**Significance:** Polymer-supported dendritic catalysts [Gn(E-Im), Gn(A-Im), Gn(T-Im)] were prepared from Wang resins and N-alkylated imidazoles (1–3), and applied to the Baylis–Hillman reaction. Thus, the Baylis–Hillman reaction of methyl vinyl ketone and 4-nitrobenzaldehyde was performed with the catalytic resin G2(A-Im) (0.1 mmol of N-alkylated imidazole units) in DMF–H2O (9:1, v/v) at room temperature for 4 h to afford adduct 4 in 91% yield.

**Comment:** The addition of water improved the catalytic activity in the Baylis–Hillman reaction. The second-generation catalysts [G2(E-Im), G2(T-Im), G2(A-Im)] exhibited higher catalytic activity than their non-dendritic counterparts [G0(E-Im), G0(T-Im), G0(A-Im)].