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**Supporting Information**

# Catalytic $CO_2$ fixation to cyclic carbonates by copper(II) complexes of N4 ligands under mild conditions

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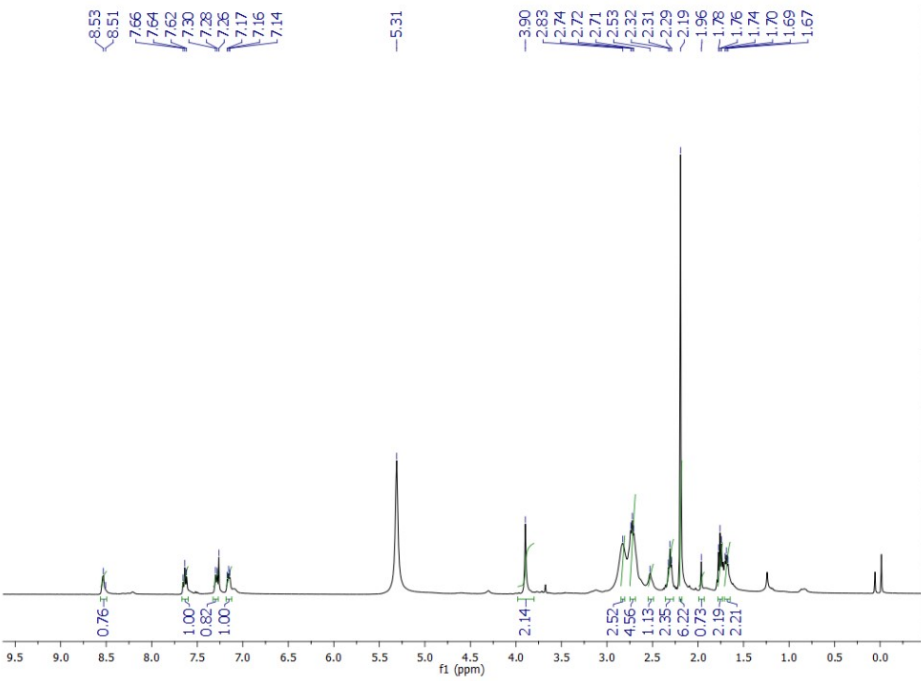



**Figure S1.** $^{1}H$ NMR Spectrum for the Ligand **1** in $CDCl_3$.

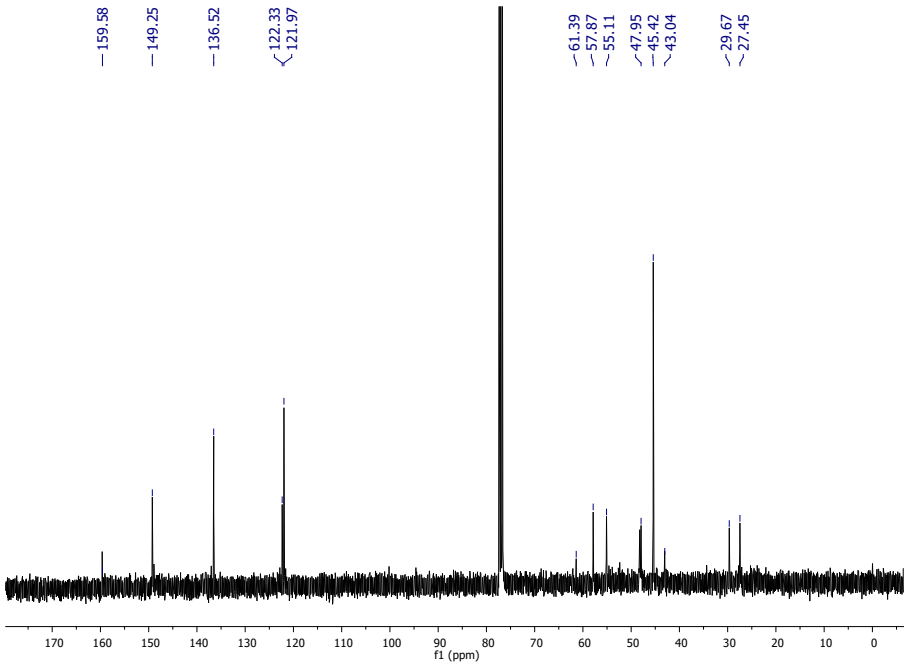



**Figure S2.** $^{13}C$ NMR Spectrum for the Ligand **1** in $CDCl_3$.

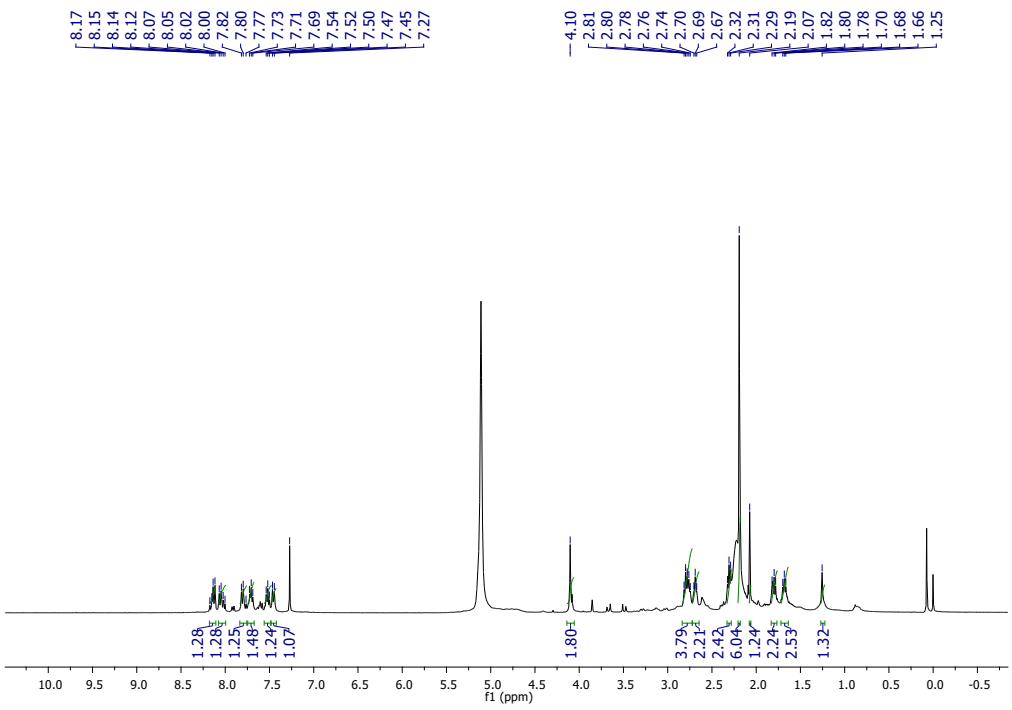



**Figure S3.** $^{1}H$ NMR Spectrum for the Ligand **2** in $CDCl_3$.

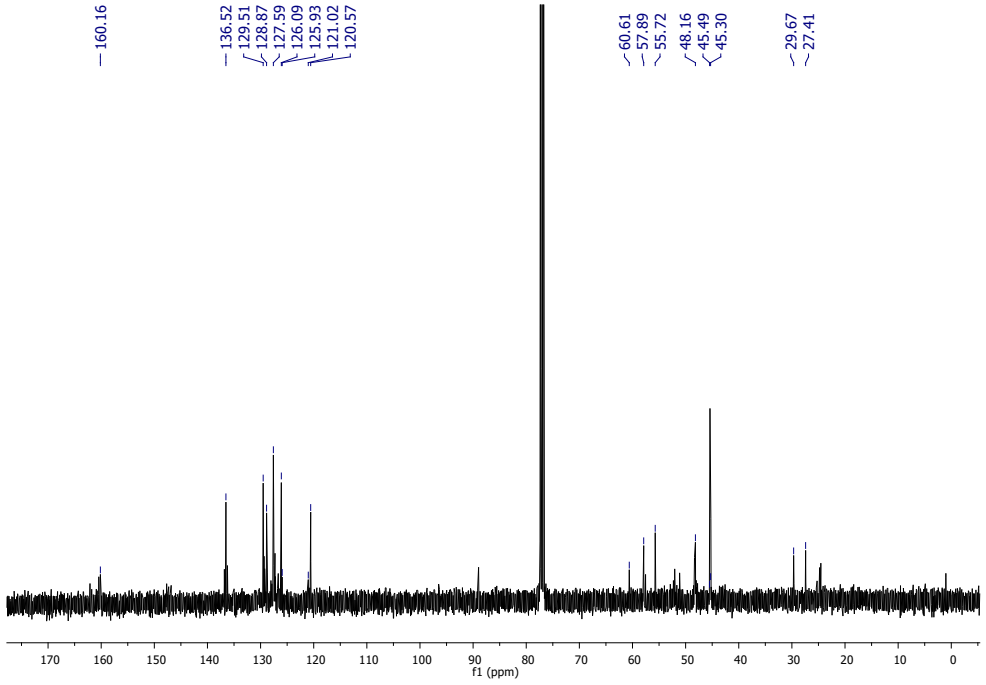



**Figure S4.** $^{13}C$ NMR Spectrum for the Ligand **2** in $CDCl_3$.

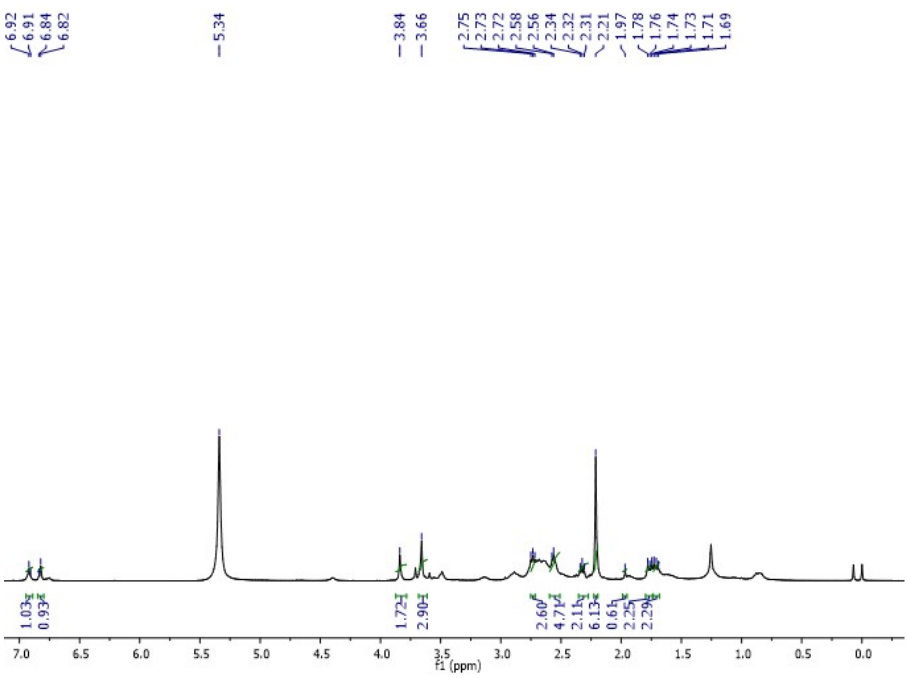



**Figure S5.** $^{1}H$ NMR Spectrum for the Ligand **3** in $CDCl_3$.

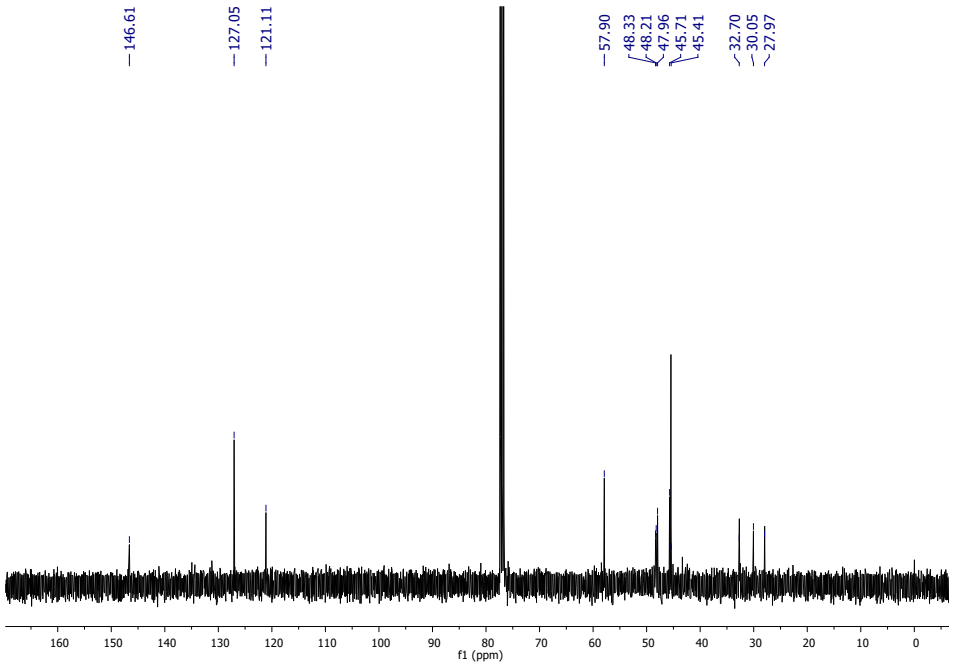



**Figure S6.** $^{13}C$ NMR Spectrum for the Ligand **3** in $CDCl_3$.

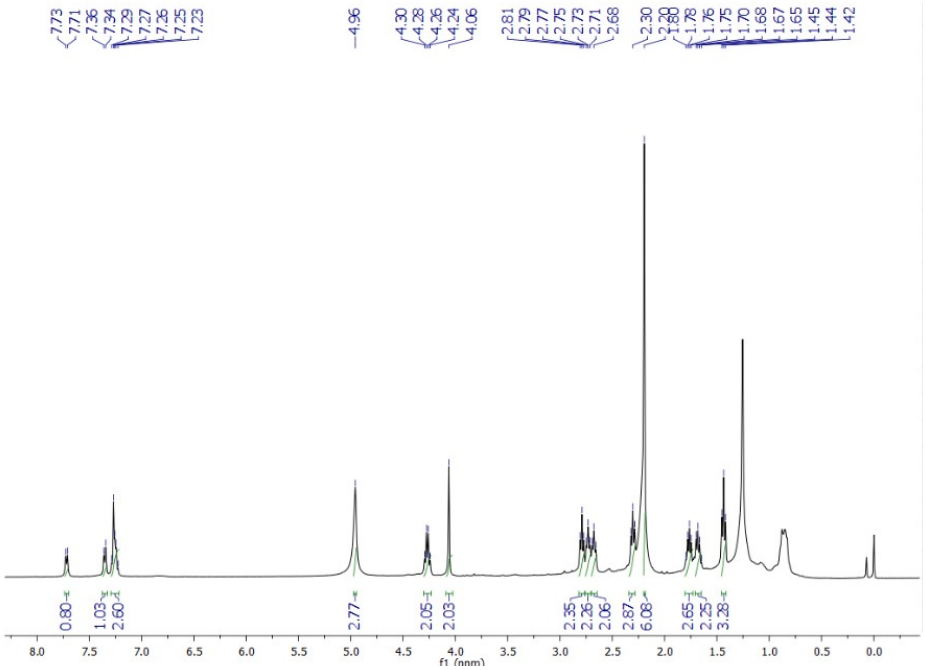


**Figure S7.** $^{1}H$ NMR Spectrum for the Ligand **4** in $CDCl_3$.

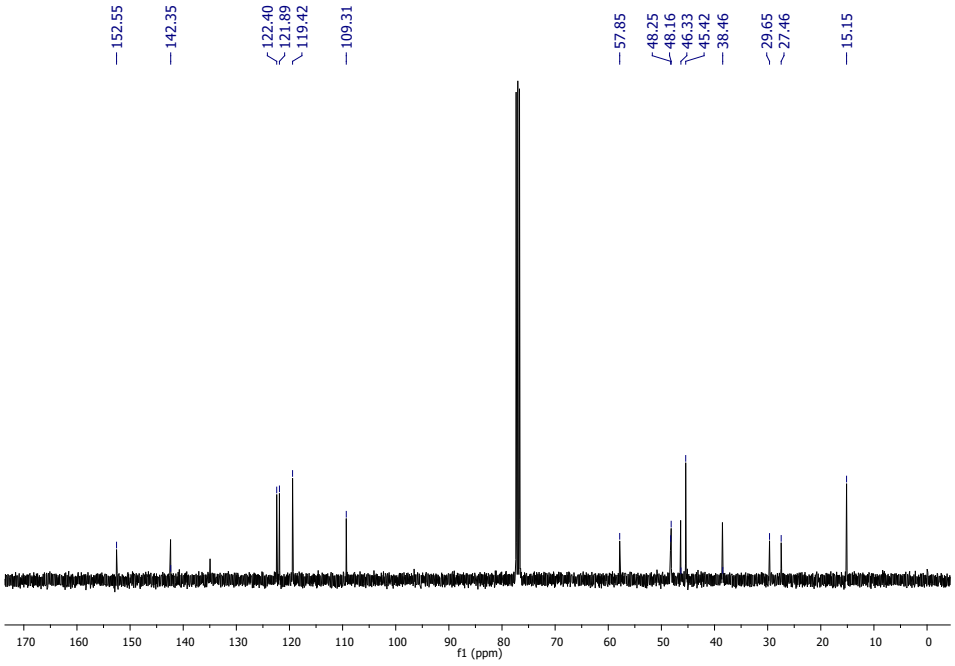


**Figure S8.** $^{13}C$ NMR Spectrum for the Ligand **4** in $CDCl_3$.

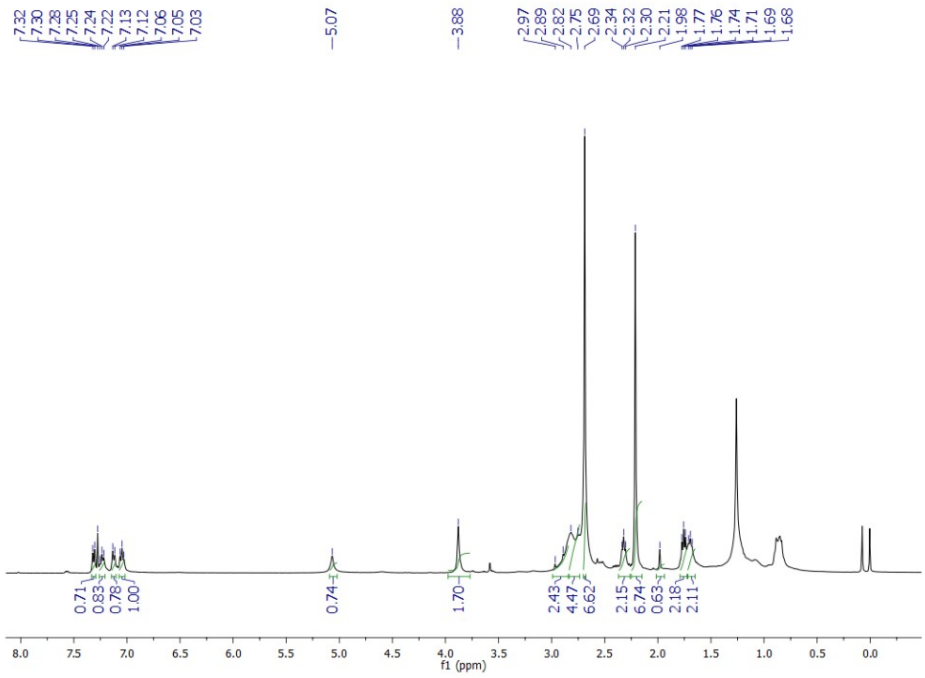



**Figure S9.** $^{1}H$ NMR Spectrum for the Ligand **5** in $CDCl_3$.

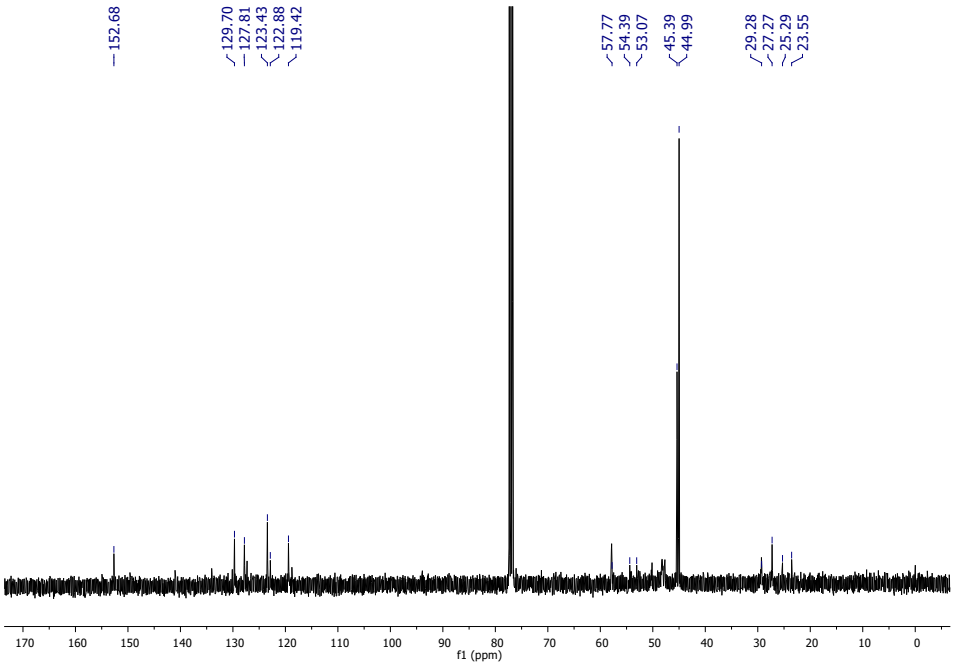



**Figure 10.** $^{13}C$ NMR Spectrum for the Ligand **5** in $CDCl_3$.

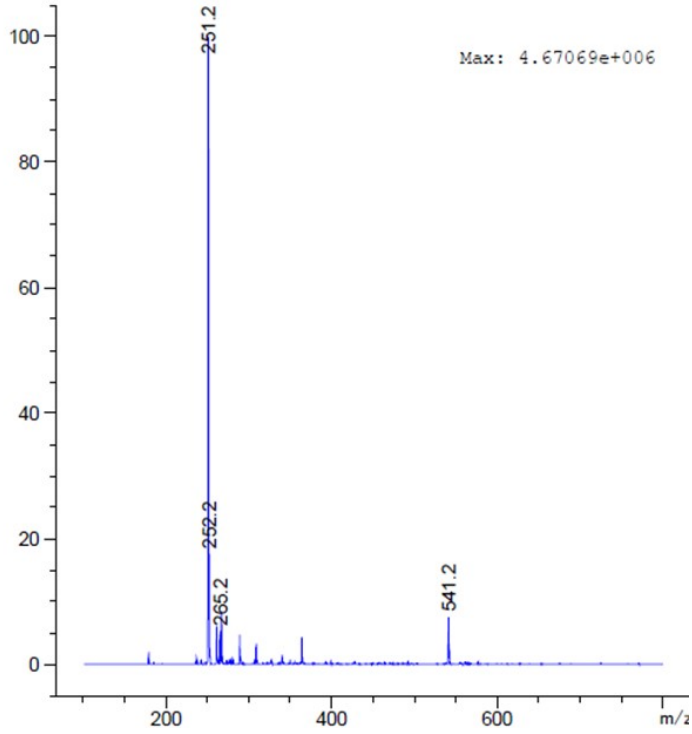



**Figure 11.** ESI-mass spectrum of **L1** in acetonitrile.

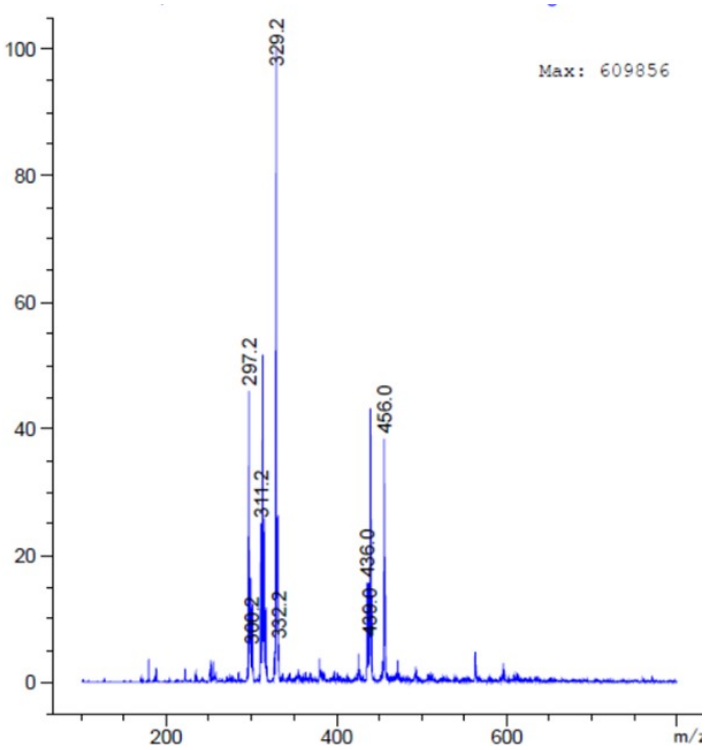



**Figure 12.** ESI-mass spectrum of **L2** in acetonitrile.

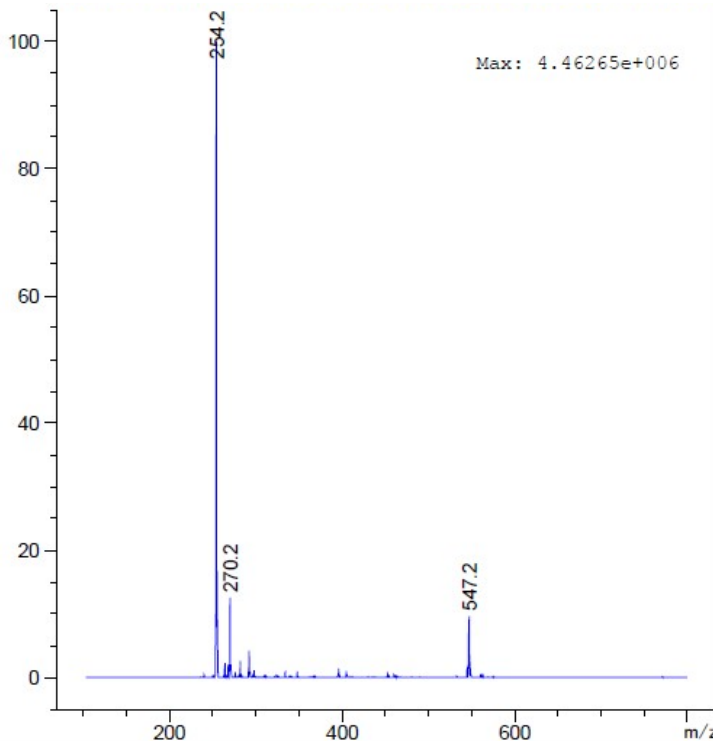



**Figure 13.** ESI-mass spectrum of **L3** in acetonitrile.

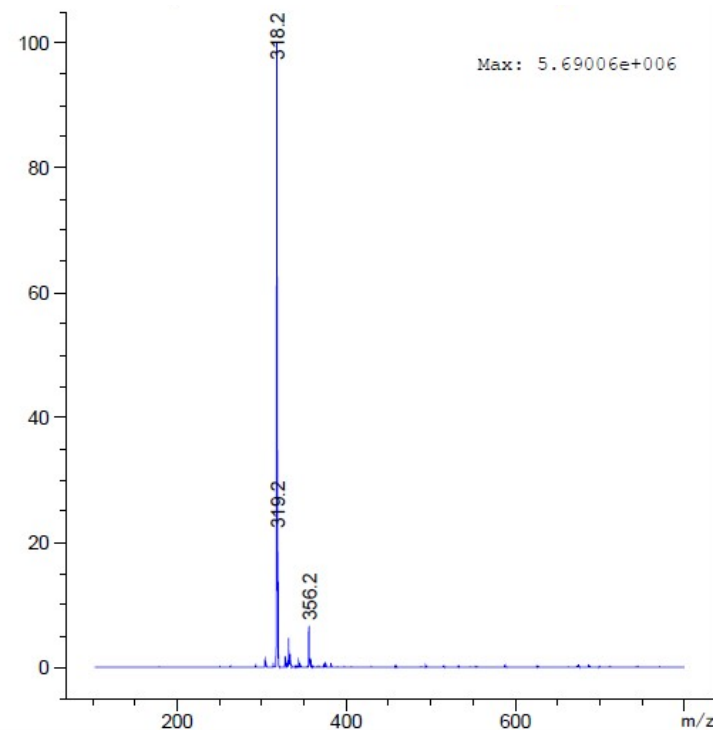



**Figure 14.** ESI-mass spectrum of **L4** in acetonitrile.

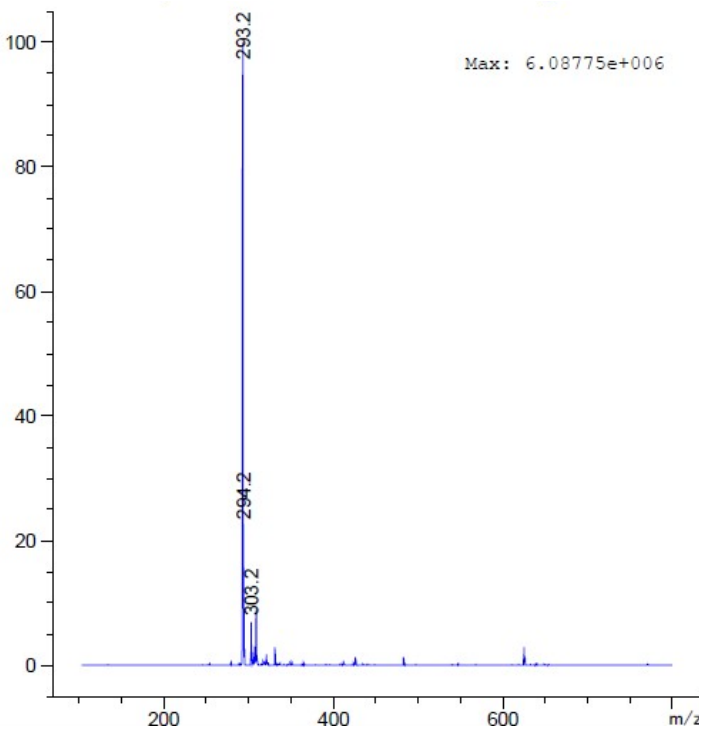



**Figure 15.** ESI-mass spectrum of **L5** in acetonitrile.

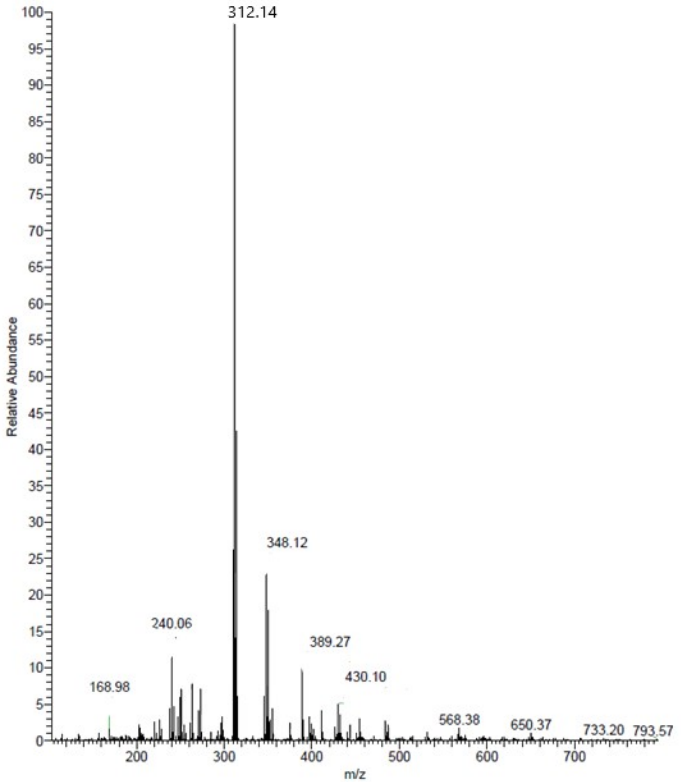



**Figure 16.** ESI-mass spectrum of complex **1** in acetonitrile.

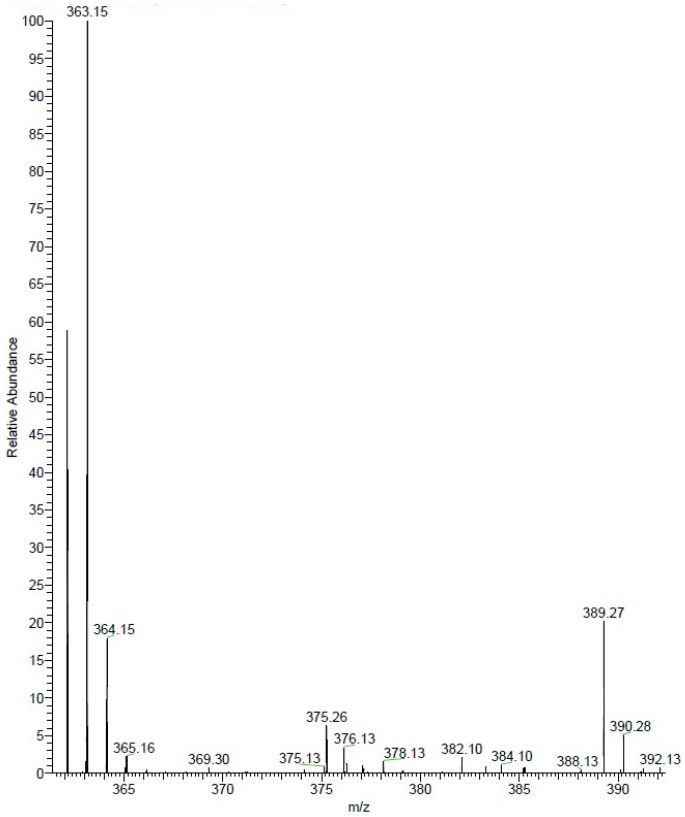



**Figure 17.** ESI-mass spectrum of complex **2** in acetonitrile.

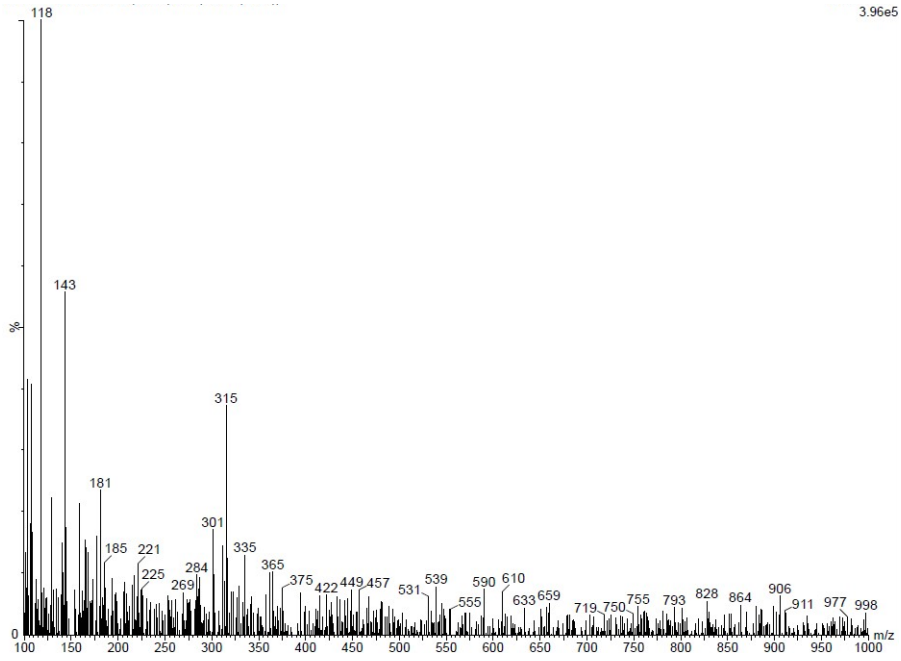



**Figure 18.** ESI-mass spectrum of complex **3** in acetonitrile.

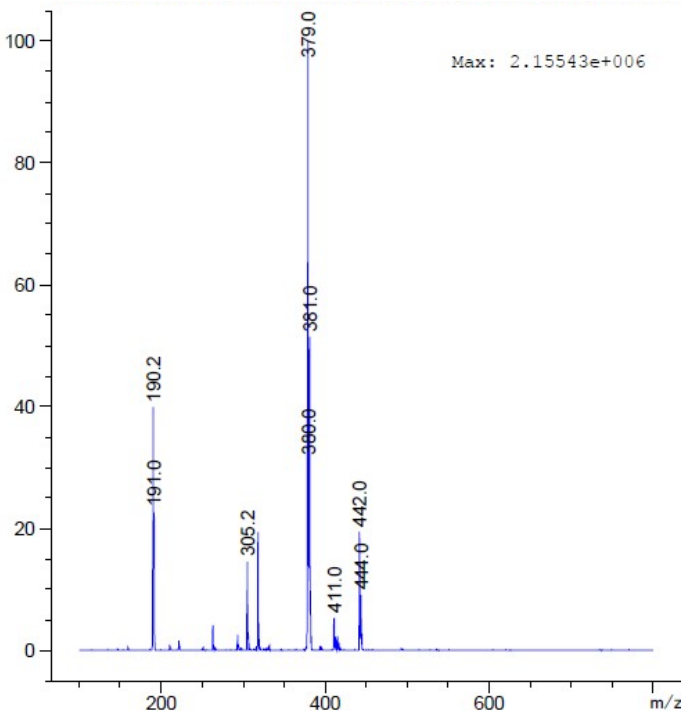



**Figure 19.** ESI-mass spectrum of complex **4** in acetonitrile.

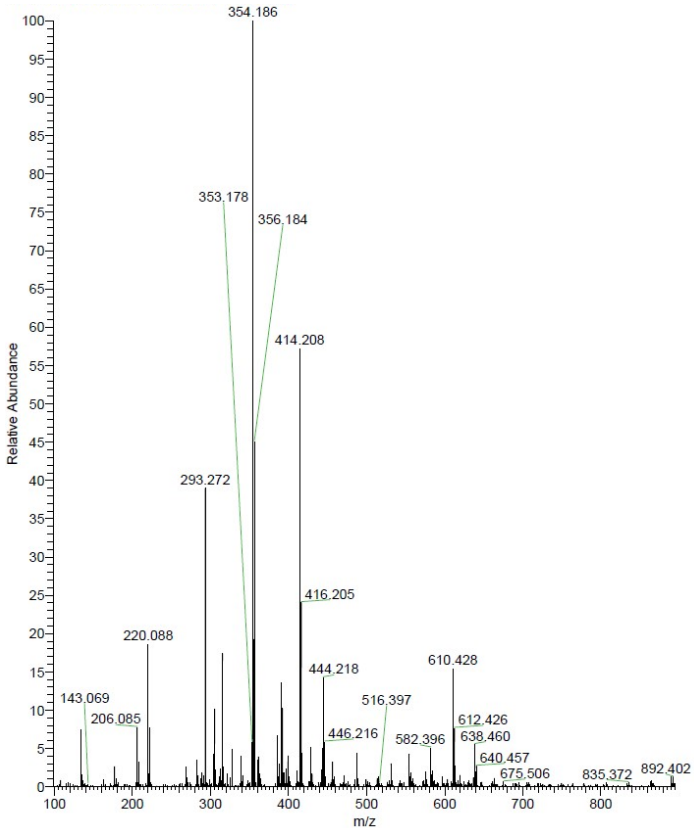



**Figure 20.** ESI-mass spectrum of complex **5** in acetonitrile.

**EPR Spectral analysis:**

EPR spectra of complexes **1** – **5** were measured in methanol:DMF mixture (8:2) at 70 K. The EPR parameters $g_{\|}$, $g_{\perp}$, $A_{\|}$, $A_{\perp}$, and the energies of d-d transition were used to determine the bonding parameters $\alpha^2$, $\beta^2$, and $\gamma^2$ which may be regarded as measures of the covalency of the in-plane σ bonds, and out-of-plane π bonds, respectively. The value of in plane sigma bonding parameter $\alpha^2$ was estimated from the following equation (**1**):

$$\alpha^2 = A_{\|}/0.036 + (g_{\|} - 2.0023) + 3/7\,(g_{\perp} - 2.0023) + 0.04. \quad \ldots\ldots\ldots \quad (\mathbf{1})$$

The orbital reduction factors $K_{\|} = \alpha^2\beta^2$ and $K_{\perp} = \alpha^2\gamma^2$ were calculated using the following equations (**2**) and (**3**):

$$K_{\|}^2 = (g_{\|} - 2.0023)\,\Delta E\,(d_{xy} - d_{x^2-y^2}) / 8\lambda_0) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (\mathbf{2})$$

$$K_{\perp}^2 = (g_{\perp} - 2.0023)\,\Delta E\,(d_{xz,yz} - d_{x^2-y^2}) / 2\lambda_0) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (\mathbf{3})$$

$$K_{\|} = \alpha^2\beta^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \mathbf{(4)}$$

$$K_{\perp} = \alpha^2\gamma^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \mathbf{(5)}$$

$$\beta^2 = K_{\|}/\alpha^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \mathbf{(6)}$$

Where, $\lambda_0$ is the spin orbit coupling constant and has the value -828 $cm^{-1}$ for a copper(II) $d^9$ system.[1-2]

Where, $K_{\|} = K_{\perp} = 0.77$ for pure σ bonding and $K_{\|} < K_{\perp}$ for in-plane π -bonding, while for the out-of-plane π bonding $K_{\|} > K_{\perp}$.[1-2] In all the copper(II) complexes, it is observed that $K_{\|} < K_{\perp}$ which indicates the presence of significant in-plane π bonding. Furthermore, $\alpha^2$, $\beta^2$ and $\gamma^2$ have values less than 1 which is expected for 100% ionic character of the bonds and become smaller with increasing covalent bonding. The evaluated values of $\alpha^2$, $\beta^2$ and $\gamma^2$ of the complexes are consistent with both strong in plane σ and in plane π bonding.

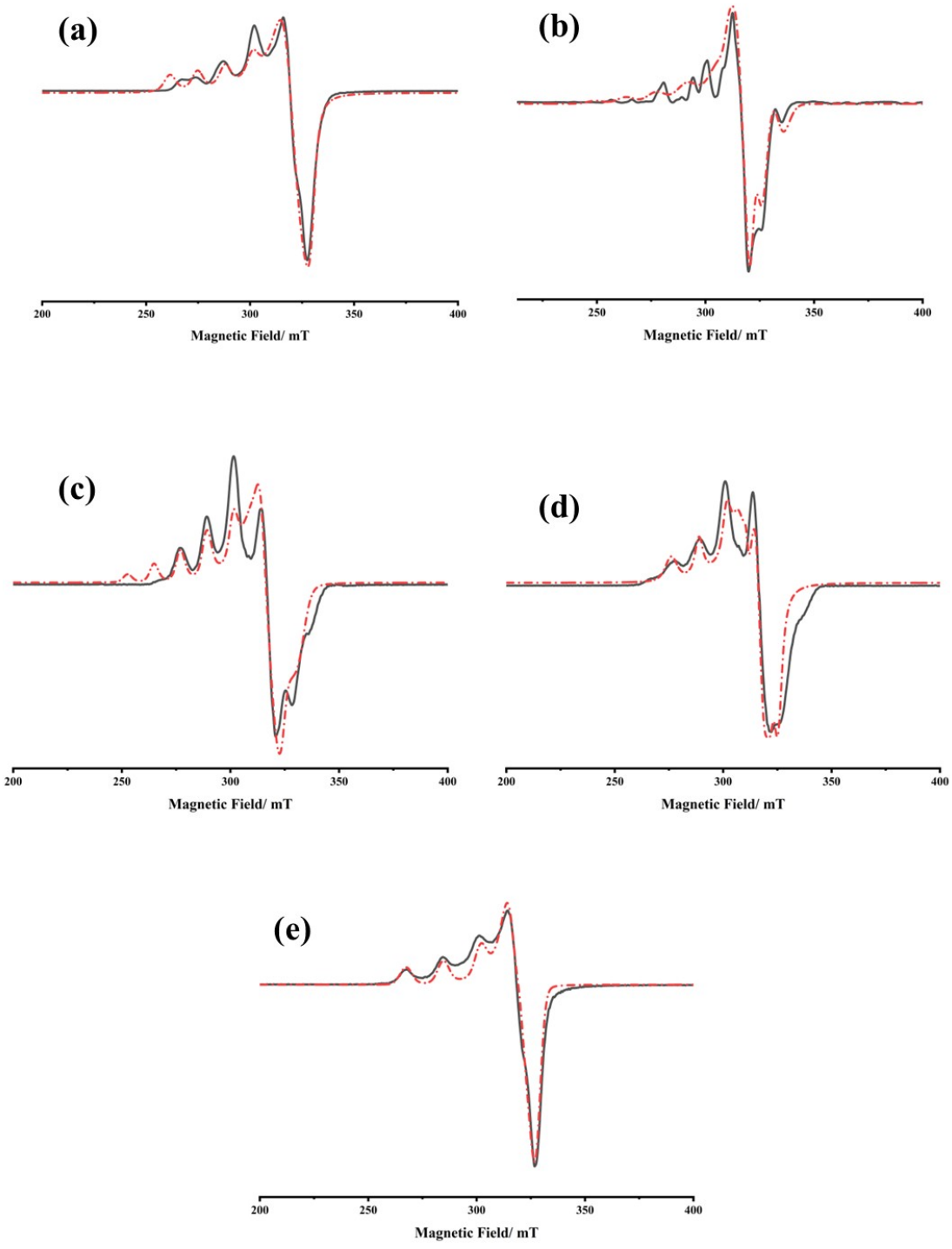



**Figure 21.** EPR spectra of **1** (a), **2** (b), **3** (c), **4** (d), and **5** (e) in methanol/DMF. Experimental (black) and simulated spectra, using EasySpin package (red), are overlaid in each case.

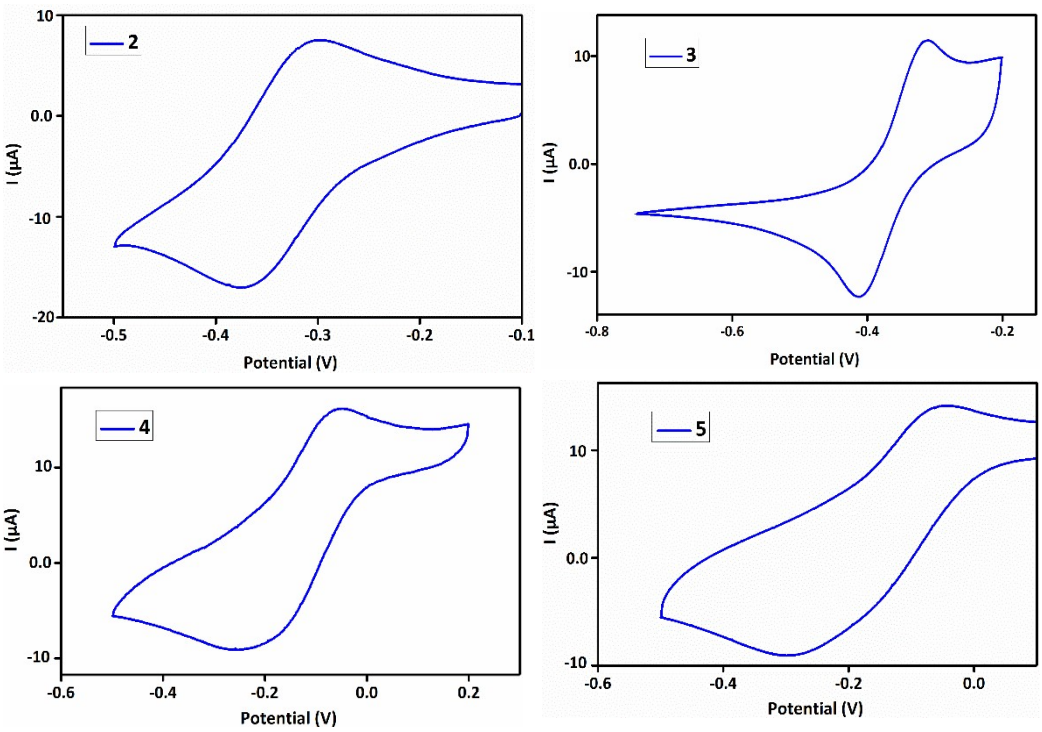

2
3
4
5
I (μA)
Potential (V)

**Figure S22.** Cyclic voltammograms of complexes **2 - 5** ($1 \times 10^{-3}$ M) in $CH_3CN$ at 25 °C. Supporting electrolyte: 0.1 M NaCl. Working electrode: Glassy carbon, Reference electrode: $Ag/Ag^+$ and counter electrode: Pt wire. Scan rate: 50 mV $s^{-1}$.

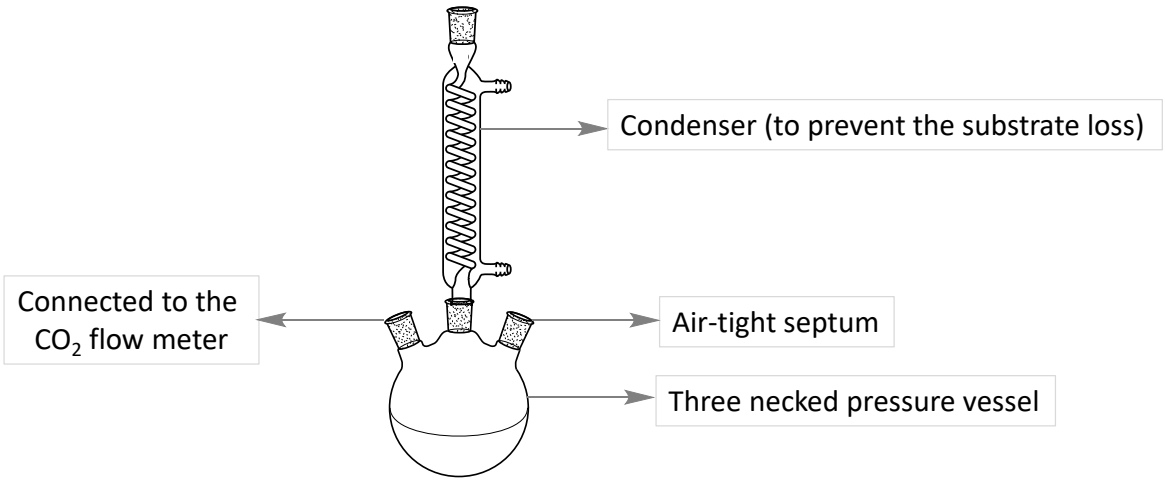



**Figure S23.** Picture of the experimental setup used in the $CO_2$ fixation reaction.

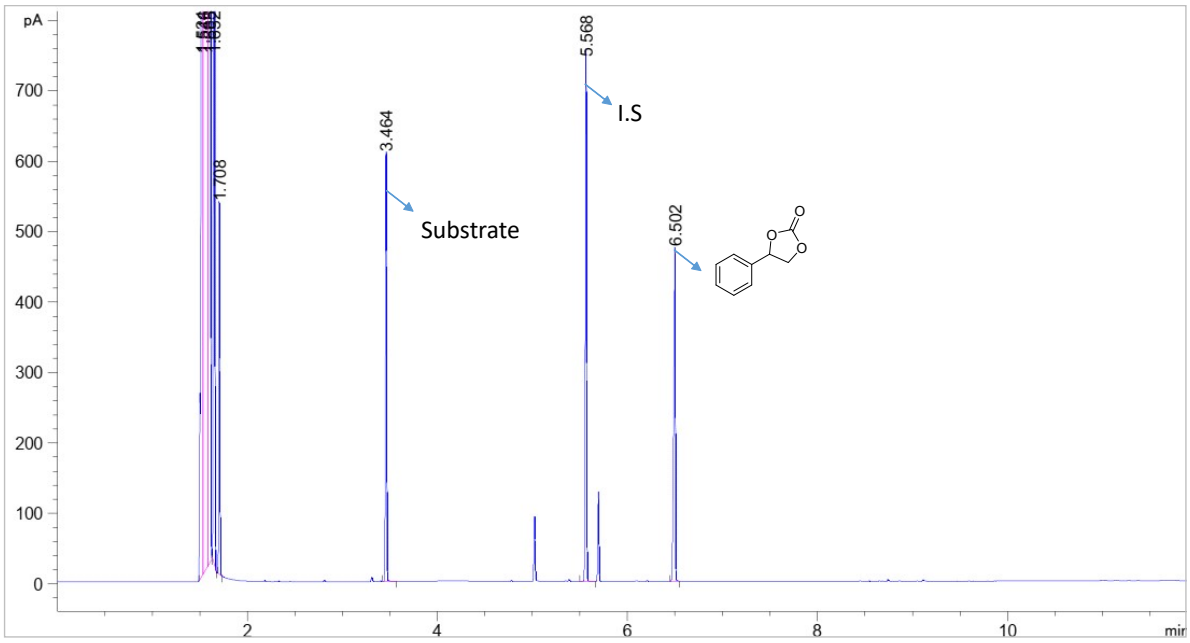



**Figure S24.** GC-Profile for the reaction of **1** with styrene oxide. Reaction condition: **1** (5 $\mu$mol, 0.05 mol%), substrate (10 mmol), $Bu_4NBr$ (0.5 mol%) under 1 atm $CO_2$ for 24 hours at 25 °C.

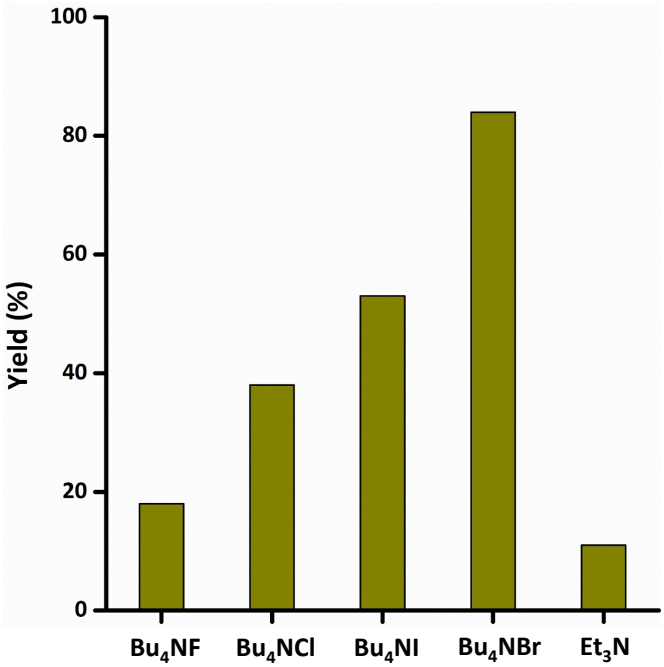
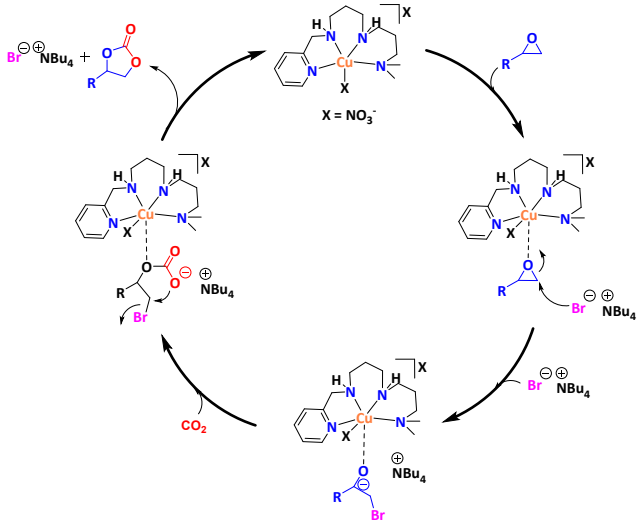



**Figure S25.** Influence of the co-catalyst in the formation of cyclic carbonate catalyzed by **1** (5 $\mu$mol, 0.05 mol%), epoxide (10 mmol), co-catalyst (0.5 mol%) under 1 atmospheric $CO_2$ at 25 °C for 24 hours.




**Scheme S1.** The proposed mechanism for the fixation of $CO_2$ into cyclic carbonate by **1**.

**Table S1.** Crystallographic data and structure refinement parameters for **1**, **3** and **4**.

| | **1** | **3** | **4** |
|---|---|---|---|
| Formula | $C_{14}H_{26}CuN_6O_6$ | $C_{13}H_{27}CuN_7O_6$ | $C_{18}H_{31}CuN_7O_6$ |
| Molecular weight | 437.95 | 440.95 | 505.03 |
| crystal system | Trigonal | Monoclinic | Triclinic |
| space group | R3c:H | P21/c | P-1 |
| *a* (Å) | 26.520(2) | 8.2096(11) | 8.509(8) |
| *b* (Å) | 26.520(2) | 21.884(2) | 11.488(10) |
| *c* (Å) | 14.3074(11) | 11.7702(15) | 23.43(2) |
| $\alpha$ (deg) | 90 | 90 | 90 |
| $\beta$ (deg) | 90 | 105.516(13) | 90 |
| $\gamma$ (deg) | 120 | 90 | 102.23(3) |
| *V* (Å$^3$) | 8714.5(16) | 2037.5(5) | 2238(3) |
| Z | 18 | 4 | 2 |
| $\mu$ (mm$^{-1}$) | 1.171 | 1.115 | 1.026 |
| R factor all | 0.0560 | 0.1013 | 0.3213 |
| R factor gt | 0.0453 | 0.0599 | 0.0992 |
| *w*R factor ref | 0.1292 | 0.1371 | 0.3055 |

| | | | |
|---|---|---|---|
| *w*R factor gt | 0.1191 | 0.1193 | 0.2047 |
| Goodness of fit ref | 1.080 | 1.087 | 0.885 |

| Complex | $Ep_a$ (V) | $Ep_c$ (V) | $\Delta Ep$ (mV) | $E_{1/2}$ (V) |
|---|---|---|---|---|
| **1** | -0.304 | -0.376 | 72 | -0.340 |
| **2** | -0.298 | -0.361 | 63 | -0.329 |
| **3** | -0.317 | -0.419 | 102 | -0.368 |
| **4** | -0.054 | -0.237 | 183 | -0.145 |
| **5** | -0.061 | -0.297 | 236 | -0.179 |

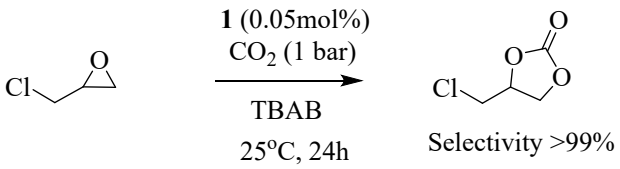
| | | | |
|---|---|---|---|
| R1[a] | 0.0453 | 0.0599 | 0.0893 |
| wR2[b] | 0.1292 | 0.1371 | 0.2416 |

[a]$R1=\sum\big|\,|F_o|-|Fc|\,\big|/\sum|F_o|$, [b]$R2=\sum w[(F_o-F_c)^2/\sum w[(F_o^2)^2]^{1/2}$.

**Table S2.** Redox data for **1 - 5** in water

[a]Concentration: $1 \times 10^{-3}$ M in aqueous solution 25 ºC (reference: $Ag/Ag^{+}$; supporting electrolyte: 0.1 M NaCl; scan rate = 50 mV $s^{-1}$).

**Table S3.** Optimization of the reaction of epichlorohydrin with 1 atm $CO_2$ using **1**



| Entry[a] | **1** (mol%) | Co-cat (mol%) | [Y][b] (%) | TON | TOF ($h^{-1}$) | [S] (%) |
|---|---|---|---|---|---|---|
| 1 | 0.025 | 0.25 | 29 | 580 | 24 | >99 |
| 2 | 0.025 | 0.50 | 57 | 1140 | 47 | >99 |
| 3 | 0.05 | 0.50 | 84 | 1680 | 70 | >99 |
| 4 | 0.05 | - | 5 | 100 | 4 | - |
| 5 | - | 0.50 | 9 | 180 | 7 | >99 |
| 6[c] | 0.05 | 0.50 | 18 | 360 | 15 | >99 |
| 7[d] | 0.05 | 0.50 | 38 | 760 | 31 | >99 |
| 8[e] | 0.05 | 0.50 | 53 | 1060 | 44 | >99 |
| 9[f] | 0.05 | 0.50 | 11 | 220 | 9 | >99 |
| 10[g] | 0.05 | 0.50 | 8 | 160 | 6 | - |
| 11[h] | 0.05 | 0.50 | 5 | 100 | 4 | - |

[a]General reaction condition: **1** (5 $\mu$mol, 0.05 mol%), epichlorohydrin (10 mmol), $Bu_4NBr$(0.5 mol%) under 1 atmospheric $CO_2$ for 24 hours at 25 °C. [b]GC Yield (average of three runs). [c]Using TBAF. [d]Using TBAC. [e]Using TBAI. [f]Using $Et_3N$. [g]Using Copper(II)acetate. [h]Using Copper(II)chloride.

**Table S4.** Comparison of the catalysts **1 – 5**

| Complex | [Substrate]/[Cu] | Co-cat (mol%) | [Y][b] (%) | TON | TOF ($h^{-1}$) | [S] (%) |
|---|---|---|---|---|---|---|

| | | | | | | |
|---|---|---|---|---|---|---|
| **1** | 2000 | 0.50 | 84 | 1680 | 70 | >99 |
| **2** | 2000 | 0.50 | 67 | 1340 | 56 | >99 |
| **3** | 2000 | 0.50 | 75 | 1500 | 62 | >99 |
| **4** | 2000 | 0.50 | 72 | 1440 | 60 | >99 |
| **5** | 2000 | 0.50 | 56 | 1120 | 47 | >99 |

[a]General reaction condition: catalyst (5 $\mu$mol, 0.05 mol%), epichlorohydrin (10 mmol), $Bu_4NBr$ (0.5 mol%) under 1 atmospheric $CO_2$ for 24 hours at 25 °C. [b]GC Yield (average of three runs).

## References


(1) (a) E. Garribba, G. Micera, *J. Chem. Educ.,* 2006, **83**, 1229; (b) S. H. Laurie, T. Lund, J. B. Raynor, *J. Chem. Soc., Dalton Trans.,* 1975, 1389-1394.

(2) (a) E. I. Solomon, *Inorg. Chem.,* 2006, **45**, 8012. (b) P. F. Rapheal, E. Manoj, M. R. P. Kurup, *Polyhedron* 2007, **26**, 818.