

Supplementary Material

Synthesis of Cobalt(III) Complexes Derived from Pyridoxal: Structural Cleavage Evaluations and In Silico Calculations for Biological Targets

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Table S3. Crystal data and data collection and refinements of ligand L1C.

Table S1. Crystal data and data collection and refinements of complexes C1'-C4'.

	C1'	C2'	C3'	C4'
Empirical formula	C ₂₉ H ₃₅ CoN ₄ O ₈ S ₂	C ₃₆ H ₄₀ CoN ₅ O ₅ S ₂	C ₃₂ H ₃₅ CoN ₄ O ₅ S ₂	C ₃₂ H ₃₃ CoN ₄ O ₄ S ₂
Formula weight	690.66	745.78	678.69	660.67
Temperature (K)	293(2)	100(2)	100(2)	293(2)
Wavelength	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
<i>a</i> (Å)	26.8620(17)	13.314(6)	8.802(4)	17.90830(10)
<i>b</i> (Å)	11.3709(6)	18.162(9)	21.554(9)	15.2987(2)
<i>c</i> (Å)	24.4690(15)	14.176(8)	17.180(9)	14.56720(10)
α (°)	90.00	90.00	90.00	90.00
β (°)	115.397(5)	97.983(16)	93.949(18)	106.9020(10)
γ (°)	90.00	90.00	90.00	90.00
Volume (Å ³) / Z	6751.6(7) / 8	3395(3) / 4	3252(2) / 4	3818.63(6) / 4
Calculated density (mg.m ⁻³)	1.359	1.459	1.386	1.149
Absorption coefficient (nm ⁻¹)	0.683	0.680	0.702	0.594
<i>F</i> (000)	2880	1560	1416	1376
Crystal size (mm)	0.273 × 0.208 × 0.185	0.365 × 0.188 × 0.089	0.32 × 0.27 × 0.1	0.277 × 0.201 × 0.108
Theta range for data collection (°)	1.84 to 28.55	2.24 to 28.29	2.23 to 30.75	2.38 to 28.61
Limiting indices	-36 ≤ <i>h</i> ≤ 35, -15 ≤ <i>k</i> ≤ 14, -32 ≤ <i>l</i> ≤ 31	-17 ≤ <i>h</i> ≤ 17, -24 ≤ <i>k</i> ≤ 24, -18 ≤ <i>l</i> ≤ 18	-12 ≤ <i>h</i> ≤ 12, -30 ≤ <i>k</i> ≤ 30, -24 ≤ <i>l</i> ≤ 24	-24 ≤ <i>h</i> ≤ 23, -20 ≤ <i>k</i> ≤ 20, -19 ≤ <i>l</i> ≤ 19
Reflections collected/unique	36343 / 8415	39138 / 8375	140942 / 10100	62251 / 9777
Completeness to theta	99.7%	99.9%	99.7%	99.8%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and Min. Transmission	0.9566 and 0.9357	0.8621 and 0.6954	0.9431 and 0.8066	0.922 and 0.8785
Data/restraints/ parameters	8587/0/397	8375/0/451	10110/0/399	9777/0/399
Goodness-of-fit on <i>F</i> ²	1.017	1.000	1.082	0.973
Índice <i>R</i> _{int}	0.0820	0.1247	0.0820	0.0875
Final <i>R</i> indices <i>R</i> ₁ and <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0745 <i>wR</i> ₂ = 0.1217	<i>R</i> ₁ = 0.0727 <i>wR</i> ₂ = 0.1313	<i>R</i> ₁ = 0.0575 <i>wR</i> ₂ = 0.1493	<i>R</i> ₁ = 0.0063 <i>wR</i> ₂ = 0.1609
<i>R</i> indices (all data) <i>R</i> ₁	<i>R</i> ₁ = 0.0959	<i>R</i> ₁ = 0.1148	<i>R</i> ₁ = 0.0938	<i>R</i> ₁ = 0.1406

and wR_2	$wR_2 = 0.143$	$wR_2 = 0.1650$	$wR_2 = 0.1382$	$wR_2 = 0.1831$
Largest diff. peak ($e^- \text{ \AA}^{-3}$) and hole	0.450 and -0.410	0.303 and -0.419	0.519 and -0.632	0.264 and -0.277

Table 2S. Crystal data and data collection and refinements of complexes C1-C4.

	C1	C2	C3	C4
Empirical formula	C ₄₅ H ₅₄ CoF ₆ N ₆ O ₆ PS ₄	C ₃₂ H ₃₄ CoF ₆ N ₄ O ₄ PS ₂	C ₃₄ H ₃₈ CoF ₆ N ₄ O ₄ PS ₂	C ₄₀ H ₅₁ CoF ₆ N ₅ O ₅ PS ₂
Formula weight	1107.08	806.65	834.70	949.88
Temperature (K)	120(2)	295(2)	100(2)	100(2)
Wavelength	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2 ₁ /n	P2 ₁ /c	P2 ₁ /c	P2 ₁ /n
a (Å)	10.095(6)	9.384(5)	9.3252(5)	10.5867(5)
b (Å)	38.52(2)	19.624(9)	20.4612(9)	21.6734(10)
c (Å)	13.335(8)	19.631(9)	18.8318(9)	19.2897(9)
α (°)	90.00	90.00	90.00	90.00
β (°)	106.54(2)	97.425(14)	93.844(2)	98.103(2)
γ (°)	90.00	90.00	90.00	90.00
Volume (Å ³)	4970(5) / 4	3585(3) / 4	3585.1(3) / 4	4381.8(4) / 4
Calculated density (mg.m ⁻³)	1.480	1.495	1.546	1.438
Absorption coefficient (nm ⁻¹)	0.621	0.713	0.716	0.597
$F(000)$	2296	1656	1720	1972
Crystal size (mm)	0.26 × 0.1 × 0.07	0.34 × 0.2 × 0.16	0.396 × 0.238 × 0.216	0.25 × 0.24 × 0.07
Theta range for data collection (°)	2.25 to 27.13	2.19 to 29.61	2.39 to 29.63	2.28 to 30.18
Limiting indices	-12 ≤ h ≤ 12, -49 ≤ k ≤ 49, -14 ≤ l ≤ 17	-13 ≤ h ≤ 13, -27 ≤ k ≤ 27, -27 ≤ l ≤ 27	-12 ≤ h ≤ 12, -28 ≤ k ≤ 26, -26 ≤ l ≤ 26	-14 ≤ h ≤ 14, -29 ≤ k ≤ 30, -27 ≤ l ≤ 27
Reflections collected/unique	57903 / 10949	46499 / 10035	53319 / 10072	122196 / 12902
Completeness to theta	99.7%	99.6%	99.7%	99.5%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and Min.	0.9678 and 0.8751	0.8844 and 0.7885	0.8622 and 0.8251	0.8594 and 0.765

Transmission				
Data/restraints/ parameters	10949/0/624	10035/0/451	10072/0/469	12902/0/544
Goodness-of-fit on F^2	1.032	1.051	1.084	1.023
Índice R_{int}	0.0705	0.0480	0.0386	0.1116
Final R indices R_1 and $wR_2[I > 2\sigma(I)]$	$R_1 = 0.0714$ $wR_2 = 0.173$	$R_1 = 0.0735$ $wR_2 = 0.1007$	$R_1 = 0.0316$ $wR_2 = 0.0797$	$R_1 = 0.0873$ $wR_2 = 0.1082$
R indices (all data) R_1 and wR_2	$R_1 = 0.119$ $wR_2 = 0.1951$	$R_1 = 0.1141$ $wR_2 = 0.1267$	$R_1 = 0.0433$ $wR_2 = 0.0878$	$R_1 = 0.1521$ $wR_2 = 0.1399$
Largest diff. peak ($e^- \text{ \AA}^{-3}$) and hole	0.827 and -0.229	0.480 and -0.567	0.562 and -0.495	0.404 and -0.225

Spectral data

NMR spectroscopy

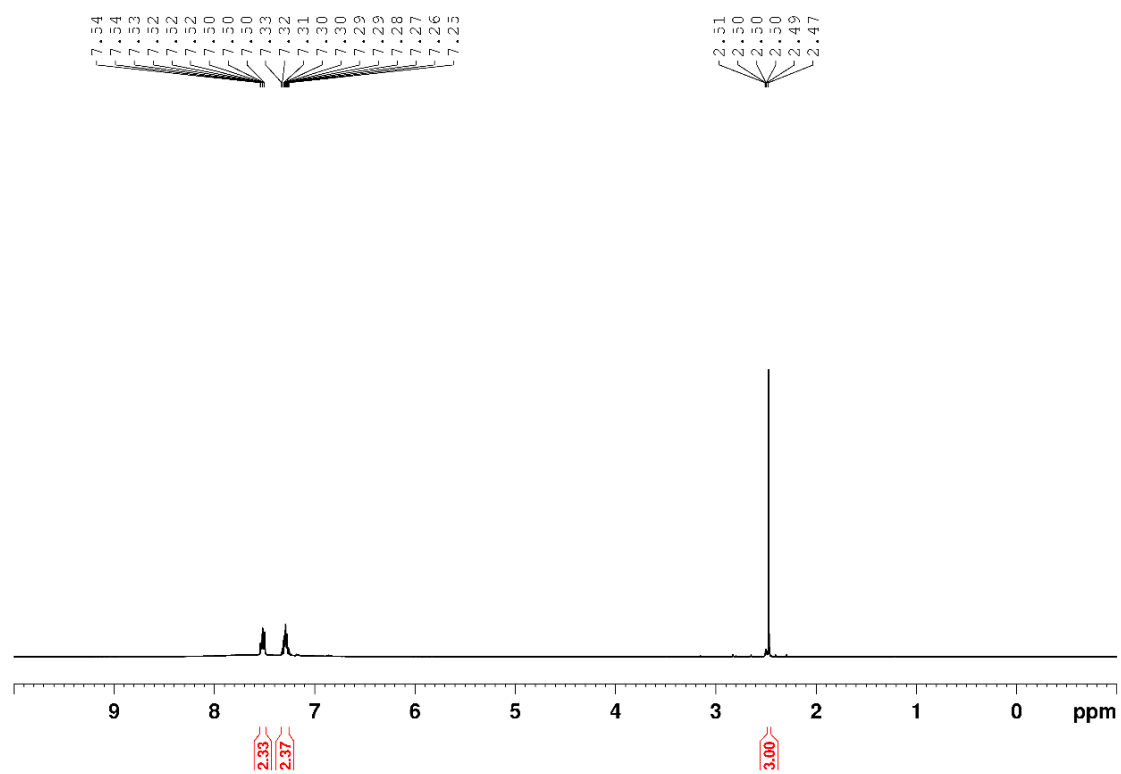


Figure S1. ^1H NMR spectra of the 2-(Methylthio)aniline hydrochloride (DMSO-d_6 , 400 MHz, 25°C).

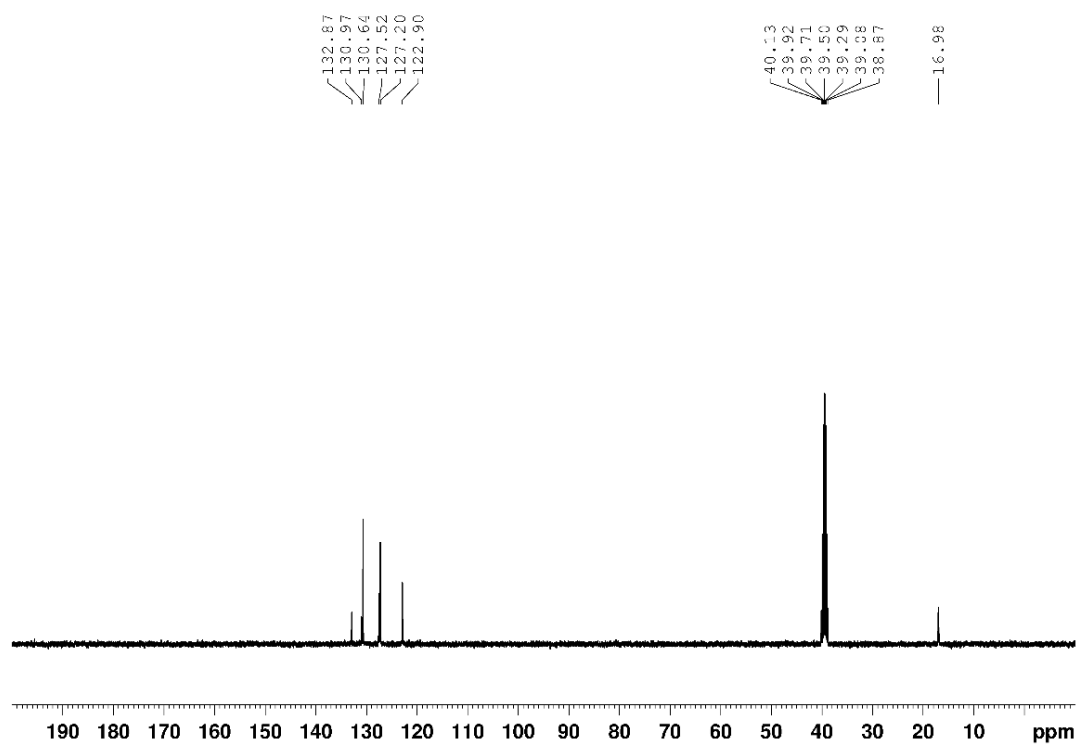


Figure S2. ^{13}C NMR spectra of the 2-(Methylthio)aniline hydrochloride (DMSO-d_6 , 100 MHz, 25°C).

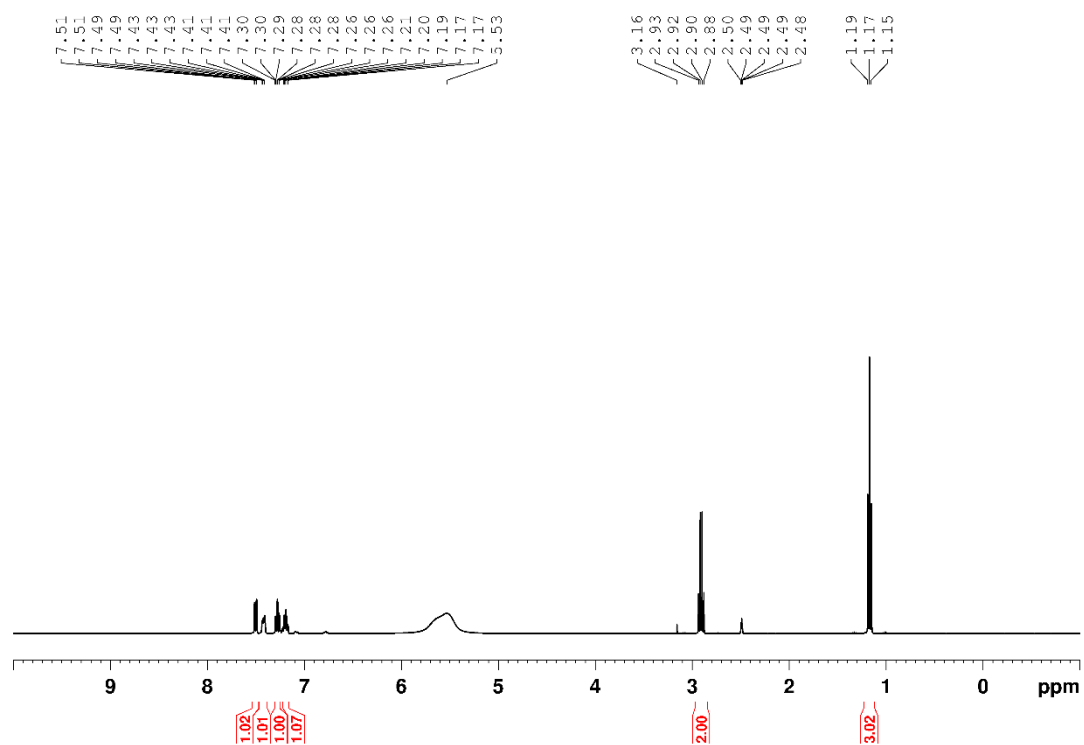


Figure S3. ¹H NMR spectra of the 2-(Ethylthio)benzenamine hydrochloride (DMSO-d₆, 400 MHz, 25°C).

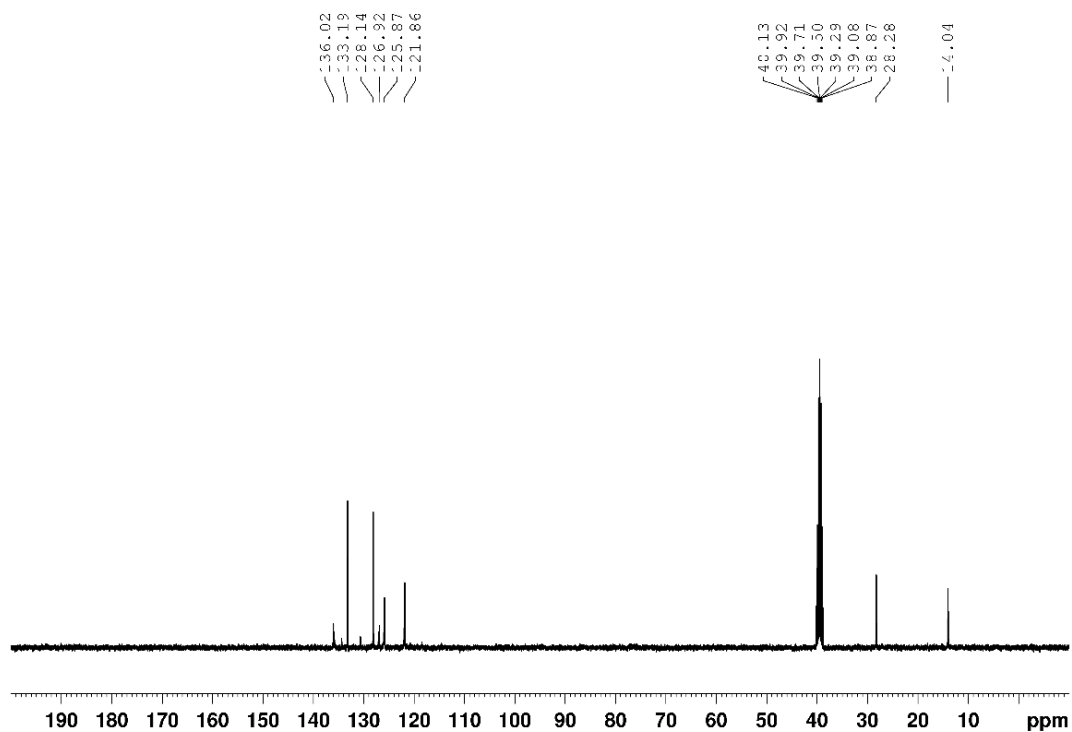


Figure S4. ¹³C NMR spectra of the 2-(Ethylthio)benzenamine hydrochloride (DMSO-d₆, 100 MHz, 25°C).

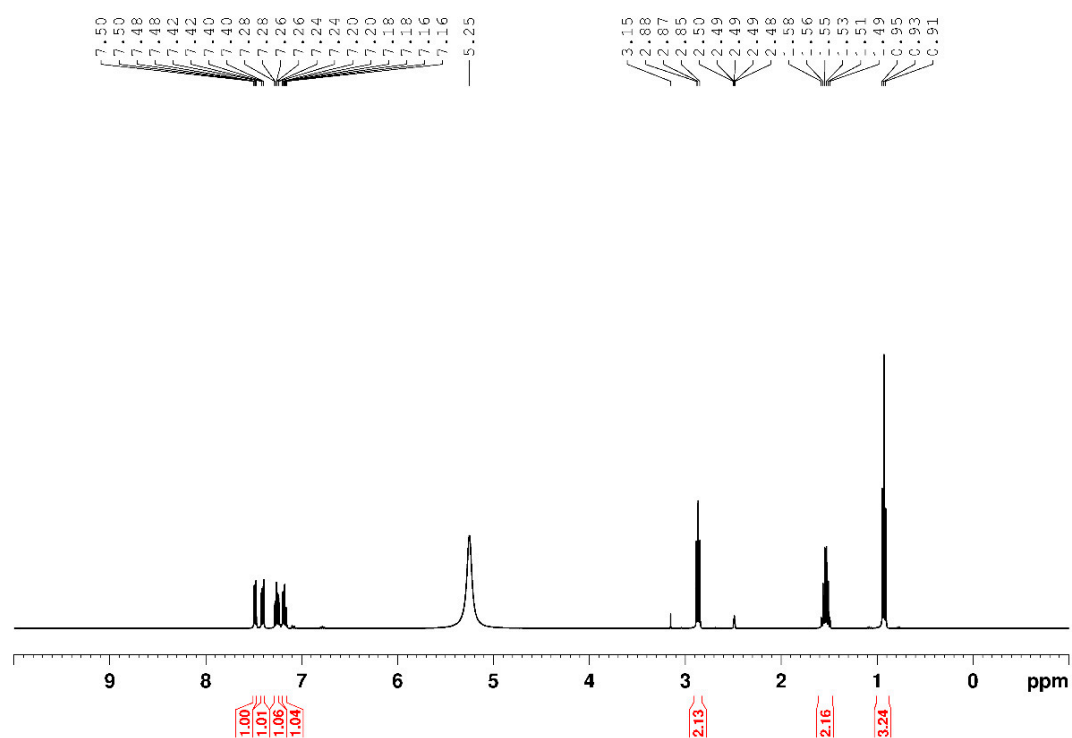


Figure S5. ¹H NMR spectra of the 2-(Propylthio)benzenamine hydrochloride (DMSO-d₆, 400 MHz, 25°C).

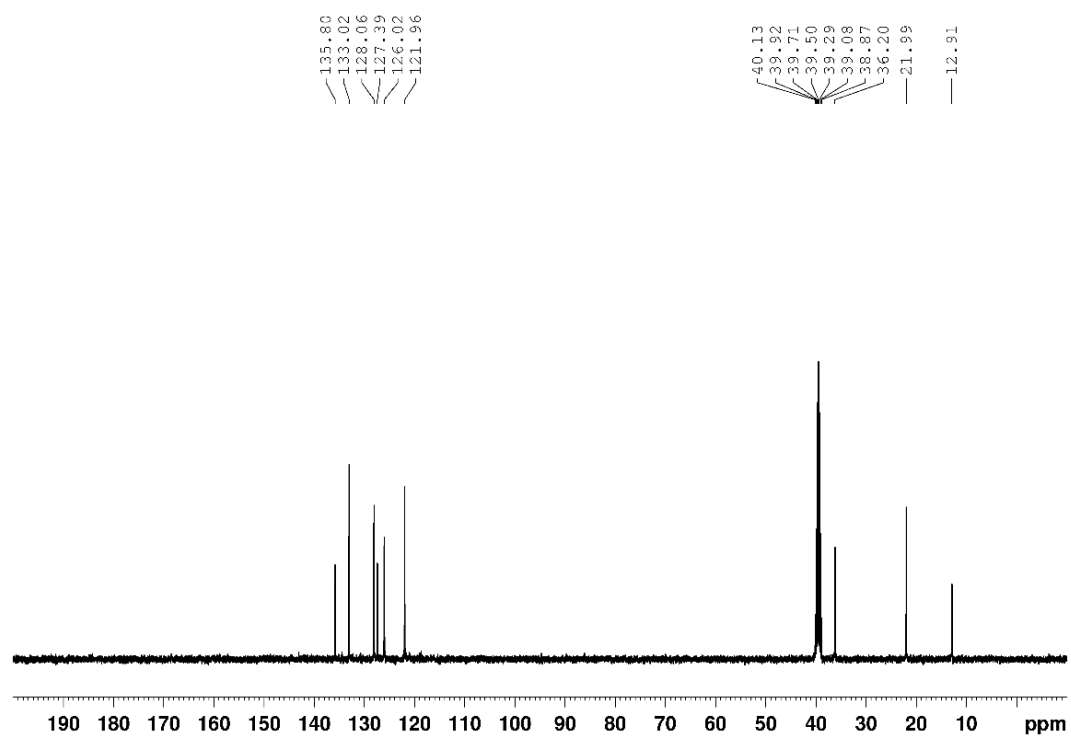


Figure S6. ^{13}C NMR spectra of the 2-(Propylthio)benzenamine hydrochloride (DMSO-d_6 , 100 MHz, 25°C).

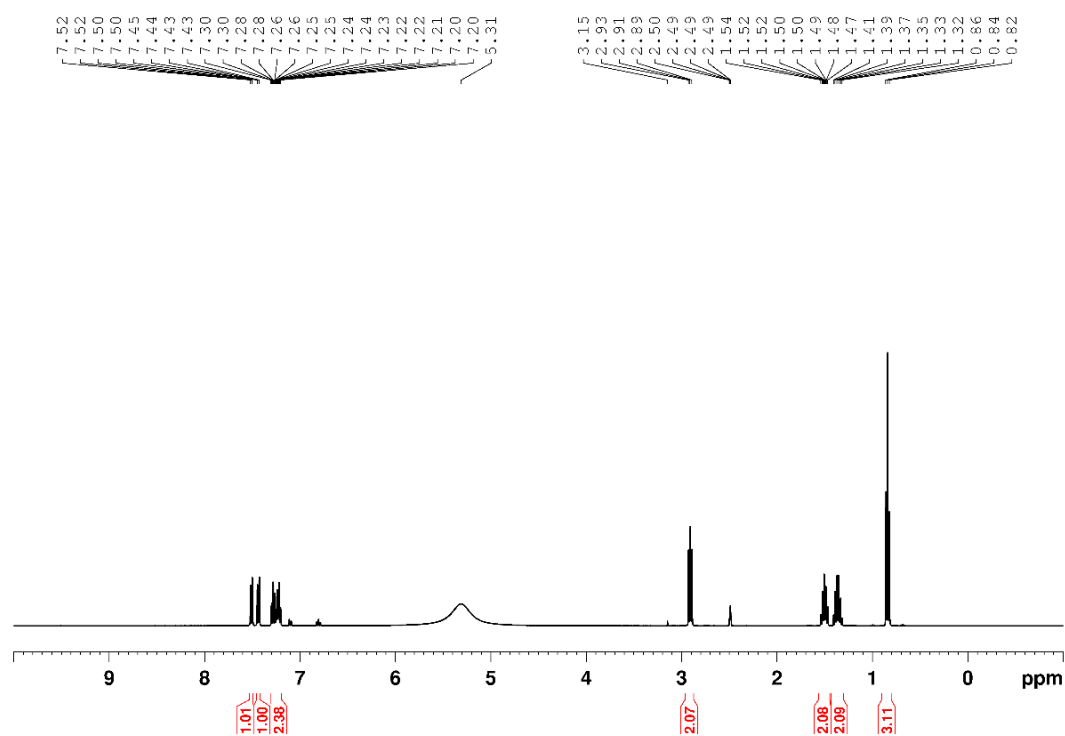


Figure S7. ¹H NMR spectra of the 2-(Butylthio)benzenamine hydrochloride (DMSO-d₆, 400 MHz, 25°C).

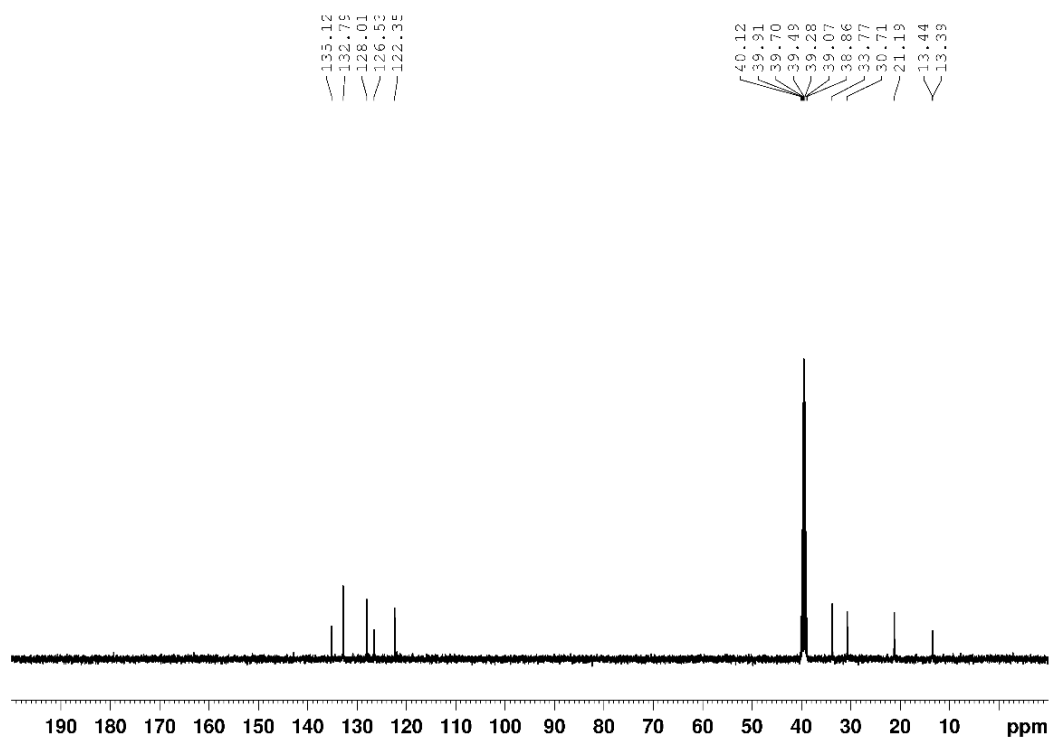


Figure S8. ¹³C NMR spectra of the 2-(Butylthio)benzenamine hydrochloride (DMSO-d₆, 100 MHz, 25°C).

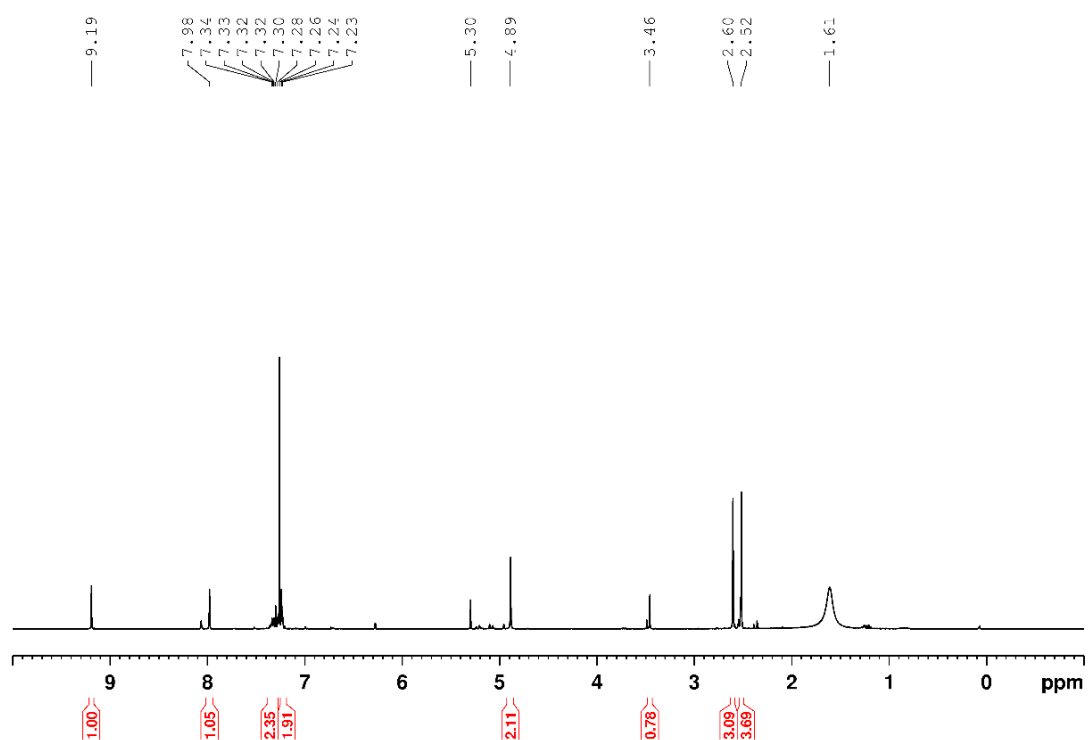


Figure S9. ^1H NMR spectra of the ligand **L1C** (CDCl_3 , 400 MHz, 25°C). Impurities: 5.30 (dichloromethane); 3.46 (methanol) and 1.61 (residual water).

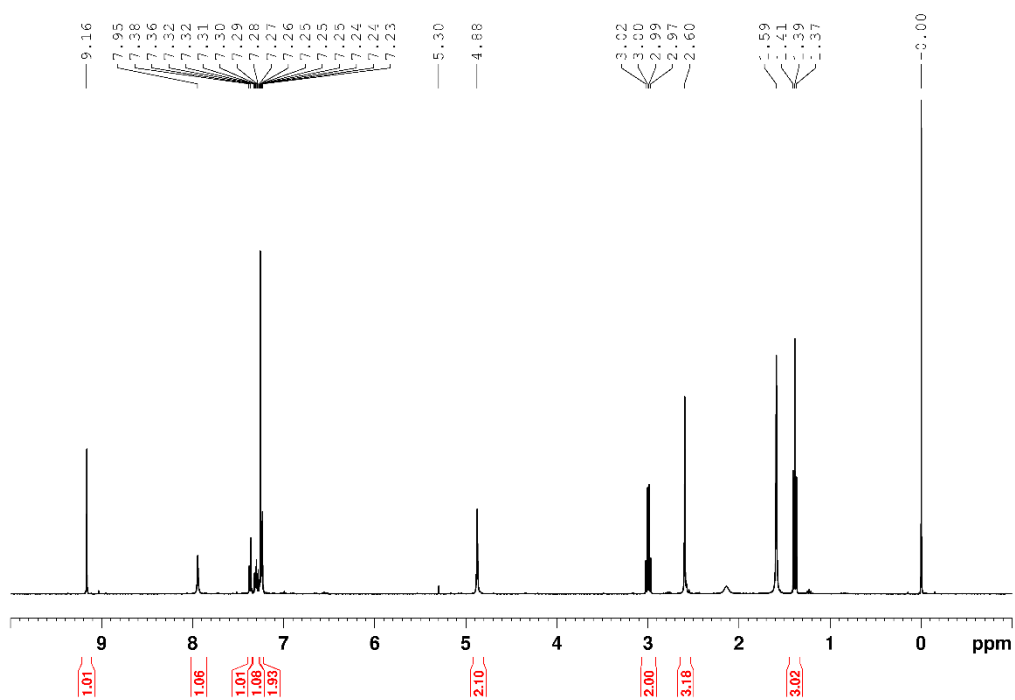


Figure S10. ^1H NMR spectra of the ligand **L2C** (CDCl_3 , 400 MHz, 25°C). Impurities: 5.30 (dichloromethane) and 1.59 (residual water).

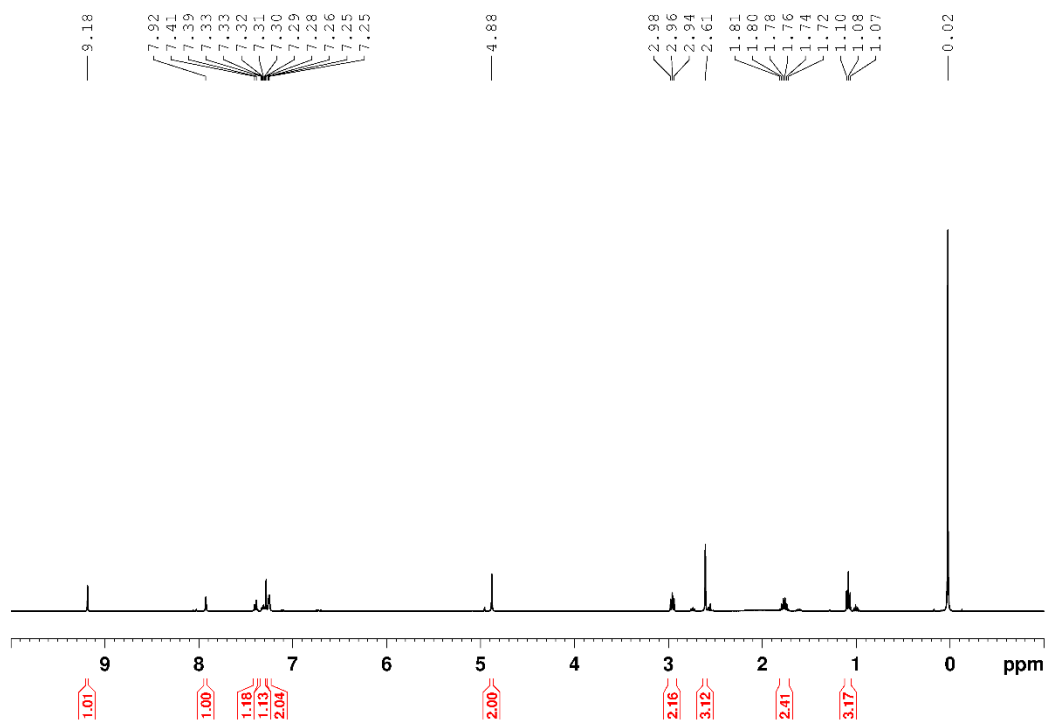


Figure S11. ^1H NMR spectra of the ligand **L3C** (CDCl_3 , 400 MHz, 25°C).

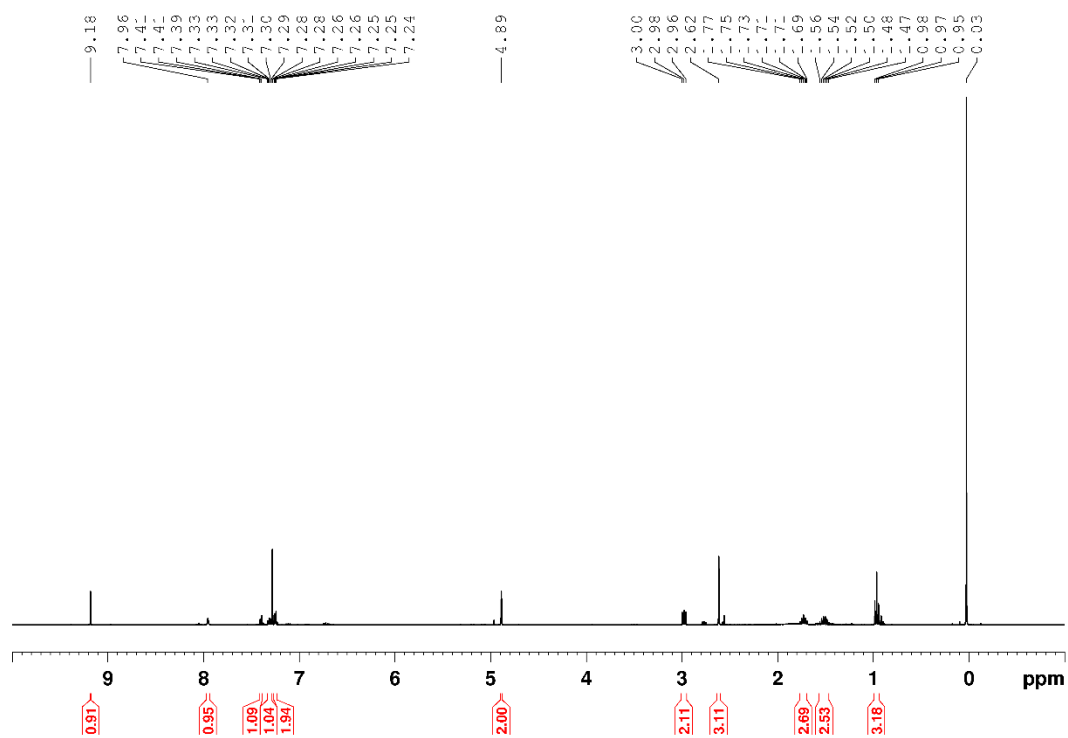


Figure S12. ¹H NMR spectra of the ligand L4C (CDCl₃, 400 MHz, 25°C).

UV/Vis spectroscopy

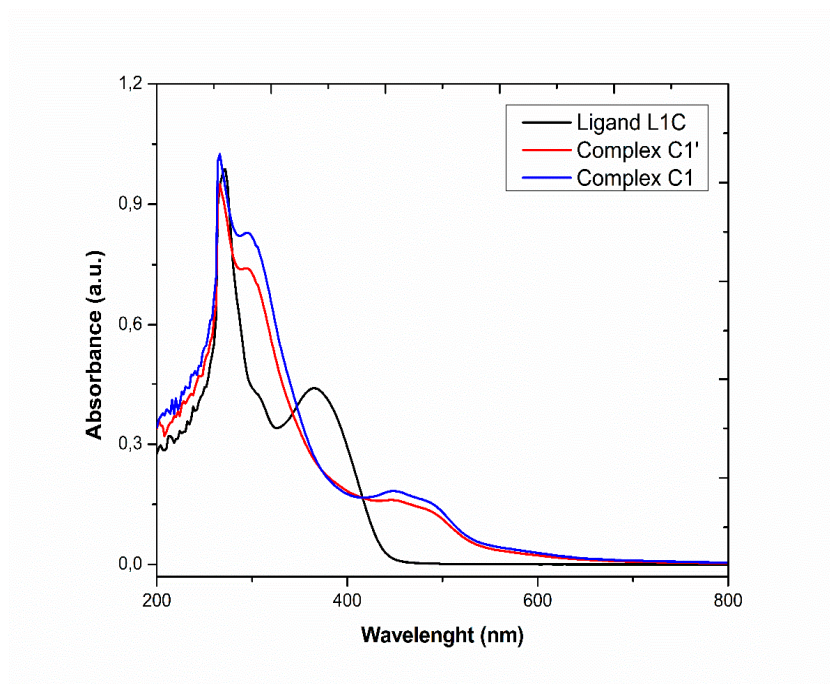


Figure S13. Steady state UV-Vis spectra of ligand **L1C**, complex **C1'** and complex **C1** (Experimental conditions: DMF, room temperature, 10^{-5} M range).

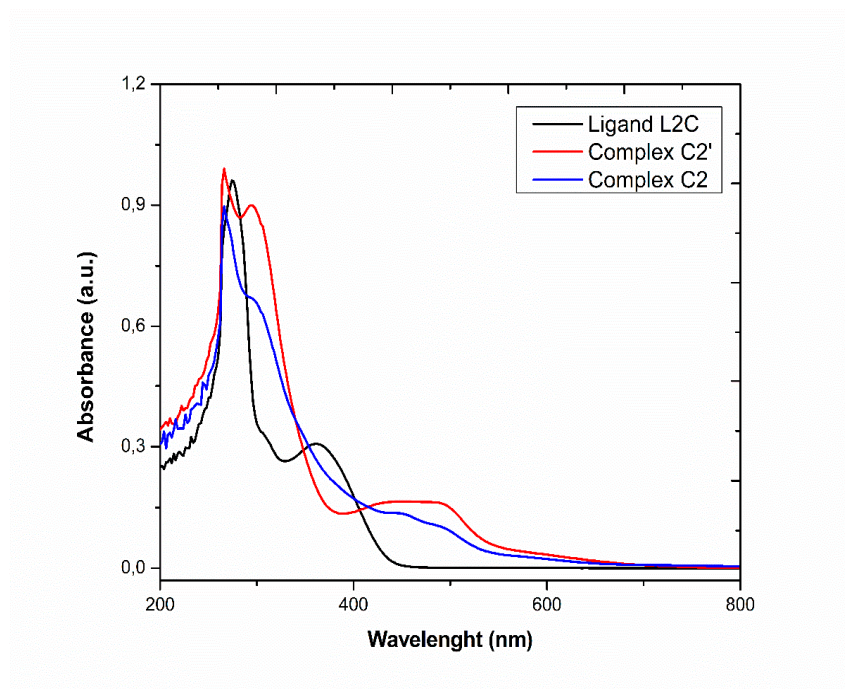


Figure S14. Steady state UV-Vis spectra of ligand **L2C**, complex **C2'** and complex **C2** (Experimental conditions: DMF, room temperature, 10^{-5} M range).

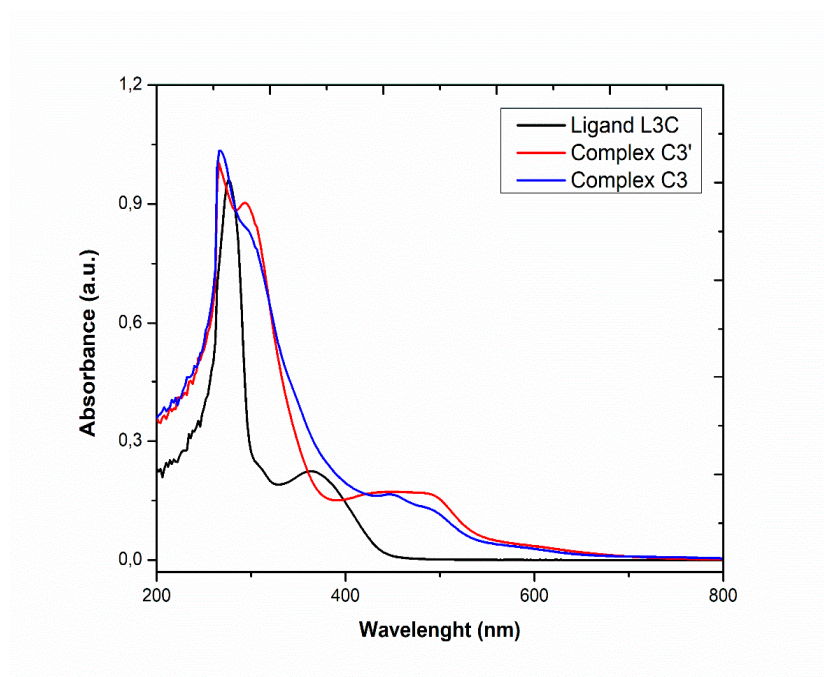


Figure S15. Steady state UV-Vis spectra of ligand **L3C**, complex **C3'** and complex **C3** (Experimental conditions: DMF, room temperature, 10^{-5} M range).

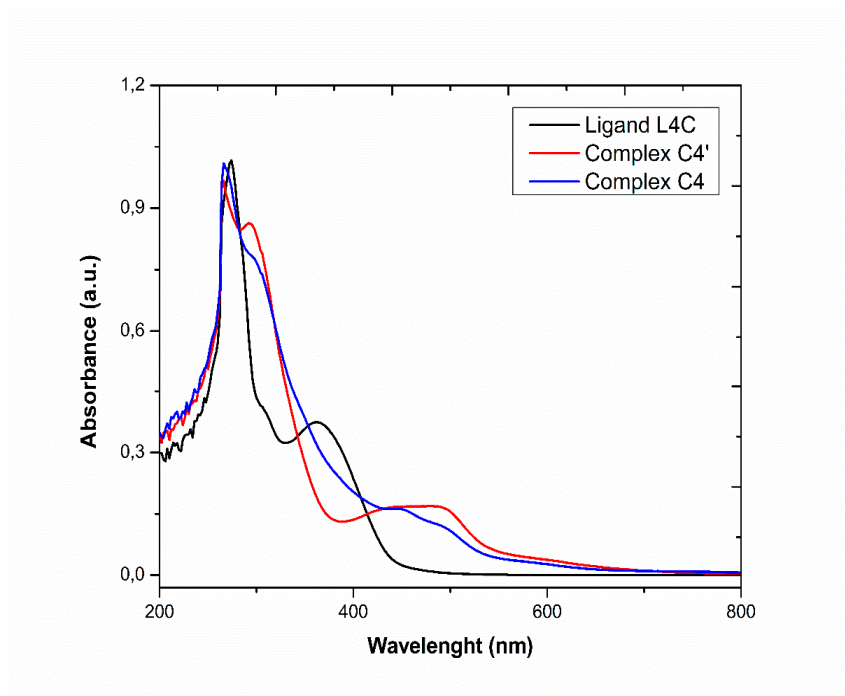


Figure S16. Steady state UV-Vis spectra of ligand **L4C**, complex **C4'** and complex **C4** (Experimental conditions: DMF, room temperature, 10^{-5} M range).

Infrared spectroscopy (FTIR)

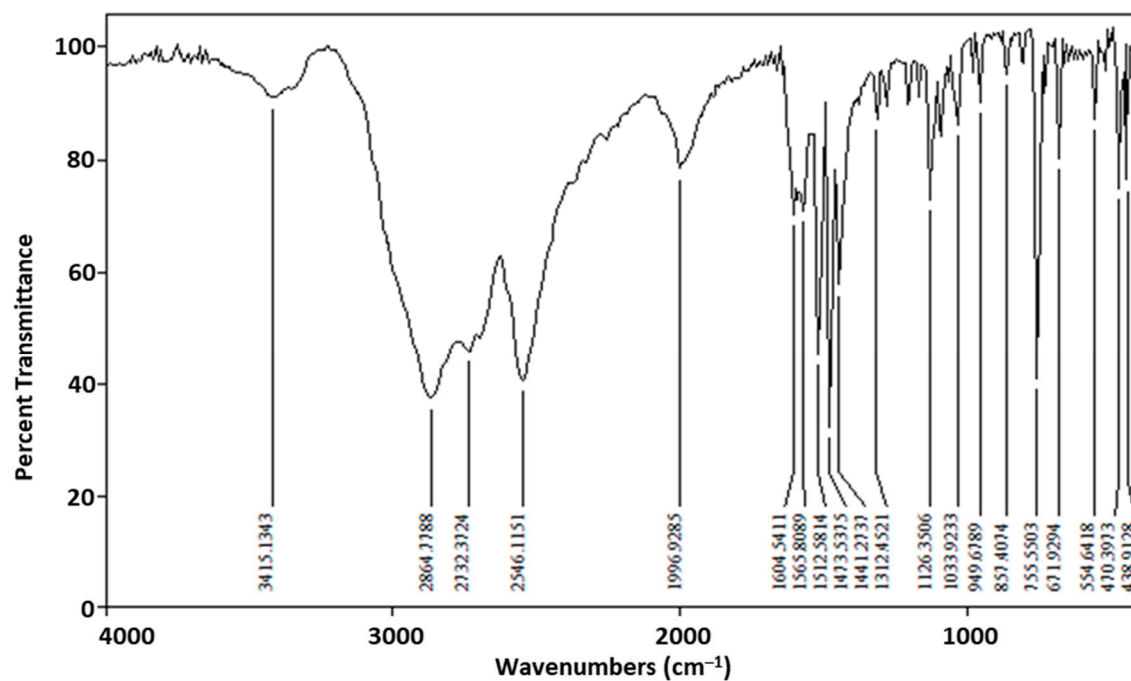


Figure S17. Infrared spectra (FTIR) of the S-alkylated aniline 2-(methylthio)aniline hydrochloride.

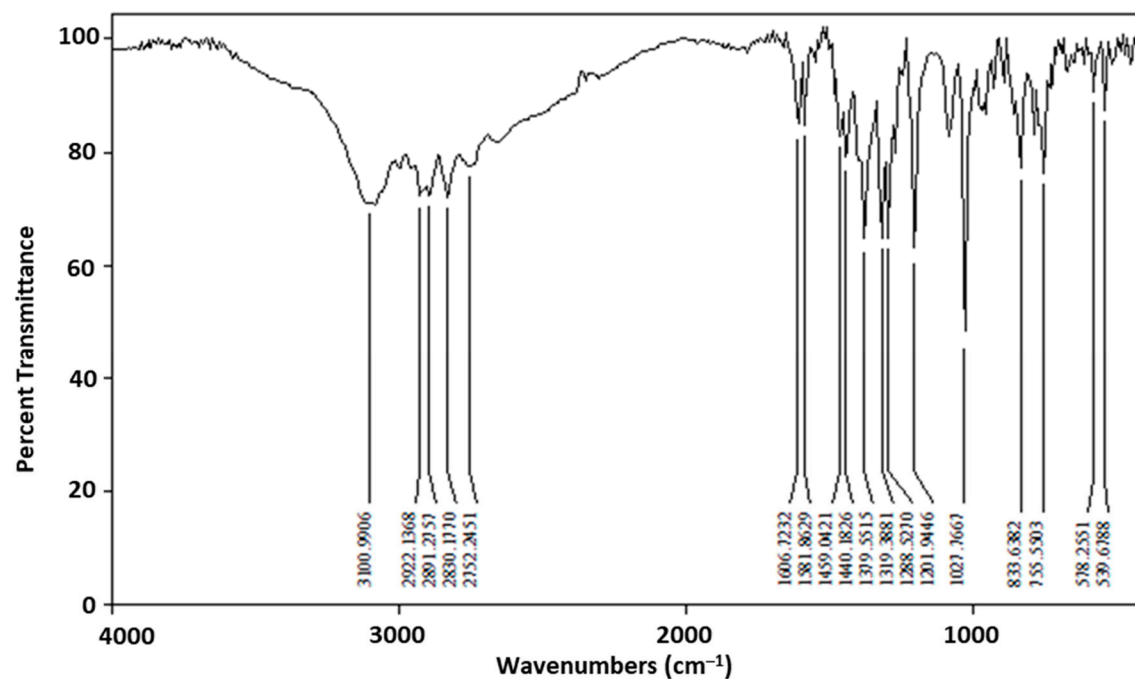


Figure S18. Infrared spectra (FTIR) of the ligand L1C.

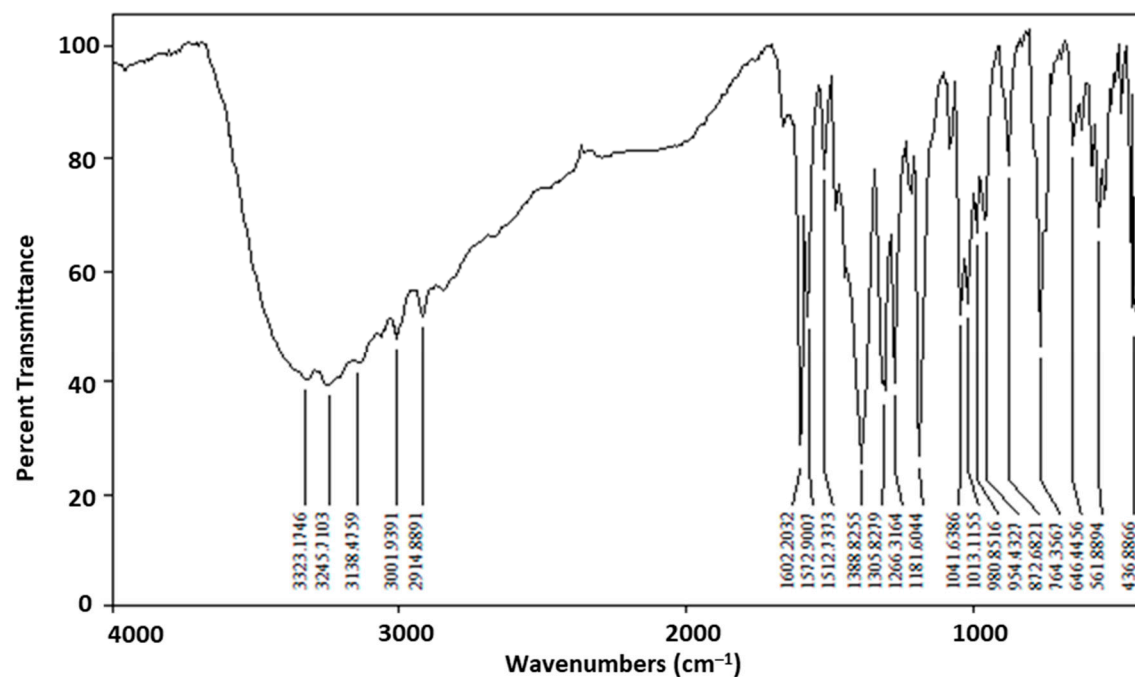


Figure S19. Infrared spectra (FTIR) of the complex C1'.

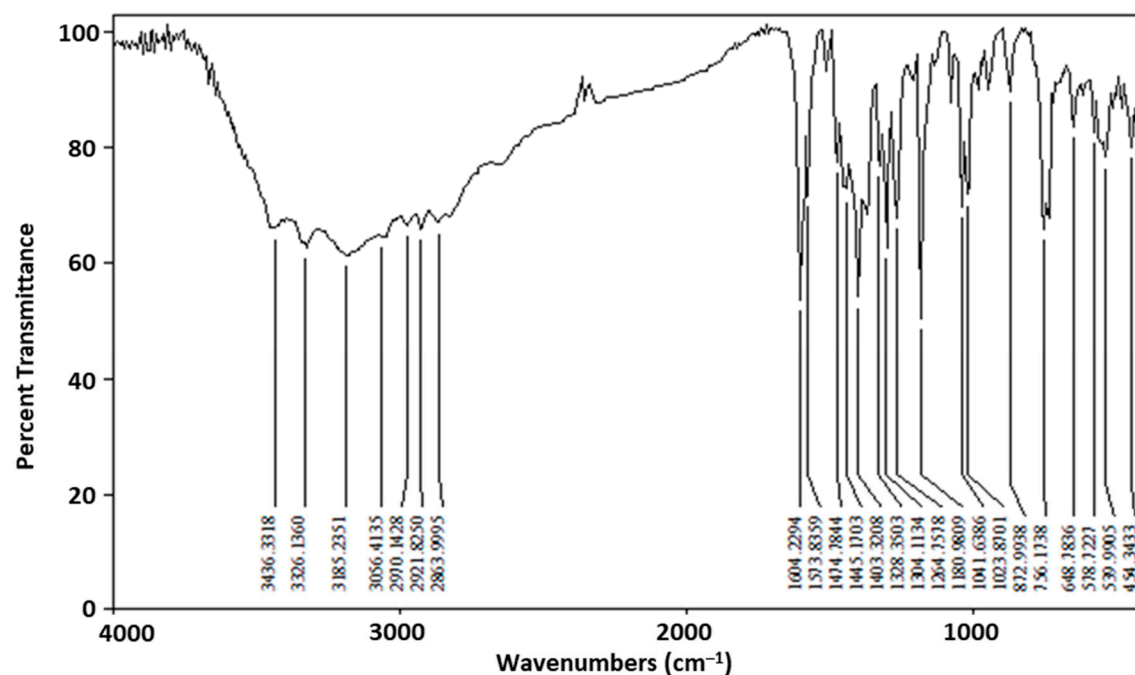


Figure S20. Infrared spectra (FTIR) of the complex C2'.

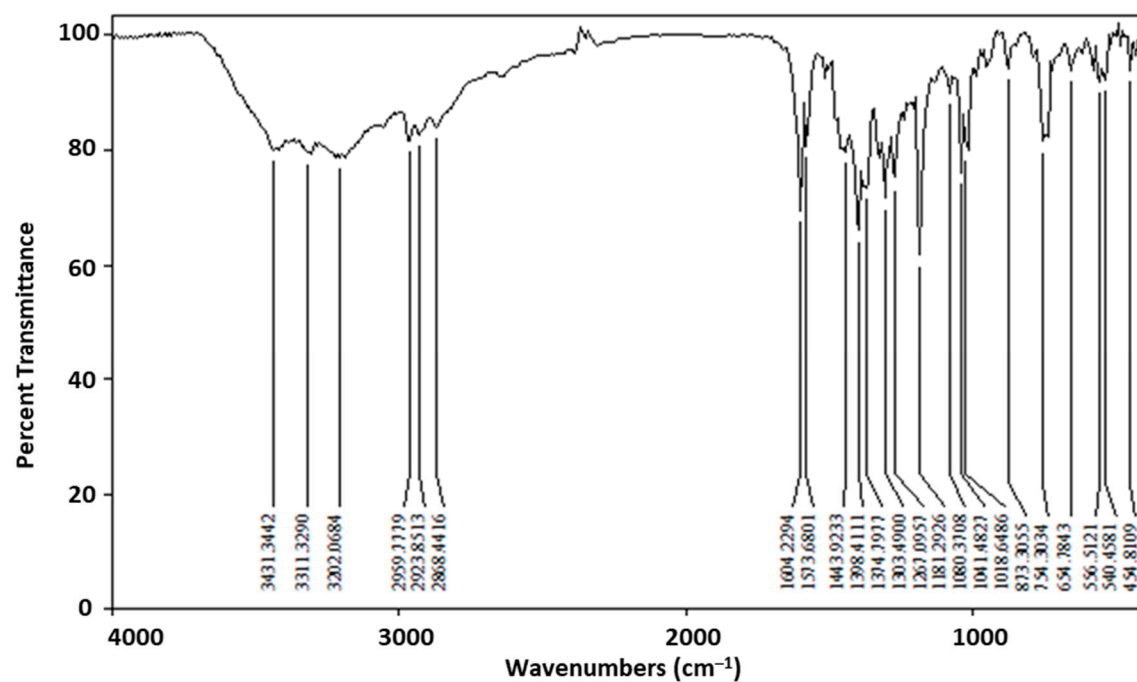


Figure S21. Infrared spectra (FTIR) of the complex C3'.

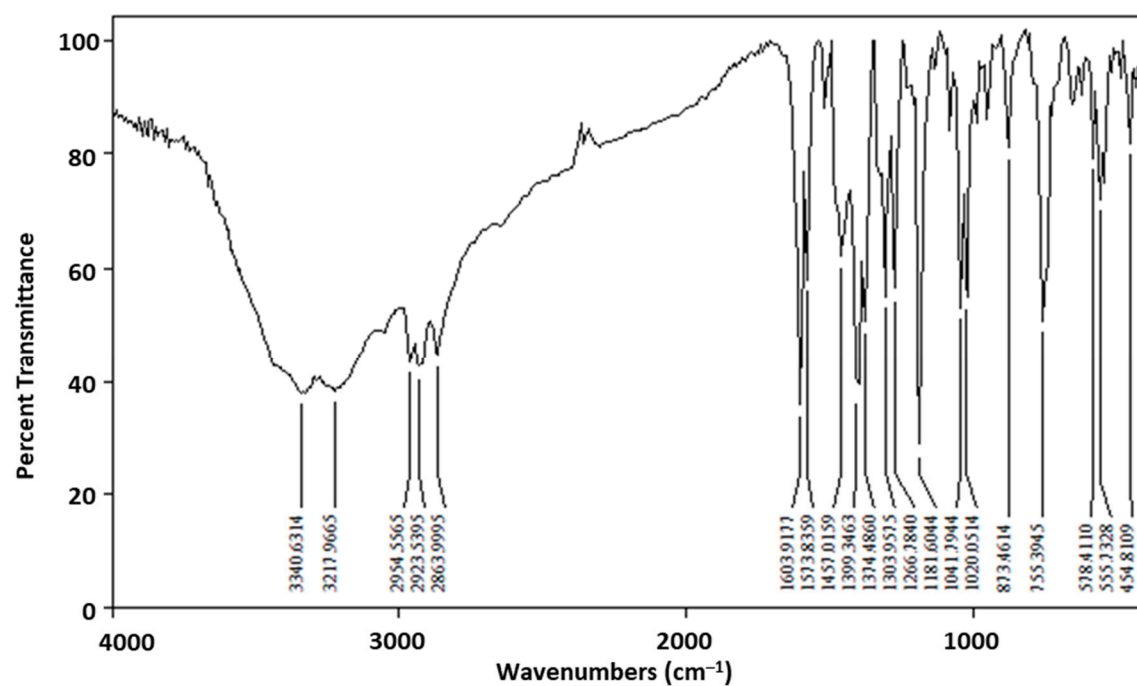


Figure S22. Infrared spectra (FTIR) of the complex C4'.

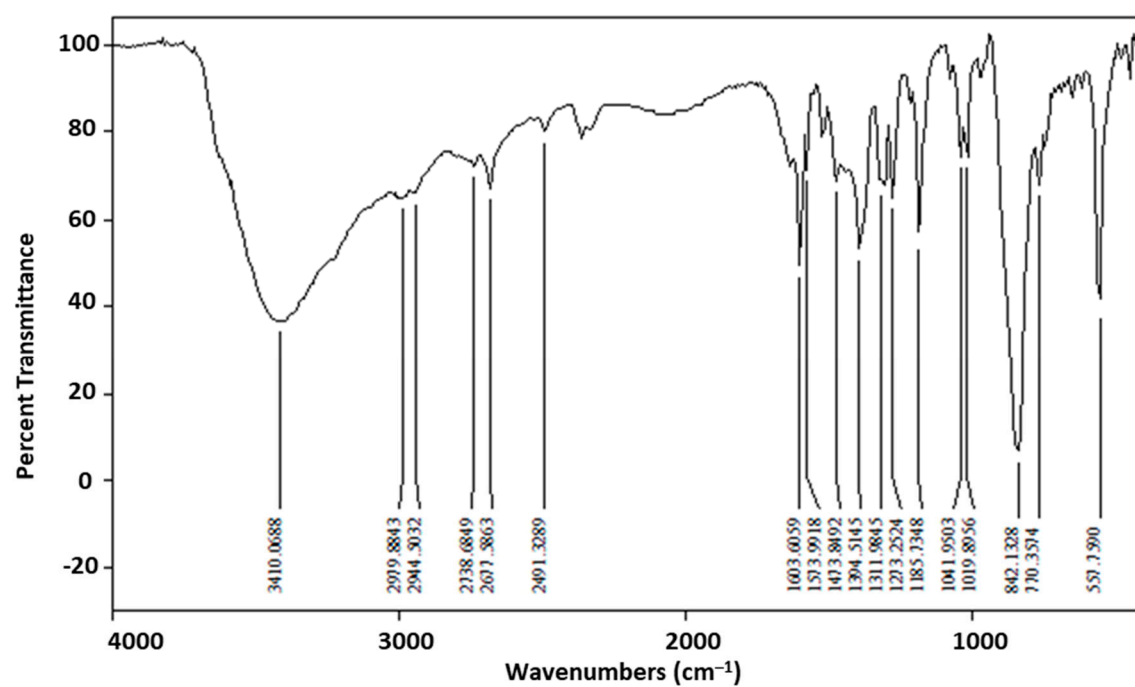


Figure S23. Infrared spectra (FTIR) of the complex C1.

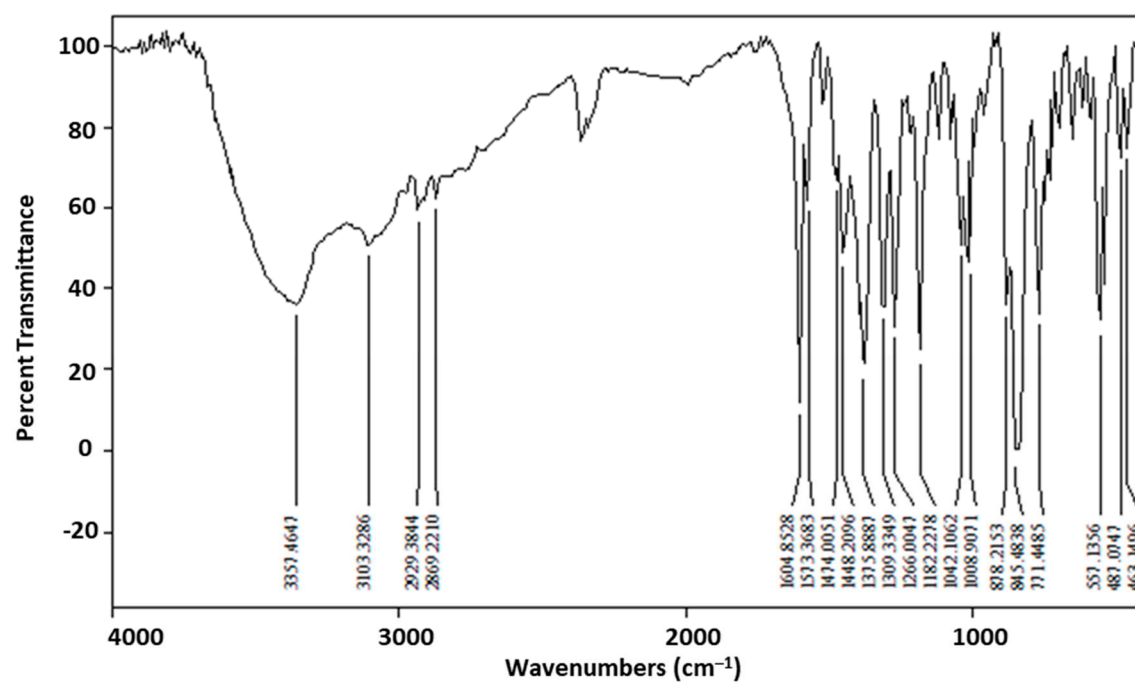


Figure S24. Infrared spectra (FTIR) of the complex C2.

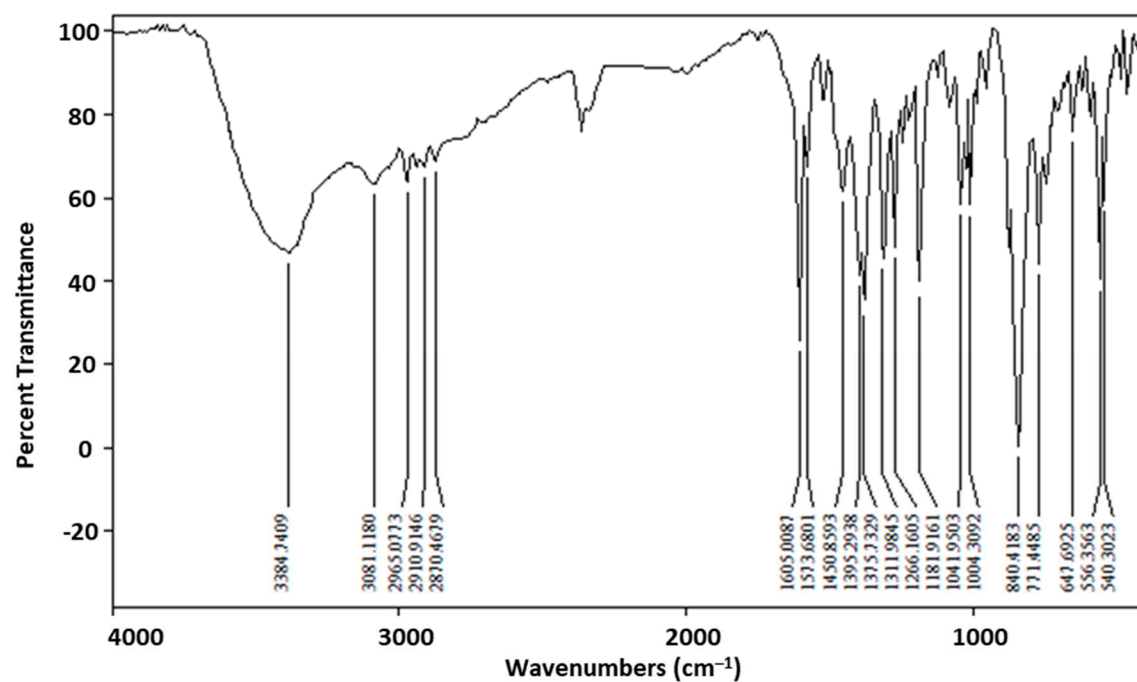


Figure S25. Infrared spectra (FTIR) of the complex C3.

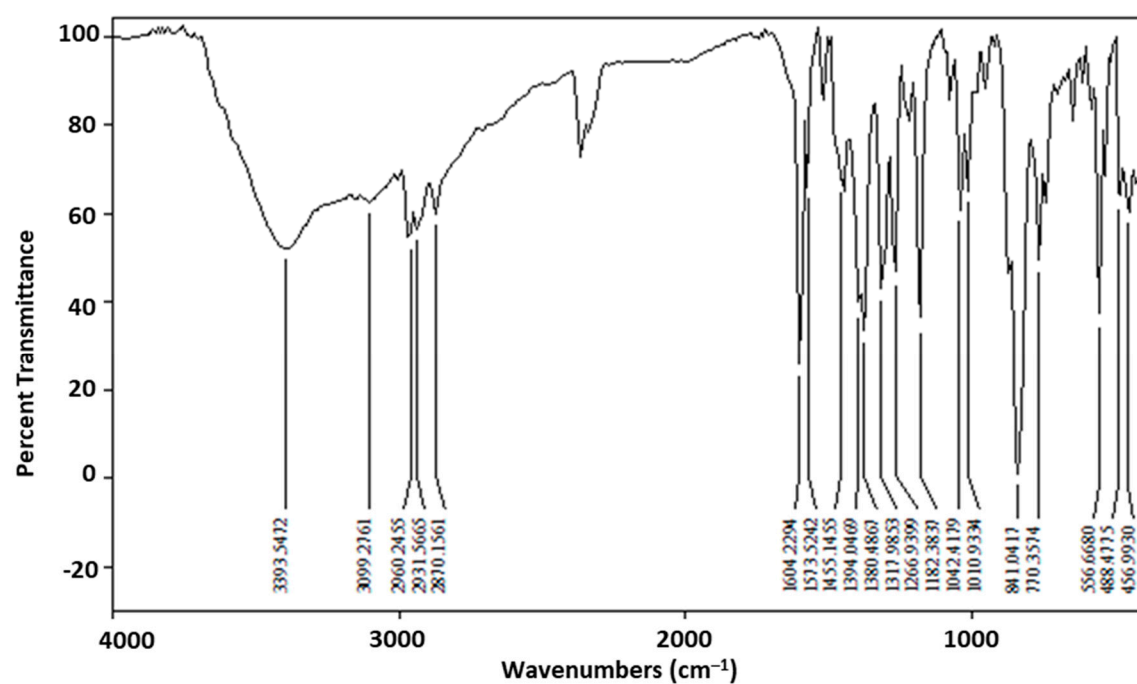


Figure S26. Infrared spectra (FTIR) of the complex C4.

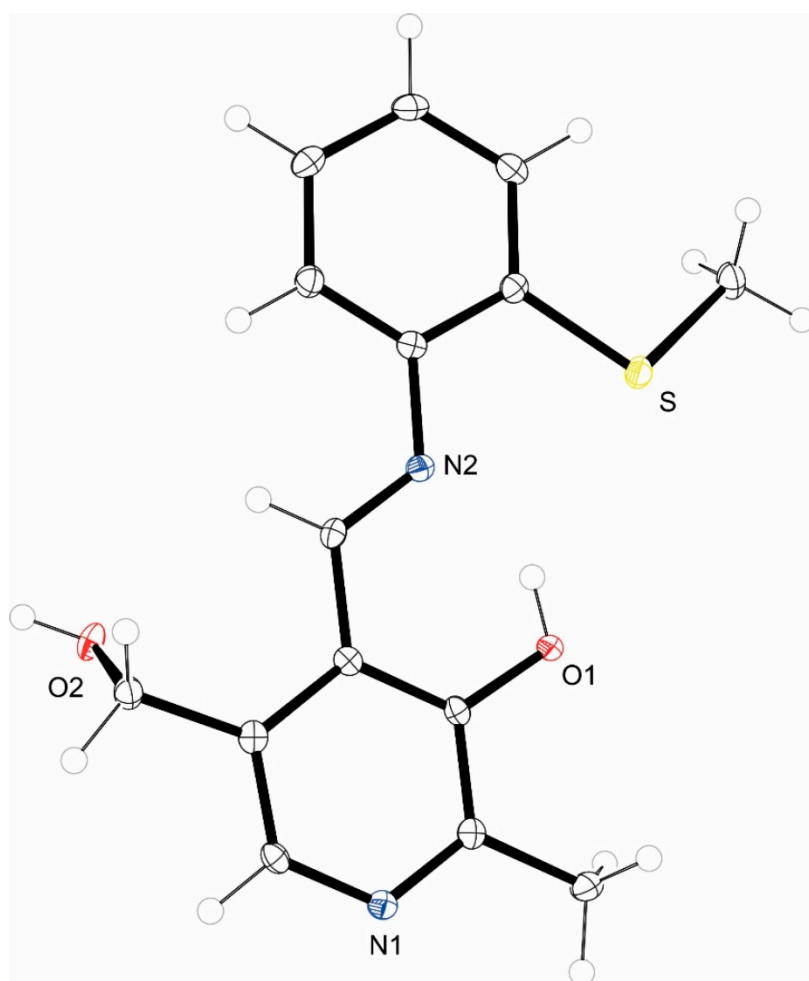


Figure S27. ORTEP-3.1 projection of the molecular structures of the ligand **L1C** in the solid state. Ellipsoids were calculated at 50% probability.

Table S3. Crystal data and data collection and refinements of ligand **L1C**.

	L1C
Empirical formula	C ₁₅ H ₁₆ N ₂ O ₂ S
Formula weight	288.36
Temperature (K)	100(2)
Wavelength	0.71073
Crystal system	Monoclinic
Space group	P2 ₁ /c
<i>a</i> (Å)	5.000(4)
<i>b</i> (Å)	27.17(2) Å
<i>c</i> (Å)	10.117(8)
α (°)	90.00
β (°)	101.16(2)
γ (°)	90.00
Volume (Å ³) / Z	1348.4(18)/ 4
Calculated density (mg.m ⁻³)	1.420
Absorption coefficient (nm ⁻¹)	0.243
<i>F</i> (000)	608
Crystal size (mm)	0.42 × 0.32 × 0.20
Theta range for data collection (°)	2.54 to 27.97
Limiting indices	-6 ≤ <i>h</i> ≤ 6, -35 ≤ <i>k</i> ≤ 35, -13 ≤ <i>l</i> ≤ 13
Reflections collected/unique	20241 / 3244
Completeness to theta	99.7%
Absorption correction	Semi-empirical from equivalents
Max. and Min. Transmission	0.9530 and 0.9049
Data/restraints/ parameters	3244 / 0 / 181
Goodness-of-fit on <i>F</i> ²	1.023
Índice <i>R</i> _{int}	0.0795
Final <i>R</i> indices <i>R</i> ₁ and <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0462 <i>wR</i> ₂ = 0.0972
<i>R</i> indices (all data) <i>R</i> ₁ and <i>wR</i> ₂	<i>R</i> ₁ = 0.0795 <i>wR</i> ₂ = 0.1055
Largest diff. peak (e ⁻ Å ⁻³) and hole	0.384 and -0.445