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Supporting Information

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**(NHC)Copper(I)-Catalyzed [3+2] Cycloaddition of Azides and Mono- or  
Disubstituted Alkynes**

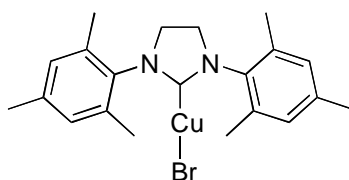
Silvia Díez-González, Andrea Correa, Luigi Cavallo and Steven P. Nolan\*

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## General Considerations

All reagents were used as purchased. Copper(I) bromide and sodium *tert*-butoxide were stored under argon in a glovebox. 1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride (SIMes·HCl) was synthesized according to literature procedures<sup>[1]</sup> or can be purchased from Strem. Flash column chromatography was performed on silica gel 60 (230-400 mesh). <sup>1</sup>H and <sup>13</sup>C Nuclear Magnetic Resonance (NMR) spectra were recorded on a 300 MHz spectrometer at room temperature. Chemical shifts (δ) are reported with respect to tetramethylsilane as internal standard in ppm. Assignments of some <sup>1</sup>H and <sup>13</sup>C NMR signals rely on COSY and/or HMBC experiments. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., Madison, NJ, USA.

## Synthesis of [(SIMes)CuBr]



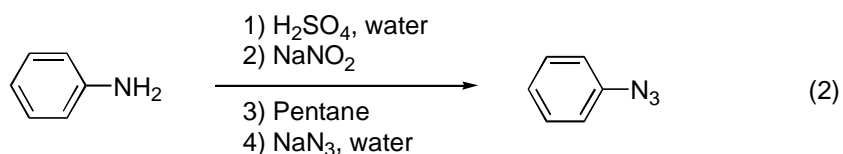
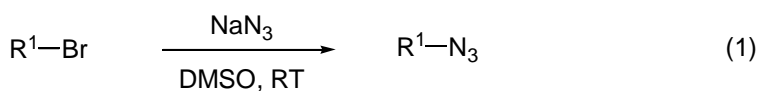
In an oven-dried vial, copper(I) bromide (0.522 g, 3.63 mmol), SIMes·HCl (0.86 g, 2.52 mmol) and sodium *tert*-butoxide (0.243 g, 2.52 mmol) were loaded inside a glovebox and stirred in dry

THF (18 mL) overnight at room temperature outside of the glovebox. After filtration of the reaction mixture through a plug of Celite, the filtrate was mixed with hexane to form a precipitate. A second filtration afforded 0.808 g (71% yield) of the title complex as an off-white solid.

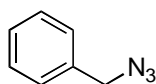
$^1\text{H}$  NMR (300 MHz, acetone- $d_6$ ):  $\delta$  = 7.01 (s, 4H,  $\text{H}^{\text{Ar}}$ ), 4.16 (s, 4H,  $\text{NCH}_2$ ), 2.37 (s, 12H,  $\text{ArCH}_3$ ), 2.29 (s, 6H,  $\text{ArCH}_3$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 202.6 (C,  $\text{NCN}$ ), 138.5 (C,  $\text{C}^{\text{Ar}}$ ), 135.3 (CH,  $\text{C}^{\text{Ar}}$ ), 135.0 (C,  $\text{C}^{\text{Ar}}$ ), 129.7 (CH,  $\text{C}^{\text{Ar}}$ ), 51.0 ( $\text{CH}_2$ ,  $\text{NCH}_2$ ), 21.0 ( $\text{CH}_3$ ,  $\text{ArCH}_3$ ), 18.0 ( $\text{CH}_3$ ,  $\text{ArCH}_3$ ); Elemental analysis calcd for  $\text{C}_{21}\text{H}_{26}\text{BrCuN}_2$  (449.89): C, 56.06; H, 5.83; N, 6.23. Found: C, 55.98; H, 5.64; N, 6.21.

### Synthesis of Azides (1)

Alkyl azides were synthesized at room temperature from the corresponding bromides by nucleophilic substitution with sodium azide in DMSO (eq. 1).<sup>[2]</sup> Phenyl azide **1k** was prepared following a previously reported combination<sup>[3]</sup> of the methods described by Nölting<sup>[4]</sup> and Lindsay<sup>[5]</sup> (eq. 5).



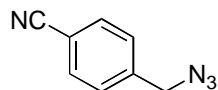
#### Benzyl azide (1a)



From benzyl bromide (3.6 mL, 30 mmol) and following the Alvarez procedure<sup>[2]</sup> (reaction time = 1 h), 3.77 g of the title compound were isolated as a light yellow oil after extraction (94%).

Spectroscopic data for **1a** were consistent with previously reported data for this compound.<sup>[2]</sup>

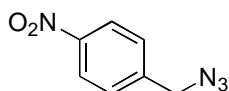
#### 4-(Azidomethyl)benzonitrile (**1d**)



From 4-(bromomethyl)benzonitrile (1.96 g, 10 mmol) and following the Alvarez procedure<sup>[2]</sup> (reaction time = 3 h), 1.48 g of the title compound were isolated as a light yellow oil after extraction (94%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): **d** = 7.68 (d, *J* = 8.5 Hz, 2H, H<sup>Ar</sup>), 7.43 (d, *J* = 8.5 Hz, 2H, H<sup>Ar</sup>), 4.45 (s, 2H, N<sub>3</sub>CH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): **d** = 140.7 (C, C<sup>Ar</sup>), 132.5 (CH, C<sup>Ar</sup>), 128.4 (CH, C<sup>Ar</sup>), 112.0 (C, CN), 109.2 (C, C<sup>Ar</sup>), 53.9 (CH<sub>2</sub>).

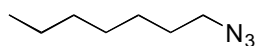
#### 1-(Azidomethyl)4-nitrobenzene (**1e**)



From 1-(bromomethyl)-4-nitrobenzene (6.18 g, 30 mmol) and following the Alvarez procedure<sup>[2]</sup> (reaction time = 4 h), 4.95 g of the title compound were isolated as a bright yellow oil after extraction (94%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): **d** = 8.23 (d, *J* = 8.6 Hz, 2H, H<sup>Ar</sup>), 7.50 (d, *J* = 8.6 Hz, 2H, H<sup>Ar</sup>), 4.51 (s, 2H, N<sub>3</sub>CH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): **d** = 147.6 (C, C<sup>Ar</sup>), 142.7 (C, C<sup>Ar</sup>), 128.5 (CH, C<sup>Ar</sup>), 123.9 (CH, C<sup>Ar</sup>), 53.6 (CH<sub>2</sub>).

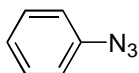
#### 1-Azidoheptane (**1g**)



From 1-bromoheptane (4.7 mL, 30 mmol) and following the Alvarez procedure<sup>[2]</sup> (reaction time = 5 h), 3.71 g of the title compound were isolated as a light yellow oil after extraction (88%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): *d* = 3.26 (t, *J* = 7.0 Hz, N<sub>3</sub>CH<sub>2</sub>), 1.65 – 1.56 (m, 2H, N<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.40 – 1.21 (m, 8H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.90 (t, *J* = 6.6 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): *d* = 51.4 (N<sub>3</sub>CH<sub>2</sub>), 31.6 (CH<sub>2</sub>), 28.8 (CH<sub>2</sub>), 26.6 (CH<sub>2</sub>), 22.5 (CH<sub>2</sub>), 14.0 (CH<sub>3</sub>).

### Phenyl azide (**1k**)

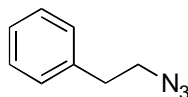


From aniline (6.20 g, 70 mmol) and following the Cwiklicki procedure,<sup>[3]</sup> 6.70 g of the title compound were isolated as a light yellow oil after extraction (80%).

<sup>1</sup>H NMR for **1k** was consistent with previously reported data for this compound.<sup>[3]</sup>

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): *d* = 139.9 (C, C<sup>Ar</sup>), 129.7 (CH, C<sup>Ar</sup>), 124.8 (CH, C<sup>Ar</sup>), 119.0 (CH, C<sup>Ar</sup>).

### (2-Azidomethyl)benzene (**1l**)

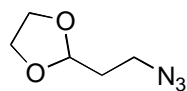


From (2-bromoethyl)benzene (4.0 mL, 30 mmol) and following the Alvarez procedure<sup>[2]</sup> (reaction time = 5 h), 4.14 g of the title compound were isolated as a light yellow oil after extraction (94%).

<sup>1</sup>H NMR for **1l** was consistent with previously reported data for this compound.<sup>[6]</sup>

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): *d* = 138.0 (C, C<sup>Ar</sup>), 128.7 (CH, C<sup>Ar</sup>), 128.6 (CH, C<sup>Ar</sup>), 126.7 (CH, C<sup>Ar</sup>), 52.4 (CH<sub>2</sub>, N<sub>3</sub>CH<sub>2</sub>), 35.3 (CH<sub>2</sub>, CH<sub>2</sub>Ph).

### 2-(2-Azidoethyl)-1,3-dioxolane (**1m**)



From 2-(2-bromoethyl)-1,3-dioxolane (1.34 mL, 10 mmol) and following the Alvarez procedure<sup>[2]</sup> (reaction time = 14 h), 1.41 g of the title compound were isolated as a light yellow oil after extraction (99%).

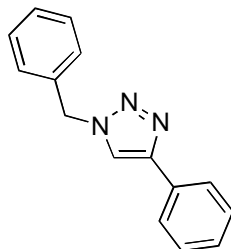
<sup>1</sup>H NMR for **1m** was consistent with previously reported data for this compound.<sup>[7]</sup>

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): *d* = 101.9 (CH, OCHO), 64.9 (CH<sub>2</sub>, OCH<sub>2</sub>), 46.5 (CH<sub>2</sub>, N<sub>3</sub>CH<sub>2</sub>), 33.0 (CH<sub>2</sub>, N<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>).





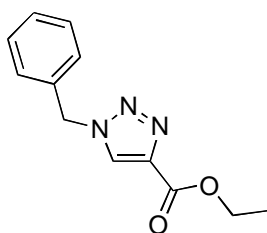
### 1-Benzyl-4-phenyl-1*H*-1,2,3-triazole (**3a**)



- A) Using the general procedure from 0.133 g of benzyl azide **1a** and 0.11 mL of phenylacetylene **2a**, 0.231 g of the title compound was isolated as a white solid after filtration (98% yield).
- B) Using the general procedure from 0.246 mL of benzyl bromide **4a** and 0.11 mL of **2a**, 0.217 g of the title compound was isolated as a white solid after filtration (92% yield).
- C) Using the general procedure from 0.115 mL of benzyl chloride **4a'** and 0.11 mL of **2a**, 0.219 g of the title compound was isolated as a white solid after filtration (93% yield).

Spectroscopic data for **3a** were consistent with previously reported data for this compound.<sup>[8]</sup>

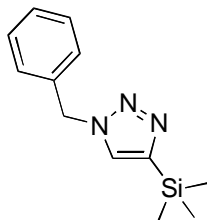
### Ethyl 1-benzyl-4-butyl-1*H*-1,2,3-triazole-4-carboxylate (**3b**)



Using the general procedure from 0.133 g of benzyl azide **1a** and 0.106 mL of ethyl propiolate **2b**, 0.183 g of the title compound was isolated as a white solid after filtration (91% yield).

Spectroscopic data for **3b** were consistent with previously reported data for this compound.<sup>[9]</sup>

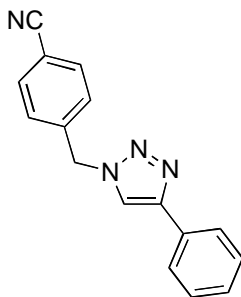
### 1-Benzyl-4-(trimethylsilyl)-1H-1,2,3-triazole (**3c**)



Using the general procedure ( $T = 45^{\circ}\text{C}$ ) from 0.133 g of benzyl azide **1a** and 0.146 mL of trimethylsilylacetylene **2c**, 0.227 g of the title compound was isolated as an off-white solid after extraction (98% yield).

Spectroscopic data for **3c** were consistent with previously reported data for this compound.<sup>[8]</sup>

### 4-[(4-Phenyl-1H-1,2,3-triazol-1-yl)methyl]benzonitrile (**3d**)

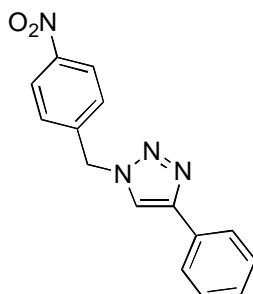


A) Using the general procedure from 0.158 g of 4-(azidomethyl)benzonitrile **1d** and 0.11 mL of phenylacetylene **2a**, 0.242 g of the title compound was isolated as a white solid after filtration (93% yield).

B) Using the general procedure from 0.196 g of 4-(bromomethyl)benzonitrile **4d** and 0.11 mL of phenylacetylene **2a**, 0.253 g of the title compound was isolated as a white solid after filtration (97% yield).

Spectroscopic data for **3d** were consistent with previously reported data for this compound.<sup>[8]</sup>

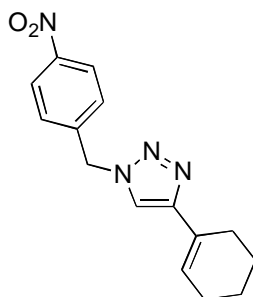
### 1-(4-Nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole (**3e**)



- A) Using the general procedure from 0.176 g of 4-(azidomethyl)-4-nitrobenzene **1e** and 0.11 mL of phenylacetylene **2a**, 0.250 g of the title compound was isolated as a yellow solid after filtration (89% yield).
- B) Using the general procedure from 0.206 g of 1-(bromomethyl)-4-nitrobenzene **4e** and 0.11 mL of phenylacetylene **2a**, 0.275 g of the title compound was isolated as a white solid after filtration (98% yield).

Spectroscopic data for **1a** were consistent with previously reported data for this compound.<sup>[8]</sup>

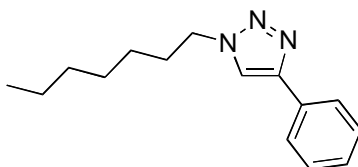
### 4-Cyclohexenyl-1-(4-nitrobenzyl)-1*H*-1,2,3-triazole (**3f**)



Using the general procedure from 0.176 g of 4-(azidomethyl)-4-nitrobenzene **1e** and 0.118 mL of 1-ethynylcyclohex-1-ene **2f**, 0.263 g of the title compound was isolated as a light yellow solid after filtration (93% yield).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.17 (d,  $J$  = 8.6 Hz, 2H,  $\text{H}^{\text{Ar}}$ ), 7.41 (s, 1H,  $\text{NCH=}$ ), 7.40 (d,  $J$  = 8.6 Hz, 2H,  $\text{H}^{\text{Ar}}$ ), 6.51 (broad s, 1H,  $=\text{CHCH}_2$ ), 5.62 (s, 2H,  $\text{NCH}_2$ ), 2.40 – 2.23 (m, 2H, cyclohexenyl), 2.23 – 2.11 (m, 2H, cyclohexenyl), 1.80 – 1.56 (m, 4H, cyclohexenyl);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 150.2 (C,  $\text{NC=}$ ), 147.8 (C,  $\text{C}^{\text{Ar}}$ ), 142.1 (C,  $\text{C}^{\text{Ar}}$ ), 128.3 (CH,  $\text{C}^{\text{Ar}}$ ), 126.8 (C,  $\text{C}=\text{CHCH}_2$ ), 125.5 (CH,  $\text{C}=\text{CHCH}_2$ ), 124.1 (CH,  $\text{C}^{\text{Ar}}$ ), 118.5 (CH,  $\text{NCH=}$ ), 52.8 ( $\text{CH}_2$ ,  $\text{NCH}_2$ ), 26.2 ( $\text{CH}_2$ ), 25.1 ( $\text{CH}_2$ ), 22.2 ( $\text{CH}_2$ ), 22.0 ( $\text{CH}_2$ ); Elemental analysis calcd for  $\text{C}_{15}\text{H}_{16}\text{N}_4\text{O}_2$  (284.31): C, 63.37; H, 5.67; N, 19.71. Found: C, 63.49; H, 5.36; N, 19.35.

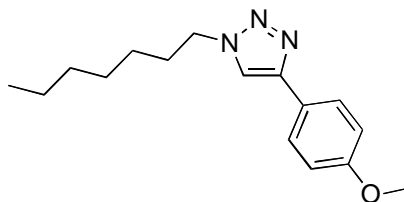
### 1-Heptyl-4-phenyl-1*H*-1,2,3-triazole (3g)



Using the general procedure from 0.176 g of 1-azidoheptane **1g** and 0.11 mL of phenylacetylene **2a**, 0.225 g of the title compound was isolated as a white solid after filtration (93% yield).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.85 (d,  $J$  = 7.1 Hz, 2H,  $\text{H}^{\text{Ar}}$ ), 7.75 (s, 1H,  $\text{NCH=}$ ), 7.48 – 7.40 (m, 2H,  $\text{H}^{\text{Ar}}$ ), 7.40 – 7.29 (m, 1H,  $\text{H}^{\text{Ar}}$ ), 4.40 (t,  $J$  = 7.2 Hz,  $\text{NCH}_2$ ), 2.04 – 1.88 (m, 2H,  $\text{NCH}_2\text{CH}_2$ ), 1.43 – 1.19 (m, 8H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.87 (t,  $J$  = 6.7 Hz,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 147.5 (C,  $\text{NC=}$ ), 130.6 (C,  $\text{C}^{\text{Ar}}$ ), 128.7 (CH,  $\text{C}^{\text{Ar}}$ ), 127.9 (CH,  $\text{C}^{\text{Ar}}$ ), 125.5 (CH,  $\text{C}^{\text{Ar}}$ ), 119.4 (CH,  $\text{NCH=}$ ), 50.2 ( $\text{CH}_2$ ,  $\text{NCH}_2$ ), 31.4 ( $\text{CH}_2$ , heptyl), 30.2 ( $\text{CH}_2$ , heptyl), 28.6 ( $\text{CH}_2$ , heptyl), 26.3 ( $\text{CH}_2$ , heptyl), 22.4 ( $\text{CH}_2$ , heptyl), 13.9 ( $\text{CH}_3$ ); Elemental analysis calcd for  $\text{C}_{15}\text{H}_{21}\text{N}_3$  (243.35): C, 74.03; H, 8.70; N, 17.27. Found: C, 73.79; H, 8.60; N, 17.18.

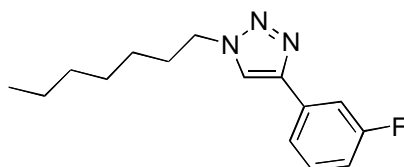
### 1-Heptyl-4-(4-methoxyphenyl)-1H-1,2,3-triazole (3h)



Using the general procedure from 0.176 g of 1-azidoheptane **1g** and 0.136 mL of 1-ethynyl-4-methoxybenzene **2g**, 0.255 g of the title compound was isolated as a white solid after filtration (93% yield).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.76 (d,  $J$  = 8.8 Hz, 2H,  $\text{H}^{\text{Ar}}$ ), 7.66 (s, 1H,  $\text{NCH=}$ ), 6.96 (d,  $J$  = 8.8 Hz, 2H,  $\text{H}^{\text{Ar}}$ ), 4.37 (t,  $J$  = 7.2 Hz,  $\text{NCH}_2$ ), 3.84 (s, 3H,  $\text{OCH}_3$ ), 2.00 – 1.83 (m, 2H,  $\text{NCH}_2\text{CH}_2$ ), 1.42 – 1.21 (m, 8H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.88 (t,  $J$  = 6.8 Hz,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 159.4 (C,  $\text{C}^{\text{Ar}}$ ), 147.5 (C,  $\text{NC=}$ ), 126.9 (CH,  $\text{C}^{\text{Ar}}$ ), 123.4 (C,  $\text{C}^{\text{Ar}}$ ), 118.6 (CH,  $\text{NCH=}$ ), 114.1 (CH,  $\text{C}^{\text{Ar}}$ ), 55.2 ( $\text{CH}_2$ ,  $\text{NCH}_2$ ), 50.3 ( $\text{CH}_3$ ,  $\text{OCH}_3$ ), 31.5 ( $\text{CH}_2$ , heptyl), 30.3 ( $\text{CH}_2$ , heptyl), 28.6 ( $\text{CH}_2$ , heptyl), 26.4 ( $\text{CH}_2$ , heptyl), 22.5 ( $\text{CH}_2$ , heptyl), 14.0 ( $\text{CH}_2\text{CH}_3$ ); Elemental analysis calcd for  $\text{C}_{16}\text{H}_{23}\text{N}_3\text{O}$  (273.37): C, 70.30; H, 8.48; N, 15.37. Found: C, 69.98; H, 8.79; N, 15.24.

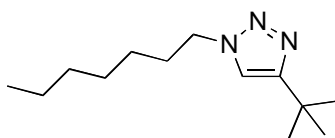
### 4-(3-Fluorophenyl)-1-heptyl-1H-1,2,3-triazole (3i)



- A) Using the general procedure from 0.176 g of 1-azidoheptane **1g** and 0.121 mL of 1-ethynyl-3-fluorobenzene **2i**, 0.233 g of the title compound was isolated as an off-white solid after extraction (89% yield).
- B) Using the general procedure from 0.157 mL of 1-bromoheptane **4g** and 0.121 mL of 1-ethynyl-3-fluorobenzene **2i**, 0.240 g of the title compound was isolated as a white solid after extraction (92% yield).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\mathbf{d}$  = 7.76 (s, 1H,  $\text{NCH=}$ ), 7.65 – 7.52 (m, 2H,  $\text{H}^{\text{Ar}}$ ), 7.43 – 7.34 (m, 1H,  $\text{H}^{\text{Ar}}$ ), 7.08 – 6.97 (m, 1H,  $\text{H}^{\text{Ar}}$ ), 4.41 (t,  $J$  = 7.3 Hz,  $\text{NCH}_2$ ), 2.02 – 1.89 (m, 2H,  $\text{NCH}_2\text{CH}_2$ ), 1.43 – 1.20 (m, 8H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.89 (t,  $J$  = 6.7 Hz,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\mathbf{d}$  = 160.4 (d,  $J$  = 244 Hz, C, C–F), 146.5 (C,  $\text{NC=}$ ), 132.8 (d,  $J$  = 8.5 Hz, C,  $\text{C}^{\text{Ar}}$ ), 130.3 (d,  $J$  = 8.5 Hz, CH,  $\text{C}^{\text{Ar}}$ ), 121.2 (CH,  $\text{C}^{\text{Ar}}$ ), 119.8 (CH,  $\text{NCH=}$ ), 114.7 (d,  $J$  = 21 Hz, CH,  $\text{C}^{\text{Ar}}$ ), 112.4 (d,  $J$  = 23 Hz, CH,  $\text{C}^{\text{Ar}}$ ), 50.4 ( $\text{CH}_2$ ,  $\text{NCH}_2$ ), 31.4 ( $\text{CH}_2$ , heptyl), 30.2 ( $\text{CH}_2$ , heptyl), 28.6 ( $\text{CH}_2$ , heptyl), 26.3 ( $\text{CH}_2$ , heptyl), 22.4 ( $\text{CH}_2$ , heptyl), 13.9 ( $\text{CH}_3$ ); Elemental analysis calcd for  $\text{C}_{15}\text{H}_{20}\text{FN}_3$  (261.34): C, 68.94; H, 7.71; N, 16.08. Found: C, 68.87; H, 7.99; N, 15.85.

#### 4-*tert*-Butyl-1-heptyl-1H-1,2,3-triazole (**3j**)

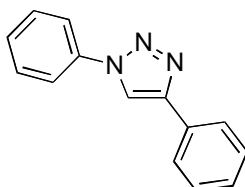


Using the general procedure from 0.176 g of 1-azidoheptane **1g** and 0.13 mL of 3,3-dimethylbut-1-yne **2j** and 2 mol % of [(SImes)CuBr], 0.212 g of the title compound was isolated as a light yellow oil after extraction (95% yield).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\mathbf{d}$  = 7.19 (s, 1H,  $\text{NCH=}$ ), 4.21 (t,  $J$  = 7.4 Hz, 2H,  $\text{NCH}_2$ ), 1.84 – 1.74 (m, 2H,  $\text{NCH}_2\text{CH}_2$ ), 1.33 – 1.21 (m,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ) and 1.26 (s,  $\text{CCH}_3$ ) (17H), 0.80 (t,  $J$  = 6.8 Hz,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\mathbf{d}$  = 157.2 (C,  $\text{NC=}$ ), 118.1 (CH,  $\text{NCH=}$ ), 49.8 ( $\text{CH}_2$ ,  $\text{NCH}_2$ ), 31.3 ( $\text{CH}_2$ , heptyl), 30.4 (C,  $\text{CCH}_3$ ), 30.1 ( $\text{CH}_3$ ,  $\text{CCH}_3$ ), 28.4 ( $\text{CH}_2$ , heptyl), 26.2

(CH<sub>2</sub>, heptyl), 22.2 (CH<sub>2</sub>, heptyl), 13.8 (CH<sub>2</sub>CH<sub>3</sub>); Elemental analysis calcd for C<sub>13</sub>H<sub>25</sub>N<sub>3</sub> (223.36): C, 69.91; H, 11.28; N, 18.81. Found: C, 70.01; H, 11.56; N, 18.76.

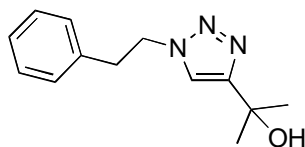
### 1,4-Diphenyl-1*H*-1,2,3-triazole (**3k**)



Using the general procedure from 0.119 g of phenyl azide **1k** and 0.11 mL of phenylacetylene **2a**, 0.189 g of the title compound was isolated as a white solid after filtration (86% yield).

Spectroscopic data for **3k** were consistent with previously reported data for this compound.<sup>[10]</sup>

### 2-(1-Phenethyl-1*H*-1,2,3-triazol-4-yl)propan-2-ol (**3l**)

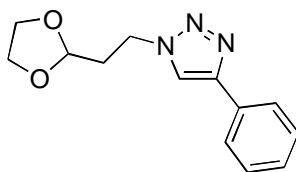


Using the general procedure from 0.147 g of (2-azidoethyl)benzene **1l** and 0.11 mL of 2-methylbut-3-yn-2-ol **2l**, 0.216 g of the title compound was isolated as a white solid after filtration (94% yield).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): *d* = 7.39 – 7.21 (m, 3H, H<sup>Ar</sup>), 7.19 (s, 1H, NCH=), 7.18 – 7.02 (m, 2H, H<sup>Ar</sup>), 4.54 (t, *J* = 7.6 Hz, PhCH<sub>2</sub>), 3.19 (t, *J* = 7.6 Hz, NCH<sub>2</sub>), 2.99 (s broad, 1H, OH), 1.59 (s, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): *d* = 155.3 (C, NC=), 137.0 (C, C<sup>Ar</sup>), 128.7 (CH, C<sup>Ar</sup>), 128.6 (CH, C<sup>Ar</sup>), 127.0 (CH, C<sup>Ar</sup>), 119.5 (CH, NCH=), 68.3 (C, COH), 51.5 (CH<sub>2</sub>, NCH<sub>2</sub>),

36.7 (CH<sub>2</sub>, PhCH<sub>2</sub>), 30.4 (CH<sub>3</sub>); Elemental analysis calcd for C<sub>13</sub>H<sub>17</sub>N<sub>3</sub>O (231.29): C, 67.51; H, 7.41; N, 18.17. Found: C, 67.45; H, 7.48; N, 17.87.

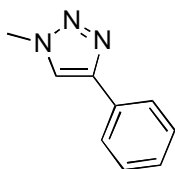
### 1-[2-(1,3-Dioxolan-2-yl)ethyl]-4-phenyl-1H-1,2,3-triazole (3m)



Using the general procedure from 0.143 g of (2-azidoethyl)-1,3-dioxolane **1m** and 0.11 mL of phenylacetylene **2a**, 0.226 g of the title compound was isolated as a white solid after filtration (92% yield).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): *d* = 7.87 – 7.73 (m, 3H, H<sup>Ar</sup> + NCH=), 7.47 – 7.28 (m, 3H, H<sup>Ar</sup>), 4.94 (t, *J* = 4.3 Hz, 1H, OCHO), 4.55 (t, *J* = 7.2 Hz, 2H, NCH<sub>2</sub>), 4.04 – 3.92 (m, 2H, OCH<sub>2</sub>), 3.92 – 3.84 (m, 2H, OCH<sub>2</sub>), 2.37 – 2.27 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): *d* = 147.4 (C, NC=), 130.6 (C, C<sup>Ar</sup>), 128.7 (CH, C<sup>Ar</sup>), 128.0 (CH, C<sup>Ar</sup>), 125.6 (CH, C<sup>Ar</sup>), 119.8 (CH, NCH=), 101.4 (CH, OCHO), 65.0 (CH<sub>2</sub>, CH<sub>2</sub>O), 45.3 (CH<sub>2</sub>, NCH<sub>2</sub>), 34.0 (CH<sub>2</sub>, NCH<sub>2</sub>CH<sub>2</sub>); Elemental analysis calcd for C<sub>13</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub> (245.28): C, 63.66; H, 6.16; N, 17.13. Found: C, 63.82; H, 6.22; N, 16.86.

### 1-Methyl-4-phenyl-1H-1,2,3-triazole (3n)

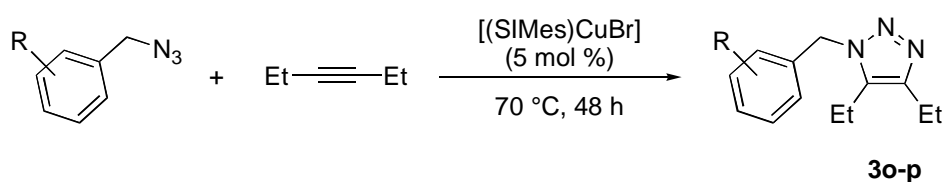




Using the general procedure from 62  $\mu\text{L}$  iodomethane **4n** and 0.11 mL of phenylacetylene **2a**, 0.143 g of the title compound was isolated as a light yellow solid after filtration (90% yield).

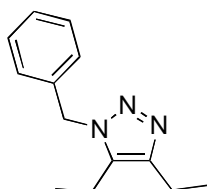
Spectroscopic data for **3n** were consistent with previously reported data for this compound.<sup>[8]</sup>

### C. General Procedure for the [3+2]-Cycloaddition of Azides and 3-Hexyne



In a vial fitted with a screw cap, azide **1a** or **1e** (1.0 mmol), 3-hexyne **2o** (0.120 mL, 1.05 mmol) and [(SIMes)CuBr] (22 mg, 5 mol %) were loaded. The reaction was allowed to proceed at 70°C for 48 h. The reaction mixture was allowed to cool down and poured on an aqueous  $\text{NH}_4\text{Cl}$ /diethyl ether mixture. After extraction of the aqueous phase with diethyl ether, the combined organic layers were washed with brine, dried over magnesium sulfate, filtered and evaporated. Due to their low melting-point, triazoles **3o** and **3p** could not be purified by recrystallization and the crude product was purified by flash chromatography on silica gel.

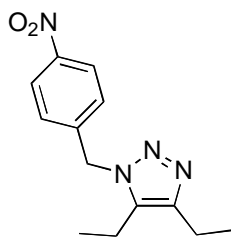
#### 1-Benzyl-4,5-diethyl-1H-1,2,3-triazole (**3o**)



Using the general procedure from 0.133 g of benzyl azide **1a** and after purification by flash chromatography on silica gel (pentane/diethyl ether: 1:1), 0.153 g of the title compound was isolated as a colorless oil (71% yield).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\mathbf{d}$  = 7.42 – 7.27 (m, 3H,  $\text{H}^{\text{Ar}}$ ), 7.21 – 7.18 (m, 2H,  $\text{H}^{\text{Ar}}$ ), 5.48 (s, 2H,  $\text{NCH}_2$ ), 2.65 (q,  $J$  = 7.6 Hz,  $\text{CH}_2\text{CH}_3$ ), 2.52 (q,  $J$  = 7.6 Hz,  $\text{CH}_2\text{CH}_3$ ), 1.28 (t,  $J$  = 7.6 Hz,  $\text{CH}_2\text{CH}_3$ ), 0.96 (t,  $J$  = 7.6 Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\mathbf{d}$  = 146.39 (C,  $\text{NC}=\text{}$ ), 146.34 (C,  $\text{NC}=\text{}$ ), 135.4 (C,  $\text{C}^{\text{Ar}}$ ), 128.88 (CH,  $\text{C}^{\text{Ar}}$ ), 128.81 (CH,  $\text{C}^{\text{Ar}}$ ), 128.1 (CH,  $\text{C}^{\text{Ar}}$ ), 51.8 ( $\text{CH}_2$ ,  $\text{NCH}_2$ ), 18.5 ( $\text{CH}_2$ ,  $\text{CH}_2\text{CH}_3$ ), 15.9 ( $\text{CH}_2$ ,  $\text{CH}_2\text{CH}_3$ ), 14.2 ( $\text{CH}_3$ ), 13.3 ( $\text{CH}_3$ ); Elemental analysis calcd for  $\text{C}_{13}\text{H}_{17}\text{N}_3$  (215.29): C, 72.52; H, 7.96; N, 19.52. Found: C, 72.43; H, 7.83; N, 19.45.

#### 4,5-Diethyl-1-(4-nitrobenzyl)-1H-1,2,3-triazole (3p)



Using the general procedure from 0.176 g of 4-(azidomethyl)-4-nitrobenzene **1e** and after purification by flash chromatography on silica gel (diethyl ether), 0.130 g of the title compound was isolated as a yellow oil (48% yield).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\mathbf{d}$  = 8.21 (d,  $J$  = 8.7 Hz,  $\text{H}^{\text{Ar}}$ ), 7.30 (d,  $J$  = 8.7 Hz,  $\text{H}^{\text{Ar}}$ ), 5.58 (s, 2H,  $\text{NCH}_2$ ), 2.67 (q,  $J$  = 7.5 Hz,  $\text{CH}_2\text{CH}_3$ ), 2.55 (q,  $J$  = 7.5 Hz,  $\text{CH}_2\text{CH}_3$ ), 1.30 (t,  $J$  = 7.5 Hz,  $\text{CH}_2\text{CH}_3$ ), 1.01 (t,  $J$  = 7.5 Hz,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\mathbf{d}$  = 147.71 (C), 147.66 (C), 147.63 (C), 142.6 (C,  $\text{C}^{\text{Ar}}$ ), 127.7 (CH,  $\text{C}^{\text{Ar}}$ ), 124.1 (CH,  $\text{C}^{\text{Ar}}$ ), 50.7 ( $\text{CH}_2$ ,  $\text{NCH}_2$ ), 18.4 ( $\text{CH}_2$ ,  $\text{CH}_2\text{CH}_3$ ), 15.8 ( $\text{CH}_2$ ,  $\text{CH}_2\text{CH}_3$ ), 14.1 ( $\text{CH}_3$ ), 13.5 ( $\text{CH}_3$ ); Elemental analysis calcd for  $\text{C}_{13}\text{H}_{16}\text{N}_4\text{O}_2$  (260.29): C, 59.99; H, 6.20; N, 21.52. Found: C, 60.34; H, 6.33; N, 21.76.

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