

Supplementary Materials

Antioxidants into Nopal (*Opuntia ficus-indica*), important inhibitors of free radicals' formation.

Romina Castañeda-Arriaga,¹ Adriana Perez-Gonzalez,² Tiziana Marino,^{*3} Nino Russo,³ Annia Galano,¹

¹*Departamento de Química. Universidad Autónoma Metropolitana-Iztapalapa. San Rafael Atlixco 186, Col. Vicentina. Iztapalapa. C. P. 09340. México D. F. México.*

²*CONACYT, Universidad Autónoma Metropolitana, Iztapalapa, San Rafael Atlixco 186, Col. Vicentina. Iztapalapa. C. P. 09340. México D. F. México.*

³*Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, I-87036 Arcavacata di Rende, Italy*

Table of Contents

Figure S1. Phenolic and poliphenolic compounds in Nopal (<i>Opuntia ficus-indica</i>).	3
Figure S2. Deprotonation routes of PhAs.....	4
Table S1. Chelation routes (ChR), chelation sites (ChS), conditional Gibbs free energies of reaction (ΔG° , at pH=7.4, in kcal/mol), and Maxwell-Boltzmann distribution (%MB) for the chelation pathways of PhAs.....	5
Figure S3. Energy scan for the <i>f</i> -HAT reactions between $\cdot\text{OH}$ and PhAs-Cu(II) at 298.15 K. Solvent=water.	24
Table S2. Gibbs free energy of reaction (ΔG , kcal/mol) and Gibbs free energy of activation (ΔG^\ddagger , kcal/mol) for the direct RAF mechanism between PhAs-Cu(II) and $\cdot\text{OH}$. Solvent=water.	25
Figure S4. Transition states structures of exergonic RAF reactions between $\cdot\text{OH}$ and $\text{H}_{n-2}\text{COA}^{2-}$ - (2)-C2 at 298.15 K. Solvent=water.	26

Figure S5. Transition states structures of exergonic RAF reactions between $\cdot\text{OH}$ and $\text{H}_{\text{n}-2}\text{FLA}^{2-}$ -(2)-C5 complexes at 298.15 K. Solvent=water.	27
Figure S6. Transition states structures of exergonic RAF reactions between $\cdot\text{OH}$ and $\text{H}_{\text{n}-2}\text{FLA}^{2-}$ -(2)-C2 complexes at 298.15 K. Solvent=water.	28
Figure S7. Transition states structures of exergonic RAF reactions between $\cdot\text{OH}$ and $\text{H}_{\text{n}-2}\text{PRA}^{2-}$ -(2)-C7 complexes at 298.15 K. Solvent=water.	29
Figure S8. Transition states structures of exergonic RAF reactions between $\cdot\text{OH}$ and $\text{H}_{\text{n}-2}\text{GAA}^{2-}$ -(2)-C7 complexes at 298.15 K. Solvent=water.	30

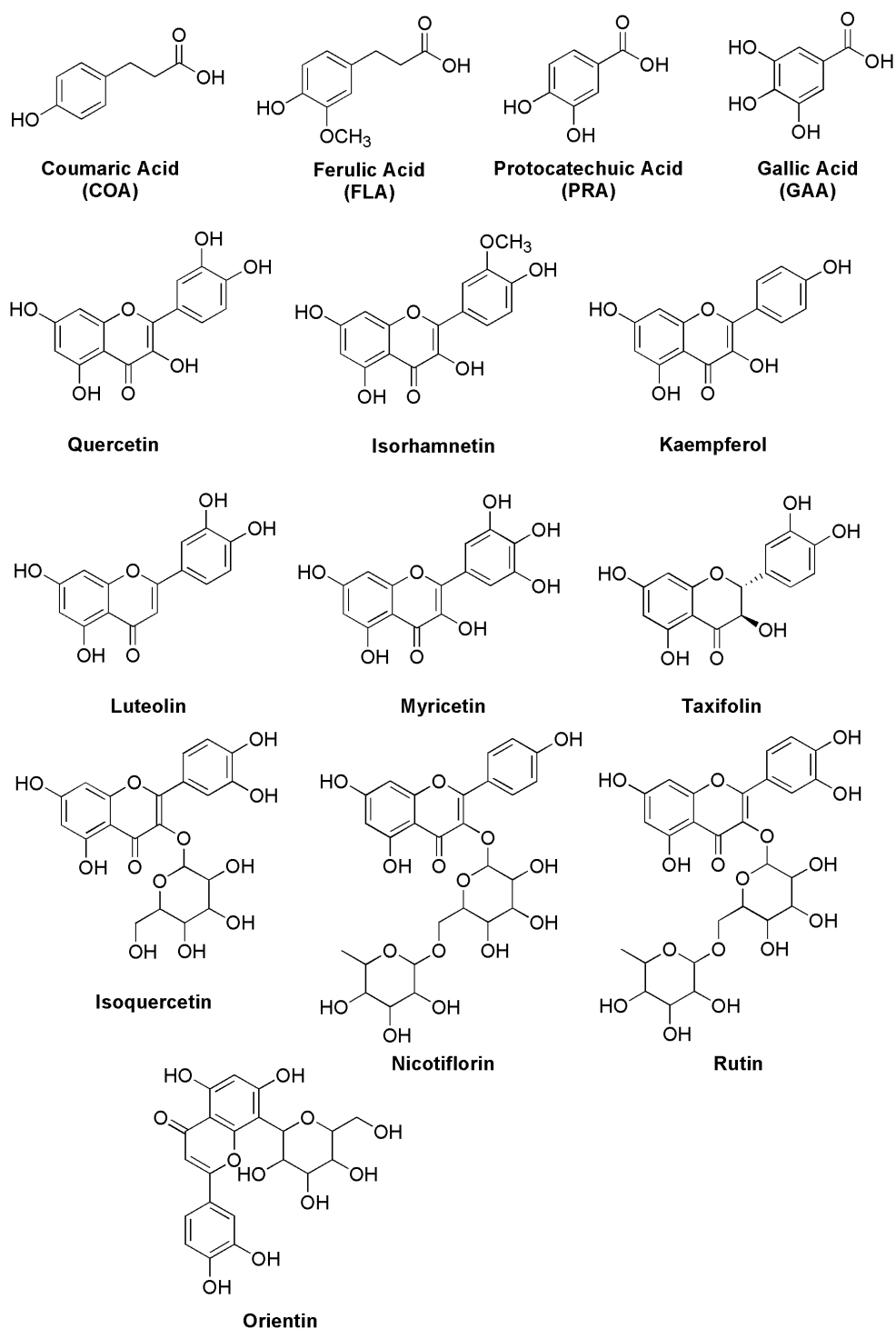


Figure S1. Phenolic and polyphenolic compounds in Nopal (*Opuntia ficus-indica*).

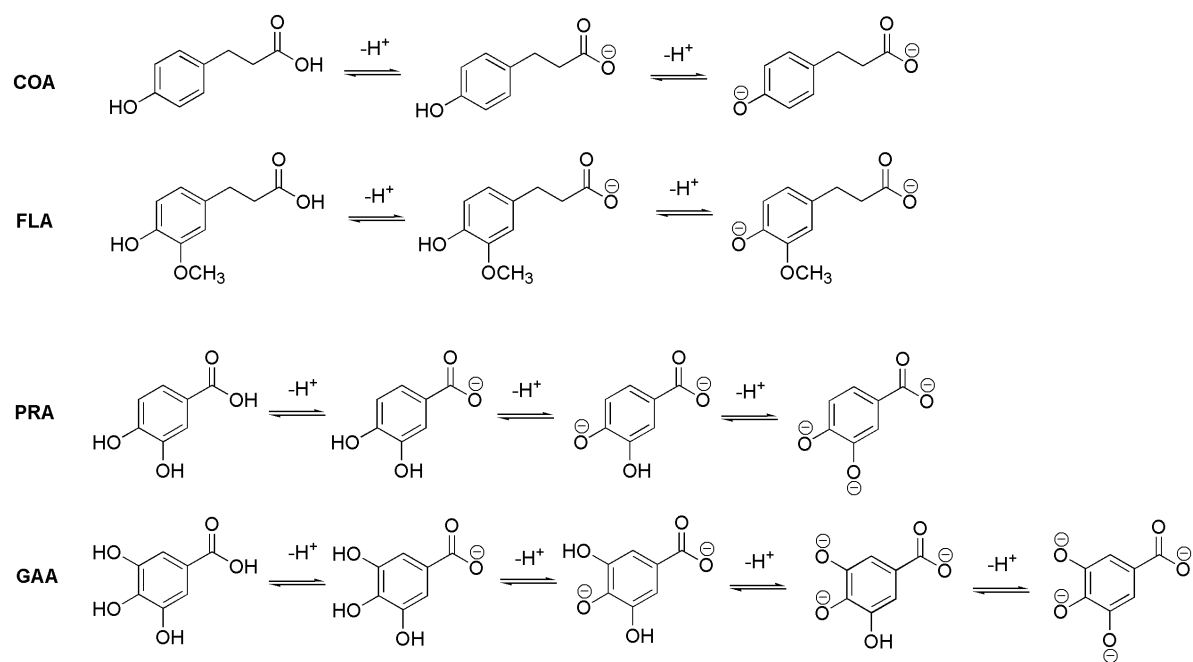
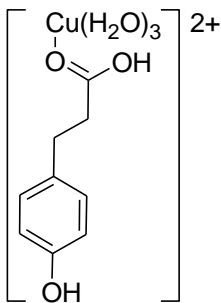
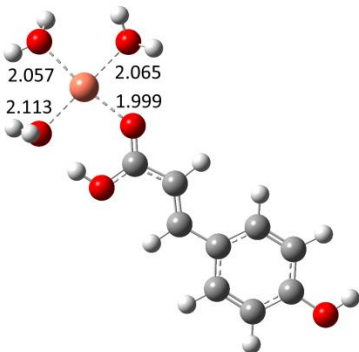
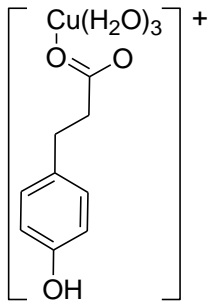
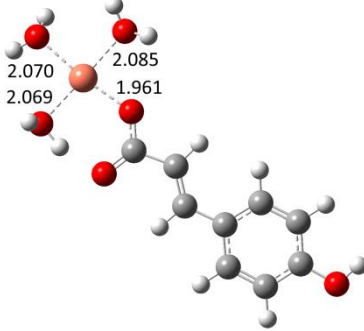
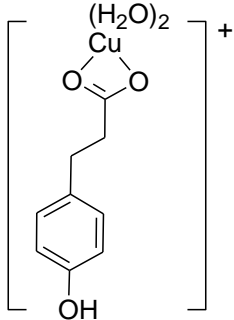
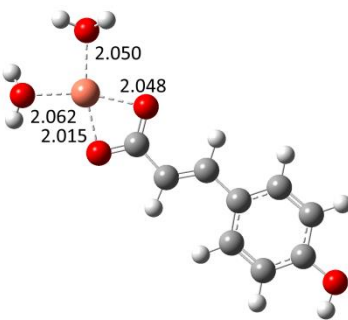
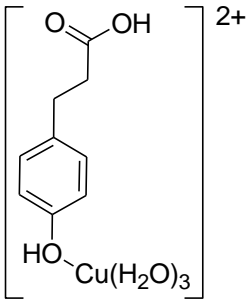
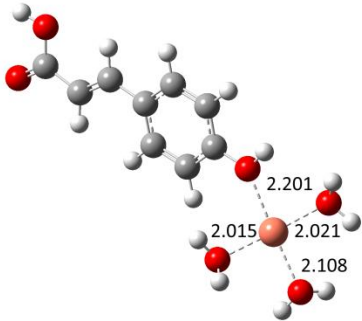
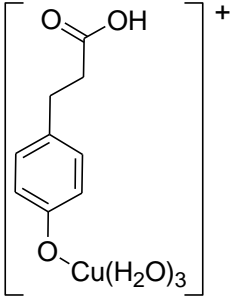
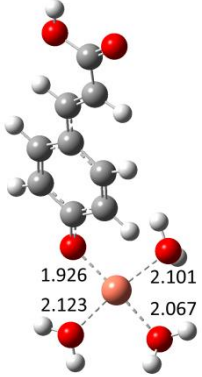
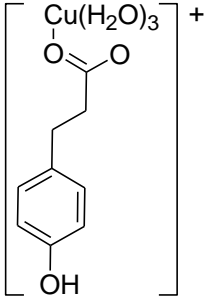
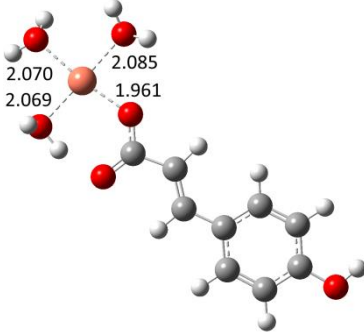
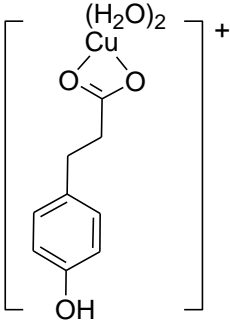
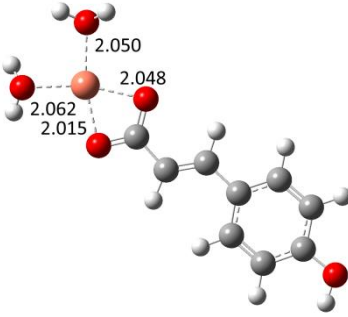
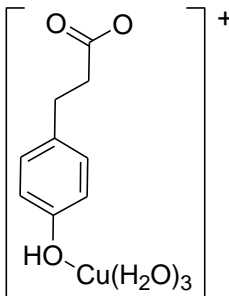
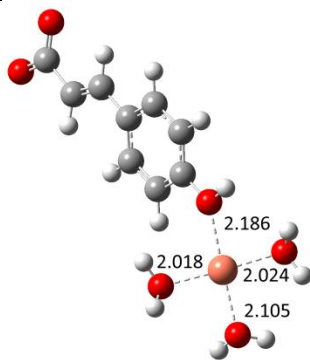
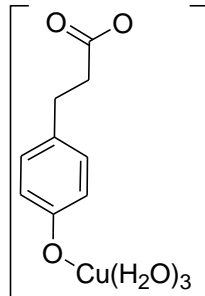
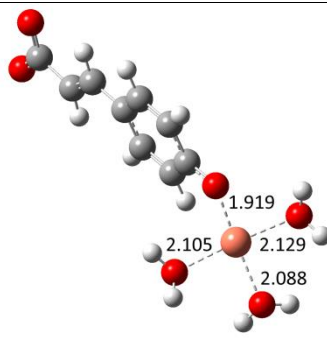
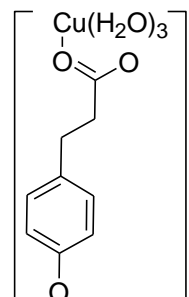
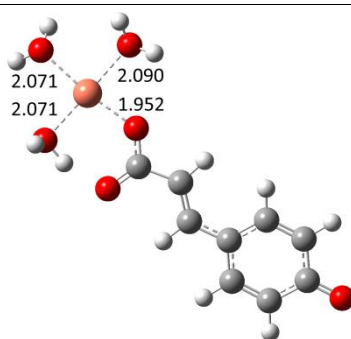
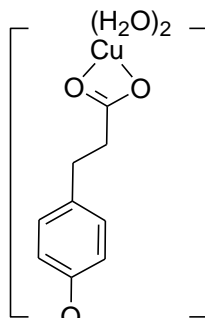
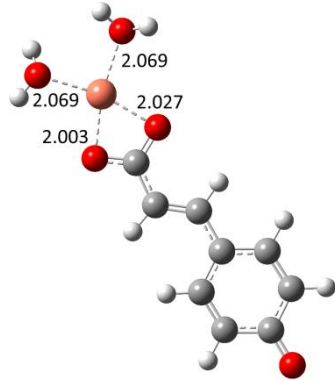


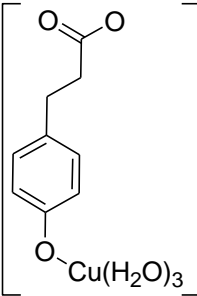
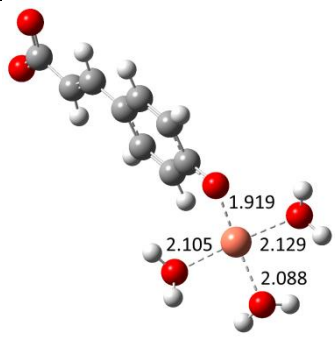
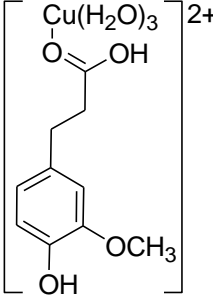
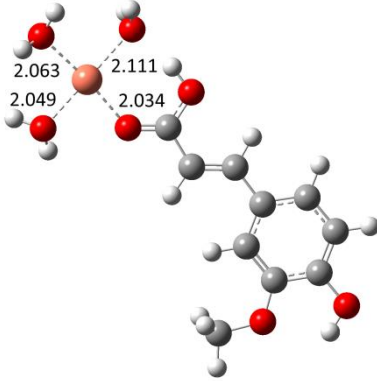
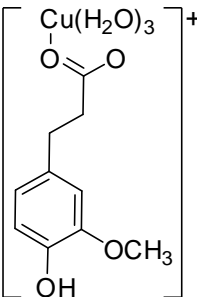
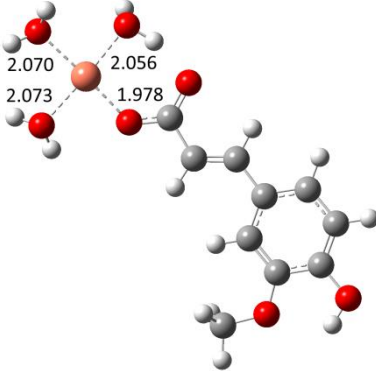
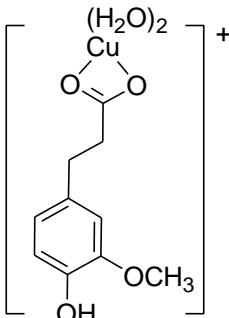
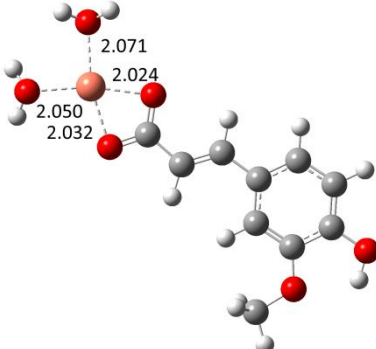
Figure S2. Deprotonation routes of PhAs

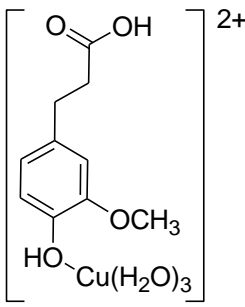
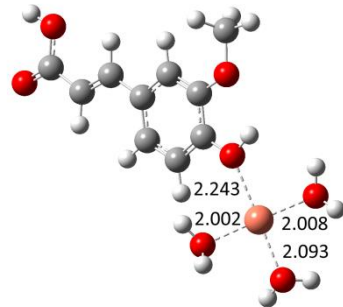
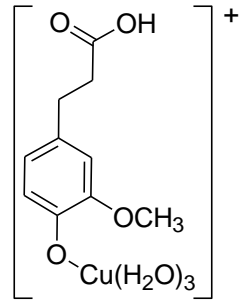
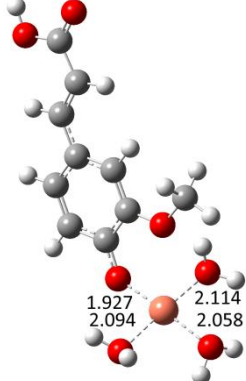
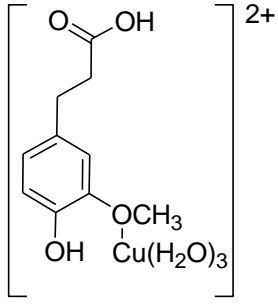
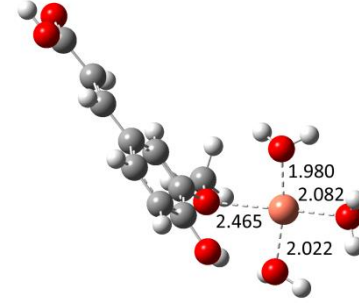
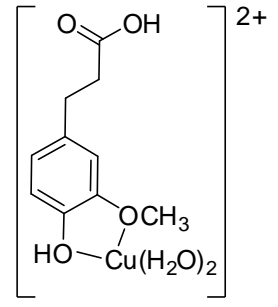
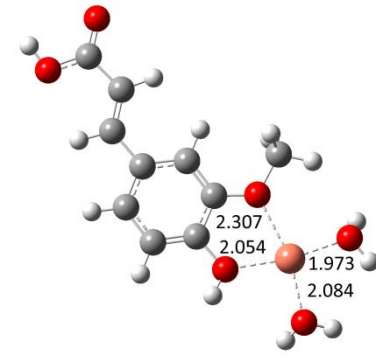
Table S1. Chelation routes (ChR), chelation sites (ChS), conditional Gibbs free energies of reaction ($\Delta G'$, at pH=7.4, in kcal/mol), and Maxwell-Boltzmann distribution (%MB) for the chelation pathways of PhAs.

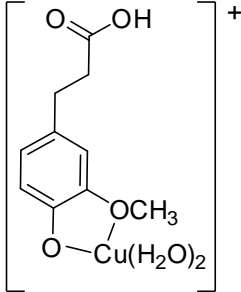
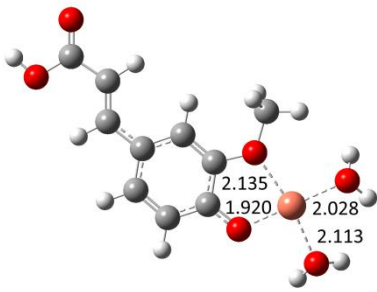
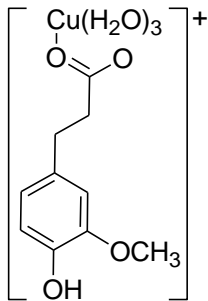
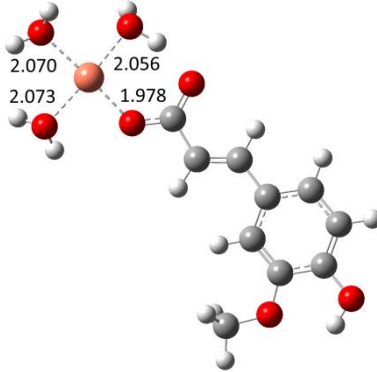
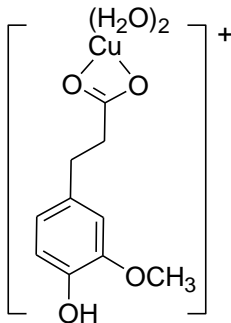
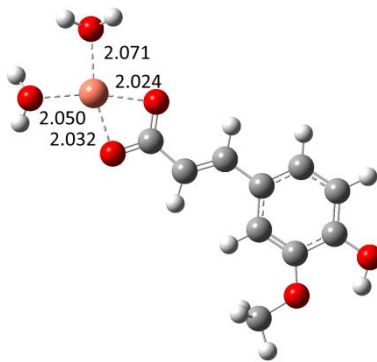
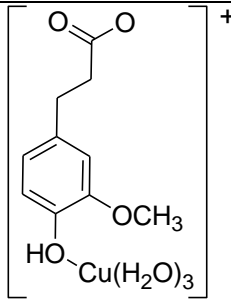
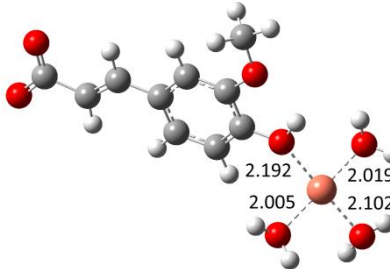
Complex	ChS	ChR	ΔG	%MB	Structure	3D View
H _n COA(1)-C1	CO	I	3.06	0		
H _n COA(1)-C2	CO	II	-11.19	0		
H _n COA(2)-C3	COO	II	-15.51	0		

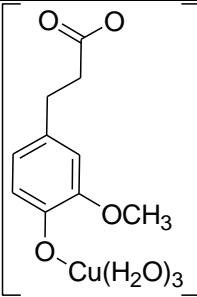
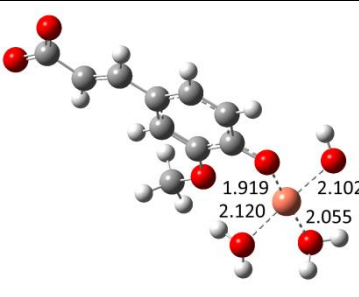
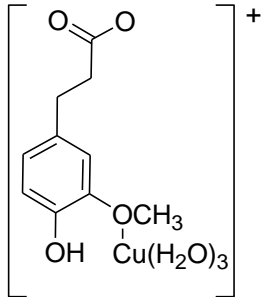
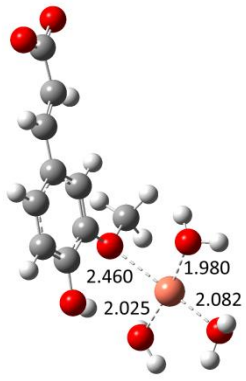
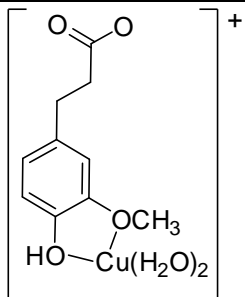
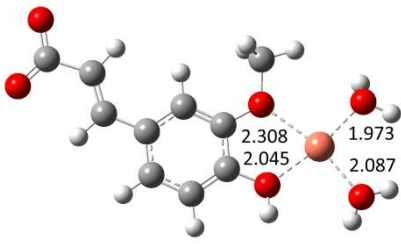
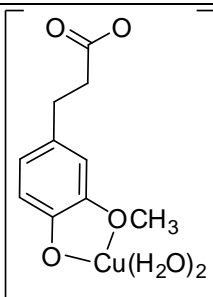
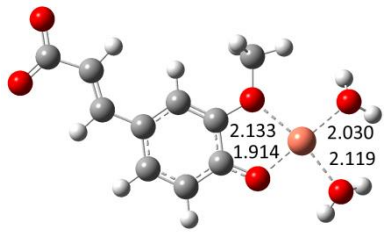
$H_n\text{COA(1)-C4}$	OH	I	7.13	0		
$H_n\text{COA(1)-C5}$	OH	II	-6.34	0		
$H_{n-1}\text{COA}^-(1)\text{-C1}$	CO	III	-10.80	0		
$H_{n-1}\text{COA}^-(2)\text{-C2}$	COO	III	-15.11	0		

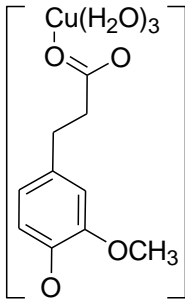
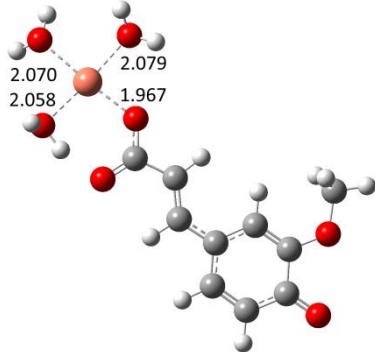
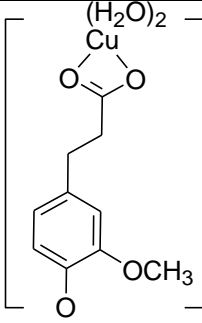
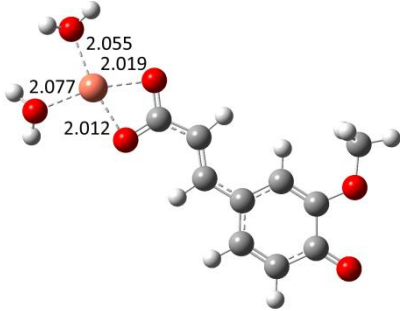
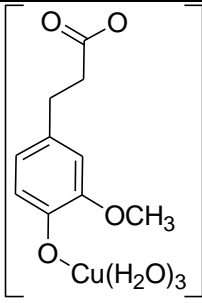
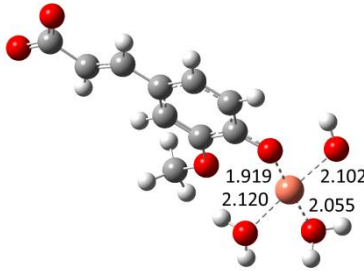
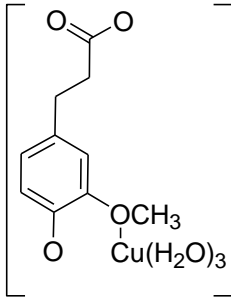
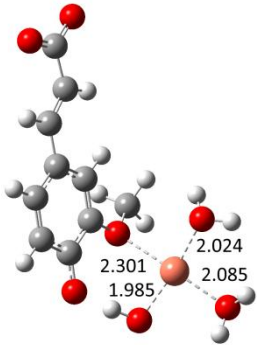
$H_{n-1}COA^-$ (1)-C3	OH	III	5.55	0		
$H_{n-1}COA^-$ (1)-C4	OH	IV	-5.93	0		
$H_{n-2}COA^{2-}$ (1)-C1	CO	V	-12.99	0		
$H_{n-2}COA^{2-}$ (2)-C2	COO	V	-22.87	~100		

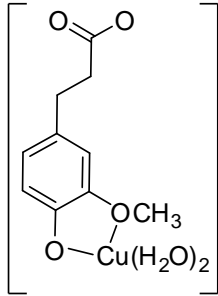
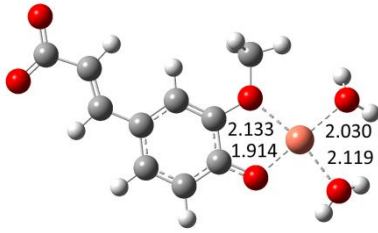
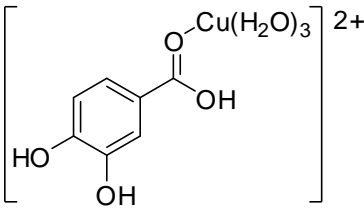
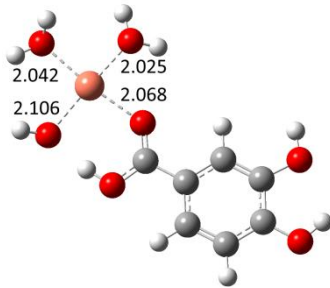
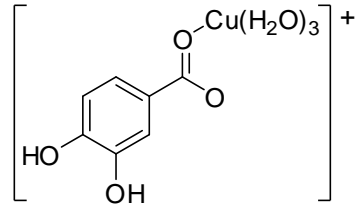
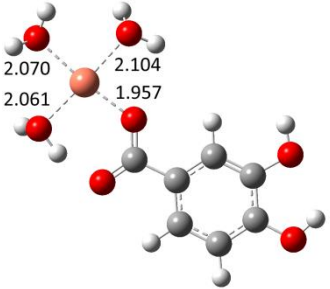
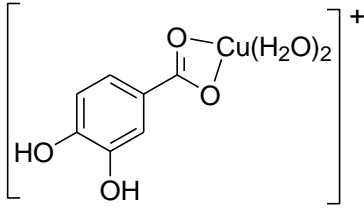
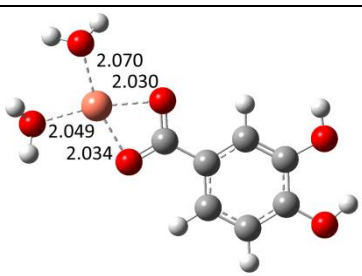
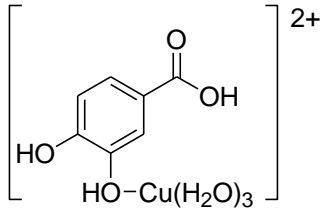
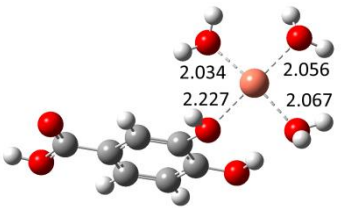
$H_{n-2}COA^{2-}$ (1)-C3	OH	V	-12.77	0		
$H_nFLA(1)$ -C1	CO	I	2.51	0		
$H_nFLA(1)$ -C2	CO	II	-10.99	0		
$H_nFLA(2)$ -C3	COO	II	-15.43	0.14		

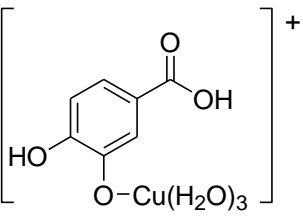
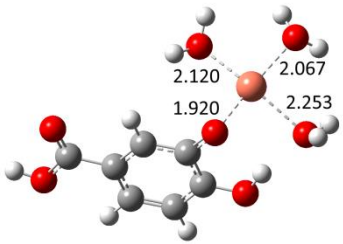
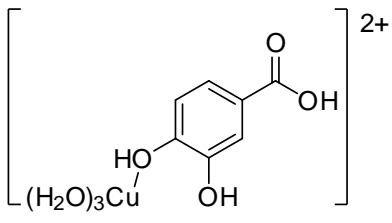
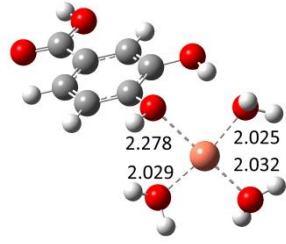
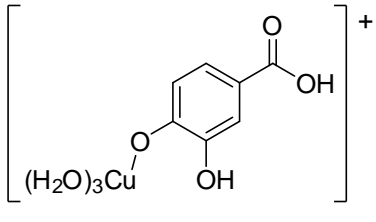
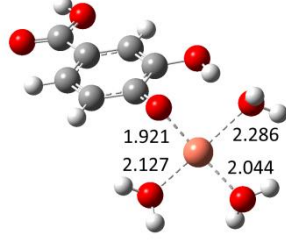
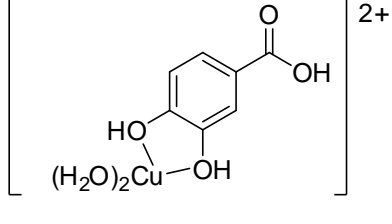
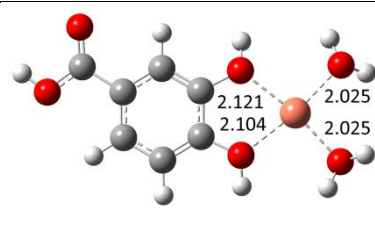
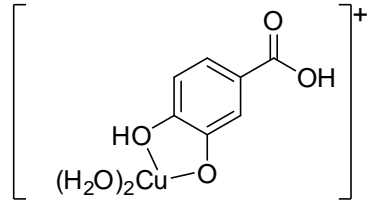
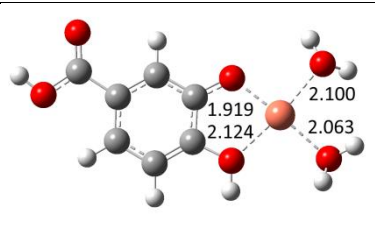
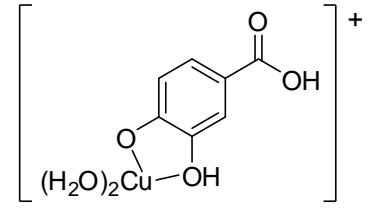
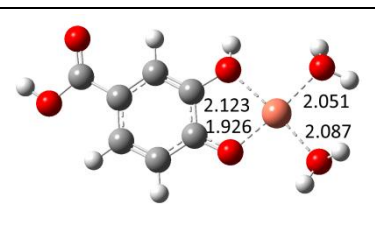
H _n FLA (1)-C4	OH	I	7.50	0		
H _n FLA (1)-C5	OH	II	-6.35	0		
H _n FLA (1)-C6	OCH ₃	I	7.05	0		
H _n FLA (2)-C7	OH, OCH ₃	I	4.40	0		

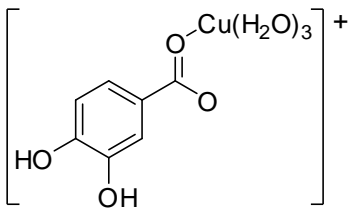
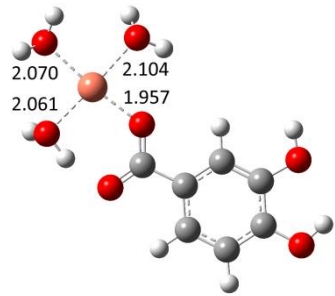
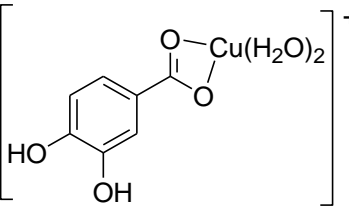
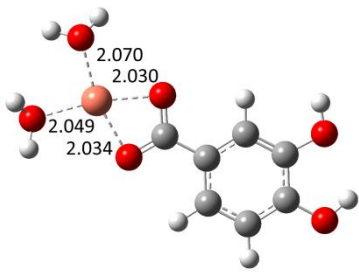
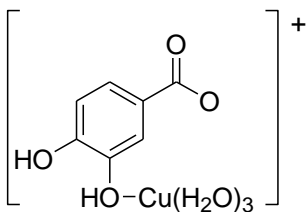
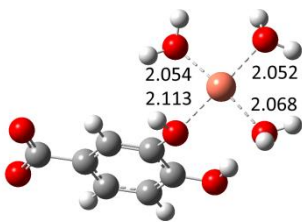
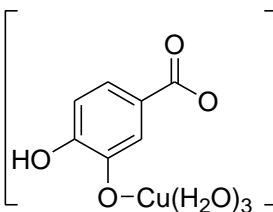
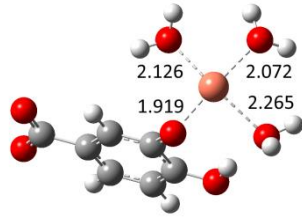
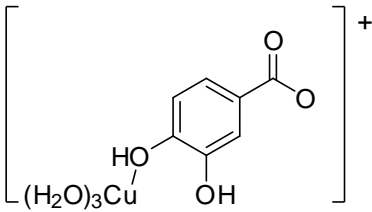
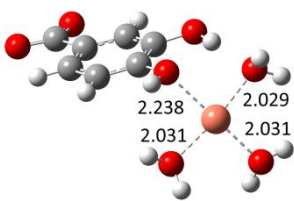
$H_nFLA(2)-C8$	OH, OCH ₃	II	-13.23	0		
$H_{n-1}FLA^-(1)-C1$	CO	III	-9.96	0		
$H_{n-1}FLA^-(2)-C2$	COO	III	-14.40	0.03		
$H_{n-1}FLA^-(1)-C3$	OH	III	6.28	0		

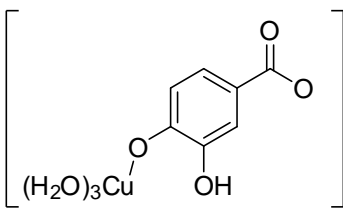
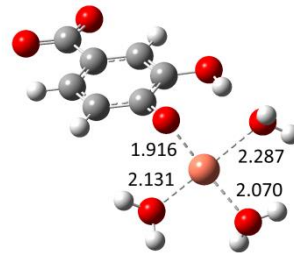
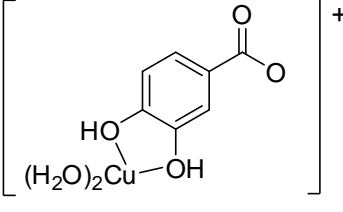
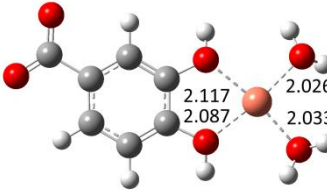
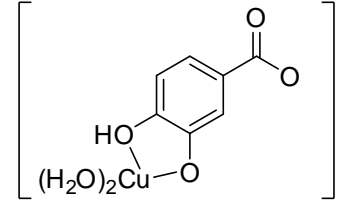
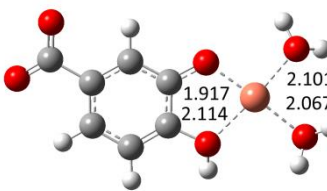
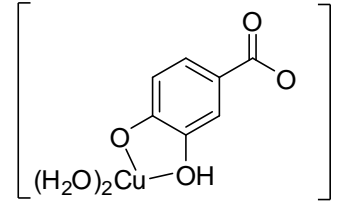
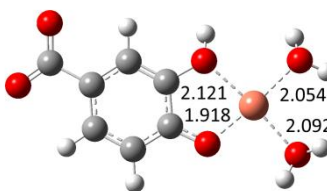
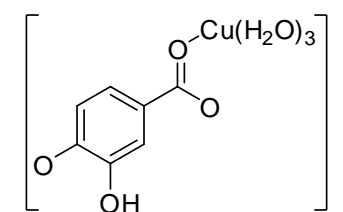
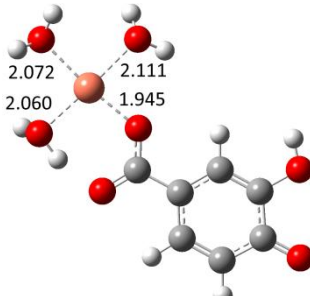
$H_{n-1}FLA^- (1)-C4$	OH	IV	-5.92	0	 <p>Chemical structure of $H_{n-1}FLA^- (1)-C4$ complex. The structure shows a central copper atom coordinated by three water molecules (H_2O) and a phenolate ligand. The phenolate ligand is substituted with a methoxy group (OCH_3) and a propionic acid side chain (CH_2CH_2COOH). The copper atom is coordinated to the phenolate oxygen and the three water molecules.</p>	 <p>3D ball-and-stick model of the $H_{n-1}FLA^- (1)-C4$ complex. The structure shows the spatial arrangement of the copper atom, water molecules, and the phenolate ligand. Bond lengths are indicated: 1.919 Å, 2.102 Å, 2.120 Å, and 2.055 Å.</p>
$H_{n-1}FLA^- (1)-C5$	OCH_3	III	6.22	0	 <p>Chemical structure of $H_{n-1}FLA^- (1)-C5$ complex. The structure shows a central copper atom coordinated by three water molecules (H_2O) and a phenolate ligand. The phenolate ligand is substituted with a methoxy group (OCH_3) and a propionic acid side chain (CH_2CH_2COOH). The copper atom is coordinated to the phenolate oxygen and the three water molecules.</p>	 <p>3D ball-and-stick model of the $H_{n-1}FLA^- (1)-C5$ complex. The structure shows the spatial arrangement of the copper atom, water molecules, and the phenolate ligand. Bond lengths are indicated: 2.460 Å, 1.980 Å, 2.025 Å, and 2.082 Å.</p>
$H_{n-1}FLA^- (2)-C6$	OH, OCH_3	III	3.13	0	 <p>Chemical structure of $H_{n-1}FLA^- (2)-C6$ complex. The structure shows a central copper atom coordinated by two water molecules (H_2O) and a phenolate ligand. The phenolate ligand is substituted with a methoxy group (OCH_3) and a propionic acid side chain (CH_2CH_2COOH). The copper atom is coordinated to the phenolate oxygen and the two water molecules.</p>	 <p>3D ball-and-stick model of the $H_{n-1}FLA^- (2)-C6$ complex. The structure shows the spatial arrangement of the copper atom, water molecules, and the phenolate ligand. Bond lengths are indicated: 2.308 Å, 1.973 Å, 2.045 Å, and 2.087 Å.</p>
$H_{n-1}FLA^- (2)-C7$	OH, OCH_3	IV	-12.4	0	 <p>Chemical structure of $H_{n-1}FLA^- (2)-C7$ complex. The structure shows a central copper atom coordinated by two water molecules (H_2O) and a phenolate ligand. The phenolate ligand is substituted with a methoxy group (OCH_3) and a propionic acid side chain (CH_2CH_2COOH). The copper atom is coordinated to the phenolate oxygen and the two water molecules.</p>	 <p>3D ball-and-stick model of the $H_{n-1}FLA^- (2)-C7$ complex. The structure shows the spatial arrangement of the copper atom, water molecules, and the phenolate ligand. Bond lengths are indicated: 2.133 Å, 2.030 Å, 1.914 Å, and 2.119 Å.</p>

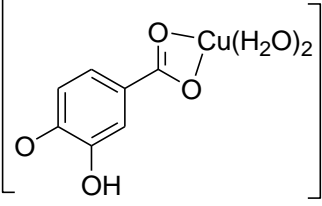
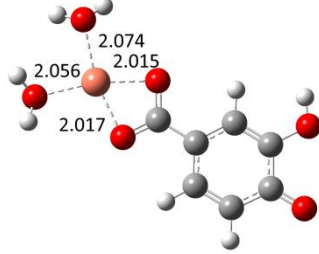
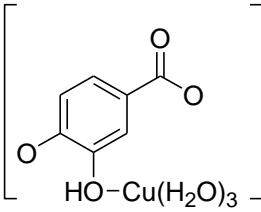
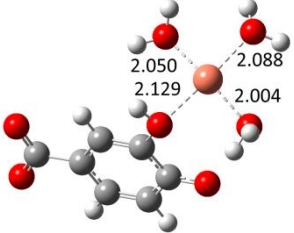
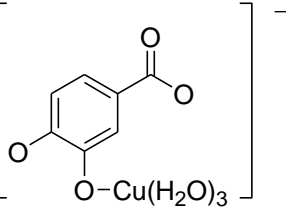
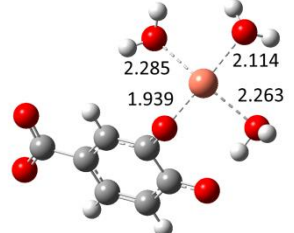
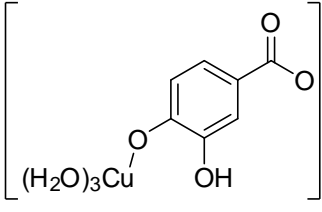
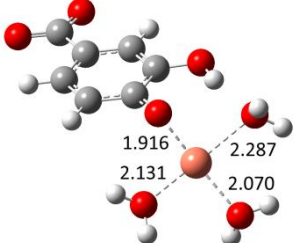
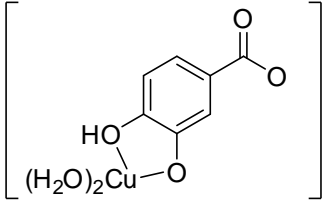
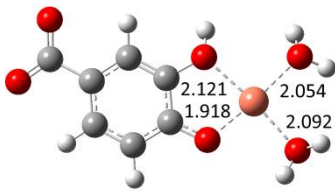
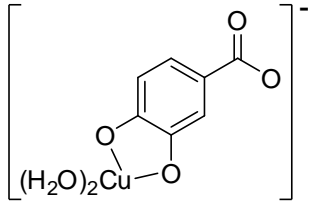
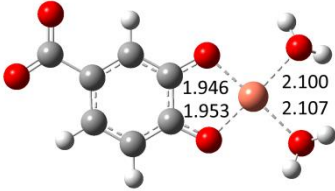
$H_{n-2}FLA^{2-}$ (1)-C1	CO	V	-12.08	0		
$H_{n-2}FLA^{2-}$ (2)-C2	COO	V	-18.30	18.21		
$H_{n-2}FLA^{2-}$ (1)-C3	OH	V	-12.67	0		
$H_{n-2}FLA^{2-}$ (1)-C4	OCH ₃	V	-3.50	0		

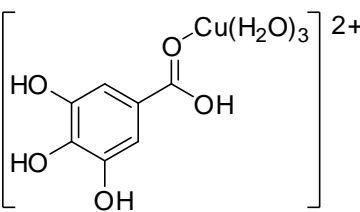
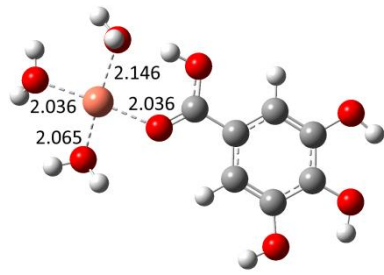
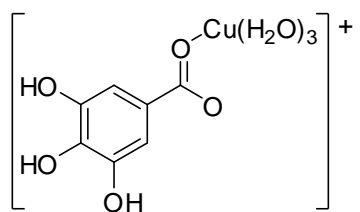
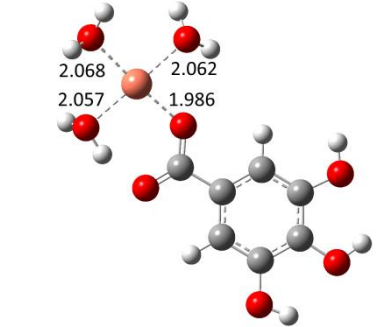
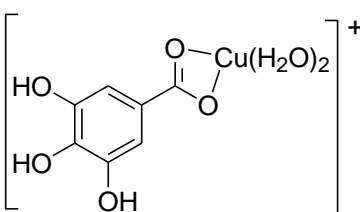
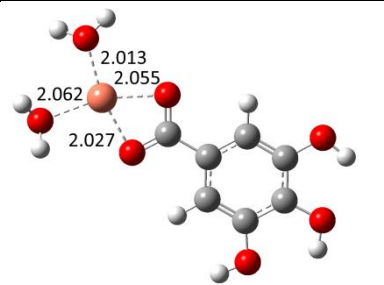
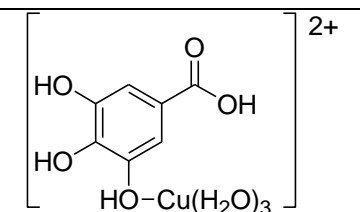
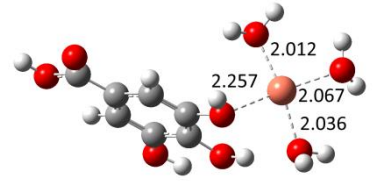
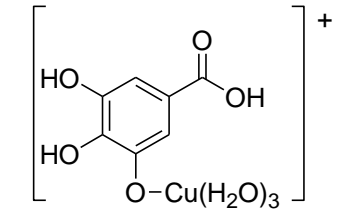
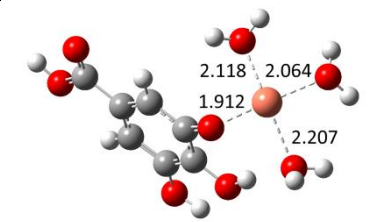
$H_{n-2}FLA^{2-}$ (2)-C5	OH, OCH ₃	V	-19.19	81.61		
$H_nPRA(1)$ -C1	CO	I	2.05	0		
$H_nPRA(1)$ -C2	CO	II	-13.54	0		
$H_nPRA(2)$ -C3	COO	II	-16.57	0		
$H_nPRA(1)$ -C4	OH (3)	I	5.51	0		

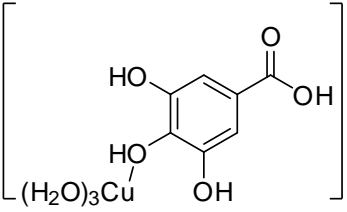
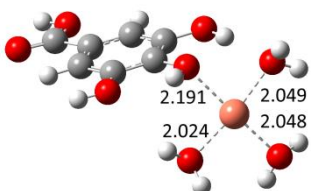
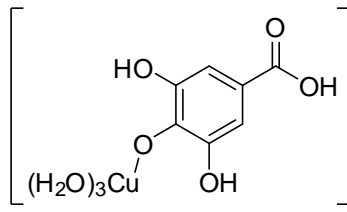
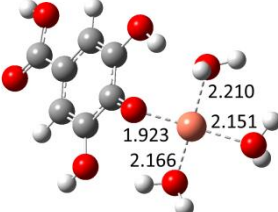
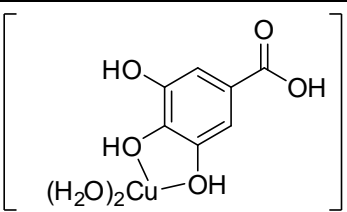
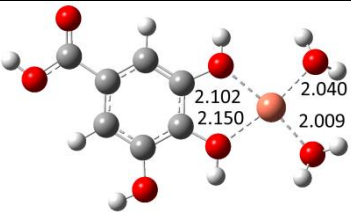
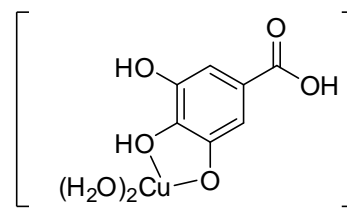
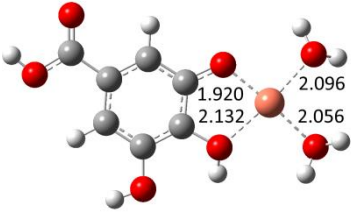
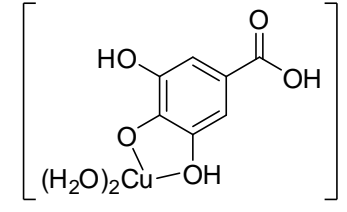
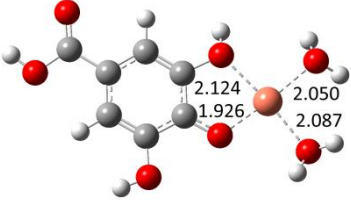
H _n PRA (1)-C5	OH (3)	II	-9.26	0		
H _n PRA (1)-C6	OH (4)	I	5.74	0		
H _n PRA (1)-C7	OH (4)	II	-9.33	0		
H _n PRA (2)-C8	OH (3), OH (4)	I	3.55	0		
H _n PRA (2)-C9	OH (3), OH (4)	II	-13.04	0		
H _n PRA (2)-C10	OH (3), OH (4)	II	-13.21	0		

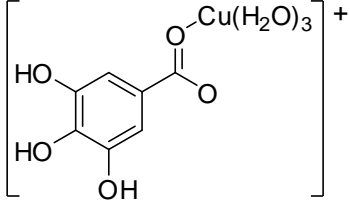
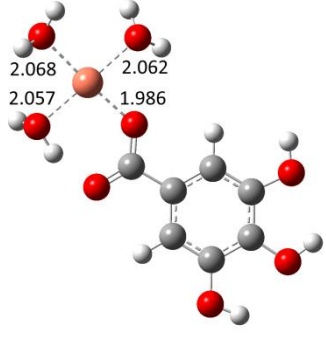
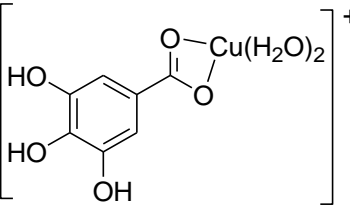
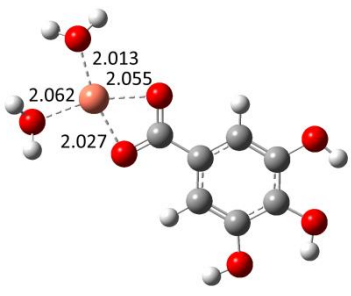
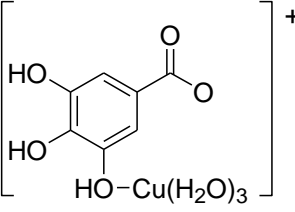
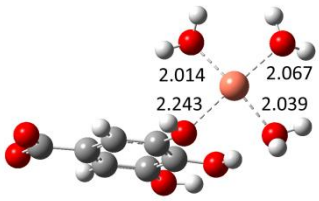
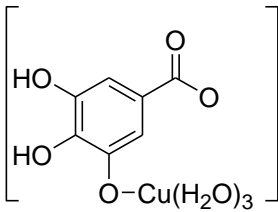
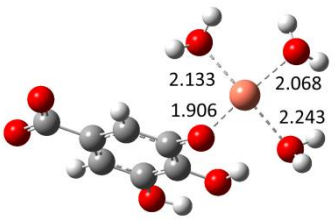
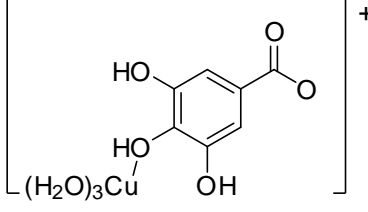
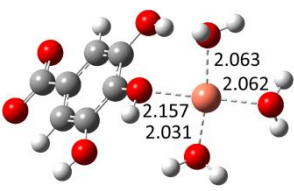
$H_{n-1}PRA^-(1)-C1$	CO	III	-11.19	0		
$H_{n-1}PRA^-(2)-C2$	COO	III	-14.22	0		
$H_{n-1}PRA^-(1)-C3$	OH (3)	III	4.30	0		
$H_{n-1}PRA^-(1)-C4$	OH (3)	IV	-8.77	0		
$H_{n-1}PRA^-(1)-C5$	OH (4)	III	6.61	0		

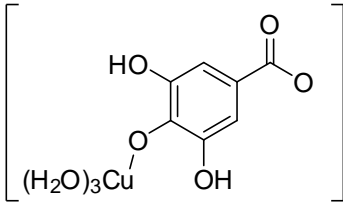
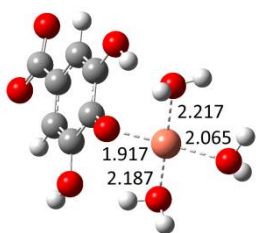
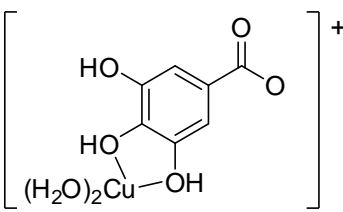
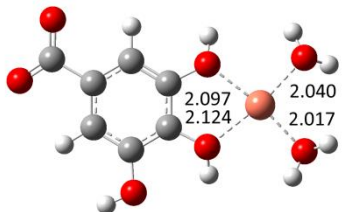
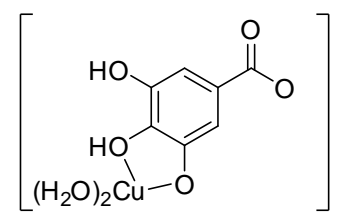
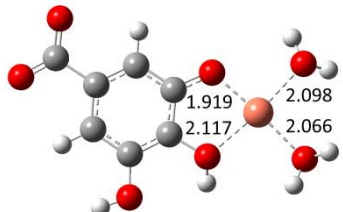
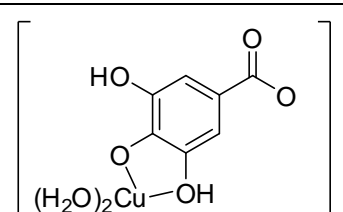
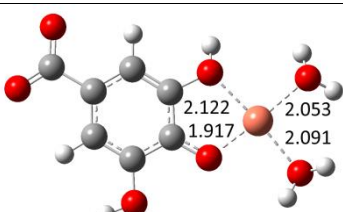
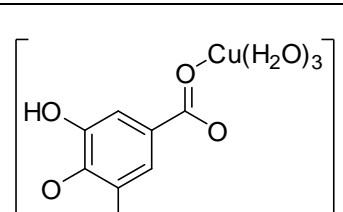
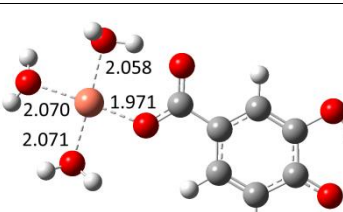
$H_{n-1}PRA^-(1)-C6$	OH (4)	IV	-9.58	0		
$H_{n-1}PRA^-(2)-C7$	OH (3), OH (4)	III	1.79	0		
$H_{n-1}PRA^-(2)-C8$	OH (3), OH (4)	IV	-12.15	0		
$H_{n-1}PRA^-(2)-C9$	OH (3), OH (4)	IV	-12.58	0		
$H_{n-2}PRA^{2-}(1)-C1$	CO	V	-10.97	0		

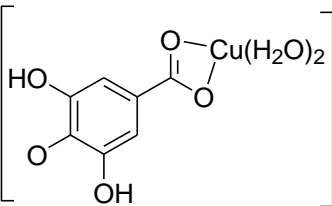
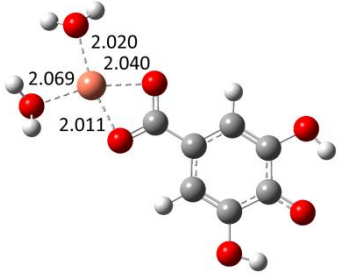
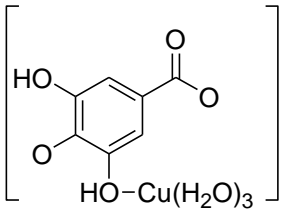
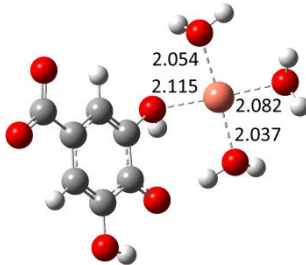
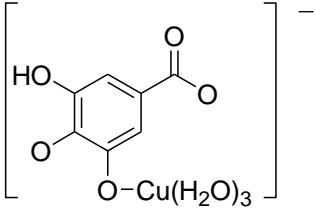
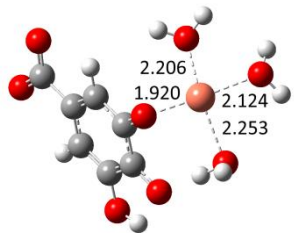
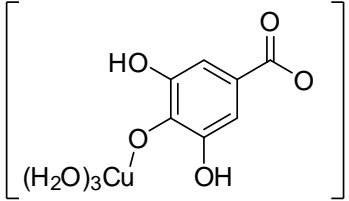
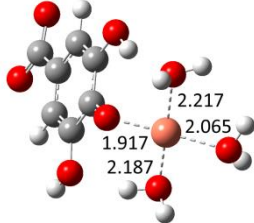
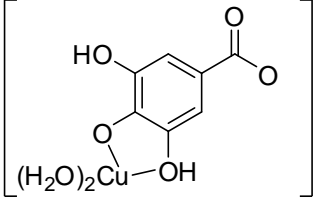
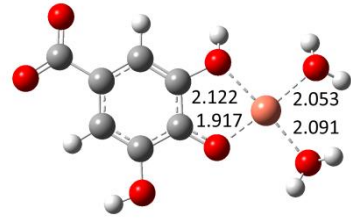
$H_{n-2}PRA^{2-}$ (2)-C2	COO	V	-16.23	0		
$H_{n-2}PRA^{2-}$ (1)-C3	OH (3)	V	-3.17	0		
$H_{n-2}PRA^{2-}$ (1)-C4	OH (3)	VI	-12.02	0		
$H_{n-2}PRA^{2-}$ (1)-C5	OH (4)	V	-14.42	0		
$H_{n-2}PRA^{2-}$ (2)-C6	OH (3), OH (4)	V	-17.42	0.01		
$H_{n-2}PRA^{2-}$ (2)-C7	OH (3), OH (4)	VI	-22.83	99.99		

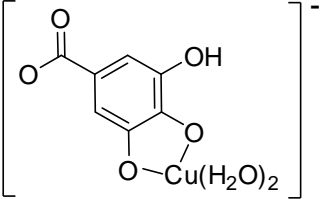
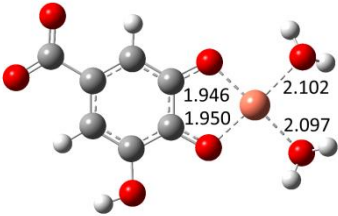
H _n GAA(1)-C1	CO	I	2.40	0		
H _n GAA (1)-C2	CO	II	-13.70	0		
H _n GAA (2)-C3	COO	II	-16.65	0.08		
H _n GAA (1)-C4	OH (3)	I	6.93	0		
H _n GAA (1)-C5	OH (3)	II	-8.26	0		

H _n GAA (1)-C6	OH (4)	I	5.55	0	 $\left[\begin{array}{c} \text{HO} \\ \text{HO} \end{array} \text{C}_6\text{H}_2\text{COOH} \right]^{2+} \\ \text{(H}_2\text{O)}_3\text{Cu}$	 2.191, 2.049, 2.048, 2.024
H _n GAA (1)-C7	OH (4)	II	-11.01	0	 $\left[\begin{array}{c} \text{HO} \\ \text{O} \end{array} \text{C}_6\text{H}_2\text{COOH} \right]^+ \\ \text{(H}_2\text{O)}_3\text{Cu}$	 2.210, 2.151, 2.166, 1.923
H _n GAA (2)-C8	OH (3), OH (4)	I	3.61	0	 $\left[\begin{array}{c} \text{HO} \\ \text{HO} \end{array} \text{C}_6\text{H}_2\text{COOH} \right]^{2+} \\ \text{(H}_2\text{O)}_2\text{Cu-OH}$	 2.102, 2.040, 2.150, 2.009
H _n GAA (2)-C9	OH (3), OH (4)	II	-13.00	0	 $\left[\begin{array}{c} \text{HO} \\ \text{HO} \end{array} \text{C}_6\text{H}_2\text{COOH} \right]^+ \\ \text{(H}_2\text{O)}_2\text{Cu-O}$	 2.096, 2.056, 2.132, 1.920
H _n GAA N(2)-C10	OH (3), OH (4)	II	-12.77	0	 $\left[\begin{array}{c} \text{HO} \\ \text{O} \end{array} \text{C}_6\text{H}_2\text{COOH} \right]^+ \\ \text{(H}_2\text{O)}_2\text{Cu-OH}$	 2.124, 2.050, 2.087, 1.926

$H_{n-1}GAA^-(1)-C1$	CO	III	-10.93	0		
$H_{n-1}GAA^-(2)-C2$	COO	III	-13.87	0		
$H_{n-1}GAA^-(1)-C3$	OH (3)	III	5.98	0		
$H_{n-1}GAA^-(1)-C4$	OH (3)	IV	-7.94	0		
$H_{n-1}GAA^-(1)-C5$	OH (4)	III	4.80	0		

$H_{n-1}GAA^-(1)-C6$	OH (4)	IV	-11.42	0		
$H_{n-1}GAA^-(2)-C7$	OH (3), OH (4)	III	2.04	0		
$H_{n-1}GAA^-(2)-C8$	OH (3), OH (4)	IV	-11.97	0		
$H_{n-1}GAA^-(2)-C9$	OH (3), OH (4)	IV	-11.57	0		
$H_{n-2}GAA^{2-}(1)-C1$	CO	V	-13.82	0		

$H_{n-2}GAA^{2-}$ (2)-C2	COO	V	-18.48	1.86		
$H_{n-2}GAA^{2-}$ (1)-C3	OH (3)	V	-2.85	0		
$H_{n-2}GAA^{2-}$ (1)-C4	OH (3)	VI	-11.54	0		
$H_{n-2}GAA^{2-}$ (1)-C5	OH (4)	V	-14.30	0		
$H_{n-2}GAA^{2-}$ (2)-C6	OH (3), OH (4)	V	-14.45	0		

$\text{H}_{n-2}\text{GAA}^{2-}$ (2)-C7	OH (3), OH (4)	VI	-20.83	98.05		
--	-------------------	----	--------	-------	--	---

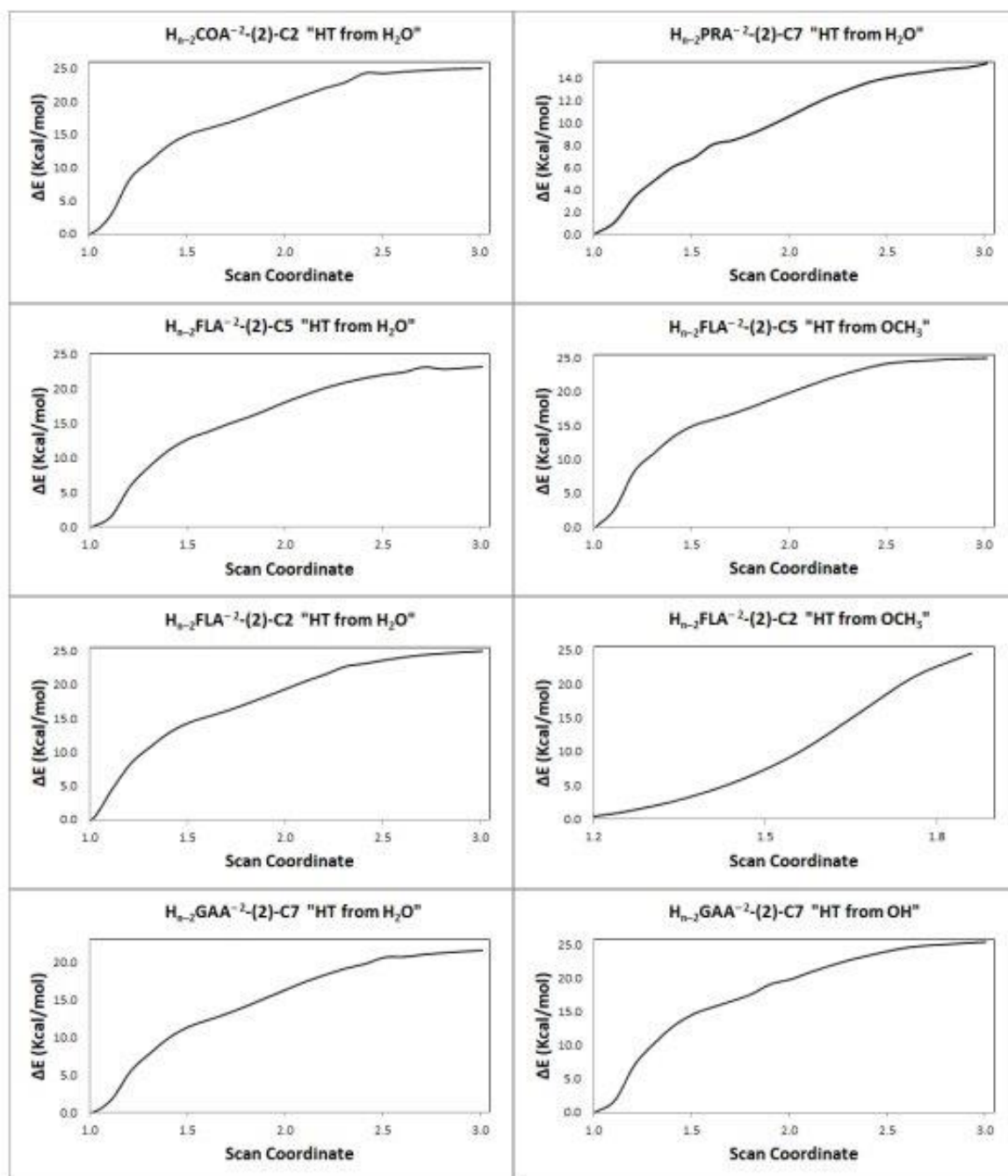


Figure S3. Energy scan for the *f*-HAT reactions between $\cdot\text{OH}$ and PhAs-Cu(II) at 298.15 K. Solvent=water.

Table S2. Gibbs free energy of reaction (ΔG , kcal/mol) and Gibbs free energy of activation (ΔG^\ddagger , kcal/mol) for the direct RAF mechanism between PhAs-Cu(II) and $\cdot\text{OH}$.

Solvent=water.

PhAs-Cu(II)		ΔG	ΔG^\ddagger
$\text{H}_{\text{n-2}}\text{COA}^{2-}$ (2)-C2	RAF-1	-8.10	-1.74
$\text{H}_{\text{n-2}}\text{COA}^{2-}$ (2)-C2	RAF-2	-12.92	-1.38
$\text{H}_{\text{n-2}}\text{COA}^{2-}$ (2)-C2	RAF-3	-17.08	-6.81
$\text{H}_{\text{n-2}}\text{COA}^{2-}$ (2)-C2	RAF-4	-13.63	-6.28
$\text{H}_{\text{n-2}}\text{FLA}^{2-}$ (2)-C5	RAF-1	-10.16	-2.48
$\text{H}_{\text{n-2}}\text{FLA}^{2-}$ (2)-C5	RAF-2	NF	--
$\text{H}_{\text{n-2}}\text{FLA}^{2-}$ (2)-C5	RAF-3	-18.40	-4.78
$\text{H}_{\text{n-2}}\text{FLA}^{2-}$ (2)-C5	RAF-4	-20.79	-8.05
$\text{H}_{\text{n-2}}\text{FLA}^{2-}$ (2)-C5	RAF-5	-15.21	-4.43
$\text{H}_{\text{n-2}}\text{FLA}^{2-}$ (2)-C5	RAF-6	-17.52	-6.38
$\text{H}_{\text{n-2}}\text{FLA}^{2-}$ (2)-C2	RAF-1	-8.11	-3.01
$\text{H}_{\text{n-2}}\text{FLA}^{2-}$ (2)-C2	RAF-2	-15.39	-3.32
$\text{H}_{\text{n-2}}\text{FLA}^{2-}$ (2)-C2	RAF-3	-20.84	-7.25
$\text{H}_{\text{n-2}}\text{FLA}^{2-}$ (2)-C2	RAF-4	-15.78	-9.98
$\text{H}_{\text{n-2}}\text{FLA}^{2-}$ (2)-C2	RAF-5	-14.96	-6.56
$\text{H}_{\text{n-2}}\text{FLA}^{2-}$ (2)-C2	RAF-6	-16.08	-5.88
$\text{H}_{\text{n-2}}\text{PRA}^{2-}$ (2)-C7	RAF-1	-15.32	-6.22
$\text{H}_{\text{n-2}}\text{PRA}^{2-}$ (2)-C7	RAF-2	-17.03	-8.33
$\text{H}_{\text{n-2}}\text{PRA}^{2-}$ (2)-C7	RAF-3	-17.50	-12.01
$\text{H}_{\text{n-2}}\text{PRA}^{2-}$ (2)-C7	RAF-4	-18.97	-12.62
$\text{H}_{\text{n-2}}\text{PRA}^{2-}$ (2)-C7	RAF-5	-14.90	-7.18
$\text{H}_{\text{n-2}}\text{PRA}^{2-}$ (2)-C7	RAF-6	-19.63	-10.62
$\text{H}_{\text{n-2}}\text{GAA}^{2-}$ (2)-C7	RAF-1	-14.88	-6.36
$\text{H}_{\text{n-2}}\text{GAA}^{2-}$ (2)-C7	RAF-2	-18.24	-7.63
$\text{H}_{\text{n-2}}\text{GAA}^{2-}$ (2)-C7	RAF-3	-15.82	-10.74
$\text{H}_{\text{n-2}}\text{GAA}^{2-}$ (2)-C7	RAF-4	-19.96	-13.07
$\text{H}_{\text{n-2}}\text{GAA}^{2-}$ (2)-C7	RAF-5	-19.19	-9.09
$\text{H}_{\text{n-2}}\text{GAA}^{2-}$ (2)-C7	RAF-6	-17.74	-9.46

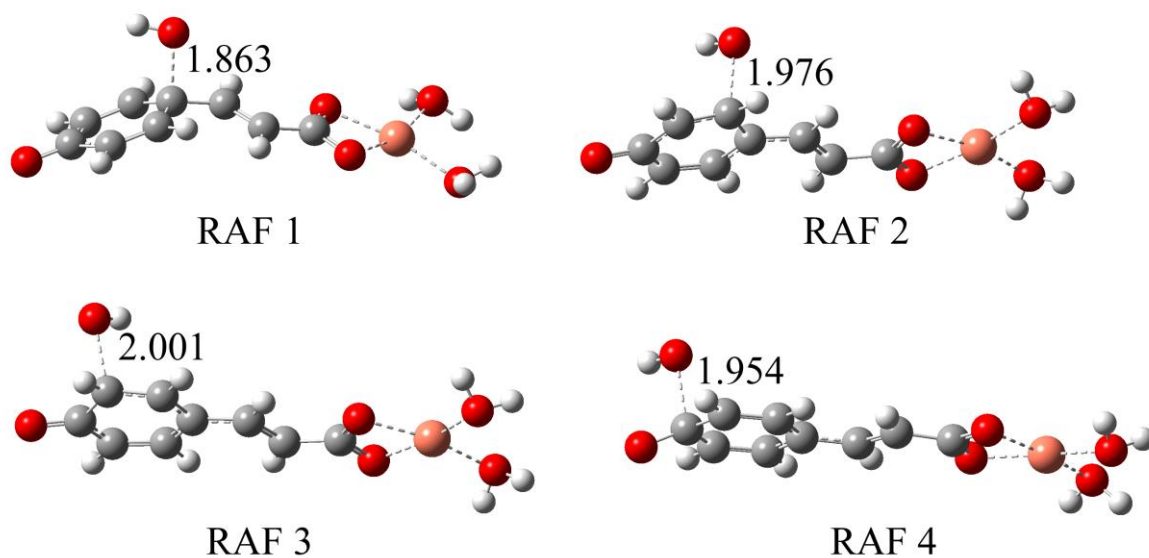
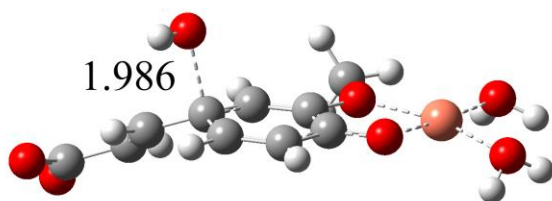
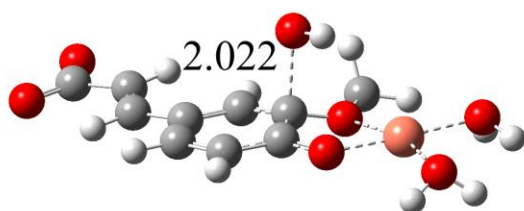


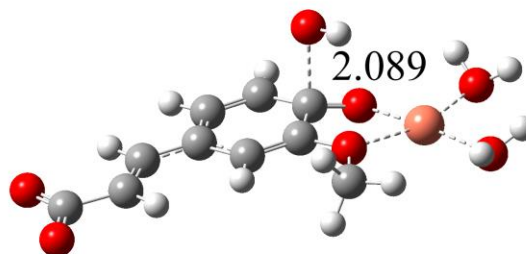
Figure S4. Transition states structures of exergonic RAF reactions between $\cdot\text{OH}$ and $\text{H}_n\text{-}_2\text{COA}^{2-}\text{-(2)-C2}$ at 298.15 K. Solvent=water.



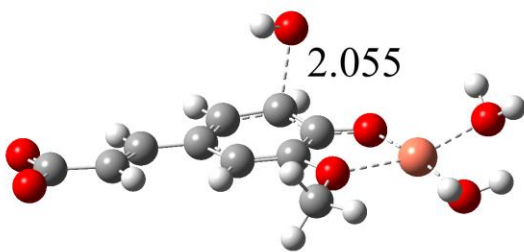
RAF 1



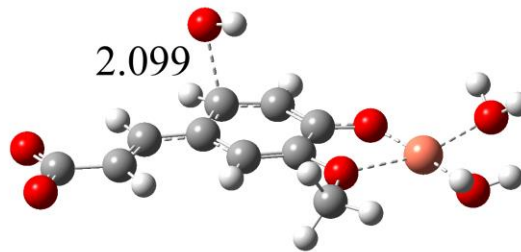
RAF 3



RAF 4



RAF 5



RAF 6

Figure S5. Transition states structures of exergonic RAF reactions between $\cdot\text{OH}$ and $\text{H}_n\text{-}_2\text{FLA}^{2-}\text{-(2)-C5}$ complexes at 298.15 K. Solvent=water.

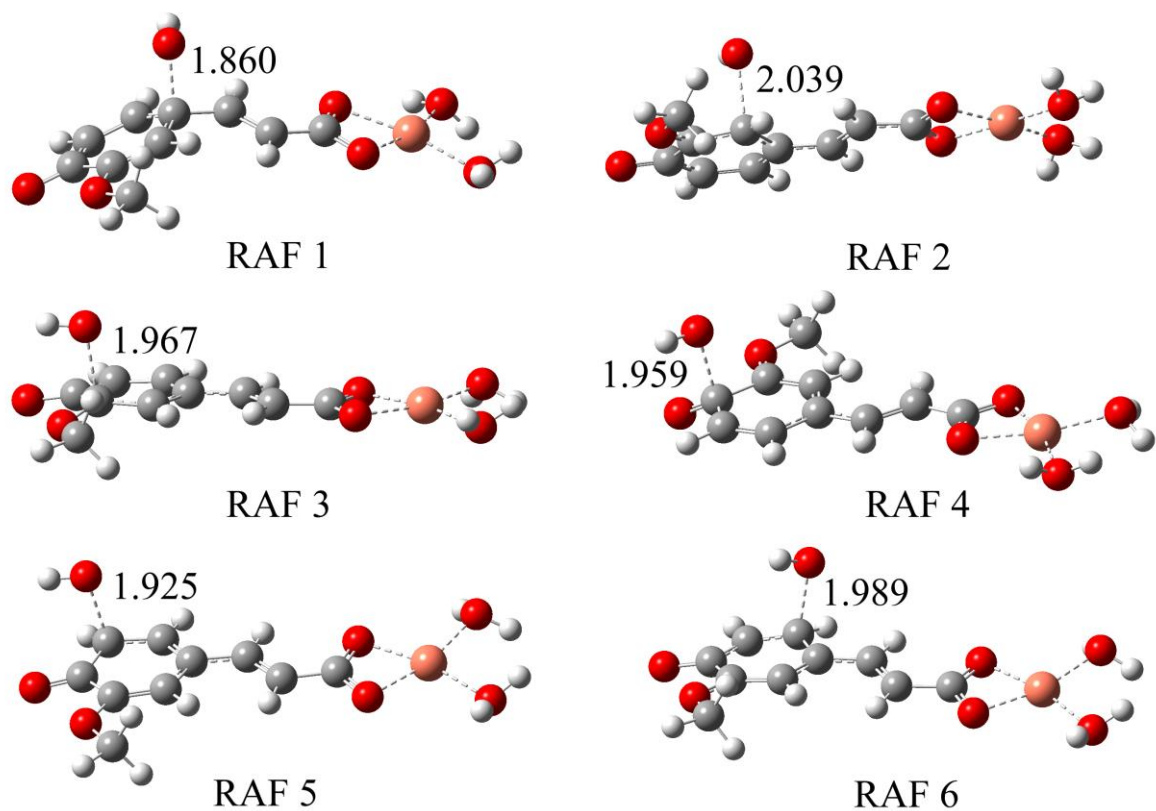


Figure S6. Transition states structures of exergonic RAF reactions between $\cdot\text{OH}$ and $\text{H}_{\text{n-2}}\text{FLA}^{2-}-(2)\text{-C2}$ complexes at 298.15 K. Solvent=water.

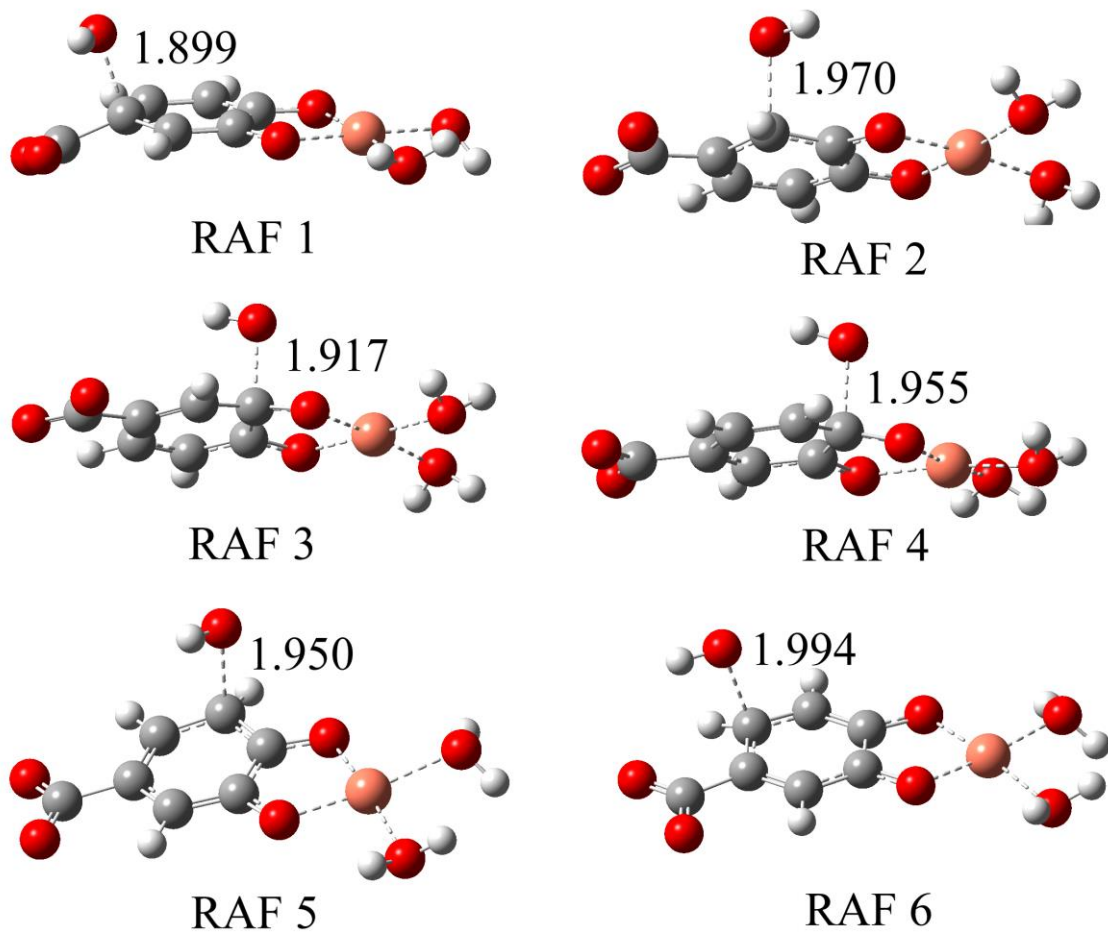


Figure S7. Transition states structures of exergonic RAF reactions between $\cdot\text{OH}$ and $\text{H}_n\text{-}_2\text{PRA}^{2-}\text{-(2)-C7}$ complexes at 298.15 K. Solvent=water.

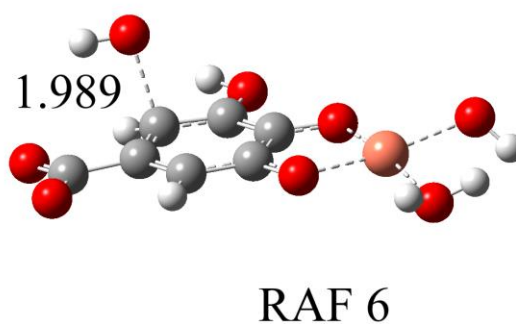
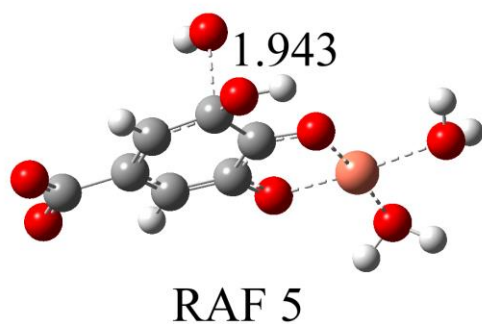
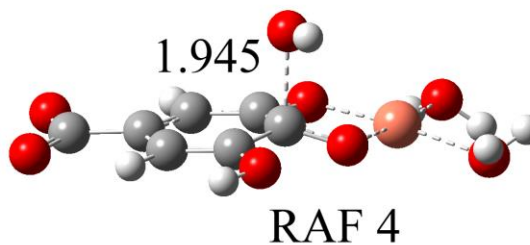
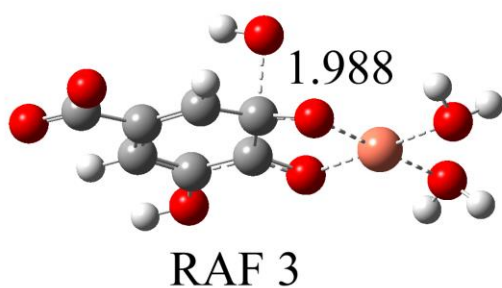
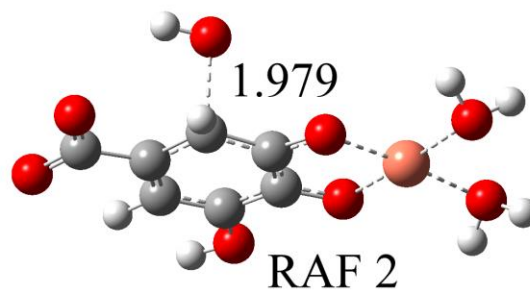
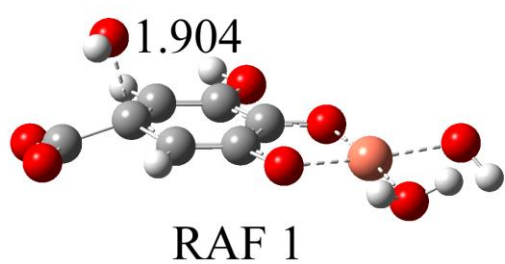


Figure S8. Transition states structures of exergonic RAF reactions between $\cdot\text{OH}$ and $\text{H}_n\text{-}_2\text{GAA}^{2-}\text{-(2)-C7}$ complexes at 298.15 K. Solvent=water.