Lignin is a heteroaromatic biopolymer that is an essential component in the cell wall of plants. The structural and chemical properties of lignin provide plants with macroscopic structural rigidity, and protection against microbial invasion leading to subsequent cell wall degradation. For this reason, lignin presents a major inhibition to the efficient harvesting of biomass. Given the variability of lignin composition and structure among species, environment, etc., the field of “lignomics” seeks to “sequence” lignin oligomers into constituent unit types (H, G, S) and linkages. This is predominantly done by means of tandem mass-spectrometry, by first generating a library of characteristic fragmentation pathways built from collision-induced dissociation of model dilignol ions, and applying them to the interpretation of fragmentation in larger ions. While these methods have proven powerful, UV photofragmentation spectroscopy of lignin ions cooled in a 22-pole cold ion trap provides an alternative approach to lignomics based on fragmentation following resonant UV excitation. This approach serves as a complimentary method to pure MS\textsuperscript{n}-based methods with the potential for unveiling dissociation pathways only accessed by UV excitation. Further, the multichromophoric nature of lignin enables site-selectivity for the energy imparted into the molecule/ion when differentiation of the site absorptions may be possible. IR spectroscopy of the cold ions can be used for detailed analysis of the preferred conformations and binding sites of metal cations. UV spectroscopy and photofragmentation mass spectrometry has been carried out on the model (G-type) β-O-4 and β-β dilignol linkages complexed with Li\textsuperscript{+} and Na\textsuperscript{+}. The UV spectral signatures were found to vary between dilignols and metal complexes, and unique photofragmentation pathways were observed among the four complexes. IR spectroscopy in the OH stretch region was used as a probe of the conformation and binding preferences. In all cases, the dominating factor driving these structures was metal\textsuperscript{+}-oxygen electrostatic interactions with the alkali metal ion bound at the linkage between the lignol sub-units.