Supporting Information
for
**Copper(I)-NHC complexes as efficient catalysts for the
synthesis of 1,4-disubstituted 1,2,3-sulfonyltriazoles in air**

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1. General Information

All reactions were performed in air. Solvents were used as received. NHC-copper(I) complexes were synthesized according to published procedure.^[1] Azides were synthesised according to published procedures.^[2] All other reagents were purchased and used as received. ¹H, ¹³C-{¹H} and ³¹P-{¹H} Nuclear Magnetic Resonance (NMR) spectra were recorded at 298K on a Bruker AVANCE 400 spectrometer using the residual solvent peak (CDCl₃: δ_H = 7.26 ppm, δ_C = 77.16 ppm) or TMS as reference. Elemental analyses were performed by the London Metropolitan University Service.

2. Synthesis and characterization of NHC-copper(I) complexes

***N,N'*-bis-{2,6-(di-*iso*-propyl)phenyl}imidazol-2-ylidene-*N,N'*-bis{2,4,6-(trimethyl)phenyl}imidazol-2-ylidene copper(I) tetrafluoroborate, [Cu(IPr)(IMes)]BF₄, **1**.**^[1]

Colorless solid, 320.7 mg, 90%.

¹H NMR (400 MHz, CD₂Cl₂, 298K): δ (ppm): 0.82 (d, 12H, ³J_{HH} = 6.9 Hz, CHCH₃), 1.10 (d, 12H, ³J_{HH} = 6.9 Hz, CHCH₃), 1.66 (s, 12H, CH₃ Mes), 2.31 (septet, 4H, ³J_{HH} = 6.9 Hz, CHCH₃), 2.39 (s, 6H, CH₃ Mes), 6.80 (s, 4H, Ar IMes), 6.88 (s, 2H, H⁴ and H⁵), 7.11 (s, 2H, H^{4'} and H^{5'}), 7.20 (d, 4H, ³J_{HH} = 7.8 Hz, Ar IPr), 7.57 (t, 2H, ³J_{HH} = 7.8 Hz, Ar IPr).

¹³C-{¹H} NMR (75 MHz, CD₂Cl₂, 298K): δ (ppm): 17.3 (s, CH₃ Mes), 21.3 (s, CH₃ Mes), 23.6 (s, CHCH₃), 24.5 (s, CHCH₃), 28.9 (s, CHCH₃), 123.9 (s, C⁴ and C⁵), 124.3 (s, C^{4'} and C^{5'}), 124.5 (s, Ar IPr), 130.1 (s, Ar IMes), 131.0 (s, Ar IPr), 134.5 (s, C^{IV}), 134.6 (s, C^{IV}), 134.8 (s, C^{IV}), 139.6 (s, C^{IV}), 145.4 (s, C^{IV}), 176.2 (s, C_{carbene}), 179.3 (s, C_{carbene}).

Anal. Calcd for C₄₈H₆₀BCuF₄N₄: C, 68.36; H, 7.17; N, 6.64. Found: C, 68.09; H, 7.24; N, 6.61.

***N,N'*-bis-{2,6-(di-*iso*-propyl)phenyl}imidazol-2-ylidene-*N,N'*-(di-*tert*-butyl)imidazol-2-ylidene copper(I) tetrafluoroborate, [Cu(IPr)(*It*Bu)]BF₄ **2**.**^[1]

Colorless solid, 274 mg, 95 %.

¹H NMR (400 MHz, CD₂Cl₂, 298K): δ (ppm): 1.19 (s, 18H, CH₃ *tert*-butyl), 1.22 (d, 12H, ³J_{HH} = 7.1 Hz, CHCH₃) overlapping with 1.24 (d, 12H, ³J_{HH} = 7.1 Hz, CHCH₃), 2.71 (septet, 4H, ³J_{HH} = 7.1 Hz, CHCH₃), 6.98 (s, 2H, H⁴ and H⁵), 7.34 (s, 2H, H⁴ and H⁵), 7.36 (d, 4H, ³J_{HH} = 7.5 Hz, Ar IPr), 7.54 (t, 2H, ³J_{HH} = 7.5 Hz, Ar IPr).

¹³C-{¹H} NMR (CD₂Cl₂, 75 MHz, 298K): δ (ppm): 24.0 (s, CHCH₃), 25.0 (s, CHCH₃), 29.1 (s, CHCH₃), 29.9 (s, C^{IV}), 31.9 (s, CH₃ *tert*-butyl), 57.3 (s, C^{IV} mesityl), 117.6 (s, C⁴ and C⁵), 124.9 (s,

C⁴ and C⁵), 125.2 (s, Ar), 131.3 (s, Ar), 135.1 (s, C^{IV} phenyl), 145.8 (s, C^{IV} phenyl), 171.6 (s, C_{carbene}), 179.6 (s, C_{carbene}).

Anal. Calcd for C₃₈H₅₆BCuF₄N₄: C, 63.46; H, 7.85; N, 7.79. Found: C, 63.55; H, 7.74; N, 7.82.

***N,N'*-bis-{2,6-(di-*iso*-propyl)phenyl}imidazol-2-ylidene-*N,N'*-(dicyclohexyl)imidazol-2-ylidene copper(I) tetrafluoroborate, [Cu(IPr)(ICy)]BF₄ 3.**^[1]

Colorless solid, 306 mg, 99 %.

¹H NMR (400 MHz, CD₂Cl₂, 298K): δ (ppm): 0.89-1.12 (m, 6H, CH₂ cyclohexyl), 1.24 (d, 12H, ³J_{HH} = 6.8 Hz, CHCH₃), 1.29 (d, 12H, ³J_{HH} = 6.8 Hz, CHCH₃), 1.31-1.42 (m, 4H, CH₂ cyclohexyl), 1.56-1.71 (m, 10H, CH₂ cyclohexyl), 2.59 (septet, 4H, ³J_{HH} = 6.8 Hz, CHCH₃), 3.10 (tt, 2H, ³J_{HH} = 12.2 Hz, ³J_{HH} = 4 Hz, CH cyclohexyl), 6.89 (s, 2H, H⁴ and H⁵), 7.29 (s, 2H, H^{4'} and H^{5'}), 7.44 (d, 4H, ³J_{HH} = 7.8 Hz, Ar), 7.64 (t, 2H, ³J_{HH} = 7.8 Hz, Ar).

¹³C-{¹H} NMR (CD₂Cl₂, 75 MHz, 298K): δ (ppm): 23.5 (s, CHCH₃), 24.9 (s, CH₂ cyclohexyl), 25.1 (s, CH₂ cyclohexyl), 25.7 (s, CHCH₃), 29.2 (s, CHCH₃), 34.5 (s, CH₂ cyclohexyl), 61.3 (s, CH cyclohexyl), 118.6 (s, C⁴ and C⁵), 124.3 (s, C^{4'} and C^{5'}), 125.0 (s, Ar), 131.6 (s, Ar), 134.6 (s, C^{IV}), 146.4 (s, C^{IV}), 171.7 (s, C_{carbene}), 179.3 (s, C_{carbene}).

Anal. Calcd for C₄₂H₆₀BCuF₄N₄: C, 65.40; H, 7.84; N, 7.26. Found: C, 65.37; H, 7.84; N, 7.17.

***(N,N'*-bis-{2,6-(di-*iso*-propyl)phenyl}imidazole-2-ylidene)tri-*tert*-butylphosphine tetrafluoroborate copper (I) [Cu(IPr)(PtBu)₃]BF₄ 4.**^[11]

Colorless solid (294 mg, 99%).

¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ (ppm): 1.06 (d, 27H, ³J_{HP} = 13.3 Hz, C(CH₃)₃), 1.23 (d, 12H, ³J_{HH} = 6.9 Hz, CHCH₃), 1.28 (d, 12H, ³J_{HH} = 6.9 Hz, CHCH₃), 2.61 (septet, 4H, ³J_{HH} = 6.9 Hz, CHCH₃), 7.35 (d, 4H, ³J_{HH} = 7.9 Hz, CH Ar), 7.39 (s, 2H, H⁴ and H⁵), 7.54 (t, 2H, ³J_{HH} = 7.9 Hz, CH Ar).

¹³C-{¹H} NMR (75 MHz, CD₂Cl₂, 298 K): δ (ppm): 24.3 (s, CHCH₃), 24.8 (s, CHCH₃), 29.2 (s, CHCH₃), 32.2 (d, ²J_{CP} = 5.2 Hz, CH₃ *tert*-butyl), 37.3 (d, ¹J_{CP} = 12.6 Hz, CCH₃ *tert*-butyl), 124.6 (s, C⁴ and C⁵), 124.8 (s, Ar), 131.3 (s, Ar), 134.7 (s, C^{IV}), 145.8 (s, C^{IV}), 178.6 (d, ²J_{CP} = 61.0 Hz, C_{carbene}).

³¹P-{¹H} NMR (162 MHz, CD₂Cl₂, 298 K): δ (ppm): 66.9 ppm.

Anal. Calcd for C₃₉H₆₃BCuF₄N₄: C, 63.19; H, 8.57; N, 3.78. Found: C, 63.12; H, 8.71; N, 3.66.

3. Sulfonyl azides

Tosyl azide ^[2]

¹H NMR (300 MHz, CDCl₃, 298K, TMS): δ (ppm): 2.48 (s, 3H, CH₃), 7.41 (d, 2H, ³J_{HH} = 8.12 Hz, CH_{Ar}), 7.84 (d, 2H, ³J_{HH} = 8.12 Hz, CH_{Ar}).

4-Methoxybenzenesulfonyl azide ^[2]

¹H NMR (300 MHz, CDCl₃, 298K, TMS): δ (ppm): 7.06 (d, 2H, ³J_{HH} = 9.14 Hz, CH_{Ar}), 7.90 (d, 2H, ³J_{HH} = 9.14 Hz, CH_{Ar}).

4-Nitrobenzenesulfonyl azide ^[2]

¹H NMR (300 MHz, CDCl₃, 298K, TMS): δ (ppm): 7.11 (d, 2H, ³J_{HH} = 8.81 Hz, CH_{Ar}), 7.19 (d, 2H, ³J_{HH} = 8.81 Hz, CH_{Ar}).

Benzenesulfonyl azide ^[2]

¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ (ppm): 7.63 (t, 2H, ³J_{HH} = 7.7 Hz, CH_{Ar}), 7.74 (t, 1H, ³J_{HH} = 7.7 Hz, CH_{Ar}), 7.97 (t, 2H, ³J_{HH} = 8.4 Hz, CH_{Ar}).

Naphthalenesulfonyl azide ^[2]

¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ (ppm): 7.55-7.64 (m, 1H, CH_{Ar}), 7.65-7.70 (m, 1H, CH_{Ar}), 7.72-7.79 (m, 1H, CH_{Ar}), 7.99 (dd, 1H, ³J_{HH} = 8.3, 3.1 Hz, CH_{Ar}), 8.20 (dd, 2H, ³J_{HH} = 8.3,

2.9 Hz, CH_{Ar}), 8.36 (dd, 1H, $^3J_{HH} = 7.3, 3.1$ Hz, CH_{Ar}), 7.50 (dd, 1H, $^3J_{HH} = 8.6, 2.9$ Hz, CH_{Ar}).

2,4,6-Tri-isopropyl-benzenesulfonyl azide ^[2]

¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ (ppm): 1.27 (d, 6H, $^3J_{HH} = 6.8$ Hz, CH(CH₃)₂) overlapped with 1.29 (d, 12H, $^3J_{HH} = 7.0$ Hz CH(CH₃)₂), 2.93 (septet, 1H, $^3J_{HH} = 6.8$ Hz, CH(CH₃)₂) 4.05 (septet, 2H, $^3J_{HH} = 7.0$ Hz, CH(CH₃)₂), 3.82-4.07 (m, 2H, CH_{Ar}).

4-Bromobenzenesulfonyl azide ^[2]

¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ (ppm): 7.74-7.80 (m, 2H, CH_{Ar}), 7.81-7.86 (m, 2H, CH_{Ar}).

Methanesulfonyl azide ^[2]

¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ (ppm): 3.27 (s, 3H, CH₃).

4. Catalysis

4.1. Procedure for table 2

A vial was charged with tosyl azide (1.00 mmol), phenylacetylene (1.05 mmol), the copper catalyst and solvent (1 mL - when stated). The reaction mixture was stirred at room temperature or 40°C for 15 hours. The solvent was removed under vacuum and the conversion was determined by ¹H-NMR based on tosyl azide.

4.2. Procedure for Scheme 2

A vial was charged with the azide (1.00 mmol), the alkyne (1.05 mmol), [Cu(IPr)(P^tBu)₃]BF₄ **4** (37.1 mg, 5 mol%) and toluene (1 mL). The reaction mixture was stirred at room temperature for 5-15 hours. Ethyl acetate was then added and the solution was filtered through a plug of celite. The solution was concentrated (0.5 mL) and hexane or diethyl ether was added (3 mL). The product was collected by filtration and washed with hexane or diethyl ether (2 x 3 mL).

4.3. 1,2,3-sulfonyltriazaoles

1-(4-Methylbenzenesulfonyl)-4-benzene-1H-1,2,3-triazole (**7aa**)^[3]

p-Toluenesulfonyl azide (153 μL, 1.00 mmol), phenylacetylene (115 μL, 1.05 mmol). 1-(4-Methylbenzenesulfonyl)-4-benzene-1H-1,2,3-triazole was obtained as a colorless solid (290 mg, 97%).

¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ (ppm): 2.45 (s, 3H, CH₃), 7.35-7.45 (m, 5H, CH_{Ar}), 7.83 (m, 2H, CH_{Ar}), 8.03 (m, 2H, CH_{Ar}), 8.31 (s, 1H, N-CH).

1-(4-Methylbenzenesulfonyl)-4-(4-fluorobenzene)-1H-1,2,3-triazole (7ab)

p-Toluenesulfonyl azide (153 μ L, 1.00 mmol), *p*-fluorophenylacetylene (110 μ L, 1.05 mmol). 1-(4-Methylbenzenesulfonyl)-4-(4-fluorobenzene)-1H-1,2,3-triazole was obtained as a colorless solid (308 mg, 97%).

^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ (ppm): 2.45 (s, 3H, CH_3), 7.12 (m, 2H, CH_{Ar}), 7.40 (d, 2H, $^3J_{\text{HH}} = 8.2$ Hz, CH_{Ar}), 7.80 (m, 2H, CH_{Ar}), 8.03 (d, 2H, $^3J_{\text{HH}} = 8.2$ Hz, CH_{Ar}), 8.28 (s, 1H, N-CH).

^{13}C - $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 298K, TMS): δ (ppm): 22.0 (s, CH_3), 116.3 (d, $J_{\text{CF}} = 22.5$ Hz, CH_{Ar}), 118.8 (s, N-CH), 125.3 (d, $J_{\text{CF}} = 2.5$ Hz, C^{IV}), 128.1 (d, $J_{\text{CF}} = 6.8$ Hz, CH_{Ar}), 128.9 (s, CH_{Ar}), 130.6 (s, CH_{Ar}), 133.1 (s, C^{IV}), 147.6 (s, C^{IV}), 163.3 (d, $J_{\text{CF}} = 255.0$ Hz, C^{IV}).

HRMS calcd. for $\text{C}_{15}\text{H}_{12}\text{FN}_3\text{O}_2\text{S}$ ($\text{M}+\text{H}$) $^+$ 318.0707, **found** 318.0707.

1-(4-Methylbenzenesulfonyl)-4-*tert*-butyl-1H-1,2,3-triazole (7ac)

p-Toluenesulfonyl azide (153 μ L, 1.00 mmol), *tert*-butylacetylene (129 μ L, 1.05 mmol). 1-(4-Methylbenzenesulfonyl)-4-*tert*-butyl-1H-1,2,3-triazole was obtained as a colorless solid (274 mg, 98%).

^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ (ppm): 1.33 (s, 9H, CCH_3), 2.45 (s, 3H, CH_3), 7.38 (d, 2H, $^3J_{\text{HH}} = 8.62$ Hz, CH_{Ar}), 7.80 (s, 1H, N-CH), 7.90 (d, 2H, $^3J_{\text{HH}} = 8.62$ Hz, CH_{Ar}).

^{13}C - $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 298K, TMS): δ (ppm): 22.0 (s, CH_3), 30.1 (s, $\text{C}(\text{CH}_3)_3$), 31.1 (s, C^{IV}), 118.3 (s, N-CH), 128.8 (s, CH_{Ar}), 130.5 (s, CH_{Ar}), 133.5 (s, C^{IV}), 147.1 (s, C^{IV}), 157.4 (s, C^{IV}).

HRMS calcd. for $\text{C}_{13}\text{H}_{17}\text{N}_3\text{O}_2\text{S}$ ($\text{M}+\text{H}$) $^+$ 280.1114, **found** 280.1111.

1-(4-Methylbenzenesulfonyl)-4-(4-*tert*-butylbenzene)-1H-1,2,3-triazole (7ad)^[6]

p-Toluenesulfonyl azide (153 μ L, 1.00 mmol), *tert*-butylphenylacetylene (189 μ L, 1.05 mmol). 1-(4-Methylbenzenesulfonyl)-4-(4-*tert*-butylbenzene)-1H-1,2,3-triazole was obtained as a colorless solid (348 mg, 98%).

¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ (ppm): 1.33 (s, 9H, CCH₃), 2.45 (s, 3H, CH₃), 7.39 (d, 2H, ³*J*_{HH} = 8.06 Hz, CH_{Ar}), 7.45 (d, 2H, ³*J*_{HH} = 8.45 Hz, CH_{Ar}), 7.75 (d, 2H, ³*J*_{HH} = 8.45 Hz, CH_{Ar}), 8.02 (d, 2H, ³*J*_{HH} = 8.06 Hz, CH_{Ar}), 8.27 (s, 1H, N-CH).

1-(4-Methylbenzenesulfonyl)-4-(2-pyridine)-1H-1,2,3-triazole (7ae)^[4]

p-Toluenesulfonyl azide (153 μ L, 1.00 mmol), 2-ethynylpyridine (106 μ L, 1.05 mmol). 1-(4-Methylbenzenesulfonyl)-4-(2-pyridine)-1H-1,2,3-triazole was obtained as a colorless solid (288 mg, 96%).

¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ (ppm): 2.48 (s, 3H, CH₃), 7.21-7.32 (m, 2H, CH_{Ar}), 7.41 (d, 2H, ³*J*_{HH} = 8.2 Hz, CH_{Ar}), 7.50 (d, 1H, ³*J*_{HH} = 7.6 Hz, CH_{Ar}), 7.67 (t, 1H, ³*J*_{HH} = 7.6 Hz, CH_{Ar}), 7.84 (d, 2H, ³*J*_{HH} = 8.2 Hz, CH_{Ar}), 8.61 (s, 1H, N-CH).

1-(4-Methylbenzenesulfonyl)-4-(2-methoxybenzene)-1H-1,2,3-triazole (7af)

p-Toluenesulfonyl azide (153 μ L, 1.00 mmol), *o*-methoxyphenylacetylene (136 μ L, 1.05 mmol). 1-(4-Methylbenzenesulfonyl)-4-(2-methoxybenzene)-1H-1,2,3-triazole was obtained as a colorless solid (313 mg, 95%).

^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ (ppm): 2.44 (s, 3H, CH_3), 3.97 (s, 3H, OCH_3), 6.99 (m, 1H, CH_{Ar}), 7.06 (m, 1H, CH_{Ar}), 7.34 (m, 1H, CH_{Ar}), 7.37 (d, 2H, $^3J_{\text{HH}} = 8.4$ Hz, CH_{Ar}), 8.03 (d, 2H, $^3J_{\text{HH}} = 8.4$ Hz, CH_{Ar}), 8.32 (m, 1H, CH_{Ar}), 8.57 (s, 1H, N-CH).

^{13}C - $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 298K, TMS): δ (ppm): 21.9 (s, CH_3), 55.6 (s, OCH_3), 110.9 (s, CH_{Ar}), 117.8 (s, C^{IV}), 121.1 (s, CH_{Ar}), 122.2 (s, N-CH), 128.1 (s, CH_{Ar}), 128.7 (s, CH_{Ar}), 130.0 (s, CH_{Ar}), 130.5 (s, CH_{Ar}), 133.5 (s, C^{IV}), 142.9 (s, C^{IV}), 147.2 (s, C^{IV}), 156.1 (s, C^{IV}).

HRMS calcd. for $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_3\text{S}$ ($\text{M}+\text{H}$) $^+$ 330.2846, **found** 330.2830.

1-(4-Methylbenzenesulfonyl)-4-(3-fluorobenzene)-1H-1,2,3-triazole (7ag) ^[6]

p-Toluenesulfonyl azide (153 μ L, 1.00 mmol), *m*-fluorophenylacetylene (121 μ L, 1.05 mmol). 1-(4-Methylbenzenesulfonyl)-4-(3-fluorobenzene)-1H-1,2,3-triazole was obtained as a colorless solid (305 mg, 96%).

^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ (ppm): 2.46 (s, 3H, CH_3), 7.07 (m, 1H, CH_{Ar}), 7.36-7.44 (m, 3H, CH_{Ar}), 7.53-7.63 (m, 2H, CH_{Ar}), 8.04 (m, 2H, CH_{Ar}), 8.33 (s, 1H, N-CH).

1-(4-Methylbenzenesulfonyl)-4-(4-methoxybenzene)-1H-1,2,3-triazole (7ah) ^[7]

p-Toluenesulfonyl azide (153 μ L, 1.00 mmol), *p*-methoxyphenylacetylene (136 μ L, 1.05 mmol). 1-(4-Methylbenzenesulfonyl)-4-(4-methoxybenzene)-1H-1,2,3-triazole was obtained as a colorless solid (306 mg, 93%).

^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ (ppm): 2.45 (s, 3H, CH_3), 3.84 (s, 3H, OCH_3), 6.95 (d, 2H, $^3J_{\text{HH}} = 8.83$ Hz, CH_{Ar}), 7.38 (d, 2H, $^3J_{\text{HH}} = 8.33$ Hz, CH_{Ar}), 7.75 (d, 2H, $^3J_{\text{HH}} = 8.83$ Hz, CH_{Ar}), 8.02 (d, 2H, $^3J_{\text{HH}} = 8.33$ Hz, CH_{Ar}), 8.21 (s, 1H, N-CH).

1-(4-Methylbenzenesulfonyl)-4-(4-methylbenzene)-1H-1,2,3-triazole (7ai) ^[3,6]

p-Toluenesulfonyl azide (153 μ L, 1.00 mmol), 4-ethynyltoluene (133 μ L, 1.05 mmol). 1-(4-Methylbenzenesulfonyl)-4-(4-methylbenzene)-1H-1,2,3-triazole was obtained as a colorless solid (301 mg, 96%).

^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ (ppm): 2.38 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 7.24 (d, 2H, $^3J_{\text{HH}} = 8.1$ Hz, CH_{Ar}), 7.39 (d, 2H, $^3J_{\text{HH}} = 8.3$ Hz, CH_{Ar}), 7.71 (d, 2H, $^3J_{\text{HH}} = 8.1$ Hz, CH_{Ar}), 8.03 (d, 2H, $^3J_{\text{HH}} = 8.3$ Hz, CH_{Ar}), 8.27 (s, 1H, N-CH).

1-(4-Methoxybenzenesulfonyl)-4-phenyl-1H-1,2,3-triazole (7ba) ^[4,5]

p-Methoxybenzenesulfonyl azide (213 mg, 1.00 mmol), phenylacetylene (115 μ L, 1.05 mmol). 1-(4-Methoxybenzenesulfonyl)-4-phenyl-1H-1,2,3-triazole was obtained as a colorless solid (303 mg, 96%).

^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ (ppm): 3.88 (s, 3H, OCH_3), 7.03 (d, 2H, $^3J_{\text{HH}} = 8.6$ Hz, CH_{Ar}), 7.37 (m, 1H, CH_{Ar}), 7.43 (m, 2H, CH_{Ar}), 7.82 (m, 2H, CH_{Ar}), 8.08 (d, 2H, $^3J_{\text{HH}} = 8.6$ Hz, CH_{Ar}), 8.30 (s, 1H, N-CH).

1-(4-Methoxybenzenesulfonyl)-4-(4-fluorobenzene)-1H-1,2,3-triazole (7bb)

p-Methoxybenzenesulfonyl azide (213 mg, 1.00 mmol), *p*-fluorophenylacetylene (110 μ L, 1.05 mmol). 1-(4-Methoxybenzenesulfonyl)-4-(4-fluorobenzene)-1H-1,2,3-triazole product was obtained as a colorless solid (313 mg, 94%).

^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ (ppm): 3.89 (s, 3H, OCH_3), 7.04 (d, 2H, $^3J_{\text{HH}} = 8.8$ Hz, CH Ar), 7.12 (m, 2H, CH Ar), 7.80 (m, 2H, CH_{Ar}), 8.08 (d, 2H, $^3J_{\text{HH}} = 8.8$ Hz, CH_{Ar}), 8.27 (s, 1H, N-CH).

^{13}C - $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 298K, TMS): δ (ppm): 56.1 (s, OCH_3), 115.2 (s, CH_{Ar}), 116.1 (d, $J_{\text{CF}} = 21.8$ Hz, CH_{Ar}), 118.7 (N-CH), 125.3 (d, $J_{\text{CF}} = 2.4$ Hz, C^{IV}), 127.0 (s, C^{IV}), 128.1 (d, $J_{\text{CF}} = 8.9$ Hz, CH_{Ar}), 131.3 (s, CH_{Ar}), 146.5 (s, C^{IV}), 163.3 (d, $J_{\text{CF}} = 254$ Hz, C^{IV}), 165.6 (s, C^{IV}).

HRMS calcd. for $\text{C}_{15}\text{H}_{12}\text{FN}_3\text{O}_3\text{S}$ ($\text{M}+\text{H}$) $^+$ 334.0656, **found** 334.0661.

1-(4-Methoxybenzenesulfonyl)-4-(4-*tert*-butylbenzene)-1H-1,2,3-triazole (7bd)

p-Methoxybenzenesulfonyl azide (213 mg, 1.00 mmol), *p-tert*-butylphenylacetylene (189 μ L, 1.05 mmol). 1-(4-Methoxybenzenesulfonyl)-4-(4-*tert*-butylbenzene)-1H-1,2,3-triazole product was obtained as a colorless solid (364 mg, 98%).

^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ (ppm): 1.34 (s, 9H, CCH_3), 3.89 (s, 3H, OCH_3), 7.03 (d, 2H, $^3J_{\text{HH}} = 9.13$ Hz, CH_{Ar}), 7.45 (d, 2H, $^3J_{\text{HH}} = 8.3$ Hz, CH_{Ar}), 7.75 (d, 2H, $^3J_{\text{HH}} = 8.3$ Hz, CH_{Ar}), 8.08 (d, 2H, $^3J_{\text{HH}} = 9.13$ Hz, CH_{Ar}), 8.26 (s, 1H, N-CH).

^{13}C - $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 298K, TMS): δ (ppm): 31.4 (s, CCH_3), 34.9 (s, C^{IV}), 56.1 (s, OCH_3), 115.2 (s, CH_{Ar}), 118.6 (s, N-CH), 126.0 (s, CH_{Ar}), 126.0 (s, CH_{Ar}), 126.2 (s, C^{IV}), 127.2 (s, C^{IV}), 131.3 (s, CH_{Ar}), 147.4 (s, C^{IV}), 152.4 (s, C^{IV}), 165.5 (s, C^{IV}).

HRMS calcd. for $\text{C}_{19}\text{H}_{21}\text{N}_3\text{O}_3\text{S}$ ($\text{M}+\text{H}$) $^+$ 372.1376, **found** 372.1380.

1-(4-Methoxybenzenesulfonyl)-4-(2-methoxybenzene)-1H-1,2,3-triazole (7bf)

p-Methoxybenzenesulfonyl azide (213 mg, 1.00 mmol), *o*-methoxyphenylacetylene (136 μ L, 1.05 mmol). 1-(4-Methoxybenzenesulfonyl)-4-(2-methoxybenzene)-1H-1,2,3-triazole was obtained as a colorless solid (332 mg, 96%).

^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ (ppm): 3.84 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 6.95 (d, 2H, $^3J_{\text{HH}} = 8.8$ Hz, CH_{Ar}), 7.03 (d, 2H, $^3J_{\text{HH}} = 9.1$ Hz, CH_{Ar}), 7.75 (d, 2H, $^3J_{\text{HH}} = 8.8$ Hz, CH_{Ar}), 8.07 (d, 2H, $^3J_{\text{HH}} = 9.1$ Hz, CH_{Ar}), 8.21 (s, 1H, N-CH).

^{13}C - $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 298K, TMS): δ (ppm): 55.5 (s, OCH_3), 56.1 (s, OCH_3), 114.5 (s, CH_{Ar}), 115.2 (s, CH_{Ar}), 118.0 (N-CH), 121.6 (s, C^{IV}), 127.2 (s, C^{IV}), 127.5 (s, CH_{Ar}), 131.3 (s, CH_{Ar}), 147.3 (s, C^{IV}), 160.4 (s, C^{IV}), 165.4 (s, C^{IV}).

HRMS calcd. for $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_4\text{S}$ ($\text{M}+\text{H}$) $^+$ 346.0856, **found** 346.0851.

1-(4-methoxybenzenesulfonyl)-4-(3-fluorobenzene)-1H-1,2,3-triazole (7bg)

p-Methoxybenzenesulfonyl azide (213 μ L, 1.00 mmol), *m*-fluorophenylacetylene (121 μ L, 1.05 mmol). 1-(4-Methoxybenzenesulfonyl)-4-(3-fluorobenzene)-1H-1,2,3-triazole was obtained as a colorless solid (320 mg, 96%).

^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ (ppm): 3.89 (s, 3H, OCH_3), 7.02-7.12 (m, 3H, CH_{Ar}), 7.40 (m, 1H, CH_{Ar}), 7.58 (m, 2H, CH_{Ar}), 8.09 (m, 2H, CH_{Ar}), 8.32 (s, 1H, N-CH).

^{13}C - $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 298K, TMS): δ (ppm): 56.1 (s, OCH_3), 113.3 (d, $J_{\text{CF}} = 22.5$ Hz, CH_{Ar}), 115.3 (s, CH_{Ar}), 116.1 (d, $J_{\text{CF}} = 21.8$ Hz, C^{IV}), 119.4 (s, N-CH), 121.8 (d, $J_{\text{CF}} = 2.6$ Hz, CH_{Ar}), 126.9 (s, C^{IV}), 130.9 (d, $J_{\text{CF}} = 8.7$ Hz, CH_{Ar}), 131.5 (s, CH_{Ar}), 165.6 (s, C^{IV}).

HRMS calcd. for $\text{C}_{15}\text{H}_{12}\text{FN}_3\text{O}_3\text{S}$ ($\text{M}+\text{H}$) $^+$ 334.0656, **found** 334.0661.

1-(4-Methoxybenzenesulfonyl)-4-(4-methoxybenzene)-1H-1,2,3-triazole (7bh)

p-Methoxybenzenesulfonyl azide (213.2 mg, 1.00 mmol), 4-ethynylanisole (136.2 μ L, 1.05 mmol). 1-(4-Methoxybenzenesulfonyl)-4-(4-methoxybenzene)-1H-1,2,3-triazole was obtained as a colorless solid (328.1 mg, 95%).

^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ (ppm): 3.84 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 6.96 (d, 2H, $^3J_{\text{HH}} = 7.9$ Hz, CH_{Ar}), 7.04 (d, 2H, $^3J_{\text{HH}} = 8.6$ Hz, CH_{Ar}), 7.75 (d, 2H, $^3J_{\text{HH}} = 7.9$ Hz, CH_{Ar}), 8.08 (d, 2H, $^3J_{\text{HH}} = 8.6$ Hz, CH_{Ar}), 8.22 (s, 1H, N-CH).

^{13}C - $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 298K, TMS): δ (ppm): 55.5 (s, OCH_3), 56.1 (s, OCH_3), 114.5 (s, CH_{Ar}), 115.2 (s, CH_{Ar}), 118.0 (N-CH), 121.7 (s, C^{IV}), 127.2 (s, C^{IV}), 127.6 (s, CH_{Ar}), 131.3 (s, CH_{Ar}), 160.4 (s, C^{IV}), 165.4 (s, C^{IV}).

HRMS calcd. for $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_4\text{S}$ ($\text{M}+\text{H}$) $^+$ 346.056, **found** 346.0860.

1-(4-Methoxybenzenesulfonyl)-4-(4-methylbenzene)-1H-1,2,3-triazole (7bi)

p-Methoxybenzenesulfonyl azide (213 mg, 1.00 mmol), 4-ethynyltoluene (133 μ L, 1.05 mmol). 1-(4-Methoxybenzenesulfonyl)-4-(4-methylbenzene)-1H-1,2,3-triazole was obtained as a colorless solid (316 mg, 96%).

^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ (ppm): 2.38 (s, 3H, CH_3), 3.88 (s, 3H, OCH_3), 7.03 (d, 2H, $^3J_{\text{HH}} = 8.92$ Hz, CH_{Ar}), 7.24 (d, 2H, $^3J_{\text{HH}} = 7.64$ Hz, CH_{Ar}), 7.71 (d, 2H, $^3J_{\text{HH}} = 7.64$ Hz, CH_{Ar}), 8.08 (d, 2H, $^3J_{\text{HH}} = 8.92$ Hz, CH_{Ar}), 8.26 (s, 1H, N-CH).

^{13}C - $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 298K, TMS): δ (ppm): 21.5 (s, CH_3), 56.1 (s, OCH_3), 115.2 (s, CH_{Ar}), 118.5 (s, N-CH), 126.1 (s, CH_{Ar}), 126.2 (s, C^{IV}), 127.2 (s, C^{IV}), 129.8 (s, CH_{Ar}), 131.3 (s, CH_{Ar}), 139.2 (s, C^{IV}), 147.5 (s, C^{IV}), 165.5 (s, C^{IV}).

HRMS calcd. for $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_3\text{S}$ ($\text{M}+\text{H}$) $^+$ 330.0907, **found** 330.0912.

1-(4-Methoxybenzenesulfonyl)-4-(3,5-trifluoromethylbenzene)-1H-1,2,3-triazole (7bj) ^[4]

p-Methoxybenzenesulfonyl azide (213 mg, 1.00 mmol), 3,5-bis(trifluoromethyl)-phenylacetylene (186 μ L, 1.05 mmol). 1-(4-Methoxybenzenesulfonyl)-4-(3,5-bis(trifluoromethyl)benzene)-1H-1,2,3-triazole product was obtained as a colorless solid (415 mg, 92%).

¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ (ppm): 3.90 (s, 3H, OCH₃), 7.06 (d, 2H, ³*J*_{HH} = 9.1 Hz, CH_{Ar}), 7.87 (s, 1H, CH_{Ar}), 8.11 (d, 2H, ³*J*_{HH} = 9.1 Hz, CH_{Ar}), 8.28 (s, 2H, CH_{Ar}), 8.47 (s, 1H, N-CH).

1-(Methylsulfonyl)-4-benzene-1H-1,2,3-triazole (7ca) ^[5, 6]

Methylsulfonyl azide (121 mg, 1.00 mmol), phenylacetylene (115 μ L, 1.05 mmol). 1-(Methylsulfonyl)-4-benzene-1H-1,2,3-triazole product was obtained as a colorless solid (216 mg, 97%).

¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ (ppm): 3.00 (s, 3H, CH₃), 7.52 (m, 3H, CH_{Ar}), 7.86 (m, 2H, CH_{Ar}), 8.37 (s, 1H, CH_{Ar}).

1-(Naphthalenesulfonyl)-4-benzene-1H-1,2,3-triazole (7da) ^[4, 6]

Naphthalenesulfonyl azide (233 mg, 1.00 mmol), phenylacetylene (115 μ L, 1.05 mmol). 1-(Naphthalenesulfonyl)-4-benzene-1H-1,2,3-triazole was obtained as a colorless solid (315 mg, 94%).

¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ (ppm): 7.36-7.46 (m, 3H, CH_{Ar}), 7.61-7.84 (m, 5H, CH_{Ar}), 7.97 (d, 1H, ³J_{HH} = 8.52 Hz, CH_{Ar}), 8.24 (d, 1H, ³J_{HH} = 8.91 Hz, CH_{Ar}), 8.41 (s, 1H, NCH), 8.66 (d, 1H, ³J_{HH} = 8.52 Hz, CH_{Ar}), 8.88 (d, 1H, ³J_{HH} = 8.91 Hz, CH_{Ar}).

1-(Naphthalenesulfonyl)-4-(4-fluorobenzene)-1H-1,2,3-triazole (7db)

Naphthalenesulfonyl azide (233 mg, 1.00 mmol), *p*-fluorophenylacetylene (110 μL, 1.05 mmol). 1-(Naphthalenesulfonyl)-4-(4-fluorobenzene)-1H-1,2,3-triazole was obtained as a colorless solid (332 mg, 94% with 10mol% of catalyst).

¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ (ppm): 7.11 (t, 2H, ³J_{HH} = 8.6 Hz, CH_{Ar}), 7.61-7.85 (m, 5H, CH_{Ar}), 7.97 (d, 1H, ³J_{HH} = 8.2 Hz, CH_{Ar}), 8.24 (d, 1H, ³J_{HH} = 8.2 Hz, CH_{Ar}), 8.37 (s, 1H, NCH), 8.65 (dd, 1H, ³J_{HH} = 7.6, 1.2 Hz, CH_{Ar}), 8.87 (dd, 1H, ³J_{HH} = 8.6, 1.2 Hz, CH_{Ar}).

¹³C-{¹H} NMR (75 MHz, CDCl₃, 298K, TMS): δ (ppm): 116.2 (d, *J*_{CF} = 21.7 Hz, CH_{Ar}), 118.9 (s, N-CH), 124.3 (s, CH_{Ar}), 127.9 (s, CH_{Ar}), 128.0 (s, C^{IV}), 128.1 (s, C^{IV}), 128.5 (s, C^{IV}), 129.7 (d, *J*_{CF} = 8.9 Hz, CH_{Ar}), 131.2 (s, C^{IV}), 132.5 (s, CH_{Ar}), 134.4 (s, CH_{Ar}), 137.9 (s, CH_{Ar}).

HRMS calcd. for C₁₈H₁₂FN₃O₂S (M+H)⁺ 354.0707, **found** 354.0710.

1-(Naphthalenesulfonyl)-4-(4-methylbenzene)-1H-1,2,3-triazole (7di)

Naphthalenesulfonyl azide (233 mg, 1.00 mmol), *p*-methylphenylacetylene (106 μL, 1.05 mmol). 1-(Naphthalenesulfonyl)-4-(4-methylbenzene)-1H-1,2,3-triazole obtained as a colorless solid (325 mg, 93%).

¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ (ppm): 2.36 (s, 3H, CH₃), 7.22 (m, 2H, CH_{Ar}), 7.69 (m, 5H, CH_{Ar}), 7.95 (m, 1H, CH_{Ar}), 8.22 (m, 1H, CH_{Ar}), 8.36 (m, 1H, N-CH), 8.64 (m, 1H, CH_{Ar}), 8.87 (s, 1H, CH_{Ar}).

¹³C-{¹H} NMR (75 MHz, CDCl₃, 298K, TMS): δ (ppm): 21.5 (s, CH₃), 118.7 (s, N-CH), 124.2 (s,

CH_{Ar}), 124.4 (s, CH_{Ar}), 126.1 (s, CH_{Ar}), 127.9 (s, CH_{Ar}), 128.5 (s, C^{IV}), 129.8 (s, CH_{Ar}), 129.5 (s, CH_{Ar}), 131.4 (s, C^{IV}), 132.4 (s, CH_{Ar}), 134.4 (s, C^{IV}), 137.8 (s, CH_{Ar}), 139.3 (s, C^{IV}), 147.6 (s, C^{IV}).
HRMS calcd. for C₁₉H₁₅N₃O₂S (M+H)⁺ 350.0958, **found** 350.0962.

1-Benzenesulfonyl-4-benzene-1H-1,2,3-triazole (7ea) ^[5]

Benzenesulfonyl azide (183 mg, 1.00 mmol), phenylacetylene (110 μ L, 1.05 mmol). 1-Benzenesulfonyl-4-benzene-1H-1,2,3-triazole product was obtained as a colorless solid (277 mg, 97%).

¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ (ppm): 7.33 (s, 1H, CH_{Ar}), 7.44 (t, 2H, ³J_{HH} = 7.7 Hz, CH_{Ar}), 7.62 (t, 2H, ³J_{HH} = 7.6 Hz, CH_{Ar}), 7.74 (t, 3H, ³J_{HH} = 7.6 Hz, CH_{Ar}), 7.83 (d, 2H, ³J_{HH} = 8.0 Hz, CH_{Ar}), 8.16 (d, 2H, ³J_{HH} = 8.0 Hz, CH_{Ar}), 8.33 (s, 1H, N-CH).

1-Benzenesulfonyl-4-fluorobenzene-1H-1,2,3-triazole (7eb)

Benzenesulfonyl azide (183 mg, 1.00 mmol), *p*-fluorophenylacetylene (110 μ L, 1.05 mmol). 1-(Benzenesulfonyl)-4-(4-fluorobenzene)-1H-1,2,3-triazole product obtained as a colorless solid (285 mg, 94%).

¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ (ppm): 7.13 (m, 2H, CH_{Ar}), 7.62 (m, 2H, CH_{Ar}), 7.70-7.86 (d, 3H, CH_{Ar}), 8.16 (d, 2H, ³J_{HH} = 8.0 Hz, CH_{Ar}), 8.29 (s, 1H, N-CH).

¹³C-{¹H} NMR (75 MHz, CDCl₃, 298K, TMS): δ (ppm): 116.1 (d, J_{CF} = 22.3 Hz, CH_{Ar}), 118.9 (N-CH), 125.0 (s, C^{IV}), 122.8 (d, J_{CF} = 8.4 Hz, CH_{Ar}), 128.8 (s, CH_{Ar}), 130.0 (s, CH_{Ar}), 135.9 (s, C^{IV}).

HRMS calcd. for C₁₄H₁₀FN₃O₂S (M+H)⁺ 304.0551, **found** 304.0556.

1-Benzenesulfonyl-4-(4-*tert*-butylbenzene)-1H-1,2,3-triazole (7ed)

Benzenesulfonyl azide (183 mg, 1.00 mmol), *tert*-butylphenylacetylene (189 μ L, 1.05 mmol). 1-(4-Methylbenzenesulfonyl)-4-(4-*tert*-butylbenzene)-1H-1,2,3-triazole product was obtained as a colorless solid (328 mg, 96% with 10 mol% of catalyst).

^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ (ppm): 1.34 (s, 9H, CCH_3), 7.46 (d, 2H, $^3J_{\text{HH}} = 8.26$ Hz, CH_{Ar}), 7.61 (m, 2H, CH_{Ar}), 7.74 (m, 2H, CH_{Ar}), 8.15 (d, 2H, $^3J_{\text{HH}} = 8.26$ Hz, CH_{Ar}), 8.29 (s, 1H, N-CH).

^{13}C - $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 298K, TMS): δ (ppm): 31.4 (s, CH_3), 34.9 (s, $\text{C}(\text{CH}_3)_3$), 118.8 (s, N-CH), 126.0 (s, CH_{Ar}), 126.1 (s, CH_{Ar}), 126.8 (s, C^{IV}), 128.8 (s, CH_{Ar}), 129.9 (s, CH_{Ar}), 135.8 (s, C^{IV}), 136.4 (s, C^{IV}), 152.6 (s, C^{IV}).

HRMS calcd. for $\text{C}_{18}\text{H}_{19}\text{FN}_3\text{O}_2\text{S}$ ($\text{M}+\text{H}$) $^+$ 342.1271, **found** 342.1269.

1-Benzenesulfonyl-3-fluorobenzene-1H-1,2,3-triazole (7eg)

Benzenesulfonyl azide (183 mg, 1.00 mmol), 3-fluorophenylacetylene (121 μ L, 1.05 mmol). 1-Benzenesulfonyl-3-fluorobenzene-1H-1,2,3-triazole product was obtained as a colorless solid (297 mg, 98%).

^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ (ppm): 7.07 (tdd, 1H, $^3J_{\text{HH}} = 1$ Hz, 2.5 Hz, 8.0 Hz, CH_{Ar}), 7.41 (m, 1H, CH_{Ar}), 7.54 - 7.67 (m, 4H, CH_{Ar}), 7.75 (tt, 1H, $^3J_{\text{HH}} = 1.8$ Hz, 7.5 Hz, CH_{Ar}), 8.17 (m, 2H, CH_{Ar}), 8.34 (s, 1H, N-CH).

^{13}C - $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 298K, TMS): δ (ppm): 113.3 (d, $J_{\text{CF}} = 23.6$ Hz, CH_{Ar}), 116.2 (d, $J_{\text{CF}} = 21$ Hz, CH_{Ar}), 119.6 (s, N-CH), 121.9 (d, $J_{\text{CF}} = 2.5$ Hz, CH_{Ar}), 128.9 (s, CH_{Ar}), 130.1 (s, CH_{Ar}), 130.8 (s, d, $J_{\text{CF}} = 8.5$ Hz, CH_{Ar}), 136.0 (s, CH_{Ar}), 136.2 (s, C^{IV}), 155.2 (s, C^{IV}), 164.5 (d, $J_{\text{CF}} = 255.0$ Hz, C^{IV}). **HRMS** calcd. for $\text{C}_{14}\text{H}_{10}\text{FN}_3\text{O}_2\text{S}$ ($\text{M}+\text{H}$) $^+$ 304.0551, **found** 304.0551.

1-Benzenesulfonyl-4-methoxybenzene-1H-1,2,3-triazole (7eh)

Benzenesulfonyl azide (183 mg, 1.00 mmol), *p*-methoxyphenylacetylene (136 μ L, 1.05 mmol). 1-(Benzenesulfonyl)-4-(4-methoxybenzene)-1H-1,2,3-triazole product was obtained as a colorless solid (309 mg, 98%).

^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ = 3.84 (s, 3H, OCH_3), 6.95 (m, 2H, CH_{Ar}), 7.60 (m, 2H, CH_{Ar}), 7.73 (m, 1H, CH_{Ar}) overlapped with 7.76 (m, 2H, CH_{Ar}), 8.15 (m, 2H, CH_{Ar}), 8.23 (s, 1H, N-CH).

^{13}C - $\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 298K, TMS): δ (ppm): 55.5 (s, OCH_3), 114.6 (s, CH_{Ar}), 118.1 (N-CH), 121.5 (s, C^{IV}), 127.6 (s, CH_{Ar}), 128.8 (s, CH_{Ar}), 130.0 (s, CH_{Ar}), 135.8 (s, CH_{Ar}), 136.4 (s, C^{IV}), 147.5 (s, C^{IV}), 160.5 (s, C^{IV}).

HRMS calcd. for $\text{C}_{15}\text{H}_{13}\text{FN}_3\text{O}_3\text{S}$ ($\text{M}+\text{H}$) $^+$ 316.0750, **found** 316.0750.

1-(2,4,6-Tri-*iso*-propyl-benzenesulfonyl)-4-benzene-1H-1,2,3-triazole (7fa) ^[8]

2,4,6-Tri-*iso*-propyl-benzenesulfonyl azide (309 mg, 1.00 mmol), phenylacetylene (115 μ L, 1.05 mmol). 1-(2,4,6-Tri-*iso*-propyl-benzenesulfonyl)-4-benzene-1H-1,2,3-triazole product was obtained as a colorless solid (403 mg, 98%).

^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ (ppm): 1.25 (m, 18H, CHCH_3), 2.92 (m, 1H, CHCH_3), 4.18 (m, 2H, CHCH_3), 7.36-7.56 (m, 5H, CH_{Ar}), 7.87 (m, 2H, CH_{Ar}), 8.40 (s, 1H, N-CH).

1-(4-Bromobenzenesulfonyl)-4-benzene-1H-1,2,3-triazole (7ga) ^[5]

p-Bromobenzenesulfonyl azide (262 mg, 1.00 mmol), phenylacetylene (115 μ L, 1.05 mmol). 1-(4-Bromobenzenesulfonyl)-4-benzene-1H-1,2,3-triazole was obtained as a colorless solid (335 mg, 92%).

¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ (ppm): 7.44 (m, 3H, CH_{Ar}), 7.76 (m, 2H, CH_{Ar}), 7.83 (m, 2H, CH_{Ar}), 8.02 (m, 2H, CH_{Ar}), 8.31 (s, 1H, N-CH).

1-(4-Bromobenzenesulfonyl)-4-(*tert*-butylmethylbenzene)-1H-1,2,3-triazole (7gd)

p-Bromobenzenesulfonyl azide (262.1 mg, 1.00 mmol), 4-*tert*-butylphenylacetylene (189 μ L, 1.05 mmol). 1-(4-Bromobenzenesulfonyl)-4-(4-*tert*-butyl-methylbenzene)-1H-1,2,3-triazole was obtained as a colorless solid (411.9 mg, 98% with 10 mol% of catalyst).

¹H NMR (400 MHz, CDCl₃, 298K, TMS): δ (ppm): 1.34 (s, 9H, CCH₃), 7.46 (m, 2H, CH_{Ar}), 7.75 (m, 4H, CH_{Ar}), 8.00 (s, 2H, CH_{Ar}), 8.27 (s, 1H, N-CH).

¹³C-{¹H} NMR (75 MHz, CDCl₃, 298K, TMS): δ (ppm): 31.4 (s, CCH₃), 34.9 (s, CCH₃), 118.7 (s, N-CH), 125.8 (s, CH_{Ar}), 126.0 (s, CH_{Ar}), 126.1 (s, CH_{Ar}), 130.1 (s, CH_{Ar}), 131.6 (s, C^{IV}), 133.4 (s, C^{IV}), 135.3 (s, C^{IV}), 152.7 (s, C^{IV}).

HRMS calcd. for C₁₈H₁₈BrN₃O₂S (M+H)⁺ 420.0376, **found** 420.0377.

1-(4-Bromobenzenesulfonyl)-4-(3-fluorobenzene)-1H-1,2,3-triazole (7gg)

p-Bromobenzenesulfonyl azide (262 mg, 1.00 mmol), *m*-fluorophenylacetylene (121 μ L, 1.05 mmol). 1-(4-Bromobenzenesulfonyl)-4-(3-fluorobenzene)-1H-1,2,3-triazole was obtained as a colorless solid (375 mg, 98% with 10 mol% of catalyst).

^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ (ppm): 7.09 (d, 1H, CH_{Ar}), 7.41 (s, 1H, CH_{Ar}), 7.53-7.62 (m, 2H, CH_{Ar}), 7.77 (m, 2H, CH_{Ar}), 8.02 (s, 2H, CH_{Ar}), 8.32 (s, 1H, N-CH).

1-(4-Bromobenzenesulfonyl)-4-(3,5-trifluoromethylbenzene)-1H-1,2,3-triazole (7gj)

p-Bromobenzenesulfonyl azide (262 mg, 1.00 mmol), 3,5-trifluoromethylphenylacetylene (186 μ L, 1.05 mmol). 1-(4-Bromobenzenesulfonyl)-4-(3,5-trifluoromethylbenzene)-1H-1,2,3-triazole product was obtained as a colorless solid (480 mg, 96%).

^1H NMR (400 MHz, CDCl_3 , 298K, TMS): δ (ppm): 7.79 (d, 2H, $^3J_{\text{HH}} = 8.9$ Hz, CH_{Ar}), 7.89 (s, 1H, CH_{Ar}), 8.04 (d, 2H, $^3J_{\text{HH}} = 8.9$ Hz, CH_{Ar}), 8.29 (s, 2H, CH_{Ar}), 8.49 (s, 1H, N-CH).

$^{13}\text{C}\{-^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 298K, TMS): δ (ppm): 120.4 (N-CH), 122.8 (s, CH_{Ar}), 123.2 (q, $J_{\text{CF}} = 275.0$ Hz, C^{IV}), 126.3 (s, CH_{Ar}), 130.3 (s, CH_{Ar}), 131.1 (s, C^{IV}), 132.4 (q, $J_{\text{CF}} = 34$ Hz, C^{IV}), 133.6 (s, CH_{Ar}), 134.7 (s, C^{IV}), 144.9 (s, C^{IV}).

HRMS calcd. for $\text{C}_{16}\text{H}_8\text{F}_6\text{N}_3\text{O}_2\text{S}$ ($\text{M}+\text{H}$) $^+$ 499.9498, **found** 499.9490.

5. Optimization

5.1. Comparison of complexes^a

L	T (°C)	[Cu] (mol%)	Solvent	Conversion (%) ^b
PtBu ₃	RT	10	toluene	100
	40	10	toluene	80
ICy	RT	10	toluene	30
	40	10	toluene	50
ItBu	RT	10	toluene	30
	40	10	toluene	90
IMes	RT	10	toluene	10
	40	10	toluene	8
PtBu ₃	RT	10	water	80
	40	10	water	100
ICy	RT	10	water	30
	40	10	water	50
ItBu	RT	10	water	50
	40	10	water	70
IMes	RT	10	water	20
	40	10	water	25
PtBu ₃	RT	10	EtOAc	80
	40	10	EtOAc	90
ICy	RT	10	EtOAc	10
	40	10	EtOAc	50
ItBu	RT	10	EtOAc	6
	40	10	EtOAc	100
IMes	RT	10	EtOAc	0
	40	10	EtOAc	10
PtBu ₃	RT	10	DCM	70
	40	10	DCM	60
ICy	RT	10	DCM	<10
	40	10	DCM	20
ItBu	RT	10	DCM	10
	40	10	DCM	40
IMes	RT	10	DCM	10
	40	10	DCM	0
PtBu ₃	RT	10	THF	100
	40	10	THF	80
ICy	RT	10	THF	10
	40	10	THF	40
ItBu	RT	10	THF	11
	40	10	THF	30
IMes	RT	10	THF	0

PtBu ₃	RT	10	Dioxane	80
	40	10	Dioxane	20
ICy	RT	10	Dioxane	5
	40	10	Dioxane	20
ItBu	RT	10	Dioxane	7
	40	10	Dioxane	14
IMes	RT	10	Dioxane	0
PtBu ₃	RT	10	Acetonitrile	40
	40	10	Acetonitrile	30
ICy	RT	10	Acetonitrile	20
	40	10	Acetonitrile	20
ItBu	RT	10	Acetonitrile	10
	40	10	Acetonitrile	90
IMes	RT	10	Acetonitrile	14
PtBu ₃	RT	10	Propanol	80
	40	10	Propanol	20
ICy	RT	10	Propanol	11
	40	10	Propanol	20
ItBu	RT	10	Propanol	25
	40	10	Propanol	35
PtBu ₃	RT	10	Chloroform	60
	40	10	Chloroform	50
ICy	RT	10	Chloroform	10
	40	10	Chloroform	10
ItBu	RT	10	Chloroform	10
	40	10	Chloroform	20
IMes	RT	10	Chloroform	10
	40	10	Chloroform	13
PtBu ₃	RT	10	Neat	100
	40	10	Neat	80
ICy	RT	10	Neat	32
	40	10	Neat	40
ItBu	RT	10	Neat	25
	40	10	Neat	90
IMes	RT	10	Neat	13
	40	10	Neat	15

^a Reaction conditions: azide (1.00 mmol), alkyne (1.05 mmol), solvent (0.5 mL). ^b Conversion determined by ¹H-NMR, minimum average of 2 reactions. EtOAc = ethyl acetate, THF = tetrahydrofuran, DCM = dichloromethane

5.2. Comparison between the [Cu(IPr)(PtBu₃)] and the bis-carbene copper (I) complexes at lower loading

Catalyst	T (°C)	[Cu] (mol%)	Solvent	Conversion (%) ^b
PtBu ₃	RT	5	toluene	100
	40	5	toluene	50
ICy	RT	5	toluene	20
	40	5	toluene	20
ItBu	RT	5	toluene	30
	40	5	toluene	20
PtBu ₃	RT	5	water	40
	40	5	water	40
ICy	RT	5	water	40
	40	5	water	30
ItBu	RT	5	water	60
	40	5	water	50
PtBu ₃	RT	5	EtOAc	60
	40	5	EtOAc	30
ICy	RT	5	EtOAc	7
	40	5	EtOAc	25
ItBu	RT	5	EtOAc	10
	40	5	EtOAc	20
PtBu ₃	RT	5	THF	20
PtBu ₃	RT	5	Dioxane	20

^a Reaction conditions: azide (1.00 mmol), alkyne (1.05 mmol), solvent (0.5 mL). ^b Conversion determined by ¹H-NMR, minimum average of 2 reactions. EtOAc = ethyl acetate, THF = tetrahydrofuran

6. NMR spectra

6.1 ^1H NMR (CD_2Cl_2) and $^{13}\text{C}\{-^1\text{H}\}$ NMR (CD_2Cl_2) of **4**

6.2. NMR Spectra of catalysis products

Compound 7aa

Compound 7ab

Compound 7ac

Compound 7ad

Compound 7ae

Compound 7af

Compound 7ag

Compound 7ah

Compound 7ai

Compound 7ba

Compound 7bb

Compound 7bd

Compound 7bf

Compound 7bg

Compound 7bh

Compound 7bi

Compound 7bj

Compound 7ca

Compound 7da

Compound 7db

Compound 7di

Compound 7ea

Compound 7eb

Compound 7ed

Compound 7eg

Compound eh

Compound 7a

Compound 7ga

Compound 7gd

Compound 7gg

Compound 7gj

7. Mechanistic studies

A mixture of $[\text{Cu}(\text{IPr})(\text{P}^t\text{Bu}_3)]$ **4** and phenylacetylene was stirred overnight in acetonitrile at RT. The solvent was removed *in vacuo* and toluene was added. The precipitate (**B**) was collected by filtration and the solvent of the supernatant solution was removed *in vacuo*.

8. References

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