Comparison of the MS/MS spectra of protonated C-14 iturin A and C-14 fluoroiturin (A and B, respectively). The possible b- and y-fragment ions of linear iturin A are shown above the mass spectra. β-AA indicates the iturinic acid. Of particular interest is the presence of the b6 ion (m/z 801) in spectrum A, which corresponds to the fragment containing the tyrosine residue, and its absence in spectrum B; a new ion fragment, m/z 819, is observed in spectrum B (indicated by x) corresponding to the fluorotyrosine-containing peptide. The lower mass regions of the MS/MS spectra for iturin and fluoroiturin are also shown (C and D, respectively). The immonium ions of the constituent amino acids are present in spectrum C: Pro (m/z 70), Asn (m/z 87), Gln (m/z 101), Tyr (m/z 136) and β-AA (m/z 184); in the spectrum for fluoroiturin (D), tyrosine is replaced by fluorotyrosine (m/z 154).
Calibration graph of authentic iturin A as determined by LC-MS; the responses of ions $m/z$ 1043.5 and $m/z$ 1057.5 were combined.