

# Chemospecific and Regioselective Ethereal Methyl-Oxygen Bond Cleavage Behavior of Aroylated Dimethoxynaphthalenes by Combined Action of AlCl<sub>3</sub> and Aroyl Group

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## ABSTRACT

AlCl<sub>3</sub>-mediated cleavage of ethereal methyl-oxygen bond in aroylated 2,7-dimethoxynaphthalene compounds proceeds chemospecifically and regioselectively. The ethereal bond at the  $\beta(2)$ -position of 1-monoaroylated 2,7-dimethoxynaphthalene is cleaved readily and predominantly against the  $\beta(7)$ -position, whereas scission of  $\beta$ -ethereal bonds of 1,8-diaroylated 2,7-dimethoxynaphthalene hardly undergoes like the non-aroylated mother frame compound of 2,7-dimethoxynaphthalene.

**Keywords:** Aroylated 2,7-Dialkoxynaphthalene; Chemospecific and Regioselective Scission of Ethereal Alkyl-Oxygen Bond; Combined Action of AlCl<sub>3</sub> and Aroyl Group; Neighboring Group Effect

## 1. Introduction

Congested molecular units having non-coplanar alignment of aromatic rings such as biphenyl, binaphthyl, and other poly (aromatic rings) compounds have been in the limelight for building block of functional molecules and polymers [1-4]. Recently, the authors' group has found that 2,7-dialkoxynaphthalenes readily undertake acid-mediated diaroylation with high peri-regioselectivity to give 1-aroyl and 1,8-diaroyl-2,7-dialkoxynaphthalenes in satisfactory yields [5,6]. In crystal, the aroyl group of the resulting molecules attaches to the naphthalene ring as nearly perpendicular manner and for diaroylated derivatives two aroyl groups are situated in opposite directions (*anti*-orientation) [7-9]. The authors' group has integrated the naphthalene-1,8-bis(carbonylarylene) unit into poly(arylene ether ketone) backbone and reported unique solubility tendency to organic solvents and characteristic thermal behavior of the resulting polymers with interpretation in relation to the spatial organization of the repeating unit [10]. In addition, some curious reactions of the 2,7-dimethoxynaphthalene and its derivatives such as reversible aroylation depending on Brønsted acid strength [5] and dual aroylation mediated by Lewis acid [6] are also revealed during the studies on aroylation of naphthalene derivatives.

In this article, the authors introduce Methyl-oxygen

bond cleavage behavior of  $\beta$ -ethereal substituent in aroylated dimethoxynaphthalenes by the combined action of AlCl<sub>3</sub> and aroyl group and discuss the regioselectivity and the chemospecificity based on the comparison of the corresponding reaction behaviors among the homologous and analogous dialkoxynaphthalene molecules.

As well known methyl aryl ether generally resists acid-mediated Methyl-oxygen bond cleavage. So deprotection of methyl group from methoxyarenes needs specific reagents such as iodotrimethylsilane with Lewis acids, or BBr<sub>3</sub> in place of AlCl<sub>3</sub>, which has almost no potential for this purpose [11-14]. Furthermore, the BBr<sub>3</sub>-mediated cleavage often suffers from low regioselectivity. Therefore, effective and regioselective cleavage of methyl aryl ether by AlCl<sub>3</sub> is of interest.

## 2. Results and Discussion

**Table 1** shows the results of AlCl<sub>3</sub>-mediated ether-cleavage reaction of 1-monoaroyl-2,7-dimethoxynaphthalene (**1aa**) in refluxing CH<sub>2</sub>Cl<sub>2</sub> solutions. The methyl-oxygen bond in 2-methoxy group of 1-monoaroylnaphthalene **1aa** was cleaved in the presence of three equimolar amounts of AlCl<sub>3</sub> or more (Entries 1 - 6). Using of five equimolar amounts of AlCl<sub>3</sub> quantitatively yielded 2-hydroxy-7-methoxy product **2ba** (Entry 5). The exclusive scission of 2-methoxy moiety leaving the other

**Table 1.** Etheral Methyl-oxygen bond cleavage reaction of 1-monoaroylnaphthalene **1aa** by AlCl<sub>3</sub><sup>[a]</sup>.

Entry	AlCl <sub>3</sub> mmol	Product Distribution (%) <sup>[b]</sup>		
		<b>1aa</b>	<b>2ba 2ab</b>	<b>2bb</b>
1	0.1	99	1/0	0
2	0.2	97	3/0	0
3	0.3	88	12/0	0
4	0.4	27	73/0	0
5	0.5	2	98(97)/0	0
6	1.0	1	99/0	0

<sup>[a]</sup>Reaction conditions: 1-Monoaroylnaphthalene **1aa** (0.1 mmol), AlCl<sub>3</sub> (0.1 - 1.0 mmol), CH<sub>2</sub>Cl<sub>2</sub> (0.25 ml), reflux, 30 min, N<sub>2</sub> atmosphere; <sup>[b]</sup>Calculated on the basis of <sup>1</sup>H NMR spectra. Isolated yield is given in parentheses.

$\beta$ -etheral substituent of 7-methoxy group unchanged was achieved even when ten equimolar amounts of AlCl<sub>3</sub> were employed against substrate **1aa** (Entry 6).

**Table 2** presents the results of treatment of non-arylated mother frame molecule of 2,7-dimethoxynaphthalene (**3aa**) and the analogous molecule of 3-monoaroyl-2,7-dimethoxynaphthalene **5aa** with AlCl<sub>3</sub>. Dimethoxynaphthalene (**3aa**) essentially gave none of alkyl ether-cleaved products (Entries 1 and 2). On the other hand, Methyl-oxygen bond in 3-monoaroyl-2,7-dimethoxynaphthalene **5aa** was readily cleaved at the 2-position leaving  $\beta$ (7)-methoxy group unchanged as well as 1-monoaroyl-2,7-dimethoxynaphthalene **1aa** (Entries 3 and 4).

The results of the reaction of monoaroyl-2,7-dimethoxynaphthalenes (**1aa** and **5aa**) and the ketonic-carbonyl-free analogue, 2,7-dimethoxynaphthalene (**3aa**), obviously indicate that the ether cleavage reaction of the monoaroyl-2,7-dimethoxynaphthalenes proceeds chemospecifically and regioselectively. Regioselective methyl-oxygen bond cleavage at 2-position of monoaroyl-2,7-dimethoxynaphthalenes **1aa** and **5aa** apparently demonstrates the presence of the neighboring effect of the aryl group.

Contrarily, no methyl-oxygen bond cleavage proceeded for 1,8-diaroyl-2,7-dimethoxynaphthalene (**7aa**) under the similar reaction conditions (**Table 3**, Entry 1). In refluxing CH<sub>2</sub>ClCH<sub>2</sub>Cl solution, only a trace amount of halfly ether-cleaved product **8ba** was detected (Entry 2). The ether cleavage reaction proceeded still scarcely even when ten equimolar amounts of AlCl<sub>3</sub> were employed (Entry 3). In refluxing toluene solution, 1,8-diaroyl-2,7-dimethoxynaphthalene **7aa** gave unidentified compounds with trace amounts of halfly and dualy methyl ether-cleaved products **8ba** and **8bb** (Entry 4).

**Table 2.** Etheral Methyl-oxygen bond cleavage reaction of dimethoxynaphthalene analogues **3aa/5aa** by AlCl<sub>3</sub><sup>[a]</sup>.

Entry	Substrate	AlCl <sub>3</sub> (mmol)	Product Distribution (%) <sup>[b]</sup>			
			<b>3aa 5aa</b>	<b>4ba</b>	<b>6ba / 6ab</b>	<b>4bb 6bb</b>
1	<b>3aa</b>	0.5	100	0		0
2	<b>3aa</b>	1.0	100	0		0
3	<b>5aa</b>	0.5	0		97(81) / 2	1
4	<b>5aa</b>	1.0	0		99/0	1

<sup>[a]</sup>Reaction conditions: Dimethoxynaphthalene analogue **3aa** or **5aa** (0.1 mmol), AlCl<sub>3</sub> (0.5 mmol or 1.0 mmol), CH<sub>2</sub>Cl<sub>2</sub> (0.25 ml), reflux, 30 min, N<sub>2</sub> atmosphere; <sup>[b]</sup>Calculated on the basis of <sup>1</sup>H NMR spectra.

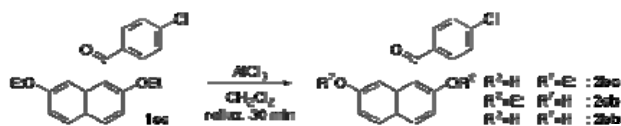
**Table 3.** Etheral Methyl-oxygen bond cleavage reaction of 1,8-diaroylnaphthalene **7aa** by AlCl<sub>3</sub><sup>[a]</sup>.

Entry	AlCl <sub>3</sub> (mmol)	solvent	Product Distribution (%) <sup>[b,c]</sup>		
			<b>7aa</b>	<b>8ba</b>	<b>8bb</b>
1	0.5	CH <sub>2</sub> Cl <sub>2</sub>	100	0	0
2	0.5	CH <sub>2</sub> ClCH <sub>2</sub> Cl	97	3	0
3	1.0	CH <sub>2</sub> ClCH <sub>2</sub> Cl	91	9	0
4 <sup>[d]</sup>	0.5	toluene	3 <sup>[c]</sup>	8 <sup>[c]</sup>	9 <sup>[c]</sup>

<sup>[a]</sup>Reaction conditions: 1,8-Diaroylnaphthalene **7aa** (0.1 mmol), AlCl<sub>3</sub> (0.5 mmol or 1.0 mmol), solvent (dichloromethane, 1,2-dichloroethane, or toluene; 0.25 ml), reflux, 30 min, N<sub>2</sub> atmosphere; <sup>[b]</sup>Calculated on the basis of <sup>1</sup>H NMR spectra; <sup>[c]</sup>Isolated yields; <sup>[d]</sup>Unidentified compounds were included.

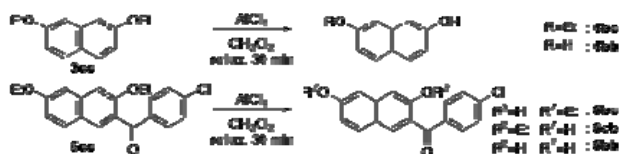
The distinct behavior that contrary to complete cleavage of  $\beta$ (2)-methyl ether bond of 1-monoaroyl-2,7-dimethoxynaphthalene **1aa**, the  $\beta$ -methyl ether bonds of 1,8-diaroyl-2,7-dimethoxynaphthalene **7aa** were essentially unchanged indicates the plausible origination of the chemospecificity from the facility of formation of the required conformation for methyl ether bond cleavage. The required conformation still remains indeterminable, however, the probable situation of AlCl<sub>3</sub> between ketonic carbonyl oxygen atom and ether oxygen atom might promote the scission of methyl-oxygen bond. In the case of 1,8-diaroyl-2,7-dimethoxynaphthalene **7aa**, the formation of the required conformation is presumably obstructed sterically compared to 1- and 3-monoaroyl-ated naphthalene derivatives.

The ethyl-oxygen bond cleavage reactions carried out against the corresponding diethoxynaphthalene homologues (**Table 4-6**) manifest the essentially similar reaction behaviors to those of 2,7-dimethoxynaphthalene

**Table 4.** Etheral ethyl-oxygen bond cleavage reaction of 1-monoaroylated naphthalene **1cc** by AlCl<sub>3</sub><sup>[a]</sup>.

Entry	AlCl <sub>3</sub> (mmol)	Product Distribution (%) <sup>[b]</sup>		
		1cc	2bc/2cb	2bb
1	0.3	28	72/0	0
2	0.5	0	86(80)/0	14(12)
3	1.0	0	54/0	46

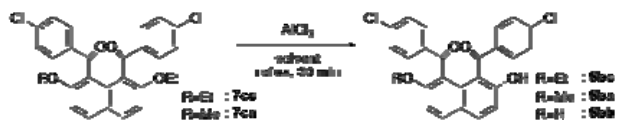
<sup>[a]</sup>Reaction conditions: 1-Monoaroylated naphthalene **1cc** (0.1 mmol), AlCl<sub>3</sub> (0.1 - 1.0 mmol), CH<sub>2</sub>Cl<sub>2</sub> (0.25 ml), reflux, 30 min, N<sub>2</sub> atmosphere; <sup>[b]</sup>Calculated on the basis of <sup>1</sup>H NMR spectra. Isolated yields are given in parentheses.

**Table 5.** Etheral ethyl-oxygen bond cleavage reaction of diethoxynaphthalene analogues **3cc/5cc** by AlCl<sub>3</sub><sup>[a]</sup>.

Entry	Substrate	AlCl <sub>3</sub> (mmol)	Product Distribution (%) <sup>[b]</sup>				
			3cc	5cc	4bc	6bc/6cb	4bb
1	3cc	0.5	100	0	-	0	
2	3cc	1.0	96	4	-	0	
3	5cc	0.5	0	-	54 (54)/0	46 (38)	
4	5cc	1.0	0	-	22 (22)/0	78 (77)	

<sup>[a]</sup>Reaction conditions: Dialkoxynaphthalene analogue **3cc** or **5cc** (0.1 mmol), AlCl<sub>3</sub> (0.5 mmol or 1.0 mmol), CH<sub>2</sub>Cl<sub>2</sub> (0.25 ml), reflux, 30 min, N<sub>2</sub> atmosphere; <sup>[b]</sup>Calculated on the basis of <sup>1</sup>H NMR spectra. Isolated yields are given in parentheses.

analogues (**1aa**, **3aa**, **5aa**, and **7aa**). Ethyl-oxygen bonds in 1-mono-, 3-mono-, and 1,8-diaroylnaphthalenes were somewhat easily cleaved than the methyl-oxygen bonds in the corresponding homologous molecules. According to the reaction conditions, halfly ether-cleaved products were obtained quantitatively or mixtures with dihydroxy derivatives were yielded. For example, 1-monoaroylated 2-hydroxy-7-ethoxynaphthalene (**2bc**) was solely formed by use of a smaller amount of AlCl<sub>3</sub> (Table 4, Entry 1 vs. 2). However, half ethyl ether cleavage of 1,8-diaroylated 2,7-diethoxynaphthalene (**7cc**) is rather difficult even under mild conditions (Table 6, Entries 2 and 6). The results of the cleavage reaction of unsymmetrically dialkoxylated molecule of 1,8-diaroyl-2-ethoxy-7-methoxy naphthalene (**7ca**) suggest that the methyl-oxygen bond cleavage is promoted after the cleavage of ethoxy group has completed (Table 6). In refluxing CH<sub>2</sub>ClCH<sub>2</sub>Cl solution, the ethyl-oxygen bond of 1,8-diaroyl-2-ethoxy-7-methoxynaphthalene (**7ca**) was cleaved in preference to the

**Table 6.** Alkyl ether cleavage reaction of 1,8-diaroylated naphthalene **7cc/7ca** by AlCl<sub>3</sub><sup>[a]</sup>.

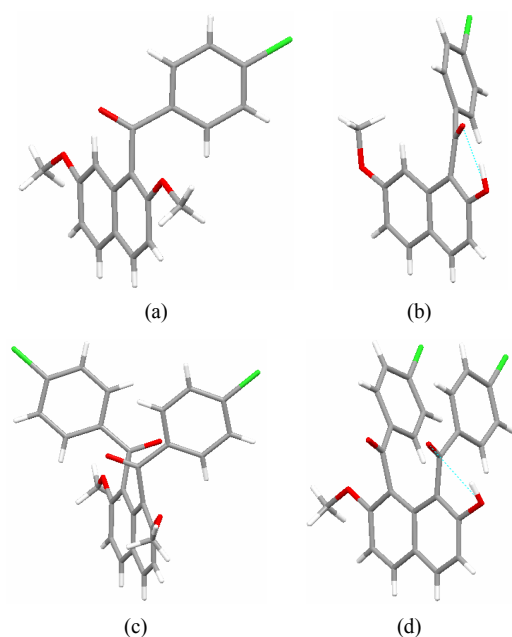
Entry	7	AlCl <sub>3</sub> (mmol)	Solvent	Product Distribution (%) <sup>[b]</sup>		
				7cc	7ca	8bc
1	cc	0.5	CH <sub>2</sub> Cl <sub>2</sub>	90	5	5
2	cc	1.0	CH <sub>2</sub> Cl <sub>2</sub>	77	6	17
3	ca	0.5	CH <sub>2</sub> Cl <sub>2</sub>	100	0	0
4	cc	0.5	CH <sub>2</sub> ClCH <sub>2</sub> Cl	43	35 (34)	22
5	cc	1.0	CH <sub>2</sub> ClCH <sub>2</sub> Cl	0	0	100
6 [c]	cc	1.0	CH <sub>2</sub> ClCH <sub>2</sub> Cl	33	33	34
7	ca	0.5	CH <sub>2</sub> ClCH <sub>2</sub> Cl	46	0	42
8	ca	1.0	CH <sub>2</sub> ClCH <sub>2</sub> Cl	15	0	70 (67)
9	cc	0.5	toluene	0	0	100 (95)
10	ca	0.5	toluene	0	7	93

<sup>[a]</sup>Reaction conditions: 1,8-Diaroylated naphthalene **7cc** or **7ca** (0.1 mmol), AlCl<sub>3</sub> (0.5 mmol or 1.0 mmol), solvent (dichloromethane, 1,2-dichloroethane, or toluene; 0.25 ml), reflux, 30 min, N<sub>2</sub> atmosphere; <sup>[b]</sup>Calculated on the basis of <sup>1</sup>H NMR spectra. Isolated yields are given in parentheses. [c] At r.t.

methyl-oxygen bond (Entries 7 and 8). In refluxing toluene solution, the two kinds of alkyl-oxygen bonds were thoroughly cleaved (Entry 10).

Figure 1 displays the crystal structures of aroylated 2,7-dimethoxynaphthalenes (**1aa** and **7aa**) [15,16] and aroylated 2-hydroxy-7-methoxynaphthalenes (**2ba** and **8ba**) [17,18]. In 1-monoaroyl-2,7-dimethoxynaphthalene **1aa**, the aroyl group non-coplanarly attaches to the naphthalene ring. On the other hand, the ketonic carbonyl moiety and hydroxy group in 1-monoaroyl-2-hydroxy-7-methoxynaphthalene **2ba** make a coplanar configuration with intramolecular hydrogen bond. The same type of intramolecular hydrogen bond between ketonic carbonyl moiety and hydroxy group is observed in X-ray crystal structure of 1,8-diaroyl-2-hydroxy-7-methoxynaphthalene **8ba**. However, in contrast to anti-orientation of 1,8-diaroylnaphthalene **7aa**, 1,8-diaroyl-2-hydroxy-7-methoxynaphthalene **8ba** has syn-orientation, *i.e.*, two aroyl groups are oriented in same directions. 1-Monoaroylnaphthalene **1aa** and 1,8-diaroylnaphthalene **7aa** have apparently same non-coplanar alignment around the aroyl connections. However, the steric hindrance around the ketonic carbonyl group might be meaningfully different to affect the rotational capability. The aroyl groups of 1,8-diaroylnaphthalene **7aa** are deviated out of the naphthalene ring plane more largely than 1-monoaroylnaphthalene **1aa**. The angles between C(carbonyl)-C(naphthalene) bond and naphthalene plane are 13.07° and 11.71° for **7aa** and 3.21° for **1aa**.

The bond lengths between ketonic carbonyl group and



**Figure 1.** X-ray crystal structures of aroylnaphthalenes: (a) molecule **1aa**; (b) molecule **2ba**; (c) molecule **7aa**; (d) molecule **8ba** (For clarity, an ethanol molecule is removed from the figure).

naphthalene ring of 1,8-diaroylnaphthalene **7aa** are longer than that of 1-monoaroylnaphthalene **1aa** (1.516 Å and 1.520 Å for **7aa**; 1.506 Å for **1aa**). About the 8-aroyle group adjacent to methoxy group in 1,8-diaroyl-2-hydroxy-7-methoxynaphthalene **8ba**, the corresponding angle and bond length are 9.13° and 1.509 Å, respectively.

These data indicate that steric hindrance around ketonic carbonyl group increases in the order of *monoaroyl*-dimethoxy derivative **1aa** < *diaroyl*-monohydroxymonomethoxy compound **8ba** < *diaroyl*-dimethoxy compound **7aa**. Furthermore, it led us to conjecture that the sterically fixed aroyle group is difficult to promote the methyl ether-cleavage. In other words, rotation ability of aroyle group presumably enables to cleave the methyl-oxygen bond by formation of the suitable arrangement of the intervening species.

### 3. Conclusion

Conclusively, the AlCl<sub>3</sub>-mediated scission behavior of alkyl-oxygen linkage of β-alkoxy groups in non-aroyleated, 1-mono-, and 1,8-diaroyl-2,7-dimethoxynaphthalenes (**3aa**, **1aa**, and **7aa**) shows distinct chemospecificity. Methyl-oxygen bond cleavage of 1-monoaroyl-2,7-dimethoxynaphthalene (**1aa**) smoothly and regioselectively proceeds at the 2-position, however, that of 1,8-diaroyl-naphthalene (**7aa**) is apparently deactivated like the inertness of 2,7-dimethoxynaphthalene (**3aa**). The single aroyle group promotes the ether cleavage of the

adjacent methoxy group, whereas the two adjacent aroyle groups situated at the peri-position disturb AlCl<sub>3</sub> mediated scission of the neighboring β-methyl ether group. Replacement of one or two methoxy groups with ethoxy ones a little blunts the chemospecificity and the regioselectivity of aroyleated naphthalenes. The observed specificity in the alkyl ether-cleavage reaction affords some hitherto-unknown aspects in structures and chemical properties relationship of these congested non-coplanar aromatic-rings-accumulated molecules.

## 4. Experimental

All reagents were of commercial quality and were used as received. Solvents were dried and purified using standard techniques.

### 4.1. Measurement

<sup>1</sup>H NMR spectra were recorded on a JEOL JNM-AL300 spectrometer (300 MHz) and a JEOL ECX400 spectrometer (400 MHz). Chemical shifts are expressed in ppm relative to internal standard of Me<sub>4</sub>Si (δ 0.00). <sup>13</sup>C NMR spectra were recorded on a JEOL JNM-AL300 spectrometer (75 MHz) and a JEOL ECX400 spectrometer (100 MHz). Chemical shifts are expressed in ppm relative to internal standard of CDCl<sub>3</sub> (δ 77.0). IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. Elemental analyses were performed on a Yanaco CHN CORDER MT-5 analyzer. High-resolution FAB mass spectra were recorded on a JEOL MStation (MS700) ion trap mass spectrometer in positive ion mode.

### 4.2. Typical Procedure of Methyl-Oxygen Bond Cleavage Reaction Mediated by AlCl<sub>3</sub>

To a solution of 1-(4-chlorobenzoyl)-2,7-dimethoxynaphthalene (**1aa**, 0.1 mmol, 32.7 mg) and in dichloromethane (0.25 ml), AlCl<sub>3</sub> (0.5 mmol, 66.7 mg) was added by portions at ambient temperature under nitrogen atmosphere. After the reaction mixture was stirred in the refluxing solution for 30 min, it was poured into iced water (20 ml) and the mixture was extracted with CHCl<sub>3</sub> (15 ml × 3). The combined extracts were washed with sat. NaCl aq. and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to give solid. The crude product was purified by recrystallization (**2ca**, hexane, isolated yield 75%).

Other ether cleavage reactions were undertaken by essentially the same procedure as above.

### 4.3. Synthetic Procedure of Aroylnaphthalenes

**1-(4-Chlorobenzoyl)-2,7-dimethoxynaphthalene (1aa).** To a solution of 2,7-dimethoxynaphthalene (0.200 mmol, 68.2 mg) and 4-chlorobenzoyl chloride (0.22 mmol, 38.5

mg) in dichloromethane (0.5 ml), AlCl<sub>3</sub> (0.22 mmol, 29.3 mg) was added by portions at 0°C under nitrogen atmosphere. After the reaction mixture was stirred at r.t. for 3 h, it was poured into iced water (20 ml) and the mixture was extracted with CHCl<sub>3</sub> (15 ml × 3). The combined extracts were washed with 2 M NaOH aq., sat. NaCl aq. and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to give powdery product. The crude product was purified by recrystallization (hexane, isolated yield 78%).

#### 3-(4-Chlorobenzoyl)-2,7-dimethoxynaphthalene (5aa).

The title compound was prepared by treatment of a mixture of 2,7-dimethoxynaphthalene (10 mmol; 1.88 g) and 4-chlorobenzoic acid (11 mmol 1.72 g) with phosphorus pentoxide–methanesulfonic acid mixture (P<sub>2</sub>O<sub>5</sub>-MsOH [1/10 w/w]; 10 ml) at 60°C for 8 hours. After the reaction mixture was stirred at 353 K for 8 h, the mixture was extracted with CHCl<sub>3</sub> (10 ml × 3). The combined extracts were washed with 2 M aqueous NaOH followed by washing with brine. The organic layers thus obtained were dried over anhydrous MgSO<sub>4</sub>. The solvent was removed under reduced pressure to give cake. The crude product was purified by recrystallization (ethanol, isolated yield 56%).

**1,8-Bis(4-chlorobenzoyl)-2,7-dimethoxynaphthalene (7aa).** To a solution of 2,7-dimethoxynaphthalene (0.200 mmol, 68.2 mg) and 4-chlorobenzoyl chloride (0.66 mmol, 116 mg) in dichloromethane (0.5 ml), TiCl<sub>4</sub> (1.8 mmol, 341 mg) was added by portions at r.t. under nitrogen atmosphere. After the reaction mixture was stirred at r.t. for 3 h, it was poured into iced water (20 ml) and the mixture was extracted with CHCl<sub>3</sub> (15 ml × 3). The combined extracts were washed with 2 M NaOH aq., sat. NaCl aq. and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to give powdery product. The crude product was purified by recrystallization (ethanol, isolated yield 88%).

**1,8-Bis(4-chlorobenzoyl)-2,7-diethoxynaphthalene (7cc).** To a solution of TiCl<sub>4</sub> (180 mmol, 34.2 g) and 4-chlorobenzoyl chloride (60 mmol, 10.5 g) in dichloromethane (25 ml), 2,7-diethoxynaphthalene/dichloromethane (20 mmol, 4.33 g/25 ml) was added by portions at r.t. under nitrogen atmosphere. After the reaction mixture was stirred at r.t. for 3 h, it was poured into iced water (200 ml) and the mixture was extracted with CHCl<sub>3</sub> (40 ml × 3). The combined extracts were washed with 2 M NaOH aq., sat. NaCl aq. and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to give powdery pale white product (94% yield). The crude product was purified by recrystallization (chloroform/ethanol, isolated yield 62%).

**1,8-Bis(4-chlorobenzoyl)-2-ethoxy-7-methoxynaphthalene (7ca).** To a solution of 1-(4-chlorobenzoyl)-2-ethoxy-7-methoxynaphthalene (0.200 mmol, 68.2 mg)

and 4-chlorobenzoyl chloride (0.44 mmol, 77.0 mg) in dichloromethane (0.5 ml), TiCl<sub>4</sub> (1.32 mmol, 248 mg) was added by portions at r.t. under nitrogen atmosphere. After the reaction mixture was stirred at r.t. for 3 h, it was poured into iced water (20 ml) and the mixture was extracted with CHCl<sub>3</sub> (15 ml × 3). The combined extracts were washed with 2 M NaOH aq., sat. NaCl aq. and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to give powdery product. The crude product was purified by silicagel column chromatography (hexane : AcOEt = 1 : 1, isolated yield 87%).

#### 4.4. Identification of the Products

##### 1-(4-Chlorobenzoyl)-2,7-dimethoxynaphthalene (1aa).

Colorless needle (hexane), Mp 121.5°C - 122°C; IR (KBr): 1667, 1628, 1586, 1512 cm<sup>-1</sup>; <sup>1</sup>H NMR δ (300 MHz, CDCl<sub>3</sub>): 3.73 (3H, s), 3.79 (3H, s), 6.78 (1H, d, *J* = 2.4 Hz), 7.02 (1H, dd, *J* = 2.4, 9.0 Hz), 7.16 (1H, d, *J* = 9.0 Hz), 7.39 (2H, d, *J* = 8.4 Hz), 7.72 (1H, d, *J* = 9.0 Hz), 7.78 (2H, d, *J* = 8.4 Hz), 7.87 (1H, d, *J* = 9.0 Hz) ppm; <sup>13</sup>C NMR δ (75 MHz, CDCl<sub>3</sub>): 55.168, 56.239, 101.88, 110.05, 117.15, 121.06, 124.34, 128.86, 129.72, 130.87, 131.28, 132.94, 136.45, 139.71, 155.02, 158.96, 196.81 ppm; Calcd for C<sub>19</sub>H<sub>15</sub>O<sub>3</sub>Cl: C, 69.83%; H, 4.63%; Found: C, 69.61%; H, 4.74%.

**1-(4-Chlorobenzoyl)-2-hydroxy-7-methoxynaphthalene (2ba).** Yellow platelet (hexane), Mp 118°C - 118.5°C; IR (KBr): 3434, 1623, 1583, 1513, 1214, 843 cm<sup>-1</sup>; <sup>1</sup>H NMR δ (300 MHz, CDCl<sub>3</sub>): 3.37 (s, 3H), 6.58 (d, 1H, *J* = 2.4 Hz), 6.91 (dd, 1H, *J* = 2.4, 9.0 Hz), 7.07 (d, 1H, *J* = 9.0 Hz), 7.40 (d, 2H, *J* = 8.7 Hz), 7.58 (d, 2H, *J* = 8.7 Hz), 7.63 (d, 1H, *J* = 9.0 Hz), 7.85 (d, 1H, *J* = 9.0 Hz), 11.35 (s, 1H) ppm; <sup>13</sup>C NMR δ (75 MHz, CDCl<sub>3</sub>): 54.5, 106.5, 113.4, 115.8, 116.4, 123.7, 128.9, 130.2, 130.7, 133.8, 136.5, 138.7, 138.8, 158.2, 162.6, 199.1 ppm; Anal. Calcd for C<sub>18</sub>H<sub>13</sub>ClO<sub>3</sub>: C 69.13, H 4.19. Found: C 69.11, H 4.09.

**1-(4-Chlorobenzoyl)-2,7-dihydroxynaphthalene (2bb).** Yellow oil; IR (KBr): 3398, 1653, 1625, 1586, 1515, 1240, 1215 cm<sup>-1</sup>; <sup>1</sup>H NMR δ (400 MHz, CDCl<sub>3</sub>): 5.18 (1H, s), 6.61 (1H, d, *J* = 2.2 Hz), 6.89 (1H, dd, *J* = 2.2, 8.6 Hz), 7.07 (1H, d, *J* = 8.8 Hz), 7.39 (2H, d, *J* = 8.2 Hz), 7.60 (2H, d, *J* = 8.2 Hz), 7.66 (1H, d, *J* = 8.8 Hz), 7.85 (1H, d, *J* = 8.8 Hz), 11.14 (1H, s) ppm; <sup>13</sup>C NMR δ (100 MHz, CDCl<sub>3</sub>): 109.62, 113.16, 115.07, 116.55, 123.75, 128.95, 130.76, 130.97, 133.92, 136.48, 138.26, 139.07, 154.53, 162.33, 198.71 ppm; HRMS (FAB; *m*-nitrobenzyl alcohol [*m*-NBA]) *m/z*: [M + H]<sup>+</sup>; Calcd for C<sub>17</sub>H<sub>12</sub>O<sub>3</sub>Cl: 299.0475; Found: 299.0502.

**3-(4-Chlorobenzoyl)-2,7-dimethoxynaphthalene (5aa).** Yellow needle (EtOH), Mp 152°C; IR (KBr): 1657, 1622, 1588, 1503 cm<sup>-1</sup>; <sup>1</sup>H NMR δ (300MHz, CDCl<sub>3</sub>): 3.82 (3H, s), 3.94 (3H, s), 7.05 (1H, dd, *J* = 2.4, 8.9 Hz), 7.10

(1H, d,  $J = 2.4$  Hz), 7.13 (1H, s), 7.40 (2H, d,  $J = 8.7$  Hz), 7.69 (1H, d,  $J = 8.7$  Hz), 7.77 (2H, d,  $J = 8.7$  Hz), 7.79 (1H, s) ppm;  $^{13}\text{C}$  NMR  $\delta$  (75 MHz,  $\text{CDCl}_3$ ): 55.349, 55.522, 105.03, 105.44, 117.17, 123.20, 127.41, 128.50, 130.08, 130.24, 131.22, 137.28, 138.83, 139.20, 155.67, 159.47, 194.81 ppm; Calcd for  $\text{C}_{19}\text{H}_{15}\text{O}_3\text{Cl}$ : C, 69.83%; H, 4.63%. Found: C, 69.75%; H, 4.83%.

**3-(4-Chlorobenzoyl)-2-hydroxy-7-methoxynaphthalene (6ba).** Yellow needle (AcOEt + hexane); Mp 177°C; IR (KBr): 3470, 1643, 1594, 1561, 1511  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  (300 MHz,  $\text{CDCl}_3$ ): 3.93 (3H, s), 6.94 (1H, br), 6.96 (1H, d,  $J = 8.4, 2.4$  Hz), 7.23 (1H, s), 7.52 (2H, d,  $J = 8.9$  Hz), 7.57 (1H, d,  $J = 8.4$  Hz), 7.69 (2H, d,  $J = 9.0$  Hz), 7.99 (1H, s), 11.26 (1H, s) ppm;  $^{13}\text{C}$  NMR  $\delta$  (75 MHz,  $\text{CDCl}_3$ ): 55.383, 103.68, 111.25, 117.80, 118.50, 122.24, 128.72, 130.78, 131.24, 136.09, 136.36, 138.43, 140.07, 158.17, 161.09, 200.01 ppm; HRMS (FAB; *m*-NBA)  $m/z$ :  $[\text{M} + \text{H}]^+$ ; Calcd for  $\text{C}_{18}\text{H}_{14}\text{O}_3\text{Cl}$ : 313.0631. Found: 313.0624.

**3-(4-Chlorobenzoyl)-2,7-dihydroxynaphthalene (6bb).** Yellow powder (AcOEt + hexane), Mp 148°C - 148.5°C; IR (KBr): 3422, 1648, 1593, 1561, 1524  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  (400 MHz,  $\text{CDCl}_3$ ): 6.01 (1H, s), 6.94 (1H, dd,  $J = 8.6, 2.4$  Hz), 6.99 (1H, d,  $J = 2.4$  Hz), 7.17 (1H, s), 7.53 (2H, d,  $J = 8.4$  Hz), 7.63 (1H, d,  $J = 9.2$  Hz), 7.69 (2H, d,  $J = 8.8$  Hz), 8.02 (1H, s), 11.22 (1H, s) ppm;  $^{13}\text{C}$  NMR  $\delta$  (100 MHz,  $\text{CDCl}_3$ ): 107.64, 110.70, 116.84, 118.76, 122.33, 128.79, 130.81, 132.00, 136.38, 136.50, 138.55, 140.02, 157.43, 158.03, 200.13 ppm; HRMS (FAB; *m*-NBA)  $m/z$ :  $[\text{M} + \text{H}]^+$ ; Calcd for  $\text{C}_{17}\text{H}_{12}\text{O}_3\text{Cl}$ : 299.0475; Found: 299.0501.

**1,8-Bis(4-chlorobenzoyl)-2,7-dimethoxynaphthalene (7aa).** Yellow needle (EtOH + AcOEt), Mp 216°C - 217°C; IR (KBr): 1665, 1611, 1588, 1512  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  (300MHz,  $\text{CDCl}_3$ ): 3.70 (6H, s), 7.21 (2H, d,  $J = 9.0$  Hz), 7.33 (4H, d,  $J = 8.6$  Hz), 7.64 (4H, d,  $J = 8.6$  Hz), 7.96 (2H, d,  $J = 9.0$  Hz) ppm;  $^{13}\text{C}$  NMR  $\delta$  (75 MHz,  $\text{CDCl}_3$ ): 56.297, 111.07, 120.57, 125.45, 128.37, 129.90, 130.40, 132.43, 137.07, 138.99, 156.39, 195.95 ppm; Calcd for  $\text{C}_{26}\text{H}_{18}\text{O}_4\text{Cl}_2$ : C, 67.11%; H, 3.90%. Found: C, 67.10%; H, 4.09%.

**1,8-Bis(4-chlorobenzoyl)-2-hydroxy-7-methoxynaphthalene (8ba).** Yellow platelet (EtOH), Mp 232.5°C - 233.5°C; IR (KBr): 1643, 1612, 1587, 1510, 1278, 1089, 831  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  (300 MHz,  $\text{CDCl}_3$ ): 3.60 (s, 3H), 6.91 (d,  $J = 8.7$  Hz, 2H), 7.20 - 7.10 (m, 6H), 7.33 (d,  $J = 8.7$  Hz, 2H), 7.94-7.86 (m, 2H), 9.34 (s, 1H) ppm;  $^{13}\text{C}$  NMR  $\delta$  (75 MHz,  $\text{CDCl}_3$ ): 56.0, 110.6, 117.3, 121.3, 124.6, 127.7, 128.5, 130.5, 131.9, 132.6, 133.7, 135.0, 136.3, 136.8, 138.4, 139.7, 157.6, 159.5, 195.1, 196.8 ppm; HRMS (FAB; *m*-NBA)  $m/z$ :  $[\text{M} + \text{H}]^+$ ; calcd for  $\text{C}_{25}\text{H}_{17}\text{O}_4\text{Cl}_2$ , 451.0504; found, 451.0520. Anal. Calcd for  $\text{C}_{25}\text{H}_{16}\text{O}_4\text{Cl}_2$ : C 66.53, H 3.57. Found: C 66.31, H 3.76.

**1,8-Bis(4-chlorobenzoyl)-2,7-dihydroxynaphthalene**

**(8bb).** Yellow powder (AcOEt), Mp 302.2°C - 307.4°C; IR (KBr): 3160 (O-H), 1643 (C=O), 1587 (Ar), 1511 (Ar)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  (300 MHz,  $\text{CDCl}_3$ ): 7.11 - 7.15 (4H, broad), 7.14 (2H,  $J = 8.7$  Hz), 7.25 - 7.28 (4H, m), 7.93 (2H, d,  $J = 9.0$  Hz), 11.13 (2H, s) ppm.  $^1\text{H}$  NMR  $\delta$  (300 MHz, DMSO): 7.09 (2H, d,  $J = 8.7$  Hz), 7.49 (4H, d,  $J = 8.4$  Hz), 7.61 (4H, d,  $J = 8.7$  Hz), 7.93 (2H, d,  $J = 9.0$  Hz), 10.12 (2H, s) ppm;  $^{13}\text{C}$  NMR  $\delta$  (75 MHz, DMSO): 115.44, 117.61, 123.76, 128.79, 131.19, 132.73, 137.65, 137.96, 155.04, 196.56 ppm; HRMS (FAB; *m*-NBA)  $m/z$ :  $[\text{M} + \text{H}]^+$ , calcd for  $\text{C}_{24}\text{H}_{14}\text{Cl}_2\text{O}_4\text{Na}$ , 459.0167; found, 459.0132.

**1-(4-Chlorobenzoyl)-2,7-diethoxynaphthalene (1cc).** Colorless needle (hexane), Mp 124°C - 125°C; IR (KBr): 1660, 1625, 1582, 1514, 1242, 1216  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  (400 MHz,  $\text{CDCl}_3$ ): 1.09 (3H, t,  $J = 6.8$  Hz), 1.36 (3H, t,  $J = 7.2$  Hz), 3.96 (2H, q,  $J = 10, 14$  Hz), 4.04 (2H, q,  $J = 10, 14$  Hz), 6.83 (1H, d,  $J = 2.4$  Hz), 7.01 (1H, dd,  $J = 2.4, 9.2$  Hz), 7.10 (1H, d,  $J = 8.8$  Hz), 7.38 (2H, d,  $J = 8.6$  Hz), 7.70 (1H, d,  $J = 8.8$  Hz), 7.76 (2H, d,  $J = 8.6$  Hz), 7.83 (1H, d,  $J = 9.2$  Hz) ppm;  $^{13}\text{C}$  NMR  $\delta$  (100 MHz,  $\text{CDCl}_3$ ): 14.577, 14.596, 63.394, 64.805, 102.78, 111.20, 117.33, 121.41, 124.32, 128.72, 129.65, 130.72, 131.30, 133.12, 136.99, 139.40, 154.63, 158.35, 196.97 ppm; HRMS (FAB; *m*-NBA)  $m/z$ :  $[\text{M} + \text{H}]^+$ ; Calcd for  $\text{C}_{21}\text{H}_{20}\text{O}_3\text{Cl}$ : 355.1101; Found: 355.1061.

**1-(4-Chlorobenzoyl)-7-ethoxy-2-hydroxynaphthalene (2cb).** Glassy yellow solid (oil); IR (KBr): 3239, 1656, 1619, 1594, 1571, 1513, 1203  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  (400 MHz,  $\text{CDCl}_3$ ): 1.22 (3H, t,  $J = 7.0$  Hz), 3.52 (2H, q,  $J = 10, 14$  Hz), 6.55 (1H, d,  $J = 2.5$  Hz), 6.90 (1H, dd,  $J = 2.5, 8.8$  Hz), 7.05 (1H, d,  $J = 8.8$  Hz), 7.40 (2H, d,  $J = 8.4$  Hz), 7.57 (2H, d,  $J = 8.4$  Hz), 7.61 (1H, d,  $J = 9.2$  Hz), 7.83 (1H, d,  $J = 9.2$  Hz), 11.29 (1H, s) ppm;  $^{13}\text{C}$  NMR  $\delta$  (100 MHz,  $\text{CDCl}_3$ ): 14.510, 62.898, 107.08, 113.42, 116.25, 116.30, 123.60, 128.93, 130.15, 130.65, 133.86, 136.52, 138.62, 138.78, 138.80, 157.61, 162.48, 199.07 ppm; HRMS (FAB; *m*-NBA)  $m/z$ :  $[\text{M} + \text{H}]^+$ ; Calcd for  $\text{C}_{19}\text{H}_{16}\text{O}_3\text{Cl}$ : 327.0788; Found: 327.0784.

**3-(4-Chlorobenzoyl)-2,7-diethoxynaphthalene (5cc).** Yellow oil (AcOEt+hexane); IR (KBr): 1663, 1626, 1585, 1504, 1211  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  (400 MHz,  $\text{CDCl}_3$ ): 1.14 (3H, t,  $J = 6.8$  Hz), 1.49 (3H, t,  $J = 6.8$  Hz), 4.04 (2H, q,  $J = 10, 14$  Hz), 4.16 (2H, q,  $J = 10, 14$  Hz), 7.04 (1H, dd,  $J = 2.4, 8.8$  Hz), 7.05 (1H, br), 7.07 (1H, s), 7.40 (2H, d,  $J = 8.4$  Hz), 7.69 (1H, d,  $J = 8.8$  Hz), 7.74 (2H, d,  $J = 8.4$  Hz), 7.83 (1H, s) ppm;  $^{13}\text{C}$  NMR  $\delta$  (100 MHz,  $\text{CDCl}_3$ ): 14.234, 14.777, 63.528, 63.804, 105.65, 106.06, 106.08, 117.35, 123.20, 127.61, 128.31, 130.14, 130.36, 130.99, 137.06, 137.46, 138.83, 154.95, 158.78, 195.18 ppm; HRMS (FAB; *m*-NBA)  $m/z$ :  $[\text{M} + \text{H}]^+$ ; Calcd for  $\text{C}_{21}\text{H}_{20}\text{O}_3\text{Cl}$ : 355.1101; Found: 355.1112.

**3-(4-Chlorobenzoyl)-7-ethoxy-2-hydroxynaphthalene (6cb).** Yellow needle, ( $\text{CHCl}_3$  + hexane); Mp 151°C;

IR (KBr): 3448, 1638, 1593, 1560, 1509, 1236, 1209  $\text{cm}^{-1}$ ;  $^1\text{H NMR } \delta$  (300 MHz,  $\text{CDCl}_3$ ): 1.49 (3H, t,  $J = 7.0$  Hz), 4.17 (2H, q,  $J = 11, 14$  Hz), 6.95 (1H, brs), 6.95 (1H, dd,  $J = 8.8, 2.4$  Hz), 7.22 (1H, s), 7.52 (2H, d,  $J = 8.4$  Hz), 7.59 (1H, d,  $J = 8.7$  Hz), 7.69 (2H, d,  $J = 8.4$  Hz), 8.00 (1H, s), 11.26 (1H, s) ppm;  $^{13}\text{C NMR } \delta$  (400 MHz,  $\text{CDCl}_3$ ): 14.663, 63.699, 104.40, 111.22, 118.09, 118.52, 122.24, 128.77, 128.92, 130.81, 131.27, 136.15, 138.46, 140.21, 158.19, 160.53, 200.05 ppm; HRMS (FAB; *m*-NBA)  $m/z$ :  $[\text{M} + \text{H}]^+$ ; Calcd for  $\text{C}_{19}\text{H}_{16}\text{O}_3\text{Cl}$ : 327.0788. Found: 327.0784.

**1,8-Bis(4-chlorobenzoyl)-2,7-diethoxynaphthalene (7cc).** Colorless needle (Chloroform/EtOH), Mp 214.1°C - 216.2°C; IR (KBr): 1660 (C=O), 1610(Ar), 1510 (Ar), 1274 (O-Et)  $\text{cm}^{-1}$ ;  $^1\text{H NMR } \delta$  (300 MHz,  $\text{CDCl}_3$ ): 0.96 (6H, t,  $J = 6.9$  Hz), 3.97 (4H, q,  $J = 7.2$  Hz), 7.15 (2H, d,  $J = 9.0$  Hz), 7.34 (4H, d,  $J = 8.4$  Hz), 7.67 (4H, d,  $J = 8.4$  Hz), 7.92 (2H, d,  $J = 8.7$  Hz) ppm;  $^{13}\text{C NMR } \delta$  (100 MHz,  $\text{CDCl}_3$ ): 14.52, 64.48, 112.19, 121.06, 125.53, 128.38, 130.45, 132.52, 137.78, 138.78, 156.10, 196.63 ppm.; HRMS (FAB; *m*-NBA)  $m/z$ :  $[\text{M} + \text{H}]^+$ ; calcd for  $\text{C}_{28}\text{H}_{23}\text{Cl}_2\text{O}_4$ , 493.0973; found, 493.0958.

**1,8-Bis(4-chlorobenzoyl)-2-ethoxy-7-methoxynaphthalene (7ca).** Pale yellow needle (silicagel column, hexane: AcOEt = 1:1), Mp 209.3°C - 210.1°C; IR (KBr): 1663, 1609, 1587, 1510, 1267, 1047, 838  $\text{cm}^{-1}$ ;  $^1\text{H NMR } \delta$  (300 MHz,  $\text{CDCl}_3$ ): 0.96 (t,  $J = 7.0$  Hz, 3H), 3.70 (s, 3H), 3.97 (q,  $J = 10, 14$  Hz, 2H), 7.21 - 7.14 (m, 2H), 7.97 - 7.91 (m, 2H), 7.33 (d,  $J = 8.7$  Hz, 4H), 7.67 - 7.63 (m, 4H) ppm;  $^{13}\text{C NMR } \delta$  (75 MHz,  $\text{CDCl}_3$ ): 14.4, 56.4, 65.0, 111.2, 112.3, 121.1, 121.3, 125.6, 128.3, 128.4, 130.2, 130.4, 130.5, 132.3, 132.4, 137.3, 137.7, 138.8, 139.0, 156.0, 156.5, 196.0, 196.1 ppm; HRMS (FAB; *m*-NBA)  $m/z$ :  $[\text{M} + \text{H}]^+$ ; calcd for  $\text{C}_{27}\text{H}_{21}\text{O}_4\text{Cl}_2$ , 479.0817; found, 479.0822. Anal. Calcd for  $\text{C}_{27}\text{H}_{20}\text{O}_4\text{Cl}_2$ : C, 67.65; H, 4.21. Found: C, 67.45; H, 4.10.

**1,8-Bis(4-chlorobenzoyl)-2-ethoxy-7-hydroxynaphthalene (8bc).** Yellow powder (silicagel column, AcOEt), Mp 200.3°C - 203.9°C; IR (KBr): 3378, 1644, 1611, 1589, 1567, 1510, 1208, 1225, 1281, 1090, 803  $\text{cm}^{-1}$ ;  $^1\text{H NMR } \delta$  (400 MHz,  $\text{CDCl}_3$ ): 0.85 (3H, t,  $J = 6.8$  Hz), 3.89 (2H, q,  $J = 10, 14$  Hz), 6.88 (2H, d,  $J = 8.0$  Hz), 7.07 (1H, d,  $J = 8.8$  Hz), 7.09 - 7.16 (3H, m), 7.18 (2H, d,  $J = 8.4$  Hz), 7.31 (2H, d,  $J = 8.4$  Hz), 7.88 (1H, d,  $J = 8.4$  Hz), 7.90 (1H, d,  $J = 8.8$  Hz), 9.53 (1H, s) ppm;  $^{13}\text{C NMR } \delta$  (100 MHz,  $\text{CDCl}_3$ ): 14.043, 69.491, 111.33, 113.98, 117.07, 121.13, 124.39, 127.46, 128.42, 130.31, 131.98, 132.68, 133.70, 135.09, 136.54, 136.73, 138.13, 139.58, 157.08, 159.57, 195.59, 197.12 ppm; HRMS (FAB; *m*-NBA)  $m/z$ :  $[\text{M} + \text{H}]^+$ , calcd for  $\text{C}_{26}\text{H}_{19}\text{Cl}_2\text{O}_4$ , 465.0660; found 465.0629.

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