Electronic Supplementary Information

Unravelling the Effects of Functional Groups on the Adsorption of 2-Mercaptobenzothiazole on the Copper Surface: A DFT Study

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Table S1. Effect of basis set selection on calculated quantum chemical parameters of MBT derivatives.

Compound	B3LYP/6-31+G(d,p)				B3LYP/Def2-TZVP			
	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)	μ (Debye)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)	μ (Debye)
MBT-H	-5.963	-1.524	4.439	5.115	-5.906	-1.431	4.475	4.804
MBT-CH_3	-5.848	-1.432	4.416	5.672	-5.795	-1.347	4.448	5.316
MBT-OH	-5.804	-1.436	4.368	6.204	-5.730	-1.343	4.387	5.953
MBT-COOH	-6.258	-2.204	4.055	2.380	-6.192	-2.085	4.107	2.194
MBT-NO_2	-6.581	-3.118	3.463	3.319	-6.504	-2.927	3.577	3.175

Table S2. HOMO and LUMO distributions of MBT derivatives.

Compound	HOMO distribution (%)				LUMO distribution (%)			
	S1	S_m	N3	R	S1	S_m	N	R
MBT-H	13.35	**44.85**	7.90	0.54	9.15	**24.04**	6.16	0.92
MBT-CH_3	11.81	**43.30**	8.21	1.92	8.76	**23.73**	6.35	2.10
MBT-OH	8.36	**39.68**	9.05	4.97	6.48	**21.32**	6.06	1.29
MBT-SH	7.10	**34.40**	8.22	14.07	7.39	**22.31**	5.61	2.65
MBT-NH_2	5.45	**32.44**	8.59	11.67	7.03	**21.82**	6.63	2.07
MBT-OCH_3	8.52	**38.17**	8.54	6.60	8.07	**23.32**	7.14	1.80
MBT-$NHCH_3$	4.55	**28.77**	7.97	15.24	7.88	**22.87**	7.36	2.00
MBT-Cl	11.32	**42.56**	8.41	4.00	7.32	**22.28**	5.33	2.13
MBT-COOH	14.60	**44.27**	7.38	2.51	5.40	**13.20**	2.55	21.68
MBT-NO_2	15.29	**45.05**	7.42	2.32	1.61	**4.76**	1.54	55.80

Table S3. Fukui indices for electrophilic attack (f^-) of MBT derivatives.

Compound	S1	S_m	N3	X in R*	H8	C4	C5	C6	C7
MBT-H	-0.1483	**-0.3482**	-0.0517	-0.0361	-0.0300	-0.0366	-0.0607	-0.0679	-0.0328
MBT-CH_3	-0.1353	**-0.3337**	-0.0525	-0.0199	-0.0293	-0.0362	-0.0596	-0.0565	-0.0266
MBT-OH	-0.1209	**-0.3200**	-0.0531	-0.0655	-0.0295	-0.0412	-0.0637	-0.0558	-0.0304
MBT-SH	-0.1072	**-0.2855**	-0.0474	-0.1722	-0.0270	-0.0375	-0.0532	-0.0423	-0.0241
MBT-NH_2	-0.1049	**-0.2881**	-0.0486	-0.0832	-0.0279	-0.0396	-0.0643	-0.0503	-0.0303
MBT-OCH_3	-0.1171	**-0.3059**	-0.0494	-0.0565	-0.0286	-0.0361	-0.0633	-0.0516	-0.0270
MBT-$NHCH_3$	-0.0953	**-0.2652**	-0.0441	-0.0812	-0.0265	-0.0369	-0.0617	-0.0414	-0.0308
MBT-Cl	-0.1308	**-0.3256**	-0.0519	-0.1170	-0.0290	-0.0372	-0.0559	-0.0499	-0.0258
MBT-COOH	-0.1475	**-0.3366**	-0.0492	-0.0162	-0.0286	-0.0341	-0.0498	-0.0549	-0.0275
MBT-NO_2	-0.1523	**-0.3400**	-0.0482	-0.0067	-0.0300	-0.0350	-0.0490	-0.0514	-0.0298

**Atom X in functional group R that bonded to C6.*

Table S4. Fukui indices for nucleophilic attack (f^+) of MBT derivatives.

Compound	S1	S_m	N3	X in R*	H8	C4	C5	C6	C7
MBT-H	-0.1186	**-0.2676**	-0.0304	-0.0410	-0.0281	-0.0747	-0.0485	-0.0691	-0.0685
MBT-CH_3	-0.1125	**-0.2587**	-0.0303	-0.0199	-0.0273	-0.0751	-0.0451	-0.0530	-0.0654
MBT-OH	-0.1062	**-0.2523**	-0.0313	-0.0382	-0.0272	-0.0890	-0.0619	-0.0469	-0.0701
MBT-SH	-0.1053	**-0.2503**	-0.0274	-0.0922	-0.0259	-0.0797	-0.0431	-0.0481	-0.0671
MBT-NH_2	-0.1062	**-0.2511**	-0.0327	-0.0335	-0.0274	-0.0848	-0.0582	-0.0457	-0.0632
MBT-OCH_3	-0.1086	**-0.2544**	-0.0333	-0.0258	-0.0278	-0.0828	-0.0601	-0.0463	-0.0607
MBT-$NHCH_3$	-0.1064	**-0.2505**	-0.0341	-0.0238	-0.0276	-0.0825	-0.0595	-0.0416	-0.0565
MBT-Cl	-0.1069	**-0.2533**	-0.0269	-0.0941	-0.0260	-0.0807	-0.0451	-0.0514	-0.0714
MBT-COOH	-0.0986	**-0.2097**	-0.0172	-0.0680	-0.0223	-0.0502	-0.0381	-0.0547	-0.0621
MBT-NO_2	-0.0728	**-0.1634**	-0.0152	-0.0929	-0.0184	-0.0418	-0.0359	-0.0296	-0.0504

**Atom X in functional group R that bonded to C6.*

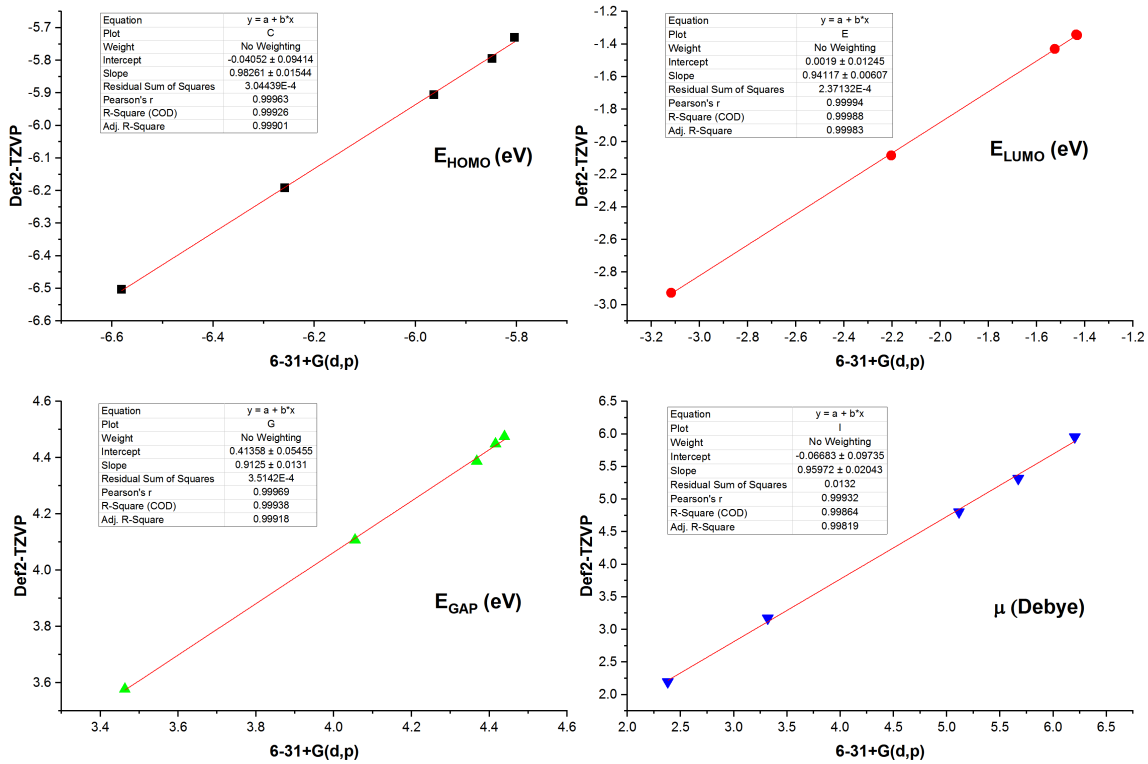

Fig. S1. Correlation between quantum chemical parameters of MBT derivatives calculated using 6-31+G(d,p) and Def2-TZVP basis sets, respectively.

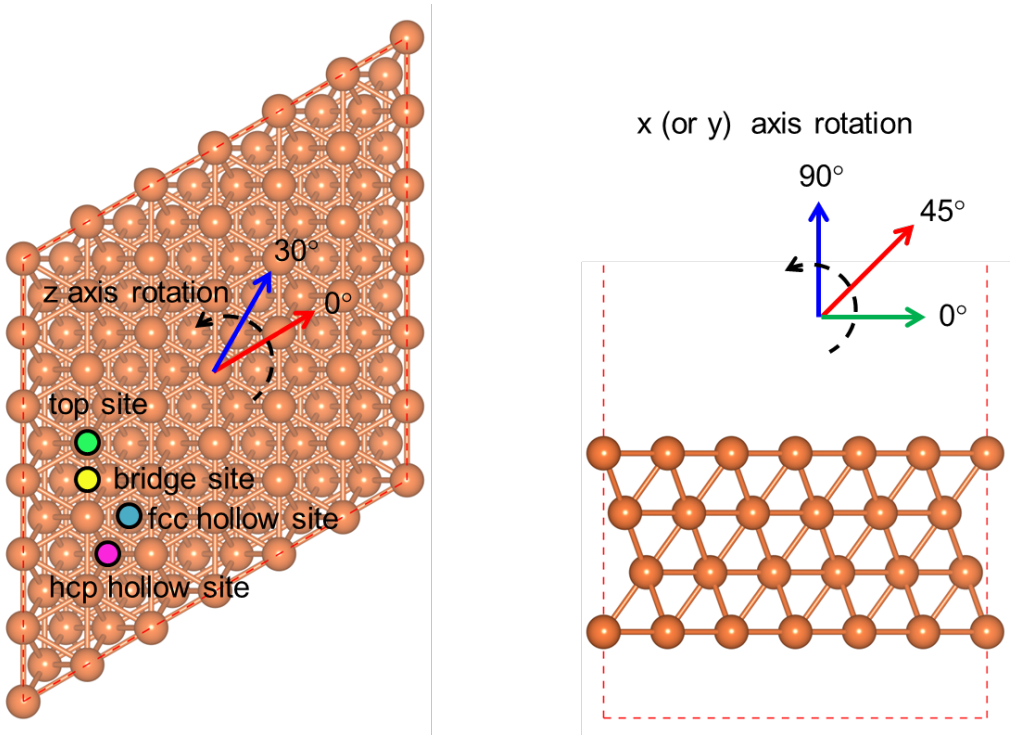

Fig. S2. The diagram illustrates high-symmetry adsorption sites and orientations.

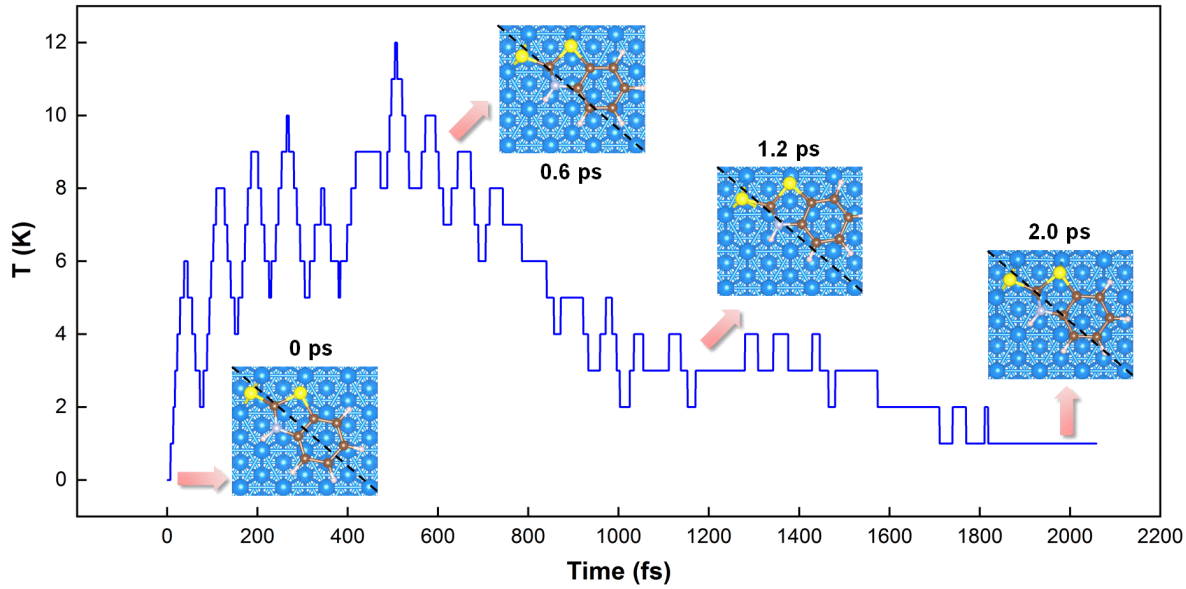

Fig. S3. The ab initio molecular dynamics simulation in NVT ensemble for MBT on Cu (111) surface around 0 K.

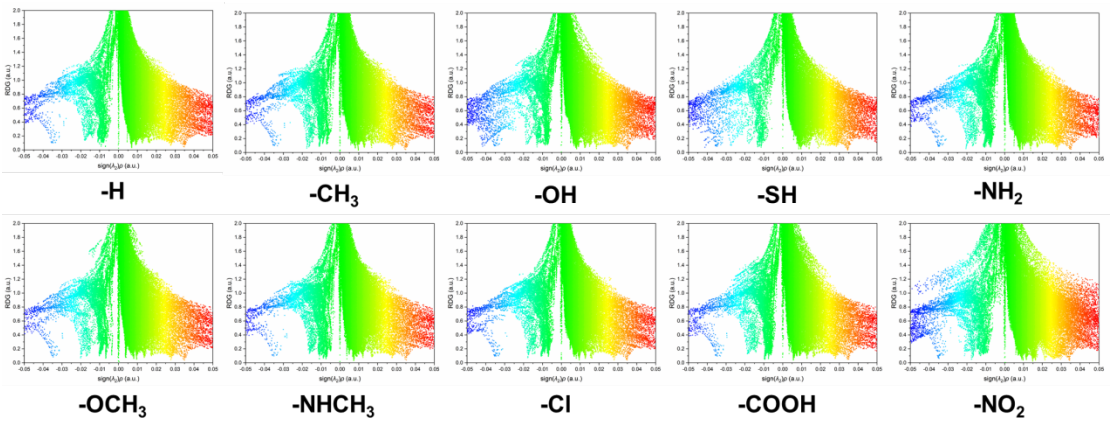

Fig. S4. RDG scatter plots for MBTs adsorbed on Cu (111) in a flat configuration. The coloration of the dots follows a blue-green-red scale corresponding to the values of sign(λ_2)ρ, ranging from -0.05 to 0.05 a.u.

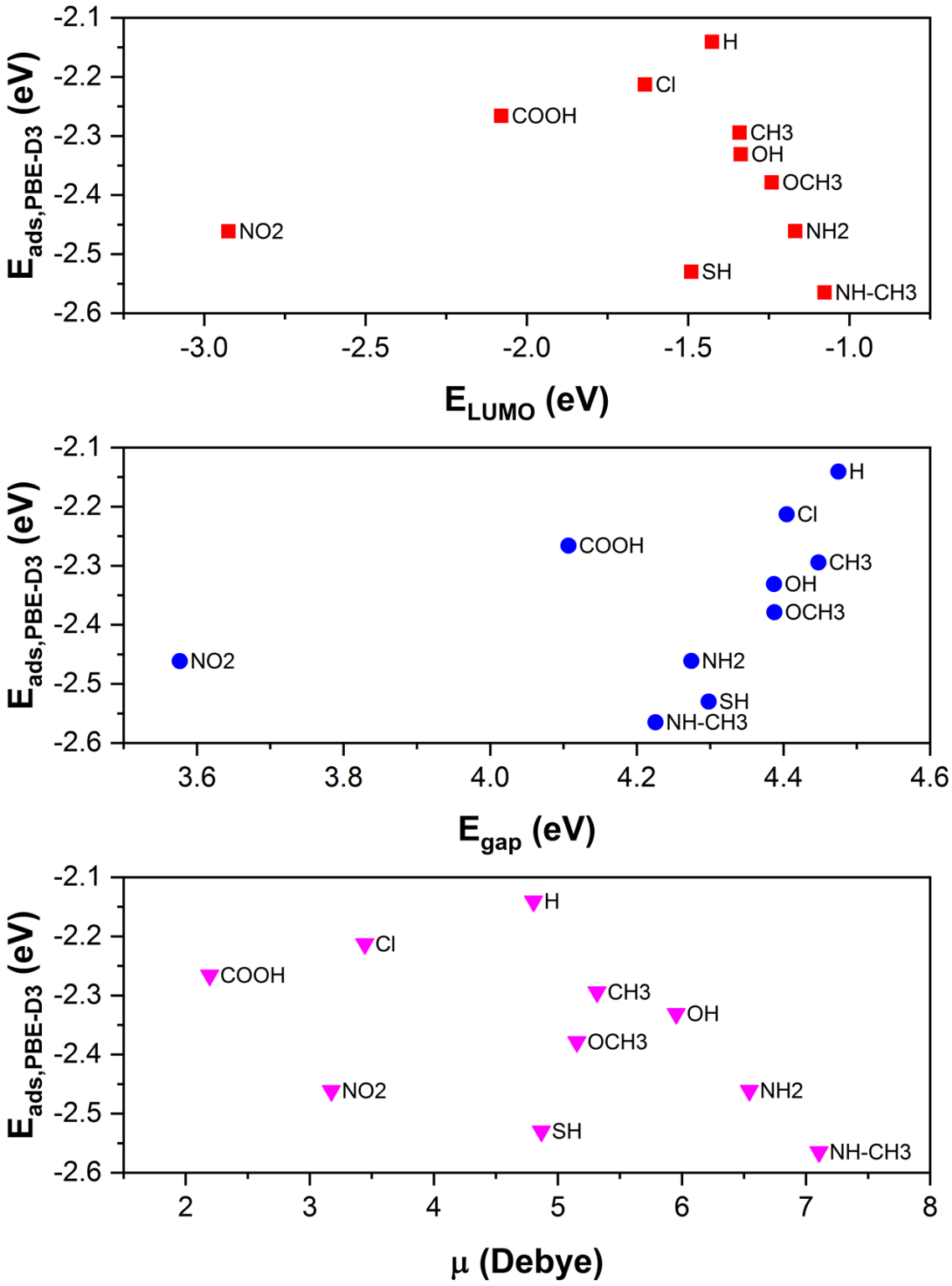

Fig. S5. Correlation between quantum chemical parameters and adsorption energies of MBT derivatives on Cu (111) in flat configuration.

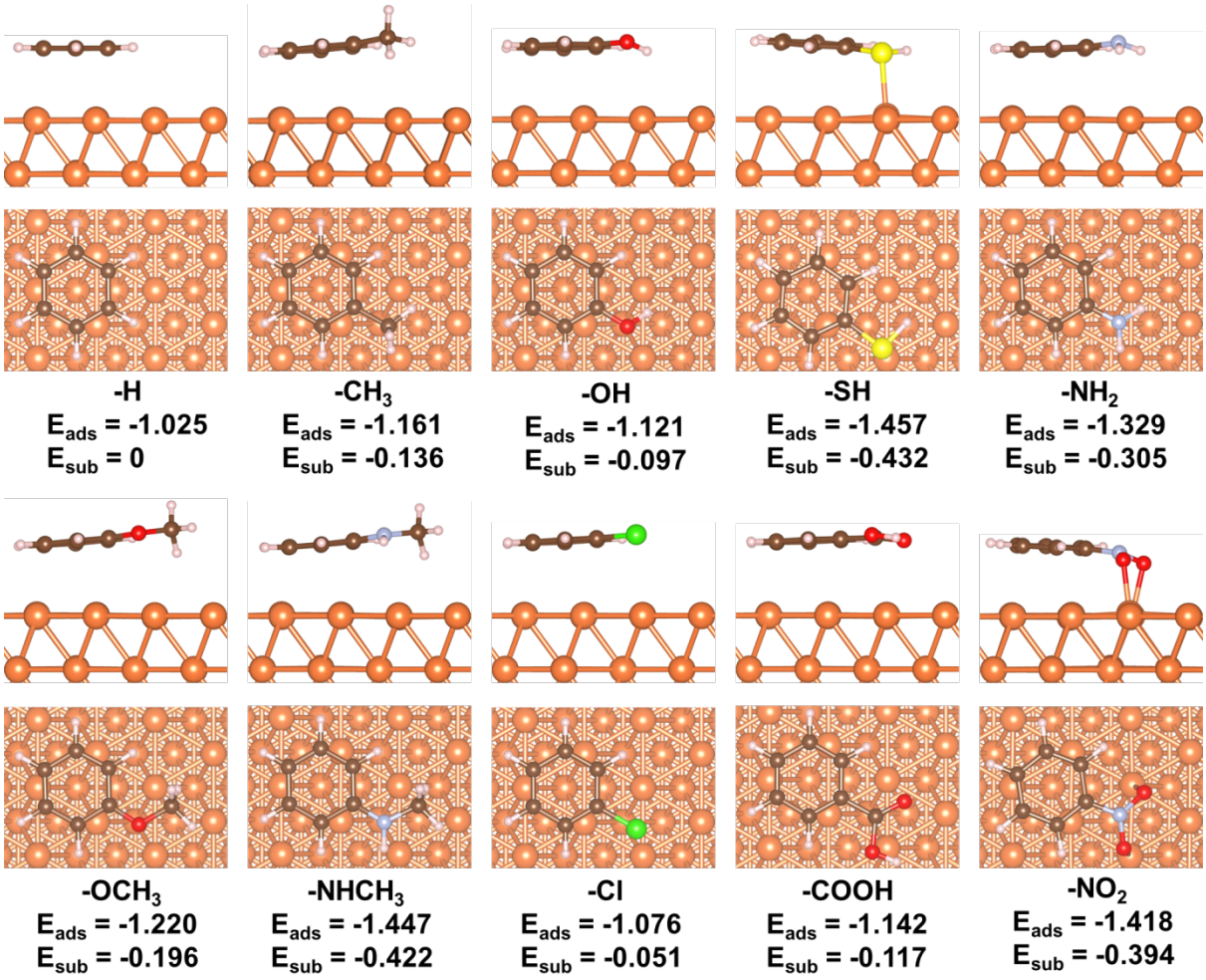

Fig. S6. Optimized structures and adsorption energies (E_{ads}, eV) of benzene derivatives adsorbed on Cu (111) in flat configuration and the corresponding substitution interaction energies (E_{sub}, eV).