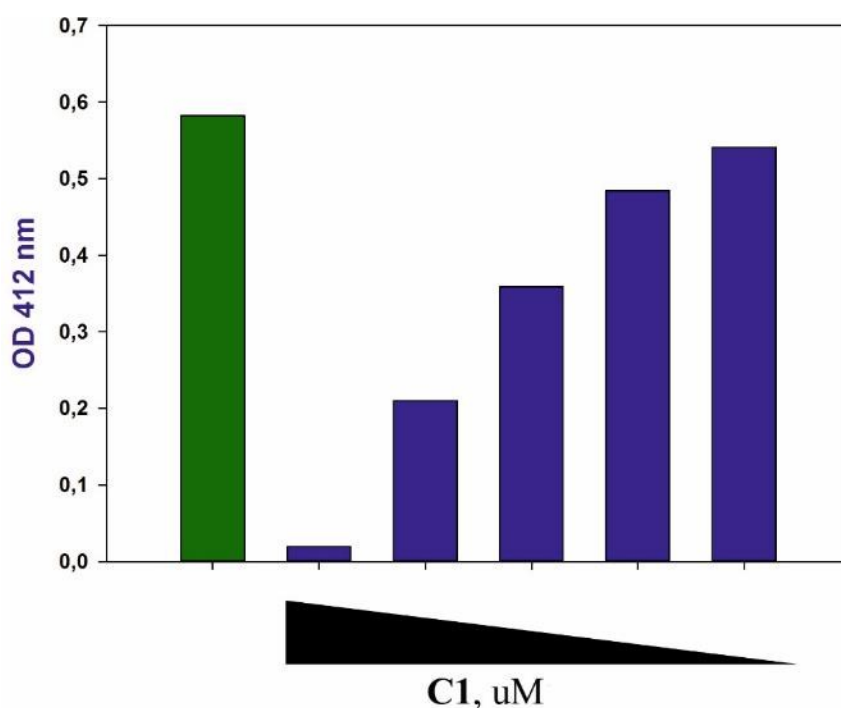


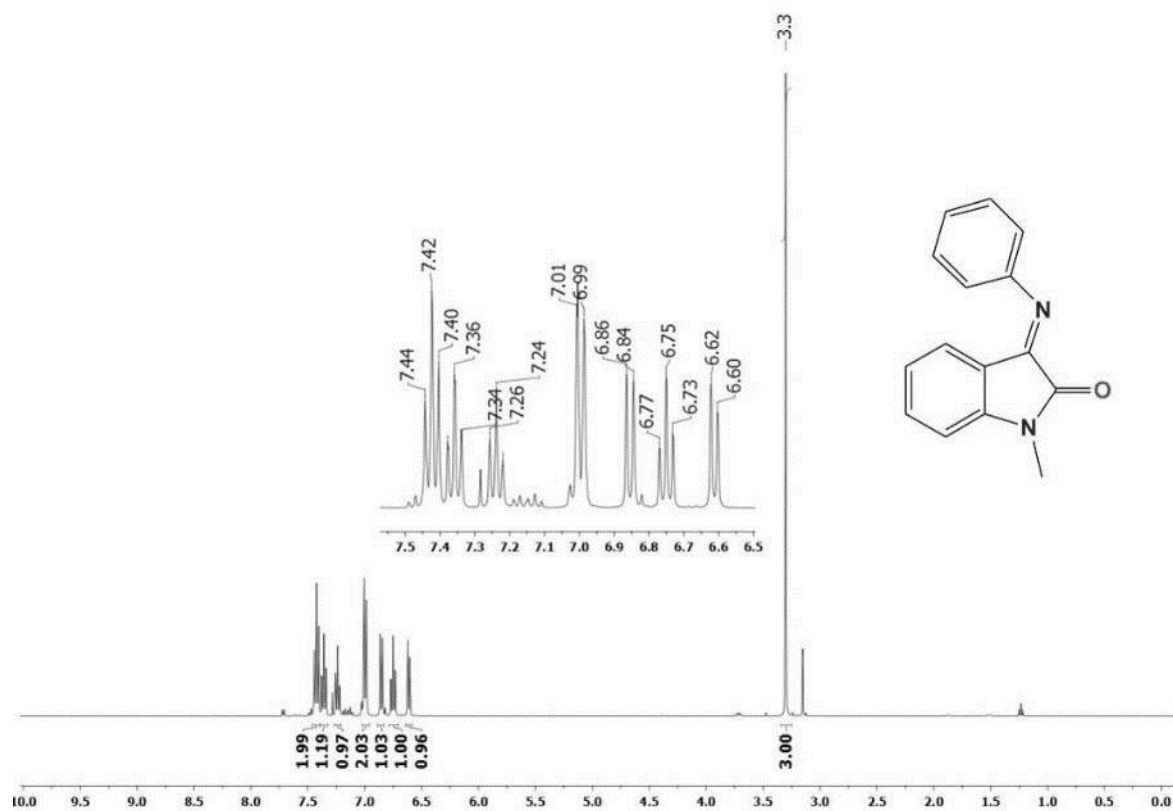
**SUPPORTING INFORMATION**

**Structure and Catalytic Properties of Novel Copper Isatin Schiff Base Complexes**

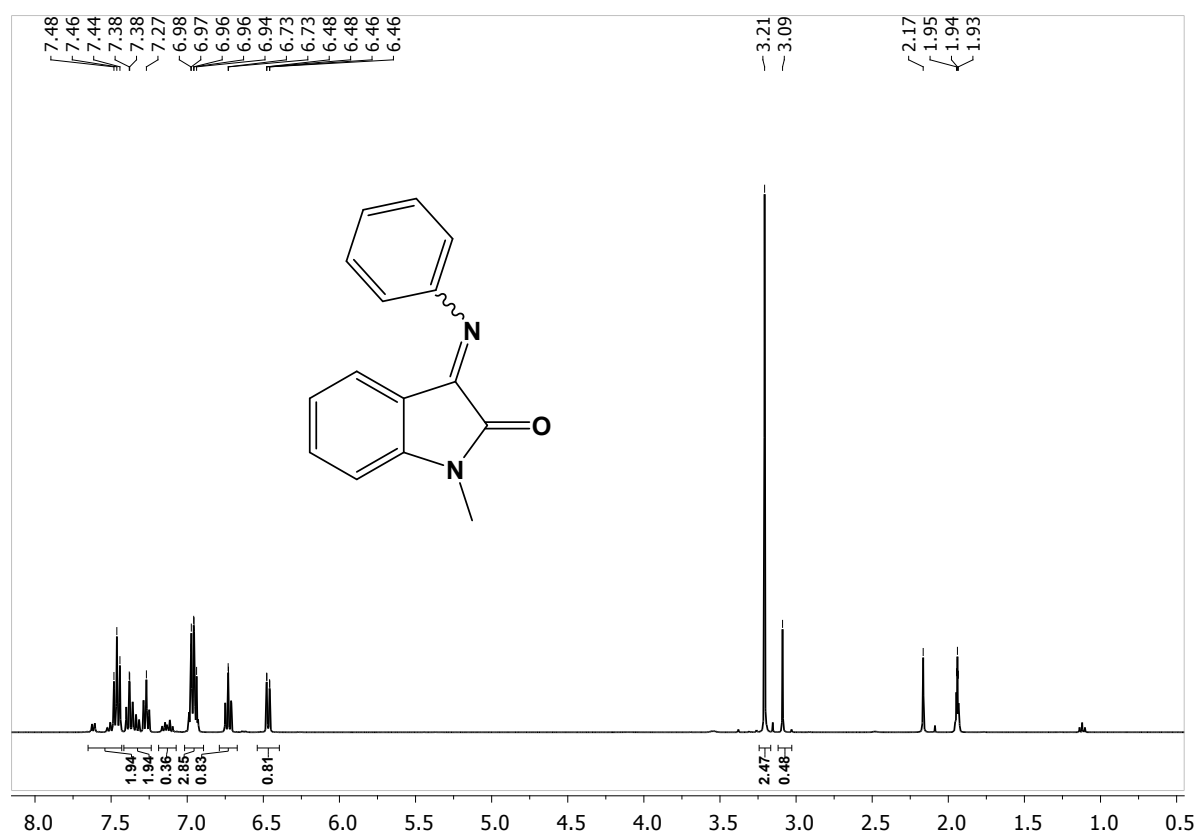
Andrey S. Smirnov, Luísa M.D.R.S. Martins, Dmitriy N. Nikolaev, Roman A. Manzhos, Vlad V. Gurzhiy, Alexander G. Krivenko,  
Kirill O. Nikolaenko, Alexander V. Belyakov, Alexander V. Garabadzhiu and Pavel B. Davidovich



**Figure S1.** Glutathione oxidation assay. Green GSH reacts with DTNB to form yellow colored product –  $\text{TNB}^{2-}$  that is detected by absorption at 412 nm. Complex **C1** (100, 50, 25, 12.5 and 6.25  $\mu\text{M}$ ) reacts 100  $\mu\text{M}$  GSH and the amount of formed  $\text{TNB}^-$  is reduced (see A.A. Dietz, H.M. Rubinstein, *Clinical Biochemistry*, V.5, 1972, pp. 136-138).



**Figure S2**  $\text{CDCl}_3$   $^1\text{H}$  NMR spectrum for L1



**Figure S3**  $\text{CD}_3\text{CN}$   $^1\text{H}$  NMR spectrum for L1

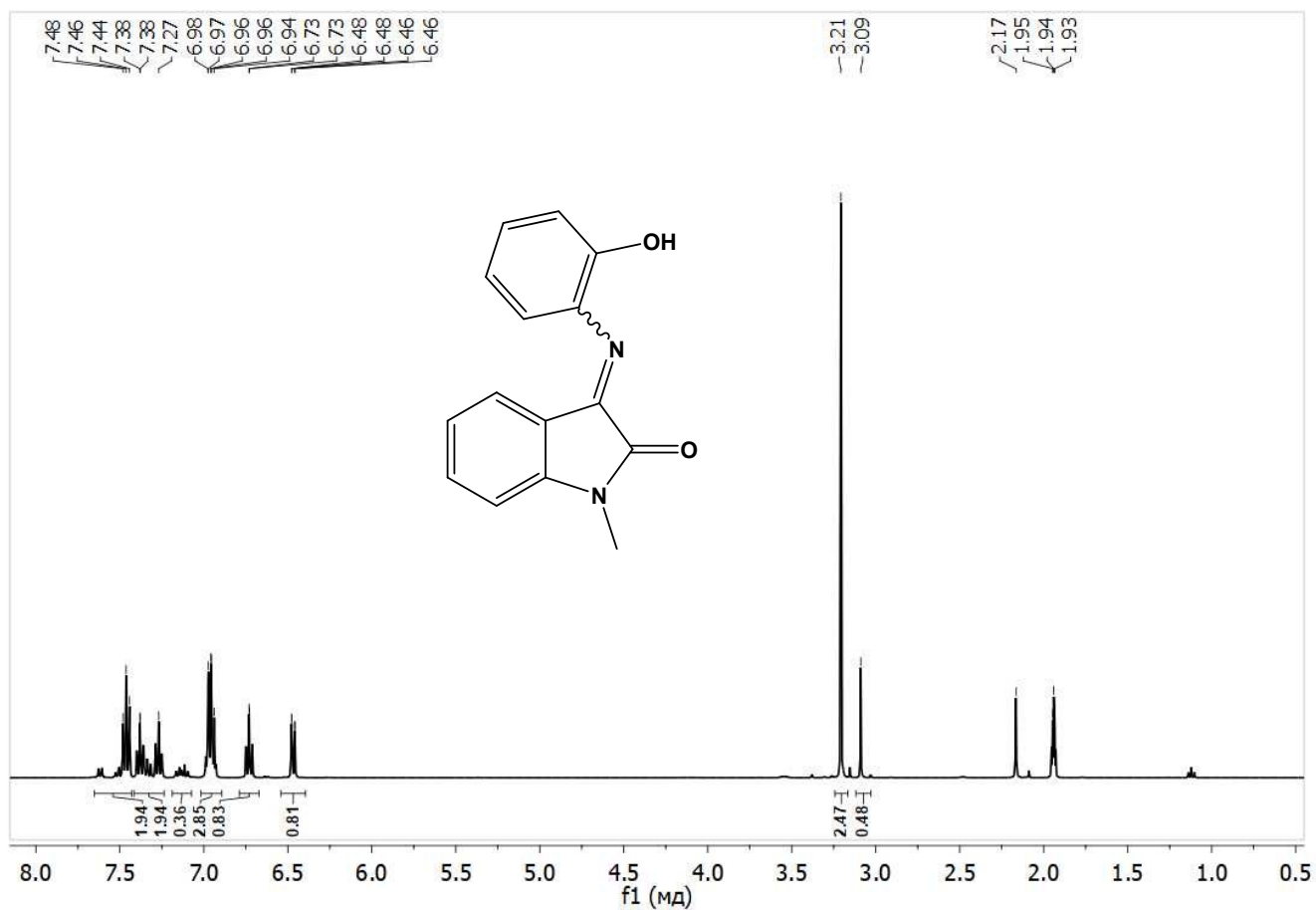


Figure S4 CD<sub>3</sub>CN <sup>13</sup>C NMR spectrum for L1

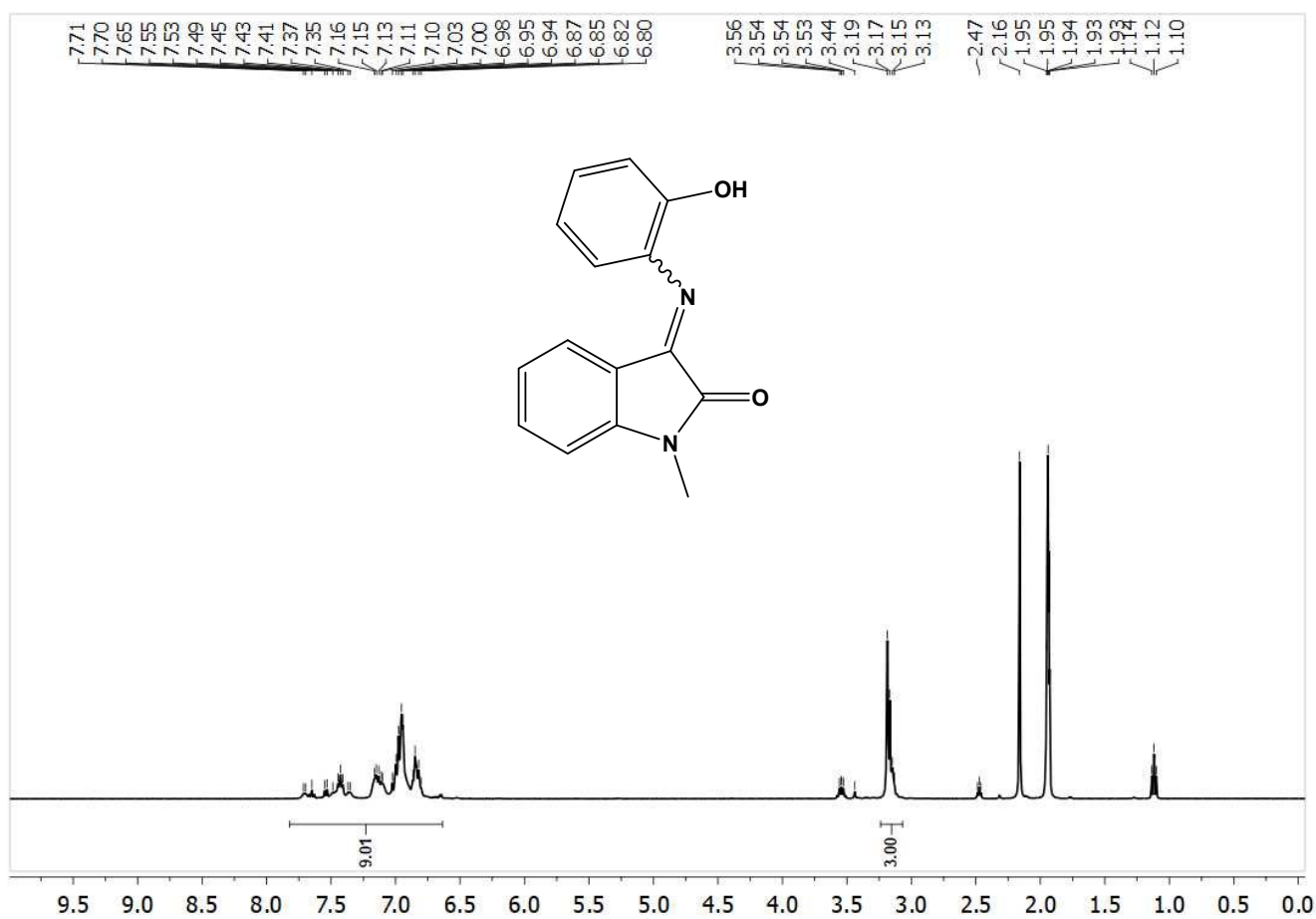
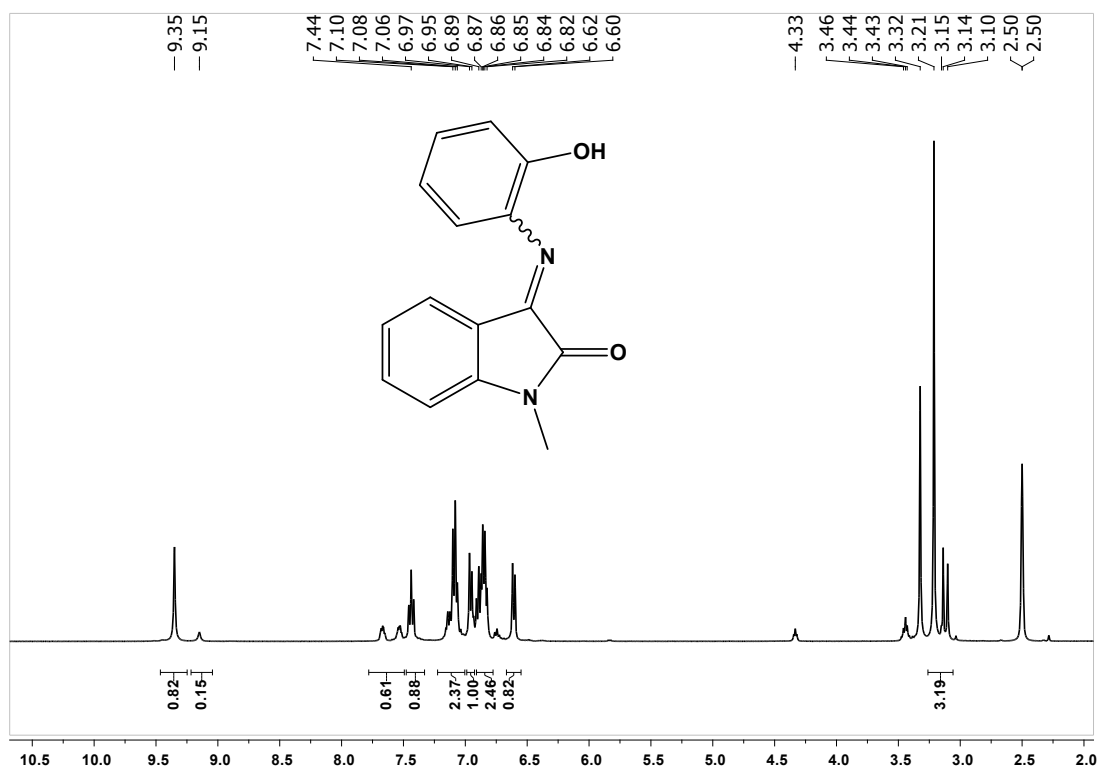
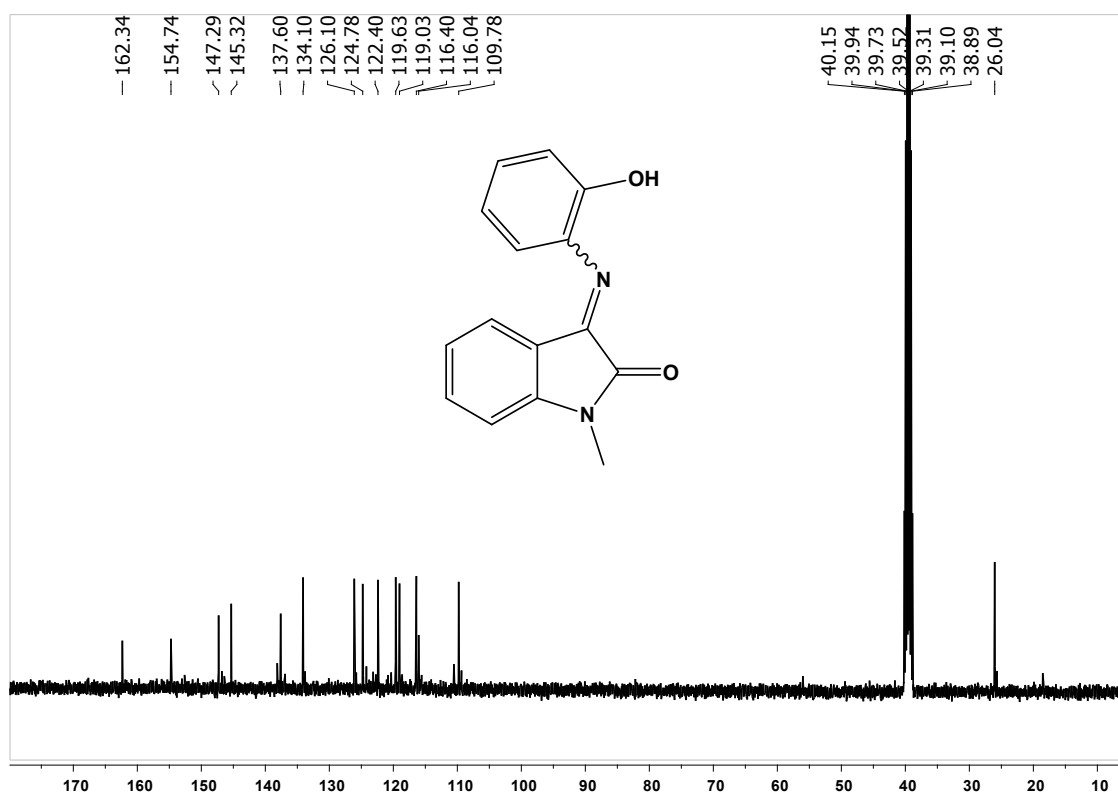


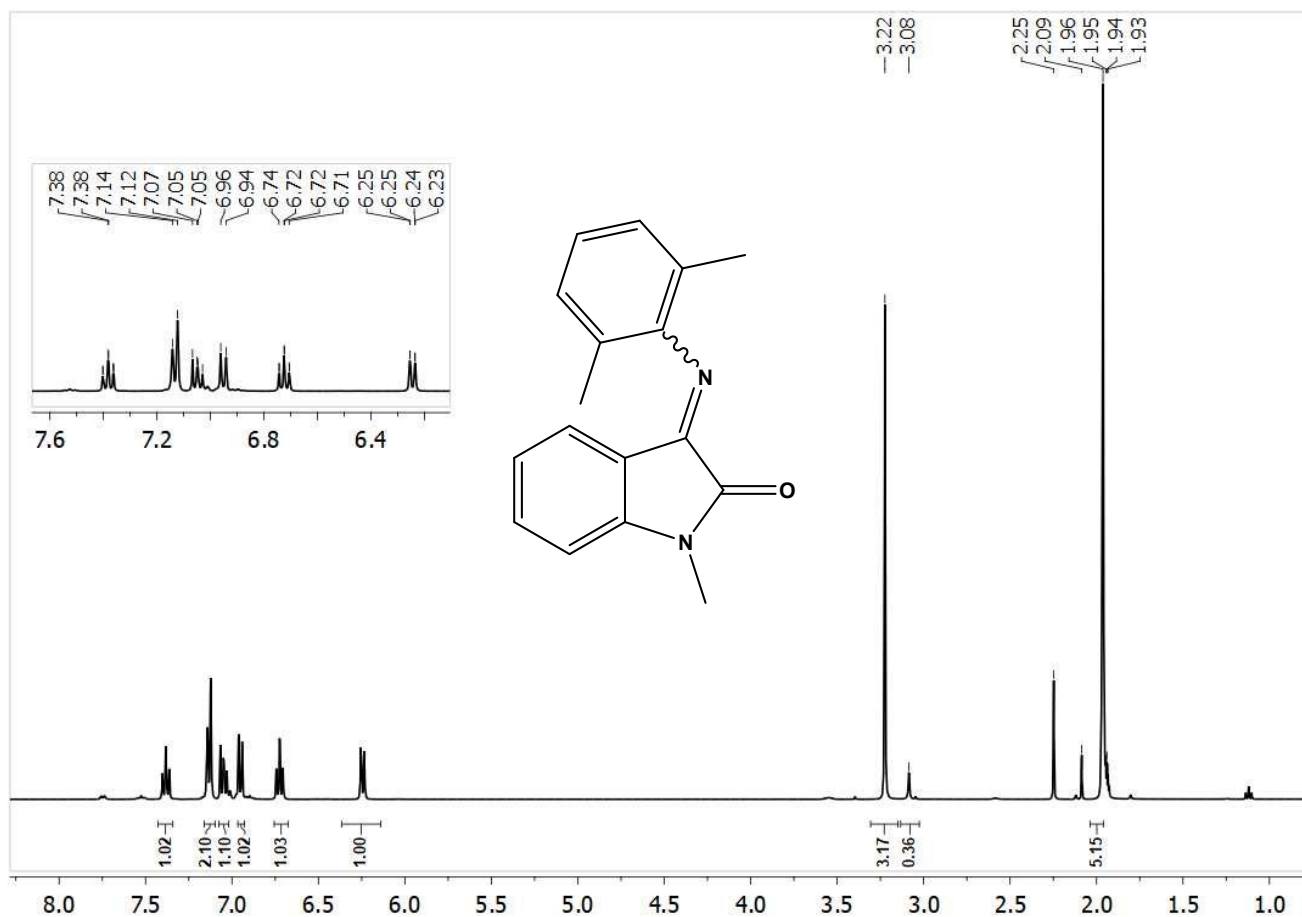
Figure S5 CDCl<sub>3</sub> <sup>1</sup>H NMR spectrum for L2



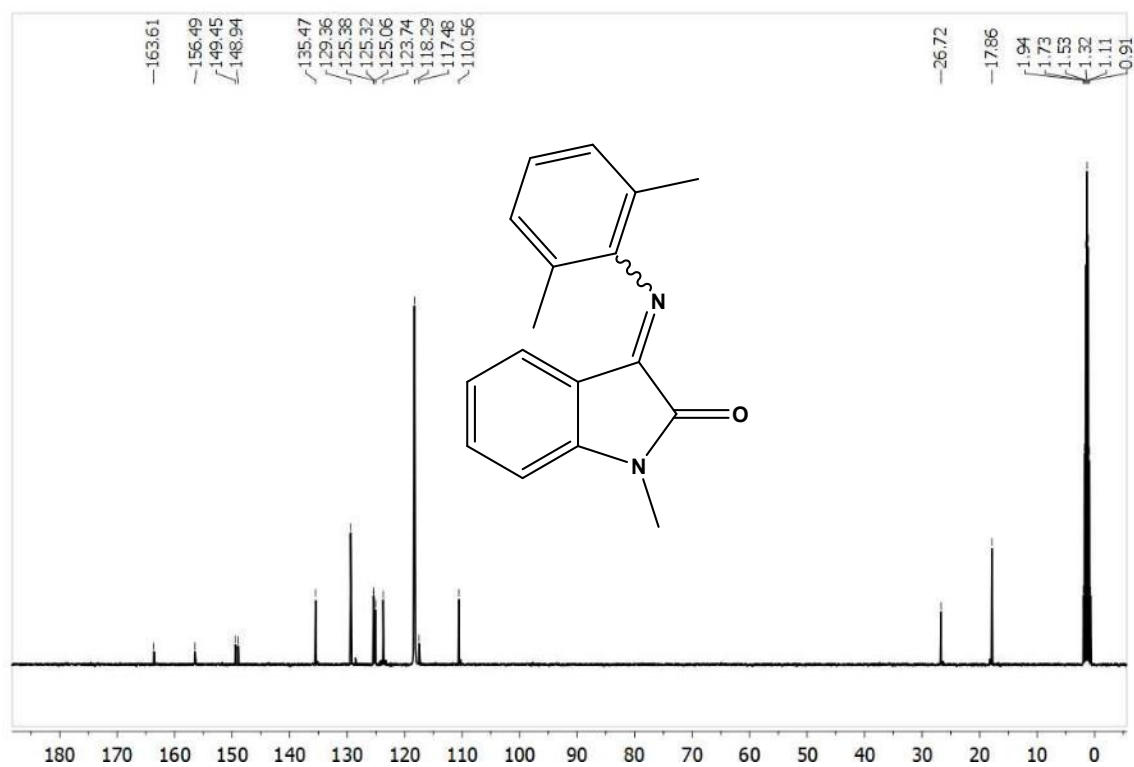
**Figure S6** DMSO-d<sub>6</sub> <sup>1</sup>H NMR spectrum for L2



**Figure S7** DMSO-d<sub>6</sub> <sup>13</sup>C NMR spectrum for L2



**Figure S8** CD<sub>3</sub>CN <sup>1</sup>H NMR spectrum for L3



**Figure S9** CD<sub>3</sub>CN <sup>13</sup>C NMR spectrum for L3

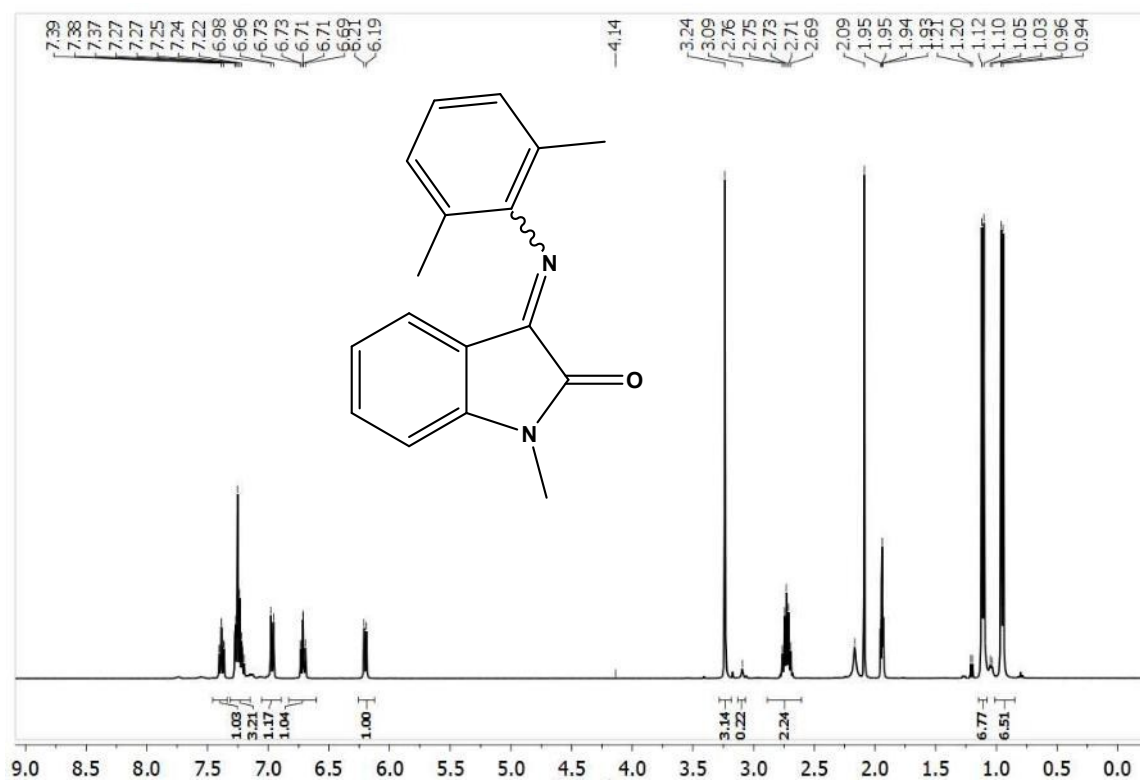


Figure S10 CD<sub>3</sub>CN <sup>1</sup>H NMR spectrum for L4

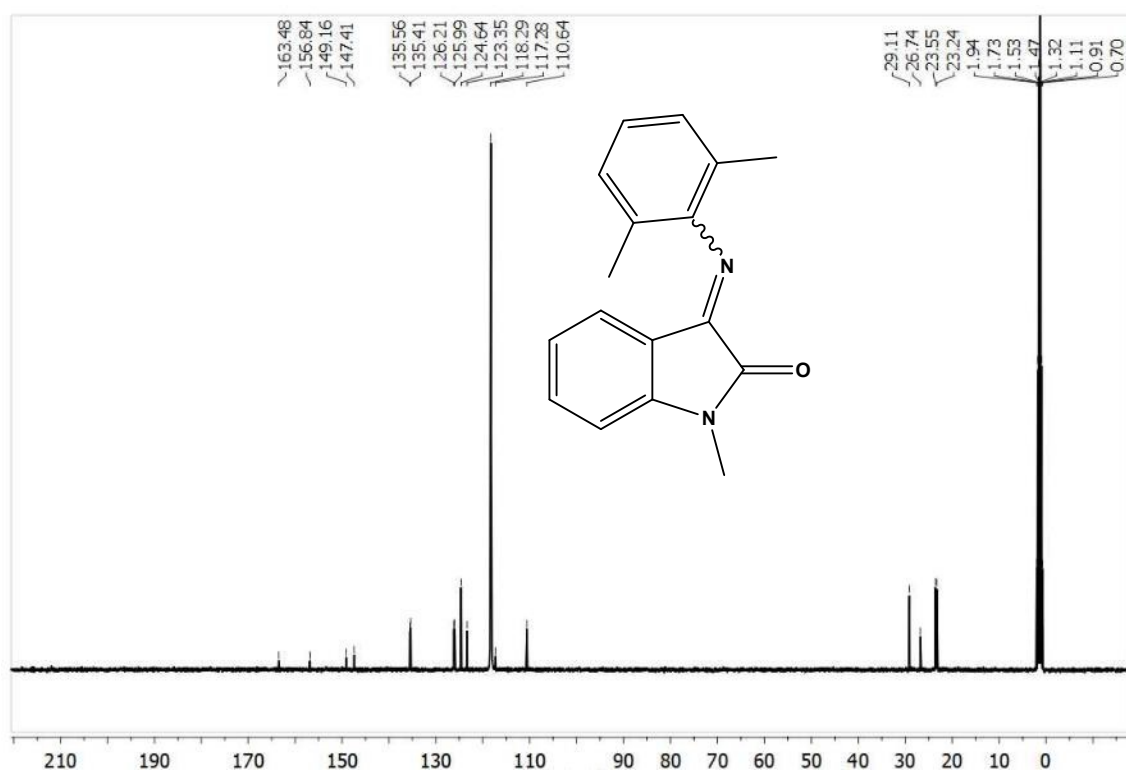


Figure S11 CD<sub>3</sub>CN <sup>13</sup>C NMR spectrum for L4

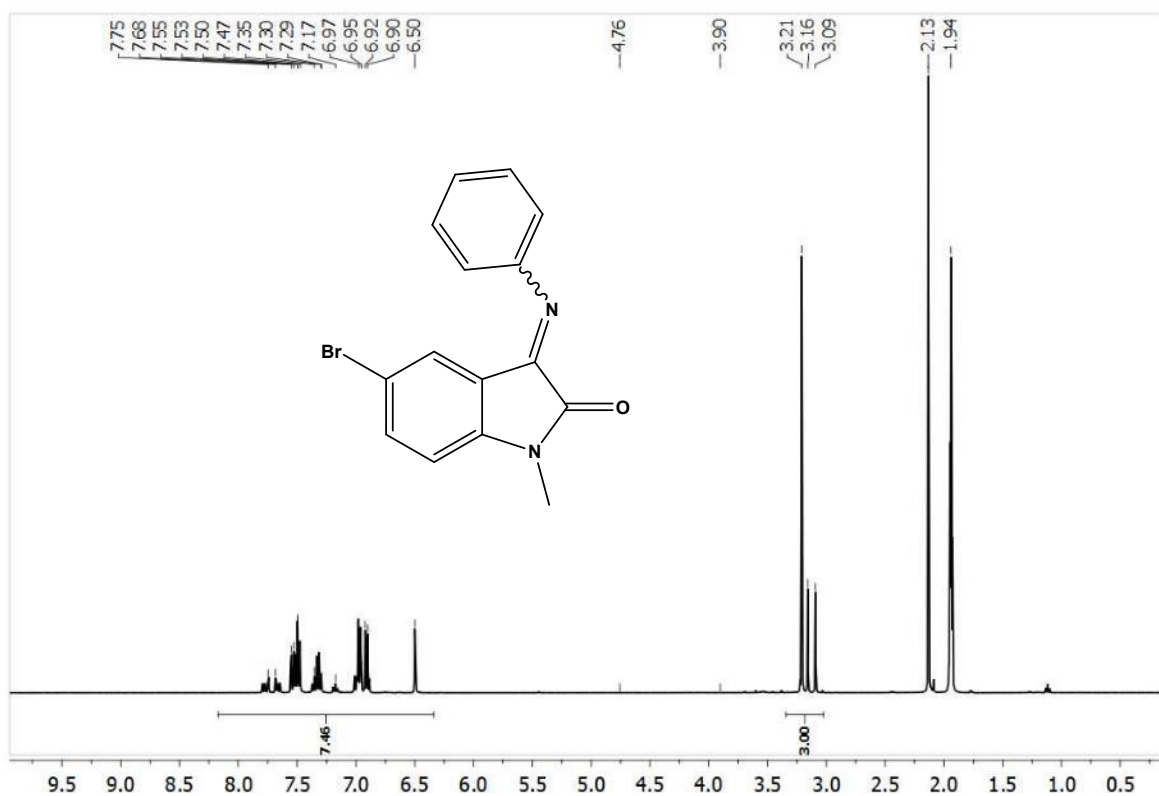


Figure S12 CD<sub>3</sub>CN <sup>1</sup>H NMR spectrum for L5

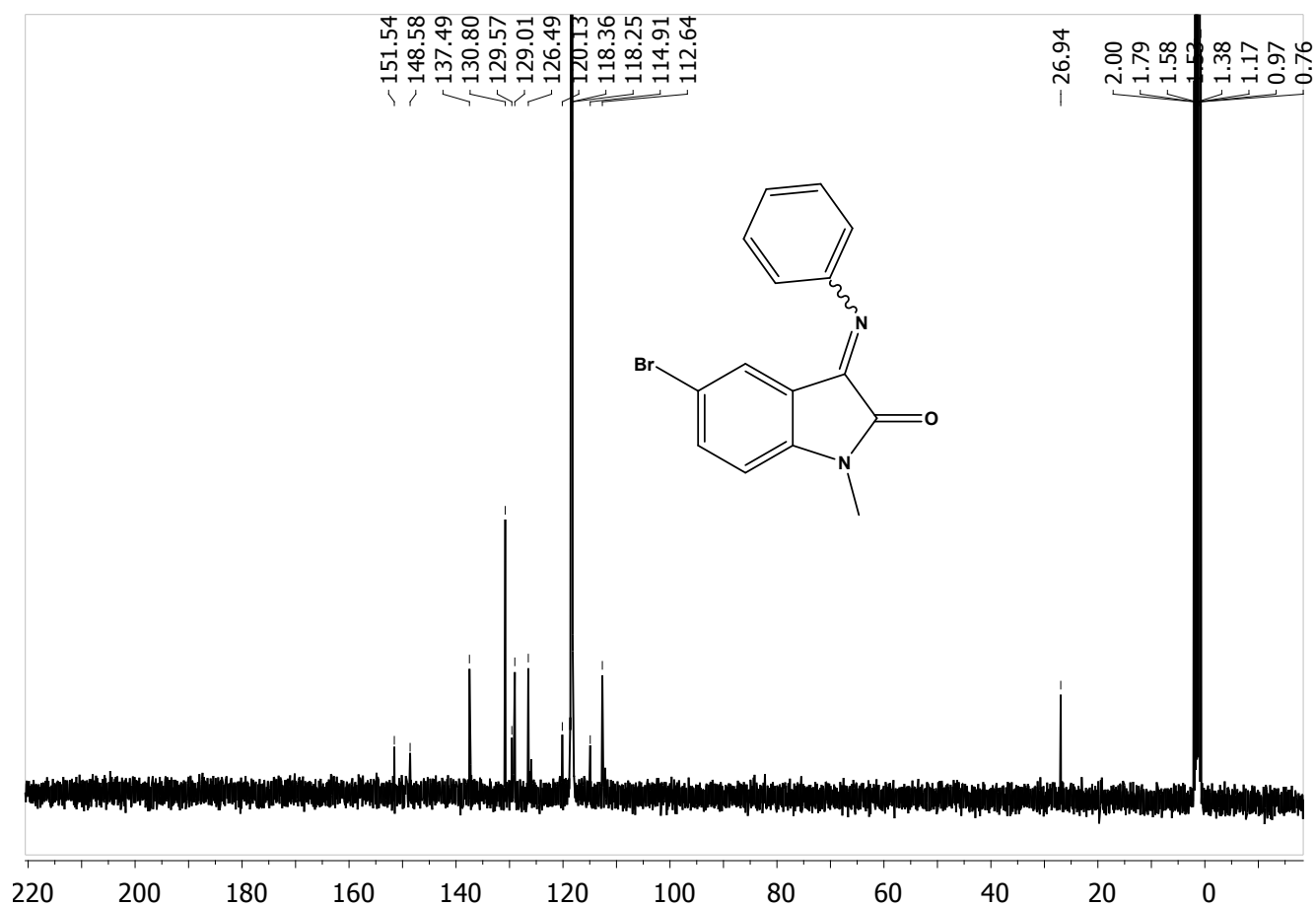


Figure S13 CD<sub>3</sub>CN <sup>13</sup>C NMR spectrum for L5

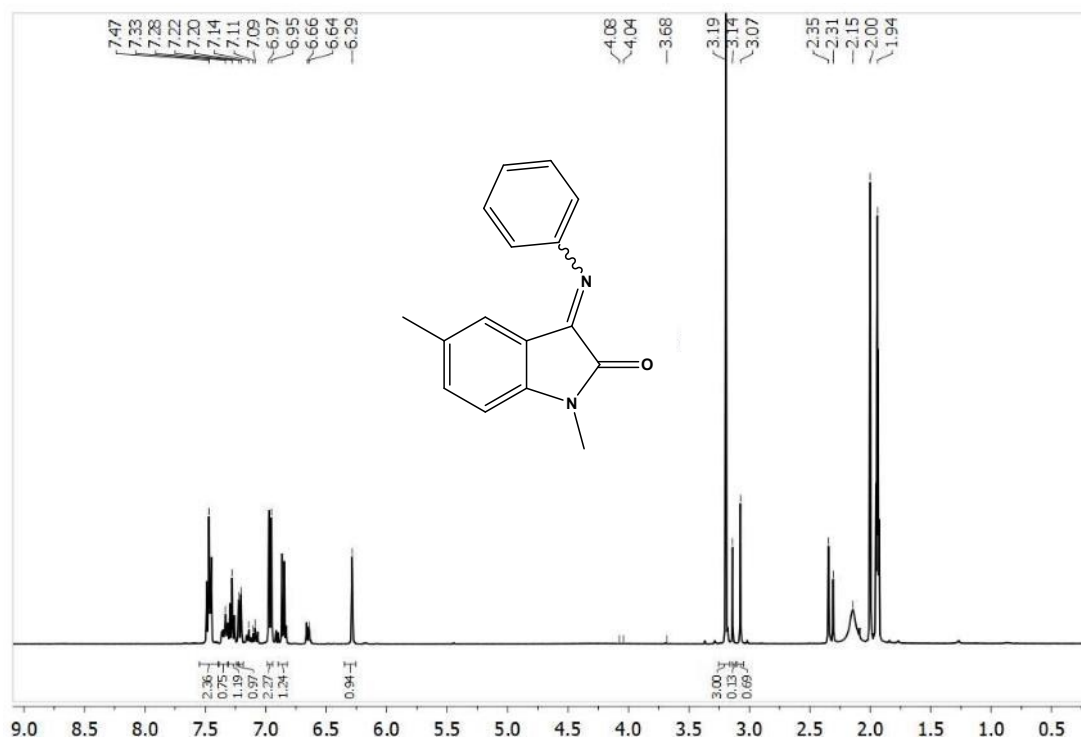


Figure S14 CD<sub>3</sub>CN <sup>1</sup>H NMR spectrum for L6

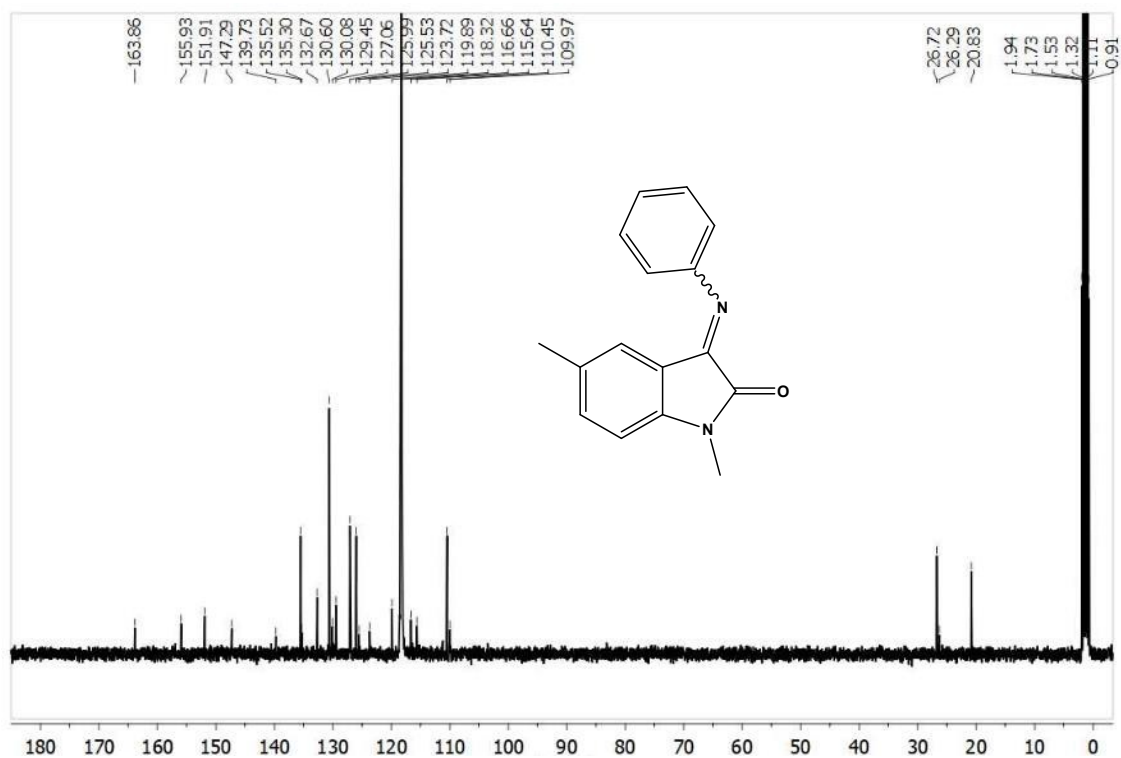
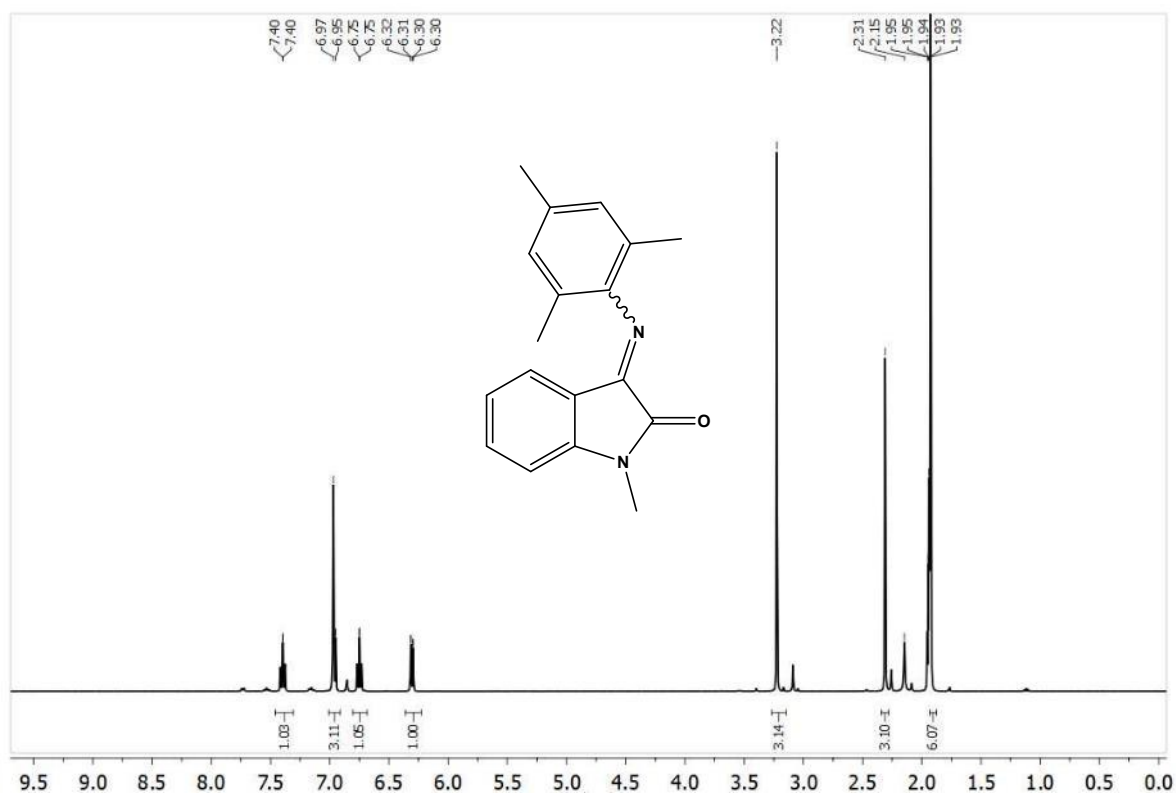
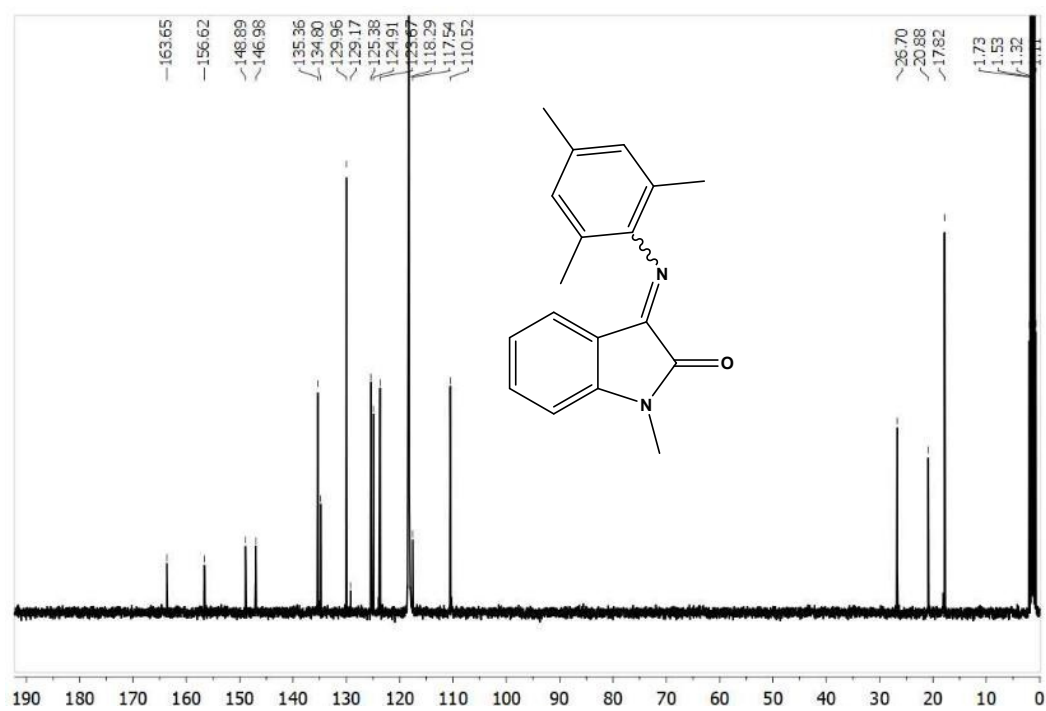


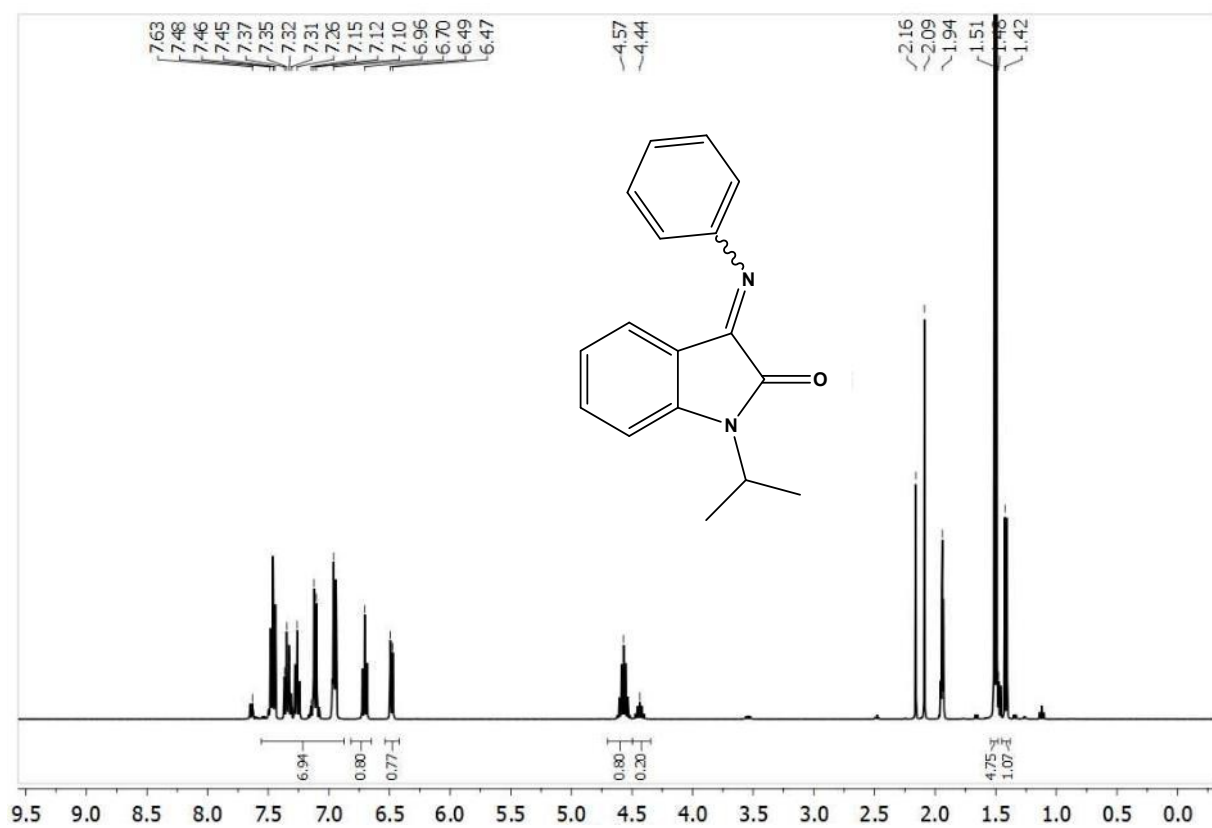
Figure S15 CD<sub>3</sub>CN <sup>13</sup>C NMR spectrum for L6



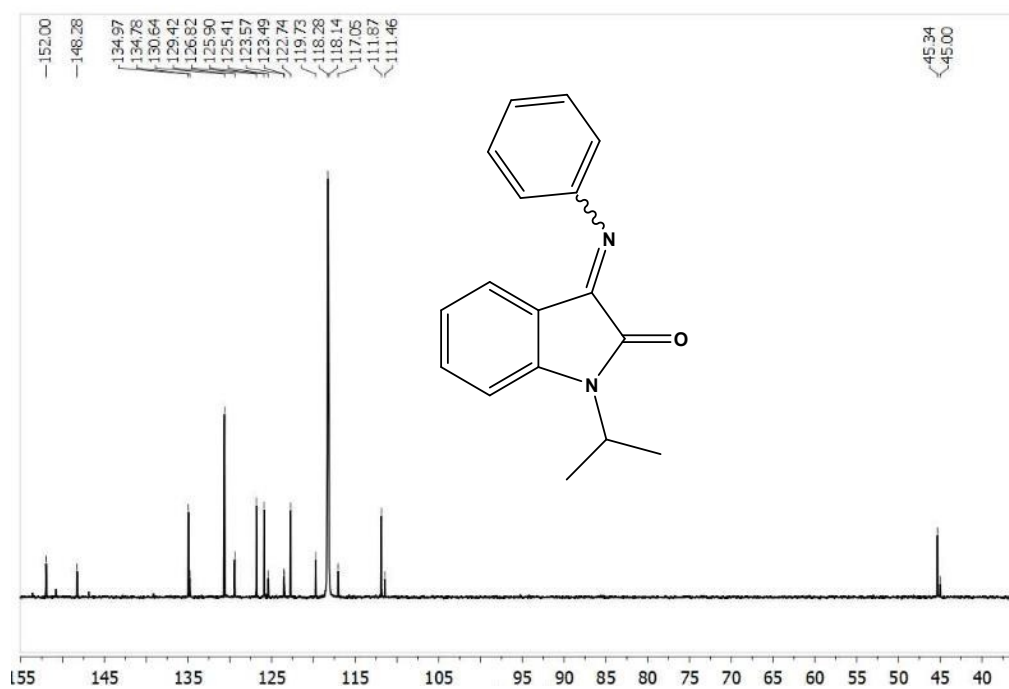
**Figure S16** CD<sub>3</sub>CN <sup>1</sup>H NMR spectrum for L7



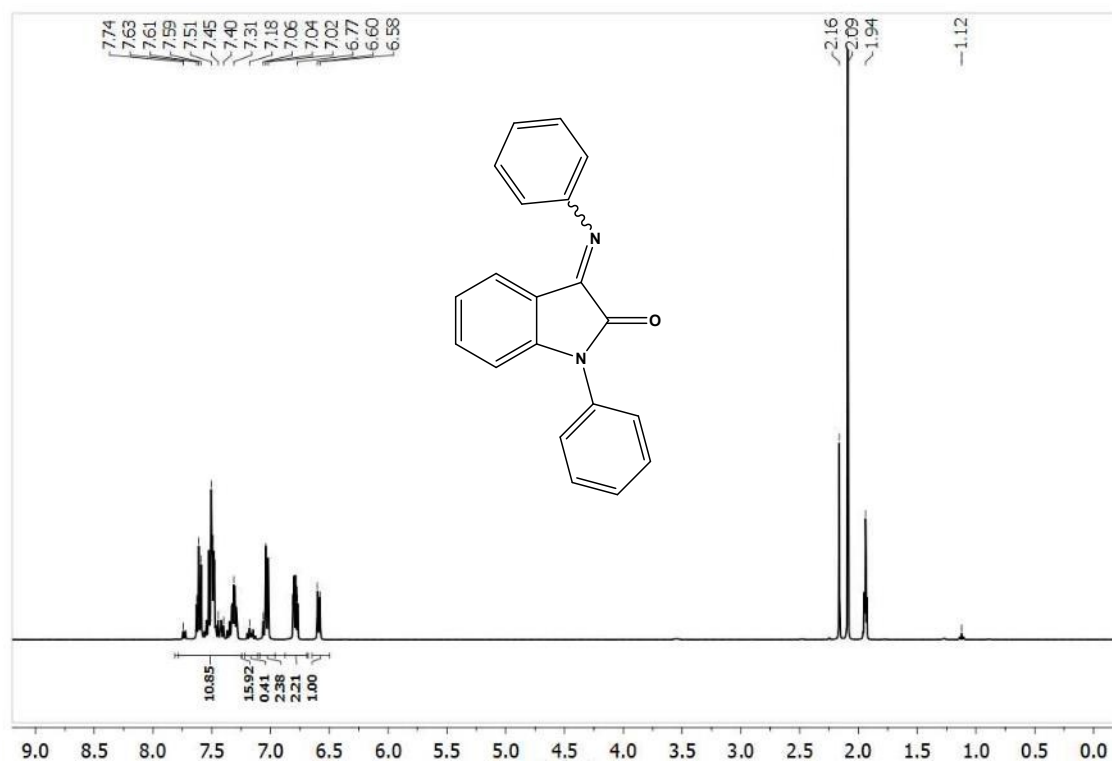
**Figure S17** CD<sub>3</sub>CN <sup>13</sup>C NMR spectrum for L7



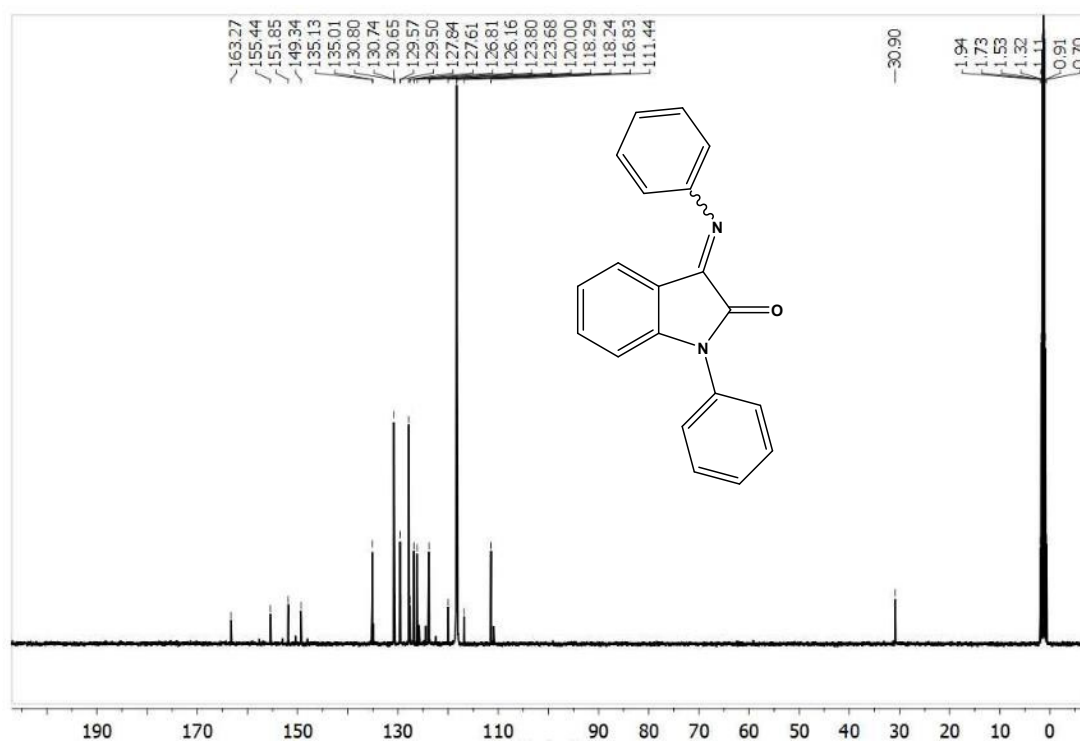
**Figure S18** CD<sub>3</sub>CN <sup>1</sup>H NMR spectrum for **L8**



**Figure S19** CD<sub>3</sub>CN <sup>13</sup>C NMR spectrum for **L8**



**Figure S20** CD<sub>3</sub>CN <sup>1</sup>H NMR spectrum for L9



**Figure S21** CD<sub>3</sub>CN <sup>13</sup>C NMR spectrum for L9

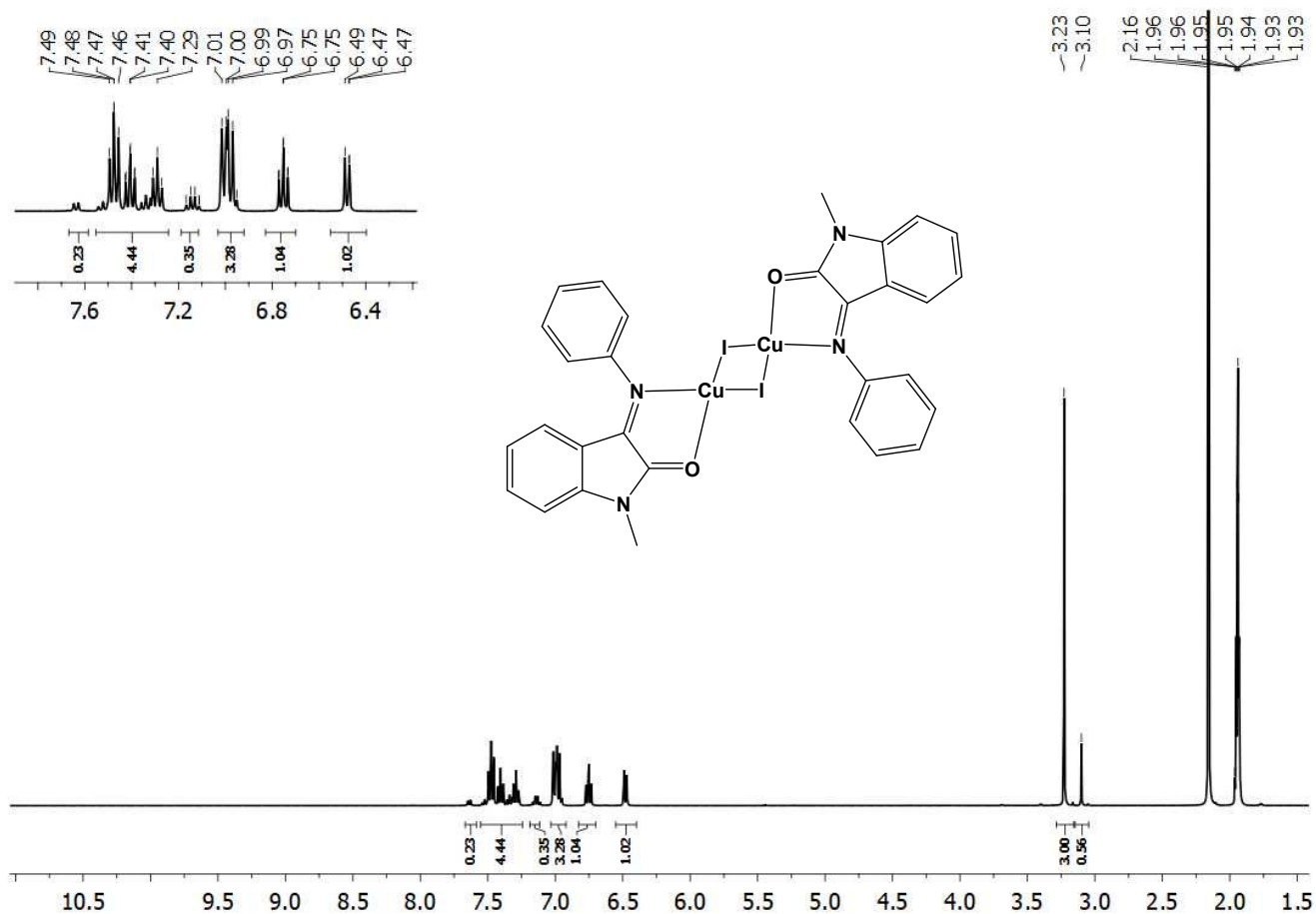


Figure S22 CD<sub>3</sub>CN <sup>1</sup>H NMR spectrum for C15

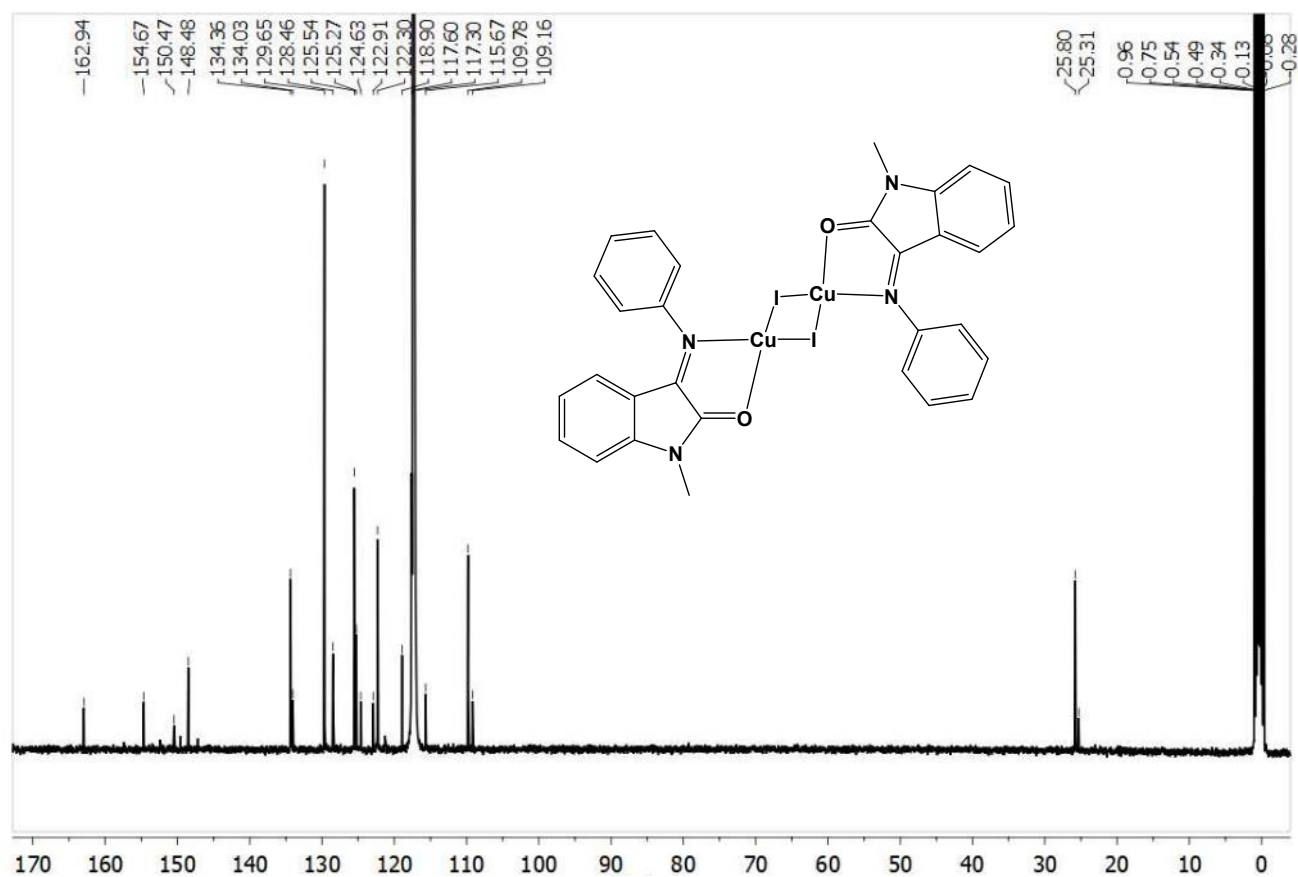
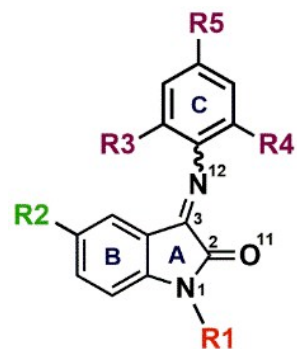


Figure S23 CD<sub>3</sub>CN <sup>13</sup>C NMR spectrum for C15

**Table S1** Selected Bond lengths (Å) for the ligands **L1-L9**

| Compound   | N1-C2    | C=O      | C2-C3    | C=N      | N12-C    |
|------------|----------|----------|----------|----------|----------|
| <b>L1</b>  | 1.372(2) | 1.210(2) | 1.531(2) | 1.275(2) | 1.419(2) |
| <b>L2</b>  | 1.354(2) | 1.228(2) | 1.532(2) | 1.227(2) | 1.422(2) |
| <b>L3</b>  | 1.369(1) | 1.215(1) | 1.527(2) | 1.274(1) | 1.422(2) |
| <b>L4*</b> | 1.366(1) | 1.217(1) | 1.531(1) | 1.269(1) | 1.423(1) |
|            | 1.368(1) | 1.215(1) | 1.535(1) | 1.270(1) | 1.422(1) |
| <b>L5</b>  | 1.371(3) | 1.212(3) | 1.535(3) | 1.270(3) | 1.417(3) |
| <b>L6</b>  | 1.378    | 1.209    | 1.525    | 1.278    | 1.417    |
| <b>L7</b>  | 1.364(2) | 1.217(2) | 1.532(2) | 1.273(2) | 1.425(2) |
| <b>L8</b>  | 1.375(2) | 1.217(2) | 1.534(3) | 1.268(2) | 1.423(2) |
| <b>L9*</b> | 1.369(2) | 1.215(2) | 1.535(2) | 1.266(2) | 1.431(2) |
|            | 1.378(2) | 1.212(2) | 1.530(2) | 1.268(2) | 1.431(2) |

\*for two independent molecules



**Table S2** Crystallographic and structure refinement data for ligands **L2-L9**\*

| Compound                                         | <b>L2</b>                                                     | <b>L3</b>                                        | <b>L4</b>                                        | <b>L5</b>                                          | <b>L6</b>                                        | <b>L7</b>                                        | <b>L8</b>                                        | <b>L9</b>                                        |
|--------------------------------------------------|---------------------------------------------------------------|--------------------------------------------------|--------------------------------------------------|----------------------------------------------------|--------------------------------------------------|--------------------------------------------------|--------------------------------------------------|--------------------------------------------------|
| CCDC #                                           | 1412864                                                       | 1538859                                          | 1538860                                          | 1538858                                            | 1538861                                          | 1538862                                          | 1538863                                          | 1538865                                          |
| Formula                                          | C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> | C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O | C <sub>21</sub> H <sub>24</sub> N <sub>2</sub> O | C <sub>15</sub> H <sub>11</sub> BrN <sub>2</sub> O | C <sub>16</sub> H <sub>14</sub> N <sub>2</sub> O | C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O | C <sub>17</sub> H <sub>16</sub> N <sub>2</sub> O | C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O |
| Crystal System                                   | Monoclinic                                                    | Monoclinic                                       | Monoclinic                                       | Monoclinic                                         | Monoclinic                                       | Monoclinic                                       | Orthorhombic                                     | Triclinic                                        |
| <i>a</i> (Å)                                     | 10.1494(6)                                                    | 13.6078(3)                                       | 8.4797 (1)                                       | 8.1114 (2)                                         | 9.0075 (8)                                       | 6.9194 (4)                                       | 9.6713 (4)                                       | 9.9809 (7)                                       |
| <i>b</i> (Å)                                     | 7.7078(5)                                                     | 19.5284(6)                                       | 15.0831 (2)                                      | 16.2246 (4)                                        | 6.8883 (8)                                       | 8.6089 (5)                                       | 9.0619 (4)                                       | 10.7407 (4)                                      |
| <i>c</i> (Å)                                     | 15.2882(7)                                                    | 11.3494(3)                                       | 28.0078 (4)                                      | 19.1312 (4)                                        | 10.3867 (11)                                     | 24.9101 (16)                                     | 15.8838 (7)                                      | 14.987 (1)                                       |
| $\alpha$ (°)                                     | 90                                                            | 90                                               | 90                                               | 90                                                 | 90                                               | 90                                               | 90                                               | 73.451 (5)                                       |
| $\beta$ (°)                                      | 101.259(6)                                                    | 108.884(3)                                       | 93.360 (1)                                       | 95.696 (2)                                         | 98.932 (8)                                       | 96.141 (6)                                       | 90                                               | 78.454 (6)                                       |
| $\gamma$ (°)                                     | 90                                                            | 90                                               | 90                                               | 90                                                 | 90                                               | 90                                               | 90                                               | 86.790 (4)                                       |
| <i>V</i> (Å <sup>3</sup> )                       | 1172.96(11)                                                   | 2853.65(14)                                      | 3576.04 (8)                                      | 2505.32 (10)                                       | 636.64 (11)                                      | 1475.34 (16)                                     | 1392.07 (11)                                     | 1508.92 (16)                                     |
| Molecular weight                                 | 252.27                                                        | 264.32                                           | 340.42                                           | 315.17                                             | 250.29                                           | 278.34                                           | 264.32                                           | 298.33                                           |
| Space group                                      | <i>P</i> 2 <sub>1</sub> / <i>c</i>                            | <i>C</i> 2/ <i>c</i>                             | <i>P</i> 2 <sub>1</sub> / <i>c</i>               | <i>C</i> 2/ <i>c</i>                               | <i>P</i> 2 <sub>1</sub> / <i>m</i>               | <i>P</i> 2 <sub>1</sub> / <i>c</i>               | <i>Pna</i> 2 <sub>1</sub>                        | <i>P</i> -1                                      |
| $\mu$ (mm <sup>-1</sup> )                        | 0.788                                                         | 0.880                                            | 0.07                                             | 4.41                                               | 0.66                                             | 0.08                                             | 0.08                                             | 0.65                                             |
| Temperature (K)                                  | 100(2)                                                        | 100(2)                                           | 100(2)                                           | 100(2)                                             | 100(2)                                           | 100(2)                                           | 100(2)                                           | 100(2)                                           |
| <i>Z</i>                                         | 4                                                             | 8                                                | 8                                                | 8                                                  | 2                                                | 4                                                | 4                                                | 4                                                |
| <i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )    | 1.429                                                         | 1                                                | 1.190                                            | 1.671                                              | 1.306                                            | 1.253                                            | 1.261                                            | 1.313                                            |
| Crystal size (mm <sup>3</sup> )                  | 0.32×0.27×0.19                                                | 0.25×0.19×0.11                                   | 0.15×0.09×0.04                                   | 0.19×0.12×0.08                                     | 0.12×0.08×0.05                                   | 0.22×0.18×0.10                                   | 0.14×0.09×0.05                                   | 0.22×0.15×0.09                                   |
| Radiation                                        | CuK $\alpha$ ( $\lambda$ = 1.54184)                           | CuK $\alpha$                                     | CuK $\alpha$                                     | CuK $\alpha$                                       | CuK $\alpha$                                     | MoK $\alpha$ ( $\lambda$ = 0.71073)              | MoK $\alpha$                                     | CuK $\alpha$                                     |
| Total reflections                                | 5151                                                          | 8586                                             | 41223                                            | 6338                                               | 5071                                             | 15790                                            | 11892                                            | 10430                                            |
| Unique reflections                               | 2236                                                          | 2881                                             | 7097                                             | 2482                                               | 1373                                             | 3379                                             | 3197                                             | 5945                                             |
| Angle range $2\theta$ (°)                        | 8.88–145.00                                                   | 4.09–75.50                                       | 6.66–145.00                                      | 9.29–145.00                                        | 8.62–145.00                                      | 5.76–55.00                                       | 6.16–55.00                                       | 6.20–145.00                                      |
| Reflections with $ F_o  \geq \sigma_F$           | 1767                                                          | 2474                                             | 6654                                             | 2213                                               | 1107                                             | 2913                                             | 3104                                             | 4799                                             |
| <i>R</i> <sub>int</sub>                          | 0.0265                                                        | 0.0288                                           | 0.049                                            | 0.0411                                             | 0.0705                                           | 0.0256                                           | 0.0174                                           | 0.0220                                           |
| <i>R</i> $\sigma$                                | 0.0302                                                        | 0.0271                                           | 0.097                                            | 0.0401                                             | 0.0465                                           | 0.0209                                           | 0.0155                                           | 0.0330                                           |
| <i>R</i> <sub>1</sub> ( $ F_o  \geq \sigma_F$ )  | 0.0370                                                        | 0.0384                                           | 0.0378                                           | 0.0346                                             | 0.0694                                           | 0.0444                                           | 0.0299                                           | 0.0435                                           |
| <i>wR</i> <sub>2</sub> ( $ F_o  \geq \sigma_F$ ) | 0.0920                                                        | 0.0975                                           | 0.0972                                           | 0.0907                                             | 0.1766                                           | 0.1101                                           | 0.0741                                           | 0.1102                                           |
| <i>R</i> <sub>1</sub> (all data)                 | 0.0516                                                        | 0.0455                                           | 0.0445                                           | 0.0399                                             | 0.0828                                           | 0.0516                                           | 0.0311                                           | 0.0559                                           |
| <i>wR</i> <sub>2</sub> (all data)                | 0.1027                                                        | 0.1035                                           | 0.1024                                           | 0.0955                                             | 0.1970                                           | 0.1158                                           | 0.0751                                           | 0.1209                                           |
| <i>S</i>                                         | 1.024                                                         | 1.035                                            | 1.03                                             | 1.050                                              | 1.062                                            | 1.030                                            | 1.071                                            | 1.023                                            |
| $\rho_{\min}, \rho_{\max}, e/\text{\AA}^3$       | −0.200, 0.248                                                 | −0.201, 0.213                                    | −0.20, 0.31                                      | −0.62, 0.89                                        | −0.31, 0.54                                      | −0.26, 0.28                                      | −0.17, 0.19                                      | −0.17/0.33                                       |

\* Crystallographic data for **L1** is available in A. S. Smirnov et al., *RSC Advances*, 2017, 7, 10070-10073.

**Table S3** Crystallographic and structure refinement data for complexes **C1-C8**

| Compound                                         | <b>C1</b>                                                                       | <b>C2</b>                                                                                     | <b>C3</b>                                                                                     | <b>C4</b>                                                                                     | <b>C5</b>                                                                                                                                                                            | <b>C6</b>                                                                                     | <b>C7</b>                                                                                     | <b>C8</b>                                                                       |
|--------------------------------------------------|---------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------|
| CCDC #                                           | 1538868                                                                         | 1538877                                                                                       | 1538873                                                                                       | 1538881                                                                                       | 1538878                                                                                                                                                                              | 1538883                                                                                       | 1538876                                                                                       | 1538871                                                                         |
| Formula                                          | C <sub>30</sub> H <sub>24</sub> Cl <sub>2</sub> CuN <sub>4</sub> O <sub>2</sub> | C <sub>36</sub> H <sub>36</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>4</sub> O <sub>2</sub> | C <sub>36</sub> H <sub>36</sub> Br <sub>2</sub> Cu <sub>2</sub> N <sub>4</sub> O <sub>2</sub> | C <sub>34</sub> H <sub>32</sub> Br <sub>2</sub> Cu <sub>2</sub> N <sub>4</sub> O <sub>2</sub> | C <sub>21</sub> H <sub>24</sub> BrCuN <sub>2</sub> O·<br>(C <sub>21</sub> H <sub>24</sub> BrCuN <sub>2</sub> O) <sub>0.7</sub> ·<br>C <sub>21</sub> H <sub>24</sub> N <sub>2</sub> O | C <sub>30</sub> H <sub>22</sub> Br <sub>4</sub> Cu <sub>2</sub> N <sub>4</sub> O <sub>2</sub> | C <sub>32</sub> H <sub>28</sub> Br <sub>2</sub> Cu <sub>2</sub> N <sub>4</sub> O <sub>2</sub> | C <sub>32</sub> H <sub>28</sub> Cl <sub>2</sub> CuN <sub>4</sub> O <sub>2</sub> |
| Crystal System                                   | Triclinic                                                                       | Monoclinic                                                                                    | Monoclinic                                                                                    | Monoclinic                                                                                    | Triclinic                                                                                                                                                                            | Triclinic                                                                                     | Triclinic                                                                                     | Triclinic                                                                       |
| <i>a</i> (Å)                                     | 8.0870(8)                                                                       | 15.435(8)                                                                                     | 15.4205(6)                                                                                    | 26.9791(11)                                                                                   | 11.0842(4)                                                                                                                                                                           | 8.5542(4)                                                                                     | 8.6213(4)                                                                                     | 8.9050(7)                                                                       |
| <i>b</i> (Å)                                     | 9.2417(10)                                                                      | 8.1831(15)                                                                                    | 7.92427(19)                                                                                   | 8.2871(3)                                                                                     | 11.7852(5)                                                                                                                                                                           | 9.5043(6)                                                                                     | 9.3911(5)                                                                                     | 9.2277(4)                                                                       |
| <i>c</i> (Å)                                     | 9.6103(10)                                                                      | 14.316(6)                                                                                     | 14.7380(5)                                                                                    | 14.1074(5)                                                                                    | 17.1333(5)                                                                                                                                                                           | 10.1464(4)                                                                                    | 10.1721(4)                                                                                    | 9.8071(7)                                                                       |
| $\alpha$ (°)                                     | 75.944(9)                                                                       | 90                                                                                            | 90                                                                                            | 90                                                                                            | 99.747(3)                                                                                                                                                                            | 90.501(4)                                                                                     | 90.122(4)                                                                                     | 74.790(5)                                                                       |
| $\beta$ (°)                                      | 75.005(9)                                                                       | 114.64(5)                                                                                     | 112.819(4)                                                                                    | 94.972(3)                                                                                     | 108.723(3)                                                                                                                                                                           | 96.474(4)                                                                                     | 97.663(3)                                                                                     | 65.400(7)                                                                       |
| $\gamma$ (°)                                     | 79.112(9)                                                                       | 90                                                                                            | 90                                                                                            | 90                                                                                            | 102.672(3)                                                                                                                                                                           | 115.484(6)                                                                                    | 115.574(5)                                                                                    | 76.151(5)                                                                       |
| <i>V</i> (Å <sup>3</sup> )                       | 666.90(13)                                                                      | 1643.5(13)                                                                                    | 1659.98(10)                                                                                   | 3142.2(2)                                                                                     | 1997.24(13)                                                                                                                                                                          | 738.40(7)                                                                                     | 734.60(7)                                                                                     | 699.24(9)                                                                       |
| Molecular weight                                 | 606.97                                                                          | 754.67                                                                                        | 843.59                                                                                        | 815.53                                                                                        | 884.71                                                                                                                                                                               | 917.23                                                                                        | 787.48                                                                                        | 635.02                                                                          |
| Space group                                      | <i>P</i> -1                                                                     | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                                            | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                                            | <i>C</i> 2/ <i>c</i>                                                                          | <i>P</i> -1                                                                                                                                                                          | <i>P</i> -1                                                                                   | <i>P</i> -1                                                                                   | <i>P</i> -1                                                                     |
| $\mu$ (mm <sup>-1</sup> )                        | 3.293                                                                           | 3.405                                                                                         | 3.728                                                                                         | 4.954                                                                                         | 3.451                                                                                                                                                                                | 8.417                                                                                         | 5.273                                                                                         | 3.167                                                                           |
| Temperature (K)                                  | 100(2)                                                                          | 100(2)                                                                                        | 100(2)                                                                                        | 100(2)                                                                                        | 100(2)                                                                                                                                                                               | 100(2)                                                                                        | 100(2)                                                                                        | 100(2)                                                                          |
| <i>Z</i>                                         | 1                                                                               | 1                                                                                             | 2                                                                                             | 4                                                                                             | 2                                                                                                                                                                                    | 1                                                                                             | 1                                                                                             | 1                                                                               |
| <i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )    | 1.511                                                                           | 1.525                                                                                         | 1.688                                                                                         | 1.724                                                                                         | 1.471                                                                                                                                                                                | 2.063                                                                                         | 1.780                                                                                         | 1.508                                                                           |
| Crystal size (mm <sup>3</sup> )                  | 0.18 × 0.16 × 0.08                                                              | 0.04 × 0.02 × 0.01                                                                            | 0.12 × 0.09 × 0.05                                                                            | 0.22 × 0.17 × 0.07                                                                            | 0.18 × 0.10 × 0.06                                                                                                                                                                   | 0.16 × 0.09 × 0.05                                                                            | 0.23 × 0.16 × 0.09                                                                            | 0.14 × 0.09 × 0.05                                                              |
| Radiation                                        | CuK $\alpha$                                                                    | CuK $\alpha$                                                                                  | MoK $\alpha$                                                                                  | CuK $\alpha$                                                                                  | CuK $\alpha$                                                                                                                                                                         | CuK $\alpha$                                                                                  | CuK $\alpha$                                                                                  | CuK $\alpha$                                                                    |
| Total reflections                                | 11073                                                                           | 5753                                                                                          | 11026                                                                                         | 11659                                                                                         | 27863                                                                                                                                                                                | 6459                                                                                          | 10404                                                                                         | 4591                                                                            |
| Unique reflections                               | 2632                                                                            | 3059                                                                                          | 3798                                                                                          | 3120                                                                                          | 7935                                                                                                                                                                                 | 2921                                                                                          | 2914                                                                                          | 2689                                                                            |
| Angle range 2 $\theta$ (°)                       | 9.73-145.00                                                                     | 6.30-140.00                                                                                   | 6.08-55.00                                                                                    | 6.58-145.00                                                                                   | 7.96-145.00                                                                                                                                                                          | 8.79-145.00                                                                                   | 8.79-145.00                                                                                   | 10.04-145.00                                                                    |
| Reflections with $ F_o  \geq \sigma_F$           | 2338                                                                            | 1493                                                                                          | 3196                                                                                          | 2698                                                                                          | 6860                                                                                                                                                                                 | 2537                                                                                          | 2532                                                                                          | 2294                                                                            |
| <i>R</i> <sub>int</sub>                          | 0.0394                                                                          | 0.1286                                                                                        | 0.0350                                                                                        | 0.0502                                                                                        | 0.0634                                                                                                                                                                               | 0.0382                                                                                        | 0.0534                                                                                        | 0.0352                                                                          |
| <i>R</i> $\sigma$                                | 0.0274                                                                          | 0.1499                                                                                        | 0.0402                                                                                        | 0.0383                                                                                        | 0.0505                                                                                                                                                                               | 0.0466                                                                                        | 0.0389                                                                                        | 0.0535                                                                          |
| <i>R</i> <sub>1</sub> ( $ F_o  \geq \sigma_F$ )  | 0.0281                                                                          | 0.1451                                                                                        | 0.0332                                                                                        | 0.0386                                                                                        | 0.0492                                                                                                                                                                               | 0.0336                                                                                        | 0.0347                                                                                        | 0.0389                                                                          |
| <i>wR</i> <sub>2</sub> ( $ F_o  \geq \sigma_F$ ) | 0.0704                                                                          | 0.3741                                                                                        | 0.0753                                                                                        | 0.0966                                                                                        | 0.1232                                                                                                                                                                               | 0.0784                                                                                        | 0.0868                                                                                        | 0.0959                                                                          |
| <i>R</i> <sub>1</sub> (all data)                 | 0.0330                                                                          | 0.2246                                                                                        | 0.0452                                                                                        | 0.0472                                                                                        | 0.0575                                                                                                                                                                               | 0.0418                                                                                        | 0.0414                                                                                        | 0.0468                                                                          |
| <i>wR</i> <sub>2</sub> (all data)                | 0.0735                                                                          | 0.4590                                                                                        | 0.0816                                                                                        | 0.1049                                                                                        | 0.1305                                                                                                                                                                               | 0.0835                                                                                        | 0.0919                                                                                        | 0.1030                                                                          |
| <i>S</i>                                         | 1.035                                                                           | 1.372                                                                                         | 1.046                                                                                         | 1.033                                                                                         | 1.040                                                                                                                                                                                | 1.042                                                                                         | 1.045                                                                                         | 1.041                                                                           |
| $\rho_{\min}, \rho_{\max}, e/\text{\AA}^3$       | -0.49, 0.33                                                                     | -2.03, 2.90                                                                                   | -0.52, 0.90                                                                                   | -0.44, 1.27                                                                                   | -0.88, 1.25                                                                                                                                                                          | -0.70, 0.79                                                                                   | -0.69, 0.93                                                                                   | -0.43, 0.62                                                                     |

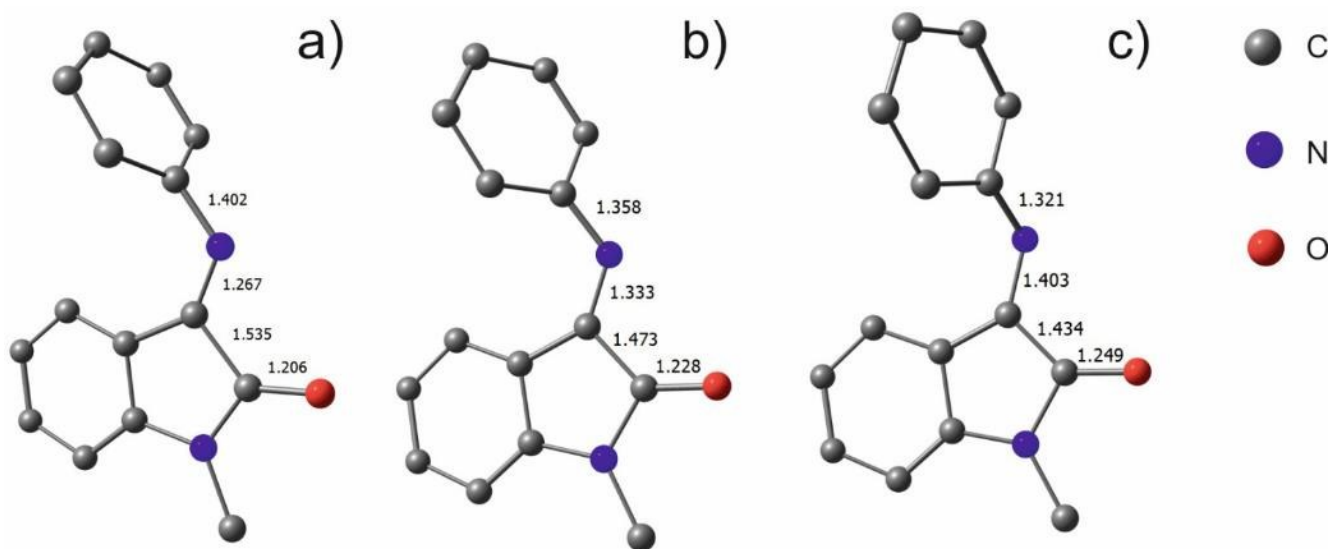
**Table S4** Crystallographic and structure refinement data for complexes **C9-C16**

| Compound                                         | <b>C9</b>                                                         | <b>C10</b>                                                       | <b>C11</b>                                                                        | <b>C12</b>                                                        | <b>C13</b>                                          | <b>C14</b>                                                                                   | <b>C15</b>                                          | <b>C16</b>                                                                                   |
|--------------------------------------------------|-------------------------------------------------------------------|------------------------------------------------------------------|-----------------------------------------------------------------------------------|-------------------------------------------------------------------|-----------------------------------------------------|----------------------------------------------------------------------------------------------|-----------------------------------------------------|----------------------------------------------------------------------------------------------|
| CCDC #                                           | 1538874                                                           | 1538872                                                          | 1538866                                                                           | 1538870                                                           | 1538882                                             | 1538875                                                                                      | 1538879                                             | 1538880                                                                                      |
| Formula                                          | C <sub>30</sub> H <sub>24</sub> BrCuN <sub>4</sub> O <sub>2</sub> | C <sub>30</sub> H <sub>24</sub> CuIn <sub>4</sub> O <sub>2</sub> | C <sub>38</sub> H <sub>39</sub> BCuF <sub>4</sub> N <sub>5</sub> O <sub>2.3</sub> | C <sub>30</sub> H <sub>24</sub> BrCuN <sub>4</sub> O <sub>4</sub> | C <sub>20</sub> H <sub>14</sub> CuIn <sub>2</sub> O | C <sub>36</sub> H <sub>36</sub> Cu <sub>2</sub> I <sub>2</sub> N <sub>4</sub> O <sub>2</sub> | C <sub>15</sub> H <sub>12</sub> CuIn <sub>2</sub> O | C <sub>34</sub> H <sub>32</sub> Cu <sub>2</sub> I <sub>2</sub> N <sub>4</sub> O <sub>2</sub> |
| Crystal System                                   | Monoclinic                                                        | Monoclinic                                                       | Monoclinic                                                                        | Monoclinic                                                        | Monoclinic                                          | Monoclinic                                                                                   | Triclinic                                           | Monoclinic                                                                                   |
| <i>a</i> (Å)                                     | 17.9841(19)                                                       | 17.9067(5)                                                       | 12.8485(3)                                                                        | 17.9161(9)                                                        | 12.7900(8)                                          | 15.5090(16)                                                                                  | 8.5695(9)                                           | 27.2980(4)                                                                                   |
| <i>b</i> (Å)                                     | 6.9520(8)                                                         | 6.9140(2)                                                        | 14.2133(3)                                                                        | 6.9866(5)                                                         | 17.0969(8)                                          | 7.8740(9)                                                                                    | 9.3493(7)                                           | 8.22746(15)                                                                                  |
| <i>c</i> (Å)                                     | 21.036(2)                                                         | 21.1065(7)                                                       | 21.2613(5)                                                                        | 21.0116(9)                                                        | 7.9810(5)                                           | 15.023(2)                                                                                    | 10.6986(11)                                         | 14.3942(3)                                                                                   |
| $\alpha$ (°)                                     | 90                                                                | 90                                                               | 90                                                                                | 90                                                                | 90                                                  | 90                                                                                           | 74.782(9)                                           | 90                                                                                           |
| $\beta$ (°)                                      | 91.011(2)                                                         | 90.872(3)                                                        | 106.297(2)                                                                        | 91.316(5)                                                         | 102.964(7)                                          | 111.451(14)                                                                                  | 75.057(9)                                           | 93.2951(13)                                                                                  |
| $\gamma$ (°)                                     | 90                                                                | 90                                                               | 90                                                                                | 90                                                                | 90                                                  | 90                                                                                           | 63.915(10)                                          | 90                                                                                           |
| <i>V</i> (Å <sup>3</sup> )                       | 2629.6(5)                                                         | 2612.82(14)                                                      | 3726.72(15)                                                                       | 2629.4(3)                                                         | 1700.72(18)                                         | 1707.5(4)                                                                                    | 732.76(14)                                          | 3227.49(9)                                                                                   |
| Molecular weight                                 | 615.98                                                            | 662.97                                                           | 752.89                                                                            | 647.98                                                            | 488.77                                              | 937.57                                                                                       | 426.71                                              | 909.51                                                                                       |
| Space group                                      | C2/c                                                              | C2/c                                                             | P2 <sub>1</sub> /n                                                                | C2/c                                                              | P2 <sub>1</sub> /c                                  | P2 <sub>1</sub> /c                                                                           | P-1                                                 | C2/c                                                                                         |
| $\mu$ (mm <sup>-1</sup> )                        | 2.386                                                             | 10.744                                                           | 0.647                                                                             | 3.330                                                             | 16.141                                              | 16.036                                                                                       | 3.592                                               | 16.944                                                                                       |
| Temperature (K)                                  | 210(2)                                                            | 100(2)                                                           | 100(2)                                                                            | 100(2)                                                            | 100(2)                                              | 100(2)                                                                                       | 100(2)                                              | 100(2)                                                                                       |
| <i>Z</i>                                         | 4                                                                 | 4                                                                | 4                                                                                 | 4                                                                 | 4                                                   | 2                                                                                            | 2                                                   | 4                                                                                            |
| D <sub>calc</sub> (g/cm <sup>3</sup> )           | 1.556                                                             | 1.685                                                            | 1.342                                                                             | 1.637                                                             | 1.909                                               | 1.824                                                                                        | 1.934                                               | 1.872                                                                                        |
| Crystal size (mm <sup>3</sup> )                  | 0.18 × 0.13 × 0.05                                                | 0.18 × 0.12 × 0.07                                               | 0.10 × 0.06 × 0.03                                                                | 0.10 × 0.05 × 0.02                                                | 0.22 × 0.07 × 0.02                                  | 0.14 × 0.06 × 0.02                                                                           | 0.27 × 0.06 × 0.01                                  | 0.28 × 0.12 × 0.02                                                                           |
| Radiation                                        | MoK $\alpha$                                                      | CuK $\alpha$                                                     | MoK $\alpha$                                                                      | Cu K $\alpha$                                                     | CuK $\alpha$                                        | CuK $\alpha$                                                                                 | MoK $\alpha$                                        | CuK $\alpha$                                                                                 |
| Total reflections                                | 13152                                                             | 9321                                                             | 25734                                                                             | 4917                                                              | 6610                                                | 9644                                                                                         | 6003                                                | 23592                                                                                        |
| Unique reflections                               | 2796                                                              | 2477                                                             | 8807                                                                              | 2547                                                              | 3217                                                | 3370                                                                                         | 3355                                                | 3212                                                                                         |
| Angle range 2 $\theta$ (°)                       | 3.87-53.45                                                        | 8.38-140.00                                                      | 6.07-56.00                                                                        | 8.42-145.00                                                       | 7.09-140.00                                         | 6.12-145.00                                                                                  | 5.65-55.00                                          | 6.49-145.00                                                                                  |
| Reflections with $ F_o  \geq \sigma_F$           | 1797                                                              | 2404                                                             | 7026                                                                              | 2011                                                              | 2521                                                | 2268                                                                                         | 2866                                                | 3041                                                                                         |
| <i>R</i> <sub>int</sub>                          | 0.0445                                                            | 0.0435                                                           | 0.0310                                                                            | 0.0701                                                            | 0.0636                                              | 0.1407                                                                                       | 0.0315                                              | 0.0676                                                                                       |
| <i>R</i> $\sigma$                                | 0.0470                                                            | 0.0342                                                           | 0.0365                                                                            | 0.0831                                                            | 0.0821                                              | 0.1389                                                                                       | 0.0583                                              | 0.0318                                                                                       |
| <i>R</i> <sub>1</sub> ( $ F_o  \geq \sigma_F$ )  | 0.0386                                                            | 0.0312                                                           | 0.0484                                                                            | 0.0757                                                            | 0.0509                                              | 0.0710                                                                                       | 0.0329                                              | 0.0354                                                                                       |
| <i>wR</i> <sub>2</sub> ( $ F_o  \geq \sigma_F$ ) | 0.0874                                                            | 0.0781                                                           | 0.1181                                                                            | 0.1958                                                            | 0.1225                                              | 0.1714                                                                                       | 0.0561                                              | 0.0978                                                                                       |
| <i>R</i> <sub>1</sub> (all data)                 | 0.0687                                                            | 0.0325                                                           | 0.0647                                                                            | 0.0892                                                            | 0.0686                                              | 0.1073                                                                                       | 0.0425                                              | 0.0373                                                                                       |
| <i>wR</i> <sub>2</sub> (all data)                | 0.0946                                                            | 0.0796                                                           | 0.1302                                                                            | 0.2125                                                            | 0.1340                                              | 0.2048                                                                                       | 0.0602                                              | 0.1004                                                                                       |
| <i>S</i>                                         | 0.893                                                             | 1.049                                                            | 1.019                                                                             | 1.021                                                             | 0.991                                               | 1.014                                                                                        | 1.015                                               | 1.065                                                                                        |
| $\rho_{\min}, \rho_{\max}, e/\text{\AA}^3$       | -0.34, 1.08                                                       | -0.87, 0.87                                                      | -0.93, 1.15                                                                       | -1.50, 1.44                                                       | -0.90, 2.21                                         | -1.24, 2.20                                                                                  | -0.79, 0.88                                         | -1.54, 1.62                                                                                  |

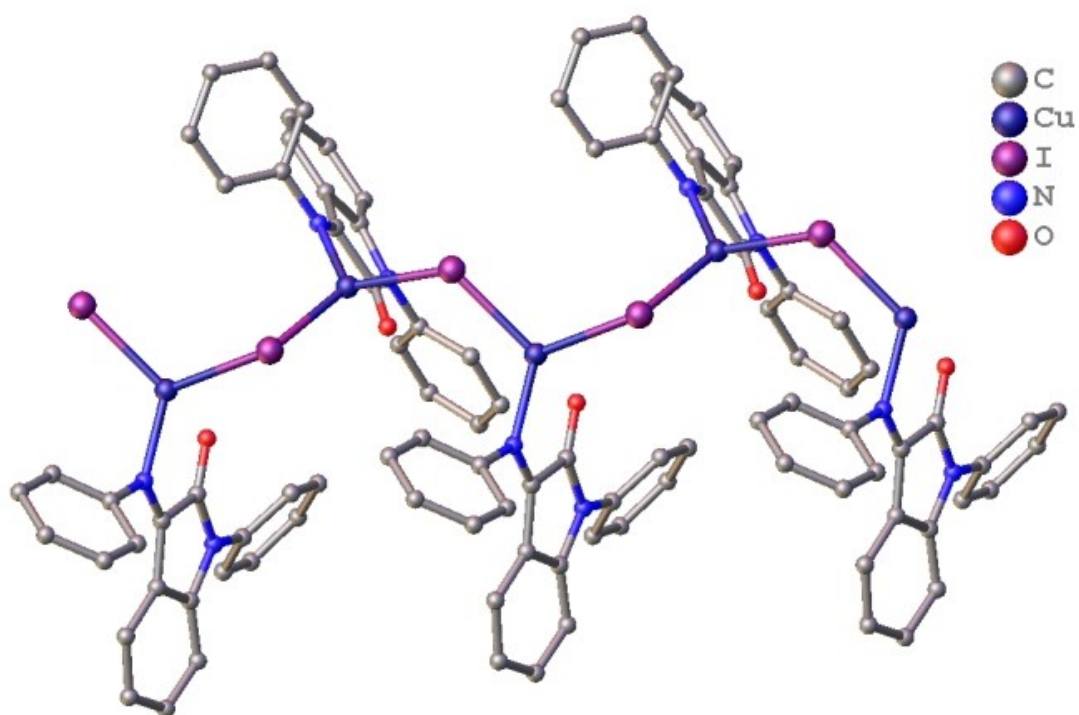
**Table S5** Calculated (B3LYP/cc-pVTZ) Mulliken charges of isatin Schiff base ligands **L0-L9**

| Compound<br>/atom | N1            | C2    | O11           | C3     | N12           | C13   |
|-------------------|---------------|-------|---------------|--------|---------------|-------|
| <b>*L0</b>        | <b>-0.112</b> | 0.210 | -0.269        | -0.067 | -0.154        | 0.177 |
| <b>L1</b>         | -0.034        | 0.222 | -0.290        | -0.078 | -0.155        | 0.173 |
| <b>L3</b>         | -0.038        | 0.217 | -0.290        | -0.072 | -0.155        | 0.060 |
| <b>L4</b>         | -0.030        | 0.208 | -0.293        | -0.059 | <b>-0.179</b> | 0.055 |
| <b>L5</b>         | -0.034        | 0.223 | -0.287        | -0.078 | -0.148        | 0.180 |
| <b>L6</b>         | -0.032        | 0.223 | -0.292        | -0.078 | -0.159        | 0.166 |
| <b>L7</b>         | -0.032        | 0.217 | -0.291        | -0.073 | -0.159        | 0.052 |
| <b>L8</b>         | -0.062        | 0.232 | -0.275        | -0.092 | -0.159        | 0.165 |
| <b>L9</b>         | <b>-0.049</b> | 0.248 | <b>-0.307</b> | -0.076 | -0.155        | 0.174 |

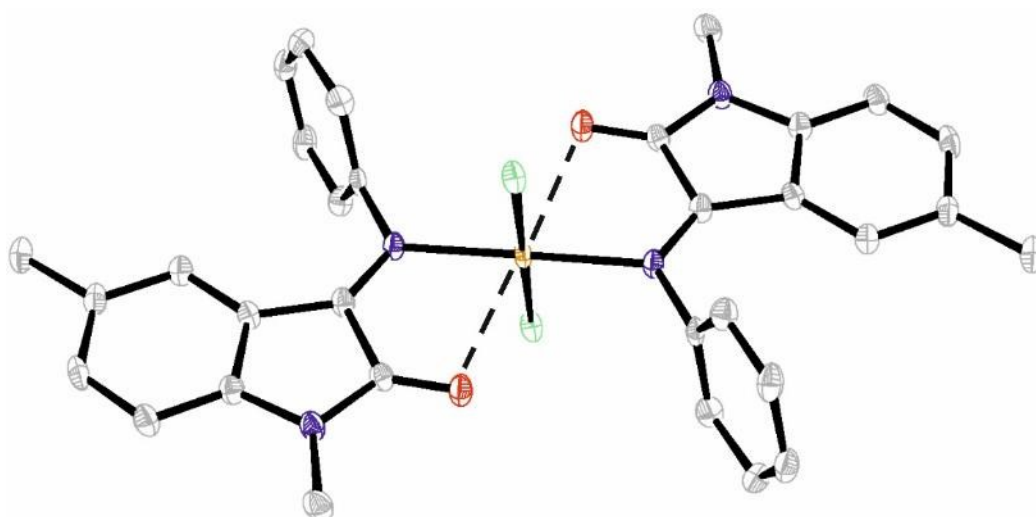
**\*L0** - 1-H-3(phenylimino)indolinone-2-one



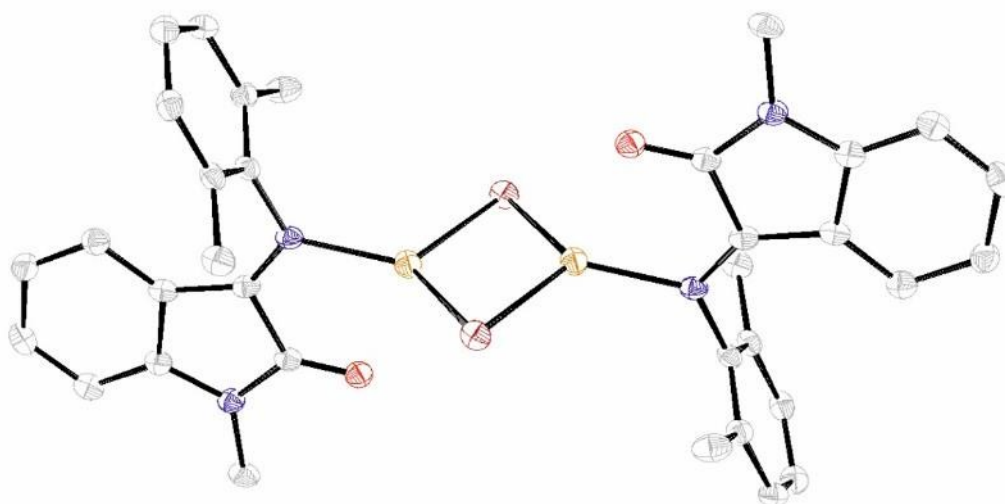
**Figure S24** DFT (B3LYP cc-PVTZ) optimized gas-phase geometries of neutral **L1** (a), single **L1<sup>-</sup>** (b) and double (c) reduced **L1<sup>2-</sup>**



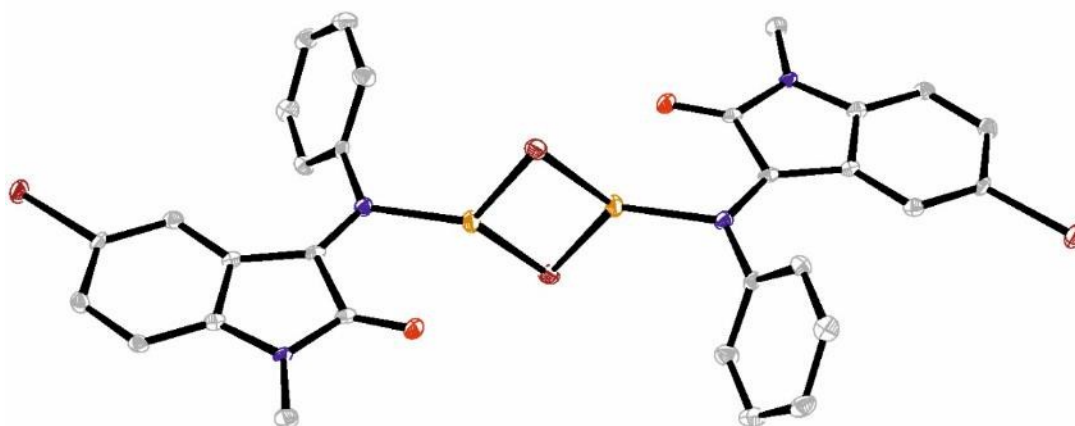
**Figure S25** Molecular structure of the complex **C13** fragment



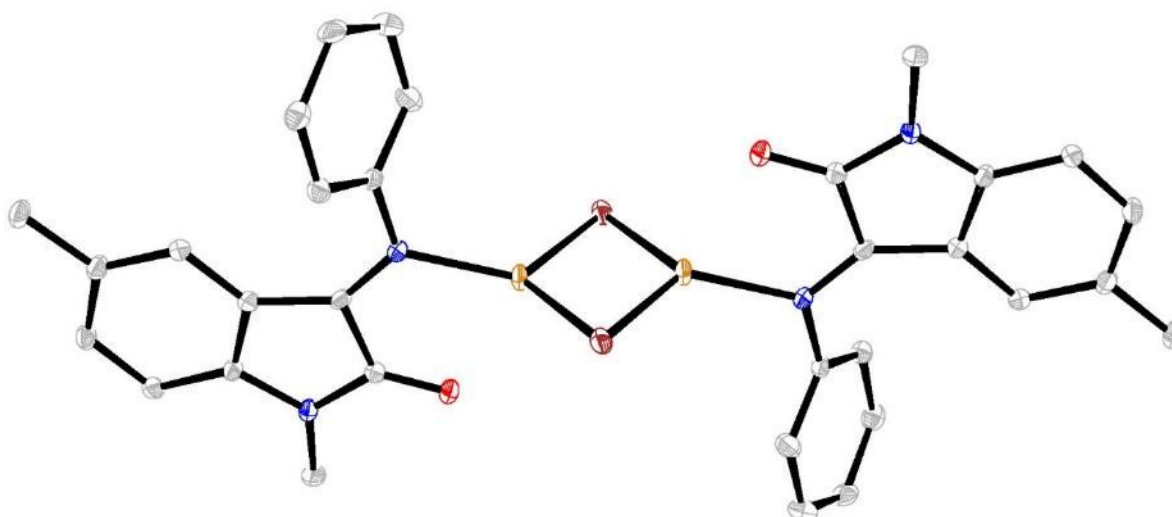
**Figure S26** ORTEP representation of X-ray resolved molecular structure of  $[\text{Cu}(\text{L6})_2]\text{Cl}_2$  (**C8**)



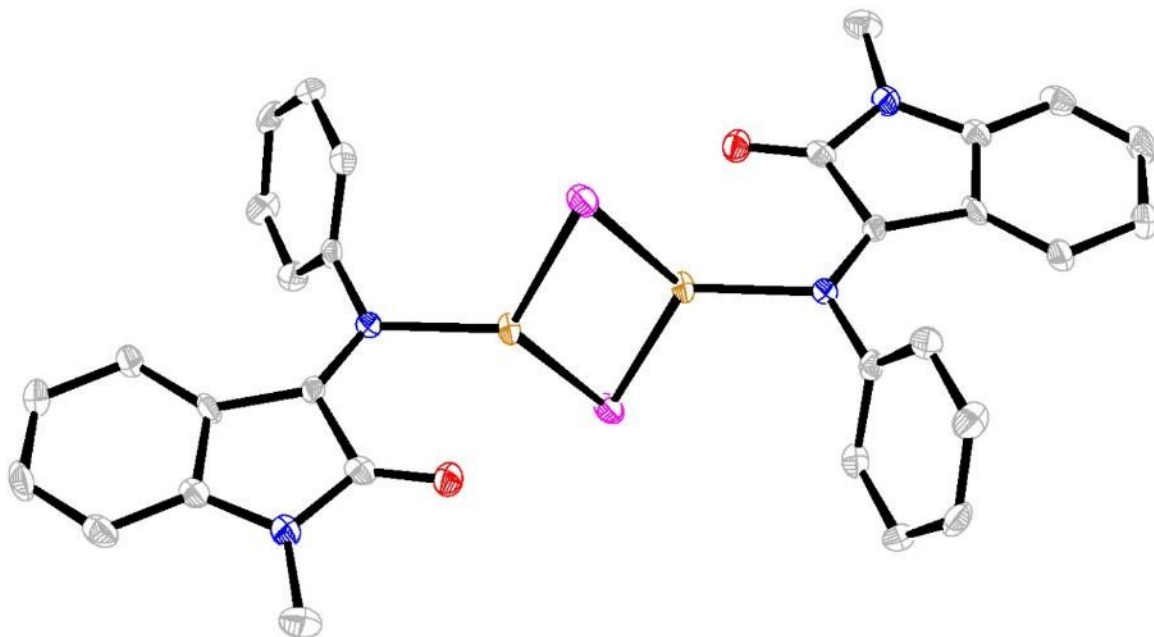
**Figure S27** ORTEP representation of X-ray resolved molecular structure of  $[\text{Cu}_2(\mu\text{-Br})_2(\text{L3})_2]$  (**C4**)



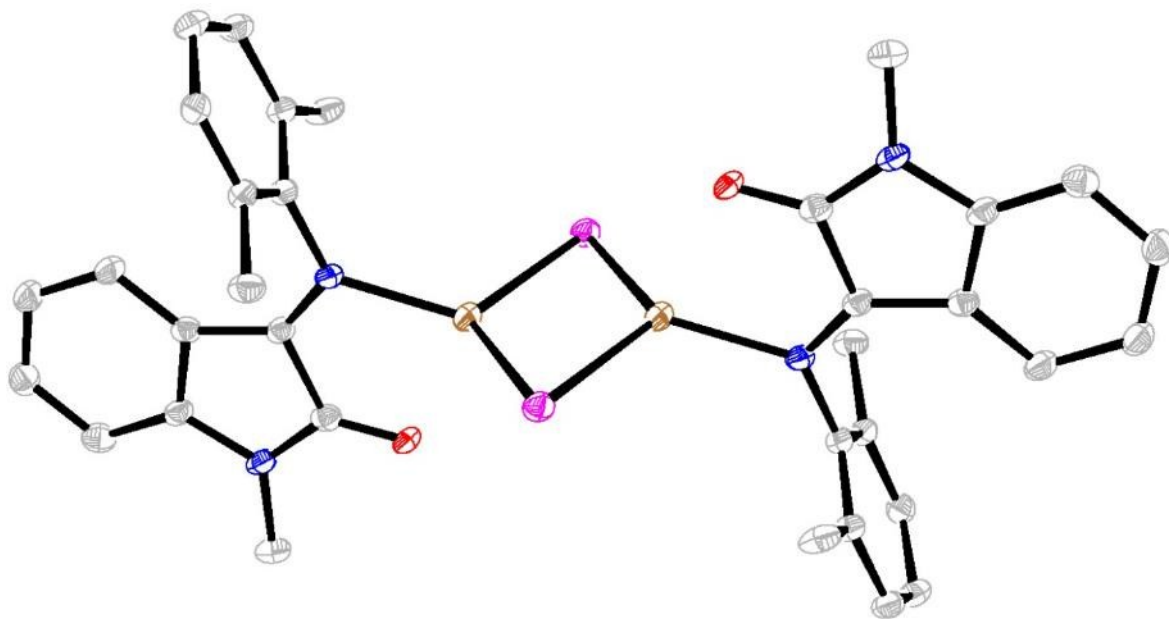
**Figure S28** ORTEP representation of X-ray resolved molecular structure of  $[\text{Cu}_2(\mu\text{-Br})_2(\text{L5})_2]$  (**C6**)



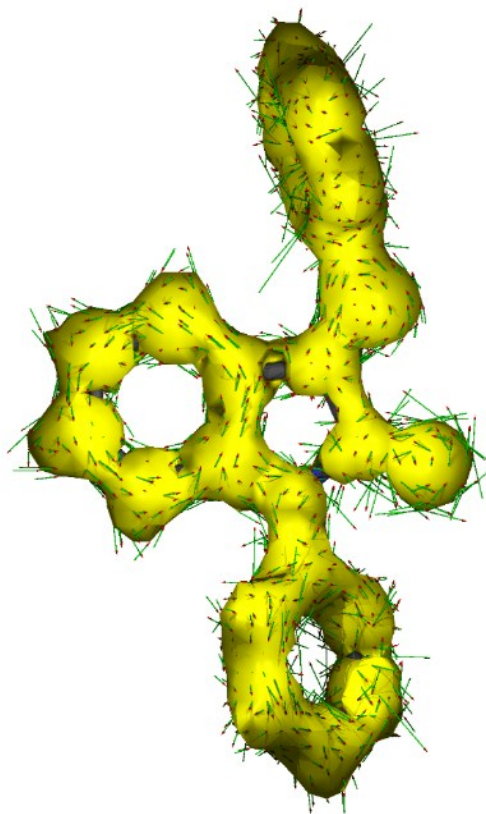
**Figure S29** ORTEP representation of X-ray resolved molecular structure of  $[\text{Cu}_2(\mu\text{-Br})_2(\text{L6})_2]$  (**C7**)



**Figure S30** ORTEP representation of X-ray resolved molecular structure of  $[\text{Cu}_2(\mu\text{-I})_2(\text{L1})_2]$  (**C15**)



**Figure S31** ORTEP representation of X-ray resolved molecular structure of  $[\text{Cu}_2(\mu\text{-I})_2(\text{L3})_2]$  (**C16**)



**Figure S32** Anisotropy of the Induced Current Density (ACID) isosurface for the **L9** at an isosurface value 0.05 a.u. Current density vectors are plotted onto the ACID isosurface to indicate dia- and paratropic ring currents. The magnetic field vector is orthogonal relative to the rings plane and points upward (clockwise currents are diatropic).