Electronic Supplementary Material (ESI) for Dalton Transactions.

Contributions of Inner and Outer Coordination Sphere Bonding in Determining the Strength of Substituted Phenolic Pyrazoles as Copper Extractants

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Electronic Supplementary Information

Experimental details: reagents and equipment and synthesis and characterisation of proligands and complexes.

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Experimental details: reagents, equipment, synthesis and characterisation of proligands and complexes.

All reagents and solvents were used as received from Sigma-Aldrich, Fischer Scientific UK, VWR international, Merck or Alfa Aesar. Toluene and THF were dried by passage through activated alumina columns using a solvent purification system and used immediately for synthesis. ^{1}H NMR were recorded at 298 K on Bruker AVA600, AVA500 or AVA400 spectrometers at 600, 500 and 400 MHz respectively, and ^{13}C NMR on Bruker AVA600, AVA500 or AVA400 spectrometers at 150.83, 125.76 and 100.55 MHz respectively. NMR were referenced internally to residual protic solvent (^{1}H) or (^{13}C) and chemical shifts are quoted in ppm (δ). Mr Stephen Boyer at London Metropolitan University determined elemental microanalyses (School of Human Sciences, Science Centre, 29, Hornsey Road, London, N7 7DD). Mass spectra were recorded on a Thermo-Fischer LCQ Classic (ESI) or MAT 900 XP spectrometer (EI). ICP-OES was carried out using a Perkin Elmer 5300DV spectrometer. 1-Methoxy-2-propanol solutions were taken up with a peristaltic pump into a Gem Tip cross flow nebuliser and a Glass Cyclonic spray chamber at a rate of 2.0 mL min^{-1}. Torch settings used a radio frequency forward power of 1500 W and argon gas flows of 20, 1.4 and 0.45 L min^{-1} for plasma, auxiliary and nebuliser flows. Data were processed using WinLab32 version 3.0.0.0103. Crystal data were collected by The University of Edinburgh Crystallography Service on a three circle Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073) equipped with an Oxford Cryosystems low temperature device operating at 150 K.

Solvent extraction experiments

Copper loading by L1H-L3H was compared with that of 5-nonylsalicylaldoxime by stirring equal volumes of 0.05 M dichloromethane (DCM) solutions of the individual extractants with an equal volume of an aqueous stock solution of $CuSO_4$ (5.00 gL^{-1} with pH 2.0) at 600 r.p.m. in tightly sealed screw top jars equipped with a magnetic stirrer for 30 min. The phases were allowed to separate and samples were diluted by a factor of 1:100 with water (aqueous phase) or white spirit (DCM phase) and their copper content analysed by ICP-AES. Stripping of copper-loaded solutions was carried out by contacting with an equal volume of aqueous H_2SO_4 (125.00 gL^{-1}) containing 5.00 gL^{-1} $CuSO_4$ using conditions for stirring and analysis as above. Note that in commercial operations, "spent electrolyte" obtained from electrowinning the copper ($CuSO_4 + H_2O = Cu + H_2SO_4$) is used to strip copper from the loaded organic phase ($CuL_{2org} + H_2SO_4 = CuSO_4 + 2LH_{org}$), generating fresh electrolyte and regenerating the extractant which is reused.[1, 2] In this work the sulphuric acid concentration in the strip solution (125 g/L) was lower than that in a typical spent electrolyte,[3] ensuring that both the phenolic oxime and the phenolic pyrazole were not fully stripped, allowing a judgement to be made on their relative ease of stripping.

The selectivity of loading of copper(II) over iron(III) was determined by contacting equal volumes of 0.05 M DCM solutions of the extractants with equal volumes of an aqueous stock solution containing $CuSO_4$ and $Fe_2(SO_4)_3$ (both at 5.00 gL^{-1}), adjusted to pH 2.0, using conditions for stirring and analysis as above.

Extractions using L4H-L9H were carried out by contacting chloroform solutions (2.5 mL) of the ligands at concentrations of 0.005 mol L^{-1} with aqueous solutions (2.5 mL) of $CuSO_4$ at concentrations of 0.005 mol L^{-1}. The pH of the aqueous copper sulphate solution was varied by adding 0.5 mL of sodium hydroxide/water or sulphuric acid/water solutions of varying concentrations to 2.0 mL of 0.00625 mol L^{-1} $CuSO_4$ solution and measured at equilibrium.

After vigorous stirring for 22 hr at 40^{o}C, the phases were separated and 0.2 mL of each evaporated and diluted into 10.00 mL 1-methoxy-2-propanol for copper analysis by ICP-OES. The equilibrium pH of the aqueous phase was measured by titration of 0.5 mL of the aqueous phase against varying concentrations of sodium hydroxide. The calculated percentage copper(II) uptake into the organic phase was plotted against the measured equilibrium pH of the aqueous phase to give S-curves.

Computational Methods

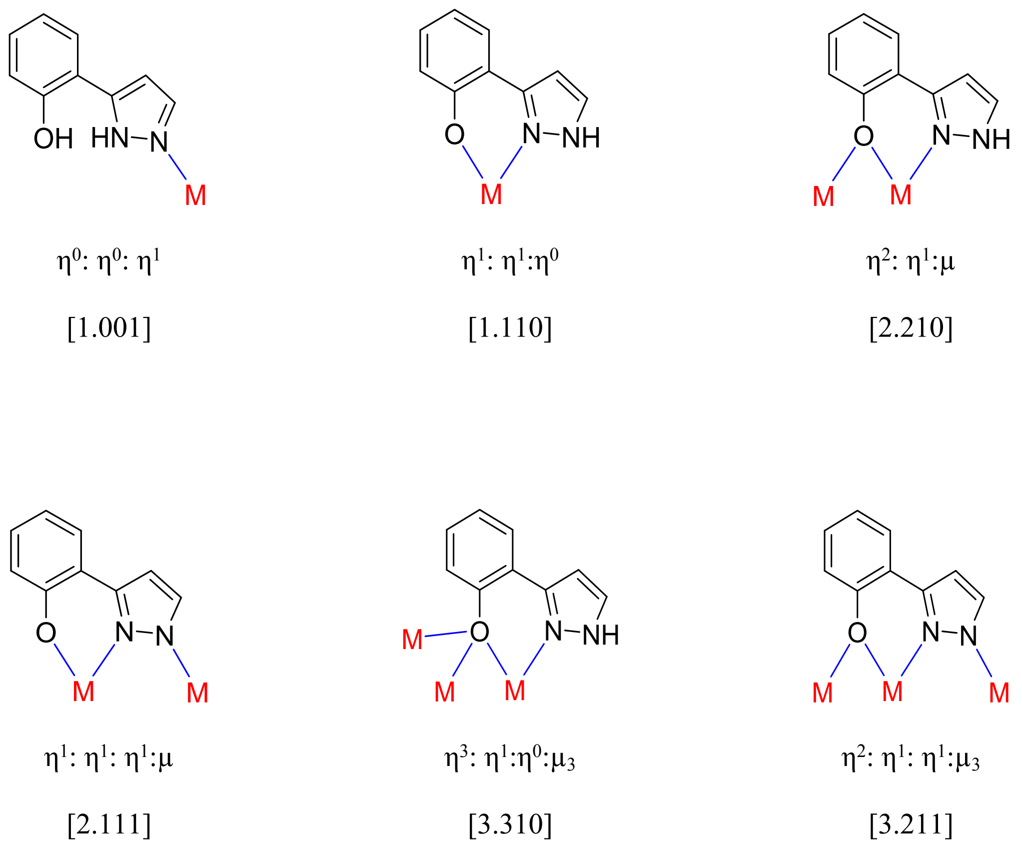
All calculations were executed using the Gaussian ’09 program.[4] Full structural optimizations and analyses were carried out using the hybrid DFT functional B[5]3LYP[6], coupled to the 6-31+G(d,p) basis set for each of the proligands, proligand dimers, ligand monomers and copper complexes. Vibrational frequency calculations were carried out on all optimized structures to ensure energy minima had been reached and to obtain thermodynamic correction terms necessary to translate internal energy values into Gibbs free energy values. Assembly formation energies, dimerization deprotonation and binding energies are calculated using the difference in free energy values based on the sum of the products and the sum of individual reactants. A correction factor for basis set superposition error (BSSE) has also been included which is determined using the counterpoise method of Boys and Bernardi.[7] Interligand bonding was studied using NBO6.[8]

Formation energies reported in Table 2 of the main text were performed in the absence of an implicit solvent model, for reasons reported in the main text. In order to verify that the justification for this is sound, calculations to derive complex formation energies were repeated for L10H, L12H and L15H using PCM=water for the species that reside in the aqueous phase (Cu^{2+}, H_2O and H_3O^+) and PCM=chloroform for the species that reside in the organic phase (L and CuL_2).

Table S1: Change in Gibbs free energies for component terms involved in complex formation, along with relative values free energy of complex formation energies, both with and without PCM correction terms

	ΔG(PCM) /Hartrees	ΔG_{form} (no PCM) /kJmol^{-1}	ΔG_{form} (PCM) /kJmol^{-1}
L10H	0.009712	–	–
L12H	0.00891	–	–
L15H	0.008495	–	–
H_2O	0.008343	–	–
H_3O^+	0.12344	–	–
Cu^{2+}	1.064819	–	–
$Cu(L10)_2$	0.010536	0.0	0.0
$Cu(L12)_2$	0.009545	-22.9	-24.5
$Cu(L15)_2$	0.011998	-0.5	-10.8

The data presented in the table confirm that the effects of including the PCM chloroform model has a minor effect on the energies of the ligand monomers and corresponding copper complexes. For the aqueous species, the cations, as would be expected shift in energy quite considerably, which has a knock-on effect on the absolute values of the formation energies. However, when the energies are expressed as a relative series the ordering remains unchanged.



η^0: η^0: η^1 [1.001]

η^1: η^1:η^0 [1.110]

η^2: η^1:μ [2.210]

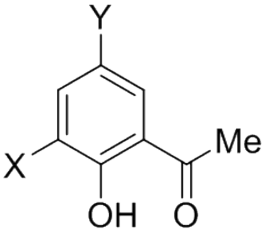
η^1: η^1: η^1:μ [2.111]

η^3: η^1:η^0:μ_3 [3.310]

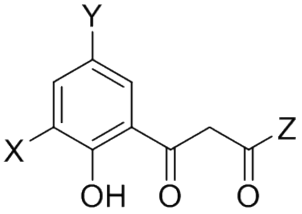
η^2: η^1: η^1:μ_3 [3.211]

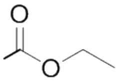
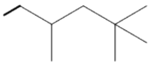
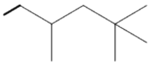
ESI Figure 1: The six modes of coordination of phenolic pyrazoles observed in structures in the Cambridge Crystallographic Database.[9] [M.xxx] is the Harris notation[10] in which “M” defines the number of metals bound to each ligand and the subsequent three digits indicate how many metal atoms are bonded to the phenol oxygen and to the pyrazole N^2 and N^1 atoms respectively.

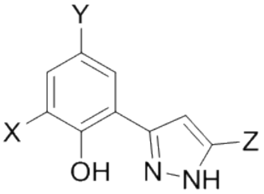
Preparation of proligands L1H-L10H and L12H

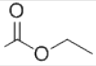
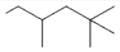
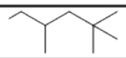
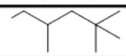
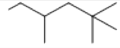
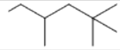
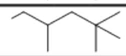


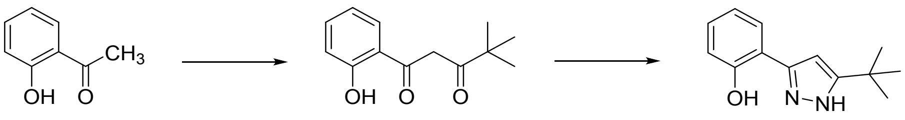
#	X	Y
1	H	H
2	NO_2	CH_3
3	Br	CH_3
4	MeO	CH_3
5	H	Br
6	Br	H



	X	Y	Z
7	H	H	
8	H	H	
9	H	H	
10	H	H	
11	H	H	H
12	NO_2	Me	
13	Br	Me	″
14	MeO	Me	″
15	H	Br	″
16	Br	H	″
17	H	Me	″
18	Br	H	H



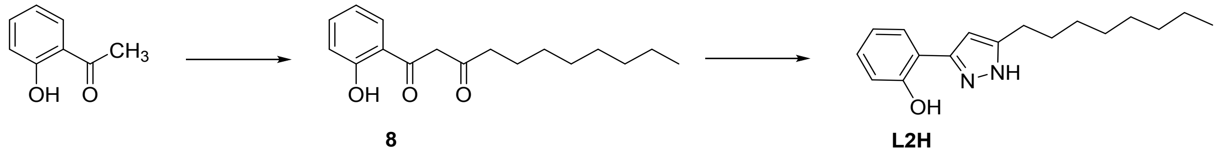
	X	Y	Z
L1H	H	H	
L2H	H	H	
L3H	H	H	
L4H	NO_2	Me	
L5H	Br	Me	
L6H	MeO	Me	
L7H	H	Br	
L8H	H	Me	
L9H	H	H	
L10H	H	H	H
L11H	NO_2	H	H
L12H	Br	H	H
L13H	MeO	H	H
L14H	H	NO_2	H
L15H	H	Br	H
L16H	H	MeO	H



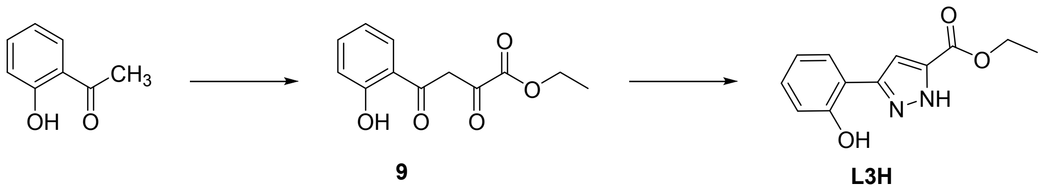
7

L1H

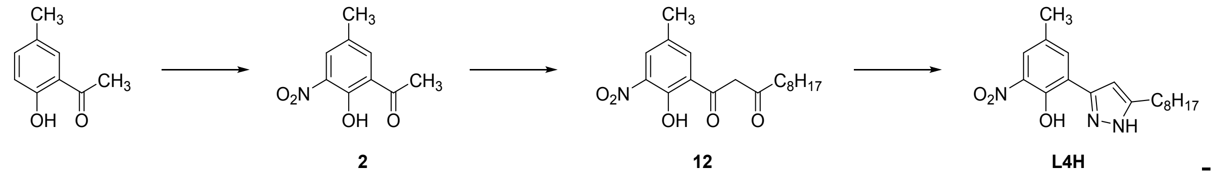
2-(5-tert-Butyl-1H-pyrazol-3-yl)phenol (L1H) was prepared from **7** by the method used below for L2H as white crystals. *Anal. Calc.* for $C_{13}H_{16}N_2O$: C, 72.19 ; H, 7.46; N, 12.95, Found: C,72.09; H, 7.54; N, 12.98. ^1H NR (400 MHz, $CDCl_3$): δ 1.38 (s, 9H, $C(CH_3)_3$), 6.45 (s, 1H, pyzH), 6.90 (t, 1H, ArH), 7.02 (d, 1H, ArH), 7.20 (t, 1H, ArH), 7.56 (d, 1H, ArH), 9.86 (br s, 1H, OH), 11.00 (br s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.1, 30.9, 98.0, 116.9, 117.0, 119.3, 126.4, 129.0, 152.1, 153.8, 155.9. MS (ESI) *m/z* 215.1185 [$(M-H)^-$].



2-(5-Octyl-1H-pyrazol-3-yl)phenol (L2H). 2'-Hydroxyacetophenone (1 g, 7 mmol) was added to a suspension of sodium hydride (60% dispersion in mineral oil, 2.7 g 70 mmol) and heated to 75 ^{o}C for 1 hr. Nonanoyl chloride (1.29 g, 7 mmol) was added over stirring and cooling *via* ice bath. The solution was heated at 75 ^{o}C for 16 h, cooled on ice and quenched with acetic acid (10 mL). THF and excess acid was removed *in vacuo* and the residue extracted into ethyl acetate (10 mL). The extract was washed with deionised water and solvent removed *in vacuo* to give **8** (2.98 g). Without further purification, **8** (2.98 g) was dissolved in ethanol (20 mL), hydrazine hydrate (0.71 g, 15 mmol) was added and the solution was left to stir under reflux for 16 hr. The solvent was removed *in vacuo* and the residue was recrystallized from toluene to obtain **L2H** as an orange oil, 1.01 g, 50.5 %. *Anal. Calc.* for $C_{17}H_{24}N_2O$: C, 74.96 ; H, 8.88; N, 10.28, Found: C, 75.10; H, 8.90; N, 10.14. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.92 (t, 1H) 1.3 (m, 10H) 1.71 (m, 2H) 2.71 (t, 1H) 6.46 (s, pyrazH) 6.94 (td, ArH) 7.05 (d, ArH) 7.24 (td, 1H) 7.58(dd, ArH). ^{13}C NMR (500 MHz, $CDCl_3$) δ 14.1 22.6 25.2 29.0 29.2 29.3 31.3 31.8 100.2 116.8 116.9 119.3 126.5 129.0 145.0 152.5 156.0. MS (ESI) *m/z* 273.2

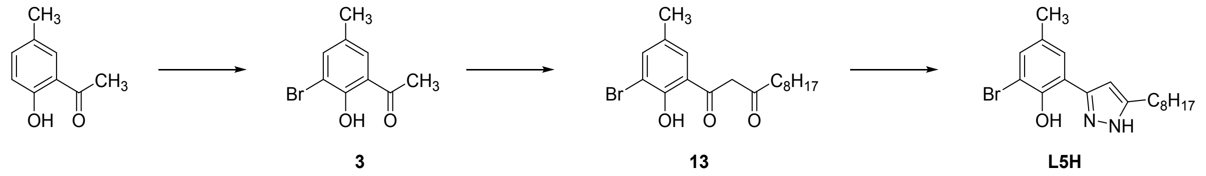


Ethyl 3-(2-hydroxyphenyl)-1H-pyrazole-5-carboxylate (L3H). 2'-Hydroxyacetophenone (5 g, 36.7 mmol) and diethyloxalate (5.95 g, 40.7 mmol) were dissolved in toluene (250 mL) to which potassium tert-butoxide (11 g, 98 mmol) was added portionwise and stirred for 1 hr at room temperature. The reaction was quenched with 1 M HCl (250 mL) and the organic layer was removed, washed with water (3 x 200 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* to give **9** as a crude yellow oil (*ca* 1 g). Without further purification, **9** was dissolved in ethanol (50 mL) to which hydrazine monohydrate (2 mL, 41 mmol) was added and refluxed overnight. After cooling, the precipitate was filtered off, and the remaining ethanolic phase retained. The solvent was removed *in vacuo* to give a red/orange oil which solidified upon standing. The orange solid was washed with toluene to give **L3H** as a pale yellow solid, 0.6 g, 7 %. *Anal. Calc.* for $C_{12}H_{12}N_2O_3$: C, 62.06 ; H, 5.21; N, 12.06, Found: C, 62.10; H, 5.19; N, 12.01. ^{1}H NMR (500 MHz, CDCl$_3$): δ 1.46 (3 H, t, CH$_2$C$\mathbf{H_3}$), 4.47 (2 H, q, C$\mathbf{H_2}$CH$_3$), 6.97 (1 H, td, ArH), 7.07 (1 H, dd, ArH), 7.24 (1 H, s, pyzH), 7.29 (1 H, td, ArH), 7.61 (1 H, dd, ArH). ^{13}C NMR (126 MHz, CDCl$_3$) δ 14.26, 61.93, 105.21, 115.74, 117.35, 119.64, 126.62, 129.96, 134.94, 152.87, 155.77, 159.25. MS (EI) *m/z* 232.1.



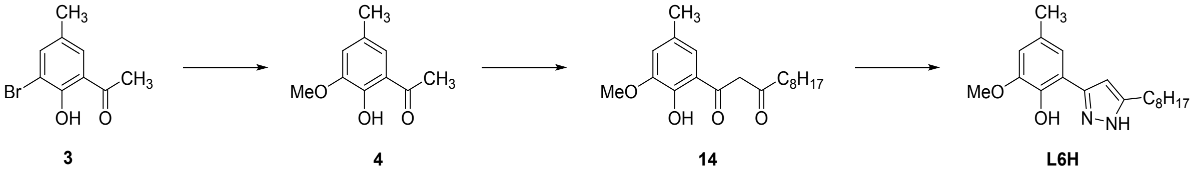
Methyl-3-nitro-2-hydroxyacetophenone (2). Nitric acid (70 %, 3.60 g, 40 mmol) was added in portions over 20 min with stirring and cooling *via* ice bath to a solution of 5-methyl-2-hydroxyacetophenone (5.00 g, 33 mmol) in acetic acid (30 mL). The mixture was allowed to warm to room temperature and then heated to 70 °C for 16 hr. Acetic acid was removed *in vacuo,* the residue dissolved in DCM, washed with a saturated aqueous NaHCO$_3$ (50 mL) and deionised water (3 x 20 mL) then dried over anhydrous MgSO$_4$. DCM was removed *in vacuo* and the residue recrystallized from toluene to yield 5-methyl-3-nitro-2-hydroxyacetophenone (**2**), 2.53 g, 39 %. Anal. Calc. for C$_9$H$_9$NO$_4$: C, 55.39; H, 4.65; N, 7.18, Found: C, 55.3; H, 4.7; N; 7.1 ^{1}H NMR (500 MHz, CDCl$_3$): δ 1.55 (s, 3H), 2.47 (s, 3H), 8.16 (s, 2H), 11.29 (s, 1H). MS (EI) *m/z* 195.0.

2-Nitro-4-methyl-6-[5-(2,4,4-trimethylpentyl)-1*H*-pyrazol-3-yl]phenol (L4H). A solution of **2** (2.00 g, 10 mmol) and 3,5,5-trimethylhexanoyl chloride (1.99 g, 11 mmol) in dry THF (60 mL) which had been stirred under reflux for 16 hr was added dropwise under nitrogen with cooling over ice/water to a suspension of sodium hydride (60% dispersion in mineral oil, 4.10 g, 103 mmol) in dry THF (10 mL) that had been left to stir for 1 hr. The resulting red solution was warmed to room temperature, heated under reflux for 16 hr, cooled on ice and quenched with glacial acetic acid (6.18 g, 103 mmol). Sufficient water was added to allow stirring to continue during the quenching. THF was removed *in vacuo* and the precipitate extracted into ethyl acetate (10 mL). The extract was washed with deionised water, dried over Na$_2$SO$_4$ and evaporated *in vacuo* to give **12** (1.87 g). Without further purification, **12** (1.4 g) was dissolved in ethanol (10 mL), hydrazine hydrate (0.21 g, 4 mmol) was added and the solution was left to stir under reflux for 16 hr. The solvent was removed *in vacuo* and the residue was recrystallized from toluene to obtain **L4H** as a yellow solid, 0.45 g, 34 %. *Anal. Calc.* for: C, 65.23; H, 7.60; N, 12.68, Found: C, 65.27; H, 7.7; N, 12.6. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.92 (s, 9H), 1.01 (d, 3H), 1.16 (dd, 2H), 1.36 (dd, 2H), 1.9 (m, 1H), 2.41 (s, 3H), 2.53 (dd, 2H), 2.72 (dd, 2H), 6.57 (s, 1H), 7.81 (dd, 1H), 7.85 (dd, 1H), ^{13}C NMR (100 MHz, CDCl$_3$): 20.41, 22.51, 30.0, 30.2, 31.1, 50.6, 103.1, 124.4, 149.7, MS (EI) *m/z* 331.1.



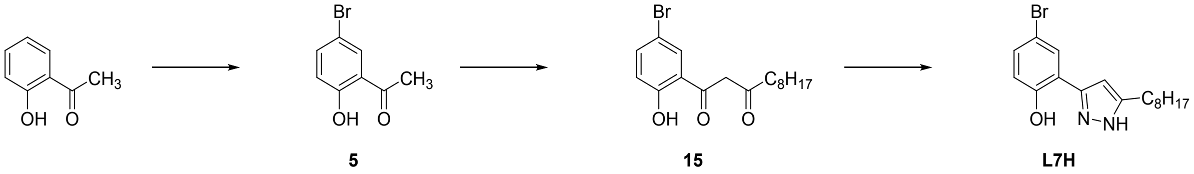
5-Methyl-3-bromo-2-hydroxyacetophenone (3). Bromine (6.62 g, 37.2 mmol) was added in portions over 20 min to a solution of 5-methyl-2-hydroxyacetophenone (5.00 g, 33 mmol) and sodium acetate (2.70 g, 33 mmol) in acetic acid (100 mL) with cooling (0 ^{o}C, ice bath) and stirring. The mixture was allowed to warm to room temperature then heated to 70 ^{o}C for 16 hr, acetic acid was removed *in vacuo*, the residue dissolved in DCM which was washed with a saturated aqueous $NaHCO_3$ (50 mL) and deionised water (3 x 20 mL) and then dried over anhydrous $MgSO_4$. DCM was removed *in vacuo* to yield 5-methyl-3-bromo-2-hydroxyacetophenone (**3**), 3.63 g, 48 %. Anal. Calc. for $C_9H_9BrO_2$: C, 47.19; H 3.96. Found: C, 47.0; H, 3.8. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.34 (s, 3H), 2.66 (s, 3H), 7.51 (dd, 1H), 7.60 (dd, 1H), 12.76 (s, 1H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.2, 26.6, 111.7, 120.1, 129.2, 129.9, 140.3, 156.8, 204.2. MS (EI) *m/z* 227.9 ($[M]^+$, ^{79}Br), 229.9 ($[M]^+$, ^{81}Br).

2-Bromo-4-methyl-6-[5-(2,4,4-trimethylpentyl)-1*H*-pyrazol-3-yl]phenol (L5H). A solution of **3** (1.13 g, 5 mmol) and 3,5,5-trimethylhexanoyl chloride (1.02 g 6 mmol) in dry THF (20 mL) which had been left to stir for 1 hr was added dropwise to a suspension of sodium hydride (60% dispersion in mineral oil, 1.92 g, 48 mmol) in dry THF (10 mL) that had been left to stir under nitrogen for 1 hr cooling over ice/water. The reaction mixture was left to warm to room temperature before being heated gently to initiate a vigorous reaction with bubbling, and repeated where the bubbling subsided until no further reaction could be observed. The reaction mixture was stirred at 50 ^{o}C for 20 hr, then cooled on ice and quenched with glacial acetic acid (2.88 g, 48 mmol). Sufficient water was added to allow stirring to continue during the quenching. THF was removed *in vacuo* and the orange precipitate extracted into ethyl acetate (100 mL). The extract was washed with deionised water, dried over Na_2SO_4 and evaporated *in vacuo.* The orange precipitate was extracted into ethyl acetate (100 mL), washed with water (20 mL) and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the residue purified via column chromatography (hexane:ethyl acetate 9:1) to give **13** (1.51 g) Without further purification, **13** (0.80 g) was dissolved in ethanol (10 mL), hydrazine hydrate (0.11 g, 2 mmol) was added and the solution was left to stir under reflux for 16 hr. The solvent removed *in vacuo* and the residue recrystallised from hexane to give **L5H** as a yellow solid, 0.65 g, 36 %. *Anal. Calc.* for $C_{18}H_{25}Br,N_2O$: C, 59.18, H, 6.90, N, 7.67, Found: C, 59.1; H, 6.8; N, 7.6. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.93 (s, 9H), 1.02 (d, 3H), 1.19 (dd, 2H), 13.4 (dd, 2H), 2.33 (s, 3H), 2.54 (dd, 2H), 2.73 (dd, 2H), 6.49 (s, 1H), 7.33 (dd, 2H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.3, 22.5, 30.2, 31.1, 35.4, 50.6, 101.2, 110.6, 117.6, 126.1, 129.4, 132.8, 144.0, 150.5, 151.7. MS (EI) *m/z* 364.0 ($[M]^+$, ^{79}Br), 366.0 ($[M]^+$, ^{81}Br).



5-Methyl-3-methoxy-2-hydroxyacetophenoneone (4). Sodium metal (1.3 g, 54 mmol) was dissolved in anhydrous methanol (21 mL) under nitrogen then heated to 60 °C. A solution of 5-methyl-3-bromo-2-hydroxyacetophenone (**3**) (1.00 g, 4.4 mmol) in anhydrous dimethylformamide (DMF, 1.5 ml) was added, to a solution of copper(I) bromide (0.31 g, 2 mmol) in anhydrous DMF (2 ml). The mixture was heated under reflux for 16 hr, quenched with water (100 mL) and extracted into DCM (100 mL). The organic phase was separated, the DCM removed *in vacuo* and the crude residue purified by column chromatography (hexane:ethyl acetate 9:1) to obtain 5-methyl-3-methoxy-2-hydroxyacetophenone (**4**) as a pale yellow solid, 0.14 g, 19 %. Anal. Calc. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71, Found: C, 6.8; H, 6.8. ^1H NMR (500 MHz, $CDCl_3$): δ 2.34 (s, 3H), 2.64 (s, 3H), 3.91 (s, 3H), 6.90 (dd, 1H). 7.13 (dd, 1H), 12.39 (s, 1H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.1, 27.0, 56.2, 118.5, 121.4, 127.6, 148.7, 150.8, 204.8. MS (EI) *m/z* 180.0.

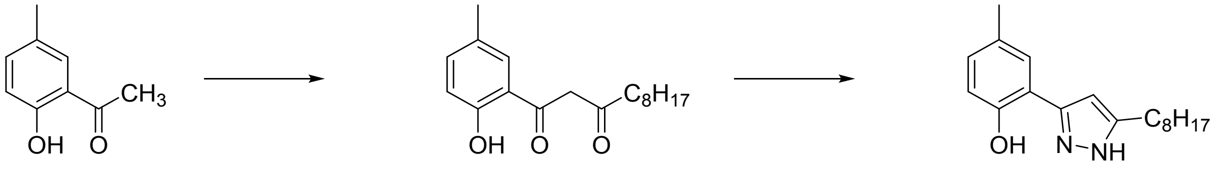
2-Methoxy-4-methyl-6-[5-(2,4,4-trimethylpentyl)-1*H*-pyrazol-3-yl]phenol (L6H). A solution of **4** (0.80 g, 4 mmol) and 3,5,5-trimethylhexanoyl chloride (0.86 g 5 mmol) in dry THF (20 mL) which had been stirred under reflux for 16 hr was added dropwise under nitrogen with cooling over ice/water to a suspension of sodium hydride (60% dispersion in mineral oil, 1.76 g, 44 mmol) that had been left to stir for 1 hr. The resulting orange solution was warmed to room temperature, heated under reflux for 16 hr, stirred for 48 hr at RT and quenched with glacial acetic acid (2.64 g, 44 mmol). Sufficient water was added to allow stirring to continue during the quenching. THF was removed *in vacuo* and the precipitate extracted into ethyl acetate (100 mL). The extract was washed with deionised water, dried over Na_2SO_4 and evaporated *in vacuo.* The orange precipitate was extracted into DCM (50 mL), washed with water (20 mL) and dried over anhydrous $MgSO_4$. The DCM was removed *in vacuo* and the residue recrystallised from hexane to give **14** as a colourless solid (0.54 g). Without further purification, **14** (0.50 g) was dissolved in ethanol (10 mL), hydrazine hydrate (0.08 g, 2 mmol) added and the solution left to stir under reflux for 16 hr. The solvent was removed *in vacuo* and the residue was recrystallised from toluene to obtain **L6H** as a yellow solid, 0.25 g, 20 %. Anal. Calc. for $C_{19}H_{28}N_2O_2$: C, 72.12; H, 8.92; N, 8.85, Found: C, 72.1; H 8.8; N, 8.78. ^1H NMR (400 MHz, $CDCl_3$): δ 0.93 (s, 9H), 1.01 (d, 3H), 1.17 (dd, 1H), 1.35 (dd, 1H), 1.85 – 1.97 (m, 1H), 2.35 (s, 6H), 2.52 (dd, 1H), 2.71 (dd, 1H), 3.93 (s, 3H), 6.45 (s, 1H), 6.69 (dd, 1H), 7.02 (dd, 1H). MS (EI) *m/z* 316.1.



5-Bromo-2-hydroxyacetophenoneone (5). N-bromosuccinimide (6.62 g, 37 mmol) was added over 20 min to a stirred solution of 2-hydroxyacetophenone (5.07 g, 37 mmol) in dry THF (100 mL) and the mixture left to stir at room temperature for 16 hr. The resulting orange solution was quenched with 100 mL saturated aqueous $Na_2S_2O_5$ to give a clear and colourless solution. The products were extracted into ether (2 x 60 mL), which was washed with saturated $Na_2S_2O_5$ (20 mL) and finally water (20 mL) before being dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo* to give a mixture of crude products that was purified by column chromatography (hexane:chloroform:ethyl acetate 9:1:0.5) to give 5-bromo-2-hydroxyacetophenone (**5**) as a yellow solid, 2.3 g, 29%. *Anal. Calc.* for $C_8H_7BrO_2$: C, 44.68; H, 3.28. Found: C, 44.8; H, 3.4. ^1H NMR (500 MHz, $CDCl_3$): δ 2.65 (s, 3H), 6.92 (d, 1H), 7.58 (dd, 1H), 7.86 (d, 1H), 12.18 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.8, 110.4, 113.3, 121.2, 132.2, 141.6, 158.2, 203.3. MS (EI) *m/z* 213.9 ($[M]^+$, ^{79}Br), 215.9 ($[M]^+$, ^{81}Br).

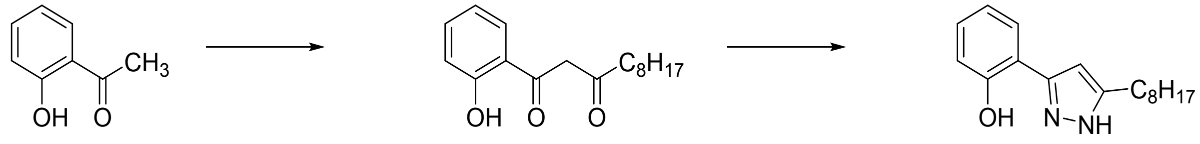
4-Bromo-2-[5-(2,4,4-trimethylpentyl)-1*H*-pyrazol-3-yl]phenol (L7H). A solution of **5** (1 g, 5 mmol) and 3,5,5-trimethylhexanoyl chloride (0.82 g, 5 mmol) in dry THF (60 mL) which had been stirred under reflux for 16 hr was added dropwise under nitrogen with cooling over ice/water to a suspension of sodium hydride (60% dispersion in mineral oil, 1.86 g, 46 mmol) in dry THF (10 mL) that had been left to stir for 1 hr. The cooled mixture was stirred for 2 hr and the resulting orange solution was warmed to RT before being heated to initiate a vigorous reaction with bubbling. Heating was repeated when the bubbling had subsided until no further reaction could be observed. The solution was stirred at 50 °C for 48 hr, cooled and quenched with glacial acetic acid (50 mL). Sufficient water was added to allow stirring to continue during the quenching. THF was removed *in vacuo* and the resulting brown oil extracted into ethyl acetate (2 x 40 mL). The extract was washed with deionised water, dried over Na_2SO_4 and evaporated *in vacuo* to give a brown oil from which **15** (0.6 g) separated as a pale brown solid on standing in hexane. Without further purification **15** (0.5 g) was dissolved in ethanol (50 mL), hydrazine hydrate (0.140 g, 1 mmol) was added and the solution was left to stir under reflux for 16 hr. The ethanol was removed *in vacuo* to give a residue that solidified at room temperature after 24 hr. The resulting yellow solid was purified by flash column chromatography (DCM) and dried under high vacuum to give **L7H**, 0.24 g. *Anal. Calc.* for $C_{17}H_{23}BrN_2O$: C, 58.12; H, 6.60; N, 7.97. Found: C, 58.27; H, 6.65; N, 7.93 %. ^1H NMR (500 MHz, $CDCl_3$): δ 0.94 (s, 9H), 1.02 (d, 3H), 1.19 (dd, 1H), 1.33 (dd, 1H), 1.92 (m, 1H), 2.55 (dd, 1H), 2.73 (dd, 1H), 6.46 (s, 1H), 6.93 (d, 1H), 7.31 (dd, 1H), 7.68 (d, 1H). ^{13}C NMR

(125 MHz, $CDCl_3$): δ 22.5, 30.0, 30.2, 31.1, 35.3, 50.5, 101.3, 111.0, 118.6, 118.9, 128.9, 131.7, 144.0, 151.4, 155.2. MS (EI) *m/z* 350.1 ([M^+], ^{79}Br), 352.1 ([M^+], ^{81}Br).



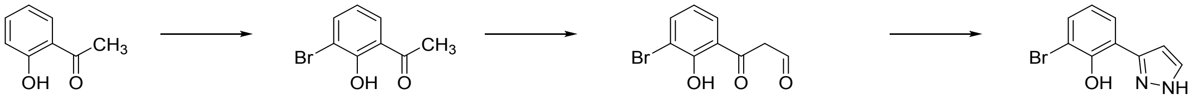
17 **L8H**

4-Methyl-2-[5-(2,4,4-trimethylpentyl)-1*H*-pyrazol-3-yl]phenol (L8H). A solution of 5-methyl-2-hydroxyacetophenone, (1.00 g, 7 mmol) and 3,5,5-trimethyhexanoyl chloride (1.41 g 8 mmol) in dry THF (60 mL) which had been stirred under reflux for 1 hr was added dropwise under nitrogen with cooling to a suspension of sodium hydride (60% dispersion in mineral oil, 2.64 g, 70 mmol) in dry THF (15 mL) that had been left to stir for 1 hr. The cooled mixture was stirred for 2 hr and the resulting yellow solution was warmed to RT before being heated to initiate a vigorous reaction with bubbling. Heating was repeated when the bubbling had subsided until no further reaction could be observed. The reaction mixture was stirred at 50°C for 20 hr, cooled on ice and quenched with glacial acetic acid (3.48 g, 70 mmol). Sufficient water was added to allow the mixture to continue to be stirred during quenching. THF was removed *in vacuo* and the product extracted into ethyl acetate (100 mL), washed with water (20 mL) and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the residue recrystallised from hexane to give **17** (1.22 g). Without further purification, **17** (1.00 g) was dissolved in ethanol (5 mL), hydrazine hydrate (0.17 g, 3 mmol) was added and the solution was left to stir under reflux for 16 hr. The ethanol was removed *in vacuo* and the residue recrystallised from hexane to yield **L8H** as a white solid, 0.62 g, 63 %. Anal. Calc. for: C, 75.48; H, 9.15; N, 9.78, Found: C, 75.2; H, 9.1, N, 9.7 ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (s, 9H), 1.00 (d, 3H), 1.15 (dd, 2H), 1.30 (dd, 2H), 1.90 (m, 1H), 2.35 (s, 3H), 2.50 (dd, 2 H), 2.69 (dd, 2H), 6.47 (s, 1H), 6.94 (d, 1H), 7.04 (dd, 1H), 7.84 (d, 1H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.6, 22.5, 30.0, 30.2, 31.1, 35.4, 50.6, 101.0, 116.3, 116.8, 126.7, 128.2, 129.9 143.7, 152.7, 153.8. MS (EI) *m/z* 286.1.



10 **L9H**

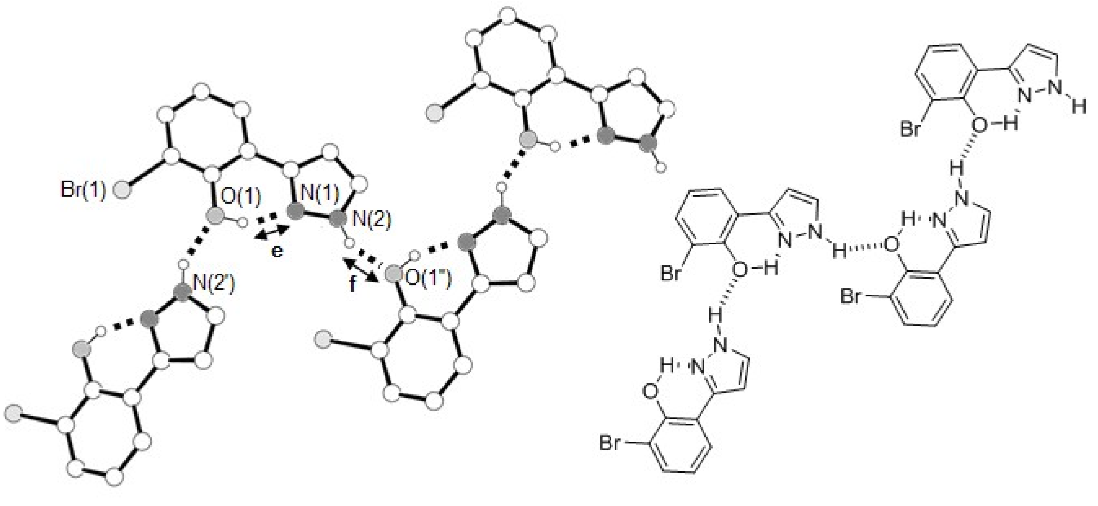
2-[5-(2,4,4-Trimethylpentyl)-1*H*-pyrazol-3-yl]phenol (L9H). A solution of 2-hydroxyacetophenone (1 g, 7 mmol) and 3,5,5-trimethylhexanoyl chloride (1.4 mL, 7 mmol) in dry THF (20 mL) which had been stirred under reflux for 1 hr was added dropwise under nitrogen with cooling over ice/water to a suspension of sodium hydride (60% dispersion in mineral oil, 2.94 g, 73 mmol) in dry THF (10 mL) that had been left to stir for 1 hr. The cooled mixture was stirred for 2 hr and the resulting orange solution was then warmed to RT before being heated to initiate a vigorous reaction with bubbling. Heating was repeated when the bubbling subsided until no further reaction could be observed. The solution was stirred under reflux for 48 hr, cooled on ice and quenched with glacial acetic acid (50 mL). The product was extracted into ethyl acetate (2 x 40 mL), washed with water (20 mL) and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* to give **10** (0.85 g). Without further purification, **10** (0.5 g) was dissolved in ethanol (50 mL), hydrazine hydrate (10 mmol, 0.1 mL) was added and the solution was left to stir under reflux for 16 hr. After standing at room temperature for 24 hr, the ethanol was removed under vacuum, the product extracted into ethyl acetate (40 mL), the solution washed with water (10 mL), dried over $MgSO_4$ and evaporated to give **L9H** as a yellow solid, 0.11 g, 5 %. *Anal. Calc.* for $C_{17}H_{24}N_2O$: C, 74.96; H, 8.88; N, 10.28, Found: C, 75.11; H, 9.02; N, 10.21 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.94 (s, 9H), 1.03 (d, 3H), 1.19 (dd, 1H), 1.35 (dd, 2H), 1.92 (m, 1H), 2.55 (dd, 1H), 2.73 (dd, 1H), 6.48 (s, 1H), 6.93 (td), 7.04 (dd), 7.24 (td, 1H), 7.59 (dd, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.5, 30.0, 30.2, 31.1, 35.4, 50.5, 101.1, 116.8, 117.0, 119.2, 126.4, 129.1, 143.7, 152.6, 156.1. MS (EI) m/z 272.1.



6 **18** **L12H**

3-Bromo-2-hydroxyacetophenone (6). N-bromosuccinimide (6.62 g, 3.7 mmol) was added over 20 min to a stirred suspension of 2-hydroxyacetophenone (5.07 g, 37 mmol) and di-isopropyl amine (0.4 mmol, 0.038 g) in carbon disulphide (100 mL) cooled on ice. The solution was allowed to warm to room temperature and left to stir for 30 minutes. Water (100 mL) was added and the products extracted into ethyl acetate (60 mL), washed with saturated aqueous $NaHCO_3$ (30 mL) and water (30 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo*, giving a crude product mixture which was purified by column chromatography (hexane:chloroform:ethyl acetate 9:1:0.5) to obtain 3-bromo-2-hydroxyacetophenone (**6**) as a yellow solid, 0.79 g, 10%. *Anal. Calc.* for $C_8H_7BrO_2$: C, 44.68; H, 3.28. Found: C, 44.5; H, 44.5 . ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.69 (s, 3H), 6.85 (t, 1H), 7.75 (dd, 1H), 7.78 (dd, 1H), 12.99 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.7, 112.2, 119.7, 120.5, 129.9, 139.6, 159.0, 204.3. MS (EI) *m/z* 213.9 ($[M]^+$, ^{79}Br), 215.9 ($[M]^+$, ^{81}Br).

2-Bromo-6-[1*H*-pyrazol-3-yl]phenol (L12H). A solution of **6** (0.5 g, 2 mmol) and ethyl formate (0.68 g 9 mmol) in dry THF (20 mL) which had been stirred for 1 hr was added dropwise to a suspension of sodium hydride (60% dispersion in mineral oil, 0.76 g, 18 mmol) in dry THF (15 mL) that had been left to stir under nitrogen with cooling over ice/water for 1 hr. The cooled mixture was stirred for 2 hr and the resulting orange solution was warmed to room temperature before being heated to initiate a vigorous reaction with bubbling. Heating was repeated when the bubbling subsided until no further reaction could be observed. The reaction mixture was stirred at 50 ^{o}C for 20 hr, cooled on ice and quenched with glacial acetic acid (1.08 g, 18 mmol). Sufficient water was added to allow the mixture to continue to be stirred during quenching. THF was removed *in vacuo* and the product extracted into ethyl acetate (100 mL), washed with water (20 mL) and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* to give **18** (0.20 g) as a colourless solid. Without further purification, **18** (0.16 g) was dissolved in ethanol (5 mL), hydrazine hydrate (0.06 g, 1 mmol) was added and the solution was left to stir under reflux for 16 hr. The ethanol was removed *in vacuo* and the residue recrystallized from toluene to give colourless crystals suitable for X-ray structure determination of **L12H**, 0.1 g, 21 % Anal. Calc. for $C_9H_7BrN_2O$: C, 45.22; H, 2.95; N, 11.72, Found: C, 45.9; H 3.0; N 11.5. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.76 (d, 1H), 6.82 (t, 1H), 7.50 (dd, 1H), 7.58 (dd, 1H), 7.70 (d, 1H), MS (EI) *m/z* 239.9 ([M]$^+$, ^{79}Br), 241.9 ([M]$^+$, ^{81}Br). Crystal data: M = $C_9H_7BrN_2O$; orthorhombic, a = 3.84135(10), b = 9.9290(2), c = 22.7560(6) Å; U = 867.94(4) Å^3; T = 137 K; space group $P2_12_12_1$; Z = 4; 15277 reflections measured, 1812 unique (R_{int} = 0.0225) which were used in all calculations; final R_w = 0.0527 (all data).



Part of the X-ray crystal structure of L12H. Hydrogen atoms were found in a Fourier difference map and modelled isotropically in the final refinement cycles. L12H adopts a ribbon arrangement where the proton attached to N(2) forms a hydrogen bond with the phenol of a neighbouring molecule whilst O(1) accepts a hydrogen from a different L12H molecule. The least squares planes of the phenyl rings of two neighbouring L12H molecules form a dihedral angle of 33.5^{o}, indicating that the ribbon arrangement is not very planar. The hydrogen atom on the pyrazole N(2) atom forms an intermolecular hydrogen bond to the phenolic oxygen O(1) with D···A is 2.821(3).

[Cu(L12)$_2$] L12H (1 equiv) and copper(II) acetate hydrate (0.5 equiv) were mixed in methanol and heated to 70^{o}C for 20 mins. Methanol was removed *in vacuo* and chloroform (10 ml) was added to the residue and washed with deionised water (2 x 10 ml). The solution was dried over sodium sulfate and filtered. The chloroform was removed *in vacuo* to give **[Cu(L12)$_2$]** as a yellow solid in 60% yield. XRD crystals were grown *via* slow evaporation of an ethanol solution of the complex (*ca* 10 mg/mL, 5 mL). Crystal data: C27 H18 Br3 Cu1.50 N6 O3: M = 809.51; monoclinic, a = 9.78868(7), b = 15.40415(13), c = 17.09116(14) Å; U = 2576.89(4) Å^3; T = 120 K; space group; P 21/c Z = 4; 21736 reflections measured, 5351 unique (R_{int} = 0.0219) which were used in all calculations; final R_w = 0.0529 (all data).

The CCDC deposition codes for **L12H** and **[Cu(L12)$_2$]** are 1430501 and 1430499 respectively.

DFT Calculations

Table S2: Gibbs Free Energy of formation

$$\Delta G_f = (G[CuL_2] + (2*G[H_3O^+])) - (G[Cu^{2+}] + (2*[HL]) + (2*[H_2O])) + BSSE$$

B3LYP/6-31+G(d,p)	L11H	L12H	L13H	L14H
Substitution	*o*-NO_2	*o*-Br	*o*-MeO	*p*-NO_2
G, Cu^{2+}/(H)	-1639.268314	-1639.268314	-1639.268314	-1639.268314
G, H_2O/(H)	-76.43040366	-76.43040366	-76.43040366	-76.43040366
G, HL/(H)	-736.9080077	-3103.54266	-646.8994995	-736.9210938
G + BSSE, $[CuL_2]$/(H)	-3113.05479	-7846.305891	-2933.01841	-3113.05766
G, H_3O^+/(H)	-76.69261269	-76.69261269	-76.69261269	-76.69261269
$\Delta G_{formation}$/(H)	-0.494878746	-0.476674697	-0.475514692	-0.471576575
$\Delta G_{formation}$ (kJ/mol)	-1299.304147	-1251.509416	-1248.463824	-1238.124297

B3LYP/6-31+G(d,p)	L15H	L10H	L16H
Substitution	*p*-Br	H	*p*-MeO
G, Cu^{2+}/(H)	-1639.268314	-1639.268314	-1639.268314
G, H_2O/(H)	-76.43040366	-76.43040366	-76.43040366
G, HL/(H)	-3103.544936	-532.4059623	-646.9029865
G + BSSE , $[CuL_2]$/(H)	-7846.301913	-2704.023759	-2933.015826
G, H_3O^+/(H)	-76.69261269	-76.69261269	-76.69261269
$\Delta G_{formation}$/(H)	-0.468145676	-0.467938644	-0.465956776
$\Delta G_{formation}$ (kJ/mol)	-1229.116472	-1228.572909	-1223.369515

Table S3: Gibbs Free Energy of Monomer Deprotonation

$\Delta G_{dep} = (G[L^-] + G[H_3O^+]) - (G[HL] + G[H_2O]) + BSSE$

B3LYP/6-31+G(d,p)	L11H	L12H	L13H	L14H
	o-NO_2	*o*-Br	*o*-MeO	*p*-NO_2
G, HL/(H)	-736.9080077	-3103.54266	-646.8994995	-736.9210938
G, H_2O/(H)	-76.43040366	-76.43040366	-76.43040366	-76.43040366
G, L^-/(H)	-736.4033267	-3103.023965	-646.3690817	-736.4191692
G, H_3O^+/(H)	-76.69261269	-76.69261269	-76.69261269	-76.69261269
(for 2 L) ΔG_{dep}/(H)	0.484943942	0.512972646	0.536417602	0.4794312
ΔG_{dep} (kJ/mol)	1273.220319	1346.809681	1408.364413	1258.746615

B3LYP/6-31+G(d,p)	L15H	L10H	L16H
	p-Br	H	*p*-MeO
G, HL/(H)	-3103.544936	-532.4059623	-646.9029865
G, H_2O/(H)	-76.43040366	-76.43040366	-76.43040366
G, L^-/(H)	-3103.024291	-531.8764701	-646.3712734
G, H_3O^+/(H)	-76.69261269	-76.69261269	-76.69261269
ΔG_{dep}/(H)	0.516870806	0.534566296	0.539008
ΔG_{dep} (kJ/mol)	1357.0443	1403.503809	1415.166081

Table S4: Gibbs Free Energy of Binding

$\Delta G_{bind} = G[CuL_2] - (G[Cu^{2+}] + (2*G[L^-]) + BSSE$

B3LYP/6-31+G(d,p)	L11H	L12H	L13H	L14H
	o-NO_2	*o*-Br	*o*-MeO	*p*-NO_2
G, Cu2+/(H)	-1639.268314	-1639.268314	-1639.268314	-1639.268314
G, L-/(H)	-736.4033267	-3103.023965	-646.3690817	-736.4191692
G + BSSE, $[CuL_2]$/(H)	-3113.05479	-7846.305891	-2933.01841	-3113.05766
ΔG_{bind}/(H)	-0.979822687	-0.989647342	-1.011932294	-0.951007774
ΔG_{bind} (kJ/mol)	-2572.524465	-2598.319097	-2656.828237	-2496.870911

B3LYP/6-31+G(d,p)	L15H	L10H	L16H
	p-Br	H	*p*-MeO
G, Cu2+/(H)	-1639.268314	-1639.268314	-1639.268314
G, L-/(H)	-3103.024291	-531.8764701	-646.3712734
G + BSSE , $[CuL_2]$/(H)	-7846.301913	-2704.023759	-2933.015826
ΔG_{bind}/(H)	-0.985016481	-1.002504939	-1.004964995
ΔG_{bind} (kJ/mol)	-2586.160772	-2632.076718	-2638.535595

Table S5: Dimerisation Energy (Internal Energy)

$\Delta U = U[L_2] - (2*U[L]) + BSSE$

B3LYP/6-31+G(d,p)	L11H	L12H	L13H	L14H
	o-NO_2	*o*-Br	*o*-MeO	*p*-NO_2
U, L (H)	-737.0283087	-3103.653556	-647.0509075	-737.0419678
U, L_2 + BSSE /(H)	-1474.085775	-6207.326549	-1294.121956	-1474.096793
ΔU_{dim}/(H)	-0.029157616	-0.019436758	-0.020140572	-0.012857775
ΔG_{bind} (kJ/mol)	-76.55332181	-51.03120893	-52.87907134	-33.75808839

B3LYP/6-31+G(d,p)	L15H	L10H	L16H
	p-Br	H	*p*-MeO
U, L (H)	-3103.655078	-532.5282963	-647.0539065
U, L_2 + BSSE /(H)	-6207.325295	-1065.072491	-1294.12427
ΔU_{dim}/(H)	-0.015139472	-0.015898548	-0.016456667
ΔU_{dim}/(kJ/mol)	-39.74868329	-41.74163696	-43.20698048

Table S6: Optimized Coordinates L10H Monomer and Deprotonated Monomer

X=H				**L10H**			
Energy		-532.528				-531.985	
Charge		0				1	
Multiplicity		1				1	
Atom	**x**	**y**	**z**	**Atom**	**x**	**y**	**z**
C	-1.15174	0.95459	0.00001	**C**	1.08471	1.01897	-0.00009
C	-0.4051	-0.2517	0.00003	**C**	0.39516	-0.26407	-0.00012
C	-1.11291	-1.46845	0.00005	**C**	1.12951	-1.46097	-0.00013
C	-2.50303	-1.50895	0.00003	**C**	2.52451	-1.48249	-0.00014
C	-3.22414	-0.30758	0.00001	**C**	3.21239	-0.25361	-0.00004
C	-2.55386	0.91069	-0.00001	**C**	2.52152	0.94924	0.00005
O	-0.57509	2.18105	0.00001	**O**	0.46577	2.14648	0.00029
C	1.06375	-0.24578	0.00001	**C**	-1.06533	-0.29649	-0.00004
H	-0.55654	-2.40084	0.00006	**N**	-1.79509	0.85195	0.00004
H	-3.01985	-2.46336	0.00004	**N**	-3.1334	0.65682	-0.00013
H	-4.3103	-0.32238	0	**C**	-2.01432	-1.33261	0.0003
H	0.40319	2.07911	0.00007	**C**	-3.26207	-0.6778	-0.00011
N	1.74667	0.91219	-0.00013	**H**	0.58593	-2.40481	-0.00014
H	-3.09178	1.85322	-0.00003	**H**	3.06385	-2.42631	-0.00017
N	3.05105	0.5683	-0.00001	**H**	4.30256	-0.24569	0.00002
C	1.97159	-1.34388	-0.00004	**H**	3.05209	1.89886	0.00021
C	3.22899	-0.7775	0.00002	**H**	-4.25251	-1.11744	-0.00018
H	3.75203	1.29259	0.00001	**H**	-1.82652	-2.39658	0.00056
H	4.21412	-1.22047	0.00007	**H**	-1.3087	1.75774	-0.00002
H	1.74459	-2.39833	-0.00005				

Table S7: Optimized Coordinates L10H Dimer and Complex

X=H				L10H			
Energy		-532.528				-531.985	
Charge		0				1	
Multiplicity		1				1	
Atom	**x**	**y**	**z**	**Atom**	**x**	**y**	**z**
C	-1.15174	0.95459	0.00001	**C**	1.08471	1.01897	-0.00009
C	-0.4051	-0.2517	0.00003	**C**	0.39516	-0.26407	-0.00012
C	-1.11291	-1.46845	0.00005	**C**	1.12951	-1.46097	-0.00013
C	-2.50303	-1.50895	0.00003	**C**	2.52451	-1.48249	-0.00014
C	-3.22414	-0.30758	0.00001	**C**	3.21239	-0.25361	-0.00004
C	-2.55386	0.91069	-0.00001	**C**	2.52152	0.94924	0.00005
O	-0.57509	2.18105	0.00001	**O**	0.46577	2.14648	0.00029
C	1.06375	-0.24578	0.00001	**C**	-1.06533	-0.29649	-0.00004
H	-0.55654	-2.40084	0.00006	**N**	-1.79509	0.85195	0.00004
H	-3.01985	-2.46336	0.00004	**N**	-3.1334	0.65682	-0.00013
H	-4.3103	-0.32238	0	**C**	-2.01432	-1.33261	0.0003
H	0.40319	2.07911	0.00007	**C**	-3.26207	-0.6778	-0.00011
N	1.74667	0.91219	-0.00013	**H**	0.58593	-2.40481	-0.00014
H	-3.09178	1.85322	-0.00003	**H**	3.06385	-2.42631	-0.00017
N	3.05105	0.5683	-0.00001	**H**	4.30256	-0.24569	0.00002
C	1.97159	-1.34388	-0.00004	**H**	3.05209	1.89886	0.00021
C	3.22899	-0.7775	0.00002	**H**	-4.25251	-1.11744	-0.00018
H	3.75203	1.29259	0.00001	**H**	-1.82652	-2.39658	0.00056
H	4.21412	-1.22047	0.00007	**H**	-1.3087	1.75774	-0.00002
H	1.74459	-2.39833	-0.00005				

X=H				L10H			
Energy		-1065.07				-2704.27	
Charge		0				0	
Multiplicity		1				2	
Atom	**x**	**y**	**z**	**Atom**	**x**	**y**	**z**
C	3.17339	0.96034	-0.00029	**C**	3.37802	0.31706	0.00001
C	3.63198	-0.38174	0.00012	**C**	4.78376	0.43398	0.00005

C	5.02047	-0.6028	0.00043	**C**	5.6204	-0.6729	0.00007
C	5.93101	0.45	0.00032	**C**	2.79097	-0.98828	-0.00001
C	5.45847	1.76764	-0.00013	**C**	5.04655	-1.9536	0.00006
C	4.08896	2.0192	-0.00044	**C**	3.66812	-2.10235	0.00002
O	1.84556	1.27021	-0.0006	**C**	2.57021	1.53573	-0.00002
C	2.68886	-1.50916	0.00013	**O**	1.48787	-1.23466	-0.00006
H	5.38827	-1.62437	0.00073	**C**	1.80193	3.64095	-0.00006
H	6.99716	0.24681	0.00056	**N**	1.22608	1.49716	0.00003
H	6.15694	2.59938	-0.00023	**C**	2.97144	2.90142	-0.0001
H	1.32485	0.42214	-0.00029	**N**	0.77398	2.76813	-0.00002
N	1.36538	-1.27491	-0.00028	**O**	-1.48789	1.23467	-0.00003
H	3.70391	3.03416	-0.00079	**N**	-1.22607	-1.49715	-0.00001
N	0.76794	-2.47931	-0.00007	**C**	-2.791	0.98828	0.00002
C	2.9274	-2.91049	0.00028	**C**	-3.66815	2.10234	0.00007
C	1.67099	-3.48869	0.0003	**C**	-3.37803	-0.31706	0.00002
H	-0.24859	-2.50675	-0.00017	**C**	-5.04658	1.95358	0.00013
H	1.36252	-4.5239	0.0005	**C**	-5.62042	0.67287	0.00013
H	3.87345	-3.42906	0.00047	**C**	-4.78376	-0.434	0.00008
C	-2.68888	1.50917	0.00009	**C**	-2.57019	-1.53573	-0.00003
C	-3.63198	0.38173	-0.00005	**N**	-0.77396	-2.76811	-0.00005
C	-3.17337	-0.96034	-0.00028	**C**	-2.97141	-2.90143	-0.00007
C	-4.08892	-2.01922	-0.00024	**C**	-1.8019	-3.64094	-0.00017
H	-3.70386	-3.03417	-0.00042	**Cu**	0.00000	0.00001	0.00000
C	-5.45844	-1.76767	-0.00004	**H**	-0.23852	2.87658	-0.00003
H	-6.15689	-2.59942	-0.00004	**H**	6.69816	-0.54630	0.00011
C	-5.93099	-0.45004	0.00015	**H**	3.21786	-3.09076	0.00000
H	-6.99715	-0.24687	0.00031	**H**	5.68103	-2.83605	0.00007
O	-1.84554	-1.2702	-0.00058	**H**	5.22562	1.42586	0.00007
H	-1.32483	-0.42213	-0.00085	**H**	-6.69817	0.54626	0.00018
C	-5.02047	0.60278	0.00014	**H**	-5.22561	-1.42589	0.00009
H	-5.38829	1.62434	0.00032	**H**	-5.68107	2.83602	0.00017
N	-1.36539	1.27494	0.00011	**H**	-3.21789	3.09076	0.00007
N	-0.76796	2.47934	0.00022	**H**	0.23855	-2.87656	-0.00006
H	0.24856	2.50677	0.00021	**H**	3.9752	3.29607	-0.00017
C	-1.67103	3.48871	0.00048	**H**	1.63648	4.70861	-0.00009
H	-1.36257	4.52393	0.00063	**H**	-1.63644	-4.7086	-0.00025
C	-2.92744	2.9105	0.0004	**H**	-3.97517	-3.29608	-0.00007
H	-3.87349	3.42906	0.00053				

Table S8: Optimized Coordinates L11H Monomer and Deprotonated Monomer

X=NO2				**L11H**			
Energy		-737.028				-736.5096787	
Charge		0				1	
Multiplicity		1				1	
Atom	**x**	**y**	**z**	**Atom**	**x**	**y**	**z**
C	-0.51332	-0.32136	-0.00199	**C**	-0.47672	-0.40389	-0.01033
C	0.56099	0.6149	0.02895	**C**	0.58795	0.61645	0.01222
C	0.26977	1.9847	0.08417	**C**	0.28374	1.97025	0.04523
C	-1.03955	2.46248	0.08881	**C**	-1.04108	2.44371	0.04932
C	-2.09453	1.55688	0.04001	**C**	-2.08075	1.52902	0.02443
C	-1.83036	0.18843	0.01518	**C**	-1.82812	0.14764	0.01449
O	-0.31668	-1.64127	-0.08936	**O**	-0.20264	-1.63361	-0.07376
C	1.95818	0.15787	-0.00219	**C**	1.98884	0.18864	-0.00051
H	1.09029	2.69422	0.11558	**N**	2.353	-1.12203	-0.04457
H	-1.2347	3.52846	0.12766	**N**	3.6869	-1.32349	-0.05047
H	-3.12691	1.88532	0.02661	**C**	3.19764	0.90108	0.02481
H	0.65422	-1.82464	-0.11884	**C**	4.20055	-0.08644	-0.00779
N	2.24775	-1.15135	-0.08494	**N**	-2.98609	-0.71121	0.00837
N	3.59192	-1.23021	-0.09331	**O**	-4.09615	-0.20469	-0.29
C	3.16008	0.91915	0.04258	**O**	-2.87105	-1.90609	0.30638
C	4.17887	-0.00886	-0.01802	**H**	1.09891	2.69059	0.06625
H	4.03284	-2.13538	-0.15022	**H**	-1.2447	3.5099	0.07786
H	5.25273	0.10621	-0.01291	**H**	-3.11457	1.85338	0.0241
H	3.27384	1.98959	0.11029	**H**	5.27547	0.04513	-0.00208
N	-2.98968	-0.71269	0.00611	**H**	3.32963	1.97242	0.06187
O	-3.9942	-0.32415	-0.60127	**H**	1.64514	-1.85792	-0.07346
O	-2.91323	-1.77323	0.62086				

Table S9: Optimized Coordinates L11H Dimer and Complex

X=NO2				**L11H**			
Energy		-737.028				-736.5096787	
Charge		0				1	
Multiplicity		1				1	
Atom	**x**	**y**	**z**	**Atom**	**x**	**y**	**z**
C	-0.51332	-0.32136	-0.00199	**C**	-0.47672	-0.40389	-0.01033
C	0.56099	0.6149	0.02895	**C**	0.58795	0.61645	0.01222
C	0.26977	1.9847	0.08417	**C**	0.28374	1.97025	0.04523
C	-1.03955	2.46248	0.08881	**C**	-1.04108	2.44371	0.04932
C	-2.09453	1.55688	0.04001	**C**	-2.08075	1.52902	0.02443
C	-1.83036	0.18843	0.01518	**C**	-1.82812	0.14764	0.01449
O	-0.31668	-1.64127	-0.08936	**O**	-0.20264	-1.63361	-0.07376
C	1.95818	0.15787	-0.00219	**C**	1.98884	0.18864	-0.00051
H	1.09029	2.69422	0.11558	**N**	2.353	-1.12203	-0.04457
H	-1.2347	3.52846	0.12766	**N**	3.6869	-1.32349	-0.05047
H	-3.12691	1.88532	0.02661	**C**	3.19764	0.90108	0.02481
H	0.65422	-1.82464	-0.11884	**C**	4.20055	-0.08644	-0.00779
N	2.24775	-1.15135	-0.08494	**N**	-2.98609	-0.71121	0.00837
N	3.59192	-1.23021	-0.09331	**O**	-4.09615	-0.20469	-0.29
C	3.16008	0.91915	0.04258	**O**	-2.87105	-1.90609	0.30638
C	4.17887	-0.00886	-0.01802	**H**	1.09891	2.69059	0.06625
H	4.03284	-2.13538	-0.15022	**H**	-1.2447	3.5099	0.07786
H	5.25273	0.10621	-0.01291	**H**	-3.11457	1.85338	0.0241
H	3.27384	1.98959	0.11029	**H**	5.27547	0.04513	-0.00208
N	-2.98968	-0.71269	0.00611	**H**	3.32963	1.97242	0.06187
O	-3.9942	-0.32415	-0.60127	**H**	1.64514	-1.85792	-0.07346
O	-2.91323	-1.77323	0.62086				

X=NO2				**L11H**			
Energy		-1474.09				-3113.3	

Charge		0				0	
Multiplicity		1				2	
Atom	**x**	**y**	**z**	**Atom**	**x**	**y**	**z**
C	-3.09425	-0.19724	-0.00044	**C**	2.94992	-1.65984	-0.02322
C	-3.14772	-1.62703	-0.00083	**N**	4.35171	1.88441	0.05604
C	-4.39381	-2.2569	-0.00078	**C**	4.16969	-2.33995	-0.04757
C	-5.58868	-1.53086	-0.00038	**C**	5.39912	-1.67594	-0.03696
C	-5.5487	-0.14522	-0.00003	**C**	2.93835	-0.21543	0.00851
C	-4.31525	0.52144	-0.00003	**C**	5.41978	-0.29133	0.00019
O	-1.92395	0.44169	-0.00059	**C**	4.22051	0.43283	0.01841
C	-1.90328	-2.41427	-0.00137	**C**	1.70634	-2.44318	-0.03128
H	-4.43218	-3.3417	-0.00106	**O**	1.8482	0.48518	0.03929
H	-6.54204	-2.04763	-0.00032	**C**	0.16146	-4.06067	-0.05543
H	-6.45369	0.44807	0.00028	**N**	0.48714	-1.87051	-0.01798
N	-0.71829	-1.77913	-0.00113	**C**	1.53102	-3.85163	-0.05469
N	0.22743	-2.72889	-0.00165	**N**	-0.43417	-2.85407	-0.03324
C	-1.69061	-3.81748	-0.00235	**O**	-1.84818	-0.48516	0.03928
C	-0.31373	-3.96848	-0.00223	**N**	-0.48714	1.87054	-0.01796
H	1.2074	-2.4442	-0.00121	**C**	-2.93834	0.21542	0.00849
H	0.30791	-4.85158	-0.00262	**C**	-4.2205	-0.43286	0.0184
H	-2.42293	-4.60988	-0.0029	**C**	-2.94993	1.65983	-0.02325
N	-4.35745	1.98443	0.00044	**C**	-5.41977	0.2913	0.00014
O	-5.46801	2.52283	-0.0008	**C**	-5.39912	1.6759	-0.03705
O	-3.30182	2.63333	0.00199	**C**	-4.1697	2.33993	-0.04764
C	4.3938	2.2569	-0.00308	**N**	-4.35169	-1.88444	0.05608
H	4.43217	3.3417	-0.00473	**C**	-1.70635	2.44319	-0.03127
C	5.58868	1.53086	-0.00341	**N**	0.43415	2.85412	-0.03318
H	6.54204	2.04762	-0.00538	**C**	-1.53106	3.85165	-0.05464
C	5.54871	0.14522	-0.00131	**C**	-0.16151	4.06071	-0.05535
H	6.45369	-0.44807	-0.00145	**Cu**	0.00001	0.00002	0.01239
C	4.31525	-0.52145	0.00089	**O**	5.48686	2.35462	0.19284
N	4.35745	-1.98443	0.00275	**O**	3.35274	2.61701	-0.05619
O	3.30182	-2.63333	-0.00103	**O**	-5.48682	-2.35465	0.19305

O	5.46799	-2.52283	0.00787	**O**	-3.35274	-2.61706	-0.05625
C	3.09425	0.19725	0.00138	**H**	-1.42636	-2.59107	-0.02967
O	1.92396	-0.4417	0.00415	**H**	6.32622	-2.2377	-0.05838
C	3.14772	1.62703	-0.00064	**H**	6.35209	0.25831	0.01249
C	1.90328	2.41427	-0.00017	**H**	4.16494	-3.42482	-0.07517
C	1.69062	3.81748	-0.0013	**H**	-0.42024	-4.97045	-0.0698
H	2.42294	4.60987	-0.00265	**H**	2.29111	-4.61621	-0.06852
C	0.31373	3.96849	-0.0001	**H**	-6.32623	2.23764	-0.0585
H	-0.3079	4.85159	-0.00034	**H**	-4.16496	3.4248	-0.07526
N	-0.22743	2.7289	0.00131	**H**	-6.35208	-0.25835	0.01244
H	-1.2074	2.44422	0.00175	**H**	-2.29116	4.61621	-0.06847
N	0.71829	1.77913	0.00137	**H**	0.42018	4.9705	-0.06968
H	-1.18362	-0.24027	-0.00079	**H**	1.42634	2.59114	-0.02958
H	1.18362	0.24026	0.00391				

Table S10: Optimized Coordinates for L12H Monomer and Deprotonated Monomer

X=Br				**L12H**			
Energy		-3103.653556				-3103.120832	
Charge		0				1	
Multiplicity		1				1	
Atom	**x**	**y**	**z**	**Atom**	**x**	**y**	**z**
C	-0.20218	-0.16602	0.00005	**C**	-0.1634	-0.2324	-0.00031
C	0.94389	0.67213	0.00018	**C**	0.97057	0.6837	0.00004
C	0.76793	2.06598	0.00012	**C**	0.78164	2.07227	0.00031
C	-0.49893	2.63859	0	**C**	-0.48824	2.64879	0.00031
C	-1.62861	1.81538	-0.00014	**C**	-1.6113	1.80588	0.00009
C	-1.47343	0.4345	-0.00017	**C**	-1.44162	0.4318	-0.00018
O	-0.13259	-1.51027	0.00022	**O**	-0.03948	-1.50156	-0.00009
C	2.29748	0.09919	0.00014	**C**	2.32496	0.13259	0.00003
H	1.64215	2.70862	0.00018	**N**	2.55017	-1.20956	0.00101
H	-0.6135	3.71757	-0.00001	**Br**	-2.99918	-0.69233	-0.00009
H	-2.6259	2.24126	-0.00021	**N**	3.8574	-1.54966	0.00035
H	0.81398	-1.78502	0.00062	**C**	3.60161	0.71704	-0.00064
N	2.48042	-1.23224	-0.00018	**C**	4.49606	-0.37113	-0.00062
Br	-3.00922	-0.68409	-0.00008	**H**	1.65762	2.71776	0.00065

N	3.81519	-1.41872	-0.00017	**H**	-0.61152	3.72809	0.00069
C	3.55812	0.76188	0.00019	**H**	-2.61397	2.22391	0.00022
C	4.49908	-0.24615	0.0001	**H**	5.5792	-0.35194	-0.00102
H	4.18225	-2.3577	-0.00035	**H**	3.84308	1.76998	-0.00142
H	5.57879	-0.21795	0.00014	**H**	1.7581	-1.8606	0.00114
H	3.75618	1.82213	0.00033				

Table S11: Optimized Coordinates for L12H Dimer and Complex

X=Br				**L12H**			
Energy		-6207.33				-7846.54	
Charge		0				0	
Multiplicity		1				2	
Atom	**x**	**y**	**z**	**Atom**	**x**	**y**	**z**
C	-3.15747	-0.5738	0.00001	**C**	2.69987	-2.04642	0.00002
C	-3.00283	-1.98577	-0.00006	**Br**	4.45866	1.75123	0.00004
C	-4.15378	-2.7881	-0.00014	**C**	3.83469	-2.87866	0.00001
C	-5.42945	-2.23102	-0.00032	**C**	5.12507	-2.36632	0.00001
C	-5.58007	-0.842	-0.00043	**C**	2.86895	-0.62428	0.00003
C	-4.45035	-0.03175	-0.00023	**C**	5.31093	-0.97817	0.00002
O	-2.1017	0.26916	0.00005	**C**	4.20577	-0.14492	0.00004
C	-1.66059	-2.58632	-0.00006	**C**	1.36911	-2.65977	0.00002
H	-4.04261	-3.86758	-0.00015	**O**	1.89235	0.25252	0.00004
H	-6.30627	-2.87008	-0.00045	**C**	-0.38125	-4.05513	0.00002
H	-6.56626	-0.39136	-0.00067	**N**	0.24105	-1.92573	0.00000
H	-1.26382	-0.27367	0.00021	**C**	1.0026	-4.0331	0.00002
N	-0.57444	-1.79417	-0.00001	**N**	-0.80593	-2.77584	0.00000
Br	-4.64262	1.86353	-0.00065	**O**	-1.89234	-0.25251	-0.00001
N	0.49124	-2.61083	-0.00008	**N**	-0.24105	1.92574	0.00002
C	-1.2584	-3.94861	-0.00009	**C**	-2.86895	0.62428	-0.00002
C	0.12475	-3.91398	0.00007	**C**	-4.20577	0.14492	-0.00004
H	1.41556	-2.1861	-0.00005	**C**	-2.69987	2.04642	-0.00001
H	0.85854	-4.70646	0.00016	**C**	-5.31093	0.97817	-0.00006
H	-1.87882	-4.83127	-0.00012	**C**	-5.12507	2.36632	-0.00005
C	3.15746	0.57379	0.00035	**C**	-3.83469	2.87866	-0.00003
O	2.1017	-0.26917	0.00014	**Br**	-4.45866	-1.75123	-0.00009
H	1.26383	0.27365	-0.00024	**C**	-1.36911	2.65977	0.00002
C	3.00282	1.98576	0.00016	**N**	0.80593	2.77584	0.00005
C	4.15377	2.7881	0.00028	**C**	-1.0026	4.0331	0.00005
H	4.0426	3.86758	0.00019	**C**	0.38125	4.05513	0.00006
C	5.42944	2.23102	0.00047	**Cu**	0.00000	0.00000	0.00001
H	6.30626	2.87009	0.00054	**H**	-1.73999	-2.36538	0.00000
C	5.58007	0.842	0.00058	**H**	5.98265	-3.03062	0.00000
H	6.56626	0.39137	0.0007	**H**	6.30951	-0.55462	0.00002
C	1.66058	2.58632	-0.00004	**H**	3.69690	-3.95506	0.00000
N	0.57442	1.79417	-0.00013	**H**	-5.98265	3.03062	-0.00007

N	-0.49125	2.61083	0.00003	**H**	-3.69689	3.95506	-0.00002
H	-1.41556	2.18609	0.00012	**H**	-6.30951	0.55462	-0.00009
C	-0.12476	3.91398	-0.00014	**H**	1.73999	2.36538	0.00006
H	-0.85855	4.70646	-0.00016	**H**	1.65405	-4.89227	0.00003
C	1.2584	3.94861	-0.00024	**H**	-1.07914	-4.87931	0.00002
H	1.87881	4.83126	-0.00033	**H**	1.07914	4.87931	0.00009
C	4.45035	0.03176	0.00048	**H**	-1.65405	4.89227	0.00006
Br	4.64263	-1.86353	0.00054				

Table S12: Optimized Coordinated for L13H Monomer and Deprotonated Monomer

X=OMe				**L13H**			
Energy		-647.051				-646.507	
Charge		0				1	
Multiplicity		1				1	
Atom	**x**	**y**	**z**	**Atom**	**x**	**y**	**z**
C	-0.62787	-0.47022	-0.00009	**C**	0.57681	-0.53445	0
C	0.37537	0.5228	-0.00008	**C**	-0.39537	0.53792	0.00001
C	-0.00584	1.88194	-0.00004	**C**	0.01021	1.88814	0.00004
C	-1.34186	2.24661	0.00003	**C**	1.35018	2.24634	0.00007
C	-2.34203	1.26131	0.00004	**C**	2.33423	1.23085	0.00007
C	-1.99437	-0.08752	-0.00002	**C**	1.96619	-0.1062	0.00002
O	-0.36863	-1.79683	-0.00028	**O**	0.26484	-1.777	-0.0001
C	1.79947	0.15972	-0.00002	**C**	-1.81773	0.2054	-0.00002
H	0.75988	2.65026	-0.00002	**N**	-2.24735	-1.08607	0.00007
H	-1.62255	3.29512	0.00007	**N**	-3.59356	-1.22183	0
H	-3.38388	1.55843	0.00009	**C**	-2.99057	0.97952	-0.0001
H	0.60605	-1.92832	-0.00055	**C**	-4.04204	0.04142	-0.00009
N	2.1866	-1.12761	0.00023	**O**	2.87295	-1.15063	-0.00001
N	3.53536	-1.10496	0.00023	**C**	4.24096	-0.82965	0.00001
C	2.9434	1.00936	0.00001	**H**	-0.75133	2.66537	0.00004
C	4.02937	0.15953	0.0001	**H**	1.64864	3.29141	0.0001
H	4.043	-1.97571	0.00034	**H**	3.38229	1.51588	0.00009
H	5.09178	0.35456	0.00011	**H**	-5.10961	0.22749	-0.00014
H	2.9739	2.08748	-0.00007	**H**	-3.06681	2.05716	-0.00016
O	-2.88401	-1.12238	-0.00005	**H**	4.53197	-0.25332	-0.89294
C	-4.26946	-0.81487	-0.00001	**H**	4.77908	-1.78206	-0.00002
H	-4.55595	-0.24817	0.89574	**H**	4.53197	-0.25338	0.893
H	-4.78597	-1.77574	-0.00004	**H**	-1.55931	-1.84792	0.0002
H	-4.556	-0.24808	-0.89568				

Table S13: Optimized Coordinates for L13H Dimer and Complex

X=OMe				**L13H**			
Energy		-1294.12				-2933.33	
Charge		0				0	
Multiplicity		1				2	
Atom	**x**	**y**	**z**	**Atom**	**x**	**y**	**z**
C	-3.23145	0.03006	0.00046	**C**	-3.04278	1.48215	0.00001
C	-3.30283	1.43975	-0.00029	**O**	-3.96193	-2.05995	0.00003
C	-4.57175	2.05319	-0.00123	**C**	-4.32165	2.08597	0.00007
C	-5.73115	1.29243	-0.00145	**C**	-5.47705	1.32704	0.00011
C	-5.65933	0.1089	-0.00074	**C**	-2.93635	0.06228	-0.00001
C	-4.41697	0.74073	0.00021	**C**	-5.39235	-0.07784	0.00009
O	-2.05388	0.64559	0.00151	**C**	-4.15101	-0.69773	0.00004
C	-2.07542	2.2507	-0.00012	**C**	-1.85599	2.34019	-0.00002
H	-4.63783	3.13611	-0.00179	**O**	-1.80957	-0.62207	-0.00003
H	-6.70207	1.77766	-0.00218	**C**	-0.39684	4.04123	-0.00016
H	-6.57292	0.69114	-0.00094	**N**	-0.60972	1.83446	-0.00004
H	-1.314	0.01994	0.00155	**C**	-1.75249	3.75949	0.00006
N	-0.87325	1.6493	0.00061	**N**	0.2614	2.86411	-0.00004
N	0.04399	2.63093	0.00043	**O**	1.80957	0.62207	-0.00004
C	-1.90307	3.66146	-0.0005	**N**	0.60972	-1.83446	-0.00001
C	-0.53287	3.85573	-0.0004	**C**	2.93635	-0.06228	0.00000
H	1.02581	2.35995	0.00065	**C**	4.15101	0.69773	-0.00001
H	0.05926	4.7591	-0.00071	**C**	3.04278	-1.48215	0.00001
H	-2.66128	4.42901	-0.00097	**C**	5.39235	0.07784	0.00001
C	3.23145	0.03006	0.0002	**C**	5.47705	-1.32704	0.00002
O	2.05387	0.64559	0.00067	**C**	4.32165	-2.08597	0.00002
H	1.314	0.01996	0.0008	**O**	3.96194	2.05995	-0.00003
C	3.30283	1.43975	-0.00016	**C**	1.85599	-2.34019	0.00002
C	4.57175	2.05319	-0.00055	**N**	-0.26140	-2.86411	-0.00001
H	4.63784	3.13611	-0.00082	**C**	1.75249	-3.75949	-0.00001
C	5.73115	1.29243	-0.00062	**C**	0.39684	-4.04123	0.00009
H	6.70207	1.77766	-0.00093	**Cu**	0.00000	0.00000	-0.00005
C	5.65933	0.1089	-0.00029	**C**	-5.11602	-2.88636	0.00007
H	6.57292	0.69114	-0.00035	**C**	5.11602	2.88636	-0.00004
C	2.07542	2.2507	-0.0002	**H**	1.25200	2.61586	-0.00004
N	0.87325	1.6493	0.00006	**H**	-6.45030	1.80715	0.00015
N	-0.04399	2.63092	-0.00008	**H**	-6.30374	-0.66444	0.00012

H	-1.02581	2.35995	0.00018	**H**	-4.39641	3.16850	0.00010
C	0.53287	3.85573	-0.00052	**H**	0.13238	4.98273	-0.00024
H	-0.05926	4.7591	-0.00072	**H**	-2.55426	4.48049	0.00015
C	1.90307	3.66146	-0.00059	**H**	6.45030	-1.80715	0.00003
H	2.66128	4.42901	-0.0009	**H**	4.39641	-3.16850	0.00003
C	4.41697	0.74074	0.00011	**H**	6.30374	0.66444	0.00000
O	4.22649	2.09703	0.00046	**H**	2.55426	-4.48049	-0.00004
O	-4.22649	2.09703	0.00094	**H**	-0.13238	-4.98273	0.00015
C	-5.37706	2.93059	0.00084	**H**	-1.252	-2.61586	-0.00005
H	-5.00291	3.95545	0.00153	**H**	-4.75045	-3.91482	0.00005
H	-5.98972	2.76832	-0.8952	**H**	-5.72959	-2.72056	-0.89511
H	-5.99052	2.76741	0.89617	**H**	-5.72952	-2.72057	0.89529
C	5.37706	2.93059	0.00043	**H**	4.75045	3.91482	-0.00005
H	5.99029	2.76766	0.89596	**H**	5.72956	2.72055	-0.89523
H	5.0029	3.95546	0.00074	**H**	5.72956	2.72058	0.89517
H	5.98994	2.76807	-0.89541				

Table S14: Optimized Coordinates for L14H Monomer and Deprotonated Monomer

Y=NO2				**L14H**			
Energy		-737.042				-736.527	
Charge		0				1	
Multiplicity		1				1	
Atom	**x**	**y**	**z**	**Atom**	**x**	**y**	**z**
C	0.24675	1.6463	0.0001	**C**	0.31677	1.68129	0.00007
C	0.43694	0.23514	0.00006	**C**	0.4562	0.22023	0.00001
C	-0.69545	-0.58516	0.00001	**C**	-0.67292	-0.58575	-0.00003
C	-1.97119	-0.02952	-0.00002	**C**	-1.96756	-0.03696	-0.00001
C	-2.16387	1.35726	0.00001	**C**	-2.14058	1.36747	0.00005
C	-1.05325	2.18398	0.00007	**C**	-1.0395	2.18784	0.0001
O	1.26879	2.51867	0.00026	**O**	1.31325	2.46744	0.00017
C	1.78186	-0.35613	0.00003	**C**	1.79016	-0.38332	0
H	-0.60126	-1.66349	-0.00003	**N**	2.9218	0.37369	-0.00009
H	-3.16892	1.76009	-0.00001	**N**	4.06335	-0.34569	-0.00009
H	2.12382	2.02381	0.00042	**C**	2.23736	-1.71121	0.00001
N	2.8693	0.43319	-0.00013	**C**	3.64254	-1.61805	0.00005
H	-1.15762	3.26341	0.00011	**N**	-3.10217	-0.89383	-0.00006
N	3.92511	-0.40314	-0.00016	**O**	-2.93158	-2.13392	-0.00011
C	2.16972	-1.72443	0.00001	**O**	-4.24657	-0.38451	-0.00004
C	3.54896	-1.70755	0	**H**	-0.57886	-1.66537	-0.00008
H	4.85831	-0.02103	-0.00027	**H**	-3.14702	1.77005	0.00007
H	4.27421	-2.50784	0.00003	**H**	-1.14881	3.26871	0.00017
H	1.53832	-2.59916	0.00006	**H**	4.36976	-2.42031	0.0001
N	-3.13082	-0.9173	-0.00009	**H**	1.63363	-2.60671	0.00004
O	-2.93015	-2.13696	-0.00008	**H**	2.87481	1.39307	-0.00017
O	-4.25299	-0.40225	-0.00007				

Table S15: Optimized Coordinates for L14H Dimer and Complex

Y=NO2				**L14H**			
Energy		-1474.1				-3113.31	
Charge		0				0	
Multiplicity		1				2	
Atom	**x**	**y**	**z**	**Atom**	**x**	**y**	**z**
C	-3.17563	-0.91547	-0.00015	**C**	3.35833	0.46423	0.00000
C	-3.62961	0.43319	0	**N**	7.04831	-0.20833	0.00000
C	-5.0083	0.66448	0.00003	**C**	4.74640	0.64520	0.00000
C	-5.90266	-0.40198	-0.00011	**C**	5.61163	-0.44152	0.00000
C	-5.46009	-1.72844	-0.00027	**C**	2.82844	-0.87114	0.00000
C	-4.09576	-1.97527	-0.00029	**C**	5.11850	-1.75468	0.00000
O	-1.85909	-1.22437	-0.00014	**C**	3.75300	-1.95238	0.00000
C	-2.67974	1.55457	0.00011	**C**	2.49864	1.64902	0.00000
H	-5.40127	1.67322	0.00014	**O**	1.54714	-1.16638	0.00000
H	-6.18113	-2.53623	-0.00038	**C**	1.65342	3.71957	0.00000
H	-1.33219	-0.37498	0.00001	**N**	1.15704	1.55422	0.00000
N	-1.35919	1.30478	0.00003	**C**	2.84981	3.02539	0.00000
H	-3.71511	-2.99098	-0.0004	**N**	0.65943	2.80767	0.00000
N	-0.75187	2.50315	0.00017	**O**	-1.54714	1.16638	0.00000
C	-2.90735	2.95572	0.00025	**N**	-1.15704	-1.55422	0.00000
C	-1.64574	3.52146	0.00026	**C**	-2.82844	0.87114	0.00000
H	0.26359	2.52497	0.00019	**C**	-3.75300	1.95238	0.00000
H	-1.32777	4.55366	0.00035	**C**	-3.35833	-0.46423	0.00000
H	-3.84888	3.48258	0.00032	**C**	-5.11850	1.75468	0.00000
C	2.67973	-1.55455	0.00014	**C**	-5.61163	0.44152	0.00000
C	3.6296	-0.43319	0.00003	**C**	-4.74640	-0.64520	0.00000
C	3.17563	0.91547	-0.00003	**N**	-7.04831	0.20833	0.00000
C	4.09577	1.97526	-0.00014	**C**	-2.49864	-1.64902	0.00000
H	3.71513	2.99097	-0.00019	**N**	-0.65943	-2.80767	0.00000
C	5.4601	1.72842	-0.00017	**C**	-2.84981	-3.02539	-0.00001
H	6.18115	2.53621	-0.00025	**C**	-1.65342	-3.71957	-0.00001
C	5.90266	0.40197	-0.00011	**Cu**	0.00000	0.00000	0.00000
O	1.8591	1.2244	-0.00002	**O**	7.45073	0.96165	0.00000
H	1.33217	0.37502	0.00005	**O**	7.79412	-1.19396	0.00000
C	5.00829	-0.66449	-0.00002	**O**	-7.79412	1.19396	0.00000
H	5.40126	-1.67323	0.00002	**O**	-7.45073	-0.96165	0.00000
N	1.35918	-1.30475	0.00019	**H**	-0.35380	2.88989	0.00000

N	0.75186	-2.50311	0.00014	**H**	3.34490	-2.95781	0.00001
H	-0.26361	-2.52494	0.00005	**H**	5.81124	-2.58743	0.00001
C	1.64572	-3.52143	0.00039	**H**	5.17589	1.63876	0.00000
H	1.32775	-4.55364	0.00052	**H**	1.44712	4.77966	0.00000
C	2.90733	-2.95571	0.00026	**H**	3.83825	3.45653	0.00000
H	3.84886	-3.48257	0.00029	**H**	-5.17589	-1.63876	0.00000
N	7.33917	0.12419	-0.00015	**H**	-5.81124	2.58743	0.00000
N	-7.33916	-0.12422	-0.00009	**H**	-3.34490	2.95781	0.00000
O	8.11206	1.08629	-0.00022	**H**	-3.83825	-3.45653	-0.00001
O	7.70133	-1.05638	-0.00009	**H**	-1.44712	-4.77966	-0.00001
O	-7.70133	1.05635	0.00014	**H**	0.35380	-2.88989	0.00000
O	-8.11205	-1.08634	-0.00017				

Table S16: Optimized Coordinates for L15H Monomer and Deprotonated Monomer

Y=Br				**L15H**			
Energy		-3103.66				-3103.12	
Charge		0				1	
Multiplicity		1				1	
Atom	**x**	**y**	**z**	**Atom**	**x**	**y**	**z**
C	-0.77796	1.71593	0	**C**	-0.86997	1.73094	0.00016
C	-0.83207	0.2991	-0.00005	**C**	-0.85441	0.2741	0.00005
C	0.37665	-0.41923	-0.00005	**C**	0.35997	-0.42878	-0.00002
C	1.59603	0.24142	-0.00001	**C**	1.57261	0.24701	-0.00004
C	1.65097	1.63733	0.00002	**C**	1.61167	1.64695	0.00004
C	0.46588	2.36331	0.00003	**C**	0.4228	2.36092	0.00017
O	-1.88089	2.49963	-0.00006	**O**	-1.95307	2.41873	0.00042
C	-2.11237	-0.42078	-0.00001	**C**	-2.11698	-0.46064	0.00007
H	0.35778	-1.50259	-0.00006	**N**	-3.31148	0.19165	-0.00009
H	2.60614	2.15054	0.00003	**N**	-4.38554	-0.62772	-0.00002
H	-2.68371	1.93048	-0.00018	**C**	-2.44345	-1.82566	0.00023
N	-3.27577	0.25261	0.00023	**C**	-3.85176	-1.85768	0.00007
H	0.47836	3.44822	0.00004	**Br**	3.22197	-0.75291	-0.00021
N	-4.2408	-0.68841	0.00009	**H**	0.34958	-1.51446	-0.00008
C	-2.36051	-1.82261	0.00007	**H**	2.56543	2.16748	0.00004
C	-3.73381	-1.94793	-0.00006	**H**	0.43593	3.44794	0.0003
H	-5.20776	-0.40316	0.00012	**H**	-4.50479	-2.72203	0.00009
H	-4.37369	-2.81806	-0.00016	**H**	-1.76397	-2.66559	0.00038
H	-1.64412	-2.62912	0.00007	**H**	-3.33043	1.2183	-0.00031
Br	3.21409	-0.77149	-0.00004				

Table S17: Optimized Coordinated for L15H Dimer Complex

Y=Br				**L15H**			
Energy		-6207.33				-7846.53	
Charge		0				0	
Multiplicity		1				2	
Atom	**x**	**y**	**z**	**Atom**	**x**	**y**	**z**
C	-3.1708	0.93196	0.00016	**C**	-3.35702	0.46681	0.00003
C	-3.6217	-0.41181	-0.00018	**Br**	-7.50945	-0.11214	-0.00003
C	-5.00567	-0.65184	-0.00027	**C**	-4.75341	0.65698	0.00001
C	-5.90934	0.40171	-0.00001	**C**	-5.62392	-0.41775	0
C	-5.46488	1.72479	0.00036	**C**	-2.82952	-0.86238	0.00004
C	-4.09687	1.98062	0.00047	**C**	-5.12953	-1.72635	0.00001
O	-1.84749	1.25135	0.00017	**C**	-3.75918	-1.93231	0.00003
C	-2.67366	-1.53451	-0.00013	**C**	-2.49784	1.64998	0.00004
H	-5.37247	-1.67135	-0.00048	**O**	-1.54096	-1.16793	0.00006
H	-6.17436	2.54445	0.00057	**C**	-1.64164	3.71857	0.00008
H	-1.3199	0.40716	-0.00045	**N**	-1.15697	1.55196	-0.00001
N	-1.35191	-1.29122	0.00047	**C**	-2.84164	3.02992	0.00009
H	-3.72648	3.0007	0.00075	**N**	-0.65212	2.8023	0.00002
N	-0.74873	-2.49194	0.00024	**O**	1.54096	1.16793	0.00001
C	-2.90554	-2.93596	-0.00021	**N**	1.15697	-1.55196	0.00003
C	-1.64599	-3.50679	-0.00017	**C**	2.82952	0.86238	-0.00002
H	0.26769	-2.51411	0.00035	**C**	3.75918	1.93231	-0.00006
H	-1.33168	-4.54018	-0.00036	**C**	3.35702	-0.46681	0
H	-3.84839	-3.46037	-0.00045	**C**	5.12953	1.72635	-0.00008
C	2.67367	1.53452	0.00002	**C**	5.62392	0.41775	-0.00005
C	3.6217	0.41181	0.00024	**C**	4.75341	-0.65698	-0.00002
C	3.1708	-0.93196	0.00034	**Br**	7.50945	0.11214	-0.0001
C	4.09686	-1.98062	0.00022	**C**	2.49784	-1.64998	0.00004
H	3.72647	-3.00069	0.00031	**N**	0.65211	-2.8023	0.00008
C	5.46487	-1.7248	0.00007	**C**	2.84164	-3.02992	0.00011
H	6.17434	-2.54446	0.00005	**C**	1.64164	-3.71857	0.00011
C	5.90934	-0.40171	-0.00003	**Cu**	0	0	0.00001
O	1.84749	-1.25135	0.00059	**H**	0.3635	2.87034	0.00001
H	1.31989	-0.40716	0.00106	**H**	-3.36151	-2.94258	0.00003
C	5.00567	0.65183	0.00006	**H**	-5.80996	-2.57105	0
H	5.37247	1.67134	-0.00005	**H**	-5.15577	1.66287	-0.00001
N	1.35192	1.29124	-0.0003	**H**	5.15577	-1.66287	0

N	0.74874	2.49196	-0.0003	**H**	5.80996	2.57105	-0.00011
H	-0.26768	2.51411	-0.00025	**H**	3.36151	2.94258	-0.00008
C	1.646	3.5068	-0.00028	**H**	-0.36351	-2.87034	0.00009
H	1.3317	4.54019	-0.00029	**H**	3.82745	-3.46759	0.00014
C	2.90555	2.93597	-0.00041	**H**	1.43067	-4.77812	0.00015
H	3.8484	3.46038	-0.00053	**H**	-1.43067	4.77812	0.00011
Br	-7.78194	0.03219	-0.00012	**H**	-3.82745	3.46759	0.00013
Br	7.78194	-0.03221	-0.00012				

Table S18: Optimized Coordinates L16H Monomer and Deprotonated Monomer

Y=OMe				**L16H**			
Energy		-647.054				-646.508	
Charge		0				1	
Multiplicity		1				1	
Atom	**x**	**y**	**z**	**Atom**	**x**	**y**	**z**
C	0.03469	1.51205	-0.00006	**C**	-0.0536	1.53435	0.00001
C	-0.27723	0.12774	-0.00006	**C**	-0.29437	0.09853	-0.00008
C	0.7779	-0.79748	0.00001	**C**	0.7782	-0.80685	-0.00003
C	2.11138	-0.38998	0.00006	**C**	2.10242	-0.37816	0.00003
C	2.41154	0.97861	0.00004	**C**	2.37566	0.99794	0.00008
C	1.37368	1.91096	-0.00001	**C**	1.32581	1.9161	0.00012
O	-0.90943	2.49124	-0.00015	**O**	-1.0044	2.4073	0.00023
C	-1.66767	-0.34817	-0.00006	**C**	-1.6675	-0.39878	-0.00011
H	0.57485	-1.8628	0.00003	**N**	-2.72144	0.46157	-0.00019
H	3.43622	1.33093	0.00008	**N**	-3.92829	-0.14637	-0.00068
H	-1.80023	2.07828	-0.00022	**C**	-2.23912	-1.6818	0.00022
N	-2.69238	0.52171	0.00009	**C**	-3.6294	-1.45417	0.00004
H	1.58946	2.97447	-0.00002	**O**	3.07938	-1.38312	0.00005
N	-3.81069	-0.23202	-0.0002	**C**	4.42514	-0.97442	0.00014
C	-2.16352	-1.68358	0.00009	**H**	0.58682	-1.87722	-0.00004
C	-3.53701	-1.56207	-0.0001	**H**	3.39745	1.36713	0.00016
H	-4.71083	0.22155	-0.00034	**H**	1.53707	2.98276	0.00025
H	-4.32208	-2.30393	-0.00018	**H**	-4.43057	-2.18373	0.00016
H	-1.6009	-2.60392	0.0002	**H**	-1.72431	-2.63164	0.00057
O	3.04776	-1.39746	0.00012	**H**	4.67691	-0.38057	0.893
C	4.41998	-1.03546	0.00021	**H**	4.67701	-0.38054	-0.89268
H	4.68431	-0.45743	0.89568	**H**	5.02623	-1.88849	0.00015
H	4.68443	-0.45747	-0.89526	**H**	-2.53778	1.47589	-0.00036
H	4.97719	-1.97353	0.00026				

Table S19: Optimized Coordinates for L16H Dimer and Complex

Y=OMe				**L16H**			
Energy		-1294.13				-2933.33	
Charge		0				0	
Multiplicity		1				2	
Atom	**x**	**y**	**z**	**Atom**	**x**	**y**	**z**
C	-3.13596	1.07992	-0.00125	**C**	-2.77551	1.02195	0.00001
C	-3.64497	-0.23699	-0.00009	**C**	-3.38312	-0.26612	0.00001
C	-5.04426	-0.42227	0.00068	**C**	-4.79671	-0.37595	0.00006
C	-5.91431	0.66512	0.0003	**C**	-5.6115	0.7463	0.00011
C	-5.39321	1.96873	-0.00093	**C**	-5.01866	2.02161	0.0001
C	-4.02021	2.16683	-0.00171	**C**	-3.64233	2.14584	0.00006
O	-1.79489	1.34869	-0.00201	**O**	-1.46615	1.25679	-0.00004
C	-2.74621	-1.40013	0.00018	**C**	-2.5954	-1.49673	-0.00003
H	-5.4302	-1.43377	0.00154	**N**	-1.25059	-1.47761	-0.00004
H	-6.08045	2.80833	-0.00125	**N**	-0.8167	-2.75439	-0.0001
H	-1.30574	0.48354	-0.00135	**C**	-3.0155	-2.85729	-0.00011
N	-1.41457	-1.2161	-0.00101	**C**	-1.85646	-3.61332	-0.00007
H	-3.60705	3.17054	-0.00267	**C**	2.5954	1.49673	-0.00008
N	-0.86292	-2.44189	-0.00032	**C**	3.38312	0.26612	-0.00004
C	-3.03657	-2.7919	0.00111	**C**	2.77551	-1.02195	-0.00008
C	-1.80258	-3.41689	0.00126	**C**	3.64232	-2.14585	-0.00004
H	0.15234	-2.50611	-0.00078	**C**	5.01865	-2.02161	0.00002
H	-1.53292	-4.46288	0.00209	**C**	5.61149	-0.74631	0.00007
H	-4.00059	-3.27636	0.00192	**O**	1.46615	-1.25679	-0.00009
C	2.74622	1.40014	0.00003	**C**	4.79671	0.37594	0.00005
C	3.64497	0.23699	-0.00037	**N**	1.25059	1.47762	-0.00004
C	3.13594	-1.07991	-0.00146	**N**	0.81671	2.7544	-0.00001
C	4.02019	-2.16683	-0.00163	**C**	1.85647	3.61332	-0.00045
H	3.60701	-3.17054	-0.00251	**C**	3.0155	2.85729	0.00006
C	5.39319	-1.96874	-0.00077	**Cu**	0	0	-0.00002
H	6.08041	-2.80835	-0.00092	**O**	6.98769	-0.72545	0.00014
C	5.9143	-0.66515	0.0003	**O**	-6.98769	0.72545	0.00016
O	1.79487	-1.34867	-0.00247	**C**	-7.63662	-0.53453	0.00016
H	1.30573	-0.48351	-0.00261	**C**	7.63662	0.53452	0.00019
C	5.04426	0.42226	0.00047	**H**	-5.2362	-1.36534	0.00007
H	5.43021	1.43376	0.0013	**H**	-5.66017	2.8975	0.00014
N	1.41458	1.21612	-0.00065	**H**	-3.18452	3.13057	0.00005

N	0.86294	2.44192	-0.00004	**H**	0.19471	-2.87528	-0.00013
H	-0.15232	2.50616	-0.00042	**H**	-1.70554	-4.6828	-0.00008
C	1.80261	3.41691	0.00146	**H**	-4.02393	-3.23914	-0.00015
H	1.53296	4.46291	0.00233	**H**	3.18451	-3.13057	-0.00006
C	3.0366	2.79191	0.00102	**H**	5.66016	-2.89751	0.00005
H	4.00062	3.27636	0.00164	**H**	5.2362	1.36533	0.0001
O	7.28429	-0.57085	0.00113	**H**	-0.1947	2.8753	0.00011
O	-7.2843	0.57081	0.001	**H**	1.70555	4.6828	-0.0007
C	7.87128	0.72126	0.00229	**H**	4.02393	3.23914	0.00019
H	7.58965	1.29019	0.89837	**H**	-7.3836	-1.1185	0.89577
H	7.59077	1.2913	-0.89343	**H**	-7.38366	-1.11847	-0.89549
H	8.95016	0.55964	0.00286	**H**	-8.7069	-0.32219	0.00019
C	-7.87127	-0.72131	0.00228	**H**	8.7069	0.32219	0.00025
H	-7.58975	-1.2901	0.89847	**H**	7.38358	1.11847	0.89581
H	-7.59065	-1.29147	-0.89333	**H**	7.38368	1.11849	-0.89545
H	-8.95016	-0.5597	0.00269				

Table S20: Additional information on bond lengths in the crystal structure of [Cu(L12)$_2$] giving the values used to calculate the average bond lengths in Figure 4 in the main text.

	[Cu(L10)$_2$]		[Cu(L12)$_2$]	
	X = H		X = Br	
	DFT	XRD	DFT	XRD
Cu-N	1.935	1.919(2)	1.941	AV: 1.924(3) 1.924(2), 1.922(2), 1.927(2)
Cu-O	1.933	1.915(2)	1.909	AV: 1.908(9) 1.901(2), 1.903(2), 1.919(2)
cis N-Cu-O (*intra*ligand)	90.4	90.9(1)	90.5	AV: 90.2(1) 90.8(1), 90.2(1), 90.4(1)
cis N-Cu-O (*inter*ligand)	89.6	89.1(1)	89.5	AV : 89.3(9) 90.05(7), 88.37(7), 89.59(7)
Br⋯HN	-	-	2.787	Av: 2.95(9) 2.855, 2.928, 3.052
OH⋯N	2.063	2.23(2)	2.118	AV: 2.22(6) 2.273, 2.162, 2.225
Br⋯N	-	-	3.794	AV: 3.768(3) 3.706(2), 3.781(2), 3.813(2)
O⋯N	2.733	2.720(2)	2.747	AV: 2.75(3) 2.719(2), 2.770(2), 2.771(2)

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