Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information For

Design of high-efficiency g-C_3N_4 based metal monoatom catalysts by two extra-NM_1 atoms: density functional theory simulations

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1 Computational details

The adsorption energies of OH, O and OOH groups on the substrates by following:

$$\Delta E_{*O} = E(\text{sub/O}) - E(\text{sub}) - [E(H_2O) - E(H_2)] \quad \text{(S1)}$$

$$\Delta E_{*OH} = E(\text{sub/OH}) - E(\text{sub}) - [E(H_2O) - E(H_2)/2] \quad \text{(S2)}$$

$$\Delta E_{*OOH} = E(\text{sub/OOH}) - E(\text{sub}) - [2\times E(H_2O) - 3\times E(H_2)/2] \quad \text{(S3)}$$

where $E(\text{sub/H}_2\text{O})$, $E(\text{sub/OH})$, $E(\text{sub/O})$ and $E(\text{sub/OOH})$ denote the total energies of H_2O, OH, O and OOH groups on the substrates. $E(\text{sub})$, $E(H_2O)$ and $E(H_2)$ are the energies of bare substrate, water, and hydrogen gas, respectively.

The detailed Gibbs free energy change can be calculated by:

$$\Delta G_1 = \Delta G_{*OH} - eU \quad \text{(S4)}$$

$$\Delta G_2 = \Delta G_{*O} - \Delta G_{*OH} - eU \quad \text{(S5)}$$

$$\Delta G_3 = \Delta G_{*OOH} - \Delta G_{*O} - eU \quad \text{(S6)}$$

$$\Delta G_4 = 4.92\text{eV} - \Delta G_{*OOH} - eU \quad \text{(S7)}$$

where the sum of $\Delta G_{1\text{-}4}$ is fixed to the negative of experimental Gibbs free energy of formation of two water molecules ($-2\Delta_{H_2O}^{exp} = 4.92$ eV). The Gibbs free energy of ($H^+ + e^-$) in solution is estimated as the half energy of H_2 molecule at standard condition.

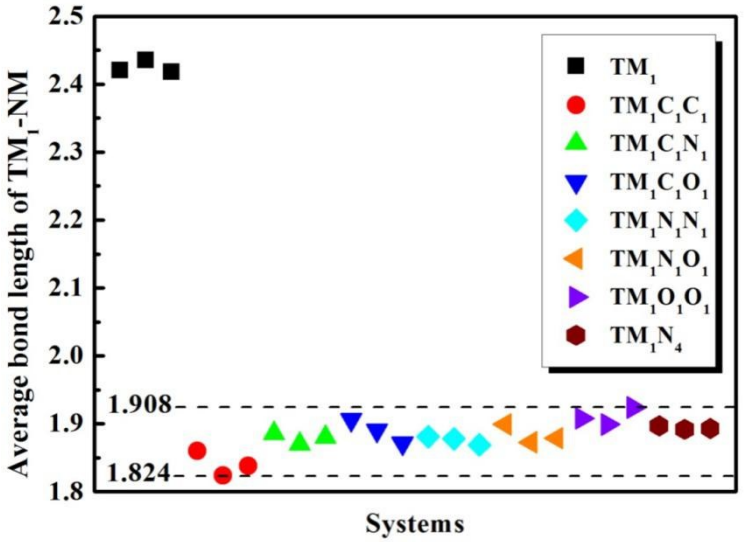

Fig. S1 Average lengths of TM_1-NM_1 bonds in all considered systems with unit of Å.

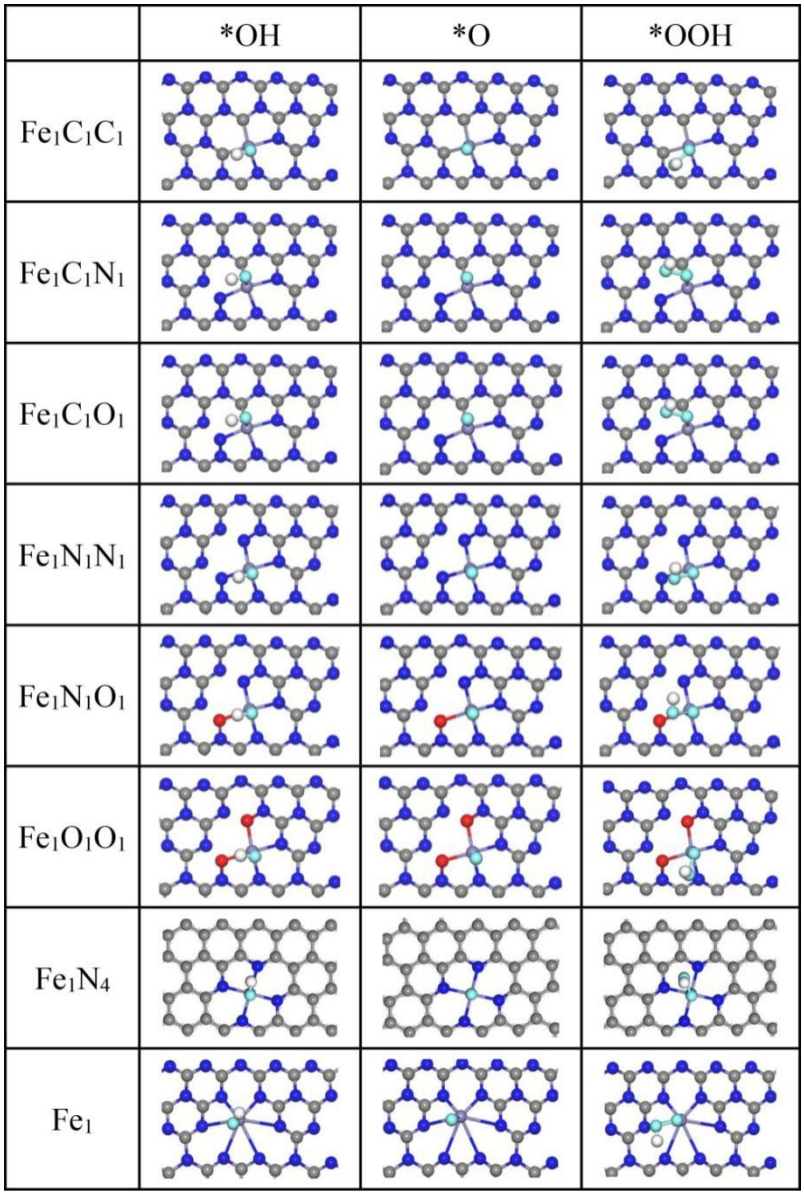

Fig. S2 Partial atom structures of *OH, *O and *OOH at active sites of Fe_1 based systems.

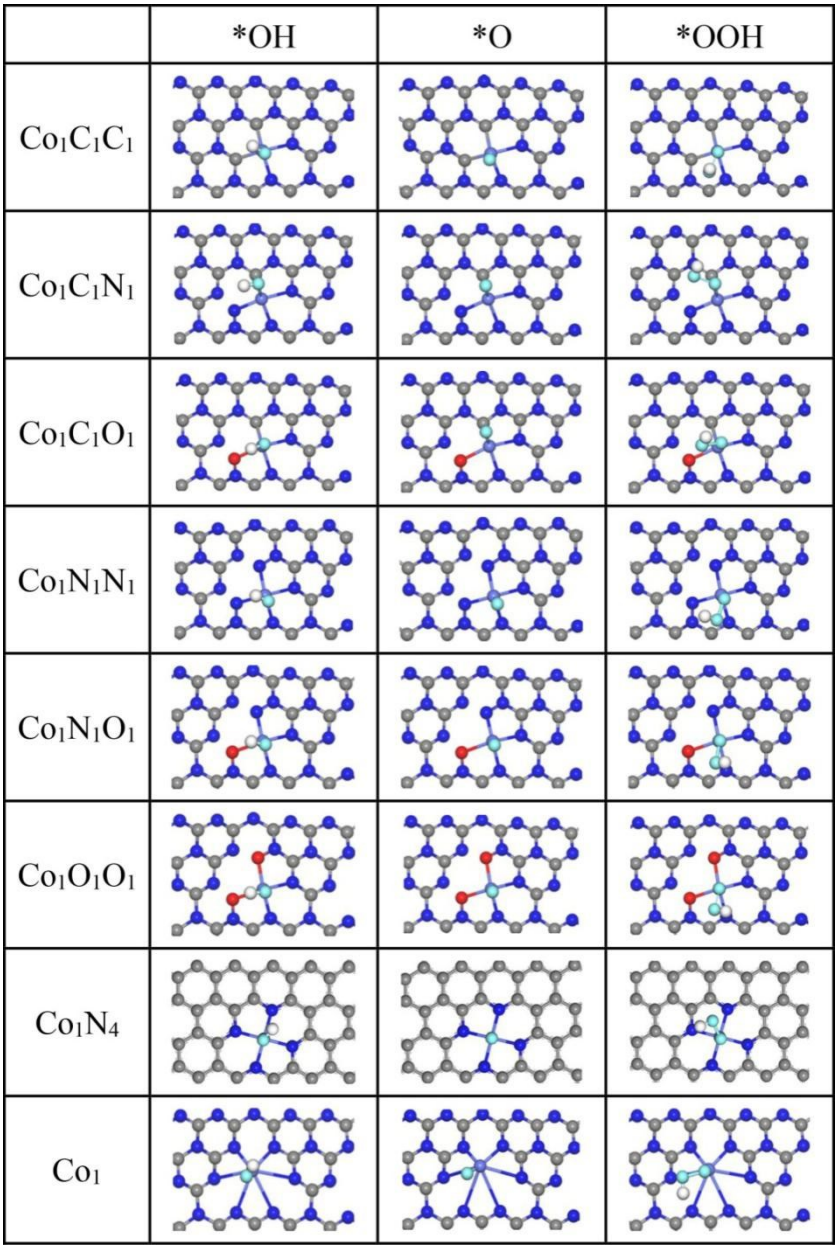

Fig. S3 Partial atom structures of *OH, *O and *OOH at active sites of Co_1 based systems.

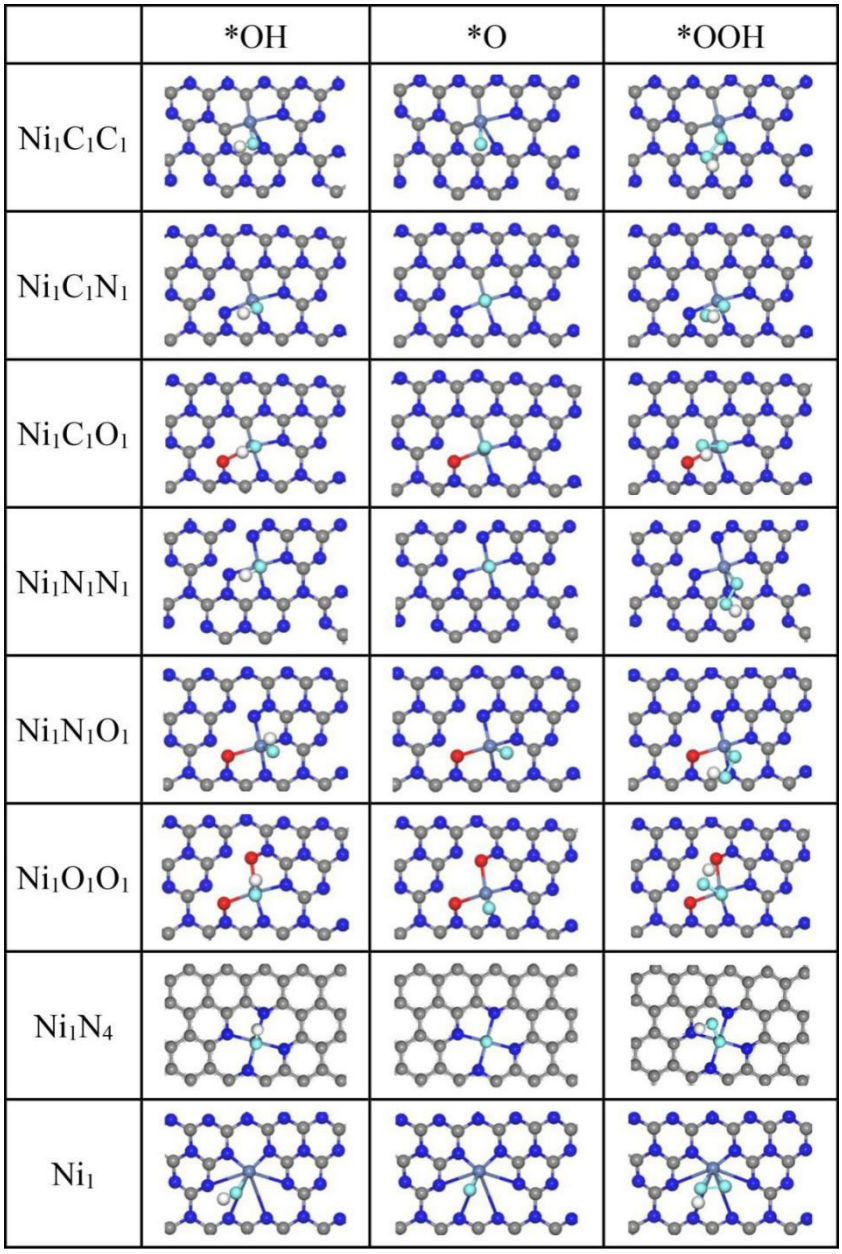

Fig. S4 Partial atom structures of *OH, *O and *OOH at active sites of Ni_1 based systems.

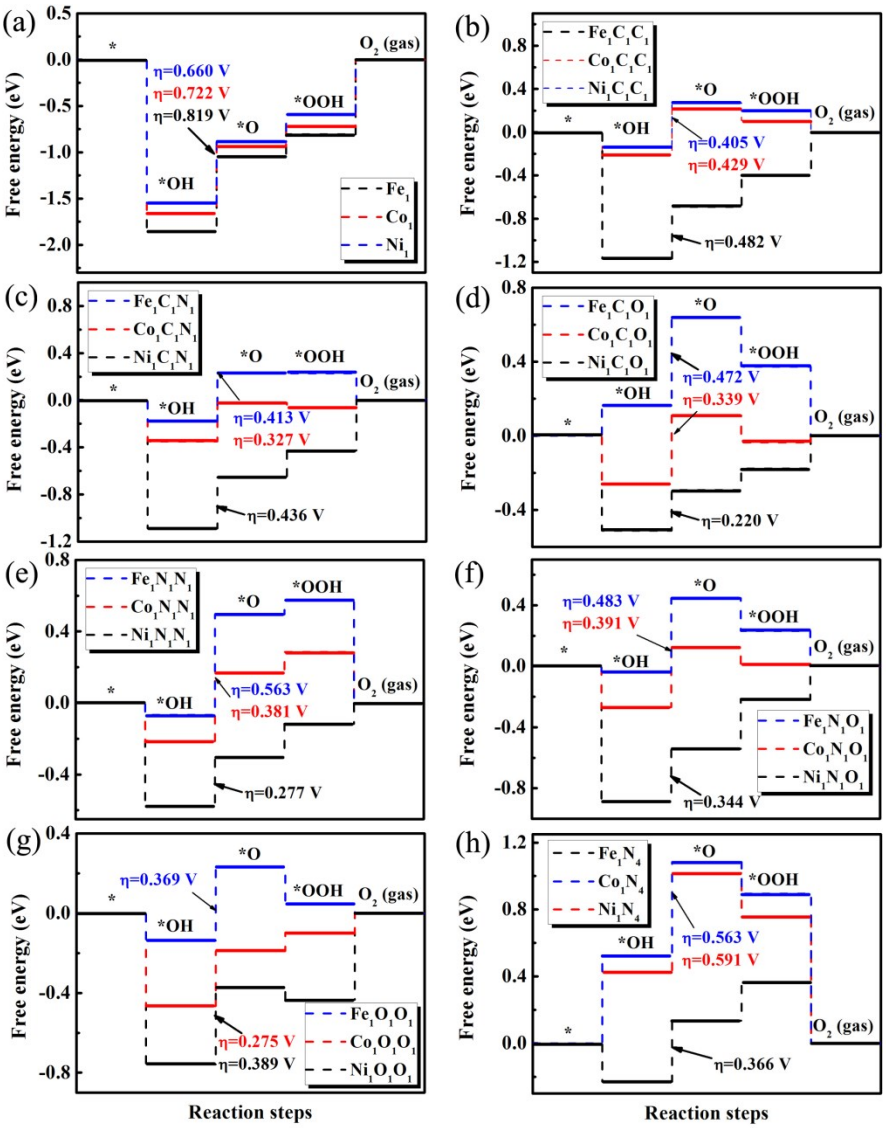

Fig. S5 Gibbs free energy change curves of all systems with potential U = 1.23 V vs RHE and without solvation effect.

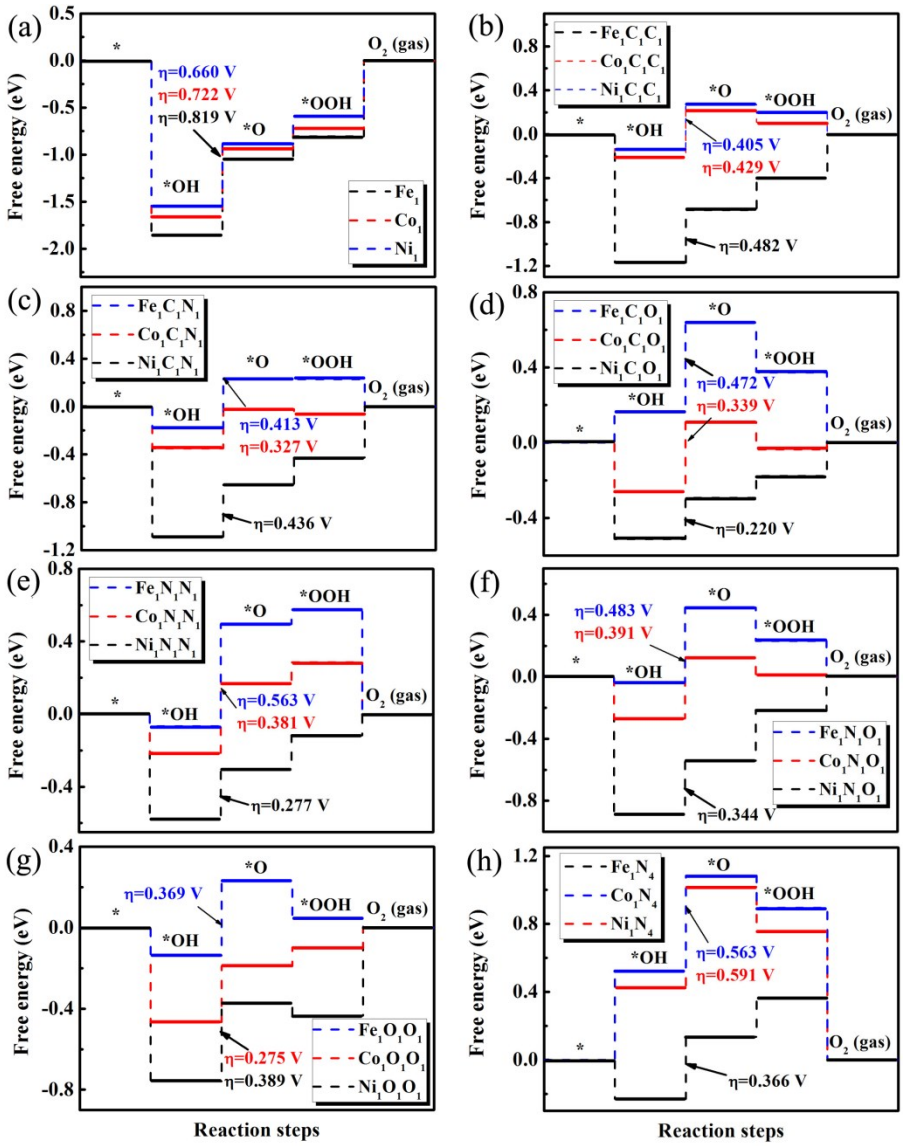

Fig. S6 Gibbs free energy change curves of all systems with potential U = 1.23 V vs RHE and with solvation effect.

Table S1 Band length ($d_{TM1\text{-}NM}$) and average bond length (d_{ave}) of the TM_1-NM bonds in all considered systems with unit of Å.

	$d_{TM1\text{-}NM}$	d_{ave}
Co_1	1.963, 1.963, 2.579, 2.585, 2.759, 2.763	2.435
$Co_1C_1C_1$	1.773, 1.788, 1.859, 1.876	1.824
$Co_1C_1N_1$	1.828, 1.842, 1.873, 1.938	1.870
$Co_1C_1O_1$	1.842, 1.892, 1.893, 1.934	1.890
$Co_1N_1N_1$	1.831, 1.871, 1.885, 1.915	1.878
$Co_1N_1O_1$	1.826, 1.837, 1.863, 1.967	1.873
$Co_1O_1O_1$	1.855, 1.879, 1.911, 1.951	1.899
Co_1N_4	1.892, 1.892, 1.892, 1.892	1.892
Fe_1	1.978, 1.978, 2.514, 2.517, 2.764, 2.766	2.420
$Fe_1C_1C_1$	1.786, 1.822, 1.896, 1.936	1.860
$Fe_1C_1N_1$	1.831, 1.841, 1.897, 1.976	1.886
$Fe_1C_1O_1$	1.848, 1.908, 1.913, 1.953	1.906
$Fe_1N_1N_1$	1.811, 1.843, 1.921, 1.950	1.881
$Fe_1N_1O_1$	1.805, 1.907, 1.908, 1.977	1.899
$Fe_1O_1O_1$	1.864, 1.893, 1.915, 1.959	1.908
Fe_1N_4	1.897, 1.897, 1.897, 1.897	1.897
Ni_1	1.984, 1.985, 2.452, 2.634, 2.701, 2.753	2.418
$Ni_1C_1C_1$	1.804, 1.810, 1.860, 1.876	1.838
$Ni_1C_1N_1$	1.843, 1.861, 1.876, 1.940	1.880
$Ni_1C_1O_1$	1.836, 1.861, 1.864, 1.924	1.871
$Ni_1N_1N_1$	1.849, 1.857, 1.884, 1.885	1.869
$Ni_1N_1O_1$	1.840, 1.867, 1.894, 1.916	1.879
$Ni_1O_1O_1$	1.882, 1.915, 1.947, 1.953	1.924
Ni_1N_4	1.893, 1.893, 1.893, 1.893	1.893

Table S2 Adsorption free energies of ΔG_{*OH}, ΔG_{*O} and ΔG_{*OOH} and theoretical η^{OER} values of all considered systems with and without solvation effect, unit of eV.

	Without solvation effect				With the solvation effect			
	ΔG_{*OH}	ΔG_{*O}	ΔG_{*OOH}	η^{OER}	ΔG_{*OH}	ΔG_{*O}	ΔG_{*OOH}	η^{OER}
Co_1	-0.431	1.521	2.970	0.722	-0.212	1.777	3.228	0.759
$Co_1C_1C_1$	1.017	2.676	3.797	0.429	1.258	2.927	4.045	0.439
$Co_1C_1N_1$	0.881	2.438	3.630	0.327	1.122	2.697	3.878	0.345
$Co_1C_1O_1$	0.972	2.541	3.655	0.339	1.215	2.814	3.901	0.369
$Co_1N_1N_1$	1.017	2.628	3.974	0.381	1.259	2.882	4.226	0.393
$Co_1N_1O_1$	0.962	2.583	3.701	0.391	1.206	2.835	3.956	0.399
$Co_1O_1O_1$	0.764	2.270	3.593	0.275	1.008	2.524	3.848	0.286
Co_1N_4	1.658	3.479	4.442	0.591	1.901	3.731	4.696	0.600
Fe_1	-0.634	1.415	2.843	0.819	-0.401	1.639	3.098	0.810
$Fe_1C_1C_1$	0.058	1.770	3.289	0.482	0.302	2.026	3.532	0.494
$Fe_1C_1N_1$	0.141	1.807	3.263	0.436	0.395	2.051	3.517	0.426
$Fe_1C_1O_1$	0.718	2.167	3.513	0.220	0.971	2.420	3.766	0.219
$Fe_1N_1N_1$	0.649	2.156	3.573	0.277	0.898	2.411	3.826	0.283
$Fe_1N_1O_1$	0.344	1.918	3.469	0.344	0.589	2.171	3.721	0.352
$Fe_1O_1O_1$	0.471	2.089	3.256	0.389	0.715	2.342	3.505	0.397
Fe_1N_4	0.999	2.595	4.057	0.366	1.242	2.858	4.306	0.386
Ni_1	-0.320	1.590	3.102	0.680	-0.098	1.838	3.326	0.706
$Ni_1C_1C_1$	1.095	2.730	3.882	0.405	1.352	2.989	4.139	0.407
$Ni_1C_1N_1$	1.050	2.692	3.919	0.413	1.399	3.097	4.172	0.368
$Ni_1C_1O_1$	1.396	3.098	4.064	0.472	1.650	3.353	4.319	0.468
$Ni_1N_1N_1$	1.163	2.956	4.264	0.563	1.415	3.212	4.518	0.567
$Ni_1N_1O_1$	1.195	2.908	3.922	0.483	1.449	3.164	4.179	0.485
$Ni_1O_1O_1$	1.093	2.692	3.735	0.369	1.347	2.951	3.989	0.374
Ni_1N_4	1.751	3.544	4.585	0.563	2.003	3.801	4.838	0.568