

Microwave-assisted synthesis and characterization of Co(II) phthalocyanine and investigation of its catalytic activity on 4-nitrophenol oxidation

Ece Tuğba SAKA*, Zekeriya BIYIKLIOĞLU, Halit KANTEKİN

Department of Chemistry, Faculty of Science, Karadeniz Technical University, Trabzon, Turkey

Received: 16.05.2014 • Accepted: 22.07.2014 • Published Online: 24.11.2014 • Printed: 22.12.2014

Abstract: In this study, new cobalt phthalocyanine containing a 2-(2-benzothiazolylthio)ethoxy group at peripheral positions has been synthesized and characterized by spectroscopic methods (IR, UV-Vis elemental analysis, and mass spectroscopies). Catalytic activity of Co(II) phthalocyanine has been investigated in the presence of oxidants such as tert-butylhydroperoxide, m-chloroperoxybenzoic acid, and H₂O₂. Co(II) phthalocyanine shows catalytically activity and product conversion under mild conditions. To find the optimal conditions in the oxidation process, substrate ratio, oxidant ratio, temperature, and oxidant type were examined over 3 h. The results exhibit the best optimum reaction conditions in this catalytic system.

Key words: Phthalocyanine, microwave irradiation, cobalt, 4-nitrophenol oxidation, oxidant

1. Introduction

Phthalocyanine molecules have been investigated for important applications in technological and scientific areas due to their color, thermal stability, and luminescence properties.^{1,2} For example, they are used in liquid crystals, photosensitizers, nonlinear optics, solar cells, catalysis, and various chemical sensing applications.³ Because phthalocyanines have planar heterocyclic systems, their primary disadvantage is their tendency to aggregate, which results in low solubility and difficulties during purification and characterization. Due to the insolubility of phthalocyanines in organic and/or inorganic solvents, one of the most significant aims of research on the chemistry of phthalocyanines is to improve their solubility in various solvents.^{4,5} Phthalocyanines obtained from substitution to the peripheral or nonperipheral positions of long or voluminous alkyl chains are provided in order to dissolve in common organic solvents. Phthalocyanines that dissolve in water are reached by adding sulfonyl, carboxyl, or quaternary amino groups.^{6,7}

Metal phthalocyanines are generally obtained in high yields by cyclotetramerization of different organic molecules with a metal salt at high temperatures.^{8,9} On the other hand, increased attention has been focused on the application of microwave irradiation in the synthesis of metal phthalocyanines for last 10 years. Various reactions including synthesis reaction of phthalocyanines are carried out under microwave-assisted conditions in which significant rate enhancements, improved yield and selectivity, and reduction in thermal by-products have been achieved.^{3,10–16}

Para-nitrophenols are employed as a raw material in several industries. Because of their toxicity to the environment and the spreading of large volumes of contamination into the environment, phenol and substituted phenol compounds are intensively studied for removal from wastewaters.¹⁷

*Correspondence: ece.t.saka@hotmail.com

Co(II) phthalocyanines complexes are catalysts widely used to carry oxygen from different oxygen donors to organic molecules in a great number of works.^{18–21} Unfortunately, Co(II) phthalocyanines are rarely available catalysts on 4-nitrophenol oxidation.²² Therefore, we report microwave-assisted synthesis and characterization of substituted Co(II) phthalocyanines peripherally containing a 2-(2-benzothiazolylthio)ethoxy group. The catalytic demeanor of this complex in oxidation of 4-nitrophenol with changing substrate/catalyst ratio, type of oxidant, and temperature is also explored.

2. Results and discussion

2.1. Syntheses and characterization

The synthetic route to novel peripherally tetra-substituted cobalt phthalocyanine **4** is demonstrated in Figure 1. Cyclotetramerization of **3** happened in the presence of CoCl₂ to reach the target complex **4**. The phthalonitrile **3** was obtained and the new cobalt phthalocyanine was purified according to the literature.²³ The product was obtained in a yield of 53% and was characterized by spectral data (IR, UV-Vis, and mass spectroscopies). The spectral data confirm the formation of complex **4**.

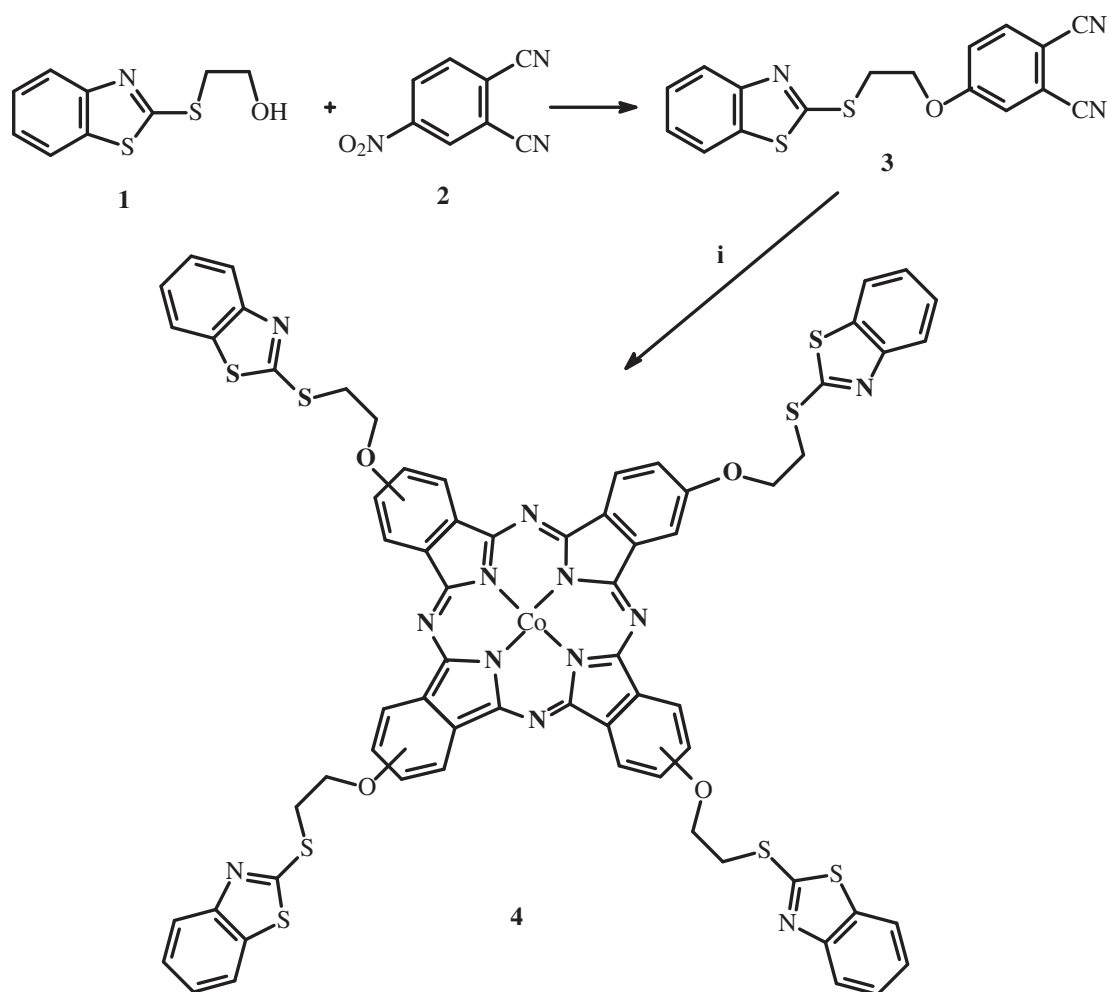


Figure 1. Chemical pathway of the cobalt(II) phthalocyanine **4**. Synthesis of (i) 2-(dimethylamino)ethanol at 175 °C and 350 W for 8 min by microwave oven.

The IR spectra reveal the formation of complex **4** with the disappearance of absorption bands at 2227 cm^{-1} ($\text{C}\equiv\text{N}$). The ^1H NMR and ^{13}C NMR spectra of complex **4** could not be taken due to the paramagnetic cobalt(II) centers. In the mass spectra of complex **4** the presence of a molecular ion peak at $m/z = 1348$ $[\text{M-Co}]^+$ confirmed the proposed structure.²⁴

UV spectra of phthalocyanines including Q and B bands are known. Q band limits are 600–720 nm and B band limits are 250–350 nm in the visible region.²⁵ The electronic absorption spectra of complex **4** in chloroform at room temperature is shown in Figure 2. In UV-Vis spectra of complex **4** (in CHCl_3) split Q bands appeared at 677 and 614 nm, while the B band remained at 281 nm.

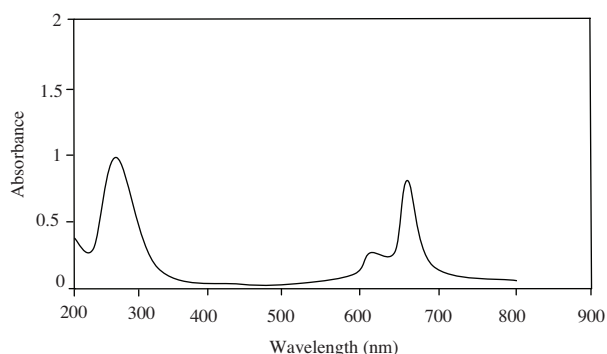


Figure 2. UV-Vis spectrum of complex **4** in CHCl_3 .

2.2. Catalytic studies

A typical catalytic reaction was carried out according to the literature.²⁶ In order to control the experiments, 4-nitrophenol oxidation with tert-buthylhydroperoxide (TBHP), m-chloroperoxybenzoic acid (m-CPBA), and H_2O_2 was done in the absence of the catalyst under the same reaction conditions. The results proved that the catalyst plays a prominent role in the oxidation process. Tables 1–3 show that comparative studies of the catalytic activity of complex **4** for oxidation of 4-nitrophenol revealed that the complex is an active catalyst in DMF. The oxidation products of 4-nitrophenol are benzoquinone as the main product and hydroquinone as a minor product (Figure 3). To achieve the highest conversion of the substrate, the catalytic reactions were carried out while changing the reaction temperature, time, oxidants, and substrate/catalyst ratio.

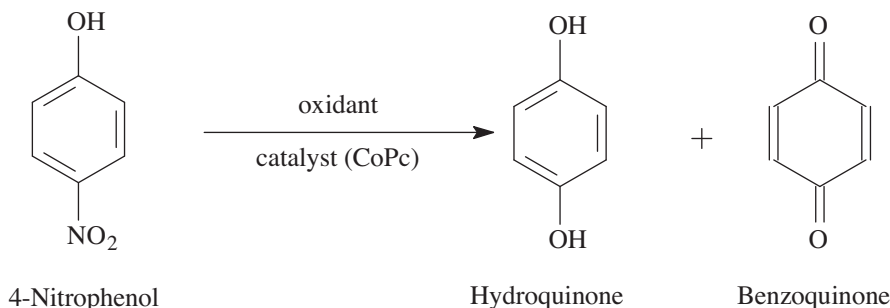


Figure 3. Product formed through oxidation of 4-nitrophenol by TBHP, m-CPBA, and H_2O_2 in the presence of complex **4**.

The results of the catalytic oxidation of 4-nitrophenol by TBHP in the presence of complex **4** are shown in Figure 4. Higher yield was obtained for benzoquinone than hydroquinone for this catalyst. The yield of

the 2 products increased, but leveled off with time. This situation occurs due to the degradation of the Co(II) phthalocyanine by the oxidant.

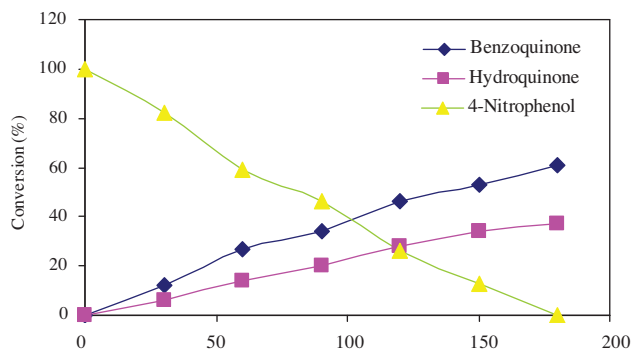


Figure 4. Time-dependent conversion of 4-nitrophenol oxidation. Reaction conditions: 0.71×10^{-3} mol 4-nitrophenol, 1.06×10^{-3} mol TBHP, 3.55×10^{-6} mol complex **4** in 10 mL DMF at 90 °C.

Table 1 shows the results when the molar ratio (substrate/catalyst) was varied (200–800). The other reaction parameters were 90 °C, 1.06×10^{-3} mol TBHP, and 0.01 L DMF for 3 h. As predicted, with a decrease in the substrate/catalyst molar ratio, the conversion amount increases. At each different substrate/catalyst ratio, the oxidation of 4-nitrophenol gives the same main product (benzoquinone) with selectivity of 57.7% for complex **4**.

Table 1. Effect of amount of substrate on 4-nitrophenol oxidation with complex **4**.

Entry	Subs./cat.	Benzoquinone	Hydroquinone	Tot. conv. (%)	TON ^a	TOF ^b (h ⁻¹)
1	200/1	61	37	98	196	65
2	300/1	54	32	86	258	86
3	400/1	48	32	80	320	106
4	500/1	39	21	60	300	100
5	600/1	26	20	56	336	112
6	800/1	19	19	38	304	101

^aTON = moles of product/moles of catalyst.

^bTOF = moles of product/moles of catalyst × time.

Conversion was determined by GC.

Reaction conditions: 90 °C, 1.06×10^{-3} mol TBHP, 3.55×10^{-6} mol complex **4**, 0.01 L DMF for 3 h.

The effect of the oxygen source on the reaction rate of 4-nitrophenol oxidation was investigated for TBHP, m-CPBA, aerobic oxygen, and H₂O₂. With the exception of the oxidant, all the experimental conditions were kept constant for the catalytic reactions. The data are given in Table 2 and Figure 5. There was no conversion for complex **4** when aerobic oxygen was used as the oxidant. The results showed that complex **4** exhibits significantly higher activity with TBHP than the other studied oxidants. The control experiment showed that the 4-nitrophenol was not oxidized in the absence of an oxidant. Study of the influence of temperature on the oxidation of 4-nitrophenol with complex **4** showed that as the reaction temperature was raised, the catalyst activity increased. The experiments were conducted at different temperatures (25 °C, 50 °C, 70 °C, 90 °C) while the other reaction parameters were unchanged (Table 3). The total conversion was increased by 43% when the temperature was raised beyond 90 °C. The highest conversion (86%) was obtained with TOF = 86 for complex **4** at 90 °C.

Table 2. Effect of different oxidants on 4-nitrophenol oxidation with complex **4**.

Entry	Oxidant	Benzoquinone	Hydroquinone	Tot. conv. (%)	TON ^a	TOF ^b (h ⁻¹)
1	TBHP	61	37	98	196	65
2	H ₂ O ₂	46	25	71	142	47
3	m-CPBA	31	19	50	100	33
4	Air oxygen	-	-	-	-	-
5	No oxidant	-	-	-	-	-
6	TBHP*	-	-	-	-	-

^aTON = moles of product/moles of catalyst.

^bTOF = moles of product/moles of catalyst × time.

Conversion was determined by GC.

*The oxidation reaction was done without complex **4**.

Reaction conditions: 90 °C, 0.71 × 10⁻³ mol 4-nitrophenol, 1.06 × 10⁻³ mol TBHP, 3.55 × 10⁻⁶ mol complex **4**, 0.01 L DMF for 3 h.

Table 3. Effect of temperature on 4-nitrophenol oxidation with complex **4**.

Entry	T (°C).	Benzoquinone	Hydroquinone	Selectivity ^a	Tot. conv. (%)	TON ^b	TOF ^c (h ⁻¹)
1	90	54	32	62	86	258	86
2	70	47	32	59	79	237	79
3	50	35	27	56	62	186	62
4	25	21	22	48	43	129	43

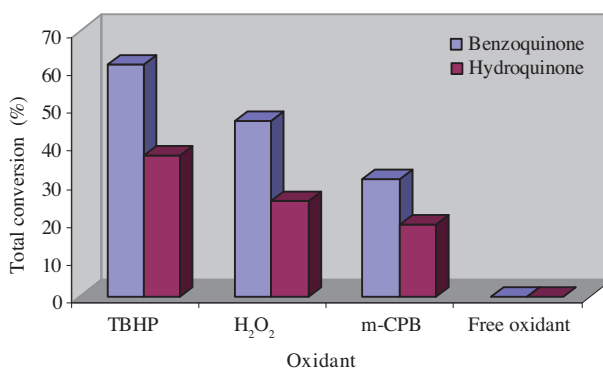
^aBenzoquinone.

^bTON = moles of product/moles of catalyst.

^cTOF = moles of product/moles of catalyst × time.

Conversion was determined by GC.

Reaction conditions: 90 °C, 1.06 × 10⁻³ mol 4-nitrophenol, 1.06 × 10⁻³ mol TBHP, 3.55 × 10⁻⁶ mol complex **4**, 0.01 L DMF for 3 h.

**Figure 5.** The oxidant effect on 4-nitrophenol oxidation.

Very few works on 4-nitrophenol oxidation with a Co(II) phthalocyanine catalyst are available. Bıyıklıođlu et al. used 4-[4-((E)-{4-(dimethylamino)phenyl}imino} methyl)phenoxy] substituted Co(II) phthalocyanine catalyst and TBHP, m-CPBA, and H₂O₂ oxidants in the oxidation of 4-nitrophenol. They observed that Co(II) phthalocyanine had high total conversion (96%) and turnover number (TON: 190). Moreover, that study demonstrated the fast degradation of the phthalocyanine ring in the complex when m-CPBA and H₂O₂ were employed as an oxidants.²² In our work, complex **4** was found to be a more active catalyst in the oxidation of 4-nitrophenol with high conversion and turnover number (98% and TON: 196).

In addition to these parameters, changing of the catalysts was studied by UV-Vis spectrophotometer during the oxidation reaction. Degradation of Co(II) phthalocyanine is a frequent situation in oxidation processes with the addition of an oxidant.^{27–29} It was seen that Co(II) phthalocyanine in chloroform has a distinctive sharp vibronic Q band due to the monomeric species in the absence of an oxygen source.¹ As the oxidation reaction proceeds, this Q band shifts to 662 nm, broadens, and disappears at the end of the reaction. The shift from 654 to 662 nm attested to the metal oxidation of M(II)-Pc to M(III)-Pc (Figure 6).³⁰ After 3 h, this oxidized intermediate decomposed. There was no further conversion of any products. As the reaction time progresses, the widening and disappearing of the Q band are seen as in Co(II) phthalocyanine.³¹ This situation is due to the result of the attack of the phthalocyanine ring by the alkyl and alkoxy radicals that are produced from TBHP. The color of the solution changed from blue to green as catalysis progressed. However, the reaction products continued to form even after the catalyst had turned yellow, suggesting that once reaction intermediates are formed, the reaction can still proceed in the presence or absence of the original form of the catalyst.

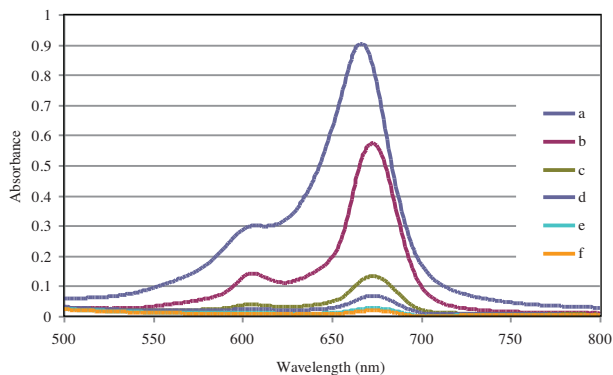


Figure 6. Time-dependent changes in the visible spectrum of oxidized complex **4** observed upon addition of TBHP (1.06×10^{-3} mol) to a reaction mixture containing 0.71×10^{-3} mol 4-nitrophenol and 3.55×10^{-6} mol complex **4** catalyst in 10 mL: (b) 36 min, (c) 72 min, (d) 108 min, (e) 144 min, (f) 180 min after addition of TBHP. All spectra for oxidized complex **4** were taken after 6-fold dilution with DMF. (a) shows the visible spectrum of (nonoxidized) complex **4**.

3. Experimental

3.1. Measurements

The general procedure for the oxidation of 4-nitrophenol and measurements were done according to the literature.²³ All materials used in this work were obtained according to the literature.^{23,32,33}

3.2. Synthesis of peripherally tetra-substituted cobalt(II) phthalocyanine (**4**)

2-(2-Benzothiazolythio)ethoxy phthalonitrile **3** (0.5 g, 1.48 mmol), CoCl_2 (95 mg, 0.74 mmol), and 2-(dimethylamino)ethanol (5 mL) were irradiated in a microwave oven at 175 °C and 350 W for 8 min. After cooling to room temperature, the reaction mixture was refluxed with ethanol to precipitate the product, which was filtered off and dried in vacuo over P_2O_5 . The obtained green solid product was purified by column chromatography on alumina with chloroform and methanol (8:2) as the solvent system. Yield: 0.280 g (53%), mp >300 °C.

(KBr tablet) ν_{max} / cm^{-1} : 3056 (Ar-H), 2955–2931 (aliph. C-H), 1664, 1609, 1522, 1483, 1343, 1277, 1237, 1096, 1070, 994, 824, 753. UV-Vis (CHCl_3), λ_{max} ($\log \epsilon$) nm: 677 (4.45), 614 (4.17), (4.60), 281 (5.10).

4. Conclusion

In this study, all spectroscopic data of Co(II) phthalocyanine showed successful synthesis. Catalytic activities of Co(II) phthalocyanine were then investigated by examining the effects of certain parameters. Co(II) phthalocyanine showed catalytic performance in 4-nitrophenol oxidation with benzoquinone conversion (61%) when using TBHP as an oxidant. In conclusion, this catalytic work is feasible and time-saving in terms of procedure and we have determined the best oxidation conditions for complex **4** with high TON and TOF values.

Acknowledgment

This study was supported by the Research Fund of Karadeniz Technical University, Project No: 9666 (Trabzon, Turkey).

References

1. Leznoff, C. C.; Lever, A. B. P. *Phthalocyanines: Properties and Applications*; VCH: New York, NY, USA, 1989.
2. Moser, F. H.; Thomas, A. *The Phthalocyanines, Vol. 1*; Boca Raton, FL, USA: CRC Press, 1983.
3. Seven, Ö.; Dindar, B.; Gültekin, B. *Turk. J. Chem.* **2009**, *33*, 123–134.
4. Sakamoto, K.; Kato, T.; Ohno-Okomura, E.; Watanabe, M.; Cook, M. J. *Dyes Pigments* **2005**, *64*, 67–75.
5. Kostka, M.; Zimcik, P.; Miletin, M.; Klemra, P.; Kopecky, K.; Musil, Z. *J. Photoch. Photobio. A* **2006**, *178*, 16–25.
6. Bıyıkhoğlu, Z.; Durmuş, M.; Kantekin, H. *J. Photochem. Photobio. A* **2011**, *222*, 87–96.
7. Acar, I.; Cakır, V.; Bıyıkhoğlu, Z.; Kantekin, H. *Synthetic Met.* **2012**, *162*, 1156–1163.
8. McKeown, N. B. *J. Mater. Chem.* **2000**, *20*, 10588–10597.
9. Agboola, B. O. PhD, Division of Chemistry, Rhodes University, Grahamstown, South Africa, 2007.
10. Lokesh, K. S.; Uma, N.; Ahcar, B. N. *Polyhedron* **2009**, *28*, 1022–1028.
11. Bıyıkhoğlu, Z.; Kantekin, H. *Transit. Metal Chem.* **2007**, *32*, 851–856.
12. Bıyıkhoğlu, Z.; Guner, E. T.; Topcu, S.; Kantekin, H. *Polyhedron* **2008**, *27*, 1707–1713.
13. Kantekin, H.; Bıyıkhoğlu, Z.; Celenk, E. *Inorg. Chem. Commun.* **2008**, *11*, 633–635.
14. Bekircan, O.; Bıyıkhoğlu, Z.; Acar, İ.; Bektaş, H.; Kantekin, H. *J. Organomet. Chem.* **2008**, *693*, 3425–3429.
15. Kantekin, H.; Dilber, G.; Bıyıkhoğlu, Z. *J. Organomet. Chem.* **2008**, *693*, 1038–1042.
16. Bıyıkhoğlu, Z.; Kantekin, H. *Dyes Pigments*, **2009**, *80*, 17–21.
17. Martin-Hernandez, M.; Carrera, J.; Suarez-Ojeda, M. E.; Besson, M.; Descorme, C. *Appl. Catal. B-Environ.* **2012**, *123*, 141–150.
18. Rao, T. V.; Rao, K. N.; Jain, S. L.; Sain, B. *Synthetic Commun.* **2012**, *32*, 1151–1157.
19. Cimen, Y.; Türk, H. *Appl. Catal. A-Gen.* **2008**, *340*, 52–58.
20. Yılmaz, F.; Özer, M.; Kani, I.; Bekaroglu O. *Catal. Lett.* **2009**, *130*, 642–647.
21. Saka, E. T.; Bıyıkhoğlu, Z.; Kantekin, H.; Kani, I. *Appl. Organometal. Chem.* **2013**, *27*, 59–67.
22. Acar, I.; Bayrak, R.; Saka, E. T.; Bıyıkhoğlu, Z.; Kantekin, H. *Polyhedron* **2013**, *50*, 345–353.
23. Saka, E. T.; Ersoy, N.; Göl, C.; Durmuş, M.; Bıyıkhoğlu, Z.; Kantekin, H. *J. Organomet. Chem.* **2013**, *723*, 1–9.

24. Durmus, M.; Erdoğan, A.; Oğunsipe, A.; Nyokong, T. *Dyes Pigments*, **2009**, *82*, 244–250.
25. Gürol, I.; Ahsen, V.; Bekaroğlu, O. *J. Chem. Soc. Dalton Trans.* **1994**, *4*, 497–500.
26. Saka, E. T.; Büyüklüoğlu, Z. *J. Organomet. Chem.* **2013**, *756–746*, 50–56.
27. Büyüklüoğlu, Z.; Kantekin, H.; Acar, İ. *Inorg. Chem. Commun.* **2008**, *11*, 1448–1451.
28. Akinbulu, I. A.; Nyokong, T. *Polyhedron* **2010**, *29*, 1257–1270.
29. Alemdar, A.; Özkaya, A. R.; Bulut, M. *Polyhedron* **2009**, *28*, 3788–3396.
30. Zhao, F.; Zhang, J.; Abe, T.; Wöhrle, D.; Kaneko, M. *J. Mol. Catal. A Chem.* **1999**, *145*, 245–256.
31. Sehlotho, N.; Nyokong, T. *J. Mol. Catal. A Chem.* **2004**, *219*, 201–207.
32. Perin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Oxford, UK, 1989.
33. Young, J. G.; Onyebugu, W. J. *J. Org. Chem.* **1990**, *55*, 2155–2159.