Supporting Information

Highly functionalized heterogeneous dendrigraft catalyst with peripheral copper moieties for the facile synthesis of 2-substituted benzimidazoles and 2, 2-disubstituted benzimidazoles

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1) GPC Profile of glycerol initiated PECH

![Auto-Scaled Chromatogram](image)

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2) EDX Spectrum of glycerol initiated PECH coupled Merrifield Resin
3) IR spectrum of PECH loaded Merrifield resin

4) IR spectrum of tosylated PECH
5) IR spectrum of PECH loaded polyazide

6) Solid State $^{13}$C NMR spectrum of tosylated PECH
7) TG-DTG plot of PECH loaded Merrifield resin

8) IR Spectrum of G0, G0.5, G1, G1.5 and G2 overlayed

9) Solid State $^{13}$C NMR spectra of GLR-G0.5, G1, G1.5 and G2 overlayed
10) EDX spectrum of GLR-G2-Cu
11) IR spectrum of GLR-G2 and GLR-G2-Cu overlayed

![IR spectrum of GLR-G2 and GLR-G2-Cu](image)

12) Experimental and simulated EPR spectra of GLR-G2-Cu

![Experimental and simulated EPR spectra of GLR-G2-Cu](image)
13) XRD pattern of GLR-G2 and GLR-G2-Cu

14) XPS wide spectra of Cu (2p$_{3/2}$) of GLR-G2-Cu

15) Bar diagram of recycling of GLR-G2-Cu catalyst
Cat.recoveryC – Catalyst recovery for Cyclohexanone substrate

PdtyieldC – Product yield for Cyclohexanone substrate

Cat.recoveryB - Catalyst recovery for Benzaldehyde substrate

PdtyieldB - Product yield for Benzaldehyde substrate

Experimental procedure

1. Estimation of Chlorine capacity

   The chloromethyl resin (250 mg) was refluxed in pyridine (5 ml) for one hour. Acetic acid (10 ml) and water (10 ml) was added to the reaction mixture. The chloride ions were displaced by the addition of conc. HNO₃ (5 ml) and precipitated with a measured excess of standard AgNO₃ (0.1N, 10 ml) solution. The AgCl formed was coated with toluene (5 ml). The excess of AgNO₃ was back titrated with standard NH₄SCN solution using ferric alum as indicator. The amount of chloride ions per gram of the resin was calculated from the titre value.

   Chlorine capacity of Merrifield resin: 5.2 mmols/g;

   Chlorine Capacity of PECH loaded resin: 12.8 mmols/g;

2. Estimation of hydroxyl group
0.5 g of the hydroxyl compound was taken in a RB flask fitted with a condenser. 10 mL of the acetylating mixture (1 volume acetic anhydride + 4 volume anhydrous pyridine) was added. It was heated on a boiling water bath for 60 min. The reaction mixture was removed from water bath, 20 ml distilled water was added, shaken well to ensure complete hydrolysis of the unchanged acetic anhydride, cooled and allowed to stand for 10 min. The solution was titrated with 1 N NaOH using phenolphthalein as indicator.

Hydroxyl Capacity of PECH loaded resin: 1.43 mmols/g.

3. Estimation of amine capacity

The polystyrene resin bearing the amino groups (100 mg) was suspended in HCl (0.1M, 40 ml) for 24 h with occasional stirring. The resin was filtered and washed with distilled water. The filtrate and washings were collected. The unreacted HCl was determined by titration against standard NaOH solution with the use of phenolphthalein indicator. A blank titration was also carried out. From the titre values, the amount of amino groups per gram of the resin was calculated.

Amine capacity of resin loaded G0 polymer: 13.45 mmols/g
Amine capacity of resin loaded G1 polymer: 22.13 mmols/g
Amine capacity of resin loaded G2 polymer: 30.24 mmols/g

Characterization of Benzimidazole derivatives

2-Phenyl-1H-benzo[d]imidazole (3a)

Off white solid, mp 293 °C.

\[
{^1}H\text{ NMR (300 MHz, DMSO-d}_{6}\] \(\delta\): 7.14-7.28 (m, 2H), 7.43-7.77 (m, 5H), 8.16-8.25 (m, 2H) ppm.

\[
{^{13}}C\text{ NMR (75 MHz, DMSO-d}_{6}\] \(\delta\): 111.2, 118.8, 121.5, 122.4, 126.3, 128.8, 129.7, 130.1, 134.9, 143.7, 151.1 ppm.

GC-MS, m/z: 194.

2-(4-Nitrophenyl)-1H-benzo[d]imidazole (3b)

Pink red solid, mp 317 °C.

\[
{^1}H\text{ NMR (300 MHz, DMSO-d}_{6}\] \(\delta\): 7.23-7.34 (m, 2H), 7.55 (d, \(J = 7.9\) Hz, 1H), 7.77 (d, \(J = 6.8\) Hz, 1H), 8.34 (d, \(J = 8.5\) Hz, 2H), 8.44 (d, \(J = 8.5\) Hz, 2H) ppm.

\[
{^{13}}C\text{ NMR (75 MHz, DMSO-d}_{6}\] \(\delta\): 111.3, 119.1, 121.9, 123.1, 123.7, 127.0, 134.9, 135.9, 143.6, 147.5, 148.7
2-(4-Methoxyphenyl)-1H-benzo[d]imidazole (3c)

Colourless solid, mp 219 °C.

$^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$: 3.83 (s, 3H), 7.11 (d, $J = 8.9$ Hz, 2H), 7.14-7.23 (m, 2H), 7.49-7.62 (m, 2H), 8.13 (d, $J = 8.9$ Hz, 2H) ppm.

$^{13}$C NMR (75 MHz, DMSO-d$_6$) $\delta$: 55.2, 114.2, 121.6, 122.6, 127.9, 151.2, 160.5 ppm.

GC-MS, m/z: 239.

2-(4-Chlorophenyl)-1H-benzo[d]imidazole (3d)

Colourless solid, mp 290 °C.

$^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$: 7.13-7.33 (m, 2H), 7.47-7.73 (m, 4H), 8.20 (d, $J = 7.1$ Hz, 2H), 12.93 (bs, 1H) ppm.

$^{13}$C NMR (75 MHz, DMSO-d$_6$) $\delta$: 111.2, 118.7, 121.5, 122.3, 126.3, 128.8, 129.7, 130.0, 134.9, 143.7, 151.1 ppm.

GC-MS, m/z: 224.

2-(4-Bromophenyl)-1H-benzo[d]imidazole (3e)

Off white solid, mp 282 °C.

$^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$: 7.14-7.29 (m, 2H), 7.46-7.71 (m, 2H), 7.76 (d, $J = 8.5$ Hz, 2H), 8.12 (d, $J = 8.5$ Hz, 2H), 12.99 (bs, 1H) ppm.

$^{13}$C NMR (75 MHz, DMSO-d$_6$) $\delta$: 121.8, 123.1, 128.2, 129.3, 130.7, 131.8, 150.1 ppm.

GC-MS, m/z: 271.99.

2-(4-Methylphenyl)-1H-benzo[d]imidazole (3f)

Colourless solid, mp 270 °C.

$^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$: 2.38 (s, 3H), 7.12-7.27 (m, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.47-7.69 (m, 2H), 8.07 (d, $J = 8.3$ Hz, 2H) ppm.

$^{13}$C NMR (75 MHz, DMSO-d$_6$) $\delta$: 20.8, 111.0, 118.5, 121.4, 122.1, 126.2, 127.3, 129.3, 139.4, 151.2 ppm.

GC-MS, m/z: 208.
2-(4-Hydroxyphenyl)-1H-benzo[d]imidazole (3g)

Colourless solid, mp 255 °C.

$^1$H NMR (500 MHz, DMSO-d$_6$) $\delta$: 9.94 (br s, 1H), 7.98 (d, $J$ = 8.0 Hz, 2H), 7.57 (d, $J$ = 7.4 Hz, 1H), 7.45 (d, $J$ = 6.9 Hz, 1H), 7.15-7.12 (m, 2H), 6.89 (d, $J$ = 8.0 Hz, 2H) ppm.

$^{13}$C NMR (125 MHz, DMSO-d$_6$) $\delta$: 159.1, 151.8, 143.9, 128.1, 121.9, 121.3, 121.1, 118.3, 115.7, 110.9 ppm.

GC-MS, m/z: 210.

2-(3-Nitrophenyl)-1H-benzo[d]imidazole (3h)

Off white solid, mp 203°C.

$^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$: 7.21-7.32 (m, 2H), 7.46-7.58 (m, 1H), 6.66-7.78 (m, 2H), 8.21-8.32 (m, 1H), 8.62 (d, $J$ = 7.7 Hz, 1H), 9.1 (s, 1H) ppm.

$^{13}$C NMR (75 MHz, DMSO-d$_6$) $\delta$: 111.6, 118.9, 121.9, 122.8, 124.9, 125.9, 129.6, 130.9, 132.3, 134.6, 149.8 ppm.

GC-MS, m/z: 239.

2-(3-Chlorophenyl)-1H-benzo[d]imidazole (3i)

Colourless solid, mp 235°C.

$^1$H NMR (300MHz, DMSO-d$_6$) $\delta$: 7.11-7.33 (m, 2H), 7.45-7.76 (m, 4H), 8.15 (d, $J$ = 6.8 Hz, 1H), 8.22 (s, 1H) ppm.

$^{13}$C NMR (75 MHz, DMSO-d$_6$) $\delta$: 111.4, 118.9, 121.9, 122.7, 124.9, 125.9, 129.4, 130.8, 132.1, 133.6, 149.6 ppm.

GC-MS, m/z: 228.

2-(2-Chlorophenyl)-1H-benzo[d]imidazole (3j)

Pink red solid, mp 232°C.

$^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$: 7.17-7.31 (m, 2H), 7.47-7.77 (m, 5H), 7.87-7.96 (m, 1H), 12.74 (bs, 1H) ppm.

$^{13}$C NMR (75 MHz, DMSO-d$_6$) $\delta$: 121.9, 127.1, 129.8, 130.1, 130.8, 131.5, 131.8, 148.9 ppm.

GC-MS, m/z: 228.

2-(2-Methoxyphenyl)-1H-benzo[d]imidazole (3k)

Colourless solid, mp 174°C.

$^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$: 4.02 (s, 3H), 7.11 (t, $J$ = 7.3 Hz, 1H), 7.16-7.30 (m, 3H), 7.48 (t, $J$ = 7.3 Hz, 1H), 7.56-7.71 (m, 2H), 8.33 (d, $J$ = 7.55, 1H) ppm.

$^{13}$C NMR (75 MHz, DMSO-d$_6$) $\delta$: 55.6, 111.9, 118.0, 120.7,
2-(2-Hydroxyphenyl)-1H-benzo[d]imidazole (3l)

Colourless solid, mp 252°C.

\( ^1 \text{H NMR } (300 \text{ MHz, DMSO-d}_6 ) \delta: 12.92 (s, 2\text{H}, \text{NH, OH}), 7.11 (t, J = 7.3 \text{ Hz, } 1\text{H}), 7.16-7.30 (m, 3\text{H}), 7.48 (t, J = 7.3 \text{ Hz, } 1\text{H}), 7.56-7.71 (m, 2\text{H}), 8.38 (d, J = 7.55, 1\text{H}) \text{ ppm.} \)

\( ^{13} \text{C NMR } (75 \text{ MHz, DMSO-d}_6 ) \delta: 112, 118.0, 120.7, 121.7, 129.7, 131.1, 148.8, 156.8 \text{ ppm.} \)

GC-MS, m/z: 224.

2,2-Dimethyl-2H-benzo[d]imidazole (3a).

Brown oil.

\( ^1 \text{H NMR } (400 \text{ MHz, CDCl}_3 ) \delta: 7.21 (dd, 2\text{H}, J = 7.3, 2.7 \text{ Hz}), 7.02 (dd, 2\text{H}, J = 7.3, 2.7 \text{ Hz}), 1.52 (s, 6\text{H}) \text{ ppm.} \)

\( ^{13} \text{C NMR } (100 \text{ MHz, CDCl}_3 ) \delta: 159.8, 134.8, 126.0, 104.6, 22 \text{ ppm.} \)

GC-MS, m/z: 146.


Yellow oil.

\( ^1 \text{H NMR } (400 \text{ MHz, CDCl}_3 ) \delta: 7.19 (dd, 2\text{H}, J = 7.3, 3.2 \text{ Hz}), 7.00 (dd, 2\text{H}, J = 7.3, 3.2 \text{ Hz}), 2.08 (q, 2\text{H}, J = 7.3 \text{ Hz}), 1.52 (s, 3\text{H}), 0.73 (t, 3\text{H}, J = 7.3 \text{ Hz}) \text{ ppm.} \)

\( ^{13} \text{C NMR } (100 \text{ MHz, CDCl}_3 ) \delta: 160, 134.5, 125.8, 107.1, 29.3, 19.9, 8.9 \text{ ppm.} \)

GC-MS, m/z: 160.


Yellow oil.

\( ^1 \text{H NMR } (400 \text{ MHz, CDCl}_3 ) \delta: 7.21 (dd, 2\text{H}, J = 7.3, 2.7 \text{ Hz}), 7.00 (dd, 2\text{H}, J = 7.3, 2.7 \text{ Hz}), 2.31 (m, 1\text{H}, J = 6.8 \text{ Hz}), 1.48 (s, 3\text{H}), 0.97 (d, 6\text{H}, J = 6.8 \text{ Hz}) \text{ ppm.} \)

\( ^{13} \text{C NMR } (100 \text{ MHz, CDCl}_3 ) \delta: 160, 134.5, 125.7, 110, 35.0, 18.8, 18.4 \text{ ppm.} \)

GC-MS, m/z: 174.

Yellow oil.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 7.19 (dd, 2H, \(J = 7.2, 2.7\) Hz), 6.9 (dd, 2H, \(J = 7.2, 2.7\) Hz), 2.01-1.97 (m, 2H), 1.50 (s, 3H), 1.22-1.10 (m, 6H), 0.82 (t, 3H, \(J = 6.8\) Hz) ppm.

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\): 159.2, 134.5, 125.8, 107.2, 36.1, 32.0, 24.1, 22.5, 20.4, 14.0 ppm.

GC-MS, m/z: 202.

2,2-Diethyl-2H-benzo[d]imidazole (3e).

Brown oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.20 (dd, 2H, \(J = 7.8, 2.7\) Hz), 7.02 (dd, 2H, \(J = 7.8, 2.7\) Hz), 2.12 (q, 4H, \(J = 7.3\) Hz), 0.69 (t, 6H, \(J = 7.3\) Hz) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 160, 134.5, 125.8, 110, 28, 8.5 ppm.

GC-MS, m/z: 174.

2,2-Dipropyl-2H-benzo[d]imidazole (3f).

Brown oil.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 7.19 (dd, 2H, \(J = 7.5, 3.1\) Hz), 7.00 (dd, 2H, \(J = 7.5, 3.1\) Hz), 2.02 (m, 4H), 1.01 (m, 4H), 0.82 (t, 6H, \(J = 7.2\) Hz) ppm.

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\): 160, 134.5, 125.6, 109.9, 37.5, 17.1, 14.1 ppm.

GC-MS, m/z: 202.

2,2-Dibutyl-2H-benzo[d]imidazole (3g).

Yellow oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 7.20 (dd, 2H, \(J = 7.3, 2.7\) Hz), 7.00 (dd, 2H, \(J = 7.3, 2.7\) Hz), 2.05 (m, 4H), 1.25 (m, 4H), 1.01 (m, 4H), 0.81 (t, 6H, \(J = 7.3\) Hz) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 160.0, 134, 125.5, 109.6, 34.8, 25.9, 22.9, 13.9 ppm.

GC-MS, m/z 230.
**Spiro[benzo[d]imidazole-2,1'-cyclopentane] (3h)**

Brown oil.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.22 (dd, 2H, $J = 7.2$, 3.1 Hz), 7.00 (dd, 2H, $J = 7.2$, 3.1 Hz), 1.94 (m, 4H), 1.61 (m, 4H) ppm.

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 159.5, 134.2, 126.0, 107.3, 32.5, 25.2 ppm.

GC-MS, m/z 172.

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**Spiro[benzo[d]imidazole-2,1'-cyclohexane] (3i)**

Brown oil.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.22 (dd, 2H, $J = 7.2$, 3.1 Hz), 7.00 (dd, 2H, $J = 7.2$, 3.1 Hz), 1.95 (m, 4H), 1.75 (m, 2H), 1.60 (m, 4H) ppm.

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 159.3, 134.3, 126.0, 107.5, 32.4, 25.5, 24.9 ppm.

GC-MS, m/z: 186.12.

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**4'-tert-Butylspiro[benzo[d]imidazole-2,1'-cyclohexane] (3j)**

White solid. mp 141-143 $^\circ$C.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.25 (m, 2H), 6.99 (dd, 2H, $J = 7.5$, 3.1 Hz), 2.45 (t, 2H), 1.99 (m, 2H), 1.78 (q, 2H), 1.35 (m, 2H), 0.97 (s, 9H), 0.90 (m, 1H) ppm.

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 159.9, 159.0, 134.1, 126.0, 125.9, 107.2, 48, 33.1, 32.9, 27.9, 26 ppm.

GC-MS, m/z: 242.

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**Spiro[benzo[d]imidazole-2,1'-cycloheptane] (3k)**

Yellow solid. mp 92-93 $^\circ$C.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.19 (dd, 2H, $J = 7.5$, 3.1 Hz), 6.95 (dd, 2H, $J = 7.5$, 3.1 Hz), 1.99 (m, 4H), 1.82 (m, 4H), 1.70 (m, 4H) ppm.

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 159, 134.5, 126.1, 111, 34.0, 30, 25.1 ppm.

GC-MS, m/z: 200.
**Spiro[benzo[d]imidazole-2,1'-cyclooctane] (3l)**

Yellow solid. mp 103-105 °C.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.19 (dd, 2H, $J = 7.5, 3.1$ Hz), 6.99 (dd, 2H, $J = 7.5, 3.1$ Hz), 2.0 (m, 4H), 1.8 (m, 6H), 1.6 (m, 4H) ppm.

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 159.5, 134.5, 126.1, 111, 30.0, 28.9, 25, 24.9 ppm.

GC-MS, m/z: 214.