

Supplementary Information

Enzyme-inspired catalysts with high activity and selectivity for oxidative polymerization of 2-phenylphenol

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S1. NMR spectra of 'Bu₂'Butacn, 'Bu'Pr₂tacn, and their precursors

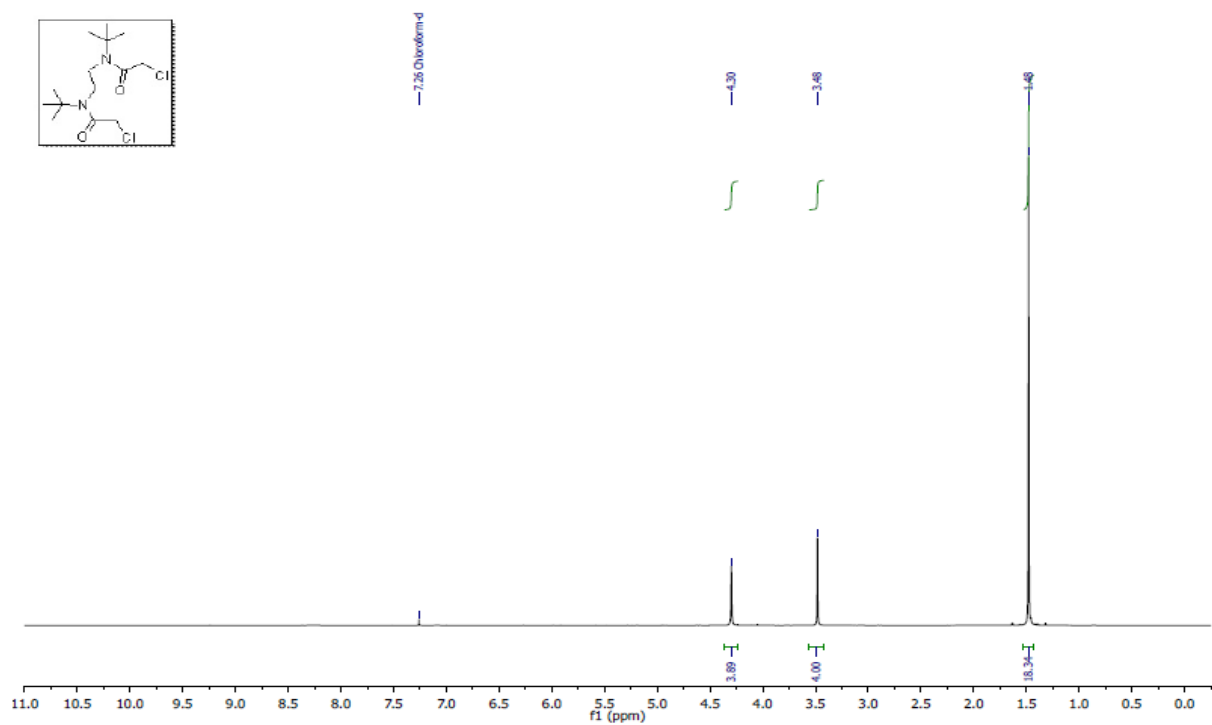


Fig. S1.1 ¹H NMR spectrum of 5a.

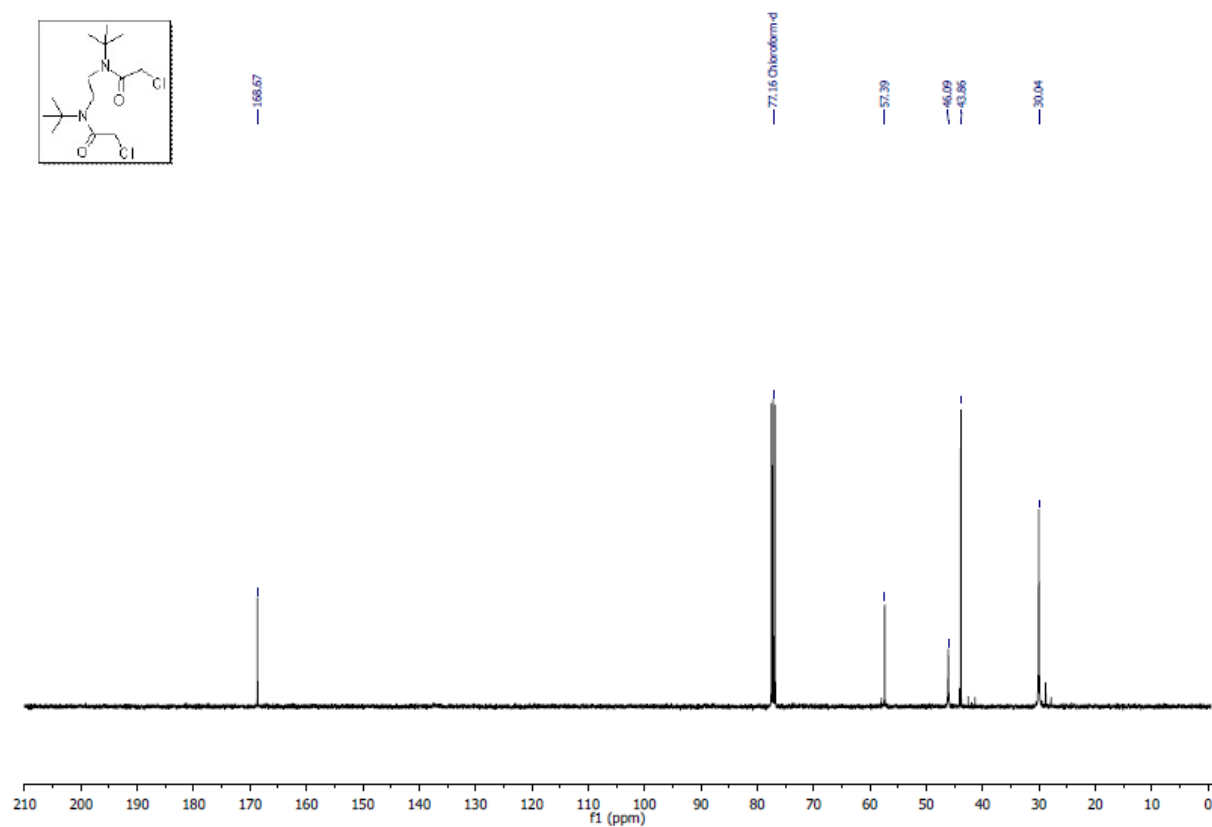


Fig. S1.2 ¹³C NMR spectrum of 5a.

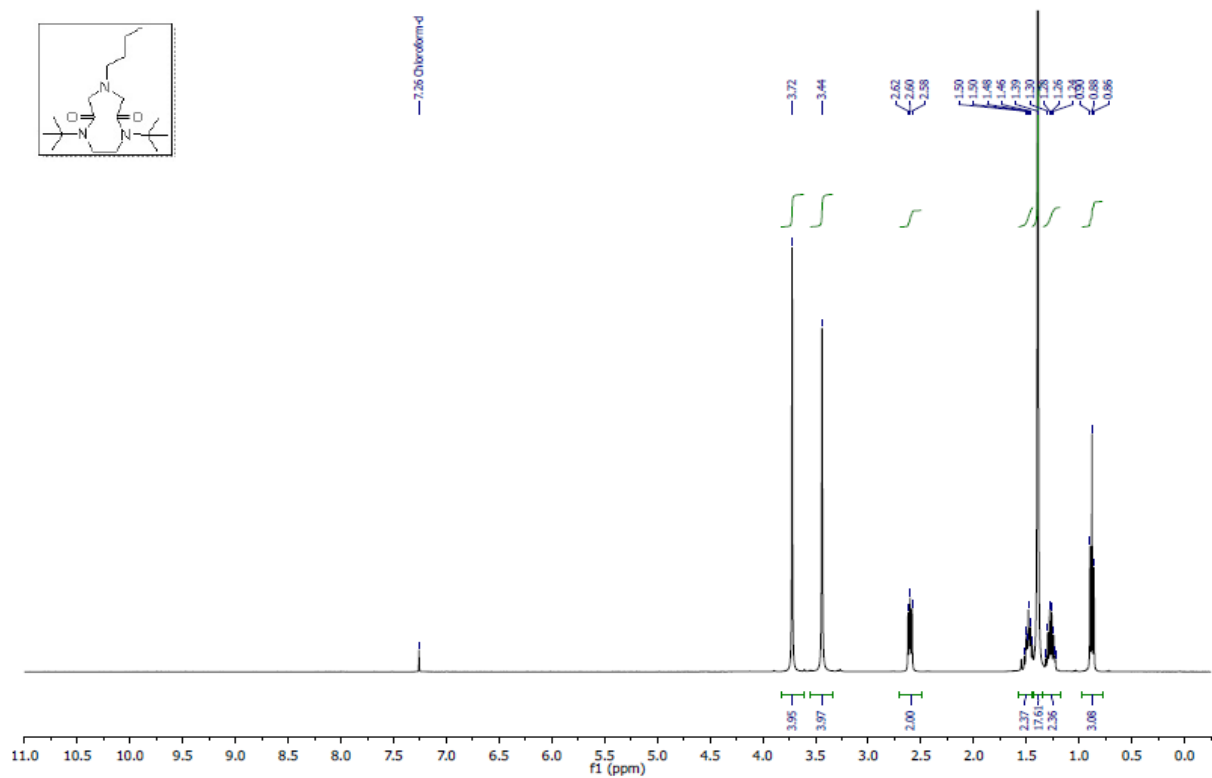


Fig. S1.3 ¹H NMR spectrum of 6a.

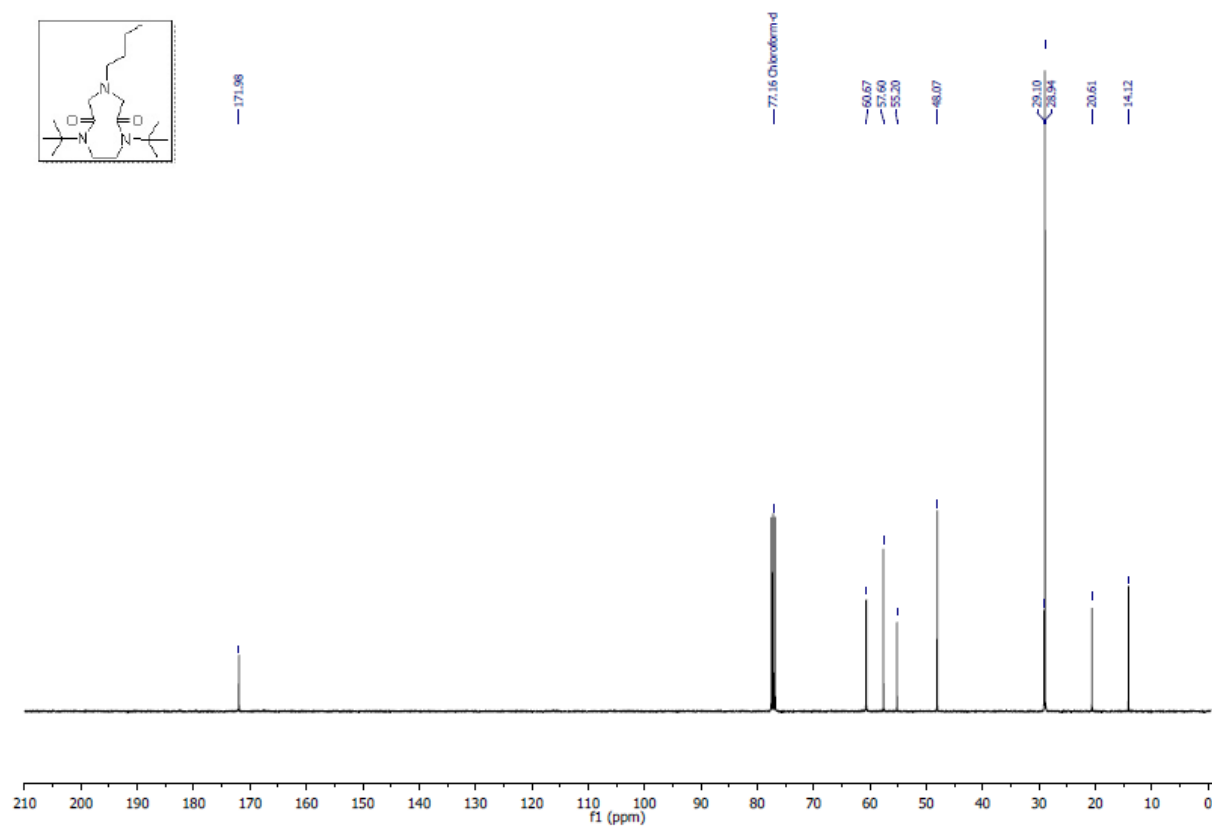


Fig. S1.4 ¹³C NMR spectrum of 6a.

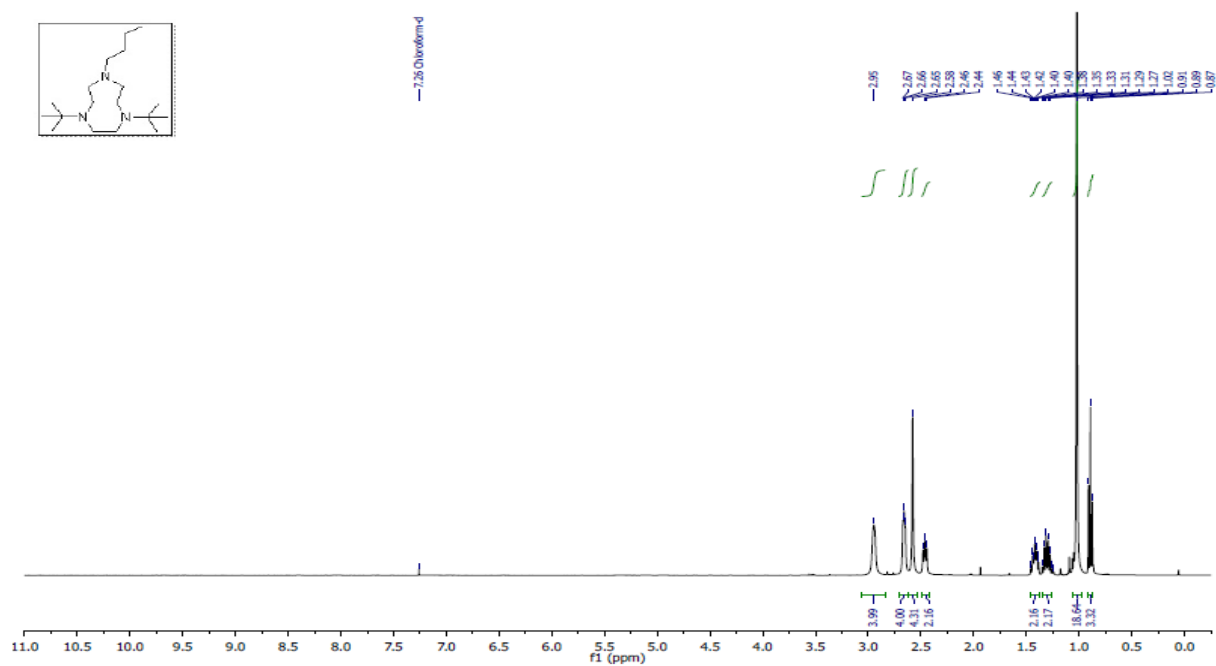


Fig. S1.5 ^1H NMR spectrum of 'Bu₂'Butacn.

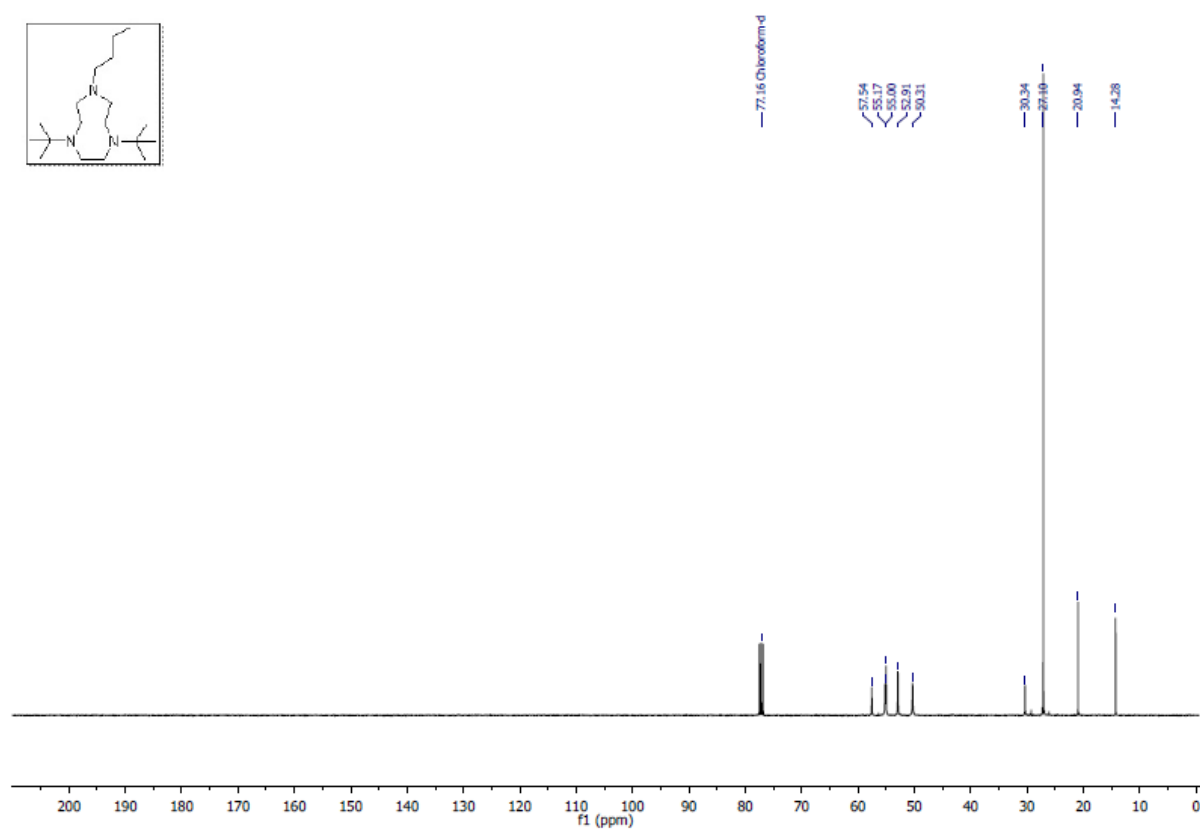


Fig. S1.6 ^{13}C NMR spectrum of 'Bu₂'Butacn.

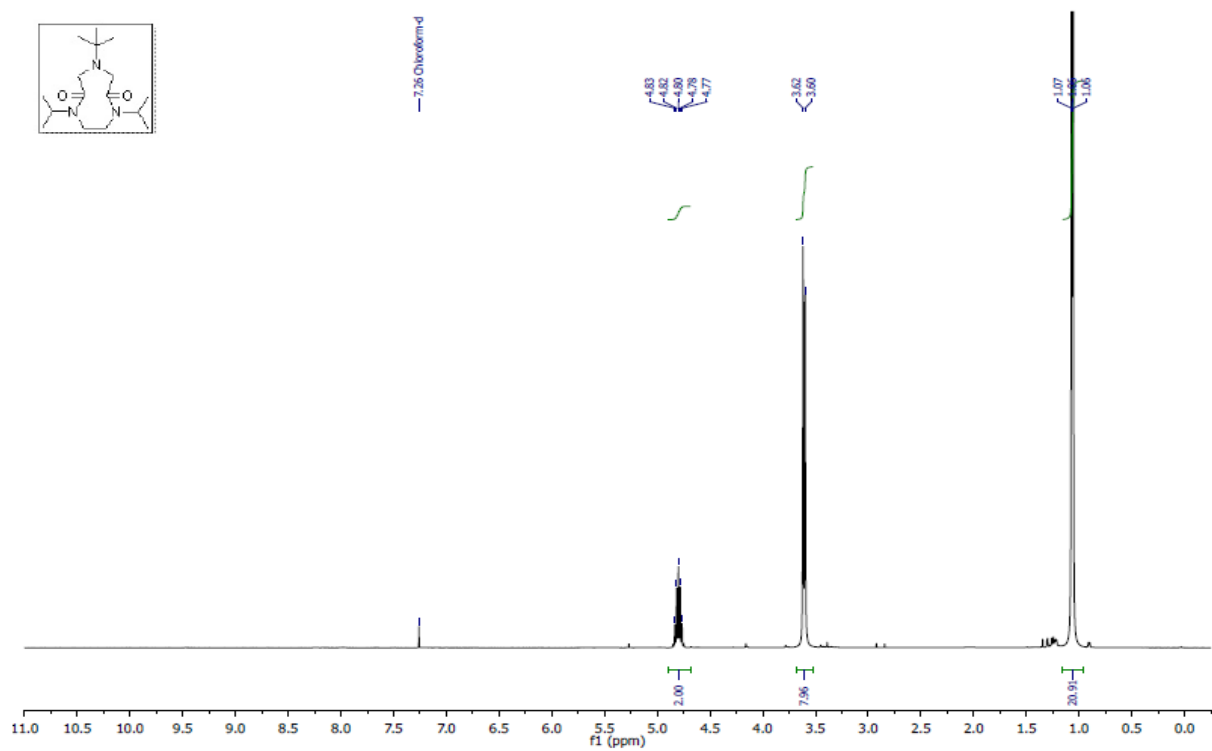


Fig. S1.9 ¹H NMR spectrum of **6b**.

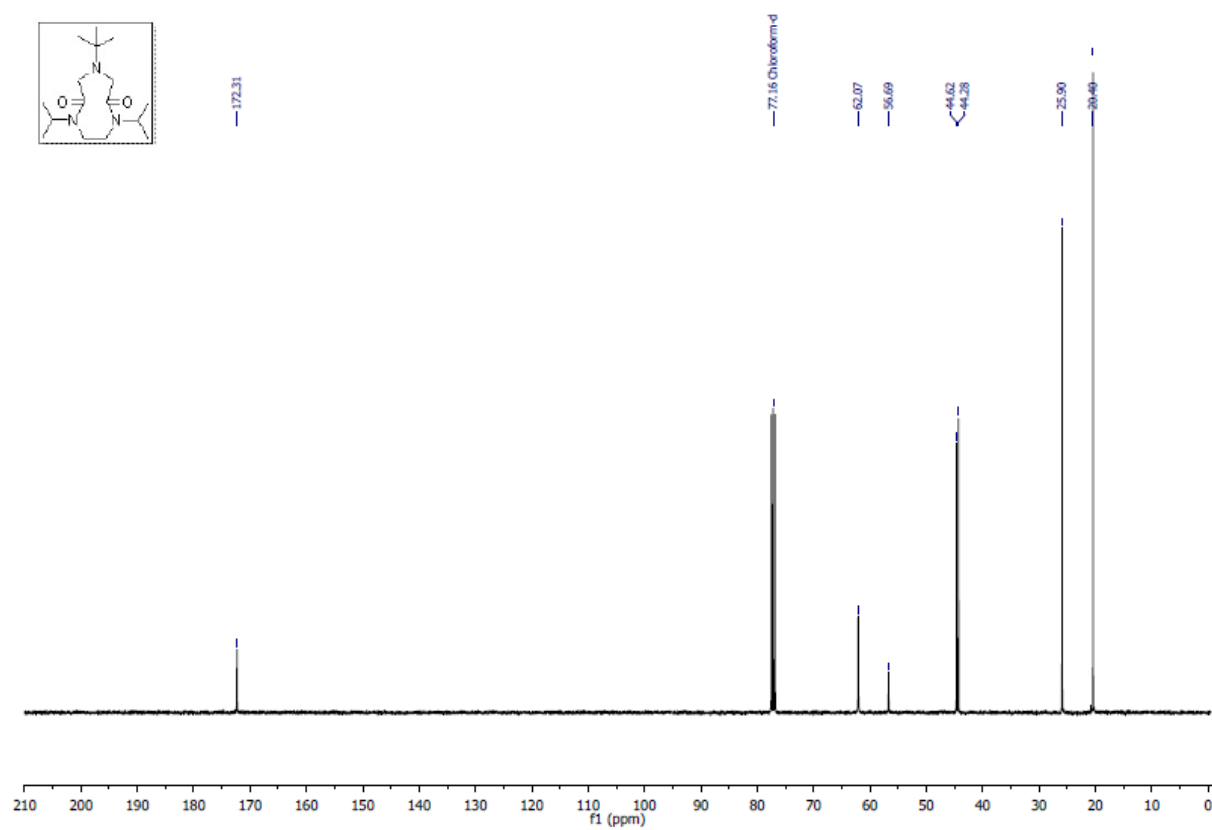


Fig. S1.10 ¹³C NMR spectrum of **6b**.

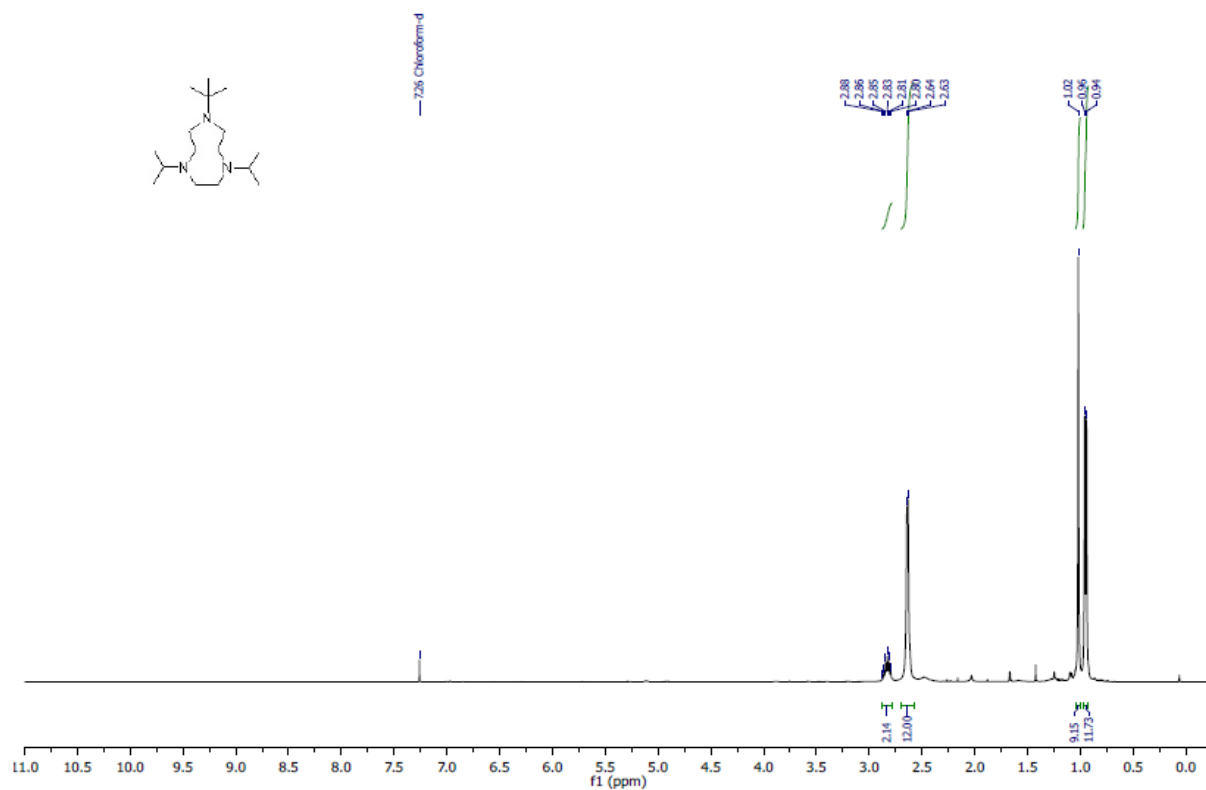


Fig. S1.11 ¹H NMR spectrum of *t*BuPr₂tacn.

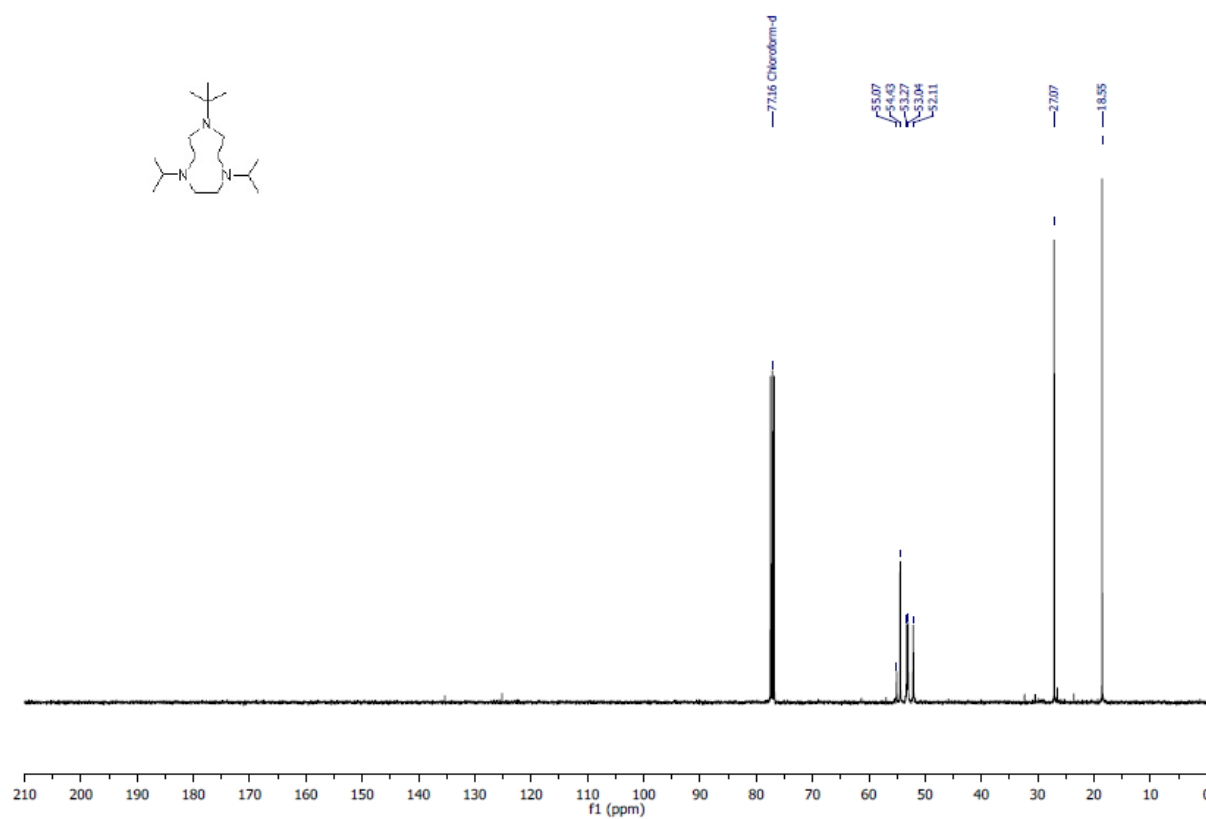


Fig. S1.12 ¹³C NMR spectrum of *t*BuPr₂tacn.

S2. X-ray structure reports of [Cu('Bu₂"Butacn)SO₄] and [Cu('Bu₃tacn)Cl][PF₆]

The diffraction data of [Cu('Bu₂"Butacn)SO₄] and [Cu('Bu₃tacn)Cl][PF₆] were on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Mo K α ($\lambda = 0.71073$ Å) radiation at -95 ± 1 °C. A crystal of suitable size and quality was coated with Paratone-N oil (Hampton Research, Aliso Viejo, USA) and mounted on a Dual-Thickness MicroLoop LD (200 μ M) (MiTeGen, New York, USA). The crystal to detector distance was *ca.* 45 mm. Data were collected using 0.5° intervals in ϕ and ω to a maximum 2θ value of 55.0°. The highly redundant data sets were reduced using CrysAlisPro.^[1] An empirical absorption correction was applied for each complex. Structures were solved by direct methods (SIR2008^[2]). The position of the silver ions and their first coordination sphere were located from a direct method E-map. And other non-hydrogen atoms were found in alternating difference Fourier syntheses, and least squares refinement cycles. During the final refinement cycles the temperature factors were refined anisotropically. Refinement was carried out by a full matrix least-squares method on F^2 . All calculations were performed with the CrystalStructure^[3] crystallographic software package except for refinement, which was performed using SHELXL 2013.^[4] Hydrogen atoms were placed in calculated positions. Crystallographic data and structure refinement parameters including the final discrepancies (R and R_w) are listed in Table 1. The structure of [Cu('Bu₃tacn)Cl][PF₆] was highly disordered. The structure of one of the two molecules (molecule 2) was too highly disordered, so that it could not be determined. This resulted in large B values, especially for the Cu2 and Cl2 atoms. The bond distances and bond angles around Cu2 in molecule 2 were incorrect due to this effect. The effect of this was that many alerts (Alert A) remained and the R and R_w values were high. Therefore, in the main text, we only discuss molecule 1.

Table S2.1 Crystal data and structure refinement of [Cu('Bu₂"Butacn)SO₄] and [Cu('Bu₃tacn)Cl][PF₆].

Complex	[Cu('Bu ₂ "Butacn)SO ₄]	[Cu('Bu ₃ tacn)Cl][PF ₆]
CCDC number	2238500	2238501
Empirical Formula	C ₁₈ H ₃₉ CuN ₃ O ₄ S	C _{19.5} H ₄₂ ClCuF ₆ N ₃ P
Formula Weight	457.13	562.53
Crystal System	Monoclinic	Trigonal
Space Group	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>P</i> -3 (#147)
<i>a</i> / Å	10.2913(2)	10.9907(8)
<i>b</i> / Å	16.4105(3)	10.9907(8)
<i>c</i> / Å	13.1029(3)	23.1929(16)
α / °	90	90
β / °	992.4886(18)	90
γ / °	90	120
<i>V</i> / Å ³	2210.80(8)	2426.3(3)
<i>Z</i>	4	4
<i>D</i> _{calc} / g cm ⁻³	1.373	1.402
μ (MoK α) / cm ⁻¹	11.095	11.290
2 θ range, °	6 – 55	6 – 55
Reflections collected	17191	11627
Unique reflections	5066	3726
<i>R</i> _{int}	0.0181	0.0339
Number of Variables	244	190
Refls. / Para. ratio	20.67	19.61
Residuals: <i>R</i> 1 (<i>I</i> > 2 σ (<i>I</i>))	0.0236	0.1213
Residuals: <i>R</i> (All refl.)	0.0256	0.1336
Residuals: <i>wR</i> 2 (All refl.)	0.0680	0.3133
Goodness of fit ind.	1.086	1.048
Max/min peak, / e Å ⁻³	0.34 / -0.29	8.09 / -2.18

$$R1 = \Sigma ||Fo| - |Fc|| / \Sigma |Fo|, wR2 = [\Sigma (w (Fo^2 - Fc^2)^2) / \Sigma w(Fo^2)^2]^{1/2}$$

S3. Oxidative polymerization of 2-PhP using [Cu('Bu₂''Butacn)SO₄] catalyst

Since [Cu('Bu₂''Butacn)SO₄] was insoluble in PhMe, anisole, and benzonitrile, but soluble in PhNO₂, PhMe and PhNO₂ were selected as the insoluble and soluble reaction solvents for the oxidative polymerization of 2-PhP. In a two-neck flask under O₂, a solution of 2-PhP (1.2 mmol), Ph₂O (160 mg), and Ph₂Py (0.60 mmol) in PhMe or PhNO₂ (2.4 g) was added to [Cu('Bu₂''Butacn)SO₄] (0.060 mmol), and each mixture was stirred at 40 °C under O₂. After 24 h, the conversions of 2-PhP were only 1% and no polymers were obtained as methanol-insoluble parts in both of the solvents.

In the case using PhMe as the solvent, [Cu('Bu₂''Butacn)SO₄] was kept insoluble for 24 h, so the complex could not work as the heterogeneous catalyst. In the case of PhNO₂, [Cu('Bu₂''Butacn)SO₄] was soluble but did not react with 2-PhP, because the SO₄²⁻ ion coordinated to Cu(II) ion as a bidentate ligand.

S4. UV-Vis analysis of the mixture of CuCl₂ and ⁱPr₃tacn in PhMe

In 20 mL vials filled with argon, the mixtures of CuCl₂ (0.24–0.12 mmol) and ⁱPr₃tacn (0.12–0.24 mmol) were stirred in dry PhMe (2.8 mL) for 30 min, and after adding dry PhMe (2.8 mL), the diluted mixtures were stirred for about 3 h. The final mixtures were filtered and the filtrates were measured by UV-Vis spectroscopy using a JASCO V-550 spectrophotometer. Isolated [Cu(ⁱPr₃tacn)Cl₂] was also analyzed in a similar way for a comparison. The absorption spectra in the ranges of 250–500 nm and 450–900 nm were shown in Fig. S4.1 and S4.2, respectively. For each spectrum, peak separation was performed as Gaussian curves using Igor Pro. Results in Fig. S4.3–S4.6 and Table S4.1.

In the UV-Vis spectra (Fig. S4.1 and S4.2), [Cu(ⁱPr₃tacn)Cl₂] had a large peak at 297 nm, a shoulder peak in 310–340 nm, a middle peak at 425 nm, and a small peak at 747 nm. As the separated peaks (Fig. S4.3 and Table S4.1), [Cu(ⁱPr₃tacn)Cl₂] possessed characteristically a broad peak at 267 nm (Peak 0) and a peak at 770 nm (Peak 5), which is the longest wavelength absorption. In the case of CuCl₂:ⁱPr₃tacn = 2:1, the UV-Vis spectrum and the separated peaks (Fig. S4.4 and Table S4.1) almost agreed with those of [Cu(ⁱPr₃tacn)Cl₂], showing the formation of the same complex as [Cu(ⁱPr₃tacn)Cl₂].

On the other hand, for CuCl₂:ⁱPr₃tacn = 1:1, a broad peak (Peak 0) shifted to 299 nm (Fig. S4.5 and Table S4.1), although the other separated peaks were observed similarly as [Cu(ⁱPr₃tacn)Cl₂]. Considering the data that the catalysis of CuCl₂:ⁱPr₃tacn = 1:1 was much more active for oxidative polymerization of 2-PhP than [Cu(ⁱPr₃tacn)Cl₂] (Fig. 3), the complex with CuCl₂:ⁱPr₃tacn = 1:1 would generate or include another reactive complex different from [Cu(ⁱPr₃tacn)Cl₂]. Moreover, only for CuCl₂:ⁱPr₃tacn = 1:2, the separated peak with the longest wavelength absorption (Peak 5) reduced to 744 nm (Fig. S4.6 and Table S4.1). The catalysis of CuCl₂:ⁱPr₃tacn = 1:2 largely decrease the activity (Fig. 3), probably forming a less reactive complex than the other copper complexes.

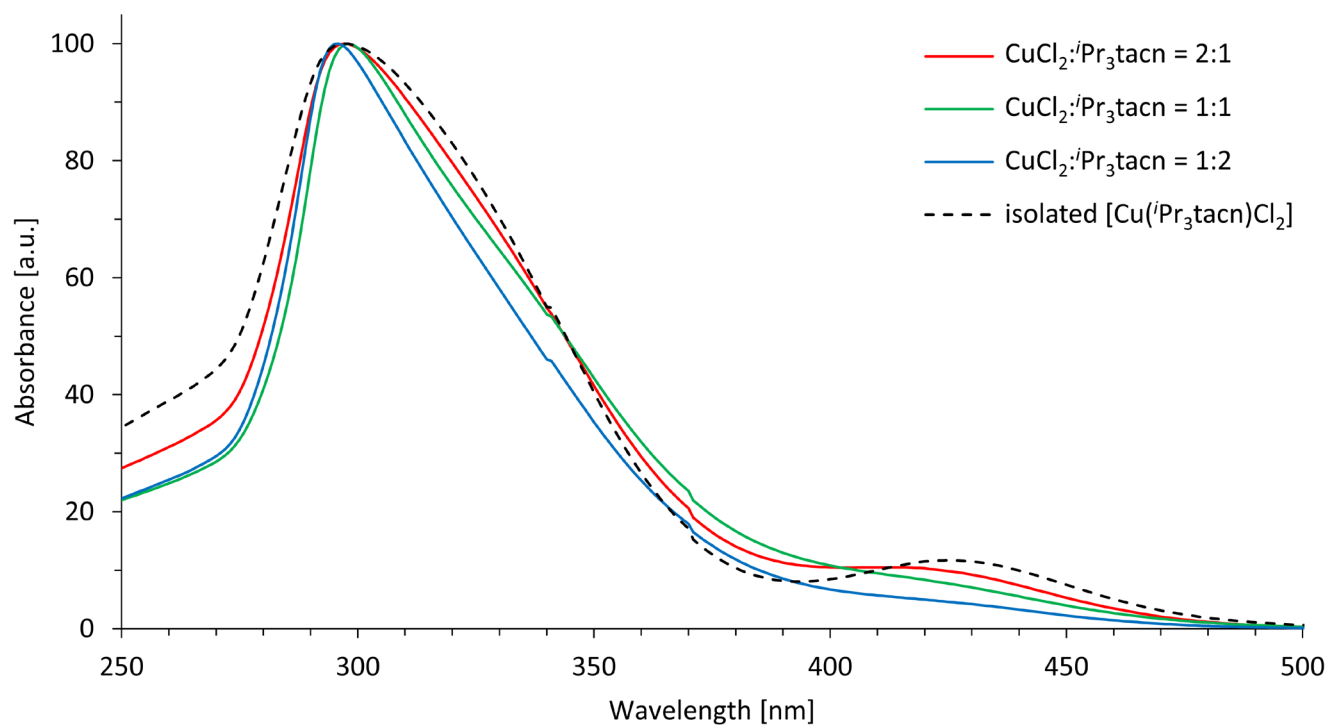


Fig. S4.1 Absorption spectra (250–500 nm) of the mixtures of CuCl₂ / *i*Pr₃tacn in PhMe; normalized by each peak maximum of 296–298 nm.

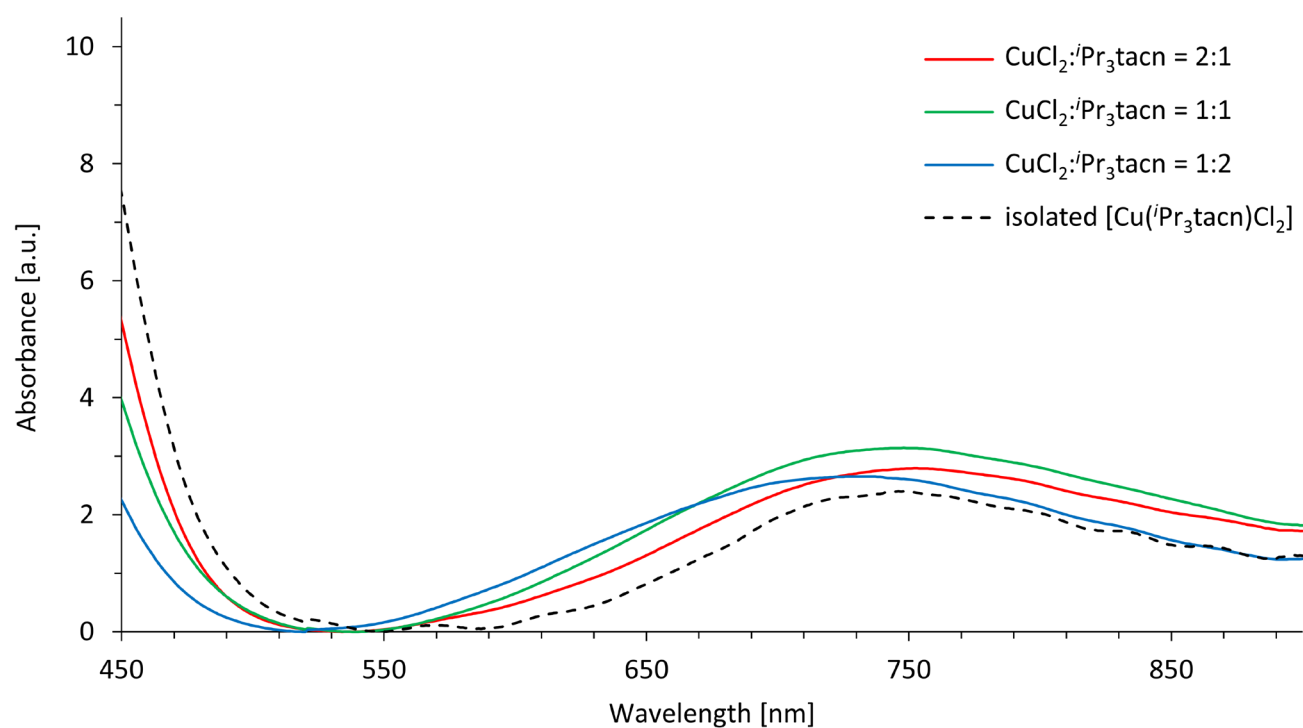


Fig. S4.2 Absorption spectra (450–900 nm) of the mixture of CuCl₂ / *i*Pr₃tacn in PhMe; normalized by each peak maximum of 296–298 nm.

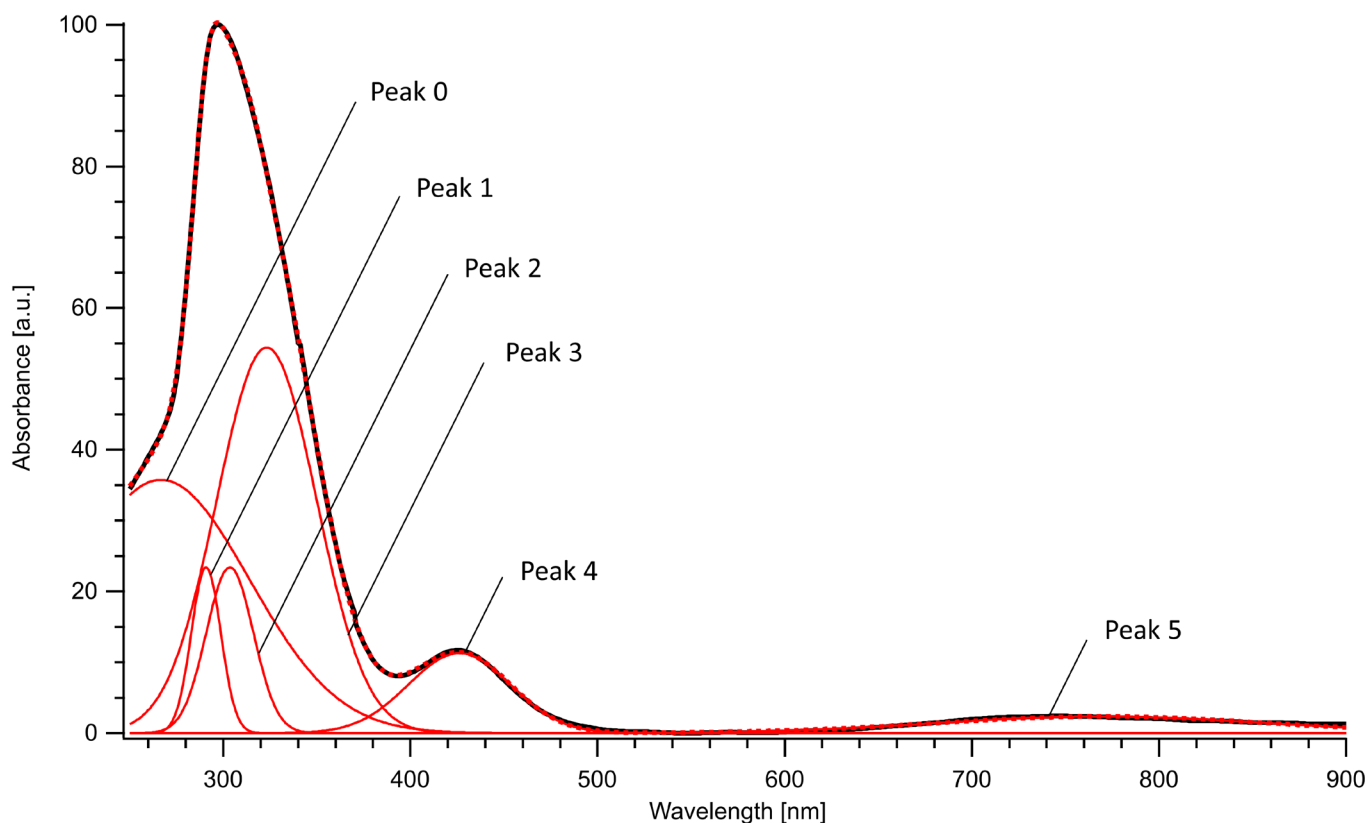


Fig. S4.3 Peak fitting results for UV-Vis spectrum of isolated $[\text{Cu}(\text{iPr}_3\text{tacn})\text{Cl}_2]$; the black solid line, the red dotted line and the red solid lines are the observed spectrum, the fitted spectrum, and the separated peaks, respectively.

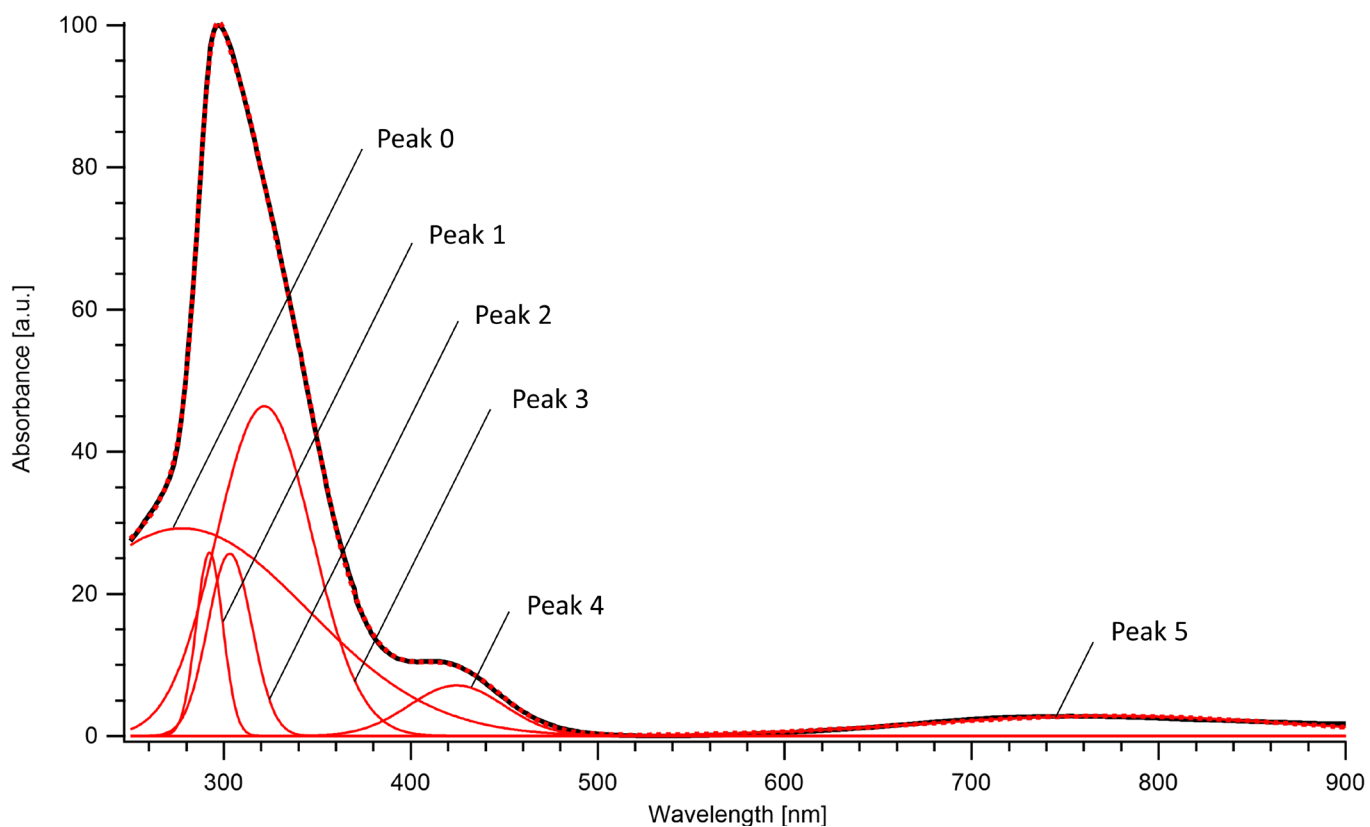


Fig. S4.4 Peak fitting results for UV-Vis spectrum of $\text{CuCl}_2:\text{iPr}_3\text{tacn} = 2:1$; the black solid line, the red dotted line and the red solid lines are the observed spectrum, the fitted spectrum, and the separated peaks, respectively.

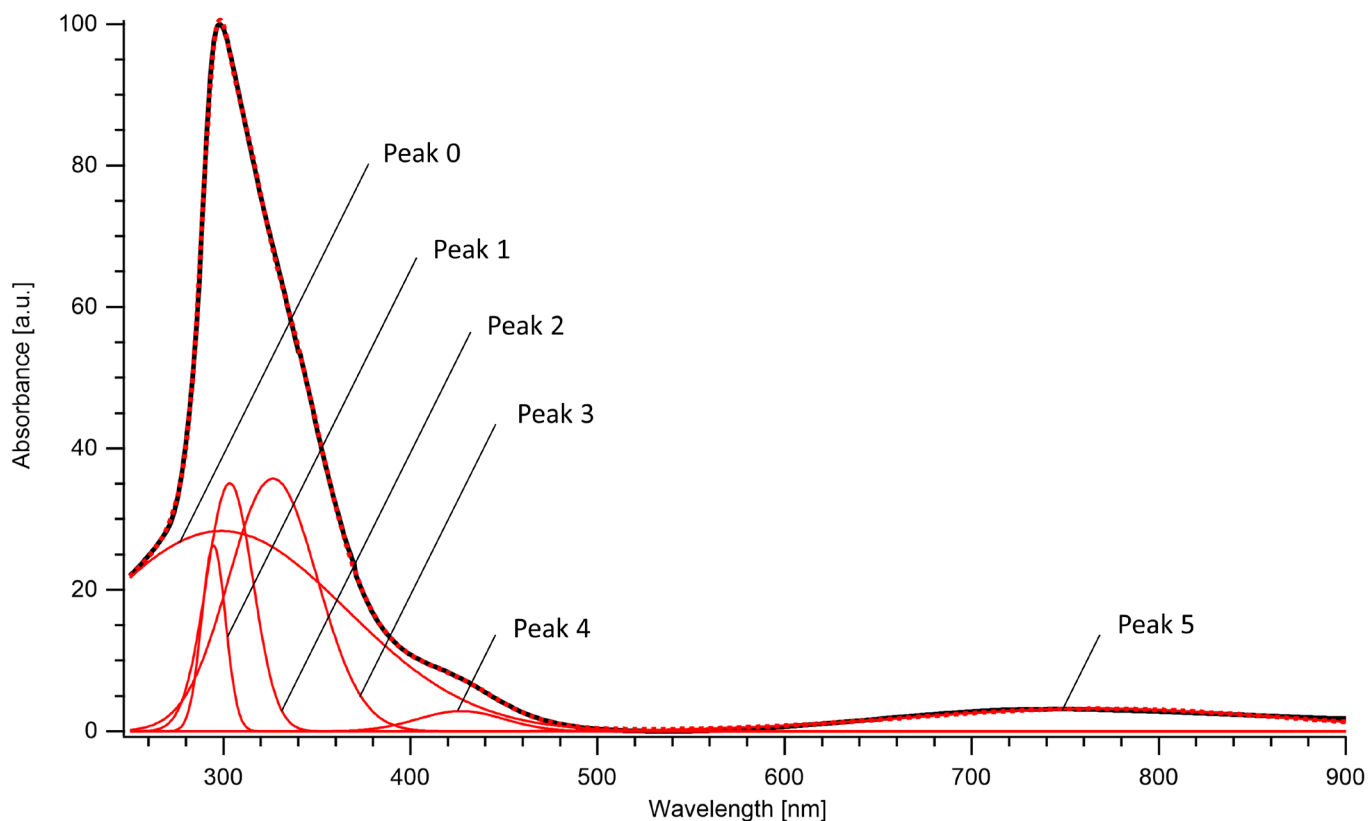


Fig. S4.5 Peak fitting results for UV-Vis spectrum of $\text{CuCl}_2:\text{Pr}_3\text{tacn} = 1:1$; the black solid line, the red dotted line and the red solid lines are the observed spectrum, the fitted spectrum, and the separated peaks, respectively.

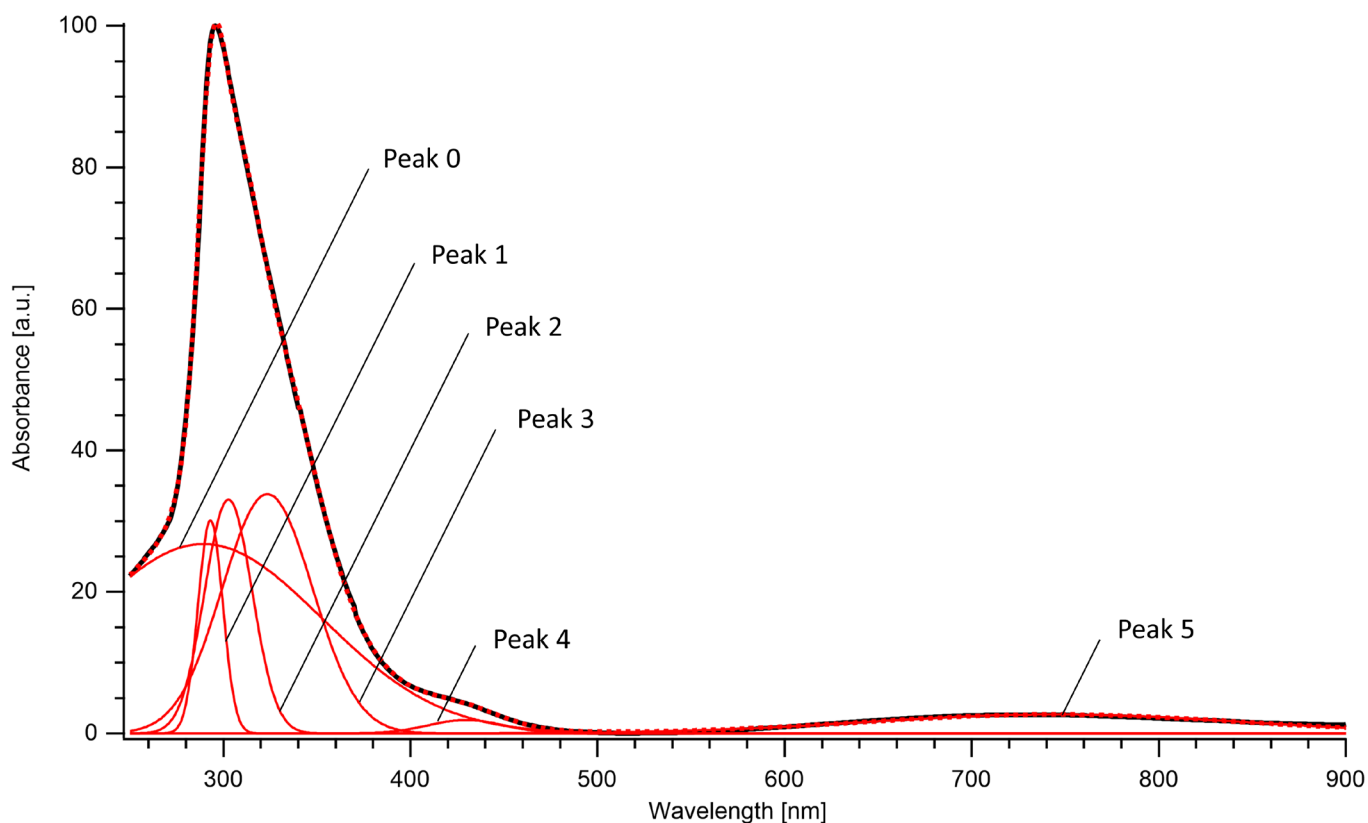


Fig. S4.6 Peak fitting results for UV-Vis spectrum of $\text{CuCl}_2:\text{Pr}_3\text{tacn} = 1:2$; the black solid line, the red dotted line and the red solid lines are the observed spectrum, the fitted spectrum, and the separated peaks, respectively.

Table S4.1 The separated peaks from each UV-Vis spectra of the Cu/ⁱPr₃tacn complexes.

CuCl ₂ : ⁱ Pr ₃ tacn	Peak 0			Peak 1			Peak 2		
	Location [nm]	Width [nm]	Height	Location [nm]	Width [nm]	Height	Location [nm]	Width [nm]	Height
(isolated)	267 (±8)	67 (±3)	36 (±3)	291 (±0)	11 (±0)	23 (±4)	304 (±2)	18 (±2)	23 (±6)
2:1	278 (±4)	95 (±4)	29 (±1)	292 (±0)	10 (±0)	26 (±2)	303 (±1)	17 (±1)	26 (±2)
1:1	299 (±1)	95 (±2)	28 (±1)	295 (±0)	9 (±0)	26 (±1)	303 (±0)	18 (±0)	35 (±2)
1:2	289 (±2)	90 (±3)	27 (±1)	293 (±0)	9 (±0)	30 (±1)	303 (±0)	18 (±0)	33 (±2)

(continued from the above table)

CuCl ₂ : ⁱ Pr ₃ tacn	Peak 3			Peak 4			Peak 5		
	Location [nm]	Width [nm]	Height	Location [nm]	Width [nm]	Height	Location [nm]	Width [nm]	Height
(isolated)	323 (±2)	38 (±2)	54(±8)	426 (±1)	39 (±0)	11 (±0)	770 (±1)	124 (±2)	2 (±0)
2:1	322 (±1)	36 (±1)	46 (±2)	424 (±0)	36 (±1)	7 (±0)	773 (±1)	141 (±1)	3 (±0)
1:1	326 (±1)	33 (±1)	36 (±1)	427 (±1)	33 (±2)	3 (±0)	767 (±1)	142 (±1)	3 (±0)
1:2	323 (±1)	34 (±1)	34 (±2)	430 (±1)	28 (±1)	2 (±0)	744 (±1)	142 (±1)	3 (±0)

S5. NMR, FT-IR, and UV-Vis spectra of the obtained polymers

The NMR spectra of the polymers produced via $\text{Cu}(^i\text{Pr}_3\text{tacn})$ (Run 7), $\text{Cu}(^t\text{Bu}^i\text{Pr}_2\text{tacn})$ (Run 8), $\text{Cu}(^t\text{Bu}_2^i\text{Butacn})$ (Run 9), and $\text{Cu}(^t\text{Bu}_3\text{tacn})$ (Run 10) catalysis were analyzed in CDCl_3 using JEOL JNM-ECS400 (^1H : 400 MHz, Fig. S5.1, ^{13}C : 101 MHz, Fig. S5.2 and S5.3). The FT-IR spectra were obtained by a KBr pellet method using a Thermo Fisher Scientific Nicolet iS50 spectrometer (Fig. S5.4). The UV-Vis spectra were measured in a polymer/ CHCl_3 solution (1.0 mg/4.0 mL) using a JASCO V-550 spectrophotometer (Fig. S5.5). The FT-IR and UV-Vis spectra of the polymer given via the catalysis with $\text{CuCl}_2:^i\text{Pr}_3\text{tacn} = 1:1$ (Run 2) were also shown for a comparison in Fig. S5.4 and S5.5.

The ^1H and ^{13}C NMR and FT-IR spectra of the polymers (Run 7–9) showed that no clear differences were detected (Fig. S5.1–S5.4), although the MWDs largely varied from 13 to 61. Therefore, these polymers would have slight amounts of the structural differences.

The polymer (Run 10) had $R_{\text{C=O/C-H}} = 0.01$, because the C=O stretching peaks at 1,645 and 1,682 cm^{-1} of quinones and diphenoquinones, respectively, were slightly larger than those for the polymers (Run 7–9) in the FT-IR spectrum (Fig. S5.4). This data was in a good agreement with the UV-Vis spectrum (Fig. S5.5), in which the absorbance in the range of 350–420 nm (Run 10) was also somewhat higher than the polymers (Run 7–9) owing to the inclusion such carbonyl structures. For a comparison, the polymer with $R_{\text{C=O/C-H}} = 0.07$ (Run 2) further increased the C=O stretching peaks and the absorbance in 350–420 nm.

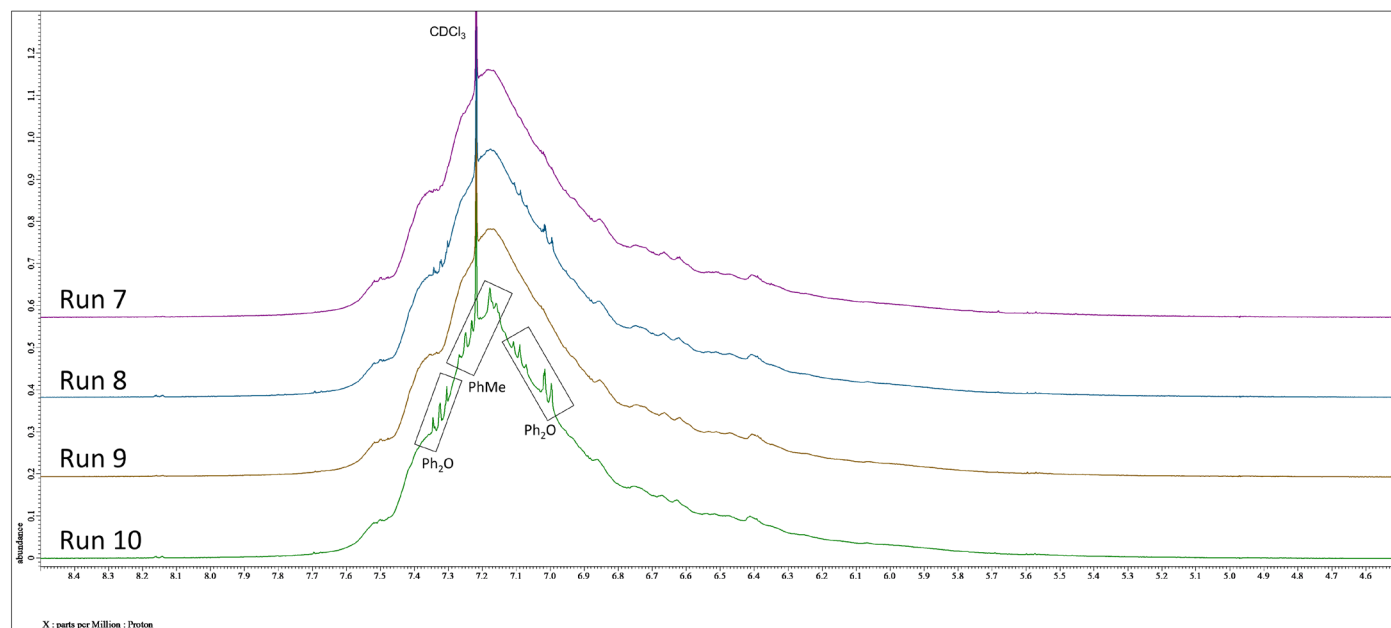


Fig. S5.1 ^1H NMR spectra of the polymers (Run 7–10).

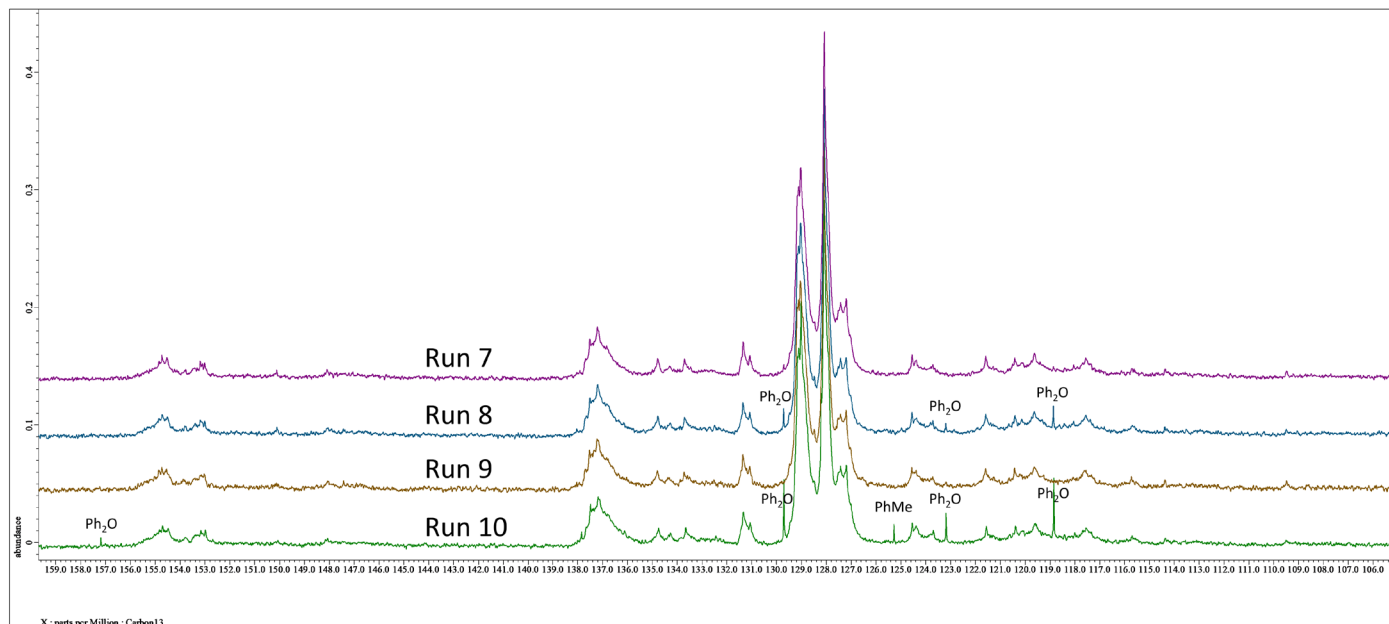


Fig. S5.2 ^{13}C NMR spectra of the polymers (Run 7–10).

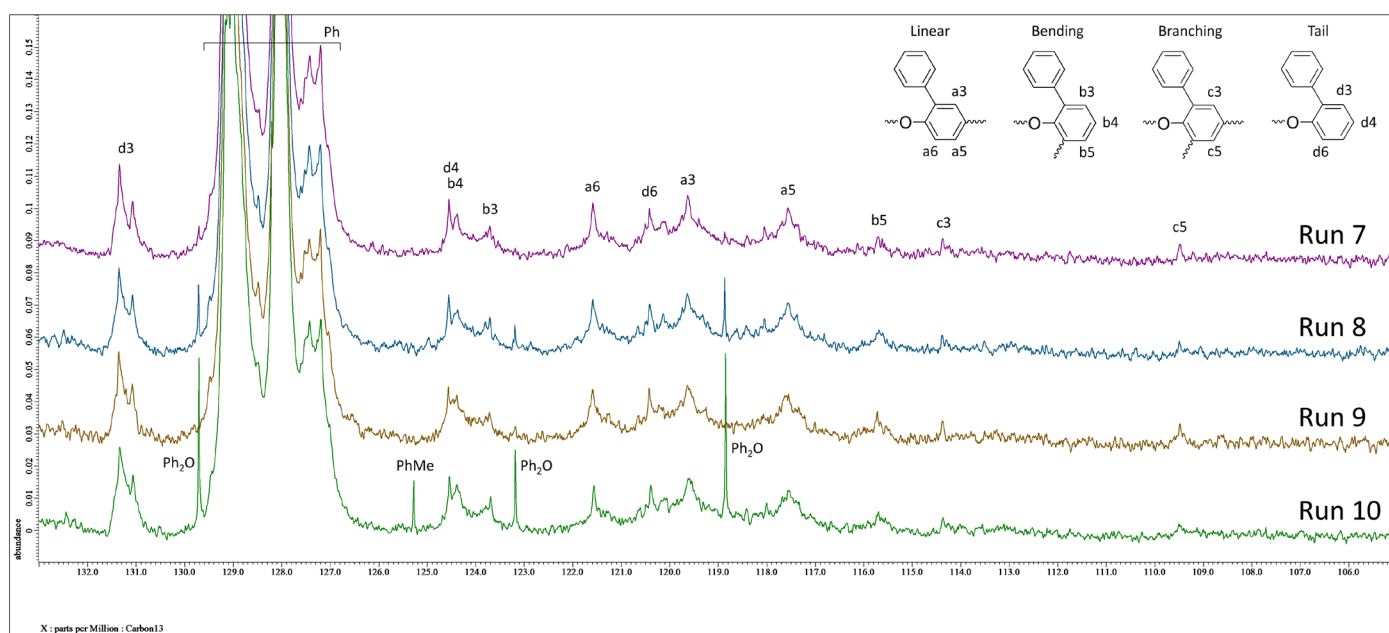


Fig. S5.3 ^{13}C NMR spectra of the polymers (Run 7–10) in 105–133 ppm; only carbon atoms individually bonded to one hydrogen atom are identified as the linear, bending, branching, and tail structures.^[5]

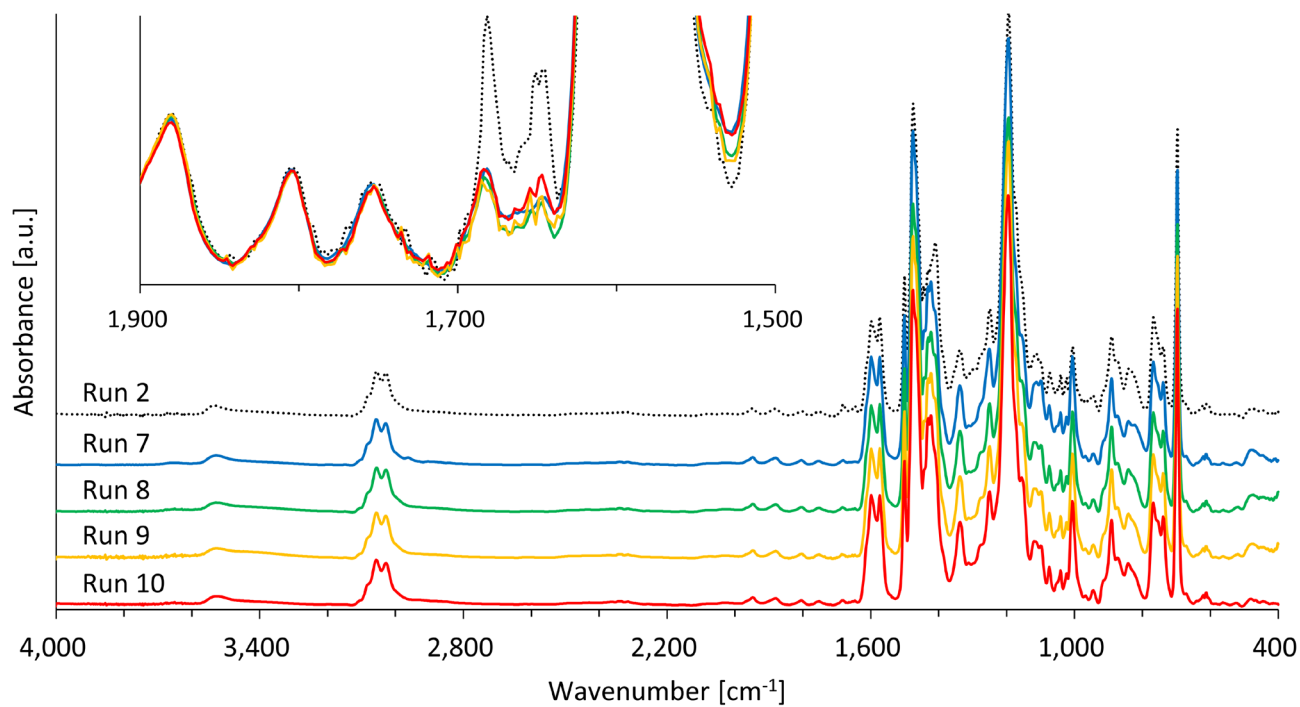


Fig. S5.4 FT-IR spectra of the polymers (Run 2, 7–10); normalized by each area of C–H peaks.

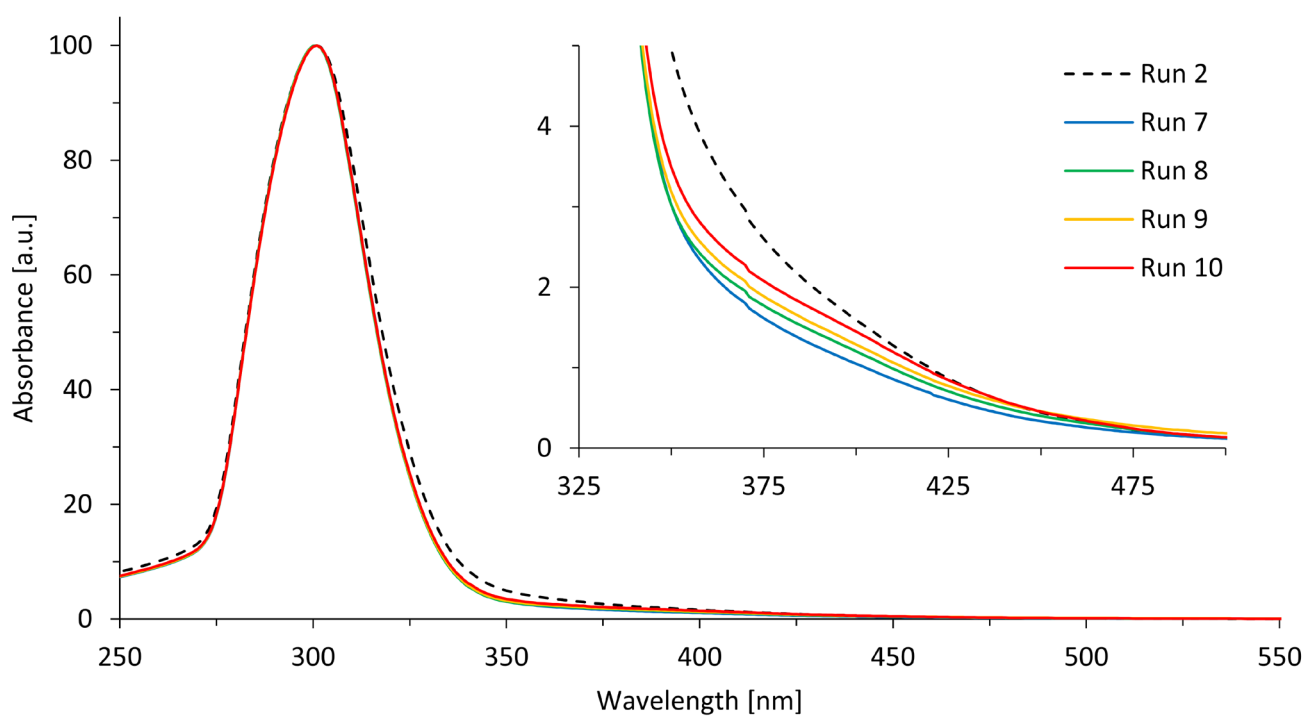


Fig. S5.5 UV-Vis spectra of the polymers (Run 2, 7–10) in a polymer/ CHCl_3 solution (1.0 mg/4.0 mL), normalized by each peak maximum at 301 nm.

S6. Oxidative polymerization of phenol by Cu(ⁱBu₃tacn) and Cu(ⁱBu₂"Butacn) catalysts

Oxidative polymerization of phenol as another monomer was performed by using Cu(R¹R²R³tacn) catalysts with two or three ⁱBu groups (Run S6.2 or S6.3, respectively). In a two-neck flask under N₂, a solution of R¹R²R³tacn (0.060 mmol) in dry PhMe (1.2 g) was added to CuCl₂ (0.12 mmol) and stirred at room temperature for 30 min. To this catalyst mixture, a solution containing phenol (1.2 mmol), Ph₂O (160 mg), and Ph₂Py (0.60 mmol) in PhMe (1.2 g) was added and purged with O₂. The reaction mixture was stirred at 40 °C under O₂. After 72 h, conc. hydrochloric acid (10 drops) and methanol (30 mL) were added to the reaction mixture, and the precipitate was filtered, washed three times with methanol, and dried under reduced pressure at 60 °C overnight. The results are summarized in Table S6.1.

It was noteworthy that the Cu(ⁱBu₃tacn)-catalyzed polymerization of phenol proceeded (Run S6.3), and including the Cu(ⁱBu₂"Butacn) catalysis (Run S6.2), a pale-yellow or pale-brown polymer was obtained in 86–88% yield with insolubility in chloroform and *T*_{d10} of 496–502 °C. In the FT-IR spectrum of the polymer (Fig. S6.1), almost none of O–H stretching peaks showed that the polymer consisted of C–O coupling structures. These data of the polymer were similar to those of the polymer obtained in the oxidative polymerization of phenol via [Cu(ⁱPr₃tacn)Cl₂] catalyst (Run S6.1 and the previous data^[6]).

Table S6.1 Cu(R¹R²R³tacn)-catalyzed oxidative polymerization of phenol.^a

Run	Cu(R ¹ R ² R ³ tacn) catalyst			Time [h]	Conv. ^c [%]	Yield ^f [%]	Solubility in CHCl ₃	<i>T</i> _{d10} ^g [°C]
	Cu salt (mmol)	Ligand (mmol)	Prep. ^b					
S6.1	[Cu(ⁱ Pr ₃ tacn)Cl ₂] (0.060)		isolated ^c	72	96	88	insoluble	476
S6.2	CuCl ₂ (0.12)	ⁱ Bu ₂ "Butacn (0.060)	<i>in situ</i> ^d	72	98	86	insoluble	502
S6.3	CuCl ₂ (0.12)	ⁱ Bu ₃ tacn (0.060)	<i>in situ</i> ^d	72	98	88	insoluble	496

^a Cu(R¹R²R³tacn)-catalyzed polymerization of phenol (1.2 mmol) in the presence of Ph₂Py (0.60 mmol) in PhMe (2.4 g in total) with stirring at 40 °C under O₂. ^b Catalyst preparation method. ^c Using isolated [Cu(ⁱPr₃tacn)Cl₂] (0.060 mmol). ^d Adding a solution of R¹R²R³tacn in PhMe (1.2 g) to CuCl₂ with stirring at room temperature under N₂ for 0.5 h. ^e Monomer conversion. ^f Polymer yield. ^g 10% weight loss temperature.

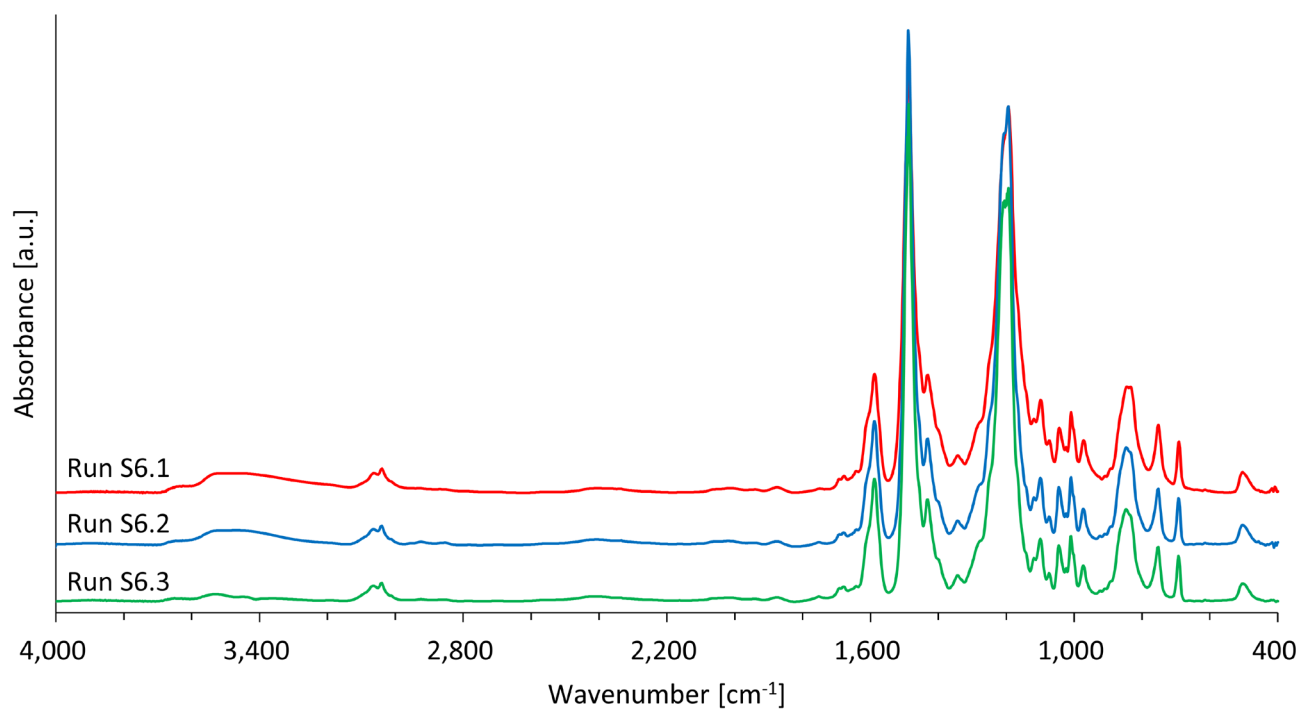


Fig. S6.1 FT-IR spectra of the polymer obtained from phenol via the $\text{Cu}(\text{R}^1\text{R}^2\text{R}^3\text{tacn})$ catalysis, normalized by C–H stretching peaks.

S7. Addition of (2,2,6,6-tetramethyl-1-piperidinyl)oxyl to Cu(^tBu₂"Butacn) catalysis

To confirm the reaction mechanism of enzyme-inspired catalysis, the addition of (2,2,6,6-tetramethyl-1-piperidinyl)oxyl (TEMPO, a free radical scavenger^[7]) (Run S7.1) to the Cu(^tBu₂"Butacn) catalysis (Run 9). In a two-neck flask under N₂, a solution of ^tBu₂"Butacn (0.060 mmol) in dry PhMe (1.2 g) was added to CuCl₂ (0.12 mmol) and stirred at room temperature for 30 min. To this catalyst mixture, a solution containing 2-PhP (1.2 mmol), Ph₂O (160 mg), Ph₂Py (0.60 mmol), and TEMPO (0.12 mmol) in PhMe (1.2 g) was added and purged with O₂. The reaction mixture was stirred at 40 °C under O₂, and after 24 h, the conversion of 2-PhP reached 99%. Then, conc. hydrochloric acid (10 drops) and methanol (30 mL) were added to the reaction mixture, and the precipitate was filtered, washed three times with methanol, and dried under reduced pressure at 60 °C overnight. The results are shown in Table S7.1.

The reaction rate (Fig. S7.1) in the presence of TEMPO (Run S7.1) did not decreased but a little increased in comparison with that in the absence (Run 9), showing that the Cu(^tBu₂"Butacn) catalysis would inherently proceed through controlled radicals not via free radicals. For Run S7.1, a pale-brown polymer was obtained in 93% yield with *M_n* of 13,500, *M_w*/*M_n* of 18, and *T_{d10}* of 534 °C, similarly as Run 9. The polymer of Run S7.1 had almost the same FT-IR spectrum (Fig. S7.2) as that for Run 9, although containing some amount of C=O stretching peaks with *R_{C=O/O-H}* of 0.11. The formation of C=O structures could be due to slightly including another reaction path such as Cu/TEMPO-catalyzed aerobic oxidation.^[8]

Table S7.1 Cu(^tBu₂"Butacn)-catalyzed oxidative polymerization of 2-PhP with or without TEMPO.^a

Run	TEMPO [mmol]	Time [h]	Conv. ^b [%]	Yield ^c [%]	<i>M_n</i> ^d	<i>M_w</i> / <i>M_n</i> ^d	<i>R_{C=O/C-H}</i> ^e	<i>T_{d10}</i> ^f [°C]
S7.1	0.12	24	99	93	13,500	18	0.11	534
9	0	24	100	96	12,500	13	0	528

^a By using the Cu(^tBu₂"Butacn) catalyst formed from ^tBu₂"Butacn (0.060 mmol) and CuCl₂ (0.12 mmol), the polymerization of 2-PhP (1.2 mmol) was performed with Ph₂Py (0.60 mmol) in the presence or absence of TEMPO in PhMe (2.4 g in total) with stirring at 40 °C under O₂. ^b Monomer conversion. ^c Polymer yield. ^d Measured by GPC. ^e Area ratio of C=O/C-H peaks in FT-IR. ^f 10% weight loss temperature.

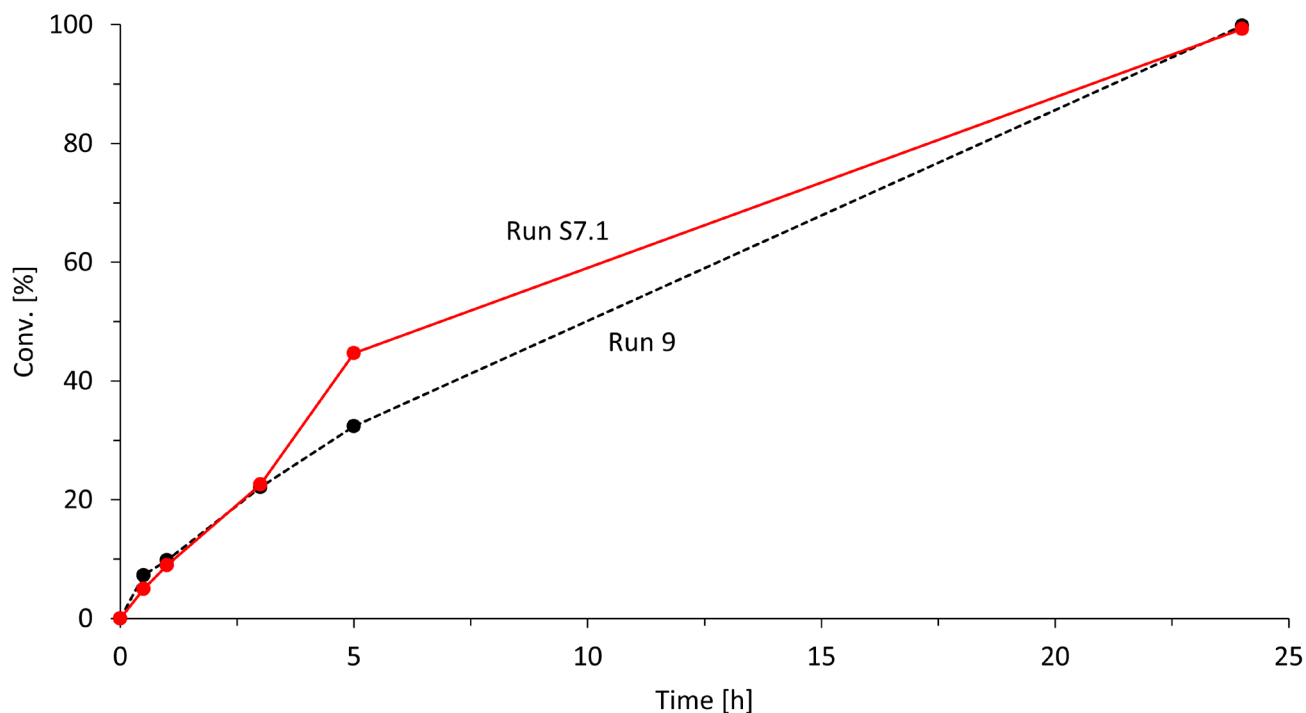


Fig. S7.1 Time-conversion curves of the Cu(*t*Bu₂Butacn) catalysis with and without TEMPO (Run S7.1 and Run 9, respectively).

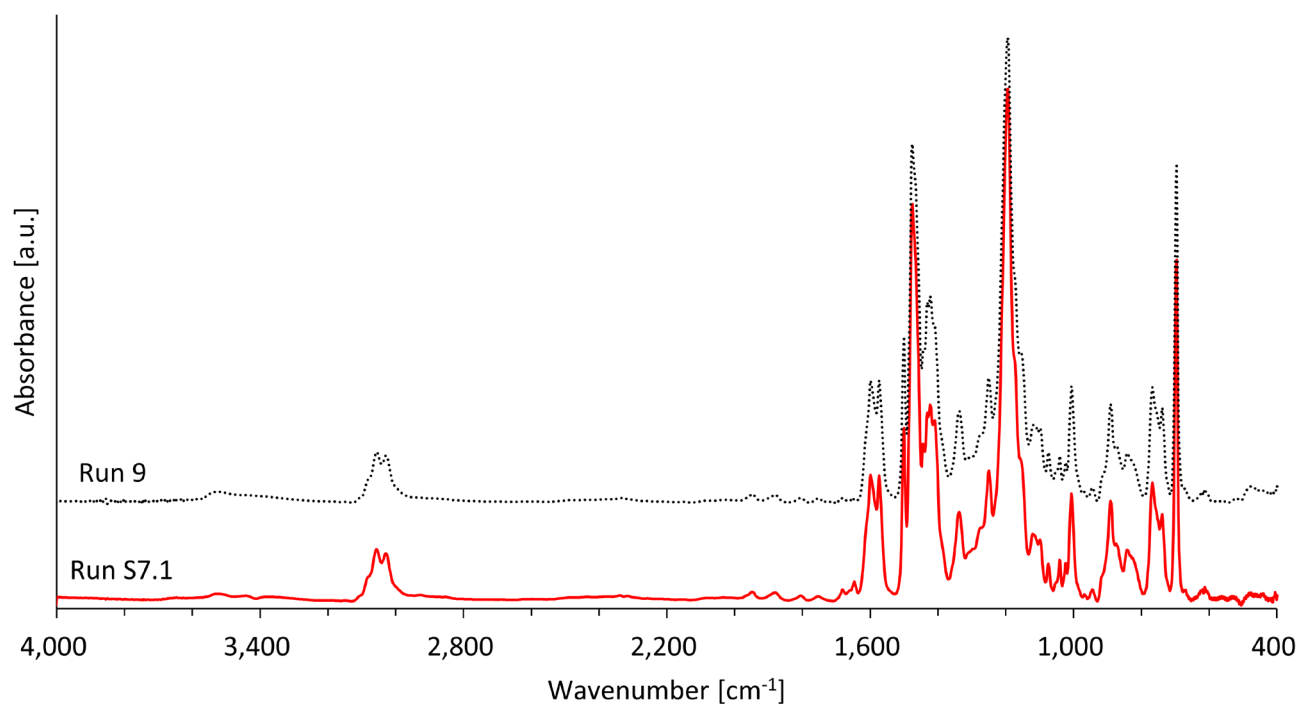


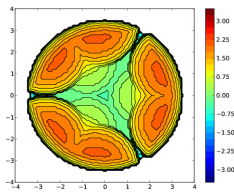
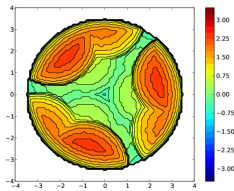
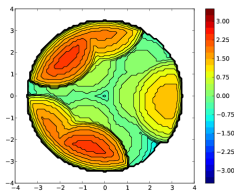
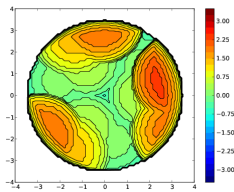
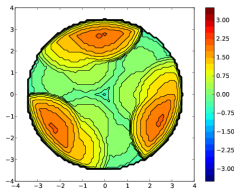
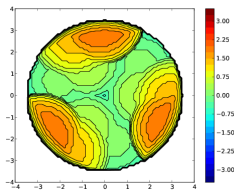
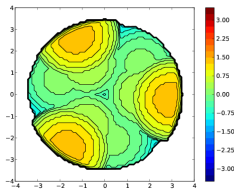
Fig. S7.2 FT-IR spectra of the polymers obtained from 2-PhP via the Cu(*t*Bu₂Butacn) catalysis with and without TEMPO (Run S7.1 and Run 9, respectively), normalized with the C–H stretching peaks.

S8. Buried volumes of R¹R²R³tacn ligands

In order to quantify the steric hindrance of R¹R²R³tacn, the buried volume (%*V*_{Bur})^[9] was applied to the Cu(R¹R²R³tacn) complex. As the complexes, [Cu(^{*t*}Bu₃tacn)Cl]⁺ was derived from the single-crystal structure of [Cu(^{*t*}Bu₃tacn)Cl][PF₆] and Cu(R¹R²R³tacn)⁺ complexes were optimized by MOPAC 2016:^[10] The used keywords were PM6, CHARGE = 1, EF, PRECISE, GNORM = 0.05, NOINTER, GRAPHF, MMOK, LET DDMIN = 0.0. The %*V*_{Bur} and the steric maps^[11] were calculated using SambVca 2.1:^[12] The sphere radius is 3.5 Å, the bond radii are scaled at 1.17, the Cu atom was defined as the center of the sphere, the z-axis was placed from the centroid of the three N atoms toward the Cu atom, H atoms were not included in the calculation, and Cu and Cl ions were removed. The results are summarized in Table S8.1.

The %*V*_{Bur} of ^{*t*}Bu₃tacn in the observed [Cu(^{*t*}Bu₃tacn)Cl]⁺ (75.7%) was almost the same as that in the optimized Cu(^{*t*}Bu₃tacn)⁺ (74.6%), although slightly larger owing to the coordination of Cl ion and the difference of Cu valence. From the comparison, the structure optimized by the semiempirical calculation seems to be meaningful for evaluating the steric hindrances of the R¹R²R³tacn. The %*V*_{Bur} values of R¹R²R³tacn ligands in the optimized Cu(R¹R²R³tacn)⁺ complexes were in the order of ^{*n*}Bu₃tacn (60.6%) < ^{*i*}Pr₃tacn (67.5%) ≈ ^{*c*}Hex₃tacn (67.6%) < ^{*t*}Bu^{*i*}Pr₂tacn (69.9%) ≈ ^{*t*}Bu₂^{*n*}Butacn (70.0%) < ^{*t*}Bu₃tacn (74.6%). The order is in a very good agreement with the present data that the steric hindrances of Cu(^{*t*}Bu₂^{*n*}Butacn) and Cu(^{*t*}Bu^{*i*}Pr₂tacn) catalysts were appropriate for depressing the *ortho* coupling of 2-PhP, that of Cu(^{*t*}Bu₃tacn) catalyst was too large, and that of Cu(^{*i*}Pr₃tacn) catalyst was too small. Furthermore, the above order is consistent with the selectivity for the para coupling of 4-phenoxyphenol in the Cu(^{*c*}Hex₃tacn) (95%), Cu(^{*i*}Pr₃tacn) (93%), and Cu(^{*n*}Bu₃tacn) (90%) catalysis.^[13]

Table S8.1 % V_{Bur} and steric maps of Cu($R^1R^2R^3\text{tacn}$) complexes.

Cu($R^1R^2R^3\text{tacn}$) complex	% V_{Bur}	Steric map
$[\text{Cu}(\textit{t}\text{Bu}_3\text{tacn})\text{Cl}]^+{}^{\text{a}}$	75.7	
$\text{Cu}(\textit{t}\text{Bu}_3\text{tacn})^+{}^{\text{b}}$	74.6	
$\text{Cu}(\textit{t}\text{Bu}_2\textit{n}\text{Bu}\text{tacn})^+{}^{\text{b}}$	70.0	
$\text{Cu}(\textit{t}\text{Bu}\textit{i}\text{Pr}_2\text{tacn})^+{}^{\text{b}}$	69.9	
$\text{Cu}(\textit{e}\text{Hex}_3\text{tacn})^+{}^{\text{b}}$	67.6	
$\text{Cu}(\textit{i}\text{Pr}_3\text{tacn})^+{}^{\text{b}}$	67.5	
$\text{Cu}(\textit{n}\text{Bu}_3\text{tacn})^+{}^{\text{b}}$	60.6	

^a Derived from the single-crystal structure of $[\text{Cu}(\textit{t}\text{Bu}_3\text{tacn})\text{Cl}][\text{PF}_6]$. ^b Optimized by PM6/MOPAC2016.

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