

Electronic Supplementary Information (ESI) for
Cellulose-Immobilized NHC–Cu(I) Complex: An Efficient
and Reusable catalyst for Multicomponent Synthesis of
1,2,3-Triazoles

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TABLE OF CONTENTS

Contents	Page
Preparation of IL	S3
Preparation of CL-IL	S3
Preparation of NHC-Cu/CL	S3
General procedure for the multicomponent 1,3-dipolar cycloaddition	S3
Characterization	S4
References	S6

Preparation of IL

In a well-dried 25 mL Schlenk flask, (3-chloropropyl)trimethoxy silane (10 mmol) was added to 1-methylimidazole (10 mmol), and then the system was evacuated and purged with argon five times. After being stirred at 90 °C for 48 h under argon atmosphere, the resulting mixture was allowed to cool down to room temperature, was washed with dry ethyl acetate four times and dried under vacuum for 24 h at room temperature. The finally obtained ionic liquid was a kind of yellowish sticky liquids.^{s1} The ¹H NMR (300 MHz) spectral data for the ionic liquid is as follows: δ = 0.43 (m, 2H), 1.81(m, 2H), 3.39 (s, 9H), 3.9 (m, 2H), 4.1 (m, 2H), 7.3 (s, 1H), 7.6 (s, 1H), 10.3 (s, 1H).

Preparation of CL-IL

The imidazolium salt was dissolved in a mixture of 80/20 (v/v) ethanol/water at a concentration of 10% (w/w) for 12 h at room temperature, and thus was hydrolyzed to form reactive silanol groups. The cellulose suspension (10% w/w with respect to the solvent) in a mixture of 80/20 (v/v) ethanol/water was added in the solution and stirred for 8 h. Subsequently, the solvent was evaporated at 40 °C for 3 h under reduced pressure. The obtained white solid thermally treated at 110 °C for 3 h, followed by thorough washing with ethanol and drying at room temperature.

Preparation of NHC-Cu/CL

The CL-IL was treated with freshly prepared CuI in dry THF for 6 h at room temperature in the presence of NaO*t*-Bu which played a role as a base for the deprotonation of the imidazolium group. The amount of NHC-Cu(I) on the supported catalysts was determined by AA after treatment with HCl 6N. HCl solution dissolves organic portions of the particles and releases copper ions into solution. The copper content of the catalyst was found to be 0.86 mmol g⁻¹ based on AA analysis. This means that 39.6% of the imidazolium groups in the cellulose support participated in the formation of Cu complex. The low loading of Cu implies that the majority of the NaO*t*-Bu may be deactivated by hydroxyl groups in surface layer of the cellulose support.

General procedure for the multicomponent 1,3-dipolar cycloaddition

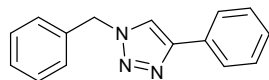
A mixture of benzyl halide or tosylate (1.0 mmol), sodium azide (1.2 mmol), phenylacetylene (1.3 mmol) in H₂O (3 mL) was heated at 50 °C for 1 h. After completion of the reaction (TLC), the heterogeneous mixture was cooled to room temperature and the ethyl acetate

was added to the flask and the catalyst was separated by filtration. The products were extracted with ethyl acetate–water mixture. The combined organic layers were dried over MgSO₄ and concentrated under reduced pressure to give the corresponding 1,2,3-triazole. Obtained triazole was purified by recrystallization from EtOAc and *n*-hexane.

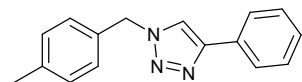
Characterization

All chemicals were purchased from commercial suppliers and all solvents were purified and dried using standard procedures. IR spectra were recorded on a Bomem MB-Series FT-IR spectrophotometer. Scanning electron microscopy and EDX mapping characterizations of NHC-Cu/CL composite were performed using an electron microscopy Philips XL-30 ESEM. ¹H-NMR spectra were recorded on a BRUKERDRX-300AVANCE spectrometer. The concentration of copper was estimated using Shimadzu AA-680 flame atomic absorption spectrophotometer. The thermal stability of the CL and NHC-Cu/CL composites were determined using a thermogravimetric analyzer (TGA/DTA Bahr: STA-503) under air and a heating rate of 10 °C min⁻¹. Elemental analysis of NHC-Cu/CL nanocomposite was performed using an Elementar Analysensysteme GmbH VarioEL CHNS. Gas chromatography was performed on a Trace GC ultra from the Thermo Company equipped with FID detector and Rtx[®]-1 capillary column. GC condition for hot filtration test: isotherm at 50 °C (1 min); ramp at 10 °C/min to 77 °C; isotherm at 77 °C (3 min); ramp at 10 °C/min to 260 °C; isotherm at 260 °C (1 min). GC analysis parameter: Injector: Mode=split, Temp.=250 °C, split flow= 10 mL/min, split ratio=10; Detector: Flame=On, Base temp.= 270 °C, ignition threshold= 0.5 pA, Flow: Air=350 mL/min, H₂=35 mL/min, Makeup (N₂)=30 mL/min; Carrier: N₂, flow mode=constant, flow=1.0 mL/min.

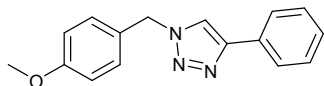
All products are known compounds and were reported previously.^{s1-4}



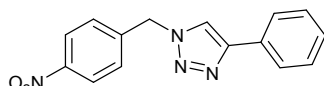
White solid, mp: 128-130 °C (lit.^{s1} mp: 130-132 °C). ¹H NMR: (300 MHz, CDCl₃) δ (ppm): 5.55 (s, 2H), 7.24-7.38 (m, 8H), 7.66 (s, 1H), 7.76-7.84 (m, 2H).



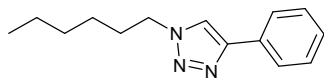
White solid, mp: 94-96 °C (lit.^{s1} 93-94 °C). ¹H NMR: (300 MHz, CDCl₃) δ (ppm): 2.34 (s, 3H), 5.46 (s, 2H), 7.19-7.22 (m, 4H), 7.29-7.41 (m, 3H), 7.65 (s, 1H), 7.80-7.82 (m, 2H).



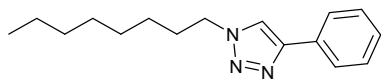
White solid, mp: 136-138 °C (lit.^{s2} mp: 139-140 °C). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 3.78 (s, 3H), 5.46 (s, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.65 (s, 1H, 5-H), 7.81 (d, *J* = 7.4 Hz, 2H).



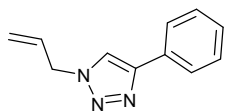
White solid, mp: 156-157 °C (lit.^{s2} mp: 157-159 °C). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 5.71 (s, 2H), 7.27-7.48 (m, 5H), 7.78 (s, 1H), 7.82 (d, *J* = 8.5 Hz, 2H), 8.25 (d, *J* = 8.5 Hz, 2H).



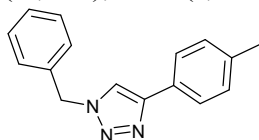
White solid, mp: 69-70 °C (lit.^{s1} mp: 67-68 °C). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 0.87 (m, 3H), 1.38 (m, 2H), 1.91-1.85 (m, 2H), 4.34 (m, 2H), 7.28-7.41 (m, 3H), 7.74 (s, 1H), 7.86 (m, 2H).



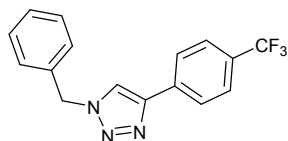
White solid, mp: 77-79 °C (lit.^{s2} mp: 78-80 °C). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 0.86 (m, 3H), 1.25-1.35 (m, 10H), 1.58-1.68 (m, 2H), 1.91-1.93 (m, 2H), 4.36-4.41 (m, 2H), 7.27-7.44 (m, 3H), 7.76 (s, 1H), 7.82 (m, 2H).



White solid, mp: 56-58 °C (lit.^{s3} mp: 57-58 °C). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 5.04 (d, *J* = 6.1 Hz, 2H), 5.28-5.40 (m, 2H), 6.06 (m, 1H), 7.28-7.37 (m, 3H), 7.46-7.52 (m, 2H), 7.76 (s, 1H).



White solid, mp: 152-153 °C (lit.^{s1} mp: 150-152 °C). Mp 154-155 °C (Lit. 151-152). ¹H-NMR (300 MHz, CDCl₃) δ (ppm): 2.36 (s, 3H), 5.56 (s, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.27-7.39 (m, 5H), 7.62 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 2H)



White solid, mp: 133-135 °C (lit.^{s4} mp: 137-138 °C). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 5.56 (s, 2H), 7.27-7.42 (m, 5H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.77 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 2H)

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