molecules

MDPI

*Supporting Information*

# A new dimeric copper(II) complex of hexyl bis(pyrazolyl)acetate ligand as efficient catalyst for allylic oxidations

**Luca Bagnarelli [1], Alessandro Dolmella [2], Carlo Santini [1], Riccardo Vallesi [1], Roberto Giacomantonio [1], Serena Gabrielli [1,*] and Maura Pellei [1,*]**

[1] School of Science and Technology, Chemistry Division, University of Camerino, via S. Agostino 1, 62032 Camerino, Italy; luca.bagnarelli@unicam.it (L.B.); carlo.santini@unicam.it (C.S.); riccardo.vallesi@unicam.it (R.V.); robert.giacomantonio@unicam.it (R.G.)

[2] Department of Pharmaceutical and Pharmacological Sciences, University of Padova, via Marzolo 5, 35131 Padova, Italy; alessandro.dolmella@unipd.it

* Correspondence: serena.gabrielli@unicam.it (S.G.); maura.pellei@unicam.it (M.P.); Tel.: +39-0737-402219 (S.G.); +39-0737-402213 (M.P.)

**Contents**

**Table S1.** Summary of crystal data and structure refinement for compound **1**.

| **Empirical formula** | **$C_{14}H_{20}N_4O_2CuBr_2$** |
|---|---|
| Formula weight | 499.70 |
| Temperature / K | 296.9(9) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| $a$ / Å | 13.0171(4) |
| $b$ / Å | 9.8111(2) |
| $c$ / Å | 15.8632(4) |
| $\alpha$ / ° | 90 |
| $\beta$ / ° | 110.248(3) |
| $\gamma$ / ° | 90 |
| Volume / Å$^3$ | 1900.73(9) |
| $Z$ | 4 |
| $\rho_{calc}$ g/cm$^3$ | 1.746 |
| $\mu$ / mm$^{-1}$ | 5.366 |
| $F$(000) | 988.0 |
| Crystal size / mm$^3$ | 0.6 × 0.4 × 0.01 |
| Radiation | Mo Kα (λ = 0.71073) |
| Index ranges | −15 ≤ h ≤ 17, −13 ≤ k ≤ 12, −19 ≤ l ≤ 20 |
| Reflections collected | 22513 |
| Independent reflections / $R_{int}$ | 4228 / 0.0437 |
| Data / restraints / parameters | 4228 / 78 / 293 |
| Goodness-of-fit on $F^2$ | 1.058 |
| Final $R$ indexes [$I$>=2$\sigma$ ($I$)] | $R_1$ = 0.0351, $wR_2$ = 0.0666 |
| Largest diff. peak / hole / e Å$^{-3}$ | 0.50 / −0.46 |

[a] Goodness-of-fit = $[\Sigma w (F_o^2 - F_c^2)^2 / (N_{obsevns} - N_{params})]^{1/2}$, based on all data;. [b] $R_1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$;. [c] $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$.

**Table S2.** Intermolecular contacts in **1**.

| **Atom (A)** | **Atom (B)** | **A⋯B (Å )** | **Symmetry [a]** |
|---|---|---|---|
| C(8) | Br(1) | 3.37 | 1 – $x$ , –1/2 + $y$, 3/2 – $z$ |
| C(7) | Br(1) | 3.43 | 1 – $x$ , –1/2 + $y$, 3/2 – $z$ |
| H(7) | Br(1) | 2.91 | 1 – $x$ , –1/2 + $y$, 3/2 – $z$ |
| H(1) | Br(1) | 2.93 | $x$, –1 + $y$, $z$ |

[a] Symmetry operator of B atom; atom A belongs to asymmetric unit.

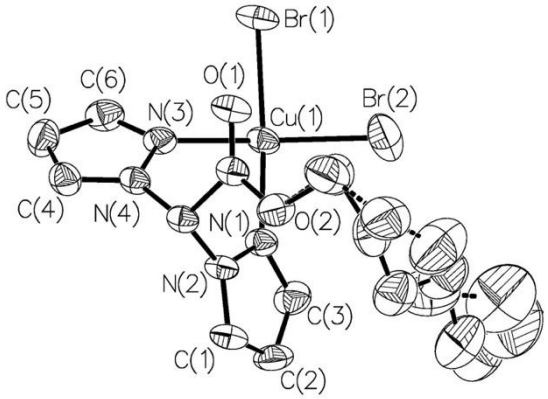


**Figure S1.** ORTEP drawing of the asymmetric unit of **1**, showing part of the selected numbering scheme. Hydrogen atoms omitted for clarity. The alternate arrangement of the disordered hexyloxy chain has dashed bonds. Thermal ellipsoids drawn at the 50% probability level.

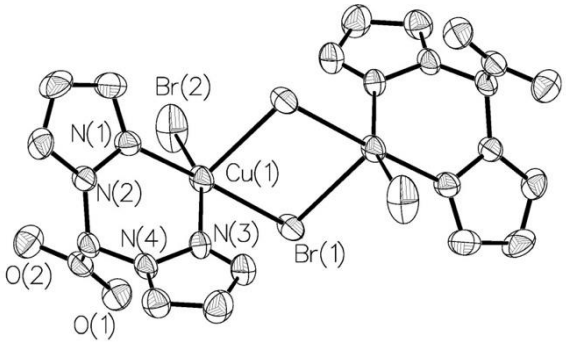


**Figure S2.** An ORTEP representation of the dimeric complex **1** showing part of the selected numbering scheme. Hydrogen atoms and disordered hexyloxy chains removed for clarity. Thermal ellipsoids drawn at the 50% probability level.

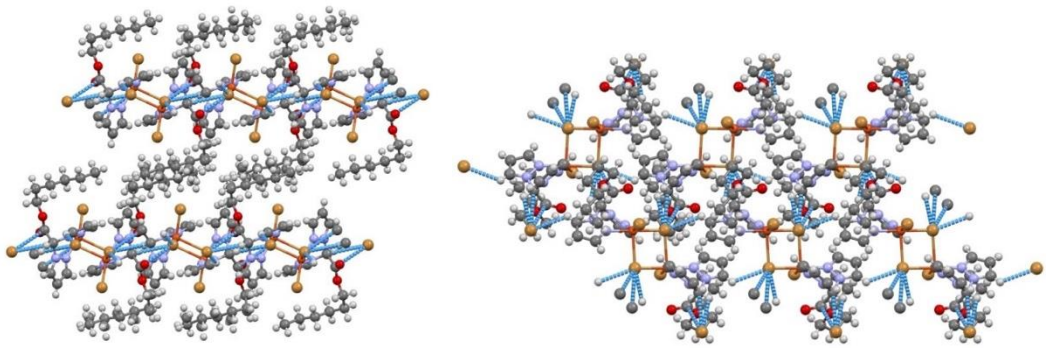

**Figure S3.** Packing diagrams for **1**. Left: the bi–dimensional network developing in the *bc* plane (view down the *a* axis). Right: the 'sandwich' motif created by the planes incorporating the hexyl aliphatic chains and the part of the molecules containing the $Cu_2Br_2$ tetramers developing along the *a* axis. Contacts colored in cyan.

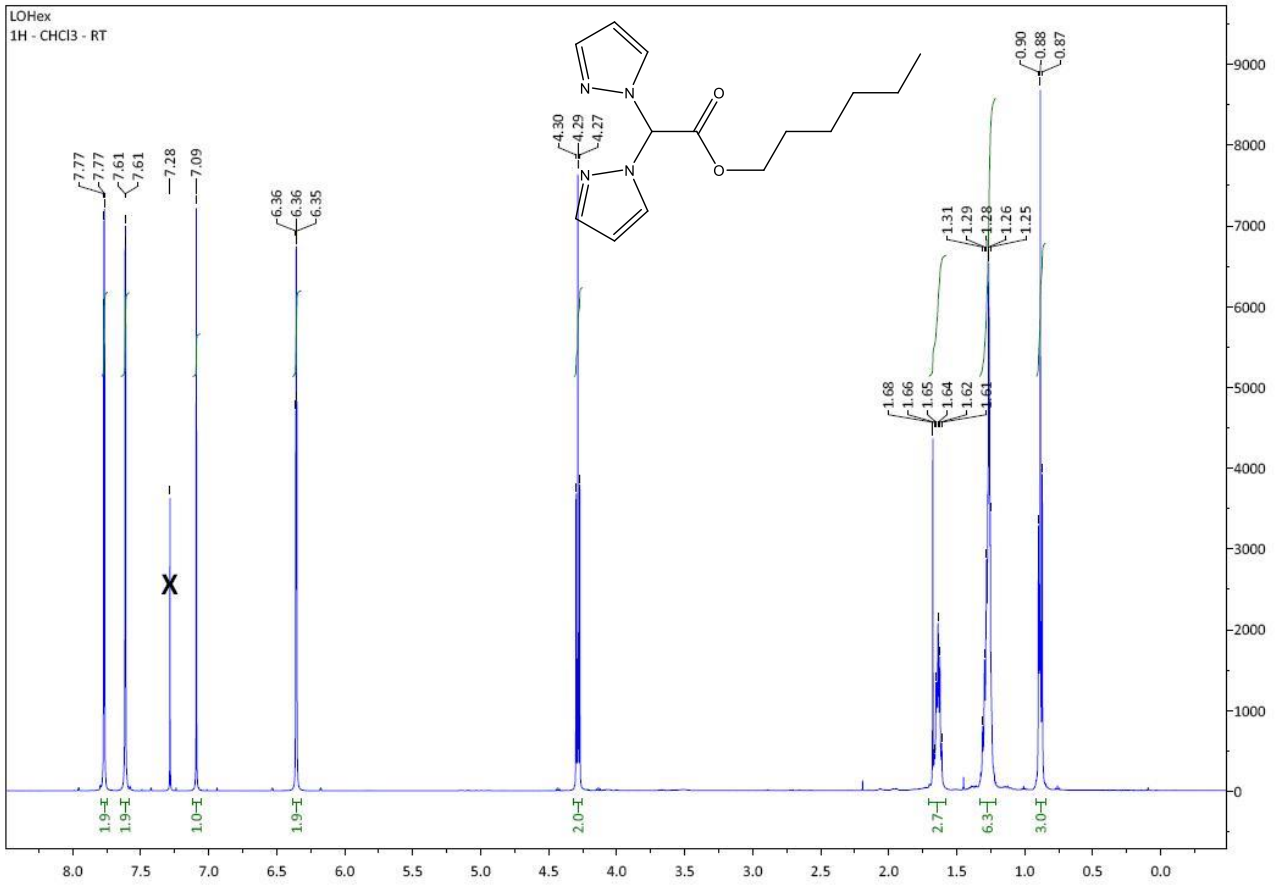


**Figure S4.** $^{1}$H-NMR of HC(COOHex)(pz)$_2$ ($L^{OHex}$) in $CDCl_3$.

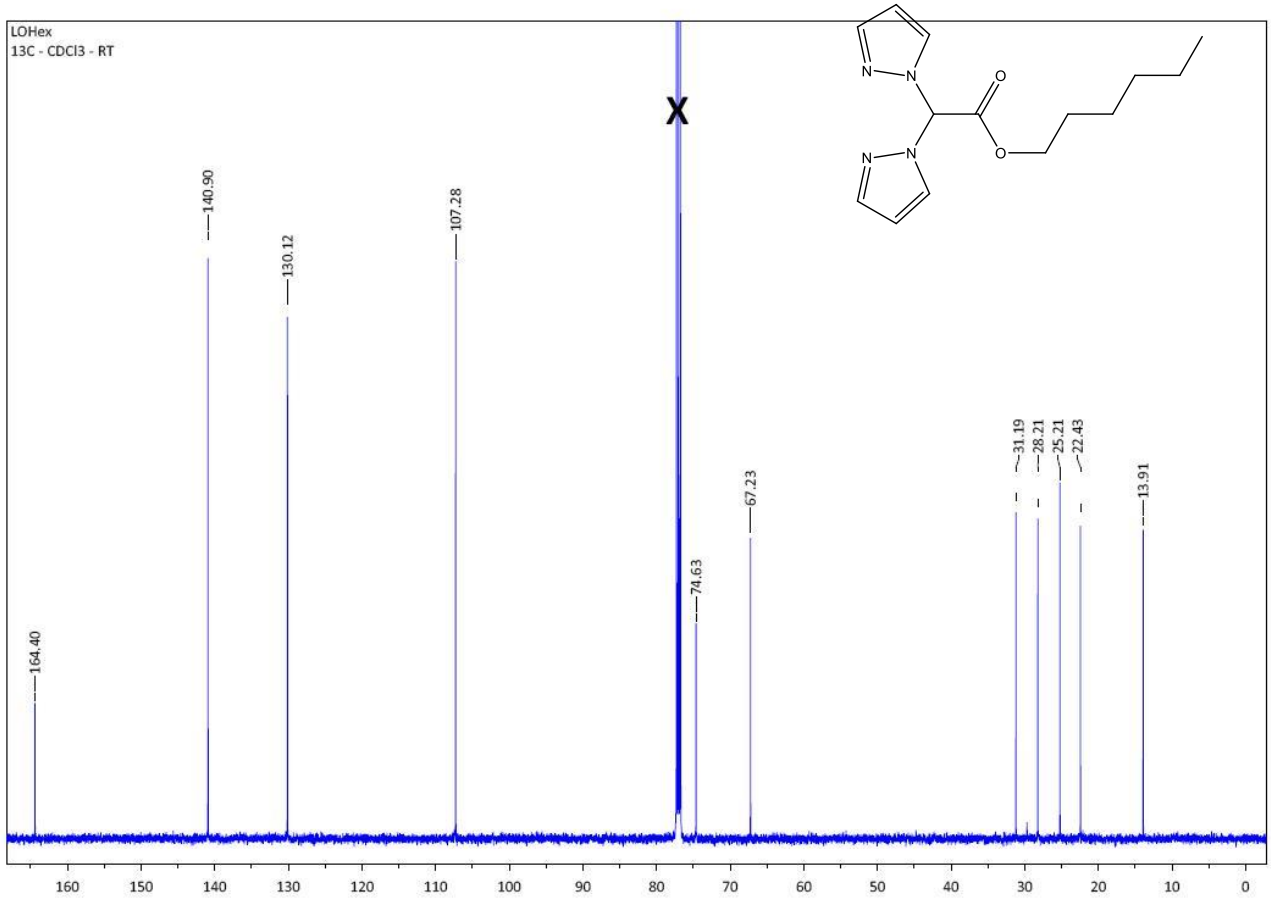


**Figure S5.** $^{13}$C-NMR of HC(COOHex)(pz)$_2$ ($L^{OHex}$) in $CDCl_3$.

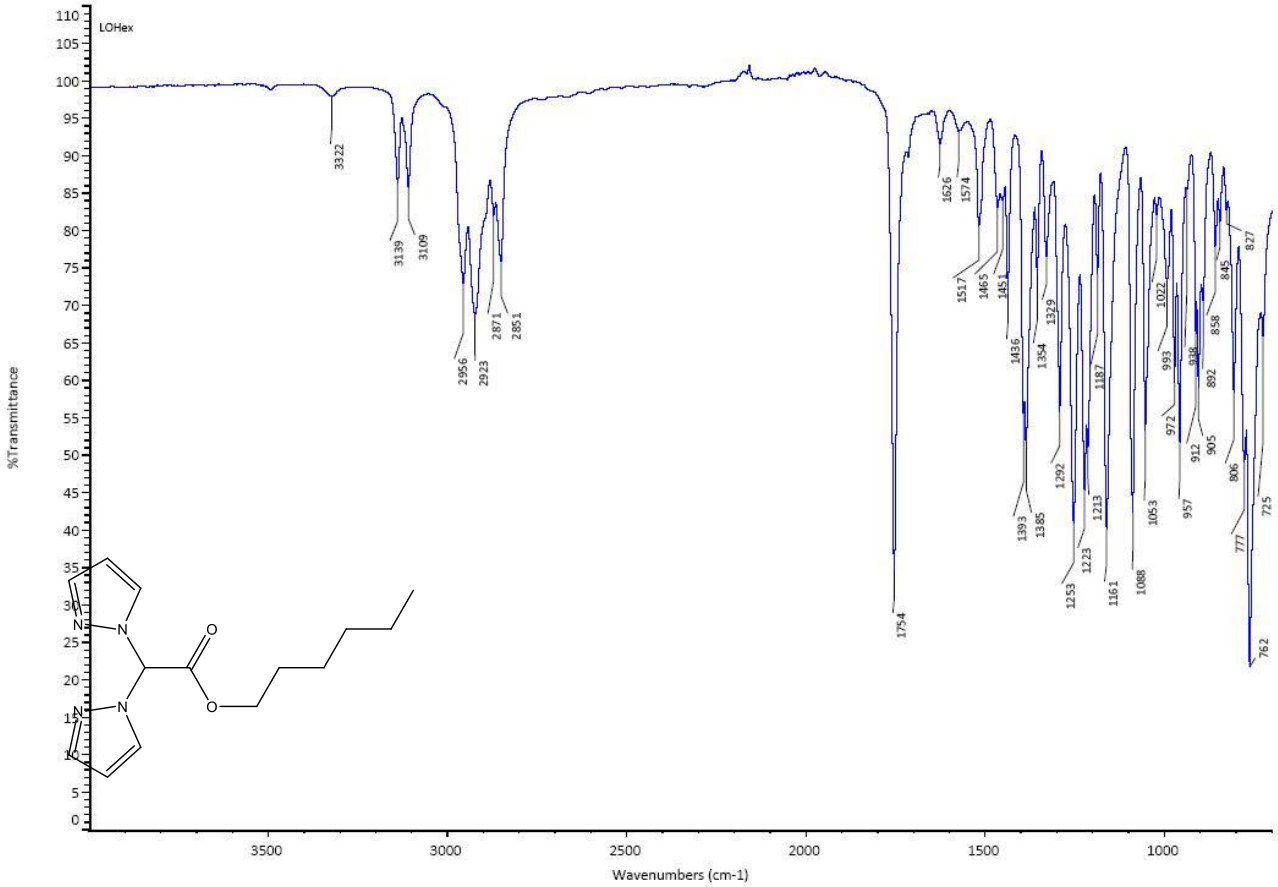


**Figure S6.** FT-IR spectrum of HC(COOHex)(pz)$_2$ ($L^{OHex}$).

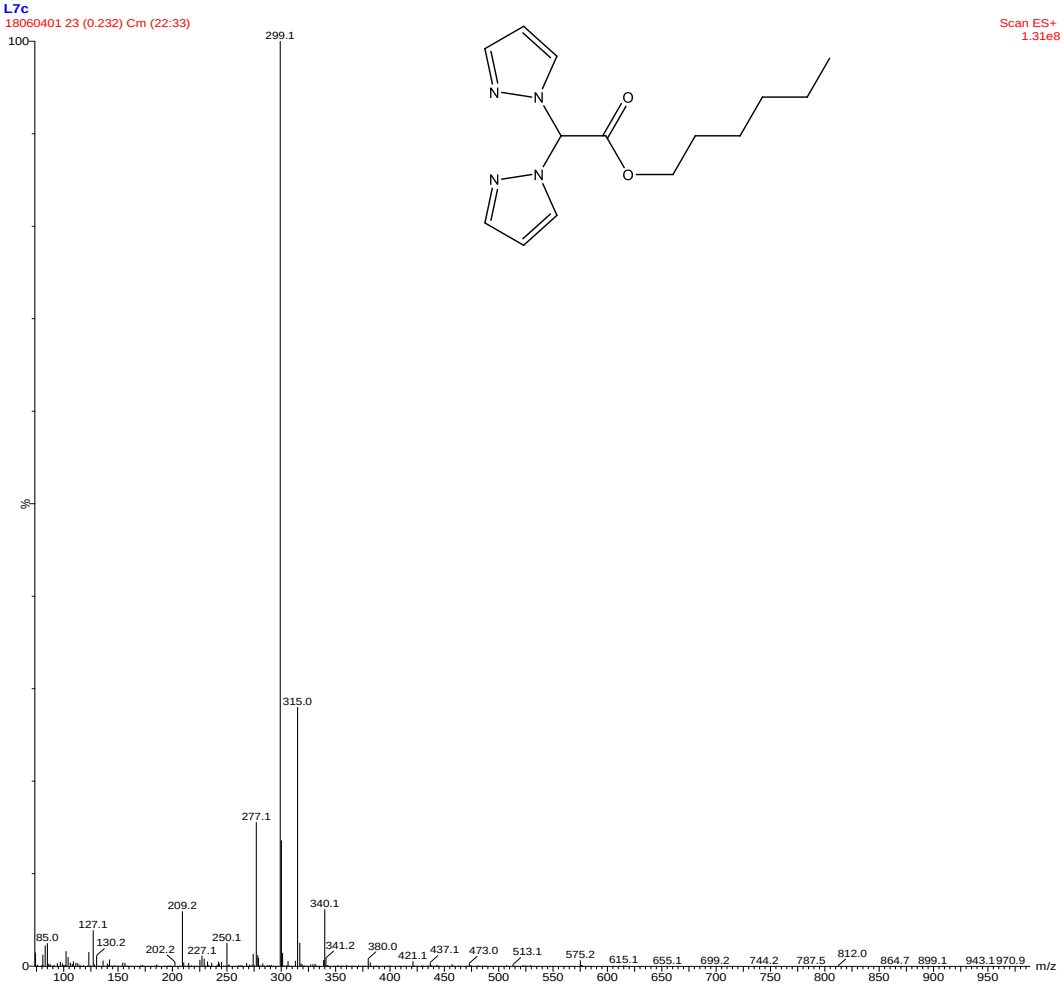


**Figure S7.** ESI-MS(+) spectrum of HC(COOHex)(pz)$_2$ ($L^{OHex}$).

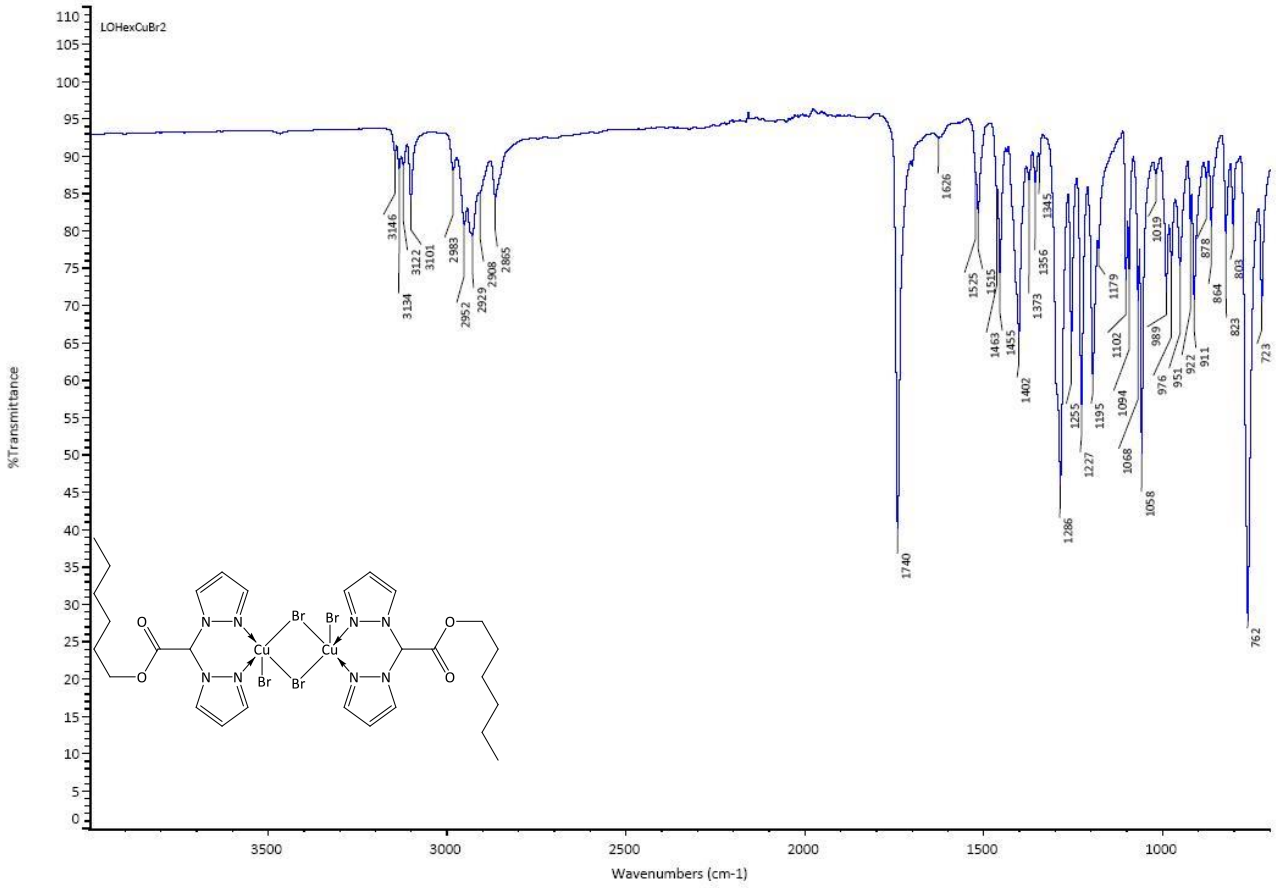


**Figure S8.** FT-IR spectrum of $[Cu(L^{OHex})Br(\mu\text{-}Br)]_2$ (**1**).

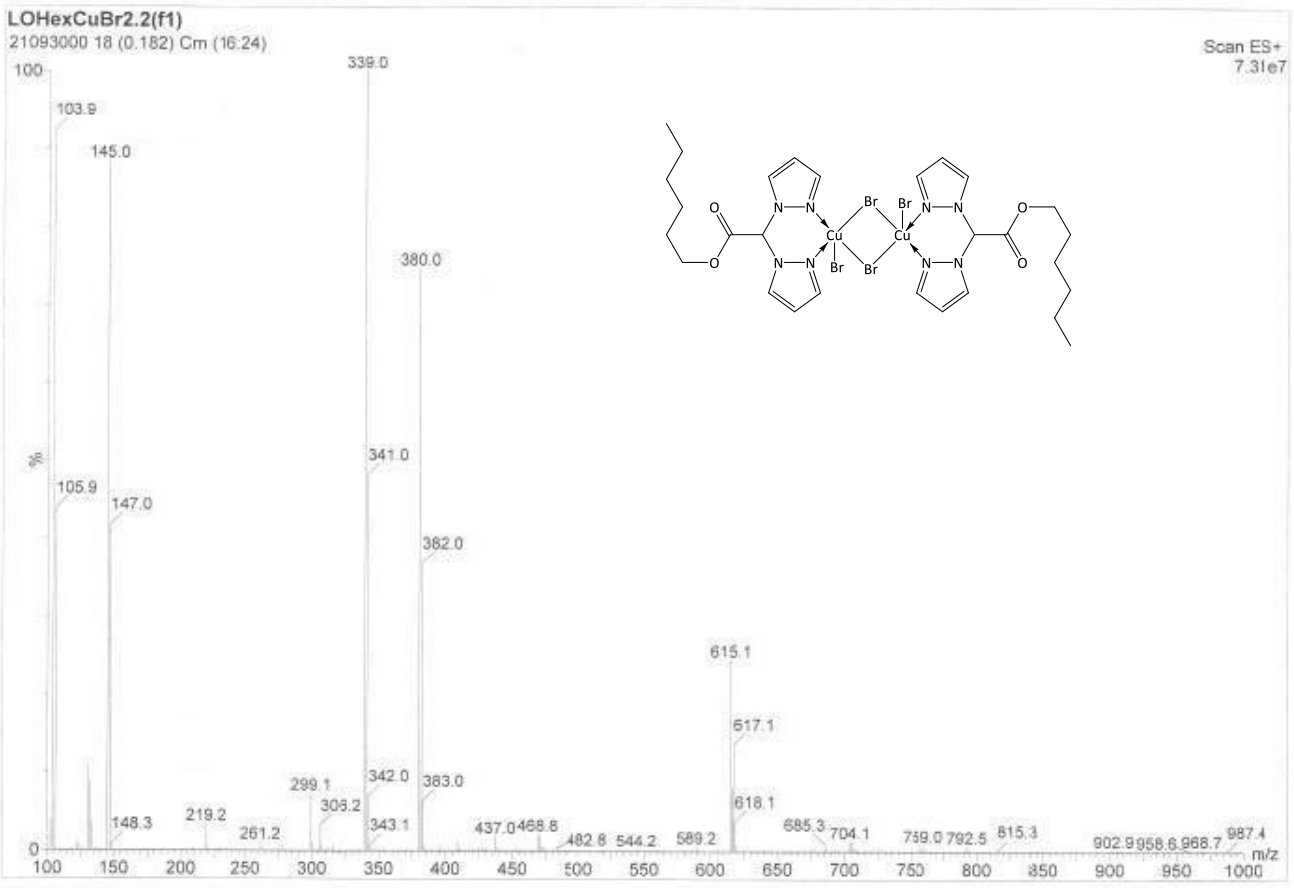


**Figure S9.** ESI-MS(+) spectrum of $[Cu(L^{OHex})Br(\mu\text{-}Br)]_2$ (**1**).

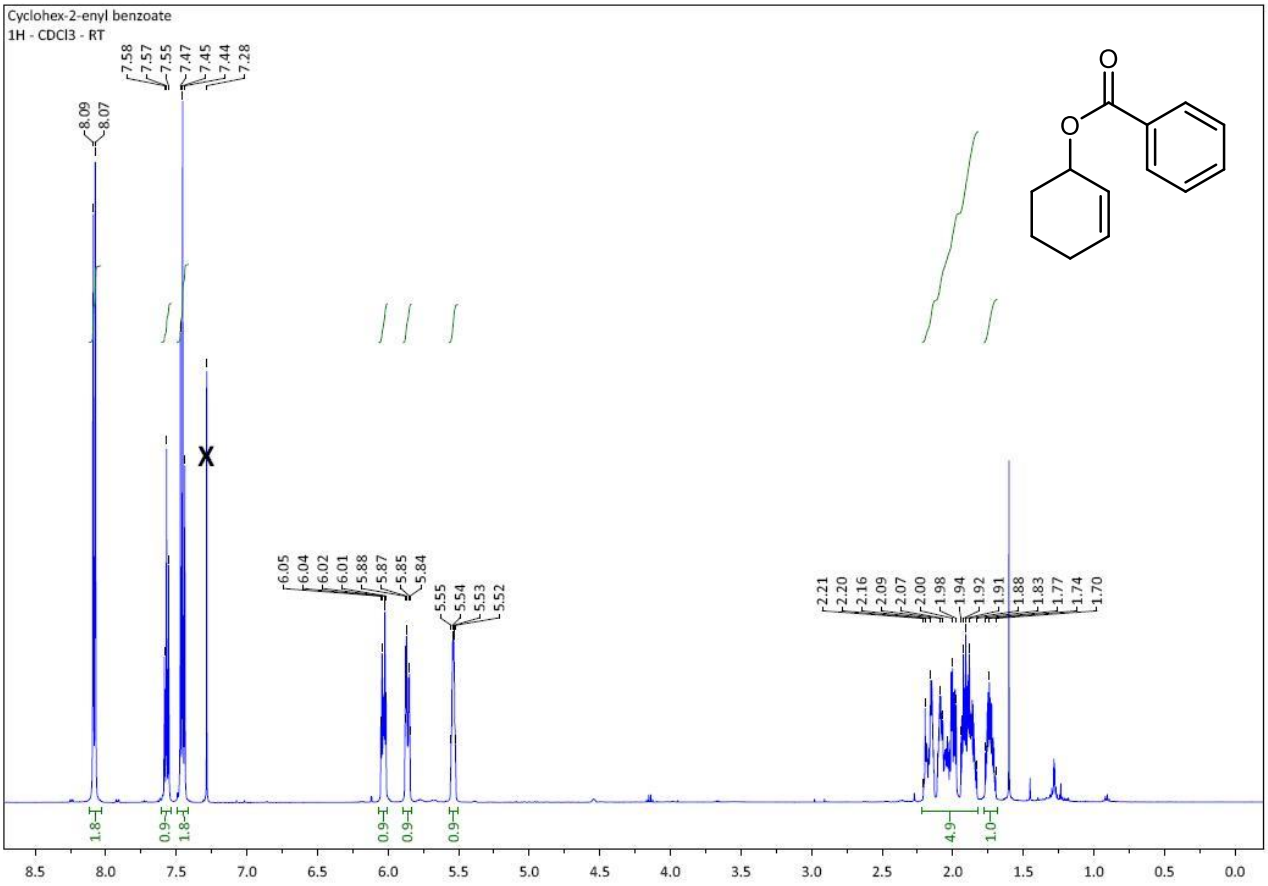


**Figure S10.** $^{1}$H-NMR of compound **4** in $CDCl_3$.

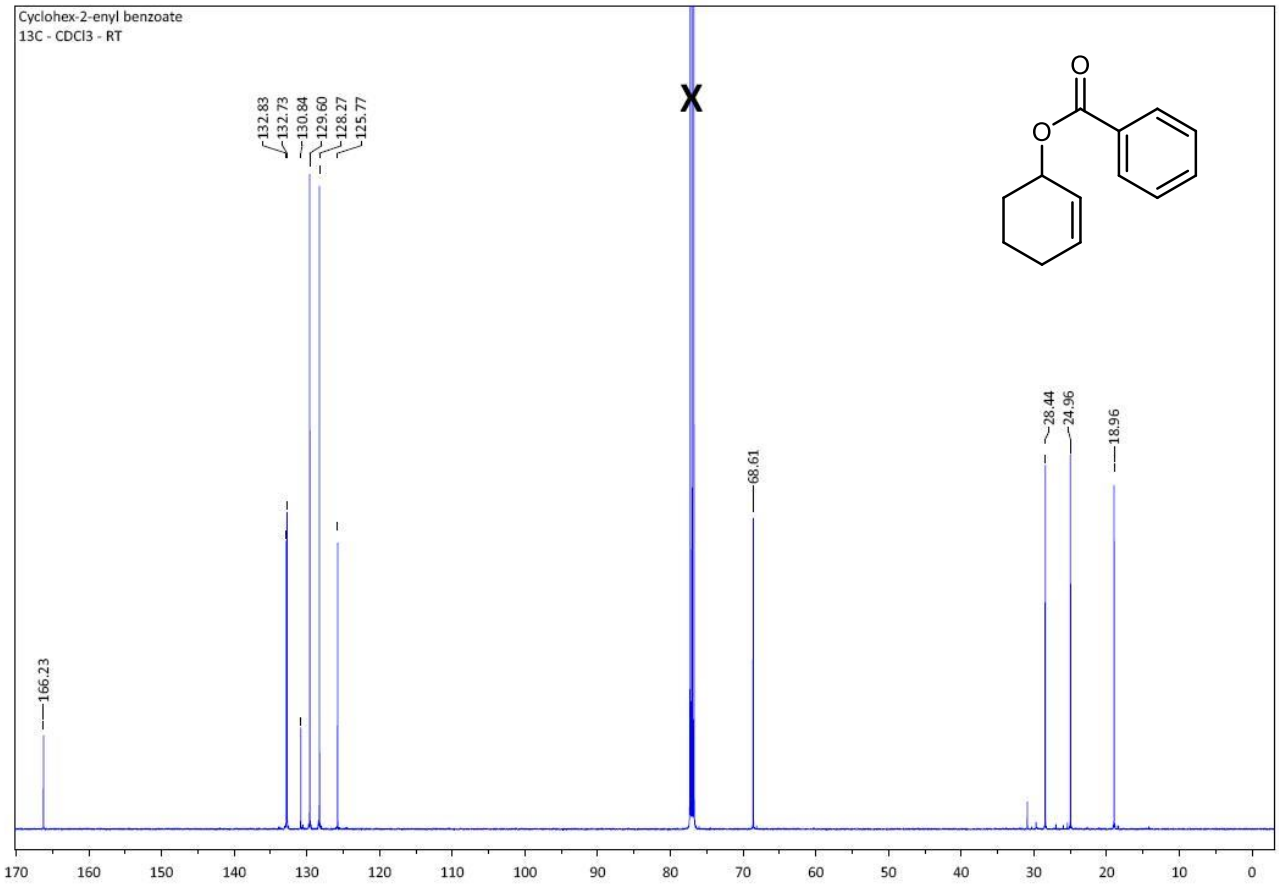


**Figure S11.** $^{13}$C-NMR of compound **4** in $CDCl_3$.

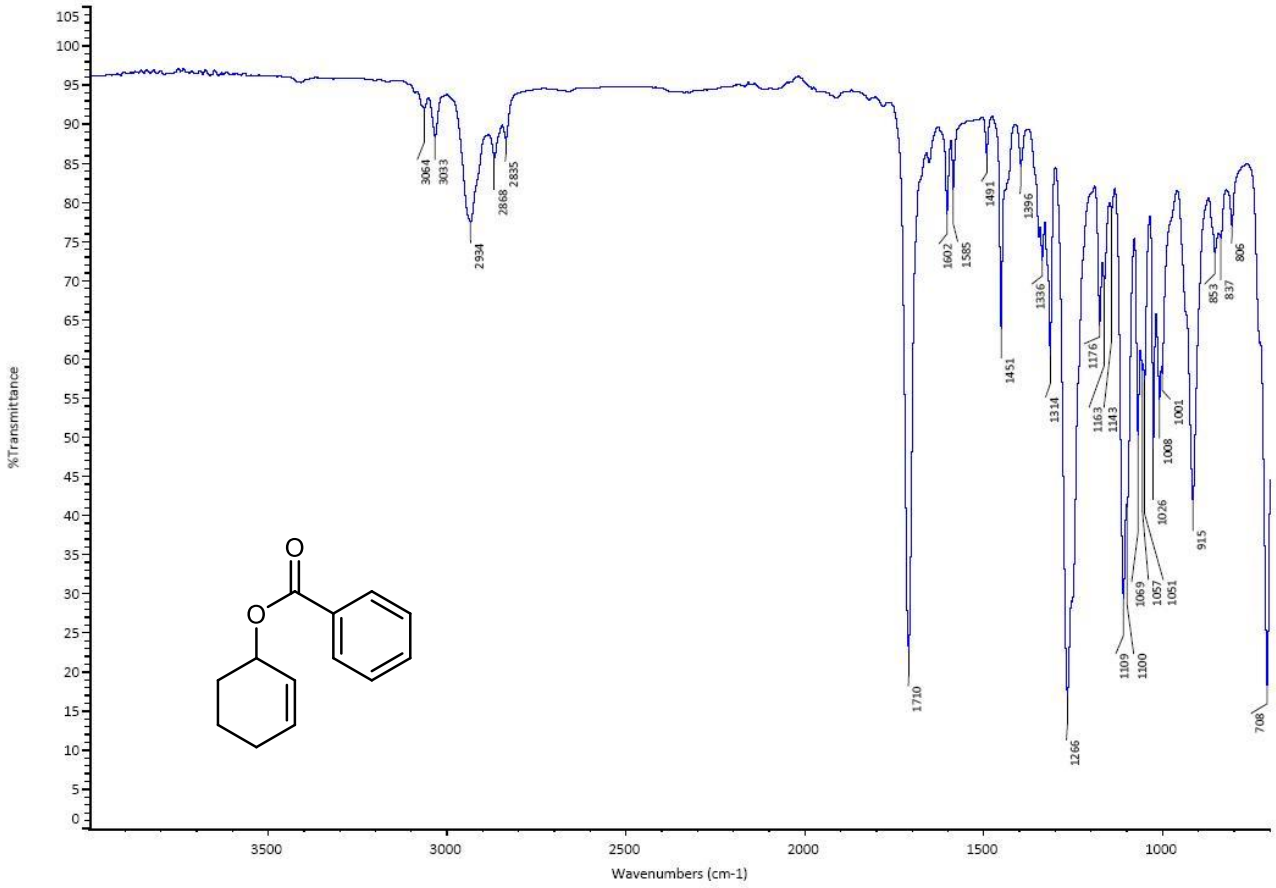


**Figure S12.** FT-IR spectrum of compound **4**.

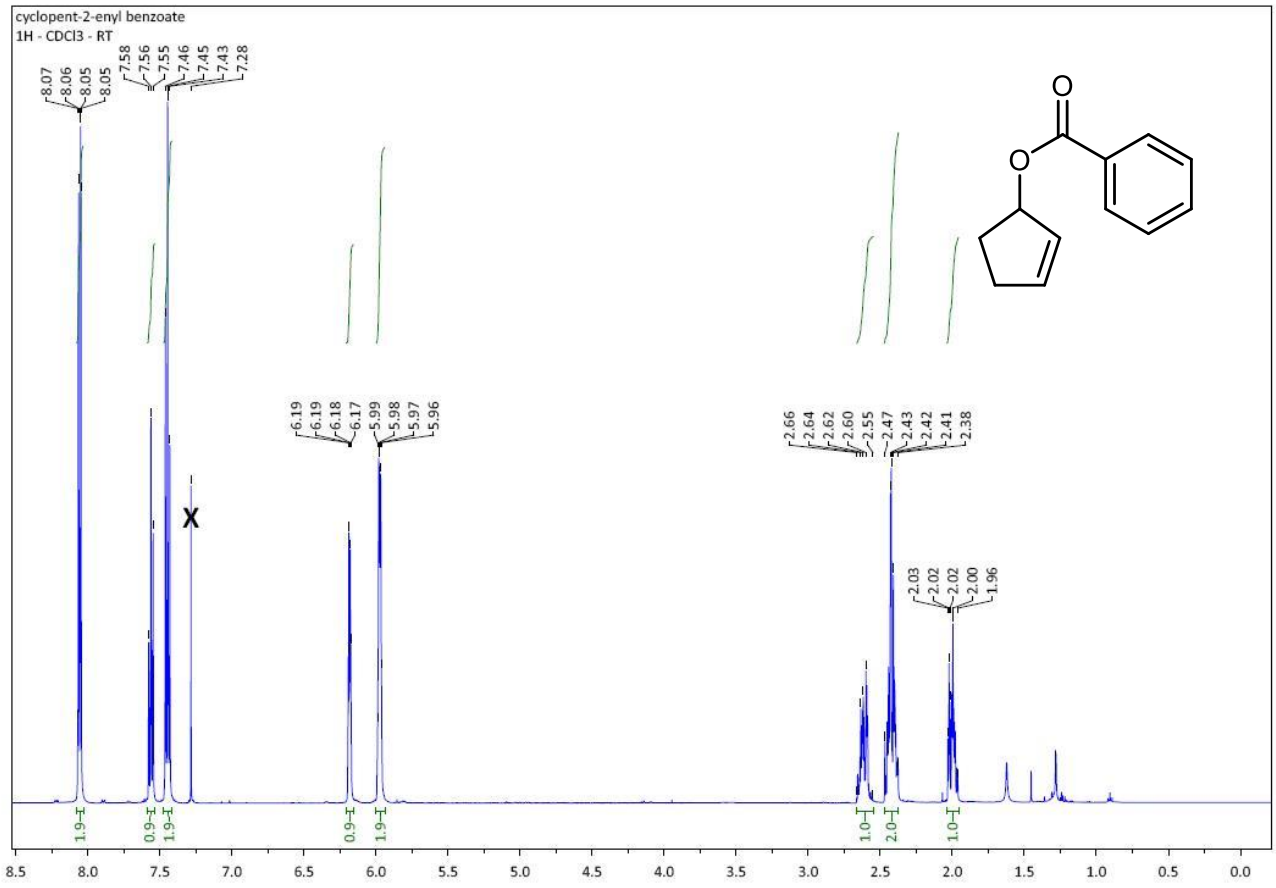


**Figure S13.** $^{1}$H-NMR of compound **5** in $CDCl_3$.

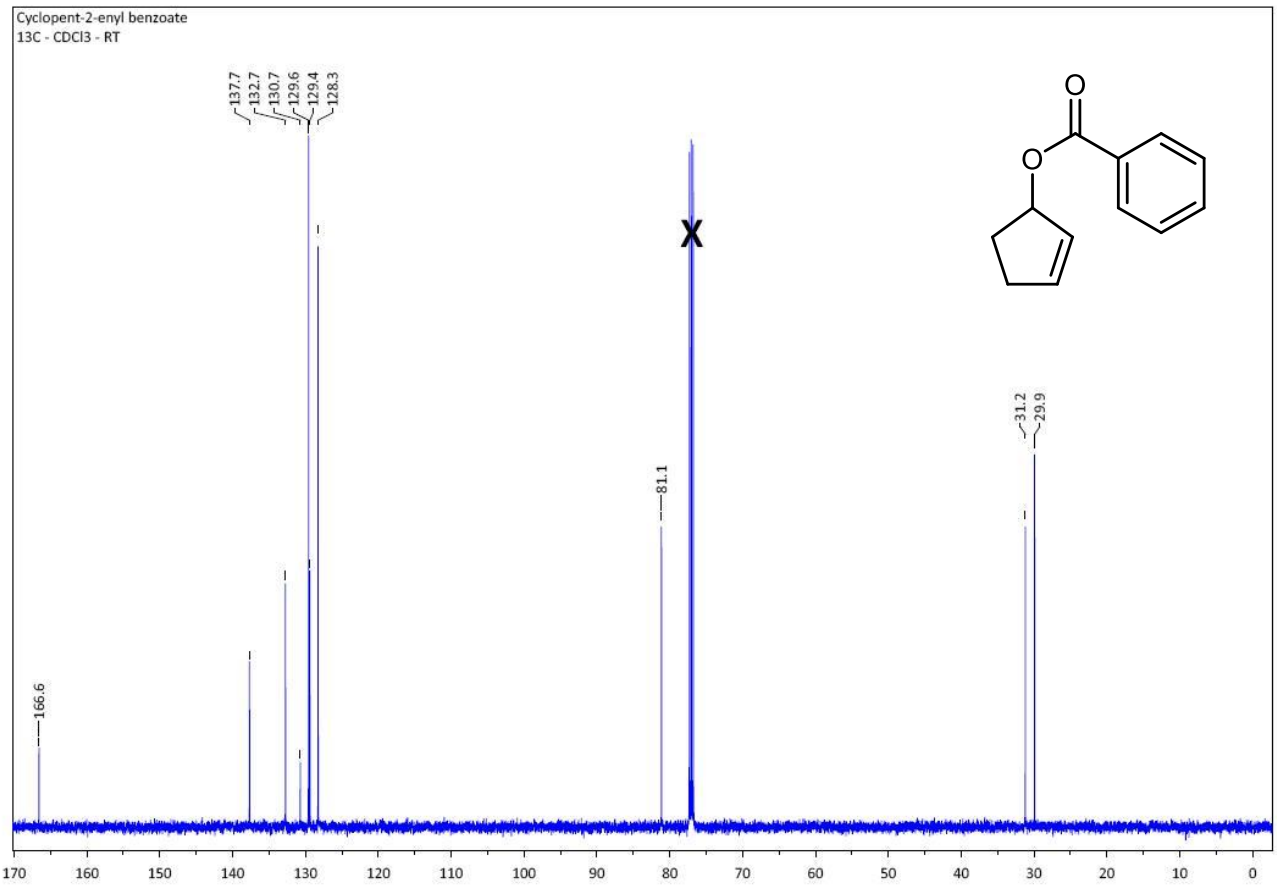


**Figure S14.** $^{13}$C-NMR of compound **5** in $CDCl_3$.

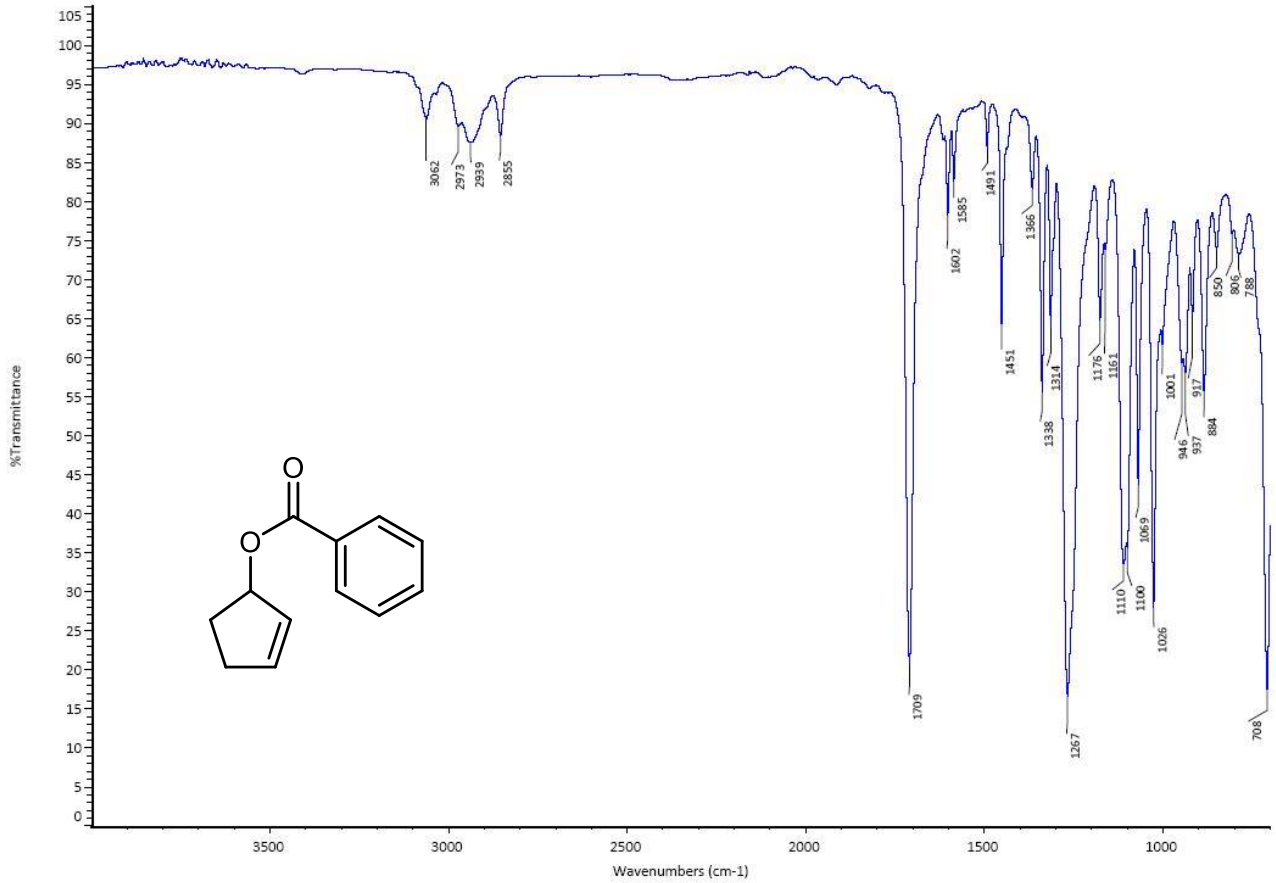


**Figure S15.** FT-IR spectrum of compound **5**.

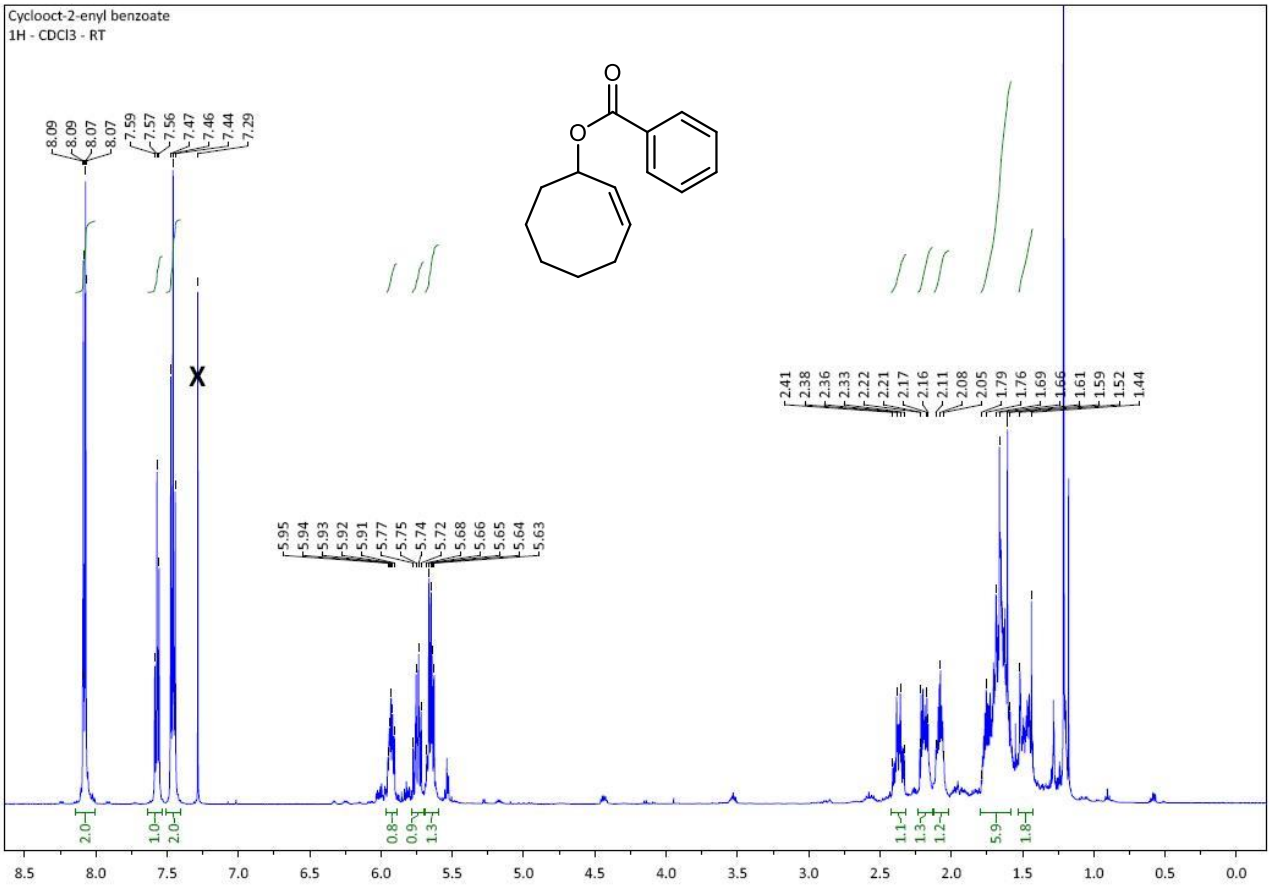


**Figure S16.** $^{1}$H-NMR of compound **6** in $CDCl_3$.

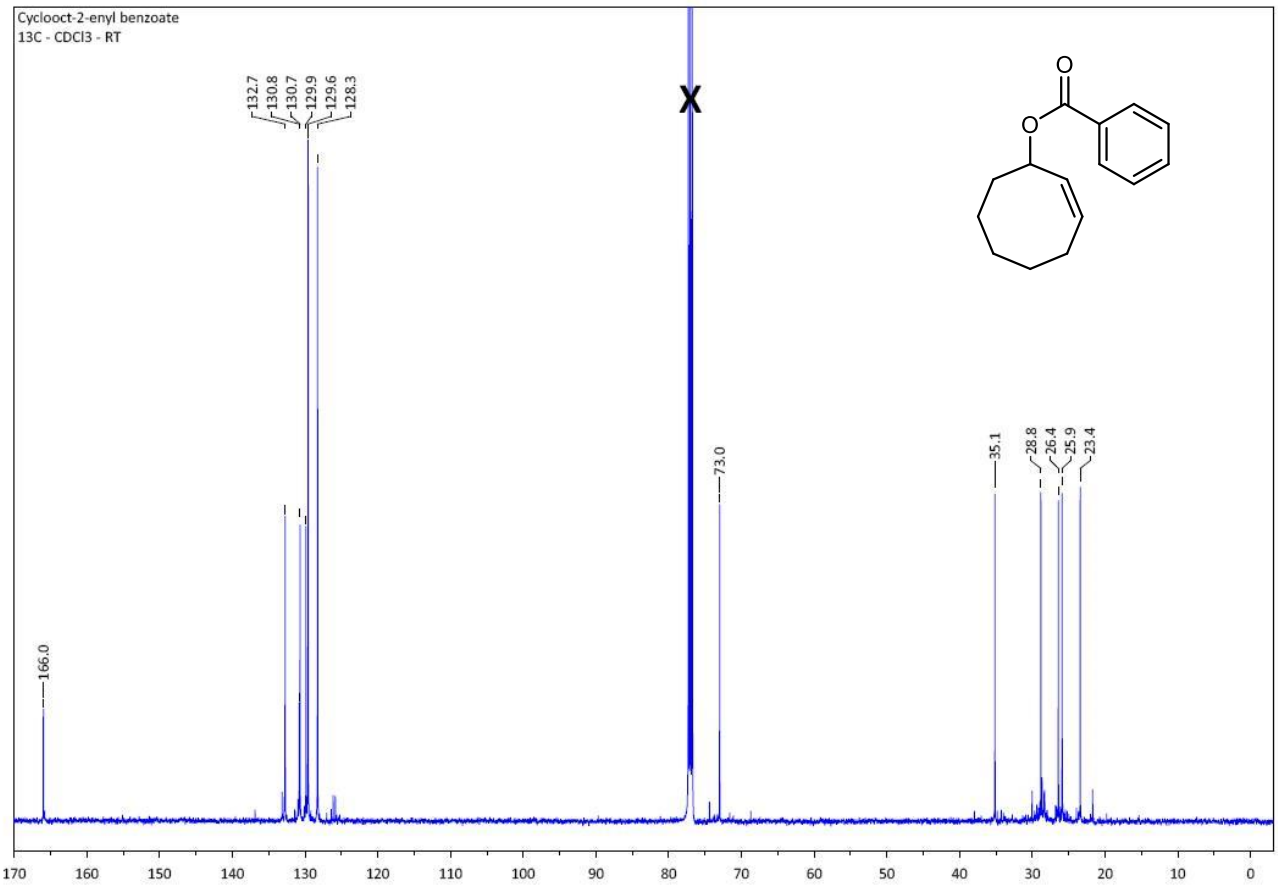


**Figure S17.** $^{13}$C-NMR of compound **6** in $CDCl_3$.

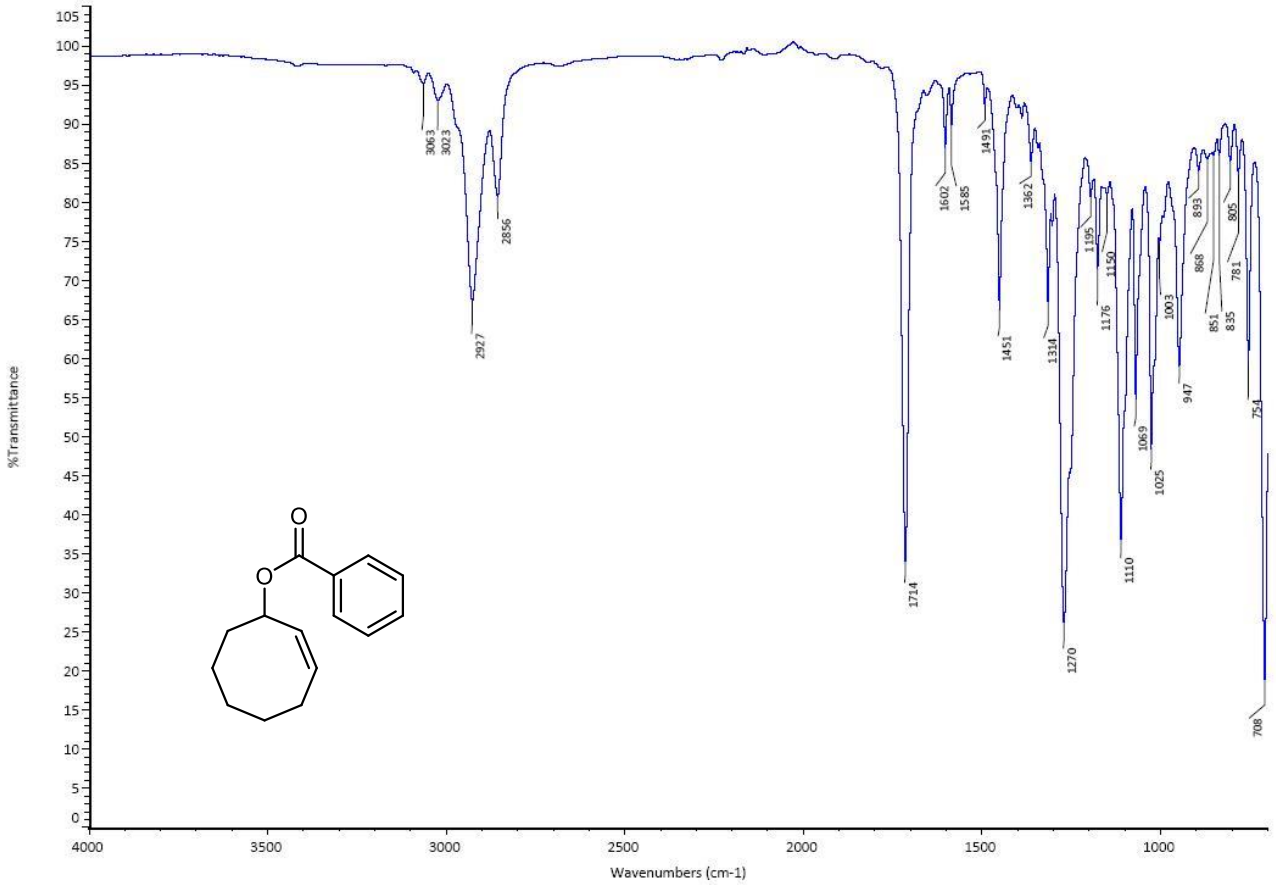


**Figure S18.** FT-IR spectrum of compound **6**.