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

Electronic Supplementary Information

The interplay between structural perfectness and CO oxidation catalysis on aluminum, phosphorous, and silicon complexes of corroles

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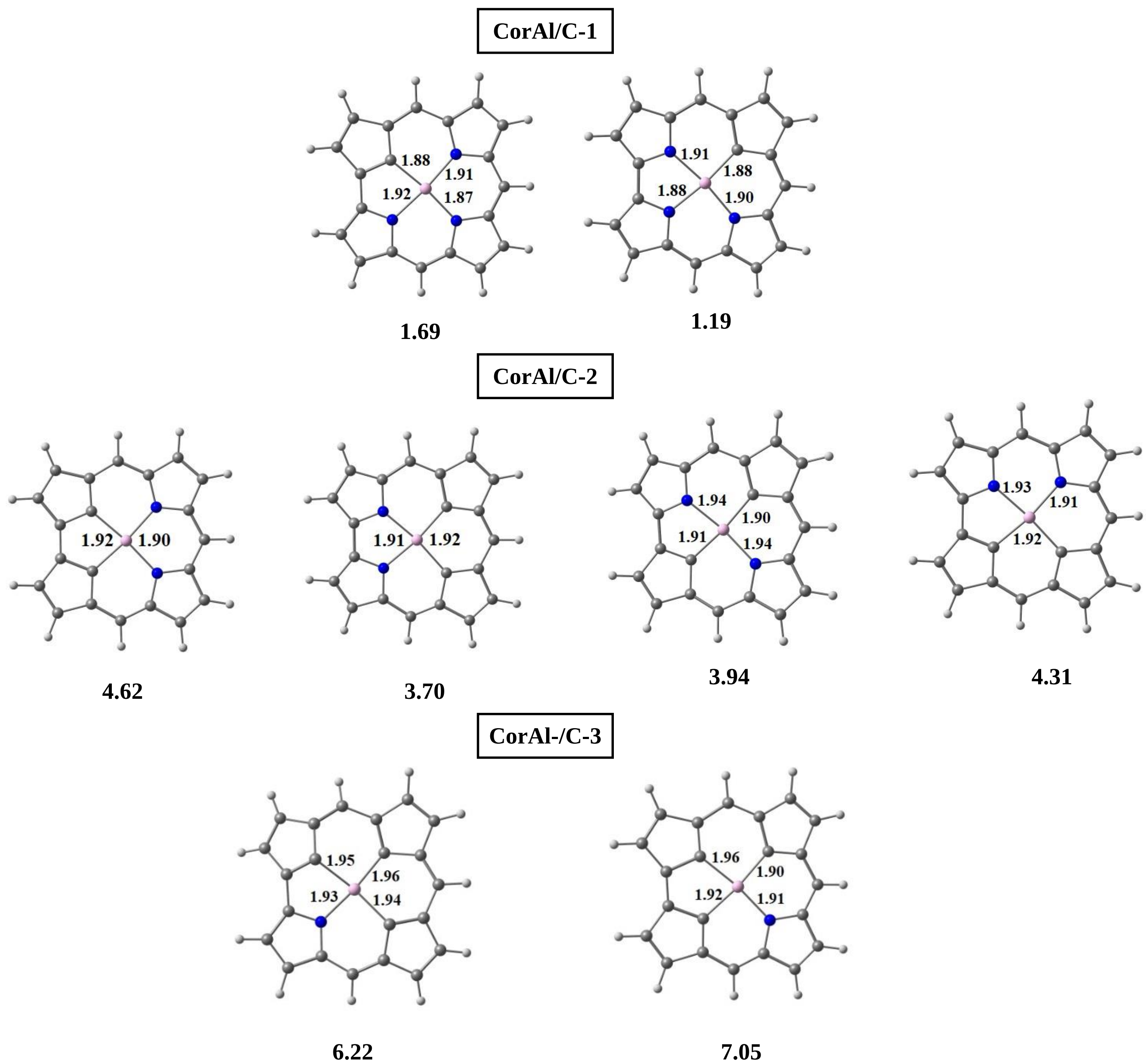

Fig. S1 Different configurations of defective corrole of type CorAl/C-*x*. The numbers are the defect formation energy in eV. In the figure, white, gray, dark blue, and pink balls represent H, C, N, and Al atoms.

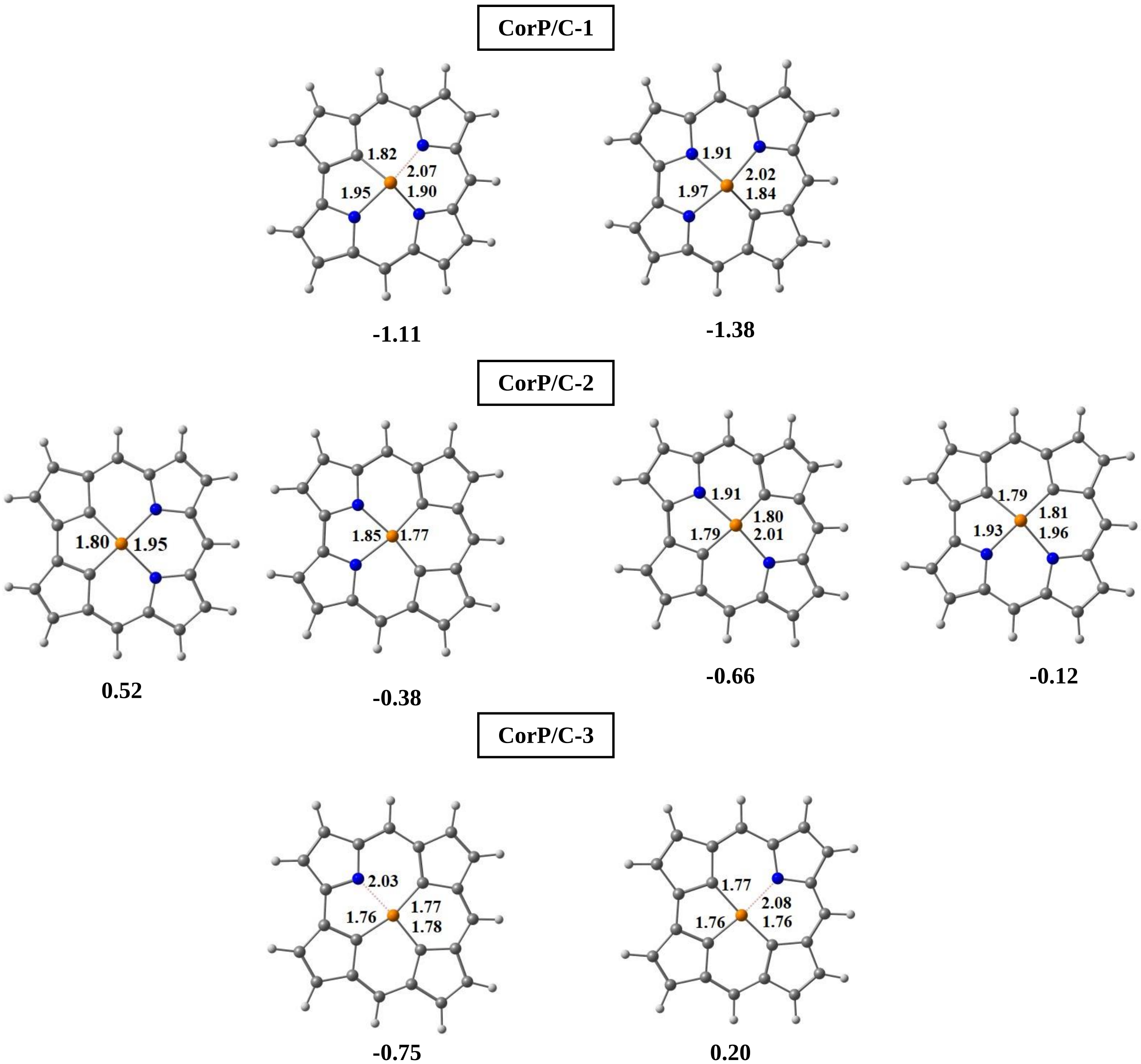

Fig. S2 Different configurations of defective corrole of type CorP/C-*x*. The numbers are the defect formation energy in eV. In the figure, white, gray, dark blue, and orange balls represent H, C, N, and P atoms.

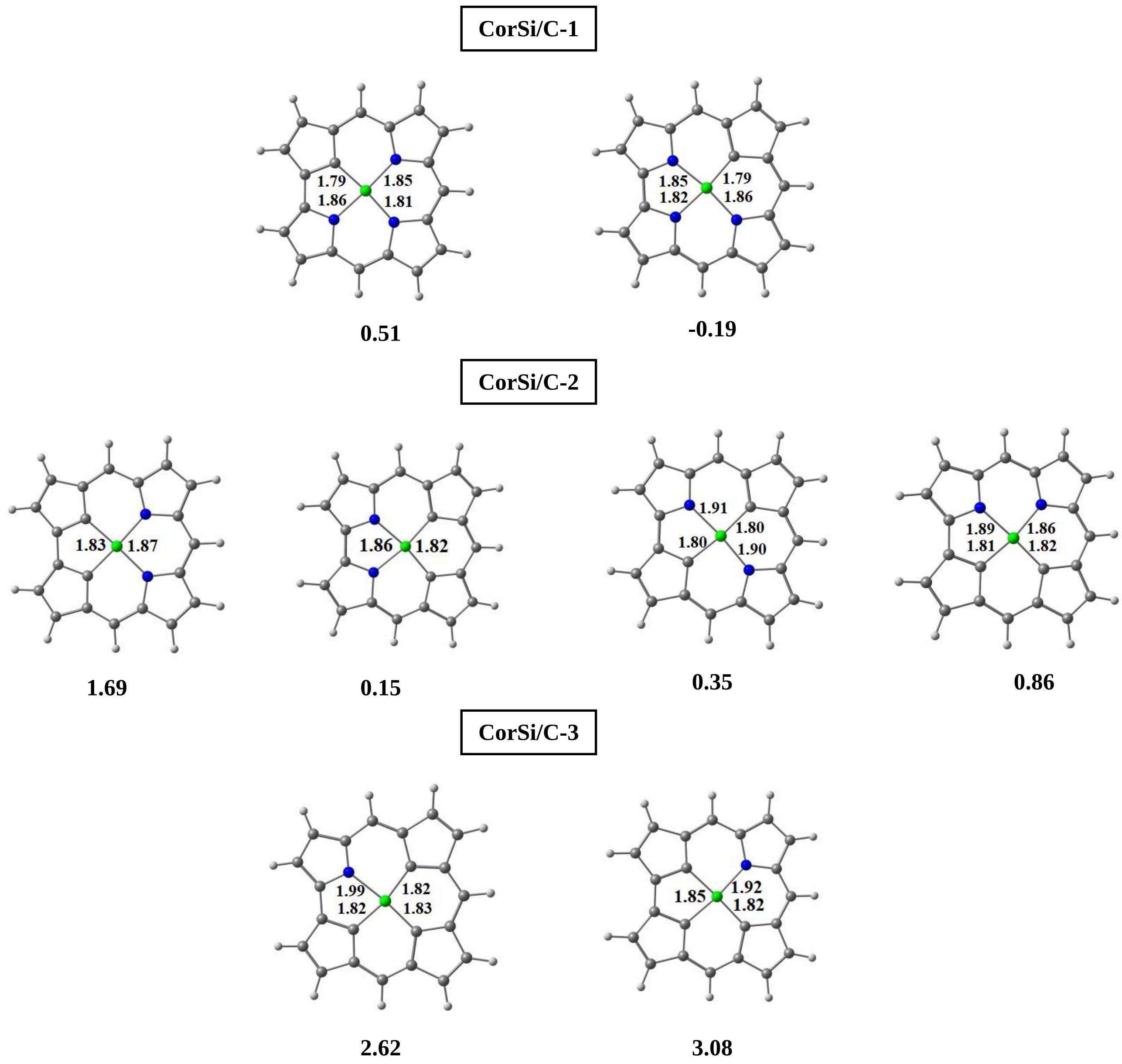

Fig. S3 Different configurations of defective corrole of type CorSi/C-*x*. The numbers are the defect formation energy in eV. In the figure, white, gray, dark blue, and green balls represent H, C, N, and Si atoms.

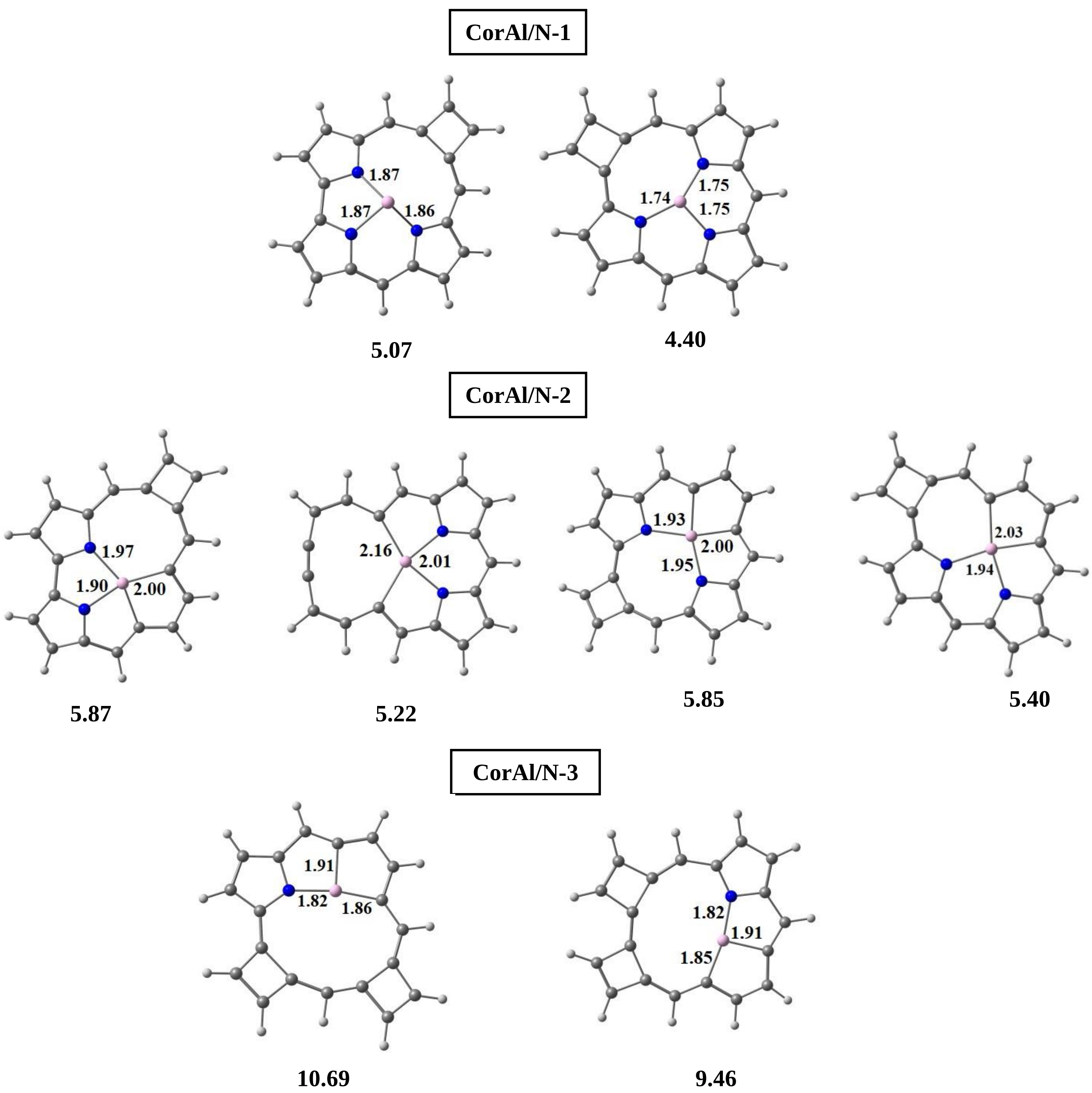

Fig. S4 Different configurations of defective corrole of type CorAl/N-*x*. The numbers are the vacancy formation energy in eV. In the figure, white, gray, dark blue, and pink balls represent H, C, N, and Al atoms.

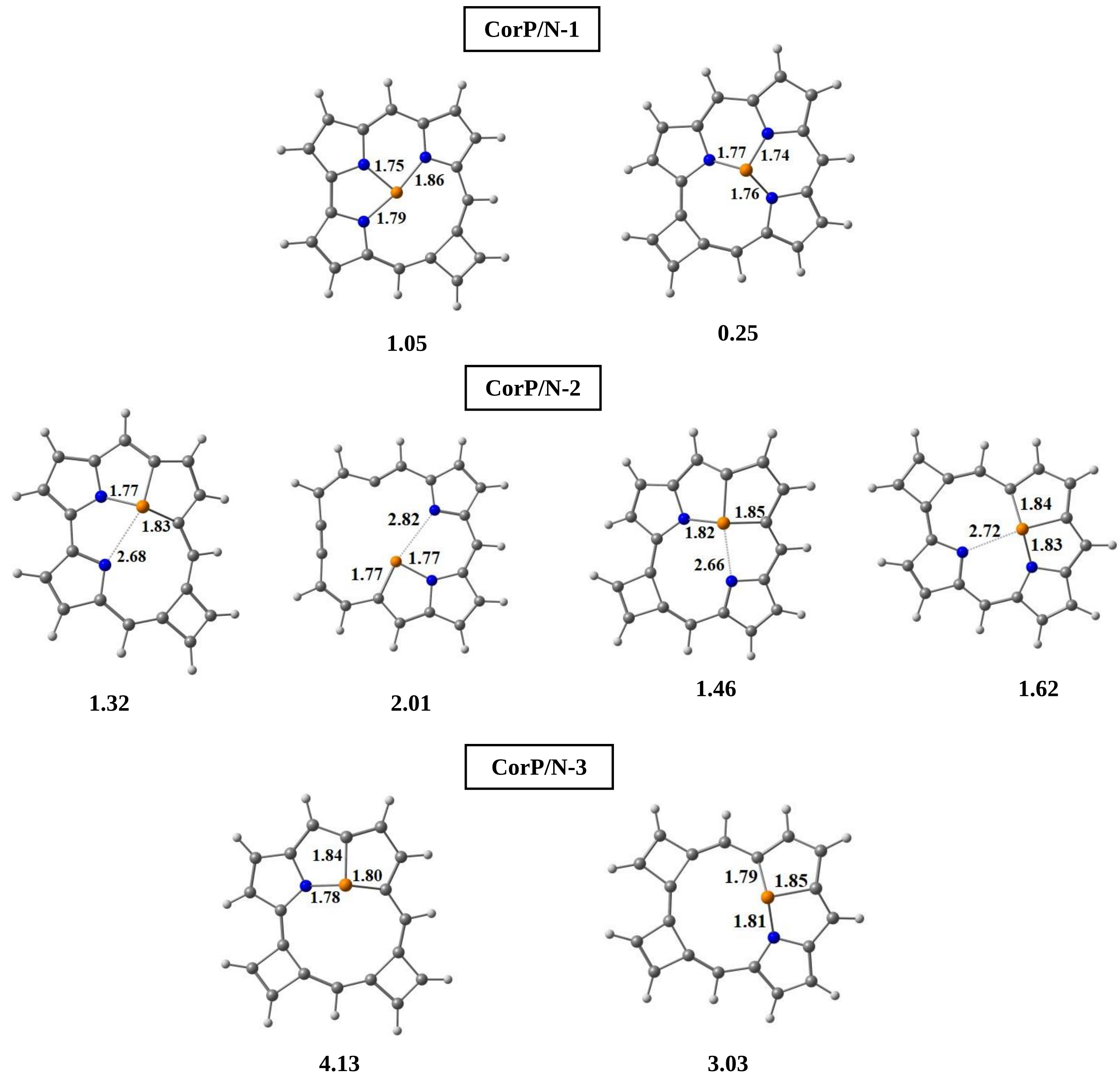

Fig. S5 Different configurations of defective corrole of type CorP/N-*x*. The numbers are the vacancy formation energy in eV. In the figure, white, gray, dark blue, and orange balls represent H, C, N, and P atoms.

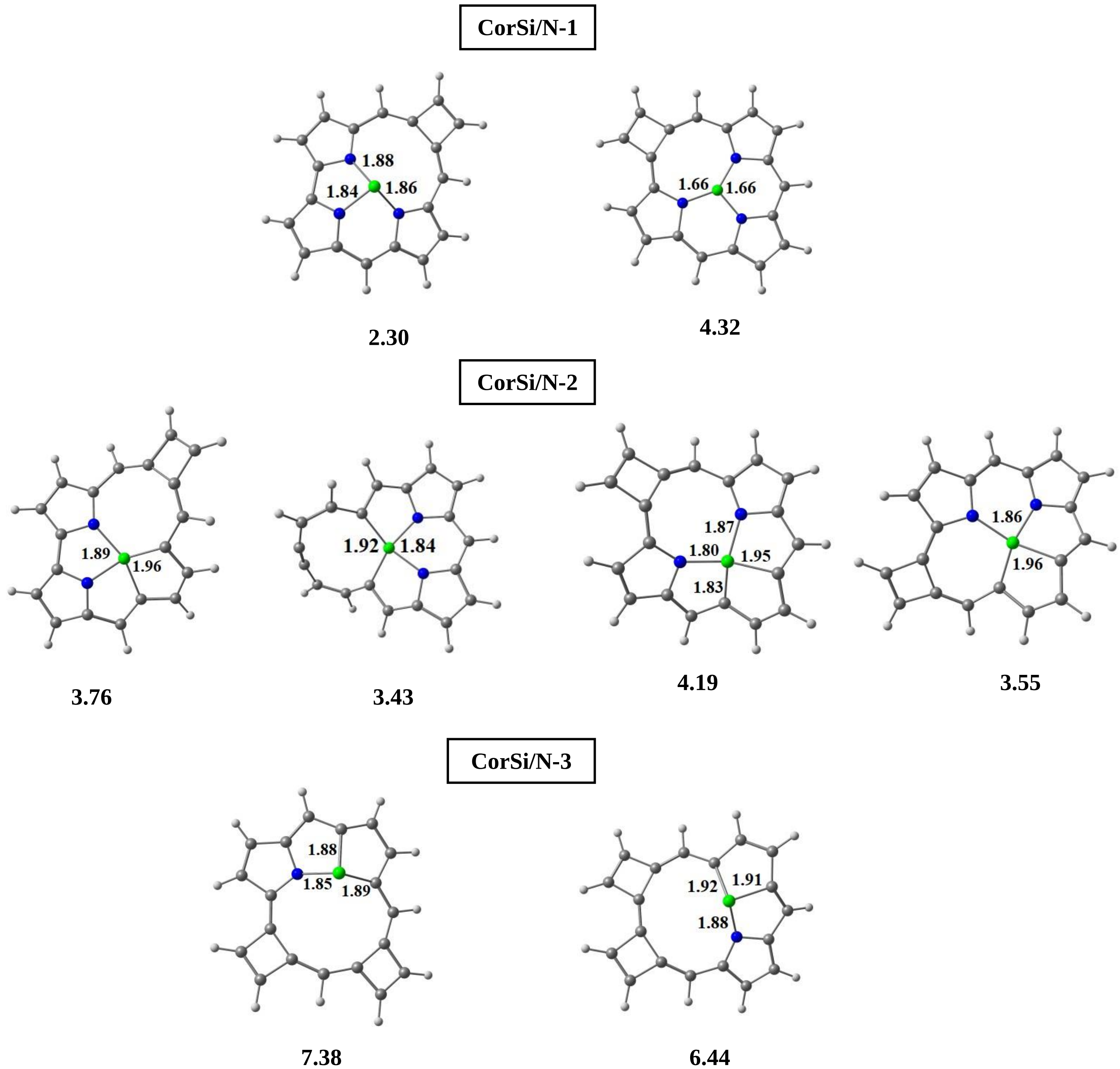

Fig. S6 Different configurations of defective corrole of type CorSi/N-*x*. The numbers are the vacancy formation energy in eV. In the figure, white, gray, dark blue, and green balls represent H, C, N, and Si atoms.

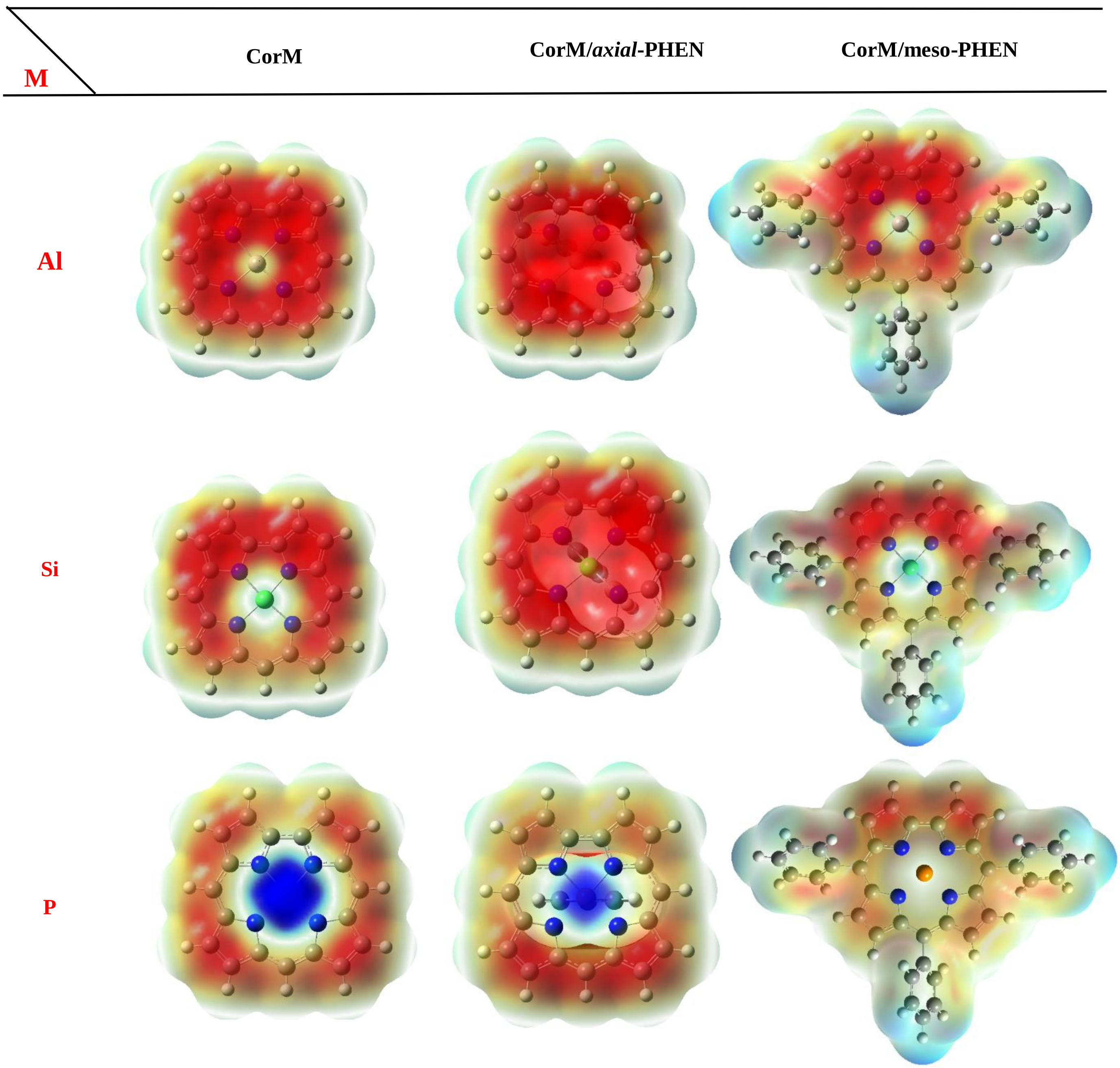

Fig. S7 The molecular electrostatic potential isosurface (0.0004 au) for CorM, CorM/*axial*-PHEN and CorM/*meso*-PHEN molecules.

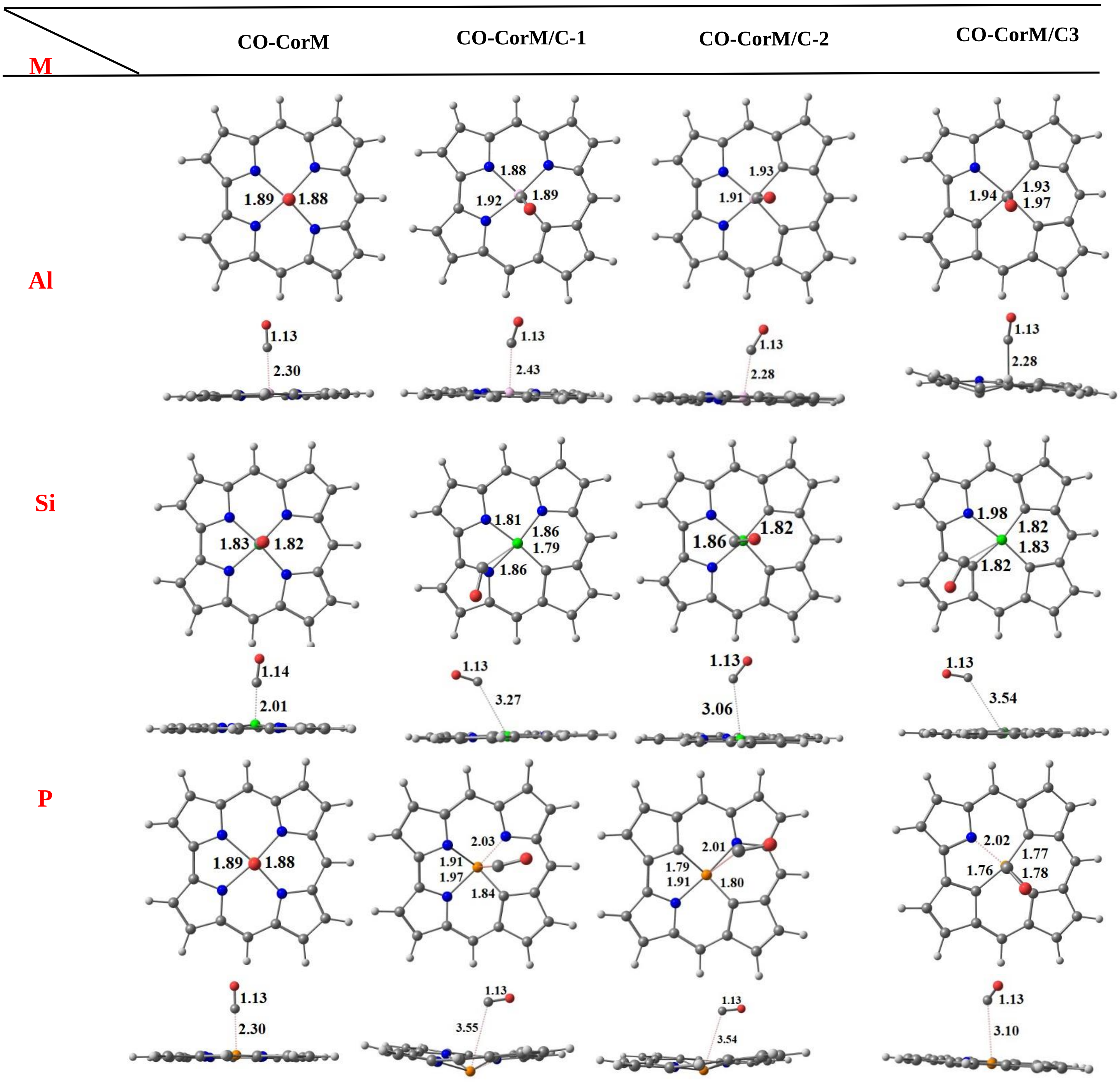

Fig. S8 Top and side views for the most stable configurations for CO adsorption on the perfect and defective corroles of type CorM/C-*x* (C: Gray; O: Red; N: Blue; H: White; Al: Pink; Si: Green; P: Orange).

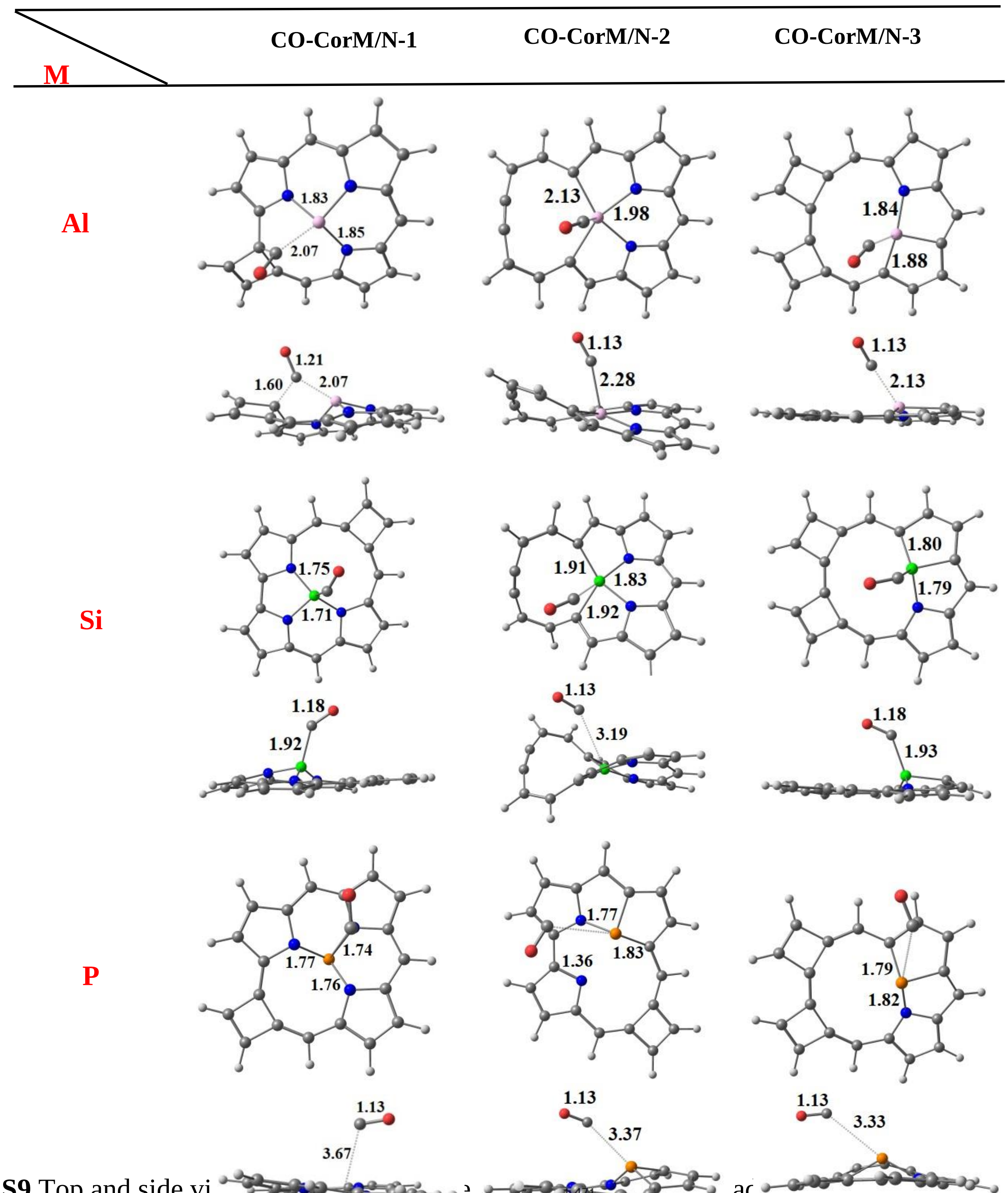

Fig. S9 Top and side vi … e … ac … defective corroles of type CorM/N-*x* (C: Gray; O: Red; N: Blue; H: White; Al: Pink; Si: Green; P: Orange).

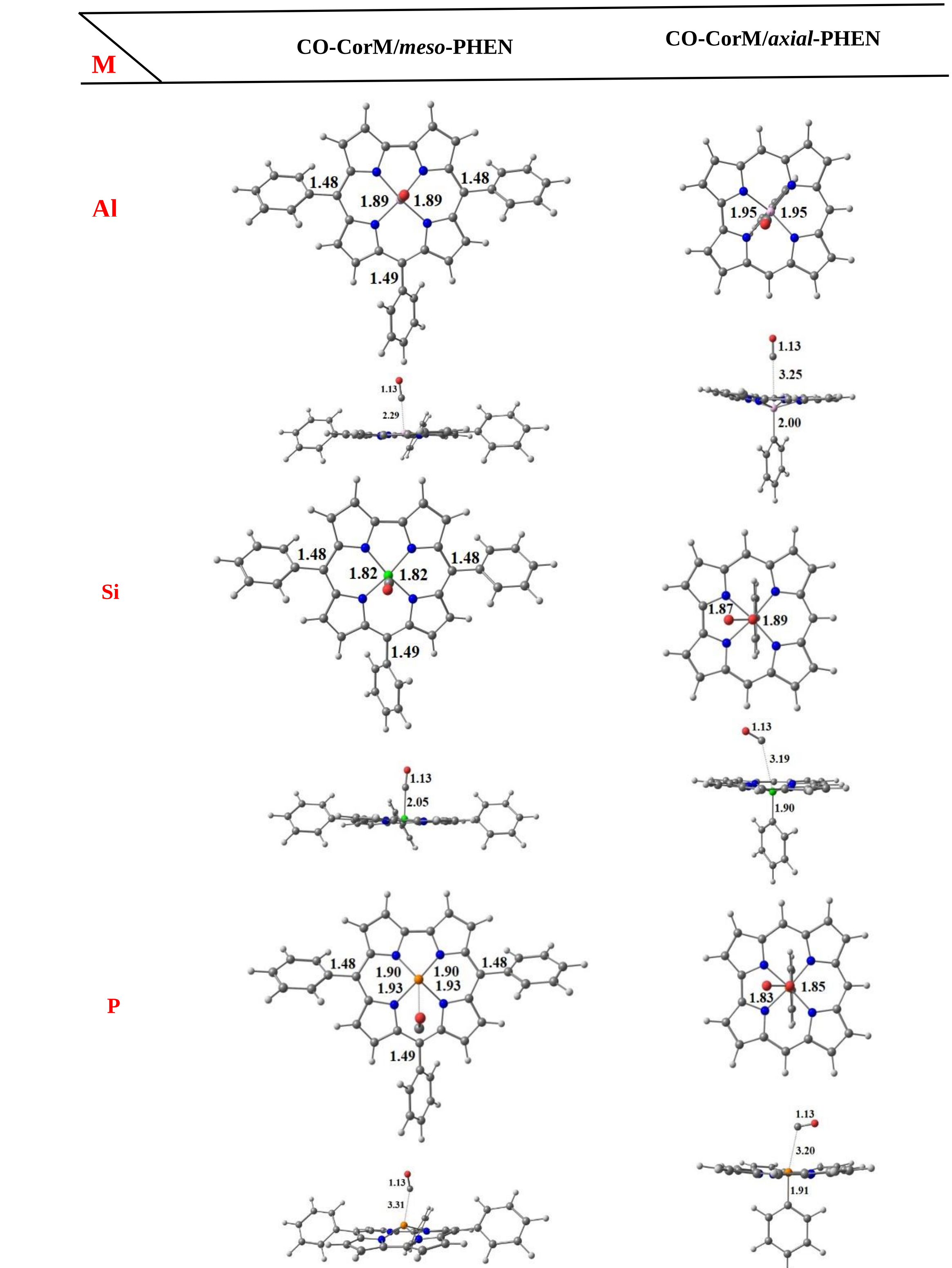

Fig. S10 Top and side views for the most stable configurations for CO adsorption on the phenyl substituted CorMs (C: Gray; O: Red; N: Blue; H: White; Al: Pink; Si: Green; P: Orange).

Table S1. The relative energies (eV) of perfect corroles with different charges and spin states calculated by different DFT methods. **Bold** values show the ground spin state.

	(Charge, multiplicity)	M06-2X	B3LYP	PBE	PBE0
CorAl	(3, 4)	33.29	32.26	31.93	32.71
	(3, 2)	31.91	30.98	31.00	31.40
	(2, 3)	17.80	17.03	17.05	17.34
	(2, 1)	17.72	17.09	17.10	17.41
	(1, 4)	9.35	8.70	8.73	8.89
	(1, 2)	7.37	6.94	6.98	7.12
	(0, 1)	0.91	0.73	0.75	0.82
	(0, 3)	2.70	2.42	2.44	2.50
	(-1, 2)	**0.00**	**0.00**	**0.00**	**0.00**
	(-1, 4)	1.82	1.71	1.77	1.67
	(-2, 1)	2.94	3.13	3.02	3.10
	(-2, 3)	3.09	3.21	3.17	3.15
	(-3, 2)	9.53	9.88	9.76	9.78
	(-3, 4)	10.96	10.38	10.89	10.22
CorP	(3, 4)	32.50	31.43	29.89	3.30
	(3, 2)	31.49	30.81	29.30	29.59
	(2, 3)	17.60	16.92	15.50	15.75
	(2, 1)	17.20	16.77	15.24	15.45
	(1, 4)	9.18	8.67	7.26	7.38
	(1, 2)	7.12	6.71	5.30	5.44
	(0, 1)	0.99	0.80	0.59	0.52
	(0, 3)	2.39	2.29	0.83	0.90
	(-1, 2)	**0.00**	**0.00**	**0.00**	**0.00**
	(-1, 4)	1.56	1.45	0.62	0.43
	(-2, 1)	2.88	3.07	1.58	1.63
	(-2, 3)	4.57	4.49	1.74	2.99
	(-3, 2)	11.05	9.82	8.27	9.55
	(-3, 4)	11.08	11.14	8.80	9.58
CorSi	(3, 3)	30.57	29.68	29.71	29.57
	(3, 1)	30.67	29.88	29.78	29.79
	(2, 4)	17.31	17.54	17.57	17.31
	(2, 2)	16.27	15.71	15.78	15.48
	(1, 3)	7.84	7.43	7.41	7.09
	(1, 1)	5.72	5.45	5.53	5.11
	(0, 2)	1.11	1.02	1.07	0.58
	(0, 4)	3.27	2.99	2.61	2.54
	(-1, 1)	**0.00**	**0.00**	**0.00**	**0.00**
	(-1, 3)	0.28	0.48	0.44	0.32
	(-2, 2)	3.41	3.07	2.99	2.50
	(-2, 4)	3.05	3.16	3.13	2.58
	(-3, 1)	10.21	9.30	9.14	8.86
	(-3, 3)	9.50	9.83	9.73	9.22

Table S2.. The relative energy (eV) of different structures for defected corroles with charge -1 and different spin states calculated by different DFT methods. Latin numbers refer to the geometrical isomers shown in Figs. S1- S6. **Bold** values show the ground spin state.

		(Charge, multiplicity)	M06-2X	B3LYP	PBE	PBE0
CorAl/C-1	**I**	(-1, 1)	0.52	0.50	0.47	0.50
		(-1, 3)	1.98	1.65	1.79	1.43
	II	**(-1, 1)**	**0.00**	**0.00**	**0.00**	**0.00**
		(-1, 3)	1.38	1.68	1.40	1.29
CorAl/C-2	**I**	(-1, 2)	0.94	0.74	0.65	0.78
		(-1, 4)	2.41	2.16	2.02	2.13
	II	**(-1, 2)**	**0.00**	**0.00**	**0.00**	**0.00**
		(-1, 4)	1.95	2.65	1.71	1.68
	III	(-1, 2)	0.24	0.22	0.17	0.23
		(-1, 4)	1.85	2.54	1.58	1.58
	IV	(-1, 2)	0.61	0.56	0.48	0.58
		(-1, 4)	2.09	2.31	1.88	1.85
CorAl/C-3	**I**	**(-1, 1)**	**0.00**	**0.00**	**0.00**	**0.00**
		(-1, 3)	0.82	1.17	0.61	0. 54
	II	(-1, 1)	0.85	0.70	0.75	0.76
		(-1, 3)	0.98	1.59	0.71	0.65
CorAl/N-1	**I**	(-1, 1)	0.62	0.49	0.63	0.51
		(-1, 3)	0.74	1.53	1.00	0.95
	II	**(-1, 1)**	**0.00**	**0.00**	**0.00**	**0.00**
		(-1, 3)	0.73	0.50	0.33	0.38
CorAl/N-2	**I**	(-1, 2)	1.89	3.39	1.57	3.43
		(-1, 4)	3.39	4.06	3.19	3.51
	II	**(-1, 2)**	**0.00**	**0.00**	**0.00**	**0.00**
		(-1, 4)	1.22	1.99	1.02	0.97
	III	(-1, 2)	0.54	0.71	0.84	0.53
		(-1, 4)	2.73	3.99	3.14	3.17
	IV	(-1, 2)	0.09	0.14	0.07	0.16
		(-1, 4)	1.98	2.67	1.74	1.92
CorAl/N-3	**I**	(-1, 1)	1.45	1.31	1.18	1.63
		(-1, 3)	**0.00**	**0.00**	**0.00**	**0.00**
	II	(-1, 1)	0.43	0.23	0.29	0.35
		(-1, 3)	0.67	0.63	0.52	0.72
CorSi/C-1	**I**	(-1, 2)	0.70	0.65	0.60	0.67

		(-1, 4)	2.64	2.40	2.31	2.44
	II	**(-1, 2)**	**0.00**	**0.00**	**0.00**	**0.00**
		(-1, 4)	2.29	2.10	2.08	2.07
CorSi/C-2	**I**	(-1, 1)	1.58	1.47	1.36	1.49
		(-1, 3)	3.24	3.16	2.37	3.16
	II	**(-1, 1)**	**0.00**	**0.00**	**0.00**	**0.00**
		(-1, 3)	2.09	1.92	1.88	1.91
	III	(-1, 1)	0.22	0.16	0.13	0.17
		(-1, 3)	1.99	1.79	1.73	1.80
	IV	(-1, 1)	0.73	0.66	0.60	0.67
		(-1, 3)	2.37	2.19	2.15	2.20
CorSi/C-3	**I**	**(-1, 2)**	**0.00**	**0.00**	**0.00**	**0.00**
		(-1, 4)	2.09	1.81	1.74	1.80
	II	(-1, 2)	0.45	0.34	0.28	0.33
		(-1, 4)	2.24	1.96	1.91	1.92
CorSi/N-1	**I**	**(-1, 2)**	**0.00**	**0.00**	**0.00**	**0.00**
		(-1, 4)	2.42	2.99	2.73	2.77
	II	(-1, 2)	0.51	0.44	0.46	0.41
		(-1, 4)	1.01	1.21	1.20	1.17
CorSi/N-2	**I**	(-1, 1)	0.30	0.43	0.38	0.27
		(-1, 3)	0.96	0.82	0.72	0.65
	II	**(-1, 1)**	**0.00**	**0.00**	**0.00**	**0.00**
		(-1, 3)	1.30	1.08	1.10	1.21
	III	(-1, 1)	0.77	0.73	0.55	0.63
		(-1, 3)	1.06	0.93	0.85	0.77
	IV	(-1, 1)	0.11	0.11	0.13	0.11
		(-1, 3)	0.71	0.51	0.40	0.36
CorSi/N-3	**I**	(-1, 2)	0.98	0.80	0.70	0.79
		(-1, 4)	1.52	1.28	1.26	1.24
	II	**(-1, 2)**	**0.00**	**0.00**	**0.00**	**0.00**
		(-1, 4)	1.57	1.69	1.57	1.55
CorP/C-1	**I**	(-1, 1)	0.28	0.27	0.25	0.27
		(-1, 3)	1.31	1.61	1.17	1.57
	II	**(-1, 1)**	**0.00**	**0.00**	**0.00**	**0.00**
		(-1, 3)	0.74	0.73	0.74	0.62
CorP/C-2	**I**	(-1, 2)	1.20	1.14	1.06	1.17
		(-1, 4)	2.60	2.28	2.21	2.33

	II	(-1, 2)	0.31	0.38	0.33	0.30
		(-1, 4)	2.54	1.93	1.92	1.96
	III	**(-1, 2)**	**0.00**	**0.00**	**0.00**	**0.00**
		(-1, 4)	1.77	1.62	1.62	1.63
	IV	(-1, 2)	0.54	0.48	0.44	0.51
		(-1, 4)	2.26	2.04	2.03	2.08
CorP/C-3	**I**	**(-1, 1)**	**0.00**	**0.00**	**0.00**	**0.00**
		(-1, 3)	1.90	1.72	1.69	1.74
	II	(-1, 1)	0.90	0.86	0.80	0.88
		(-1, 3)	2.35	2.13	2.03	2.14
CorP/N-1	**I**	(-1, 1)	0.84	0.87	0.62	0.85
		(-1, 3)	1.27	1.25	1.18	1.21
	II	**(-1, 1)**	**0.00**	**0.00**	**0.00**	**0.00**
		(-1, 3)	1.24	0.71	0.69	0.68
CorP/N-2	**I**	**(-1, 2)**	**0.00**	**0.00**	**0.00**	**0.00**
		(-1, 4)	2.11	1.89	1.84	1.85
	II	(-1, 2)	0.75	0.59	0.65	0.73
		(-1, 4)	2.08	1.69	2.04	2.19
	III	(-1, 2)	0.17	0.17	0.19	0.18
		(-1, 4)	2.04	1.74	1.64	1.74
	IV	(-1, 2)	0.33	0.22	0.18	0.26
		(-1, 4)	1.66	1.37	1.33	1.42
CorP/N-3	**I**	(-1, 1)	1.16	1.12	0.97	1.00
		(-1, 3)	1.36	1.10	1.06	1.06
	II	**(-1, 1)**	**0.00**	**0.00**	**0.00**	**0.00**
		(-1, 3)	1.33	1.13	1.09	1.16

Table S3. Adsorption energy (eV) of C-end on and O-end on configurations of CO with different charge and multiplicities on perfect and defective CorMs at M062X/6-31G(d) level.

	(Charge, multiplicity)	CO	OC
CorAl	(-1, 1)	**-0.38**	-0.27
	(-1, 3)	1.31	1.59
CorAl/C-1	(-1, 2)	**-0.27**	-0.23
	(-1, 4)	0.93	-0.01
CorAl/C-2	(-1, 1)	**-0.34**	-0.16
	(-1, 3)	1.55	1.78
CorAl/C-3	(-1, 1)	**-0.24**	0.19
	(-1, 3)	0.44	0.67
CorAl/N-1	(-1, 1)	**-1.02**	-0.92
	(-1, 3)	-0.84	-0.49
CorAl/N-2	(-1, 2)	**-0.31**	-0.27
	(-1, 4)	1.58	1.73
CorAl/N-3	(-1, 1)	**-0.60**	-0.31
	(-1, 3)	-0.13	0.15
CorSi	(-1, 1)	**-0.40**	-0.13
	(-1, 3)	-1.13	-0.26
CorSi/C-1	(-1, 2)	**-0.22**	0.34
	(-1, 4)	1.09	2.00
CorSi/C-2	(-1, 1)	**-0.14**	0.07
	(-1, 3)	1.73	1.85
CorSi/C-3	(-1, 2)	**-0.19**	-0.06
	(-1, 4)	1.80	2.66
CorSi/N-1	(-1, 2)	**0.69**	1.68
	(-1, 4)	1.13	3.04
CorSi/N-2	(-1, 1)	**-0.24**	-0.19
	(-1, 3)	0.99	1.02
CorSi/N-3	(-1, 2)	**0.05**	1.08
	(-1, 4)	0.10	2.13
CorP	(-1, 2)	**-0.22**	-0.16
	(-1, 4)	-0.19	-0.10
CorP/C-1	(-1, 1)	**-0.21**	0.05
	(-1, 3)	0.53	0.54
CorP/C-2	(-1, 2)	**-0.19**	-0.15
	(-1, 4)	1.57	1.57

CorP/C-3	(-1, 1)	**-0.03**	0.10
	(-1, 3)	1.71	1.71
CorP/N-1	(-1, 1)	**-0.21**	-0.18
	(-1, 3)	0.63	0.64
CorP/N-2	(-1, 2)	**-0.18**	-0.15
	(-1, 4)	1.96	1.89
CorP/N-3	(-1, 1)	**-0.17**	-0.12
	(-1, 3)	1.15	1.15

Table S4. Adsorption energy (eV) of end-on and side-on configurations of O_2 with different charge and multiplicities on perfect and defective CorMs at M062X/6-31G(d) level.

	(Charge, multiplicity)	End-on	Side-on
CorAl	(-1, 2)	**-2.11**	–
	(-1, 4)	-0.73	–
CorAl/C-1	(-1, 1)	0.51	**-1.40**
	(-1, 3)	-0.67	-0.49
CorAl/C-2	(-1, 2)	**-0.65**	–
	(-1, 4)	0.04	–
CorAl/C-3	(-1, 1)	–	**-1.84**
	(-1, 3)	0.00	-1.01
CorAl/N-1	(-1, 1)	**-3.44**	–
	(-1, 3)	-3.24	–
CorAl/N-2	(-1, 2)	**-1.47**	-1.31
	(-1, 4)	-0.32	-0.28
CorAl/N-3	(-1, 1)	–	**-3.70**
	(-1, 3)	–	-2.67
CorSi	(-1, 1)	**-3.92**	-3.37
	(-1, 3)	-3.16	-1.73
CorSi/C-1	(-1, 2)	**-2.24**	-1.88
	(-1, 4)	-0.93	0.00
CorSi/C-2	(-1, 1)	–	-0.09
	(-1, 3)	**-0.49**	0.73
CorSi/C-3	(-1, 2)	**-0.64**	–
	(-1, 4)	-0.28	–
CorSi/N-1	(-1, 2)	–	**-3.60**
	(-1, 4)	-0.29	-1.49
CorSi/N-2	(-1, 1)	**-2.16**	-1.96
	(-1, 3)	–	–
CorSi/N-3	(-1, 2)	-1.17	**-1.79**
	(-1, 4)	-0.55	-0.75
CorP	(-1, 2)	**-2.11**	-1.03
	(-1, 4)	-1.72	-0.84
CorP/C-1	(-1, 1)	**-0.89**	-1.00
	(-1, 3)	-0.07	-0.52
CorP/C-2	(-1, 2)	**-1.15**	-0.98
	(-1, 4)	1.32	0.4

CorP/C-3	(-1, 1)	–	**1.02**
	(-1, 3)	–	1.68
CorP/N-1	(-1, 1)	–	**-1.78**
	(-1, 3)	–	-1.04
CorP/N-2	(-1, 2)	-0.09	**-0.72**
	(-1, 4)	0.65	1.14
CorP/N-3	(-1, 1)	–	**-1.79**
	(-1, 3)	0.29	0.27