

SUPPORTING INFORMATION

Dinuclear Cu(I) Halides with Terphenyl Phosphines: Synthesis, Photophysical Studies and Catalytic Applications in CuAAC Reactions

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1. General methods.

All preparations and manipulations were carried out under oxygen-free nitrogen, using conventional Schlenk techniques. Solvents were rigorously dried and degassed before use. Ligands **L1-L5**,¹ organic azides² and the iodide alkynes³ were synthesized following previously reported procedures. Reagents were purchased from commercial suppliers and used without further purification.

NMR spectra were recorded on Bruker Avance DPX-300, Avance DRX-400, Avance DRX-500, and 400 Ascend/R spectrometers. The ¹H and ¹³C resonances of the solvent were used as the internal standard and the chemical shifts are reported relative to TMS while ³¹P was referenced to external H₃PO₄. Elemental analyses were performed by the Servicio de Microanálisis of Instituto de Investigaciones Químicas (IIQ). CITIUS. X-ray diffraction studies were accomplished at Centro de Investigación Tecnología e Innovación, CITIUS (Universidad de Sevilla) and Centro de Investigación en Química Sostenible, CIQSO (Universidad de Huelva).

Diffuse reflectance spectra were acquired in a Shimadzu UV-2501PC equipped with an integrating sphere. The powdered samples were smashed between two quartz lamellae, accommodated on a BaSO₄ filled support and the spectra run using an identical BaSO₄ filled support as blank. The remission function, F(R), was calculated using the Kubelka–Munk equation for optically thick samples. UV–vis absorbance spectra were acquired on a UV–vis–NIR Varian Cary 5000 spectro-photometer and emission spectra were recorded on a SPEX Fluorolog-3 Model FL3–22 spectrofluorimeters. Time-resolved emission spectra were acquired in the same apparatus, using a pulsed xenon lamp with a full-width of 3 μs. Spectra and decays were collected with a minimum 50 μs delay to remove any interference from the lamp. Luminescence quantum efficiencies were measured by the absolute method with an Integrated Sphere. Films for optical characterization were prepared in zeonex (10% in toluene) matrix by drop-casting onto a quartz substrate with an emitter concentration of

¹ (a) Ortega-Moreno, L.; Fernández-Espada, M.; Moreno, J. J.; Navarro-Gilabert, C.; Campos, J.; Conejero, S.; López-Serrano, J.; Maya, C.; Peloso, R.; Carmona, E. *Polyhedron*, **2016**, *116*, 170-181. (b) Marín, M.; J. Moreno, J.; Navarro-Gilabert, C.; Álvarez, E.; Maya, C.; Peloso, R.; Nicasio, M. C.; Carmona, E. *Chem. Eur. J.* **2019**, *25*, 260-272

² a) Alvarez, S. G.; Alvarez, M. T. *Synthesis* **1997**, 413-414. b) Tao, C-Z.; Cui, X.; Li, J.; Liu, A-X.; Liu, L.; Guo, Q-X. *Tetrahedron Lett.* **2007**, *48*, 3525-3529. c) Campbell-Verduyn, L.; Mirfeizi, L.; Dierckx, R. A.; Elsinga, P. H.; Feringa, B. L. *Chem. Commun.* **2009**, 2139-2141.

³ Hein, J. E.; Tripp, J. C.; Krasnova, L. B.; Sharpless, B. K.; Fokin, V. V. *Angew. Chem. Int. Ed.* **2009**, *48*, 8018-8021.

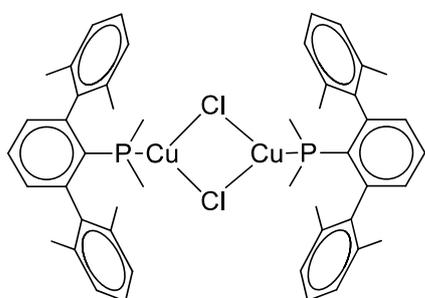
1% (m/m). The Raman analysis was carried out using a Labram 300 Jobin Yvon spectrometer, equipped with a HeNe laser 17mW operating at 633 nm. The laser beam was focused with a 50x Olympus objective lens. The laser power at the surface of the samples was varied with the aid of a set of neutral density filters (D 0.6).

DFT calculations have been carried out with the program Gaussian 09 using the B3LYP functional, 6-31G** basis set for C, H and a standard double- ζ polarized basis set, namely, the LANL2DZ set for Cu, I and P augmented with polarization functions on P (a d orbital with exponent 0.364 for P, upon EMSL basis set ex-change database). For Cu, P and I we applied also Effective Core Potentials. Geometry optimization and TD-DFT calculations were performed in cyclohexane with the PCM solvation method. Molecular Orbital visualization for all the complexes was performed using Avogadro 1.2.0.

2. General procedure for the synthesis of $[\text{Cu}(\mu\text{-X})(\text{PR}_2\text{Ar}')_2]_2$ complexes, 1-5.

Dichloromethane (*ca.* 5 mL) was added to an equimolar mixture (*ca.* 0.1-0.3 mmol) of the ligand (**L1-L5**) and the copper halide. The reaction mixture was stirred at room temperature for 12 h. After filtration, the resulting solution was evaporated to dryness affording a colorless or pale yellow solid, which was washed with petroleum ether (*ca.* 5 mL) and dried *under vacuum*. In most cases, the crude product was pure enough for subsequent use; otherwise, analytically pure samples were obtained by recrystallization as detailed below.

$[\text{CuCl}(\text{PMe}_2\text{Ar}^{\text{Xyl}_2})_2]_2$, **1a**. Colourless solid. Yield: 98%.



^1H NMR (300 MHz, CDCl_3): δ 7.57 (t, $^3J_{\text{HH}} = 7.6$ Hz, 1H, *p*- C_6H_3), 7.30 (t, 2H, *p*-Xyl), 7.18 (d, $^3J_{\text{HH}} = 7.6$ Hz, 4H, *m*-Xyl), 7.07 (dd, $^3J_{\text{HH}} = 7.6$ Hz, $^4J_{\text{HP}} \sim 1$ Hz, 2H, *m*- C_6H_3), 2.05 (s, 12 H, CH_3 -Xyl), 1.14 (d, $^2J_{\text{HP}} = 6.8$ Hz, 6H, P- CH_3).

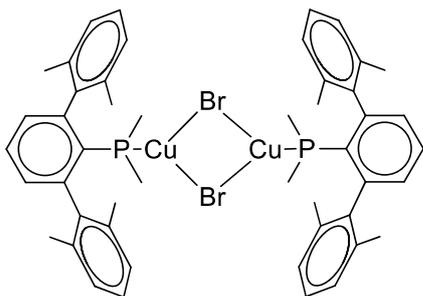
$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 147.1 (br s, *o*-

C₆H₃), 140.2 (br s, *ipso*-Xyl), 135.4 (*o*-Xyl), 131.8 (*p*-C₆H₃), 130.5 (d, ³J_{CP} = 6 Hz, *m*-C₆H₃), *ipso*-C₆H₃ masked by more intense signals, 128.7 (*m*-Xyl), 128.6 (*p*-Xyl), 21.5 (CH₃-Xyl), 14.0 (d, ¹J_{CP} = 23 Hz, P-CH₃).

³¹P{¹H} NMR (121 MHz, CDCl₃): δ -34.3 (br s).

Elemental analysis calculated (found) for C₂₄H₂₇ClPCu: C 64.71 (64.5), H 6.11 (6.2) %.

[CuBr(PMe₂Ar^{Xyl})₂]₂, **1b**. Colourless solid. Yield: 92%.



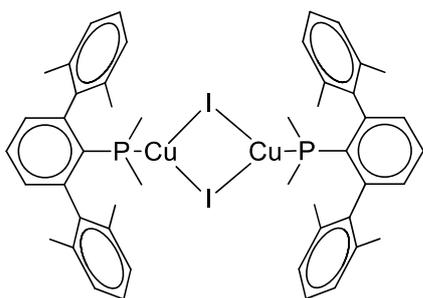
¹H NMR (300 MHz, CDCl₃): δ 7.56 (t, ³J_{HH} = 7.6 Hz, 1H, *p*-C₆H₃), 7.30 (t, 2H, *p*-Xyl), 7.19 (d, ³J_{HH} = 7.6 Hz, 4H, *m*-Xyl), 7.07 (d, ³J_{HH} = 7.6 Hz, 2H, *m*-C₆H₃), 2.08 (s, 12 H, CH₃-Xyl), (d, ²J_{HP} = 6.8 Hz, 6H, P-CH₃).

¹³C{¹H} NMR (75 MHz, CDCl₃): δ 147.1 (d, ²J_{CP} = 13 Hz, *o*-C₆H₃), 140.5 (d, ³J_{CP} = 6 Hz, *ipso*-Xyl), 135.5 (*o*-Xyl), 131.5 (*p*-C₆H₃), 130.5 (d, ³J_{CP} = 6 Hz, *m*-C₆H₃), 129.2 (d, ¹J_{CP} = 24 Hz, *ipso*-C₆H₃), 128.6 (*m*-Xyl), 128.4 (*p*-Xyl), 21.6 (CH₃-Xyl), 14.2 (d, ¹J_{CP} = 24 Hz, P-CH₃).

³¹P{¹H} NMR (121 MHz, CDCl₃): δ -34.8 (br s).

Elemental analysis calculated (found) for C₂₄H₂₇CuBrP: C 58.84 (58.8), H 5.56 (5.6).

[CuI(PMe₂Ar^{Xyl})₂]₂, **1c**. Colourless solid. Yield: 93%.



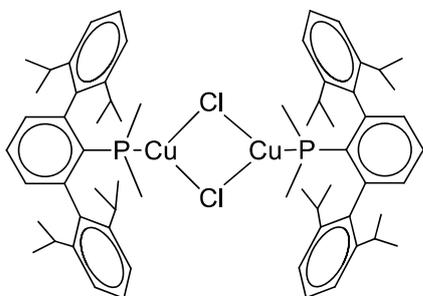
¹H NMR (300 MHz, CDCl₃): δ 7.48 (td, ³J_{HH} = 7.6 Hz, ⁴J_{HP} = 1.3 Hz, 1H, *p*-C₆H₃), 7.21-7.10 (m, 6H, H_{ar}), 6.99 (dd, ³J_{HH} = 7.6, ³J_{HP} = 2.7 Hz, 2H, *m*-C₆H₃), 2.07 (s, 12H, CH₃-Xyl), 1.01 (d, ²J_{HP} = 5.2 Hz, 6H, P-CH₃).

¹³C{¹H} NMR (75 MHz, CDCl₃): δ 147.0 (d, ²J_{CP} = 13 Hz, *o*-C₆H₃), 141.2 (d, ³J_{CP} = 6 Hz, *ipso*-Xyl), 135.7 (*o*-Xyl), 130.8 (*p*-C₆H₃), 130.3 (d, ³J_{CP} = 6 Hz, *m*-C₆H₃), 129.4 (d, ¹J_{CP} = 24 Hz, *ipso*-C₆H₃), 128.4 (*m*-Xyl), 128.0 (*p*-Xyl), 22.0 (CH₃-Xyl), 14.8 (d, ¹J_{CP} = 21 Hz, P-CH₃).

³¹P{¹H} NMR (121 MHz, CDCl₃): δ -40.0 (br s).

Elemental analysis calculated (found) for C₂₄H₂₇CuIP: C 53.69 (54.0), H 5.07 (5.3).

[CuCl(PMe₂Ar^{Dipp})₂]₂, **2a**. Pale-yellow crystals obtained by recrystallization at 5 °C from pentane: CH₂Cl₂ (3:1) mixtures. Yield: 84%.



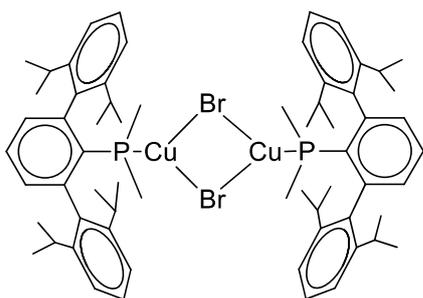
¹H NMR (300 MHz, CDCl₃): δ 7.53 (m, 3H, *p*-C₆H₃ and *p*-Dipp), 7.31 (d, ³J_{HH} = 7.5 Hz, 4H, *m*-Dipp), 7.21 (dd, ³J_{HH} = 7.5 Hz, ³J_{HP} = 2.7 Hz, 2H, *m*-C₆H₃), 2.47 (sept, ³J_{HH} = 6.8 Hz, 4H, *CH*-*i*Pr), 1.33 (d, ³J_{HH} = 6.8 Hz, 12H, *CH*₃-*i*Pr), 1.19 (d, ²J_{HP} = 6.4 Hz, 6H, P-CH₃), 1.05 (d, ³J_{HH} = 6.8 Hz, 12H, *CH*₃-*i*Pr).

¹³C{¹H} NMR (75 MHz, CDCl₃): δ 146.0 (d, ²J_{CP} = 15 Hz, *o*-C₆H₃), 145.8 (*o*-Dipp), 137.2 (d, ³J_{CP} = 7 Hz, *ipso*-Dipp), 131.9 (d, ³J_{CP} = 6 Hz, *m*-C₆H₃), 129.7 (s, *p*-C₆H₃), 129.6 (s, *p*-Dipp), 124.1 (s, *m*-Dipp), *ipso*-C₆H₃ masked by more intense signals, 31.2 (s, *CH*-*i*Pr), 25.4 (s, *CH*₃-*i*Pr), 22.8 (s, *CH*₃-*i*Pr), 13.9 (d, ¹J_{CP} = 26 Hz, P-CH₃).

³¹P{¹H} NMR (121 MHz, CDCl₃): δ -35.7 (br s).

Elemental analysis calculated (found) for C₃₂H₄₃CuClP:bC 68.92 (68.9), H 7.77 (7.5).

[CuBr(PMe₂Ar^{Dipp})₂]₂, **2b**. Pale-yellow crystals obtained by recrystallization at 5 °C from pentane: CH₂Cl₂ (3:1) mixtures. Yield: 85%.



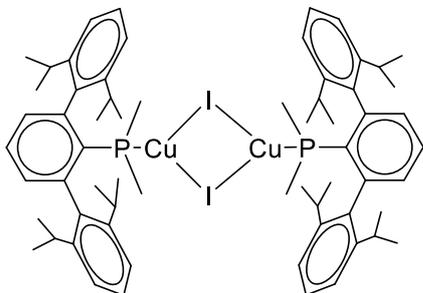
¹H NMR (300 MHz, CDCl₃): δ 7.53 (m, 3H, *p*-C₆H₃ and *p*-Dipp), 7.32 (d, ³J_{HH} = 7.5 Hz, 4H, *m*-Dipp), 7.20 (dd, ³J_{HH} = 7.5 Hz, ³J_{HP} = 2.7 Hz, 2H, *m*-C₆H₃), 2.49 (sept, ³J_{HH} = 6.8 Hz, 4H, *CH*-*i*Pr), 1.33 (d, ³J_{HH} = 6.8 Hz, 12H, *CH*₃-*i*Pr), 1.18 (d, ²J_{HP} = 6.4 Hz, 6H, P-CH₃), 1.07 (d, ³J_{HH} = 6.8 Hz, 12H, *CH*₃-*i*Pr).

¹³C{¹H} NMR (75 MHz, CDCl₃): δ 146.1 (d, ²J_{CP} = 15 Hz, *o*-C₆H₃), 145.7 (*o*-Dipp), 137.1 (d, ³J_{CP} = 7 Hz, *ipso*-Dipp), 131.8 (d, ³J_{CP} = 6 Hz, *m*-C₆H₃), 129.6 (*p*-C₆H₃), 129.6 (*p*-Dipp), 124.3 (*m*-Dipp), *ipso*-C₆H₃ masked by more intense signals, 31.2 (*CH*-*i*Pr), 25.4 (*CH*₃-*i*Pr), 22.8 (*CH*₃-*i*Pr), 13.8 (d, ¹J_{CP} = 25 Hz, P-CH₃).

³¹P{¹H} NMR (121 MHz, CDCl₃): δ -34.9 (br s).

Elemental analysis calculated (found) for C₃₂H₄₃CuBrP: C 63.83 (63.5), H 7.20 (7.6).

[CuI(PMe₂Ar^{Dipp})₂], **2c**. Pale-yellow solid. Yield: 93%.

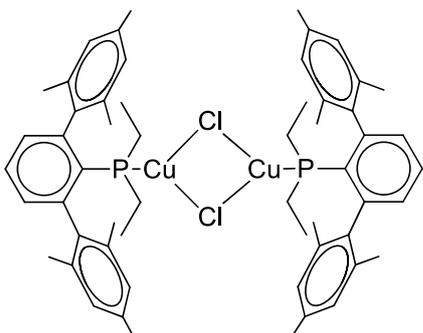


¹H NMR (300 MHz, CDCl₃): δ 7.52 (m, 3H, *p*-C₆H₃ and *p*-Dipp), 7.34 (d, ³J_{HH} = 7.6 Hz, 4H, *m*-Dipp), 7.20 (dd, ³J_{HH} = 7.6 Hz, ³J_{HP} = 2.8 Hz, 2H, *m*-C₆H₃), 2.49 (sept, ³J_{HH} = 6.8 Hz, 4H, *CH*-*i*Pr), 1.34 (d, ³J_{HH} = 6.8 Hz, 12H, *CH*₃-*i*Pr), 1.17 (d, ²J_{HP} = 6.2 Hz, 6H, P-CH₃), 1.07 (d, ³J_{HH} = 6.8 Hz, 12H, *CH*₃-*i*Pr).

³¹P{¹H} NMR (121 MHz, CDCl₃): δ -32.9 (br s).

Elemental analysis calculated (found) for C₃₂H₄₃CuIP: C 59.21 (59.0), H 6.68 (6.7).

[CuCl(PEt₂Ar^{Mes})₂], **3a**. Colorless solid. Yield: 98%.



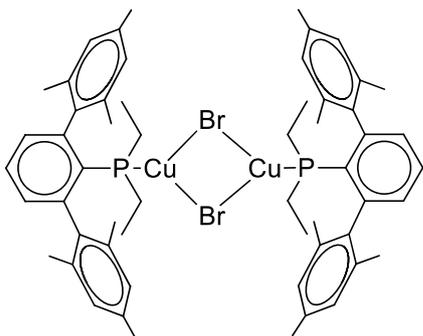
¹H NMR (300 MHz, CDCl₃): δ 7.53 (td, ³J_{HH} = 7.7, ⁴J_{HP} = 1.5 Hz, 1H, *p*-C₆H₃), 7.07 (dd, ³J_{HH} = 7.7, ³J_{HP} = 2.8 Hz, 2H, *m*-C₆H₃), 7.03 (s, 4H, *m*-Mes), 2.40 (s, 6H, *p*-CH₃), 2.00 (s, 12H, *o*-CH₃), 1.67-1.51 (ABX₃Y system, 2H, *CHH*-Et), 1.46-1.30 (ABX₃Y, 2H, *CHH*-Et), 1.05 (dt, ³J_{HP} = 21.6, ³J_{HH} = 7.6 Hz, 6H, CH₂CH₃).

¹³C{¹H} NMR (75 MHz, CDCl₃): δ 148.2 (d, ²J_{CP} = 13 Hz, *o*-C₆H₃), 138.7 (*p*-Mes), 137.3 (d, ³J_{CP} = 6 Hz, *ipso*-Mes), 135.3 (*o*-Mes), 131.7 (*p*-C₆H₃), 130.9 (d, ³J_{CP} = 6 Hz, *m*-C₆H₃), 129.5 (*m*-Mes), 127.8 (d, ¹J_{CP} = 31 Hz, *ipso*-C₆H₃), 21.3 (*p*-CH₃), 18.9 (d, ¹J_{CP} = 22 Hz, CH₂CH₃), 12.9 (d, ²J_{CP} = 9 Hz, CH₂CH₃).

³¹P{¹H} NMR (121 MHz, CDCl₃): δ 2.6 (br s).

Elemental analysis calculated (found) for C₂₈H₃₅CuClP: C 67.05 (67.4), H 7.03 (7.4).

[CuBr(PEt₂Ar^{Mes2})₂], **3b**. Colourless solid. Yield: 90 %.



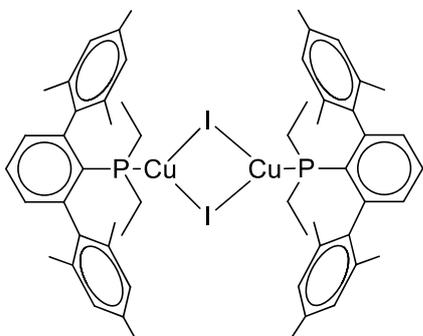
¹H NMR (300 MHz, CDCl₃): δ 7.53 (td, ³J_{HH} = 7.7, ⁴J_{HP} = 1.4 Hz, 1H, *p*-C₆H₃), 7.07 (dd, ³J_{HH} = 7.7, ³J_{HP} = 2.8 Hz, 2H, *m*-C₆H₃), 7.03 (s, 4H, *m*-Mes), 2.40 (s, 6H, *p*-CH₃), 2.00 (s, 12H, *o*-CH₃), 1.70-1.51 (ABX₃Y system, 2H, CHH-Et), 1.48-1.29 (ABX₃Y system, 2H, CHH-Et), 1.06 (dt, ³J_{HP} = 21.6, ³J_{HH} = 7.6 Hz, 6H, CH₂CH₃).

¹³C{¹H} NMR (75 MHz, CDCl₃): δ 148.3 (d, ²J_{CP} = 13 Hz, *o*-C₆H₃), 138.8 (*p*-Mes), 137.3 (d, ³J_{CP} = 6 Hz, *ipso*-Mes), 135.5 (*o*-Mes), 131.7 (*p*-C₆H₃), 130.9 (d, ³J_{CP} = 6 Hz, *m*-C₆H₃), 129.7 (*m*-Mes), 128.1 (d, ¹J_{CP} = 31 Hz, *ipso*-C₆H₃), 21.4 (*p*-CH₃), 18.9 (d, ¹J_{CP} = 22 Hz, CH₂CH₃), 12.8 (d, ²J_{CP} = 9 Hz, CH₂CH₃) ppm.

³¹P NMR (121 MHz, CDCl₃): δ 2.1 (br s).

Elemental analysis calculated (found) for C₂₈H₃₅CuBrP: C 61.59 (61.6), H 6.46 (6.7).

[CuI(PEt₂Ar^{Mes2})₂], **3c**. Colourless solid. Yield: 98 %.



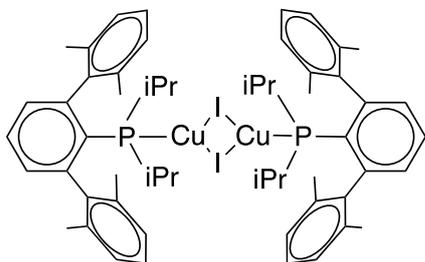
¹H NMR (300 MHz, CDCl₃): δ 7.53 (td, ³J_{HH} = 7.7, ⁴J_{HP} = 1.5 Hz, 1H, *p*-C₆H₃), 7.08-7.02 (m, 6H, H_{ar}), 2.40 (s, 6H, CH₃-Mes), 2.00 (s, 12 H, CH₃-Mes), 1.69-1.52 (m, 2H, CH₂CH₃), 1.50-1.33 (m, 2H, CH₂CH₃), 1.08 (dt, ²J_{HP} = 21.3; ³J_{HH} = 7.6 Hz, 6H, CH₂CH₃).

¹³C{¹H} NMR (75 MHz, CDCl₃): δ 148.0 (d, ²J_{CP} = 13 Hz, *o*-C₆H₃), 138.4 (*p*-Mes), 137.3 (d, ³J_{CP} = 6 Hz, *ipso*-Mes), 135.0 (*o*-Mes), 131.3 (*p*-C₆H₃), 130.7 (d, ³J_{CP} = 6 Hz, *m*-C₆H₃), 129.8 (*m*-Mes), 128.5 (d, ¹J_{CP} = 31 Hz, *ipso*-C₆H₃), 21.4, 21.3 (CH₃-Mes), 18.6 (d, ¹J_{CP} = 22 Hz, CH₂CH₃), 12.2 (d, ²J_{CP} = 9 Hz, CH₂CH₃).

³¹P{¹H} NMR (121 MHz, CDCl₃): δ 0.7 (br s).

Elemental analysis calculated (found) for C₂₈H₃₅CuIP: C 56.71 (56.4), H 5.95 (6.5).

[CuI(PiPr₂Ar^{Xyl})₂]₂, 4c. Pale-yellow crystals obtained by recrystallization at 5 °C from pentane: CH₂Cl₂ (3:1) mixtures. Yield: 90%.

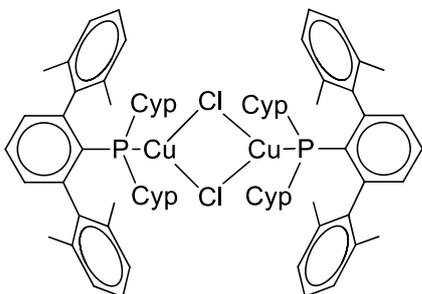


¹H NMR (300MHz, CDCl₃): δ 7.56 (t, ³J_{HH} = 7.7 Hz, 1H, *p*-C₆H₃), 7.35 (t, ³J_{HH} = 7.7 Hz, 2H, *p*-Xyl), 7.24 (d, *J* = 7.7 Hz, 4H, *m*-Xyl), 7.12 (dd, ³J_{HH} = 7.6 Hz, ³J_{HP} = 2.6 Hz, 2H, *m*-C₆H₃), 2.20 (m, 2H, CH-*i*Pr), 2.08 (s, 12H, CH₃-Xyl), 1.13 (dd, ³J_{HH} = 7.2 Hz, ³J_{HP} = 21.3 Hz, 6H, CH₃-*i*Pr), 0.75 (dd, ³J_{HH} = 7.2 Hz, ³J_{HP} = 15.5 Hz, 6H, CH₃-*i*Pr).

³¹P{¹H} NMR (121 MHz, CDCl₃): δ 25.7 (br s).

Elemental analysis calculated (found) for C₂₈H₃₅CuIP: C 56.71 (56.7), H 5.95 (5.8).

[CuCl(PCyp₂Ar^{Xyl})₂]₂, 5a. Pale-yellow crystals obtained by recrystallization at 5 °C from pentane: CH₂Cl₂ (3:1) mixtures. Yield: 89 %.



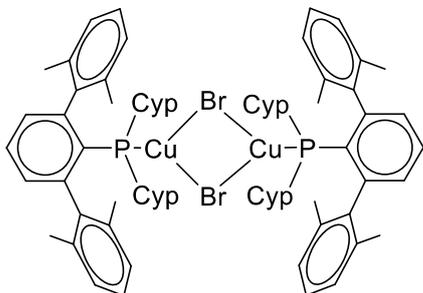
¹H NMR (300 MHz, CDCl₃): δ 7.53 (t, ³J_{HH} = 7.7 Hz, 1H, *p*-C₆H₃), 7.32 (t, ³J_{HH} = 7.7 Hz, 2H, *p*-Xyl), 7.23 (d, ³J_{HH} = 7.7 Hz, 4H, *m*-Xyl), 7.05 (d, ³J_{HH} = 7.7 Hz, 2H, *m*-C₆H₃), 2.03 (s, 12 H, CH₃-Xyl), 1.99-1.10 (m, 18H, Cyp).

¹³C{¹H} NMR (75 MHz, CDCl₃): δ 148.0 (d, ²J_{CP} = 13 Hz, *o*-C₆H₃), 140.6 (d, ³J_{CP} = 6 Hz, *ipso*-Xyl), 135.6 (*o*-Xyl), 131.1 (d, ⁴J_{HP} = 1 Hz, *p*-C₆H₃), 130.5 (d, ¹J_{CP} = 24 Hz, *ipso*-C₆H₃), 128.7 (*p*-Xyl), 128.5 (*m*-Xyl), 35.7-35.2 various signals (CH₂Cyp), 31.5 (d, ¹J_{CP} = 9 Hz, CHCyp), 25.4-25.1 various signals (CH₂Cyp), 21.5 (CH₃-Xyl).

³¹P{¹H} NMR (121 MHz, CDCl₃): δ 20.9 (br s).

Elemental analysis calculated (found) for C₃₂H₃₉CuClIP: C 69.42 (69.6), H 7.10 (7.0).

[CuBr(PCyp₂Ar^{Xyl₂)₂)]₂, 5b.} Pale-yellow crystals obtained by recrystallization at 5 °C from pentane: CH₂Cl₂ (3:1) mixtures. Yield: 91 %.



Following the general procedure, the synthesis was carried out in CHCl₃.

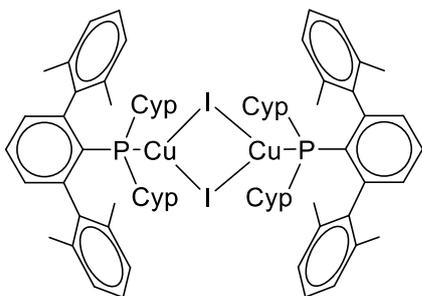
¹H NMR (400 MHz, CDCl₃): δ 7.54 (t, ³J_{HH} = 7.6 Hz, 1H, *H*_{ar}), 7.33 (t, ³J_{HH} = 7.6 Hz, 2H, *H*_{ar}), 7.19 (d, ³J_{HH} = 7.6 Hz, 4H, *H*_{ar}), 7.11 (dd, ³J_{HH} = 7.6, ³J_{HP} = 2.6 Hz, 2H, *H*_{ar}), 2.07 (s, 12H, CH₃-Xyl), 2.04-0.80 (m, 18H, Cyp).

¹³C NMR (100 MHz, CDCl₃): δ 148.1 (d, ²J_{CP} = 13 Hz, *o*-C₆H₃), 140.6 (d, ³J_{CP} = 6 Hz, *ipso*-Xyl), 135.5 (*o*-Xyl), 131.3 (d, ⁴J_{HP} = 1 Hz, *p*-C₆H₃), 131.2 (*m*-C₆H₃), 130.7 (d, ¹J_{CP} = 24 Hz, *ipso*-C₆H₃), 128.9 (*p*-Xyl), 128.6 (*m*-Xyl), 35.7-35.3 various signals (CH₂Cyp), 31.4 (d, ¹J_{CP} = 9 Hz, CHCyp), 25.7-25.4 various signals (CH₂Cyp), 21.6 (CH₃-Xyl).

³¹P NMR (121 MHz, CDCl₃): δ 19.4 (br s).

Elemental analysis calculated (found) for C₃₂H₃₉CuBrP: C 64.26 (64.1), H 6.57 (6.6).

[CuI(PCyp₂Ar^{Xyl₂)₂)]₂, 5c.} Pale-yellow crystals obtained by recrystallization at 5 °C from pentane: CH₂Cl₂ (3:1) mixtures. Yield: 90 %.



Following the general procedure, the synthesis was carried out in CHCl₃.

¹H NMR (400 MHz, CDCl₃): δ 7.53 (t, ³J_{HH} = 8.0, Hz, 1H, *H*_{ar}), 7.31 (t, ³J_{HH} = 7.7 Hz, 2H, *H*_{ar}), 7.20 (d, ³J_{HH} = 7.6 Hz, 4H, *H*_{ar}), 7.10 (d, ³J_{HH} = 7.6 Hz, 2H, *H*_{ar}), 2.07 (s, 12H, CH₃-Xyl), 1.78-1.31 (m, 18H, Cyp).

¹³C NMR (100 MHz, CDCl₃): δ 148.1 (d, ²J_{CP} = 13 Hz, *o*-C₆H₃), 140.5 (d, ³J_{CP} = 6 Hz, *ipso*-Xyl), 135.4 (*o*-Xyl), 131.3 (d, ⁴J_{HP} = 1 Hz, *p*-C₆H₃), 131.2 (*m*-C₆H₃), 130.9 (d, ¹J_{CP} = 24 Hz, *ipso*-C₆H₃), 129.3 (*p*-Xyl), 128.6 (*m*-Xyl), 35.6-35.3 various signals (CH₂Cyp), 31.1 (d, ¹J_{CP} = 9 Hz, CHCyp), 25.8-25.5 various signals (CH₂Cyp), 21.6 (CH₃-Xyl).

³¹P NMR (160 MHz, CDCl₃): δ 16.8. ³¹P NMR (160 MHz, CDCl₃): δ 16.8..

Elemental analysis calculated (found) for C₃₂H₃₉CuIP: C 59.21 (59.0), H 6.68 (7.0).

3. Catalytic procedures and characterization of triazoles.

3.1. General catalytic procedure for the [3+2] cycloaddition of azides and terminal alkynes. Procedure A.

A vial fitted with a screw cap was loaded with the alkyne (1.2 mmol), the azide (1 mmol), the copper complex (0.5 mol% Cu) and water (3 mL) under air. The reaction mixture was stirred at room temperature for 5-12 h. The product was extracted with ethyl acetate, the combined organic layers were washed with brine, dried over anhydrous MgSO₄ and the solvent was removed under vacuum. When required, the product was purified by flash column chromatography.

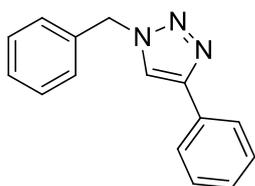
3.2. General catalytic procedure for the [3+2] cycloaddition of *in situ* generated azides and terminal alkynes. Procedure B.

A vial fitted with a screw cap was loaded with the alkyne (1 mmol), the aryl halide (1 mmol), sodium azide (1.3 mmol), the copper complex (0.5 mol% Cu) and water (3 mL) under air. The reaction mixture was stirred at room temperature for 5-12 h. The product was extracted with ethyl acetate, the combined organic layers were washed with brine, dried over anhydrous MgSO₄ and the solvent was removed under vacuum. When required, the product was purified by flash column chromatography.

3.3. Characterization data for compounds shown in Tables 4, and 5.

Most of triazoles products have already been described in the literature. However, ¹H NMR spectra of these compounds used to identify them have been included herein, along with the references to their full spectroscopic characterization. For novel compounds, all relevant spectroscopic and analytical data are provided.

1-Benzyl-4-phenyl-1*H*-1,2,3-triazole⁴ (Table 4 and Table 5, 14a)



Following the general catalytic procedure A, phenylacetylene (0.110 mL, 1 mmol), benzyl azide (133.1 mg, 1 mmol) and the catalyst **1c** or **3c** (0.005 mmol of Cu) were stirred in water (3 mL)

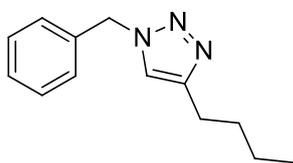
⁴Appukkuttan, P.; Dehaen, W.; Fokin, V. V.; Van der Eycken, E. *Org. Lett.* **2004**, *6*, 4223-4225.

for 6 h at room temperature. The title compound was isolated as a white powder after purification by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). Yield: 226.3 mg, 96% (**1c**); 221,6 mg, 94% (**3c**).

Following the general catalytic procedure B: phenylacetylene (0.110 mL, 1 mmol), benzyl bromide (0.120 mL, 1mmol), NaN₃ (84.2 mg, 1.3 mmol) and the catalyst **3c** (0.005 mol of Cu) were reacted for 12 h at room temperature. Yield: 233.4 mg (99%).

¹H NMR (300 MHz, CDCl₃): δ 7.80 (m, 2H), 7.66 (s, 1H), 7.42-7.35 (m, 5H), 7.33-7.29 (m, 3H), 5.58 (s, 2H).

1-Benzyl-4-(n-butyl)-1H-1,2,3-triazole⁵ (Table 4 and Table 5, 14b)

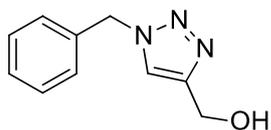


Following the general catalytic procedure A, 1-hexyne (0.115 mL, 1 mmol), benzyl azide (133.1 mg, 1 mmol) and the catalyst **1c** or **3c** (0.005 mmol of Cu) were stirred in water (3 mL) for 6 h at room temperature. The title compound was isolated as a white powder after purification by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). Yield: 209.9 mg, 97% (**1c**); 203,4 mg, 94% (**3c**).

Following the general catalytic procedure B: 1-hexyne (0.115 mL, 1 mmol), benzyl bromide (0.120 mL, 1mmol), NaN₃ (84.2 mg, 1.3 mmol) and the catalyst **3c** (0.005 mol of Cu) were reacted for 12 h at room temperature. Yield: 204 mg (95%).

¹H NMR (300 MHz, CDCl₃): δ 7.38 (m, 3H), 7.27 (m, 2H), 7.19 (s, 1H), 5.51 (s, 2H), 2.71 (t, *J* = 7.0 Hz, 2H), 1.65 (m, 2H), 1.38 (m, 2H), 0.93 (t, *J* = 7.0 Hz, 3H).

(1-Benzyl-1H-1,2,3-triazol-4-yl)methanol⁶ (Table 4 and Table 5 14c)



Following the general catalytic procedure A, propargyl alcohol (0.058 mL, 1 mmol) benzyl azide (133 mg, 1 mmol) and the catalyst **1c** or **3c** (0.005 mmol of Cu) were stirred in water (3 mL) for 6 h at room temperature. The title compound was isolated as a white powder

⁵ Candelon, N.; Lastécouères, D.; Diallo, A. K.; Aranzaes, J. R.; Astruc, D.; Vincent, J.-M. *Chem. Commun.* 2008, 741-743.

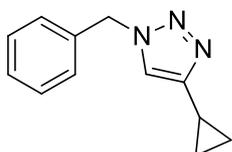
⁶ Buckley, B. R.; Dann, S. E.; Harris, D. P.; Heaney, H.; Stubbs, E. C. *Chem. Commun.* 2010, 46, 2274-2276.

after purification by flash chromatography (petroleum ether : ethyl acetate = 1 : 1). Yield: 175 mg, 92% (**1c**); 173 mg, 91% (**3c**).

Following the general catalytic procedure B: propargyl alcohol (0.058 mL, 1 mmol), benzyl bromide (0.120 mL, 1mmol), NaN₃ (84.2 mg, 1.3 mmol) and the catalyst **3c** (0.005 mol of Cu) were reacted for 12 h at room temperature. Yield: 179 mg (95%).

¹H NMR (300 MHz, CDCl₃): δ 7.44 (s, 1H), 7.38-7.34 (m, 3H), 7.29-7.25 (m, 2H), 5.52 (s, 2H), 4.77 (d, *J* = 5.9 Hz, 2H), 2.41 (t, *J* = 5.9 Hz, 1H).

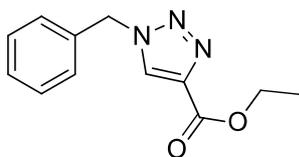
1-Benzyl-4-cyclopropyl-1*H*-1,2,3-triazole⁷ (Table 4, 14d)^d



Following the general catalytic procedure A, cyclopropyl acetylene (0.085 mL, 1 mmol), benzyl azide (133 mg, 1 mmol) and the catalyst **1c** or **3c** (0.005 mmol of Cu) were stirred in water (3 mL) for 6 h at room temperature. The title compound was isolated as a white powder after purification by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). Yield: 180 mg, 90% (**1c**); 176 mg, 88% (**3c**).

¹H NMR (300 MHz, CDCl₃): δ 7.37 (m, 3H), 7.26 (m, 2H), 7.15 (s, 1H), 5.47 (s, 2H), 1.92 (m, 1H), 0.92 (m, 2H), 0.82 (m, 2H).

Ethyl 1-benzyl-1*H*-1,2,3-triazole-4-carboxylate⁴ (Table 4, 14e)

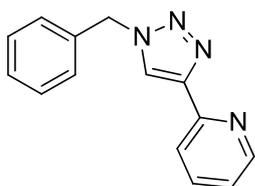


Following the general catalytic procedure A, ethyl propiolate (0.099 mL, 1 mmol), benzyl azide (133 mg, 1 mmol) and the catalyst **1c** or **3c** (0.005 mmol of Cu) were stirred in water (3 mL) for 6 h at room temperature. The title compound was isolated as a white powder after purification by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). Yield: 218 mg, 94% (**1c**); 213 mg, 92% (**3c**).

¹H NMR (300 MHz, CDCl₃): δ 7.97 (s, 1H), 7.37 (m, 3H), 7.27 (m, 2H), 5.56 (s, 2H), 4.37 (q, *J* = 7.0, 2H), 1.36 (t, *J* = 7.0, 3H).

⁷ Namitharan, K.; Kumarraja, M.; Pitchumani, K. *Chem. Eur. J.* **2009**, *15*, 2755-2758.

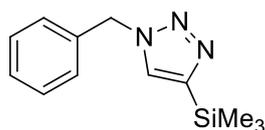
2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)pyridine⁸ (Table 4, 14f)



Following the general catalytic procedure A, 2-ethynylpyridine (0.101 mL, 1 mmol), benzyl azide (133 mg, 1 mmol) and the catalyst **1c** or **3c** (0.005 mmol of Cu) were stirred in water (3 mL) for 6 h at room temperature. The title compound was isolated as a white powder after purification by flash chromatography (petroleum ether : ethyl acetate = 2 : 1). Yield: 220 mg, 93% (**1c**); 227 mg, 96% (**3c**).

¹H NMR (300 MHz, CDCl₃): δ 8.53 (ddd, *J* = 4.9, 1.8, 1.2 Hz, 1H), 8.18 (dt, *J* = 7.8, 1.2 Hz, 1H), 8.04 (s, 1H), 7.76 (td, *J* = 7.8, 1.8 Hz, 1H), 7.36 (m, 5H), 7.21 (ddd, *J* = 7.8, 4.9, 1.2 Hz, 1H), 5.58 (s, 2H).

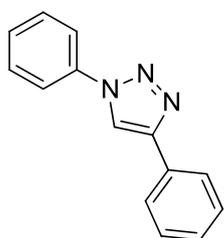
1-Benzyl-4-(trimethylsilyl)-1*H*-1,2,3-triazole⁴ (Table 4, 14g)



Following the general catalytic procedure A, ethynyltrimethylsilane (0.141 mL, 1 mmol), benzyl azide (133 mg, 1 mmol) and the catalyst **1c** or **3c** (0.005 mmol of Cu) were stirred in water (3 mL) for 6 h at room temperature. The title compound was isolated as a white powder after purification by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). Yield: 210 mg, 91% (**1c**); 206 mg, 89% (**3c**).

¹H NMR (300 MHz, CDCl₃): δ 7.45 (s, 1H), 7.37 (m, 3H), 7.28 (m, 2H), 5.56 (s, 2H), 0.30 (m, 9H).

1,4-Diphenyl-1*H*-1,2,3-triazole⁵ (Table 4, 14h)

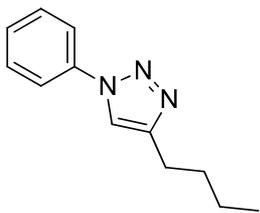


Following the general catalytic procedure A, phenylacetylene (0.024 mL, 0.221 mmol), azidobenzene (26 mg, 0.221 mmol) and the catalyst **1c** or **3c** (0.005 mmol of Cu) were stirred in water (3 mL) for 5 h at room temperature. The title compound was isolated as a white powder after purification by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). Yield: 44 mg, 91% (**1c**); 46 mg, 94% (**3c**).

¹H NMR (300 MHz, CDCl₃): δ 8.20 (s, 1H), 7.92 (d, *J* = 7.3 Hz, 2H), 7.80 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.47 (m, 3H), 7.37 (t, *J* = 7.3 Hz, 1H).

⁸ Richardson, C.; Fitchett, C. M.; Keene, F. R.; Steel, P. J. *Dalton Trans.* **2008**, 2534-2537.

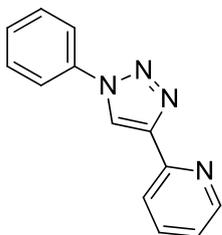
4-(*n*-Butyl)-1-phenyl-1*H*-1,2,3-triazole (Table 4, 14i)



Following the catalytic general procedure A, 1-hexyne (0.035 mL, 0.301 mmol), azidobenzene (36 mg, 0.301 mmol) and the catalyst **1c** or **3c** (0.005 mmol of Cu) were stirred in water (3 mL) for 5 h at room temperature. The title compound was isolated as a white powder after purification by flash chromatography (ethyl petroleum ether : ethyl acetate = 5 : 1). Yield: 56 mg, 92% (**1c**); 57 mg, 93% (**3c**).

¹H NMR (300 MHz, CDCl₃): δ 7.71 (m, 3H), 7.49 (m, 2H), 7.40 (m, 1H), 2.79 (t, *J* = 7.6 Hz, 2H), 1.71 (m, 2H), 1.41 (m, 2H), 0.95 (t, *J* = 7.6 Hz, 3H).

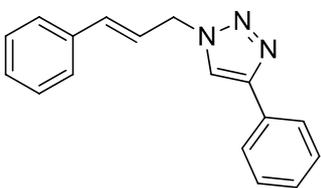
2-(1-Phenyl-1*H*-1,2,3-triazol-4-yl)pyridine⁹ (Table 4, 14j)



Following the general catalytic procedure A, 2-ethynylpyridine (0.030 mL, 0.298 mmol), azidobenzene (36 mg, 0.298 mmol) and the catalyst **1c** or **3c** (0.005 mmol of Cu) were stirred in water (3 mL) for 5 h at room temperature. The title compound was isolated as a white powder after purification by flash chromatography (ethyl petroleum ether : ethyl acetate = 5 : 1). Yield: 61 mg, 92% (**1c**); 63 mg, 95% (**3c**).

¹H NMR (300 MHz, CDCl₃): δ 8.61 (m, 2H), 8.25 (d, *J* = 7.9 Hz, 1H), 7.81 (m, 3H), 7.55 (m, 2H), 7.45 (m, 1H), 7.26 (m, 1H).

1-Cinnamyl-4-phenyl-1*H*-1,2,3-triazole¹⁰ (Table 4, 14k)



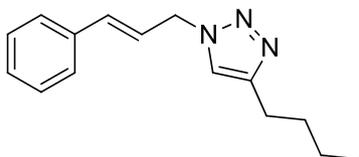
Following the general catalytic procedure A, phenylacetylene (0.110 mL, 1 mmol), cinnamyl azide (159 mg, 1 mmol) and the catalyst **1c** or **3c** (0.005 mmol of Cu) were stirred in water (3 mL) for 5 h at room temperature. The title compound was isolated as a white powder after purification by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). Yield: 249 mg, 95% (**1c**); 244 mg, 93% (**3c**).

⁹ Kacprzak, K. *Synlett* **2005**, 943-946.

¹⁰ Nunes, A.; Djakovitch, L. Khrouz, L.; Felpin, F.-X. Dufaud, V. *J. Mol. Catal. A: Chem.* **2017**, 437, 150-157.

^1H NMR (300 MHz, CDCl_3): δ 7.84 (m, 2H), 7.81 (s, 1H), 7.44-7.28 (m, 8H), 6.71 (d, J = 15.8 Hz, 1H), 6.39 (dt, J = 15.8, 6.6 Hz, 1H), 5.19 (dd, J = 6.6, 1.2 Hz, 3H).

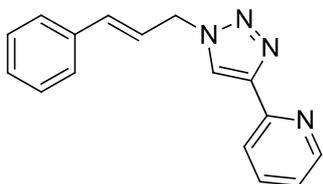
4-(*n*-Butyl)-1-cinnamyl-1*H*-1,2,3-triazole¹¹ (Table 4, 14l)



Following the general catalytic procedure A, 1-hexyne (0.115 mL, 1 mmol), cinnamyl azide (159 mg, 1 mmol) and the catalyst **1c** or **3c** (0.005 mmol of Cu) were stirred in water (3 mL) for 5 h at room temperature. The title compound was isolated as a white powder after purification by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). Yield: 227 mg, 94% (**1c**); 222 mg, 92% (**3c**).

^1H NMR (300 MHz, CDCl_3): δ 7.31-7.26 (m, 6H), 6.60 (d, J = 15.8 Hz, 1H), 6.30 (dt, J = 15.8, 6.6 Hz, 1H), 5.05 (d, J = 5.6 Hz, 2H), 2.70 (t, J = 7.7 Hz, 2H), 1.64 (m, 2H), 1.37 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H).

2-(1-Cinnamyl-1*H*-1,2,3-triazol-4-yl)pyridine (Table 4, 14m)



Following the general catalytic procedure A, 2-ethynylpyridine (0.101 mL, 1 mmol), cinnamyl azide (159 mg, 1 mmol) and the catalyst **1c** or **3c** (0.005 mmol of Cu) were stirred in water (3 mL) for 5 h at room temperature. The title compound was isolated as a white powder after purification by flash chromatography (petroleum ether : ethyl acetate = 2 : 1). Yield: 242 mg, 92% (**1c**); 252 mg, 96% (**3c**).

^1H NMR (300 MHz, CDCl_3): δ 8.54 (d, J = 3.4 Hz, 1H), 8.18 (m, 2H), 7.74 (td, J = 7.8, 1.6 Hz, 1H), 7.37-7.17 (m, 6H), 6.69 (d, J = 15.8 Hz, 1H), 6.36 (dt, J = 15.8, 6.7 Hz, 1H), 5.16 (dd, J = 6.7, 1.2 Hz, 2H).

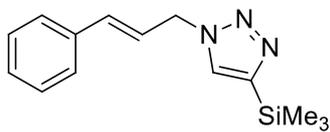
^{13}C NMR (75 MHz, CDCl_3): δ 150.3, 149.4, 148.7, 137.0, 135.9, 135.5, 128.8, 128.6, 126.8, 122.9, 121.8, 121.6, 120.3, 52.5.

IR (nujol): 3123, 2953, 2853, 1460, 1376, 1222, 1196, 1062, 979, 741, 722, 665 cm^{-1} .

¹¹ Alonso, F.; Moglie, Y.; Radivoy, G.; Yus, M. *Eur. J. Org. Chem.* **2010**, 1875-1884.

Elemental analysis calculated (found) for C₁₆H₁₄N₄: C 73.26 (73.2), H 5.38 (5.5), N 21.36 (21.2).

1-Cinnamyl-4-(trimethylsilyl)-1*H*-1,2,3-triazole (Table 4, 14n)



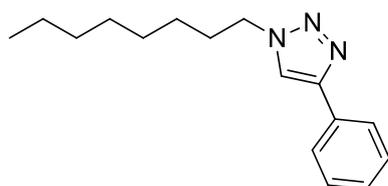
Following the general catalytic procedure A, ethynyltrimethylsilane (0.141 mL, 1 mmol), cinnamyl azide (159 mg, 1 mmol) and the catalyst **1c** or **3c** (0.005 mmol of Cu) were stirred in water (3 mL) for 5 h at room temperature. The title compound was isolated as a white powder after purification by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). Yield: 232 mg, 90% (**1c**); 240 mg, 93% (**3c**).

¹H NMR (300 MHz, CDCl₃): δ 7.56 (s, 1H), 7.40-7.25 (m, 5H), 6.67 (d, *J* = 15.8 Hz, 1H), 6.35 (dt, *J* = 15.8, 6.7 Hz, 1H), 5.16 (dd, *J* = 6.7, 1.2 Hz, 2H), 0.32 (s, 9H).

¹³C NMR (75 MHz, CDCl₃): δ 135.8, 135.3, 128.9, 128.8, 128.7, 126.9, 122.5, 51.9, -0.92. IR (nujol): 3118, 3027, 2956, 2854, 1488, 1450, 1376, 1250, 1193, 1109, 967, 843, 759, 691, 668 cm⁻¹.

Elemental analysis calculated (found) for C₁₄H₁₉N₃Si: C 65.32 (65.6), H 7.44 (7.3), N 16.32 (16.0).

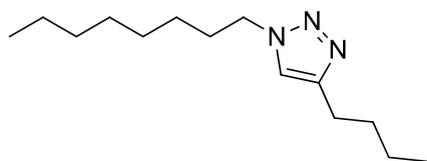
1-(*n*-Octyl)-4-phenyl-1*H*-1,2,3-triazole⁹ (Table 4, 14o)



Following the general catalytic procedure A, phenylacetylene (0.110 mL, 1 mmol), 1-azidooctane (155 mg, 1 mmol) and the catalyst **1c** or **3c** (0.005 mmol of Cu) were stirred in water (3 mL) for 12 h at room temperature. The title compound was isolated as a white powder after purification by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). Yield: 242 mg, 94% (**1c**); 239 mg, 93% (**3c**).

¹H NMR (300 MHz, CDCl₃): δ 7.84 (m, 2H), 7.74 (s, 1H), 7.43 (m, 2H), 7.33 (m, 1H), 4.40 (t, *J* = 7.2 Hz, 2H), 1.94 (m, 2H), 1.37-1.25 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H).

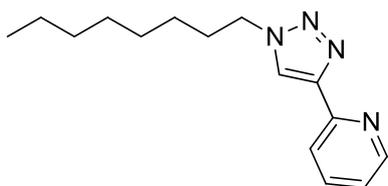
4-(*n*-Butyl)-1-(*n*-octyl)-1*H*-1,2,3-triazole¹² (Table 4, 14p)



Following the general catalytic procedure procedure A, 1-hexyne (0.115 mL, 1 mmol), 1-azidooctane (155 mg, 1 mmol) and the catalyst **1c** or **3c** (0.005 mmol of Cu) were stirred in water (3 mL) for 12 h at room temperature. The title compound was isolated as a white powder after purification by flash chromatography (petroleum ether : ethyl acetate = 2 : 1). Yield: 221 mg, 93% (**1c**); 219 mg, 92% (**3c**).

¹H NMR (300 MHz, CDCl₃): δ 7.24 (s, 1H), 4.30 (t, *J* = 7.2 Hz, 2H), 2.72 (t, *J* = 7.4 Hz, 2H), 1.87 (m, 2H), 1.65 (m, 2H), 1.42-1.25 (m, 12H), 0.90 (dt, *J* = 13.5, 7.2 Hz, 6H).

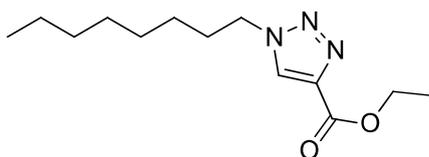
2-(1-(*n*-Octyl)-1*H*-1,2,3-triazol-4-yl)pyridine¹³ (Table 4, 14q)



Following the general catalytic procedure A, 2-ethynylpyridine (0.101 mL, 1 mmol), 1-azidooctane (155 mg, 1 mmol) and the catalyst **1c** or **3c** (0.005 mmol of Cu) were stirred in water (3 mL) for 12 h at room temperature. The title compound was isolated as a white powder after purification by flash chromatography (petroleum ether : ethyl acetate = 2 : 1). Yield: 243 mg, 94% (**1c**); 243 mg, 93% (**3c**).

¹H NMR (300 MHz, CDCl₃): δ 8.57 (d, *J* = 4.9 Hz, 1H), 8.17 (dt, *J* = 7.8, 1.1 Hz, 1H), 8.12 (s, 1H), 7.76 (td, *J* = 7.8, 1.8 Hz, 1H), 7.21 (ddd, *J* = 7.8, 4.9, 1.1 Hz, 1H), 4.40 (t, *J* = 7.2 Hz, 2H), 1.94 (m, 2H), 1.35-1.17 (m, 10H), 0.86 (t, *J* = 6.7 Hz, 3H).

Ethyl 1-(*n*-octyl)-1*H*-1,2,3-triazole-4-carboxylate¹⁴ (Table 4, 14r)



Following the general catalytic procedure A, ethyl propiolate (0.099 mL, 1 mmol), 1-azidooctane (155 mg, 1 mmol) and the catalyst **1c** or **3c** (0.005 mmol

¹² Hu, H.; Sun, Z. *Adv. Synth. Catal.* **2016**, *358*, 1736-1740.

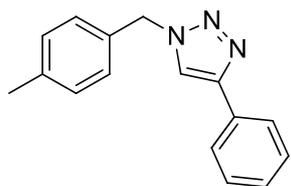
¹³ Crowley, J. D.; Bandeen, P. H.; Hanton, L. R. *Polyhedron* **2010**, *29*, 70-83.

¹⁴ Özçubukçu, S.; Ozkal, E.; Jimeno, C.; Pericàs, M. A. *Org. Lett.* **2009**, *11*, 4680-4683.

of Cu) were stirred in water (3 mL) for 12 h at room temperature. The title compound was isolated as a white powder after purification by flash chromatography (petroleum ether : ethyl acetate = 5 : 1). Yield: 125 mg, 99% (**1c**); 123 mg, 97% (**3c**).

¹H NMR (300 MHz, CDCl₃): δ 8.06 (s, 1H), 4.41 (m, 4H), 1.92 (m, 2H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.31-1.22 (m, 10H), 0.87 (t, *J* = 6.8, 3H).

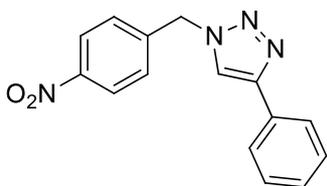
1-(4-Methylbenzyl)-4-phenyl-1*H*-1,2,3-triazole¹⁵ (Table 5, 14s)



Following the general catalytic procedure B, phenylacetylene (0.110 mL, 1 mmol), 4-methylbenzyl bromide (185 mg, 1 mmol), sodium azide (84.1 mg, 1.3 mmol) and the catalyst **3c** (0.005 mmol of Cu) were stirred in water (3 mL) for 12 h at room temperature. The title compound was isolated as a white powder after washing with hexane. Yield: 243 mg, 98%.

¹H NMR (300 MHz, CDCl₃): δ 7.84-7.79 (m, 2H), 7.71 (br s, 1H), 7.40-7.27 (m, 3H), 7.23-7.16 (m, 4H), 5.49 (s, 2H), 2.35 (s, 3H).

1-(4-Nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole¹⁶ (Table 5, 14t)



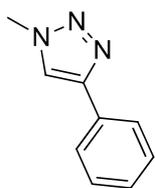
Following the general catalytic procedure B, phenylacetylene (0.110 mL, 1 mmol), 4-nitrobenzyl bromide (216 mg, 1 mmol), sodium azide (84.1 mg, 1.3 mmol) and the catalyst **3c** (0.005 mmol of Cu) were stirred in water (3 mL) for 12 h at room temperature. The title compound was isolated as a white powder after washing with hexane. Yield: 203 mg, 72%.

¹H NMR (300 MHz, CDCl₃): δ 8.23 (d, *J* = 8.7 Hz, 2H), 7.84-7.76 (m, 3H), 7.46-7.32 (m, 5H), 5.70 (s, 2H).

¹⁵ Zhou, C. J.; Zhang, J.; Liu, P.; Xie, J. W.; Dai, B. *RSC Adv.* **2015**, 5, 6661-6665.

¹⁶ Reddy, V. H.; Reddy, Y. V. R.; Sridhar, B.; Reddy, B. V. S. *Adv. Synth. Catal.* **2016**, 358, 1088-1092.

1-Methyl-4-phenyl-1*H*-1,2,3-triazole⁴ (Table 5, 14u)



Following the general catalytic procedure B, phenylacetylene (0.055 mL, 0.5 mmol), iodomethane (0.031 mL, 0.5 mmol), sodium azide (22 mg, 0.65 mmol) and the catalyst **3c** (0.005 mmol of Cu) were stirred in water (3 mL) for 12 h at room temperature. The title compound was isolated as a white powder after washing with hexane. Yield: 62 mg, 78%.

¹H NMR (300 MHz, CDCl₃): δ 8.29 (s, 1H), 7.56-7.43 (m, 5H), 4.18 (s, 3H).

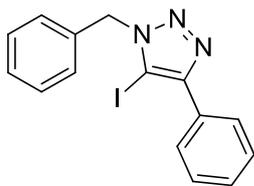
3.4. General procedure for the [3+2] cycloaddition of azides and iodoalkynes.

In a vial fitted with a screw cap, the catalyst **1c** (1-2 mol% Cu) was added to a mixture of iodoalkyne (1 mmol), 2,6-lutidine (4 mol%) and azide (1 mmol) in water (3 mL) under air. The reaction mixture was stirred at room temperature for 24 h. The reaction was quenched by adding aqueous NH₄OH (1 mL, 10% solution). The volatile components were removed by evaporation, and the crude residue was extracted with diethyl ether and washed with water. The solvent was removed under vacuum and the product was purified by flash column chromatography.

3.5. Characterization of iodo-triazoles.

Most of iodotriazoles products have already been described in the literature. However, ¹H NMR spectra of these compounds used to identify them have been included herein, along with the references to their full spectroscopic characterization. For novel compounds, all relevant spectroscopic and analytical data are provided.

1-Benzyl-5-iodo-4-phenyl-1*H*-1,2,3-triazole¹⁷ (Table 7, 15a)

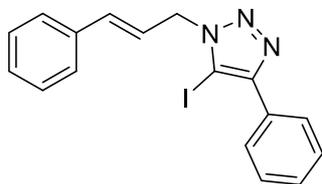


Following the general catalytic procedure, iodoethynylbenzene (114 mg, 0.5 mmol), benzyl azide (66.6 mg, 0.5 mmol) and the catalyst **1c** (1 mol% Cu) afford the title compound as a white powder after purification by flash chromatography (petroleum ether : ethyl acetate 5:1). Yield: 176 mg, 98%.

¹⁷ Dinér, P.; Andersson, T.; Kjellén, J.; Elbing, K.; Hohmann, S.; Grøtli, M. *New J. Chem.* **2009**, *33*, 1010-1016.

^1H NMR (300 MHz, CDCl_3): δ 7.94 (m, 2H), 7.49-7.30 (m, 8H), 5.68 (s, 2H).

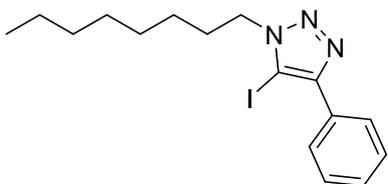
1-Cinnamyl-5-iodo-4-phenyl-1*H*-1,2,3-triazole¹⁸ (Table 7, 15b)



Following the general procedure from iodoethynylbenzene (114 mg, 0.5 mmol) and cinnamyl azide (80 mg, 0.5 mmol) and the catalyst **1c** (2 mol% Cu), the title compound was isolated as a white powder after purification by flash chromatography (petroleum ether). Yield: 132 mg, 68%.

^1H NMR (300 MHz, CDCl_3): δ 8-7.94 (m, 2H), 7.53-7.29 (m, 8H), 6.68 (d, J = 15.2 Hz, 1H), 6.37 (dt, J = 15.9, 6.2 Hz, 1H), 5.28 (dd, J = 6.2, 1.3 Hz, 2H).

1-Octyl-5-iodo-4-phenyl-1*H*-1,2,3-triazole (Table 7, 15c)



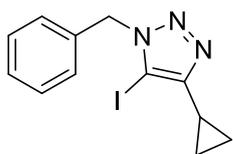
Following the general procedure from iodoethynylbenzene (114 mg, 0.5 mmol), octyl azide (78 mg, 0.5 mmol) and the catalyst **1c** (2 mol% Cu), the title compound was isolated as a white powder after purification by flash chromatography (petroleum ether : ethyl acetate 20:1). Yield: 126 mg, 65%.

^1H NMR (300 MHz, CDCl_3): δ 7.99-7.92 (m, 2H), 7.53-7.40 (m, 3H), 2.01-1.91 (m, 2H), 1.48-1.22 (m, 10H), 0.95-0.85 (m, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 149.8, 130.3, 128.7, 127.6, 76.3, 50.9, 31.8, 30.0, 29.1, 29.0, 26.4, 22.6, 14.1.

HR-MS (ESI): m/z calculated for $\text{C}_{16}\text{H}_{23}\text{IN}_3^+$ $[\text{MH}]^+$ 384.0931, found 384.0924.

1-Benzyl-5-iodo-4-cyclopropyl-1*H*-1,2,3-triazole³ (Table 7, 15d)



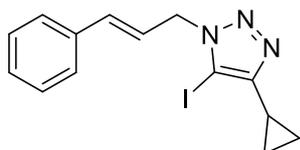
Following the general procedure from iodoethynylcyclopropane (96 mg, 0.5 mmol), benzyl azide (67 mg, 0.5 mmol) and the catalyst **1c** (1 mol% Cu), the title compound was isolated as a white powder

¹⁸ Steven Lal, Henry S. Rzepa, and Silvia Díez-González. *ACS Catal.* **2014**, 4, 2274–2287.

after purification by flash chromatography (petroleum ether : ethyl acetate 15:1). Yield: 141 mg, 87%.

^1H NMR (300 MHz, CDCl_3): δ 7.37-7.25 (m, 5H), 5.57 (s, 2H), 1.84-1.74 (m, 1H), 1.10-0.95 (m, 4H).

1-Cinnamyl-5-iodo-4-cyclopropyl-1H-1,2,3-triazole (Table 7, 15e)



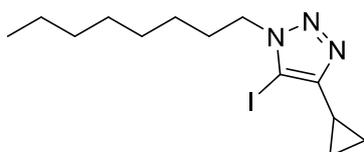
Following the general procedure from iodoethynylcyclopropane (96 mg, 0.5 mmol), cinnamyl azide (80 mg, 0.5 mmol) and the catalyst **1c** (1 mol% Cu), the title compound was isolated as a white powder after purification by flash chromatography (petroleum ether). Yield: 167 mg, 95%.

^1H NMR (300 MHz, CDCl_3): δ 7.41-7.29 (m, 5H), 6.62 (d, $J = 15.9$ Hz, 1H), 6.29 (dt, $J = 15.8, 6.3$ Hz, 1H), 5.15 (dd, $J = 6.3, 1.4$ Hz, 2H), 1.88-1.77 (m, 1H), 1.09-0.97 (m, 4H).

^{13}C NMR (300 MHz, CDCl_3): δ 153.1, 135.7, 134.9, 128.7, 128.4, 126.7, 122.0, 77.8, 52.6, 7.6, 7.3.

HR-MS (ESI): m/z calculated for $\text{C}_{14}\text{H}_{16}\text{IN}_3^+$ $[\text{MH}]^+$ 352.0305, found 352.0301.

1-Octyl-5-iodo-4-cyclopropyl-1H-1,2,3-triazole (Table 7, 15f)

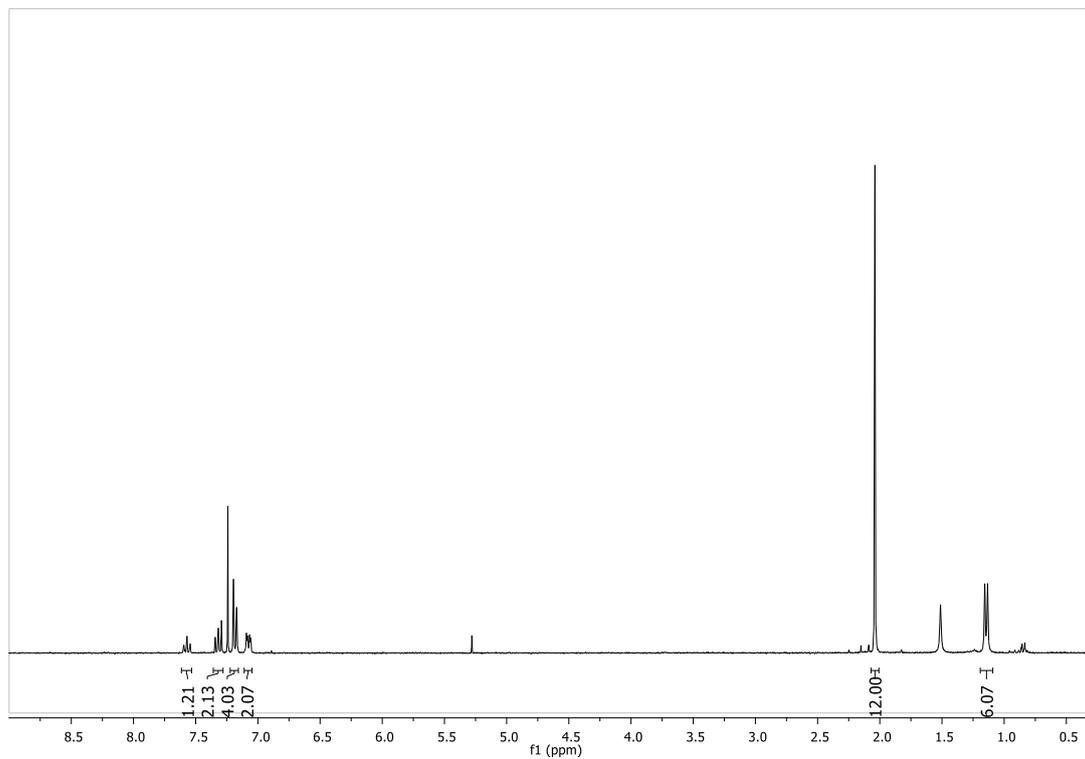


Following the general procedure from iodoethynylcyclopropane (96 mg, 0.5 mmol), octyl azide (78 mg, 0.5 mmol) and the catalyst **1c** (1 mol% Cu), the title compound was isolated as a white powder after purification by flash chromatography (petroleum ether : ethyl acetate 20:1). Yield: 78 mg, 45%.

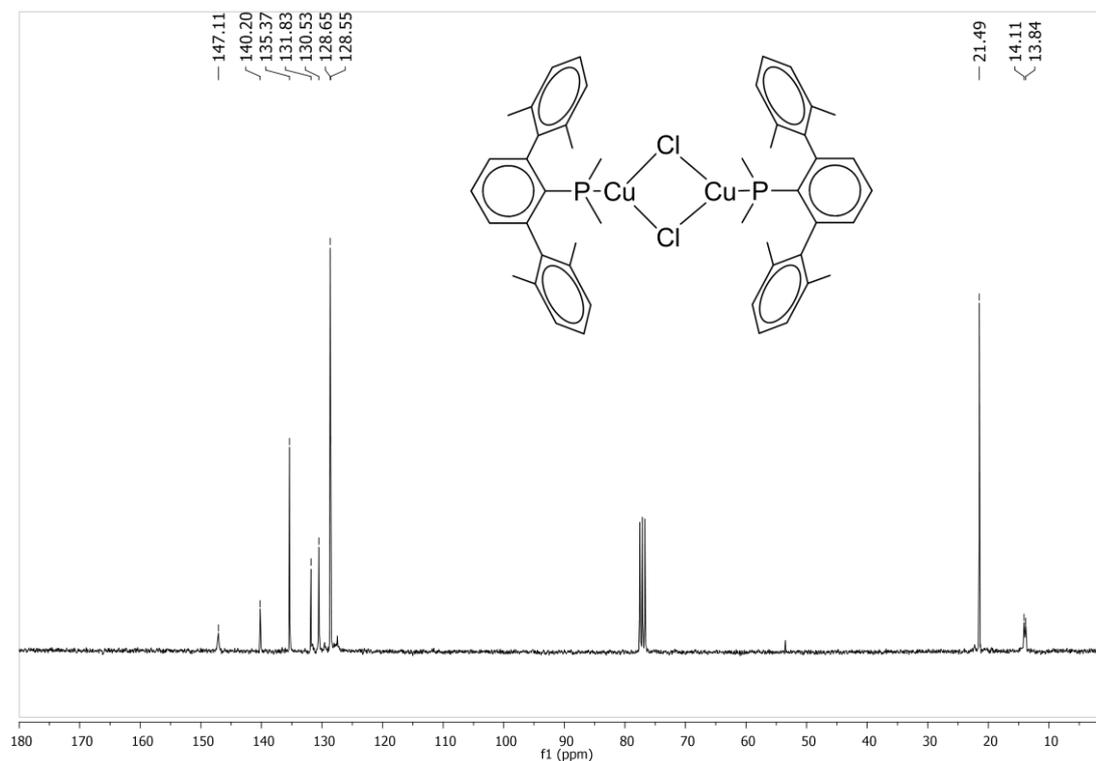
^1H NMR (300 MHz, CDCl_3): δ 7.99-7.92 (m, 2H), 7.53-7.40 (m, 3H), 2.01-1.91 (m, 2H), 1.48-1.22 (m, 10H), 0.95-0.85 (m, 3H), 1.88-1.77 (m, 1H), 1.09-0.97 (m, 4H).

4. NMR spectra of compounds.

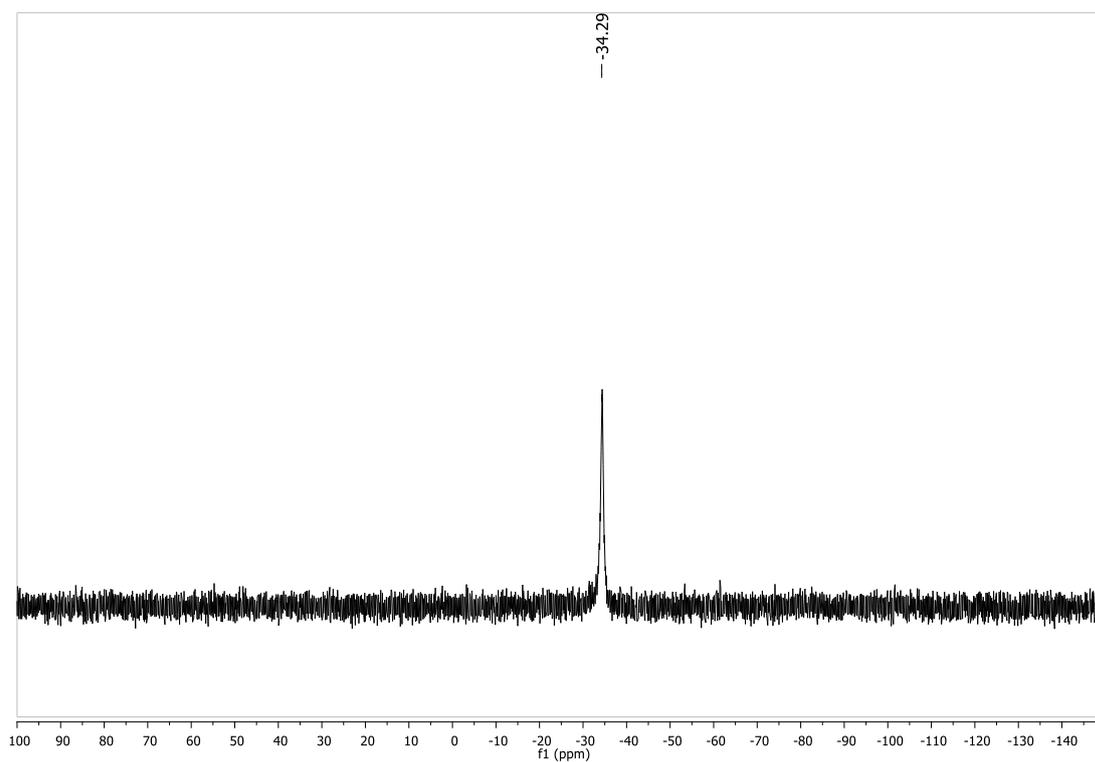
^1H NMR spectrum of $[\text{CuCl}(\text{PMe}_2\text{Ar}^{\text{Xyl}_2})_2]_2$, **1a**



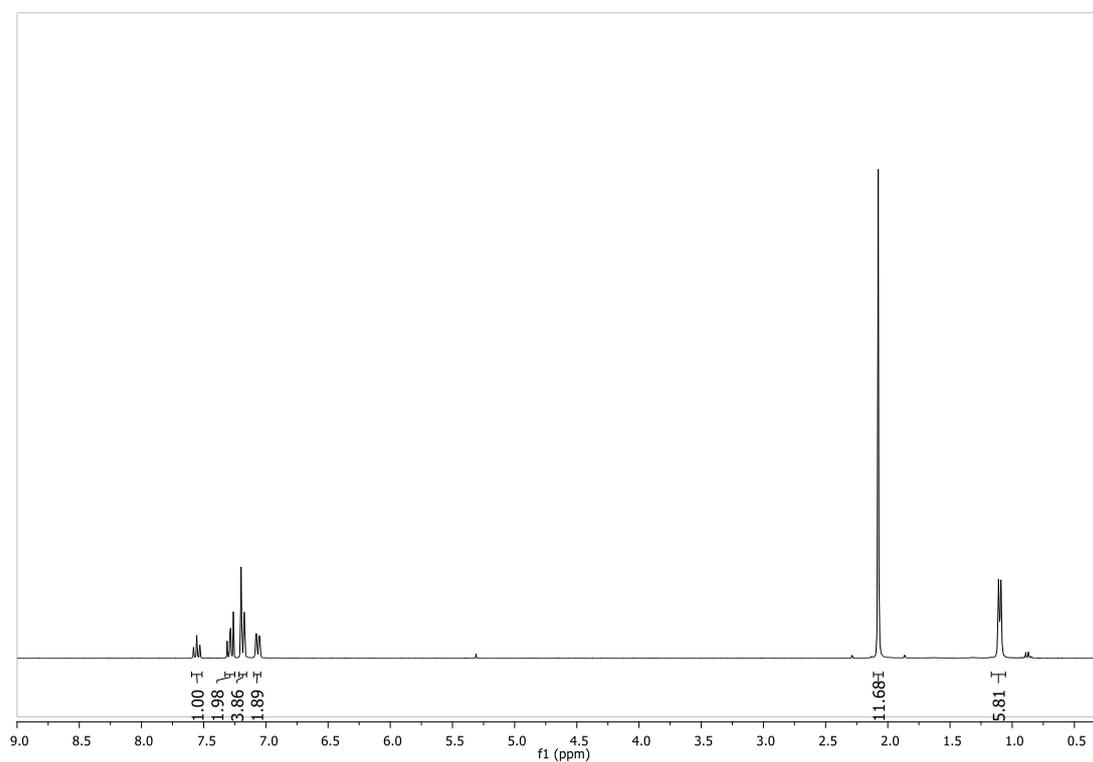
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{CuCl}(\text{PMe}_2\text{Ar}^{\text{Xyl}_2})_2]_2$, **1a**



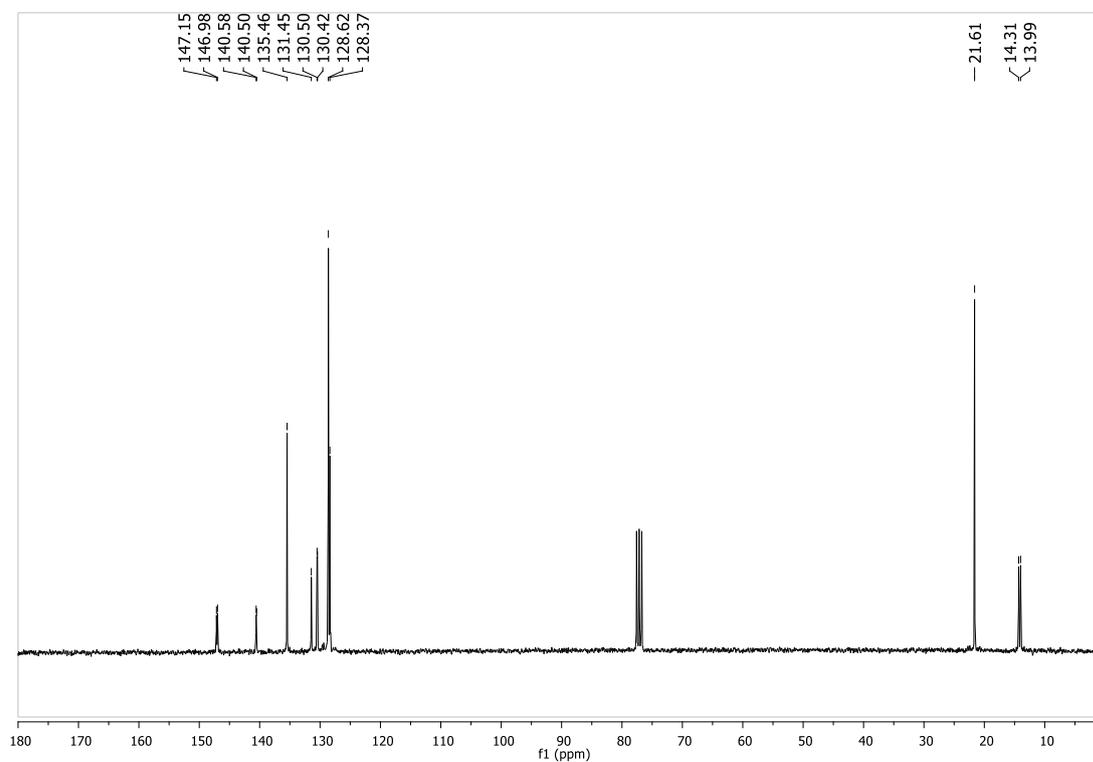
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{CuCl}(\text{PMe}_2\text{Ar}^{\text{Xyl}_2})_2]$, **1a**



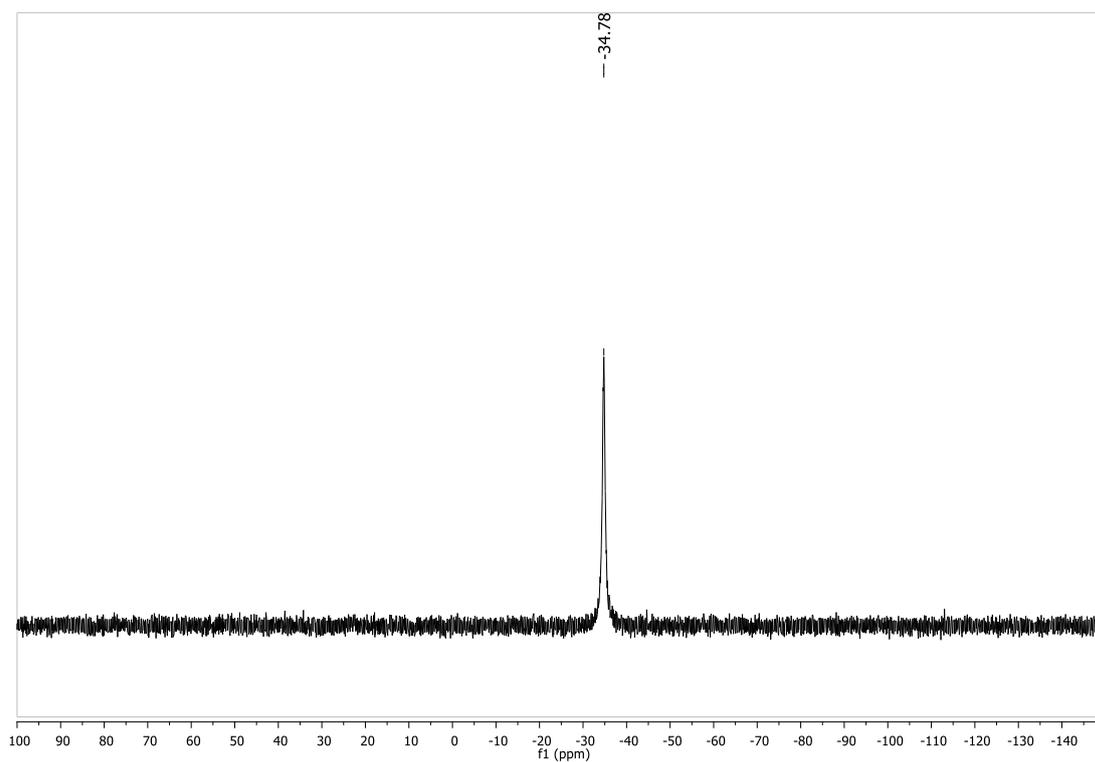
^1H NMR spectrum of $[\text{CuBr}(\text{PMe}_2\text{Ar}^{\text{Xyl}_2})_2]$, **1b**



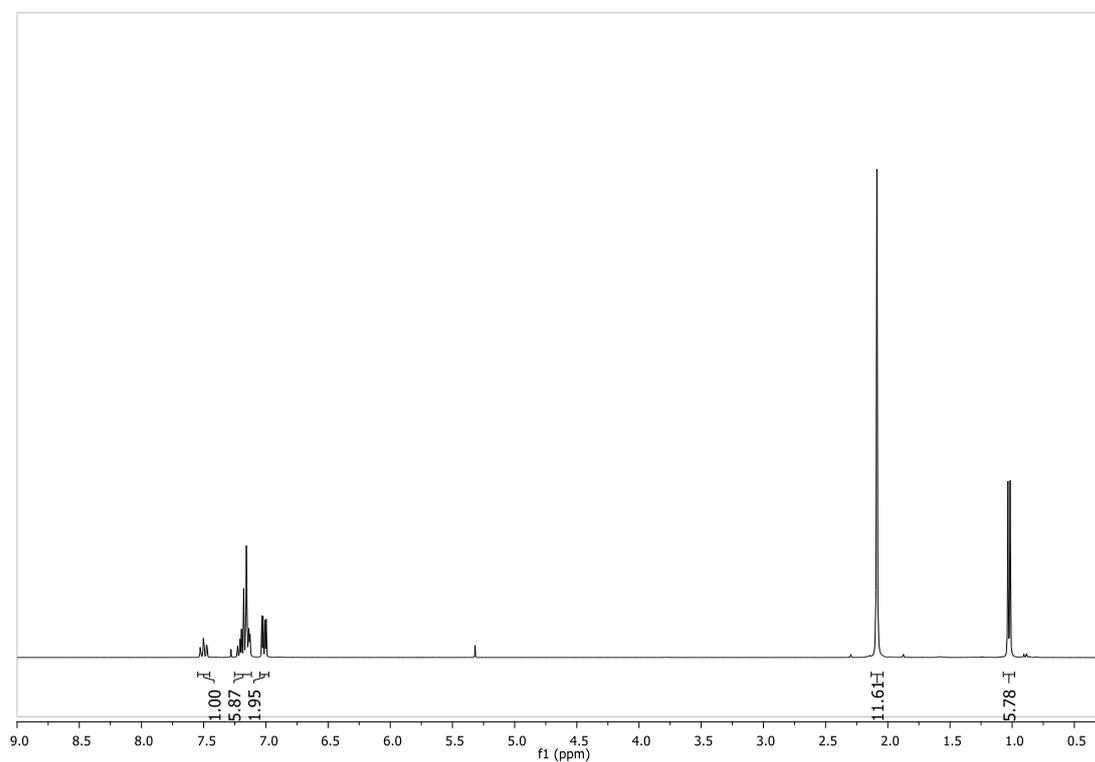
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{CuBr}(\text{PMe}_2\text{Ar}^{\text{Xyl}_2})_2]$, **1b**



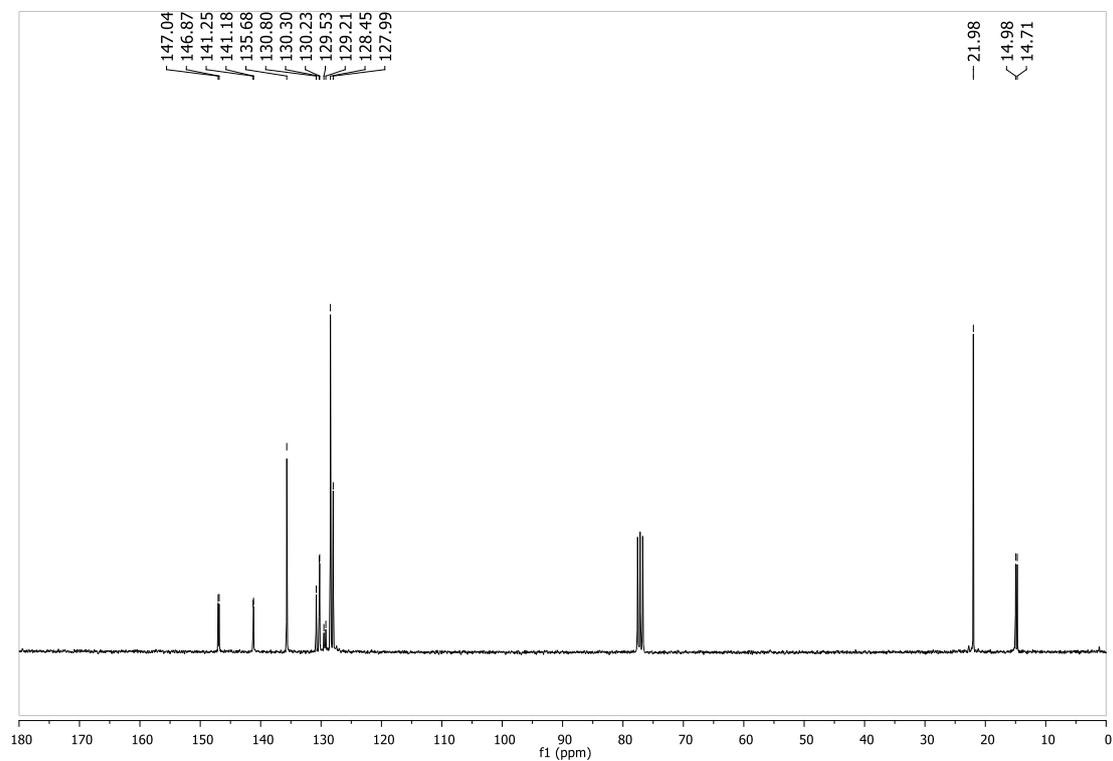
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{CuBr}(\text{PMe}_2\text{Ar}^{\text{Xyl}_2})_2]$, **1b**



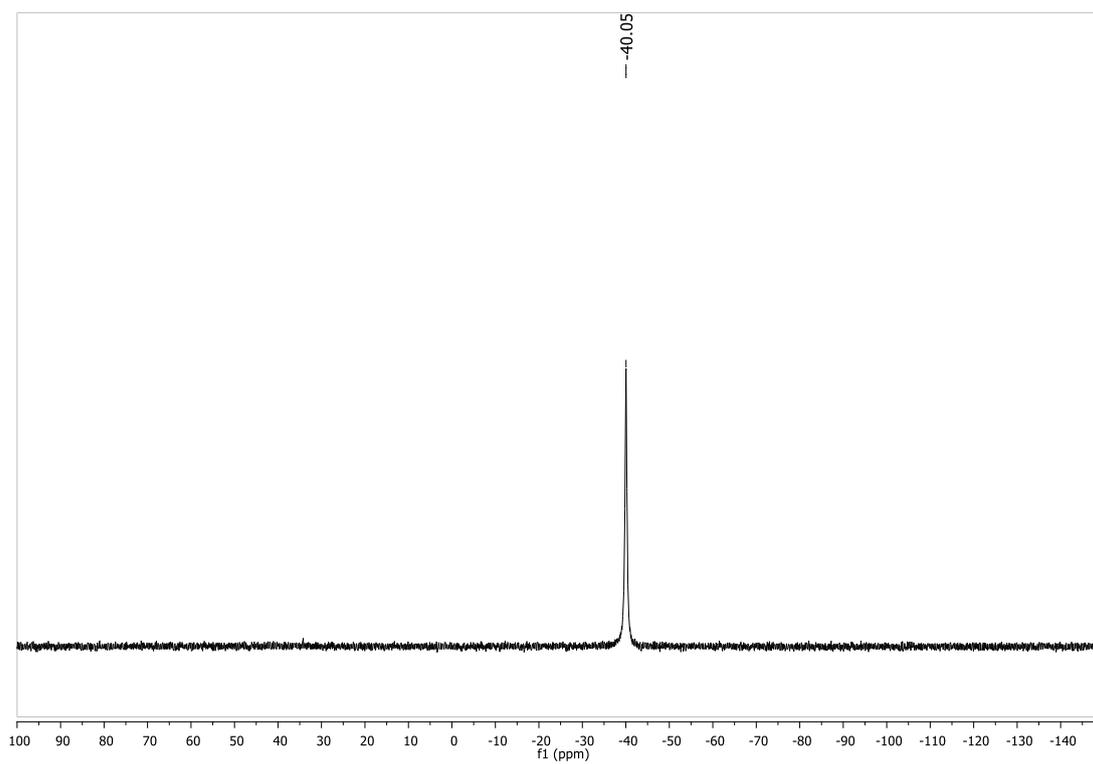
^1H NMR spectrum of $[\text{CuI}(\text{PMe}_2\text{Ar}^{\text{Xyl}_2})_2]$, **1c**



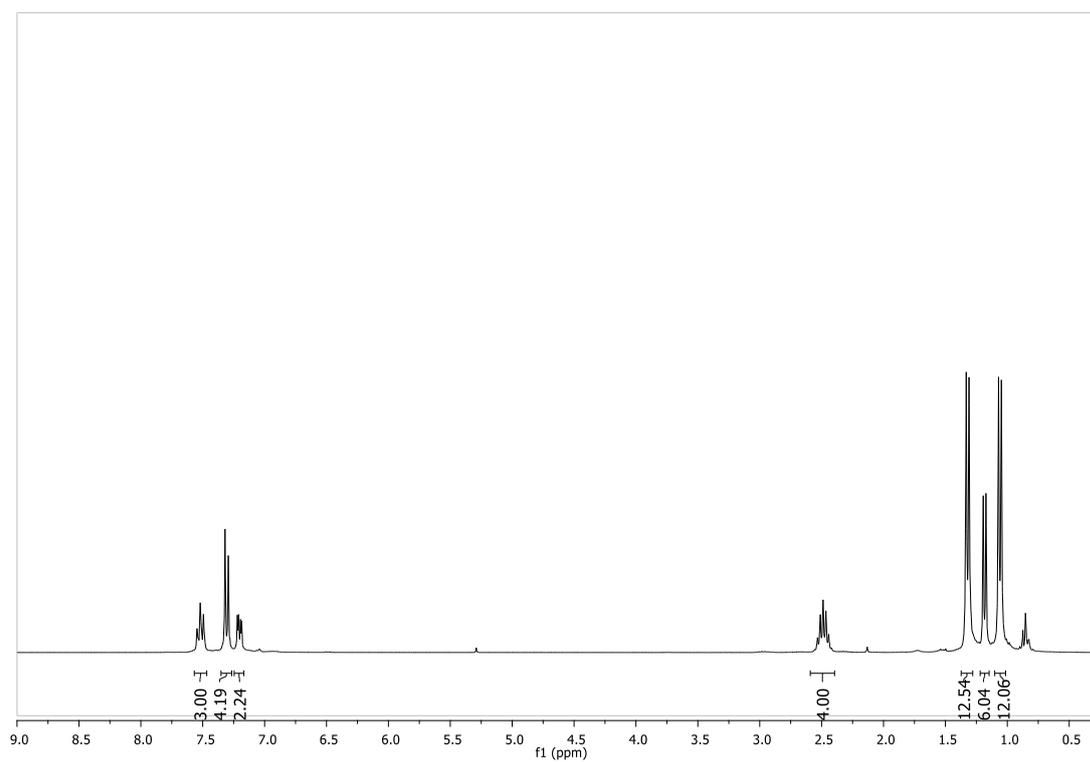
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{CuI}(\text{PMe}_2\text{Ar}^{\text{Xyl}_2})_2]$, **1c**



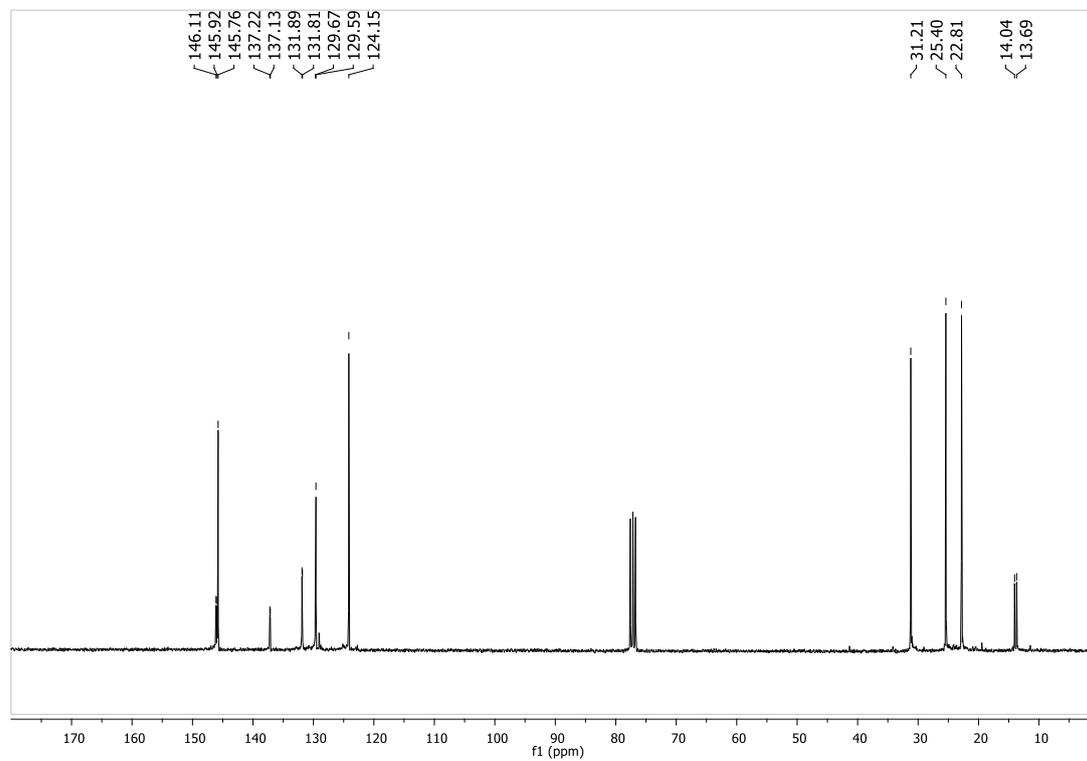
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{CuI}(\text{PMe}_2\text{Ar}^{\text{Xyl}_2})_2]$, **1c**



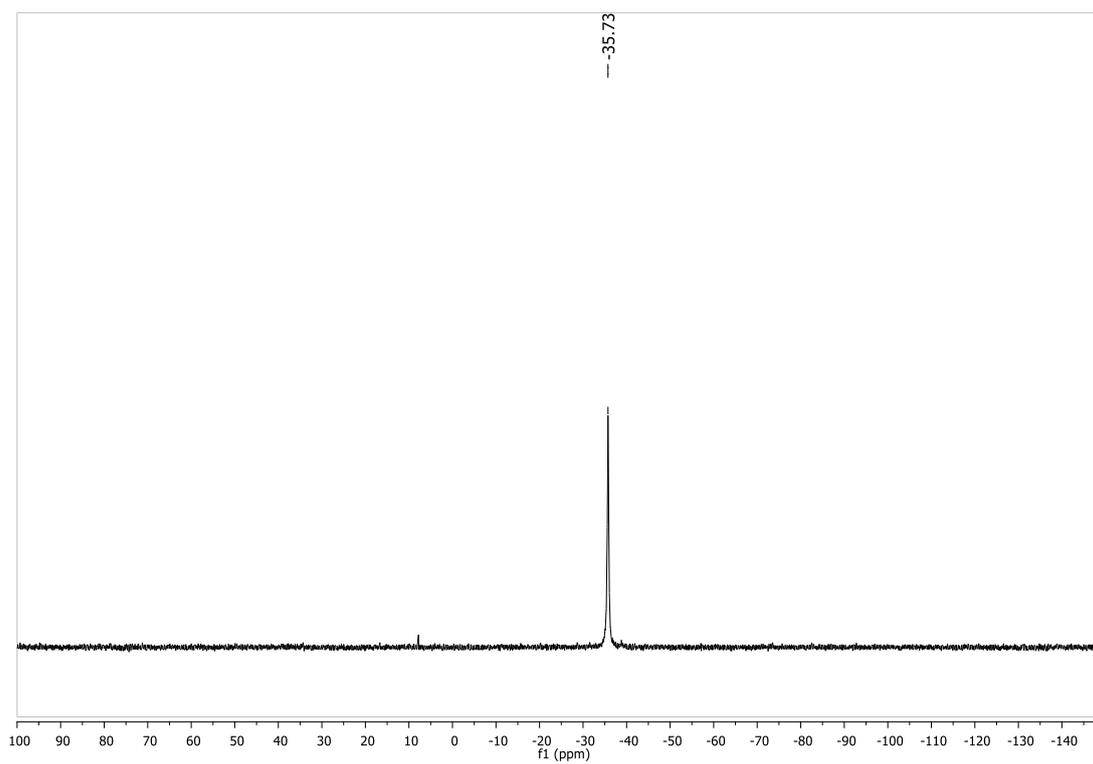
^1H NMR spectrum of $[\text{CuCl}(\text{PMe}_2\text{Ar}^{\text{Dipp}_2})_2]$, 2a



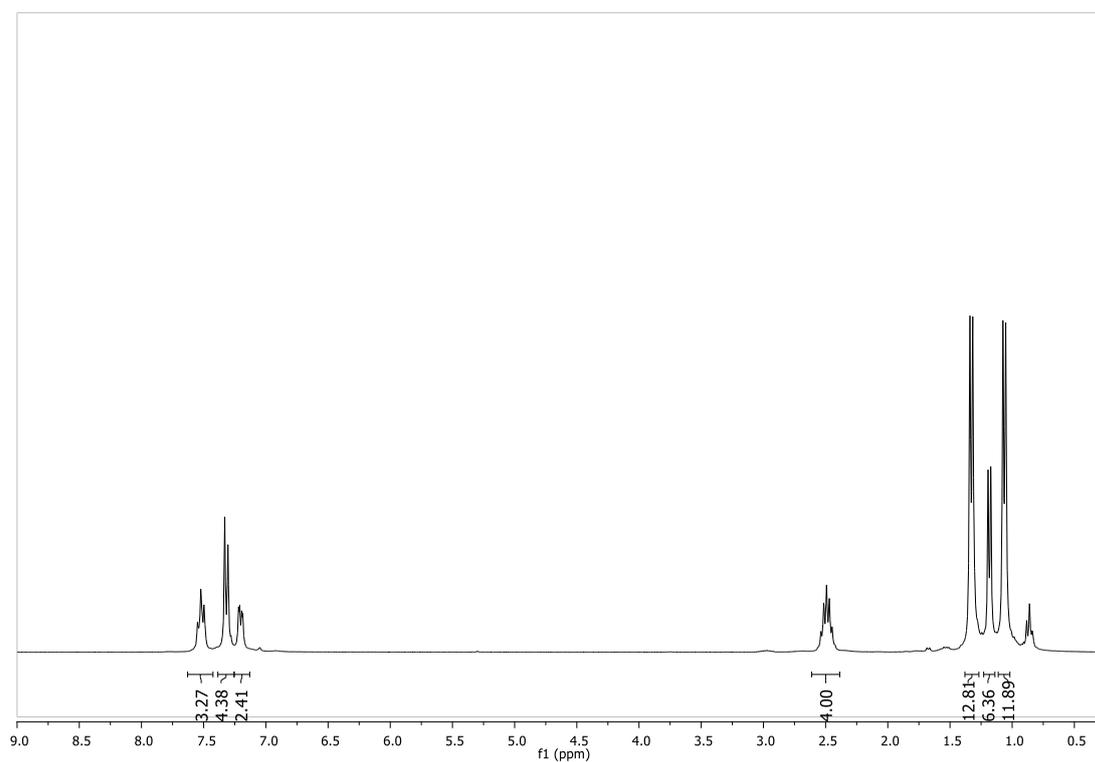
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{CuCl}(\text{PMe}_2\text{Ar}^{\text{Dipp}_2})_2]$, 2a



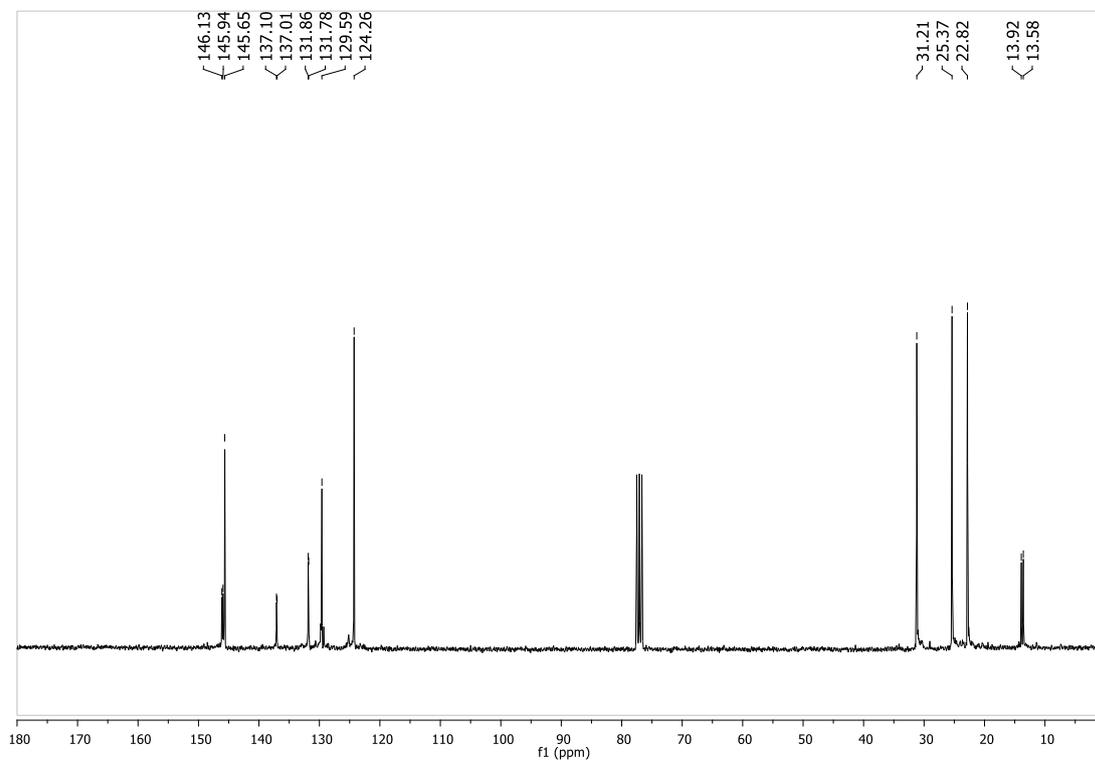
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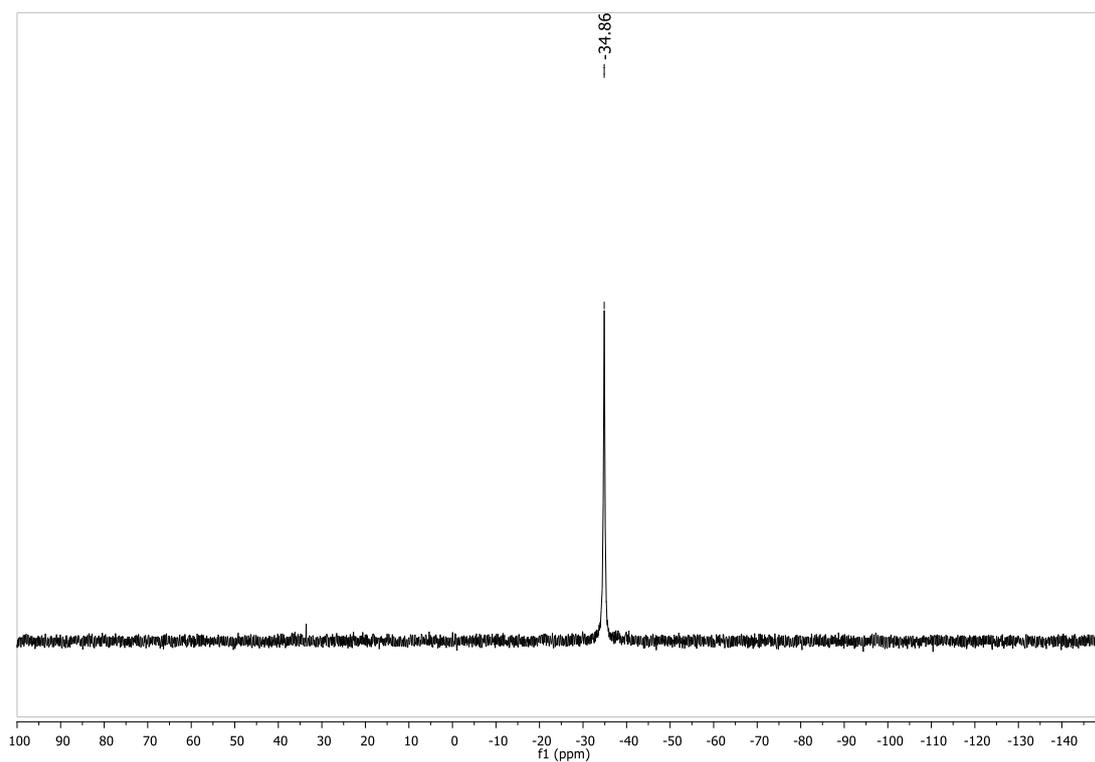
^1H NMR spectrum of $[\text{CuBr}(\text{PMe}_2\text{Ar}^{\text{Dipp}_2})_2]$, 2b



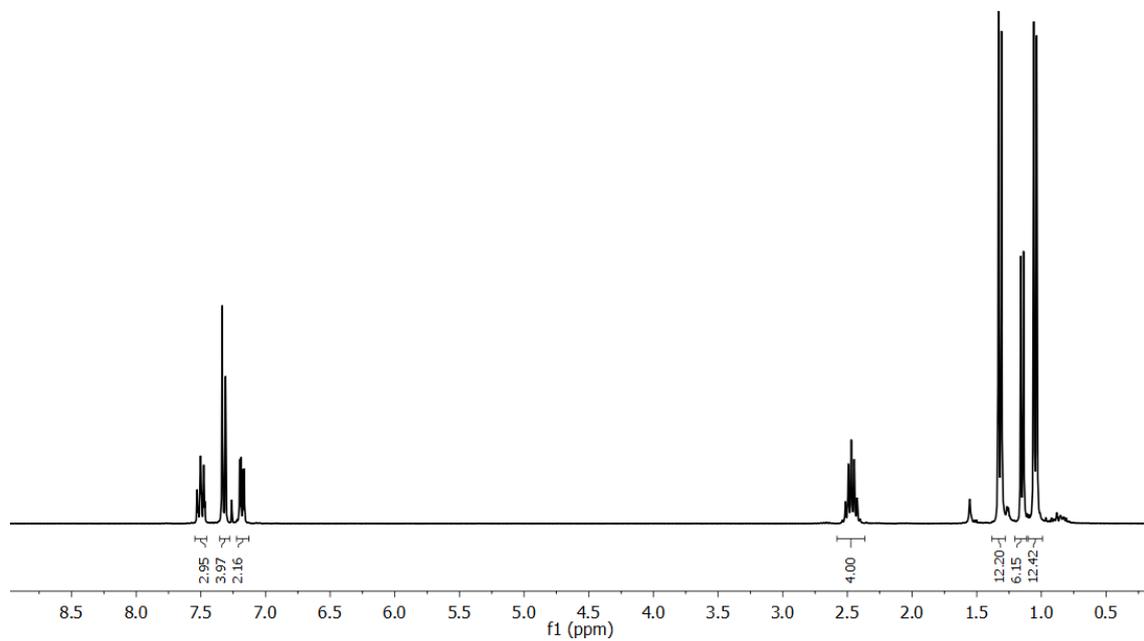
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{CuBr}(\text{PMe}_2\text{Ar}^{\text{Dipp}_2})_2]$, 2b



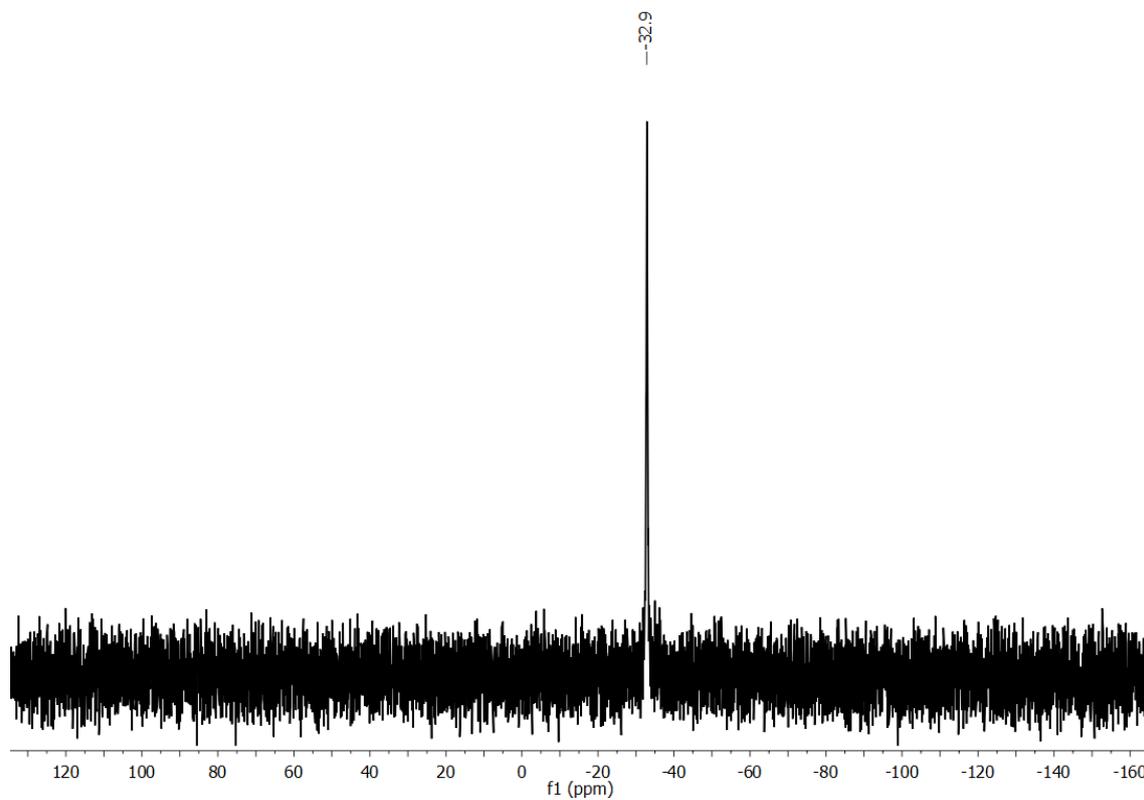
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{CuBr}(\text{PMe}_2\text{Ar}^{\text{Dipp}_2})_2]$, **2b**



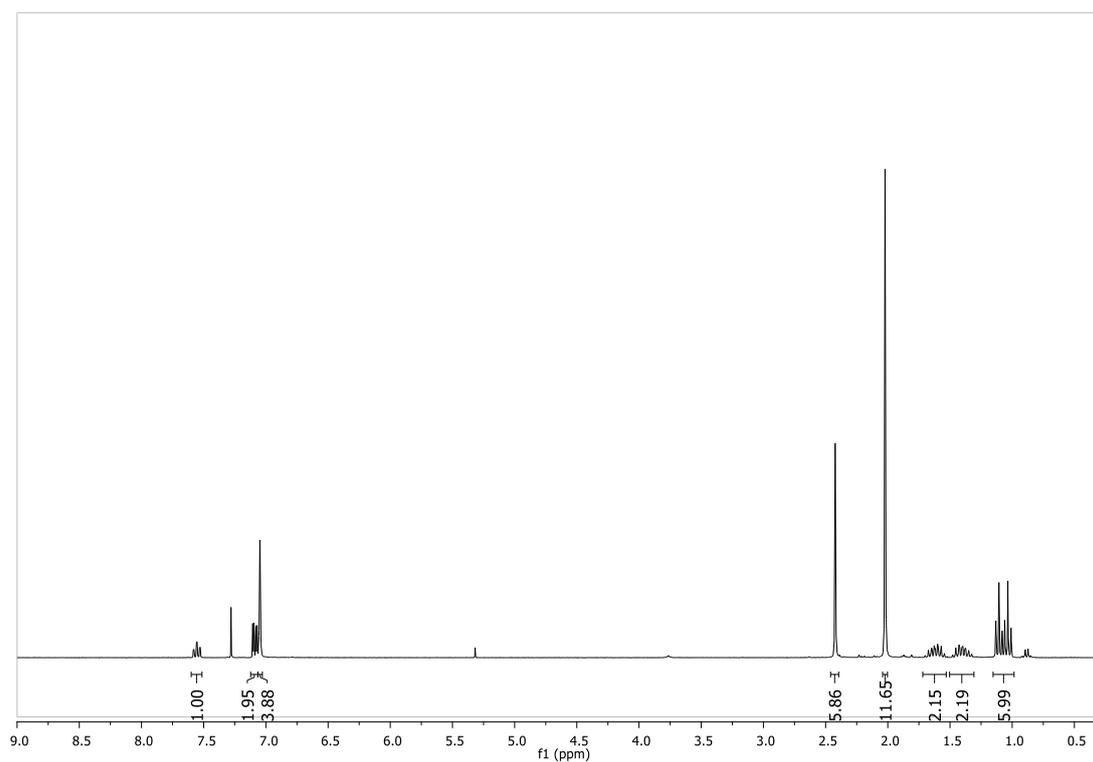
^1H NMR spectrum of $[\text{CuI}(\text{PMe}_2\text{Ar}^{\text{Dipp}_2})_2]_2$, **2c**



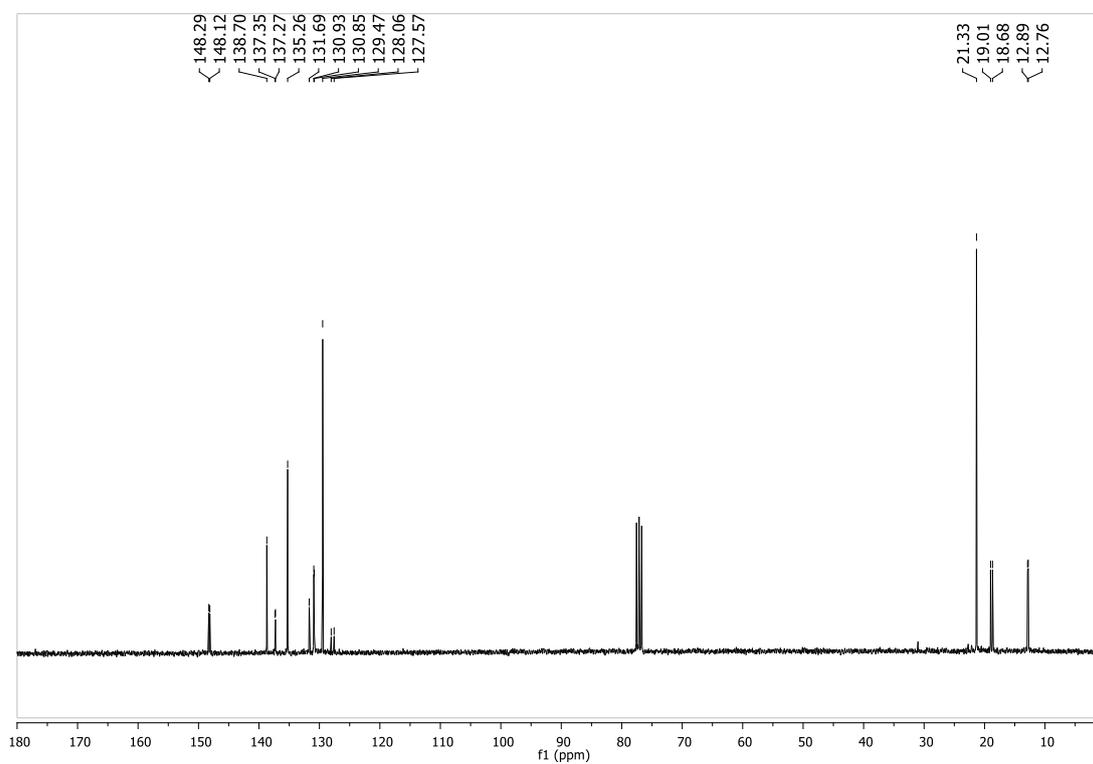
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{CuI}(\text{PMe}_2\text{Ar}^{\text{Dipp}_2})_2]_2$, **2c**



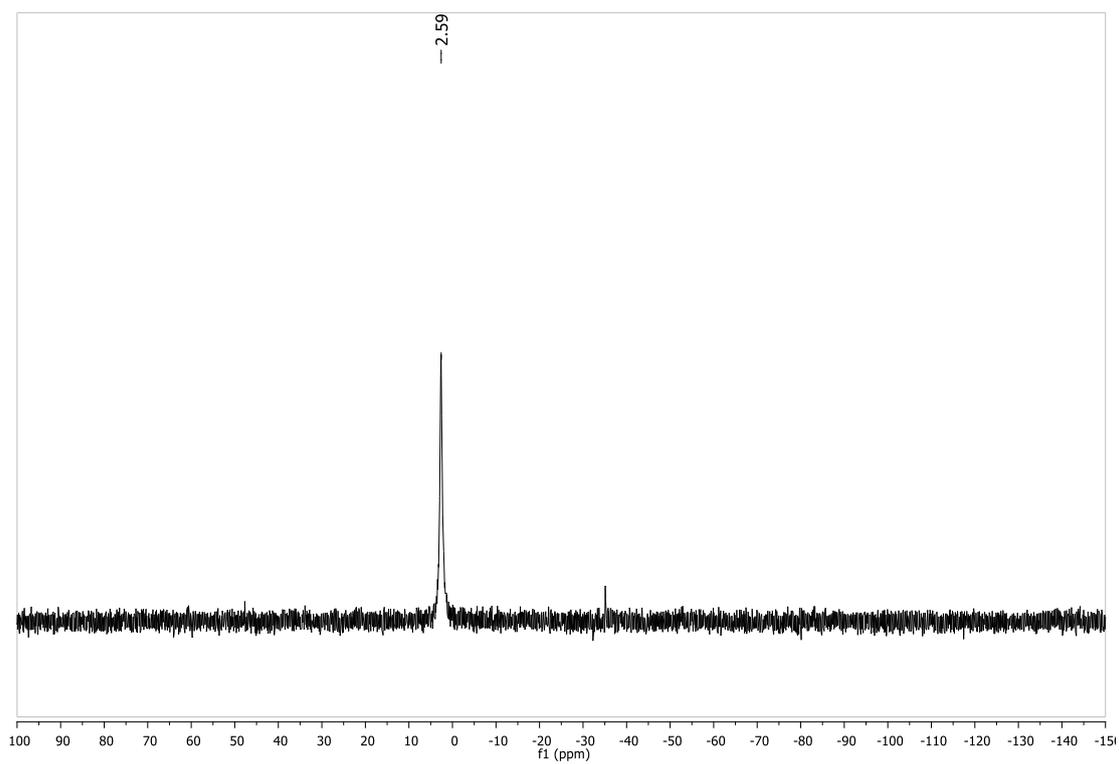
^1H NMR spectrum of $[\text{CuCl}(\text{PEt}_2\text{Ar}^{\text{Mes}_2})_2]$, 3a



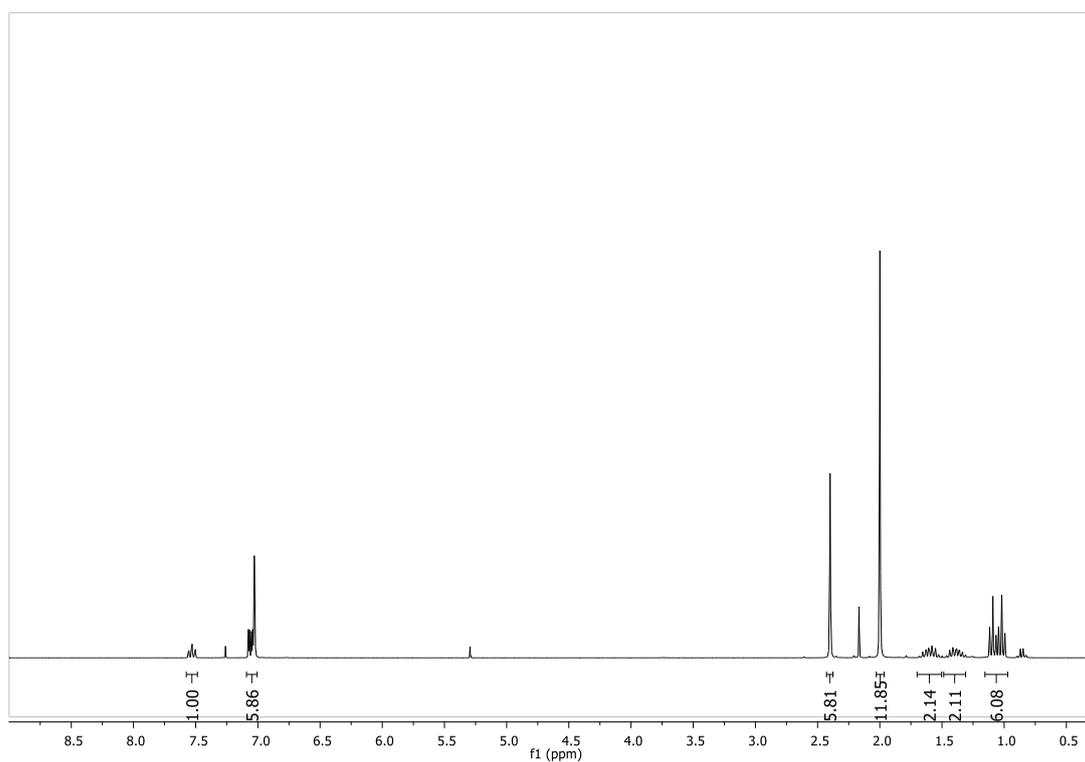
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{CuCl}(\text{PEt}_2\text{Ar}^{\text{Mes}_2})_2]$, 3a



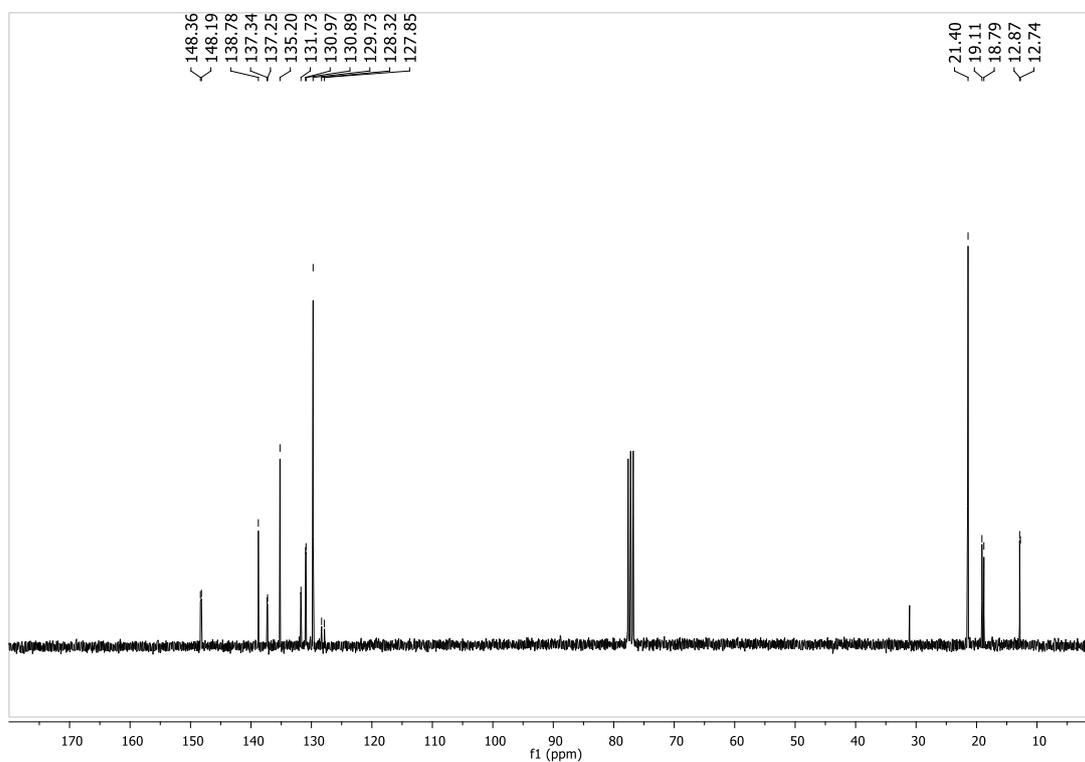
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{CuCl}(\text{PEt}_2\text{Ar}^{\text{Mes}_2})_2]$, **3a**



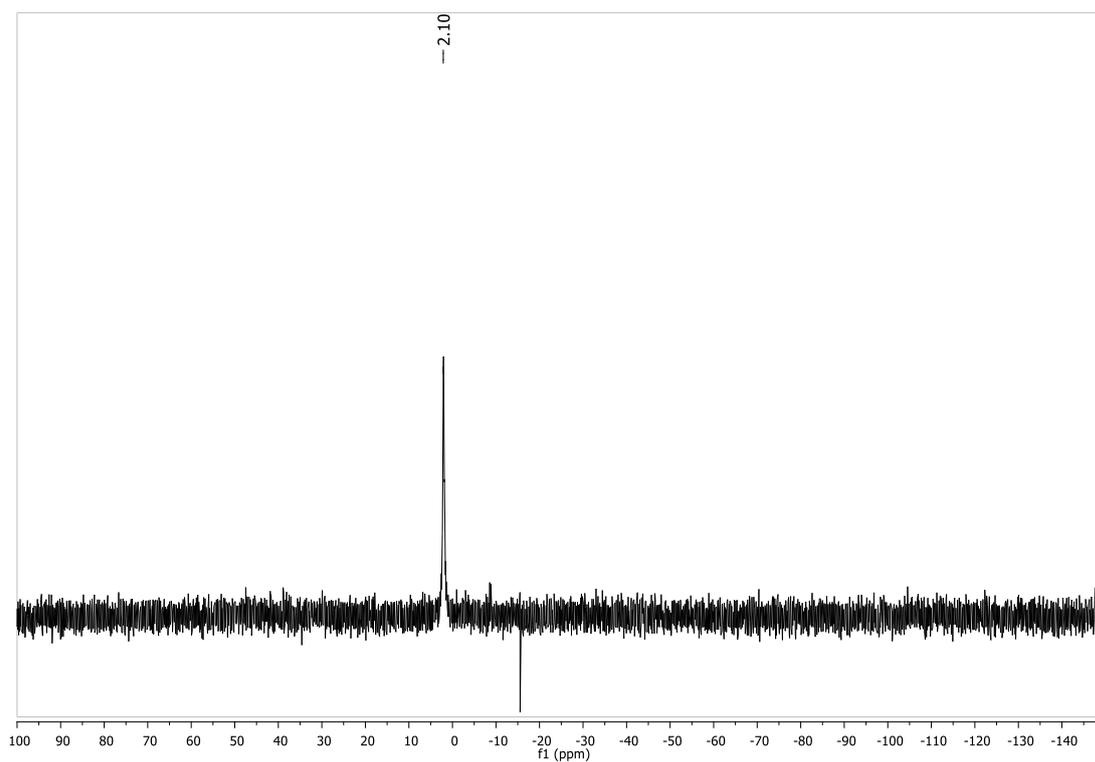
^1H NMR spectrum of $[\text{CuBr}(\text{PEt}_2\text{Ar}^{\text{Mes}_2})_2]$, **3b**



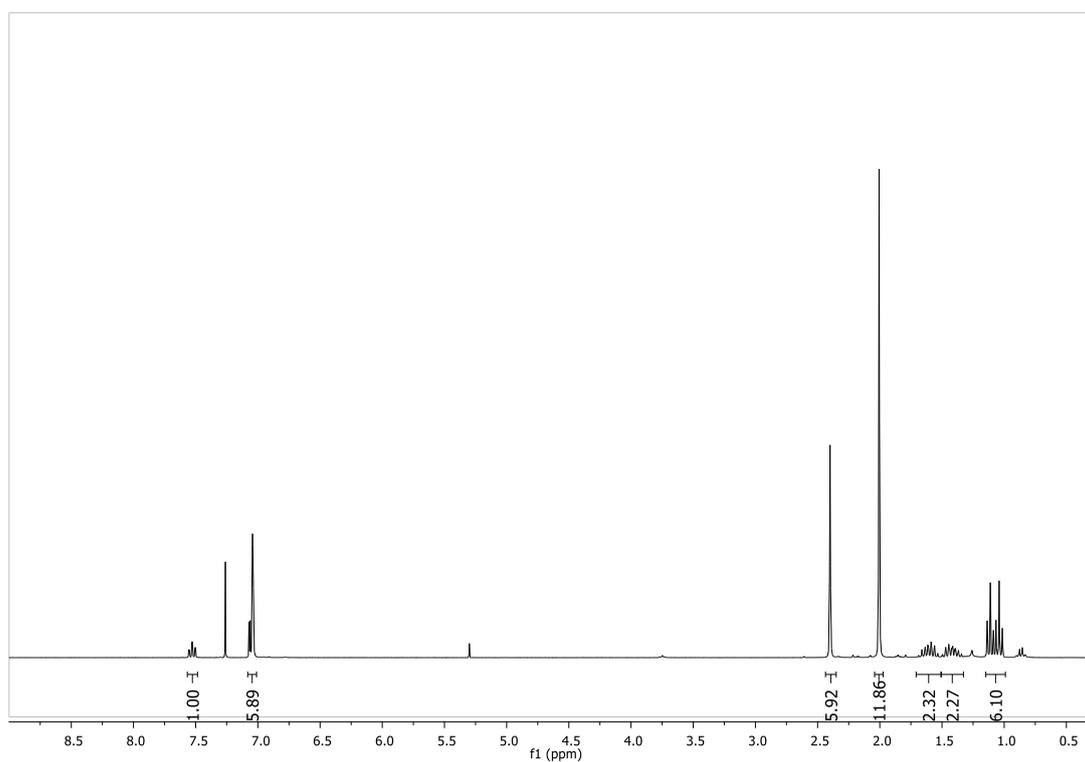
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{CuBr}(\text{PEt}_2\text{Ar}^{\text{Mes}_2})_2]$, **3b**



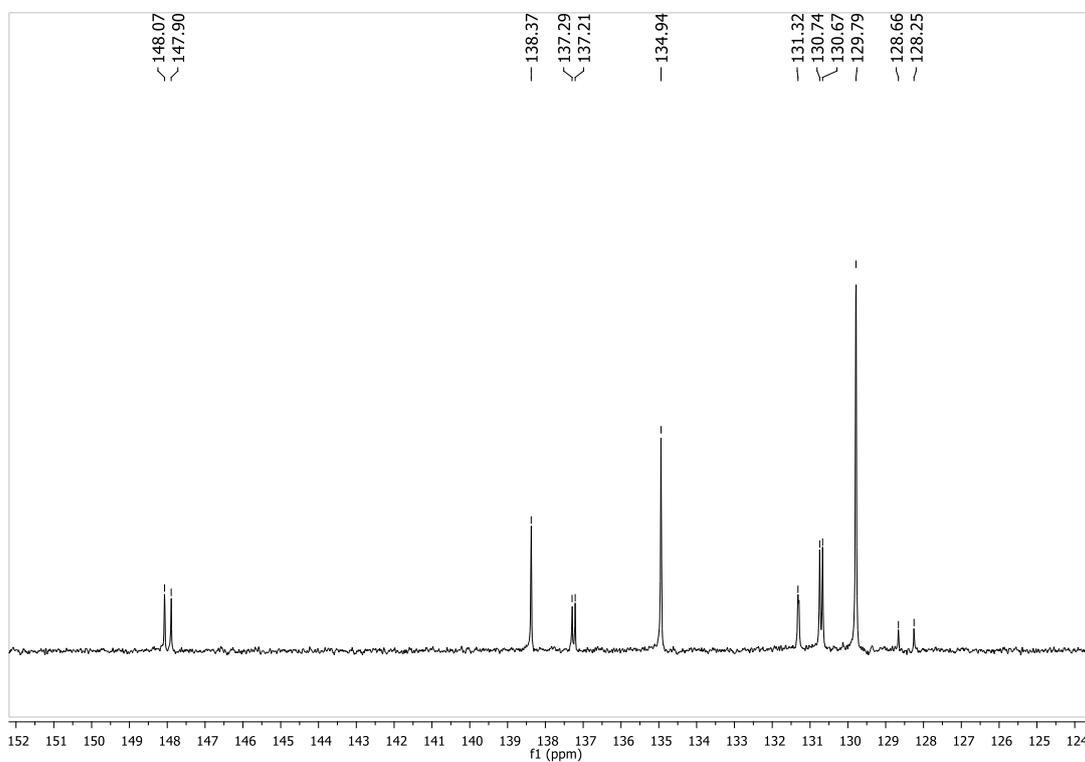
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{CuBr}(\text{PEt}_2\text{Ar}^{\text{Mes}_2})_2]$, **3b**



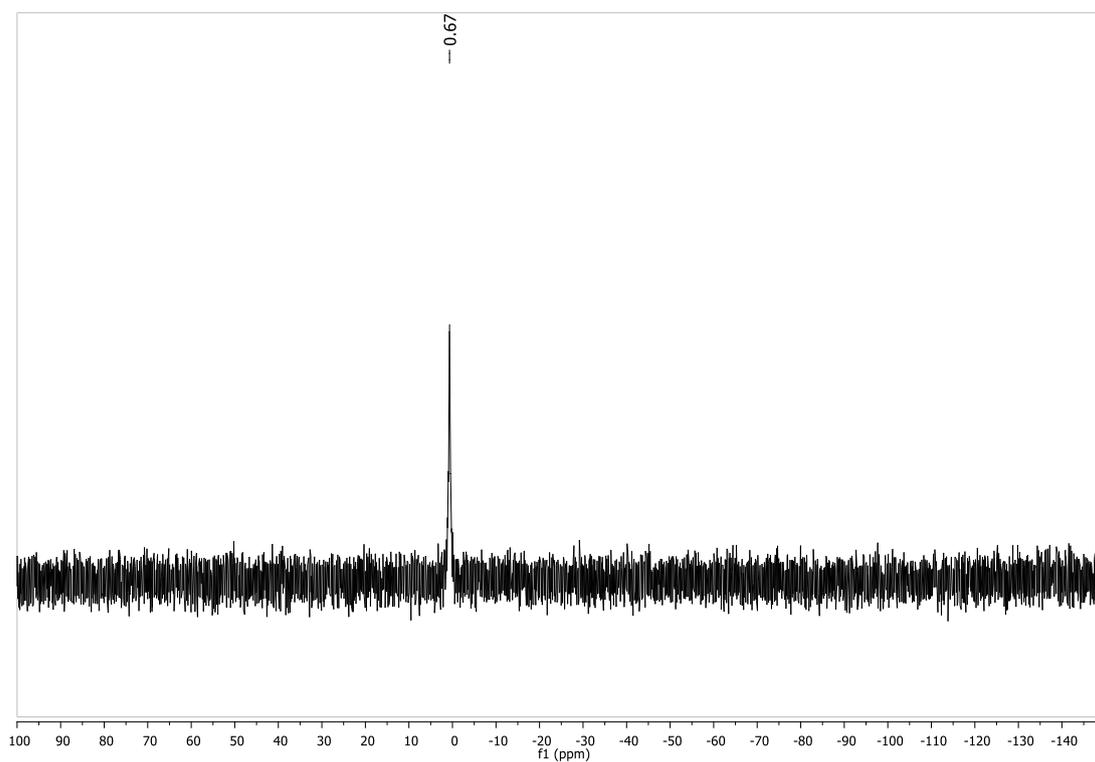
^1H NMR spectrum of $[\text{CuI}(\text{PEt}_2\text{Ar}^{\text{Mes}_2})_2]$, **3c**



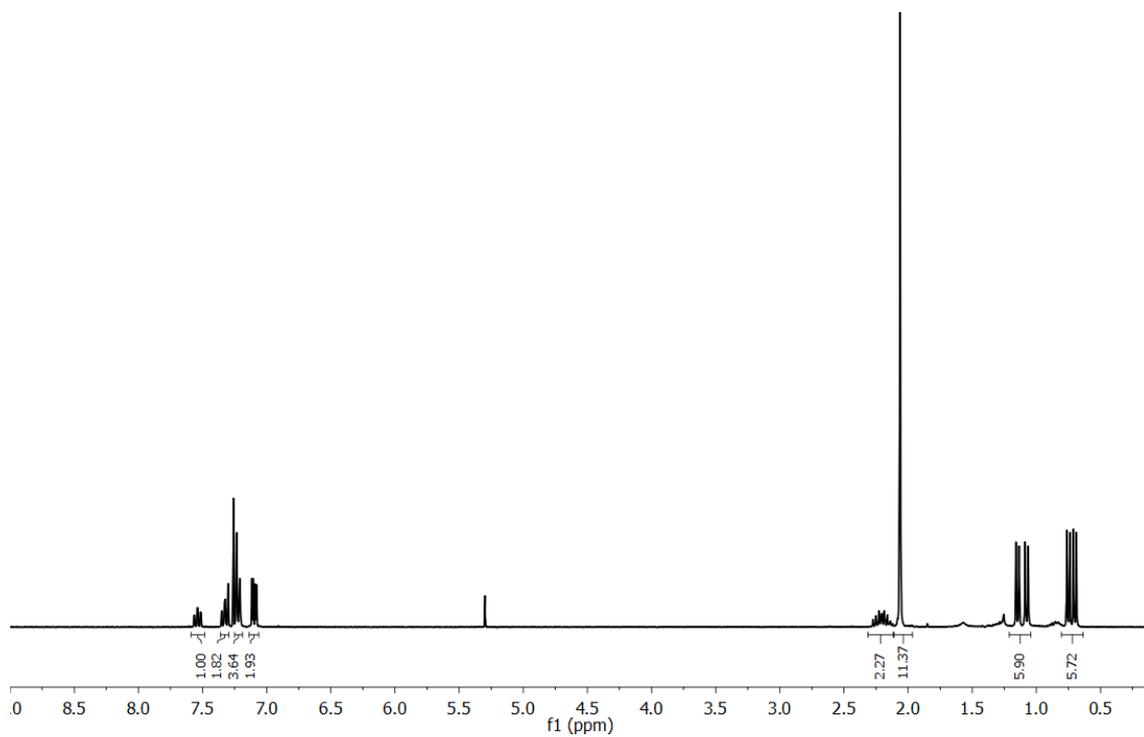
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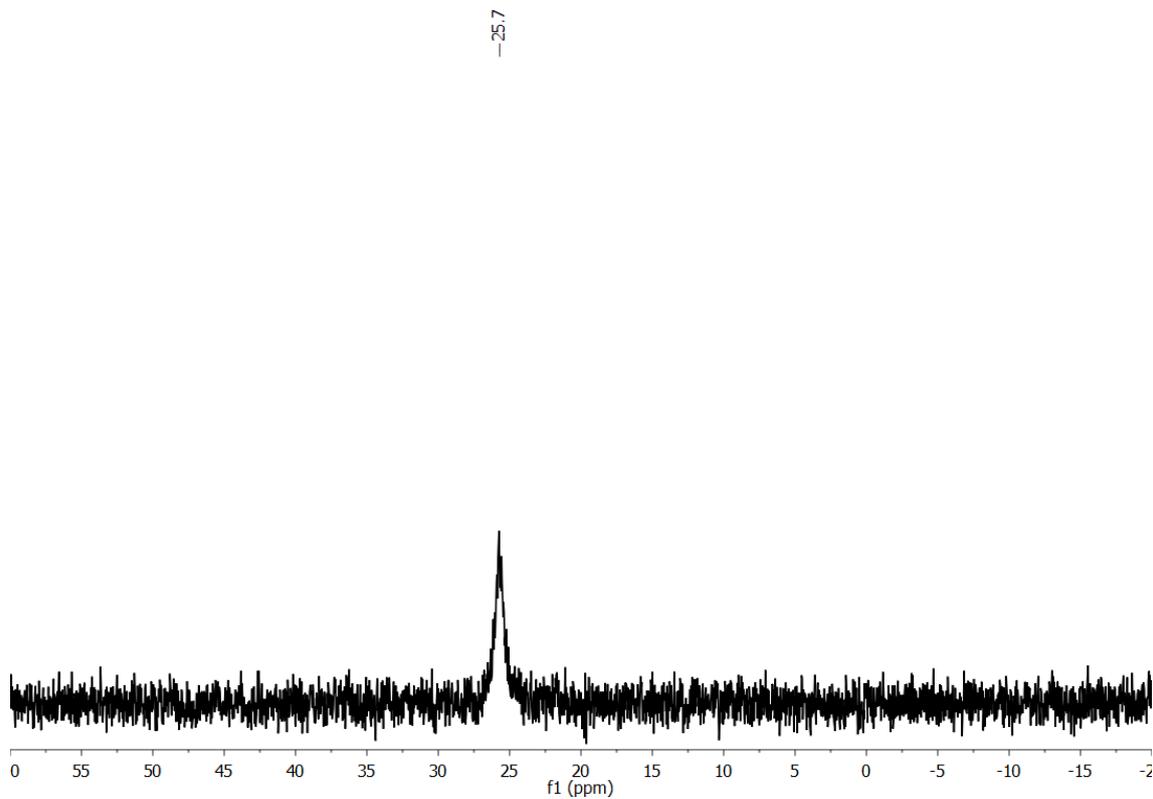
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{CuBr}(\text{PEt}_2\text{Ar}^{\text{Mes}_2})_2]$, **3c**



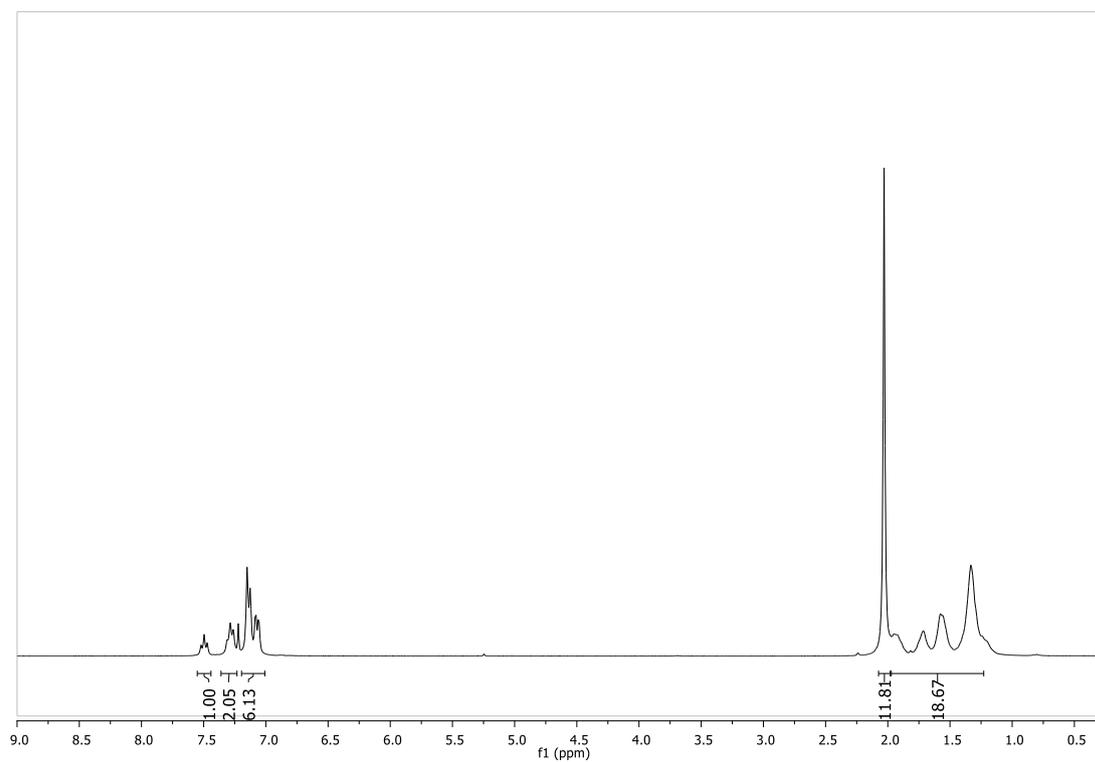
^1H NMR spectrum of $[\text{CuI}(\text{PiPr}_2\text{Ar}^{\text{Xyl}_2})_2]$, **4c**



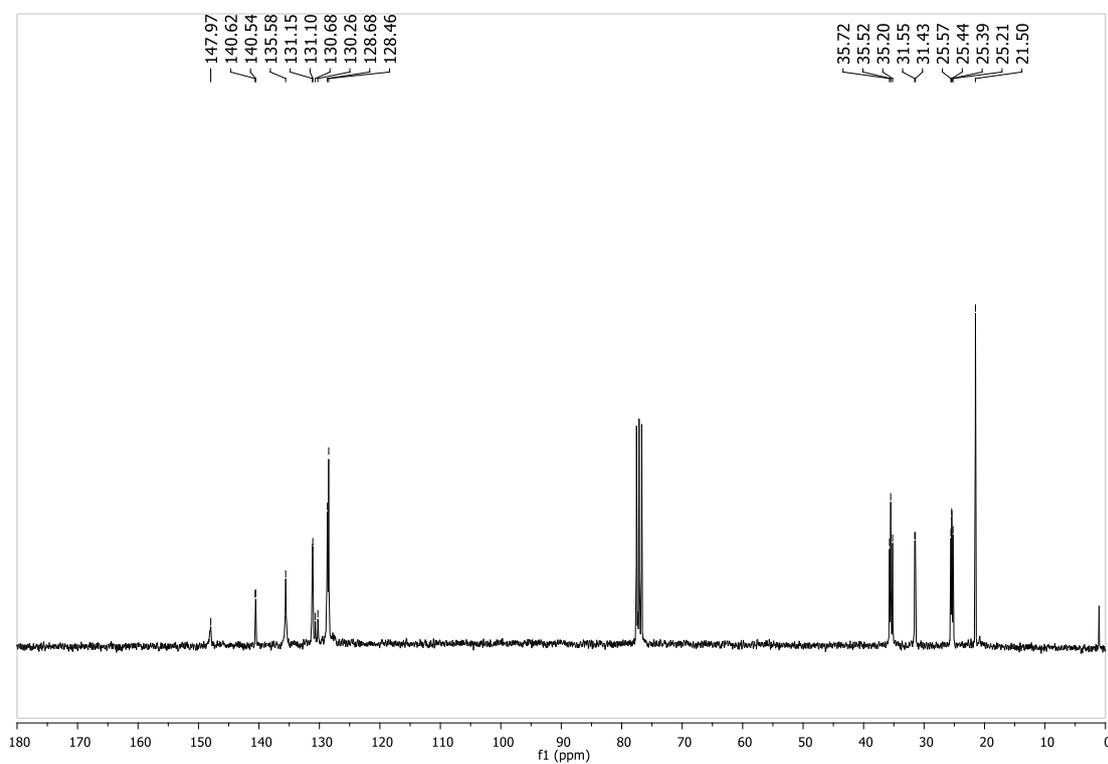
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{CuI}(\text{PiPr}_2\text{Ar}^{\text{Xyl}_2})_2]$, **4c**



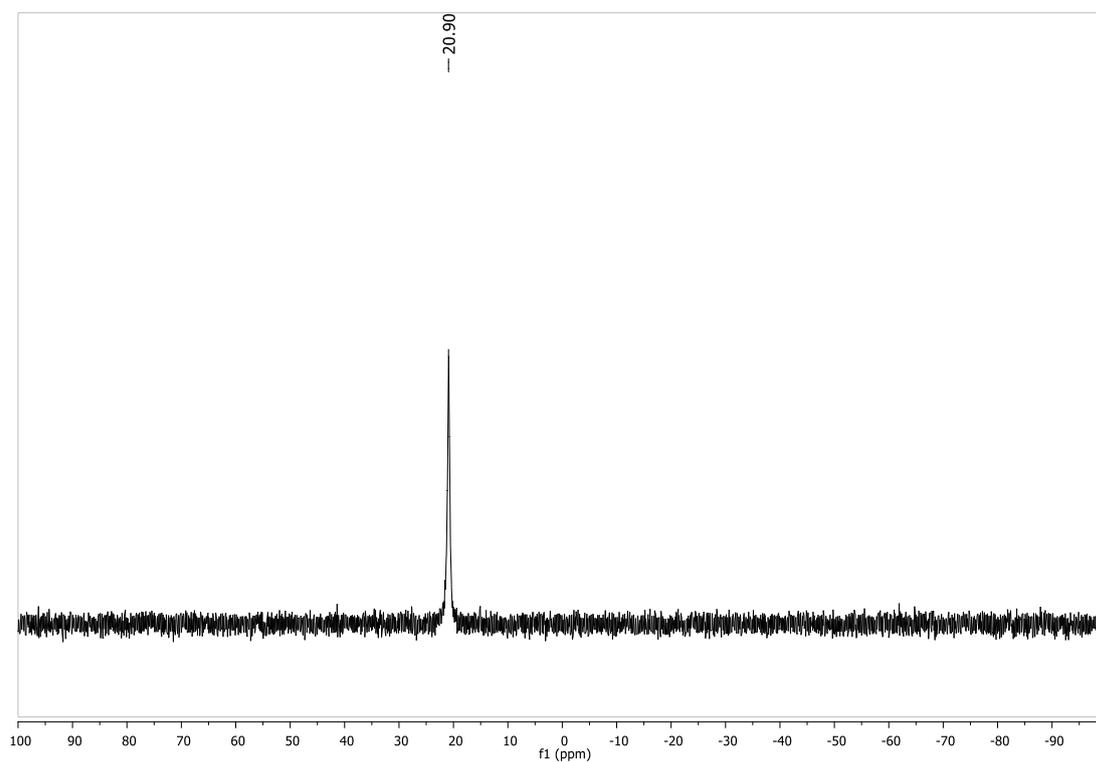
^1H NMR spectrum of $[\text{CuCl}(\text{PCyp}_2\text{Ar}^{\text{Xyl}_2})_2]$, 5a



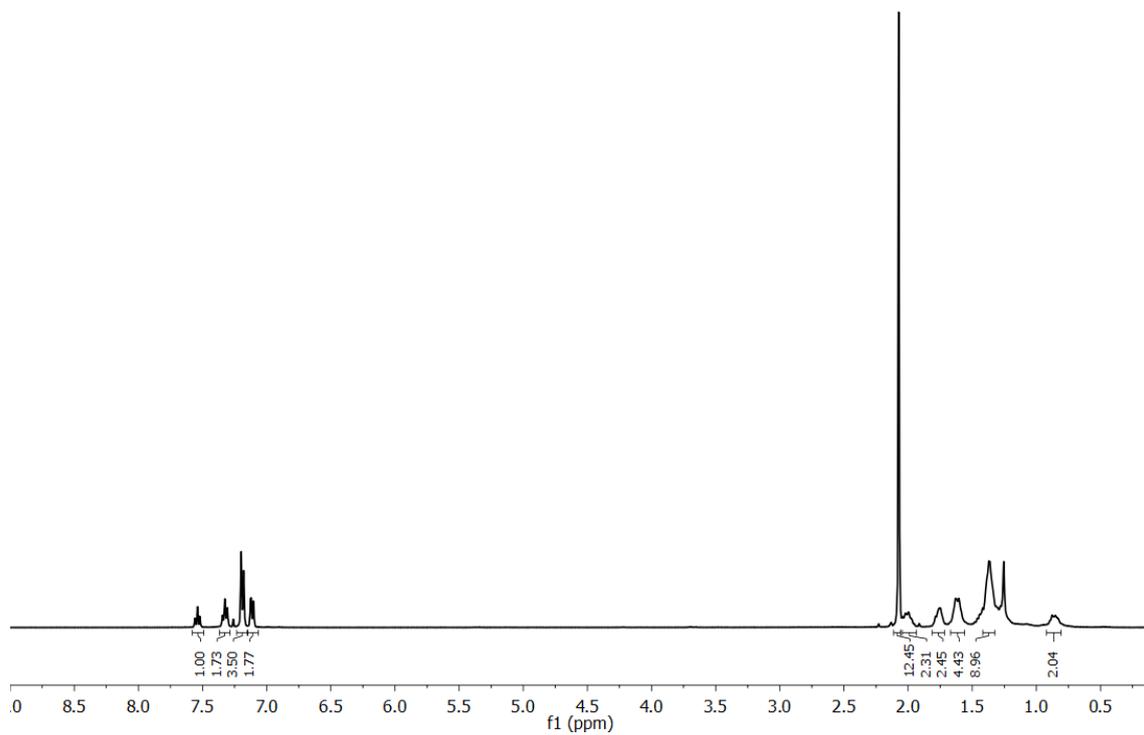
$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{CuCl}(\text{PCyp}_2\text{Ar}^{\text{Xyl}_2})_2]$, 5a



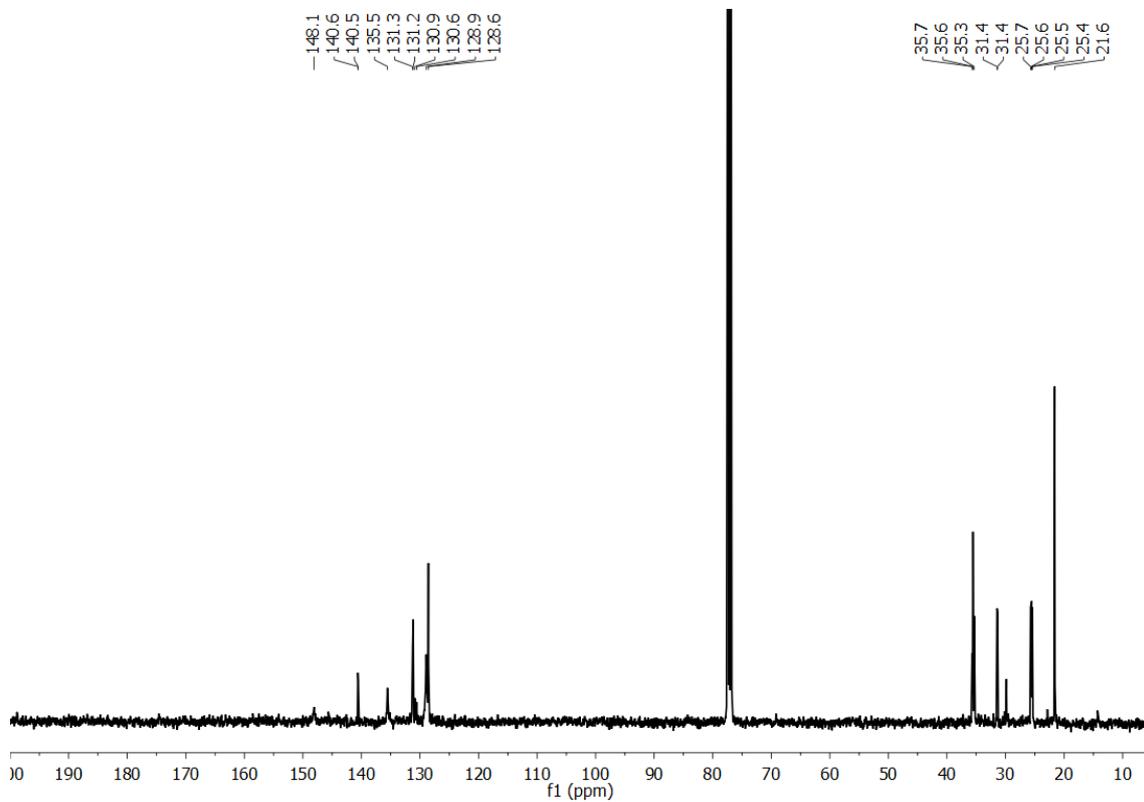
$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{CuCl}(\text{PCyp}_2\text{Ar}^{\text{Xyl}_2})_2]$, 5a



^1H NMR spectrum of $[\text{CuBr}(\text{PCyp}_2\text{Ar}^{\text{Xyl}_2})_2]$, **5b**

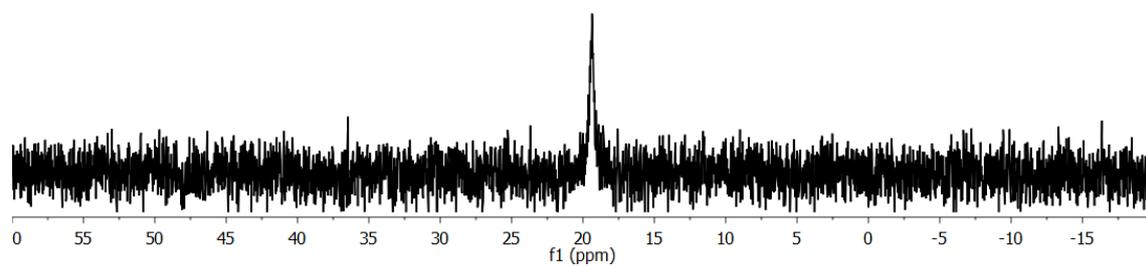


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{CuBr}(\text{PCyp}_2\text{Ar}^{\text{Xyl}_2})_2]$, **5b**

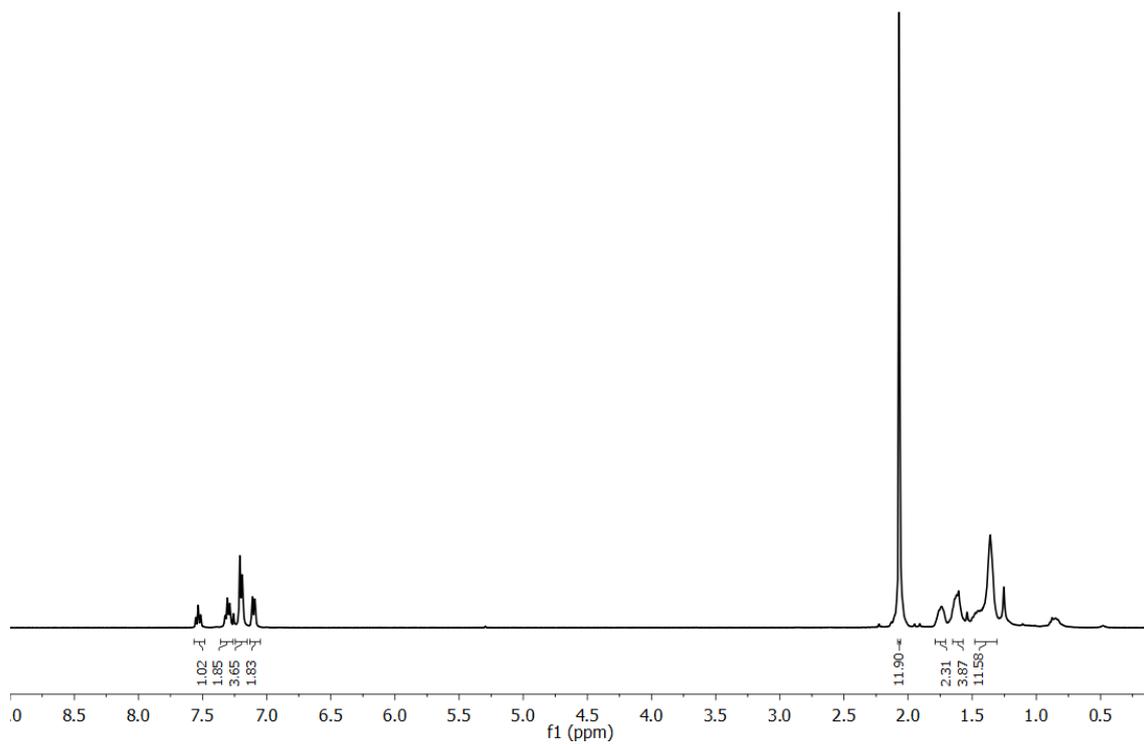


$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{CuBr}(\text{PCyp}_2\text{Ar}^{\text{Xyl}_2})_2]$, **5b**

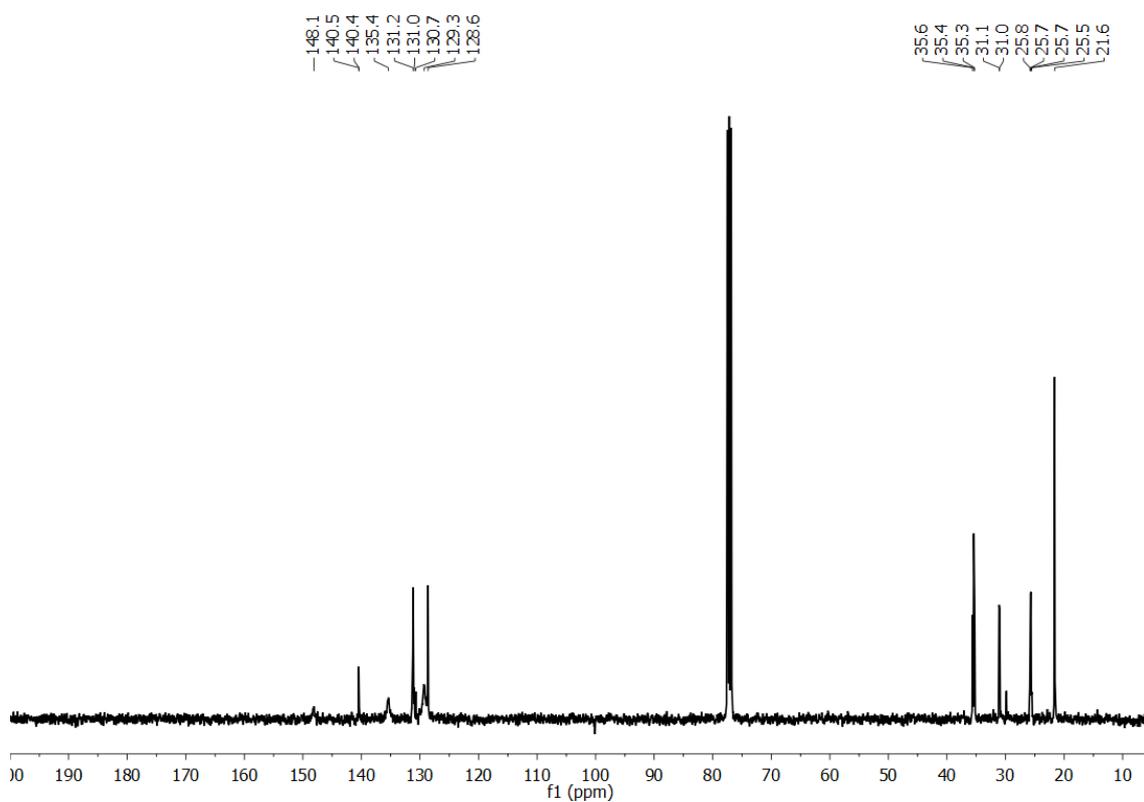
-19.4



^1H NMR spectrum of $[\text{CuI}(\text{PCyp}_2\text{Ar}^{\text{Xyl}_2})_2]$, **5c**

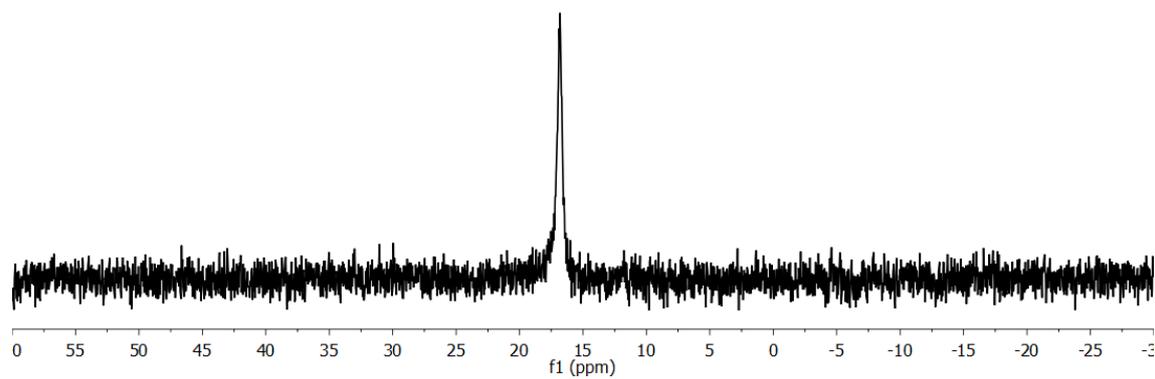


$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{CuI}(\text{PCyp}_2\text{Ar}^{\text{Xyl}_2})_2]$, **5c**

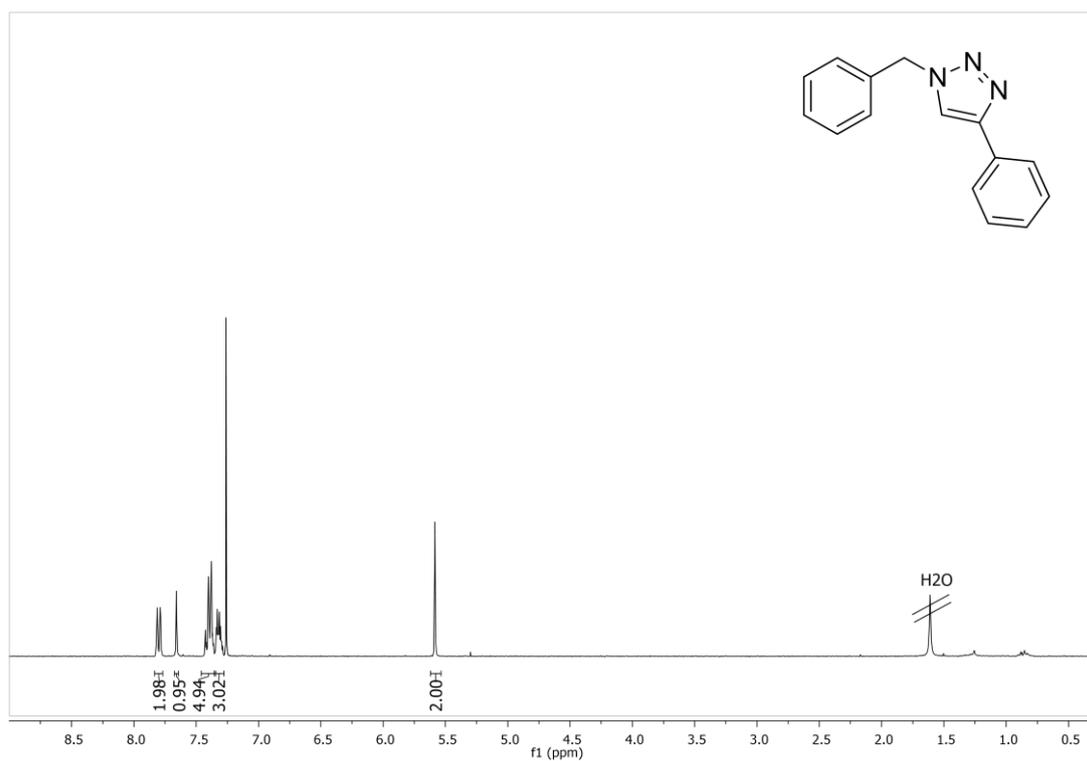


$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{CuI}(\text{PCyp}_2\text{Ar}^{\text{Xyl}_2})_2]$, **5c**

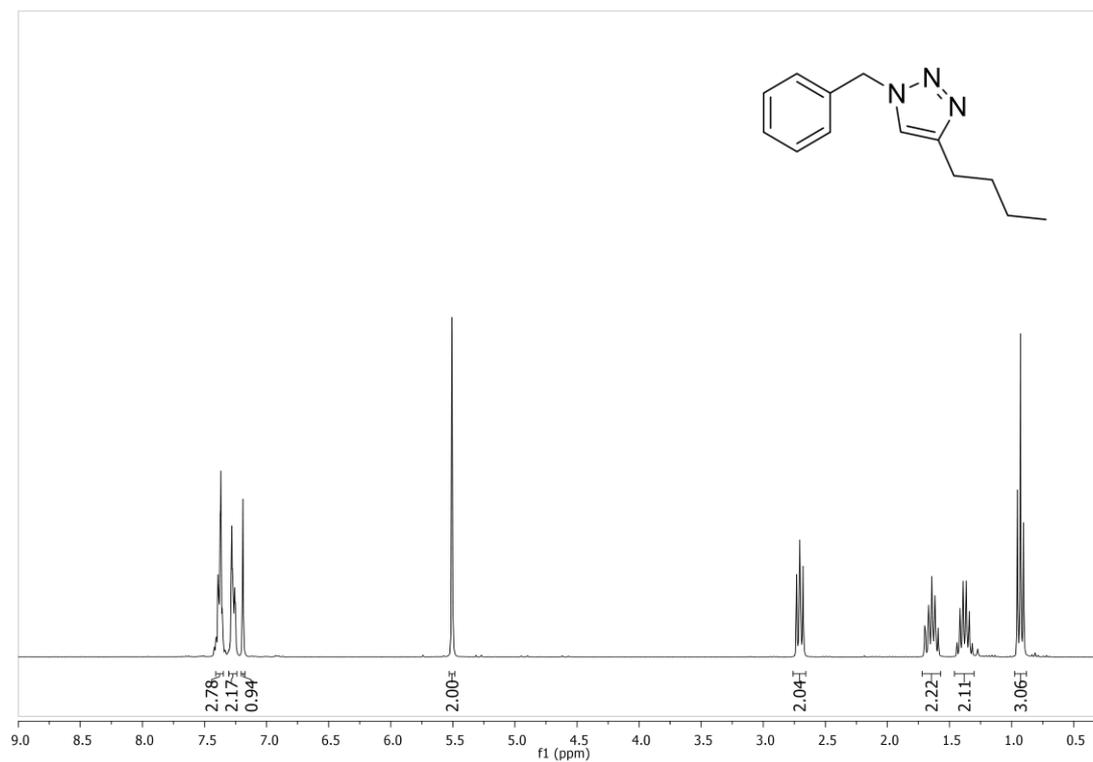
-16.8



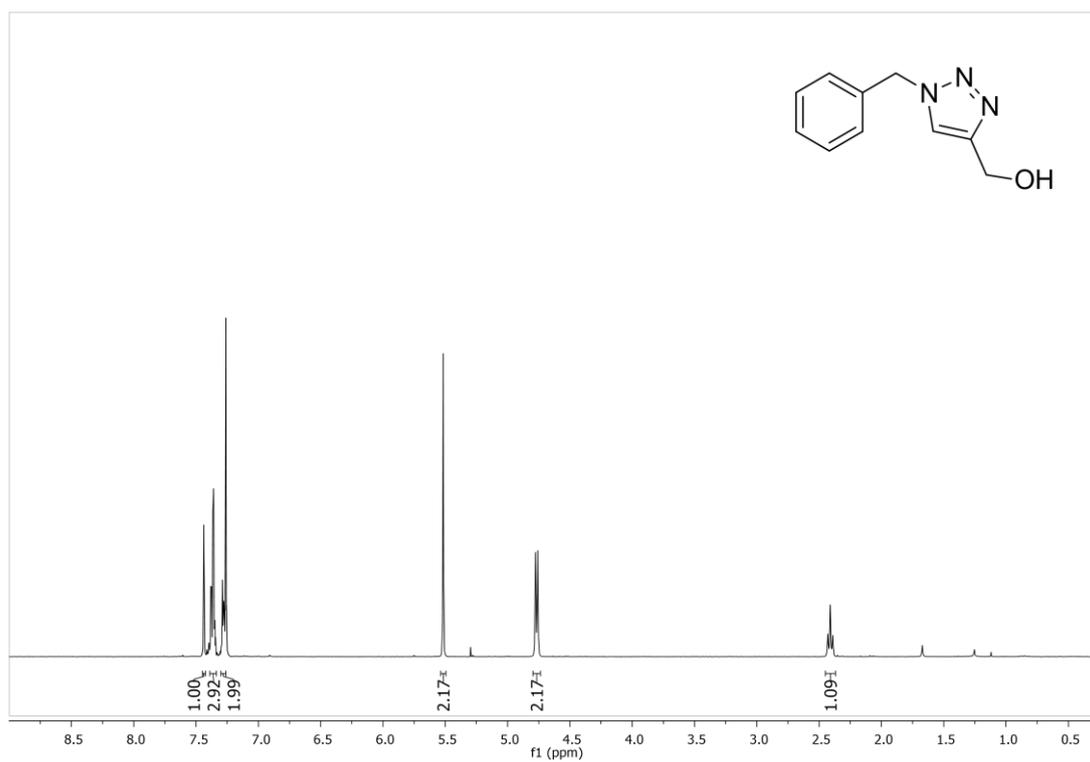
1-Benzyl-4-phenyl-1*H*-1,2,3-triazole, 14a



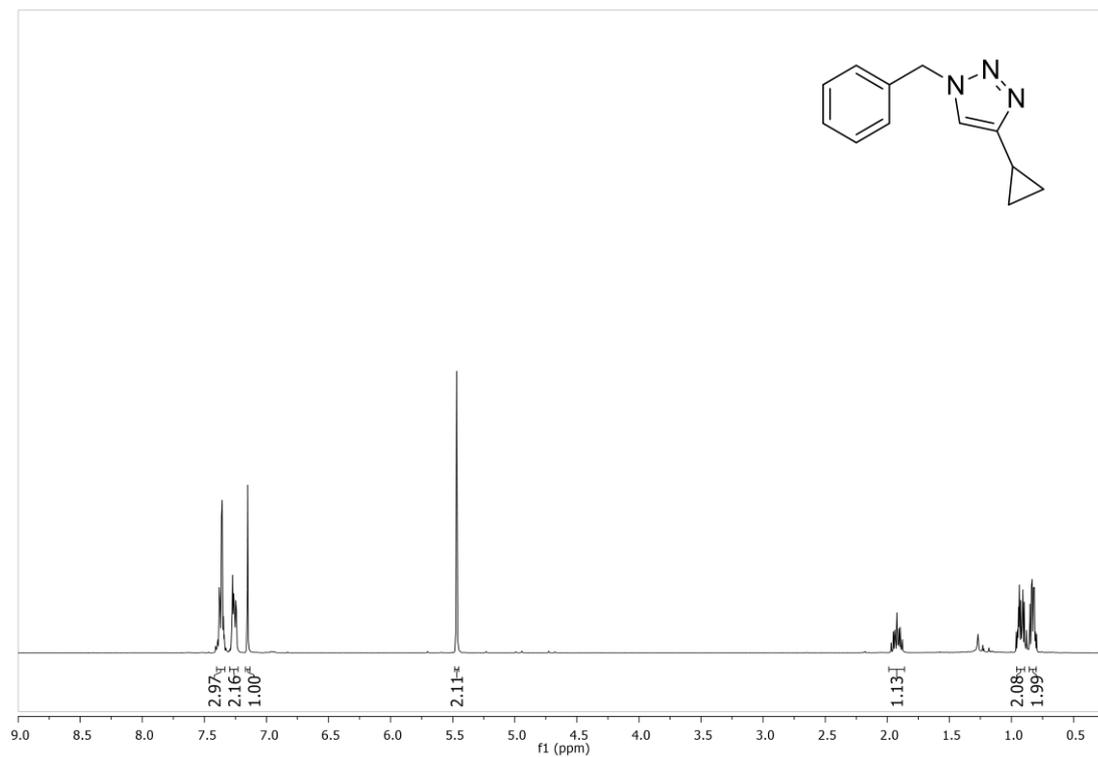
1-Benzyl-4-butyl-1*H*-1,2,3-triazole, 14b



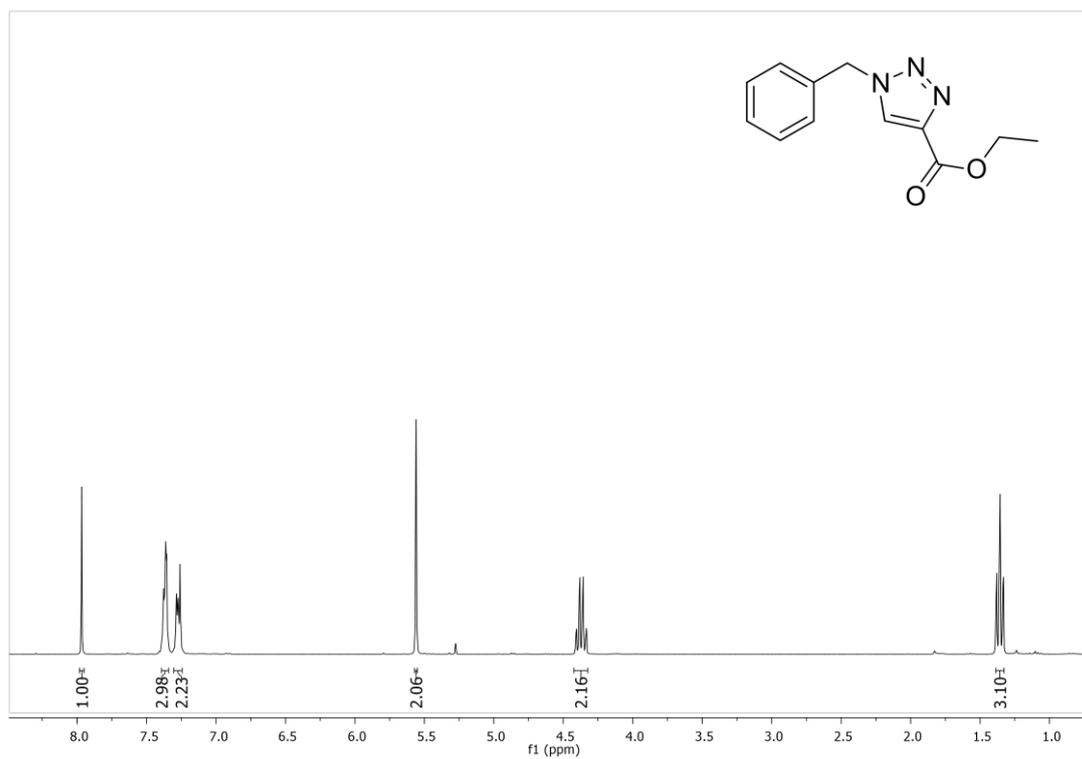
(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methanol, 14c



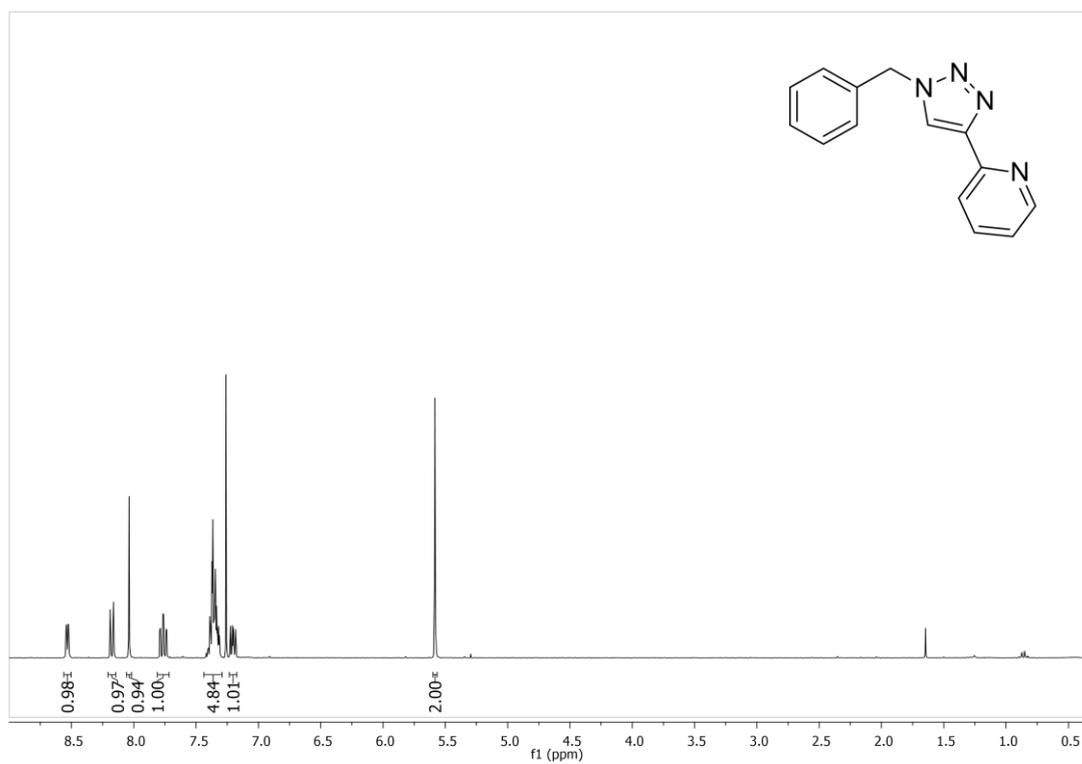
1-Benzyl-4-cyclopropyl-1*H*-1,2,3-triazole, 14d



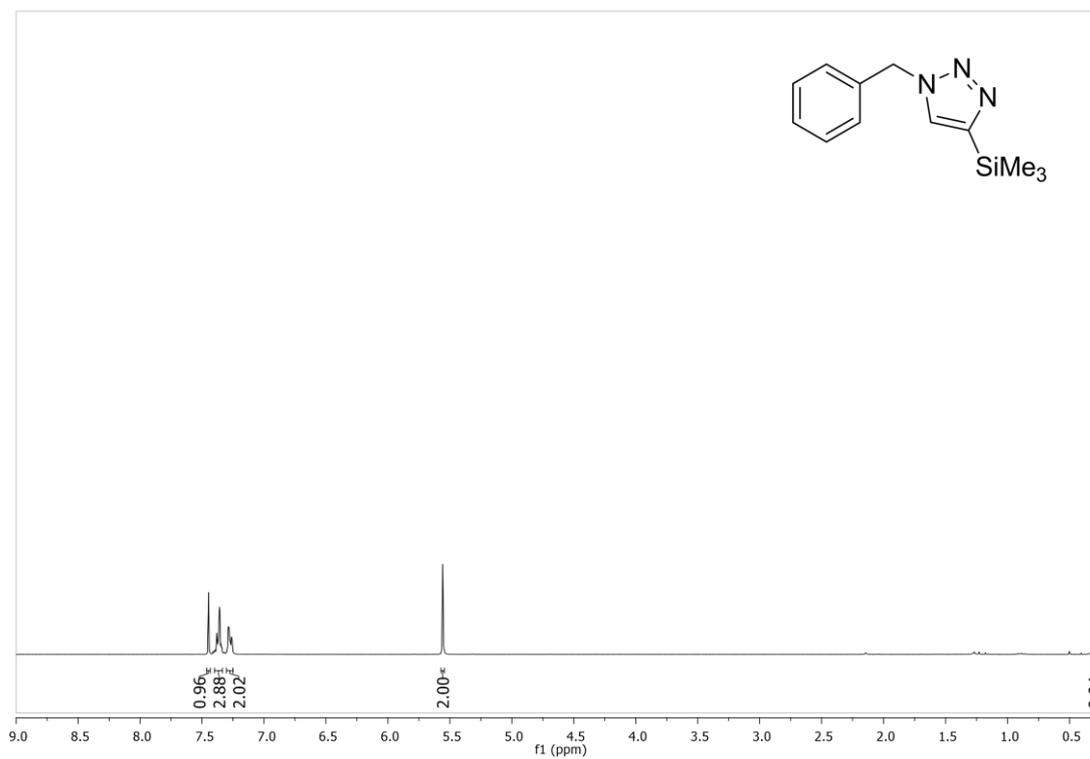
Ethyl 1-benzyl-1*H*-1,2,3-triazole-4-carboxylate, 14e



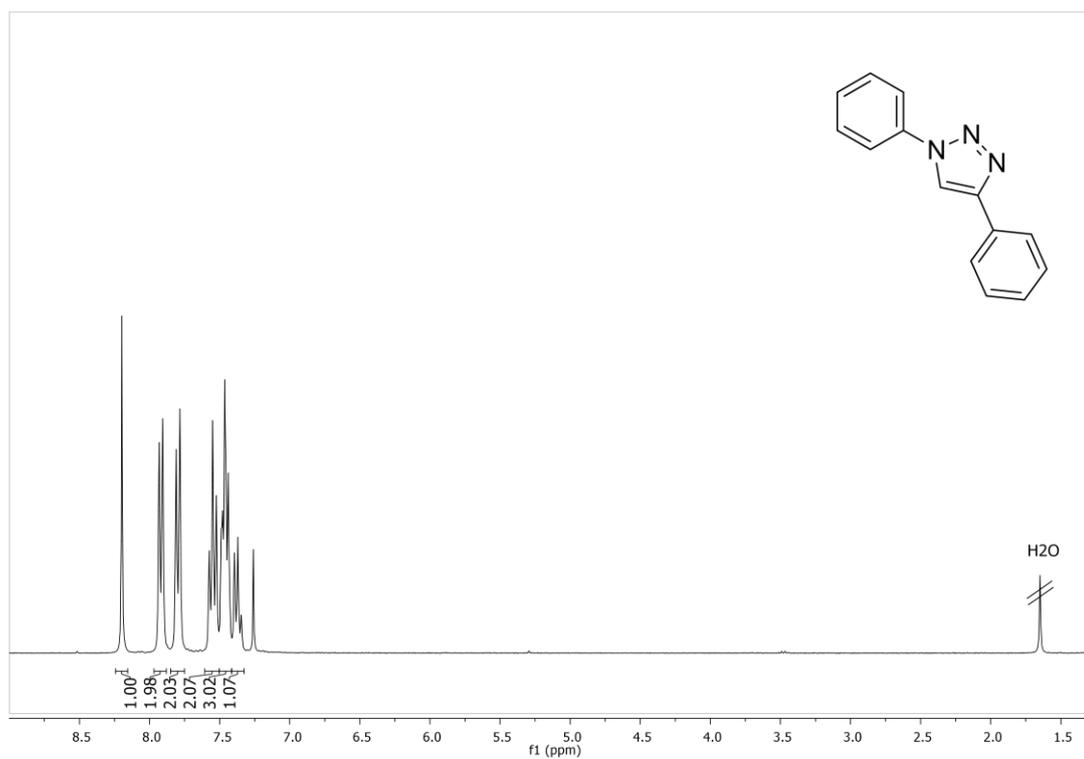
2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)pyridine, 14f



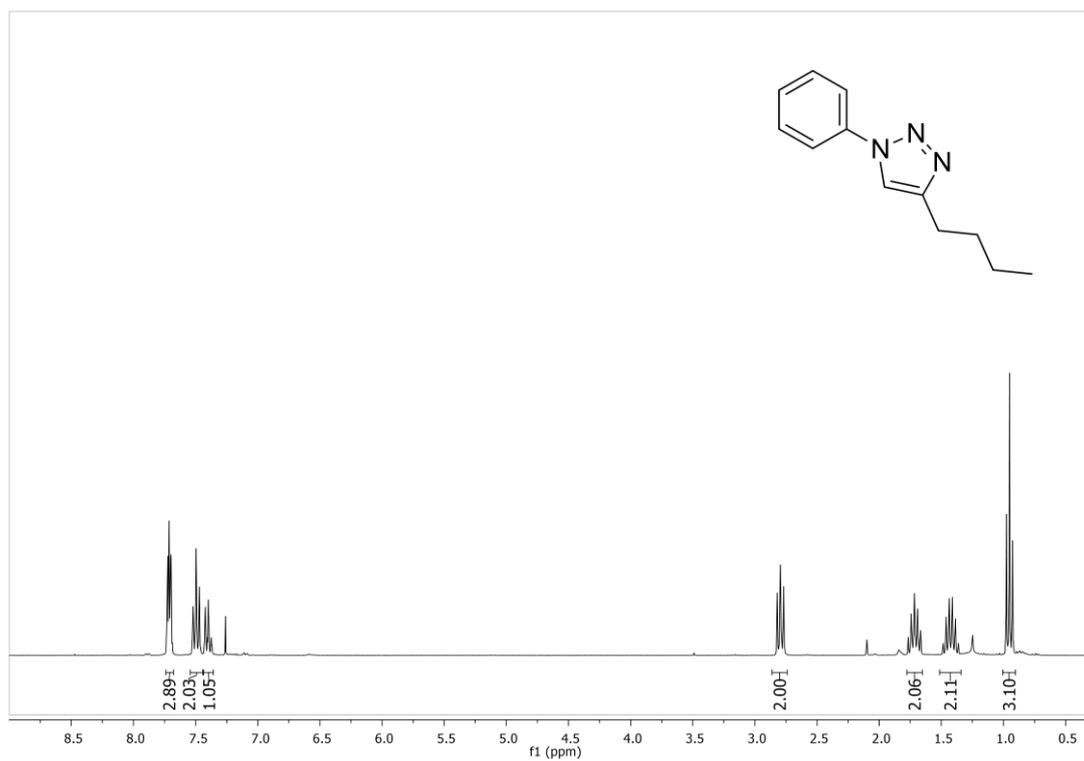
1-Benzyl-4-(trimethylsilyl)-1H-1,2,3-triazole, 14g



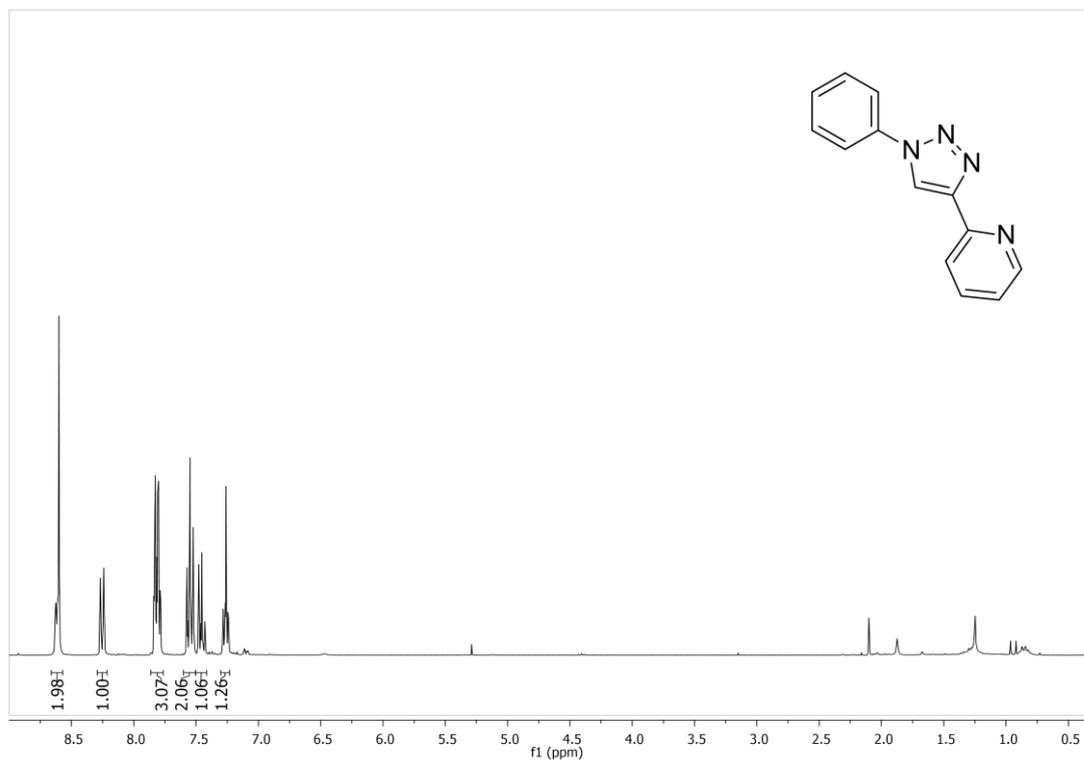
1,4-Diphenyl-1H-1,2,3-triazole, 14h



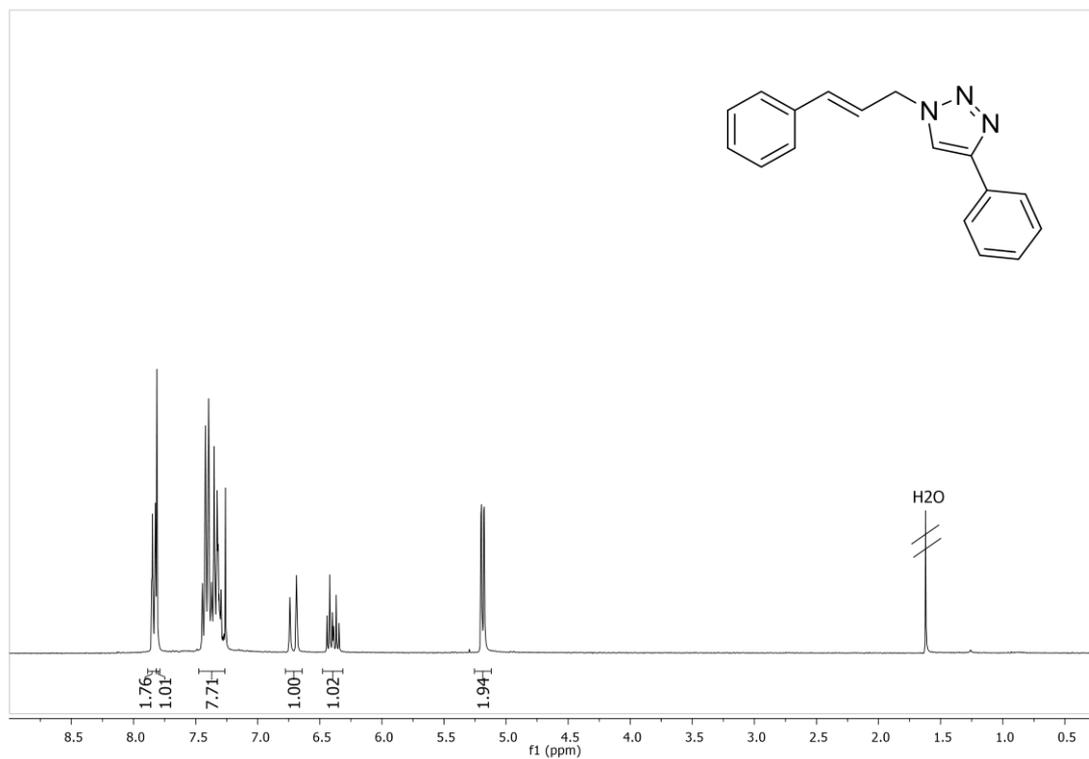
4-(*n*-Butyl)-1-phenyl-1*H*-1,2,3-triazole, 14i



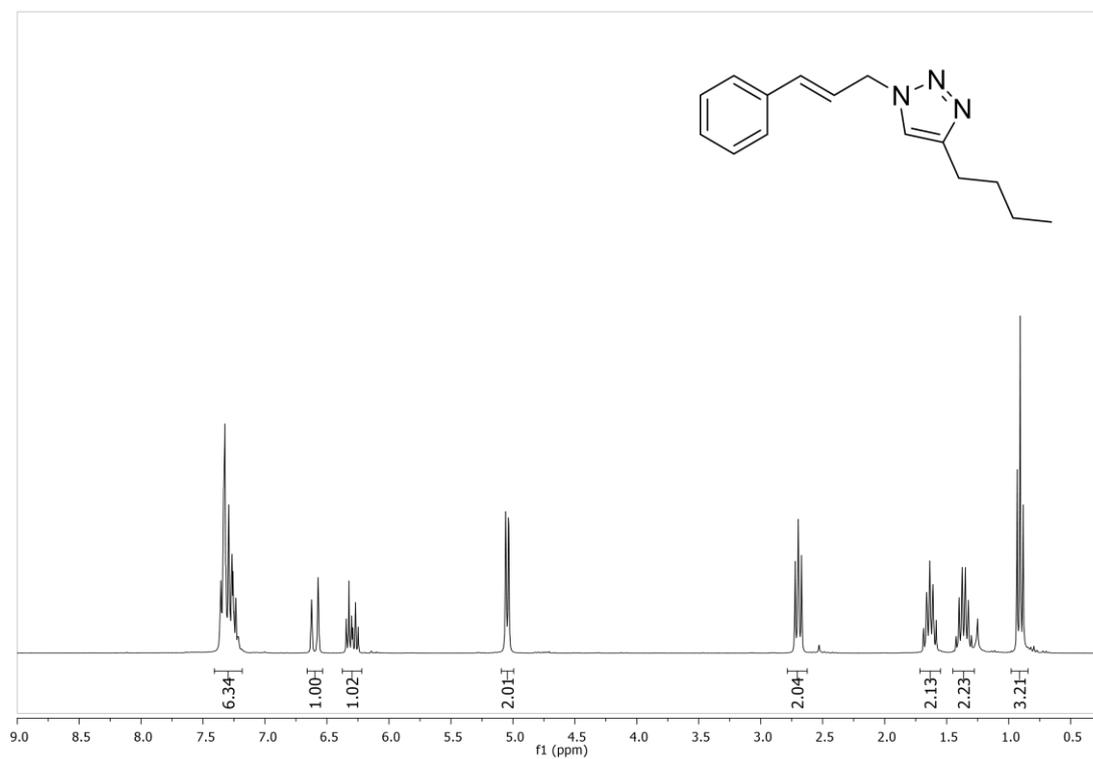
2-(1-Phenyl-1*H*-1,2,3-triazol-4-yl)pyridine, 14j



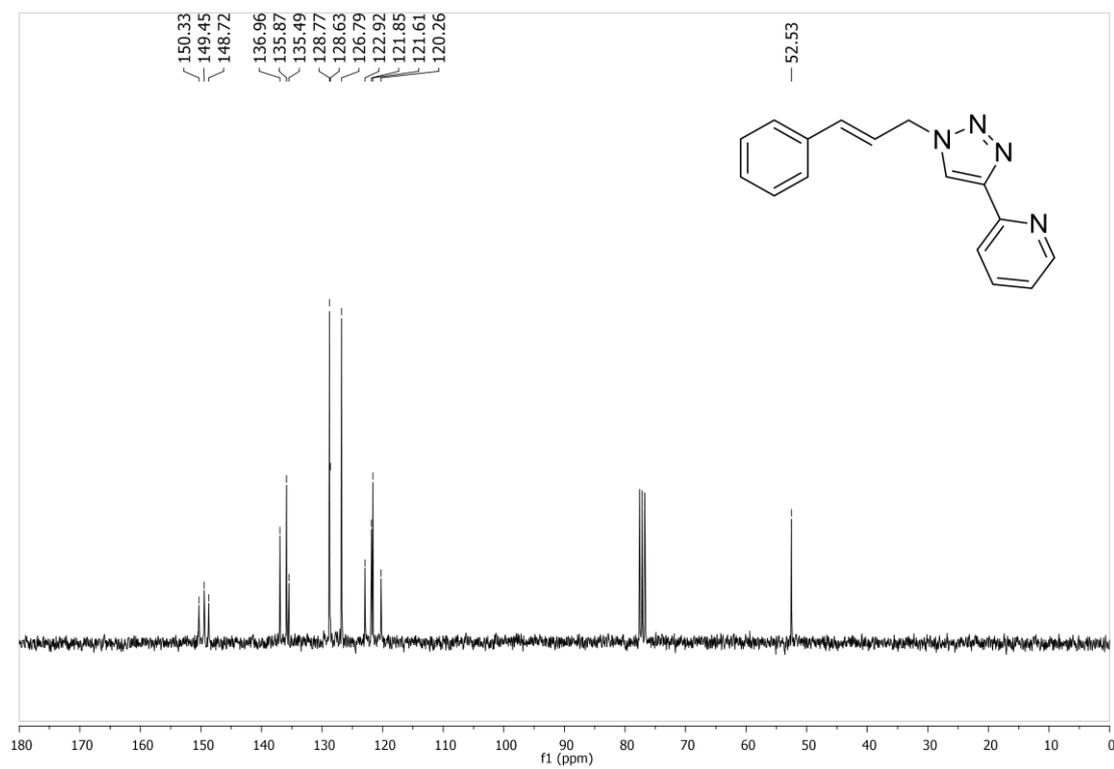
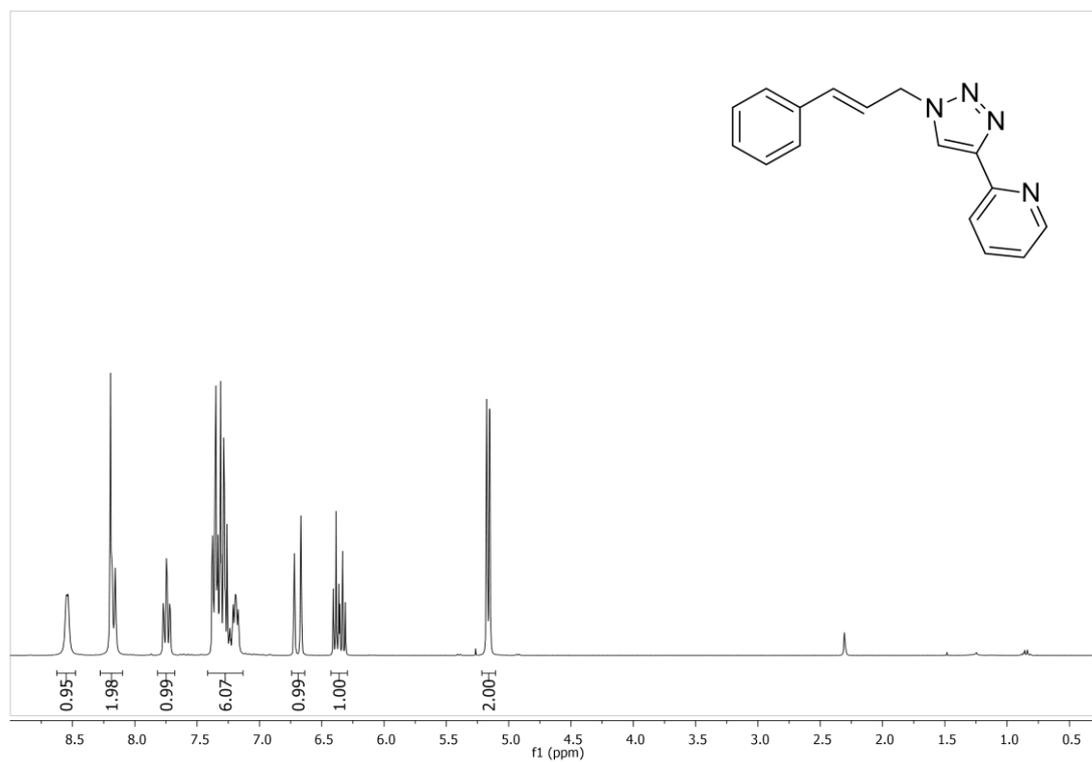
1-Cinnamyl-4-phenyl-1*H*-1,2,3-triazole, 14k



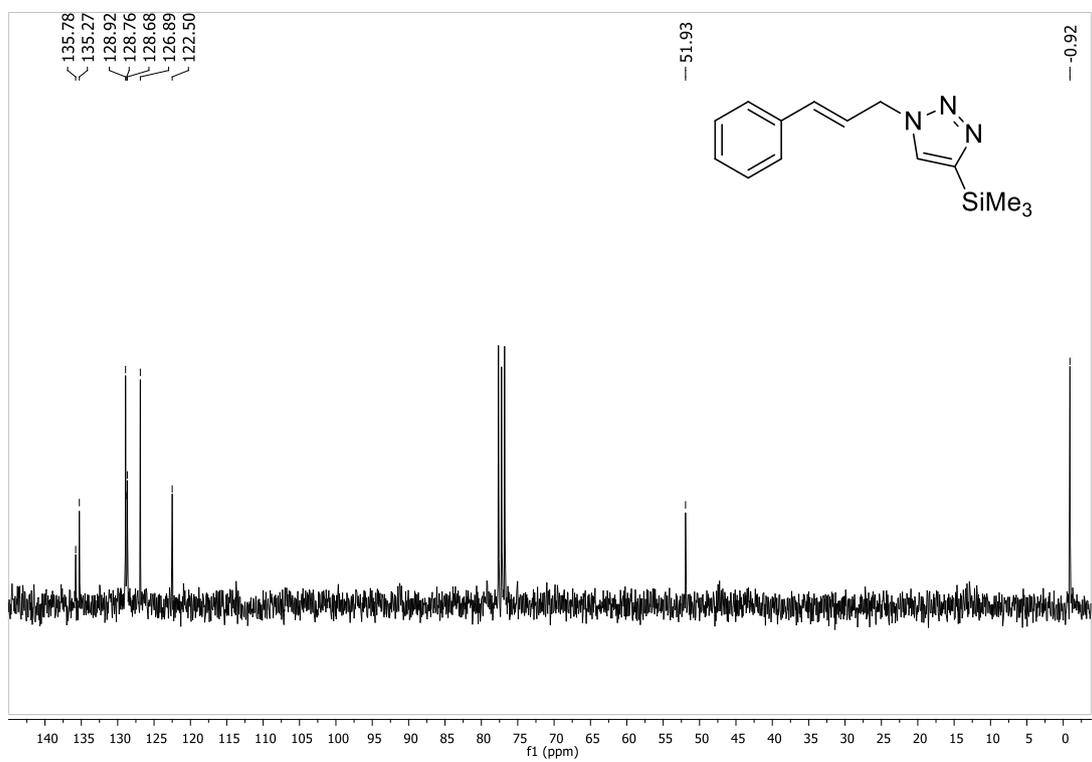
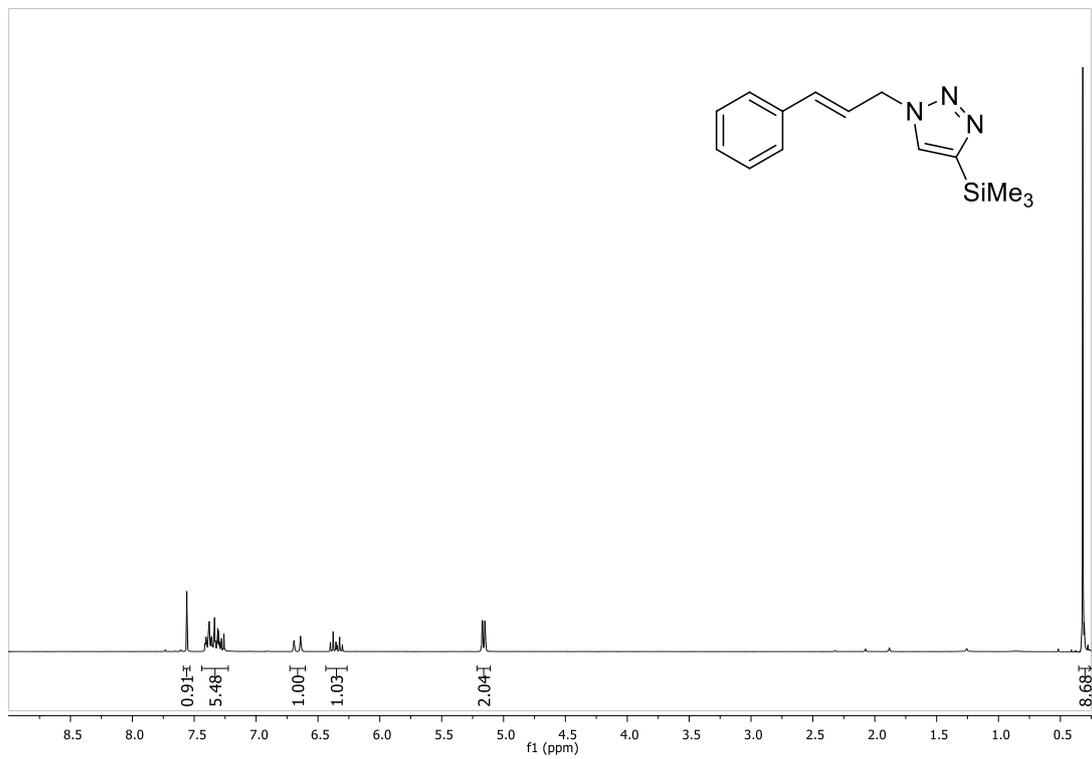
4-(*n*-Butyl)-1-cinnamyl-1*H*-1,2,3-triazole, 14l



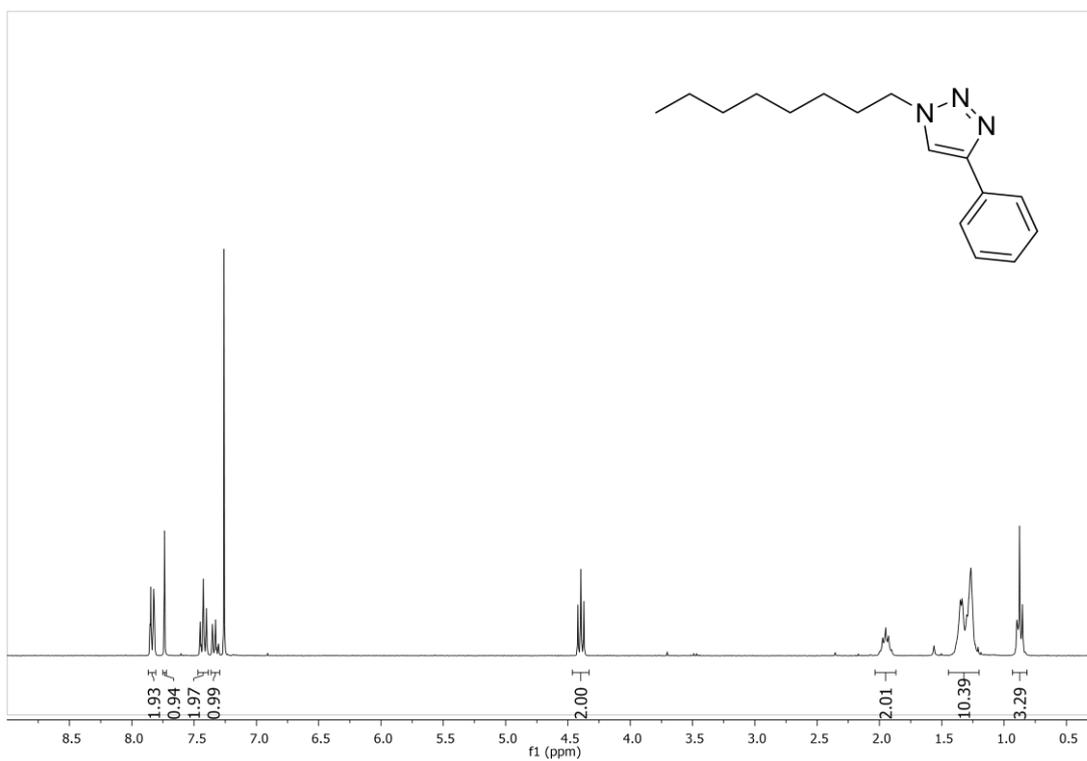
2-(1-Cinnamyl-1H-1,2,3-triazol-4-yl)pyridine, 14m



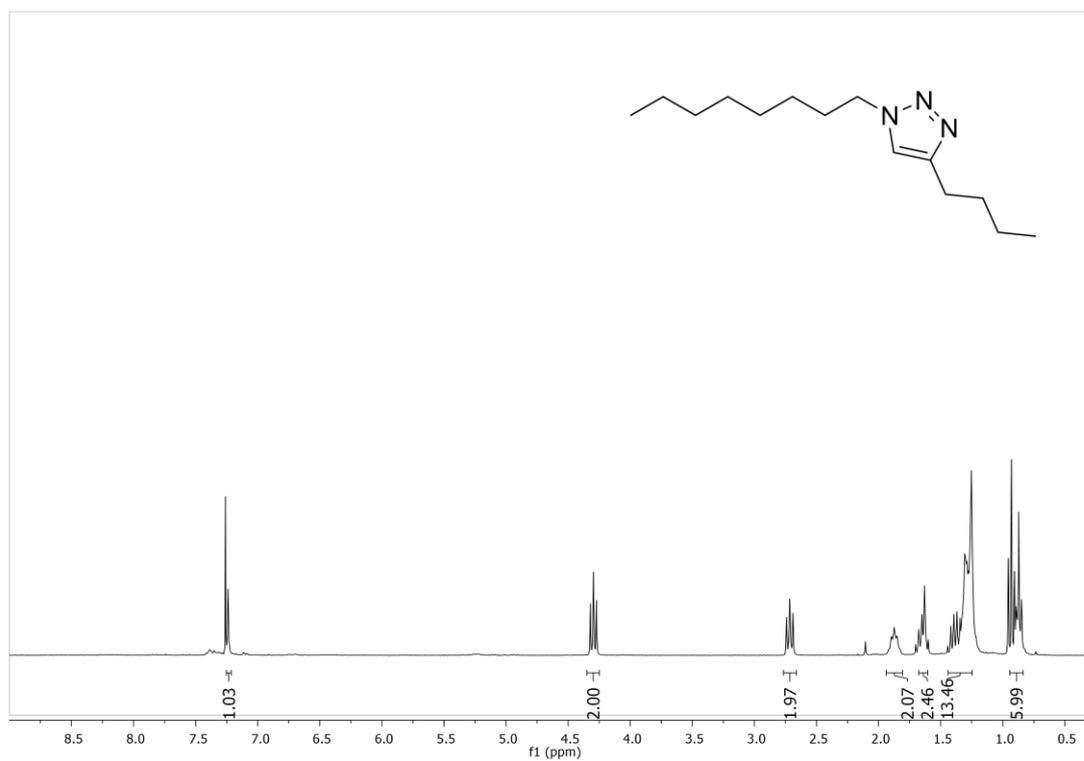
1-Cinnamyl-4-(trimethylsilyl)-1H-1,2,3-triazole, 14n



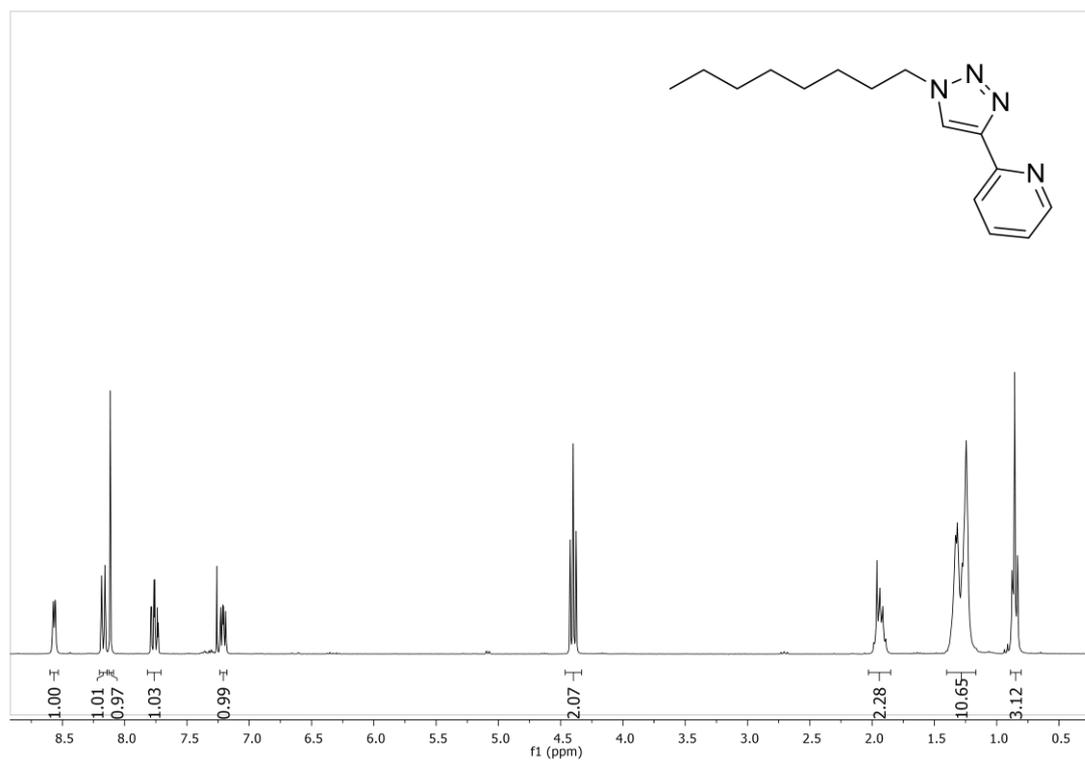
1-Octyl-4-phenyl-1*H*-1,2,3-triazole, 14o



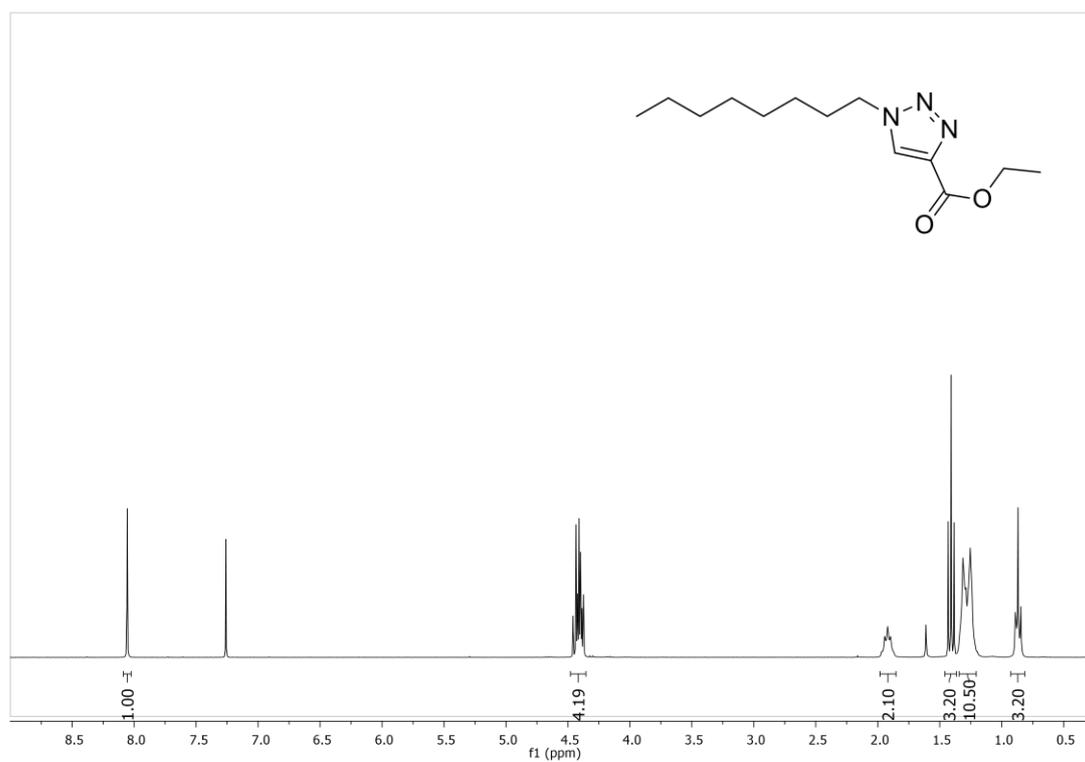
1-Octyl-4-*n*-butyl-1*H*-1,2,3-triazole, 14p



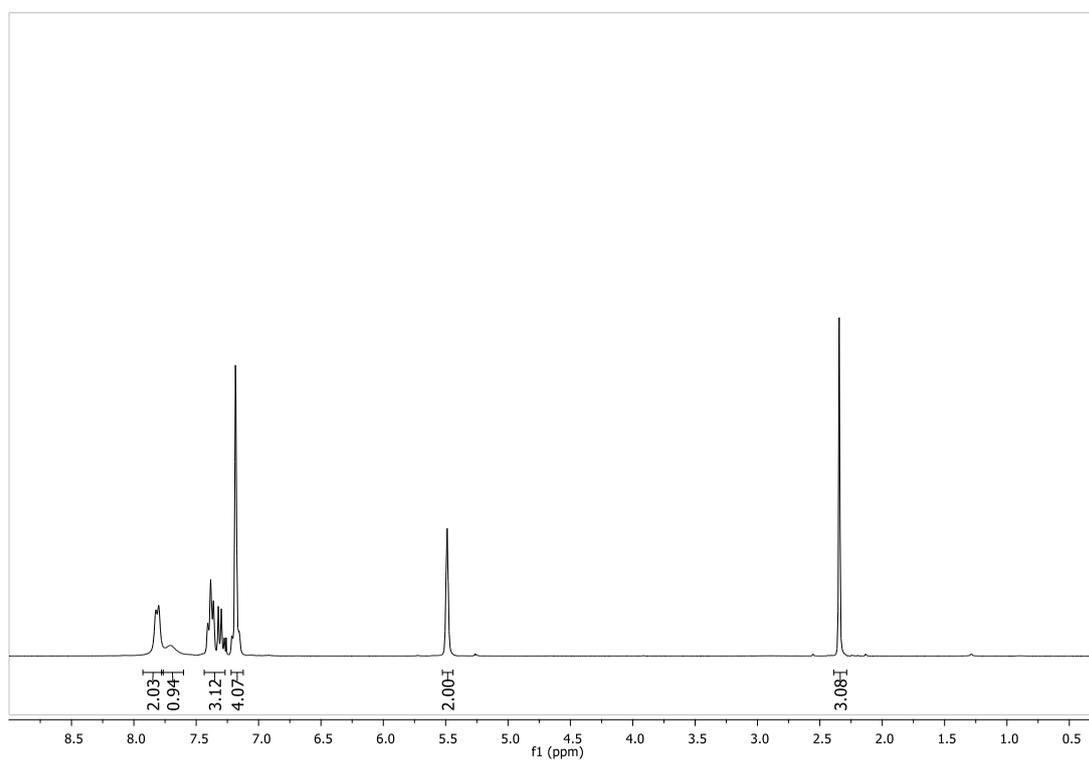
2-(1-Octyl-1*H*-1,2,3-triazol-4-yl)pyridine, 14q



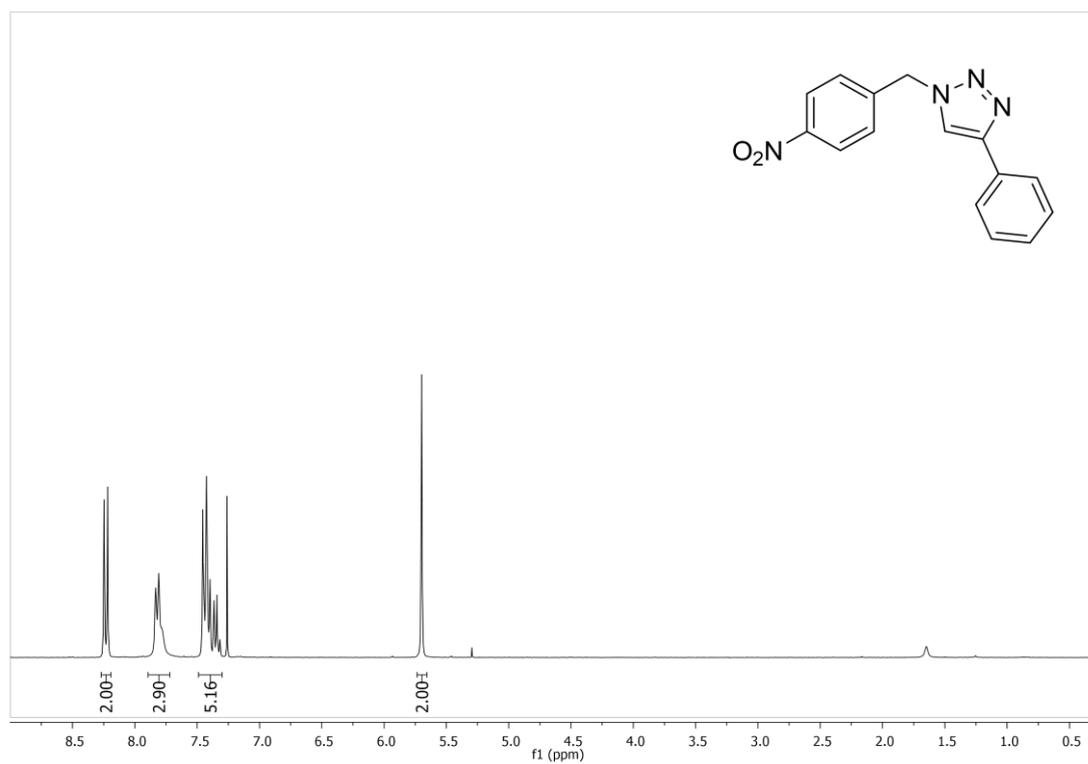
Ethyl 1-octyl-1*H*-1,2,3-triazole-4-carboxylate, 14r



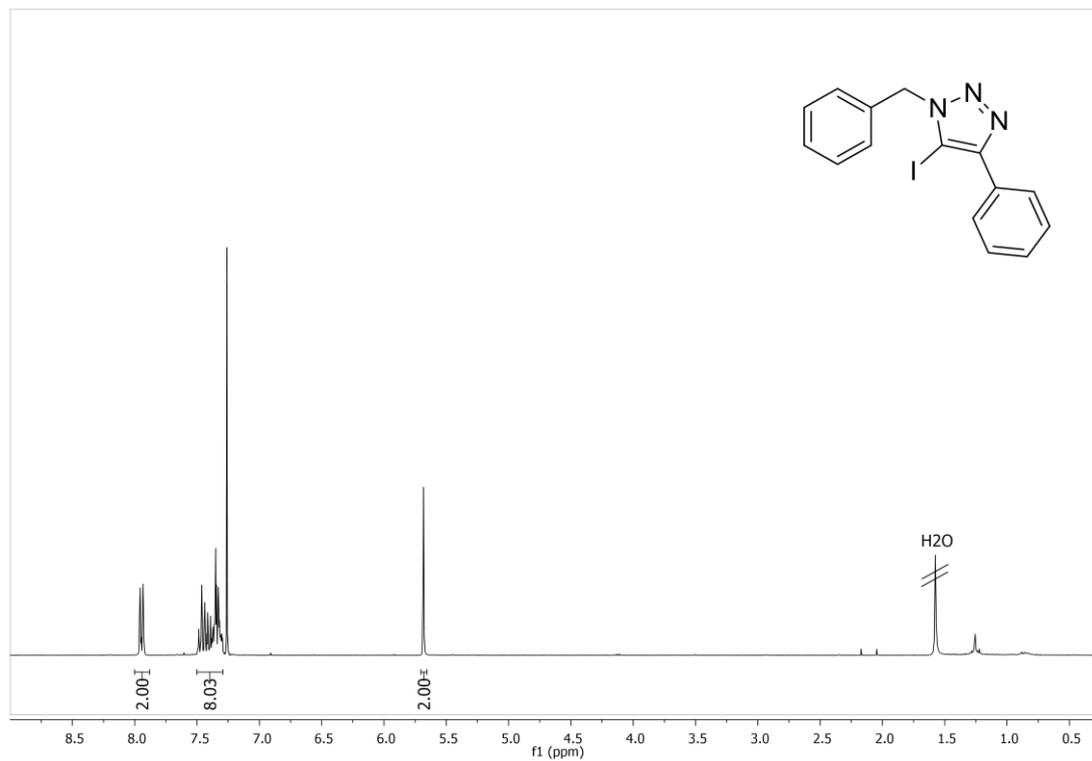
1-(4-Methylbenzyl)-4-phenyl-1*H*-1,2,3-triazole, 14s



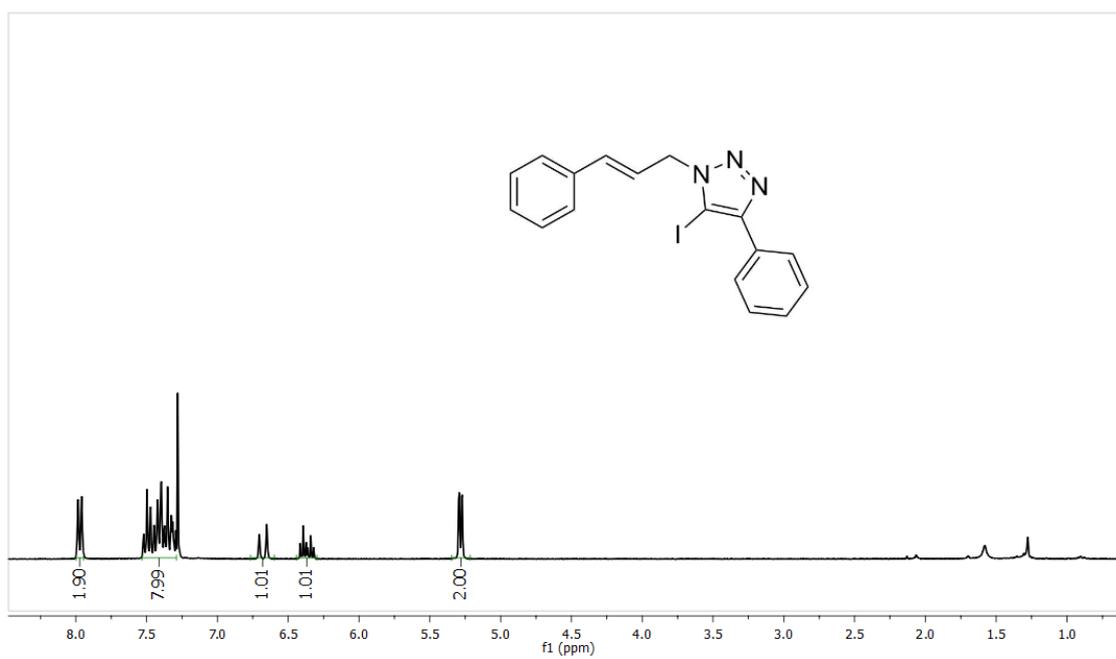
1-(4-Nitrobenzyl)-4-phenyl-1*H*-1,2,3-triazole, 14t



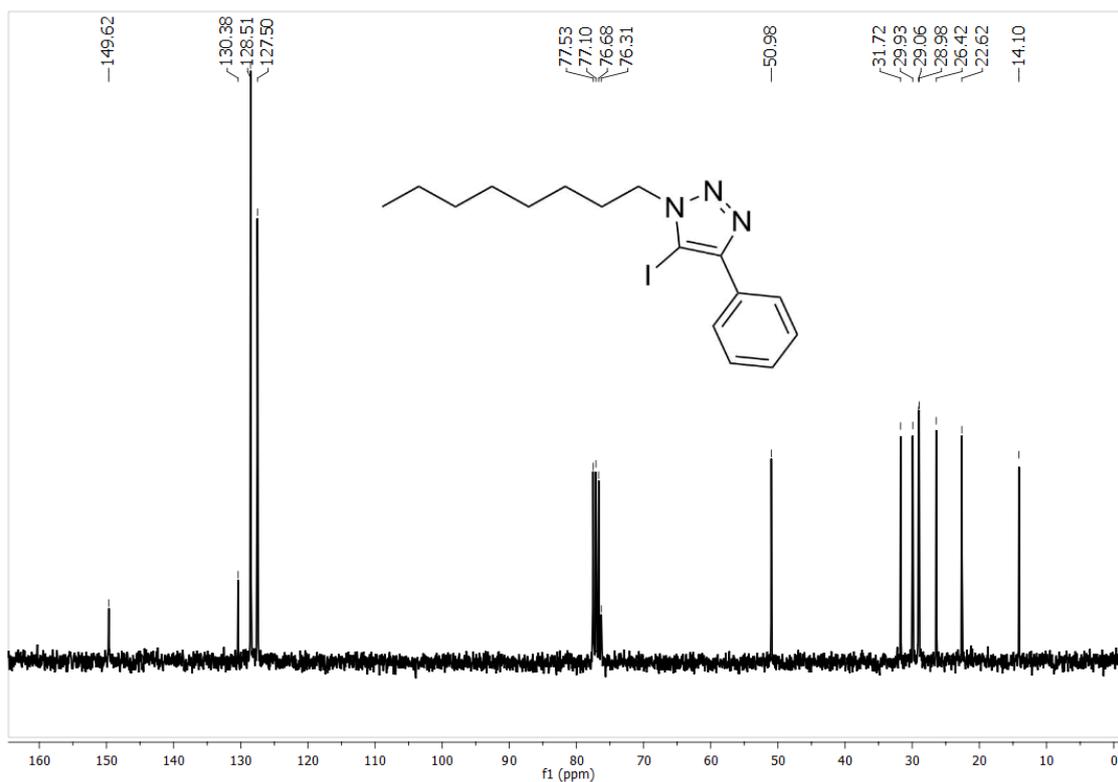
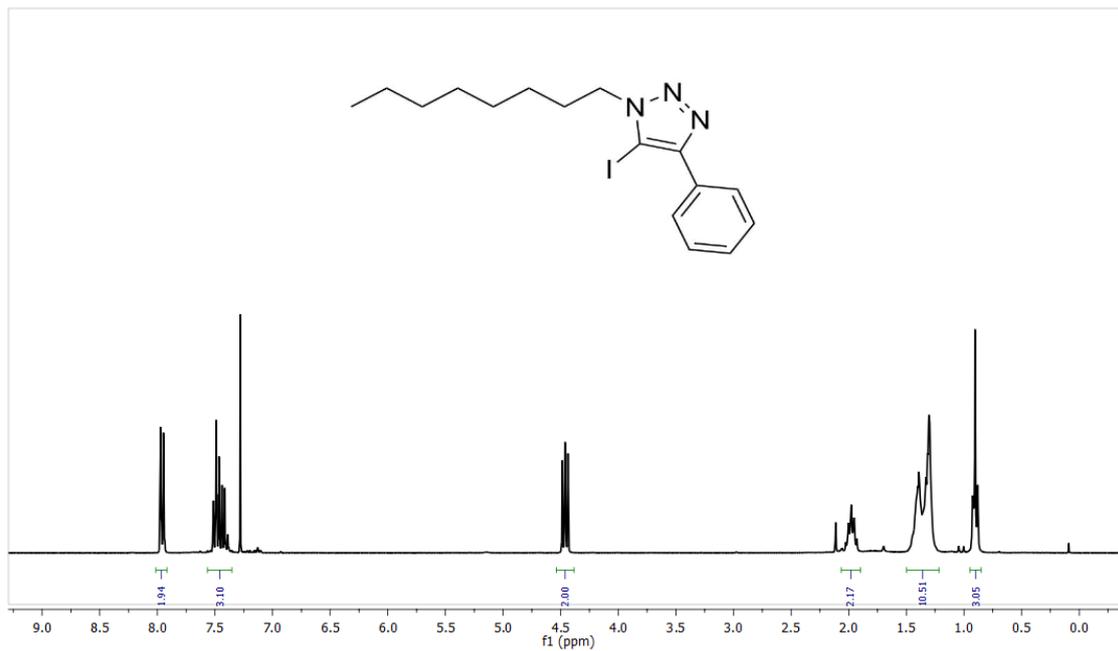
1-Benzyl-5-iodo-4-phenyl-1H-1,2,3-triazole, 15a



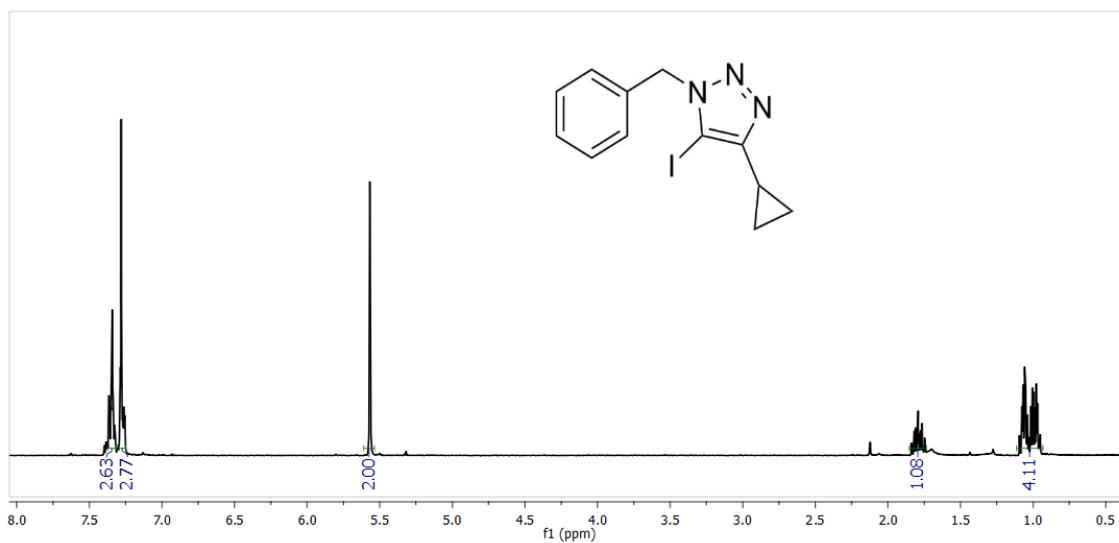
1-Cinnamyl-5-iodo-4-phenyl-1H-1,2,3-triazole, 15b



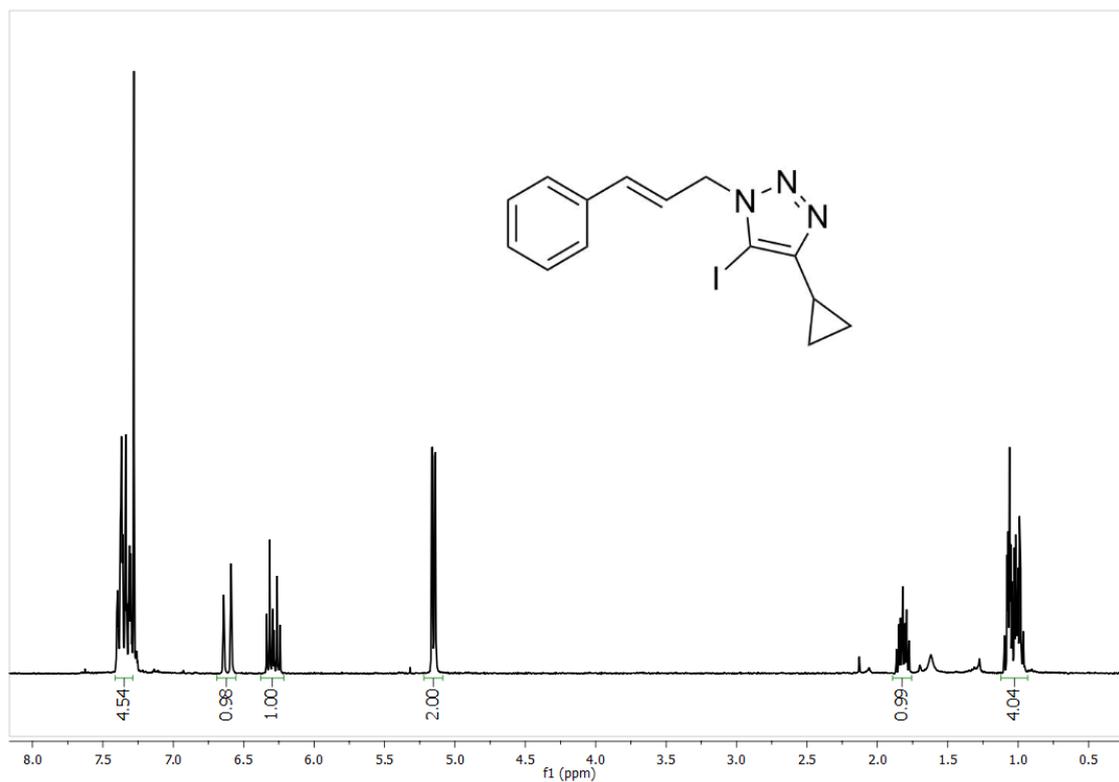
1-Octyl-5-iodo-4-phenyl-1H-1,2,3-triazole, 15c



1-Benzyl-5-iodo-4-cyclopropyl-1H-1,2,3-triazole, 15d



1-Cinnamyl-5-iodo-4-cyclopropyl-1H-1,2,3-triazole, 15e



5. DOSY NMR experiments

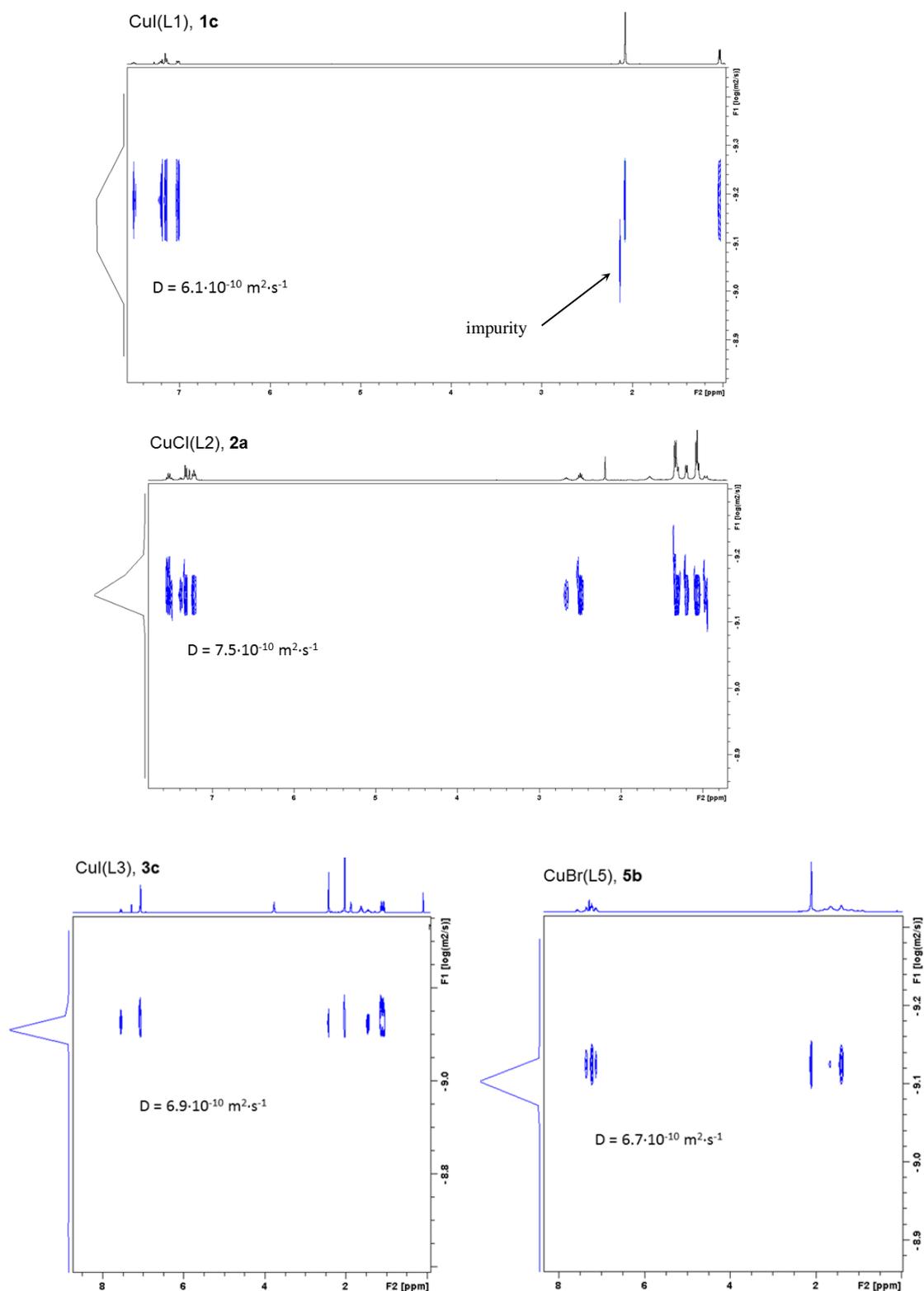


Figure S1. DOSY ¹H NMR spectra of complexes **1c**, **2a**, **3c**, and **5b** in CDCl₃ at 25 °C with the corresponding calculated diffusion coefficients.

6. X-ray structural data of new complexes

Single crystals of suitable size for X-ray diffraction analysis of **1**, **2c**, **3b**, **3c**, **4c** and **5c** were obtained from slow diffusion of pentane into a solution of the complex in dichloromethane. Crystals were coated with FOMBLIN oil, mounted on a glass fibre and fixed in a cold nitrogen stream ($T = 100\text{ K}$) to the goniometer head. Data collection have been performed on two diffractometers: a Bruker-AXSX8Kappa diffractometer equipped with an Apex-II CCD area detector, using a graphite monochromator $\text{Ag K}\alpha_1$ ($\lambda=0.56086\text{ \AA}$) and a Bruker Cryo-Flex low-temperature device (used with **1c**, **3b** and **3c**), and a Bruker Chi-Fixed QUEST diffractometer equipped with a Photon II CMOS detector, using $\text{MoK}\alpha_1$ ($\lambda=0.71073\text{ \AA}$, microfocus sealed x-ray tube) and an Oxford Cryosystems low-temperature device (Cryostream 800), (used with **1a**, **1b**, **2c**, **4c** and **5c**).

Data collections were processed with APE-W2D-ND (Bruker, 2004), cell refinement and data reduction with SAINT-Plus (Bruker, 2004) and the absorption was corrected by multiscan method applied by SADABS.¹⁹ The space-group assignment was based upon systematic absences, E statistics, and successful refinement of the structure. The structures **4b**, **4d** and **4e** were solved by direct methods, and **1a**, **1c**, **3d** and **3e** by Charge Flipping. The structure was refined against all F_2 data by full-matrix least-squares techniques (SHELXTL-6.12)²⁰ minimizing $w[F_o^2 - F_c^2]^2$.

Thermal parameters for all non-hydrogen atoms were refined anisotropically while hydrogen atoms were included in calculated positions and allowed to ride on the attached atoms with the isotropic temperature factors (U_{iso} values) fixed at 1.2 times (1.5 times for methyl groups) those U_{eq} values of the corresponding attached atoms. Some geometric restraints (DFIX command), the ADP restrain SIMU and the rigid bond restraint DELU and RIGU were used in order to obtain more reasonable geometric and ADP values of the atoms on groups moderately librating. It was also employed ISOR command to restrain the anisotropic U-values of these atoms to behave more isotropically.

A summary of the fundamental crystal and refinement data are given in the Tables S1-S2. Atomic coordinates, anisotropic displacement parameters and bond

¹⁹ G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data. Göttingen: University of Göttingen, 1996.

²⁰ G. M. Sheldrick, SHELXTL, versión 6.14. Program for solution and refinement of crystal structures, Universität Göttingen, Germany, 2000.

lengths and angles can be found in the cif files, which have been deposited in the Cambridge Crystallographic Data Centre with no. 2001351 (for **1a**), 2001349 (for **1b**), 2001231 (for **1c**), 2003447 (for **2c**), 2001230 (for **3b**), 2001229 (for **3c**), 2001352 (for **4c**) and 2001348 (for **5c**). These data can be obtained free for charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table S1. Crystal data and Structure Refinement for compounds **1c**, **3b**, and **3c**.

| | 1c | 3b | 3c |
|--|--|---|--|
| formula | C ₂₄ H ₂₇ Cu I P | C ₂₈ H ₃₅ Cu Br P | C ₂₈ H ₃₅ Cu I P |
| fw | 536.86 | 545.98 | 592.97 |
| cryst.size, mm | 0.34×0.22×0.14 | 0.29×0.29×0.12 | 0.21×0.18×0.11 |
| crystal system | Monoclinic | Triclinic | Monoclinic |
| space group | P2 ₁ /n | P-1 | P2 ₁ /c |
| <i>a</i> , Å | 8.3060(4) | 11.5683(8) | 18.5195(6) |
| <i>b</i> , Å | 19.0384(8) | 11.8831(8) | 8.7781(4) |
| <i>c</i> , Å | 14.4683(7) | 12.4332(9) | 16.3617(6) |
| α , deg | 90 | 112.584(3) | 90 |
| β , deg | 96.369(2) | 104.394(3) | 100.320(2) |
| γ , deg | 90 | 97.745(3) | 90 |
| <i>V</i> , Å ³ | 2273.79(18) | 1477.04(18) | 2616.83(18) |
| <i>T</i> , K | 173(2) | 100(2) | 173(2) |
| <i>Z</i> | 4 | 2 | 4 |
| ρ_{calc} , g cm ⁻³ | 1.568 | 1.228 | 1.505 |
| μ , mm ⁻¹ (MoK α) | 1.267 | 1.150 | 1.106 |
| <i>F</i> (000) | 1072 | 564 | 1200 |
| absorption corrections | multi-scan, 0.63-0.74 | multi-scan, 0.65-0.74 | multi-scan, 0.66-0.74 |
| θ range, deg | 1.40 – 21.36 | 1.48 – 23.69 | 1.76 – 21.99 |
| no. of rflns measd | 38180 | 48388 | 43948 |
| <i>R</i> _{int} | 0.066 | 0.070 | 0.072 |
| no. of rflns unique | 5195 | 8914 | 6502 |
| no. of params / restraints | 250 / 0 | 288 / 0 | 288 / 0 |
| <i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>)) ^a | 0.036 | 0.038 | 0.039 |
| <i>R</i> ₁ (all data) | 0.054 | 0.061 | 0.063 |
| <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>)) | 0.108 | 0.105 | 0.112 |
| <i>wR</i> ₂ (all data) | 0.129 | 0.126 | 0.135 |
| Diff.Fourier.peaks min/max, eÅ ⁻³ | -0.913 / 0.559 | -0.648 / 0.677 | -0.908 / 0.821 |
| CCDC number | 2001231 | 2001230 | 2001229 |

Table S2 Crystal data and Structure Refinement for compounds **1a**, **1b**, **2c**, **4c**, **5c**.

| | 1a | 1b | 2c | 4c | 5c |
|---|--|--|--|---|--|
| Empirical formula | C ₄₉ H ₅₆ Cl ₄ Cu ₂ P ₂ | C ₄₈ H ₅₄ Br ₂ Cu ₂ P ₂ | C ₆₄ H ₈₆ Cu ₂ I ₂ P ₂ | C ₅₆ H ₇₀ Cu ₂ I ₂ P ₂ | C ₆₄ H ₇₈ Cu ₂ I ₂ P ₂ |
| Formula weight | 975.75 | 979.75 | 1298.14 | 1185.94 | 1290.08 |
| Temperature (K) | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Triclinic | Monoclinic | Triclinic | Triclinic | Monoclinic |
| Space group | P-1 | P ₂ /c | P-1 | P-1 | P ₂ /n |
| Unit cell dimensions | a = 11.266(3) Å b = 11.920(3) Å c = 18.935(4) Å α = 96.527(8)° β = 94.614(8)° γ = 112.882(9)° | a = 16.0513(7) Å b = 12.0946(5) Å c = 24.0943(10) Å α = 90° β = 106.354(2) γ = 90 | a = 12.6353(11) Å b = 15.1087(14) Å c = 25.294(2) Å α = 106.683(3)° β = 90.503(3)° γ = 95.859(3)° | a = 9.7059(7) Å b = 10.6028(7) Å c = 12.6274(9) Å α = 87.294(3)° β = 87.732(3)° γ = 81.145(3)° | a = 10.3096(5) Å b = 12.7129(6) Å c = 21.7860(10) Å α = 90° β = 101.509(2)° γ = 90° |
| Volume (Å ³) | 2305.9(9) | 4488.3(3) | 4597.6(7) Å ³ | 1281.88(16) | 2798.0(2) |
| Z | 2 | 4 | 3 | 1 | 2 |
| ρ _{calc} , g cm ⁻³ | 1.405 | 1.450 | 1.407 | 1.536 | 1.531 |
| Absorption coefficient (mm ⁻¹) | 1.257 | 2.831 | 1.790 | 2.132 | 1.960 |
| F(000) | 1012 | 2000 | 1992 | 600 | 1312 |
| Crystal size (mm ³) | 0.12×0.05×0.02 | 0.285×0.165×0.1 | 0.49 x 0.28 x 0.165 | 0.365×0.22×0.065 | 0.29×0.15×0.08 |
| Theta range for data collection (°) | 2.185 to 26.119 | 2.141 to 33.253 | 2.246 to 30.158° | 2.477 to 33.335 | 2.492 to 32.155 |
| Index ranges | -13<=h<=13, -14<=k<=14, -23<=l<=23 | -24<=h<=24, -18<=k<=18, -37<=l<=37 | -17<=h<=17, -21<=k<=21, -35<=l<=35 | -15<=h<=15, -16<=k<=16, -19<=l<=19 | -15<=h<=15, -19<=k<=19, -32<=l<=32 |
| Reflections collected | 89551 | 226365 | 96575 | 113965 | 140181 |
| Independent reflections | 9117 [R _{int} = 0.0768] | 17246 [R _{int} = 0.0576] | 27067 [R _{int} = 0.0506] | 9911 [R _{int} = 0.0466] | 9827 [R _{int} = 0.0452] |
| Completeness to theta = 25.242° | 99.9 % | 99.9 % | 99.9% | 99.9 % | 99.9 % |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents |
| Max. and min. transmission | 0.0926 and 0.0640 | 0.2694 and 0.1860 | 0.0232 and 0.0045 | 0.0734 and 0.0340 | 0.1586 and 0.1140 |
| Refinement method | Full-matrix least-squares on F ² | Full-matrix least-squares on F ² | Full-matrix least-squares on F ² | Full-matrix least-squares on F ² | Full-matrix least-squares on F ² |
| Data/restraints/params | 9117 / 906 / 749 | 17246 / 360 / 574 | 27067 / 0 / 976 | 9911 / 0 / 288 | 9827 / 0 / 320 |
| Goodness-of-fit on F ² | 1.099 | 1.024 | 1.047 | 1.034 | 1.069 |
| Final R indices (I > 2σ(I)) | R ₁ = 0.0519, wR ₂ = 0.1199 | R ₁ = 0.0325, wR ₂ = 0.0755 | R ₁ = 0.0795, wR ₂ = 0.2185 | R ₁ = 0.0288, wR ₂ = 0.0652 | R ₁ = 0.0240, wR ₂ = 0.0538 |
| R indices (all data) | R ₁ = 0.0704, wR ₂ = 0.1279 | R ₁ = 0.0518, wR ₂ = 0.0849 | R ₁ = 0.0983, wR ₂ = 0.2404 | R ₁ = 0.0406, wR ₂ = 0.0701 | R ₁ = 0.0317, wR ₂ = 0.0573 |
| Largest diff. peak and hole (eÅ ⁻³) | 0.786 and -0.685 | 0.948 and -0.768 | 6.837 and -0.869 | 1.541 and -0.507 | 1.089 and -0.473 |
| CCDC number | | 2001349 | | 2001352 | 2001348 |

Figure S2. Molecular structure of complex **1a**.

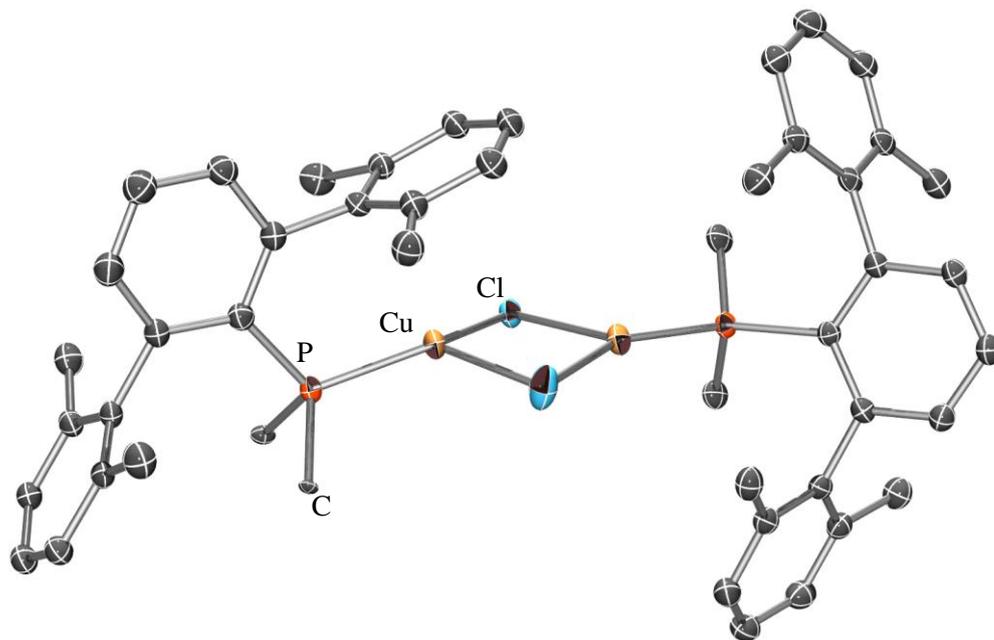


Figure S3. Molecular structure of complex **1b**.

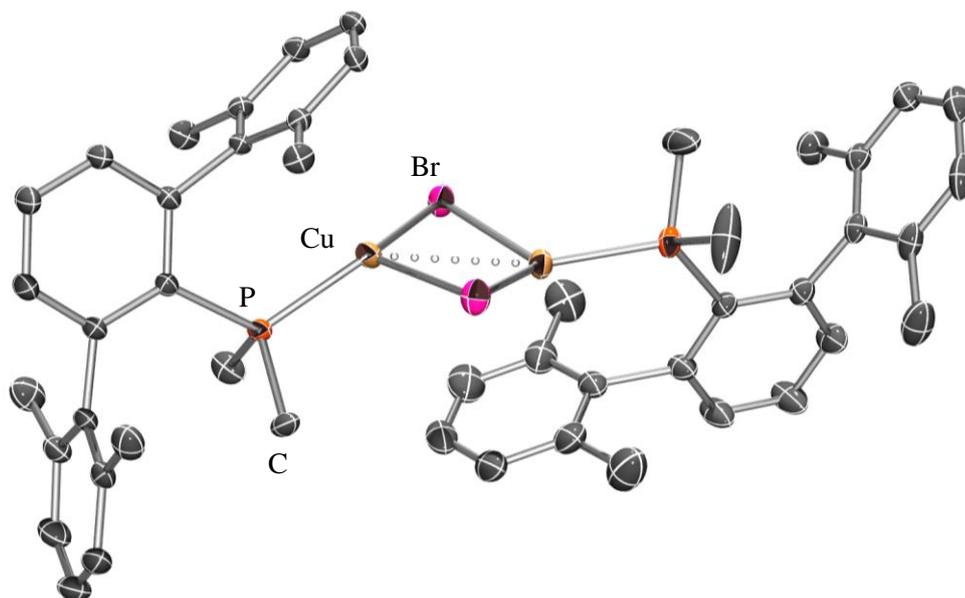


Figure S4. Molecular structure of complex **2c**.

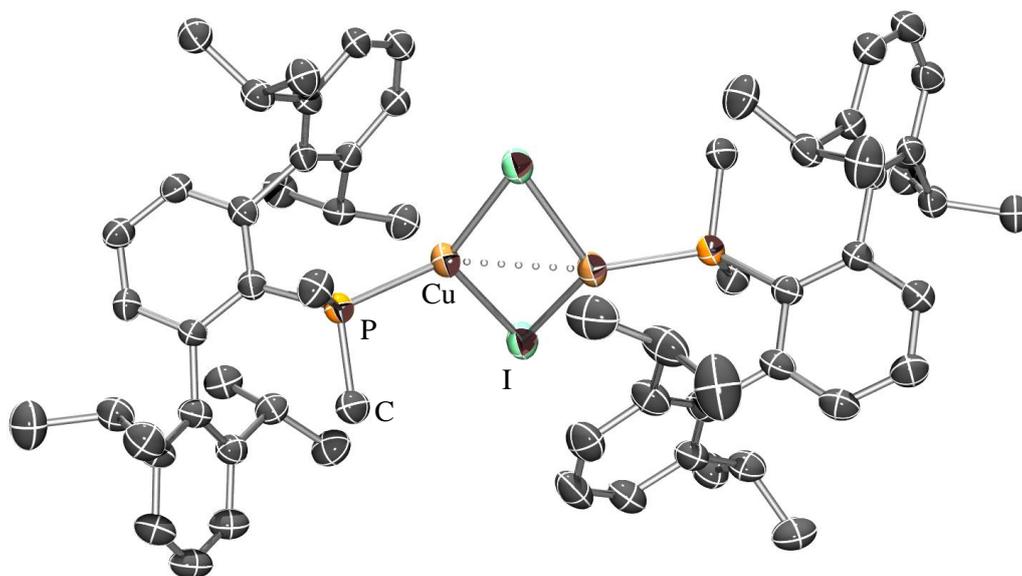


Figure S5. Molecular structure of complex **3b**.

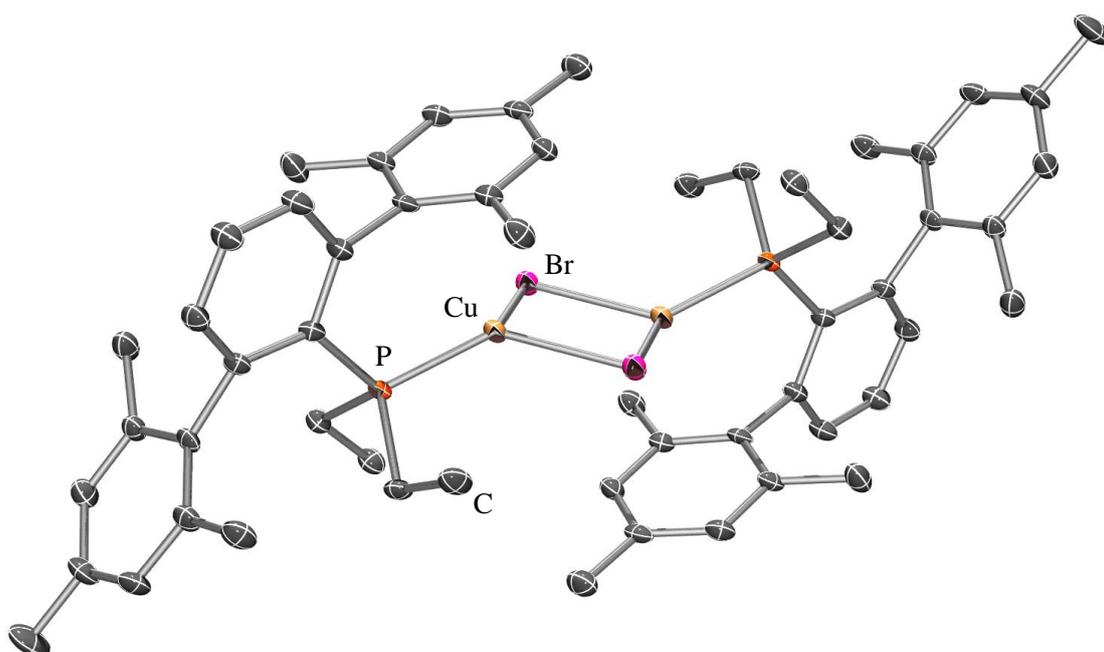


Figure S6. Molecular structure of complex **4c**.

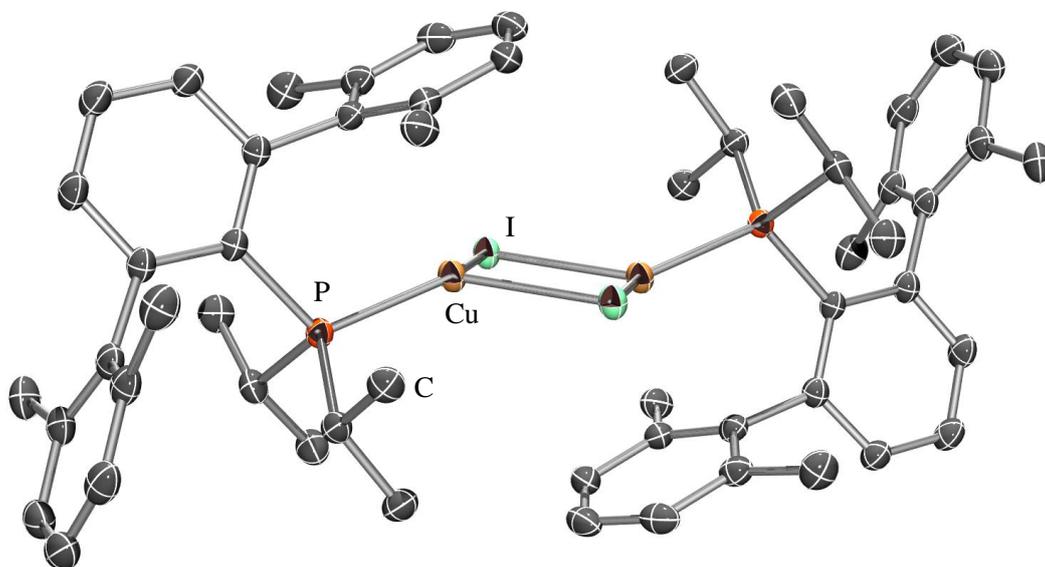
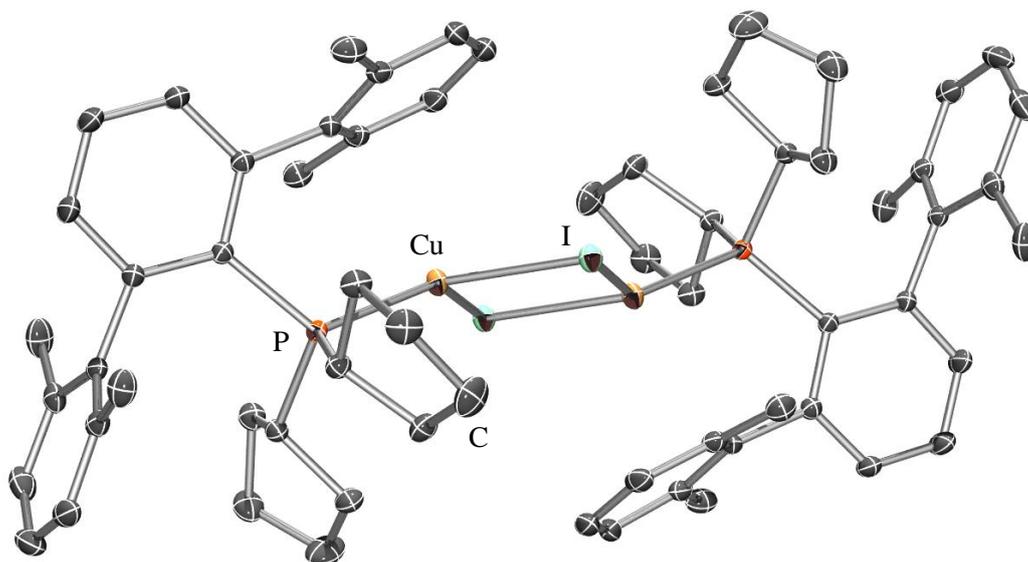


Figure S7. Molecular structure of complex **5c**.



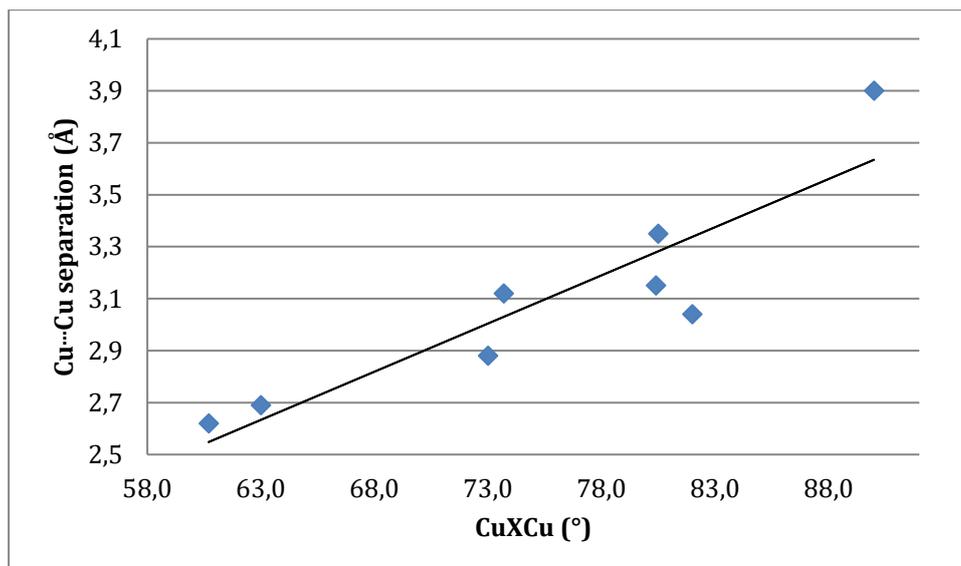


Figure S8. Correlation between the metal-metal separation and the Cu1-X-Cu1' angle for complexes **1-5**.

Table S3. Triplet states close to S_2 in energy with (HOMO,LUMO+1) participation in their configuration set.

| State | 1c | | 3c | |
|-------|----------------|------------|----------------|------------|
| | HOMO,LUMO+1(%) | Energy(nm) | HOMO,LUMO+1(%) | Energy(nm) |
| S_2 | 79% | 338 | 92% | 334 |
| T_8 | 20% | 340 | 80% | 339 |
| T_7 | 0% | 340 | 0% | 340 |
| T_6 | 24% | 342 | 0% | 346 |
| T_5 | 4% | 342 | 0% | 346 |
| T_4 | 5% | 346 | 0% | 349 |
| T_3 | 3% | 347 | 0% | 349 |
| T_2 | 6% | 348 | 0% | 353 |
| T_1 | 26% | 350 | 7% | 353 |

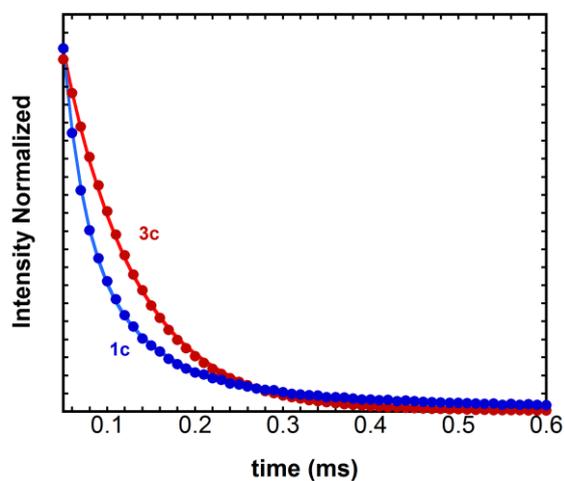


Figure S9. Decay profile of **1c** and **3c** in Zeonex placed in vacuum, with lifetime of 56 μ s for **1c** and 82 μ s for **3c**.

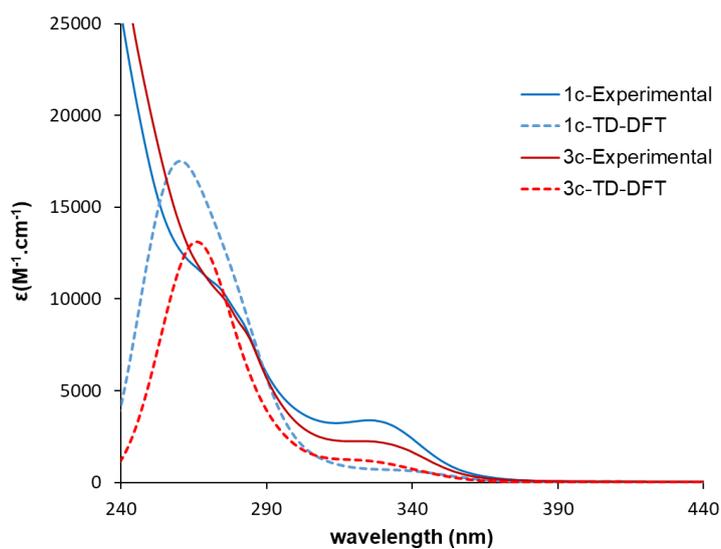


Figure S10 TD-DFT simulated electronic spectra of complexes **1c** and **3c** (dashed lines) plotted against the experimental UV-Vis spectra in cyclohexane.

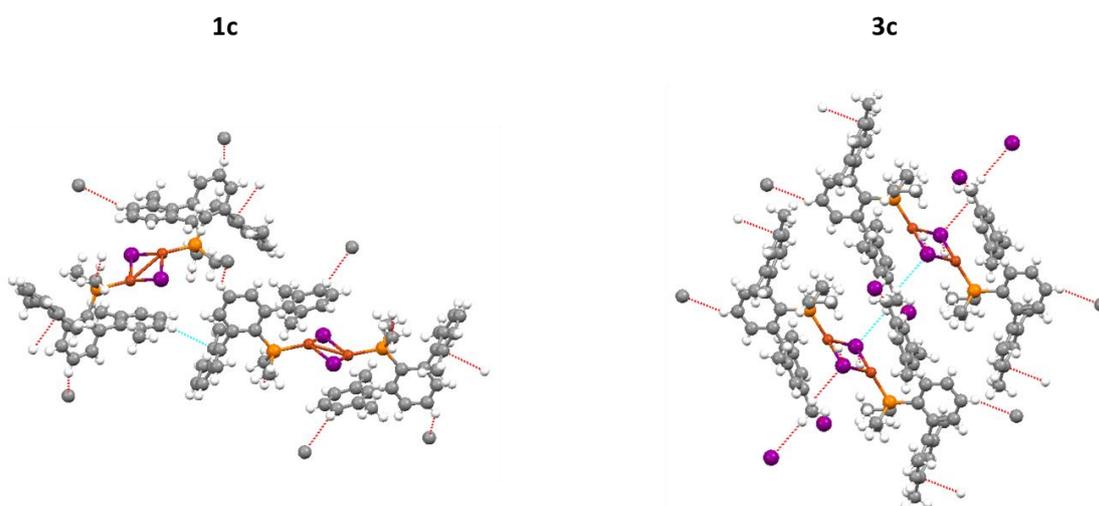


Figure S11 X-ray structure of the complexes **1c** [CuI(PMe₂Ar^{Xyl})]₂ and **3c** [CuI(PEt₂Ar^{Mes})]₂ and their packing in crystalline network. **1c** interacts to adjacent molecules through aromatic H while **3c** interacts through I atoms.

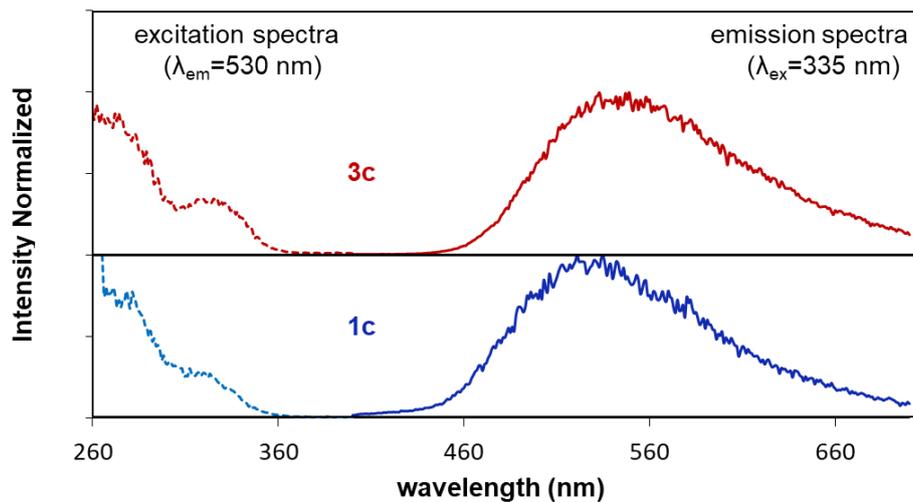


Figure S12 Excitation and Emission spectra of complexes **1c** and **3c** in frozen cyclohexane solution (5.00×10^{-5} M) at 77 K.