Electronic Supplementary Material (ESI) for Green Chemistry.
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Supplementary Information

NMR spectroscopy was performed on a Bruker instrument (600 MHz for ^{1}H) equipped with an inverse cryoprobe. TMS and D_2O were used as internal standards for ^{1}H experiments and calibrated at δ 0.00 and 4.80 ppm, respectively.

Synthesis of cholinium lysinate

To a flask containing 100 mL of 46% aqueous choline hydroxide (46 g, 380 mmol) was slowly added to a solution of lysine 66.5 g (1.2 eq, 450 mmol) in 100 mL of deionized water. The flask containing the choline hydroxide was cooled in an ice bath before addition of lysine and the reaction was allowed to warm to room temperate, in the dark, with stirring. After 48 hr, water was removed under reduced pressure at 55 ^{o}C and the resulting material was dissolved in 1.6 L of 9:1 acetonitrile:water. Residual lysine was removed by centrifugation (8000 RPM, 5 min, 0 ^{o}C). Another 1 L of 9:1 acetonitrile:water was added, and the resulting mixture was centrifuged, to remove any additional lysine. Solvent was removed under reduced pressure to yield cholinium lysinate as a light brown oil. The material was resuspended in 475 mL of methanol and vacuum filtered over a bed of activated carbon (20 g) at the top of neutral alumina (20 g) to yield a yellow oil (83g, 330 mmol, 88% yield). ^{1}H NMR (D_2O) δppm relative to D_2O: 1.38 (m, 2H), 1.51 (m, 2H), 1.59 (m, 1H), 1.66 (m, 1H), 2.68 (td, 2H, *J*= 7.2Hz, 3.2Hz), 3.24 (s, 10H), 3.55 (m, 2H), 4.09 (m, 2H).

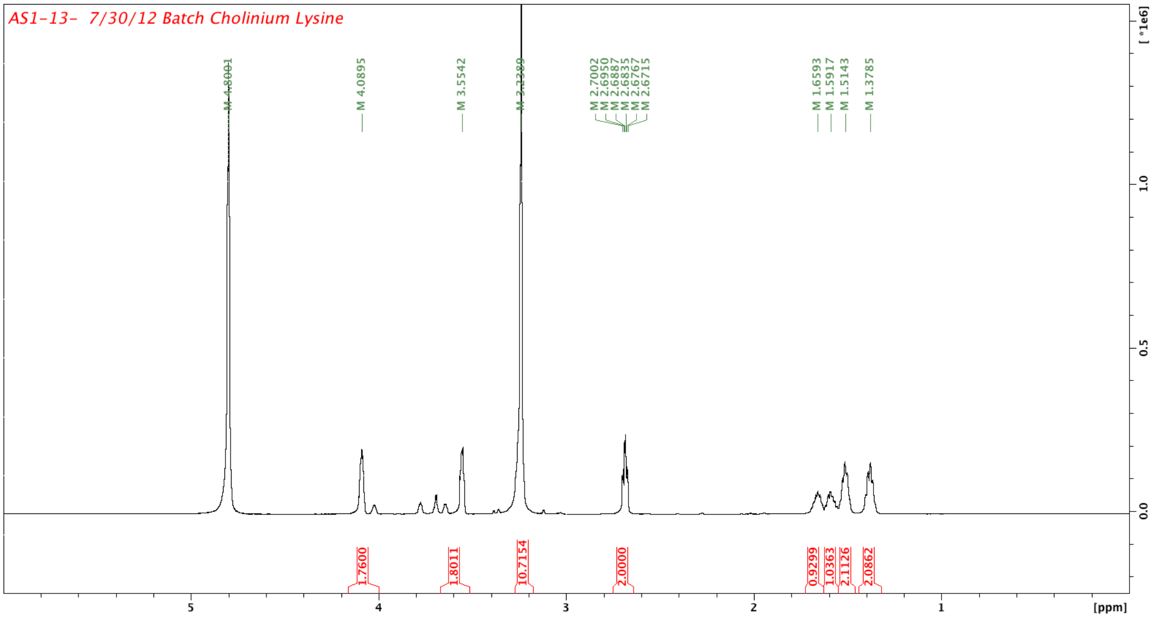


Figure S1 ^{1}H NMR spectra of [Ch][Lys] in D_2O.

Synthesis of 1-ethyl-3-methylimidazolium lysinate

To an ice bath cooled solution of 1-ethyl-3-methylimidazolium hydrogen sulfate (20 g, 96.0 mmol) in 60 mL deionized water was added 16.44 g (1 eq, 96.0 mmol) $Ba(OH)_2$. The resulting slurry was stirred vigorously for 10 min and centrifuged (4000 RPM, 5 min) to remove the resulting $BaSO_4$ precipitate. The 1-ethyl-3-methylimidazolium hydroxide supernatant was cooled to 0^oC, to which a solution of L-lysine 15.44 g (1.1 eq, 105.6 mmol) in 50 mL deionized water was added dropwise. The reaction was allowed to warm to room temperate, in the dark, with stirring. After 48 hr, water was removed under reduced pressure at 55^oC and the resulting material was dissolved in 700 mL of 9:1 acetonitrile:water. Residual lysine was removed by centrifugation (8000 RPM, 5 min, 0^oC). Another 400 mL of 9:1 acetonitrile:water was added, and the resulting mixture was centrifuged, to remove any additional lysine. Solvent was removed under reduced pressure to yield 1-ethyl-3-methylimidazolium lysinate (20.9 g, 81.5 mmol, 85% yield) as a pale yellow oil. ^1H NMR (DMSO-d_6) δ ppm relative to TMS: 1.24 (m, 2H) 1.28 (m, 3H), 1.41 (t, 3H, *J*= 7.3Hz), 1.53 (m, 1H), 2.48 (m, 2H), 2.79 (m, 1H), 3.90 (s, 3H), 4.24 (q, 2H, *J*= 14.4Hz, 7.2Hz), 7.77 (s, 1H), 7.85 (s, 1H), 9.91 (s, 1H). ^{13}C NMR, δ ppm relative to DMSO-d_6: 178.0, 137.4, 123.6, 121.9, 56.2, 44.0 (2C), 41.5, 35.6, 33.1, 23.4, 15.3.

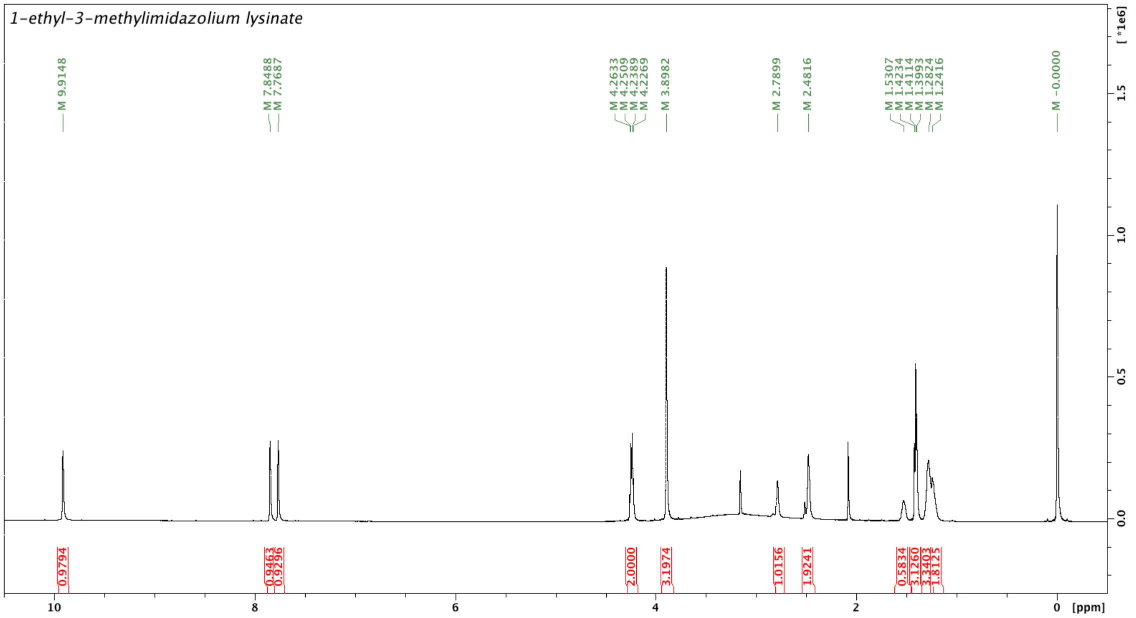


Figure S2 ^1H NMR spectra of $[C_2mim][Lys]$ in DMSO-d_6.

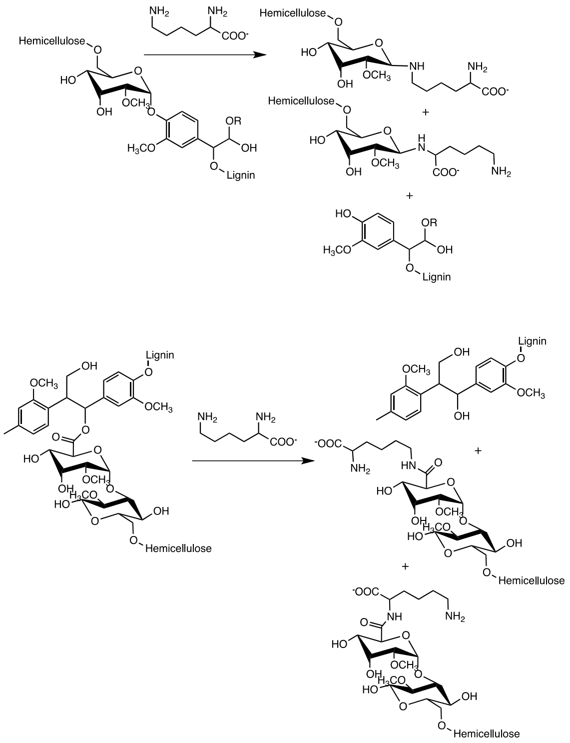


Figure S3. Proposed reactions between amino acid anion and lignin-carbohydrate linkage.

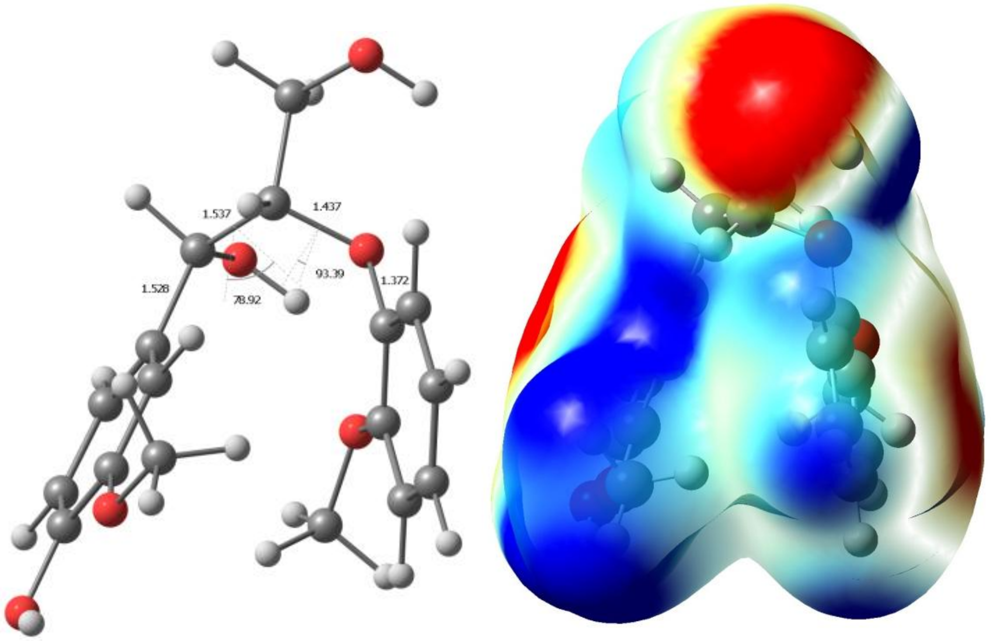
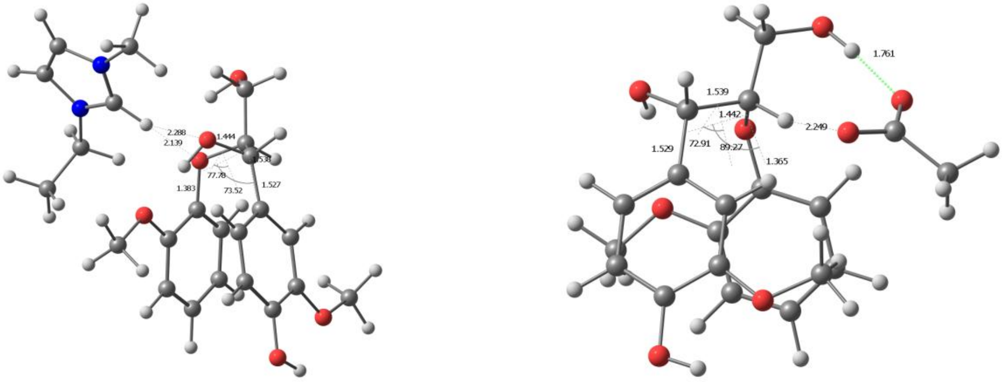


Figure S4. Optimized geometry for dilignol model compound and molecular electrostatic potentials at the ±0.04 au isosurface. The color scale indicates charges on the atoms: red = most electronegative, green = neutral, blue = most electropositive.

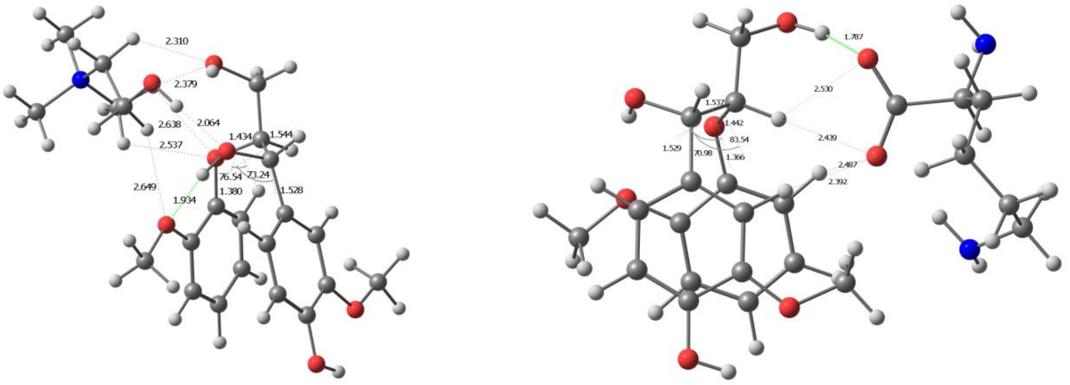


$[C_2mim]^+$— dilignol

IE=21.26

$[OAc]^-$— dilignol

IE=43.92



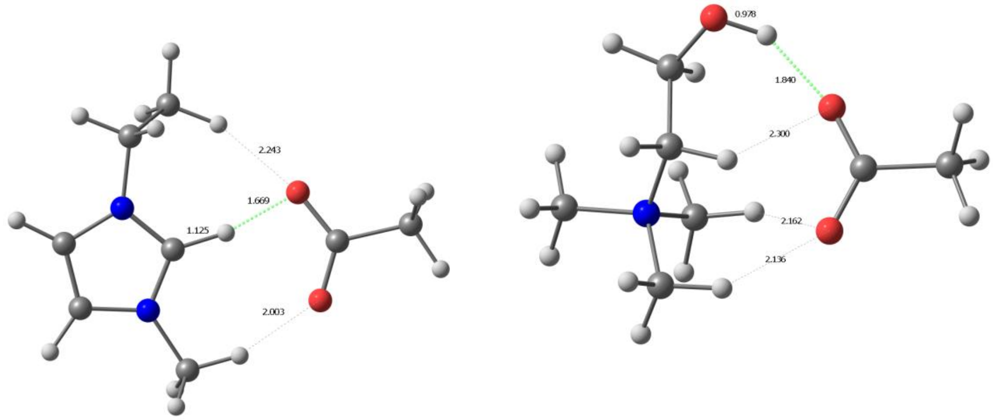
$[Ch]^+$— dilignol

IE=28.14

$[Lys]^-$— dilignol

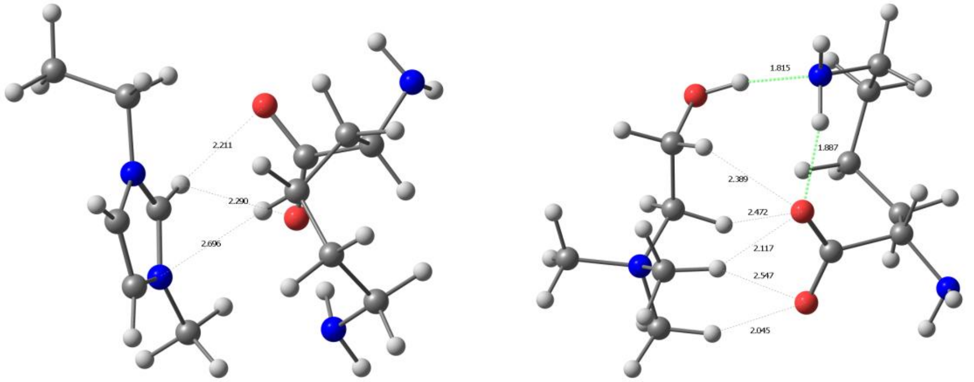
IE=38.87

Figure S5. Most stable geometries of dilignol with cations and anions calculated at M06-2x/6-31+G(d,p) level. Interaction energy (IE) is reported in kcal/mol.



[C_2mim]$^{+}$[OAc]$^{-}$
IE=106.42

[Ch]$^{+}$ [OAc]$^{-}$
IE=117.4



[C_2mim]$^{+}$[Lys]$^{-}$
IE=102.14

[Ch]$^{+}$[Lys]$^{-}$
IE=114.3

Figure S6. Most stable geometries calculated at M06-2x/6-311++G(d,p) level of four ILs. Interaction energy (IE) is reported in kcal/mol. The dotted lines denote molecular interactions between IL anions and cations.

Complete citation of Ref 28

Gaussian 09, revision A.01; Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Montgomery, J.A., Jr.; Vreven, T.; Kudin, K.; Burant, J.C.; Millam, J.M.; Iyengay, S.S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G.A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J.E.; Hratchian, H.P.; Cross, J.B.; Adamo, C.; Jaramillo, J.; Comperts, R.; Startmann, R.E.; Yazyev, O.; Austin, A.J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Ayala, P.Y.; Morokuma, K.; Voth, G.A.; Salvador, P.; Dannenbuerg, J.J.; Zakrzewski, V.G.; Dapprich, S.; Daniels, A.D.; Strain, M.C.; Farkas, O.; Malick, D.K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J.B.; Ortiz, J.V.; Cui, Q.; Baboul, A.G.; Clifford, S.; Cioslowski, J.; Stefanov, B.B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R.L.; Fox, D.J.; Keith, T.; Al-Laham, M.A.; Peng, C.Y.; Nanayakkara, A.; Challacombe, M.; Gill, P.M.W.; Johnson, B.; Chem, W.; Wong, M.W., Gonzalez, C.; Pople, J.A.; Gaussian, Inc.: Wallingford CT, 2009.

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