Supporting Information for

A Mn Bipyrimidine Catalyst Predicted to Reduce CO2 at Lower Overpotential

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Computational Methods

Density functional theory (DFT) calculations for geometry optimizations, electronic energy, solvation energy, and vibrational frequencies were performed using the (U)B3LYP hybrid exchange-correlation functional[1] with the D3 dispersion correction,[2] as implemented in the Jaguar software version 7.9.[3] Solvation effects were modeled using the Poisson-Boltzmann continuum (PBF) approximation[4] for acetonitrile ($\varepsilon = 37.5$, $r = 2.18$).

Geometry optimizations were performed in the gas phase (for CO_2, water, CO, and the TFEH complexes of **2a** and **2b**) or acetonitrile (all other species, including transition states) using 6-311G**++ basis sets[5] for C, H, N and O, the LACV3P++ basis set and effective core

potential[6] (ECP) augmented with two *f*-functions[7] for Mn. Default van der Waals' radii were used during optimization on all atoms, except TFEH, TFE^-, the TFE^-/TFE homoconjugate, $F_3CCH_2OCO_2^-$, **2a**, and **2b**, which were optimized with non-standard van der Waals' radii on anionic O atoms (2.0 or 2.2 Å) and protic H atoms (0.75 Å). These radii were chosen because they correctly predicted pK_a's for various neutral organic oxy-acids (e.g., phenol) and ΔG_{solv}'s for their conjugate bases (e.g., phenoxide; vide infra). Finally, single-point energy calculations with the aforementioned non-standard van der Waals' radii were performed. Vibrational frequencies were obtained with the same basis sets but without *f*-functions (LACV3P++ for Mn). No optimized ground-state structure had any imaginary frequency. Most optimized transition state structures had one imaginary frequency; a few had an additional weak (between 30*i* and 0 cm^{-1}) imaginary frequency arising from the rotation of loosely-bound solvent molecules. For example, the TS for dehydroxylation of **3a** to **4a** containing two TFEH molecules had two imaginary frequencies, one at 496*i* cm^{-1} associated with the reaction coordinate and another at 17*i* cm^{-1} arising from the rotation of a loosely associated TFEH molecule.

Thermodynamic parameters were calculated using the harmonic oscillator, ideal gas and rigid rotor approximations;[8] in computing vibrational entropies, all vibrations < 50 cm^{-1} not associated with the reaction coordinate of a transition state were replaced with 50 cm^{-1} to avoid spurious fluctuations in entropy arising from low frequency modes. Standard reduction potentials are reported versus the standard calomel electrode (SCE), taking its absolute potential to be -4.422 V.[9] Potentials vs SCE can be converted to values vs SHE by adding 0.24 V.

Calculation of pK_as for Neutral Organic Acids and ΔG_{solv}s for their Conjugate Bases

Since proton transfer is an integral part of the catalytic cycles, computational methods were benchmarked against experimentally determined pK_a values for neutral organic oxyacids, including TFE, and ΔG_{solv}s of their anionic conjugate bases. For the calculation of pK_as, the free energy of H^+ at 1 M in MeCN (G = -264.6 kcal/mol) was taken to be its gas-phase value ($G(H^+$, 1atm) = H – TS = 2.5 k_BT – T * 26.04 = -6.3 kcal/mol) plus the empirical solvation energy in acetonitrile ($\Delta G(1atm \rightarrow 1M,MeCN) = -260.2 + k_BTln(24.5)$). [10]

The default van der Waals' radii in Jaguar 7.9 gave rather unsatisfactory agreement with experimental results (Figure S1, Table S1)-- pK_as were underestimated by 12.5±0.9 units and ΔG_{solv}s were overestimated (too exergonic). Increasing the van der Waals' radii on anionic oxygen atoms decreased ΔG_{solv}s—a radius of 2.0 Å gave excellent agreement with experimental values for phenoxide, and satisfactory agreement for acetate (Figure S2, Table S2). Decreasing the van der Waals' radius on protic hydrogen atoms increased pK_as by increasing the exergonicity of solvation for the acid—a radius of 0.75 Å gave satisfactory to excellent values for phenol, acetic acid and TFE (Figure S3, Table S3).

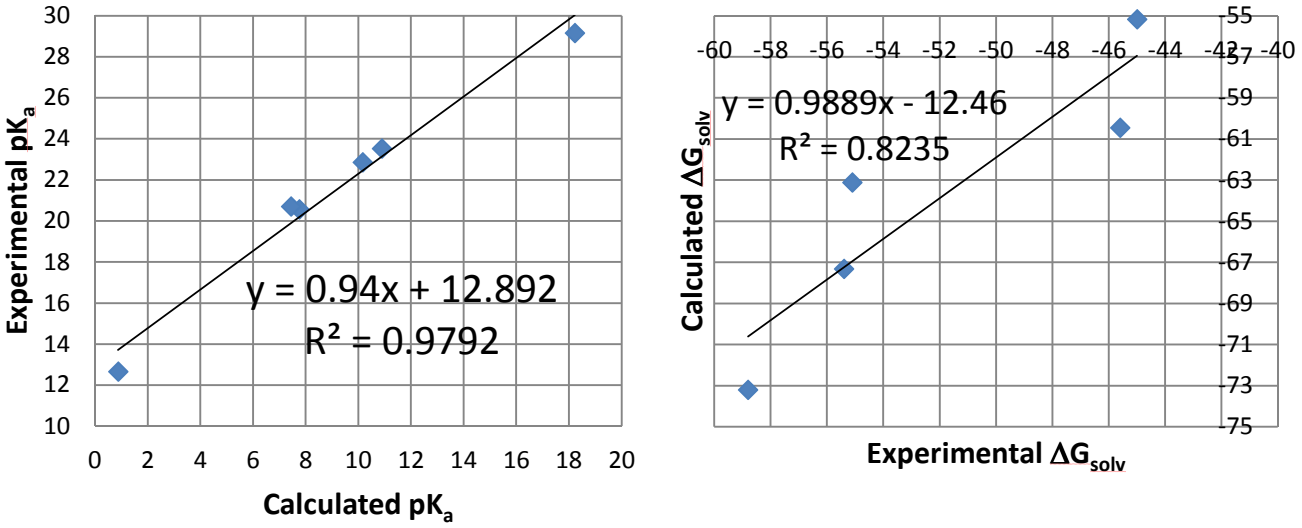


Figure S1: Calculations using default van der Waals' radii in Jaguar 7.9 underestimate pK_as and overestimate the exergonicity of anion solvation in acetonitrile.

Table S1: Calculations using default van der Waals' radii in Jaguar 7.9 underestimate pK_as and overestimate the exergonicity of anion solvation in acetonitrile.

pK_a			**ΔG_{solv}**		
Acid	**Calculated**	**Experimental[11]**	**Anion**	**Calculated**	**Experimental[12]**
Phenol	18.2	29.4	Phenoxide	-63.1	-55.1
Acetic acid	10.9	23.5	Acetate	-73.2	-58.8, -62.7[13]
4-nitrophenol	10.2	22.9	4-nitrophenoxide	-55.2	-45
Benzoic acid	7.4	20.7	Benzoate	-67.3	-55.4
$(F_3C)_3COH$	7.8	20.6	$(F_3C)_3CO^-$	-50.8	Not available
Trifluoroacetic acid	0.9	12.7	Trifluoroacetate	-60.5	-45.6

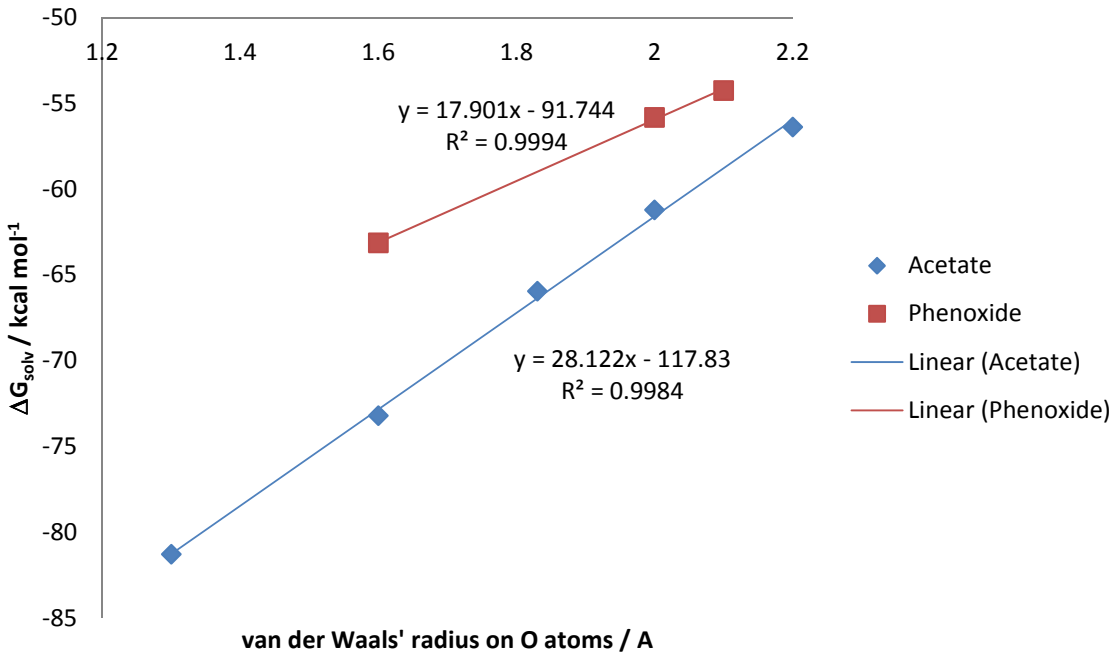


Figure S2: Increasing the van der Waals' radii on oxygen atoms decreased the calculated exergonicity of solvation in acetonitrile.

Table S2: Increasing the van der Waals' radii on oxygen atoms decreased the calculated exergonicity of solvation in acetonitrile.

	Acetate		**Phenoxide**	
	ΔG_{solv} / kcal mol^{-1}			
van der Waals' radius on O / Å	**Calculated**	**Experimental**	**Calculated**	**Experimental**
1.3	-81.3	-56.9, [11] -62.7[12]	N/A	-55.1[11]
1.6	-73.2		-63.1	
1.83	-65.9		N/A	
2	-61.2		-55.8	
2.1	N/A		-54.3	
2.2	-56.4		N/A	

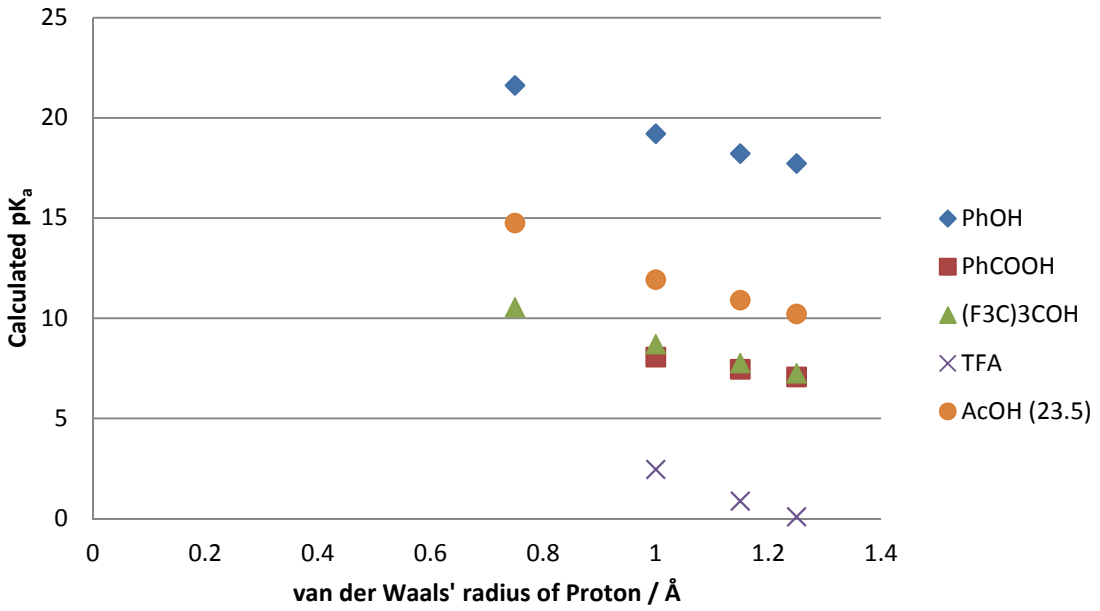


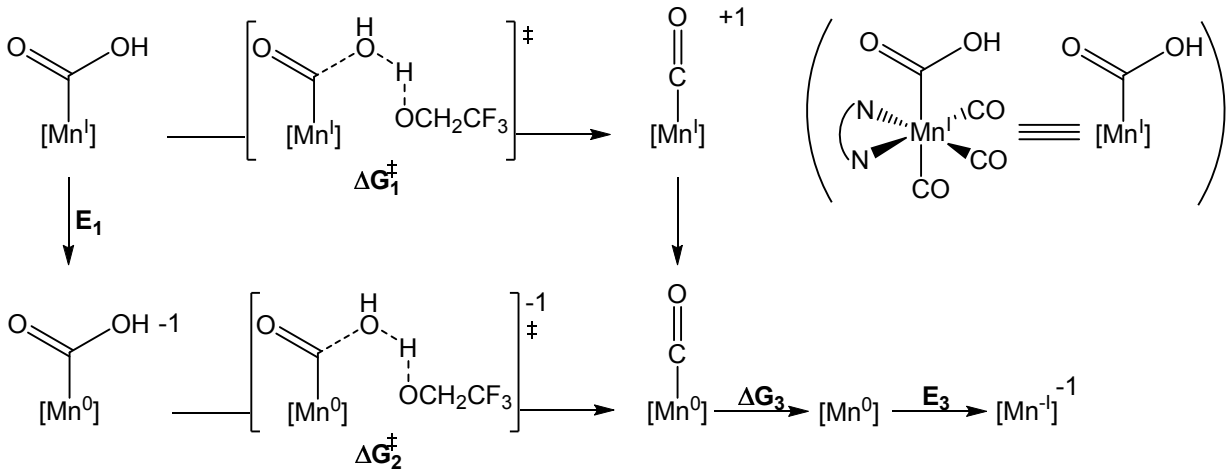
Figure S3: Decreasing the van der Waals' radius of the protic hydrogen increases calculated pK_a. Calculations were performed in acetonitrile with standard van der Waals' radii on all other atoms.

Table S3: pK_as calculated in acetonitrile with different van der Waals' radii on oxygen atoms and protons.

		Van der Waals' radius of Proton / Å				
Acid	**Van der Waals' radius of O / Å**	**1.25**	**1.15 (default)**	**1.0**	**0.75**	**Experimental pK_a**[11]
Acetic Acid	1.3	4.3	5.0	6.0	8.8	23.5
	1.6	10.2	10.9	11.9	14.8	
	2.0	19.0	19.7	20.7	23.5	
	2.2	22.6	23.2	24.3	27.1	
Phenol	1.6	17.7	18.2	19.2	21.6	29.1
	2.0	23.1	23.6	24.6	27.0	
	2.1	24.2	24.7	25.7	28.1	
TFE	1.6	N/A	22.1	N/A	26.2	35.4[14]
	2.0	N/A	29.2	N/A	33.3	
	2.2	N/A	31.7	N/A	35.8	

Comparison of computational methods

Table S4: Key thermodynamic values calculated with a variety of methods regarding solvation, basis set and functional



Geometry		Energy		$\Delta G^{\ddagger}_1$	$\Delta G^{\ddagger}_2$	ΔG_3	E_1	E_2
Functional	**Basis/solvation**	**Functional**	**Basis/solvation**	**kcal/mol**			**(V vs SCE)**	
B3LYP-d3	6-31G** vacuum	B3LYP-d3	6-311G**++ MeCN	19.4	15.4	-2.0	-1.58	-1.20
		B3LYP-d3	6-311G**++ MeCN (alt. radii)	26.7	24.1		-1.58	
		B3LYP-d3	6-311G**++(+2f) MeCN			-2.0	-1.57	-1.19
		M06	6-311G**++ MeCN	25.6	21.5	-1.9	-1.50	-1.08
B3LYP-d3	6-311G**++ MeCN	B3LYP-d3	6-311G**++ MeCN			-2.5	-1.59	-1.21
B3LYP-d3	6-311G**++ MeCN (alt. radii)	B3LYP-d3	6-311G**++ MeCN (alt. radii)	27.8	26.8		-1.54	
B3LYP-d3	6-311G**++(+2f) MeCN	B3LYP-d3	6-311G**++(+2f) MeCN			-2.5	-1.58	-1.20
M06	6-311G**++ MeCN	M06	6-311G**++ MeCN			-2.8	-1.50	-1.09

Cartesian coordinates (in Å) for optimized structures of species discussed in the text

CO_2

C	0.0000000000	0.0000000000	0.0000000000
O	0.0000000000	0.0000000000	1.1611091236
O	0.0000000000	0.0000000000	-1.1611091236

CO

C	0.0000000000	0.0000000000	0.6443005121
O	0.0000000000	0.0000000000	-0.4833790194

TFE

O	0.15551597	2.0342135324	0.0000000000
C	0.93278282	0.8469239510	0.0000000000
C	-0.00654804	-0.3451943424	0.0000000000
F	-0.81477911	-0.3806472090	1.0850575988
F	-0.81477911	-0.3806472090	-1.0850575988
F	0.70815521	-1.4967544041	0.0000000000
H	1.56029966	0.7540145054	0.8936374264
H	1.56029966	0.7540145054	-0.8936374264
H	0.75200128	2.7997573239	0.0000000000

TFE^-

O	0.20376031	2.1280314461	0.0000000000
C	0.88181018	0.9381760810	0.0000000000
C	-0.00300825	-0.3145609790	0.0000000000
F	-0.81771586	-0.4037617888	1.0884259988
F	-0.81771586	-0.4037617888	-1.0884259988
F	0.74561570	-1.4593420781	0.0000000000
H	1.53812989	0.7668817364	0.8818140461
H	1.53812989	0.7668817364	-0.8818140461

B, i.e., homoconjugate of TFE and TFE^-

O	-2.044092708	2.3706356443	-1.5992894256
C	-1.215435634	3.4632634181	-1.3172400466
H	-0.790317615	3.9290636381	-2.2123496255
H	-1.768069660	4.2336460431	-0.7668742321
C	-0.031822681	3.0871045355	-0.4355218213
F	-0.413394990	2.6230400425	0.7831027604
F	0.756626039	2.1325197622	-0.9770057600
F	0.761526295	4.1704899844	-0.2070505003
O	-1.295831713	1.0135935125	-3.5926631293
H	-1.676227373	1.8167742858	-2.4155212250
C	-1.056952571	1.8354930126	-4.6706855399
H	-1.272229390	1.3691048627	-5.6498055780
H	-1.630895871	2.7835782650	-4.6559231483
C	0.398126944	2.2930980803	-4.7998625914
F	0.825900075	3.0464308057	-3.7523425373
F	1.276238619	1.2633766678	-4.9069952685
F	0.578780493	3.0670315396	-5.9142717688

$ROCO_2^-$, R= F_3CCH_2

O	-0.08167804	0.9347311084	0.0000000000
C	0.62403242	-0.2977216735	0.0000000000
C	-0.41535896	-1.4000495269	0.0000000000
F	-1.22259070	-1.3630693007	1.0855738052
F	-1.22259070	-1.3630693007	-1.0855738052
F	0.19194249	-2.6134445982	0.0000000000
H	1.24471643	-0.4246386497	0.8922036682
H	1.24471643	-0.4246386497	-0.8922036682
C	0.69558987	2.1234099624	0.0000000000
O	-0.011914954	3.1504953864	0.0000000000
O	1.934669951	1.9911930827	0.0000000000

$TS_{B\rightarrow[F_3CCH_2OCO_2]^-}$

O	-1.3119433429	2.0168360530	-1.5026138450
C	-0.5204843688	3.1387289695	-1.3710445987
H	0.4851956342	3.0313490664	-1.8089918553
H	-0.9650242443	4.0462225666	-1.8181845947
C	-0.2861949148	3.5040141204	0.0875062011
F	-1.4386266377	3.7478461156	0.7632257504
F	0.3633835095	2.5336790413	0.7830504528
F	0.4739920269	4.6326747264	0.2044335707
O	-1.5210035312	1.0952566370	-3.8912075472
H	-1.3905019118	1.4431055515	-2.9372698138
C	-1.2576024407	2.1433117391	-4.7846952082
H	-1.8394718941	2.0217729241	-5.7042795521
H	-1.4846080998	3.1319613541	-4.3666260863
C	0.2073976737	2.1697900482	-5.1962832883
F	1.0413849896	2.3550514137	-4.1424955175
F	0.6005231601	1.0216683210	-5.7989944539
F	0.4519424121	3.1789480305	-6.0726883113
C	-3.4451466080	2.5297220297	-1.5239822284
O	-3.4004702551	3.6591153042	-1.8445747788
O	-3.8771161933	1.4811785937	-1.2180005122

1a $[(bpy)Mn(CO)_3]^-$			
Mn	0.0429656104	1.6719999167	1.6534183620
C	2.7118959135	0.6514890637	1.1017961628
C	2.7544955039	2.9793244706	1.4096980549
C	4.1136597280	3.0315415675	1.2335819218
C	4.8241059497	1.8311037854	0.9710041048
C	4.1149867183	0.6549704807	0.9138211477
C	-0.3115996109	-1.3072289927	1.3082542014
N	0.5400204958	-0.2366388796	1.2881649516
C	1.8837959661	-0.5067696051	1.0735526016
C	2.3383075516	-1.8298014683	0.8555632683
C	1.4531101512	-2.8814559831	0.8607075879
C	0.0820005801	-2.6047889980	1.1007879766
N	2.0161928362	1.8292113218	1.3382980275
H	2.1943600844	3.8802874750	1.6234066801
H	4.6235347504	3.9859820123	1.2981096221
H	5.8985111445	1.8407868249	0.8249907962
H	4.6289390770	-0.2803552658	0.7244803024
H	-1.3494237182	-1.0735284260	1.5069872490
H	3.3939124203	-2.0091545446	0.6865774670
H	1.7947525111	-3.8967038345	0.6926543484
H	-0.6575287824	-3.3970831062	1.1255141811
C	-0.1691219539	1.7489698405	3.4015507750
O	-0.3728595282	1.8433728933	4.5529688974
O	-0.4761673397	4.5285586452	1.1102262472
C	-0.2533495904	3.3973495301	1.3225020926
O	-2.7990228128	1.2710409462	0.9552293254
C	-1.6671574872	1.4146584652	1.2270874327

1b $[(bpymd)Mn(CO)_3]^-$			
Mn	0.0309058255	1.6784487527	1.6367640675
C	2.7068930024	0.6465546914	1.1109823771
C	2.7573724848	2.9650551200	1.3752505724
C	4.1180897457	2.9588838870	1.1985040129
C	4.7403463371	1.7037017886	0.9754970347
N	4.0571525784	0.5780779619	0.9391990049
C	-0.2981428333	-1.3062962631	1.2627961087
N	0.5299286021	-0.2274772719	1.2722667400
C	1.8852448802	-0.5023018198	1.0819286074
N	2.3908161060	-1.7516909456	0.8803313936
C	1.5459523167	-2.7621479975	0.8601284228
C	0.1518604968	-2.5855641705	1.0524757306
N	2.0039672302	1.8337327633	1.3249044784
H	2.2261828982	3.8887943589	1.5686593326
H	4.6916491731	3.8769690772	1.2340933069
H	5.8156190449	1.6374496354	0.8326180324
H	-1.3489323902	-1.1080322807	1.4347922097
H	1.9598068813	-3.7531758243	0.6942681508
H	-0.5323479524	-3.4250844470	1.0399909085
C	-0.1626365076	1.7685344927	3.3906271572
O	-0.3233437749	1.8527247086	4.5445037998
O	-0.4880148665	4.5460784491	1.1475665760
C	-0.2684777239	3.4142007788	1.3342261039
O	-2.8350117782	1.2573089725	1.0524149782
C	-1.6988963963	1.4103591962	1.2762114945

$TS_{\mathbf{1a}\rightarrow\mathbf{2a}}$			
Mn	-4.2483749169	1.9966879917	-0.3938834533
C	-3.0537110516	-0.5541921167	-1.0986277785
C	-1.8813527244	0.4593567100	0.6535727368
C	-0.9813266981	-0.5798610592	0.7245617464
C	-1.1214448118	-1.6665122040	-0.1655653515
C	-2.1613479299	-1.6479896313	-1.0697182420
C	-6.0238499859	0.8844840729	-2.5722332283
N	-4.9056544099	0.7309148254	-1.7981144554
C	-4.1840067714	-0.4346484051	-1.9759664054
C	-4.5550459657	-1.3937520064	-2.9396710640
C	-5.6718842856	-1.1983822640	-3.7239282289
C	-6.4296440050	-0.0223257246	-3.5200465237
N	-2.9042863176	0.5050767784	-0.2397800967
H	-1.8113387669	1.3029812775	1.3289949533
H	-0.1859505796	-0.5508968058	1.4606844316
H	-0.4305898918	-2.5023070430	-0.1348178621
H	-2.2978518166	-2.4744584054	-1.7571050505
H	-6.5925701652	1.7884989365	-2.4016382274
H	-3.9594527582	-2.2911987193	-3.0595402290
H	-5.9657418070	-1.9309461868	-4.4676599339
H	-7.3258298697	0.1780994156	-4.0970957951
C	-5.0045209805	1.7283447197	1.1714577626
O	-5.4800331876	1.6254807112	2.2404259650
O	-2.3079493943	4.0867645323	0.3661132323
C	-3.0662603604	3.2501571948	0.0464080666
O	-6.0941360426	4.1788032402	-1.1319914593

$TS_{\mathbf{1b}\rightarrow\mathbf{2b}}$			
Mn	-4.1401511689	2.2512475353	-0.7999806440
C	-3.1064671105	-0.3431567190	-1.5608356604
C	-1.7445504070	0.6208257264	0.0545121975
C	-0.9113434651	-0.4696756752	0.0061434141
C	-1.2467669571	-1.5023568190	-0.8977610569
N	-2.3272234414	-1.4451148172	-1.6575071760
C	-6.1653924438	1.1285778245	-2.7378740664
N	-4.9820077383	0.9774649942	-2.0849284064
C	-4.3091367957	-0.2040273316	-2.3220023893
N	-4.7228663388	-1.1651306567	-3.1797577258
C	-5.8604937989	-0.9669372310	-3.8236988054
C	-6.6434939485	0.1913625699	-3.6192931531
N	-2.8451475960	0.7311660431	-0.7357695628
H	-1.5549493902	1.4420398486	0.7344450734
H	-0.0357107533	-0.5336013405	0.6414368274
H	-0.6235612969	-2.3884314139	-0.9848557586
H	-6.7201344957	2.0338833385	-2.5260528952
H	-6.1827434307	-1.7401195906	-4.5160678902
H	-7.5869055127	0.3366592763	-4.1322577364
C	-5.0731965267	2.0136765812	0.6758031971
O	-5.6892026672	1.9090113313	1.6625328418
O	-2.2302154792	4.1898945993	0.3499709330
C	-2.9755443266	3.4156738981	-0.0980133265
O	-5.6889571089	4.5751446934	-1.7633887053
C	-5.0908224875	3.6500097438	-1.3880364119
C	-2.6423804338	2.8485830938	-3.1692283904

C	-5.3761776731	3.3056492489	-0.8423900817	O	-2.5589165422	4.0354664906	-3.2146809291
C	-2.9246111932	2.6432770080	-2.9181347426	O	-2.4326336657	1.7587312564	-3.5861504916
O	-2.1043909714	1.7946035273	-2.9494018059				
O	-3.5318449657	3.5805190515	-3.3101683729				
2a $[(bpy)Mn(CO)_3(CO_2)]^-$				**2b** $[(bpymd)Mn(CO)_3(CO_2)]^-$			
Mn	-4.3506265444	2.1392017947	-0.2694496046	Mn	0.2267110040	1.6820694481	1.4483448778
C	-2.8499676167	-0.2476188540	-0.9971959759	C	2.8469704313	0.7500834829	0.6441974778
C	-1.9292251550	0.7193023299	0.9074956812	C	2.9462877271	3.0077884366	1.1176120426
C	-0.9318164625	-0.2370341252	0.9771140603	C	4.2746715003	3.0274936323	0.7449271432
C	-0.8873893091	-1.2358283650	-0.0034813507	C	4.8322967563	1.8224408476	0.2966751063
C	-1.8591707887	-1.2411206625	-0.9906165254	N	4.1314417338	0.6916947019	0.2623591891
C	-6.0055243201	0.7927565243	-2.4403207571	C	0.0046020392	-1.3532174880	1.3613818984
N	-4.8713995663	0.7758252611	-1.7088571540	N	0.7653828498	-0.2535377456	1.1698405616
C	-3.9797328390	-0.2275812378	-1.9247745983	C	2.0316383312	-0.4586168052	0.7122744322
C	-4.2010549236	-1.2006007660	-2.9112334332	N	2.5494670665	-1.6546027207	0.3952538414
C	-5.3581828840	-1.1574278401	-3.6714500770	C	1.7693566168	-2.7210042344	0.5539165357
C	-6.2891099829	-0.1419100100	-3.4202249360	C	0.4676064911	-2.6183591967	1.0626920049
N	-2.8678536435	0.7392152121	-0.0621142952	N	2.2052732651	1.8803795456	1.0506830941
H	-1.9973622410	1.5000042876	1.6541790121	H	2.4489228212	3.8980389043	1.4819649895
H	-0.2096958119	-0.2003899736	1.7851794544	H	4.8577599961	3.9392017450	0.7997593754
H	-0.1184110649	-2.0008726813	0.0154643494	H	5.8683975510	1.7714975120	-0.0256959233
H	-1.8578492898	-2.0177172146	-1.7453899216	H	-0.9878754004	-1.1962607431	1.7650358607
H	-6.7069776497	1.5859843582	-2.2157250146	H	2.1901128285	-3.6856447844	0.2847595678
H	-3.4785306033	-1.9909942065	-3.0723737726	H	-0.1529135973	-3.4930622016	1.2177725067
H	-5.5434787739	-1.9060632758	-4.4344229691	C	0.3390328398	1.7076252884	3.2247259139
H	-7.2213313560	-0.0759146852	-3.9700941383	O	0.3628527362	1.7581192899	4.3878115448
C	-5.4099323592	1.4814187512	1.0032411618	O	-0.3612465717	4.5626737755	1.1778559227
O	-6.1192101515	1.1236884224	1.8576287261	C	-0.1221625832	3.4326696584	1.2858628413
O	-3.0559540922	4.1453200441	1.4646507136	O	-2.6741805744	1.1370917184	1.3774019455
C	-3.5596734598	3.3514443511	0.7819038607	C	-1.5329607522	1.3428787227	1.4072985181
O	-6.2545486293	4.2055411840	-1.1708928332	C	-0.0118047320	1.7051871169	-0.9570828658
C	-5.5064010363	3.3879491462	-0.8216468901	O	-0.9795655645	2.3293053694	-1.4093844811
C	-2.9546509281	3.1230689203	-1.9436895848	O	0.8979396060	1.0633968139	-1.4847224159
O	-2.8923500641	4.3677717668	-1.9841941847				
O	-2.4023706438	2.2624360127	-2.6417243540				
2a/2TFEH $[(bpy)Mn(CO)_3(CO_2)]^-$/2TFEH				**2b**/2TFEH $[(bpymd)Mn(CO)_3(CO_2)]^-$/2TFEH			
Mn	-4.9623026159	2.4588117984	-0.7657750295	Mn	-3.3050652207	1.9690937522	-1.9435717567
C	-2.5199023193	1.6377052574	0.5920886221	C	-2.5032775348	-0.1189889319	-0.0209452268
C	-3.6733066906	3.1840363577	1.8755950460	C	-1.1370921634	1.7127211034	0.2160216592
C	-2.6664451620	3.2225766555	2.8245087567	C	-0.4794275629	1.0835933926	1.2603747728
C	-1.5294819353	2.4354926169	2.6303739524	C	-0.9031023818	-0.2003591819	1.6016305747
C	-1.4611032127	1.6314954045	1.5075518706	N	-1.9197790071	-0.7960746862	0.9652992739
C	-3.7391571141	0.3808531636	-2.5724808173	C	-5.3399065873	-0.2874397799	-2.2525563099
N	-3.6601565143	1.0445578355	-1.3974255520	N	-4.2353154286	0.1474043219	-1.6249249943
C	-2.5467713872	0.8503683412	-0.6330167907	C	-3.6866233756	-0.6798148368	-0.7123823204
C	-1.5134819041	-0.0003295129	-1.0387698037	N	-4.1487910099	-1.8874303125	-0.3891802244
C	-1.6055295095	-0.6647566826	-2.2487870957	C	-5.2499621813	-2.3116629536	-1.0234573790
C	-2.7504995647	-0.4683152913	-3.0291223571	C	-5.8925950643	-1.5274321448	-1.9780749747
N	-3.6129120114	2.4200282776	0.7741998686	N	-2.1454166823	1.1141600544	-0.4445564329
H	-4.5591244099	3.7964277861	1.9742435009	H	-0.8780242134	2.7137154666	-0.0939372955
H	-2.7636668299	3.8760545972	3.6824679872	H	0.3189133242	1.5819123358	1.7995888706
H	-0.6997604122	2.4687109134	3.3253699897	H	-0.4317175265	-0.7565295745	2.4069453207
H	-0.5733929778	1.0483986244	1.3085598474	H	-5.7958095665	0.3884347288	-2.9574106453
H	-4.6222796811	0.5747934869	-3.1629517521	H	-5.6242266325	-3.2952053940	-0.7542341090
H	-0.6281875393	-0.1045015628	-0.4282097130	H	-6.7940505957	-1.8633195920	-2.4786337829

H	-0.8019402514	-1.3098273626	-2.5837321386
H	-2.8709803770	-0.9548368212	-3.9892741660
C	-6.1711656214	1.5112343284	0.1785552695
O	-6.9773917879	0.9448371793	0.7902231076
O	-5.9641833699	5.1664418176	-0.1376523992
C	-5.5821177891	4.1007166272	-0.3799634099
O	-6.7073607571	2.4149675303	-3.1540830681
C	-6.0118761701	2.4373552392	-2.2336355578
C	-3.4505362400	3.6109717903	-1.9286250126
O	-2.4675049119	4.0029535872	-1.2306613677
O	-3.5745549102	3.6394063186	-3.1537384978
O	-0.3262085312	2.9716967354	-2.0248906097
H	-1.1597225443	3.4680696055	-1.6726775390
C	-0.4067957579	2.9068109550	-3.4216924028
H	-0.5068395564	1.8728475946	-3.7756143116
H	-1.2583720141	3.4851254173	-3.7969466318
C	0.8687342919	3.4585689998	-4.0233736608
F	1.0933800183	4.7486387195	-3.7006952776
F	1.9690152879	2.7630304802	-3.6139689558
F	0.8448652644	3.3791644197	-5.3811444691
O	1.2380908652	1.4794737726	-0.5208906508
H	0.5655412615	1.9298222972	-1.0941848640
C	2.2199307098	2.4360912966	-0.2488048574
H	3.1586143252	1.9380389282	0.0102480421
H	2.3953753714	3.1073156963	-1.0963603570
C	1.8423699225	3.3118989559	0.9374031525
F	0.6869935226	3.9659590827	0.7497540722
F	1.7134731203	2.5909545943	2.0862314031
F	2.8123350735	4.2404972987	1.1710565420
C	-4.3302600534	2.8281388011	-0.7112327015
O	-4.9701431375	3.4306706120	0.0401703420
O	-1.7493113654	4.4069235748	-2.5419764885
C	-2.3234627467	3.4447080016	-2.2664659739
O	-5.0766190366	2.8773850307	-4.1220253765
C	-4.3798826737	2.4993915086	-3.2857850603
C	-2.0649523867	1.0273848787	-3.4455315176
O	-0.8177415081	1.2950179299	-3.5114043836
O	-2.5944579566	0.2503634789	-4.3002688980
O	1.3902622158	1.8443272873	-2.1720024137
H	0.4733144678	1.7187572463	-2.5392203235
C	1.8469521380	3.1355011029	-2.4804413454
H	2.8807904181	3.1106298261	-2.8425695972
H	1.2246237963	3.6392015437	-3.2272203392
C	1.8482254301	4.0181507057	-1.2358279742
F	0.6018404985	4.2646183207	-0.7521330826
F	2.5446809871	3.4689060677	-0.2152152089
F	2.4067401088	5.2276340875	-1.5106576759
O	-3.6541175654	1.3274212288	-6.5652028360
H	-3.3567640387	0.9198187030	-5.7150596548
C	-4.5700671036	0.4762386778	-7.1981282730
H	-4.6198888743	0.7318942472	-8.2613121670
H	-4.3203378162	-0.5879144243	-7.1072876101
C	-5.9751558040	0.6572968680	-6.6430943000
F	-6.0655386679	0.2997654090	-5.3393380728
F	-6.4177546809	1.9318692825	-6.7325737879
F	-6.8602782081	-0.1174398003	-7.3268323592

$TS_{2a/2TFEH \rightarrow 3a}$

Mn	-4.0878739468	2.5095479924	-1.2391346112
C	-2.4683978609	0.1336701433	-0.5669618284
C	-1.6266851628	2.0058609264	0.5131215338
C	-0.6789062917	1.2489806377	1.1905122947
C	-0.6264304842	-0.1232380010	0.9614313678
C	-1.5338595076	-0.6873758111	0.0716765264
C	-5.3808593325	0.1973770889	-2.7316741675
N	-4.3822256757	0.5740927980	-1.9164959005
C	-3.5145563450	-0.3684962249	-1.4733272418
C	-3.6443225467	-1.7113144160	-1.8396063408
C	-4.6922258363	-2.0951339535	-2.6681173990
C	-5.5778434807	-1.1202052772	-3.1235812129
N	-2.5036223173	1.4719271777	-0.3522973482
H	-1.6872778400	3.0707828691	0.6628317451
H	0.0061989489	1.7392923233	1.8712253656
H	0.1017609399	-0.7461969718	1.4707649950
H	-1.5211070366	-1.7549521778	-0.1082011984
H	-6.0486547309	0.9758569252	-3.0732181937
H	-2.9406336864	-2.4514947128	-1.4794294186
H	-4.8136981111	-3.1353707738	-2.9497254686
H	-6.4134078832	-1.3664687930	-3.7688542248
C	-5.0599398355	2.2599419539	0.2770330126
O	-5.6951385188	2.1663039653	1.2378954903
O	-3.3037416241	5.2513957784	-0.4654701258
C	-3.5845946163	4.1691130372	-0.7452849307
O	-6.3973779230	3.7423551881	-2.6006656606

$TS_{2b/2TFEH \rightarrow 3b}$

Mn	-4.1297118237	2.5247517206	-1.1756945530
C	-2.4707703496	0.1733330828	-0.5375872755
C	-1.6477841806	2.0108630042	0.5667478102
C	-0.7092074175	1.2062422624	1.1955631719
C	-0.7120997144	-0.1462801742	0.8758510705
N	-1.5922830512	-0.6657457671	0.0084606689
C	-5.3411959617	0.1983755083	-2.7490242089
N	-4.3824916027	0.6028672031	-1.8965467656
C	-3.5091655753	-0.3335346051	-1.4666842023
N	-3.5314147782	-1.6207731543	-1.8038033049
C	-4.4994543883	-2.0174969523	-2.6391033335
C	-5.4393356716	-1.1254254946	-3.1481706067
N	-2.5373839537	1.5006830457	-0.3031555127
H	-1.7100483416	3.0679996347	0.7642073923
H	0.0051244769	1.6276670425	1.8909911533
H	0.0004343304	-0.8319523244	1.3248505530
H	-6.0380988509	0.9449757673	-3.1044866679
H	-4.5197350077	-3.0704522387	-2.9025466106
H	-6.2215332243	-1.4460908041	-3.8261791160
C	-5.1120138661	2.2469074426	0.3331990493
O	-5.7481825714	2.1347301304	1.2900433157
O	-3.4323476608	5.2880968190	-0.3949938334
C	-3.6705066159	4.1952202322	-0.6711585294
O	-6.4499950218	3.7227982912	-2.5519072264
C	-5.5441922598	3.2457431557	-2.0208222165
C	-3.0760648734	2.9120553536	-2.9947899499

C	-5.4941951970	3.2489815679	-2.0762608022
C	-3.0588030337	2.8621473605	-3.0816780146
O	-1.9276825872	3.5497990747	-3.1279576595
O	-3.5736544624	2.5349888259	-4.1708482156
O	-0.1930103218	3.4543283302	-1.4501075973
H	-1.1936635408	3.5441633118	-2.2335929425
C	0.5634220081	2.3809863991	-1.8935611837
H	1.0470707181	1.8382381776	-1.0686964704
H	-0.0256969551	1.6468948701	-2.4661582571
C	1.6914590680	2.8171819365	-2.8168020487
F	1.2497469212	3.4107547227	-3.9516611243
F	2.5362152595	3.7006062027	-2.2308879142
F	2.4524156338	1.7511253967	-3.2061519292
O	1.2667269815	4.1858061399	0.6422995685
H	0.6630280316	4.0100403355	-0.1361387598
C	1.0828959684	5.4942674391	1.1116137380
H	1.9940985045	5.8439485815	1.6084097709
H	0.8201205374	6.2092425130	0.3244499085
C	-0.0277601142	5.5402496970	2.1497569721
F	-1.2290159932	5.1832870413	1.6354920800
F	0.2065414037	4.7059219502	3.1924100421
F	-0.1727204106	6.7875501477	2.6681788518

3a [(bpy)Mn(CO)$_3$(CO$_2$H)]

Mn	0.19615489	1.7061251249	1.5740837495
C	2.89303502	0.7466417746	0.9721644297
C	2.93868660	3.0439680495	1.3231300512
C	4.29714459	3.1118447203	1.0423104707
C	4.96665702	1.9396648238	0.6962948811
C	4.25755590	0.7442999044	0.6682284699
C	-0.01756614	-1.3470365761	1.5783765612
N	0.77997490	-0.2787426148	1.4079342467
C	2.06916289	-0.4758168321	1.0407614983
C	2.567221885	-1.7597101214	0.7998919394
C	1.730450176	-2.8585415874	0.9570673014
C	0.414836637	-2.6497807063	1.3666100776
N	2.242647105	1.8952489270	1.2779580558
H	2.392436259	3.9379157177	1.5971061134
H	4.808169903	4.0665492003	1.0960304358
H	6.025780778	1.9519416729	0.4614141957
H	4.766817612	-0.1776529791	0.4174965962
H	-1.033453650	-1.1543393565	1.8998977311
H	3.596349029	-1.9061217246	0.4969387231
H	2.103866423	-3.8603691187	0.7722426847
H	-0.272255758	-3.4741314531	1.5214632976
C	0.415301427	1.6701866570	3.3874951518
O	0.533947619	1.6619839935	4.5325071121
O	-0.391565408	4.6029807796	1.5743761371
C	-0.154457932	3.4748407094	1.5702497101
O	-2.703895241	1.1764070472	1.7871428352
C	-1.571341228	1.3730319216	1.6996082441
C	0.048633980	1.6836563849	-0.5174452468
O	-1.012551492	2.3711599744	-1.0892731581
O	0.818149482	1.1215457146	-1.2867902059
H	-0.945519923	2.2804556846	-2.0620906411

3’a [(bpy)Mn(CO)$_3$(CO$_2$H)]$^-$

O	-1.9199032685	3.5509225879	-3.0097294649
O	-3.5984176428	2.6272301800	-4.0924701410
O	-0.1782014710	3.2585349170	-1.3656272371
H	-1.1680875684	3.4558755763	-2.1206972428
C	0.5622281012	2.2342743222	-1.9355221968
H	1.0315335835	1.5826606452	-1.1823756852
H	-0.0362376561	1.5945091808	-2.6007525076
C	1.7046514386	2.7650318200	-2.7895306087
F	1.2805423888	3.5380980910	-3.8168293385
F	2.5841013398	3.5176399543	-2.0826880529
F	2.4221465047	1.7426836583	-3.3388147681
O	1.2678396312	3.9052490968	0.7775043753
H	0.6938292565	3.7217948410	-0.0187769082
C	1.2203752465	5.2808260291	1.0561344447
H	2.1099741902	5.5801173636	1.6192196118
H	1.1510671533	5.9016512017	0.1548505578
C	0.0123554047	5.6074323380	1.9199325462
F	-1.1535651220	5.2671898890	1.3164197196
F	0.0331594873	4.9526931476	3.1081361740
F	-0.0558185330	6.9332286696	2.2009841420

3b [(bpymd)Mn(CO)$_3$(CO$_2$H)]

Mn	0.1848420447	1.7013046715	1.3165985138
C	2.8679578653	0.7535025098	0.6776303873
C	2.9525342495	3.0214960837	1.0596650227
C	4.2949235451	3.0265862105	0.7127472460
C	4.8558396696	1.8106959925	0.3289824863
N	4.1487966967	0.6737066245	0.3265748593
C	-0.0079676208	-1.3696014633	1.3081479293
N	0.7641130830	-0.2804580429	1.1481496438
C	2.0378637643	-0.4773858393	0.7475377822
N	2.5752775571	-1.6596583367	0.4583994757
C	1.7902069930	-2.7365924290	0.5867124717
C	0.4742396569	-2.6401506172	1.0330938081
N	2.2271437508	1.8898981499	1.0237785995
H	2.4473523515	3.9281204323	1.3699023520
H	4.8759438281	3.9414308728	0.7364038054
H	5.8958847068	1.7424595755	0.0234481720
H	-1.0205891905	-1.2155244552	1.6605516853
H	2.2292450902	-3.6970160465	0.3327025669
H	-0.1524120202	-3.5159666741	1.1573748482
C	0.3775739564	1.6769562047	3.1371018273
O	0.4782570546	1.6752324658	4.2822736985
O	-0.3954009347	4.6014693505	1.2914705161
C	-0.1633277766	3.4739307878	1.2978852209
O	-2.7167620916	1.1556333149	1.4924780140
C	-1.5865039331	1.3617774919	1.4206511264
C	0.0696679606	1.6581827333	-0.7776341154
O	-0.9718254328	2.3289822208	-1.3867821991
O	0.8644382103	1.0795477950	-1.5099292665
H	-0.8857663329	2.2181531612	-2.3567376957

3’b [(bpymd)Mn(CO)$_3$(CO$_2$H)]$^-$

Mn	0.18811058	1.7133533449	1.5373514995
C	2.89676867	0.7176456446	0.9971864573
C	2.93177001	3.0603357175	1.2237793414
C	4.29829998	3.1326906124	1.0124538250
C	4.99592596	1.9219491239	0.7599697135
C	4.30106511	0.7371435339	0.7544372041
C	-0.03422933	-1.3487894628	1.4793324731
N	0.75450580	-0.2714669194	1.3383903229
C	2.10529201	-0.4590030711	1.0660614006
C	2.605558183	-1.7830780048	0.9010516630
C	1.773515848	-2.8672086971	1.0364627897
C	0.404526644	-2.6552235986	1.3461484339
N	2.226635284	1.9177758033	1.2104341363
H	2.370168932	3.9674995168	1.4180476294
H	4.802856800	4.0908209740	1.0413171620
H	6.066290495	1.9286009824	0.5789376062
H	4.826628071	-0.1927099436	0.5715817670
H	-1.074517467	-1.1530678910	1.7151119425
H	3.653984514	-1.9356125830	0.6737883848
H	2.162704764	-3.8729424844	0.9132667775
H	-0.288539939	-3.4773234216	1.4757825403
C	0.507232720	1.6042625675	3.3276674135
O	0.710271886	1.5370425977	4.4614204069
O	-0.366669393	4.6094170452	1.6834738354
C	-0.144624929	3.4755523364	1.6142309418
O	-2.694435717	1.1671630798	1.8649337059
C	-1.563438725	1.3726634113	1.7281073467
C	-0.036492953	1.7402942601	-0.5451962892
O	-1.098248154	2.5024472235	-1.0509524982
O	0.649661460	1.1689669291	-1.3845444447
H	-1.082976419	2.4243147175	-2.0263721146

Mn	0.1791207471	1.7033195277	1.2622492260
C	2.8841052186	0.7024670188	0.7140945167
C	2.9311401332	3.0194421812	0.9434727557
C	4.3074248236	3.0278915684	0.7168564996
C	4.9036571513	1.7813668025	0.4665116038
N	4.2313607010	0.6402141218	0.4622632421
C	-0.0214463070	-1.3571080771	1.1898634508
N	0.7446595017	-0.2793854065	1.0585763113
C	2.0924476386	-0.4705271901	0.7793688946
N	2.6426872677	-1.7134080295	0.5915780992
C	1.8396565541	-2.7591862161	0.7190262758
C	0.4756457426	-2.6510786177	1.0349373956
N	2.2150677523	1.9000623613	0.9351029855
H	2.3984915223	3.9435618306	1.1390420489
H	4.8774145961	3.9480576212	0.7294672313
H	5.9709514769	1.7165174232	0.2653610721
H	-1.0660416211	-1.1923061824	1.4299042531
H	2.2898794713	-3.7381145947	0.5679004022
H	-0.1608088563	-3.5192530190	1.1481705428
C	0.4706573533	1.6098970195	3.0627080118
O	0.6345106337	1.5637712643	4.2026544244
O	-0.3860110712	4.5999738078	1.3859298860
C	-0.1568574089	3.4688184191	1.3272789079
O	-2.7055173751	1.1595966521	1.5912700605
C	-1.5767517117	1.3635947535	1.4521164732
C	-0.0446599350	1.7364409341	-0.8165621905
O	-1.1500159273	2.4260932643	-1.3197574204
O	0.6877142669	1.2163389735	-1.6503950571
H	-1.1270109179	2.3594310750	-2.2962501053

$TS_{3a \rightarrow 4a}$			
Mn	-4.5873188586	2.2440365976	-0.8015528248
C	-2.7892058683	-0.0517787744	-0.4707232941
C	-2.7949207322	1.2559511669	1.4544317371
C	-1.9549682563	0.3679644664	2.1162853577
C	-1.5329807234	-0.7790712837	1.4487828432
C	-1.9499769322	-0.9879215334	0.1376177852
C	-4.4385139626	0.9054444622	-3.5679673848
N	-4.0259012676	0.8820310116	-2.2890136228
C	-3.2479268519	-0.1475348375	-1.8703833741
C	-2.9001004372	-1.1914689446	-2.7303531600
C	-3.3413521506	-1.1667067171	-4.0492265432
C	-4.1164600438	-0.0927734867	-4.4798973028
N	-3.2161382713	1.0492075152	0.1970855208
H	-3.1239127299	2.1674770537	1.9302371682
H	-1.6443528319	0.5849112195	3.1320087052
H	-0.8800130158	-1.4973174253	1.9339225302
H	-1.6177480339	-1.8670420524	-0.4001943879
H	-5.0465808031	1.7471576703	-3.8741623333
H	-2.2913421185	-2.0163270692	-2.3817053272
H	-3.0801285648	-1.9723302193	-4.7276533867
H	-4.4770723240	-0.0217571038	-5.5000784859
C	-5.9565640515	1.1061115995	-0.3040945566
O	-6.8203036519	0.4199772357	-0.0055776384
O	-5.2118836718	4.0638083885	1.4671448865

$TS_{3b \rightarrow 4b}$			
Mn	-4.6103766319	2.2848524595	-0.9118338172
C	-3.0537668286	-0.1954645786	-0.7215530507
C	-2.7463595285	1.0526829838	1.1888513577
C	-1.9387919663	0.0479909596	1.7036771177
C	-1.7665056001	-1.0935481928	0.9259137982
N	-2.3160587884	-1.2114013623	-0.2909286283
C	-4.7607859721	0.9621868634	-3.7156761764
N	-4.2922238369	0.8998851826	-2.4547672265
C	-3.6117183792	-0.2140273386	-2.1024554013
N	-3.3955299374	-1.2599630977	-2.8920974142
C	-3.8770845878	-1.1982209020	-4.1409683982
C	-4.5661842773	-0.0819241381	-4.6081583038
N	-3.3204851111	0.9256572010	-0.0188339325
H	-2.9215402364	1.9758110725	1.7213032416
H	-1.4715589001	0.1533703216	2.6765394744
H	-1.1707880221	-1.9309130495	1.2780778250
H	-5.2974670846	1.8558755004	-4.0102796706
H	-3.7044640753	-2.0611614635	-4.7779304876
H	-4.9450063541	-0.0273846394	-5.6226655105
C	-6.0845614857	1.3040333527	-0.3633116597
O	-7.0077647406	0.7204961238	-0.0310934096
O	-4.9512797135	4.0875584494	1.4340448290
C	-4.7864887667	3.3935740150	0.5412505681
O	-6.3723422508	4.0699240510	-2.4990734950

C	-4.9507035243	3.3600391372	0.6035960679
O	-6.4813758884	3.7684308276	-2.5015482000
C	-5.7480514054	3.1793231738	-1.8451972316
C	-3.1588933882	3.4963662209	-1.4107648464
O	-2.6809023778	4.1624345818	-2.2113438109
O	0.3051212208	3.5309065747	-0.4804719684
H	-0.6644782287	3.7706633208	-0.1483980277
C	0.4296050438	2.1387077323	-0.4886146669
H	1.4257210075	1.8214233544	-0.1579381006
H	-0.3116827616	1.6499527431	0.1538119538
C	0.2433029350	1.5439150752	-1.8782099382
F	-0.9795961710	1.7922503247	-2.4045926375
F	1.1493385138	2.0091233962	-2.7731409610
F	0.3811364035	0.1899331764	-1.8434712024
O	-2.0122608383	4.0374971053	0.3810470720
H	-2.1440855465	4.9879160693	0.2618706290

C	-5.6941604014	3.3808233109	-1.8843738712
C	-3.0521176776	3.3427586562	-1.5584803848
O	-2.4469294720	3.8820624310	-2.3652471424
O	0.4487619482	3.6094816267	-0.5155361403
H	-0.5517412575	3.7291407378	-0.2044594171
C	0.8156429476	2.2770778098	-0.3106934685
H	1.8986900250	2.1818856829	-0.1737678428
H	0.3255444054	1.8303533982	0.5645496491
C	0.4624921290	1.3888711154	-1.4972258555
F	-0.8666630477	1.3869672466	-1.7749654634
F	1.0896681904	1.7590134472	-2.6389621231
F	0.8065700011	0.0952407676	-1.2554713542
O	-1.9255764406	3.8381982371	0.2949932118
H	-2.1337717195	4.7823693809	0.3084139105

4a $[(bpy)Mn(CO)_4]^+$

Mn	-1.34459633	1.7005029884	0.9600376218
C	0.52771293	0.2630818486	2.7106996081
C	0.66806627	2.5544602436	3.1137391308
C	1.64516422	2.3719898555	4.0847539814
C	2.07177368	1.0773694610	4.3698881228
C	1.50646858	0.0125718986	3.6753137287
C	-1.71149336	-1.2684196693	0.2742288617
N	-1.06048788	-0.3653404026	1.0301221676
C	-0.13226248	-0.7975656274	1.9225467167
C	0.156057836	-2.1571185264	2.0632072494
C	-0.518950892	-3.0854283379	1.2767469830
C	-1.470727149	-2.6339478239	0.3659618422
N	0.117829765	1.5290715033	2.4382328252
H	0.320160778	3.5517811434	2.8763282036
H	2.054067231	3.2348073520	4.5987292615
H	2.832917497	0.8942506970	5.1214020892
H	1.828744334	-0.9992706007	3.8876887255
H	-2.447893417	-0.8941157804	-0.4256503581
H	0.897925911	-2.4950527078	2.7760640812
H	-0.302128391	-4.1439700396	1.3769379234
H	-2.024072755	-3.3168861073	-0.2692063739
C	-2.677756356	1.5379891237	2.2909190893
O	-3.482411273	1.4446635485	3.0856504465
O	-1.558262692	4.6709923695	1.0572775984
C	-1.470726270	3.5330538613	1.0262731904
O	-3.421559428	1.6623786094	-1.1756304056
C	-2.625758636	1.6706195070	-0.3570941644
C	0.020350442	1.8199011803	-0.3426184582
O	0.835217781	1.8957230869	-1.1287147105

4b $[(bpymd)Mn(CO)_4]^+$

Mn	-1.3510837440	1.7098853347	0.9530965435
C	0.5213923852	0.2788034671	2.7070143997
C	0.6929424778	2.5397003816	3.1255682701
C	1.6602128485	2.2822392229	4.0853557774
C	2.0081381958	0.9508395277	4.2981401307
N	1.4385394080	-0.0465623553	3.6085007222
C	-1.6931622864	-1.2932819238	0.2784597088
N	-1.0645628664	-0.3601707127	1.0199032269
C	-0.1444575647	-0.7915920054	1.9112834804
N	0.1864618289	-2.0605886855	2.1105648770
C	-0.4396618768	-2.9860424119	1.3711242686
C	-1.4032900190	-2.6414430399	0.4269164744
N	0.1173724480	1.5386038042	2.4307153979
H	0.3761401499	3.5530185237	2.9112056668
H	2.1215355061	3.0896063349	4.6429178370
H	2.7570575284	0.6739702027	5.0343825602
H	-2.4329325063	-0.9577115181	-0.4380212522
H	-0.1611093910	-4.0218426820	1.5415730727
H	-1.9106043826	-3.3899052264	-0.1712656156
C	-2.6875765493	1.5501279476	2.2867775275
O	-3.4916070719	1.4590321694	3.0809137394
O	-1.5473114390	4.6817442726	1.0779575038
C	-1.4715699496	3.5449586820	1.0307613380
O	-3.4348042879	1.6377912239	-1.1776628668
C	-2.6379335069	1.6671199320	-0.3627852331
C	0.0089135099	1.8384922596	-0.3598125575
O	0.8182878828	1.9202368570	-1.1495517632

$TS_{\mathbf{3'a \rightarrow 5a}}$

Mn	-4.4022698380	2.1647187317	-0.6753011832
C	-2.7355550954	-0.2524899749	-0.6788812598
C	-2.5239738502	0.8794212110	1.3809057289
C	-1.6620822601	-0.0717294218	1.8892992332
C	-1.3140925289	-1.1721966759	1.0615959558
C	-1.8462861805	-1.2558503526	-0.2003627420
C	-4.8100170514	0.8578408296	-3.4301406547
N	-4.2022607490	0.8038285299	-2.2295362265

$TS_{\mathbf{3'b \rightarrow 5b}}$

Mn	-3.9735333772	1.9847702362	-0.9307192375
C	-3.2793478813	-0.8308466106	-1.4593171995
C	-2.2351992261	-0.1206935726	0.4970437804
C	-1.6917339715	-1.3871263672	0.6840100493
C	-1.9941672062	-2.3469312262	-0.2962128837
N	-2.7632552060	-2.0953073077	-1.3439070137
C	-5.4491381109	1.1774139228	-3.5117127045
N	-4.6282008716	0.8194113173	-2.5245033578

C	-3.3380406273	-0.2525252039	-1.9646927297	C	-4.1503103440	-0.4879149863	-2.5236587927
C	-3.1118324749	-1.2404509422	-2.9643367339	N	-4.4990819448	-1.4077753549	-3.4781937413
C	-3.7444050918	-1.1605982086	-4.1798539870	C	-5.3203339960	-1.0108898790	-4.4362416582
C	-4.6272164730	-0.0780335131	-4.4302169946	C	-5.8375845960	0.2945853919	-4.5154371554
N	-3.0514313234	0.8285740088	0.1413994851	N	-3.0068697403	0.1812895454	-0.5459307011
H	-2.8028192500	1.7346631274	1.9848208298	H	-2.0461226493	0.6690950547	1.2140344335
H	-1.2651739662	0.0372928288	2.8907900235	H	-1.0660402842	-1.6131057202	1.5373904234
H	-0.6352790276	-1.9392834602	1.4199435340	H	-1.5958743256	-3.3562640554	-0.2165207207
H	-1.5885370037	-2.0913304060	-0.8401915072	H	-5.8129494634	2.1988564587	-3.5060204538
H	-5.4757451330	1.6973517931	-3.5929795404	H	-5.5911149289	-1.7543814706	-5.1831473735
H	-2.4316076114	-2.0593212251	-2.7642179022	H	-6.5066685471	0.6002035971	-5.3093390933
H	-3.5679489691	-1.9167019101	-4.9384075082	C	-5.3898939011	1.4013494167	0.0819001621
H	-5.1510238524	0.0266608469	-5.3724777295	O	-6.2786352187	1.0425823319	0.7098628097
C	-5.7391901934	1.1525063980	0.0452424229	O	-2.7290526835	3.4089267810	1.3537813972
O	-6.5801521421	0.5062117627	0.4824065324	C	-3.2167471876	2.8659899485	0.4674786445
O	-4.3947406152	4.0340225025	1.6285229410	O	-5.4266761284	4.4488372683	-1.7080939307
C	-4.3779910224	3.3111773842	0.7357006445	C	-4.8630936535	3.4923472486	-1.4118177564
O	-6.3955545403	3.8696395916	-2.0471235605	C	-2.4867651146	2.5411219625	-2.1725844387
C	-5.6115431516	3.2106419250	-1.5188540198	O	-1.8957265784	2.3453900674	-3.1398982337
C	-2.9622066279	3.2169093791	-1.6717623054	O	0.6145629723	4.2383338459	-0.7645322717
O	-2.5893437942	3.5123713861	-2.7213797653	H	-0.3717133736	4.2843562145	-1.0818099047
O	0.4260532938	3.1381922201	-0.1882207149	C	0.7441948352	3.2882057170	0.2564379381
H	-0.4439572222	3.6864861629	-0.2601243001	H	1.6051094348	3.5223573060	0.8916011763
C	0.1156170281	1.8546879190	-0.6624132369	H	-0.1422239262	3.2258574449	0.8988335108
H	0.5925364496	1.0783500391	-0.0560169657	C	0.9835155306	1.8855266120	-0.2866831737
H	-0.9602698163	1.6757476271	-0.6601859470	F	-0.0334026118	1.4405339831	-1.0584482188
C	0.5744705154	1.6266158481	-2.0939011849	F	2.1083496705	1.8019879257	-1.0415437961
F	0.1760595940	2.6002149163	-2.9419454845	F	1.1244743568	0.9909613600	0.7292816848
F	1.9300566179	1.5519651837	-2.2083063463	O	-1.8201723898	4.4423293723	-1.5473295449
F	0.0760973455	0.4552422643	-2.5713170700	H	-1.7125617221	4.8103418155	-2.4357342917
O	-1.8048951682	4.4061312675	-0.3908170674				
H	-1.5902159504	5.0723507786	-1.0593433641				
5a $[(bpy)Mn(CO)_4]^0$				**5b** $[(bpymd)Mn(CO)_4]^0$			
Mn	-1.4364191210	1.8201146673	0.8817653905	Mn	-1.3558179696	1.7126281196	0.9489874807
C	0.6034136365	0.1833663901	2.7835869786	C	0.5049540318	0.2536453858	2.6865446771
C	0.7490785659	2.4572677532	3.1936036738	C	0.6718923558	2.5463327418	3.1080560242
C	1.7310011035	2.2812236521	4.1638941319	C	1.6438476299	2.3087005642	4.0718508315
C	2.1574584097	0.9836444058	4.4414694837	C	2.0001468533	0.9640072462	4.2859774723
C	1.5882829630	-0.0782103114	3.7450231768	N	1.4578896900	-0.0436389465	3.6233842427
C	-1.6238573886	-1.3629976253	0.3492956639	C	-1.6988373955	-1.2676515407	0.2738775534
N	-0.9806760124	-0.4625117338	1.1006193440	N	-1.0796312006	-0.3395704680	1.0071824762
C	-0.0627294932	-0.8845894790	1.9907140142	C	-0.1291986518	-0.7648916400	1.9308402857
C	0.2292776182	-2.2462541794	2.1439079859	N	0.1850374756	-2.0851253603	2.1104645873
C	-0.4429198627	-3.1784294222	1.3592127700	C	-0.4508867316	-2.9726658235	1.3645962262
C	-1.3907279387	-2.7317839929	0.4404025906	C	-1.4228089774	-2.6226112445	0.4085127377
N	0.1995382958	1.4405098140	2.5204995270	N	0.0998146084	1.5576622461	2.4165645327
H	0.3847040020	3.4470909635	2.9410149246	H	0.3487159964	3.5582087231	2.8910553121
H	2.1446344790	3.1400859614	4.6812138625	H	2.0983326193	3.1200659635	4.6254564631
H	2.9220499573	0.7972938515	5.1888696826	H	2.7556225454	0.7093819347	5.0261560710
H	1.9123595261	-1.0902521301	3.9535294360	H	-2.4370214531	-0.9248017535	-0.4423860194
H	-2.3517490231	-0.9660957394	-0.3495648576	H	-0.1885734296	-4.0166774852	1.5210178898
H	0.9674616419	-2.5833626001	2.8610492901	H	-1.9327649769	-3.3642082798	-0.1927893818
H	-0.2277827336	-4.2367540258	1.4660134653	C	-2.6644345515	1.5275138191	2.2951709397
H	-1.9393761848	-3.4201325095	-0.1932144582	O	-3.4466964201	1.4114444315	3.1111342784
C	-2.7352122567	1.6473214358	2.1944066997	O	-1.5557929202	4.6784726416	1.0679569242
O	-3.5449423300	1.5490137086	3.0045768957	C	-1.4751808734	3.5377260771	1.0263056651

O	-1.6148060268	4.7725152432	1.0221480006	O	-3.4353603600	1.6595239320	-1.1779926556
C	-1.4812078594	3.6174662281	1.0335212794	C	-2.6352704162	1.6722875414	-0.3602729063
O	-3.4953714597	1.7353449720	-1.2444337137	C	0.0205667484	1.8151455479	-0.3367896928
C	-2.6824094713	1.6760335140	-0.4152418972	O	0.8550899305	1.8724226390	-1.1058199780
C	-0.0850683430	1.9309392464	-0.3832914560				
O	0.7474919162	2.0077103418	-1.1726536599				
6a [(bpy)MnH(CO)$_3$]				**6b** [(bpymd)MnH(CO)$_3$]			
Mn	-4.5330392464	2.0390186902	0.2707679218	Mn	-4.5272514999	2.0560528502	0.2728453129
C	-2.8124915850	-0.0512513883	-0.8643845250	C	-2.8373107721	-0.0681496582	-0.8385134242
C	-2.1642738154	0.4162259763	1.3167638510	C	-2.1597409030	0.3858418644	1.3108346271
C	-1.1201446544	-0.4978522899	1.2566654363	C	-1.1503895542	-0.5563084302	1.1878907358
C	-0.9178520786	-1.2061978488	0.0732421662	C	-1.0461096335	-1.2232568282	-0.0303085514
C	-1.7769776460	-0.9823327956	-0.9962279733	N	-1.8924887316	-0.9843181114	-1.0391430591
C	-5.7087556643	1.4296849959	-2.4825386851	C	-5.7053564436	1.4087678532	-2.4965453695
N	-4.7406983627	1.1494105064	-1.5927036884	N	-4.7516564157	1.1510550874	-1.5823093117
C	-3.7991895344	0.2313269856	-1.9225064122	C	-3.8296613304	0.2186372327	-1.9046842501
C	-3.8022300956	-0.3998887821	-3.1708049110	N	-3.7725039470	-0.4401246286	-3.0600288230
C	-4.7987784339	-0.0934431316	-4.0900061442	C	-4.7132013303	-0.1631333165	-3.9708540271
C	-5.7766157187	0.8346784867	-3.7358389538	C	-5.7229756958	0.7637471594	-3.7234769393
N	-2.9906068310	0.6498985364	0.2822717091	N	-3.0034129037	0.6465194223	0.2948523363
H	-2.3508633413	0.9766295740	2.2239364768	H	-2.3028488268	0.9377489701	2.2313047102
H	-0.4862281589	-0.6440999679	2.1241292199	H	-0.4736785632	-0.7607118708	2.0096076693
H	-0.1101936239	-1.9252382783	-0.0150064561	H	-0.2742389573	-1.9677067749	-0.2016557280
H	-1.6422956982	-1.5318892609	-1.9194758348	H	-6.4623540547	2.1376092686	-2.2352626187
H	-6.4557965154	2.1510473468	-2.1768476710	H	-4.6578781214	-0.6993063165	-4.9135727923
H	-3.0396243611	-1.1253947232	-3.4250864802	H	-6.4938347453	0.9763218426	-4.4552731872
H	-4.8135536432	-0.5754716493	-5.0618828905	C	-5.7385120820	0.9780094527	1.1067317579
H	-6.5821962609	1.0999452069	-4.4114701827	O	-6.5286696676	0.3516210197	1.6676852405
C	-5.7224354672	0.9269938467	1.0864045556	O	-3.6570252591	3.4548859457	2.7196235101
O	-6.5005802219	0.2763039281	1.6393924192	C	-4.0119231749	2.8864891432	1.7791657488
O	-3.7166997309	3.4287956382	2.7399231030	O	-6.4211560778	4.2542837655	-0.2563145742
C	-4.0443062172	2.8621965851	1.7871301340	C	-5.7030802061	3.3760644430	-0.0404284290
O	-6.4695115861	4.2119206135	-0.2012954613	H	-3.4731371177	3.0315275276	-0.4471574437
C	-5.7313724162	3.3417715950	-0.0157077355				
H	-3.4870438622	3.0302036809	-0.4443741461				
$TS_{\mathbf{1a}\rightarrow\mathbf{6a}}$				$TS_{\mathbf{1b}\rightarrow\mathbf{6b}}$			
Mn	-3.3116850936	2.3988995093	-0.0381108574	Mn	-3.3963209738	2.4491908138	-0.1832716594
C	-2.0571491629	-0.0165752542	-1.1634975518	C	-2.2431562618	0.0050163738	-1.3198666979
C	-1.0441554764	0.5392397871	0.8516341087	C	-1.0769003681	0.5865668113	0.5783329309
C	-0.2127161697	-0.5653283901	0.7961327340	C	-0.2926526272	-0.5393876205	0.4388696242
C	-0.3113457316	-1.4350293676	-0.2959347148	C	-0.5535423467	-1.3773103790	-0.6523194492
C	-1.2435151992	-1.1513708711	-1.2814752548	N	-1.5249014002	-1.1059370685	-1.5219184486
C	-4.7841127076	1.8603645492	-2.6333203865	C	-5.0602741972	1.8274344645	-2.6553184112
N	-3.7951419120	1.4629310638	-1.8074439668	N	-4.0150225334	1.4760202360	-1.8750109530
C	-3.0813271898	0.3557495336	-2.1388251012	C	-3.3421665297	0.3506473156	-2.2245709211
C	-3.3360782646	-0.3522590760	-3.3210904185	N	-3.6237541952	-0.4173288800	-3.2830351101
C	-4.3464052914	0.0733822838	-4.1691219026	C	-4.6470387902	-0.0470495939	-4.0532024661
C	-5.0912942410	1.2018183131	-3.8124556202	C	-5.4114949758	1.0894552636	-3.7690324616
N	-1.9610555859	0.8313026248	-0.1006686427	N	-2.0665583757	0.8883464954	-0.2991761143
H	-0.9870110070	1.2247433581	1.6865750529	H	-0.9279270968	1.2702863140	1.4040464606
H	0.4972915194	-0.7393925631	1.5973856609	H	0.4934389887	-0.7631993814	1.1513277250
H	0.3221688591	-2.3125932454	-0.3716337301	H	0.0269670006	-2.2798484147	-0.8205999845
H	-1.3433409862	-1.8094691231	-2.1358264660	H	-5.6119722367	2.7119550670	-2.3621070094
H	-5.3397130198	2.7352488347	-2.3208123344	H	-4.8690990202	-0.6724548574	-4.9131903222
H	-2.7485892165	-1.2257529342	-3.5754840904	H	-6.2496031753	1.3808243573	-4.3914364282

H	-4.5542472368	-0.4642534556	-5.0885057563
H	-5.8982610158	1.5688041012	-4.4367141219
C	-4.7480072844	1.7675585421	0.7600511102
O	-5.7558376707	1.4731318868	1.2820021243
O	-2.3595588565	3.5146402601	2.5215914558
C	-2.7227435226	3.0765404080	1.5056835399
O	-4.2291764381	5.0887281933	-0.8499131914
C	-3.7595357394	4.0243044120	-0.5752627004
O	-1.1841850563	4.5855835918	-1.5930170908
H	-2.3760493702	3.9011050913	-0.9655474306
C	-0.4218251470	3.4703845188	-1.8560265288
H	0.6674909692	3.6305072555	-1.7824501751
H	-0.6614095872	2.6290155680	-1.1807325783
C	-0.6431813611	2.8997020153	-3.2578152346
F	-1.9439376974	2.8630910384	-3.6241400474
F	0.0012699005	3.6063196076	-4.2357685091
F	-0.1799588342	1.6152796703	-3.3522597715

C	-4.7225946128	1.8082950737	0.8020922355
O	-5.6469041475	1.5114045115	1.4508059991
O	-2.1267771174	3.6660766590	2.1901183008
C	-2.6231727867	3.1924967711	1.2539406465
O	-4.4681018028	5.0702806291	-1.0111687346
C	-3.9834136488	4.0315027392	-0.7091489103
O	-1.4399155852	4.6476961409	-1.8709575789
H	-2.5972920753	3.8310982093	-1.2158365346
C	-0.4033257011	3.7848536485	-1.6098222249
H	0.5697334479	4.2741743366	-1.4284833034
H	-0.5985714738	3.1393839788	-0.7317243822
C	-0.1413336987	2.7928880499	-2.7420729269
F	-1.2691361794	2.2059036534	-3.2091355640
F	0.4612905348	3.3607428854	-3.8268996051
F	0.6809353752	1.7762967932	-2.3408741647

$TS_{\mathbf{1a}\rightarrow\mathbf{2a}}$, closed shell

Mn	-4.2497194616	1.9953186778	-0.3936890016
C	-3.0538508721	-0.5546783248	-1.0985132805
C	-1.8803827270	0.4602660383	0.6520483499
C	-0.9797226832	-0.5784269164	0.7226657628
C	-1.1199908019	-1.6654007895	-0.1669325076
C	-2.1607348285	-1.6478067408	-1.0701937080
C	-6.0245909510	0.8826312283	-2.5721762016
N	-4.9077979946	0.7284401034	-1.7962952445
C	-4.1850483437	-0.4360572317	-1.9749636334
C	-4.5554708277	-1.3953624406	-2.9386558936
C	-5.6715280751	-1.1998739048	-3.7239966852
C	-6.4292148977	-0.0237129745	-3.5210798296
N	-2.9042412627	0.5050548620	-0.2403744202
H	-1.8100201896	1.3042670109	1.3269315998
H	-0.1836501394	-0.5486177636	1.4580349175
H	-0.4286368520	-2.5008176287	-0.1365038737
H	-2.2973950915	-2.4748267177	-1.7569207306
H	-6.5941318599	1.7860777716	-2.4011235588
H	-3.9599625229	-2.2929717213	-3.0577552858
H	-5.9648693972	-1.9325144189	-4.4679026664
H	-7.3246643680	0.1770342705	-4.0992259460
C	-5.0062130494	1.7278176574	1.1715754028
O	-5.4821477596	1.6265918814	2.2405868346
O	-2.3083872170	4.0857865793	0.3632863468
C	-3.0669501268	3.2487402605	0.0450639973
O	-6.0919116647	4.1789987003	-1.1360888725
C	-5.3759333949	3.3048081602	-0.8445810736
C	-2.9192311028	2.6491091788	-2.9165143043
O	-2.1159748985	1.7851828016	-2.9596736925
O	-3.5097567767	3.6019253665	-3.2961820276

$TS_{\mathbf{1b}\rightarrow\mathbf{2b}}$, closed shell

Mn	-4.1415843338	2.2508576487	-0.7980799168
C	-3.1080484500	-0.3441425637	-1.5585241583
C	-1.7477636163	0.6194544225	0.0581333035
C	-0.9134401768	-0.4701280725	0.0089273353
C	-1.2477633525	-1.5025017988	-0.8951342738
N	-2.3283544234	-1.4457575541	-1.6551645123
C	-6.1638340289	1.1303372221	-2.7421806083
N	-4.9824155936	0.9780241701	-2.0851680969
C	-4.3098696488	-0.2038651408	-2.3217892221
N	-4.7213425391	-1.1638505873	-3.1815947292
C	-5.8564562076	-0.9643457095	-3.8295614991
C	-6.6389819559	0.1945351970	-3.6267877282
N	-2.8476677973	0.7291162646	-0.7326695265
H	-1.5599309073	1.4404513714	0.7387588164
H	-0.0376020834	-0.5331914256	0.6437445718
H	-0.6237819003	-2.3879209168	-0.9822631545
H	-6.7193272572	2.0353889923	-2.5312026358
H	-6.1769199043	-1.7368496953	-4.5234035776
H	-7.5800139023	0.3415598935	-4.1434471667
C	-5.0630874555	2.0147624905	0.6846672599
O	-5.6720788122	1.9119605428	1.6760449621
O	-2.2227406667	4.1956927964	0.3253589501
C	-2.9716881010	3.4180507306	-0.1111630641
O	-5.7030724508	4.5718082069	-1.7470015628
C	-5.0999855404	3.6476087759	-1.3769253099
C	-2.6473792457	2.8444076332	-3.1694402832
O	-2.5624715436	4.0313513473	-3.2181628017
O	-2.4379923577	1.7550111369	-3.5876390877

$TS_{\mathbf{1a}\rightarrow\mathbf{2a}}$''

Mn	-4.2686905479	1.9906283600	-0.4140562243
C	-3.0590201149	-0.5380942658	-1.1438044528
C	-1.8367575463	0.4974992319	0.5610224667
C	-0.9219206540	-0.5276758141	0.6007450753
C	-1.0725076375	-1.6181306988	-0.2859250859
C	-2.1475438384	-1.6156991702	-1.1474675304

$TS_{\mathbf{1a}\rightarrow\mathbf{2a}}$'''

Mn	-4.2469588101	1.9925978011	-0.4283104087
C	-3.0646957134	-0.5758158838	-1.1196414211
C	-1.7819188873	0.5235183443	0.4958358034
C	-0.8840016879	-0.5168467325	0.5636130451
C	-1.0820628659	-1.6522207234	-0.2509110349
C	-2.1794949299	-1.6720976332	-1.0858964844

C	-6.1420270057	0.8024421128	-2.4585257367	C	-6.0645351326	0.8427792607	-2.5345416675
N	-4.9774306712	0.6840876799	-1.7588293983	N	-4.9334773265	0.6886565355	-1.7894799038
C	-4.2311545290	-0.4541072402	-1.9670170055	C	-4.2333124380	-0.4873299441	-1.9496410348
C	-4.6308312690	-1.4340409867	-2.9008785933	C	-4.6538017274	-1.4776956345	-2.8598969710
C	-5.7970104761	-1.2753044298	-3.6170421475	C	-5.7943335044	-1.2893412916	-3.6128328795
C	-6.5788857306	-0.1221219937	-3.3769259809	C	-6.5192829411	-0.0911895786	-3.4361509575
N	-2.8930271661	0.5370449871	-0.3002223466	N	-2.8646676543	0.5360212226	-0.3314111358
H	-1.7518317229	1.3377477025	1.2380021147	H	-1.6586363196	1.3953244558	1.1243843696
H	-0.1038998519	-0.4861712626	1.3114582119	H	-0.0427508617	-0.4510566668	1.2444814999
H	-0.3678241366	-2.4426197406	-0.2796176791	H	-0.3945037298	-2.4903441690	-0.2167304556
H	-2.3000980284	-2.4461789380	-1.8266680030	H	-2.3660301134	-2.5331557820	-1.7168035289
H	-6.7278397690	1.6879260942	-2.2483832601	H	-6.6118203556	1.7621153407	-2.3764143153
H	-4.0184626912	-2.3156708855	-3.0500839223	H	-4.0775737782	-2.3894778536	-2.9663621995
H	-6.1126213284	-2.0223903860	-4.3373237898	H	-6.1264823056	-2.0439455388	-4.3175804472
H	-7.5145784698	0.0451994063	-3.8992479729	H	-7.4272457059	0.1066089589	-3.9951297744
C	-5.2604714411	1.7034644896	1.0057273385	C	-5.2279853672	1.6474789623	0.9880437693
O	-5.9254676984	1.5960154832	1.9677910760	O	-5.8869889401	1.5011111596	1.9486558639
O	-2.4906793734	4.0317200372	0.7653497156	O	-2.5126268961	4.0403159968	0.8059344136
C	-3.1860850103	3.2123763321	0.3033310055	C	-3.1927716175	3.2228670047	0.3176600259
O	-5.8228056116	4.2524354254	-1.5052164740	O	-5.8549410722	4.2612984827	-1.4240349493
C	-5.2163717338	3.3471974822	-1.0799508207	C	-5.2209533532	3.3558829544	-1.0394458865
C	-2.5940493090	2.7322890851	-2.7827549808	C	-2.6649493599	2.7940431831	-2.7837335609
O	-2.3858438535	1.6447110252	-3.1860814729	O	-1.5641123107	2.8038228726	-2.3481441505
O	-2.5387140109	3.9144889712	-2.7546915767	O	-3.4949384612	2.9031005593	-3.6193254857

References

Becke, A. D.; *J. Chem. Phys.*, **1993**, *98*, 5648-5652..

[2] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H.; *J. Chem. Phys.,* **2010**, *132*, 154104-154119.

[3] Jaguar; Schrödinger, LLC: New York, NY, 2012

[4] Marten, B.; Kim, K.; Cortis, C.; Friesner, R. A.; Murphy, R. B.; Ringnalda, M. N.; Sitko, D.; Honig, B.; *J. Phys. Chem.,* **1996**, *100*, 11775-11788.

[5] Hay, P. J.; Wadt, W. R.; *J. Chem. Phys.* **1985**, *82*, 299-310.

[6] Hay, P. J.; Wadt, W. R.; *J. Chem. Phys.* **1985**, *82*, 270-283.

[7] Martin, J. M. L.; Sundermann, A.; *J. Chem. Phys.* **2001**, *114*, 3408-3420.

[8] McQuarrie, D. A. *Statistical Mechanics*; University Science Books: Sausalito, CA, **2000.**

[9] Isse, A. A.; Gennaro, A. *J. Phys. Chem. B* **2010**, *114*, 7894– 7899.

[10]Kelly, C.P.; Cramer, C. J.; Truhlar, D.G.; *J. Phys. Chem. B* **2007**, *111*, 408-422.

[11] Kütt, A.; Leito, I.; Kaljurand, I.; Sooväli, L.; Vlasov, V. M.; Yagupolskii, L. M.; Koppel, I. A.; *J. Org. Chem.*, **2006**, *71*, 2829–2838, unless otherwise noted.

[12] Marenich, A. V.; Kelly, C. P.; Thompson, J. D.; Hawkins, G. D.; Chambers, C. C.; Giesen, D. J.; Winget, P.; Cramer, C. J.; Truhlar, D. G.; Minnesota Solvation Database – version 2012, University of Minnesota, Minneapolis, 2012., unless otherwise noted.

[13] Böes, E. S.; Livotto, R. S.; Stassen, H.; *Chem. Phys.*, **2006**, *331*, 142-158

[14] Personal correspondence with Prof. Ivo Leito. Estimated by correlation analysis from pK_a values measured in dimethylsulfoxide (DMSO)— pK_a values in acetonitrile and DMSO are known to be well-correlated—with an estimated uncertainty of ca. 1.0 pK_a units.