Electronic Supplementary Information for:

Theoretical investigation of the gas-phase Mn^+- and Co^+-catalyzed oxidation of benzene by N_2O

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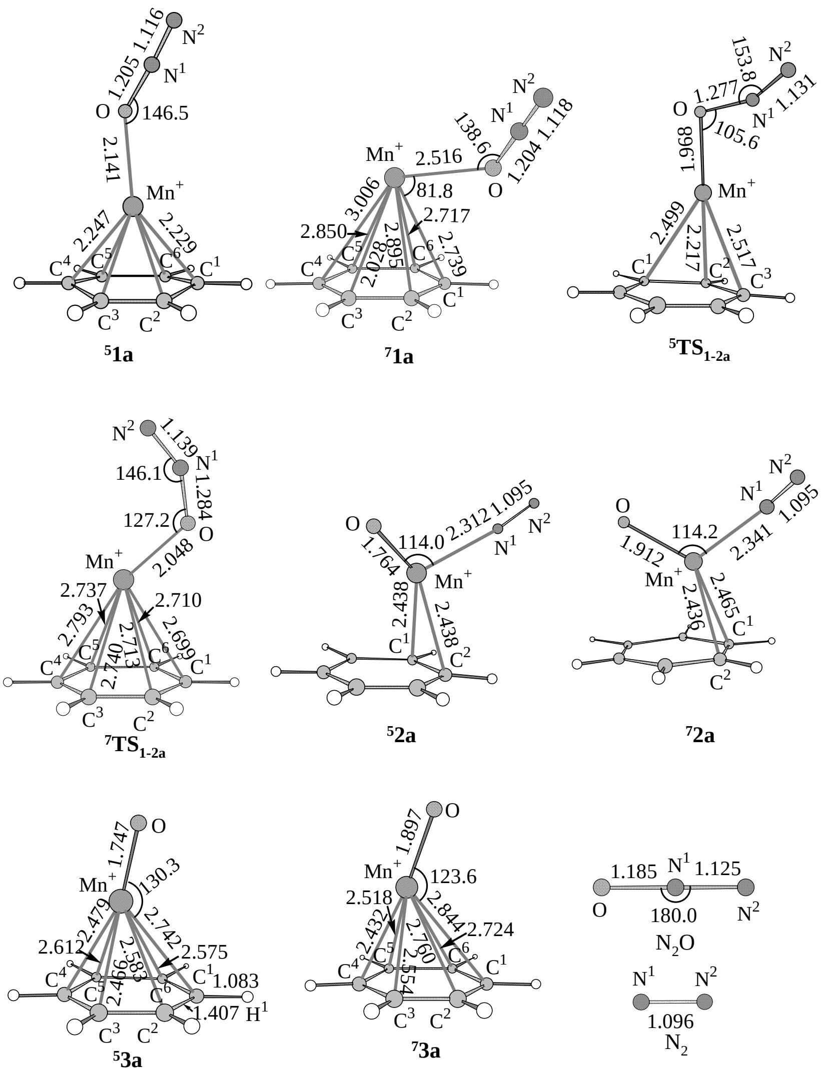

Fig. 1. Optimized geometries and selected structural parameters (Å and deg) for all the reactants, intermediates, saddle points and products involved in the coordination of benzene to Mn^+ followed by N_2O reduction relevant to the Mn^+-catalyzed oxidation of benzene by N_2O at the B3LYP/DZVP(opt)+6-311+G** level.

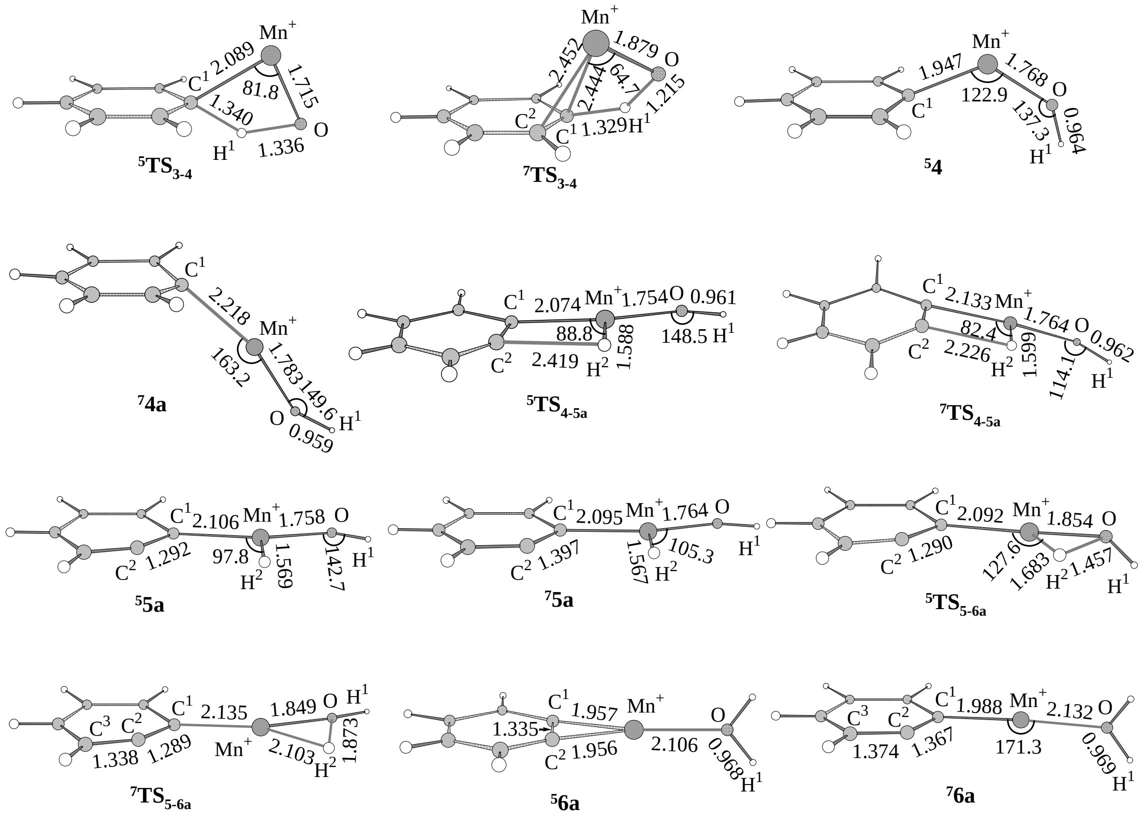

Fig. 2. Optimized geometries and selected structural parameters (Å and deg) for all the intermediates, saddle points and products involved in the reaction of $OMn^+(C_6H_6)$ via the nonradical mechanism associated with the Mn^+-catalyzed oxidation of benzene by N_2O at the B3LYP/DZVP(opt)+6-311+G** level.

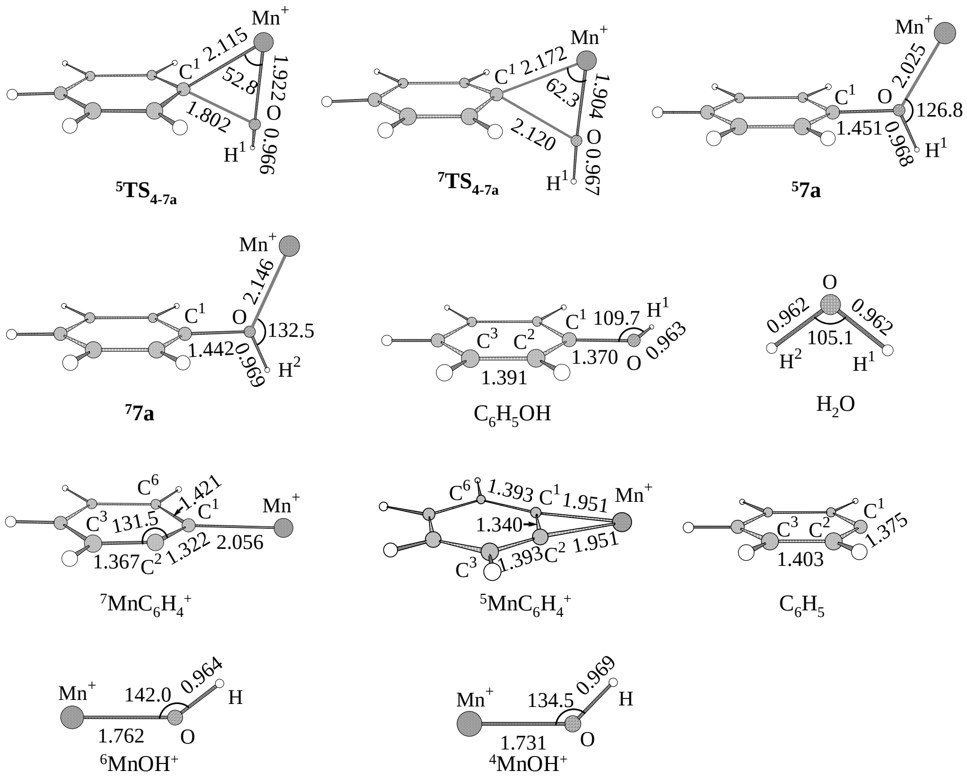

Fig. 2. Continued.

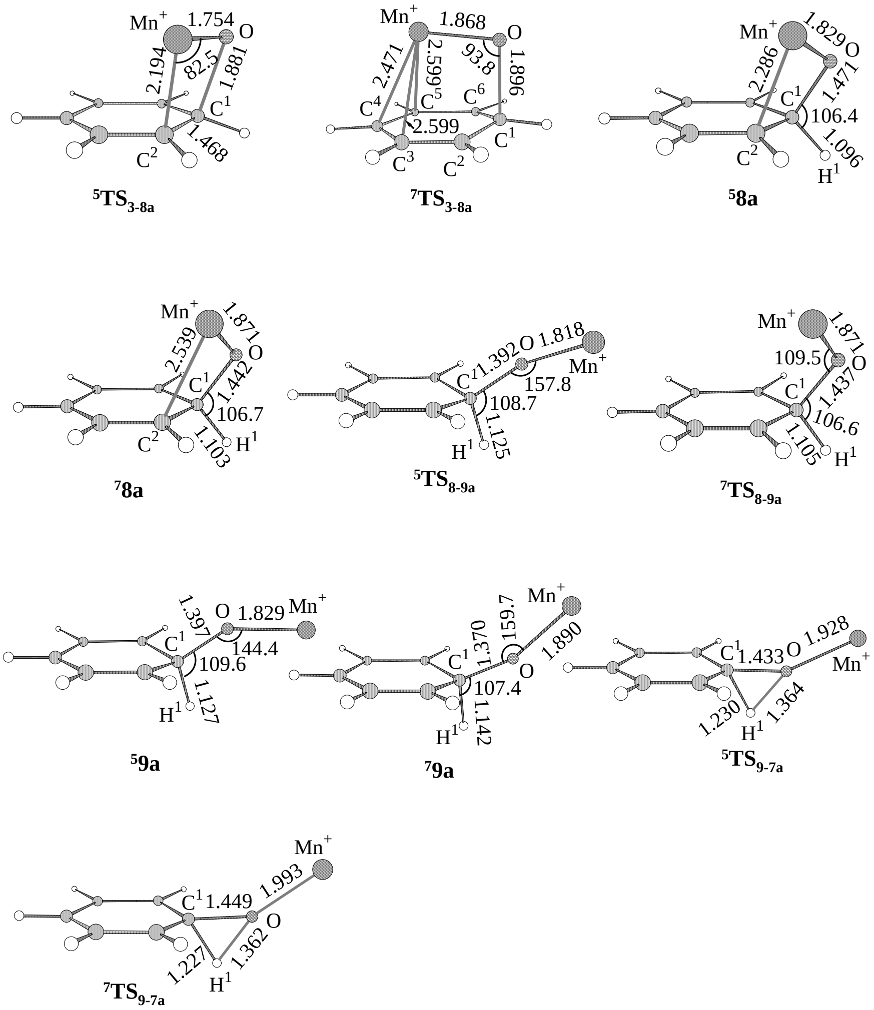

Fig. 3. Optimized geometries and selected structural parameters (Å and deg) for all the intermediates, saddle points and products involved in the reaction of $OMn^+(C_6H_6)$ via the oxygen-insertion mechanism associated with the Mn^+-catalyzed oxidation of benzene by N_2O at the B3LYP/DZVP(opt)+6-311+G** level.

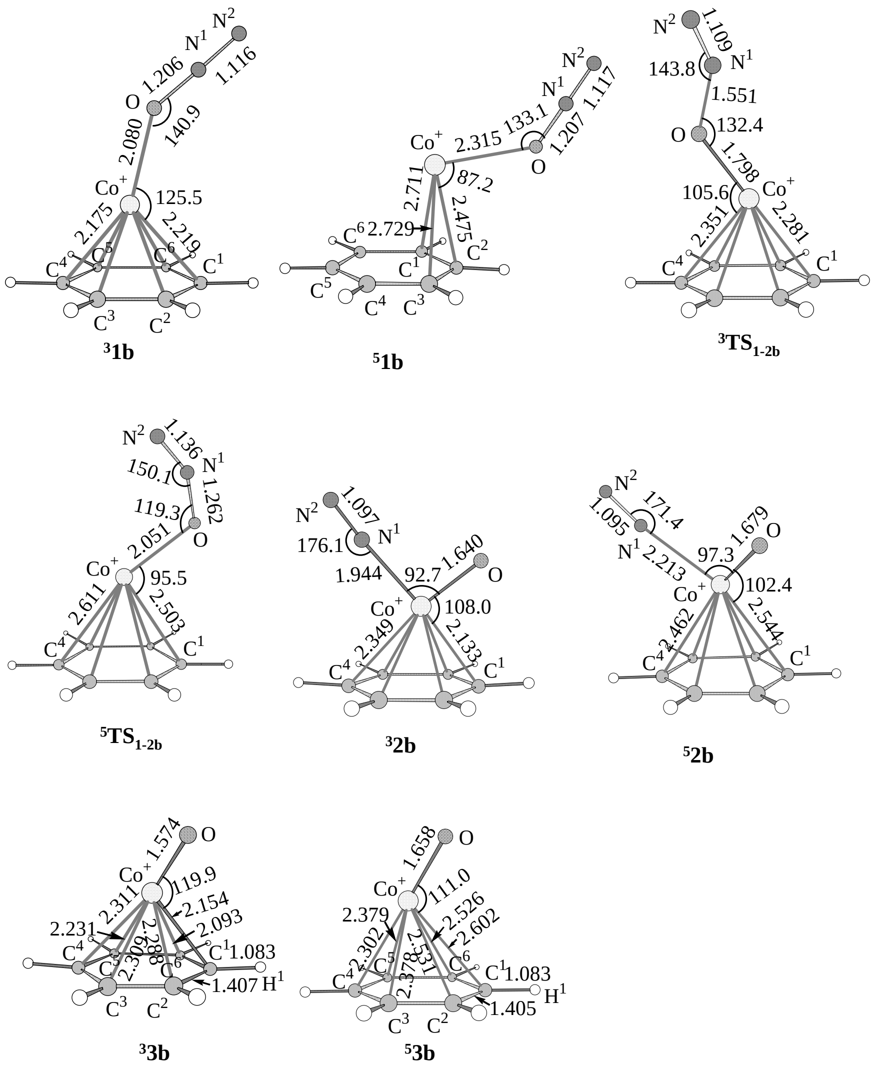

Fig. 4. Optimized geometries and selected structural parameters (Å and deg) involved in the coordination of benzene to Co^{+} followed by N_2O reduction relevant to the Co^{+}-catalyzed oxidation of benzene by N_2O at the B3LYP/DZVP(d)(opt)+6-311+G** level.

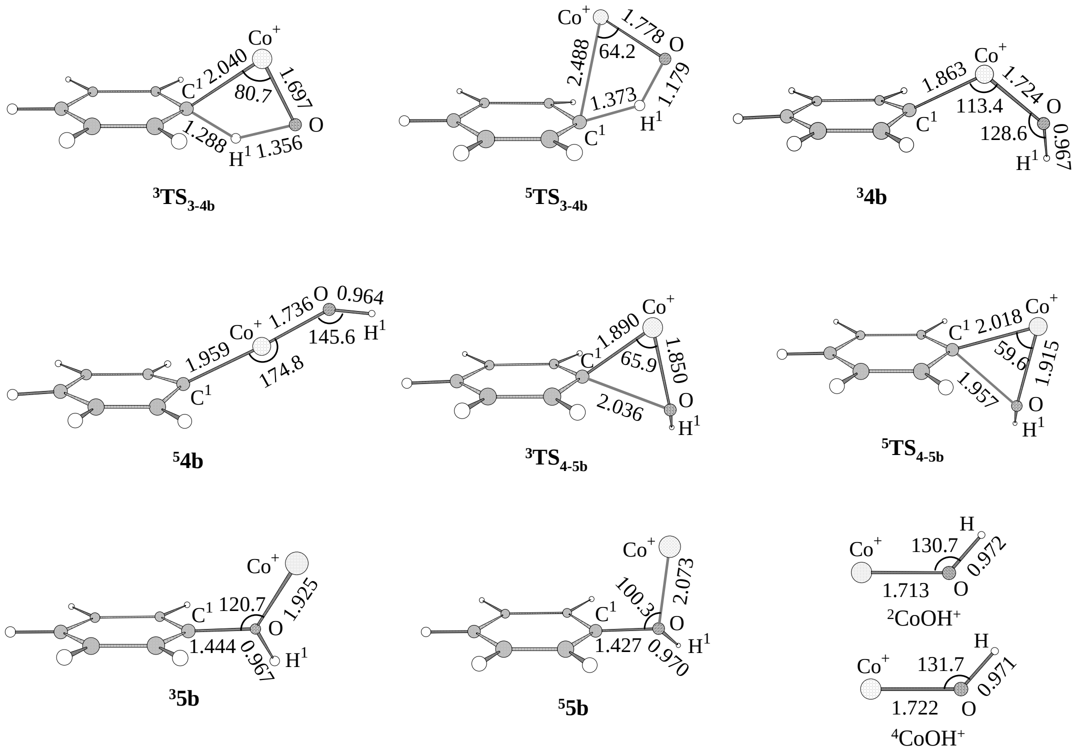

Fig. 5. Optimized geometries and selected structural parameters (Å and deg) for all the intermediates, saddle points and products involved in the reaction of $OCo^{+}(C_6H_6)$ via the nonradical mechanism associated with the Co^{+}-catalyzed oxidation of benzene by N_2O at the B3LYP/DZVP(d)(opt)+6-311+G** level.

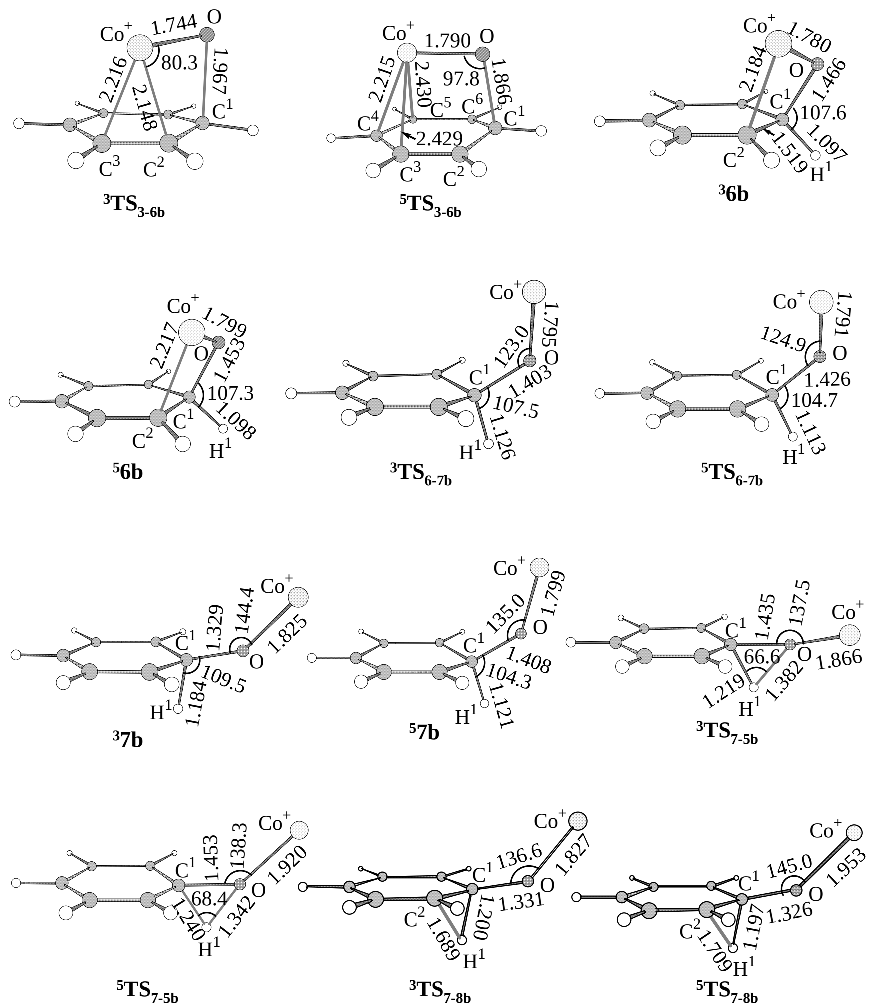

Fig. 6. Optimized geometries and selected structural parameters (Å and deg) for all the intermediates, saddle points and products involved in the reaction of $OCo^+(C_6H_6)$ via the oxygen-insertion mechanism associated with the Co^+-catalyzed oxidation of benzene by N_2O at the B3LYP/DZVP(opt)+6-311+G** level.

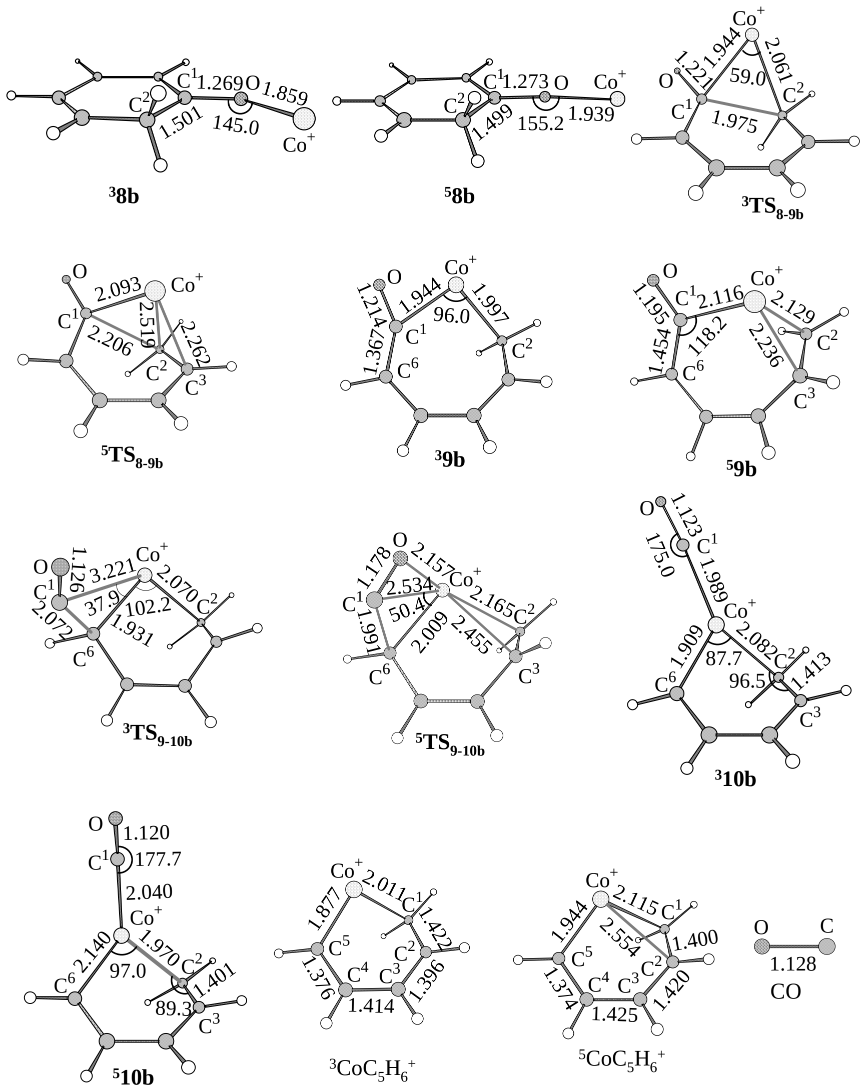

Fig. 6. Continued.

Table 1. Calculated energies E (Hartree), zero-point energies ZPE (Hartree), and <S^2> for all species involved in the Mn^+ and Co^+-catalyzed oxidation of benzene by N_2O

Species	Level 1[a]			Level 2[b]	
	E	ZPE	<S^2>[c]	E	<S^2>[a]
N_2O	-184.71823	0.01101	0.0	-184.72427	0.0
N_2	-109.55969	0.0056	0.0	-109.56344	0.0
C_6H_6	-232.31127	0.10018	0.00	-232.32061	0.0
C_6H_5OH	-307.55863	0.10414	0.0	-307.57053	0.0
C_6H_5	-231.62233	0.08697	0.09	-231.63122	0.76
H_2O	-76.45846	0.02129	0.0	-76.46204	0.0
CO	-113.34905	0.00504	0.0	-113.35200	0.0
$^5Mn^+$	-1150.50474	0.0	7.00	-1150.48251	6.01
$^7Mn^+$	-1150.54013	0.0	12.00	-1150.54010	12.00
$^5MnO^+$	-1225.71885	0.0014	6.79	-1225.73137	6.78
$^7MnO^+$	-1225.70082	0.00146	12.01	-1225.71210	12.01
$^4MnOH^+$	-1226.32492	0.01176	3.79	-1226.34918	3.78
$^6MnOH^+$	-1226.41575	0.01146	8.76	-1226.42684	8.76
$^5Mn(C_6H_4)^+$	-1381.61025	0.07689	6.24	-1381.62780	6.23
$^7Mn(C_6H_4)^+$	-1381.58094	0.07548	12.07	-1381.59320	12.07
$^5Mn(C_6H_6)^+$	-1382.87584	0.10057	6.51	-1382.89337	6.31
$^7Mn(C_6H_6)^+$	-1382.90089	0.10102	12.00	-1382.91399	12.00
^{5}**1a**	-1567.62959	0.11183	6.19	-1567.65720	6.15
^{7}**1a**	-1567.62846	0.11246	12.00	-1567.64593	12.00
$^5\mathbf{TS_{1\text{-}2a}}$	-1567.61985	0.11076	6.33	-1567.64483	6.31
$^7\mathbf{TS_{1\text{-}2a}}$	-1567.61210	0.10997	12.02	-1567.63252	12.02
^{5}**2a**	-1567.68714	0.10984	6.71	-1567.71420	6.71
^{7}**2a**	-1567.67000	0.10982	12.01	-1567.69528	12.01
^{5}**3a**	-1458.11774	0.10271	6.69	-1458.14355	6.68
^{7}**3a**	-1458.09762	0.10282	12.01	-1458.12105	12.01
$^5\mathbf{TS_{3\text{-}4a}}$	-1458.06551	0.09777	6.29	-1458.09082	6.26
$^7\mathbf{TS_{3\text{-}4a}}$	-1458.04815	0.09670	12.02	-1458.07016	12.02
^{5}**4a**	-1458.13149	0.10092	6.31	-1458.15351	6.30
^{7}**4a**	-1458.11642	0.09929	12.01	-1458.13641	12.01
$^5\mathbf{TS_{4\text{-}5a}}$	-1458.04127	0.09348	6.11	-1458.06326	6.11
$^7\mathbf{TS_{4\text{-}5a}}$	-1457.97891	0.09118	12.14	-1458.00042	12.14
^{5}**5a**	-1458.04316	0.09350	6.12	-1458.06467	6.11
^{7}**5a**	-1457.98792	0.09255	12.13	-1458.00846	12.13
$^5\mathbf{TS_{5\text{-}6a}}$	-1458.01981	0.09255	6.27	-1458.04108	6.26
$^7\mathbf{TS_{5\text{-}6a}}$	-1457.98480	0.08916	12.01	-1458.00352	12.01
^{5}**6a**	-1458.12983	0.10175	6.23	-1458.14867	6.229
^{7}**6a**	-1458.09271	0.10075	12.04	-1458.10756	12.04
$^5\mathbf{TS_{4\text{-}7a}}$	-1458.08222	0.10007	6.61	-1458.10223	6.51
$^7\mathbf{TS_{4\text{-}7a}}$	-1458.07959	0.10007	12.03	-1458.09597	12.03

$^{5}\mathbf{7a}$	-1458.12940	0.10470	6.71	-1458.12138	6.01
$^{7}\mathbf{7a}$	-1458.14904	0.10470	12.00	-1458.16094	12.00
$^{5}\mathbf{TS_{3\text{-}8a}}$	-1458.08398	0.10215	6.60	-1458.10805	6.59
$^{7}\mathbf{TS_{3\text{-}8a}}$	-1458.07735	0.10205	12.05	-1458.10042	12.05
$^{5}\mathbf{8a}$	-1458.09649	0.10325	6.79	-1458.11835	6.79
$^{7}\mathbf{8a}$	-1458.09127	0.10293	12.03	-1458.11134	12.03
$^{5}\mathbf{TS_{8\text{-}9a}}$	-1458.08340	0.10243	6.84	-1458.09936	6.83
$^{7}\mathbf{TS_{8\text{-}9a}}$	-1458.09126	0.10281	12.03	-1458.11076	12.02
$^{5}\mathbf{9a}$	-1458.08372	0.10264	6.80	-1458.10027	6.78
$^{7}\mathbf{9a}$	-1458.09945	0.10222	12.01	-1458.11372	12.01
$^{5}\mathbf{TS_{9\text{-}7a}}$	-1458.04657	0.09920	6.74	-1458.06080	6.69
$^{7}\mathbf{TS_{9\text{-}7a}}$	-1458.06614	0.09905	12.01	-1458.07888	12.01
$^{5}\mathbf{10a}$	-1335.25436	0.01154	6.75	-1335.26229	6.00
$^{5}\mathbf{TS_{10\text{-}11a}}$	-1335.23300	0.00834	6.60	-1335.24705	6.571
$^{5}\mathbf{11a}$	-1335.31433	0.00877	6.77	-1335.30719	6.54
$^{7}\mathbf{10a}$	-1335.27966	0.01129	12.00	-1335.28437	12.00
$^{7}\mathbf{TS_{10a}}$	-1335.23559	0.00702	12.01	-1335.24584	12.01
$^{3}Co^{+}$	-1382.20776	0.0	2.00	-1382.20881	2.00
$^{5}Co^{+}$	-1382.19804	0.0	6.00	-1382.19920	6.00
$^{3}CoO^{+}$	-1457.34922	0.00165	2.38	-1457.35698	2.00
$^{5}CoO^{+}$	-1457.41001	0.00179	6.01	-1457.41928	6.01
$^{3}CoC_6H_6^{+}$	-1614.60749	0.10091	2.01	-1614.62414	2.02
$^{5}CoC_6H_6^{+}$	-1614.57637	0.10105	6.00	-1614.57637	6.00
$^{2}CoOH^{+}$	-1458.05736	0.01167	1.69	-1458.06679	1.69
$^{4}CoOH^{+}$	-1458.08769	0.01169	3.76	-1458.07503	3.76
$^{3}CoC_5H_6^{+}$	-1576.42559	0.09106	2.10	-1576.44042	2.10
$^{5}CoC_5H_6^{+}$	-1576.39785	0.09021	6.02	-1576.40874	6.02
$^{3}\mathbf{1b}$	-1799.37305	0.11352	2.03	-1799.39471	2.03
$^{5}\mathbf{1b}$	-1799.29769	0.11258	6.00	-1799.32025	6.00
$^{3}\mathbf{TS_{1\text{-}2b}}$	-1799.32913	0.10971	2.31	-1799.35289	2.32
$^{5}\mathbf{TS_{1\text{-}2b}}$	-1799.29232	0.11083	6.01	-1799.31337	6.01
$^{3}\mathbf{2b}$	-1799.39053	0.11264	2.05	-1799.41869	2.05
$^{5}\mathbf{2b}$	-1799.39628	0.11074	6.03	-1799.42130	6.03
$^{3}\mathbf{3b}$	-1689.80227	0.10427	2.02	-1689.82853	2.02
$^{5}\mathbf{3b}$	-1689.82225	0.10345	6.02	-1689.84502	6.02
$^{3}\mathbf{TS_{3\text{-}4b}}$	-1689.74799	0.09749	2.38	-1689.76862	2.39
$^{5}\mathbf{TS_{3\text{-}4b}}$	-1689.74092	0.09658	6.02	-1689.75737	6.02
$^{3}\mathbf{4b}$	-1689.81826	0.10146	2.23	-1689.83798	2.23
$^{5}\mathbf{4b}$	-1689.81071	0.10065	6.02	-1689.83018	6.02
$^{3}\mathbf{TS_{4\text{-}5b}}$	-1689.79650	0.10173	2.10	-1689.81562	2.09
$^{5}\mathbf{TS_{4\text{-}5b}}$	-1689.76448	0.10116	6.03	-1689.78167	6.03
$^{3}\mathbf{5b}$	-1689.842597	0.10524	2.05	-1689.85696	2.04
$^{5}\mathbf{5b}$	-1689.81906	0.10473	6.00	-1689.83247	6.00

^{3}TS$_{3\text{-}6b}$	-1689.77356	0.10252	2.72	-1689.77550	2.27
^{5}TS$_{3\text{-}6b}$	-1689.77524	0.10242	6.06	-1689.79527	6.06
^{3}6b	-1689.78857	0.10379	2.67	-1689.80990	2.42
^{5}6b	-1689.78104	0.10331	6.02	-1689.79732	6.02
^{3}TS$_{6\text{-}7b}$	-1689.78170	0.10285	2.40	-1689.78496	2.26
^{5}TS$_{6\text{-}7b}$	-1689.77394	0.10294	6.02	-1689.77379	6.02
^{3}7b	-1689.78801	0.10138	2.14	-1689.79162	2.03
^{5}7b	-1689.77424	0.10296	6.02	-1689.77903	6.01
^{3}TS$_{7\text{-}5b}$	-1689.75549	0.09943	2.08	-1689.77074	2.07
^{5}TS$_{7\text{-}5b}$	-1689.73794	0.09906	6.01	-1689.75130	6.01
^{3}TS$_{7\text{-}8b}$	-1689.78139	0.10078	2.30	-1689.79107	2.03
^{5}TS$_{7\text{-}8b}$	-1689.74253	0.10044	6.00	-1689.77561	6.00
^{3}8b	-1689.84318	0.10443	2.06	-1689.84491	2.02
^{5}8b	-1689.81299	0.10402	6.00	-1689.83321	6.00
^{3}TS$_{8\text{-}9b}$	-1689.78116	0.10104	2.02	-1689.79988	2.02
^{5}TS$_{8\text{-}9b}$	-1689.73459	0.09904	6.06	-1689.75132	6.06
^{3}9b	-1689.79951	0.10110	2.05	-1689.81890	2.05
^{5}9b	-1689.76277	0.09930	6.05	-1689.77979	6.05
^{3}TS$_{9\text{-}10b}$	-1689.75872	0.09782	2.04	-1689.77684	2.04
^{5}TS$_{9\text{-}10b}$	-1689.71865	0.09632	6.03	-1689.73919	6.03
^{3}10b	-1689.81397	0.09938	2.06	-1689.82624	2.09
^{5}10b	-1689.78186	0.09719	6.03	-1689.80133	6.03
^{3}11b	-1566.95698	0.01170	2.16	-1566.97387	2.04
^{3}TS$_{11\text{-}12b}$	-1566.92203	0.00763	2.33	-1566.93273	2.35
^{3}12b	-1566.98844	0.00927	3.013	-1566.95989	2.01
^{5}11b	-1566.94234	0.01146	6.001	-1566.94900	6.00
^{5}TS$_{11\text{-}12b}$	-1566.90852	0.00708	6.01	-1566.91887	6.01
^{5}12b	-1567.01318	0.00939	6.02	-1567.02711	6.02

[a] B3LYP in conjunction with the DZVP(opt) set for Mn^{+}, the DZVP(d)(opt) set for Ni and the 6-311+G** set for the nonmetal atoms. [b] The B3LYP/DZVP(d)(opt+3f)+6-311++G(2d,2p)//DZVP(opt)+6-311+G** level for Mn^{+}-containing species and the B3LYP/DZVP(d)(opt+3f)+6-311++G(2d,2p)//DZVP(d)(opt)+6-311+G** level for Co^{+}-containing species. [c] Values before annihilation.