ESI

for

A new “Bicycle Helmet”-like copper(II),sodiumphenylsilsesquioxane. Synthesis, structure and catalytic activity

by

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Experiments

Synthesis.

$PhSi(OMe)_3$, solvents, and 2,2’-bipyridine were purchased from Acros Organics and used as received. All manipulations required no inert atmosphere. IR spectrum for **1** was recorded on Shimadzu IR Prestige21 FTIR spectrometer in KBr pellets. Set of signals: 1120 cm^{-1} (νPh–Si), 940–1100 cm^{-1} (νasSi–O, νasSi–O–Si), 900 cm^{-1} (νasSi–O in Si–O–M fragment), 720–680 cm^{-1} (σC–H of mono-substituted phenyl group).

$PhSi(OMe)_3$ (1.5 g, 7.56 mmol), NaOH (0.30 g, 7.56 mmol), and 20 mL of an ethanol were placed in a three-neck round-bottom flask (equipped with magnetic stirrer and condenser). The resulting solution was heated under reflux for 1 h and then was cooled to room temperature, and 0.34 g (2.52 mmol) of $CuCl_2$ was added at once. The mixture was stirred for 4 h and filtered from NaCl. The filtrate was mixed with 0.24 g (1.51 mmol) of 2,2′-bipyridine in 60 mL of THF. The resulting solution was intensely stirred for 3 h with a magnetic stirrer and then filtered from the insoluble precipitate. After approximately 7 days the formation of crystalline material was observed; several single crystals were used for X-ray diffraction analysis (for details of the X-ray diffraction study see below). The rest of the crystalline fraction was separated from the solution, washed with *n*-heptane, and dried under vacuum. Dried crystalline material was used for XRF analysis (spectrometer VRA-30). Anal. Calcd for $[(PhSiO_{1.5})_{12}(CuO)_5(NaO_{0.5})(HO_{0.5})(C_{10}H_8N_2)_3]$: Cu, 12.93; Na, 0.94; N, 3.42; Si, 13.72. Found (for vacuum-dried sample): Cu, 12.93; Na, 0.94; N, 3.42; Si, 13.72. Yield: 0.38 g (24%).

Crystal data for 1: crystals are monoclinic (space group $P2_1/c$), chemical composition $C_{124}H_{131.67}Cu_5N_6NaO_{30.83}Si_{12}$, a = 28.8235(9), b = 24.5281(8), c = 20.8021(7) Å, β = 105.820(2)°, V = 14149.7(8) Å ^{3}, Z = 4, d_{calc}= 1.266 g·cm^{-3}, F(000) = 5551, M = 2696.17. Single crystal (blue irregular-shaped, dimensions 0.15 × 0.25 × 0.5 mm) was selected and intensities of 242229 reflections were measured with Bruker APEX-II CCD diffractometer in the centre for molecular composition studies of INEOS RAS at 120K (ϕ and ω scans, microfocus source, λ[CuKα] = 1.54178 Å, μ = 2.377 mm^{-1}, $2\theta_{max}$ = 144.24°). After merging of equivalents and absorption correction 27370 independent reflections (R_{int} = 0.0702) were used for the structure solution and refinement. The structure was solved by direct method and refined by full-matrix technique against F^2 in anisotropic approximation. The positions of hydrogen atoms in methyl and methylene groups were calculated geometrically and refined in rigid body approximation. Final R factors: R_1 = 0.0910, (23778 reflections with I>σ(I)), wR_2 = 0.2395 (all reflections), GOF = 1.012. The structure was solved with the ShelXT[S1] program and refined with the ShelXL[S2] program. Molecular graphics was drawn using OLEX2[S3] program.

CCDC 1852742 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures.

Catalytic oxidation of alkanes. Experimental.

CAUTION. The combination of air or molecular oxygen and H_2O_2 with organic compounds at elevated temperatures may be explosive! The reactions (an example is demonstrated by Figure 2) after addition of nitromethane as a standard compound were analyzed by GC. The samples obtained in the alkane oxidation were typically analyzed twice (before and after their treatment with PPh_3) by GC (the chromatograph-3700; fused silica capillary column FFAP/OV-101 20/80 w/w, 30 m × 0.2 μm × 0.3 μm; argon as a carrier gas). This method (the comparison of chromatograms of the same sample obtained before and after addition of PPh_3) which was proposed by one of us earlier [13] allows us to estimate real concentration of alkyl hydroperoxide, ketone (aldehyde) and alcohol present in the reaction solution. Attribution of peaks was made by comparison with chromatograms of authentic samples and by GC–MS.

Structure discussion

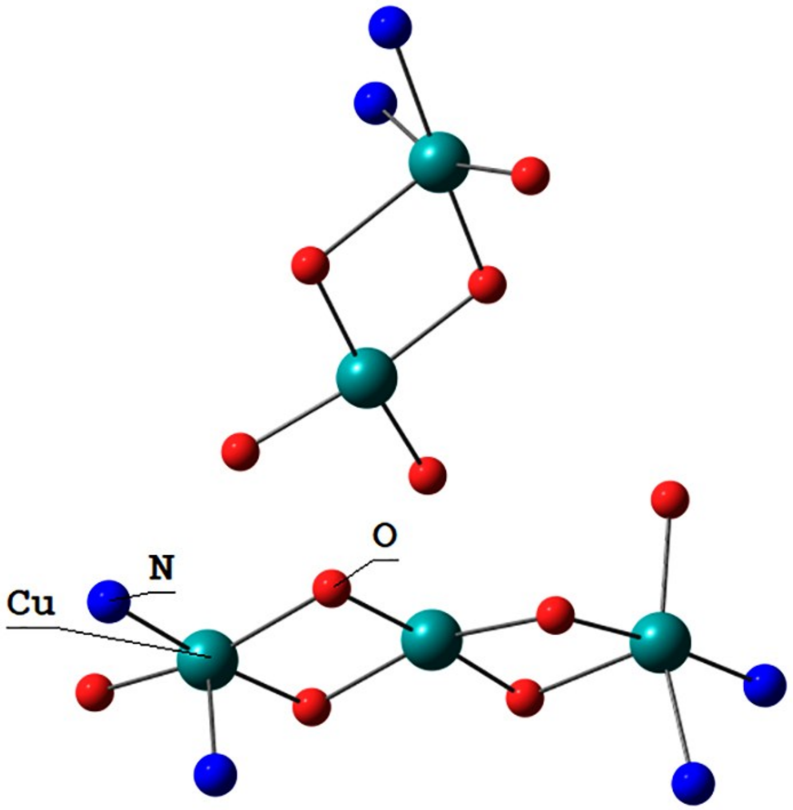


Figure S1. Location of copper(II) centers in the structure of **1**

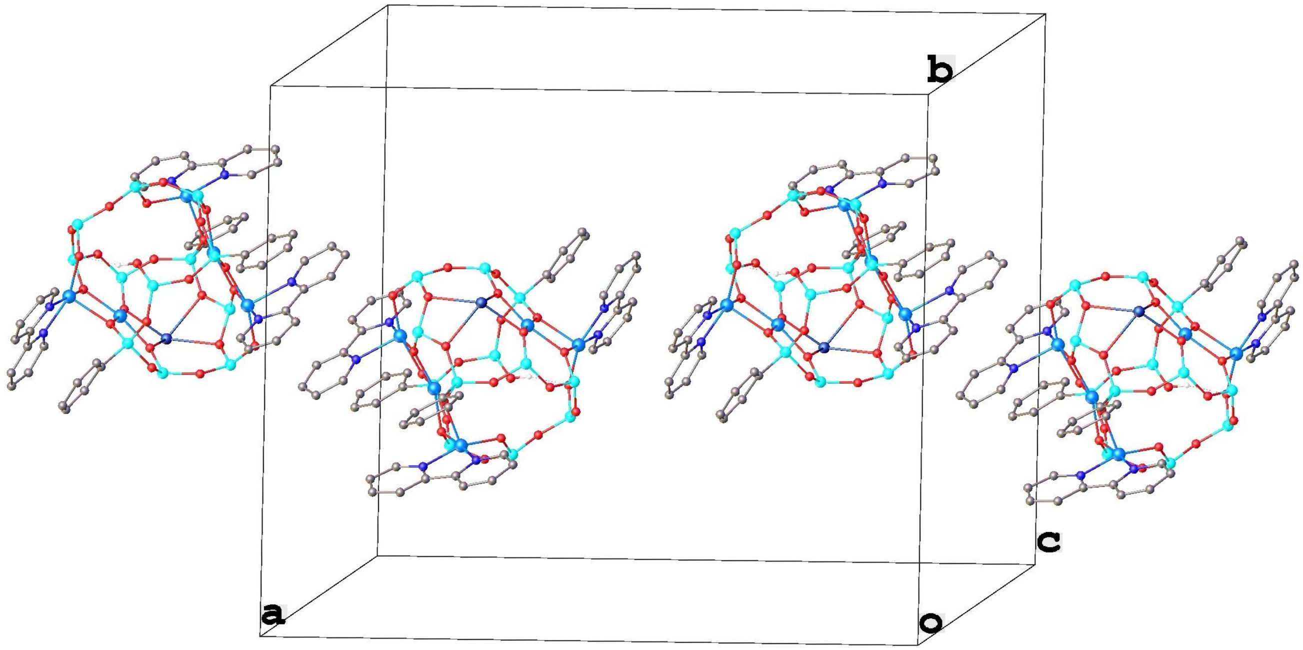


Figure S2. “Bipy-Bipy-phenyl” stacking fashion of **1** in crystal

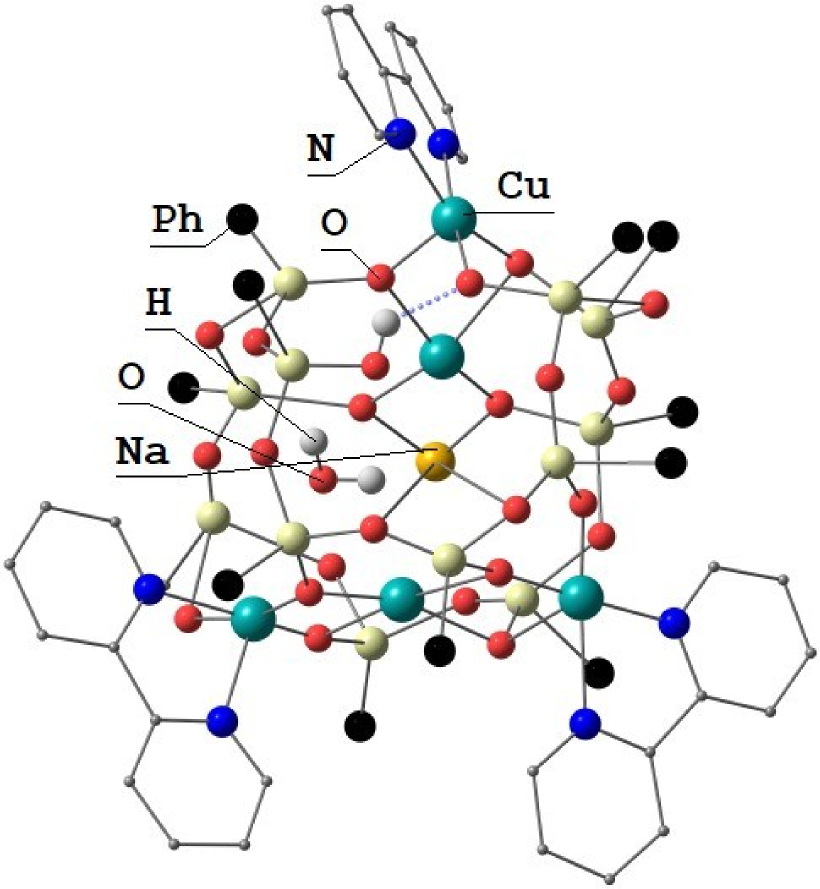


Figure S3. Molecular structure of **1**, showing encapsulation of water molecule

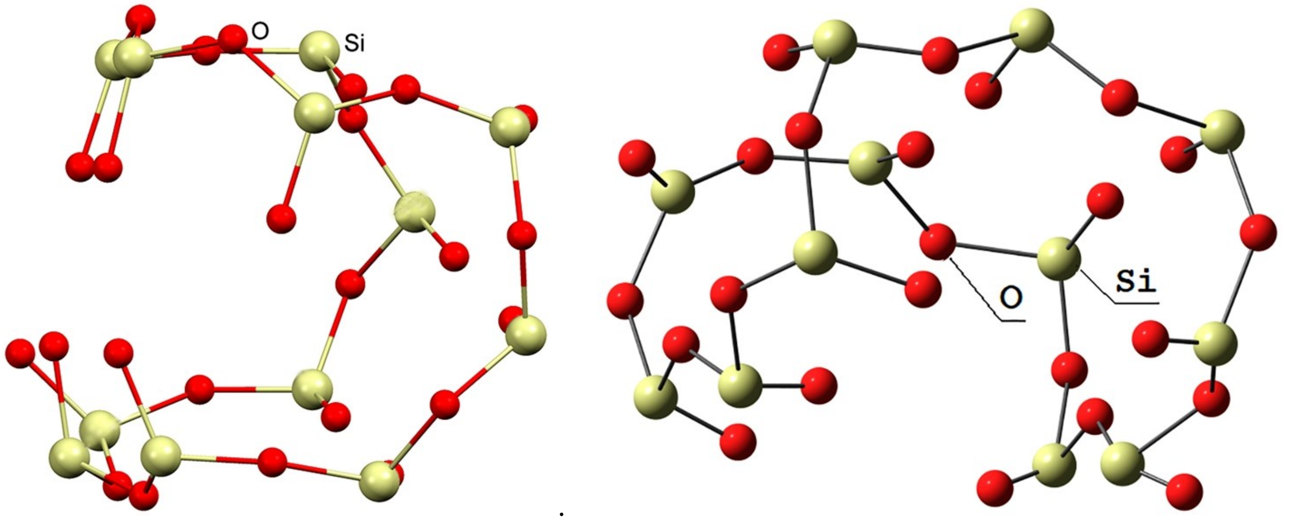


Figure S4. Comparison of silsesquioxane ligands in **1** (left) and in globular Cu-silsesquioxane cage (right, Ref. 10)

Table 1. Selected bond lengths(Å) and angles (deg) in **1** and in globular Cu-silsesquioxane cage (Ref. 10)

	1	Ref. 10b
Si-O in cyclic fragments Si-O-Si	1.614(4) – 1.658(4)	1.62- 1.66
Si-O in fragment Si-O-M	1.591(4) – 1.619(4)	1.58 – 1.60
∠ SiOSi	104.7(2) – 113.5(2)	127.2 – 136.2
The longest Si-Si distance in cyclic fragments Si-O-Si	8.253(2)	7.50, 7.50

Table 2. Hydrogen bonds for **1**

D	**H**	**A**	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**
O36	H36	O26	0.84	1.89	2.647(6)	149.3
O24	H24C	O23	0.85	2.08	2.861(6)	151.5
O24	H24D	O36	0.85	2.01	2.855(7)	176.6

Analysis of short interatomic contacts allowed us to reveal three intermolecular hydrogen bonds. The strongest one is O36-H36…O26 bond between hydroxyl group at silicon atom Si7 that is characterized by O…O distance equal to 2.647(6) Å. The water molecule in central cavity of **1** is held by two hydrogen bonds (Table 2) which are weaker (mean O…O distance is equal to 2.858(7) Å)

General procedure for the formation of amides

General considerations

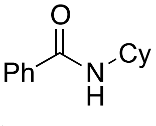
All reagents were purchased from Aldrich Chemical Co., Fluka and Alfa Aesar and used without further purification. Analyses were performed at the 'Plateforme Technologique Laboratoire de Mesures Physiques' (IBMM, Université de Montpellier). ^1H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Chemical shifts are reported in ppm and referenced to the solvent peak ($CDCl_3$ at 7.26 ppm). Data are reported as s = singlet, d = doublet, t = triplet, q = quadruplet, qt = quintuplet, sept = septuplet, m = multiplet; coupling constant in Hz; integration. ^{13}C NMR spectra were recorded on Bruker Avance III HD 100 MHz spectrometer. Chemical shifts are reported in ppm and referenced to the solvent peak ($CDCl_3$ at 77.16 ppm).

General procedure

In a sealed tube were added successively amine hydrochloride (0.5 mmol), $CaCO_3$ (25.0 mg, 0.25 mmol), CH_3CN (1mL), **1** (1.0 mg, 0.0004 mmol), benzylic alcohol (105 µL, 1.0 mmol) and TBHP (5.5M in nonane, 225 µL, 1.25mmol). The mixture was stirred at 80°C for 2h and TBHP (5.5M in nonane, 225 µL, 1.25mmol) were again added to the mixture. After 24h at 80°C, the mixture was cooled to room temperature and 1N HCl and EtOAc were added. The mixture was extracted twice with EtOAc, and the combined organic phases were washed with a saturated solution of $NaHCO_3$ and brine, and concentrated under reduced pressure. To remove the excess of benzylic alcohol, 80 mL of H_2O were added and evaporated under reduced pressure. Crude product was then purified using silica gel chromatography using gradients of cyclohexane/EtOAc to yield the pure compounds.

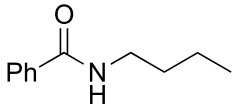
Description of amides

N-Cyclohexylbenzamide [S4]



^1H NMR (300 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 2H, $H_{Ar\text{-}ortho}$), 7.48 – 7.42 (m, 1H, $H_{Ar\text{-}para}$), 7.41 – 7.34 (m, 2H, $H_{Ar\text{-}meta}$), 6.19 (d, *J* = 7.2 Hz, 1H, N*H*), 4.00 – 3.89 (m, 1H, NHC*H*), 2.03 – 1.95 (m, 2H, $CH_{2\text{-}Cy}$), 1.77 – 1.60 (m, 3H, $CH_{2\text{-}Cy}$), 1.44 – 1.13 (m, 5H, $CH_{2\text{-}Cy}$).
^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8 (*C*(O)NH), 135.1 (C_{Ar}), 131.3 ($CH_{Ar\text{-}para}$), 128.5 (CH_{Ar}), 127.0 (CH_{Ar}), 48.8 (CH_{Cy}), 33.2 ($CH_{2\text{-}Cy}$), 25.6 ($CH_{2\text{-}Cy}$), 25.0 ($CH_{2\text{-}Cy}$).

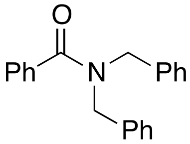
N-n-butylbenzamide [S4]



^{1}H NMR (300 MHz, CDCl$_3$) δ 7.78 – 7.73 (m, 2H, $H_{\text{Ar-ortho}}$), 7.50 – 7.32 (m, 3H, $H_{\text{Ar-meta/para}}$), 6.60 (s, 1H, NH), 3.49 – 3.35 (m, 2H, NHCH_2), 1.65 – 1.48 (m, 2H, NHCH$_2$CH_2), 1.47 – 1.29 (m, 2H, NHCH$_2$CH$_2$CH_2), 0.99 – 0.85 (m, 3H, NHCH$_2$CH$_2$CH$_2$CH_3).

^{13}C NMR (75 MHz, CDCl$_3$) δ 167.8 (C(O)NH), 134.9 (C_{Ar}), 131.4 (CH$_{\text{Ar-para}}$), 128.6 (CH$_{\text{Ar}}$), 127.0 (CH$_{\text{Ar}}$), 40.0 (NHCH$_2$CH$_2$CH$_2$CH$_3$), 31.8 (NHCH$_2$$CH_2CH_2CH_3$), 20.1 (NHCH$_2CH_2$$CH_2CH_3$), 13.9 (NHCH$_2CH_2CH_2$$CH_3$).

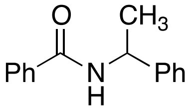
N,*N*-Dibenzylbenzamide [S4]



^{1}H NMR (300 MHz, CDCl$_3$) δ 7.55 – 7.50 (m, 2H, H_{Ar}), 7.42 – 7.29 (m, 11H, H_{Ar}), 7.20 – 7.11 (m, 2H, H_{Ar}), 4.73 (s, 2H, CH_2Ph), 4.43 (s, 2H, CH_2Ph).

^{13}C NMR (75 MHz, CDCl$_3$) δ 172.3 (C(O)N), 137.0 (C_{Ar}), 136.5 (C_{Ar}), 136.2 (C_{Ar}), 129.7 (CH$_{\text{Ar}}$), 128.9 (CH$_{\text{Ar}}$), 128.8 (CH$_{\text{Ar}}$), 128.6 (CH$_{\text{Ar}}$), 128.5 (CH$_{\text{Ar}}$), 127.7 (CH$_{\text{Ar}}$), 127.1 (CH$_{\text{Ar}}$), 126.8 (CH$_{\text{Ar}}$), 51.6 (CH$_2$Ph), 46.9 (CH$_2$Ph).

N-[(±)-1-phenylethyl]benzamide[S4]



^{1}H NMR (300 MHz, CDCl$_3$) δ 7.67 (d, J = 7.7 Hz, 2H, $H_{\text{Ar-ortho}}$), 7.39 – 7.33 (m, 1H, $H_{\text{Ar-para}}$), 7.32 – 7.20 (m, 6H, H_{Ar}), 7.19 – 7.13 (m, 1H, $H_{\text{Ar-para}}$), 6.54 (d, J = 6.7 Hz, 1H, NH), 5.22 (sept, J = 6.7 Hz, 1H, NHCHCH$_3$Ph), 1.48 (d, J = 6.7 Hz, 3H, NHCHCH_3Ph).

^{13}C NMR (126 MHz, CDCl$_3$) δ 166.7 (C(O)NH), 143.3 (C_{Ar}), 134.6 (C_{Ar}), 131.5 (CH$_{\text{Ar}}$), 128.8 (CH$_{\text{Ar}}$), 128.6 (CH$_{\text{Ar}}$), 127.4 (CH$_{\text{Ar}}$), 127.0 (CH$_{\text{Ar}}$), 126.3 (CH$_{\text{Ar}}$), 49.3 (CHCH$_3$), 21.8 (CHCH$_3$).

Calculation of TON and TOF

TON (Turnover Number) is defined, for the copper-catalyzed oxidative amidation, as follow:

$$\text{TON} = \frac{mmol\ of\ product}{mmol\ of\ copper}$$

<u>Example:</u>

With a 88% yield on a reaction started using 0.5 mmol of amine,

mmol of product = 0.88 x 0.5 = 0.44 mmol

Using 0.4 mol% of Cu compared to the amine,

mmol of copper = 0.5 x 0.004 = 0.002 mmol.

$$\text{So TON} = \frac{0.44}{0.002} = 220$$

TOF (Turnover Frequency) is defined in the IUPAC Gold Book "as molecules reacting per active site in unit time". This definition is quite simple and more detailed description of the TOF can be found in literature.[S5] In this publication, and for comparison purpose with our previous publications on cage-like compounds-catalyzed oxidative amidation, TOF values were calculated at full conversion of the substrate, using the following equation:

$$\text{TOF} = \frac{mmol\ of\ product}{mmol\ of\ copper\ .\ reaction\ time}\ (\text{h}^{-1})$$

Reaction time was set to 24h to obtain full conversion of the substrates.

<u>Example:</u>

With a 88% yield on a reaction started using 0.5 mmol of amine,

mmol of product = 0.88 x 0.5 = 0.44 mmol

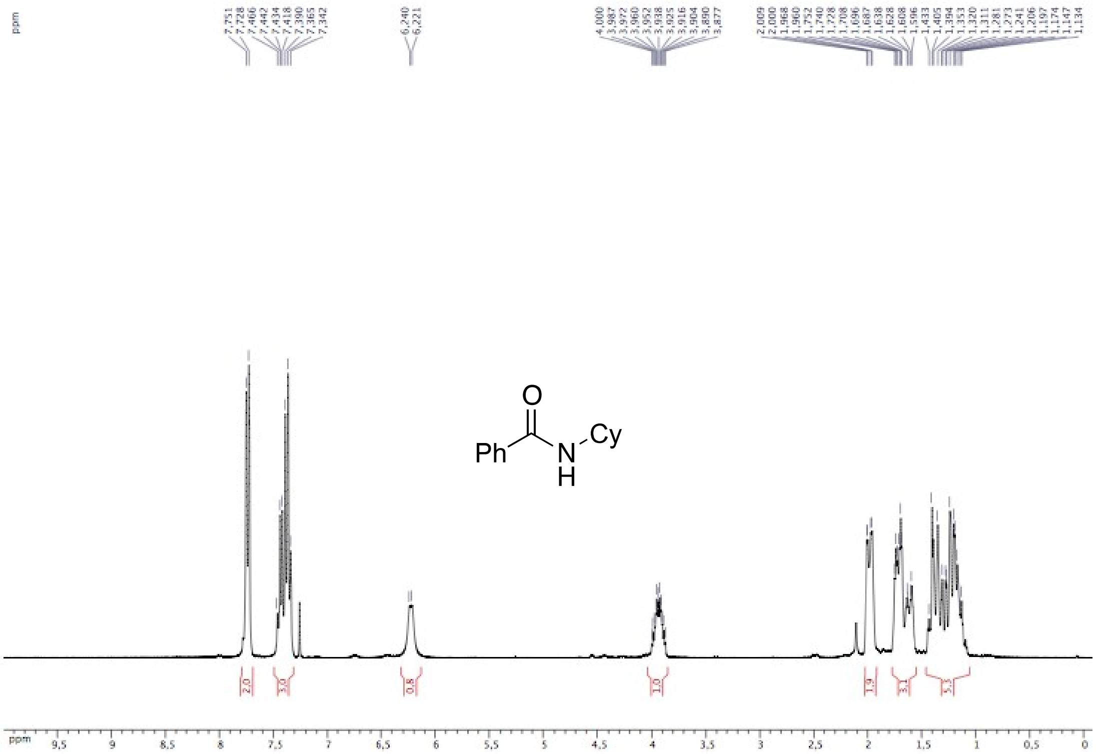
Using 0.4 mol% of Cu compared to the amine,

mmol of copper = 0.5 x 0.004 = 0.002 mmol.

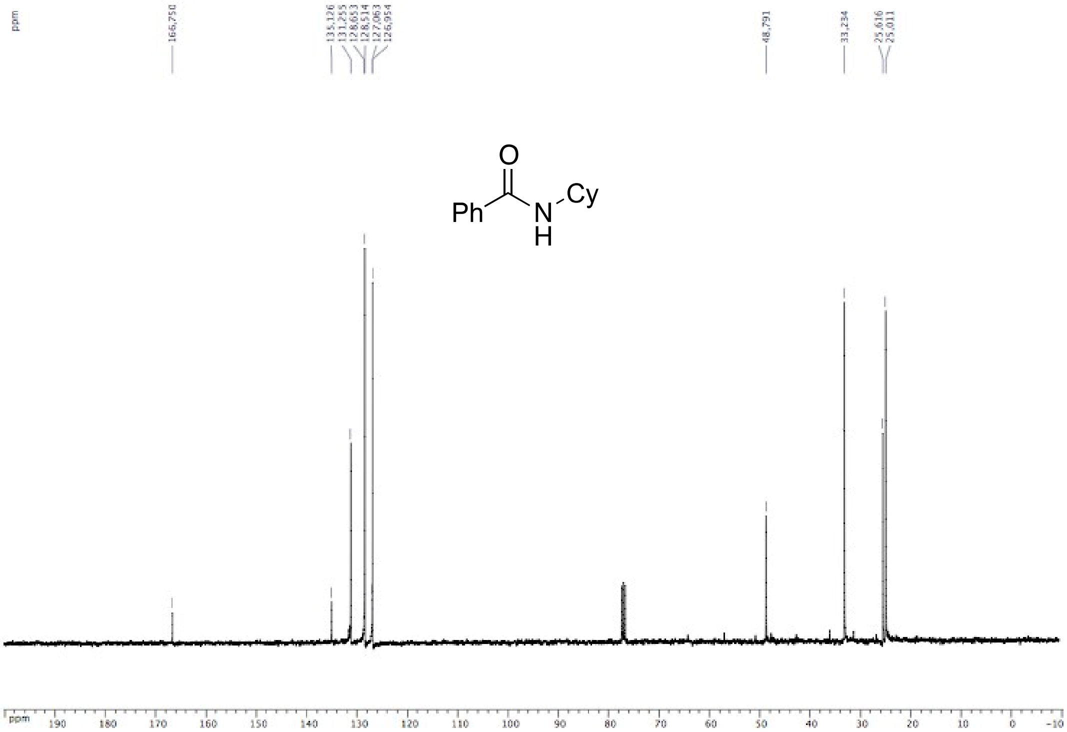
$$\text{So TOF} = \frac{0.44}{0.002\ .\ 24} = 9.2\ \text{h}^{-1}$$

NMR of amides

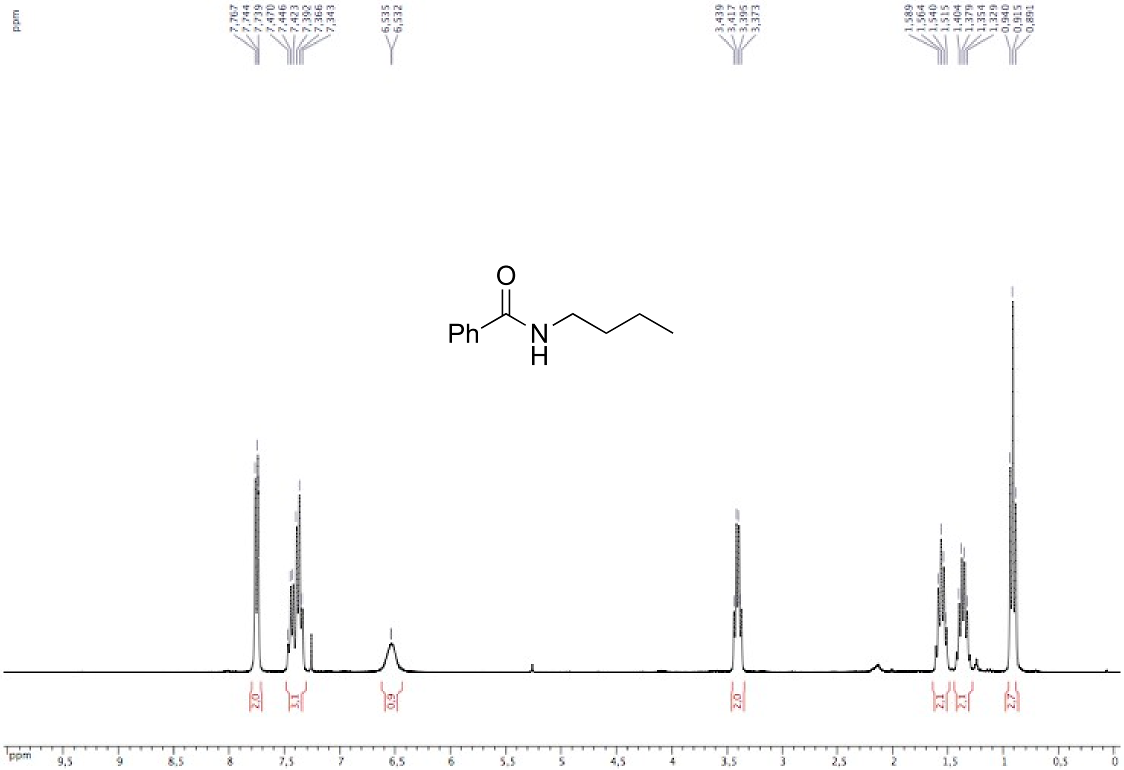
^{1}H NMR (300 MHz, $CDCl_3$) of ***N*-Cyclohexylbenzamide**



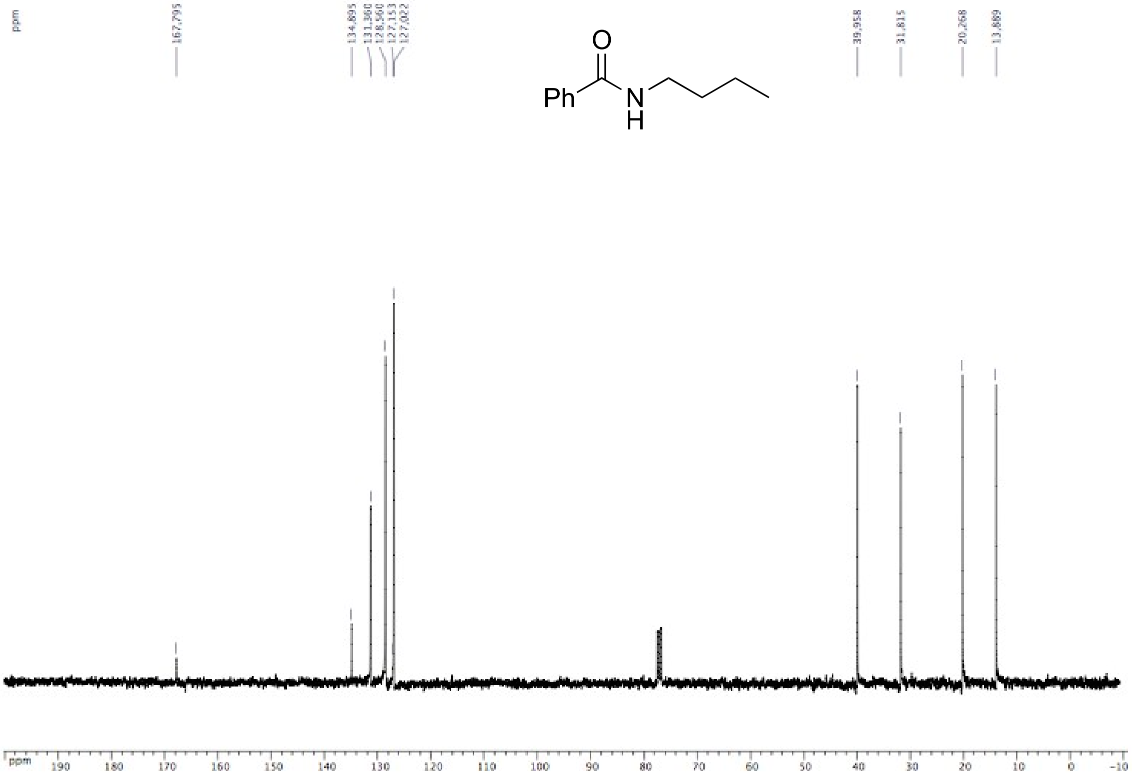
^{13}C NMR (100 MHz, $CDCl_3$) of ***N*-Cyclohexylbenzamide**



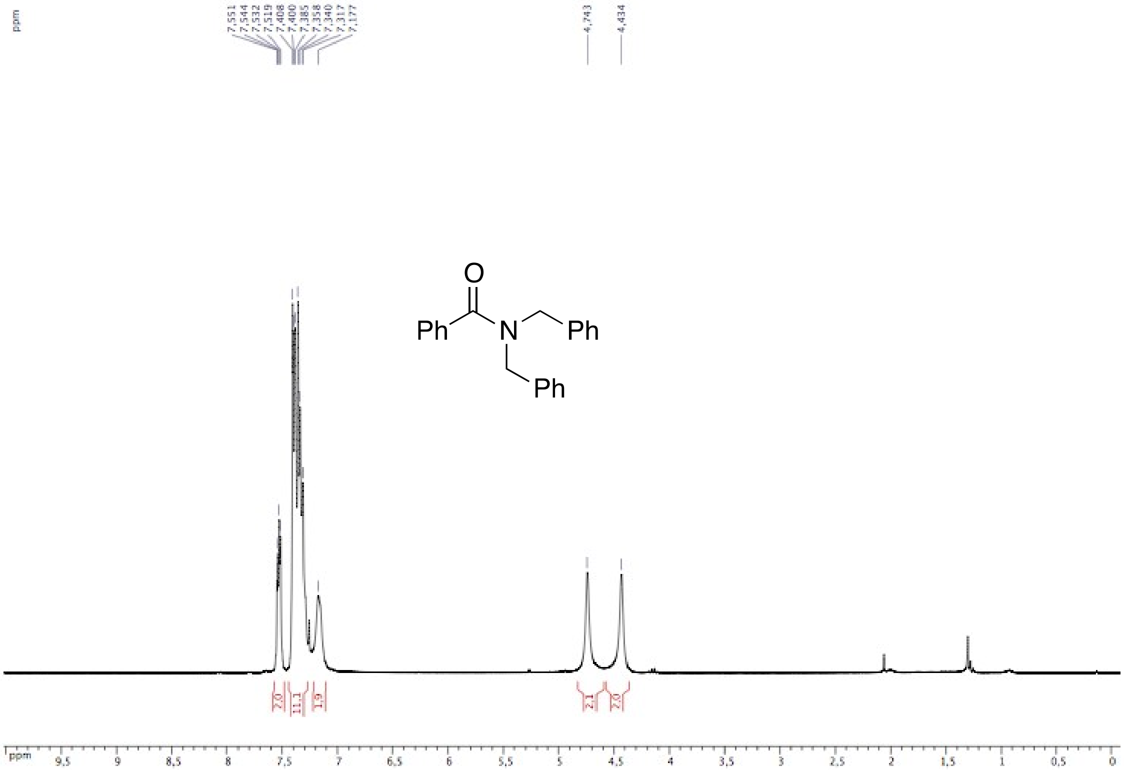
^{1}H NMR (300 MHz, CDCl$_3$) of ***N*-n-butylbenzamide**



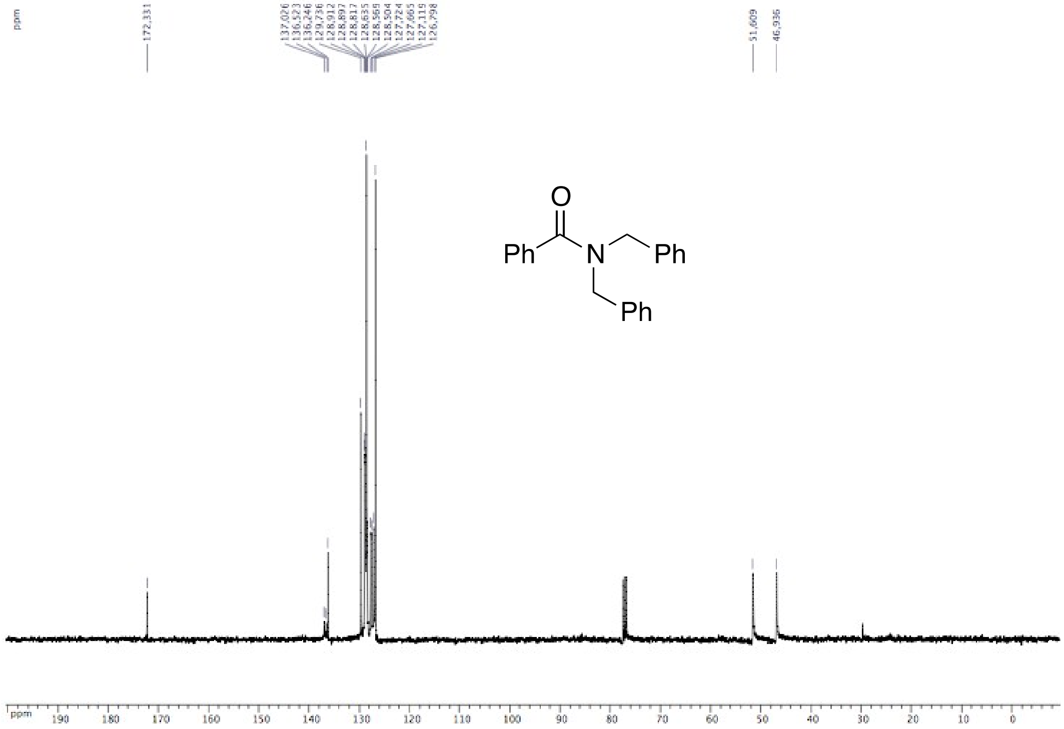
^{13}C NMR (126 MHz, CDCl$_3$) of ***N*-n-butylbenzamide**



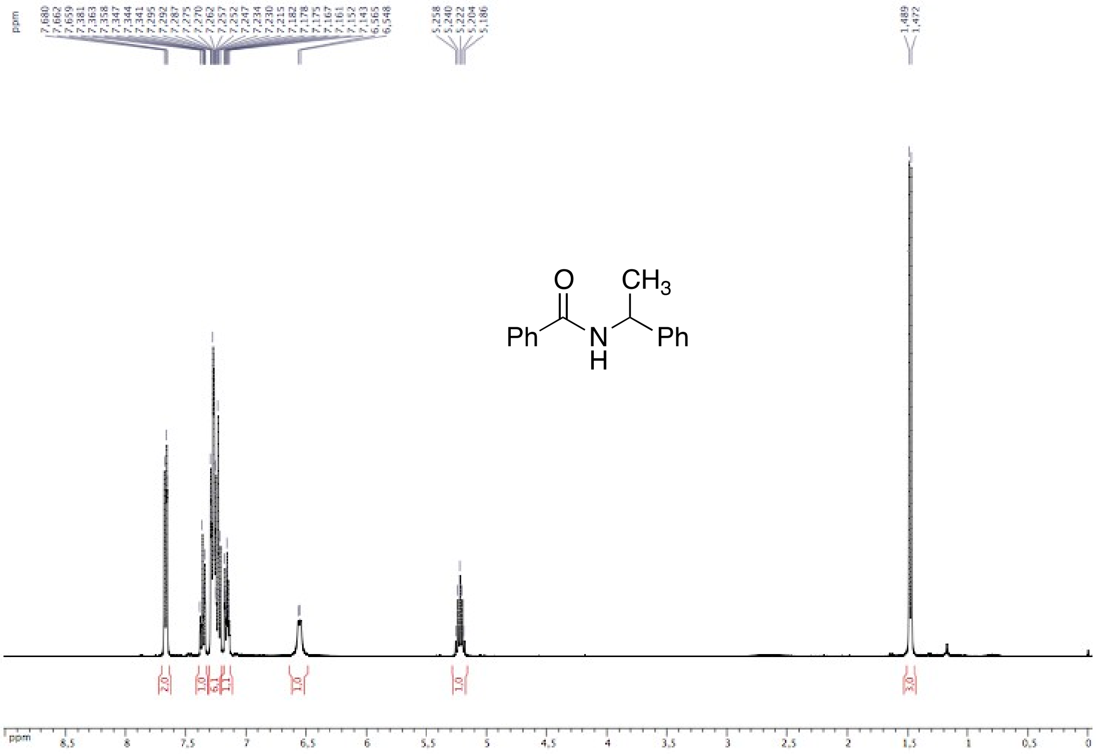
^{1}H NMR (300 MHz, $CDCl_3$) of ***N*,*N*-Dibenzylbenzamide**



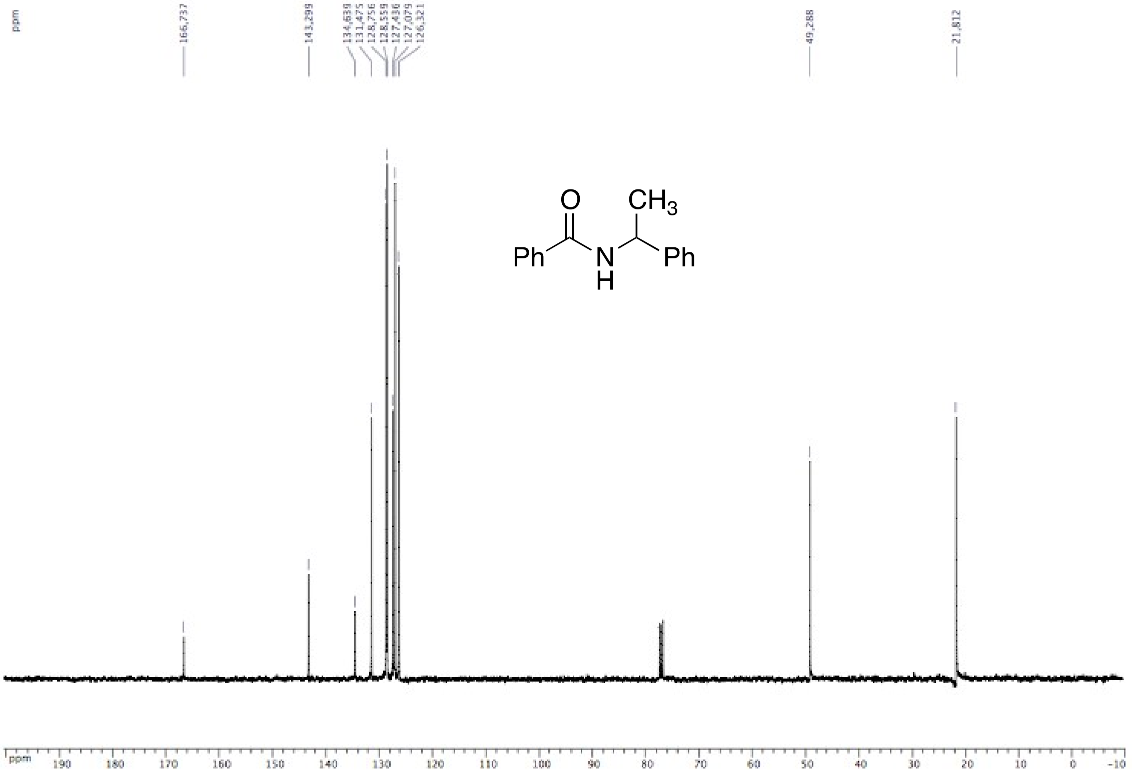
^{13}C NMR (75 MHz, $CDCl_3$) of ***N*,*N*-Dibenzylbenzamide**



^{1}H NMR (400 MHz, CDCl$_3$) of ***N*-[(±)-1-phenylethyl]benzamide**



^{13}C NMR (75 MHz, CDCl$_3$) of ***N*-[(±)-1-phenylethyl]benzamide**



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