

Peripherally 1,2-dinaphthyl ethanediol substituted phthalocyanine complexes: synthesis, characterization, aggregation, and application in benzyl alcohol oxidation at room temperature

Halil Zeki GÖK^{1,*} , Mustafa Kemal YILMAZ² 

¹Department of Biomedical Engineering, Bucak Faculty of Technology, Burdur Mehmet Akif Ersoy University, Bucak, Burdur, Turkey

²Department of Chemistry, Faculty of Arts and Sciences, Mersin University, Mersin, Turkey

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Abstract: In this study, the synthesis of a novel 1,2-dinaphthyl ethanediol substituted phthalonitrile (**2**) together with tetra-substituted zinc(II) phthalocyanine (Pc) (**3**) and cobalt(II) Pc (**4**) bearing 1,2-dinaphthyl ethanediol at peripheral positions was described. The aggregation behaviors of metallophthalocyanines **3** and **4** in solution were investigated by carrying out Beer–Lambert experiments at different concentrations. In addition, the catalytic activity of new cobalt(II) Pc **4** was investigated for benzyl alcohol oxidation. Benzyl alcohol was converted to benzaldehyde using cobalt(II) Pc **4** as a catalyst by a conversion of 99% with selectivity of 100% at room temperature in 1 h. Several spectroscopic techniques such as FT-IR, UV-Vis, ¹H and ¹³C NMR, and MALDI-TOF MS were used for the characterization of the newly synthesized compounds.

Key words: Metallophthalocyanine, catalysis, C₂-symmetric, benzyl alcohol oxidation, aggregation

1. Introduction

Phthalocyanines (Pcs) are one of the most popular chemical materials studied in chemistry and have been applied widely in advanced technologies due to the unique properties of Pcs such as chemical and thermal stability, electron transfer ability, UV-Vis light absorption, and high molar absorption coefficients [1]. Pcs can be synthesized either in polymeric form or monomeric form by using bis-phthalonitrile or phthalonitrile derivatives, respectively, in the presence or absence of metal ions [2–4]. Monomeric or polymeric Pcs have been widely used in many research areas, such as catalysts for many chemical reactions [5], precious metal recovery [6], and conversion of solar energy to electric power [7].

Catalysis is another attractive area for both scientific researchers and industrial applications, and one of the most important applications for Pc metal complexes as well [8]. For instance, production of aldehydes from their corresponding alcohols involves catalytic oxidation of alcohols in the presence of Pcs with redox active metal centers such as cobalt and iron [9]. The solubility of a Pc compound in solvent used for oxidation reaction determines its usability as a catalyst in catalytic oxidation. The solubility of Pc compounds can be improved by incorporation of various substituents to either the nonperipheral or peripheral positions of the Pc skeleton. This appropriation is one of the most used synthetic strategies to obtain highly soluble and nonaggregated Pc metal complexes [10–18].

*Correspondence: halilzekigok@gmail.com

The aim of the present work was to synthesize a phthalonitrile precursor derived from sterically hindered phenols. The 1,2-di(naphthalen-1-yl)ethane-1,2-diol unit of Pc, an analog of 1,2-diphenylethane-1,2-diol (hydrobenzoin), was chosen because of being sterically hindered and straightforwardly accessible. It was anticipated that this would result in Pcs containing bulky substituents placed at sites where they can interfere best with cofacial self-association and therefore enhance solubility. A reduction in the tendency of Pcs to aggregate in solution could be advantageous in a number of applications, including catalytic applications [15]. Catalytic activity of cobalt(II) Pc **4** in benzyl alcohol oxidation was also examined, with the aim of improving the benzaldehyde selectivity and increasing the range of products, and comparing their catalytic activity in the presence of different oxidants at different temperatures. Moreover, other factors affecting benzyl alcohol oxidation, such as solvent type, substrate to catalyst ratio, and oxidant amount, were also discussed in this work.

2. Experimental

2.1. Materials and methods

1,2-Dinaphthyl ethanediol and 4-nitrophthalonitrile were prepared by following the procedures given in the literature, respectively [19,20]. The reagents and solvents used during this study were purchased from commercial suppliers. Drying and purification of all solvents was performed according to the procedures given by Perrin and Armarego [21]. The purification of compounds was carried out on silica gel (Merck, Kieselgel 60, 400–630 mesh).

A PerkinElmer Spectrum 65 spectrometer, Varian Mercury 400 MHz spectrometer, Micromass Quatro LC/ULTIMA LC-MS/MS and Bruker Daltonics MALDI-TOF spectrometer, a PG-T80+ spectrophotometer, and a LECO Elemental Analyzer were used to record the spectral data of the newly synthesized compounds. The KBr pellet technique was used for the FT-IR measurements. NMR spectra were collected using CDCl₃ and THF-d₈ (99.9%). UV-Vis measurements were performed at room temperature in 1-cm path-length cuvettes. The melting points of the compounds were determined on a melting point apparatus and are reported uncorrected. The gas chromatography analyses were monitored on a Shimadzu GC-2010 Plus gas chromatograph.

2.2. Synthesis

2.2.1. 4-(2-Hydroxy-1,2-dinaphthylethoxy)phthalonitrile (**2**)

4-Nitrophthalonitrile (0.28 g; 1.6 mmol) was added to stirring DMSO (3.0 mL) containing 1,2-dinaphthyl ethanediol (**1**) (0.5 g, 1.6 mmol) under nitrogen atmosphere at room temperature and stirred for a further 15 min. Then oven-dried finely ground K₂CO₃ (0.22 g; 1.6 mmol) was added to the stirring reaction mixture at room temperature and the resulting mixture was kept stirring for a further 3 h. The reaction medium was monitored by thin-layer chromatography. At the end of 3 h, the reaction mixture was transferred to a beaker containing 1 portion of water and 3 portions of ice. The precipitate formed in the beaker was separated by vacuum filtration. This precipitate was extracted with dichloromethane and water. The organic phases were combined and then dried over anhydrous Na₂SO₄. By filtration, sodium sulfate was separated from the organic phase. The solvent was evaporated under reduced pressure in order to obtain the crude product. The purification of the crude product was performed on silica gel by flash column chromatography. Dichloromethane was used as the mobile phase and the target product was obtained as a white solid. Yield: 0.59 g, (83%); mp: 115–116 °C. Anal. Calc. C₃₀H₂₀N₂O₂: C 81.80%, H 4.58%, N, 6.36%. Found: C 81.93%, H 4.66%, N 6.37%. FT-IR (KBr disk) v_{max}/cm^{-1} : 3473, 3416 (OH), 3049, 2931, 2230 (C≡N), 1712, 1596, 1561, 1490, 1294, 1249,

1092, 1041, 778, 735; ^1H NMR (400 MHz, CDCl_3 , ppm) δ : 7.89 (d, $J = 8.4$ Hz, H), 7.79 (d, $J = 8.4$ Hz, H), 7.75–7.67 (m, 4H), 7.62 (d, $J = 7.0$ Hz, H), 7.50–7.46 (m, 2H), 7.42–7.26 (m, 2H), 7.07 (dd, $J = 8.9$ Hz, $J = 2.2$ Hz, H), 6.22 (d, $J = 6.4$ Hz, H), 6.01 (d, $J = 6.4$ Hz, H), 3.12 (br, s, OH); ^{13}C NMR (100 MHz, CDCl_3 , ppm) δ : 160.7, 135.2, 134.1, 133.7, 133.6, 130.8, 130.7, 130.3, 129.8, 129.2, 128.7, 126.6, 125.9, 125.6, 125.4, 125.0, 124.9, 122.8, 121.2, 120.1, 117.3, 115.4, 115.0, 82.7, 74.5; MS (ESI) MS Calc.: 475.1; Found: 475.1 $[\text{M} + \text{Cl}]^-$.

2.2.2. 2(3),9(10),16(17),23(24)-Tetrakis-{(2-hydroxy-1,2-dinaphthylethoxy)} phthalocyaninato zinc(II) (3)

A Schlenk tube containing 4-(2-hydroxy-1,2-dinaphthylethoxy)phthalonitrile (**2**) (0.22 g; 0.5 mmol), anhydrous $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ (0.046 g; 0.25 mmol), a catalytic amount of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), and 2.5 mL of n-pentanol as reaction solvent was heated to 140 °C for 24 h under inert atmosphere to give the desired zinc(II) Pc compound (**3**). At the end of 24 h, the reaction mixture was cooled to room temperature. The reaction mixture was transferred to an evaporating flask and the solvent of the reaction mixture was removed under reduced pressure. The remaining green crude product was purified by silica gel column chromatography with methanol followed by a chloroform-methanol (98:2) solvent system as eluting solvents. Further purification of compound **3** was performed by preparative thin-layer silica gel chromatography with a methanol-chloroform (2:98) solvent system. Yield was 0.026 g (12%). mp: >300 °C. IR (KBr disk) $\nu_{\text{max}}/\text{cm}^{-1}$: 3557, 3381 (OH), 3030, 2922, 1611, 1484, 1395, 1335, 1223, 1090, 1050, 1008, 836, 763, 738, 696. ^1H NMR (400 MHz, d_8 -THF, ppm) δ : 7.80–7.31 (m, 68H), 6.00 (m, 4H), 5.46 (m, 4H); UV-Vis (DMF): λ_{max} , nm (log ϵ): 356 (5.13), 616 (4.69), 684 (5.43); MALDI-TOF (ESI⁺) (m/z): Calc.: 1824.5; Found: 1824.5 $[\text{M}]^+$.

2.2.3. 2(3),9(10),16(17),23(24)-Tetrakis-{(2-hydroxy-1,2-dinaphthylethoxy)} phthalocyaninato cobalt(II) (4)

Cobalt(II) Pc (**4**) was synthesized by following the procedure for **3**. For this purpose, CoCl_2 was used instead of $\text{Zn}(\text{CH}_3\text{CO}_2)_2$. The amount of CoCl_2 was 0.035 g. Purification: Flash column chromatography on silica gel with a solvent mixture of diethyl ether-hexane (8:2), then methanol-chloroform (1:99). Yield was 0.030 g (14%); mp: >300 °C. IR (KBr disk) $\nu_{\text{max}}/\text{cm}^{-1}$: 3553, 3415 (OH), 3059, 3030, 2901, 1610, 1520, 1482, 1407, 1342, 1276, 1230, 1098, 1066, 1006, 835, 755, 696; UV-Vis (DMF): λ_{max} , nm (log ϵ): 326 (5.25), 610 (4.82), 672 (5.38); MS (MALDI-TOF) (m/z): Calc.: 1819.5; Found: 1819.3 $[\text{M}]^+$.

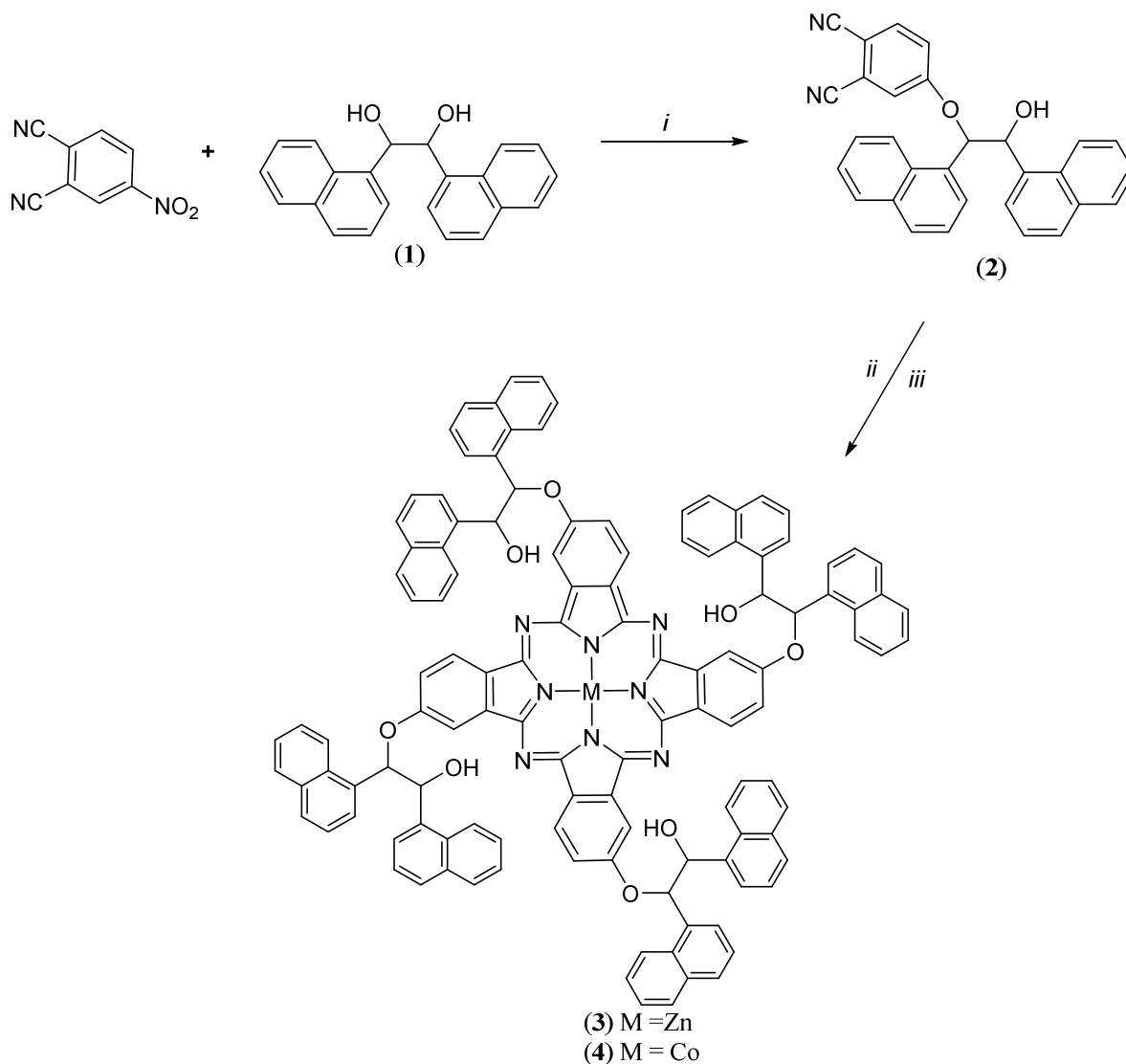
2.3. Procedure for the application of cobalt(II) Pc (4) in benzyl alcohol oxidation

Cobalt(II) Pc (**4**) as a catalyst, benzyl alcohol, and solvent were put together in a standard Schlenk tube. To remove oxygen, nitrogen gas was bubbled into the Schlenk tube. The oxidant was then added to the Schlenk tube and the resulting reaction mixture was stirred for the desired time. Monitoring of the reaction and calculation of the conversion amount of the benzyl alcohol to benzaldehyde was performed by comparison of 1,4-benzoquinone, benzaldehyde, and benzoic acid standards on a Shimadzu GC-2010 Plus gas chromatograph equipped with a 30 m \times 0.25 mm \times 0.25 μm capillary column (Rxi - 5ms, 95% diphenyl, 95% dimethyl polysiloxane).

3. Results and discussion

3.1. Synthesis and characterization

The synthetic pathway for the synthesis of phthalonitrile **2** and its Pc derivatives **3** and **4** is given in the Scheme. Obtaining phthalonitrile derivative **2** was the first step of the synthetic pathway. The reaction of 1,2-dinaphthyl ethanediol (**1**) with 4-nitrophthalonitrile in a flask containing K_2CO_3 as the base and DMSO as the solvent of the reaction afforded substituted phthalonitrile derivative **2**, namely 4-(2-hydroxy-1,2-dinaphthylethoxy)phthalonitrile, with a yield of 83%.



Scheme. Syntheses of phthalonitrile derivative **2** and metallo-Pcs **3** and **4**. Reagents and conditions: (i) DMSO, K_2CO_3 , rt; (ii) $Zn(CH_3COO)_2$, n-pentanol, DBU, 140 °C; (iii) $CoCl_2$, n-pentanol, DBU, 140 °C.

The characterization of new phthalonitrile compound **2** was done first by IR spectrum. The IR spectrum of **2** showed the vibration bands for $C\equiv N$ at 2230 cm^{-1} and OH at 3473 and 3416 cm^{-1} , respectively, which is in agreement with the structure of **2**. The disappearance of strong stretching vibration bands of $-NO_2$ in the

IR spectrum of **2** confirmed the formation of **2** as well (see Supplementary Figure 1). The ^1H NMR spectrum acquired in CDCl_3 (see Supplementary Figure 2) gave us the opportunity to characterize the structure of **2**. The broad singlet that appeared at $\delta = 3.12$ ppm was attributed to the $-\text{OH}$ group of **2**. The aliphatic $-\text{CH}$ protons of **2** were expected to give two separate doublets with the same coupling constant. The observation of peaks at 6.22 and 6.01 ppm with a coupling constant of $J = 6.4$ Hz was in agreement with our expectations. The other sets of protons corresponding to the naphthyl moieties appeared together between 7.90 and 7.07 ppm. Structural characterization of the same compound was additionally performed by ^{13}C (APT) NMR spectrum. Carbon resonances of the nitrile carbons that substituted the benzene moiety appeared as two peaks at $\delta = 115.4$ and 115.0 ppm due to the C_1 symmetry of phthalonitrile derivative **2** in the ^{13}C (APT) NMR spectrum (see Supplementary Figure 3). The carbon resonances observed at $\delta = 82.7$ and 74.5 ppm were attributed to CH carbons containing a hydroxyl group and oxygen atom, respectively, confirming the proposed structure. In the ES/MS spectrum of **2**, the expected molecular ion peak appeared at $m/z = 475.1$ $[\text{M} + \text{Cl}]^+$ (see Supplementary Figure 4), which is in agreement with the proposed formula.

In a Schlenk tube containing 2.5 mL of n-pentanol and a catalytic amount of DBU, the cyclotetramerization reaction of 4-(2-hydroxy-1,2-dinaphtylethoxy)phthalonitrile **2** with metal salts $\text{Zn}(\text{CH}_3\text{CO}_2)_2$ and CoCl_2

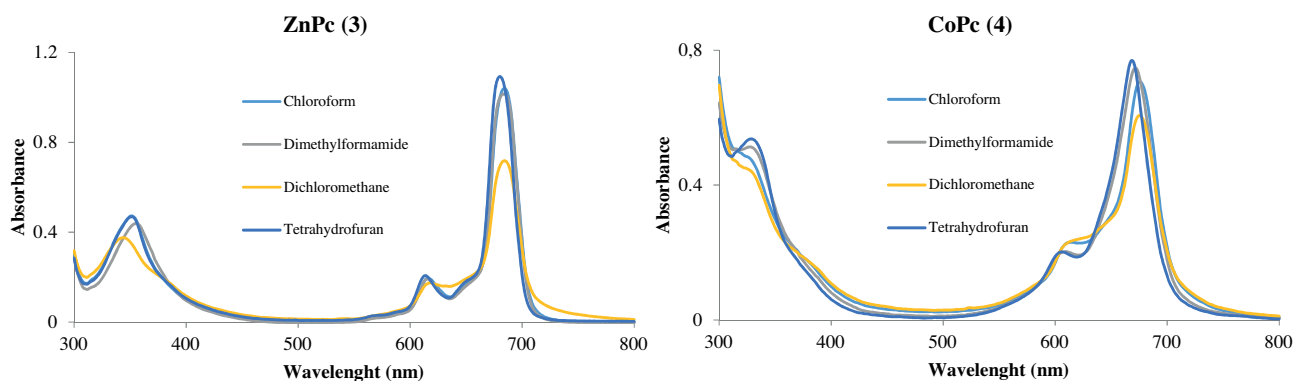


Figure 1. UV-Vis spectra of zinc(II) Pc (**3**) and cobalt(II) Pc (**4**) in different solvents.

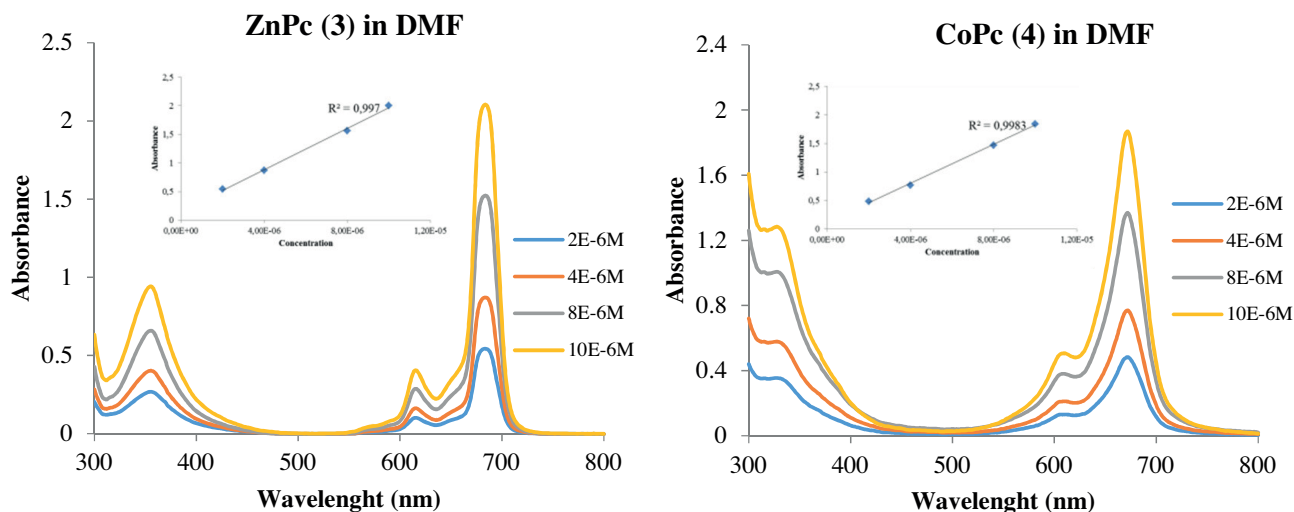


Figure 2. Aggregation properties of Pc complexes **3** and **4** at different concentrations in DMF.

afforded peripherally substituted metallo-Pcs **3** and **4**, respectively. Flash silica gel column chromatography and/or preparative thin-layer chromatography using silica gel were applied to the crude Pc products in order to remove impurities. Pc complexes were characterized by a combination of FT-IR, UV-Vis, ^1H NMR (for compound **3**), and MALDI-TOF techniques. In the IR spectra of **3** and **4** (see Supplementary Figure 5 for **3** and Supplementary Figure 8 for **4**), the vibration at around 2230 cm^{-1} related to the $\text{C}\equiv\text{N}$ group was not observed after the cyclotramerization of phthalonitrile derivative **2**, which confirms the formation of the desired Pc compounds. The IR spectra of **3** and **4** are very similar, but small shifts in wavenumbers were observed. The $-\text{OH}$ group of metallo-Pcs **3** and **4** was characterized by a vibration band at 3381 cm^{-1} for **3** and 3415 cm^{-1} in their IR spectra. The ^1H NMR spectrum of **3** showed expected protons between at $\delta = 7.80\text{--}5.46$ ppm. The interpretation of the ^1H NMR spectrum of **3** was a challenge due to the overlapped peaks of Pc and the attached naphthyl moiety. Thus, multiplet analysis was used for the integration of the peaks in the ^1H NMR spectrum of **3** (see Supplementary Figure 6). In the case of the cobalt(II) Pc (**4**), the ^1H NMR spectrum of **4** could not be collected since the cobalt(II) ion is paramagnetic [22]. The mass measurements of Pcs **3** and **4** were performed by using MALDI-TOF techniques. The mass spectra of **3** and **4** showed expected molecular ion peaks at $m/z = 1824.5\text{ [M]}^+$ for **3** and $m/z = 1819.3\text{ [M]}^+$ for **4**, which agree with the proposed structures (see Supplementary Figure 7 for **3** and Supplementary Figure 9 for **4**).

The solubility of metallo-Pcs **3** and **4** in common organic solvents such as CH_2Cl_2 , CHCl_3 , DMF, and THF is good enough to investigate their aggregation properties in those solvents. Hence, the electronic spectra of Pc complexes **3** and **4** were recorded in those solvents at a concentration of $4 \times 10^{-6}\text{ M}$ in order to compare the effect of solvent on the position and absorption of Q bands of synthesized metallo-Pcs **3** and **4**. The recorded spectra can be seen in Figure 1.

The appearance of Q bands as unsplit and single in the recorded UV-Vis spectra of **3** and **4** confirmed the D_{4h} symmetry of **3** and **4**, which is expected for Pcs containing a metal in their center [23]. The absorptions related to Q bands of **3** and **4** were observed at 684 and 672 nm with shoulders at 616 and 610 nm, respectively, while the B band was at 356 and 326 nm in the recorded UV-Vis spectra in DMF, respectively. It is well known in the literature that the increasing size of the central metal [24] and number of electrons in the d-orbitals [25] cause a redshift in the Q band. A smaller HOMO-LUMO gap in zinc(II) Pcs than cobalt(II) Pcs causes the larger redshift for the Q band in zinc(II) Pc **3** than that of **4**. If the UV-Vis spectra of **3** in CHCl_2 and **4** in CHCl_3 and CHCl_2 are carefully reviewed, it can be seen that the shape of the main Q bands broadened, and the intensity of the main Q bands decreased in the recorded UV-Vis spectra of **3** and **4**. These kinds of changes for the main Q band are referred to as aggregation, the reason for which is the presence of dimers or higher order complexes of Pcs [26–28].

To investigate the aggregation behavior of synthesized Pc complexes **3** and **4** in solution, Beer-Lambert experiments were performed with Pc complexes **3** and **4** at concentrations in the range of 10×10^{-6} to $2 \times 10^{-6}\text{ mol dm}^{-3}$ by scanning the spectral window between 300 and 800 nm on a UV-Vis spectrophotometer. From the results of the experiment, it is clearly seen from Figure 2 that the absorption intensity of the main Q band of **3** and **4** increased by increasing the concentration of the solution containing Pc compounds. These results confirmed that there were no new bands blue-shifted due to the presence of aggregated species for Pc compounds **3** and **4** [29].

3.2. Application of cobalt(II) Pc (4) in benzyl alcohol oxidation

In a typical run, the cobalt(II) Pc (4) as catalyst, benzyl alcohol, and solvent were placed in a Schlenk tube. To remove the oxygen, nitrogen gas was bubbled into the Schlenk tube. The oxidant was then added to the reaction mixture and the resulting reaction mixture was stirred for 1 h at the desired temperature. Monitoring of the reaction and calculation of the conversion amount of the benzyl alcohol to benzaldehyde was performed by comparison of standards on a Shimadzu GC-2010 Plus gas chromatograph.

Table 1. Solvent, oxidant, and temperature effect on the oxidation of benzyl alcohol with complex 4^{a*}.

Entry	Solvent	Oxidant	Temp. (°C)	Total conversion (%) ^b	Benzaldehyde (%)	Benzoic acid (%)	1,4-Benzoquinone (%)	Selectivity (%)	TON ^c
1	DMF	TBHP	80	21	18	-	-	86	42
2	DMF	m-CPBA	80	89	37	-	-	41	178
3	ACN	TBHP	80	100	86	-	11	86	200
4	ACN	m-CPBA	80	100	83	17	-	83	200
5	ACN	H ₂ O ₂	80	100	8	92	-	8	200
6	ACN	TBHP	60	100	95	-	4	95	200
7	ACN	TBHP	40	100	95	-	3	95	200
8	ACN	TBHP	25	99	99	-	-	100	198

^aReaction conditions: benzyl alcohol (2.90×10^{-4} mol), oxidant (2.90×10^{-4} mol), catalyst (1.45×10^{-6} mol), solvent 5.0 mL. Reactions were conducted for 1 h in all cases. ^bConversions were determined by GC based on benzyl alcohol. ^cTurnover number (TON: moles of substrate converted per mole of metal in the catalyst). *GC chromatograms related to Table 1 can be found in the Supplementary file.

To evaluate the catalytic activity of complex 4, the effects of solvent, oxidant, reaction temperature, oxidant to catalyst ratio (O/C), and substrate to catalyst ratio (S/C) were investigated on the selective oxidation of benzyl alcohol to benzaldehyde. For initial tests, the molar ratio of catalyst, oxidant, and benzyl alcohol was chosen as 1/200/200 and reaction time was kept constant for 1 h at 80 °C. The influence of the solvent, oxidant, and reaction temperature was first determined and the results are illustrated in Table 1. After screening the effect of the solvent, we found 89% conversion but poor selectivity (41%) for 1 h of the reaction in dimethylformamide (DMF) when m-chloroperoxybenzoic acid (m-CPBA) was used as an oxidant (entry 2). With the same oxidant, good benzaldehyde selectivity (83%) was obtained in acetonitrile (ACN) with a full conversion when comparing the result obtained from DMF as solvent (entries 2 and 4). When *tert*-butylhydroperoxide (TBHP) was used as an oxidant, total conversion was very poor in DMF (entry 1). On the other hand, complete conversion and better selectivity (86%) were obtained in ACN when TBHP was used as oxidant, but the formation of benzoquinone was also observed (entry 3). In all cases, the use of ACN as a solvent gave better conversion and selectivity compared to DMF as it allows for the higher solubility of the substrate and catalyst used depending on the high polarity. Otherwise, in the presence of hydrogen peroxide (H₂O₂) as an oxidant in ACN, oxidation of benzyl alcohol gave benzaldehyde as the minor product while benzoic acid was the major (92%, entry 5). It is noted that the color of the reaction went from the blue of the catalyst to colorless suddenly following the addition of H₂O₂; therefore, the catalytic process was not studied effectively in the presence of this oxidant. This situation

is probably due to the degradation of the CoPc catalyst (**4**) by the oxidant at the beginning of the reaction. Besides that, a control experiment was carried out in the absence of oxidant, and benzyl alcohol was not oxidized to related corresponding products. After determining the best solvent and oxidant, we decided to investigate the role of the reaction temperature on the oxidation of benzyl alcohol. Therefore, three experiments were done at different temperatures in the range of 25–80 °C (entries 6–8). Normally, the reaction temperature has a strong influence on the oxidation of benzyl alcohol and the reaction rate is also reduced due to decrease in reaction temperature [30]. Surprisingly, decreasing temperature did not affect the total conversion of benzyl alcohol, and due to the decrease in temperature benzaldehyde selectivity was gradually increased and finally reached 100% (compare entries 3 and 6–8). Thus, room temperature was chosen to be the optimum temperature to achieve the highest benzaldehyde selectivity for our catalyst. Under the framework of this study, the successful application of CoPc as an oxidation catalyst for the selective oxidation of benzyl alcohol to benzaldehyde at room temperature with only 1 h of the reaction was achieved.

To extend the catalytic tests of catalyst **4**, the effect of the oxidant amount on the selective oxidation of benzyl alcohol was also studied by varying the oxidant to catalyst ratio from 100/1 to 900/1 while other parameters were kept constant (Table 2). We found that increasing the oxidant to catalyst ratio from 100/1 to 200/1 led to the selective oxidation of benzyl alcohol to benzaldehyde with total conversion of 99% and 100% selectivity (TON = 198), but further increasing the oxidant ratio led to a decrease in the catalytic activity (up to 27%) (compare entries 1–7). These results support that in the presence of a higher amount of oxidant, the active sites of cobalt ion are blocked and this effect leads to the generation of inactive intermediate species during the catalytic reaction [31–36].

Table 2. The effect of oxidant amount on benzyl alcohol oxidation with complex **4**^{a*}.

Entry	Oxidant/ catalyst	Total conversion (%) ^b	Benzaldehyde (%)	Benzoic acid (%)	1,4-Benzoquinone (%)	Selectivity (%)	TON ^c
1	100/1	82	68	10	-	83	164
2	200/1	99	99	-	-	100	198
3	300/1	58	46	11	1	79	116
4	400/1	45	41	3	1	91	90
5	500/1	34	34	-	-	100	68
6	700/1	29	29	-	-	100	58
7	900/1	27	26	-	-	96	54

^aReaction conditions: benzyl alcohol (2.90×10^{-4} mol), oxidant (TBHP), catalyst (1.45×10^{-6} mol), acetonitrile (5.0 mL), 25 °C, time: 1 h. ^bConversions were determined by GC based on benzyl alcohol. ^cTurnover number (TON: moles of substrate converted per mole of metal in the catalyst). *GC chromatograms related to Table 2 can be found in the Supplementary file.

For the amounts of catalyst used influencing the results of the selective oxidation of benzyl alcohol, the effect of substrate to catalyst ratio was also investigated by varying from 200/1 to 1500/1 under optimized conditions (Table 3). First of all, a blank experiment was carried out under the optimized conditions without catalyst for comparison, and we did not observe any benzaldehyde formation in the reaction mixture (entry 1). The results show that benzyl alcohol was converted to benzaldehyde with full conversion and 96% selectivity, achieving a TON of 400, even when the substrate to catalyst ratio was 400/1 (entry 3). On further increasing

the substrate to catalyst ratio, the catalytic activity decreased for the oxidation of benzyl alcohol, as expected (entry 4–7). This study showed that a 400/1 ratio of substrate to catalyst was needed for the oxidation of benzyl alcohol to get complete conversion and high selectivity.

Table 3. The effect of substrate to catalyst ratio on benzyl alcohol oxidation with complex **4**^{a*}.

Entry	Substrate/ catalyst	Total conversion (%) ^b	Benzaldehyde (%)	Benzoic acid (%)	1,4-Benzoquinone (%)	Selectivity (%)	TON ^c
1	200/1 ^d	-	-	-	-	-	-
2	200/1	99	99	-	-	100	198
3	400/1	100	96	-	2	96	400
4	600/1	53	52	-	1	98	318
5	800/1	32	31	-	-	96	256
6	1000/1	17	16	-	-	94	170
7	1500/1	9	9	-	-	99	135

^aReaction conditions: benzyl alcohol, TBHP (2.90×10^{-4} mol), catalyst (1.45×10^{-6} mol), acetonitrile (5.0 mL), 25 °C, time: 1 h. ^bConversions were determined by GC based on benzyl alcohol. ^cTurnover number (TON: moles of substrate converted per mole of metal in the catalyst). ^dWithout catalyst. *GC chromatograms related to Table 3 can be found in the Supplementary file.

Table 4 was summarized by catalytic activity studies of some previously reported CoPc catalysts substituted with peripheral units for the oxidation of cyclohexene or benzyl alcohol. Additionally, Çakır et al. investigated the catalytic performance of (2-{2-[3-(diethylamino)phenoxy]ethoxy}ethoxy) substituted Fe(II) and Co(II) phthalocyanines on selective oxidation of benzyl alcohol in ACN at 70 °C. Product conversion of 94% and 77% benzaldehyde selectivity were obtained using FePc as catalyst under their optimized conditions in

Table 4. Catalytic activities towards the oxidation of benzyl alcohol and cyclohexene of some previously reported CoPc catalysts.

Catalyst	Substrate	React. time (h)	React. temp. (°C)	Oxidant	Conversion (%)	Selectivity (%)	Ref.
Co(tbpch ₂)	cyclohexene	24	25	O ₂	30	nr	[39]
CoPc ^b	cyclohexene	3	90	TBHP	92	60 ^f	[31]
CoPc ^c					98	68 ^f	
CoPc ^d	Benzyl alcohol	3	50	TBHP	97	86 ^g	[9]
CoPc ^e	Benzyl alcohol	1	25	TBHP	99	100 ^g	-

^a tbpCH₂: tetra-*tert*-butylphthalocyanine.

^b Pc: tetrakis-[2-(1,4-dioxo-8-azaspiro[4.5]dec-8-yl)ethoxy]phthalocyanine.

^c Pc: tetrakis-(3,3-diphenylpropoxy)phthalocyanine.

^d Pc: {2-[2-(2,3,5,6-tetrafluorophenoxy)ethoxy]ethoxy}phthalocyanine.

^e Pc: {1,2-di(naphthalen-1-yl)ethane-1,2-diol}phthalocyanine.

^f for 2-cyclohexene-1-ol.

^g for benzaldehyde.

nr: not reported.

3 h of reaction [30]. Özer et al. reported the catalytic behavior of novel Co(II) and Pd(II)-perfluoroalkyl Pc complexes for benzyl alcohol oxidation in perfluoromethylcyclohexane (PFMCH) or using different organic-fluorous biphasic systems such as n-hexane-PFMCH, acetone-PFMCH, and toluene-PFMCH. They tested the selective oxidation of benzyl alcohol with TBHP, H₂O₂, m-CPBA, aerobic O₂, and oxone as oxidants and they found that TBHP was the best one. They also tested the effect of reaction temperature using 1.24×10^{-2} mol TBHP with substrate/catalyst ratio of 520 for CoPc in an n-hexane-PFMCH system. After 24 h, they obtained 92.7% aldehyde selectivity with only 39.4% total conversion between 30 and 70 °C [37]. Kamiloğlu et al. investigated catalytic activity of tetra-{2-(2,3,5,6-tetrafluorophenoxy)ethoxy} substituted Co(II) and Fe(II)Pc complexes for the oxidation of benzyl alcohol, changing different parameters to determine the optimal conditions. They observed that for this catalyst system, TBHP was the best oxidant and the maximum conversion was obtained (95%) with product distribution of 74% benzaldehyde, 5% benzoquinone, and 16% benzoic acid at 50 °C for the Co(II)Pc complex in 3 h [38]. Based on the performance of our 1,2-dinaphthyl ethanediol substituted CoPc catalyst towards benzyl alcohol oxidation, it can be said that it is a more successful catalyst than some other catalysts mentioned above. The best reported results were obtained in terms of reaction temperature (25 °C), reaction time (1 h), and benzaldehyde selectivity (100%) in literature for oxidation of benzyl alcohol with TBHP as an oxidant. On the other hand, the presence of a bulky 1,2-di(naphthalen-1-yl)ethane-1,2-diol group on the Pc unit seems to enhance the product selectivity and catalyst activity, possibly due to the increased steric crowding in CoPc complex **4**. In addition to the overall rating, improved conversions and activities were achieved while milder reaction conditions were employed compared to the previously reported complexes.

3.3. Conclusions

This study describes the synthesis of a novel phthalonitrile, 4-(2-hydroxy-1,2-dinaphthylethoxy)phthalonitrile, and its zinc(II) and cobalt(II) Pc derivatives. All synthesized compounds were characterized by using spectroscopic techniques such as FT-IR, UV-Vis, ¹H and ¹³C NMR, and mass analysis. Pc complexes **3** and **4** were examined to understand the aggregation behavior in different organic solvents by using Beer-Lambert experiments. The experiments showed that the zinc(II) Pc **3** and cobalt(II) Pc **4** did not exhibit any aggregation behavior in DMF and THF solvent at concentrations of 10×10^{-6} and 2×10^{-6} mol dm⁻³. In addition to that, the catalytic performance of cobalt(II) Pc **4** was investigated in benzyl alcohol oxidation. Reaction conditions such as oxidant and solvent type, reaction temperature, substrate to catalyst ratio, and oxidant to catalyst ratio were investigated in an effort to establish optimum catalytic conditions. The most exciting observation is that benzaldehyde was found as a major product in all of the catalytic tests. Also, the optimization studies showed that benzyl alcohol gave benzaldehyde with full selectivity in only 1 h of reaction at room temperature using an oxidant/substrate/catalyst ratio of 200/200/1 in the presence of 4-(2-hydroxy-1,2-dinaphthylethoxy)phthalonitrile substituted cobalt(II) Pc (**4**).

Acknowledgments

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SUPPLEMENTARY INFORMATION

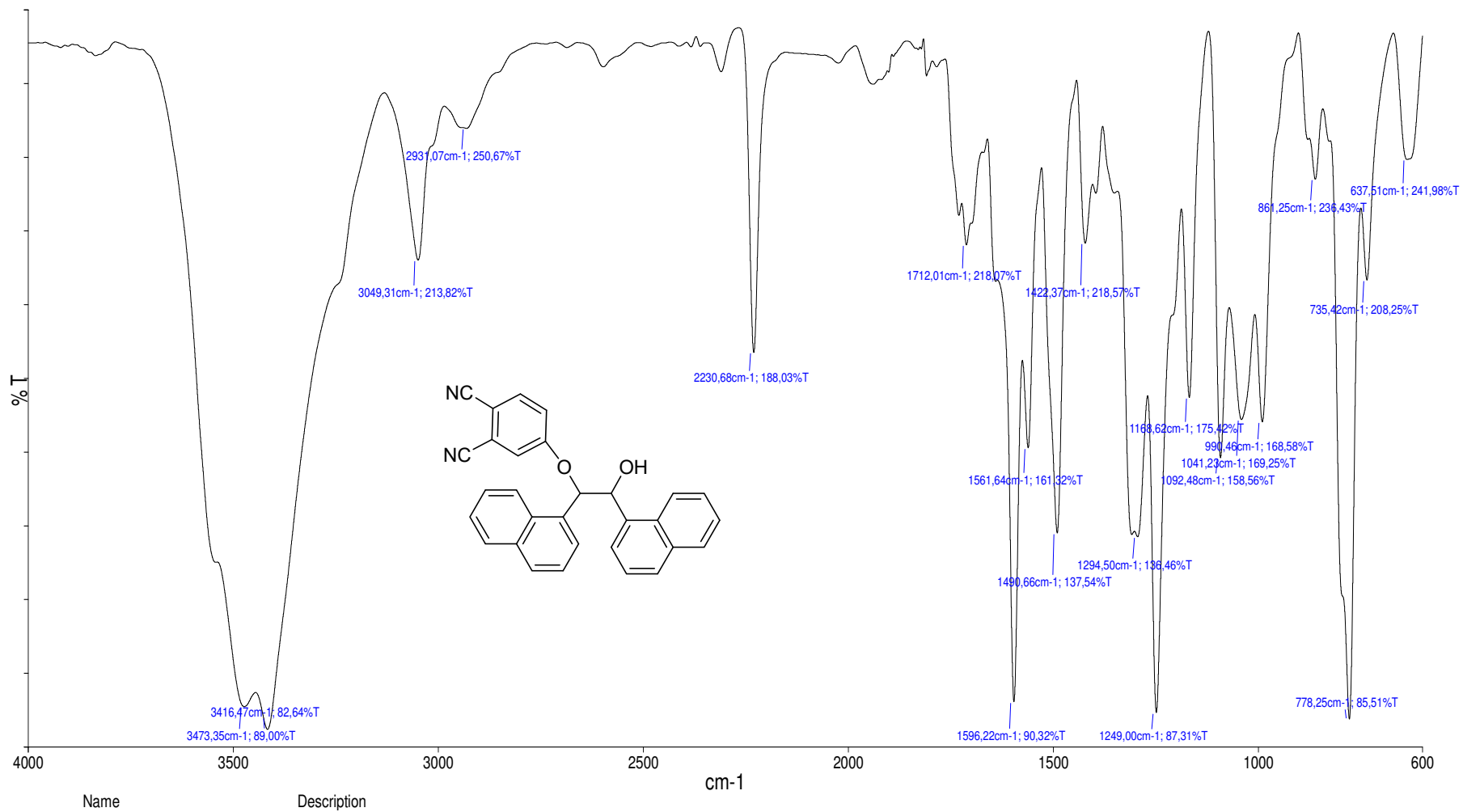
Peripherally 1,2-dinaphthyl ethanediol substituted phthalocyanine complexes: Synthesis, characterization, aggregation and application in benzyl alcohol oxidation at room temperature

Halil Zeki Gök^{1*}, Mustafa Kemal Yılmaz²

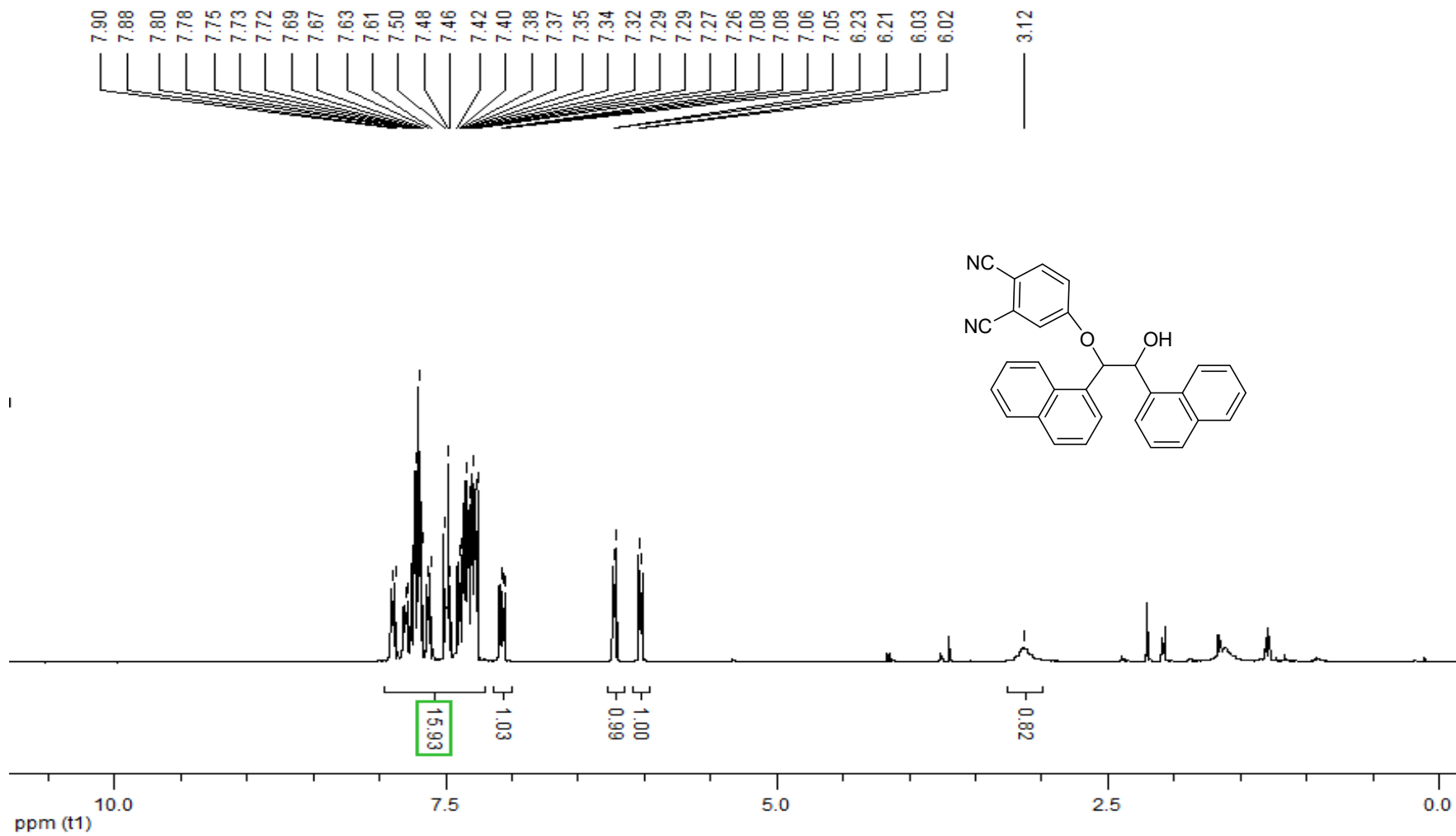
¹Department of Biomedical Engineering, Bucak Faculty of Technology, Mehmet Akif Ersoy University,
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²Department of Chemistry, Faculty of Arts and Sciences, Mersin University, Mersin, Turkey

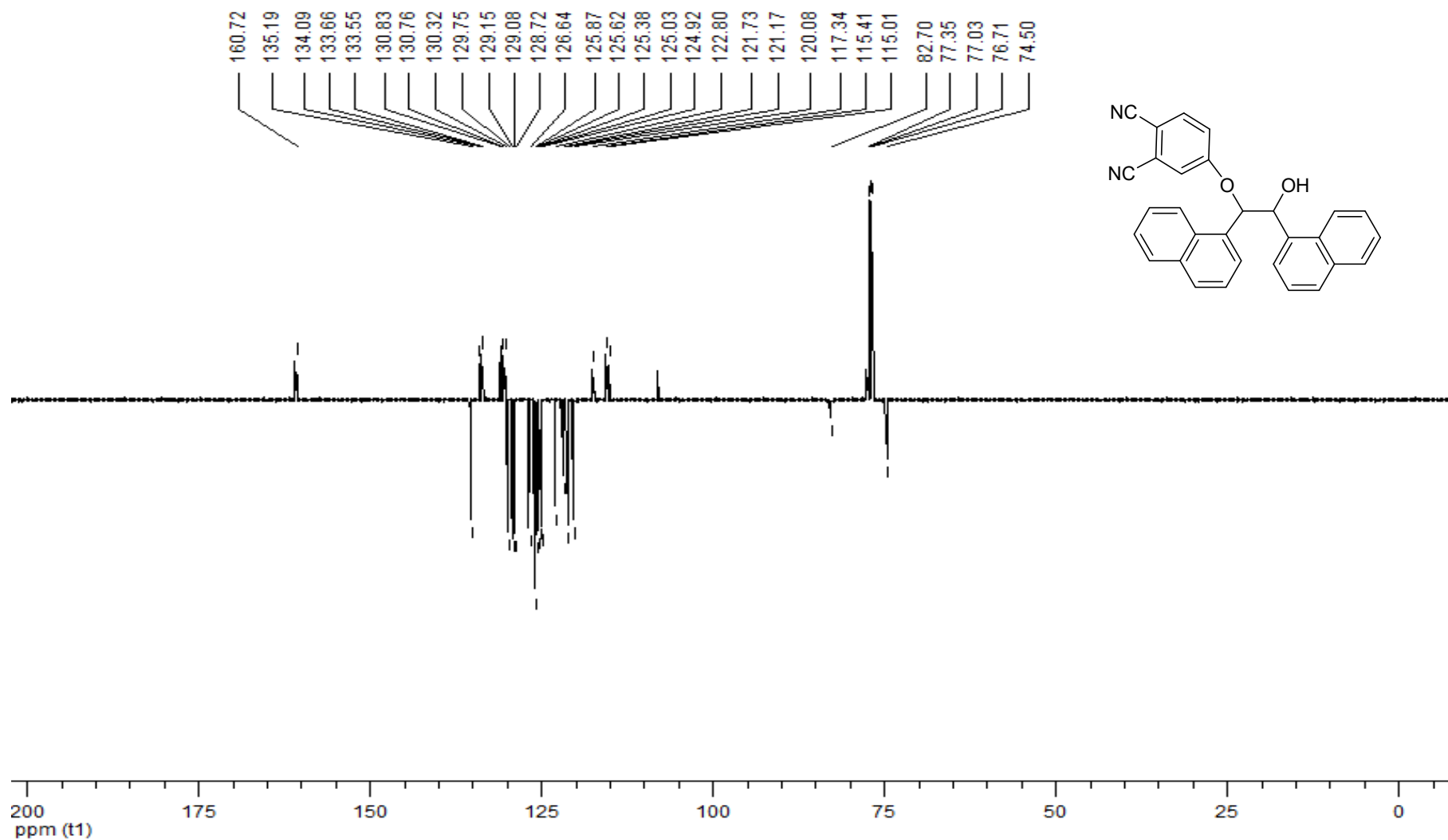
*Correspondence: halilzekigok@gmail.com



Supplementary Figure 1. FT-IR spectrum of (2)



Supplementary Figure 2. ¹H-NMR spectrum of (2)

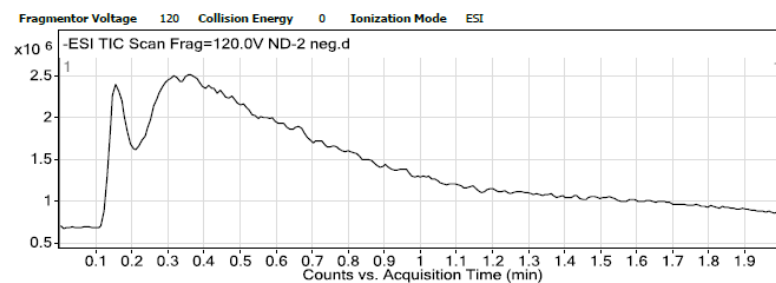


Supplementary Figure 3. ¹³C-NMR (APT) spectrum of (2)

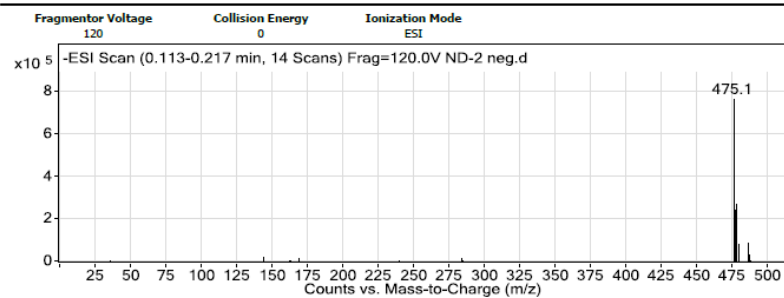
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Sample Type Sample **Position** P1-A2
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Comment

Sample Group Info.

User Chromatograms

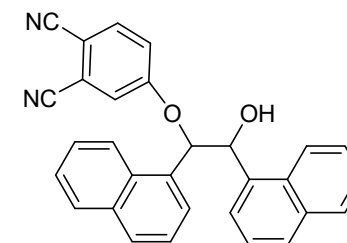


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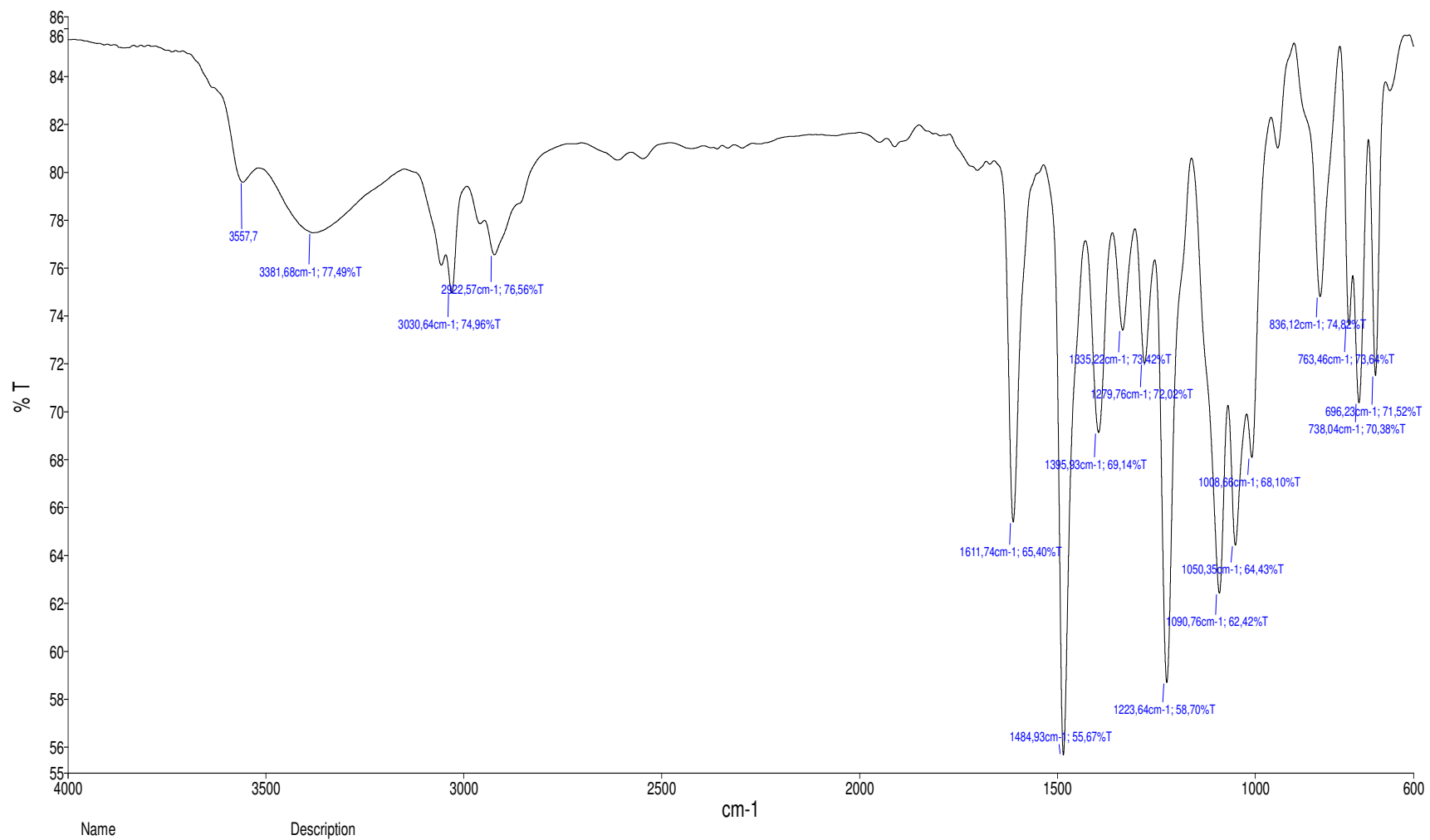


Peak List

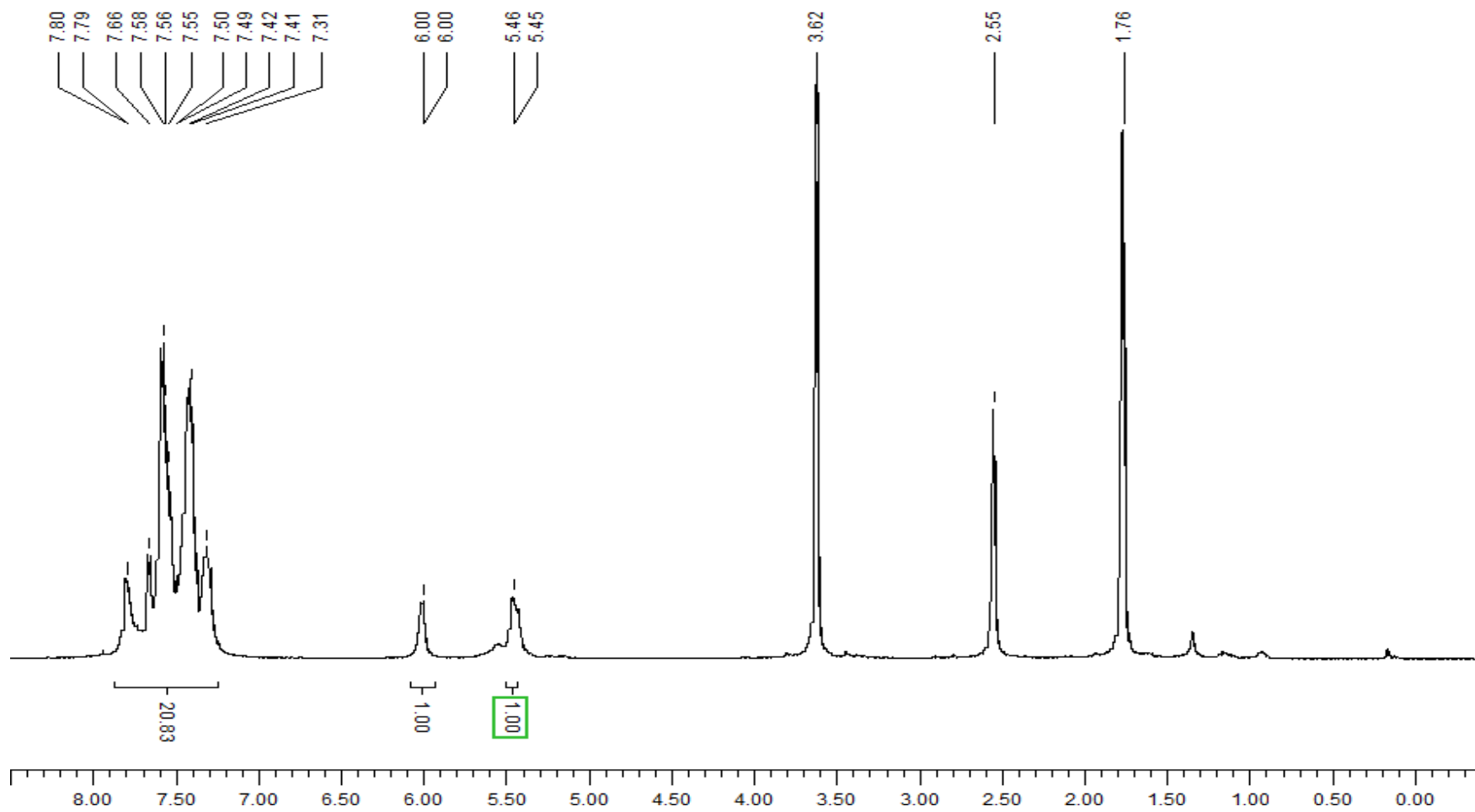
m/z	z	Abund
475.1	1	764349.9
476.2	1	247095.4
477.1	1	276479.5
478.2	1	83967.4
485.2		92463.1



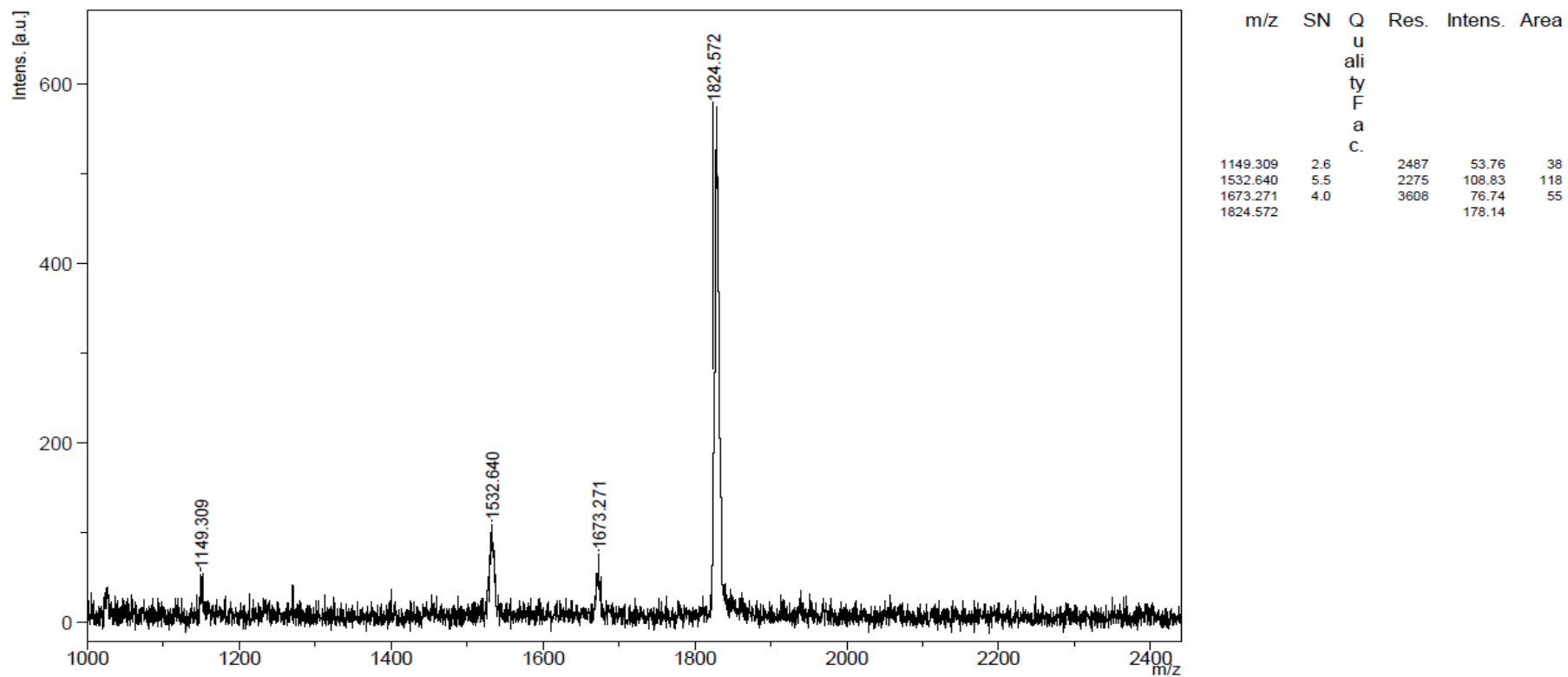
Supplementary Figure 4. LC-MS/MS spectrum of (2)



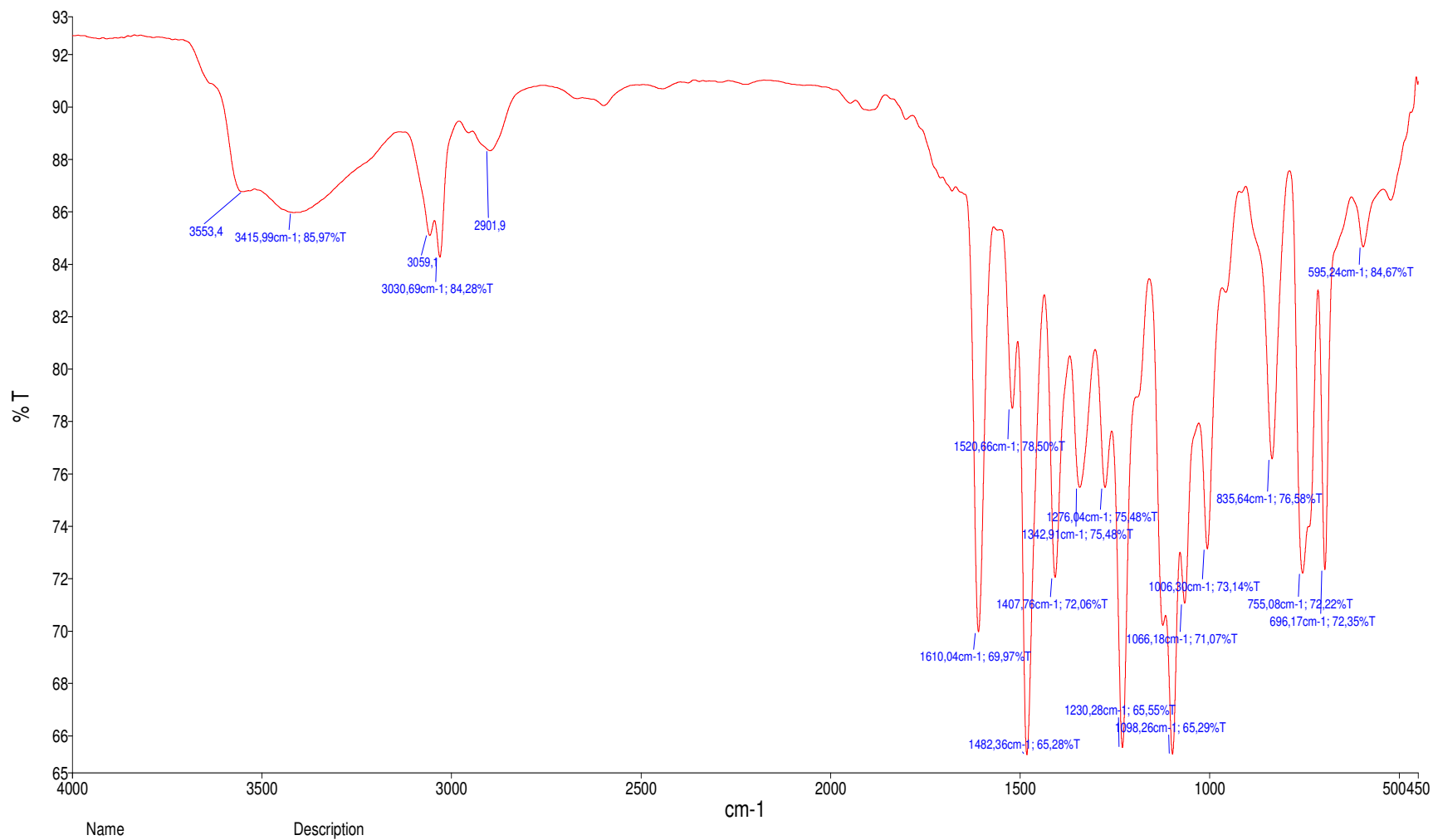
Supplementary Figure 5. FT-IR spectrum of (3)



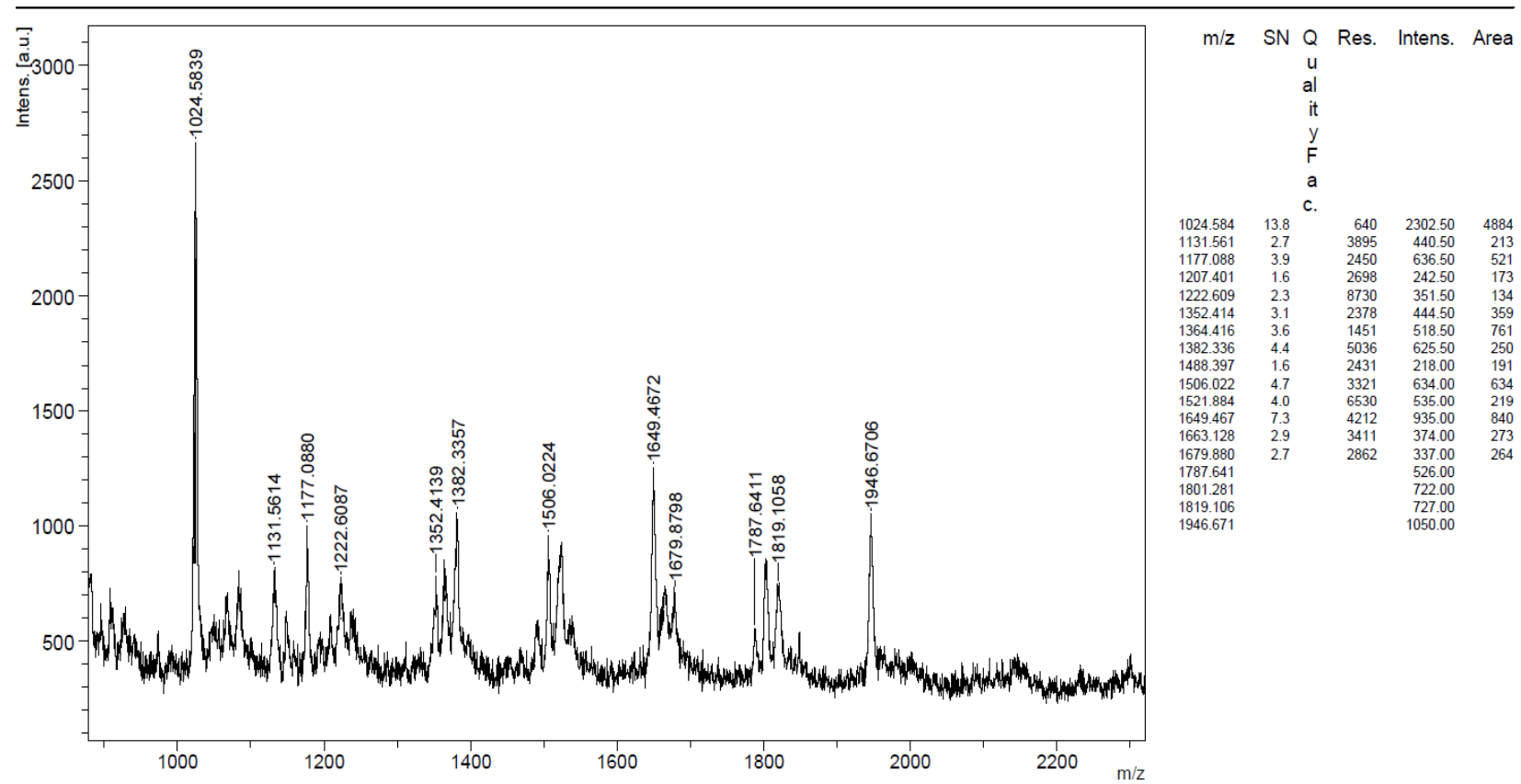
Supplementary Figure 6. ¹H-NMR spectrum of (3)



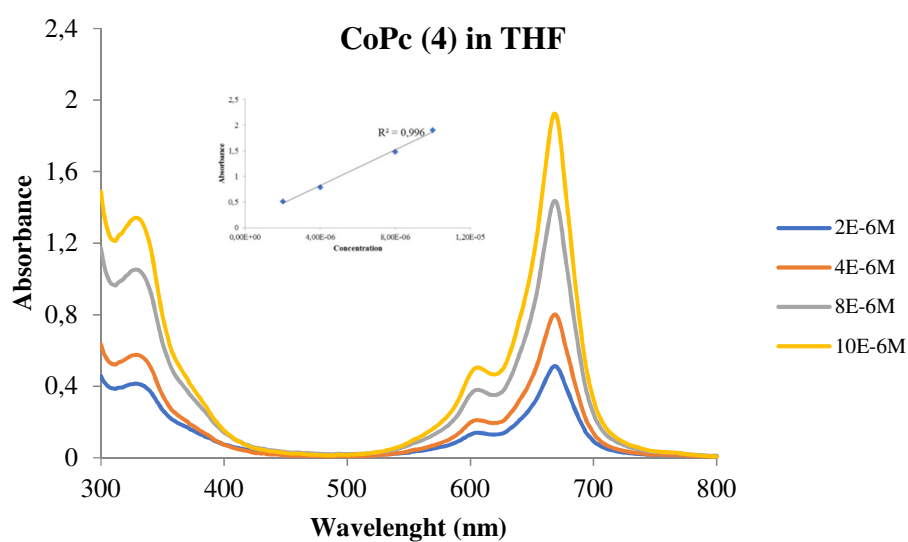
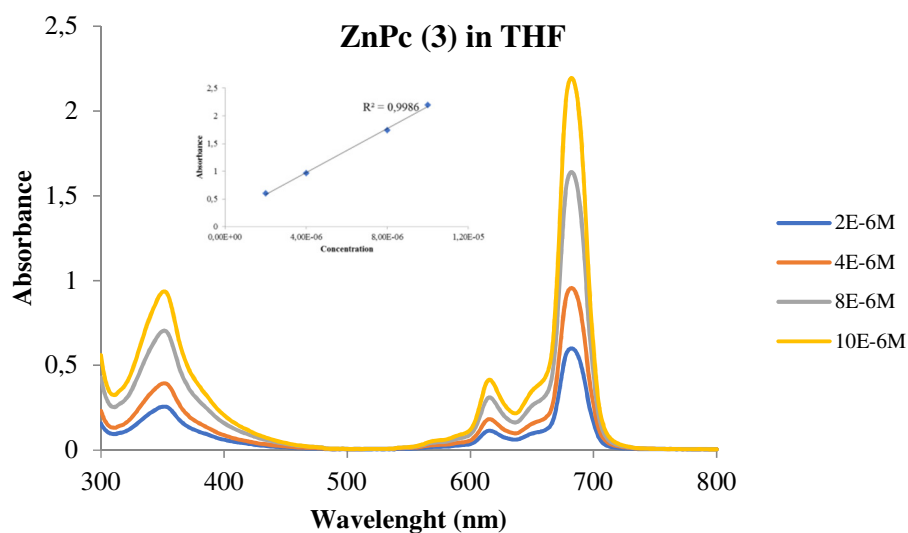
Supplementary Figure 7. MALDI-TOF spectrum of (3)



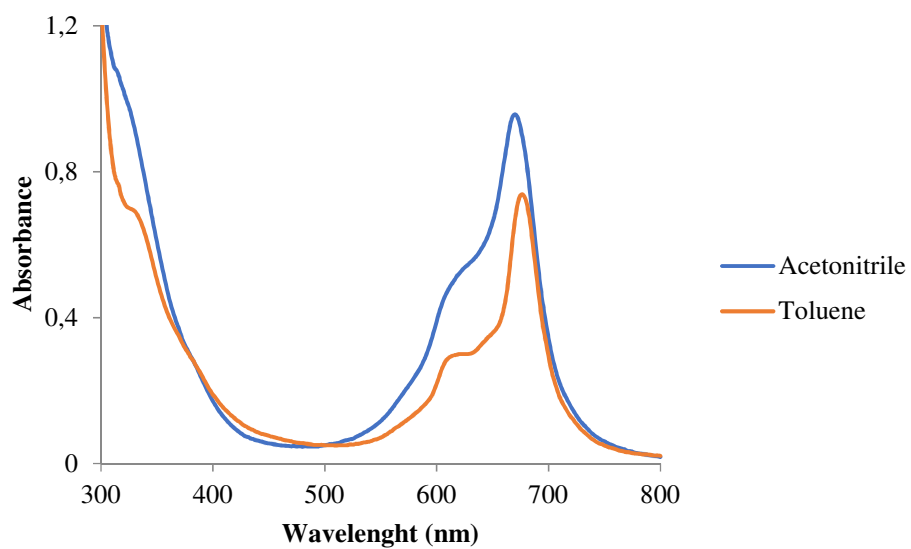
Supplementary Figure 8. FT-IR spectrum of (4)



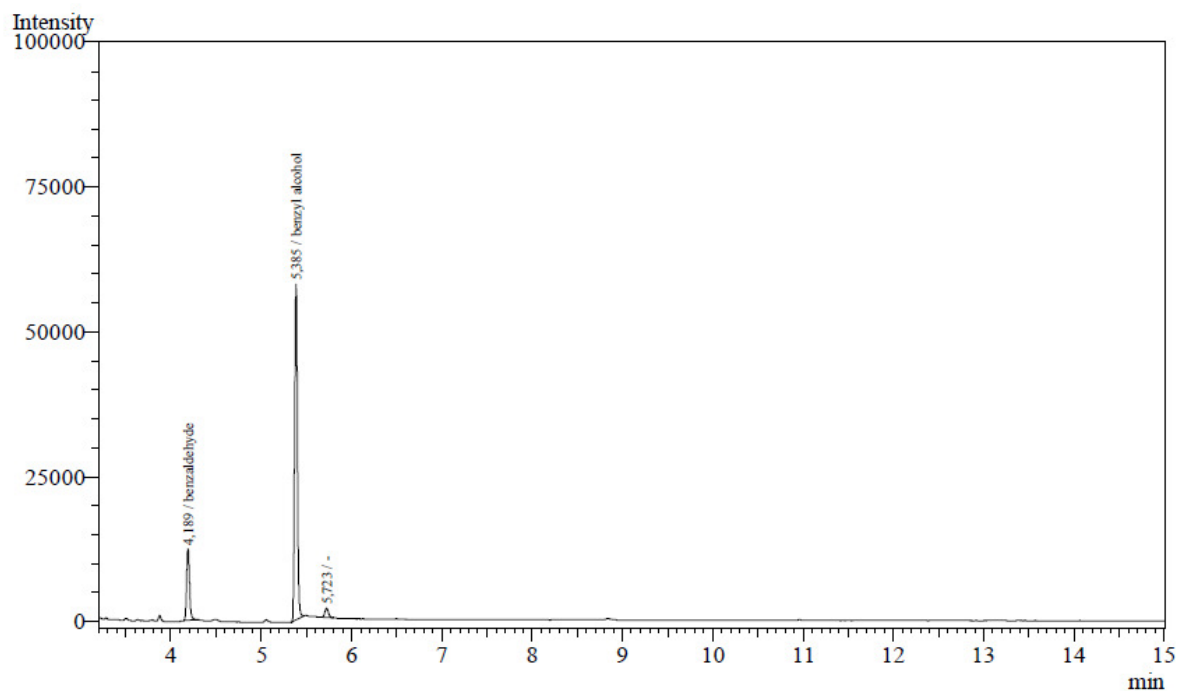
Supplementary Figure 9. MALDI-TOF spectrum of (4)



Supplementary Figure 10. Aggregation properties of phthalocyanine complexes (3) and (4) in THF at different concentrations (Concentration: 2×10^{-6} , 4×10^{-6} , 8×10^{-6} , 10×10^{-6} M). Inset: Beer-Lambert plot.

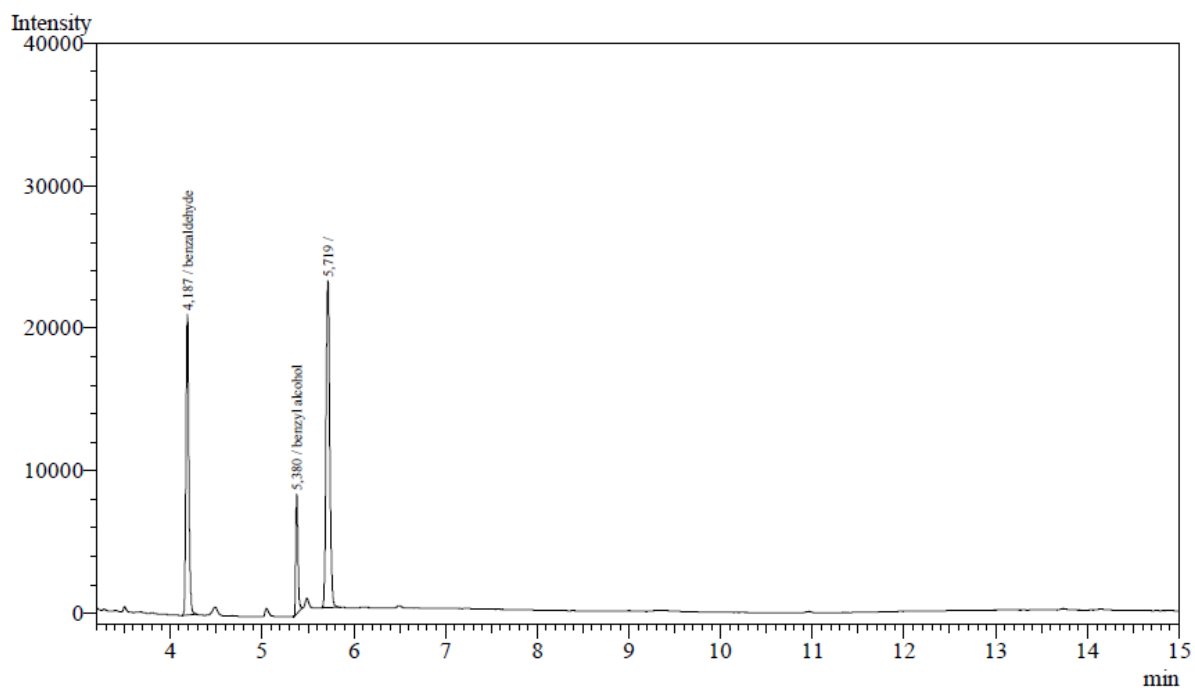


Supplementary Figure 11. UV-vis spectra of cobalt(II) phthalocyanine (**4**) in acetonitrile and toluene.



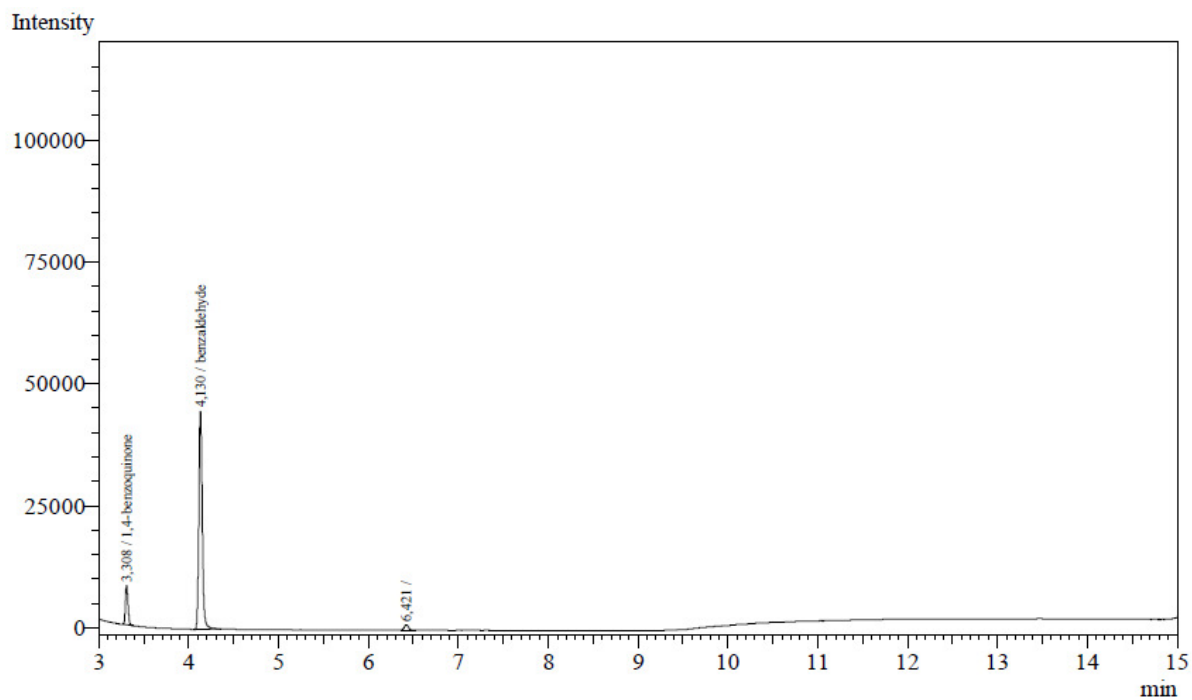
Peak#	Ret.Time	Compound name	Area	Height	Area%
1	4,189	benzaldehyde	27704	12309	17,9
2	5,385	benzyl alcohol	122488	57275	79,2
3	5,723	-	4455	1577	2,9
Total			154647	71161	100,0

Supplementary Figure 12. GC chromatogram of Table 1 entry 1



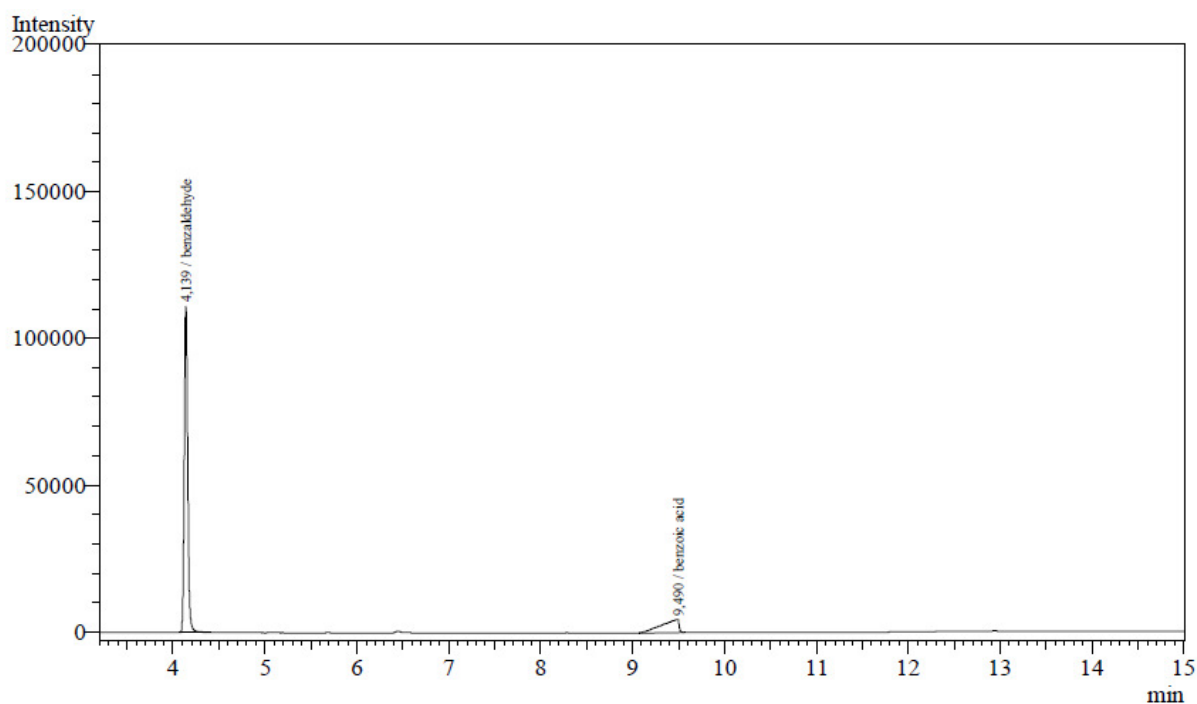
Peak#	Ret.Time	Compound name	Area	Height	Area%
1	4,187	benzaldehyde	45737	20820	36,9
2	5,380	benzyl alcohol	13660	8322	11,0
3	5,719		64408	22880	52,0
Total			123805	52022	100,0

Supplementary Figure 13. GC chromatogram of Table 1 entry 2



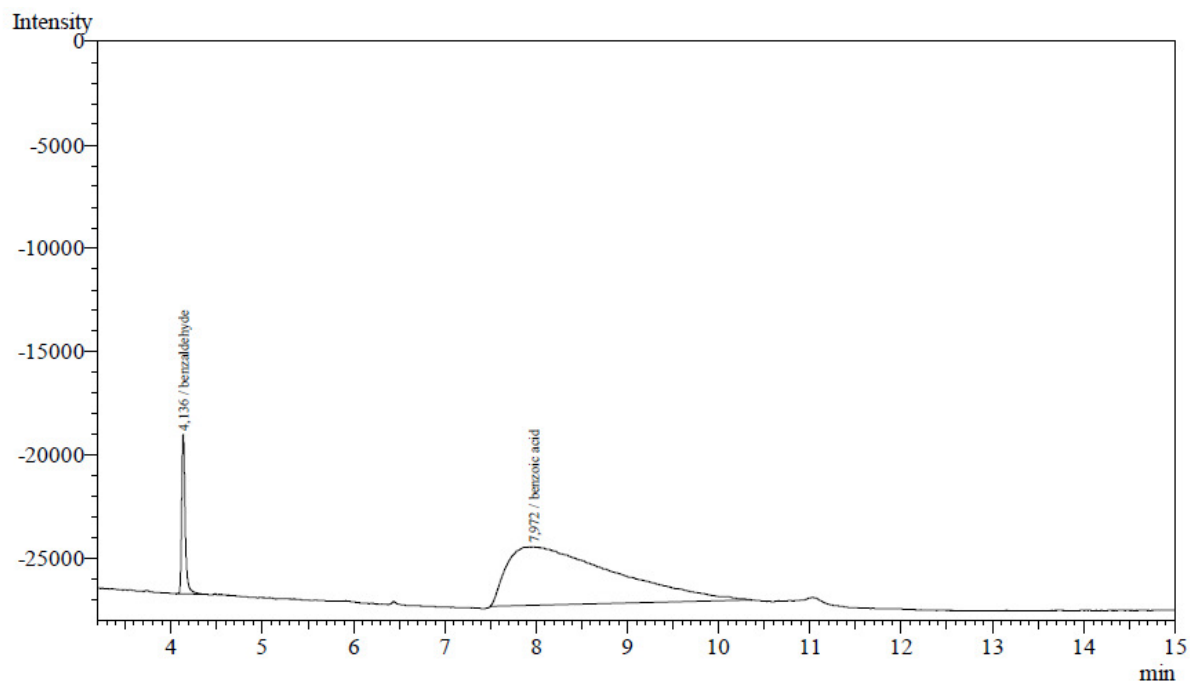
Peak#	Ret. Time	Compound name	Area	Height	Area%
1	3,308	1,4-benzoquinone	15940	7937	11,4
2	4,130	benzaldehyde	120129	44383	85,9
3	6,421		3723	1120	2,7
Total			139792	53440	100,0

Supplementary Figure 14. GC chromatogram of Table 1 entry 3



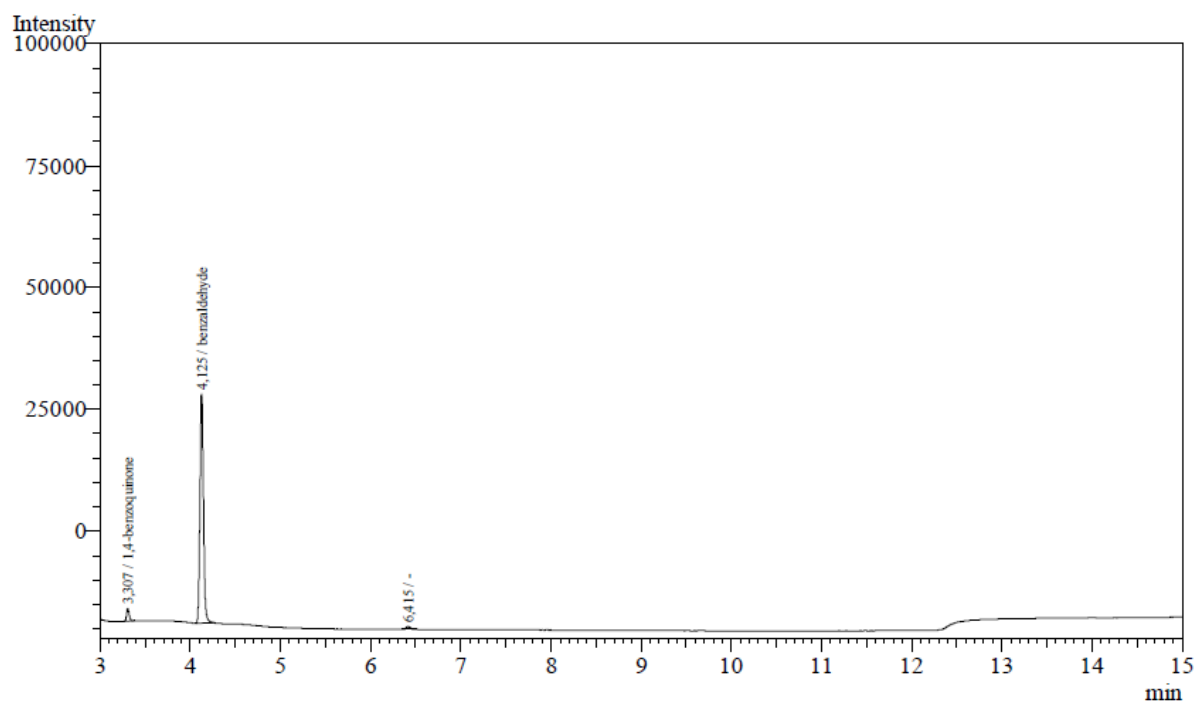
Peak#	Ret. Time	Compound name	Area	Height	Area%
1	4,139	benzaldehyde	290948	110579	83,3
2	9,490	benzoic acid	58211	4512	16,7
Total			349159	115091	100,0

Supplementary Figure 15. GC chromatogram of Table 1 entry 4



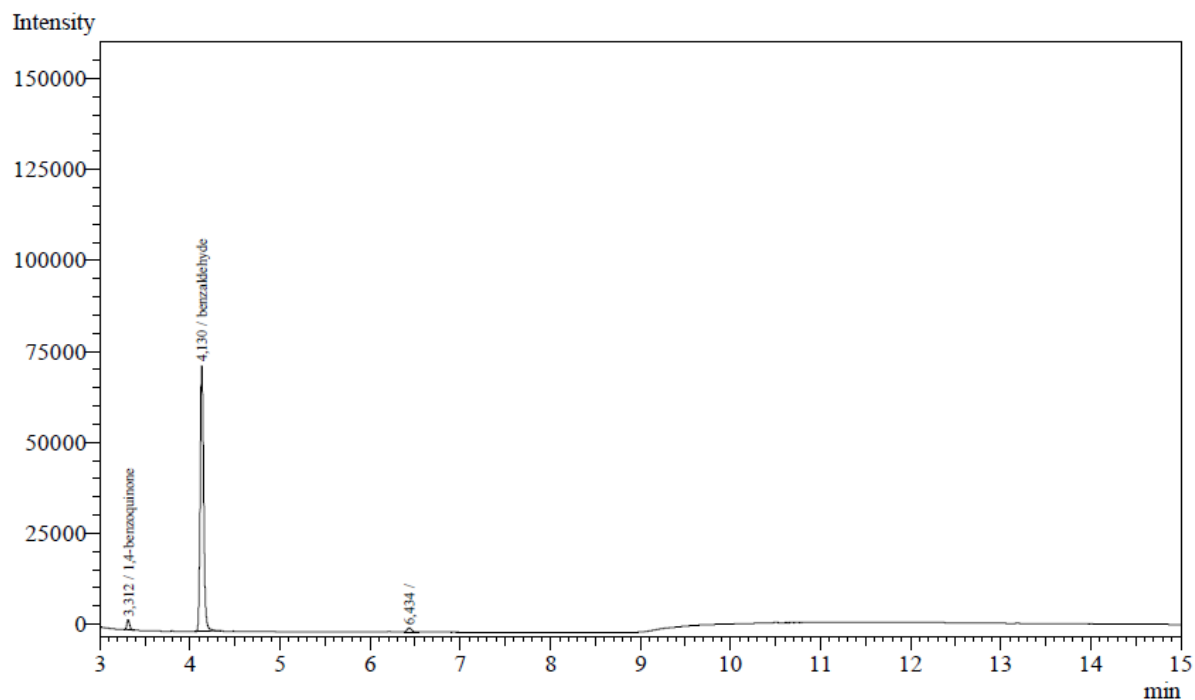
Peak#	Ret.Time	Compound name	Area	Height	Area%
1	4,136	benzaldehyde	20742	7659	8,3
2	7,972	benzoic acid	230095	2827	91,7
Total			250837	10486	100,0

Supplementary Figure 16. GC chromatogram of Table 1 entry 5



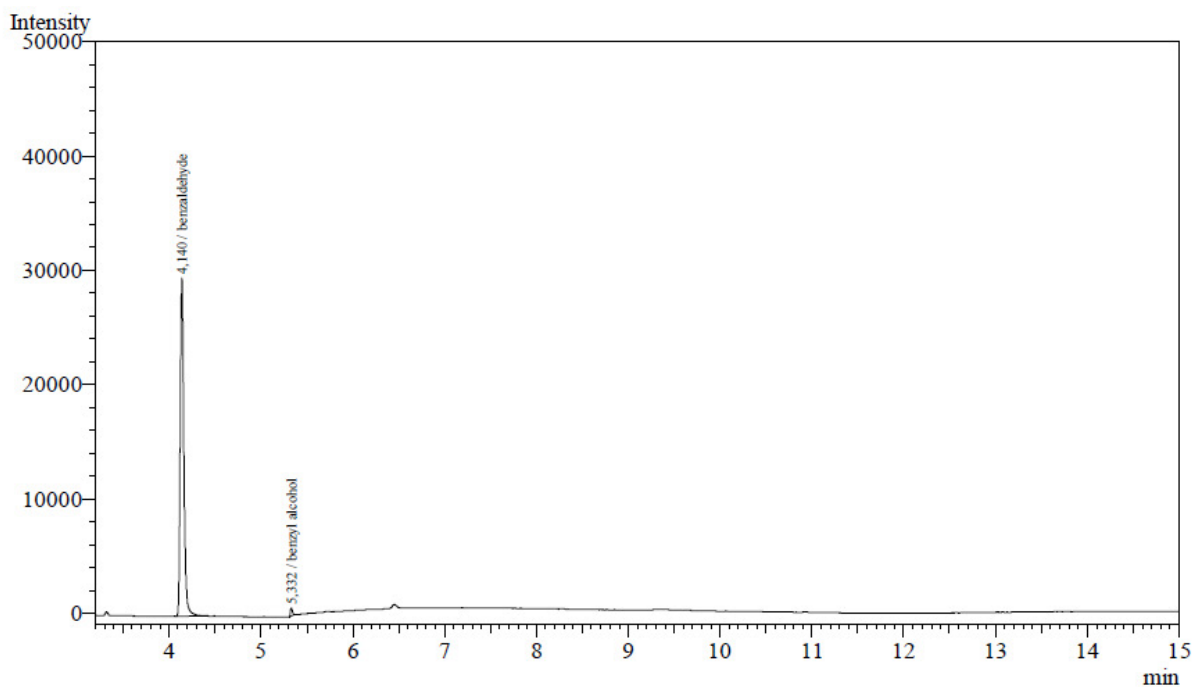
Peak#	Ret.Time	Compound name	Area	Height	Area%
1	3,307	1,4-benzoquinone	5354	2590	4,0
2	4,125	benzaldehyde	127148	46589	94,6
3	6,415	-	1879	568	1,4
Total			134381	49747	100,0

Supplementary Figure 17. GC chromatogram of Table 1 entry 6



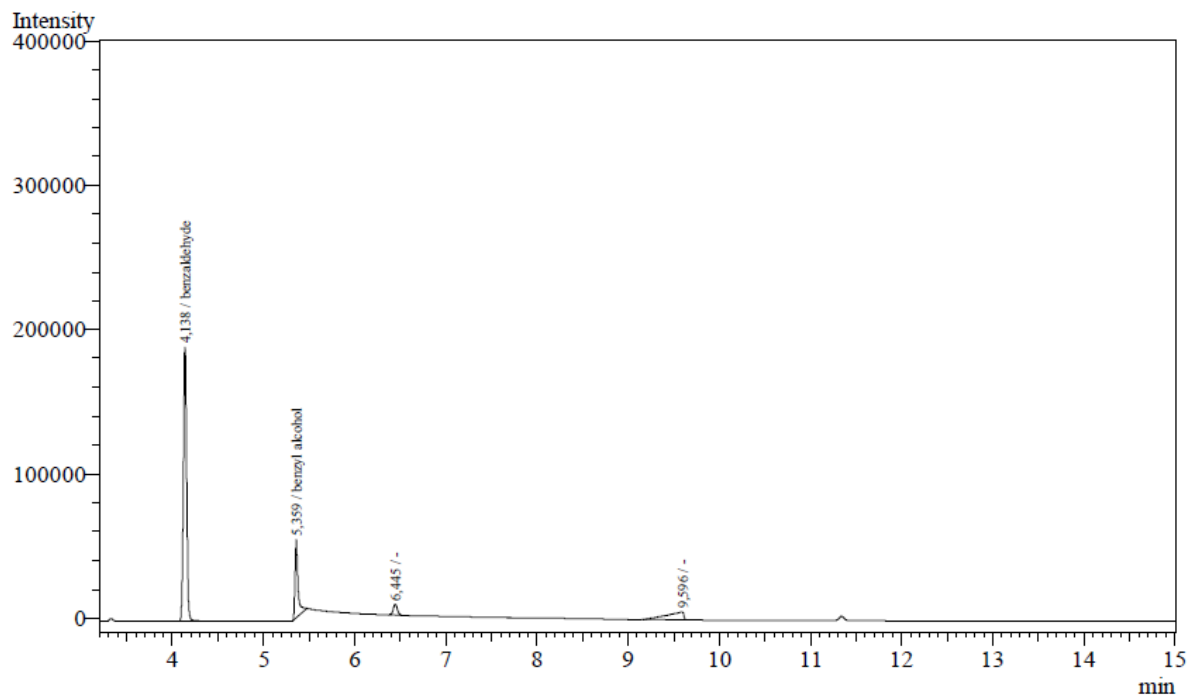
Peak#	Ret.Time	Compound name	Area	Height	Area%
1	3,312	1,4-benzoquinone	5846	2816	2,8
2	4,130	benzaldehyde	198153	72455	95,4
3	6,434		3813	1125	1,8
Total			207812	76396	100,0

Supplementary Figure 18. GC chromatogram of Table 1 entry 7



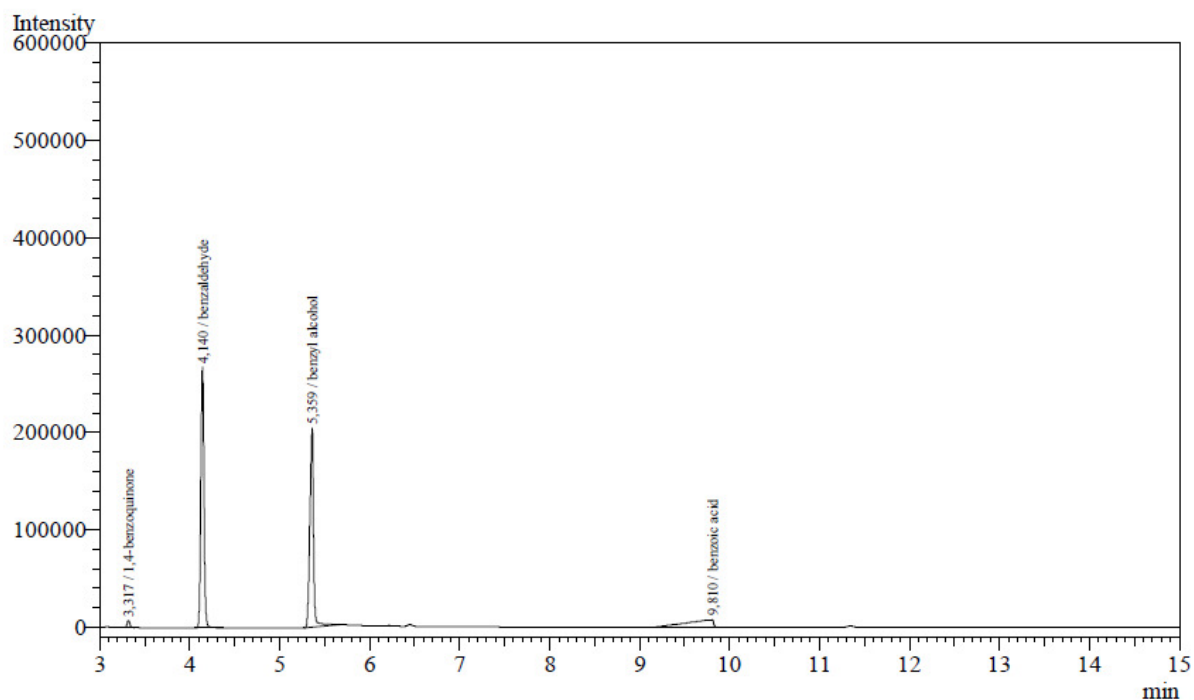
Peak#	Ret.Time	Compound name	Area	Height	Area%
1	4,140	benzaldehyde	82102	29266	98,7
2	5,332	benzyl alcohol	1044	693	1,3
Total			83146	29959	100,0

Supplementary Figure 19. GC chromatogram of Table 1 entry 8, Table 2 entry 2 and Table 3 entry 2



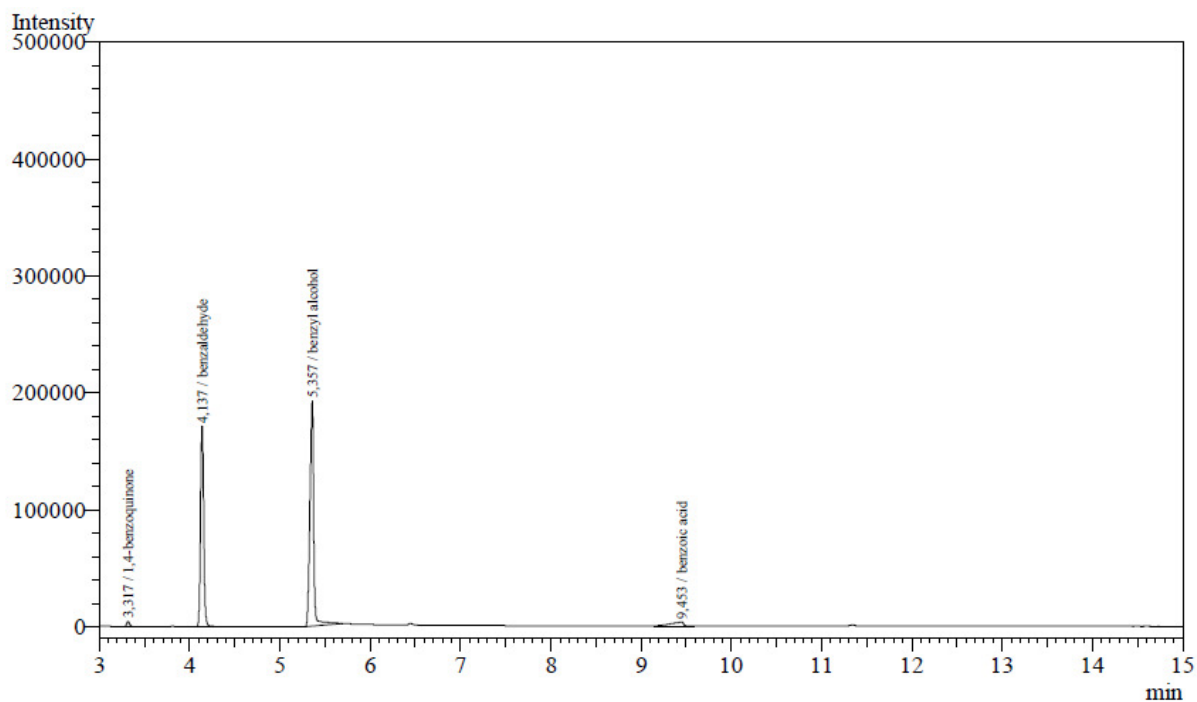
Peak#	Ret.Time	Compound name	Area	Height	Area%
1	4,138	benzaldehyde	470025	189447	68,1
2	5,359	benzyl alcohol	124696	53385	18,1
3	6,445	-	23226	7388	3,4
4	9,596	-	72192	5270	10,5
Total			690139	255490	100,0

Supplementary Figure 20. GC chromatogram of Table 2 entry 1



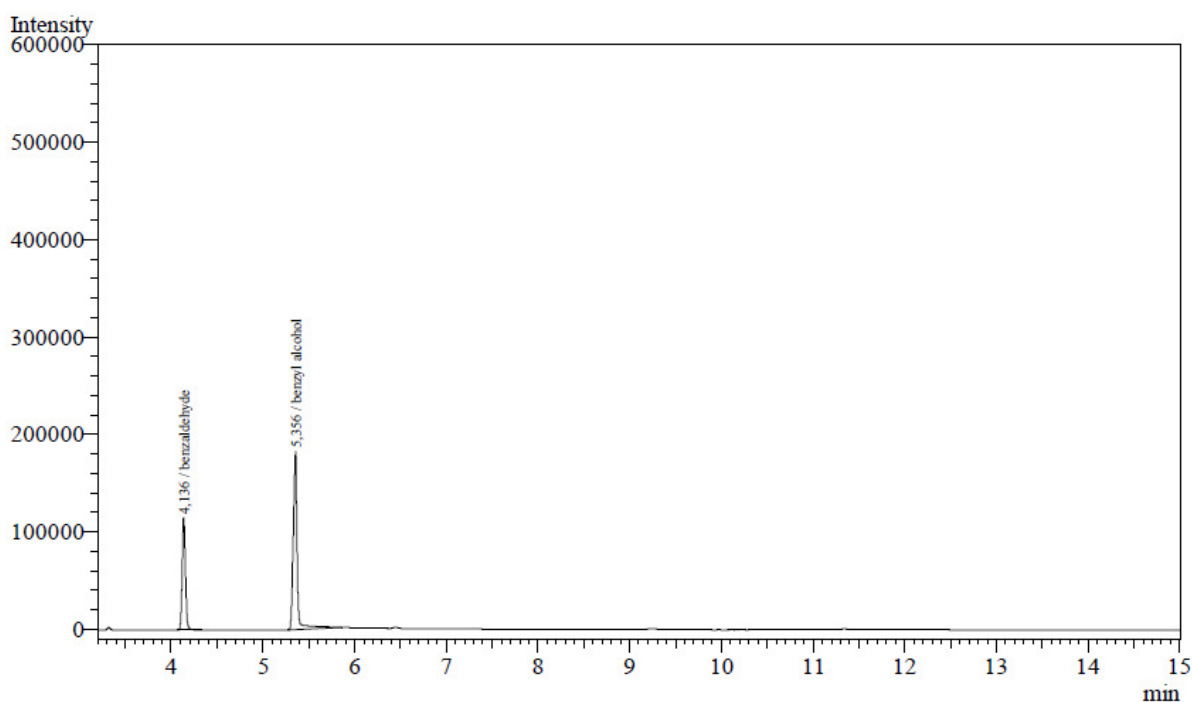
Peak#	Ret.Time	Compound name	Area	Height	Area%
1	3,317	1,4-benzoquinone	14470	7199	1,0
2	4,140	benzaldehyde	649898	264577	46,0
3	5,359	benzyl alcohol	588457	203619	41,6
4	9,810	benzoic acid	160637	7697	11,4
Total			1413462	483092	100,0

Supplementary Figure 21. GC chromatogram of Table 2 entry 3



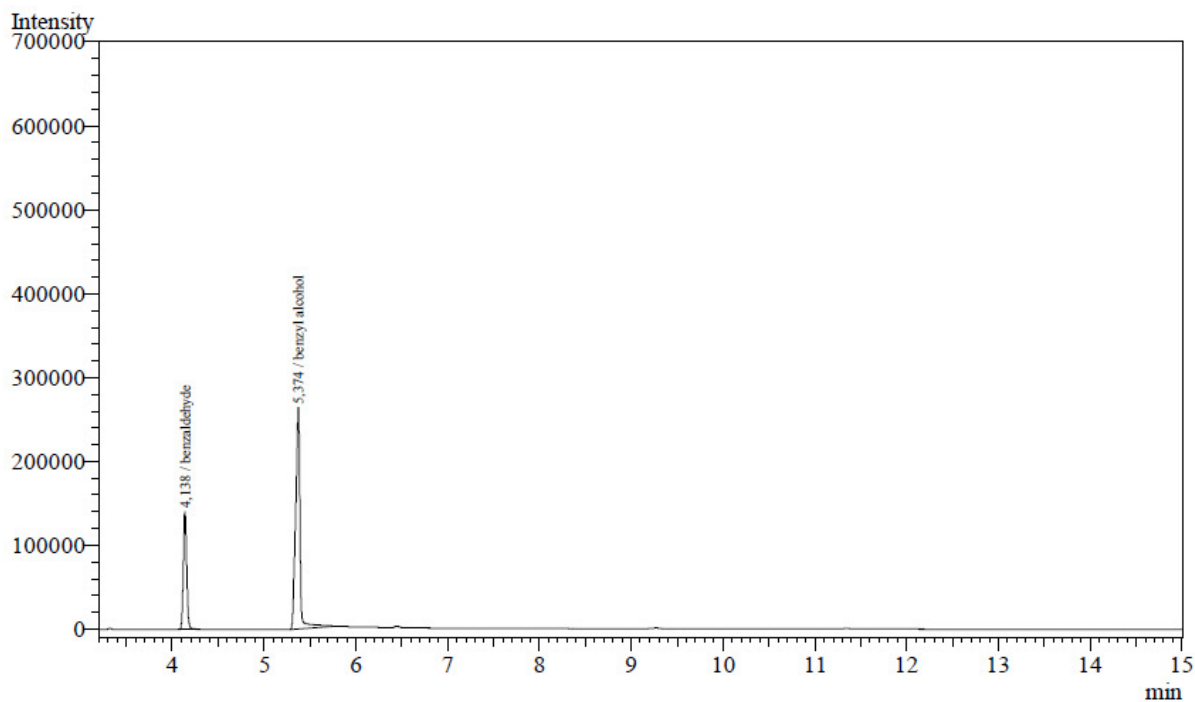
Peak#	Ret. Time	Compound name	Area	Height	Area%
1	3,317	1,4-benzoquinone	9059	4546	0,9
2	4,137	benzaldehyde	421143	171231	40,8
3	5,357	benzyl alcohol	564948	191045	54,8
4	9,453	benzoic acid	36557	3487	3,5
Total			1031707	370309	100,0

Supplementary Figure 22. GC chromatogram of Table 2 entry 4



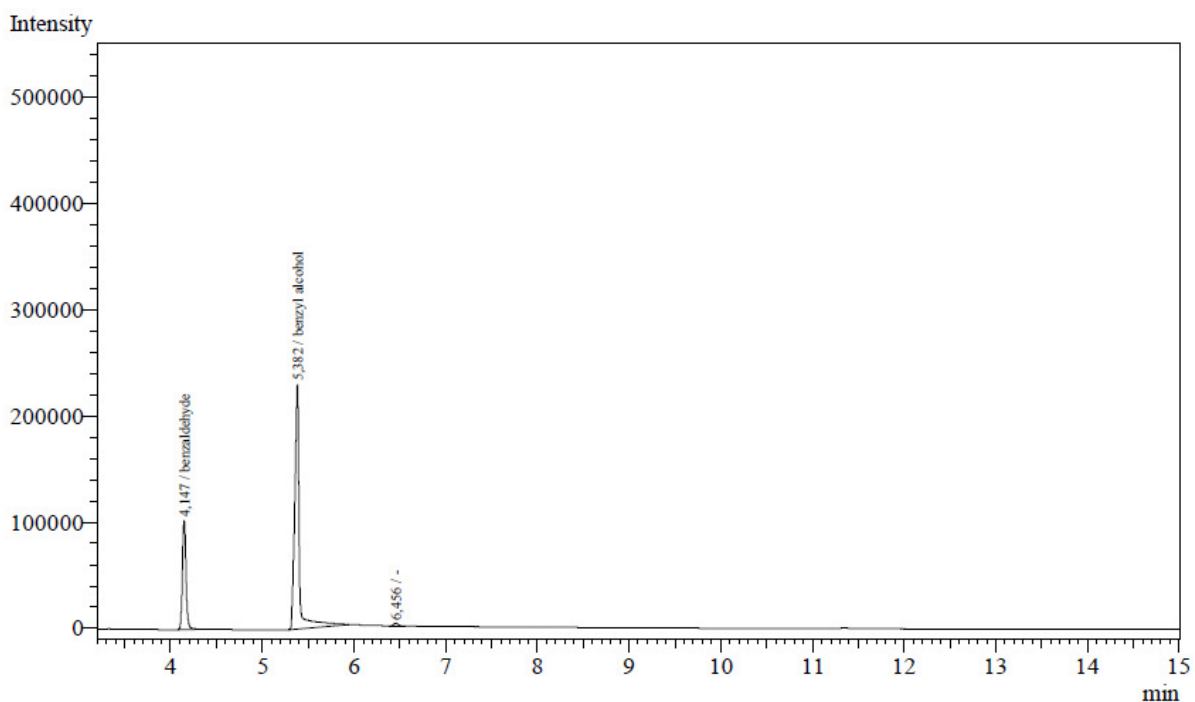
Peak#	Ret. Time	Compound name	Area	Height	Area%
1	4,136	benzaldehyde	286158	114034	34,0
2	5,356	benzyl alcohol	555249	182148	66,0
Total			841407	296182	100,0

Supplementary Figure 23. GC chromatogram of Table 2 entry 5



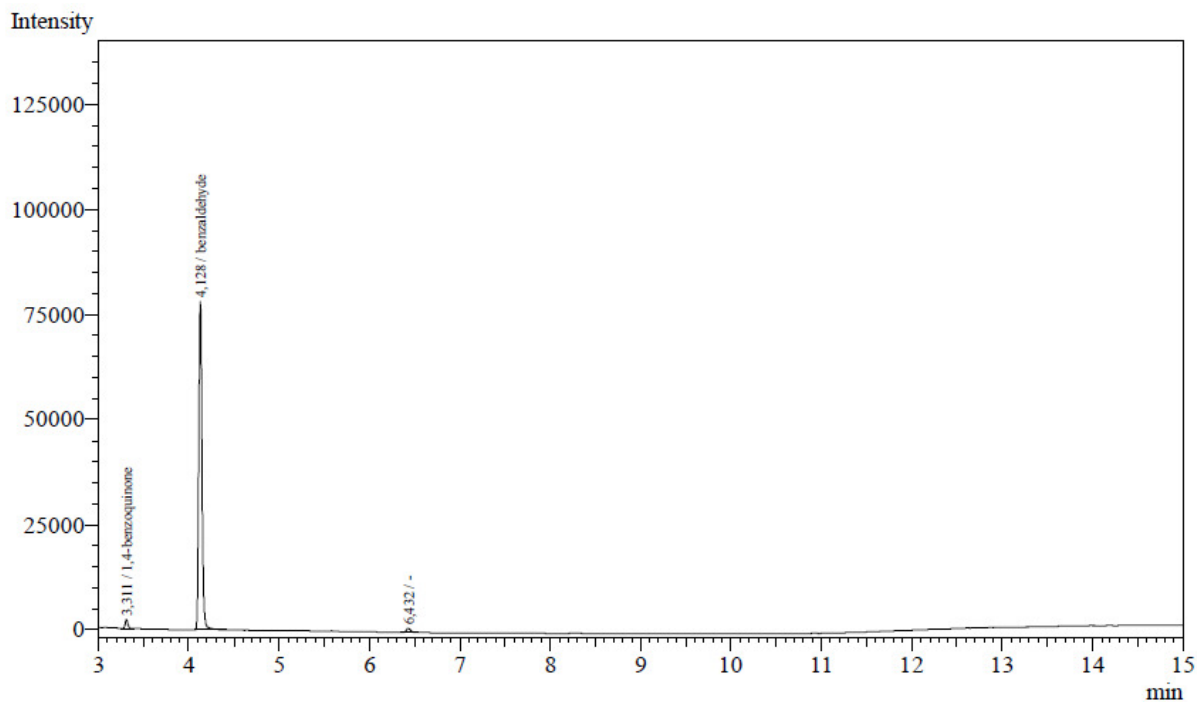
Peak#	Ret. Time	Compound name	Area	Height	Area%
1	4,138	benzaldehyde	360135	139850	29,0
2	5,374	benzyl alcohol	880435	263326	71,0
Total			1240570	403176	100,0

Supplementary Figure 24. GC chromatogram of Table 2 entry 6



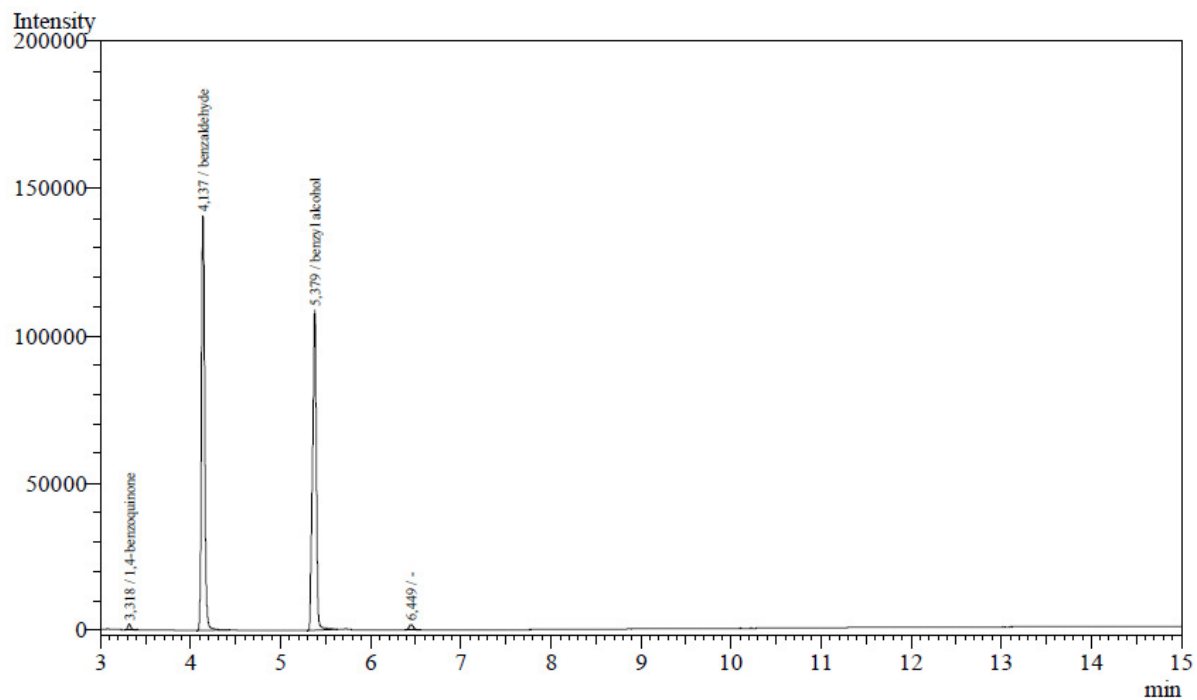
Peak#	Ret. Time	Compound name	Area	Height	Area%
1	4,147	benzaldehyde	282616	102085	25,8
2	5,382	benzyl alcohol	805741	228389	73,5
3	6,456	-	8063	2357	0,7
Total			1096420	332831	100,0

Supplementary Figure 25. GC chromatogram of Table 2 entry 7



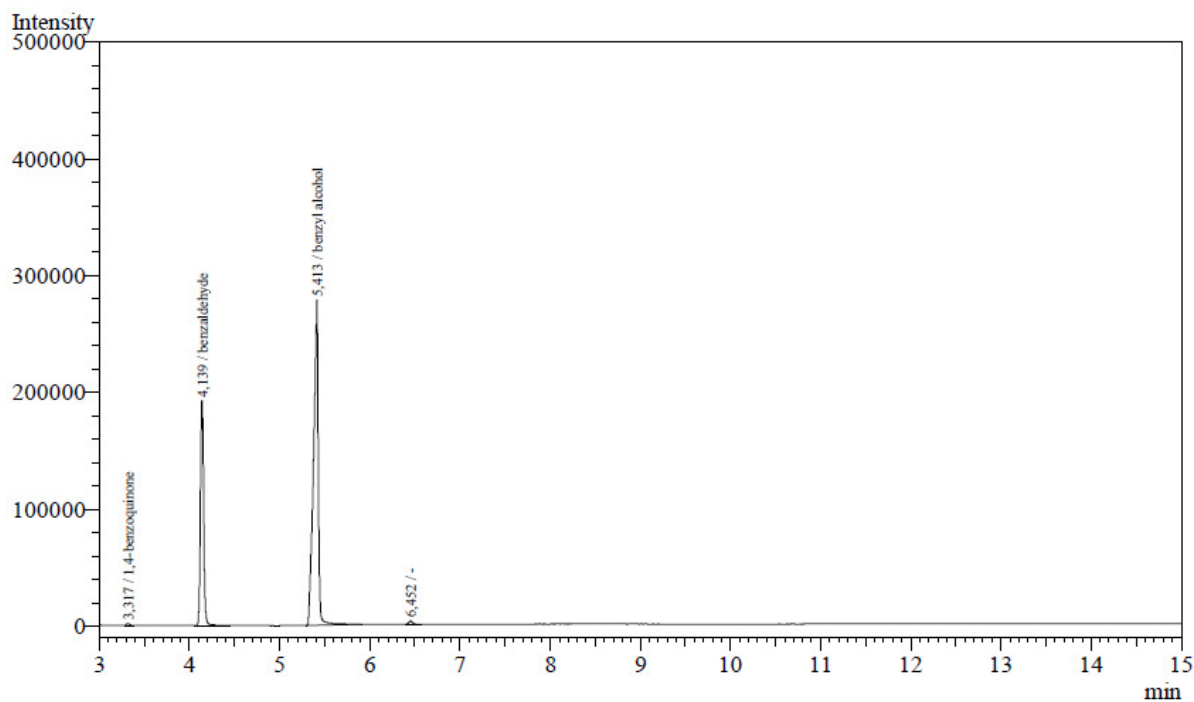
Peak#	Ret.Time	Compound name	Area	Height	Area%
1	3,311	1,4-benzoquinone	4043	2053	2,0
2	4,128	benzaldehyde	195589	77857	96,3
3	6,432	-	3388	1001	1,7
Total			203020	80911	100,0

Supplementary Figure 26. GC chromatogram of Table 3 entry 3



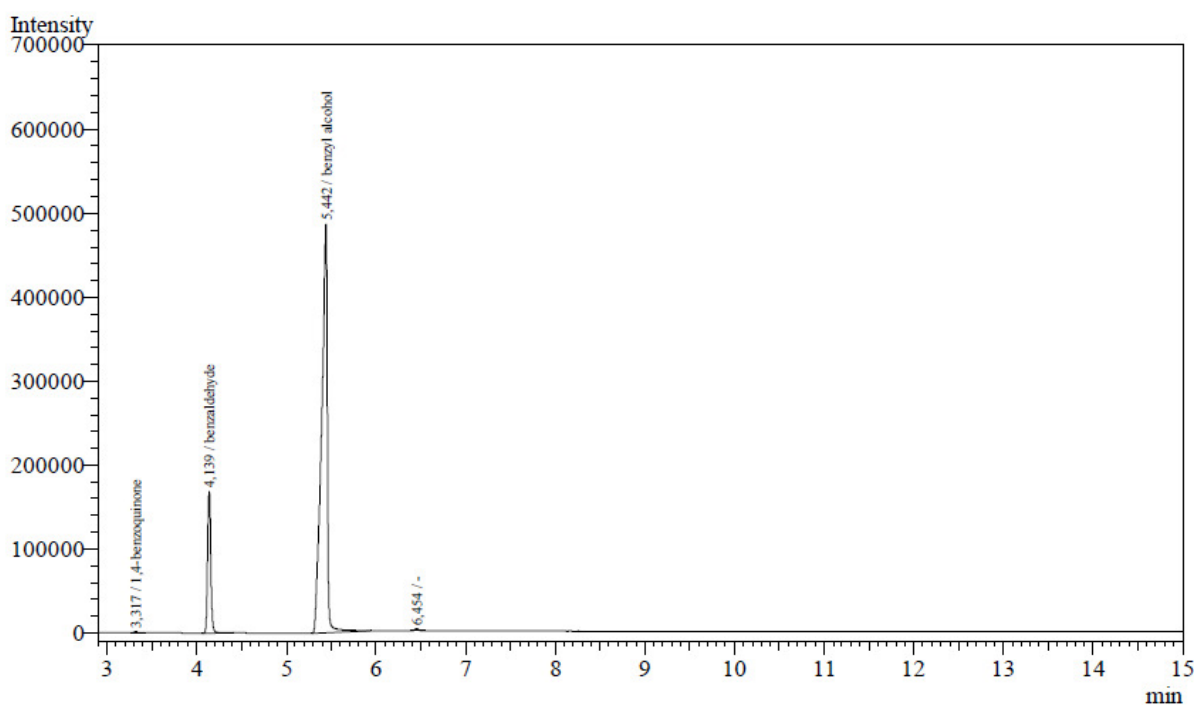
Peak#	Ret.Time	Compound name	Area	Height	Area%
1	3,318	1,4-benzoquinone	3899	1889	0,6
2	4,137	benzaldehyde	349635	140304	51,6
3	5,379	benzyl alcohol	318629	108374	47,0
4	6,449	-	6077	1836	0,9
Total			678240	252403	100,0

Supplementary Figure 27. GC chromatogram of Table 3 entry 4



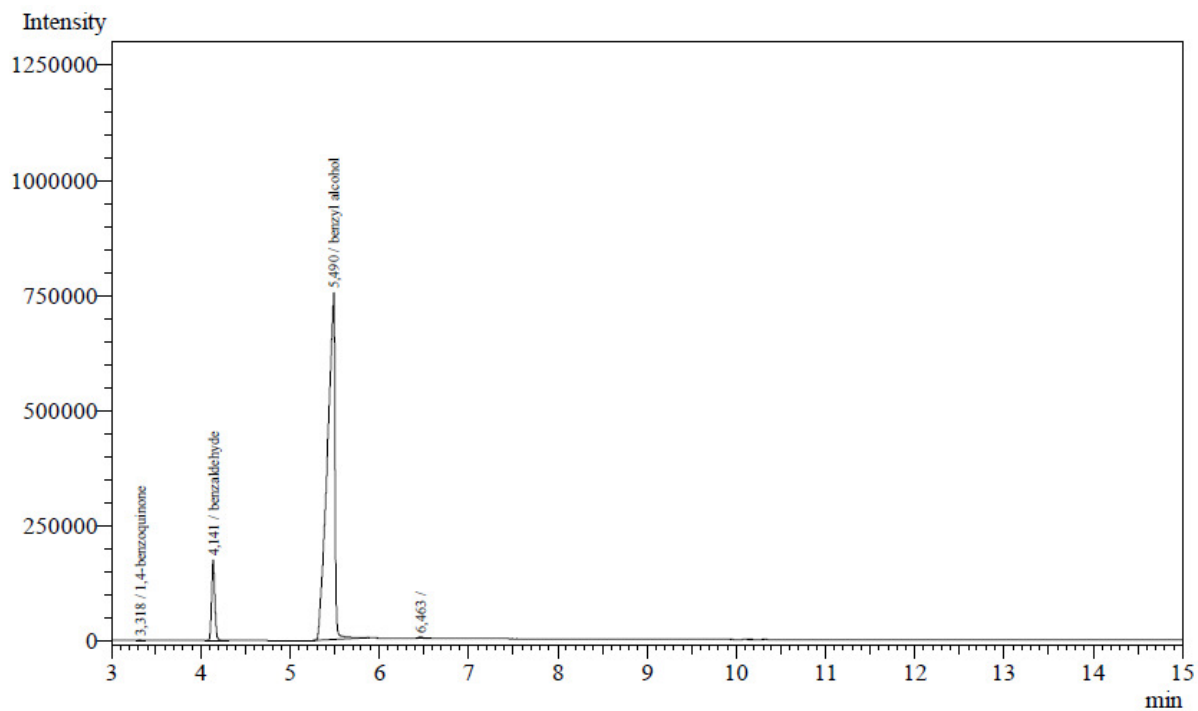
Peak#	Ret. Time	Compound name	Area	Height	Area%
1	3,317	1,4-benzoquinone	3364	1702	0,2
2	4,139	benzaldehyde	477762	191646	31,5
3	5,413	benzyl alcohol	1029038	277047	67,8
4	6,452	-	8218	2613	0,5
Total			1518382	473008	100,0

Supplementary Figure 28. GC chromatogram of Table 3 entry 5



Peak#	Ret. Time	Compound name	Area	Height	Area%
1	3,317	1,4-benzoquinone	3963	1985	0,2
2	4,139	benzaldehyde	419001	167077	16,2
3	5,442	benzyl alcohol	2161689	482909	83,4
4	6,454	-	7905	2588	0,3
Total			2592558	654559	100,0

Supplementary Figure 29. GC chromatogram of Table 3 entry 6



Peak#	Ret. Time	Compound name	Area	Height	Area%
1	3,318	1,4-benzoquinone	3490	1731	0,1
2	4,141	benzaldehyde	439583	173606	8,9
3	5,490	benzyl alcohol	4487476	752030	90,8
4	6,463		9262	3072	0,2
Total			4939811	930439	100,0

Supplementary Figure 30. GC chromatogram of Table 3 entry 7