Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Interaction of the trinuclear copper(I) pyrazolate with alkynes and carbon-carbon triple bond activation

Aleksei A. Titov,†*[a] Vladimir A. Larionov,†*[ab] Alexander F. Smol'yakov,[a] Maria I. Godovikova,[a] Ekaterina M. Titova,[ab] Victor I. Maleev,[a] Elena S. Shubina[a]

[a] A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (INEOS RAS), Vavilov St. 28, 119991 Moscow, Russian Federation.

[b] Department of Inorganic Chemistry, Peoples' Friendship University of Russia (RUDN University), Miklukho-Maklaya Street 6, 117198 Moscow, Russian Federation

† Both authors contributed equally to this work.

E-mail: *tit@ineos.ac.ru

*larionov@ineos.ac.ru

General Information

All solvents purchased from commercial suppliers were used without further purification (CH_2Cl_2, CD_2Cl_2, hexane). Purchased 1-octyne (**1**) and phenylacetylene (**2**) from commercial suppliers were used without further purification. The trinuclear copper(I) *bis*-(trifluoromethyl)pyrazolate ({[3,5-$(CF_3)_2$Pz]Cu}$_3$]) (**[CuL]$_3$**) was prepared according to a published procedure.[S1] *ortho*-Fluorobenzyl azide (**5**) was synthesized according to a literature procedure.[S2] If not stated otherwise, flash column chromatography was performed with silica gel 60 M from Macherey-Nagel.

Instrumentation and Methods

Proton nuclear magnetic resonance (^{1}H-NMR) spectra and carbon nuclear magnetic resonance (^{13}C-NMR) spectra were recorded on Bruker Avance-III-500 spectrometer with CryoProbe Prodigy operating at 500.13 MHz (^{1}H) and 125.76 MHz ($^{13}C\{^1H\}$) and Bruker Avance 600 spectrometer operating at 600.22 MHz (^{1}H) and 150.93 MHz ($^{13}C\{^1H\}$). Chemical shifts are reported in ppm relative to the residual solvent peak (CD_2Cl_2: $\delta = 5.32$ ppm for ^{1}H-NMR, $\delta = 53.4$ for ^{13}C-NMR, $CDCl_3$: $\delta = 7.26$ ppm for ^{1}H-NMR, $\delta = 77.2$ for ^{13}C-NMR;). NMR data are reported as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant, integration, and nucleus. IR spectra were recorded on Shimadzu IRPrestige-21 FTIR spectrophotometer using CaF_2 cuvettes and nujol. Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART APEX II diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, ω-scan technique). The APEX II software[S3] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling and absorption correction, while SHELXTL[S4] and OLEX2[S5] was applied for space group and structure determination, refinements, graphics, and structure reporting. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were placed geometrically and included in the structure factor calculations in the riding motion approximation. Crystallographic data for complexes **3** and **4** are presented in Table S1. CCDC 1871238, 1871239 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Experimental details and refinement parameters of complexes **3** and **4**.

Compound	**3**	**4**
Empirical formula	$C_{36}H_{16}Cu_3F_{24}N_8$	$C_{36}H_{32}Cu_3F_{24}N_8$
Formula weight	1207.19	1223.31
Temperature, K	120(2)	120(2)
Wavelength, Å	0.71073	0.71073
Crystal size, mm	0.15×0.12×0.05	0.21×0.14×0.05
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a, Å	9.1317(11)	8.550(9)
b, Å	11.0607(13)	10.660(12)
c, Å	11.7651(14)	13.468(14)
α deg.	72.527(2)	107.62(3)
β, deg.	70.675(3)	100.88(2)
γ, deg.	69.170(3)	95.18(2)
V, Å^3	1025.4(2)	1135(2)
Z	1	1
D_{calc}, g·cm^{-3}	1.955	1.790
Absorption coefficient, μ, cm^{-1}	1.693	1.531
F(000)	591	607
Theta range for data collection	1.88-29.0	1.63-30.57
Reflections collected	19293	15153
Independent reflections	5444	6937
Reflections observed with $I > 2\sigma(I)$	4233	6032
Parameters	1242	327
Goodness-of-fit on F^2	1.032	1.045
R_1 [$I > 2\sigma(I)$]	0.0378	0.0263
wR_2 [all data]	0.1017	0.717
Largest diff. peak and hole	3.637 / -0.392	0.63 / -0.416

IR spectra

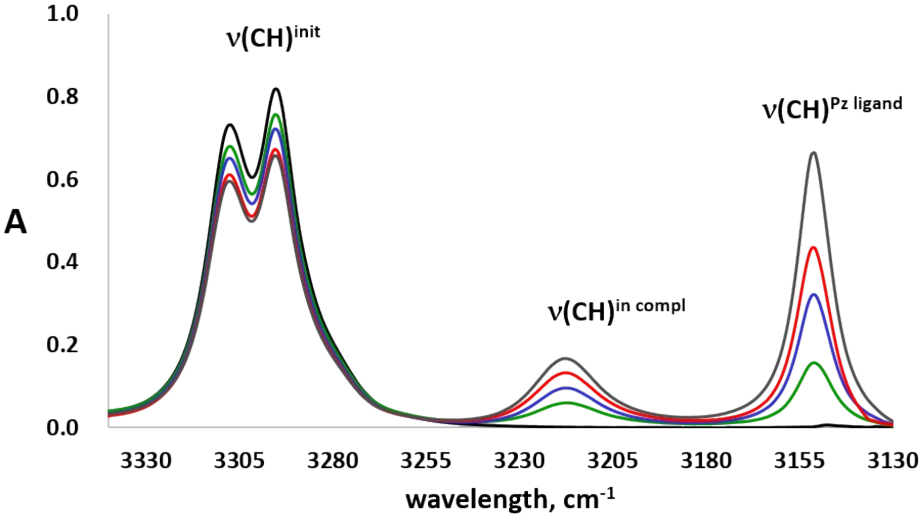


Figure S1. IR spectra (*the area of C≡C-H stretching vibrations*) of phenylacetylene **2** (c = 0.05 M, *black*) and **2** in the presence of the increasing amount of **[CuL]$_3$** (0.25 equiv.: *green*, 0.5 equiv.: *blue*, 0.75 equiv.: *red*, 1 equiv.: *grey*) in CH$_2$Cl$_2$, d = 2 mm, T = 298 K.

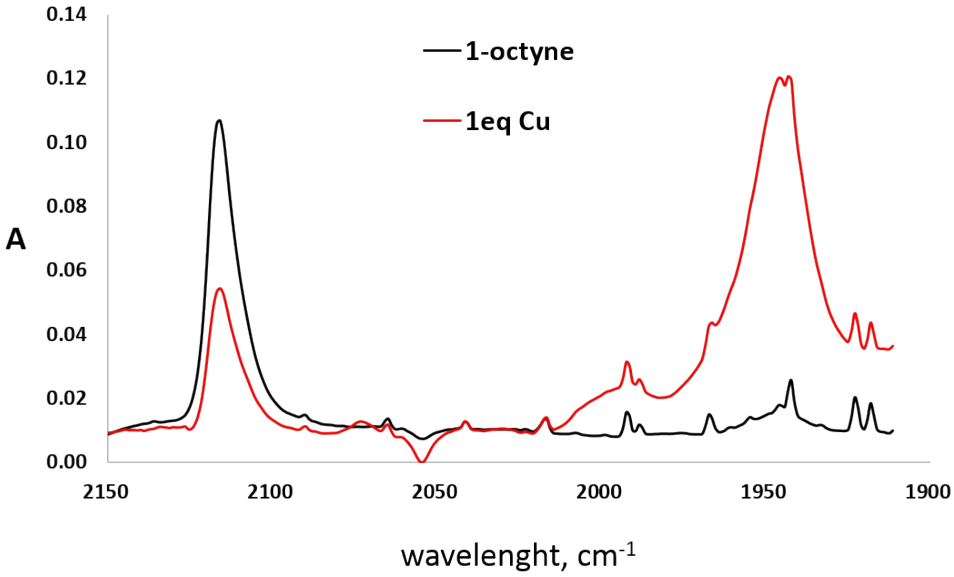


Figure S2. IR spectra (the range of C≡C stretching vibrations) of 1-octyne **1** (c = 0.05 M, *black*) and **1** in the presence of a one equivalent of **[CuL]$_3$** (*red*) in CH$_2$Cl$_2$, d = 2 mm, T = 298 K.

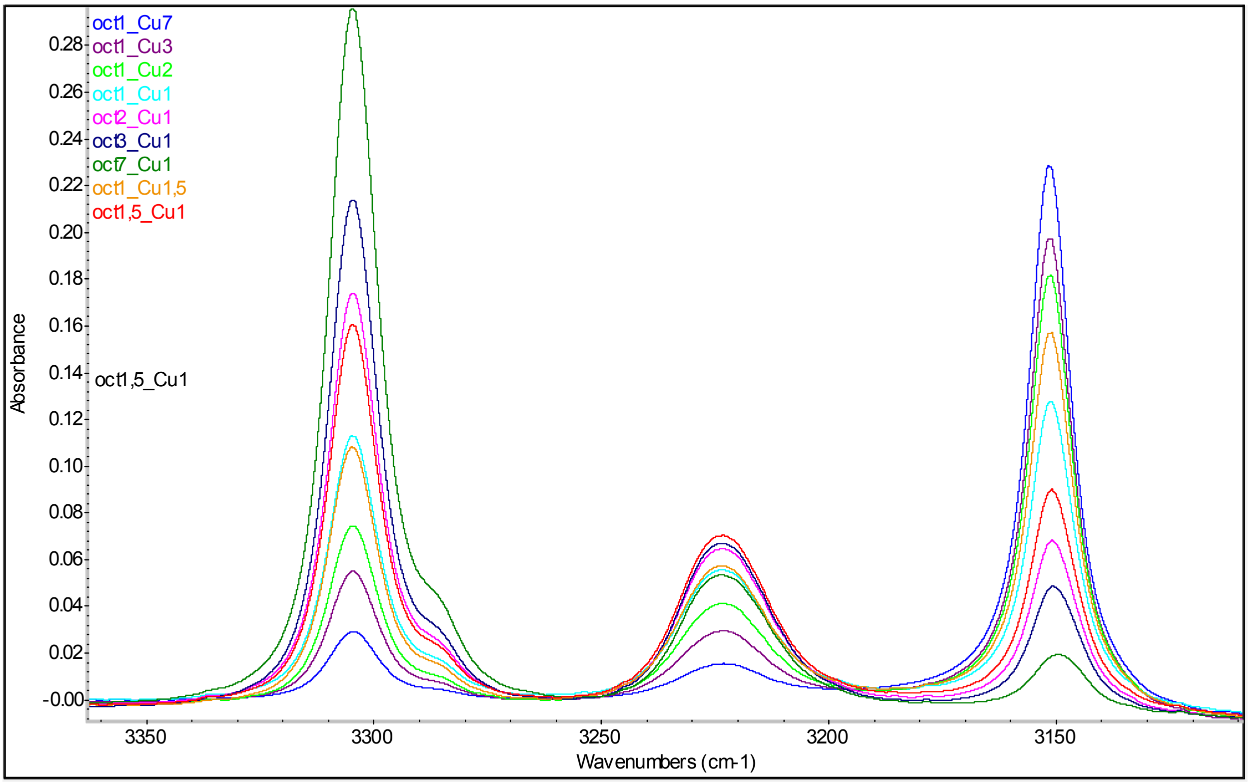


Figure S3. IR spectra of isomolar series of 1-octyne (**1**) and $[CuL]_3$ in CH_2Cl_2. d = 0.4 mm, C([**1**]+$[CuL]_3$) = 0.05 M.

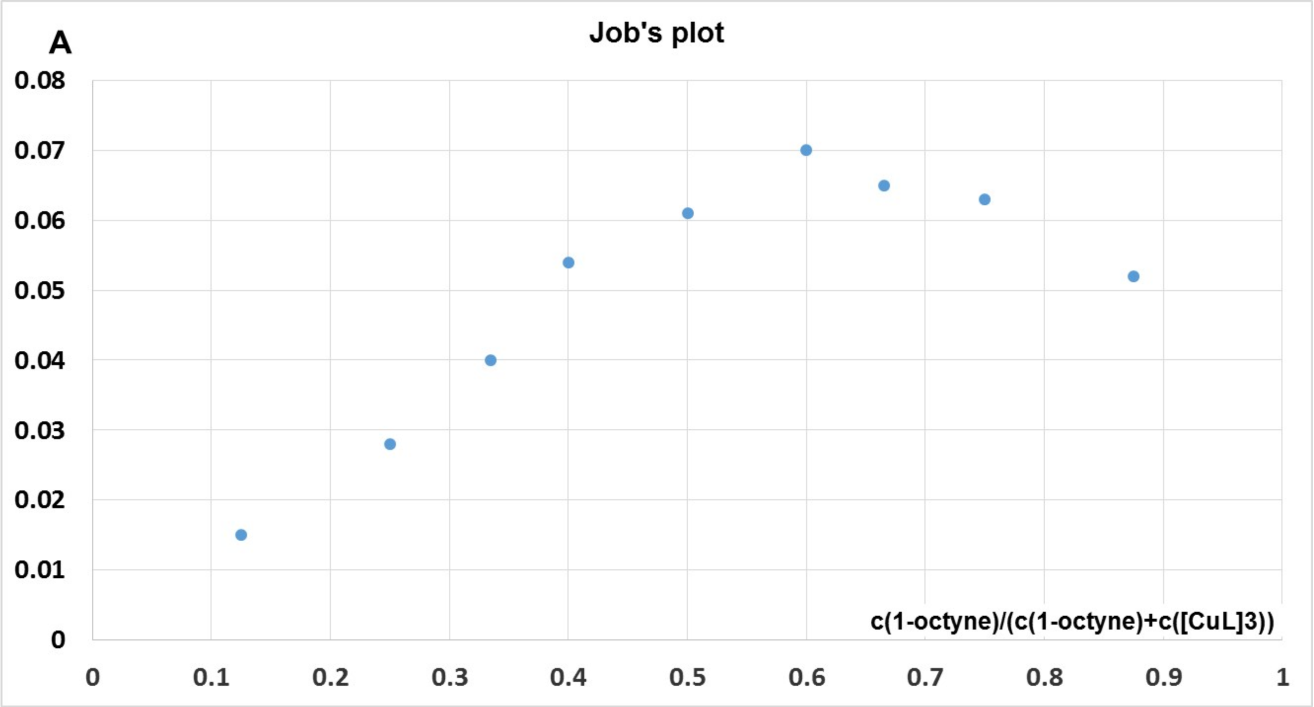


Figure S4. Job's plot: dependence of the band intensity of 1-octyne **1** (3222 cm^{-1}) on the composition of the isomolar solution of 1-octyne and $[CuL]_3$

NMR spectra

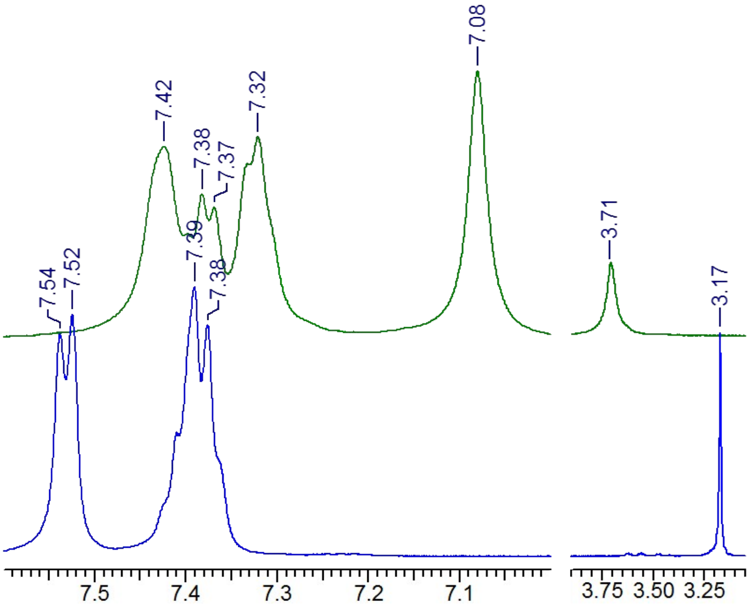


Figure S5. ^{1}H NMR spectra of phenylacetylene **2** (c = 0.05 M, *blue*) and **2** in the presence of one equivalent of **[CuL]$_3$** (*green*) in CD_2Cl_2, T = 298 K.

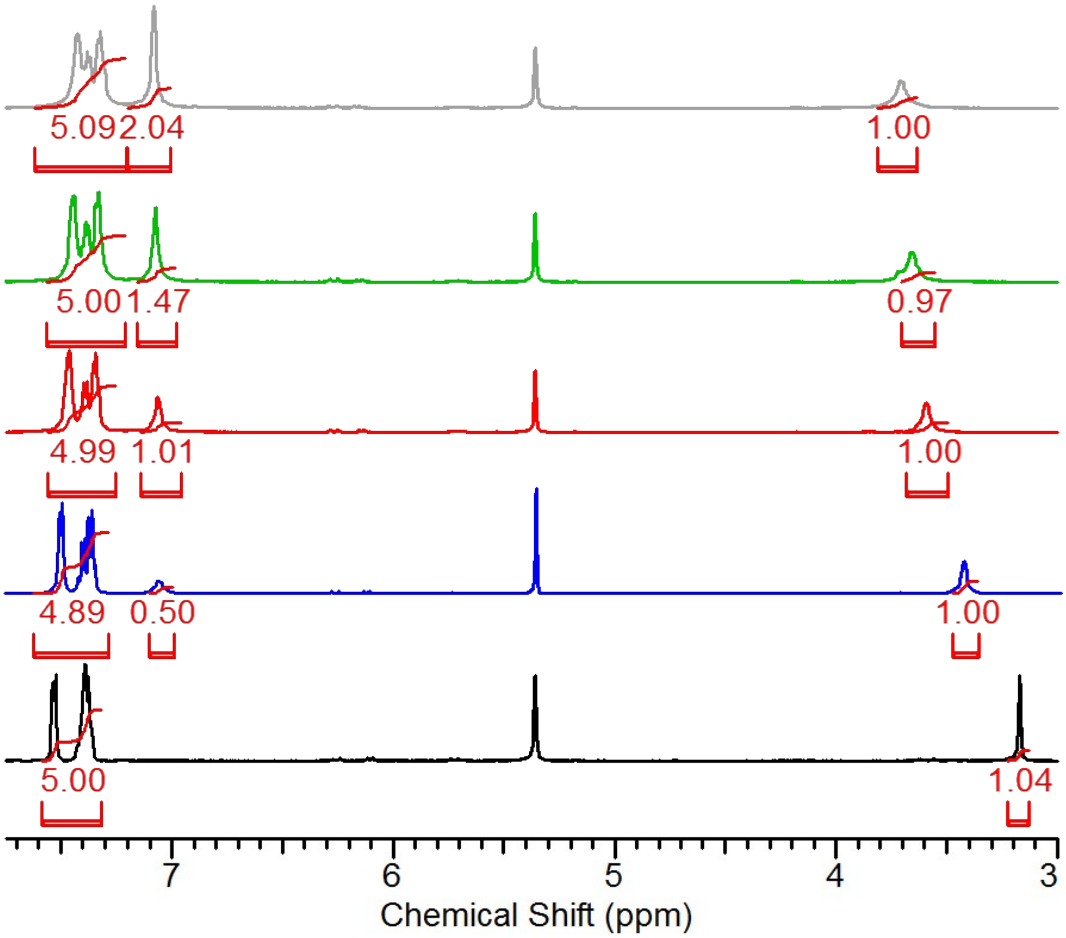


Figure S6. ^{1}H NMR spectra of phenylacetylene **2** (c = 0.05 M, *black*) and **2** in the presence of different amount of **[CuL]$_3$** (0.25 equiv.: *blue*, 0.5 equiv.: *red*, 0.75 equiv: *green*, 1 equiv.: *grey*) in CD_2Cl_2, T = 298 K. Common integrals are red.

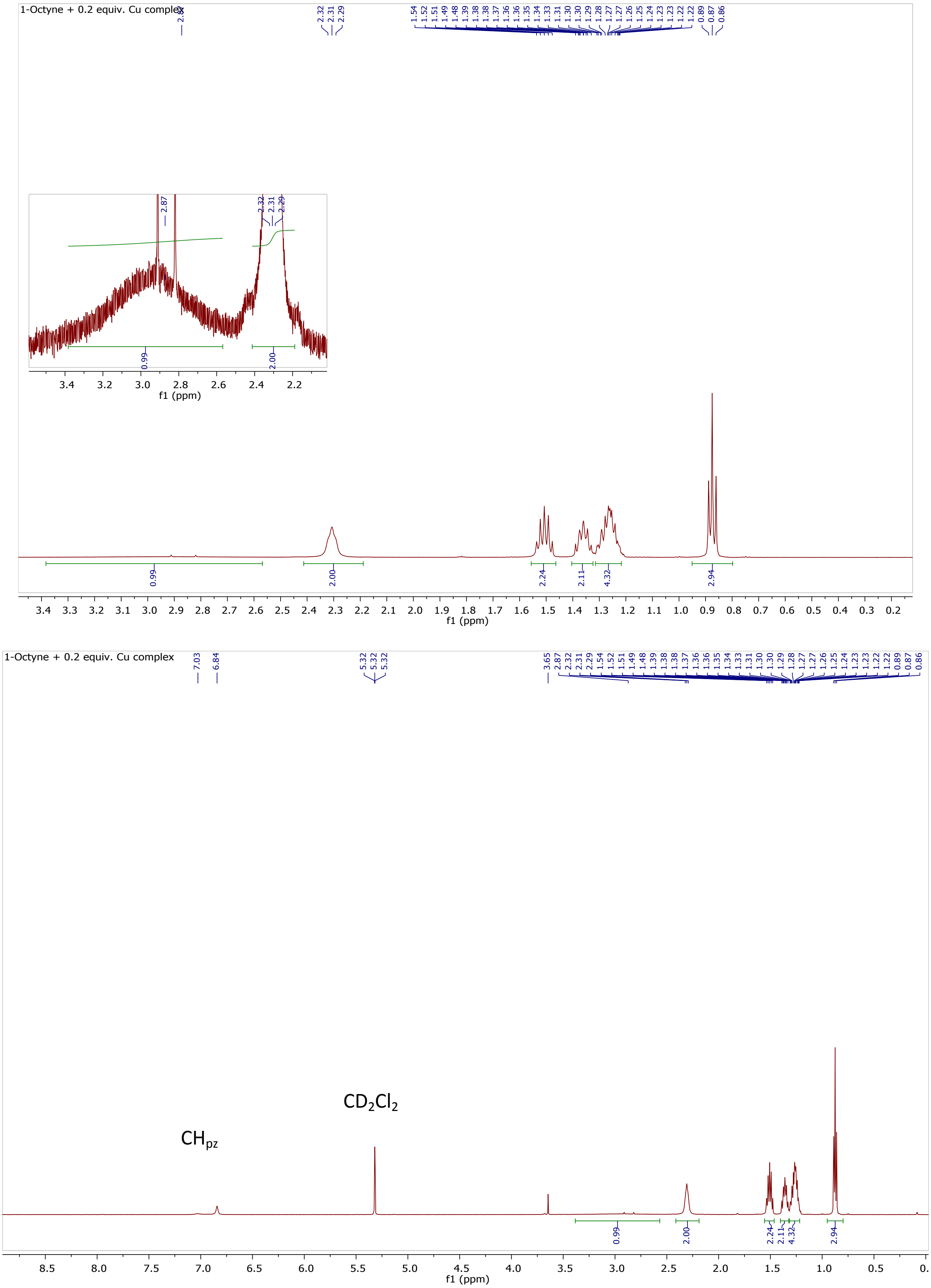


Figure S7. ^{1}H NMR spectra of 1-octyne **1** (c = 0.05 M) in the presence of 0.2 equivalent of **[CuL]$_3$** in CD$_2$Cl$_2$, T = 298 K. Common integrals are green.

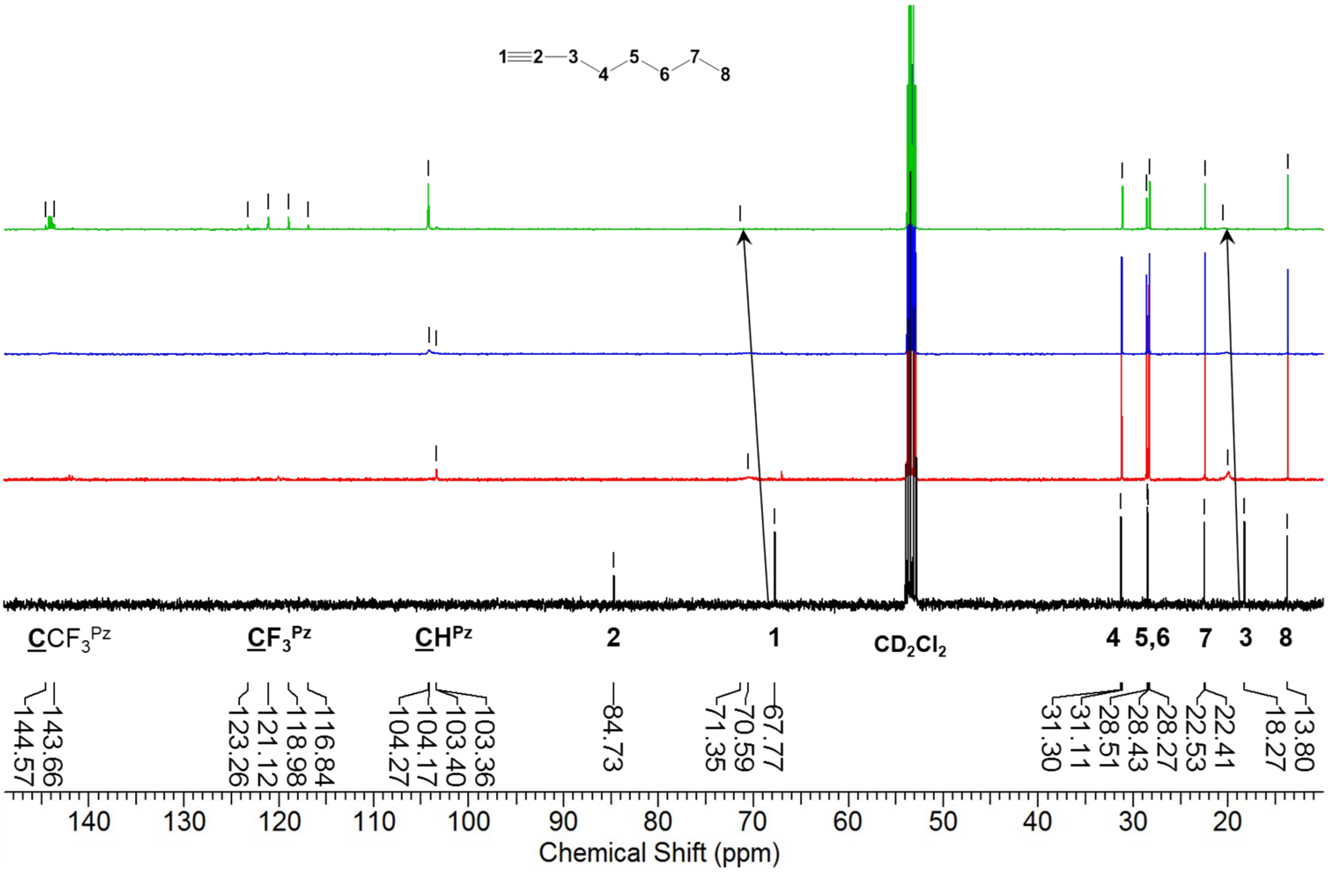


Figure S8. ^{13}C NMR spectra of 1-octyne **1** (c = 0.05 M, *black*) and **1** in the presence of different amount of **[CuL]$_3$** (0.25 equiv.: *red*, 0.5 equiv.: *blue*, 1 equiv.: *green*) in CD_2Cl_2, T = 298 K.

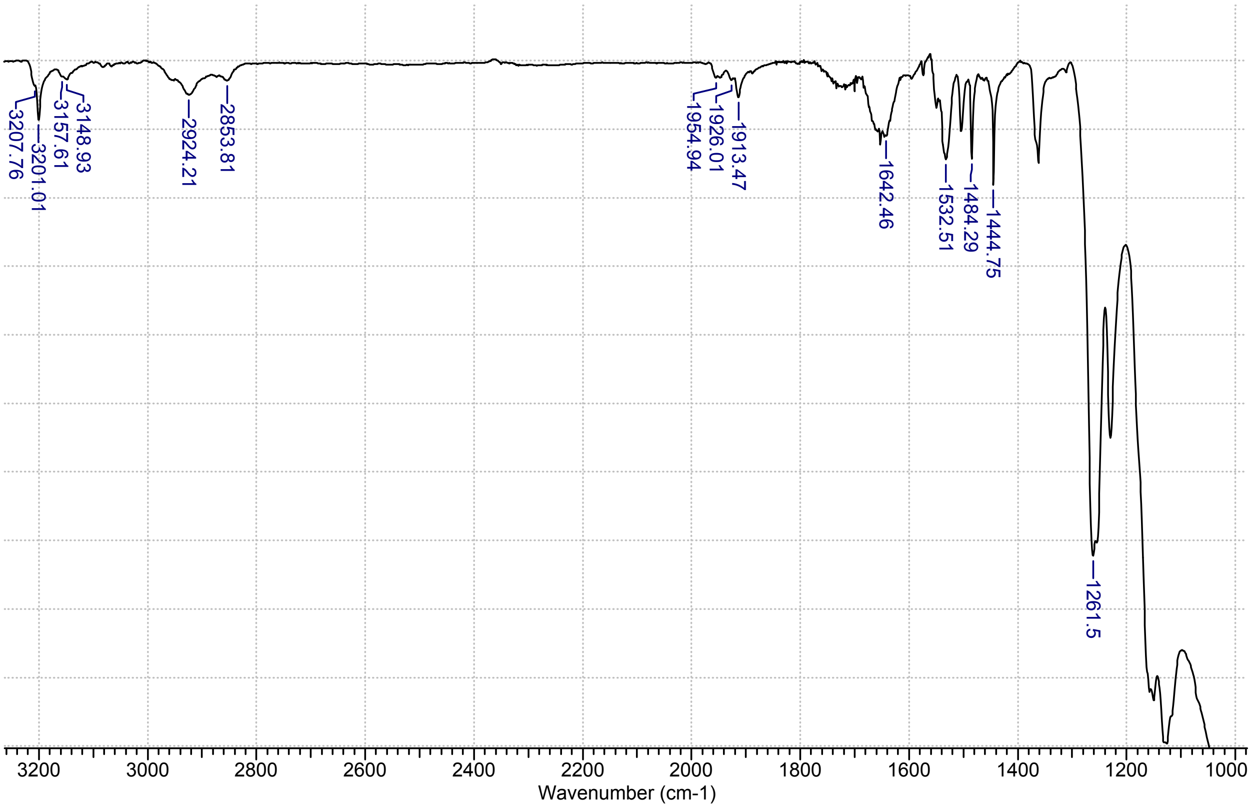


Figure S9. IR spectrum of the crystal **3**, thin film.

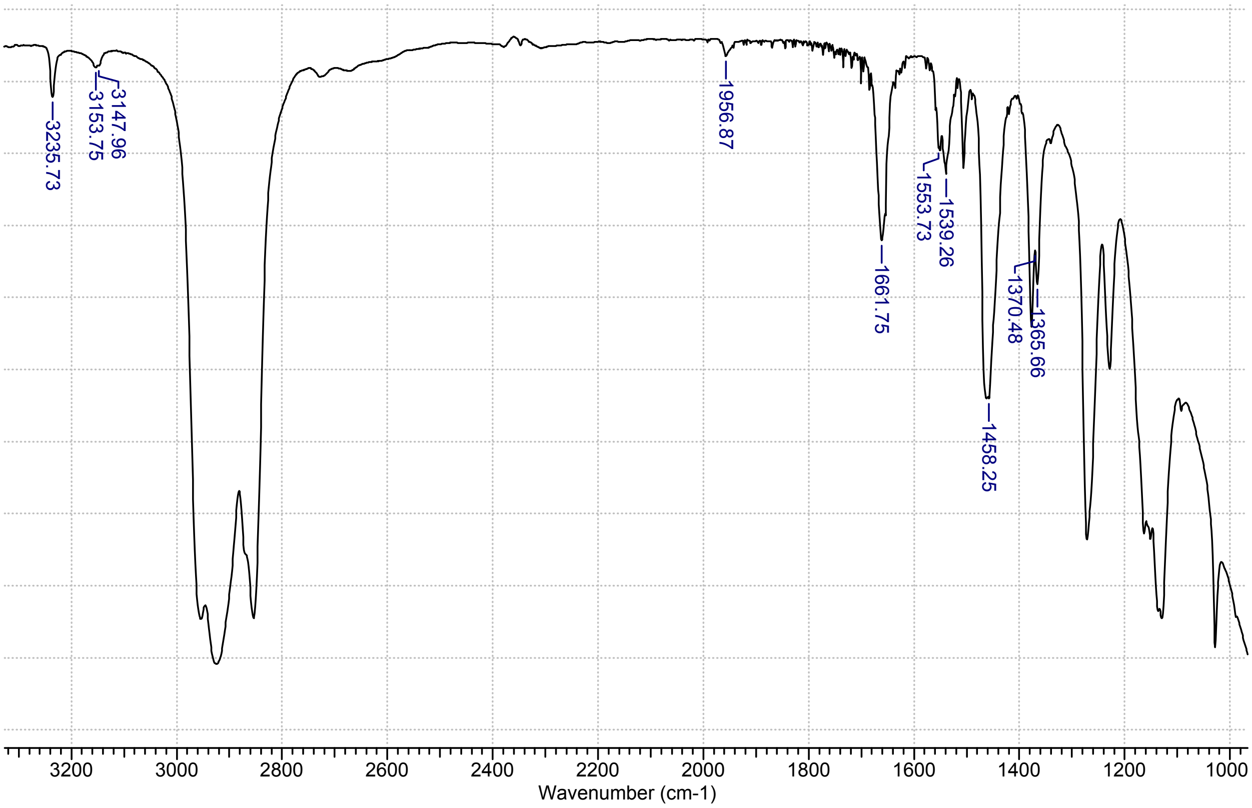


Figure S10. IR spectrum of the crystal **4**, nujol.

Procedure for the reaction between phenylacetylene (2) and *ortho*-fluorobenzyl azide (5) in the presence of one equivalent of complex [CuL]$_3$

To a solution of complex **[CuL]$_3$** (40.0 mg, 0.05 mmol) and phenylacetylene (**2**) (5.1 mg, 0.05 mmol) in CD_2Cl_2 (0.5 mL) in NMR tube was added *ortho*-fluorobenzyl azide (**5**) (10.2 mg, 0.065 mmol) under air. The reaction was monitored by NMR measurement. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford the triazole (**6**) as white powder (99% yield).

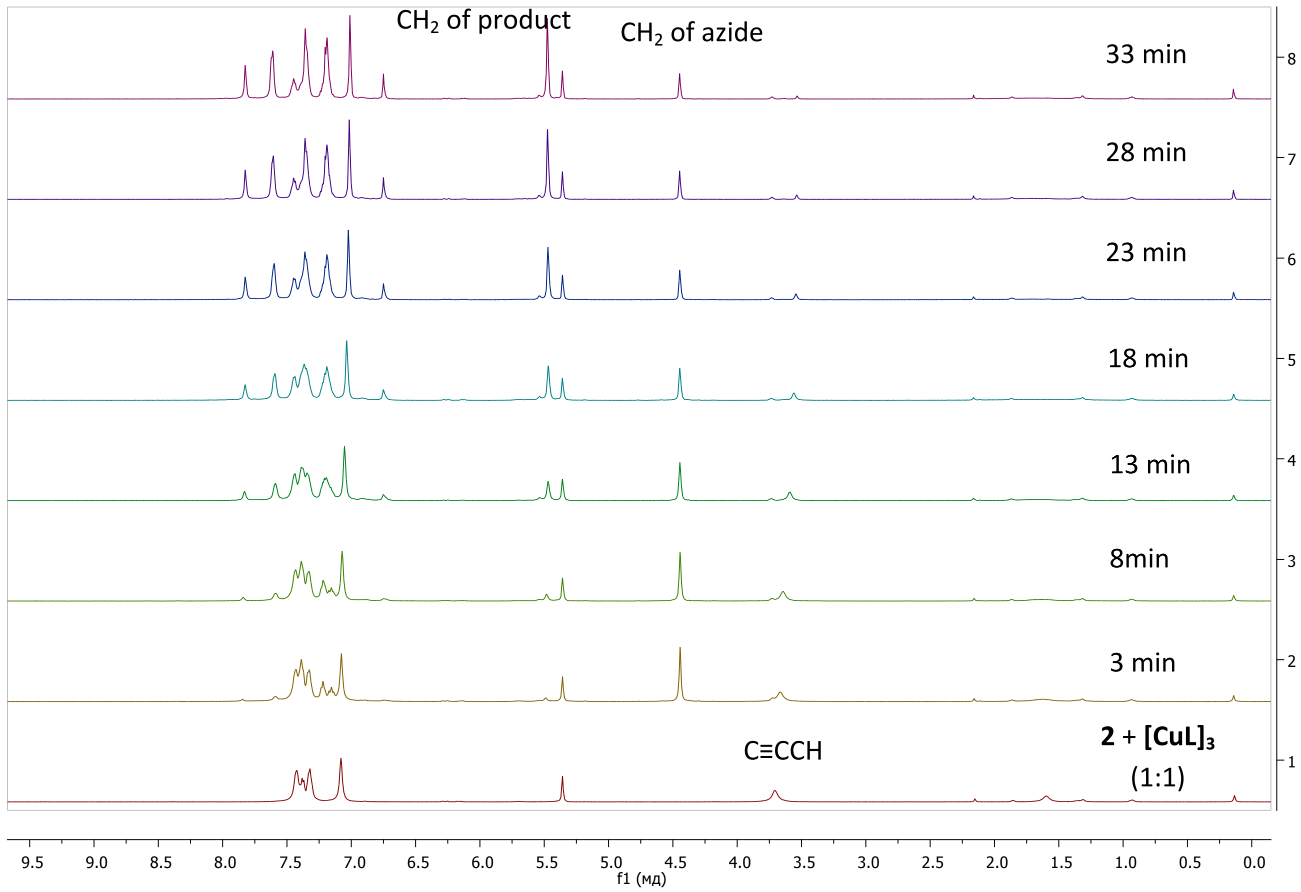


Figure S11. ^{1}H NMR spectra of the reaction between phenylacetylene (**2**) and *ortho*-fluorobenzyl azide (**5**) (c = 0.05 M) in the presence of one equivalent of **[CuL]$_3$** in CD_2Cl_2, d = 2 mm, T = 298 K.

Procedure for the click reaction between 1-octyne (1) or phenylacetylene (2) and *ortho*-fluorobenzyl azide (5) catalyzed by complex [CuL]$_3$

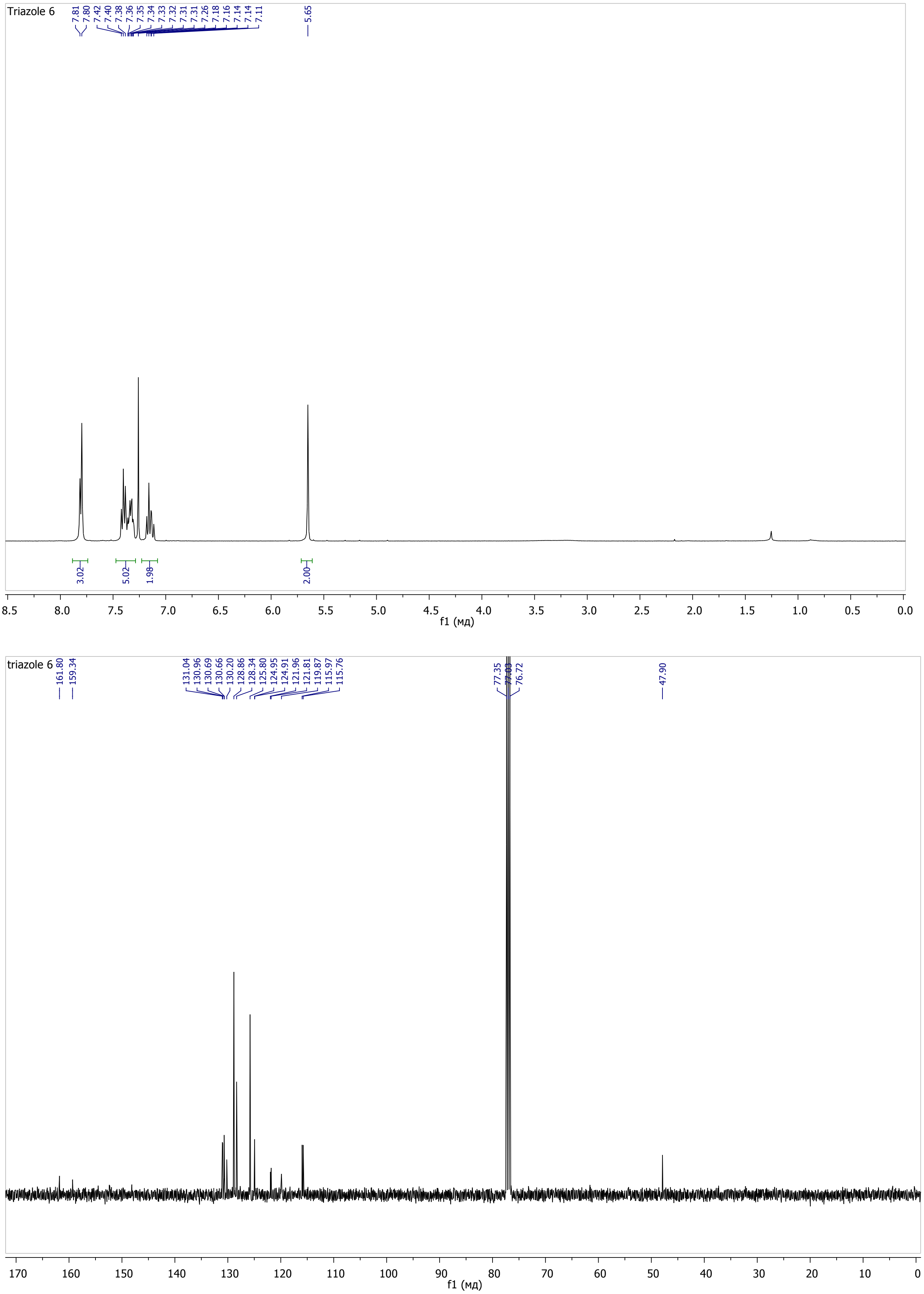
To a solution of complex **[CuL]$_3$** (1 mol%, 2.7 mg, 3.4 10^{-3} mmol) and acetylene (**1** or **2**) (0.34 mmol) in CH_2Cl_2 (1 mL) in a vial was added *ortho*-fluorobenzyl azide (**5**) (53.2 mg, 0.34 mmol) under air. The vial was then tightly capped with a rubber-sealed screw cap and the mixture was stirred at room temperature for 3 h. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (CH_2Cl_2) to afford the triazole (**6** or **7**) as white powder (99% yield).

1-(2-fluorobenzyl)-4-phenyl-1*H*-1,2,3-triazole (6)

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.88–7.77 (m, 3H), 7.47–7.29 (m, 5H), 7.21–7.08 (m, 2H), 5.65 (s, 2H) ppm.

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 161.8, 159.3, 131.0 (d, J = 8.1 Hz), 130.7 (d, J = 3.1 Hz), 130.2, 128.9, 128.3, 125.8, 124.9 (d, J = 3.7 Hz), 121.8, 119.9, 115.9 (d, J = 21.1 Hz) ppm.

^{19}F-NMR (376 MHz, $CDCl_3$): δ = -118.1 ppm.



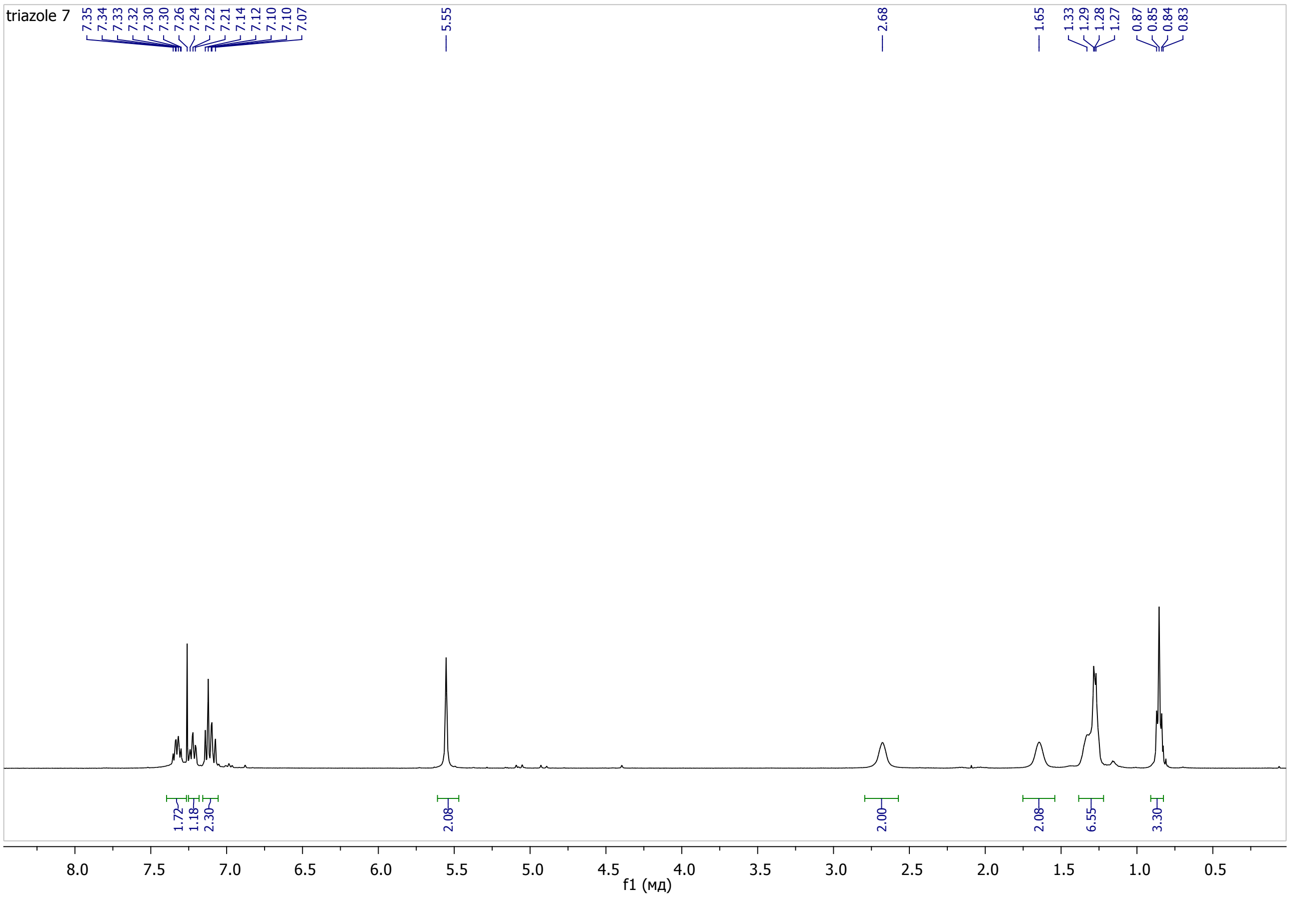
^{1}H NMR and ^{13}C NMR spectra of triazole **6**.

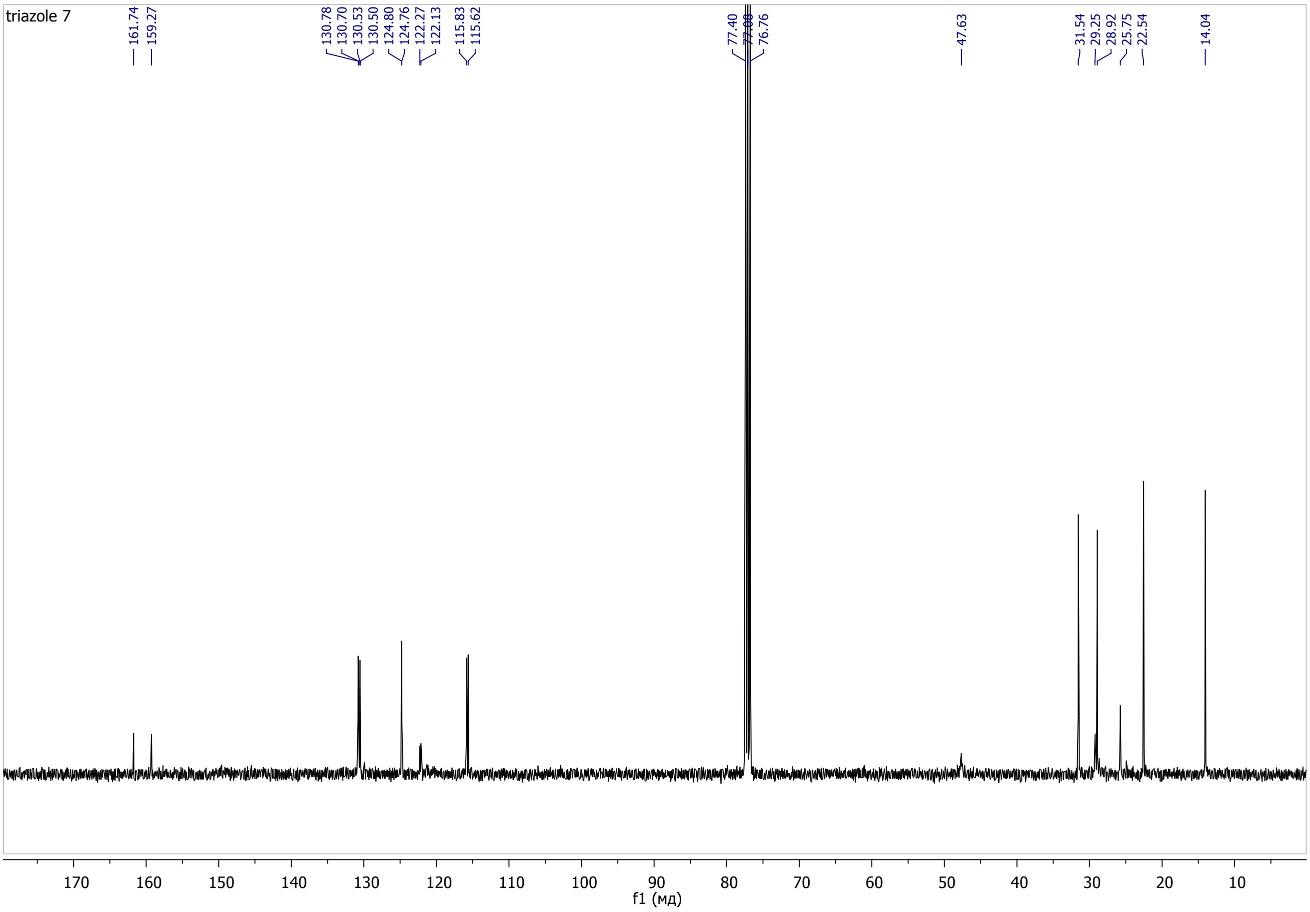
1-(2-fluorobenzyl)-4-hexyl-1*H*-1,2,3-triazole (7)

^{1}H-NMR (400 MHz, CDCl$_3$): δ = 7.40–7.27 (m, 2H), 7.23 (t, J = 6.9 Hz, 1H), 7.16–7.07 (m, 2H), 5.55 (s, 2H), 2.78–2.60 (m, 2H), 1.73–1.56 (m, 2H), 1.38–1.22 (m, 6H), 0.86 (t, J = 6.7 Hz, 3H) ppm.

^{13}C-NMR (101 MHz, CDCl$_3$): δ = 161.7, 159.3, 130.7 (d, J = 8.2 Hz), 130.5 (d, J = 3.0 Hz), 124.8 (d, J = 3.4 Hz), 122.2 (d, J = 14.4 Hz), 115.7 (d, J = 21.1 Hz), 47.6, 31.5, 29.3, 28.9, 25.8, 22.5, 14.0 ppm.

^{19}F-NMR (376 MHz, CDCl$_3$): δ = -118.3 ppm.





^{1}H NMR and ^{13}C NMR spectra of triazole **7**.

References

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S2. C. Büll, T. Heise, N. van Hilten, J. F. A. Pijnenborg, V. Bloemendal, L. Gerrits, E. D. Kers-Rebel, T. Ritschel, M. H. den Brok, G. J. Adema, T. J. Boltje, *Angew. Chem. In. Ed.* **2017**, *56*, 3309.

S3. APEX II Software Package; Bruker AXS Inc.: Madison, WI, **2005**.

S4. G. M. Sheldrick, *Acta Crystallogr., Sect. A,* **2008**, 64, 112.

S5. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, 42, 339.