Electronic Supporting Information

Substituent-induced post-assembly modification cascade of a metallosupramolecular imine-type Co-complex

Grzegorz Markiewicz, [#ab] Bartosz Orwat, [#ab] Miłosz Piechocki,[ab] Kamila Jankowska,[ab] Ireneusz Kownacki *[ab] and Artur R. Stefankiewicz *[ab]

[a] *Faculty of Chemistry, Adam Mickiewicz University, Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland*

[b] *Center for Advanced Technologies, Adam Mickiewicz University, Uniwersytetu Poznańskiego 10, 61-614 Poznań, Poland*

[#] These authors contributed equally to this work.
E mail: irekk@o365.amu.edu.pl, ars@amu.edu.pl

Table of contents

1. General

1.1. Materials and methods

Chemicals and solvents were purchased from commercial suppliers (mainly Sigma-Aldrich and Fluorochem) and used as received, unless otherwise stated. Deoxygenated solvents (DCM, MeOH, *n*-hexane and H_2O) used for the synthesis of Co(II) complexes were obtained by a sonification under argon atmosphere (2 h), followed by a reflux under the same inert gas (4 h) prior to use. Triethylamine and (triisopropylsilyl)acetylene were dried over calcium hydride, distilled and stored under inert gas prior to use. Reactions accelerated with microwave irradiation were conducted in CEM microwave 10 mL vials with the use of CEM Discover, a pressure microwave reactor. Chromatographic purifications were carried out with preparative flash chromatogram Isolera One from Biotage, using self-packed columns with silica gel 60 Å 230-400 mesh (Merck). Celite 545 0.02 – 0.1 mm (Merck) was used as a Samplet® filler.

1.2. NMR spectroscopy

NMR solvents were purchased from Deutero GmbH (Germany) and used as received. NMR spectra were acquired on Bruker Fourier 300 MHz, Bruker Avance IIIHD 400 MHz, and Bruker Avance IIIHD 600 MHz spectrometers and referenced on solvent residual peaks.

1.3. IR spectroscopy

IR spectra were acquired on Thermo Fisher Nicolet iS50 FT-IR spectrometer with attenuated total reflectance (ATR) unit.

1.4. UV-Vis spectroscopy

UV-Vis spectra were acquired on Agilent Cary 60 spectrophotometer, in quartz cuvettes with 10 mm path length.

1.5. Gas chromatography

Coupling reaction progress was monitored on gas chromatograph Bruker Scion 436-GC. For determination of conversion, α,α,α-trifluorotoluene was used as an internal standard. Reaction products were identified with gas chromatograph Varian 450-GC coupled to mass spectrometer Bruker 320-MS equipped with direct insertion probe for low-volatility compounds.

1.6. ESI-MS

ESI-MS spectra were recorded on Bruker HD Impact and ABSciex QTOF 5600 spectrometer in positive ion mode, using acetonitrile as a solvent.
Theoretical MS spectra were predicted using Mestrelab Research MNova software ver. 11.0.

1.7. Computational methods

The ground states of the cobalt complexes were optimised using Density Functional Theory (DFT)[1] with B3LYP functional.[2] The calculations were performed using 6-311+G(d) basis set[3] for H, C, N, O, Si and Br atoms, while LANL2DZ basis set with effective core pseudopotential was applied for Co.[4] All calculations were carried out with Gaussian09 software package[5] in PL-Grid infrastructure.

1.8. Cyclic Voltammetry (CV)

CV measurements were performed on an Autolab PGSTAT M101. Measurements were carried out on a classic three electrode assembly. Pt wire was used as a working electrode, Pt spiral as a counter electrode and silver wire as a pseudo-reference electrode. The scan rate was 100 mV/s. Potentials were calibrated by ferrocene as an internal standard. Solutions of 0.2 M tetrabutylammonium hexafluorophosphate in dichloromethane (HPLC grade) or THF were used as a supporting electrolyte. The concentration $1 \cdot 10^{-3}$ M of the studied compounds was used. The solutions were deoxidised by argon bubbling prior to the measurement. The measured redox potentials are referred to ferrocene as an internal standard.

1.9. X-ray photoelectron spectroscopy (XPS)

XPS analysis was performer on SPECS UHV system, with monochromatic source and charge compensation. Data were processed using CasaXPS software.

2. Synthesis

2.1. Synthesis of the aldehyde

5-bromo-2-pyridinecarboxaldehyde was purchased from commercial source and used as received. 5-[(triisopropylsilyl)ethynyl]- derivative was synthesised *via* Sonogashira coupling of 5-bromo-2-pyridinecarboxaldehyde with corresponding acetylene, as follows:

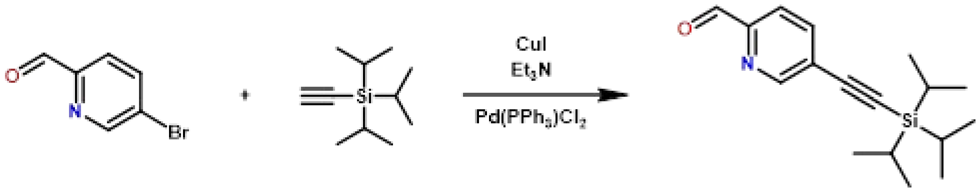


Figure S1. *Synthesis of 5-[(triisopropylsilyl)ethynyl]2-pyridinecarboxaldehyde.*

***5-[(triisopropylsilyl)ethynyl]2-pyridinecarboxaldehyde**:* A Schlenk flask equipped with magnetic stirrer was loaded with 5-bromo-2-pyridinecarboxaldehyde (500 mg, 2.69 mmol, 1.0 equiv), bis(triphenylphosphine)palladium(II) chloride (38 mg, 54 µmol, 2 mol%) and copper(I) iodide (26 mg, 134 µmol, 5 mol%). The flask was then evacuated and backfilled with argon three times. Next, triethylamine (5 mL) and (triisopropylsilyl)acetylene (556 mg, 2.96 mmol, 1.1 equiv) were added under argon atmosphere and the reaction vessel was closed. The mixture was heated at 70°C in an oil bath for 12 h. After reaction was complete, all volatiles were removed under reduced pressure. The residue was dissolved in dichloromethane and filtered through silica plug. The obtained solution was concentrated under reduced pressure to a minimal volume, adsorbed on celite and loaded into a Biotage Samplet®. The product was purified by column chromatography using gradient elution from 100% hexanes to 50% DCM: 50% hexanes. The fractions containing desired product were collected and concentrated under reduced pressure, giving pure product as a colourless oil (668 mg, 2.32 mmol) with 86% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.81 (s, 1H), 7.90 (s, 2H), 1.15 – 1.13 (m, 21H). ^{13}C NMR (75 MHz, MeCN-d_3) δ 192.76, 153.06, 151.06, 139.95, 125.08, 120.99, 102.82, 99.82, 18.74, 11.33. ESI-MS: Calcd for $C_{17}H_{25}NNaOSi^+$: 310.1598 m/z; Found: $[M+Na]^+ = 310.1598$ m/z. Elem. Anal. Calcd for $C_{17}H_{25}NOSi$: C, 71.03; H, 8.77; N, 4.87; Found: C, 71.06; H, 8.84; N, 4.84.

2.2. Synthesis of the ligands

Ligands were synthesised by condensation of 2-aminophenol with the corresponding aldehydes in anhydrous ethanol under mild acidic conditions (acetic acid), as follows:

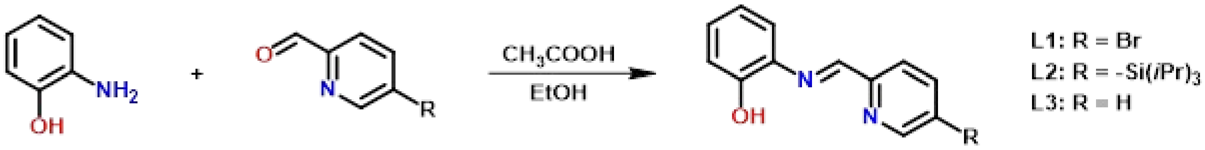
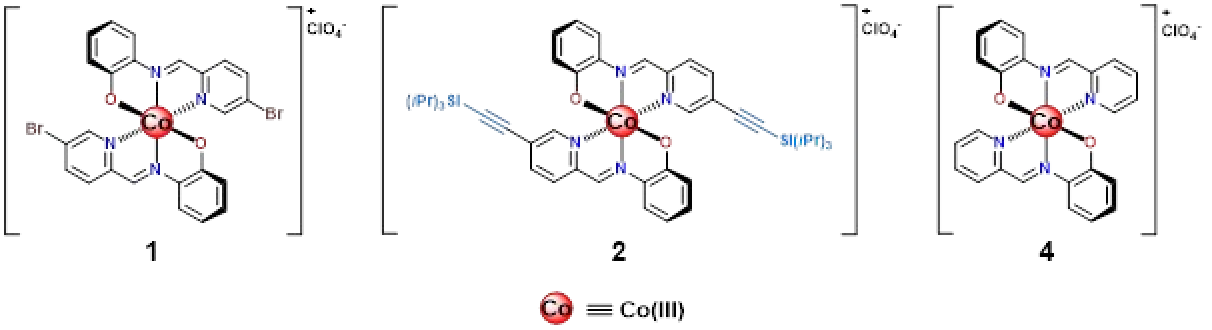


Figure S2. *General synthesis method of **L1**, **L2** and **L3** ligands.*

Synthesis of L1: 2-aminophenol (10.9 mg, 0.1 mmol) and 5-bromo-2-pyridinecarboxaldehyde (18.6 mg, 0.1 mmol) were dissolved in 10 mL of anhydrous ethanol and 2 drops of glacial acetic acid were added. The obtained orange-brown solution was stirred for 24 h at room temperature. After solvent removal, the pure product was obtained as a brown solid in quantitative yield. ^{1}H NMR (600 MHz, MeCN-d_3) δ 8.79 (d, J = 1.9 Hz, 1H), 8.76 (s, 1H), 8.31 (d, J = 8.5 Hz, 1H), 8.08 (dd, J = 8.5, 2.1 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.23 (t, J = 7.8 Hz, 1H), 7.03 – 6.85 (m, 2H). ^{13}C NMR (151 MHz, MeCN-d_3) δ 158.27, 154.24, 153.57, 151.68, 140.42, 136.10, 130.71, 123.80, 123.38, 121.13, 118.29, 116.50. ESI-MS: Calcd for $C_{12}H_9BrN_2NaO^+$: 298.9790, 300.9771 m/z; Found: $[M+Na]^+$ = 298.9771, 300.9750 m/z. Elem. Anal. Calcd for $C_{12}H_9BrN_2O$: C, 52.01; H, 3.27; N, 10.11; Found: C, 52.12; H, 3.38; N, 10.05.
Synthesis of L2*:* 2-aminophenol (10.9 mg, 0.1 mmol) and 5-[(triisopropylsilyl)ethynyl]-2-pyridinecarboxaldehyde (28.7 mg, 0.1 mmol) were dissolved in 10 mL of anhydrous ethanol and 2 drops of glacial acetic acid were added. The obtained red solution was stirred for 24 h at room temperature. After solvent removal, the pure product was obtained as a red-solid in quantitative yield. ^{1}H NMR (600 MHz, MeCN-d_3) δ 8.78 (s, 1H), 8.74 (d, J = 2.0 Hz, 1H), 8.33 (d, J = 8.2 Hz, 1H), 7.91 (dd, J = 8.2, 2.1 Hz, 1H), 7.43 (dd, J = 8.0, 1.5 Hz, 1H), 7.26 – 7.19 (m, 1H), 6.95 (dd, J = 8.1, 1.3 Hz, 1H), 6.94 – 6.89 (m, 1H), 1.20 – 1.10 (m, 22H). ^{13}C NMR (151 MHz, MeCN-d_3) δ 158.33, 154.48, 153.67, 153.22, 140.23, 136.12, 130.73, 122.40, 121.98, 121.09, 118.16, 116.49, 104.59, 97.69, 18.95, 12.02. ESI-MS: Calcd for $C_{23}H_{30}N_2NaOSi^+$: 401.2010 m/z; Found: $[M+Na]^+$ = 401.2026 m/z. Elem. Anal. Calcd for $C_{23}H_{30}N_2OSi$: C, 72.97; H, 7.99; N, 7.40; Found: C, 72.99; H, 8.04; N, 7.37.
Synthesis of L3: 2-aminophenol (10.9 mg, 0.1 mmol) and 2-pyridinecarboxaldehyde (10.7 mg, 9.5 µL 0.1 mmol) were dissolved in 10 mL of anhydrous ethanol and 2 drops of glacial acetic acid were added. The obtained orange solution was stirred for 24 h at room temperature. After solvent removal, the pure product was obtained as an orange solid in quantitative yield. ^{1}H NMR (300 MHz, MeCN-d_3) δ 8.80 (s, 1H), 8.70 (d, J = 4.6 Hz, 1H), 8.35 (d, J = 7.9 Hz, 1H), 7.89 (td, J = 7.6, 1.1 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.22 (td, J = 7.6, 1.5 Hz, 1H), 7.00 – 6.87 (m, 2H). ^{13}C NMR (151 MHz, MeCN-d_3) δ 159.55, 155.50, 153.47, 150.70, 137.72, 136.44, 130.39, 126.38, 122.62, 121.08, 118.23, 116.41. ESI-MS: Calcd for $C_{12}H_{11}N_2O^+$: 199.0866 m/z; Found: $[M+H]^+$ = 199.0869 m/z. Elem. Anal. Calcd for $C_{12}H_{10}N_2O$: C, 72.71; H, 5.09; N, 14.13; Found: C, 72.75; H, 5.17; N, 14.09.

2.3. Synthesis of Co(III) complexes

Although ligands **L1, L2** and **L3** might be isolated in pure forms, the Co(III) complexes were synthesised by the subcomponent self-assembly of 2-aminophenol, with the corresponding aldehyde, and cobalt(II) perchlorate in DCM:MeOH mixture (1:1 v/v) under mildly basic conditions (Et_3N). Free access of air to the reaction mixture, enabled quantitative oxidation of the Co(II) into Co(III).



1 2 4

Figure S3. *Structures of Co(III) complexes obtained by the subcomponent self-assembly:* ***1**, **2** and **4**.*

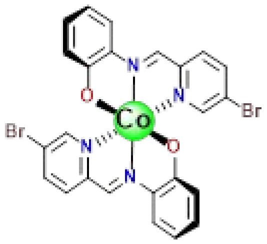
Synthesis of 1: 2-aminophenol (100 mg, 0.92 mmol) and 5-bromo-2-pyridinecarboxaldehyde (171 mg, 0.92 mmol) were dissolved in 30 mL of DCM/MeOH (1:1 v/v) and then Et_3N (128 µL, 93 mg, 0.92 mmol) was added. To this mixture, a solution of cobalt(II) perchlorate hexahydrate (168 mg, 0.46 mmol) in 10 mL of DCM/MeOH (1:1 v/v) was added dropwise under vigorous stirring. After 24 h at room temperature, the dark red precipitate was filtered off, washed with small amount of DCM/MeOH (1:1 v/v), and dried *in vacuo*. Yield 277 mg, 85%. ^{1}H NMR (300 MHz, MeCN-*d*$_3$) δ 9.08 (s, 1H), 8.21 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.98 – 7.90 (m, 3H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 6.80 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 8.6 Hz, 1H). ESI-MS: Calcd for $C_{24}H_{16}Br_2CoN_4O_2^+$: 608.8967, 610.8948 m/z; Found: $[M-ClO_4^-]^+$ = 608.8962, 610.8936 m/z. Elem. Anal. Calcd for $C_{24}H_{16}Br_2ClCoN_4O_6$: C, 40.57; H, 2.27; N, 7.88; Found: C, 40.60; H, 2.36; N, 7.82.

Synthesis of 2: 2-aminophenol (65.5 mg, 0.6 mmol) and 5-[(triisopropylsilyl)ethynyl]-2-pyridinecarboxaldehyde (172.5 mg, 0.6 mmol) were dissolved in 30 mL of DCM/MeOH (1:1 v/v) and then Et_3N (88.5 µL, 64.2 mg, 0.6 mmol) was added. To this mixture, a solution of cobalt(II) perchlorate hexahydrate (109.6 mg, 0.3 mmol) in 10 mL of DCM/MeOH (1:1 v/v) was added dropwise under vigorous stirring. After 24 h at room temperature, the dark violet solution was evaporated. The solid obtained was suspended in *n*-hexane and then evaporated under reduced pressure. This process was repeated 3 times, to remove the residual triethylamine salts giving pure product as a violet solid. Yield 210 mg, 76 %. ^{1}H NMR (600 MHz, MeCN-*d*$_3$) δ 9.16 (s, 1H), 8.04 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.86 (s, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.80 (t, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 8.5 Hz, 1H), 1.08 – 1.04 (m, 21H).ESI-MS: Calcd for $C_{46}H_{58}CoN_4O_2Si_2^+$: 813.3425 m/z; Found: $[M-ClO_4^-]^+$ = 813.3447 m/z. Elem. Anal. Calcd for $C_{46}H_{58}ClCoN_4O_6Si_2$: C, 60.48; H, 6.40; N, 6.13; Found: C, 60.40; H, 6.55; N, 6.14.

Synthesis of 4: 2-aminophenol (65.5 mg, 0.6 mmol) and 2-pyridine-carboxaldehyde (64.3 mg, 0.6 mmol) were dissolved in 30 mL of DCM/MeOH (1:1 v/v) and then Et_3N (88.5 µL, 64.2 mg, 0.6 mmol) was added. To this mixture, a solution of cobalt(II) perchlorate hexahydrate (109.6 mg, 0.3 mmol) in 10 mL of DCM/MeOH (1:1 v/v) was added dropwise under vigorous stirring. After 24 h at room temperature, the dark violet precipitate was filtered off, washed with small amount of DCM/MeOH mixture (1:1 v/v), and dried in vacuo. Yield 116 mg, 70%. ^{1}H NMR (600 MHz, MeCN-*d*$_3$) δ 9.16 (s, 1H), 8.04 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.86 (s, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.80 (t, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 8.5 Hz, 1H), 1.08 – 1.04 (m, 21H). ESI-MS: Calcd for $C_{46}H_{58}CoN_4O_2Si_2^+$: 453.0756 m/z; Found: $[M-ClO_4^-]^+$ = 453.0767 m/z. Elem. Anal. Calcd for $C_{24}H_{18}ClCoN_4O_6$: C, 52.14; H, 3.28; N, 10.14; Found: C, 52.10; H, 3.35; N, 6.11.

2.4. Synthesis of Co(II) complexes

Although ligand **L1** might be isolated in pure form, its Co(II) complex **5** was synthesised by the subcomponent self-assembly of 2-aminophenol, with the appropriate aldehyde, and cobalt(II) perchlorate in DCM:MeOH mixture (1:1 v/v) under mildly basic conditions (Et_3N). To avoid the oxidation of the central ion, the synthesis was conducted in Schlenk-type vial under argon atmosphere using solvents deoxygenated as described in General section.



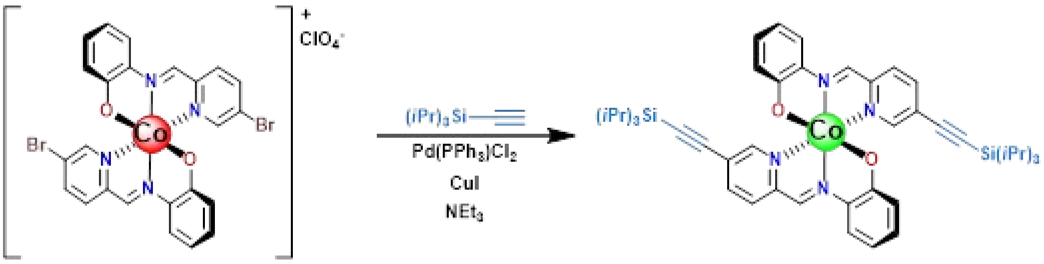
5

Co ≡ Co(II)

Figure S4. *Structure of complex* ***5****.*

Synthesis of 5: 2-aminophenol (109 mg, 1.0 mmol) and 5-bromo-2-pyridinecarboxaldehyde (186 mg, 1 mmol) were dissolved in 25 mL of deoxygenated DCM/MeOH (1:1 v/v) and then Et_3N (139 µL, 101 mg, 0.1 mmol) was added. To this mixture, a solution of cobalt(II) perchlorate hexahydrate (186 mg, 0.5 mmol) in 10 mL of deoxidised DCM/MeOH (1:1 v/v) was added dropwise under vigorous stirring. After 24 h at room temperature, the solvents were evaporated, and the dark-red solid was washed 2 times with deoxygenated *n*-hexane, dried, and then sonicated 2 times with deoxygenated water to remove the triethylamine salts. The resulting dark-red solid was dried in vacuo. Yield 262 mg, 84%. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 251.16, 141.70, 62.18, 25.83, 20.80, 15.07, 9.03, 2.47. ESI-MS: Calcd for $C_{24}H_{16}Br_2CoN_4O_2^+$: 608.8967, 610.8948 m/z; Found: $[M]^+$ = 608.8978, 610.8960 m/z. Elem. Anal. Calcd for $C_{24}H_{16}Br_2CoN_4O_2$: C, 47.17; H, 2.64; N, 9.17; Found: C, 47.23; H, 2.71; N, 9.14.

Synthesis of 3 *via* cascade reaction: A CEM microwave vial equipped with magnetic stirrer was loaded with complex **1** (50 mg, 70 µmol, 1.0 equiv), bis(triphenylphosphine)palladium(II) chloride (4.94 mg, 7.04 µmol, 10 mol %) and copper(I) iodide (2.01 mg, 10.55 µmol, 15 mol%). The vial was placed in a bigger Schlenk flask and then evacuated and backfilled with argon three times. Subsequently, anhydrous α,α,α-trifluorotoluene (2 mL), triethylamine (1 mL) and (triisopropylsilyl)acetylene (52.9 mg, 281 µmol, 4.0 equiv) were added under argon atmosphere and the vial was closed with a cap. The reaction vessel was placed in a microwave reactor and heated with a maximum power of 100 W, at 70°C, for 20 h. After, the reaction mixture was cooled to room temperature and diluted with 3 mL of hexanes and then centrifuged. The precipitate obtained was washed and centrifuged four times with biphasic mixture of 2 mL hexanes and 2 mL deionised water. The product was dried in an oven at 60°C overnight and finally under reduced pressure to constant mass. Pure product was obtained as a purple-black solid (50 mg, 61 µmol) with 87% yield. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 253.04, 132.91, 53.33, 25.46, 22.55, 14.72, 10.29, 2.21, 1.21, 0.11, -4.69. ESI-MS: Calcd for $C_{46}H_{58}CoN_4O_2Si_2^+$: 813.3425; Found: $[M]^+$ = 813.3423. Elem. Anal. Calcd for $C_{46}H_{58}CoN_4O_2Si_2$: C, 67.87; H, 7.18; N, 6.88; Found: C, 67.93; H, 7.27; N, 6.86.



1

3

Co ≡ Co(II)   Co ≡ Co(III)

Figure S5. *Sonogashira coupling and simultaneous Glaser reduction performed on* ***1****.*

2.5. Reduction attempts of complex 1 without alkyne additive

A CEM microwave vial equipped with magnetic stirrer was loaded with **1** (50 mg, 70 μmol, 1.0 equiv), and nothing more in case (1), anhydrous lithium iodide (10.4 mg, 77 μmol, 1.1 equiv) in case (2), copper(I) iodide (14.74 mg, 77 μmol, 1.1 equiv) in case (3), and copper(I) iodide (2.01 mg, 10.55 μmol, 15 mol%) with bis(triphenylphosphine)palladium(II) chloride (4.94 mg, 7.04 μmol, 10 mol %) in case (4). In all cases, the vial was placed in a bigger Schlenk flask and then evacuated and backfilled with argon three times. Subsequently, anhydrous α,α,α-trifluorotoluene (2 mL) and triethylamine (1 mL) were added under argon atmosphere and the vial was closed with a cap. The reaction vessel was placed in a microwave reactor and heated with a maximum power of 100 W, at 70°C, for 20 h. After indicated time, the reaction mixture was cooled to room temperature and diluted with 3 mL of hexanes and then centrifuged. The precipitate obtained was washed and centrifuged four times with biphasic mixture of 2 mL hexanes and 2 mL deionised water. The product obtained was dried in an oven at 60°C overnight and finally under reduced pressure to constant mass. IR analysis of the obtained purple-black solid confirmed recovery of the unreacted substrate in all cases.

2.6. Reduction attempts of Co(III) complexes *via* Glaser reaction

Reduction attempt of 1: A CEM microwave vial equivuipped with magnetic stirrer was loaded with complex **1** (50 mg, 70 μmol, 1.0 equiv) and copper(I) iodide (2.01 mg, 10.55 μmol, 15 mol%). The vial was placed in a Schlenk flask and then evacuated and backfilled with argon three times. Subsequently, anhydrous α,α,α-trifluorotoluene (2 mL), triethylamine (1 mL) and (triisopropylsilyl)acetylene (52.9 mg, 281 μmol, 4.0 equiv) were added under argon atmosphere and the vial was closed with a cap. The reaction vessel was placed in a microwave reactor and heated with a maximum power of 100 W, at 70°C, for 20 h. After indicated time, the reaction mixture was cooled to room temperature and diluted with 3 mL of hexanes and then centrifuged. The formed precipitate was washed and centrifuged four times with biphasic mixture of 2 mL hexanes and 2 mL of deionised water. The product obtained was dried in an oven at 60°C overnight and finally under reduced pressure to constant mass. IR analysis of the obtained purple-black solid confirmed recovery of the unreacted substrate.

Reduction attempt of 2: A CEM microwave vial equivuipped with magnetic stirrer was loaded with complex **2** (64 mg, 70 μmol, 1.0 equiv) and copper(I) iodide (2.01 mg, 10.55 μmol, 15 mol%). The vial was placed in a Schlenk flask and then evacuated and backfilled with argon three times. Subsequently, anhydrous α,α,α-trifluorotoluene (2 mL), triethylamine (1 mL) and (triisopropylsilyl)acetylene (52.9 mg, 281 μmol, 4.0 equiv) were added under argon atmosphere and the vial was closed with a cap. The reaction vessel was placed in a microwave reactor and heated with a maximum power of 100 W, at 70°C, for 20 h. After indicated time, the reaction mixture was cooled to room temperature and diluted with 3 mL of hexanes and then centrifuged. The formed precipitate was washed and centrifuged four times with biphasic mixture of 2 mL hexanes and 2 mL of deionised water. The product obtained was dried in an oven at 60°C overnight and finally under reduced pressure to constant mass. IR analysis of the obtained purple-black solid confirmed recovery of the unreacted substrate.

Reduction of 2: A CEM microwave vial equipped with magnetic stirrer was loaded with complex **2** (64 mg, 70 μmol, 1.0 equiv), bis(triphenylphosphine)palladium(II) chloride (4.94 mg, 7.04 μmol, 10 mol %) and copper(I) iodide (2.01 mg, 10.55 μmol, 15 mol%). The vial was placed in a Schlenk flask and then evacuated and backfilled with argon three times. Subsequently, anhydrous α,α,α-trifluorotoluene (2 mL), triethylamine (1 mL) and (triisopropylsilyl)acetylene (52.9 mg, 281 μmol, 4.0 equiv) were added under argon atmosphere and the vial was closed with a cap. The reaction vessel was placed in a microwave reactor and heated with a maximum power of 100 W, at 70°C, for 20 h. After indicated time, the reaction mixture was cooled to room temperature and diluted with 3 mL of hexanes and then centrifuged. The formed precipitate was washed and centrifuged four times with biphasic mixture of 2 mL hexanes and 2 mL deionised water. The product obtained was dried in an oven at 60°C overnight and finally under reduced pressure to constant mass. Pure product was obtained as a purple-black solid (24 mg, 29 μmol) with 54% yield. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 253.04, 132.91, 53.33, 25.46, 22.55, 14.72, 10.29, 2.21, 1.21, 0.11, -4.69. ESI-MS: Calcd for $C_{46}H_{58}CoN_4O_2Si_2^+$: 813.3425; Found: $[M]^+$ =

813.3423. Elem. Anal. Calcd for $C_{46}H_{58}CoN_4O_2Si_2$: C, 67.87; H, 7.18; N, 6.88; Found: C, 67.93; H, 7.27; N, 6.86.

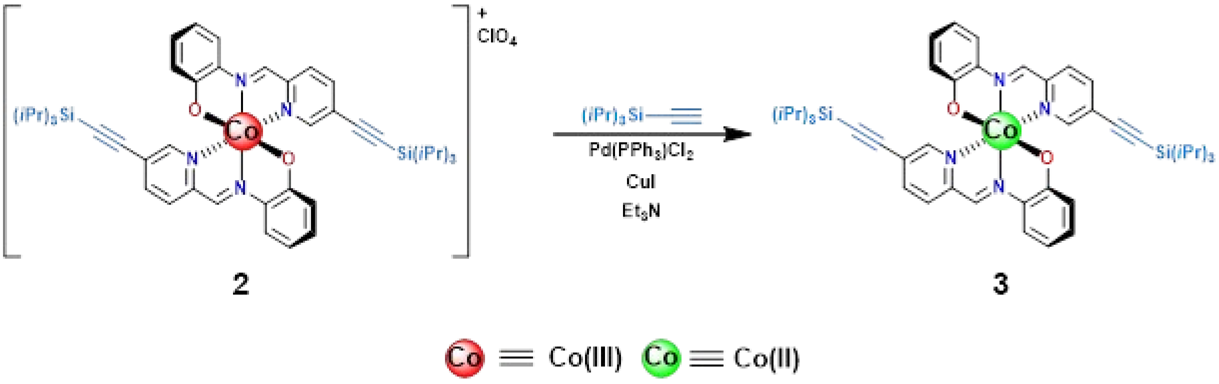


Figure S6. *Reduction of complex **2** via Glaser reaction.*

Reduction attempt of complex 4: A CEM microwave vial equipped with magnetic stirrer was loaded with complex **4** (39 mg, 70 µmol, 1.0 equiv) and copper(I) iodide (2.01 mg, 10.55 µmol, 15 mol%). The vial was placed in a Schlenk flask and then evacuated and backfilled with argon three times. Subsequently, anhydrous α,α,α-trifluorotoluene (2 mL), triethylamine (1 mL) and (triisopropylsilyl)acetylene (52.9 mg, 281 µmol, 4.0 equiv) were added under argon atmosphere and the vial was closed with a cap. The reaction vessel was placed in a microwave reactor chamber and heated with a maximum power of 100 W, at 70°C, for 20 h. After that, the reaction mixture was cooled to room temperature and diluted with 3 mL of diethyl ether and then centrifuged. The formed precipitate was washed and centrifuged two times with biphasic mixture of 2 mL diethyl ether and 2 mL deionised water and finally two times with 2 mL portions of diethyl ether. The product obtained was dried in an oven at 60°C overnight and finally under reduced pressure to constant mass. IR analysis of the obtained purple-black solid confirmed recovery of the unreacted substrate.

Reduction attempt of complex 4: A CEM microwave vial equipped with magnetic stirrer was loaded with $[Co^{III}(\mathbf{L3})_2]ClO_4$ (39 mg, 70 µmol, 1.0 equiv), bis(triphenylphosphine)-palladium(II) chloride (4.94 mg, 7.04 µmol, 10 mol %) and copper(I) iodide (2.01 mg, 10.55 µmol, 15 mol%). The vial was placed in a Schlenk flask and then evacuated and backfilled with argon three times. Subsequently, anhydrous α,α,α-trifluorotoluene (2 mL), triethylamine (1 mL) and (triisopropylsilyl)acetylene (52.9 mg, 281 µmol, 4.0 equiv) were added under argon atmosphere and the vial was closed with a cap. The reaction vessel was placed in a microwave reactor chamber and heated with a maximum power of 100 W, at 70°C, for 20 h. After that, the reaction mixture was cooled to room temperature and diluted with 3 mL of diethyl ether and then centrifuged. The formed precipitate was washed and centrifuged two times with biphasic mixture of 2 mL diethyl ether and 2 mL deionised water and finally two times with 2 mL portions of diethyl ether. The product obtained was dried in an oven at 60°C overnight and finally under reduced pressure to constant mass. IR analysis of the obtained purple-black solid confirmed recovery of the unreacted substrate.

3. NMR Spectra

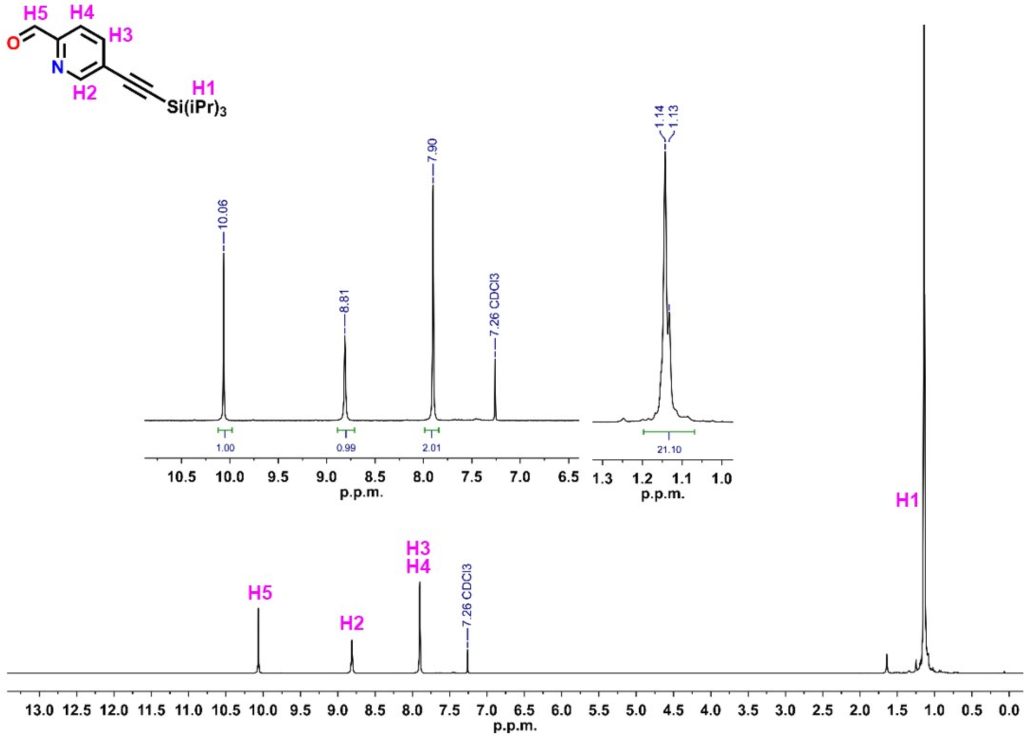


Figure S7. *^{1}H NMR (300 MHz, MeCN-d_3, 298 K) spectrum of 5-[(triisopropylsilyl)ethynyl]-2-pyridinecarboxaldehyde.*

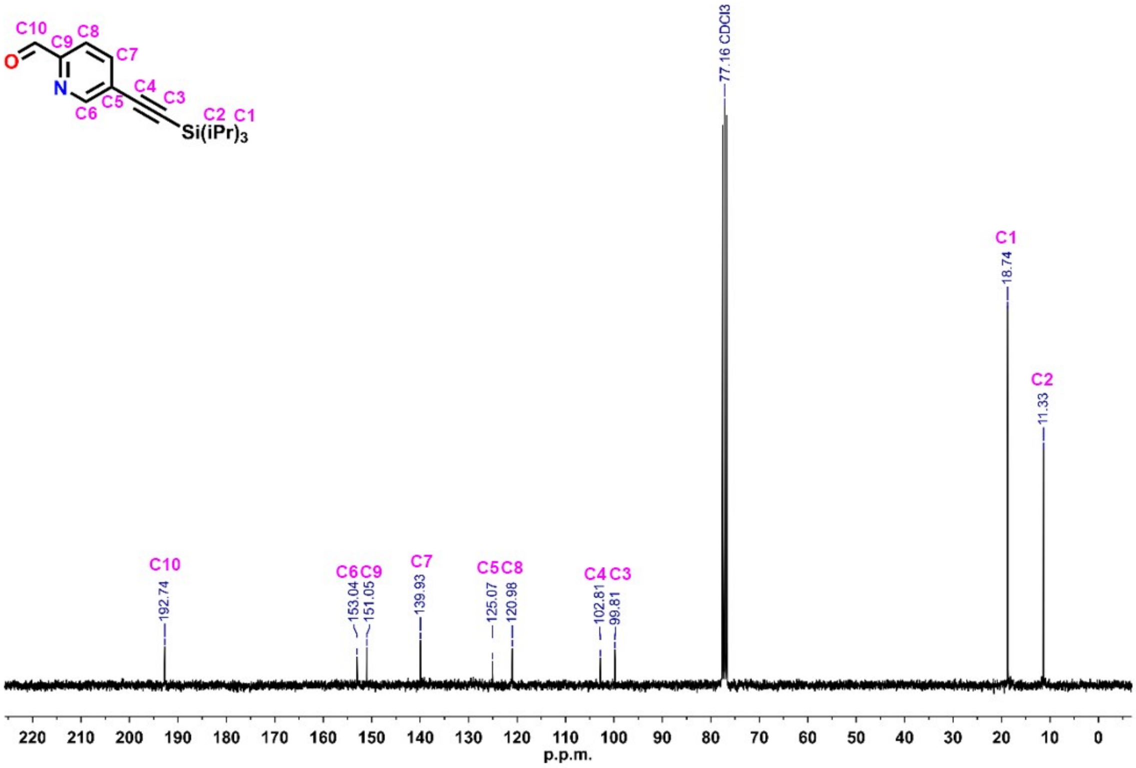


Figure S8. *^{13}C NMR (75 MHz, MeCN-d_3, 298 K) spectrum of 5-[(triisopropylsilyl)ethynyl]-2-pyridinecarboxaldehyde.*

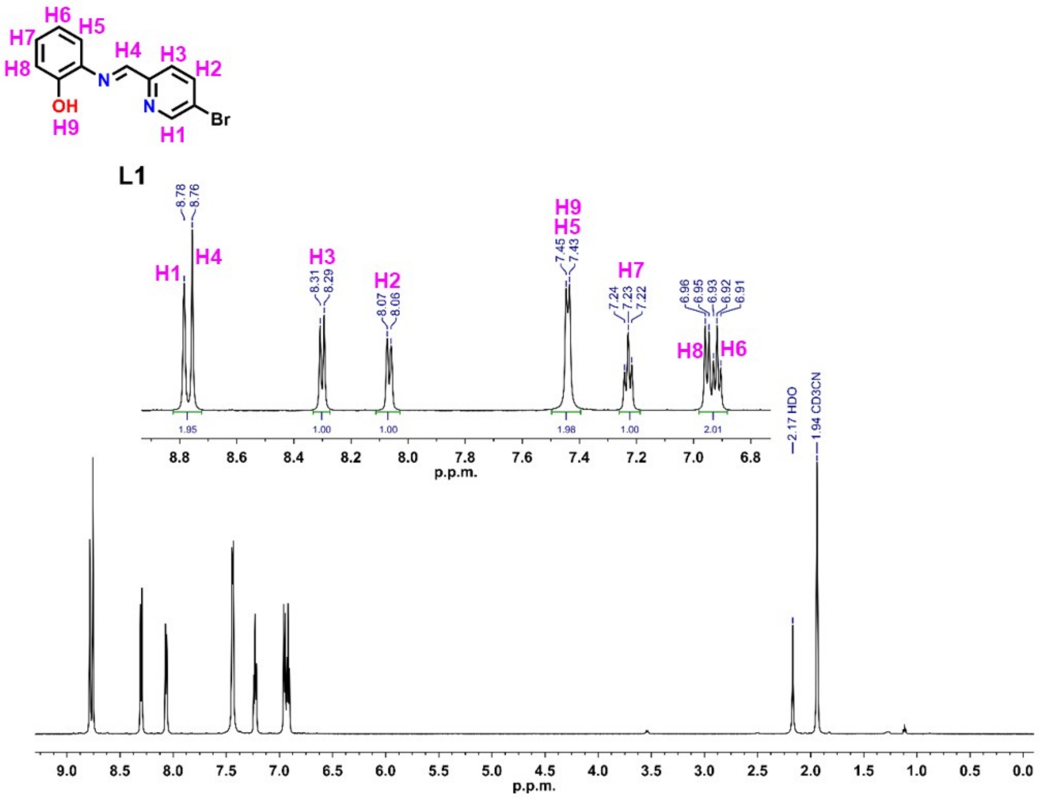


Figure S9. *^{1}H NMR (600 MHz, MeCN-d_3, 298 K) spectrum of* ***L1.***

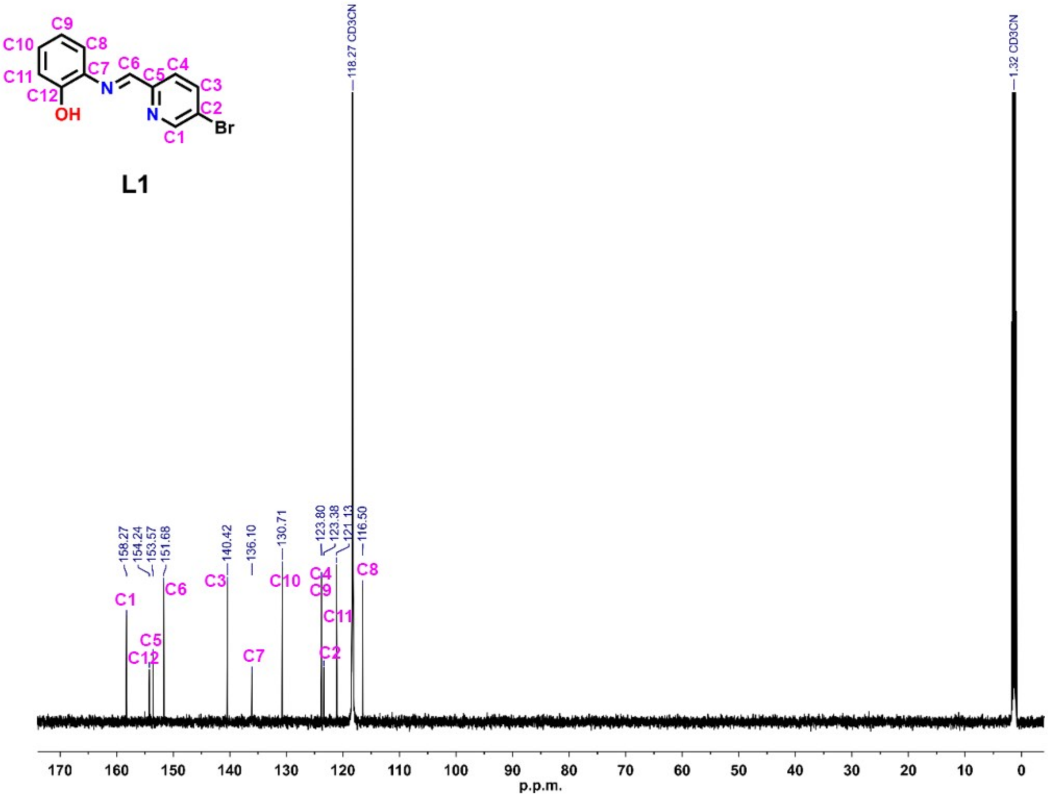


Figure S10. *^{13}C NMR (151 MHz, MeCN-d_3, 298 K) spectrum of* ***L1.***

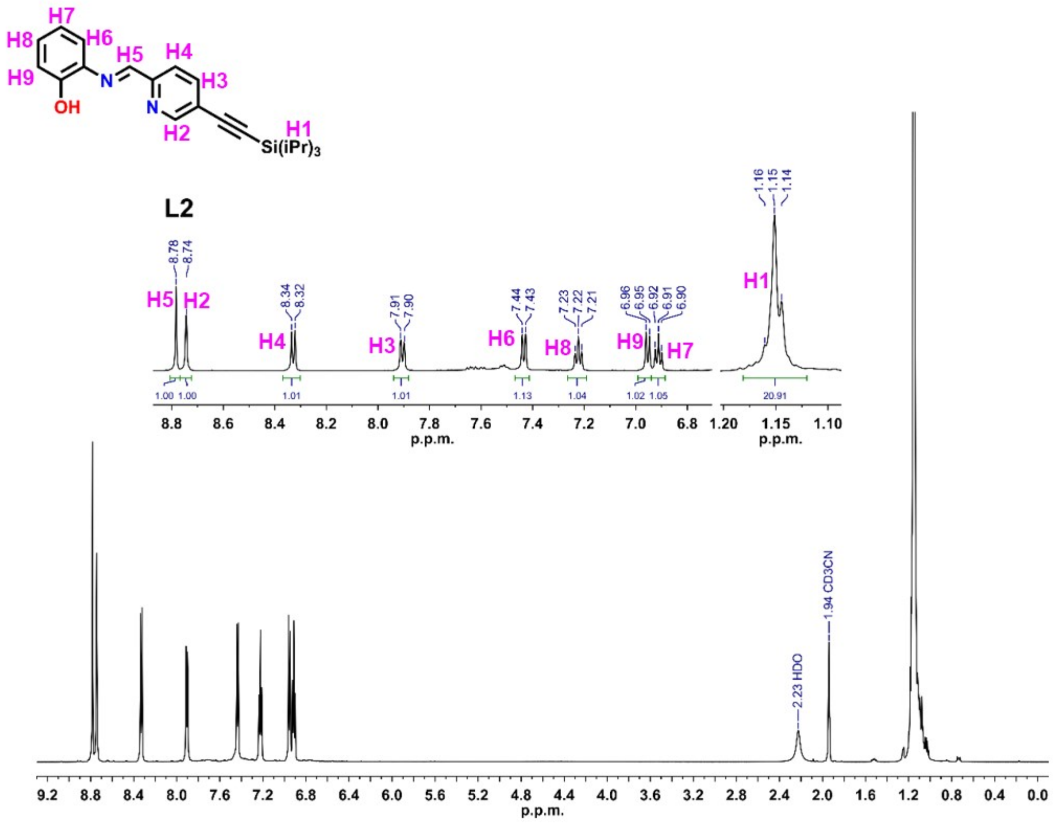


Figure S11. *^{1}H NMR (600 MHz, MeCN-d_3, 298 K) spectrum of* ***L2.***

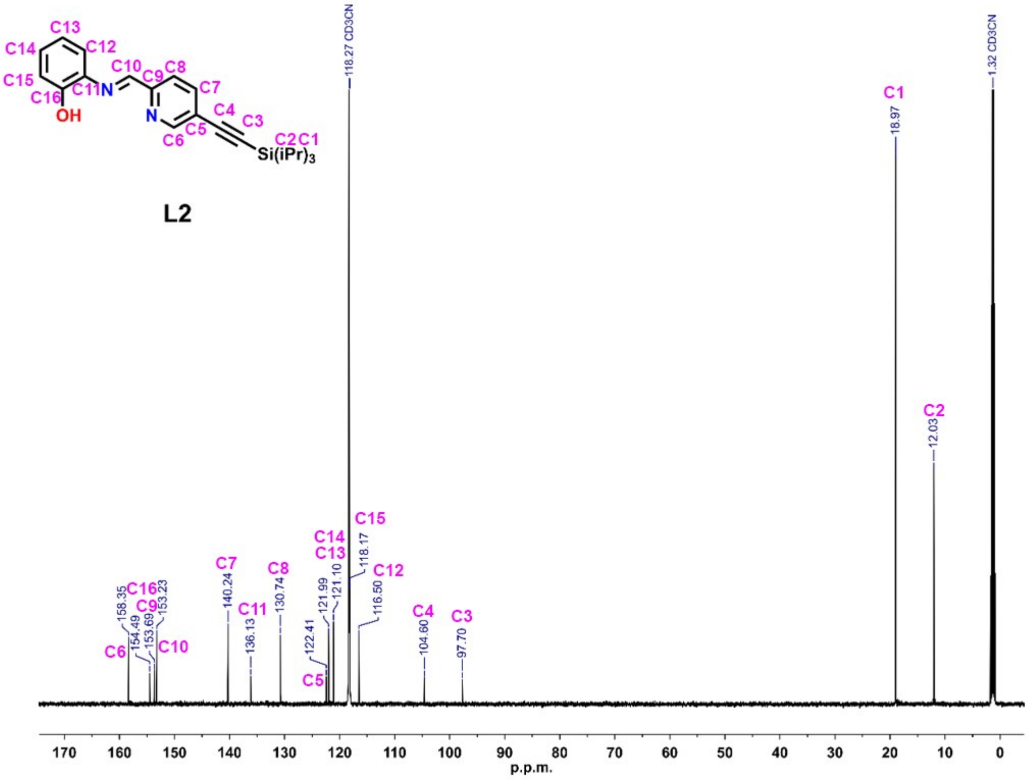


Figure S12. *^{13}C NMR (151 MHz, MeCN-d_3, 298 K) spectrum of* ***L2.***

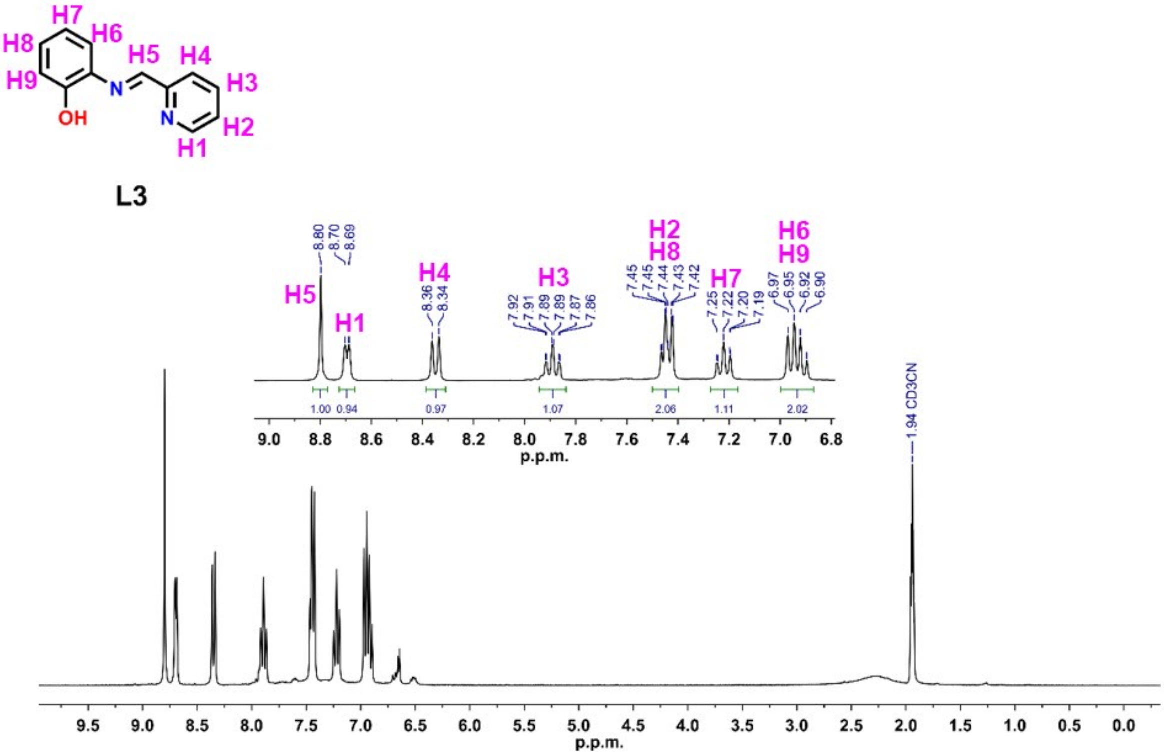


Figure S13. *^{1}H NMR (300 MHz, MeCN-d_3, 298 K) spectrum of* ***L3***.

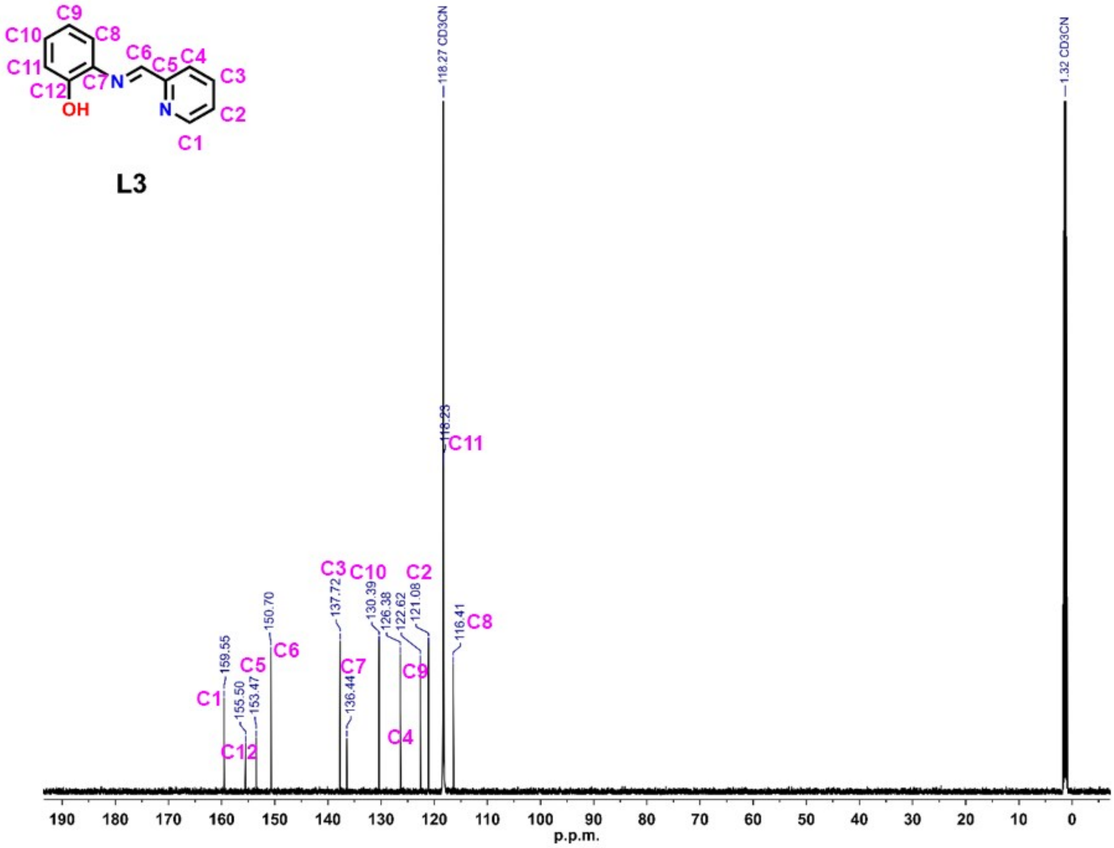


Figure S14. *^{13}C NMR (151 MHz, MeCN-d_3, 298 K) spectrum of* ***L3.***

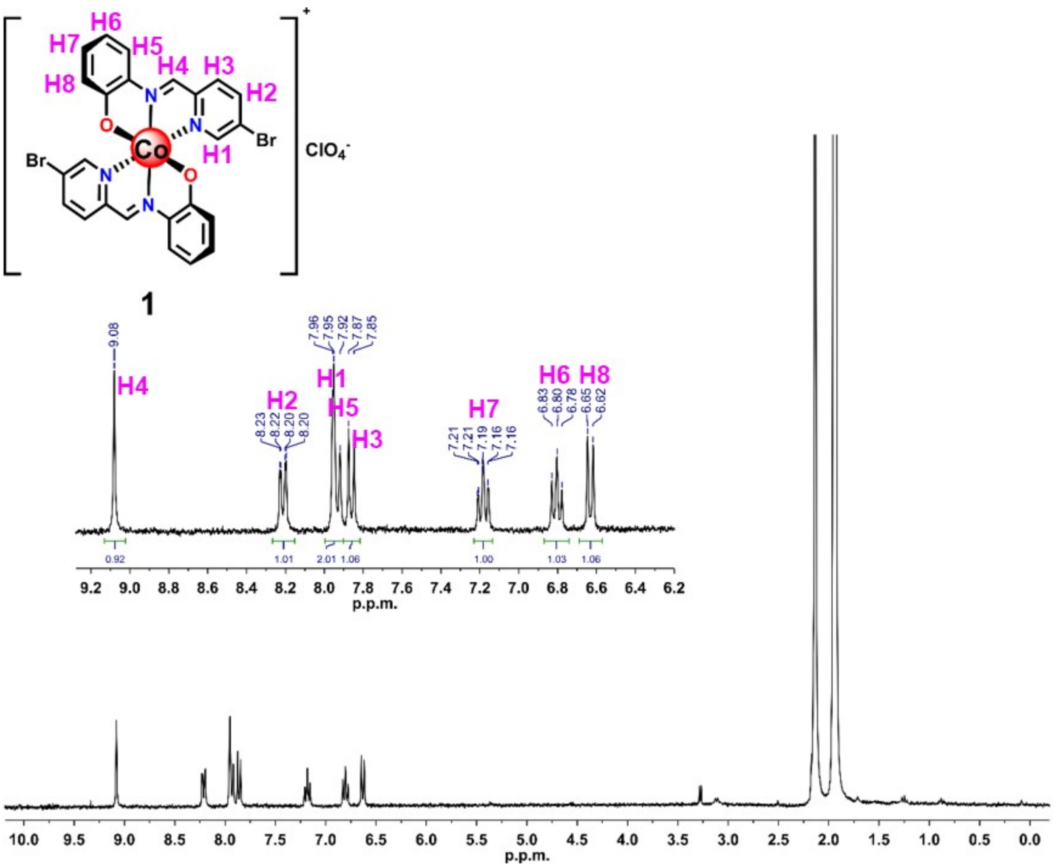


Figure S15. *^{1}H NMR (300 MHz, MeCN-d_3, 298 K) spectrum of complex **1**.*

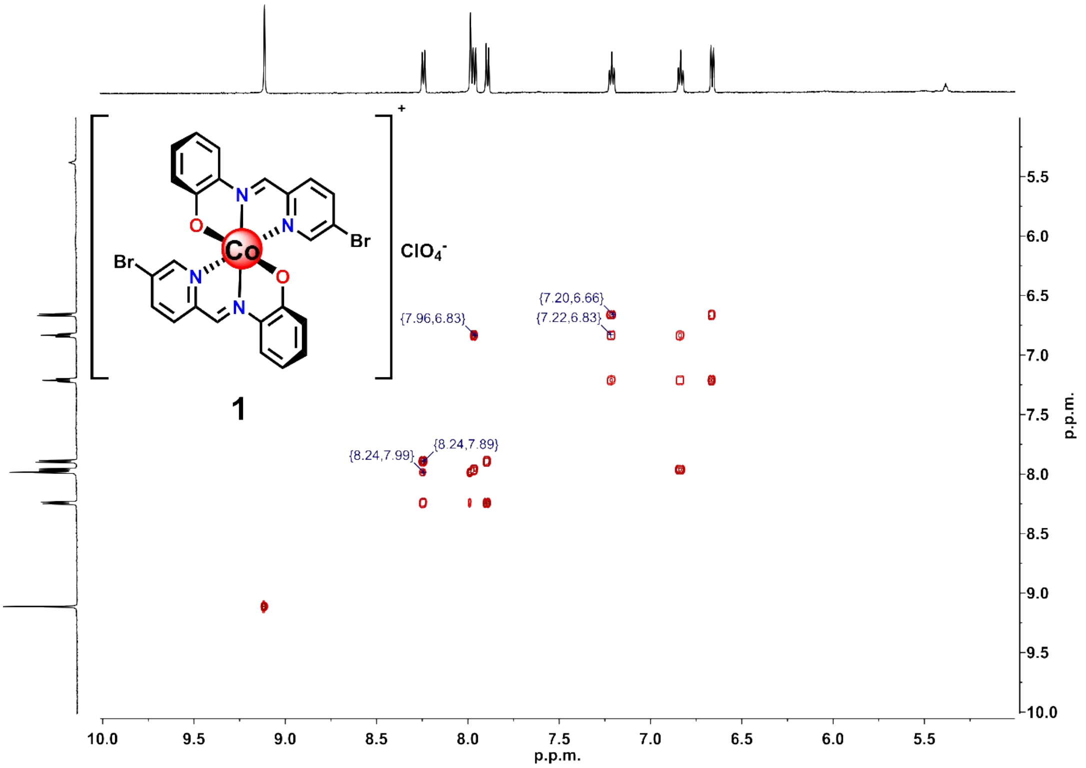


Figure S16. *^{1}H-^{1}H COSY NMR (600 MHz, MeCN-d_3, 298 K) spectrum of complex **1**.*

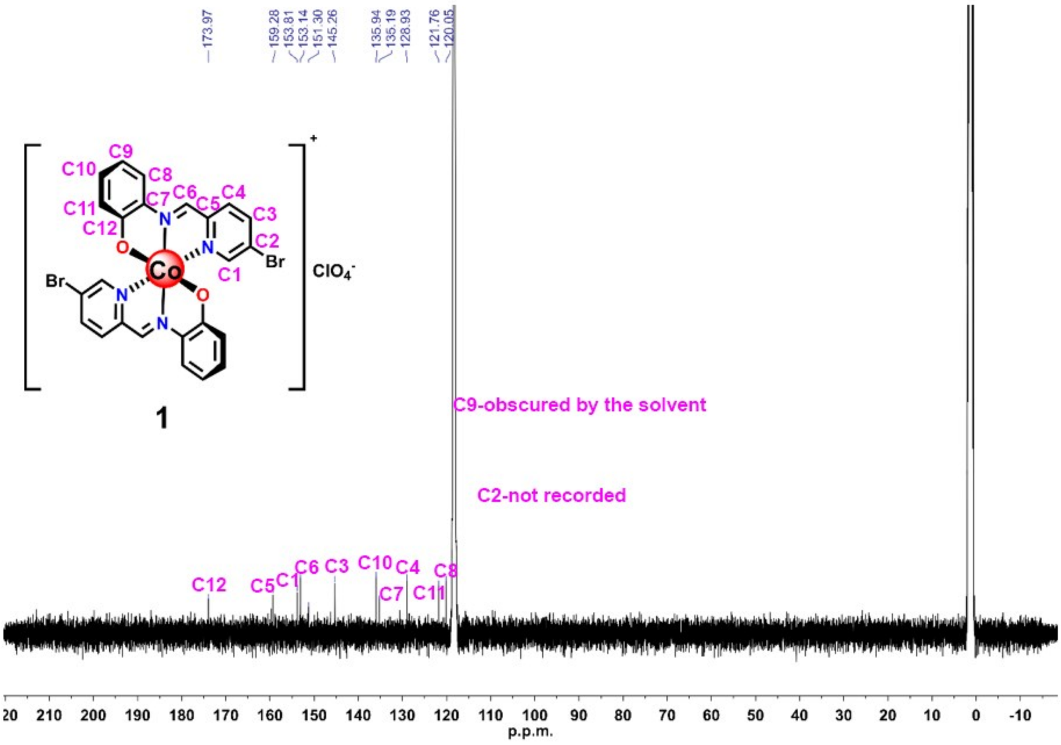


Figure S17. *^{13}C NMR (100 MHz, MeCN-d$_3$, 298 K) spectrum of complex **1** (aq. time ≈ 16 h).*

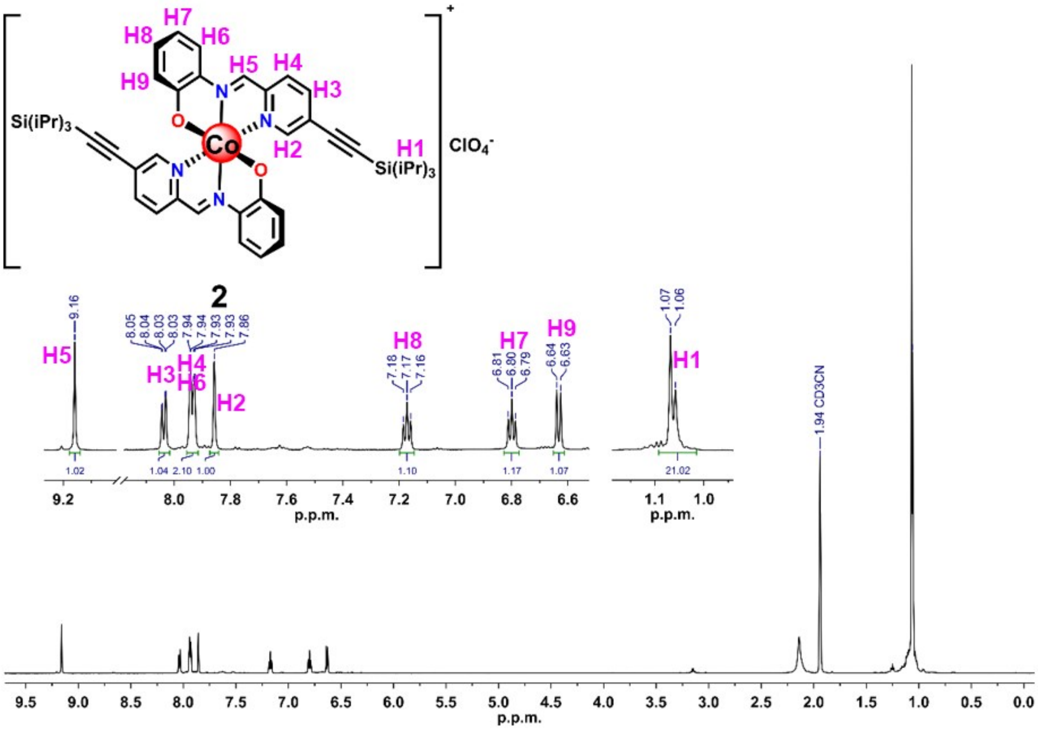


Figure S18. *^{1}H NMR (300 MHz, MeCN-d$_3$, 298 K) spectrum of complex **2**.*

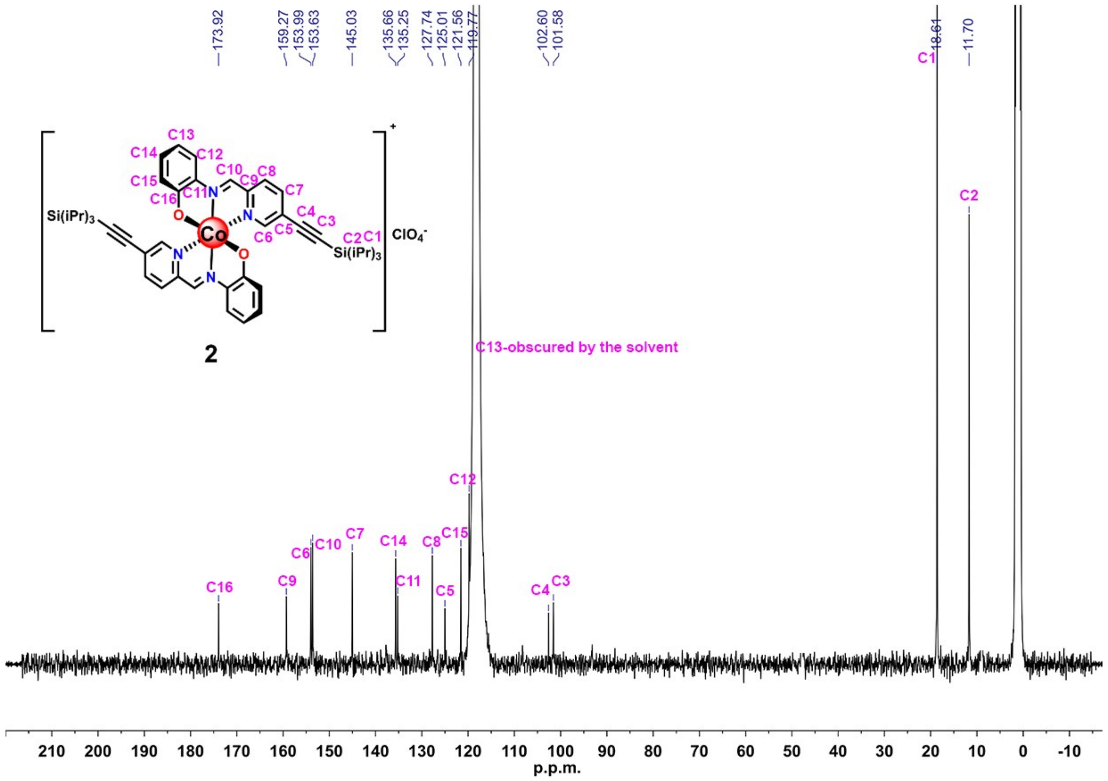


Figure S19. ^{13}C NMR (100 MHz, MeCN-d_3, 298 K) spectrum of complex **2** (aq. time ≈ 8 h).

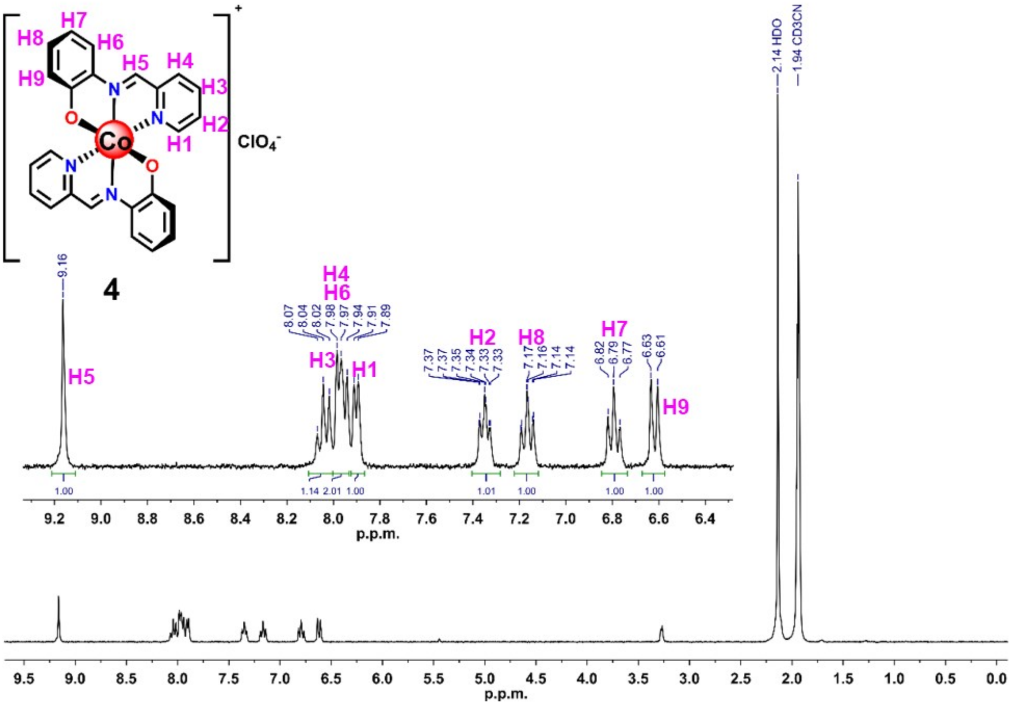
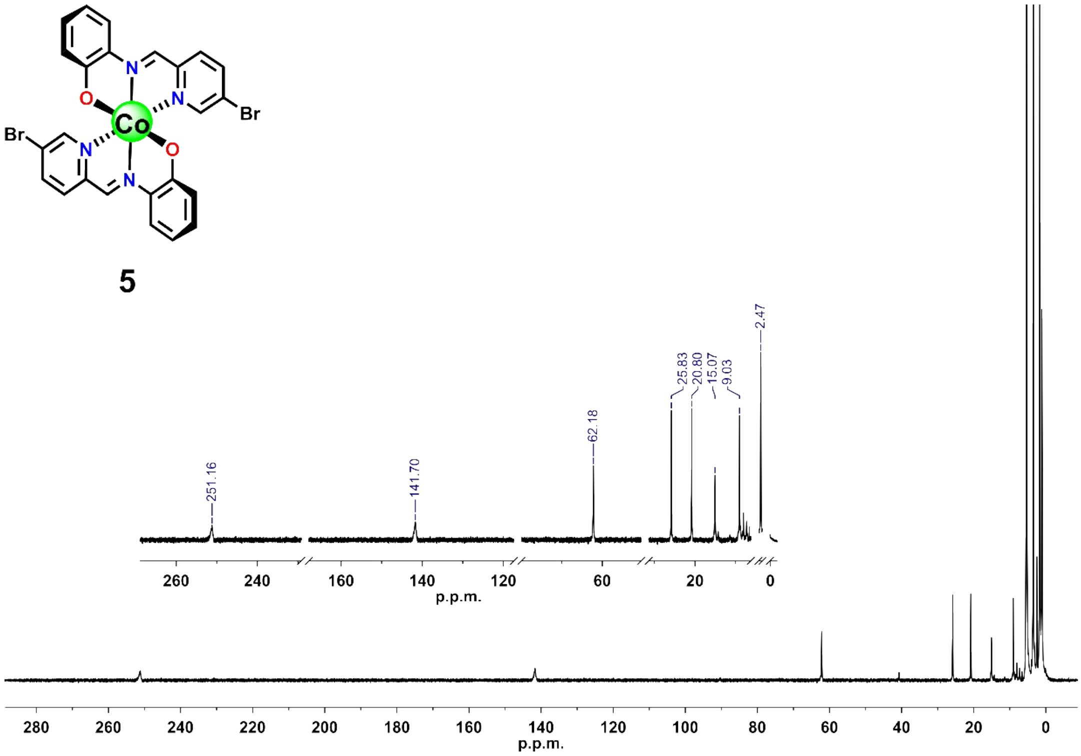
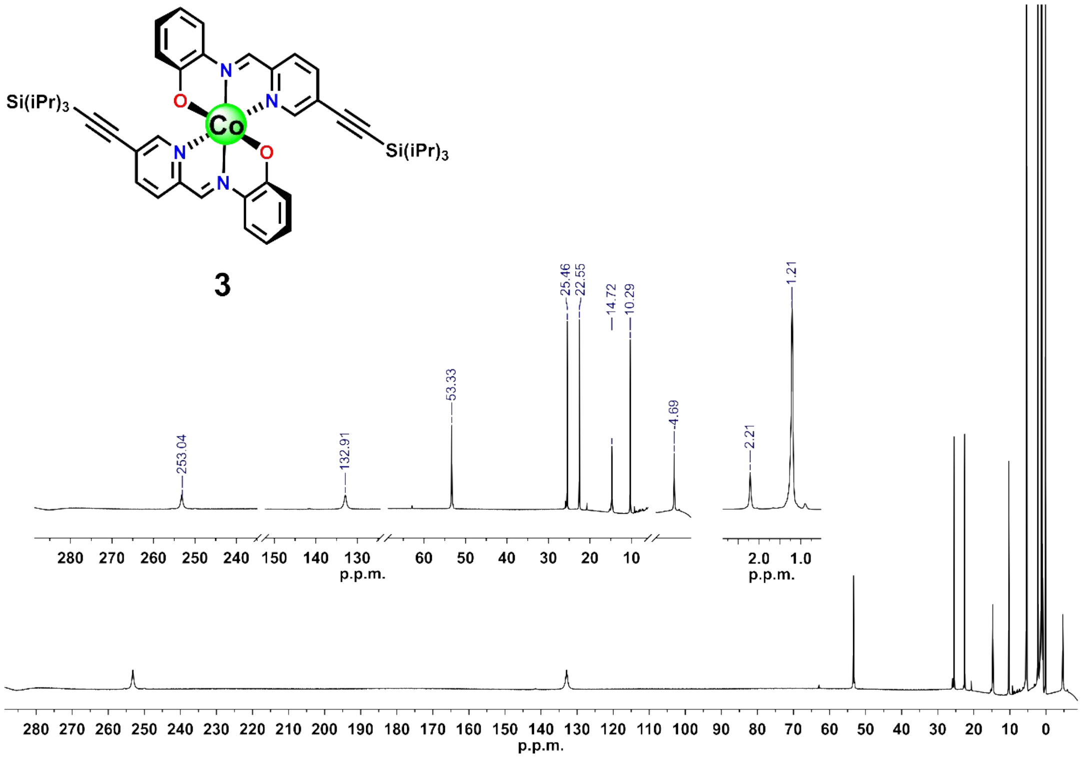


Figure S20. ^{1}H NMR (300 MHz, MeCN-d_3, 298 K) spectrum of complex **4**.



5

Figure S21. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) spectrum of complex **5**.



3

Figure S22. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K) spectrum of **3**.

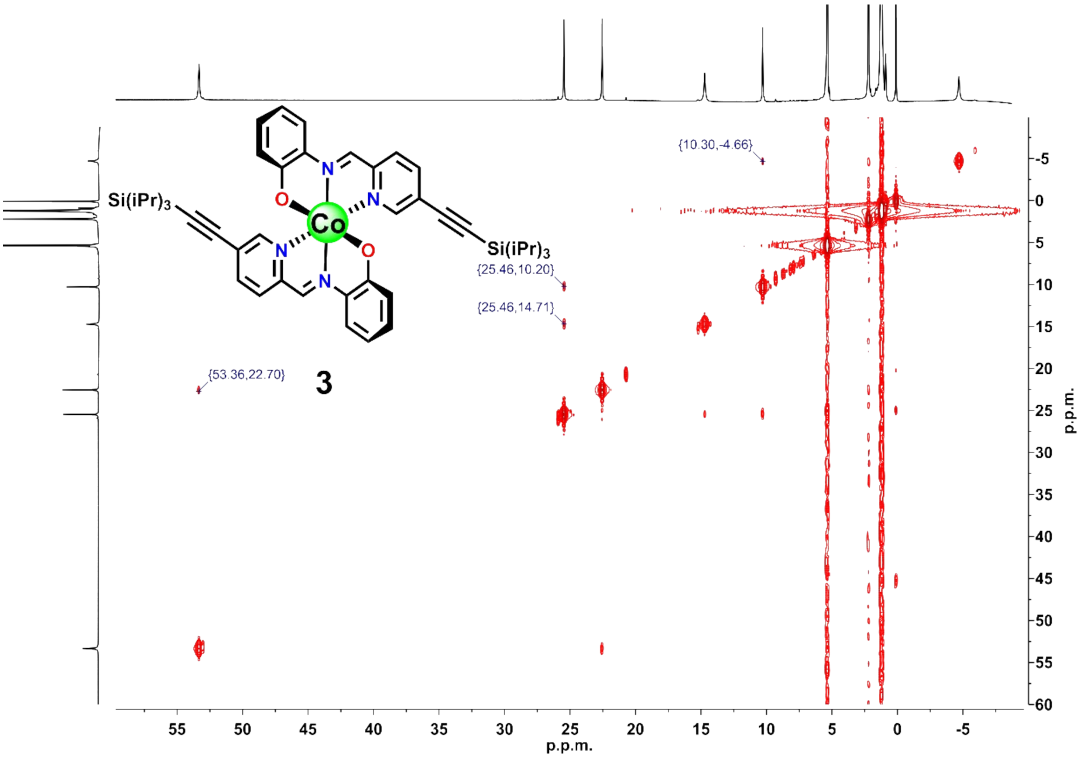


Figure S23. *^1H-^1H COSY NMR (600 MHz, CD_2Cl_2, 298 K) spectrum of complex **3**.*

Both **1** and **2** complexes have been tested for direct reduction of Co(III) metal centre by Pd(0) species. Tris(dibenzylideneacetone) dipalladium(0) $[Pd_2(DBA)_3]$ was chosen as a reductant, due to its sufficient solubility in CD_3CN and tendency to exchange ligands around Pd(0) core. As shown below, the addition of $[Pd_2(DBA)_3]$ to the solutions of **1** and **2** induced the Co(III) to Co(II) redox reaction only in the latter case, proving that indeed the silylalkynyl substituents are responsible for intramolecular electron transfer.

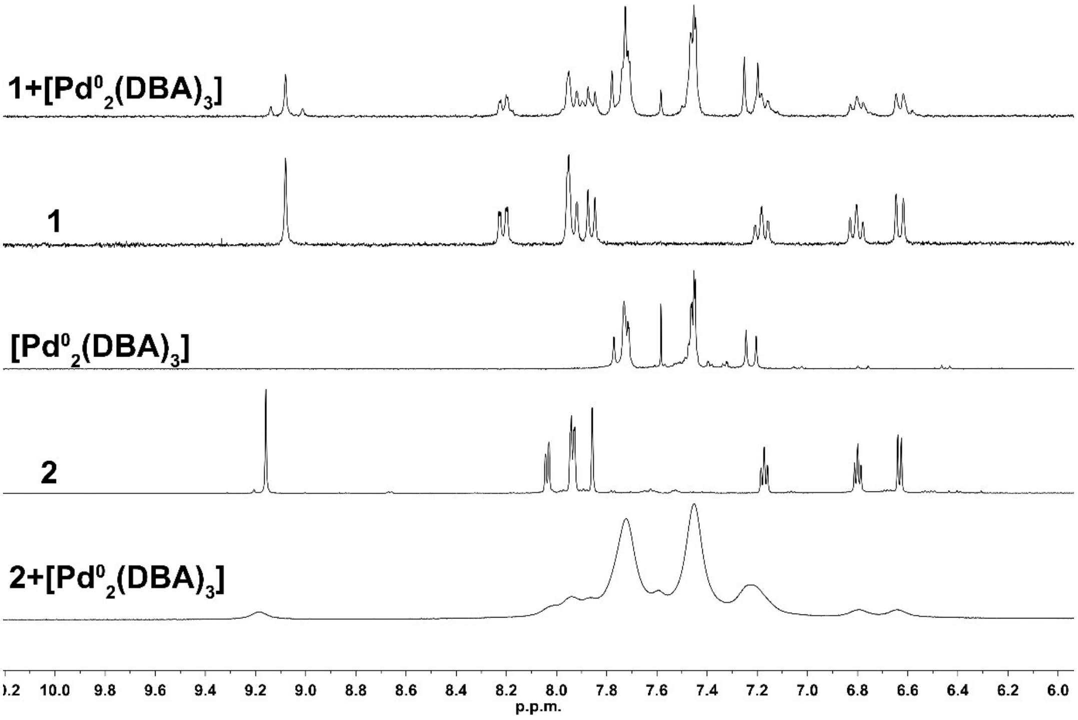


Figure S24. *Stacked ^{1}H NMR spectra (400 MHz, MeCN-d_3, 298 K) of **1** and **2** before and after addition of stoichiometric amount of tris(dibenzylideneacetone) dipalladium(0) [$Pd_2(DBA)_3$].The mixture of **2** and [$Pd_2(DBA)_3$] was found to be paramagnetic, as a result of substituent mediated Co(III)/Co(II) reduction.*

4. IR spectra

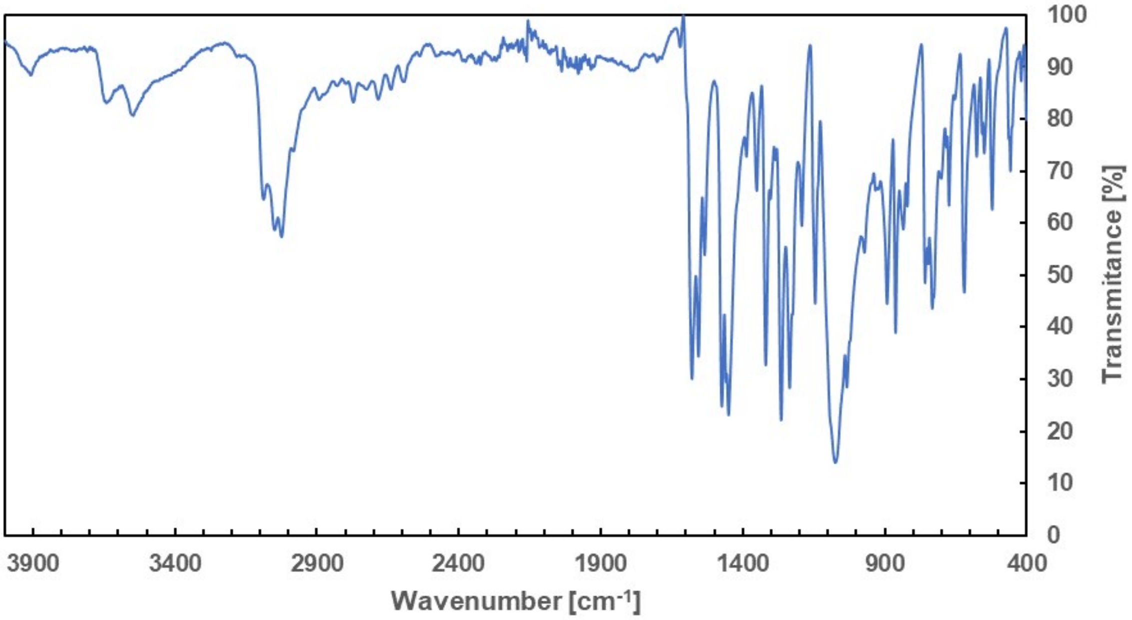


Figure S25. *FT-IR(ATR) spectrum of complex **1**.*

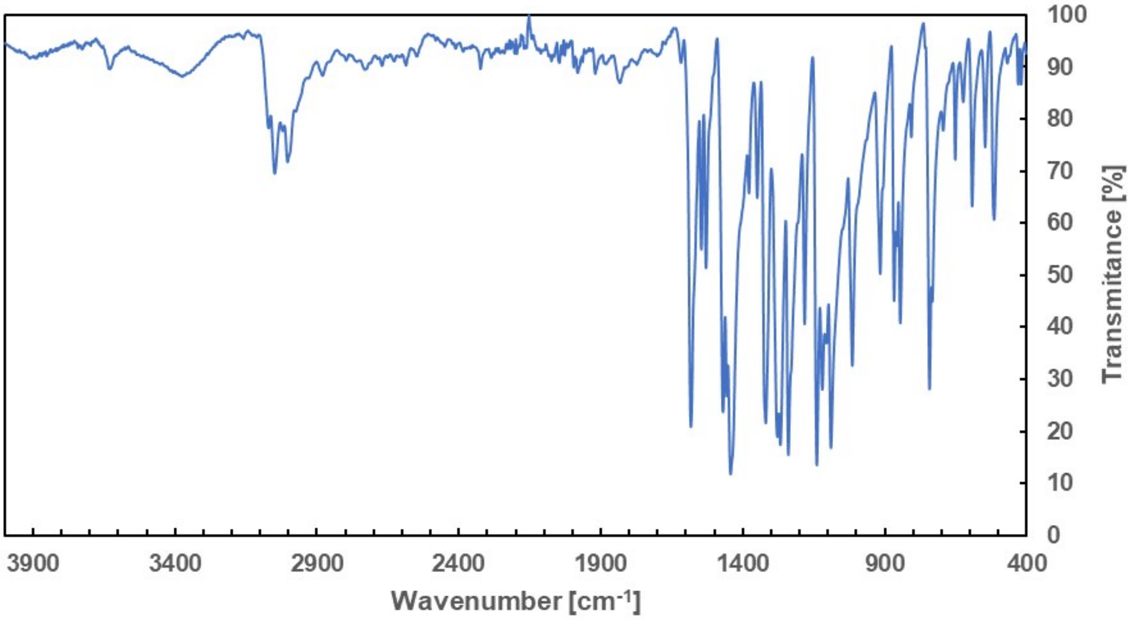


Figure S26. *FT-IR(ATR) spectrum of complex **5**.*

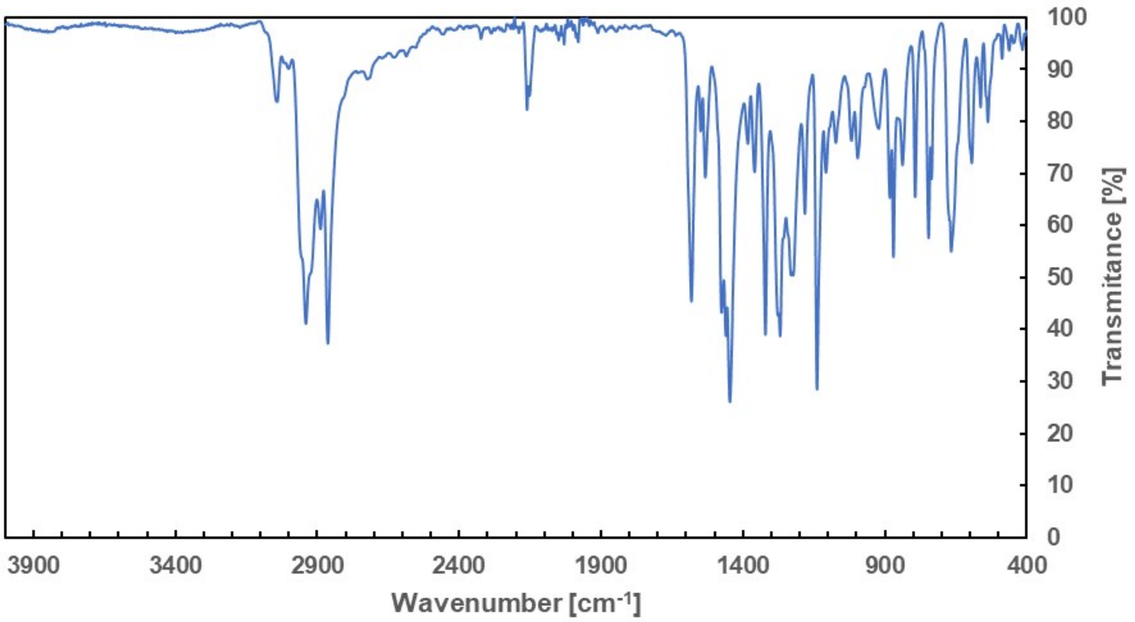


Figure S27. *FT-IR(ATR) spectrum of complex **3** obtained via microwave-accelerated synthesis.*

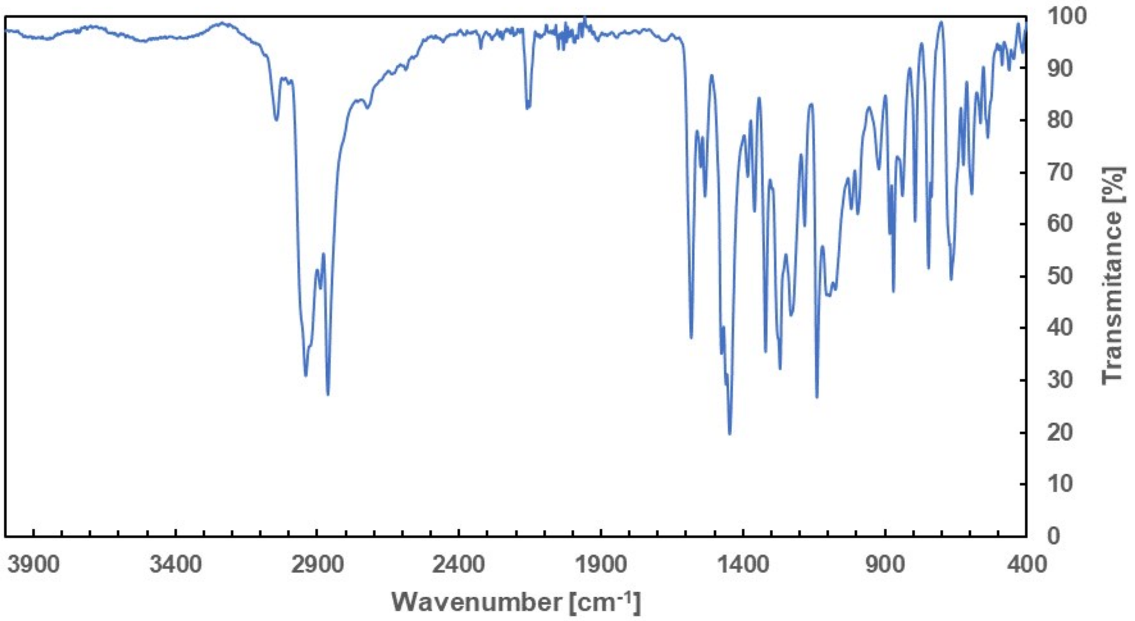


Figure S28. *FT-IR(ATR) spectrum of complex **3** obtained by heating in the oil bath.*

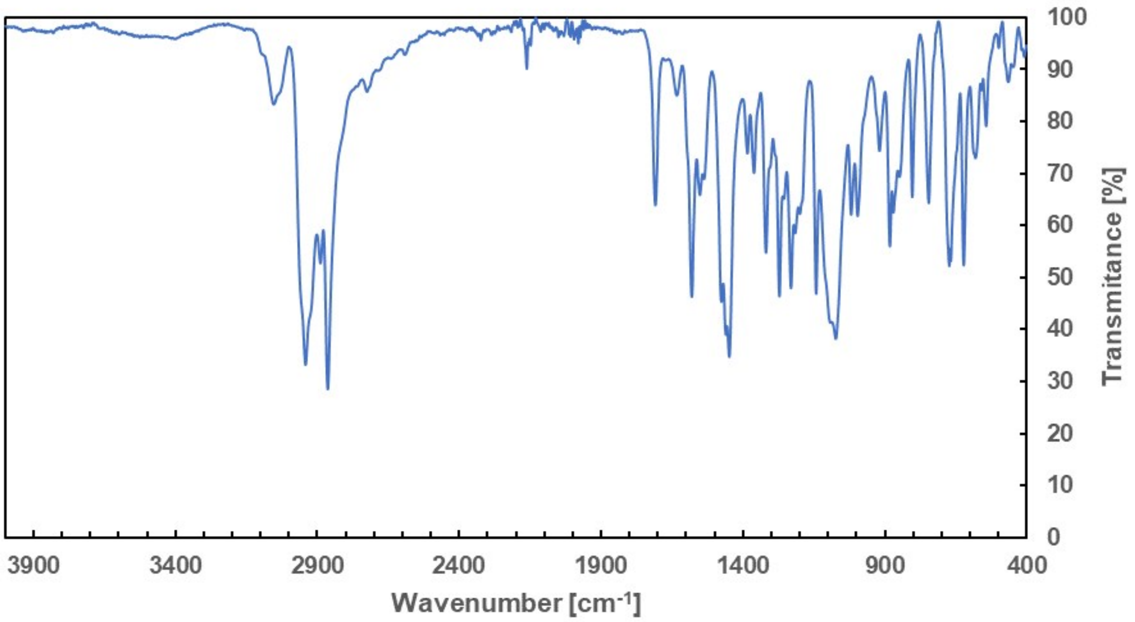


Figure S29. *FT-IR(ATR) spectrum of complex **2**.*

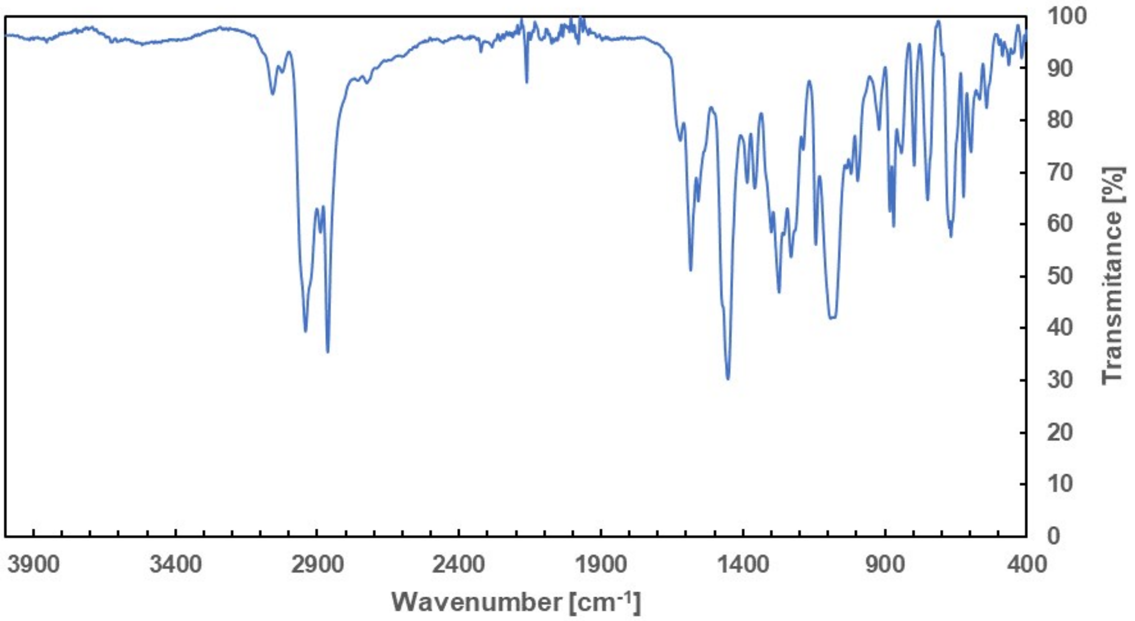


Figure S30. *FT-IR(ATR) spectrum of complex **2** after reduction reaction without palladium catalyst.*

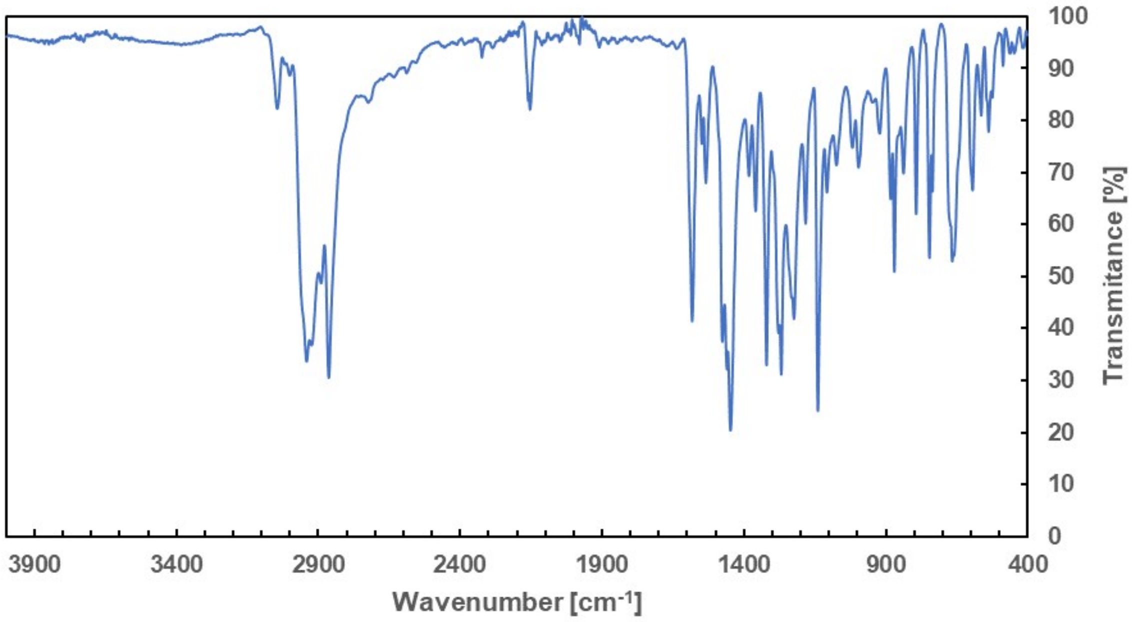


Figure S31. *FT-IR(ATR) spectrum of complex **2** after reduction reaction with palladium catalyst.*

5. UV-Vis spectra

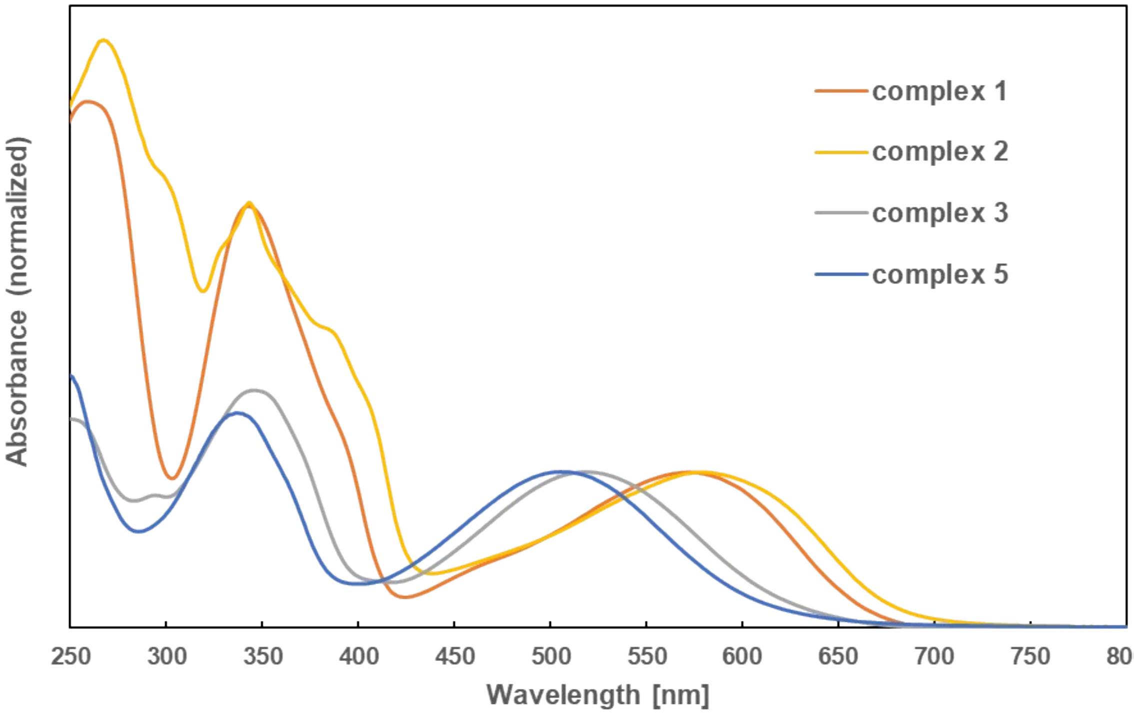


Figure S32. *UV-Vis spectra of complexes: **1**, **2**, **3** and **5** measured in DCM solutions at* 5×10^{-6} *M.*

6. Gas chromatography

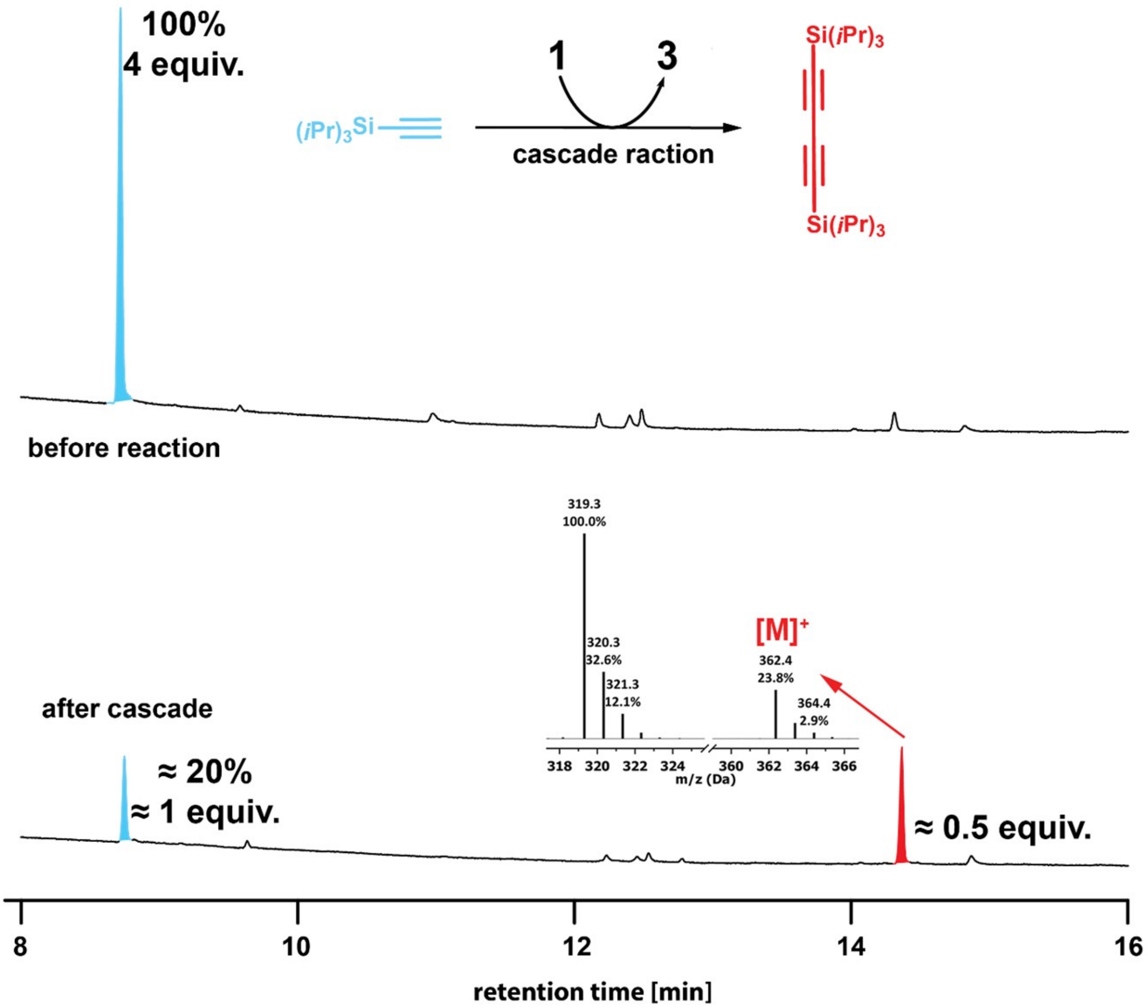


Figure S33. *GC(TCD) chromatograms of Sonogashira coupling and simultaneous Glaser reduction performed on **1**. Top: reaction mixture before reaction. Bottom: reaction mixture after cascade. Inset: EI-MS spectrum of* $(iPr)_3SiC{\equiv}C\text{-}C{\equiv}CSi(iPr)_3$.

7. ESI-MS

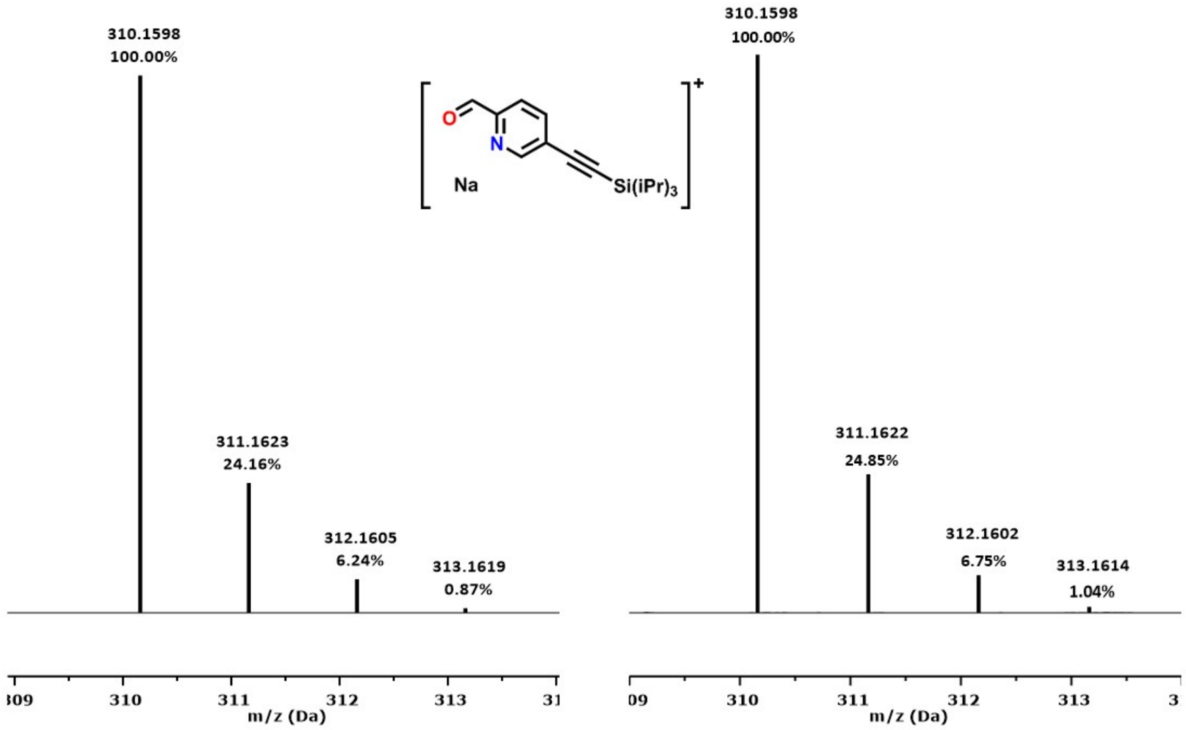


Figure S34. *ESI-HRMS spectrum of 5-[(triisopropylsilyl)ethynyl]2-pyridinecarbox-aldehyde, prediction (left) and measurement (right, normalised).*

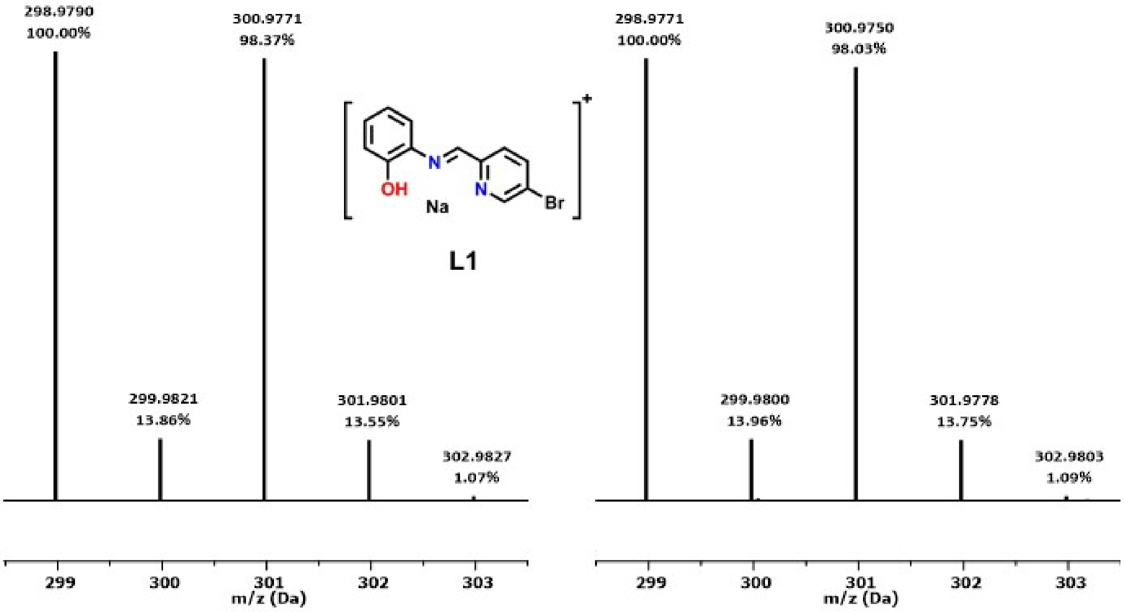


Figure S35. *ESI-HRMS spectrum of* ***L1****, prediction (left) and measurement (right).*

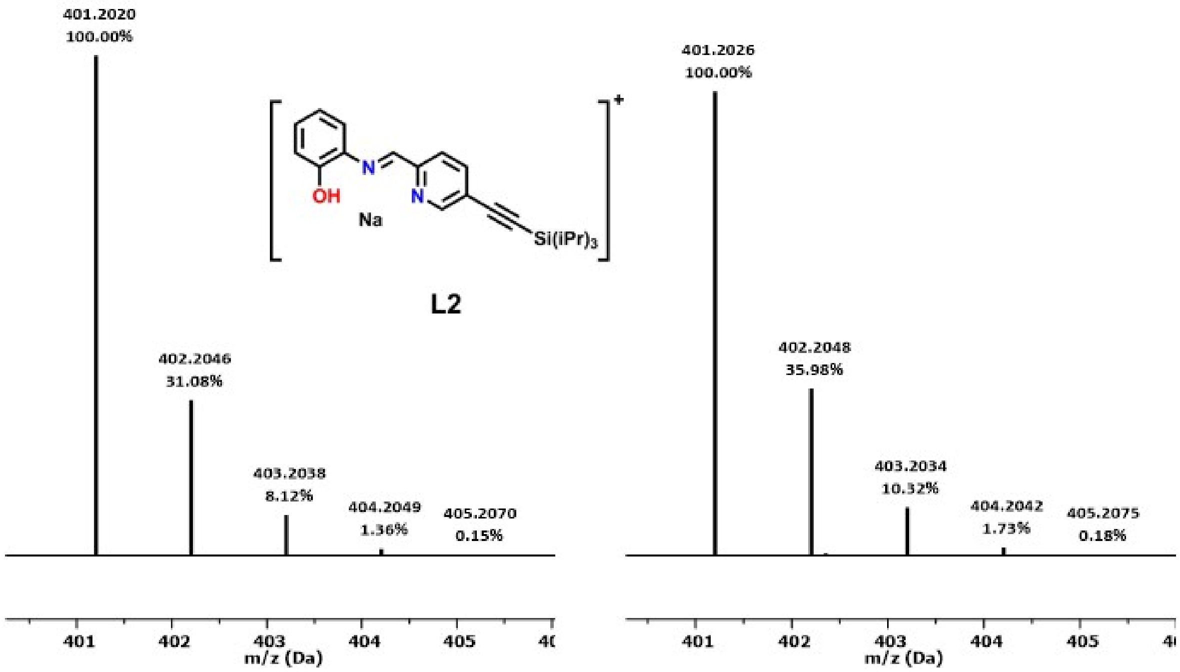


Figure S36. *ESI-HRMS spectrum of **L2**, prediction (left) and measurement (right).*

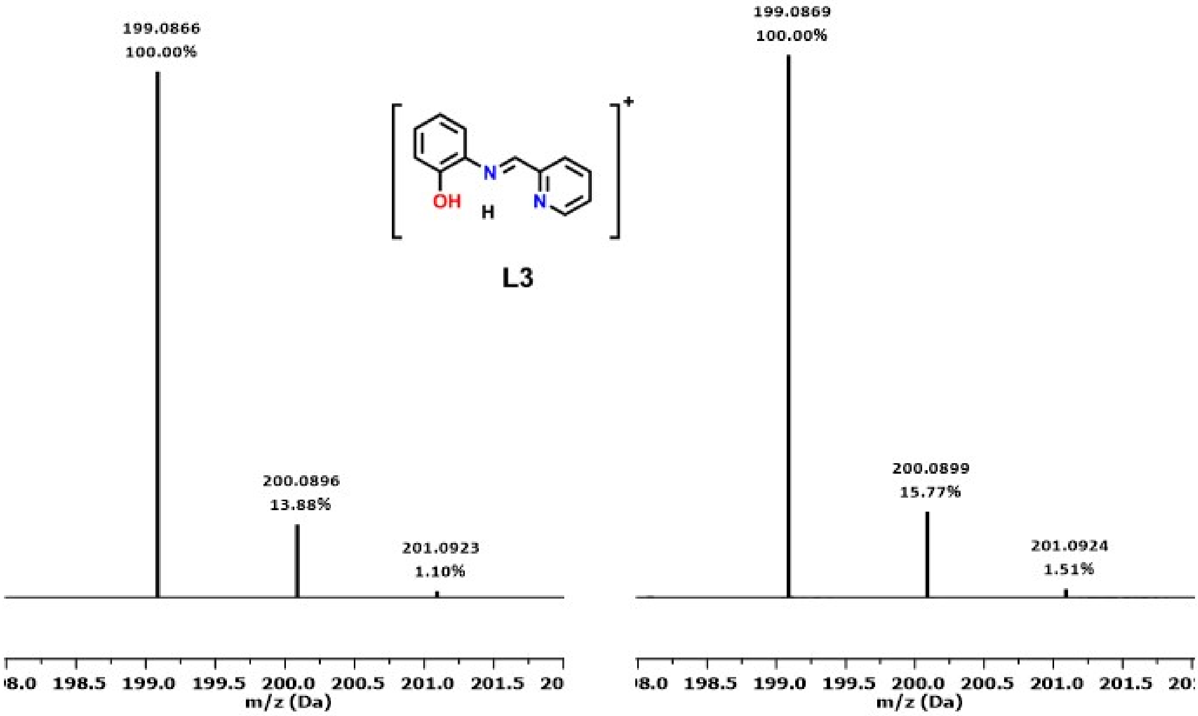


Figure S37. *ESI-HRMS spectrum of **L3**, prediction (left) and measurement (right).*

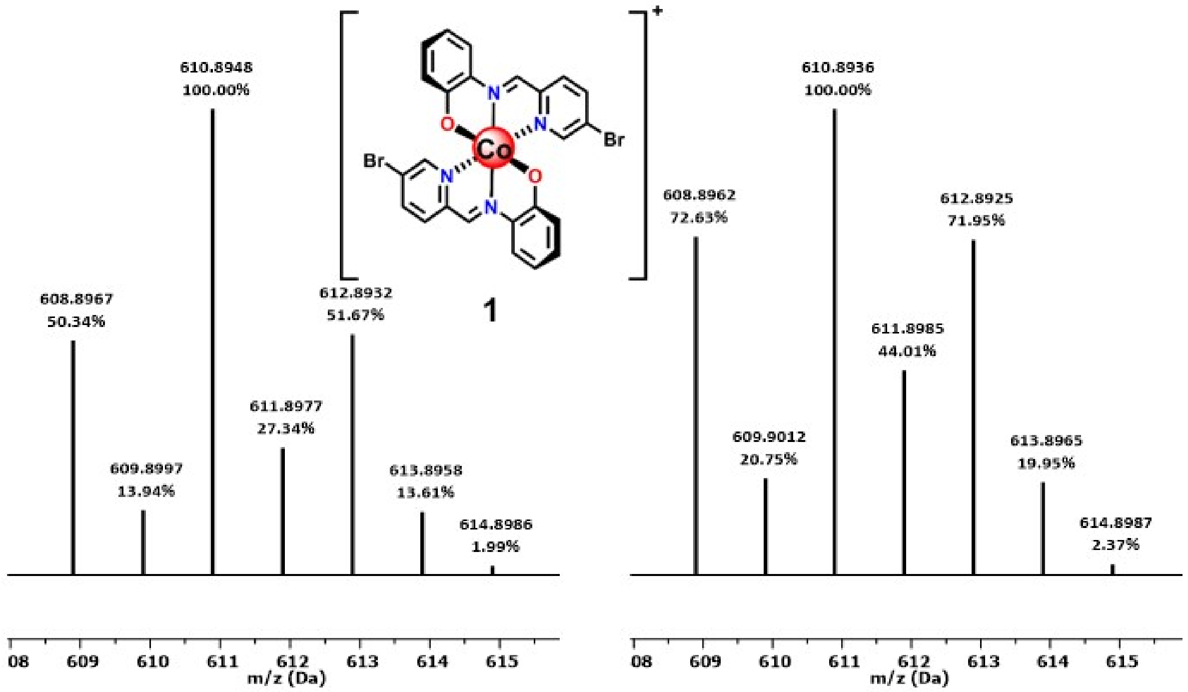


Figure S38. *ESI-HRMS spectrum of complex **1**, prediction (left) and measurement (right).*

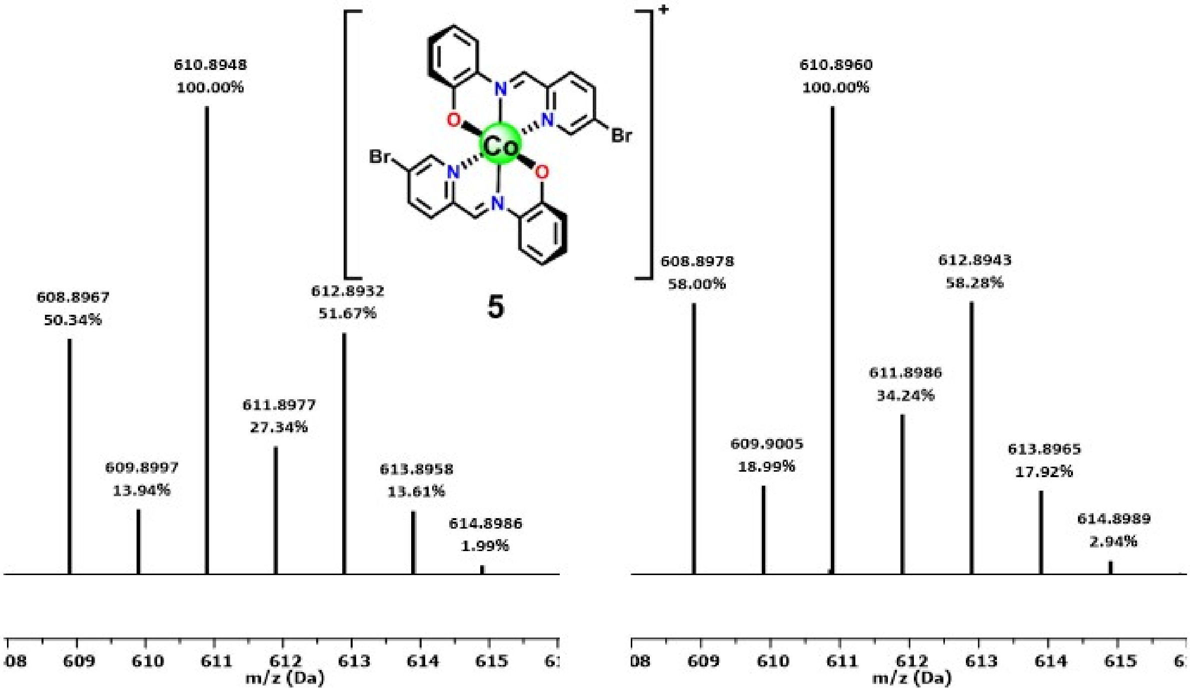


Figure S39. *ESI-HRMS spectrum of complex **5**, prediction (left) and measurement (right).*

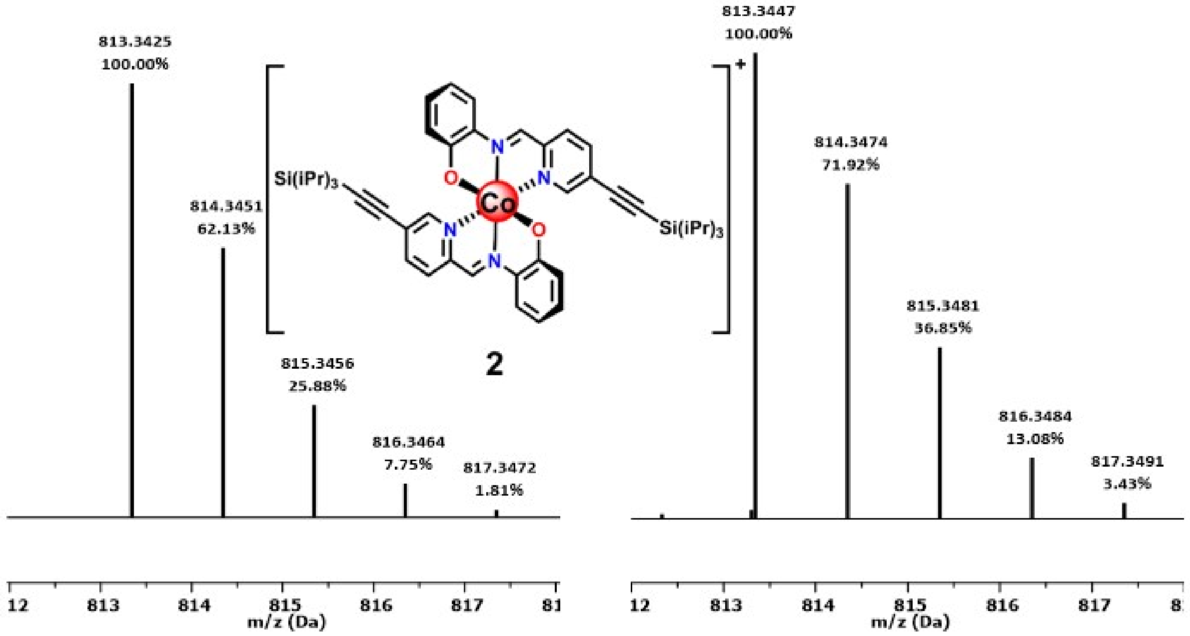


Figure S40. *ESI-HRMS spectrum of complex **2**, prediction (left) and measurement (right).*

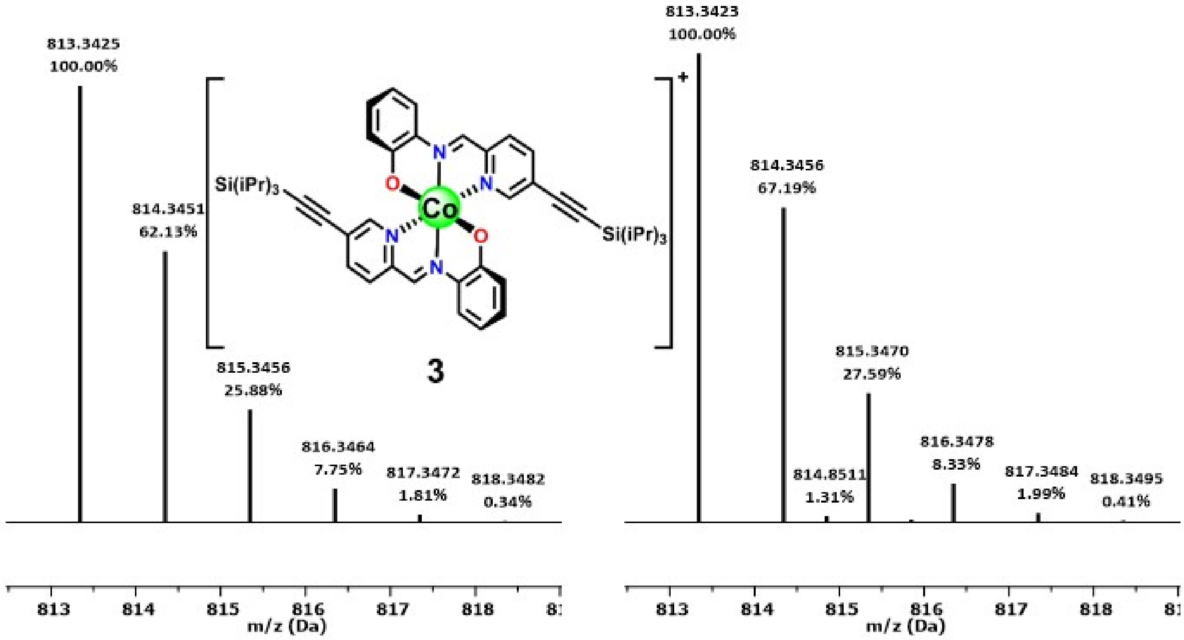


Figure S41. *ESI-HRMS spectrum of complex **3**, prediction (left) and measurement (right).*

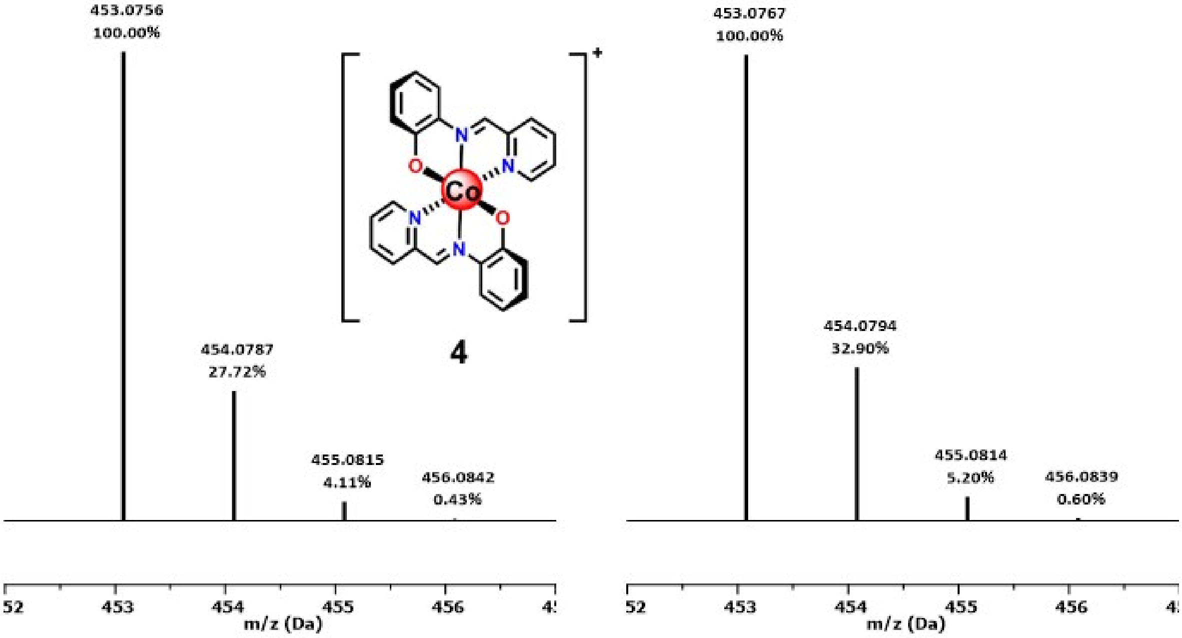


Figure S42. *ESI-HRMS spectrum of complex **4**, prediction (left) and measurement (right).*

8. DFT calculations

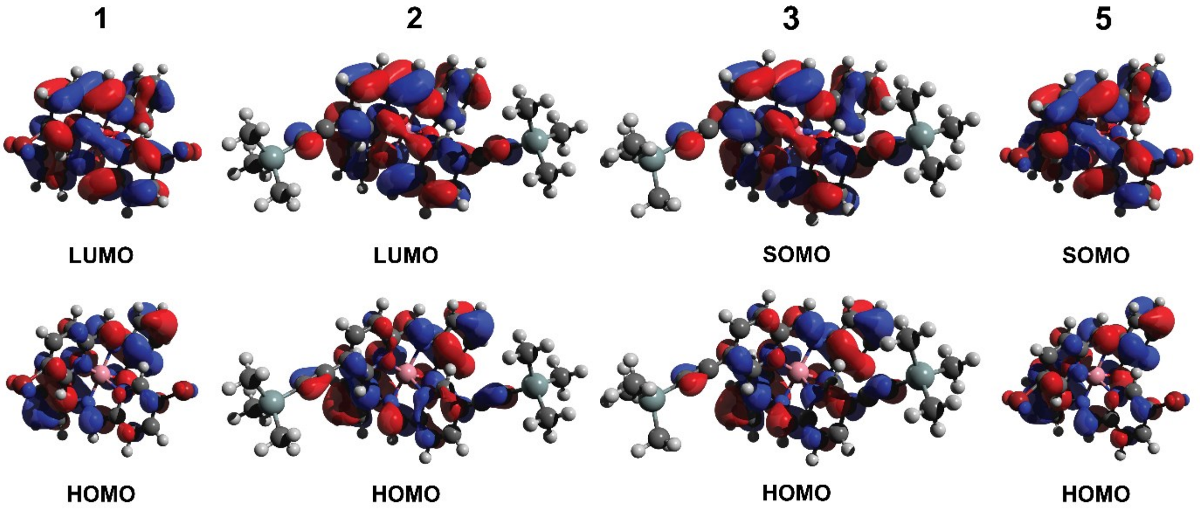


Figure S43. *Shapes of the calculated molecular orbitals (HOMO, LUMO and SOMO stand for Highest, Lowest Unoccupied and Single Occupied Molecular Orbitals) of 1, 2, 3, and* ***5****. iPr groups were simplified to Me in* ***2*** *and* ***3*** *in order to reduce computational cost.*

Table S1. Optimised ground state geometry of **5** (atom symbol, x, y, z Cartesian coordinates)

C	-2.72507	-4.43411	-1.90664
N	-2.54125	-3.51418	-0.89737
C	-1.31670	-3.26787	-0.42764
C	-0.19876	-3.91620	-0.93076
C	-0.34856	-4.86040	-1.95924
C	-1.61670	-5.11510	-2.44209
C	-4.08071	-4.61795	-2.31322
N	-4.97456	-3.94117	-1.62639
C	-6.34523	-3.84050	-1.75453
C	-7.16866	-4.56988	-2.62835
C	-8.53306	-4.33417	-2.63295
C	-9.07855	-3.36533	-1.76891
C	-8.28077	-2.63391	-0.90371
C	-6.88821	-2.85831	-0.86874
O	-6.08856	-2.20269	-0.06111
B	r 1.52695	-3.50039	-0.23644
C	-3.97604	-3.14625	2.38040
N	-4.33244	-3.86337	1.25878
C	-4.66169	-5.15255	1.36186
C	-4.66101	-5.80966	2.58300
C	-4.30232	-5.11073	3.74686
C	-3.95959	-3.77781	3.63739
C	-3.63182	-1.78279	2.13787
N	-3.63317	-1.41489	0.87531
C	-3.38954	-0.19638	0.27440
C	-2.94232	0.98025	0.89823
C	-2.75487	2.12360	0.13997
C	-3.01920	2.09746	-1.24280
C	-3.46468	0.94692	-1.87368
C	-3.65457	-0.23687	-1.13003
O	-4.05996	-1.35717	-1.68022
B	r -5.1719	7 -7.6440	4 2.66870
C	o -4.2703	2 -2.7178	1 -0.35331
H	-1.23669	-2.52955	0.35998
H	0.51386	-5.37764	-2.36169
H	-1.76779	-5.84228	-3.23221
H	-4.34462	-5.27058	-3.14006
H	-6.73867	-5.31304	-3.29289
H	-9.17957	-4.89219	-3.30122
H	-10.1493	7 -3.1858	8 -1.78129
H	-8.70135	-1.88383	-0.24315
H	-4.93896	-5.65918	0.44609
H	-4.29367	-5.61001	4.70808
H	-3.67199	-3.21092	4.51594
H	-3.39200	-1.10185	2.94909
H	-2.74279	0.99232	1.96544
H	-2.40739	3.03711	0.60980
H	-2.87153	2.99960	-1.82869
H	-3.67302	0.92897	-2.93770

Table S2. Optimised ground state geometry of **1** (atom symbol, x, y, z Cartesian coordinates)

C	-2.68710	-4.42957	-1.91807
N	-2.50139	-3.53351	-0.90540
C	-1.27264	-3.24700	-0.48238
C	-0.14551	-3.84827	-1.04499
C	-0.30921	-4.76863	-2.07797
C	-1.59462	-5.05999	-2.51642
C	-4.06779	-4.63904	-2.30215
N	-4.94649	-3.95801	-1.63230
C	-6.31714	-3.85101	-1.74800
C	-7.14664	-4.56400	-2.63744
C	-8.50184	-4.32183	-2.62441
C	-9.03972	-3.36652	-1.72911
C	-8.24386	-2.65735	-0.85296
C	-6.84901	-2.88363	-0.84156
O	-6.04452	-2.24091	-0.03075
B	r 1.57319	-3.39650	-0.39211
C	-3.99660	-3.17213	2.40300
N	-4.33162	-3.89230	1.29299
C	-4.71703	-5.16072	1.40932
C	-4.78581	-5.79418	2.65131
C	-4.44554	-5.08128	3.79876
C	-4.04704	-3.75692	3.66960
C	-3.61343	-1.79905	2.14678
N	-3.62969	-1.43500	0.90104
C	-3.38576	-0.22324	0.28829
C	-2.95809	0.96663	0.91196
C	-2.77014	2.09264	0.14245
C	-3.01031	2.04347	-1.25161
C	-3.43121	0.88916	-1.87955
C	-3.63152	-0.28393	-1.11754
O	-4.02587	-1.40953	-1.66102
B	r -5.3419	2 -7.6016	3 2.74414
C	o -4.2402	3 -2.7529	5 -0.33444
H	-1.18091	-2.52221	0.31613
H	0.55055	-5.24625	-2.53216
H	-1.75285	-5.76843	-3.32118
H	-4.33179	-5.30444	-3.11894
H	-6.72502	-5.29168	-3.32305
H	-9.15834	-4.85724	-3.29983
H	-10.1094	7 -3.1849	8 -1.73526
H	-8.65939	-1.92160	-0.17458
H	-4.98101	-5.68320	0.49883
H	-4.49320	-5.55093	4.77383
H	-3.78013	-3.17617	4.54486
H	-3.35850	-1.12322	2.95789
H	-2.77953	0.99667	1.98183
H	-2.44236	3.01808	0.60070
H	-2.86139	2.94140	-1.84227
H	-3.62002	0.85770	-2.94612

Table S3. Optimised ground state geometry of **3** (atom symbol, x, y, z Cartesian coordinates) (*i*Pr simplified to Me groups).

C	-2.65890	-4.46590	-1.86920
N	-2.49890	-3.54290	-0.85560
C	-1.28930	-3.27760	-0.37910
C	-0.12390	-3.89510	-0.85860
C	-0.27850	-4.84980	-1.89590
C	-1.53230	-5.12950	-2.39090
C	-4.00500	-4.66750	-2.28950
N	-4.91680	-3.99590	-1.62120
C	-6.28630	-3.91440	-1.76790
C	-7.08870	-4.66010	-2.64750
C	-8.45590	-4.44220	-2.67190
C	-9.02560	-3.47540	-1.82110
C	-8.24910	-2.72850	-0.95000
C	-6.85380	-2.93380	-0.89530
O	-6.07380	-2.26310	-0.08200
C	-4.00420	-3.17120	2.40120
N	-4.33070	-3.89950	1.27530
C	-4.66140	-5.18000	1.38100
C	-4.70530	-5.86210	2.60670
C	-4.36450	-5.12460	3.76880
C	-4.01740	-3.79640	3.66250
C	-3.66040	-1.81060	2.15570
N	-3.64230	-1.44740	0.89200
C	-3.39290	-0.23140	0.29000
C	-2.96380	0.95110	0.91590
C	-2.76850	2.09160	0.15560
C	-3.00580	2.05700	-1.23220
C	-3.43240	0.90100	-1.86550
C	-3.63100	-0.28040	-1.11950
O	-4.02040	-1.40460	-1.67110
C	o -4.2436	0 -2.7634	0 -0.34080
H	-1.23170	-2.53980	0.41170
H	0.59660	-5.35270	-2.29100
H	-1.66500	-5.85930	-3.18200
H	-4.25120	-5.33090	-3.11340
H	-6.64030	-5.40170	-3.30160
H	-9.08600	-5.01260	-3.34540
H	-10.0985	0 -3.3103	0 -1.84870
H	-8.68820	-1.98040	-0.29930
H	-4.91210	-5.69280	0.46050
H	-4.38100	-5.61570	4.73490
H	-3.75150	-3.22180	4.54290
H	-3.43480	-1.12450	2.96690
H	-2.78520	0.96970	1.98670
H	-2.43570	3.00970	0.62730
H	-2.85170	2.95700	-1.81970
H	-3.61970	0.87640	-2.93330
C	-5.08580	-7.22530	2.65960
C	-5.41350	-8.39710	2.70930
C	1.14440	-3.56250	-0.32320
C	2.24030	-3.28620	0.13020
S	i 3.89860	-2.85840	0.81520
C	5.13890	-4.13720	0.19880
C	4.37260	-1.13480	0.21730
C	3.79410	-2.89460	2.69740
H	5.19450	-4.14810	-0.89350
H	3.64560	-0.38460	0.54140
H	3.50170	-3.88300	3.06300
S	i -5.9360	0 -10.165	10 2.76900
C	-5.11680	-10.9782	0 4.25950
C	-7.81270	-10.2326	0 2.93150
C	-5.38320	-10.9996	0 1.17160
H	-5.40700	-10.4879	0 5.19330
H	-8.30530	-9.73660	2.09040
H	-4.29740	-10.9521	0 1.04940
H	3.06050	-2.17480	3.07180
H	4.75990	-2.64670	3.15010
H	4.42560	-1.08940	-0.87410
H	5.35120	-0.83820	0.60910
H	6.14400	-3.92460	0.57780
H	4.87010	-5.14600	0.52500
H	-5.67130	-12.0560	0 1.15910
H	-5.83440	-10.5249	0 0.29550
H	-8.16880	-11.2679	0 2.95990
H	-8.15360	-9.74090	3.84700
H	-5.40260	-12.0323	0 4.33850
H	-4.02600	-10.9361	0 4.19080

Table S4. Optimised ground state geometry of **2** (atom symbol, x, y, z Cartesian coordinates) (*i*Pr simplified to Me groups).

C	-2.72120	-4.35094	-1.90775
N	-2.52502	-3.47732	-0.87512
C	-1.29474	-3.19896	-0.46347
C	-0.14754	-3.77509	-1.04324
C	-0.34764	-4.67654	-2.10321
C	-1.63327	-4.96269	-2.53357
C	-4.10443	-4.55623	-2.27703
N	-4.97746	-3.89734	-1.57833
C	-6.35085	-3.79530	-1.67171
C	-7.18893	-4.48759	-2.56821
C	-8.54620	-4.25610	-2.52830
C	-9.07690	-3.33218	-1.59741
C	-8.27185	-2.64304	-0.71347
C	-6.87490	-2.85794	-0.72994
O	-6.06280	-2.23211	0.08539
C	-3.96156	-3.21837	2.45873
N	-4.31669	-3.90852	1.33380
C	-4.69766	-5.17635	1.42320
C	-4.75232	-5.87201	2.64683
C	-4.38117	-5.16553	3.80411
C	-3.98651	-3.84077	3.70826
C	-3.58946	-1.83883	2.23441
N	-3.63228	-1.43787	1.00071
C	-3.40678	-0.20658	0.41900
C	-2.97682	0.96740	1.06895
C	-2.80899	2.11746	0.32972
C	-3.07142	2.10690	-1.06056
C	-3.49514	0.96775	-1.71408
C	-3.67613	-0.22869	-0.98354
O	-4.07374	-1.33982	-1.55228
C	o -4.2574	3 -2.7241	4 -0.25965
H	-1.19691	-2.49325	0.35165
H	0.50837	-5.14037	-2.57878
H	-1.80148	-5.65207	-3.35284
H	-4.37727	-5.20303	-3.10604
H	-6.77257	-5.19134	-3.28163
H	-9.20866	-4.77619	-3.20999
H	-10.1479	2 -3.1584	4 -1.58154
H	-8.68178	-1.93049	-0.00735
H	-4.97821	-5.67154	0.50215
H	-4.41048	-5.66317	4.76617
H	-3.70319	-3.28291	4.59330
H	-3.32047	-1.18545	3.05953
H	-2.78189	0.96792	2.13649
H	-2.48070	3.03162	0.80993
H	-2.93842	3.02241	-1.62771
H	-3.70154	0.96541	-2.77793
C	1.14380	-3.44478	-0.56278
C	2.25638	-3.16806	-0.15684
C	-5.17183	-7.22471	2.68706
C	-5.53457	-8.38465	2.73361
S	i 3.97198	-2.75214	0.44845
C	5.14040	-4.05418	-0.23903
C	4.39222	-1.03506	-0.19287
C	3.92591	-2.79194	2.32890
H	5.13694	-4.06473	-1.33246
H	3.68738	-0.28209	0.17040
H	3.63408	-3.77617	2.70560
S	i -6.1017	1 -10.159	92 2.83118
C	-6.03780	-10.6691	9 4.63932
C	-7.85480	-10.2260	1 2.15359
C	-4.92098	-11.1836	3 1.78356
H	-6.69586	-10.0520	5 5.25724
H	-7.90035	-9.89542	1.11220
H	-3.89230	-11.1151	2 2.14798
H	4.87577	-5.05822	0.10399
H	6.16835	-3.85902	0.08251
H	4.91251	-2.56244	2.74383
H	3.22304	-2.05801	2.73317
H	5.39178	-0.73577	0.13818
H	4.38425	-0.99727	-1.28556
H	-8.53652	-9.59645	2.73187
H	-8.24300	-11.2488	7 2.19006
H	-6.35696	-11.7092	7 4.75974
H	-5.02653	-10.5884	6 5.04750
H	-5.20589	-12.2403	5 1.80451
H	-4.92570	-10.8648	1 0.73744

9. Cyclic Voltammetry (CV)

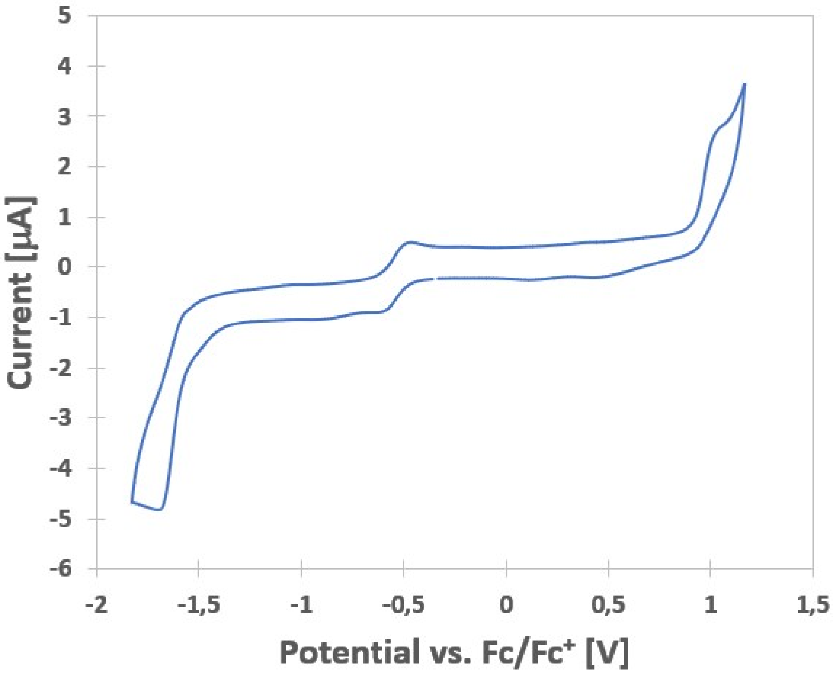


Figure S44. *Cyclic voltammogram of **1**. Co(III)/Co(II) redox potential was calculated to be – 0.55 V.*

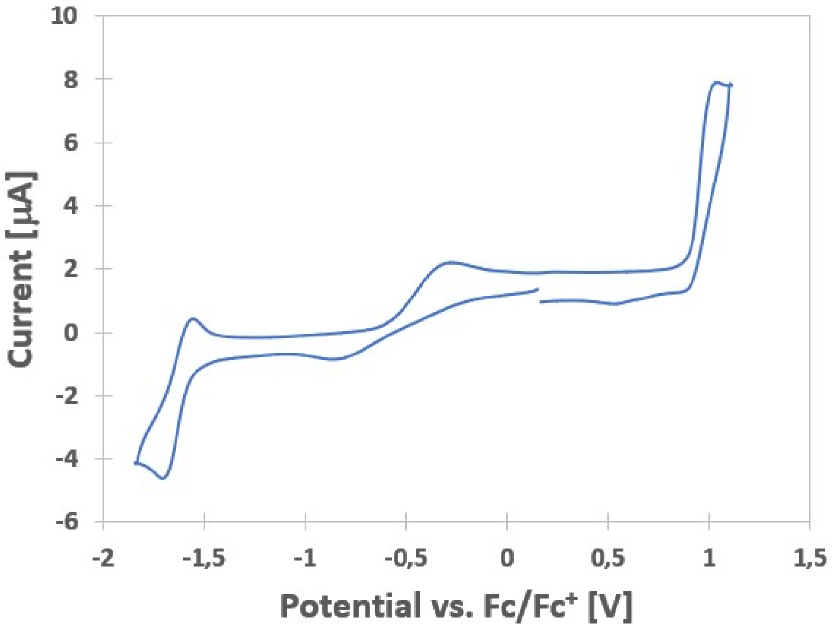


Figure S45. *Cyclic voltammogram of **2**. Co(III)/Co(II) redox potential was calculated to be – 0.57 V.*

10. X-ray photoelectron spectroscopy spectra (XPS)

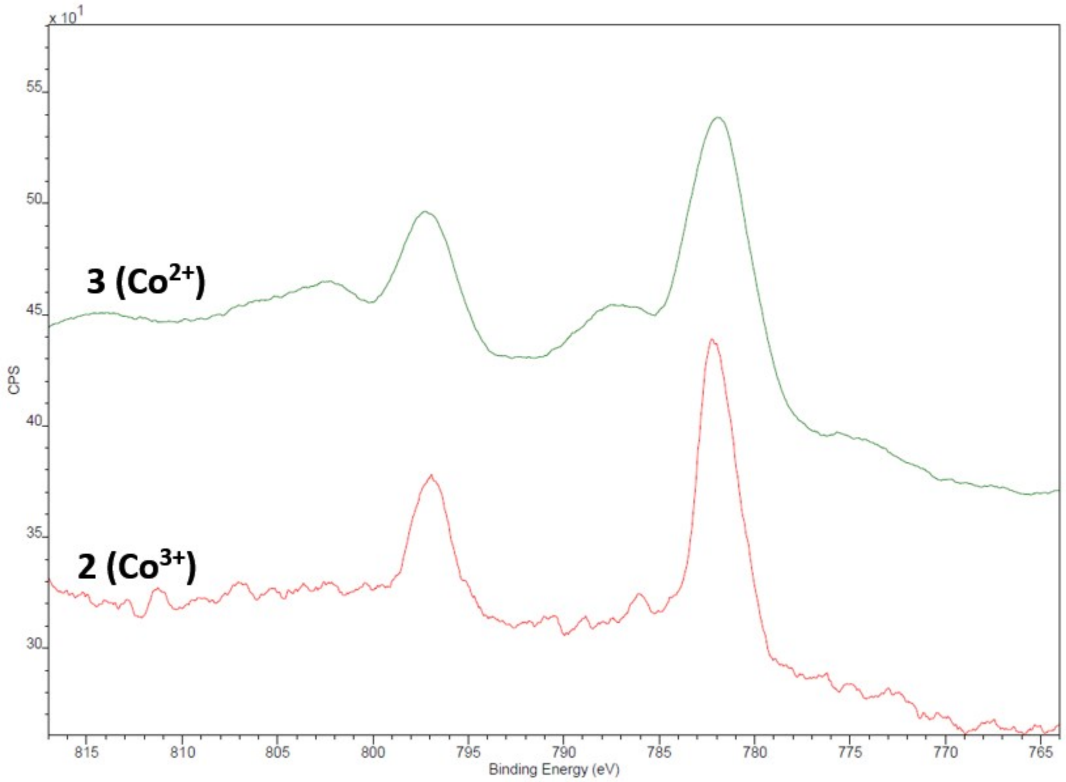


Figure S46. *Stacked XPS spectra of **2** (red) and **3** (green) complexes (Co binding energy range).*

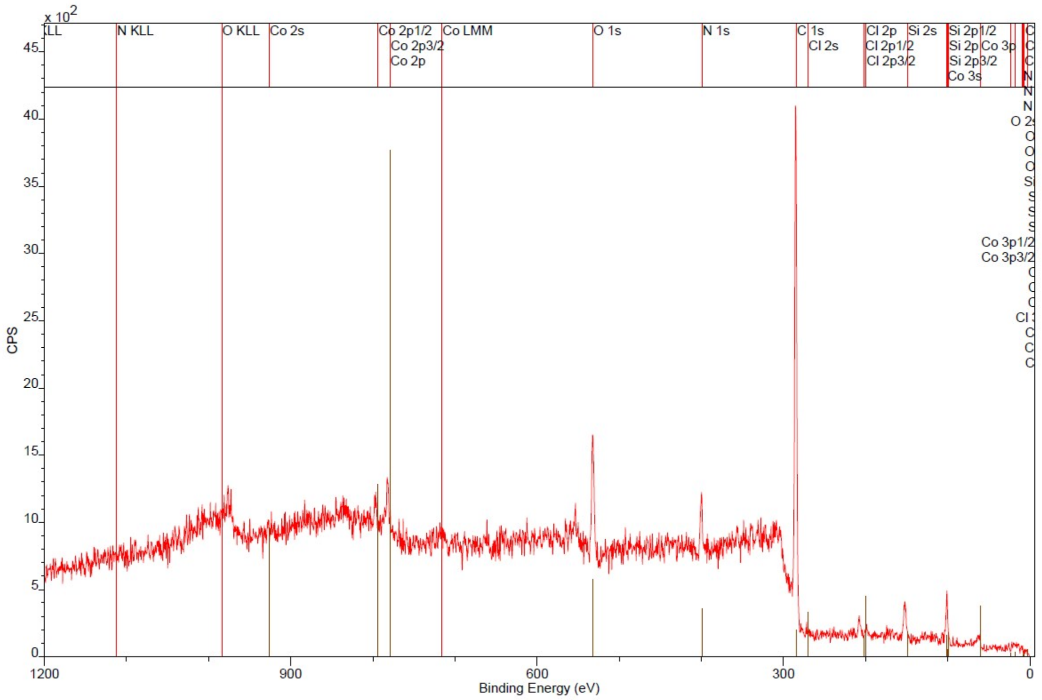


Figure S47. *XPS spectrum of **2** (survey mode).*

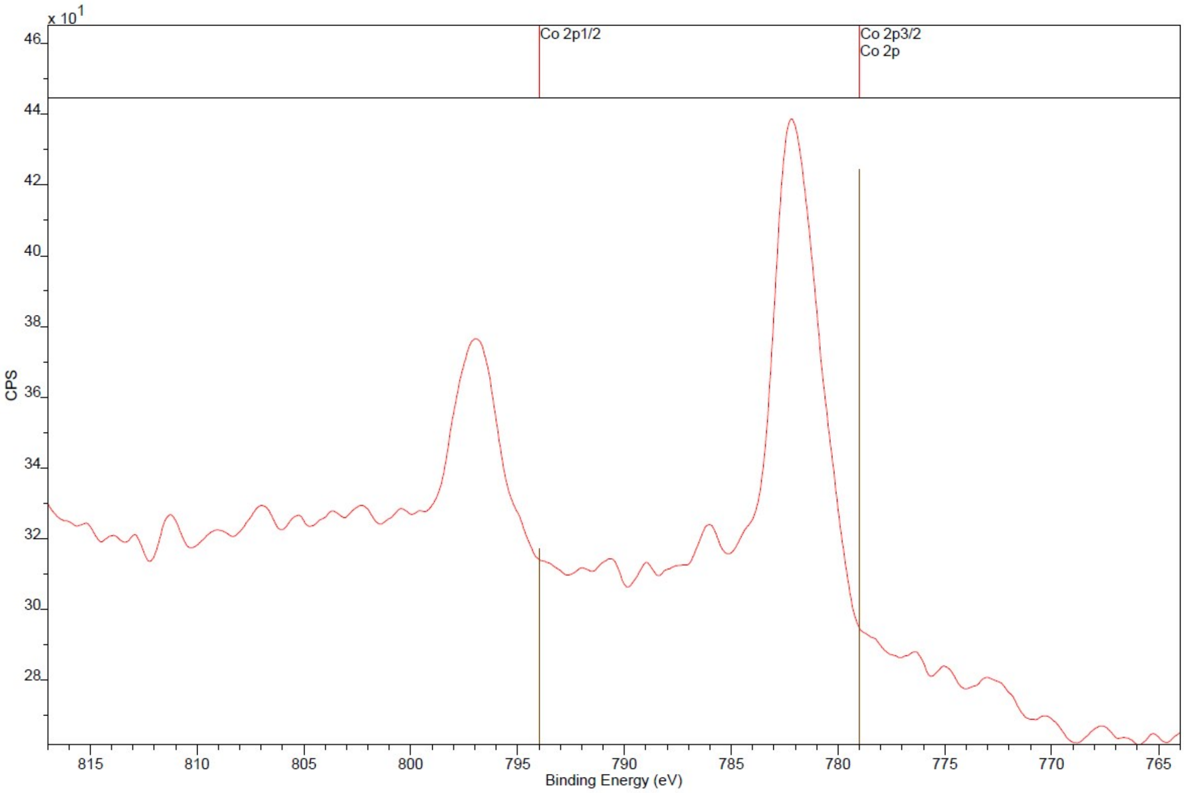


Figure S48. *XPS spectrum of **2** (Co binding energy range).*

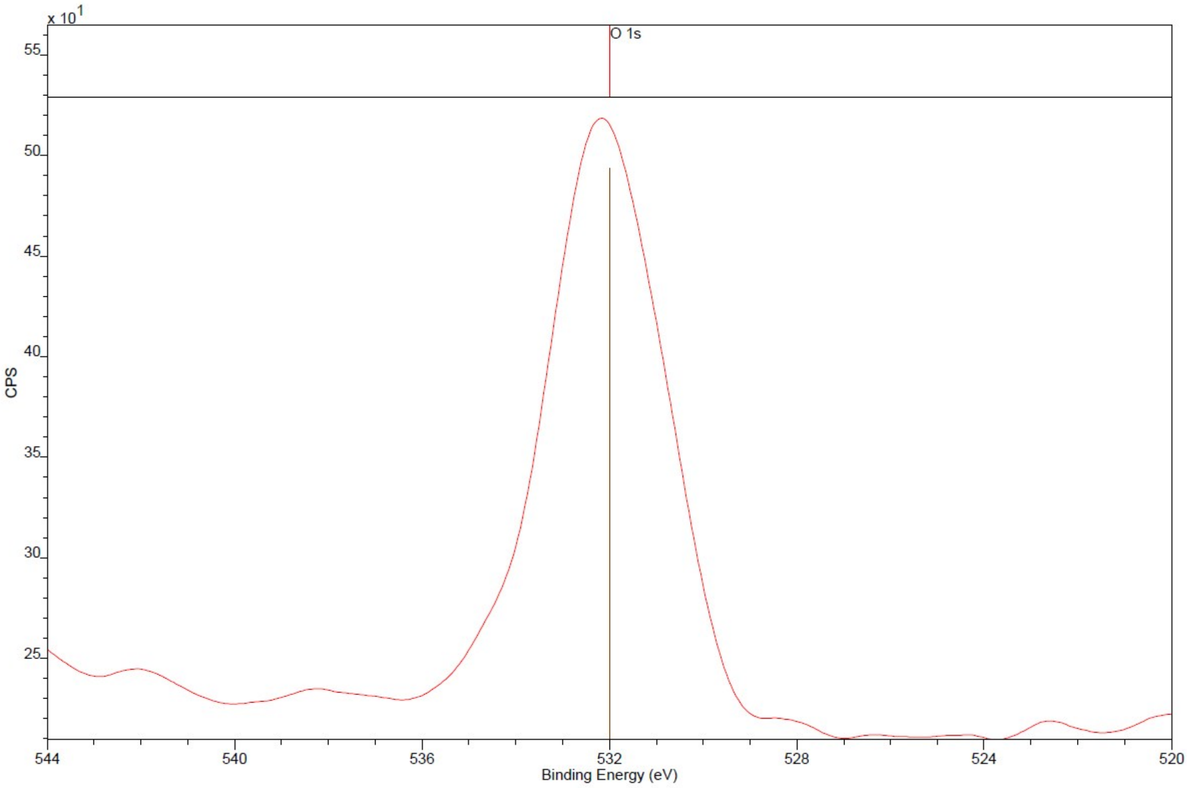


Figure S49. *XPS spectrum of **2** (O binding energy range).*

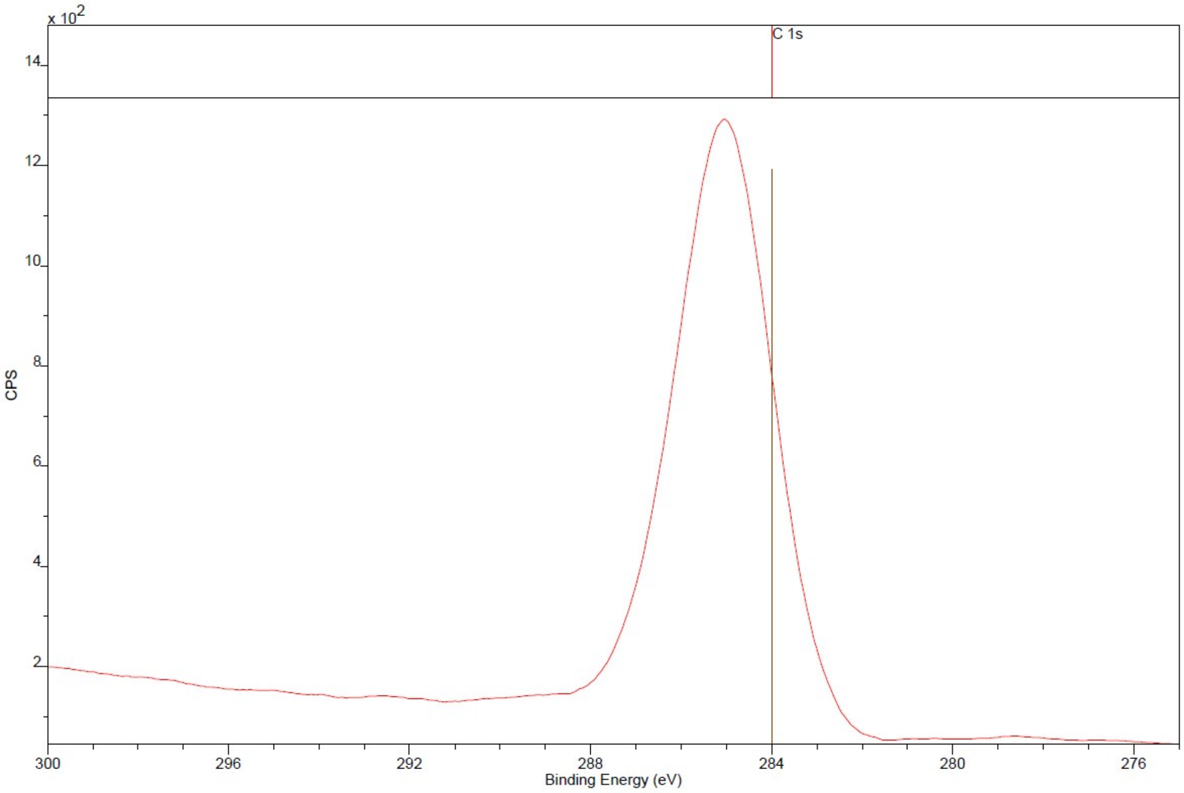


Figure S50. *XPS spectrum of* ***2*** *(C binding energy range).*

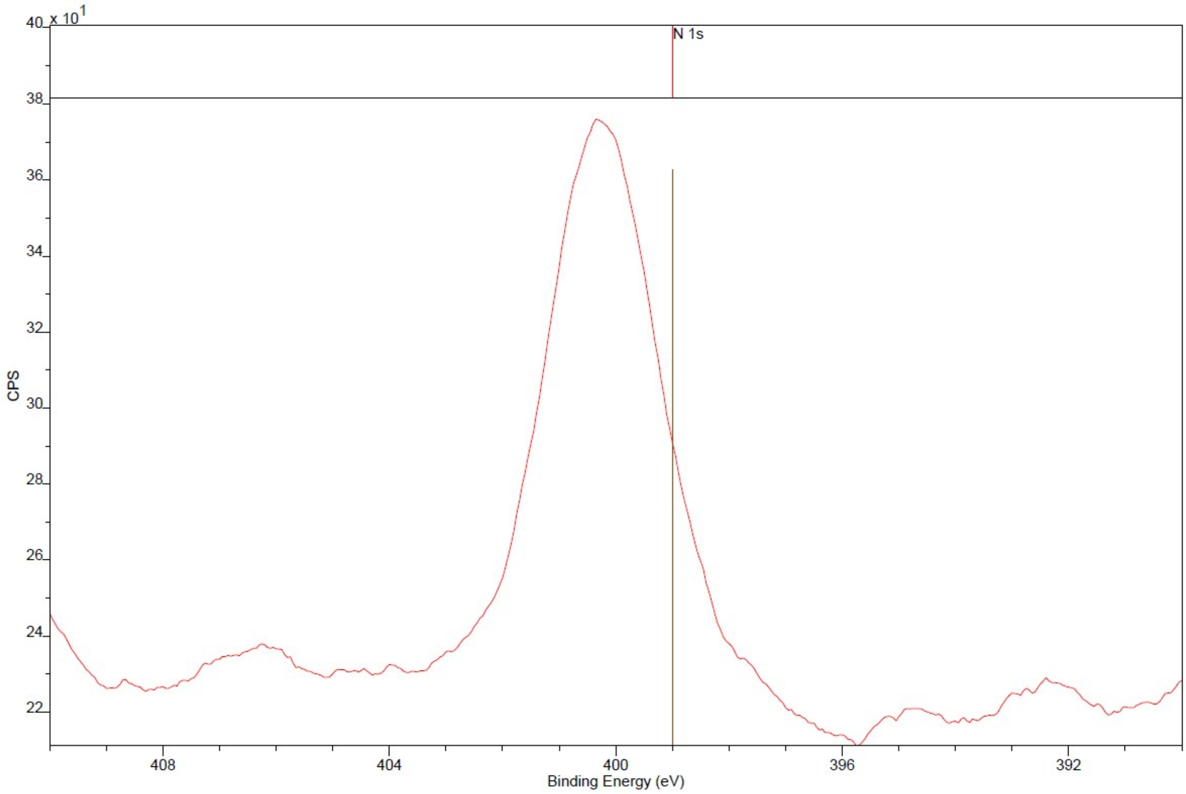


Figure S51. *XPS spectrum of* ***2*** *(N binding energy range).*

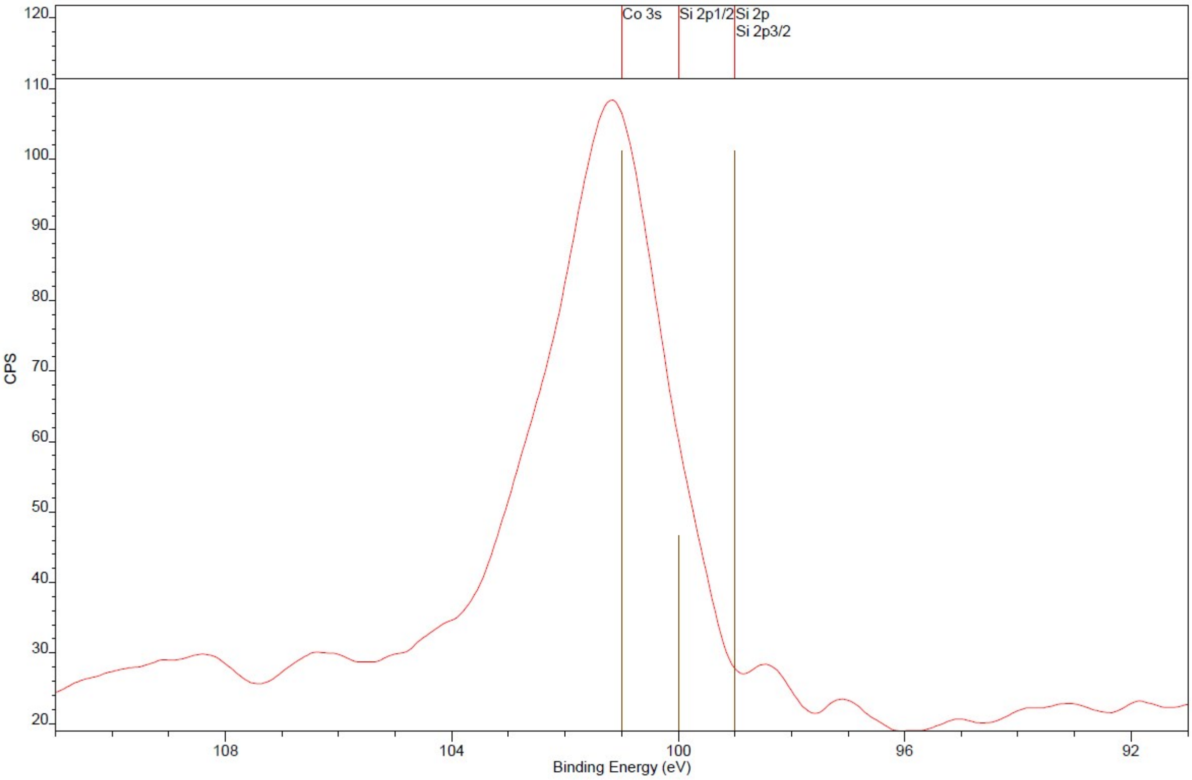


Figure S52. *XPS spectrum of* ***2*** *(Co and Si binding energy range).*

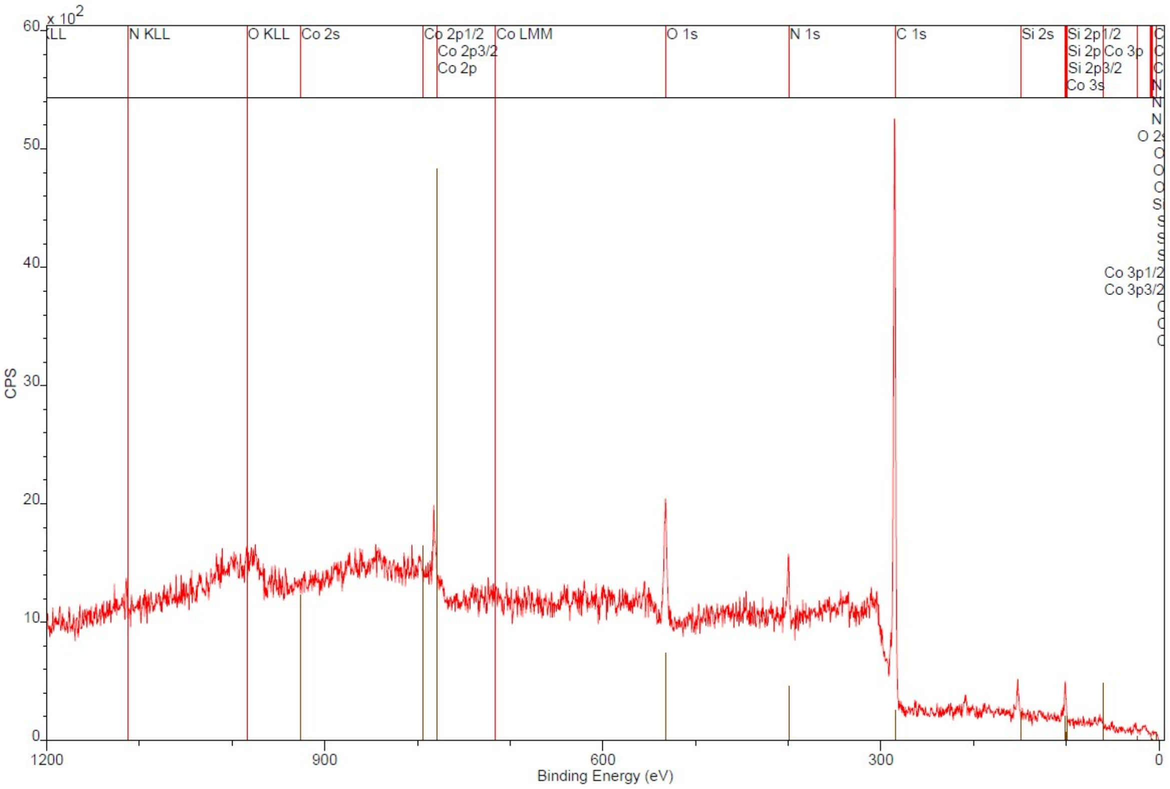


Figure S53. *XPS spectrum of* ***3*** *(survey mode).*

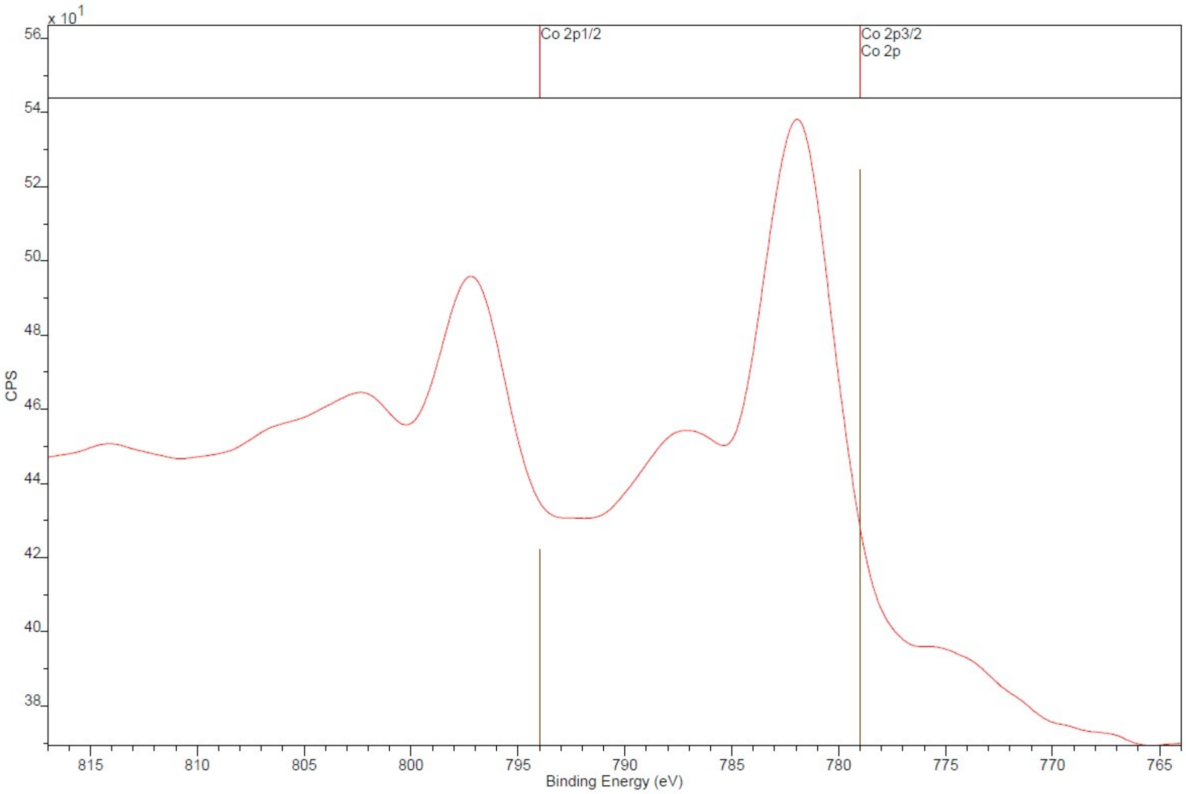


Figure S54. *XPS spectrum of **3** (Co binding energy range).*

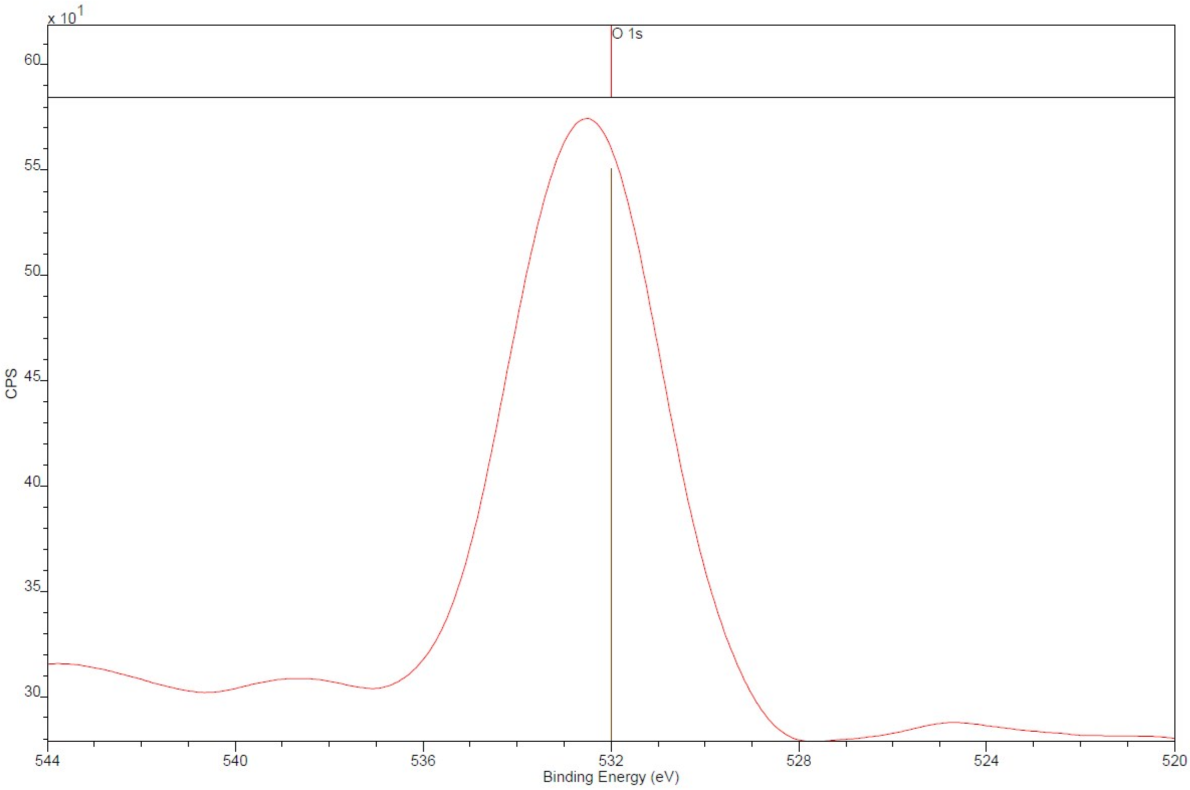


Figure S55. *XPS spectrum of **3** (O binding energy range).*

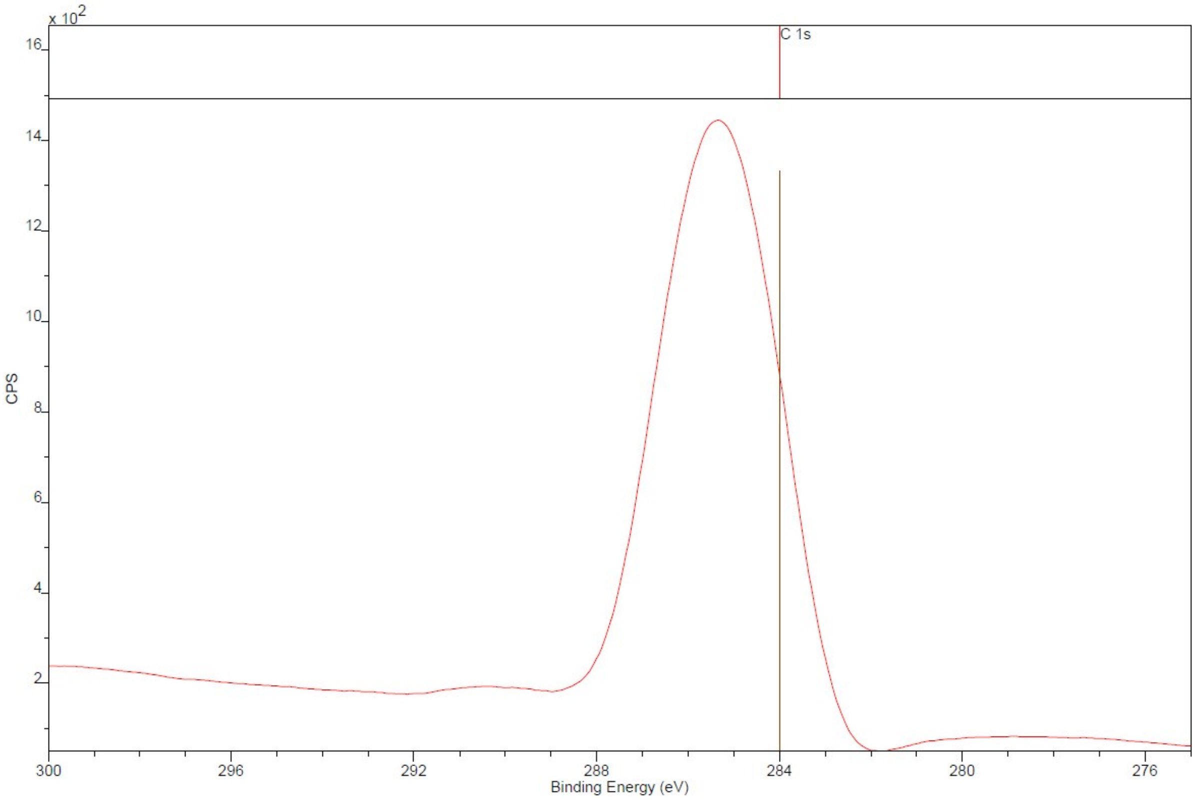


Figure S56. *XPS spectrum of* ***3*** *(C binding energy range).*

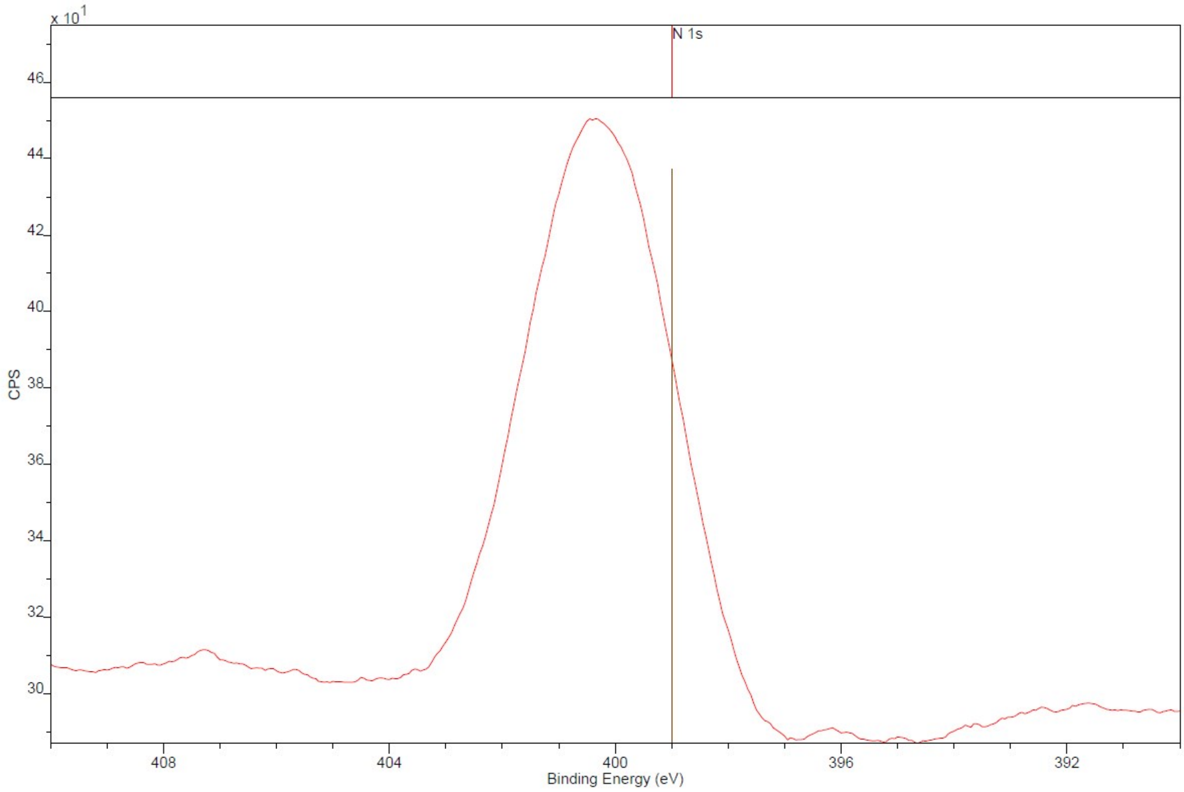


Figure S57. *XPS spectrum of* ***3*** *(N binding energy range).*

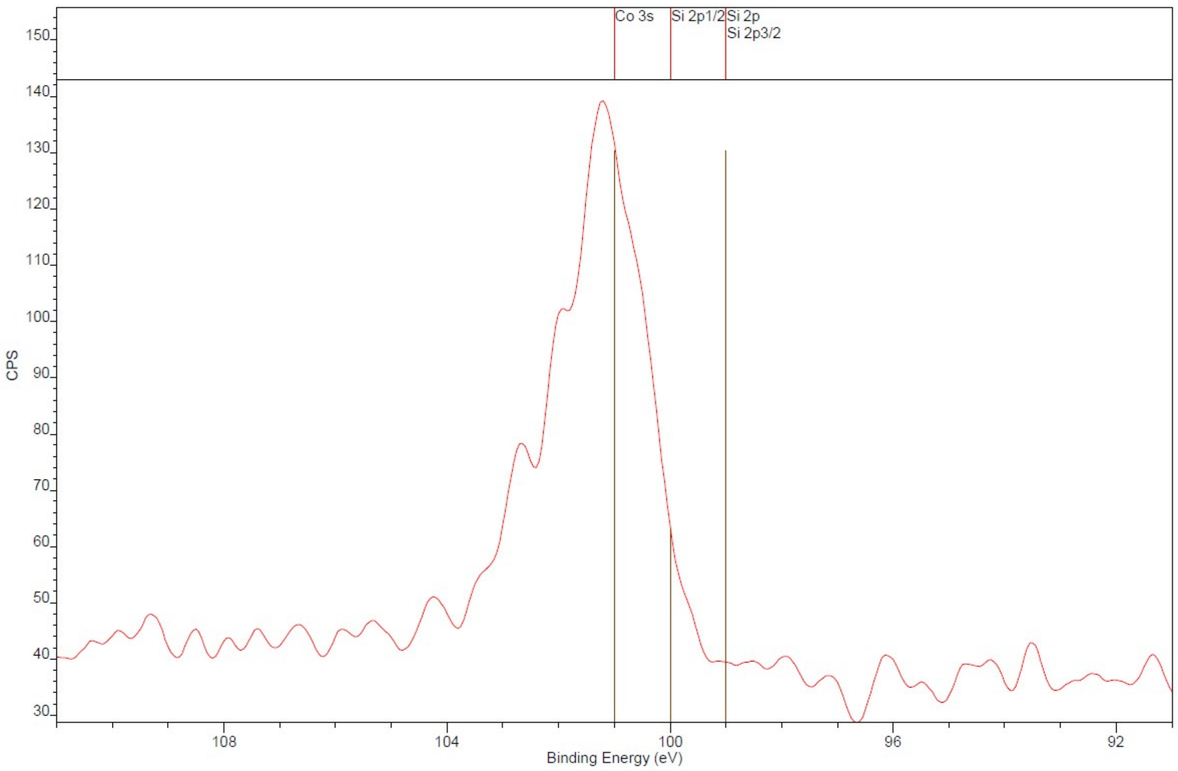


Figure S58. *XPS spectrum of **3** (Co and Si binding energy range).*

11. References

---

[1] A.D. Becke. J. Chem. Phys. 1993, **98**, 5648–5652

[2] (a) P.J. Stephens. F.J. Devlin. C.F. Chabalowski. M.J. Frisch. *J. Phys. Chem.* 1994, **98,** 11623–11627; (b) K. Kim. K.D. Jordan. *J. Phys. Chem.,* 1994, **98**, 10089–10094; (c) T. Clark. J. Chandrasekhar. G.W. Spitznagel. P.V.R. Schleyer. Li–F. *J. Comput. Chem.*, 1993, **4**, 294–301

[3] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654–3665

[4] W. R. Wadt, P. J. Hay, *J. Chem. Phys.*, **1985**, *82*, 270 + 284 + 299

[5] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.