**SUPPORTING INFORMATION**

# "Comprehensive enhancement in electrocatalytic oxygen evolution performance of nickel and cobalt complexes derived from π–conjugated N–heterocyclic carbene ligands through carbon composite strategy"

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## *General considerations*

All the reactions including starting materials (**1–3**) and triazolium salts (**4** and **5**) were carried out under aerobic conditions in oven–dried glassware with magnetic stirring. 1,2,4–Triazole, 3–chloro–2–methyl–1–propene, potassium hydroxide, dicyclopentadienylnickel(II), anhydrous cobalt(II) chloride anhydrous were procured commercially from Merck chemical company and were used without further purification. Further, the carbon composite was commercially procured from Shilpent enterprises. Heating was accomplished by a silicone oil

bath maintaining desired temperature. Reactions were monitored by thin–layer chromatography (TLC) performed on 0.25 mm Merck TLC silica gel plates. For the removal of volatile solvents rotary evaporator attached to a dry diaphragm pump (10–15 mm Hg) was used. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer and have been outlined corresponding to DMSO–$d_6$. $^{1}H$ NMR coupling constants ($J$) are reported in Hertz (Hz) and peak splitting have been assigned as singlet (s), doublet (d), triplet (t) and multiplet (m). FT–IR spectra were recorded on a Nicolet FT–IR spectrometer using KBr pellet method and the spectral responses were measured in the range of 400–6000 $cm^{-1}$. The molar conductivity measurements were recorded using a digital ELICO-CM-82 conductivity bridge using 0.001 M aqueous potassium chloride solution for calibration. The melting points were assessed using a Stuart scientific (UK) instrument with an accuracy of ± 0.3 $^{o}C$.

The single crystal data of the respective NHC precursors have been obtained through X–ray diffraction analysis. The crystals were mounted on a Gemini A Ultra Oxford Diffraction automatic diffractometer equipped with a CCD detector for data collection. X–ray intensity data were collected with graphite monochromated MoKa radiation (kL’0.71073 Å) at 295(2) K with ω scan mode. Lorentz, polarization and empirical absorption correction using spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm (CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.37.46) were applied. All non–hydrogen atoms were refined anisotropically using full–matrix, least squares. All hydrogen atoms were added geometrically and refined as “riding” on the adjacent carbon with individual isotropic temperature factor equal to 1.2 times the value of equivalent temperature factor of the parent atom. Olex2[1] and SHELXS[2] programs were used for all calculations. The molecular graphic designs and packing diagram were performed using OLEX2 software.

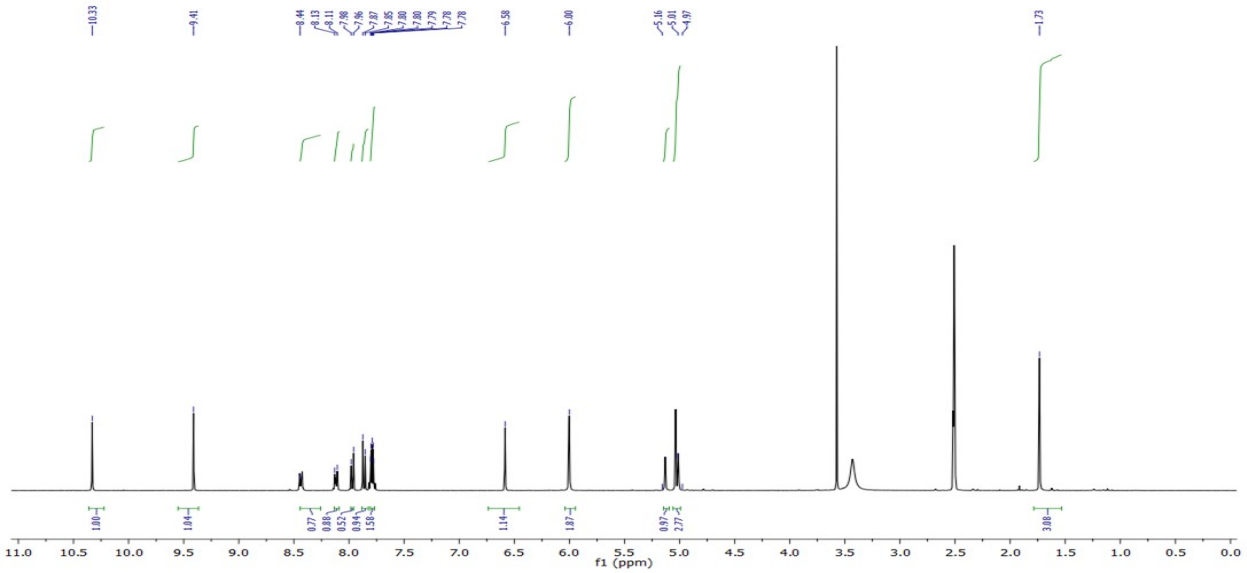


Figure SI1: [1]H NMR spectrum of salt 7,8 –benzocoumarin substituted salt **4** recorded in $d_6$–DMSO at room temperature.

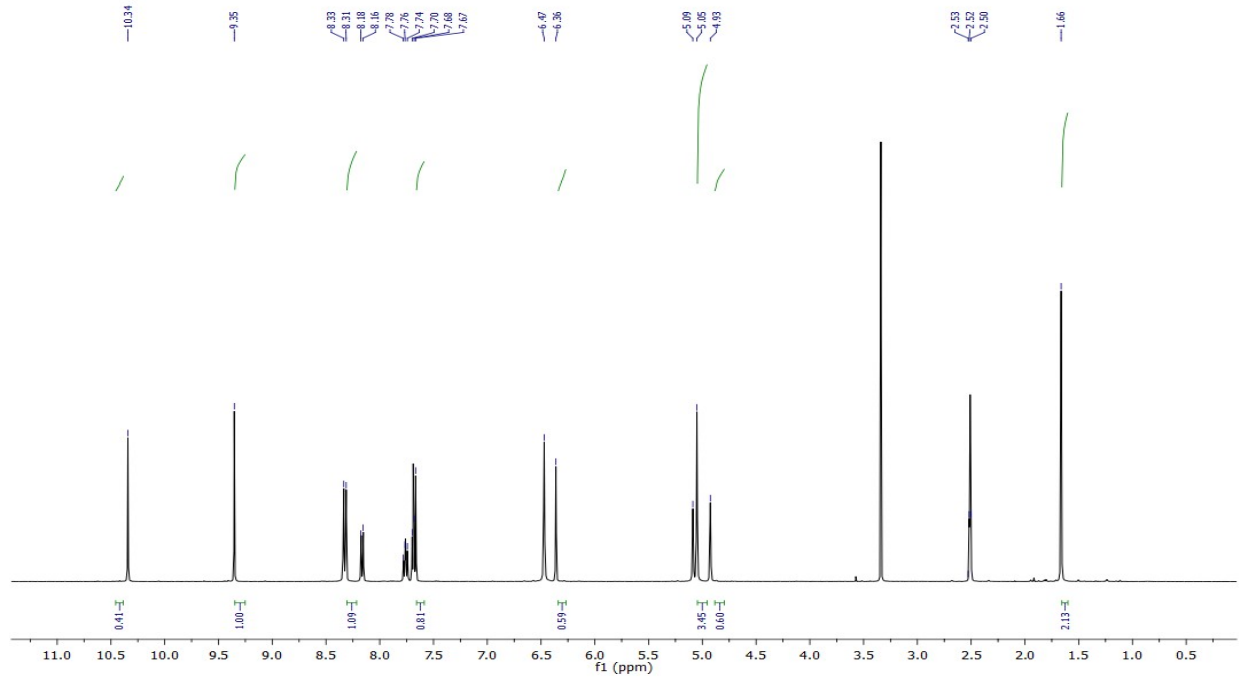


Figure SI2: [1]H NMR spectrum of 5,6 –benzocoumarin substituted salt **5** recorded in $d_6$–DMSO at room temperature.

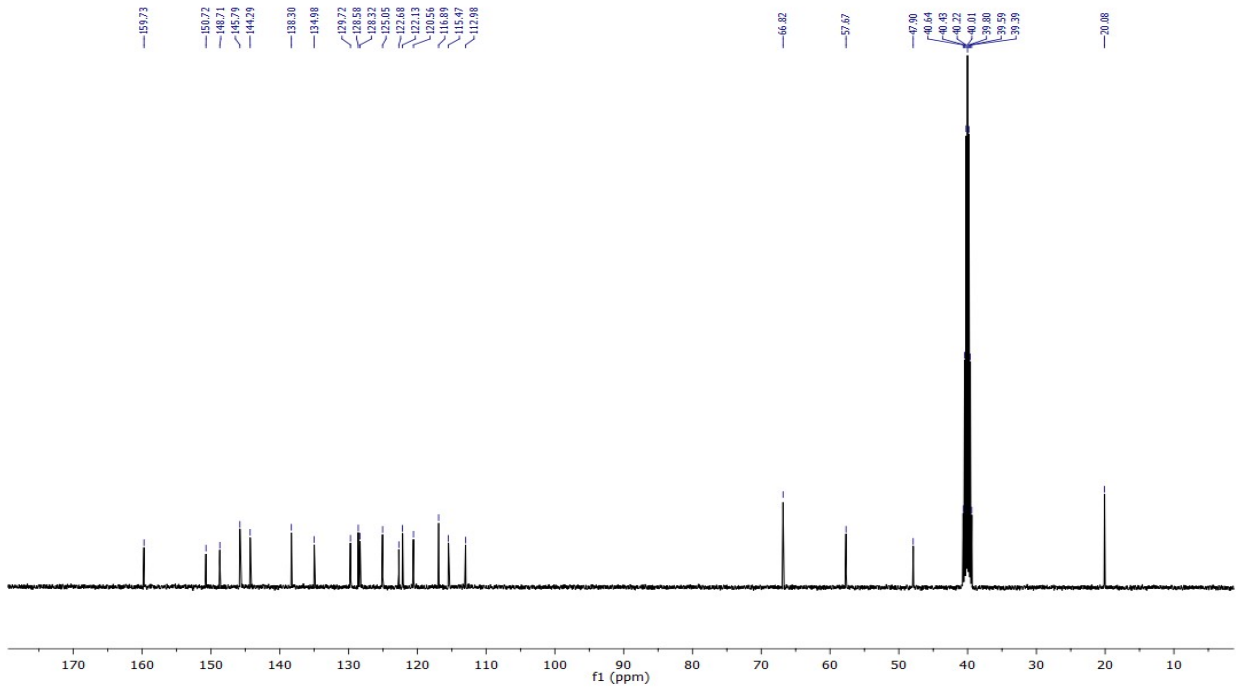


Figure SI3: $^{13}C$ NMR spectrum of 7,8 –benzocoumarin substituted salt **4** recorded in $d_6$–DMSO at room temperature.

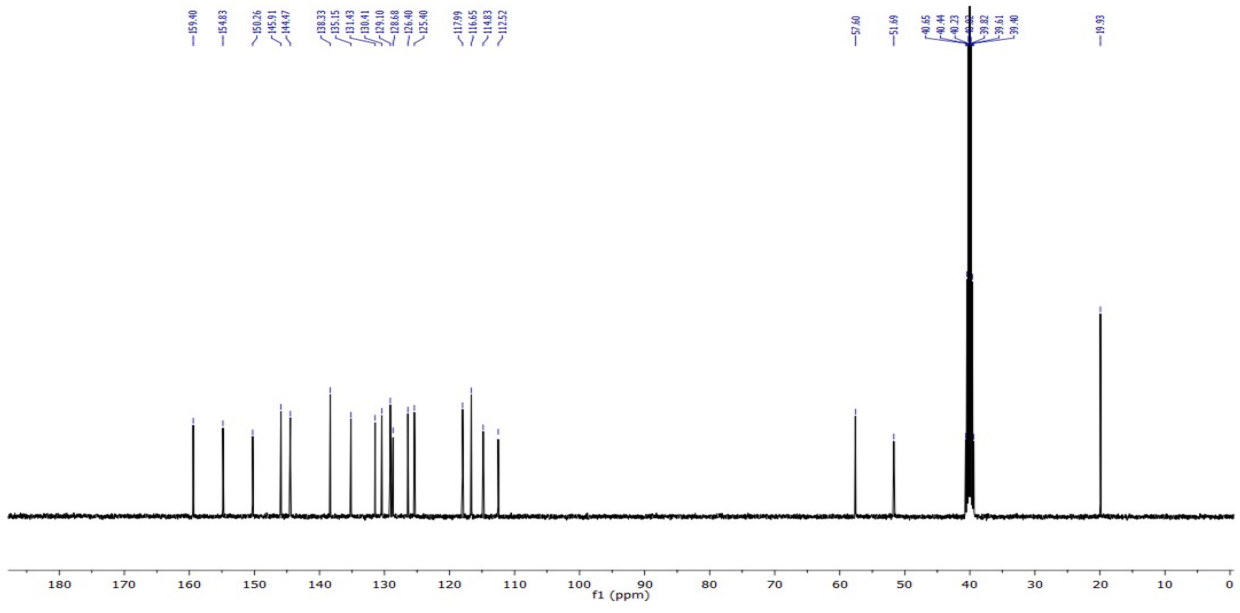


Figure SI4: $^{13}C$ NMR spectrum of 5,6–benzocoumarin substituted salt **5** recorded in $d_6$–DMSO at room temperature.

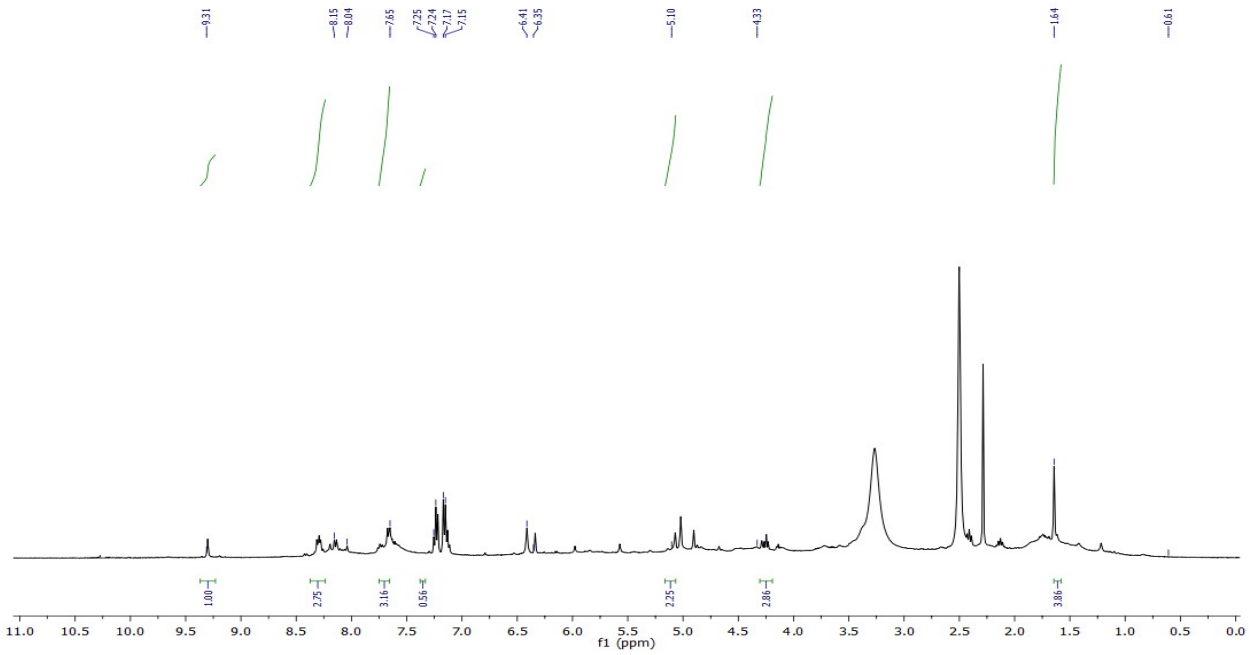


Figure SI5: $^{1}$H NMR spectrum of nickel(II) complex **6** recorded in $d_6$–DMSO at room temperature.

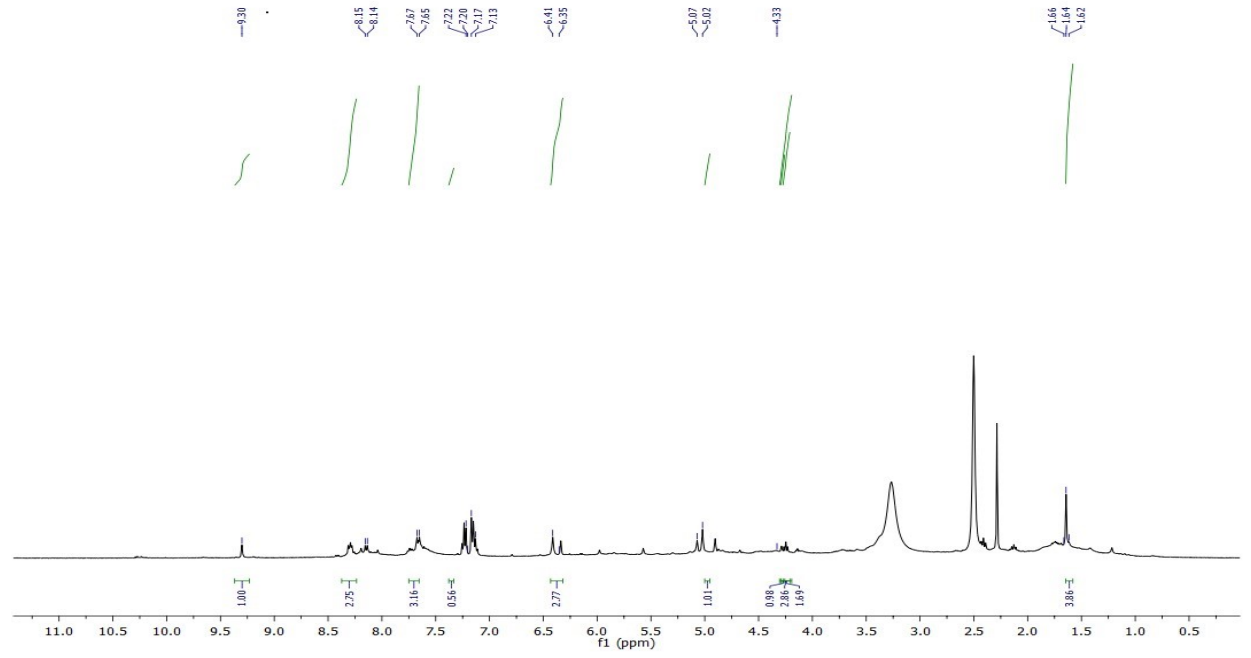


Figure SI6: $^{1}$H NMR spectrum of complex nickel(II) **7** recorded in $d_6$–DMSO at room temperature.

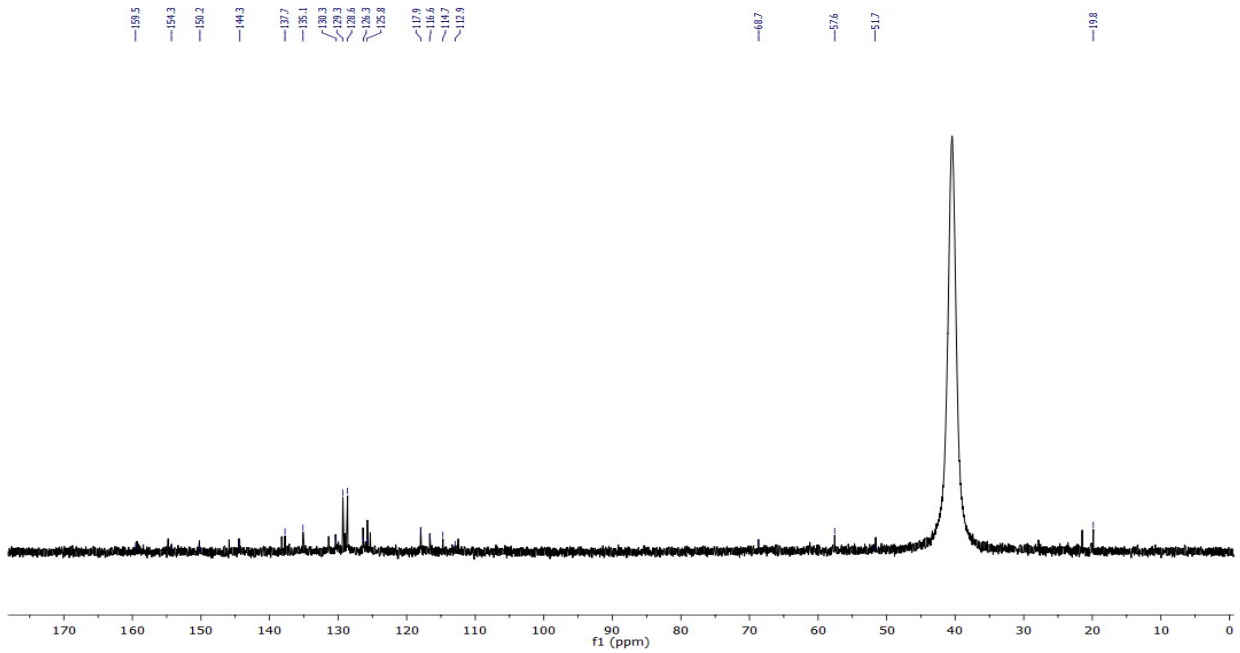


Figure SI7: $^{13}C$ NMR spectrum of nickel(II) complex **6** recorded in $d_6$–DMSO at room temperature.

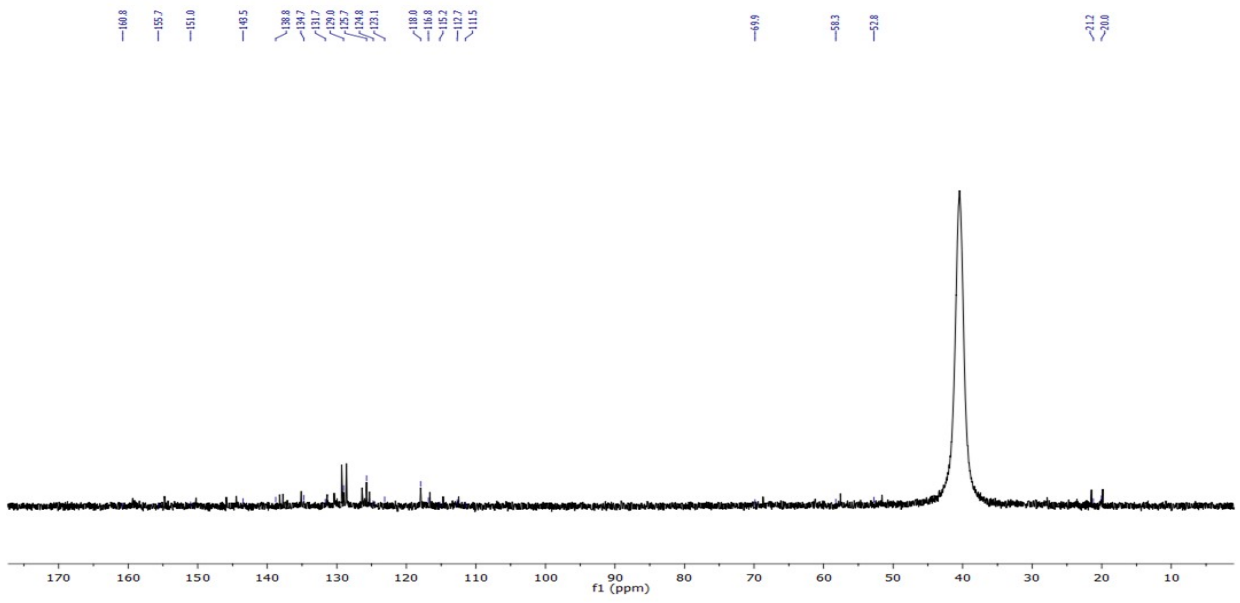


Figure SI8: $^{13}C$ NMR spectrum of complex nickel(II) **7** recorded in $d_6$–DMSO at room temperature.

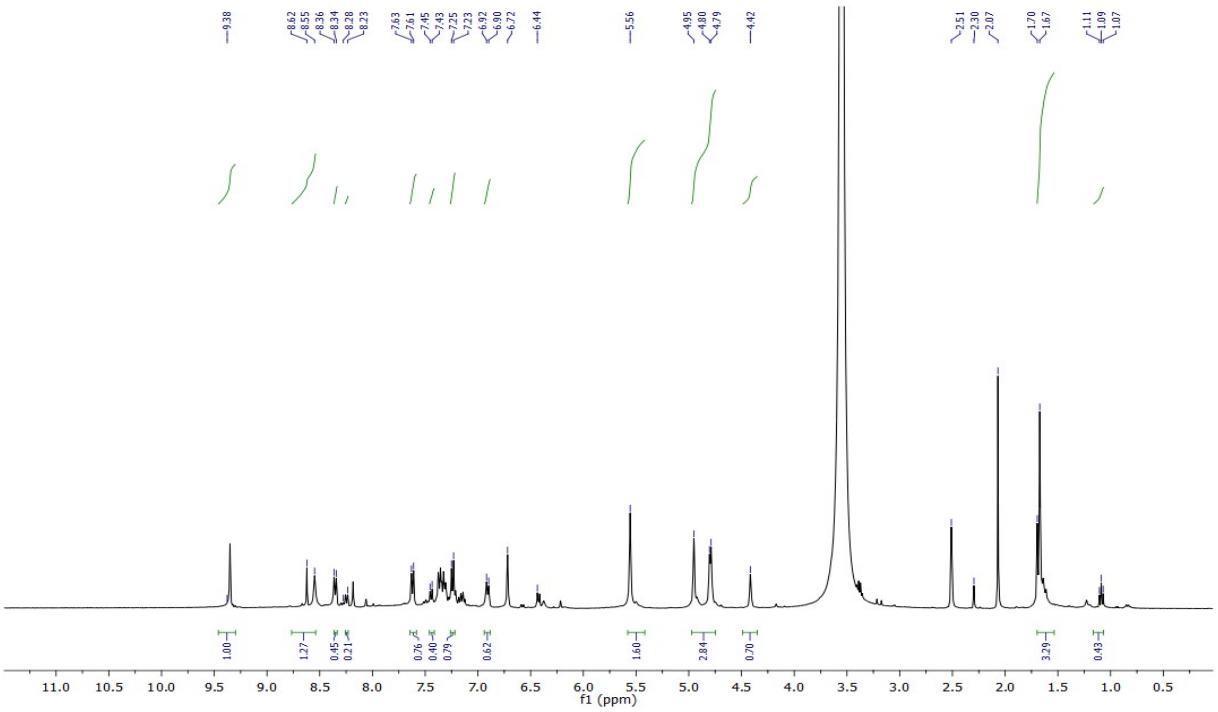


Figure SI9: $^{1}$H NMR spectrum of complex cobalt(III) **8** recorded in $d_6$–DMSO at room temperature.

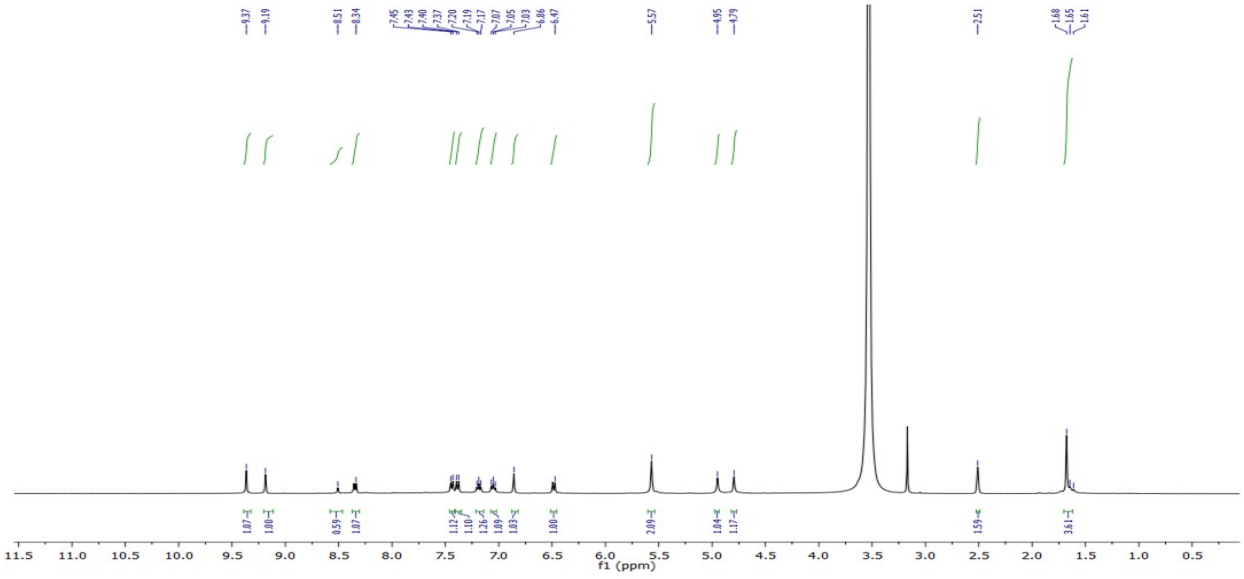


Figure SI10: $^{1}$H NMR spectrum of complex cobalt(III) **9** recorded in $d_6$–DMSO at room temperature.

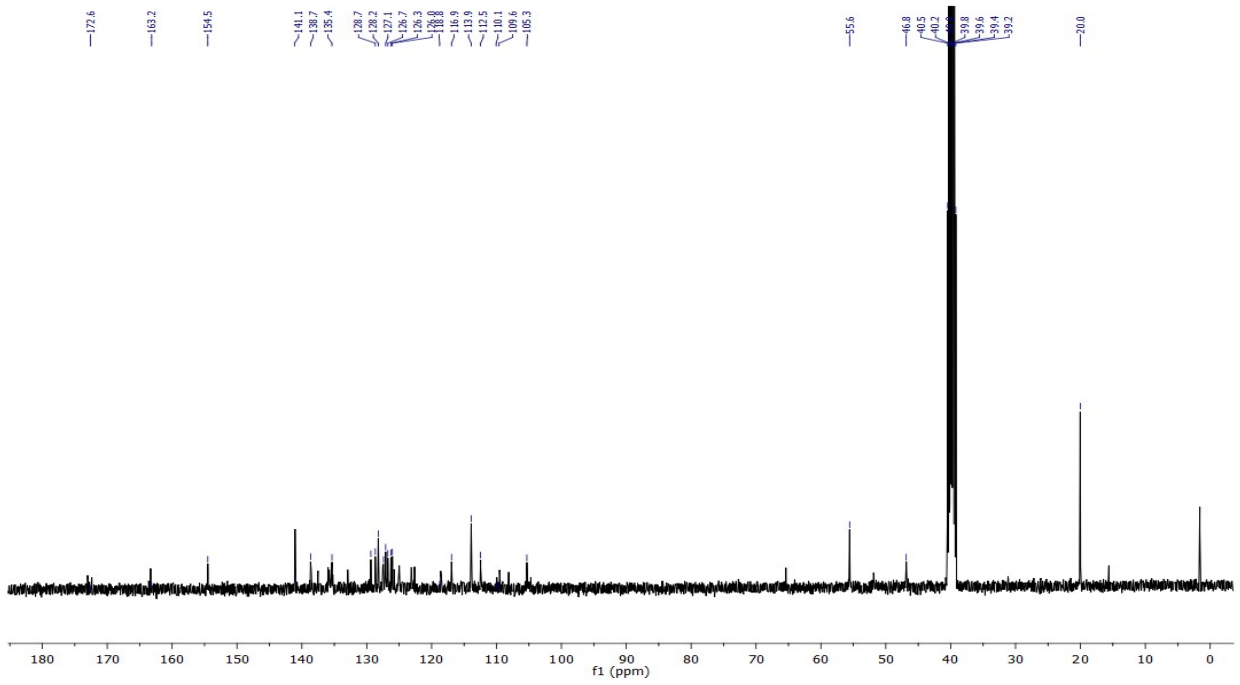


Figure SI11: $^{13}C$ NMR spectrum of cobalt(III) complex **8** recorded in $d_6$–DMSO at room temperature.

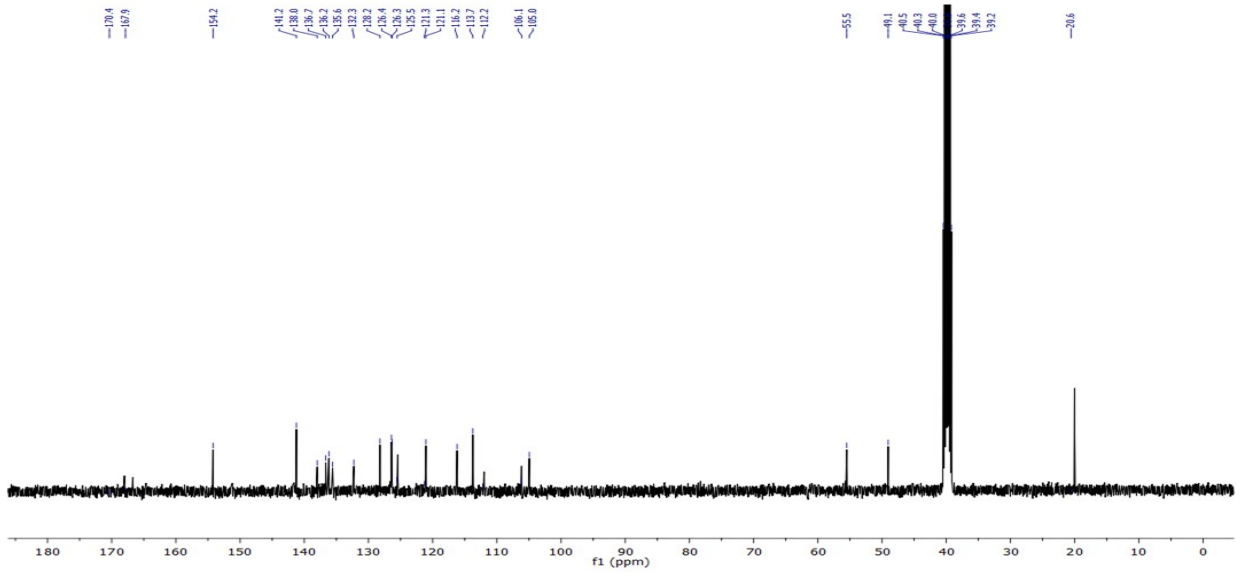


Figure SI12: $^{13}C$ NMR spectrum of cobalt(III) complex **9** recorded in $d_6$–DMSO at room temperature.

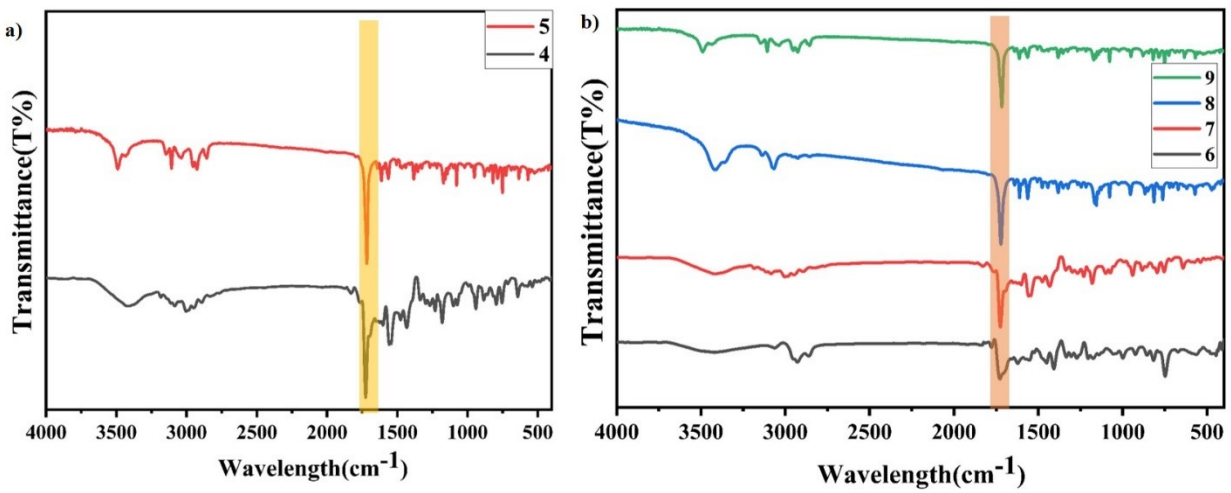


Figure SI13: **(a)**FT-IR of corresponding triazolium bromide salts (**4** and **5**); **(b)** FT-IR of corresponding nickel(II) and cobalt(III) NHC complexes (**6-9)**.

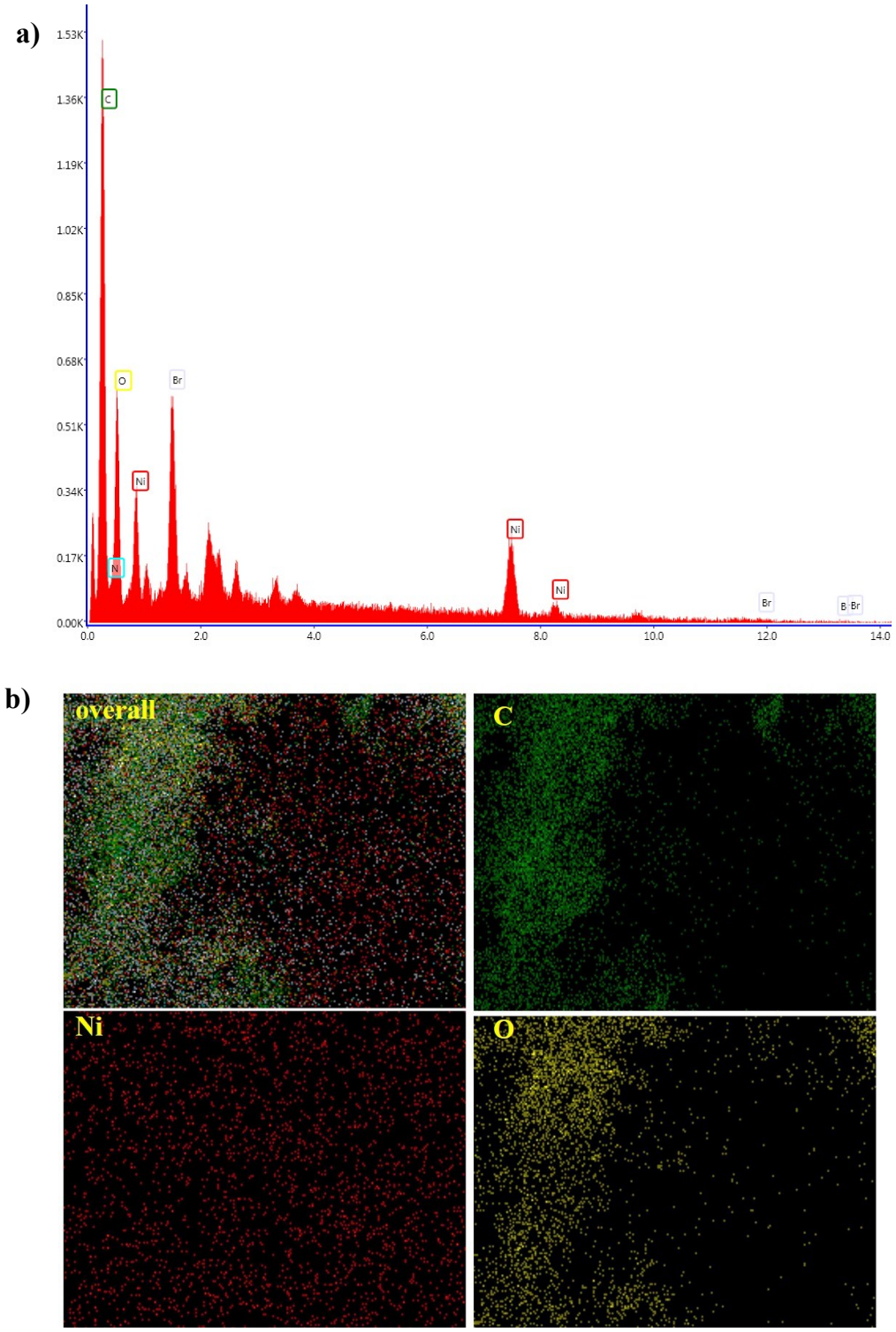


Figure SI14: EDX spectra (**a**) and elemental mapping (**b**) analysis of nickel(II) complex **6**

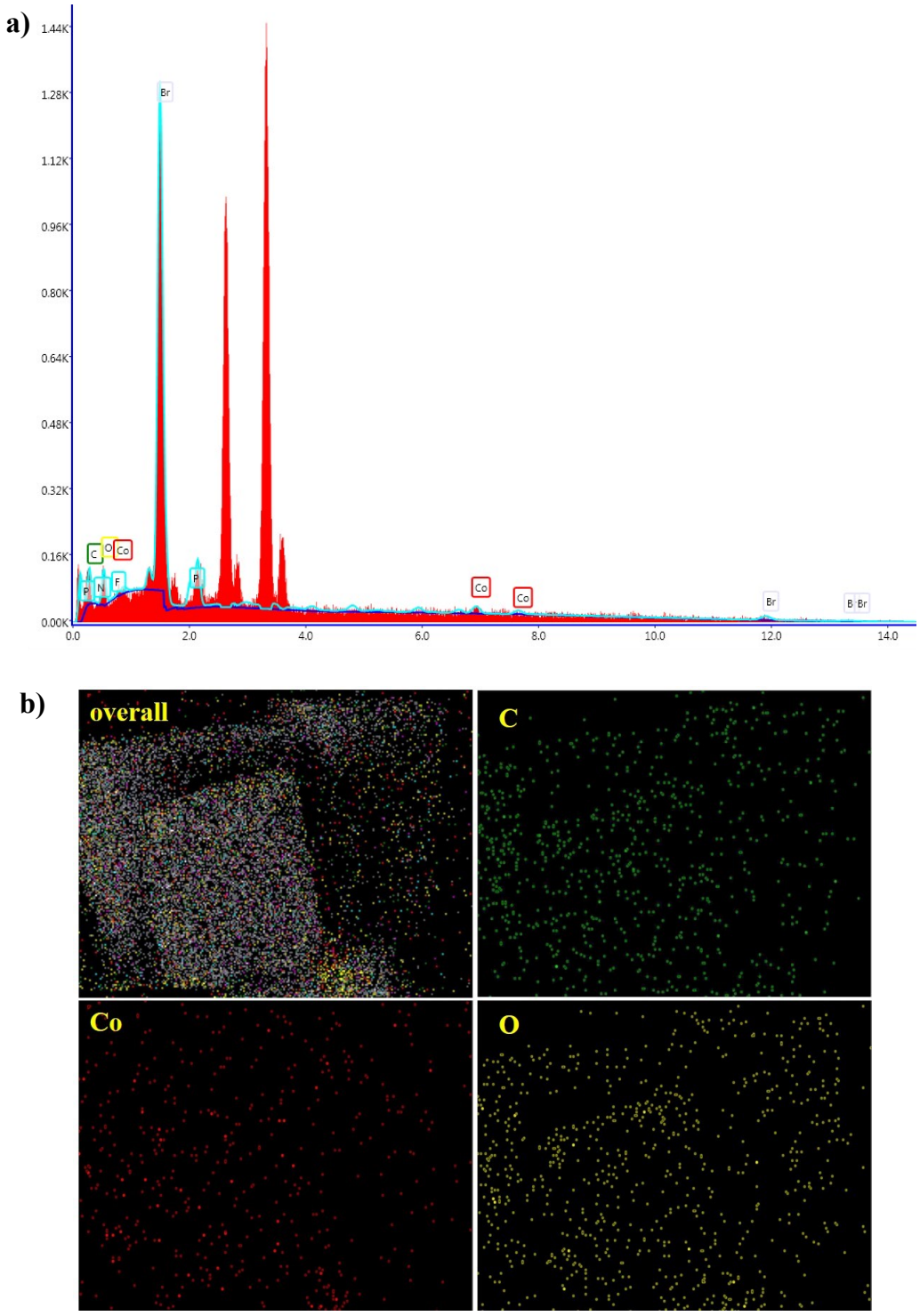


Figure SI15: EDX spectra (**a**) and elemental mapping (**b**) analysis of cobalt(III) complex **8**

Table SI1: Crystal parameters and details of the X–ray data collection, structure and refinement parameters of triazolium bromide salts **4** and **5**.

| | **4** | **5** |
|---|---|---|
| Formula | $C_{20}\,H_{18}\,BrN_3O_2$ | $C_{20}\,H_{18}\,BrN_3O_2$ |
| Molecular weight | 412.288 | 412.288 |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ |
| Unit Cell dimensions | | |
| a (Å) | 10.7857 (16) | 13.4985 (8) |
| b (Å) | 14.519 (2) | 16.3402 (11) |
| c (Å) | 11.7467 (18) | 8.5914 (4) |
| α (°) | 90 | 90 |
| β (°) | 103.727 (15) | 99.883 (5) |
| γ (°) | 90 | 90 |
| Density(calcd) (g/cm$^3$) | 1.532 | 1.467 |
| Abs.coeff. (mm$^{-1}$) | 2.320 | 2.221 |
| *F*(000) | 839.5 | 840.0 |
| Crystal size (mm) | 0.29 x 0.22 x 0.14 | 0.23 x 0.14 x 0.08 |
| Tempertaure | N/A | 295(2) |
| Radiation (Å) | 0.71073 | 0.71073 |
| Θ Min, Max (°) | 6.82, 58.78 | 6.616, 58.716 |
| Data set | –14:11, –20:18, –11:15 | –16:18, –22:16, –11:10 |
| Tot., Uniq. Data | 9181 | 9246 |
| R (int) | 0.0678 | 0.0287 |
| $N_{ref}$, $N_{par}$ | 4160, 237 | 4428, 244 |
| R, wR2, S | 0.0525, 0.1105, 0.0882 | 0.0518, 0.0995, 0.0506 |

Table SI2: Important bond lengths corresponding to salt **4**.

| **Atom** | **Atom** | **Length/Å** |
|---|---|---|
| O1 | C18 | 1.366(4) |
| O1 | C19 | 1.377(4) |
| O2 | C19 | 1.186(5) |
| N1 | N2 | 1.352(4) |
| N1 | C1 | 1.297(4) |
| N1 | C3 | 1.464(4) |
| N2 | C2 | 1.300(4) |
| N3 | C1 | 1.313(4) |
| N3 | C2 | 1.342(4) |
| N3 | C7 | 1.459(4) |

Table SI3: Important bond lengths corresponding to salt **5**.

| **Atom** | **Atom** | **Length/Å** |
|---|---|---|
| O1 | C6 | 1.359(4) |
| O1 | C7 | 1.368(3) |
| O2 | C6 | 1.208(4) |
| N1 | N2 | 1.342(4) |
| N1 | C1 | 1.297(4) |
| N1 | C17 | 1.453(4) |
| N2 | C2 | 1.294(5) |
| N3 | C1 | 1.319(3) |
| N3 | C2 | 1.346(4) |
| N3 | C3 | 1.473(4) |

Table SI4: Important bond angles corresponding to salt **4**.

| **Atom** | **Atom** | **Atom** | **Angle/°** |
|---|---|---|---|
| C19 | O1 | C18 | 121.8(3) |
| C1 | N1 | N2 | 110.7(3) |
| C3 | N1 | N2 | 121.3(3) |
| C3 | N1 | C1 | 128.0(3) |
| C2 | N2 | N1 | 103.5(3) |
| C2 | N3 | C1 | 105.6(3) |
| C7 | N3 | C1 | 125.5(3) |
| C7 | N3 | C2 | 128.8(3) |
| N3 | C1 | N1 | 108.3(3) |
| N3 | C2 | N2 | 111.9(3) |
| O2 | C19 | O1 | 117.4(4) |
| C4 | C3 | N1 | 112.7(3) |

Table SI5: Important bond angles corresponding to salt **5**.

| Atom | Atom | Atom | Angle/° |
|---|---|---|---|
| C6 | O1 | C7 | 122.7(2) |
| N2 | N1 | C17 | 120.4(3) |
| C1 | N1 | N2 | 110.8(3) |
| C1 | N1 | C17 | 128.7(3) |
| C2 | N2 | N1 | 103.6(3) |
| C1 | N3 | C2 | 104.6(3) |
| C1 | N3 | C3 | 125.7(3) |
| C2 | N3 | C3 | 129.7(3) |
| N1 | C1 | N3 | 108.6(3) |
| N2 | C2 | N3 | 112.4(3) |
| N3 | C3 | C4 | 110.0(2) |
| O1 | C6 | C5 | 115.8(3) |
| O2 | C6 | O1 | 117.9(3) |
| O2 | C6 | C5 | 126.2(3) |

Table SI6: Electrochemical impedance data of complexes **6–9** and their carbon composites.

| Molecular Electrocatalyst | $R_s$ in Ω | $R_{ct}$ in Ω | $C_{dl}$ in μF/cm² |
|---|---|---|---|
| **6** | 12.28 | 15.57 | 173.0 |
| **7** | 13.39 | 20.74 | 197.2 |
| **8** | 15.86 | 16.43 | 292.3 |
| **9** | 12.45 | 17.58 | 130.5 |
| **6–CP** | 10.29 | 15.10 | 26.0 |
| **7–CP** | 12.29 | 16.69 | 22.0 |

| | | | |
|---|---|---|---|
| **8-CP** | 12.31 | 15.46 | 33.0 |
| **9–CP** | 12.47 | 17.47 | 38.0 |

Table SI7: OER activity of materials reported in literatures, onset potentials, overpotentials at 50 mA $cm^{-2}$, Tafel slopes

| Catalyst | Onset potential (mV) | Overpotential (mV) | Tafel slope (mV $dec^{-1}$) | Reference |
|---|---|---|---|---|
| **6** | **243** | **373** | **89.1** | **In this work** |
| **6-CP** | **162** | **323** | **39.5** | **In this work** |
| **8** | **265** | **415** | **100.2** | **In this work** |
| **8-CP** | **242** | **348** | **55.9** | **In this work** |
| Co–SA/NG | 280 | 412 | 125 | 3 *et.al* |
| Ni–SA/NG | 300 | 499 | 143 | 3 *et.al* |
| CoNi–DS/NG | 190 | 332 | 81 | 4 *et.al* |
| FC | 370 | 555 | 237 | 4 *et.al* |
| FCCD25 | 220 | 390 | 191 | 4 *et.al* |

## REFERENCES


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