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Oxidation of benzyl alcohol by novel peripherally and non-peripherally modular C_2-symmetric diol substituted cobalt (II) phthalocyanines

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In this study, a modular ligand structure was designed by altering the binding position of the phenyl group at backbone of hydrobenzoin. A series of regio isomeric substituted phthalonitriles derived from this modular C_2-symmetric ligand was synthesized and characterized. Then, eight cobalt (II) phthalocyanines (CoPc) were obtained from the reaction of phthalonitrile derivatives with cobalt (II) chloride. The catalytic activities of synthesized cobalt (II) phthalocyanines were tested for benzyl alcohol oxidation in acetonitrile using *tert*-butylhydroperoxide as the oxygen source and in the presence of *N*-bromosuccinimide as an additive at 80 °C for 5 hr of the reaction. In this sense, the effect of substrate to catalyst ratio and oxidant to catalyst ratio have been studied in detail for getting the highest benzaldehyde selectivity (up to 83%). The effect of structural design of substituents at peripheral or non-peripheral positions of phthalocyanine skeleton on the catalytic activity performance of cobalt (II) phthalocyanines in benzyl alcohol oxidation was also clarified. All newly synthesized compounds are characterized by FT-IR, ^{1}H NMR, IR, UV–Vis and MALDI-TOF MS spectral data.

KEYWORDS

benzyl alcohol, C_2-symmetric-diol, oxidation, phthalocyanine, synthesis

1 | INTRODUCTION

The researches on the activation of C-H bonds such as in alkane and alcohol are very important for the development of clean oxidation process from the point of view of chemistry and industry.[1] The activation of a bond in a chemical reaction are mostly performed by a catalyst which is capable of driving the chemical reaction under mild condition. Numerous biochemical reactions in living cells are being come true every day, and these reactions are operated by enzymes which are very attractive biocatalysts. The catalytic oxidation of steroids, fatty acids, and the synthesis and breakdown of some of hormone in mammals are operated by cytochrome P-450.[2] Many researchers directed their effort to reveal mechanism of dioxygen activation of cytochrome P-450.[3] In those studies, metalloporphyrins have been investigated extensively for the elucidating the activity of cytochrome P-450 due to their closely relevant catalytic chemistry to cytochrome P-450.[4, 5] Therefore, the chemistry of porphyrins has been well documented in numerous research article, reviews and books.[6–9] Development of efficient catalysts for the activation of C-H bonds in this manner can be achieved by mimicking the active sites of biocatalysts and natural products such as cytochrome P-450 and porphyrin, respectively. At this point, phthalocyanines have been synthesized by bioinspired approach and studied for a long time as the analogues of porphyrin

molecules.[10] The structure of metallophthalocyanines is very similar to the structure of porphyrin but former have high chemical and thermal stability in contrast to naturally occurring porphyrins.[11–13] Not only because of the chemical and thermal stability of phthalocyanines but also due to their cost-efficient synthesis on large scales in terms of ease accessibility and cheap precursors make the phthalocyanines very attractive compounds as catalysts.

On account of the unique properties of phthalocyanines above mentioned, they have been applied widely in advanced technologies such as molecular photovoltaics,[14] electro-catalysts,[15] thin-film transistors,[16] solar cell material,[17, 18] optical imaging,[19] photodynamic therapy[20] and as catalysts for the oxidation of alkane,[21] olefins,[22] phenols,[23] alcohols[24] and sulfur compounds[25] in homogenous and heterogenous catalytic reactions. The catalytic oxidation of above-mentioned chemicals by phthalocyanine complexes is very important for industry to prepare valuable chemicals and also an attractive topic for research. The catalytic activity of metallophthalocyanines depends on the substituents attached to phthalocyanines and the metal in its center.[1] The solubility of metallophthalocyanines is also another important factor for the catalytic activity, especially in homogenous catalysis. To overcome the solubility problem of metallophthalocyanines, the nature and the position of the substituents are the key in the design of phthalocyanines. Therefore, incorporation of electron donating or electron withdrawing substituents to the peripheral and non-peripheral position of phthalocyanine skeleton is a fruitful approach for not only obtaining the desired solubility properties of metallophthalocyanines but also tuning the catalytic properties of them.[26–28]

Although more than 70 different metals located in the center cavity of metallophthalocyanines have been described, metallophthalocyanines with metals such as Co, Fe, Ru, Mn and Cr are the most studied class of phthalocyanines for the catalytic oxidation process due to the redox activity of those metal ions. While inserting the redox active metal ion in the center of phthalocyanines is the necessity for the catalytic steps which are taking places at the metal site, substitution of peripheral or non-peripheral positions of phthalocyanine with bulky groups improves the solubility and decrease the tendency to aggregate in solution which limits the application of phthalocyanines.

In this study, we report the synthesis and characterization of eight cobalt (II) phthalocyanines bearing positional isomers of phenyl substituted hydrobenzoin at peripheral and non-peripheral positions of phthalocyanine skeleton as bulky groups, and investigation of their catalytic activity in the oxidation of benzyl alcohol.

2 | EXPERIMENTAL SECTION

2.1 | Materials and equipment

(*R*,*R*)-hydrobenzoin **4**[29] and its derivatives **1–3**,[30] 3-nitrophthalonitrile,[31] 4-nitrophthalonitrile,[32] C_2-symmetric diol substituted phthalonitriles **6**, **10** and **8**, **12**, and cobalt (II) phthalocyanines **16, 20**[33] and **14, 18**[34] were synthesized according to the published literatures. All reagents and solvents were reagent grade quality and were obtained from commercial suppliers. All solvents were dried and purified as described by Perrin and Armarego.[35] Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 400–630 mesh).

FTIR spectra were measured on a Perkin Elmer Spectrum 65 spectrometer using potassium bromide (KBr) pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer using deuterochloroform ($CDCl_3$) and deuterated tetrahyrofuran (THF-d_8, 99.95%). Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC–MS/MS and a Bruker Daltonics MALDI-TOF spectrometer. Optical spectra were recorded in the UV–Vis region with a PG-T80+ spectrophotometer using 1 cm path length cuvettes at room temperature. The catalytic reactions were monitored by GC-FID chromatography equipped with a 30 m × 0.25 μm × 0.25 μm capillary column (Rxi-5 ms, 95% diphenyl, 95% dimethyl polysiloxane) by comparison standards (benzaldehyde, benzoic acid and 1,4-benzoquinone). Elemental analyses were obtained with a LECO Elemental Analyser (CHNS 0932) spectrophotometer. Melting points were determined with an electrothermal apparatus and are uncorrected.

2.2 | Synthesis

2.2.1 | General procedure for the synthesis of phenyl-substituted hydrobenzoin derived 3- or 4-phthalonitrile (5, 7, 9 and 11, *Scheme 1*)

3-nitrophthalonitrile or 4-nitrophthalonitrile (1.0 mmol, 1.0 equiv.) were added at once into two-necked flask containing a stirring solution of phenyl-substituted hydrobenzoin derivatives (**1** or **3**, 1.0 mmol, 1.0 equiv.) in 4 mL of dimethyl sulfoxide (DMSO) under inert atmosphere at room temperature. Then, the mixture was kept 15 min stirred. At the end of this period, to the reaction mixture was added 1.0 equivalent of finely ground anhydrous potassium carbonate (K_2CO_3) and stirred further 2 hr. The formation of product was evaluated by thin layer chromatography. The reaction was kept stirring till the

consumption of one of the reactants. Then, the reaction mixture was poured into ice-water (3:1 *v*/v) to assist the precipitation of the crude product. The filtration of the solution afforded the crude product as light-yellow precipitate which was then dissolved in dichloromethane. The organic phase was washed twice with a portion of 50 mL of water and then dried over anhydrous sodium sulfate (Na_2SO_4). The organic solvent was evaporated under reduced pressure in order to obtain the crude product which was finally purified by silica gel flash column chromatography. The elution was carried out with dichloromethane (DCM)-ethylacetate (EtOAc) (95:5).

4-((1′R,2′R)-2′- hydroxy-1′,2′-di(2″-phenylphenyl)ethoxy) phthalonitrile (5)

Synthesis of **5** was performed by following the general procedure by using 4-nitrophthalonitrile (0.181 g, 1.04 mmol), **1** (0.384 g, 1.04 mmol) and K_2CO_3 (0.144 g, 1.04 mmol). The product was obtained as a white solid. Yield: 0.325 g, (64%); mp: 80–81 °C. Found: C, 82.54; H, 4.98; N, 5.32%; 'molecular formula $C_{34}H_{24}N_2O_2'$ requires C, 82.94; H, 4.91; N, 5.69%. $[\alpha]_D^{20} =$ +21.98 (c = 1, $CHCl_3$); retention time 8.84 min, Chiral ART Amylose-C, 30:70 *n*-hexane-*i*PrOH, flow rate of 0.5 mL/min, 254 nm, t = 40 °C; IR (KBr disc) ν_{max}/cm^{-1}: 3439 (OH), 3035, 2952, 2231 (C ≡ N), 1597, 1486, 1315, 1250, 1059, 751, 703; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 7.6 (dd, J = 7.2 Hz, J = 2.0 Hz, H), 7.51 (d, J = 9.0 Hz, H), 7.42–7.25 (m, 10H), 7.20 (dt, J = 7.5 Hz, J = 1.5 Hz, H), 7.12–7.09 (m, H), 7.01–6.87 (m, 6H), 6.36 (br, s, H), 5.57 (d, J = 8.0 Hz, H), 5.23 (d, J = 8.0 Hz, H), 2.89 (br, OH); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ: 160.5, 142.2, 140.5, 139.7, 135.5, 134.8, 132.1, 130.4, 130.2, 129.3, 129.1, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 126.9, 121.5, 120.7, 117.2, 115.5, 114.9, 107.9, 82.5, 73.2; MS (ESI^-) MS calculated $[M + Cl]^-$ for $C_{34}H_{24}N_2O_2Cl$: 527.1 found: 527.1.

4-((1′R,2′R)-2′ - hydroxy-1′,2′-di(4″-phenylphenyl) ethoxy) phthalonitrile (7)

Synthesis of **7** was performed by following the general procedure by using 4-nitrophthalonitrile (0.36 g, 2.11 mmol), **3** (0.77 g, 2.11 mmol) and K_2CO_3 (0.29 g, 2.11 mmol). The product was obtained as a white solid. Yield: 0.745 g, (72%); mp: 87–89 °C. Found: C, 82.28; H, 4.68; N, 5.01%; 'molecular formula $C_{34}H_{24}N_2O_2'$ requires C, 82.94; H, 4.91; N, 5.69%. $[\alpha]_D^{20} =$ +79.88 (c = 1, $CHCl_3$); retention time 23.50 min, Chiral ART Amylose-C, 30:70 *n*-hexane-*i*PrOH, flow rate of 0.5 mL/min, 254 nm, t = 40 °C; IR (KBr disc) ν_{max}/cm^{-1}: 3465 (OH), 3031, 2954, 2918, 2871, 2231 (C ≡ N), 1597, 1488, 1313, 1249, 1092, 837, 696; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 7.62–7.12 (m, 21H), 5.30 (d, J = 7.3 Hz, H), 5.10 (d, J = 7.3 Hz, H), 2.95 (br, OH); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ: 160.8, 141.9, 141.4, 140.4, 139.9, 137.0, 135.2, 133.8, 128.9, 127.8, 127.7, 127.5, 127.4, 127.0, 126.9, 121.1, 120.6, 117.4, 115.4, 115.1, 108.1, 86.1, 76.1; MS (ESI^-) MS calculated $[M + Cl]^-$ for $C_{34}H_{24}N_2O_2Cl$: 527.1 found: 527.1.

3-((1′R,2′R)-2′ - hydroxy-1′,2′-di(2″-phenylphenyl) ethoxy) phthalonitrile (9)

Synthesis of **9** was performed by following the general procedure by using 3-nitrophthalonitrile (0.181 g, 1.04 mmol), **1** (0.384 g, 1.04 mmol) and K_2CO_3 (0.144 g, 1.04 mmol). The product was obtained as a white solid. Yield: 0.376 g, (74%); mp: 202–203 °C. Found: C, 82.58; H, 4.67; N, 5.52%; 'molecular formula $C_{34}H_{24}N_2O_2'$ requires C, 82.94; H, 4.91; N, 5.69%. $[\alpha]_D^{20} =$ +65.94 (c = 1, $CHCl_3$); retention time 7.63 min, Chiral ART Amylose-C, 30:70 *n*-hexane-*i*PrOH, flow rate of 0.5 mL/min, 254 nm, t = 40 °C; IR (KBr disc) ν_{max}/cm^{-1}: 3465 (OH), 3088, 2932, 2232 (C ≡ N), 1580, 1465, 1281, 1029, 761, 700; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 7.58–7.56 (m, H), 7.39–7.17 (m, 13H), 7.10–7.00 (m, 4H), 6.96 (dd, J = 7.5 Hz, J = 0.8 Hz, H), 6.79 (d, J = 8.3 Hz, H), 6.30 (br, s, H), 5.59 (d, J = 8.5 Hz, H), 5.33 (d, J = 8.3 Hz, H), 3.04 (br, OH); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ: 160.1, 142.3, 141.8, 140.4, 139.8, 135.5, 133.8, 132.1, 130.3, 130.1, 129.1,129.0, 128.4, 128.3, 128.2, 128.2, 128.1, 127.9, 126.9, 125.8, 119.9, 116.8, 115.1, 113.0, 83.7, 73.1; MS (ESI^-) MS calculated $[M + Cl]^-$ for $C_{34}H_{24}N_2O_2Cl$: 527.1 found: 527.1.

3-((1′R,2′R)-2′ - hydroxy-1′,2′-di(4″-phenylphenyl) ethoxy) phthalonitrile (11)

Synthesis of **11** was performed by following the general procedure by using 3-nitrophthalonitrile (0.34 g; 1.98 mmol), **3** (0.73 g, 1.98 mmol) and K_2CO_3 (0.27 g; 1.98 mmol). The product was obtained as a white solid. Yield: 0.79 g, (81%); mp: 93–95 °C. Found: C, 82.15; H, 5.09; N, 5.79%; 'molecular formula $C_{34}H_{24}N_2O_2'$ requires C, 82.94; H, 4.91; N, 5.69%. $[\alpha]_D^{20} =$ +325.49 (c = 1, $CHCl_3$); retention time 26.34 min, Chiral ART Amylose-C, 30:70 *n*-hexane-*i*PrOH, flow rate of 0.5 mL/min, 254 nm, t = 40 °C; IR (KBr disc) ν_{max}/cm^{-1}: 3465 (OH), 3030, 2921, 2231 (C ≡ N), 1579, 1463, 1282, 1042, 761, 696; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ: 7.58–7.40 (m, 14H), 7.36–7.30 (m, 2H), 7.24 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 5.36 (d, J = 7.3 Hz, H), 5.19 (d, J = 7.3 Hz, H), 3.16 (s, OH); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ: 160.39, 141.8, 141.2, 140.7, 136.9, 134.3, 133.9, 128.9, 128.8, 127.8, 127.6, 127.5, 127.4, 127.1, 127.0, 126.9, 125.8, 119.0, 117.1, 115.2, 113.2, 105.9, 87.1, 77.7; MS (ESI^-) MS calculated $[M + Cl]^-$ for $C_{34}H_{24}N_2O_2Cl$: 527.1 found: 527.1.

2.2.2 | General procedure for the synthesis of cobalt (II) phthalocyanines (13, 15, 17 and 19)

Cobalt (II) phthalocyanines **13, 15, 17** and **19** were synthesized by the reaction of anhydrous $CoCl_2$ (0.5 mmol, 0.5 equiv.) with the corresponding phthalonitrile derivatives in 2.5 mL of n-pentanol at 140 °C for 24 hr in a Schlenk tube under inert atmosphere in the presence of catalytic amount of 1,8-diazabicyclo(5.4.0) undec-7-ene (DBU). Then, the resulting reaction mixture was cooled to the room temperature. The solvent of the reaction mixture was removed under reduced pressure. The remaining crude product was purified by chromatography over silica gel column with a solvent mixture hexane-diethyl ether (7:3) followed by methanol and chloroform solvents as eluents.

2(3),9(10),16(17),23(24)-Tetrakis-{((1′R,2′R)-2′-hydroxy-1′,2′-di(2″-phenylphenyl)ethoxy)} phthalocyaninato cobalt (II) (13)

According to the general procedure of the synthesis of cobalt (II) phthalocyanines, 4-((1′*R*,2′*R*)-2′-hydroxy-1′,2′-di(2″-phenylphenyl)ethoxy phthalonitrile **5** (0.47 g; 0.95 mmol) and $CoCl_2$ (0.062 g; 0.48 mmol) gave a blue solid cobalt (II) phthalocyanine **13**. The yield was 0.085 g (17%). mp: 268–270 °C. Found: C, 79.22; H, 4.41; N, 5.61%; 'molecular formula $C_{136}H_{96}N_8O_8Co$' requires C, 80.50; H, 4.77; N, 5.52%. IR (KBr disc) ν_{max}/cm^{-1}: 3547, 3453 (OH), 3058, 2927, 1656, 1612, 1476, 1410, 1230, 1096, 750, 702; UV–Vis (DMF): λ_{max}, nm (log ε): 330 (4.96), 610 (4.59), 672 (5.18); MS (MALDI-TOF) (*m/z*): calculated $[M]^+$ for $C_{136}H_{96}N_8O_8Co$: 2027.6 found: 2027.4 $[M]^+$.

2(3),9(10),16(17),23(24)-Tetrakis-{((1′R,2′R)-2′-hydroxy-1′,2′-di(4″-phenylphenyl)ethoxy)} phthalocyaninato cobalt (II) (15)

According to the general procedure of the synthesis of cobalt (II) phthalocyanines, 4-((1′*R*,2′*R*)-2′-hydroxy-1′,2′-di(4″-phenylphenyl)ethoxy phthalonitrile **7** (0.37 g; 0.74 mmol) and $CoCl_2$ (0.049 g; 0.37 mmol) gave a green solid cobalt (II) phthalocyanine **15**. The yield was 0.088 g (22%). mp: 261–262 °C. Found: C, 80.13; H, 4.81; N, 5.08%; 'molecular formula $C_{136}H_{96}N_8O_8Co$' requires C, 80.50; H, 4.77; N, 5.52%. IR (KBr disc) ν_{max}/cm^{-1}: 3553, 3416 (OH), 3059, 3030, 2901, 1610, 1520, 1482, 1407, 1230, 1098, 1068, 835, 755, 696; UV–Vis (DMF): λ_{max}, nm (log ε): 326 (4.93), 610 (4.51), 672 (5.00); MS (MALDI-TOF) (*m/z*): calculated $[M]^+$ for $C_{136}H_{96}N_8O_8Co$: 2027.6 found: 2027.9 $[M]^+$.

1(4),8(11),15(18),22(25)-Tetrakis-{((1′R,2′R)-2′-hydroxy-1′,2′-di(2″-phenylphenyl)ethoxy)} phthalocyaninato cobalt (II) (17)

According to the general procedure of the synthesis of cobalt (II) phthalocyanines, 3-((1′*R*,2′*R*)-2′-hydroxy-1′,2′-di(2″-phenylphenyl)ethoxy phthalonitrile **9** (0.4 g; 0.81 mmol) and $CoCl_2$ (0.053 g; 0.41 mmol) gave a green solid cobalt (II) phthalocyanine **17**. The yield was 0.045 g (11%). mp: 246–247 °C. Found: C, 79.03; H, 4.26; N, 5.09%; 'molecular formula $C_{136}H_{96}N_8O_8Co$' requires C, 80.50; H, 4.77; N, 5.52%. IR (KBr disc) ν_{max}/cm^{-1}: 3383 (OH), 3057, 2925, 1597, 1481, 1330, 1145, 1092, 746, 701; UV–Vis (DMF): λ_{max}, nm (log ε): 312 (4.74), 632 (4.44), 694 (4.96); MS (MALDI-TOF) (*m/z*): calculated $[M]^+$ for $C_{136}H_{96}N_8O_8Co$: 2027.6 found: 2027.9 $[M]^+$.

1(4),8(11),15(18),22(25)-Tetrakis-{((1′R,2′R)-2′-hydroxy-1′,2′-di(4″-phenylphenyl)ethoxy)} phthalocyaninato cobalt (II) (19)

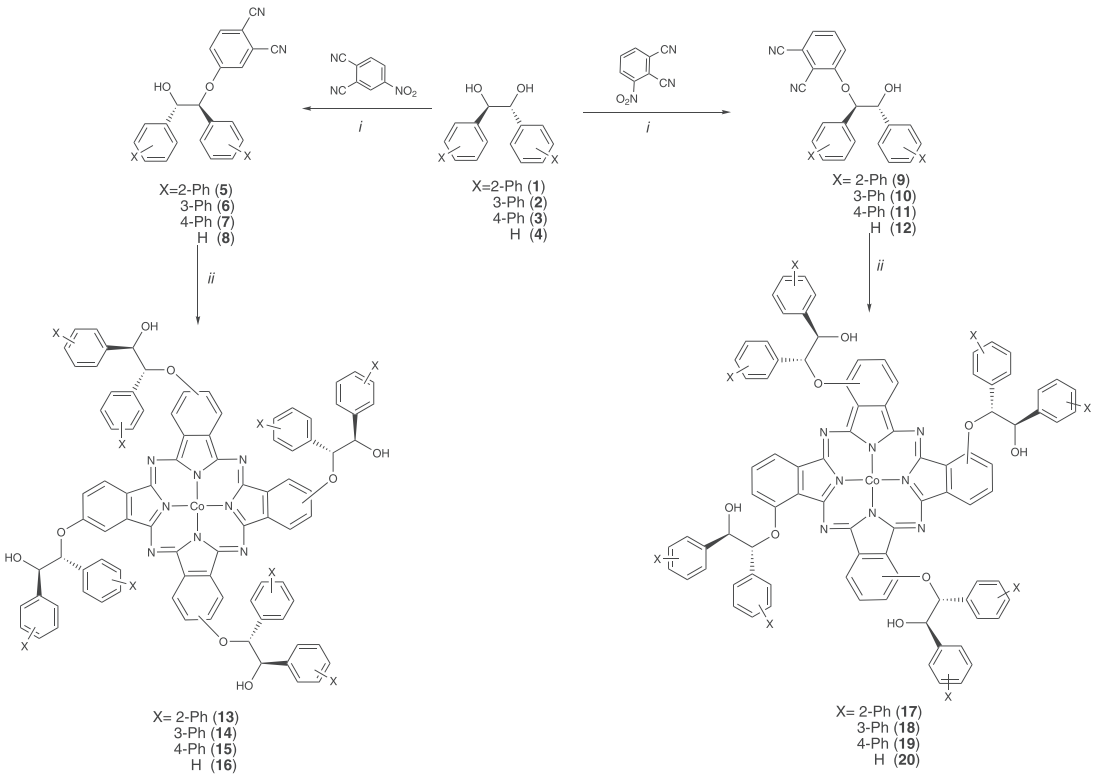
According to the general procedure of the synthesis of cobalt (II) phthalocyanines, 3-((1′*R*,2′*R*)-2′-hydroxy-1′,2′-di(4″-phenylphenyl)ethoxy phthalonitrile **11** (0.42 g; 0.85 mmol) and $CoCl_2$ (0.055 g; 0.42 mmol) gave a green solid cobalt (II) phthalocyanine **19**. The yield was 0.027 g (6%). mp: 237–238 °C. Found: C, 79.36; H, 4.18; N, 5.49%; 'molecular formula $C_{136}H_{96}N_8O_8Co$' requires C, 80.50; H, 4.77; N, 5.52%. IR (KBr disc) ν_{max}/cm^{-1}: 3352 (OH), 3059, 3030, 2923, 2854,1599, 1485, 1330, 1263, 1091, 762, 737, 694; UV–Vis (DMF): λ_{max}, nm (log ε): 314 (4.86), 638 (4.22), 702 (4.64); MS (MALDI-TOF) (*m/z*): calculated $[M]^+$ for $C_{136}H_{96}N_8O_8Co$: 2027.6 found: 2033.6 $[M + 6H]^+$.

3 | RESULTS AND DISCUSSION

3.1 | Synthesis and characterization

The synthesis of optically active chiral phthalonitriles **5–12** and their cobalt (II) phthalocyanine derivatives **13–20** was illustrated in Scheme 1. The synthesis of four phthalonitriles among them was reported before in literature.[33, 34] The syntheses of new phthalonitriles **5**, **7**, **9** and **11** were performed by the reaction of 3-nitrophthalonitrile or 4-nitrophthalonitrile with the corresponding phenyl-substituted C_2 symmetric diol in the presence of potassium carbonate in DMSO at room temperature. These reactions gave the desired phthalonitriles **5**, **7**, **9** and **11** with the yield of around 70%.

To characterize the phthalonitriles **5**, **7**, **9** and **11**, a combination of spectroscopic techniques such as FT-IR, ^1H and ^{13}C NMR and mass analyses was applied (see



SCHEME 1 Syntheses of phthalonitrile derivatives (**5-12**) and metallophthalocyanines (**13-20**). Reagents and conditions: (i) DMSO, K_2CO_3, rt; (ii) $CoCl_2$, n-pentanol, DBU, 140 °C

Supporting Information). The FT-IR measurements of optically active phthalonitriles **5**, **7**, **9** and **11** were performed by using KBr pellet technique. The appearances of strong intense stretching vibration band at around 2230 cm^{-1} due to the C ≡ N group for all the phthalonitriles in their FT-IR spectra are in good agreement with the proposed structures. In addition to that, the observation of a broad vibrational band at around 3400 cm^{-1} corresponding to the -OH group in the FT-IR spectra of phthalonitriles **5**, **7**, **9** and **11** also confirmed the formation of desired phthalonitriles. Acquiring the ^1H and ^{13}C NMR in $CDCl_3$ allow us to determine the exact structures of phthalonitriles. It was expected to obtain very similar NMR spectra for all phthalonitriles since phthalonitriles **5**, **7**, **9** and **11** were isomers and have the same number of protons and carbons in their structures. The only difference between the spectra was the small change in chemical shift values. The common point of ^1H NMR spectra for all phthalonitriles is the observation of two doublets with the same coupling constant value between 5–6 ppm for the aliphatic -CH protons due to the C_1 symmetry of chiral phthalonitriles **5**, **7**, **9** and **11**. Additionally, the observation of a broad singlet peak at around δ = 3.00 ppm for the proton of -OH group in the ^1H NMR spectra of **5**, **7**, **9** and **11** confirmed the proposed structures. The rest of the protons for the phthalonitriles were observed in aromatic region as expected. In the ^{13}C NMR spectra of **5**, **7**, **9** and **11**, the specific carbon resonances such as aliphatic -CH carbons bounded to the oxygen atom and hydroxyl group appeared as two different carbon signals in a region of δ = 75–85 ppm as expected. The existence of C ≡ N group in the case of phthalonitriles was characterized carbon resonances at around δ = 115.00 ppm.[33] The observation of two carbon resonances at around δ = 115.00 ppm for all the synthesized phthalonitriles in their ^{13}C NMR spectra is consistent with the general expectation for the structures of **5**, **7**, **9** and **11**. The rest of the aromatic carbons was observed between δ = 105–160 ppm. The last measurement for the phthalonitriles to confirm their structures was mass analyses. The mass measurements of phthalonitriles on a LC–MS system gave the same molecular ion peaks at m/z = 527.1 $[M + Cl]^-$ as expected due to the isomeric nature of the phthalonitriles **5**, **7**, **9** and **11**. In addition to the mass analyses, the results of found and calculated elemental analyses values were consistent, which confirmed the successive synthesis of the desired phthalonitriles.

As the last step of the synthetic pathway, the desired cobalt (II) phthalocyanines **13–20** were synthesized from the corresponding phthalonitriles **5–12** by the reaction of phthalonitrile derivative with cobalt (II) chloride in the

presence of catalytic amount of DBU in 2.5 mL of n-pentanol at 140 °C for 24 hr in a Schlenk tube under inert atmosphere. The new four cobalt (II) phthalocyanines **13, 15, 17** and **19** were purified by flash silica gel column chromatography and characterized by FT-IR, UV–Vis and mass measurements (see Supporting Information). By taking account of the FT-IR measurements of cobalt (II) phthalocyanines **13, 15, 17** and **19**, we can conclude that the synthesis of desired cobalt (II) phthalocyanines was performed successfully due to the disappearance of C ≡ N group in their FT-IR spectra. The presence of a vibrational band at around 3400 cm^{-1} attributed to the -OH group of phthalocyanines can be also taken as clear evidence for the formation of cobalt (II) phthalocyanines **13, 15, 17** and **19**. The ^{1}H NMR spectra of cobalt (II) phthalocyanines could not be acquired due to the paramagnetic nature of cobalt (II) ion.[33] The mass analyses of newly synthesized cobalt (II) phthalocyanines were performed on a Bruker Daltonics MALDI-TOF spectrometer. The observation of molecular ion peaks at m/z = 2027 $[M + H]^{+}$ for regio isomer cobalt (II) phthalocyanines **13, 15, 17** and **19** confirmed the proposed structures of the phthalocyanines.

Phthalocyanines have characteristic UV–Vis absorption spectra with two bands in the spectral window between 300–800 nm.[10] One of these absorption bands is called as B band and it was expected to observe at around 300 nm. The other absorption band appeared between 600–800 nm and is called as the Q band.[10] The appearance of the Q band varies depending on whether there is a metal in the center of phthalocyanine compound. In general, the phthalocyanines containing a metal in their center give an unsplitted Q band due to their D_{4h} symmetry whereas metal-free phthalocyanines give the two splitted Q band due to their D_{2h} symmetry.[10] The UV–Vis spectra of all cobalt (II) phthalocyanines recorded in THF were given in Figure 1. As seen from Figure 1, all phthalocyanines gave two main absorptions bands as expected. The UV–Vis absorption spectra of peripherally substituted CoPc **13–16** showed the main Q absorption band at around λ_{max} = 670 with the shoulder at around 610 nm while the Q absorption band was observed at around λ_{max} = 700 with the shoulder at around 640 for the non-peripherally substituted CoPc **17–20**. It was also noted that the main Q absorption band of the non-peripheral substituted CoPc **17–20** was seen in red-shifted compared to that of peripherally substituted of CoPc **13–16**. This is well known as the effect of α-substitution of phthalocyanine skeleton. The substitution at non-peripheral positions of phthalocyanine causes the electron density enhancement and resulted in red shifting of spectra of metallophthalocyanines.[36, 37]

3.2 | Catalytic studies

The catalytic activities of cobalt (II) phthalocyanines **13, 15** and **17, 19** were examined for the selective oxidation of benzyl alcohol to benzaldehyde together with their regio-isomers (**14** and **18**) as we have previously reported.[34] In all catalytic experiments, benzaldehyde was obtained as the main product and the other oxidation products (1,4-benzoquinone and benzoic acid) were formed very little or trace amount and yields were determined by gas chromatography analyses using the standards of these compounds (Scheme 2).

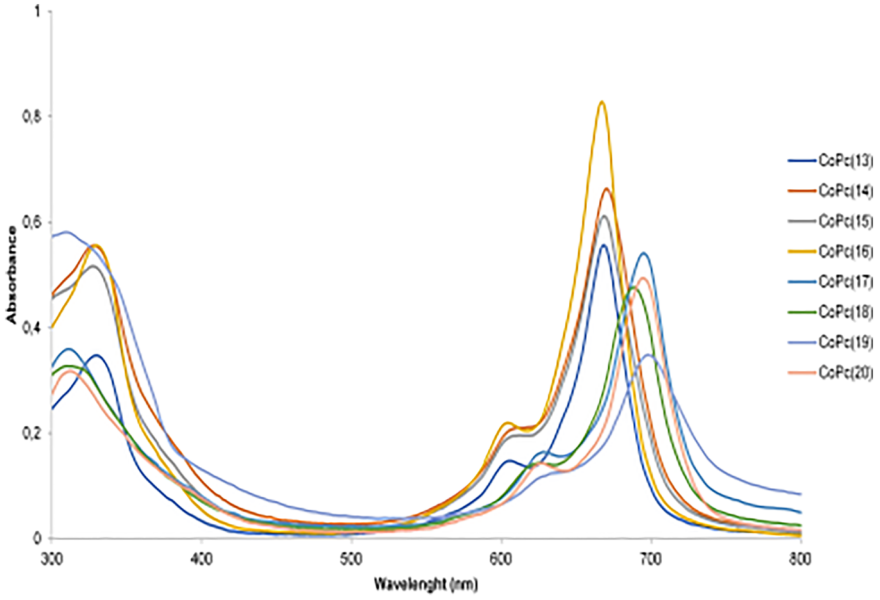
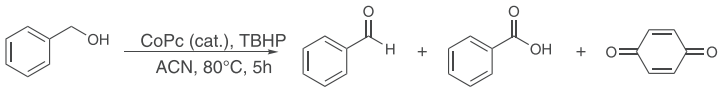


FIGURE 1 UV–Vis spectra of cobalt(II) phthalocyanines **13-20** in tetrahydrofuran [Colour figure can be viewed at wileyonlinelibrary.com]

SCHEME 2 Oxidation of benzyl alcohol using cobalt(II)phthalocyanines 13-15 and 17-20 as catalysts



One of the most important factors for the performance of cobalt (II) phthalocyanines on the oxidation of benzyl alcohol in homogenous catalysis is their solubility in reaction solvent. The solubility of phthalocyanine compounds can be improved by incorporation of various substituents to the either non–peripheral or peripheral positions of phthalocyanine skeleton.[1, 10, 27, 28, 33, 34] We have recently focused on synthesizing of phthalocyanines with bulky C_2-symmetric diols either peripheral or non-peripheral positions of phthalocyanine skeleton to overcome the solubility and aggregation problems of phthalocyanines.[33, 34] The results showed that the phthalocyanines substituted with C_2-symmteric diols have good solubility in common organic solvents such as diethyl ether, chloroform, dichloromethane, tetrahydrofuran, acetonitrile etc.

The effectiveness of a metal complex in catalysis varies depending on the interaction between the metal in the center and the ligand coordinated to the metal center. The ligand structure coordinated around the metal center directly affects the reactivity and selectivity of the metal complex. As a traditional approach for catalysis reactions, performance of the catalyst can be tuned by changing the steric and electronic properties of the ligand coordinated to the metal center.[38] Studies have demonstrated that the catalytic activity of the metal ion is directly related to the number of electrons in the d shell.[39] 1st, 2nd and 3rd order transition metals are used as metal centers in catalytic reactions due to their unfilled d shells. 1st order transition metals are more preferred in catalyst synthesis since they are cheaper and less toxic than 2nd and 3rd order transition metals.[1, 38]

Very recently, we reported two cobalt (II) phthalocyanine complexes having both non-substituted hydrobenzoin moieties at the peripheral (**16**) and non-peripheral (**20**) positions and the catalytic activity of these complexes for the selective oxidation of benzyl alcohol to benzaldehyde were studied in detail.[33] For this purpose, we made a conscious effort to optimize the selective oxidation process of benzyl alcohol and the efficiency of several oxidants (tertiary butyl hydroperoxide; TBHP, *m*-chloroperoxybenzoic acid; *m*-CPBA, and hydrogen peroxide; H_2O_2), solvents (dimethylformamide; DMF and acetonitrile; ACN), reaction temperature (25 and 80 °C) and the effect of using an additive (potassium bromide; KBr, N-bromosuccinimide; NBS and tetrabutylammonium bromide; Bu_4NBr) on the catalyst activity was explored for 5 hours of the reaction. We found that the reaction gave the best conversion (94%) and benzaldehyde selectivity (82%) for both non-substituted catalysts (**16** and **20**) in the presence of the catalytic amount of NBS as an additive with TBHP as the source of oxidant in ACN solvent at 80 °C. It should also be noted that no oxidation product was observed in the blank experiment which was carried out in the absence of any catalyst under optimized conditions. So, to evaluate the catalytic activity of each novel cobalt (II) phthalocyanine complexes having phenyl substituted hydrobenzoin units at peripheral and non-peripheral positions, oxidant amount and substrate to catalyst ratio were determined under certain conditions[33] for selective oxidation of benzyl alcohol to benzaldehyde.

The efficiency of cobalt (II) phthalocyanine complexes **13–15** and **17–19** in the oxidation of benzyl alcohol to corresponding products was studied by varying the oxidant to catalyst ratio from 100/1 to 900/1 (increasing by 100 units) for the reaction period of 5 hr and consequently the highest percentage conversion and benzaldehyde selectivity was determined for each catalyst. Results were presented in Table 1. For all peripheral and non-peripheral substituted cobalt (II) phthalocyanine complexes, full or higher conversions (≥84%) were obtained in every case but benzaldehyde selectivity of the reaction was decreased with depending on the rising concentration of oxidant. Maximal benzaldehyde selectivity (ca 58%) was obtained when using 100/1 oxidant to catalyst ratio with catalyst **13** (Table 1, entry 1). A slightly decrease of the benzaldehyde selectivity (43–54%) was observed with other catalysts in the presence of the same amount of TBHP (Table 1, entries 7, 13, 19, 25, and 31). However, a significant decrease (to 18%) was determined for the benzaldehyde selectivity with an increasing oxidant ratio due to the generation of nonactive species around the cobalt ion depending on the excess amount of oxidant during the catalytic cycle.[33, 40–44]

Substrate to catalyst ratio is another important factor effecting the total conversion and benzaldehyde selectivity for the oxidation of benzaldehyde. So, the effect of the substrate concentration was next examined for our cobalt (II) phthalocyanine complexes and related results are illustrated in Table 2. The results show that the conversion of benzyl alcohol decreased with an increasing amount of substrate until the minimum conversion of 9–22% when 2000/1 substrate to catalyst ratio was used (Table 2, entries 7 and 14). Whereas increasing ratio beyond 2000/1, the selectivity of benzaldehyde generally

TABLE 1 The effect of oxidant amount on the selective oxidation of benzyl alcohol[a]

Entry	Catalyst	Oxidant/catalyst	Conv. (%)[b]	Benzaldehyde (%)[b]	Benzoic acid (%)[b]	1,4-benzoquinone (%)[b]	Selectivity (Benzaldehyde) (%)	TON[c]	TOF[d] (h^{-1})
1	**13**	100/1	93	54	33	6	58	107	21
2		200/1	89	45	34	7	51	102	20
3		300/1	84	40	32	8	48	97	19
4		500/1	98	40	33	8	41	113	23
5		700/1	93	44	30	10	47	107	21
6		900/1	99	28	27	10	28	114	23
7	**14**	100/1	90	49	36	1	54	103	21
8		200/1	100	45	43	7	45	115	23
9		300/1	100	43	41	7	43	115	23
10		500/1	100	44	39	8	44	115	23
11		700/1	100	36	37	9	36	115	23
12		900/1	100	30	28	8	30	115	23
13	**15**	100/1	100	50	40	4	50	115	23
14		200/1	100	50	31	5	50	115	23
15		300/1	100	43	40	6	43	115	23
16		500/1	100	44	34	5	44	115	23
17		700/1	100	33	33	6	33	115	23
18		900/1	100	18	33	10	18	115	23
19	**17**	100/1	96	49	36	2	51	110	22
20		200/1	100	45	40	3	45	115	23
21		300/1	88	46	32	2	52	101	20
22		500/1	94	44	37	4	46	108	22
23		700/1	95	45	36	5	47	109	22
24		900/1	99	43	36	5	43	114	23
25	**18**	100/1	96	41	37	4	43	110	22
26		200/1	97	43	34	5	44	111	22
27		300/1	97	38	44	7	39	111	22
28		500/1	99	40	44	7	40	114	23
29		700/1	100	25	48	12	25	115	23
30		900/1	100	41	43	4	41	115	23

TABLE 1 (Continued)

Entry	Catalyst	Oxidant/ catalyst	Conv. (%)[b]	Benzaldehyde (%)[b]	Benzoic acid (%)[b]	1,4-benzoquinone (%)[b]	Selectivity (Benzaldehyde) (%)	TON[c]	TOF[d] (h^{-1})
31	**19**	100/1	91	47	36	4	52	105	21
32		200/1	100	46	46	3	46	115	23
33		300/1	100	45	45	4	45	115	23
34		500/1	100	47	40	3	47	115	23
35		700/1	98	47	35	3	48	113	23
36		900/1	99	39	41	4	39	114	23

[a]Reaction conditions: Benzyl alcohol ($3.23x10^{-4}$ mol), TBHP (oxidant), catalyst ($2.81x10^{-6}$ mol), Acetonitrile (ACN, 5.0 ml), N-Bromosuccinimide (NBS, 5.0 mg).
[b]Conversions were determined by GC analyses using standards of the oxidation products.
[c]TON: mole of product/mole of catalyst
[d]TOF: mole of product/(mole of catalyst x time).

TABLE 2 The effect of catalyst amount on the selective oxidation of benzyl alcohol[a]

Entry	Catalyst	Substrate/catalyst	Conv. (%)[b]	Benzaldehyde (%)[b]	Benzoic acid (%)[b]	1,4-benzoquinone (%)[b]	Selectivity (Benzaldehyde) (%)	TON[c]	TOF[d] (h^{-1})
1	**13**	115/1	96	54	31	3	56	110	22
2		300/1	66	41	18	2	62	198	40
3		600/1	36	26	7	1	72	216	43
4		900/1	36	26	7	1	72	324	65
5		1200/1	15	11	2	-	73	180	36
6		1500/1	15	11	2	-	73	225	45
7		2000/1	11	8	1	-	73	220	44
8	**14**	115/1	46	30	13	1	65	53	11
9		300/1	34	23	8	-	68	102	20
10		600/1	26	18	5	-	69	156	31
11		900/1	25	17	5	-	68	225	45
12		1200/1	16	10	3	-	63	192	38
13		1500/1	11	7	2	-	64	165	33
14		2000/1	9	6	1	-	67	180	36
15	**15**	115/1	44	34	8	-	77	51	10
16		300/1	38	29	6	-	76	114	23
17		600/1	35	25	6	-	71	210	42
18		900/1	35	24	6	-	69	315	63
19		1200/1	18	13	2	-	72	216	43
20		1500/1	18	13	2	-	72	270	54
21		2000/1	16	11	2	-	69	320	64
22	**17**	115/1	81	43	26	2	53	93	19
23		300/1	66	37	9	2	56	198	40
24		600/1	56	36	9	1	64	336	67
25		900/1	26	20	4	-	77	234	47
26		1200/1	24	18	4	-	75	288	58
27		1500/1	23	17	3	-	74	345	69
28		2000/1	18	15	2	-	83	360	72
29	**18**	115/1	26	18	7	-	69	30	6
30		300/1	26	19	5	-	73	78	16

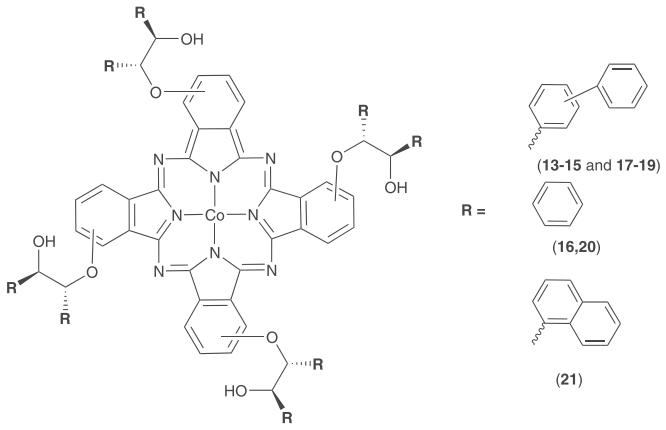
TABLE 2 (Continued)

Entry	Catalyst	Substrate/ catalyst	Conv. (%)[b]	Benzaldehyde (%)[b]	Benzoic acid (%)[b]	1,4-benzoquinone (%)[b]	Selectivity (Benzaldehyde) (%)	TON[c]	TOF[d] (h^{-1})
31		600/1	20	14	4	-	70	120	24
32		900/1	32	20	7	-	63	288	58
33		1200/1	26	17	4	-	65	312	62
34		1500/1	16	11	3	-	69	240	48
35		2000/1	14	10	2	-	71	280	56
36	**19**	115/1	100	44	48	1	44	115	23
37		300/1	73	42	22	2	58	219	44
38		600/1	43	27	11	1	63	258	52
39		900/1	49	28	11	1	57	441	88
40		1200/1	57	32	13	1	56	684	137
41		1500/1	18	12	3	-	67	270	54
42		2000/1	22	15	4	-	68	440	88

[a]Reaction conditions: Benzyl alcohol, TBHP (The best ratio for each catalyst from Table 1), catalyst ($2.81x10^{-6}$ mol), Acetonitrile (ACN, 5.0 ml), N-Bromosuccinimide (NBS, 5.0 mg).
[b]Conversions were determined by GC analyses using standards of the oxidation products.
[c]TON: mole of product/mole of catalyst.
[d]TOF: mole of product/(mole of catalyst x time).

remained steady for peripherally substituted catalyst **18** and non-peripherally substituted catalysts **14** and **15** (entries; 8–21 and 29–35). On the other hand, for catalysts **13, 17** and **19**, benzaldehyde selectivity was positively affected (from 68 to 83%) by increasing amount of substrate (2000/1) in spite of the fact that conversion is low (≤22%). However, conversion of benzyl alcohol inclined to decrease while substrate to catalyst ratio was processing from 300/1 to 2000/1 and the best conversion was obtained at 115/1 substrate/catalyst ratio for all catalysts (entries, 1, 8, 15, 22, 29, and 36).

Another purpose of this study is to explore the effects of the substituent patterns on benzyl alcohol oxidation by comparing other results obtained from our previously synthesized hydrobenzoin (**16, 20**) and hydronaphtoin (**21**) substituted cobalt (II) phthalocyanines. It is noteworthy, however, that our newly examined cobalt (II) phthalocyanines **13–15** and **17–19** having phenyl substituted on hydrobenzoin units at different positions gave better benzaldehyde selectivity when compared to the non-substituted analogues **16** and **20**. We could not conclude a direct comparison with the results obtained with binding position of the phenyl substituents on hydrobenzoin skeleton, since in every situation that we reported in this paper there is no distinct differences in conversion and selectivity been quoted. The best catalytic activity among the synthesized cobalt (II) phthalocyanines (**13–21**) was observed in the case of hydronaphtoin substituted cobalt (II) phthalocyanines **21** which converts benzyl alcohol to benzaldehyde by a conversion of 99% with selectivity of 100% at room temperature in 1 hr.[40] The common point of the phthalocyanines **13–21** are O-R groups at either peripheral or non-peripheral positions of phthalocyanine structure and cobalt (II) ion as center metal. It is noted that the structures of **13–15** and **17–19** are not same as the structure of **21**, but quite similar to that of **21**. The general structures for C_2-symmetric diol substituted phthalocyanine **13–21** are given in Scheme 3. The only difference between the structures of **13–15, 17–19** and **21** is the pattern of substituents. In the case of **21**, the phenyl ring was fused with the phenyl of hydrobenzoin unit to form the naphthyl pattern while the same phenyl group was bounded to the 2, 3 or 4-position of phenyl of hydrobenzoin unit in the structures of **13–15** and **17–19**. The detailed catalytic activity studies of closely related structures **13–15, 17–19** and **21** in the oxidation of benzyl alcohol showed that the catalytic activity of the phthalocyanine molecule can be affected by a very small modification in molecule such as fusing a phenyl ring with the phenyl ring of hydrobenzoin unit to form the naphthyl pattern instead of binding of the phenyl ring to the hydrobenzoin structure at 2, 3 or 4-position. From these experimental results, we can conclude that the structural design of R group covalently bounded to the peripheral or non-peripheral position of phthalocyanine skeleton can play a crucial role in the catalytic activity of cobalt (II) phthalocyanines.



SCHEME 3 The structures of C_2-symmetric diol substituted cobalt(II) phthalocyanines **13-21**.[33, 34, 40]

Previously published oxidation studies were listed in Table 3 and the results that we noted on this paper are considered together. Our cobalt (II) phthalocyanine complexes which have phenyl substituted hydrobenzoin units at peripheral and non-peripheral positions on phthalonitrile skeleton were active, selective, robust and suitable catalysts for the oxidation of benzyl alcohol. Although the mechanism of this selective oxidation of benzyl alcohol has not been studied in detail, this probably proceeds over the formation of $PcCo^{III}$-O-O-^{t}Bu complex in the first step interacting tertiary butyl hydroperoxide (TBHP) with Co (II)-Pc catalyst (Scheme 4). During the catalysis process, the attack of the RO. and ROO. radicals, which are derived from TBHP, on the Pc ring probably leads to the decomposition of the phthalocyanine complex, resulting in the solution color turns from blue to green. However, the continuation of the catalysis process, even when the reaction medium turns yellow, gives the impression that once the catalytically active species have been formed, the reaction can continue, whether the original form of Co (II)-Pc catalysts is in the reaction medium or not.[41–43]

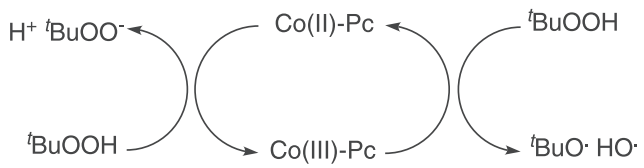
4 | CONCLUSIONS

A series of cobalt (II) phthalocyanines was synthesized by introduction of phenyl-substituted hydrobenzoin moieties to the peripheral and non-peripheral positions of phthalocyanine and inserting cobalt ion as redox active

TABLE 3 Catalytic activities towards the homogeneous oxidation of benzyl alcohol and cyclohexene of some previously reported CoPc catalysts

Catalyst	Substrate	Time (h)	Temp. (°C)	Oxidant	Conv. (%)	Selectivity (%)	Ref.
CoPc[a]	cyclohexene	3	90	TBHP	92	60[j]	[45]
CoPc[b]					98	68[j]	
CoPc[c]	benzyl alcohol	1	25	TBHP	99	100[k]	[38]
CoPc[d]	benzyl alcohol	3	90	TBHP	90	80[k]	[46]
Co ($tbpcH_2$)	cyclohexene	24	25	O_2	30	nr	[47]
CoPc[e]	benzyl alcohol	3	50	TBHP	97	86[k]	[41]
CoPc[f]	benzyl alcohol	3	70	TBHP	89	78[k]	[48]
CoPc[g]	benzyl alcohol	3	90	TBHP	91	82[k]	[49]
CoPc[h]	benzyl alcohol	5.5	70	TBHP	27	91[k]	[50]

$tbpcH_2$: tetra-*tert*-butylphthalocyanine, For Pcs;
[a]tetrakis-[2-(1,4-dioxa-8-azaspiro[4.5]dec-8-yl)ethoxy]phthalocyanine,
[b]tetrakis-(3,3-diphenylpropoxy)phthalocyanine,
[c]{1,2-di (naphthalene-1-yl)ethane-1,2-diol}phthalonitrile,
[d](2-{2-[3-(trifluoromethyl)phenoxy]ethoxy} ethoxy),
[e]{2-[2-(2,3,5,6-Tetrafluorophenoxy)ethoxy]ethoxy},
[f](2-{2-[3-(diethylamino) phenoxy]ethoxy}ethoxy),
[g]2-(2-(4-allyl-2-methoxyphenoxy)ethoxy)ethoxy,
[h]4-(Heptadeca fluorononyloxy).
[j]for 2-cyclohexene-1-ol,
[k]for benzaldehyde, nr: not reported.



SCHEME 4 Proposed reaction mechanism for the formation of active species from Co(II)-Pc and TBHP

metal to the center of phthalocyanine. Novel cobalt (II) phthalocyanines were characterized and investigated their catalytic activity in oxidation of benzyl alcohol. The better benzaldehyde selectivity were obtained in the presence of phenyl ring on hydrobenzoin in case cobalt (II) phthalocyanines **13–15** and **17–19** compared to cobalt (II) phthalocyanines **16** and **20** containing non-substituted hydrobenzoin at peripheral or non-peripheral positions, respectively. According to experimental results, changing the binding positions of phenyl ring on hydrobenzoin did not affect the conversion and selectivity of benzyl alcohol to benzaldehyde indicating that the positional isomerism has no critical effect on the oxidation of benzyl alcohol. Hence, it can be said that structural isomerism has no critical effect on the oxidation of benzyl alcohol in the case of phthalocyanine ring substituted with hydrobenzoin units at different positions. But, the structural design of R group covalently bounded to the peripheral or non-peripheral position of phthalocyanine skeleton can play a crucial role in the oxidation of benzyl alcohol when compare the results in this study with our previous studies.[33, 40] In conclusion, we have shown the importance of structural design of R group substituted to phthalocyanine skeleton for high conversion efficiency in the oxidation of benzyl alcohol.

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DISCLOSURE STATEMENT

There is no conflict of interest between the authors.

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