Supported N-alkylimidazole-decorated dendrons as heterogeneous catalysts for the Baylis-Hillman reaction.

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Supporting Information
Experimental:

All reactions were conducted under an atmosphere of nitrogen in oven-dried glassware in dry solvents. $^1$H NMR (200, 400 MHz) and $^{13}$C NMR (50, 100 MHz) spectra were recorded on Bruker AVANCE-200 and AVANCE-400 spectrometers, in CDCl$_3$ or CDCl$_3$:trifluoroacetic acid (1:1) with residual CHCl$_3$ ($^1$H, 7.26 ppm), or CDCl$_3$ ($^{13}$C, 77.0 ppm) as an internal standard. Gel-phase $^{13}$C NMR (100 MHz) spectra were recorded in benzene-d$_6$ on Bruker AVANCE-400 using solvent as an internal standard (126.0 ppm).

For solid-phase synthesis, Wang Bromo polystyrene (1% crosslinked with divinylbenzene,100-200 mesh, loading 0.9 mmol Br/g) was used as a starting material for the dendrons and catalysts synthesis, except for the preparation of G1(E-Im) which was prepared from Wang polystyrene resin (1% crosslinked with divinylbenzene,100-200 mesh, loading 0.96 mmol OH/g). Yields were determined using the $^1$H NMR spectra of trifluoroacetic acid:CDCl$_3$ (1:1) cleavage solutions with 11mM C$_6$H$_6$ (7.36ppm) as an internal standard. Alcohols were fully or partially converted to trifluoroacetate esters under these conditions.

Synthesis of 1-(2-(prop-2-ynyloxy)ethyl)-1H-imidazole:
Sodium hydride (1.38 g, 35.6 mmol, 2 equiv, 60% in oil) and 1-(2-hydroxyethyl)-imidazole (2 g, 17.8 mmol, 1 equiv) were mixed in dry THF. The solution was mixed for 0.5 h and propargyl bromide (2.33 mL, 21.4 mmol, 1.2 equiv, 80% in toluene) was added. The solution was mixed at room temperature for 4 h, refluxed for 3 h, cooled to room temperature and mixed overnight. The reaction completion was confirmed by TLC analysis. The solvent was evaporated and the crude residue was extracted with ethyl acetate (30 mL), washed with water (20 mL x 3) and saturated aqueous NH$_4$Cl solution (20 mL x 2). The organic phase was dried on MgSO$_4$, the solvent was evaporated and the crude material was separated on a silica gel column (50% EtOAc : 50% Hexanes) to give the pure product (yield 90%) as an orange oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.47 (s, 1H); 7.03 (s, 1H); 6.98 (s, 1H); 4.11 (m, 4H); 3.78 (t, $J = 5.1$ Hz, 2H); 2.45 (s, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 138.2, 129.9, 120.1, 79.6, 75.9, 69.7, 59.2, 47.6.

Characterization of the catalytic resins

G0(T-Im)
Starting material G0(N$_3$),$^1$ azido group loading 0.92 mmol/g.
Conversion 100%, internal reference-based yield 92%, loading 0.75 mmol/g.

Following trifluoroacetic acid-induced cleavage (the compound is cleaved with the linker attached):

$^1$H NMR (400 MHz, CDCl$_3$/trifluoroacetic acid 1:1): $\delta$ 8.72 (br s, 1H); 7.69 (bs, 1H); 7.43 (m, 2H); 7.33 (d, J = 7.2 Hz, 2H); 7.02 (d, J = 7.2 Hz, 2H); 5.67 (s, 2H); 4.80 (m, 2H); 4.56 (m, 2H); 4.05 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$/trifluoroacetic acid 1:1): $\delta$ 156.5, 135.6, 134.8, 131.7, 128.9, 123.8, 122.8, 120.7, 69.7 (x 2), 58.6, 50.3.

**G1(T-Im)**
Starting material G1(N$_3$),$^1$ dendron loading 0.81 mmol/g, azido group loading 1.62 mmol/g.
Conversion 100%, internal reference-based yield 59%, dendron loading 0.38 mmol/g, imidazole group loading 0.76 mmol/g.

Following trifluoroacetic acid-induced cleavage:

$^1$H NMR (400 MHz, CDCl$_3$/trifluoroacetic acid 1:1): $\delta$ 8.76 (br s, 2H); 7.70 (m, 4H); 7.40 (m, 8H); 7.11 (m, 9H); 5.72 (m, 8H); 5.02 (m, 4H); 4.81 (m, 8H); 4.52 (m, 8H); 4.07 (m, 8H).

**G2(T-Im)**
Starting material G2(N$_3$),$^1$ dendron loading 0.26 mmol/g, azido group loading 1.04 mmol/g.
Conversion 100%, internal reference-based yield 58%, dendron loading 0.14 mmol/g, imidazole group loading 0.56 mmol/g.

Following trifluoroacetic acid-induced cleavage:

$^1$H NMR (200 MHz, CDCl$_3$/trifluoroacetic acid 1:1): $\delta$ 8.71 (br s, 4H); 7.70 (m, 4H); 7.40 (m, 8H); 7.11 (m, 9H); 5.72 (m, 8H); 5.02 (m, 4H); 4.81 (m, 8H); 4.52 (m, 8H); 4.07 (m, 8H).

**G0(E-Im)**
Starting material Wang polysterene resin, hydroxy group loading 0.96 mmol/g.
Conversion 100%, internal reference-based yield 99%, loading 0.85 mmol/g.
Partial gel-phase $^{13}$C NMR (100 MHz, C$_6$D$_6$): $\delta$ 166.8, 158.9, 137.6, 119.5, 114.6, 69.4, 66.5, 49.7.

Following trifluoroacetic acid-induced cleavage:
\(^1\)H NMR (400 MHz, CDCl\(_3\)/trifluoroacetic acid 1:1): \(\delta\) 8.82 (br s, 1H); 7.72 (s, 1H); 7.54 (s, 1H); 5.25 (s, 2H).

**G1(E-Im)**
Starting material G1(OH),
\(^2\) dendron loading 0.73 mmol/g, hydroxy group loading 1.46 mmol/g.
Conversion 100%, internal reference-based yield 99 %, dendron loading 0.63 mmol/g, imidazole group loading 1.26 mmol/g.
Following trifluoroacetic acid-induced cleavage:
\(^1\)H NMR (200 MHz, CDCl\(_3\)/trifluoroacetic acid 1:1): \(\delta\) 8.69 (br s, 2H); 7.42 (s, 2H); 7.36 (s, 2H); 6.92 (m, 3H); 5.21 (s, 4H); 5.11 (s, 4H).
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)/trifluoroacetic acid 1:1): \(\delta\) 171.2, 155.3, 136.7, 136.5, 123.7, 121.0, 120.8, 116.9, 69.7, 50.1.

**G2(E-Im)**
Starting material G2(OH),
\(^2\) dendron loading 0.56 mmol/g, hydroxy group loading 2.24 mmol/g.
Conversion 100%, internal reference-based yield 100 %, dendron loading 0.45 mmol/g, imidazole group loading 1.8 mmol/g.
Following trifluoroacetic acid-induced cleavage:
\(^1\)H NMR (400 MHz, CDCl\(_3\)/trifluoroacetic acid 1:1): \(\delta\) 8.76 (br s, 4H); 7.50 (s, 4H); 7.47 (s, 4H); 7.04 (m, 9H); 5.10 - 5.41 (m, 20H).
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)/trifluoroacetic acid 1:1): \(\delta\) 167.3, 159.3, 155.1, 136.9, 136.7, 136.5, 123.8, 122.8, 122.5, 120.6, 116.9, 116.7, 70.9, 69.4, 50.4.

**G0(A-Im)**
Starting material Wang Bromo polysterene resin, bromo group loading 0.9 mmol/g.
Conversion 100%, internal reference-based yield 95%, loading 0.82 mmol/g.
Partial gel-phase \(^{13}\)C NMR (100 MHz, C\(_6\)D\(_6\)): \(\delta\) 137.8, 119.4, 115.5, 69.9, 53.8, 46.0, 44.8, 32.1.
Following trifluoroacetic acid-induced cleavage (the compound is cleaved with the linker attached):
\(^1\)H NMR (200 MHz, CDCl\(_3\)/trifluoroacetic acid 1:1): \(\delta\) 8.69 (br s, 1H); 7.81 (m, 2H); 7.46 (s, 1H); 7.42 (s, 1H); 7.28 (d, J = 7.6 Hz, 2H); 7.00 (d, J = 7.9 Hz, 2H); 4.40 (m, 2H); 4.27 (m, 2H); 3.33 (m, 2H); 2.46 (m, 2H).
**G1(A-Im)**
Starting material G1(Cl), dendron loading 0.63 mmol/g, chloro group loading 1.26 mmol/g.
Conversion 100%, internal reference-based yield 72%, dendron loading 0.41 mmol/g, imidazole group loading 0.82 mmol/g.
Partial gel-phase $^{13}$C NMR (100 MHz, C$_6$D$_6$): $\delta$ 138.6, 120.6, 115.9, 58.5, 47.2, 46.0, 32.0.
Following trifluoroacetic acid-induced cleavage:
$^1$H NMR (200 MHz, CDCl$_3$/trifluoroacetic acid 1:1): $\delta$ 8.64 (br s, 2H); 7.88 (m, 4H); 7.42 (m, 2H); 7.43 (m, 2H); 7.10 (m, 3H); 4.37 (m, 4H); 4.24 (m, 4H); 3.36 (m, 4H), 2.45 (m, 4H).
$^{13}$C NMR (50 MHz, CDCl$_3$/trifluoroacetic acid 1:1): $\delta$ 156.2, 134.4, 132.1, 121.5, 120.6, 118.7, 111.3, 52.6, 46.3, 45.2, 26.6.

**G2(A-Im)**
Starting material G2(Cl), dendron loading 0.13 mmol/g, chloro group loading 0.52 mmol/g.
Conversion 100%, internal reference-based yield 70%, dendron loading 0.08 mmol/g, imidazole group loading 0.32 mmol/g.
Following trifluoroacetic acid-induced cleavage:
$^1$H NMR (200 MHz, CDCl$_3$/trifluoroacetic acid 1:1): $\delta$ 8.68 (br s, 4H); 7.92 (m, 8H); 7.46 (m, 4H); 7.43 (m, 4H); 7.10 (m, 9H); 5.10 (s, 4H); 4.41 (m, 8H); 4.26 (m, 8H); 3.38 (m, 8H), 2.48 (m, 8H).
Partial $^{13}$C NMR (100 MHz, CDCl$_3$/trifluoroacetic acid 1:1): $\delta$ 135.1, 133.0, 122.3, 121.3, 117.4, 117.2, 70.2, 52.9, 46.1, 45.0, 30.7.

For the general procedure (with 10 molar % of catalysts) we applied the following amounts of resins (mg):

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<th>Resin Type</th>
<th>Amount (mg)</th>
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<tr>
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