 -0.86896
N 0.66077 1.60349 1.84885
N -0.66044 -0.77669 0.88530
N 2.41339 1.57191 -0.44780
N 1.05923 -0.78226 -1.43795
C 1.42004 2.70490 2.15397
C -1.15191 -1.89980 0.27279
C -0.23293 1.43539 2.87557
C -1.36629 -0.61308 2.04798
C 2.92406 2.67844 0.17826
C 0.32249 -1.90254 -1.72634
C 3.14731 1.38281 -1.58963
C 1.98468 -0.64103 -2.44150
C 0.98590 3.25875 3.41610
C -2.20547 -2.47419 1.08132
C -0.03814 2.47192 3.86338
C -2.33872 -1.67619 2.18175
C 4.02670 3.20958 -0.59327
C 0.79102 -2.48714 -2.96204
C 4.16596 2.40566 -1.68888
C 1.82151 -1.70585 -3.40503
H 1.42414 4.13495 3.89191
H -2.76109 -3.37564 0.82656
H -0.61459 2.56867 4.78237
H -3.02611 -1.78600 3.01939
H 4.61285 4.08470 -0.31604
H 0.37905 -3.38653 -3.41768
H 4.88982 2.48347 -2.49899
H 2.43022 -1.83133 -4.29947
C 2.46383 3.21486 1.38125
C -0.70698 -2.42399 -0.94116
C 2.95183 0.36241 -2.52131
C -1.18043 0.41555 2.97215
H -1.82113 0.41371 3.85564
H -1.19975 -3.32768 -1.30390
H 3.61990 0.34147 -3.38415
H 2.97469 4.10213 1.75919
Mn 0.74781 0.51046 0.12362
C -5.97697 0.81186 -0.45014
C -4.66651 1.13863 -0.17458
C -3.64002 0.89714 -1.12301
C -3.96967 0.32853 -2.33528
C -5.30962 -0.03168 -2.67868
C -6.33110 0.22372 -1.69706
H -0.62348 1.34898 -1.78324
H -2.59629 1.16271 -0.90399
Cl -2.67619 0.03751 -3.49985
H -4.40066 1.58929 0.78490
H -6.76394 0.99967 0.28487
C -5.68365 -0.62002 -3.91959
C -6.99981 -0.94166 -4.18206
C -7.67796 -0.12253 -2.00529
C -8.00828 -0.69158 -3.21734
H -4.91025 -0.81386 -4.66390
H -7.26757 -1.39281 -5.14081
H -9.04672 -0.95120 -3.43772
H -8.45036 0.07313 -1.25656
O 2.38924 -0.97531 1.31508
S 3.02125 -0.94425 2.66608
O 2.09960 -1.18858 3.79414
O 4.01629 0.12859 2.86697
C 4.06916 -2.49544 2.62740
F 4.73225 -2.64822 3.78166
F 3.31243 -3.58460 2.44001
F 4.97090 -2.44401 1.63834

**[$Mn^{IV}OH(Por^{+\bullet})OTf]^+$ with H bonding to OTf, electrophilic reaction at $C_1$**

74
RC (-1/5)
O -0.58131 0.30107 -0.20952
N 1.24658 2.32693 0.07777
N 0.73866 0.45370 2.16751
N 1.66018 0.17180 -1.75019
N 1.18713 -1.70101 0.35544
C 1.65032 3.06601 -1.00764
C 0.72803 -0.57302 3.07984
C 0.80773 3.21633 1.02916
C 0.38722 1.59777 2.84211
C 2.03036 1.20173 -2.57955
C 1.10263 -2.43715 1.51114
C 1.66396 -0.97518 -2.50599
C 1.24311 -2.59248 -0.68840
C 1.48972 4.47046 -0.71994
C 0.36914 -0.05703 4.37789
C 0.94763 4.56245 0.53104
C 0.13432 1.28039 4.22574
C 2.29407 0.68480 -3.90106
C 1.12573 -3.84303 1.18808
C 2.04603 -0.65862 -3.86074
C 1.18952 -3.93918 -0.17274
H 1.74533 5.27388 -1.40894
H 0.29162 -0.66084 5.28061
H 0.67608 5.45779 1.08798
H -0.16315 2.00704 4.98003
H 2.61279 1.29034 -4.74805
H 1.07271 -4.64445 1.92278
H 2.12915 -1.38799 -4.66494
H 1.21644 -4.83650 -0.78881
C 2.06114 2.55016 -2.23312
C 0.93688 -1.91762 2.79099
C 1.43157 -2.26211 -2.02713
C 0.37398 2.88263 2.30840
H 0.06747 3.69733 2.96561
H 0.88143 -2.62496 3.61885
H 1.46975 -3.08111 -2.74662
H 2.36218 3.26159 -3.00316
Mn 1.12735 0.30889 0.20081
H -1.15220 -0.16181 0.46774
C -3.70409 1.85442 -5.65660
C -2.41635 2.33463 -5.83541
C -1.44260 2.15570 -4.82787
C -1.76650 1.50301 -3.64719
C -3.07485 1.00984 -3.43858
C -4.06243 1.18005 -4.46100
H -1.02183 1.36617 -2.85974
H -0.42905 2.53399 -4.97990
Cl -4.02666 2.28454 -0.65221
H -2.15033 2.85233 -6.76017
H -4.45726 1.98690 -6.43769
C -3.44285 0.34179 -2.22386
C -4.73553 -0.19786 -2.07196
C -5.37096 0.64780 -4.25104
C -5.69501 -0.03106 -3.08559
H -2.66163 0.09849 -1.50341
H -4.96862 -0.74332 -1.15491
H -6.69854 -0.44159 -2.95400
H -6.12015 0.77663 -5.03696
O 3.12198 0.22299 0.64555
S 4.13860 1.22528 1.18272
O 3.71798 1.91971 2.40539
O 4.78189 2.01993 0.12946
C 5.45535 0.02280 1.74785
F 6.47776 0.70094 2.27327
F 4.97024 -0.80227 2.67646
F 5.90693 -0.70203 0.72425
O -2.28448 -0.88627 1.48355
S -3.14554 -2.00878 0.99769
O -2.60017 -2.74102 -0.16155
C -3.05179 -3.23739 2.40647
O -4.58808 -1.68917 0.94727
F -3.82322 -4.29780 2.14419
F -1.79954 -3.67304 2.59187
F -3.47313 -2.68474 3.54790

74
TS (-1/5)
O -2.49865 3.19818 2.39840
N -0.39601 5.09832 2.43877
N -0.79719 3.30970 4.64729
N -0.34619 2.86029 0.64027
N -0.71273 1.07147 2.86221
C -0.12601 5.78009 1.27753
C -0.84898 2.30565 5.58349
C -0.58428 6.03944 3.42124
C -0.91295 4.49888 5.32663
C -0.06872 3.85044 -0.26870
C -0.78982 0.37576 4.04335
C -0.45090 1.68672 -0.06427
C -0.77853 0.14830 1.84706
C -0.12170 7.19898 1.54023
C -0.99566 2.88005 6.89851
C -0.41947 7.36001 2.86438
C -1.05095 4.23585 6.73818
C 0.01878 3.28136 -1.59262
C -0.89024 -1.03678 3.76614
C -0.23102 1.94349 -1.46777
C -0.89802 -1.17663 2.40754
H 0.07472 7.96494 0.79161
H -1.05839 2.30287 7.81967
H -0.51162 8.28537 3.43092
H -1.16032 5.00510 7.50101
H 0.23397 3.84966 -2.49617
H -0.96574 -1.81060 4.52791
H -0.25488 1.18264 -2.24637
H -0.96783 -2.09091 1.82025
C 0.05848 5.20678 0.02213
C -0.81881 0.94047 5.31488
C -0.67719 0.42667 0.48624
C -0.84408 5.76937 4.76223
H -0.95922 6.62198 5.43291
H -0.88353 0.26072 6.16481
H -0.73719 -0.41728 -0.20249
H 0.27333 5.87970 -0.80909
Mn -0.64935 3.08749 2.64304
H -2.99572 2.77419 3.14652
C -3.94551 4.78328 -2.94974
C -3.67828 6.11384 -2.66771
C -3.72764 6.57109 -1.33732
C -4.04587 5.69229 -0.30354
C -4.32519 4.34276 -0.56552
C -4.27371 3.87095 -1.91239
H -4.09300 6.05307 0.72587
H -3.51509 7.61884 -1.11185
Cl -5.93151 4.06044 1.69261
H -3.42905 6.80656 -3.47509
H -3.90652 4.41689 -3.97889
C -4.62709 3.38262 0.54020
C -4.97783 2.01342 0.14239
C -4.56201 2.49929 -2.19556
C -4.90423 1.60122 -1.17411
H -3.72959 3.32238 1.25443
H -5.22681 1.31290 0.94356
H -5.12375 0.56029 -1.42401
H -4.52502 2.15923 -3.23332
O 1.48697 2.86506 2.87351
S 2.61262 3.83791 3.15146
O 2.46887 4.59313 4.40540
O 3.06689 4.58228 1.96662
C 4.00108 2.63239 3.49747
F 5.12321 3.30307 3.77498
F 3.70596 1.85528 4.54244
F 4.22878 1.85080 2.43918
O -4.02383 2.05396 4.39253
S -5.00826 0.97503 4.08544

O -4.65777 0.14003 2.91278
C -4.79932 -0.19797 5.53090
O -6.42281 1.37394 4.19494
F -5.67276 -1.20766 5.43751
F -3.56730 -0.72344 5.57037
F -5.01605 0.43371 6.68998

74
PC (-1/5)
O -1.04652 0.46098 0.04780
N 1.40321 2.19785 0.17997
N 0.88592 0.34686 2.33032
N 1.38332 0.01876 -1.69892
N 0.92854 -1.83817 0.45990
C 1.64162 2.91920 -0.96530
C 0.67960 -0.68139 3.21896
C 1.33507 3.10119 1.21337
C 0.89848 1.51030 3.06219
C 1.64040 1.04223 -2.58100
C 0.71561 -2.56205 1.60848
C 1.36115 -1.14416 -2.43269
C 0.96345 -2.73915 -0.57740
C 1.73521 4.32237 -0.64345
C 0.55187 -0.14935 4.55415
C 1.54322 4.43522 0.70516
C 0.68466 1.20747 4.45673
C 1.77262 0.50975 -3.91499
C 0.61895 -3.96527 1.28692
C 1.59829 -0.84366 -3.82363
C 0.77191 -4.07512 -0.06613
H 1.92140 5.11223 -1.36954
H 0.38110 -0.75097 5.44556
H 1.54024 5.33684 1.31573
H 0.64708 1.95042 5.25194
H 1.97759 1.10741 -4.80186
H 0.44420 -4.75498 2.01548
H 1.63203 -1.58604 -4.61957
H 0.75394 -4.97469 -0.67939
C 1.75771 2.39058 -2.24905
C 0.60160 -2.03365 2.89243
C 1.16064 -2.42537 -1.92073
C 1.09853 2.79112 2.55105
H 1.07706 3.62051 3.25952
H 0.42509 -2.73598 3.70788
H 1.16761 -3.25355 -2.63094
H 1.95591 3.09055 -3.06201
Mn 1.16890 0.17882 0.32265
H -1.67083 -0.08550 0.59428
C -2.24920 1.87867 -5.28552
C -2.69318 3.04944 -5.86371
C -3.84497 3.70036 -5.35453
C -4.53115 3.17240 -4.27976
C -4.09937 1.96600 -3.66103
C -2.93054 1.30237 -4.17563
H -5.41658 3.67580 -3.88974
H -4.19159 4.62790 -5.81695
Cl -6.18858 2.13063 -1.86625
H -2.15905 3.47873 -6.71496
H -1.36102 1.37155 -5.67136
C -4.75911 1.36343 -2.54424
C -4.30922 0.19230 -1.97347
C -2.48295 0.09252 -3.57223
C -3.15942 -0.45122 -2.49998
H -1.38057 0.39973 -0.86016
H -4.82482 -0.24277 -1.11513
H -2.82734 -1.37949 -2.02820
H -1.59419 -0.39932 -3.97532
O 3.35049 -0.12746 0.61332
S 4.52675 0.81338 0.68187
O 4.54264 1.67705 1.87399
O 4.87212 1.44333 -0.60326
C 5.91891 -0.39923 0.98136
F 7.08172 0.25401 1.07529
F 5.72570 -1.07638 2.11686
F 6.01120 -1.27687 -0.02199
O -2.78337 -0.95497 1.51828
S -3.58960 -2.09986 0.99748
O -2.93827 -2.87312 -0.08151
C -3.59484 -3.27866 2.44968
O -5.02230 -1.79616 0.80130
F -4.29544 -4.37758 2.15282
F -2.34977 -3.65224 2.76940
F -4.14685 -2.70591 3.52302

**[$Mn^{IV}$OH(Por$^{+\bullet}$)OTf]$^+$ with H bonding to OTf, nucleophilic reaction at $C_2$**

74
RC (-1/5)
N -2.01141 -1.46001 1.57503
N -2.25042 1.28190 2.34775
N -0.74947 -0.65973 -0.85667
N -1.03136 2.08342 -0.11325
C -1.91521 -2.69996 0.99075
C -2.43224 2.63767 2.46978
C -2.45296 -1.65605 2.86256
C -2.67353 0.71162 3.52254
C -0.84167 -2.00560 -1.11689
C -1.35968 3.33037 0.35685
C -0.03221 -0.09942 -1.88770
C -0.25461 2.26698 -1.23007
C -2.33933 -3.70888 1.92924
C -3.00154 2.93238 3.76257
C -2.65371 -3.06554 3.09229
C -3.13123 1.74240 4.42185
C -0.18147 -2.30103 -2.36380
C -0.79148 4.33702 -0.50925
C 0.33698 -1.12602 -2.82992
C -0.08695 3.67960 -1.47826
H -2.36671 -4.77605 1.71537
H -3.25002 3.93289 4.11328
H -3.00471 -3.49314 4.03013
H -3.51946 1.56069 5.42281
H -0.11634 -3.29412 -2.80544
H -0.90705 5.41003 -0.36350
H 0.90794 -0.94876 -3.73991
H 0.50783 4.08326 -2.29616
C -1.41143 -2.95907 -0.27907
C -2.05211 3.59672 1.53488
C 0.23678 1.25592 -2.05119
C -2.73579 -0.65404 3.78471
H -3.09241 -0.96212 4.76852
H -2.24719 4.64194 1.77852
H 0.85269 1.55867 -2.89957
H -1.39766 -3.99673 -0.61433
C 7.43814 0.07024 -3.30760
C 6.43902 -0.31212 -2.42502
C 5.51945 0.64178 -1.91967
C 5.63356 2.00710 -2.33773
C 6.66322 2.37133 -3.23433
C 7.55191 1.41742 -3.71230
H 4.41220 -0.75835 -0.66800
H 8.14203 -0.67227 -3.69067
H 6.35105 -1.35318 -2.10460
C 4.49547 0.28226 -0.99307
C 4.69564 2.96403 -1.82627
H 6.74595 3.41269 -3.55504
H 8.34359 1.70981 -4.40614
C 3.71918 2.57084 -0.88899
C 3.61582 1.23252 -0.48524
H 3.03706 3.32057 -0.48440
H 2.84408 0.92205 0.22091
O 0.13430 0.25940 1.56065
H 0.74606 -0.45132 1.21352
Mn -1.43446 0.30660 0.77362
Cl 2.96006 3.24085 -3.74866
H 4.85426 4.02224 -2.03236
O -3.24324 0.45683 -0.18239
S -4.60593 -0.20225 -0.00685
O -5.16338 -0.09020 1.34670
O -4.72074 -1.49694 -0.68947
C -5.62966 0.97464 -1.03906
F -6.90574 0.58297 -1.02311
F -5.55950 2.21304 -0.54865
F -5.20574 0.99007 -2.30287
O 1.90481 -1.50211 0.64658
S 2.91321 -2.17189 1.53022
O 4.04746 -2.75514 0.78473
O 3.24074 -1.43144 2.76077
C 1.97218 -3.66679 2.14689
F 2.74463 -4.41292 2.94303
F 0.89513 -3.28761 2.84545
F 1.56170 -4.42933 1.12790

74
TS (-1/5)
N -0.38165 -1.73769 0.95844
N 0.08311 1.08947 0.80902
N -1.33718 -1.73184 -1.73618
N -0.88861 1.10243 -1.89236
C -0.76510 -3.05561 0.88193
C 0.11857 2.44469 0.59060
C 0.22365 -1.56699 2.18222
C 0.60256 0.87181 2.06033
C -1.60141 -3.04607 -1.43886
C -0.69710 2.45361 -1.74507
C -1.64900 -1.54920 -3.06250
C -1.25510 0.88962 -3.19822
C -0.40158 -3.73480 2.10003
C 0.66597 3.10710 1.75103
C 0.22327 -2.81862 2.89770
C 0.97888 2.13161 2.65515
C -2.10859 -3.71397 -2.61241
C -0.96947 3.12043 -2.99654
C -2.12356 -2.79235 -3.62092
C -1.30236 2.15058 -3.89974
H -0.59120 -4.78819 2.29762
H 0.79720 4.18423 1.84233
H 0.64273 -2.95985 3.89249
H 1.41489 2.24075 3.64687
H -2.40086 -4.76228 -2.64717
H -0.89924 4.19602 -3.15148
H -2.43982 -2.92320 -4.65462
H -1.56995 2.26438 -4.94914
C -1.36566 -3.66333 -0.21500
C -0.25730 3.08940 -0.58584
C -1.59060 -0.34255 -3.75518
C 0.70188 -0.36464 2.69295
H 1.14539 -0.38540 3.68933
H -0.15969 4.17556 -0.61547
H -1.87217 -0.35665 -4.80906
H -1.61371 -4.72138 -0.12965
C 6.09217 0.87729 1.72594
C 6.01340 -0.13231 0.77363
C 5.11446 -0.03340 -0.31510
C 4.29468 1.12526 -0.42744
C 4.38225 2.12935 0.54495
C 5.26988 2.01095 1.61611
H 5.59716 -1.98746 -1.16731
H 6.78935 0.78656 2.56248
H 6.64138 -1.02285 0.86022
C 4.98006 -1.09350 -1.27577
C 3.38233 1.26883 -1.59766
H 3.75181 3.01741 0.45507
H 5.32424 2.80182 2.36803
C 3.18246 0.05911 -2.41391
C 4.02867 -1.03631 -2.29129
H 2.44644 0.10982 -3.21494
H 3.90324 -1.89706 -2.94831
O 1.15040 -0.62928 -1.12745
H 1.33608 -1.59674 -1.25406
Mn -0.55028 -0.34089 -0.49249
Cl 4.18138 2.57642 -2.82057
H 2.44941 1.78806 -1.36068
O -2.55128 0.08440 0.14116
S -3.36058 -0.26797 1.37252
O -2.78354 0.21142 2.63713
O -3.90821 -1.63255 1.35608
C -4.84863 0.83211 1.09765
F -5.71821 0.67343 2.09949
F -4.48661 2.11668 1.05347
F -5.46342 0.52525 -0.04684
O 1.72524 -3.29065 -1.63387
S 2.84801 -4.06531 -1.02599
O 3.99321 -4.29936 -1.93293
O 3.18549 -3.68561 0.36029
C 2.11384 -5.78003 -0.85256
F 3.02905 -6.62945 -0.37127
F 1.06803 -5.78475 -0.01465
F 1.69737 -6.24333 -2.03621

74
PC (-1/5)
N -0.77255 -0.54388 1.59964
N -0.56161 2.28392 1.09142
N -1.44598 -0.99055 -1.15414
N -1.23316 1.83672 -1.66453
C -0.95445 -1.90569 1.65720
C -0.57344 3.59572 0.67557
C -0.39010 -0.14010 2.85768
C -0.22301 2.29229 2.42462
C -1.53560 -2.28919 -0.71528
C -1.15071 3.21056 -1.70104
C -1.69869 -1.00994 -2.50480
C -1.52782 1.42230 -2.94300
C -0.67910 -2.37536 2.99225
C -0.22345 4.45645 1.77808
C -0.32409 -1.28347 3.73396
C -0.00064 3.64923 2.85922
C -1.86076 -3.15533 -1.82192
C -1.39669 3.67476 -3.04389
C -1.95746 -2.36440 -2.93111
C -1.62392 2.56775 -3.81371
H -0.74710 -3.41537 3.30735
H -0.15637 5.54156 1.71770
H -0.04386 -1.24118 4.78531
H 0.28274 3.93551 3.87087
H -1.98094 -4.23455 -1.74601
H -1.38885 4.72055 -3.34720
H -2.18387 -2.65700 -3.95524
H -1.84454 2.51751 -4.87887
C -1.31925 -2.72200 0.58975
C -0.85055 4.03416 -0.61801
C -1.73056 0.10246 -3.34279
C -0.12315 1.17061 3.24517
H 0.16399 1.33605 4.28453
H -0.81632 5.10907 -0.80057
H -1.95274 -0.07171 -4.39660
H -1.41514 -3.79040 0.78601
C 6.40631 0.21271 1.49966
C 5.97324 -0.08164 0.20496
C 4.80039 0.49672 -0.30803
C 4.06477 1.39092 0.50351
C 4.50160 1.67553 1.80130
C 5.66809 1.08943 2.30311
H 4.94553 -0.44372 -2.28831
H 7.31905 -0.24755 1.88640
H 6.53817 -0.78094 -0.41670
C 4.30233 0.16295 -1.64556
C 2.85210 2.05989 -0.07494
H 3.92558 2.36775 2.42164
H 6.00047 1.31718 3.31886
C 2.12021 1.25023 -1.15805
C 3.07701 0.52117 -2.06627
H 1.50843 1.95403 -1.74297
H 2.70660 0.20412 -3.04386
O 1.22701 0.33318 -0.51198
H 1.45786 -0.61122 -0.73567
Mn -1.03614 0.64842 -0.02471
Cl 3.36767 3.67514 -0.83138
H 2.13874 2.34377 0.70568
O -3.18109 0.93664 0.39725
S -4.05376 0.56715 1.57226
O -3.69437 1.24446 2.82857
O -4.37699 -0.86621 1.65327
C -5.66438 1.37169 1.06558
F -6.59522 1.15660 2.00042
F -5.51193 2.69119 0.92083
F -6.10614 0.86879 -0.09042
O 1.60740 -2.18162 -1.22542
S 2.80670 -3.07013 -1.33190
O 3.39560 -3.14224 -2.68275
O 3.75452 -2.96454 -0.20653
C 2.03491 -4.76055 -1.10177
F 2.97113 -5.71426 -1.17047
F 1.43304 -4.85580 0.09062
F 1.12132 -5.00726 -2.04871

**[$Mn^{IV}$OH(TDCPP$^{+\bullet}$)OTf]$^+$ w/o H bonding to OTf, electrophilic reaction at $C_1$**

106
RC (0/5)
O -1.35415 -0.08582 -0.55303
N 0.18505 1.77530 0.67439
N -0.36252 -0.71306 1.92053
N 1.10186 0.42012 -1.64594
N 0.50636 -2.06458 -0.41731
C 0.74239 2.85691 0.03161
C -0.34706 -1.98700 2.43867
C -0.48486 2.25926 1.77404
C -0.97204 0.09542 2.85029
C 1.51183 1.68332 -1.99400
C 0.41607 -3.16156 0.41019
C 1.23683 -0.37081 -2.76208
C 0.74873 -2.53631 -1.68887
C 0.42245 4.05911 0.75925
C -0.94957 -1.97503 3.74881
C -0.36217 3.69474 1.81381
C -1.36617 -0.69870 3.98772
C 1.94762 1.68318 -3.36997
C 0.61852 -4.35930 -0.36381
C 1.74748 0.42373 -3.85295
C 0.79251 -3.97548 -1.66241
H 0.74236 5.05990 0.48057
H -1.06050 -2.84421 4.39213
H -0.79944 4.33779 2.57342
H -1.87378 -0.31684 4.86987
H 2.33216 2.54922 -3.90265
H 0.60662 -5.37004 0.03618
H 1.94932 0.05310 -4.85480
H 0.96418 -4.61077 -2.52771
C 1.41092 2.83214 -1.19834
C 0.06447 -3.14416 1.76648
C 1.03622 -1.75553 -2.81584
C -1.08740 1.48979 2.77745
C -1.80267 2.20234 3.88401
C 0.02183 -4.45050 2.49798
C 1.22090 -2.45011 -4.12920
C 1.94217 4.11924 -1.75062
Mn 0.31305 -0.13905 0.11957
H -1.71856 -0.98630 -0.58846
C -6.22524 0.18137 -4.20226
C -5.09147 0.47840 -4.94454
C -3.85899 0.67765 -4.30035
C -3.76397 0.59602 -2.89714
C -4.91670 0.24946 -2.11679
C -6.17049 0.05635 -2.78116
H -2.78931 0.61792 -2.40707
H -2.96280 0.89836 -4.88233
Cl -3.67912 3.16108 -2.75122
H -5.15469 0.55668 -6.03188
H -7.18409 0.02859 -4.70472
C -4.84505 0.09679 -0.71274
C -5.97955 -0.22749 0.01764
C -7.31433 -0.27177 -2.00889
C -7.21963 -0.40965 -0.63297
H -3.88404 0.24528 -0.21474
H -5.91414 -0.33732 1.10260
H -8.10671 -0.66235 -0.04738
H -8.27222 -0.41786 -2.51458
O 2.18886 -0.22777 0.80914
S 2.89806 0.25631 2.08426
O 2.51875 -0.49154 3.28587
O 2.99570 1.71515 2.18091
C 4.62614 -0.32823 1.66465
F 5.44738 -0.00422 2.66310
F 4.64716 -1.65009 1.50290
F 5.05913 0.25168 0.54681
C 2.48003 -2.90812 -4.56454
C 2.65217 -3.55353 -5.79161
C 1.54584 -3.75517 -6.61800
C 0.27969 -3.31958 -6.22480
C 0.13215 -2.67725 -4.99322
Cl 3.88187 -2.67117 -3.54384
H 3.64568 -3.89146 -6.08818
H 1.67173 -4.25849 -7.57906
H -0.59210 -3.47287 -6.86172
Cl -1.46779 -2.14467 -4.51798
C 3.28618 4.49843 -1.56697
C 3.79504 5.69587 -2.07685
C 2.95215 6.54519 -2.79481
C 1.61562 6.20324 -3.00661
C 1.12695 5.00150 -2.48806
Cl 4.36440 3.44445 -0.67931
H 4.84192 5.95100 -1.90882
H 3.34217 7.48309 -3.19638
H 0.94943 6.85694 -3.57074
Cl -0.54753 4.57975 -2.77417
C -3.17259 2.51506 3.78737
C -3.86116 3.17588 4.80741
C -3.17441 3.54418 5.96485
C -1.81566 3.25790 6.10194
C -1.14805 2.59566 5.06859
Cl -4.05848 2.07551 2.34125
H -4.92235 3.39619 4.68714
H -3.70350 4.06147 6.76816
H -1.26775 3.54315 7.00061
Cl 0.55617 2.25447 5.26500
C -1.15556 -5.22009 2.58142
C -1.20199 -6.43842 3.26311
C -0.04626 -6.91799 3.88118
C 1.14367 -6.19238 3.81614
C 1.16699 -4.97594 3.12880
Cl -2.61668 -4.64772 1.80330
H -2.13635 -6.99931 3.30254
H -0.07283 -7.86935 4.41696
H 2.05395 -6.55935 4.29149
Cl 2.67410 -4.09208 3.05113

106
TS (0/5)
O -2.21466 3.27570 1.79027
N -0.54048 5.18783 3.00032
N -1.06648 2.69016 4.29113
N 0.28338 3.80169 0.64226
N -0.27160 1.30306 1.92504
C -0.05035 6.26595 2.30248
C -1.11978 1.40939 4.79061
C -1.10585 5.67891 4.15184
C -1.58451 3.52069 5.25730
C 0.62975 5.07051 0.24996
C -0.42522 0.20922 2.74508
C 0.43201 2.98661 -0.45363
C -0.03157 0.82533 0.65666
C -0.30568 7.47551 3.04664
C -1.67269 1.43761 6.12257
C -0.97989 7.11598 4.17544
C -1.98279 2.73600 6.40035
C 1.03423 5.05192 -1.13593
C -0.25540 -0.99603 1.97217
C 0.88949 3.76946 -1.57673
C -0.03555 -0.61625 0.68018
H -0.01683 8.47521 2.73211
H -1.82020 0.56675 6.75626
H -1.34265 7.76242 4.97062
H -2.42622 3.13534 7.30889
H 1.36779 5.91812 -1.70183
H -0.31467 -2.00637 2.36904
H 1.09144 3.37919 -2.57109
H 0.12956 -1.25600 -0.18310
C 0.53076 6.23234 1.02838
C -0.78811 0.23743 4.09875
C 0.25877 1.59643 -0.47690
C -1.64590 4.91965 5.19854
C -2.26733 5.64765 6.35137
C -0.92443 -1.07079 4.81578
C 0.43912 0.88731 -1.78353
C 1.01113 7.51806 0.42800
Mn -0.44516 3.24813 2.44990
H -2.62091 2.40618 1.94860
C -5.94646 3.45541 -1.96617
C -4.80859 4.22744 -2.24562

C -4.02247 4.72632 -1.22622
C -4.30403 4.43696 0.18617
C -5.52253 3.61468 0.46200
C -6.31670 3.13681 -0.62241
H -3.40344 3.96627 0.68692
H -3.15022 5.34560 -1.44627
Cl -4.35763 6.06569 1.12939
H -4.54790 4.44597 -3.28372
H -6.56971 3.08672 -2.78436
C -5.86890 3.26240 1.77347
C -6.98848 2.47025 2.02659
C -7.45522 2.33671 -0.34181
C -7.78868 2.01108 0.96403
H -5.25338 3.62084 2.60132
H -7.24356 2.20555 3.05547
H -8.66638 1.39352 1.16827
H -8.06193 1.97300 -1.17500
O 1.55711 3.16701 3.09543
S 2.31751 3.64591 4.32324
O 2.09025 2.82216 5.51774
O 2.32064 5.10454 4.49519
C 4.06184 3.23215 3.78476
F 4.91959 3.58227 4.74572
F 4.18967 1.92397 3.55763
F 4.38151 3.89194 2.66977
C 1.69084 0.39462 -2.20142
C 1.86054 -0.26648 -3.42056
C 0.75875 -0.44763 -4.25765
C -0.49972 0.02579 -3.88372
C -0.64477 0.68340 -2.65980
Cl 3.08791 0.61104 -1.16944
H 2.84856 -0.63161 -3.70292
H 0.88233 -0.96331 -5.21246
H -1.36754 -0.10952 -4.53010
Cl -2.23406 1.27021 -2.21285
C 2.36299 7.90633 0.51494
C 2.83188 9.09783 -0.04456
C 1.93990 9.93500 -0.71565
C 0.59305 9.58746 -0.82886
C 0.14672 8.39193 -0.26055
Cl 3.50317 6.87195 1.34615
H 3.88667 9.35825 0.04953
H 2.29816 10.86804 -1.15609
H -0.11330 10.23250 -1.35248
Cl -1.54972 7.98241 -0.41393
C -3.61920 6.04335 6.32431
C -4.22205 6.71546 7.39036
C -3.46497 7.01270 8.52411
C -2.12060 6.64547 8.59173
C -1.53945 5.97278 7.51363
Cl -4.59061 5.70254 4.90711
H -5.27258 7.00025 7.32344
H -3.92697 7.53820 9.36272
H -1.51731 6.87585 9.47047
Cl 0.14948 5.53207 7.62387
C -2.14480 -1.77427 4.84839
C -2.28413 -2.99428 5.51418
C -1.18072 -3.54217 6.17012
C 0.04802 -2.88125 6.16023
C 0.16357 -1.66172 5.48762
Cl -3.54349 -1.11087 4.02805
H -3.24882 -3.50278 5.51320
H -1.27964 -4.49552 6.69378
H 0.91734 -3.30059 6.66784
Cl 1.71492 -0.85458 5.48578

106
PC (0/5)
O -1.86533 -0.15324 -0.82034
N 0.07044 1.75768 0.54174
N -0.45193 -0.76761 1.79873
N 0.95362 0.40212 -1.82293
N 0.41877 -2.12501 -0.57148
C 0.53071 2.85487 -0.15046
C -0.55891 -2.05892 2.26185
C -0.47435 2.22854 1.71389
C -0.95764 0.04973 2.78270
C 1.24298 1.68872 -2.21418
C 0.22193 -3.23042 0.22596
C 1.20867 -0.40961 -2.90488
C 0.79460 -2.59247 -1.81104
C 0.26795 4.05145 0.61068
C -1.13950 -2.05251 3.58228
C -0.37324 3.66683 1.75087
C -1.40092 -0.75169 3.89712
C 1.68487 1.68853 -3.58715
C 0.48673 -4.42708 -0.53312
C 1.64753 0.39497 -4.01875
C 0.82838 -4.03372 -1.79402
H 0.53009 5.06013 0.30161
H -1.33344 -2.93596 4.18531
H -0.73213 4.29879 2.55928
H -1.84533 -0.36321 4.80996
H 1.97442 2.57111 -4.15194
H 0.41180 -5.44136 -0.14922
H 1.90666 0.01364 -5.00325
H 1.09164 -4.66391 -2.63982
C 1.09874 2.84383 -1.43156
C -0.22370 -3.22174 1.55511
C 1.13294 -1.80931 -2.92354
C -1.00411 1.45034 2.75223
C -1.63144 2.15797 3.91448
C -0.40582 -4.54066 2.24202
C 1.47563 -2.51561 -4.19932
C 1.55960 4.14358 -2.01704
Mn 0.31749 -0.18302 0.01560
H -2.12782 -0.98328 -1.24744
C -4.49601 -0.69508 -3.13163
C -3.67486 0.21387 -3.76512
C -3.61938 1.56032 -3.32414
C -4.39559 1.96542 -2.25586
C -5.25938 1.06151 -1.56241
C -5.29979 -0.30080 -2.02451
H -2.04813 0.53074 -1.48481
H -2.96768 2.27736 -3.82536
Cl -4.30822 3.64237 -1.74585
H -3.05294 -0.09388 -4.60826
H -4.53975 -1.73289 -3.47088
C -6.06543 1.43514 -0.45120
C -6.87321 0.50921 0.17647
C -6.14853 -1.22588 -1.35227
C -6.91760 -0.83313 -0.27738
H -6.03198 2.46650 -0.09876
H -7.48293 0.81221 1.03097
H -7.56280 -1.55534 0.22859
H -6.17736 -2.25971 -1.70596
O 2.36492 -0.24251 0.72607
S 3.09448 0.25244 1.95594
O 2.90586 -0.60002 3.13884
O 3.01910 1.70752 2.15430
C 4.86616 -0.04889 1.43754
F 5.69476 0.32794 2.41508
F 5.07471 -1.34274 1.18287
F 5.16326 0.65196 0.33953
C 2.80521 -2.83888 -4.53627
C 3.13360 -3.49323 -5.72632
C 2.11737 -3.84345 -6.61618
C 0.78596 -3.54757 -6.32073
C 0.48308 -2.89377 -5.12413
Cl 4.09874 -2.41871 -3.43480
H 4.17705 -3.72297 -5.94464
H 2.36530 -4.35459 -7.54895
H -0.01733 -3.81906 -7.00642
Cl -1.19927 -2.54863 -4.77154
C 2.90963 4.54133 -1.93717
C 3.36457 5.74399 -2.48384
C 2.45997 6.58456 -3.13360
C 1.11419 6.23007 -3.23607
C 0.68213 5.02323 -2.68052
Cl 4.06575 3.50615 -1.12825
H 4.41831 6.01083 -2.39607
H 2.80720 7.52631 -3.56422
H 0.39749 6.87879 -3.74077
Cl -1.01581 4.61137 -2.81357
C -3.00674 2.46347 3.92607
C -3.61539 3.12378 4.99600
C -2.84115 3.49562 6.09596
C -1.47568 3.21021 6.12828
C -0.88880 2.54867 5.04620
Cl -4.00276 1.99904 2.56080
H -4.68380 3.33929 4.95998
H -3.30742 4.01248 6.93759
H -0.86094 3.49438 6.98303
Cl 0.82376 2.20093 5.11142
C -1.61948 -5.25229 2.16966
C -1.80112 -6.48260 2.80583
C -0.74855 -7.03213 3.53933
C 0.47147 -6.36200 3.63671
C 0.62950 -5.13235 2.99192
Cl -2.95588 -4.58374 1.25511
H -2.75893 -6.99727 2.72260
H -0.88080 -7.99357 4.04039
H 1.30102 -6.78193 4.20657
Cl 2.16812 -4.31151 3.12686

**[$Mn^{IV}$OH(TDCPP$^{+\bullet}$)OTf]$^+$ w/o H bonding to OTf, nucleophilic reaction at $C_2$**

106
RC (0/5)
N -0.01972 -0.61694 1.80356
N -0.27770 1.91508 0.55015
N -0.67569 -1.88551 -0.65695
N -0.99397 0.64705 -1.89269
C -0.12670 -1.90344 2.27664
C -0.70058 3.03520 -0.13001
C 0.52101 0.14227 2.81388
C 0.25662 2.34545 1.74225
C -0.72623 -3.00030 0.15091
C -1.27114 1.93968 -2.26303
C -0.81007 -2.32341 -1.95707
C -1.03824 -0.11766 -3.03388
C 0.34069 -1.95020 3.64063
C -0.43313 4.20517 0.66715
C 0.77178 -0.69692 3.96015
C 0.18622 3.78299 1.80663
C -0.91318 -4.17159 -0.66555
C -1.52924 1.98717 -3.68224
C -0.93419 -3.75758 -1.96640
C -1.35460 0.72321 -4.16290
H 0.35795 -2.84053 4.26400
H -0.67374 5.22492 0.37769
H 1.20078 -0.35854 4.89978
H 0.54104 4.38815 2.63702
H -0.99612 -5.18777 -0.28844
H -1.78558 2.88429 -4.24005
H -1.05008 -4.36796 -2.85847
H -1.45313 0.37954 -5.18953
C -0.51033 -3.02689 1.53488
C -1.20365 3.06822 -1.43590
C -0.91699 -1.51098 -3.09293
C 0.69981 1.53140 2.79203
C 1.31963 2.19009 3.98566
C -1.59553 4.39138 -2.01845
C -0.96784 -2.17349 -4.43424
C -0.57971 -4.35112 2.23170
C 6.26384 -2.61868 1.31119
C 6.98138 -2.26777 0.17856
C 6.43536 -1.36543 -0.77029
C 5.13461 -0.81403 -0.53554
C 4.42153 -1.19145 0.62582
C 4.97698 -2.08158 1.53398
H 8.12396 -1.43334 -2.13796
H 6.69247 -3.31624 2.03461
H 7.97486 -2.68745 0.00113
C 7.13305 -1.00619 -1.96259
C 4.59023 0.10838 -1.49066
H 3.42966 -0.76760 0.79688
H 4.41458 -2.37087 2.42454
C 5.30108 0.40734 -2.66948
C 6.57285 -0.14440 -2.89479
H 4.85390 1.07821 -3.40510
H 7.11969 0.10555 -3.80634
O 1.28894 -0.01785 -0.53156
H 1.53888 -0.93400 -0.73817
Mn -0.44520 0.01944 -0.05661
Cl 5.16344 2.40934 -0.52247
H 3.55416 0.43046 -1.37730
O -2.39178 0.03180 0.40722
S -3.21512 0.52536 1.60781
O -3.20839 1.98278 1.76143
O -3.04985 -0.29587 2.80988
C -4.91773 0.10337 0.95420
F -5.82960 0.46337 1.85708
F -5.15923 0.75298 -0.18294
F -5.02311 -1.20602 0.73552
C -2.18081 -2.56090 -5.03636
C -2.22406 -3.17825 -6.28894
C -1.03120 -3.42196 -6.97109
C 0.19313 -3.05501 -6.41063
C 0.21172 -2.43942 -5.15689
Cl -3.68898 -2.26843 -4.19782
H -3.18595 -3.46181 -6.71741
H -1.05603 -3.90382 -7.95089
H 1.13116 -3.24081 -6.93482
Cl 1.75945 -1.98703 -4.47259
C -1.79038 -4.84359 2.75765
C -1.86844 -6.07509 3.41362
C -0.71622 -6.84925 3.55367
C 0.50265 -6.40301 3.04067
C 0.55672 -5.16926 2.38818
Cl -3.25065 -3.89753 2.58491
H -2.82701 -6.41555 3.80665
H -0.76872 -7.81247 4.06582
H 1.40882 -7.00149 3.13967
Cl 2.09628 -4.64004 1.73964
C 2.69047 2.51703 4.00388
C 3.29437 3.12104 5.10972
C 2.52168 3.41838 6.23291
C 1.15808 3.12227 6.25185
C 0.57439 2.51726 5.13588
Cl 3.67447 2.18332 2.59495
H 4.35928 3.35447 5.08075
H 2.98603 3.89046 7.10151
H 0.54239 3.35742 7.12067
Cl -1.14071 2.17227 5.17960
C -0.65248 5.25641 -2.60841
C -1.01405 6.49144 -3.15204
C -2.35189 6.88697 -3.11644
C -3.31981 6.05763 -2.54889
C -2.93576 4.82634 -2.01149
Cl 1.03028 4.77832 -2.67969
H -0.24965 7.12871 -3.59785
H -2.64359 7.85123 -3.53833
H -4.36874 6.35440 -2.51886
Cl -4.17004 3.80082 -1.31509

106
TS (0/5)
N -0.11513 -0.50015 1.71579
N -0.41743 2.03155 0.42869
N -0.68866 -1.82070 -0.76040
N -1.05310 0.71301 -2.04042
C -0.10369 -1.79647 2.17576
C -0.76585 3.13951 -0.30869
C 0.29677 0.29676 2.75891
C -0.00982 2.48563 1.66126
C -0.63748 -2.93409 0.04927
C -1.25827 2.00684 -2.44942
C -0.88456 -2.27118 -2.04806
C -1.14422 -0.07974 -3.15862
C 0.31263 -1.81394 3.55675
C -0.57590 4.32668 0.48765
C 0.57835 -0.52504 3.91058
C -0.09260 3.92448 1.69688
C -0.81544 -4.11780 -0.75202
C -1.51184 2.02931 -3.87083
C -0.95089 -3.71006 -2.04695
C -1.42342 0.74284 -4.31174
H 0.40228 -2.70672 4.17033
H -0.77962 5.34105 0.15444
H 0.92246 -0.15462 4.87281
H 0.17025 4.54406 2.55048
H -0.82504 -5.13500 -0.36891
H -1.71532 2.92310 -4.45514
H -1.10022 -4.32845 -2.92842
H -1.54782 0.37464 -5.32698
C -0.38205 -2.94530 1.42626
C -1.17520 3.15203 -1.64743
C -1.05792 -1.47674 -3.18823
C 0.37100 1.69530 2.75292
C 0.81108 2.38672 4.00827
C -1.48635 4.47360 -2.27945
C -1.19500 -2.16505 -4.51115
C -0.32953 -4.27285 2.11861
C 5.85530 -3.19049 0.56766
C 5.59361 -2.78327 -0.73523
C 4.98319 -1.53205 -0.99306
C 4.65655 -0.68572 0.10523
C 4.91971 -1.11586 1.41180
C 5.51024 -2.35890 1.64658
H 4.90866 -1.77794 -3.15945
H 6.32300 -4.16021 0.75356
H 5.84703 -3.43229 -1.57751
C 4.63788 -1.12447 -2.32654
C 4.07838 0.66273 -0.15480
H 4.66567 -0.46283 2.25058
H 5.70521 -2.68366 2.67123
C 3.56878 0.89308 -1.51686
C 3.91786 0.04823 -2.56321
H 3.01755 1.81454 -1.70230
H 3.60187 0.29251 -3.57990
O 1.26067 0.11682 -0.64877
H 1.55340 -0.80254 -0.77093
Mn -0.52448 0.10762 -0.17456
Cl 5.51005 1.98093 0.08586
H 3.38979 0.99697 0.62427
O -2.55062 0.07249 0.23954
S -3.45578 0.53318 1.37692
O -3.43940 1.98401 1.59877
O -3.40985 -0.34165 2.55429
C -5.11866 0.19405 0.58806
F -6.08939 0.52477 1.44172
F -5.26663 0.91444 -0.52460
F -5.24275 -1.09761 0.28177
C -2.45147 -2.51970 -5.04037
C -2.58439 -3.15895 -6.27558
C -1.43979 -3.45964 -7.01514
C -0.17478 -3.12821 -6.52771
C -0.06725 -2.49020 -5.28975
Cl -3.90130 -2.15750 -4.12942
H -3.57762 -3.41502 -6.64590
H -1.53449 -3.95874 -7.98197
H 0.72658 -3.35921 -7.09637
Cl 1.53221 -2.08870 -4.69691
C -1.47767 -4.85235 2.69335
C -1.44048 -6.09058 3.34005
C -0.23131 -6.78189 3.42289
C 0.93025 -6.24512 2.86557
C 0.86896 -5.00606 2.22355
Cl -3.00545 -4.00648 2.59869
H -2.35454 -6.50065 3.77084
H -0.19355 -7.75011 3.92686
H 1.88071 -6.77663 2.92336
Cl 2.34070 -4.35393 1.53164
C 2.14311 2.80228 4.20178
C 2.56487 3.44197 5.37000
C 1.64056 3.68534 6.38616
C 0.30917 3.29664 6.23604
C -0.08960 2.65746 5.05935
Cl 3.33515 2.53332 2.94416
H 3.60783 3.74336 5.47288
H 1.96065 4.18500 7.30305
H -0.42449 3.48461 7.02065
Cl -1.76689 2.19082 4.89868
C -0.48385 5.27853 -2.85481
C -0.76731 6.51222 -3.44569
C -2.08606 6.96830 -3.47166
C -3.11119 6.20138 -2.91656
C -2.80377 4.97041 -2.33142
Cl 1.17998 4.72833 -2.84410
H 0.04138 7.10180 -3.87882
H -2.31729 7.93184 -3.93098
H -4.14533 6.54708 -2.93248
Cl -4.10627 4.02468 -1.64512

106
PC (0/5)
N 0.00614 -0.55105 1.93043
N -0.17504 1.96106 0.56876
N -0.44100 -1.92911 -0.55664
N -0.65244 0.59214 -1.91254
C 0.06866 -1.84348 2.40016
C -0.37047 3.06322 -0.23569
C 0.27469 0.27012 3.00139
C 0.06468 2.44040 1.83827
C -0.35427 -3.02907 0.26784
C -0.72680 1.88306 -2.38172
C -0.65640 -2.40742 -1.83071
C -0.79566 -0.23319 -3.00461
C 0.38060 -1.83335 3.80839
C -0.24532 4.26518 0.54943
C 0.51402 -0.52824 4.17828
C 0.02920 3.88075 1.82839
C -0.52139 -4.23126 -0.50937
C -0.92206 1.87031 -3.81072
C -0.70425 -3.84758 -1.80564
C -0.95977 0.56297 -4.19610
H 0.48924 -2.71729 4.43161
H -0.35321 5.27659 0.16610
H 0.75176 -0.13501 5.16335
H 0.18750 4.51577 2.69632
H -0.49840 -5.24233 -0.11081
H -1.01360 2.75335 -4.43801
H -0.86117 -4.48362 -2.67315
H -1.09047 0.16730 -5.20009
C -0.10960 -3.01112 1.64738
C -0.61666 3.05008 -1.61402
C -0.80363 -1.63396 -2.98953
C 0.31095 1.67046 2.98175
C 0.63887 2.38549 4.25710
C -0.74984 4.36584 -2.31693
C -0.96719 -2.34994 -4.29459
C 0.00726 -4.32673 2.35394
C 6.59550 -3.01789 -1.03863
C 5.99876 -2.13590 -1.94307
C 5.17505 -1.09265 -1.48895
C 4.96978 -0.93536 -0.09705
C 5.56654 -1.82565 0.80077
C 6.37487 -2.86828 0.33488
H 4.78581 -0.24175 -3.47849
H 7.23098 -3.82715 -1.40649
H 6.16103 -2.25921 -3.01715
C 4.49591 -0.18807 -2.42504
C 4.14929 0.22892 0.38125
H 5.40091 -1.69958 1.87402
H 6.83425 -3.56063 1.04426
C 3.04984 0.65851 -0.60005
C 3.52217 0.65314 -2.03118
H 2.68308 1.65021 -0.30539
H 2.99627 1.29093 -2.74533
O 1.91920 -0.22067 -0.44640
H 2.09165 -1.05651 -0.90785
Mn -0.40799 0.02141 0.02417
Cl 5.26642 1.68053 0.64598
H 3.70391 0.04096 1.36504
O -2.53776 0.01207 0.31813
S -3.48962 0.53026 1.37649
O -3.51328 1.99616 1.48542
O -3.46480 -0.24477 2.62513
C -5.12936 0.09516 0.58905
F -6.12936 0.47971 1.38632
F -5.26716 0.70989 -0.58801
F -5.22681 -1.22186 0.39408
C -2.23591 -2.68418 -4.80663
C -2.39406 -3.35139 -6.02406
C -1.26269 -3.70109 -6.76244
C 0.01401 -3.38936 -6.29235
C 0.14662 -2.72223 -5.07233
Cl -3.66888 -2.25649 -3.89727
H -3.39614 -3.59022 -6.38187
H -1.37704 -4.22262 -7.71523
H 0.90495 -3.65763 -6.86111
Cl 1.75933 -2.34016 -4.50227

C -1.10761 -4.95551 2.94163
C -1.00618 -6.18263 3.60229
C 0.23664 -6.81149 3.68693
C 1.36781 -6.22370 3.11847
C 1.24159 -4.99687 2.46269
Cl -2.67601 -4.18587 2.84640
H -1.89650 -6.63294 4.04251
H 0.32495 -7.77073 4.20166
H 2.34393 -6.70619 3.17856
Cl 2.67626 -4.27871 1.75639
C 1.95793 2.77922 4.55746
C 2.28723 3.44048 5.74306
C 1.28036 3.72652 6.66610
C -0.04029 3.35779 6.40795
C -0.34612 2.69618 5.21557
Cl 3.24204 2.44295 3.41269
H 3.32284 3.72484 5.93260
H 1.52769 4.24339 7.59593
H -0.83612 3.57783 7.12033
Cl -2.00867 2.24830 4.91378
C 0.37151 5.05207 -2.82207
C 0.26070 6.27838 -3.48162
C -1.00160 6.84998 -3.64833
C -2.14000 6.20529 -3.16296
C -2.00385 4.97880 -2.50759
Cl 1.97033 4.36033 -2.62384
H 1.15724 6.77319 -3.85653
H -1.09874 7.80890 -4.16201
H -3.13108 6.64315 -3.28661
Cl -3.44535 4.18996 -1.90650

**[$Mn^{IV}$OH(TDCPP$^{\bullet-}$)OTf]$^{+}$ with H bonding to OTf, electrophilic reaction at $C_1$ of 1-chloro-1,2-dihydronaphthalen-2-ol**

116
RC (0/5)
C -6.48362 3.16545 -0.88353
C -5.89428 2.36430 -1.86398
C -5.32973 1.11989 -1.53757
C -5.34802 0.68182 -0.18822
C -5.93242 1.49702 0.78519
C -6.50502 2.72859 0.44337
H -4.55566 0.70269 -3.55640
H -6.92428 4.12804 -1.15505
H -5.86937 2.69973 -2.90420
C -4.71766 0.26904 -2.56524
C -4.61423 -0.61016 0.13411
H -5.94403 1.16340 1.82326
H -6.96424 3.34583 1.21961
C -4.69892 -1.66117 -0.98598
C -4.40286 -1.01346 -2.32164
H -5.74670 -2.02527 -1.00885
H -3.96227 -1.65803 -3.08748
O -3.89388 -2.78343 -0.73435
H -2.98579 -2.61836 -1.06126
Cl -5.18832 -1.37392 1.69623
H -3.54941 -0.38606 0.31956
O -0.94903 -0.13667 -0.62747
H -0.91829 -0.99195 -1.13946
N -0.34017 2.09727 0.70621
N 0.08641 -0.45217 1.90176
N 1.18020 1.29201 -1.56170
N 1.49180 -1.29723 -0.41860
C -0.65877 3.16202 -0.12519
C 0.27252 -1.74188 2.26230
C -0.90317 2.35796 1.90909
C -0.37536 0.21736 3.02860
C 0.82817 2.52401 -1.99630
C 1.35234 -2.54288 0.18589
C 2.15393 0.82073 -2.42923
C 2.26918 -1.47821 -1.51570
C -1.49696 4.09366 0.59804
C -0.05869 -1.92702 3.65797
C -1.62596 3.60928 1.86404
C -0.43054 -0.71058 4.13807
C 1.60543 2.88472 -3.16183
C 2.03643 -3.53232 -0.61533
C 2.44638 1.84489 -3.41084
C 2.62479 -2.87175 -1.64702
H -1.90492 5.01431 0.18879
H 0.00575 -2.86898 4.19578
H -2.16939 4.04766 2.69684
H -0.74088 -0.45657 5.14816
H 1.52305 3.82399 -3.70217
H 2.06719 -4.59616 -0.39805
H 3.18604 1.75926 -4.20206
H 3.22519 -3.28664 -2.45128
C -0.13023 3.38480 -1.38599
C 0.78306 -2.77916 1.42582
C 2.67533 -0.46409 -2.43656
C -0.83620 1.52124 3.06348
Mn 0.55048 0.38199 0.12580
S 3.26072 0.55710 1.96622
O 4.09202 -0.53893 1.46522
O 2.69750 0.43891 3.31402
O 2.24978 1.07269 0.92462
C 4.37720 2.05895 2.02228
F 3.69326 3.13261 2.41129
F 5.35890 1.83284 2.89308
F 4.90641 2.29065 0.82386
C 4.30041 -1.38853 -5.78693
C 3.34274 -1.02812 -4.83499
C 5.63081 -1.54982 -5.40006
H 6.38069 -1.83086 -6.14260
C 3.68389 -0.83005 -3.48021
C 6.01077 -1.34906 -4.07248
H 7.04893 -1.46145 -3.75849
C 5.04150 -0.99384 -3.13327
H 3.99414 -1.53954 -6.82250
Cl 5.53481 -0.72773 -1.47811
Cl 1.69350 -0.82184 -5.36956
C -1.26683 6.94706 -3.54474
C -0.25760 7.01891 -2.58327
C -1.90503 5.73585 -3.81677
H 0.25095 7.95950 -2.36933
H -2.69157 5.66896 -4.56908
C 0.10657 5.86407 -1.88732
C -1.52461 4.59254 -3.11159
C -0.51908 4.62547 -2.12675
H -1.55723 7.84638 -4.09201
C 0.75673 -4.17427 1.96579
C -0.43409 -4.92801 1.95118
C 1.89617 -4.78252 2.52958
C -0.48405 -6.23476 2.44056
C 1.86317 -6.08700 3.02769
H -1.42326 -6.78757 2.40224
H 2.76673 -6.52190 3.45607
C 0.67055 -6.80960 2.97344
H 0.63891 -7.83112 3.35845
Cl 3.38998 -3.88088 2.64208
Cl -1.89314 -4.20876 1.31418
Cl -2.31925 3.07538 -3.46619
Cl 1.38666 5.96492 -0.69970
C -1.34305 2.08561 4.35325
C -2.62298 1.77971 4.85568
C -0.55181 2.97358 5.10933
C -3.09018 2.31766 6.05720
C -1.00007 3.51831 6.31416
H -4.08793 2.05647 6.41133
H -0.35369 4.19673 6.87185
C -2.27156 3.18393 6.78296
H -2.63031 3.60650 7.72392
Cl 1.03806 3.41140 4.52826
Cl -3.66955 0.70736 3.95339
S -1.11415 -3.24208 -3.08840
O 0.25918 -3.20951 -3.61175
O -1.29352 -2.50034 -1.78572
O -2.19939 -3.01447 -4.05894
C -1.35217 -5.02045 -2.54940
F -1.19616 -5.83153 -3.59994
F -2.57272 -5.20793 -2.04800
F -0.45346 -5.36425 -1.61998

116
TS (0/5)
C -5.87078 3.33700 -1.74262
C -5.47346 2.37794 -2.67091
C -4.88699 1.16986 -2.25365
C -4.69332 0.93512 -0.85562
C -5.08378 1.92339 0.06431
C -5.67432 3.10768 -0.37153
H -4.43912 0.43933 -4.27433
H -6.33130 4.26792 -2.08167
H -5.61750 2.55479 -3.73946
C -4.46964 0.15896 -3.21787
C -3.99569 -0.31864 -0.47136
H -4.92796 1.75108 1.12947
H -5.98489 3.85855 0.35868
C -4.29487 -1.52227 -1.39460
C -4.15653 -1.09584 -2.83280
H -5.36918 -1.75591 -1.22353
H -3.83308 -1.85900 -3.54602
O -3.58529 -2.67197 -1.06731
H -2.68104 -2.61571 -1.44918
Cl -4.16675 -0.78362 1.25350
H -2.81465 -0.12408 -0.58757
O -1.36086 0.01464 -0.76421
H -1.17269 -0.72308 -1.38980
N -0.61013 2.46280 0.67063
N -0.12806 -0.09421 1.86744
N 0.87087 1.66403 -1.65433
N 1.26722 -0.93246 -0.50697
C -0.85516 3.58162 -0.11272
C 0.12733 -1.36750 2.24016
C -1.14867 2.71756 1.88826
C -0.60798 0.56167 2.99323
C 0.58000 2.93302 -2.03478
C 1.21710 -2.15774 0.14844
C 1.75914 1.16073 -2.59232
C 1.95118 -1.13682 -1.65944
C -1.64447 4.52884 0.64165
C -0.19705 -1.56114 3.63652
C -1.80787 4.00274 1.88811
C -0.62694 -0.35954 4.10874
C 1.31350 3.27890 -3.23046
C 1.88689 -3.15335 -0.65676
C 2.05379 2.18736 -3.56700
C 2.34994 -2.52164 -1.76698
H -2.00108 5.48508 0.26780
H -0.08779 -2.49456 4.18203
H -2.32979 4.43983 2.73525
H -0.94995 -0.11432 5.11718
H 1.27317 4.23983 -3.73605
H 1.98318 -4.20355 -0.39719
H 2.73810 2.07817 -4.40389
H 2.88652 -2.95264 -2.60559
C -0.29687 3.83175 -1.35965
C 0.69230 -2.38513 1.41067
C 2.24419 -0.14121 -2.64169
C -1.07190 1.86662 3.03412
Mn 0.30053 0.74799 0.06353
S 3.20267 0.95819 1.81650
O 4.06368 -0.02874 1.15092
O 2.74018 0.64453 3.17649
O 2.11879 1.52899 0.91953
C 4.28874 2.46872 2.02015
F 3.60640 3.47535 2.57147
F 5.32165 2.17336 2.81158
F 4.75956 2.87216 0.83915
C 3.35298 -1.11634 -6.17592
C 2.55726 -0.71134 -5.10145
C 4.71488 -1.34476 -5.97811
H 5.33864 -1.66052 -6.81707
C 3.09355 -0.53855 -3.80678
C 5.28704 -1.16345 -4.71851
H 6.35308 -1.32323 -4.55402
C 4.47760 -0.76511 -3.65354
H 2.89839 -1.24779 -7.15829
Cl 5.21755 -0.51462 -2.08963
Cl 0.86589 -0.40191 -5.41063
C -1.05120 7.63853 -3.26006
C -0.09900 7.55130 -2.24352
C -1.75387 6.50573 -3.67318
H 0.46327 8.42849 -1.92186
H -2.49504 6.56145 -4.47109
C 0.14012 6.31788 -1.63335
C -1.49784 5.28140 -3.05273
C -0.55798 5.15373 -2.01208
H -1.24395 8.60031 -3.74009
C 0.75299 -3.77102 1.97385
C -0.37215 -4.61632 1.91882
C 1.91282 -4.28124 2.58810
C -0.34448 -5.91422 2.43318
C 1.95881 -5.57598 3.11055
H -1.23537 -6.53948 2.36535
H 2.87600 -5.93452 3.57893
C 0.82679 -6.38800 3.02627
H 0.85696 -7.40186 3.43114
Cl 3.33214 -3.26952 2.72036
Cl -1.84305 -4.02165 1.18758
Cl -2.36945 3.86543 -3.59274
Cl 1.35999 6.22675 -0.38327
C -1.48614 2.45217 4.35069
C -2.75814 2.24693 4.91801
C -0.58786 3.26185 5.07621
C -3.12041 2.80776 6.14519
C -0.92989 3.82902 6.30538
H -4.11706 2.62265 6.54700
H -0.20180 4.44454 6.83469
C -2.19978 3.59685 6.83505
H -2.47559 4.03714 7.79562
Cl 1.00563 3.56730 4.42668
Cl -3.93312 1.26689 4.07316
S -0.92286 -3.31161 -3.44307
O 0.44637 -3.31165 -3.98088
O -1.11218 -2.45255 -2.21950
O -2.01903 -3.19982 -4.42385
C -1.11851 -5.04416 -2.75372
F -0.96596 -5.93772 -3.73504
F -2.32851 -5.21214 -2.21551
F -0.20101 -5.29549 -1.81332

116
PC (0/5)
C -6.22594 3.21745 -1.20692
C -5.74683 2.31692 -2.14778
C -5.53729 0.96626 -1.80953
C -5.83324 0.54519 -0.45267
C -6.31558 1.50349 0.49451
C -6.51160 2.81196 0.12010
H -4.75095 0.41112 -3.76498
H -6.38315 4.26028 -1.49216
H -5.52224 2.65086 -3.16209
C -5.01573 0.03315 -2.77537
C -5.57044 -0.78901 -0.11171
H -6.53125 1.17990 1.51274
H -6.88794 3.53958 0.84105
C -5.25889 -1.82610 -1.15040
C -4.84127 -1.27380 -2.47084
H -6.33659 -2.10066 -1.37657
H -4.44283 -1.99785 -3.18652
O -4.62116 -2.95838 -0.71091
H -3.67031 -2.93057 -1.00198
Cl -5.71426 -1.35837 1.48226
H -1.97952 -0.17830 0.02794
O -1.29950 -0.29094 -0.65041
H -1.46884 -1.18257 -1.03953
N -0.26618 2.13451 0.73954
N 0.16441 -0.43655 1.93075
N 1.21962 1.30866 -1.58014
N 1.57624 -1.28372 -0.42450
C -0.48410 3.24785 -0.03935
C 0.42617 -1.73069 2.30661
C -0.86626 2.37390 1.95338
C -0.38326 0.19354 3.02404
C 0.90634 2.58749 -1.97990
C 1.51405 -2.50084 0.21783
C 2.10563 0.80709 -2.50671
C 2.28873 -1.48020 -1.58508
C -1.27647 4.20271 0.69543
C 0.03173 -1.92427 3.68143
C -1.49903 3.66930 1.93210
C -0.45369 -0.73151 4.12896
C 1.61854 2.90144 -3.19451
C 2.16517 -3.50319 -0.59052
C 2.37427 1.81086 -3.50800
C 2.65571 -2.87115 -1.69288
H -1.60450 5.16786 0.31761
H 0.12772 -2.85464 4.23537
H -2.04910 4.11114 2.75928
H -0.83773 -0.49743 5.11869
H 1.55827 3.84568 -3.72991
H 2.23979 -4.55793 -0.33972
H 3.04566 1.68908 -4.35386
H 3.20465 -3.30924 -2.52226
C 0.05840 3.48143 -1.31152
C 0.99794 -2.72889 1.50161
C 2.61188 -0.50065 -2.53866
C -0.88457 1.50144 3.05248
Mn 0.71620 0.44288 0.18265
S 3.61256 0.73974 2.03627
O 4.64507 -0.09673 1.40764
O 3.09382 0.30093 3.34105
O 2.54892 1.22802 1.07806
C 4.48564 2.35105 2.41020
F 3.64442 3.22892 2.96426
F 5.49157 2.13659 3.26306
F 4.98560 2.89061 1.29584
C 4.01707 -1.49727 -5.97821
C 3.12915 -1.12367 -4.96561
C 5.37486 -1.62474 -5.68653
H 6.07468 -1.91631 -6.47274
C 3.55462 -0.87743 -3.64214
C 5.84412 -1.37218 -4.39751
H 6.90451 -1.45563 -4.15709
C 4.94027 -1.00227 -3.39874
H 3.63699 -1.68202 -6.98351
Cl 5.57143 -0.66763 -1.80122
Cl 1.43901 -0.94712 -5.38396
C -0.83897 7.25095 -3.24301
C 0.21990 7.17336 -2.33750
C -1.60681 6.12193 -3.53135
H 0.82934 8.04791 -2.10724
H -2.43528 6.16958 -4.23890
C 0.50355 5.95257 -1.71969
C -1.30420 4.91288 -2.90052
C -0.24698 4.78807 -1.97752
H -1.06735 8.20116 -3.73067
C 1.11780 -4.10628 2.07915
C 0.01820 -4.98695 2.13411
C 2.33310 -4.58848 2.60796
C 0.11986 -6.27732 2.66009
C 2.45807 -5.87473 3.13918
H -0.75901 -6.92272 2.67626
H 3.42024 -6.20145 3.53505
C 1.34652 -6.71755 3.15793
H 1.43538 -7.72535 3.56943
Cl 3.74196 -3.54953 2.62443
Cl -1.54475 -4.46011 1.54657
Cl -2.28190 3.50884 -3.28246
Cl 1.84610 5.88180 -0.59888
C -1.51484 1.99121 4.31934
C -2.86623 1.73725 4.62427
C -0.78544 2.73938 5.26544
C -3.46654 2.19377 5.79977
C -1.36337 3.20594 6.44911
H -4.51701 1.97252 5.99168
H -0.75948 3.77893 7.15362
C -2.70590 2.92912 6.70995
H -3.16479 3.29055 7.63280
Cl 0.89972 3.09944 4.96327
Cl -3.84384 0.81724 3.49442
S -1.67059 -3.41064 -2.87651
O -0.32029 -3.04092 -3.31331
O -2.08223 -2.75946 -1.56890
O -2.73765 -3.39218 -3.89326
C -1.53702 -5.21757 -2.39885
F -1.28679 -5.95100 -3.48639
F -2.67780 -5.64975 -1.85438
F -0.54688 -5.40744 -1.52668

**[$Mn^{IV}$OH(TDCPP$^{\bullet-}$)OTf]$^{+}$ with H bonding to OTf, nucleophilic reaction at $C_2$ of 1-chloronaphthalene**

113
RC (0/5)
N -0.87691 -0.66850 1.72364
N -0.62028 1.97706 0.64235
N -1.09092 -1.73025 -0.94007
N -0.80146 0.91499 -2.01231
C -0.98672 -2.00286 2.04884
C -0.47015 3.15608 -0.05234
C -0.79673 0.02056 2.91264
C -0.57430 2.30072 1.97974
C -1.18238 -2.91527 -0.24371
C -0.65716 2.24545 -2.34141
C -1.20390 -2.04805 -2.27489
C -0.96922 0.23412 -3.20013
C -0.95943 -2.15586 3.48197
C -0.31207 4.24932 0.87445
C -0.84750 -0.90618 4.01551
C -0.38337 3.72230 2.12920
C -1.34854 -4.00860 -1.16845
C -0.72010 2.40161 -3.77236
C -1.36397 -3.47267 -2.42299
C -0.91514 1.16054 -4.30233
H -1.01918 -3.10359 4.01083
H -0.16856 5.28994 0.59494
H -0.79642 -0.63166 5.06597
H -1.44265 -5.05494 -0.88956
H -0.63190 3.34644 -4.30250
H -1.47210 -3.99533 -3.36999
H -1.01597 0.89155 -5.35071
C -1.12825 -3.06612 1.14841
C -0.48205 3.30731 -1.44486
C -1.15344 -1.14593 -3.34598
C -0.66500 1.40806 3.05519
C 7.42213 -1.91630 -1.30247
C 6.21790 -2.59585 -1.44141
C 4.99428 -1.94084 -1.22561
C 5.02152 -0.54025 -0.85572
C 6.27959 0.12674 -0.71259
C 7.45626 -0.54981 -0.93611
H 3.78055 -3.72087 -1.56090
H 8.36087 -2.44767 -1.47635
H 6.21306 -3.65169 -1.71777
C 3.74410 -2.65163 -1.34504
C 3.80042 0.09797 -0.60751
H 6.29175 1.17906 -0.42963
H 8.41402 -0.03721 -0.83338
C 2.47615 -0.55464 -0.90809
C 2.56499 -2.02711 -1.16087
H 2.21415 -0.11355 -1.90211
H 1.61346 -2.55478 -1.23382
O 1.46510 -0.18697 -0.01535
H 1.80153 -0.45862 0.88106
Mn -0.95160 0.13647 -0.14158
Cl 3.72499 1.70875 -0.08215
O -3.09235 0.23001 -0.09918
S -4.24858 1.16196 0.19074
O -5.32044 0.51220 0.95612
C -4.97159 1.37362 -1.52293
F -5.97692 2.25224 -1.48991
F -4.04839 1.82197 -2.37897
F -5.44291 0.21098 -1.98185
C 1.12600 6.45168 -2.93870
C 0.01831 7.28759 -3.08364
C 0.94890 5.17054 -2.41084
H 0.14548 8.29126 -3.49514
C -1.25103 6.84733 -2.70813
C -0.31225 4.68527 -2.01202
H -2.12553 7.48924 -2.81968
C -1.40353 5.56165 -2.18171
H 2.12351 6.78158 -3.23079
Cl -3.00819 5.03862 -1.72730
Cl 2.35858 4.14251 -2.25254
Cl -3.95130 -4.05866 1.80277
C -2.49912 -5.00785 2.03693
C -1.24802 -4.45208 1.70469
C -0.11758 -5.26585 1.91428
Cl 1.47474 -4.64348 1.53686

H 0.68226 -7.15592 2.57434
C -0.22027 -6.56186 2.42651
H -1.56865 -8.08548 3.14357
C -1.47955 -7.07353 2.74241
C -2.62582 -6.30099 2.55031
H -3.61507 -6.68995 2.79390
Cl -3.99673 -1.37289 -4.45922
C -2.56012 -1.84227 -5.34050
C -1.29781 -1.69369 -4.73257
C -0.18070 -2.08595 -5.49497
Cl 1.42789 -1.93319 -4.81360
C -0.30265 -2.59900 -6.78844
H 0.59134 -2.89013 -7.34089
C -1.57286 -2.72973 -7.35176
H -1.67900 -3.12968 -8.36250
C -2.70781 -2.35263 -6.63279
H -3.70513 -2.44957 -7.06314
C -0.60613 1.96835 4.44356
C 0.61531 2.12710 5.12715
Cl 2.10528 1.64881 4.34405
C 0.68034 2.65020 6.42111
H 1.64847 2.75459 6.91214
C -0.49894 3.02883 7.06409
H -0.45756 3.43850 8.07572
H -2.65908 3.17668 6.91756
C -1.73090 2.88603 6.42434
C -1.77189 2.36072 5.13023
H -0.30760 4.24628 3.07852
O 4.27913 -2.96842 1.87619
S 3.71570 -1.88411 2.70160
O 3.06669 -0.78127 1.91062
O 2.96864 -2.27629 3.90557
C 5.22822 -1.00610 3.36722
F 5.95367 -1.84201 4.11478
F 6.00054 -0.56486 2.36535
F 4.88402 0.04147 4.12063
Cl -3.32828 2.18862 4.34926
O -3.85124 2.51714 0.59514

113
TS (0/5)
N -0.69690 -0.81257 2.04100
N -0.35415 1.81528 1.02106
N -1.07717 -1.80709 -0.62377
N -0.69592 0.83993 -1.64715
C -0.80632 -2.15662 2.33748
C -0.15418 2.99932 0.34126
C -0.66785 -0.14402 3.24557
C -0.41848 2.13615 2.36065
C -1.12753 -3.01028 0.04261
C -0.38730 2.14454 -1.95880
C -1.32899 -2.07410 -1.95036
C -0.98457 0.20413 -2.83672
C -0.80885 -2.33254 3.76659
C -0.06234 4.08423 1.28406
C -0.73607 -1.09231 4.32515
C -0.24476 3.55555 2.52539
C -1.40972 -4.06717 -0.89563
C -0.45960 2.32853 -3.38579
C -1.54838 -3.48772 -2.12270
C -0.84577 1.13778 -3.92515
H -0.87089 -3.29051 4.27583
H 0.09895 5.12609 1.02079
H -0.71534 -0.83440 5.38053
H -1.50029 -5.11995 -0.64130
H -0.25385 3.26033 -3.90592
H -1.76913 -3.97420 -3.06935
H -1.01402 0.90302 -4.97305
C -0.99194 -3.19950 1.42491
C -0.12264 3.17500 -1.04556
C -1.30973 -1.14744 -3.00144
C -0.58665 1.24163 3.42138
C 7.17897 -1.34537 -0.10896
C 6.12623 -2.25420 0.01684
C 4.84044 -1.93033 -0.43582
C 4.61851 -0.64278 -1.03540
C 5.70602 0.26809 -1.14787
C 6.96589 -0.08183 -0.68906
H 3.96154 -3.84983 0.09800
H 8.17390 -1.61722 0.25053
H 6.29548 -3.22882 0.47820
C 3.75267 -2.87098 -0.33395
C 3.31957 -0.36881 -1.52922
H 5.53631 1.24662 -1.59824
H 7.79311 0.62490 -0.77891
C 2.22054 -1.28623 -1.34588
C 2.50158 -2.57442 -0.78794
H 1.38253 -1.18030 -2.02991
H 1.69628 -3.30623 -0.72898
O 1.17643 -0.33983 0.01338
H 1.70083 -0.44206 0.86776
Mn -0.67040 0.00774 0.20469
Cl 2.99494 1.06106 -2.41763
O -2.67607 0.21343 0.30367
S -3.77560 1.20209 0.70603
O -4.72087 0.59369 1.64534
C -4.72741 1.32357 -0.90170
F -5.68380 2.24373 -0.77456
F -3.92325 1.67950 -1.90311
F -5.29574 0.15504 -1.19623
C 1.62027 6.42084 -2.12872
C 0.53954 7.17654 -2.58237
C 1.39645 5.13464 -1.63083
H 0.70534 8.18284 -2.97303
C -0.75320 6.65536 -2.53154
C 0.11003 4.55913 -1.57555
H -1.60944 7.23881 -2.87149
C -0.95461 5.36664 -2.03094
H 2.63546 6.81813 -2.15357
Cl -2.59598 4.76549 -1.96219
Cl 2.78059 4.23706 -1.04563
Cl -3.84735 -4.25381 1.80715
C -2.40237 -5.17632 2.16281
C -1.13549 -4.59131 1.96257
C -0.01617 -5.37786 2.29995
Cl 1.58884 -4.70018 2.14154
H 0.75209 -7.25322 3.03337
C -0.14318 -6.68111 2.78748
H -1.52426 -8.24486 3.33656
C -1.41613 -7.22680 2.95617
C -2.55248 -6.47701 2.64983
H -3.55297 -6.88831 2.78774
Cl -4.25175 -1.16757 -3.83713
C -2.94051 -1.69036 -4.86773
C -1.61748 -1.64264 -4.38360
C -0.61184 -2.08863 -5.26366
Cl 1.06349 -2.07843 -4.74944
C -0.89535 -2.54959 -6.55145
H -0.08164 -2.88375 -7.19588
C -2.21944 -2.57503 -6.99038
H -2.45115 -2.93354 -7.99562
C -3.24868 -2.14711 -6.15167
H -4.28801 -2.16407 -6.48129
C -0.70962 1.79141 4.81093
C 0.40882 2.16957 5.57976
Cl 2.01359 2.00108 4.91184
C 0.28241 2.67979 6.87489
H 1.17782 2.95648 7.43247
C -0.98766 2.82525 7.43285
H -1.09403 3.22303 8.44447
H -3.12202 2.57809 7.12785
C -2.12291 2.46661 6.70527
C -1.97471 1.95811 5.41264
H -0.25534 4.07737 3.47851
O 3.96801 -2.63317 2.57412
S 3.42540 -1.36518 3.10612
O 2.78726 -0.47624 2.08427
O 2.69990 -1.46332 4.38314
C 4.96642 -0.39042 3.53706
F 5.70730 -1.06885 4.41954
F 5.71310 -0.16918 2.44797
F 4.66220 0.79576 4.07390
Cl -3.41463 1.52446 4.52030
O -3.30314 2.56377 0.96653

113
PC (0/5)
N -1.27284 -0.94349 1.98685
N -0.55235 1.62731 1.00410
N -1.53935 -1.91244 -0.70121
N -0.78707 0.66995 -1.69510
C -1.48777 -2.28381 2.27268
C -0.14724 2.75267 0.36375
C -1.23564 -0.29842 3.18059
C -0.69582 1.96558 2.34043
C -1.77080 -3.08471 -0.06011
C -0.26247 1.92069 -1.97253
C -1.69357 -2.16536 -2.05296
C -0.98805 0.06162 -2.89168
C -1.55497 -2.46351 3.70262
C -0.00910 3.84176 1.29887
C -1.41853 -1.23019 4.26389
C -0.37142 3.36001 2.51958
C -2.10790 -4.11984 -1.00861
C -0.14239 2.08547 -3.40148
C -2.07065 -3.54688 -2.24330
C -0.60879 0.94007 -3.97157
H -1.70715 -3.41488 4.20515
H 0.30695 4.84947 1.04358
H -1.42584 -0.96915 5.31848
H -2.34412 -5.14961 -0.75506
H 0.24386 2.97115 -3.89832
H -2.26644 -4.01414 -3.20477
H -0.67685 0.69852 -5.02867
C -1.71433 -3.29242 1.34660
C 0.05837 2.89615 -1.03704
C -1.44900 -1.26987 -3.08657
C -1.03444 1.09795 3.36851
C 8.55838 0.28850 -3.09835
C 7.92892 -0.25879 -2.00024
C 6.50870 -0.34669 -1.93340
C 5.73308 0.14996 -3.03985
C 6.41326 0.70895 -4.15828
C 7.79129 0.77623 -4.18652
H 6.44814 -1.27573 0.03018
H 9.64901 0.34791 -3.13348
H 8.51388 -0.63705 -1.15763
C 5.84743 -0.90933 -0.80593
C 4.31086 0.04895 -2.93988
H 5.82626 1.08532 -4.99701
H 8.29605 1.20867 -5.05401
C 3.69113 -0.50240 -1.83794
C 4.47203 -0.98890 -0.76014
H 2.60288 -0.55960 -1.78518
H 3.97182 -1.42512 0.10648
O 0.69734 -0.62896 0.11763
H 1.18457 -0.63568 1.00812
Mn -0.97615 -0.15262 0.15059
Cl 3.30844 0.64597 -4.25793
O -2.93960 0.29407 0.10928
S -3.92374 1.44892 0.32070
O -5.05267 1.03819 1.15704
C -4.64351 1.61342 -1.39903
F -5.52438 2.61248 -1.41055
F -3.68426 1.88019 -2.28712
F -5.26288 0.48984 -1.75503
C 2.56010 5.63096 -1.95379
C 1.71340 6.63020 -2.43622
C 2.00886 4.43033 -1.50238
H 2.13593 7.57274 -2.79078
C 0.33150 6.43703 -2.46733
C 0.62087 4.19461 -1.52443
H -0.33792 7.21420 -2.83747
C -0.20103 5.22806 -2.01377
H 3.64090 5.77263 -1.92431
Cl -1.93461 5.00717 -2.04586
Cl 3.07546 3.18568 -0.89450
Cl -4.61223 -4.10116 1.88316
C -3.24168 -5.16098 2.12442
C -1.94731 -4.68365 1.84814
C -0.87181 -5.56926 2.04926
Cl 0.75095 -5.01421 1.72426
H -0.21516 -7.53014 2.65522
C -1.07292 -6.87272 2.50918
H -2.53580 -8.32821 3.13539
C -2.37142 -7.31045 2.77503
C -3.46261 -6.46038 2.58541
H -4.48025 -6.79406 2.79080
Cl -4.16740 -0.85070 -4.41432
C -2.80525 -1.60859 -5.20315
C -1.59756 -1.75418 -4.49615
C -0.52548 -2.36964 -5.17066
Cl 1.00290 -2.57230 -4.34573
C -0.64670 -2.82256 -6.48596
H 0.20684 -3.29415 -6.97402
C -1.86192 -2.66179 -7.15361
H -1.96441 -3.01361 -8.18237
C -2.94683 -2.05542 -6.51876
H -3.90016 -1.92543 -7.03199
C -1.20727 1.64662 4.75121
C -0.12399 1.84530 5.62801
Cl 1.48923 1.43005 5.10731
C -0.30730 2.35740 6.91509
H 0.55697 2.49559 7.56555
C -1.59404 2.68074 7.34727
H -1.74246 3.08217 8.35202
H -3.70326 2.74183 6.83557
C -2.69332 2.49350 6.50764
C -2.49142 1.97891 5.22579
H -0.40324 3.89125 3.46709
O 3.09699 -2.83094 1.87760
S 2.67386 -1.85831 2.90599
O 2.00312 -0.63348 2.34957
O 2.03253 -2.40814 4.11073
C 4.28883 -1.15441 3.54139
F 5.02157 -2.12401 4.09586
F 4.99856 -0.60930 2.54683
F 4.07298 -0.21234 4.46481
Cl -3.86989 1.74320 4.17729
O -3.28474 2.74158 0.58462

**Naphthalene**

19
Naphthalene (0/1)
C 2.43900 -0.70977 0.00000
C 2.43913 0.70972 0.00000
C 1.24773 1.40585 0.00000
C 0.00000 0.71848 0.00000
C -0.00003 -0.71864 0.00000
C 1.24766 -1.40604 0.00000
C -1.24774 -1.40588 0.00000
C -2.43913 -0.70957 0.00000
C -2.43904 0.70988 0.00000
C -1.24757 1.40598 0.00000
H 3.38921 -1.24993 0.00000
H 3.38941 1.24965 0.00000
H 1.24579 2.49943 0.00000
H -1.24636 -2.49946 0.00000
H -3.38932 -1.24970 0.00000
H -3.38925 1.24998 0.00000
H -1.24570 2.49954 0.00000
H 1.24616 -2.49958 0.00000

**Naphthalene radical**

18
Ionized naphthalene (1/2)
C 0.69679 -2.45381 0.00000
C -0.69679 -2.45381 0.00000
C -1.40481 -1.23716 0.00000
C -0.71713 -0.00000 0.00000
C 0.71713 0.00000 0.00000
C 1.40481 -1.23716 0.00000
C 1.40481 1.23716 0.00000
C 0.69679 2.45381 0.00000
C -0.69679 2.45381 0.00000
C -1.40481 1.23716 0.00000
H 1.24545 -3.39740 0.00000
H -1.24545 -3.39740 0.00000
H -2.49717 -1.24281 0.00000
H 2.49717 1.24281 0.00000
H 1.24545 3.39740 0.00000
H -1.24545 3.39739 0.00000
H -2.49717 1.24281 0.00000
H 2.49717 -1.24281 0.00000

**$Cl^-$ + Naphthalene in complex**

19
Complex (-1/1)
Cl -1.78665 2.31664 -0.44472
C -1.81571 -1.43467 0.88725
C -1.68572 -1.83174 -0.46936
C -0.54858 -1.51157 -1.18240
C 0.51251 -0.78011 -0.57547
C 0.38082 -0.37815 0.79799
C -0.80623 -0.72509 1.50494
C 1.44191 0.35326 1.40479
C 2.57906 0.67337 0.69158
C 2.70908 0.27633 -0.66499
C 1.69947 -0.43326 -1.28252
H -2.72127 -1.69423 1.44157
H -2.49236 -2.39342 -0.94729
H -0.44660 -1.81660 -2.22762
H 1.34044 0.65853 2.44998
H 3.38559 1.23507 1.16971
H 3.61463 0.53591 -1.21926
H 1.79801 -0.73992 -2.32757
H -0.90511 -0.41859 2.54998

**$Cl^-$ + Naphthalene complex radical**

19
Complex radical (0/2)
Cl -2.38406 1.37317 -0.81752
C 2.97827 0.28431 -0.42287
C 2.45042 1.39472 0.27218
C 1.14708 1.36979 0.74649
C 0.32979 0.23442 0.54106
C 0.86487 -0.89657 -0.15648
C 2.19993 -0.84257 -0.63332
C 0.04424 -2.05077 -0.33441
C -1.25169 -2.09823 0.15852
C -1.78759 -0.99190 0.83815
C -1.02444 0.17857 1.00911
H 4.00539 0.31574 -0.79378
H 3.07302 2.27756 0.43505
H 0.73545 2.23202 1.27676
H 0.46034 -2.91165 -0.86431
H -1.85715 -2.99642 0.02081
H -2.80333 -1.02899 1.23561
H -1.39790 0.98224 1.64352
H 2.60790 -1.70502 -1.16647

**$[Mn^{IV}OH(Por^{+\bullet})OTf]^+$**

47
Non-reduced (1/5)
N 1.42595 1.04581 -1.19314
N -1.15531 1.95952 -0.35532
N 0.40475 -1.61629 -1.41314
N -2.15660 -0.72516 -0.50445
C 2.53928 0.45125 -1.77174
C -2.44745 2.22461 -0.04555
C 1.74558 2.34749 -0.99298
C -0.46126 3.15159 -0.21055
C 1.65817 -1.85795 -1.87690
C -3.34789 -0.07859 -0.21019
C -0.20767 -2.85600 -1.26696
C -2.43332 -2.04998 -0.54041
C 3.58650 1.43735 -1.92009
C -2.60913 3.61641 0.30529
C 3.09841 2.60987 -1.42395
C -1.37451 4.18911 0.21611
C 1.86389 -3.27305 -2.06281
C -4.40156 -1.06005 -0.06533
C 0.71354 -3.89329 -1.67075
C -3.83087 -2.28357 -0.25541
H 4.56958 1.23338 -2.34024
H -3.55329 4.07575 0.59151
H 3.59098 3.57782 -1.35558
H -1.08795 5.22195 0.40564
H 2.78425 -3.71982 -2.43370
H -5.43709 -0.82166 0.17025
H 0.48533 -4.95751 -1.65877
H -4.29861 -3.26553 -0.21846
C 2.65306 -0.87847 -2.10111
C -3.49614 1.27528 -0.01438
C -1.50335 -3.06819 -0.85493
C 0.87413 3.33751 -0.48291
H 1.28734 4.33632 -0.33823
H -4.49324 1.64571 0.22689
H -1.85544 -4.09929 -0.80345
H 3.59788 -1.21761 -2.52754
O -0.87186 0.50026 -2.58886
H -0.83008 -0.29555 -3.14681
Mn -0.38549 0.17261 -0.91206
O 0.03859 -0.18423 0.97709
S 1.35638 -0.08470 1.77934
O 1.69267 1.29623 2.13110
O 2.40774 -0.95822 1.25270
C 0.76618 -0.89065 3.36297
F 1.77679 -0.92317 4.22671
F -0.23604 -0.19475 3.88962
F 0.35853 -2.13294 3.12168

**$[Mn^{IV}OH(Por)OTf]$**

47
Reduced (0/4)
N 1.18376 1.43736 -1.07014
N -1.51404 1.74947 -0.17477
N 0.68927 -1.33347 -1.56615
N -1.97670 -1.04700 -0.57732
C 2.36631 1.14005 -1.70640
C -2.85935 1.72623 0.10976
C 1.24911 2.76064 -0.70335
C -1.07042 3.02307 0.09012
C 1.95591 -1.25880 -2.10089
C -3.25929 -0.68305 -0.24576
C 0.33855 -2.66571 -1.55015
C -1.97106 -2.41296 -0.72160
C 3.21149 2.30794 -1.72343
C -3.27873 3.02981 0.56127
C 2.52776 3.30497 -1.08766
C -2.16901 3.82707 0.56539
C 2.40504 -2.57970 -2.45736
C -4.09085 -1.85999 -0.17475
C 1.41428 -3.45078 -2.09902
C -3.29015 -2.93162 -0.45128
H 4.20747 2.34103 -2.16187
H -4.29708 3.28239 0.85219
H 2.84031 4.33128 -0.90233
H -2.08668 4.87450 0.85096
H 3.37227 -2.80039 -2.90576
H -5.15115 -1.85089 0.07251
H 1.39481 -4.53454 -2.20181
H -3.55682 -3.98658 -0.48909
C 2.72686 -0.10584 -2.20674
C -3.68505 0.60785 0.05121
C -0.88631 -3.17936 -1.13631
C 0.21990 3.49605 -0.12657
H 0.42196 4.53922 0.11902
H -4.73567 0.74447 0.31009
H -1.02537 -4.25934 -1.19735
H 3.71138 -0.19934 -2.66668
O -0.97774 0.58276 -2.55014
H -0.78399 -0.16951 -3.13462
Mn -0.42173 0.21248 -0.89592
O 0.10438 -0.24343 0.98614
S 1.38403 -0.04655 1.80732
O 1.50663 1.30239 2.36845
O 2.57232 -0.66189 1.20754
C 0.94802 -1.14315 3.25914
F 1.95598 -1.13224 4.13154
F -0.15125 -0.70283 3.86821
F 0.74510 -2.39593 2.85410