Electronic Supplementary Material Information

Synthesis of Discrete Catalytic Oligomers and their Potential in Silica-Supported Cooperative Catalysis

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1 General considerations

Reagents were obtained from commercial sources and used without further purification. \textsuperscript{1, 2} \textsuperscript{11, 12} and 2-azidoethylamine were synthesized according to previous literature reports.\textsuperscript{1-3} All reactions were carried out under argon. Flash column chromatography was carried out using silica gel 230-400 mesh (Sigma-Aldrich) as the stationary phase. Spherical silica gel (40-75 µm, 100 Å) was purchased from Sorbtech Technologies. Milli-Q water (resistivity 18.2 MΩ.cm) was obtained from a Milli-Q Reference system (Merck). FT-IR was measured on a Thermo Scientific FTIR Nexus 870 spectrometer. TGA was measured on a Mettler Toledo TGA/SDTA 851\textsuperscript{e} instrument. ICP-AES was performed on a Thermo Scientific ICAP 6500 spectrometer. Prior to analysis, the samples were treated with HNO\textsubscript{3}-HF at 120 °C overnight. The residue was taken up in 1 mL HNO\textsubscript{3} and diluted to 25 mL with ultrapure water. NMR spectra were recorded on a Bruker-300 or a Bruker-500 spectrometer. Chemical shifts (\(\delta\)) are reported in parts per million (ppm) from low to high field and referenced to residual solvent. Coupling constants (\(J\)) are reported in hertz (Hz). Standard abbreviations indicating multiplicity are used as follows: b= broad, s= singlet, d= doublet, t= triplet, q= quartet, quint= quintet, m= multiplet. Compounds with TEMPO radical were mixed with 1,2-diphenylhydrazine (2.0 equiv.) prior to NMR analysis. Specific surface area and pore size were obtained through nitrogen adsorption-desorption experiments using a Micromeritics Tristar 3000. Before analysis, the samples were degassed overnight under vacuum at 60 °C. BET and BJH approaches were applied to process the raw data. X-ray photoelectron spectroscopy (XPS) measurements were performed on a SSX 100/206 photoelectron spectrometer from Surface Science Instruments equipped with a monochromatized microfocused Al X-ray source (1486.6 eV operated at 20 mA and 10 kV). All binding energies were referenced to the C-(C, H) component of the C 1s peak fixed at 284.8 eV. The base pressure in the spectrometer was in the low 10\textsuperscript{-8} Torr range. Peak decomposition was achieved with Casa XPS (Casa Software Ltd., UK). GC was performed on a Shimadzu GC-2010 equipped with a FID detector. Aerobic oxidation experiments were performed under O\textsubscript{2} bubbling (5.5 mL/min) using a SLA5850 thermal mass flow controller from Brooks.
2 Synthesis

2.1 Chain elongation

![Chemical structure](image)

To a solution of 2 (4.85 g, 17.96 mmol) in degassed DMF (90 mL) was added glycidyl propargyl ether (2.6 mL, 1.2 equiv.), DIPEA (16.0 mL, 5.0 equiv.) and CuI (341 mg, 0.1 equiv.). The solution was heated at 55 °C overnight. After cooling to room temperature, 0.05 M Na₂EDTA (150 mL) was added and the reaction mixture was stirred at room temperature under bubbling with air for 30 min. The aqueous layer was extracted with DCM (4 × 100 mL), dried with anhydrous Na₂SO₄ and concentrated under vacuum. The crude product was purified by flash chromatography over silica gel (ethyl acetate/hexane) to give 3 (5.38 g, 79 %) as a faint yellow oil.

$^1$H NMR (300 MHz, CDCl₃): $\delta =$ 7.70 (s, 1H, H7), 4.67 and 4.62 (d, AB system, 2H, $J = 12.0$ Hz, H8), 4.53 (dd, 1H, $J = 14.0$ Hz, $J = 3.5$ Hz, H6), 4.36 (dd, 1H, $J = 14.0$ Hz, $J = 7.4$ Hz, H6), 4.19 (bs, 3H, H3+5), 3.82 (dd, 1H, $J = 11.5$ Hz, $J = 2.8$ Hz, H3), 3.58 (dd, 1H, $J = 9.7$ Hz, $J = 4.8$ Hz, H9), 3.50 (dd, 1H, $J = 9.7$ Hz, $J = 5.6$ Hz, H4), 3.41 (dd, 1H, $J = 11.5$ Hz, $J = 6.1$ Hz, H9), 3.14 (dd, 1H, $J = 6.8$ Hz, $J = 5.1$ Hz, $J = 2.7$ Hz, H10), 2.77 (dd, 1H, $J = 4.9$ Hz, $J = 4.2$ Hz, H11), 2.59 (dd, 1H, $J = 5.0$ Hz, $J = 2.7$ Hz, H11), 0.90 (s, 9H, H1), 0.09 (s, 6H, H2); $^{13}$C NMR (75 MHz, CDCl₃): $\delta =$ 144.6, 124.4, 101.4, 90.7, 77.4, 71.2, 70.7, 69.1, 64.6, 59.6, 53.1, 50.8, 44.3, 26.1, 16.5, -4.6; HRMS m/z = 382.2155 (calcd. for 382.2157 C₁₈H₃₂O₄N₃²⁸Si [M+H]$^+$).

![Chemical structure](image)

To a solution of 3 (6.44 g, 16.86 mmol) in DMF (45 mL) was added NaN₃ (6.60 g, 6.0 equiv.) and NH₄Cl (1.40 g, 1.5 equiv.). The reaction was heated to 65 °C and allowed to stir for 6 h. The solvent was evaporated and the residue was dissolved in water (80 mL) and extracted with ethyl acetate (4 × 100 mL), dried over Na₂SO₄ and concentrated under vacuum and purified by flash column chromatography (ethyl acetate/hexane) to give 4 (5.34 g, 74 %) as a faint yellow oil.
\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.69\) (s, 1H, H\(_7\)), 4.62 (bs, 2H, H\(_8\)), 4.54 (dd, J= 14.0 Hz, J= 3.1 Hz, H\(_6\)), 4.35 (dd, 1H, J= 14.0 Hz, J= 7.5 Hz, H\(_6\)), 4.18 (bs, 3H, H\(_{3+5}\)), 3.92 (dd, 1H, J= 10.3 Hz, J= 5.1 Hz, H\(_{10}\)), 3.79 (bs, 1H, H\(_{OH}\)), 3.61-3.48 (m, 5H, H\(_{4+9+OH}\)), 3.32-3.30 (m, 2H, H\(_{11}\)), 0.89 (s, 9H, H\(_1\)), 0.08 (s, 6H, H\(_2\)); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 144.3, 124.3, 101.5, 90.5, 77.4, 71.9, 70.8, 69.6, 69.1, 64.6, 59.5, 53.5, 53.2, 26.1, 16.5, -4.7; HRMS m/z= 425.2327 (calcd. for 425.2327 C\(_{18}\)H\(_{33}\)O\(_3\)N\(_6\)\(^{28}\)Si [M+H\(^+\)].

To a solution of 4 (5.34 g, 12.59 mmol) in degassed DMF (125 mL) was added glycidyl propargyl ether (1.8 mL, 1.2 equiv.), DIPEA (11.2 mL, 5.0 equiv.) and CuI (239 mg, 0.1 equiv.). The solution was heated at 55 °C overnight. After cooling to room temperature, 0.05 M Na\(_2\)EDTA (150 mL) was added and the reaction mixture was stirred at room temperature under bubbling with air for 30 min. The aqueous layer was extracted with DCM (4 \times 100 mL), dried over anhydrous Na\(_2\)SO\(_4\) and concentrated under vacuum. The crude product was purified by flash chromatography (methanol/DCM) to give 5 (3.75 g, 56%) as a faint yellow oil.

\(^1\)H NMR (300 Hz, CDCl\(_3\)): \(\delta = 7.72\) (s, 1H, H\(_7\)), 7.69 (s, 1H, H\(_7\)), 4.58 and 4.55 (bs, 4H, H\(_8\)), 4.53-4.28 (m, 6H, H\(_{6+7+H\_OH}\)), 4.18 (bs, 3H, H\(_{3+5}\)), 4.15-4.06 (m, 1H, H\(_9\)), 3.78 (ddd, 1H, J= 11.5 Hz, J= 2.7 Hz, J= 0.9 Hz, H\(_8\)), 3.55 (dd, 2H, J= 5.1 Hz, J= 0.9 Hz, H\(_4\)), 3.49-3.32 (m, 3H, H\(_{4+9}\)), 3.14-3.08 (m, 1H, H\(_{10}\)), 2.74 (dd, 1H, J= 4.8 Hz, J= 4.5 Hz, H\(_{11}\)), 2.56 (dd, 1H, J= 5.0 Hz, J= 2.7 Hz, H\(_{11}\)), 0.89 (s, 9H, H\(_1\)), 0.07 (s, 6H, H\(_2\)); \(^{13}\)C NMR (75 Hz, CDCl\(_3\)): \(\delta = 144.3, 144.0, 124.5, 101.6, 90.4, 77.4, 71.1, 71.0 \times 2\), 68.9 \times 2\), 64.5, 64.4, 59.5, 53.5, 52.9, 50.8, 44.3, 26.1, 16.5, -4.7; HRMS m/z= 537.2842 (calcd. for 537.2851 C\(_{28}\)H\(_{41}\)O\(_3\)N\(_6\)\(^{28}\)Si [M+H\(^+\)].

To a solution of 5 (3.40 g, 6.33 mmol) in DMF (15 mL) was added NaN\(_3\) (2.50 g, 6.0 equiv.) and NH\(_4\)Cl (0.51 g, 1.5 equiv.). The reaction mixture was heated at 65 °C and allowed to stir for 6 h. The solvent was evaporated and the residue was dissolved in water (70 mL) and extracted with ethyl acetate (4 \times 100 mL), dried over anhydrous Na\(_2\)SO\(_4\) and concentrated.
under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to give 6 (3.20 g, 87 %) as a faint yellow oil.

$^1$H NMR (300 Hz, CDCl$_3$): $\delta$ = 7.72 (s, 1H, H$_7$), 7.69 (s, 1H, H$_7$), 4.70-4.64 (m, 1H, H$_{OH}$), 4.58-4.46 (m, 6H, H$_{6-8}$), 4.43-4.29 (m, 3H, H$_{6-8}$,OH), 4.24-4.21 (bs, 3H, H$_{3+OH}$), 4.15-4.09 (m, 2H, H$_3$), 3.92 (dT, 1H, $J$= 10.3 Hz, H$_7$), 3.60-3.55 (m, 2H, H$_4$), 3.53-3.46 (m, 2H, H$_4$), 3.41 (bt, 2H, $J$= 5.7 Hz, H$_9$), 0.91 (s, 9H, H$_1$), 0.09 (s, 6H, H$_2$); $^{13}$C NMR (75 Hz, CDCl$_3$): $\delta$ = 144.2, 143.9, 124.7, 124.6, 124.5, 124.3, 101.6, 90.5, 77.4, 72.1, 71.1, 70.9, 69.6, 69.0, 68.9, 64.5, 64.2, 59.6, 53.7, 53.5, 52.9, 26.1, 16.5, -4.6; HRMS m/z = 580.3024 (calcd. for C$_{24}$H$_{42}$O$_6$N$_9$Si [M+H$^+$]).

2.2 Chain termination

To a solution of 4 (8.70 g, 20.52 mmol) in degassed DMF (100 mL) was added phenylacetylene (2.70 mL, 1.2 equiv.), DIPEA (18.2 mL, 5.0 equiv.) and CuI (389 mg, 0.1 equiv.). The solution was heated and stirred at 55 °C overnight. After cooling to room temperature, 0.05 M Na$_2$EDTA (200 mL) was added and the reaction mixture was stirred at room temperature under bubbling with air for 30 min. The aqueous layer was extracted with DCM (4 $\times$ 150 mL), dried over anhydrous Na$_2$SO$_4$ and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to give 7 (8.30 g, 77 %) as a white solid.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.90 (s, 1H, H$_{12}$), 7.72-7.69 (m, 3H, H$_{7+13}$), 7.37-7.24 (m, 3H, H$_{14+15}$), 4.67-4.24 (m, 10H, H$_{5+8+11+11+OH}$), 4.17 (bs, 4H, H$_{3+5+10}$), 3.55-3.41 (m, 4H, H$_4$-9), 0.90 (s, 9H, H$_1$), 0.08 (s, 6H, H$_2$); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 147.3, 143.9, 130.4, 128.9, 128.2, 125.7, 124.5, 121.7, 101.6, 90.4, 77.4, 71.2, 71.1, 70.9, 69.0, 68.9, 64.4, 64.3, 59.5, 53.6, 53.0, 26.1, 16.5, -4.6; HRMS m/z = 527.2795 (calcd. for 527.2797 C$_{26}$H$_{39}$O$_4$N$_6$Si [M+H$^+$]).
To a solution of 6 (3.00 g, 5.18 mmol) in degassed DMF (52 mL) was added phenyl acetylene (680 µL, 1.2 equiv.), DIPEA (4.6 mL, 5.0 equiv.) and CuI (98 mg, 0.1 equiv.). The solution was heated and stirred at 55 °C overnight. After cooling to room temperature, 0.05 M Na₂EDTA (100 mL) was added and the reaction mixture was stirred at room temperature under bubbling with air for 30 min. The aqueous layer was extracted with DCM (4 × 100 mL), dried over anhydrous Na₂SO₄ and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to give 8 (3.52 g, quant.) as a white solid.

**1H NMR** (300 MHz, DMF-d7): δ = 8.54 (s, 1H, H₁₂), 8.13 (s, 2H, H₇), 7.96-7.92 (m, 2H, H₁₃), 7.50-7.45 (m, 2H, H₁₄), 7.37-7.33 (m, 1H, H₁₅), 5.61 (dd, 3H, J= 11.7 Hz, J= 5.8 Hz, H₁OH), 4.67 (d, 4H, J= 5.1 Hz, H₈), 4.64-4.37 (m, 6H, H₆+₁₁), 4.32 (bs, 2H, H₃), 4.26-4.12 (m, 3H, H₅+₁₀), 3.61-3.53 (m, 6H, H₄+₉), 0.94 (s, 9H, H₁), 0.12 (s, 6H, H₂); **13C NMR** (75 Hz, DMF-d7): δ = 146.8, 131.6, 129.1, 128.0, 125.4, 122.4, 103.4, 89.1, 79.4, 72.2, 71.8, 69.2, 64.6, 59.1, 53.5, 25.8, 16.4, -5.0; **HRMS m/z** = 682.3489 (calcd. for C₃₂H₄₈O₆N₉²⁸Si [M+H]+).

### 2.3 Lateral chain functionalization

![Diagram of molecular structure]

To a solution of 7 (8.30 g, 15.78 mmol) in DMF (80 mL) was added DSC (9.70 mg, 2.4 equiv.) and triethylamine (6.6 mL, 3.0 equiv.) and the reaction mixture was stirred at room temperature overnight. On the second day, a solution of 2-azidoethylamine (4.00 g, 3.0 equiv.) and triethylamine (6.6 mL, 3.0 equiv.) in DMF (20 mL) was added and the solution was stirred overnight at room temperature. To the resulting reaction mixture DCM (100 mL) was added and the organic layer washed with water (3 × 50 mL). The aqueous layer was back-extracted with DCM (2 × 100 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to give 9 (9.30 g, 79 %) as a yellowish orange viscous liquid.

**1H NMR** (300 MHz, CD₃OD): δ = 8.29 (s, 1H, H₁₂), 8.00 (s, 1H, H₇), 7.86-7.83 (m, 2H, H₁₃), 7.48-7.37 (m, 3H, H₁₄+₁₅), 5.27 (bs, 2H, H₅+₁₀), 4.76-4.61 (m, 6H, H₆+₈+₁₁), 4.26 (bs, 2H, H₃),
3.68-3.67 (m, 4H, H_{4+9}), 3.44-3.26 (m, 8H, H_{16+17}), 0.97 (s, 9H, H_{1}), 0.14 (s, 6H, H_{2}); \textbf{^{13}C NMR} (75 MHz, CD_{3}OD): \delta = 157.3, 148.8, 131.6, 130.0, 129.3, 126.7, 126.1, 123.3, 103.1, 90.8, 72.5, 70.0, 69.8, 69.4, 65.2, 60.1, 54.4, 51.7, 51.4, 41.4, 26.5, 17.2, -4.5; \textbf{HRMS} m/z = 751.3505 (calc. for 751.3567 C_{32}H_{47}O_{6}N_{14}^{28}Si [M+H]^+) 

To a solution of 8 (500 mg, 0.734 mmol) in DMF (15 mL) was added DSC (846 mg, 4.5 equiv.) and triethylamine (613 \mu L, 6 equiv.) and the reaction mixture was stirred at room temperature overnight. On the second day, a solution of 2-azidoethylamine (284 \mu L, 4.5 equiv.) and triethylamine (613 \mu L, 6 equiv.) in DMF (4 mL) was added and the solution was stirred overnight at room temperature. To the resulting reaction mixture DCM (100 mL) was added and the organic layer was washed with water (3 \times 50 mL). The aqueous layer was back-extracted with (2 \times 100 mL) DCM. The combined organic layers were dried over anhydrous Na_{2}SO_{4} and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to give 10 (550 mg, 74 %) as a yellowish orange viscous liquid.

\textbf{^{1}H NMR} (300 MHz, CD_{3}OD): \delta = 8.27 (s, 1H, H_{12}), 7.97 (s, 1H, H_{7}), 7.95 (s, 1H, H_{2}), 7.81 (d, 2H, J = 7.1 Hz, H_{13}), 7.46-7.32 (m, 3H, H_{14+15}), 5.30-5.20 (m, 3H, H_{5+10}), 4.74-4.63 (m, 10H, H_{6+8+11}), 4.25 (bs, 2H, H_{3}), 3.68-3.59 (m, 6H, H_{4+9}), 3.37-3.23 (m, 12 H, H_{16+17}), 0.95 (s, 9H, H_{1}), -0.11 (s, 6H, H_{2}); \textbf{^{13}C NMR} (75 Hz, CD_{3}OD) \delta = 157.4, 148.8, 145.5, 131.6, 130.0, 129.3, 126.7, 126.2, 123.2, 103.1, 90.8, 72.5, 69.8, 69.4, 65.1, 60.0, 51.7, 41.4, 26.5, 17.2, -4.5; \textbf{HRMS} m/z = 1018.4651 (calc. for 1018.4647 C_{41}H_{60}O_{9}N_{21}^{28}Si [M+H]^+).
To a solution of 9 (1.5 g, 2.00 mmol) in degassed DMF (20 mL) was added 11 (1.02 g, 2.4 equiv.), Et₃N (2.8 mL, 10.0 equiv.) and CuI (77 mg, 0.2 equiv.). The solution was heated and stirred at 55 °C overnight. After cooling to room temperature, 0.05 M Na₂EDTA (100 mL) was added and the reaction mixture was stirred at room temperature under bubbling with air for 30 min. The aqueous layer was extracted with DCM (3 × 100 mL), dried over anhydrous Na₂SO₄ and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to give S1 (1.8 g, 77 %) as an orange viscous liquid.

**¹H NMR** (500 MHz, CDO₃D, 1,2-diphenylhydrazine): δ = 8.31 (s, 1H, H₁₂), 8.01-7.87 (m, 4H, H₇₋₁₃+₁₈), 7.48-7.39 (m, 3H, H₁₄+₁₅), 5.45-5.26 (m, 2H, H₅₋₁₀), 4.72-4.49 (m, 14H, H₆+8+₁₁+₁₇₋₁₉), 4.28 (s, 2H, H₁₉), 3.84 (bs, 2H, H₂₀), 3.73-3.53 (m, 8H, H₄₋₉+₁₆), 2.00 (bs, 4H, H₂₁), 1.49 (bs, 4H, H₂₁), 1.25-1.19 (m, 24H, H₂₂), 1.00 (s, 9H, H₁), 0.17 (s, 6H, H₂); ¹³C NMR (125 MHz, CDO₃D, 1,2-diphenylhydrazine): δ = 157.1 (×2), 153.7, 151.1, 148.6, 148.4, 146.3, 145.4, 132.2, 131.6, 131.5, 130.2, 129.9, 129.3, 129.2, 126.6 (×2), 126.2, 125.3, 125.1, 123.7, 123.3, 119.6, 113.2, 103.4, 103.1, 90.8, 79.4, 72.6, 72.4, 72.2, 71.8, 71.3, 70.0, 69.9, 69.6, 69.3, 65.1, 62.0, 60.0, 59.9, 54.3, 52.6, 51.7, 51.6, 50.7, 45.5, 41.8, 39.4, 32.6, 28.8, 26.5, 21.2, 17.2, -4.4; HRMS m/z = 1171.6537 (calcd. for 1171.6555 C₅₆H₈₇O₁₀N₁₆²⁸Si [M+H]+).

To a solution of 10 (660 mg, 0.65 mmol) in degassed DMF (7 mL) was added 11 (491 mg, 3.6 equiv.), Et₃N (1.4 mL, 15 equiv.) and CuI (37 mg, 0.3 equiv.). The solution was heated and stirred at 55 °C overnight. After cooling to room temperature, 0.05 M Na₂EDTA (100 mL) was added and reaction mixture was stirred at room temperature under bubbling with air for 30 min. The aqueous layer was extracted with DCM (4 × 100 mL), dried over anhydrous Na₂SO₄ and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to give S2 (620 mg, 58 %) as a orange-white solid.
**1H NMR** (500 MHz, DMF-$d_7$, 1,2-diphenylhydrazine): δ = 8.53 (s, 1H, H$_{12}$), 8.16-8.11 (m, 4H, H$_{7+13+18}$), 7.51-7.46 (m, 3H, H$_{14+15}$), 5.24 (bs, 3H, H$_{5+10}$), 4.78-4.69 (m, 10H, H$_{6+8+11}$), 4.61 (m, 6H, H$_{19}$), 4.52 (m, 6H, H$_{17}$), 4.32 (bs, 2H, H$_{3}$), 3.84-3.62 (m, 12H, H$_{4+9+16+20}$), 1.96 (d, 6H, J = 12.3 Hz, H$_{21}$), 1.33 (t, 6H, J = 11.6 Hz, H$_{21}$), 1.13-1.12 (m, 36H, H$_{22}$), 0.94 (s, 9H, H$_{1}$), -0.13 (s, 6H, H$_{2}$); 
**13C NMR** (125 MHz, DMF-$_d_7$, 1,2-diphenylhydrazine): δ = 155.9, 1532.5, 150.7, 147.2, 145.4, 144.4, 131.8, 129.7, 129.1, 128.1, 125.6, 125.2, 124.2, 123.0, 122.6, 120.4, 118.2, 112.2, 103.1, 89.5, 71.5, 70.4, 68.8, 64.5, 61.4, 59.2, 58.5, 50.5, 49.4, 45.1, 41.3, 32.5, 25.9, 20.6, 16.4, -5.0; 
**HRMS** m/z = 1647.9037 (calcd. for 1647.9051 C$_{77}$H$_{119}$O$_5$N$_{24}$Si$^{+}$ [M+H$^+$]).

To a solution of 9 (1.20 g, 1.6 mmol) in degassed DMF (16 mL) was added 12 (407 mg, 2.4 equiv.), Et$_3$N (2.2 mL, 10.0 equiv.) and Cul (61 mg, 0.2 equiv.). The solution was heated and stirred at 55 °C overnight. After cooling to room temperature, 0.05 M Na$_2$EDTA (150 mL) was added and the reaction mixture was stirred at room temperature under bubbling with air for 30 min. The aqueous layer was extracted with DCM (3 × 100 mL), dried over anhydrous Na$_2$SO$_4$ and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to give S3 (1.00 g, 65 %) as a pale brown solid.

**1H NMR** (500 MHz, CD$_3$OD): δ = 8.26 (s, 1H, H$_{12}$), 7.98-7.96 (m, 3H, H$_{7+18}$), 7.81-7.72 (m, 4H, H$_{13+22}$), 7.42-7.33 (m, 3H, H$_{14+15}$), 7.16-7.14 (m, 2H, H$_{20}$), 6.94 (s, 2H, H$_{21}$), 5.30-5.27 (m, 4H, H$_{19}$), 5.14 (bs, 2H, H$_{5+10}$), 4.77-4.53 (m, 8H, H$_{6+8+11}$), 4.51-4.34 (m, 4H, H$_{17}$), 4.23-4.21 (m, 2H, H$_{3}$), 3.75-3.38 (m, 8H, H$_{4+9+16}$), 0.93 (s, 9H, H$_{1}$), 0.10 (s, 6H, H$_{2}$); 
**13C NMR** (500 MHz, CD$_3$OD): δ = 157.4 (×2), 148.8, 145.5, 144.3, 144.2, 138.4, 131.7, 130.0, 129.4, 129.3, 129.2, 126.7 (×2), 126.4, 125.6, 123.4, 120.8, 103.2, 90.8, 72.7, 72.5, 72.3, 70.1, 69.8, 69.4, 65.2, 60.1, 58.5, 54.5, 52.8, 51.8, 51.0, 47.8, 42.6 (×2), 41.9, 37.4, 26.8, 26.5, 24.8, 17.2, 13.9, -4.5; 
**HRMS** m/z = 963.4626 (calcd. for 963.4629 C$_{44}$H$_{59}$O$_6$N$_{18}$Si$^{+}$ [M+H$^+$]).
To a solution of 10 (700 mg, 0.69 mmol) in degassed DMF (7 mL) was added 12 (263 mg, 3.6 equiv.), Et₃N (15 equiv., 1.45 mL) and Cul (40 mg, 0.3 equiv.). The reaction mixture was stirred at 55 °C overnight. After cooling to room temperature, 0.05 M Na₂EDTA (100 mL) was added and reaction mixture was stirred at room temperature under bubbling with air for 30 min. The aqueous layer was extracted with DCM (4 × 100 mL), dried using anhydrous Na₂SO₄ and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to give S₄ (400 mg, 44 %) as a orange-white solid.

¹H NMR (500 MHz, CD₃OD): δ = 8.27 (s, 1H, H₁₂), 7.97-7.95 (m, 5H, H₇+18), 7.81-7.75 (m, 5H, H₁₃+22), 7.43-7.29 (m, 3H, H₁₄+₁₅), 7.16 (s, 3H, H₂₀), 6.94 (s, 3H, H₂₁), 5.31-5.26 (m, 6H, H₁₉), 5.18-5.09 (m, 3H, H₁₅+₁₀), 4.71-4.57 (m, 10H, H₆+₁₈+₁₁), 4.42 (bs, 6H, H₁₇), 4.21 (s, 2H, H₅), 3.61-3.41 (m, 12H, H₉+₁₆), 0.92 (s, 9H, H₁), 0.09 (s, 6H, H₂); ¹³C NMR (125 MHz, CD₃OD): δ = 157.3, 148.8, 145.5, 144.3 (×2), 138.4, 131.7, 130.1, 129.4, 129.3, 126.7, 126.4, 125.6, 123.5, 120.8, 103.2, 90.7, 72.5, 69.8, 69.5, 65.1, 60.1, 51.7, 51.0, 47.8, 42.6, 41.9, 26.5, 17.2, 9.3, -4.5; HRMS m/z = 1336.6236 (calcd. for 1336.6226 C₅₇H₇₆O₈N₃₀Si [M+H]⁺).

To a solution of 9 (1.56 g, 2.08 mmol) in degassed DMF (13 mL) was added 2-ethynylpyridine (505 µL, 2.4 equiv.), Et₃N (2.8 mL, 10.0 equiv.) and Cul (77 mg, 0.2 equiv.). The solution was heated and stirred at 55 °C overnight. After cooling to room temperature, 0.05 M Na₂EDTA (100 mL) was added and the reaction mixture was stirred at room
temperature under bubbling with air for 30 min. The aqueous layer was extracted with DCM (3 × 100 mL), dried over anhydrous Na₂SO₄ and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to give S5 (1.38 g, 69 %) as a orange solid.

**1H NMR** (300 MHz, DMF-d₇): δ = 8.64-8.51 (m, 4H, H₁₈-H₂₂), 8.15-7.93 (m, 6H, H₇-H₁₀, H₁₂-H₁₅+19+20), 7.67-7.34 (m, 5H, H₁₄+15+21), 5.63-5.24 (m, 2H, H₅-H₆), 4.84-4.58 (m, 10H, H₆+H₈+H₁₁+H₁₇), 4.31 (bs, 2H, H₃), 3.75-3.53 (m, 8H, H₄-H₉+H₁₆), 0.92 (s, 9H, H₁), 0.11 (s, 6H, H₂); **13C NMR** (75 MHz, DMF-d₇): δ = 155.9, 155.8, 147.1, 137.2, 131.4, 129.0, 128.0, 125.6, 125.4, 125.1, 123.8, 122.4, 122.3, 103.3, 102.9, 89.4, 89.1, 79.3, 71.8, 71.3 (×2), 69.2, 69.0, 68.7, 64.6, 64.4, 59.1, 59.0, 53.6, 53.4, 51.5, 50.5 (×2), 49.8, 46.3, 41.2, 41.1, 28.2, 26.1, 25.8, 16.3, -5.1; **HRMS** m/z = 957.4409 (calcd. for C₄₆H₇₀O₆N₁₆₂₈Si [M+H]+).

To a solution of 10 (700 mg, 0.69 mmol) in degassed DMF (7 mL) was added 2-ethynylpyridine (250 µL, 3.6 equiv.), Et₃N (1.5 mL, 15 equiv.) and CuI (40 mg, 0.3 equiv.). The reaction mixture was stirred at 55 °C overnight. After cooling to room temperature 0.05 M Na₂EDTA (100 mL) was added and reaction mixture was stirred at room temperature under bubbling with air for 30 min. The aqueous layer was extracted with DCM (4 × 100 mL), dried using anhydrous Na₂SO₄ and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM/Et₃N) to give S6 (620 mg, 68 %) as a brownish-black solid.

**1H NMR** (500 MHz, CD₃OD): δ = 8.51 (bs, 3H, H₂₂), 8.44-8.40 (m, 3H, H₁₈), 8.23 (d, 1H, J= 3.5 Hz, H₁₂), 8.02-7.74 (m, 10H, H₇+H₁₃+H₁₉+H₂₀), 7.36-7.27 (m, 6H, H₁₄+H₁₅+H₂₁), 5.27-5.10 (m, 3H, H₅+H₁₀), 4.72-4.53 (m, 16H, H₆+H₈+H₁₁+H₁₇), 4.18 (bs, 2H, H₃), 3.66-3.50 (m, 12H, H₄+H₉+H₁₆), 0.90 (s, 9H, H₁), 0.07 (s, 6H, H₂); **13C NMR** (125 MHz, CD₃OD) δ = 157.4, 157.3, 151.1, 1504, 148.8, 145.6, 138.8, 131.6, 130.0, 129.3, 126.7, 126.3, 124.8, 124.5, 123.4, 121.5, 103.2,
90.7, 79.5, 72.6, 69.7, 69.4, 65.1, 60.1, 51.8, 51.7, 51.6, 51.1, 42.0, 35.8, 32.2, 26.5, 17.2, -4.5; HRMS \textit{m/z} = 1327.5914 (calcd. for 1327.5913 C\textsubscript{62}H\textsubscript{75}O\textsubscript{9}N\textsubscript{24}Si [M+H]+).

To a solution of \textbf{S1} (1.80 g, 1.54 mmol) in THF (25 mL) was added TBAF (1.0 M in THF, 1.6 mL, 1.05 equiv.) and the solution was kept for stirring overnight at room temperature. The reaction mixture was diluted with ethyl acetate (100 mL) and washed with NH\textsubscript{4}Cl (3 × 50 mL) and water (2 × 50 mL). The organic layer was dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and concentrated under vacuum to yield \textbf{13} (1.20 g, 74 %).

\textbf{\textsuperscript{1}H NMR} (300 MHz, CD\textsubscript{3}OD, 1,2-diphenylhydrazine): \(\delta = 8.25\) (s, 1H, H\textsubscript{11}), 7.97-7.92 (m, 3H, H\textsubscript{6}+17), 7.81 (t, 2H, \(J = 8.2\) Hz, H\textsubscript{12}), 7.42 (t, 2H, \(J = 7.4\) Hz, H\textsubscript{13}), 7.33 (t, 1H, \(J = 7.0\) Hz, H\textsubscript{14}), 5.19-5.15 (m, 2H, H\textsubscript{4/9}), 4.71-4.35 (m, 14H, H\textsubscript{5/7/10/16/18}), 4.22-4.13 (m, 2H, H\textsubscript{2}), 3.78-3.75 (m, 2H, H\textsubscript{10}), 3.67-3.45 (m, 8H, H\textsubscript{3/8/15}), 3.31 (m, 1H, H\textsubscript{1}) 1.94-1.91 (m, 4H, H\textsubscript{20}), 1.44-1.36 (m, 4H, H\textsubscript{20}), 1.17-1.12 (m, 24H, H\textsubscript{21}); \textbf{\textsuperscript{13}C NMR} (75 MHz, CD\textsubscript{3}OD, 1,2-diphenylhydrazine): \(\delta = 157.2\) (×2), 153.8, 148.7, 148.4, 146.4, 132.2, 131.7, 131.6, 130.2, 130.0, 129.8, 129.3, 129.2, 126.7, 126.6, 126.3, 126.2, 125.4, 123.7, 123.3, 121.4, 79.5, 72.6, 72.4, 72.1, 71.9, 70.1, 69.9, 69.6, 69.3, 65.1, 62.0, 60.0, 59.4, 59.3, 54.4, 54.3, 52.6, 51.6, 50.8, 45.5, 41.9, 32.6, 21.2; HRMS \textit{m/z} = 1057.5690 (calcd. for C\textsubscript{50}H\textsubscript{73}O\textsubscript{10}N\textsubscript{16} 1057.5690 [M+H]+).
To a solution of S2 (1.50 g, 0.91 mmol) in THF (30 mL) was added TBAF (1.0 M in THF, 1.0 mL, 1.05 equiv.) and the solution was kept for stirring overnight at room temperature. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with NH4Cl (2 × 50 mL) and water (2 × 50 mL). The organic layer was dried over anhydrous Na2SO4 and concentrated under vacuum to yield 14 (1.25 g, 89 %).

1H NMR (500 MHz, DMF-d7, 1,2-diphenylhydrazine): \( \delta = 8.53 \) (s, 1H, \( H_{11} \)), 8.17-8.12 (m, 5H, \( H_{5+17} \)), 7.95-7.94 (m, 2H, \( H_{12} \)), 7.53-7.46 (m, 3H, \( H_{13+14} \)), 5.22 (bs, 3H, \( H_4+9 \)), 4.82-4.68 (m, 10H, \( H_{5+7+10} \)), 4.64-4.61 (m, 6H, \( H_{18} \)), 4.55-4.48 (m, 6H, \( H_{16} \)), 4.27 (d, 2H, \( J = 1.6 \text{ Hz}, H_2 \)), 3.83-3.77 (m, 3H, \( H_{19} \)), 3.71-3.50 (m, 12H, \( H_{3+8+15} \)), 1.97-1.95 (m, 6H, \( H_{20} \)), 1.35-1.31 (m, 6H, \( H_{20} \)), 1.13-1.11 (m, 36H, \( H_{21} \)); 13C NMR (125 MHz, DMF-d7, 1,2-diphenylhydrazine): \( \delta = 155.8, 152.7, 150.6, 147.1, 145.4, 144.4, 144.0, 131.8, 131.5, 129.7, 129.1, 128.1, 128.0, 127.4, 125.6, 125.5, 125.3, 124.2, 122.9, 122.5, 122.4, 120.3, 118.2, 112.1, 80.3, 80.0, 79.4, 76.9, 76.6, 72.2, 71.8, 71.5, 71.4, 70.3, 69.2, 69.1, 68.9, 68.8, 68.7, 64.6, 64.5, 61.4, 58.5 (×2), 58.4, 53.7, 53.4, 50.6, 50.5, 49.4, 45.0, 44.9, 41.3, 32.5, 20.4; HRMS m/z = 1534.8268 (calcd. for 1534.8264 C73H106O15N24 [M+H]+).

To a solution of S3 (1.00 g, 1.04 mmol) in THF (25 mL) was added TBAF (1.0 M in THF, 1.1 mL, 1.05 equiv.) and the solution was kept for stirring overnight at room temperature. The reaction mixture was concentrated under reduced pressure followed by purification by flash column chromatography (methanol/DCM) to yield 15 (0.620 g, 70 %).

1H NMR (500 MHz, CD3OD): \( \delta = 8.29 \) (s, 1H, \( H_{11} \)), 7.99-7.97 (m, 4H, \( H_{6+17} \)), 7.82-7.76 (m, 4H, \( H_{12+21} \)), 7.42-7.31 (m, 3H, \( H_{13+14} \)), 7.16 (s, 2H, \( H_{19} \)), 6.95 (s, 2H, \( H_{20} \)), 5.31-5.27 (m, 4H, \( H_{18} \)), 5.16-5.11 (m, 2H, \( H_4+9 \)), 4.67-4.53 (m, 8H, \( H_{5+7+10} \)), 4.43-4.42 (m, 4H, \( H_{16} \)), 4.16 (s, 2H, \( H_2 \)), 3.64-3.44 (m, 10H, \( H_{3+8+15+NH} \)), 2.91 (s, 1H, \( H_1 \)); 13C NMR (125 MHz, CD3OD): \( \delta = 157.3 \) (×2), 148.7, 145.5, 144.2 (×2), 131.6, 130.0, 129.4, 129.2, 126.7, 126.5, 125.6, 123.5,
To a solution of S4 (1.00 g, 0.75 mmol) in THF (30 mL) was added TBAF (1.0 M in THF, 0.8 mL, 1.05 equiv.) and the solution was kept for stirring overnight at room temperature. The reaction mixture was concentrated under vacuum followed by purification by flash column chromatography (methanol/DCM/Et3N) to yield 16 (0.81 g, 89%).

\[
\text{HRMS } m/z = 849.3761 \text{ (calcd. for } 849.3764 \text{ C}_{38}H_{45}O_6N_{18} [M+H]^+).
\]

\[
\begin{align*}
\text{1H NMR (500 MHz, CD}_3\text{OD): } & \delta = 8.27 (s, 1H, H_{11}), 7.98-7.90 (m, 5H, H_{6+17}), 7.81-7.77 (m, 4H, H_{12+21}), 7.41-7.31 (m, 3H, H_{13+14}), 7.18 (bs, 3H, H_{19}), 6.97 (s, 3H, H_{20}), 5.31-5.27 (m, 6H, H_{18}), 5.17-5.09 (m, 3H, H_{4+9}), 4.73-4.57 (m, 10H, H_{5+7+10}), 4.42 (bs, 6H, H_{16}), 4.17 (bs, 2H, H_2), 3.70-3.43 (m, 12H, H_{3+8+15}), 2.90 (bs, 1H, H_1); \\
\text{13C NMR (125 MHz, CD}_3\text{OD): } & \delta = 157.3, 148.8, 145.5, 144.3, 144.2, 131.7, 130.0, 129.4, 126.7, (\times 2), 126.4, 125.6, 123.5, 80.2, 76.6, 76.4, 72.5, 70.1, 69.8, 69.4, 65.1, 62.6, 59.4, 54.4, 51.7, 51.0, 47.8, 42.7, 41.9, 29.6, 24.8, 20.7, 13.9, 9.2; \\
\text{HRMS } m/z = 1222.5374 \text{ (calcd. for } 1222.5375 \text{ C}_{53}H_{64}O_9N_{27} [M+H]^+).
\end{align*}
\]

To a solution of S5 (1.38 g, 1.44 mmol) in THF (25 mL) was added TBAF (1.0 M in THF, 1.5 mL, 1.05 equiv.) and the solution was kept for stirring overnight at room temperature. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with NH4Cl (4 × 50 mL) and NaHCO3 (2× 50 mL). The organic layer was dried over anhydrous Na2SO4 and concentrated under vacuum to yield 17 (1.04 g, 85%).
**H NMR** (500 MHz, CD$_3$OD): $\delta$ = 8.58-8.41 (m, 2H, H$_{21}$), 8.42-8.41 (m, 2H, H$_{17}$), 8.27-8.26 (m, 1H, H$_{11}$), 8.01-7.96 (m, 3H, H$_{6+18}$), 7.87-7.78 (m, 4H, H$_{12+19}$), 7.44-7.31 (m, 5H, H$_{13+14+20}$), 5.20-5.16 (m, 2H, H$_{4+9}$), 4.68-4.39 (m, 10H, H$_{5+7+10+16}$), 4.20-4.16 (m, 2H, H$_2$), 3.64-3.53 (m, 8H, H$_{3+8+15}$), 2.89 (s, 1H, H$_1$); $^{13}$C NMR (125 Hz, CD$_3$OD): $\delta$ = 157.3, 157.2, 150.9, 150.3, 148.6, 148.4, 145.6, 145.4, 145.3, 145.1, 138.7 ($\times$2), 131.6, 131.4, 129.9, 129.2 ($\times$2), 126.6 ($\times$2), 126.3, 126.2, 124.6, 124.3, 123.3, 121.4, 80.3, 80.1, 79.4, 76.6, 76.3, 72.6, 72.4, 72.1, 70.0, 69.9, 69.5, 69.2, 65.1 ($\times$2), 59.3, 54.3, 54.2, 51.6, 50.9, 47.8, 41.9, 26.8, 24.7, 20.6, 13.9, 9.2; HRMS $m/z$ = 843.3544 (calcd. for C$_{40}$H$_{43}$O$_6$N$_{16}$Si [M+H]$^+$).

To a solution of S6 (0.8 g, 0.60 mmol) in THF (25 mL) was added TBAF (1.0 M in THF, 0.6 mL, 1.05 equiv.) and the solution was kept for stirring overnight at room temperature. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with saturated NaHCO$_3$ (2 $\times$ 50 mL) and saturated NH$_4$Cl (2 $\times$ 50 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated under vacuum. The crude product was purified by flash column chromatography (methanol/DCM) to yield 18 (0.65 g, 89%).

$^1$H NMR (500 MHz, CD$_3$OD): $\delta$ = 8.52-8.50 (m, 3H, H$_{21}$), 8.39-8.38 (m, 3H, H$_{17}$), 8.21 (m, 1H, H$_{11}$), 8.04-7.74 (m, 10H, H$_{6+12+18+19}$), 7.36-7.27 (m, 6H, H$_{13+14+20}$), 5.26-5.09 (m, 3H, H$_{4+9}$), 4.70-4.52 (m, 16H, H$_{5+7+10+16}$), 4.14 (s, 2H, H$_2$), 3.72-3.45 (m, 12H, H$_{3+7+10+16}$), 2.86 (s, 1H, H$_1$); $^{13}$C NMR (125 MHz, CD$_3$OD): $\delta$ = 157.3, 151.1, 150.5, 148.7, 145.5, 138.8, 131.6, 130.0, 129.3, 126.7, 126.3, 124.7, 124.4, 123.4, 121.5, 80.2, 79.5, 76.6, 72.5, 69.7, 69.4, 65.1, 59.4, 51.7, 51.0, 42.0, 32.1, 13.9; HRMS $m/z$ = 1213.5049 (calcd. for 1213.5048 C$_{56}$H$_{61}$O$_9$N$_{24}$[M+H]$^+$).
3 $^1$H and $^{13}$C NMR spectra

Figure S1. $^1$H NMR of 3.

Figure S2. $^{13}$C NMR of 3.
Figure S3. $^1$H NMR of 4.

Figure S4. $^{13}$C NMR of 4.
Figure S5. $^1$H NMR of 5.

Figure S6. $^{13}$C NMR of 5.
Figure S7. $^1$H NMR of 6.

Figure S8. $^{13}$C NMR of 6.
Figure S9. $^1$H NMR of 7.

Figure S10. $^{13}$C NMR of 7.
Figure S11. $^1$H NMR of 8.

Figure S12. $^{13}$C NMR of 8.
Figure S13. $^1$H NMR of 9.

Figure S14. $^{13}$C NMR of 9.
Figure S15. $^1$H NMR of 10.

Figure S16. $^{13}$C NMR of 10.
Figure S17. $^1$H NMR of S1.

Figure S18. $^{13}$C NMR of S1.
Figure S19. $^1$H NMR of S2.

Figure S20. $^{13}$C NMR of S2.
Figure S21. $^1$H NMR of S3.

Figure S22. $^{13}$C NMR of S3.
Figure S23. $^1$H NMR of S4.

Figure S24. $^{13}$C NMR of S4.
Figure S25. $^1$H NMR of S5.

Figure S26. $^{13}$C NMR of S5.
Figure S27. $^1$H NMR of S6.

Figure S28. $^{13}$C NMR of S6.
Figure S29. $^1$H NMR of 13.

Figure S30. $^{13}$C NMR of 13.
Figure S31. $^1$H NMR of 14.

Figure S32. $^{13}$C NMR of 14.
Figure S33. $^1$H NMR of 15.

Figure S34. $^{13}$C NMR of 15.
Figure S35. $^1$H NMR of 16.

Figure S36. $^{13}$C NMR of 16.
Figure S37. $^1$H NMR of 17.

Figure S38. $^{13}$C NMR of 17.
Figure S39. $^1$H NMR of 18.

Figure S40. $^{13}$C NMR of 18.
4 Preparation of supported catalysts

4.1 Preparation of azide functionalized silica
Azide functionalized silica (SiO$_2$-N$_3$/TMS) was prepared from activated silica (SiO$_2$) according to our previous literature report.$^2$ Commercially available spherical silica gel (Sorbtech Technologies, 40-75 μm, 100 Å) was activated by boiling in HCl 6 M for 1 day. The silica was filtered and washed with deionized water until neutral pH and dried in oven for 2 days at 120 °C. The resulting silica was then placed in a round-bottom flask and heated at 120 °C under vacuum for 2 hours. The flask was then allowed to cool to room temperature and toluene (20 mL/g) was added together with AzPTMS (2 mmol/g) and the resulting mixture refluxed overnight. The silica was then filtered, washed with toluene and CH$_2$Cl$_2$. The obtained azide functionalized silica was dried in vacuum oven at 50 °C overnight. The flask was then cooled with liquid nitrogen and HMDS (1.5 mL/g) was added under vacuum. The resulting mixture was finally heated at 80 °C for 8 hours. The silica was filtered, washed with CH$_2$Cl$_2$ and dried under vacuum oven to give SiO$_2$-N$_3$/TMS.

4.2 Preparation of catalyst 19
SiO$_2$-N$_3$/TMS was suspended in degassed DMF (15 mL/g). 11, 12 and 2-ethynyl pyridine were added (1:1:1 molar ratio, 1.2 equiv. vs N$_3$ loading) subsequently followed by Et$_3$N (5.0 equiv. vs N$_3$ loading) and CuI (0.4 equiv. vs N$_3$ loading). The reaction was stirred at 55 °C for 2 days and monitored by FT-IR and TGA. The functionalized silica was recovered by filtration and washed with CH$_3$CN (150 mL) and CH$_2$Cl$_2$ (150 mL) and keep in glovebox.

4.3 Preparation of catalyst 20
SiO$_2$-N$_3$/TMS was suspended in degassed DMF (15 mL/g). Dimers 13, 15 and 17 were added (1:1:1 molar ratio, 1.2 equiv. vs N$_3$ loading) subsequently followed by Et$_3$N (5.0 equiv. vs N$_3$ loading) and CuI (0.4 equiv. vs N$_3$ loading). The reaction was stirred at 55 °C for 2 days and monitored by FT-IR and TGA. The functionalized silica was recovered by filtration and washed with CH$_3$CN (150 mL) and CH$_2$Cl$_2$ (150 mL) and keep in glovebox.

4.4 Preparation of catalyst 21
SiO$_2$-N$_3$/TMS was suspended in degassed DMF (15 mL/g). Trimers 14, 16 and 18 were added (1:1:1 molar ratio, 1.2 equiv. vs N$_3$ loading) subsequently followed by Et$_3$N (5.0 equiv. vs N$_3$ loading) and CuI (1.2 equiv. vs N$_3$ loading). The reaction was stirred at 55 °C for 2 days and monitored by FT-IR and TGA. The functionalized silica was recovered by filtration and washed with CH$_3$CN (150 mL) and CH$_2$Cl$_2$ (150 mL) and keep in glovebox.
5 TGA

Figure S41. (a) TGA and (b) DTG curves of silica, silica-N$_3$, silica-N$_3$/TMS, 19, 20 and 21.

6 FT-IR

Figure S42. FT-IR spectra of silica, silica-N$_3$, silica-N$_3$/TMS, 19, 20 and 21.
Figure S43. XPS survey scan of 19, 20 and 21.

Figure S44. (a) C 1s, (b) N 1s and (c) Cu 2p HR XPS spectra of 19, 20 and 21.
8 ICP-AES

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9 Physisorption

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10 References