

*Supplementary Materials*

# Copper(II) Perfluorinated Carboxylate Complexes with Small Aliphatic Amines as Universal Precursors for Nanomaterial Fabrication

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**Citation:** Szymańska, I.B.; Madajska, K.; Butrymowicz, A.; Barwiołek, M. Copper(II) Perfluorinated Carboxylate Complexes with Small Aliphatic Amines as Universal Precursors for Nanomaterial Fabrication. *Materials* **2021**, *14*, 7451. <https://doi.org/10.3390/ma14237451>

Academic Editor: Piotr Smoleński

Received: 2 November 2021

Accepted: 30 November 2021

Published: 4 December 2021

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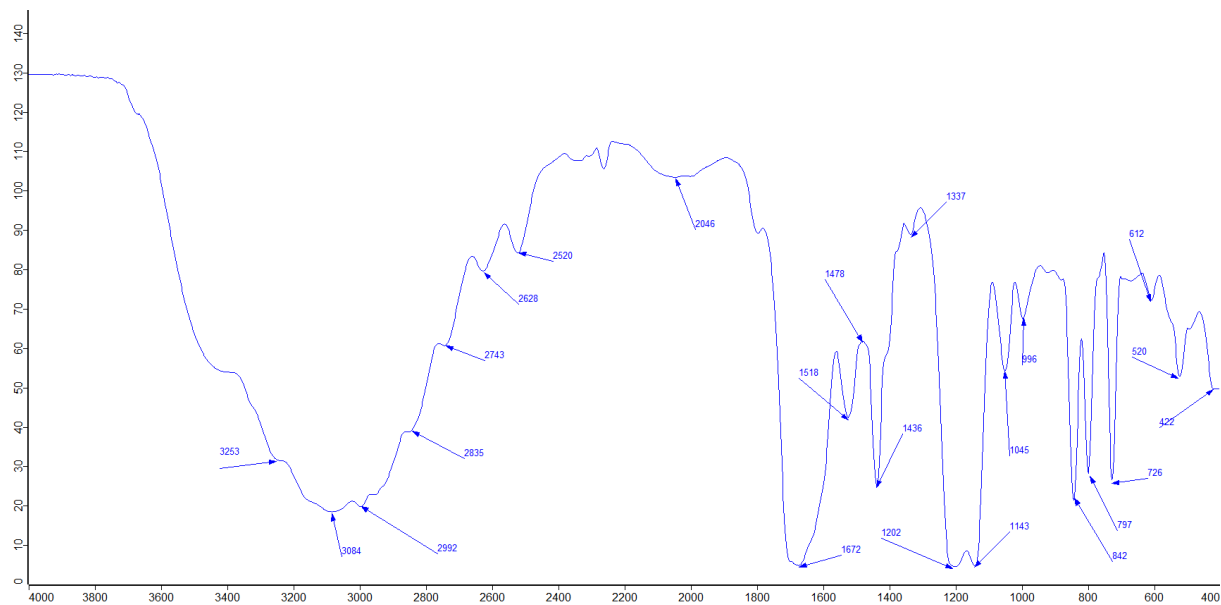


Figure S1. Infrared spectrum (thin film on KBr plates) of [Cu<sub>2</sub>(EtNH<sub>2</sub>)<sub>2</sub>(μ-O<sub>2</sub>CCF<sub>3</sub>)<sub>4</sub>] (1).

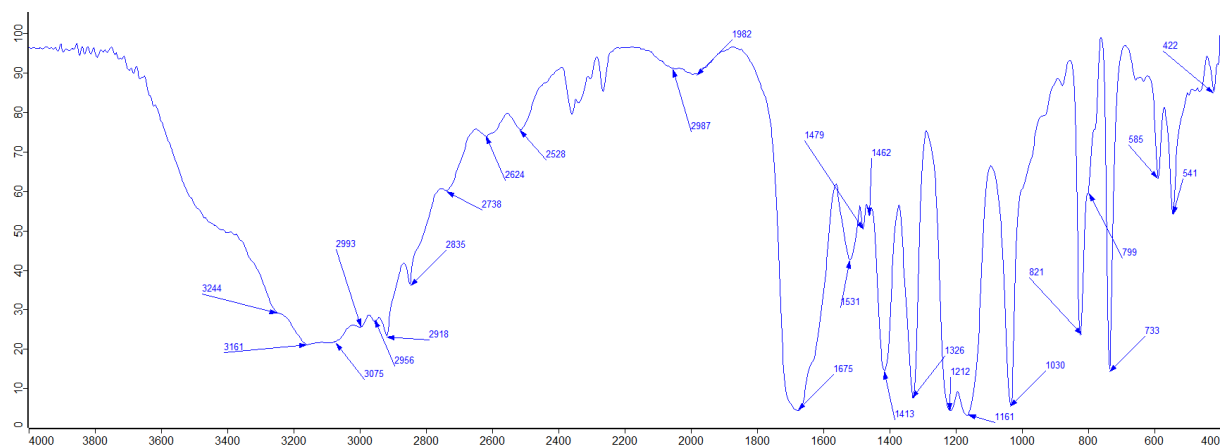
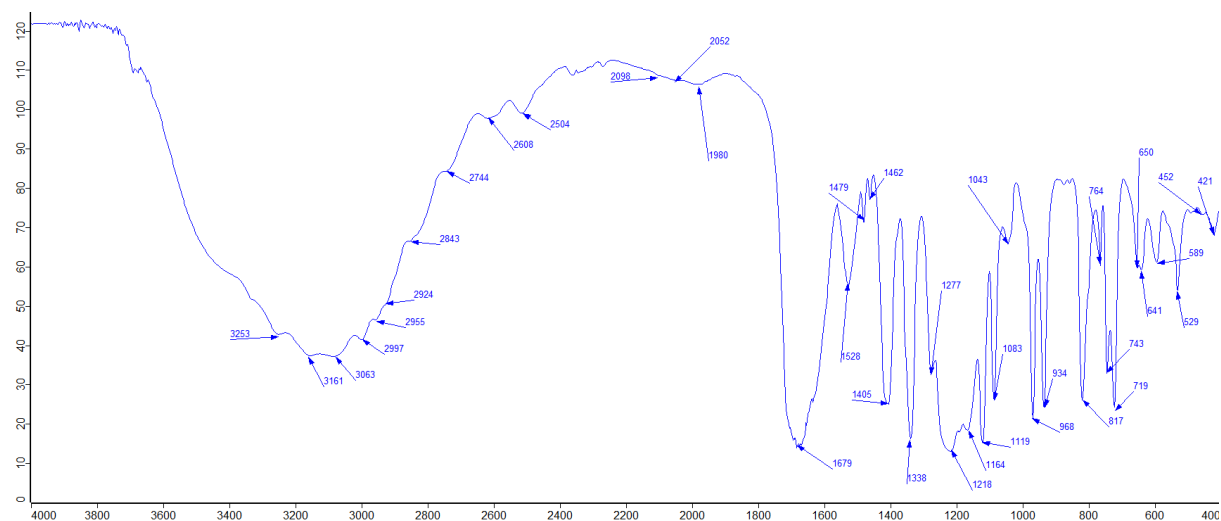
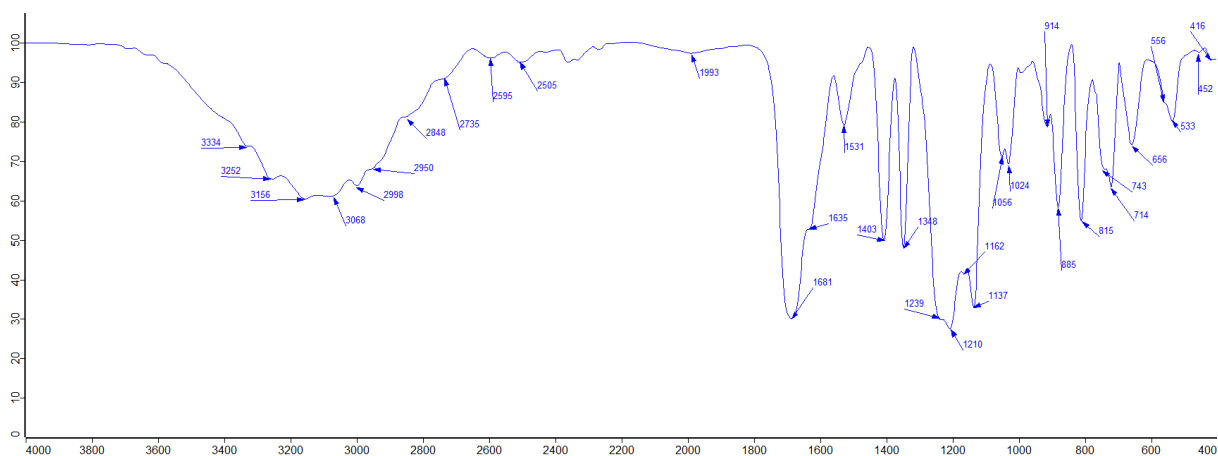


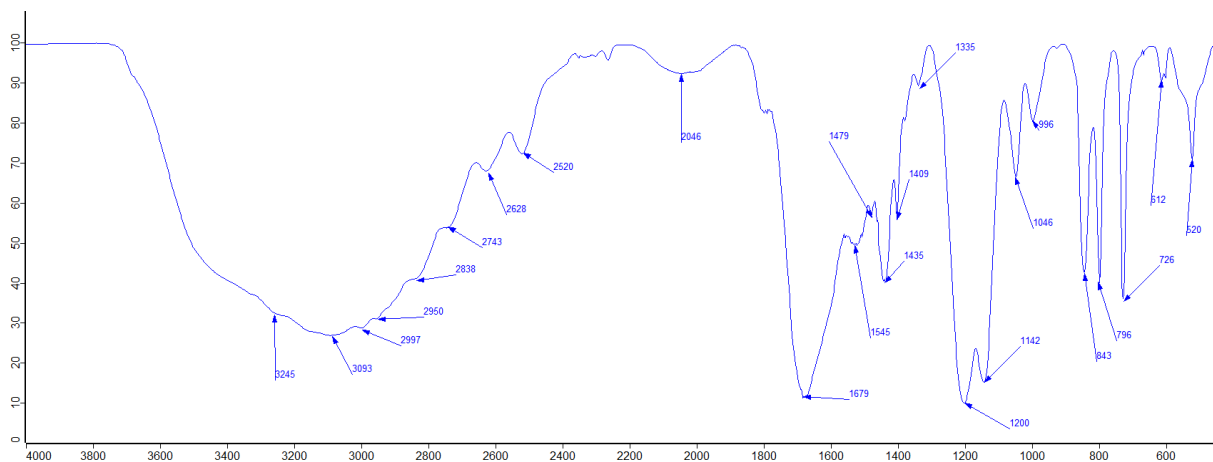
Figure S2. Infrared spectrum (thin film on KBr plates) of [Cu<sub>2</sub>(EtNH<sub>2</sub>)<sub>2</sub>(μ-O<sub>2</sub>CC<sub>2</sub>F<sub>5</sub>)<sub>4</sub>] (2).



**Figure S3.** Infrared spectrum (thin film on KBr plates) of  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_3\text{F}_7)_4]$  (3).



**Figure S4.** Infrared spectrum (thin film on KBr plates) of  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_4\text{F}_9)_4]$  (4).



**Figure S5.** Infrared spectrum (thin film on KBr plates) of  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_5\text{F}_{11})_4]$  (5).

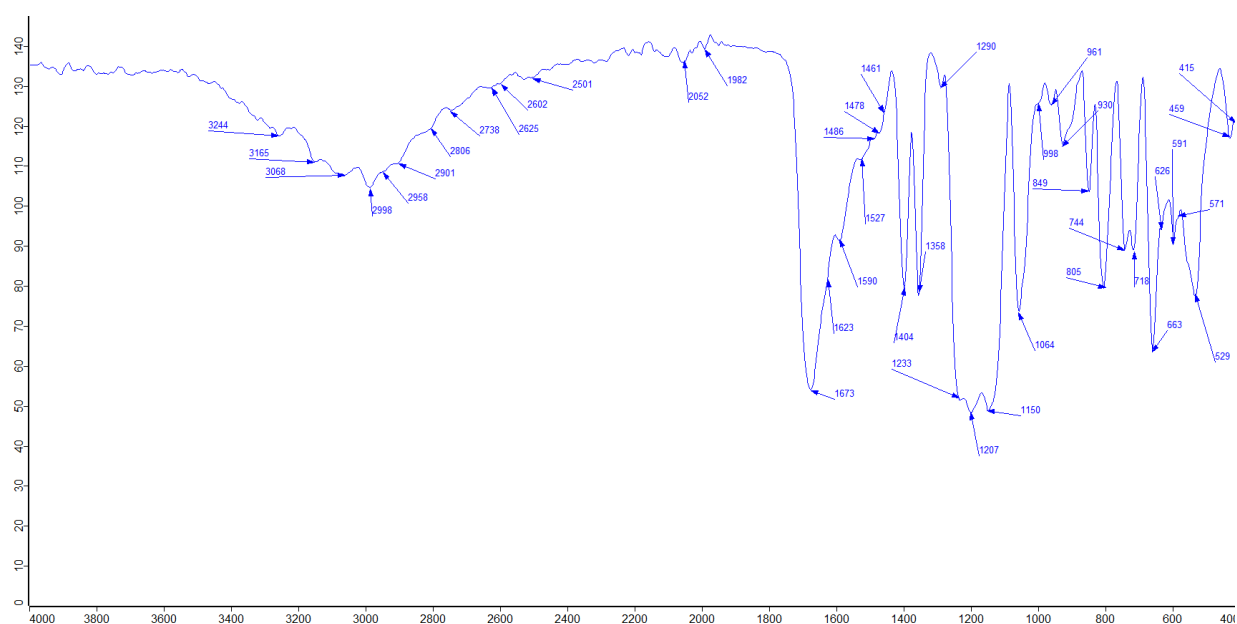


Figure S6. ATR-IR spectrum  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_6\text{F}_{13})_4]$  (6).

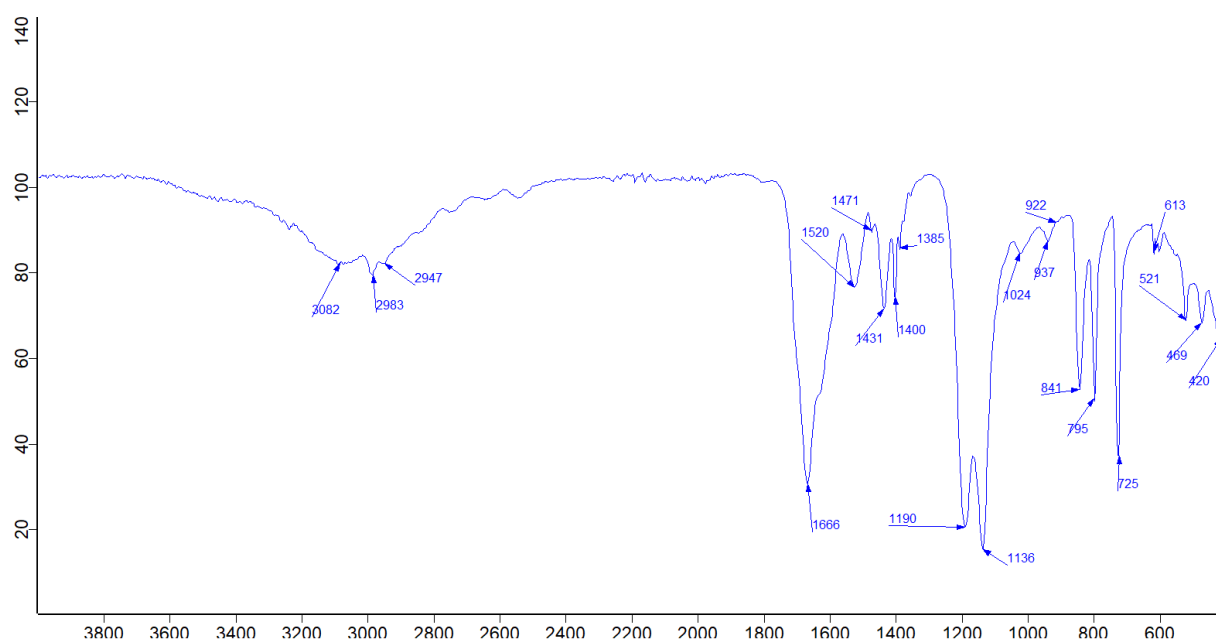


Figure S7. ATR-IR spectrum of  $[\text{Cu}_2(\text{iPrNH}_2)_2(\mu\text{-O}_2\text{CCF}_3)_4]$  (7).

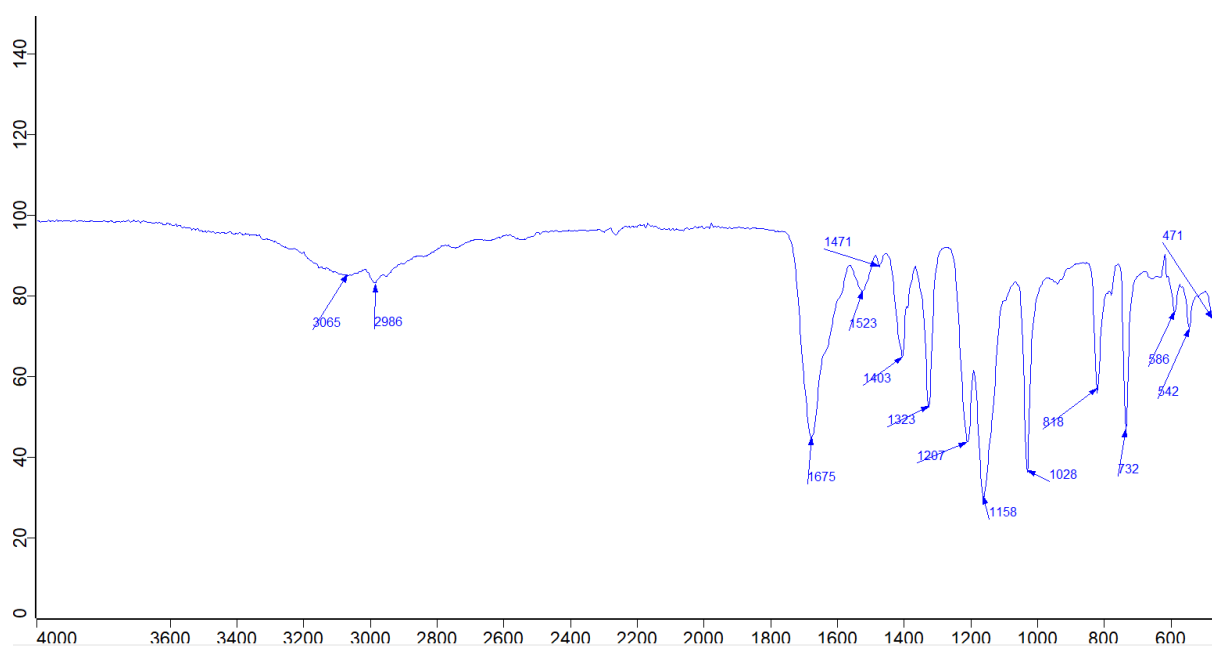


Figure S8. ATR-IR spectrum of [Cu<sub>2</sub>(iPrNH<sub>2</sub>)<sub>2</sub>(μ-O<sub>2</sub>CC<sub>2</sub>F<sub>5</sub>)<sub>4</sub>] (8).

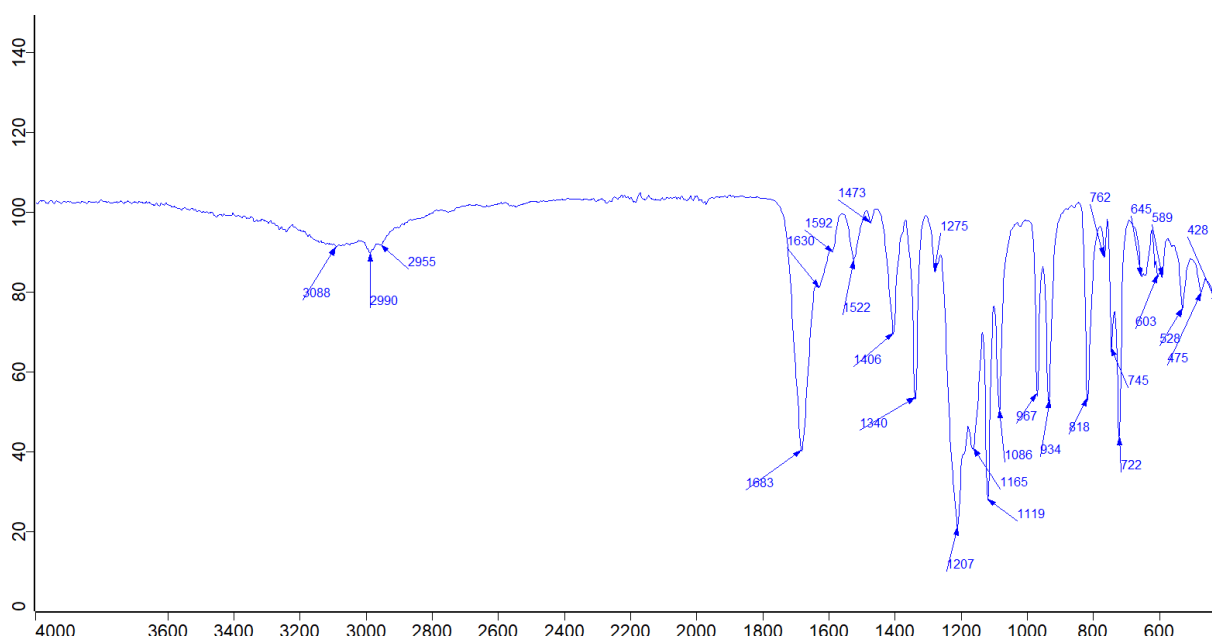


Figure S9. ATR-IR spectrum of [Cu<sub>2</sub>(iPrNH<sub>2</sub>)<sub>2</sub>(μ-O<sub>2</sub>CC<sub>3</sub>F<sub>7</sub>)<sub>4</sub>] (9).

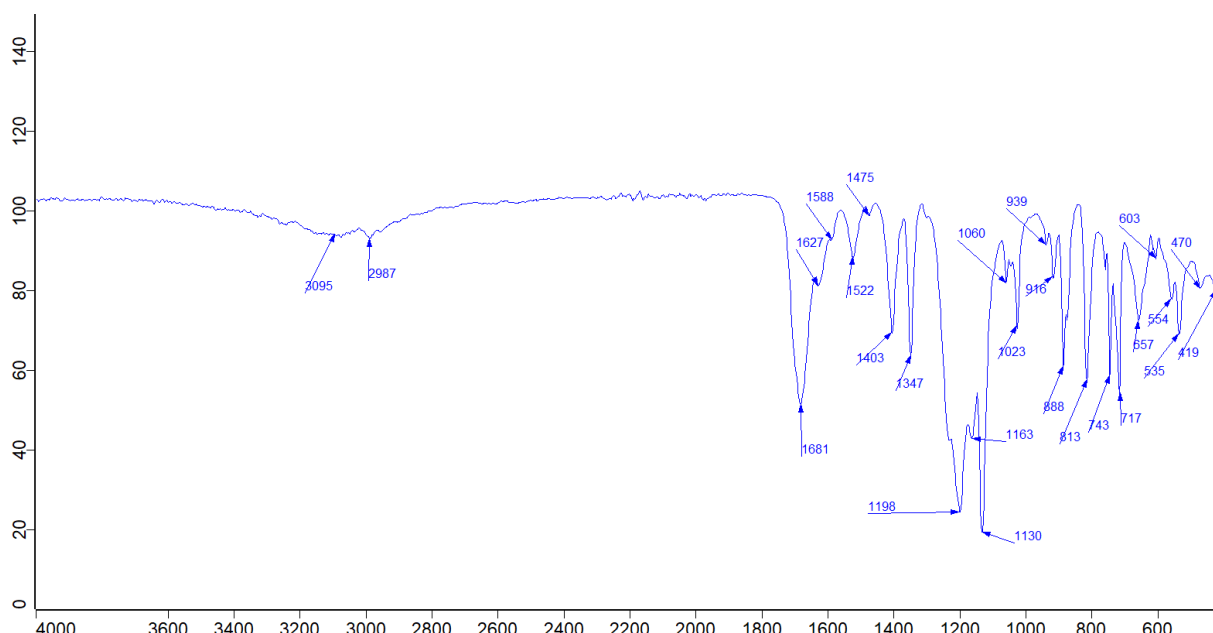


Figure S10. ATR-IR spectrum of  $[\text{Cu}_2(\text{iPrNH}_2)_2(\mu\text{-O}_2\text{CC}_3\text{F}_7)_4]$  (10).

Table S1. Mass spectrometry EI MS data of  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$  (2).

| Fragments                                                             | $m/z$ | RI [%] |       |       |       |
|-----------------------------------------------------------------------|-------|--------|-------|-------|-------|
|                                                                       |       | 310 K  | 331 K | 357 K | 542 K |
| $[\text{C}_2\text{H}_4\text{N}]^+$                                    | 42    | 3      | 1     | 2     | -     |
| $[\text{CO}_2]^+$                                                     | 44    | 10     | 3     | 6     | 27    |
| $[\text{C}_2\text{H}_7\text{N}]^+ / [\text{COOH}]^+$                  | 45    | 25     | 5     | 23    | 23    |
| $[\text{CF}_2]^+$                                                     | 50    | 6      | 1     | 6     | 5     |
| $[\text{CF}_3]^+$                                                     | 69    | 34     | 11    | 38    | 32    |
| $[\text{CF}_3\text{CO}]^+$                                            | 97    | 12     | 4     | 12    | 9     |
| $[\text{C}_2\text{F}_4]^+$                                            | 100   | 33     | 11    | 33    | 30    |
| $[\text{C}_2\text{F}_5]^+$                                            | 119   | 41     | 21    | 45    | 35    |
| $[\text{Cu}]^+$                                                       | 63    | 14     | 6     | 11    | 12    |
| $[\text{Cu}(\text{O}_2\text{C})]^+$                                   | 107   | 6      | 5     | 4     | 2     |
| $[\text{Cu}(\text{EtNH}_2)]^+$                                        | 108   | 4      | 3     | 3     | -     |
| $[\text{Cu}_2\text{F}]^+$                                             | 145   | 16     | 13    | 16    | 17    |
| $[\text{Cu}_2(\text{O}_2\text{CC}_2\text{F}_5)]^+$                    | 289   | 100    | 100   | 100   | 100   |
| $[\text{Cu}_2(\text{EtNH}_2)(\text{O}_2\text{CC}_2\text{F}_5)]^+$     | 334   | 2      | 3     | 2     | -     |
| $[\text{Cu}_2(\text{O}_2\text{CC}_2\text{F}_5)_2]^+$                  | 452   | 39     | 40    | 28    | 38    |
| $[\text{Cu}_2(\text{EtNH}_2)(\text{O}_2\text{CC}_2\text{F}_5)_3]^+$   | 660   | 3      | 2     | 2     | -     |
| $[\text{Cu}_2(\text{EtNH}_2)_2(\text{O}_2\text{CC}_2\text{F}_5)_3]^+$ | 705   | 7      | 4     | 5     | -     |

**Table S2.** Mass spectrometry EI MS data of  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_3\text{F}_7)_4]$  (3).

| Fragments                                                             | <i>m/z</i> | RI [%] |       |       |       |
|-----------------------------------------------------------------------|------------|--------|-------|-------|-------|
|                                                                       |            | 357 K  | 417 K | 463 K | 542 K |
| $[\text{C}_2\text{H}_4\text{N}]^+$                                    | 42         | 15     | 2     | 1     | -     |
| $[\text{CO}_2]^+$                                                     | 44         | 36     | 8     | 7     | 9     |
| $[\text{C}_2\text{H}_7\text{N}]^+ / [\text{COOH}]^+$                  | 45         | 38     | 7     | 3     | 4     |
| $[\text{CF}_2]^+$                                                     | 50         | 3      | 4     | 3     | 3     |
| $[\text{CF}_3]^+$                                                     | 69         | 45     | 33    | 23    | 23    |
| $[\text{C}_2\text{F}_4]^+$                                            | 100        | 30     | 25    | 22    | 21    |
| $[\text{C}_2\text{F}_5]^+$                                            | 119        | 34     | 12    | 7     | 7     |
| $[\text{C}_3\text{F}_5]^+$                                            | 131        | 77     | 4     | 3     | 6     |
| $[\text{C}_3\text{F}_7]^+$                                            | 169        | 25     | 19    | 8     | 11    |
| $[\text{Cu}]^+$                                                       | 63         | 6      | 17    | 15    | 12    |
| $[\text{Cu}(\text{O}_2\text{C})]^+$                                   | 107        | 2      | 8     | 7     | 2     |
| $[\text{Cu}(\text{EtNH}_2)]^+$                                        | 108        | 3      | 3     | 2     | -     |
| $[\text{Cu}_2\text{F}]^+$                                             | 145        | 12     | 17    | 17    | 17    |
| $[\text{Cu}_2(\text{O}_2\text{CC}_3\text{F}_7)]^+$                    | 339        | 100    | 100   | 100   | 100   |
| $[\text{Cu}_2(\text{EtNH}_2)(\text{O}_2\text{CC}_3\text{F}_7)]^+$     | 384        | 2      | 2     | 1     | -     |
| $[\text{Cu}_2(\text{O}_2\text{CC}_3\text{F}_7)_2]^+$                  | 552        | 29     | 28    | 27    | 26    |
| $[\text{Cu}_2(\text{EtNH}_2)(\text{O}_2\text{CC}_3\text{F}_7)_3]^+$   | 810        | 1      | 2     | 2     | -     |
| $[\text{Cu}_2(\text{EtNH}_2)_2(\text{O}_2\text{CC}_3\text{F}_7)_3]^+$ | 855        | 8      | 3     | 1     | -     |

**Table S3.** Mass spectrometry EI MS data of [Cu<sub>2</sub>(EtNH<sub>2</sub>)<sub>2</sub>(μ-O<sub>2</sub>CC<sub>4</sub>F<sub>9</sub>)<sub>4</sub>] (4).

| Fragments                                                                                                                       | <i>m/z</i> | RI [%] |       |       |       |
|---------------------------------------------------------------------------------------------------------------------------------|------------|--------|-------|-------|-------|
|                                                                                                                                 |            | 305 K  | 345 K | 424 K | 590 K |
| [C <sub>2</sub> H <sub>4</sub> N] <sup>+</sup>                                                                                  | 42         | 4      | 3     | 1     | -     |
| [CO <sub>2</sub> ] <sup>+</sup>                                                                                                 | 44         | 45     | 34    | 20    | 27    |
| [C <sub>2</sub> H <sub>7</sub> N] <sup>+</sup> /[COOH] <sup>+</sup>                                                             | 45         | 10     | 10    | 3     | 1     |
| [CF <sub>2</sub> ] <sup>+</sup>                                                                                                 | 50         | 7      | 5     | 3     | 2     |
| [CF <sub>3</sub> ] <sup>+</sup>                                                                                                 | 69         | 92     | 73    | 46    | 34    |
| [C <sub>2</sub> F <sub>3</sub> ] <sup>+</sup>                                                                                   | 81         | 4      | 3     | 2     | 2     |
| [C <sub>3</sub> F <sub>3</sub> ] <sup>+</sup>                                                                                   | 93         | 8      | 5     | 4     | 7     |
| [CF <sub>3</sub> CO] <sup>+</sup>                                                                                               | 97         | 1      | 1     | 1     | -     |
| [C <sub>2</sub> F <sub>4</sub> ] <sup>+</sup>                                                                                   | 100        | 84     | 66    | 42    | 18    |
| [C <sub>2</sub> F <sub>5</sub> ] <sup>+</sup>                                                                                   | 119        | 16     | 14    | 9     | 4     |
| [C <sub>3</sub> F <sub>5</sub> ] <sup>+</sup>                                                                                   | 131        | 100    | 80    | 52    | 100   |
| [C <sub>3</sub> F <sub>6</sub> ] <sup>+</sup>                                                                                   | 150        | 12     | 11    | 7     | 4     |
| [C <sub>4</sub> F <sub>7</sub> ] <sup>+</sup>                                                                                   | 181        | 6      | 5     | 3     | 13    |
| [C <sub>4</sub> F <sub>9</sub> ] <sup>+</sup>                                                                                   | 219        | 15     | 15    | 10    | 2     |
| [Cu] <sup>+</sup>                                                                                                               | 63         | 6      | 7     | 7     | -     |
| [Cu <sub>2</sub> ] <sup>+</sup>                                                                                                 | 126        | 1      | 1     | 1     | -     |
| [Cu <sub>2</sub> F] <sup>+</sup>                                                                                                | 145        | 9      | 12    | 12    | -     |
| [Cu <sub>2</sub> (O <sub>2</sub> CC <sub>4</sub> F <sub>9</sub> )] <sup>+</sup>                                                 | 389        | 69     | 100   | 100   | 1     |
| [Cu <sub>2</sub> (EtNH <sub>2</sub> )(O <sub>2</sub> CC <sub>4</sub> F <sub>9</sub> )] <sup>+</sup>                             | 434        | 1      | 1     | -     | -     |
| [Cu <sub>2</sub> (O <sub>2</sub> CC <sub>4</sub> F <sub>9</sub> ) <sub>2</sub> ] <sup>+</sup>                                   | 652        | 16     | 25    | 26    | -     |
| [Cu <sub>2</sub> (EtNH <sub>2</sub> )(O <sub>2</sub> CC <sub>4</sub> F <sub>9</sub> ) <sub>3</sub> ] <sup>+</sup>               | 960        | 3      | 3     | -     | -     |
| [Cu <sub>2</sub> (EtNH <sub>2</sub> ) <sub>2</sub> (O <sub>2</sub> CC <sub>4</sub> F <sub>9</sub> ) <sub>3</sub> ] <sup>+</sup> | 1005       | 1      | 1     | -     | -     |
| [Cu <sub>3</sub> (O <sub>2</sub> CC <sub>4</sub> F <sub>9</sub> ) <sub>5</sub> ] <sup>+</sup>                                   | 1506       | <1     | <1    | 1     | -     |



**Table S4.** Mass spectrometry EI MS data of [Cu<sub>2</sub>(EtNH<sub>2</sub>)<sub>2</sub>(μ-O<sub>2</sub>CC<sub>5</sub>F<sub>11</sub>)<sub>4</sub>] (5).

| Fragments                                                                                                                        | <i>m/z</i> | RI [%] |       |       |
|----------------------------------------------------------------------------------------------------------------------------------|------------|--------|-------|-------|
|                                                                                                                                  |            | 319 K  | 425 K | 590 K |
| [C <sub>2</sub> H <sub>3</sub> N] <sup>+</sup>                                                                                   | 41         | 1      | -     | 1     |
| [C <sub>2</sub> H <sub>4</sub> N] <sup>+</sup>                                                                                   | 42         | 2      | -     | -     |
| [CO <sub>2</sub> ] <sup>+</sup>                                                                                                  | 44         | 11     | 3     | 16    |
| [C <sub>2</sub> H <sub>7</sub> N] <sup>+</sup> /[COOH] <sup>+</sup>                                                              | 45         | 28     | 8     | 2     |
| [CF <sub>2</sub> ] <sup>+</sup>                                                                                                  | 50         | 4      | 2     | 1     |
| [CF <sub>3</sub> ] <sup>+</sup>                                                                                                  | 69         | 70     | 33    | 30    |
| [C <sub>2</sub> F <sub>3</sub> ] <sup>+</sup>                                                                                    | 81         | 3      | 1     | 2     |
| [C <sub>3</sub> F <sub>3</sub> ] <sup>+</sup>                                                                                    | 93         | 6      | 5     | 11    |
| [C <sub>2</sub> F <sub>4</sub> ] <sup>+</sup>                                                                                    | 100        | 39     | 24    | 7     |
| [C <sub>2</sub> F <sub>5</sub> ] <sup>+</sup>                                                                                    | 119        | 24     | 13    | 5     |
| [C <sub>3</sub> F <sub>5</sub> ] <sup>+</sup>                                                                                    | 131        | 100    | 67    | 100   |
| [C <sub>3</sub> F <sub>6</sub> ] <sup>+</sup>                                                                                    | 150        | 3      | 2     | 1     |
| [C <sub>3</sub> F <sub>7</sub> ] <sup>+</sup>                                                                                    | 169        | 6      | 3     | 3     |
| [C <sub>4</sub> F <sub>7</sub> ] <sup>+</sup>                                                                                    | 181        | 24     | 17    | 47    |
| [C <sub>4</sub> F <sub>9</sub> ] <sup>+</sup>                                                                                    | 219        | 3      | 2     | 1     |
| [C <sub>5</sub> F <sub>9</sub> ] <sup>+</sup>                                                                                    | 231        | 5      | 4     | 8     |
| [C <sub>5</sub> F <sub>11</sub> ] <sup>+</sup>                                                                                   | 269        | 14     | 8     | -     |
| [Cu] <sup>+</sup>                                                                                                                | 63         | 6      | 3     | -     |
| [Cu <sub>2</sub> ] <sup>+</sup>                                                                                                  | 126        | 1      | 1     | -     |
| [Cu <sub>2</sub> F] <sup>+</sup>                                                                                                 | 145        | 9      | 8     | -     |
| [Cu <sub>2</sub> (O <sub>2</sub> CC <sub>5</sub> F <sub>11</sub> )] <sup>+</sup>                                                 | 439        | 94     | 100   | -     |
| [Cu <sub>2</sub> (EtNH <sub>2</sub> )(O <sub>2</sub> CC <sub>5</sub> F <sub>11</sub> )] <sup>+</sup>                             | 484        | 2      | -     | -     |
| [Cu <sub>2</sub> (O <sub>2</sub> CC <sub>5</sub> F <sub>11</sub> ) <sub>2</sub> ] <sup>+</sup>                                   | 752        | 22     | 21    | -     |
| [Cu <sub>2</sub> (EtNH <sub>2</sub> )(O <sub>2</sub> CC <sub>5</sub> F <sub>11</sub> ) <sub>3</sub> ] <sup>+</sup>               | 1110       | 4      | 1     | -     |
| [Cu <sub>2</sub> (EtNH <sub>2</sub> ) <sub>2</sub> (O <sub>2</sub> CC <sub>5</sub> F <sub>11</sub> ) <sub>3</sub> ] <sup>+</sup> | 1155       | 2      | -     | -     |
| [Cu <sub>3</sub> (O <sub>2</sub> CC <sub>5</sub> F <sub>11</sub> ) <sub>5</sub> ] <sup>+</sup>                                   | 1756       | -      | 2     | -     |

**Table S5.** Mass spectrometry EI MS data of  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_6\text{F}_{13})_4]$  (6).

| Fragments                                                                | $m/z$ | RI [%] |       |       |       |
|--------------------------------------------------------------------------|-------|--------|-------|-------|-------|
|                                                                          |       | 305 K  | 398 K | 431 K | 616 K |
| $[\text{C}_2\text{H}_4\text{N}]^+$                                       | 42    | 9      | 2     | 1     | -     |
| $[\text{CO}_2]^+$                                                        | 44    | 41     | 21    | 13    | 18    |
| $[\text{C}_2\text{H}_7\text{N}]^+ / [\text{COOH}]^+$                     | 45    | 25     | 8     | 4     | -     |
| $[\text{CF}_2]^+$                                                        | 50    | 4      | 4     | 4     | 1     |
| $[\text{CF}_3]^+$                                                        | 69    | 81     | 78    | 65    | 34    |
| $[\text{C}_2\text{F}_3]^+$                                               | 81    | 3      | 4     | 3     | 1     |
| $[\text{C}_3\text{F}_3]^+$                                               | 93    | 9      | 8     | 8     | 8     |
| $[\text{C}_2\text{F}_4]^+$                                               | 100   | 39     | 56    | 55    | 10    |
| $[\text{C}_2\text{F}_5]^+$                                               | 119   | 23     | 29    | 25    | 10    |
| $[\text{C}_3\text{F}_5]^+$                                               | 131   | 100    | 96    | 81    | 100   |
| $[\text{C}_3\text{F}_6]^+$                                               | 150   | 3      | 5     | 4     | 1     |
| $[\text{C}_3\text{F}_7]^+$                                               | 169   | 9      | 14    | 12    | 2     |
| $[\text{C}_4\text{F}_7]^+$                                               | 181   | 20     | 22    | 19    | 26    |
| $[\text{C}_5\text{F}_7]^+$                                               | 193   | 1      | 2     | 2     | 2     |
| $[\text{C}_5\text{F}_9]^+$                                               | 231   | 12     | 19    | 17    | 16    |
| $[\text{C}_6\text{F}_{13}]^+$                                            | 319   | 3      | 9     | 10    | -     |
| $[\text{Cu}]^+$                                                          | 63    | 3      | 6     | 6     | -     |
| $[\text{Cu}(\text{O}_2\text{C})]^+$                                      | 107   | 1      | 3     | 4     | -     |
| $[\text{Cu}(\text{EtNH}_2)]^+$                                           | 108   | 1      | 2     | 1     | -     |
| $[\text{Cu}_2\text{F}]^+$                                                | 145   | 5      | 11    | 10    | -     |
| $[\text{Cu}_2(\text{O}_2\text{CC}_6\text{F}_{13})]^+$                    | 489   | 34     | 100   | 100   | -     |
| $[\text{Cu}_2(\text{EtNH}_2)(\text{O}_2\text{CC}_6\text{F}_{13})]^+$     | 534   | -      | 2     | 1     | -     |
| $[\text{Cu}_2(\text{O}_2\text{CC}_6\text{F}_{13})_2]^+$                  | 852   | 4      | 18    | 20    | -     |
| $[\text{Cu}_2(\text{EtNH}_2)(\text{O}_2\text{CC}_6\text{F}_{13})_3]^+$   | 1260  | -      | 2     | 2     | -     |
| $[\text{Cu}_2(\text{EtNH}_2)_2(\text{O}_2\text{CC}_6\text{F}_{13})_3]^+$ | 1305  | 1      | 1     | -     | -     |

**Table S6.** Mass spectrometry EI MS data of  $[\text{Cu}_2(\text{iPrNH}_2)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$  (8).

| Fragments                                                              | <i>m/z</i>        | RI [%] |       |       |       |
|------------------------------------------------------------------------|-------------------|--------|-------|-------|-------|
|                                                                        |                   | 357 K  | 404 K | 458 K | 505 K |
| $[\text{C}_2\text{H}_4\text{N}]^+$                                     | 42                | 1      | 1     | 47    | 21    |
| $[\text{C}_3\text{H}_7]^+$                                             | 43                | 86     | 87    | 18    | 6     |
| $[\text{CO}_2]^+$                                                      | 44                | 7      | 5     | 4     | 80    |
| $[\text{C}_2\text{H}_7\text{N}]^+ / [\text{COOH}]^+$                   | 45                | 68     | 41    | 52    | 40    |
| $[\text{CF}_2]^+$                                                      | 50                | 14     | -     | 100   | 66    |
| $[\text{C}_3\text{H}_7\text{N}]^+$                                     | 57                | 30     | 14    | 4     | 3     |
| $[\text{C}_3\text{H}_8\text{N}]^+$                                     | 58                | 1      | 1     | 33    | 7     |
| $[\text{C}_3\text{H}_9\text{N}]^+$                                     | 59                | 40     | 46    | 8     | 2     |
| $[\text{CF}_3]^+$                                                      | 69                | 77     | 4     | 3     | 2     |
| $[\text{CF}_3\text{CO}]^+$                                             | 97                | 26     | 74    | 27    | 19    |
| $[\text{C}_2\text{F}_4]^+$                                             | 100               | 66     | 2     | -     | 100   |
| $[\text{C}_2\text{F}_5]^+$                                             | 119               | 63     | 3     | 1     | -     |
| $[\text{Cu}]^+$                                                        | 63                | 3      | -     | 22    | 16    |
| $[\text{Cu}(\text{O}_2\text{C})]^+$                                    | 107               | -      | 45    | 4     | 3     |
| $[\text{Cu}(\text{iPrNH}_2)]^+$                                        | 122               | 32     | 53    | 10    | -     |
| $[\text{Cu}_2]^+$                                                      | 126               | 1      | 4     | 7     | 4     |
| $[\text{Cu}_2\text{F}]^+$                                              | 145               | 2      | -     | 19    | 13    |
| $[\text{Cu}(\text{iPrNH}_2)(\text{O}_2\text{CC}_2\text{F}_5)]^+$       | 285               | 10     | 24    | 7     | -     |
| $[\text{Cu}_2(\text{O}_2\text{CC}_2\text{F}_5)]^+$                     | 289               | 14     | 3     | 60    | 38    |
| $[\text{Cu}_2(\text{iPrNH}_2)(\text{O}_2\text{CC}_2\text{F}_5)]^+$     | 348               | 9      | 16    | 2     | -     |
| $[\text{Cu}_2(\text{O}_2\text{CC}_2\text{F}_5)_2]^+$                   | 452               | 5      | -     | 16    | 11    |
| $[\text{Cu}_2(\text{iPrNH}_2)(\text{O}_2\text{CC}_2\text{F}_5)_3]^+$   | 674 <sup>a)</sup> | -      | -     | -     | -     |
| $[\text{Cu}_2(\text{iPrNH}_2)_2(\text{O}_2\text{CC}_2\text{F}_5)_3]^+$ | 733               | 65     | 72    | 1     | -     |

a) The  $[\text{Cu}_2(\text{iPrNH}_2)(\text{O}_2\text{CC}_2\text{F}_5)_3]^+$  ion (674 *m/z*) was detected but not at the temperatures selected for Table S6.

**Table S7.** Mass spectrometry EI MS data of  $[\text{Cu}_2(\text{iPrNH}_2)_2(\mu\text{-O}_2\text{CC}_3\text{F}_7)_4]$  (9).

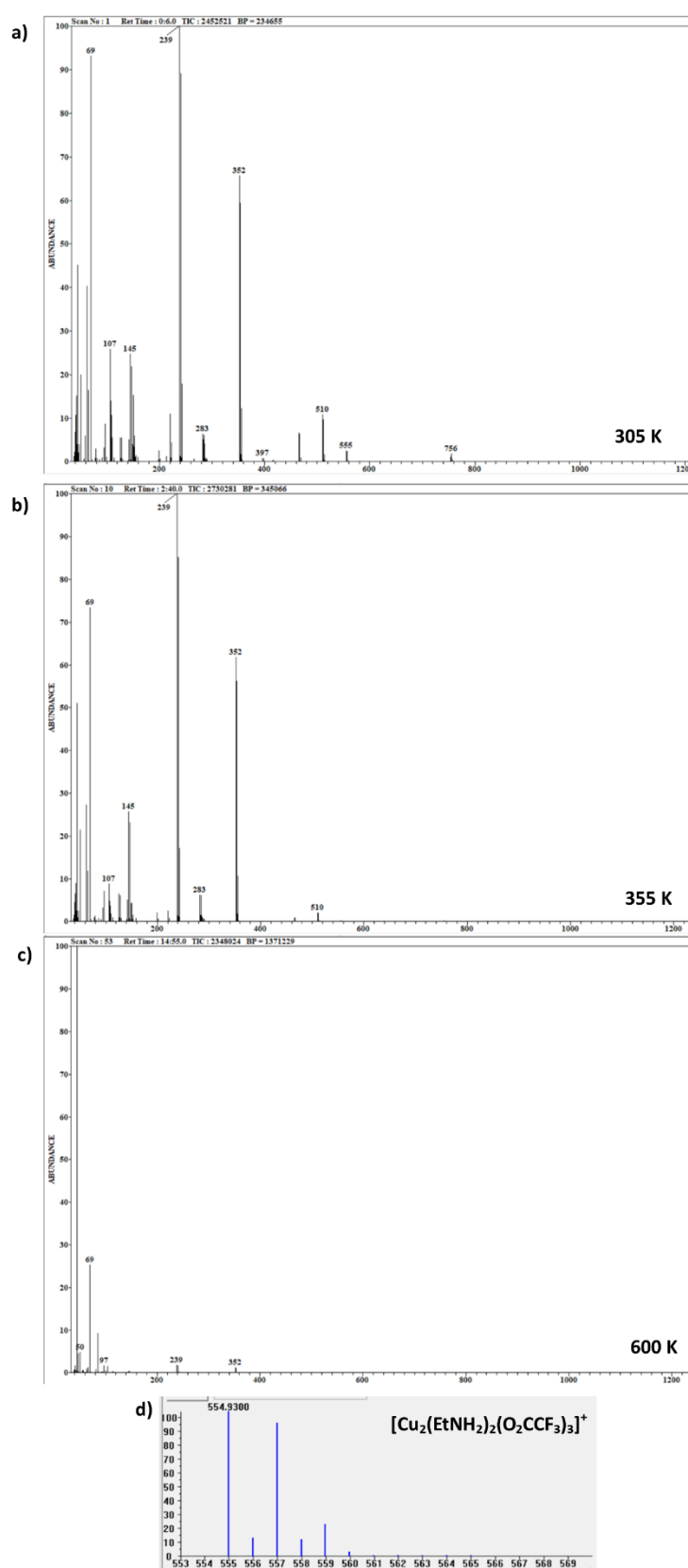
| Fragments                                                              | $m/z$ | RI [%] |       |       |       |
|------------------------------------------------------------------------|-------|--------|-------|-------|-------|
|                                                                        |       | 340 K  | 372 K | 499 K | 544 K |
| $[\text{C}_2\text{H}_4\text{N}]^+$                                     | 42    | 67     | 95    | 100   | 10    |
| $[\text{CO}_2]^+$                                                      | 44    | 2      | 3     | 2     | 14    |
| $[\text{C}_2\text{H}_7\text{N}]^+ / [\text{COOH}]^+$                   | 45    | 12     | 19    | 20    | 22    |
| $[\text{CF}_2]^+$                                                      | 50    | 10     | 5     | 44    | 49    |
| $[\text{C}_3\text{H}_7\text{N}]^+$                                     | 57    | 4      | 6     | 7     | -     |
| $[\text{C}_3\text{H}_8\text{N}]^+$                                     | 58    | 61     | 100   | 42    | 1     |
| $[\text{C}_3\text{H}_9\text{N}]^+$                                     | 59    | 10     | 16    | 10    | -     |
| $[\text{CF}_3]^+$                                                      | 69    | 100    | -     | 2     | 2     |
| $[\text{C}_2\text{F}_4]^+$                                             | 100   | 48     | -     | 1     | 1     |
| $[\text{C}_2\text{F}_5]^+$                                             | 119   | 27     | 63    | 98    | 100   |
| $[\text{C}_3\text{F}_5]^+$                                             | 131   | 54     | 59    | 97    | 79    |
| $[\text{C}_3\text{F}_7]^+$                                             | 169   | 10     | 29    | 47    | 50    |
| $[\text{Cu}]^+$                                                        | 63    | -      | 13    | 26    | 32    |
| $[\text{Cu}(\text{iPrNH}_2)]^+$                                        | 122   | 17     | 25    | 11    | -     |
| $[\text{Cu}_2]^+$                                                      | 126   | -      | 2     | 1     | 5     |
| $[\text{Cu}_2\text{F}]^+$                                              | 145   | 2      | 9     | 20    | 23    |
| $[\text{Cu}(\text{iPrNH}_2)(\text{O}_2\text{CC}_3\text{F}_7)]^+$       | 335   | 2      | 4     | 3     | -     |
| $[\text{Cu}_2(\text{O}_2\text{CC}_3\text{F}_7)]^+$                     | 339   | 5      | 24    | 51    | 54    |
| $[\text{Cu}_2(\text{iPrNH}_2)(\text{O}_2\text{CC}_3\text{F}_7)]^+$     | 398   | 3      | 5     | 1     | -     |
| $[\text{Cu}_2(\text{O}_2\text{CC}_3\text{F}_7)_2]^+$                   | 552   | -      | 4     | 10    | 9     |
| $[\text{Cu}_2(\text{iPrNH}_2)(\text{O}_2\text{CC}_3\text{F}_7)_3]^+$   | 824   | -      | 2     | 2     | -     |
| $[\text{Cu}_2(\text{iPrNH}_2)_2(\text{O}_2\text{CC}_3\text{F}_7)_3]^+$ | 883   | 16     | 24    | -     | -     |

The  $[\text{Cu}_3(\text{O}_2\text{CC}_3\text{F}_7)_5]^+$  ion (1256  $m/z$ ) was detected but not at the temperatures selected for Table S7.

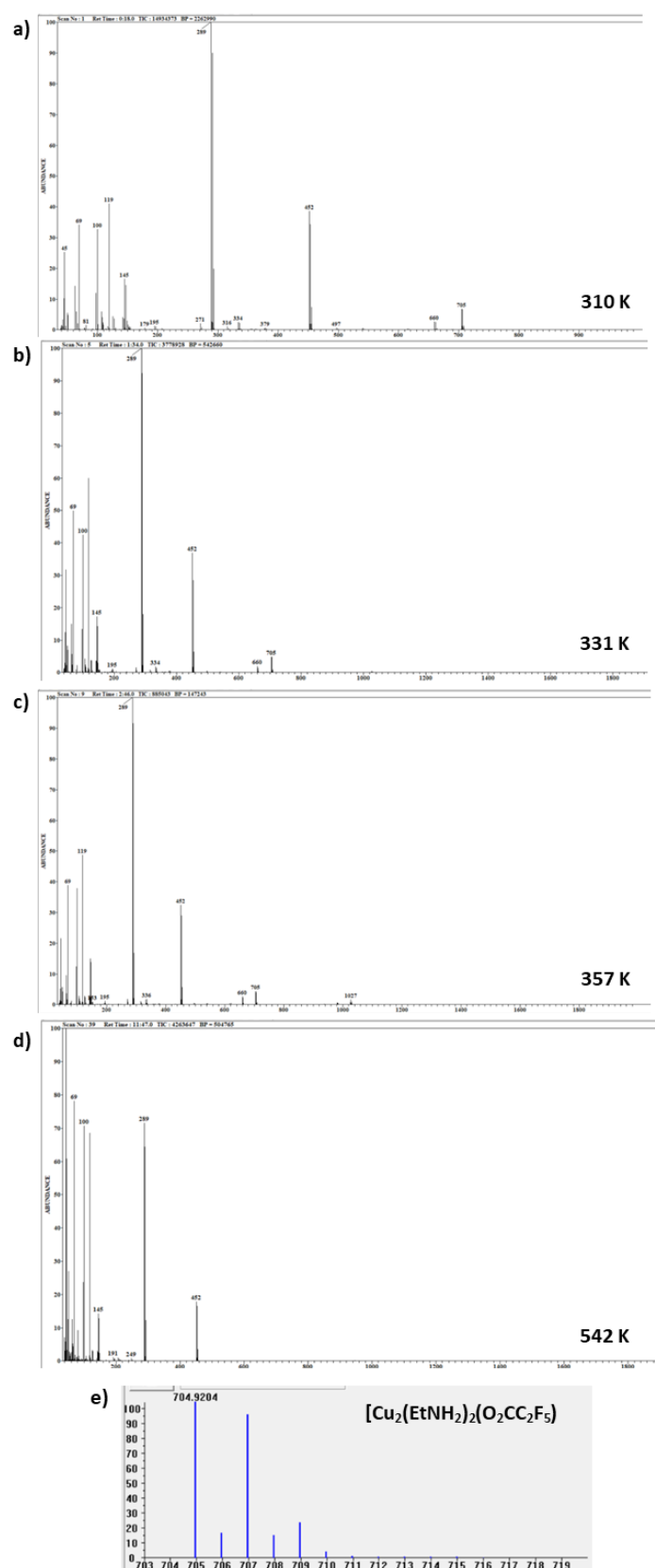
**Table S8.** Mass spectrometry EI MS data of  $[\text{Cu}_2(\text{iPrNH}_2)_2(\mu\text{-O}_2\text{CC}_4\text{F}_9)_4]$  (10).

| Fragments                                                              | $m/z$ | RI [%] |       |       |       |
|------------------------------------------------------------------------|-------|--------|-------|-------|-------|
|                                                                        |       | 369 K  | 388 K | 401 K | 490 K |
| $[\text{C}_2\text{H}_4\text{N}]^+$                                     | 42    | 4      | 6     | 4     | 14    |
| $[\text{C}_3\text{H}_7]^+$                                             | 43    | 41     | 84    | 71    | 3     |
| $[\text{CO}_2]^+$                                                      | 44    | 3      | 5     | 5     | 37    |
| $[\text{C}_2\text{H}_7\text{N}]^+ / [\text{COOH}]^+$                   | 45    | 25     | 42    | 68    | 9     |
| $[\text{CF}_2]^+$                                                      | 50    | 9      | 12    | 19    | 20    |
| $[\text{C}_3\text{H}_7\text{N}]^+$                                     | 57    | 11     | 20    | 15    | 1     |
| $[\text{C}_3\text{H}_8\text{N}]^+$                                     | 58    | 93     | -     | -     | 4     |
| $[\text{C}_3\text{H}_9\text{N}]^+$                                     | 59    | 15     | 21    | 23    | 1     |
| $[\text{CF}_3]^+$                                                      | 69    | 43     | 1     | 72    | 4     |
| $[\text{C}_2\text{F}_3]^+$                                             | 81    | 4      | 6     | 10    | 8     |
| $[\text{C}_3\text{F}_3]^+$                                             | 93    | 12     | 17    | 27    | 31    |
| $[\text{CF}_3\text{CO}]^+$                                             | 97    | 3      | 6     | 10    | 7     |
| $[\text{C}_2\text{F}_4]^+$                                             | 100   | 51     | 100   | 1     | 100   |
| $[\text{C}_2\text{F}_5]^+$                                             | 119   | 27     | 43    | 69    | 44    |
| $[\text{C}_3\text{F}_5]^+$                                             | 131   | 90     | 1     | 1     | -     |
| $[\text{C}_3\text{F}_6]^+$                                             | 150   | 7      | 15    | 30    | 13    |
| $[\text{C}_4\text{F}_7]^+$                                             | 181   | 8      | 10    | 17    | 7     |
| $[\text{C}_4\text{F}_9]^+$                                             | 219   | 6      | 13    | 27    | 7     |
| $[\text{Cu}]^+$                                                        | 63    | 4      | 7     | 13    | 3     |
| $[\text{Cu}_2]^+$                                                      | 126   | 2      | 5     | 3     | -     |
| $[\text{Cu}_2\text{F}]^+$                                              | 145   | 2      | 8     | 18    | 2     |
| $[\text{Cu}(\text{iPrNH}_2)(\text{O}_2\text{CC}_4\text{F}_9)]^+$       | 385   | 2      | 2     | 3     | -     |
| $[\text{Cu}_2(\text{O}_2\text{CC}_4\text{F}_9)]^+$                     | 389   | 6      | 29    | 64    | 5     |
| $[\text{Cu}_2(\text{iPrNH}_2)(\text{O}_2\text{CC}_4\text{F}_9)]^+$     | 448   | 3      | 4     | 5     | -     |
| $[\text{Cu}_2(\text{O}_2\text{CC}_4\text{F}_9)_2]^+$                   | 652   | 1      | 5     | 9     | 1     |
| $[\text{Cu}_2(\text{iPrNH}_2)(\text{O}_2\text{CC}_4\text{F}_9)_3]^+$   | 974   | 1      | 1     | 2     | -     |
| $[\text{Cu}_2(\text{iPrNH}_2)_2(\text{O}_2\text{CC}_4\text{F}_9)_3]^+$ | 1033  | 18     | 20    | 21    | -     |

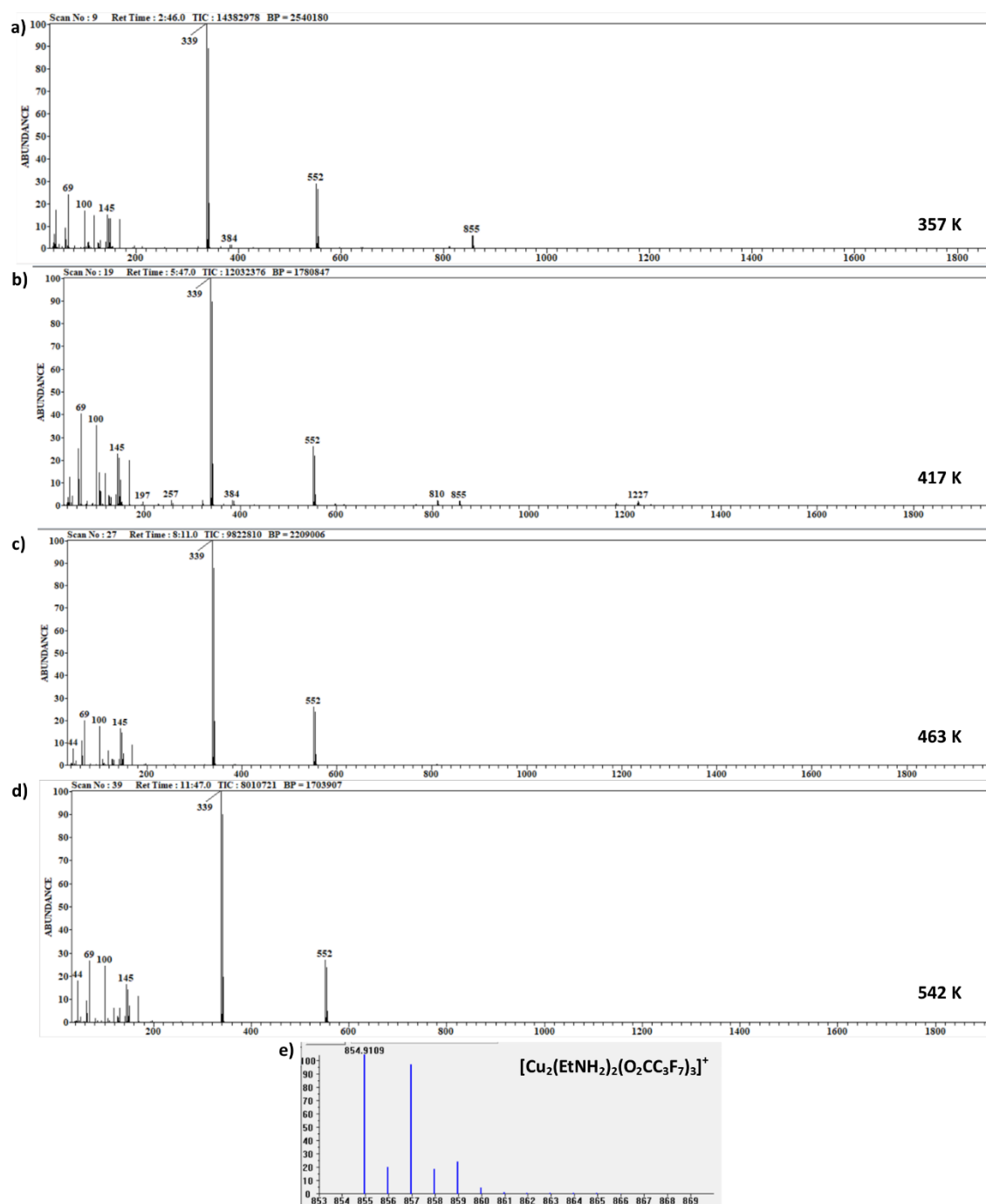
The  $[\text{Cu}_3(\text{O}_2\text{CC}_4\text{F}_9)_5]^+$  ion (1506  $m/z$ ) was detected but not at the temperatures selected for Table S8.



**Figure S11.** Mass spectrometry EI MS spectra of  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CCF}_3)_4]$  (1) at temperature: a) 305 K, b) 355 K, c) 600 K and d) simulation of isotopic pattern for a pseudomolecular ion  $[\text{Cu}_2(\text{EtNH}_2)_2(\text{O}_2\text{CCF}_3)_3]^+$ .

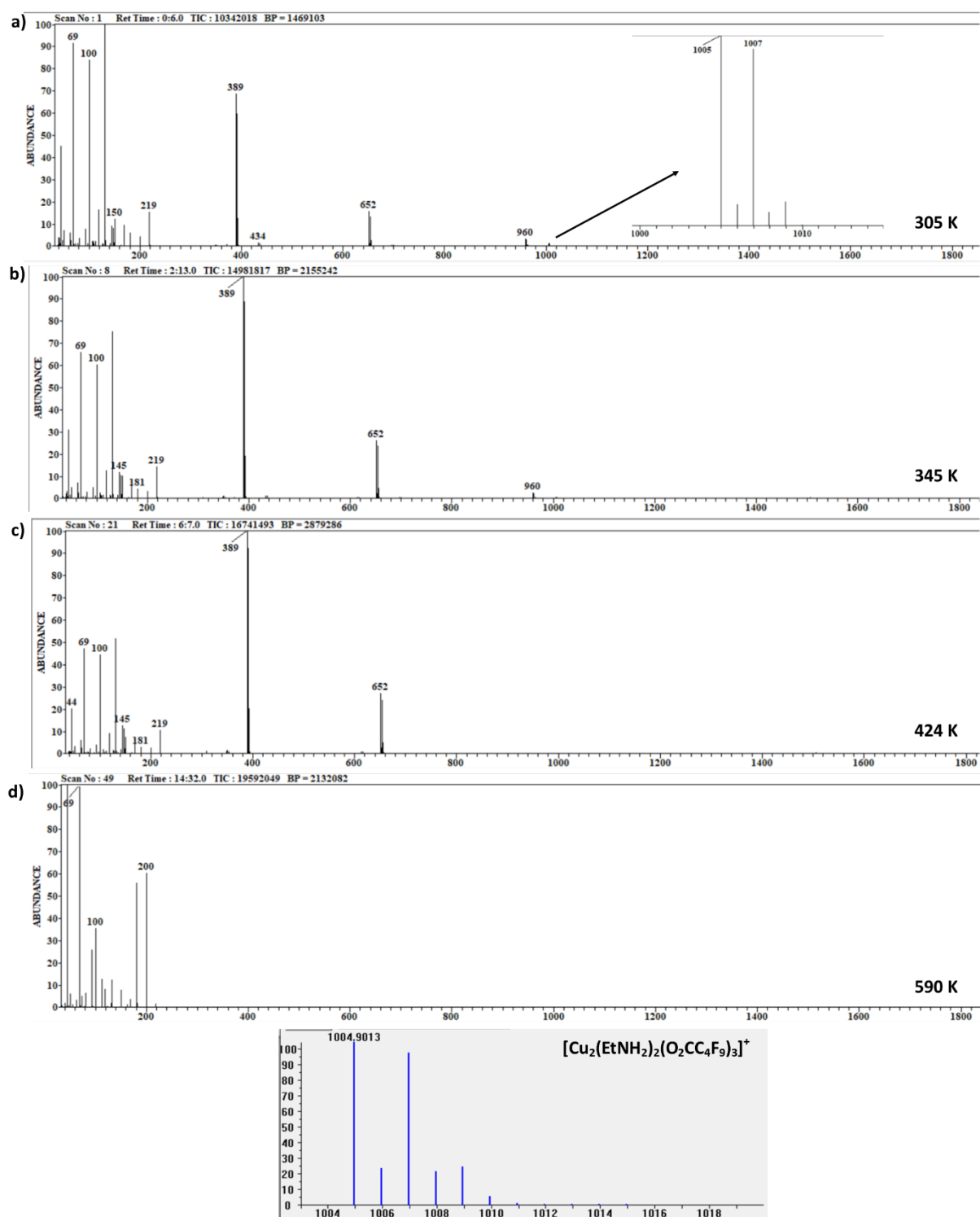


**Figure S12.** Mass spectrometry EI MS spectra of  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$  (2) at temperature: a) 310 K, b) 331 K, c) 357 K d) 542 K and e) simulation of isotopic pattern for a pseudomolecular ion  $[\text{Cu}_2(\text{EtNH}_2)_2(\text{O}_2\text{CC}_2\text{F}_5)_3]^+$ .

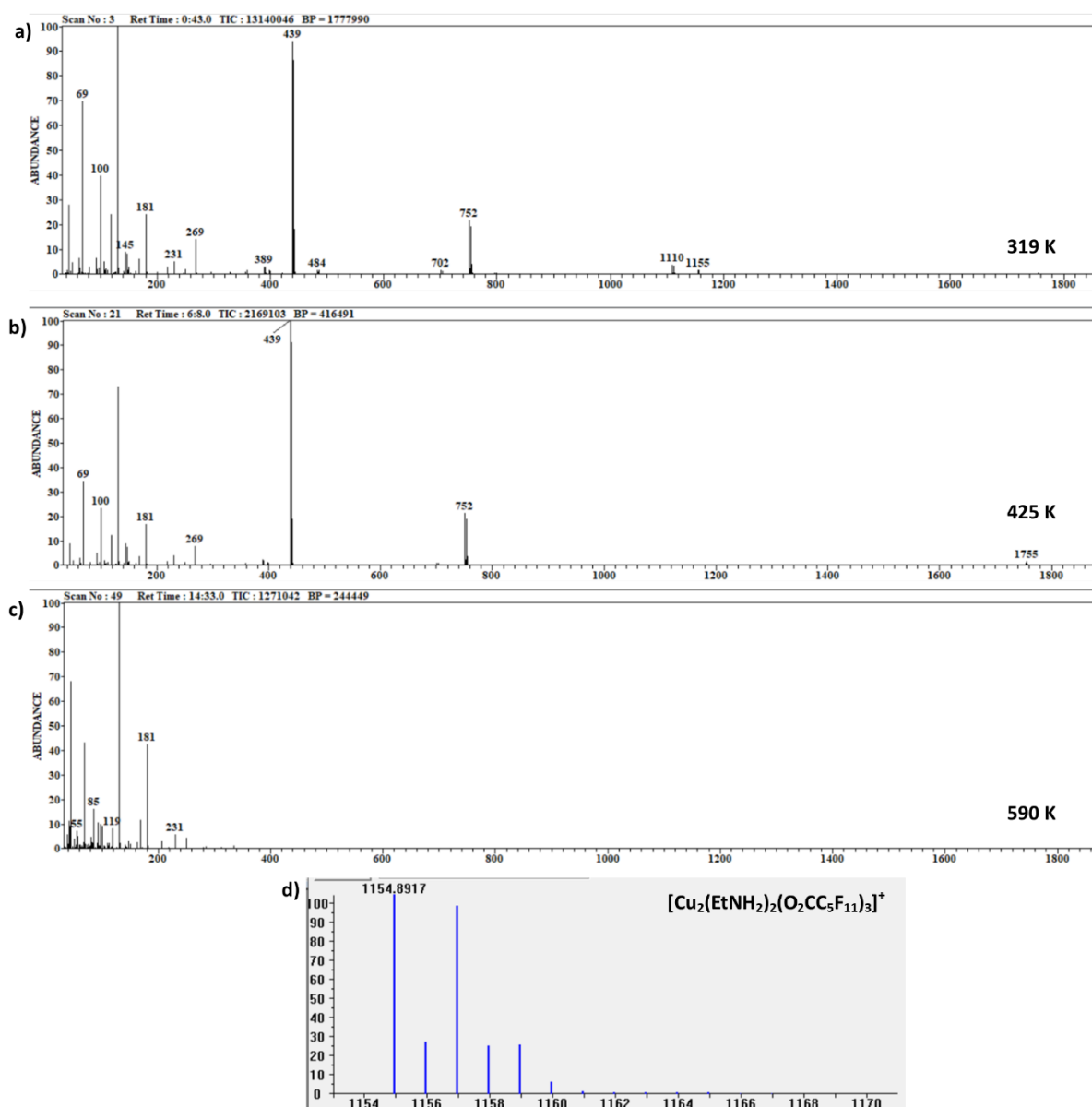


**Figure S13.** Mass spectrometry EI MS spectra of  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_3\text{F}_7)_4]$  (3) at temperature: a) 357 K, b) 417 K, c) 463 K d) 542 K, and e) simulation of isotopic pattern for a pseudomolecular ion  $[\text{Cu}_2(\text{EtNH}_2)_2(\text{O}_2\text{CC}_3\text{F}_7)_3]^+$ .

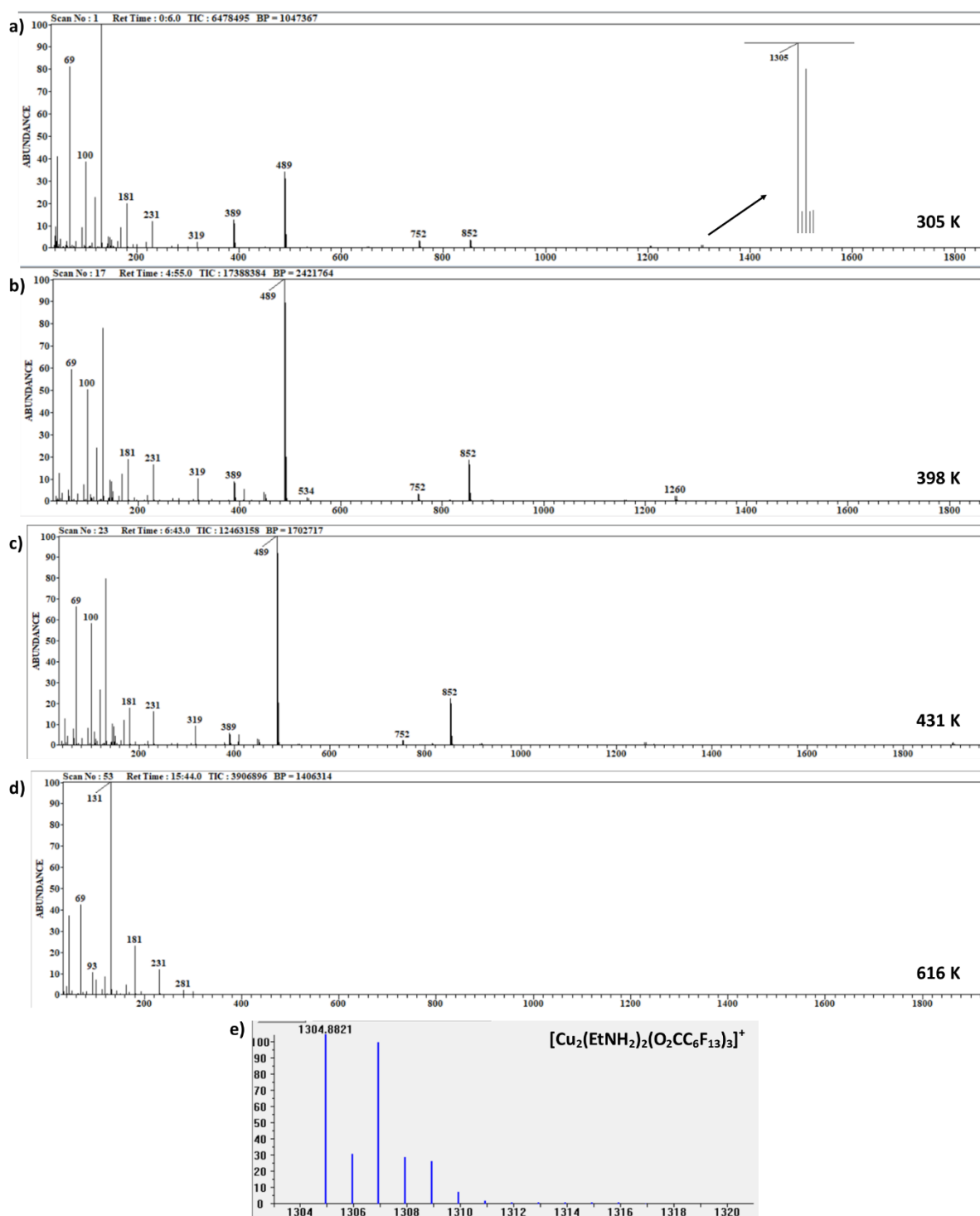




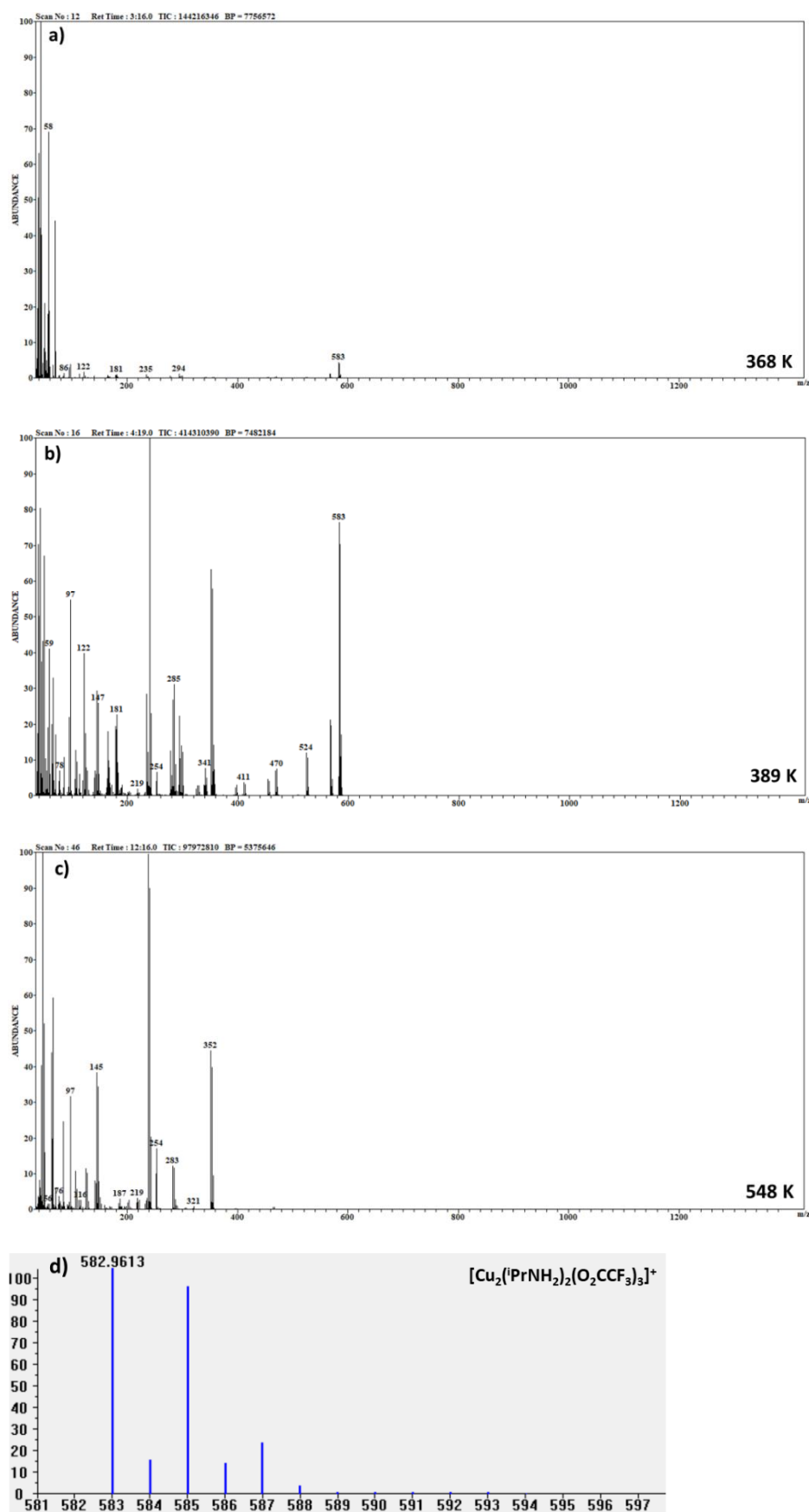
**Figure S14.** Mass spectrometry EI MS spectra of  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_4\text{F}_9)_4]$  (4) at temperature: a) 305 K, b) 345 K, c) 424 K d) 590 K, and e) simulation of isotopic pattern for a pseudomolecular ion  $[\text{Cu}_2(\text{EtNH}_2)_2(\text{O}_2\text{CC}_4\text{F}_9)_3]^+$ .



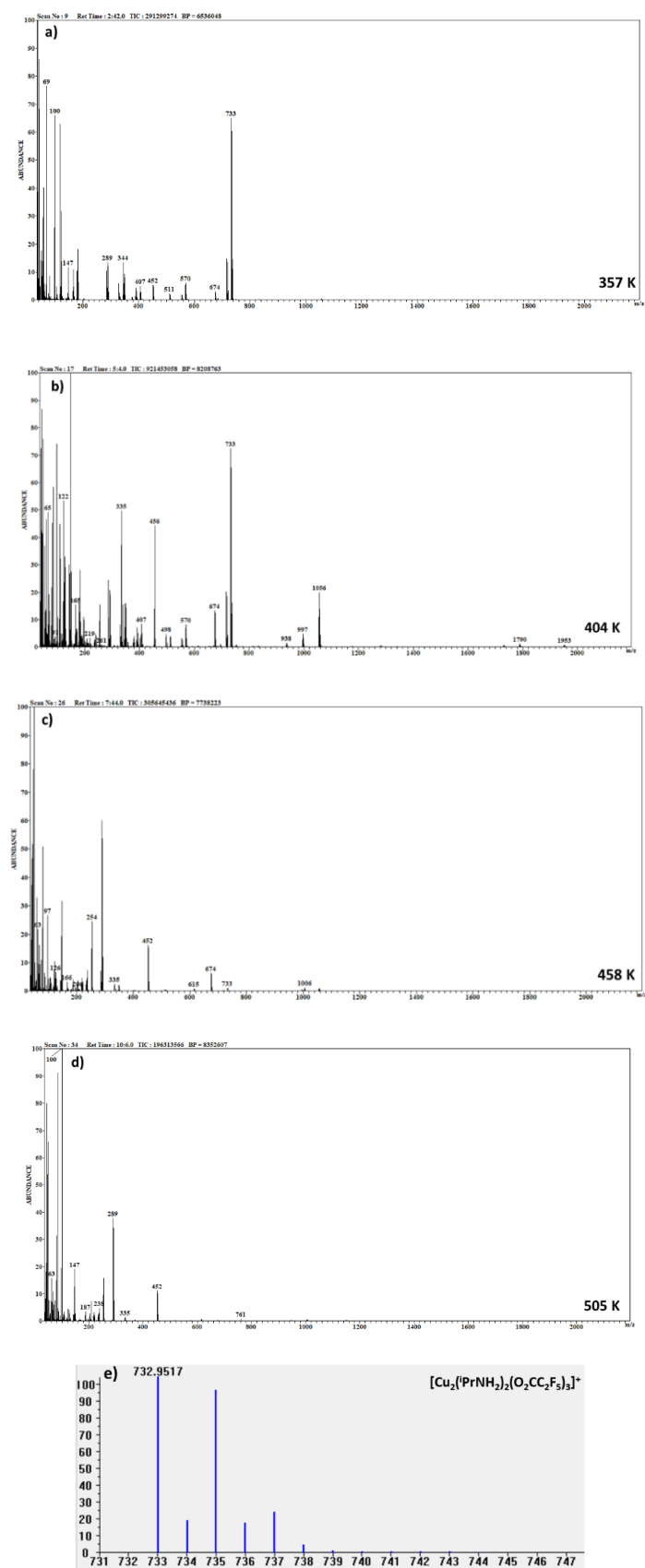
**Figure S15.** Mass spectrometry EI MS spectra of  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_5\text{F}_{11})_4]$  (5) at temperature: a) 319 K, b) 425 K, c) 590 K, and d) simulation of isotopic pattern for a pseudomolecular ion  $[\text{Cu}_2(\text{EtNH}_2)_2(\text{O}_2\text{CC}_5\text{F}_{11})_3]^+$ .



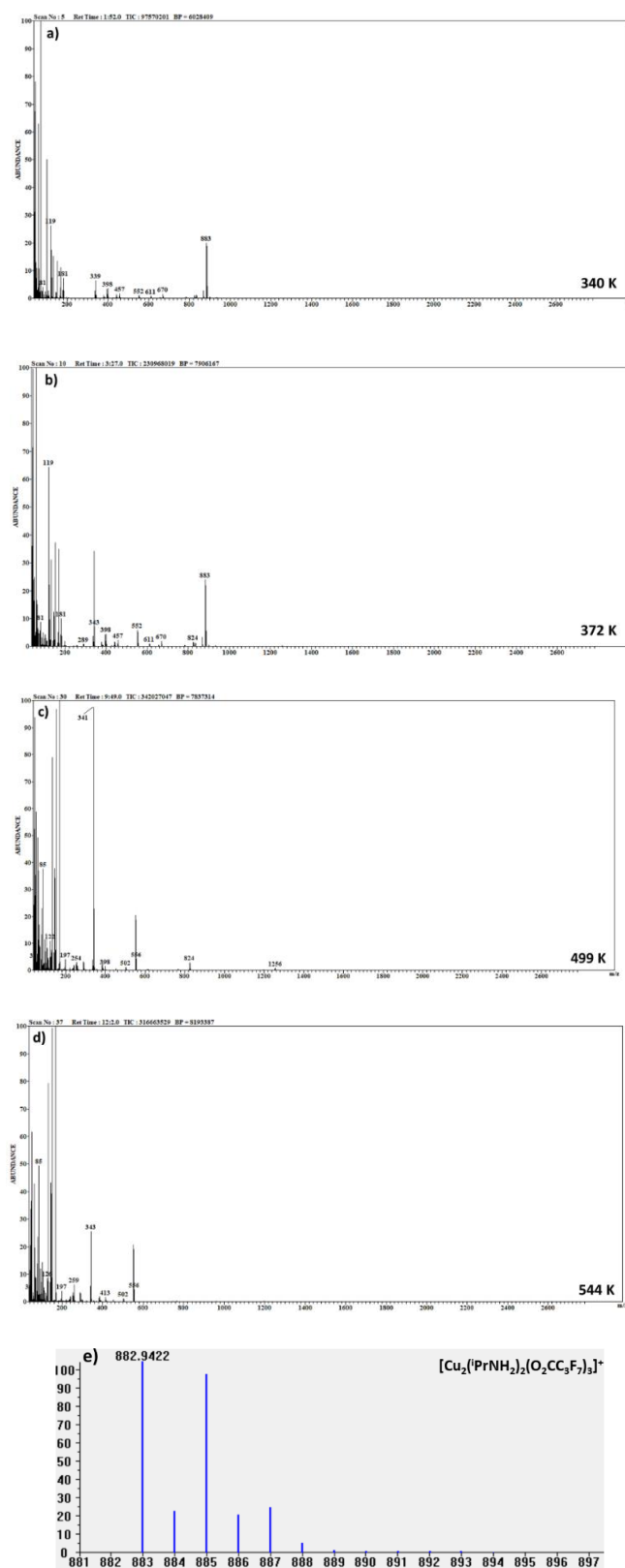
**Figure S16.** Mass spectrometry EI MS spectra of  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_6\text{F}_{13})_4]$  (6) at temperature: a) 305 K, b) 398 K, c) 431 K d) 616 K, and e) simulation of isotopic pattern for a pseudomolecular ion  $[\text{Cu}_2(\text{EtNH}_2)_2(\text{O}_2\text{CC}_6\text{F}_{13})_3]^+$ .



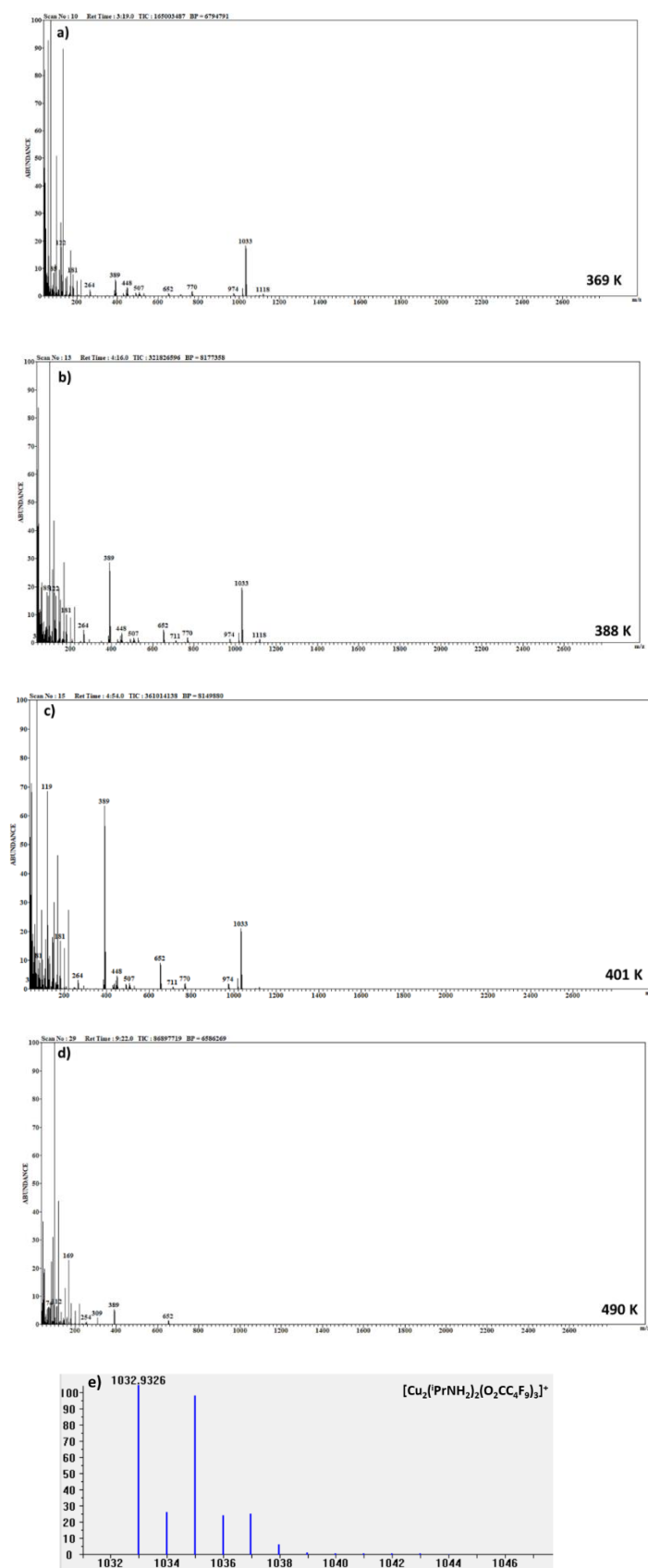
**Figure S17.** Mass spectrometry EI MS spectra of  $[\text{Cu}_2(\text{iPrNH}_2)_2(\mu\text{-O}_2\text{CCF}_3)_4]$  (7) at temperature: a) 368 K, b) 389 K, c) 548, and d) simulation of isotopic pattern for a pseudomolecular ion  $[\text{Cu}_2(\text{iPrNH}_2)_2(\text{O}_2\text{CCF}_3)_3]^+$ .



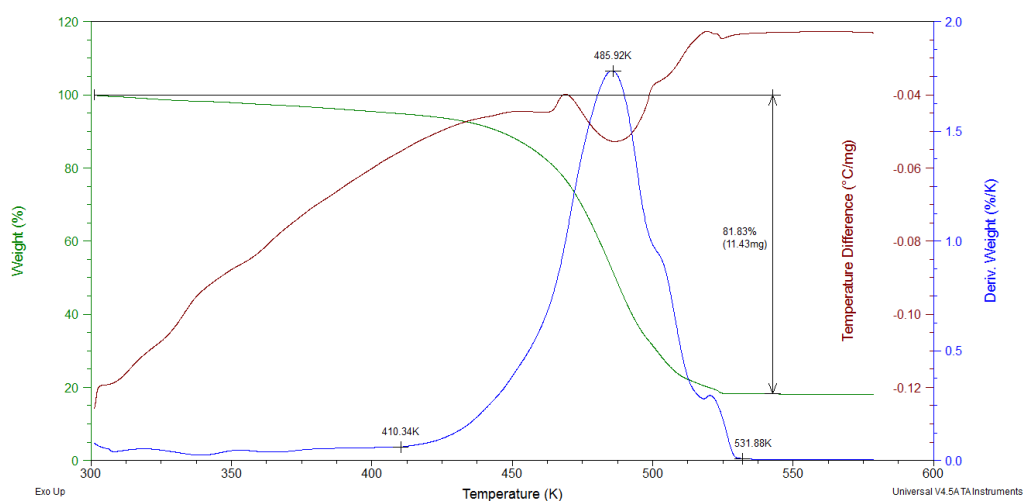
**Figure S18.** Mass spectrometry EI MS spectra of  $[\text{Cu}_2(\text{iPrNH}_2)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$  (8) at temperature: a) 357 K, b) 404 K, c) 458 K, d) 505 K, and e) simulation of isotopic pattern for a pseudomolecular ion  $[\text{Cu}_2(\text{iPrNH}_2)_2(\text{O}_2\text{CC}_2\text{F}_5)_3]^+$ .



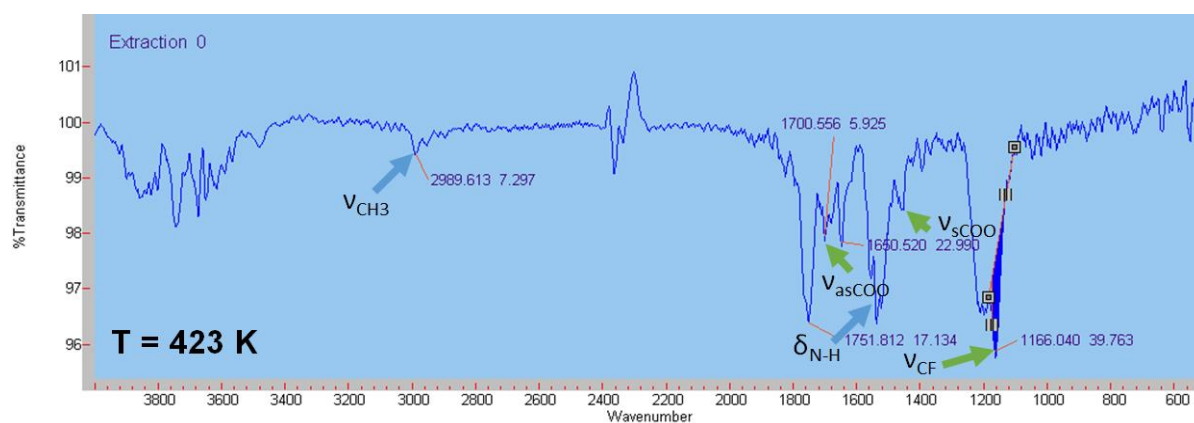
**Figure S19.** Mass spectrometry EI MS spectra of  $[\text{Cu}_2(\text{iPrNH}_2)_2(\mu\text{-O}_2\text{CC}_3\text{F}_7)_4]$  (9) at temperature: a) 340 K, b) 372 K, c) 499 K, d) 544 K, and e) simulation of isotopic pattern for a pseudomolecular ion  $[\text{Cu}_2(\text{iPrNH}_2)_2(\text{O}_2\text{CC}_3\text{F}_7)_3]^+$ .



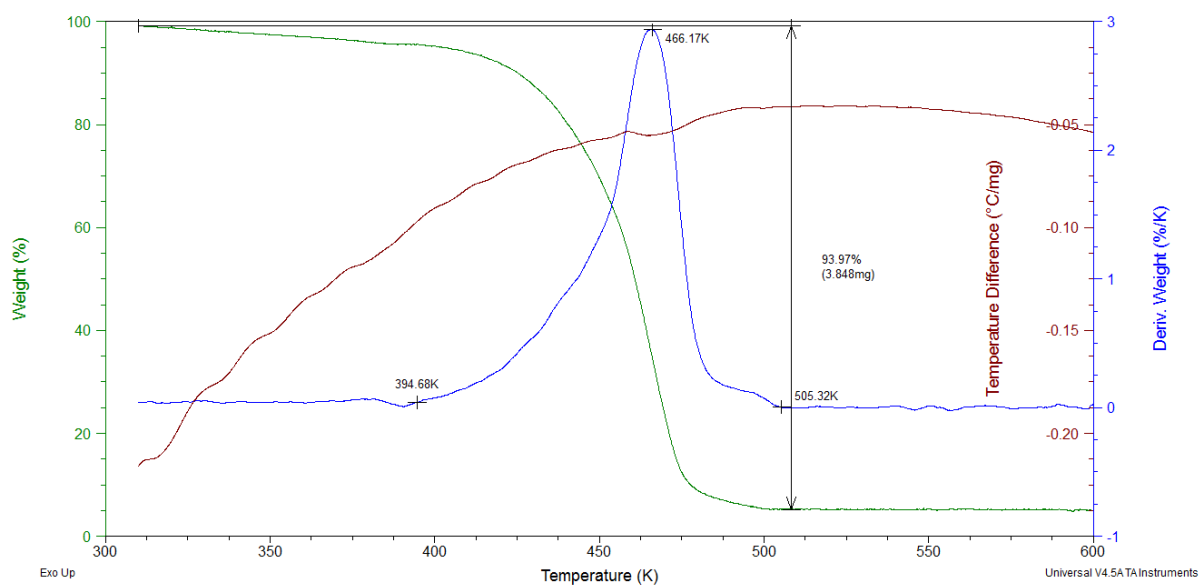
**Figure S20.** Mass spectrometry EI MS spectra of  $[\text{Cu}_2(\text{PrNH}_2)_2(\mu\text{-O}_2\text{CC}_4\text{F}_9)_4]$  (10) a) 369 K, b) 388 K, c) 401 K, d) 490 K, and e) simulation of isotopic pattern for a pseudomolecular ion  $[\text{Cu}_2(\text{PrNH}_2)_2(\text{O}_2\text{CC}_4\text{F}_9)_3]^+$ .



**Figure S21.** Thermal decomposition of  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CCF}_3)_4]$  (1) (TG, DTG, DTA curves).

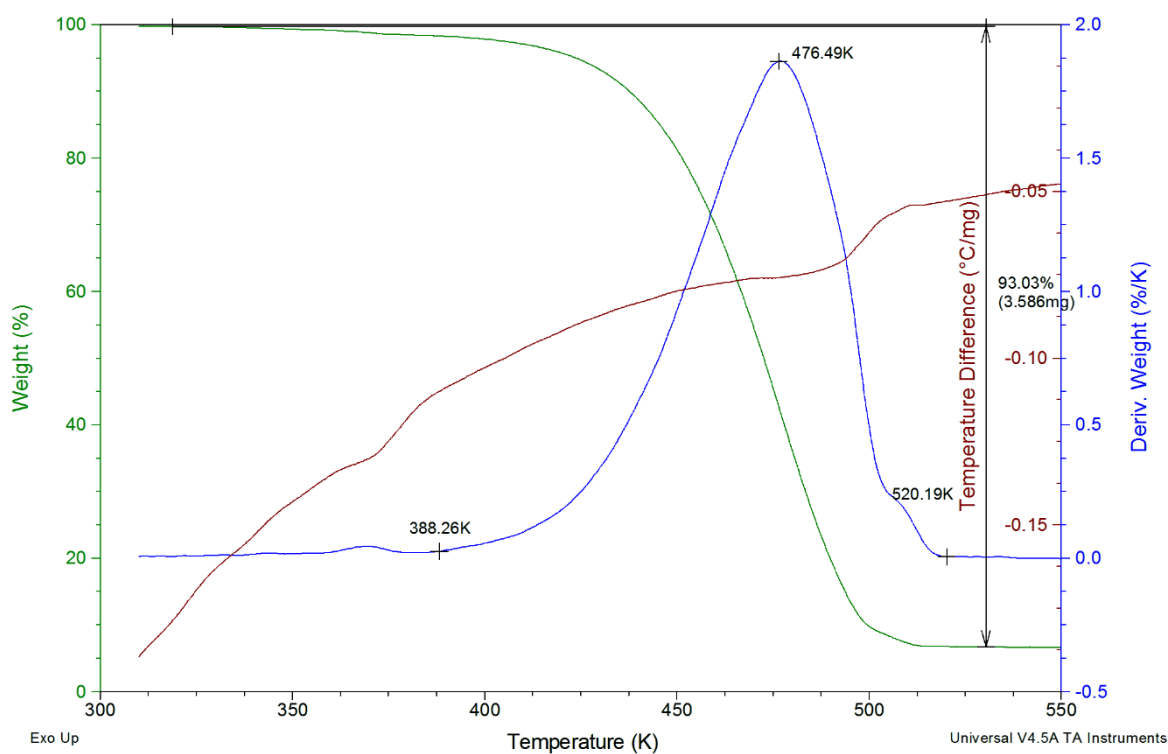


**Figure S22.** TGA/IR spectrum of  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CCF}_3)_4]$  (1) registered at temperature 423 K.

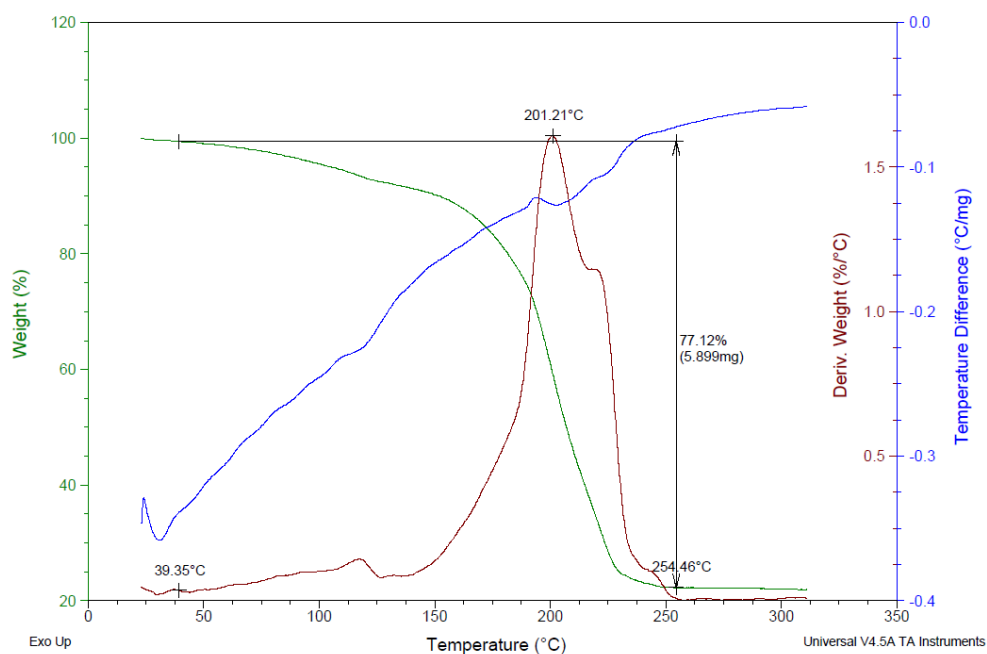


**Figure S23.** Thermal decomposition of  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_3\text{F}_7)_4]$  (3) (TG, DTG, DTA curves).





**Figure S24.** Thermal decomposition of  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_4\text{F}_9)_4]$  (4) (TG, DTG, DTA curves).



**Figure S25.** Thermal decomposition of  $[\text{Cu}_2(\text{iPrNH}_2)_2(\mu\text{-O}_2\text{CCF}_3)_4]$  (7).

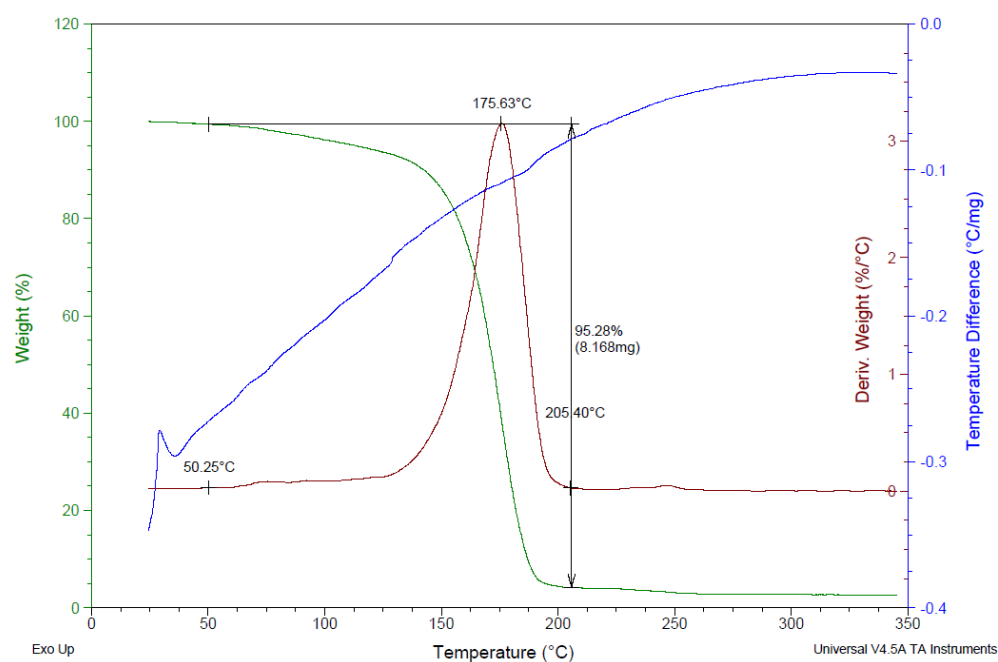


Figure S26. Thermal decomposition of  $[\text{Cu}_2(\text{iPrNH}_2)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$  (8).

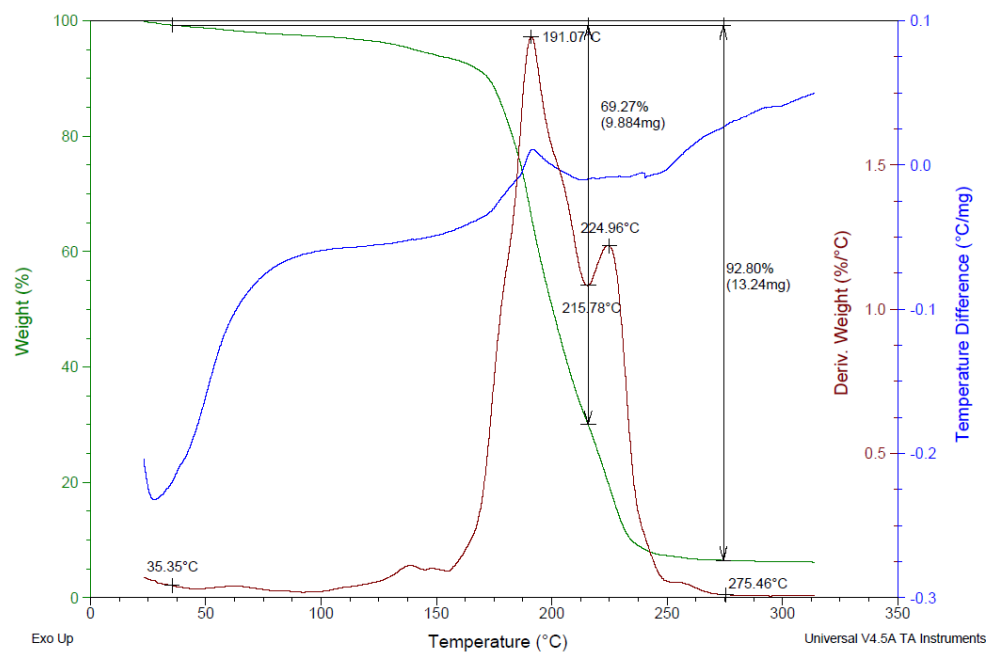


Figure S27. Thermal decomposition of  $[\text{Cu}_2(\text{iPrNH}_2)_2(\mu\text{-O}_2\text{CC}_3\text{F}_7)_4]$  (9).

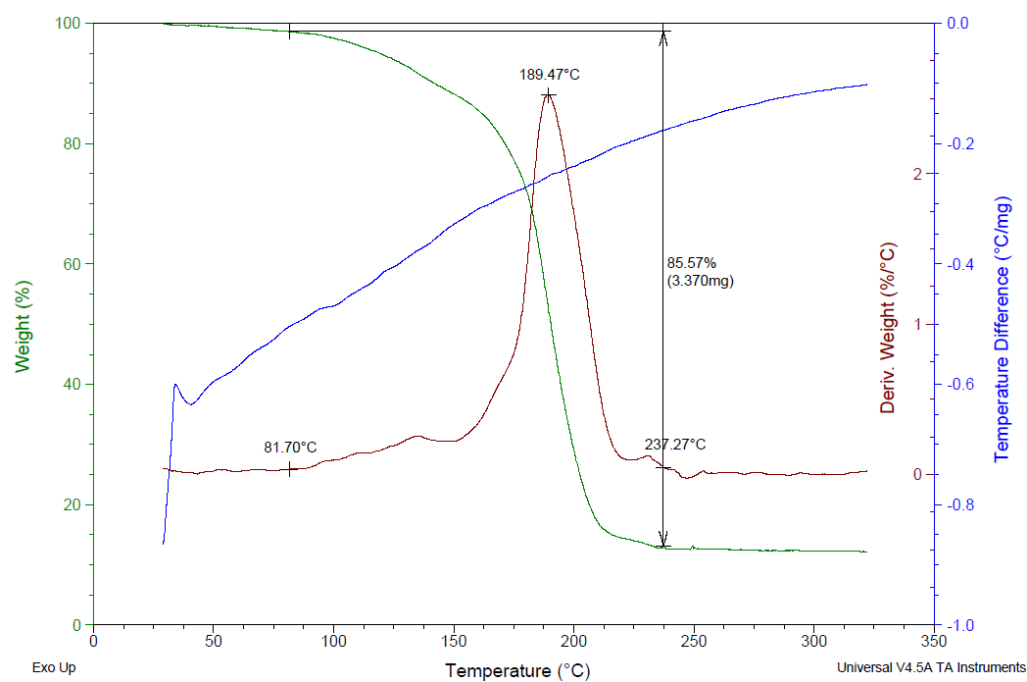


Figure S28. Thermal decomposition of  $[\text{Cu}_2(\text{iPrNH}_2)_2(\mu\text{-O}_2\text{CC}_3\text{F}_7)_4]$  (10).

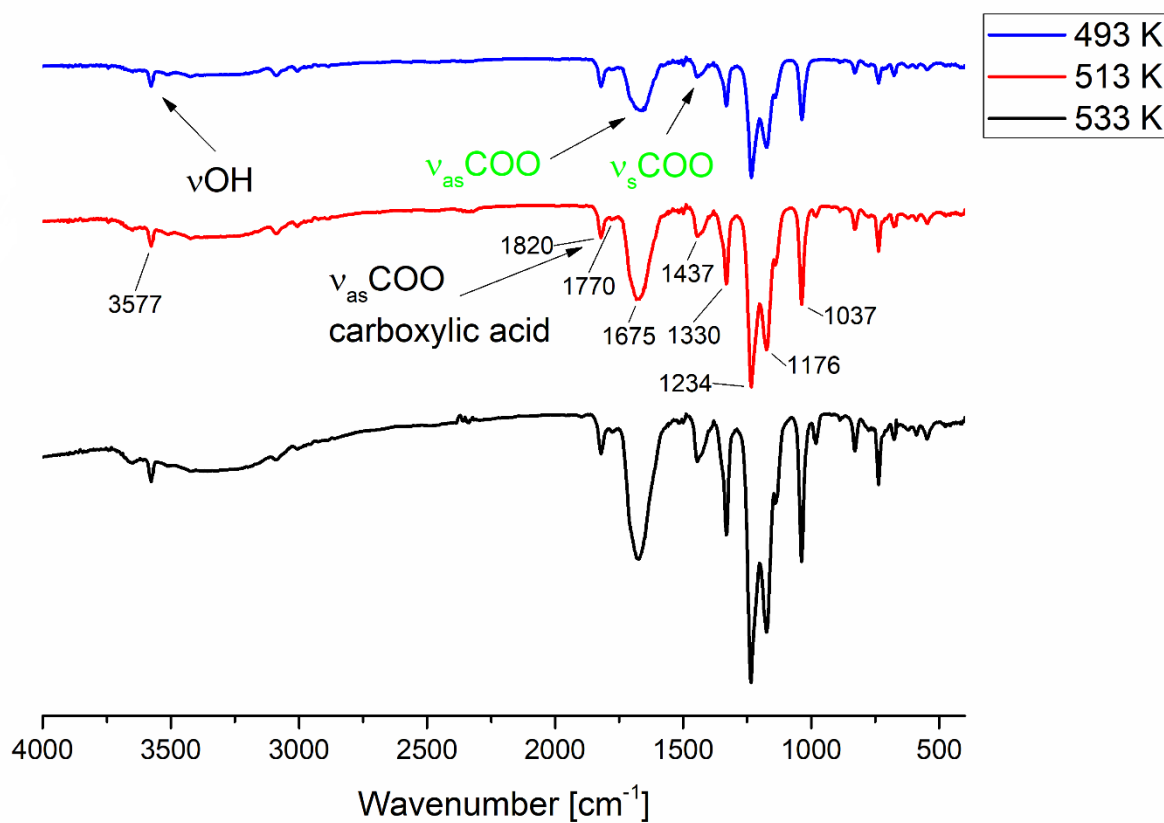


Figure S29. Temperature variable infrared spectra VT IR of vapors formed during the  $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$  compound heating.

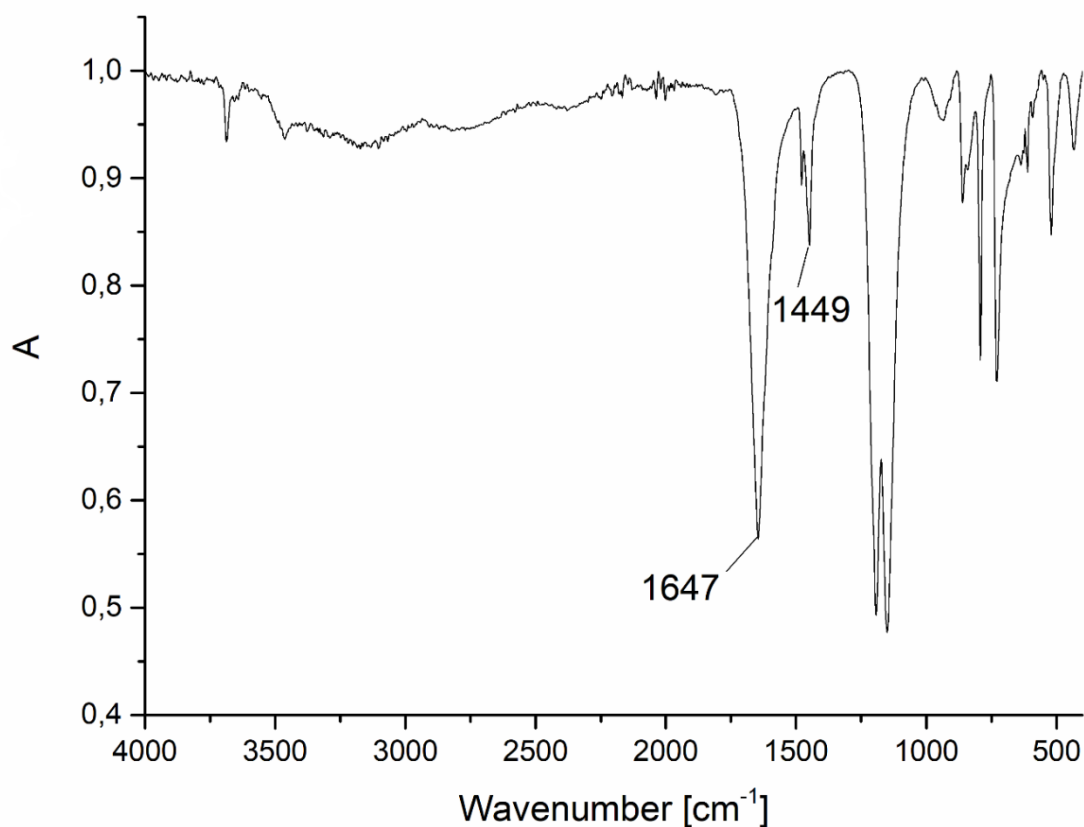


Figure S30. Infrared spectra for the  $[\text{Cu}_2(\mu\text{-O}_2\text{CCF}_3)_4]$  in the solid state.

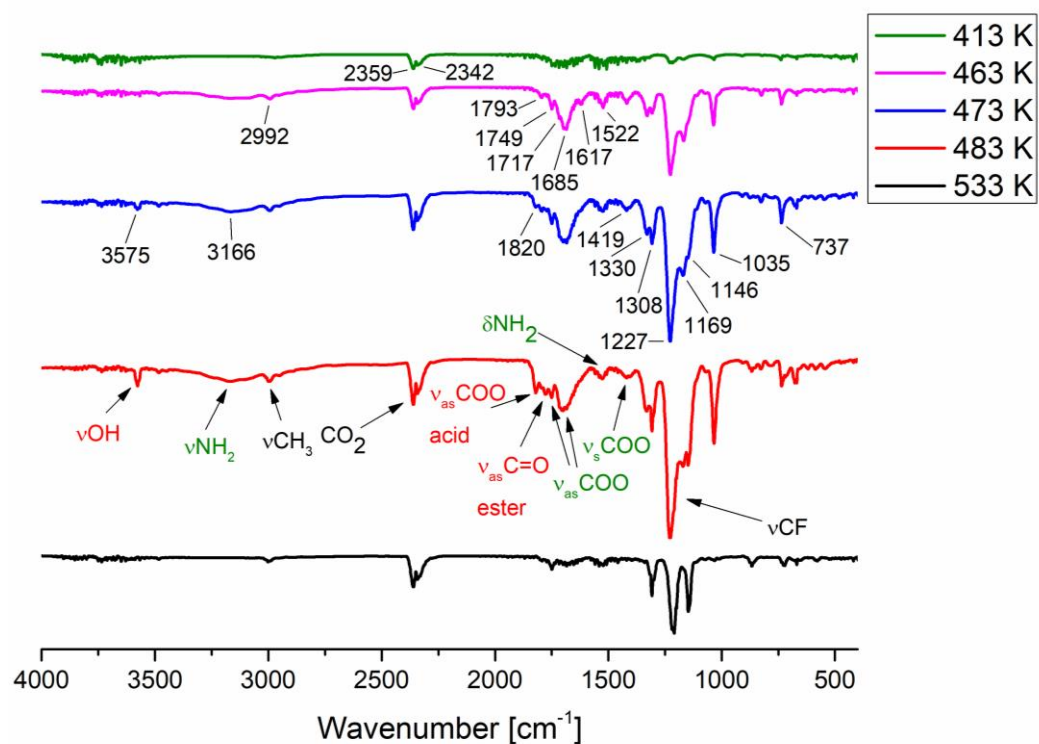
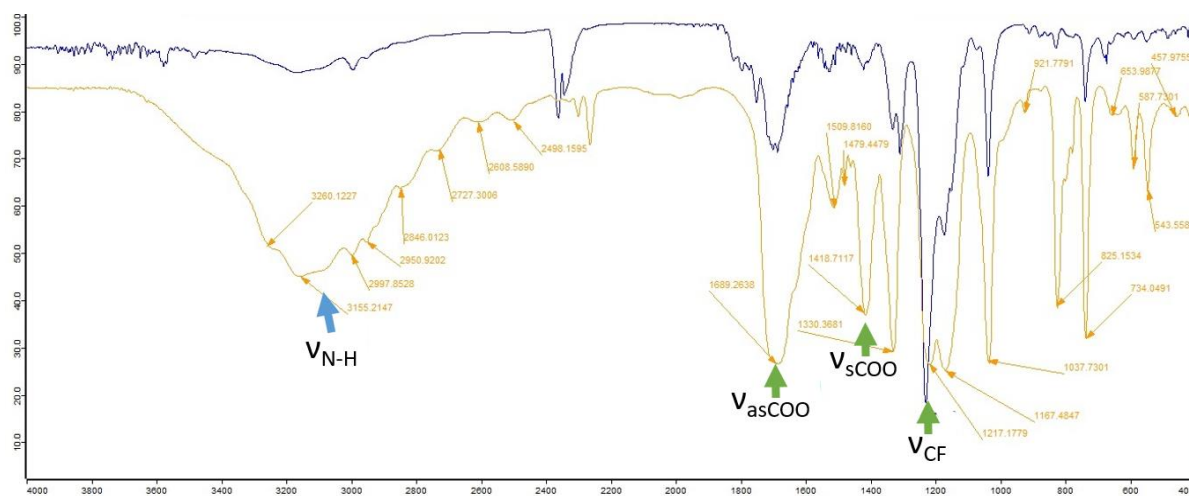
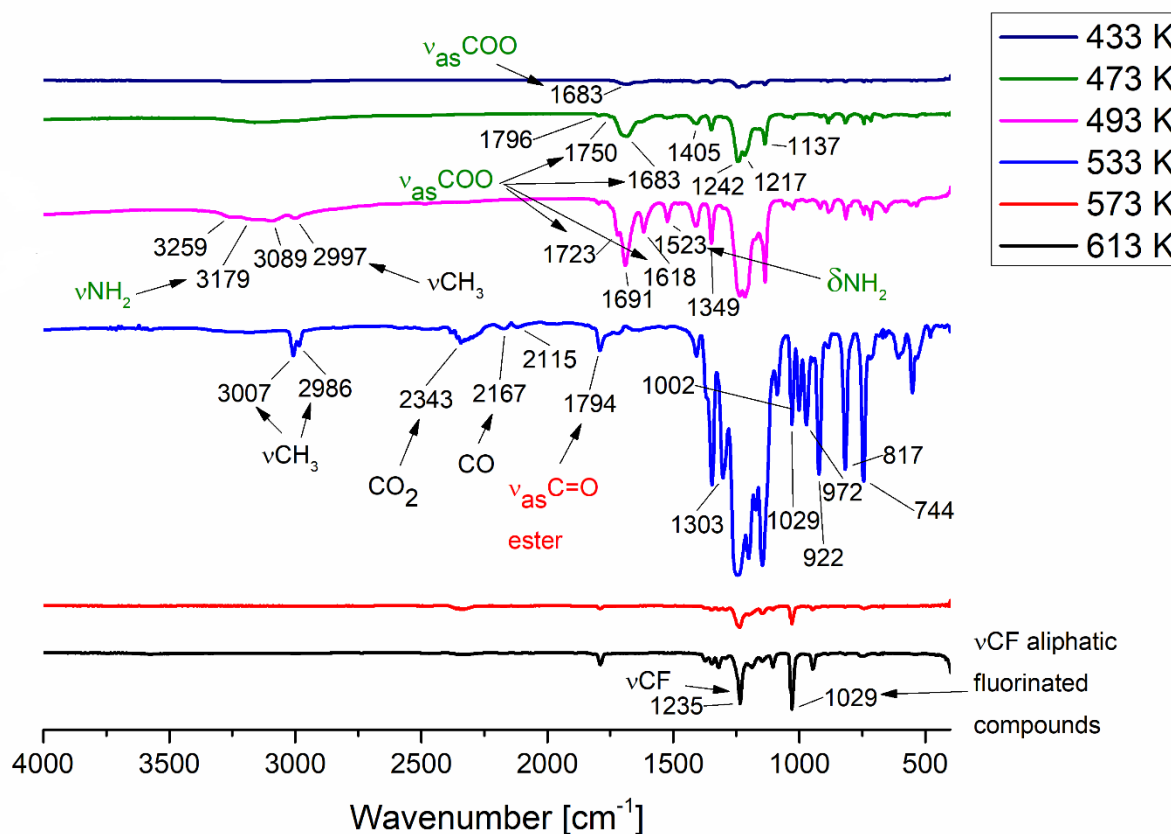


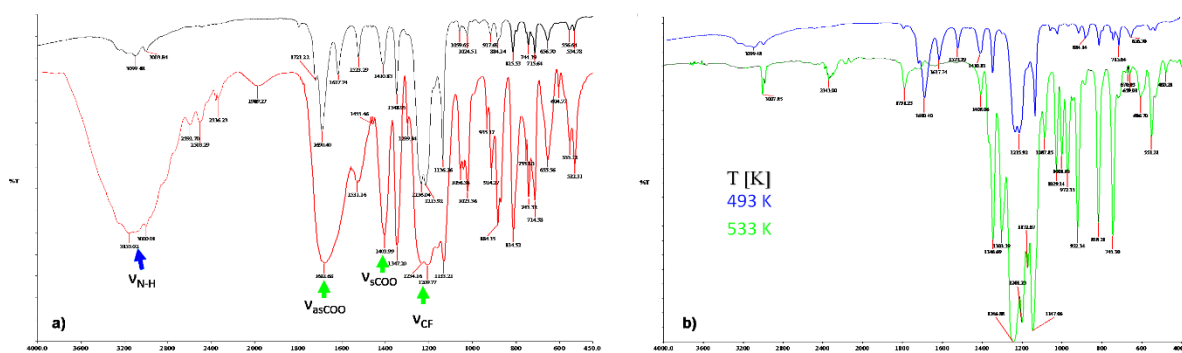
Figure S31. Temperature variable infrared spectra VT IR of vapors formed during the  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$  complex (2) heating.



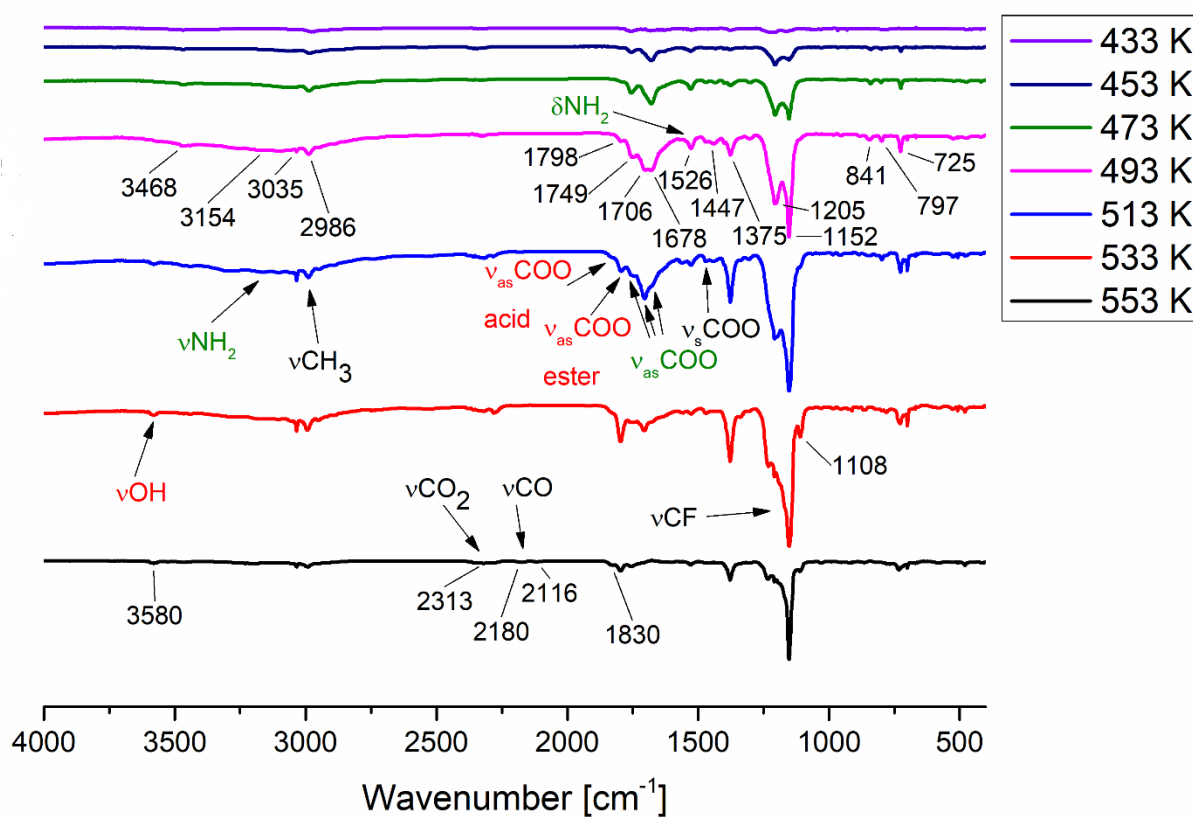
**Figure S32.** The spectra comparison for the  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$  complex (2) in the solid state (orange line) and in the gas phase at 473 K (blue line).



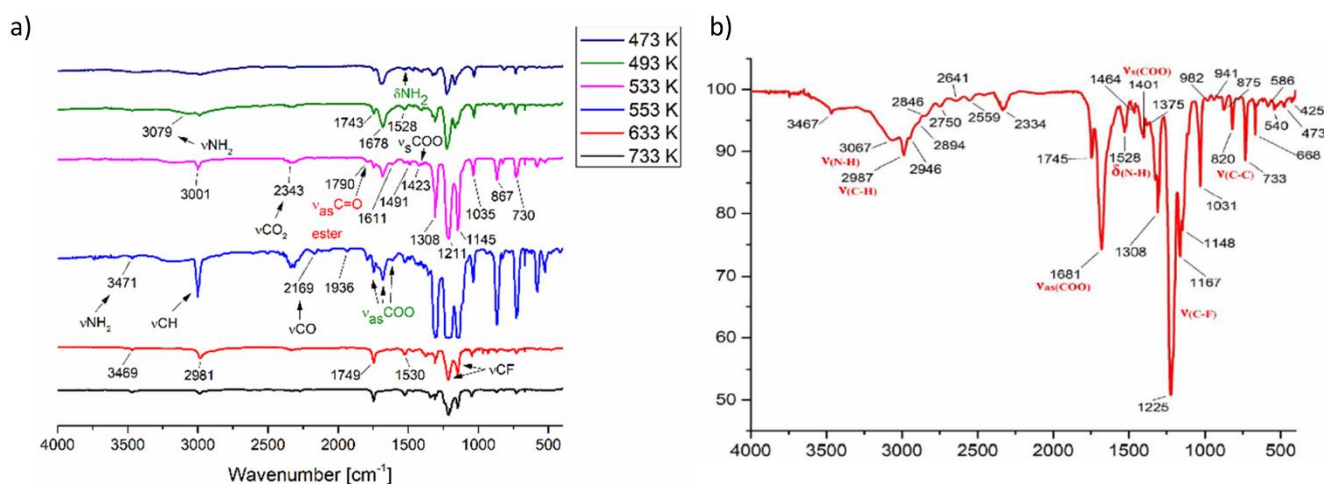
**Figure S33.** Temperature variable infrared spectra VT IR of vapors formed during the  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_4\text{F}_9)_4]$  complex (4) heating.



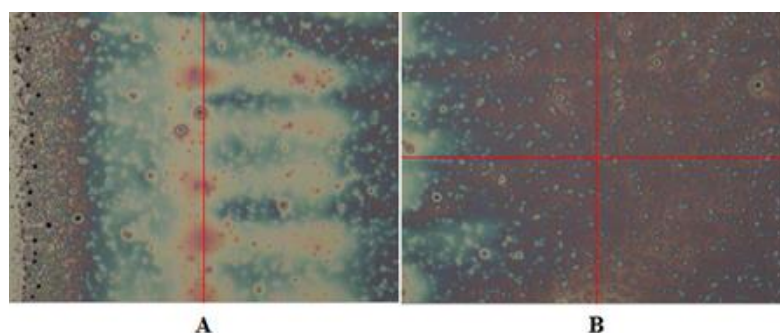
**Figure S34.** The spectra comparison for the  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_4\text{F}_9)_4]$  complex (4) a) in the solid state (red line) and in the gas phase at 493 K (black line) b) at temperature 493 K and 533 K.



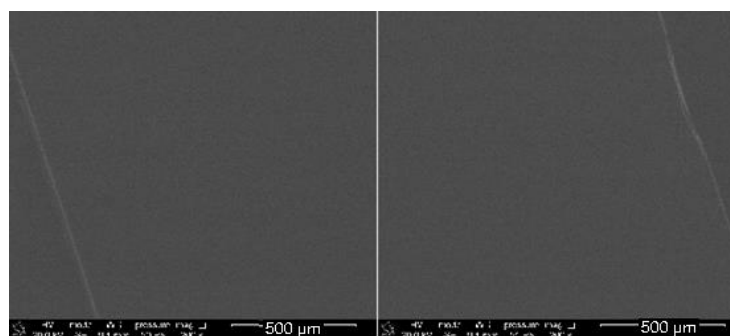
**Figure S35.** Temperature variable infrared spectra VT IR for the vapor formed during the  $[\text{Cu}_2(\text{iPrNH}_2)_2(\mu\text{-O}_2\text{CCF}_3)_4]$  complex (7) heating.



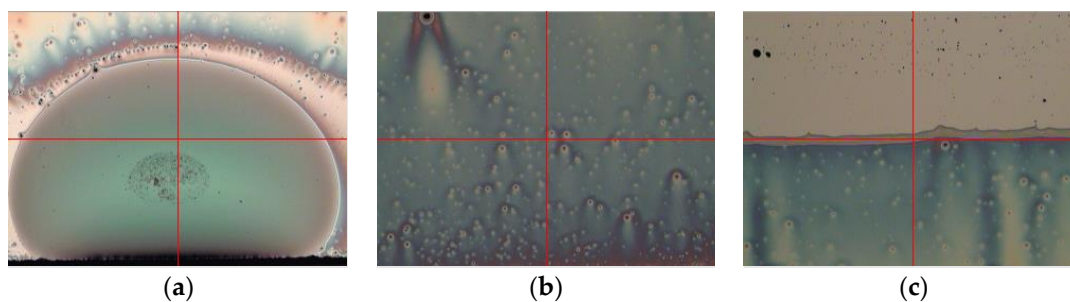
**Figure S36.** Temperature variable infrared spectra VT IR of vapors formed a) during the  $[\text{Cu}_2(\text{iPrNH}_2)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4]$  complex (8) heating 433–733 K and b) at temperature 493 K (red line).



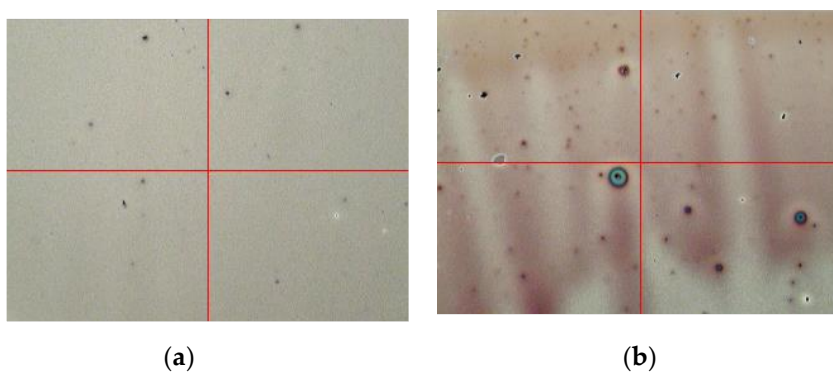
**Figure S37.** Optical microscope images of dip-coated  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_3\text{F}_7)_4](3)/\text{Si}$  before heating, immersion time 30 s, before heating (A) the immersion line, (B) middle of the layer.



**Figure S38.** SEM image of dip-coated  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_3\text{F}_7)_4](3)/\text{Si}$  immersion time 30 s, Mag = 200×, before heating.



**Figure S39.** Optical microscope images of dip-coated  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_3\text{F}_7)_4](\mathbf{3})/\text{Si}$ , before heating, immersion time 20 s, coating count 10, Mag 5x, the lower part of the substrate (A), middle of the layer (B), immersion line (C).



**Figure S40.** Images from optical microscope after heating dip-coated (A)  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_3\text{F}_7)_4](\mathbf{3})/\text{Si}$  immersion time 20 s; (B)  $[\text{Cu}_2(\text{EtNH}_2)_2(\mu\text{-O}_2\text{CC}_2\text{F}_5)_4](\mathbf{2})/\text{Si}$  immersion time 20 s.