[(NHC)CuX] Complexes: Synthesis, Structural Studies and Catalytic Activities in Hydrosilylation and Click Chemistry. On the Advantage of Using Well-Defined Catalytic Systems

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Supporting Information

GENERAL CONSIDERATIONS

All reagents were used as received. Solid reagents for the preparation of [(NHC)CuX] complexes were stored under argon in a glovebox containing less than 1 ppm oxygen. Imidazolium and imidazolinium salts and free carbenes were synthesized according to literature procedures.[1] [(NHC)AgCl] complexes were prepared following the reported conditions.[2] ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer at room temperature. Chemical shifts (δ) are reported with respect to tetramethylsilane as internal standard in ppm. Elemental analyses were performed by Robertson Microlit Laboratories, Inc., Madison, NJ (USA) and at the Centro de Microanálisis Elemental of the Universidad Complutense de Madrid (Spain). All reported yields are isolated yields and in the catalytic studies are the average of at least two runs.

Table 1. SYNTHESIS OF [(NHC)CuX] COMPLEXES

[(NHC)CuX]		NHC source	Cu source [equiv]	Base [equiv]	Solvent [T]	Yield (%)
[(IPr)CuCl]	**1a**	IPr·HCl	CuCl [1 equiv]	NaO*t*-Bu [1 equiv]	THF [RT]	94
[(IPr)CuBr]	**1b**	IPr·HCl	CuBr [1 equiv]	NaO*t*-Bu [1 equiv]	THF [RT]	80
[(IPr)CuI]	**1c**	IPr·HCl	CuI [1.1 equiv]	KOMe [1.2 equiv]	Toluene [RT]	81
[(SIPr)CuCl]	**2a**	SIPr·HCl	CuCl [1.1 equiv]	KOMe [1.4 equiv]	Toluene [RT]	80
		[(SIPr)AgCl]	CuCl [5 equiv]	--	MeCN [RT]	83
[(SIPr)CuBr]	**2b**	SIPr·HCl	$CuBr\cdot SMe_2$ [1.1 equiv]	KOMe [1.25 equiv]	Toluene [115ºC]	84
		[(SIPr)AgCl]	CuBr [5 equiv]	--	MeCN [RT]	84
[(SIPr)CuI]	**2c**	SIPr·HCl	CuI [1.1 equiv]	KOMe [1.2 equiv]	Toluene [RT]	77
		[(SIPr)AgCl]	CuI [5 equiv]	--	MeCN [RT]	90
[(IAd)CuCl]	**3a**	$IAd\cdot HBF_4$	CuCl [1.2 equiv]	KOMe [1.5 equiv]	Toluene [RT]	81
[(IAd)CuBr]	**3b**	$IAd\cdot HBF_4$	$CuBr\cdot SMe_2$ [1.2 equiv]	KOMe [1.4 equiv]	Toluene [115ºC]	81
[(IAd)CuI]	**3c**	$IAd\cdot HBF_4$	CuI [1.5 equiv]	KOMe [1.5 equiv]	Toluene [RT]	75
[(IMes)CuCl]	**4a**	IMes·HCl	CuCl [1.1 equiv]	NaO*t*-Bu [1 equiv]	THF [RT]	64
[(IMes)CuBr]	**4b**	IMes·HCl	CuBr [1.4 equiv]	NaO*t*-Bu [1 equiv]	THF [RT]	62

Table 1. (cont.)

[(NHC)CuX]		NHC source	Cu source [equiv]	Base [equiv]	Solvent [T]	Yield (%)
[(SIMes)CuCl]	**5a**	SIMes·HCl	CuCl [1 equiv]	NaO*t*-Bu [1 equiv]	THF [RT]	70
[(SIMes)CuBr]	**5b**	SIMes·HCl	CuBr [1.4 equiv]	NaO*t*-Bu [1 equiv]	THF [RT]	71
[(ICy)CuCl]	**6a**	ICy·HBF_4	CuCl [1 equiv]	NaO*t*-Bu [1 equiv]	THF [RT]	76
		ICy	CuCl [1 equi]	--	THF [RT]	71
[(ICy)CuBr]	**6b**	ICy	CuBr [1 equi]	--	THF [RT]	82
[(ICy)CuI]	**6c**	ICy	CuI [1 equi]	--	THF [RT]	82
[(ItBu)CuCl]	**7a**	ItBu	CuCl [1 equi]	--	THF [RT]	73
[(ItBu)CuBr]	**7b**	ItBu	CuBr [1 equi]	--	THF [RT]	85
[(ItBu)CuI]	**7c**	ItBu	CuI [1 equi]	--	THF [RT]	80

CRYSTALLOGRAPHIC TABLES

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes **1a-c**, **2a**,**c**, **3a-b**, **4a-b**, **5a-b** and **6a**.

	[(IPr)CuCl] 1a[a]	**[(IPr)CuBr] 1b**	**[(IPr)CuI] 1c**	**[(SIPr)CuCl] 2a**[b]	**[(SIPr)CuI] 2c**	**[(IAd)CuCl] 3a**
Cu(1)–C(1)	1.953(8)	1.884(2)	1.869(8)	1.896(7)	1.8874(17)	1.894(2)
N(1)–C(1)	1.320(7)	1.352(2)	1.364(7)	1.337(6)	1.3322(14)	1.361(3)
N(2)–C(1)	1.320(7)	1.352(2)	1.364(7)	1.337(6)	1.3322(14)	1.365(2)
C(2)–C(3)	1.368(15)	1.352(2)	1.368(11)	1.511(12)	1.533(3)	1.355(3)
Cu(1)–X	2.089(4)	2.2090(4)	2.3803(10)	2.114(2)	2.3804(2)	2.1114(6)
N(1)–C(1)–N(2)	108.9(8)	104.5(2)	103.6(6)	108.0(6)	108.58(14)	104.56(17)
C(1)–Cu(1)–X	180.0	180.0	180.0	174.4(2)	180.0	177.39(6)

	[(IAd)CuBr] 3b	**[(IMes)CuCl] 4a**	**[(IMes)CuBr] 4b**[c]	**[(SIMes)CuCl] 5a**[d]	**[(SIMes)CuBr] 5b**	**[(ICy)CuCl] 6a**[d]
Cu(1)–C(1)	1.912(6)	1.956(10)	1.897(6)	1.882(4)	1.884(7)	2.114(11)
N(1)–C(1)	1.350(8)	1.310(8)	1.343(5)	1.332(5)	1.323(10)	1.284(11)
N(2)–C(1)	1.365(8)	1.310(8)	1.343(5)	1.341(5)	1.345(9)	1.280(11)
C(2)–C(3)	1.367(9)	1.399(12)	1.372(9)	1.519(7)	1.510(11)	1.260(19)
Cu(1)–X	2.2386(12)	2.091(2)	2.2101(7)	2.0990(11)	2.1903(14)	2.136(6)
N(1)–C(1)–N(2)	105.0(5)	109.3(8)	105.1(5)	108.2(3)	108.7(6)	111.4(14)
C(1)–Cu(1)–X	177.02(17)	180.000(1)	180.0	178.48(13)	177.7(2)	170.6(3)

[a] Data from ref. [3]; [b] Data from ref. [4]. [c] Data from ref. [5]. [d] Data from ref. [6].

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complexes **3c**, and **6c**.

	[(IAd)CuI] **3c**	[(ICy)CuBr] **6b**	[(ICy)CuI] **6c**
Cu(1)–C(1)	1.9463(12)	2.022(16)	1.927(8)
N(1)–C(1)	1.3653(14)	1.37(3)	1.349(10)
N(2)–C(1)	1.3625(15)	1.38(2)	1.359(10)
Cu(1)–X(1)	2.62654(19)	2.471(3)	2.5487(11)
Cu(2)–C(2)		1.86(2)	1.973(8)
Cu(1)–C(2)			2.165(8)
N(3)–C(2)		1.37(3)	1.373(10)
N(4)–C(2)		1.39(3)	1.369(10)
Cu(2)–X(2)		2.199(5)	2.6206(12)
Cu(3)–C(1)		2.08(2)	1.928(8)
N(5)–C(3)			1.355(10)
N(6)–C(3)			1.355(10)
Cu(3)–X(3)		2.503(3)	2.8509(13)
Cu(1)–Cu(2)	2.9510(3)		2.4528(15)
Cu(1)–Cu(3)		2.503(3)	
Cu(2)–Cu(3)		2.767(5)	2.5332(14)
N(1)–C(1)–N(2)	104.60(10)	104.8(14)	104.2(7)
N(3)–C(2)–N(4)		109(2)	103.6(6)
N(5)–C(3)–N(6)			107.1(7)
Cu(1)–C(1)–Cu(3)		75.3(6)	
Cu(1)–C(2)–Cu(2)			72.5(3)
C(1)–Cu(1)–X(1)	131.91(3)	124.6(6)	128.2(2)
C(2)–Cu(2)–X(2)		140.7(7)	128.9(2)
C(3)–Cu(3)–X(3)			110.5(3)

Table 4. Crystallographic Data for **1b-c**, **2c**, **3a-c**, **4a**, **5b**, and **6b-c**.

	[(IPr)CuBr] 1b	**[(IPr)CuI] 1c**	**[(SIPr)CuI] 2c**	**[(IAd)CuCl] 3a**	**[(IAd)CuBr] 3b**
chemical formula	$C_{27}H_{36}BrCuN_2$	$C_{27}H_{36}CuIN_2$	$C_{27}H_{38}CuIN_2$	$C_{23}H_{32}ClCuN_2$	$C_{23}H_{32}BrCuN_2$
M (g/mol)	532.03	579.02	581.03	435.50	479.96
T (K)	150(2)	150(2)	100(2)	100(2)	100(2)
crystalline system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	*Pccn*	*Pccn*	*Pccn*	*Pca2(1)*	*Pna2(1)*
a (Å)	10.7030(4)	10.9153(7)	10.9969(3)	14.7293(6)	11.5621(5)
b (Å)	12.7140(5)	12.6813(8)	12.5666(3)	21.9562(8)	26.7715(12)
c (Å)	19.4880(7)	20.1285(12)	19.9092(5)	12.4897(6)	6.4838(3)
α (deg)	90.00	90.00	90.00	90.00	90.00
β (deg)	90.00	90.00	90.00	90.00	90.00
γ (deg)	90.00	90.00	90.00	90.00	90.00
V (Å^3)	2651.89(17)	2786.2(3)	2751.32(12)	4039.2(3)	2006(16)
Z	4	4	4	8	4
density(calcd) (g.cm^{-3})	1.333	1.380	1.403	1.432	1.588
absorp coeff (mm^{-1})	2.346	1.907	1.931	1.224	3.090
F(000)	1104	1176	1184	1840	992
crystal size (mm)	0.65×0.45×0.20	0.40×0.35×0.35	0.40×0.40×0.20	0.40×0.40×0.10	0.30×0.20×0.02
θ (deg)	2.49 – 30.50	2.02 – 22.49	3.87 – 39.79	2.83 – 37.07	2.88 – 36.37
index range *hkl*	±15	±11	-18 to 19	±24	-15 to 19
	±18	±13	-19 to 20	-30 to 36	-42 to 44
	±27	±21	-12 to 35	-6 to 21	-5 to 10
data/restraints/params	4052/130/214	1821/130/181	7571/0/142	13057/1/487	6889/1/245
goodness-of-fit on F^2	1.092	1.098	1.069	0.987	1.185
Final R values	$R_1 = 0.0352$	$R_1 = 0.0416$	$R_1 = 0.0321$	$R_1 = 0.0369$	$R_1 = 0.0423$
[I>2sigma(I)]	$wR_2 = 0.0931$	$wR_2 = 0.1013$	$wR_2 = 0.0818$	$wR_2 = 0.0811$	$wR_2 = 0.0761$
R values (all data)	$R_1 = 0.0486$	$R_1 = 0.0492$	$R_1 = 0.0481$	$R_1 = 0.0562$	$R_1 = 0.0946$
	$wR_2 = 0.1056$	$wR_2 = 0.1013$	$wR_2 = 0.0890$	$wR_2 = 0.0893$	$wR_2 = 0.2223$

Table 4. (cont.)

	[(IAd)CuI] 3c	**[(IMes)CuCl] 4a**	**[(SIMes)CuBr] 5b**	**[(ICy)CuBr] 6b**	**[(ICy)CuI] 6c**
chemical formula	$C_{46}H_{64}Cu_2I_2N_4$	$C_{21}H_{24}ClCuN_2$	$C_{21}H_{26}BrCuN_2$	$C_{30}H_{48}Br_3Cu_3N_4$	$C_{48.5}H_{78.5}Cu_3I_3N_7$
M (g/mol)	1053.89	403.41	449.89	895.07	1331.00
T (K)	100(2)	150(2)	93(2)	93(2)	93(2)
crystalline system	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	*P1*	*Fdd2*	*P2(1)/n*	*P2(1)/c*	*P2(1)/c*
a (Å)	9.6305(2)	14.694(3)	8.348(2)	12.051(5)	12.542(2)
b (Å)	9.9465(2)	28.998(5)	21.934(6)	23.197(10)	17.245(3)
c (Å)	11.4681(3)	9.4788(17)	11.275(3)	12.516(5)	26.111(5)
α (deg)	73.5890(10)	90.00	90.00	90.00	90.00
β (deg)	81.0420(10)	90.00	90.127(9)	92.761(12)	100.885(8)
γ (deg)	88.3730(10)	90.00	90.00	90.00	90.00
V (Å^3)	1040.78(4)	4038.8(13)	2064.5(9)	3495(3)	5546.0(17)
Z	1	8	4	4	4
density(calcd) (g.cm^{-3})	1.681	1.327	1.447	1.319	1.594
absorp coeff (mm^{-1})	2.543	1.219	2.999	5.264	2.847
F(000)	532	1680	920	1792	2658
crystal size (mm)	0.50×0.40×0.40	0.30×0.20×0.15	0.06×0.06×0.03	0.15×0.15×0.02	0.03×0.03×0.03
θ (deg)	3.00 – 39.91	2.65 – 25.00	2.59 – 25.35	1.91 – 25.32	2.29 – 25.35
index range *hkl*	±16	±17	±10	-14 to 12	-13 to 14
	-17 to 15	±34	-26 to 19	-27 to 24	-20 to 16
	±20	±11	-13 to 11	±15	-24 to 31
data/restraints/params	10904 / 0 / 244	1784/34/130	3739/0/233	6339/0/363	9944/0/544
goodness-of-fit on F^2	1.032	1.057	1.067	1.381	1.032
Final R values	$R_1 = 0.0273$	$R_1 = 0.0321$	$R_1 = 0.0755$	$R_1 = 0.1628$	$R_1 = 0.0609$
[I>2sigma(I)]	$wR_2 = 0.0742$	$wR_2 = 0.0927$	$wR_2 = 0.1771$	$wR_2 = 0.4124$	$wR_2 = 0.1178$
R values (all data)	$R_1 = 0.0296$	$R_1 = 0.0404$	$R_1 = 0.1162$	$R_1 = 0.2312$	$R_1 = 0.1032$
	$wR_2 = 0.0760$	$wR_2 = 0.0987$	$wR_2 = 0.1966$	$wR_2 = 0.4486$	$wR_2 = 0.1331$

CATALYTIC ACTIVITY: HYDROSILYLATION OF KETONES

General Procedure for the [(SIMes)CuCl]-Catalyzed Hydrosilylation of Ketones

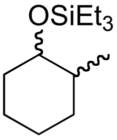
In a vial fitted with a septum screw cap, [(SIMes)CuCl] **5a** (8 mg, 0.02 mmol, 2 mol %) and sodium *tert*-butoxide (2.5 mg, 2 mol %) were charged inside a glove box and stirred in dry THF (1 mL) at the reaction outside of the glove box for 5 minutes before adding triethylsilane (0.2 mL, 1.2 mmol, 1.2 equiv) through the septum using a syringe. After 5 more minutes of stirring, the ketone (1 mmol) was added. When the starting material was a solid, it was added as a solution in THF. The reaction was monitored by GC, after consumption of the starting material or no further conversion, the reaction mixture was opened to air and filtered through a plug of active charcoal and celite using DCM as solvent. The organic phase was concentrated *in vacuo* and the purity of the residue established by GC and ^{1}H NMR analyses. Flash chromatography was then performed unless crude product was estimated to be greater than 95% pure.

Synthesis and Characterization of Silyl Ethers

(Cyclohexyloxy)triethysilane (Table 7, entry 1)

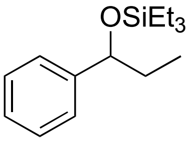
Using the general procedure at room temperature, cyclohexanone (0.100 mL, 1 mmol) was hydrosilylated by triethylsilane. The residue was purified by flash chromatography on silica gel (pentane) to afford 0.199 g (93% yield) of the title compound as a colorless oil. Spectroscopic data were consistent with previously reported data for this compound.[7]

(2-Methylcyclohexyloxy)triethylsilane (Table 7, entry 2)



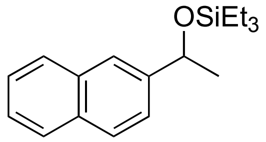
Using the general procedure at room temperature, 2-methylcyclohexanone (0.121 mL, 1 mmol) was hydrosilylated by triethylsilane. The residue was purified by flash chromatography on silica gel (pentane) to afford the title compound as a colorless oil and in a mixture 78:22 of *trans:cis* diastereoisomers (0.218 g, 95% yield). Spectroscopic data were consistent with previously reported data for this compound.[8]

(1-Phenylpropoxy)triethylsilane (Table 7, entry 3)



Using the general procedure at room temperature, propiophenone (0.133 mL, 1 mmol) was hydrosilylated by triethylsilane. The residue was purified by flash chromatography on silica gel (pentane) to afford 0.241 g (96% yield) of the title compound as a colorless oil. Spectroscopic data were consistent with previously reported data for this compound.[3]

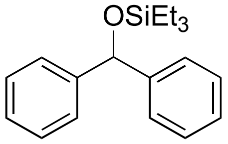
[1-(Naphthalen-2-yl)ethoxy]triethylsilane (Table 7, entry 4)



Using the general procedure at room temperature, 2'-acetonaphtone (0.170 g, 1 mmol) was hydrosilylated by triethylsilane. The residue was purified by flash chromatography on silica gel (pentane) to afford 0.259 g (90% yield) of the title compound as a colorless oil.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.96–7.73 (m, 4H, C^{Ar}), 7.67–7.48 (m, 3H, C^{Ar}), 5.12 (q, J = 6.3 Hz, 1H, C*H*–CH$_3$), 1.60 (d, J = 6.3 Hz, 3H, CH–C*H*$_3$), 1.03 (t, J = 8.0 Hz, 9H, SiCH$_2$C*H*$_3$), 0.78–0.62 ppm (m, 6H, SiC*H*$_2$CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 144.4 (C, C^{Ar}), 133.3 (C, C^{Ar}), 132.7 (C, C^{Ar}), 127.9 (CH, C^{Ar}), 127.8 (CH, C^{Ar}), 127.6 (CH, C^{Ar}), 125.8 (CH, C^{Ar}), 125.4 (CH, C^{Ar}),124.0 (CH, C^{Ar}), 123.4 (CH, C^{Ar}), 70.7 (CH, *C*H–CH$_3$), 27.2 (CH$_3$, CH–*C*H$_3$), 6.8 (CH$_3$, CH$_2$–*C*H$_3$), 4.8 ppm (CH$_2$, *C*H$_2$–CH$_3$). Elemental analysis calcd (%) for C$_{18}$H$_{26}$OSi (286.18): C, 75.46; H, 9.15; found: C, 75.81; H, 9.36.

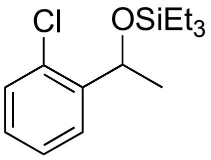
(Diphenylmethoxy)triethylsilane (Table 7, entry 5)



(A) Using the general procedure at 80ºC, benzophenone (0.182 g, 1 mmol) was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.294 g, 98% yield). (B) Using the general procedure at room temperature, benzophenone (0.182 g, 1 mmol) at room temperature was hydrosilylated by triethylsilane. A colorless oil was obtained as the pure product after concentration of the filtrate (0.293 g, 98% yield). Spectroscopic data were consistent with previously reported data for this compound.[6]

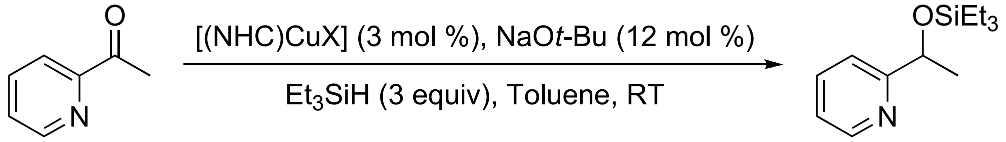
(Dicyclopropylmethoxy)triethylsilane (Table 7, entry 6). Using the general procedure at 80°C, dicyclopropyl ketone (0.114 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane/Et$_2$O : 80/20) to afford 0.209 g the title compound as a colorless oil (92% yield). Spectroscopic data were consistent with previously reported data for this compound.[6]

[1-(2-Chlorophenyl)ethoxy]triethylsilane (Table 7, entry 7)



Using the general procedure at 80ºC, 2'-chloroacetophenone (0.130 mL, 1 mmol) was hydrosilylated by triethylsilane. The crude product was purified by flash chromatography on silica gel (pentane) to afford 0.247 g (91% yield) of the title compound as a colorless oil. Spectroscopic data were consistent with previously reported data for this compound.[6]

Catalyst Screening for the Hydrosilylation of 2-Acetylpyridine



[(NHC)CuX]		Time (h)	Conv. (%)[a]
[(IPr)CuCl]	**1a**	23	>99
[(IPr)CuBr]	**1b**	24	90
[(IPr)CuI]	**1c**	23	89
[(SIPr)CuCl]	**2a**	24	92
[(SIPr)CuBr]	**2b**	24	64
[(SIPr)CuI]	**2c**	24	66
[(IAd)CuCl]	**3a**	2	>99
[(IAd)CuBr]	**3b**	5	>99
[(IAd)CuI]	**3c**	24	>99

[(NHC)CuX]		Time (h)	Conv. (%)[a]
[(IMes)CuCl]	**4a**	0.5	>99
[(IMes)CuBr]	**4b**	0.75	>99
[(SIMes)CuCl]	**5a**	0.5	>99
[(SIMes)CuBr]	**5b**	0.5	>99
[(ICy)CuCl]	**6a**	0.5	>99
[(ICy)CuBr]	**6b**	1	91
[(ICy)CuI]	**6c**	4	>99
[(ItBu)CuCl]	**7a**	23	95
[(ItBu)CuBr]	**7b**	23	94
[(ItBu)CuI]	**7c**	23	91

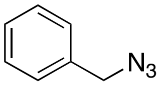
[a] GC conversions are the average of at least two independent runs.

CATALYTIC ACTIVITY: [3+2] CYCLOADDITION OF AZIDES AND ALKYNES

Synthesis of Azides

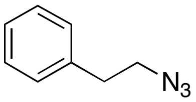
Alkyl azides were synthesized at room temperature from the corresponding bromides by nucleophilic substitution with sodium azide in DMSO.[9]

Benzyl azide



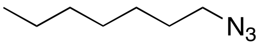
From benzyl bromide (3.6 mL, 30 mmol) and following the Alvarez procedure[9] (reaction time = 1 h), 3.77 g of the title compound were isolated as a light yellow oil after extraction (94%). Spectroscopic data were consistent with previously reported data for this compound.[9]

(2-Azidomethyl)benzene



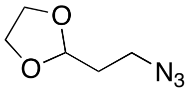
From (2-bromoethyl)benzene (4.0 mL, 30 mmol) and following the Alvarez procedure[9] (reaction time = 5 h), 4.14 g of the title compound were isolated as a light yellow oil after extraction (94%). Spectroscopic data were consistent with previously reported data for this compound.[10,11]

1-Azidoheptane



From 1-bromoheptane (4.7 mL, 30 mmol) and following the Alvarez procedure[9] (reaction time = 5 h), 3.71 g of the title compound were isolated as a light yellow oil after extraction (88%). Spectroscopic data were consistent with previously reported data for this compound.[10]

2-(2-Azidoethyl)-1,3-dioxolane



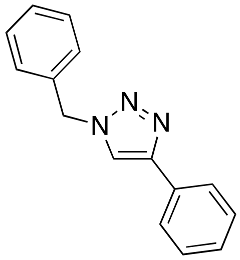
From 2-(2-bromoethyl)-1,3-dioxolane (1.34 mL, 10 mmol) and following the Alvarez procedure[9] (reaction time = 14 h), 1.41 g of the title compound were isolated as a light yellow oil after extraction (99%). Spectroscopic data were consistent with previously reported data for this compound.[10,12]

General Procedure for the [(NHC)CuX]-Catalyzed [3+2] Cycloaddition of Azides and Alkynes

In a vial fitted with a screw cap, azide (1.0 mmol), alkyne (1.1 mmol) and [(NHC)CuX] (4.4 mg if **3c**, or 3.6 mg if **5b**) were loaded. The reaction was allowed to proceed at room temperature and monitored by ^{1}H NMR or GC analysis of aliquots. After total consumption of the starting azide, the solid product was simply dissolved in EtOAc and concentrated or alternatively collected by filtration and washed with pentane. In all examples, the crude products were estimated to be greater than 95% pure by ^{1}H NMR. Reported yields are isolated yields and are the average of at least two independent runs.

Synthesis and Characterization of [1,2,3]-triazoles

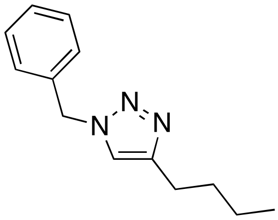
1-Benzyl-4-phenyl-1*H*-1,2,3-triazole (Table 9, entry 1)



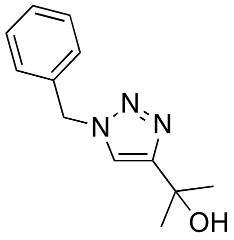
Using the general procedure from 0.125 mL of benzyl azide, 0.11 mL of phenylacetylene and **3c**, and after 10 min of reaction, 0.232 g of the title compound were isolated as a white solid after evaporation of EtOAc (99% yield). Spectroscopic data were consistent with previously reported data for this compound.[13]

1-Benzyl-4-butyl-1*H*-1,2,3-triazole (Table 9, entry 2)

Using the general procedure from 0.125 mL of benzyl azide, 0.118 mL of 1-hexyne and **3c**, and after 90 min of reaction, 0.202 g of the title compound were isolated as a white solid after evaporation of EtOAc (95% yield). Spectroscopic data were consistent with previously reported data for this compound.[14]



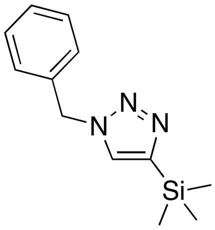
2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)propan-2-ol (Table 9, entry 3)



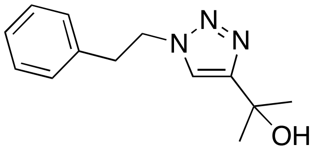
(A) Using the general procedure from 0.125 mL of benzyl azide, 0.102 mL of 2-methylbut-3-yn-2-ol and **3c**, and after 2 h of reaction, 0.200 g of the title compound were isolated as a white solid after washing with pentane (92% yield). (B) Using the general procedure from 0.125 mL of benzyl azide, 0.102 mL of 2-methylbut-3-yn-2-ol and **5b**, and after 18 h of reaction, 0.166 g of the title compound were isolated as a white solid after washing with pentane (76% yield). Spectroscopic data were consistent with previously reported data for this compound.[13]

1-Benzyl-4-(trimethylsilyl)-1*H*-1,2,3-triazole (Table 9, entry 4)

Using the general procedure from 0.125 mL of benzyl azide, 0.146 mL of trimethylsilylacetylene and **3c,** 0.220 g of the title compound was isolated as an off-white solid after extraction with diethyl ether (95% yield). Spectroscopic data were consistent with previously reported data for this compound.[13]

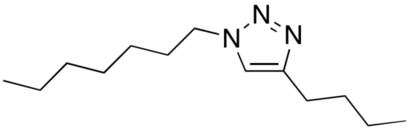


2-(1-Phenethyl-1*H*-1,2,3-triazol-4-yl)propan-2-ol (Table 9, entry 5)



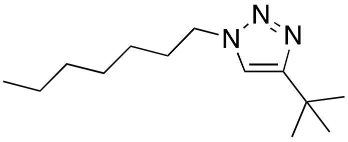
Using the general procedure from 0.147 g of (2-azidoethyl)benzene, 0.102 mL of 2-methylbut-3-yn-2-ol and **3c**, 0.202 g of the title compound was isolated as a white solid after filtration (92% yield). Spectroscopic data were consistent with previously reported data for this compound.[10]

4-Butyl-1-heptyl-1*H*-1,2,3-triazole (Table 9, entry 6)



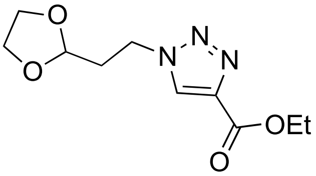
Using the general procedure from 0.141 g of 1-azidoheptane, 0.12 mL, of 1-hexyne and **3c**, 0.205 g of the title compound were isolated as a light yellow oil after extraction with ethyl acetate (98% yield). Spectroscopic data were consistent with previously reported data for this compound.[4]

4-*tert*-Butyl-1-heptyl-1*H*-1,2,3-triazole (Table 9, entry 7)



Using the general procedure from 0.141 g of 1-azidoheptane, 0.13 mL of 3,3-dimethylbut-1-yne and **3c**, 0.215 g of the title compound was isolated as a light yellow oil after extraction with ethyl acetate (96% yield). Spectroscopic data were consistent with previously reported data for this compound.[10]

Ethyl 1-(2-(1,3-dioxolan-2-yl)ethyl)-1*H*-1,2,3-triazole-4-carboxylate (Table 9, entry 8)



Using the general procedure from 0.143 g of 2-(2-azidoethyl)-1,3-dioxolane, 0.106 mL of ethyl propiolate and **3c**, 0.214 g of the title compound was isolated as a light yellow oil after washing with pentane (93% yield). Spectroscopic data were consistent with previously reported data for this compound.[15]

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