Molecular View on Lignin Fractionation in Organic-water Co-solvent: Effect of the Ratio of Van Der Waals over Electrostatic of Lignin-Solvent Interactions

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Table S1-Table S8

Figure S1-Figure S18

Reference

Table S1. The lignin removal rate in water, organic and organic-water co-solvent according to previous experimental results (473.15 K, 2 MPa).[1, 2]

Solvent	Lignin Removal Rate
GBL-H_2O (v7/v3)	0.96
GVL-H_2O (v7/v3)	0.93
THF-H_2O (v7/v3)	0.9
THF-H_2O (v6/v4)	0.9
EAC-H_2O (v7/v3)	0.88
MTHF-H_2O (v7/v3)	0.73
GBL	0.67
GVL	0.62
THF	0.4
EAC	0.28
MTHF	0.28
H_2O	0.12

Table S2. Average H-bond number of lignin model LG1 in different solvents.

Solvent	Lignin-Lignin	Lignin-Solvent	Lignin-Organic	Lignin-Water
GBL-H_2O (v7/v3)	8.9	33.5	9.0	24.5
GVL-H_2O (v7/v3)	9.1	34.4	7.8	26.6
THF-H_2O (v7/v3)	9.9	34.4	2.9	31.4
THF-H_2O (v6/v4)	9.5	37.6	2.7	34.9
EAC-H_2O (v7/v3)	9.2	31.0	7.5	23.4
MTHF-H_2O (v7/v3)	9.5	36.8	3.8	32.9
GBL	8.5	15.8	15.8	0.0
GVL	9.3	15.6	15.6	0.0
THF	12.7	4.8	4.8	0.0
EAC	9.6	13.7	13.7	0.0
MTHF	12.5	6.1	6.1	0.0
H_2O	8.6	60.1	0.0	60.1

Table S3. Average H-bond number of lignin model LG2 in different solvents.

Solvent	Lignin-Lignin	Lignin-Solvent	Lignin-Organic	Lignin-Water
GBL-H_2O (v7/v3)	7.6	30.4	7.6	22.8
GVL-H_2O (v7/v3)	7.3	30.7	7.1	23.6
THF-H_2O (v7/v3)	8.2	33.7	2.4	31.3
THF-H_2O (v6/v4)	8.5	24.7	3.0	21.7
EAC-H_2O (v7/v3)	7.3	28.7	6.7	22.0
MTHF-H_2O (v7/v3)	8.3	31.4	3.2	28.2
GBL	7.1	15.7	15.7	0.0
GVL	8.0	13.6	13.6	0.0
THF	11.0	4.2	4.2	0.0
EAC	8.0	12.2	12.2	0.0
MTHF	10.6	5.6	5.6	0.0
H_2O	6.8	54.7	0.0	54.7

Table S4. Average H-bond number of lignin model LG3 in different solvents.

Solvent	Lignin-Lignin	Lignin-Solvent	Lignin-Organic	Lignin-Water
GBL-H_2O (v7/v3)	5.8	29.3	7.4	21.9
GVL-H_2O (v7/v3)	6.4	28.6	6.1	22.4
THF-H_2O (v7/v3)	6.8	32.4	2.3	30.1
THF-H_2O (v6/v4)	6.7	32.2	2.3	30.0
EAC-H_2O (v7/v3)	6.9	24.2	6.2	18.0
MTHF-H_2O (v7/v3)	7.4	26.6	2.9	23.7
GBL	6.1	14.7	14.7	0.0
GVL	7.2	12.5	12.5	0.0
THF	8.7	5.8	5.8	0.0
EAC	6.5	12.2	12.2	0.0
MTHF	9.2	5.6	5.6	0.0
H_2O	6.7	48.3	0.0	48.3

Table S5. Average H-bond number of lignin model LG4 in different solvents.

Solvent	Lignin-Lignin	Lignin-Solvent	Lignin-Organic	Lignin-Water
GBL-H_2O (v7/v3)	5.1	23.5	5.8	17.7
GVL-H_2O (v7/v3)	5.6	22.5	5.4	17.0
THF-H_2O (v7/v3)	6.1	23.2	1.9	21.3
THF-H_2O (v6/v4)	5.5	27.3	1.7	25.6
EAC-H_2O (v7/v3)	5.5	21.0	5.2	15.9
MTHF-H_2O (v7/v3)	6.3	20.5	2.6	17.9
GBL	5.0	11.7	11.7	0.0
GVL	5.6	10.3	10.3	0.0
THF	8.2	3.1	3.1	0.0
EAC	5.8	9.1	9.1	0.0
MTHF	7.2	4.4	4.4	0.0
H_2O	5.1	43.4	0.0	43.4

Table S6. Average H-bond number of lignin model LG5 in different solvents.

Solvent	Lignin-Lignin	Lignin-Solvent	Lignin-Organic	Lignin-Water
GBL-H_2O (v7/v3)	4.2	23.4	5.9	17.6
GVL-H_2O (v7/v3)	4.5	22.7	5.0	17.7
THF-H_2O (v7/v3)	5.2	24.4	1.7	22.8
THF-H_2O (v6/v4)	5.5	24.5	1.7	22.9
EAC-H_2O (v7/v3)	5.3	20.3	4.5	15.8
MTHF-H_2O (v7/v3)	5.4	23.1	2.1	20.9
GBL	4.6	10.5	10.5	0.0
GVL	4.9	10.1	10.1	0.0
THF	8.1	3.1	3.1	0.0
EAC	5.1	9.7	9.7	0.0
MTHF	6.4	5.2	5.2	0.0
H_2O	4.3	40.2	0.0	40.2

Table S7. Energy decomposition analysis for weak interaction with typical lignin dimers (*β*-O-4, *β*-*β*, *β*-5) and typical solvent molecules (kcal/mol).

Items	Molecules	Electrostatic ΔE_{elec}	Dispersion ΔE_{disp}	Exchange-repulsion	Orbital ΔE_{orb}	Total Energy	$\Delta E_{disp}/\Delta E_{elec}$
a	*β*-*β*···*β*-*β*	-14.18	-30.73	37.31	-4.84	-12.44	**2.17**
b	*β*-O-4···*β*-O-4	-13.65	-28.13	34.05	-5.76	-13.49	**2.06**
c	*β*-5···*β*-5	-10.10	-28.27	31.32	-5.03	-12.10	**2.80**
d	*β*-5···*β*-5	-20.50	-22.44	37.19	-8.72	-14.47	**1.09**
e	*β*-*β*···H_2O	-12.11	-8.96	18.89	-5.38	-7.56	**0.74**
f	*β*-*5*···H_2O	-11.64	-5.37	15.52	-4.12	-5.61	**0.46**
g	*β*-*5*···THF	-14.65	-10.80	22.11	-6.62	-9.95	**0.74**
h	*β*-*β*···GBL	-13.56	-15.72	23.07	-4.52	-10.74	**1.76**
i	*β*-O-4···GBL	-6.45	-11.33	17.02	-3.05	-3.82	**2.01**
j	*β*-*5*···THF	-6.56	-13.19	16.71	-2.43	-5.46	**1.16**

Table S8. The proportion of E_{vdw} in Lignin-Solvent interaction for the six lignin dimer models with DES based on previous work.[3]

Lignin Dimers	Solvents	Interaction Energy			Proportion of E_{vdw}
		vdW	coulomb	total	
β-5	3c-DES-0	-238.327	-167.357	-405.684	**0.587**
	3c-DES-2	-235.715	-170.945	-406.660	**0.580**
	3c-DES-4	-238.362	-184.024	-422.386	**0.564**
	3c-DES-6	-254.319	-169.739	-424.058	**0.600**
β-1	3c-DES-0	-261.003	-169.269	-430.272	**0.607**
	3c-DES-2	-252.587	-190.407	-442.994	**0.570**
	3c-DES-4	-259.617	-186.516	-446.133	**0.582**
	3c-DES-6	-260.383	-185.406	-445.789	**0.584**
β-O-4	3c-DES-0	-236.988	-150.843	-387.831	**0.611**
	3c-DES-2	-236.165	-151.398	-387.563	**0.609**
	3c-DES-4	-235.130	-161.770	-396.900	**0.592**
	3c-DES-6	-228.132	-170.456	-398.588	**0.572**
β-*β*	3c-DES-0	-299.452	-153.236	-452.688	**0.661**
	3c-DES-2	-297.210	-155.020	-452.230	**0.657**
	3c-DES-4	-298.852	-162.933	-461.785	**0.647**
	3c-DES-6	-298.171	-188.527	-486.698	**0.613**
β-*β*-2*γ*-OH	3c-DES-0	-292.077	-227.911	-519.988	**0.562**
	3c-DES-2	-291.465	-239.199	-530.664	**0.549**
	3c-DES-4	-283.586	-239.064	-522.650	**0.543**
	3c-DES-6	-288.947	-239.182	-528.129	**0.547**
β-*β*-2*pCA*	3c-DES-0	-461.576	-315.900	-777.476	**0.594**
	3c-DES-2	-469.783	-332.205	-801.988	**0.586**
	3c-DES-4	-478.988	-337.154	-816.142	**0.587**
	3c-DES-6	-466.786	-387.582	-854.368	**0.546**

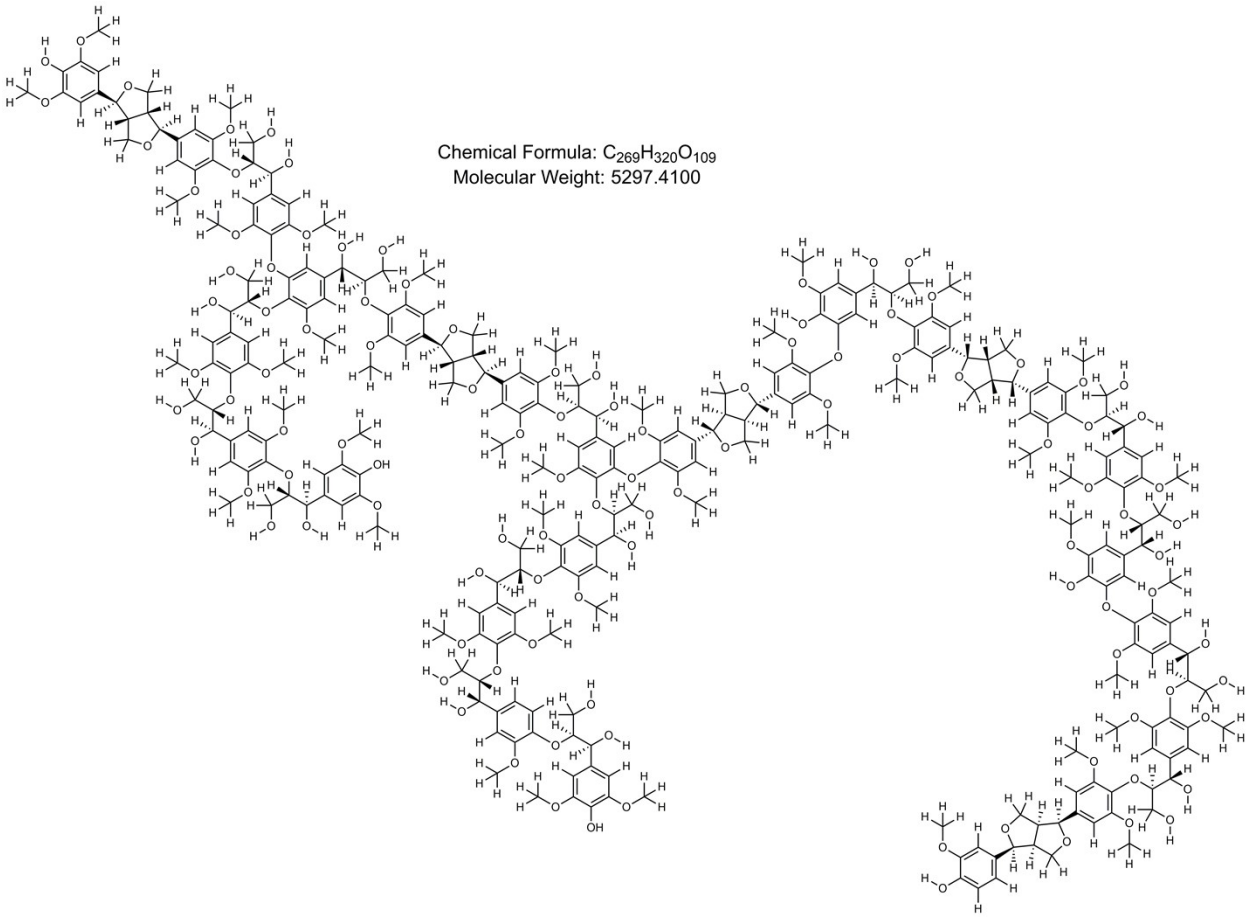

Figure S1. The chemical structure of lignin model LG1.

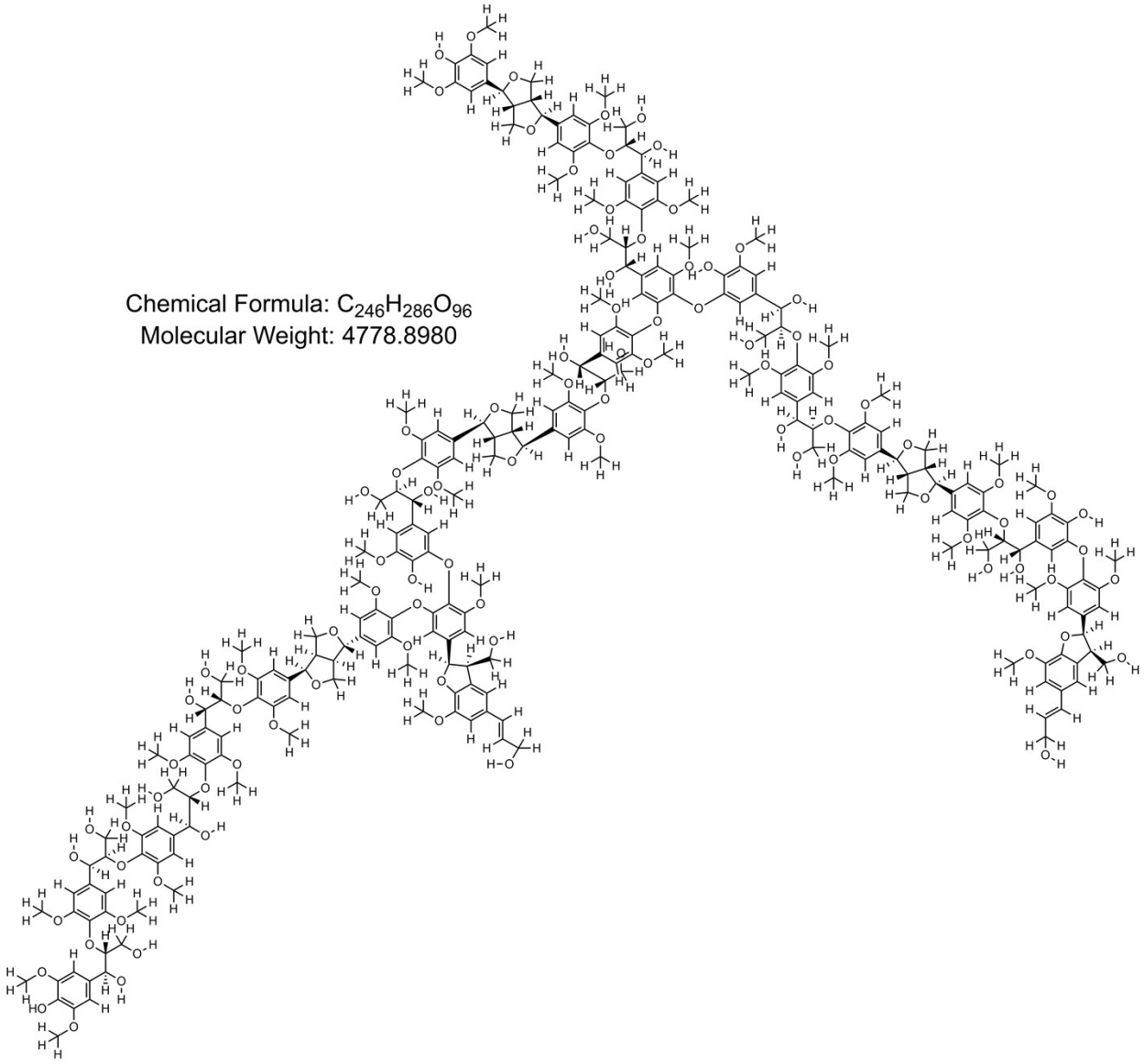

Figure S2. The chemical structure of lignin model LG2.

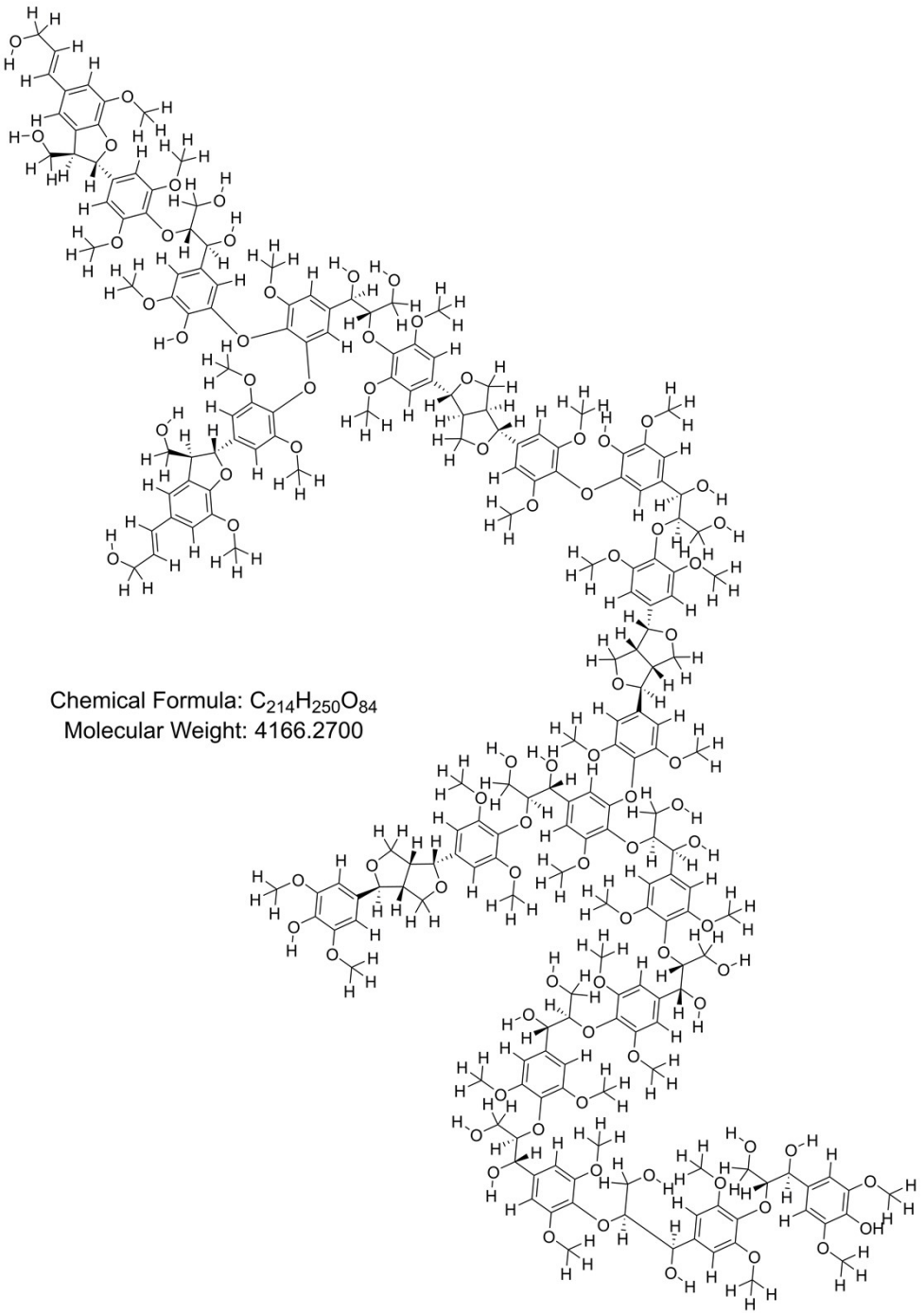

Figure S3. The chemical structure of lignin model LG3.

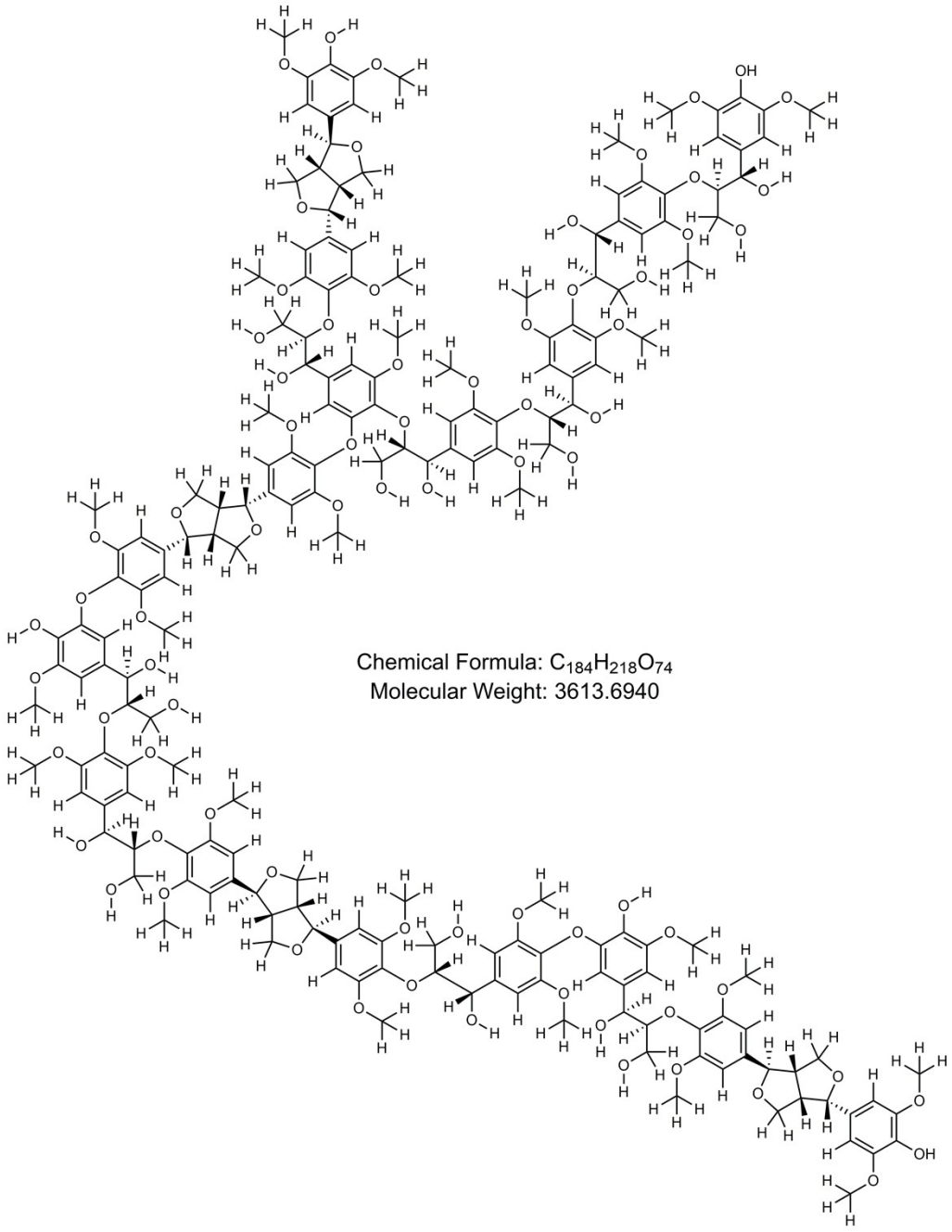

Figure S4. The chemical structure of lignin model LG4.

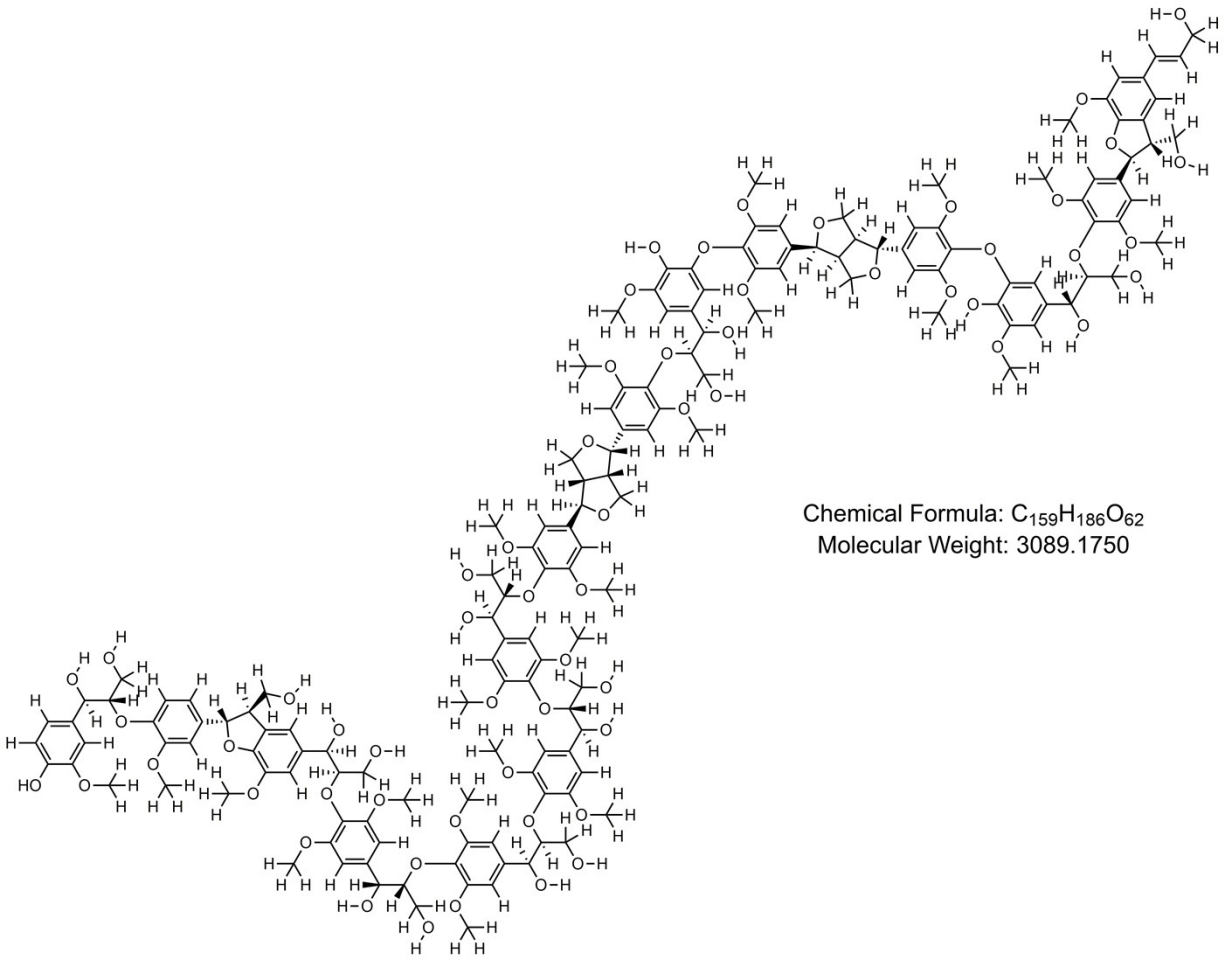

Figure S5. The chemical structure of lignin model LG5.

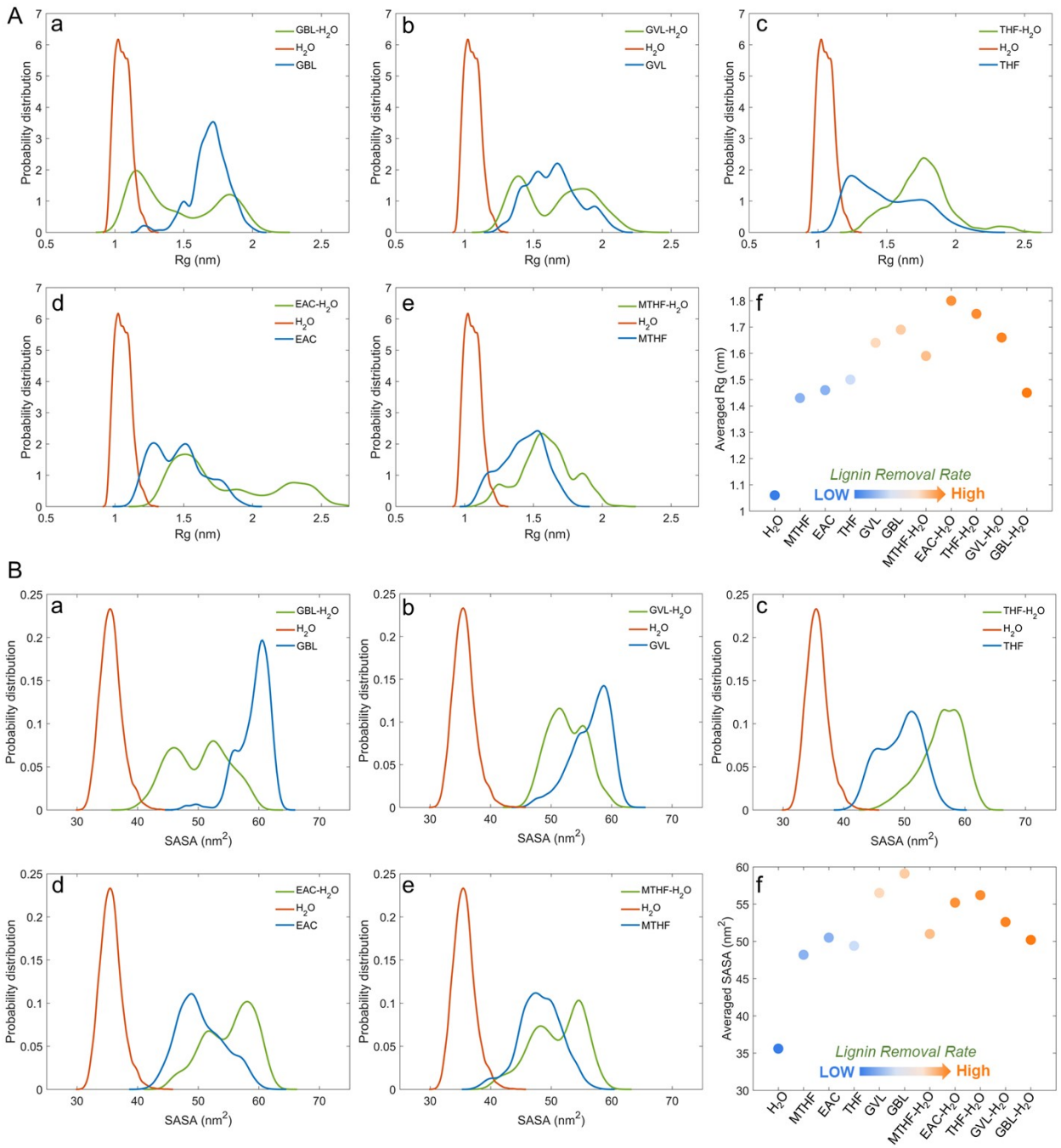

Figure S6. **A**. The probability distribution of Rg of lignin model chain LG2 in different solvents during 10 ns Production MD simulation. **B**. The probability distribution of SASA of lignin model chain LG2 in different solvents during 10 ns Production MD simulation. **a**. Organic part: GBL. **b**. Organic part: GVL. **c**. Organic part: THF. **d**. EAC. **e**. MTHF. The volume ratio of co-solvent was 7:3 (organic part: water). **f.** Averaged Rg/SASA in different solvent with the relative experimental lignin removal rate.

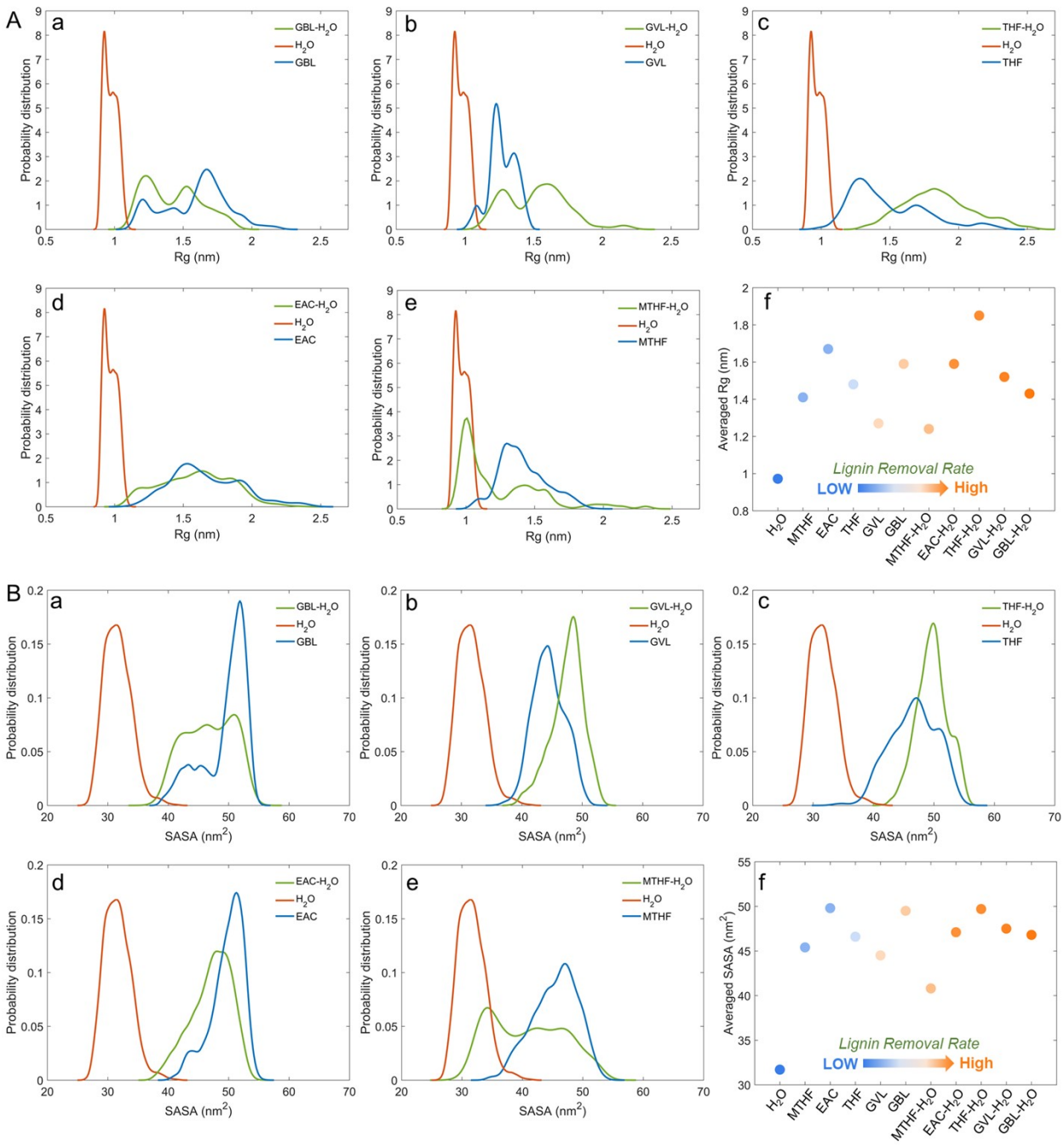

Figure S7. **A**. The probability distribution of Rg of lignin model chain LG3 in different solvents during 10 ns Production MD simulation. **B**. The probability distribution of SASA of lignin model chain LG3 in different solvents during 10 ns Production MD simulation. **a**. Organic part: GBL. **b**. Organic part: GVL. **c**. Organic part: THF. **d**. EAC. **e**. MTHF. The volume ratio of co-solvent was 7:3 (organic part: water). **f.** Averaged Rg/SASA in different solvent with the relative experimental lignin removal rate.

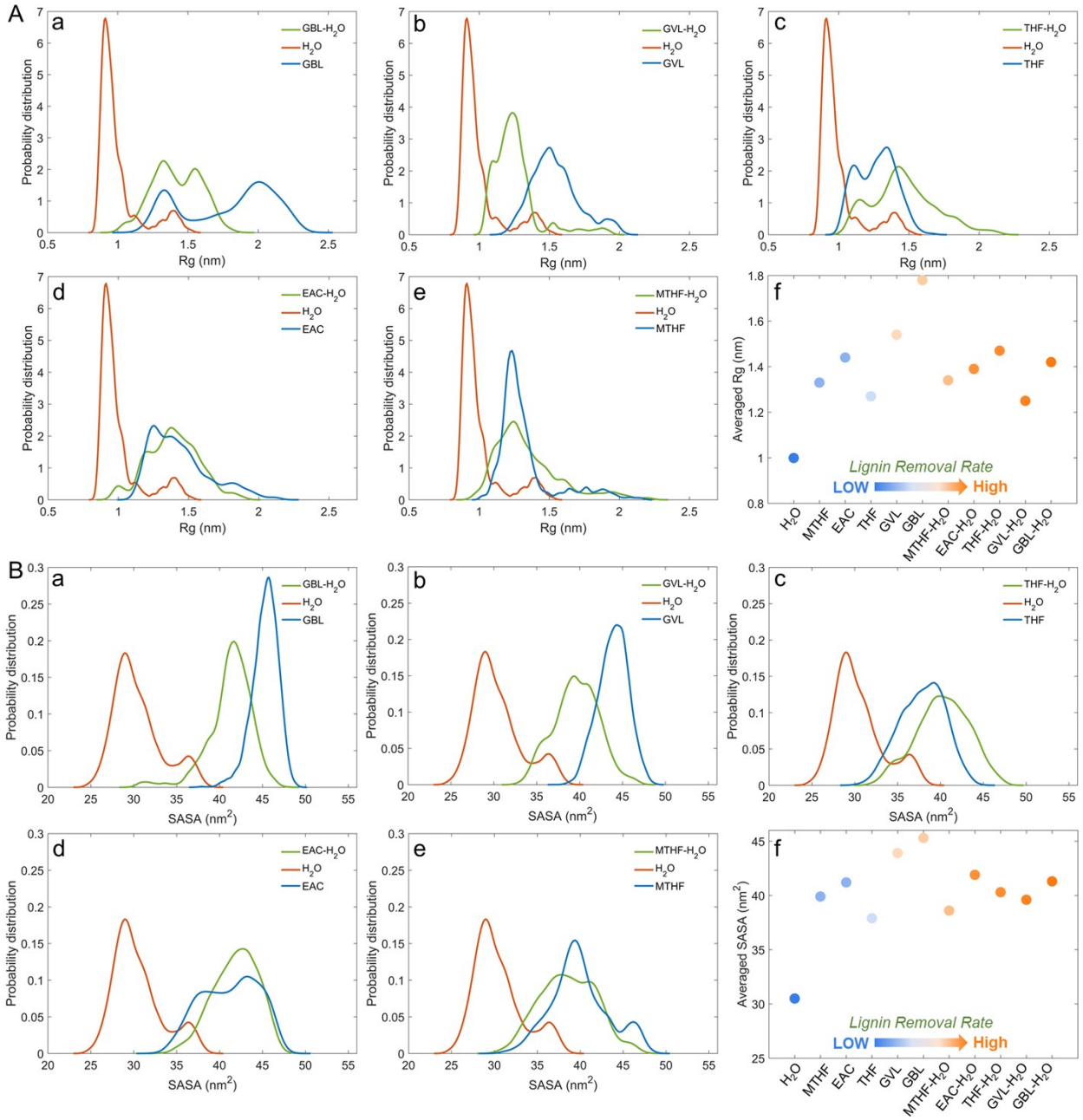

Figure S8. **A**. The probability distribution of Rg of lignin model chain LG4 in different solvents during 10 ns Production MD simulation. **B**. The probability distribution of SASA of lignin model chain LG4 in different solvents during 10 ns Production MD simulation. **a**. Organic part: GBL. **b**. Organic part: GVL. **c**. Organic part: THF. **d**. EAC. **e**. MTHF. The volume ratio of co-solvent was 7:3 (organic part: water). **f.** Averaged Rg/SASA in different solvent with the relative experimental lignin removal rate.

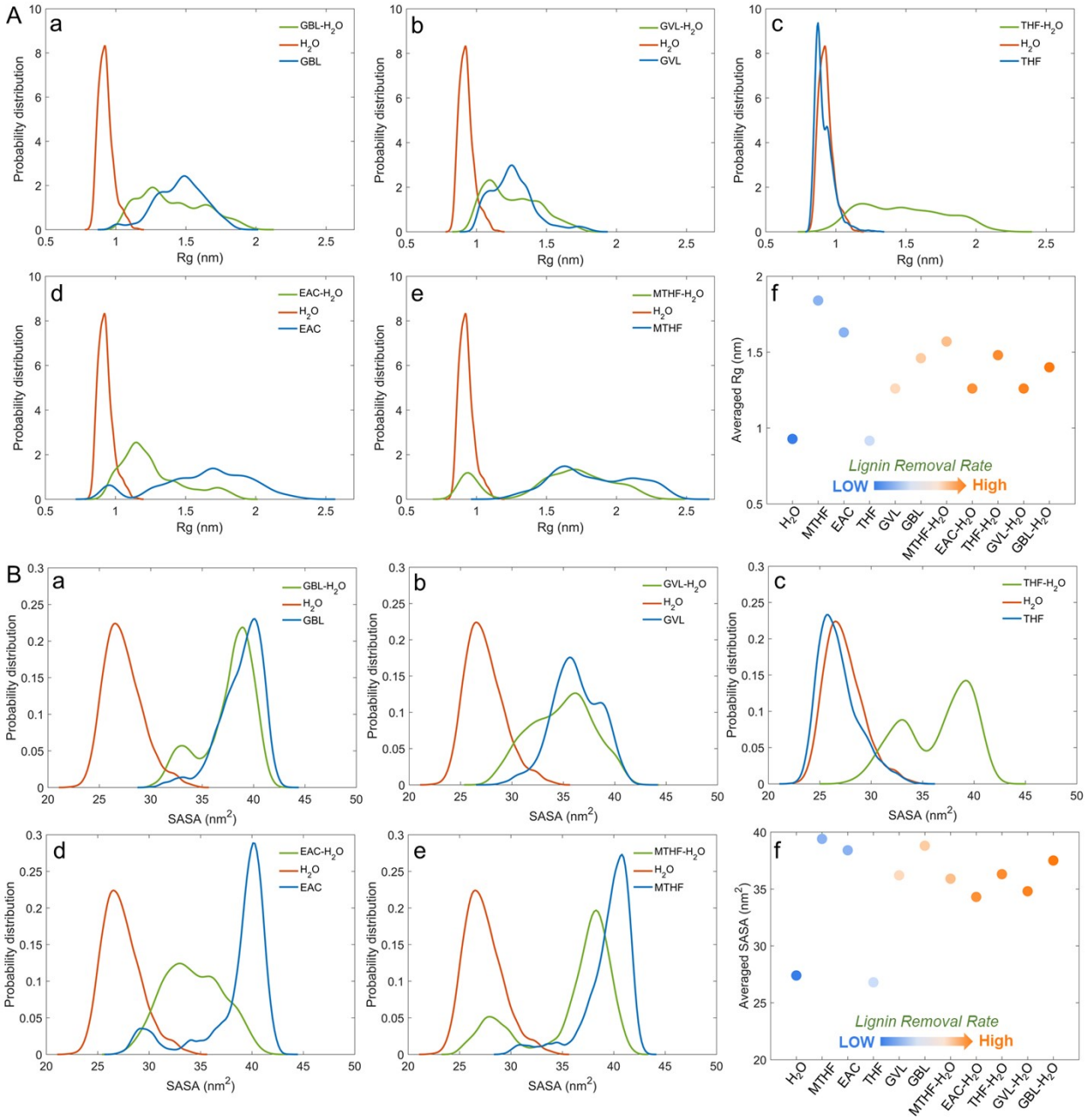

Figure S9. **A**. The probability distribution of Rg of lignin model chain LG5 in different solvents during 10 ns Production MD simulation. **B**. The probability distribution of SASA of lignin model chain LG5 in different solvents during 10 ns Production MD simulation. **a**. Organic part: GBL. **b**. Organic part: GVL. **c**. Organic part: THF. **d**. EAC. **e**. MTHF. The volume ratio of co-solvent was 7:3 (organic part: water). **f.** Averaged Rg/SASA in different solvent with the relative experimental lignin removal rate.

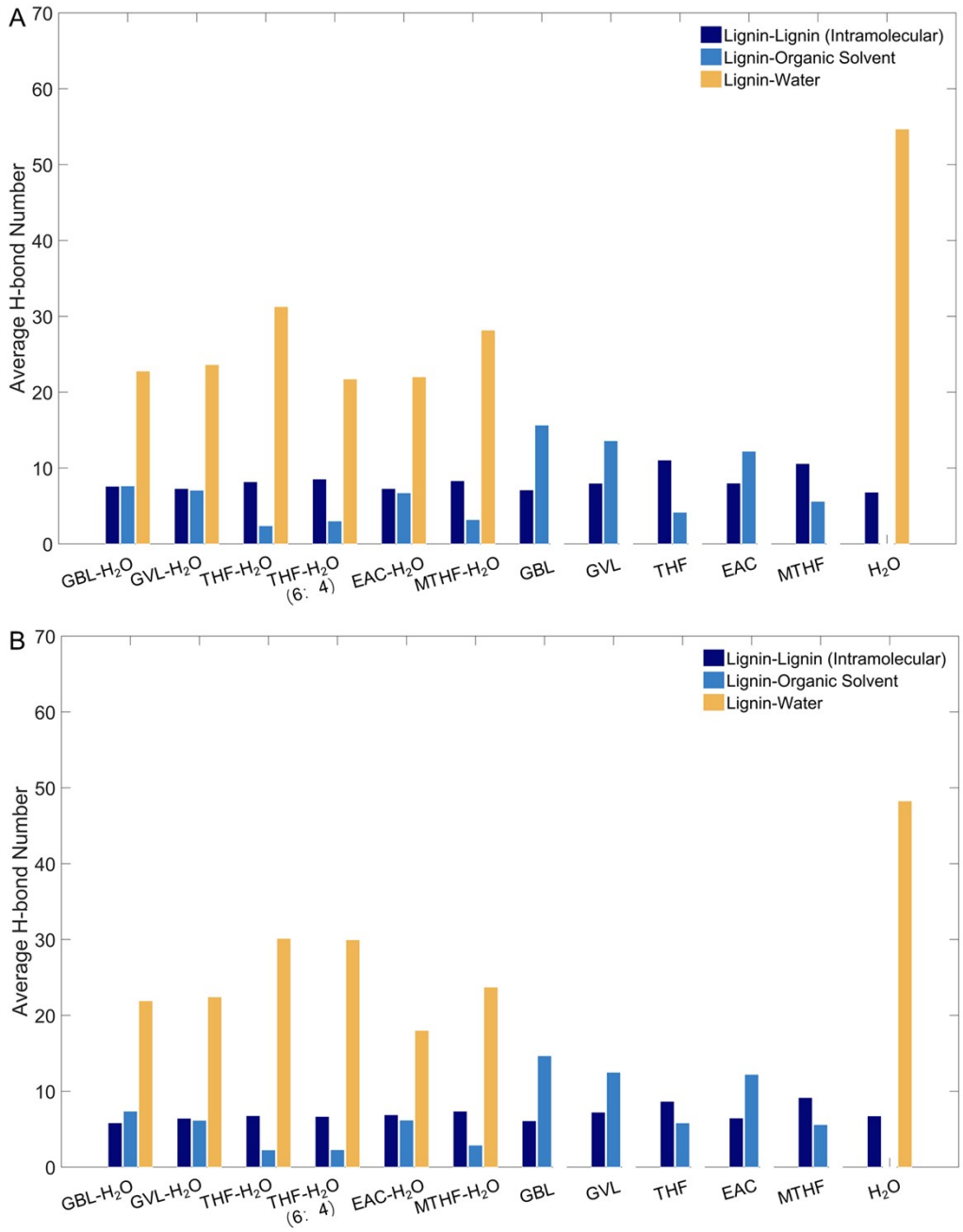

Figure S10. Average H-bond numbers of lignin models in different solvent. Dark blue for Lignin-Lignin. Blue for Lignin-Organic Part. Orange for Lignin-Water. **A**. LG2. **B**. LG3.

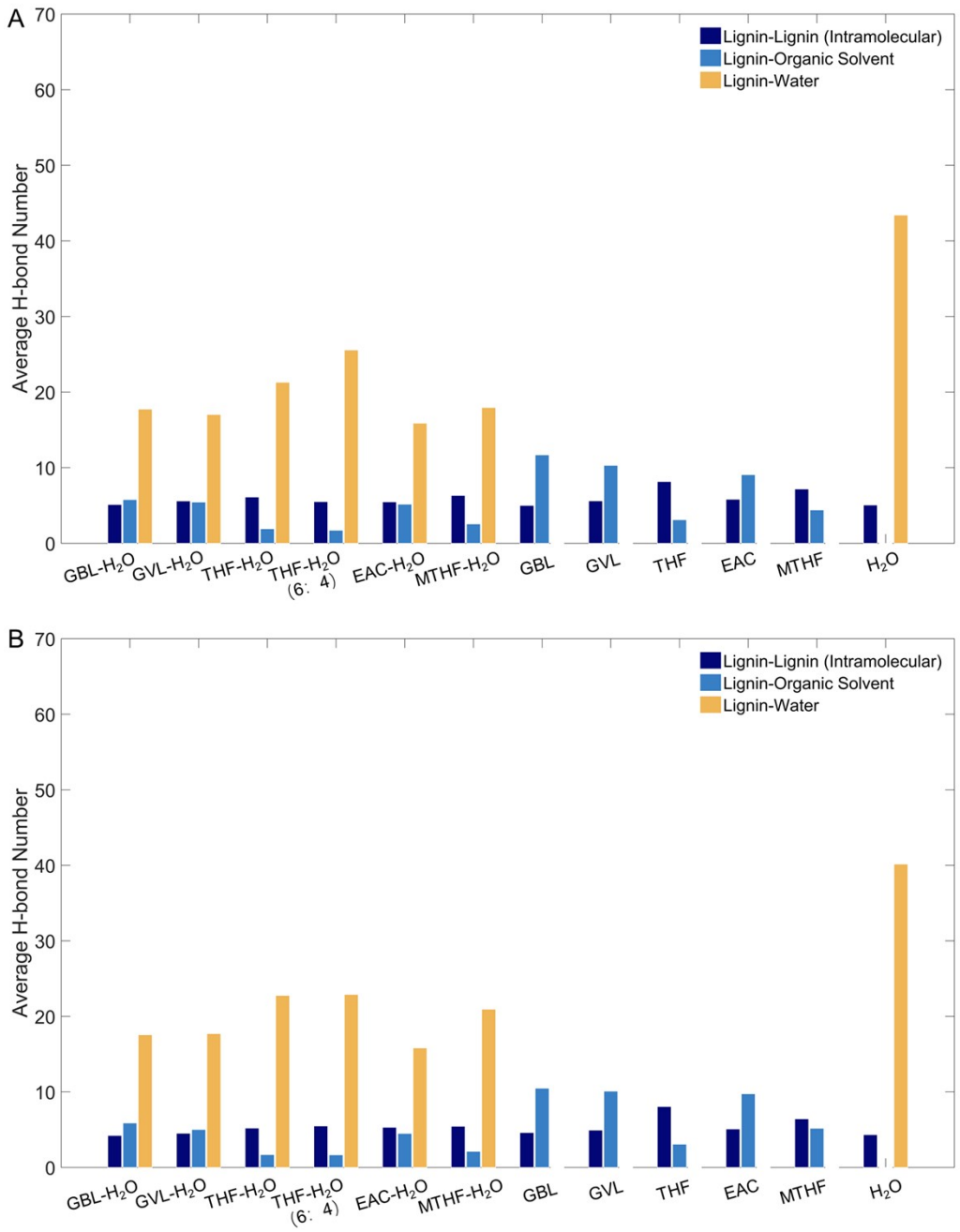

Figure S11. Average H-bond numbers of lignin models in different solvent. Dark blue for Lignin-Lignin. Blue for Lignin-Organic Part. Orange for Lignin-Water. **A**. LG4. **B**. LG5.

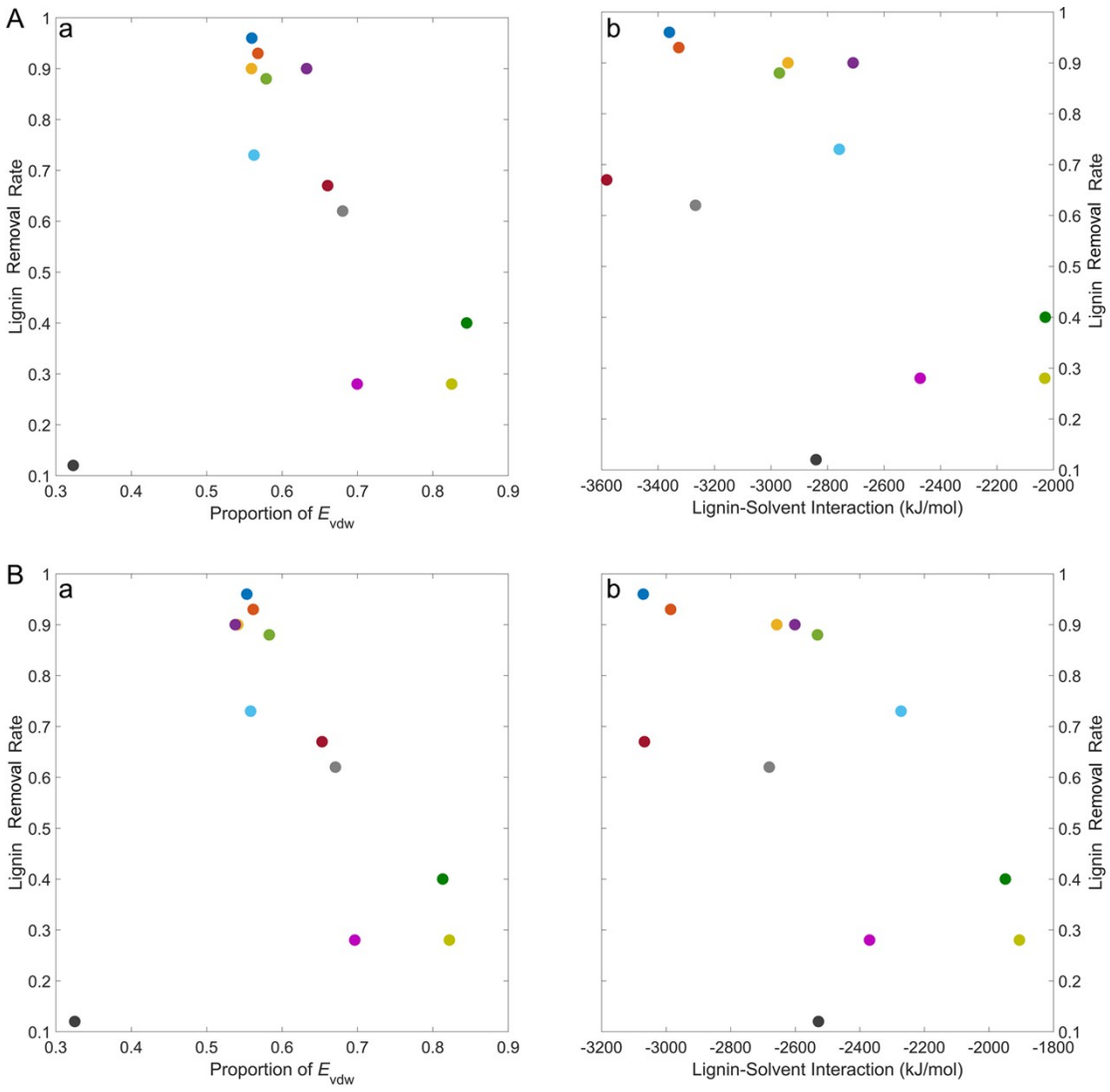

Figure S12. Lignin removal rate with proportion of E_{vdw} and lignin solvent interaction for lignin models. **A**. LG2. **B**. LG3 **a**. Proportion of E_{vdw}. **b**. Whole lignin solvent interaction.

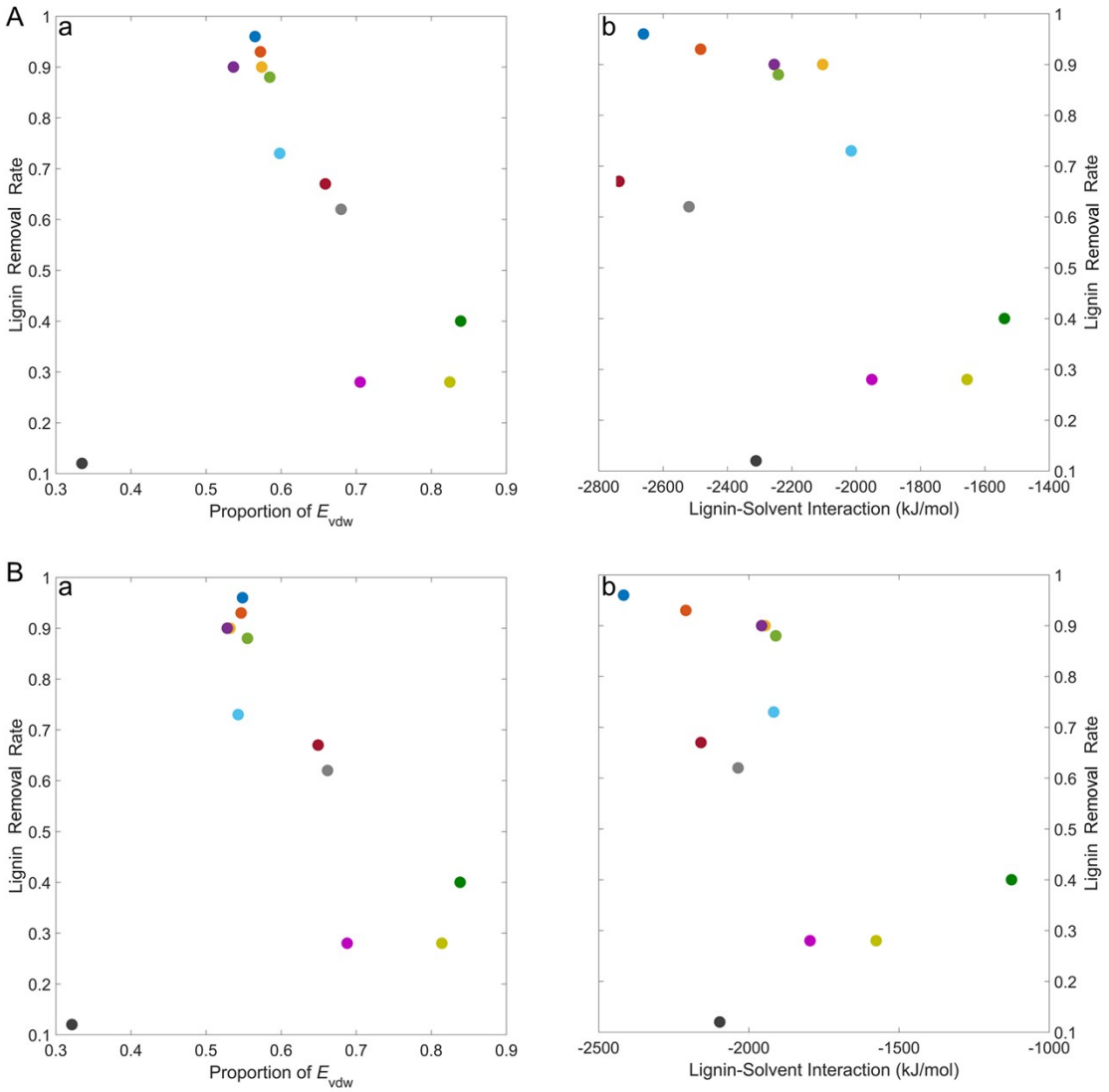

Figure S13. Lignin removal rate with proportion of E_{vdw} and lignin solvent interaction for lignin models. **A**. LG4. **B**. LG5 **a**. Proportion of E_{vdw}. **b**. Whole lignin solvent interaction.

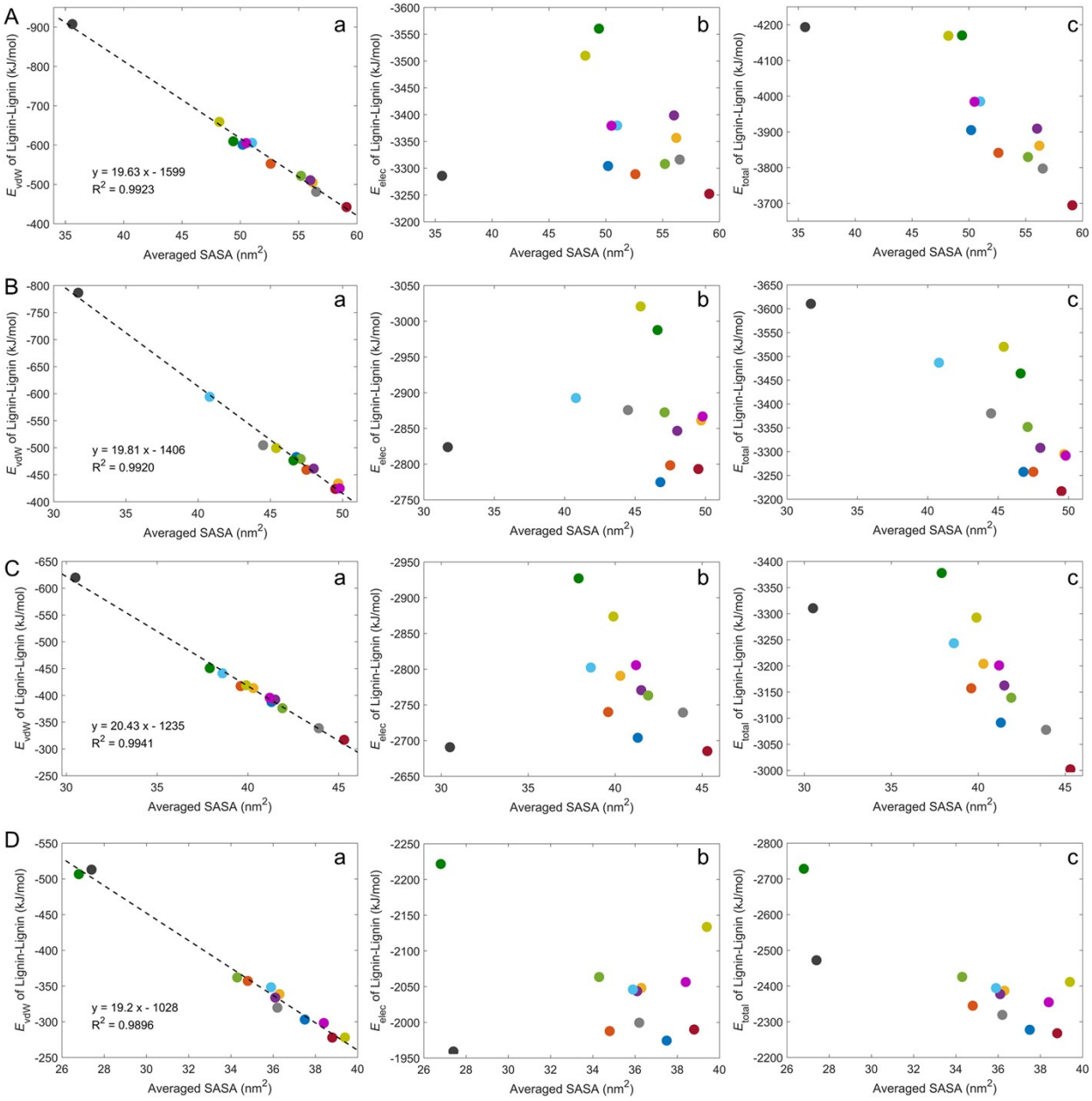

Figure S14. Relations between average solvent accessible surface areas (SASA) of lignin models and Lignin-Lignin Intramolecular interaction. **A**. LG2. **B**. LG3. **C**. LG4. **D**. LG5. **a**. Van der Waals. **b**. Electrostatic. **c**. Total.

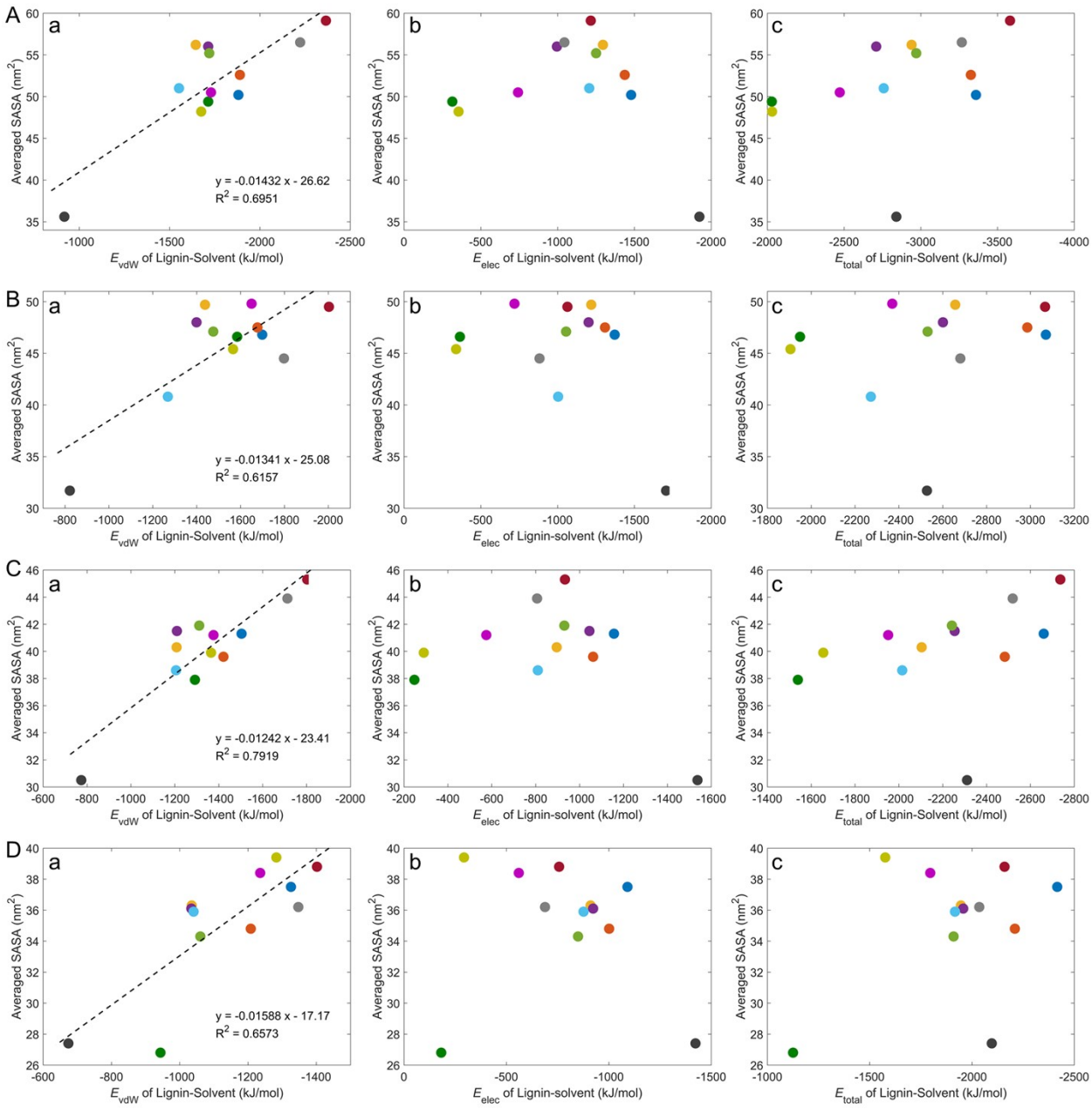

Figure S15. Relations between Lignin-Solvent interaction and average solvent accessible surface areas (SASA) of lignin models. **A**. LG2. **B**. LG3. **C**. LG4. **D**. LG5. **a**. Van der Waals. **b**. Electrostatic. **c**. Total.

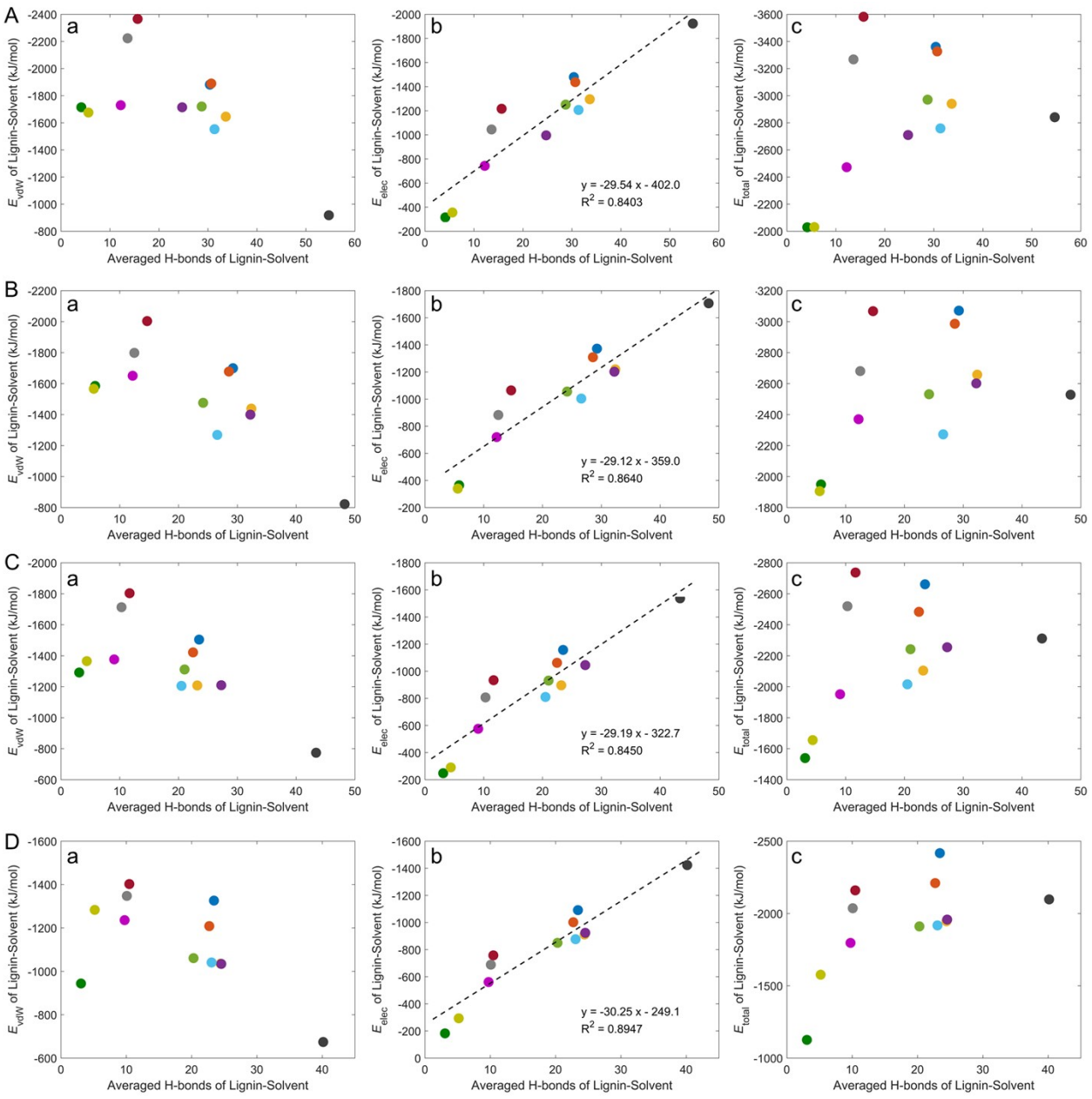

Figure S16. Relations between average number of Lignin-Solvent H-bond and Lignin-Solvent interaction of lignin models. **A**. LG2. **B**. LG3. **C**. LG4. **D**. LG5. **a**. Van der Waals. **b**. Electrostatic. **c**. Total.

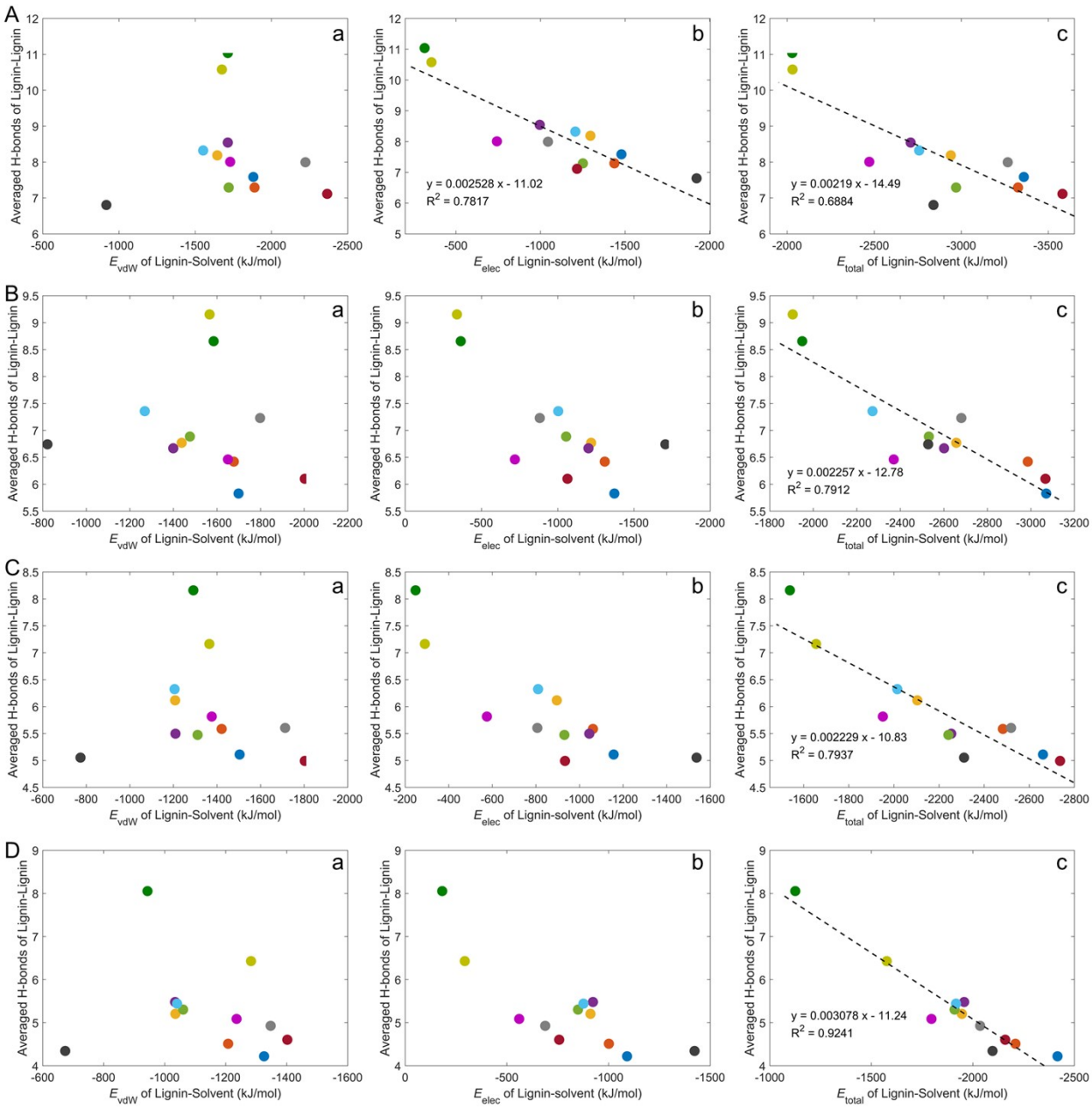

Figure S17. Relations between Lignin-Solvent interaction and average number of Lignin-Lignin intramolecular H-bond of lignin models. **A**. LG2. **B**. LG3. **C**. LG4. **D**. LG5. **a**. Van der Waals. **b**. Electrostatic. **c**. Total.

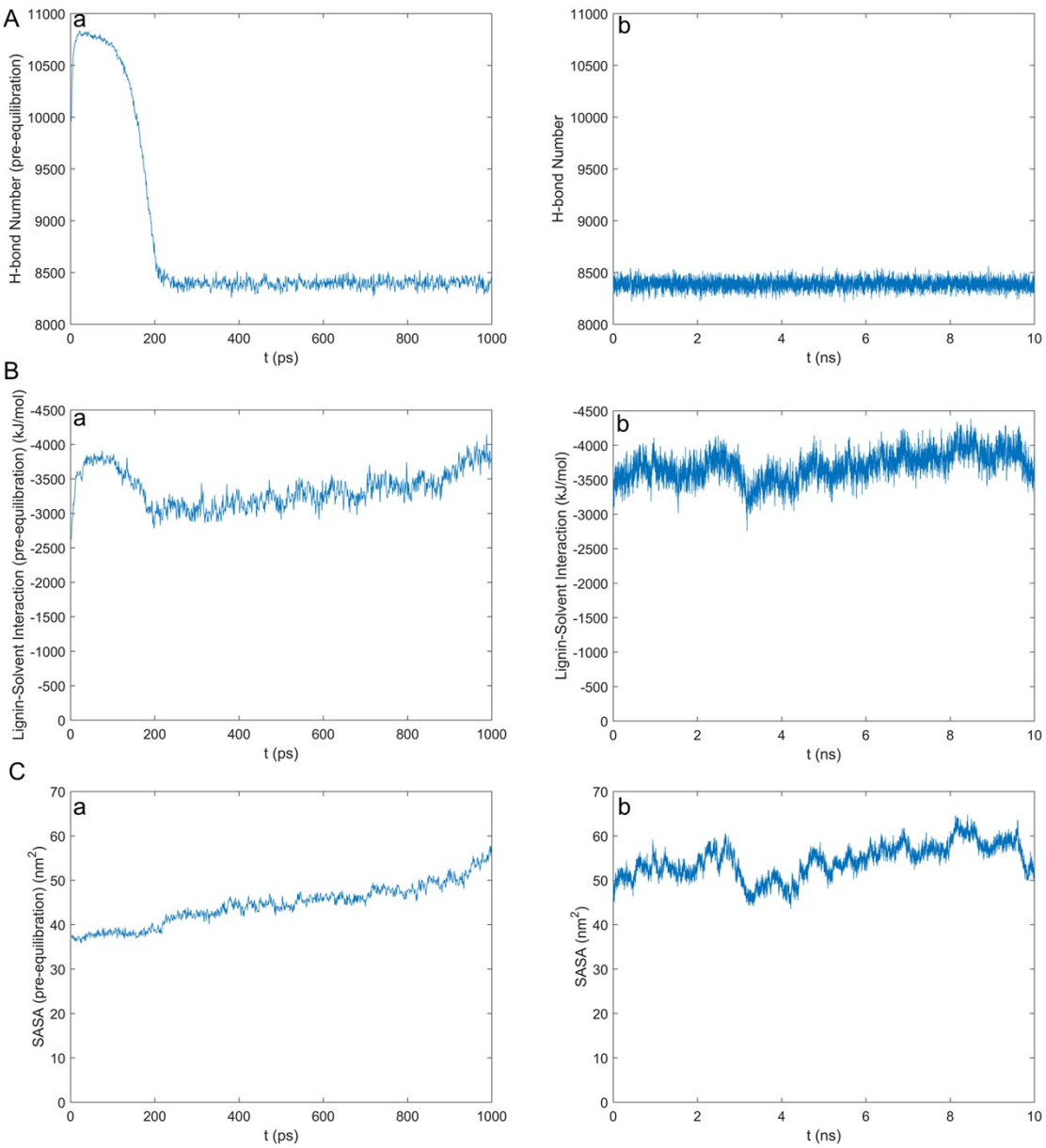

Figure S18. Detailed situation of LG1 in GBL-H_2O solvent. A. H-bond analysis for whole system. B. Lignin-Solvent interaction. C. SASA of lignin. (a. pre-equilibration NPT. b. Production MD)

Reference

1. Zhang, H.; Liu, X. D.; Li, J. M.; Jiang, Z. C.; Hu, C. W., Performances of Several Solvents on the Cleavage of Inter- and Intramolecular Linkages of Lignin in Corncob Residue. *ChemSusChem* **2018,** *11* (9), 1494-1504.

2. Jiang, Z. C.; He, T.; Li, J. M.; Hu, C. W., Selective conversion of lignin in corncob residue to monophenols with high yield and selectivity. *Green Chem.* **2014,** *16* (9), 4257-4265.

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