Supporting Information

Efficient Heterogeneous Copper-Catalyzed Alder-Ene Reaction of Allenynamides to Pyrrolines

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General information

Unless otherwise noted, all reagents were used as received from commercial suppliers. Reactions were monitored using thin-layer chromatography (SiO$_2$). TLC plates were visualized with UV light (254 nm) or KMnO$_4$ stain. Flash chromatography was carried out with 60Å (particle size 35-70 μm) normal flash silica gel. NMR spectra were recorded on a Bruker 400 or 500 MHz spectrometer unless otherwise stated. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in CDCl$_3$ (H = 7.26 ppm and C = 77.0 ppm) as internal standard, and coupling constants (J) are given in Hz. HRMS were recorded on a Bruker micrOTOF instrument using ESI technique. Scanning transmission electron microscopy (STEM) was carried out using a 200 kV JEOL 2100F microscope, which eqips with a Schottky field-emission gun and ultrahigh-resolution pole-piece (Cs=0.5 mm). Bright-field (BF) and High angle annular dark field (HAADF) were acquired simultaneously using Gatan BF and JEOL ADF detectors, respectively, through Gatan DigitalMicrograph. The samples in vials were shaken, in order to have small pieces. Then the samples were dispersed onto Cu TEM supporting grid with holey carbon films without using solvent. X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation state of the Cu nanoparticles. All XPS data were processed using Kratos software. XPS spectral data were collected using a Kratos Axis Ultra DLD electron spectrometer with a monochromatized Al-Kα source operating at 120W. The binding energies (BE) were scaled with regards to the aliphatic C 1s carbon set to 285.0 eV. The concentration of copper was determined with inductively coupled plasmaoptical emission spectrometry (ICP-OES) by Medac Ltd. (UK) on Varian Vista MPZ.
Preparation of Cu-AmP-MCC

Preparation of amino-functionalized microcrystalline cellulose (AmP-MCC):[1] In an oven dried flask, MCC (1.0 g), tartaric acid (97.6 mg, 5 mol% to silane) was dispersed in dry toluene (20 mL). Next, 3-aminopropyltrimethoxysilane (2.27 mL, 13.0 mmol) was added and the mixture was stirred at 82 °C for 48 h. The suspension was then centrifuged and the crude AmP-MCC was washed using soxhleted extraction with acetone. After 16h, the resulting AmP-MCC was dried under vacuum for 24 h.

Preparation of the mixed valence Cu(I/II) nanocatalyst Cu-AmP-MCC:[2] To a suspension of AmP-MCC (1.0 g) in pH-adjusted H₂O solution (25 ml, pH 9) by the use of 0.1 N LiOH, was added a suspension of copper(II) trifluoromethanesulfonate (Cu(OTf)₂, 0.3 g) in deionized water (20 mL, pH 9) at room temperature. After stirring for 24 h, the formed Cu(II)-AmP-MCC with pale-blue color was recovered by centrifugation and was washed with deionized H₂O (3 × 30 mL) and acetone (3 × 30 mL) by using centrifuge. The washed Cu(II)-AmP-MCC was collected by decantation and dried overnight under vacuum.

In the next step, the dry Cu(II)-AmP-MCC was suspended in deionized water (35 mL), and NaBH₄ (190.0 mg, 5.0 mmol, 3.7 equiv to copper) in deionized water (15 mL) was added slowly at room temperature. After vigorous stirring for 1 h, the resulting mixed valence Cu(I/II) nanocatalyst Cu-AmP-MCC was recovered by centrifugation and was washed with deionized H₂O (3×30 mL) and acetone (3×30 mL) by the use of a centrifuge. The washed Cu-AmP-MCC was collected by decantation, dried for 48 h under vacuum and obtained as dark blue amorphous powder. The Cu-AmP-MCC was characterized by STEM and XPS (see Figures S1 and S2).
Characterizations of Cu-AmP-MCC by STEM

Figure S1. STEM bright-field images of Cu-AmP-MCC catalyst, a) with 200 nm scale bar and b) with 100 nm scale bar, c) with 50 nm scale bar and d) with 20 nm scale bar. Moiré fringes given by overlapping of crystalline particles are observed.
Figure S2. XPS spectrum of the Cu2p state of Cu-AmP-MCC nanocatalyst
Table S1. Cu 2p spectrum components of Cu-AmP-MCC nanocatalyst

| BE, eV  | FWHM, eV | AC, at% | Component                  |
|---------|----------|---------|---------------------------|
| 932.5   | 1.25     | 4.05    | Cu 2p 3/2 Cu(I)           |
| 952.3   | 1.4      | 1.66    | Cu 2p 1/2 Cu(I)           |
|         |          | ∑ = 5.71|                           |
| 934.6   | 2.4      | 2.1     | Cu 2p 3/2 Cu(II)          |
| 954.2   | 2.45     | 0.98    | Cu 2p 1/2 Cu(II)          |
| 936.2   | 2.1      | 0.21    | Cu 3/2 Cu(II) “tail”      |
| 956.2   | 2.25     | 0.16    | Cu 1/2 Cu(II) “tail”      |
| 941.4   | 2.7      | 0.48    | Cu 2p 3/2 Cu(II) satellite|
| 943.9   | 2.7      | 0.68    | Cu 2p 3/2 Cu(II) satellite|
| 962.6   | 2.45     | 0.59    | Cu 2p 1/2 Cu(II) satellite|
|         |          | ∑ = 5.2 |                           |

The high resolution spectra for the Cu2p region revealed two main peaks located at 932.5 eV and 952.3 eV belonging to Cu(I) as well as peaks at 934.6 eV and 954.2 eV that are characteristic of Cu(II) (Figure S2). Moreover, a collection of satellite features of these peaks are clearly observed at 936.2 eV, 941.4 eV, 943.9 eV, 956.2 eV and 962.6 eV, which also indicated the presence of Cu(II) species. The atomic ratio between Cu(I) and Cu(II) can be calculated from their atomic concentrations based on the ratio of the combined integrals of the peaks belonging to Cu(I) to those of the peaks belonging to Cu(II). Thus Cu(I) : Cu(II) = 5.71 : 5.2 = 1.1 : 1 (Table S1).
General procedure for the preparation of allenynamide 3

The allenic sulfonamides S1 were prepared according to a procedure described in the literature.\[3\]

To a flame-dried 25 mL Schlenk flask were added (in the following order) allenic sulfonamide S1 (2.0 mmol, 1.0 equiv), copper(I) thiophene-2-carboxylate (CuTc) (38.1 mg, 0.20 mmol, 10 mol%) and Cs2CO3 (1.30 g, 4.0 mmol) under argon atmosphere. The flask was evacuated under vacuum and flushed with argon for three times. To this mixture toluene (10.0 mL) was added, followed by DMEDA (43.1 µL, 0.40 mmol, 20 mol%) and the alkynyl bromide S2 (2.4 mmol, 1.2 equiv). The reaction mixture was stirred under argon at 40 °C. After 4 h, the reaction mixture was cooled to rt, filtered through a pad of celite, concentrated in vacuo and purified by flash silica gel column chromatography (petroleum ether/EtOAc with 3% Et3N as eluent) to give allenynamide 3.

*N-(hept-1-yn-1-yl)-4-methyl-N-(2-(2-methylprop-1-en-1-ylidene)hexyl)benzenesulfonamide* (3a)

85% isolated yield, colorless oil. 1H NMR (400 MHz, CDCl3) δ ppm 7.77 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 3.78 (s, 2H), 2.44 (s, 3H), 2.24 (t, J = 7.0 Hz, 2H), 1.90 (t, J = 6.9 Hz, 2H), 1.63 (s, 2H), 1.49 – 1.42 (m, 2H), 1.37 – 1.28 (m, 8H), 0.88 (t, J = 7.0 Hz, 2H), 0.87 (t, J = 7.2 Hz, 2H); 13C NMR (100 MHz, CDCl3) δ 201.43, 144.03, 134.86, 129.47, 127.65, 96.91, 96.65, 73.04, 70.21, 55.13, 30.94, 29.59, 29.37, 28.71, 22.20 (2C), 21.58, 20.55, 18.49, 13.96, 13.95; HRMS (ESI): calc. for C24H35NNaO2S [M+Na]+ 424.2281; found: 424.2283.

*N-(hept-1-yn-1-yl)-4-methyl-N-(2-(2-(methyl-d3)prop-1-en-1-ylidene-3,3,3-d3)hexyl)benzenesulfonamide* (d6-3a)
83% isolated yield, colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ ppm 7.77 (d, $J = 8.3$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 3.77 (s, 2H), 2.43 (s, 3H), 2.23 (t, $J = 7.1$ Hz, 2H), 1.90 (t, $J = 6.9$ Hz, 2H), 1.49 – 1.43 (m, 2H), 1.37 – 1.26 (m, 8H), 0.88 (t, $J = 7.1$ Hz, 2H), 0.87 (t, $J = 7.2$ Hz, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 201.42, 144.02, 134.82, 129.45, 127.61, 96.57 (2C), 77.25, 77.00, 76.75, 73.02, 70.17, 55.12, 30.90, 29.57, 29.33, 28.67, 22.17 (2C), 21.54, 18.46, 13.93, 13.92; HRMS (ESI): calc. for C$_{24}$H$_{29}$D$_6$NNaO$_2$S [M+Na]$^+$ 430.2657; found: 430.2654.

$^{N}$-(hept-1-ynyl)-4-methyl-$N$-(4-methyl-2-phenylpenta-2,3-dien-1-yl)benzenesulfonamide (3b)

92% isolated yield, colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ ppm δ 7.77 (d, $J = 8.2$ Hz, 2H), 7.30 (d, $J = 8.3$ Hz, 2H), 7.28 – 7.23 (m, 3H), 7.16 (d, $J = 6.8$ Hz, 2H), 3.80 (s, 2H), 2.75 – 2.63 (m, 2H), 2.42 (s, 3H), 2.31 – 2.18 (m, 4H), 1.56 (s, 6H), 1.45 (dt, $J = 14.2$, 7.0 Hz, 2H), 1.36 – 1.27 (m, 4H), 0.88 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 201.89, 144.26, 142.06, 134.94, 129.66, 128.55, 128.27, 127.79, 125.74 , 97.80, 96.28, 73.15, 70.47, 55.33, 33.81, 31.17, 28.86, 22.34, 21.75, 20.63, 18.64, 14.14; HRMS (ESI): calc. for C$_{28}$H$_{35}$NNaO$_2$S [M+Na]$^+$ 472.2281; found: 472.2283.

$^{N}$-(hept-1-yn-1-yl)-4-methyl-$N$-(4-methyl-2-phenylpenta-2,3-dien-1-yl)benzenesulfonamide (3c)

76% isolated yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.77 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 7.1$ Hz, 2H), 7.33 – 7.28 (m, 4H), 7.19 (t, $J = 7.2$ Hz, 1H), 4.25 (s, 2H), 2.45 (s, 3H), 2.20 (t, $J = 7.0$ Hz, 2H), 1.77 (s, 6H), 1.44 – 1.38 (m, 2H), 1.30 – 1.24 (m, 4H), 0.87 (t, $J$
= 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 204.39, 144.15, 135.46, 134.45, 129.52, 128.34, 127.77, 126.63, 126.21, 99.84, 98.28, 72.92, 70.66, 52.56, 30.90, 28.64, 22.18, 21.60, 20.12, 18.51, 13.95; HRMS (ESI): calc. for C$_{26}$H$_{31}$NaN$_2$O$_2$S $[M+Na]^+$ 444.1968; found: 444.1971.

$N$-(2,4-dimethylpenta-2,3-dien-1-yl)-$N$-(hept-1-yn-1-yl)-4-methylbenzenesulfonamide (3d)

81% isolated yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.75 (d, $J = 8.4$ Hz, 2H), 7.29 (d, $J = 8.1$ Hz, 2H), 3.75 (s, 2H), 2.41 (s, 3H), 2.22 (t, $J = 7.0$ Hz, 2H), 1.61 (s, 3H), 1.60 (s, 6H), 1.48 – 1.41 (m, 2H), 1.33 – 1.24 (m, 4H), 0.86 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 201.58, 144.02, 134.70, 129.40, 127.48, 95.49, 91.65, 72.89, 70.00, 56.10, 30.79, 28.57, 22.05, 21.43, 20.43, 18.34, 16.37, 13.84; HRMS (ESI): calc. for C$_{21}$H$_{29}$NaN$_2$O$_2$S $[M+Na]^+$ 382.1811; found: 382.1813.

Ethyl 3-(((N-(hept-1-yn-1-yl)-4-methylphenyl)sulfonamido)methyl)-5-methylhexa-3,4-dienoate (3e)

72% isolated yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.77 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 4.14 (q, $J = 7.1$ Hz, 2H), 3.89 (s, 2H), 2.98 (s, 2H), 2.43 (s, 3H), 2.23 (t, $J = 7.0$ Hz, 2H), 1.65 (s, 6H), 1.49 – 1.42 (m, 2H), 1.31 – 1.29 (m, 4H), 1.26 (t, $J = 7.1$ Hz, 3H), 0.88 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 202.96, 171.18, 144.18, 134.68, 129.54, 127.64, 97.88, 90.72, 72.96, 70.30, 60.60, 54.80, 35.92, 30.94, 28.66, 22.17, 21.59, 20.26, 18.45, 14.17, 13.96; HRMS (ESI): calc. for C$_{24}$H$_{35}$NaN$_2$O$_4$S $[M+Na]^+$ 454.2023; found: 454.2021.

$N$-(2-(cyclopentylidenemethylene)hexyl)-$N$-(hept-1-yn-1-yl)-4-methylbenzenesulfonamide (3f)
78% isolated yield, colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ ppm 7.77 (d, $J = 8.3$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 3.81 (s, 2H), 2.42 (s, 3H), 2.29 – 2.26 (m, 4H), 2.23 (t, $J = 7.0$ Hz, 2H), 1.90 (t, $J = 7.0$ Hz, 2H), 1.64 – 1.61 (m, 4H), 1.48 – 1.42 (m, 2H), 1.35 – 1.25 (m, 8H), 0.88 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 196.63, 143.98, 134.92, 129.41, 127.59, 105.60, 99.12, 73.14, 70.09, 31.06, 30.87, 29.53, 29.50, 28.66, 26.94, 22.17, 22.15, 21.51, 18.45, 13.92, 13.90; HRMS (ESI): calc. for C$_{26}$H$_{37}$NaO$_2$S [M+Na]$^+$ 450.2437; found: 450.2436.

4-methyl-N-(2-(2-methylprop-1-en-1-ylidene)hexyl)-N-(phenylethynyl)benzenesulfonamide (3g)

61% isolated yield, colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ ppm 7.78 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 8.3$ Hz, 2H), 3.78 (s, 2H), 2.43 (s, 3H), 1.90 (t, $J = 7.2$ Hz, 2H), 1.71 (dd, $J = 21.8$, 13.4 Hz, 3H), 1.63 (s, 6H), 1.45 – 1.19 (m, 11H), 0.87 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 201.63, 144.58, 134.98, 131.43, 129.83, 128.33, 127.84, 127.68, 123.34, 97.56, 96.61, 82.75, 70.96, 55.35, 29.76, 22.35, 21.78, 20.75, 14.11; HRMS (ESI): calc. for C$_{25}$H$_{29}$NaO$_3$S [M+Na]$^+$ 430.1811; found: 430.1810.

$\text{N-((4-methoxyphenyl)ethynyl)-4-methyl-N-(2-(2-methylprop-1-en-1-ylidene)hexyl)benzenesulfonamide (3h)}$

55% isolated yield, colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) δ ppm 7.86 (d, $J = 8.3$ Hz, 2H), 7.36 (d, $J = 8.4$ Hz, 2H), 7.33 – 7.29 (m, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 3.92 (s, 2H), 3.83 (s, 3H), 2.47 (s, 3H), 1.96 (q, $J = 6.7$ Hz, 2H), 1.63 (s, 6H), 1.40 – 1.30 (m, 4H), 0.90 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 201.69, 159.43, 144.46, 134.99, 133.43, 130.72, 129.77, 129.18, 128.35, 127.65, 113.96, 97.42, 96.62, 81.17, 70.52, 55.41, 29.77, 22.35, 21.77, 20.72, 14.11; HRMS (ESI): calc. for C$_{26}$H$_{31}$NaO$_3$S [M+Na]$^+$ 460.1917; found: 460.1919.

$\text{N-(cyclohexylethynyl)-4-methyl-N-(2-(2-methylprop-1-en-1-ylidene)hexyl)benzenesulfonamide (3i)}$
50% isolated yield, colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ ppm 7.78 (d, $J = 8.1$ Hz, 2H), 7.31 (d, $J = 8.3$ Hz, 2H), 3.78 (s, 2H), 2.43 (s, 3H), 1.90 (t, $J = 7.2$ Hz, 2H), 1.71 (dd, $J = 21.8$, 13.4 Hz, 3H), 1.63 (s, 6H), 1.45 – 1.19 (m, 11H), 0.87 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 201.43, 144.17, 134.93, 129.56, 127.83, 96.98, 74.18, 73.61, 55.29, 33.02, 29.73, 29.48, 28.98, 26.05, 24.83, 22.34, 21.72, 20.71, 14.09; HRMS (ESI): calc. for C$_{25}$H$_{35}$NNaO$_2$S [M+Na]$^+$ 436.2281; found: 436.2280.

4-Methyl-N-(2-(2-methylprop-1-en-1-ylidene)hexyl)-N-((trimethylsilyl)ethynyl)benzenesulfonamide (3j)

71% isolated yield, colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ ppm 7.77 (d, $J = 8.3$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 3.82 (s, 2H), 2.43 (s, 3H), 1.87 (t, $J = 7.0$ Hz, 2H), 1.63 (s, 6H), 1.36 – 1.25 (m, 4H), 0.86 (t, $J = 7.1$ Hz, 3H), 0.13 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 201.29, 144.36, 134.70, 129.43, 127.73, 97.10, 96.32, 95.14, 77.26, 77.00, 76.75, 72.92, 54.93, 29.52, 29.31, 22.13, 21.55, 20.55, 13.89, 0.11; HRMS (ESI): calc. for C$_{22}$H$_{33}$NNaO$_2$SSi [M+Na]$^+$ 426.1893; found: 426.1895.

N-(3-((tert-butyldimethylsilyl)oxy)prop-1-yn-1-yl)-4-methyl-N-(2-(2-methylprop-1-en-1-ylidene)hexyl)benzenesulfonamide (3k)

83% isolated yield, colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ ppm 7.78 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 4.42 (s, 2H), 3.83 (s, 2H), 2.43 (s, 3H), 1.88 (t, $J = 6.9$ Hz, 2H), 1.64 (s, 6H), 1.37 – 1.27 (m, 4H), 0.87 (s, 9H), 0.06 (s, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 201.40, 144.30, 135.01, 129.62, 127.61, 97.29, 96.43, 78.06, 77.25, 77.00, 76.75, 70.07, 54.99, 51.83,
29.55, 29.38, 25.76, 22.19, 21.57, 20.54, 18.18, 13.94, -5.17; HRMS (ESI): calc. for C_{26}H_{41}N_{2}O_{3}SSi [M+Na]^+ 498.2469; found: 498.2471.
Optimization of reaction conditions

Table S2. Optimization of reaction conditions for the Alder-ene reaction of 3a.\(^a\)

| Entry | Catalyst | Base | Solvent | T (°C) | Yield of 4a (%)\(^b\) | Yield of 5a (%)\(^b\) |
|-------|----------|------|---------|--------|----------------------|----------------------|
| 1     | Cu-AmP-MCC | Cs₂CO₃ | Toluene | 60     | 65                   | 0                    |
| 2     | Cu-AmP-MCC | -     | Toluene | 60     | 61                   | <5                   |
| 3     | Cu-AmP-MCC | Cs₂CO₃ | Toluene | 60     | 61                   | 0                    |
| 4\(^c\) | Cu(OTf)₂ | Cs₂CO₃ | Toluene | 60     | 65                   | 0                    |
| 5\(^c\) | AgOTf   | Cs₂CO₃ | Toluene | 60     | 48                   | 0                    |
| 6\(^c\) | Sc(OTf)₃ | Cs₂CO₃ | Toluene | 60     | 53                   | 0                    |
| 7     | -        | Cs₂CO₃ | Toluene | 60     | 9                    | 0                    |
| 8     | Cu-AmP-MCC | K₂CO₃ | Toluene | 60     | 57                   | 0                    |
| 9     | Cu-AmP-MCC | K₃PO₄ | Toluene | 60     | 49                   | 0                    |
| 10    | Cu-AmP-MCC | Na₂CO₃ | Toluene | 60     | 42                   | 0                    |
| 11    | Cu-AmP-MCC | Et₃N  | Toluene | 60     | 64                   | 0                    |
| 12    | Cu-AmP-MCC | DIPEA | Toluene | 60     | 61                   | 0                    |
| 13    | Cu-AmP-MCC | Cs₂CO₃ | THF     | 60     | 36                   | 0                    |
| 14    | Cu-AmP-MCC | Cs₂CO₃ | MeOH    | 60     | 21                   | 0                    |
| 15    | Cu-AmP-MCC | Cs₂CO₃ | CH₃CN   | 60     | 18                   | 0                    |
| 16    | Cu-AmP-MCC | Cs₂CO₃ | DCE     | 60     | 43                   | 8                    |
| 17    | Cu-AmP-MCC | -     | DCE     | 60     | 28                   | 19                   |
| 18    | Cu-AmP-MCC | -     | CHCl₃   | 60     | 18                   | 35                   |
| 19    | Cu-AmP-MCC | Cs₂CO₃ | Toluene | 80     | 91(88)\(^d\)        | 0                    |
| 20\(^e\) | Cu-AmP-MCC | Cs₂CO₃ | Toluene | 80     | 78                   | 0                    |
| 21    | Cu-AmP-MCC | -     | CHCl₃   | 80     | 3                    | 71 (68)\(^d\)       |
| 22    | -        | Cs₂CO₃ | Toluene | 80     | 29                   | 0                    |
| 23    | -        | -     | Toluene | 80     | 18                   | 8                    |

\(^a\)The reaction was carried out in the indicated solvent (1 mL) using 3a (0.1 mmol) and base (0.2 mmol) in the presence of metal catalyst (5.4 mol%). \(^b\)Determined by NMR using 1,1,2,2-tetrachloroethane as the standard. \(^c\)5.0 mol% metal catalyst was used. \(^d\)Isolated yield. \(^e\)Reaction time: 12 h. CPG = controlled pore glass.
General procedure for the Cu-AmP-MCC-catalyzed Alder-ene reaction of 3 to 2,5-dihydropyrroles 4

To an oven-dried microwave vial equipped with a magnetic stir bar were added Cu-AmP-MCC (8.0 mg, 5.4 mol% of Cu) and Cs₂CO₃ (130.3 mg, 0.40 mmol, 2.0 equiv). The vial was then sealed and evacuated under vacuum and flushed with argon three times before the solution of allenynamide 3 (0.20 mmol, 1.0 equiv) in toluene (2.0 mL) was added. The reaction mixture was stirred under argon at 80 °C. After 24 h, the reaction mixture was cooled to rt, filtered through a pad of celite, concentrated in vacuo and purified by flash column chromatography (petroleum ether/EtOAc as eluent) to give 2,5-dihydropyrroles 4.

(Z)-4-Butyl-2-hexylidene-3-(prop-1-en-2-yl)-1-tosyl-2,5-dihydro-1H-pyrrole (4a)

The general procedure was followed using 3a (80.2 mg, 0.2 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 30 : 1) yielded 4a (70.6 mg, 88%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ ppm 7.64 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 7.8Hz, 2H), 5.07 – 5.06 (m, 1H), 5.04 (t, J = 7.3 Hz, 1H), 4.57 – 4.56 (m, 1H), 4.11 (s, 2H), 2.52 (dt, J = 7.5, 7.3 Hz, 2H), 2.37 (s, 3H), 1.88 (t, J = 7.0 Hz, 2H), 1.59 (s, 3H), 1.45 – 1.38 (m, 2H), 1.34 – 1.30 (m, 4H), 1.02 – 0.92 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H), 0.75 (t, J = 6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 143.58, 142.44, 138.44, 138.26, 137.54, 134.99, 133.77, 129.00, 127.95, 118.12, 116.98, 58.10, 31.67, 30.06, 29.78, 29.27, 26.29, 22.57, 22.43, 22.24, 21.46, 14.07, 13.85; HRMS (ESI): calc. for C₂₄H₃₅NNaO₂S [M+Na]⁺ 424.2281; found: 424.2282.

(Z)-2-Hexylidene-4-phenethyl-3-(prop-1-en-2-yl)-1-tosyl-2,5-dihydro-1H-pyrrole (4b)
The general procedure was followed using **3b** (89.8 mg, 0.2 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20 : 1) yielded **4b** (76.3 mg, 85%) as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ ppm 7.67 (d, $J$ = 8.2 Hz, 2H), 7.29 – 7.20 (m, 5H), 7.05 (d, $J$ = 7.1 Hz, 2H), 5.14 – 5.05 (m, 2H), 4.53 (d, $J$ = 1.0 Hz, 1H), 4.22 (s, 2H), 2.62 – 2.51 (m, 2H), 2.41 (s, 3H), 2.36 – 2.29 (m, 2H), 2.26 – 2.18 (m, 2H), 1.58 (d, $J$ = 13.4 Hz, 3H), 1.50 – 1.42 (m, 2H), 1.39 – 1.32 (m, 4H), 0.96 – 0.90 (m, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 143.82, 142.34, 141.20, 139.03, 137.50, 134.23, 133.89, 129.20, 128.60, 128.15, 126.33, 118.87, 117.28, 58.38, 34.52, 31.82, 29.89, 29.39, 28.95, 22.73, 22.53, 21.67, 14.26; HRMS (ESI): calc. for C$_{28}$H$_{35}$NNaO$_2$S $[M+Na]^+$ 472.2281; found: 472.2280.

(Z)-2-Hexyldiene-4-phenyl-3-(prop-1-en-2-yl)-1-tosyl-2,5-dihydro-1H-pyrrole (4c)

The general procedure was followed using **3c** (84.2 mg, 0.2 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20 : 1) yielded **4c** (75.8 mg, 90%) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.62 (d, $J$ = 8.2 Hz, 2H), 7.26 – 7.20 (m, 3H), 7.15 (d, $J$ = 7.8 Hz, 2H), 7.13 – 7.10 (m, 2H), 5.35 (t, $J$ = 7.4 Hz, 1H), 5.16 – 5.15 (m, 1H), 4.67 – 4.66 (m, 1H), 4.60 (s, 2H), 2.60 (dt, $J$ = 7.5, 7.3 Hz, 2H), 2.34 (s, 3H), 1.53 (s, 3H), 1.49 – 1.42 (m, 2H), 1.37 – 1.33 (m, 4H), 0.91 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.73, 143.35, 138.69, 138.29, 133.55, 133.45, 131.29, 129.08, 128.26, 127.85, 127.69, 126.51, 120.73, 118.04, 58.19, 31.68, 29.67, 29.37, 22.57, 22.00, 21.46, 14.09; HRMS (ESI): calc. for C$_{26}$H$_{31}$NNaO$_2$S [M+Na]$^+$ 444.1968; found: 444.1969.

(Z)-2-Hexyldiene-4-methyl-3-(prop-1-en-2-yl)-1-tosyl-2,5-dihydro-1H-pyrrole (4d)
The general procedure was followed using 3d (71.8 mg, 0.2 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 30 : 1) yielded 4d (58.2 mg, 81%) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.61 (d, $J = 8.3$ Hz, 2H), 7.19 (d, $J = 7.9$ Hz, 2H), 5.07 – 5.05 (m, 1H), 5.02 (d, $J = 7.3$ Hz, 1H), 5.54 – 5.53 (m, 1H), 4.12 (s, 2H), 2.51 (dt, $J = 7.5$, 7.2 Hz, 2H), 2.37 (s, 3H), 1.52 (s, 3H), 1.46 (s, 3H), 1.42 – 1.37 (m, 2H), 1.35 – 1.29 (m, 4H), 0.88 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.55, 142.24, 138.15, 137.37, 133.73, 130.83, 128.98, 127.76, 118.14, 117.04, 60.00, 31.64, 29.73, 29.11, 22.54, 22.05, 21.47, 14.06, 11.90; HRMS (ESI): calc. for C$_{21}$H$_{29}$NNO$_2$S $[M+Na]^+$ 382.1811; found: 382.1810.

Ethyl (Z)-2-(5-hexylidene-4-(prop-1-en-2-yl)-1-tosyl-2,5-dihydro-1H-pyrrol-3-yl)acetate (4e)

The general procedure was followed using 3e (86.2 mg, 0.2 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10 : 1) yielded 4e (41.5 mg, 48%) as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ ppm 7.63 (d, $J = 8.3$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 5.11 – 5.08 (m, 2H), 4.60 – 4.59 (m, 1H), 4.33 (s, 2H), 4.06 (q, $J = 7.2$ Hz, 2H), 2.92 (s, 2H), 2.52 (dt, $J = 7.5$, 7.4 Hz, 2H), 2.38 (s, 3H), 1.52 (s, 3H), 1.45 – 1.39 (m, 2H), 1.35 – 1.31 (m, 4H), 1.22 (t, $J = 7.1$ Hz, 3H), 1.22 (t, $J = 7.1$ Hz, 3H), 0.89 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 169.49, 143.58, 141.60, 141.52, 136.78, 133.77, 129.01, 127.94, 126.93, 120.06, 117.87, 60.93, 58.53, 32.99, 31.66, 29.63, 29.19, 22.55, 22.14, 21.50, 14.13, 14.07; HRMS (ESI): calc. for C$_{24}$H$_{33}$NNO$_4$S $[M+Na]^+$ 454.2023; found: 454.2023.

(Z)-4-Butyl-3-(cyclopent-1-en-1-yl)-2-hexylidene-1-tosyl-2,5-dihydro-1H-pyrrole (4f)

The general procedure was followed using 3f (85.5 mg, 0.2 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 30 : 1) yielded 4f (66.6 mg, 78%) as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ ppm 7.62 (d, $J = 8.3$ Hz, 2H), 7.19 (d, $J = 8.1$ Hz, 2H), 5.45 – 5.43 (m, 1H), 5.05 (t, $J = 7.3$ Hz, 1H), 4.08 (s, 2H), 2.51 (dt, $J = 7.5$, 7.4 Hz, 2H),

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2.41 – 2.37 (m, 2H), 2.38 (s, 3H), 2.19 – 2.15 (m, 2H), 2.19 – 1.84 (m, 4H), 1.44 – 1.38 (m, 2H), 1.34 – 1.31 (m, 4H), 0.94 – 0.86 (m, 7H), 0.73 (t, J = 6.9 Hz, 3H); 13C NMR (126 MHz, CDCl3) δ 143.48, 142.76, 135.85, 135.58, 133.77, 133.69, 131.43, 128.95, 127.92, 118.45, 58.04, 35.36, 32.93, 31.71, 30.08, 29.79, 29.33, 26.45, 22.57, 22.18, 21.48, 14.07, 13.83; HRMS (ESI): calc. for C26H37NNaO2S [M+Na]+ 450.2437; found: 450.2434.

(Z)-2-Benzylidene-4-butyl-3-(prop-1-en-2-yl)-1-tosyl-2,5-dihydro-1H-pyrrole (4g)

The general procedure was followed using 3g (81.4 mg, 0.2 mmol). The reaction was performed for 4 h. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20 : 1) yielded 4g (62.7 mg, 77%) as a colorless oil. The NMR data are in accordance with those reported in the literature.[3] 1H NMR (500 MHz, CDCl3) δ ppm 7.78 (d, J = 7.3 Hz, 2H), 7.67 (d, J = 8.3 Hz, 2H), 7.33 (t, J = 7.7 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.19 (t, J = 7.4 Hz, 1H), 6.01 (s, 1H), 5.18 (s, 1H), 4.65 (s, 1H), 4.25 (s, 2H), 2.39 (s, 3H), 1.95 (t, J = 7.3 Hz, 2H), 1.72 (s, 3H), 1.03 – 0.93 (m, 4H), 0.79 (t, J = 7.0 Hz, 3H); 13C NMR (126 MHz, CDCl3) δ 143.98, 143.17, 139.42, 137.80, 137.24, 136.81, 133.15, 129.26, 129.11, 128.17, 127.75, 126.62, 117.68, 115.04, 58.38, 30.18, 26.57, 22.72, 22.33, 21.53, 13.93; HRMS (ESI): calc. for C25H29NNaO2S [M+Na]+ 430.1811; found: 430.1814.

(Z)-4-Butyl-2-(4-methoxybenzylidene)-3-(prop-1-en-2-yl)-1-tosyl-2,5-dihydro-1H-pyrrole (4h)

The general procedure was followed using 3h (87.4 mg, 0.2 mmol). The reaction was performed for 5 h. Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20 : 1) yielded 4h (65.6 mg, 75%) as a colorless oil. 1H NMR (500 MHz, CDCl3) δ ppm 7.71 (d, J = 8.8 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 5.93 (s, 1H), 5.15 (d, J = 1.5 Hz, 1H), 4.61 (s, 1H), 4.22 (s, 2H), 3.81 (s, 3H), 2.38
(s, 3H), 1.91 (t, J = 7.0 Hz, 2H), 1.68 (s, 3H), 1.04 – 0.90 (m, 4H), 0.77 (t, J = 6.8 Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 158.44, 143.97, 141.58, 139.57, 137.46, 136.71, 133.30, 130.70, 129.36, 129.15, 128.33, 117.62, 115.12, 58.46, 55.28, 30.30, 26.65, 22.81, 22.45, 21.61, 14.00; HRMS (ESI): calc. for C$_{26}$H$_{31}$NNaO$_3$S [M+Na]$^+$ 460.1917; found: 460.1916.

(Z)-4-Butyl-2-(cyclohexylmethylen)-3-(prop-1-en-2-yl)-1-tosyl-2,5-dihydro-1H-pyrrole (4i)

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\text{\includegraphics[width=0.2\textwidth]{4i.png}}
\]

The general procedure was followed using 3i (82.6 mg, 0.2 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 30 : 1) yielded 4i (57.9 mg, 70%) as a colorless oil. The NMR data are in accordance with those reported in the literature.$^{[3]}$ $^1$H NMR (500 MHz, CDCl$_3$) δ ppm 7.64 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.3 Hz, 2H), 5.05 (s, 1H), 4.87 (d, J = 10.5 Hz, 1H), 4.55 (d, J = 1.0 Hz, 1H), 4.11 (s, 2H), 3.02 – 2.94 (m, 1H), 1.87 (t, J = 7.4 Hz, 4H), 1.72 – 1.65 (m, 3H), 1.57 (s, 3H), 1.39 (dt, J = 22.2, 9.6 Hz, 2H), 1.21 – 1.13 (m, 1H), 1.10 – 0.82 (m, 7H), 0.75 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 143.69, 140.66, 138.51, 137.74, 135.12, 133.98, 129.17, 128.08, 123.86, 117.14, 58.36, 37.33, 33.60, 30.22, 26.46, 25.96, 22.62, 22.44, 21.64, 14.03; HRMS (ESI): calc. for C$_{25}$H$_{35}$NNaO$_2$S [M+Na]$^+$ 436.2281; found: 436.2276.

(Z)-4-Butyl-3-(prop-1-en-2-yl)-1-tosyl-2-((trimethylsilyl)methylene)-2,5-dihydro-1H-pyrrole (4j)

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\text{\includegraphics[width=0.2\textwidth]{4j.png}}
\]

The general procedure was followed using 3j (80.6 mg, 0.2 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 30 : 1) yielded 4j (66.1 mg, 82%) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.62 (d, J = 8.3 Hz, 2H), 7.20 (d, J = 7.8 Hz, 2H), 5.12 – 5.10 (m, 1H), 4.93 (s, 1H), 4.56 – 4.55 (m, 1H), 4.08 (s, 2H), 2.37 (s, 3H), 1.92 (t, J = 7.6 Hz, 2H), 1.61 (s, 3H), 1.01 – 0.97 (m, 2H), 0.90 – 0.82 (m, 2H), 0.74 (t, J = 7.1 Hz, 4H), 0.25 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.40, 143.64, 139.95, 138.08, 137.64,
133.74, 129.01, 127.91, 117.21, 111.73, 57.40, 29.99, 26.56, 22.56, 22.12, 21.48, 13.85, 0.43;
HRMS (ESI): calc. for C\textsubscript{22}H\textsubscript{33}NNaO\textsubscript{2}SSi [M+Na]\textsuperscript{+} 426.1893; found: 426.1899.

(Z)-4-Butyl-2-((tert-butyldimethylsilyl)oxy)ethylidene)-3-(prop-1-en-2-yl)-1-tosyl-2,5-dihydro-1H-pyrrole (4k)

The general procedure was followed using 3k (95.1 mg, 0.2 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20 : 1) yielded 4k (69.4 mg, 73%) as a colorless oil. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) ppm 7.60 (d, \(J = 7.6\) Hz, 2H), 7.21 (d, \(J = 7.9\) Hz, 2H), 5.19 (t, \(J = 6.0\) Hz, 1H), 5.10 (s, 1H), 4.63 (d, \(J = 6.0\) Hz, 2H), 4.60 (s, 1H), 4.09 (s, 2H), 2.38 (s, 3H), 1.90 (t, \(J = 7.2\) Hz, 2H), 1.62 (s, 3H), 1.00 – 0.86 (m, 4H), 0.90 (s, 9H), 0.74 (t, \(J = 7.3\) Hz, 3H), 0.08 (s, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 143.89, 142.46, 137.99, 136.96, 136.74, 133.40, 129.12, 127.96, 117.44, 116.44, 61.53, 58.01, 30.06, 26.32, 26.00, 22.39, 22.16, 21.49, 18.35, 13.84, -5.01; HRMS (ESI): calc. for C\textsubscript{26}H\textsubscript{41}NNaO\textsubscript{3}SSi [M+Na]\textsuperscript{+} 498.2469; found: 498.2470.
General procedure for the Cu-AmP-MCC-catalyzed Alder-ene reaction of 3 to pyrroles 5

![Chemical structure](image)

To an oven-dried microwave vial equipped with a magnetic stir bar were added Cu-AmP-MCC (8.0 mg, 5.4 mol% of Cu). The vial was then sealed and evacuated under vacuum and flushed with argon for three times before the solution of allenynamide 3 (0.20 mmol, 1.0 equiv) in CHCl₃ (2.0 mL) was added. The reaction mixture was stirred under argon at 80 °C. After 24 h, the reaction mixture was cooled to rt, filtered through a pad of celite, concentrated in vacuo and purified by flash column chromatography (petroleum ether/EtOAc as eluent) to give pyroles 5.

4-Butyl-2-hexyl-3-(prop-1-en-2-yl)-1-tosyl-1H-pyrrole (5a)

![Chemical structure](image)

The general procedure was followed using 3a (80.2 mg, 0.2 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 50:1) yielded 5a (54.5 mg, 68%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ ppm 7.59 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 7.9 Hz, 2H), 6.96 (s, 1H), 5.14 (s, 1H), 4.73 (s, 1H), 2.57 (t, J = 8.0 Hz, 2H), 2.40 (s, 3H), 2.31 (t, J = 7.6 Hz, 2H), 1.87 (s, 3H), 1.54 – 1.46 (m, 2H), 1.34 – 1.20 (m, 10H), 0.90 (t, J = 7.3 Hz, 3H), 0.86 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 144.21, 138.76, 137.09, 131.57, 130.08, 129.74, 126.68, 126.47, 118.33, 116.48, 31.47, 31.39, 31.21, 29.35, 25.85, 25.33, 24.23, 22.58, 22.47, 21.57, 14.07, 13.92; HRMS (ESI): calc. for C₂₄H₃₅N₄O₂S [M+Na]^+ 424.2281; found: 424.2280.
2-Hexyl-4-phenethyl-3-(prop-1-en-2-yl)-1-tosyl-1H-pyrrole (5b)

The general procedure was followed using 3b (89.8 mg, 0.2 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 30 : 1) yielded 5b (63.8 mg, 71%) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.54 (d, $J = 8.4$ Hz, 2H), 7.29 – 7.25 (m, 4H), 7.21 – 7.14 (m, 3H), 6.96 (s, 1H), 5.17 – 5.16 (m, 1H), 4.75 – 4.74 (m, 1H), 2.84 (t, $J = 7.3$ Hz, 2H), 2.64 (t, $J = 8.1$ Hz, 2H), 2.57 (t, $J = 8.1$ Hz, 2H), 2.42 (s, 3H), 1.89 (s, 3H), 1.43 – 1.36 (m, 2H), 1.28 – 1.19 (m, 6H), 0.87 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.26, 141.88, 138.58, 137.01, 131.61, 129.84, 129.79, 128.38, 128.27, 126.50, 125.84, 125.50, 118.59, 116.77, 35.61, 31.47, 31.16, 29.34, 27.62, 25.81, 24.24, 22.58, 21.59, 14.07; HRMS (ESI): calc. for C$_{28}$H$_{35}$NNaO$_2$S [M+Na]$^+$ 472.2281; found: 472.2279.

2-Hexyl-4-phenyl-3-(prop-1-en-2-yl)-1-tosyl-1H-pyrrole (5c)

The general procedure was followed using 3c (84.2 mg, 0.2 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20 : 1) yielded 5c (61.5 mg, 73%) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.69 (d, $J = 8.4$ Hz, 2H), 7.49 – 7.46 (m, 2H), 7.36 (s, 1H), 7.35 – 7.23 (m, 5H), 5.22 – 5.21 (m, 1H), 4.94 – 4.93 (m, 1H), 2.69 (t, $J = 8.0$ Hz, 2H), 2.42 (s, 3H), 1.69 (s, 3H), 1.47 – 1.40 (m, 2H), 1.30 – 1.21 (m, 6H), 0.88 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.67, 139.26, 136.69, 134.36, 132.52, 129.93, 128.44, 128.36, 127.11, 126.73, 126.71, 126.42, 118.91, 116.96, 31.46, 31.29, 29.36, 25.50, 24.15, 22.57, 21.59, 14.07; HRMS (ESI): calc. for C$_{26}$H$_{31}$NNaO$_2$S [M+Na]$^+$ 444.1968; found: 444.1970.

2-hexyl-4-methyl-3-(prop-1-en-2-yl)-1-tosyl-1H-pyrrole (5d)

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The general procedure was followed using 3d (71.8 mg, 0.2 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 30 : 1) yielded 5d (45.4 mg, 63%) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.61 (d, $J = 8.4$ Hz, 2H), 7.26 (d, $J = 8.0$ Hz, 2H), 6.97 (q, $J = 1.1$ Hz, 1H), 5.16 – 5.14 (m, 1H), 4.74 – 4.73 (m, 1H), 2.60 (t, $J = 8.0$ Hz, 2H), 2.40 (s, 3H), 1.94 (d, $J = 1.2$ Hz, 3H), 1.88 (s, 3H), 1.44 – 1.37 (m, 2H), 1.29 – 1.19 (m, 6H), 0.86 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.27, 138.62, 137.06, 131.63, 130.37, 129.77, 126.53, 121.35, 118.83, 116.33, 31.46, 31.22, 29.33, 25.91, 23.99, 22.58, 21.55, 14.06, 10.80; HRMS (ESI): calc. for C$_{21}$H$_{29}$NNaO$_2$S [M+Na]$^+$ 382.1811; found: 382.181.

**Ethyl 2-(5-hexyl-4-(prop-1-en-2-yl)-1-tosyl-IH-pyrrol-3-yl)acetate (5e)**

![Diagram of 5e](image)

The general procedure was followed using 3e (86.2 mg, 0.2 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 15 : 1) yielded 5e (35.5 mg, 41%) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.62 (d, $J = 8.1$ Hz, 2H), 7.27 (d, $J = 8.8$ Hz, 2H), 7.20 (s, 1H), 5.17 (s, 1H), 4.74 (s, 1H), 4.13 (q, $J = 7.1$ Hz, 2H), 3.35 (s, 2H), 2.56 (t, $J = 8.0$ Hz, 2H), 2.40 (s, 3H), 1.86 (s, 3H), 1.42 – 1.35 (m, 2H), 1.24 (t, $J = 7.1$ Hz, 3H), 1.24 – 1.18 (m, 6H), 0.86 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.33, 144.49, 137.99, 136.88, 131.60, 129.85, 129.55, 126.61, 120.24, 118.11, 117.35, 60.72, 31.44, 31.41, 31.00, 29.34, 25.92, 24.18, 22.56, 21.58, 14.16, 14.06; HRMS (ESI): calc. for C$_{24}$H$_{33}$NNaO$_4$S [M+Na]$^+$ 454.2023; found: 454.2021.

**4-Butyl-3-(cyclopent-1-en-1-yl)-2-hexyl-1-tosyl-1H-pyrrole (5f)**

![Diagram of 5f](image)

The general procedure was followed using 3f (85.5 mg, 0.2 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 30 : 1) yielded 5f (45.4 mg, 53%) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.60 (d, $J = 8.4$ Hz, 2H), 7.25 (d, $J = 8.0$ Hz, 2H), 6.98 (s, 1H), 5.55 – 5.53 (m, 1H), 2.58 (t, $J = 8.0$ Hz, 2H), 2.45 – 2.40 (m, 4H), 2.40 (s,
3H), 2.31 (t, J = 7.0 Hz, 2H), 1.92 (tt, J = 7.2, 7.2 Hz, 2H), 1.52 – 1.44 (m, 2H), 1.41 – 1.19 (m, 10H), 0.90 (t, J = 7.3 Hz, 3H), 0.86 (t, J = 7.2 Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 144.21, 137.09, 136.79, 132.23, 129.75, 129.68, 127.24, 126.53, 125.00, 118.36, 77.32, 77.00, 76.68, 36.47, 32.93, 31.43, 31.37, 31.10, 29.23, 25.99, 25.77, 23.97, 22.57, 22.50, 21.56, 14.07, 13.95; HRMS (ESI): calc. for C\(_{26}\)H\(_{37}\)NNaO\(_2\)S [M+Na]\(^+\) 450.2437; found: 450.2435.

\(2\)-Benzyl-4-butyl-3-(prop-1-en-2-yl)-1-tosyl-1H-pyrrole (5g)

![Image of 5g]

The general procedure was followed using 3g (81.4 mg, 0.2 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 20 : 1) yielded 5g (57.8 mg, 71%) as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm 7.28 (d, J = 7.7 Hz, 2H), 7.09 – 7.06 (m, 4H), 7.02 (d, J = 8.1 Hz, 2H), 6.89 – 6.87 (m, 2H), 5.13 (s, 1H), 4.80 (s, 1H), 4.19 (s, 2H), 2.40 (t, J = 7.4 Hz, 2H), 2.34 (s, 3H), 1.87 (s, 3H), 1.58 (tt, J = 7.8, 7.8 Hz, 2H), 1.44 – 1.35 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.82, 139.75, 138.46, 136.16, 131.65, 129.38, 128.01, 127.96, 127.82, 126.68, 126.33, 125.40, 118.63, 116.76, 31.46, 30.72, 25.44, 24.21, 22.55, 21.47, 13.95; HRMS (ESI): calc. for C\(_{25}\)H\(_{29}\)NNaO\(_2\)S [M+Na]\(^+\) 430.1811; found: 430.1810.

\(4\)-Butyl-3-(prop-1-en-2-yl)-1-tosyl-2-((trimethylsilyl)methyl)-1H-pyrrole (5j)

![Image of 5j]

The general procedure was followed using 3j (80.6 mg, 0.2 mmol). Purification by column chromatography on silica gel (petroleum ether/EtOAc = 30 : 1) yielded 5j (61.4 mg, 76%) as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) ppm 7.55 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 6.86 (s, 1H), 5.15 – 5.13 (m, 1H), 4.73 – 4.71 (m, 1H), 2.39 (s, 3H), 2.29 (t, J = 7.4 Hz, 2H), 2.22 (s, 2H), 1.86 (s, 3H), 1.45 (tt, J = 7.7, 7.7 Hz, 2H), 1.30 – 1.21 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H), 0.02 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 144.03, 138.89, 136.95, 130.35, 129.61, 128.12, 127.64, 126.31, 117.69, 116.83, 31.21, 25.47, 23.87, 22.31, 21.54, 15.90, 13.90, -0.70; HRMS (ESI): calc. for C\(_{22}\)H\(_{33}\)NNaO\(_2\)Si [M+Na]\(^+\) 426.1893; found: 426.1895.
Deuterium-labeling experiments

To an oven-dried microwave vial equipped with a magnetic stir bar were added Cu-AmP-MCC (8.0 mg, 5.4 mol% of Cu) and Cs$_2$CO$_3$ (130.3 mg, 0.40 mmol, 2.0 equiv). The vial was then sealed and evacuated under vacuum and flushed with argon for three times before H$_2$O (7.2 µL, 0.40 mmol, 2.0 equiv) and the solution of $d^6$-3a (81.5 mg, 0.2 mmol, 1.0 equiv) in toluene (2.0 mL) was added. The reaction mixture was stirred under argon at 80 ºC. After 24 h, the reaction mixture was cooled to rt, filtered through a pad of celite, concentrated in vacuo and purified by flash column chromatography (petroleum ether/EtOAc = 30 : 1 as eluent) to give $d^6$-4a.

(Z)-4-Butyl-2-(hexylidene-1-d)-3-(prop-1-en-2-yl-d5)-1-tosyl-2,5-dihydro-1H-pyrrole ($d^6$-4a)

$d^6$-4a: 52.9 mg, 65% isolated yield, colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.63 (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 4.10 (s, 2H), 2.52 (t, $J = 7.6$ Hz, 2H), 2.37 (s, 3H), 1.88 (t, $J = 7.5$ Hz, 2H), 1.43 – 1.38 (m, 2H), 1.34 – 1.31 (m, 4H), 1.01 – 0.91 (m, 4H), 0.89 (t, $J = 7.1$ Hz, 3H), 0.75 (t, $J = 6.9$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.57, 142.40, 138.18, 137.23, 134.94, 133.75, 128.99, 127.93, 117.73 (t, $J = 22.0$ Hz), 116.68 – 116.20 (m), 58.09, 31.67, 30.06, 29.74, 29.16, 26.27, 22.56, 22.22, 21.46, 14.07, 13.85. HRMS (ESI): calc. for C$_{24}$H$_{29}$D$_6$NNaO$_2$S [M+Na]$^+$ 430.2657; found: 430.2658.
Recycling experiments and leaching test

To an oven-dried microwave vial equipped with a magnetic stir bar were added Cu-AmP-MCC (8.0 mg, 5.4 mol% of Cu) and Cs$_2$CO$_3$ (130.3 mg, 0.40 mmol, 2.0 equiv). The vial was then sealed and evacuated under vacuum and flushed with argon three times before the solution of 3a (80.2 mg, 0.2 mmol, 1.0 equiv) in toluene (2.0 mL) was added. The reaction mixture was stirred under argon at 80 °C. After 24 h, the reaction mixture was cooled to rt and centrifuged for 3 min at 10000 rpm. The catalyst was washed with toluene (2 × 2 mL), H$_2$O (2 × 2 mL), and acetone (3 × 2 mL) and dried for 12 h under vacuum before being used in the next run or for characterizations. The supernatant of toluene was combined for the determination of yield by NMR using 1,1,2,2-tetrachloroethane as the internal standard. The leaching test of the copper nanocatalyst was carried out by ICP-OES analysis of the recovered solution from the 1st run and the amount of copper in the reaction mixture was determined to be <1 ppm.
References

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NMR spectra

\[ \text{\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz)} \]

\[ \text{\textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz)} \]
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 126 MHz)
$\text{Ph}_2\text{C} = \text{N} - \text{Ts}$

$\text{Ph}_2\text{C} = \text{N} - \text{n-C}_3\text{H}_7$

$^1\text{H NMR (CDCl}_3\text{, 400 MHz)}$

$\text{Ph}_2\text{C} = \text{N} - \text{Ts}$

$\text{Ph}_2\text{C} = \text{N} - \text{n-C}_6\text{H}_{11}$

$^{13}\text{C NMR (CDCl}_3\text{, 100 MHz)}$
$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)

S30
$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
**1H NMR (CDCl₃, 400 MHz)**

**13C NMR (CDCl₃, 100 MHz)**
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 126 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 126 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 126 MHz)

S35
$^{1}$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 126 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 126 MHz)
$\text{H NMR (CDCl}_3, \ 400 \text{ MHz}}$

$\text{C NMR (CDCl}_3, \ 100 \text{ MHz}}$
\[4b\]

\[\text{H NMR (CDCl}_3, 500 \text{ MHz)}\]

\[\text{13C NMR (CDCl}_3, 126 \text{ MHz)}\]
\[ \text{Ph}^+ \text{Ts}^- \]

**4c**

\(^{1}H\) NMR (CDCl\(_3\), 400 MHz)

\[ \text{Ph}^+ \text{Ts}^- \]

**4c**

\(^{13}C\) NMR (CDCl\(_3\), 100 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 126 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 126 MHz)

4g

n-Bu

NTs

n-Bu

NTs

4g
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 126 MHz)
$^1$H NMR (CDCl$_3$, 500 MHz)

$^{13}$C NMR (CDCl$_3$, 126 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
$^{1}$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)

S54
$\text{H NMR (CDCl}_3, 400 \text{ MHz)}$

$\text{C NMR (CDCl}_3, 100 \text{ MHz)}$

S55
$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)
$^1$H NMR (CDCl$_3$, 400 MHz)

$^{13}$C NMR (CDCl$_3$, 100 MHz)