Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Cu-tetracatechol metallopolymer catalyst for three component click reactions and β-borylation of α, β-unsaturated carbonyl compounds

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1. Experimental procedures

1.1 Materials and Methods

All the chemicals were purchased from commercial sources and used without further purification. Dichloromethane (DCM), chloroform, methanol, hexane, dimethylformamide (DMF), ethanol, toluene and acetonitrile (ACN), *t*-butyl alcohol were purchased from VWR Chemicals. Deuterated methanol-d_4 and $CDCl_3$ were obtained from Cambridge Isotope Laboratories for ^{1}H NMR and ^{13}C NMR analyses. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 300 NMR, Bruker DRX 400 NMR and Bruker AV 500 NMR, respectively, using methanol-d_4 and $CDCl_3$ as solvents. Mass spectrometric analyses of the compounds were performed with the Bruker Autoflex III TOF/MALDI analyser. The optical properties of the compounds were investigated using Shimadzu UV-VIS-NIR Spectrophotometer. FTIR spectra were recorded using KBr as a matrix using the Bruker-alpha instrument. Electrochemical properties of the polymer and ligand were measured with a CH Instruments Electrochemical Analyzer using platinum (Pt) as the working electrode, Pt wire as the counter electrode, and Ag/AgCl as the reference electrode. Crystal analysis was done by using a Bruker D8 venture single crystal X-ray diffractometer with the X-ray intensity (λ = 0.71073 Å). The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS).The structure was solved and refined using the Bruker SHELXTL Software.

1.2 Synthesis of Compound 1

Catechol (3 g, 27.5 mmol) was dissolved in 36 mL of methanol under N_2 atmosphere. Terephthalaldehyde (0.609 g, 4.54 mmol) was added in the mixture, followed by 9.3 mL of 12 M HCl. The reaction mixture was stirred and refluxed at 80 °C for overnight under the inert atmosphere. After completion of the reaction, the excess solvent was removed under reduced pressure and mixed with water to yield gummy solid. This solid was washed with chloroform (3 x 50 mL) followed by extraction in diethyl ether (3 x 50 mL). The organic layer was dried over anhydrous Na_2SO_4, and pure product was obtained via column chromatography [MeOH : DCM, 6:94], yield = 60 %. Crystallization was done in DCM/methanol/water mixture to yield white crystals.^{1}H NMR (500 MHz, Methanol-d_4, δ ppm) 6.99 (s, 4H), 6.65 (d, J = 8.1 Hz, 4H), 6.52 (d, J = 2.2 Hz, 4H), 6.42 (d, J = 2.1 Hz, 2H), 6.40 (d, J = 2.0 Hz, 2H), 5.20 (s, 2H).^{13}C NMR (126 MHz, Methanol-d_4, δ ppm) 145.90, 144.45, 144.12, 137.84, 130.06, 121.78, 117.68, 115.94, 56.57. HRMS-ESI (m/z): Observed $[M-H]^-$ = 537.1558, Calculated $[M-H]^-$ = 537.1555

Interfacial Polymerization

Compound **1** (0.010 g, 0.0186 mmol) was dissolved in ethyl acetate (EA, 5 mL) and copper acetate (0.0074 g, 0.0371 mmol) in water (5 mL). Interface polymerization was achieved at the interface of aqueous solution of copper acetate and EA solution of the compound **1**. After 24 hr, the film from the interface was either collected on a glass slide or deposited onto a substrate (e.g. glass slide) placed at the bottom of the beaker by slowly removing the bottom layer followed by top layer. The polymer film deposited substrate was washed with ethanol, water and dried at 65 °C for overnight. This dried film was further used for full characterization.

Bulk Polymerization

Compound **1** (0.350 g, 0.650 mmol) and copper acetate (0.260 g, 1.30 mmol) were dissolved separately in ethanol (10 mL each). Both solutions were cooled to 5 °C before mixing for bulk polymerization. After mixing the two solutions, the mixture was kept at room temperature for overnight for completing the polymerization. The solid polymer was collected after centrifuging the solution, washed three times with water, followed by ethanol to remove unreacted reactants. The polymer was dried in an oven at 65 °C for 24 hr.

GPC Analysis

Polymer film and polymer powder (0.005 g) were dispersed separately in DMF (1.5 mL), sonicated for 30 min and kept at room temperature for 24 hr to achieve maximum solubility. The solutions were filtered using 0.22 µm PTFE filter and used for GPC analyses.

Spectroscopic Characterization

The polymer (0.001 g) was dissolved in DMF(1 mL), sonicated for the 10 min to dissolve the solid, centrifuged and UV-VIS spectra were recorded from 250 nm to 800 nm.

For recording the UV spectrum of the solid film, the a few drops of the solution of polymer in DMF was drop casted on a quartz substrate, dried, and UV-Vis spectra was recorded at room temperature from 250 nm to 800 nm.

BET Analysis

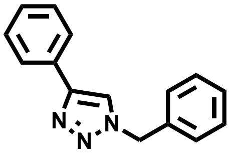
The N_2sorption isotherm of the polymer solid was measured by Quantachrome Autosorb iQ C-XR (Quantachrome® ASiQwin™) at 77K. The sample (90 mg) was degassed at 110 °C for overnight under vacuum before the gas isotherm analysis. Surface area was calculated from N_2adsorption data. Pore size was calculated by DFT (slit pore, NLDFT equilibrium model).

Three component click reaction catalyzed by Cu-tetracatechol polymer

We used a previously reported protocol for the reaction with some modifications.[1] Briefly, 10 mL vial was charged with alkyne (0.5 mmol), sodium azide (0.5 mmol), and an alkyl halide (0.5 mmol) into a water /*t*-butyl alcohol mixture (1.5/0.5 mL) with or without sodium ascorbate (10 mg, 10 mol %). The Cu-tetracatechol polymer solid (10 mg) was added and the reaction mixture was stirred at 50 °C for 2.5 hr. After completion, the mixture was diluted with water (2 mL), transferred into a separating funnel and the product was extracted with DCM (3 × 2mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the desired 1, 2, 3-triazole. Purification of the obtained triazole was accomplished via recrystallization from EtOAc:hexane (1 : 1) mixture.

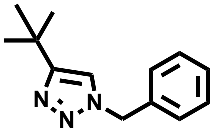
For recycling of catalyst, the products were extracted in DCM layer and both DCM and water fractions were centrifuged separately. The collected solid was added in water and the next batch of reactants dissolved in appropriate organic solvent were added in it, and the above process was repeated. Crude NMR spectra were used for the characterization of the products and calculating the % conversion after each cycle.

All compounds were previously reported (1a-6a) and characterized by ^{1}H NMR.[1-5]



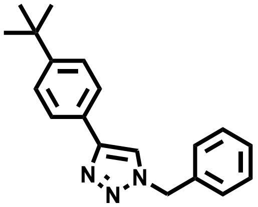
1a

1-benzyl-4-phenyl-1H-1,2,3-triazole.[1] All peaks are in accordance with literature.[1] ^{1}H NMR (400 MHz, Chloroform-*d*, δ ppm) 7.81 (d, *J* = 7.5 Hz, 2H), 7.69 (s, 1H), 7.43 – 7.35 (m, 5H), 7.34 – 7.29 (m, 3H), 5.58 (s, 2H).



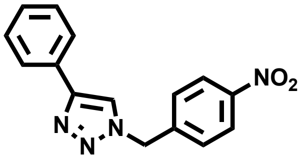
2a

1-benzyl-4-(tert-butyl)-1H-1,2,3-triazole.[2] All peaks are in accordance with literature.[2] ^{1}H NMR (400 MHz, Chloroform-*d*, δ ppm) 7.42 – 7.34 (m, 5H), 7.24 (s, 1H), 5.48 (s, 2H), 1.32 (s, 9H).



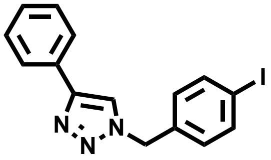
3a

1-benzyl-4-(4-(tert-butyl)phenyl)-1H-1,2,3-triazole.[3] All peaks are in accordance with literature.[3] ^{1}H NMR (400 MHz, Chloroform-*d*, δ ppm) 7.74 (d, *J* = 8.5 Hz, 2H), 7.66 (s, 1H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.38 – 7.34 (m, 3H), 7.30 – 7.27 (m, 2H), 5.55 (s, 2H), 1.33 (s, 9H).



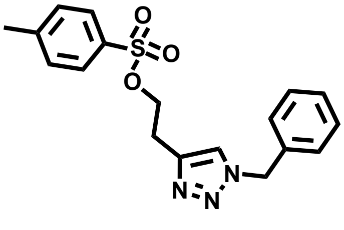
4a

1-(4-nitrobenzyl)-4-phenyl-1H-1,2,3-triazole.[1] All peaks are in accordance with literature.[1] ^{1}H NMR (400 MHz, Chloroform-*d*, δ ppm) 8.22 (d, *J* = 2.4 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.79 (s, 1H), 7.46 – 7.40 (m, 4H), 7.34 (m, 1H), 5.70 (s, 2H).



5a

1-(4-iodobenzyl)-4-phenyl-1H-1,2,3-triazole.[4] All peaks are in accordance with literature.[4] ^{1}H NMR (400 MHz, Chloroform-*d*, δ ppm) 7.80 (d, *J* = 1.4 Hz, 1H), 7.79 – 7.78 (m, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.67 (s, 1H), 7.36 – 7.32 (m, 3H), 7.06 (d, *J* = 8.4 Hz, 2H), 5.52 (s, 2H).



6a

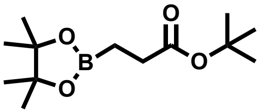
2-(1-benzyl-1H-1,2,3-triazol-4-yl)ethyl 4-methylbenzenesulfonate.[5] All peaks are in accordance with literature.[5] ^{1}H NMR (400 MHz, Chloroform-*d*, δ ppm) 7.69 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.30 (m, 8H), 5.47 (s, 2H), 4.25 (t, *J* = 6.4 Hz, 2H), 3.06 (t, *J* = 6.5 Hz, 2H), 2.42 (s, 3H).

β-borylation of α,β-unsaturated carbonyl compound catalyzed by Cu-tetracatechol polymer

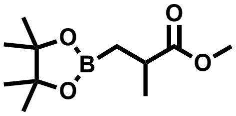
A previously reported procedure was followed for carrying out the reaction with some modifications.[6] A glass vial (10 mL) was charged with a mixture of bis(pinacolato)diboron (99 mg, 1 equ.), acrylate (56.6 µL, 1.0 equ.) and DMAP (2.38 mg, 0.05 equ.) in water (3 mL) along with the solid Cu-tetracatechol polymer (5 mg). The reaction mixture was stirred at room temperature for 3 h, ethyl acetate (3 mL) was added in the reaction mixture, the organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 × 2 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to give the corresponding β-borylated product. Crude NMR spectrum was used for the characterization of the product formed and analysis of % conversion.

For continuous catalysis, after the compounds were extracted in EA, both aqueous and organic fractions were centrifuged to collect the polymer solid and used for the next reaction. Crude NMR spectrum was used for the characterization of the product formed and analysis of % conversion after each cycle.

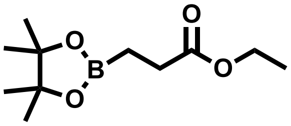
All compounds were previously reported (1b-5b) and characterized by ^{1}H NMR.[6-8]


1b

tert-butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate.[7] All peaks are compared with literature.[7] ^{1}H NMR (300 MHz, Chloroform-*d*, δ ppm) 2.31 (t, *J* = 7.5 Hz, 2H), 1.40 (s, 9H), 1.23 (s, 6H), 1.20 (s, 6H), 0.93 (t, *J* = 7.4 Hz, 2H).

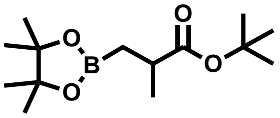

2b

methyl 2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate.[6] All peaks are compared with literature.[6] ^{1}H NMR (400 MHz, Chloroform-*d*, δ ppm) 3.62 (s, 3H), 2.65 (h, *J* = 7.2 Hz, 1H), 1.21 – 1.20 (m, 12H), 1.17 (d, *J* = 7.0 Hz, 3H), 1.09 (dd, *J* = 15.9, 7.6 Hz, 1H), 0.90 (dd, *J* = 15.8, 7.3 Hz, 1H).



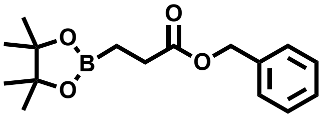
3b

ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate.[7] All peaks are compared with literature.[7] ^{1}H NMR (400 MHz, Chloroform-*d*, δ ppm) 4.05 (q, *J* = 7.1 Hz, 2H), 2.36 (t, *J* = 7.5 Hz, 2H), 1.19 (d, *J* = 7.4 Hz, 15H), 0.95 (t, *J* = 7.5 Hz, 2H).



4b

tert-butyl 2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate.[8] All peaks are compared with literature.[8] ^{1}H NMR (400 MHz, Chloroform-*d*, δ ppm) 2.54 (h, *J* = 7.2 Hz, 1H), 1.41 (s, 9H), 1.22 (d, *J* = 3.3 Hz, 12H), 1.14 (d, *J* = 7.1 Hz, 3H), 1.07 (dd, *J* = 15.8, 7.4 Hz, 1H), 0.85 (dd, *J* = 15.9, 7.5 Hz, 1H).



5b

benzyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate.[6] All peaks are compared with literature.[6] ^{1}H NMR (400 MHz, Chloroform-*d*, δ ppm) 7.31 – 7.18 (m, 5H), 5.03 (s, 2H), 2.42 (t, *J* = 7.5 Hz, 2H), 1.14 (s, 12H), 0.97 (t, *J* = 7.5 Hz, 2H).

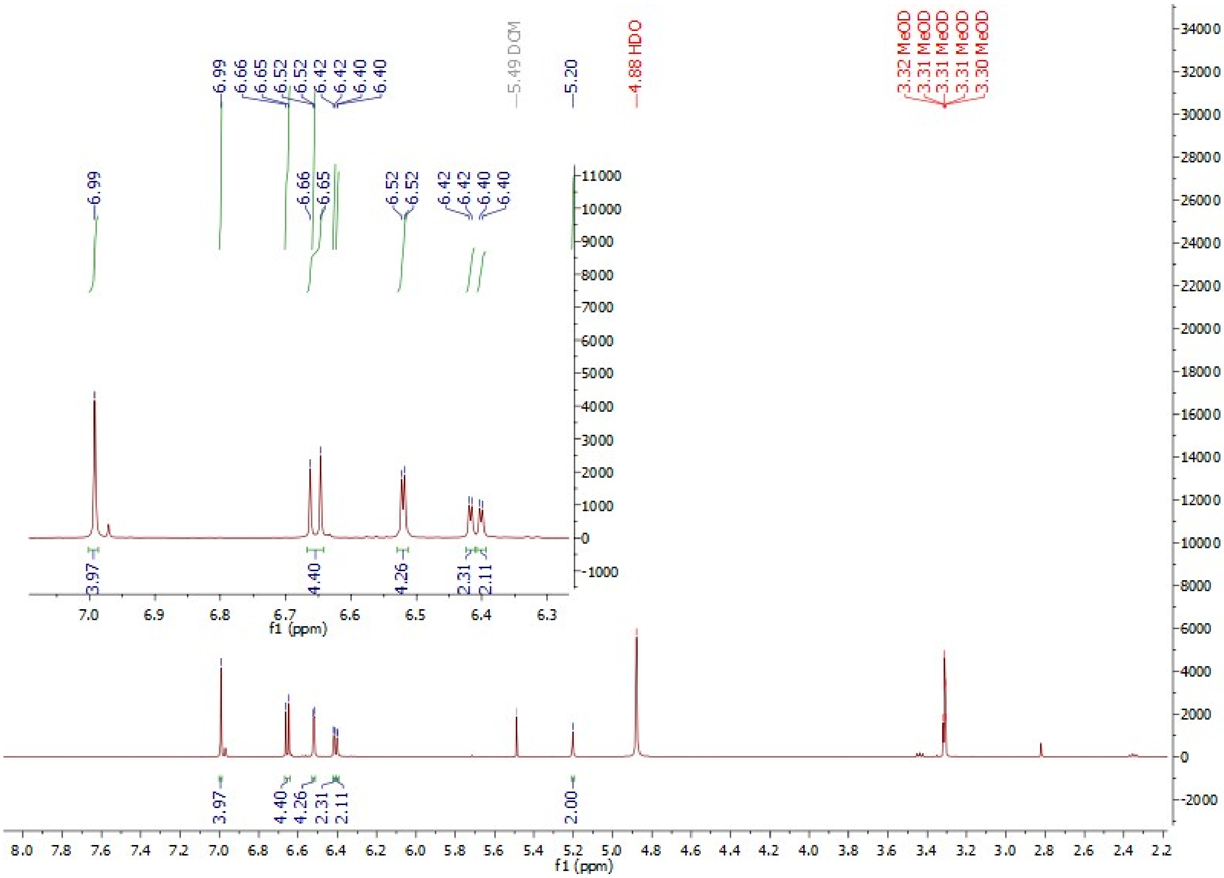


Figure S1. ^{1}H NMR spectrum of the compound **1** in MeOD.

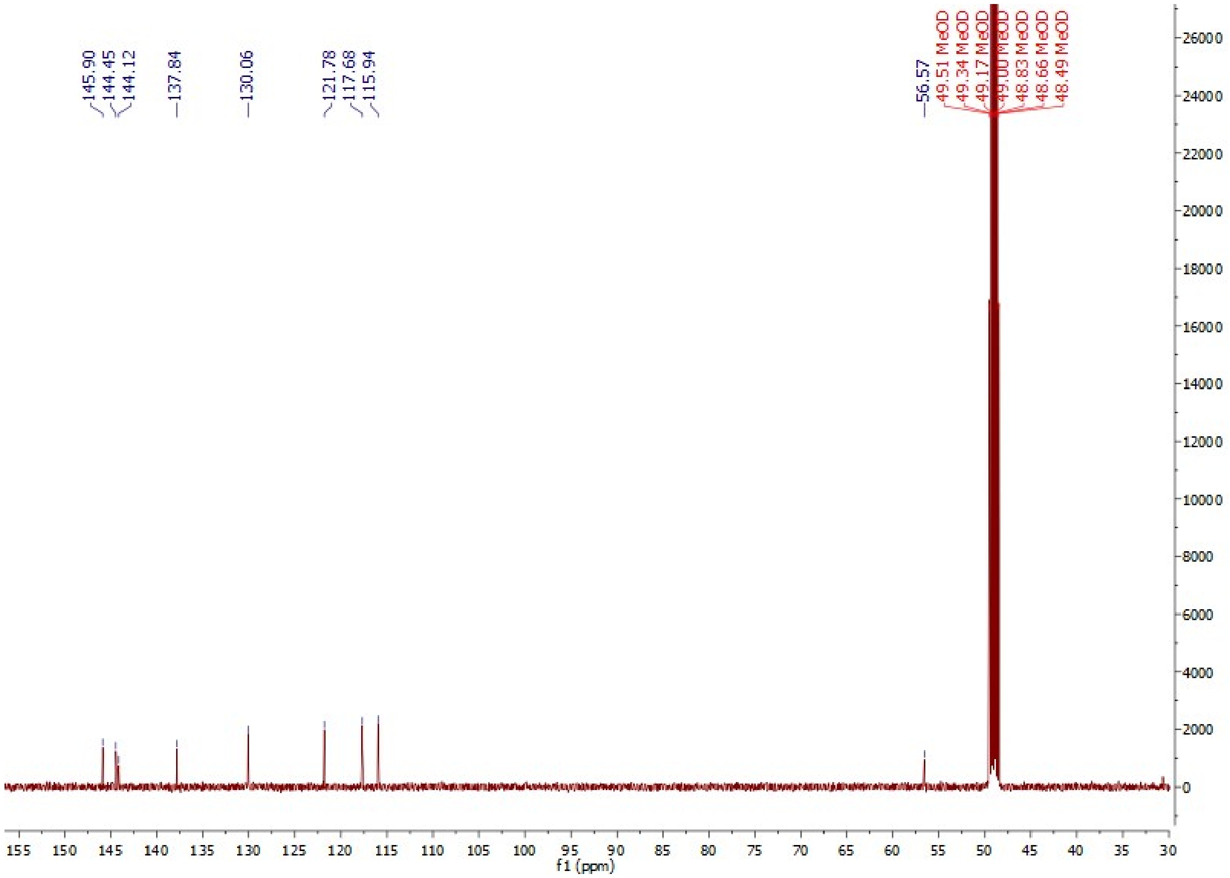


Figure S2. ^{13}C NMR spectrum of compound **1** in MeOD.

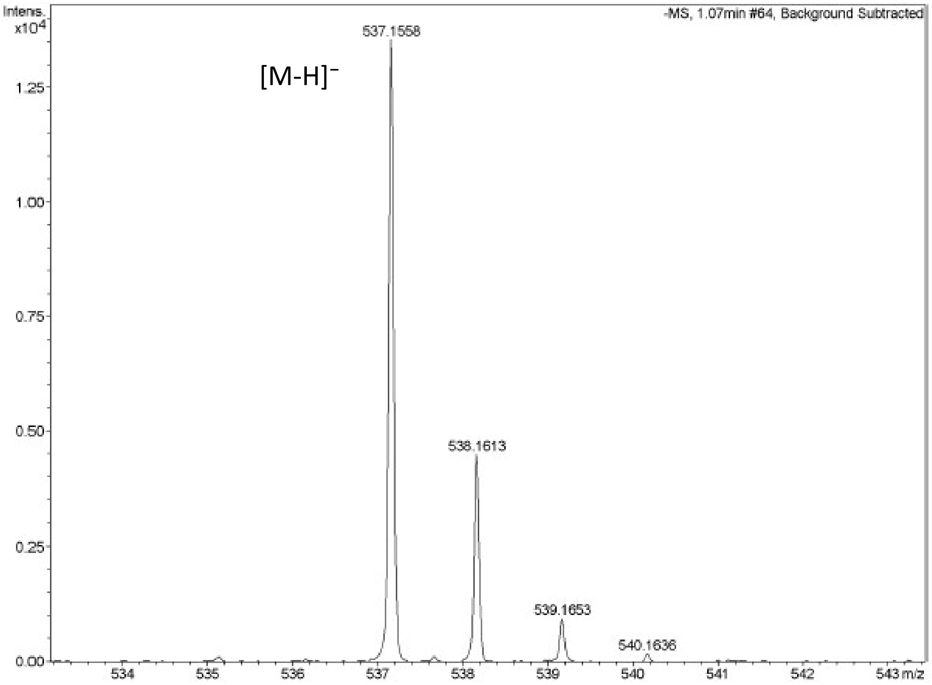


Figure S3. HRMS-ESI for compound **1**

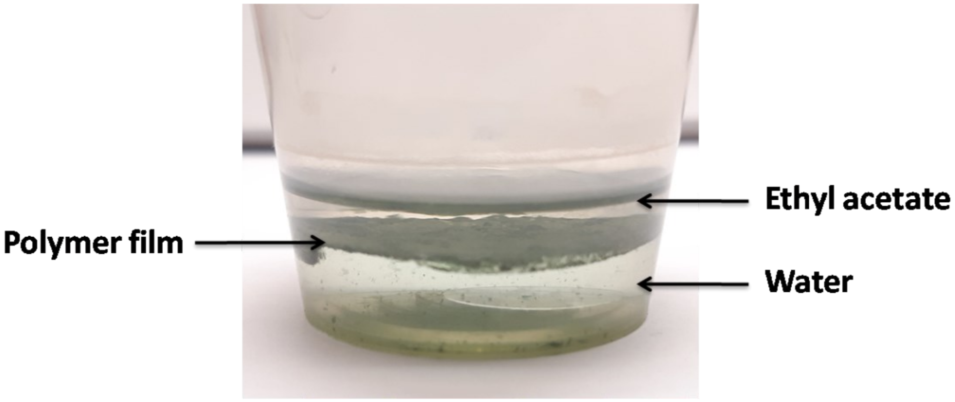


Figure S4. Interfacial polymerization at the biphasic interface of two immiscible liquids (EA and water). The polymer film formed at the interfaceis green in color.

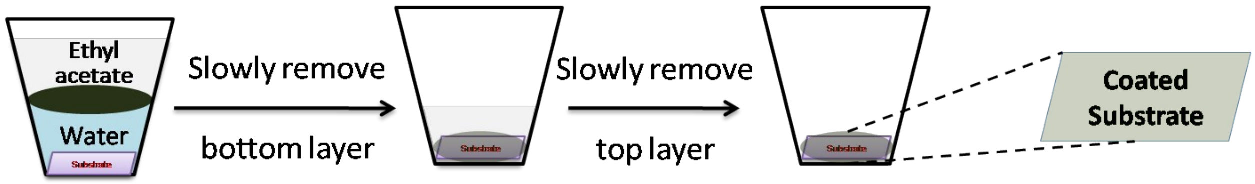
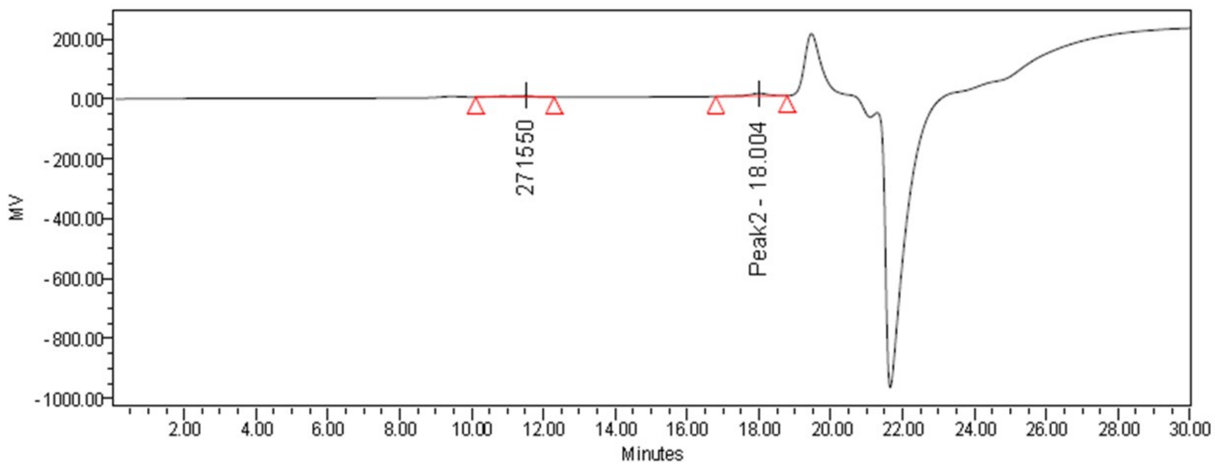


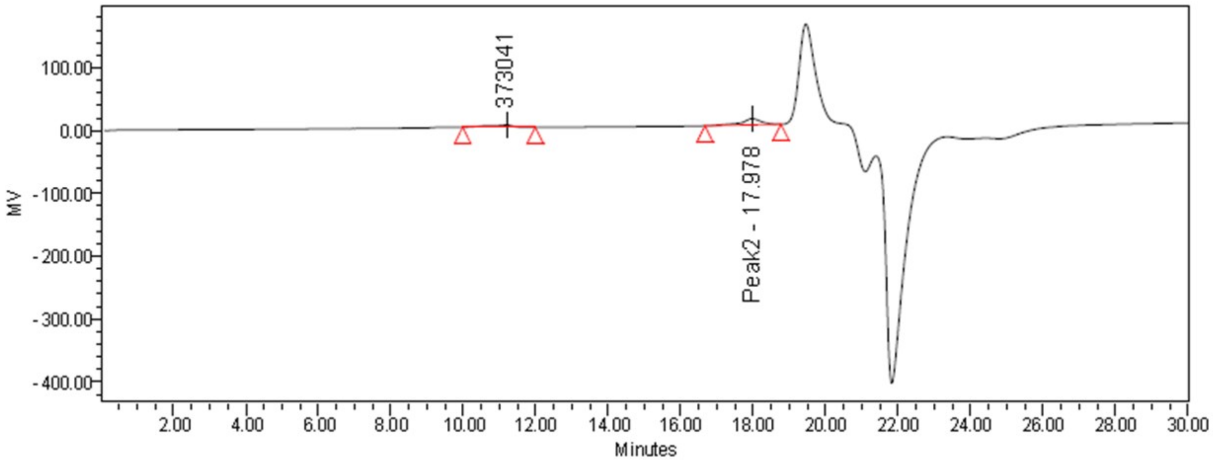
Figure S5. Process of deposition of film on the substrate by removing bottom layer first using a syringe followed by top layer.



GPC Results

	Retention Time (min)	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	11.517	357014	428061	271550	522299	629448		1.199001		
2	18.004	788	868		969	1085		1.101295		

Figure S6. GPC trace for the soluble portion in DMF of the Cu-tetracatechol film obtained from interfacial polymerization.



GPC Results

	Retention Time (min)	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1	11.204	487522	568090	373041	671886	788973		1.165260		
2	17.978	825	930		1064	1213		1.127682		

Figure S7. GPC traces of the soluble portion in DMF of the Cu-tetracatechol powder via bulk polymerization

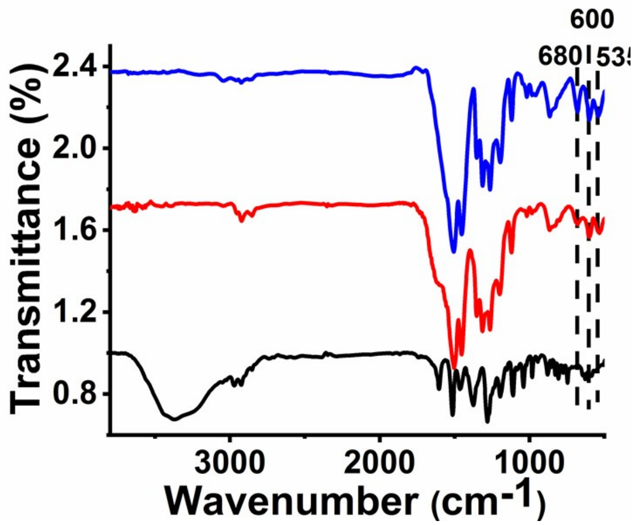


Figure S8. IR spectra of catechol derivative **1** (▬) with interfacial film (▬) and bulk polymer (▬).

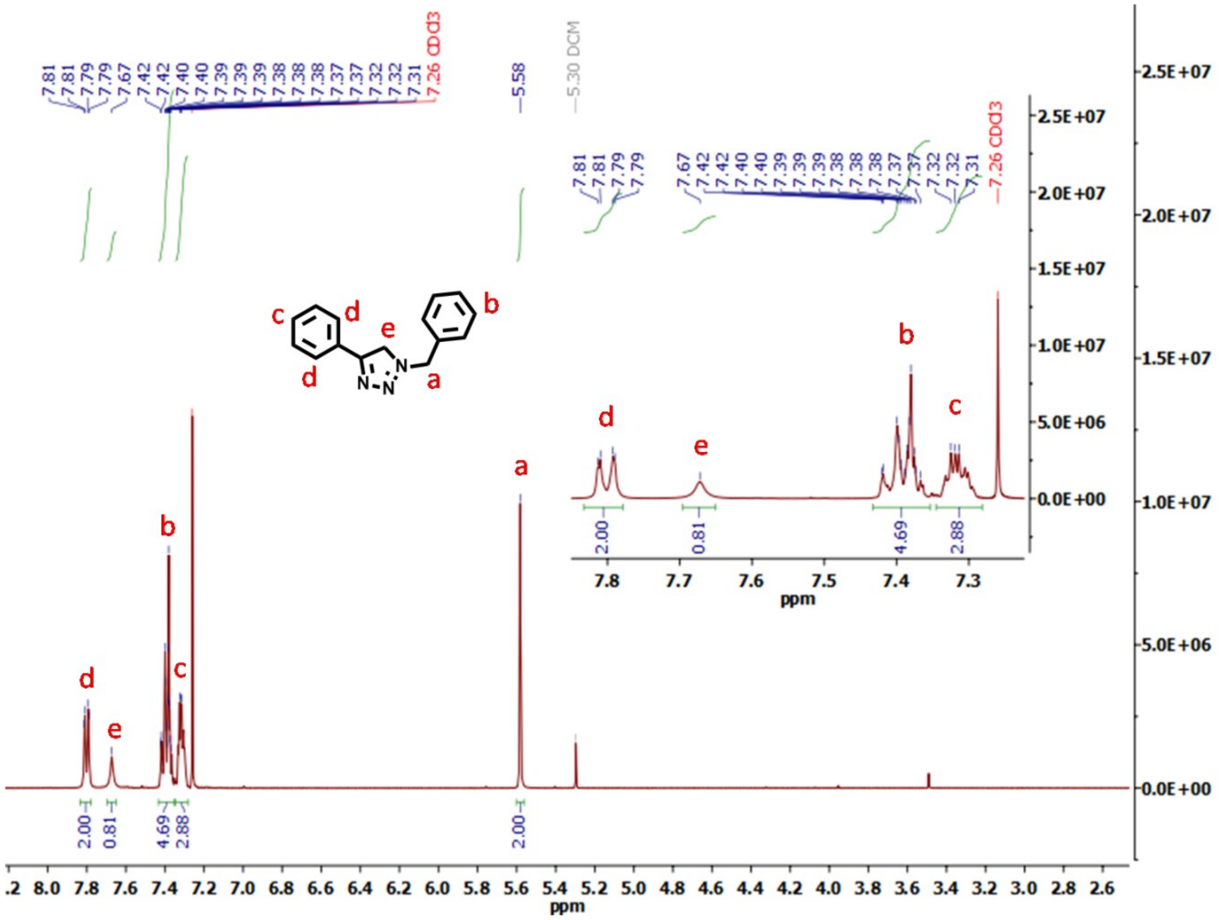


Figure S9. Crude NMR spectrum ($CDCl_3$) of the product from click reaction catalyzed by Cu-catechol polymer in presence of sodium ascorbate. No peaks from the reactants and all observed peaks are from the products confirmed using reported literature data.[1]

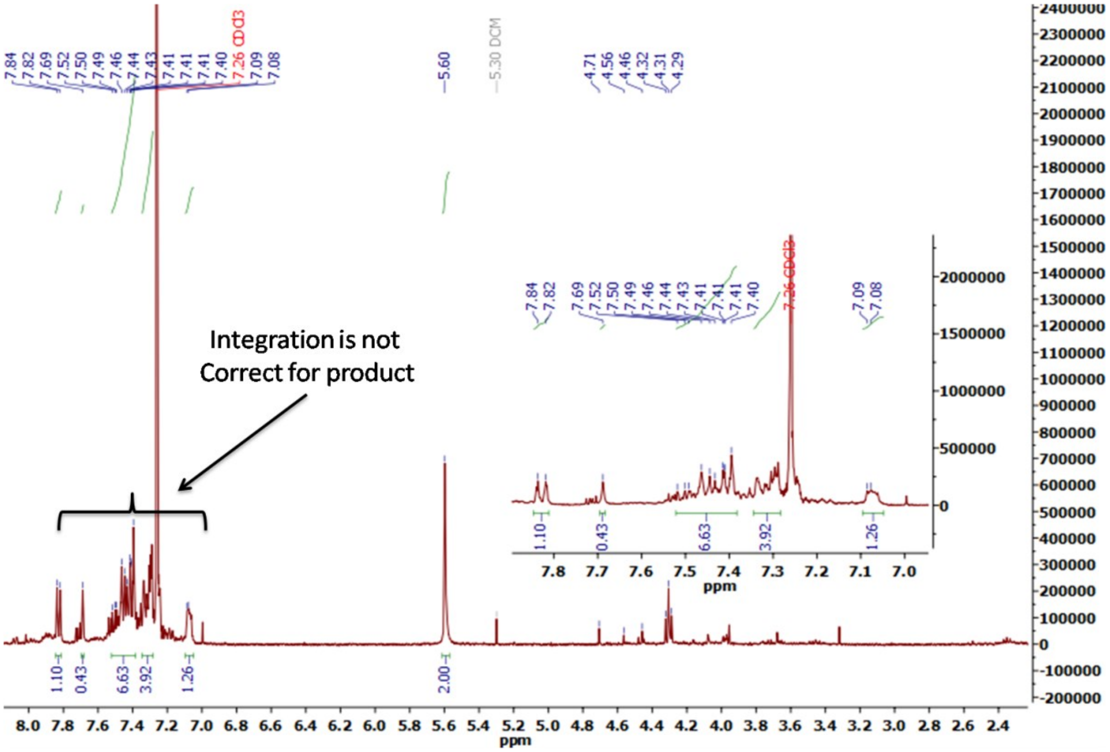
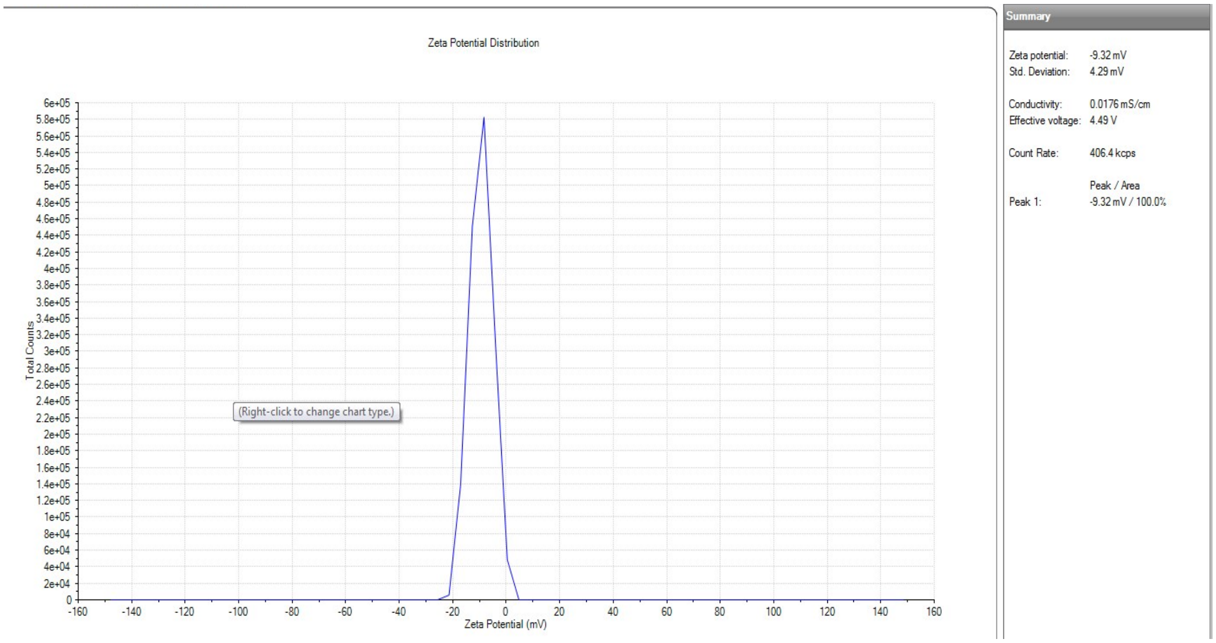


Figure S10. Crude NMR spectrum ($CDCl_3$) of the product from the click reaction in the absence of Cu-tetracatechol polymer in presence of sodium ascorbate. Peak numbers and integrations are not matching with the product. Additional peaks are observed.



Zeta potential: -9.32 mV
Std. Deviation: 4.29 mV

Conductivity: 0.0176 mS/cm
Effective voltage: 4.49 V

Count Rate: 406.4 kcps

Peak / Area
Peak 1: -9.32 mV / 100.0%

Figure S11. Zeta potential of the Cu polymer in water dispersion.

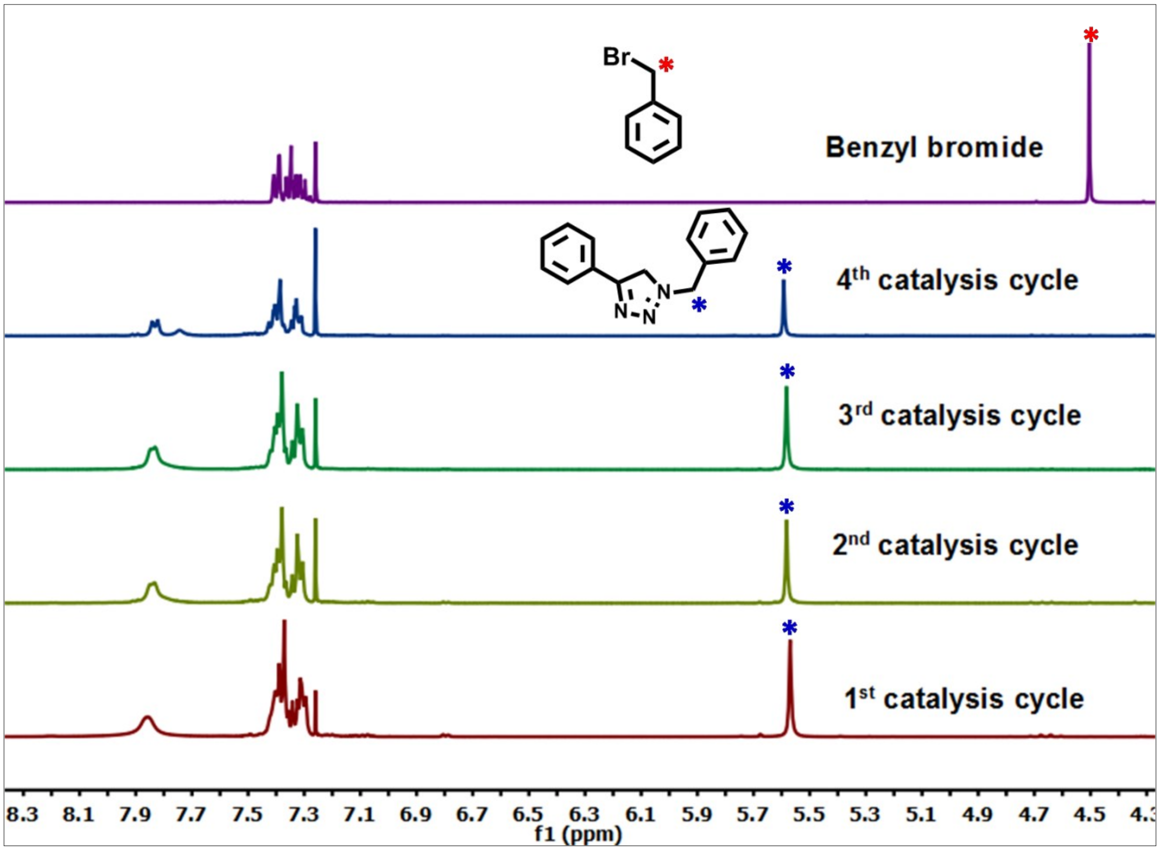


Figure S12. Stacked crude NMR spectra ($CDCl_3$) of continuous catalysis cycles for click reaction, catalyzed by Cu-tetracatechol polymer in the absence of sodium ascorbate. No peak from reactants are present in the crude NMR spectra.

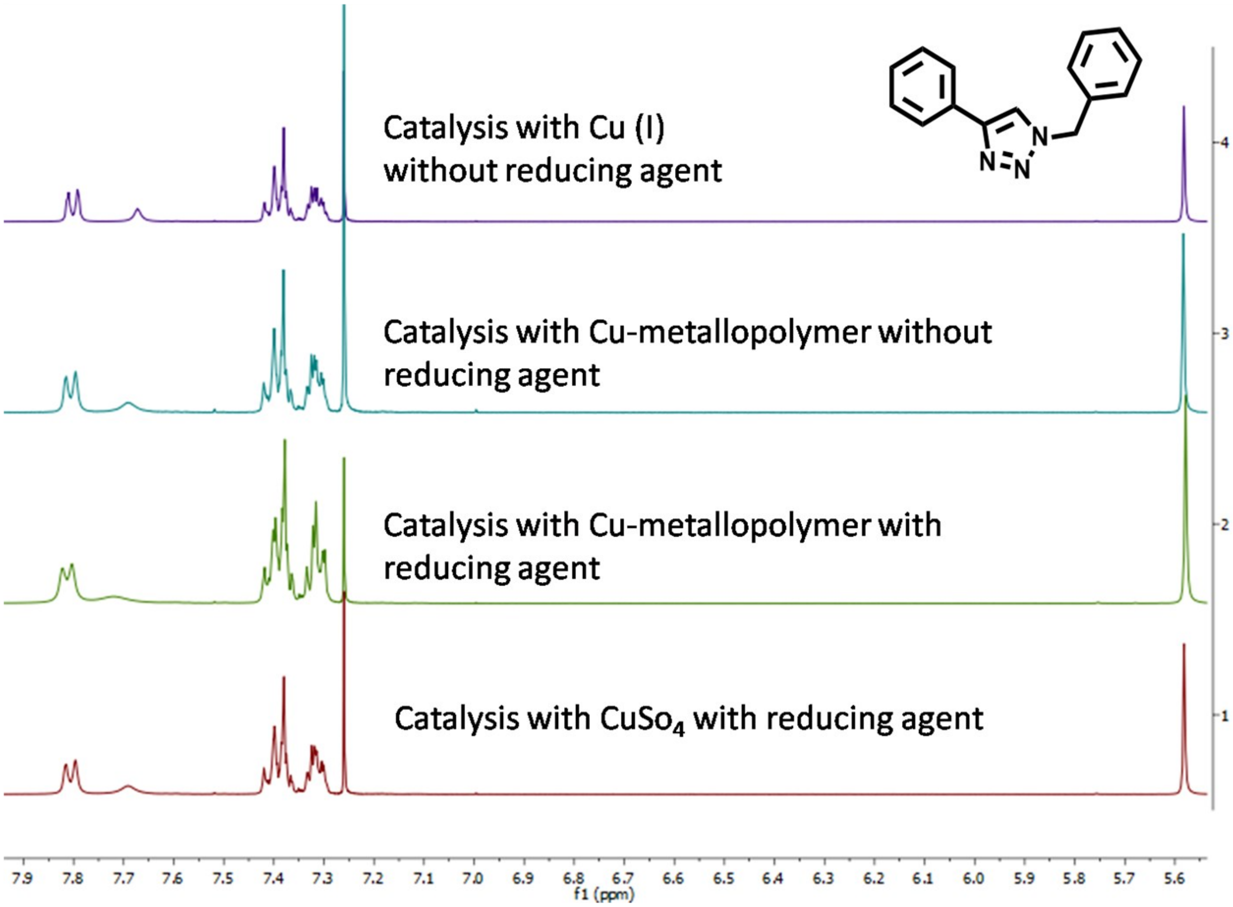


Figure S13. NMR spectra ($CDCl_3$) from click reaction in presence and absence of the ascorbic acid, the reducing agent. As observed from the NMR spectra, Cu-tetracatechol polymer catalyze the reactions in the absence of ascorbic acid.

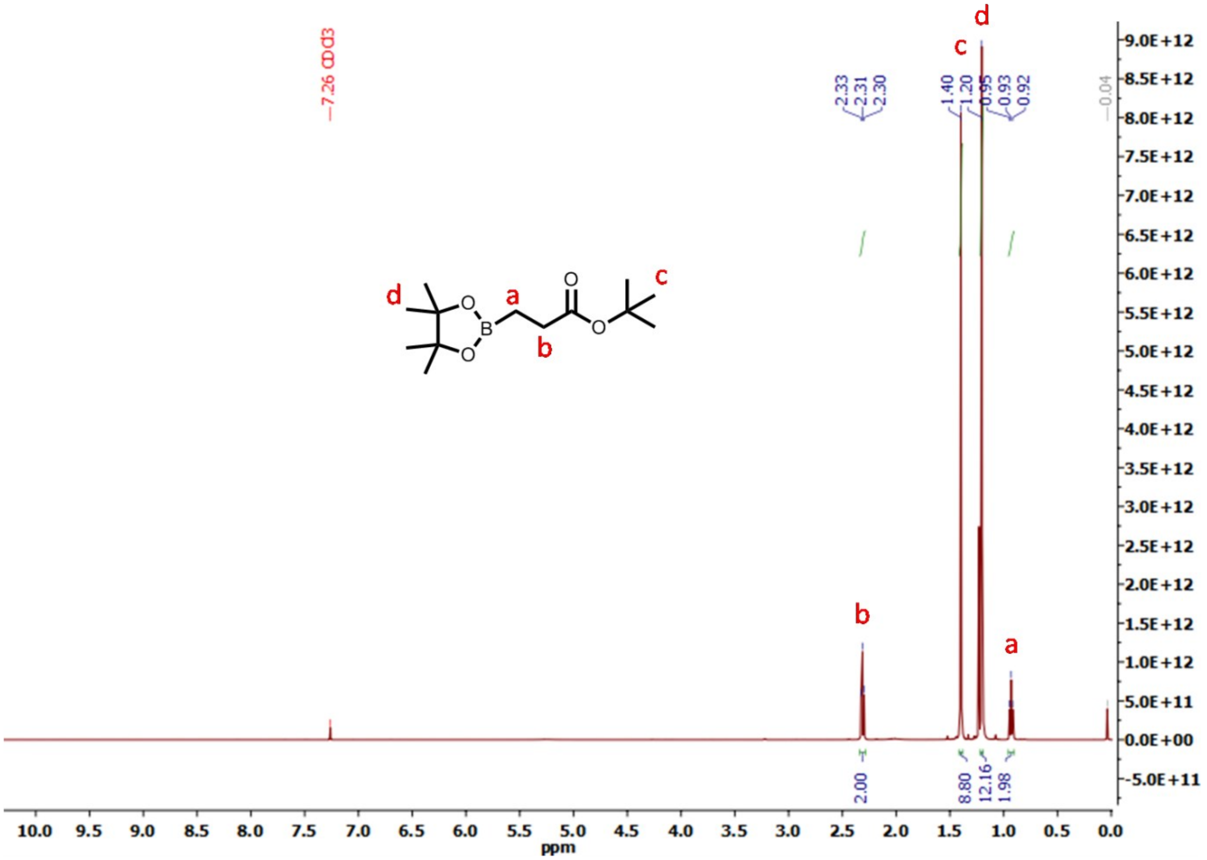


Figure S14. Crude NMR spectrum ($CDCl_3$) of the β-borylation reaction of *t*-butyl acrylate catalyzed by Cu-tetracatechol polymer. No peaks belonging to the reactants were present. All peaks corresponding to the product are confirmed using literature data.[9]

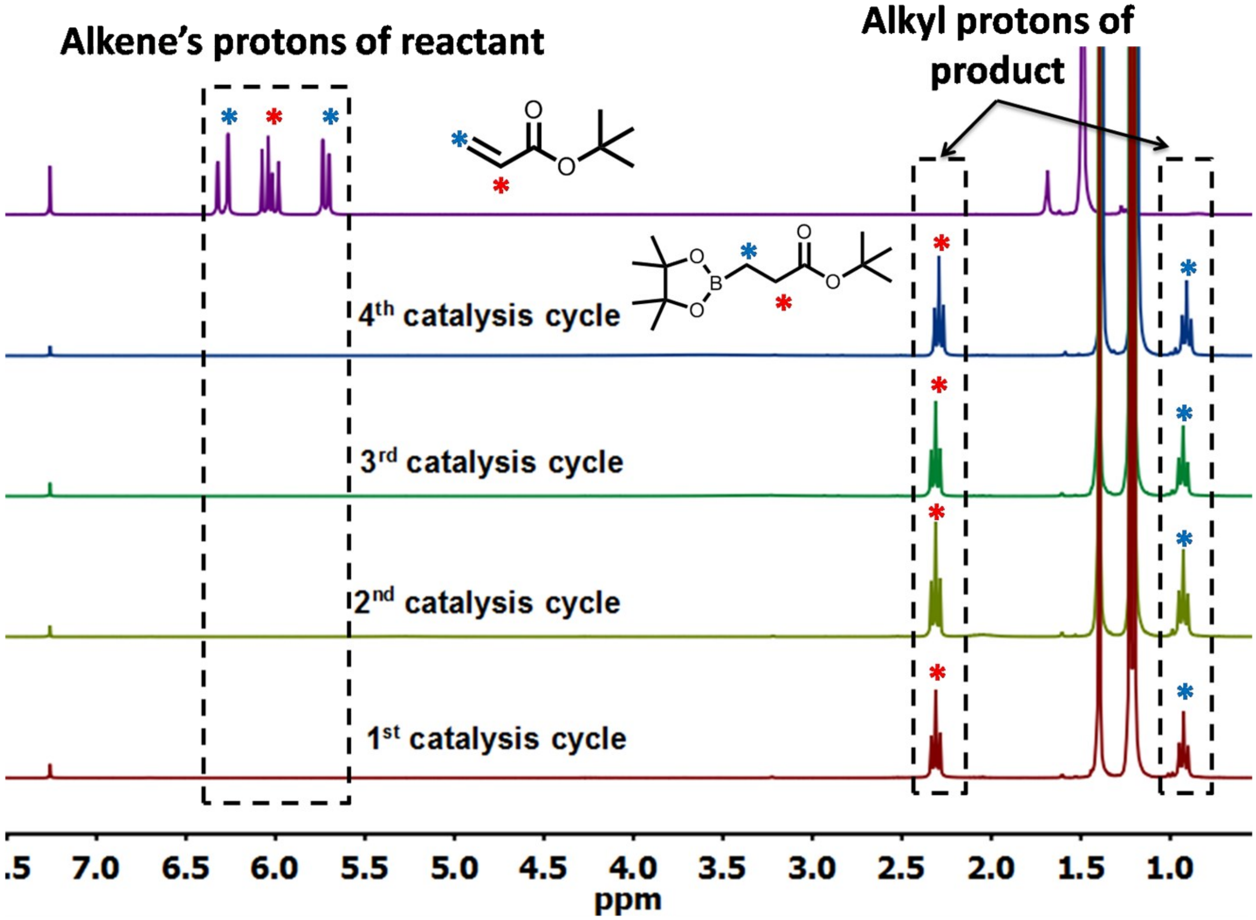


Figure S15. Stacked crude NMR spectra ($CDCl_3$) of repeated catalysis cycles of β-borylation reaction catalyzed by Cu-tetracatechol polymer. No peaks from the starting material, acrylate compound were present in the NMR spectra of crude products.

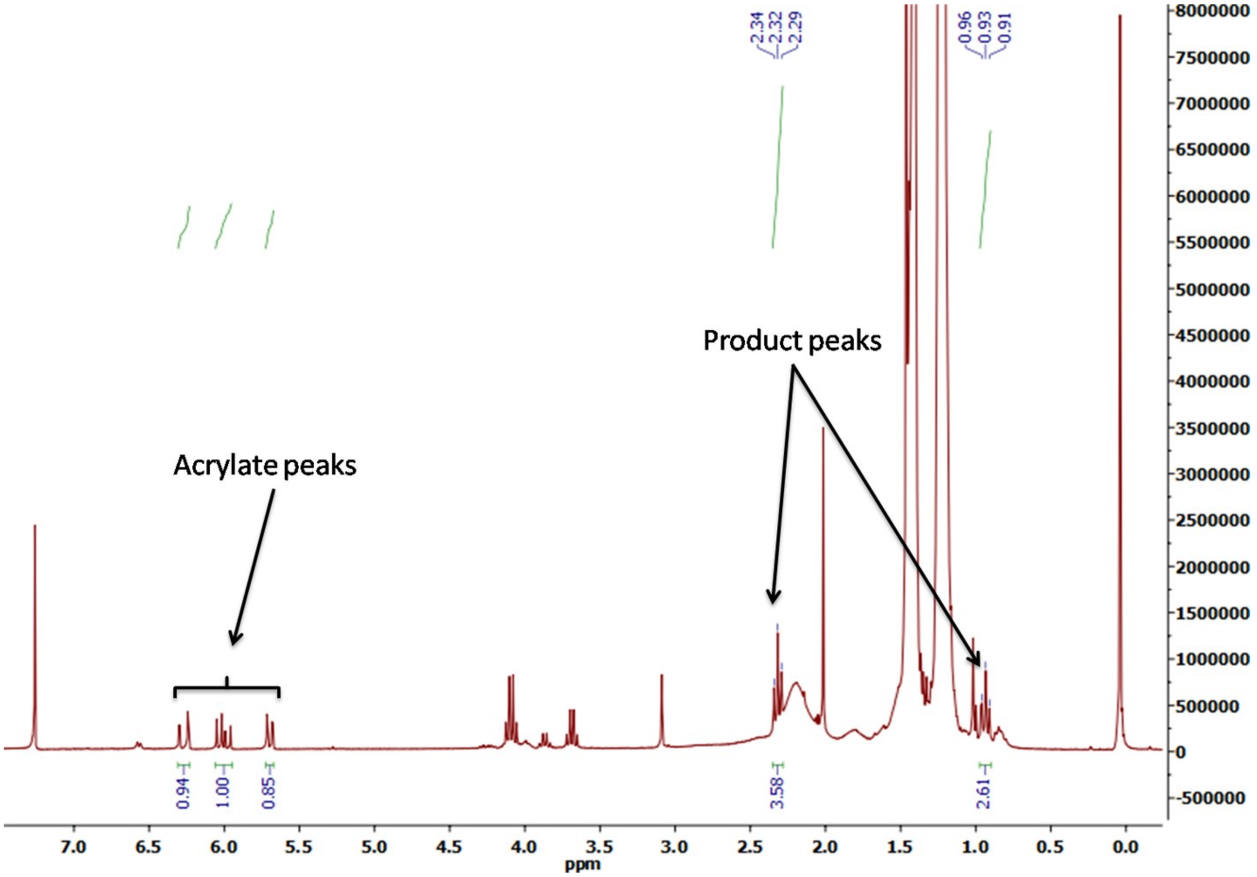


Figure S16. Crude NMR spectrum ($CDCl_3$) of the β−borylation reaction in the absence of Cu-tetracatechol polymer. The observed peaks from the acrylate starting material in the range of 5.5 to 6.5 ppm indicate incomplete transformation. The peaks from products are also present, but with lower intensities.

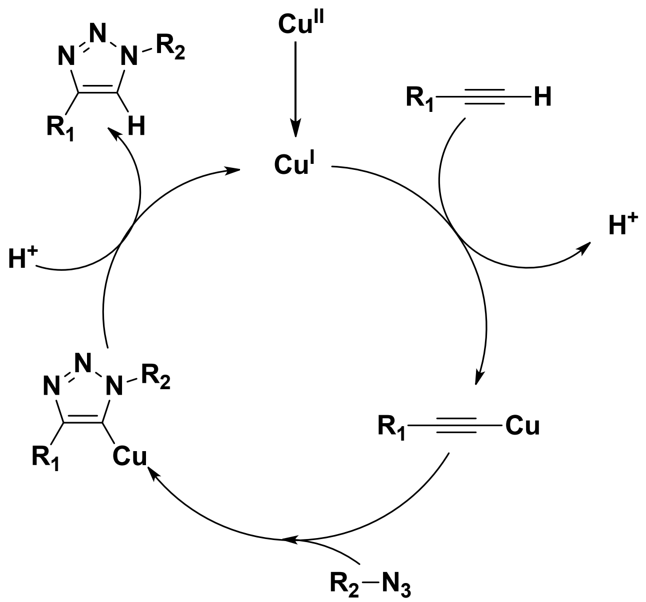


Figure S17. Plausible mechanism for the three component click reaction catalyzed by Cu-tetracatechol polymer.[1]

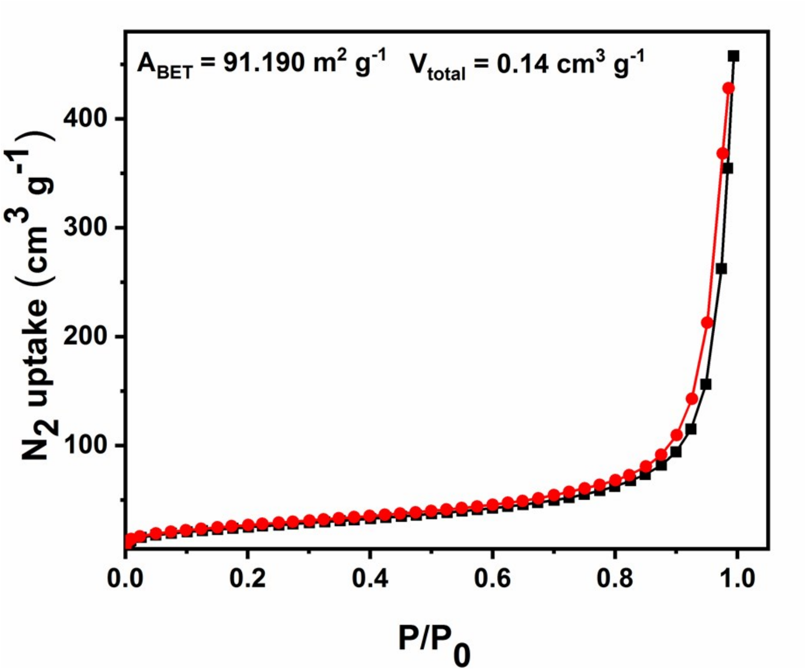


Figure S18. N_2 sorption curve from BET experiment for Cu-tetracatechol polymer – adsorption **(-o-)** and desorption (-●-) experiments.

Table 1S. Comparison of the catalytic activity of the Cu-tetracatechol polymer for the click reaction with a few reported Cu-polymer based catalysts.

Catalyst	**Reaction condition**	**Time (h)**	**% Conversion**	**Reducing agent/e$^-$ donor**	**Resusability (% conversion in 4th run)**	**References**
Cu(I)-AMPS[10]	Water, RT	1	82	NA	Decreases with no. cycles (50% in 4th cycle)	*Appl Organometal Chem. 2019; **33**, e4669.*
$CuSO_4$-PEG-PS[11]	Water, RT	12	97	Na Ascorbate	Recyclable	*ACS Sustainable Chem. Eng. 2017, **5**, 11, 10722-10734*
Cu(II)-cellulose-poly (hydroxamic acid)[12]	Water, 70°C	3	95	Na Ascorbate	Decreases with no. of cycles (93 % in 4th cycle)	*Carbohydr. Polym., 2017, **156**, 175-181*
Cu(I)-C22-PS[13]	Water, RT	15	99	NA	Decreases with no. of cycles cycle (71% in 4th cycle)	*Tetrahedron, 2014, **70**, 8885-8892*
Polymeric Imidazole-Cu (II)[1]	Water:*t*-BuOH, 50°C	2.5	99	Na Ascorbate	Recyclable (99% in 4th run)	*J. Am. Chem. Soc., 2012, **134**, 9285-9290*
Cu (II) –TCTA coordination polymer[14]	$CDCl_3$, light	6	93.5	NEt_3	2 times only (90% in 2nd cycle)	*RSC Adv., 2017, 7, 52907-52913*
$[Cu^I_4(SiW_{12}O_{40})(L)]\cdot 6H_2O\cdot 2$ DMF (MOF)[15]	MeOH, 80°C (* 50°C)	12	99 (*44)	NA	Recyclable (approx. 95% in 4th run)	*ACS Appl. Mater. Interfaces, 2018, **10**, 2628-2636*
Cu – tetracatechol polymer	Water:*t*-BuOH, 50°C	2.5	99	-	Recyclable without processing (99% in 4th run)	**This work**

AMPS = aminomethyl polystyrene; PEG-PS = polystyrene–poly(ethylene glycol); C22-PS = polystyrene-cryptand-22; TCTA = 5,5’,5”-(nitrilotris(benzene-4,1- diyl))tris(thiophene-2-carboxylic acid)

Table 2S. Comparison of the catalytic activity of the Cu-tetracatechol polymer for the β-borylation reaction with a few reported Cu-polymer based catalysts.

Catalyst	**Reaction condition**	**Time (in hr)**	**% Conversion**	**Resusability**	**References**
CP@Cu NPs[16]	Acetone/H_2O	12	95	Reusable	*Nanomaterials*, 2018, **8**, 326
CSM@Cu[17]	MeOH/H_2O	8	93	Reusable but decreases with no. of runs (92% in 4th run)	*Polymers*, 2019, **11**, 1417
Cu-tetracatechol polymer	H_2O	3	99	Recyclable without processing (99% in 4th run)	**This Work**

CP = chitosan/poly (vinyl alcohol); CSM = Chitosan microsphere

Table 3. Sample and crystal data for tetracatechol ligand 1 (code - J457).

Identification code	J457	
Chemical formula	C34H34Cl4O10	
Formula weight	744.41 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.124 x 0.188 x 0.204 mm	
Crystal system	orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 10.5190(5) Å	α = 90°
	b = 14.5588(7) Å	β = 90°
	c = 22.7509(10) Å	γ = 90°
Volume	3484.2(3) Å3	
Z	4	
Density (calculated)	1.419 g/cm3	

Absorption coefficient	0.396 mm-1
F(000)	1544

Table 4. Data collection and structure refinement for Ligand 1 (code - J457).

Theta range for data collection	2.64 to 28.28°
Index ranges	-13<=h<=14, -19<=k<=19, -30<=l<=30
Reflections collected	68486
Independent reflections	4310 [R(int) = 0.0376]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.7459 and 0.7057
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick 2008)
Refinement method	Full-matrix least-squares on F2
Refinement program	SHELXL-2017/1 (Sheldrick, 2017)
Function minimized	Σ w(Fo2 - Fc2)2
Data / restraints / parameters	4310 / 60 / 267
Goodness-of-fit on F2	1.074
Final R indices	3809 data; I>2σ(I) R1 = 0.0816, wR2 = 0.2590
	all data R1 = 0.0884, wR2 = 0.2702
Weighting scheme	w=1/[σ2(Fo2)+(0.1722P)2+4.8478P] where P=(Fo2+2Fc2)/3
Largest diff. peak and hole	0.903 and -1.147 eÅ-3
R.M.S. deviation from mean	0.125 eÅ-3

Table 5. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for tetracatechol ligand 1 (code - J457).

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x/a	y/b	z/c	U(eq)
O1	0.23634(19)	0.75832(13)	0.35174(8)	0.0292(4)
O2	0.3042(2)	0.57630(12)	0.35193(8)	0.0294(4)
O3	0.41478(18)	0.86050(18)	0.75115(8)	0.0392(6)
O4	0.16181(18)	0.82890(15)	0.75015(8)	0.0314(5)
C1	0.6193(2)	0.02429(16)	0.47970(10)	0.0236(5)
C2	0.5964(2)	0.93512(16)	0.49922(10)	0.0223(5)
C3	0.4770(2)	0.90959(15)	0.51975(9)	0.0180(4)
C4	0.4550(2)	0.81100(15)	0.54034(9)	0.0185(4)
C5	0.4103(2)	0.74821(15)	0.49080(9)	0.0186(4)
C6	0.3402(2)	0.78064(15)	0.44332(9)	0.0206(5)
C7	0.3044(2)	0.72211(16)	0.39780(9)	0.0211(5)
C8	0.3402(2)	0.62964(16)	0.39901(10)	0.0233(5)
C9	0.4099(3)	0.59676(16)	0.44640(11)	0.0263(5)
C10	0.4442(2)	0.65569(16)	0.49209(10)	0.0233(5)
C11	0.3708(2)	0.80964(15)	0.59464(9)	0.0190(4)
C12	0.4273(2)	0.83211(18)	0.64850(10)	0.0241(5)
C13	0.3557(2)	0.83852(18)	0.69923(10)	0.0246(5)
C14	0.2249(2)	0.82219(18)	0.69766(10)	0.0239(5)
C15	0.1676(2)	0.80090(19)	0.64426(10)	0.0266(5)
C16	0.2405(2)	0.79431(18)	0.59306(10)	0.0243(5)

C1S	0.3179(8)	0.4337(5)	0.1567(3)	0.0525(14)
Cl1	0.2124(3)	0.42891(12)	0.21780(9)	0.0614(7)
Cl2	0.4741(3)	0.4150(2)	0.17471(15)	0.0842(8)
C1X	0.377(2)	0.4333(15)	0.1662(10)	0.078(4)
Cl3	0.2961(9)	0.4221(4)	0.2292(2)	0.091(2)
Cl4	0.5355(11)	0.4381(7)	0.1648(4)	0.124(3)
O1W	0.4152(3)	0.41190(16)	0.36177(13)	0.0443(7)
O2W	0.523(3)	0.4166(16)	0.3399(13)	0.0443(7)

Table 6. Bond lengths (Å) for Ligand 1 (code - J457).

O1-C7	1.374(3)	O1-H11	0.857(18)
O2-C8	1.376(3)	O2-H21	0.858(18)
O3-C13	1.372(3)	O3-H31	0.825(19)
O4-C14	1.370(3)	O4-H41	0.828(19)
C1-C2	1.393(3)	C1-C3	1.398(3)
C1-H1	0.95	C2-C3	1.390(3)
C2-H2	0.95	C3-C4	1.527(3)
C4-C11	1.520(3)	C4-C5	1.525(3)
C4-H4	1.0	C5-C6	1.391(3)
C5-C10	1.394(3)	C6-C7	1.393(3)
C6-H6	0.95	C7-C8	1.398(3)
C8-C9	1.389(3)	C9-C10	1.395(3)
C9-H9	0.95	C10-H10	0.95
C11-C16	1.389(3)	C11-C12	1.401(3)
C12-C13	1.381(3)	C12-H12	0.95

C13-C14	1.397(3)	C14-C15	1.391(3)
C15-C16	1.398(3)	C15-H15	0.95
C16-H16	0.95	C1S-Cl2	1.715(8)
C1S-Cl1	1.781(7)	C1S-H1S1	0.99
C1S-H1S2	0.99	C1X-Cl4	1.67(2)
C1X-Cl3	1.68(2)	C1X-H1X1	0.99
C1X-H1X2	0.99	O1W-H1W	0.86(2)
O1W-H2W	0.842(19)		

Table 7. Bond angles (°) for tetracatechol ligand 1 (code - J457).

C7-O1-H11	114.(3)	C8-O2-H21	111.(3)
C13-O3-H31	105.(3)	C14-O4-H41	118.(3)
C2-C1-C3	120.9(2)	C2-C1-H1	119.6
C3-C1-H1	119.6	C3-C2-C1	120.8(2)
C3-C2-H2	119.6	C1-C2-H2	119.6
C2-C3-C1	118.3(2)	C2-C3-C4	119.43(19)
C1-C3-C4	122.29(19)	C11-C4-C5	114.39(18)
C11-C4-C3	110.48(17)	C5-C4-C3	112.54(17)
C11-C4-H4	106.3	C5-C4-H4	106.3
C3-C4-H4	106.3	C6-C5-C10	118.7(2)
C6-C5-C4	122.27(19)	C10-C5-C4	119.00(19)
C5-C6-C7	120.9(2)	C5-C6-H6	119.6
C7-C6-H6	119.6	O1-C7-C6	118.2(2)
O1-C7-C8	121.7(2)	C6-C7-C8	120.1(2)
O2-C8-C9	123.7(2)	O2-C8-C7	117.0(2)

C9-C8-C7	119.3(2)	C8-C9-C10	120.2(2)
C8-C9-H9	119.9	C10-C9-H9	119.9
C5-C10-C9	120.8(2)	C5-C10-H10	119.6
C9-C10-H10	119.6	C16-C11-C12	118.6(2)
C16-C11-C4	123.78(19)	C12-C11-C4	117.43(19)
C13-C12-C11	121.0(2)	C13-C12-H12	119.5
C11-C12-H12	119.5	O3-C13-C12	119.2(2)
O3-C13-C14	120.5(2)	C12-C13-C14	120.3(2)
O4-C14-C15	124.6(2)	O4-C14-C13	116.3(2)
C15-C14-C13	119.2(2)	C14-C15-C16	120.3(2)
C14-C15-H15	119.8	C16-C15-H15	119.8
C11-C16-C15	120.6(2)	C11-C16-H16	119.7
C15-C16-H16	119.7	Cl2-C1S-Cl1	113.8(4)
Cl2-C1S-H1S1	108.8	Cl1-C1S-H1S1	108.8
Cl2-C1S-H1S2	108.8	Cl1-C1S-H1S2	108.8
H1S1-C1S-H1S2	107.7	Cl4-C1X-Cl3	121.8(13)
Cl4-C1X-H1X1	106.9	Cl3-C1X-H1X1	106.9
Cl4-C1X-H1X2	106.9	Cl3-C1X-H1X2	106.9
H1X1-C1X-H1X2	106.7	H1W-O1W-H2W	103.(5)

Table 8. Torsion angles (°) for Ligand 1 (code - J457).

C3-C1-C2-C3	0.0(4)	C1-C2-C3-C1	0.0(4)
C1-C2-C3-C4	179.5(2)	C2-C3-C4-C11	140.6(2)
C1-C3-C4-C11	-39.9(3)	C2-C3-C4-C5	-90.1(2)
C1-C3-C4-C5	89.3(2)	C11-C4-C5-C6	97.9(2)

C3-C4-C5-C6	-29.3(3)	C11-C4-C5-C10	-84.2(2)
C3-C4-C5-C10	148.7(2)	C10-C5-C6-C7	-0.1(3)
C4-C5-C6-C7	177.9(2)	C5-C6-C7-O1	-179.3(2)
C5-C6-C7-C8	-0.8(3)	O1-C7-C8-O2	0.0(3)
C6-C7-C8-O2	-178.5(2)	O1-C7-C8-C9	179.5(2)
C6-C7-C8-C9	1.0(3)	O2-C8-C9-C10	179.1(2)
C7-C8-C9-C10	-0.4(4)	C6-C5-C10-C9	0.7(3)
C4-C5-C10-C9	-177.3(2)	C8-C9-C10-C5	-0.5(4)
C5-C4-C11-C16	-31.0(3)	C3-C4-C11-C16	97.2(3)
C5-C4-C11-C12	154.1(2)	C3-C4-C11-C12	-77.7(2)
C16-C11-C12-C13	0.4(4)	C4-C11-C12-C13	175.6(2)
C11-C12-C13-O3	179.8(2)	C11-C12-C13-C14	0.3(4)
O3-C13-C14-O4	-0.4(4)	C12-C13-C14-O4	179.2(2)
O3-C13-C14-C15	179.4(2)	C12-C13-C14-C15	-1.0(4)
O4-C14-C15-C16	-179.1(2)	C13-C14-C15-C16	1.2(4)
C12-C11-C16-C15	-0.2(4)	C4-C11-C16-C15	-175.1(2)
C14-C15-C16-C11	-0.6(4)		

Table 9. Anisotropic atomic displacement parameters (Å^2) for Ligand 1 (code - J457).

The anisotropic atomic displacement factor exponent takes the form: -2π2[h2 a*2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O1	0.0375(10)	0.0322(9)	0.0180(8)	-0.0042(7)	-0.0102(7)	0.0006(7)
O2	0.0462(11)	0.0243(9)	0.0177(8)	-0.0046(6)	-0.0023(7)	-0.0066(7)
O3	0.0245(9)	0.0804(16)	0.0127(8)	-0.0110(9)	-0.0035(6)	0.0042(9)
O4	0.0247(9)	0.0555(12)	0.0141(8)	0.0067(7)	0.0028(6)	0.0073(8)
C1	0.0192(10)	0.0268(11)	0.0248(11)	0.0013(8)	0.0020(8)	0.0006(8)
C2	0.0197(10)	0.0261(11)	0.0211(10)	-0.0002(8)	0.0009(8)	0.0023(8)
C3	0.0203(10)	0.0225(10)	0.0113(9)	-0.0018(7)	-0.0018(7)	-0.0013(8)
C4	0.0208(9)	0.0217(10)	0.0129(9)	-0.0013(7)	-0.0012(7)	0.0001(7)
C5	0.0211(10)	0.0217(10)	0.0131(9)	-0.0018(7)	0.0001(7)	-0.0021(8)
C6	0.0237(10)	0.0227(10)	0.0153(9)	-0.0021(8)	-0.0018(7)	-0.0012(8)
C7	0.0238(10)	0.0258(11)	0.0138(9)	-0.0006(8)	-0.0009(7)	-0.0046(8)
C8	0.0313(11)	0.0241(11)	0.0146(9)	-0.0035(8)	0.0025(8)	-0.0068(9)
C9	0.0390(13)	0.0198(10)	0.0201(11)	0.0004(8)	0.0007(9)	-0.0023(9)
C10	0.0296(11)	0.0242(11)	0.0162(9)	0.0009(8)	-0.0009(8)	-0.0006(8)
C11	0.0215(10)	0.0235(10)	0.0120(9)	0.0006(7)	-0.0012(7)	0.0012(8)
C12	0.0201(10)	0.0383(13)	0.0138(10)	-0.0021(8)	-0.0023(8)	0.0021(9)
C13	0.0231(11)	0.0387(13)	0.0121(10)	-0.0017(8)	-0.0043(8)	0.0032(9)
C14	0.0233(11)	0.0358(12)	0.0126(10)	0.0035(8)	0.0006(8)	0.0030(9)
C15	0.0210(10)	0.0406(13)	0.0183(11)	0.0009(9)	-0.0011(8)	-0.0031(9)
C16	0.0241(11)	0.0343(12)	0.0145(9)	-0.0006(8)	-0.0017(8)	-0.0045(9)
C1S	0.072(4)	0.048(3)	0.037(3)	-0.009(2)	-0.001(3)	-0.006(3)

Cl1	0.0725(14)	0.0619(9)	0.0497(9)	-0.0035(6)	0.0063(8)	-0.0099(8)
Cl2	0.0658(14)	0.0864(15)	0.1003(18)	-0.0308(12)	-0.0082(13)	-0.0079(11)
C1X	0.072(7)	0.086(6)	0.077(7)	-0.012(6)	-0.020(6)	0.005(7)
Cl3	0.123(6)	0.091(3)	0.060(2)	-0.0053(19)	-0.015(3)	-0.011(3)
Cl4	0.117(6)	0.146(6)	0.107(5)	-0.026(4)	-0.016(5)	0.019(5)
O1W	0.0566(16)	0.0268(11)	0.0494(16)	-0.0033(10)	-0.0038(12)	-0.0064(10)
O2W	0.0566(16)	0.0268(11)	0.0494(16)	-0.0033(10)	-0.0038(12)	-0.0064(10)

Table 10. Hydrogen atomic coordinates and isotropic atomic displacement paramete (Å^2) for Ligand 1 (code - J457).

	x/a	y/b	z/c	U(eq)
H11	0.216(3)	0.719(2)	0.3257(13)	0.035
H21	0.333(3)	0.5215(15)	0.3556(16)	0.035
H31	0.357(3)	0.877(3)	0.7731(16)	0.047
H41	0.0832(18)	0.831(3)	0.7496(18)	0.038
H1	0.7016	1.0404	0.4658	0.028
H2	0.6632	0.8912	0.4985	0.027
H4	0.5398	0.7871	0.5531	0.022
H6	0.3163	0.8435	0.4419	0.025
H9	0.4342	0.5340	0.4477	0.032
H10	0.4913	0.6325	0.5245	0.028
H12	0.5162	0.8431	0.6502	0.029
H15	0.0784	0.7908	0.6426	0.032

H16	0.2006	0.7792	0.5569	0.029
H1S1	0.2914	0.3872	0.1274	0.063
H1S2	0.3104	0.4949	0.1379	0.063
H1X1	0.3516	0.3813	0.1407	0.094
H1X2	0.3455	0.4899	0.1469	0.094
H1W	0.480(4)	0.405(4)	0.339(2)	0.053
H2W	0.368(4)	0.367(2)	0.353(2)	0.053

Table 11. Hydrogen bond distances (Å) and angles (°) for Ligand 1 (code - J457).

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
O1-H11...O4	0.857(18)	1.94(2)	2.751(2)	158.(4)
O2-H21...O1W^a	0.858(18)	1.820(19)	2.672(3)	172.(4)
O2-H21...O2W^b	0.858(18)	2.54(4)	3.28(3)	146.(3)
O3-H31...O2	0.825(19)	1.99(3)	2.731(3)	148.(4)
O3-H31...O4	0.825(19)	2.23(4)	2.700(3)	116.(4)
O4-H41...O3	0.828(19)	1.82(2)	2.639(3)	168.(4)
C9-H9...O1W^a	0.95	2.65	3.310(4)	127.0
O1Wa-H1Wa...Cl1^a	0.86(2)	2.79(3)	3.622(4)	163.(5)
O1Wa-H2Wa...O1	0.842(19)	1.93(2)	2.755(3)	167.(5)

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