Electronic Supplementary Information

Catalytic Activity of new Heteroleptic [Cu(PPh₃)₂(β-oxidithioester)] Complexes: Click derived Triazolyl Glycoconjugates†‡

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**S1: Figure S1.** Simulated (in red, generated from single crystal data) and experimental (in black) PXRD patterns of 1-6
S2: $^1$H, $^{13}$C and $^{31}$P NMR spectra of complexes 1-6

Spectrum 1: $^1$H NMR of Complex 1

Spectrum 2: $^{13}$C NMR of Complex 1
Spectrum 3: $^{31}$P NMR of Complex 1

Spectrum 4: $^1$H NMR of Complex 2
Spectrum 5: $^{13}$C NMR of Complex 2

Spectrum 6: $^{31}$P NMR of Complex 2
Spectrum 7: $^1$H NMR of Complex 3

Spectrum 8: $^{13}$C NMR of Complex 3
**Spectrum 9:** $^{31}$P NMR of Complex 3

**Spectrum 10:** $^{1}$H NMR of Complex 4
**Spectrum 11:** $^{13}$C NMR of Complex 4

**Spectrum 12:** $^{31}$P NMR of Complex 4
Spectrum 13: $^1$H NMR of Complex 5

Spectrum 14: $^{13}$C NMR of Complex 5
Spectrum 15: $^{31}$P NMR of Complex 5

Spectrum 16: $^1$H NMR of Complex 6
Spectrum 17: $^{13}$C NMR of Complex 6

Spectrum 18: $^{31}$P NMR of Complex 6
S3: Figure S3. Molecular structures of 2-6 with ellipsoids at 30% probability showing the atom numbering scheme.
**S4: Figure S4.** Supramolecular structure of complex 1 sustained by the H⋯H interactions.

**S5: Figure S5.** Supramolecular structure of complex 3 sustained via H⋯H interactions giving a zig-zag appearance.
**S6: Figure S6.** Supramolecular structure of complex 4 sustained by the H···H interactions.

![Diagram of supramolecular structure of complex 4](image)

**S7: Figure S7.** Supramolecular structure of complex 1 sustained via C−H···O interactions giving a zig-zag appearance.

![Diagram of supramolecular structure of complex 1](image)
**S8: Figure S8.** UV-Vis. absorption spectra of ligands L1–L6 in CH$_2$Cl$_2$ solution.

**S9: Figure S9.** Details of the orbitals and transitions for 1.

- HOMO (-0.22806)
- HOMO-1 (-0.21492)
- HOMO-2 (-0.21274)
HOMO-3 (-0.19481)  HOMO-4 (-0.18652)

LUMO (-0.06711)  LUMO+1 (-0.02590)  LUMO+2 (-0.02535)

LUMO+3(-0.02334)  LUMO+4 (-0.02215)

Frontier Orbitals – Energies (a.u.) in Brackets
Uv spectra

Homo 199, Lumo 200

Excited State 4: Singlet-A 2.6979 eV 459.56 nm f=0.0412
198 ->200 -0.38440
199 ->200  0.52571

Excited State 10: Singlet-A 3.5136 eV 352.87 nm f=0.4237
197 ->200  0.62074

Excited State 14: Singlet-A 3.5894 eV 345.42 nm f=0.0176
199 ->201  0.64466

Excited State 15: Singlet-A 3.6777 eV 337.12 nm f=0.0628
199 ->202  0.60033
199 ->203  -0.27797

Excited State 16: Singlet-A 3.7498 eV 330.64 nm f=0.0241
199 ->202  0.26638
199 ->203  0.59831

Excited State 17: Singlet-A 3.7832 eV 327.72 nm f=0.0498
193 ->200  -0.57294
195 ->200  -0.33958

Excited State 18: Singlet-A 3.8171 eV 324.82 nm f=0.1438
193 ->200  -0.27610
195 ->200  0.47246
199 ->204  0.30994

Figure S10: UV-Vis Spectrum of I showing transition from HOMO-3 to LUMO.
S11: $^1$H and $^{13}$C NMR spectra of triazolyl glycoconjugates (9a-h)

**Spectrum 1:** 500 MHz $^1$H NMR of compound 9a
Spectrum 2: 125 MHz $^{13}$C NMR of compound 9a
Spectrum 3: 500 MHz $^1$H NMR of compound 9b
Spectrum 4: 125 MHz $^{13}$C NMR of compound 9b
Spectrum 5: 500 MHz $^1$H NMR of compound 9c
Spectrum 6: 125 MHz $^1$H NMR of compound 9c
Spectrum 7: 500 MHz $^1$H NMR of compound 9d
Spectrum 8: 125 MHz $^{13}$C NMR of compound 9d
Spectrum 9: 500 MHz $^1$H NMR of compound 9e
Spectrum 10: 125 MHz $^{13}$C NMR of compound 9e
Spectrum 11: 500 MHz $^1$H NMR of compound 9f
Spectrum 12: 125 MHz $^{13}$C NMR of compound 9f
Spectrum 13: 500 MHz $^1$H NMR of compound 9g
Spectrum 14: 125 MHz $^{13}$C NMR of compound 9g
Spectrum 15: 500 MHz $^{13}$C NMR of compound 9h
Spectrum 16: 125 MHz $^{13}$C NMR of compound 9h
S12: Synthesis of triazolyl glycoconjugates (9a-h)

1-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-4-phenyl-[1,2,3]-triazole (9a)

Path-a: 2,3,4,6-Tetra-O-acetyl-β-d-glucopyranosyl azide (100mg, 0.268 mmol) and phenylacetylene (35 μl, 0.321 mmol) were taken in dry CH₂Cl₂ (1 mL) in presence of Cu-catalyst 1 (2mg, 2.7μmol) and the mixture was stirred at room temperature for 5 h. Completion of the reaction was monitored by TLC and reaction mass was concentrated under reduced pressure to obtain crude. Purification of crude mass by flash chromatography (ethyl acetate: hexane) afforded triazole derivative. Yield (96%).

Path-b: 2,3,4,6-Tetra-O-acetyl-β-d-glucopyranosyl azide (100mg, 0.268 mmol) and phenylacetylene (35 μl, 0.321 mmol) were taken in dry CH₂Cl₂ (1 mL) in presence of Cu-catalyst 6 (2mg, 2.7μmol) and the mixture was stirred at room temperature for 3 h. Completion of the reaction was monitored by TLC and reaction mass was concentrated under reduced pressure to obtain crude. Purification of crude mass by flash chromatography (ethyl acetate: hexane) afforded triazole derivative. Yield (97%). White solid, m.p. 200-202 ºC, R₇ = 0.5, (50% ethyl acetate/n-hexane); ¹H NMR (500 MHz, CDCl₃): δ 8.02 (s, 1H), 7.84 (d, J = 7.5 Hz, 2H), 7.45-7.42 (m, 2H), 7.36 (d, J = 7.5 Hz, 1H), 5.95 (d, J = 9.5 Hz, 1H), 5.53 (t, J = 9.5 Hz, 1H), 5.47-5.43 (m, 1H), 5.28 (t, J = 9.5 Hz, 1H), 4.35-4.31 (m, 1H), 4.18-4.15 (m, 1H), 4.06-4.03 (m, 1H), 2.08 (d, J = 4.0 Hz, 6H), 2.04 (s, 3H), 1.88 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 170.5, 170.0, 169.4, 169.1, 148.6, 129.9, 128.9, 128.6, 125.9, 117.8, 85.9, 75.2, 72.8, 70.2, 67.8, 61.6, 20.7, 20.6, 20.6 and 20.2 ppm.

1-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(1-cyclohexenyl)- [1,2,3]-triazole (9b)

Path-a: 2,3,4,6-Tetra-O-acetyl-β-d-glucopyranosyl azide (100mg, 0.268 mmol) and 1-Ethynylcyclohexene (38 μl, 0.321 mmol) were taken in dry CH₂Cl₂ (1 mL) in presence of Cu-catalyst 1 (2mg, 2.7μmol) and the mixture was stirred at room temperature for 5 h. Completion of the reaction was monitored by TLC and reaction mass was concentrated under reduced pressure to obtain crude. Purification of crude mass by flash chromatography (ethyl acetate: hexane) afforded triazole derivative. Yield (94%).

Path-b: 2,3,4,6-Tetra-O-acetyl-β-d-glucopyranosyl azide (100mg, 0.268 mmol) and 1-Ethynylcyclohexene (38 μl, 0.321 mmol) were taken in dry CH₂Cl₂ (1 mL) in presence of Cu-catalyst 6 (2mg, 2.7μmol) and the mixture was stirred at room temperature for 3 h. Completion of the reaction was monitored by TLC and
reaction mass was concentrated under reduced pressure to obtain crude. Purification of crude mass by flash chromatography (ethyl acetate: hexane) afforded triazole derivative. Yield (98%); solid; m.p. 196-198 °C; R_f = 0.5, (40% ethyl acetate/n-hexane); 1H NMR (500 MHz, CDCl3): δ 7.61 (s, 1H), 6.59 (d, J = 4.0 Hz, 1H), 5.88 (d, J = 9.5 Hz, 1H), 5.49-5.39 (m, 2H), 5.26-5.22 (m, 1H), 4.32-4.29 (m, 1H), 4.15-4.12 (m, 1H), 4.02-3.99 (m, 1H), 2.36 (s, 2H), 2.21-2.20 (m, 2H), 2.08-2.03 (m, 9H), 1.88 (s, 3H), 1.78-1.75 (m, 2H), 1.69-1.65 (s, 2H); 13C NMR (125 MHz, CDCl3): δ 170.5, 169.9, 169.4, 169.0, 150.2, 126.7, 126.1, 116.2, 85.7, 75.0, 72.8, 70.2, 67.8, 61.6, 26.3, 25.3, 22.1, 22.1, 20.7, 20.6, 20.5 and 20.2 ppm.

1-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(2-(trifluoromethyl)phenyl)[1,2,3]-triazole (9c)

Path-a: 2,3,4,6-Tetra-O-acetyl-β-d-glucopyranosyl azide (100mg, 0.268 mmol), 1-Ethynyl-4-trifluorobenzene (44 μl, 0.321 mmol) were taken in dry CH2Cl2 (1 mL) in presence of Cu-catalyst 1 (2mg, 2.7μmol) and the mixture was stirred at room temperature for 5 h. Completion of the reaction was monitored by TLC and reaction mass was concentrated under reduced pressure to obtain crude. Purification of crude mass by flash chromatography (ethyl acetate: hexane) afforded triazole derivative. Yield (98%).

Path-b: 2,3,4,6-Tetra-O-acetyl-β-d-glucopyranosyl azide (100mg, 0.268 mmol), 1-Ethynyl-4-trifluorobenzene (44 μl, 0.321 mmol) were taken in dry CH2Cl2 (1 mL) in presence of Cu-catalyst 6 (2mg, 2.7μmol) and the mixture was stirred at room temperature for 3 h. Completion of the reaction was monitored by TLC and reaction mass was concentrated under reduced pressure to obtain crude. Purification of crude mass by flash chromatography (ethyl acetate: hexane) afforded triazole derivative. Yield (98%); solid; m.p. 130-132 °C; R_f = 0.4, (20% ethyl acetate/n-hexane); 1H NMR (500 MHz, CDCl3): δ 7.98 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 7.5 Hz, 1H), 7.65-7.62 (m, 1H), 7.53-7.50 (m, 1H), 5.98 (d, J = 9.5 Hz, 1H), 5.59-5.55 (m, 1H), 5.46 (t, J = 9.5 Hz, 1H), 5.30 (t, J = 9.5 Hz, 1H), 4.35-4.31 (m, 1H), 4.21-4.08 (m, 1H), 4.07-4.05 (m, 1H), 2.09-2.08 (m, 6H), 2.04 (m, 3H), 1.89 (s, 3H); 13C NMR (125 MHz, CDCl3): δ 170.5, 170.0, 169.4, 168.8, 145.0, 132.0, 131.9, 128.8, 128.7, 127.9, 127.6, 126.3, 126.2, 125.1, 122.9, 121.3, 121.2, 85.8, 75.2, 72.8, 70.1, 67.7, 61.5, 20.7, 20.6, 20.5 and 20.0 ppm.

1-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(4-(dimethylamino)phenyl)[1,2,3]-triazole (9d)
Path-a: 2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl azide (100mg, 0.268mmol), 4-ethynyl-N,N-dimethylaniline (46mg, 0.321mmol) were taken in dry CH₂Cl₂ (1 mL) in presence of Cu-catalyst 1 (2mg, 2.7μmol) and the mixture was stirred at room temperature for 5 h. Completion of the reaction was monitored by TLC and reaction mass was concentrated under reduced pressure to obtain crude. Purification of crude mass by flash chromatography (ethyl acetate: hexane) afforded triazole derivative. Yield (95%) Path-b: 2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl azide (100mg, 0.268mmol), 4-ethynyl-N,N-dimethylaniline (46mg, 0.321mmol) were taken in dry CH₂Cl₂ (1 mL) in presence of Cu-catalyst 6 (2mg, 2.7μmol) and the mixture was stirred at room temperature for 3 h. Completion of the reaction was monitored by TLC and reaction mass was concentrated under reduced pressure to obtain crude. Purification of crude mass by flash chromatography (ethyl acetate: hexane) afforded triazole derivative. Yield (92%); solid; m.p. 204-208 °C; R_f = 0.5, (50% ethyl acetate/n-hexane); ^1H NMR (500 MHz, CDCl₃): δ 7.83 (s, 1H), 7.68 (d, J = 9.0 Hz, 2H), 6.74 (d, J = 8.5 Hz, 2H), 5.90 (d, J = 10.0 Hz, 1H), 5.54-5.50 (m, 1H), 5.41 (t, J = 9.5 Hz, 1H), 5.25 (t, J = 9.5 Hz, 1H), 4.31-4.28 (m, 1H), 4.13 (d, J = 12.5 Hz, 1H), 4.01-3.98 (m, 1H), 2.96 (s, 6H), 2.06 (d, J = 5.0 Hz 6H), 2.01 (m, 3H), 1.85 (s, 3H); ^13C NMR (125 MHz, CDCl₃): δ 170.6, 170.0, 169.4, 169.0, 150.7, 149.0, 126.9, 118.0, 116.0, 112.4, 85.7, 75.1, 72.9, 70.2, 67.8, 61.7, 40.5, 20.7, 20.6, 20.6 and 20.2 ppm.

1-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(4-pentylphenyl)-[1,2,3]-triazole (9e)

Path-a: 2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl azide (100mg, 0.268 mmol), 1-ethynyl-4-pentylbenzene (49μl, 0.321 mmol) were taken in dry CH₂Cl₂ (1 mL) in presence of Cu-catalyst 1 (2mg, 2.7μmol) and the mixture was stirred at room temperature for 5 h. Completion of the reaction was monitored by TLC and reaction mass was concentrated under reduced pressure to obtain crude. Purification of crude mass by flash chromatography (ethyl acetate: hexane) afforded triazole derivative. Yield (91%). Path-b: 2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl azide (100mg, 0.268 mmol), 1-ethynyl-4-pentylbenzene (49μl, 0.321 mmol) were taken in dry CH₂Cl₂ (1 mL) in presence of Cu-catalyst 6 (2mg, 2.7μmol) and the mixture was stirred at room temperature for 3 h. Completion of the reaction was monitored by TLC and reaction mass was concentrated under reduced pressure to obtain crude. Purification of crude mass by flash chromatography (ethyl acetate: hexane) afforded triazole derivative. Yield (94%); solid; m.p. 170-176 °C; R_f = 0.5, (30% ethyl acetate/n-hexane); ^1H NMR (500 MHz, CDCl₃): δ 7.97 (s, 1H),
7.74 (d, $J = 7.5$ Hz, 2H), 7.26-7.24 (m, 2H), 5.94 (d, $J = 9.5$ Hz, 1H), 5.55-5.51 (m, 1H), 5.46-5.42 (m, 1H), 5.29-5.25 (m, 1H), 4.35-4.31 (m, 1H), 4.17-4.14 (m, 1H), 4.03-3.99 (m, 1H), 4.17-4.14 (m, 1H), 3.83 (m, 1H), 2.64-2.61 (m, 2H), 2.09-2.04 (m, 9H), 1.88 (s, 3H), 1.64-1.61 (m, 2H), 1.35-1.25 (m, 4H), 0.91-0.88 (m, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 170.6, 170.0, 169.4, 169.0, 148.7, 143.6, 129.0, 127.3, 125.9, 117.4, 85.8, 75.2, 72.8, 70.2, 67.8, 61.6, 35.8, 31.5, 31.1, 29.7, 22.6, 20.7, 20.6, 20.6, 20.2 and 14.1 ppm.

1-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(4-Bromophenyl)-[1,2,3]-triazole (9f)

**Path-a:** 2,3,4,6-Tetra-O-acetyl-β-d-glucopyranosyl azide (100mg, 0.268mmol), 1-bromo-4-ethynylbenzene (60mg, 0.321 mmol) were taken in dry CH$_2$Cl$_2$ (1mL) in presence of Cu-catalyst 1 (2mg, 2.7μmol) and the mixture was stirred at room temperature for 5 h. Completion of the reaction was monitored by TLC and reaction mass was concentrated under reduced pressure to obtain crude. Purification of crude mass by flash chromatography (ethyl acetate: hexane) afforded triazole derivative. Yield (95%).

**Path-b:** 2,3,4,6-Tetra-O-acetyl-β-d-glucopyranosyl azide (100mg, 0.268mmol), 1-bromo-4-ethynylbenzene (60mg, 0.321 mmol) were taken in dry CH$_2$Cl$_2$ (1mL) in presence of Cu-catalyst 6 (2mg, 2.7μmol) and the mixture was stirred at room temperature for 3 h. Completion of the reaction was monitored by TLC and reaction mass was concentrated under reduced pressure to obtain crude. Purification of crude mass by flash chromatography (ethyl acetate: hexane) afforded triazole derivative. Yield (96%); solid; m.p. 214-218°C; R$_f$ = 0.5, (30% ethyl acetate/n-hexane); $^1$H NMR (500 MHz, CDCl$_3$): δ 8.01 (s, 1H), 7.72-7.70 (m, 2H), 7.57-7.55 (m, 2H), 5.93 (d, $J = 8.5$ Hz, 1H), 5.52-5.43 (m, 2H), 5.27 (t, $J = 9.5$ Hz, 1H), 4.35-4.31 (m, 1H), 4.17-4.14 (dd, $J = 1.2$, 10.5 Hz, 1H), 4.05-4.02 (m, 1H), 2.11-2.08 (s, 6H), 2.04 (m, 3H), 1.89 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 170.5, 169.9, 169.4, 169.1, 147.5, 132.1, 128.9, 127.5, 127.3, 122.6, 117.9, 85.9, 75.3, 72.7, 70.3, 67.7, 61.6, 20.7, 20.6, 20.6 and 20.2 ppm.

1-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-4-(4-Bromophenyl carbamoyloxymethyl)-[1,2,3]-triazole (9g)

**Path-a:** 2,3,4,6-Tetra-O-acetyl-β-d-glucopyranosyl azide (100mg, 0.268 mmol), prop-2-yn-1-yl (4-bromophenyl)carbamate (81mg, 0.321 mmol) were taken in dry CH$_2$Cl$_2$ (1 mL) in presence of Cu-catalyst 1 (2mg, 2.7μmol) and the mixture was stirred at room temperature for 5 h.
Completion of the reaction was monitored by TLC and reaction mass was concentrated under reduced pressure to obtain crude. Purification of crude mass by flash chromatography (ethyl acetate: hexane) afforded triazole derivative. Yield (97%); oil, R\textsubscript{f} = 0.5, (50% ethyl acetate/n-hexane); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 7.98 (s, 1H), 7.42 (d, \(J = 9.0\) Hz, 2H), 7.31-7.29 (m, 2H), 7.00 (bs, 1H), 5.84 (d, \(J = 9.5\) Hz, 1H), 5.55-5.52 (m, 2H), 5.36 (d, \(J = 9.5\) Hz, 1H), 5.28-5.24 (m, 2H), 4.24-4.14 (m, 3H), 2.22 (s, 3H), 2.04-2.01 (m, 6H), 1.87 (s, 3H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \(\delta\) 170.4, 170.0, 169.8, 169.1, 153.0, 143.5, 136.8, 132.1, 122.6, 120.4, 116.3, 86.4, 74.2, 70.7, 67.9, 66.8, 61.2, 58.0, 20.7, 20.7, 20.5 and 20.3 ppm.

1-(2,3,4,6-Tetra-O-acetyl-\(\beta\)-D-galactopyranosyl)-4-phenyl-[1,2,3]-triazole (9h)

Path-a: 2,3,4,6-Tetra-O-acetyl-\(\beta\)-d-galactopyranosyl azide (100mg, 0.268mmol) and phenylacetylene (35\(\mu\)l, 0.321mmol) were taken in dry CH\textsubscript{2}Cl\textsubscript{2} (1 ml) in presence of Cu-catalyst \textbf{1} (2mg, 2.7\(\mu\)mol) and the mixture was stirred at room temperature for 5 h. Completion of the reaction was monitored by TLC and reaction mass was concentrated under reduced pressure to obtain crude. Purification of crude mass by flash chromatography (ethyl acetate: hexane) afforded triazole derivative. Yield (93%); white solid, m.p. 200-202 °C, R\textsubscript{f} = 0.5, (50% ethyl acetate/n-hexane); \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 8.06 (s, 1H), 7.86 (d, \(J = 7.5\) Hz, 2H), 7.45-7.42 (m, 2H), 7.36-7.33 (m, 1H), 5.92 (d, \(J = 9.5\) Hz, 1H), 5.65 (t, \(J = 7.5\) Hz, 1H), 5.58 (d, \(J = 3.0\) Hz, 1H), 5.31-5.28 (m, 1H), 4.29-4.27 (m, 1H), 4.23-4.15 (m, 2H), 2.24 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.90 (s, 3H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): \(\delta\) 170.2, 169.9, 169.7, 169.0, 148.3, 129.8, 128.7, 128.4, 125.8, 117.7, 86.2, 73.9, 70.7, 67.7, 66.8, 61.1, 20.6, 20.5, 20.4 and 20.1 ppm.
**S13**: Characterization data of the synthesized ligands L1–L6

[L1] Yield: (0.178 g, 89%). Anal. Calcd for C₈H₆O₂S₂ (200.27): C 46.12, H 7.74%. Found: C 46.02, H 7.79%. IR (KBr, cm⁻¹): 1158 (ν(C=O)), 1613 (ν(C=C)), 1226 (ν(C=S)). ¹H NMR (500.15 MHz, CDCl₃, ppm): δ 2.64 (s, 3H, −SCH₃), 6.56 (s, 1H, −CH=−C=−), 6.91-7.57 (m, 3H, −C₆H₃O), 14.70 (s, 1H, −C(OH)−). ¹³C NMR (125.76 MHz, CDCl₃, ppm): δ 17.18 (−SCH₃), 106.54 (−CH=−C=−), 112.91, 115.31, 145.87, 148.74 (−C₆H₃O), 159.37 (−C(OH)−), 216.81 (−C=S).

[L2] Yield: (0.184 g, 85%). Anal. Calcd for C₈H₆O₃S (216.33): C 44.41, H 3.73%. Found: C 44.35, H 3.78%. IR (KBr, cm⁻¹): 1150 (ν(C=O)), 1576 (ν(C=C)), 1232 (ν(C=S)). ¹H NMR (500.15 MHz, CDCl₃, ppm): δ 2.55 (s, 3H, −SCH₃), 6.77 (s, 1H, −CH=−C=−), 7.02-7.64 (m, 3H, −C₆H₃S), 14.97 (s, 1H, −C(OH)−). ¹³C NMR (125.76 MHz, CDCl₃, ppm): δ 16.93 (−SCH₃), 106.95 (−CH=−C=−), 128.36, 129.22, 134.96, 138.32 (−C₆H₃S), 164.01 (−C(OH)−), 215.68 (−C=S).

[L3] Yield: (0.194 g, 81%). Anal. Calcd for C₁₁H₁₂O₂S₂ (240.34): C 57.11, H 4.79%. Found: C 57.02, H 4.84%. IR (KBr, cm⁻¹): 1177 (ν(C=O)), 1603 (ν(C=C)), 1232 (ν(C=S)). ¹H NMR (500.15 MHz, CDCl₃, ppm): δ 2.65 (s, 3H, −SCH₃), 3.87 (s, 3H, −OCH₃), 6.94 (s, 1H, −CH=−C=−), 6.96-7.87 (m, 4H, −C₆H₄OCH₃), 15.18 (s, 1H, −C(OH)−). ¹³C{¹H} NMR (125.76 MHz, CDCl₃, ppm): δ 17.03 (−SCH₃), 107.20 (−CH=−C=−), 107.20, 114.26, 128.76, 130.68 (−C₆H₄OCH₃), 169.63 (−C(OH)−), 215.75 (−C=S).

[L4] Yield: (0.247 g, 85%). Anal. Calcd for C₁₀H₆Br₁O₁S₂ (289.21): C 41.53, H 3.14%. Found: C 41.45, H 3.24%. IR (KBr, cm⁻¹): 1178 (ν(C=O)), 1584 (ν(C=C)), 1236 (ν(C=S)). ¹H NMR (500.15 MHz, CDCl₃, ppm): δ 2.66 (s, 3H, −SCH₃), 6.90 (s, 1H, −CH=−C=−), 7.57-7.83 (m, 4H, −C₆H₄Br), 15.04 (s, 1H, −C(OH)−). ¹³C{¹H} NMR (125.76 MHz, CDCl₃, ppm): δ 17.33 (−SCH₃), 107.69 (−CH=−C=−), 126.57, 128.17, 129.93, 132.13 (−C₆H₄Br), 167.84 (−C(OH)−), 217.73 (−C=S).

[L5] Yield: (0.187 g, 89%). Anal. Calcd for C₁₀H₁₀O₁S₂ (210.31): C 57.11, H 4.79%. Found: C 57.02, H 4.84%. IR (KBr, cm⁻¹): 1159 (ν(C=O)), 1590 (ν(C=C)), 1238 (ν(C=S)). ¹H NMR (500.15 MHz, CDCl₃, ppm): δ 2.63 (s, 3H, −SCH₃), 6.94 (s, 1H, −CH=−C=−), 7.42-7.94 (m, 5H, −C₆H₅), 15.08 (s, 1H, −C(OH)−). ¹³C{¹H} NMR (125.76 MHz, CDCl₃, ppm): δ 17.24 (−SCH₃), 107.93 (−CH=−C=−), 126.77, 128.86, 131.98, 133.19 (−C₆H₅), 169.29 (−C(OH)−), 217.33 (−C=S).
[L6] Yield: (0.187 g, 89%). Anal. Calcd for C₉H₉N₁O₁S₂ (211.30): C 51.16, H 4.29, N 6.63%. Found: C 51.06, H 4.36, N 6.54%. IR (KBr, cm⁻¹): 1124 (νc=oh), 1591 (νc=c), 1263 (νc=s). ¹H NMR (500.15 MHz, CDCl₃, ppm): δ 2.63 (s, 3H, –SCH₃), 6.82 (s, 1H, –CH=CH₂), 7.31, 8.04, 8.62, 8.99 (m, 4H, –C₅H₄N), 14.89 (s, 1H, –COH–). ¹³C[¹H] NMR (125.76 MHz, CDCl₃, ppm): δ 17.39 (–SCH₃), 107.98 (–CH=CH₂), 123.70, 130.31, 134.01, 147.86, 152.19 (–C₅H₄N), 166.17 (–COH–), 218.39 (–C=S).

S14: Scheme 14. Generalized methodology for the synthesis of complexes 1-6