Electronic Supplementary Material (ESI) for RSC Advances.


# Electronic Supplementary Information

## A novel method for copper(II) mediated regionselective bromination of aromatic rings under mild conditions

**Samim Khan, Subrata Jana, Michael G. B. Drew, Antonio Bauza, Antonio Frontera and Shouvik Chattopadhyay**

**Table S1:** Crystal data and refinement details of the complex.

| | |
|---|---|
| Formula | $C_{18}H_{22}Br_2CuN_2O$ |
| Formula Weight | 505.73 |
| Crystal Size [mm] | 0.04 x 0.05 x 0.21 |
| Temperature (K) | 150 |
| Crystal system | Monoclinic |
| Space group | P21/c |
| a(Å) | 7.3937(5) |
| b(Å) | 12.4939(13) |
| c(Å) | 19.6733(16) |
| α (deg) | (90) |
| β(deg) | 91.432(6) |
| γ (deg) | (90) |
| Z | 4 |
| $d_{calc}$ (g $cm^{-3}$) | 1.849 |
| μ (mm-1) | 5.608 |
| *F*(000) | 1004 |
| Total Reflections | 9915 |
| Unique Reflections | 5211 |
| Observed data [I > 2 σ (I)] | 3506 |
| No. of parameters | 220 |
| R(int) | 0.057 |
| R1, wR2 ( all data) | 0.1198, 0.1960 |
| R1, wR2 [I > 2 σ (I)] | 0.0739, 0.1779 |
| Min. and Max. Resd. Dens. [e/Ang^3] | -2.02, 1.47 |

**Table S2:** Selected bond lengths (Å) and bond angles (º) of the complex.

| | |
|---|---|
| Br(1)-Cu(1) | 2.4168(11) |
| Cu(1)-O(11) | 1.869(6) |
| Cu(1)-N(23) | 1.968(6) |
| Cu(1)-N(26) | 2.030(6) |
| Br(1)-Cu(1)-O(11) | 87.52(16) |
| Br(1)-Cu(1)-N(23) | 169.17(19) |
| Br(1)-Cu(1)-N(26) | 95.59(18) |
| O(11)-Cu(1)-N(23) | 91.7(2) |
| O(11)-Cu(1)-N(26) | 176.7(2) |
| N(23)-Cu(1)-N(26) | 85.1(3) |

**Table S3:** Geometric features (distances in Å and angles in degrees) of the C–H···π and anion···π interactions.

| C–H···π | | | | |
|---|---|---|---|---|
| C–H···Cg(Ring) | H···Cg (Å) | C–H···Cg (°) | C···Cg (Å) | Symmetry transformation |
| C(221)-H(22C)···Cg(4) | 2.70 | 148 | 3.549(8) | 1-x,2-y,1-z |
| C(27)-H(27B)···Cg(3) | 3.00 | 159 | 3.919(9) | 1-x,1/2+y,1/2-z |
| C(30)-H(30A)···Cg(4) | 2.91 | 123 | 3.530(12) | 1-x,1/2+y,1/2-z |
| anion···π | | | | |
| Y–X···Cg(Ring) | X···Cg (Å) | Y–X···Cg (°) | Y···Cg (Å) | Symmetry transformation |
| C(19)-Br(19)···Cg(2) | 3.629(3) | 68.9(2) | 3.437(7) | 1-x,2-y,1-z |

Cg(2)=Centre of gravity of ring [Cu(1)–O(11)–C(12)–C(21)–C(22)–N(23)]; Cg(3)=Centre of gravity of ring [C(12)–C(13)–C(18)–C(19)–C(20)–C(21)]; Cg(4)=Centre of gravity of ring [C(13)–C(14)–C(15)–C(16)–C(17)–C(18)].

**Table S4:** Geometric features (distances in Å and angles in degrees) of the π···π interactions.

| Cg(I)···Cg(J) | $D_p$ | α | β | γ | $D1_p$ | $D2_p$ | Symmetry transformation |
|---|---|---|---|---|---|---|---|
| Cg(2)···Cg(3) | 3.901(4) | 0.5(3) | 29.9 | 29.5 | 3.397(2) | 3.381(3) | 1-x,2-y,1-z |
| Cg(3)···Cg(3) | 3.715(4) | 0 | 23.9 | 23.9 | 3.396(3) | 3.396(3) | 1-x,2-y,1-z |

α=Dihedral Angle between ring I and ring J(º); β=Angle Cg(I)→Cg(J) vector and normal to plane I (º); γ=Angle Cg(I)→Cg(J) vector and normal to plane J (º); $D_p$= distance between the centroids of ring I and ring J; $D1_p$=Perpendicular distance of Cg(I) to ring J; $D2_p$=Perpendicular distance of Cg(J) to ring I.