# Synthesis of Functionalized Arenes based on [3+3] Cyclizations of 1,3-Bis(silyloxy)-1,3-butadienes with Sulfone-, Ester-, Amino-, and Nitro- substituted Enones and Antimicrobial Activity of Pyridyl Enones

**DISSERTATION**

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**Eidesstattliche Erklärung**

Hiermit erkläre ich, die vorliegende Dissertationsschrift eigenständig und nur unter Verwendung der angegebenen Hilfsmittel und Literaturquellen angefertigt zu haben.

Abdol Majid Riahi

Rostock, 30. März 2009

*Affectionately Dedicated to*

*"My Wife Arezoo"*

*&*

*"My parents, Brothers and Sisters"*

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# Acknowledgements

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*Abdol Majid Riahi 06.April 2009*

# List of used abbreviations

| | |
|---|---|
| Ar | Aromatic |
| APT | Attached Proton Test |
| ATCC | American Type Culture Collection |
| *n*BuLi | *n*-Butylithium |
| DEPT | Distortionless Enhancement by Polarisation Transfer |
| EI | Electronic Ionization |
| ESI | Electrospray Ionization |
| EtOAc | Ethylacetate |
| HRMS | High Resolution Mass Spectroscopy |
| IR | Infrared spectroscopy |
| LDA | Lithium diisopropylamide |
| MS | Mass Spectrometry |
| Ph | Phenyl |
| $NEt_3$ | Triethylamine |
| NMR | Nuclear Magnetic Resolution |
| HMQC | Heteronuclear Multiple Quantum Coherence |
| HMBC | Heteronuclear Multiple Bond Correlation |
| COSY | Correlated Spectroscopy |
| NOESY | Nuclear Overhauser and Exchange Spectroscopy |
| $Me_3SiOTf$ | Trimethylsilyl-trifluoro methanesulfonate |
| $Me_3SiCl$ | Trimethylsilylchloride |
| mp. | Melting point |
| RCM | Ring Closing Metathesis |
| TBAI | Tetrabutyl amonium iodie |

| | |
|---|---|
| TFA | Trifluoroacetic acid |
| $Tf_2O$ | Trifluoromethanesulfonic anhydride |
| THF | Tetrahydrofurane |
| TLC | Thin Layer Chromatography |
| TMS | Trimethylsilane |
| UV | Ultraviolet Spectroscopy |

# General Introduction

The impact of chemistry is ubiquitous in our everyday lives although the average citizen may not recognize or appreciate that fact. Advances in the chemical sciences are directly responsible for many of the improvements in the standard of living we enjoy. In no area is this truer than in modern medicine, especially as it relates to the development of new drugs.

Although the pharmaceutical industry is less than two centuries old, its roots are firmly embedded in the chemical industry [1]. In fact, in its early history, the pharmaceutical industry was considered a special branch of the chemical industry, especially in Europe where large chemical companies also were the leading manufacturers of medicines. During the first century of the drug industry, chemistry was involved in two primary ways. One was the domain of the analytical chemist who was concerned with the isolation and purification of the active ingredients of medicinal plants. One of the earliest examples of this was in 1815 when morphine was isolated from opium extract. A modern example of this type of chemistry is the isolation of taxol (paclitaxel) from the bark of the Pacific Yew tree [2]. The second domain was that of the synthetic chemist who was concerned both with making compounds that occur in nature and with creating new compounds. A modern example of this type of chemistry is the invention by Robert A. Holton of the semi-synthesis process for making taxol, which allowed taxol to be used clinically on a large scale, thus saving or extending millions of lives [3], [4], [5].

Modern chemistry is characterized by the ability to both examine and manipulate matter at the molecular scale. The modern synthetic chemist is increasingly able to construct molecules with specific atoms in specific locations and having a particular structure or shape. Synthetic organic chemistry is one of the cornerstones of the modern pharmaceutical industry. Synthetic organic chemists work hand-in-hand with biologists and doctors to invent, manufacture and test new chemical compounds that can treat human disease. The tremendous improvements in life spans are a testament to the success of this partnership.

My studies are focused on the development of new and reliable synthetic strategies and their application to the preparation of natural products analogues, and pharmacologically active

carba- and heterocycles. The target structures include functionalized arenes like arylsulfonyl-phenols, nitro-substituted biaryls, benzodioates, and also pyridyl-enones

# Summary

A significant part of the present dissertation has been recently published. The work presented in this dissertation is concerned with the synthesis of functionalized arenes based on [3+3] cyclizations of 1,3-bis(silyloxy)-1,3-butadienes and related transformations. Regioselective syntheses of highly functionalized of 4-(arylsulfonyl)phenols, benzodioates, amino- and nitro-substituted biaryls based on [3+3] cyclocondensations with 1,3-bis(silyloxy)-1,3-butadienes and also the synthesis and antimicrobial activity of functionalized 4-hydroxypyridyl-enones is reported.

**Synthesis of Functionalized Arenes based on [3+3] Cyclizations of 1,3-Bis(silyloxy)-1,3-butadienes with Sulfone-, Ester-, amino-, and Nitro- substituted Enones and Antimicrobial Activity of Pyridyl Enones**

**1**. This chapter includes the synthesis of amino- and nitro-substituted biaryls **9, 10a-l** based on formal $TiCl_4$ mediated [3+3] regioselective cyclocondensations of masked dianions, with 3-nitroaryl-3-silyloxy-2-en-1-ones, a methodology developed by Chan and coworkers, and subsequent reduction using $H_2$ and Pd/C.

**2.** Chapter two deals with the formal [3+3] cyclizations of 1,3-bis(silyl enol ethers) with 2-arylsulfonyl-3-ethoxy-2-en-1-ones which afforded regioselectively 4-(arylsulfonyl)phenols **13a-ag**.

**3.** In this chapter, I have described the regioselective synthesis of 4-acyl-1-hydroxy-2,3-benzodioates **17a-al** by chelation-controlled [3+3] annulation of 3-acyl-4-ethoxy-2-oxo-3-enoates with 1,3-bis(trimethylsilyloxy)-1,3-butadienes.

**4**. In chapter 4, I have reported the synthesis and antimicrobial activity of 4-hydroxy-4-(pyridyl)alk-3-en-2-ones **21a-f, 22a-e.**

**5**. This chapter includes the experimental, spectroscopic data and full characterization of all new products.

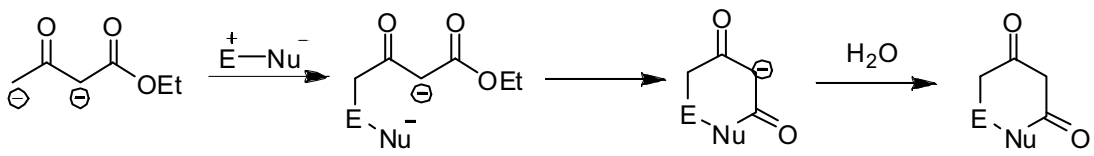
# 1 Synthesis of amino- and nitro-substituted biaryls based on regioselective cyclocondensations of 1,3-bis(silyloxy)-1,3-butadienes with 3-nitroaryl-3-silyloxy-2-en-1-ones

## 1.1 Synthesis of 4-alkyl-1,3-bis(trimethylsiloxy)buta-1,3-dienes

### 1.1.1 Introduction

The cyclization of 1,3-dicarbonyl compounds with electrophiles prepare a convenient approach to various heterocyclic and carbacyclic ring systems. 1,3-dicarbonyl compounds can react in two ways, free dianions and masked dianions. Free dianions are organic substrates containing two delocalized negative charges and they can be generated by reaction of 1,3-dicarbonyl compounds in the presence of strong base, such as LDA or *n*-BuLi [6]. To avoid the high basicity and reactivity of free dianions, these are masked by using some masking agents. 1,3-Bis(silyl enol ethers) commonly known as masked dianions, are considered as the synthetic equivalent of the corresponding 1,3-dicarbonyl compounds [7]. The observed regioselectivity for reactions of free and masked dianions is in most of the cases the same. The functionalization of the terminal carbon atom of 1,3-dicarbonyl compounds by reaction of the corresponding dianions with electrophiles represents an important synthetic method which has been used in the synthesis of natural products. The terminal carbon atom of the dianion can be regioselectively coupled with one equivalent of an electrophile $E^+$ to give a monoanion which can be subsequently trapped by addition of a second electrophile. The cyclization reactions of dianions follow the two general mechanistic pathways [6] (Scheme 1.1, Schem 1.2).

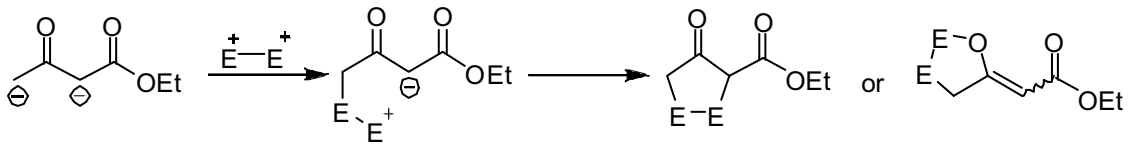
**Mechanism type A**: the dianion can react with monofunctional electrophiles with transposition of a negative charge from the dianion to the electrophile. This carbanion attacks an $E^+$ centre of the former dianion moiety (e.g. the ester group) to give a cyclic monoanion which is subsequently quenched with water.




**Scheme 1.1**: Possible mechanism for cyclization reactions of 1,3-dicarbonyl dianions.

Nu = nucleophile center, E = electrophile center

**Mechanism type B**: the dianion can also react as a dinucleophile with a dielectrophile. A monoanion is formed, followed by attack of the latter onto a second $E^+$ center.




**Scheme 1.2**: Possible mechanism for cyclization reactions of 1,3-dicarbonyl dianions. E = electrophile center

Cyclization reactions of dianions with dielectrophiles are synthetically important and useful. However, problems can arise since both starting materials are highly reactive compounds which have low reactivity matching. In addition, 1,2-dielectrophiles are often rather labile, and reactions with nucleophiles can often lead to polymerization, decomposition, formation of open-chained products, elimination or SET-process. These limitations can be overcome by two methods: a) a proper tuning of the reactivity of dianion and dieletrophile and b) the use of eletroneutral dianion equivalents (masked dianions) in Lewis acid catalyzed reactions [6].

Recent studies proved that 1,3-bis(silyl enol ethers) can be considered as equivalents of the corresponding 1,3-dicarbonyl dianions [7]. The chemistry of bis silyl enol ethers has been developed during the last two decades [7d]. It is, for example, known that silyl enol ethers can condense with various carbonyl compounds in the presence of Lewis acids [8]. These Lewis-acid-mediated reactions [9] (e. g. alkylation and aldol condensation) provide useful alternatives to classical enolate chemistry. In cyclization reactions, 1,3-bis(silyl enol ethers) can react as 1,3-dinucleophiles or, similar to the well-known Danishefsky diene [10], as

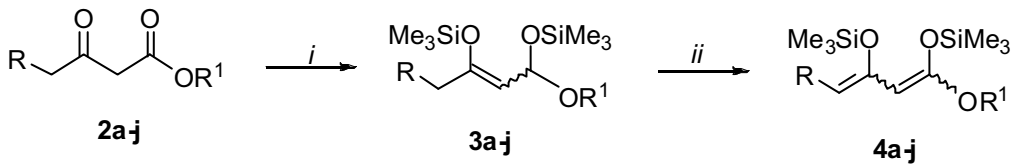
functionalized butadienes. 1,3-Bis(silyl enol ethers) undergo reactions with electrophiles at the terminal carbon atom followed by reaction of the central carbon or the oxygen atom. Silyl enol ethers can be cleaved with nucleophiles such as MeLi, $LiNH_2$ or $R_4N^+F^-$ to give enolates. They can be reacted with halides ($Br_2$, $Cl_2$, $I_2$) or pseudohalides (PhSCl, PhSeCl, Cl-N=O) [11], whereas enolates can be alkylated only by primary or secondary halides, enol silyl ethers can be alkylated by tertiary halides [12].

The preparation of 1,3-bis(silyl enol ethers) mainly follows the procedures reported by Chan and Molander. These syntheses rely on the preparation of 1,3-mono(silyl enol ethers) which are subsequently transformed into 1,3-bis(silyl enol ethers) by deprotonation with LDA and subsequent silylation [13].

In this chapter, I present the synthesis of novel 4-alkyl-1,3-bis(trimethylsilyoxy)-1,3-butadiens following the procedure of Chan.

### 1.1.2 Results and discussion

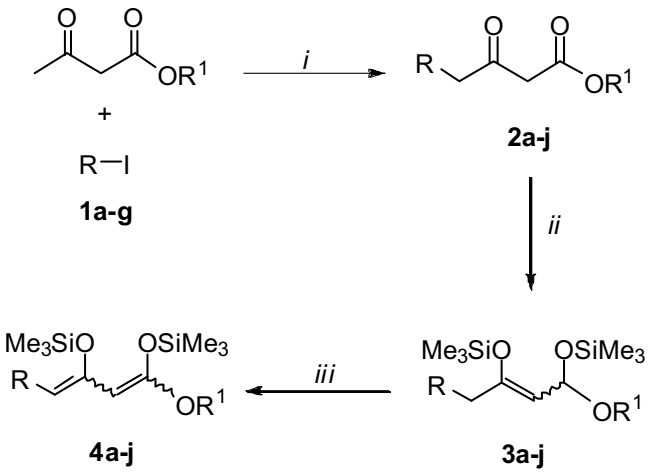
Following the procedures of Chan and Molander, 1,3-bis(trimethylsilyloxy)-1,3-butadienes **4a-j** were prepared from the respective 1,3-dicarbonyl compounds **2a-j** in two steps, which were commercially available. Treatment of the β-ketoesters with $NEt_3$, $Me_3SiCl$ afforded 1,3-mono(silyl enol ethers) **3a-j**. Deprotonation of the latter with LDA and subsequent addition of $Me_3SiCl$ afforded the diene **4a-j** (Scheme 1.3, Table 1.1)




**Scheme 1.3**: Synthesis of 1,3-bis(silyl enol ethers) **4a-j**; *i*) 1) $NEt_3$ (1.5 equiv.); 2) $Me_3SiCl$ (1.5 equiv.), $C_6H_6$, 20 °C, 12 - 48 h; *ii*) 1) LDA (1.5 equiv.), THF, 0 °C, 2 h; 2) $Me_3SiCl$ (1.5 equiv.), –78 → 20 °C, 6 - 12 h.

The synthesis of alkyl-substituted-1,3-bis(silyl enol ether) derivatives require the synthesis of the respective β-ketoesters **2a-j**. It is known that the regioselectivities of the reactions of monoanions and dianions generally differ greatly. 1,3-Dicarbonyl monoanions are generally alkylated at the central carbon or at the oxygen atom, whereas the formation of dianions

allows the functionalization of the terminal carbon atom. Based on this, the 4-alkyl-3-oxobutanoates **2a-j** were prepared by reactions of the dianion of methyl acetoacetate with the respective alkylhalides **1a-g** (RI). These compounds were transformed, according to a known procedure [9], into the desired 1,3-bis(silyl enol ethers) **4a-j** via the respective mono(silyl enol ethers) **3a-j** (Scheme 1.3, Table 1.1).




**Scheme 1.4**: Synthesis of alkyl-substituted 1,3-bis(silyl enol ethers) derivatives **4h-j**; *i*: 1) 2.5 LDA, THF, 0 °C, 1 h; 2) **1a-g**, –78 → 20 °C; *ii*: $Me_3SiCl$ (1.5 equiv.), $NEt_3$ (1.5 equiv.), $C_6H_6$, 20 °C, 48 h; *iii*: 1) LDA (1.5 equiv.), THF, –78 °C, 1 h; 2) $Me_3SiCl$ (1.5 equiv.), 20 °C, –78 → 20 °C.

All 4-alkyl-1,3-bis(silyl enol ethers) prepared could be stored at suitable conditions (-20 $^{o}$C, dry, inert gas atmosphere) for several months without decomposition. The 1,3-bis(silyl enol ethers) **4** of β-keto esters used in this thesis are listed in the following table.

**Table 1.1**: 1,3-Bis(silyl enol ethers) **4a-j**

| **4** | R | $R^1$ |
|---|---|---|
| **a** | H | Me |
| **b** | Me | Me |
| **c** | Et | Et |
| **d** | *n*Bu | Me |
| **e** | *n*Pen | Me |
| **f** | *n*Hex | Me |
| **g** | *n*Hep | Me |
| **h** | *n*Oct | Me |
| **i** | *n*Non | Me |
| **j** | *n*Dec | Me |

### 1.1.3 Conclusions

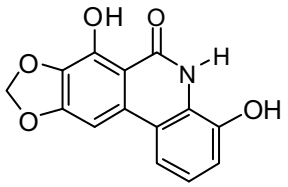
The application of known procedures allowed the synthesis of novel 1,3-bis(silyl enol ethers). These masked dianions will be used in cyclization reactions for the synthesis heterocycles and aromatic rings which represent important building blocks and natural product analogues.

## 1.2 Synthesis of amino- and nitro-substituted biaryls

### 1.2.1 Introduction

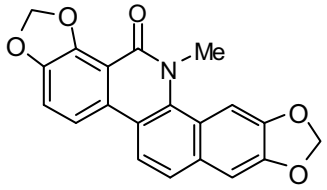
Amino- and nitro-substituted biaryls are of considerable current interest, due to their anti-hepatitis and antimalarial activity, binding affinity to C5 a receptor (human monocyte cell line U937), inhibition of cyclic nucleotide phosphorodiesterases (PDEs), and activity for topoisomerases I and II-mediated DNA cleavage [14]. Dibenzo[*b*,*d*]pyrid-6-ones (6(5*H*)-phenanthridinones) can be regarded as lactams derived from amino-substituted biaryls. Similar to amino-substituted biaryls, they are of considerable pharmacological relevance and occur in a variety of natural products. For example, sanguinarinone (Figure 1.2) shows anti-proliferative activity against leukemia HL-60 cells, antiparasitic activity, and anticoagulant activity [15]. Anti-proliferative activity against P-388 and human colon carcinoma HT-29 cells has been reported for oxotoddaline [16]. Oxynitidine possesses cytotoxic activity [17]. Several other biologically active natural products, such as narciprimine (Figure 1.1), chelirubinone, oxychelirubine, arolycoricidine, pratosine, turraeanthin B, or kalbretorine, are known [18]. A number of other pharmacologically active natural products, e. g. cytotoxic

oxynitidine [17], have been reported [18], [19]. Recently Cho *et al*. [20j] reported the total synthesis of oxyavicine, oxynitidine and oxyfagaronine alkaloids (Figure 1.3 - 1.5).




Narciprimine

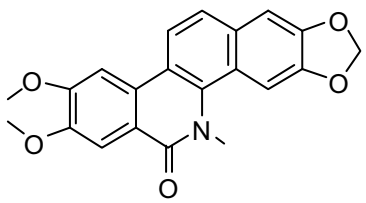
**Figure 1.1**: Narciprimine




Sanguinarinone

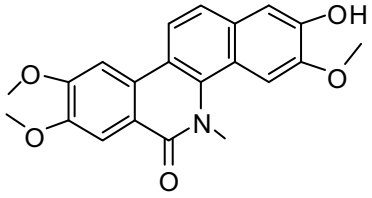
**Figure 1.2**: Sanguinarinone

The synthesis of nitro- and amino-substituted biaryls by nitration [21].of biphenyls suffers from the low regioselectivity. An additional problem arises form the fact that, due to the harsh reaction conditions, several side-reaction are possible for more complex substrates. Nitro-substituted biaryls are available by Ullmann-type reactions and by nucleophilic aromatic substitutions [22]. However, the scope of these reactions is limited by steric and electronic effects (low conversion, formation of regioisomeric mixtures). The synthesis of amino-substituted biaryls by palladium(0)-catalyzed coupling reactions [23]. suffers from the fact that electron-rich arenes, in particular sterically encumbered substrates, often react sluggishly or not at all. Last but not the least, the synthesis of the required starting materials, highly functionalized or sterically encumbered aryl halides or triflates (the latter derived from the corresponding phenols), can be a difficult and tedious task. 6(5*H*)-Phenanthridinones have been prepared from 2-alkoxycarbonyl-2-nitrobiaryls by reduction of the nitro into an amino group (using Fe/AcOH, Fe/THF, Zn/HOAc, Raney-Ni, or $H_2$-Pd/C) and subsequent cyclization [20]. Whereas this process is straightforward, problems are, as described above, associated with the synthesis of the functionalized biaryl system.



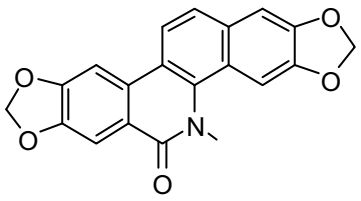
Oxynitidine

**Figure 1.3**: Oxynitidine



Oxyfagaronine

**Figure 1.4**: Oxyfagaronine



Oxyavicine

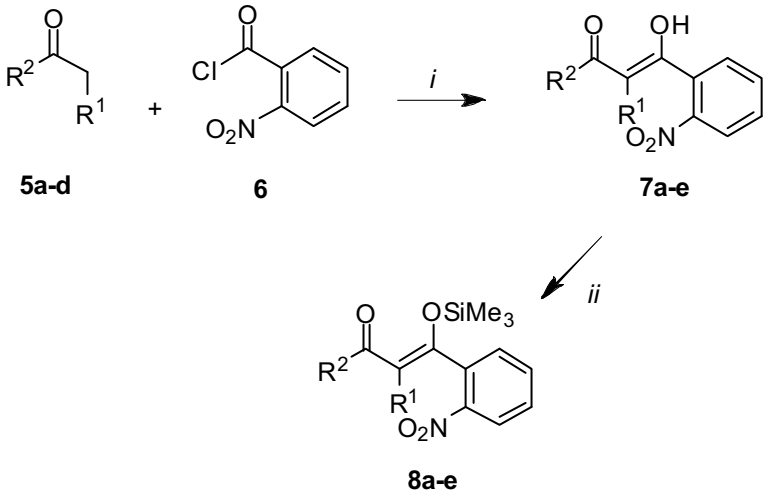
**Figure1.5**: Oxyavicine

All biaryl syntheses outlined above rely on the functionalization of a suitable arene. An interesting alternative is based on the use of synthetic building blocks in cyclocondensation reactions. To the best of our knowledge, only a single application of this strategy to the synthesis of a nitro-substituted biaryl has been reported to date. Ashburn and coworkers reported the synthesis of 2-nitro-2'-alkoxycarbonyl-biphenyls by Diels-Alder reaction [24]. Chan and coworkers were the first to report [25]. a convenient synthesis of functionalized phenols by $TiCl_4$-mediated [3+3] cyclization [26]. of 1,3-bis(trimethylsilyloxy)-1,3-butadienes [27]. with 3-silyloxy-2-en-1-ones. In recent years, Langer *et al.* studied the application of this reaction to the synthesis of various functionalized arenes. Herein, I wish to report what is, to the best of my knowledge, the first synthesis of nitro- and amino-substituted biaryls and of 6(5*H*)-phenanthridinones by application of a [3+3]-cyclocondensation / lactamization strategy.

Although recently Cho *et al.*[20j] reported the synthesis oxyphenanthridinones, which they synthesised in fourteen steps, and I like to present an efficient methodology to prepare the same skeleton in two steps. Noteworthy, the products are formed with very good regioselectivity and are not readily available by other methods.

### 1.2.2 Results and discussion

The novel nitro-substituted benzoylacetones **7a-e** were prepared in 40-85% yields by LDA-mediated reaction of ketones **5a-d** with benzoyl chlorides **6** (Scheme 1.5, Table 1.2). The reaction of **7b** with *N*-chlorosuccinimide (NCS) gave the chlorinated benzoylacetone **7e**. The silylation of **7a-e** afforded the 1-aryl-1-silyloxy-1-en-3-ones **8a-e** in high yields.




**Scheme 1.5:** Synthesis of **7a-e** and **8a-e**; *i*: LDA (1.5 equiv.), THF; *ii*: 1) $NEt_3$ (1.6 equiv.), $Me_3SiCl$ (1.8 equiv.), $C_6H_6$, 20 °C, 3 d. Products **8** exist as mixtures of *E/Z* isomers.

Table 1.2: Synthesis of **7, 8a-e**

| **5** | **7,8** | $R^1$ | $R^2$ | $R^3$ | % (**7**)[a] | % (**8**)[a] |
|---|---|---|---|---|---|---|
| **a** | **b** | H | Et | $NO_2$ | 45 | 95 |
| **b** | **c** | H | *n*Pr | $NO_2$ | 45 | 88 |
| **c** | **d** | H | *n*Bu | $NO_2$ | 40 | 93 |
| **d** | **e** | Me | Et | $NO_2$ | 48 | 94 |
| **e** | **f** | Cl | *n*Pr | $NO_2$ | 85 | 92 |

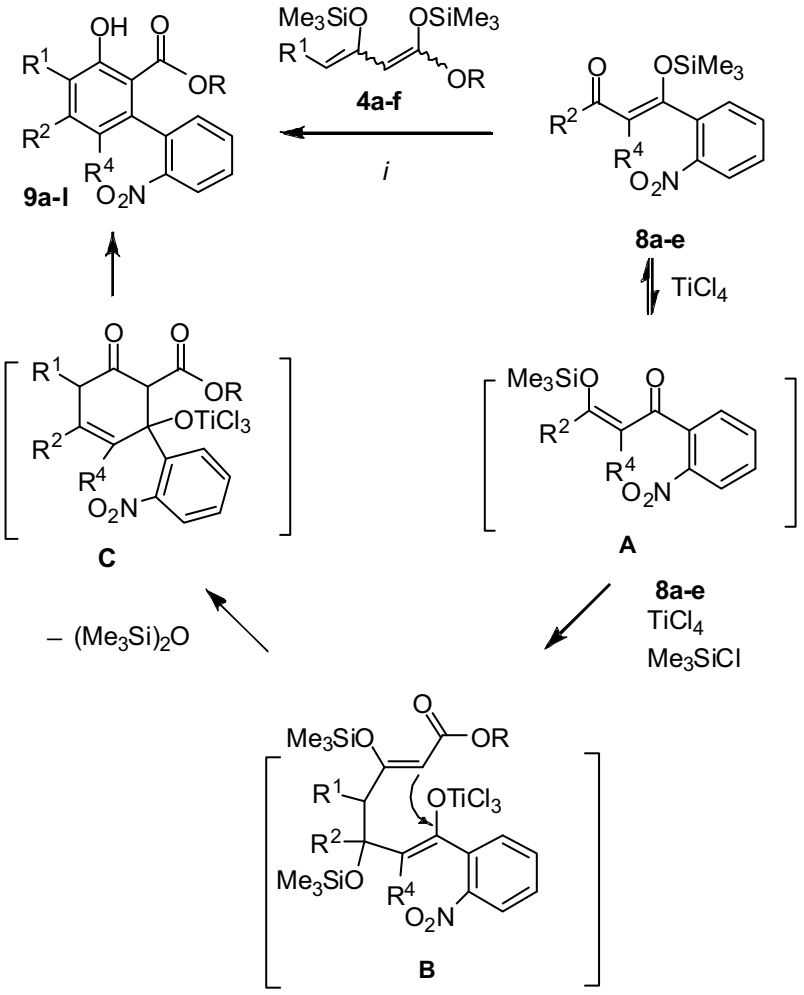
[a] Yields of isolated products, **7e** prepared by chlorination of **7b**, conditions: NCS (1.0 equiv.), $CCl_4$, 8 h, 75 – 80 °C

The $TiCl_4$-mediated cyclization of **8a-e** with 1,3-bis(trimethylsilyloxy)-1,3-butadienes **4a-f**, readily available in two steps from the corresponding β-ketoesters [7], afforded the novel nitro-substituted biaryls **9a-l** (Scheme 1.6, Table 1.3).

The formation of the product can be explained by the mechanism depicted in Scheme 1.6. During the optimization, it proved to be important to carry out the reactions in a highly concentrated solution. We have observed earlier that employment of other Lewis acids results in a decrease of the yield of [3+3] cyclocondensation reactions. It is important to be noted that all the cyclizations proceeded with very good regioselectivity. The moderate yields can be explained by competing, $TiCl_4$-mediated oxidative dimerization of the 1,3-bis(silyloxy)-1,3-butadiene and by partial hydrolysis of the starting materials during the reaction. No clear trend is observed for the yield with respect to the influence of the substitution pattern.

1.2.2.1 Possible mechanism for synthsis of **9a-l**

The regioselective formation of products **9a-l** can be explained, following a mechanism first suggested by Chan [7], by $TiCl_4$-mediated isomerization of **8** into intermediate type **A**, $TiCl_4$-mediated attack of the terminal carbon atom of 1,3-bis(silyl enol ether) **4** onto the carbon located next to substituent $R^1$ to give intermediate type **B** (conjugate addition), cyclization (intermediate type **C**), and subsequent aromatization (Scheme 1.6, Table 1.3).



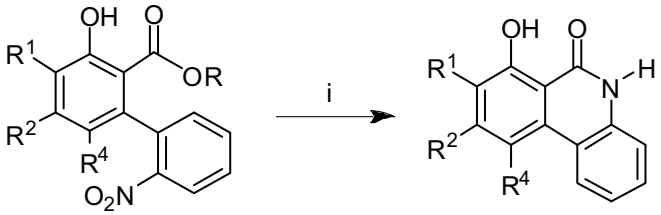

**Scheme 1.6:** Synthesis of **9a-l**; *i*: **8** (1.0 equiv.), **4** (1.1 equiv.), $TiCl_4$, $CH_2Cl_2$, –78 → 20 °C

Table 1.3: Synthesis of **9, 10a-l**

| **8** | **4** | **9,10** | $R^1$ | $R^2$ | $R^3$ | $R^4$ | % (**9**)[a] | % (**10**)[a] |
|---|---|---|---|---|---|---|---|---|
| **a** | **a** | **a** | Me | H | Et | H | 43 | 75 |
| **a** | **b** | **b** | Me | Me | Et | H | 42 | 53 |
| **a** | **c** | **c** | Et | Et | Et | H | 38 | 52 |
| **a** | **d** | **d** | Me | nHex | Et | H | 41 | 51 |
| **a** | **e** | **e** | Me | nHept | Et | H | 39 | 49 |
| **a** | **f** | **f** | Me | nOct | Et | H | 38 | 50 |
| **b** | **c** | **g** | Et | Et | nPr | H | 37 | 63 |
| **c** | **a** | **h** | Me | H | nBu | H | 42 | 70 |
| **c** | **b** | **i** | Me | Me | nBu | H | 39 | 54 |
| **c** | **d** | **j** | Me | nHex | nBu | H | 38 | 50 |
| **d** | **d** | **k** | Me | nHex | Et | Me | 38 | 50 |
| **e** | **a** | **l** | Me | H | nPr | Cl | 55 | 49 |

[a] Yields of isolated products

The configuration of all products was established by spectroscopic methods. The structure of **10g** was independently confirmed by X-ray crystal structure analysis (Figure 1.6).




**9a-l** **10a-l**

**Scheme 1.7:** Synthesis of **10a-l**; *i*: $H_2$, Pd/C (10 mol-%), 25 °C, 48 h.

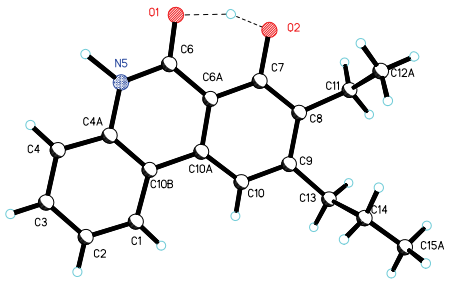



**Figure 1.6,** Ortep plot of **10g** (hydrogen at O3 found in the difference map and refined freely)

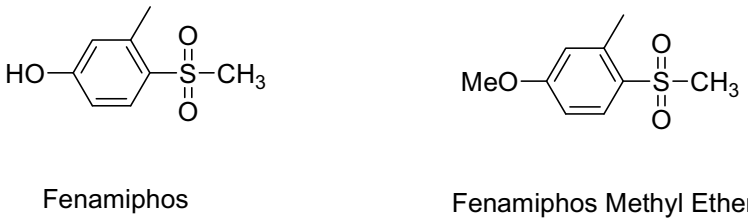
### 1.2.3 Conclusions

In conclusion, I have reported a regioselective approach to functionalized nitro and amino substituted biaryls and 6(5*H*)-phenanthridinones by application of a [3+3] cyclization / lactamization strategy. The products are not readily available by other methods.

# 2 First synthesis of 4-(arylsulfonyl)phenols by regioselective [3+3] cyclocondensations of 1,3-bis(silyloxy)-1,3-butadienes with 2-arylsulfonyl-3-ethoxy-2-en-1-ones

## 2.1 Introduction

A number of pharmacologically active compounds contain a 4-(arylsulfonyl)phenol substructure. The wide range of pharmacological activities reported include, for example, antibacterial activity [29], inhibition of phospholipidase $A_2$ [30], inhibition of catechol O-methyltransferase [31], inhibition of dihydropteroate synthase of *Escherichia coli* [32], hypolipidemic activity [33], cytotoxicity against HeLa cells and the antipicornavirus [34], neuropeptide $Y_1$ receptor binding activity [35], anti-HIV activity [36], anticholesteremic activity [37], binding to human muscarinic $M_1$ and $M_2$ receptors [38], histamine $H_3$-receptor antagonistic activity [39], antiprotozoal activity [40], binding to neuroblastoma cells [41], binding to the human cannabinoid $CB_1$ receptor [42], and inhibition of the main protease of the recombinant SARS coronavirus [43]. In addition, highly functionalized sulfone derivatives, such as hydroxylated benzoates, are considered as lead structures in agricultural chemistry. For example, Fenamiphos (Figure 2.1) has been widely used as an insecticide [44].




Fenamiphos

Fenamiphos Methyl Ether

**Figure 2.1**: Fenamiphos sulfone phenol and his related Ether

A number of synthetic approaches to diaryl sulfones have been reported. Classic approaches include, for example, the oxidation of diaryl sulfides [45]. In addition, the Friedel-Crafts-type acylation of anisole with phenylsulfonic acid chloride has been reported [46]. However, this reaction proceeds with low regioselectivity. The reaction of phenol with benzenesulfonic acid requires harsh conditions (240 °C) [47]. In recent years, transition metal mediated syntheses of diaryl sulfones have been developed. Examples include the CuI/proline-mediated reaction of aryl iodides with sodium benzenesulfinate [48], the Suzuki reaction of 4-

methoxybenzeneboronic acid with phenylsulfonic acid chloride [49], and the copper(II)acetate-catalyzed reaction of 4-methoxybenzeneboronic acid with sodium benzenesulfinate (in the presence of 1,10-phenanthroline and oxygen) [50].

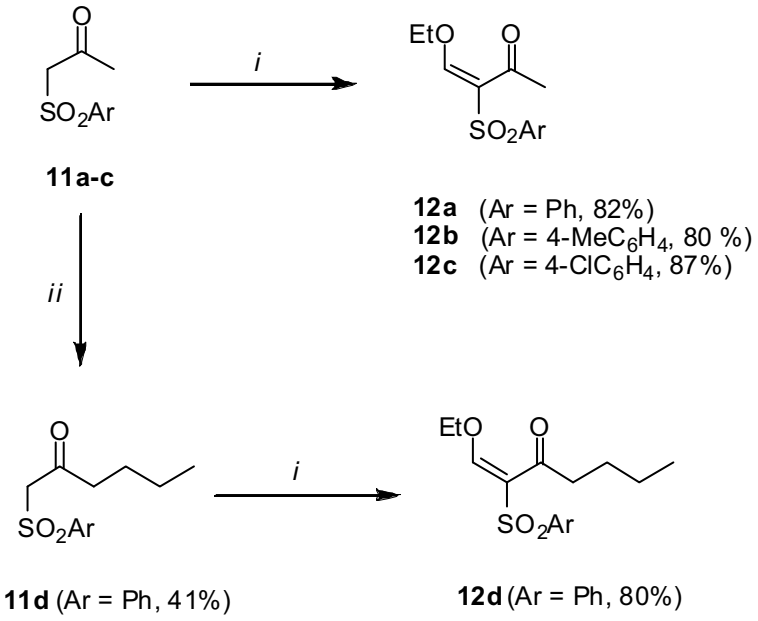
Despite their great synthetic utility, the sulfonations outlined above, which all rely on the coupling of two arene moieties, can suffer from several drawbacks, such as harsh reaction conditions, low regioselectivity, and narrow synthetic scope. In addition, it is important to note that the synthesis of the required starting materials, functionalized or highly substituted aryl halides or triflates, can be a difficult and tedious task, due to the low *o/p*-regioselectivity of electrophilic substitutions, competing isomerization reactions, and other problems.

An interesting alternative approach to diaryl sulfones is based on the application of a ′building block strategy′. Examples include the reaction of diethyl 2,4-diaryl-3-(arylsulfonyl)buta-1,3-diene-1,1-dicarboxylates with malononitrile [51], 6π-electrocyclizations of 1-(1-chlorohexa-1,3,5-triene-3-sulfonyl)benzenes [52], [4+2] cycloadditions of 3*H*-isobenzofuran-1-one with (1-benzenesulfonyl-vinyl)trimethylsilanes [53], reactions of enamines with 1,2,4-tris(phenylsulfonyl)-2-butene [54], the [4+2] cycloaddition of Danishefsky's diene with a sulfonyl-substituted allene [55], the [4+2] cycloaddition of a 1,2-bis(arylsulfonyl)ethylene with thiophene-1,1-dioxide [56], the cyclization of a 1-trimetyhsilyloxy-1,3-butadiene with an arylvinylsulfone [57], 6π-electrocyclizations of 2-[2,2-diaryl-4-sulfonyl)vinyl]furans [58], and the [4+2] cycloaddition of furan with 1,3-bis(phenylsulfonyl)allene [59].

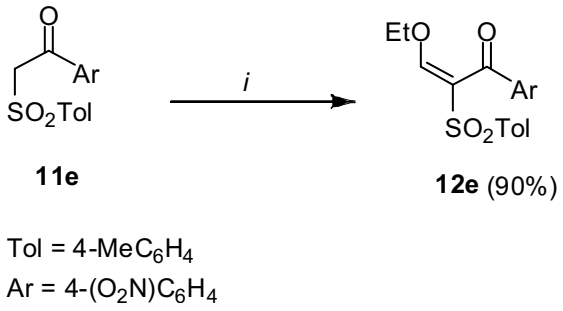
Chan and coworkers were the first to report [25] the $TiCl_4$-mediated [3+3] cyclization [26] of 1,3-bis(trimethylsilyloxy)-1,3-butadienes [27] with 3-silyloxy-2-en-1-ones which allows a convenient synthesis of salicylates. In recent years, the application of this methodology to the synthesis of various functionalized arenes has been reported [26]. Most of the $TiCl_4$-mediated [3+3] cyclizations of 1,3-bis(trimethylsilyloxy)-1,3-butadienes reported to date involve the usage of 3-*silyloxy*-2-en-1-ones as starting materials. Although a few regioselective cyclizations have been reported, these reactions are generally *not* regioselective, due to $TiCl_4$-mediated isomerization (silyl shift) of the 3-silyloxy-2-en-1-ones. In their early work in 1980 [25], Chan and Brownbridge reported an isolated example of a successful and regioselective cyclization of a 3-*alkoxy*-2-en-1-one, i. e. 1-ethoxybut-1-en-3-one. Based on this observation, we have recently started a synthetic program directed to regioselective [3+3] cyclizations of acceptor-substituted 3-alkoxy-2-en-1-ones. Our strategy takes advantage of the fact that the required enones are readily available by reaction of acceptor-substituted ketones (such as β-ketoesters or β-etosulfones) with triethyl orthoformiate.

## 2.2 Results and discussion

1,3-Bis(silyloxy)-1,3-butadienes **4a-m** were prepared from the corresponding β-ketoesters in two steps [25]. 2-Arylsulfonyl-3-ethoxy-2-en-1-ones **12a-e** were prepared, following a known procedure [61], by reaction of β-ketosulfones **11a-e** with triethyl orthoformate and acetic anhydride (Schemes 2.1 and 2.2).




**Scheme 2.1:** Synthesis of 1**2a-d**; *i*: **11a-d** (1.0 equiv.), $HC(OEt)_3$ (1.2 equiv.), $Ac_2O$, reflux, 2 h, ii: LDA, $CH_3(CH_2)_2I$ (-78 - r.t.), 14 hr



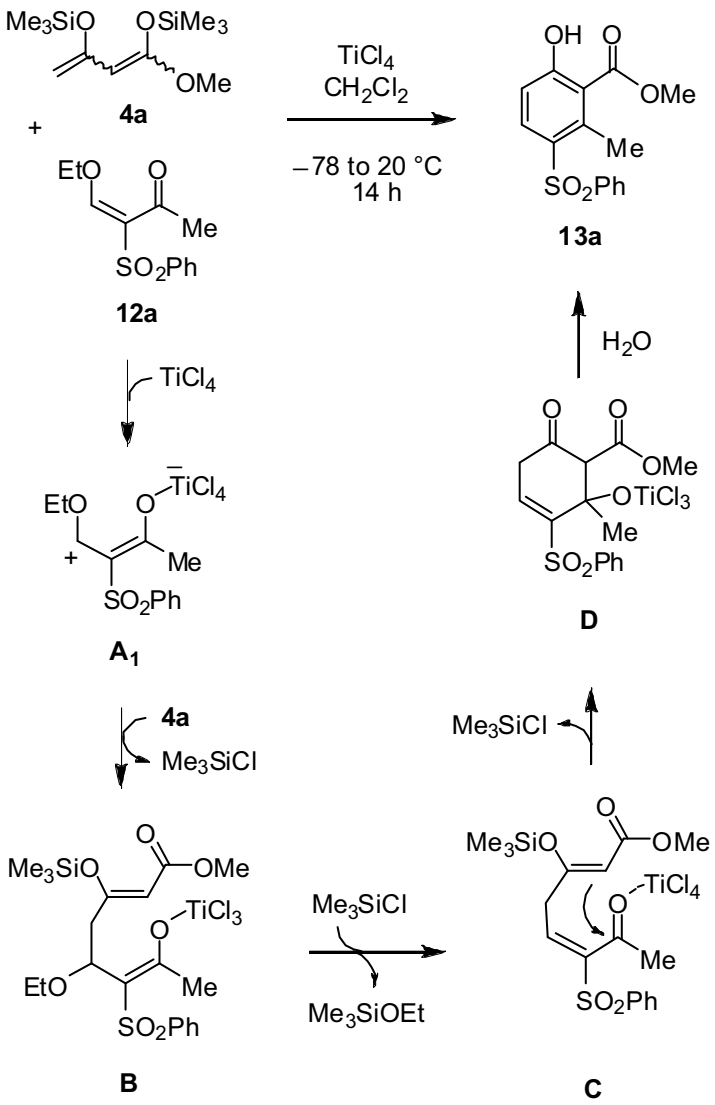

**Scheme 2.2:** Synthesis of **12e**; *i*: **11e** (1.0 equiv.), $HC(OEt)_3$ (1.2 equiv.), $Ac_2O$, reflux, 2 h

Table 2.1: Synthesis of **12a-e**

| **11,12** | $R^1$ | Ar | % (**12**)[a] |
|---|---|---|---|
| **a** | Me | Ph | 82 |
| **b** | Me | 4-$MeC_6H_4$ | 80 |
| **c** | Me | 4-$ClC_6H_4$ | 87 |
| **d** | *n*Bu | Ph | 80 |
| **e** | 4-$NO_2C_6H_4$ | 4-$MeC_6H_4$ | 90 |

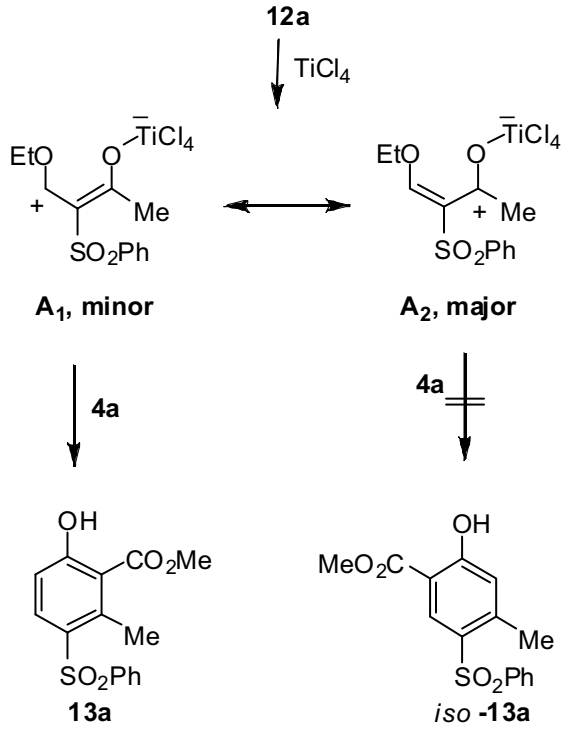
[a] Yields of isolated products

The $TiCl_4$-mediated cyclization of **12a** with **4a** afforded the novel 4-(arylsulfonyl)phenol **13a** in up to 80% yield (Scheme 2.3). The best yield was obtained when the reaction was carried out in a highly concentrated solution. It is worth to be noted that the cyclization proceeded with excellent regioselectivity. The formation of product **13a** might be explained by reaction of **12a** with $TiCl_4$ to give intermeidate $\mathbf{A_1}$, attack of the terminal carbon atom of **4a** onto $\mathbf{A_1}$ to give intermediate **B**, formation of intermediate **C**, cyclization via the central carbon (intermediate **D**) and subsequent aromatization.



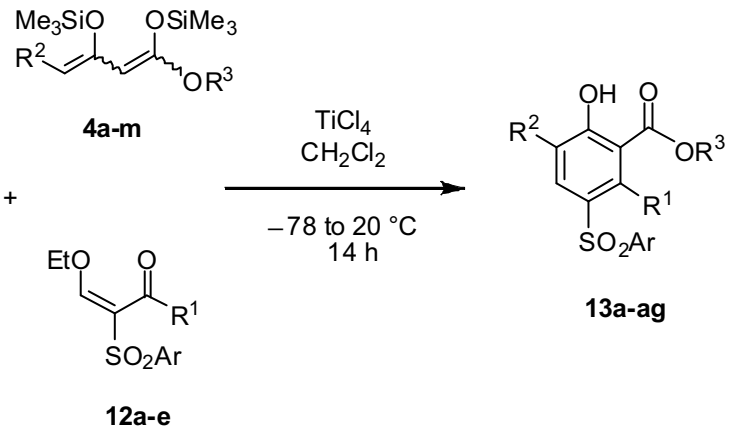

**Scheme 2.3:** Possible mechanism of the formation of **13a**

The regioselectivity of the formation of **13a** might be explained as follows. The chelation of $TiCl_4$ by the carbonyl oxygen atom of **12a** results in the formation of intermediate **A** containing an allylic cation (Scheme 2.4). We assume that resonance structure $\mathbf{A_2}$ is predominantly present, due to the σ-donating effect of the methyl group. On the other hand, the observed product is formed by attack of the terminal carbon atom of **4a** onto $\mathbf{A_1}$. This might be explained by the steric hindrance of the allylic carbon attached to the methyl group and by the reduced positive charge density.




**Scheme 2.4:** Possible explanation of the regioselectivity of the cyclization of **12a** with **4a**

The formal [3+3] cyclization of 2-arylsulfonyl-3-ethoxy-2-en-1-ones **12a-e** with 1,3-bis(silyloxy)-1,3-butadienes **4a-m** afforded the 4-(arylsulfonyl)phenols **13a-ag** in 42-80% yield (Scheme 2.5, Table 2.2). The aryl groups located at the sulfonyl group of enones **12** have some influence on the yields. The best yields were obtained for products **13a-j** and **13ab-ad** which are derived from phenyl-substituted enones **12a** and **12d**, respectively. In contrast, the presence of a substituent located at carbon atom C-4 of the 1,3-bis(silyloxy)-1,3-butadiene has no significant effect on the yield. This can be seen by comparison of the yield of product **13a** with the yields of products **13b-j** and **13ab-ad** and by comparison of the yields of products **13k**, **13s**, and **13ab** with those of the corresponding substituted derivatives. All products were formed with excellent regioselectivity. The formation of only one regioisomer was observed.




**Scheme 2.5:** Synthesis of **4a-ag**

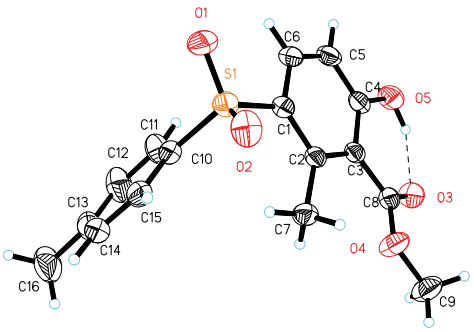
Table 2.1: Synthesis of **13a-ag**

| **12** | **4** | **13** | Ar | $R^1$ | $R^2$ | $R^3$ | % (**13**)[a] |
|---|---|---|---|---|---|---|---|
| **a** | **a** | **a** | Ph | Me | H | Me | 80 |
| **a** | **b** | **b** | Ph | Me | Me | Me | 80 |
| **a** | **c** | **c** | Ph | Me | Et | Et | 77 |
| **a** | **d** | **d** | Ph | Me | *n*Bu | Me | 76 |
| **a** | **e** | **e** | Ph | Me | *i*-Bu | Me | 70 |
| **a** | **f** | **f** | Ph | Me | *n*Hex | Me | 78 |
| **a** | **g** | **g** | Ph | Me | *n*Hep | Me | 75 |
| **a** | **h** | **h** | Ph | Me | *n*Oct | Me | 75 |
| **a** | **i** | **i** | Ph | Me | *n*Non | Me | 75 |
| **a** | **j** | **j** | Ph | Me | *n*Dec | Me | 78 |
| **b** | **a** | **k** | 4-$MeC_6H_4$ | Me | H | Me | 57 |
| **b** | **b** | **l** | 4-$MeC_6H_4$ | Me | Me | Me | 56 |
| **b** | **c** | **m** | 4-$MeC_6H_4$ | Me | Et | Et | 46 |
| **b** | **d** | **n** | 4-$MeC_6H_4$ | Me | *n*Bu | Me | 65 |
| **b** | **f** | **o** | 4-$MeC_6H_4$ | Me | *n*Hex | Me | 61 |
| **b** | **g** | **p** | 4-$MeC_6H_4$ | Me | *n*Hep | Me | 60 |
| **b** | **h** | **q** | 4-$MeC_6H_4$ | Me | *n*Oct | Me | 59 |
| **b** | **k** | **r** | 4-$MeC_6H_4$ | Me | OMe | Me | 42 |
| **c** | **a** | **s** | 4-$ClC_6H_4$ | Me | H | Me | 47 |
| **c** | **b** | **t** | 4-$ClC_6H_4$ | Me | Me | Me | 48 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **c** | **c** | **u** | 4-$ClC_6H_4$ | Me | Et | Et | 47 |
| **c** | **d** | **v** | 4-$ClC_6H_4$ | Me | *n*Bu | Me | 54 |
| **c** | **f** | **w** | 4-$ClC_6H_4$ | Me | *n*Hex | Me | 50 |
| **c** | **g** | **x** | 4-$ClC_6H_4$ | Me | *n*Hep | Me | 51 |
| **c** | **h** | **y** | 4-$ClC_6H_4$ | Me | *n*Oct | Me | 52 |
| **c** | **l** | **z** | 4-$ClC_6H_4$ | Me | 4-$ClC_6H_4$ | Me | 49 |
| **c** | **m** | **aa** | 4-$ClC_6H_4$ | Me | 4-$MeC_6H_4$ | Me | 53 |
| **d** | **a** | **ab** | Ph | n-Bu | H | Me | 77 |
| **d** | **b** | **ac** | Ph | n-Bu | Me | Me | 79 |
| **d** | **m** | **ad** | Ph | n-Bu | 4-$MeC_6H_4$ | Me | 75 |
| **e** | **a** | **ae** | 4-$MeC_6H_4$ | 4-$O_2NC_6H_4$ | H | Me | 45 |
| **e** | **b** | **af** | 4-$MeC_6H_4$ | 4-$O_2NC_6H_4$ | Me | Me | 49 |
| **e** | **d** | **ag** | 4-$MeC_6H_4$ | 4-$O_2NC_6H_4$ | nBu | Me | 47 |

[a] Yields of isolated products

The structures of all products were confirmed by spectroscopic methods. The structures of products **4k**, **4s**, **4ab**, and **4ae**, all containing a hydrogen atom located at carbon atom C-6, are evident by the presence of large coupling constants for the two neighbouring hydrogen atoms. The structures of **4k**, **4s** and **4ae** were independently confirmed by X-ray crystal structure analyses (Figures 2.2 - 2.4) [60].



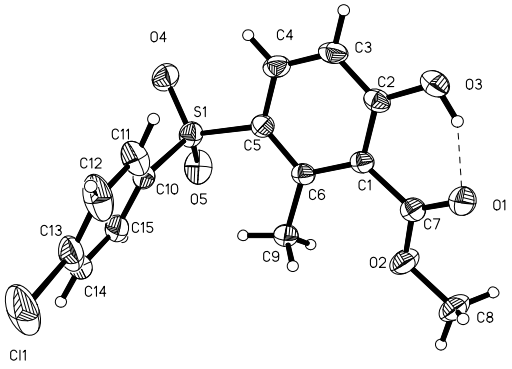




**Figure 2.2:** Ortep plot of **4k** (30% probability level)

**Figure 2.3:** Ortep plot of **4s** (30% probability level)

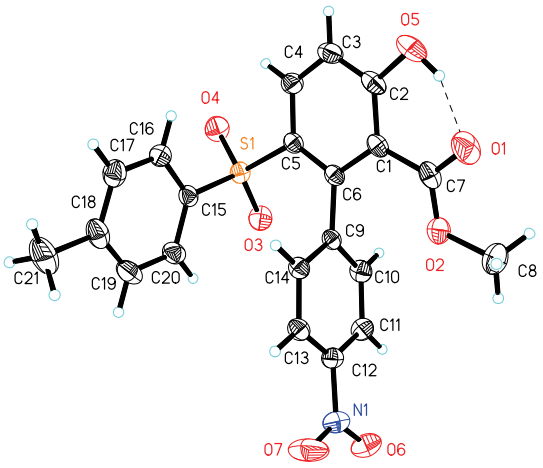
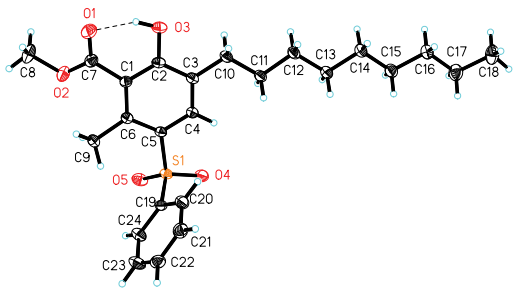



**Figure 2.4:** Ortep plot of **4ae** (30% probability level)

The elucidation of the structures of all other derivatives, containing an alkyl group located at carbon C-6, was not so easy and had to rely on extensive 2D NMR experiments (NOESY, HMBC). The structures of **4i**, and **4m** were unambigiously confirmed by X-ray crystal structure analyses (Figures 2.5, 2.6) [60].



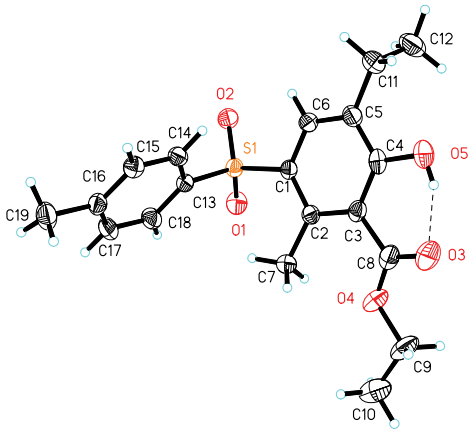




**Figure 2.5:** Ortep plot of **4i** (30% probability level)

**Figure 2.6:** Ortep plot of **4m** (30% probability level)

## 2.3 Conclusions

In conclusion, I have reported a convenient and regioselective synthesis of functionalized 4-(arylsulfonyl)phenols by what are, to the best of my knowledge, the first formal [3+3] cyclizations of 1,3-bis(silyloxy)-1,3-butadienes with 2-arylsulfonyl-3-ethoxy-2-en-1-ones, which are not readily available by other methods. In contrast to the C-S coupling reactions this method constitutes a new building block methodology and involves the formation of one of the two arene moieties by formation of two C-C bonds. The reactions are easy to be carried out and the starting materials are readily available.

# 3 Regioselective synthesis of 4-acyl-1-hydroxy-2,3- benzodioates by chelation-controlled [3+3] annulation of 3-acyl-4-ethoxy-2-oxo-3-enoates with 1,3-bis(trimethylsilyloxy)-1,3-butadienes

## 3.1 Introduction

Highly functionalized benzene derivatives, such as hydroxylated benzoates and benzodioates, are of considerable interest as lead structures and synthetic building blocks in medicinal and agricultural chemistry [61], [62]. Classical syntheses of such compounds are based on electrophilic substitution and oxidation reactions. Despite their great utility, electrophilic substitutions have several drawbacks (e. g., low regioselectivity and low reactivity of electron-poor substrates). Oxidations of toluene to benzoic acid derivatives often require drastic conditions. Transition metal-catalyzed functionalizations of functionalized benzene derivatives proceed under relatively mild conditions [63]. However, the synthesis of the required starting materials, highly functionalized or sterically encumbered benzene derivatives, can be a difficult task.

Functionalized benzene derivatives have been prepared also by application of a 'building block' strategy. Examples include base-mediated cyclizations of acetone-1,3-dicarboxylates [30], condensations of 1,3-dicarbonyl dianions with carboxylic acid derivatives and subsequent intramolecular aldol reactions of the polyketides thus formed [65], and [4+2] cycloadditions [66]. Chan and Brownbridge were the first to report [25] the synthesis of salicylates by formal [3+3] cyclizations of 1,3-bis(silyloxy)-1,3-butadienes [30] with 3-silyloxy-2-en-1-ones. This strategy has been widely applied in recent years [26].

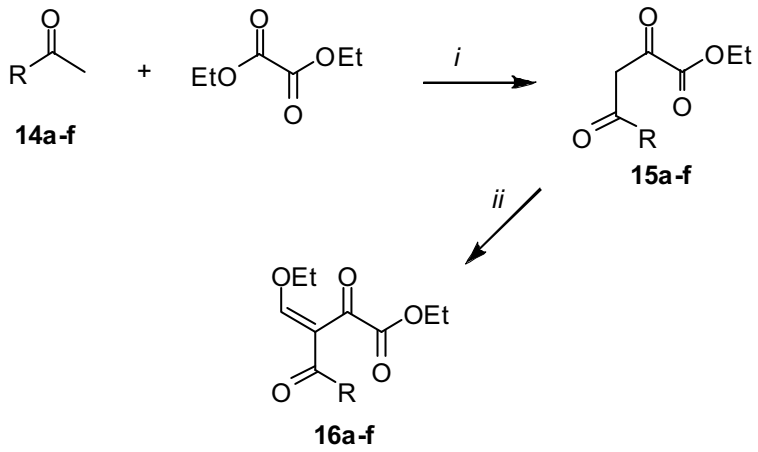
However, its scope is mainly limited to 3-silyloxy-2-en-1-ones derived from symmetrical 1,3-diketones. Although a few exceptions have been reported [25], cyclizations of 3-silyloxy-2-en-1-ones derived from unsymmetrical 1,3-diketones often proceed with low regioselectivity, due to $TiCl_4$-mediated isomerization of the 3-silyloxy-2-en-1-one.

In their early work, Chan and Brownbridge reported [25] an isolated example of a regioselective cyclocondensation of a 3-alkoxy- rather than a 3-silyloxy-2-en-1-one. Based on this observation, we recently started a program directed towards the development of new cyclizations of acceptor-substituted 3-alkoxy-2-en-1-ones. Herein, we report, for the first time, a convenient synthesis of 4-acyl-1-hydroxy-2,3-benzodioates by [3+3] cyclization of 1,3-(bis)trimethylsilyloxy-1,3-butadienes with 4-acyl-1-hydroxy-2,3-benzodioates. Although several electrophilic sites are present in the starting materials, the cyclizations proceed with excellent regioselectivity which can be explained by the regiodirecting effect of the 2-

oxoester moiety (chelation-control) [67], [68]. The products reported herein are not readily available by other methods.

## 3.2 Results and discussion

4-Acyl-1-hydroxy-2,3-benzodioates **16a-f** were prepared in good yield by reaction of the known 2,4-diketoesters **15a-f**, available from diethyl oxalate, with triethyl orthoformiate and acetic anhydride (Scheme 3.1, Table 3.1).



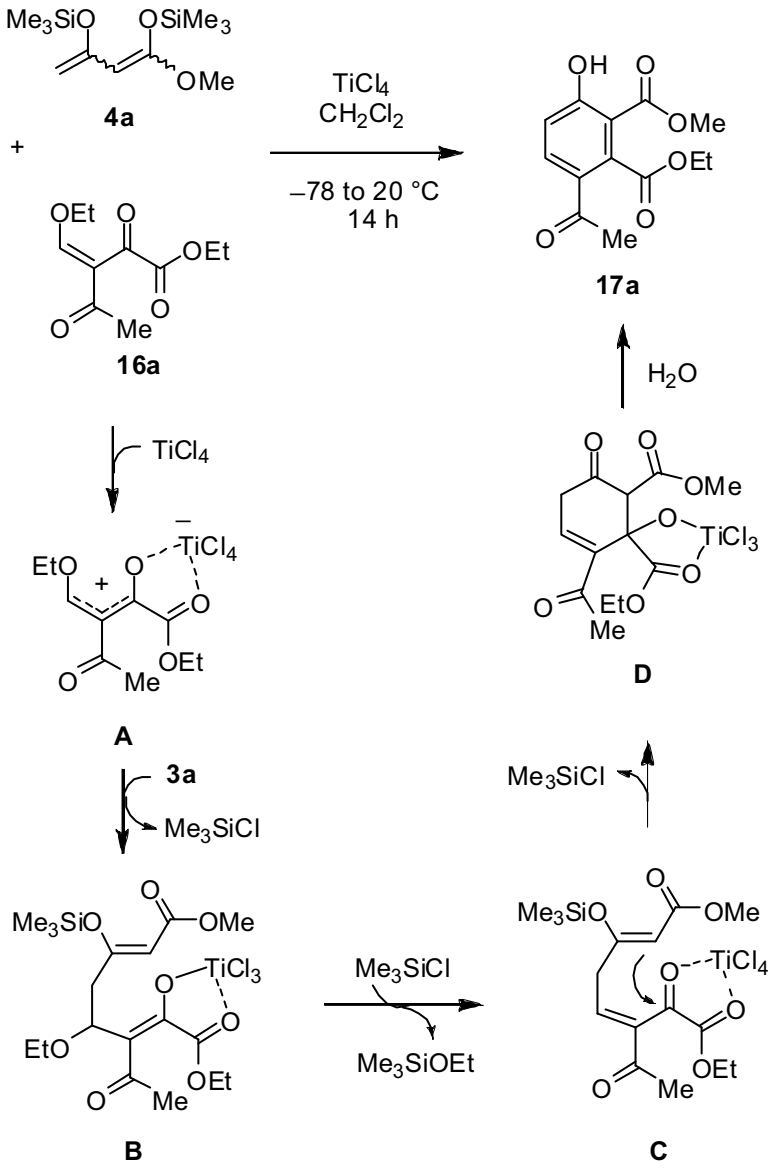

**Scheme 3.1:** Synthesis of **16a-f**;i: Diethyl oxalate (1.0 equiv.), **14a-f** (1.0 equiv.), NaOEt (1.0 equiv.), *ii*: **15a-f** (1.0 equiv.), $HC(OEt)_3$ (1.2 equiv.), $Ac_2O$, reflux, 2-4 h, products exist as mixtures of *E/Z* isomers

**Table 3.1:** Synthesis of **3a-f**

| **14,15,16** | R | **% (15)[a]** | **% (16)[a]** |
|---|---|---|---|
| **a** | Me | 76 | 97 |
| **b** | Ph | 79 | 96 |
| **c** | 4-$MeC_6H_4$ | 80 | 98 |
| **d** | 4-$MeOC_6H_4$ | 82 | 95 |
| **e** | 4-$BrC_6H_4$ | 75 | 92 |
| **f** | OEt | 74 | 99 |

[a] Yields of isolated products

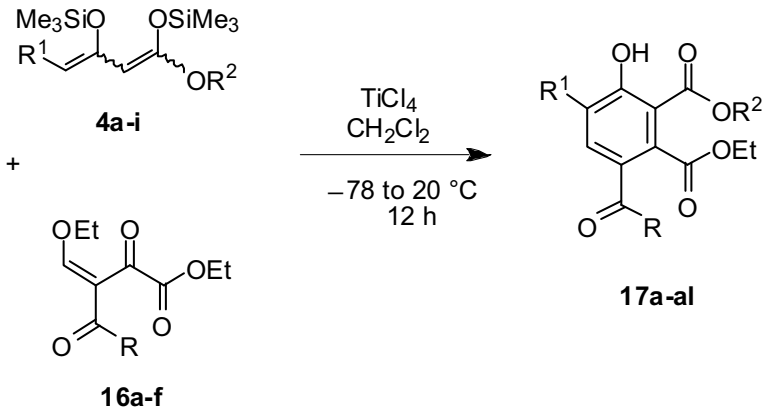
The $TiCl_4$-mediated cyclization of **3a** with **4a** afforded the 4-acetyl-1-hydroxy-2,4-benzodioate **5a** with excellent regioselectivity (Scheme 3.2). The best yield was obtained when the reaction was carried out in a highly concentrated solution [75]. The formation of **5a** can be explained by reaction of **3a** with $TiCl_4$ to give allylic cation **A**. The attack of the terminal carbon atom of **4a** onto **A** resulted in the formation of intermediate **B**. The elimination of (ethoxy)trimethylsilane (intermediate **C**) and subsequent cyclization gave intermediate **D**. The elimination of titanium hydroxide and aromatization resulted in the formation of product **5a**.




**Scheme 3.2:** Possible mechanism of the formation of **17a**

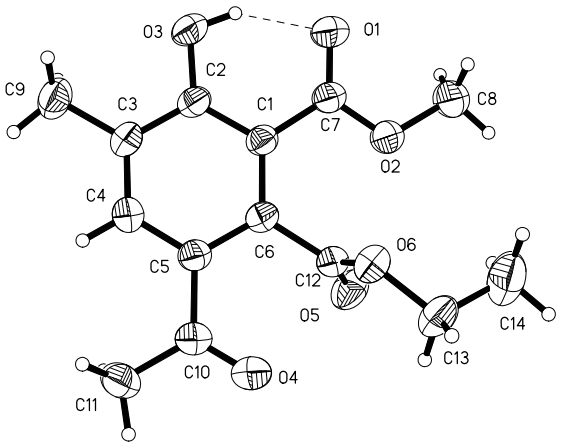
The regioselectivity of the first step (**A→B**) might be explained by the low steric hindrance and by the high positive charge density of the allylic carbon atom attached to the ethoxy group. The regioselectivity of the cyclization (**C→D**) might be explained by selective activation of the 2-oxoester moiety rather than the acetyl group, due to the formation of a chelate complex with $TiCl_4$ (intermediates **A**, **B** and **C**).

The $TiCl_4$-mediated cyclization of 4-acyl-1-hydroxy-2,3-benzodioates **16a-f** with 1,3-bis(trimethylsilyloxy)-1,3-butadienes **4a-i** afforded the 4-acyl-1-hydroxy-2,3-benzodioates **17a-al** in 48-70% yield (Scheme 3.3, Table 3.2). The best yields are obtained for aroyl derivatives **17g-ak** and for ester derivative **17l**.




**Scheme 3.3** Synthesis of **17a-al**

The structures of all products were confirmed by spectroscopic methods. The structures of **17a** and **17b** were independently confirmed by X-ray crystal structure analyses (Figures 3.1, 3.2).



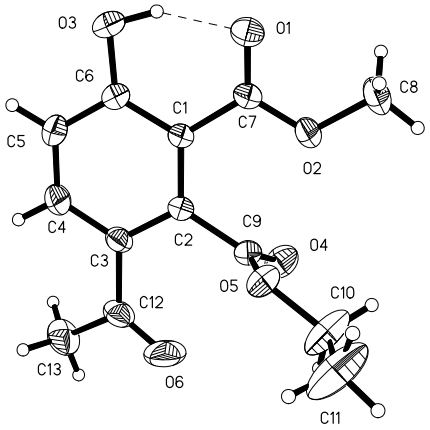
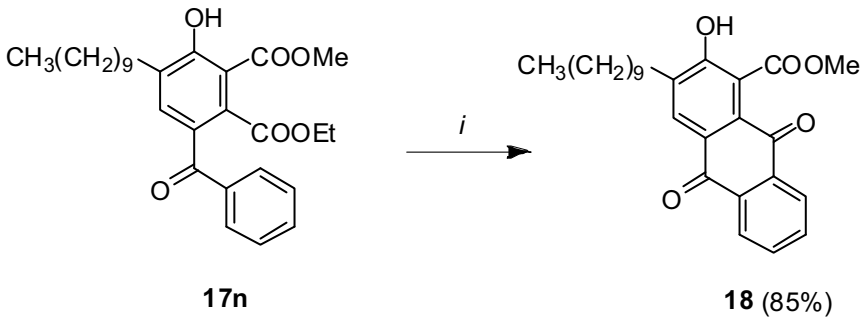




**Figure 3.1:** Ortep plot of **17a** (30% probability level)

**Figure 3.2:** Ortep plot of **17b** (30% probability level)

Treatment of **17n** with conc. sulfuric acid resulted in an intramolecular Friedel-Crafts acylation to give the anthraquinone **18** (Scheme 3.4).




**17n** **18** (85%)

**Scheme 3.4:** Synthesis of **18**; *i*: conc. sulfuric acid, 1h

**Table 3.2:** Synthesis of **17a-al**

| 4 | 16 | 17 | R | $R^1$ | $R^2$ | % (**17**)[a] |
|---|---|---|---|---|---|---|
| **a** | **a** | **a** | Me | H | Me | 48 |
| **b** | **a** | **b** | Me | Me | Me | 50 |
| **c** | **a** | **c** | Me | Et | Et | 50 |
| **d** | **a** | **d** | Me | *n*Bu | Me | 58 |
| **f** | **a** | **e** | Me | *n*Hex | Me | 59 |
| **g** | **a** | **f** | Me | *n*Oct | Me | 59 |
| **a** | **b** | **g** | Ph | H | Me | 65 |
| **b** | **b** | **h** | Ph | Me | Me | 67 |
| **c** | **b** | **i** | Ph | Et | Et | 62 |
| **d** | **b** | **j** | Ph | *n*Bu | Me | 65 |
| **f** | **b** | **k** | Ph | *n*Hex | Me | 65 |
| **g** | **b** | **l** | Ph | *n*Oct | Me | 66 |
| **h** | **b** | **m** | Ph | *n*Non | Me | 67 |
| **i** | **b** | **n** | Ph | *n*Dec | Me | 66 |
| **a** | **c** | **o** | 4-$MeC_6H_4$ | H | Me | 69 |
| **b** | **c** | **p** | 4-$MeC_6H_4$ | Me | Me | 70 |
| **d** | **c** | **q** | 4-$MeC_6H_4$ | *n*Bu | Me | 70 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **f** | **c** | **r** | 4-Me$C_6H_4$ | *n*Hex | Me | 65 |
| **g** | **c** | **s** | 4-Me$C_6H_4$ | *n*Oct | Me | 64 |
| **h** | **c** | **t** | 4-Me$C_6H_4$ | *n*Non | Me | 66 |
| **i** | **c** | **u** | 4-Me$C_6H_4$ | *n*Dec | Me | 65 |
| **a** | **d** | **v** | 4-MeO$C_6H_4$ | H | Me | 62 |
| **b** | **d** | **w** | 4-MeO$C_6H_4$ | Me | Me | 63 |
| **c** | **d** | **x** | 4-MeO$C_6H_4$ | Et | Et | 56 |
| **e** | **d** | **y** | 4-MeO$C_6H_4$ | *n*Pen | Me | 64 |
| **f** | **d** | **z** | 4-MeO$C_6H_4$ | *n*Hex | Me | 61 |
| **h** | **d** | **aa** | 4-MeO$C_6H_4$ | *n*Non | Me | 63 |
| **i** | **d** | **ab** | 4-MeO$C_6H_4$ | *n*Dec | Me | 64 |
| **a** | **e** | **ac** | 4-Br$C_6H_4$ | H | Me | 63 |
| **b** | **e** | **ad** | 4-Br$C_6H_4$ | Me | Me | 66 |
| **c** | **e** | **ae** | 4-Br$C_6H_4$ | Et | Et | 65 |
| **e** | **e** | **af** | 4-Br$C_6H_4$ | *n*Pen | Me | 66 |
| **f** | **e** | **ag** | 4-Br$C_6H_4$ | *n*Hex | Me | 70 |
| **h** | **e** | **ah** | 4-Br$C_6H_4$ | *n*Non | Me | 68 |
| **i** | **e** | **ai** | 4-Br$C_6H_4$ | *n*Dec | Me | 69 |
| **a** | **f** | **aj** | OEt | H | Me | 68 |
| **b** | **f** | **ak** | OEt | Me | Me | 69 |
| **e** | **f** | **al** | OEt | *n*Pen | Me | 69 |

[a] Yields of isolated products

## 3.3 Conclusions

In conclusion, I have reported the regioselective synthesis of 4-acyl-1-hydroxy-2,3-benzodioates by the first chelation-controlled [3+3] cyclizations of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with 4-acyl-1-hydroxy-2,3-benzodioates.

# 4 Synthesis and Antimicrobial Activity of 4-Hydroxy-4-(pyridyl)alk-3-en-2-ones

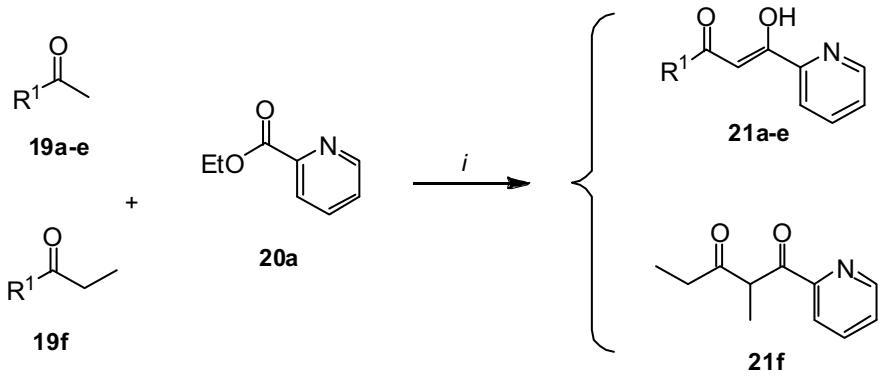
## 4.1 Intoduction

Serious infections by resistant and multiresistant microbes are dramatically increased during the recent years [70], [71] and represent the second leading cause of death [72]. Multiresistant strains of *Staphylococcus aureus*, such as MRSA (Methicillin resistant *S. aureus*), are often responsible for severe and life-threatening infections in patients during their stay in hospitals or in immunosuppressed persons. Therefore, the development of new antimicrobial agents represents an important task in medicinal chemistry. Its success crucially relies on the search for new chemical entities (NCEs). Unfortunately, pharmaceutical companies are more and more leaving this area, due to economic reasons [73]. Genomics, combinatorial synthesis, and high throughput screening (HTS) are used to identify new lead structures. However, success is limited as chemical companies have been unable to identify new and valid antimicrobial agents by random screening of compound libraries [73]. In fact no innovative antibiotics have been launched on the market for several decades. It was not before 2000 and 2003 that the first new NCEs, the oxazolidinone linezolid and the lipopeptide daptomycin, appeared on the market, respectively [74], [75]. Recently, we have reported that 2-vinylchroman-4-ones show a remarkable activity against several humanpathogenic bacteria, including multiresistant strains [76]. Herein, I report, for the first time, the synthesis of novel 4-hydroxy-4-(pyridyl)alk-3-en-2-ones and their antimicrobial activity against Gram-positive and Gram-negative bacteria

## 4.2 Result and discussion

### 4.2.1 Chemistry

The NaH-mediated condensation of ketones **19a-f** with ethyl pyridine-2-carboxylate (**20a**) afforded the 4-hydroxy-4-(pyrid-2-yl)alk-3-en-2-ones **21a-f** (Scheme 4.1, Table 4.1). Products **21a-e** exclusively exist in their enol tautomeric form. Product **21f** exclusively resides in the keto form which is often the case for 2-substituted 1,3-diketones.



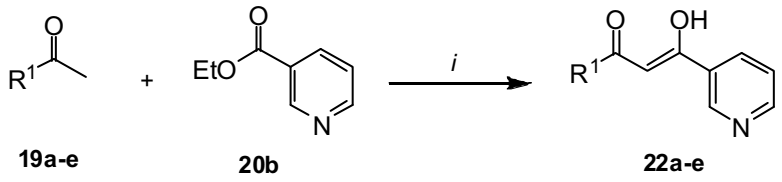

**Scheme 4.1:** Synthesis of **21a-f**; *i*: NaH (4.0 equiv.), **20a** (1.0 equiv.), **19a-f** (2.0 equiv), $Et_2O$, reflux, 2 h.

**Table 4.1:** Synthesis of **21a-f**

| 1 | 2 | 3 | $R^1$ | % (3)[a] |
|---|---|---|---|---|
| **a** | **a** | **a** | Me | 65 |
| **b** | **a** | **b** | Et | 55 |
| **c** | **a** | **c** | *n*Pr | 66 |
| **d** | **a** | **d** | *n*Bu | 50 |
| **e** | **a** | **e** | Ph | 61 |
| **f** | **a** | **f** | Et | 55 |

[a] Yields of isolated products

The condensation of ketones **19a-e** with ethyl pyridine-3-carboxylate (**20b**) afforded the 4-hydroxy-4-(pyrid-3-yl)alk-3-en-2-ones **22a-e** (Scheme 4.2, Table 4.2). Products **22a-e** exclusively exist in their enol tautomeric form.




**Scheme 4.2:** Synthesis of **22a-e**; *i*: NaH (4.0 equiv.), **20b** (1.0 equiv.), **19a-e** (2.0 equiv), $Et_2O$, reflux, 2 h.

**Table 4.2:** Synthesis of **4a-e**

| 1 | 2 | 3 | $R^1$ | % (4)a |
|---|---|---|---|---|
| **a** | **a** | **a** | Me | 53 |
| **b** | **a** | **b** | Et | 67 |
| **c** | **a** | **c** | *n*Pr | 70 |
| **d** | **a** | **d** | *n*Bu | 62 |
| **e** | **a** | **e** | Ph | 65 |

[a] Yields of isolated products

### 4.2.2 Biological Activity

The biological activity of compounds **21** and **22** were evaluated using an initial antimicrobial screening (agar diffusion test). During these studies some derivatives showed remarkable antibacterial properties. Especially the growth of Gram-positive bacteria *Staphylococcus aureus* and *Bacillus subtilis* and the Gram-negative *Escherichia coli* was inhibited. The minimal inhibitory concentrations of all compounds were further investigated. The results of these studies are summarized in Table 4.3. The antimicrobial activity of the 4-hydroxy-4-(pyridyl)alk-3-en-2-ones is promising, albeit lower compared to the standard antibiotic Ampicillin, and shows an interesting influence of the substitution pattern.

The presence of the pyridine moiety is mandatory for the pharmacological activity. The antibacterial activities strongly depend on the substitution pattern of the pyridine moiety. The pyrid-2-yl derivatives **21a**, **21b**, **21c**, and **21d** are the most active compounds in this study. Interestingly, only derivatives which exist in their enol tautomeric form exhibit a good

antimicrobial activity. In contrast, **21f** (which exclusively resides in the keto form) possesses the lowest antibacterial activity against Gram-positive bacteria. Compound **21f** only shows a weak activity against Gram-negative *E. coli*. This suggests that the formation of the enol tautomeric form is essential for the antibiotic activity of the pyridyl compounds. Considering the influence of substituent $R^1$ it was found that more bulky residues lead to a stronger growth inhibition. This is especially the case for *B. subtilis*. In *S. aureus* this tendency is also observable but to a lower extent. Beside this observation the highest antibacterial activity was found for compounds **22e** and **21e**. The latter showed the highest activity against all tested bacteria. The phenyl substitution seems to be a strong inducer for the antibacterial activity. This might be explained by a better binding to unpolar residues at the cellular target. The *n*-butyl-substituted derivatives **22d** and **21e** also show a remarkable growth inhibition which further supports this assumption. The mechanism of action might be based on binding of the enol moiety to the cellular receptor and interaction with an aromatic residue of the latter. More investigation towards the mechanism of action should concentrate on the role of the substitution pattern of the 1,3-diketo moiety. The derivatisation of the phenyl group should give more insight into the mode of action. Furthermore the investigation of possible alterations of the metabolism under influence of the pyridyl-derivatives in the tested bacteria is interesting and will be topic of future work.

**Table 4.3:** Minimal inhibitory concentrations of selected compounds **21** and **22** (values given in mM) [a]

| Compond | ***S. aureus*** *ATCC 6538* | ***B. subtilis*** *ATCC 11229* | ***E. coli*** *ATCC 6051* |
|---|---|---|---|
| **21a** | 0.29 | 1.16 | 2.32 |
| **21b** | 0.13 | 1.19 | 1.1 |
| **21c** | 1 | 0.51 | 0.51 |
| **21d** | 0.47 | 0.23 | 0.23 |
| **21e** | 0.21 | 0.11 | 0.11 |
| **21f** | 3.97 | 4.11 | 2.01 |
| **22a** | 2.4 | 2.43 | 2.46 |
| **22b** | 2.15 | 2.11 | 2.14 |
| **22c** | 1.01 | 1.05 | 0.49 |
| **22d** | 0.46 | 0.47 | 0.47 |
| **22e** | 0.42 | 0.42 | 0.43 |
| **Ampicillin** | 0.009 | 0.034 | 0.019 |

[a] Minimal inhibitory concentrations were determined by a dilution assay (results are averages of 3 independent experiments).

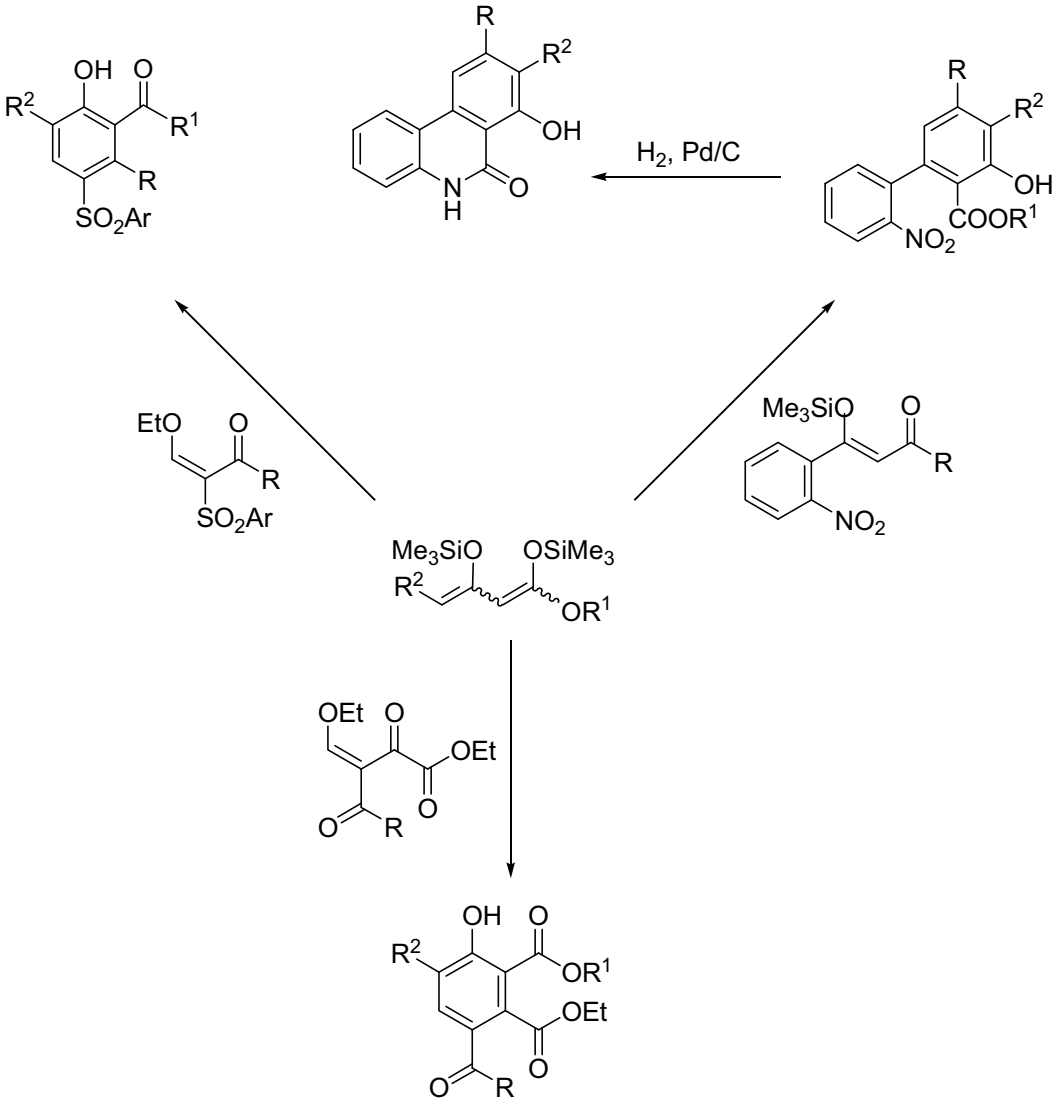
## 4.3 Conclusions

A variety of novel 4-hydroxy-4-(pyrid-2-yl)alk-3-en-2-ones were prepared by base-mediated condensation of ketones with pyridinecarboxylates. Several derivatives show a significant antimicrobial activity against Gram-positive and Gram-negative bacteria.

# 5 Abstract

Regioselective cyclocondensation reactions of 1,3-bis(silyl enol ethers) with different mono(silyl enol ethers) provide an elegant approach for the synthesis of various complex carba- and heterocycles from simple starting materials. 2-Nitro-substituted biaryls are prepared based on [3+3] cyclocondensations of 1,3-bis(silyl enol ethers) with 3-nitroaryl-3-silyloxy-2-en-1-ones. Subsequently, 2-nitro-substituted biaryls are transformed into biaryl lactams [6(5*H*)-phenanthridinones] by reduction using hydrogen (Pd/C-catalysis). The cyclocondensation reaction of 1,3-bis(silyl enol ethers) with 2-arylsulfonyl-3-ethoxy-2-en-1-ones yielded 4-(arylsulfonyl)phenols. 4-Acyl-1-hydroxy-2,3-benzodioates were synthesized by chelation-controlled [3+3] annulation of 3-acyl-4-ethoxy-2-oxo-3-enoates with 1,3-bis(trimethylsilyloxy)-1,3-butadienes. Furthermore the synthesis and antimicrobial activity of 4-hydroxy-4-(pyridyl)alk-3-en-2-ones is reported.

Regioselektive Cyclokondensationsreaktionen von 1,3-Bis(silylenolethern) mit unterschiedlichen Mono(silylenolethern) bieten einen eleganten Zugang zu einer Vielzahl unterschiedlicher Carba- und Heterocyclen ausgehend von einfachen Ausgangsstoffen. 2-Nitro-substituierte Biaryle werden durch [3+3] Cyclokondensationen von 1,3-Bis(silylenolethern) und 3-Nitroaryl-3-silyloxy-2-en-1-ones hergestellt. Anschließend werden nitrosubstituierte Biaryle in Lactame [6(5*H*)-Phenanthridinone] durch Hydrierung mit Wasserstoff (Pd/C-Katalyse) umgewandelt. Die Cyclokondensation von 1,3-Bis(silylenolethern) mit 2-Arylsulfonyl-3-ethoxy-2-en-1-onen lieferte 4-(Arylsulfonyl)phenole. 4-Acyl-1-hydroxy-2,3-benzodioate werden durch chelatkontrollierte [3+3] Cyclisierungen von 1,3-Bis(silylenolethern) hergestellt. Weiterhin wurden antimikrobiell aktive 4-Hydroxy-4-(pyridyl)alk-3-en-2-one hergestellt.




**General Scheme**: Some main results of the present thesis

# 6 Experimental Section

## 6.1 General: Equipment, chemicals and work technique

**$^{1}$H NMR Spectroscopy:**

Bruker: AM 250, Avance 250, AC 250 (250 MHz); ARX 300, Avance 300 (300 MHz); Varian VXR 500 S, Avance 500 (500 MHz); δ = 0.00 ppm for Tetramethylsilane; δ = 2.04 ppm for Acetone d-6; δ = 7.26 ppm for Deuterochloroform (CDCl3) and δ = 2.50 ppm for DMSO- $d_6$; Characterization of the signal fragmentations: s = singlet, d = doublet, dd = double of doublet, ddd = doublet of a double doublet, t = triplet, q = quartet, quint = quintet; sext = Sextet, sept = Septet, m = multiplet, br = broadly. Spectra were evaluated according to first order rule. All coupling constants are indicated as (*J*).

**$^{13}$C NMR Spectroscopy:**

Bruker: AM 250, Avance 250, AC 250 (62.9 MHz); ARX 300, Avance 300 (75 MHz); Varian VXR 500 S, Avance 500 (125 MHz); δ = 128.00 ppm for Acetone d-6; δ = 77.00 ppm for CDCl3, δ = 39.7 ppm for DMSO- $d_6$. The multiplicity of the carbon atoms was determined by the DEPT 135 and APT technique (APT = Attached Proton Test) and quoted as $CH_3$, $CH_2$, CH and C for primary, secondary, tertiary and quaternary carbon atoms. Characterization of the signal fragmentations: quart = quartet the multiplicity of the signals was determined by the DEPT recording technology and/or the APT recording technology.

**Mass Spectroscopy:**

AMD MS40, AMD 402 (AMD Intectra), Varian MAT CH 7, MAT 731.

**High Resolution mass spectroscopy:**

Finnigan MAT 95 or Varian MAT 311; Bruker FTCIR, AMD 402 (AMD Intectra).

**Infrared spectroscopy (IR):**

Bruker IFS 66 (FT IR), Nicolet 205 FT IR; Nicolet Protege 460, Nicolet 360 Smart Orbit (ATR); KBr, KAP, Nujol, and ATR; Abbreviations for signal allocations: w = weak, m = medium, s = strong, br = broad.

**Elementary analysis:**

LECO CHNS-932, Thermoquest Flash EA 1112.

**X-ray crystal structure analysis: B**

ruker X8Apex Diffractometer with CCD-Kamera (Mo-$K_a$ und Graphit Monochromator, $\lambda = 0.71073$ Å).

**Melting points:**

Micro heating table HMK 67/1825 Kuestner (Büchi apparatus); Meltingpoints are uncorrected.

**Column chromatography:**

Chromatography was performed over Merck silica gel 60 (0,063 -0,200 mm, 70 - 230 mesh) as normal and/or over mesh silica gel 60 (0,040 - 0,063 mm, 200 -400 mesh) as Flash Chromatography. All solvent were distilled before use.

**TLC:**

Merck DC finished foils silica gel 60 F254 on aluminum foil and Macherey finished

foils Alugram® Sil G/UV254. Detection under UV light with 254 nm and/or 366 nm without dipping reagent, as well as with anisaldehyde sulfuric acid reagent (1 mL anisaldehyde consisting in 100 mL stock solution of 85% methanol, 14% acetic acid and 1% sulfuric acid).

**Chemicals and work technique:**

All solvents for using were distilled by standard methods. All reactions were carried out under an inert atmosphere, oxygen and humidity exclusion. All of the chemicals are standard, commercially available from Merck®, Aldrich®, Arcos® and others. The order of the characterized connections effected numerically, but does not correspond to the order in the main part of dissertation.

**Biological testing:**

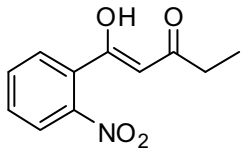
Evaluation of the biological activity was described earlier [85[a]].

## 6.2 Procedures and spectroscopic data

**General procedure for the synthesis of 1,3-dicarbonyl compounds 7a-e:**

To a stirred solution of LDA (75.0 mmol) in THF (1.2 mL/1.0 mmol of LDA) was added ketone **5** (50.0 mmol) at ~ 78 °C. After the solution was stirred for 1 h, the acid chloride **6** (60.0 mmol) was added. The temperature of the solution was allowed to rise to 20 °C during 12 h. A saturated solution of $NH_4Cl$ was added, the layers were separated, and the aqueous layer was extracted with EtOAc (3×50 mL). The combined organic layers were dried ($Na_2SO_4$) and filtered, and the solvent was removed in *vacuo*. The residue was purified by chromatography (silica gel, *n*-heptane/EtOAc = 30:1 → 20:1) to give **7.** Compounds **6** were commercially available.

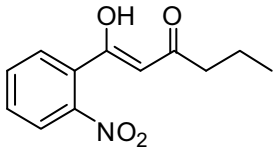
**1-hydroxy-1-(2-nitrophenyl)pent-1-en-3-one (7a):**




Chemical Formula: $C_{11}H_{11}NO_4$
Exact Mass: 221.069

Reaction starting with LDA (1.5 equiv.) in THF (62 mL), **5a** [2-Butanone] (4.47 mL, 50 mmol), and **6** [2-Nitrobezoylchloride] (7.89 mL, 60.0 mmol), **7a** was isolated as a yellowish solid (11.93 g, 45 %), m.p 58 – 60 °C. $^1$H NMR (250 MHz, $CDCl_3$): δ = 1.10 (t, $^3J$ = 7.7 Hz, 3 H, $CH_2CH_3$), 2.58 (q, $^3J$ = 7.1 Hz, 2 H, $CH_2CH_3$), 5.73 (s, 1 H, CH), 7.45 - 7.55 (m, 3 H, $CH_{Ar}$), 7.80 – 7.83 (m, 1 H, $CH_{Ar}$), 15.10 ($s_{(br)}$, 1 H, OH).$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 9.6 ($CH_3$), 31.5 ($CH_2$), 98.5 (CH), 124.4, 129.1, 130.8, 132.8 ($CH_{Ar}$), 134.2, 148.1 ($C_{Ar}$), 186.6 (COH), 194.5 (CO). MS (EI 70 eV): *m/z* (%) = 221 ($[M]^+$, 2), 151 (11), 150 (100), 136 (24), 135 (24), 134 (11), 104 (16), 92 (17), 79 (10), 77 (14), 76 (18), 57 (43), 51 (16), 43 (300). HRMS (EI): Calcd. for $C_{11}H_{11}O_4N$: 221.06826; found: 221.068437.

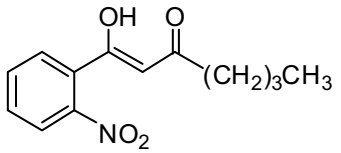
**1-hydroxy-1-(2-nitrophenyl)hex-1-en-3-one (7b):**



Chemical Formula: $C_{12}H_{13}NO_4$
Exact Mass: 235.084

Reaction starting with LDA (1.5 equiv.) in THF (62 mL), **5b** [2-Pentanone] (5.32 mL, 50 mmol), and **6** [2-Nitrobezoylchloride] (7.89 mL, 60.0 mmol), **7b** was isolated as a yellowish oil (5.98 g, 46 %). $^1$H NMR (250 MHz, $CDCl_3$): δ = 1.12 (t, $^3J$ = 7.6 Hz, 3 H, $CH_2CH_2\mathit{CH_3}$), 1.40 - 1.45 (m, 2 H, $CH_2\mathit{CH_2}CH_3$), 2.40 (t, $^3J$ = 7.4 Hz, 2 H, $\mathit{CH_2}CH_2CH_3$), 5.70 (s, 1 H, CH), 7.46 ─ 7.56 (m, 3 H, $CH_{Ar}$), 7.83 - 7.86 (m, 1 H, $CH_{Ar}$), 15.12 ($s_{(br)}$, 1 H, OH).$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 13.5 ($CH_3$), 18.5, 32.5 ($CH_2$), 98.4 (CH), 124.4, 129.2, 130.9, 132.9 ($CH_{Ar}$), 134.1, 148.1 ($C_{Ar}$), 186.5 (COH), 194.6 (CO).

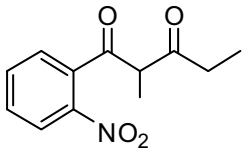
**1-hydroxy-1-(2-nitrophenyl)hept-1-en-3-one (7c):**



Chemical Formula: $C_{13}H_{15}NO_4$
Exact Mass: 249.100

Reaction starting with LDA (1.5 equiv.) in THF (62 mL), **5c** [2-Hexnone] (6.18 mL, 50 mmol), and **6** [2-Nitrobezoylchloride] (7.89 mL, 60.0 mmol), **7c** was isolated as a red-yellowish oil (5.98 g, 40 %). $^1$H NMR (250 MHz, $CDCl_3$): δ = 0.95 (t, $^3J$ = 7.4 Hz, 3 H, $CH_2CH_2CH_2\mathit{CH_3}$), 1.35 – 1.44 (m, 2 H, $CH_2$), 1.59 - 1.70 (m, 2 H, $CH_2$), 2.38 (t, $^3J$ = 7.8 Hz, 2 H, $\mathit{CH_2}CH_2CH_2CH_3$), 5.79 (s, 1 H, CH), 7.54 - 7.64 (m, 3 H, $CH_{Ar}$), 7.90 - 7.93 (m, 1 H, $CH_{Ar}$), 15.24 ($s_{(br)}$, 1 H, OH). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 13.7 ($CH_3$), 22.2, 27.8, 37.5 ($CH_2$), 99.1 (CH), 124.4, 129.1, 131.0, 132.8 ($CH_{Ar}$), 134.6, 147.8 ($C_{Ar}$), 186.9 (COH), 193.2 (CO).

**2-methyl-1-(2-nitrophenyl)pentane-1,3-dione (7d):**

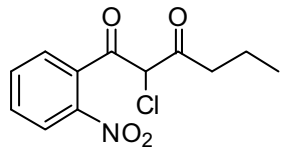


Chemical Formula: $C_{12}H_{13}NO_4$
Exact Mass: 235.084

Reaction starting with LDA (1.5 equiv.) in THF (24 mL), **5d** [3-Pentanone] (2.11 mL, 20 mmol), and **6** [2-Nitrobezoylchloride] (3.15 mL, 24.0 mmol), **7d** was isolated as a red-yellowish oil (2.70 g, 48 %). $^1$H NMR (250 MHz, $CDCl_3$): δ = 1.12 (t, $^3J$ = 7.0 Hz, 3 H, $CH_2\mathit{CH_3}$), 1.41 (d, $^3J$ = 6.7 Hz, 3 H, $\mathit{CH_3}CHCOC_2H_5$), 2.46 (q, $^3J$ = 7.3 Hz, 2 H, $\mathit{CH_2}CH_3$), 4.04 (q, $^3J$ = 7.1 Hz, 1 H, $\mathit{CH}CH_3$), 7.34 - 7.67 (m, 3 H, $CH_{Ar}$), 8.05 - 8.08 (m, 1 H, $CH_{Ar}$).$^{13}$C NMR (75 MHz, $CDCl_3$):

δ = 7.5, 13.6 ($CH_3$), 34.9 ($CH_2$), 60.0 (CH), 124.3, 128.4, 130.6, 134.6 ($CH_{Ar}$), 137.0, 145.4 ($C_{Ar}$), 196.3, 207.6 (CO). MS (EI 70 eV): *m/z* (%) = 235 ($[M]^+$, 2), 151 (10), 150 (78), 136 (15), 135 (13), 104 (13), 92 (12), 79 (13), 77 (16), 76 (31), 57 (100), 51 (22), 50 (14),43 (9), 29 (25).HRMS (EI): Calcd. for $C_{12}H_{13}NO_4$: 235.08391; found: 235.083664.

**2-chloro-1-(2-nitrophenyl)hexane-1,3-dione (7e):**




Chemical Formula: $C_{12}H_{12}ClNO_4$
Exact Mass: 269.045

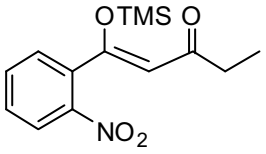
A mixture of **7b** (2.00 g, 8.50 mmol) and NCS (1.04 g, 7.80 mmol) in $CCl_4$ (18 mL) was heated at reflux for 8 h. After cooling, the precipitate of succinimide was filtered off and water was added, the layers were separated, and the aqueous layer was extracted with $CH_2Cl_2$ (3×150 mL). The combined organic layers were dried ($Na_2SO_4$) and filtered, and the solvent was removed in vacuo. The residue was purified by chromatography (silica gel, *n*-heptane/EtOAc 30:1 → 20:1) to give **7e** as yellowish oil (1.95 g, 85 %). $^1$H NMR ($CDCl_3$, 250 MHz): δ = 0.96 (t, $^3J$ = 7.1 Hz, 3 H, $CH_2CH_2\mathit{CH_3}$), 1.61 - 1.73 (m, 2 H, $CH_2\mathit{CH_2}CH_3$), 2.55 (t, $^3J$ = 7.4 Hz, 2 H, $\mathit{CH_2}CH_2CH_3$), 5.23 (s, 1 H, CH), 7.53 - 7.78 (m, 3 H, $CH_{Ar}$), 8.23 - 8.27 (m, 1 H, $CH_{Ar}$).$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.7 ($CH_3$), 18.6, 37.3 ($CH_2$), 69.6 (CH), 124.4, 130.0, 131.7, 134.9 ($CH_{Ar}$), 139.5, 145.4 ($C_{Ar}$), 189.5, 199.8 (CO).

**General procedure for the synthesis of silyl enol ethers 8a-e:**

To a stirred benzene solution (2.5 mL/1.0 mmol of **3**) of **3** (10.0 mmol) was added triethylamine (16.0 mmol). After stirring of the solution for 2 h, trimethylchlorosilane (18.0 mmol) was added. After stirring of the solution for 72 h, the solvent was removed in *vacuo* and hexane (25 mL) was added to the residue to give a suspension. The latter was filtered under argon atmosphere. The filtrate was concentrated in *vacuo* to give silyl enol ethers **8a-e**.

Due to the unstable nature of the silyl enol ethers, they were characterized only by NMR spectroscopy.

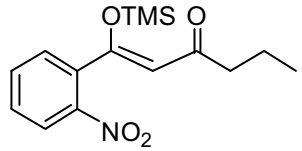
**1-(2-nitrophenyl)-1-(trimethylsilyloxy)pent-1-en-3-one (8a):**




Chemical Formula: $C_{14}H_{19}NO_4Si$
Exact Mass: 293.108

Starting with benzene (52.0 mL), **7a** (4.62 g, 20.88 mmol), triethylamine (4.65 mL, 33.41 mmol) and trimethylchlorosilane (4.74 mL, 37.59 mmol), **8a** was isolated as a reddish oil (5.80 g, 95 %). $^1$H NMR (250 MHz, $CDCl_3$): δ =0.21 - 0.31 (m, 9 H, $Si(CH_3)_3$), 0.98 (t, $^3J$ = 7.6 Hz, 3 H, $CH_2CH_3$), 2.58 (q, $^3J$ = 7.1 Hz, 2 H, $CH_2CH_3$), 5.81 (s, 1 H, CH), 7.44 - 7.53 (m, 3 H, $CH_{Ar}$), 7.80 - 7.83 (m, 1 H, $CH_{Ar}$). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 0.3 ($Si(CH_3)_3$), 7.8 ($CH_3$), 36.8 ($CH_2$), 98.4 (CH), 123.6, 127.9, 129.4, 131.9 ($CH_{Ar}$), 134.6, 145.0 ($C_{Ar}$), 177.4 (COTMS), 198.5 (CO).

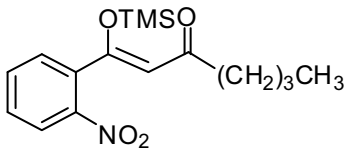
**1-(2-nitrophenyl)-1-(trimethylsilyloxy)hex-1-en-3-one(8b):**




Chemical Formula: $C_{15}H_{21}NO_4Si$
Exact Mass: 307.124

Starting with benzene (63.0 mL), **7b** (4.83 g, 20.2 mmol), triethylamine (4.50 mL, 43.0 mmol) and trimethylchlorosilane (4.64 mL, 33.1 mmol), **8b** was isolated as a reddish oil(5.60 g, 88%). $^1$H NMR (250 MHz, $CDCl_3$): δ = 0.21 - 0.43 (m, 9 H, $Si(CH_3)_3$), 1.06 - 1.14 (m, 3 H, $CH_3$), 1.69 - 1.85 (m, 2 H, $CH_2$), 2.43 - 2.53 (m, 2 H, $CH_2$), 5.85 (s, 1 H, CH), 7.50 - 8.00 (m, 3 H, $CH_{Ar}$), 8.07 ─ 8.19 (m, 1 H, $CH_{Ar}$), $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 0.2 ($Si(CH_3)_3$), 13.8 ($CH_3$), 36.4, 39.5 ($CH_2$), 98.9 (CH), 124.1, 128.1, 129.3, 131.6 ($CH_{Ar}$), 139.4, 148.3, ($C_{Ar}$), 178.0 (COTMS), 193.2 (C=O).

**1-(2-nitrophenyl)-1-(trimethylsilyloxy)hept-1-en-3-one (8c):**

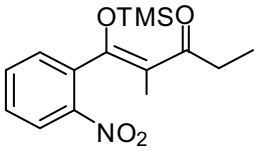



Chemical Formula: $C_{16}H_{23}NO_4Si$
Exact Mass: 321.140

Starting with benzene (22.5 mL), **7c** (2.20 g, 8.89 mmol), triethylamine (1.99 mL, 14.23 mmol) and trimethylchlorosilane (2.02 mL, 16.0 mmol), **8c** was isolated as a reddish oil (2.66 g, 93 %). $^1$H NMR (250 MHz, $CDCl_3$): δ =0.24 - 0.27 (m, 9 H, $Si(CH_3)_3$), 0.89 (t, $^3J$ = 7.6 Hz, 3 H, $CH_2CH_2CH_2CH_3$), 1.31 - 1.38 (m, 2 H, $CH_2$), 1.51 - 1.60 (m, 2 H, $CH_2$), 2.34 (t, $^3J$ = 6.8 Hz, 2 H, $CH_2CH_2CH_2CH_3$), 5.79 (s, 1 H, CH), 7.53 - 7.65 (m, 3 H, $CH_{Ar}$), 7.91 - 7.94 (m, 1 H, $CH_{Ar}$). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 0.3 ($Si(CH_3)_3$), 13.6

($CH_3$), 22.1, 27.7, 37.4 ($CH_2$), 99.0 (CH), 124.1, 129.0, 131.1, 132.8 ($CH_{Ar}$), 133.4, 139.1 ($C_{Ar}$), 176.5 (COTMS), 193.3 (CO).

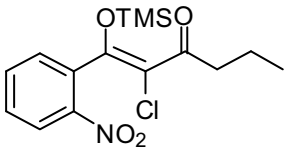
**2-methyl-1-(2-nitrophenyl)-1-(trimethylsilyloxy)pent-1-en-3-one (8d):**




Chemical Formula: $C_{15}H_{21}NO_4Si$
Exact Mass: 307.124

Starting with benzene (29.0 mL), **7d** (2.70 g, 11.50 mmol), triethylamine (2.57 mL, 18.4 mmol) and trimethylchlorosilane (2.61 mL, 20.70 mmol), **8d** was isolated as a yellowish oil (3.31 g, 94 %). $^1$H NMR (250 MHz, $CDCl_3$): δ =0.1 - 0.29 (m, 9 H, $Si(CH_3)_3$), 0.88 (t, $^3J$ = 6.8 Hz, 3 H, $CH_2CH_3$), 2.02 (s, 3 H, $CH_3$), 2.36 (q, $^3J$ = 8.7 Hz, 2 H, $CH_2CH_3$), 7.28 - 7.54 (m, 3 H, $CH_{Ar}$), 8.00 - 8.03 (m, 1 H, $CH_{Ar}$). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 0.2 ($Si(CH_3)_3$), 7.1, 12.5 ($CH_3$), 34.0 ($CH_2$), 118.2 (C), 123.6, 128.9, 130.5, 132.6 ($CH_{Ar}$), 145.6, 152.9 ($C_{Ar}$), 168.5 (COTMS), 202.8 (CO).

**2-chloro-1-(2-nitrophenyl)-1-(trimethylsilyloxy)hex-1-en-3-one (8e):**




Chemical Formula: $C_{15}H_{20}ClNO_4Si$
Exact Mass: 341.085

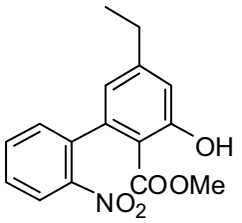
Starting with benzene (52.0 mL), **7e** (1.95 g, 7.22 mmol), triethylamine (1.62 mL, 11.56 mmol) and trimethylchlorosilane (1.64 mL, 13.01 mmol), **8e** was isolated as a yellowish oil (2.27 g, 92 %). $^1$H NMR (250 MHz, $CDCl_3$): δ =0.10 - 0.23 (m, 9 H, $Si(CH_3)_3$), 0.93 (t, $^3J$ = 7.4 Hz, 3 H, $CH_2CH_2CH_3$), 1.58 – 1.69 (m, 2 H, $CH_2$), 2.53 (t, $^3J$ = 7.6 Hz, 2 H, $CH_2CH_2CH_3$), 7.42 - 7.63 (m, 3 H, $CH_{Ar}$), 8.13 - 8.23 (m, 1 H, $CH_{Ar}$). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 0.1 ($Si(CH_3)_3$), 13.4 ($CH_3$), 18.2, 37.0 ($CH_2$), 108.9 (CCl), 124.2, 129.9, 131.2, 132.8 ($CH_{Ar}$), 143.2, 147.6 ($C_{Ar}$), 165.1 (COTMS), 189.1 (CO).

**General procedure for the synthesis of salicylates 9a-l:**

To a $CH_2Cl_2$ solution of silyl enol ether **8** (1.0 equiv.) and 1,3-bis(silyl enol ether) **4** (1.1 equiv.) was dropwise added $TiCl_4$ (1.1 equiv.) at –78 $^o$ C under argon atmosphere. The solution was stirred at –78 $^o$ C for 30 min and then allowed to warm to 20 °C during 18 h. To the solution was added a saturated aqueous solution of 10 % HCl. The organic layer was separated and the aqueous layer was repeatedly extracted with $CH_2Cl_2$. The combined organic

extracts were dried ($Na_2SO_4$) and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography (silica gel, *n*-hexane/EtOAc) to give salicylates **9.**

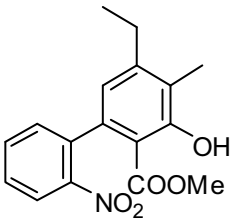
**methyl 5-ethyl-3-hydroxy-2'-nitrobiphenyl-2-carboxylate (9a):**




Chemical Formula: $C_{16}H_{15}NO_5$
Exact Mass: 301.095

Starting with bis silyl-enol ether **4a** (1.720 g, 6.6 mmol), $TiCl_4$ (1.251 g, 6.6 mmol) $CH_2Cl_2$ (12 mL) and monosilyl enol ether **8a** (1.760 g, 6.0 mmol), **9a** was isolated (0.780 g, 43 %) as a yellowish oil. $^1$H NMR ($CDCl_3$, 250 MHz): δ = 1.05 (t, $^3J$ = 7.5 Hz, 3 H, $CH_2CH_3$), 2.45 (q, $^3J$ = 7.5 Hz, 2 H, $CH_2CH_3$), 3.27 (s, 3 H, $OCH_3$), 6.31 (d, $^4J$ = 2.0 Hz, 1 H, $CH_{Ar}$), 6.70 (d, $^4J$ = 1.7 Hz, 1 H, $CH_{Ar}$), 7.07 (dd, $^3J$ = 7.7 Hz, $^4J$ = 1.3 Hz, 1 H, $CH_{Ar}$), 7.31 (ddd, $^3J$ = 7.0 Hz, $^3J$ = 7.0 Hz, $^4J$ = 1.5 Hz, 1 H, $CH_{Ar}$), 7.43 (ddd, $^3J$ = 7.5 Hz, $^3J$ = 7.5 Hz, $^4J$ = 1.5 Hz, 1 H, $CH_{Ar}$), 7.87 (dd, $^3J$ = 8.4 Hz, $^4J$ = 1.3 Hz, 1 H, $CH_{Ar}$), 11.05 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 14.6 ($CH_3$), 28.9 ($CH_2$), 52.4 ($OCH_3$), 108.8 ($CCOOCH_3$), 117.2, 121.5, 123.8, 127.8, 131.3, 132.5 ($CH_{Ar}$), 138.5, 140.4, 148.1, 151.8, 162.8 ($C_{Ar}$), 170.4 (CO).IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 3022 (w), 2949 (w), 2872 (w), 1659 (s), 1607 (m), 1571 (m), 1522 (s), 1436 (m), 1417 (w), 1386 (w), 1344 (s), 1272 (m), 1211 (s), 1160 (m), 1145 (m), 1102 (m), 1039 (w), 947 (w), 870 (w), 804 (m), 743 (s), 688 (s), 635 (m), 544 (w).GC-MS (EI 70 eV): *m/z* (%) = 301 ($[M]^+$, 45), 270 (15), 269 (86), 256 (17), 255 (100), 242 (14), 241 (16), 240 (18), 213 (18), 198 (10), 197 (17), 196 (14), 195 (21), 181 (14), 180 (12), 170 (16), 168 (16), 167 (16), 166 (10), 165 (26), 153 (12), 152 (36), 151 (14), 139 (15), 128 (12), 127 (11), 115 (24), 77 (11), 76 (10). HRMS (EI): Calcd. for $C_{16}H_{15}NO_5$: 301.09447; found: 301.094496.

**methyl 5-ethyl-3-hydroxy-4-methyl-2'-nitrobiphenyl-2-carboxylate (9b):**



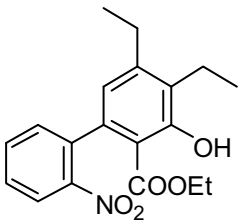

Chemical Formula: $C_{17}H_{17}NO_5$
Exact Mass: 315.111

Starting with bis silyl-enol ether **4b** (1.207 g, 4.4 mmol), $TiCl_4$ (0.834 g, 4.4 mmol) $CH_2Cl_2$ (8 mL) and monosilyl enol ether **8a** (1.170 g, 4.0 mmol), **9b** was isolated (0.530 g, 42 %) as a yellowish oil. $^1$H NMR ($CDCl_3$, 250 MHz): δ = 1.05 (t, $^3J$ = 7.4 Hz, 3 H, $CH_2CH_3$), 2.12 (s, 3 H, $CH_3$), 2.52 (q, $^3J$ = 7.5 Hz, 2 H, $CH_2CH_3$), 3.32 (s, 3 H, $OCH_3$), 6.35 (s, 1 H, $CH_{Ar}$), 7.12 (dd, $^3J$ = 7.3 Hz, $^4J$ = 1.4 Hz, 1 H, $CH_{Ar}$), 7.34 (ddd, $^3J$ = 7.6 Hz, $^3J$ = 7.6 Hz, $^4J$ = 1.8 Hz, 1 H, $CH_{Ar}$), 7.46 (ddd, $^3J$ = 7.3 Hz, $^3J$ = 7.3 Hz, $^4J$ = 1.6 Hz, 1 H, $CH_{Ar}$), 7.90 (dd, $^3J$ = 8.3 Hz, $^4J$ =

1.4 Hz, 1 H, $CH_{Ar}$), 11.48 (s, 1 H, OH). $^{13}C$ NMR ($CDCl_3$, 75 MHz): δ = 11.0, 14.1 ($CH_3$), 27.0 ($CH_2$), 51.9 ($OCH_3$), 108.0 (*C*$COOCH_3$), 121.0, 123.5, 124.4, 127.6, 131.3, 132.6 ($CH_{Ar}$), 137.1, 138.7, 143.3, 149.2, 160.8 ($C_{Ar}$), 170.4 (CO).IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 3065 (w), 2967 (w), 2874 (w), 1659 (s), 1606 (m), 1567 (m), 1522 (s), 1437 (m), 1397 (m), 1345 (s), 1269 (s), 1214 (m), 1173 (m), 1144 (m), 1108 (w), 1044 (w), 927 (w), 867 (w), 809 (m), 730 (s), 683 (m), 632 (w), 605 (w).GC-MS (EI 70 eV): *m/z* (%) = 315 ($[M]^+$, 59), 284 (19), 283 (100), 269 (21), 254 (12), 238 (28), 224 (22), 222 (20), 195 (10), 194 (38), 193 (10), 181 (10), 178 (10), 168 (10), 167 (16), 166 (12), 165 (32), 153 (10), 152 (20), 151 (9), 139 (10), 128 (9), 127 (8), 115 (12), 77 (8), 76 (7).

HRMS (EI): Calcd. for $C_{17}H_{17}NO_5$: 315.11012; found: 315.110575.

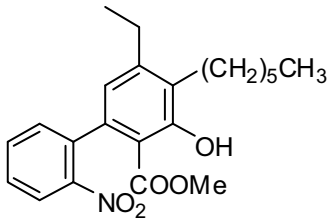
**ethyl 4,5-diethyl-3-hydroxy-2'-nitrobiphenyl-2-carboxylate (9c):**




Chemical Formula: $C_{19}H_{21}NO_5$
Exact Mass: 343.142

Starting with bis silyl-enol ether **4c** (1.996 g, 6.6 mmol), $TiCl_4$ (1.251 g, 6.6 mmol) $CH_2Cl_2$ (12 mL) and monosilyl enol ether **8a** (1.760 g, 6.0 mmol), **9c** was isolated (0.782 g, 38 %) as a yellowish oil. $^1H$ NMR ($CDCl_3$, 250 MHz): δ = 0.54 - 0.62 (m, 6 H, 2×$CH_2CH_3$), 1.10 (t, $^3J$ = 6.9 Hz, 3 H, $OCH_2CH_3$), 2.52 (q, $^3J$ = 7.7 Hz, 2 H, $CH_2CH_3$), 2.65 (q, $^3J$ = 7.7 Hz, 2 H, $CH_2CH_3$), 3.76 (q, $^3J$ = 7.5 Hz, 2 H, $OCH_2CH_3$), 6.34 (s, 1 H, $CH_{Ar}$), 6.99 (dd, $^3J$ = 7.4 Hz, $^4J$ = 1.3 Hz, 1 H, $CH_{Ar}$), 7.34 (ddd, $^3J$ = 7.3 Hz, $^3J$ = 7.2 Hz, $^4J$ = 1.4 Hz, 1 H, $CH_{Ar}$), 7.42 (ddd, $^3J$ = 7.5 Hz, $^3J$ = 7.5 Hz, $^4J$ = 1.5 Hz, 1 H, $CH_{Ar}$), 7.94 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.4 Hz, 1 H, $CH_{Ar}$), 11.43 (s, 1 H, OH). $^{13}C$ NMR ($CDCl_3$, 62 MHz): δ = 13.3, 13.8, 17.2 ($CH_3$), 19.0, 19.8 ($CH_2$), 60.9 ($OCH_2$), 108.0 (*C*$COOC_2H_5$), 124.1, 123.8, 127.4, 131.2, 132.6 ($CH_{Ar}$), 125.8, 135.4, 137.1, 142.6, 148.5, 158.4 ($C_{Ar}$), 170.7 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 3066 (w), 2965 (w), 2873 (w), 1656 (m), 1606 (m), 1563 (w), 1525 (s), 1463 (w), 1396 (m), 1347 (m), 1276 (s), 1212 (m), 1177 (m), 1111 (w), 1056 (w), 906 (w), 838 (s), 784 (m), 680 (m), 649 (w), 632 (w).GC-MS (EI 70 eV): *m/z* (%) = 344 ($[M]^+$+1, 25),343 ($[M]^+$, 100), 298 (11), 297 (52), 280 (10), 270 (11), 269 (20), 253 (16), 252 (35), 250 (11), 238 (16), 237 (16), 235 (16), 234 (18), 224 (17), 222 (11), 221 (24), 220 (49), 218 (11), 210 (11), 208 (56), 207 (63), 206 (26), 196 (11), 194 (18), 193 (25), 192 (15), 181 (21), 180 (29), 178 (25), 168 (12), 167 (20), 166 (14), 165 (47), 153 (12), 152 (25), 151 (10), 139 (11), 128 (12), 115 (14), 77 (11), 29 (20). HRMS (EI): Calcd. for $C_{19}H_{21}NO_5$: 343.14142; found: 343.141422.

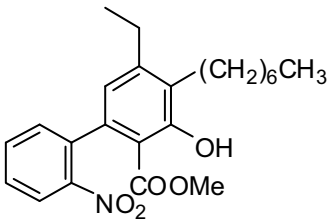
**methyl 5-ethyl-4-hexyl-3-hydroxy-2'-nitrobiphenyl-2-carboxylate (9d):**




Chemical Formula: $C_{22}H_{27}NO_5$
Exact Mass: 385.189

Starting with bis silyl-enol ether **4d** (1.516 g, 4.4 mmol), $TiCl_4$ (0.834 g, 4.4 mmol) $CH_2Cl_2$ (8 mL) and monosilyl enol ether **8a** (1.170 g, 4.0 mmol),**9d** was isolated (0.631 g, 41 %) as a yellowish oil. $^1$H NMR ($CDCl_3$, 250 MHz): δ = 0.78 (t, $^3J$ = 7.3 Hz, 3 H, $(CH_2)_5CH_3$), 1.06 (t, $^3J$ = 7.6 Hz, 3 H, $CH_2CH_3$), 1.08 - 1.14 (m, 8 H, 4×$CH_2$), 2.46 (q, $^3J$ = 7.2 Hz, 2 H, $CH_2CH_3$), 2.48 - 2.52 (m, 2 H, $CH_2$), 3.32 (s, 3 H, $OCH_3$), 6.35 (s, 1 H, $CH_{Ar}$), 6.99 (dd, $^3J$ = 7.6 Hz, $^4J$ = 1.3 Hz, 1 H, $CH_{Ar}$), 7.35 (ddd, $^3J$ = 7.0 Hz, $^3J$ = 7.0 Hz, $^4J$ = 1.5 Hz, 1 H, $CH_{Ar}$), 7.45 (ddd, $^3J$ = 7.5 Hz, $^3J$ = 7.5 Hz, $^4J$ = 1.5 Hz, 1 H, $CH_{Ar}$), 7.88 (dd, $^3J$ = 8.5 Hz, $^4J$ = 1.3 Hz, 1 H, $CH_{Ar}$), 11.43 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 62 MHz): δ = 14.9, 17.3 ($CH_3$), 22.6, 25.9, 26.1, 29.4, 29.8, 31.7 ($CH_2$), 51.8 ($OCH_3$), 108.1 ($C$COOCH$_3$), 121.2, 123.5, 127.5, 131.2, 132.1 ($CH_{Ar}$), 129.3, 137.0, 138.7, 142.9, 148.9, 160.7 ($C_{Ar}$), 170.0 (CO). IR (Neat, cm$^{-1}$): $\widetilde{\nu}$ = 3066 (w), 2954 (w), 2856 (w), 1661 (s), 1606 (w), 1564 (w), 1526 (s), 1439 (m), 1399 (m), 1349 (m), 1273 (m), 1213 (m), 1175 (m), 1118 (w), 1035 (w), 908 (m), 854 (w), 786 (w), 732 (s), 708 (w), 633 (w).GC-MS (EI 70 eV): *m/z* (%) = 386 ([M]$^+$+1, 25), 385 ([M]$^+$, 100), 339 (21), 338 (64), 336 (23), 292 (29), 290 (10), 282 (47), 268 (20), 253 (10), 252 (10), 250 (15), 249 (36), 248 (27), 240 (11), 239 (50), 238 (21), 237 (30), 235 (18), 234 (12), 224 (14), 223 (19), 222 (53), 221 (13), 210 (20), 208 (39), 207 (38), 195 (13), 194 (42), 193 (22), 181 (10), 180 (12), 179 (19), 178 (37), 167 (14), 166 (13), 153 (11), 152 (20), 115 (12), 43 (20), 41 (15), 29 (12). HRMS (EI): Calcd. for $C_{22}H_{27}NO_5$: 385.18837; found: 385.187845.

**methyl 5-ethyl-4-heptyl-3-hydroxy-2'-nitrobiphenyl-2-carboxylate (9e):**

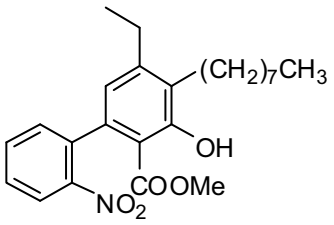



Chemical Formula: $C_{23}H_{29}NO_5$
Exact Mass: 399.205

Starting with bis silyl-enol ether **4e** (2.367 g, 6.6 mmol), $TiCl_4$ (1.251 g, 6.6 mmol) $CH_2Cl_2$ (12 mL) and monosilyl enol ether **8a** (1.760 g, 6.0 mmol), **9e** was isolated (0.934 g, 39 %) as a yellowish oil. $^1$H NMR ($CDCl_3$, 250 MHz): δ = 0.79 - 0.80 (m, 3 H, $(CH_2)_6CH_3$), 1.12 (t, $^3J$ = 7.6 Hz, 3 H, $CH_2CH_3$), 1.21 - 1.26 (m, 10 H, 5×$CH_2$), 2.57 (q, $^3J$ = 7.3 Hz, 2 H, $CH_2CH_3$), 2.61 – 2.66 (m, 2 H, $CH_2$), 3.37 (s, 3 H, $OCH_3$), 6.40 (s, 1 H, $CH_{Ar}$), 7.17 (dd, $^3J$ = 7.4 Hz, $^4J$ = 1.4 Hz, 1 H, $CH_{Ar}$), 7.38 (ddd, $^3J$ = 7.1 Hz, $^3J$ = 7.2 Hz, $^4J$ = 1.5 Hz, 1 H, $CH_{Ar}$), 7.51 (ddd, $^3J$ = 7.6 Hz, $^3J$ = 7.5 Hz, $^4J$ = 1.5 Hz, 1 H, $CH_{Ar}$), 7.92 (dd, $^3J$ = 7.9 Hz, $^4J$ = 1.3 Hz, 1 H, $CH_{Ar}$), 11.48 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 62 MHz): δ = 13.1,

16.3 ($CH_3$), 21.7, 24.9, 25.1, 28.2, 28.5, 29.1, 30.9 ($CH_2$), 50.8 ($OCH_3$), 107.1 (*C*$COOCH_3$), 120.2, 122.5, 126.5, 130.3, 131.1 ($CH_{Ar}$), 124.9, 136.1, 137.6, 141.9, 147.8, 159.7 ($C_{Ar}$), 170.0 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 3066 (w), 2953 (w), 2853 (w), 1660 (m), 1606 (w), 1564 (w), 1525 (s), 1438 (m), 1399 (m), 1347 (m), 1281 (m), 1212 (m), 1174 (m), 1118 (w), 1055 (w), 907 (m), 854 (w), 782 (w), 730 (s), 708 (m), 633 (w).GC-MS (EI 70 eV): *m/z* (%) = 400 ($[M]^+$+1, 28), 399 ($[M]^+$, 100), 353 (20), 350 (22), 322 (10), 306 (27), 282 (48), 268 (20), 264 (10), 263 (10), 253 (15), 252 (12), 250 (15), 249 (33), 248 (27), 240 (11), 239 (51), 238 (25), 237 (32), 236 (17), 235 (18), 234 (12), 224 (20), 223 (20), 222 (53), 221 (13), 210 (17), 209 (17), 208 (45), 207 (36), 195 (13), 194 (38), 193 (20), 181 (10), 180 (12), 179 (17), 178 (33), 167 (14), 166 (50), 165 (15), 153 (9), 152 (17), 115 (11), 43 (26), 41 (17), 29 (13). HRMS (EI): Calcd. for $C_{23}H_{29}NO_5$: 399.20402; found: 399.202985.

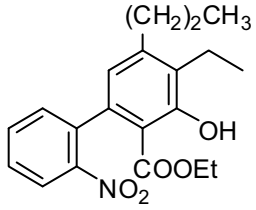
**methyl 5-ethyl-3-hydroxy-2'-nitro-4-octylbiphenyl-2-carboxylate (9f):**



Chemical Formula: $C_{24}H_{31}NO_5$
Exact Mass: 413.220

Starting with bis silyl-enol ether **4f** (1.639 g, 4.4 mmol), $TiCl_4$ (0.834 g, 4.4 mmol) $CH_2Cl_2$ (8 mL) and monosilyl enol ether **8a** (1.173 g, 4.0 mmol), **9f** was isolated (0.627 g, 38 %) as a yellowish oil. $^1$H NMR ($CDCl_3$, 250 MHz): δ = 0.71 (t, $^3J$ = 7.3 Hz, 3 H, $(CH_2)_7CH_3$), 1.02 (t, $^3J$ = 7.5 Hz, 3 H, $CH_2CH_3$), 1.04 - 1.12 (m, 12 H, 6×$CH_2$), 2.47 (q, $^3J$ = 7.3 Hz, 2 H, $CH_2CH_3$), 2.52 - 2.55 (m, 2 H, $CH_2$), 3.27 (s, 3 H, $OCH_3$), 6.30 (s, 1 H, $CH_{Ar}$), 7.08 (dd, $^3J$ = 7.3 Hz, $^4J$ = 1.1 Hz, 1 H, $CH_{Ar}$), 7.28 (ddd, $^3J$ = 7.7 Hz, $^3J$ = 7.7 Hz, $^4J$ = 1.3 Hz, 1 H, $CH_{Ar}$), 7.40 (ddd, $^3J$ = 7.3 Hz, $^3J$ = 7.3 Hz, $^4J$ = 1.3 Hz, 1 H, $CH_{Ar}$), 7.84 (dd, $^3J$ = 8.5 Hz, $^4J$ = 1.5 Hz, 1 H, $CH_{Ar}$), 11.38 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 62 MHz): δ = 15.2, 16.1 ($CH_3$), 23.8, 27.1, 27.3, 30.3, 30.4, 30.5, 30.7, 33.1 ($CH_2$), 50.0 ($OCH_3$), 109.4 (*C*$COOCH_3$), 122.3, 124.7, 128.7, 132.4, 133.3 ($CH_{Ar}$), 130.4, 138.2, 139.9, 149.3, 150.0, 162.2 ($C_{Ar}$), 172.2 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 2953 (w), 2853 (w), 1753 (w), 1661 (m), 1606 (m), 1563 (w), 1526 (s), 1437 (m), 1398 (m), 1348 (m), 1275 (m), 1213 (m), 1174 (m), 1120 (w), 1053 (w), 904 (m), 841 (w), 753 (m), 706 (m), 630 (w). GC-MS (EI 70 eV): *m/z* (%) = 414 ($[M]^+$+1, 28), 413 ($[M]^+$, 100), 368 (11), 367 (42), 354 (13), 353 (22), 352 (91), 336 (19), 320 (14), 306 (20), 283 (14), 282 (82), 266 (20), 253 (21), 252 (16), 250 (15), 249 (15), 248 (20), 240 (12), 239 (46), 238 (25), 237 (27), 236 (24), 235 (23), 234 (12), 224 (34), 223 (16), 222 (49), 221 (20), 210 (14), 209 (14), 208 (35), 207 (23), 206 (11), 205 (10), 196 (12), 194 (30), 193 (29), 192 (14), 181 (12), 180 (12), 179 (14), 178 (26), 167 (14), 166 (12), 165 (54), 153 (9), 152 (20), 55 (12), 43 (26), 41 (25), 29 (16). HRMS (EI): Calcd. for $C_{24}H_{31}NO_5$: 413.21967; found: 413.220441.

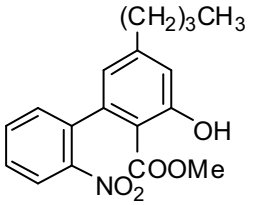
**Ethyl 4-ethyl-3-hydroxy-2'-nitro-5-propylbiphenyl-2-carboxylate (9g):**




Chemical Formula: $C_{20}H_{23}NO_5$
Exact Mass: 357.158

Starting with bis silyl-enol ether **4c** (0.998 g, 3.3 mmol), $TiCl_4$ (0.625 g, 3.3 mmol) $CH_2Cl_2$ (7 mL) and monosilyl enol ether **8b** (0.876 g, 3.0 mmol), **9g** was isolated (0.400 g, 37 %) as a yellowish oil.$^1$H NMR ($CDCl_3$, 250 MHz): δ = 0.59 (t, $^3J$ = 7.3 Hz, 3 H, $CH_3$), 0.83 (t, $^3J$ = 6.5 Hz, 3 H, $CH_3$), 1.07 (t, $^3J$ = 7.4 Hz, 3 H, $CH_3$), 1.39 - 1.48 (m, 2 H, $CH_2$), 2.43 - 2.50 (m, 2 H, $CH_2$), 2.57 - 2.66 (m, 2 H, $CH_2$), 3.82 (q, $^3J$ = 6.5 Hz, 2 H, $OCH_2$), 6.32 (s, 1 H, $CH_{Ar}$), 7.12 (dd, $^3J$ = 7.5 Hz, $^4J$ = 1.5 Hz, 1 H, $CH_{Ar}$), 7.34 (ddd, $^3J$ = 8.0 Hz, $^3J$ = 7.5 Hz, $^4J$ = 1.5 Hz, 1 H, $CH_{Ar}$), 7.44 (ddd, $^3J$ = 7.5 Hz, $^3J$ = 7.4 Hz, $^4J$ = 1.5 Hz, 1 H, $CH_{Ar}$), 7.88 (dd, $^3J$ = 7.6 Hz, $^4J$ = 1.3 Hz, 1 H, $CH_{Ar}$), 11.58 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 62 MHz): $\delta_C$ = 8.9, 14.4, 15.2 ($CH_3$), 20.3, 25.1, 36.3 ($CH_2$), 62.0 ($OCH_2$), 109.4 ($C_{Ar}$), 123.1, 124.7, 128.6 ($CH_{Ar}$), 131.7 ($C_{Ar}$), 132.4, 133.2 ($CH_{Ar}$), 137.9, 140.1, 148.1, 149.1, 162.0 ($C_{Ar}$), 171.8 (C=O). GC-MS (EI 70 eV): *m/z* (%) = 357 ([M]$^+$, 100), 311 (54), 283 (21), 266 (38), 250 (43), 235 (20), 220 (58), 194 (20), 180 (39), 165 (39), 152 (27), 115 (15), 77 (11). HRMS (EI): Calcd. for $C_{20}H_{23}NO_5$: 357.15707; found: 329.15710.

**methyl 5-butyl-3-hydroxy-2'-nitrobiphenyl-2-carboxylate (9h):**



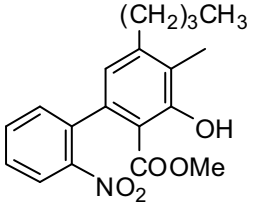

Chemical Formula: $C_{18}H_{19}NO_5$
Exact Mass: 329.126

Starting with bis silyl-enol ether **4a** (1.289 g, 4.95 mmol), $TiCl_4$ (0.938 g, 4.95 mmol) $CH_2Cl_2$ (9 mL) and monosilyl enol ether **8c** (1.446 g, 4.5 mmol), **9h** was isolated (0.621 g, 42 %) as a yellowish oil. $^1$H NMR ($CDCl_3$, 250 MHz): δ = 0.78 (t, $^3J$ = 7.3 Hz, 3 H, $(CH_2)_3CH_3$), 1.17 - 1.26 (m, 2 H, $CH_2$), 1.41 - 1.53 (m, 2 H, $CH_2$), 2.46 (t, $^3J$ = 7.9 Hz, 2 H, $CH_2(CH_2)_2CH_3$), 3.32 (s, 3 H, $OCH_3$), 6.35 (d, $^4J$ = 1.7 Hz, 1 H, $CH_{Ar}$), 6.74 (d, $^4J$ = 1.7 Hz, 1 H, $CH_{Ar}$), 7.12 (dd, $^3J$ = 7.5 Hz, $^4J$ = 1.6 Hz, 1 H, $CH_{Ar}$), 7.36 (ddd, $^3J$ = 7.7 Hz, $^3J$ = 8.1 Hz, $^4J$ = 1.6 Hz, 1 H, $CH_{Ar}$), 7.47 (ddd, $^3J$ = 7.5 Hz, $^3J$ = 7.7 Hz, $^4J$ = 1.5 Hz, 1 H, $CH_{Ar}$), 7.92 (dd, $^3J$ = 7.7 Hz, $^4J$ = 1.2 Hz, 1 H, $CH_{Ar}$), 11.10 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 12.9 ($CH_3$), 21.3, 31.6, 34.6 ($CH_2$), 50.9 ($OCH_3$), 107.6 ($C$COOCH$_3$), 116.4, 120.9, 122.7, 126.9, 130.1, 131.3 ($CH_{Ar}$), 137.3, 139.2, 146.9, 149.5, 161.5 ($C_{Ar}$), 169.4 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 3066 (w), 2954 (w), 2859 (w), 1662 (s), 1608 (m), 1570 (m), 1522 (s), 1438 (m), 1417 (m), 1346 (s), 1266 (s), 1216 (s), 1161 (m), 1146 (m), 1103 (m), 1008 (w), 950 (w), 856 (w), 808 (m), 753 (m), 702 (s), 632 (w), 545 (w).GC-MS (EI 70 eV): *m/z* (%) = 329 ([M]$^+$, 43), 297 (32), 284 (20), 283 (100), 270 (14), 256 (10),

255 (56), 226 (12), 182 (12), 181 (15), 180 (15), 166 (10), 165 (13), 154 (26), 153 (12), 152 (27), 151 (10), 139 (10), 115 (15), 97 (12).

HRMS (EI): Calcd. for $C_{18}H_{19}NO_5$: 329.12577; found: 329.125715.

**methyl 5-butyl-3-hydroxy-4-methyl-2'-nitrobiphenyl-2-carboxylate (9i):**

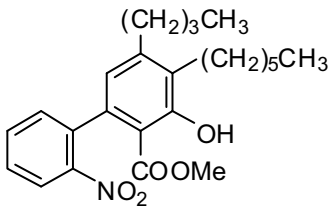



Chemical Formula: $C_{19}H_{21}NO_5$
Exact Mass: 343.142

Starting with bis silyl-enol ether **4b** (1.509 g, 5.5 mmol), $TiCl_4$ (1.043 g, 5.5 mmol) $CH_2Cl_2$ (10 mL) and monosilyl enol ether **8c** (1.607 g, 5.0 mmol), **9i** was isolated (0.670 g, 39 %) as a yellowish oil. $^1$H NMR ($CDCl_3$, 250 MHz): δ = 0.79 (t, $^3J$ = 7.1 Hz, 3 H, $(CH_2)_3CH_3$), 1.19 - 1.28 (m, 2 H, $CH_2$), 1.30 - 1.44 (m, 2 H, $CH_2$), 2.12 (s, 3 H, $CH_3$), 2.49 (t, $^3J$ = 7.1 Hz, 2 H, $CH_2(CH_2)_2CH_3$), 3.32 (s, 3 H, $OCH_3$), 6.34 (s, 1 H, $CH_{Ar}$), 7.11 (dd, $^3J$ = 7.4 Hz, $^4J$ = 1.3 Hz, 1 H, $CH_{Ar}$), 7.34 (ddd, $^3J$ = 8.0 Hz, $^3J$ = 8.1 Hz, $^4J$ = 1.6 Hz, 1 H, $CH_{Ar}$), 7.45 (ddd, $^3J$ = 8.0 Hz, $^3J$ = 7.7 Hz, $^4J$ = 1.6 Hz, 1 H, $CH_{Ar}$), 7.88 (dd, $^3J$ = 8.2 Hz, $^4J$ = 1.6 Hz, 1 H, $CH_{Ar}$), 11.48 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.3, 16.0 ($CH_3$), 24.7, 34.1, 35.8 ($CH_2$), 53.9 ($OCH_3$), 110.0 ($CCOOCH_3$), 124.0, 125.6, 129.7, 133.4, 134.3 ($CH_{Ar}$), 126.7, 136.5, 138.9, 140.7, 150.2, 163.0 ($C_{Ar}$), 173.0 (CO).IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 2953 (w), 2870 (w), 1659 (s), 1606 (m), 1566 (m), 1522 (s), 1437 (m), 1397 (m), 1345 (s), 1267 (s), 1196 (m), 1173 (m), 1144 (m), 1112 (m), 1010 (m), 962 (w), 852 (m), 809 (m), 752 (m), 705 (m), 633 (w), 546 (w).GC-MS (EI 70 eV): *m/z* (%) = 344 ($[M]^+$+1, 11), 343 ($[M]^+$, 53), 312 (20), 311 (100), 297 (22), 225 (19), 224 (18), 208 (24), 207 (10), 195 (11), 194 (14), 181 (10), 180 (15),167 (11), 166 (10), 165 (26), 152 (18), 115 (10).

HRMS (EI): Calcd. for $C_{19}H_{21}NO_5$: 343.14142; found: 343.141424.

**methyl 5-butyl-4-hexyl-3-hydroxy-2'-nitrobiphenyl-2-carboxylate (9j):**

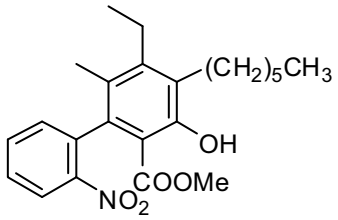



Chemical Formula: $C_{24}H_{31}NO_5$
Exact Mass: 413.220

Starting with bis silyl-enol ether **4d** (2.274 g, 6.6 mmol), $TiCl_4$ (1.251 g, 6.6 mmol) $CH_2Cl_2$ (12 mL) and monosilyl enol ether **8c** (1.928 g, 6 mmol), **9j** was isolated (0.941 g, 38 %) as a yellowish oil. $^1$H NMR ($CDCl_3$, 250 MHz): δ = 0.74 (m, 6 H, 2×$CH_3$), 1.08 - 1.25 (m, 12 H, 6×$CH_2$), 2.42 (t, $^3J$ = 7.4 Hz, 2 H, $CH_2(CH_2)_2CH_3$), 2.48 - 2.55 (m, 2 H, $CH_2$), 3.26 (s, 3 H, $OCH_3$), 6.28 (s, 1 H, $CH_{Ar}$), 7.07 (dd, $^3J$ = 8.1 Hz, $^4J$ = 1.6 Hz,

1 H, $CH_{Ar}$), 7.28 (ddd, $^3J$ = 7.4 Hz, $^3J$ = 7.4 Hz, $^4J$ = 1.6 Hz, 1 H, $CH_{Ar}$), 7.42 (ddd, $^3J$ = 7.1 Hz, $^3J$ = 7.7 Hz, $^4J$ = 1.6 Hz, 1 H, $CH_{Ar}$), 7.83 (dd, $^3J$ = 8.1 Hz, $^4J$ = 1.6 Hz, 1 H, $CH_{Ar}$), 11.38 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 15.1, 15.2 ($CH_3$), 23.8, 23.9, 27.2, 30.6, 31.0, 32.9, 34.2, 34.3 ($CH_2$), 52.9 ($OCH_3$), 109.3 (*C*$COOCH_3$), 123.2, 124.7, 128.7, 132.5, 133.4 ($CH_{Ar}$), 130.7, 138.0, 139.9, 148.9, 149.3, 162.1 ($C_{Ar}$), 172.2 (CO).IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 2954 (m), 2856 (m), 1933 (w), 1702 (w), 1661 (m), 1606 (m), 1562 (w), 1525 (s), 1437 (m), 1397 (m), 1347 (s), 1271 (m), 1228 (m), 1174 (m), 1145 (m), 1121 (m), 1009 (w), 954 (w), 842 (m), 813 (m), 754 (m), 706 (m), 632 (w), 562 (w).GC-MS (EI 70 eV): *m/z* (%) = 414 ($[M]^+$+1, 27), 413 ($[M]^+$, 98), 368 (11), 367 (38), 364 (11), 336 (19), 325 (22), 324 (100), 320 (20), 310 (26), 300 (10), 280 (11), 278 (25), 276 (16), 264 (14), 252 (13), 250 (22), 249 (17), 248 (11), 239 (13), 238 (13), 236 (20), 235 (26), 234 (19), 233 (10), 226 (11), 225 (54), 224 (15), 223 (15), 222 (16), 221 (15), 220 (20), 210 (13), 209 (12), 208 (26), 207 (15), 206 (10), 196 (12), 195 (14), 194 (33), 193 (14), 181 (13), 180 (22), 179 (12), 178 (20), 167 (14), 166 (14), 165 (36), 152 (21), 43 (23), 41 (20), 29 (13). HRMS (EI): Calcd. for $C_{24}H_{31}NO_5$: 413.21967; found: 413.219007.

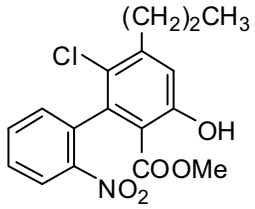
**methyl 5-ethyl-4-hexyl-3-hydroxy-6-methyl-2'-nitrobiphenyl-2-carboxylate (9k):**




Chemical Formula: $C_{23}H_{29}NO_5$
Exact Mass: 399.205

Starting with bis silyl-enol ether **4d** (2.274 g, 6.6 mmol), $TiCl_4$ (1.251 g, 6.6 mmol) $CH_2Cl_2$ (12 mL) and monosilyl enol ether **8d** (1.844 g, 6.0 mmol), **6r** was isolated (0.577 g, 38 %) as a yellowish oil. $^1$H NMR ($CDCl_3$, 250 MHz): δ = 0.78 - 0.81 (m, 3 H, $(CH_2)_5CH_3$), 1.07 (t, $^3J$ = 7.6 Hz, 3 H, $CH_2CH_3$), 1.29 - 1.33 (m, 8 H, 4×$CH_2$), 2.49 (s, 3 H, $CH_3$), 2.56 – 2.68 (m, 4 H, 2×$CH_2$), 3.28 (s, 3 H, $OCH_3$), 7.04 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.5 Hz, 1 H, $CH_{Ar}$), 7.40 (ddd, $^3J$ = 7.8 Hz, $^3J$ = 7.8 Hz, $^4J$ = 1.5 Hz, 1 H, $CH_{Ar}$), 7.51 (ddd, $^3J$ = 7.5 Hz, $^3J$ = 7.2 Hz, $^4J$ = 1.5 Hz, 1 H, $CH_{Ar}$), 8.0 (dd, $^3J$ = 8.1 Hz, $^4J$ = 1.5 Hz, 1 H, $CH_{Ar}$), 11.19 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 62 MHz): δ = 13.9, 14.1, 16.4 ($CH_3$), 22.4, 25.8, 28.5, 29.9, 31.4, 31.8 ($CH_2$), 51.8 ($OCH_3$), 108.5 (*C*$COOCH_3$), 123.7, 127.5, 131.1, 132.6 ($CH_{Ar}$), 125.1, 129.3, 136.1, 138.5, 148.3, 148.4, 158.6 ($C_{Ar}$), 171.6 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 2954 (w), 2926 (m), 2856 (w), 1753 (m), 1659 (s), 1594 (w), 1525 (s), 1438 (m), 1411 (m), 1348 (s), 1263 (m), 1211 (s), 1175 (m), 1119 (w), 1016 (w), 919 (w), 853 (w), 788 (w), 752 (m), 707 (w), 627 (w).GC-MS (EI 70 eV): *m/z* (%) = 400 ($[M]^+$+1, 15), 399 ($[M]^+$, 59), 339 (23), 338 (100), 296 (27), 292 (23), 263 (11), 253 (10), 252 (10), 250 (10), 249 (21), 238 (17), 236 (13), 234 (10), 222 (14), 221 (10), 208 (14), 207 (21), 179 (13), 178 (21), 165 (14), 152 (9), 43 (13), 41 (10). HRMS (EI): Calcd. for $C_{23}H_{29}NO_5$: 399.20402; found: 399.203491.

**methyl 6-chloro-3-hydroxy-2'-nitro-5-propylbiphenyl-2-carboxylate (9l):**



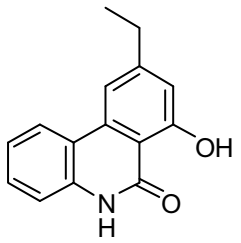

Chemical Formula: $C_{17}H_{16}ClNO_5$
Exact Mass: 349.072

Starting with bis silyl-enol ether **4a** (1.260 g, 4.84 mmol), $TiCl_4$ (0.920 g, 4.84 mmol) $CH_2Cl_2$ (9 mL) and monosilyl enol ether **8e** (1.50 g, 4.4 mmol), **9l** was isolated (0.841 g, 55 %) as a yellowish oil. $^1$H NMR ($CDCl_3$, 250 MHz): δ = 0.87 (t, $^3J$ = 7.5 Hz, 3 H, $(CH_2)_2CH_3$), 1.51 - 1.59 (m, 2 H, $CH_2$), 2.58 (t, $^3J$ = 7.5 Hz, 2 H, $CH_2CH_2CH_3$), 3.28 (s, 3 H, $OCH_3$), 6.84 (s, 1 H, $CH_{Ar}$), 7.03 (dd, $^3J$ = 7.5 Hz, $^4J$ = 1.8 Hz, 1 H, $CH_{Ar}$), 7.42 (ddd, $^3J$ = 8.1 Hz, $^3J$ = 8.1 Hz, $^4J$ = 1.8 Hz, 1 H, $CH_{Ar}$), 7.55 (ddd, $^3J$ = 8.1 Hz, $^3J$ = 8.1 Hz, $^4J$ = 1.7 Hz, 1 H, $CH_{Ar}$), 8.08 (dd, $^3J$ = 7.8 Hz, $^4J$ = 1.8 Hz, 1 H, $CH_{Ar}$), 10.94 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.8 ($CH_3$), 22.2, 36.4 ($CH_2$), 52.3 ($OCH_3$), 69.68 ($CH_{Ar}$), 110.3 ($C$COOOCH$_3$), 124.4, 130.0, 131.7, 134.9 ($CH_{Ar}$), 128.3, 136.3, 138.9, 145.3, 148.2, 160.7 ($C_{Ar}$), 169.8 (CO).IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 3102 (w), 3017 (w), 2959 (w), 2862 (w), 1723 (m). 1668 (w), 1601 (w), 1569 (w), 1524 (s), 1440 (m), 1340 (s), 1297 (m), 1266 (m), 1196 (m), 1164 (w), 1144 (m), 1113 (w), 1040 (w), 997 (m), 857 (m), 787 (s), 762 (m), 717 (m), 698 (s), 650 (m), 634 (s), 555 (w) .GC-MS (EI 70 eV): *m/z* (%) = 351 ([M$^+$], $^{37}$Cl, 25), 349 ([M$^+$], $^{35}$Cl, 71), 317 (20), 314 (44), 313 (11), 305 (12), 303 (35), 290 (10), 283 (18), 282 (100), 274 (18), 272 (24), 257 (16), 255 (13), 254 (70), 246 (11), 244 (20), 231 (14), 230 (13), 227 (17), 226 (33), 225 (38), 218 (15), 216 (13), 215 (14), 214 (15), 209 (18), 208 (11), 198 (21), 195 (13), 193 (24), 186 (11), 182 (13), 181 (17), 180 (22), 178 (23), 177 (34), 170 (10), 168 (21), 167 (19), 166 (10), 165 (26), 163 (13), 158 (10), 155 (16), 153 (24), 152 (49), 151 (33), 149 (17), 139 (40), 131 (13), 128 (15), 126 (16), 124 (21), 115 (12), 114 (10), 77 (11), 76 (12), 75 (11), 67 (14), 29 (10). HRMS (EI): Calcd. for $C_{17}H_{16}NO_5Cl$: 349.07115; found: 349.070500.

**General procedure for the synthesis of phenanthridinones 10a-l:**

To a stirred methanol suspension (25 mL) of Pd/C (10 mol-%) was added **9a-l** (1.0 equiv.). The mixture was set under a hydrogen atmosphere. After stirring for 48 h at 20 °C, the reaction mixture was filtered (celite) and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, heptanes heptanes/EtOAc = 2:1).

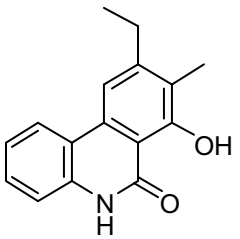
**9-ethyl-7-hydroxyphenanthridin-6(5H)-one (10a):**



Chemical Formula: $C_{15}H_{13}NO_2$
Exact Mass: 239.095

Starting with **9a** (0.190 g, 0.63 mmol),**10a** was isolated (0.113 g, 75 %) by column chromatography (silica gel, heptanes/EtOAc = 30:1 → 20:1) as a colorless solid, m.p 260 - 261 °C.$^1$H NMR (DMSO, 250 MHz): δ = 1.27 (t, $^3J$ = 7.7 Hz, 3 H, $CH_2CH_3$), 2.75 (q, $^3J$ = 7.2 Hz, 2 H, $CH_2CH_3$), 6.85 ($s_{(br)}$, 1 H, $CH_{Ar}$), 7.28 - 7.34 (m, 1 H, $CH_{Ar}$), 7.38 - 7.41 (m, 1 H, $CH_{Ar}$), 7.49 - 7.55 (m, 1 H, $CH_{Ar}$), 7.76 ($s_{(br)}$, 1 H, $CH_{Ar}$), 8.36 (d, $^3J$ = 8.3 Hz, 1 H, $CH_{Ar}$), 12.02 ($s_{(br)}$, 1 H, NH), 13.25 (s, 1 H, OH). $^{13}$C NMR (DMSO, 62 MHz): δ = 15.0 ($CH_3$), 28.8 ($CH_2$), 107.9 ($C_{Ar}$), 111.7 113.7, 116.5 ($CH_{Ar}$), 118.1 ($C_{Ar}$), 123.0, 123.7, 129.6 ($CH_{Ar}$), 135.2, 135.5, 151.8, 161.5 ($C_{Ar}$), 165.4 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 3172 (w), 3042 (w), 2956 (m), 2928 (m), 2867 (m), 1650 (s), 1620 (m), 1594 (w), 1556 (m), 1462 (w), 1453 (m), 1430 (m), 1371 (w), 1347 (m), 1299 (m), 1224 (m), 1174 (m), 1128 (w), 1100 (w), 1058 (w), 1014 (m), 948 (w), 909 (w), 846 (m), 770 (w), 747 (s), 720 (m), 680 (m), 633 (m), 553 (m).MS (EI 70 eV): *m/z* (%) = 240 ([M]$^+$+1, 17), 239 ([M]$^+$, 100), 238 (32), 207 (13), 196 (11).HRMS (EI): Calcd. for $C_{15}H_{13}NO_2$: 239.09408; found: 239.094189.

**9-ethyl-7-hydroxy-8-methylphenanthridin-6(5H)-one (10b):**

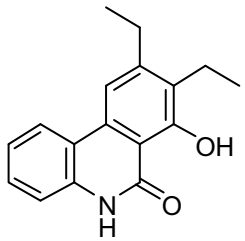


Chemical Formula: $C_{16}H_{15}NO_2$
Exact Mass: 253.110

Starting with **9b** (0.228 g, 0.723 mmol), **10b** was isolated (0.097 g, 53 %) by column chromatography (silica gel, heptanes/EtOAc = 30:1 → 20:1) as a colorless solid, m.p 265 - 267 °C. $^1$H NMR (DMSO, 250 MHz): δ = 1.14 (t, $^3J$ = 7.0 Hz, 3 H, $CH_2CH_3$), 2.18 (s, 3 H, $CH_3$), 2.77 (q, $^3J$ = 7.1 Hz, 2 H, $CH_2CH_3$), 7.26 - 7.32 (m, 1 H, $CH_{Ar}$), 7.36 - 7.39 (m, 1 H, $CH_{Ar}$), 7.45 - 7.51 (m, 1 H, $CH_{Ar}$), 7.70 (s, 1 H, $CH_{Ar}$), 8.34 (d, $^3J$ = 7.8 Hz, 1 H, $CH_{Ar}$), 11.95 ($s_{(br)}$, 1 H, NH), 13.62 (s, 1 H, OH). $^{13}$C NMR (DMSO, 62 MHz): δ = 13.8, 15.4 ($CH_3$), 28.8 ($CH_2$), 107.4 ($C_{Ar}$), 111.8, 116.4 ($CH_{Ar}$), 118.1 ($C_{Ar}$), 123.0, 123.3 ($CH_{Ar}$), 126.0 ($C_{Ar}$), 129.2 ($CH_{Ar}$), 132.4, 135.1, 149.5, 159.3, ($C_{Ar}$), 165.0 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 3172 (w), 3041 (w), 2955 (m), 2930 (m), 2866 (m), 1651 (s), 1622 (m), 1590 (w), 1550 (m), 1457 (w), 1435 (m), 1369 (w), 1345 (m), 1300 (m), 1220 (m), 1170 (m), 1128 (w), 1098 (w), 1060 (w), 1012 (m), 945 (w), 908 (w), 845 (m), 770 (w), 746 (s), 719 (m), 682 (m), 633 (m), 552 (m). MS (EI 70 eV): *m/z* (%) = 255 ([M]$^+$+2, 11), 254 ([M]$^+$+1, 26), 253 ([M]$^+$, 100), 252 (45), 239 (10), 238 (13), 226 (10), 225 (18), 224 (24), 84 (10), 66

(18), 44 (35), 43 (12).Anal.: Calcd for $C_{16}H_{15}NO_2$: C 75.30, H 5.48, N 5.85; found.: C 75.38, H 5.43, N 5.75

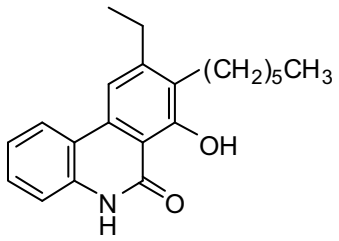
**8,9-diethyl-7-hydroxyphenanthridin-6(5H)-one (10c):**




Chemical Formula: $C_{17}H_{17}NO_2$
Exact Mass: 267.126

Starting with **9c** (0.171 g, 0.5 mmol), **10c** was isolated (0.069 g, 52 %) by column chromatography (silica gel, heptanes/EtOAc = 30:1 → 20:1) as a colorless solid, m.p 242 - 244 °C. $^1$H NMR (DMSO, 250 MHz): δ = 1.13 (t, $^3J$ = 7.0 Hz, 3 H, $CH_2CH_3$), 1.27 (t, $^3J$ = 7.0 Hz, 3 H, $CH_2CH_3$), 2.66 - 2.74 (m, 2 H, $CH_2CH_3$), 2.76 - 2.83 (m, 2 H, $CH_2CH_3$), 7.26 - 7.29 (m, 1 H, $CH_{Ar}$), 7.36 - 7.40 (m, 1 H, $CH_{Ar}$), 7.44 - 7.49 (m, 1 H, $CH_{Ar}$), 7.74 (s, 1 H, $CH_{Ar}$), 8.34 (d, $^3J$ = 7.8 Hz, 1 H, $CH_{Ar}$), 11.96 ($s_{(br)}$, 1 H, NH), 13.62 (s, 1 H, OH). $^{13}$C NMR (DMSO, 62 MHz): δ = 15.4, 16.8 ($CH_3$), 18.1, 26.0 ($CH_2$), 107.4 ($C_{Ar}$), 111.9, 116.4 ($CH_{Ar}$), 118.3 ($C_{Ar}$), 123.0, 123.3 ($CH_{Ar}$), 128.2 ($C_{Ar}$), 129.2 ($CH_{Ar}$), 132.4, 135.1, 149.5, 159.2, ($C_{Ar}$), 165.7 (CO).IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 3173 (w), 3035 (w), 2953 (m), 2927 (m), 2865 (m), 1651 (s), 1628 (m), 1592 (w), 1562 (m), 1460 (w), 1455 (m), 1433 (m), 1370 (w), 1347 (m), 1297 (m), 1222 (m), 1170 (m), 1123 (w), 1115 (w), 1058 (w), 1012 (m), 945 (w), 909 (w), 845 (m), 768 (w), 745 (s), 723 (m), 678 (m), 630 (m), 552 (m).MS (EI 70 eV): *m/z* (%) = 267 ([M]$^+$, 41), 253 (17), 252 (100).HRMS (EI): Calcd. for $C_{17}H_{17}NO_2$: 267.12538; found: 267.125175.

**9-ethyl-8-hexyl-7-hydroxyphenanthridin-6(5H)-one (10d):**

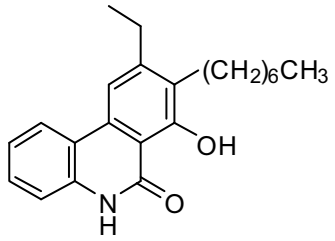



Chemical Formula: $C_{21}H_{25}NO_2$
Exact Mass: 323.189

Starting with **9d** (0.255 g, 0.66 mmol), **10d** was isolated (0.109 g, 51 %) by column chromatography (silica gel, heptanes/EtOAc = 30:1 → 20:1) as a colorless solid, m.p 230 - 232 °C. $^1$H NMR ($CD_3OD$, 250 MHz): δ = 0.96 - 0.99 (m, 3 H, $(CH_2)_5CH_3$), 1.03 - 1.08 (m, 3 H, $CH_2CH_3$), 1.34 - 1.41 (m, 8 H, 4×$CH_2$), 2.87 - 2.95 (m, 4 H, 2×$CH_2$), 7.24 - 7.30 (m, 1 H, $CH_{Ar}$), 7.44 - 7.45 (m, 1 H, $CH_{Ar}$), 7.48 - 7.51 (m, 1 H, $CH_{Ar}$), 7.74 (s, 1 H, $CH_{Ar}$), 8.29 (d, $^3J$ = 7.8 Hz, 1 H, $CH_{Ar}$). $^{13}$C NMR ($CD_3OD$, 62 MHz): δ = 14.5, 15.4 ($CH_3$), 23.5, 26.4, 27.1, 27.6, 29.8, 32.8 ($CH_2$), 108.8 ($C_{Ar}$), 124.4, 117.0 ($CH_{Ar}$), 120.0 ($C_{Ar}$), 122.7, 124.1 ($CH_{Ar}$), 129.1 ($C_{Ar}$), 130.0 ($CH_{Ar}$), 134.0, 136.9, 151.0, 161.1, ($C_{Ar}$), 167.5 (CO).IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 2971 (m), 2910 (w), 2831 (m), 2758 (m), 2719 (m), 2487 (m), 2096 (w), 1586 (w), 1467 (m), 1397 (w), 1330 (w), 1202 (w), 1151 (m), 1103

(m), 978 (m), 957 (m), 840 (w), 805 (w), 612 (m).MS (EI 70 eV): *m/z* (%) = 324 ($[M]^+$+1, 11), 323 ($[M]^+$, 31), 266 (11), 254 (19), 253 (78), 252 (100), 237 (10) .HRMS (EI): Calcd. for $C_{21}H_{25}NO_2$: 323.18798; found: 323.18.7220.

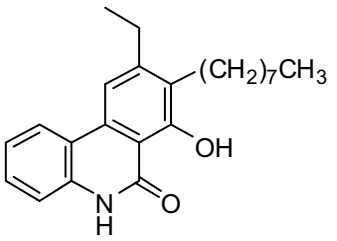
**9-ethyl-8-heptyl-7-hydroxyphenanthridin-6(5H)-one (10e):**




Chemical Formula: $C_{22}H_{27}NO_2$
Exact Mass: 337.204

Starting with **9e** (0.265 g, 0.66 mmol), **10e** was isolated (0.109 g, 49 %) by column chromatography (silica gel, heptanes/EtOAc = 30:1 → 20:1) as a colorless solid, m.p 232 – 234 °C. $^1$H NMR (DMSO, 250 MHz): δ = 0.85 - 0.86 (m, 3 H, $(CH_2)_6CH_3$), 1.10 (t, $^3J$ = 7.1 Hz, 3 H, $CH_2CH_3$), 1.26 - 1.29 (m, 10 H, 5×$CH_2$), 2.63 - 2.72 (m, 2 H, $CH_2$), 2.78 (q, $^3J$ = 7.7 Hz, 2 H, $CH_2CH_3$), 7.23 − 7.29 (m, 1 H, $CH_{Ar}$), 7.36 – 7.41 (m, 1 H, $CH_{Ar}$), 7.46 - 7.52 (m, 1 H, $CH_{Ar}$), 7.74 (s, 1 H, $CH_{Ar}$), 8.34 (d, $^3J$ = 7.7 Hz, 1 H, $CH_{Ar}$), 11.94 ($s_{(br)}$, 1 H, NH), 13.63 (s, 1 H, OH). $^{13}$C NMR (DMSO, 62 MHz): δ = 13.9, 15.4 ($CH_3$), 22.0, 26.0, 28.5, 28.6, 29.1, 29.3, 31.3 ($CH_2$), 107.4 ($C_{Ar}$), 111.8, 116.4 ($CH_{Ar}$), 118.3 ($C_{Ar}$), 123.1, 123.3 ($CH_{Ar}$), 126.1 ($C_{Ar}$), 129.3 ($CH_{Ar}$), 132.4, 135.2, 149.5, 159.3 ($C_{Ar}$), 165.7 (CO).IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 3172 (w), 3062 (w), 3022 (w), 2956 (m), 2926 (m), 2867 (m), 1717 (w), 1651 (s), 1623 (m), 1595 (m), 1554 (m), 1460 (w), 1455 (m), 1437 (m), 1370 (m), 1347 (m), 1300 (m), 1225 (m), 1180 (m), 1126 (w), 1098 (w), 1056 (w), 1015 (m), 948 (w), 908 (w), 845 (m), 770 (w), 747 (s), 720 (m), 682 (m), 635 (m), 552 (m). MS (EI 70 eV): *m/z* (%) = 338 ($[M]^+$+1, 8), 337 ($[M]^+$, 34), 308 (12), 266 (13), 254 (15), 253 (72), 252 (100), 237 (10), 209 (9), 208 (12), 207 (39), 191 (9), 44 (11). HRMS (EI): Calcd. for $C_{22}H_{27}NO_2$: 337.20363; found: 337.203119.

**9-ethyl-7-hydroxy-8-octylphenanthridin-6(5H)-one (10f):**

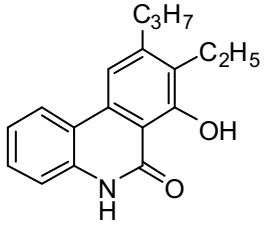



Chemical Formula: $C_{23}H_{29}NO_2$
Exact Mass: 351.220

Starting with **9f** (0.347 g, 0.84 mmol),**10f** was isolated (0.147 g, 50 %) by column chromatography (silica gel, heptanes/EtOAc = 30:1 → 20:1) as a colorless solid, m.p 241 – 243 °C. $^1$H NMR (DMSO, 250 MHz): δ = 0.85 - 0.87 (m, 3 H, $(CH_2)_7CH_3$), 1.08 (t, $^3J$ = 7.1 Hz, 3 H, $CH_2CH_3$), 1.24 - 1.27 (m, 12 H, 6×$CH_2$), 2.60 - 2.67 (m, 2 H, $CH_2$), 2.78 (q, $^3J$ = 7.4 Hz, 2 H, $CH_2CH_3$), 7.26 - 7.32 (m, 1 H, $CH_{Ar}$), 7.36 - 7.42 (m, 1 H, $CH_{Ar}$), 7.46 – 7.49 (m, 1 H, $CH_{Ar}$), 7.74 (s, 1 H, $CH_{Ar}$),

8.33 (d, $^3J$ = 7.7 Hz, 1 H, $CH_{Ar}$), 11.96 ($s_{(br)}$, 1 H, NH), 13.62 (s, 1 H, OH). $^{13}$C NMR (DMSO, 62 MHz): δ = 13.8, 15.3 ($CH_3$), 22.0, 26.0, 26.8, 28.5, 28.6, 29.1, 29.3, 31.3 ($CH_2$), 107.3 ($C_{Ar}$), 111.6, 116.4 ($CH_{Ar}$), 118.3 ($C_{Ar}$), 123.0, 123.3 ($CH_{Ar}$), 128.3 ($C_{Ar}$), 129.3 ($CH_{Ar}$), 132.3, 135.2, 150.0, 159.2 ($C_{Ar}$), 165.7 (CO).IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 3169 (w), 3082 (w), 3020 (w), 2963 (m), 2921 (m), 2875 (m), 1716 (w), 1650 (s), 1594 (m), 1500 (m), 1430 (m), 1408 (s), 1372 (m), 1330 (m), 1319 (m), 1295 (m), 1235 (m), 1194 (m), 1112 (w), 1091 (m), 1047 (w), 1008 (w), 940 (w), 912 (w), 853 (m), 810 (s), 798 (m), 750 (s), 698 (m), 687 (m), 639 (m), 592 (m), 529 (m). MS (EI 70 eV): *m/z* (%) = 352 ([M]$^+$+1, 11), 351 ([M]$^+$, 49), 253 (88), 252 (100), 237 (8). HRMS (EI): Calcd. for $C_{23}H_{29}NO_2$: 351.22063; found: 351.220119.

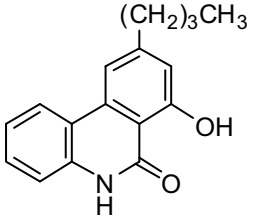
**8-Ethyl-7-hydroxy-9-propylphenanthridin-6(5H)-one (10g):**



Chemical Formula: $C_{18}H_{19}NO_2$
Exact Mass: 281.142

Starting with **9g** (0.202 g, 0.57 mmol), **10g** was isolated (0.100 g, 63%) by column chromatography (silica gel, heptanes/EtOAc = 30:1 → 20:1) as a colorless solid, m.p 232 - 234 °C. $^1$H NMR (DMSO, 250 MHz): δ = 1.00 (t, $^3J$ = 8.1 Hz, 3 H, $CH_3$), 1.13 (t, $^3J$ = 7.2 Hz, 3 H, $CH_3$), 1.66 (q, $^3J$ = 7.3 Hz, 2 H, $CH_2$), 2.66 - 2.77 (m, 4 H, $CH_2$), 7.26 - 7.36 (m, 2 H, $CH_{Ar}$), 7.49 - 7.58 (m, 2 H, $CH_{Ar}$), 8.34 (d, $^3J$ = 8.0 Hz, 1 H, $CH_{Ar}$), 11.90 ($s_{(br)}$, 1 H, NH), 13.62 (s, 1 H, OH). $^{13}$C NMR (DMSO, 62 MHz): δ = 13.9, 14.0 ($CH_3$), 18.3, 24.0, 35.0 ($CH_2$), 107.5 ($C_{Ar}$), 112.6, 116.6 ($CH_{Ar}$), 118.4, 121.6 ($C_{Ar}$), 123.0, 123.8, 131.3 ($CH_{Ar}$), 132.3, 135.2, 147.8, 159.2 ($C_{Ar}$), 165.7 (C=O). MS (EI 70 eV): *m/z* (%) = 281 ([M]$^+$, 100), 238 (76), 207 (12), 224 (30), 190 (7), 165 (5), 78 (40), 63 (23), 43 (8). HRMS (EI): Calcd. for $C_{17}H_{17}NO_2$: 267.12535; found: 267.12538. Anal.: Calcd for $C_{18}H_{19}NO_2$: C 76.84, H 6.81, N 4.98; found.: C 76.90, H 6.60, N 4.90.

**9-butyl-7-hydroxyphenanthridin-6(5H)-one (10h):**

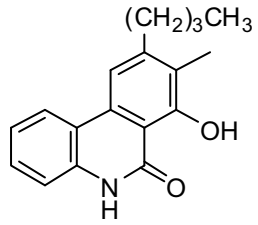


Chemical Formula: $C_{17}H_{17}NO_2$
Exact Mass: 267.126

Starting with **9h** (0.164 g, 0.5 mmol),**10h** was isolated (0.931 g, 70 %) by column chromatography (silica gel, heptanes/EtOAc = 30:1 → 20:1) as a colorless solid, m.p 234 - 235 °C. $^1$H NMR (DMSO, 250 MHz): δ = 0.92 (t, $^3J$ = 7.1 Hz, 3 H, $(CH_2)_3CH_3$), 1.27 - 1.41 (m, 2 H, $CH_2$), 1.59 - 1.71 (m, 2 H, $CH_2$), 2.71 (t, $^3J$ = 7.6 Hz, 2 H, $CH_2(CH_2)_2CH_3$), 6.83 (s, 1 H, $CH_{Ar}$), 7.28v7.33 (m, 1 H, $CH_{Ar}$), 7.38 - 7.41 (m, 1 H,

$CH_{Ar}$), 7.49 - 7.55 (m, 1 H, $CH_{Ar}$), 7.75 (s, 1 H, $CH_{Ar}$), 8.35 (d, $^3J$ = 8.8 Hz, 1 H, $CH_{Ar}$), 12.02 ($s_{(br)}$, 1 H, NH), 13.26 (s, 1 H, OH). $^{13}$C NMR (DMSO, 62 MHz): δ = 13.7 ($CH_3$), 21.7, 32.6, 35.5 ($CH_2$), 107.9 ($C_{Ar}$), 112.2, 114.2, 116.5 ($CH_{Ar}$), 118.2 ($C_{Ar}$), 123.0, 123.7, 129.7 ($CH_{Ar}$), 135.1, 135.5, 150.5, 161.5 ($C_{Ar}$) 165.4 (CO).IR (Neat, cm$^{-1}$): $\widetilde{\nu}$ = 3170 (w), 3075 (w), 3012 (w), 2953 (m), 2923 (m), 2856 (m), 1659 (s), 1626 (m), 1595 (m), 1552 (m), 1503 (m), 1455 (w), 1426 (m), 1406 (m), 1378 (m), 1349 (m), 1296 (m), 1229 (m), 1163 (m), 1126 (w), 1078 (w), 1037 (w), 1006 (m), 938 (w), 916 (w), 862 (m), 805 (m), 774 (m), 747 (s), 680 (m), 639 (m), 617 (m), 553 (m).MS (EI 70 eV): *m/z* (%) = 268 ([M]$^+$+1, 8), 267 ([M]$^+$, 53), 226 (24), 225 (100), 224 (23), 196 (10), 178 (8), 78 (24), 63 (26), 44 (10).HRMS (EI): Calcd. for $C_{17}H_{17}NO_2$: 267.12538; found: 267.125349.

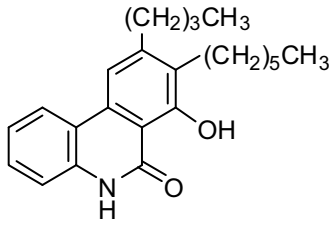
**9-butyl-7-hydroxy-8-methylphenanthridin-6(5H)-one (10i):**



Chemical Formula: $C_{18}H_{19}NO_2$
Exact Mass: 281.142

Starting with **9i** (0.171 g, 0.5 mmol), **10i** was isolated (0.0756 g, 54 %) by column chromatography (silica gel, heptanes/EtOAc = 30:1 → 20:1) as a colorless solid, m.p 257 - 259 °C. $^1$H NMR (DMSO, 250 MHz): δ = 0.94 (t, $^3J$ = 7.1 Hz, 3 H, $(CH_2)_3CH_3$), 1.36 - 1.44 (m, 2 H, $CH_2$), 1.52 - 1.61 (m, 2 H, $CH_2$), 2.20 (s, 3 H, $CH_3$), 2.76 (t, $^3J$ = 7.4 Hz, 2 H, $CH_2(CH_2)_2CH_3$), 7.26 - 7.32 (m, 1 H, $CH_{Ar}$), 7.36 - 7.39 (m, 1 H, $CH_{Ar}$), 7.46 - 7.52 (m, 1 H, $CH_{Ar}$), 7.73 (s, 1 H, $CH_{Ar}$), 8.34 (d, $^3J$ = 8.1 Hz, 1 H, $CH_{Ar}$), 11.96 ($s_{(br)}$, 1 H, NH), 13.62 (s, 1 H, OH). $^{13}$C NMR (DMSO, 62 MHz): δ = 10.6, 13.7 ($CH_3$), 22.1, 31.9, 33.5 ($CH_2$), 107.3 ($C_{Ar}$), 112.4, 116.4 ($CH_{Ar}$), 118.3, 121.3 ($C_{Ar}$), 123.0, 123.3, 129.2 ($CH_{Ar}$), 132.1, 135.1, 148.6, 159.2 ($C_{Ar}$) 165.6 (CO).IR (Neat, cm$^{-1}$): $\widetilde{\nu}$ = 3305 (w), 3169 (w), 3017 (w), 2953 (m), 2932 (m), 2860 (m), 1731 (w), 1657 (s), 1651 (s), 1632 (m), 1595 (m), 1553 (m), 1503 (m), 1449 (w), 1409 (m), 1372 (m), 1348 (m), 1304 (m), 1268 (m), 1236 (m), 1195 (m), 1113 (m), 1098 (m), 1057 (m), 935 (m), 857 (m), 843 (m), 805 (s), 789 (s), 743 (s), 713 (m), 668 (m), 629 (m), 620 (m), 560 (s), 539 (s).MS (EI 70 eV): *m/z* (%) = 282 ([M]$^+$+1, 12), 281 ([M]$^+$, 57), 252 (15), 240 (16), 239 (100), 238 (15), 224 (31).HRMS (EI): Calcd. for $C_{18}H_{19}NO_2$: 281.14103; found: 281.141039.

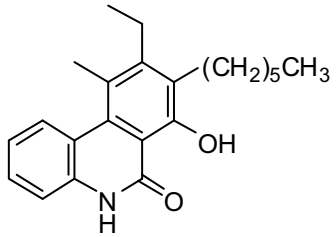
**9-butyl-7-hydroxy-8-methylphenanthridin-6(5H)-one (10j):**




Chemical Formula: $C_{23}H_{29}NO_2$
Exact Mass: 351.220

Starting with **9j** (0.098 g, 0.55 mmol), **10j** was isolated (0.097 g, 50 %) by column chromatography (silica gel, heptanes/EtOAc = 30:1 → 20:1) as a colorless solid, m.p 220 – 222 °C. $^1$H NMR (DMSO, 250 MHz): δ = 0.84 - 0.90 (m, 3 H, $(CH_2)_5CH_3$),0.95 (t, $^3J$ = 7.3 Hz, 3 H, $(CH_2)_3CH_3$), 1.22 - 1.31 (m, 6 H, 3×$CH_2$), 1.37 - 1.43 (m, 4 H, 2×$CH_2$), 1.57 - 1.64 (m, 2 H, $CH_2$), 2.63 - 2.77 (m, 4 H, 2×$CH_2$), 7.26 - 7.32 (m, 1 H, $CH_{Ar}$), 7.36 - 7.39 (m, 1 H, $CH_{Ar}$), 7.46 - 7.51 (m, 1 H, $CH_{Ar}$), 7.73 (s, 1 H, $CH_{Ar}$), 8.33 (d, $^3J$ = 8.7 Hz, 1 H, $CH_{Ar}$), 11.95 ($s_{(br)}$, 1 H, NH), 13.63 (s, 1 H, OH).$^{13}$C NMR (DMSO, 62 MHz): δ = 13.7, 13.9 ($CH_3$), 21.9, 22.2, 24.9, 28.9, 30.6, 31.0, 32.7, 33.0 ($CH_2$), 107.4 ($C_{Ar}$), 112.5, 116.4 ($CH_{Ar}$), 118.3 ($C_{Ar}$), 121.3, 123.3 ($CH_{Ar}$), 126.2 ($C_{Ar}$), 129.2 ($CH_{Ar}$), 132.3, 135.1, 148.2, 159.3 ($C_{Ar}$) 165.7 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 3166 (w), 2951 (m), 2923 (m), 2867 (m), 1714 (w), 1650 (s), 1626 (m), 1597 (m), 1551 (w), 1502 (m), 1454 (w), 1409 (m), 1376 (w), 1349 (m), 1309 (m), 1267 (m), 1233 (m), 1195 (m), 1101 (w), 1041 (w), 1014 (w), 937 (w), 872 (m), 845 (m), 809 (m), 786 (s), 747 (s), 729 (m), 672 (m), 659 (m), 621 (w), 559 (m), 535 (w). MS (EI 70 eV): *m/z* (%) = 352 ([M]$^+$+1, 27), 351 ([M]$^+$, 90), 322 (17), 294 (29), 281 (42), 280 (86), 266 (13), 252 (18), 250 (18), 240 (18), 239 (87), 238 (100), 226 (11), 225 (13), 224 (12), 210 (15), 63 (13). HRMS (EI): Calcd. for $C_{23}H_{29}NO_2$: 351.21958; found: 351.219174.

**9-ethyl-8-hexyl-7-hydroxy-10-methylphenanthridin-6(5H)-one (10k):**

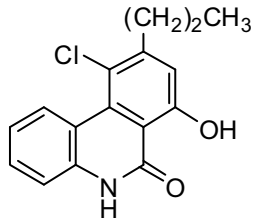



Chemical Formula: $C_{22}H_{27}NO_2$
Exact Mass: 337.204

Starting with **9k** (0.199 g, 0.5 mmol), **10k** was isolated (0.084 g, 50 %) by column chromatography (silica gel, heptanes/EtOAc = 30:1 → 20:1) as a colorless solid, m.p 193 - 194 °C. $^1$H NMR (DMSO, 250 MHz): δ = 0.87 (t, $^3J$ = 6.5 Hz, 3 H, $CH_2CH_3$), 1.16 (t, $^3J$ = 7.1 Hz, 3 H, $(CH_2)_5CH_3$), 1.25 - 1.36 (m, 6 H, 3×$CH_2$), 2.50 (s, 3 H, $CH_3$), 2.67 - 2.73 (m, 4 H, 2×$CH_2$), 2.82 (q, $^3J$ = 7.7 Hz, 2 H, $CH_2CH_3$), 7.23 − 7.29 (m, 1 H, $CH_{Ar}$), 7.38 - 7.41 (m, 1 H, $CH_{Ar}$), 7.43 - 7.49 (m, 1 H, $CH_{Ar}$), 8.23 (d, $^3J$ = 8.0 Hz, 1 H, $CH_{Ar}$), 11.93 ($s_{(br)}$, 1 H, NH), 13.95 (s, 1 H, OH). $^{13}$C NMR (DMSO, 62 MHz): δ = 13.8, 14.1, 19.5 ($CH_3$), 22.0, 23.2, 25.5, 29.0, 29.3, 31.1 ($CH_2$), 108.1 ($C_{Ar}$), 116.1 ($CH_{Ar}$) 119.3 ($C_{Ar}$), 121.8 ($CH_{Ar}$), 122.1, 126.6 ($C_{Ar}$), 128.3, 128.4 ($CH_{Ar}$), 132.1, 135.8, 149.0, 157.7 ($C_{Ar}$), 166.1 (CO).IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 3305 (w), 3169 (w), 3033 (w), 2955 (m), 2921 (m), 2856

(m), 1722 (w), 1656 (m), 1586 (m), 1549 (m), 1503 (m), 1465 (m), 1408 (s), 1376 (m), 1344 (m), 1291 (m), 1275 (m), 1261 (m), 1180 (m), 1164 (m), 1128 (m), 1113 (m), 1011 (m), 981 (w), 945 (w), 911 (m), 857 (m), 810 (s), 751 (m), 720 (m), 692 (m), 665 (m), 634 (w), 591 (m), 556 (m), 538 (m). MS (EI 70 eV): *m/z* (%) = 338 ($[M]^+$+1, 25), 337 ($[M]^+$, 84), 308 (10), 280 (15), 267 (86), 266 (100), 250 (14), 238 (12), 237 (12). HRMS (EI): Calcd. for $C_{22}H_{27}NO_2$: 337.20363; found: 337.203114.

**10-chloro-7-hydroxy-9-propylphenanthridin-6(5H)-one (10l):**




Chemical Formula: $C_{16}H_{14}ClNO_2$
Exact Mass: 287.071

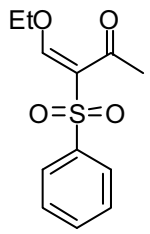
Starting with **9l** (0.174 g, 0.5 mmol), **10l** was isolated (0.070 g, 49 %) by column chromatography (silica gel, heptanes/EtOAc = 30:1 → 20:1) as a colorless solid, m.p 258 - 260 °C. $^1$H NMR (DMSO, 250 MHz): δ = 0.99 (t, $^3J$ = 8.1 Hz, 3 H, $CH_3$), 1.62 - 1.71 (m, 2 H, $CH_2CH_2CH_3$), 2.82 (t, $^3J$ = 7.4 Hz, 2 H, $CH_2CH_2CH_3$), 7.02 (s, 1 H, $CH_{Ar}$), 7.28 – 7.34 (m, 1 H, $CH_{Ar}$), 7.42 - 7.46 (m, 1 H, $CH_{Ar}$), 7.54 - 7.60 (m, 1 H, $CH_{Ar}$), 9.35 (d, $^3J$ = 8.7 Hz, 1 H, $CH_{Ar}$), 12.27 ($s_{(br)}$, 1 H, NH), 14.00 (s, 1 H, OH). $^{13}$C NMR (DMSO, 62 MHz): δ = 13.7 ($CH_3$), 22.1, 36.7 ($CH_2$), 110.1 ($C_{Ar}$), 116.7, 117.0 ($CH_{Ar}$) 117.5, 118.6 ($C_{Ar}$), 122.3, 127.3, 130.0 ($CH_{Ar}$), 131.9, 136.2, 149.1, 160.4 ($C_{Ar}$), 165.0 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 3116 (w), 3129 (w), 3078 (w), 3014 (w), 2957 (m), 2933 (m), 2868 (m), 2743 (m), 1656 (s), 1610 (m), 1580 (m), 1552 (m), 1503 (m), 1465 (m), 1408 (s), 1338 (m), 1290 (m), 1275 (m), 1242 (m), 1190 (m), 1174 (m), 1134 (m), 1090 (m), 1040 (w), 1018 (w), 944 (w), 923 (w), 872 (m), 850 (m), 808 (s), 784 (m), 772 (m), 755 (s), 711 (s), 661 (m), 627 (m), 610 (w), 598 (m), 548 (m). MS (EI 70 eV): *m/z* (%) = 289 ($[M^+]$ $^{37}$Cl, 27), 287 ($[M^+]$ $^{35}$Cl, 88), 261 (30), 260 (15), 259 (100), 253 (12), 252 (31), 225 (40), 224 (40), 211 (10), 196 (20), 178 (10), 177 (11), 84 (12), 78 (70), 66 (11), 63 (78), 61 (13), 45 (10), 44 (12).

HRMS (EI): Calcd. for $C_{16}H_{14}NO_2Cl$: 287.07076; found: 287.070305.

**General procedure for the synthesis of enones 12a-e:**

A solution of ketosulfone **11** (1 equiv.) in triethyl orthoformiate (1.2 equiv.) and acetic anhydride was stirred for 1.5 h at 120 °C and, subsequently, for 1.5 h at 140 °C. The acetic anhydride was removed in vacuo and the resulting solid residue was recrystallized (ethanol).

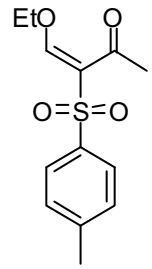
**4-Ethoxy-3-(phenylsulfonyl)but-3-en-2-one (12a).**



Chemical Formula: $C_{12}H_{14}O_4S$
Exact Mass: 254.061

Starting with **11a** (2.00 g, 10.1 mmol) and triethyl orthoformiate (12.1 mmol, 1.79 g, 2.0 ml), **12a** was isolated (2.10 g, 82%) as a slightly brown solid, mp. = 46-48 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ = 1.40 (t, $^3J$ = 7.5 Hz, 3H, $OCH_2CH_3$), 2.25 (s, 3H, $COCH_3$), 4.34 (q, $^3J$ = 7.1 Hz, 2H, $OCH_2CH_3$), 7.38 - 7.50 (m, 3H, $3CH_{Ar}$), 7.88 - 7.91 (m, 2 H, $2CH_{Ar}$), 8.20 (s, 1H, $CH_{vin}$). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 15.4 ($OCH_2CH_3$), 31.9 ($COCH_3$), 74.6 ($OCH_2CH_3$), 122.0 ($C_{olf}$), 128.20 ($2CH_{Ar}$), 128.58 ($2CH_{Ar}$), 129.4 ($CH_{Ar}$), 133.4 ($C_{Ar}$), 167.7 ($CH_{olf.}$), 191.0 (CO). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ = 3066 (w), 2986 (w), 2254 (w), 1667 (m), 1599 (s), 1477 (w), 1446 (m), 1393 (m), 1354 (m), 1302 (s), 1189 (m), 1148 (s), 1090 (m), 1047 (m), 998 (m), 906 (s), 849 (m), 724 (s), 686 (s), 647 (m), 612 (s), 600 (s), 563 (s), 543 (s). GC-MS (EI, 70 eV): *m/z* (%) = 211 (41), 190 (30), 189 (74), 175 (20), 162 (10), 161 (55), 147 (17), 141 (43), 125 (14), 105 (17), 97 (39), 78 (23), 77 (100), 69 (32), 51 (31), 43 (38), 29 (16). HRMS (EI): Calcd. for $C_{12}H_{14}O_4S$ ($[M]^+$): 254.06073; found: 254.060618.

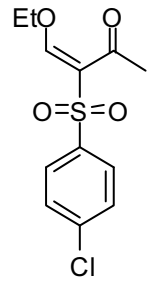
**4-Ethoxy-3-tosylbut-3-en-2-one (12b).**



Chemical Formula: $C_{13}H_{16}O_4S$
Exact Mass: 268.077

Starting with **11b** (2.00 g, 9.4 mmol) and triethyl orthoformiate (11.3 mmol, 1.67 g, 1.9 ml), **12b** was isolated (2.02 g, 80%) as a slightly brown solid, mp. = 134-135 °C. $^1$H NMR (250 MHz, $CDCl_3$): δ = 1.41 (t, $^3J$ = 7.4Hz, 3H, $OCH_2CH_3$), 2.24 (s, 3H, $COCH_3$), 2.32 (s, 3H, $PhCH_3$), 4.33 (q, $^3J$ = 7.3 Hz, 2H, $OCH_2CH_3$), 7.19 - 7.22 (m, 2H, $2CH_{Ar}$), 7.76 - 7.79 (m, 2 H, $2CH_{Ar}$), 8.18 (s, 1H, $CH_{vin}$). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 15.3 ($OCH_2CH_3$), 21.5 ($PhCH_3$), 32.0 ($COCH_3$), 74.5 ($OCH_2CH_3$), 122.2 ($C_{olf}$), 128.2 ($2CH_{Ar}$), 129.2 ($2CH_{Ar}$), 138.4, 143.7 ($C_{Ar}$), 167.3 ($CH_{olf.}$), 191.1 (CO). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ = 3056 (w), 2984 (w), 2925 (w), 2871 (w), 1666 (m), 1597 (s), 1494 (w), 1473 (w), 1394 (m), 1300 (s), 1265 (m), 1187 (m), 1144 (s), 1047 (m), 927 (w), 849 (m), 734 (m), 666 (s), 606 (m), 562 (s), 531 (s). GC-MS (EI, 70 eV): *m/z* (%) = 225 (25), 204 (20), 203 (16), 190 (10), 189 (75), 175 (36), 161 (15), 155 (48), 139 (15), 119 (12), 97 (80), 92 (24), 91 (100), 89 (11), 77 (10), 69 (47), 65 (35), 63 (10), 43 (32), 39 (11). 29 (15). HRMS (EI): Calcd. for $C_{13}H_{16}O_4S$ ($[M]^+$): 268.07638; found: 268.076825.

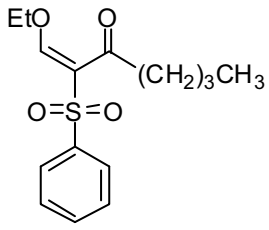
**3-(4-Chlorophenylsulfonyl)-4-ethoxybut-3-en-2-one (12c):**




Chemical Formula: $C_{12}H_{13}ClO_4S$
Exact Mass: 288.022

Starting with **11c** (2.00 g, 8.6 mmol) and triethyl orthoformiate (10.3 mmol, 1.50 g, 1.7 ml), **12c** was isolated (2.16 g, 87%) as a dark brown solid, mp. = 120-121 °C. $^1$HNMR (250 MHz, $CDCl_3$): δ = 1.42 (t, $^3J$ = 7.8 Hz, 3H, $OCH_2CH_3$), 2.26 (s, 3H, $COCH_3$), 4.35 (q, $^3J$ = 7.3 Hz, 2H, $OCH_2CH_3$), 7.35 - 7.41 (m, 2H, $2CH_{Ar}$), 7.81 - 7.86 (m, 2 H, $2CH_{Ar}$), 8.19 (s, 1H, $CH_{vin}$). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 15.2 ($OCH_2CH_3$), 31.9 ($COCH_3$), 74.7 ($OCH_2CH_3$), 122.1 ($C_{olf}$), 129.0 ($2CH_{Ar}$), 130.0 ($2CH_{Ar}$), 139.5, 140.1 ($C_{Ar}$), 168.1 ($CH_{olf}$), 191.1 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 3087 (w), 2972 (w), 2982 (w), 1657 (m), 1597 (m), 1475 (w), 1438 (w), 1395 (w), 1357 (w), 1330 (m), 1296 (m), 1260 (m), 1193 (m), 1176 (m), 1139 (m), 1085 (m), 1041 (m), 1009 (w), 927 (w), 841 (m), 808 (w), 762 (m), 708 (w), 642 (m), 612 (m), 591 (m), 553 (m). GC-MS (EI, 70 eV): *m/z* (%) = 247 (12), 245 (36), 224 (35), 223 (17), 209 (12), 195 (29), 189 (16), 177 (16), 175 (38), 159 (11), 133 (11), 113 (17), 112 (14), 111 (62), 97 (100), 75 (23), 69 (48), 43 (50). HRMS (EI): Calcd. for $C_{12}H_{13}O_4ClS$ ($[M]^+$): 288.02176; found: 288.021693.

**1-Ethoxy-2-(phenylsulfonyl)hept-1-en-3-one (12d).**

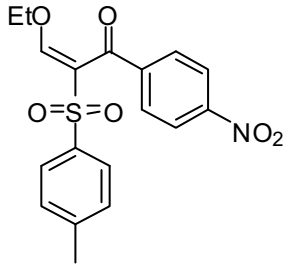



Chemical Formula: $C_{15}H_{20}O_4S$
Exact Mass: 296.108

Starting with **11d** (2.00 g, 8.3 mmol) and triethyl orthoformiate (10.0 mmol, 1.47 g, 1.66 ml), **12d** was isolated (1.97 g, 80%) as a dark brown solid, mp. = 79-81 °C. $^1$HNMR (250 MHz, $CDCl_3$): δ = 0.77 (t, $^3J$ = 7.4 Hz, 3H, $(CH_2)_3CH_3$), 1.09-1.24 (m, 3H, $OCH_2CH_3$), 1.37-1.43 (m, 4H, $2CH_2$), 2.57 (t, $^3J$ = 7.6 Hz, 2H, $COCH_2$), 4.34 (q,$^3J$ = 7.4 Hz, 2H, $OCH_2CH_3$), 7.37 - 7.48 (m, 3H, $3CH_{Ar}$), 7.87 - 7.91 (m, 2 H, $2CH_{Ar}$), 8.15 (s, 1H, $CH_{vin}$). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.8, 15.4 ($CH_3$), 22.1, 25.4 ($CH_2$), 43.6 ($COCH_2$), 74.4 ($OCH_2CH_3$), 121.3 ($C_{olf.}$), 128.2 ($2CH_{Ar}$), 128.5 ($2CH_{Ar}$), 132.9 ($CH_{Ar}$), 141.5 ($C_{Ar}$), 166.6 ($CH_{olf.}$), 194.2 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 3303 (w), 3071 (w), 2952 (m), 2871 (w), 1721 (w), 1660 (s), 1595 (s), 1448 (m), 1396 (m), 1382 (m), 1340 (m), 1271 (s), 1150 (s), 1113 (s), 1077 (s), 1024 (s), 962 (m), 891 (w), 838 (s), 787 (m), 753 (s), 718 (s), 682 (s), 595 (s), 543 (s). GC-MS (EI, 70 eV): *m/z* (%) = 239 (36), 232 (12), 231 (27), 212 (11), 211 (100), 203 (15), 190 (15), 175 (10), 161 (37), 141 (41), 105 (10), 78 (10), 77 (68), 51 (11), 29 (13). HRMS (EI): Calcd. $(M+H)^+$ for $C_{15}H_{21}O_4S$: 297.11551; found: 297.11542. Calcd. $(M+Na)^+$

for $C_{15}H_{20}NaO_4S$: 319.09745; found: 319.09738. Calcd. $(2M+Na)^+$ for $C_{30}H_{40}NaO_8S_2$: 615.20568; found: 615.20573.

**3-Ethoxy-1-(4-nitrophenyl)-2-tosylprop-2-en-1-one (12e).**



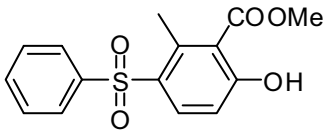

Chemical Formula: $C_{18}H_{17}NO_6S$
Exact Mass: 375.078

Starting with **11e** (2.00 g, 6.3 mmol) and triethyl orthoformiate (7.6 mmol, 1.12 g, 1.3 ml), **12c** was isolated (2.128 g, 90%) as a yellow solid, mp. = 133-134 °C. $^1$HNMR (250 MHz, $CDCl_3$): δ = 1.11 (t, $^3J$ = 7.2 Hz, 3H, $OCH_2CH_3$), 2.30 (s, 3H, $CH_3$), 4.07 (q, $^3J$ = 7.1 Hz, 2H, $OCH_2CH_3$), 7.24 - 7.29 (m, 2H, $2CH_{Ar}$), 7.74 - 7.83 (m, 4 H, $4CH_{Ar}$), 7.97 (s, 1H, $CH_{vin}$), 8.15-8.20 (m, 2H, $2CH_{Ar}$). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 15.0 ($OCH_2CH_3$), 21.6 ($PhCH_3$), 73.6 ($OCH_2CH_3$), 120.4 ($C_{olf}$), 123.5 ($2CH_{Ar}$), 128.1 ($2CH_{Ar}$), 129.64 ($2CH_{Ar}$), 129.9 ($2CH_{Ar}$), 138.4, 142.4, 144.3, 150.2 ($C_{Ar}$), 163.8 ($CH_{olf}$), 187.1 (CO). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ = 3103 (w), 3069 (w), 2999 (w), 2939 (w), 2866 (w), 1658 (m), 1585 (m), 1523 (m), 1444 (w), 1391 (w), 1348 (m), 1269 (m), 1219 (m), 1147 (m), 1073 (m), 1006 (m), 924 (w), 857 (m), 813 (m), 775 (w), 726 (m), 690 (w), 656 (m), 582 (m), 541 (m). GC-MS (EI, 70 eV): *m/z* (%) = 312 (11), 311 (68), 310 (11), 296 (64), 283 (11), 282 (38), 204 (93), 176 (100), 155 (10), 150 (25), 139 (14), 104 (19), 92 (19), 91 (73), 76 (11), 65 (16). HRMS (EI): Calcd. for $C_{18}H_{17}NO_6S$ ($[M]^+$): 375.07711; found: 375.077049.

**General procedure for the synthesis of 4-(arylsulfonyl)phenols 13a-ag.**

To a $CH_2Cl_2$ solution (2 mL / 1 mmol of **12a-e**) of **2a-e** was added **4a-m** (1.1 mmol) and, subsequently, $TiCl_4$ (1.1 mmol) at ~78 °C. The temperature of the solution was allowed to warm to 20 °C during 14 h with stirring. To the solution was added hydrochloric acid (10%, 20 mL) and the organic and the aqueous layer were separated. The latter was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic layers were dried ($Na_2SO_4$), filtered and the filtrate was concentrated in vacuo. The residue was purifed by chromatography (silica gel, heptanes / EtOAc) to give **4a-ag**.

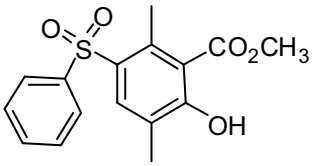
**Methyl 6-hydroxy-2-methyl-3-(phenylsulfonyl)benzoate (13a).**




Chemical Formula: $C_{15}H_{14}O_5S$
Exact Mass: 306.05619

Starting with **12a** (0.381 g, 1.5 mmol) and **4a** (0.429 g, 1.7 mmol), **13a** was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish solid (0.365 g, 80%), mp. = 80-83 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ = 2.52 (s, 3 H, Ph*CH*$_3$), 3.87 (s, 3 H, $OCH_3$), 6.96 (d, $^3J$ = 7.6 Hz, 1 H, $CH_{Ar}$), 7.40 - 7.50 (m, 3 H, $3CH_{Ar}$), 7.73 - 7.77 (m, 2 H, $2CH_{Ar}$), 8.30 (d, $^3J$ = 7.5 Hz, 1 H, $CH_{Ar}$), 11.21 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 19.0 ($CH_3$), 52.8 ($OCH_3$), 115.3 (*C*$COOCH_3$), 115.7 ($CH_{Ar}$), 127.2 ($2CH_{Ar}$), 129.1 ($2CH_{Ar}$), 131.4 ($C_{Ar}$), 132.9 ($CH_{Ar}$), 135.3 ($CH_{Ar}$), 141.9, 142.7 ($C_{Ar}$), 165.3 (COH), 171.0 (CO). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ = 3070 (w), 3003 (w), 2950 (w), 2923 (w), 2848 (w), 1722 (w), 1667 (m), 1572 (m), 1537 (w), 1461 (w), 1445 (m), 1383 (w), 1349 (m), 1286 (m), 1222 (m), 1140 (s), 1108 (m), 1082 (m), 994 (m), 842 (m), 805 (m), 756 (w), 729 (m), 688 (s), 628 (w), 607 (s), 593 (m), 547 (s). GC-MS (EI, 70 eV): *m/z* (%) = 306 ($[M]^+$, 28), 275 (25), 274 (100), 257 (16), 256 (10), 255 (27), 241 (21), 209 (15), 208 (12), 181 (14), 153 (14), 152 (12), 149 (10), 121 (13), 105 (11), 77 (33), 51 (22). HRMS (EI): Calcd. for $C_{15}H_{14}O_5S$ ($[M]^+$): 306.05565; found: 306.055771.

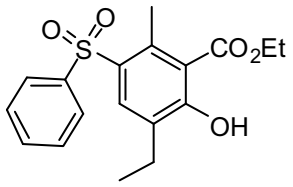
**Methyl 2-hydroxy-3,6-dimethyl-5-(phenylsulfonyl)-benzoate (13b).**




Chemical Formula: $C_{16}H_{16}O_5S$
Exact Mass: 320.072

Starting with **12a** (0.381 g, 1.5 mmol) and **4b** (0.452 g, 1.7 mmol), **13b** was isolated after chromatography (silica gel, heptanes/EtOAc) as a white solid (0.384 g, 80%), mp. = 160-161 °C. $^1$H NMR (250 MHz, $CDCl_3$): δ = 2.24 (s, 3 H, Ph*CH*$_3$), 2.46 (s, 3 H, Ph*CH*$_3$), 3.85 (s, 3 H, $OCH_3$), 7.37-7.52 (m, 3 H, $3CH_{Ar}$), 7.71-7.76 (m, 2 H, $2CH_{Ar}$), 8.19 (s, 1H, $CH_{Ar}$), 11.39 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 15.9, 18.8 ($CH_3$), 52.7 ($OCH_3$), 114.4 (*C*$COOCH_3$), 125.1 ($C_{Ar}$), 127.1 ($2CH_{Ar}$), 129.0 ($2CH_{Ar}$), 130.3 ($C_{Ar}$), 132.8, 135.5 ($CH_{Ar}$), 139.8, 142.2 ($C_{Ar}$), 163.9 (COH), 171.6 (CO). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ = 3066 (w), 2955 (w), 2255(w), 1736 (w), 1665 (m), 1604 (w), 1571 (w), 1445 (m), 1381 (w), 1344 (m), 1303 (s), 1252 (m), 1201 (m), 1165 (m), 1144 (s), 1087 (m), 1062 (w), 1031 (w), 996 (w), 975 (w), 908 (s), 826 (w), 729 (s), 688 (m), 637 (w), 579 (s), 556 (m). GC-MS (EI, 70 eV): *m/z* (%) = 320 ($[M]^+$, 26), 289 (22), 288 (100), 260 (30), 77(13). HRMS (EI): Calcd. for $C_{16}H_{16}O_5S_1$ ($[M]^+$) : 320.07130; found: 320.071232.

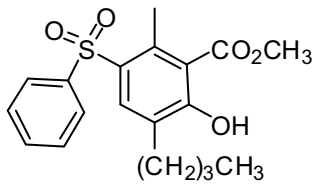
**Ethyl 3-ethyl-2-hydroxy-6-methyl-5-(phenylsulfonyl)-benzoate (13c).**



Chemical Formula: $C_{18}H_{20}O_5S$
Exact Mass: 348.103

Starting with **12a** (0.381 g, 1.5 mmol) and **4c** (0.499 g, 1.7 mmol), **13c** was isolated after chromatography (silica gel, heptanes/EtOAc) as a white solid (0.402 g, 77%), mp. = 95-97 °C. $^1$H NMR (250 MHz, $CDCl_3$): δ = 1.26 (t, $^3J$ = 7.6 Hz, 3H, $CH_2CH_3$), 1.36 (t, $^3J$ = 7.6 Hz, 3H, $OCH_2CH_3$), 2.55 (s, 3 H, $PhCH_3$), 2.73 (q, $^3J$ = 7.7 Hz, 2H, $PhCH_2CH_3$), 4.40 (q, $^3J$ = 7.2 Hz, 2H, $OCH_2CH_3$), 7.45 - 7.59 (m, 3 H, $3CH_{Ar}$), 7.79 - 7.82 (m, 2 H, $2CH_{Ar}$), 8.26 (s, 1H, $CH_{Ar}$), 11.53 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.4, 14.0, 19.0 ($CH_3$), 23.1 ($CH_2$), 62.4 ($OCH_3$), 114.7 ($CCOOCH_3$), 127.1 ($2CH_{Ar}$), 129.0 ($2CH_{Ar}$), 130.4, 130.8 ($C_{Ar}$), 132.79, 134.01 ($CH_{Ar}$), 139.7, 142.2 ($C_{Ar}$), 163.5 (COH), 171.16 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 3066 (w), 2970 (w), 2934 (w), 2254 (w), 1730 (w), 1658 (m), 1603 (w), 1565 (w), 1445 (m), 1373 (m), 1303 (m), 1288 (m), 1241 (m), 1200 (m), 1143 (s), 1086 (m), 1017 (m), 907 (w), 866 (w), 819 (w), 718 (m), 688 (m), 647 (w), 579 (s), 556 (m). GC-MS (EI, 70 eV): *m/z* (%) = 349 (13), 348 ([M]$^+$, 64), 303 (13), 302 (18), 281 (14), 275 (14), 274 (68), 237 (17), 210 (32), 209 (18), 208 (28), 207 (100), 195 (15), 191 (14), 181 (44), 165 (13), 152 (11), 133 (12), 105 (14), 103 (15), 91 (17), 79 (12), 78(14), 77 (33), 51 (15), 45 (12), 44 (90), 39 (10), 32 (36), 31 (15), 29 (11). HRMS (EI): Calcd. for $C_{18}H_{20}O_5S$ ([M]$^+$): 348.10260; found: 348.102403.

**Methyl 3-butyl-2-hydroxy-6-methyl-5-(phenylsulfonyl)-benzoate (13d).**

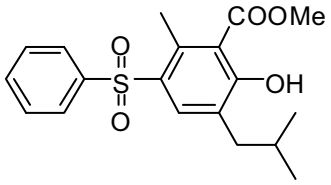


Chemical Formula: $C_{19}H_{22}O_5S$
Exact Mass: 362.119

Starting with **12a** (0.381 g, 1.5 mmol) and **4d** (0.522 g, 1.7 mmol), **13d** was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish solid (0.413 g, 76%), mp. = 95-97 °C. $^1$H NMR (250 MHz, $CDCl_3$): δ = 0.83 (t, $^3J$ = 7.5 Hz, 3H,$CH_3$), 1.23-1.32 (m, 2H, $CH_2$), 1.44-1.56 (m, 2 H, $CH_2$), 2.42 (s, 3H, $PhCH_3$), 2.58 (t, $^3J$ = 7.6 Hz, 2H, $PhCH_2$), 3.80 (s, 3H, $OCH_3$), 7.33 - 7.43 (m, 3 H, $3CH_{Ar}$), 7.66 - 7.69 (m, 2 H, $2CH_{Ar}$), 8.13 (s, 1H, $CH_{Ar}$), 11.38 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 18.8 ($CH_3$), 22.5, 29.5, 31.2 ($CH_2$), 52.6 ($OCH_3$), 114.6 ($CCOOCH_3$), 127.1 ($2CH_{Ar}$), 128.9 ($2CH_{Ar}$), 129.6, 130.4 ($C_{Ar}$), 132.7, 134.8 ($CH_{Ar}$), 139.7, 142.2 ($C_{Ar}$), 163.5 (COH), 171.7 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 3078 (w), 2958 (w), 2927 (w), 1666 (s), 1594 (w), 1567 (w), 1461 (w), 1438 (m), 1402 (m), 1381 (w), 1301 (s), 1215 (m), 1141 (s), 1085 (s), 1022 (w), 997 (m), 903 (w), 885 (w), 834 (m), 808 (m), 754 (m), 723 (m), 686 (m), 649 (m), 632 (m), 582 (s), 555 (s), 532 (s). GC-MS (EI, 70

eV): *m/z* (%) = 363 (12), 362 ([M]$^+$, 68), 330 (14), 313 (11), 303 (11), 302 (71), 301 (16), 289 (21), 288 (100), 287 (29), 260 (30), 188 (10), 77 (18). HRMS (EI): Calcd. for $C_{19}H_{22}O_5S$ ([M]$^+$) : 362.11825; found: 362.117561

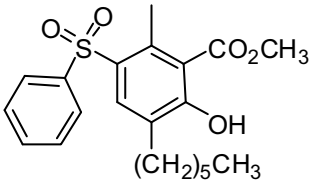
**Methyl 2-hydroxy-3-isobutyl-6-methyl-5-(phenylsulfonyl)-benzoate (13e).**




Chemical Formula: $C_{19}H_{22}O_5S$
Exact Mass: 362.11879

Starting with **12a** (0.381 g, 1.5 mmol) and **4e** (0.522 g, 1.7 mmol), **13e** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a slightly yellow solid (0.379 g, 70%), mp. = 109-110 °C. $^1$H NMR (250 MHz, $CDCl_3$): δ = 0.87 (d, $^3J$ = 6.8 Hz, 6 H, $2CH_3$), 1.88 – 1.99 (m, 1 H, CH), 2.47 (s, 3 H, Ph*CH*$_3$), 2.52 (d, $^3J$ = 7.2 Hz, 2 H, Ph*CH*$_2$), 3.85 (s, 3 H, $OCH_3$), 7.37 - 7.52 (m, 3 H, $3CH_{Ar}$), 7.69- 7.76 (m, 2 H, $2CH_{Ar}$), 8.14 (s, 1 H, $CH_{Ar}$), 11.33 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 17.9, 21.4, 21.4 ($CH_3$), 27.1 (CH), 37.9 ($CH_2$), 51.7 ($OCH_3$), 113.7 (*C*$COOCH_3$), 126.1 ($2CH_{Ar}$), 127.4 ($C_{Ar}$), 128.0 ($2CH_{Ar}$), 129.2 ($C_{Ar}$), 131.7, 134.8 ($CH_{Ar}$), 138.8, 141.1 ($C_{Ar}$) , 162.6 (COH), 170.6 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 2955 (w), 2932 (w), 2870 (w), 1716 (w), 1659 (m), 1600 (w), 1556 (w), 1427 (m), 1383 (w), 1355 (m), 1300 (s), 1254 (m), 1216 (m), 1165 (m), 1141 (s), 1084 (m), 1064 (m), 988 (m), 918 (w), 850 (w), 820 (m), 766 (w), 718 (s), 692 (s), 646 (w), 589 (s), 550 (s). GC-MS (EI, 70 eV): *m/z* (%) = 362 ([M]$^+$, 40), 331 (12), 330 (28), 315 (15), 303 (18), 302 (100), 288 (33), 287 (84), 260 (13), 238 (14), 219 (25), 188 (11), 129 (17), 125 (11), 116 (22), 99 (33), 97 (10), 81 (32), 71 (15), 69 (19), 57 (18), 55 (12). HRMS (EI): Calcd. for $C_{19}H_{22}O_5S$ ([M]$^+$) : 362.11825; found: 362.117994.

**Methyl 3-hexyl-2-hydroxy-6-methyl-5-(phenylsulfonyl)-benzoate (13f).**

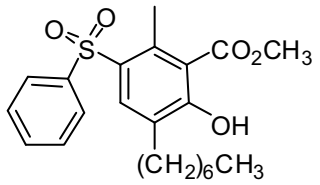



Chemical Formula: $C_{21}H_{26}O_5S$
Exact Mass: 390.150

Starting with **12a** (0.381 g, 1.5 mmol) and **4f** (0.568 g, 1.7 mmol), **13f** was isolated after chromatography (silica gel, heptanes/EtOAc) as a slightly yellow viscous oil (0.456 g, 78%). $^1$H NMR (250 MHz, $CDCl_3$): δ = 0.82 (t, $^3J$ = 7.1 Hz, 3H,$CH_3$), 1.17-1.35 (m, 6H, $3CH_2$), 1.50-1.62 (m, 2 H, $CH_2$), 2.45 (s, 3H, Ph*CH*$_3$), 2.62 (t, $^3J$ = 7.5 Hz, 2H, Ph*CH*$_2$), 3.91 (s, 3H, $OCH_3$), 7.37 - 7.47 (m, 3 H, $3CH_{Ar}$), 7.70 - 7.74 (m, 2 H, $2CH_{Ar}$), 8.17 (s, 1H, $CH_{Ar}$), 11.38 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 18.9 ($CH_3$), 22.6, 29.0, 29.1, 29.8, 31.6 ($CH_2$), 52.7($OCH_3$), 114.6 (*C*$COOCH_3$), 127.1 ($2CH_{Ar}$), 129.0 ($2CH_{Ar}$), 129.6, 130.4 ($C_{Ar}$), 132.7, 134.8 ($CH_{Ar}$), 139.7, 142.2 ($C_{Ar}$), 163.5 (COH), 171.6 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ =

3067 (w), 2926 (m), 2856 (w), 2256 (w), 1737 (w), 1665 (m), 1602 (w), 1567 (w), 1444 (m), 1345 (m), 1303 (m), 1245 (m), 1201 (m), 1143 (s), 1086 (m), 997 (w), 906 (s), 811 (w), 725 (s), 687 (s), 648 (m), 580 (s), 558 (m). GC-MS (EI, 70 eV): *m/z* (%) = 390 ([M]$^+$, 41), 359 (10), 358 (27), 341 (10), 330 (51), 329 (20), 301 (12), 289 (18), 288 (100), 287 (30), 260 (34), 97 (10), 85 (10), 83 (15), 71 (16), 70 (10), 69 (23), 57 (22), 55 (10), 43 (10). HRMS (EI): Calcd. for $C_{21}H_{26}O_5S$ ([M]$^+$): 390.14955; found: 390.149235.

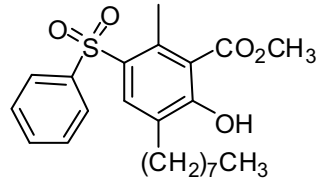
**Methyl 3-heptyl-2-hydroxy-6-methyl-5-(phenyl-sulfonyl)benzoate (13g).**



Chemical Formula: $C_{22}H_{28}O_5S$
Exact Mass: 404.166

Starting with **12a** (0.254 g, 1.0 mmol) and **4g** (0.395 g, 1.1 mmol), **13g** was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish oil (0.303 g, 75%). $^1$H NMR (250 MHz, $CDCl_3$): δ = 0.82 (t, $^3J$ = 7.4 Hz, 3 H, $CH_3$), 1.19 - 1.28 (m, 8 H, 4$CH_2$), 1.54 – 1.60 ( m, 2 H, $CH_2$), 2.46 (s, 3 H, Ph*CH$_3$*), 2.63 (t, $^3J$= 7.4 Hz, 2 H, Ph*CH$_2$*), 3.85 ( s, 3 H, $OCH_3$), 7.37 – 7.49 (m, 3 H, 3$CH_{Ar}$), 7.71 – 7.75 ( m, 2 H, 2$CH_{Ar}$), 8.18 ( s, 1 H, $CH_{Ar}$), 11.36 ( s, 1 H, OH ). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.1, 17.9 ($CH_3$), 21.7, 28.1, 28.2, 28.5, 28.9, 30.8 ($CH_2$), 51.7 ($OCH_3$), 113.7( *C*$COOCH_3$ ), 126.2 (2$CH_{Ar}$), 128.0 (2$CH_{Ar}$ ), 128.6, 129.4 ($C_{Ar}$), 131.8, 133.9 ($CH_{Ar}$), 138.7, 141.2 ($C_{Ar}$), 162.6 (COH), 170.7 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 3066 (w), 2955 (w), 2926 (m), 2855 (w), 2257 (w), 1734 (w), 1666 (m), 1603 (w), 1568 (w), 1446 (m), 1346 (m), 1305 (m), 1248 (w), 1202 (m), 1161 (m), 1145 (s), 1087 (m), 1064 (w), 1025 (w), 998 (w), 908 (m), 811 (w), 731 (s), 689 (m), 648 (w), 583 (s), 560 (m). GC-MS (EI, 70 eV): *m/z* (%) = 404 ([M$^+$], 81), 372 (40), 355 (15), 344 (61), 329 (28), 301 (19), 288 (100), 260 (40), 230 (9), 188 (8), 165 (7), 146 (8), 125 (7), 91 (8), 77 (13), 41 (9). HRMS (EI): Calcd. for $C_{22}H_{28}O_5S$ ([M]$^+$): 404.16520; found: 404.165132.

**Methyl 3-heptyl-2-hydroxy-6-methyl-5-(phenyl-sulfonyl)benzoate (13h).**

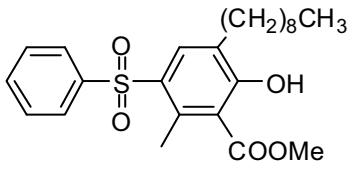


Chemical Formula: $C_{23}H_{30}O_5S$
Exact Mass: 418.181

Starting with **12a** (0.381 g, 1.5 mmol) and **4h** (0.614 g, 1.7 mmol), **13h** was isolated after chromatography (silica gel, heptanes/EtOAc) as a slightly yellow viscous oil (0.471 g, 75%). $^1$HNMR (250 MHz, $CDCl_3$): δ = 0.82 (t, $^3J$ = 7.4 Hz, 3H,$CH_3$), 1.19-1.27 (m, 10H, 5*C*$H_2$), 1.51-1.60 (m, 2 H, $CH_2$), 2.46 (s, 3H, Ph*CH$_3$*), 2.63 (t, $^3J$ = 7.4 Hz, 2H, Ph*CH$_2$*), 3.85 (s, 3H, $OCH_3$), 7.38 - 7.49 (m, 3 H, 3$CH_{Ar}$), 7.71 - 7.75 (m, 2 H, 2$CH_{Ar}$), 8.18 (s, 1H, $CH_{Ar}$),

11.31 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 14.0, 18.8 ($CH_3$), 22.6, 29.0, 29.2, 29.4, 29.4, 29.8, 31.8 ($CH_2$), 52.7 (O*C*H$_3$), 114.6 (*C*COOCH$_3$), 127.1 (2CH$_{Ar}$), 128.9 (2CH$_{Ar}$), 129.6, 130.40 ($C_{Ar}$), 132.7, 134.8 (CH$_{Ar}$), 139.6, 142.2 ($C_{Ar}$), 163.5 (COH), 171.6 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 3066 (w), 2925 (m), 2854 (w), 2255 (w), 1737 (w), 1665 (m), 1602 (w), 1567 (w), 1445 (m), 1304 (m), 1247 (w), 1144 (s), 1087 (m), 1064 (w), 998 (w), 907 (m), 811 (w), 729 (s), 688 (m), 648 (w), 582 (s), 560 (m). GC-MS (EI, 70 eV): *m/z* (%) = 419 (13), 418 ([M]$^+$, 52), 387 (13), 386 (31), 369 (12), 359 (11), 358 (45), 329 (26), 301 (12), 289 (21), 288 (100), 287 (40), 274 (16), 261 (12), 260 (26). HRMS (EI): Calcd. for $C_{23}H_{30}O_5S$ ([M]$^+$): 418.18085; found: 418.180994.

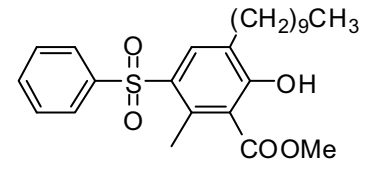
**Methyl 2-hydroxy-6-methyl-3-nonyl-5-(phenylsulfonyl)-benzoate (13i).**



Chemical Formula: $C_{24}H_{32}O_5S$
Exact Mass: 432.197

Starting with **12a** (0.381 g, 1.5 mmol) and **4i** (0.638 g, 1.7 mmol), **13i** was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish solid (0.485 g, 75%), mp. = 70-71 °C. $^1$H NMR (250 MHZ, $CDCl_3$): δ = 0.81 (t, $^3J$ = 7.8 Hz, 3 H, ($CH_3$), 1.18 – 1.26 (m, 12 H, 6$CH_2$), 1.50 – 1.60 (m, 2 H, $CH_2$), 2.46 (s, 3 H, Ph*CH$_3$*), 2.63 (t, $^3J$ = 7.2 Hz, 2 H, Ph$CH_2$), 3.85 (s, 3 H, $OCH_3$), 7.38 - 7.50 (m, 3 H, 3CH$_{Ar}$), 7.71- 7.75 (m, 2 H, 2CH$_{Ar}$), 8.18 (s, 1 H, CH$_{Ar}$), 11.35 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 14.0, 18.8 ($CH_3$), 22.6, 29.0, 29.2, 29.4, 29.4, 29.5, 29.8, 31.8 ($CH_2$), 52.7 ($OCH_3$), 114.5 (*C*COOCH$_3$), 127.1 (2CH$_{Ar}$), 128.9 (2CH$_{Ar}$), 129.6, 130.4 ($C_{Ar}$), 132.7 (CH$_{Ar}$), 134.8 (CH$_{Ar}$), 139.7, 142.2 ($C_{Ar}$) , 163.5 (COH), 171.6 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 2952 (w), 2922 (m), 2852 (w), 1737 (w), 1663 (m), 1602 (w), 1566 (w), 1441 (m), 1344 (m), 1303 (s), 1247 (m), 1200 (m), 1142 (s), 1086 (s), 1062 (m), 997 (m), 887 (m), 809 (m), 751 (m), 718 (m), 687 (s), 630 (w), 579 (s), 550 (s). GC-MS (EI, 70 eV): *m/z* (%) = 432 ([M]$^+$, 49), 401 (12), 400 (28), 383 (10), 372 (32), 331 (10), 329 (23), 301 (12), 289 (21), 288 (100), 287 (38), 274 (16), 261 (13), 260 (20). HRMS (EI): Calcd. for $C_{24}H_{32}O_5S$ ([M]$^+$): 432.19650; found: 432.196759.

**Methyl 3-decyl-2-hydroxy-6-methyl-5-(phenylsulfonyl)-benzoate (13j).**

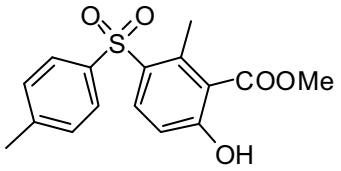


Chemical Formula: $C_{25}H_{34}O_5S$
Exact Mass: 446.21269

Starting with **12a** (0.381 g, 1.5 mmol) and **4j** (0.661 g, 1.7 mmol), **13j** was isolated after chromatography (silica gel, heptanes/EtOAc) as a white solid (0.521 g, 78%), mp. = 94-95 °C. $^1$H NMR (250 MHz, $CDCl_3$) : δ = 0.80 (t, $^3J$ = 6.8 Hz, 3 H, ($CH_3$), 1.15 – 1.26 (m, 14 H, 7$CH_2$), 1.50 – 1.56 (m, 2 H,

$CH_2$), 2.46 (s, 3 H, Ph*CH*$_3$), 2.62 (t, $^3J$ = 7.7 Hz, 2 H, Ph*CH*$_2$), 3.86 (s, 3 H, $OCH_3$), 7.37 - 7.52 (m, 3 H, 3$CH_{Ar}$), 7.69- 7.74 (m, 2 H, 2$CH_{Ar}$), 8.17 (s, 1 H, $CH_{Ar}$), 11.35 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 18.9 ($CH_3$), 22.7, 29.0, 29.3, 29.4, 29.4, 29.5, 29.5, 29.8, 31.8 ($CH_2$), 52.6 ($OCH_3$), 114.7 (*C*$COOCH_3$), 127.2 (2$CH_{Ar}$), 129.0 (2$CH_{Ar}$), 129.6, 130.4 ($C_{Ar}$), 132.7, 134.8 ($CH_{Ar}$), 139.7, 142.2 ($C_{Ar}$) , 163.5 (COH), 171.6 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 2953 (w), 2923 (m), 2853 (w), 1734 (w), 1664 (m), 1602 (w), 1567 (w), 1444 (m), 1344 (w), 1303 (s), 1246 (m), 1201 (m), 1143 (s), 1086 (m), 1063 (w), 998 (w), 906 (m), 811 (w), 763 (w), 722 (s), 688 (s), 648 (w), 581 (s), 558 (s). GC-MS (EI, 70 eV): *m/z* (%) = 446 ([M]$^+$, 46), 415 (12), 414 (26), 386 (12), 378 (18), 331 (39), 330 (10), 329 (28), 318 (14), 302 (14), 301 (15), 289 (25), 288 (100), 287 (44), 275 (13), 274 (19), 261 (19), 260 (20), 234 (25), 233 (17), 206 (21), 187 (14), 147 (11), 121 (11), 43 (10). HRMS (EI): Calcd. for $C_{25}H_{34}O_5S$ ([M]$^+$): 446.21215; found: 446.211947.

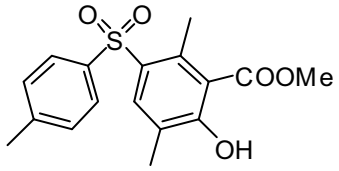
**Methyl 6-hydroxy-2-methyl-3-tosylbenzoate (13k).**



Chemical Formula: $C_{16}H_{16}O_5S$
Exact Mass: 320.07184

Starting with **12b** (0.402 g, 1.5 mmol) and **4a** (0.429 g, 1.7 mmol), **13k** was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish solid (0.274 g, 57%), mp. = 109-110 °C. $^1$H NMR (250 MHz, $CDCl_3$): δ = 2.28 (s, 3 H, Ph*CH*$_3$), 2.47 (s, 3 H, Ph*CH*$_3$), 3.81 (s, 3 H, $OCH_3$), 6.87 (d, $^3J$ = 8.4 Hz, 1 H, $CH_{Ar}$), 7.14 - 7.17 (m, 2 H, 2 $CH_{Ar}$), 7.35 - 7.58 (m, 2 H, 2$CH_{Ar}$), 8.22 (d, $^3J$ = 8.7 Hz, 1H, $CH_{Ar}$), 11.03 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 19.0, 21.5 ($CH_3$), 52.7 ($OCH_3$), 115.1 (*C*$COOCH_3$), 115.6 ($CH_{Ar}$), 127.3 (2$CH_{Ar}$), 129.6 (2$CH_{Ar}$), 131.8 ($C_{Ar}$), 135.2 ($CH_{Ar}$), 138.9, 142.6, 143.8 ($C_{Ar}$), 165.2 (COH), 171.0 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 3072 (w), 3029 (w), 2953 (w), 2922 (w), 2852 (w), 1715 (w), 1673 (m), 1592 (m), 1574 (m), 1495 (w), 1435 (m), 1348 (m), 1300 (m), 1286 (m), 1218 (m), 1188 (m), 1155 (m), 1142 (s), 1109 (m), 1081 (m), 1040 (w), 1018 (w), 997 (m), 939 (m), 848 (w), 815 (m), 759 (w), 709 (m), 692 (m), 649 (m), 597 (w), 587 (m), 565 (m), 549 (m), 533 (s). GC-MS (EI, 70 eV): *m/z* (%) = 320 ([M]$^+$, 34), 289 (27), 288 (100), 271 (23), 269 (18), 256 (9), 255 (48), 224 (16), 223 (20), 222 (17), 181 (10), 152 (11), 149 (12), 121 (12), 105 (10), 91 (19), 77 (22), 65 (20), 51 (14). HRMS (EI): Calcd. for $C_{16}H_{16}O_5S$ ([M]$^+$) : 320.07130; found: 320.071076.

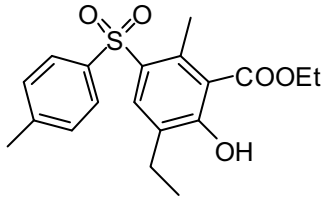
**Methyl 2-hydroxy-3,6-dimethyl-5-tosylbenzoate (13l).**




Chemical Formula: $C_{17}H_{18}O_5S$
Exact Mass: 334.087

Starting with **12b** (0.402 g, 1.5 mmol) and **4b** (0.452 g, 1.7 mmol), **13l** was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish solid (0.327 g, 65%), mp. = 175-177 °C. $^1$HNMR (250 MHz, $CDCl_3$) : δ = 2.23 (s, 3 H, Ph*CH*$_3$), 2.33 (s, 3 H, Ph*CH*$_3$), 2.47 (s, 3 H, Ph*CH*$_3$), 3.81 (s, 3 H, $OCH_3$), 7.18 - 7.21 (m, 2 H, $2CH_{Ar}$), 7.60 - 7.63 (m, 2 H, $2CH_{Ar}$), 8.17 (s, 1H, $CH_{Ar}$), 11.37 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 15.9, 18.8, 21.5 ($CH_3$), 52.7 ($OCH_3$), 114.3 (*C*$COOCH_3$), 124.9 ($C_{Ar}$), 127.2 ($2CH_{Ar}$), 129.5 ($2CH_{Ar}$), 130.8 ($C_{Ar}$), 135.4 ($CH_{Ar}$), 139.2, 139.7, 143.6 ($C_{Ar}$), 163.7 (COH), 171.5 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 3091 (w), 3054 (w), 2963 (w), 2921 (w), 2853 (w), 1667 (m), 1596 (w), 1568 (w), 1496 (w), 1434 (m), 1374 (m), 1337 (m), 1288 (m), 1247 (m), 1198 (m), 1138 (m), 1120 (m), 1088 (m), 1030 (m), 969 (m), 885 (w), 829 (w), 802 (m), 760 (m), 705 (m), 680 (m), 659 (m), 567 (s), 534 (s). GC-MS (EI, 70 eV): *m/z* (%) = 334 ([M]$^+$, 31), 303 (23), 302 (100), 274 (31), 91 (12). HRMS (EI): Calcd. for $C_{17}H_{18}O_5S$ ([M]$^+$): 334.08695; found: 334.087082.

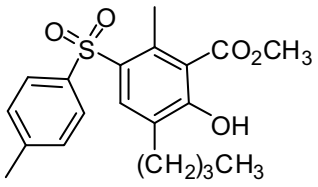
**Ethyl 3-ethyl-2-hydroxy-6-methyl-5-tosylbenzoate (13m).**




Chemical Formula: $C_{19}H_{22}O_5S$
Exact Mass: 362.119

Starting with **12b** (0.402 g, 1.5 mmol) and **4c** (0.500 g, 1.7 mmol), **13m** was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish solid (0.250 g, 46%), mp. = 112-114 °C. $^1$H NMR (250 MHz, $CDCl_3$): δ = 1.13 (t, $^3J$ = 7.3 Hz, 3H, $CH_2$*CH*$_3$), 1.24 (t, $^3J$ = 7.2 Hz, 3H, $OCH_2$*CH*$_3$), 2.28 (s, 3 H, Ph*CH*$_3$), 2.43 (s, 3 H, Ph*CH*$_3$), 2.59 (q, $^3J$ = 7.5 Hz, 2H, *CH*$_2$$CH_3$), 4.27 (q, $^3J$ = 7.2 Hz, 2H, O*CH*$_2$$CH_3$), 7.13 - 7.17 (m, 2 H, $2CH_{Ar}$), 7.55 - 7.58 (m, 2 H, $2CH_{Ar}$), 8.12 (s, 1H, $CH_{Ar}$), 11.38 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 15.8, 15.9, 18.8, 21.5 ($CH_3$), 23.0 ($CH_2$), 62.4 ($OCH_2$), 114.3 (*C*$COOCH_3$), 124.9 ($C_{Ar}$), 127.2 ($2CH_{Ar}$), 129.5 ($2CH_{Ar}$), 130.8 ($C_{Ar}$), 135.4 ($CH_{Ar}$), 139.2, 139.7, 143.6 ($C_{Ar}$), 163.7 (COH), 171.5 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 3078 (w), 2968 (w), 2927 (w), 2872 (w), 1650 (m), 1597 (w), 1556 (w), 1496 (w), 1450 (w), 1417 (m), 1372 (m), 1334 (m), 1287 (m), 1243 (m), 1180 (m), 1141 (m), 1087 (m), 1055 (m), 1017 (m), 973 (m), 925 (w), 867 (w), 842 (w), 815 (m), 785 (m), 705 (m), 678 (m), 663 (m), 569 (m), 545 (m). GC-MS (EI, 70 eV): *m/z* (%) = 362 ([M]$^+$, 36), 317 (31), 316 (96), 290 (10), 289 (19), 288 (100), 91 (25), 77 (13), 57 (33), 289 (19), 41 (10). HRMS (EI): Calcd. for $C_{19}H_{22}O_5S_1$ ([M]$^+$) : 362.11825; found: 362.117378.

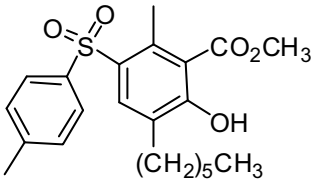
**Methyl 3-butyl-2-hydroxy-6-methyl-5-tosylbenzoate (4n).**



Chemical Formula: $C_{20}H_{24}O_5S$
Exact Mass: 376.134

Starting with **12b** (0.402 g, 1.5 mmol) and **4d** (0.522 g, 1.7 mmol), **13n** was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish solid (0.367 g, 65%), mp. = 95-96 °C. $^1$HNMR (300 MHz, $CDCl_3$): δ = 0.83 (t, $^3J$ = 7.4 Hz, 3H,$CH_3$), 1.21-1.33 (m, 2H, $2CH_2$), 1.44-1.52 (m, 2 H, $CH_2$), 2.27 (s, 3H, Ph*CH*$_3$), 2.41 (s, 3H, Ph*CH*$_3$), 2.57 (t, $^3J$ = 7.5 Hz, 2H, Ph*CH*$_2$), 3.89 (s, 3H, $OCH_3$), 7.13 - 7.17 (m, 2 H, $2CH_{Ar}$), 7.53 - 7.57 (m, 2 H, $2CH_{Ar}$), 8.10 (s, 1H, $CH_{Ar}$), 11.12 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 18.9, 21.5 ($CH_3$), 22.5, 29.6 31.2 ($CH_2$), 52.7 ($OCH_3$), 114.5 (*C*$COOCH_3$), 127.2 ($2CH_{Ar}$), 129.4 ($C_{Ar}$), 129.6 ($2CH_{Ar}$), 130.8 ($C_{Ar}$), 134.7 ($CH_{Ar}$), 139.2, 139.5, 143.6 ($C_{Ar}$), 163.3 (COH), 171.6 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 3068 (w), 2932 (w), 2875 (w), 1665 (m), 1595 (w), 1566 (w), 1495 (w), 1439 (m), 1377 (w), 1349 (m), 1299 (m), 1246 (m), 1200 (m), 1161 (m), 1138 (s), 1086 (m), 1002 (w), 980 (m), 946 (w), 884 (w), 832 (w), 808 (m), 761 (m), 730 (m), 705 (m), 684 (m), 664 (m), 629 (m), 573 (s), 555 (s), 532 (s). GC-MS (EI, 70 eV): *m/z* (%) = 377 (12), 376 ([M]$^+$, 49), 344 (16), 327 (12), 317 (19), 316 (87), 315 (16), 303 (19), 302 (100), 301 (23), 274 (32), 188 (11), 91 (14). HRMS (EI): Calcd. for $C_{20}H_{24}O_5S_1$ ([M]$^+$) : 376.13390; found: 376.133616.

**Methyl 3-hexyl-2-hydroxy-6-methyl-5-tosylbenzoate (13o).**

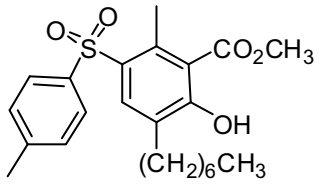


Chemical Formula: $C_{22}H_{28}O_5S$
Exact Mass: 404.166

Starting with **12b** (0.402 g, 1.5 mmol) and **4f** (0.568 g, 1.7 mmol), **13o** was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish solid (0.370 g, 61%), mp. = 95-97 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ = 0.83(t, $^3J$ = 7.1 Hz, 3H,$CH_3$), 1.21-1.32 (m, 6H, $3CH_2$), 1.49-1.56 (m, 2 H, $CH_2$), 2.33 (s, 3H, Ph*CH*$_3$), 2.46 (s, 3H, Ph*CH*$_3$), 2.62 (t, $^3J$ = 7.4 Hz, 2H, Ph*CH*$_2$), 3.85 (s, 3H, $OCH_3$), 7.19 - 7.21 (m, 2 H, $2CH_{Ar}$), 7.59 - 7.62 (m, 2 H, $2CH_{Ar}$), 8.16 (s, 1H, $CH_{Ar}$), 11.21 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 14.0, 18.8, 21.5 ($CH_3$), 22.6, 29.0, 29.1, 29.8, 31.6 ($CH_2$), 52.6 ($OCH_3$), 114.5 (*C*$COOCH_3$), 127.2 ($2CH_{Ar}$), 129.5 ($C_{Ar}$), 129.6 ($2CH_{Ar}$), 130.8 ($C_{Ar}$), 134.79 ($CH_{Ar}$), 139.2, 139.6, 143.6 ($C_{Ar}$), 163.3 (COH), 171.6 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 3086 (w), 2954 (w), 2925 (w), 2859 (w), 1660 (m), 1596 (w), 1564 (w), 1495 (w), 1434 (m), 1369 (w), 1335 (m), 1300 (m), 1289 (m), 1243 (m), 1220 (m), 1189 (m), 1138 (s), 1086 (m), 1062 (m), 997 (w), 970 (m), 885 (w), 837 (w), 814 (m), 760 (m), 705 (m), 681 (m), 656 (m), 574 (s), 550 (m), 534 (s). GC-MS (EI, 70 eV):

*m/z* (%) = 405 (13), 404 ([M]$^+$, 51), 373 (11), 372 (23), 355 (12), 345 (14), 344 (62), 343 (17), 316 (10), 315 (15), 303 (21), 302 (100), 301 (29), 274 (29), 91 (13). HRMS (EI): Calcd. for $C_{22}H_{28}O_5S_1$ ([M]$^+$) : 404.16250; found: 404.165338.

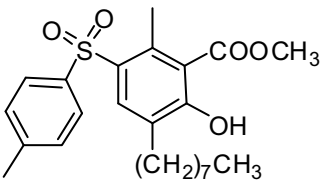
**Methyl 3-heptyl-2-hydroxy-6-methyl-5-tosylbenzoate (13p).**




Chemical Formula: $C_{23}H_{30}O_5S$
Exact Mass: 418.181

Starting with **12b** (0.268 g, 1.0 mmol) and **4g** (0.395 g, 1.1 mmol), **13p** was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish solid (0.251 g, 60%), mp. = 67-69 °C. $^1$HNMR (250 MHz, $CDCl_3$) : δ = 0.83 (t, $^3J$ = 7.03 Hz, 3H, $CH_3$ ), 1.19–1.28 (m, 8 H, 4$CH_2$), 1.54–1.60 (m, 2 H, $CH_2$), 2.34 (s, 3 H, Ph*CH*$_3$ ), 2.48 (s, 3 H, Ph*CH*$_3$), 2.64 (t, $^3J$ = 7.5 Hz, 2 H, Ph*CH*$_2$), 3.86 (s, 3 H, $OCH_3$ ), 7.22 (d, $^3J$ = 6.0 Hz, 2 H, 2$CH_{Ar}$), 7.62 (d, $^3J$ = 9.0 Hz, 2 H, 2$CH_{Ar}$), 8.17 (s, 1 H, $CH_{Ar}$), 11.33 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 14.1, 18.9, 21.5 ($CH_3$), 22.6, 29.1, 29.2, 29.4, 29.9, 31.8 ($CH_2$), 52.7 ($OCH_3$), 114.6 (*C*$COOCH_3$), 127.2 (2$CH_{Ar}$), 129.5 ($C_{Ar}$), 129.6 (2$CH_{Ar}$), 130.8 ($C_{Ar}$), 134.8 ($CH_{Ar}$), 139.2, 139.6, 143.7 ($C_{Ar}$), 163.4 (COH), 171.7 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 2954(w), 2925 (w), 2855 (w), 2256 (w), 1737 (w), 1665 (m), 1599 (w), 1567 (w), 1494 (w), 1439 (m), 1345 (w), 1311 (m), 1301 (m), 1288 (m), 1247 (w), 1201 (m), 1160 (m), 1142 (s), 1087 (m), 1063 (w), 1000 (w), 907 (m), 811 (m), 728 (s), 706 (m), 682 (m), 659 (m), 649 (m), 574 (s), 537 (m). GC-MS (EI, 70 eV): *m/z* (%) = 418 ([M$^+$], 90), 386 (32), 358 (82), 343 (25), 315 (20), 302 (100), 288 (15), 274 (34), 230 (8), 188 (8), 165 (8), 139 (11), 121 (6), 91 (21), 77 (9), 43 (10). HRMS (EI): Calcd. for $C_{23}H_{30}O_5S$ ([M]$^+$): 418.18085; found: 418.180657.

**Methyl 2-hydroxy-6-methyl-3-octyl-5-tosylbenzoate (13q).**

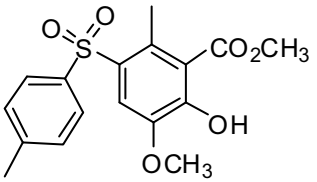



Chemical Formula: $C_{24}H_{32}O_5S$
Exact Mass: 432.197

Starting with **12b** (0.402 g, 1.5 mmol) and **4h** (0.614 g, 1.7 mmol), **13q** was isolated after chromatography (silica gel, heptanes/EtOAc) as a white solid (0.383 g, 59%), mp. = 79-81 °C. $^1$HNMR (300 MHz, $CDCl_3$): δ = 0.76 (t, $^3J$ = 7.4 Hz, 3H,$CH_3$), 1.14-1.26 (m, 10H, 5$CH_2$), 1.45-1.56 (m, 2 H, $CH_2$), 2.27 (s, 3H, Ph*CH*$_3$), 2.41 (s, 3H, Ph*CH*$_3$), 2.56 (t, $^3J$ = 7.6 Hz, 2H, Ph*CH*$_2$), 3.92 (s, 3H, $OCH_3$), 7.13 - 7.16 (m, 2 H, 2$CH_{Ar}$), 7.52 - 7.58 (m, 2 H, 2$CH_{Ar}$), 8.13 (s, 1H, $CH_{Ar}$), 11.22 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 14.1 18.8, 21.5 ($CH_3$), 22.6, 29.1, 29.2, 29.4, 29.4, 29.8, 31.8 ($CH_2$), 52.6 ($OCH_3$), 114.5 (*C*$COOCH_3$),

127.2 ($2CH_{Ar}$), 129.5 ($C_{Ar}$), 129.6 ($2CH_{Ar}$), 130.8 ($C_{Ar}$), 134.8 ($CH_{Ar}$), 139.2, 139.5, 143.6 ($C_{Ar}$), 163.3 (COH), 171.6 (CO). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ = 3077 (w), 2921 (m), 2851 (m), 1659 (m), 1597 (m), 1495 (w), 1438 (m), 1385 (w), 1348 (m), 1298 (s), 1247 (m), 1199 (s), 1142 (s), 1086 (s), 999 (m), 892 (w), 835 (w), 811 (s), 759 (m), 707 (m), 682 (s), 625 (m), 573 (s), 538 (s). GC-MS (EI, 70 eV): *m/z* (%) = 433 (17), 432 ($[M]^+$, 60), 401 (13), 400 (25), 383 (12), 373 (14), 372 (56), 343 (21), 316 (20), 315 (15), 303 (23), 302 (100), 301 (40), 288 (17), 275 (13), 274 (25), 91 (14). HRMS (EI): Calcd. for $C_{24}H_{32}O_5S_1$ ($[M]^+$) : 432.19650; found: 432.196903.

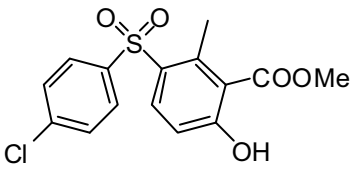
**Methyl 2-hydroxy-3-methoxy-6-methyl-5-tosylbenzoate (13r).**




Chemical Formula: $C_{17}H_{18}O_6S$
Exact Mass: 350.082

Starting with **12b** (0.402 g, 1.5 mmol) and **4k** (0.479 g, 1.7 mmol), **13r** was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish solid (0.221 g, 42%), mp. = 179-181 °C. $^1$H NMR (250 MHz, $CDCl_3$): δ = 2.30 (s, 3H, Ph*CH*$_3$), 2.33 (s, 3H, Ph*CH*$_3$), 3.84 (s, 3H, $OCH_3$), 3.93 (s, 3H, $CO_2$*CH*$_3$), 7.19-7.23 (m, 2 H, $2CH_{Ar}$), 7.60 - 7.63 (m, 2 H, $2CH_{Ar}$), 7.86 (s, 1H, $CH_{Ar}$), 9.36 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 17.4, 21.5 ($CH_3$), 52.7 (COO*C*H$_3$), 56.6 ($OCH_3$), 114.4 ($CH_{Ar}$), 118.4 (*C*COOCH$_3$), 127.30 ($2CH_{Ar}$), 129.6 ($2CH_{Ar}$), 130.80, 131.6, 138.8, 143.8, 145.6 ($C_{Ar}$), 152.4 (COH), 169.52 (CO). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ = 3411 (w), 3090 (w), 2946 (w), 2845 (w), 1709 (m), 1580 (w), 1483 (m), 1440 (m), 1345 (w), 1289 (m), 1203 (m), 1138 (m), 1089 (m), 1069 (m), 1018 (w), 993 (w), 973 (w), 894 (w), 878 (w), 824 (m), 783 (w), 749 (w), 705 (w), 672 (m), 643 (w), 625 (w), 575 (m), 556 (m). GC-MS (EI, 70 eV): *m/z* (%) = 350 ($[M]^+$, 50), 320 (11), 319 (40), 318 (100), 290 (45), 289 (11), 288 (11). HRMS (EI): Calcd. for $C_{17}H_{18}O_6S$ ($[M]^+$): 350.08186; found: 350.081087.

**Methyl 3-(4-chlorophenylsulfonyl)-6-hydroxy-2-methylbenzoate (13s).**

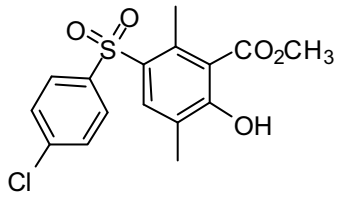



Chemical Formula: $C_{15}H_{13}ClO_5S$
Exact Mass: 340.017

Starting with **12c** (0.433 g, 1.5 mmol) and **4a** (0.429 g, 1.7 mmol), **13s** was isolated after chromatography (silica gel, heptanes/EtOAc) as a white solid (0.240 g, 47%), mp. = 126-127 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ = 2.46 (s, 3 H, Ph*CH*$_3$), 3.82 (s, 3 H, $OCH_3$), 6.90 (d, $^3J$ = 7.5 Hz, 1 H, $CH_{Ar}$), 7.33 - 7.35 (m, 2 H, $2CH_{Ar}$), 7.60 - 7.63 (m, 2 H, 2CH $_{Ar}$), 8.23 (d, $^3J$ = 7.5 Hz, 1H, $CH_{Ar}$), 11.11 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 19.2 ($CH_3$), 52.9 ($OCH_3$), 115.2 (*C*COOCH$_3$), 116.0 ($CH_{Ar}$), 128.7 ($2CH_{Ar}$), 129.4 ($2CH_{Ar}$), 131.0 ($C_{Ar}$), 135.3 ($CH_{Ar}$), 139.5, 140.4, 142.7 ($C_{Ar}$), 165.5 (COH), 171.0 (CO). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ = 3078 (w), 3024 (w), 2956

(w), 2848 (w), 2789 (w), 1673 (m), 1578 (m), 1503 (w), 1478 (w), 1435 (m), 1351 (m), 1309 (s), 1292 (m), 1223 (m), 1191 (m), 1158 (m), 1145 (s), 1109 (m), 1080 (s), 1031 (m), 995 (m), 936 (m), 848 (w), 830 (m), 763 (m), 708 (m), 685 (m), 620 (s), 564 (m), 548 (s). GC-MS (EI, 70 eV): *m/z* (%) = 342 ([$M^+$], $^{37}$Cl, 10), 340 ([$M^+$], $^{35}$Cl, 25), 310 (40), 309 (24), 308 (100), 291 (16), 289 (12), 275 (11), 255 (28), 243 (10), 242 (11), 152 (14), 149 (10), 121 (13), 111 (14), 105 (22), 77 (24), 76 (13), 75 (16), 51(17). HRMS (EI): Calcd. for $C_{15}H_{13}O_5ClS$ ([$M]^+$): 340.01667; found: 340.017220.

**Methyl 3-(4-chlorophenylsulfonyl)-6-hydroxy-2,5-dimethylbenzoate (13t).**

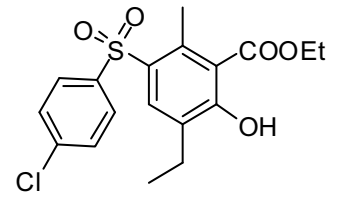


Chemical Formula: $C_{16}H_{15}ClO_5S$
Exact Mass: 354.033

Starting with **12c** (0.433 g, 1.5 mmol) and **4b** (0.452 g, 1.7 mmol), **13t** was isolated after chromatography (silica gel, heptanes/EtOAc) as a white solid (0.255 g, 48%), mp. = 180-182 °C. $^1$H NMR (250 MHz, $CDCl_3$): δ = 2.24 (s, 3 H, Ph*CH*$_3$), 2.46 (s, 3 H, Ph*CH*$_3$), 3.86 (s, 3H, $OCH_3$), 7.35-7.41 (m, 2 H, $2CH_{Ar}$), 7.64-7.70 (m, 2 H, $2CH_{Ar}$), 8.16 (s, 1H, $CH_{Ar}$), 11.38 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 15.9, 18.9 ($CH_3$), 52.8 ($OCH_3$), 114.43 (*C*$COOCH_3$), 125.30 ($C_{Ar}$), 128.68 ($2CH_{Ar}$), 129.32 ($2CH_{Ar}$), 129.94 ($C_{Ar}$), 135.45 ($CH_{Ar}$), 139.37, 139.79, 140.69 ($C_{Ar}$), 164.04 (COH), 171.48 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 3099 (w), 2969 (w), 2872 (w), 1665 (m), 1602 (w), 1580 (w), 1471 (w), 1415 (m), 1393 (m), 1370 (m), 1304 (m), 1280 (m), 1244 (m), 1202 (m), 1176 (m), 1145 (s), 1086 (s), 1011 (m), 931 (w), 843 (m), 825 (m), 802 (m), 787 (m), 765 (m), 749 (m), 707 (m), 670 (w), 650 (m), 634 (m), 591 (s), 561 (s), 534 (m). GC-MS (EI, 70 eV): *m/z* (%) = 356 (17), 354 ([$M]^+$, 51), 325 (11), 324 (78), 323 (36), 322 (100), 296 (12), 294 (39), 91 (10).

HRMS (EI): Calcd. for $C_{16}H_{15}O_5ClS$ ([$M]^+$): 354.03232; found: 354.031731.

**Ethyl 3-(4-chlorophenylsulfonyl)-5-ethyl-6-hydroxy-2-methylbenzoate (13u).**

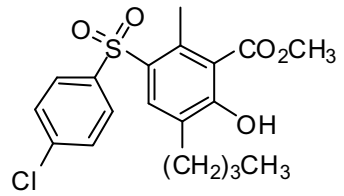


Chemical Formula: $C_{18}H_{19}ClO_5S$
Exact Mass: 382.064

Starting with **12c** (0.433 g, 1.5 mmol) and **4c** (0.500 g, 1.7 mmol), **13u** was isolated after chromatography (silica gel, heptanes/EtOAc) as a white Solid (0.269 g, 47%), mp. = 144-146 °C. $^1$H NMR (250 MHz, $CDCl_3$): δ = 1.19 (t, $^3J$ = 7.5 Hz, 3 H, $CH_2CH_3$), 1.31 (t, $^3J$ = 7.1 Hz, 3 H, $OCH_2CH_3$), 2.48 (s, 3 H, Ph*CH*$_3$), 2.66 (q, $^3J$ = 7.6 Hz, 2 H, *CH*$_2$CH$_3$), 4.35 (q, $^3J$ = 7.1 Hz, 2 H, O*CH*$_2$CH$_3$), 7.36 - 7.42 (m, 2 H, $2CH_{Ar}$), 7.65 - 7.70 (m, 2 H, $2CH_{Ar}$), 8.16 (s, 1 H, $CH_{Ar}$), 11.51 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 12.3, 13.3, 17.9 ($CH_3$),

22.0, 61.5 ($CH_2$), 113.7 (*C*$COOCH_3$), 127.6 ($2CH_{Ar}$), 128.3 ($2CH_{Ar}$), 129.0, 130.6 ($C_{Ar}$), 132.9 ($CH_{Ar}$), 138.3, 138.7, 139.7 ($C_{Ar}$), 162.8 (COH), 170.0 (CO). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ = 3100 (w), 2968 (w), 2872 (w), 1666 (m), 1603 (w), 1564 (w), 1471 (w), 1416 (w), 1393 (m), 1370 (m), 1304 (m), 1280 (m), 1254 (m), 1203 (m), 1177 (m), 1145 (s), 1085 (s), 1010 (m), 931 (w), 866 (w), 787 (m), 756 (m), 707 (m), 652 (m), 591 (s), 561 (s). GC-MS (EI, 70 eV): *m/z* (%) = 384 (16), 382 ([M]$^+$, 46), 339 (10), 338 (52), 337 (31), 336 (100), 310 (43), 309 (16), 308 (94). HRMS (EI): Calcd. for $C_{18}H_{19}O_5ClS$ ([M]$^+$): 382.06362; found: 382. 063783.

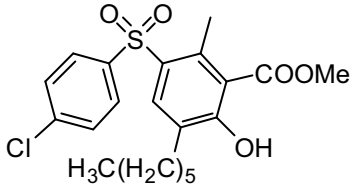
**Methyl 3-(4-chlorophenylsulfonyl)-5-butyl-6-hydroxy-2-methylbenzoate (13v).**



Chemical Formula: $C_{19}H_{21}ClO_5S$
Exact Mass: 396.080

Starting with **12c** (0.433g, 1.5mmol ) and **4d** (0.522g, 1.7 mmol ), **13v** was isolated after chromatography (silica gel, heptanes/EtOAc) as a white solid (0.321 g, 54%), mp. = 88 – 90 °C. $^1$H NMR (250 MHz, $CDCl_3$): δ = 0.81 (t, $^3J$ = 6.9 Hz, 3 H, $CH_3$), 1.18–1.33 (m, 2 H, $CH_2$), 1.42–1.54 (m, 2 H, $CH_2$), 2.39 (s, 3 H, Ph*CH*$_3$), 2.56 (t, $^3J$ = 8.1 Hz, 2 H, Ph*CH*$_2$), 3.79 (s, 3 H, $OCH_3$), 7.21 – 7.42 (m, 2 H, $2CH_{Ar}$), 7.52 – 7.67 (m, 2 H, $2CH_{Ar}$), 8.08 (s, 1 H, $CH_{Ar}$), 11.31 (s, 1 H, OH ). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 18.9 ($CH_3$), 22.5, 29.6, 31.2 ($CH_2$), 52.8 ($OCH_3$), 114.7 (*C*$COOCH_3$), 128.7 ($2CH_{Ar}$), 129.3 ($2CH_{Ar}$), 129.8, 130.0 ($C_{Ar}$), 134.8 ($CH_{Ar}$), 139.4, 139.7, 140.7 ($C_{Ar}$), 163.8 (COH), 171.5 (CO). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ = 2956 (w), 2929 (w), 2860 (w), 2257 (w), 1737 (w), 1665 (m), 1602 (w), 1572 (w), 1477 (w), 1439 (m), 1394 (w), 1346 (m), 1310 (m), 1294 (m), 1278 (m), 1245 (w), 1201 (m), 1162 (m), 1144 (s), 1086 (s), 1064 (w), 1014 (w), 1002 (w), 906 (m), 827 (m), 764 (m), 728 (s), 707 (m), 678 (w), 649 (m), 597 (s), 565 (s). GC-MS (EI, 70 eV): *m/z* (%) = 398 ([M$^+$], $^{37}$Cl, 13), 396 ([M$^+$], $^{35}$Cl, 35), 364 (18), 336 (53), 322 (100), 294 (28), 220 (3), 188 (15), 165 (5), 116 (3), 91 (5), 77 (5), 57 (4), 43 (5). HRMS (EI): Calcd. for $C_{19}H_{21}O_5ClS$ ([M]$^+$, $^{35}$Cl): 396.07927; found: 396.079088.

**Methyl 3-(4-chlorophenylsulfonyl)-5-hexyl-6-hydroxy-2-methylbenzoate (13w).**

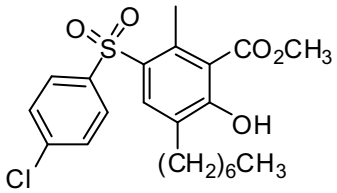


Chemical Formula: $C_{21}H_{25}ClO_5S$
Exact Mass: 424.111

Starting with **12c** (0.288 g, 1.0 mmol) and **4f** (0.379 g, 1.1 mmol), **13w** was isolated after chromatography (silica gel, heptanes/EtOAc) as a white solid (0.212 g, 50%), mp. = 91-93 °C. $^1$H NMR (250 MHz, $CDCl_3$): δ = 0.83 (t, $^3J$ = 7.0 Hz, 3 H, $CH_3$), 1.21 – 1.31 (m, 6 H, $3CH_2$), 1.53 – 1.57 (m, 2 H, $CH_2$), 2.46 (s, 3 H, Ph*CH*$_3$), 2.63 (t, $^3J$ = 7.4 Hz, 2

H, Ph$CH_2$), 3.87 (s, 3 H, $OCH_3$), 7.36 - 7.42 (m, 2 H, $2CH_{Ar}$), 7.46 - 7.70 (m, 2 H, $2CH_{Ar}$), 8.15 (s, 1H, $CH_{Ar}$), 11.40 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 14.0, 18.9 ($CH_3$), 22.6, 29.0, 29.1, 29.8, 31.6 ($CH_2$), 52.7 ($OCH_3$), 114.3 (*C*$COOCH_3$), 128.6 ($2CH_{Ar}$), 129.3 ($2CH_{Ar}$), 129.8, 130.0 ($C_{Ar}$), 134.8 ($CH_{Ar}$), 139.3, 139.6, 140.7 ($C_{Ar}$), 163.7 (COH), 171.5 (CO). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ = 3076 (w), 2954 (w), 2923 (w), 2858 (w), 1660 (m), 1564 (w), 1503 (w), 1479 (w), 1430 (m), 1414 (m), 1395 (m), 1336 (m), 1277 (m), 1243 (m), 1199 (m), 1158 (m), 1139 (s), 1086 (m), 1064 (m), 1011 (m), 970 (m), 885 (w), 828 (m), 807 (m), 764 (m), 705 (m), 653 (m), 641 (m), 600 (m), 563 (s), 547 (m). GC-MS (EI, 70 eV): *m/z* (%) = 426 ([$M^+$], $^{37}$Cl, 25), 424 ([$M^+$], $^{35}$Cl, 73), 394 (14), 392 (35), 375 (15), 366 (16), 365 (17), 364 (47), 363 (25), 336 (12), 335 (18), 324 (61), 323 (45), 322 (100), 321 (44), 296 (14), 294 (40). HRMS (EI): Calcd. for $C_{21}H_{25}O_5ClS$ ([$M]^+$, $^{35}$Cl): 424.11057; found: 424.109531.

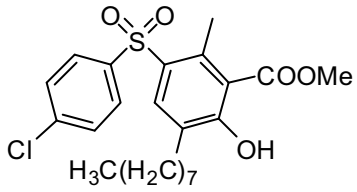
**Methyl 3-(4-chlorophenylsulfonyl)-5-heptyl-6-hydroxy-2-methylbenzoate (13x).**



Chemical Formula: $C_{22}H_{27}ClO_5S$
Exact Mass: 438.127

Starting with **12c** (0.433 g, 1.5 mmol) and **4g** (0.591 g, 1.7 mmol), **13x** was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish oil (0.335 g, 51%). $^1$H NMR (250 MHz, $CDCl_3$): δ = 0.82 (t, $^3J$ = 7.3 Hz, 3H, $CH_3$), 1.18-1.28 (m, 8H, $4CH_2$), 1.51-1.59 (m, 2 H, $CH_2$), 2.46 (s, 3H, Ph$CH_3$), 2.62 (t, $^3J$ = 7.5 Hz, 2H, Ph$CH_2$), 3.84 (s, 3H, $OCH_3$), 7.37 - 7.40 (m, 2 H, $2CH_{Ar}$), 7.65 - 7.68 (m, 2 H, $2CH_{Ar}$), 8.15 (s, 1H, $CH_{Ar}$), 11.38 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.0, 17.9 ($CH_3$), 21.6, 28.0, 28.1, 28.4, 28.9, 30.8 ($CH_2$), 51.8($OCH_3$), 113.6 (*C*$COOCH_3$), 127.6 ($2CH_{Ar}$), 128.3 ($2CH_{Ar}$), 128.8, 129.0 ($C_{Ar}$), 133.8 ($CH_{Ar}$), 138.3, 138.7, 139.7 ($C_{Ar}$), 162.7 (COH), 170.5 (CO). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ = 2954 (w), 2926 (m), 2855 (w), 2257 (w), 1737 (w), 1666 (m), 1602 (w), 1572 (w), 1477 (w), 1439 (w), 1346 (w), 1314 (m), 1247 (w), 1202 (m), 1146 (m), 1088 (m), 1013 (w), 908 (m), 826 (w), 732 (s), 678 (w), 598 (m), 565 (w). GC-MS (EI, 70 eV): *m/z* (%) = 440 (18), 439 (11), 438 ([$M]^+$, 46), 408 (14), 407 (14), 406 (31), 389 (13), 380 (13), 379 (10), 378 (35), 365 (11), 364 (10), 363 (27), 336 (11), 335 (14), 324 (37), 323 (31), 322 (100), 321 (33), 308 (12), 296 (14), 295 (12), 294 (31), 288 (11), 231 (10), 230 (11), 111 (11), 97 (13), 85 (12), 83 (13), 71 (17), 69 (17), 59 (15), 57 (24), 55 (16). HRMS (EI): Calcd. for $C_{22}H_{27}Cl\ O_5S$ ([$M]^+$): 438.12622; found: 438.126117.

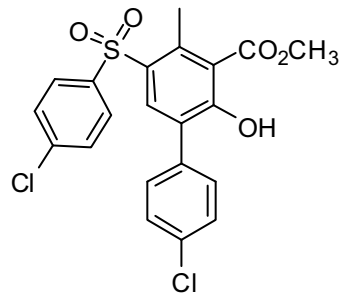
**Methyl 3-(4-chlorophenylsulfonyl)-6-hydroxy-2-methyl-5-octylbenzoate (13y).**




Chemical Formula: $C_{23}H_{29}ClO_5S$
Exact Mass: 452.142

Starting with **12c** (0.288 g, 1.0 mmol) and **4h** (0.409 g, 1.1 mmol), **13y** was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish solid (0.235 g, 52%), mp. = 82-82 °C. $^1$H NMR (250 MHz, $CDCl_3$): δ = 0.81 (t, $^3J$ = 6.8 Hz, 3 H, $CH_3$), 1.16 – 1.25 (m, 10 H, $5CH_2$), 1.50 – 1.55 (m, 2 H, $CH_2$), 2.46 (s, 3 H, $PhCH_3$), 2.62 (t, $^3J$ = 7.6 Hz, 2 H, $PhCH_2$), 3.86 (s, 3 H, $OCH_3$), 7.36 - 7.41 (m, 2 H, $2CH_{Ar}$), 7.63 - 7.69 (m, 2 H, $2CH_{Ar}$), 8.15 (s, 1H, $CH_{Ar}$), 11.39 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.0, 17.9 ($CH_3$), 21.6, 28.0, 28.2, 28.4, 28.5, 28.8, 30.8 ($CH_2$), 51.7 ($OCH_3$), 113.6 (*C*$COOCH_3$), 127.6 ($2CH_{Ar}$), 128.3 ($2CH_{Ar}$), 128.8, 129.0 ($C_{Ar}$), 133.7 ($CH_{Ar}$), 138.3, 138.6, 139.7 ($C_{Ar}$) , 162.7 (COH), 170.5 (CO). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ = 2953 (w), 2923 (m), 2853 (w), 1663 (m), 1568 (w), 1476 (w), 1436 (m), 1393 (w), 1345 (m), 1312 (m), 1293 (m), 1246 (m), 1200 (m), 1143 (s), 1085 (s), 1062 (m), 1012 (m), 1000 (m), 920 (w), 887 (w), 810 (m), 762 (m), 749 (m), 676 (w), 651 (m), 641 (w), 595 (s), 563 (s). GC-MS (EI, 70 eV): *m/z* (%) = 454 ([$M^+$], $^{37}$Cl, 23), 452 ([$M^+$], $^{35}$Cl, 68), 422 (13), 420 (30), 403 (11), 394 (10), 392 (28), 363 (23), 335 (13), 324 (44), 322 (100), 308 (15). HRMS (EI): Calcd. for $C_{23}H_{29}O_5ClS$ ([M]$^+$, $^{35}$Cl): 452.14187; found: 452.141122.

**Methyl 4'-chloro-5-(4-chlorophenylsulfonyl)-2-hydroxy-4-methylbiphenyl-3-carboxylate (13z).**

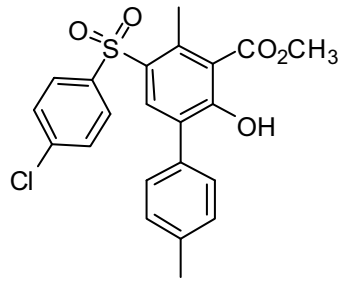



Chemical Formula: $C_{21}H_{16}Cl_2O_5S$
Exact Mass: 450.010

Starting with **12c** (0.433 g, 1.5 mmol) and **4i** (0.612 g, 1.7 mmol), **13z** was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellow solid (0.325 g, 48%), mp. = 178-180 °C. $^1$HNMR (250 MHz, $CDCl_3$): δ = 2.53 (s, 3 H, Ph*CH*$_3$), 3.90 (s, 3 H, $OCH_3$), 7.33–7.48 (m, 6 H, $6CH_{Ar}$), 7.54–7.82 (m, 2 H, $2CH_{Ar}$), 8.35 (s, 1 H, $CH_{Ar}$), 11.55 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 19.1 ($CH_3$), 53.1 ($OCH_3$), 115.9 (*C*$COOCH_3$), 127.6 ($C_{Ar}$), 128.6 ($2CH_{Ar}$), 128.8 ($2CH_{Ar}$), 129.5 ($2CH_{Ar}$), 130.7 ($2CH_{Ar}$), 130.9, 131.1, 134.1 ($C_{Ar}$), 135.4 ($CH_{Ar}$), 139.7, 140.3, 141.6 ($C_{Ar}$), 162.4 (COH), 171.3 (CO). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ = 3070 (w), 3004 (w), 2955 (w), 2929 (w), 2852 (w), 2256 (w), 1741 (w), 1723 (w), 1665 (m), 1583 (w), 1552 (w), 1492 (w), 1477 (w), 1434 (m), 1393 (m), 1311 (m), 1279 (w), 1206 (m), 1178 (m), 1148 (m), 1090 (m), 1042 (w), 1014 (m), 956 (w), 907 (m), 870 (w), 831 (m), 785 (w), 763 (m), 729 (s), 709 (m), 648 (m), 630 (w), 596 (m), 563 (m). GC-MS (EI, 70

eV): *m/z* (%) = 452 ([$M^+$], $^{37}$Cl, 9), 450 ([$M^+$], $^{35}$Cl, 12), 422 (10), 421 (14), 420 (66), 419 (23), 418 (100), 384 (2), 291 (3), 214 (12), 186 (13), 152 (26), 139 (12), 111 (11), 86 (12), 67 (15), 43 (27). HRMS (EI): Calcd. for $C_{21}H_{16}O_5Cl_2S$ ([$M]^+$, $^{35}$Cl): 450.00900; found: 450.008249.

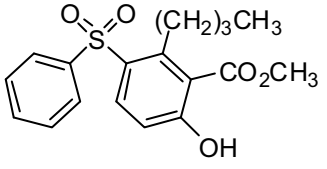
**Methyl 5-(4-chlorophenylsulfonyl)-2-hydroxy-4,4'-dimethylbiphenyl-3-carboxylate (13aa).**




Chemical Formula: $C_{22}H_{19}ClO_5S$
Exact Mass: 430.064

Starting with **12c** (0.433 g, 1.5 mmol) and **4m** (0.578 g, 1.7 mmol), **13aa** was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellow solid (0.342 g, 53%), mp. = 186-189 °C. $^1$H NMR (250 MHz, $CDCl_3$): δ = 2.34 (s, 3 H, Ph*CH*$_3$), 2.52 (s, 3 H, Ph*CH*$_3$), 3.89 (s, 3 H, $OCH_3$), 7.18-7.22 (m, 2 H, $2CH_{Ar}$), 7.37–7.40 (m, 2 H, $2CH_{Ar}$), 7.41–7.42 (m, 2 H, $2CH_{Ar}$), 7.62–7.73 (m, 2 H, $2CH_{Ar}$), 8.35 (s, 1 H, $CH_{Ar}$), 11.19 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 19.0, 21.3 ($CH_3$), 53.0 ($OCH_3$), 116.2 (*C*$COOCH_3$), 128.7 ($C_{Ar}$), 128.9 ($2CH_{Ar}$), 129.2 ($2CH_{Ar}$), 129.3 ($2CH_{Ar}$), 129.4 ($2CH_{Ar}$), 130.9, 132.6 ($C_{Ar}$), 135.4 ($CH_{Ar}$), 138.1, 139.6, 140.4, 140.7 ($C_{Ar}$), 162.1 (COH), 171.2 (CO). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ = 3101 (w), 3007 (w), 2951 (w), 2919 (w), 2855 (w), 1738 (w), 1664 (m), 1631 (w), 1604 (w), 1573 (w), 1547 (w), 1514 (w), 1477 (w), 1441 (m), 1431 (m), 1394 (w), 1348 (w), 1308 (s), 1281 (m), 1206 (m), 1178 (m), 1148 (s), 1120 (w), 1090 (m), 1043 (w), 1021 (w), 1012 (w), 1000 (w), 955 (w), 909 (w), 871 (w), 841 (w), 824 (m), 765 (m), 731 (w), 723 (w), 707 (w), 674 (w), 651 (w), 639 (w), 627 (w), 599 (s), 565 (s), 533 (w). GC-MS (EI, 70 eV): *m/z* (%) = 432 ([$M^+$], $^{37}$Cl, 8), 430 ([$M^+$], $^{35}$Cl, 20), 398 (100), 362 (4), 320 (19), 293 (4), 275 (6), 233 (26), 219 (10), 189 (10), 165 (14), 128 (57), 105 (37), 97 (6), 86 (73), 69 (16). HRMS (EI): Calcd. for $C_{22}H_{19}O_5ClS$ ([$M]^+$, $^{35}$Cl): 430.07145 ; found: 430.07204.

**Methyl 2-butyl-6-hydroxy-3-(phenylsulfonyl)benzoate (13ab).**

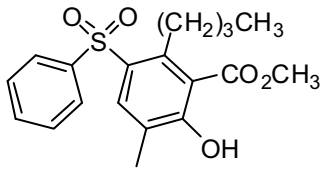



Chemical Formula: $C_{18}H_{20}O_5S$
Exact Mass: 348.103

Starting with **12d** (0.445g, 1.5 mmol) and **4a** (0.429 g, 1.7 mmol), **13ab** was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish oil (0.403 g, 77%). $^1$H NMR (250 MHz, $CDCl_3$): δ = 0.68 (t, $^3J$ = 7.4 Hz, 3 H, $CH_3$), 1.05–1.17 (m, 2 H, $CH_2$), 1.31-1.43 (m, 2 H, $CH_2$), 3.01 (t, $^3J$ = 8.03 Hz, 2 H, Ph*CH*$_2$), 3.82 (s, 3 H, $OCH_3$), 6.90 ( d, $^3J$ = 9.0 Hz, 1 H, $CH_{Ar}$), 7.35–7.47 (m, 3

H, 3$CH_{Ar}$), 7.68 –7.72 (m, 2 H, 2$CH_{Ar}$), 8.28 (d, $^3J$ = 9.0 Hz, 1 H, $CH_{Ar}$), 10.97 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.7 ($CH_3$), 23.3, 30.9, 33.9 ($CH_2$), 52.9 ($OCH_3$), 115.1 (*C*$COOCH_3$), 115.9 ($CH_{Ar}$), 127.2 (2$CH_{Ar}$), 129.2 (2$CH_{Ar}$), 131.1 ($C_{Ar}$), 132.9 ($CH_{Ar}$), 135.6 ($H_{Ar}$), 142.5, 147.8 ($C_{Ar}$), 165.3 (COH), 170.9 (CO). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ = 3339 (w, br), 3065 (w), 2956 (w), 2931 (w), 2872 (w), 2256 (w), 1732 (m), 1665 (m), 1598 (m), 1576 (m), 1446 (m), 1396 (w), 1380 (w), 1347 (w), 1302 (s), 1225 (m), 1210 (m), 1143 (s), 1107 (s), 1076 (m), 1012 (m), 999 (w), 964 (w), 951 (w), 910 (m), 832 (m), 755 (m), 721 (s), 687 (s), 648 (m), 608 (m), 583 (m), 556 (s). GC-MS (EI, 70 eV): *m/z* (%) = 348 ([$M^+$], 9), 331 (6), 313 (18), 306 (6), 281 (22), 254 (8), 239 (50), 231 (14), 211 (100), 198 (12), 165 (55), 141 (82), 125 (54), 98 (18), 85 (29), 77 (97), 69 (28), 57 (38), 43 (28). HRMS (EI): Calcd. for $C_{18}H_{20}O_5S$ ([$M]^+$): 348.11042; found: 348.11064.

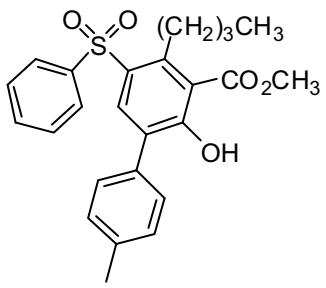
**Methyl 2-butyl-6-hydroxy-5-methyl-3-(phenylsulfonyl)-benzoate (13ac).**



Chemical Formula: $C_{19}H_{22}O_5S$
Exact Mass: 362.119

Starting with **12d** (0.445g, 1.5 mmol) and **4b** (0.452 g, 1.7 mmol), **13ac** was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish solid (0.430 g, 79%), mp. = 113-115 °C. $^1$H NMR (250 MHz, $CDCl_3$): δ = 0.71 (t, $^3J$ = 7.4 Hz, 3 H, $CH_3$), 0.91–0.99 (m, 2 H, $CH_2$), 1.10–1.18 (m, 2 H, $CH_2$), 2.25 (s, 3 H, Ph*CH*$_3$), 3.04 (t, $^3J$ = 7.4 Hz, 2 H, Ph*CH*$_2$), 3.86 (s, 3 H, $OCH_3$), 7.39– 7.52 (m, 3 H, 3$CH_{Ar}$), 7.72-7.75 (m, 2 H, 2$CH_{Ar}$), 8.23 (s, 1 H, $CH_{Ar}$), 11.41 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.7, 16.1 ($CH_3$), 23.4, 30.8, 34.0 ($CH_2$), 52.8 ($OCH_3$), 113.7 (*C*$COOCH_3$), 125.3 ($C_{Ar}$), 127.1 (2$CH_{Ar}$), 129.1 (2$CH_{Ar}$), 130.1 ($C_{Ar}$), 132.8 ($CH_{Ar}$), 136.0 ($CH_{Ar}$), 142.9, 145.1($C_{Ar}$ ), 164.2 (COH), 171.6 (CO). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ = 3067 (w), 2957 (w), 2930 (w), 2872 (w), 1737 (w), 1664 (w), 1604 (w), 1568 (w), 1446 (w), 1439 (w), 1381 (w), 1347 (w), 1304 (m), 1250 (w), 1200 (w), 1163 (m), 1144 (m), 1087 (m), 1042 (w), 999 (w), 982 (w), 909 (w), 889 (w), 834 (w), 814 (w), 754 (w), 731 (m), 722 (m), 689 (w), 649 (w), 585 (m), 572 (w), 562 (w). GC-MS (EI, 70 eV): *m/z* (%) = 362 ([$M^+$], 37), 345 (6), 330 (90), 313 (8), 295 (26), 260 (6), 239 (4), 211 (10), 189 (89), 179 (100), 161 (34), 147 (55), 125 (26), 119 (12), 91 (15), 69 (26), 57 (16), 43 (22). HRMS (EI): Calcd. for $C_{19}H_{22}O_5S$ ([$M]^+$): 362.12607; found: 362.12619.

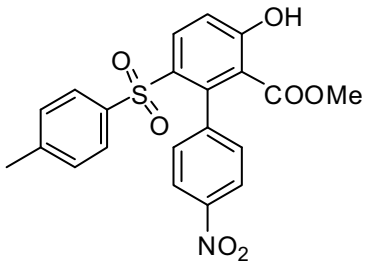
**Methyl 4-butyl-2-hydroxy-4'-methyl-5-(phenylsulfonyl)-biphenyl-3-carboxylate (13ad).**



Chemical Formula: $C_{25}H_{26}O_5S$
Exact Mass: 438.150

Starting with **12d** (0.445 g, 1.5 mmol) and **4m** (0.578 g, 1.7 mmol), **13ad** was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish oil (0.494 g, 75%). $^1$H NMR (250 MHz, $CDCl_3$): δ = 0.69 (t, $^3J$ = 7.0 Hz, 3 H, $CH_3$), 0.91–1.04 (m, 2 H, $CH_2$), 1.09–1.18 (m, 2 H, $CH_2$ ), 2.28 (s, 3 H, Ph*CH*$_3$), 3.01 (t, $^3J$= 8.0 Hz, 2 H, Ph*CH*$_2$), 3.82 (s, 3 H, $OCH_3$), 7.15 (d, $^3J$ = 7.8 Hz, 2 H, $2CH_{Ar}$), 7.34–7.44 (m, 5 H, $5CH_{Ar}$), 7.70–7.74 (m, 2 H, $2CH_{Ar}$), 8.35 (s, 1 H, $CH_{Ar}$), 10.93 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.72, 21.3 ($CH_3$), 23.4, 30.9, 33.9 ($CH_2$), 52.9 ($OCH_3$), 115.8 (*C*$COOCH_3$ ), 127.2 ($2CH_{Ar}$), 128.6 ($C_{Ar}$), 129.1 ($2CH_{Ar}$), 129.2 ($4CH_{Ar}$), 131.1, 132.8 ($C_{Ar}$), 132.9, 135.8 ($CH_{Ar}$), 138.0, 142.7, 145.8 ($C_{Ar}$), 161.9 ( COH ), 171.2 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 2956 (w), 2929 (w), 2872 (w), 2255 (w), 1736 (w), 1664 (m),1601 (w), 1573 (w), 1551 (w), 1514 (w), 1446 (m), 1437 (m), 1399 (w), 1307 (m), 1202 (m), 1178 (m), 1147 (s), 1093 (m), 1023 (w), 962 (w), 908 (m), 872 (w), 824 (m), 730 (s), 689 (m), 648 (w), 586 (s), 563 (w), 548 (w). GC-MS (EI, 70 eV): *m/z* (%) = 438 ([$M^+$], 60), 408 (21), 407 (73), 406 (100), 377 (8), 335 (3), 223 (15), 195 (62), 165 (14), 119 (10), 91 (7)**.** HRMS (EI): Calcd. for $C_{25}H_{26}O_5S$ ([$M$]$^+$): 438.15737; found: 438.15819.

**Methyl 3-hydroxy-4'-nitro-6-tosylbiphenyl-2-carboxylate (13ae).**

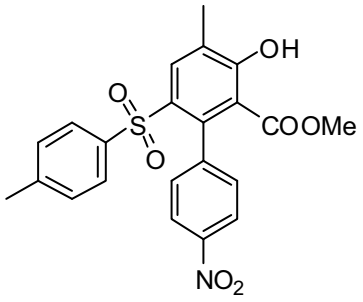


Chemical Formula: $C_{21}H_{17}NO_7S$
Exact Mass: 427.07257

Starting with **12e** (0.563 g, 1.5 mmol) and **4a** (0.429 g, 1.7 mmol), **13ae** was isolated after chromatography (silica gel, heptanes/EtOAc) as a white solid (0.289 g, 45%), mp. = 196-198 °C. $^1$H NMR (300 MHz, $CDCl_3$): δ = 2.30 (s, 3 H, Ph*CH*$_3$), 3.20 (s, 3 H, $OCH_3$), 6.91 – 6.94 (m, 2 H, $2CH_{Ar}$), 6.96 – 7.02 (m, 4 H, $4CH_{Ar}$), 7.19 (d, $^3J$ = 8.5 Hz, 1 H, $CH_{Ar}$), 7.89 – 7.92 (m, 2 H, $2CH_{Ar}$), 8.47 (d, $^3J$ = 8.5 Hz, 1H, $CH_{Ar}$), 11.28 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 21.7 ($CH_3$), 52.9 ($OCH_3$), 113.9 (*C*$COOCH_3$), 118.4 ($CH_{Ar}$), 121.5 ($2CH_{Ar}$), 127.2 ($2CH_{Ar}$), 129.2 ($2CH_{Ar}$), 130.8 ($2CH_{Ar}$), 132.2 ($C_{Ar}$), 135.0 ($CH_{Ar}$), 138.2. 142.4, 143.4, 144.1, 147.0 ($C_{Ar}$) , 165.0 (COH), 169.7 (CO).IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 3400 (w), 3106 (w), 3018 (w), 2924 (w), 2857 (w), 1703 (m), 1650 (w), 1593 (w), 1576 (m), 1515 (m), 1445 (w), 1433 (w), 1380 (w), 1347 (m), 1286 (m), 1183 (w), 1147 (m), 1119 (m), 1079 (m), 1017 (w), 966 (w), 918 (w), 866 (m), 825 (m), 790 (w), 746 (w), 692 (m), 643 (m), 617 (w), 569 (m), 554 (s). GC-MS (EI, 70 eV): *m/z* (%) = 427

([M]$^+$, 36), 396 (19), 395 (100), 139 (12), 91 (8). HRMS (EI): Calcd. for $C_{21}H_{17}O_7NS$ ([M]$^+$): 427.07202; found: 427.071814.

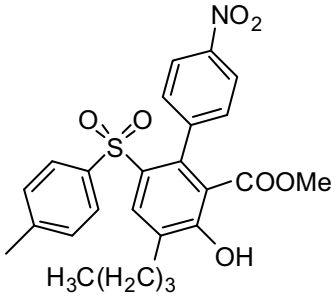
**Methyl 3-hydroxy-4-methyl-4'-nitro-6-tosylbiphenyl-2-carboxylate (13af).**




Chemical Formula: $C_{22}H_{19}NO_7S$
Exact Mass: 441.088

Starting with **12e** (0.563 g, 1.5 mmol) and **4b** (0.452 g, 1.7 mmol), **13af** was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellow solid (0.324 g, 49%), mp. = 180-182 °C. $^1$HNMR (250 MHz, $CDCl_3$): δ = 2.30 (s, 3H, Ph*CH*$_3$), 2.35 (s, 3H, Ph*CH*$_3$), 3.24 (s, 3H, $OCH_3$), 6.87-7.02 (m, 6 H, 6$CH_{Ar}$), 7.86 - 7.91 (m, 2 H, 2$CH_{Ar}$), 8.35(s, 1H, $CH_{Ar}$), 11.53 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 16.2, 21.6 ($CH_3$), 52.5 ($OCH_3$), 113.1 (*C*$COOCH_3$), 121.5 (2$CH_{Ar}$), 127.1 (2$CH_{Ar}$), 128.2 ($C_{Ar}$), 129.2 (2$CH_{Ar}$), 131.0 ($CH_{Ar}$), 131.2 ($C_{Ar}$), 135.1(2$CH_{Ar}$), 138.4, 139.8, 143.8, 143.9, 146.9 ($C_{Ar}$), 163.5 (COH), 170.3 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 3078 (w), 2925 (w), 2854 (w), 2256 (w), 1668 (m), 1597 (w), 1564 (w), 1518 (m), 1440 (w), 1380 (w), 1346 (s), 1302 (m), 1251 (m), 1148 (s), 1117 (m), 1084 (w), 1017 (w), 983 (w), 945 (w), 907 (s), 860 (w), 812 (w), 728 (s), 664 (w), 602 (w), 596 (s), 551 (w). GC-MS (EI, 70 eV): *m/z* (%) = 441 ([M]$^+$, 37), 411 (10), 410 (23), 409 (100), 363 (20), 254 (22), 253 (19). HRMS (EI): Calcd. for $C_{22}H_{19}NO_7S$ ([M]$^+$): 441.08767; found: 441.087563.

**Methyl 4-butyl-3-hydroxy-4'-nitro-6-tosylbiphenyl-2-carboxylate (13ag).**




Chemical Formula: $C_{25}H_{25}NO_7S$
Exact Mass: 483.13517

Starting with **12e** (0.563 g, 1.5 mmol) and **4d** (0.522 g, 1.7 mmol), **13ag** was isolated after chromatography (silica gel, heptanes/EtOAc) as a yellowish solid (0.340 g, 47%), mp. = 130-133 °C. $^1$H NMR (250 MHz, $CDCl_3$): δ = 0.60 (t, $^3J$ = 6.3 Hz, 3 H, $CH_3$), 1.22 – 1.30 (m, 2 H, $CH_2$), 1.59 – 1.63 (m, 2 H, $CH_2$), 2.30 (s, 3 H, Ph*CH*$_3$), 2.75 (t, $^3J$ = 6.9 Hz, 2 H, Ph*CH*$_2$), 3.25 (s, 3 H, $OCH_3$), 6.90 – 6.93 (m, 2 H, 2$CH_{Ar}$), 6.95 – 7.02 (m, 4 H, 4$CH_{Ar}$), 7.83 – 7.91 (m, 2 H, 2$CH_{Ar}$), 8.36 (s, 1H, $CH_{Ar}$), 11.70 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 12.2, 20.5 ($CH_3$), 22.2, 28.6, 32.3 ($CH_2$), 52.8 ($OCH_3$), 112.2 (*C*$COOCH_3$), 120.5 (2$CH_{Ar}$), 126.1 (2$CH_{Ar}$), 126.9 ($C_{Ar}$), 128.2 (2$CH_{Ar}$), 130.2 (2$CH_{Ar}$), 132.5 ($CH_{Ar}$), 132.8, 137.5, 138.7, 142.9, 143.0, 146.0 ($C_{Ar}$), 163.7 (COH), 169.0 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 3115 (w), 3088 (w),

2917 (w), 2850 (w), 1731 (w), 1651 (m), 1596 (m), 1516 (m), 1493 (w), 1465 (w), 1398 (m), 1344 (m), 1288 (m), 1181 (m), 1149 (m), 1121 (m), 1081 (m), 1012 (m), 953 (w), 930 (w), 867 (m), 851 (m), 796 (m), 764 (m), 701 (m), 658 (m), 621 (w), 565 (m), 549 (s). GC-MS (EI, 70 eV): *m/z* (%) = 483 ($[M]^+$, 35), 424 (33), 406 (27), 395 (100), 165 (11), 139 (16), 91 (16). HRMS (EI): Calcd. for $C_{25}H_{25}O_7NS$ ($[M]^+$): 483.13485; found: 483.133950.

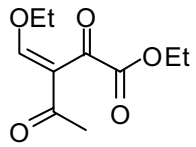
**General procedure for the synthesis of 15a-f**:

To a suspension of sodium ethoxide (1.0 equiv.) in benzene (0.5 mL / 1.0 mmol EtONa), was added dropwise Diethyl oxalate (1.0 equiv.) at 0 °C followed by the dropwise addition of **14a-f** (1.0 equiv.) in 30 minutes. The temperature of the solution was allowed to warm to 20 °C during 14 h with stirring. To the solution was added hydrochloric acid (10%, 20 mL) and the organic and the aqueous layer were separated. The later was extracted with Ether (3×20 mL) and washed with brine. The combined organic layers were dried ($Na_2SO_4$), filtered and the filtrate was concentrated in vacuo. to give **15**.

**General procedure for the synthesis of 16a-f**:

To a sulution of **15a-f** (1.0 equiv.) in Acetic anhydride (2.0 equiv.) was added triethylorthoformate (1.2 equiv.). the mixture was refluxed for 2h at 120 °C and another 2h at 140°C. The resulting raw product was dried in vacuo.to give **16** (92-99 %).

**ethyl 3-(ethoxymethylene)-2,4-dioxopentanoate(16a)**



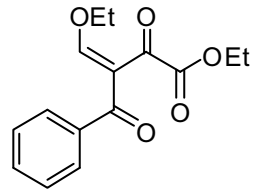

Chemical Formula: $C_{10}H_{14}O_5$
Exact Mass: 214.084

Reaction starting with **15a** (4.30 g, 27.20 mmol), triethyl orthoformate (5.16 g, 32.64 mmol), and acetic anhydride (8.60 g, 54.4 mmol), was refluxed for 6-hours at 120-140°C. After evaporation the solvents under vacuum the product was collected as a redish oil (5.64 g, 97%).$^1$HNMR (300 MHz, $CDCl_3$): δ = 1.28 (t, $^3J$ = 7.2 Hz, 3 H, $OCH_2\mathit{CH_3}$), 1.40 (t, $^3J$ = 7.1 Hz, 3 H, $OCH_2\mathit{CH_3}$), 2.36 (s, 3 H, $CH_3$), 4.24 (q, $^3J$= 7.2 Hz, 2 H, $O\mathit{CH_2}CH_3$), 4.35 (q, $^3J$= 7.1 Hz, 2 H, $O\mathit{CH_2}CH_3$), 7.85 (s, 1 H, $CH_{Olf}$). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.7, 15.0, 30.4 ($CH_3$), 61.8, 74.4 ($OCH_2$), 117.4 (CO*C*CO), 164.5 (CO), 169.4 ($CH_{Olf}$), 186.8, 195.8 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 2984 (w), 2940 (w), 2255 (w), 1780 (w), 1732 (m), 1661 (m), 1577 (m), 1473 (w), 1389 (w), 1367 (w), 1312 (m), 1255 (m), 1224 (m), 1172 (m), 1097 (m), 1022 (m), 907 (s), 862 (w), 725 (s), 684

(w), 648 (m), 601 (w).GC-MS (EI, 70 eV): *m/z* (%) = 214 ([M]$^+$, 1.4), 141 (100), 113 (55), 99 (23), 71 (82), 43 (48), 29 (20).

HRMS (EI): Calcd. for $C_{10}H_{14}O_5$ ([M]$^+$): 214.08358; found: 214.083886.

**ethyl 3-benzoyl-4-ethoxy-2-oxobut-3-enoate(16b)**

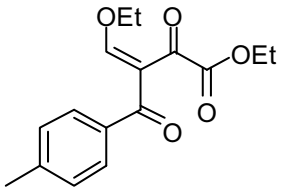



Chemical Formula: $C_{15}H_{16}O_5$
Exact Mass: 276.100

Reaction starting with **15b** (4.20 g, 19.08 mmol), triethyl orthoformate (5.04 g, 22.90 mmol), and acetic anhydride (8.40 g, 38.16 mmol), was refluxed for 6-hours at 120-140°C. After evaporation the solvents under vacuum the product was collected as a redish oil (5.0 g, 96%).$^1$HNMR (300 MHz, $CDCl_3$): δ = 1.15-1.33 (m, 6 H, 2×$OCH_2CH_3$), 4.10-4.29 (m, 4 H, 2×$OCH_2CH_3$), 7.35-7.53 (m, 3 H, 3×$CH_{Ph}$), 7.76-7.87 (m, 2 H, 2×$CH_{Ph}$), 7.93 (s, 1 H, $CH_{Olf}$).$^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.8, 15.2 ($CH_3$), 62.0, 73.4 ($OCH_2$), 117.9 (CO*C*CO), 128.5 (2×$CH_{Ar}$), 129.2 (2×$CH_{Ar}$), 133.2 ($CH_{Ar}$), 137.9 ($C_{Ar}$), 162.8 (CO), 166.4 ($CH_{Olf}$), 183.4, 192.2 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 3062 (w), 2983 (w), 2928 (w), 1740 (m), 1681 (m), 1598 (m), 1489 (w), 1447 (m), 1387 (w), 1360 (m), 1264 (s), 1183 (s), 1157 (m), 1061 (m), 1010 (m), 954 (w), 893 (w), 760 (m), 690 (s), 631 (w), 587 (m). GC-MS (EI, 70 eV): *m/z* (%) = 276 ([M]$^+$, 2), 175 (11), 106 (10), 105 (100), 77 (39).

HRMS (EI): Calcd. for $C_{15}H_{16}O_5$ ([M]$^+$): 276.09923; found: 276.099378.

**ethyl 4-ethoxy-3-(4-methylbenzoyl)-2-oxobut-3-enoate(16c)**

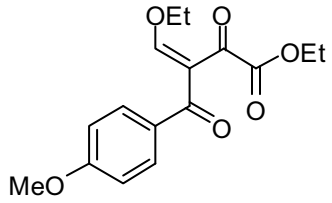



Chemical Formula: $C_{16}H_{18}O_5$
Exact Mass: 290.115

Reaction starting with **15c** (4.50 g, 19.22 mmol), triethyl orthoformate (3.40 g, 23.0 mmol), and acetic anhydride (5.68 g, 38.44 mmol), was refluxed for 6-hours at 120-140°C. After evaporation the solvents under vacuum the product was collected as a redish oil (5.46 g, 98%). $^1$HNMR (300 MHz, $CDCl_3$): δ = 1.16-1.23 (m, 6 H, 2×$OCH_2CH_3$), 2.33 (s, 3 H, $CH_3$), 4.10-4.17 (m, 4 H, 2×$OCH_2CH_3$), 7.17-7.19 (m, 2 H, 2×$CH_{Ar}$), 7.67-7.70 (m, 2 H, 2×$CH_{Ar}$), 7.89 (s, 1 H, $CH_{Olf}$). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.8, 15.2 21.7 ($CH_3$), 61.9, 73.3 ($OCH_2$), 118.1 (CO*C*CO), 129.2 (2×$CH_{Ar}$), 129.4 (2×$CH_{Ar}$), 135.3, 144.2 ($C_{Ar}$), 162.8 (CO), 166.6 ($CH_{Olf}$), 183.3, 191.8 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 2981 (w), 2923 (w), 2871 (w), 1733 (m), 1677 (m), 1604 (s), 1579 (m), 1502 (m), 1447 (m), 1384

(m), 1265 (s), 1237 (s), 1180 (s), 1112 (m), 1059 (s), 1015 (s), 896 (m), 831 (m), 752 (m), 710 (m), 674 (m), 623 (m), 590 (m), 567 (m). GC-MS (EI, 70 eV): *m/z* (%) = 290 ([M]$^+$, 3), 175 (11), 218 (10), 217 (67), 120 (17), 119 (100), 91 (42), 65 (13). HRMS (EI): Calcd. for $C_{16}H_{18}O_5$ ([M]$^+$): 290.115247; found: 290.11488.

**ethyl 4-ethoxy-3-(4-methoxybenzoyl)-2-oxobut-3-enoate(16d)**

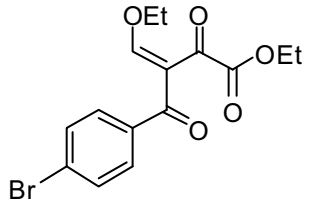


Chemical Formula: $C_{16}H_{18}O_6$
Exact Mass: 306.110

Reaction starting with **15d** (3.80 g, 15.19 mmol), triethyl orthoformate (2.69 g, 18.23 mmol), and acetic anhydride (3.09 g, 30.38 mmol), was refluxed for 6-hours at 120-140°C. After evaporation the solvents under vacuum the product was collected as a redish oil (4.41 g, 95%). $^1$HNMR (250 MHz, $CDCl_3$) : δ = 1.19 (t, $^3J$ = 7.1 Hz, 3 H, $OCH_2CH_3$), 1.20 (t, $^3J$ = 7.1 Hz, 3 H, $OCH_2CH_3$), 3.79 (s, 3 H, $OCH_3$), 4.12 (q, $^3J$= 7.2 Hz, 2 H, $OCH_2CH_3$), 4.19 (q, $^3J$= 7.1 Hz, 2 H, $OCH_2CH_3$), 6.83–6.87 (m, 2 H, $CH_{PhOMe}$), 7.76–7.79 (m, 2 H, $CH_{PhOMe}$), 7.89 (s, 1 H, $CH_{Olf}$). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 12.9, 14.3 ($CH_3$), 54.5 ($OCH_3$), 61.3, 72.3 ($OCH_2$), 112.7 (2×$CH_{PhOMe}$), 117.2 (CO*C*CO), 129.6 ($C_{Ar}$), 130.7 (2×$CH_{PhOMe}$), 162.9 (CO), 164.8 ($CH_{Olf}$), 182.5 ($C_{Ar}$), 189.7, 195.9 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 2983 (w), 2939 (w), 2905 (w), 2842 (w), 2254 (w), 1733 (m), 1674 (m), 1646 (m), 1599 (s), 1576 (m), 1510 (m), 1464 (w), 1444 (w), 1422 (w), 1385 (w), 1362 (w), 1309 (m), 1257 (s), 1170 (m), 1113 (w), 1029 (m), 911 (w), 846 (w), 806 (w), 777 (w), 731 (m), 648 (w), 609 (w). GC-MS (EI, 70 eV): *m/z* (%) = 306 ([M$^+$], 2), 278 (3), 270 (1), 249 (2), 233 (26), 210 (3), 189 (2), 135 (100), 107 (8), 92 (8), 77 (14), 69 (3), 44 (2).

HRMS (EI): Calcd. for $C_{16}H_{18}O_6$ ([M]$^+$) : 306.10979; found: 306.110424

**Ethyl 3-(4-bromobenzoyl)-4-ethoxy-2-oxobut-3-enoate(16e)**

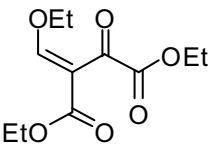


Chemical Formula: $C_{15}H_{15}BrO_5$
Exact Mass: 354.010

Reaction starting with **15e** (4.35 g, 14.60 mmol), triethyl orthoformate (2.60 g, 17.57 mmol), and acetic anhydride (3.73 g, 36.6 mmol), was refluxed for 6-hours at 120-140°C. After evaporation the solvents under vacuum the product was collected as a redish oil (4.72 g, 92%). $^1$HNMR (300 MHZ, $CDCL_3$) : δ = 1.29 (t, $^3J$ = 7.0 Hz, 3 H, $OCH_2CH_3$), 1.39 (t, $^3J$ = 6.9 Hz, 3 H, $OCH_2CH_3$), 4.21 (q, $^3J$ = 7.2 Hz, 2 H,

$OCH_2CH_3$), 4.35 (q, $^3J$ = 7.0 Hz, 2 H, $OCH_2CH_3$), 7.72-7.74 (m, 2 H, $CH_{PhBr}$), 7.82 -7.85 (m, 2 H, $CH_{PhBr}$), 8.01 (S, 1 H, $CH_{Olf}$). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.8, 15.1 ($CH_3$), 62.4, 73.6 ($OCH_2$), 117.4 (CO*C*CO), 128.3 ($C_{Ar}$), 129.8 (2×$CH_{PhBr}$), 131.8 (2×$CH_{PhBr}$), 136.0 ($C_{Ar}$), 162.7 (CO), 166.4 ($CH_{Olf}$), 183.1, 191.2 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 3064 (w), 2982 (w), 2938 (w), 2873 (w), 1824 (w), 1732 (m), 1683 (m), 1651 (m), 1584 (s), 1481 (w), 1444 (w), 1395 (m), 1367 (m), 1302 (w), 1185 (m), 1068 (m), 1007 (s), 957 (m), 920 (m), 907 (m), 896 (m), 843 (m), 748 (m), 675 (m), 626 (m), 606 (m), 587 (m). GC-MS (EI, 70 eV): *m/z* (%) = 356 ([M]$^+$, $Br^{81}$ ,10), 354 ([M]$^+$, $Br^{79}$ ,16) 283 (60), 281 (62), 185 (98), 183 (100), 157 (18), 155 (19). HRMS (EI): Calcd. for $C_{15}H_{16}O_5{}^{79}Br$ ([MH]$^+$): 355.01756; found: 355.01667.

**diethyl 2-(ethoxymethylene)-3-oxosuccinate(16f)**



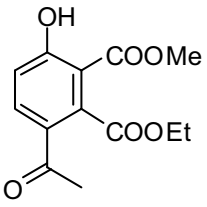
Chemical Formula: $C_{11}H_{16}O_6$
Exact Mass: 244.095

Reaction starting with **15f** (7.09 g, 37.22 mmol), triethyl orthoformate (7.53 mL, 45.0 mmol), and acetic anhydride (8.85 mL, 94.2 mmol), was refluxed for 6-hours at 120-140°C. After evaporation the solvents under vacuum the product was collected as a redish oil (9.7 g, 99%). $^1$HNMR (250 MHz, $CDCl_3$): δ = 1.21 (t, $^3J$ = 7.8 Hz, 3 H, $OCH_2CH_3$), 1.30 (t, $^3J$ = 6.9 Hz, 6 H, 2×$OCH_2CH_3$), 4.16 (q, $^3J$ = 6.9 Hz, 2 H, $OCH_2CH_3$), 4.28 (q, $^3J$ = 7.1 Hz, 4 H, 2×$OCH_2CH_3$), 7.84 (s, 1 H, $CH_{Olf}$). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 12.9, 13.1, 14.3 ($CH_3$), 62.2, 62.2, 73.5 ($OCH_2$), 108.5 (CO*C*CO), 170.0 ($CH_{Olf}$), 175.6, 182.1, 184.1 (CO). IR (KBr, cm$^{-1}$): $\tilde{\nu}$ = 2985 (w), 2941 (w), 2908 (w), 1764 (m), 1737 (m), 1702 (m), 1582 (m), 1468 (w), 1447 (w), 1390 (w), 1370 (w), 1296 (m), 1240 (m), 1184 (s), 1156 (m), 1102 (s), 1009 (s), 866 (m), 852 (m), 784 (m), 755 (m), 657 (w), 605 (w). GC-MS (EI, 70 eV): *m/z* (%) = 244 ([M$^+$], 3), 144 (1), 113 (82), 85 (100), 83 (5), 55 (5), 39

**General procedure for the synthesis of 17a-al**.

To a $CH_2Cl_2$ solution (2 mL / 1 mmol of **16a-f**) of **16a-f** was added **4a-i** (1.1 mmol) and, subsequently, $TiCl_4$ (1.1 mmol) at ~78 °C. The temperature of the solution was allowed to warm to 20 °C during 14 h with stirring. To the solution was added hydrochloric acid (10%, 20 mL) and the organic and the aqueous layer were separated. The latter was extracted with $CH_2Cl_2$ (3 × 20 mL). The combined organic layers were dried ($Na_2SO_4$), filtered and the filtrate was concentrated in vacuo. The residue was purifed by chromatography (silica gel, heptanes / EtOAc) to give **17a-al**.

**2-ethyl 1-methyl 3-acetyl-6-hydroxyphthalate (17a)**

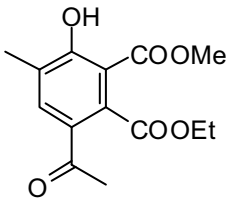



Chemical Formula: $C_{13}H_{14}O_6$
Molecular Weight: 266.247

Starting with **16a** (0.321 g, 1.5 mmol) and **4a** (0.429 g, 1.65 mmol), **17a** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a very yellowish solid (0.191 g, 48 %) m.p: 95 - 97 °C. $^1$HNMR (300 MHz, $CDCl_3$): δ = 1.17 (t, $^3J$ = 7.2 Hz, 3 H, $OCH_2CH_3$), 2.32 (s, 3 H, $CH_3$), 3.72 (s, 3 H, $OCH_3$), 4.20 (q, $^3J$ = 7.7 Hz, 2 H, $OCH_2CH_3$), 6.87 (d, $^3J$ = 9.0 Hz, 1 H, $CH_{Ar}$), 7.73 (d, $^3J$ = 9.0 Hz, 1 H, $CH_{Ar}$), 11.37 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 14.0, 27.5 ($CH_3$), 53.2 ($OCH_3$), 61.8 ($OCH_2$), 110.5 ($C$COOCH$_3$), 118.5 ($CH_{Ar}$), 126.9 ($C$COCH$_3$), 136.2 ($CH_{Ar}$), 137.4 ($C$COOC$_2$H$_5$), 164.9 ($C$OH), 168.3, 169.4, 195.7 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 3119 (w), 3076 (w), 2981 (w), 2919 (w), 2850 (w), 1729 (m), 1674 (s), 1580 (m), 1470 (w), 1443 (m), 1389 (w), 1362 (m), 1328 (m), 1304 (m), 1248 (s), 1207 (s), 1155 (m), 1137 (s), 1100 (m), 1026 (m), 965 (m), 937 (m), 872 (m), 847 (m), 811 (m), 757 (m), 733 (m), 706 (m), 688 (m), 647 (m), 598 (m), 580 (m), 540 (m). GC-MS (EI, 70 eV): *m/z* (%) = 266 ([M]$^+$, 24), 251 (11), 221 (27), 220 (33), 192 (10), 191 (100), 190 (18), 189 (42), 188 (15), 162 (39), 120 (12), 119 (29), 43 (10).

HRMS (EI): Calcd. for $C_{13}H_{14}O_6$ ([M]$^+$): 266.07849; found: 266.079233.

**1-ethyl 2-methyl 6-acetyl-3-hydroxy-4-methylphthalate (17b)**

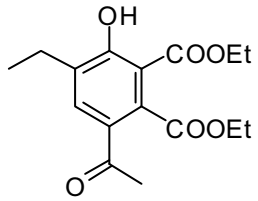



Chemical Formula: $C_{14}H_{16}O_6$
Exact Mass: 280.095

Starting with **16a** (0.321 g, 1.5 mmol) and **4b** (0.457 g, 1.65 mmol), **17b** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a very yellowish solid (0.210 g, 50%) m.p: 76 - 78°C. $^1$HNMR (300 MHz, $CDCl_3$): δ = 1.22 (t, $^3J$ = 7.3 Hz, 3 H, $OCH_2CH_3$), 2.25 (s, 3 H, $CH_3$), 2.47 (s, 3 H, $CH_3$), 3.88 (s, 3 H, $OCH_3$), 4.34 (q, $^3J$ = 7.4 Hz, 2 H, $OCH_2CH_3$), 7.73 (s, 1 H, $CH_{Ar}$), 11.78 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 14.0, 15.9, 27.5 ($CH_3$), 53.1 ($OCH_3$), 61.5 ($OCH_2$), 109.7 ($C$COOCH$_3$), 126.2, 128.1 ($C_{Ar}$), 135.0 ($C$COOC$_2$H$_5$), 136.5 ($CH_{Ar}$), 163.4 ($C$OH), 168.4, 170.0, 195.9 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 3067 (w), 2964 (w), 2929 (w), 2863 (w), 1726 (m), 1674 (s), 1564 (m), 1443 (m), 1407 (m), 1381 (w), 1363 (m), 1321 (m), 1251 (s), 1205 (s), 1172 (m), 1135 (s), 1090 (m), 1036 (s), 988 (m), 960 (m), 898 (m), 859 (m), 810 (m), 736 (m), 714 (m), 634 (m), 615 (m), 595 (m), 537 (s). GC-MS (EI, 70 eV): *m/z* (%) = 280 ([M]$^+$, 27), 248 (11), 235 (29), 234 (52), 206 (10), 205 (100), 204 (16), 203 (47), 202 (66), 176 (33), 134 (10), 133 (25), 105 (11), 77 (11), 43 (12).

HRMS (EI): Calcd. for $C_{14}H_{16}O_6$ ([M]$^+$): 280.09414; found: 280.094215.

**diethyl 6-acetyl-4-ethyl-3-hydroxyphthalate (17c)**

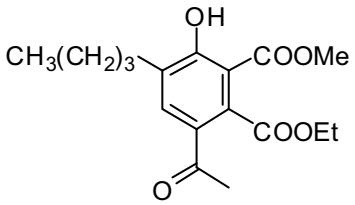



Chemical Formula: $C_{16}H_{20}O_6$
Exact Mass: 308.126

Starting with **16a** (0.321 g, 1.5 mmol) and **4c** (0.499 g, 1.65 mmol), **17c** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a white solid (0.231 g, 50%) m.p: 57 - 59°C. $^1$HNMR (300 MHz, $CDCl_3$): δ = 1.17 (t, $^3J$ = 7.6 Hz, 3 H, $CH_2CH_3$), 1.29-1.34 (m, 6 H, 2 $OCH_2CH_3$), 2.48 (s, 3 H, $CH_3$), 2.67 (t, $^3J$ = 7.7 Hz, 2 H, $CH_2CH_3$), 4.30- 4.38 (m, 4 H, 2×$OCH_2CH_3$), 7.72 (s, 1 H, $CH_{Ar}$), 11.91 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.5, 13.8, 13.9 ($CH_3$), 23.2 ($CH_2$), 27.7 ($CH_3$), 61.6, 62.8 ($OCH_2$), 109.9 ($C$COOCH$_3$), 126.5, 133.7, 134.8 ($C_{Ar}$), 134.9 ($CH_{Ar}$), 163.1 ($C$OH), 168.5, 169.6, 196.1 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 2981 (w), 2928 (w), 2894 (w), 1733 (s), 1659 (s), 1610 (w), 1555 (w), 1441 (m), 1423 (m), 1377 (w), 1363 (m), 1331 (s), 1257 (s), 1215 (s), 1144 (m), 1110 (w), 1034 (m), 1023 (s), 991 (m), 904 (m), 869 (m), 817 (m), 799 (m), 720 (m), 622 (m), 598 (w), 540 (m). GC-MS (EI, 70 eV): *m/z* (%) = 308 ([M]$^+$, 23), 263 (17), 262 (10), 219 (44), 217 (39), 216 (99), 190 (11), 189 (15), 188 (100), 147 (16), 43 (13).

HRMS (EI): Calcd. for $C_{16}H_{20}O_6$ ([M]$^+$): 308.12544; found: 308.124935.

**1-ethyl 2-methyl 6-acetyl-4-butyl-3-hydroxyphthalate (17d)**

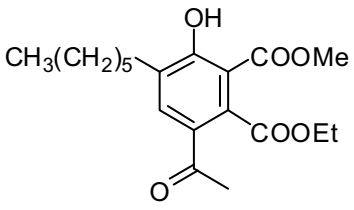



Chemical Formula: $C_{17}H_{22}O_6$
Exact Mass: 322.142

Starting with **16a** (0.321 g, 1.5 mmol) and **4d** (0.522 g, 1.65 mmol), **17d** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.280 g, 58%). $^1$HNMR (300 MHz, $CDCl_3$): δ = 0.85 (t, $^3J$ = 7.2 Hz, 3 H, $(CH_2)_3CH_3$), 1.29 (t, $^3J$ = 7.9 Hz, 3 H, $OCH_2CH_3$), 1.32-1.26 (m, 2 H, $CH_2$), 1.47-1.58 (m, 2 H, $CH_2$), 2.47 (s, 3 H, $CH_3$), 2.65 (t, $^3J$ = 7.9 Hz, 2 H, $CH_3(CH_2)_2CH_2$Ph), 3.86 (s, 3 H, $OCH_3$), 4.35 (q, $^3J$ = 7.4 Hz, 2 H, $OCH_2CH_3$), 7.70 (s, 1 H, $CH_{Ar}$), 11.76 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 12.8, 13.1 ($CH_3$), 21.5 ($CH_2$), 26.5 ($CH_3$), 28.6, 30.2 ($CH_2$), 52.1 ($OCH_3$), 60.7 ($OCH_2$), 108.8 ($C$COOCH$_3$), 125.3, 131.5, 133.8 ($C_{Ar}$), 134.8 ($CH_{Ar}$), 162.1 (COH), 167.6, 169.1, 195.2 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 2955 (w), 2929 (w), 2895 (w), 1732 (m), 1671(s), 1604 (w), 1569 (w), 1438 (m), 1340 (m), 1300 (w), 1255 (s), 1218 (s), 1164 (m), 1140 (m), 1093 (w), 1034 (m), 964 (w), 814 (m), 776 (w), 719 (m), 614 (w), 593 (w), 550 (w). GC-MS (EI, 70 eV): *m/z* (%) = 322 ([M]$^+$, 17), 277 (20), 248 (19), 247 (35), 245 (35), 244 (96), 234 (31), 217 (16), 216 (100), 215 (16), 202 (51), 175 (15), 147 (13), 43 (14).

HRMS (EI): Calcd. for $C_{17}H_{22}O_6$ ([M]$^+$): 322.14109; found: 322.141032.

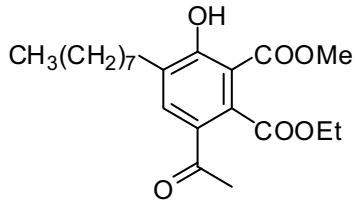
**1-ethyl 2-methyl 6-acetyl-4-hexyl-3-hydroxyphthalate (17e)**




Chemical Formula: $C_{19}H_{26}O_6$
Exact Mass: 350.173

Starting with **16a** (0.321 g, 1.5 mmol) and **4f** (0.568 g, 1.65 mmol), **17e** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish solid (0.310 g, 59%) m.p: 76 - 78°C. $^1$HNMR (300 MHz, $CDCl_3$): δ = 0.77 (t, $^3J$ = 6.9 Hz, 3 H, $(CH_2)_5CH_3$ ), 1.13-1.24 (m, 6 H, 3×$CH_2$),1.27 (t, $^3J$ = 6.9 Hz, 3 H, $OCH_2CH_3$), 1.44-1.54 (m, 2 H, $CH_2$), 2.43 (s, 3 H, $CH_3$), 2.57 (t, $^3J$ = 7.4 Hz, 2 H, $PhCH_2(CH_2)_4CH_3$ ), 3.82 (s, 3 H, $OCH_3$), 4.30 (q, $^3J$ = 7.1 Hz, 2 H, $OCH_2CH_3$), 7.65 (s, 1 H, $CH_{Ar}$), 11.72 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 14.0, 14.1, 27.6 ($CH_3$), 22.6, 29.0, 29.1, 30.0, 31.7 ($CH_2$), 53.2 ($OCH_3$), 61.8 ($OCH_2$), 110.0 (*C*$COOCH_3$), 126.4, 132.7 ($C_{Ar}$), 135.0 (*C*COOEt), 135.9 ($CH_{Ar}$), 163.4 (*C*OH), 168.9, 170.1, 196.2 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 2955 (w), 2927 (m), 2856 (w), 1733 (m), 1671 (s), 1606 (w), 1569 (w), 1439 (m), 1421 (m), 1340 (m), 1255 (s), 1218 (s), 1162 (m), 1140 (m), 1098 (m), 1034 (m), 964 (m), 909 (w), 884 (w), 863 (w), 814 (m), 776 (m), 724 (m), 647 (w), 615 (w), 594 (w), 554 (w). GC-MS (EI, 70 eV): *m/z* (%) = 350 ($[M]^+$, 10), 335 (4), 305 (17), 272 (100), 248 (14), 234 (39), 215 (14), 202 (57), 187 (35), 176 (7), 146 (9), 105 (5), 77 (6), 43 (15). HRMS (EI): Calcd. for $C_{19}H_{26}O_6$ ($[M]^+$): 350.17239; found: 350.172364.

**1-ethyl 2-methyl 6-acetyl-3-hydroxy-4-octylphthalate (17f)**



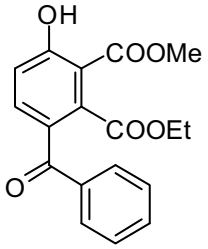

Chemical Formula: $C_{21}H_{30}O_6$
Exact Mass: 378.204

Starting with **16a** (0.321 g, 1.5 mmol) and **4g** (0.614 g, 1.65 mmol), **17f** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a brown solid (0.334 g, 59%) m.p: 105-107°C. $^1$HNMR (300 MHz, $CDCl_3$): δ = 0.82 (t, $^3J$ = 7.2 Hz, 3 H, $(CH_2)_7CH_3$), 1.22 (t, $^3J$ = 7.0 Hz, 3 H, $OCH_2CH_3$), 1.35-1.39 (m, 10 H, 5×$CH_2$), 1.47-1.58 (m, 2 H, $CH_2$), 2.47 (s, 3 H, $CH_3$), 2.62 (t, $^3J$ = 7.9 Hz, 2 H, $CH_3(CH_2)_6CH_2Ph$), 3.86 (s, 3 H, $OCH_3$), 4.33 (q, $^3J$ = 7.4 Hz, 2 H, $OCH_2CH_3$), 7.70 (s, 1 H, $CH_{Ar}$), 11.77 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.8, 14.0 ($CH_3$), 22.6 ($CH_2$), 27.6 ($CH_3$), 28.6, 29.1, 29.2, 29.4, 29.9, 31.9 ($CH_2$), 53.1 ($OCH_3$), 61.7 ($OCH_2$), 109.8 (*C*$COOCH_3$), 126.3, 132.5, 134.8 ($C_{Ar}$), 134.8 ($CH_{Ar}$), 163.2 (*C*OH), 168.5, 170.2, 196.3 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 2954 (w), 2924 (m), 2854 (w), 1734 (m), 1672 (s), 1606 (w), 1569 (w), 1439 (m), 1421 (m), 1342 (m), 1257 (m), 1220 (s), 1173 (w), 1141 (m), 1103 (w), 1036 (m), 965 (w), 907 (w), 814 (w), 777 (w), 724 (w), 724 (w), 647 (w), 615 (w), 594 (w), 557 (w). GC-MS (EI, 70 eV): *m/z* (%) = 378

([M]$^+$, 9), 333 (16), 303 (19), 301 (29), 300 (100), 248 (15), 234 (42), 215 (13), 203 (10), 202 (50), 188 (11), 187 (19), 176 (20), 43 (14).

HRMS (EI): Calcd. for $C_{21}H_{30}O_6$ ([M]$^+$): 378.20369; found: 378.203766.

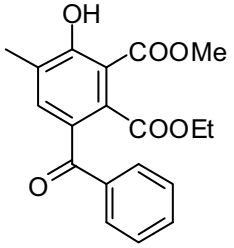
**2-ethyl 1-methyl 3-benzoyl-6-hydroxyphthalate (17g)**




Chemical Formula: $C_{18}H_{16}O_6$
Exact Mass: 328.095

Starting with **16b** (0.414 g, 1.5 mmol) and **4a** (0.429 g, 1.65 mmol), **17g** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.212 g, 65 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 1.22 (t, $^3J$ = 8.8 Hz, 3 H, $OCH_2CH_3$), 3.88 (s, 3 H, $OCH_3$), 4.17 (q, $^3J$ = 7.5 Hz, 2 H, $OCH_2CH_3$), 6.99 (d, $^3J$ = 9.0 Hz, 1 H, $CH_{Ar}$), 7.36-7.42 (m, 3 H, $CH_{Ph}$), 7.49-7.56 (m, 2 H, $CH_{Ph}$), 7.66 (d, $^3J$ = 9.0 Hz, 1 H, $CH_{Ar}$), 11.14 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.9 ($CH_3$), 53.1 ($OCH_3$), 61.9 ($OCH_2$), 110.7 (*C*$COOCH_3$), 118.1 ($CH_{Ar}$), 128.3 (2×$CH_{Ph}$), 128.7 ($C_{Ar}$), 129.9 (2×$CH_{Ph}$), 132.9 ($CH_{Ph}$), 136.4 ($CH_{Ar}$), 137.2 (*C*COOEt), 137.6 ($C_{Ar}$), 163.6 (*C*OH), 167.6, 169.3, 194.7 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 3241 (w), 3078 (w), 2976 (w), 2952 (w), 2851 (w), 1732 (m), 1662 (s), 1579 (m), 1444 (m), 1389 (w), 1332 (m), 1313 (m), 1280 (m), 1237 (s), 1177 (s), 1146 (m), 1112 (s), 1025 (m), 950 (m), 939 (m), 923 (m), 847 (m), 810 (m), 784 (m), 740 (m), 718 (m), 691 (s), 633 (s), 566 (m), 544 (m). GC-MS (EI, 70 eV): *m/z* (%) = 328 ([M]$^+$, 44), 296 (14), 283 (25), 282 (35), 252 (33), 251 (38), 225 (16), 224 (100), 223 (12), 196 (19), 195 (19), 191 (33), 168 (19), 139 (26), 119 (21), 105 (58), 77 (47), 51 (10). HRMS (EI): Calcd. for $C_{18}H_{16}O_6$ ([M]$^+$): 328.09414; found: 328.094310.

**1-ethyl 2-methyl 6-benzoyl-3-hydroxy-4-methylphthalate (17h)**



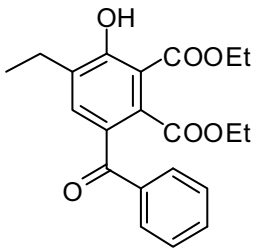

Chemical Formula: $C_{19}H_{18}O_6$
Exact Mass: 342.110

Starting with **16b** (0.414 g, 1.5 mmol) and **4b** (0.457 g, 1.65 mmol), **17h** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.343 g, 67 %).

$^1$HNMR (300 MHz, $CDCl_3$): δ = 1.23 (t, $^3J$ = 7.9 Hz, 3 H, $OCH_2CH_3$), 2.21 (s, 3 H, $CH_3$), 3.89 (s, 3 H, $OCH_3$), 4.17 (q, $^3J$ = 7.6 Hz, 2 H, $OCH_2CH_3$), 7.37-7.42 (m, 3 H, $CH_{Ph}$), 7.50 (s, 1 H, $CH_{Ar}$) 7.54-7.70 (m, 2 H, $CH_{Ph}$), 11.32 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.8, 16.0 ($CH_3$), 52.9 ($OCH_3$), 61.8 ($OCH_2$), 110.2 (*C*$COOCH_3$), 128.0 ($C_{Ar}$), 128.4 (3×$CH_{Ph}$), 129.9 (2×$CH_{Ph}$), 132.4, 135.1

($C_{Ar}$), 136.3 ($CH_{Ar}$), 144.0 ($C_{Ar}$), 161.6 (*C*OH), 167.7, 170.1, 194.8 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 3062 (w), 2980 (w), 2926 (w), 2853 (w), 1729 (m), 1666 (w), 1597 (s), 1493 (w), 1448 (m), 1391 (w), 1366 (m), 1262 (s), 1236 (s), 1181 (m), 1124 (m), 1096 (m), 1076 (m), 1055 (m), 1013 (m), 961 (m), 931 (m), 894 (m), 870 (m), 833 (m), 763 (s), 700 (s), 628 (m). GC-MS (EI, 70 eV): *m/z* (%) = 342 ([M]$^+$, 9), 264 (14), 238 (13), 199 (9), 147 (100), 105 (65), 91 (13), 85 (16), 84 (10), 77 (24), 71 (18), 69 (36), 57 (26), 55 (10), 43 (14). HRMS (EI): Calcd. for $C_{19}H_{18}O_6$ ([M]$^+$): 342.10979; found: 342.109901.

**diethyl 6-benzoyl-4-ethyl-3-hydroxyphthalate (17i)**

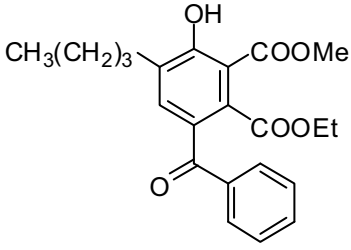


Chemical Formula: $C_{21}H_{22}O_6$
Exact Mass: 370.142

Starting with **16b** (0.414 g, 1.5 mmol) and **4c** (0.499 g, 1.65 mmol), **17i** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.345 g, 62 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 0.98 (t, $^3J$ = 7.0 Hz, 3 H, $CH_2CH_3$), 1.18 (t, $^3J$ = 7.2 Hz, 3 H, $OCH_2CH_3$), 1.33 (t, $^3J$ = 7.9 Hz, 3 H, $OCH_2CH_3$), 2.59 (q, $^3J$ = 7.5 Hz, 2 H, $CH_2CH_3$), 4.09 (q, $^3J$ = 7.2 Hz, 2 H, $OCH_2CH_3$), 4.32 (q, $^3J$ = 7.5 Hz, 2 H, $OCH_2CH_3$), 7.0 (s, 1 H, $CH_{Ar}$), 7.40-7.45 (m, 3 H, $CH_{Ph}$), 7.91-7.94 (m, 2 H,$CH_{Ph}$), 11.48 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.4, 14.0, 14.0 ($CH_3$), 22.7 ($CH_2$), 61.6, 62.5 ($OCH_2$), 110.1 (*C*COOEt), 128.5 ($C_{Ar}$), 128.9 (3×$CH_{Ph}$), 129.9 (2×$CH_{Ph}$), 132.4, 134.5 ($C_{Ar}$), 136.3 ($CH_{Ar}$), 144.1 ($C_{Ar}$), 162.1 (*C*OH), 167.6, 169.7, 190.6 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 3062 (w), 2961 (w), 2925 (w), 2851 (w), 1729 (m), 1666 (w), 1598 (m), 1448 (m), 1391 (w), 1367 (m), 1262 (s), 1238 (s), 1181 (m), 1125 (m), 1095 (m), 1014 (m), 971 (w), 868 (w), 833 (w), 792 (w), 764 (m), 700 (m), 684 (m), 628 (m). GC-MS (EI, 70 eV): *m/z* (%) = 370 ([M]$^+$, 24), 325 (13), 324 (10), 279 (31), 278 (92), 251 (24), 250 (100), 194 (12), 165 (16), 152 (11), 147 (10), 105 (28), 77 (29), 29 (10).

HRMS (EI): Calcd. for $C_{21}H_{22}O_6$ ([M]$^+$): 370.14109; found: 370.141006.

**diethyl 6-benzoyl-4-ethyl-3-hydroxyphthalate (17j)**



Chemical Formula: $C_{22}H_{24}O_6$
Exact Mass: 384.157

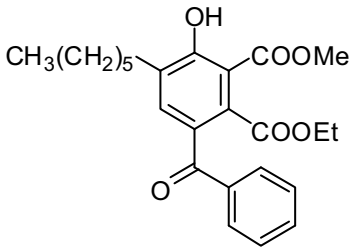
Starting with **16b** (0.414 g, 1.5 mmol) and **4d** (0.522 g, 1.65 mmol), **17j** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.375 g, 65 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 0.80 (t, $^3J$ = 7.1 Hz, 3 H, $(CH_2)_3CH_3$), 1.18 (t, $^3J$ = 8.2 Hz, 3 H, $OCH_2CH_3$), 1.22-1.27 (m, 2 H, $(CH_2)_2CH_2CH_3$), 1.45-1.55 (m, 2 H, $PhCH_2CH_2CH_2CH_3$),

2.58 (t, $^{3}J$ = 7.0 Hz, 2 H, Ph$CH_2(CH_2)_2CH_3$), 3.85 (s, 3 H, $OCH_3$), 4.14 (q, $^{3}J$ = 7.5 Hz, 2 H, $OCH_2CH_3$), 7.17-7.20 (m, 3 H, $CH_{Ph}$), 7.23 (s, 1 H, $CH_{Ar}$), 7.58 (d, $^{3}J$ = 8.8 Hz, 2 H, $CH_{Ph}$), 11.32 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 21.6 ($CH_3$), 22.6, 29.7, 31.6 ($CH_2$), 52.9 ($OCH_3$), 61.7 ($OCH_2$), 110.1 (*C*COOMe), 128.4 ($C_{Ar}$), 129.0 (3×$CH_{Ph}$), 130.2 (2×$CH_{Ph}$), 132.2, 134.6 ($C_{Ar}$), 135.9 ($CH_{Ar}$), 144.1 ($C_{Ar}$), 161.3 (*C*OH), 168.1, 170.1, 194.9 (CO).

IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 2953 (w), 2925 (w), 2856 (w), 1734 (m), 1662 (m), 1604 (m),1572 (w), 1439 (m), 1346 (m), 1234 (s), 1168 (m), 1096 (m), 1057 (m), 1016 (m), 956 (m), 915 (w), 865 (w), 812 (m), 761 (m), 721 (m), 585 (m). GC-MS (EI, 70 eV): *m/z* (%) = 384 ([M]$^{+}$, 24), 339 (14), 310 (10), 307 (28), 306 (100), 296 (18), 279 (17), 278 (70), 277 (13), 265 (14), 264 (56), 263 (13), 249 (11), 237 (10), 152 (12), 105 (18), 77 (19).

HRMS (EI): Calcd. for $C_{22}H_{24}O_6$ ([M]$^{+}$): 384.15674; found: 384.156760.

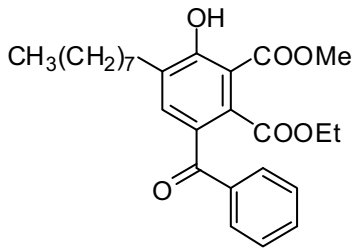
**1-ethyl 2-methyl 6-benzoyl-4-hexyl-3-hydroxyphthalate (17k)**



Chemical Formula: $C_{24}H_{28}O_6$
Exact Mass: 412.189

Starting with **16b** (0.414 g, 1.5 mmol) and **4f** (0.568 g, 1.65 mmol), **17k** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.401 g, 65 %). $^{1}$HNMR (300 MHz, $CDCl_3$): δ = 0.80 (t, $^{3}J$ = 7.8Hz, 3 H, $(CH_2)_5CH_3$), 1.18 (t, $^{3}J$ = 8.5 Hz, 3 H, $OCH_2CH_3$), 1.23-1.28 (m, 6 H, 3×$CH_2$), 1.45-1.55 (m, 2 H, $CH_2$), 2.58 (t, $^{3}J$ = 7.1 Hz, 2 H, Ph$CH_2(CH_2)_4CH_3$), 3.86 (s, 3 H, $OCH_3$), 4.16 (q, $^{3}J$ = 7.2 Hz, 2 H, $OCH_2CH_3$), 7.37-7.42 (m, 3 H, $CH_{Ph}$), 7.51 (s, 1 H, $CH_{Ar}$), 7.54-7.70 (m, 2 H, $CH_{Ph}$), 11.35 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 14.0 ($CH_3$), 22.6, 28.8, 28.9, 29.7, 31.6 ($CH_2$), 52.9 ($OCH_3$), 61.7 ($OCH_2$), 110.2 (*C*COOEt), 128.0 ($C_{Ar}$), 129.9 (3×$CH_{Ph}$), 132.2 (2×$CH_{Ph}$), 132.9, 134.9 ($C_{Ar}$), 135.9 ($CH_{Ar}$), 137.3 ($C_{Ar}$), 161.7 (*C*OH), 167.8, 169.9, 195.1 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 3059 (w), 2954 (w), 2926 (w), 2855 (w), 1733 (m), 1664 (s), 1597 (w), 1576 (w), 1439 (m), 1345 (m), 1232 (s), 1199 (m), 1169 (m), 1097 (w), 1056 (m), 1026 (w), 958 (m), 914 (w), 815 (m), 711 (m), 692 (m), 628 (m), 585 (m). GC-MS (EI, 70 eV): *m/z* (%) = 412 ([M]$^{+}$, 14), 367 (13), 335 (29), 334 (100), 310 (11), 306 (17), 296 (27), 277 (11), 265 (17), 264 (60), 250 (13), 249 (43), 152 (14), 105 (24), 77 (21). HRMS (EI): Calcd. for $C_{24}H_{28}O_6$ ([M]$^{+}$): 412.18804; found: 412.187659.

**1-ethyl 2-methyl 6-benzoyl-3-hydroxy-4-octylphthalate (17l)**

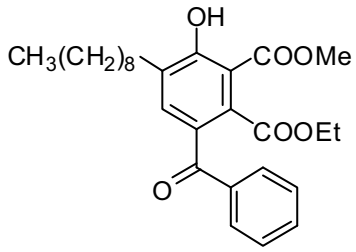



Chemical Formula: $C_{26}H_{32}O_6$
Exact Mass: 440.220

Starting with **16b** (0.414 g, 1.5 mmol) and **4g** (0.614 g, 1.65 mmol), **17l** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.435 g, 66 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 0.81 (t, $^3J$ = 7.7 Hz, 3 H, $CH_3$), 1.20-1.26 (m, 13 H, 1×$CH_3$, 5×$CH_2$), 1.46-1.52 (m, 2 H, $CH_2$), 2.58 (t, $^3J$ = 7.1 Hz, 2 H, Ph$CH_2$($CH_2$)$_6$$CH_3$), 3.86 (s, 3 H, $OCH_3$), 4.15 (q, $^3J$ = 7.4 Hz, 2 H, O$CH_2$$CH_3$), 7.37-7.41 (m, 3 H, $CH_{Ph}$), 7.49 (s, 1 H, $CH_{Ar}$) 7.66-7.69 (m, 2 H, $CH_{Ph}$), 11.36 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 14.0 ($CH_3$), 22.6, 29.0, 29.1, 29.2, 29.3, 29.8, 31.8 ($CH_2$), 53.0 ($OCH_3$), 61.7 ($OCH_2$), 110.2 (*C*COOEt), 128.0 ($C_{Ar}$), 128.3 (3×$CH_{Ph}$), 130.0 (2×$CH_{Ph}$), 132.9, 134.9 ($C_{Ar}$), 135.9 ($CH_{Ar}$), 137.2 ($C_{Ar}$), 161.7 (*C*OH), 167.8, 169.8, 195.1 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 3060 (w), 2953 (m), 2924 (w), 2853 (w), 1733 (m), 1665 (s), 1596 (w), 1576 (w), 1500 (w), 1440 (m), 1346 (m), 1252 (s), 1232 (s), 1199 (m), l 1169 (m), 1097 (w), 1055 (m), 1026 (w), 1016 (w), 959 (m), 915 (w), 865 (w), 814 (m), 773 (w), 711 (m), 691 (m), 665 (w), 628 (w), 585 (w). GC-MS (EI, 70 eV): *m/z* (%) = 440 ([M]$^+$, 12), 395 (14), 363 (30), 362 (100), 310 (12), 296 (32), 277 (11), 265 (16), 264 (54), 263 (12), 250 (14), 249 (25), 238 (28), 152 (12), 105 (25), 77 (17), 43 (8).

HRMS (EI): Calcd. for $C_{26}H_{32}O_6$ ([M]$^+$): 440.21934; found: 440.218868.

**1-ethyl 2-methyl 6-benzoyl-3-hydroxy-4-nonylphthalate (17m)**



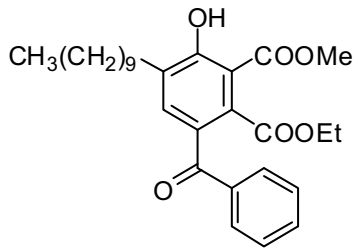

Chemical Formula: $C_{27}H_{34}O_6$
Exact Mass: 454.236

Starting with **16b** (0.414 g, 1.5 mmol) and **4h** (0.638 g, 1.65 mmol), **17m** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.456 g, 67 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 0.80 (t, $^3J$ = 6.4 Hz, 3 H, ($CH_2$)$_8$$CH_3$), 1.18 (t, $^3J$ = 7.4 Hz, 3 H, $OCH_2CH_3$), 1.20-1.25 (m, 12 H, 6×$CH_2$), 1.45-1.52 (m, 2 H, $CH_2$), 2.58 (t, $^3J$ = 7.4 Hz, 2 H, $CH_2$($CH_2$)$_7$$CH_3$), 3.86 (s, 3 H, $OCH_3$), 4.14 (q, $^3J$ = 7.4 Hz, 2 H, O$CH_2$$CH_3$), 7.36-7.41 (m, 3 H, $CH_{Ph}$), 7.51 (s, 1 H, $CH_{Ar}$), 7.68 (d, $^3J$ = 8.0 Hz, 2 H, $CH_{Ph}$), 11.35 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): = 13.9, 14.1 ($CH_3$), 22.6, 29.0, 29.2, 29.3, 29.4, 29.5, 29.8, 31.9 ($CH_2$), 53.0 ($OCH_3$), 61.8 ($OCH_2$), 110.2 (*C*COOMe), 128.1 ($C_{Ar}$), 128.3 (2×$CH_{Ph}$), 130.0 (2×$CH_{Ph}$), 132.4 ($C_{Ar}$), 132.9 ($CH_{Ph}$), 135.0 (*C*COOEt), 136.0 ($CH_{Ar}$), 137.3 ($C_{Ar}$), 161.8 (*C*OH), 167.8, 169.9, 195.1 (CO).

IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 3059 (w), 2953 (w), 2923 (m), 2853 (m), 1734 (m), 1665 (m), 1597 (w), 1476 (w), 1440 (m), 1421 (m), 1346 (m), 1252 (m), 1233 (s), 1200 (m), 1170 (m), 1056 (m), 1026 (m), 960 (m), 865 (w), 768 (m), 711 (m), 692 (m), 665 (w), 628 (w), 586 (w). GC-MS (EI, 70 eV): *m/z* (%) = 454 ($[M]^+$, 10), 409 (5), 376 (40), 296 (10), 264 (15), 242 (12), 169 (15), 129 (33), 116 (80), 105 (100), 97 (13), 84 (24), 77 (50), 57 (23), 43 (55).

HRMS (EI): Calcd. for $C_{27}H_{34}O_6$ ($[M]^+$): 454.23499; found: 454.236232.

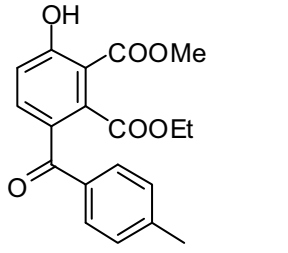
**1-ethyl 2-methyl 6-benzoyl-4-decyl-3-hydroxyphthalate (17n)**



Chemical Formula: $C_{28}H_{36}O_6$
Exact Mass: 468.251

Starting with **16b** (0.414 g, 1.5 mmol) and **4i** (0.661 g, 1.65 mmol), **17n** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.463 g, 66%). $^1$HNMR (300 MHz, $CDCl_3$): δ = 0.80 (t, $^3J$ = 7.1 Hz, 3 H, $(CH_2)_9CH_3$), 1.18 (t, $^3J$ = 7.7 Hz, 3 H, $OCH_2CH_3$), 1.20-1.25 (m, 14 H, 7×$CH_2$), 1.45-1.52 (m, 2 H, $CH_2$), 2.58 (t, $^3J$ = 7.2 Hz, 2 H, $CH_2(CH_2)_8CH_3$), 3.86 (s, 3 H, $OCH_3$), 4.14 (q, $^3J$ = 7.7 Hz, 2 H, $OCH_2CH_3$), 7.36-7.41 (m, 3 H, $CH_{Ph}$), 7.51 (s, 1 H, $CH_{Ar}$), 7.67 (d, $^3J$ = 8.9 Hz, 2 H, $CH_{Ph}$), 11.35 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 14.1 ($CH_3$), 22.7, 29.0, 29.3, 29.4, 29.5, 29.6, 29.7, 29.9, 31.9 ($CH_2$), 53.0 ($OCH_3$), 61.8 ($OCH_2$), 110.2 (*C*COOMe), 128.1 ($C_{Ar}$), 128.3 (2×$CH_{Ph}$), 130.0 (2×$CH_{Ph}$), 132.3 ($C_{Ar}$), 132.9 ($CH_{Ph}$), 135.0 (*C*COOEt), 136.0 ($CH_{Ar}$), 137.3 ($C_{Ar}$), 161.7 (*C*OH), 167.8, 169.9, 195.1 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 2953 (w), 2922 (m), 2853 (m), 1734(m), 1665 (m), 1597 (w),1576 (w), 1440 (m), 1346 (m), 1252 (s), 1233 (s), 1200 (m), 1056 (m), 1026 (m), 959 (m), 926 (w), 866 (w), 815 (m), 711 (m), 692 (m), 586 (m). GC-MS (EI, 70 eV): *m/z* (%) = 468 ($[M]^+$, 32), 422 (23), 407 (8), 390 (100), 363 (13), 296 (55), 277 (13), 264 (75), 249 (26), 238 (48), 209 (6), 180 (7), 152 (7), 105 (15), 77 (5). HRMS (EI): Calcd. for $C_{28}H_{36}O_6$ ($[M]^+$): 468.25064; found: 468.251834.

**1-ethyl 2-methyl 3-hydroxy-6-(4-methylbenzoyl)phthalate (17o)**

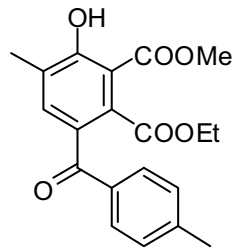


Chemical Formula: $C_{19}H_{18}O_6$
Exact Mass: 342.110

Starting with **16c** (0.435 g, 1.5 mmol) and **4a** (0.429 g, 1.65 mmol), 17**9o** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish solid (0.353 g, 69 %), m.p:70-72°C. $^1$HNMR (300 MHz, $CDCl_3$): δ = 1.22 (t, $^3J$ = 8.8 Hz, 3 H, $OCH_2CH_3$), 2.35 (s, 3 H, $CH_3$), 3.87 (s, 3 H, $OCH_3$), 4.17 (q, $^3J$ = 7.5 Hz, 2 H, $OCH_2CH_3$), 6.99 (d, $^3J$ = 9.0 Hz, 1 H, $CH_{Ar}$),

7.17-7.20 (m, 2 H, $CH_{Tol}$), 7.50-7.59 (m, 3 H, $CH_{Ar,Tol}$), 11.10 (s, 1 H, OH). $^{13}C$ NMR ($CDCl_3$, 75 MHz): δ = 13.9, 21.6 ($CH_3$), 53.0 ($OCH_3$), 61.8 ($OCH_2$), 110.7 (*C*$COOCH_3$), 118.0 ($CH_{Ar}$), 128.0 ($C_{Ar}$), 129.0 (2×$CH_{Tol}$), 130.1 (2×$CH_{Tol}$), 133.4 ($C_{Ar}$), 136.2 ($CH_{Ar}$), 137.4 (*C*COOEt), 143.9 ($C_{Ar}$), 163.4 (*C*OH), 167.6, 169.3, 194.4 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 3030 (w), 2981 (w), 2955 (w), 2851 (w), 1731 (m), 1658 (s), 1604 (m), 1582 (m), 1441 (m), 1324 (m), 1245 (s), 1213 (s), 1181 (s), 1146 (m), 1114 (s), 1029 (s), 959 (m), 937 (m), 833 (m), 811 (m), 759 (m), 728 (m), 686 (m), 639 (m), 587 (s), 534 (m). GC-MS (EI, 70 eV): *m/z* (%) = 342 ($[M]^+$, 42), 297 (22), 296 (28), 266 (30), 265 (32), 251 (12), 239 (16), 238 (100), 223 (16), 210 (14), 191 (23), 182 (11), 181 (15), 153 (13), 152 (11), 120 (10), 119 (75), 91 (43), 65 (13). HRMS (EI): Calcd. for $C_{19}H_{18}O_6$ ($[M]^+$): 342.10979; found: 342.10099.

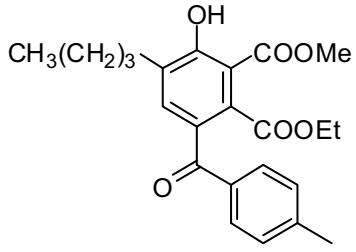
**1-ethyl 2-methyl 3-hydroxy-4-methyl-6-(4-methylbenzoyl)phthalate (17p)**



Chemical Formula: $C_{20}H_{20}O_6$
Exact Mass: 356.126

Starting with **16c** (0.435 g, 1.5 mmol) and **4b** (0.457 g, 1.65 mmol), **17p** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.373 g, 70 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 1.19 (t, $^3J$ = 8.4 Hz, 3 H, $OCH_2CH_3$), 2.20 (s, 3 H, $CH_3$), 2.35 (s, 3 H, $CH_3$), 3.86 (s, 3 H, $OCH_3$), 4.15 (q, $^3J$ = 7.5 Hz, 2 H, $OCH_2CH_3$), 7.17-7.21 (m, 2 H, $CH_{Tol}$), 7.37 (s, 1 H, $CH_{Ar}$), 7.56-7.59 (m, 2 H, $CH_{Tol}$), 11.32 (s, 1 H, OH). $^{13}C$ NMR ($CDCl_3$, 75 MHz): δ = 14.0, 16.0, 21.7 ($CH_3$), 52.9 ($OCH_3$), 61.7 ($OCH_2$), 110.1 (*C*$COOCH_3$), 127.8 ($C_{Ar}$), 129.0 (2×$CH_{Tol}$), 129.7 (2×$CH_{Tol}$), 132.2, 134.6, 134.7 ($C_{Ar}$), 136.6 ($CH_{Ar}$), 143.9 ($C_{Ar}$), 161.9 (*C*OH), 167.7, 170.0, 194.8 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 3030 (w), 2980 (w), 2954 (w), 1731 (m), 1660 (s), 1604 (m), 1573 (w), 1439 (m), 1408 (m), 1379 (w), 1408 (w), 1379 (w), 1338 (m), 1308 (m), 1236 (s), 1200 (m), 1167 (s), 1113 (w), 1054 (s), 1014 (m), 959 (m), 910 (w), 886 (w), 866 (w), 810 (m), 761 (m), 711 (m), 658 (w), 642 (w), 628 (w), 601 (m), 582 (m). GC-MS (EI, 70 eV): *m/z* (%) = 356 ($[M]^+$, 57), 324 (26), 311 (27), 310 (55), 280 (24), 279 (49), 278 (100), 253 (13), 252 (83), 250 (11), 224 (11), 205 (13), 165 (10), 161 (17), 119 (55), 91 (30), 71 (11), 69 (14), 57 (16), 55 (10), 43 (10). HRMS (EI): Calcd. for $C_{20}H_{20}O_6$ ($[M]^+$): 356.12544; found: 356.125057.

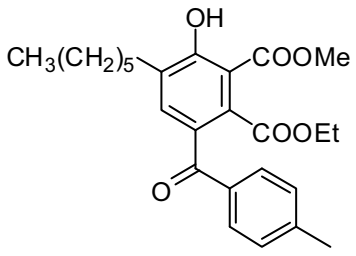
**1-ethyl 2-methyl 4-butyl-3-hydroxy-6-(4-methylbenzoyl)phthalate (17q)**




Chemical Formula: $C_{23}H_{26}O_6$
Exact Mass: 398.173

Starting with**16c** (0.435 g, 1.5 mmol) and **4d** (0.522 g, 1.65 mmol), **17q** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.481 g, 70 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 0.80 (t, $^3J$ = 7.7 Hz, 3 H, $(CH_2)_3CH_3$), 1.18 (t, $^3J$ = 8.8 Hz, 3 H, $OCH_2CH_3$), 1.22-1.27 (m, 2 H, $(CH_2)_2CH_2CH_3$), 1.45-1.55 (m, 2 H, $CH_2$), 2.36 (s, 3 H, $CH_3$), 2.61 (t, $^3J$ = 7.7 Hz, 2 H, $PhCH_2(CH_2)_2CH_3$), 3.85 (s, 3 H, $OCH_3$), 4.16 (q, $^3J$ = 7.6 Hz, 2 H, $OCH_2CH_3$), 7.17-7.21 (m, 2 H, $CH_{Tol}$), 7.36 (s, 1 H, $CH_{Ar}$), 7.56-7.59 (m, 2 H, $CH_{Tol}$), 11.32 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 14.0, 21.6 ($CH_3$), 22.9, 29.8, 31.3 ($CH_2$), 53.0 ($OCH_3$), 62.1 ($OCH_2$), 110.1 ($C$COOCH$_3$), 128.2 ($C_{Ar}$), 129.2 (2×$CH_{Tol}$), 130.5 (2×$CH_{Tol}$), 132.2, 134.6, 134.8 ($C_{Ar}$), 136.6 ($CH_{Ar}$), 143.7 ($C_{Ar}$), 162.2 ($C$OH), 168.1, 170.3, 195.1 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 2955 (w), 2926 (w), 2858 (w), 1732 (m), 1662 (m), 1604 (m), 1572 (w), 1439 (m), 1421 (m), 1346 (m), 1310 (m), 1234 (s), 1206 (m), 1167 (m), 1093 (w), 1055 (m), 1016 (m), 960 (m), 911 (w), 865 (w), 836 (w), 812 (m), 761 (w), 729 (w), 664 (w), 585 (w). GC-MS (EI, 70 eV): *m/z* (%) = 398 ([M]$^+$, 28), 353 (16), 324 (12), 321 (29), 320 (100), 310 (32), 293 (17), 292 (75), 291 (17), 279 (21), 278 (81), 277 (31), 263 (18), 251 (14), 250 (10), 165 (16), 119 (30), 91 (33). HRMS (EI): Calcd. for $C_{23}H_{26}O_6$ ([M]$^+$): 398.17239; found: 398.172357.

**1-ethyl 2-methyl 4-hexyl-3-hydroxy-6-(4-methylbenzoyl)phthalate (17r)**



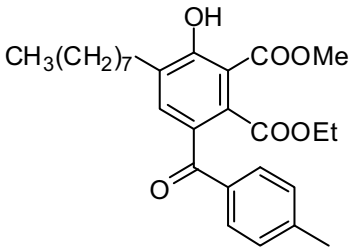

Chemical Formula: $C_{25}H_{30}O_6$
Exact Mass: 426.204

Starting with **16c** (0.435 g, 1.5 mmol) and **4f** (0.568 g, 1.65 mmol), **17r** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.415 g, 65 %).

$^1$HNMR (300 MHz, $CDCl_3$): δ = 0.80 (t, $^3J$ = 7.1 Hz, 3 H, $(CH_2)_5CH_3$), 1.18 (t, $^3J$ = 8.8 Hz, 3 H, $OCH_2CH_3$), 1.20-1.24 (m, 6 H, 3×$CH_2$), 1.46-1.52 (m, 2 H, $CH_2$), 2.36 (s, 3 H, $CH_3$), 2.58 (t, $^3J$ = 7.0 Hz, 2 H, $CH_2(CH_2)_4CH_3$), 3.86 (s, 3 H, $OCH_3$), 4.15 (q, $^3J$ = 7.6 Hz, 2 H, $OCH_2CH_3$), 7.18-7.20 (m, 2 H, $CH_{Tol}$), 7.36 (s, 1 H, $CH_{Ar}$), 7.57-7.60 (m, 2 H, $CH_{Tol}$), 11.32 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 14.0, 21.6 ($CH_3$), 22.5, 29.0, 29.0, 29.7, 31.6 ($CH_2$), 52.9 ($OCH_3$), 61.7 ($OCH_2$), 110.1 ($C$COOMe), 128.4 ($C_{Ar}$), 129.0 (2×$CH_{Tol}$), 130.2 (2×$CH_{Tol}$), 132.2, 134.6, 134.7 ($C_{Ar}$), 135.9 ($CH_{Ar}$), 143.8 ($C_{Ar}$), 161.5 ($C$OH), 167.8, 170.0, 194.9 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 2953 (w), 2925 (w), 2856 (w), 1734

(m), 1663 (m), 1604 (m), 1572 (w), 1439 (m), 1419 (m), 1346 (m), 1234 (s), 1169 (m), 1096 (m), 1057 (m), 1016 (m), 956 (m), 914 (w), 866 (w), 812 (m), 762 (m), 722 (m), 585 (m). GC-MS (EI, 70 eV): *m/z* (%) = 426 ([M]$^+$, 16), 381 (14), 349 (31), 348 (100), 324 (12), 320 (23), 310 (38), 291 (14), 279 (25), 278 (73), 277 (14), 264 (17), 263 (59), 252 (11), 203 (11), 165 (15), 119 (29), 91 (28), 29 (10). HRMS (EI): Calcd. for $C_{25}H_{30}O_6$ ([M]$^+$): 42620369; found: 426.203912.

**1-ethyl 2-methyl 3-hydroxy-6-(4-methylbenzoyl)-4-octylphthalate (17s)**

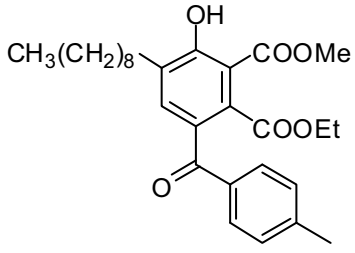


Chemical Formula: $C_{27}H_{34}O_6$
Exact Mass: 454.236

Starting with **16c** (0.435 g, 1.5 mmol) and**4g** (0.614 g, 1.65 mmol), **17s** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.435 g, 64 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 0.80 (t, $^3J$ = 7.1 Hz, 3 H, $(CH_2)_7CH_3$), 1.18 (t, $^3J$ = 8.9 Hz, 3 H, $OCH_2CH_3$), 1.20-1.27 (m, 10 H, 5×$CH_2$), 1.46-1.53 (m, 2 H, $CH_2$), 2.36 (s, 3 H, $CH_3$), 2.58 (t, $^3J$ = 7.0 Hz, 2 H, $CH_2(CH_2)_6CH_3$), 3.86 (s, 3 H, $OCH_3$), 4.14 (q, $^3J$ = 7.5 Hz, 2 H, $OCH_2CH_3$), 7.17-7.20 (m, 2 H, $CH_{Tol}$), 7.36 (s, 1 H, $CH_{Ar}$), 7.57-7.60 (m, 2 H, $CH_{Tol}$), 11.32 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.8, 14.0, 21.6 ($CH_3$), 22.6, 29.0, 29.2, 29.3, 29.3, 29.7, 31.8 ($CH_2$), 52.9 ($OCH_3$), 61.7 ($OCH_2$), 110.1 (*C*COOMe), 128.4 ($C_{Ar}$), 129.0 (2×$CH_{Tol}$), 130.2 (2×$CH_{Tol}$), 132.2, 134.6, 134.7 ($C_{Ar}$), 135.8 ($CH_{Ar}$), 143.8 ($C_{Ar}$), 161.5 (*C*OH), 167.8, 169.9, 194.8 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 2953 (w), 2923 (w), 2853 (w), 1735 (m), 1663 (m), 1605 (m), 1572 (w), 1439 (m), 1419 (m), 1346 (m), 1234 (s), 1169 (m), 1055 (m), 1016 (m), 960 (m), 915 (w), 866 (w), 812 (m), 761 (m), 719 (m), 585 (m). GC-MS (EI, 70 eV): *m/z* (%) = 454 ([M]$^+$, 13), 409 (16), 408 (13), 377 (32), 376 (100), 348 (324), 311 (11), 310 (47), 291 (16), 279 (25), 278 (71), 277 (20), 265 (11), 264 (20), 263 (43), 253 (10), 252 (27), 250 (10), 207 (16), 165 (15), 119 (36), 91 (28), 44 (11), 43 (10), 41 (10), 29 (11) .

HRMS (EI): Calcd. for $C_{27}H_{34}O_6$ ([M]$^+$): 454.23499; found: 454.234275.

**1-ethyl 2-methyl 3-hydroxy-6-(4-methylbenzoyl)-4-nonylphthalate (17t)**

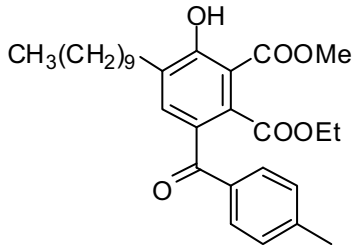


Chemical Formula: $C_{28}H_{36}O_6$
Exact Mass: 468.251

Starting with **16c** (0.435 g, 1.5 mmol) and **4h** (0.638 g, 1.65 mmol), **17t** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.463 g, 66 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 0.80 (t, $^3J$ = 7.1 Hz, 3 H, $(CH_2)_8CH_3$), 1.18 (t, $^3J$ = 8.9 Hz, 3 H, $OCH_2CH_3$), 1.20-1.27 (m, 12 H, 6×$CH_2$), 1.46-1.53 (m, 2 H, $CH_2$), 2.36 (s, 3 H, $CH_3$), 2.58 (t,

$^3J$ = 7.0 Hz, 2 H, $CH_2(CH_2)_7CH_3$), 3.86 (s, 3 H, $OCH_3$), 4.14 (q, $^3J$ = 7.5 Hz, 2 H, $OCH_2CH_3$), 7.17-7.20 (m, 2 H, $CH_{Tol}$), 7.36 (s, 1 H, $CH_{Ar}$), 7.57-7.60 (m, 2 H, $CH_{Tol}$), 11.32 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.8, 14.0, 21.6 ($CH_3$), 22.6, 29.0, 29.2, 29.3, 29.3, 29.4, 29.7, 31.8 ($CH_2$), 52.9 ($OCH_3$), 61.7 ($OCH_2$), 110.1 (*C*COOMe), 128.4 ($C_{Ar}$), 129.0 (2×$CH_{Tol}$), 130.2 (2×$CH_{Tol}$), 132.2, 134.6, 134.7 ($C_{Ar}$), 135.8 ($CH_{Ar}$), 143.8 ($C_{Ar}$), 161.5 (*C*OH), 167.8, 169.9, 194.8 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 2953 (w), 2923 (w), 2853 (w), 1735 (m), 1663 (m), 1605 (m), 1572 (w), 1439 (m), 1419 (m), 1346 (m), 1234 (s), 1169 (m), 1055 (m), 1016 (m), 960 (m), 915 (w), 866 (w), 812 (m), 761 (m), 719 (m), 585 (m). GC-MS (EI, 70 eV): *m/z* (%) = 468 ($[M]^+$, 23), 423 (13), 390 (86), 363 (9), 324 (10), 310 (31), 291 (8), 278 (39), 263 (20), 169 (14), 135 (50), 119 (100), 91 (46), 84 (12), 57 (15). HRMS (EI): Calcd. for $C_{28}H_{37}O_6$ $[(M+H)]^+$: 469.25847; found: 469.25827

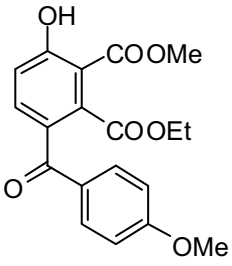
**1-ethyl 2-methyl 4-decyl-3-hydroxy-6-(4-methylbenzoyl)phthalate (17u)**



Chemical Formula: $C_{29}H_{38}O_6$
Exact Mass: 482.267

Starting with **16c** (0.435 g, 1.5 mmol) and **4i** (0.661 g, 1.65 mmol), **17u** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.470 g, 65 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 0.80 (t, $^3J$ = 6.4 Hz, 3 H, $(CH_2)_9CH_3$), 1.18 (t, $^3J$ = 7.5 Hz, 3 H, $OCH_2CH_3$), 1.20-1.25 (m, 14 H, 7×$CH_2$), 1.45-1.51 (m, 2 H, $CH_2$), 2.35 (s, 3 H, $CH_3$), 2.58 (t, $^3J$ = 7.5 Hz, 2 H, $CH_2(CH_2)_8CH_3$), 3.85 (s, 3 H, $OCH_3$), 4.14 (q, $^3J$ = 7.2 Hz, 2 H, $OCH_2CH_3$), 7.17-7.19 (m, 2 H, $CH_{Tol}$), 7.36 (s, 1 H, $CH_{Ar}$), 7.57-7.59 (m, 2 H, $CH_{Tol}$), 11.32 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 14.1, 21.7 ($CH_3$), 22.7, 29.1, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 31.9 ($CH_2$), 53.0 ($OCH_3$), 61.7 ($OCH_2$), 110.2 (*C*COOMe), 128.5 ($C_{Ar}$), 129.0 (2×$CH_{Tol}$), 130.3 (2×$CH_{Tol}$), 132.3, 134.7 ($C_{Ar}$), 134.8 (*C*COOEt), 136.0 ($CH_{Ar}$), 143.8 ($C_{Ar}$), 161.5 (*C*OH), 167.9, 169.9, 194.8 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 2953 (w), 2922 (m), 2853 (m), 1735 (m), 1664 (m), 1605 (m), 1573 (w), 1439 (m), 1420 (m), 1347 (m), 1235 (s), 1169 (m), 1057 (m), 1018 (m), 960 (m), 888 (w), 866 (w), 813 (m), 762 (m), 719 (m), 586 (m). GC-MS (EI, 70 eV): *m/z* (%) = 482 ($[M]^+$, 14), 436 (14), 404 (74), 377 (18), 324 (11), 310 (32), 291 (13), 278 (62), 263 (29), 223 (9), 194 (11), 165 (16), 135 (100), 119 (84), 91 (49), 55 (22), 43 (91). HRMS (EI): Calcd. for $C_{29}H_{38}O_6$ ($[M]^+$): 482.26629; found: 482.267429.

**1-ethyl 2-methyl 3-hydroxy-6-(4-methoxybenzoyl)phthalate (17v)**

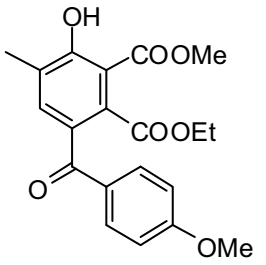


Chemical Formula: $C_{19}H_{18}O_7$
Exact Mass: 358.105

Starting with **16d** (0.459 g, 1.5 mmol) and **4a** (0.429 g, 1.65 mmol), **17v** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.333 g, 62 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 1.21 (t, $^3J$ = 7.7 Hz, 3 H, $OCH_2\mathit{CH_3}$), 3.80 (s, 3 H, $OCH_3$), 3.87 (s, 3 H, $OCH_3$), 4.18 (q, $^3J$ = 7.8 Hz, 2 H, $O\mathit{CH_2}CH_3$), 6.84-6.87 (m, 2 H, $CH_{PhOMe}$), 7.0 (d, $^3J$ = 8.8 Hz, 1 H, $CH_{Ar}$), 7.51 (d, $^3J$ = 8.5 Hz, 1 H, $CH_{Ar}$), 7.64-7.69 (m, 2 H, $CH_{PhOMe}$), 11.56 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.7 ($CH_3$), 52.7, 55.4 ($OCH_3$), 61.7 ($OCH_2$), 110.7 ($\mathit{C}COOCH_3$), 113.0 (2×$CH_{PhOMe}$), 118.2 ($CH_{Ar}$), 129.3, 129.7, 132.0 ($C_{Ar}$), 132.5 (2×$CH_{PhOMe}$), 135.9 ($CH_{Ar}$), 137.0 ($C_{Ar}$), 163.6 (*C*OH), 167.4, 169.4, 193.4 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 3076 (w), 2979 (w), 2955 (w), 2903 (w), 2841 (w), 1729 (m), 1676 (m), 1655 (m), 1596 (s), 1509 (m), 1441 (m), 1310 (m), 1246 (s), 1218 (s), 1162 (s), 1146 (s), 1114 (m), 1025 (s), 958 (m), 912 (m), 842 (m), 811 (m), 771 (m), 728 (m), 689 (w), 635 (w), 593 (m), 535 (w). GC-MS (EI, 70 eV): *m/z* (%) = 358 ([M]$^+$, 60), 313 (21), 312 (22), 282 (36), 281 (33), 255 (18), 254 (100), 253 (31), 226 (17), 225 (14), 191 (26), 135 (86), 119 (15), 107 (11), 92 (20), 77 (26).

HRMS (EI): Calcd. for $C_{19}H_{18}O_7$ ([M]$^+$): 358.10470; found: 358.104802.

**1-ethyl 2-methyl 3-hydroxy-6-(4-methoxybenzoyl)-4-methylphthalate (17w)**



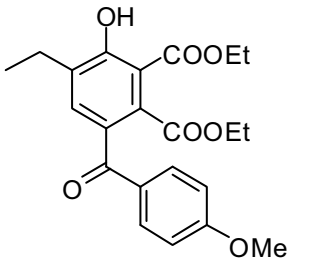
Chemical Formula: $C_{20}H_{20}O_7$
Exact Mass: 372.121

Starting with **16d** (0.459 g, 1.5 mmol) and **4b** (0.457 g, 1.65 mmol), **17w** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.351 g, 63 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 1.18 (t, $^3J$ = 7.4 Hz, 3 H, $OCH_2\mathit{CH_3}$), 2.21 (s, 3 H, $CH_3$), 3.81 (s, 3 H, $OCH_3$), 3.85 (s, 3 H, $OCH_3$), 4.11 (q, $^3J$ = 7.5 Hz, 2 H, $O\mathit{CH_2}CH_3$), 6.84-6.87 (m, 2 H, $CH_{PhOMe}$), 7.36 (s, 1 H, $CH_{Ar}$), 7.65-7.70 (m, 2 H, $CH_{PhOMe}$), 11.26 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.8, 14.0 ($CH_3$), 53.0, 55.8 ($OCH_3$), 61.8, ($OCH_2$), 110.1 ($\mathit{C}COOCH_3$), 113.5 (2×$CH_{PhOMe}$), 127.7, 128.9, 129.9 ($C_{Ar}$), 132.7 (2×$CH_{PhOMe}$), 134.6 ($C_{Ar}$), 136.1 ($CH_{Ar}$), 161.6 ($C_{Ar}$), 163.4 (*C*OH), 168.1, 170.3, 193.9 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 2979 (w), 2955 (w), 2936 (w), 2841 (w), 2254 (w), 1731 (m), 1671 (m), 1655 (m), 1596 (s), 1573 (m), 1509 (m), 1439 (m), 1413 (m), 1380 (w), 1340 (m), 1305 (m), 1238 (s), 1200 (m), 1161 (s), 1111 (m), 1054 (s), 1018 (m), 959 (m), 910 (m), 844 (m), 810

(m), 746 (m), 728 (m), 645 (m), 604 (m). GC-MS (EI, 70 eV): *m/z* (%) = 372 ($[M]^+$, 80), 340 (21), 327 (29), 326 (58), 296 (33), 295 (55), 294 (100), 269 (13), 268 (81), 267 (25), 240 (19), 239 (12), 238 (10), 205 (12), 135 (65), 133 (11), 92 (12), 77 (16).

HRMS (EI): Calcd. for $C_{20}H_{20}O_7$ ($[M]^+$): 372.12035; found: 372.120601.

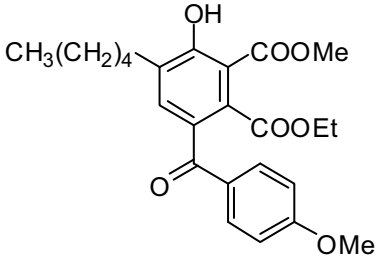
**diethyl 4-ethyl-3-hydroxy-6-(4-methoxybenzoyl)phthalate (17x)**



Chemical Formula: $C_{22}H_{24}O_7$
Exact Mass: 400.152

Starting with **16d** (0.459 g, 1.5 mmol) and **4c** (0.499 g, 1.65 mmol), **17x** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.335 g, 56 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 1.11 (t, $^3J$ = 7.5 Hz, 3 H, $CH_2CH_3$), 1.15 (t, $^3J$ = 7.3 Hz, 3 H, $OCH_2CH_3$), 1.31 (t, $^3J$ = 7.9 Hz, 3 H, $OCH_2CH_3$), 2.63 (q, $^3J$ = 7.5 Hz, 2 H, $CH_2CH_3$), 3.80 (s, 3 H, $OCH_3$), 4.09 (q, $^3J$ = 7.1 Hz, 2 H, $OCH_2CH_3$), 4.32 (q, $^3J$ = 7.2 Hz, 2 H, $OCH_2CH_3$), 6.85-6.87 (m, 2 H, $CH_{PhOMe}$), 7.35 (s, 1 H, $CH_{Ar}$), 7.66-7.69 (m, 2 H, $CH_{PhOMe}$), 11.38 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.4, 13.7, 13.7 ($CH_3$), 22.9 ($CH_2$), 55.5 ($OCH_3$), 61.5, 62.5 ($OCH_2$), 110.1 (*C*COOEt), 113.5 (2×$CH_{PhOMe}$), 128.9, 129.9 ($C_{Ar}$), 132.4 (2×$CH_{PhOMe}$), 133.5, 134.3 ($C_{Ar}$), 134.4 ($CH_{Ar}$), 161.3 ($C_{Ar}$), 163.5 (*C*OH), 167.7, 169.5, 194.0 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 2975 (w), 2935 (w), 2840 (w), 1731 (m), 1657 (m), 1596 (s), 1573 (m), 1509 (m), 1442 (m), 1417 (m), 1374 (m), 1339 (m), 1305 (m), 1251 (s), 1235 (s), 1185 (m), 1163 (s), 1095 (m), 1053 (w), 1020 (s), 986 (m), 908 (m), 846 (m), 772 (m), 762 (m), 704 (m), 605 (m), 586 (m). GC-MS (EI, 70 eV): *m/z* (%) = 400 ($[M]^+$, 29), 355 (16), 354 (17), 310 (13), 309 (32), 308 (100), 282 (14), 281 (16), 280 (65), 279 (11), 219 (18), 147 (12), 135 (62), 107 (12), 92 (14), 77 (14). HRMS (EI): Calcd. for $C_{22}H_{24}O_7$ ($[M]^+$): 400.15165; found: 400.151332.

**1-ethyl 2-methyl 3-hydroxy-6-(4-methoxybenzoyl)-4-pentylphthalate (17y)**



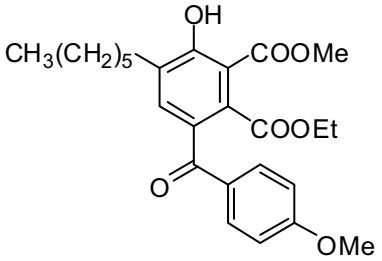
Chemical Formula: $C_{24}H_{28}O_7$
Exact Mass: 428.184

Starting with **16d** (0.459 g, 1.5 mmol) and **4e** (0.456 g, 1.65 mmol), **17y** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.411 g, 64 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 0.75 (t, $^3J$ = 7.2 Hz, 3 H, $(CH_2)_4CH_3$), 1.14 (t, $^3J$ = 7.3 Hz, 3 H, $OCH_2CH_3$), 1.17-1.21 (m, 4 H, 2×$CH_2$), 1.43-1.51 (m, 2 H, $CH_2$), 2.54 (t, $^3J$ = 6.9 Hz, 2 H,

Ar*CH*$_2$(CH$_2$)$_3$CH$_3$), 3.75 (s, 3 H, OCH$_3$), 3.80 (s, 3 H, OCH$_3$), 4.08 (q, $^3J$ = 7.3 Hz, 2 H, O*CH*$_2$CH$_3$), 6.79-6.84 (m, 2 H, CH$_{PhOMe}$), 7.30 (s, 1 H, CH$_{Ar}$), 7.60-7.65 (m, 2 H, CH$_{PhOMe}$), 11.21 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): δ = 13.9, 14.0, (CH$_3$), 22.4, 28.7, 29.7, 31.6 (CH$_2$), 52.9, 55.5 (OCH$_3$), 61.7 (OCH$_2$), 110.1 (*C*COOMe), 113.6 (2×CH$_{PhOMe}$), 128.8, 130.0, 132.3 (C$_{Ar}$), 132.4 (2×CH$_{PhOMe}$), 134.5 (*C*COOEt), 135.5 (CH$_{Ar}$), 161.3 (C$_{Ar}$), 163.6 (*C*OH), 167.8, 169.9, 193.9 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 2955 (w), 2930 (w), 2858 (w), 1732 (m), 1659 (m), 1598 (m), 1573 (w), 1510 (w), 1440 (m), 1418 (m), 1351 (m), 1254 (s), 1242 (s), 1165 (s), 1057 (m), 1027 (m), 961 (w), 846 (m), 814 (m), 775 (w), 706 (w), 586 (w). GC-MS (EI, 70 eV): *m/z* (%) = 428 ([M]$^+$, 27), 383 (12), 350 (97), 340 (14), 326 (60), 294 (100), 239 (6), 203 (9), 147 (6), 135 (56), 92 (7), 77 (11), 41 (5).

HRMS (EI): Calcd. for C$_{24}$H$_{28}$O$_7$ ([M]$^+$): 428.18295; found: 428.182763

**1-ethyl 2-methyl 4-hexyl-3-hydroxy-6-(4-methoxybenzoyl)phthalate (17z)**

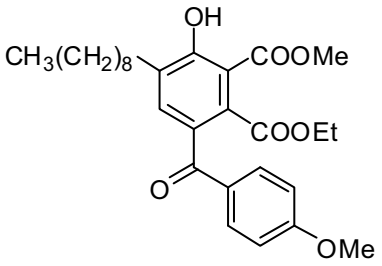


Chemical Formula: C$_{25}$H$_{30}$O$_7$
Exact Mass: 442.199

Starting with **16d** (0.459 g, 1.5 mmol) and **4f** (0.568 g, 1.65 mmol), **17z** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.404 g, 61 %). $^1$HNMR (300 MHz, CDCl$_3$): δ = 0.80 (t, $^3J$ = 6.3 Hz, 3 H, (CH$_2$)$_5$*CH*$_3$), 1.19 (t, $^3J$ = 7.2 Hz, 3 H, OCH$_2$*CH*$_3$), 1.21-1.28 (m, 6 H, 3×CH$_2$), 1.48-1.52 (m, 2 H, CH$_2$), 2.59 (t, $^3J$ = 7.5 Hz, 2 H, *CH*$_2$(CH$_2$)$_4$CH$_3$), 3.80 (s, 3 H, OCH$_3$), 3.85 (s, 3 H, OCH$_3$), 4.12 (q, $^3J$ = 7.2 Hz, 2 H, O*CH*$_2$CH$_3$), 6.85-6.87 (m, 2 H, CH$_{PhOMe}$), 7.34 (s, 1 H, CH$_{Ar}$), 7.66-7.69 (m, 2 H, CH$_{PhOMe}$), 11.26 (s, 1 H, OH). $^{13}$C NMR (CDCl$_3$, 75 MHz): δ = 13.8, 14.0 (CH$_3$), 22.5, 28.9, 29.0, 29.7, 31.6 (CH$_2$), 52.9, 55.4 (OCH$_3$), 61.6 (OCH$_2$), 110.1 (*C*COOMe), 113.5 (2×CH$_{PhOMe}$), 128.7, 130.3, 132.1 (C$_{Ar}$), 132.4 (2×CH$_{PhOMe}$), 134.4 (C$_{Ar}$), 135.4 (CH$_{Ar}$), 161.2 (C$_{Ar}$), 163.5 (*C*OH), 167.8, 169.8, 194.8 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 2954 (w), 2926 (w), 2855 (w), 1732 (m), 1659 (m), 1609 (w) 1439 (m), 1351 (m), 1252 (s), 1240 (s), 1221 (m), 1164 (s), 1097 (w), 1058 (m), 1026 (m), 960 (w), 845 (w), 775 (w), 726 (w), 606 (w), 529 (w). GC-MS (EI, 70 eV): *m/z* (%) = 442 ([M]$^+$, 27), 397 (15), 365 (27), 364 (100), 342 (12), 340 (13), 336 (19), 327 (11), 326 (64), 307 (12), 295 (17), 294 (83), 280 (11), 279 (40), 135 (39), 94 (42), 55 (16).

HRMS (ESI): Calcd. for C$_{25}$H$_{31}$O$_7$ ([M+H]$^+$): 443.20643; found: 443.20632.

**1-ethyl 2-methyl 3-hydroxy-6-(4-methoxybenzoyl)-4-nonylphthalate (17aa)**

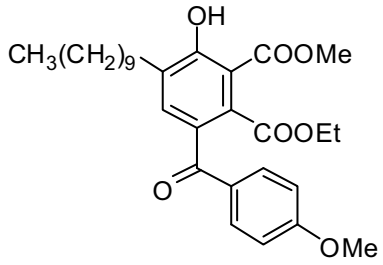



Chemical Formula: $C_{28}H_{36}O_7$
Exact Mass: 484.246

Starting with **16d** (0.459 g, 1.5 mmol) and **4h** (0.638 g, 1.65 mmol), **17aa** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.457 g, 63 %).

$^1$HNMR (300 MHz, $CDCl_3$): δ = 0.79 (t, $^3J$ = 7.1 Hz, 3 H, $(CH_2)_8CH_3$), 1.19 (t, $^3J$ = 7.5 Hz, 3 H, $OCH_2CH_3$), 1.21-1.26 (m, 12 H, 6×$CH_2$), 1.45-1.52 (m, 2 H, $CH_2$), 2.58 (t, $^3J$ = 7.5 Hz, 2 H, $ArCH_2(CH_2)_7CH_3$), 3.80 (s, 3 H, $OCH_3$), 3.85 (s, 3 H, $OCH_3$), 4.13 (q, $^3J$ = 7.1 Hz, 2 H, $OCH_2CH_3$), 6.83-6.88 (m, 2 H, $CH_{PhOMe}$), 7.34 (s, 1 H, $CH_{Ar}$), 7.65-7.70 (m, 2 H, $CH_{PhOMe}$), 11.26 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 14.1 ($CH_3$), 22.6, 29.0, 29.2, 29.3, 29.4, 29.5, 29.8, 31.9 ($CH_2$), 52.9, 55.5 ($OCH_3$), 61.7 ($OCH_2$), 110.1 (*C*COOMe), 113.6 (2×$CH_{PhOMe}$), 128.8, 130.0, 132.3 ($C_{Ar}$), 132.5 (2×$CH_{PhOMe}$), 134.5 (*C*COOEt), 135.5 ($CH_{Ar}$), 161.3 ($C_{Ar}$), 163.6 (*C*OH), 167.8, 169.9, 193.8 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 2954 (w), 2924 (m), 2853 (w), 2255 (w), 1732 (m), 1672 (m), 1659 (m), 1598 (m), 1574 (w), 1509 (w), 1440 (m), 1418 (m), 1348 (m), 1306 (m), 1253 (s), 1240 (s), 1201 (m), 1164 (s), 1111 (w), 1058 (m), 1028 (m), 961 (w), 907 (m), 867 (w), 845 (m), 727 (s), 647 (m), 606 (m), 586 (w). GC-MS (EI, 70 eV): *m/z* (%) = 484 ([M]$^+$, 23), 438 (26), 406 (100), 384 (19), 340 (15), 326 (80), 307 (14), 294 (83), 279 (35), 268 (17), 239 (17), 203 (7), 135 (34), 77 (4), 43 (7). HRMS (EI): Calcd. for $C_{28}H_{36}O_7$ ([M]$^+$): 484.24555; found: 484.245787.

**1-ethyl 2-methyl 4-decyl-3-hydroxy-6-(4-methoxybenzoyl)phthalate (17ab)**



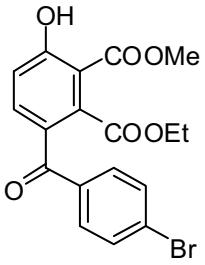

Chemical Formula: $C_{29}H_{38}O_7$
Exact Mass: 498.262

Starting with **16d** (0.459 g, 1.5 mmol) and **4i** (0.661 g, 1.65 mmol), **17ab** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.477 g, 64 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 0.81 (t, $^3J$ = 7.2 Hz, 3 H, $(CH_2)_9CH_3$), 1.15 (t, $^3J$ = 8.9 Hz, 3 H, $OCH_2CH_3$), 1.17-1.22 (m, 14 H, 7×$CH_2$), 1.45-1.52 (m, 2 H, $CH_2$), 2.58 (t, $^3J$ = 7.5 Hz, 2 H, $CH_2(CH_2)_8CH_3$), 3.80 (s, 3 H, $OCH_3$), 3.85 (s, 3 H, $OCH_3$), 4.15 (q, $^3J$ = 7.5 Hz, 2 H, $OCH_2CH_3$), 6.84-6.87 (m, 2 H, $CH_{PhOMe}$), 7.34 (s, 1 H, $CH_{Ar}$), 7.66-7.69 (m, 2 H, $CH_{PhOMe}$), 11.26 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 14.0 ($CH_3$), 22.6, 29.0, 29.3, 29.3, 29.4, 29.4, 29.5, 29.7, 31.8 ($CH_2$), 52.9, 55.4 ($OCH_3$), 61.6 ($OCH_2$), 110.1 (*C*COOMe), 113.5 (2×$CH_{PhOMe}$), 128.8, 129.9, 132.2 ($C_{Ar}$), 132.4 (2×$CH_{PhOMe}$), 134.4 ($C_{Ar}$), 135.4 ($CH_{Ar}$), 161.2 ($C_{Ar}$), 163.5 (*C*OH),

167.8, 169.8, 193.8 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 2954 (w), 2923 (w), 2853 (w), 1732 (m), 1673 (m), 1658 (w) 1598 (m), 1509 (m), 1440 (m), 1417 (m), 1306 (m), 1253 (s), 1240 (s), 1164 (s), 1057 (m), 1027 (m), 907 (m), 844 (m), 812 (m), 727 (s), 605 (w), 585 (w). GC-MS (EI, 70 eV): *m/z* (%) = 499 ($[M+H]^+$), 4.3), 498 (13), 453 (20), 452 (31), 421 (19), 420 (100), 392 (15), 340 (15), 327 (15), 326 (93), 307 (14), 295 (23), 294 (97), 280 (11), 279 (41), 268 (23), 135 (80), 77 (13), 55 (16), 44 (13), 43 (35), 41 (24).

HRMS (ESI): Calcd. for $C_{29}H_{39}O_7$ ($[M+H]^+$): 499.26903; found: 499.26915.

**2-ethyl 1-methyl 3-(4-bromobenzoyl)-6-hydroxyphthalate (17ac)**

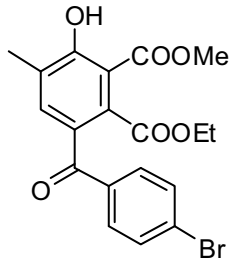


Chemical Formula: $C_{18}H_{15}BrO_6$
Exact Mass: 406.005

Starting with **16e** (0.532 g, 1.5 mmol) and **4a** (0.429 g, 1.65 mmol), **17ac** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.383 g, 63 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 1.23 (t, $^3J$ = 7.5 Hz, 3 H, $OCH_2CH_3$), 3.87 (s, 3 H, $OCH_3$), 4.19 (q, $^3J$ = 7.5 Hz, 2 H, $OCH_2CH_3$), 7.0 (d, $^3J$ = 9.0 Hz, 1 H, $CH_{Ar}$), 7.50 (d, $^3J$ = 8.5 Hz, 1 H, $CH_{Ar}$), 7.54 ($S_{br}$, 4 H, $CH_{PhBr}$), 11.56 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.9 ($CH_3$), 53.1 ($OCH_3$), 62.0 ($OCH_2$), 110.9 ($C$COOCH$_3$), 118.2 ($CH_{Ar}$), 128.2, 130.7 ($C_{Ar}$), 131.4 (2×$CH_{PhBr}$), 131.7 (2×$CH_{PhBr}$), 135.8 ($C$COOEt), 136.1 ($CH_{Ar}$), 137.6 ($C_{Ar}$), 163.7 ($C$OH), 167.4, 169.2, 193.7 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 3085 (w), 2980 (w), 2955 (w), 2902 (w), 1729 (m), 1663 (s), 1583 (s), 1441 (m), 1394 (m), 1325 (m), 1248 (s), 1217 (s), 1174 (m), 1146 (m), 1118 (m), 1068 (m), 1029 (s), 959 (m), 937 (m), 838 (m), 811 (m), 762 (m), 731 (m), 679 (m), 630 (m), 583 (m), 533 (m). GC-MS (EI, 70 eV): *m/z* (%) = 408 ($[M^+]$, $^{81}$Br, 57), 406 ($[M^+]$, $^{79}$Br, 58), 376 (25), 374 (24), 363 (27), 362 (47), 361 (28), 360 (42), 335 (44), 333 (30), 331 (31), 330 (30), 329 (26), 308 (20), 305 (16), 304 (98), 303 (55), 302 (100), 301 (43), 280 (13), 276 (15), 275 (14), 274 (17), 273 (11), 251 (34), 250 (20), 249 (11), 238 (16), 223 (31), 222 (30), 219 (11), 217 (11), 194 (20), 191 (42), 185 (41), 183 (44), 167 (10), 157 (20), 155 (22), 139 (20), 138 (17), 119 (22).

HRMS (EI): Calcd. for $C_{18}H_{15}O_6Br$ ($[M]^+$, $^{79}$Br) : 406.00465; found: 406.003513.

**1-ethyl 2-methyl 6-(4-bromobenzoyl)-3-hydroxy-4-methylphthalate (17ad)**

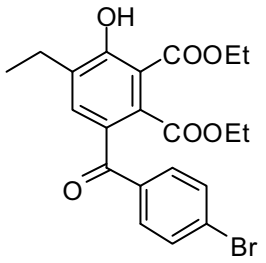



Chemical Formula: $C_{19}H_{17}BrO_6$
Exact Mass: 420.021

Starting with **16e** (0.532 g, 1.5 mmol) and **4b** (0.457 g, 1.65 mmol), **17ad** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.415 g, 66 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 1.20 (t, $^3J$ = 7.6 Hz, 3 H, $OCH_2CH_3$), 2.21 (s, 3 H, $CH_3$), 3.86 (s, 3 H, $OCH_3$), 4.14 (q, $^3J$ = 7.5 Hz, 2 H, $OCH_2CH_3$), 7.34 (s, 1 H, $CH_{Ar}$), 7.54 ($S_{br}$, 4 H, $CH_{PhBr}$), 11.36 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 15.9 ($CH_3$), 53.0 ($OCH_3$), 61.8 ($OCH_2$), 110.0 ($C$COOCH$_3$), 127.0, 128.0, ($C_{Ar}$), 131.4 (2×$CH_{PhBr}$), 131.6 (2×$CH_{PhBr}$), 134.2 ($C_{Ar}$), 135.0 ($C$COOEt), 136.0 ($C_{Ar}$), 136.1 ($CH_{Ar}$), 162.0 ($C$OH), 167.5, 169.7, 194.1 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 3056 (w), 2980 (w), 2955 (w), 1731 (m), 1663 (s), 1583 (m), 1439 (m), 1395 (m), 1337 (m), 1231 (s), 1199 (m), 1166 (s), 1110 (w), 1095 (w), 1069 (m), 1053 (s), 1008 (m), 958 (m), 910 (m), 865 (w), 873 (m), 810 (m), 765 (m), 731 (m), 679 (m), 635 (m), 579 (m). GC-MS (EI, 70 eV): *m/z* (%) = 422 ([M$^+$], $^{81}$Br, 51), 420 ([M$^+$], $^{79}$Br, 61), 391 (12), 390 (44), 389 (10), 388 (43), 377 (29), 376 (56), 375 (30), 374 (52), 346 (17), 345 (34), 343 (31), 342 (65), 319 (14), 318 (93), 317 (21), 316 (100), 290 (14), 288 (17), 265 (22), 264 (25), 252 (20), 237 (20), 235 (11), 205 (26), 185 (41), 183 (42), 181 (14), 180 (14), 157 (25), 155 (25), 152 (36), 151 (15), 133 (23), 76 (12).

HRMS (EI): Calcd. for $C_{19}H_{17}O_6Br$ ([M]$^+$, $^{79}$Br) : 420.02030; found: 420.019964.

**diethyl 6-(4-bromobenzoyl)-4-ethyl-3-hydroxyphthalate (17ae)**



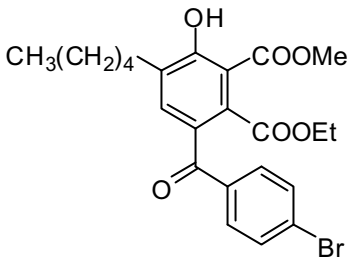

Chemical Formula: $C_{21}H_{21}BrO_6$
Exact Mass: 448.052

Starting with **16e** (0.532 g, 1.5 mmol) and **4c** (0.499 g, 1.65 mmol), **17ae** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.436 g, 65 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 1.10 (t, $^3J$ = 7.6 Hz, 3 H, $CH_2CH_3$), 1.15 (t, $^3J$ = 7.1 Hz, 3 H, $OCH_2CH_3$), 1.29 (t, $^3J$ = 7.2 Hz, 3 H, $OCH_2CH_3$), 2.63 (q, $^3J$ = 7.5 Hz, 2 H, $CH_2CH_3$), 4.12 (q, $^3J$ = 7.4 Hz, 2 H, $OCH_2CH_3$), 4.32 (q, $^3J$ = 7.5 Hz, 2 H, $OCH_2CH_3$), 7.33 (s, 1 H, $CH_{Ar}$), 7.54 ($S_{br}$, 4 H, $CH_{PhBr}$), 11.50 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.3, 13.7, 13.8 ($CH_3$), 22.9 ($CH_2$), 61.7, 62.7 ($OCH_2$), 110.2 ($C$COOEt), 127.0, 128.0, ($C_{Ar}$), 131.4 (2×$CH_{PhBr}$), 131.6 (2×$CH_{PhBr}$), 133.7 ($C_{Ar}$), 134.6 ($CH_{Ar}$), 134.8, 136.0 ($C_{Ar}$), 161.8 ($C$OH), 167.6, 169.4, 194.1 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 3056 (w), 2977 (w), 2934 (w), 2873 (w), 1731 (m), 1662 (s), 1583 (m), 1442 (w),

1421 (m), 1394 (m), 1374 (m), 1337 (m), 1300 (m), 1227 (s), 1172 (s), 1095 (m), 1068 (m), 1052 (m), 1009 (m), 907 (m), 844 (m), 815 (m), 730 (m), 687 (m), 620 (m), 579 (m). GC-MS (EI, 70 eV): *m/z* (%) = 450 ([$M^+$], $^{81}$Br, 36), 448 ([$M^+$], $^{79}$Br, 38), 405 (18), 404 (18), 403 (19), 402 (18), 359 (30), 358 (100), 357 (33), 356 (95), 335 (10), 334 (10), 331 (19), 330 (89), 329 (23), 328 (84), 305 (11), 294 (10), 288 (13), 278 (25), 277 (70), 274 (11), 272 (11), 261 (10), 259 (11), 253 (10), 251 (11), 250 (10), 249 (21), 221 (12), 219 (17), 185 (71), 184 (14), 183 (71), 165 (28), 158 (33), 157 (27), 155 (27), 153 (10), 152 (14), 147 (19), 141 (13), 140 (12), 139 (16), 135 (12), 130 (23), 119 (10), 115 (22), 111 (10), 105 (10), 97 (14), 95 (11), 91 (12), 85 (11), 84 (14), 83 (15), 81 (12), 77 (15), 76 (13), 75 (13), 73 (20), 71 (52), 70 (13), 69 (25), 67 (11), 57 (23), 55 (24), 45 (12), 43 (87), 42 (10), 41 (29).

HRMS (EI): Calcd. for $C_{21}H_{21}O_6Br$ ([$M]^+$, $^{79}$Br) : 448.05160; found: 448.051626.

**1-ethyl 2-methyl 6-(4-bromobenzoyl)-3-hydroxy-4-pentylphthalate (17af)**

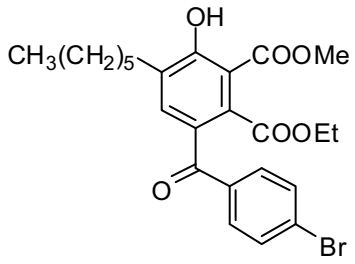


Chemical Formula: $C_{23}H_{25}BrO_6$
Exact Mass: 476.083

Starting with **16e** (0.532 g, 1.5 mmol) and **4e** (0. 0.546 g, 1.65 mmol), **17af** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.465 g, 65 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 0.80 (t, $^3J$ = 7.1 Hz, 3 H, $(CH_2)_4CH_3$), 1.15 (t, $^3J$ = 6.9 Hz, 3 H, $OCH_2CH_3$), 1.18-1.23 (m, 4 H, 2×$CH_2$), 1.41-1.49 (m, 2 H, $CH_2$), 2.53 (t, $^3J$ = 7.2 Hz, 2 H, $CH_2(CH_2)_3CH_3$), 3.81 (s, 3 H, $OCH_3$), 4.10 (q, $^3J$ = 7.6 Hz, 2 H, $OCH_2CH_3$), 7.26 (S, 1 H, $CH_{Ar}$), 7.48 ($S_{br}$, 4 H, $CH_{PhBr}$), 11.30 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 14.0 ($CH_3$), 22.4, 28.7, 29.7, 31.5 ($CH_2$), 53.0 ($OCH_3$), 61.8 ($OCH_2$), 110.3 ($C$COOCH$_3$), 127.6, 128.1 ($C_{Ar}$), 131.4 (2×$CH_{PhBr}$), 131.7 (2×$CH_{PhBr}$), 132.5 ($C_{Ar}$), 135.0 ($C$COOEt), 135.6 ($CH_{Ar}$), 136.0 ($C_{Ar}$), 161.8 ($C$OH), 167.6, 169.7, 194.0 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ =2955 (w), 2929 (w), 2858 (w), 1731 (m), 1668 (m), 1585 (w) 1440 (m), 1348 (m), 1256 (s), 1174 (m), 1070 (w), 1055 (m), 1010 (m), 907 (m), 842 (w), 814 (w), 730 (m), 648 (w), 584 (w). GC-MS (EI, 70 eV): *m/z* (%) = 478 ([$M^+$], $^{81}$Br, 16), 476 ([$M^+$], $^{79}$Br, 16), 433 (14), 431 (13), 401 (27), 400 (100), 399 (29), 398 (94), 390 (12), 388 (13), 376 (25), 374 (26), 372 (37), 370 (35), 345 (12), 344 (45), 343 (21), 342 (45), 341 (13), 329 (20), 328(11), 319 (21), 316 (12), 264 (14), 261 (14), 235 (11), 185 (22), 183 (22), 155 (15), 152 (16), 151 (10).

HRMS (EI): Calcd. for $C_{23}H_{25}O_6Br$ ([$M]^+$, $^{79}$Br) : 476.08290; found: 476.082300.

**1-ethyl 2-methyl 6-(4-bromobenzoyl)-4-hexyl-3-hydroxyphthalate (17ag)**

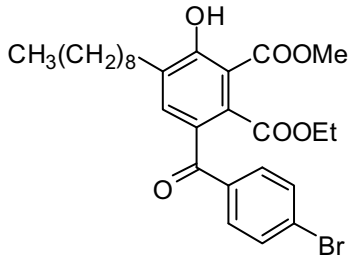



Chemical Formula: $C_{24}H_{27}BrO_6$
Exact Mass: 490.099

Starting with **16e** (0.532 g, 1.5 mmol) and **4f** (0.569 g, 1.65 mmol), **17ag** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.516 g, 70 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 0.81 (t, $^3J$ = 7.1 Hz, 3 H, $(CH_2)_5CH_3$), 1.21 (t, $^3J$ = 7.3 Hz, 3 H, $OCH_2CH_3$), 1.23-1.27 (m, 6 H, 3×$CH_2$), 1.45-1.52 (m, 2 H, $CH_2$), 2.58 (t, $^3J$ = 6.7 Hz, 2 H, $ArCH_2(CH_2)_4CH_3$), 3.86 (s, 3 H, $OCH_3$), 4.15 (q, $^3J$ = 7.5 Hz, 2 H, $OCH_2CH_3$), 7.32 (s, 1 H, $CH_{Ar}$), 7.54 ($S_{br}$, 4 H, $CH_{PhBr}$), 11.37 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 14.0 ($CH_3$), 22.6, 29.0, 29.1, 29.8, 31.6 ($CH_2$), 53.0 ($OCH_3$), 61.8 ($OCH_2$), 110.3 (*C*$COOCH_3$), 127.6, 128.1 ($C_{Ar}$), 131.5 (2×$CH_{PhBr}$), 131.7 (2×$CH_{PhBr}$), 132.6 ($C_{Ar}$), 135.0 (*C*COOEt), 135.6 ($CH_{Ar}$), 136.1 ($C_{Ar}$), 161.9 (*C*OH), 167.7, 169.8, 194.1 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 2955 (w), 2928 (w), 2856 (w), 1736 (w), 1672 (w), 1586 (w), 1441 (w), 1396 (w), 1350 (w), 1258 (w), 1235 (w), 1175 (w), 1058 (w), 962 (w), 909 (w), 732 (w), 649 (w), 586 (w). GC-MS (EI, 70 eV): *m/z* (%) = 492 ([$M^+$], $^{81}$Br, 21), 490 ([$M^+$], $^{79}$Br, 20), 445 (11), 414 (100), 376 (19), 355 (5), 344 (32), 263 (14), 235 (6), 200 (13), 183 (53), 155 (14), 129 (12), 116 (23), 57 (29), 43 (40).

HRMS (EI): Calcd. for $C_{24}H_{27}O_6Br$ ([$M]^+$, $^{79}$Br) : 490.09855; found: 490.098727.

**1-ethyl 2-methyl 6-(4-bromobenzoyl)-3-hydroxy-4-nonylphthalate (17ah)**



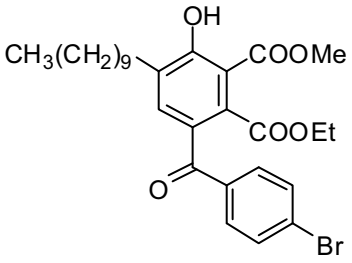

Chemical Formula: $C_{27}H_{33}BrO_6$
Exact Mass: 532.146

Starting with **16e** (0.532 g, 1.5 mmol) and **4h** (0.614 g, 1.65 mmol), **17ah** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.543 g, 68 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 0.80 (t, $^3J$ = 7.2 Hz, 3 H, $(CH_2)_7CH_3$), 1.18 (t, $^3J$ = 8.7 Hz, 3 H, $OCH_2CH_3$), 1.21-1.25 (m, 12 H, 6×$CH_2$), 1.46-1.51 (m, 2 H, $CH_2$), 2.58 (t, $^3J$ = 7.0 Hz, 2 H, $CH_2(CH_2)_7CH_3$), 3.86 (s, 3 H, $OCH_3$), 4.14 (q, $^3J$ = 7.6 Hz, 2 H, $OCH_2CH_3$), 7.31 (S, 1 H, $CH_{Ar}$), 7.53 ($S_{br}$, 4 H, $CH_{PhBr}$), 11.36 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 13.9, 14.1 ($CH_3$), 22.6, 29.0, 29.2, 29.3, 29.4, 29.5, 29.7, 31.8 ($CH_2$), 53.0 ($OCH_3$), 61.8 ($OCH_2$), 110.3 (*C*$COOCH_3$), 127.6, 128.1 ($C_{Ar}$), 131.4 (2×$CH_{PhBr}$), 131.7 (2×$CH_{PhBr}$), 132.0 ($C_{Ar}$), 135.0 (*C*COOEt), 135.6 ($CH_{Ar}$), 136.0 ($C_{Ar}$), 161.9 (*C*OH), 167.7, 169.8, 194.3 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 3085 (w), 2980 (w), 2955 (w), IR (KBr, $cm^{-1}$): $\tilde{\nu}$ = 2953 (w), 2924 (w), 2853 (w), 1734 (m), 1670 (m), 1585 (w)

1440 (m), 1349 (m), 1256 (s), 1174 (m), 1070 (w), 1010 (m), 961 (m), 842 (w), 814 (w), 733 (m), 648 (w), 584 (w). GC-MS (EI, 70 eV): *m/z* (%) = 534 ([$M^+$], $^{81}$Br, 26), 532 ([$M^+$], $^{79}$Br, 26), 489 (17), 488 (19), 487 (19), 486 (16), 457 (37), 456 (100), 454 (97), 390 (19), 388 (19), 376 (38), 375 (18), 374 (35), 345 (12), 344 (50), 343 (16), 342 (49), 330 (10), 329 (23), 327(19), 317 (11), 316 (34), 264 (12), 263 (19), 185 (24), 183 (24), 43 (16), 41 (13).

HRMS (EI): Calcd. for $C_{27}H_{34}O_6{}^{79}Br$ ([M+H]$^+$) : 533.15333; found: 533.15235.

**1-ethyl 2-methyl 6-(4-bromobenzoyl)-4-decyl-3-hydroxyphthalate (17ai)**

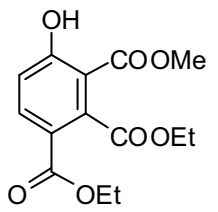


Chemical Formula: $C_{28}H_{35}BrO_6$
Exact Mass: 546.162

Starting with **16e** (0532 g, 1.5 mmol) and **4i** (0.661 g, 1.65 mmol), **17ai** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish oil (0.567 g, 69 %). $^1$HNMR (300 MHz, $CDCl_3$): δ = 0.80 (t, $^3J$ = 7.3 Hz, 3 H, $(CH_2)_9CH_3$), 1.18 (t, $^3J$ = 8.9 Hz, 3 H, $OCH_2CH_3$), 1.20-1.25 (m, 14 H, 7×$CH_2$), 1.44-1.52 (m, 2 H, $CH_2$), 2.58 (t, $^3J$ = 8.0 Hz, 2 H, $CH_2(CH_2)_8CH_3$), 3.86 (s, 3 H, $OCH_3$), 4.15 (q, $^3J$ = 7.3 Hz, 2 H, $OCH_2CH_3$), 7.32 (s, 1 H, $CH_{Ar}$), 7.54 ($S_{br}$, 4 H, $CH_{PhBr}$), 11.36 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 12.9, 13.1 ($CH_3$), 21.7, 28.0, 28.3, 28.4, 28.5, 28.6, 28.7, 28.8, 30.9 ($CH_2$), 52.1 ($OCH_3$), 60.8 ($OCH_2$), 109.3 (*C*$COOCH_3$), 126.6, 127.1 ($C_{Ar}$), 130.5 (2×$CH_{PhBr}$), 130.7 (2×$CH_{PhBr}$), 131.5, 134.0 ($C_{Ar}$), 134.6 ($CH_{Ar}$), 135.0 (*C*COOEt), 160.9 (*C*OH), 166.7, 168.8, 193.0 (CO). IR (Neat, cm$^{-1}$): $\tilde{\nu}$ = 2955 (w), 2926 (w), 2854 (w), 1734 (w), 1670 (w), 1586 (w), 1559 (w), 1507 (w), 1457 (w), 1438 (w), 1419 (w), 1351 (w), 1258 (w), 1238 (w), 1174 (w), 1070 (w), 1057 (w), 962 (w), 909 (w), 842 (w), 814 (w), 734 (w).GC-MS (EI, 70 eV): *m/z* (%) = 548 ([$M^+$], $^{81}$Br, 24), 546 ([$M^+$], $^{79}$Br, 23), 502 (25), 487 (8), 470 (100), 442 (7), 390 (24), 376 (40), 361 (8), 344 (51), 316 (38), 263 (22), 235 (9), 183 (21), 152 (8), 43 (20).

HRMS (EI): Calcd. for $C_{28}H_{35}O_6Br$ ([M]$^+$, $^{79}$Br) : 546.16115; found: 546.162377.

**1,2-diethyl 3-methyl 4-hydroxybenzene-1,2,3-tricarboxylate (17aj)**

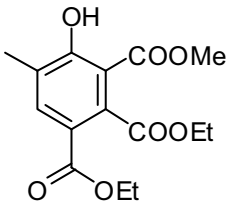


Chemical Formula: $C_{14}H_{16}O_7$
Exact Mass: 296.090

Starting with **16f** (0.366 g, 1.5 mmol) and **4a** (0.429 g, 1.65 mmol), **17aj** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish solid (0.302 g, 68 %) m.p: 70-72°C. $^1$HNMR (300 MHz, $CDCl_3$): δ = 1.29 (t, $^3J$ = 7.2 Hz, 3 H, $OCH_2CH_3$), 1.33 (t, $^3J$ = 7.4 Hz, 3 H, $OCH_2CH_3$), 3.88 (s, 3 H, $OCH_3$), 4.26 (q, $^3J$ = 7.1 Hz, 2 H, $OCH_2CH_3$), 4.35 (q, $^3J$ = 7.2 Hz, 2 H, $OCH_2CH_3$), 7.00 (d, $^3J$ = 9.0 Hz, 1 H, $CH_{Ar}$),

8.07 (d, $^{3}J$ = 9.0 Hz, 1 H, $CH_{Ar}$), 11.54 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 14.0, 14.2 ($CH_3$), 53.1 ($OCH_3$), 61.4, 61.8 ($OCH_2$), 109.7 (*C*$COOCH_3$), 118.7 ($CH_{Ar}$), 119.6 ($C_{Ar}$), 137.0 ($CH_{Ar}$), 138.7 (*C*$COOC_2H_5$), 164.3 (*C*OH), 165.1, 167.8, 169.4 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 3078 (w), 2983 (w), 2966 (w), 2940 (w), 2873 (w), 1729 (m), 1714 (s), 1682 (m), 1585 (m), 1443 (m), 1385 (w), 1346 (m), 1329 (m), 1304 (m), 1239 (s), 1202 (s), 1175 (m), 1148 (s), 1110 (m), 1024 (s), 983 (m), 938 (m), 867 (m), 855 (m), 811 (m), 752 (m), 708 (s), 648 (m), 632 (m), 562 (m). GC-MS (EI, 70 eV): *m/z* (%) = 296 ($[M]^+$, 29), 264 (14), 250 (55), 222 (11), 208 (13), 191 (100), 164 (27), 148 (16), 119 (43), 92 (10). HRMS (ESI): Calcd. for $C_{14}H_{16}O_6Na$ ($[M+Na]^+$): 319.07882; found: 319.0787.

**1,2-diethyl 3-methyl 4-hydroxy-5-methylbenzene-1,2,3-tricarboxylate (17ak)**

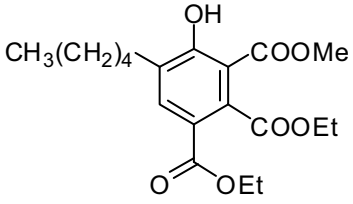


Chemical Formula: $C_{15}H_{18}O_7$
Exact Mass: 310.105

Starting with **16f** (0.366 g, 1.5 mmol) and **4b** (0.457 g, 1.65 mmol), **17ak** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a yellowish solid (0.321 g, 69%) m.p: 73 - 75°C. $^{1}$HNMR (300 MHz, $CDCl_3$): δ = 1.29 (t, $^{3}J$ = 7.2 Hz, 3 H, $OCH_2CH_3$), 1.32 (t, $^{3}J$ = 7.2 Hz, 3 H, $OCH_2CH_3$), 2.22 (s, 3 H, $CH_3$), 3.87 (s, 3 H, $OCH_3$), 4.25 (q, $^{3}J$ = 7.4 Hz, 2 H, $OCH_2CH_3$), 4.33 (q, $^{3}J$ = 7.4 Hz, 2 H, $OCH_2CH_3$),7.93 (s, 1 H, $CH_{Ar}$), 11.81 (s. 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 14.0, 14.2, 15.8 ($CH_3$), 53.0 ($OCH_3$), 61.3, 61.7 ($OCH_2$), 108.9 (*C*$COOCH_3$), 118.7, 128.2 ($C_{Ar}$), 136.3 (*C*COOOEt), 137.1 ($CH_{Ar}$), 163.6 (*C*OH), 164.7, 168.1, 169.9 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 2984 (w), 2964 (w), 2936 (w), 2873 (w), 1753 (m), 1716 (m), 1662 (m), 1434 (m), 1416 (m), 1381 (m), 1367 (m), 1339 (m), 1271 (m), 1221 (s), 1194 (m), 1151 (m), 1097 (m), 1030 (m), 981 (m), 913 (m), 882 (w), 864 (w), 812 (m), 771 (m), 759 (m), 699 (m), 671 (m), 626 (m), 573 (m). GC-MS (EI, 70 eV): *m/z* (%) = (310 ($[M]^+$, 19), 278 (14), 264 (39), 236 (8), 204 (100), 178 (11), 162 (7), 133 (21), 105 (8), 77 (5).

HRMS (EI): Calcd. for $C_{15}H_{18}O_7$ ($[M]^+$): 310.10470; found: 310.104607.

**1,2-diethyl 3-methyl 4-hydroxy-5-pentylbenzene-1,2,3-tricarboxylate (17al)**



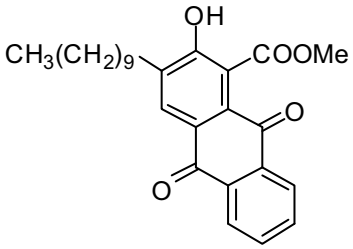
Chemical Formula: $C_{19}H_{26}O_7$
Exact Mass: 366.168

Starting with **16f** (0.366 g, 1.5 mmol) and **4e** (0.546 g, 1.65 mmol), **17al** was isolated after chromatography (silica gel, *n*-heptane/EtOAc) as a very yellowish solid (0.379 g, 69%) m.p: 76 - 78°C. $^{1}$HNMR (300 MHz, $CDCl_3$): δ = 0.78 (t, $^{3}J$ = 7.3 Hz, 3 H, $(CH_2)_4CH_3$), 1.18 – 1.29 (m, 10 H, 2×$OCH_2CH_3$,

2×$CH_2$), 1.44 – 1.54 (m, 2 H, $CH_2$), 2.55 (t, $^3J$ = 7.7 Hz, 2 H, $CH_2(CH_2)_3CH_3$), 3.81 (s, 3 H, $OCH_3$), 4.20 (q, $^3J$ = 7.4 Hz, 2 H, $OCH_2CH_3$), 4.28 (q, $^3J$ = 7.4 Hz, 2 H, $OCH_2CH_3$), 7.85 (s, 1 H, $CH_{Ar}$), 11.75 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 14.0, 14.1, 14.2 ($CH_3$), 22.4, 28.7, 29.7, 31.5 ($CH_2$), 53.0 ($OCH_3$), 61.3, 61.7 ($OCH_2$), 109.1 (*C*$COOCH_3$), 118.8, 132.8 ($C_{Ar}$), 136.2 (*C*COOOEt), 136.4 ($CH_{Ar}$), 163.4 (*C*OH), 164.8, 168.2, 169.9 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 2956 (w), 2930 (w), 2859 (w), 1739 (w), 1721 (m), 1671 (m), 1578 (w), 1440 (m), 1391 (w), 1368 (m), 1346 (m), 1251 (s), 1220 (s), 1197 (s), 1150 (2), 1111 (m), 1095 (m), 1044 (m), 922 (w), 894 (w), 865 (w), 815 (m), 768 (m), 731 (m), 700 (m), 630 (w), 590 (w), 534 (w). GC-MS (EI, 70 eV): *m/z* (%) = 366 ($[M]^+$, 13), 321 (27), 291 (24), 278 (38), 264 (100), 232 (17), 217 (31), 204 (65), 189 (16), 131 (11), 105 (5).

HRMS (ESI): Calcd. for $C_{19}H_{27}O_7$ ($[M+H]^+$): 367.17513; found: 367.17459.

**methyl 3-decyl-2-hydroxy-9,10-dioxo-9,10-dihydroanthracene-1-carboxylate(18).**




Chemical Formula: $C_{26}H_{30}O_5$
Exact Mass: 422.209

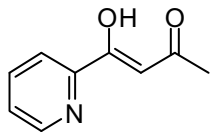
A mixture of **17n** (0.252 mg, 0.538 mmol) and of concentrated sulfuric acid (6.5 mL) was stirred at 20 °C for 1 h. The solution was poured into ice water and the mixture was extracted with Dichloromethane. The combined organic layers were dried ($Na_2SO_4$), filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography (silica gel, heptanes/EtOAc = 20:1) to give **18** as a yellowish oil (0.193 mg, 85%).$^1$HNMR (300 MHz, $CDCl_3$): δ = 0.78 (t, $^3J$ = 6.6 Hz, 3 H, $(CH_2)_9CH_3$), 1.14-1.18 (m, 14 H, 7×$CH_2$), 1.45-1.50 (m, 2 H, $CH_2$), 2.56 (t, $^3J$ = 6.8 Hz, 2 H, Ar$CH_2(CH_2)_8CH_3$), 3.93 (s, 3 H, $OCH_3$), 7.33-7.38 (m, 3 H, $CH_{Ar}$), 7.63-7.65 (m, 2 H, $CH_{Ar}$), 11.42 (s, 1 H, OH). $^{13}$C NMR ($CDCl_3$, 75 MHz): δ = 14.1 ($CH_3$), 22.6, 28.9, 29.2, 29.3, 29.3, 29.5, 29.5, 29.7, 31.9 ($CH_2$), 53.2 ($OCH_3$), 110.4 (*C*COOMe), 127.4 ($C_{Ar}$), 128.4 (2×$CH_{Ar}$), 128.7, 129.8, 130.0 ($CH_{Ar}$), 131.0, 132.5, 136.3, 137.0 ($C_{Ar}$), 161.9 (*C*OH), 170.9, 192.4, 194.9 (CO). IR (Neat, $cm^{-1}$): $\tilde{\nu}$ = 2953 (w), 2921 (m), 2851 (m), 1707(m), 1662 (m), 1597 (w),1575 (w), 1440 (m), 14266 (m), 1344 (m), 1271 (m), 1234 (m), 1170 (m), 1054 (m), 1026 (m), 1000 (w), 959 (m), 927 (w), 819 (m), 766 (m), 723 (m), 693 (m), 652 (m), 607 (m), 585 (m).GC-MS (EI, 70 eV): *m/z* (%) = 422 ($[M]^+$, 100), 405 (23), 404 (44), 391 (36), 345 (11), 309 (15), 296 (28), 278 (10), 265 (16), 264 (11), 238 (21), 231 (11), 165 (20), 152 (11), 105 (64), 77 (27), 43 (10), 41 (12).

HRMS (ESI): Calcd. for $C_{26}H_{31}O_5$ ($[M+H]^+$) : 423.2166; found: 423.21684.

**General procedure for the synthesis of 1,3-dicarbonyl compounds 21a-f and 22a-e.**

To a stirred suspension of NaH (4.0 equiv.) in anhydrous diethyl ether (1.0 mL/2.5 mmol of **19**) at 0 °C was added **20a** or **20b** (1.0 equiv.) and ketone **19a-f** (2.0 equiv.) at 20 °C. The mixture was refluxed for 2 h, cooled and a diluted aqueous solution of $NH_4Cl$ was added. The organic and the aqueous layer were separated and the latter was extracted with diethylether (3 × 20 mL). The combined organic layers were washed with brine, dried ($Na_2SO_4$), filtered and the solvent of the filtrate was removed in vacuo. The residue was purified by chromatography (silica gel, heptanes/EtOAc = 30:1 → 20:1) to give products **21** or **22**. Compounds **19a-f** and **20a-b** are commercially available.

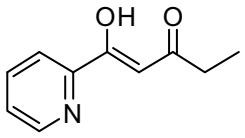
**4-Hydroxy-4-(pyrid-2-yl)but-3-en-2-one (21a).**



Chemical Formula: $C_9H_9NO_2$
Exact Mass: 163.063

Starting with NaH (2.30 g, 96.0 mmol), diethyl ether (18 mL), acetone (3.5 mL, 48.0 mmol) and **20a** (3.3 mL, 24.0 mmol), **21a** was isolated as a yellowish solid, mp. = 48-50 °C (2.055 g, 65%). $^1$H NMR (250 MHz, $CDCl_3$): δ = 2.23 (s, 3 H, $CH_3$), 6.82 (s, 1 H, CH), 7.38-7.43 (m, 1 H, $CH_{py}$), 7.80-7.86 (m, 1 H, $CH_{py}$), 8.06-8.09 (m, 1 H, $CH_{py}$), 8.65-8.66 (m, 1 H, $CH_{py}$), 15.69 ($s_{(br)}$, 1 H, OH). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 26.1 ($CH_3$), 97.2 (CH), 122.1, 126.2, 137.0, 149.0 ($CH_{py}$), 152.1 ($C_{py}$), 180.7 (COH), 195.0 (CO). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ = 3117 (w), 3066 (w), 2957 (w), 2870 (w), 1605 (m), 1579 (m), 1463 (m), 1416 (m), 1353 (m), 1284 (m), 1245 (m), 1183 (m), 1158 (m), 1079 (m), 1043 (w) 990 (m), 907 (m), 848 (m), 784 (s), 746 (m), 620 (m), 584 (w), 545 (m). GC-MS (EI, 70 eV): *m/z* (%) = 163 ($M^+$, 46), 148 (84), 134 (8), 121 (28), 106 (64), 96 (14), 85 (15), 79 (75), 78 (100), 52 (25), 51 (31), 50 (10), 43 (35), 39 (10). HRMS (EI): Calcd. for $C_9H_9O_2N$: 163.06278; found: 163.063192.

**1-Hydroxy-1-(pyridin-2-yl)pent-1-en-3-one (21b).**

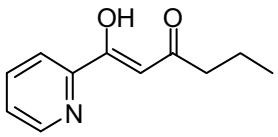


Chemical Formula: $C_{10}H_{11}NO_2$
Exact Mass: 177.079

Starting with NaH (2.30 g, 96.0 mmol), diethyl ether (18 mL), 2-butanone (4.37 mL, 48.0 mmol) and **20a** (3.3 mL, 24.0 mmol), **21b** was isolated as a yellowish oil (2.10 g, 55%). $^1$H NMR (250 MHz, $CDCl_3$): δ = 1.21 (t, $^3J$ = 7.4 Hz, 3 H, $CH_2CH_3$), 2.50 (q, $^3J$ = 7.7, 2 H, $CH_2CH_3$), 6.82 (s, 1 H, CH), 7.37−7.42 (m, 1 H, $CH_{py}$), 7.79−7.86 (m, 1 H, $CH_{py}$), 8.05-8.08 (m, 1 H, $CH_{py}$),

8.64−8.66 (m, 1 H, $CH_{py}$), 15.69 ($s_{(br)}$, 1 H, OH). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 9.4 ($CH_2\mathit{CH_3}$), 32.4 ($\mathit{CH_2}CH_3$), 96.2 (CH), 122.0, 126.1, 137.2, 149.5 ($CH_{py}$), 152.3 ($C_{py}$), 180.4 (COH), 199.6 (CO). IR (neat, $cm^{-1}$): $\tilde{\nu}$ = 2976 (w), 2879 (w), 1601 (m), 1577 (s), 1577 (s), 1460 (m), 1413 (m), 1312 (m), 1241 (m), 1044 (m), 993 (m), 829 (m), 781 (s), 742 (s), 689 (m), 543 (w). GC-MS (EI, 70 eV): *m/z* (%) = 177 ([$M^+$], 12), 162 (4), 148 (100), 106 (68), 79 (25), 78 (77), 52 (10), 51 (15). HRMS (EI): Calcd. for $C_{10}H_{11}O_2N$: 177.07843; found: 177.078306.

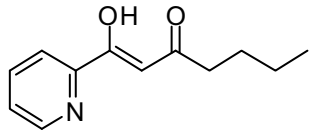
**1-Hydroxy-1-(pyridin-2-yl)hex-1-en-3-one (21c).**



Chemical Formula: $C_{11}H_{13}NO_2$
Exact Mass: 191.095

Starting with NaH (2.30 g, 96.0 mmol), diethyl ether (18 mL), 2-pentanone (5.1 mL, 48.0 mmol) and **20a** (3.26 mL, 24.0 mmol), **21c** was isolated as a yellowish oil (3.04 g, 66%). $^1H$ NMR (250 MHz, $CDCl_3$): δ = 0.98 (t, $^3J$ = 7.4 Hz, 3 H, $CH_2CH_2\mathit{CH_3}$), 1.66-1.80 (m, 2 H, $CH_2\mathit{CH_2}CH_3$), 2.44 (t, $^3J$ = 7.2 Hz, 2 H, $\mathit{CH_2}CH_2CH_3$), 6.81 (s, 1 H, CH), 7.36-7.42 (m, 1 H, $CH_{py}$), 7.78−7.85 (m, 1 H, $CH_{py}$), 8.05-8.09 (m, 1 H, $CH_{py}$), 8.63-8.66 (m, 1 H, $CH_{py}$), 15.77 ($s_{(br)}$, 1 H, OH). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 13.9 ($CH_2CH_2\mathit{CH_3}$), 19.3 ($CH_2\mathit{CH_2}CH_3$), 41.6 ($\mathit{CH_2}CH_2CH_3$), 97.0 (CH), 122.3, 126.4, 137.3, 149.5 ($CH_{py}$), 152.7 ($C_{py}$), 180.6 (COH), 198.3 (CO). IR (neat $cm^{-1}$): $\tilde{\nu}$ = 2962 (w), 2873 (w), 1720 (w), 1601 (m), 1577 (s), 1577 (s), 1458 (m), 1430 (m), 1333 (m), 1283 (m), 1086 (m), 993 (m), 827 (w), 785 (s), 742 (s), 690 (m), 618 (m). GC-MS (EI, 70 eV): *m/z* (%) = 191 ([$M^+$], 9), 163 (13), 148 (100), 121 (17), 106 (78), 93 (15), 79 (30), 78 (87), 52 (11), 51 (16), 43 (13). HRMS (EI): Calcd. for $C_{11}H_{13}O_2N$: 191.09408; found: 191.093919.

**1-Hydroxy-1-(pyridin-2-yl)hept-1-en-3-one (21d).**

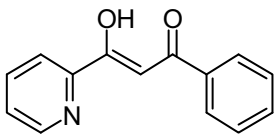


Chemical Formula: $C_{12}H_{15}NO_2$
Exact Mass: 205.110

Starting with NaH (2.30 g, 96.0 mmol), diethyl ether (18 mL), 2-hexanone (5.9 mL, 48.0 mmol) and **20a** (3.3 mL, 24.0 mmol), **21d** was isolated as a light yellow oil (2.46 g, 50%). $^1H$ NMR (250 MHz, $CDCl_3$): δ = 0.86 (t, $^3J$ = 7.3 Hz, 3 H, $(CH_2)_3\mathit{CH_3}$), 1.25-1.40 (m, 2 H, $CH_2CH_2\mathit{CH_2}CH_3$), 1.56-1.67 (m, 2 H, $CH_2\mathit{CH_2}CH_2CH_3$), 2.40 (t, $^3J$ = 7.5 Hz, 2 H, $\mathit{CH_2}CH_2CH_2CH_3$), 6.75 (s, 1 H, CH), 7.30-7.36 (m, 1 H, $CH_{py}$), 7.72−7.79 (m, 1 H, $CH_{py}$), 8.99-8.02 (m, 1 H, $CH_{py}$), 8.57-8.60 (m, 1 H, $CH_{py}$), 15.66 ($s_{(br)}$, 1 H, OH). $^{13}C$ NMR (75 MHz, $CDCl_3$): δ = 14.1 ($CH_3$), 22.5, 28.0,

39.17 ($CH_2$), 96.8 (CH), 122.1, 126.2, 137.1, 149.3 ($CH_{py}$), 152.3 ($C_{py}$), 180.8 (COH), 198.5 (CO). IR (neat $cm^{-1}$): $\tilde{\nu}$ = 2956 (w), 2871 (w), 1720 (w), 1720 (m), 1578 (m), 1563 (m), 1461 (m), 1430 (m), 1378 (w), 1281 (m), 1146 (w), 1087 (m), 1043 (w), 991 (w), 825 (w), 785 (s), 742 (m), 692 (w), 618 (m). GC-MS (EI, 70 eV): *m/z* (%) = 205 ([$M^+$], 7), 163 (30), 149 (12), 148 (100), 135 (13), 122 (11), 121 (35), 120 (18), 106 (78), 93 (27), 79 (37), 78 (100), 52 (12), 51 (16), 41 (12). HRMS (EI): Calcd. for $C_{12}H_{15}O_2N$: 205.11029; found: 205.110456.

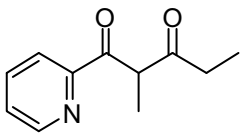
**3-Hydroxy-1-phenyl-3-(pyridin-2-yl)prop-2-en-1-one (21e).**



Chemical Formula: $C_{14}H_{11}NO_2$
Exact Mass: 225.079

Starting with NaH (2.30 g, 96.0 mmol), diethyl ether (18 mL), acetophenone (5.6 mL, 48.0 mmol) and **20a** (3.3 mL, 24.0 mmol), **21e** was isolated as a light yellow solid mp. = 81-83 °C (3.30 g, 61%). $^1$H NMR (250 MHz, $CDCl_3$): δ = 7.44-7.55 (m, 4 H, $CH_{Ar}$), 7.59 (s, 1 H, CH), 7.82-7.89 (m, 1 H, $CH_{Ar}$), 8.05-8.09 (m, 2 H, $CH_{Ar}$), 8.14-8.18 (m, 1 H, $CH_{Ar}$), 8.69-8.72 (m, 1 H, $CH_{Ar}$), 16.59 ($s_{(br)}$, 1 H, OH). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 93.6 (CH), 122.1, 126.2 ($CH_{Ar}$), 127.3 (2×$CH_{Ar}$), 128.5 (2×$CH_{Ar}$), 132.7 ($CH_{Ar}$), 135.4 ($C_{Ph}$), 137.1, 149.3 ($CH_{Ar}$), 152.6 ($C_{py}$), 183.6 (COH), 186.3 (CO). IR (neat $cm^{-1}$): $\tilde{\nu}$ = 3120 (w), 3055 (w), 2959 (w), 2872 (w), 1681 (w), 1598 (m), 1455 (m), 1417 (m), 1278 (m), 1250 (m), 1212 (m), 1178 (m), 1145 (m), 1086 (m), 1041 (w) 992 (m), 908 (m), 831 (w), 770 (s), 749 (m), 686 (m), 608 (m). GC-MS (EI, 70 eV): *m/z* (%) = 225 ($M^+$, 53), 208 (10), 198 (9), 197 (20), 196 (49), 180 (29), 168 (15), 147 (37), 120 (11), 105 (100), 98 (16), 96 (23), 92 (19), 89 (10), 84 (43), 79 (41), 78 (51), 77 (46), 75 (11), 72 (23), 69 (62), 65 (17). HRMS (EI): Calcd. for $C_{14}H_{11}O_2N$: 225.07843; found: 225.078442.

**2-Methyl-1-(pyridin-2-yl)pentane-1,3-dione (21f).**

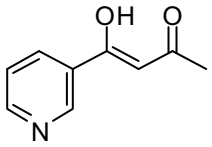


Chemical Formula: $C_{11}H_{13}NO_2$
Exact Mass: 191.095

Starting with NaH (2.30 g, 96 mmol), diethyl ether (18 mL), 3-pentanone (5.1 mL, 48.0 mmol) and **20a** (3.3 mL, 24.0 mmol), **21f** was isolated as a light red oil (2.52 g, 55%). $^1$H NMR (250 MHz, $CDCl_3$): δ = 1.08 (t, $^3J$ = 7.4 Hz, 3 H, $CH_2CH_3$), 1.39 (d, $^3J$ = 7.6 Hz, 3 H, $CH_3$), 2.70 (q, $^3J$ = 7.0, 2 H, $CH_2CH_3$), 4.86 (q, $^3J$ = 7.1, 1 H, $CHCH_3$), 7.42−7.47 (m, 1 H, $CH_{py}$), 7.79−7.86 (m, 1 H, $CH_{py}$), 8.03-8.07 (m, 1 H, $CH_{py}$), 8.60−8.63 (m, 1 H, $CH_{py}$). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 7.8, 12.7 ($CH_3$), 35.3 ($CH_2$), 54.1 (CH), 122.4, 127.3, 137.1, 148.7 ($CH_{py}$), 152.3 ($C_{py}$), 198.5, 208.9 (CO). IR (neat $cm^{-1}$): $\tilde{\nu}$ = 2978 (w), 2877 (w), 1716 (s), 1697 (s), 1584 (m), 1569 (w), 1455 (m), 1410

(w), 1324 (m), 1286 (w), 1223 (m), 1113 (w), 1038 (w), 995 (m), 950 (m), 790 (w), 781 (w), 742 (m), 667 (w), 618 (m). GC-MS (EI, 70 eV): *m/z* (%) = 191 ([$M^+$], 1), 163 (10), 162 (93), 135 (91), 134 (30), 107 (27), 106 (69), 80 (11), 79 (67), 78 (100), 57 (25), 52 (15), 51(24), 29 (19). HRMS (EI): Calcd. for $C_{11}H_{13}O_2N$: 191.09408; found: 191.093912.

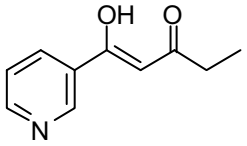
**4-Hydroxy-4-(pyridin-2-yl)but-3-en-2-one (22a).**



Chemical Formula: $C_9H_9NO_2$
Exact Mass: 163.063

Starting with NaH (2.30 g, 96.0 mmol), diethyl ether (18 mL), acetone (3.5 mL, 48.0 mmol) and **20b** (3.3 mL, 24.0 mmol), **22a** was isolated as a light orange solid, mp. = 50-52 °C (2.07 g, 53%). $^1$H NMR (250 MHz, $CDCl_3$): δ = 2.17 (s, 3 H, $CH_3$), 6.13 (s, 1 H, CH), 7.32-7.37 (m, 1 H, $CH_{py}$ ), 8.08-8.12 (m,1 H, $CH_{py}$), 8.66-6.68 (m,1 H, $CH_{py}$), 9.01 (s,1 H, $CH_{py}$), 15.92 (s,1 H, OH). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 26.0 ($CH_3$), 97.2 (CH), 123.7, 128.5, 148.4, 152.7, ($CH_{Ar}$), 134.5 ($C_{py}$ ), 181.2 (*C*OH), 194.6 (CO). IR (neat, cm$^{-1}$): $\tilde{\nu}$ = 2952 (w), 2919 (w), 1926 (w), 1584 (s), 1411 (m), 1371 (s), 1204 (m), 1077 (s), 824 (m), 872 (s), 695 (s), 543 (w). GC-MS (EI, 70 eV): *m/z* (%) = 163 ([$M^+$], 67), 162 (100), 148 (97), 106 (66), 104 (9), 85 (25), 79 (26), 78 (53), 69 (18), 65 (10), 51 (29), 50 (13), 43 (33), 39 (11). HRMS (EI): Calcd. for $C_9H_9O_2N$: 163.06278; found: 163.062897.

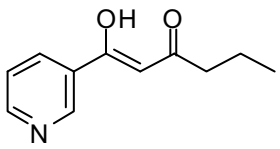
**1-Hydroxy-1-(pyridin-3-yl)pent-1-en-3-one (22b).**



Chemical Formula: $C_{10}H_{11}NO_2$
Exact Mass: 177.079

Starting with NaH (2.30 g, 96.0 mmol), diethyl ether (18 mL), 2-butanone (4.4 mL, 48.0 mmol) and **20b** (3.3 mL, 24.0 mmol), **22b** was isolated as a yellowish oil (2.86 g, 67%). $^1$H NMR (250 MHz, $CDCl_3$): δ = 1.21 (t, $^3J$ = 7.4 Hz, 3 H, $CH_2CH_3$), 2.48 (q, $^3J$ = 8.5, 2 H, $CH_2CH_3$), 6.17 (s, 1 H, CH), 7.38−7.41 (m, 1 H, $CH_{py}$), 8.13−8.18 (m, 1 H, $CH_{py}$), 8.71-8.73 (m, 1 H, $CH_{py}$), 9.06 (s, 1 H, $CH_{py}$), 15.94 ($s_{(br)}$, 1 H, OH). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 9.6 ($CH_2CH_3$), 32.5 ($CH_2CH_3$), 95.9 (CH), 123.4 ($CH_{py}$), 130.7 ($C_{py}$), 134.4, 148.2, 152.6 ($CH_{py}$), 180.5 (COH), 198.6 (CO). IR (neat cm$^{-1}$): $\tilde{\nu}$ = 2975 (w), 2879 (w), 1720 (w), 1587 (s), 1461 (m), 1412 (m), 1320 (m), 1268 (m), 1153 (w), 1087 (w), 1022 (m), 993 (w), 907 (w), 804 (w), 710 (m), 620 (w), 543 (w). GC-MS (EI, 70 eV): *m/z* (%) = 177 ([$M^+$], 37), 176 (11), 149 (14), 148 (100), 106 (43), 78 (27), 69 (12), 51 (14). HRMS (EI): Calcd. for $C_{10}H_{11}O_2N$: 177.07843; found: 177.078509.

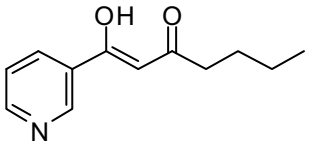
**1-Hydroxy-1-(pyridin-3-yl)hex-1-en-3-one (22c).**



Chemical Formula: $C_{11}H_{13}NO_2$
Exact Mass: 191.095

Starting with NaH (2.30 g, 96.0 mmol), diethyl ether (18 mL), 2-pentanone (5.1 mL, 48.0 mmol) and **20b** (3.3 mL, 24.0 mmol), **22c** was isolated as a light yellow oil (3.20 g, 70%). $^1$H NMR (250 MHz, $CDCl_3$): δ = 0.93 (t, $^3J$ = 7.4 Hz, 3 H, $CH_2CH_2\mathit{CH_3}$), 1.58-1.73 (m, 2 H, $CH_2\mathit{CH_2}CH_3$), 2.36 (t, $^3J$ = 7.2 Hz, 2 H, $\mathit{CH_2}CH_2CH_3$), 6.10 (s, 1 H, CH), 7.30-7.35 (m, 1 H, $CH_{py}$), 8.07−8.12 (m, 1 H, $CH_{py}$), 8.64-8.67 (m, 1 H, $CH_{py}$), 9.0 (s, 1 H, $CH_{py}$), 15.96 ($s_{(br)}$, 1 H, OH). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 13.8 ($CH_2CH_2\mathit{CH_3}$), 19.3 ($CH_2\mathit{CH_2}CH_3$), 41.0 ($\mathit{CH_2}CH_2CH_3$), 96.2 (CH), 123.4 ($CH_{py}$), 130.8 ($C_{py}$), 134.3, 148.5, 152.6 ($CH_{py}$), 181.4 (COH), 197.4 (CO). IR (neat cm$^{-1}$): $\tilde{\nu}$ = 3041 (w), 2963 (w), 2873 (w), 1720 (w), 1587 (s), 1462 (m), 1410 (m), 1380 (w), 1339 (w), 1264 (m), 1193 (m), 1090 (w), 1021 (m), 906 (m), 825 (w), 773 (m), 700 (s), 649 (w), 563 (w). GC-MS (EI, 70 eV): *m/z* (%) = 191 ([$M^+$], 26), 163 (15), 149 (12), 148 (100), 106 (38), 78 (25), 69 (12), 51 (11). HRMS (EI): Calcd. for $C_{11}H_{13}O_2N$: 191.09408; found: 191.093962.

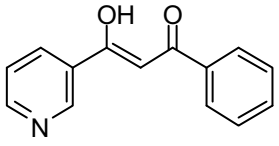
**1-Hydroxy-1-(pyridin-3-yl)hept-1-en-3-one (22d).**



Chemical Formula: $C_{12}H_{15}NO_2$
Exact Mass: 205.110

Starting with NaH (2.30 g, 96.0 mmol), diethyl ether (18 mL), 2-hexanone (5.9 mL, 48.0 mmol) and **20b** (3.3mL, 24.0 mmol), **22d** was isolated as a yellowish oil (3.05 g, 62%). $^1$H NMR (250 MHz, $CDCl_3$): δ = 0.94 (t, $^3J$ = 7.2 Hz, 3 H, $(CH_2)_3\mathit{CH_3}$), 1.32-1.47 (m, 2 H, $CH_2CH_2\mathit{CH_2}CH_3$), 1.61-1.73 (m, 2 H, $CH_2\mathit{CH_2}CH_2CH_3$), 2.45 (t, $^3J$ = 7.3 Hz, 2 H, $\mathit{CH_2}CH_2CH_2CH_3$), 6.17 (s, 1 H, CH), 7.36-7.42 (m, 1 H, $CH_{py}$), 8.13−8.18 (m, 1 H, $CH_{py}$), 8.71-8.73 (m, 1 H, $CH_{py}$), 9.06 (s, 1 H, $CH_{py}$), 16.02 ($s_{(br)}$, 1 H, OH). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 13.8 ($CH_3$), 22.3, 27.7, 39.1 ($CH_2$), 96.5 (CH), 123.4 ($CH_{py}$), 130.8 ($C_{py}$), 134.3, 148.5, 152.6 ($CH_{py}$), 181.1 (COH), 197.7 (CO). IR (neat cm$^{-1}$): $\tilde{\nu}$ = 3041 (w), 2957 (w), 2871 (w), 1586 (s), 1464 (m), 1410 (m), 1378 (w), 1270 (m), 1128 (w), 1093 (m), 1021 (m), 946 (w), 853 (w), 770 (s), 699 (s), 620 (w), 565 (w). GC-MS (EI, 70 eV): *m/z* (%) = 205 ([$M^+$],5), 176 (12), 163 (65), 162 (28), 149 (10), 148 (100), 121 (13), 106 (67), 78 (33), 69 (15), 51 (14), 41 (8). HRMS (EI): Calcd. for $C_{12}H_{15}O_2N$: 205.11029; found: 205.110456.

**3-Hydroxy-1-phenyl-3-(pyridin-3-yl)prop-2-en-1-one (22e).**




Chemical Formula: $C_{14}H_{11}NO_2$
Exact Mass: 225.079

Starting with NaH (2.30 g, 96.0 mmol), diethyl ether (18 mL), acetophenone (5.6 mL, 48.0 mmol) and **20b** (3.3 mL, 24.0 mmol), **22e** was isolated as a light yellow solid, mp. = 118-120 $^{o}$C (3.50 g, 65%). $^{1}$H NMR (250 MHz, $CDCl_3$): δ = 6.86 (s, 1 H, CH), 7.41-7.62 (m, 4 H, $CH_{Ar}$), 7.98-8.01 (m, 2 H, $CH_{Ar}$), 8.25-8.28 (m, 1 H, $CH_{Ar}$), 8.76-8.78 (m, 1 H, $CH_{Ar}$), 9.19 (s, 1 H, $CH_{Ar}$), 16.50 ($s_{(br)}$, 1 H, OH). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 93.65 (CH), 123.5 ($CH_{Ar}$), 127.3 (2×$CH_{Ar}$), 128.8 (2×$CH_{Ar}$), 131.2 ($C_{Ph}$), 132.8, 133.4 ($CH_{Ar}$), 135.1 ($C_{py}$), 148.4, 152.9 ($CH_{Ar}$), 183.5 (COH), 186.4 (CO). IR (neat cm$^{-1}$): $\tilde{\nu}$ = 3108 (w), 3056 (w), 2917 (w), 1587 (m), 1519 (m), 1463 (m), 1404 (m), 1279 (m), 1240 (m), 1188 (m), 1154 (m), 1115 (m), 1063 (m), 1036 (w) 963 (m), 841 (w), 804 (m), 769 (s), 717 (m), 683 (s), 607 (m). GC-MS (EI, 70 eV): *m/z* (%) = 225 ([$M^+$], 83), 224 (100), 196 (24), 148 (23), 147 (24), 106 (25), 105 (40), 79 (19), 78 (30), 77 (46), 69 (40), 51 (29). HRMS (EI): Calcd. for $C_{14}H_{11}O_2N$: 225.07843; found: 225.078866.

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# X-Ray Crystals Data

**Data for compound 13k Chapter 2**

**Table 1. Crystal data and structure refinement for 13k**.

Identification code **13k**

Empirical formula $C_{16}\ H_{16}\ O_5\ S$

Formula weight 320.35

Temperature 298(2) K

Wavelength 0.71073 Å

Crystal system Triclinic

Space group (H.-M.) $P\bar{1}$

Space group (Hall) -P 1

Unit cell dimensions a = 7.3898(3) Å α= 96.046(2)°.

b = 8.1060(4) Å β= 104.955(2)°.

c = 13.4273(6) Å γ = 97.200(2)°.

Volume 762.95(6) Å3

Z 2

Density (calculated) 1.394 Mg/m3

Absorption coefficient 0.233 mm-1

F(000) 336

Crystal size0.99 x 0.97 x 0.62 mm3

Θ range for data collection 3.70 to 30.00°.

Index ranges $-10\leq h\leq 9$, $-11\leq k\leq 11$, $-18\leq l\leq 18$

Reflections collected 15836

| | |
|---|---|
| Independent reflections | 4343 [R(int) = 0.0537] |
| Completeness to Θ = 30.00° | 97.5 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.8691 and 0.8022 |
| Refinement method | Full-matrix least-squares on F2 |
| Data / restraints / parameters | 4343 / 0 / 205 |
| Goodness-of-fit on F2 | 1.124 |
| Final R indices [I>2σ(I)] | R1 = 0.0537, wR2 = 0.1371 |
| R indices (all data) | R1 = 0.0711, wR2 = 0.1710 |
| Largest diff. peak and hole | 0.268 and -0.335 e.Å-3 |

Table 2. Atomic coordinates ( x 104) and equivalent isotropic displacement parameters (Å2x 103)

for **13k**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| S(1) | 1732(1) | 10054(1) | 2749(1) | 60(1) |
| O(1) | 498(3) | 10155(3) | 3411(1) | 85(1) |
| O(2) | 2590(3) | 11604(2) | 2520(1) | 79(1) |
| O(3) | -430(2) | 5597(2) | -1755(1) | 68(1) |
| O(4) | 2028(2) | 7612(2) | -1205(1) | 74(1) |
| O(5) | -3108(2) | 5481(2) | -914(1) | 69(1) |
| C(1) | 392(3) | 8734(2) | 1585(1) | 50(1) |
| C(2) | 1123(2) | 8371(2) | 738(1) | 45(1) |
| C(3) | -70(2) | 7279(2) | -141(1) | 45(1) |
| C(4) | -1917(2) | 6576(2) | -123(2) | 52(1) |

| | | | | |
|---|---|---|---|---|
| C(5) | -2585(3) | 6986(3) | 730(2) | 59(1) |
| C(6) | -1441(3) | 8051(3) | 1578(2) | 59(1) |
| C(7) | 3127(3) | 9098(3) | 785(2) | 58(1) |
| C(8) | 485(3) | 6749(2) | -1097(2) | 50(1) |
| C(9) | 2591(4) | 7078(4) | -2133(2) | 86(1) |
| C(10) | 3560(3) | 8957(3) | 3317(1) | 53(1) |
| C(11) | 3175(4) | 7270(3) | 3366(2) | 71(1) |
| C(12) | 4632(5) | 6429(4) | 3789(2) | 88(1) |
| C(13) | 6481(4) | 7267(4) | 4183(2) | 79(1) |
| C(14) | 6812(3) | 8960(4) | 4162(2) | 74(1) |
| C(15) | 5380(3) | 9817(3) | 3720(2) | 63(1) |
| C(16) | 8083(6) | 6340(6) | 4642(3) | 123(1) |

Table 4. Anisotropic displacement parameters (Å2x 103)for **13k.** The anisotropic displacement factor exponent takes the form: -2π2[ h2a*2U11 + ... + 2 h k a* b* U12 ]

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| S(1) | 59(1) | 68(1) | 55(1) | 4(1) | 17(1) | 19(1) |
| O(1) | 71(1) | 122(2) | 66(1) | -6(1) | 28(1) | 32(1) |
| O(2) | 95(1) | 58(1) | 77(1) | 7(1) | 10(1) | 13(1) |
| O(3) | 67(1) | 65(1) | 66(1) | -2(1) | 16(1) | 6(1) |
| O(4) | 72(1) | 88(1) | 61(1) | -6(1) | 34(1) | -11(1) |
| O(5) | 47(1) | 77(1) | 75(1) | 5(1) | 9(1) | -3(1) |
| C(1) | 45(1) | 59(1) | 52(1) | 14(1) | 15(1) | 17(1) |
| C(2) | 40(1) | 49(1) | 50(1) | 17(1) | 13(1) | 13(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(3) | 38(1) | 47(1) | 51(1) | 16(1) | 11(1) | 12(1) |
| C(4) | 38(1) | 54(1) | 63(1) | 19(1) | 8(1) | 10(1) |
| C(5) | 37(1) | 71(1) | 75(1) | 23(1) | 19(1) | 14(1) |
| C(6) | 45(1) | 76(1) | 64(1) | 21(1) | 23(1) | 22(1) |
| C(7) | 44(1) | 71(1) | 56(1) | 7(1) | 16(1) | 2(1) |
| C(8) | 49(1) | 51(1) | 53(1) | 14(1) | 13(1) | 15(1) |
| C(9) | 87(2) | 111(2) | 65(1) | -2(1) | 42(1) | 0(2) |
| C(10) | 51(1) | 66(1) | 42(1) | 6(1) | 14(1) | 9(1) |
| C(11) | 66(1) | 64(1) | 70(1) | 5(1) | -1(1) | 5(1) |
| C(12) | 100(2) | 72(2) | 78(2) | 5(1) | -4(1) | 27(1) |
| C(13) | 76(2) | 108(2) | 52(1) | 2(1) | 8(1) | 42(1) |
| C(14) | 52(1) | 113(2) | 55(1) | 11(1) | 15(1) | 12(1) |
| C(15) | 56(1) | 81(1) | 54(1) | 14(1) | 17(1) | 2(1) |
| C(16) | 113(3) | 166(4) | 88(2) | 4(2) | 1(2) | 83(3) |

Table 7. Hydrogen bonds for **13k** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(5)-H(5O)...O(3) | 0.91(3) | 1.69(3) | 2.515(2) | 149(3) |

Symmetry transformations used to generate equivalent atoms

**Data for compound 13s Chapter 2**

**Table 1. Crystal data and structure refinement for 13s.**

Identification code **13s**

Empirical formula $C_{15}\ H_{13}\ Cl\ O_5\ S$

Formula weight 340.76

Temperature 173(2) K

Wavelength 0.71073 Å

Crystal system Triclinic

Space group (H.-M.) $P\bar{1}$

Space group (Hall) -P 1

Unit cell dimensions a = 7.38910(10) Å α= 78.0980(10)°.

b = 8.0483(2) Å β= 75.3040(10)°.

c = 13.2408(3) Å γ = 82.3680(10)°.

Volume 742.59(3) Å3

Z 2

Density (calculated) 1.524 Mg/m3

Absorption coefficient 0.418 mm-1

F(000) 352

Crystal size0.46 x 0.3 x 0.12 mm3

Θ range for data collection 2.60 to 30.00°.

Index ranges $-10\leq h\leq 6$, $-11\leq k\leq 11$, $-18\leq l\leq 18$

Reflections collected 17901

Independent reflections4274 [R(int) = 0.0179]

Completeness to Θ = 30.00° 98.6 %

Absorption correction None

| | |
|---|---|
| Refinement method | Full-matrix least-squares on F2 |
| Data / restraints / parameters | 4274 / 0 / 205 |
| Goodness-of-fit on F2 | 1.046 |
| Final R indices [I>2σ(I)] | R1 = 0.0422, wR2 = 0.1069 |
| R indices (all data) | R1 = 0.0504, wR2 = 0.1173 |
| Largest diff. peak and hole | 0.695 and -0.901 e.Å-3 |

Table 2. Atomic coordinates ( x 104) and equivalent isotropic displacement parameters (Å2x 103)

for **13s**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Cl(1) | 3562(1) | 3941(1) | 4626(1) | 111(1) |
| S(1) | -940(1) | -251(1) | 2779(1) | 32(1) |
| O(1) | 1217(2) | 4600(2) | -1797(1) | 38(1) |
| O(2) | 3185(2) | 2514(2) | -1224(1) | 42(1) |
| O(3) | -2250(2) | 4667(2) | -982(1) | 38(1) |
| O(4) | -2817(2) | -410(2) | 3423(1) | 45(1) |
| O(5) | 216(2) | -1785(2) | 2568(1) | 48(1) |
| C(1) | 44(2) | 2762(2) | -169(1) | 24(1) |
| C(2) | -1815(2) | 3488(2) | -177(1) | 28(1) |
| C(3) | -3310(2) | 3006(2) | 675(1) | 32(1) |
| C(4) | -2979(2) | 1850(2) | 1540(1) | 32(1) |
| C(5) | -1150(2) | 1145(2) | 1574(1) | 27(1) |
| C(6) | 398(2) | 1577(2) | 728(1) | 24(1) |
| C(7) | 1518(2) | 3375(2) | -1128(1) | 27(1) |

| | | | | |
|---|---|---|---|---|
| C(8) | 4606(3) | 3142(3) | -2164(2) | 46(1) |
| C(9) | 2360(2) | 834(2) | 799(1) | 32(1) |
| C(10) | 265(2) | 884(2) | 3381(1) | 30(1) |
| C(11) | -409(3) | 2536(2) | 3505(2) | 42(1) |
| C(12) | 609(4) | 3489(3) | 3895(2) | 59(1) |
| C(13) | 2242(4) | 2739(3) | 4176(2) | 59(1) |
| C(14) | 2875(3) | 1078(4) | 4102(2) | 59(1) |
| C(15) | 1884(3) | 129(3) | 3690(1) | 45(1) |

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**Data for compound 13ae Chapter 2**

**Table 1. Crystal data and structure refinement for 13ae**.

Identification code **13ae**

Empirical formula $C_{21}\ H_{17}\ N\ O_7\ S$

Formula weight 427.42

Temperature 173(2) K

Wavelength 0.71073 Å

Crystal system Monoclinic

Space group (H.-M.) $P2_1/c$

Space group (Hall) -P 2ybc

Unit cell dimensions a = 10.4360(2) Å $\alpha$= 90°.

b = 12.8373(2) Å $\beta$= 97.3080(10)°.

c = 14.5886(3) Å $\gamma$ = 90°.

Volume 1938.56(6) Å3

Z 4

Density (calculated) 1.464 Mg/m3

Absorption coefficient 0.213 mm-1

F(000) 888

Crystal size0.70 x 0.56 x 0.27 mm3

Θ range for data collection 2.53 to 29.99°.

Index ranges -14≤h≤14, -18≤k≤17, -20≤l≤20

Reflections collected 33786

Independent reflections5647 [R(int) = 0.0201]

Completeness to Θ = 29.99° 99.9 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.9448 and 0.8653

Refinement method Full-matrix least-squares on F2

Data / restraints / parameters 5647 / 0 / 277

Goodness-of-fit on F2 1.050

Final R indices [I>2σ(I)] R1 = 0.0352, wR2 = 0.0968

R indices (all data) R1 = 0.0416, wR2 = 0.1049

Largest diff. peak and hole 0.369 and -0.356 e.Å-3

Table 2. Atomic coordinates ( x 104) and equivalent isotropic displacement parameters (Å2x 103)

for **13ae**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| S(1) | -280(1) | 8481(1) | 2257(1) | 25(1) |
| O(1) | 3674(1) | 4724(1) | 1741(1) | 46(1) |
| O(2) | 3499(1) | 5471(1) | 3090(1) | 38(1) |

| | | | | |
|---|---|---|---|---|
| O(3) | -272(1) | 8376(1) | 3240(1) | 34(1) |
| O(4) | -1500(1) | 8649(1) | 1689(1) | 37(1) |
| O(5) | 2017(1) | 5036(1) | 355(1) | 41(1) |
| O(6) | 4507(1) | 7798(1) | 6275(1) | 43(1) |
| O(7) | 5537(1) | 8810(1) | 5436(1) | 59(1) |
| N(1) | 4665(1) | 8195(1) | 5529(1) | 33(1) |
| C(1) | 2043(1) | 6011(1) | 1788(1) | 25(1) |
| C(2) | 1510(1) | 5761(1) | 871(1) | 30(1) |
| C(3) | 421(1) | 6281(1) | 448(1) | 32(1) |
| C(4) | -125(1) | 7064(1) | 909(1) | 29(1) |
| C(5) | 432(1) | 7370(1) | 1796(1) | 24(1) |
| C(6) | 1521(1) | 6859(1) | 2247(1) | 22(1) |
| C(7) | 3148(1) | 5357(1) | 2199(1) | 30(1) |
| C(8) | 4473(2) | 4749(1) | 3504(1) | 54(1) |
| C(9) | 2224(1) | 7263(1) | 3136(1) | 21(1) |
| C(10) | 1995(1) | 6894(1) | 4000(1) | 27(1) |
| C(11) | 2782(1) | 7202(1) | 4794(1) | 28(1) |
| C(12) | 3771(1) | 7906(1) | 4705(1) | 25(1) |
| C(13) | 3978(1) | 8330(1) | 3867(1) | 26(1) |
| C(14) | 3199(1) | 7995(1) | 3077(1) | 24(1) |
| C(15) | 757(1) | 9516(1) | 2041(1) | 24(1) |
| C(16) | 909(1) | 9746(1) | 1126(1) | 30(1) |
| C(17) | 1708(1) | 10565(1) | 938(1) | 35(1) |
| C(18) | 2348(1) | 11162(1) | 1661(1) | 36(1) |
| C(19) | 2188(1) | 10910(1) | 2567(1) | 37(1) |
| C(20) | 1401(1) | 10090(1) | 2767(1) | 31(1) |
| C(21) | 3194(2) | 12061(1) | 1457(2) | 54(1) |

**Data for compound 13m Chapter 2**

**Table 1. Crystal data and structure refinement for 13m.**.

| | |
|---|---|
| Identification code | **13m.** |
| Empirical formula | $C_{19} H_{22} O_5 S$ |
| Formula weight | 362.43 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group (H.-M.) | $P2_1/c$ |
| Space group (Hall) | -P 2ybc |
| Unit cell dimensions | a = 11.6509(2) Å α= 90°. |
| | b = 20.4405(4) Å β= 99.9380(10)°. |
| | c = 7.7229(2) Å γ = 90°. |
| Volume | 1811.61(7) Å3 |
| Z | 4 |
| Density (calculated) | 1.329 Mg/m3 |
| Absorption coefficient | 0.205 mm-1 |
| F(000) | 768 |
| Crystal size | 0.55 x 0.22 x 0.09 mm3 |
| Θ range for data collection | 2.67 to 30.00°. |
| Index ranges | -16≤h≤16, -25≤k≤28, -10≤l≤10 |
| Reflections collected | 22664 |
| Independent reflections | 5273 [R(int) = 0.0371] |
| Completeness to Θ = 30.00° | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9818 and 0.8958 |

| | |
|---|---|
| Refinement method | Full-matrix least-squares on F2 |
| Data / restraints / parameters | 5273 / 0 / 234 |
| Goodness-of-fit on F2 | 1.006 |
| Final R indices [I>2σ(I)] | R1 = 0.0437, wR2 = 0.0988 |
| R indices (all data) | R1 = 0.0758, wR2 = 0.1145 |
| Largest diff. peak and hole | 0.314 and -0.365 e.Å-3 |

Table 2. Atomic coordinates ( x 104) and equivalent isotropic displacement parameters (Å2x 103)

for **13m.** U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| S(1) | 10544(1) | 6165(1) | -1279(1) | 27(1) |
| O(1) | 10941(1) | 6623(1) | -2465(2) | 37(1) |
| O(2) | 10614(1) | 5478(1) | -1670(2) | 35(1) |
| O(3) | 5881(1) | 7690(1) | -203(2) | 58(1) |
| O(4) | 7409(1) | 8171(1) | -1020(2) | 42(1) |
| O(5) | 5649(1) | 6461(1) | -437(2) | 46(1) |
| C(1) | 9070(1) | 6329(1) | -1085(2) | 25(1) |
| C(2) | 8648(1) | 6962(1) | -902(2) | 26(1) |
| C(3) | 7454(1) | 7014(1) | -741(2) | 28(1) |
| C(4) | 6770(1) | 6441(1) | -676(2) | 32(1) |
| C(5) | 7231(1) | 5814(1) | -835(2) | 32(1) |
| C(6) | 8373(1) | 5773(1) | -1051(2) | 29(1) |
| C(7) | 9446(1) | 7551(1) | -804(2) | 34(1) |
| C(8) | 6847(2) | 7648(1) | -621(2) | 35(1) |
| C(9) | 6863(2) | 8806(1) | -865(3) | 51(1) |
| C(10) | 7763(2) | 9316(1) | -1028(3) | 57(1) |
| C(11) | 6505(2) | 5207(1) | -753(3) | 44(1) |
| C(12) | 5804(2) | 5014(1) | -2520(3) | 51(1) |
| C(13) | 11346(1) | 6295(1) | 850(2) | 25(1) |
| C(14) | 11006(1) | 5982(1) | 2277(2) | 27(1) |
| C(15) | 11673(1) | 6058(1) | 3932(2) | 30(1) |

| | | | | |
|---|---|---|---|---|
| C(16) | 12687(1) | 6433(1) | 4183(2) | 31(1) |
| C(17) | 13012(1) | 6739(1) | 2738(2) | 38(1) |
| C(18) | 12343(1) | 6680(1) | 1069(2) | 35(1) |
| C(19) | 13413(2) | 6501(1) | 5991(2) | 43(1) |

**Data for compound 13i Chapter 2**

**Table 1. Crystal data and structure refinement for 13i.**

Identification code **13i.**

Empirical formula $C_{24}H_{32}O_5S$

Formula weight 432.56

Temperature 173(2) K

Wavelength 0.71073 Å

Crystal system Monoclinic

Space group (H.-M.) $P2_1/c$

Space group (Hall) -P 2ybc

Unit cell dimensions a = 8.2550(2) Å $\alpha$= 90°.

b = 7.7231(2) Å $\beta$= 92.9080(10)°.

c = 35.2964(7) Å $\gamma$ = 90°.

Volume 2247.40(9) Å3

Z 4

Density (calculated) 1.278 Mg/m3

Absorption coefficient 0.176 mm-1

F(000) 928

Crystal size 0.69 x 0.45 x 0.10 mm3

$\Theta$ range for data collection 2.67 to 30.00°.

Index ranges $-11 \leq h \leq 11$, $-10 \leq k \leq 10$, $-49 \leq l \leq 49$

| | |
|---|---|
| Reflections collected | 36666 |
| Independent reflections | 6537 [R(int) = 0.0223] |
| Completeness to Θ = 30.00° | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9826 and 0.8880 |
| Refinement method | Full-matrix least-squares on F2 |
| Data / restraints / parameters | 6537 / 0 / 278 |
| Goodness-of-fit on F2 | 1.162 |
| Final R indices [I>2σ(I)] | R1 = 0.0430, wR2 = 0.1080 |
| R indices (all data) | R1 = 0.0470, wR2 = 0.1108 |
| Largest diff. peak and hole | 0.438 and -0.410 e.Å-3 |

Table 2. Atomic coordinates ( x 104) and equivalent isotropic displacement parameters (Å2x 103)

for **13i.** U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| S(1) | 6690(1) | 1957(1) | 1896(1) | 20(1) |
| O(1) | 4255(2) | 8776(1) | 993(1) | 38(1) |
| O(2) | 3554(1) | 8095(1) | 1575(1) | 29(1) |
| O(3) | 5032(1) | 6291(2) | 564(1) | 31(1) |
| O(4) | 6958(1) | 282(1) | 1728(1) | 28(1) |
| O(5) | 5511(1) | 2072(1) | 2184(1) | 29(1) |
| C(1) | 5107(1) | 6044(2) | 1249(1) | 19(1) |
| C(2) | 5372(2) | 5378(2) | 883(1) | 21(1) |
| C(3) | 6003(1) | 3707(2) | 831(1) | 19(1) |

| | | | | |
|---|---|---|---|---|
| C(4) | 6353(1) | 2726(2) | 1152(1) | 19(1) |
| C(5) | 6162(1) | 3399(2) | 1518(1) | 18(1) |
| C(6) | 5586(1) | 5077(2) | 1578(1) | 18(1) |
| C(7) | 4306(2) | 7766(2) | 1260(1) | 23(1) |
| C(8) | 2757(2) | 9765(2) | 1593(1) | 38(1) |
| C(9) | 5589(2) | 5856(2) | 1971(1) | 26(1) |
| C(10) | 6283(2) | 3091(2) | 433(1) | 23(1) |
| C(11) | 6976(2) | 1269(2) | 407(1) | 23(1) |
| C(12) | 7209(2) | 698(2) | -2(1) | 23(1) |
| C(13) | 7899(2) | -1126(2) | -24(1) | 25(1) |
| C(14) | 8168(2) | -1754(2) | -427(1) | 25(1) |
| C(15) | 8787(2) | -3613(2) | -434(1) | 28(1) |
| C(16) | 9228(2) | -4251(2) | -825(1) | 27(1) |
| C(17) | 9848(2) | -6112(2) | -823(1) | 36(1) |
| C(18) | 10378(2) | -6720(2) | -1209(1) | 40(1) |
| C(19) | 8588(2) | 2675(2) | 2096(1) | 20(1) |
| C(20) | 9861(2) | 2915(2) | 1858(1) | 27(1) |
| C(21) | 11388(2) | 3346(2) | 2016(1) | 31(1) |
| C(22) | 11631(2) | 3485(2) | 2407(1) | 30(1) |
| C(23) | 10355(2) | 3246(2) | 2641(1) | 33(1) |
| C(24) | 8812(2) | 2847(2) | 2487(1) | 28(1) |

**Data for compound 17a Chapter 3**

**Table 1. Crystal data and structure refinement for 17a.**

| | | |
|---|---|---|
| Identification code | **17a** | |
| Empirical formula | $C_{13}H_{14}O_6$ | |
| Formula weight | 266.24 | |
| Temperature | 298(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group (H.-M.) | $P2_1/n$ | |
| Space group (Hall) | -P 2yn | |
| Unit cell dimensions | a = 7.5013(3) Å | α= 90°. |
| | b = 14.4449(5) Å | β= 103.259(2)°. |
| | c = 12.5436(4) Å | γ = 90°. |
| Volume | 1322.94(8) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.337 $Mg/m^3$ | |
| Absorption coefficient | 0.107 $mm^{-1}$ | |
| F(000) | 560 | |
| Crystal size | 0.68 x 0.40 x 0.18 $mm^3$ | |
| Θ range for data collection | 2.82 to 30.00°. | |
| Index ranges | -10≤h≤10, -20≤k≤20, -17≤l≤12 | |
| Reflections collected | 17182 | |
| Independent reflections | 3865 [R(int) = 0.0262] | |
| Completeness to Θ = 30.00° | 99.8 % | |
| Absorption correction | None | |
| Refinement method | Full-matrix least-squares on $F^2$ | |

| | |
|---|---|
| Data / restraints / parameters | 3865 / 0 / 179 |
| Goodness-of-fit on $F^2$ | 1.028 |
| Final R indices [I>2σ(I)] | R1 = 0.0614, wR2 = 0.1560 |
| R indices (all data) | R1 = 0.0924, wR2 = 0.1843 |
| Largest diff. peak and hole | 0.310 and -0.225 e.$Å^{-3}$ |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$)

for **17a**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 4238(2) | 851(1) | 10205(2) | 104(1) |
| O(2) | 3482(2) | 2245(1) | 10618(1) | 67(1) |
| O(3) | 1828(2) | -250(1) | 9064(2) | 73(1) |
| O(4) | 90(2) | 3354(1) | 10454(1) | 71(1) |
| O(5) | 1438(2) | 3522(1) | 9055(1) | 60(1) |
| O(6) | -2570(3) | 3549(1) | 8407(2) | 112(1) |
| C(1) | 1249(2) | 1370(1) | 9395(1) | 42(1) |
| C(2) | -9(2) | 2108(1) | 9181(1) | 40(1) |
| C(3) | -1770(2) | 1971(1) | 8526(2) | 46(1) |
| C(4) | -2239(3) | 1091(2) | 8084(2) | 57(1) |
| C(5) | -1021(3) | 372(1) | 8261(2) | 62(1) |
| C(6) | 726(3) | 496(1) | 8921(2) | 51(1) |
| C(7) | 3123(2) | 1458(1) | 10101(2) | 50(1) |
| C(8) | 5326(3) | 2371(2) | 11273(2) | 77(1) |
| C(9) | 498(2) | 3061(1) | 9652(2) | 46(1) |

| | | | | |
|---|---|---|---|---|
| C(10) | 1864(5) | 4486(2) | 9389(3) | 108(1) |
| C(11) | 2687(7) | 4932(2) | 8623(5) | 161(2) |
| C(12) | -3094(3) | 2759(2) | 8263(2) | 60(1) |
| C(13) | -5076(3) | 2566(2) | 7820(2) | 81(1) |

**Data for compound 17b Chapter 3**

**Table 1. Crystal data and structure refinement for 17b**

Identification code **17b**

Empirical formula $C_{14}\ H_{16}\ O_6$

Formula weight 280.27

Temperature 523(2) K

Wavelength 0.71073 Å

Crystal system Monoclinic

Space group (H.-M.) $P2_1/n$

Space group (Hall) -P 2yn

Unit cell dimensions a = 7.9698(3) Å $\alpha$= 90°.

b = 21.4476(7) Å $\beta$= 92.581(2)°.

c = 16.2244(6) Å $\gamma$ = 90°.

Volume 2770.47(17) Å3

Z 8

Density (calculated) 1.344 Mg/m3

Absorption coefficient 0.106 mm-1

F(000) 1184

Crystal size0.68 x 0.54 x 0.33 mm3

$\Theta$ range for data collection 2.28 to 30.00°.

Index ranges $-8\leq h\leq 11$, $-29\leq k\leq 30$, $-22\leq l\leq 21$

Reflections collected 30295

Independent reflections 8045 [R(int) = 0.0267]

Completeness to Θ = 30.00° 99.6 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.9660 and 0.9316

Refinement method Full-matrix least-squares on F2

Data / restraints / parameters 8045 / 0 / 369

Goodness-of-fit on F2 1.041

Final R indices [I>2σ(I)] R1 = 0.0562, wR2 = 0.1420

R indices (all data) R1 = 0.1108, wR2 = 0.1883

Largest diff. peak and hole 0.286 and -0.236 e.Å-3

Table 2. Atomic coordinates ( x 104) and equivalent isotropic displacement parameters (Å2x 103)

for **17b**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 4597(3) | 3259(1) | 4728(1) | 73(1) |
| O(2) | 2991(2) | 3605(1) | 3685(1) | 59(1) |
| O(3) | 4976(2) | 2077(1) | 4940(1) | 52(1) |
| O(4) | 1751(3) | 2130(1) | 1279(1) | 86(1) |
| O(5) | 671(2) | 3085(1) | 2390(1) | 56(1) |
| O(6) | 3296(2) | 3239(1) | 1974(1) | 45(1) |
| C(1) | 3643(2) | 2533(1) | 3706(1) | 35(1) |
| C(2) | 4231(2) | 2017(1) | 4184(1) | 37(1) |
| C(3) | 4030(2) | 1404(1) | 3888(1) | 39(1) |
| C(4) | 3307(3) | 1322(1) | 3107(1) | 40(1) |

C(5) 2740(2) 1818(1) 2605(1) 38(1)

C(6) 2884(2) 2427(1) 2917(1) 35(1)

C(7) 3809(3) 3160(1) 4090(1) 42(1)

C(8) 3068(4) 4222(1) 4044(2) 68(1)

C(9) 4583(3) 861(1) 4421(1) 54(1)

C(10)2002(3) 1702(1) 1754(1) 47(1)

C(11)1582(3) 1048(1) 1492(2) 58(1)

C(12)2132(3) 2953(1) 2401(1) 38(1)

C(13)2679(3) 3693(1) 1368(1) 58(1)

C(14)2461(4) 4322(1) 1742(2) 78(1)

O(7) 8874(3) -172(1) 4222(1) 75(1)

O(8) 7568(2) -475(1) 3063(1) 60(1)

O(9) 9496(2) 981(1) 4493(1) 56(1)

O(10) 6006(3) 1160(1) 884(1) 76(1)

O(11) 5100(2) 116(1) 1924(1) 51(1)

O(12) 7644(2) 18(1) 1382(1) 53(1)

C(15)8111(2) 601(1) 3226(1) 34(1)

C(16)8751(3) 1084(1) 3745(1) 38(1)

C(17)8615(3) 1711(1) 3503(1) 40(1)

C(18)7918(3) 1839(1) 2730(1) 39(1)

C(19)7290(2) 1377(1) 2188(1) 36(1)

C(20)7368(2) 752(1) 2446(1) 33(1)

C(21)8228(3) -45(1) 3551(1) 42(1)

C(22)7625(3) -1116(1) 3339(2) 65(1)

C(23)9225(3) 2212(1) 4091(1) 56(1)

C(24)6553(3) 1552(1) 1358(1) 46(1)

C(25)6499(4) 2228(1) 1118(2) 65(1)

| | | | |
|---|---|---|---|
| C(26)6553(3) | 259(1) | 1896(1) | 38(1) |
| C(27)6943(4) | -402(1) | 744(2) | 69(1) |
| C(28)6741(4) | -1047(1) | 1048(2) | 80(1) |

# Curriculum Vitae

## Personal Information


| | |
|---|---|
| First Name: | Abdol Majid |
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| Phone: | +49 381 461 49 02 |
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| E-mail: | majid.riahi@gmail.com<br>Majid.Riahi@catalysis.de |
| Place of Birth: | Abadan / Iran |
| Date of Birth: | 21.03.1968 |
| Gender: | Male |
| Nationality: | Iranian |
| Marital Status: | married |
| Present Position | Research fellow |


## Education

| | |
|---|---|
| Since 2006 | Ph.D. Student at University of Rotock, Institute of Chemistry, Organic Chemistry, Germany |
| 10/ 2003 - 10/ 2006 | Master Degree (M. Sc) in Metalorganic and Catalysis chemistry (Leibniz Institute for Catalysis "LIKAT" e.V. at Uni. Rostock, Rostock/ Germany)<br>Title of Thesis: "Catalytic Synthesis of active agents" |
| 09/ 1993 - 10/ 1997 | Bachelor Degree in Pure Chemistry (Azad University of Mashhad, Mashhad/ Iran) |
| 06/ 1988 | High School Degree, Neyshabour/ Iran |

## Technical Skills

- Organic Synthesis Procedures and modern purification techniques of organic compounds
- Organometallic and Catalysis reactions; “Homogeneous catalysis”

- Chromatography: Gas Chromatography, Thin Layer Chromatography, Column Chromatography, HPLC Analytic and Preparative

- Spectroscopy: 1D and 2D NMR ($^{1}$H-NMR, $^{13}$C-NMR, DEPT), IR and MS
- Traning of Undergraduate and Graduate Studens

## Professional Experience

| | |
|---|---|
| 11/ 1997 – 06/ 1999 | Control quality of Colours, “Dideh Co. Tehran/ Iran” |
| 07/ 1999 – 06/ 2003 | Control quality of Polymers (Polyethylen, Polystyren and Polyurethan) “Institute of Standard and Industrial “ISIRI”– Tehran / Iran |
| 10/ 1989 - 09/ 1992 | military service at the Iran’s army |

## Computer & Software:

- System: Windows, Internet resources
- Software: Word, Excel, PowerPoint, CorelDraw, ChemDraw
- Databases: Beilstein, SciFinder Scholar

## Languages:

Persian (native speaker), German (fluently in writing, reading and speaking), English (good), Arabic (good knowledge)

## Hobbies:

Music, Photography and Several types of team sport, especially Football and Volleyball

## Publications:

**Abdolmajid Riahi**, Mirza A. Yawer, Ibrar Hussain, Olumide Fatunsin, Alexander Villinger, Christine Fischer, Peter Langer; "Synthesis of 3- and 4-amino-3′-hydroxybiaryls and dibenzo[b,d]pyrid-6-ones based on regioselective cyclocondensations of 1,3-bis(silyloxy)-1,3-butadienes with 3-(nitrophenyl)-3-silyloxy-2-en-1-ones", *Tetrahedron* **2009***,* accepted.

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