Electronic Supplementary Material (ESI) for Dalton Transactions
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SUPPLEMENTARY INFORMATION

Title: Copper(II) and Triphenylphosphine Copper(I) Ethylene Glycol Carboxylates: Synthesis, Characterisation and Copper Nanoparticle Generation

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Content

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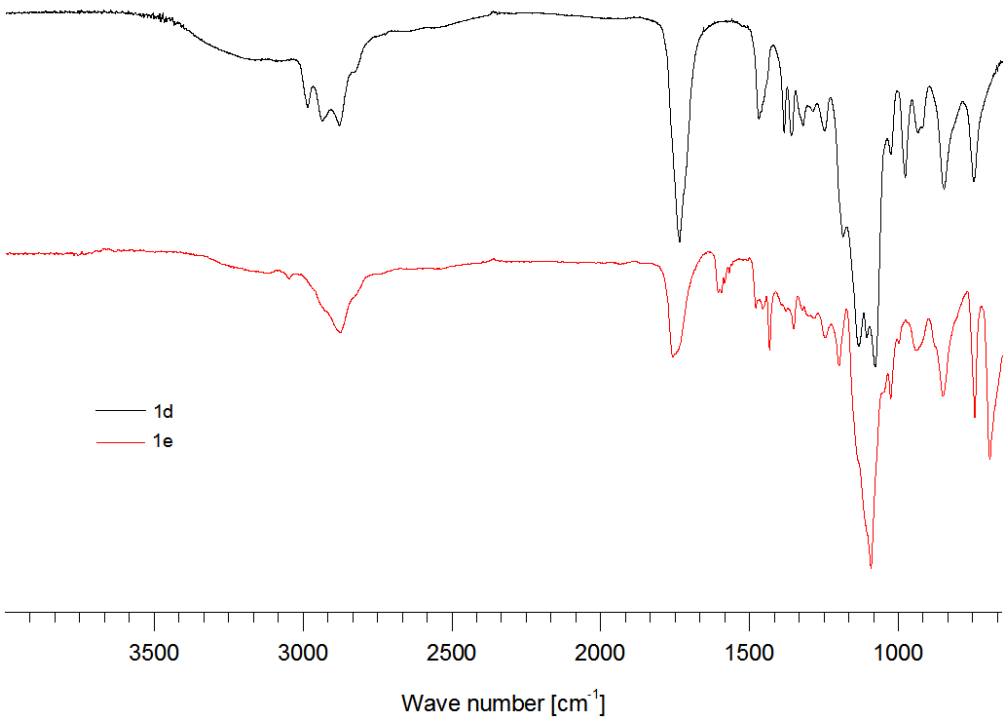
1 Precursor Characterisation

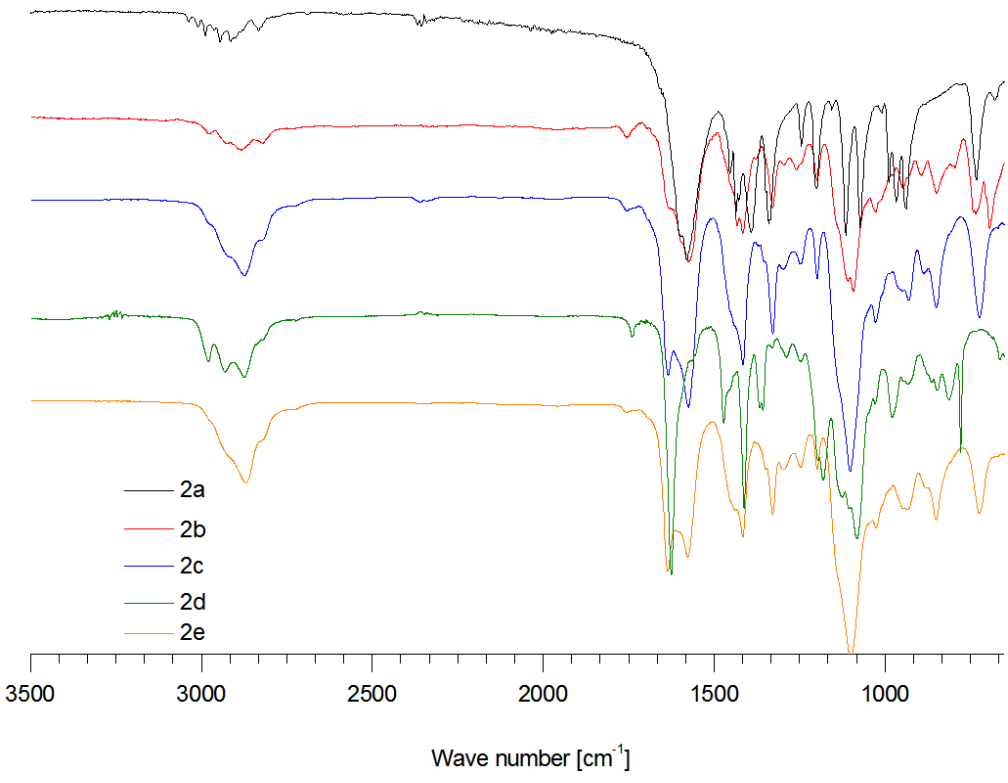
1.1 IR Spectra

All infrared spectra were recorded at ambient conditions as ATR-FTIR spectra by using a Biorad FTS-165 or a Nicolet iS 10 spectrometer from Thermo Scientific.

IR spectra of the carbonic acids **1d** and **1e**:



IR spectra of the copper(II) carboxylates **2a–e**:



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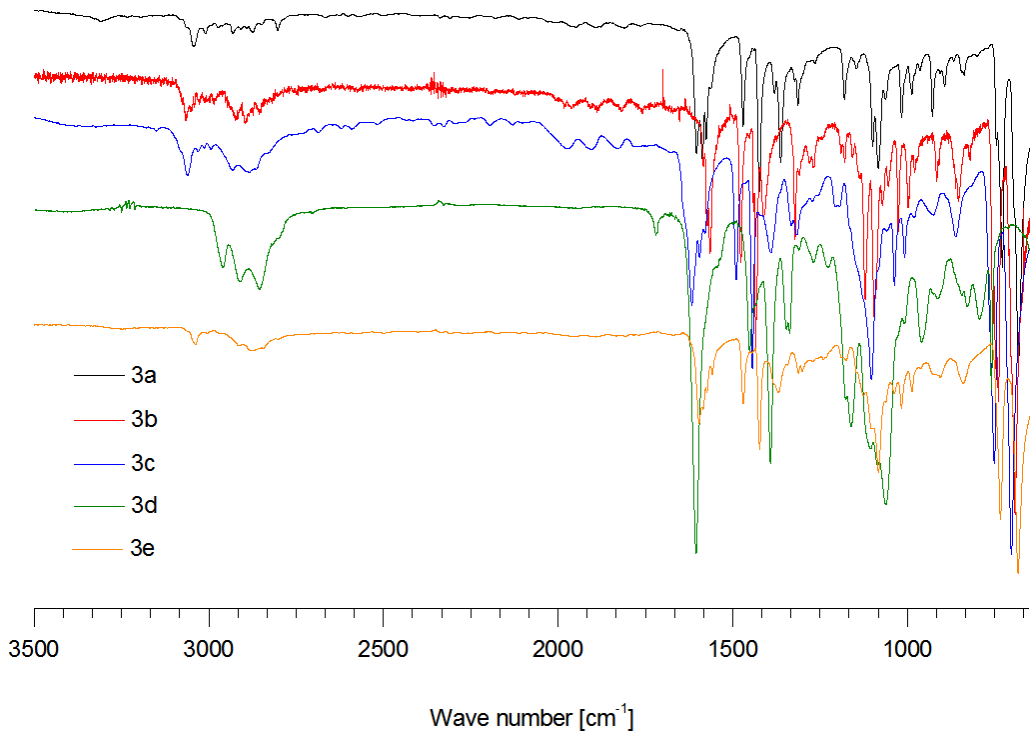
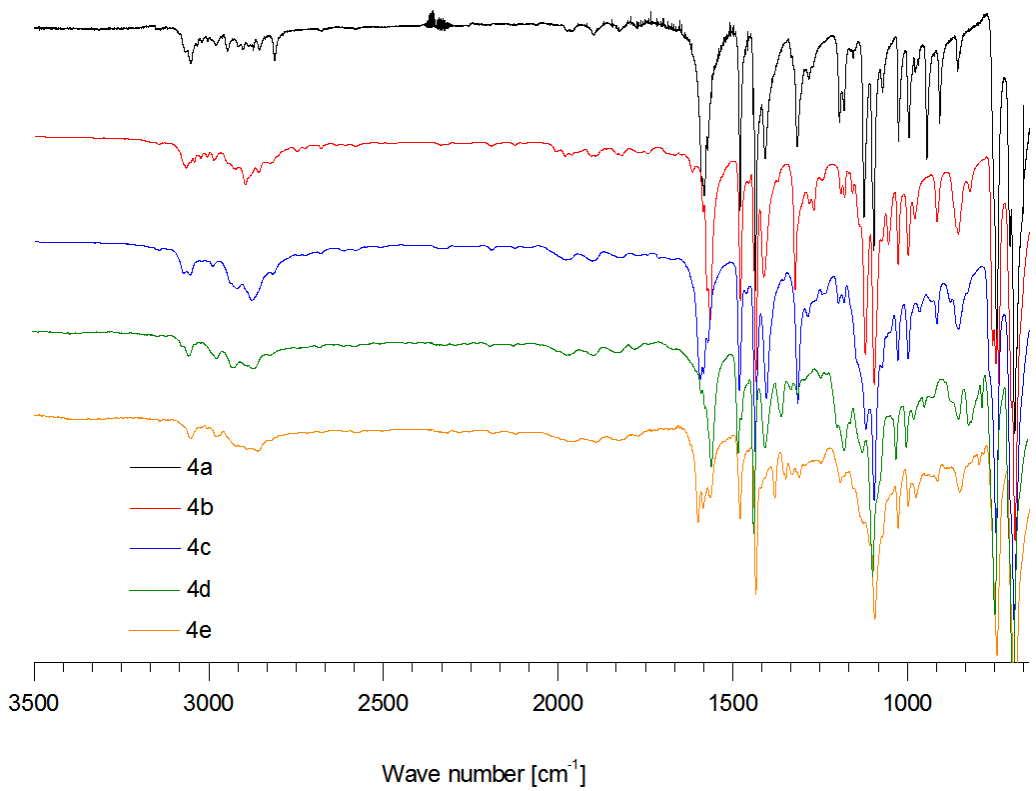
IR spectra of the tris(triphenylphosphine)copper(I) carboxylates **3a–e**:



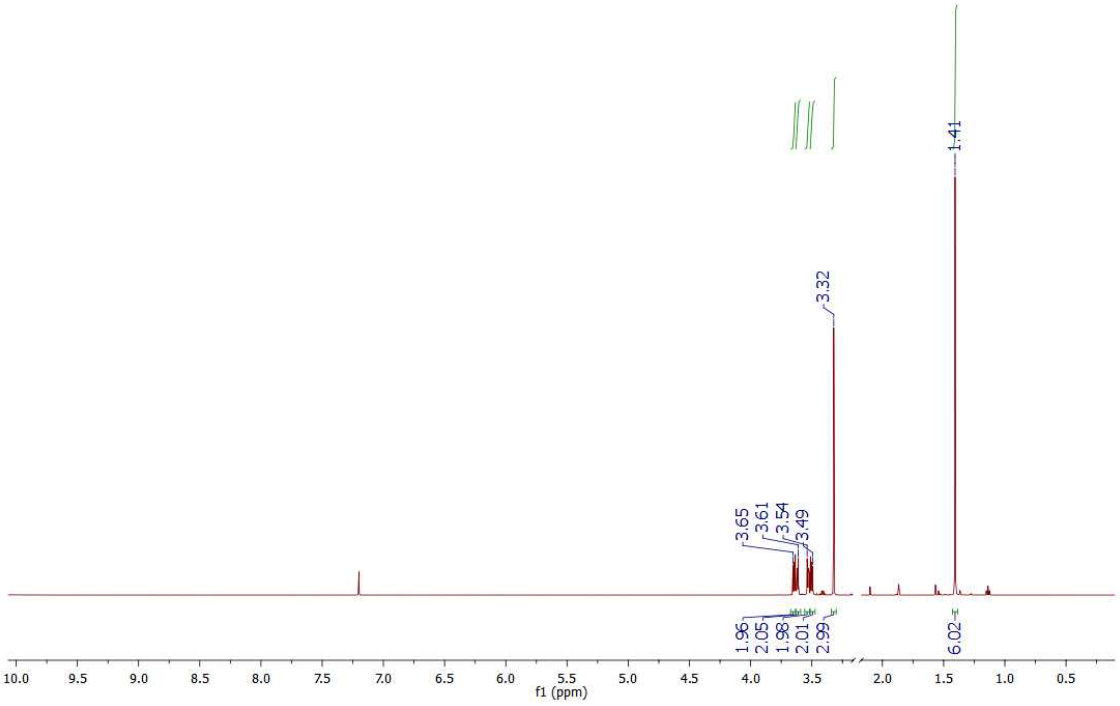
IR Spectra of the bis(triphenylphosphine)copper(I) carboxylates **4a–e**:

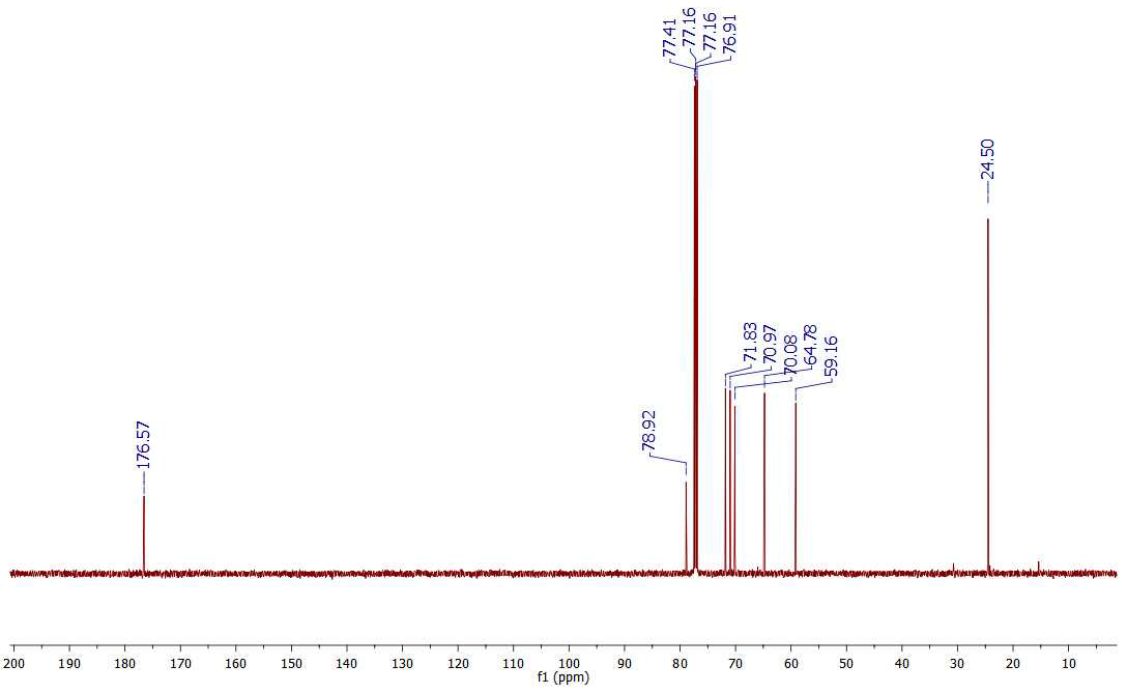


1.2 NMR Spectra

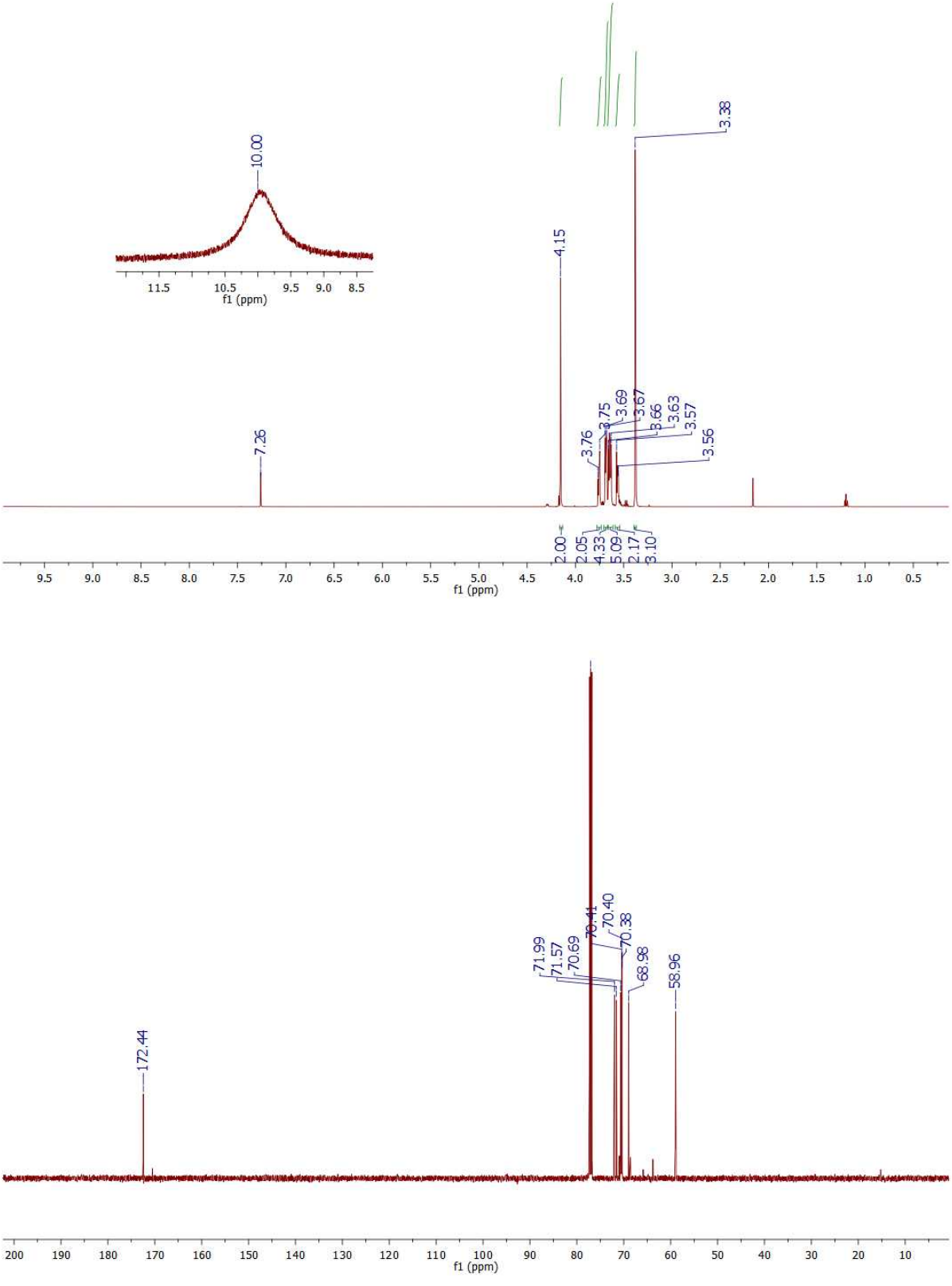
All ^{1}H NMR spectra were recorded in $CDCl_3$ at 25 °C with a Bruker Avance III 500 spectrometer operating at 500.30 MHz in the Fourier transform mode; $^{13}C\{^{1}H\}$ NMR spectra were recorded at 125.80 MHz. Chemical shifts are given relative to the internal standard tetramethylsilane (δ = 0. 00 ppm).

^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of 2-[2-(2-methoxyethoxy)ethoxy]-2-methylpropanoic acid (**1d**):

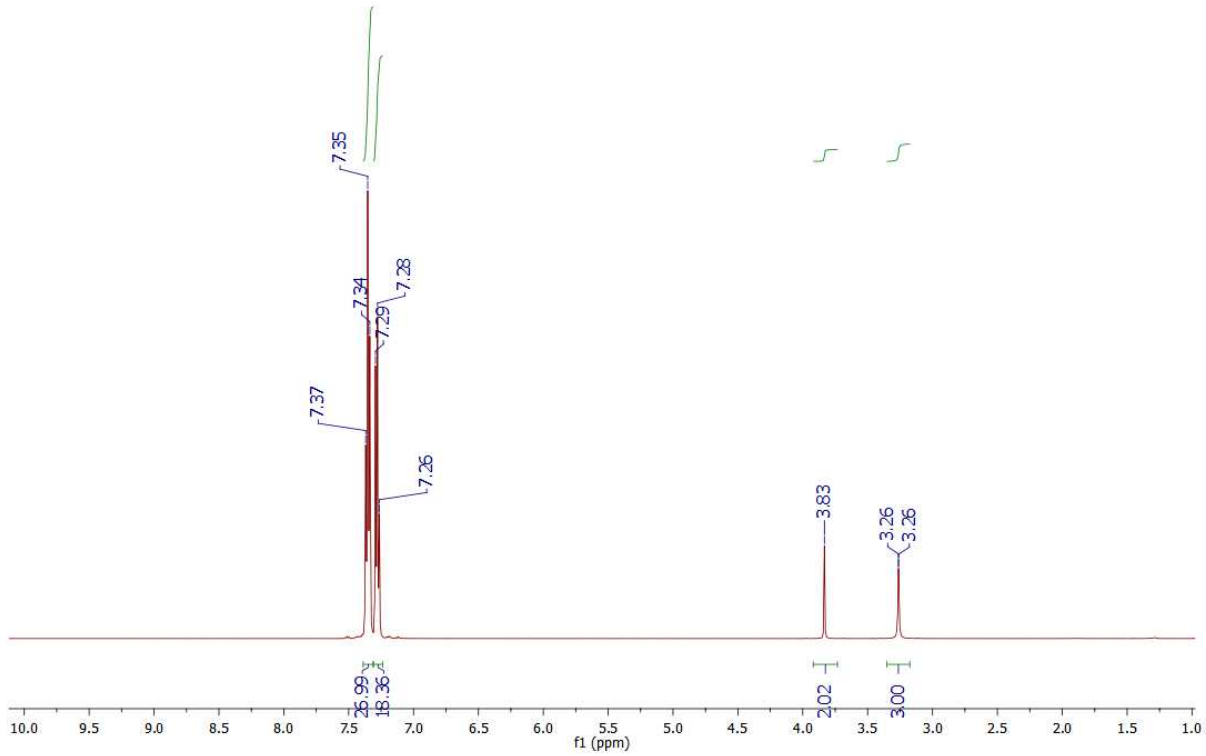


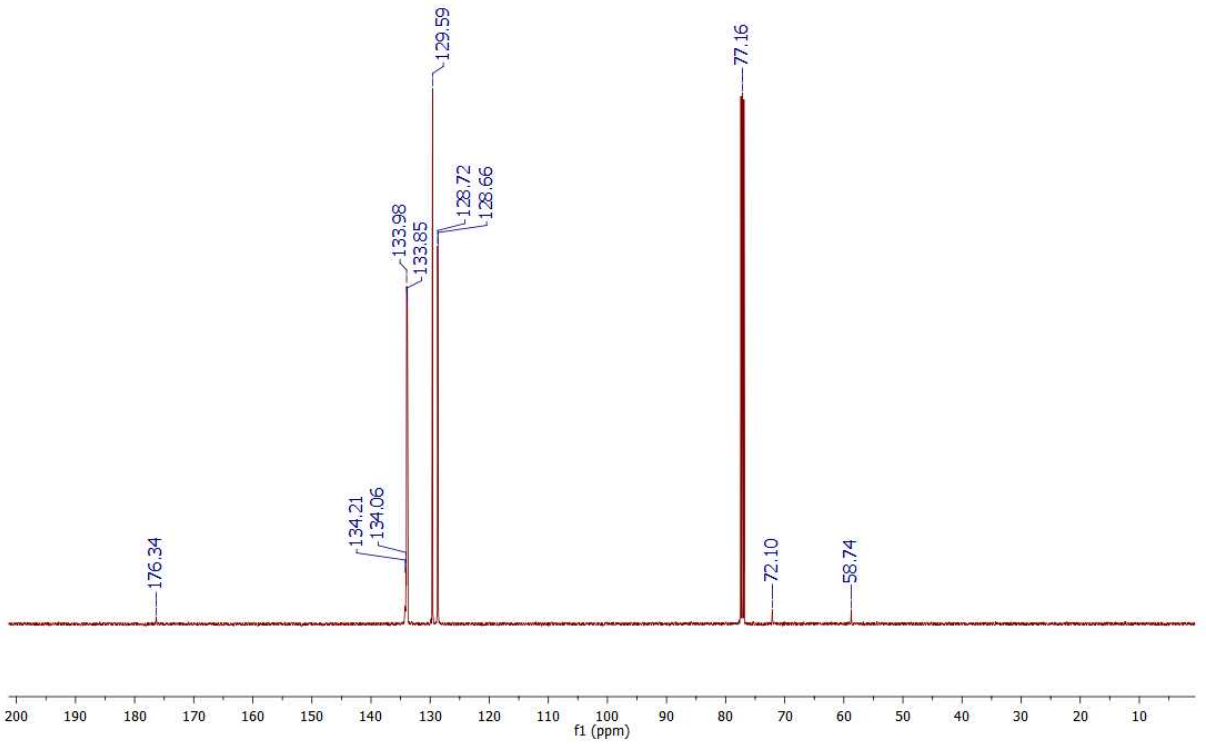


^{1}H (top) and ^{13}C{^{1}H} (bottom) NMR spectra of 2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}acetic acid (**1e**):



^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of tris(triphenylphosphine)copper(I)-2-methoxyacetate (**3a**):





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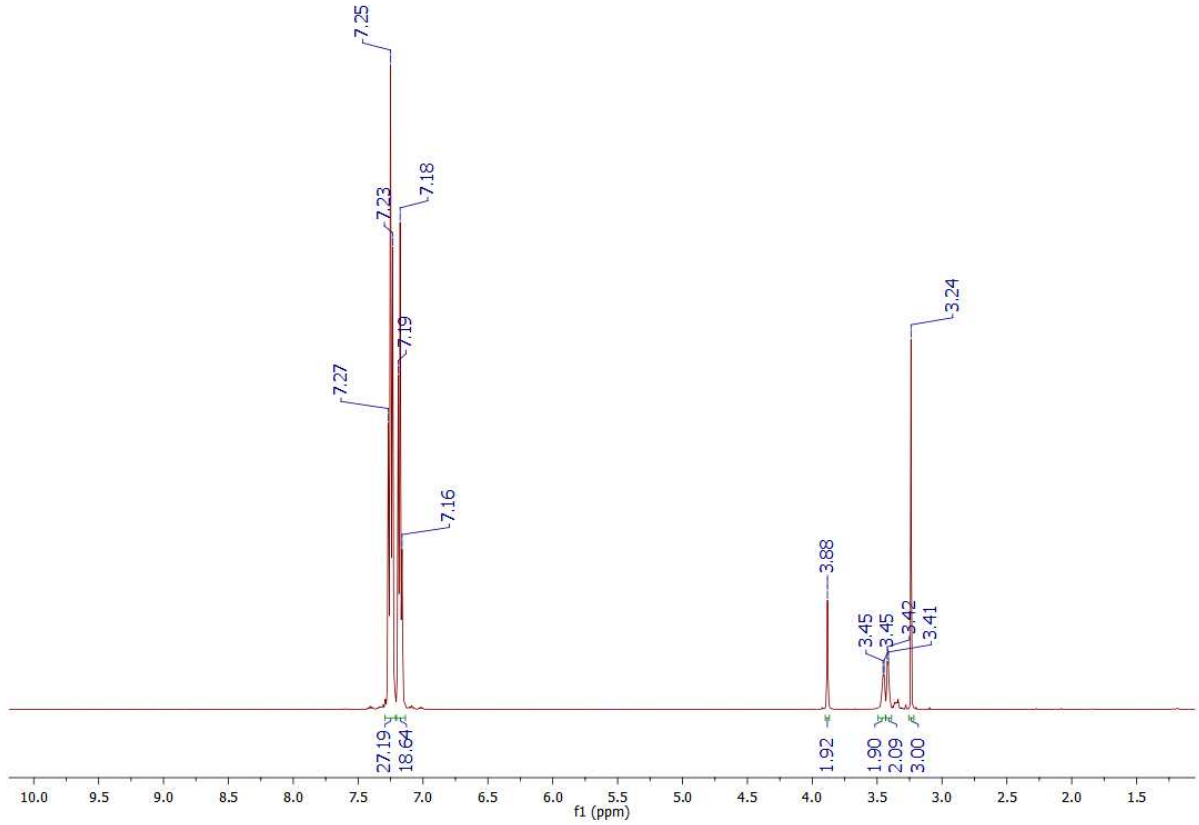
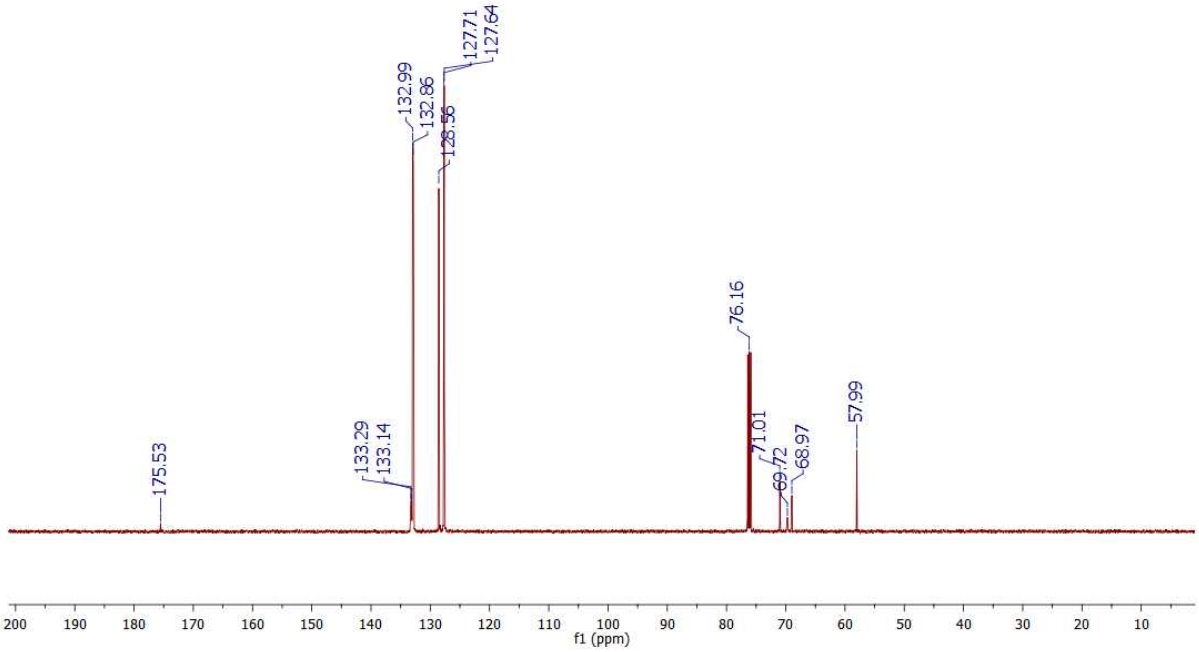
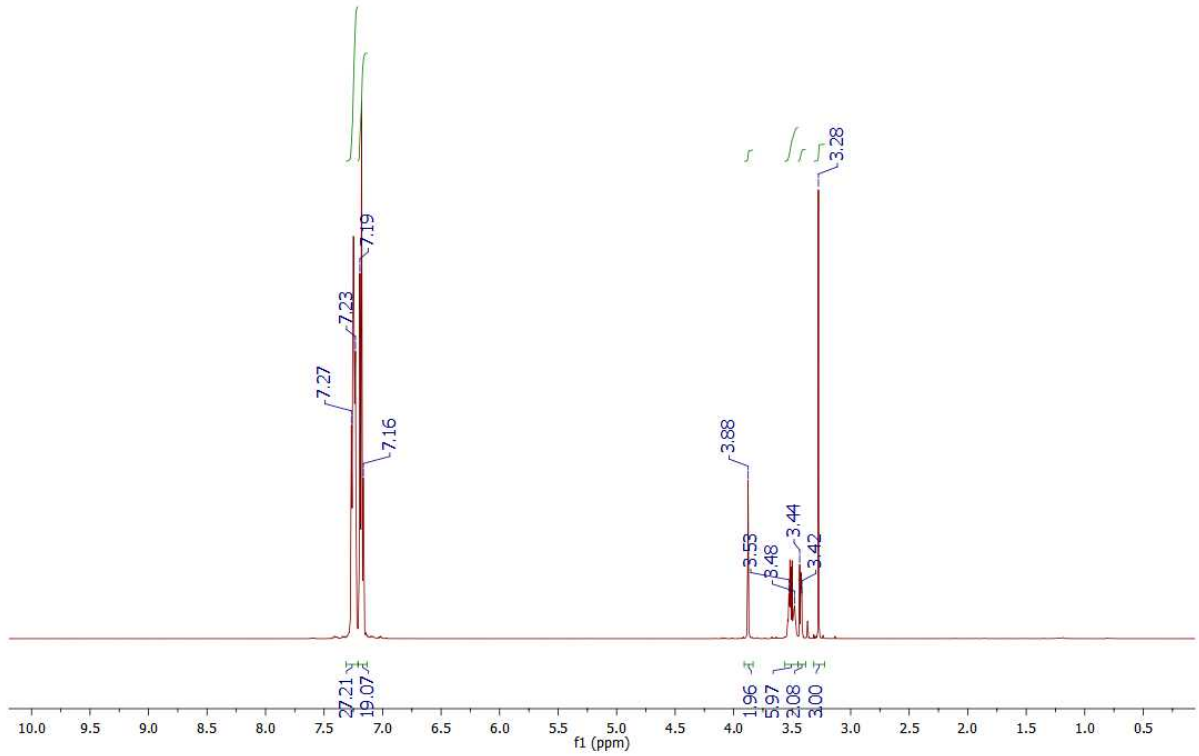
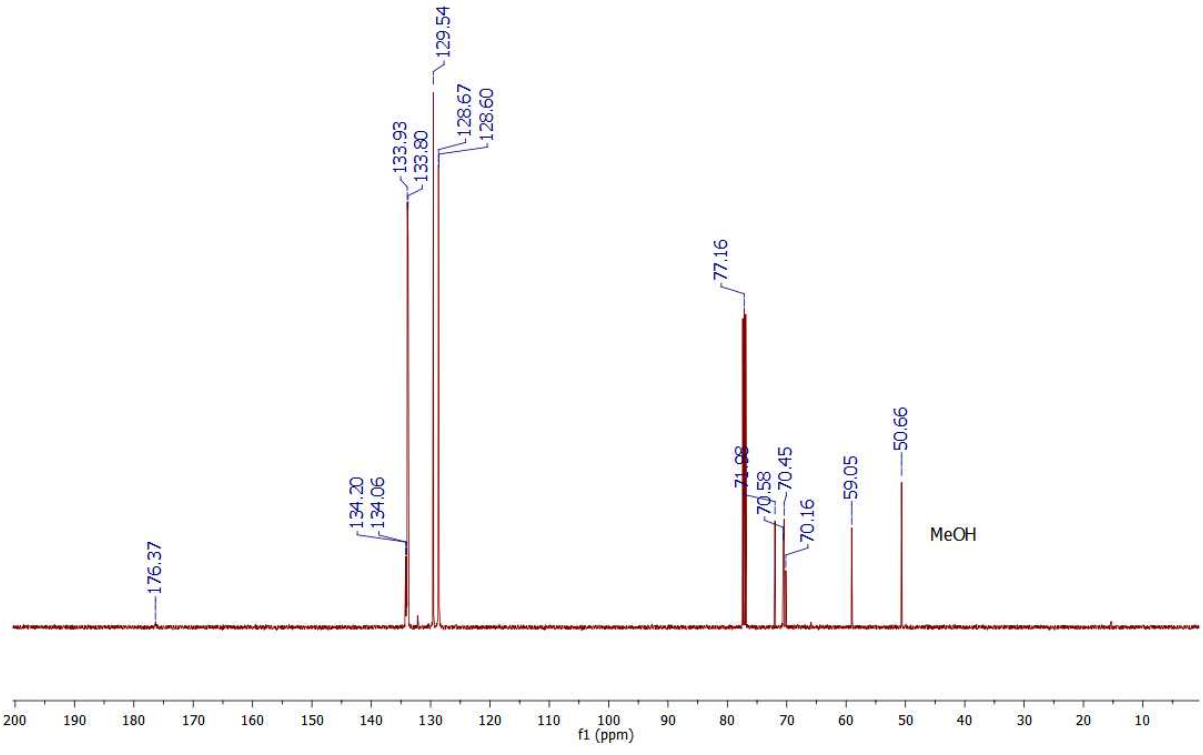
^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of tris(triphenylphosphine)copper(I)-2-(2-methoxy-ethoxy)acetate (**3b**):



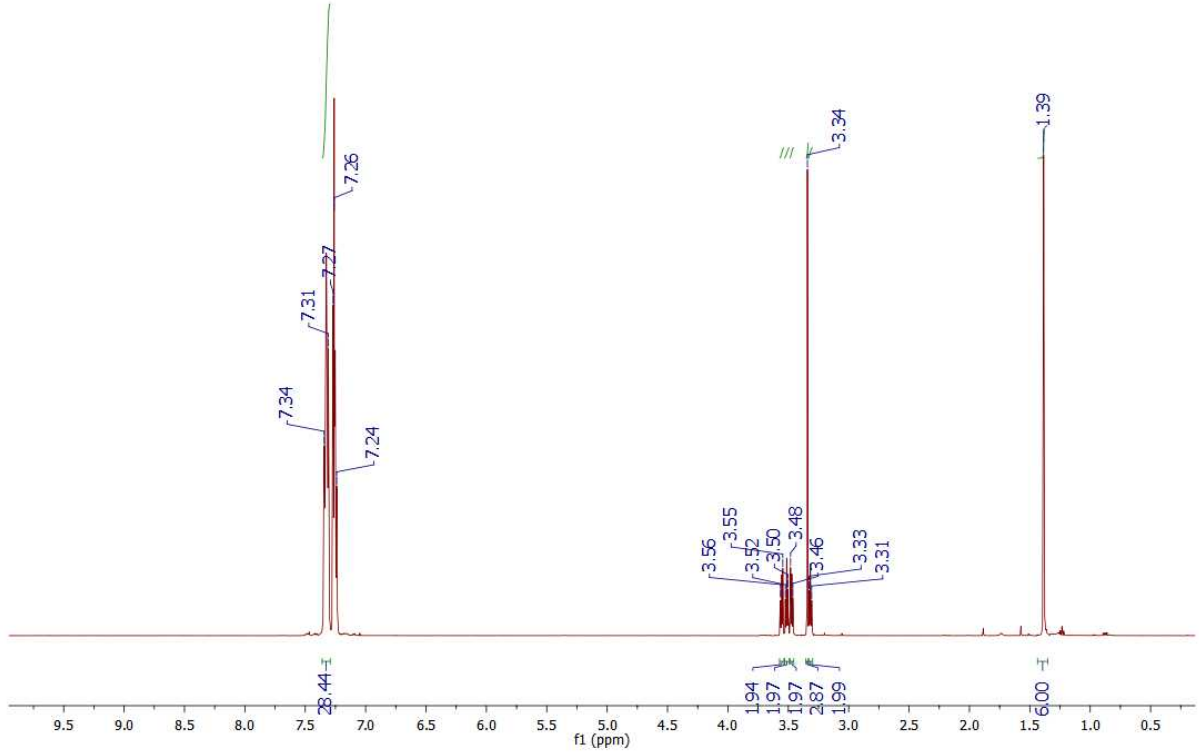


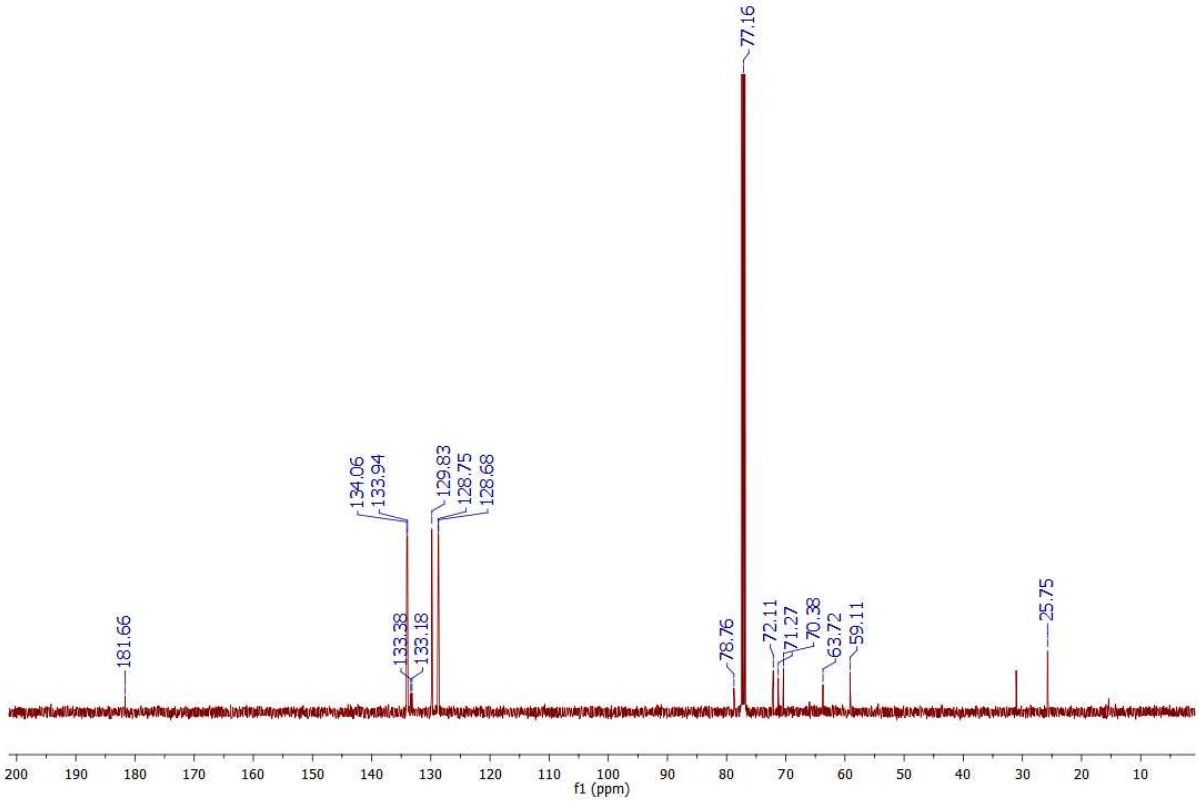
^{1}H (top) and ^{13}C{^{1}H} (bottom) NMR spectra of tris(triphenylphosphine)copper(I)-2-[2-(2-methoxy-ethoxy)ethoxy]acetate (**3c**):



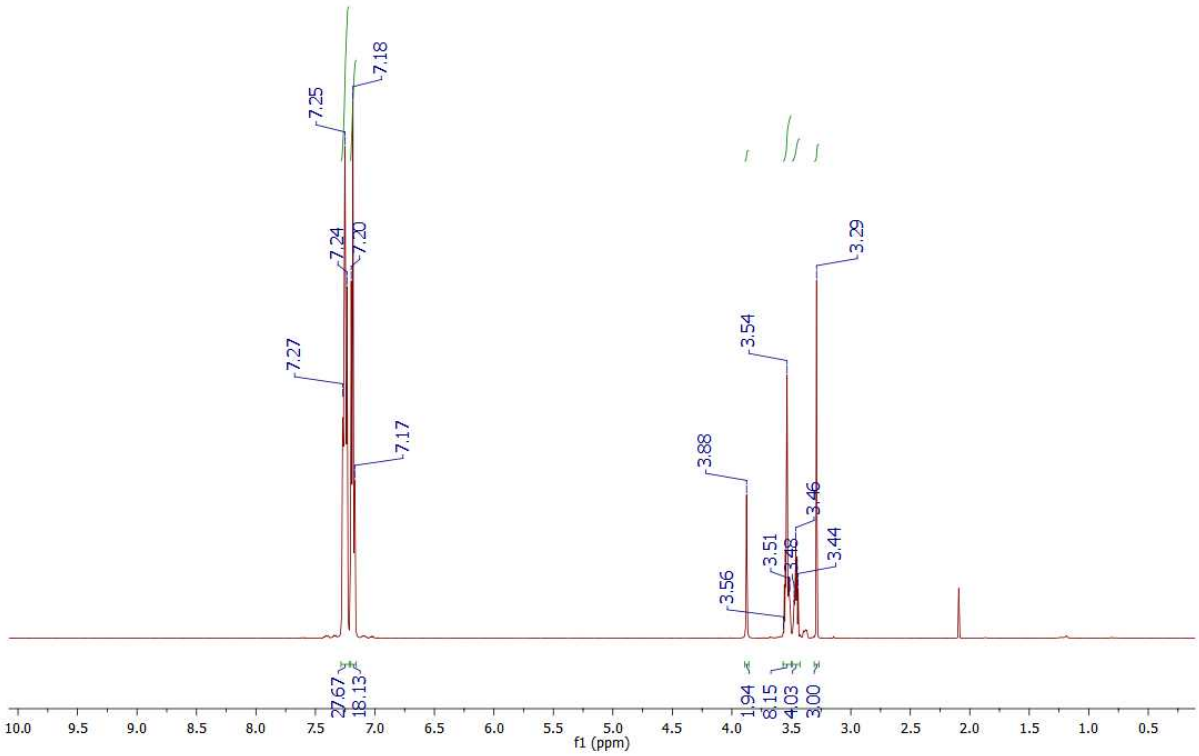


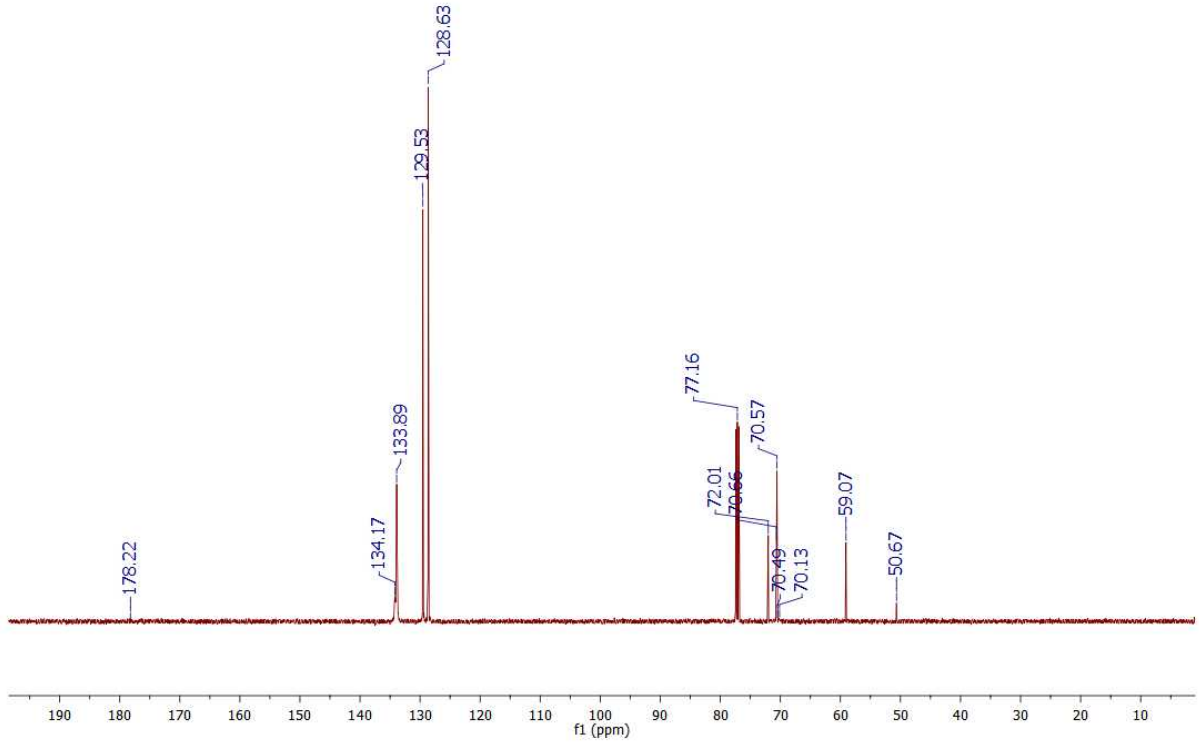
^{1}H (top) and ^{13}C{^{1}H} (bottom) NMR spectra of tris(triphenylphosphine)copper(I)-2-[2-(2-methoxy-ethoxy)ethoxy]-2-methylpropanoate (**3d**):





^{1}H (top) and ^{13}C{^{1}H} (bottom) NMR spectra of tris(triphenylphosphine)copper(I)-2-{2-[2-(2-methoxy-ethoxy)ethoxy]ethoxy}acetate (**3e**):





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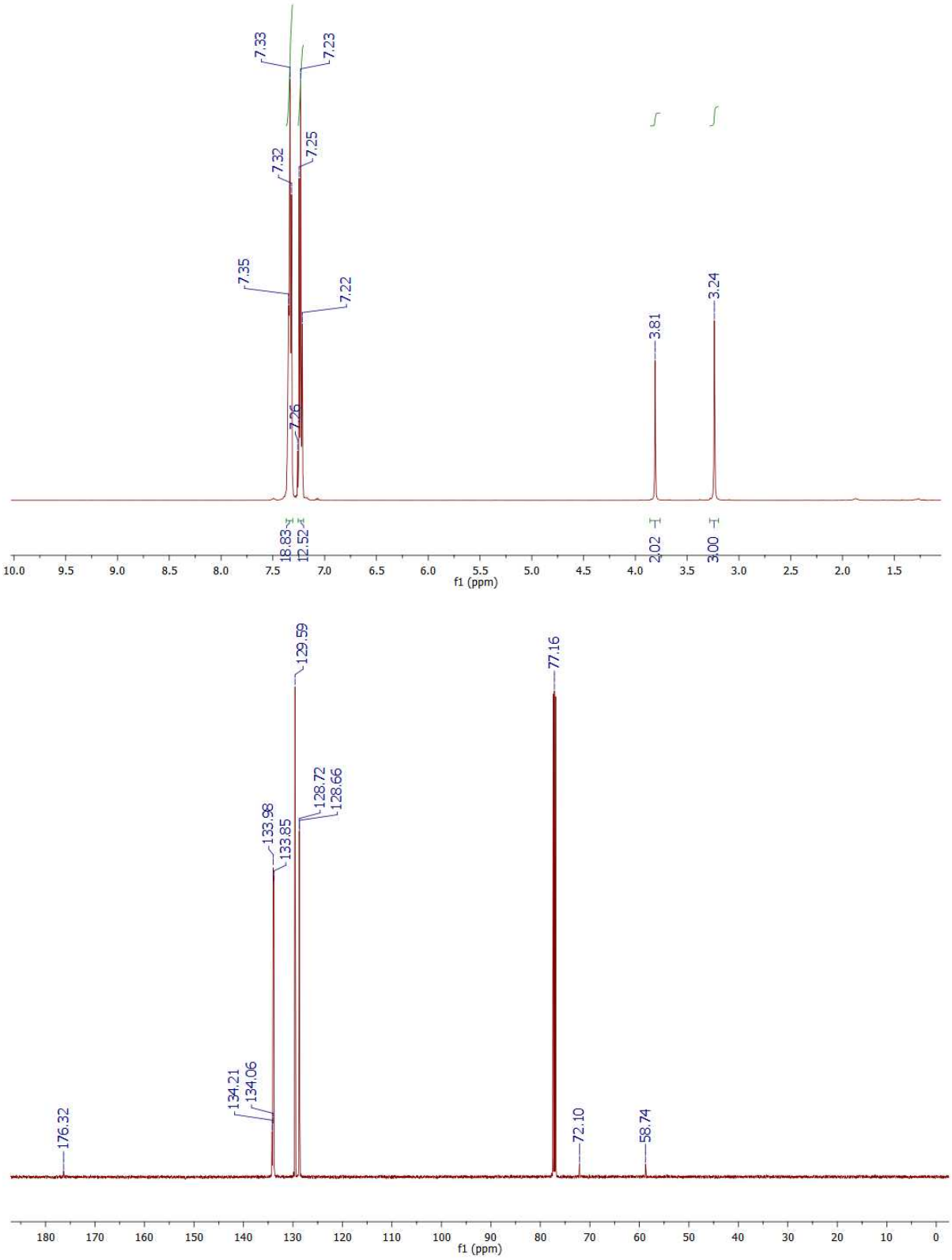
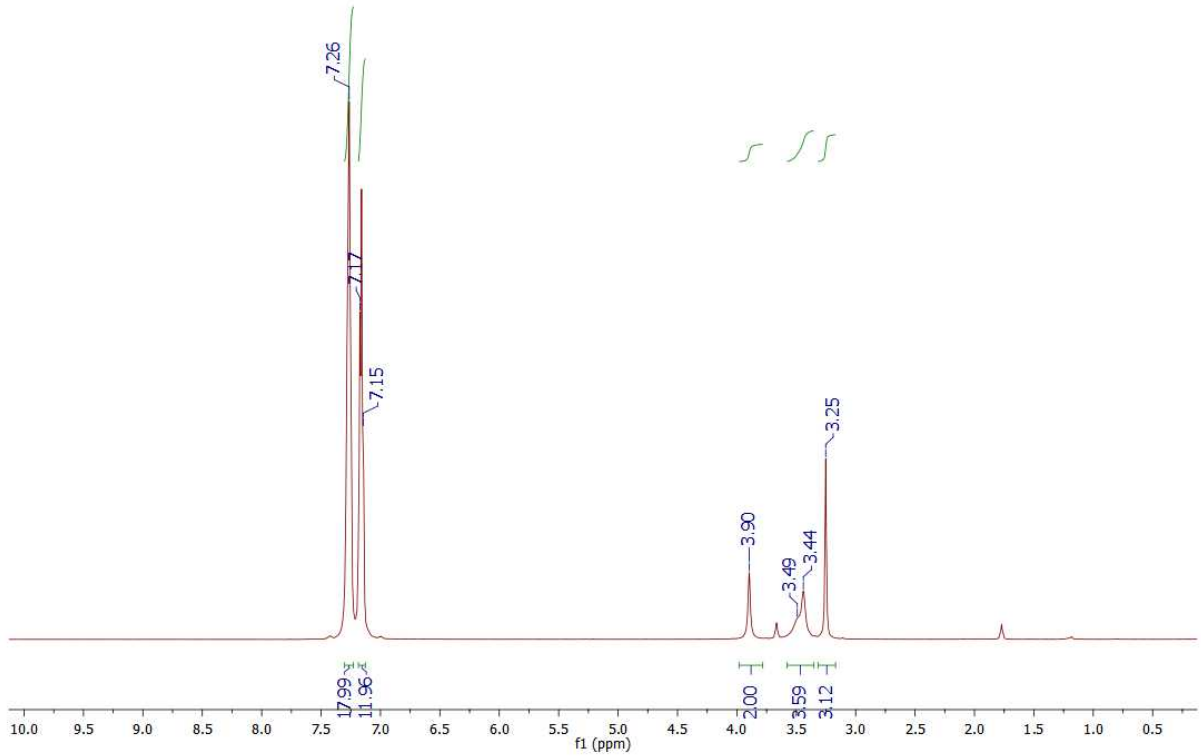
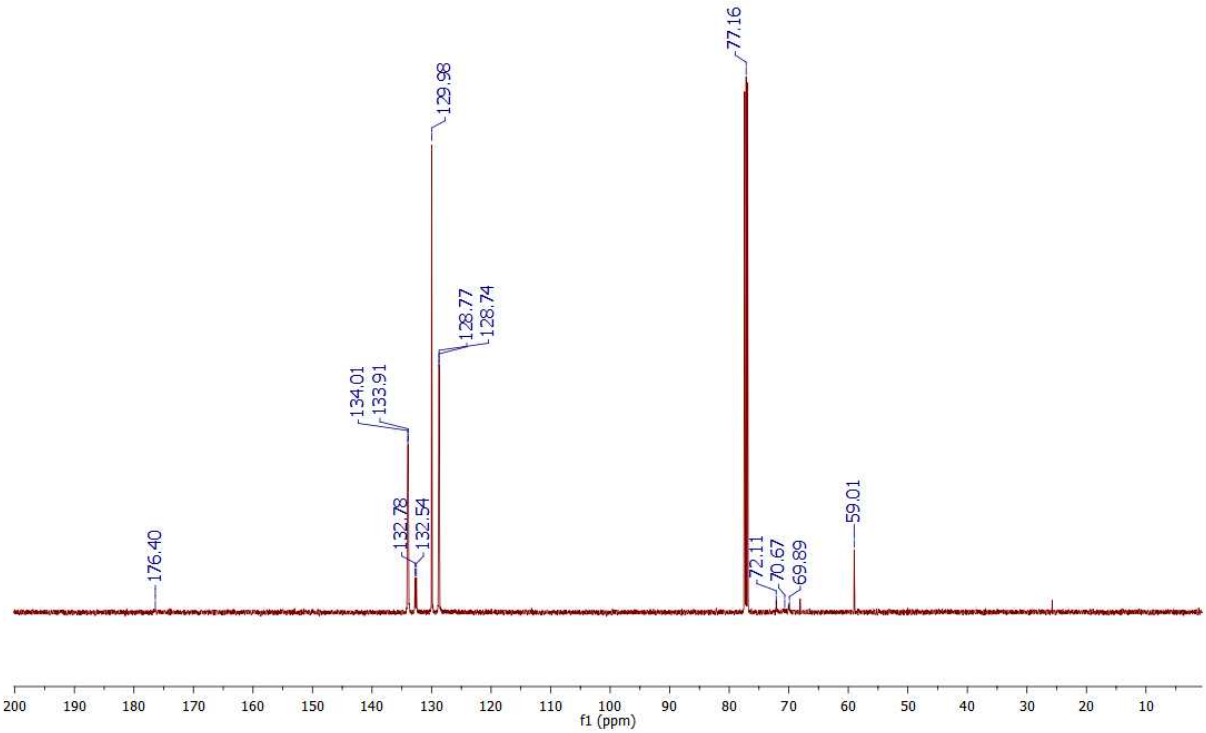
^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of bis(triphenylphosphine)copper(I)-methoxyacetate (**4a**):

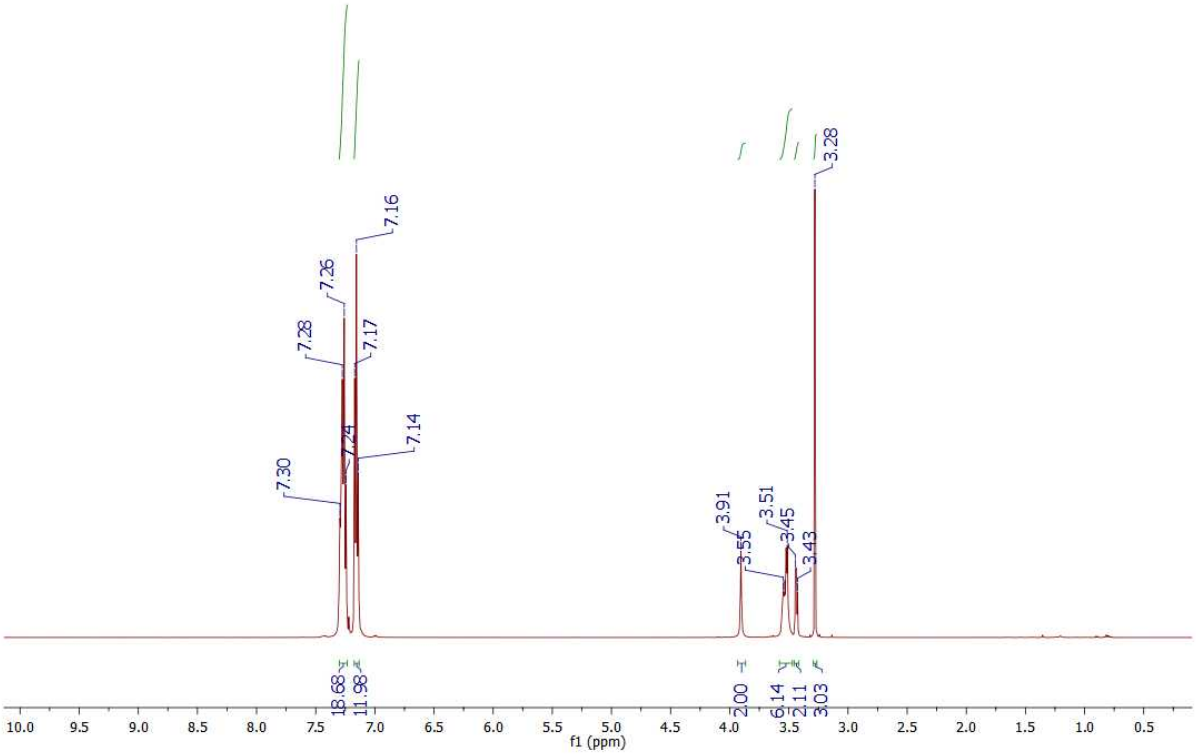


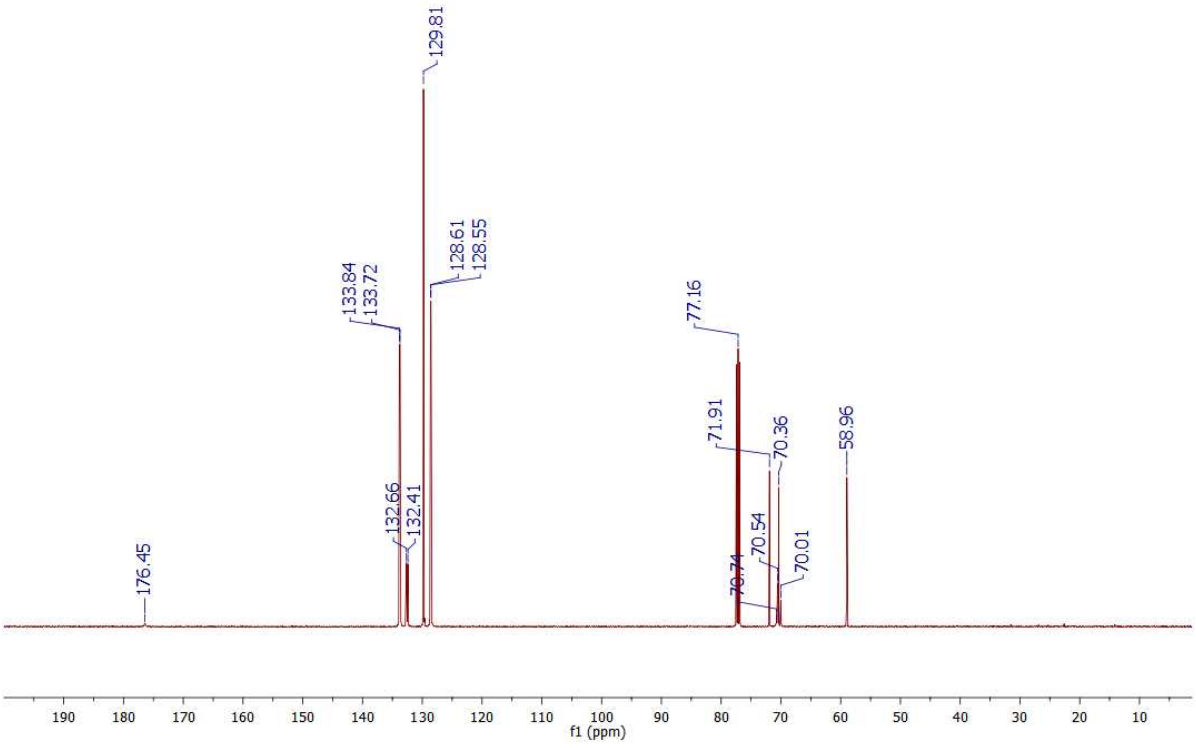
^{1}H (top) and ^{13}C{^{1}H} (bottom) NMR spectra of bis(triphenylphosphine)copper(I)-2-(2-methoxyethoxy)-acetate (**4b**):





^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of bis(triphenylphosphine)copper(I)-2-[2-(2-methoxy-ethoxy)ethoxy]acetate (**4c**):





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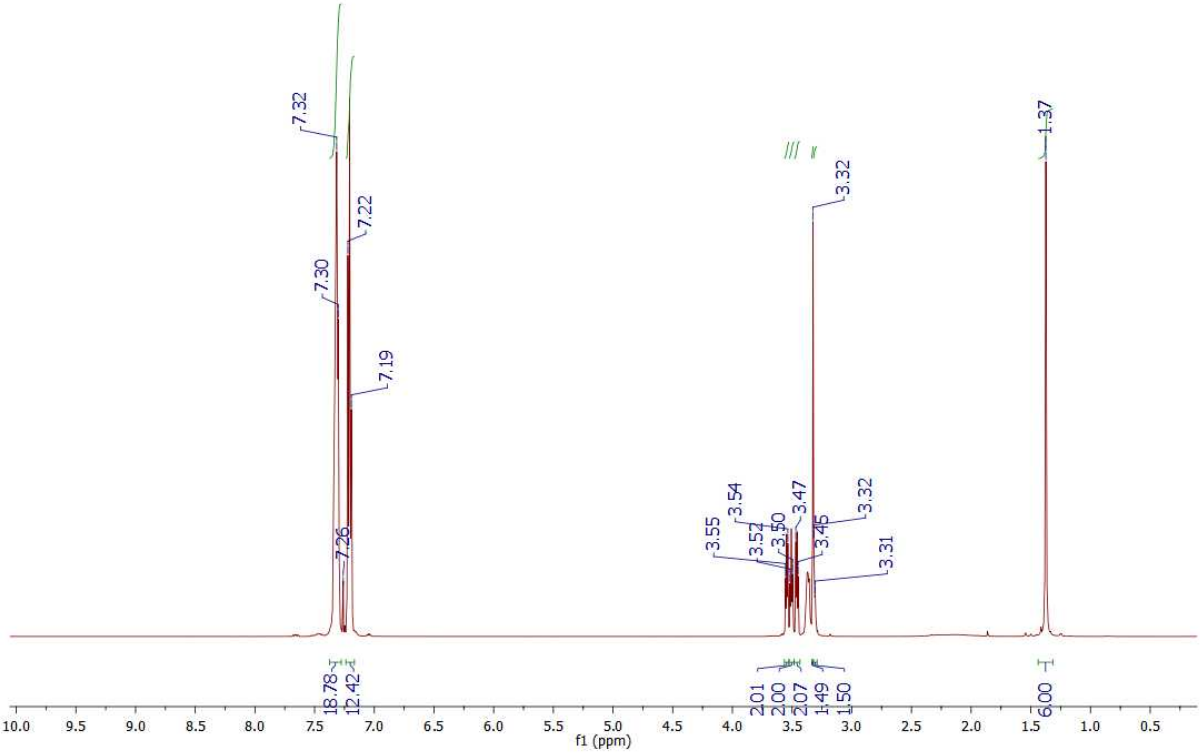
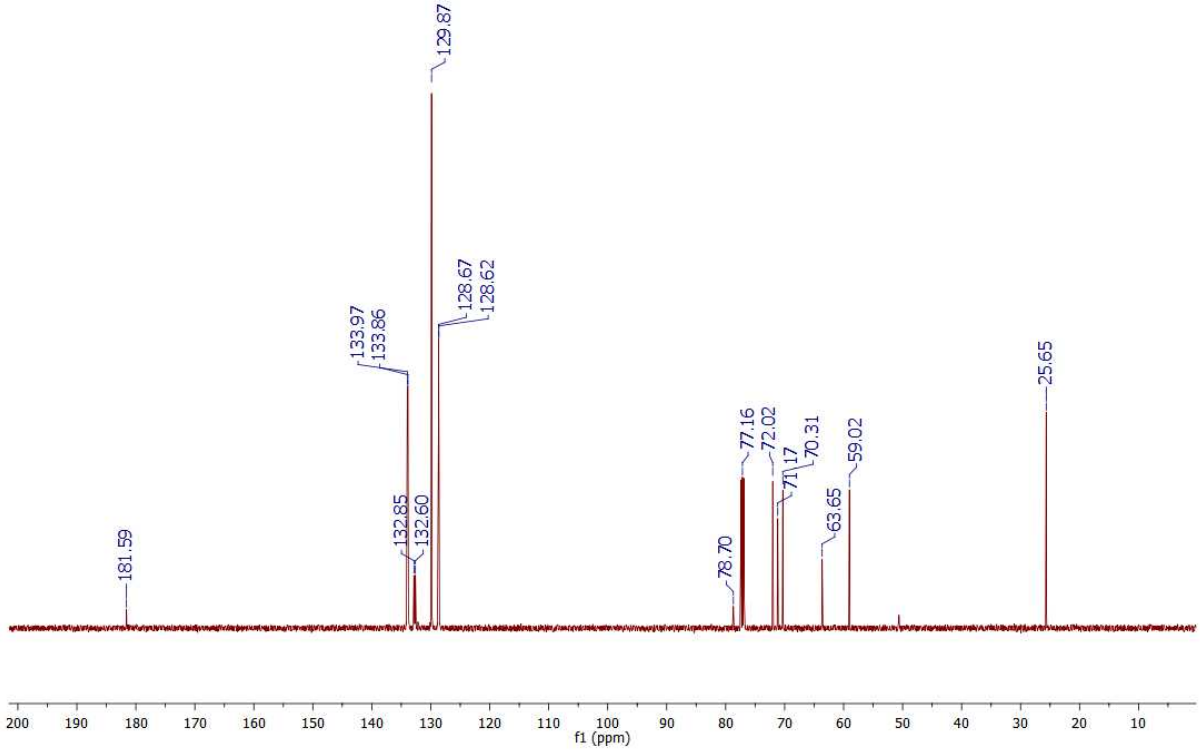
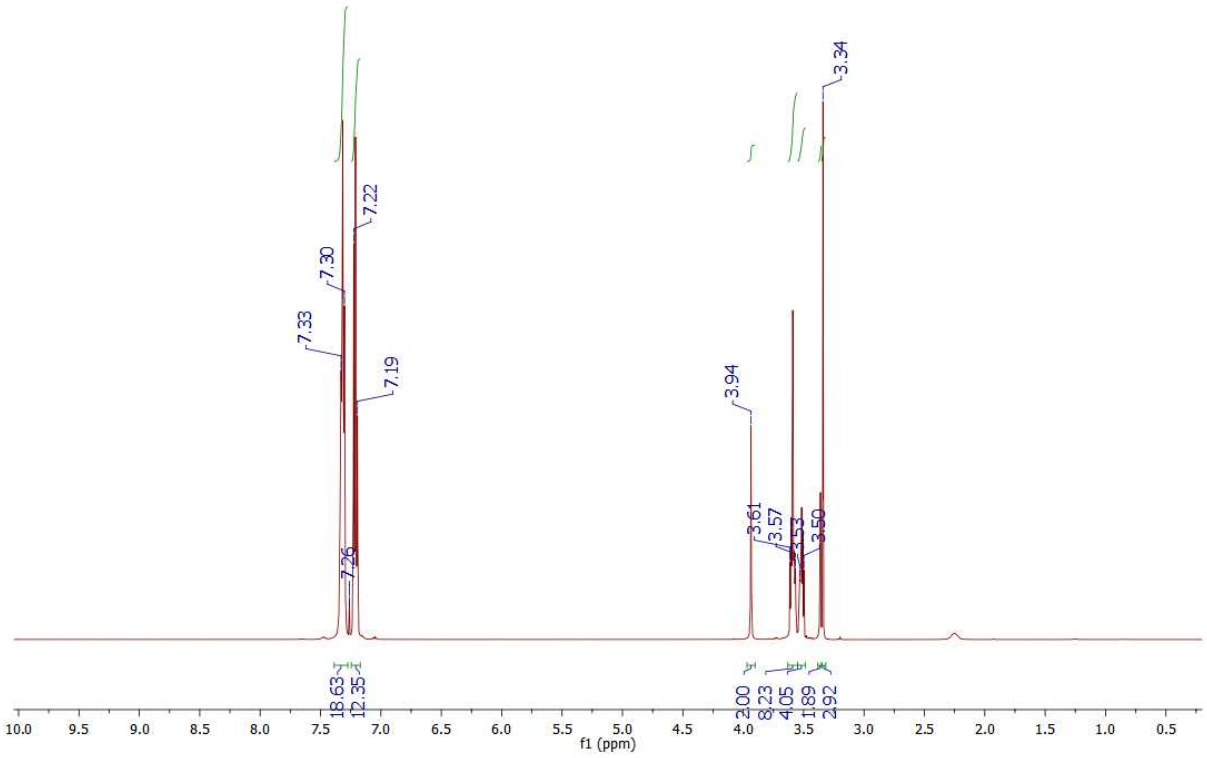
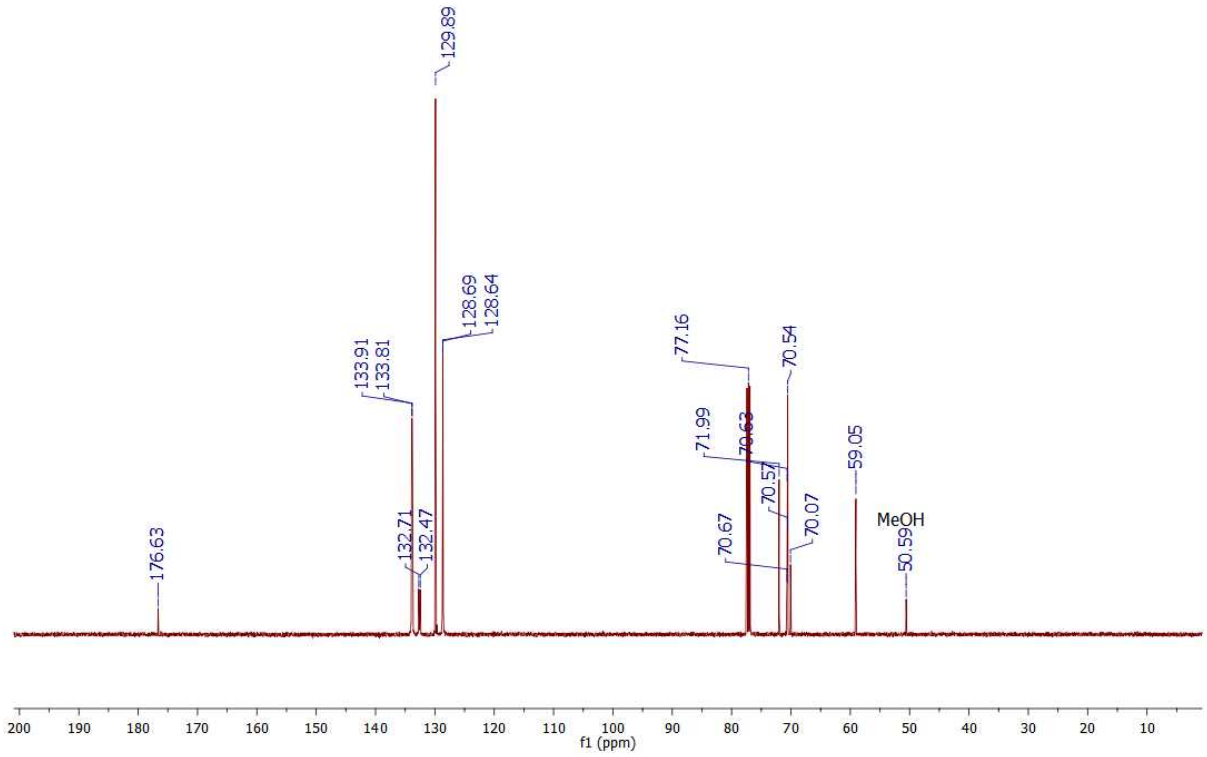
^{1}H (top) and $^{13}C\{^{1}H\}$ (bottom) NMR spectra of bis(triphenylphosphine)copper(I)-2-[2-(2-methoxy-ethoxy)ethoxy]-2-methylpropanoate (**4d**):





^{1}H (top) and ^{13}C{^{1}H} (bottom) NMR spectra of bis(triphenylphosphine)copper(I)-2-{2-[2-(2-methoxy-ethoxy)ethoxy]ethoxy}acetate (**4e**):





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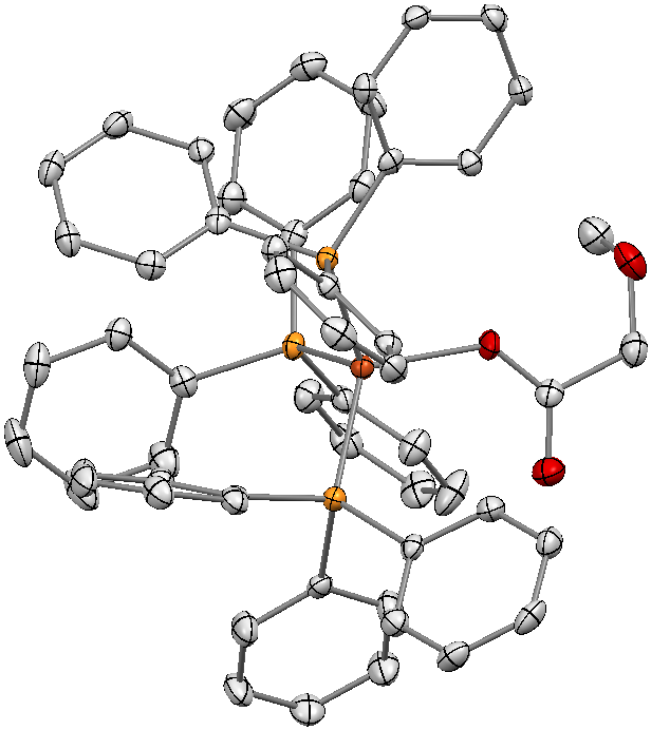
1.3 X-Ray structure analysis

Data for single crystal X-ray diffraction analysis were collected with an Oxford Gemini S diffractometer at 110 K using Cu K_α (λ = 154.184 pm) radiation. All figures show ORTEP diagrams with 50 % probability level. Hydrogen atoms and solvent molecules are omitted for clarity. In case of disordered atoms, only one conformation is shown. Colour code: gray – carbon, red – oxygen, yellow – phosphorus, orange – copper.

Crystal structure of tris(triphenylphosphine)copper(I)-methoxyacetate (**3a**, CCDC 932853):



Crystal Data for 3a: $C_{57}H_{50}CuO_3P_3$, M_r = 939.42 g · mol^{-1}, crystal dimensions 0.40 · 0.38 · 0.30 mm, T = 115 K, λ = 154.184 pm, orthorhombic, $Pna2_1$, a = 18.31189(10) Å, b = 13.00000(10) Å, c = 19.6264(2) Å, V = 4672.13(6) Å³, Z = 4, $\rho_{calcd.}$ = 1.336 g · cm^{-3}, μ = 1.984 mm^{-1}, ϑ range = 4.08 – 62.91 °, reflections collected: 9408, independent: 5316 (R_{int} = 0.0209), R_1 = 0.0340, wR_2 = 0.0887 [I>2$\sigma(I)$].

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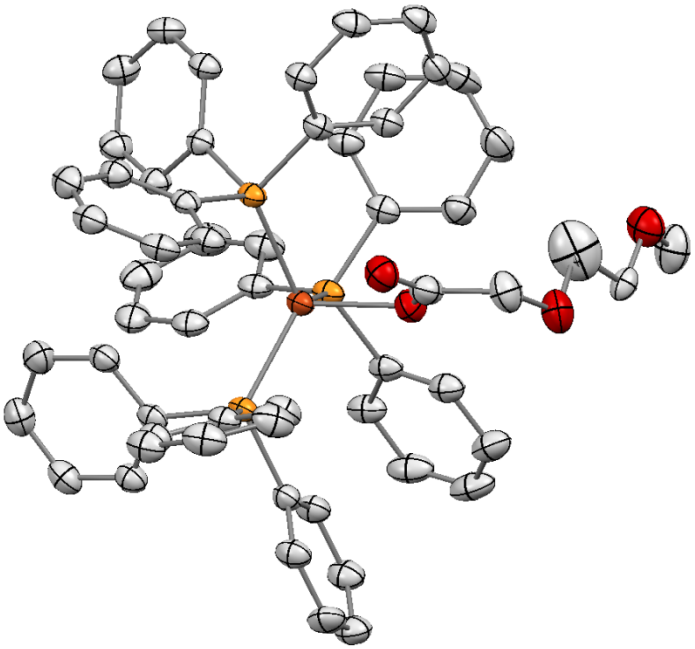
Crystal structure of tris(triphenylphosphine)copper(I)-2-(2-methoxyethoxy)acetate (**3b**, CDCC 932858):



Crystal Data for 3b: $C_{255.60}H_{294.40}Cu_4O_{35.60}P_{12}$, M_r = 4561.91 g · mol^{-1}, crystal dimensions 0.40 · 0.40 · 0.20 mm, T = 110 K, λ = 154.184 pm, monoclinic, C2/c, a = 41.396(3) Å, b = 12.6912(4) Å, c = 26.4725(18) Å, β = 227.373(8) °, V = 12350.6(12) Å³, Z = 2, $\rho_{calcd.}$ = 1.227 g · cm^{-3}, μ = 1.659 mm^{-1}, ϑ range = 3.41 – 64.10 °, reflections collected: 32252, independent: 10102 (R_{int} = 0.0415), R_1 = 0.0653, wR_2 = 0.1801 [I>2σ(I)].

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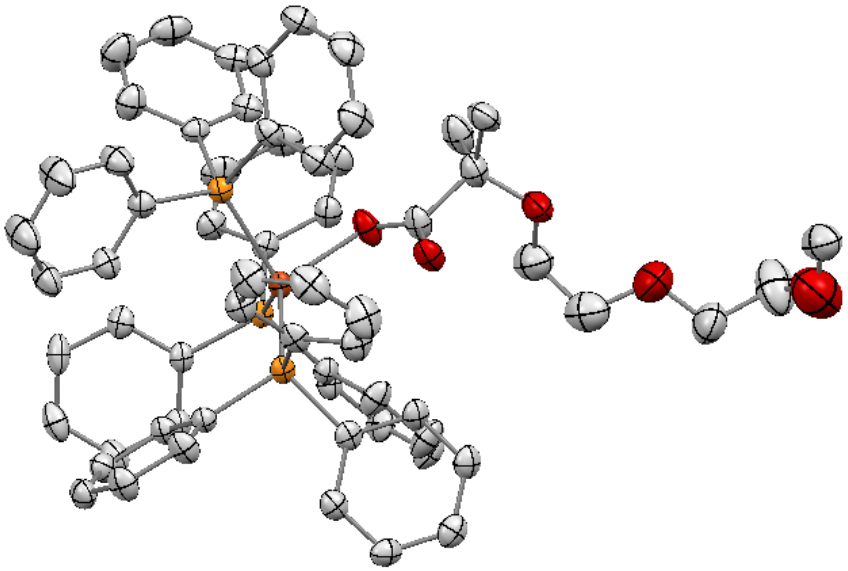
Crystal structure of tris(triphenylphosphine)copper(I)-2-[2-(2-methoxyethoxy)ethoxy]2-methyl-propanoate (**3d**, CDCC 932854):



Crystal Data for 3a: $C_{64}H_{63}CuO_5P_3$, M_r = 1174.94 g · mol^{-1}, crystal dimensions 0.40 · 0.38 · 0.38 mm, T = 100 K, λ = 154.184 pm, monoclinic, $P2_1/n$, a = 13.1082(6) Å, b = 22.7413(12) Å, c = 19.7501(11) Å, β = 104.039(5)°, V = 5711.6(5) Å³, Z = 4, $\rho_{calcd.}$ = 1.366 g · cm^{-3}, μ = 3.022 mm^{-1}, ϑ range = 3.68 – 62.50 °, reflections collected: 18682, independent: 9054 (R_{int} = 0.0613), R_1 = 0.0816, wR_2 = 0.2237 [I>2$\sigma(I)$].

Crystal Data for 4a: $C_{39}H_{35}CuO_3P_2$, M_r = 677.15 g · mol^{-1}, crystal dimensions 0.20 · 0.10 · 0.05 mm, T = 110 K, λ = 71.073 pm, triclinic, $P\bar{1}$, a = 12.4723(6) Å, b = 12.4970(7) Å, c = 12.7037(6) Å, α = 67.651(5)°, β = 75.301(4)°, γ = 62.402(5)°, V = 1615.69(14) Å³, Z = 2, $\rho_{calcd.}$ = 1.392 g · cm^{-3}, μ = 0.813 mm^{-1}, ϑ range = 2.97–25.75 °, reflections collected: 12298, independent: 6090 (R_{int} = 0.0380), R_1 = 0.0390, wR_2 = 0.0805 [I>2$\sigma(I)$].

Crystal Data for 4b: $C_{41}H_{39}CuO_4P_2$, M_r = 721.20 g · mol^{-1}, crystal dimensions 0.30 · 0.20 · 0.20 mm, T = 110 K, λ = 154.184 pm, orthorhombic, *Pbca*, a = 21.2391(2) Å, b = 10.7028(1) Å, c = 30.5782(3) Å, V = 6950.97(11) Å³, Z = 8, $\rho_{calcd.}$ = 1.378 g · cm^{-3}, μ = 2.090 mm^{-1}, ϑ range = 3.56–62.94 °, reflections collected: 11178, independent: 6420 (R_{int} = 0.0223), R_1 = 0.0507, wR_2 = 0.1381 [I>2$\sigma(I)$].

Crystal Data for 4d: $C_{45}H_{47}CuO_5P_2$, M_r = 793.31 g · mol^{-1}, crystal dimensions 0.30 · 0.25 · 0.20 mm, T = 105 K, λ = 154.184 pm, triclinic, $P\bar{1}$, a = 12.0902(10) Å, b = 13.2571(9) Å, c = 13.3691(10) Å, α = 86.456(6)°, β = 89.537(7)°, γ = 64.306(7)°, V = 1926.8(3) Å³, Z = 2, $\rho_{calcd.}$ = 1.367 g · cm^{-3}, μ = 1.954 mm^{-1}, ϑ range = 3.31–66.98 °, reflections collected: 14265, independent: 6810 (R_{int} = 0.0362), R_1 = 0.0549, wR_2 = 0.1424 [I>2$\sigma(I)$].

Crystal Data for 4e: $C_{45}H_{47}CuO_6P_2$, M_r = 809.31 g · mol^{-1}, crystal dimensions 0.20 · 0.10 · 0.10 mm, T = 104 K, λ = 71.073 pm, monoclinic, $P2_1/n$, a = 15.9464(8) Å, b = 10.6978(3) Å, c = 23.2985(11) Å, V = 3972.8(3) Å³, Z = 4, $\rho_{calcd.}$ = 1.353 g · cm^{-3}, μ = 0.679 mm^{-1}, ϑ range = 2.88–25.50 °, reflections collected: 19549, independent: 7368 (R_{int} = 0.0399), R_1 = 0.0354, wR_2 = 0.0814 [I>2$\sigma(I)$].

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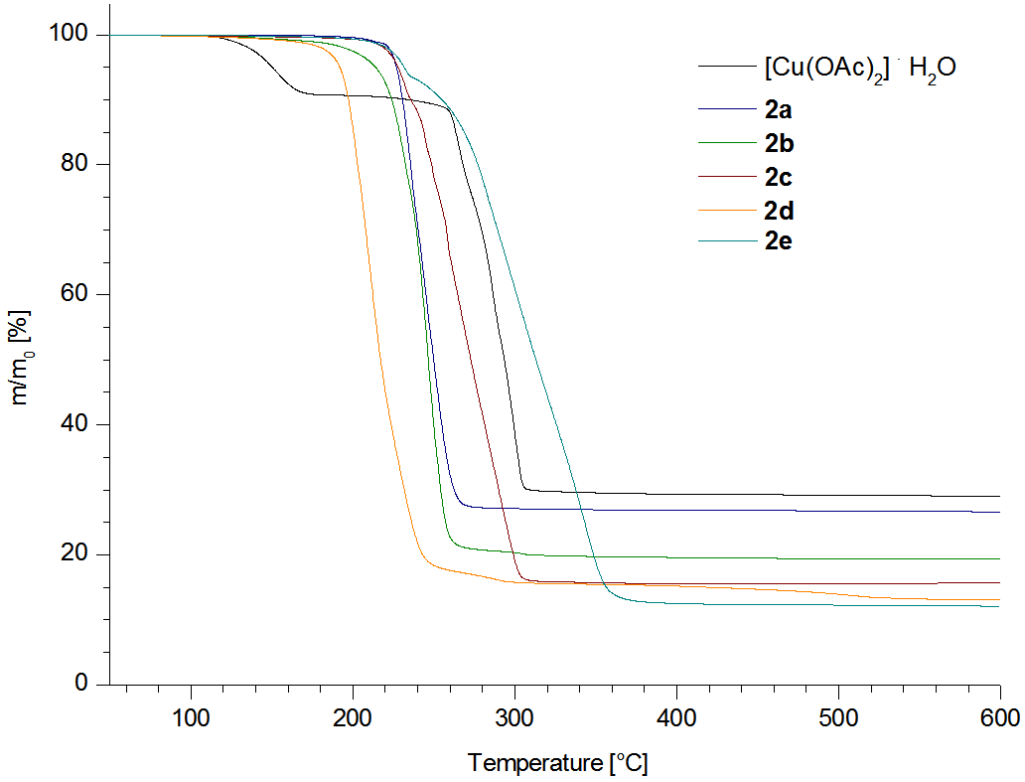
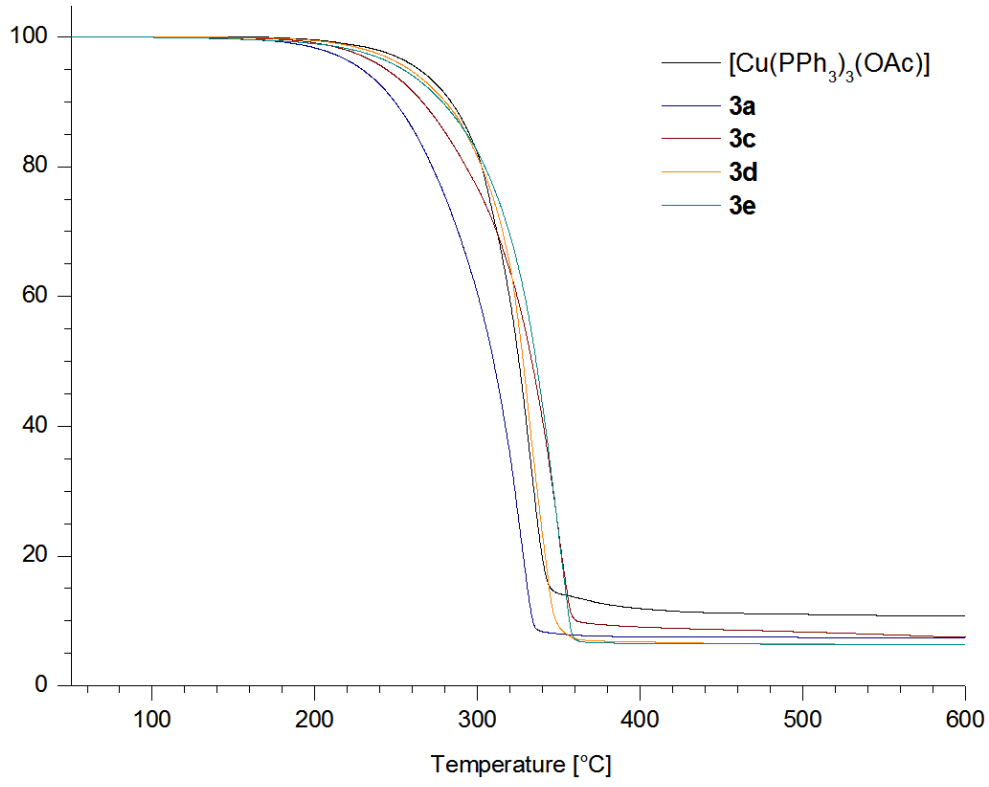
2 Thermal Decomposition

All thermogravimetric measurements were performed under N_2 flow (60 mL · min^{-1}) with a heating rate of 10 K · min^{-1} with a Mettler Toledo TGA/DSC1 1600 system.

TG traces of copper(II) acetate hydrate as well as complexes **2a–e**:



TG traces of tris(triphenylphosphine)copper(I) acetate hydrate as well as complexes 3**a,c–e**:



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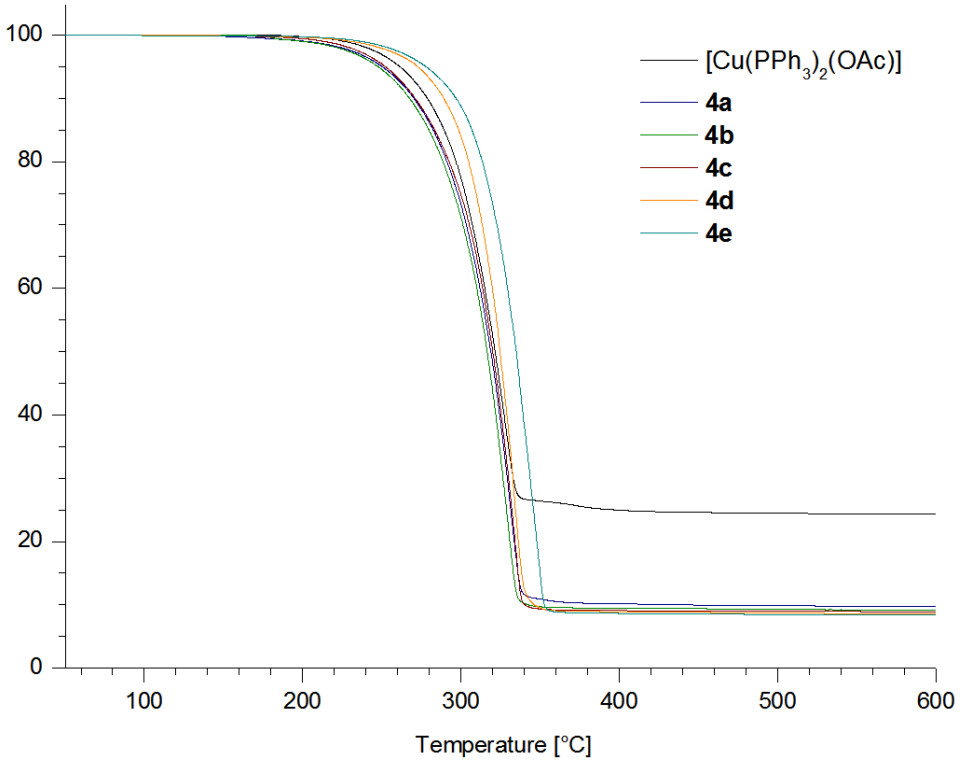
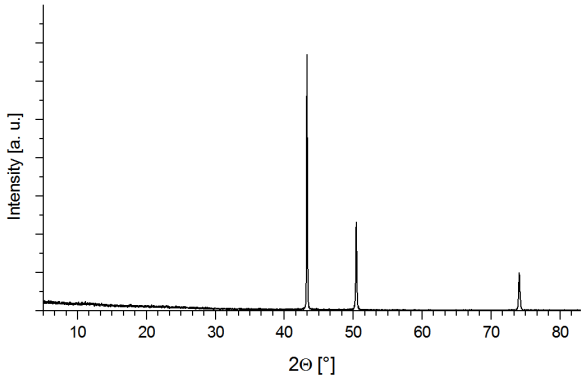
TG traces of bis(triphenylphosphine)copper(I) acetate hydrate as well as compounds **4a–e**:

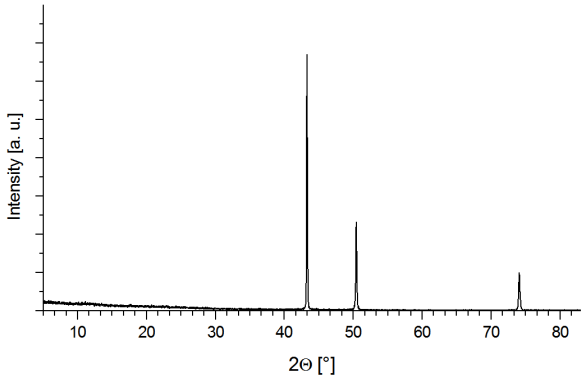


The non-volatile decomposition products of the thermal decompositions have been investigated by X-ray powder diffraction using a STOE-STAD IP device with Cu K_α (λ = 154.184 pm) radiation.

X-ray powder diffractogram of the non-volatile decomposition products of **2c**:



X-ray powder diffractogram of the non-volatile decomposition products of **4c**:



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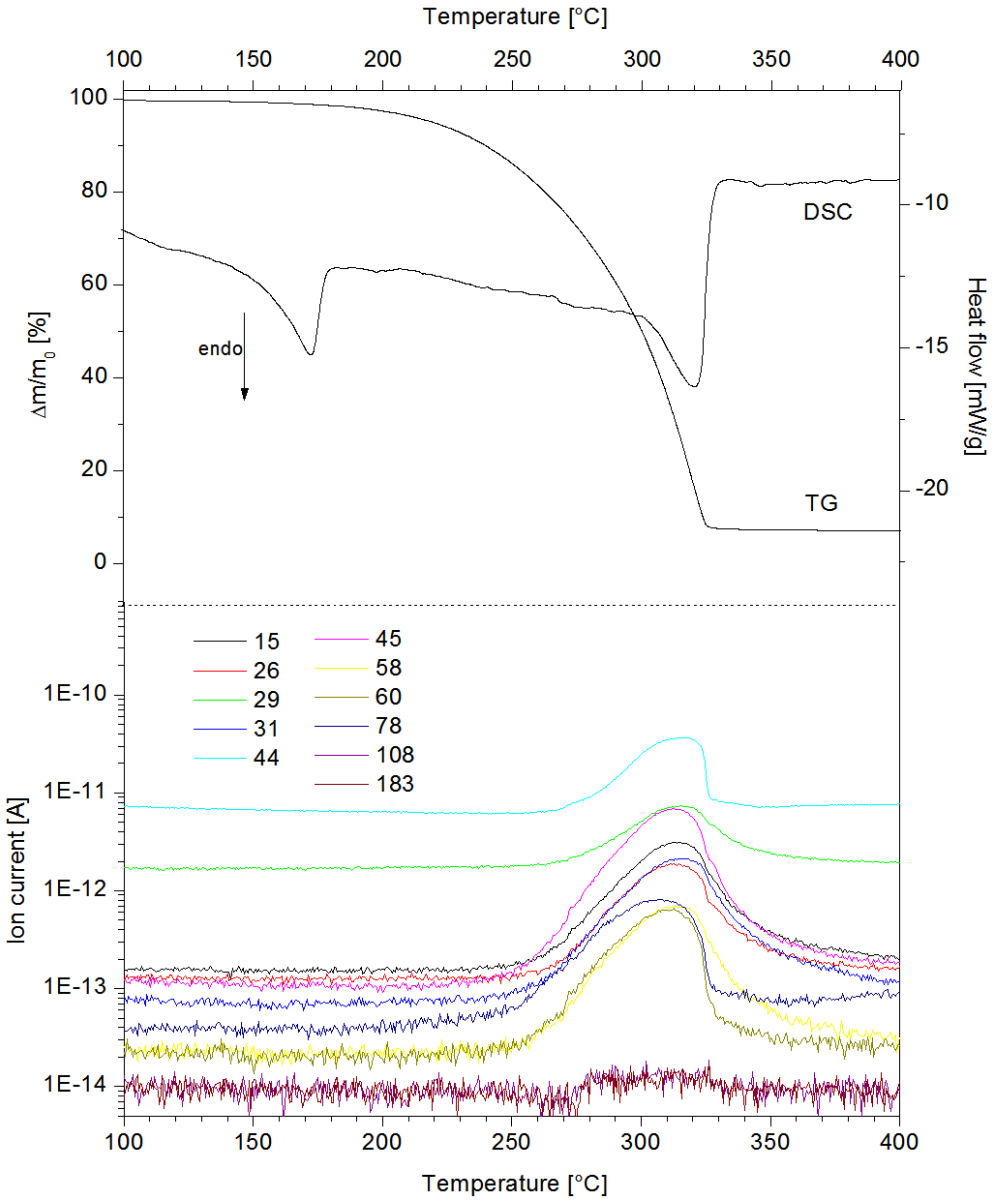
TG-MS characterisation of tris(triphenylphosphine)copper(I) 2-(2-methoxyethoxy)acetate (**3b**), measured by using a Pfeiffer Vacuum MS ThermoStar GSC 301 TS mass spectrometer coupled to the TG system:



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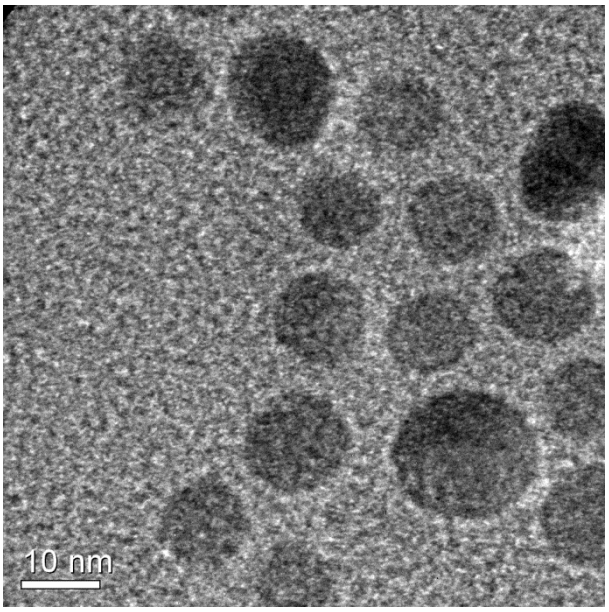
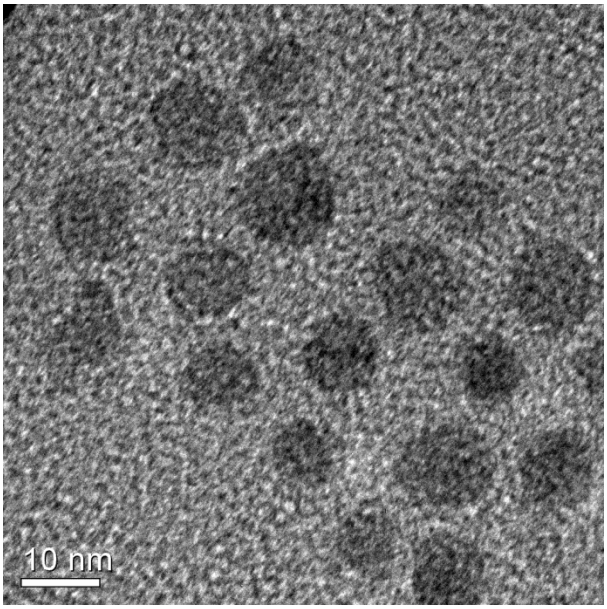
3 Additional TEM images

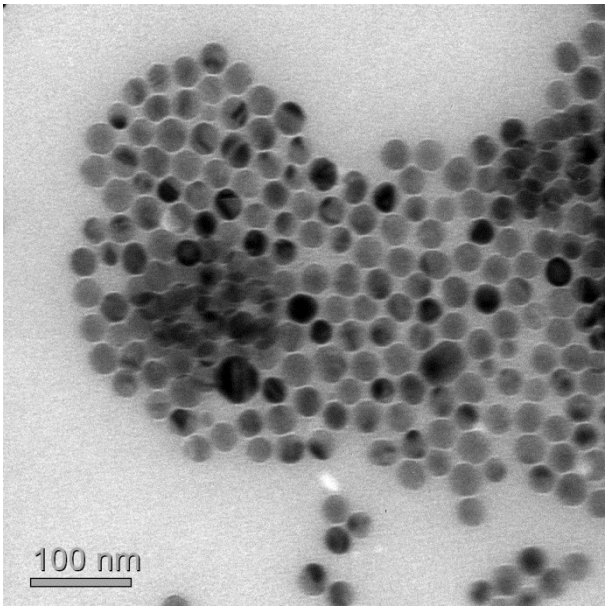
All TEM measurements were performed with a PHILIPS CM 20 FEG instrument operated at 200 kV.

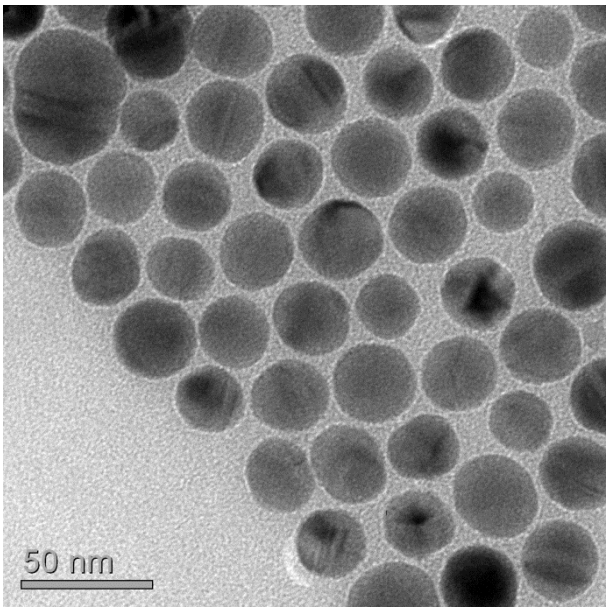
0.5 mM sample:





1.0 mM sample:





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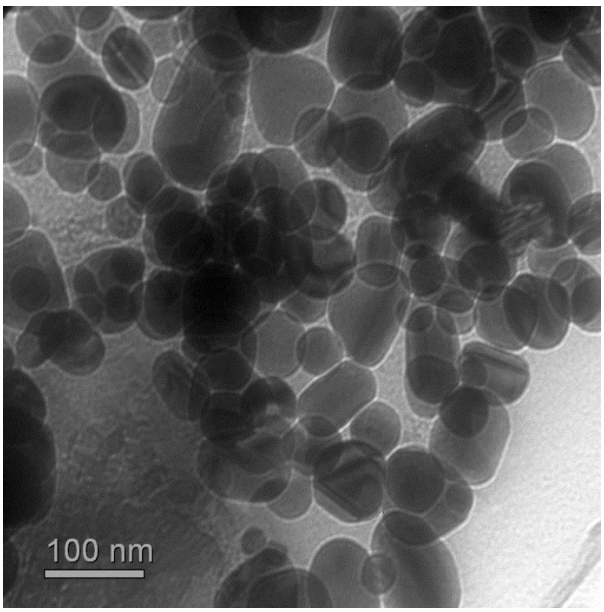
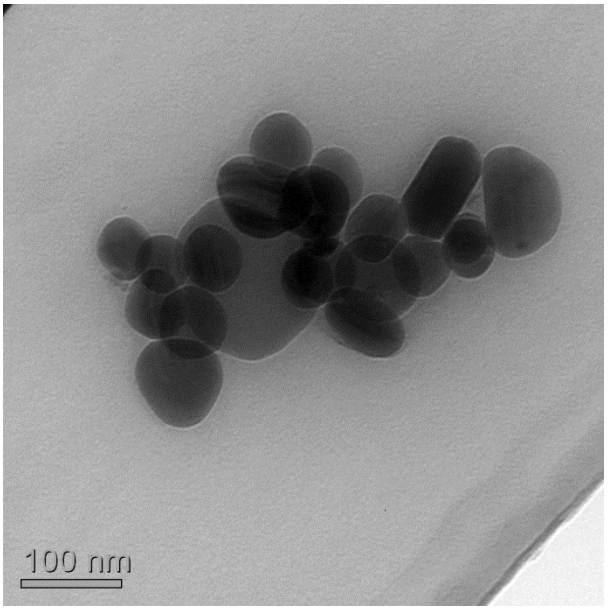
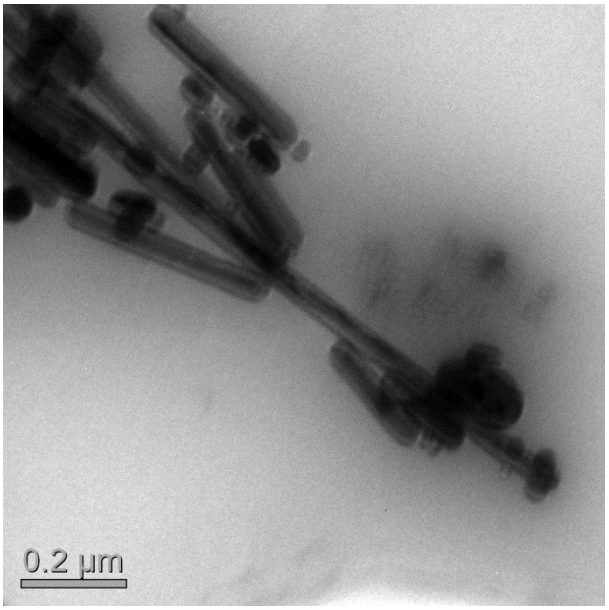
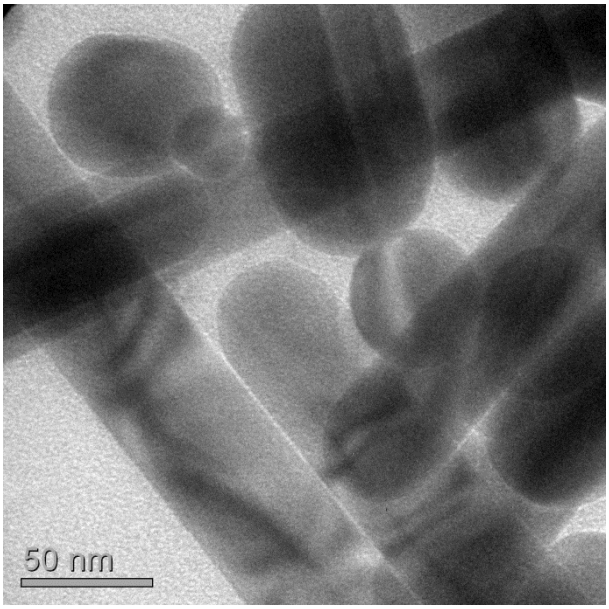
2. 0 mM sample:





10 mM sample:





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Electron diffractogram of 1.0 mM sample (red rings: copper, fcc, a = 3.61 Å):