

Supporting Information for Mechanistic Insights into Catalytic CO₂ Hydrogenation using Mn(I)-complexes with Pendant Oxygen Ligands

Shubhajit Das,[†] and Swapan K. Pati^{*,‡}

*New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore
560064, India*

*, and Theoretical Sciences Unit and New Chemistry Unit, Jawaharlal Nehru Centre for Advanced
Scientific Research, Bangalore 560064, India*

E-mail: pati@jncasr.ac.in

*To whom correspondence should be addressed

[†]New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India

[‡]Theoretical Sciences Unit and New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India

Comment on the catalyst deactivation channels

One interesting experimental observation is that a related Mn-complex, **Mn-BP** ($\text{Mn}(\text{BP})\text{Br}(\text{CO})_3$; BP=2,2'-bipyridine), which does not have any pendant oxygen ligands, has been found to be inactive towards hydrogenation of CO_2 in presence of DBU. Experimentally, a catalyst decomposition pathway was found to be at play in which formation of a Mn(0) dimer ($\text{Mn}_2(\text{BP})_2(\text{CO})_6$) was observed. This explains the lack of reactivity of the catalyst. We anticipated that such decomposition route may also be viable in other Mn-complexes bearing the pendant oxygen ligands. Since the Mn(0) dimer formation usually proceeds through a bimolecular decomposition of the Mn-hydride species with the release of H_2 , we have estimated the propensity of such side reactions for **Mn-DMBP** complex employing the equation $3_{\text{OMe}} + 3_{\text{OMe}} \rightarrow \text{Mn}_2(\text{DMBP})_2(\text{CO})_6 + \text{H}_2$. The decomposition reaction is found to be slightly endergonic by 2.1 kcal/mol, which stands in contrast with the **Mn-BP** complex for which the process is computed to be moderately exergonic by 12.0 kcal/mol. Since we did not locate the TSs for such reactions, we refrain from making a pertinent kinetic conclusion. In the case of **Mn-DHBP** we could not even optimize a Mn(0)-dimer. Such bimolecular process most likely is unfavorable for **Mn-DHBP**, presumably, due to the fact that the corresponding hydride, **3** bears a negative charge of 2 and hence the bimolecular quenching seems unlikely owing to the repulsion of the anionic ligands.

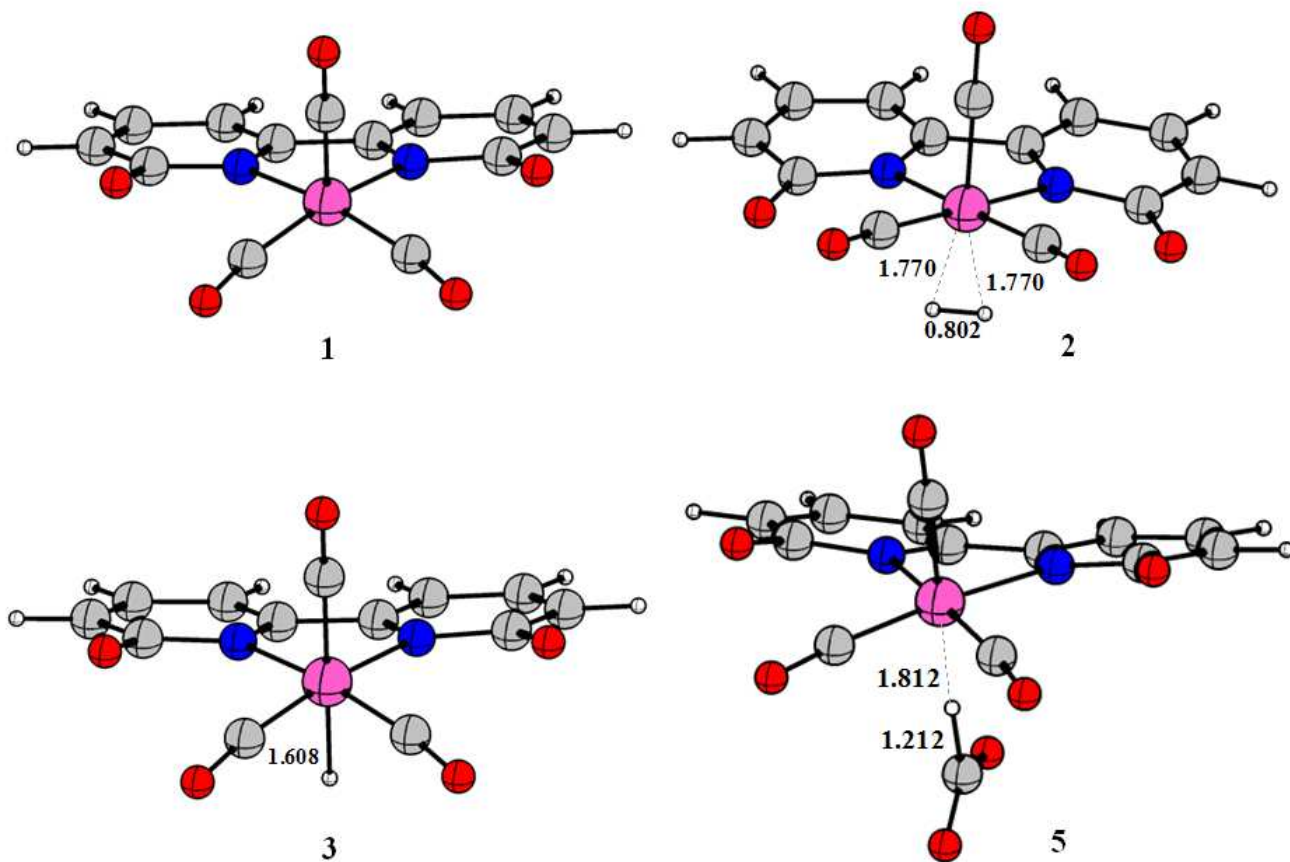


Fig. S1: Geometry optimized structures of the key intermediates in the P_A pathway of the Mn-DHBP catalyzed hydrogenation of CO_2 . All distances are given in Å. Solvent-corrected Gibbs free energy values (in kcal/mol) are given in parenthesis.

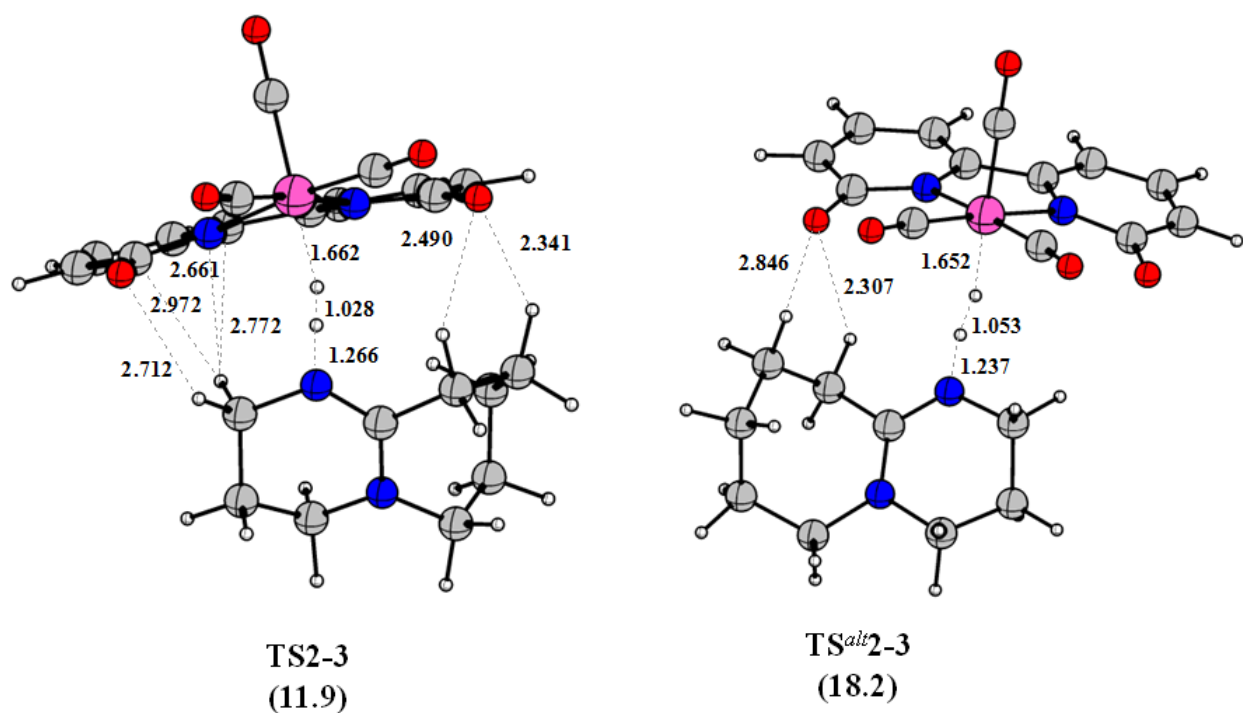


Fig. S2: Geometry optimized structures of the two TSs for DBU assisted H₂ cleavage in the **P_A** pathway of the **Mn-DHBP** catalysed hydrogenation of CO₂. Noncovalent contacts are shown explicitly in the TS structures. All distances are given in Å. Solvent-corrected Gibbs free energy values (in kcal/mol) are given in parenthesis.

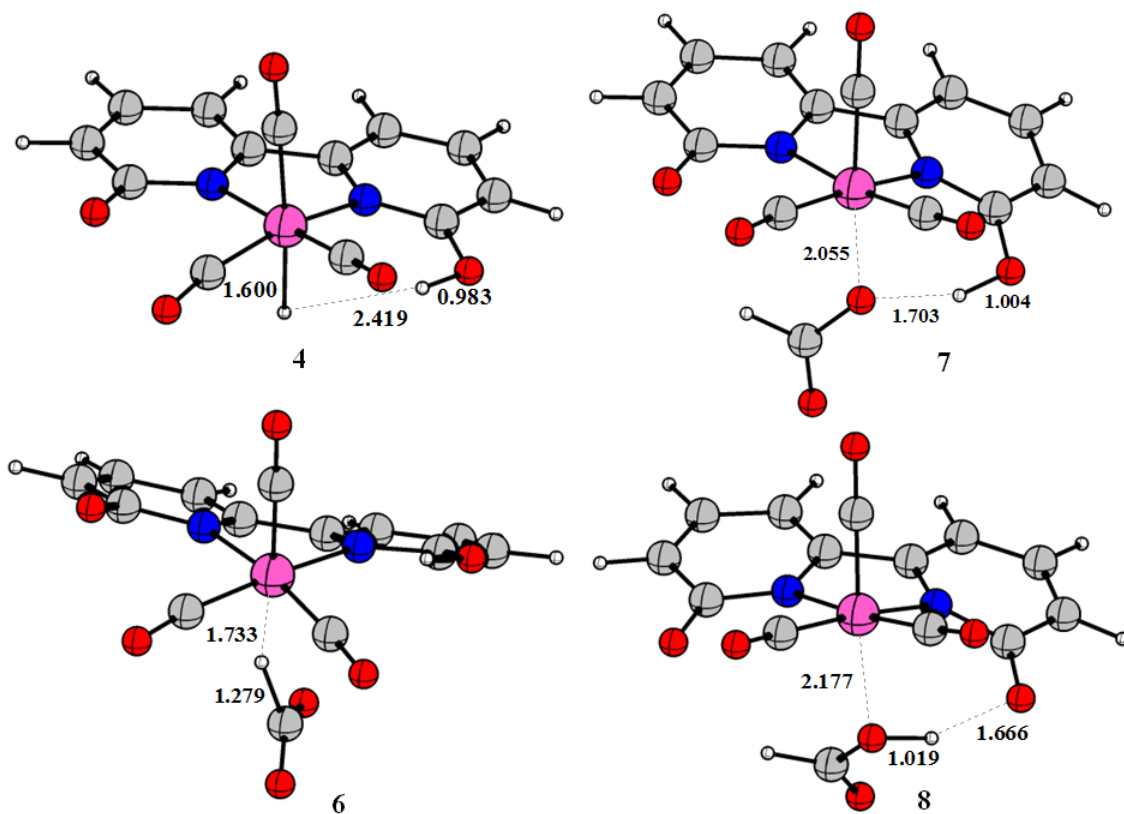


Fig. S3: Geometry optimized structures of the key intermediates in the P_B pathway of the **Mn-DHBP** catalysed hydrogenation of CO_2 . All distances are given in Å. Solvent-corrected Gibbs free energy values (in kcal/mol) are given in parenthesis.

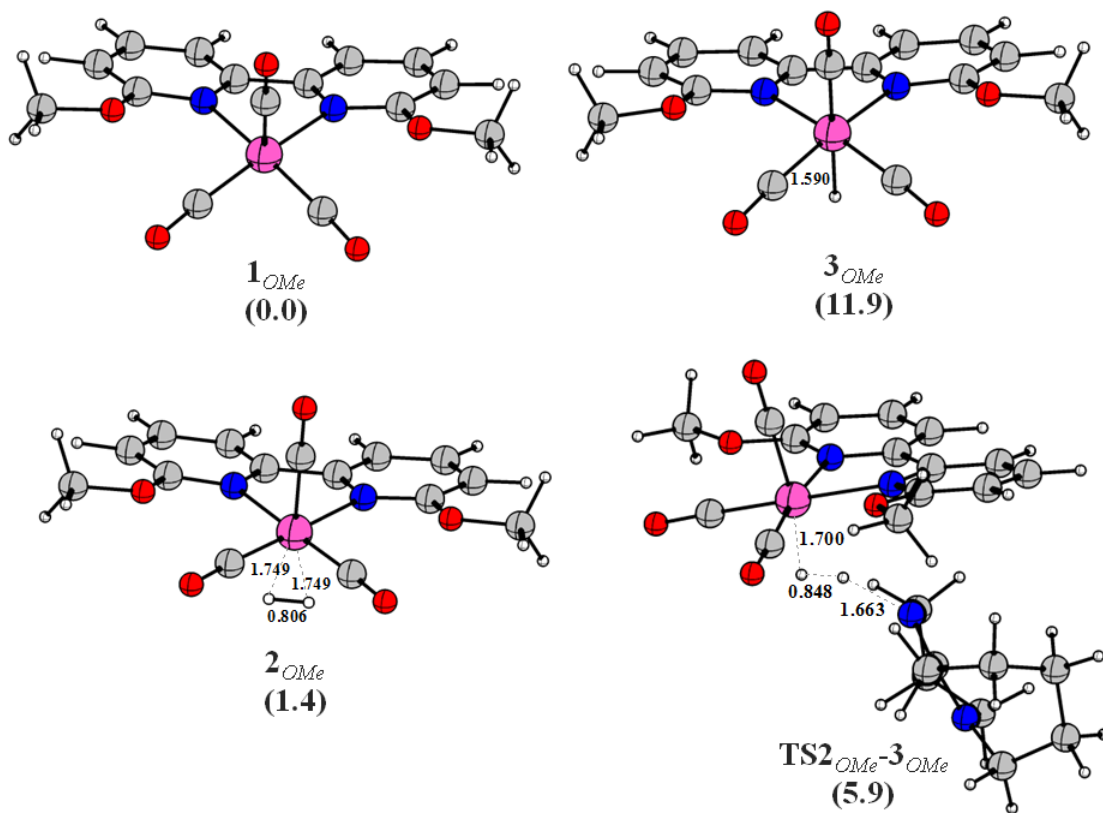


Fig. S4: Geometry optimized structures of the key intermediates in the P_A pathway of the **Mn-DMBP** catalyzed hydrogenation of CO_2 . All distances are given in Å. Solvent-corrected Gibbs free energy values (in kcal/mol) are given in parenthesis.

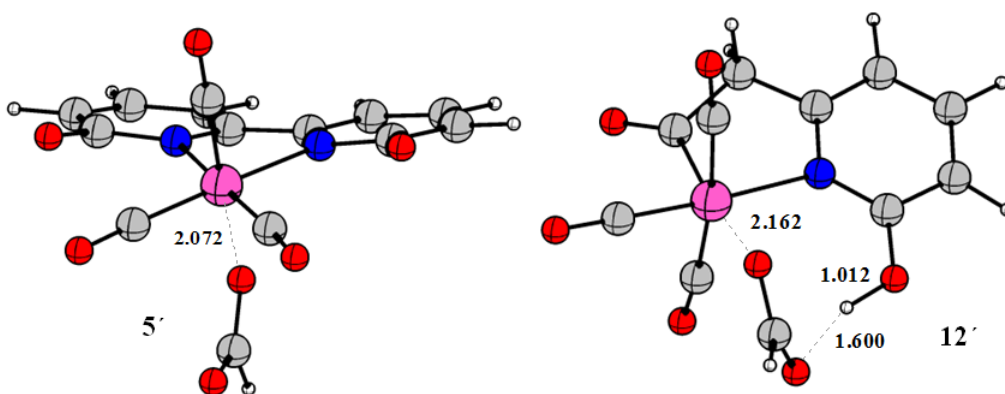


Fig. S5: Geometry optimized structures of the O-bound formate complex of **1** and **9**. All distances are given in Å. Solvent-corrected Gibbs free energy values (in kcal/mol) are given in parentheses.

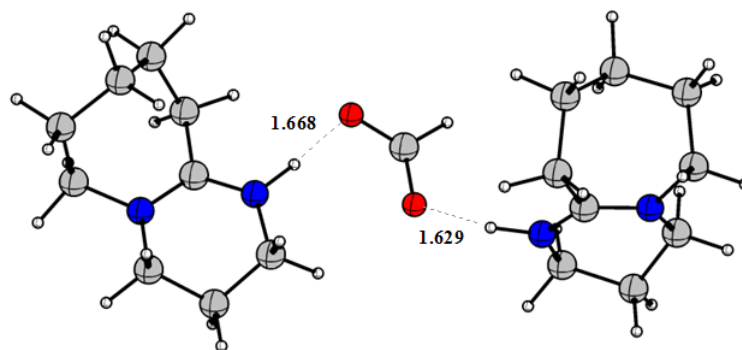


Fig. S6: Geometry optimized structure of 2DBUH⁺HCOO⁻. All distances are given in Å.

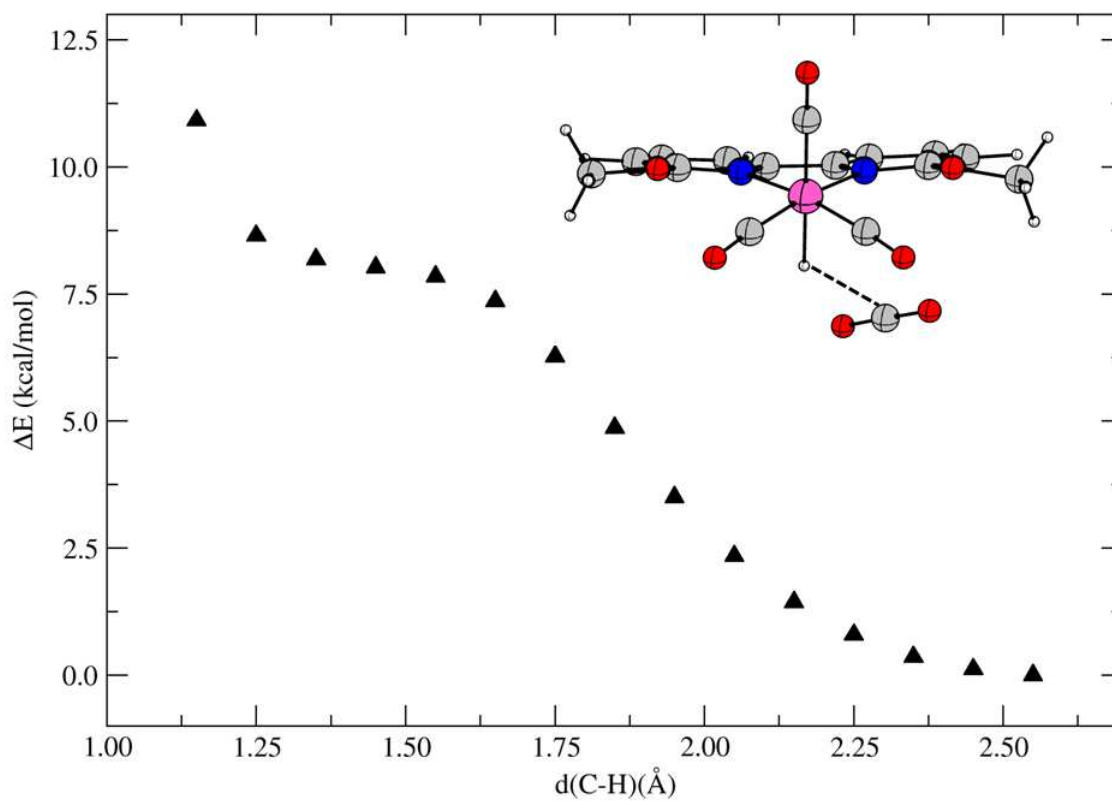


Fig. S7: Potential energy profile along (Mn)H-C(CO₂) distance in a weak 3OMe-CO₂ complex. The data points are obtained by performing relaxed potential energy scan calculations at the M06/BS-I level of theory. Inset shows geometry optimized structure of the 3OMe-CO₂ complex.

Cartesian coordinates of computed structures

2

H2

H 0.00000000 0.00000000 0.37103100

H 0.00000000 0.00000000 -0.37103100

27

DBU

N -0.30440500 0.61691700 -0.55976100

N -1.22189800 -1.47811500 0.11319200

C 0.93302000 1.34075400 -0.80324600

C 1.87600100 1.37484400 0.40034500

C -0.27964000 -0.76310100 -0.38753800

C 1.99621700 0.01248300 1.07931700

C -1.36967900 1.34951500 0.10398500

C 0.98868100 -1.45350300 -0.81446200

C 2.19525200 -1.15498000 0.11274400

C -2.65880500 0.56162700 -0.01291700

C -2.43825300 -0.82704600 0.56699900

H 1.44473000 0.89227300 -1.66372800

H 0.66467300 2.35929000 -1.11312600

H 1.53026800 2.11950900 1.13188400

H 2.86330900 1.71616500 0.05459100

H 2.82954200 0.03728600 1.79352200

H 1.09481600 -0.17779000 1.68234500

H -1.12593800 1.51882400 1.17114700

H -1.45640100 2.33680800 -0.36965900

H 1.22221600 -1.18132700 -1.85230900
H 0.76177500 -2.52285100 -0.81260800
H 2.40858200 -2.05227700 0.70599200
H 3.09386200 -0.97256600 -0.49541000
H -2.93149000 0.48585900 -1.07463200
H -3.47656500 1.07980600 0.50295100
H -3.28627100 -1.48179200 0.32564600
H -2.40975300 -0.77239500 1.66802200

29

Mn(DHBP)(CO)₃

Mn -0.00002200 -1.00978800 -0.23254700
N -1.29602200 0.54811300 0.02318400
C -2.62090600 0.47282600 0.20545200
C -3.45683300 1.59228700 0.12116700
H -4.52862200 1.48284400 0.26443100
C -2.88487200 2.82082900 -0.13957300
H -3.50859200 3.70690200 -0.21832000
C -1.49961100 2.92301100 -0.27450400
H -1.03774600 3.88922100 -0.44419200
C -0.73516300 1.77474300 -0.16696200
O -1.98000800 -3.01123700 -1.14270400
C -1.24072300 -2.21619700 -0.76892300
O -0.00065400 -2.13268000 2.45824800
C -0.00043400 -1.71347400 1.38737600
N 1.29618000 0.54794900 0.02323700
C 2.62106300 0.47247300 0.20538600

C 3.45714200 1.59181900 0.12108800
H 4.52893200 1.48221400 0.26422500
C 2.88533200 2.82045500 -0.13953900
H 3.50916300 3.70645500 -0.21822800
C 1.50008000 2.92282500 -0.27442000
H 1.03834000 3.88910800 -0.44403100
C 0.73548500 1.77465100 -0.16692600
O 1.97958900 -3.01202300 -1.14187500
C 1.24050300 -2.21660800 -0.76851600
O -3.07934800 -0.74585300 0.48113300
H -4.04151500 -0.75869800 0.57571700
O 3.07936600 -0.74626100 0.48105400
H 4.04153300 -0.75918800 0.57564000

27

1

Mn 0.99224700 -0.15596400 0.00000000
N -0.53042200 -0.05328600 1.28719400
O 0.75098100 0.16524600 3.18624100
C -0.36988900 0.04504700 2.67483000
C -1.57665200 -0.00260300 3.47353800
H -1.43961400 0.04805200 4.55061800
C -2.80979300 -0.08637500 2.89433700
H -3.70664800 -0.11102100 3.51378700
C -2.93089400 -0.12988800 1.49082500
H -3.90571300 -0.17791600 1.01697900
C -1.77501400 -0.10160000 0.73644400

O 3.09960700 -0.99130600 1.89193500
C 2.21687900 -0.62863100 1.23572100
O 2.02897200 2.55434500 0.00000000
C 1.63780800 1.45961000 0.00000000
N -0.53042200 -0.05328600 -1.28719400
O 0.75098100 0.16524600 -3.18624100
C -0.36988900 0.04504700 -2.67483000
C -1.57665200 -0.00260300 -3.47353800
H -1.43961400 0.04805200 -4.55061800
C -2.80979300 -0.08637500 -2.89433700
H -3.70664800 -0.11102100 -3.51378700
C -2.93089400 -0.12988800 -1.49082500
H -3.90571300 -0.17791600 -1.01697900
C -1.77501400 -0.10160000 -0.73644400
O 3.09960700 -0.99130600 -1.89193500
C 2.21687900 -0.62863100 -1.23572100

29

2

Mn 0.00007600 -1.06316500 -0.18697500
N -1.29334600 0.51924200 -0.20692200
O -3.16416600 -0.73792300 -0.63654000
C -2.66828400 0.36916400 -0.36342000
C -3.46906200 1.55898000 -0.19808700
H -4.54495600 1.43258300 -0.28896000
C -2.89181400 2.77552800 0.04640200
H -3.51487600 3.66292100 0.16166900

C -1.49370900 2.89087800 0.13597200
H -1.02037300 3.85352800 0.29773700
C -0.73763500 1.73869500 -0.00381900
O -1.90456500 -3.32446400 -0.19098800
C -1.24507300 -2.37373100 -0.21650000
O -0.00013000 -1.09219900 2.74431600
C -0.00003100 -1.08763100 1.58613700
N 1.29329400 0.51938200 -0.20689700
O 3.16421600 -0.73768700 -0.63648000
C 2.66823800 0.36938000 -0.36344400
C 3.46892900 1.55927000 -0.19809400
H 4.54483500 1.43291400 -0.28889800
C 2.89157200 2.77579100 0.04626400
H 3.51455600 3.66324600 0.16147200
C 1.49345300 2.89104200 0.13580200
H 1.02004900 3.85367000 0.29748900
C 0.73747500 1.73877200 -0.00384900
O 1.90491800 -3.32427500 -0.19050900
C 1.24540200 -2.37358600 -0.21629500
H 0.40122800 -0.92687400 -1.90515700
H -0.40096600 -0.92616200 -1.90505100

29

TS2-3

Mn 1.10955900 -0.17442800 0.91763200
N 1.69255700 1.48388100 -0.14274500
O -0.13677600 2.78267700 0.36053500

C 1.00967900 2.69199500 -0.13085300
C 1.68525700 3.82034300 -0.71967000
H 1.17721400 4.77990500 -0.65415500
C 2.89479800 3.67371500 -1.35024400
H 3.38542700 4.53829000 -1.79943500
C 3.49270500 2.40809800 -1.44274900
H 4.42260500 2.26440000 -1.98331800
C 2.84573200 1.34038800 -0.83413500
O -1.02714800 0.95769400 2.58504700
C -0.16744800 0.59664200 1.88288700
O 3.08726200 0.29268000 3.05462400
C 2.31547700 0.11312100 2.20296200
N 2.51202800 -0.96258800 -0.34616600
O 1.86517700 -3.15382800 -0.08906500
C 2.67549800 -2.32775600 -0.55224700
C 3.82622900 -2.72485100 -1.32768200
H 3.98303000 -3.79436900 -1.44843900
C 4.65887300 -1.79513700 -1.89473200
H 5.51768600 -2.11826500 -2.48483000
C 4.39749500 -0.42450300 -1.73910300
H 5.01507300 0.32361800 -2.22547800
C 3.30332500 -0.05942600 -0.96595700
O 0.13824700 -2.60650300 2.25575500
C 0.59266100 -1.70673700 1.67083600
N -4.19865900 -0.75967200 -0.88742700
N -1.98507900 -1.05214000 -0.22998500
C -5.42353100 0.00445300 -1.14211100

C -5.47856600 1.48099000 -0.75790100
C -2.95530200 -0.27692400 -0.61010600
C -4.76392300 1.79576700 0.55210000
C -4.43752600 -2.20392200 -0.86779300
C -2.65754100 1.18414600 -0.76171500
C -3.27635400 2.06201200 0.32849500
C -3.15898200 -2.98937200 -1.08114500
C -2.11070500 -2.49072700 -0.10770400
H -5.70615200 -0.12492700 -2.20083800
H -6.20134800 -0.51142700 -0.55404700
H -6.54710600 1.72766500 -0.69114500
H -5.07745000 2.11431200 -1.56079000
H -5.22572700 2.66470200 1.03799900
H -4.90195900 0.95338700 1.24849400
H -4.90855000 -2.48064300 0.09132500
H -5.16687200 -2.42703800 -1.66030700
H -2.99713800 1.49989200 -1.75795900
H -1.57066200 1.33324800 -0.71992900
H -2.70216900 1.93435500 1.25319700
H -3.11422500 3.10404100 0.02395600
H -2.80190000 -2.84338500 -2.11000500
H -3.35357700 -4.05944700 -0.94682200
H -1.11635000 -2.92193300 -0.29077900
H -2.37495500 -2.74926100 0.92886400
H -0.81940900 -0.63835800 -0.20554900
H 0.17842100 -0.39009300 -0.43031400

28

3

Mn 0.00006800 -1.07076200 -0.17129700

N -1.30530400 0.53453200 -0.03309000

O -3.23627000 -0.70158100 0.24616200

C -2.69355500 0.40632000 0.08597000

C -3.46972100 1.62344500 0.01426000

H -4.55052300 1.50844100 0.08124500

C -2.86932900 2.85101700 -0.11791900

H -3.47605300 3.75935000 -0.16445700

C -1.47425900 2.94075900 -0.18130800

H -0.97949000 3.90334300 -0.26116000

C -0.73943600 1.75253500 -0.12669900

O -1.89872400 -3.14132800 -1.00677700

C -1.20847800 -2.27466000 -0.62865900

O -0.00135300 -1.91294400 2.67123600

C -0.00071800 -1.51378400 1.56819400

N 1.30545400 0.53447200 -0.03292500

O 3.23638400 -0.70165400 0.24662800

C 2.69371200 0.40621200 0.08605700

C 3.46994300 1.62327300 0.01388000

H 4.55075000 1.50821500 0.08073200

C 2.86961500 2.85084600 -0.11854600

H 3.47639000 3.75912600 -0.16545300

C 1.47453700 2.94066200 -0.18173600

H 0.97980200 3.90324300 -0.26181800

C 0.73966300 1.75249400 -0.12675000

O 1.89892500 -3.14241900 -1.00397100
C 1.20875400 -2.27516200 -0.62711600
H 0.00030800 -0.76004000 -1.74856100

28

DBUH⁺

N -0.27761800 0.70213600 -0.17031100
N -1.30983900 -1.36073300 -0.04299500
C 0.86412900 1.63338700 -0.36291300
C 2.28373200 1.10684600 -0.14272200
C -0.24769000 -0.61035700 -0.33069100
C 2.37731400 -0.00989200 0.89016600
C -1.51971400 1.38583200 0.24225300
C 0.98230500 -1.30994200 -0.80806800
C 2.07262800 -1.37427500 0.27060500
C -2.74773700 0.56893100 -0.09363600
C -2.58415400 -0.83532400 0.44670700
H 0.75481700 2.09768000 -1.35254500
H 0.67570700 2.42177200 0.37642100
H 2.87526500 1.97124400 0.17839500
H 2.73684800 0.78364200 -1.08847600
H 3.37852000 -0.03146800 1.33220700
H 1.69064100 0.19880900 1.72377200
H -1.45403900 1.59611900 1.31944000
H -1.54196700 2.34894800 -0.27933100
H 1.35104400 -0.78972000 -1.69940500
H 0.71242100 -2.31965900 -1.13566400

H 1.78629800 -2.09539900 1.04615900
H 2.97151700 -1.77874000 -0.21009700
H -2.89122400 0.53374000 -1.18092200
H -3.63307700 1.04422000 0.33805200
H -3.38040200 -1.50012900 0.10203700
H -2.58729800 -0.84505700 1.54478800
H -1.21775000 -2.35706200 -0.19188000

31

TS3-5

Mn -0.00015600 -1.08545600 -0.21313500
N 1.30458400 0.50647400 -0.38242300
O 3.22914400 -0.74545200 -0.61676400
C 2.69132400 0.36994600 -0.49274500
C 3.46984400 1.58634800 -0.45677100
H 4.55050000 1.46726700 -0.51433900
C 2.87053700 2.81750200 -0.36623800
H 3.47882100 3.72527000 -0.34382600
C 1.47507700 2.91305700 -0.31208700
H 0.98215300 3.87783100 -0.25360000
C 0.73880800 1.72823100 -0.32731300
O 1.89889300 -3.19975400 0.52257900
C 1.21529700 -2.31084900 0.19778900
O -0.00113900 -1.87984100 -3.05734000
C -0.00075900 -1.51829200 -1.94369400
N -1.30533300 0.50623100 -0.38149500
O -3.22983300 -0.74604400 -0.61445800

C -2.69212500 0.36945400 -0.49086600
C -3.47083200 1.58572400 -0.45443500
H -4.55150600 1.46644900 -0.51129100
C -2.87168200 2.81698900 -0.36434600
H -3.48011400 3.72465000 -0.34157200
C -1.47620400 2.91278900 -0.31111000
H -0.98340300 3.87764900 -0.25299500
C -0.73973800 1.72809300 -0.32680500
O -1.89826900 -3.20007200 0.52406500
C -1.21507300 -2.31106000 0.19872400
H 0.00037800 -0.75383900 1.39731200
C 0.00237000 0.14698400 3.05834100
O 0.00171100 1.26651900 2.69323500
O 0.00339900 -0.78877000 3.77936600

31

5

Mn 0.00105400 -1.02359700 -0.18130100
N 1.29472300 0.53251800 -0.36949000
O 3.18332800 -0.72059800 -0.78134700
C 2.67101800 0.38933500 -0.54877400
C 3.46085000 1.59497800 -0.45632700
H 4.53740300 1.47495200 -0.56090900
C 2.87426500 2.81786200 -0.25584400
H 3.49136000 3.71669300 -0.18910700
C 1.48047900 2.92297700 -0.14892200
H 0.99837800 3.88370800 -0.00214000

C 0.73514400 1.75314200 -0.21657200
O 1.93696900 -3.14435400 0.49303200
C 1.24148500 -2.25781600 0.21185300
O 0.00201300 -1.82546000 -2.99131800
C 0.00155400 -1.49568200 -1.87186300
N -1.29767400 0.52850400 -0.36805700
O -3.18303000 -0.73051500 -0.77682300
C -2.67376500 0.38109600 -0.54552700
C -3.46712000 1.58438600 -0.45275900
H -4.54340900 1.46106400 -0.55623400
C -2.88401500 2.80910600 -0.25324400
H -3.50375400 3.70609300 -0.18620400
C -1.49045500 2.91842700 -0.14767400
H -1.01113700 3.88065600 -0.00163000
C -0.74164300 1.75085100 -0.21584800
O -1.92711900 -3.15120000 0.49347800
C -1.23493700 -2.26205800 0.21224000
H -0.00031700 -0.55802600 1.57024300
C 0.00329100 -0.12719000 2.70263600
O -0.00051700 1.10205100 2.72696300
O 0.00946600 -1.03978300 3.52865500

31

5'

Mn -0.00225800 -0.87157300 0.24216200
N -1.30443700 0.72784100 0.22088700
O -3.20461400 -0.41057400 0.85442900

C -2.67993900 0.63059700 0.42136000
C -3.46295700 1.80508200 0.10368600
H -4.54094700 1.71371200 0.22478900
C -2.86784300 2.96636400 -0.31669400
H -3.47761800 3.84360600 -0.54691100
C -1.47236000 3.03841800 -0.43722600
H -0.98337200 3.95941400 -0.73792700
C -0.73627200 1.89136000 -0.14999800
O -1.96319100 -3.07096700 0.07410000
C -1.24382000 -2.16179200 0.12354900
O -0.00216000 -1.09782100 3.15876800
C -0.00215400 -0.99768900 1.99417800
N 1.30842100 0.72090900 0.22040500
O 3.20269500 -0.42739000 0.85382800
C 2.68341400 0.61652200 0.42085200
C 3.47250800 1.78691300 0.10316800
H 4.55002200 1.68990300 0.22411800
C 2.88341100 2.95136700 -0.31691900
H 3.49772700 3.82545600 -0.54705200
C 1.48830900 3.03072500 -0.43722400
H 1.00410100 3.95436700 -0.73754400
C 0.74627400 1.88746400 -0.15013200
O 1.94711200 -3.08116900 0.07305000
C 1.23252200 -2.16826400 0.12289200
H -0.00322400 -0.89576000 -3.74905500
C -0.00437100 -1.38297500 -2.73400200
O -0.00205700 -0.52198300 -1.80019000

O -0.00759400 -2.61599500 -2.68378900

29

TS2-4

Mn 0.04768300 -1.10003600 -0.08313200

N -1.16920900 0.59351300 -0.35041100

O -3.06631000 -0.55023600 -0.94732800

C -2.53849200 0.51193300 -0.58249700

C -3.30126500 1.72475100 -0.36952700

H -4.36680200 1.66316900 -0.57782900

C -2.71753700 2.86894400 0.10292400

H -3.32221900 3.75858300 0.28157300

C -1.33351100 2.90096500 0.35536600

H -0.84204500 3.79610200 0.72544000

C -0.61298400 1.74660300 0.10134500

O -1.80351500 -3.24469100 -0.92420800

C -1.15311300 -2.34997100 -0.58707700

O -0.98711400 -0.96856800 2.66769000

C -0.58025700 -1.00806900 1.58027600

N 1.33607300 0.44701100 -0.06371300

O 2.83887400 -0.82416100 -1.15690100

C 2.59505800 0.27923600 -0.54614900

C 3.52657200 1.33856400 -0.40593800

H 4.55541200 1.17006800 -0.71034500

C 3.07564900 2.56238500 0.04725200

H 3.77482700 3.39184500 0.14613100

C 1.71150700 2.77326300 0.28989300

H 1.32436300 3.76680100 0.49486300
C 0.85557400 1.68619100 0.17395200
O 1.79940200 -3.25570000 0.87080700
C 1.13536300 -2.39582400 0.45276900
H 1.62792400 -1.17048600 -1.44986800
H 0.66233800 -1.24582900 -1.68878100

29

4

Mn -0.12296000 -1.08438000 -0.11607100
N -1.15869200 0.71412900 -0.22407200
O -3.23532900 -0.24183200 -0.46391400
C -2.54914200 0.77965700 -0.31512500
C -3.14418500 2.09517500 -0.22335800
H -4.22694000 2.13564400 -0.31424300
C -2.38820700 3.21603800 -0.01271900
H -2.86369400 4.19394000 0.06810500
C -0.99288500 3.10528700 0.09758200
H -0.37408700 3.98171100 0.26032500
C -0.43786300 1.83681400 -0.02170200
O -2.24551800 -2.91229400 -0.99788000
C -1.49851700 -2.11333100 -0.61444300
O -0.68671000 -1.15271000 2.79903700
C -0.44796900 -1.08598000 1.66191300
N 1.39695400 0.33145700 -0.15911400
O 3.06512000 -1.15462300 -0.68819200
C 2.69883000 0.07799800 -0.35044000

C 3.69418400 1.05169200 -0.23138400
H 4.73030400 0.75995900 -0.37103200
C 3.30158500 2.35139600 0.03699200
H 4.04563600 3.13860300 0.14047100
C 1.94739800 2.64991700 0.13264900
H 1.61636800 3.67118000 0.28736800
C 1.01350600 1.62236800 0.00676700
O 1.19013300 -3.68410000 0.19465100
C 0.71881400 -2.61754200 0.05129300
H 2.23420200 -1.65715800 -0.83816000
H 0.04952500 -1.08592200 -1.70651800

32

TS4-6

Mn 0.22371000 -1.07359600 -0.09935500
N 1.33063300 0.63879000 -0.20031600
O 3.36564300 -0.42165800 -0.24206700
C 2.72317800 0.63812700 -0.18890300
C 3.36708300 1.93136600 -0.11527500
H 4.45351800 1.92241700 -0.07737500
C 2.64672200 3.09394300 -0.10767000
H 3.15690500 4.05594800 -0.05880900
C 1.24329400 3.04957600 -0.17690200
H 0.65465800 3.96059300 -0.20523300
C 0.64416400 1.80174500 -0.22494400
O 2.29384400 -2.75386200 1.15146800
C 1.55746100 -2.03757600 0.62066100

O 0.92527000 -2.00343500 -2.81897200
C 0.64063500 -1.60993900 -1.76328000
N -1.20646300 0.35646700 -0.58473000
O -2.86718100 -1.11730600 -1.17810800
C -2.49086200 0.12347500 -0.87445700
C -3.46298300 1.12677800 -0.88869300
H -4.49137300 0.85695100 -1.10526700
C -3.06187700 2.41885000 -0.60362000
H -3.79257700 3.22443400 -0.57986500
C -1.71790800 2.68764300 -0.36338500
H -1.38167200 3.69740100 -0.15387300
C -0.80485900 1.63827000 -0.38370500
O -1.37641000 -3.39333200 0.72200100
C -0.78314800 -2.46049300 0.34634900
H -2.07711700 -1.68639600 -1.08982400
H -0.09819300 -0.62126100 1.45826500
C -1.00921100 0.23579600 2.46477300
O -2.08664900 -0.27043900 2.40550400
O -0.23404700 1.03973700 2.87835900

32

6

Mn 0.26515200 -0.98592900 -0.19197300
N 1.24957500 0.78494900 -0.18286500
O 3.34156100 -0.13170400 -0.39332300
C 2.63892000 0.87465300 -0.21403300
C 3.20006700 2.19386500 -0.02622300

H 4.28517500 2.25647500 -0.02044200
C 2.40430200 3.29580500 0.12236500
H 2.85152600 4.28045800 0.25740400
C 1.00386700 3.16532600 0.08509400
H 0.35788800 4.03263100 0.16983900
C 0.48282800 1.89436100 -0.07590300
O 2.48439800 -2.60883800 0.88692500
C 1.68446300 -1.91156900 0.43550500
O 1.00343700 -1.63136800 -2.96471400
C 0.70166900 -1.36832100 -1.87540600
N -1.26837400 0.36185400 -0.55273300
O -2.84431000 -1.16156900 -1.25968300
C -2.54155100 0.07025200 -0.84232000
C -3.57672200 1.00043100 -0.75203500
H -4.58898200 0.68128200 -0.97739800
C -3.25354600 2.29269700 -0.37505400
H -4.03487400 3.04338700 -0.27918400
C -1.92842600 2.62992200 -0.13629400
H -1.65399100 3.63812400 0.15354800
C -0.95374800 1.64341100 -0.23313300
O -1.15021700 -3.51634700 0.32089700
C -0.63404400 -2.49744700 0.09727600
H -2.01959200 -1.68121200 -1.25982000
H -0.03056800 -0.57911700 1.46614000
C -0.73963600 -0.34596400 2.50525900
O -0.73528200 -1.32831400 3.22094800
O -1.17389400 0.79364600 2.45742900

32

TS6-7

Mn 0.00209500 -0.99777400 -0.27762600
N 1.44245000 0.37876500 0.06910400
O 3.08993000 -1.13800700 0.56160200
C 2.75882300 0.04148100 0.36749500
C 3.70614300 1.13300400 0.43211100
H 4.73292600 0.86341700 0.66500400
C 3.32178200 2.42539100 0.21432500
H 4.05210100 3.23210200 0.27275600
C 1.97529500 2.72266900 -0.07425800
H 1.64620000 3.74763500 -0.20989000
C 1.08221600 1.66989500 -0.12763500
O 1.60910500 -3.47792500 -0.20957400
C 1.07923500 -2.45260300 -0.19636400
O 0.40334200 -0.83459900 -3.14720400
C 0.23836100 -0.91640000 -1.99844800
N -1.11450200 0.75548400 -0.13094800
O -3.18833700 -0.12306600 0.37238200
C -2.45364700 0.88132800 -0.04262000
C -3.09593500 2.08525400 -0.38664900
H -4.17988200 2.11575400 -0.33946100
C -2.32586400 3.17960600 -0.71732900
H -2.80019800 4.12205300 -0.98410400
C -0.93501300 3.09006300 -0.65418100
H -0.31094600 3.95549500 -0.85066700

C -0.36083100 1.86961600 -0.32928000
O -2.17956100 -2.93262900 -0.74341600
C -1.35839300 -2.14821000 -0.52382100
H -2.67073900 -0.67721600 1.06868200
H 0.29803300 -1.11019400 1.98449300
C -0.68995400 -0.69751600 2.39441200
O -1.71137700 -1.36150100 2.01559800
O -0.61920200 0.29949100 3.10313600

32

7

Mn 0.02107400 -0.92280000 -0.44254000
N 1.25032600 0.64659000 0.12733000
O 3.11988000 -0.62489400 0.49795700
C 2.61272600 0.49864000 0.35882100
C 3.39224400 1.71768500 0.42557600
H 4.45479200 1.59720200 0.62127800
C 2.82219400 2.94506100 0.23269500
H 3.43384600 3.84626300 0.27337000
C 1.43828200 3.04947700 -0.00893300
H 0.96124800 4.01553400 -0.14241600
C 0.70574600 1.87706000 -0.04108100
O 1.97126000 -3.14085000 -0.52438900
C 1.28033900 -2.21754300 -0.47506100
O 0.64286600 -0.12751600 -3.19298900
C 0.39590400 -0.44766600 -2.10231600
N -1.29884100 0.62792000 -0.06389100

O -3.02253900 -0.70260200 0.63927000
C -2.59354700 0.48335900 0.24064800
C -3.48223100 1.56609500 0.16812000
H -4.53526300 1.39622400 0.36943000
C -2.95723800 2.81975400 -0.09277000
H -3.61759000 3.68313900 -0.14625600
C -1.57706600 2.99255400 -0.20489800
H -1.14468700 3.98338400 -0.30191500
C -0.76310000 1.86660200 -0.14710100
O -1.84807100 -2.89595700 -1.57036100
C -1.13448100 -2.11730100 -1.08630200
H -2.23776000 -1.17371200 1.05230800
H 1.21643300 -1.31108100 2.33166200
C 0.12529100 -1.42042100 2.52869700
O -0.60049300 -1.41001000 1.45509100
O -0.30148600 -1.54425200 3.66859500

32

TS7-8

Mn 0.05932000 -1.04209100 -0.30111600
N 1.26610100 0.57679800 0.10577800
O 3.03022800 -0.59884900 0.96825500
C 2.59295200 0.46683600 0.50056100
C 3.41116800 1.64926400 0.34201800
H 4.45470200 1.55692000 0.63259600
C 2.89146600 2.81524900 -0.15003300
H 3.52968200 3.69144000 -0.26530600

C 1.52695000 2.89703800 -0.49135100
H 1.08579500 3.82432000 -0.84430500
C 0.75869500 1.76022900 -0.33333600
O 2.00656100 -3.24858900 0.02835500
C 1.30476400 -2.33708500 -0.07434500
O 0.82258700 -0.72073600 -3.09756700
C 0.52087000 -0.85632200 -1.98327600
N -1.24355600 0.52503600 -0.23733200
O -2.92174400 -0.65857900 0.73023500
C -2.55493700 0.39829800 0.11820400
C -3.42932500 1.48376100 -0.17882200
H -4.48977700 1.35224500 0.01688100
C -2.89883900 2.67734400 -0.61401100
H -3.55892500 3.52166600 -0.80966300
C -1.50909600 2.84432200 -0.72935500
H -1.07527100 3.81620400 -0.94374700
C -0.70721200 1.73957000 -0.49513500
O -1.83345200 -3.11542900 -1.20225000
C -1.11844000 -2.29371600 -0.80451400
H -1.77456400 -1.04148000 1.42615500
H 0.87434300 -0.55145000 2.69222800
C -0.22679000 -0.45425800 2.64941600
O -0.73185800 -1.23483700 1.69678000
O -0.87984400 0.25531900 3.37716600

32

8

Mn 0.04507300 -1.04891800 -0.29198500
N 1.25619800 0.57180600 0.05198700
O 3.02893400 -0.57032400 0.93784800
C 2.58864900 0.47692300 0.42913100
C 3.40372100 1.65033300 0.21070100
H 4.45583200 1.56521700 0.47093700
C 2.86571500 2.80565800 -0.28838000
H 3.49894700 3.67942000 -0.44319600
C 1.48979000 2.88271700 -0.58065300
H 1.03585700 3.80559000 -0.92872100
C 0.72767700 1.74823000 -0.38125000
O 2.04178800 -3.22602200 -0.09050100
C 1.31512200 -2.32890600 -0.14005400
O 0.61081100 -0.77326800 -3.13708500
C 0.38680100 -0.89233300 -2.00280400
N -1.26661400 0.50430000 -0.19667700
O -2.94192400 -0.67302600 0.79590800
C -2.58021100 0.36991000 0.18325300
C -3.45615700 1.46391600 -0.11603200
H -4.51493200 1.32983400 0.08877300
C -2.93724200 2.65447100 -0.56464100
H -3.60224000 3.49657500 -0.75506300
C -1.54864900 2.82108300 -0.71347600
H -1.11945900 3.79032200 -0.94815600
C -0.74341000 1.71838400 -0.48864900
O -1.89064200 -3.15775500 -1.00874600
C -1.16158500 -2.31772100 -0.68362700

H -1.56543500 -1.03838100 1.65955000
H 1.10825100 -0.47239100 2.62278200
C 0.01049200 -0.35661600 2.66408600
O -0.56818800 -1.19971500 1.79166200
O -0.59515700 0.39482600 3.38340400

32

DBUH⁺HCOO⁻

N 1.32556700 0.83307600 -0.53104500
N -0.86230200 0.18969500 0.09816800
C 2.68329500 0.36946100 -0.78204000
C 3.30906300 -0.35189100 0.41253600
C 0.30041800 -0.07397200 -0.39723500
C 2.33709600 -1.32209300 1.07998800
C 1.17437100 2.14455700 0.08490600
C 0.59236300 -1.48169200 -0.83991300
C 1.57252300 -2.22047200 0.10791900
C -0.26928200 2.59099300 -0.02861800
C -1.16489100 1.53035400 0.58346300
H 2.68057100 -0.28912700 -1.65894500
H 3.28139100 1.24382700 -1.06650200
H 3.66089200 0.37931300 1.15420700
H 4.20168200 -0.88909500 0.05984600
H 2.88696700 -1.94963600 1.79272800
H 1.61259500 -0.75547000 1.68583100
H 1.48163900 2.10874800 1.14691300
H 1.85165500 2.84044800 -0.42728200

H 0.98253900 -1.46382200 -1.86528900
H -0.36342200 -2.01161200 -0.88348900
H 1.00236300 -2.94883500 0.69632600
H 2.28806100 -2.80420900 -0.48910300
H -0.52090800 2.72573600 -1.08936200
H -0.41041800 3.55719700 0.46911100
H -2.22506900 1.72272700 0.37701300
H -1.05863500 1.53288400 1.68042300
H -2.10249000 -0.84052100 0.06288600
C -4.03416000 -0.88073800 -0.02085200
O -4.19423200 0.32056400 0.02839500
O -2.88326800 -1.51464300 0.00657300
H -4.87705000 -1.59235100 -0.09583400

22

9

C 2.98028000 1.31118100 -0.21860400
C 3.80601100 0.18197000 -0.04289400
C 3.28265000 -1.07569000 0.17209700
C 1.85908500 -1.25791300 0.22082000
C 1.60985100 1.10099900 -0.16520500
H 3.39036000 2.30387400 -0.38771000
H 4.88928000 0.30702800 -0.07869200
H 3.91824600 -1.94802400 0.30595500
C 0.52589000 2.12342200 -0.31031900
H 0.55296700 2.85349800 0.51320700
H 0.62205500 2.70851600 -1.23624200

C -0.90492600 1.49847200 -0.29057700
O -1.83707900 2.25303900 -0.49479100
N 1.11601000 -0.11974100 0.04164100
O 1.23038000 -2.32753200 0.40400000
C -0.92112200 -0.68028300 -1.72811800
C -0.95978200 0.02697600 1.85352800
C -2.59876300 -0.65923600 0.11071100
O -1.04740800 -0.80029400 -2.87321900
O -3.75667700 -0.81281700 0.12893900
O -1.10817800 0.35636400 2.95494900
Mn -0.84433300 -0.40624700 0.08097300

24

10

C 2.85889100 1.39265400 -0.51312400
C 3.82100700 0.41690000 -0.19905000
C 3.43131100 -0.81161300 0.26909900
C 2.03988700 -1.13771200 0.44142900
C 1.52639100 1.06486200 -0.32726000
H 3.13180200 2.37692600 -0.88583600
H 4.88126700 0.63710000 -0.32987600
H 4.14629400 -1.59210800 0.51744500
C 0.41682500 2.02561300 -0.59901900
H 0.33077500 2.73958100 0.23812300
H 0.58891400 2.62952200 -1.50146900
C -0.95348800 1.33865900 -0.66939700
O -1.86738800 1.94038500 -1.20686200

N 1.12236300 -0.13940600 0.12511000
O 1.65134200 -2.25335300 0.84849200
C -0.87022000 -1.12831900 -1.46638400
C -0.99307800 0.51843300 1.77681700
C -2.69742000 -0.54947200 0.21131900
O -0.86123200 -1.51304500 -2.55740600
O -3.86098900 -0.61159900 0.19428200
O -1.05078700 1.18364000 2.72523200
Mn -0.92946900 -0.42848400 0.22277500
H -1.04462300 -1.94310000 1.02210200
H -0.22245700 -1.90824200 0.91788500

24

TS10-11

C 2.93926100 1.33922900 -0.42251700
C 3.83716700 0.30129100 -0.14560300
C 3.37406400 -0.93352900 0.25871300
C 1.97818100 -1.14797400 0.37892500
C 1.58232900 1.08430300 -0.27662700
H 3.27771100 2.32297000 -0.73807800
H 4.90910400 0.46833700 -0.24839500
H 4.03923100 -1.76266500 0.48246700
C 0.50746000 2.09053000 -0.50509900
H 0.43740100 2.75879100 0.36977200
H 0.70585200 2.73580900 -1.37326700
C -0.89500600 1.43857300 -0.61361900
O -1.77426300 2.11929500 -1.11714200

N 1.12405700 -0.12270900 0.10275800
O 1.48024200 -2.27718300 0.73470300
C -0.93204600 -1.03141700 -1.53036400
C -1.02496900 0.42286900 1.79571500
C -2.66519400 -0.56333700 0.19348900
O -1.00126100 -1.40918300 -2.62570900
O -3.82707600 -0.68388700 0.20908300
O -1.13989500 0.97905900 2.81042900
Mn -0.91338700 -0.38080800 0.17065400
H -0.74498500 -1.91471100 0.85552900
H 0.23250200 -2.05741300 0.77731300

24

11

C 2.93582100 1.37188900 -0.46716900
C 3.84671900 0.35206700 -0.19125100
C 3.39110900 -0.87779900 0.24838300
C 2.00778000 -1.06329700 0.38823500
C 1.57883300 1.12245100 -0.29084800
H 3.26170800 2.35068700 -0.80978400
H 4.91476600 0.52157500 -0.31834800
H 4.05456400 -1.70550700 0.47988500
C 0.50846300 2.11778600 -0.53949500
H 0.35624500 2.72546100 0.36768000
H 0.75680200 2.81295900 -1.35544200
C -0.87553900 1.42812900 -0.76135600
O -1.68388900 2.07163500 -1.41457600

N 1.12771200 -0.08366700 0.11978100
O 1.54290100 -2.23183800 0.78677600
C -0.93033100 -1.31533200 -1.33564900
C -1.07229700 0.44057400 1.81881300
C -2.70106300 -0.38634400 0.12537500
O -0.96704700 -1.98746800 -2.28493300
O -3.86917700 -0.41638100 0.08080300
O -1.18972200 0.88890600 2.88788800
Mn -0.94960700 -0.32031200 0.18027500
H -0.83188900 -1.73014400 1.00616900
H 0.53248800 -2.12113700 0.86660700

27

TS11-12

C 3.64902000 -0.42557400 -0.24110100
C 4.06594200 0.90318400 -0.16203900
C 3.12490300 1.90710100 -0.03949300
C 1.76997300 1.54892400 0.00345500
C 2.28861500 -0.70402900 -0.20782600
H 4.36063100 -1.24266900 -0.32620500
H 5.12558700 1.15025700 -0.19032300
H 3.38540200 2.95797700 0.03892000
C 1.73202500 -2.07856500 -0.25894600
H 1.60322800 -2.39106800 -1.30809800
H 2.39530900 -2.81520600 0.21751300
C 0.29569700 -2.12802100 0.33681900
O -0.05336800 -3.18946800 0.82565200

N 1.35959600 0.27561500 -0.09353600
O 0.87810700 2.51373100 0.16080800
C -0.66595700 -0.02736400 1.82287200
C -0.73719800 -0.75956200 -1.74230000
C -2.21787800 -1.14197300 0.23635400
O -0.73154400 0.18766000 2.96102000
O -3.25315500 -1.65623100 0.37905700
O -0.84378600 -0.99027000 -2.87494000
Mn -0.62939100 -0.40588200 0.04025200
H -1.22393800 1.10384400 -0.41018700
H -0.03132400 2.12975500 0.14448900
C -2.44417800 2.11606200 -0.38808000
O -3.23770100 1.67377200 -1.15710000
O -2.07893800 2.96877700 0.37101000

27

12

C 3.57690000 -0.61112500 -0.04281900
C 4.06550100 0.70445900 -0.07695900
C 3.18837900 1.75965200 -0.10421300
C 1.77388800 1.53753400 -0.09621200
C 2.20509100 -0.79069600 -0.05614300
H 4.23851000 -1.47295400 -0.00423500
H 5.13985200 0.88823800 -0.07242900
H 3.52009200 2.79450100 -0.11535500
C 1.57317300 -2.14316900 -0.02222500
H 1.58279400 -2.59033800 -1.03038400

H 2.11394300 -2.84066200 0.63230700
C 0.09006700 -2.09005900 0.38132800
O -0.42036200 -3.08593400 0.85618200
N 1.32884600 0.23660000 -0.09469500
O 0.96094400 2.50334700 -0.09363200
C -0.70286800 -0.03819000 1.77709200
C -0.63923900 -0.90602400 -1.77744200
C -2.32699800 -0.97235000 0.08600400
O -0.73758000 0.07003800 2.92622500
O -3.39465200 -1.42167700 0.17869100
O -0.63148500 -1.34591400 -2.84978600
Mn -0.66670100 -0.35275000 -0.03619100
H -1.34651600 1.38742800 -0.88886400
H -0.49263400 2.84247000 0.26666500
C -2.07932900 2.13072900 -0.43980900
O -3.25541800 2.08611800 -0.70123900
O -1.48867600 3.02768600 0.30960000

60

2DBUH⁺HCOO⁻

N 4.99102000 0.84735400 0.04069900
N 2.71432500 0.40686700 0.08247300
C 6.33266800 0.39175800 -0.33689400
C 6.72006900 -0.90891900 0.36311100
C 3.91433200 0.18600200 -0.40250400
C 5.58081100 -1.92587500 0.38740700
C 4.86665300 1.76722100 1.17408800

C 4.07966300 -0.86389400 -1.45648600
C 4.85990300 -2.10596700 -0.94802100
C 3.50671200 2.43882400 1.15374600
C 2.42045800 1.38347700 1.12422300
H 6.36885400 0.27370900 -1.42552000
H 7.02990600 1.20014500 -0.09451700
H 7.04630700 -0.70094800 1.39108900
H 7.59201200 -1.32512500 -0.15921300
H 5.97478400 -2.89559500 0.71276300
H 4.84797500 -1.63995800 1.15929800
H 5.01727200 1.21018400 2.11391900
H 5.67347300 2.50374600 1.09403500
H 4.58732200 -0.40641400 -2.31426000
H 3.08244000 -1.15169400 -1.80339400
H 4.15181800 -2.93549100 -0.84850800
H 5.58223000 -2.41096600 -1.71665400
H 3.43164400 3.07994500 0.26596500
H 3.39428900 3.08036000 2.03300500
H 1.42879200 1.79353100 0.90646400
H 2.35316300 0.86314100 2.09034400
H 1.91422700 -0.12417200 -0.34586500
C -0.33826300 -0.40628300 -0.95793700
O -0.53786700 0.58312600 -0.19752900
O 0.74439500 -0.98470300 -1.16718000
H -1.23322100 -0.81006600 -1.50056500
N -5.23538700 0.34381600 0.36685000
N -3.15761000 1.13213700 -0.31139300

C -5.99637500 -0.71315600 1.04348100
C -5.83631200 -2.06991200 0.35842500
C -3.90049300 0.35672100 0.44873200
C -4.40205700 -2.34483100 -0.08849900
C -5.91129900 1.10557000 -0.68705700
C -3.21929800 -0.57179800 1.40442700
C -3.33344100 -2.05568300 0.96495800
C -5.13673700 2.37147800 -0.99465400
C -3.70249500 2.01960300 -1.33247100
H -5.67381000 -0.76227200 2.08893300
H -7.04366300 -0.39552100 1.06262300
H -6.50513600 -2.13409200 -0.51021400
H -6.17165100 -2.84332500 1.06231100
H -4.31968900 -3.39284600 -0.39834700
H -4.18144800 -1.76098500 -0.99756300
H -6.00892300 0.47321900 -1.58506100
H -6.92209100 1.33673700 -0.33457500
H -3.65573800 -0.42048800 2.39862100
H -2.16860300 -0.27394000 1.47353900
H -2.36240700 -2.36919700 0.56390500
H -3.51238900 -2.67478700 1.85363100
H -5.16341600 3.03629800 -0.12177800
H -5.60542300 2.90416200 -1.82740600
H -3.06839900 2.91010400 -1.37886100
H -3.63795400 1.52184300 -2.31089300
H -2.10820500 1.01613800 -0.23842600

1_{iso}

Mn 0.22650300 -1.13400100 0.00001100
N 0.92822700 0.78573200 -0.00018000
O 3.15849000 0.23492000 -0.00010500
C 2.28308200 1.11257700 -0.00017800
C 2.59517300 2.52735500 -0.00011500
H 3.65275400 2.78035700 -0.00000900
C 1.61823700 3.48516400 -0.00021200
H 1.88826300 4.54156400 -0.00022500
C 0.26218900 3.10817600 -0.00028900
H -0.53854600 3.84229200 -0.00039800
C -0.02979800 1.75700000 -0.00022600
O 2.66602600 -2.80917000 0.00093600
C 1.73982400 -2.11062600 0.00049100
O 0.40851200 -1.15461000 -2.99045800
C 0.30156400 -1.14609900 -1.84146400
N -1.41878000 -0.09329300 -0.00020600
O -2.26168400 -2.14158700 0.00003000
C -2.50911000 -0.90476200 -0.00002800
C -3.77115200 -0.22942100 0.00006700
H -4.68676000 -0.81560900 0.00021200
C -3.79169600 1.15420100 0.00003700
H -4.75498600 1.66518900 0.00013300
C -2.61702800 1.93046600 -0.00008600
H -2.65443300 3.01597100 -0.00004300
C -1.41081800 1.23789900 -0.00020000

C 0.30121000 -1.14517500 1.84147800

O 0.40802400 -1.15297000 2.99048700

29

2_{iso}

Mn -0.35487500 -1.15118700 0.00041900

N -0.93009100 0.79458200 -0.00015400

O -3.18200400 0.33761900 -0.00053500

C -2.26955800 1.18050700 -0.00051300

C -2.52777800 2.60097200 -0.00087200

H -3.57378300 2.89718200 -0.00117100

C -1.50876400 3.51456000 -0.00087200

H -1.73030200 4.58218200 -0.00117900

C -0.17326700 3.07964300 -0.00050800

H 0.64792700 3.78860000 -0.00059200

C 0.06547800 1.71407000 -0.00015100

O -2.95265600 -2.56413200 0.00070800

C -1.98608000 -1.92483500 0.00088800

O -0.40508000 -1.09928900 2.99113900

C -0.36963700 -1.12624700 1.83832200

N 1.46089500 -0.20504400 -0.00026500

O 2.65645100 -2.15842900 -0.00111400

C 2.65683100 -0.90730600 -0.00054900

C 3.86316800 -0.12500700 -0.00016900

H 4.80155800 -0.67352400 -0.00030800

C 3.81447700 1.24579900 0.00035300

H 4.73971700 1.82248300 0.00068300

C 2.58088300 1.91491900 0.00045300
H 2.53129800 2.99858900 0.00085200
C 1.42626000 1.14571100 0.00007400
C -0.36973200 -1.12789900 -1.83753500
O -0.40525000 -1.10183000 -2.99036400
H 0.03344300 -2.76901200 0.00133900
H 0.80101700 -2.41443900 0.00062800

29

TS2_{iso}-4_{iso}

Mn -0.34088900 -1.12337200 0.00000700
N -0.92315500 0.83873800 0.00001000
O -3.18024600 0.39971000 0.00005800
C -2.26152300 1.23266400 0.00003300
C -2.50991700 2.65827800 0.00002700
H -3.55460200 2.96001600 0.00004200
C -1.48907100 3.56950100 0.00000300
H -1.70720900 4.63789400 0.00000000
C -0.15475000 3.12784900 -0.00001500
H 0.67273300 3.83037200 -0.00003200
C 0.07029000 1.75977400 -0.00001100
O -2.88732200 -2.60274000 0.00003300
C -1.92341600 -1.95598000 0.00002400
O -0.46074300 -1.26837800 2.98130800
C -0.38923700 -1.18830500 1.82950900
N 1.44376400 -0.15872800 -0.00001600
O 2.53414900 -2.14559100 -0.00001600

C 2.60714700 -0.86855700 -0.00002500
C 3.83546000 -0.15722000 -0.00004400
H 4.75852500 -0.72969600 -0.00005100
C 3.81846000 1.22217900 -0.00005500
H 4.75871200 1.77266500 -0.00007000
C 2.60817400 1.92354800 -0.00004600
H 2.58879100 3.00860400 -0.00005400
C 1.42798000 1.18803500 -0.00002500
C -0.38927300 -1.18831300 -1.82949400
O -0.46080100 -1.26839100 -2.98129100
H 0.29642700 -2.64612100 0.00000300
H 1.20232800 -2.36710500 -0.00000200

29

4_{iso}

Mn -0.39578100 -1.09451700 0.00005900
N -0.94638900 0.89194500 0.00002000
O -3.21423700 0.49585300 -0.00005300
C -2.28001600 1.30988600 -0.00001700
C -2.51099200 2.73890000 0.00001000
H -3.55237200 3.05227500 -0.00001700
C -1.48087400 3.64011400 0.00006900
H -1.68557400 4.71121100 0.00008700
C -0.15431500 3.18034400 0.00010400
H 0.67896400 3.87572700 0.00014300
C 0.04870100 1.80503400 0.00008100
O -2.98485900 -2.47852700 0.00000700

C -2.00261000 -1.85720800 0.00001800
O -0.32056300 -1.69581500 2.90952000
C -0.35049900 -1.37820700 1.79141800
N 1.43454500 -0.12346700 -0.00000400
O 2.62270900 -2.07907700 -0.00062100
C 2.61784400 -0.75568600 -0.00019800
C 3.83593800 -0.06650800 -0.00019600
H 4.76045400 -0.63529500 -0.00039000
C 3.79926100 1.31742300 0.00000000
H 4.72713100 1.88635000 -0.00000800
C 2.57627600 1.98006600 0.00010800
H 2.53468300 3.06402800 0.00018800
C 1.40070500 1.22962500 0.00008100
C -0.35038600 -1.37835600 -1.79127300
O -0.32035400 -1.69609700 -2.90933500
H 0.20150900 -2.56986300 0.00026800
H 1.65690500 -2.36412000 0.00076700

35

1_{OMe}

Mn 0.00001300 -0.90649800 -0.29618400
N -1.29657300 0.64661800 -0.02294600
O -3.06255500 -0.67077000 0.38010300
C -2.62949700 0.55774700 0.14561600
C -3.46222100 1.68309700 0.08432300
H -4.53414300 1.58530000 0.21456900
C -2.88274700 2.91842000 -0.13380000

H -3.50648000 3.80646200 -0.18985900
C -1.49850300 3.02764300 -0.25415300
H -1.03556600 3.99825200 -0.39245800
C -0.73550100 1.87492100 -0.17381300
O -1.98871200 -2.90098100 -1.20029500
C -1.24339300 -2.10598600 -0.83396300
O -0.00073700 -2.04972900 2.38430200
C -0.00036600 -1.62162200 1.31613200
N 1.29668800 0.64654900 -0.02289400
O 3.06261200 -0.67091200 0.38015100
C 2.62961300 0.55761700 0.14563400
C 3.46239700 1.68292000 0.08427000
H 4.53431700 1.58506900 0.21450100
C 2.88298600 2.91826100 -0.13391300
H 3.50676600 3.80626500 -0.19004000
C 1.49874500 3.02755100 -0.25425100
H 1.03585800 3.99817500 -0.39262400
C 0.73568000 1.87487700 -0.17382500
O 1.98868400 -2.90132300 -1.19971300
C 1.24338500 -2.10626400 -0.83348400
C -4.46359100 -0.93396900 0.46942400
H -4.97760000 -0.61212300 -0.44293500
H -4.54945700 -2.01584600 0.57329500
H -4.89288000 -0.44461100 1.35046100
C 4.46362800 -0.93416800 0.46959700
H 4.54943100 -2.01604200 0.57355100
H 4.97772300 -0.61241300 -0.44274600

H 4.89287300 -0.44476200 1.35063000

37

2_{OMe}

Mn -0.00001100 -0.96144800 -0.31595400

N -1.31072800 0.64884100 -0.09507200

O -3.10661900 -0.66833100 0.15466400

C -2.64692000 0.56959400 0.03221700

C -3.46680100 1.70497700 0.03669300

H -4.54210100 1.60913500 0.13690200

C -2.87137000 2.94608000 -0.08349000

H -3.48319100 3.84400100 -0.08913700

C -1.48647200 3.04135500 -0.17657500

H -1.01039700 4.01276900 -0.24393700

C -0.73519500 1.87474700 -0.16364500

O -1.95084300 -3.14371200 -0.73856800

C -1.23078000 -2.26280900 -0.57328900

O -0.00113800 -1.45980700 2.59787700

C -0.00064300 -1.27595200 1.46624700

N 1.31094500 0.64868300 -0.09504900

O 3.10679300 -0.66861100 0.15451500

C 2.64713900 0.56934600 0.03212500

C 3.46712800 1.70465300 0.03653100

H 4.54242500 1.60870700 0.13667500

C 2.87181400 2.94580600 -0.08368500

H 3.48371900 3.84366900 -0.08942000

C 1.48692200 3.04119500 -0.17672600

H 1.01093000 4.01264500 -0.24414800
C 0.73554500 1.87465300 -0.16368400
O 1.95046500 -3.14444200 -0.73667500
C 1.23055300 -2.26325300 -0.57228600
H -0.40229400 -0.58059900 -1.97519800
H 0.40363900 -0.58357100 -1.97553800
C -4.50957400 -0.91308100 0.24027300
H -5.02705700 -0.52540300 -0.64429700
H -4.61133100 -1.99842500 0.27541300
H -4.92440800 -0.47443500 1.15452900
C 4.50971400 -0.91339500 0.24044900
H 4.92440400 -0.47457200 1.15468600
H 4.61142400 -1.99873600 0.27584300
H 5.02738300 -0.52593500 -0.64411000

64

TS₂_{OMe}-3_{OMe}

Mn 1.64716000 0.82627600 -0.65039000
N 2.07695600 -0.79705800 0.59484100
O 3.89911300 -1.38643100 -0.57044300
C 3.06525900 -1.69043400 0.41605200
C 3.19671700 -2.83403100 1.21293300
H 4.00229100 -3.53877800 1.03977100
C 2.28537100 -3.03170400 2.23429700
H 2.36525300 -3.90843900 2.87138800
C 1.28385700 -2.09363600 2.45381900
H 0.58018600 -2.22644300 3.26796800

C 1.21231000 -0.98501900 1.61915000
O 3.44540100 0.22265600 -2.90905000
C 2.75978500 0.41908800 -2.00373900
O 3.68900100 2.58189600 0.55742800
C 2.89299600 1.89509300 0.09008500
N 0.35255500 1.13465900 0.95839400
O -0.17812300 3.21258000 0.30546700
C -0.41060800 2.22116800 1.15949300
C -1.36119200 2.29286400 2.18455300
H -1.95922200 3.18730800 2.32222700
C -1.50822500 1.20091700 3.02140100
H -2.24328100 1.22475600 3.82179900
C -0.69429800 0.08834300 2.84891900
H -0.77979200 -0.76014500 3.51840500
C 0.23682000 0.09699900 1.81779800
O 0.69279800 2.97509800 -2.42788600
C 1.05020600 2.15557300 -1.69931200
H 0.65468900 -0.21388800 -1.55818500
H 0.02363600 -0.32843900 -1.00403500
C 4.96633900 -2.26530600 -0.90917100
H 4.58563200 -3.25578200 -1.18415900
H 5.45221600 -1.81006400 -1.77320300
H 5.68294200 -2.34488500 -0.08362500
C -0.95997400 4.40030700 0.35021000
H -0.80048900 4.93910500 1.29133700
H -0.60938200 5.00918500 -0.48425100
H -2.02483300 4.17462900 0.21359900

N -3.53178300 -1.66742600 -1.23242400
N -1.33492900 -1.15970600 -0.52609900
C -4.88564200 -1.16201900 -1.44415300
C -5.52308000 -0.63472700 -0.16097500
C -2.50452200 -0.80874300 -0.97203500
C -4.56608500 0.26021000 0.62406800
C -3.39078900 -3.07184400 -0.86526300
C -2.76779800 0.65433900 -1.21177600
C -3.81971200 1.26827300 -0.24945300
C -1.95339200 -3.50319500 -1.06844900
C -1.05097400 -2.56716600 -0.28546000
H -4.85866000 -0.37733800 -2.20964100
H -5.47852000 -1.97774600 -1.87282100
H -5.85236900 -1.47058300 0.47139900
H -6.42948100 -0.07582200 -0.43243400
H -5.12548700 0.79653800 1.40099700
H -3.83248400 -0.36325500 1.16250500
H -3.69624500 -3.22274300 0.18596600
H -4.07466400 -3.65737200 -1.49110000
H -3.07312300 0.79321800 -2.25687000
H -1.80735600 1.17158300 -1.10386800
H -3.31167000 1.98106400 0.41312300
H -4.54686300 1.85622600 -0.82692600
H -1.70915100 -3.45213200 -2.13793800
H -1.81634900 -4.54165000 -0.74759000
H 0.00666500 -2.74910500 -0.53516900
H -1.14843800 -2.76769700 0.79601800

36

3_{OMe}

Mn 0.00009900 -0.96205300 -0.22310100

N -1.29326800 0.64498800 -0.01158300

O -3.08553800 -0.66098000 0.32741600

C -2.62890900 0.57266600 0.11724100

C -3.45764700 1.69570500 0.04696700

H -4.53324500 1.59666800 0.14391400

C -2.87102100 2.93902000 -0.13577300

H -3.49045300 3.82994100 -0.19849500

C -1.49044300 3.03512700 -0.21524000

H -1.01305200 4.00183300 -0.33233900

C -0.73217400 1.86844600 -0.13558100

O -1.97197300 -2.91070700 -1.17198400

C -1.21309600 -2.13096900 -0.76292300

O -0.00241100 -1.96540100 2.57628600

C -0.00131100 -1.52182300 1.50338900

N 1.29349600 0.64489700 -0.01118300

O 3.08568600 -0.66099000 0.32854500

C 2.62916600 0.57253000 0.11741000

C 3.45803200 1.69539700 0.04596300

H 4.53365800 1.59627500 0.14252200

C 2.87151600 2.93865100 -0.13754400

H 3.49105300 3.82942900 -0.20125700

C 1.49092000 3.03488500 -0.21652900

H 1.01361300 4.00155600 -0.33426600

C 0.73252900 1.86836400 -0.13576400
O 1.97251800 -2.91212500 -1.16842000
C 1.21350000 -2.13172600 -0.76086800
C -4.47602100 -0.91377200 0.28964900
H -4.91520900 -0.56412700 -0.65346500
H -4.57845300 -1.99837500 0.35315300
H -4.98949700 -0.44612400 1.14009600
C 4.47612600 -0.91399100 0.29079000
H 4.98984600 -0.44540500 1.14057300
H 4.57841900 -1.99853300 0.35553600
H 4.91515700 -0.56553200 -0.65283600
H 0.00081500 -0.58490300 -1.76812600

70

$\text{Mn}_2(\text{DMBP})_2(\text{CO})_6$

Mn 0.40172700 0.95462700 -1.47847300
N -1.18813100 -0.34740100 -1.63915200
O -2.69858600 1.30691900 -1.77012900
C -2.48390300 -0.00428500 -1.81787200
C -3.49552700 -0.93456800 -2.04470500
H -4.51759900 -0.60506100 -2.19994400
C -3.16071600 -2.28589100 -2.10302700
H -3.92889200 -3.03204300 -2.29036700
C -1.84696100 -2.66139300 -1.91348100
H -1.56627700 -3.70837600 -1.94953400
C -0.88066900 -1.67302800 -1.68650900
O -0.95501700 3.56241000 -1.46661600

C -0.48822700 2.50006100 -1.43085400
O 0.86219300 1.31528000 -4.34280600
C 0.67421000 1.15426300 -3.20603300
N 1.33296200 -0.87826600 -1.39722600
O 3.39981800 0.01318500 -1.27301000
C 2.66923600 -1.10353300 -1.36967100
C 3.23987000 -2.36629800 -1.44196900
H 4.31638700 -2.48845700 -1.39744200
C 2.39953900 -3.47538700 -1.54456600
H 2.81863400 -4.47718900 -1.59312100
C 1.03712600 -3.27723000 -1.60200300
H 0.36316400 -4.12120200 -1.70383600
C 0.53005700 -1.97170000 -1.53713500
O 2.69126900 2.72349200 -0.95649000
C 1.81426600 1.97781700 -1.11909600
C -4.00693500 1.82759300 -1.86725600
H -4.64456300 1.44354000 -1.05931800
H -3.89943200 2.90804800 -1.75319200
H -4.45389900 1.59901300 -2.84390200
C 4.80308500 -0.05323300 -1.39323100
H 5.09962700 -0.52215200 -2.34072100
H 5.14848300 0.98376200 -1.38064000
H 5.25140400 -0.60350600 -0.55243900
Mn -0.40170500 0.95510100 1.47814800
N 1.18809900 -0.34694700 1.63916400
O 2.69850600 1.30739800 1.76967700
C 2.48385700 -0.00379900 1.81783300

C 3.49546000 -0.93403000 2.04500200
H 4.51752700 -0.60449300 2.20020300
C 3.16060800 -2.28532500 2.10374500
H 3.92875400 -3.03144200 2.29134400
C 1.84685100 -2.66086000 1.91424400
H 1.56615100 -3.70782800 1.95058600
C 0.88059100 -1.67254600 1.68691800
O 0.95543200 3.56268600 1.46589100
C 0.48833900 2.50047100 1.43017100
O -0.86184100 1.31613200 4.34248800
C -0.67403900 1.15501400 3.20570100
N -1.33301300 -0.87778000 1.39741100
O -3.39981000 0.01377300 1.27310400
C -2.66929900 -1.10297700 1.36997900
C -3.23998600 -2.36570400 1.44259600
H -4.31650900 -2.48783100 1.39815200
C -2.39970200 -3.47480500 1.54541800
H -2.81884100 -4.47657700 1.59420800
C -1.03727600 -3.27669900 1.60278200
H -0.36335100 -4.12067800 1.70479200
C -0.53015100 -1.97121000 1.53758500
O -2.69124900 2.72385400 0.95579000
C -1.81420600 1.97827400 1.11861500
C 4.00681600 1.82819600 1.86658000
H 4.64449100 1.44380000 1.05883200
H 3.89923800 2.90858800 1.75199700
H 4.45380800 1.60010000 2.84332700

C -4.80307000 -0.05250600 1.39352700
H -5.09952600 -0.52106600 2.34122100
H -5.14838700 0.98451000 1.38061100
H -5.25153600 -0.60304000 0.55298700

54

$\text{Mn}_2(\text{BP})_2(\text{CO})_6$

Mn -0.97977400 1.03264600 -1.12379400
N -2.46394900 0.18643200 -0.03906600
C -3.41465700 0.84897600 0.65639800
C -4.44859900 0.21581300 1.31569900
H -5.17040000 0.80986100 1.86776500
C -4.54173400 -1.17814000 1.25412700
H -5.34730200 -1.70670100 1.75674500
C -3.58785000 -1.86986600 0.53354900
H -3.63162500 -2.95343300 0.46386900
C -2.55389500 -1.17025600 -0.10057000
O -1.63850700 3.78893900 -0.32813800
C -1.35407500 2.70539000 -0.63150500
O -2.52109700 1.36244800 -3.59085700
C -1.92438500 1.21744800 -2.60528700
N -0.60118900 -0.92606800 -1.40956000
C 0.40014200 -1.43671500 -2.15547100
C 0.54019400 -2.78701000 -2.41791900
H 1.37283100 -3.12502900 -3.02896100
C -0.39578100 -3.68118700 -1.89536200
H -0.32175500 -4.74803700 -2.08893700

C -1.42497900 -3.17478100 -1.12131600
H -2.16808800 -3.84323500 -0.69503800
C -1.50875200 -1.80004100 -0.88670600
O 1.42678400 1.95531700 -2.53459600
C 0.49341900 1.59939500 -1.93412800
Mn 0.98156700 1.03282300 1.12281900
N 2.46442600 0.18294900 0.03919000
C 3.41657300 0.84315000 -0.65653700
C 4.44932800 0.20749800 -1.31529900
H 5.17240600 0.79975700 -1.86761500
C 4.53965000 -1.18659900 -1.25285100
H 5.34418300 -1.71710300 -1.75508000
C 3.58436400 -1.87594300 -0.53185400
H 3.62598800 -2.95954900 -0.46146200
C 2.55174500 -1.17386900 0.10172600
O 1.64676400 3.78683200 0.32454100
C 1.35943000 2.70433000 0.62889800
O 2.52303600 1.36236700 3.58981700
C 1.92629900 1.21737400 2.60426200
N 0.59932900 -0.92496600 1.41031600
C -0.40297300 -1.43318700 2.15656000
C -0.54550800 -2.78300600 2.42012700
H -1.37883600 -3.11897800 3.03135500
C 0.38890700 -3.67932700 1.89844600
H 0.31292000 -4.74587600 2.09291500
C 1.41908300 -3.17542700 1.12407200
H 2.16101400 -3.84558900 0.69843400