Electronic Supplementary Information

Transition metal complexes with phosphine-oxide appended aza-macrocycles – effects of ring size and denticity

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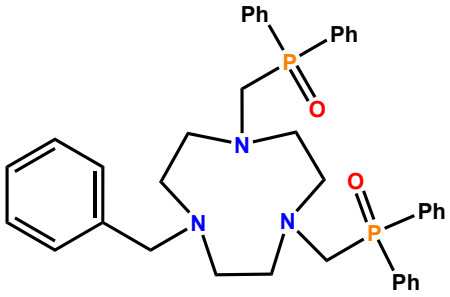
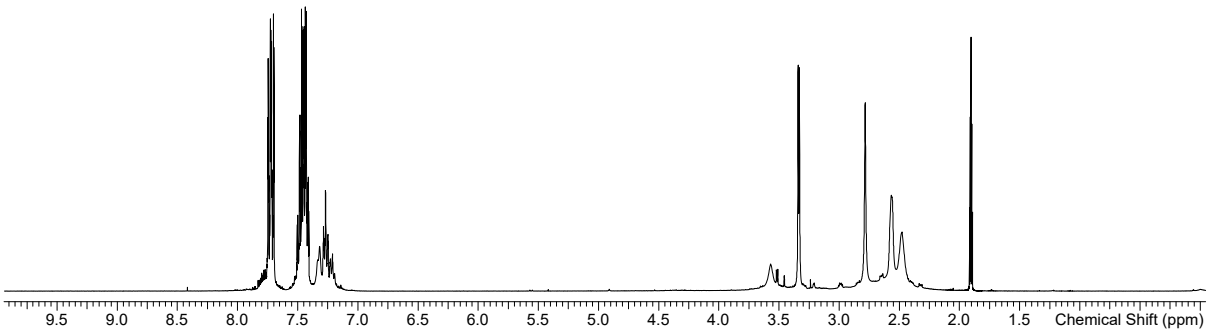
[b]*GE HealthCare, Pollards Wood, Nightingales Lane, Chalfont St Giles, Bucks, HP8 4SP, UK.*

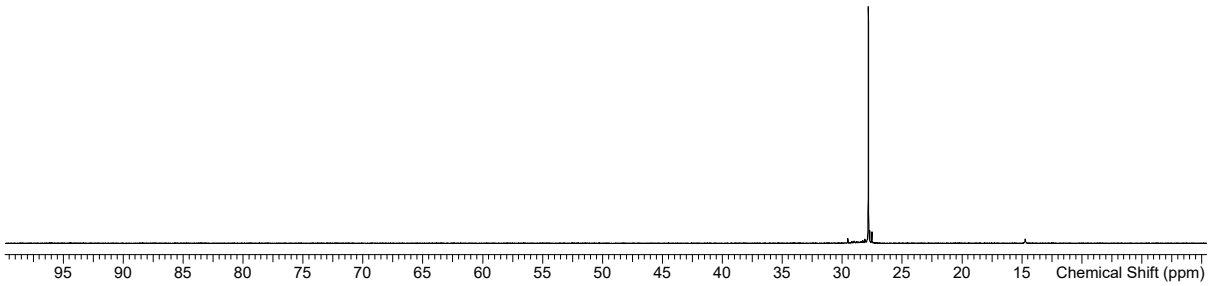
Figure S:1 Spectroscopic data for L^1



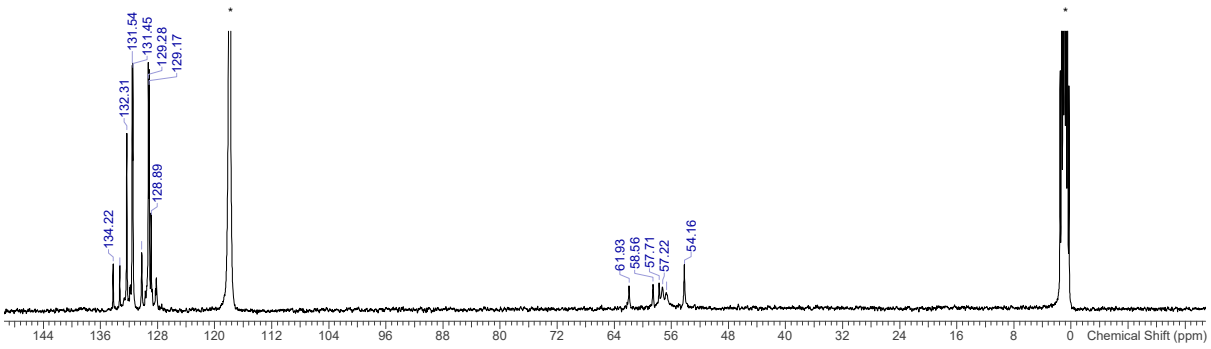
S1.1 ^{1}H NMR spectrum of $\mathbf{L^1}$ (d_3-MeCN)



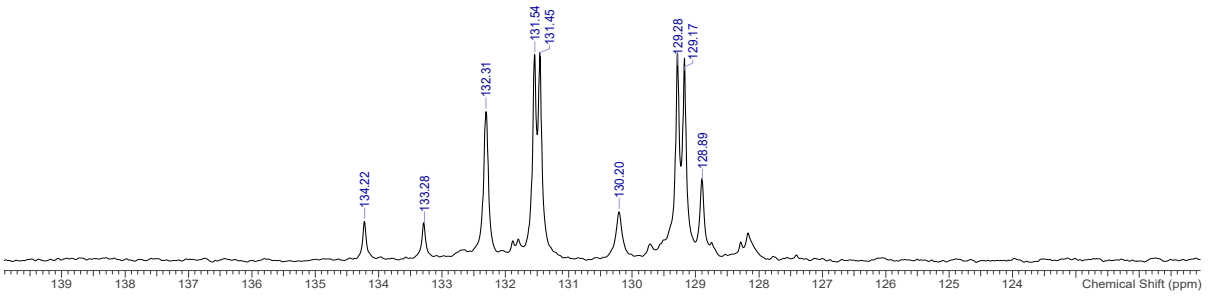
S1.2 $^{31}P\{^{1}H\}$ NMR spectrum of **L¹** (d_3-MeCN)



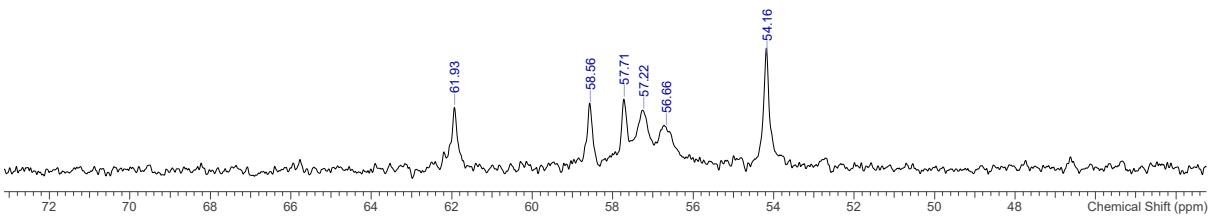
S1.3 $^{13}C\{^{1}H\}$ NMR spectrum of **L¹** (*d_3-MeCN)



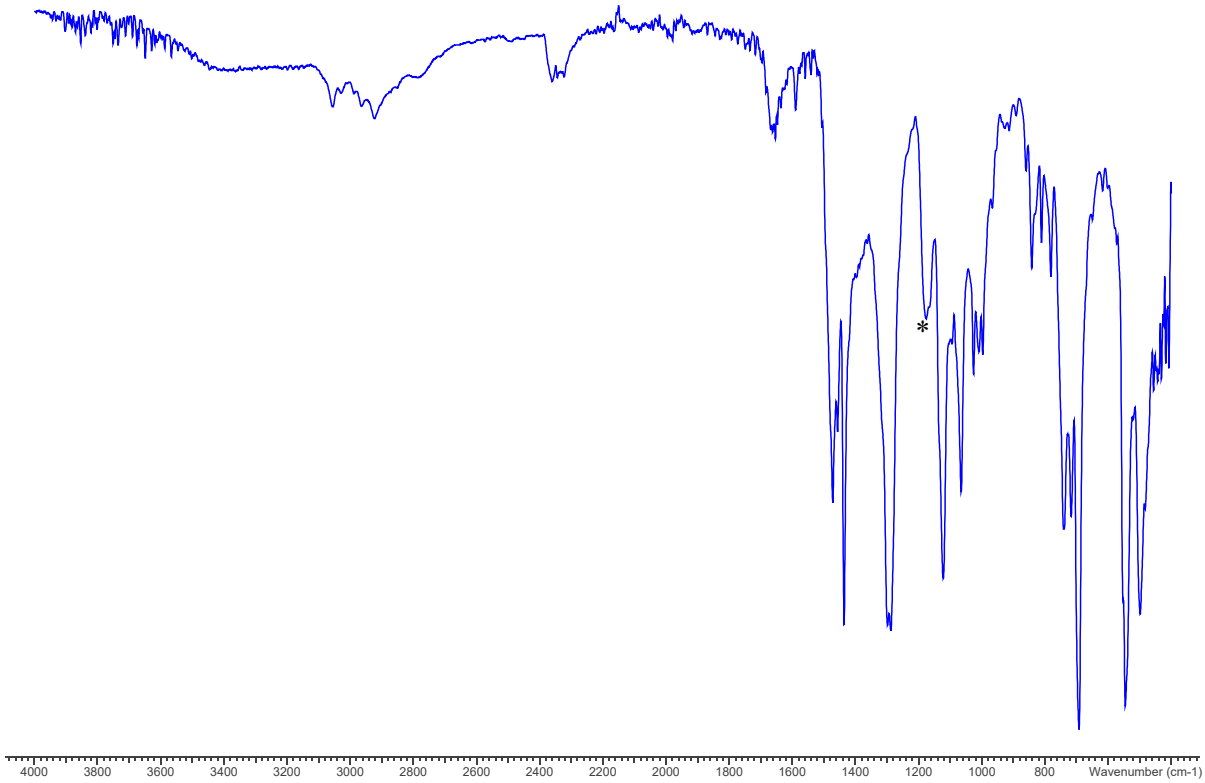
S1.3.1 Expansion of the aromatic region of $^{13}C\{^{1}H\}$ NMR spectrum of **L¹** (d_3-MeCN)



S1.3.2 Expansion of the aliphatic region of $^{13}C\{^{1}H\}$ NMR spectrum of **L¹** (d_3-MeCN)



S1.4 IR spectrum of **L¹** (* P=O stretch)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Wavenumber (cm-1)

S1.5 HR ESI+ MS of **L**[1] (MeOH)

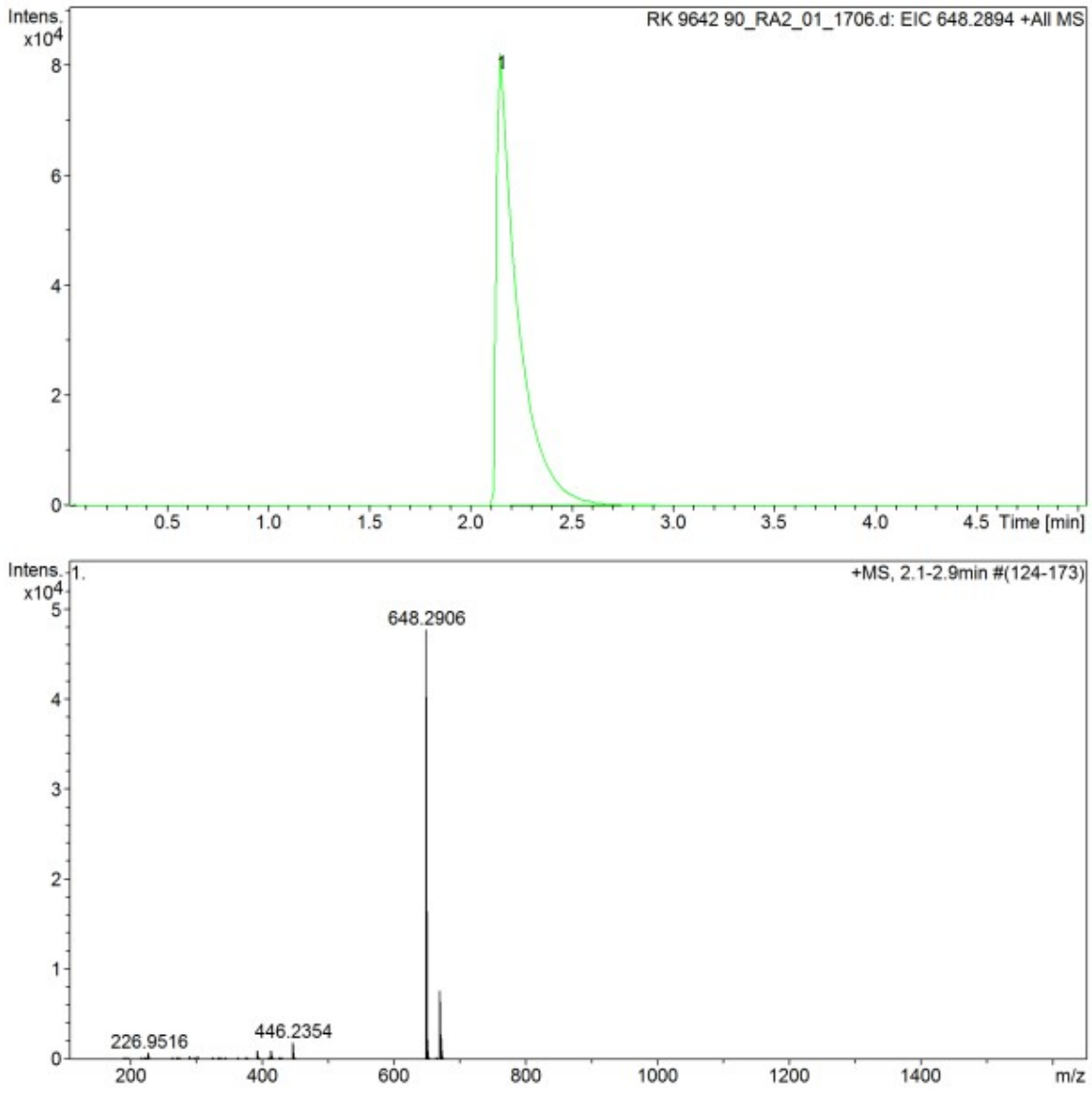
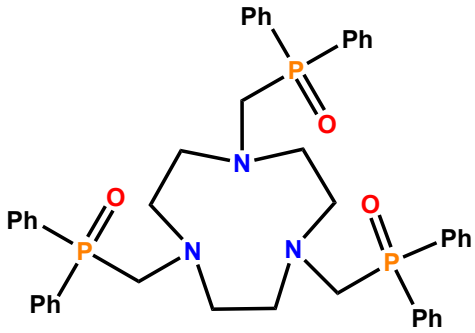
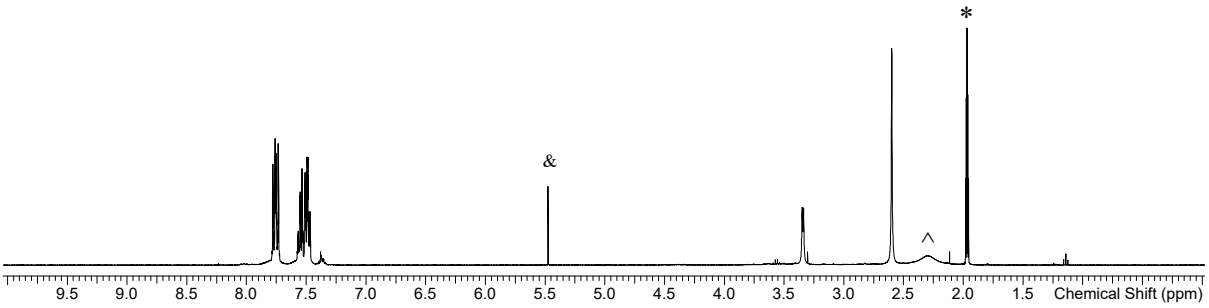


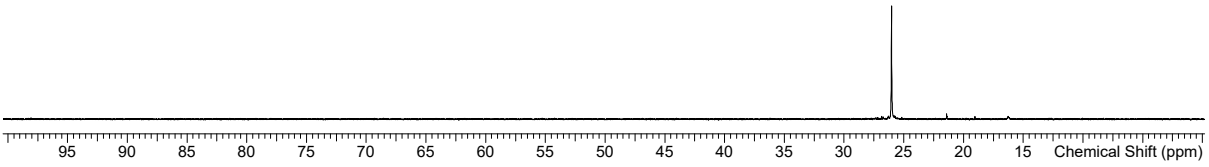
Figure S2: Spectroscopic data for L^2



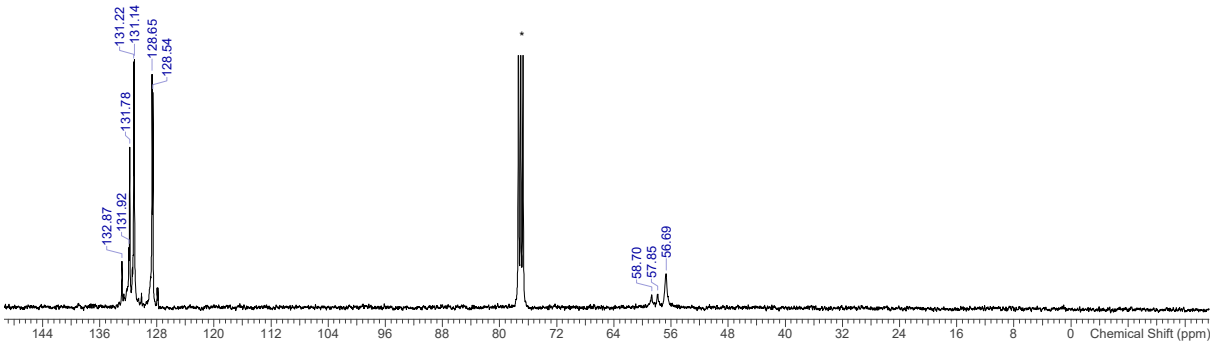
S2.1 ^{1}H NMR spectrum of $\mathbf{L^2}$ (d_3-MeCN) (*MeCN; ^H_2O; &CH_2Cl_2)



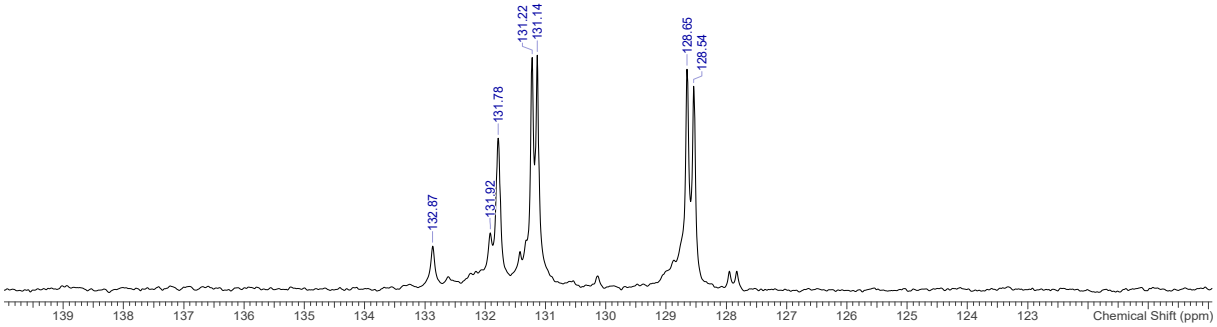
S2.2 ^{31}P{^{1}H} NMR spectrum of $\mathbf{L^2}$ (d_3-MeCN)



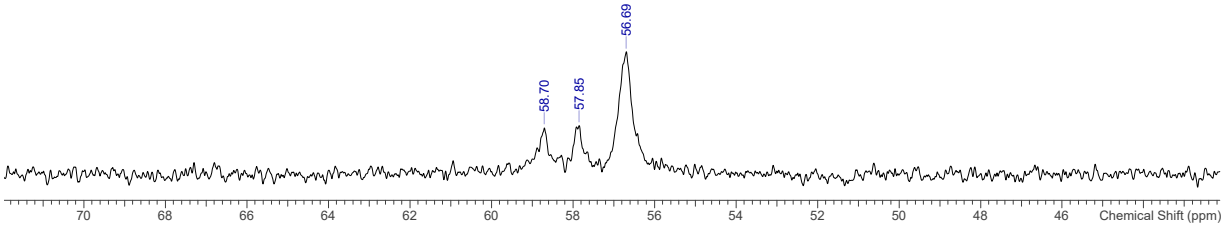
S2.3 ^{13}C{^{1}H} NMR spectrum of $\mathbf{L^2}$ (*d-$CHCl_3$)



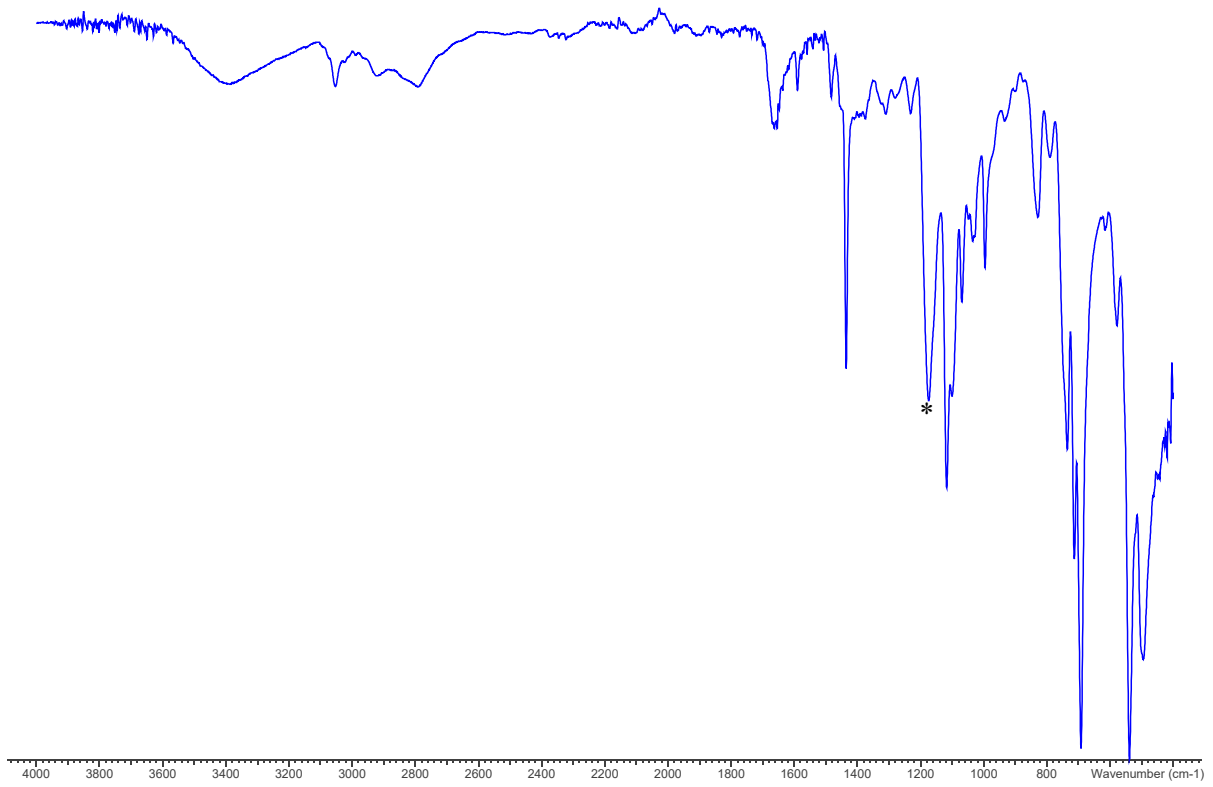
S2.3.1 Expansion of the aromatic region of $^{13}C\{^{1}H\}$ NMR spectrum of **L²** (d-$CHCl_3$)



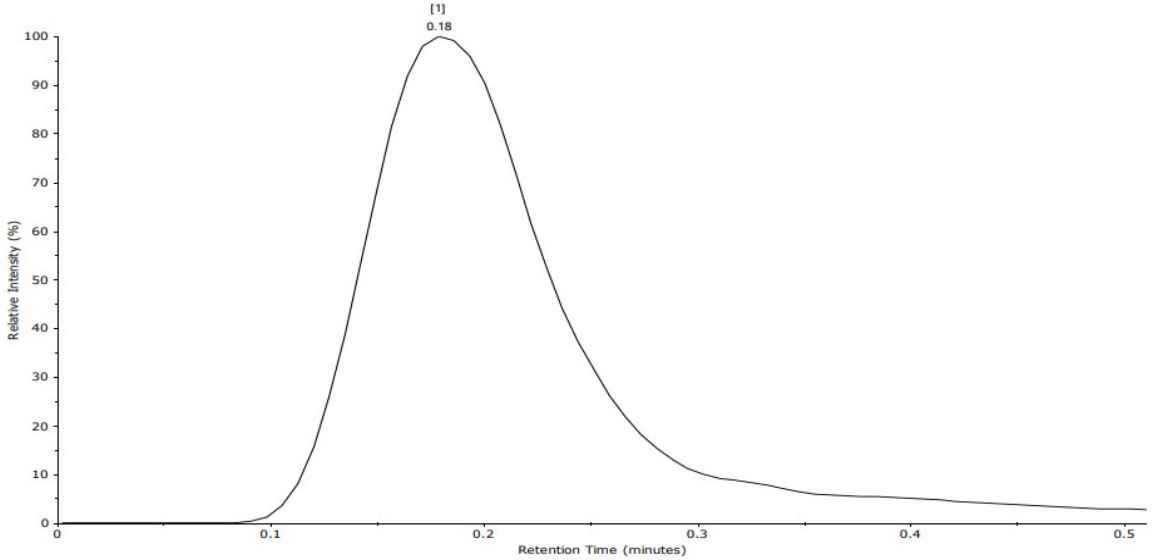
S2.3.2 Expansion of the aliphatic region of $^{13}C\{^{1}H\}$ NMR spectrum of **L²** (d-$CHCl_3$)

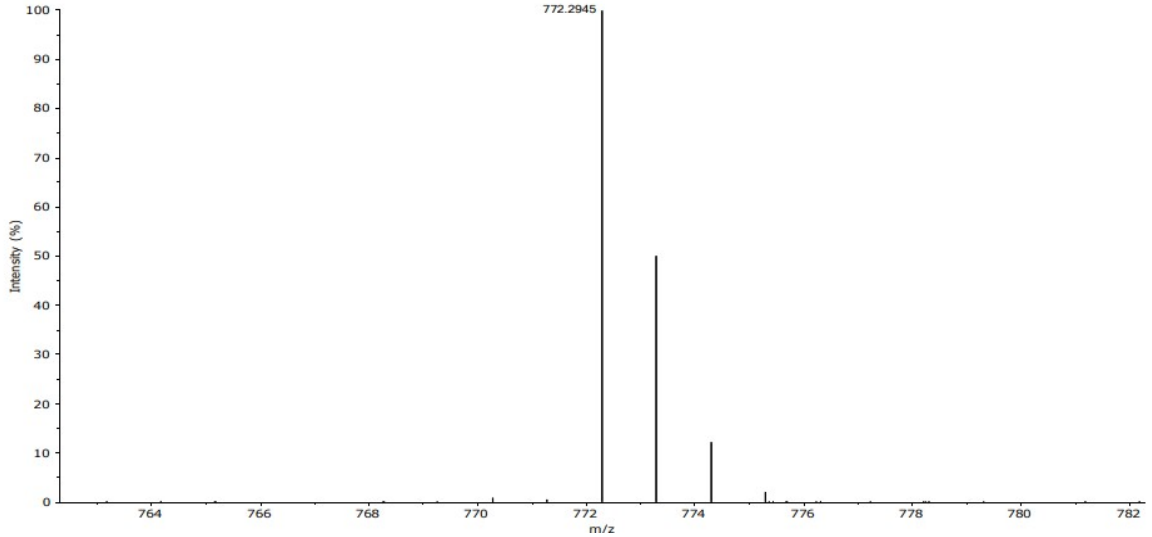


S2.4 IR spectrum of **L²** (* P=O)



S2.5 HR ESI+ MS of **L²** (MeOH)





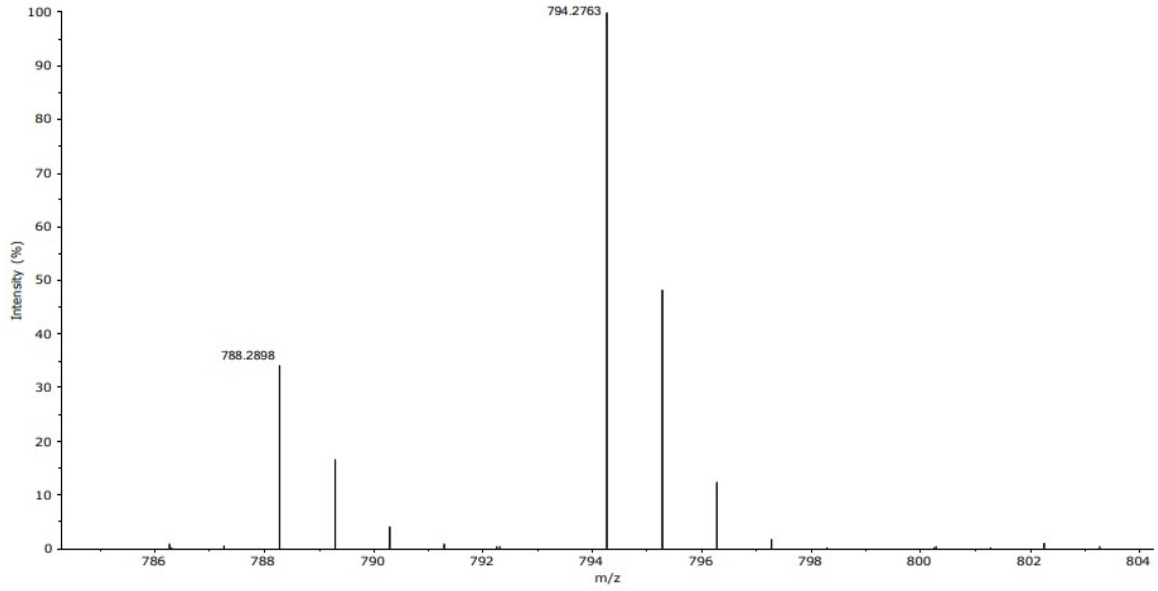
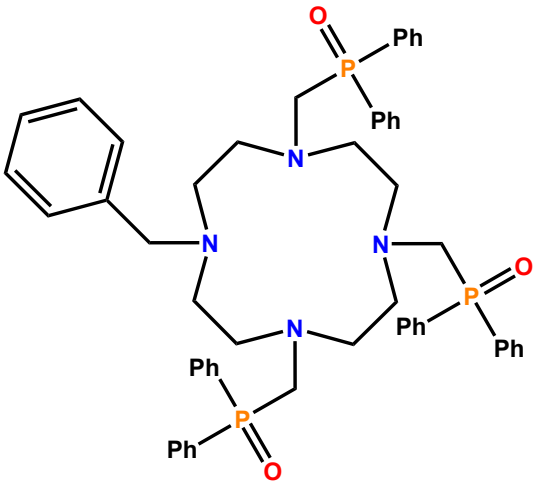
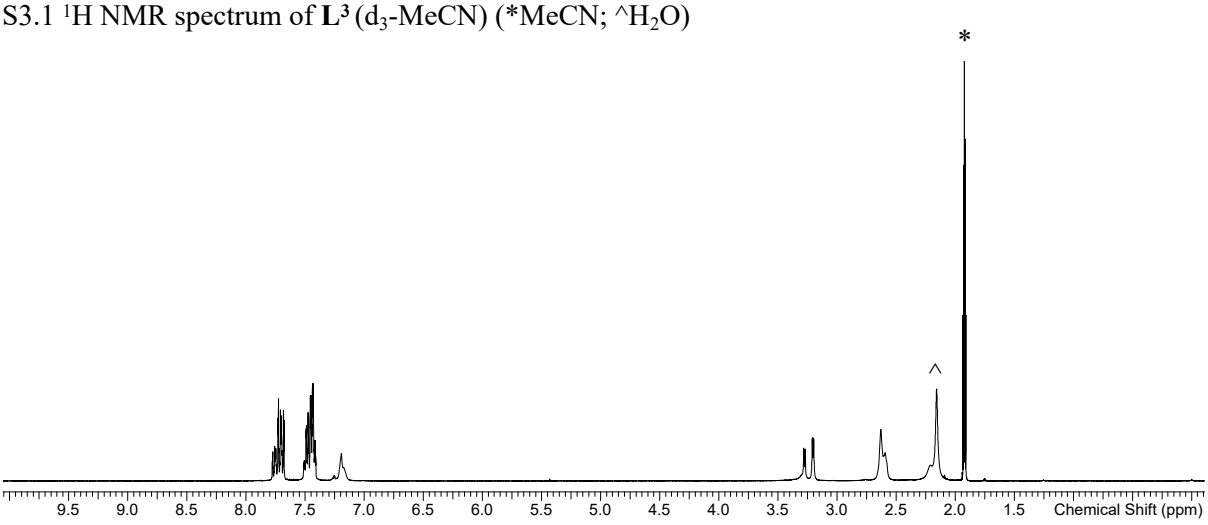


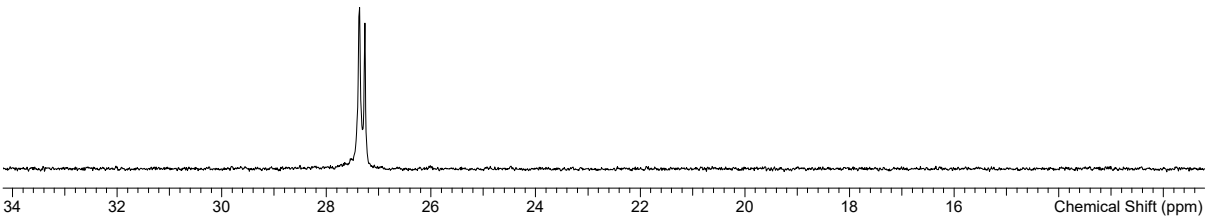
Figure S3: Spectroscopic data for L^3



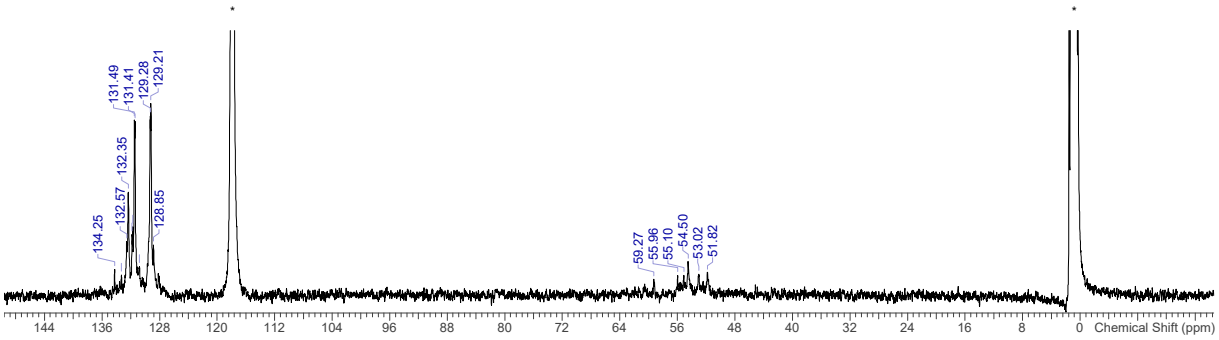
S3.1 ^{1}H NMR spectrum of $\mathbf{L^3}$ (d_3-MeCN) (*MeCN; ^H_2O)



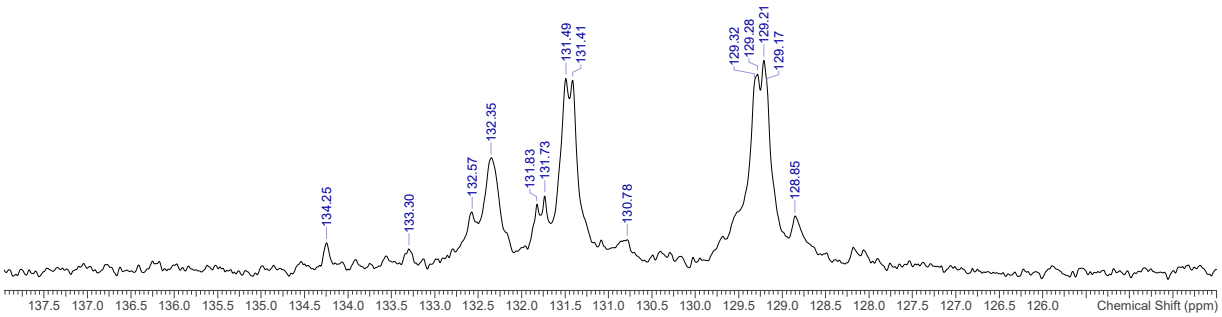
S3.2 ^{31}P{^{1}H} NMR spectrum of $\mathbf{L^3}$ (d_3-MeCN)



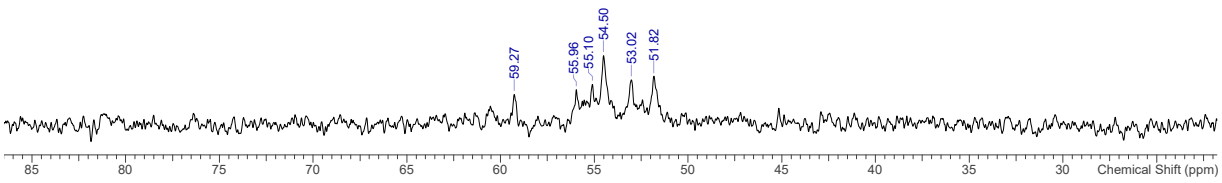
S3.3 ^{13}C{^{1}H} NMR spectrum of $\mathbf{L^3}$ (*d_3-MeCN)



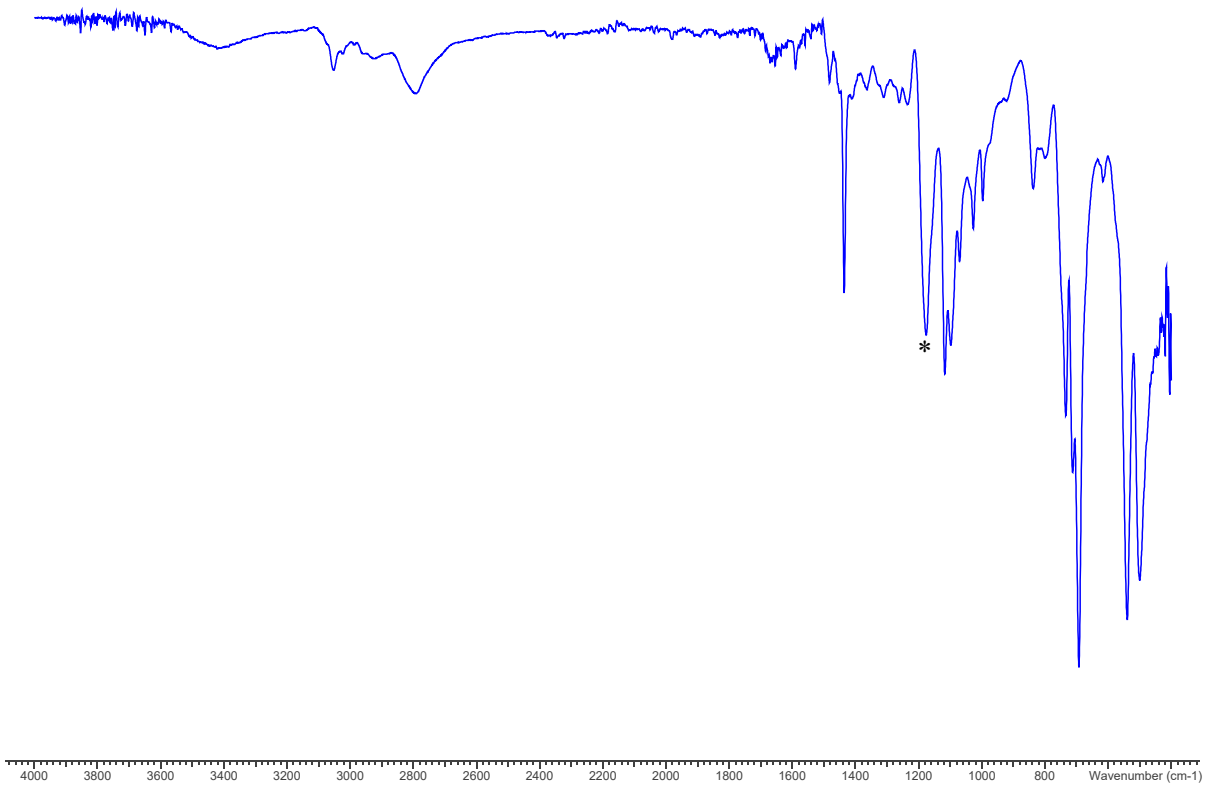
S3.3.1 Expansion of the aromatic region of $^{13}C\{^{1}H\}$ NMR spectrum of **L³** (d_3-MeCN)



S3.3.2 Expansion of the aliphatic region of $^{13}C\{^{1}H\}$ NMR spectrum of **L³** (d_3-MeCN)



S3.4 IR spectrum of **L³** (* P=O stretch)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Wavenumber (cm-1)

S3.5 HR ESI+ MS of **L³** (MeOH)

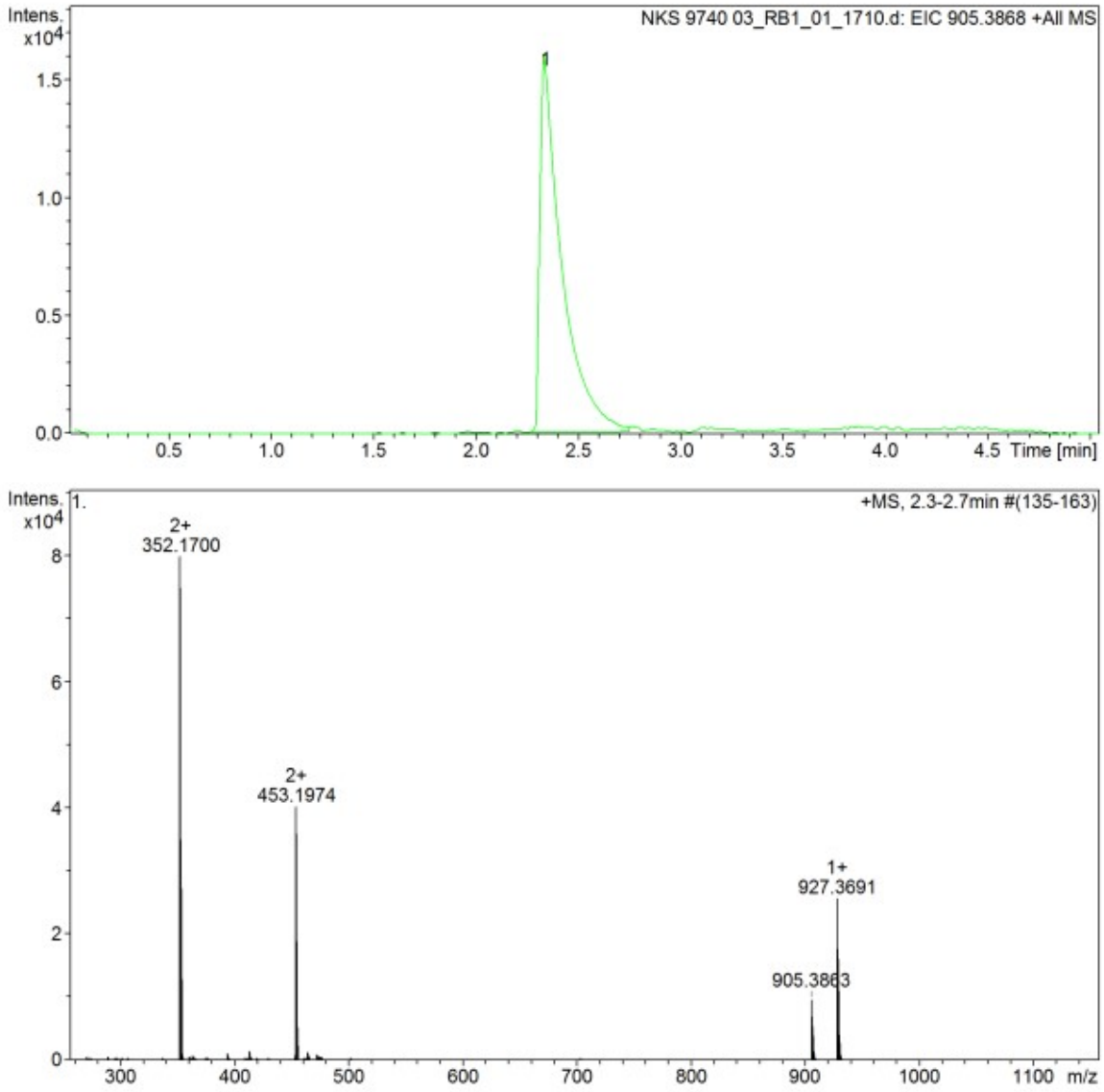
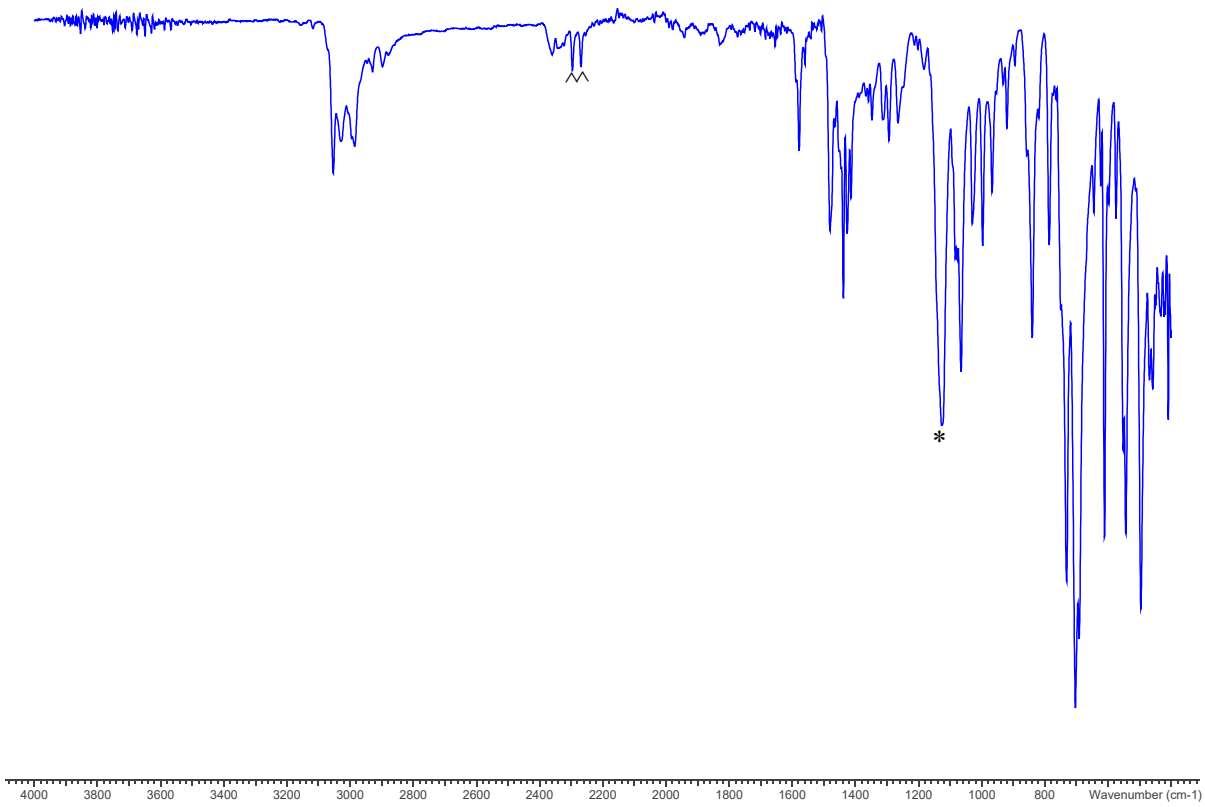
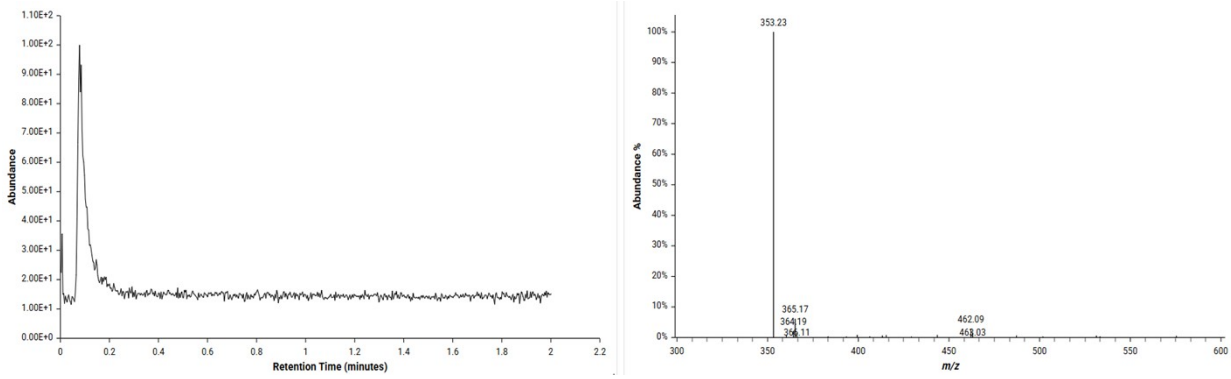


Figure S4: Spectroscopic data for $[Co(L^1)(MeCN)][BPh_4]_2$

S4.1 IR spectrum of $[Co(\mathbf{L^1})(MeCN)][BPh_4]_2$ (* P=O stretch, ^ C≡N stretch)



S4.2 ESI^+ MS (MeCN) of $[Co(\mathbf{L^1})(MeCN)][BPh_4]_2$



S4.3 UV-vis spectrum (MeCN) of [Co(**L**^{1})(MeCN)][BPh_4]$_2$

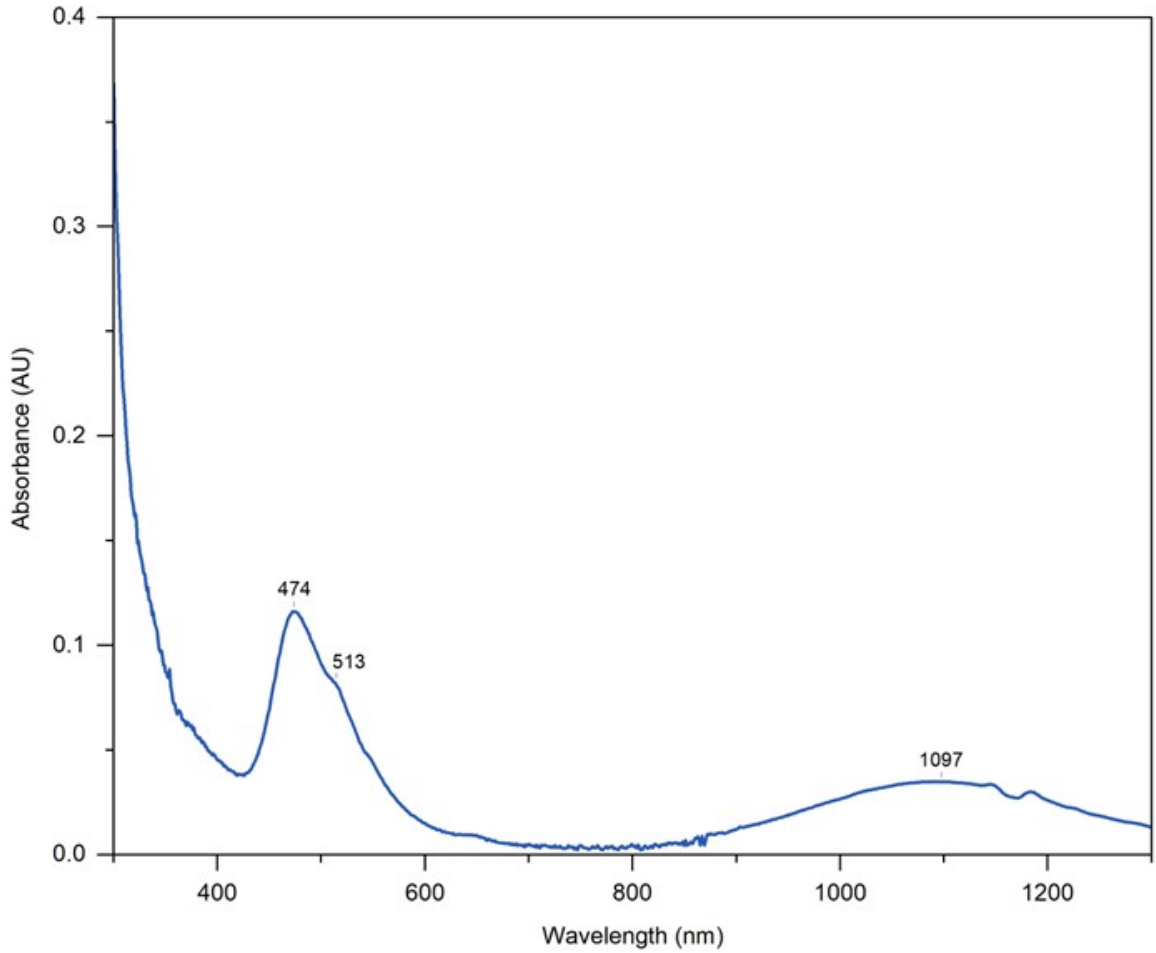
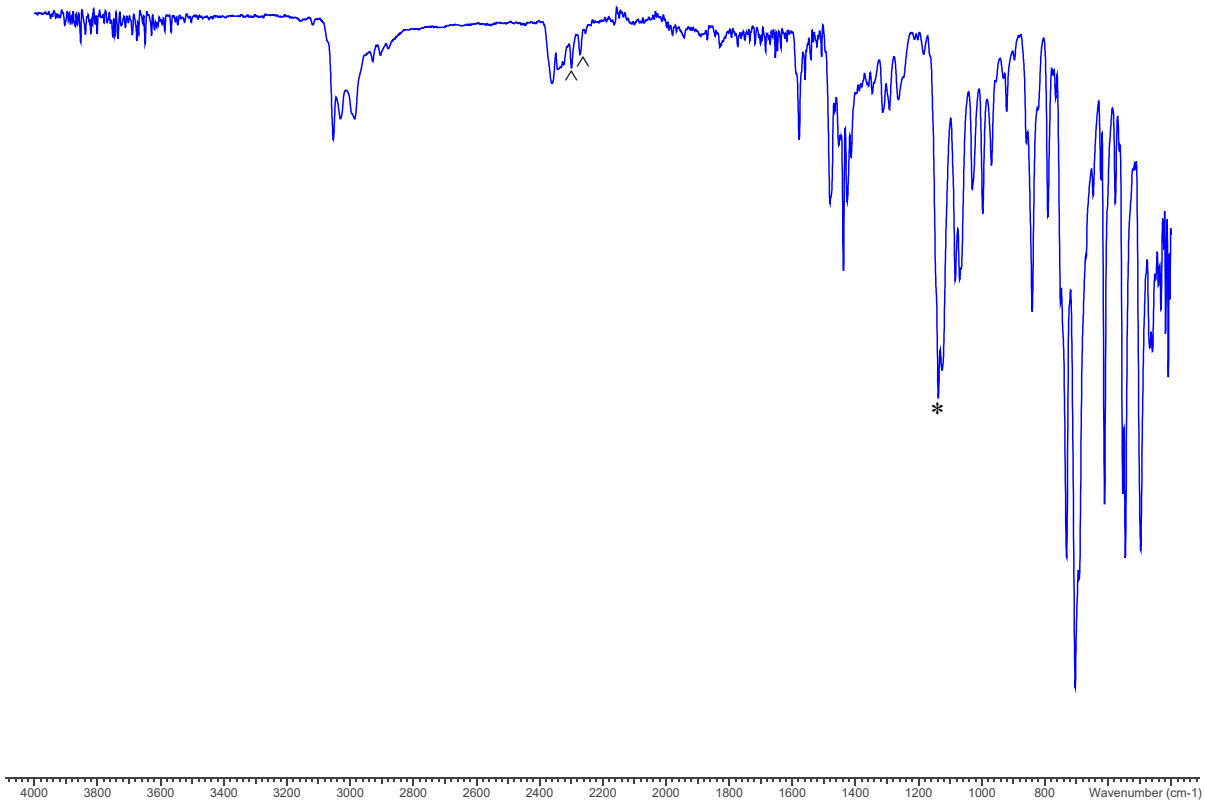
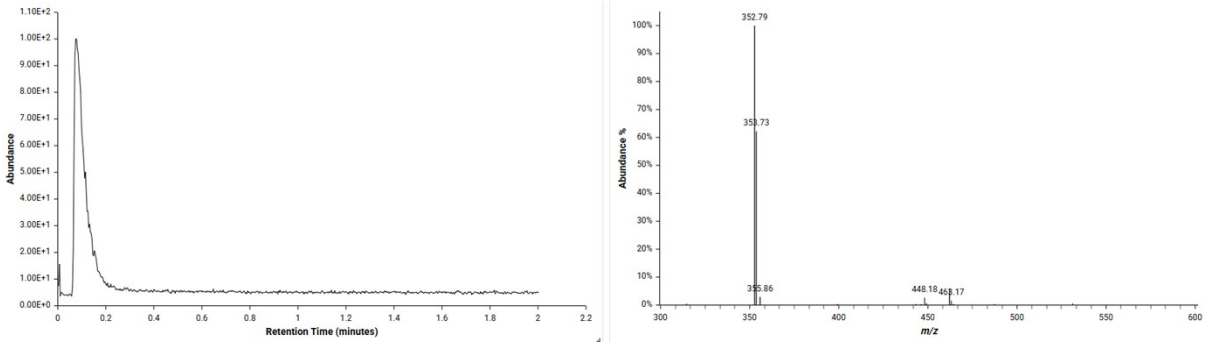


Figure S5: Spectroscopic data for [Ni(L¹)(MeCN)][BPh$_4$]$_2$

S5.1 IR spectrum of [Ni(**L¹**)(MeCN)][BPh$_4$]$_2$ (* P=O stretch, ^ C≡N stretch)



S5.2 ESI$^+$ MS (MeCN) of [Ni(**L¹**)(MeCN)][BPh$_4$]$_2$



S5.3 UV-vis spectrum (MeCN) of [Ni(**L¹**)(MeCN)][BPh$_4$]$_2$

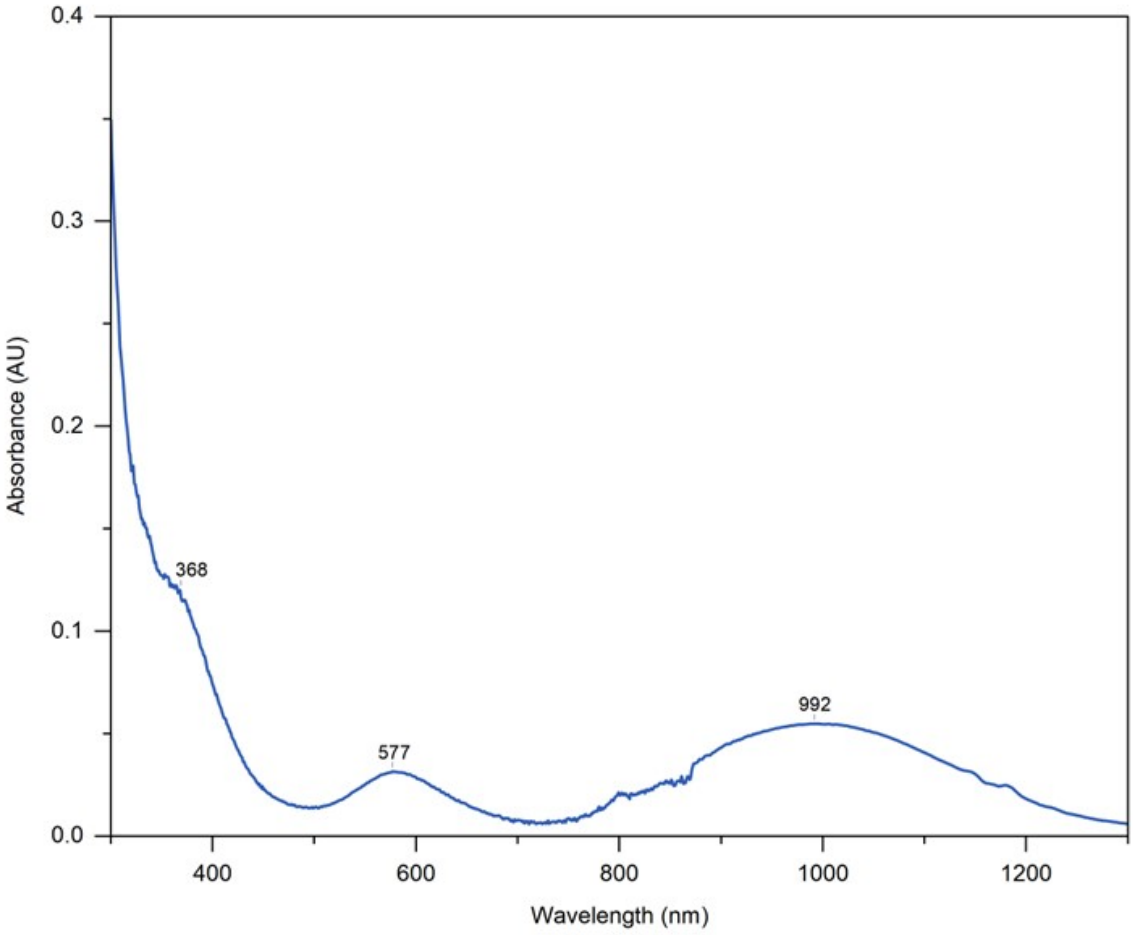
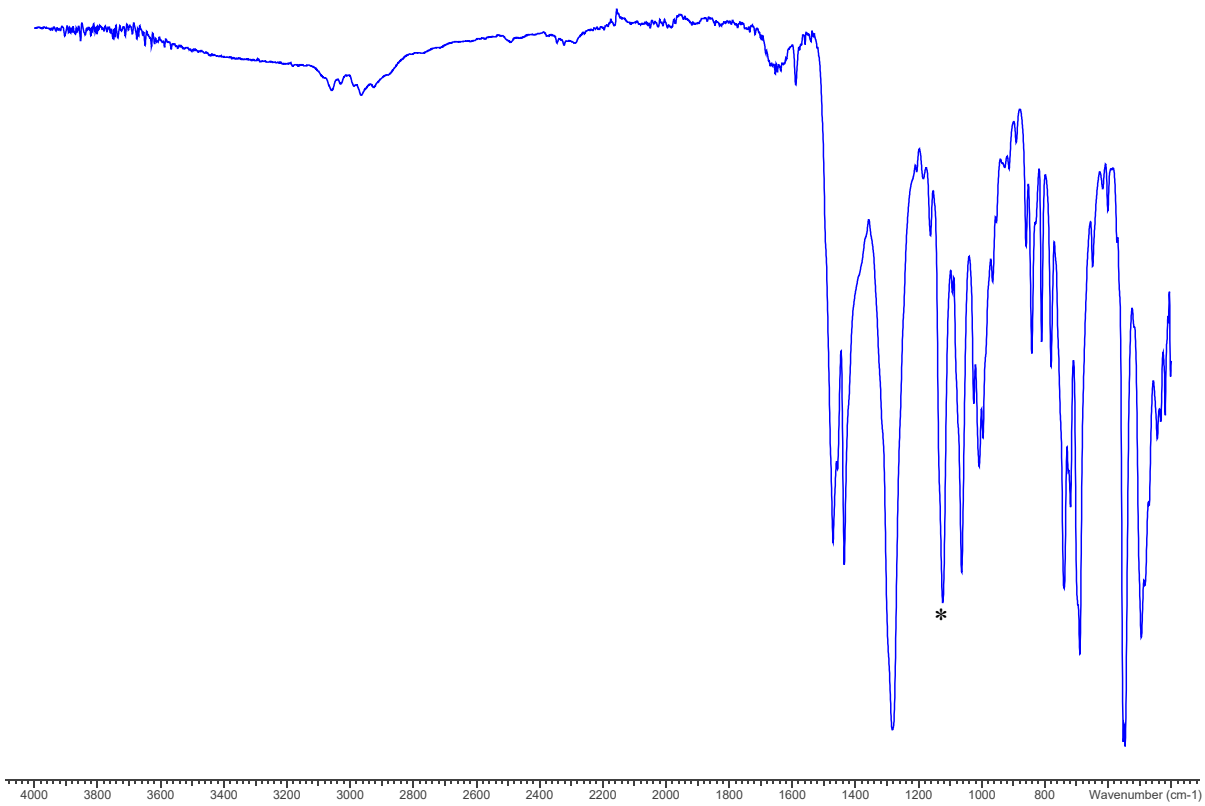
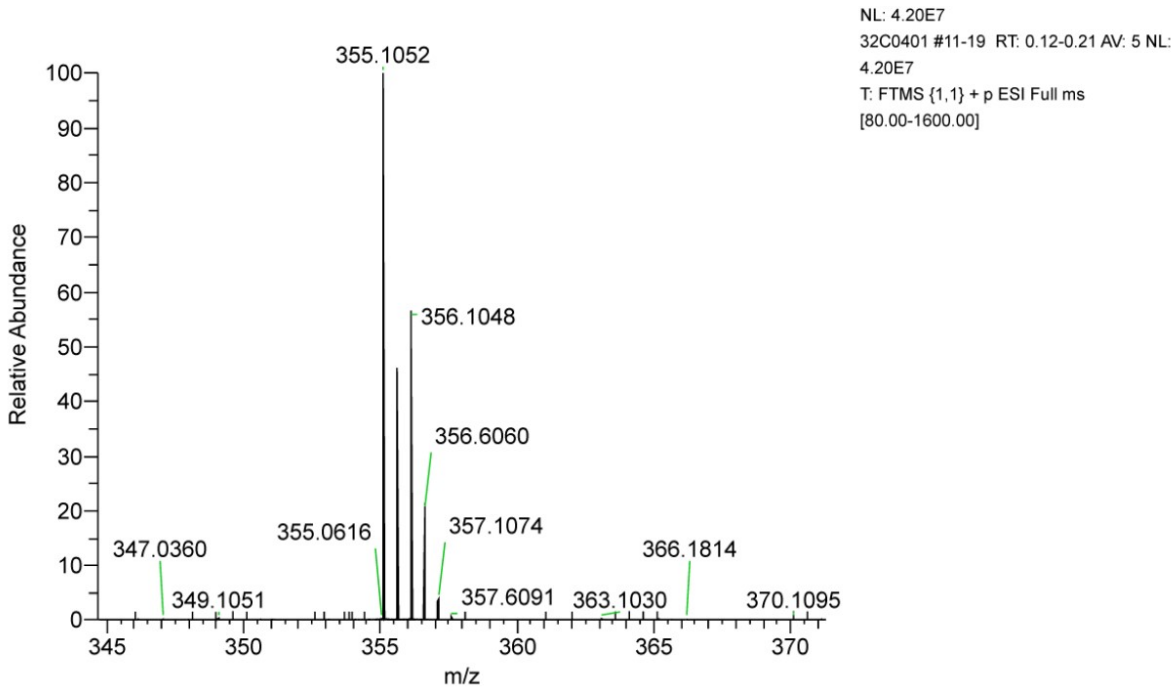

0.4
0.3
0.2
0.1
0.0
Absorbance (AU)
368
577
992
400
600
800
1000
1200
Wavelength (nm)

Figure S6: Spectroscopic data for [Cu(L¹){Cu(NO$_3$)$_4$}]

S6.1 IR spectrum of [Cu(**L¹**){Cu(NO$_3$)$_4$}] (*coordinated P=O)



S6.2 ESI$^+$ MS (MeCN) of [Cu(**L¹**){Cu(NO$_3$)$_4$}]



S6.3 UV-vis spectrum (MeCN) of [Cu(**L**^{1}){Cu(NO_3)$_4$}]

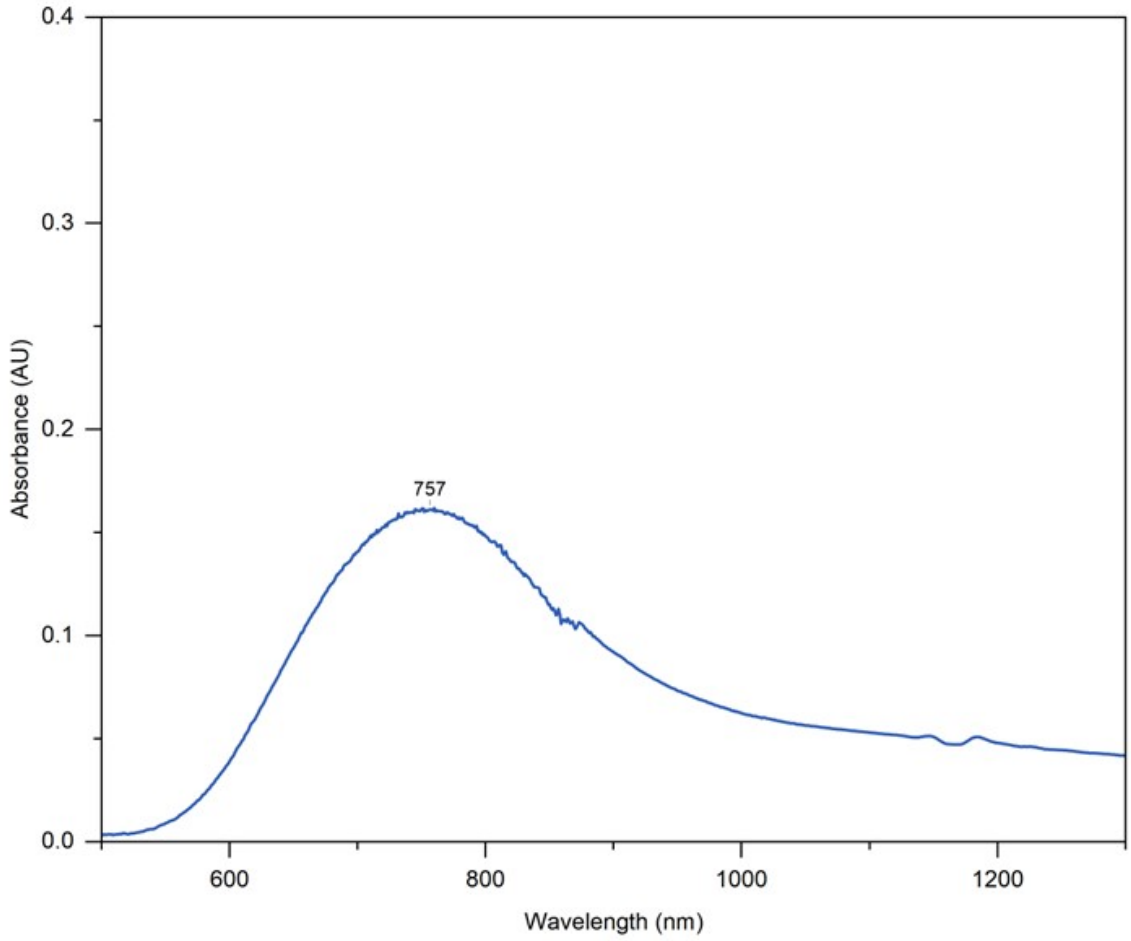
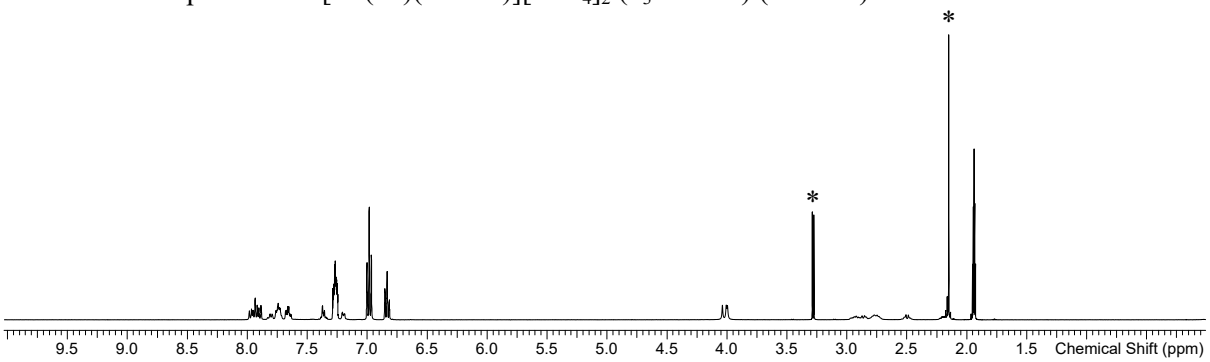
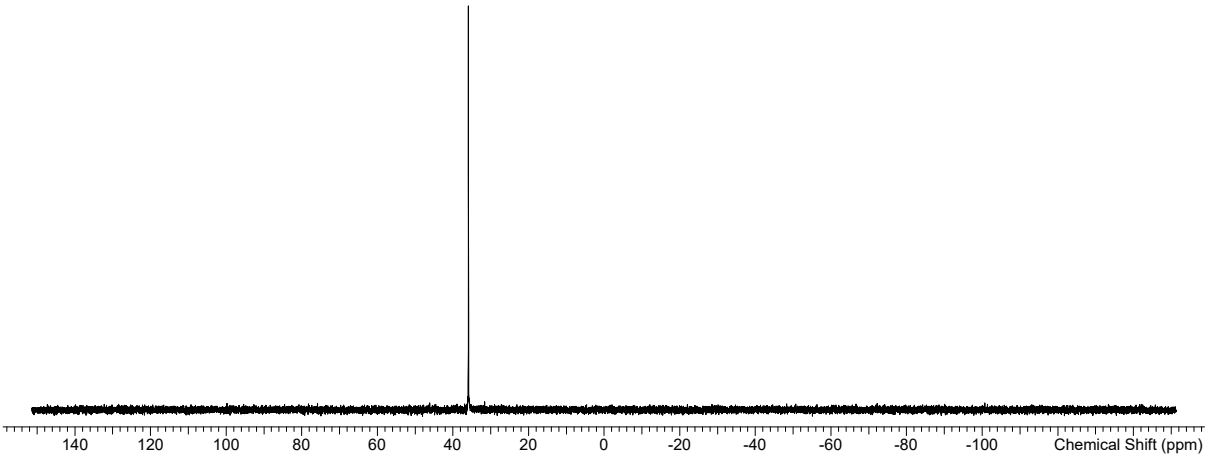


Figure S7: Spectroscopic data for $[Zn(L^1)(MeCN)][BPh_4]_2$

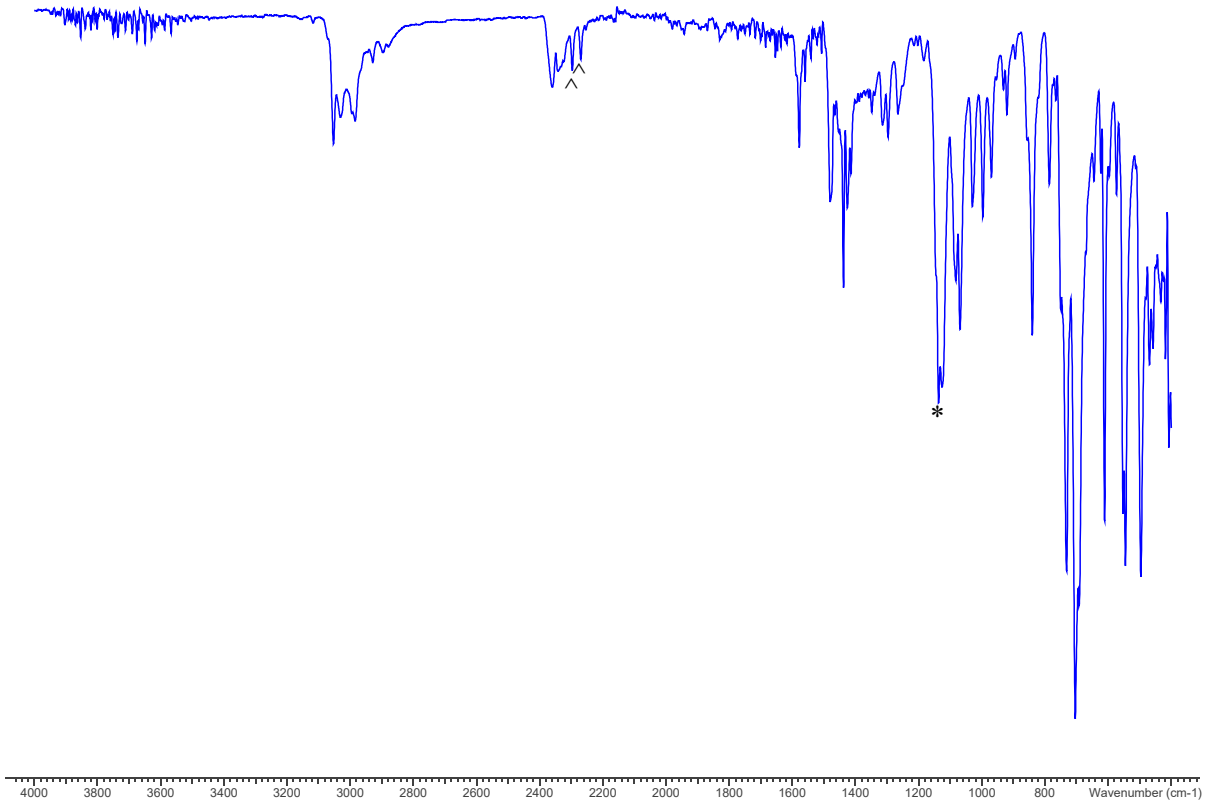
S7.1 ^1H NMR spectrum of $[Zn(\mathbf{L^1})(MeCN)][BPh_4]_2$ (d_3-MeCN) (*MeOH)



S7.2 $^{31}P\{^1H\}$ NMR spectrum of $[Zn(\mathbf{L^1})(MeCN)][BPh_4]_2$ (d_3-MeCN)



S7.3 IR spectrum of [Zn(**L**^{1})(MeCN)][BPh_4]$_2$ (* P=O stretch, ^ C≡N stretch)



S7.4 ESI^{+} MS (MeCN) of [Zn(**L**^{1})(MeCN)][BPh_4]$_2$

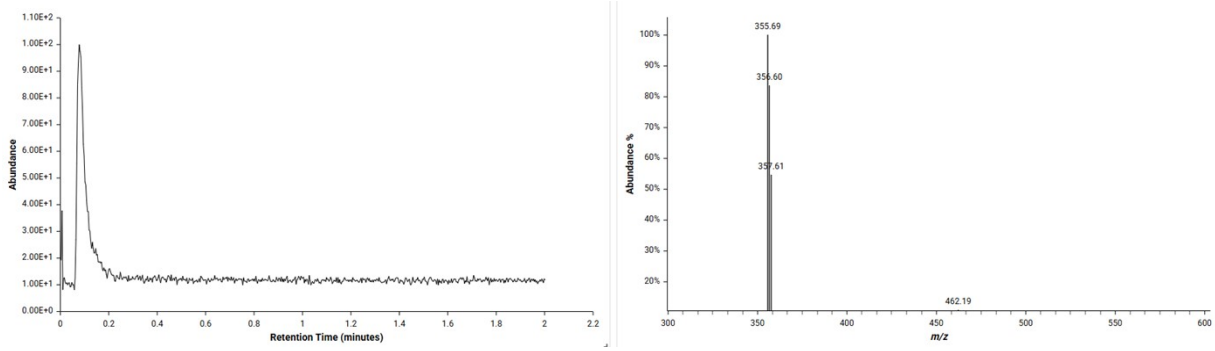
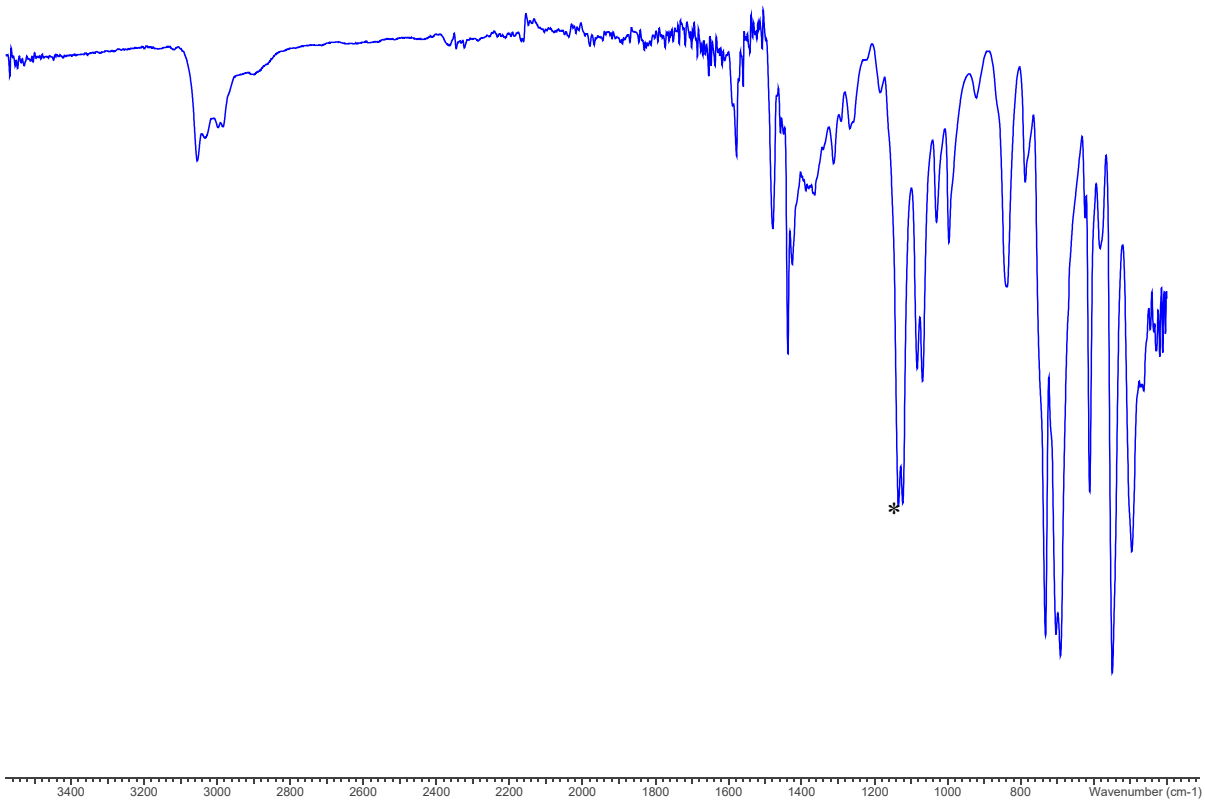
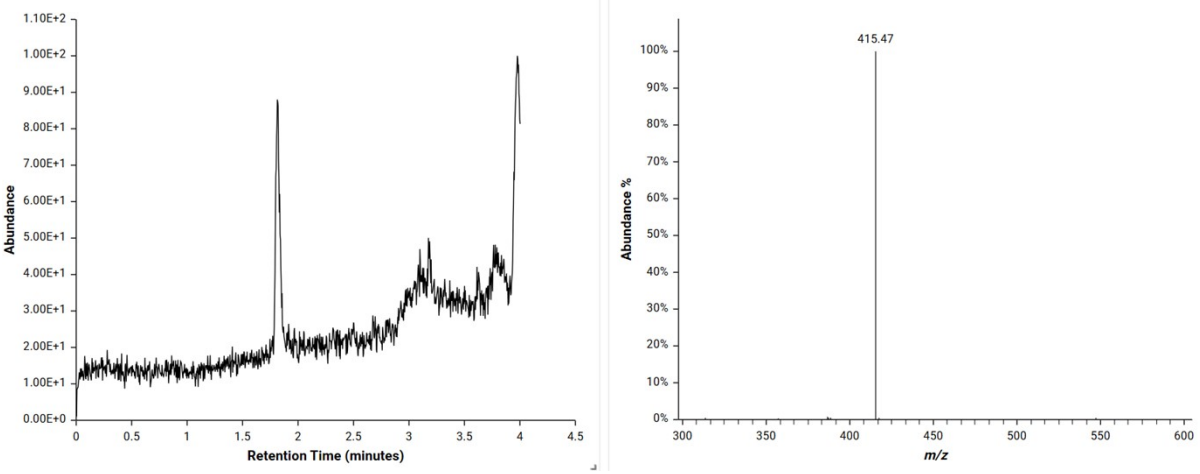


Figure S8: Spectroscopic data for [Co(L^{2})][BPh_4]$_2$

S8.1 IR spectrum of [Co(**L²**)][BPh_4]$_2$ (*coordinated P=O)



S8.2 ESI+ MS of [Co(**L²**)][BPh_4]$_2$ (MeCN)



S8.3 UV-vis spectrum (MeCN) of $[Co(\mathbf{L}^2)][BPh_4]_2$

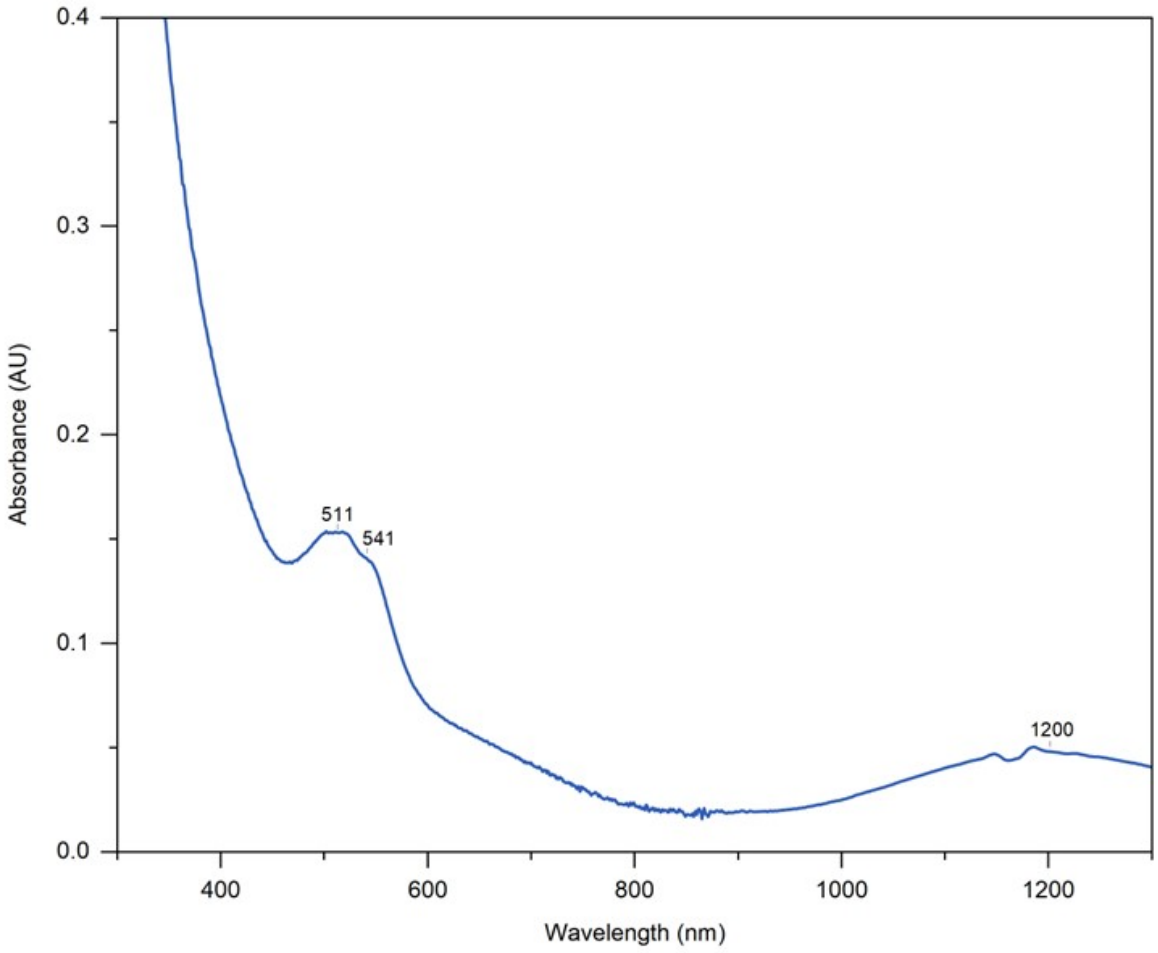
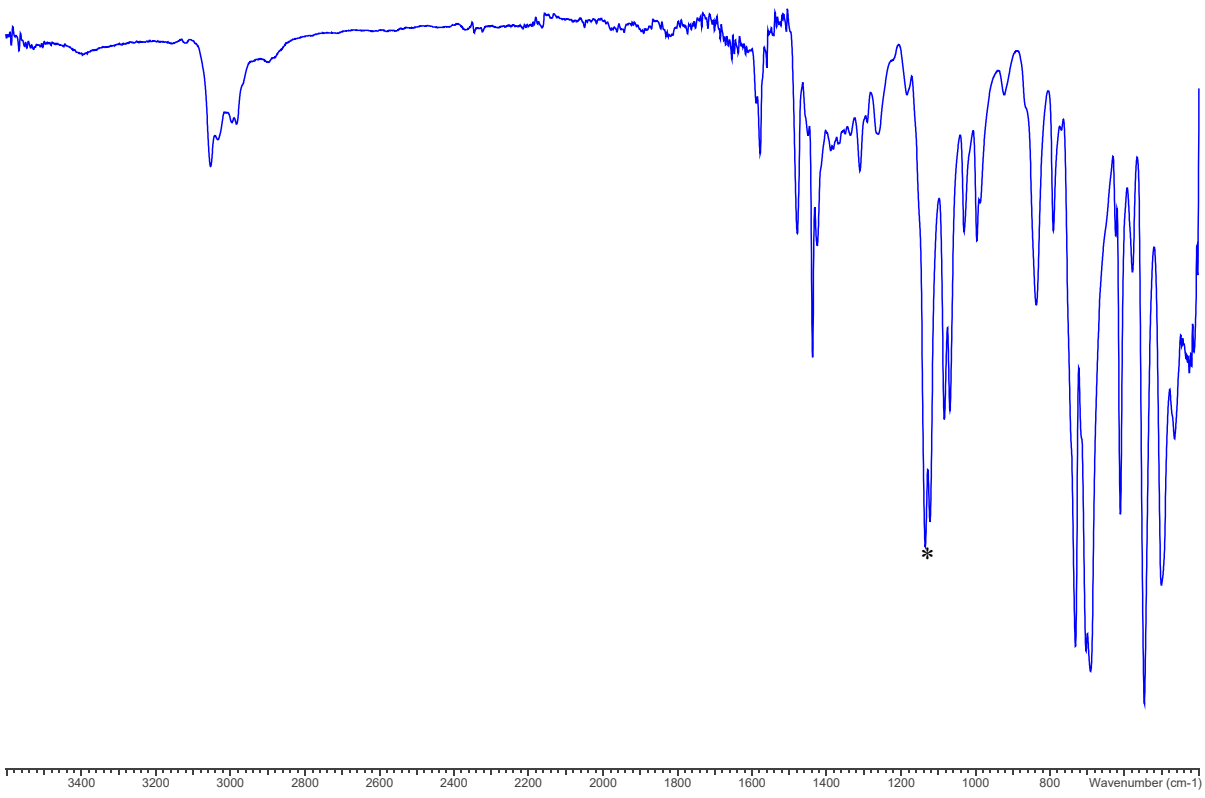
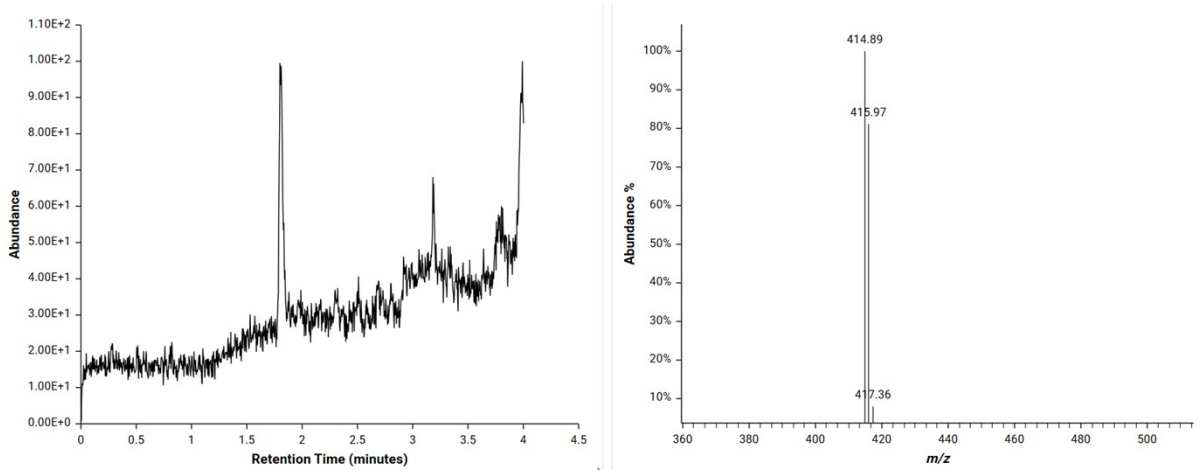


Figure S9: Spectroscopic data for [Ni(L²)][BPh₄]₂

S9.1 IR spectrum of [Ni(**L²**)][BPh_4]$_2$ (*coordinated P=O)



S9.2 ESI+ MS of [Ni(**L²**)][BPh_4]$_2$ (MeCN)



S9.3 UV-vis spectrum (MeCN) of [Ni($\mathbf{L^2}$)][BPh_4]$_2$

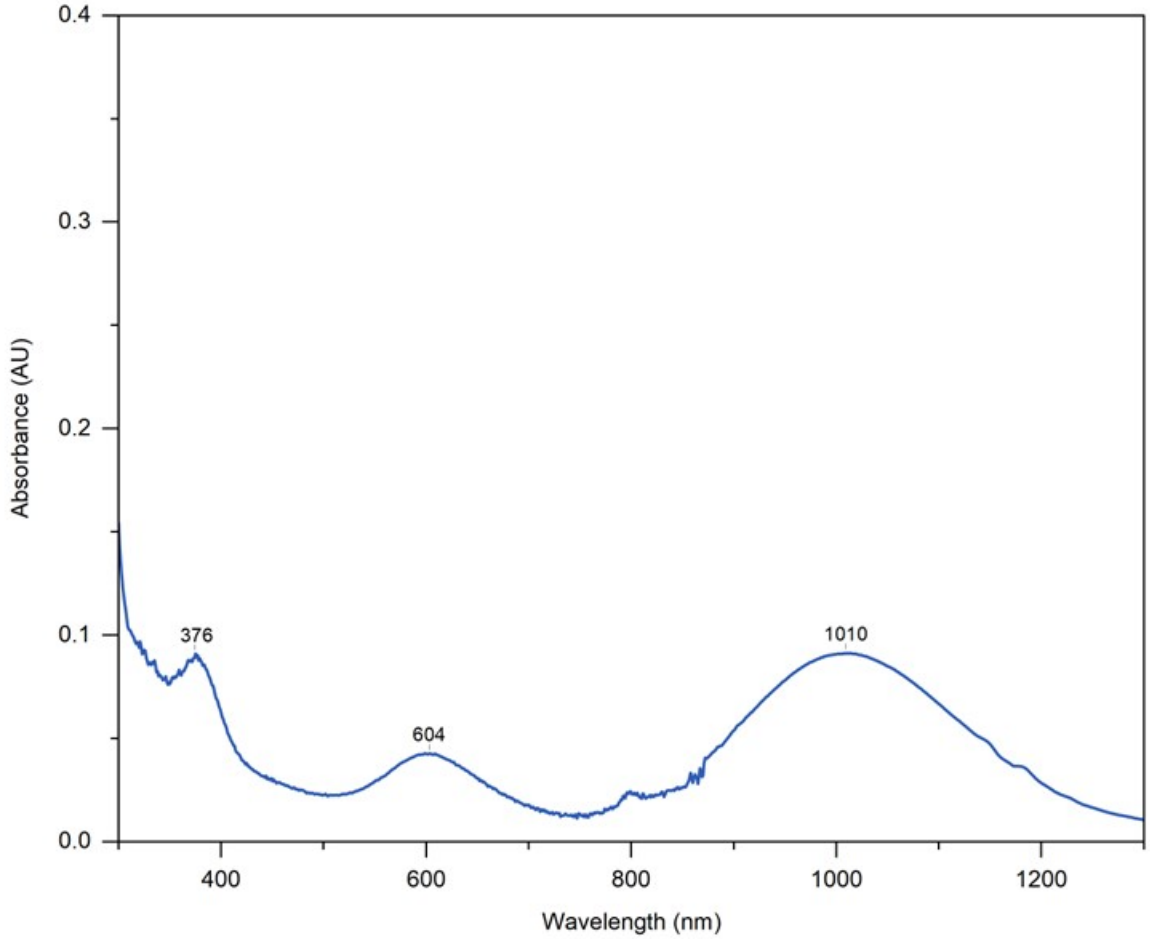
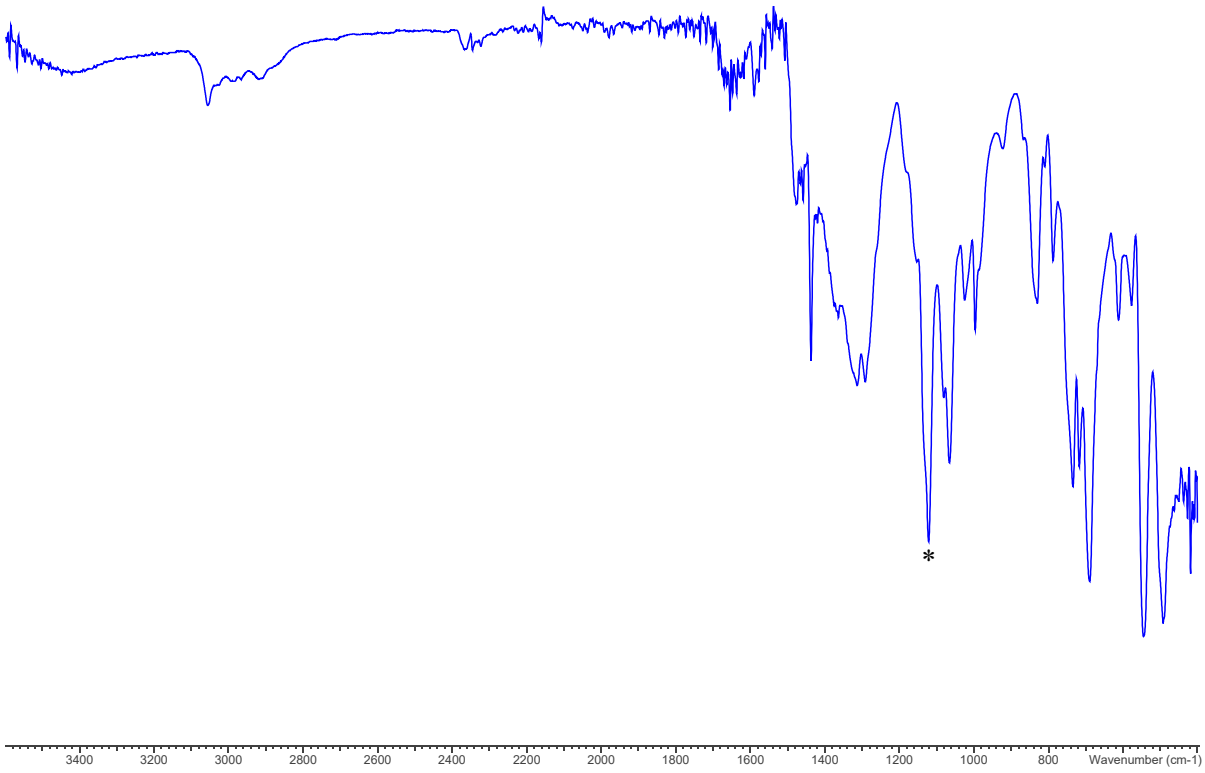
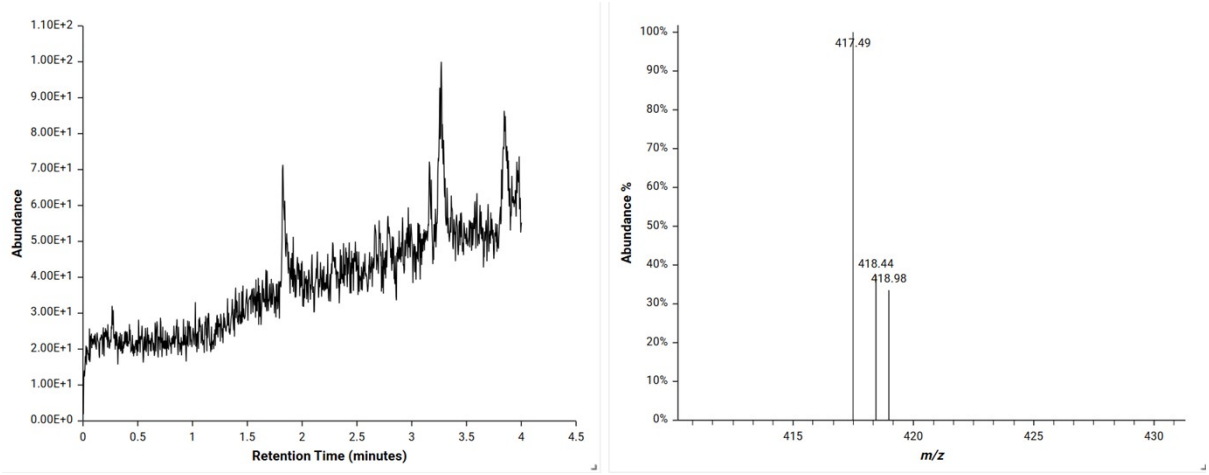


Figure **S10: Spectroscopic data for [Cu(L²)][Cu(NO₃)₄]**

S10.1 IR spectrum of [Cu(**L²**)][Cu(NO_3)$_4$] (*coordinated P=O)



S10.2 ESI+ MS of [Cu(**L²**)][Cu(NO_3)$_4$] (MeCN)



S10.3 UV-vis spectrum of $[Cu(\mathbf{L^2})][Cu(NO_3)_4]$

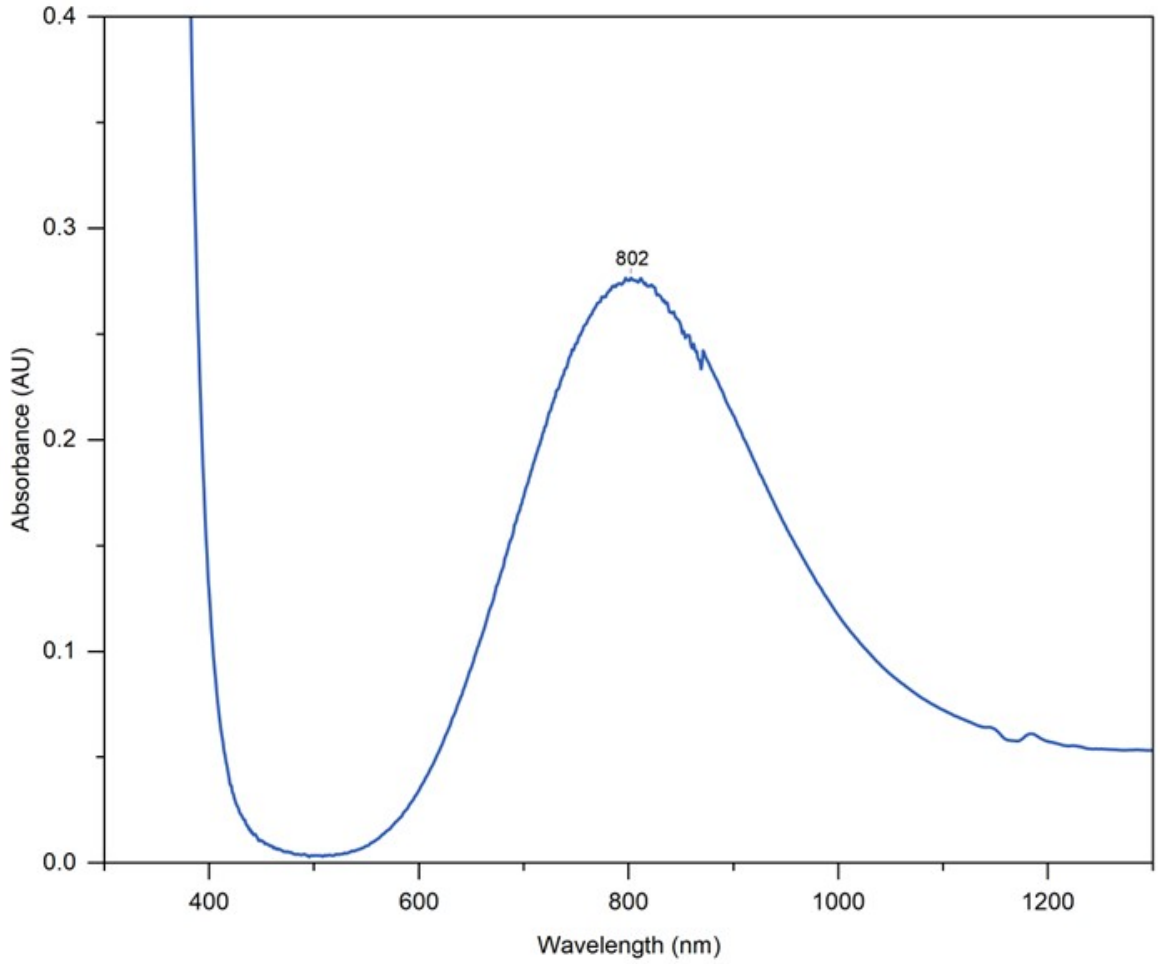
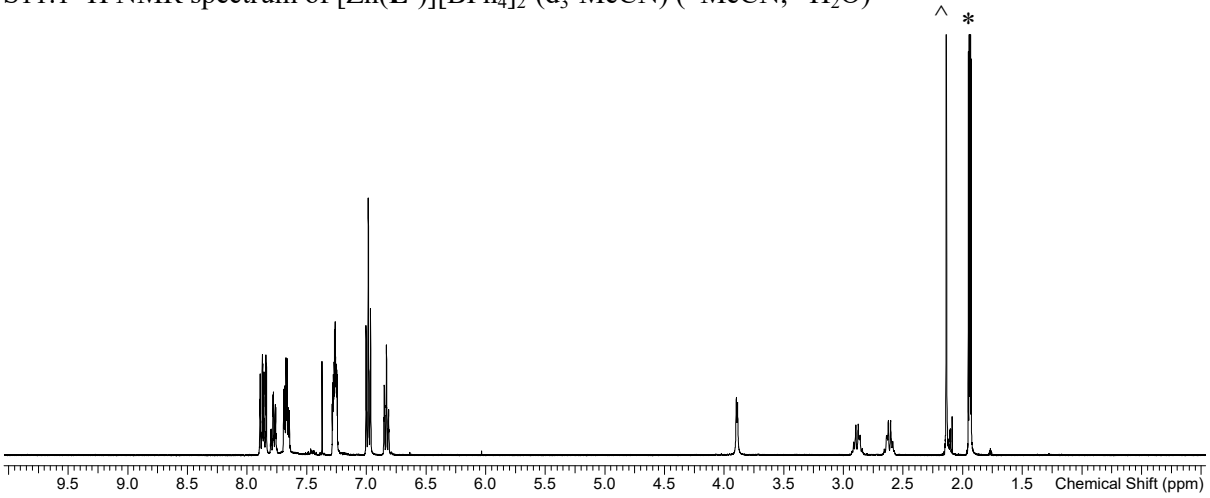
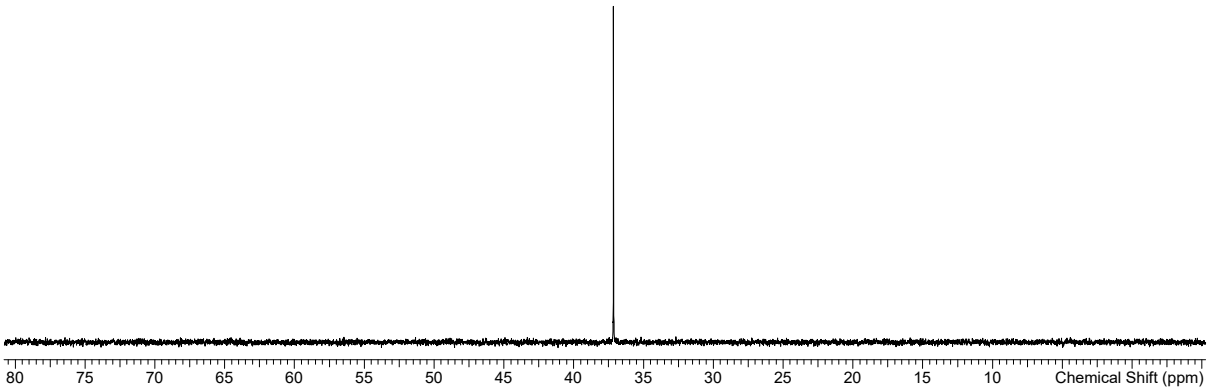


Figure S11: Spectroscopic data for $[Zn(\mathbf{L^2})][BPh_4]_2$

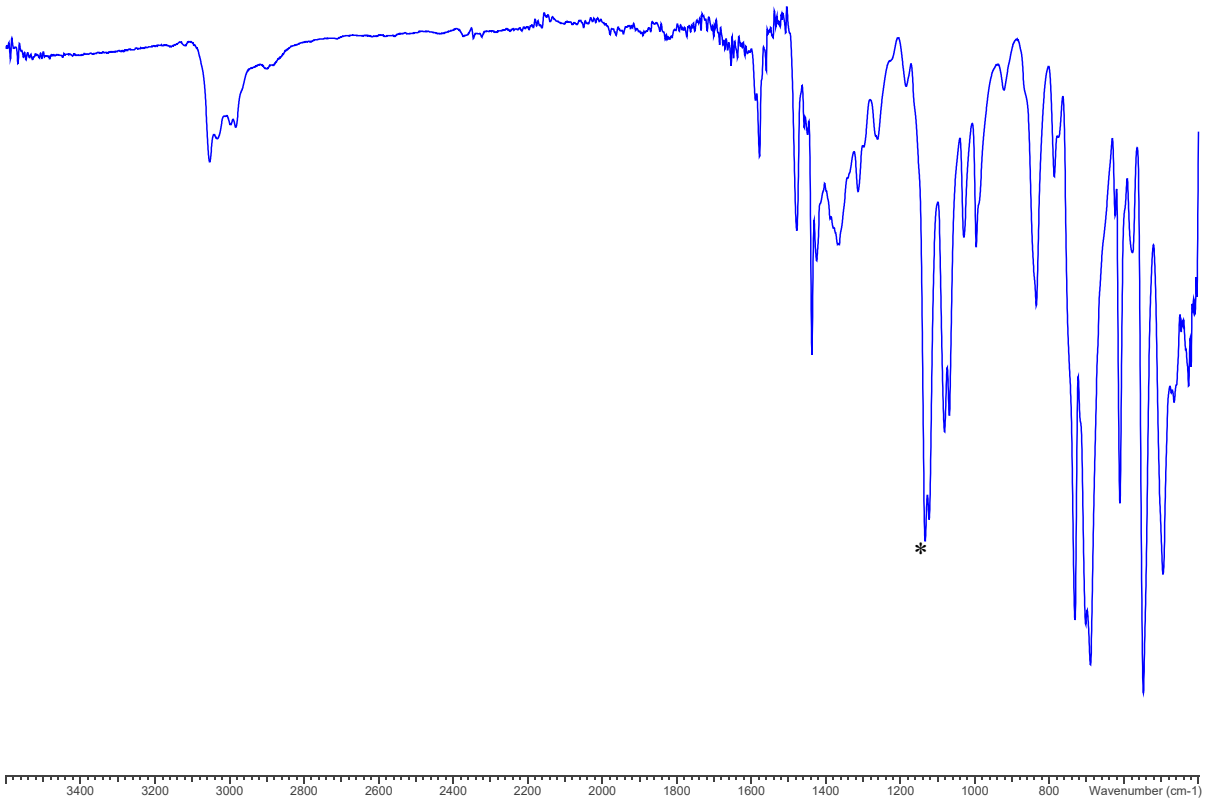
S11.1 ^{1}H NMR spectrum of $[Zn(\mathbf{L^2})][BPh_4]_2$ (d_3-MeCN) (*MeCN; ^H_2O)



S11.2 $^{31}P\{^{1}H\}$ NMR spectrum of $[Zn(\mathbf{L^2})][BPh_4]_2$ (d_3-MeCN)



S11.3 IR spectrum of $[Zn(\mathbf{L^2})][BPh_4]_2$ (*P=O)



S11.4 ESI+ MS of $[Zn(\mathbf{L^2})][BPh_4]_2$ (MeCN)

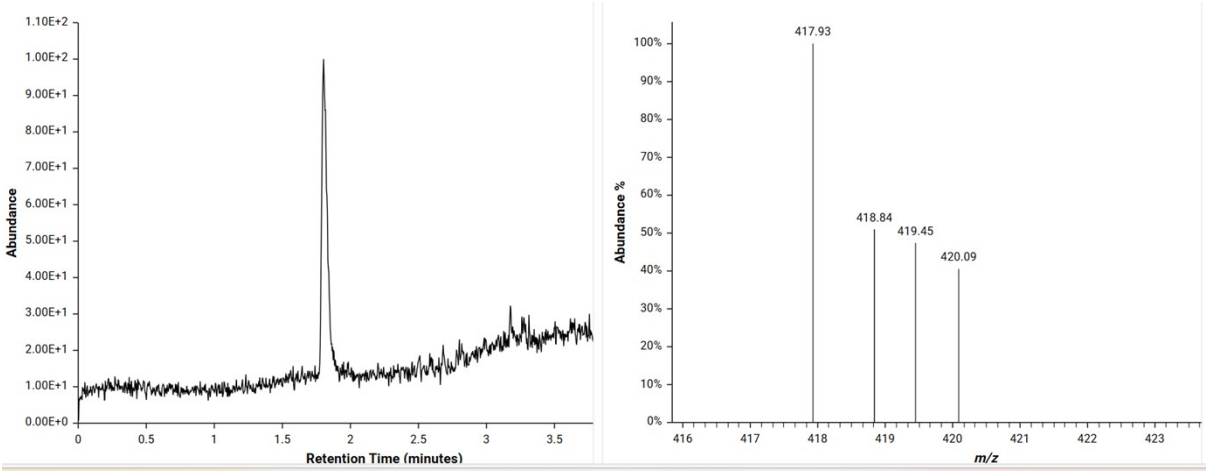
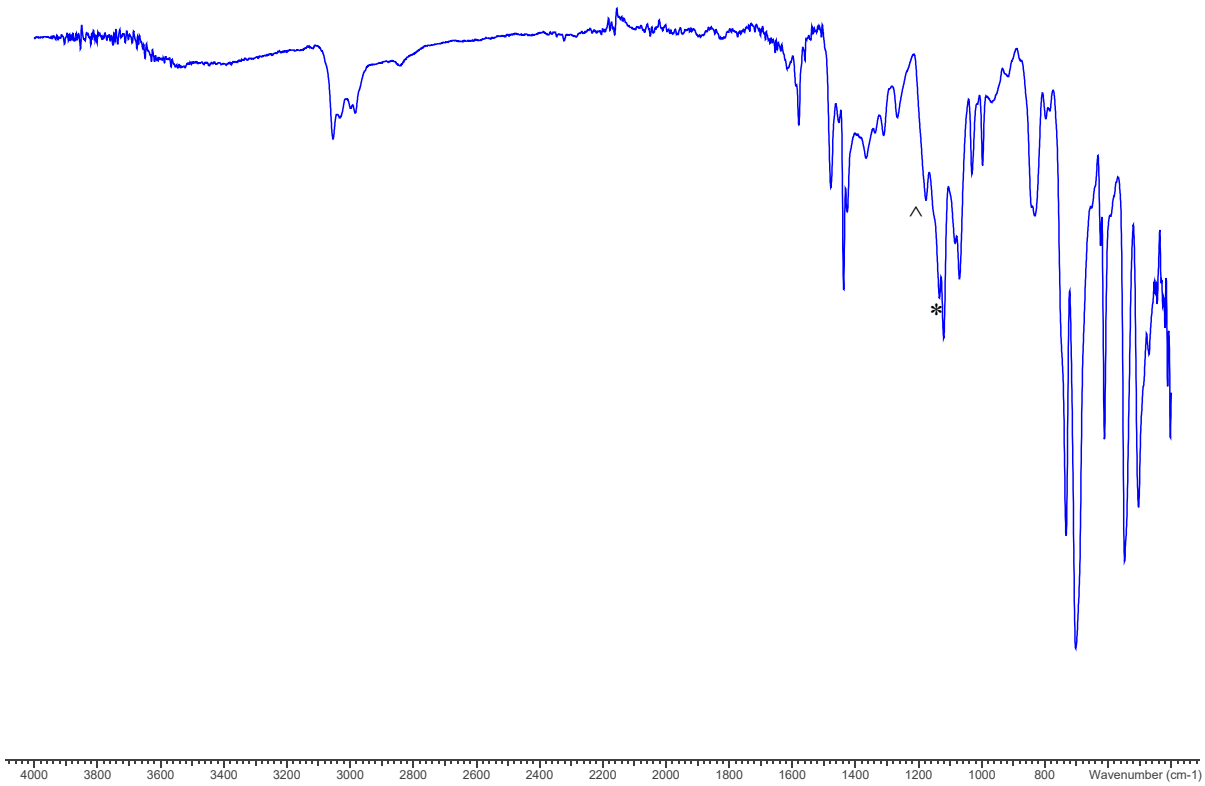
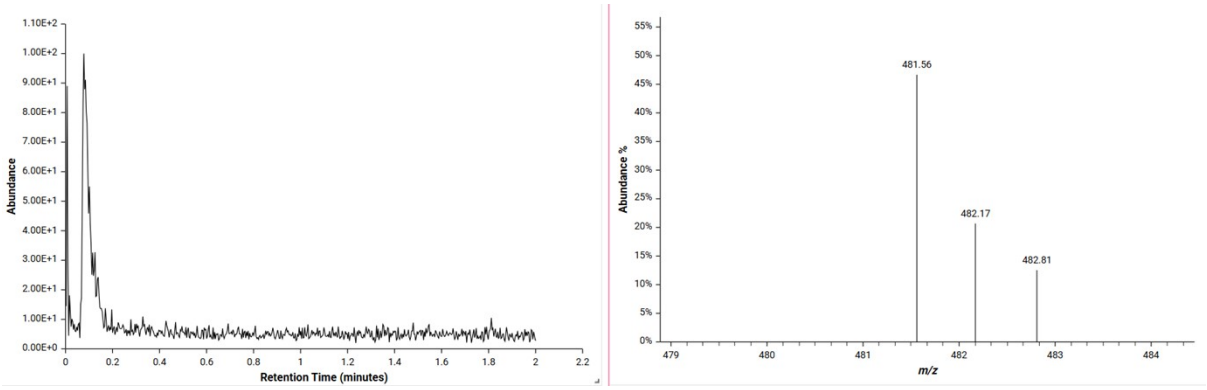


Figure S12: Spectroscopic data for $[Co(L^3)][BPh_4]_2$

S12.1 IR spectrum of $[Co(\mathbf{L^3})][BPh_4]_2$ (*coordinated P=O, ^uncoordinated P=O)



S12.2 ESI+ MS of $[Co(\mathbf{L^3})][BPh_4]_2$ (MeCN)



S12.3 UV-vis spectrum of $[Co(\mathbf{L}^3)][BPh_4]_2$

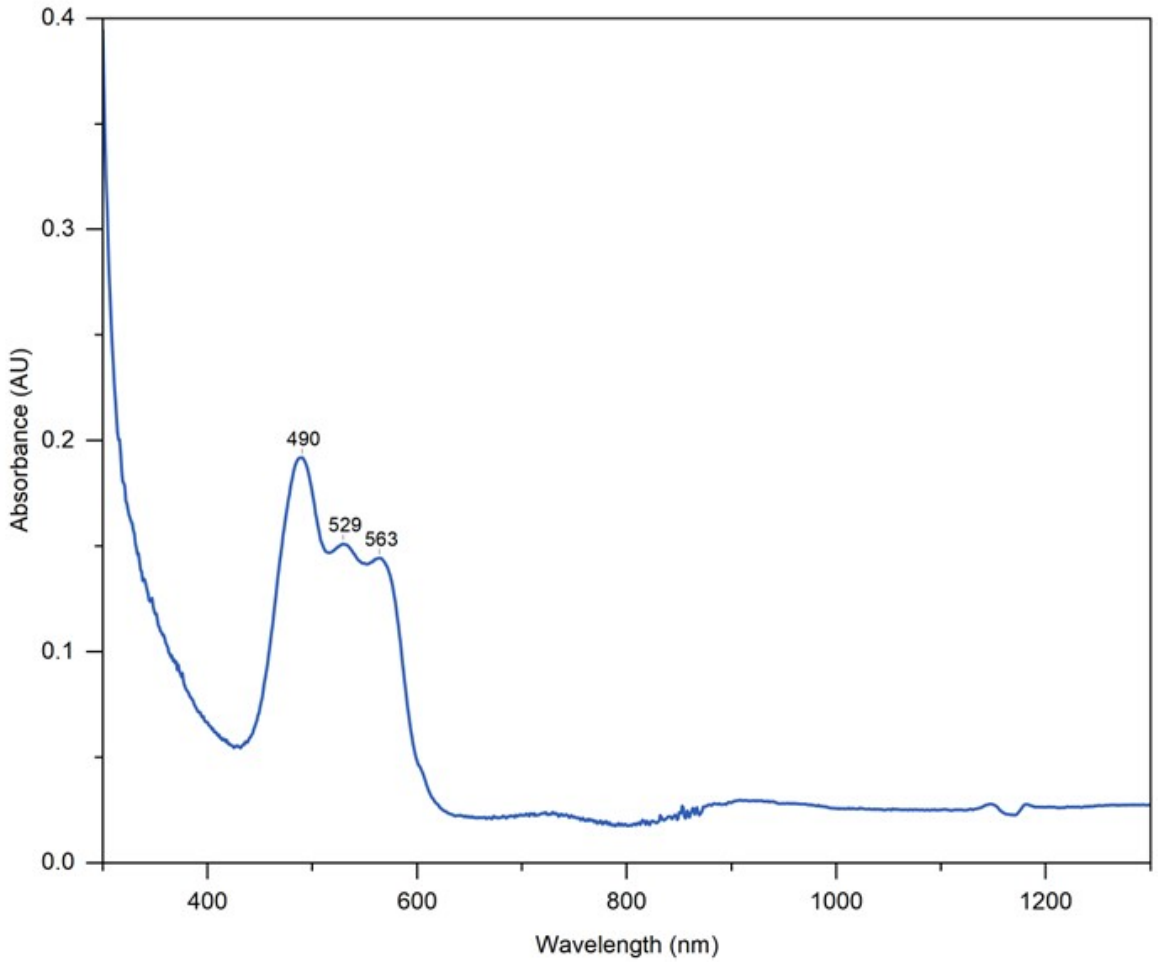
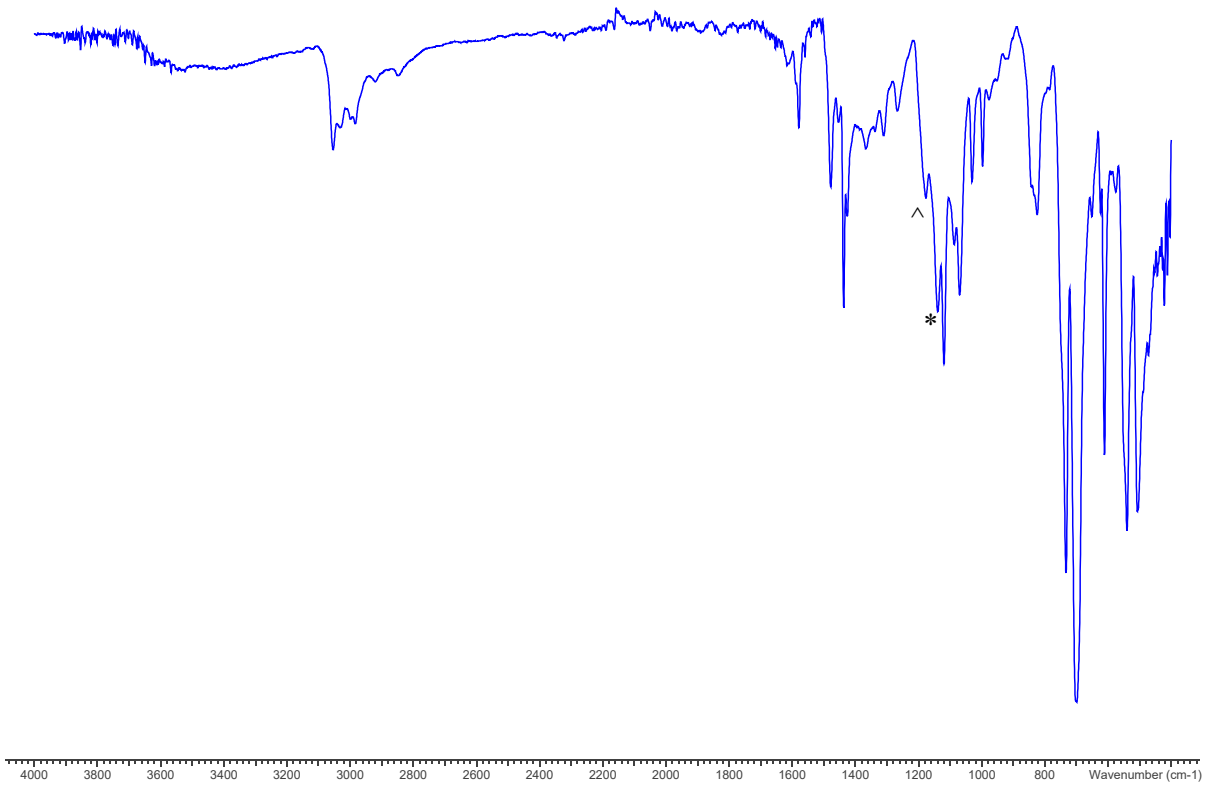
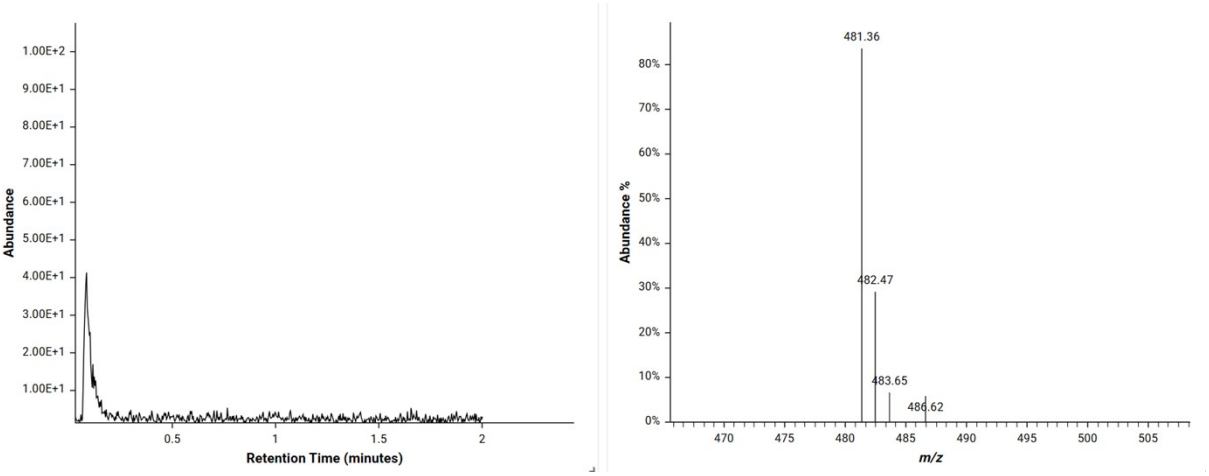


Figure S13: Spectroscopic data for [Ni(L^3)][BPh$_4$]$_2$

S13.1 IR spectrum of [Ni(**L$_3$**)][BPh$_4$]$_2$ (*coordinated P=O, ^uncoordinated P=O)



S13.2 ESI+ MS (MeCN) of [Ni(**L^3**)][BPh$_4$]$_2$



S13.3 UV-vis spectrum of [Ni(**L$_3$**)][BPh$_4$]$_2$

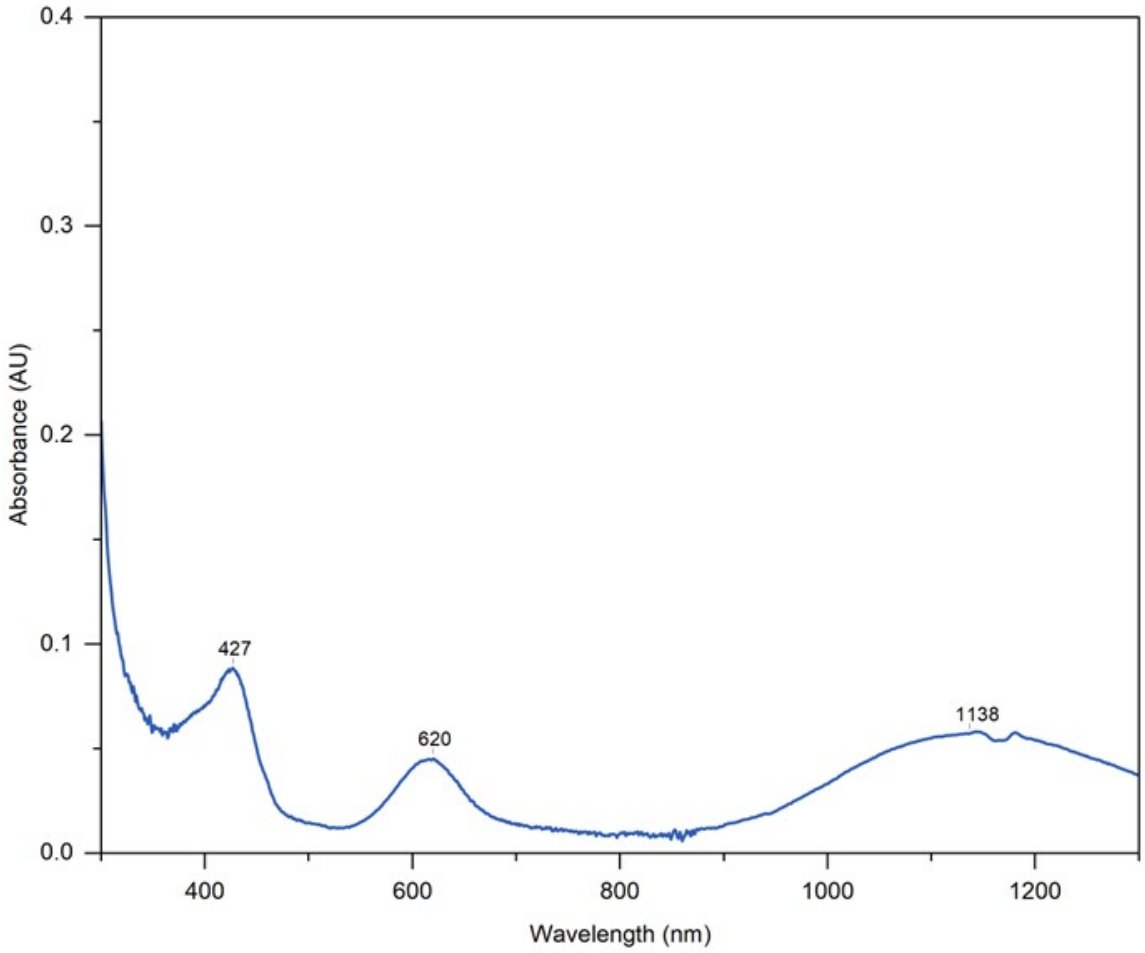
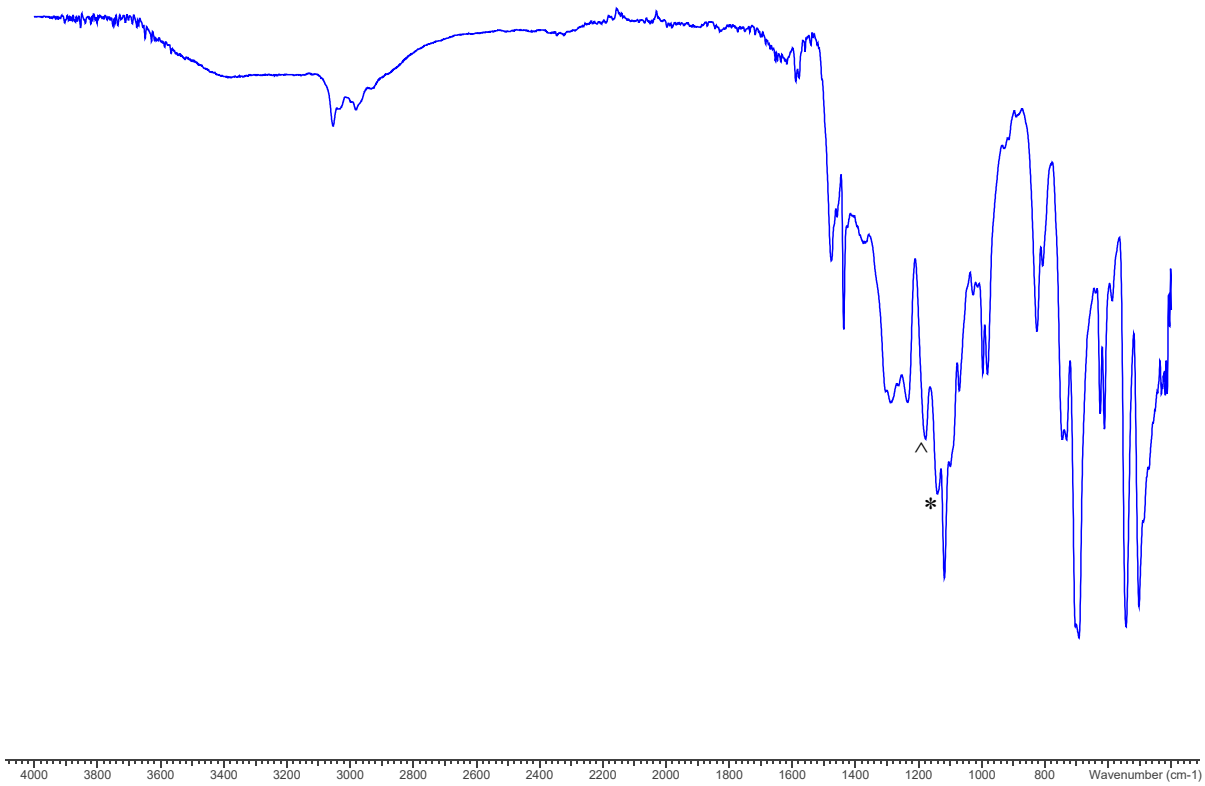
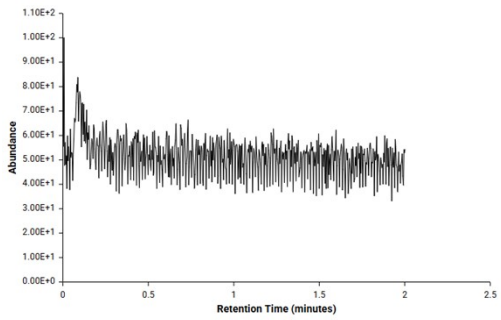

0.4
0.3
0.2
0.1
0.0
Absorbance (AU)
427
620
1138
400
600
800
1000
1200
Wavelength (nm)

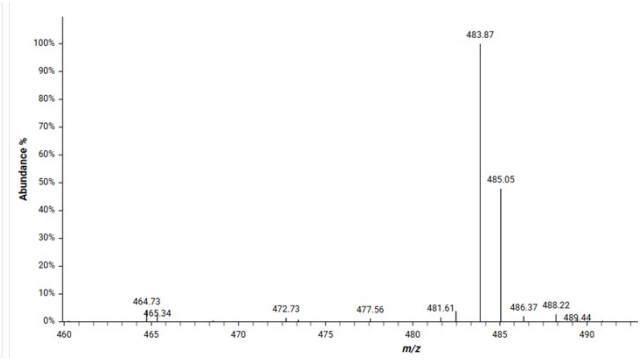
Figure S14: Spectroscopic data for [Cu(L³)][Cu(NO₃)₄]

S14.1 IR spectrum of [Cu(**L³**)][Cu(NO_3)$_4$] (*coordinated P=O, ^uncoordinated P=O)



S14.2 ESI+ MS of [Cu(**L³**)][Cu(NO_3)$_4$] (MeCN)





S14.3 UV-vis spectrum of [Cu(**L³**)][Cu(NO_3)$_4$]

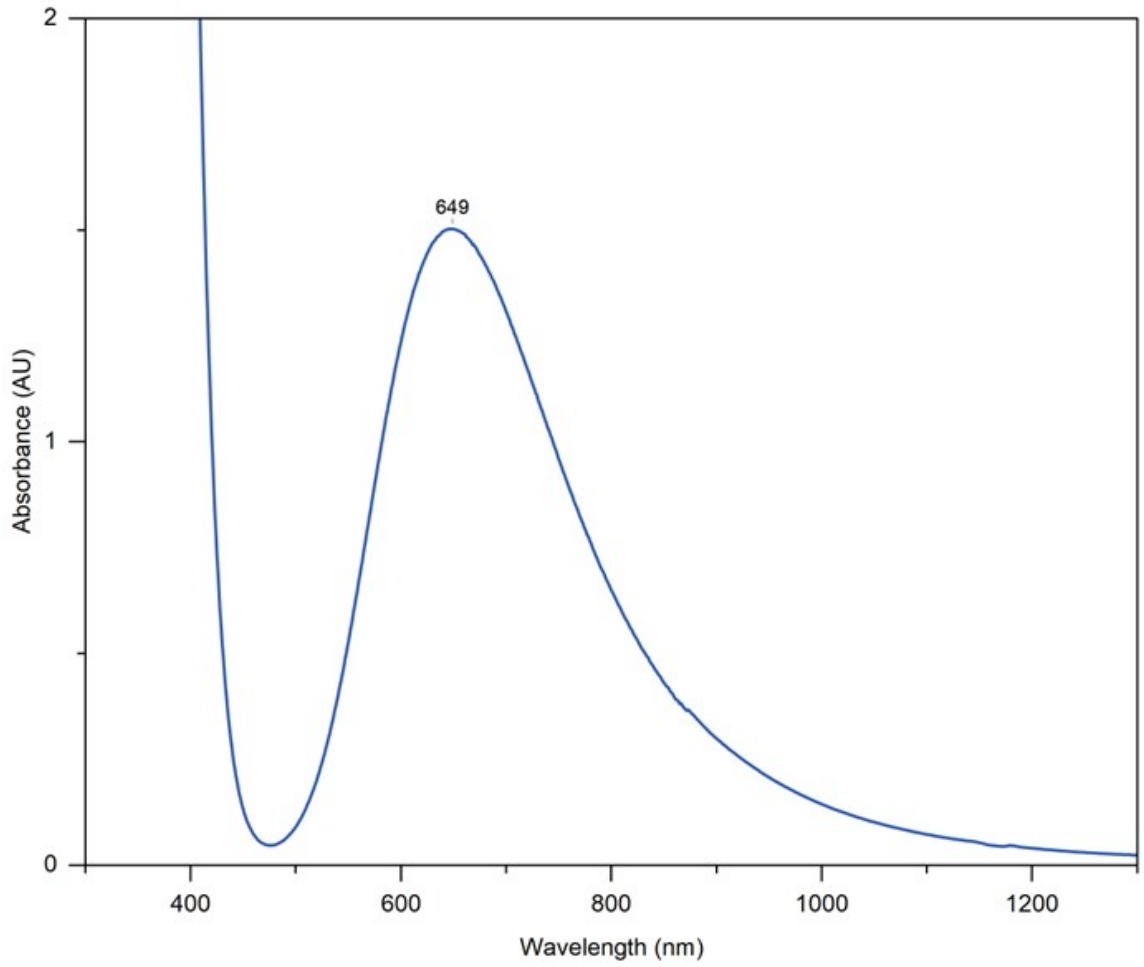
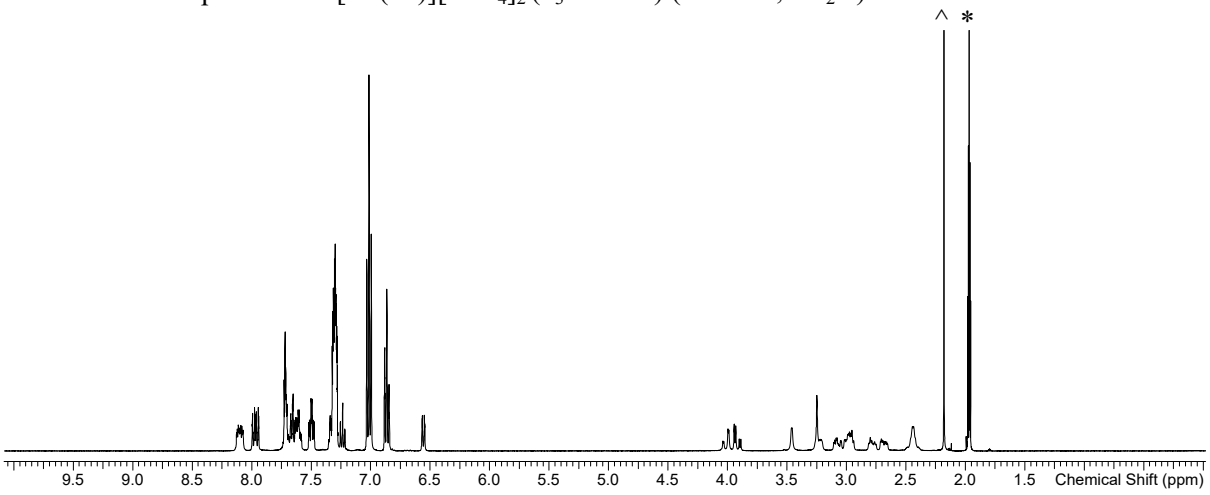
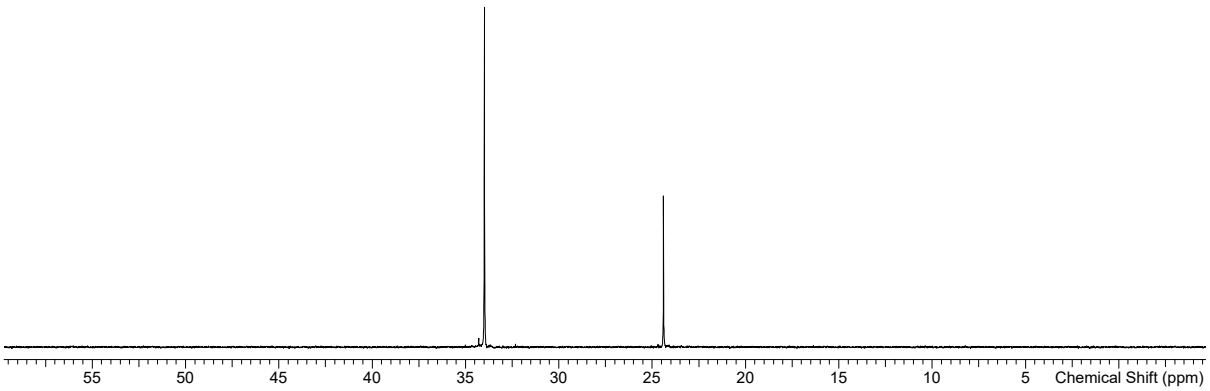

649
Absorbance (AU)
Wavelength (nm)
0
1
2
400
600
800
1000
1200

Figure S15: Spectroscopic data for $[Zn(L^3)][BPh_4]_2$

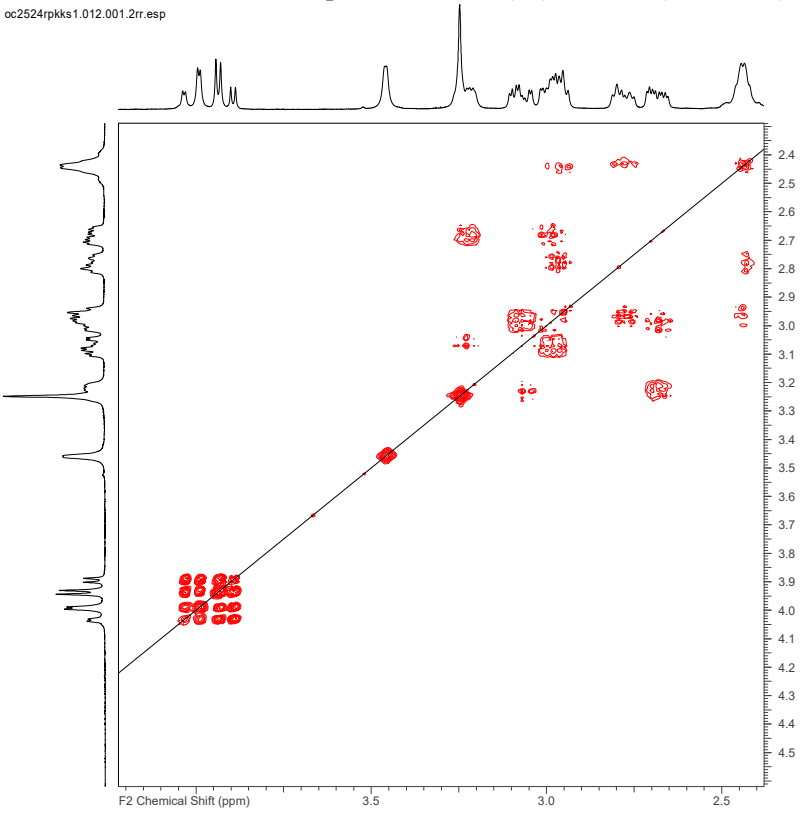
S15.1 ^1H NMR spectrum of $[Zn(\mathbf{L^3})][BPh_4]_2$ (d_3-MeCN) (*MeCN; ^H_2O)



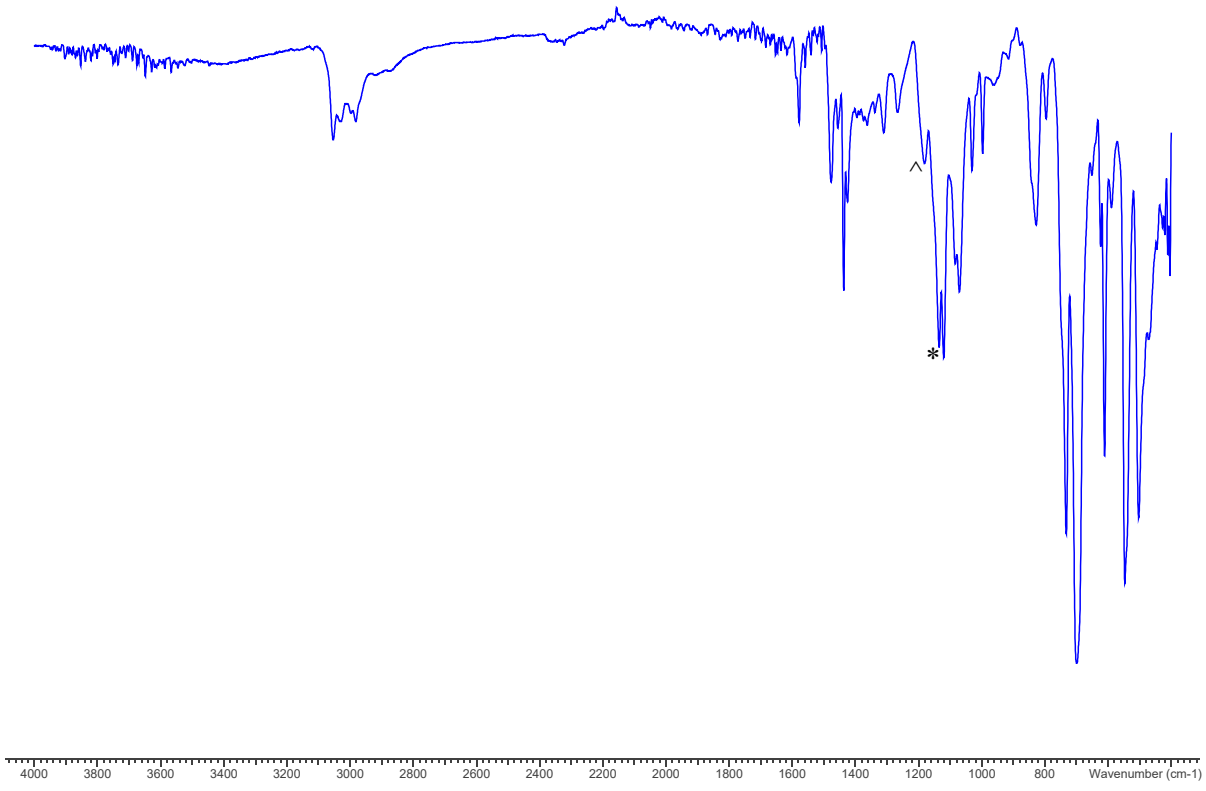
S15.2 $^{31}P\{^1H\}$ NMR spectrum of $[Zn(\mathbf{L_3})][BPh_4]_2$ (d_3-MeCN)



S15.3 ^{1}H-^{1}H COSY NMR spectrum of [Zn(**L**^{3})][BPh_4]$_2$ (d_3-MeCN)



S15.4 IR spectrum of [Zn(**L**^{3})][BPh_4]$_2$ (*coordinated P=O, ^uncoordinated P=O)



S15.5 ESI+ MS of $[Zn(\mathbf{L^3})][BPh_4]_2$ (MeCN)

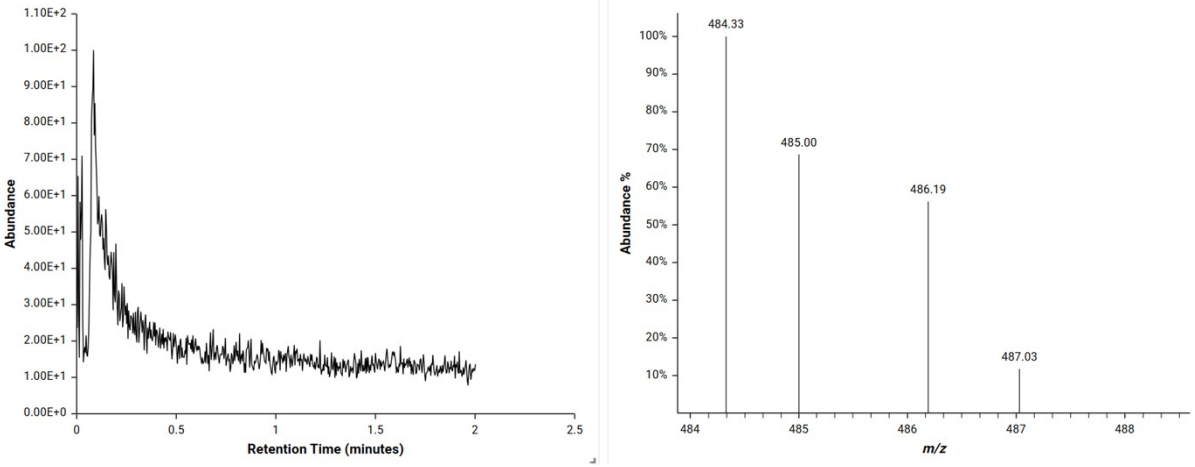
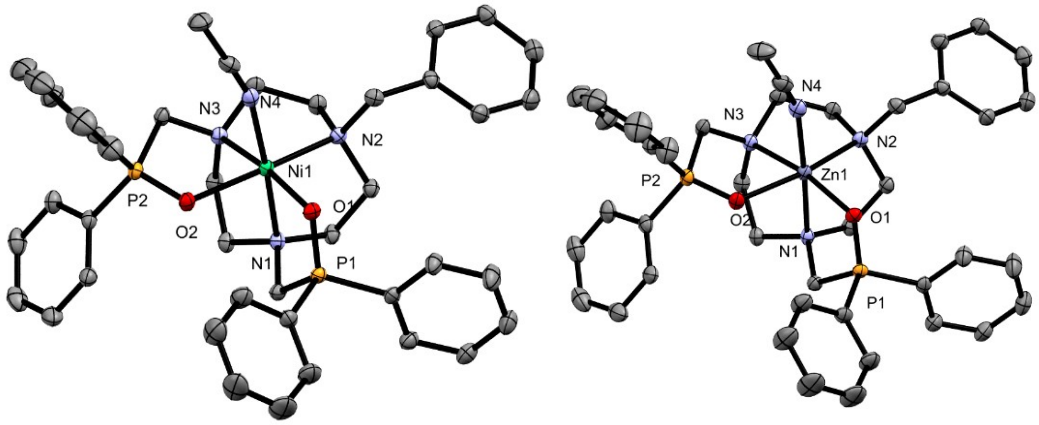
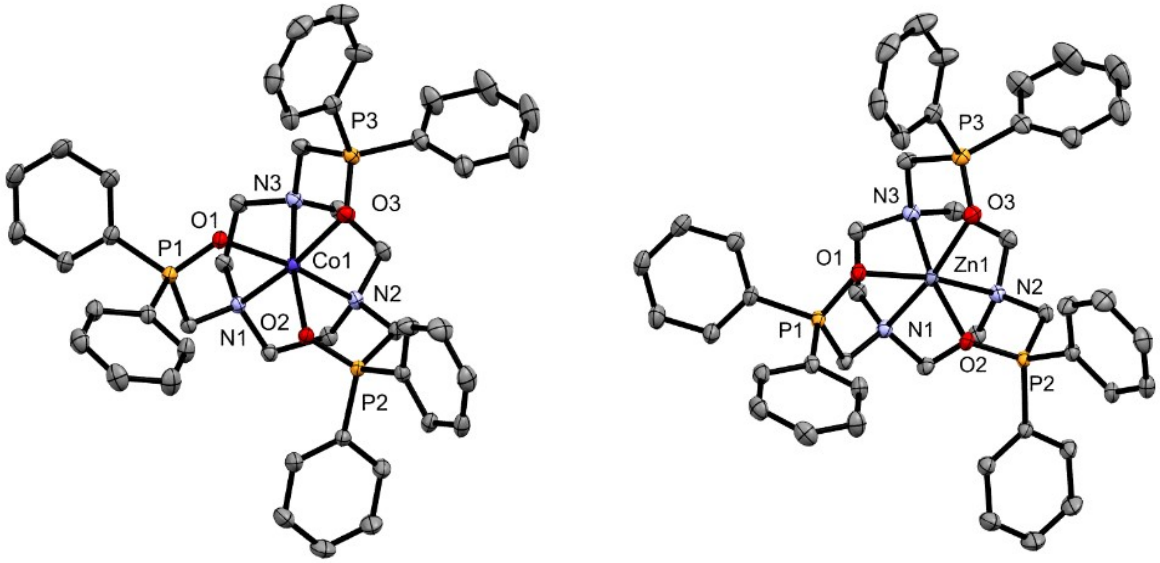


Figure S16: Crystal structures of the cations in $[M(\mathbf{L^1})(MeCN)][BPh_4]_2 \cdot MeCN$ (M = Ni (a), Zn (b)). Counter anions and solvate and hydrogens are omitted for clarity, ellipsoids drawn at 50% probability. Selected bond lengths and angles are listed in Table 1.



(a) (b)

Figure S17: Crystal structures of the cations in $[M(\mathbf{L^1})(MeCN)][BPh_4]_2 \cdot Et_2O$ (M = Co (a), Zn (b)). Counter anions, lattice solvent and hydrogen atoms are removed for clarity, ellipsoids drawn at 50% probability. Selected bond lengths and angles are listed in Table 1.



(a) (b)

Figure S18: Views showing the differences in the Jahn-Teller effect in [Cu(**L²**)][Cu(NO_3)$_4$] (left) and [Cu(**L¹**){Cu(NO_3)$_4$}] (right).

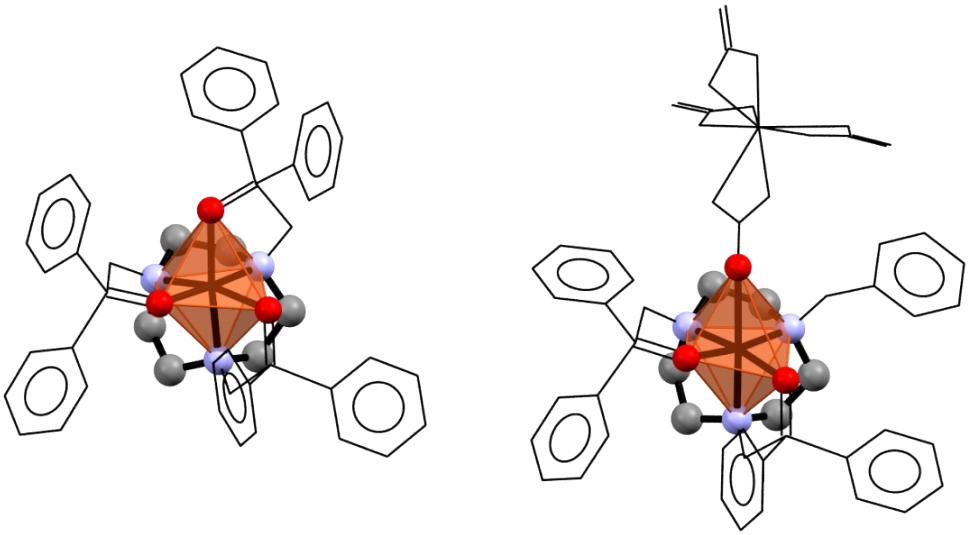


Figure S19: Crystal structure of the cation in $[Co(\mathbf{L^3})][NO_3]_2$. Counter anions, lattice solvent and H atoms are omitted for clarity, ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (°): Co1-N1 = 2.194(3), Co1-N2 = 2.395(4), Co1-N3 = 2.162(3), Co1-N4 = 2.330(3), Co1-O2 = 2.046(3), Co1-O3 = 2.087(3), P1-O1 = 1.492(3), P2-O2 = 1.477(4), P3-O3 = 1.512(4), N2- Co1-O3 = 149.66(13), N4-Co1-O2 = 151.46(15), N1-Co1-N3 = 127.02(13); mean twist angle = 11.35(10)°.

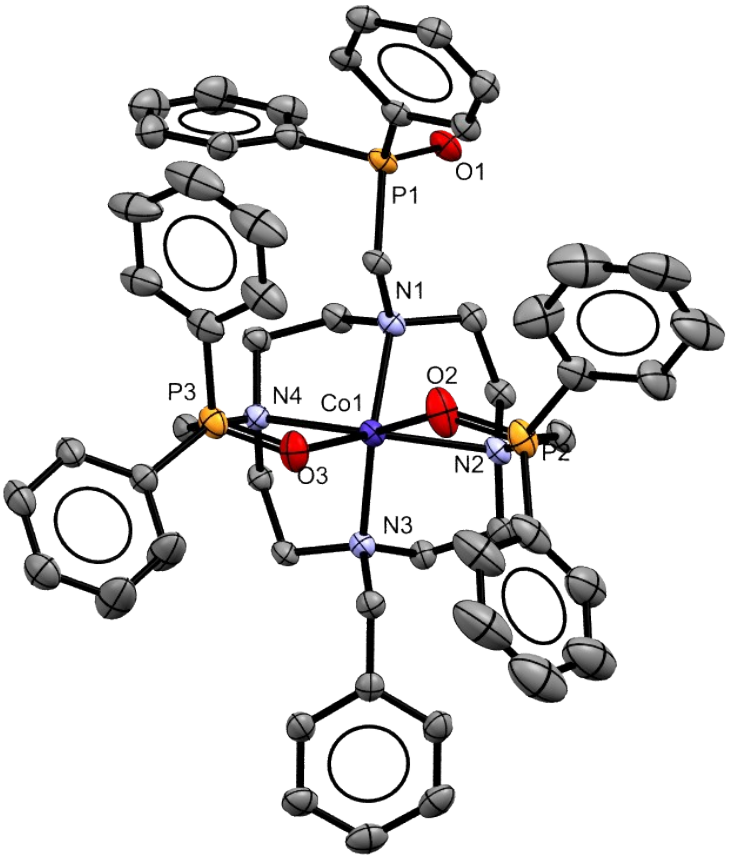


Table S1: Table of X-Ray Crystallographic Parameters

Compound	[Zn(**L**[1])(MeCN)][BPh_4]$_2$·MeCN	[Ni(**L**[1])(MeCN)][BPh_4]$_2$·MeCN	[Co(**L**[1])(MeCN)][BPh_4]$_2$·½MeCN
Formula	$C_{91}H_{89}B_2N_5O_2P_2Zn$	$C_{91}H_{89}B_2N_5NiO_2P_2$	$C_{180}H_{175}B_4Co_2N_9O_4P_4$
M	1433.60	1426.94	2813.26
Crystal system	monoclinic	monoclinic	monoclinic
Space gp (no.)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P2_1/c$ (14)
a /Å	13.3820(2)	13.5349(2)	13.4741(2)
b /Å	35.6112(6)	35.3829(7)	35.5051(4)
c /Å	16.4596(3)	16.3968(3)	16.4405(2)
α /°	90	90	90
β /°	106.049(2)	106.020(2)	105.9370(10)
γ /°	90	90	90
U /Å^3	7538.1(2)	7547.5(2)	7562.82(17)
Z	4	4	2
μ(Mo-K_α) /mm^{-1}	0.422	0.353	0.322
F(000)	3024	3016	2969
Total no. reflns	124576	124747	247513
R_{int}	0.049	0.062	0.054
Unique reflns	26172	26475	27432
No. params, restraints	930, 0	930, 0	1002, 0
GOF	1.026	1.014	1.153
R_1, wR_2 [I > 2σ(I)][b]	0.058, 0.138	0.059, 0.127	0.067, 0.160
R_1, wR_2 (all data)	0.085, 0.150	0.092, 0.139	0.081, 0.166

Table 1 (Continued)

Compound	[Cu(**L**^{1})][Cu(NO_3)$_4$]	[Zn(**L**^{2})][BPh_4]$_2$·Et_2O	[Ni(**L**^{2})][BPh_4]$_2$·Et_2O
Formula	$C_{39}H_{43}Cu_2N_7O_{14}P_2$	$C_{97}H_{98}B_2N_3O_4P_3Zn$	$C_{97}H_{98}B_2N_3NiO_4P_3$
M	1022.82	1549.68	1543.02
Crystal system	Monoclinic	Triclinic	Triclinic
Space gp (no.)	$P2_1/n$ (14)	P-1 (2)	P-1 (2)
a /Å	10.01010(10)	16.1174(2)	16.0832(3)
b /Å	17.9328(2)	18.4228(2)	18.3082(3)
c /Å	24.3639(3)	18.4245(2)	18.3795(3)
α /°	90	118.0920(10)	117.583(2)
β /°	94.3010(10)	106.1320(10)	97.1660(10)
γ /°	90	97.1690(10)	105.699(2)
U /Å^3	4361.23(8)	4420.25(10)	4415.16(16)
Z	4	2	2
μ(Mo-K_α) /mm^{-1}	1.123	0.383	0.325
F(000)	2104	1636	1632
Total number reflns	71809	132520	132615
R_{int}	0.029	0.056	0.049
Unique reflns	15301	29283	29193
No. of params, restraints	577, 0	1048, 0	1040, 0
GOF	1.055	1.014	1.016
R_1, wR_2 [I > 2σ(I)][b]	0.033. 0.083	0.051, 0.124	0.066, 0.179
R_1, wR_2 (all data)	0.045, 0.088	0.076, 0.134	0.090, 0.192

Table 1 (Continued)

Compound	[Co(**L**^{2})][BPh_4]$_2$·Et_2O	[Cu(**L**^{2})][Cu(NO_3)$_4$]	**L**^{3}·MeCN
Formula	$C_{97}H_{98}B_2CoN_3O_4P_3$	$C_{45}H_{48}Cu_2N_7O_{15}P_3$	$C_{56}H_{62}N_5O_3P_3$

M	1543.24	1146.89	946.01
Crystal system	Triclinic	Monoclinic	Triclinic
Space gp (no.)	P-1 (2)	$P2_1/n$ (14)	P-1 (2)
a /Å	16.13080(10)	12.1326(2)	12.82860(10)
b /Å	18.2809(2)	20.3581(3)	12.83880(10)
c /Å	18.4056(2)	19.3113(4)	17.7410(2)
α /°	117.7140(10)	90	76.1760(10)
β /°	106.0810(10)	96.213(2)	79.8520(10)
γ /°	97.3950(10)	90	62.7780(10)
U /Å^3	4400.22(8)	4741.81(14)	2515.53(5)
Z	2	4	2
μ(Mo-K_α) /mm^{-1}	0.301	1.077	0.168
F(000)	1630	2360.0	1004
Total number reflns	132450	42926	162859
R_{int}	0.036	0.035	0.037
Unique reflns	29045	14892	18282
No. of params, restraints	1044, 0	649, 0	605, 0
GOF	1.036	1.019	1.094
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.049, 0.141	0.056, 0.132	0.044, 0.113
R_1, wR_2 (all data)	0.068, 0.153	0.079, 0.014	0.051, 0.116

Table 1 (Continued)

Compound	[Co(**L**^{3})][NO_3]$_2$·2Et_2O	[Zn(**L**^{3})][NO_3]$_2$·6MeCN
Formula	$C_{62}H_{79}CoN_6O_{11}P_3$	$C_{66}H_{77}N_{12}O_9P_3Zn$
M	1236.207	1340.739
Crystal system	monoclinic	monoclinic

Space gp (no.)	$P2_1/c$ (14)	$P2_1/c$ (14)
a /Å	12.9014(3)	12.9010(2)
b /Å	19.0597(3)	19.0309(3)
c /Å	24.0169(5)	24.1395(4)
α /°	90	90
β /°	90.483(2)	90.696(2)
γ /°	90	90
U /Å^3	5905.5(2)	5926.24(16)
Z	4	4
μ(Mo-K_α) /mm^{-1}	0.439	0.569
F(000)	2616	2820
Total number reflns	75995	74586
R_{int}	0.066	0.050
Unique reflns	14779	14769
No. of params, restraints	665, 773	658, 62
GOF	1.047	1.068
R_1, wR_2 [$I > 2\sigma(I)$][b]	0.094, 0.238	0.065, 0.159
R_1, wR_2 (all data)	0.120, 0.255	0.084, 0.168

[a] Common items: T = 100 K; θ(max) = 27.5°; wavelength (Mo-K_α) = 0.71073 Å;

[b] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{1/2}$