Efficient synthesis of 2-alkyl-2-hydroxy-6-X-1-tetralones

Marek Pažický, Vladislav Semak, Boris Gášpár, Adela Bílešová, Marta Sališová,* and Andrej Boháč

Comenius University in Bratislava, Faculty of Natural Sciences, Department of Organic Chemistry, Mlynská dolina CH-2, 842 15 Bratislava, Slovakia
E-mail: salisova@fns.uniba.sk

Dedicated to Professor Arlette Solladié-Cavallo on her 70th anniversary

Abstract
Synthesis of 2-alkyl-2-hydroxy-6-X-1-tetralones by oxidation of 2-alkyl-6-X-1-tetralones with oxygen or air is described. The oxidation is performed in phase–transfer conditions (TEBA) with utilization of $P(OCH_3)_3$. Convenient synthesis of 2-alkyl-6-X-1-tetralones *via* 2-methoxycarbonyl-6-X-1-tetralone is also described.

Keywords: 2-Alkyl-6-X-1-tetralone, dimethylcarbonate (DMC), 2-alkyl-2-hydroxy-6-X-1-tetralone, phase–transfer conditions, TEBA, $P(OCH_3)_3$

Introduction

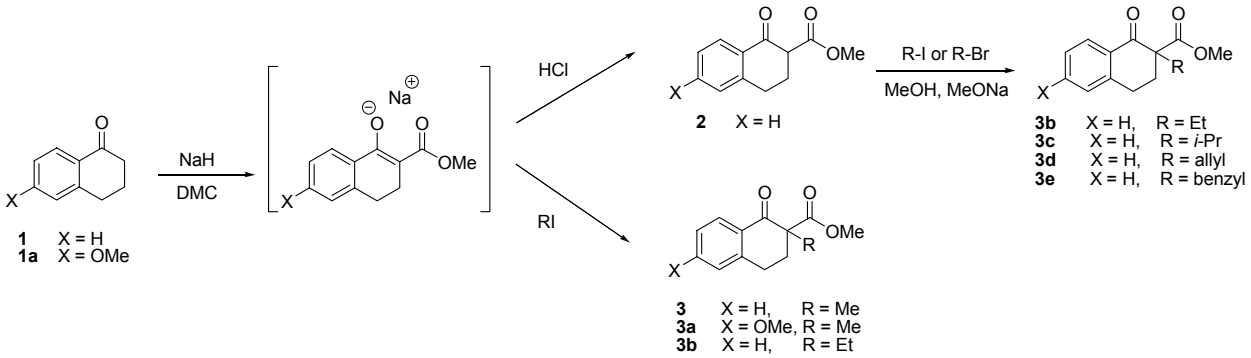
The possibility to use 2-hydroxy-2-methyl-1-tetralone (**5**) as chiral auxiliary for the epimerization or deracemization of alpha-amino acids was presented in our previous papers[1]. The synthesis of 2-hydroxy-2-methyl-1-tetralone (**5**) in racemic[2] as well as in enantiomerically enriched form[3] has been already described. Furthermore, the synthesis of the prerequisite 2-methyl-1-tetralone (**4**) is quite demanding[4].

The simplest method for the synthesis of 2-methyl-1-tetralone is direct methylation of 1-tetralone, under basic conditions. Unfortunately, this synthesis is accompanied by the formation of dimethylated product, which needs to be separated from monomethylated one (with very similar R_f) by column chromatography[5]. Another method leading to almost quantitative yield of 2-metyl-1-tetralone (**2**) is the reaction using bulky and expensive phosphazene base for abstraction of the proton from 1-tetralone[2]. Recently we published another suitable method for preparation of **2** *via* Friedel-Crafts reaction of benzene with α-methyl-γ-butyrolactone[6].

In this paper, we describe efficient and economical methods for the synthesis of 2-alkyl-6-X-1-tetralones and their oxidation to 2-alkyl-2-hydroxy-6-X-1-tetralones by oxygen or air, under phase–transfer conditions (TEBA) with utilization of $P(OCH_3)_3$.

Results and Discussion

Inspired by the reports of Loewenthal[7] and Brown et al[8] we have carried out the synthesis of 2-alkyl-6-X-1-tetralones *via* 2-methoxycarbonyl-6-X-1-tetralone (Scheme 1, Table 1).



Scheme 1

Sodium salt of 2-methoxycarbonyl-6-X-1-tetralone (**2**) was prepared from the corresponding tetralone and DMC under basic conditions. Products (**3-3e**) obtained after alkylation of 2-methoxycarbonyl-6-X-1-tetralones were obtained in varying yields. This diversity was due to the differential reactivity of the alkyl halide used. While methyl and ethyl derivatives had been prepared in almost quantitative yield, alkylation of corresponding ester with more bulky alkyl halides in methanol diminished the yield considerably. Alkylation with allyl bromide gave 52% yield of compound **3d**. While ethylation of **2** in methanol gave almost quantitative yield, the best yield of **3c** was rather low - 28%. What more, in these conditions formation of O-alkylated product **O-3c** was in some cases observed (Figure 1).

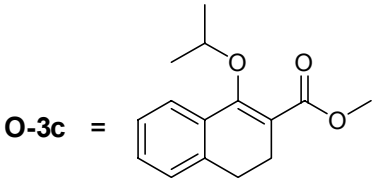


Figure 1

Alkylation with benzyl bromide in the same conditions did not give the desired product **3e**. Under these conditions, formation of benzylmethylether was observed. Reasonable results were obtained by changing the solvent and reaction conditions. When the benzylation was carried out under phase-transfer conditions (TEBA, toluene), the desired product **3e** was isolated in 77 % yield. Similar procedure was reported by Park et al.[9]

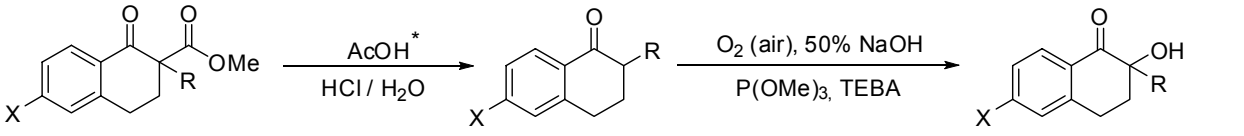
Table 1. Preparation of 2-alkyl-2-methoxycarbonyl-6-X-1-tetralones (**3-3e**)

Entry	R-X	Yield
1	MeI	**3** (98%)[a]
2	MeI	**3a** (98%)[a]
3	EtI	**3b** (99%)[b]
4	*i*-PrBr	**3c** (28%)[b]
5	AllylBr	**3d** (52%)[b]
6	BnBr	**3e** (77%)[c]

Reagent and conditions: (a) General method I, NaH in DMC; (b) General method II, NaOMe in MeO;. (c) Phase transfer conditions.

The 2-alkyl-1-tetralones (**4-4e)** were prepared *via* hydrolysis and decarboxylation of the corresponding esters **3-3e**. Under acidic conditions, the corresponding 2-alkylated-1-tetralones were directly prepared. We also found that basic hydrolysis followed by acidification and decarboxylation were in some cases more efficient (see experimental part). Krapcho described the dealkoxycarbonylation of β-keto esters in wet DMSO, containing sodium chloride[10].

As the oxidation of racemic 2-methyl-1-tetralone (**4**) by *m*-CPBA is rather expensive and risky, we decided to examine the oxidation of the corresponding 2-alkyl-1-tetralones **4-4e** with oxygen or air, under phase-transfer conditions (TEBA) using $P(OCH_3)_3$ inspired by Masui[3c]. Various 2-alkyl-2-hydroxy-6-X-1-tetralones (**5-5e**) are easily accessible following the method reported here (Scheme 2, Table 2). In some cases, the reaction takes a long time.



3	X = H	R = Me	**4**	X = H	R = Me	**5**	X = H	R = Me
3a	X = OMe	R = Me	**4a**	X = OMe	R = Me	**5a**	X = OMe	R = Me
3b	X = H	R = Et	**4b**	X = H	R = Et	**5b**	X = H	R = Et
3c	X = H	R = *i*-Pr	**4c**	X = H	R = *i*-Pr	**5c**	X = H	R = *i*-Pr
3d	X = H	R = allyl	**4d**	X = H	R = allyl	**5d**	X = H	R = allyl
3e	X = H	R = benzyl	**4e**	X = H	R = benzyl	**5e**	X = H	R = benzyl

* in some cases basic hydrolysis was more efficient

Scheme 2

Similar procedures using chiral phase transfer catalysts are also known from literature[3]. Hence, enantioselective oxidation by air to obtain the corresponding hydroxy ketone can be readily carried out by chiral crown ether catalyst as described by Vries et al.[11]

Table 2. Preparation of 2-alkyl-2-hydroxy-6-X-1-tetralones

Entry	Substrate	Decarboxylation (Yield)	PTC Oxidation (Yield)
1	**3**	**4** (96%)[a]	**5** (95%)
2	**3a**	**4a** (98%)[a]	**5a** (49%)
3	**3b**	**4b** (65%)[a]	**5b** (78%)
4	**3c**	**4c** (86%)[a]	**5c** (50%)
5	**3d**	**4d** (87%)[b]	**5d** (95%)
6	**3e**	**4e** (93%)[b]	**5e** (89%)

Reagent and conditions: (a) acidic hydrolysis and decarboxylation; (b) basic hydrolysis conditions followed by decarboxylation and acidification.

Conclusions

In conclusion, we developed a valuable methodology for the synthesis of 2-alkyl-1-tetralones and 2-alkyl-2-hydroxy-1-tetralones by alkylation of 2-metoxycarbonyl-1-tetralone, subsequent –COOMe removing and mild oxidation under PTC conditions. The synthetic method described here avoids difficulties encountered in direct alkylation of tetralones enolate**.**

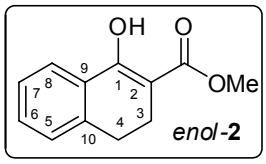
Experimental Section

General Procedure. ^{1}H and ^{13}C NMR spectra were measured on Varian Gemini (300 MHz and 75 MHz) apparatus. Chemical shifts are stated in ppm and tetramethysilane (TMS) was used as internal standard. The course of the reactions was monitored by TLC (Merck Silica gel 60 F_{254} or *SILUFOL*-UV254); for visualization an UV lamp 254 nm and iodine vapor or 10% solution of phosphomolybdic acid in EtOH were used. For column chromatography silica gel Merck 60 (40-63μm) was employed. Melting points were determined on a Kofler apparatus and are not corrected. Infrared spectra were measured on an apparatus FT-IR-ATR REACT IR 1000 (ASI Applied Systems) with a diamond probe and MTS detector.
The solvents CH_2Cl_2, MeCN and MeOH were dried by distillation from CaH_2. Benzene, Hexsol ("C6" fractions 35-100 °C, Microchem) and THF were dried by distillation from sodium. Purification of solvents was performed in accordance with usual methods[12]. 1-Tetralone (**1**) and 6-methoxy-1-tetralone (**1a**), commercially available (Acros), were distilled before use.

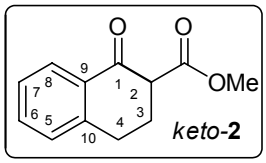
Preparation of Methyl 1,2,3,4-tetrahydro-1-oxonaphthalene-2-carboxylate (2). (2-Methoxycarbonyl-1-tetralone). 1-Tetralone (**1**) (2.8 mL, 20.88 mmol, 1.0 equiv.) was added dropwise (during 15 min) to a vigorously stirred suspension of NaH (60% dispersion in oil, 900

mg, 22.50 mmol, 1.1 equiv.) in freshly dried and distilled DMC (20 mL, 237 mmol, 11.3 equiv.), under nitrogen atmosphere. The reaction mixture was heated to reflux for 20 min while a lilac-white solid was formed and evolvement of hydrogen was observed. After this period the reaction mixture stiffed. [Warning: This experiment has to be set in a flask with higher capacity because of gas evolution; *e. g.* a 250 mL round bottomed flask was used in this experiment.] The solid was allowed to cool down to rt, dissolved in hydrochloric acid (1 M, 60 mL, to pH ≈ 5) and extracted with EtOAc (4 x 50 mL). Combined extracts were dried (Na_2SO_4), filtered and concentrated *in vacuo* to yield a brown solid (4.5 g). [Ratio of *keto* : *enol* tautomers 34 : 66 was determined by ^{1}H-NMR of crude material.] This crude product was purified by column chromatography (short column of SiO_2, Hexsol:EA - 5:1) to yield a white crystalline solid **2** (4.4 g, 97%) m.p. 73.0 – 77.4 °C. Brown[8] refers m.p. 61.5 – 69.5 °C.

[Note: As it was expected, separation of tautomers was not possible, just enriched fractions were collected for spectral analysis.]



^{1}H-NMR (300 MHz, $CDCl_3$, δ) [*keto* : *enol* tautomer = 11 : 89] *enol* form: 12.40 (s, 1H, OH); 7.80 (dd, 1H, ^4J(8,6) = 1.7, ^3J(8,7) = 7.4 Hz, H-(C8)); 7.28 – 7.33 (m, 2H, H-(C6) + H-(C7)); 7.17 (dd, 1H, ^4J (5,7) = 0.8, ^3J (5,6) = 7.3 Hz, H-(C5)); 3.83 (s, 3H, CH_3O-); 2.82 (t, 2H, ^3J(3,4) = 7.2 Hz, 2 x H-(C4)); 2.57 (t, 2H, J(3,4) = 7.2 Hz, 2 x H-(C3)).



^{1}H-NMR (300 MHz, $CDCl_3$, δ) [*keto* : *enol* = 35 : 65] *keto* form: 8.05 (dd, 1H, ^4J(6,8) = 1.5, ^3J(7,8) = 7.8 Hz, H-(C8)); 7.50 (dt, 1H, ^4J(6,8) = 1.5, ^3J = 7.5 Hz, H-(C6)); 7.24-7.35 (m, 2H, 2 x H-Ar)); 3.79 (s, 3H, CH_3O-); 3.63 (dd, 1H, ^3J = 4.8, ^3J = 10.2 Hz, H-(C2)); 2.94- 3.13 (m, 2H, 2 x H-(C4)); 2.45-2.58 (m, 1H, H-(C3)); 2.32-2.41 (m, 1H, H-(C3)). **^{13}C-NMR** (75 MHz, $CDCl_3$, δ) [just signals for *keto* form were detected; probably (when the sample was left in $CDCl_3$) equilibrium was markedly shifted to *keto* form]: 193.10 (C=O, C1), 170.60 (COO), 143.62 (C10-Ar), 133.89 (C6), 131.67 (C9-Ar), 128.78 (CHAr), 127.74 (CHAr), 126.89 (CHAr), 54.41 (C2), 52.33 (CH_3O-), 27.59 (C4), 26.34 (C3). **IR**: ($CHCl_3$, cm^{-1}): 2975 (m, C-$H_{alif.}$), 1740 (s, ester C=O,), 1675 (s, α-aryl ketone C=O), 1455 (m), 1312 (s), 1215 (s), 1151 (s), 737 (s, C-$H_{arom.}$).
Infrared, ^{1}H NMR and ^{13}C NMR spectral data are in agreement with those reported previously.[8]

Preparation of Methyl 2-alkyl-1,2,3,4-tetrahydro-1-oxonaphthalene-2-carboxylates (3-3e). (2-Alkyl-2-methoxycarbonyl-1-tetralones)

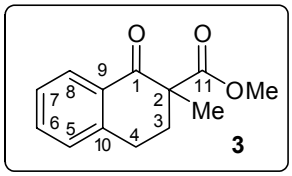
General procedure I - according to the procedure of Loewenthal[7]. Two-necked flask with magnetic stirring bar, short column and small reflux-distillation head was flamed out under argon

atmosphere. After cooling NaH (95%, 2.21 g, 87.50 mmol, 1.17 equiv.) was added to the anhyd. DMC (210 mL). To the formed suspension 1-tetralone (**1**) was added (10.2 mL, 74.65 mmol, 1.0 equiv.) under argon. The reaction was initiated by addition 10 drops of absolute methanol and by warming to 65-70°C (oil bath). When hydrogen evolution had subsided the bath temperature was gradually raised and MeOH-DMC azeotrope was very slowly distilled off until the distillation temperature remained above 89°C and 50 mL distillate had been collected. The apparatus was then raised from the oil bath and allowed to cool. To the solidified mixture was added alkyl iodide (1.28 equiv.) and the suspension was heated under reflux with stirring for 3 h and 80 mL of the distillate was collected. Reaction mixture was poured on the ice and extracted by Et_2O (3 x 150 mL) and by 100 mL of benzene. Combined organic layers were washed with 2M NaOH (80 mL) and saturated NaCl solution, dried over Na_2SO_4 and concentrated.

General procedure II. To the stirred solution of β-keto ester **2** (1.0 g, 4.9 mmol, 1.0 equiv.) in absolute MeOH (20 mL) was added MeONa (5.63mmol, 1.15 equiv.) and the reaction mixture was heated to reflux for 30 min. After cooling to rt alkyl iodide (7.35 mmol, 1.5 equiv.) was added and the mixture was refluxed for further 18 h. After cooling to rt reaction mixture was poured into water and extracted by $CHCl_3$ (3 x 15 mL). After common workup desired product was isolated.

General procedure III (inspired by Park et al.[9]). To a stirred mixture of β-keto ester **2** (1.0 g, 4.90 mmol, 1.0 equiv.) in toluene (50 mL) alkyl halide (8.36 mmol, 1.7 equiv.), KOH (notch; 1.93 g, 34.38 mmol, 7.0 equiv.), and TEBA (130 mg, 0.57 mmol, 0.12 equiv.) were added at rt. The reaction mixture was vigorously stirred at rt overnight (17.5 h). Reaction mixture was diluted with saturated NH_4Cl solution (20 mL) and extracted with EtOAc (3 x 20 mL). Combined organic layers were dried over Na_2SO_4, filtered, concentrated and purified by column chromatography.

Methyl 2-methyl-1,2,3,4-tetrahydro-1-oxonaphthalene-2-carboxylate (3). (2-Methoxycarbonyl-2-methyl-1-tetralone). Compound **3** was prepared according to the "General procedure I" and isolated as colorless oil in 98 % yield**.**

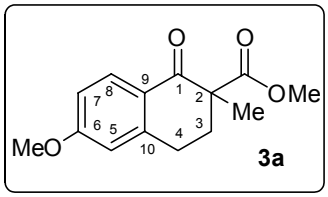


3

^{1}H NMR ($CDCl_3$, 300 MHz, δ): 8.07 (dd, 1H, J(7,8) = 8.0, J(6,8) = 1.5, H-(C8)); 7.48 (ddd, 1H, J(5,6) = 8.0, J(6,7) = 7.5, J(6,8) = 1.5, H-(C6)); 7.32 (dd, 1H, J(7,8) = 8.0, J(6,7) = 7.5, H-(C7)); 7.22 (d, 1H, J(5,6) = 7.5, H-(C5)); 3.68 (s, 3H, MeO-(C11)); 3.05 (ddd, 1H, ^2J = 17.5, J(3,4) = 9.5, J(3,4) = 5.0, H-(C4)); 2.93 (ddd, 1H, ^2J = 17.5, J(3,4) = 5.5, J(3,4) = 5.0, H-(C4)); 2.61 (ddd, 1H, ^2J = 13.5, J(3,4) = 9.5, J(3,4) = 5.0, H-(C3)); 2.61 (ddd, 1H, ^2J = 13.5, J(3,4) = 5.5, J(3,4) = 5.0, H-(C3)); 1.51 (s, 3H, Me-(C2)). **^{13}C NMR** ($CDCl_3$, 75 MHz, δ): 196.26 (C1), 173.62 (C11), 143.39 (C10), 133.69 (CH), 131.82 (C9), 128.94 (CH), 128.28

(CH), 127.01 (CH), 54.09 (MeO-(C11)), 52.69 (C2), 34.17 (C3), 26.23 (C4), 20.96 (Me-(C2)). **IR** ($CHCl_3$, cm^{-1}): 1730 (s, O-C=O), 1682 (s, C=O), 1600 (m, C=C), 1425 (m), 1373 (w), 1304 (w), 1212 (s), 921 (m), 760 (s). **Elemental analysis** ($C_{13}H_{14}O_3$): calc. C 71.54 %; H 6.47 %; found C 71.03 %; H 6.36 %.
Infrared, ^{1}H NMR and ^{13}C NMR spectral data are in agreement with those reported previously.[13]

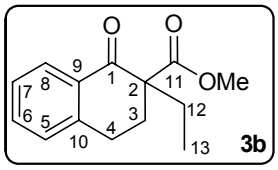
Methyl 6-methoxy-2-methyl-1,2,3,4-tetrahydro-1-oxonaphthalene-2-carboxylate (3a). (6-Methoxy-2-methoxycarbonyl-2-methyl-1-tetralone). Compound **3a** was prepared according to the "General procedure I" and isolated as white crystalline product, m.p. 89-91ºC, in 98 % yield. Mandal[14] refers m.p. 92 °C.



3a

^{1}H NMR ($CDCl_3$, 300 MHz, δ): 8.04 (d, 1H, ^3J = 8.7 Hz, H-(C8)); 6.84 (dd, 1H, ^3J = 8.8 Hz, ^4J = 2.7 Hz, H-(C7)); 6.67 (d, 1H, ^4J = 2.4 Hz, H-(C5)); 3.86 (s, 3H, (C6)-OCH_3); 3.86 (s, 3H, (C11)-OCH_3); 2.95 (ddd, 2H, 2x ^3J = 4.5 Hz, ^3J = 9.45 Hz, 2x ^2J = 17.1 Hz, ^3J = 5.7 Hz, 2 x H-(C4));, 2.59 (ddd, 1H, ^3J = 5.7 Hz, ^3J = 4.5 Hz, ^2J = 13.5 Hz, H-(C3)); 2.03 (ddd, 1H, ^3J = 4.8 Hz, ^3J = 9.45 Hz, ^2J = 13.7 Hz, H-(C3)); 1.50 (s, 3H, -CH_3).
^{1}H NMR spectral data are in agreement with those reported previously.[14]

Methyl 2-ethyl-1,2,3,4-tetrahydro-1-oxonaphthalene-2-carboxylate (3b). (2-Ethyl-2-methoxycarbonyl-1-tetralone). By the reaction conditions described in „General procedure I" only 25 % yield of compound **3b** was determined in the reaction mixture according to the ^{1}H NMR. Reaction mixture contained also **3b** and starting ester **2** in both – keto-enol forms. Separation of this mixture by chromatography was not effective. Therefore all fractions were collected, solvent evaporated and the crude mixture was used for further ethylation according to the „General procedure II".
Reaction mixture was dissolved in anhydrous MeOH and excess of *in situ* prepared MeONa was added. This mixture was heated to relux for 30 min, then cooled to rt and excess of ethyl iodide was added. The reaction mixture was monitored by TLC and quenched after 20 h when starting material was not present any more. After cooling to rt the reaction mixture was poured into water and extracted with Et_2O. Combined organic layers were dried (Na_2SO_4), filtered and concentrated. By this way almost quantitative yield of the desired product **3b** was isolated as reddish-brown oil.



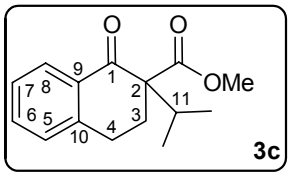
3b

^{1}H NMR ($CDCl_3$, 300 MHz, δ): 8.05 (dd, 1H, J(7,8) = 7.5, J(6,8) = 1.5, H-(C8)); 7.47 (ddd, 1H, J(5,6) = 7.5, J(6,7) = 7.5, J(6,8) = 1.5, H-(C6)); 7.31 (ddd, 1H, J(6,7) = 7.5,

J(7,8) = 7.5, *J*(5,7) = 1.0, H-(C7)); 7.22 (dd, 1H, *J*(5,6) = 7.5, *J*(5,7) = 1.0, H-(C5)); 3.68 (s, 3H, MeO-(C11)); 3.08 (ddd, 1H, ^2J = 17.5, *J*(3,4) = 10.0, *J*(3,4) = 5.0, H-(C4)); 2.92 (ddd, 1H, ^2J = 17.5, *J*(3,4) = 5.5, *J*(3,4) = 5.0, H-(C4)); 2.56 (ddd, 1H, ^2J = 14.0, *J*(3,4) = 5.5, *J*(3,4) = 5.0, H-(C3)); 2.14 (ddd, 1H, ^2J = 14.0, *J*(3,4) = 10.0, *J*(3,4) = 5.0, H-(C3)); 2.07 (dq, 1H, ^2J = 15.0, *J*(12,13) = 7.5, H-(C12)); 1.95 (dq, 1H, ^2J = 15.0, *J*(12,13) = 7.5, H-(C12)); 0.98 (t, 3H, *J*(12,13) = 7.5, H-(C13)). **^{13}C NMR** ($CDCl_3$, 75 MHz, *δ*): 195.74 (C1), 172.61 (C11), 143.35 (C10), 133.62 (CH), 132.21 (C9), 128.92 (CH), 128.26 (CH), 126.93 (CH), 58.06 (C2), 52.55 (*Me*O-(C11)), 30.17 (C3), 27.25 (CH_2), 26.09 (CH_2), 9.40 (C13). **IR** ($CHCl_3$, cm^{-1}): 1720 (s, O-C=O), 1674 (s, C=O), 1593 (m, C=C), 1435 (m), 1280 (w), 1280 (w), 1210 (s), 893 (w), 766 (s), 689 (w). **Elemental analysis** ($C_{14}H_{16}O_3$): calc. C 72.39 %; H 6.94 %; found C 72.51 %; H 6.89 %.

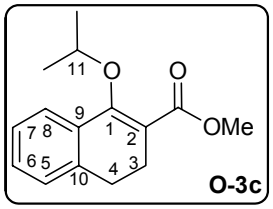
Methyl 2-isopropyl-1,2,3,4-tetrahydro-1-oxonaphthalene-2-carboxylate (3c). (2-Isopropyl-2-methoxycarbonyl-1-tetralone). Reaction was carried out according to the „General procedure II". After common work-up the crude product (yellow oil) contained only 17 % of the desired product **3c** (according to the ^{1}H NMR). What more, also 16 % of O-alkylated product **O-3c** was present in the crud product and it was impossible to separate it from the product **3c**.

Note 1. When the amount of MeONa increased to 1.5 equiv. and reaction time was prolonged to 40h, O-alkylated product **O-3c** was not present in reaction mixture. In these conditions desired product **3c** was isolated in 28 % yield as yellowish oil.



3c

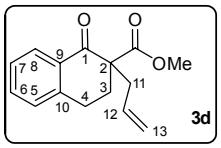
^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.05 (dd, 1H, ^3J = 7.5 Hz, ^4J = 1.5 Hz, H-(C8)); 7.45 (dt, 1H, ^3J = 7.5 Hz, ^4J = 1.5 Hz, H-(C6)); 7.29 (t, 1H, ^3J = 7.5 Hz, H-(C7)); 7.20 (d, 1H, ^3J = 7.5Hz, H-(C5)); 3.64 (s, 3H, O-CH_3); 3.21 (ddd, 1H, ^2J = 15.3 Hz, ^3J = 12 Hz, ^3J = 4.5 Hz, H-(C4)); 2.89 (ddd, 1H, ^2J = 17.1 Hz, ^3J = 4.5 Hz, ^3J = 3 Hz, H-(C4)); 2.71 (sept., 1H, ^3J = 6.6 Hz, H-(C11)); 2.47 (ddd, 1H, ^2J = 15.3 Hz, ^3J = 5.1 Hz, ^3J = 3 Hz, H-(C3)); 2.12 (ddd, 1H, ^2J = 17.1 Hz, ^3J = 12 Hz, ^3J = 5.1 Hz, H-(C3)); 0.99 (d, 3H, ^3J = 6.6 Hz, C*H*$_3$-(*i-Pr*)); 0.96 (d, 3H, ^3J = 6.6 Hz, C*H*$_3$-(*i-Pr*)). **^{13}C NMR** (300 MHz, $CDCl_3$, δ): 194.86 (C=O), 171.57 (O=C-O), 143.81 (C9), 143.81 (C9), 133.58 (CH_{Ar}), 132.84 (C10), 128.90 (CH_{Ar}), 128.26 (CH_{Ar}), 126.78 (CH_{Ar}), 61.19 (C2), 52.47 (O-CH_3), 32.70 (C11), 26.57 (CH_2), 26.26 (CH_2), 18.78 (*C*H$_3$-(*i-Pr*)), 17.77 (*C*H$_3$-(*i-Pr*)). **IR** ($CHCl_3$, cm^{-1}): 2950 (s, C_{Ar}-H), 1740 (m, O-C=O), 1680 (m, C=O), 1580 (w, C=C), 1475 (s), 1370 (m), 1275 (w), 1215 (s, C-O), 1135 (m), 755 (s). **Elemental analysis** ($C_{15}H_{18}O_3$): calc. C 73.15%; H 7.37%; found C 73.42%; H 7.54%.



^{1}H NMR spectrum of **O-3c** was described from the mixed sample containing 70 % of **3c** and 30 % **O-3c.**

^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.02-8.05 (m, 1H, H-(C8)); 7.54-7.57 (m, 1H, H_{Ar}); 7.16-7.32 (m, 2H, 2xH_{Ar}); 4.33 (sept., 1H, ^3J = 6 Hz, H-(C11)); 3.81 (s, 3H, O-CH_3); 2.60-2.78 (m, 4H, 2xCH_2), 1.31 (d, 6H, ^3J = 6 Hz, 2xCH_3-(*i-Pr*)).

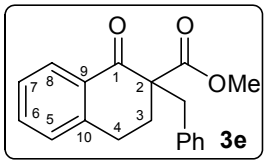
Methyl 2-allyl-1,2,3,4-tetrahydro-1-oxonaphthalene-2-carboxylate (3d). (2-Allyl-2-methoxycarbonyl-1-tetralone). The reaction was carried out according to the "General procedure II". After addition of allyl bromide the reaction mixture was heated to reflux for 20 h. After common work-up and chromatography (SiO_2, Hexol:Et_2O - 4:1) 52% of desired product **3d** was isolated as colorless oil.



^{1}H NMR (300 MHz , $CDCl_3$, δ): 8.05 (dd, 1H, ^3J = 7.8 Hz, ^4J = 1.2 Hz, H-(C8)); 7.47 (dt, 1H, ^3J = 7.5 Hz, ^4J = 1.2 Hz, H-(C6)); 7.31 (t, 1H, ^3J = 7.8 Hz, H-(C7)); 7.22 (d, 1H, ^3J = 7.5 Hz, H-(C5)); 5.82 (ddt, 1H, ^3J = 17.4 Hz, ^3J = 10.2 Hz, ^3J = 7.2 Hz, H-(C12)); 5.09-5.18 (m, 2H, 2xH-(C13)); 3.67 (s, 3H, OCH_3); 3.07 (ddd, 1H, ^2J = 17.4 Hz, ^3J = 10.2 Hz, ^3J = 4.8 Hz, H-(C4)); 2.92 (ddd, 1H, ^2J = 17.4 Hz, ^3J = 5.1 Hz, ^3J = 5.1 Hz, H-(C4)); 2.75 (dd, 1H, ^2J = 13.8 Hz, ^3J = 7.2 Hz, H-(C11)); 2.68 (dd, 1H, ^2J = 13.8 Hz, ^3J = 7.2 Hz, H-(C11)); 2.53 (ddd, 1H, ^2J = 13.8 Hz, ^3J = 5.1 Hz, ^3J = 5.1 Hz, H-(C3)); 2.14 (ddd, 1H, ^2J = 15.3 Hz, ^3J = 10.2 Hz, ^3J = 5.1 Hz, H-(C3)). **^{13}C NMR** (300 MHz, $CDCl_3$, δ): 195.14 (C=O), 172,20 (O-C=O), 143.45 (C), 133.75 (CH_{Ar}), 133.56 (CH_{Ar}), 132.10 (C), 128.96 (CH_{Ar}), 128.30 (CH_{Ar}), 126.97 (C12), 119.13 (C13), 57.64 (C2), 52.66 (OCH_3), 68.92 (CH_2), 30.73 (CH_2), 26.04 (CH_2). **Elemental analysis** ($C_{15}H_{16}O_3$): calc. C 73.75%; H 6.60%; found C 72.33%; H 6.63%.

^{1}H NMR and ^{13}C NMR spectral data are in agreement with those reported previously.[9]

Methyl 2-benzyl-1,2,3,4-tetrahydro-1-oxonaphthalene-2-carboxylate (3e). (2-Benzyl-2-methoxycarbonyl-1-tetralone). Product **3e** was prepared according to the „General procedure III". After common work-up and purification by column chromatography (SiO_2, Hexsol:Et_2O – 5:1) α-benzylated β-keto ester **3e** was isolated as a white solid, m.p. 95.3 – 96.6 °C in 77% yield.



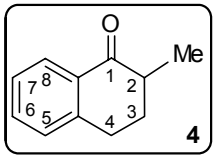
^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.08 (dd, 1H, ^4J(8,6) = 1.2, ^3J(8,7) = 7.9 Hz, H-(C8)); 7.45 (ddd, 1H, ^4J(6,8) = 1.2, ^3J(6,5) =^3J(6,7) = 7.5 Hz, H-(C6)); 7.15 (m, 7H, H-

(C5) + H-(C7) + 5 x H-(Ph)); 3.66 (s, 3H, CH_3O-); 3.45 (d, 1H, ^2J = 13.6 Hz, -CH_2-Ph); 3.32 (d, 1H, ^2J = 13.6 Hz, -CH_2-Ph); 3.08 (ddd, 1H, ^3J(3,4) = 4.7, ^3J(3,4) = 11.7, ^2J = 16.7 Hz, H-(C3)); 2.85 (ddd, 1H, ^3J(3,4) = 4.3, ^3J(3,4) = 4.7, ^2J = 16.7 Hz, H-(C3)); 2.49 (ddd, 1H, ^3J(4,3) = 4.3, ^3J(4,3) = 4.7, ^2J = 13.8 Hz, H-(C4)); 1.99 (ddd, 1H, ^3J(4,3) = 4.7, ^3J(4,3) = 11.7, ^2J = 13.8 Hz, H-(C4)). **^{13}C-NMR** (75 MHz, $CDCl_3$, δ): 194.44 (C1, C=O), 171.83 (COO), 143.25 (C10-Ar), 136.43 (C9-Ar), 133.51 (CHAr), 132.11 (C-Ar, -Ph), 130.68 (2 x CHAr), 128.71 (CHAr), 128.19 (CHAr), 128.12 (2 x CHAr), 126.76 (CHAr), 126.69 (CHAr), 58.72 (C2), 52.56 (CH_3O-),40.14 (-CH_2-Ph), 30.39 (C3), 26.05 (C4). **IR** (CH_2Cl_2, cm^{-1}): 2925 (m, C-$H_{alif.}$), 1746 (s, ester C=O,), 1675 (s, α-aryl ketone C=O), 1455 (m), 1215 (s), 1151 (s), 737 (s, C-$H_{arom.}$), 706 (s, C-$H_{arom.}$). ^{1}H NMR and ^{13}C NMR spectral data are in agreement with those reported previously.[9]

Preparation of 2-alkyl-3,4-dihydronaphthalen-1(2*H*)-ones (4-4e). (2-alkyl-1-tetralones) General procedure I - acid hydrolysis and decarboxylation. Corresponding 2-alkyl β-keto ester (**3-3e**) (73.04 mmol, 1.0 equiv.) was dissolved in the solution containing: glacial acetic acid (127 mL, 2132 mmol, 28.8 equiv.), HCl 37 % (32 mL, 288 mmol, 3.9 equiv.) and distilled water (25 mL). Reaction mixture was heated into reflux and was monitored by TLC. After 4 h starting material was not present in the reaction mixture. After cooling to the rt reaction mixture was poured into 200 mL of distilled water and 100 mL of CH_2Cl_2 was added. Neutralization of the solution has been done by slow addition of 96 g Na_2CO_3 (906 mmol, 12.24 equiv.). Water layer was extracted by CH_2Cl_2 (4 x 100 mL). Combined organic layers were dried over Na_2SO_4, filtered and concentrated.

General procedure II - basic hydrolysis and decarboxylation. To the stirred solution of 2-alkylated β-keto ester (**3-3e**) (2.07 mmol, 1.0 equiv.) in MeOH (3 mL) KOH (1.16 g, 20.7 mmol, 10 equiv.) in water (2.3 mL) was added and the reaction mixture was heated to refluxed for 75 min. After cooling to rt reaction mixture was neutralized by slow addition of 10% HCl and extracted by CH_2Cl_2 (3 x 20 mL). Combined organic layers were washed with saturated solution of NaCl (20 mL), dried over Na_2SO_4, filtered and concentrated. Crude product was purified by column chromatography (SiO_2, Hexsol:Et_2O – 4:1).

2-Methyl-3,4-dihydro-2*H*-naphthalen-1-one (4). (2-Methyl-1-tetralone). Reaction was carried out according to the „General procedure I“. After common work-up crude reaction mixture was distilled on Büchi apparatus (80-130 °C/ ~27 Pa). By this way 11.29 g (96 %) of colorless oil was isolated.

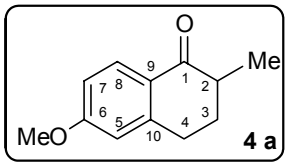


4

^{1}H NMR ($CDCl_3$, 300 MHz, *δ*): 8.05 (1H, dd, *J*(7,8) = 8.0, *J*(6,8) = 1.0, H-C(8)); 7.47 (1H, ddd, *J*(5,6) = 7.5, *J*(6,7) = 7.5, *J*(6,8) = 1.0, H-C(6)); 7.31 (1H, dd, *J*(7,8) = 8.0, *J*(6,7) = 7.5, H-C(7)); 7.25 (1H, d, *J*(5,6) = 7.5, H-C(5)); 3.12 – 2.91 (2H, m, with measurable

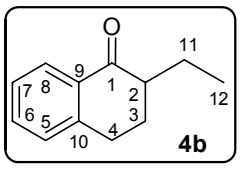
$J(3^{Me\text{-}C(2)},4^{Me\text{-}C(2)})$ = 11.0, $J(3^{H\text{-}C(2)},4^{H\text{-}C(2)})$ = 9.0, $J(3^{Me\text{-}C(2)},4^{H\text{-}C(2)})$ = 5.0, $J(3^{H\text{-}C(2)},4^{Me\text{-}C(2)})$ ~ 0.0, 2x H-C(4)); 2.61 (1H, dqd, $J(2,3^{Me\text{-}C(2)})$ = 12.0, J(Me,2) = 7.0, $J(2,3^{H\text{-}C(2)})$ = 4.5, H-C(2)); 2.21 (1H, ddd, ^2J = 13.0, $J(3^{H\text{-}C(2)},4^{H\text{-}C(2)})$ = 9.0, $J(2,3^{H\text{-}C(2)})$ = 4.5, $J(3^{H\text{-}C(2)},4^{Me\text{-}C(2)})$ ~ 0.0, $H^{H\text{-}C(2)}$-C(3)); 1.90 (1H, dddd, ^2J = 13.0, $J(2,3^{Me\text{-}C(2)})$ = 12.0, $J(3^{Me\text{-}C(2)},4^{Me\text{-}C(2)})$ = 11.0, $J(3^{Me\text{-}C(2)},4^{H\text{-}C(2)})$ = 5.0, $H^{Me\text{-}C(2)}$-C(3)); 1.28 (1H, d, J(Me,2) = 7.0, Me-C(2)).
^{1}H NMR spectral data are in agreement with those reported previously.[2]

6-Methoxy-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (4a). (6-Methoxy-2-methyl-1-tetralone). Reaction was carried out according to the „General procedure I". After common work-up the desired product **4a** was isolated as yellow oil in 98% yield.



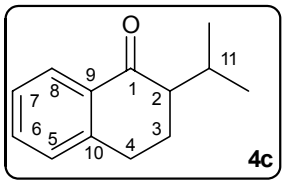
^{1}H NMR ($CDCl_3$, 300 MHz, δ) 8.01 (d, 1H, ^3J = 8.7 Hz, H-(C8)); 6.81 (dd, 1H, ^4J = 2.7 Hz, ^3J = 8.7, H-(C7)); 6.68 (d, 1H, ^4J = 2.4 Hz, H-(5)); 3.85 (s, 3H, -OCH_3); 2.93 (ddd, 1H, ^3J = 4.6 Hz, ^3J = 4.7 Hz, ^2J = 16.7 Hz, H-(4)); 3.00 (ddd, 1H, ^2J = 16.7 Hz, ^2J = 16.7 Hz, ^3J = 4.7 Hz, H-(C4)); 2.54 (ddq, 1H, ^3J = 12.5 Hz, ^3J = 4.5 Hz, ^3J = 7.2 Hz, H-(C2)); 2.16 (dq, 1H, ^3J = 4.5 Hz, ^3J = 9.0 Hz, ^2J = 13.0 Hz, H-(C3)); 1.86 (dddd, 1H, ^3J = 5.1 Hz, ^2J =13.0 Hz, ^3J = 11.0 Hz, ^3J = 12.0 Hz, H-(C3)); 1.25 (d, 3H, J = 7.0 Hz, C2-CH_3).
^{1}H NMR spectral data are in agreement with those reported previously.[15]

2-Ethyl-3,4-dihydro-2*H*-naphthalen-1-one (4b). (2-Ethyl-1-tetralone). Reaction was carried out according to the „General procedure I". After common work-up the desired product **4b** was isolated as colorless oil in 65% yield.



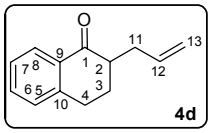
^{1}H NMR ($CDCl_3$, 300 MHz, δ): 8.03 (dd, 1H, J(7,8) = 8.0, J(6,8) = 1.5, H-(C8)); 7.45 (ddd, 1H, J(5,6) = 7.5, J(6,7) = 7.5, J(6,8) = 1.5, H-(C6)); 7.29 (dd, 1H, J(7,8) = 8.0, J(6,7) = 7.5, H-(C7)); 7.23 (d, 1H, J(5,6) = 7.5, H-(C5)); 3.03-2.95 (m, 2H, H-(C4)); 2.46-2.35 (m, H, H-(C2)); 2.24 (ddd, 1H, ^2J = 13.5, ^3J = 9.5, ^3J = 4.5, H-(C3)); 2.05-1.83 (m, 2H, H-(C3, C11)); 1.58 (dq, 1H, ^2J = 21.5, J(11,12) = 7.5, H-(C11)); 1.00 (t, 3H, J(11,12) = 7.5, H-(C12))
^{13}C NMR ($CDCl_3$, 75 MHz, δ): 200.46(C1), 144.18 (C10), 133.23 (CH), 132.81 (C9), 128.84 (CH), 127.62 (CH), 126.72 (CH), 49.12 (C2), 28.58 (CH_2), 27.94 (CH_2), 22.63 (C11), 11.64 (C12). **IR** ($CHCl_3$, cm^{-1}): 2910 (m, C-$H_{Alif.}$), 1669 (s, C=O), 1592 (s, C=C), 1445 (s), 1424 (w), 1350 (m), 1286 (m), 1205 (s), 1148 (m), 1119 (w), 1086 (w), 1020 (w), 974 (m), 898 (s), 760 (s).
Elemental analysis ($C_{12}H_{14}O$): calc. C 82.72 %; H 8.10 %; found C 82.48 %; H 8.06 %.
^{1}H NMR and ^{13}C NMR spectral data are in agreement with those reported previously.[15]

2-Isopropyl-3,4-dihydronaphthalen-1(2*H*)-one (4c). (2-Isopropyl-1-tetralone). (a) Reaction was carried out according to the „General procedure I". After common work-up the desired product **4c** was isolated as colorless oil in 51 % yield. Ecke gives b.p. 162 ^{o}C (18 mm)[16].
(b) By basic hydrolysis and decarboxylation the yield was 86 %.



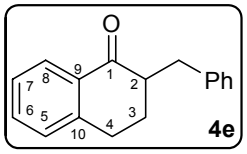
^{1}H NMR (300 MHz , $CDCl_3$, δ): 8.03 (dd, 1H, ^{3}J = 7.8 Hz, ^{4}J = 1.2 Hz, H-(C8)); 7.45 (dt, 1H, ^{3}J = 7.5 Hz, ^{4}J = 1.2 Hz, H-(C6)); 7.29 (t, 1H, ^{3}J = 8.1 Hz, H-(C7)); 7.23 (d, 1H, ^{3}J = 7.5 Hz, H-(C5)); 2.89-3.08 (m, 2H, H-(C3), H-(C4)); 2.53 (dsept., 1H, ^{3}J = 6.9 Hz, ^{3}J = 4.8 Hz, H-(C11)); 2.33 (ddd, 1H, ^{3}J = 11.4 Hz, ^{3}J = 4.8 Hz, ^{3}J = 4.5Hz, H-(C4)); 2.11-2.20 (m, 1H, H-(C2)); 1.95 (dddd, 1H, ^{2}J = 21 Hz, ^{3}J = 11.4 Hz, ^{3}J = 9.9 Hz, ^{3}J = 4.5 Hz, H-(C3)); 1.01 (d, 3H, ^{3}J = 7.2 Hz, CH_3-(*i-Pr*)); 0.91 (d, 3H, ^{3}J = 6.6 Hz, CH_3-(*i-Pr*)). **^{13}C NMR** (300 MHz, $CDCl_3$, δ): 200.10 (C=O), 144.13 (CH_{Ar}), 133.22 (CH_{Ar}), 133.18 (CH_{Ar}), 128.79 (CH_{Ar}), 127.62 (CH_{Ar}), 126.72 (CH_{Ar}), 53.95 (CH (C2)), 28.76 (CH_2), 26.39 (CH-(*i-Pr*)), 23.70 (CH_2), 20.89 (CH_3), 18.71 (CH_3). **Elemental analysis** ($C_{13}H_{16}O$): calc. C 82.94%; H 8.57%; found C 83.84%; H 9.27%.
^{1}H NMR and ^{13}C NMR spectral data are in agreement with those reported previously.[17]

2-Allyl-3,4-dihydronaphthalen-1(2*H*)-one (4d). (2-Allyl-1-tetralone). Reaction was carried out according to the „General procedure II". After common work-up the desired product **4d** was isolated as colorless oil in 87% yield.



^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.04 (dd, 1H, ^{3}J = 7.8 Hz, ^{4}J = 1.2 Hz, H-(C8)); 7.46 (dt, 1H, ^{3}J = 7.5 Hz, ^{4}J = 1.2 Hz, H-(C6)); 7.30 (t, 1H, ^{3}J = 7.2 Hz, H-(C7)); 7.23 (d, 1H, ^{3}J = 7.5 Hz, H-(C5)); 5.78-5.92 (m, 1H, H-(C12)); 5.05-5.14 (m, 2H, 2xH-(C13)); 2.98-3.02 (m, 2H, 2xH-(C4)); 2.72-2.81 (m, 1H, H-(C2)); 2.50-2.60 (m, 1H, H-(C11)); 2.20-2.32 (m, 2H, H-(C3), H-(C11)); 1.80-1.94 (m, 1H, H-(C3)). **^{13}C NMR** (300 MHz, $CDCl_3$, δ): 199.65 (C=O), 144.26 (C), 136.43 (CH_{Ar}), 133.40 (CH_{Ar}), 132.73 (C), 128.91 (CH_{Ar}), 127.68 (CH_{Ar}), 126.79 (C13), 117.03 (C12), 47.40 (C2), 34.26 (CH_2), 28.83 (CH_2), 28.18 (CH_2). **Elemental analysis** ($C_{13}H_{14}O$): calc. C 83.83%; H 7.58%; found C 82.73%; H 7.50%.

2- Benzyl -3,4-dihydronaphthalen-1(2*H*)-one (4e). (2-Benzyl-1-tetralone). Reaction was carried out according to the „General procedure II". After common work-up and column chromatography (SiO_2, Hexsol:EtOAc – 5:1 to 5:2) desired product **4e** was isolated as yellowish oil in 93% yield.



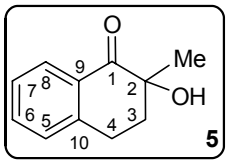
^{1}H-NMR (300 MHz, $CDCl_3$, δ): 8.07 (dd, 1H, ^4J(8,6) = 1.2, ^3J(8,7) = 7.8 Hz, H-(C8)); 7.46 (ddd, ^4J(6,8) = 1.3, ^3J(6,5) = ^3J(6,7) = 7.5 Hz, H-(C6)); 7.20 – 7.35 (m, 7H, H-(C5) + H-(C7) + 5x*H*-(Ph)); 3.50 (dd, 1H, ^3J(2, PhCH_2-) = ^3J(2,3) = 4.5, ^3J(2, -CH_2-Ph) = ^3J(2,3) = 13.4 Hz, H-(C2)); 2.93 (dd, 1H, ^3J(-CH_2-Ph,2) =4.5, ^2J = 10.0 Hz, -CH_2-Ph); 2.70 – 2.95 (m, 2H, 2xH-(C4)); 2.64 (dd, 1H, ^2J = 10.0, ^3J(-CH_2-Ph,2) = 13.4 Hz, -CH_2-Ph); 2.12 (m, 1H, with measurable ^3J(3,2) = 4.3, ^2J = 11.5 Hz, H-(C3)); 1.79 [dddd, 1H, ^3J(3,4) = 6.0, ^3J(3,4) = 9.6Hz, ^2J = 11.5, ^3J(3,2) = 13.4 Hz, H-(C3)). **IR** (CH_2Cl_2, cm^{-1}): 2913 (m, C-$H_{alif.}$), 1679 (s, C=O), 1269 (m), 1223 (m), 737 (s, C-$H_{arom.}$), 706 (s, C-$H_{arom.}$).

^{1}H NMR spectral data are in agreement with those reported previously.[5]

Preparation of 2-hydroxy-2-alkyl-3,4-dihydronaphthalen-1(2*H*)-ones (5-5e). (2-hydroxy-2-alkyl-1-tetralones)

General procedure. The corresponding 2-alkyl-1-tetralone (**4-4e**) (2.37 mmol, 1.0 equiv.) was dissolved in toluene (15 mL) covered with freshly prepared 50% solution of NaOH (10 mL). Triethylbenzylammonium chloride (TEBA) (0.36 mmol, 0.15 equiv.) and trimethoxy phosphite ($P(OMe)_3$), (2.96 mmol, 1.25 equiv.) were successively added. Reaction mixture was vigorously stirred at rt and oxygen (or air *via* small pumping device) was bubbled *via* a syringe through the mixture. After 4 - 24 h starting material was not detected (TLC control). Solution was diluted with water (30 mL) and EtOAc (20 mL). Aqueous layer was extracted with EtOAc (3 x 20 mL). Combined organic layers were washed with 10% HCl (30 mL), water (30 mL) and dried over Na_2SO_4. After filtration and removal of the solvent, the crude product was isolated and purified.

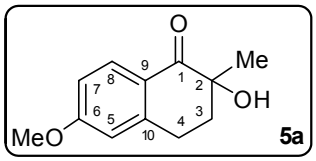
2-Hydroxy-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (5). (2-Hydroxy-2-methyl-1-tetralone). Crude product was distilled at reduced pressure (85-90°C / 8 Pa). Desired 2-hydroxy-2-methyltetralone (**5**) was isolated as yellowish oil in 95 % yield.



^{1}H NMR ($CDCl_3$, 300 MHz, *δ*): 8.05 (dd, 1H, *J*(7,8) = 8.0, *J*(6,8) = 1.5, H-(C8)); 7.53 (ddd, 1H, *J*(5,6) = 7.5, *J*(6,7) = 7.5, *J*(6,8) = 1.5, H-(C6)); 7.35 (dd, 1H, *J*(7,8) = 8.0, *J*(6,7) = 7.5, H-(C7)); 7.27 (d, 1H, *J*(5,6) = 7.5, H-(C5)); 3.86 (bs, 1H, HO-(C2)); 3.12 (ddd, 1H, ^2J = 17.5, $J(3^{Me\text{-}C(2)},4^{OH})$ = 11.0, $J(3^{OH},4^{OH})$ = 6.0, H^{OH}-(C4)); 3.02 (ddd, 1H, ^2J = 17.5, $J(3^{Me\text{-}C(2)},4^{Me\text{-}C(2)})$ = 5.5, $J(3^{C(2)},4^{Me\text{-}C(2)})$ = 3.5, $H^{Me\text{-}C(2)}$-(C4)); 2.28 (ddd, 1H, ^2J = 13.0, $J(3^{OH},4^{OH})$ = 6.0, $J(3^{OH},4^{Me\text{-}C(2)})$ = 3.5, H^{OH}-(C3)); 2.22 (ddd, 1H, ^2J = 13.0, $J(3^{Me\text{-}C(2)},4^{OH})$ = 11.0, $J(3^{Me\text{-}C(2)},4^{Me\text{-}C(2)})$ = 5.5, $H^{Me\text{-}C(2)}$-(C3)); 1.40 (s, 3H, Me-(C2)).**^{13}C NMR** ($CDCl_3$, 75 MHz, *δ*): 201.82 (C1), 143.42 (C10), 134.08 (CH), 129.92 (C9), 129.01 (CH), 128.03 (CH), 126.91 (CH), 73.60

(C2), 35.88 (C3), 26.83 (C4), 23.91 (Me-(C2)). ^{1}H NMR and ^{13}C NMR spectral data are in agreement with those reported previously.[2]

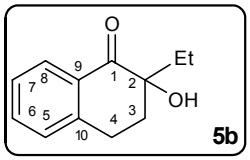
2-Hydroxy--6-methoxy-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (5a). (2-Hydroxy-6-methoxy-2-methyl-1-tetralone). Product **5a** was prepared in 49% yield like light yellow crystalline compound, with m.p. 74-76ºC.



5a

^{1}H NMR ($CDCl_3$, 300MHz, δ): 8.00 (d, 1H, ^{3}J = 8.7 Hz, H-(C8)); 6.86 (dd, 1H, ^{4}J = 2.4 Hz, ^{3}J = 8.7 Hz, H-(C7)); 6.69 (d, 1H, ^{4}J = 2.1 Hz, H-(C5)); 3.89 (bs, 1H, -OH); 3.87 (s, 3H, -OCH_3); 3.09 (ddd, 1H, ^{3}J = 6.0 Hz, ^{3}J = 11.0 Hz, ^{2}J = 17.4 Hz, H-(C4)); 2.98 (ddd, 1H, ^{3}J = 5.4 Hz, ^{2}J = 17.7 Hz, ^{3}J = 2.7 Hz, H-(C4));, 2.24 (ddd, 1H, ^{3}J = 3.0 Hz, ^{2}J = 13.2 Hz, ^{3}J = 6.0 Hz, H-(C3)); 2.20 (ddd, 1H, ^{3}J = 5.4 Hz, ^{3}J = 11.0 Hz, ^{2}J = 13.0 Hz, H-(C3)); 1.38 (s, 3H, (C2)-CH_3);. **^{13}C NMR** ($CDCl_3$, 75MHz, δ): 200.63 (C1), 164.41 (C6), 146.21 (C_{Ar}), 130.67 (CH), 123.48 (C_{Ar}), 113.95 (CH), 112.89 (CH), 73.49 (C2), 55.71 (-OMe), 36.09 (C3), 27.41 (C4), 24.40 (Me-(C2)). **IR** ($CHCl_3$. cm^{1-}): 3400 (w, O-H); 3000 (m, C_{alk}-H); 1660 (s, C=O); 1250 (-OCH_3). **Elemental analysis** ($C_{12}H_{14}O_3$): calc. C 69.89%; H 6.84%; found C 69.96%; H 6.95%.

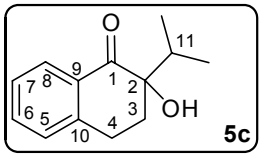
2-Ethyl-2-hydroxy-3,4-dihydronaphthalen-1(2H)-one (5b). (2-Ethyl-2-hydroxy-1-tetralone) Product **5b** was isolated in 78% yield like colorless oil.



5b

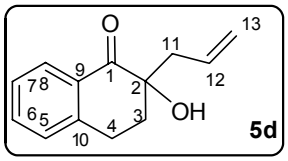
^{1}H NMR ($CDCl_3$, 300 MHz, *δ*) 8.01 (dd, 1H, *J*(7,8) = 7.5, *J*(6,8) = 1.5, H-(C8)); 7.52 (ddd, 1H, *J*(6,7) = 8.0, *J*(5,6) = 7.5, *J*(6,8) = 1.5, H-(C6)); 7.34 (dd, 1H, *J*(6,7) = 8.0, *J*(7,8) = 7.5, H-(C7)); 7.25 (d, 1H, *J*(5,6) = 7.5, H-(C5)); 3.82 (s, 1H, HO-(C2)); 3.10 (ddd, 1H, ^{2}J = 17.5, $J(3^{Et\text{-}C(2)},4^{OH})$ = 13.0, $J(3^{OH},4^{OH})$ = 5.0, H^{OH}-(C4)); 2.99 (ddd, 1H, ^{2}J = 17.5, $J(3^{Et\text{-}C(2)},4^{Et\text{-}C(2)})$ = 6.0, $J(3^{OH},4^{Et\text{-}C(2)})$ = 2.5, $H^{Et\text{-}C(2)}$-(C4)); 2.34 (ddd, 1H, ^{2}J = 13.5, $J(3^{OH},4^{OH})$ = 5.0, $J(3^{OH},4^{Et\text{-}C(2)})$ = 2.5, H^{OH}-(C3)); 2.16 (ddd, 1H, ^{2}J = 13.5, $J(3^{Et\text{-}C(2)},4^{OH})$ = 13.0, $J(3^{Et\text{-}C(2)},4^{Et\text{-}C(2)})$ = 6.0, $H^{Et\text{-}C(2)}$-(C3)); 1.73 (dq, 1H, ^{2}J = 14.5, *J*(11,12) = 7.5, H-(C11)); 1.65 (dq, 1H, ^{2}J = 14.5, *J*(11,12) = 7.5, H-(C11)); 0.94 (t, 3H, *J*(11,12) = 7.5, H-(C12)). **^{13}C NMR** ($CDCl_3$, 75 MHz, *δ*): 202.15 (C1), 143.62 (C10), 134.14 (CH), 130.47 (C9), 129.17 (CH), 128.07 (CH), 127.05 (CH), 76.00 (C2), 33.77 (C3), 28.57 (C11), 26.69 (C4), 7.38 (C12). ^{1}H NMR and ^{13}C NMR spectral data are in agreement with those reported previously.[11]

2-Isopropyl-2-hydroxy-3,4-dihydronaphthalen-1(2H)-one (5c). (2-Isopropyl-2-hydroxy-1-tetralone). Product **5c** was prepared in 50% yield like white crystalline compound, with m.p. 59-62°C (Et_2O). Carnduff[18] refers m.p. 66-68°C (from petroleum).



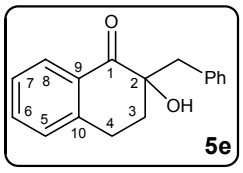
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.97 (dd, 1H, ^3J = 7.5Hz, ^4J = 1.5Hz, H-(C8)); 7.51 (dt, 1H, ^3J = 7.5Hz, ^4J = 1.5Hz, H-(C6)); 7.33 (t, 1H, ^3J = 7.5Hz, H-(C7)); 7.24 (d, 1H, ^3J = 8.1 Hz, H-(C5)); 3.76 (s, 1H, -OH); 3.10 (ddd, 1H, ^2J = 17.7 Hz, ^3J = 12.6 Hz, ^3J = 4.8 Hz, H-(C4)); 2.97 (ddd, 1H, ^2J = 17.7 Hz, ^3J = 5.7 Hz, ^3J = 2.1 Hz, H-(C4)); 2.46 (ddd, 1H, ^2J = 14.1 Hz, ^3J = 4.8 Hz, ^3J = 2.1 Hz, H-(C3)); 2.08 (ddd, 1H, ^2J = 18.6 Hz, ^3J = 12.6 Hz, ^3J = 5.7 Hz, H-(C3)); 2.01 (sept., 1H, ^3J = 6.6 Hz, H-(C11)); 1.08 (d, 3H, ^3J = 6.6 Hz, CH_3-(*i-Pr*)); 0.73 (d, 3H, ^3J = 6.6 Hz, CH_3-(*i-Pr*)). **^{13}C NMR** (300 MHz, $CDCl_3$, δ): 202.87 (C=O), 143.64 (C), 133.99 (CH_{Ar}), 130.99 (C), 129.11 (CH_{Ar}), 128.03 (CH_{Ar}), 127.04 (CH_{Ar}), 77.63 (C2), 32.86 (CH_2), 29.63 (CH), 26.42 (CH_2), 16.44 (CH_3), 16.18 (CH_3). **IR** ($CHCl_3$, cm^{-1}) 3500 (w, O-H), 2880 (s, C_{Ar}-H), 1695 (s, C=O), 1625 (w, C=C), 1480 (m), 1380 (m), 1275 (s, C-O), 995 (m), 445 (s). **Elemental analysis** ($C_{13}H_{16}O_2$): calc. C 76.44%; H 7.90%; found C 76.87%; H 8.06%.
Infrared and ^{1}H NMR spectral data are in agreement with those reported previously.[18]

2-Allyl-2-hydroxy-3,4-dihydronaphthalen-1(2H)-one (5d). (2-Allyl-2-hydroxy-1-tetralone). Product **5d** was isolated after purification by chromatography (SiO_2, Hexsol:Et_2O - 5:1) in 95% yield like yellowish oil.



^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.02 (dd, 1H, ^3J = 7.8 Hz, ^4J = 1.5 Hz, H-(C8)); 7.53 (dt, 1H, ^3J = 7.8 Hz, ^4J = 1.5 Hz, H-(C6)); 7.35 (t, 1H, ^3J = 7.8 Hz, H-(C7)); 7.26 (d, 1H, ^3J = 7.8 Hz, H-(C5)); 5.88 (dddd, 1H, ^3J = 23.1 Hz, ^3J = 14.1 Hz, ^3J = 7.8 Hz, ^3J = 6.3 Hz, H-(C12)); 5.05-5.19 (m, 2H, 2xH-(C13)); 3.81 (s, 1H, -OH); 3.11 (ddd, 1H, ^2J = 17.7 Hz, ^3J = 12.6 Hz, ^3J = 5.1 Hz, H-(C4)); 2.99 (ddd, 1H, ^2J = 17.7 Hz, ^3J = 6 Hz, ^3J = 2.4 Hz, H-(C4)); 2.32-2.48 (m, 3H, 2xH-(C11) + H-(C3)); 2.16 (ddd, 1H, ^2J = 18.9 Hz, ^3J = 12.9 Hz, ^3J = 6 Hz, H-(C3)). **^{13}C NMR** (300 MHz, $CDCl_3$, δ): 201.25 (C=O), 143.62 (C), 134.30 (CH_{Ar}), 132.27 (CH_{Ar}), 130.29 (C), 129.25 (CH_{Ar}), 128.18 (CH_{Ar}), 127.14 (C12), 119.38 (C13), 75.57 (C2), 40.51 (CH_2), 33.68 (CH_2), 26.36 (CH_2). **Elemental analysis** ($C_{13}H_{14}O_2$): calc. C 77.20%; H 6.98%; found C 76.08%; H 6.99%.
^{1}H NMR and ^{13}C NMR spectral data are in agreement with those reported previously.[11]

2-Benzyl-2-hydroxy-3,4-dihydronaphthalen-1(2H)-one (5e). (2-Benzyl-2-hydroxy-1-tetralone). Product **5e** was prepared in 89% yield like yellowish crystalline compound, m.p. 104.0 – 105.1 °C (Hexsol / Et_2O).



5e **^{1}H-NMR** (300 MHz, $CDCl_3$, δ): 8.02 (dd, 1H, ^4J(8,6) = 1.3, ^3J(8,7) = 7.8 Hz, H-(C8)); 7.57 (ddd, 1H, ^4J(6,8) = 1.3, ^3J(6,5) = ^3J(6,7) = 7.5 Hz, H-(C6)); 7.13 – 7.41 (m, 7H, H-(C5) + H-(C7) + 5 x H-(Ph)); 3.76 (bs, 1H, -OH); 3.27 (ddd, 1H, ^3J(4,3) = 5.7, ^3J(4,3) = 12.2, ^2J = 18.0 Hz, H-(C4)); 3.04 (ddd, 1H, ^3J(4,3) = 2.4, ^3J(4,3) = 5.4, ^2J = 18.0 Hz, H-(C4)); 2.92 (d, 1H, ^2J = 13.8Hz, -CH_2Ph); 3.00 (d, 1H, ^2J = 13.8Hz, -CH_2Ph); 2.20 – 2.32 (m, 1H, with measurable ^3J(3,4) = 2.4, ^3J(3,4) = 5.7, J = 7.8 Hz, H-(C3)); 2.14 – 2.28 (m, 1H, with measurable ^3J(3,4) = 5.4, ^3J(3,4) = 12.2 Hz, H-(C3)). **^{13}C-NMR** (75 MHz, $CDCl_3$, δ): 200.87 (C1, C=O), 143.18 (C10-Ar), 135.32 (C9-Ar), 134.12 (CHAr), 130.39 (C-Ar, Ph), 130.35 (2 x CHAr), 129.10 (CHAr), 128.09 (2 x CHAr), 128.00 (CHAr), 127.06 (CHAr), 126.86 (CHAr), 76.04 (C2), 41.95 (-CH$_2$-Ph), 33.82 (C3), 26.38 (C4). **IR** (CH_2Cl_2, cm^{-1}): 3315 (s, -OH), 3010 (m, C-$H_{alif.}$), 1679 (s, C=O), 1277 (s, C-O, doublet), 760 (s, C-$H_{arom.}$), 706 (s, C-$H_{arom.}$).

Acknowledgements

This work was supported by the Slovak Research and Development Agency under the contract No. APVT-20-031904, APVV LPP 0153-06 and VEGA 1/4467/07.

References and Notes

1. (a) Solladié-Cavallo, A.; Šedý, O.; Sališová, M.; Schmitt, M. *Eur. J. Org. Chem.* **2002**, 3042. See also supporting information. (b) Pažický, M.; Gášpár, B.; Solladié-Cavallo, A.; Sališová, M.; Boháč, A; Hutta, M.; Addová, G. *Synthesis* **2006**, 2013.
2. Solladié-Cavallo, A.; Šedý, O.; Sališová, M.; Biba, M.; Welch, J.; Nafié, L.; Freedman, T. *Tetrahedron*: *Asymmetry* **2001**, *12*, 2703; and references therein.
3. (a) Davis, F. A.; Weismiller, M. C. *J. Org. Chem*. **1990**, *55*, 3715. (b) Takikawa, H.; Hachisu, Y.; Bode, J. W.; Suzuki, K. *Angew. Chem. Int. Ed.* **2006**, *45*, 3492. (c) Masui, M.; Ando, A.; Shioiri, T. *Tetrahedron Lett.* **1988**, *29*, 2835.
4. (a) Davis, F. A.; Zhou, P.; Murphy, C. K.; Sundarababu, G.; Qi, H.; Han, W.; Przeslawski, R.M.; Chen, B.-C.; Carroll, P. J. *J. Org. Chem.* **1998,** *63,* 2273. (b) Murphy, J. A.; Mahesh, M.; McPheators, G.; Anand, R. V.; McGuire, T. M.; Carling, R.; Kennedy, A. R. *Org. Lett.* **2007**, *9*, 3233.
5. (a) Streitwieser, A.; Kim, Y.-J.; Wang, D. Z.-R. *Org. Lett.* **2001**, *3*, 2599. See also supporting information. (b) Goto, M.; Akimoto, K.-I.; Aoki, K.; Shindo, M.; Koga, K *Tetrahedron Lett.* **1999**, *40*, 8129. (c) Adamczyk, M.; Watt, D. S.; Netzel, D. A. *J. Org. Chem.* **1984**, *49*, 4226.

6. Semak, V.; Boháč, A.; Sališová, M.; Addová, G.; Danko, P. *Chem. Papers* **2008**, *62*, 275.
7. Loewenthal, H. J. E. *Guide for the Perplexed Organic Experimentalist*; Heyden: London, 1980; pp 125-128.
8. Brown D. S.; Marples, B. A.; Smith, P.; Walton, L. *Tetrahedron* **1995**, *51*, 3587.
9. Park, E. L; Kim, M. H; Kim, D. Y. *J. Org. Chem*. **2004**, *69*, 6897 and references therein.
10. Krapcho, A. P. *Synthesis* **1982**, 805 and 893.
11. de Vries, E. F. J.; Ploeg, L.; Colao, M.; Brussee, J.; van der Gen, A. *Tetrahedron: Asymmetry* **1995**, *6*, 1123.
12. Amarego, W. *Purification of Laboratory Chemicals*; Butterworth Heinemann: Burlington, 2003.
13. Klinkmüller, K.-D.; Marschall, H.; Weyerstahl, P. *Chem. Ber.* **1975**, *108*, 203.
14. Mandal, A. N.; Raychaudhuri, S. R.; Chatterjee, A. *Synthesis* **1983**, 727.
15. Mitsuhashi, K.; Ito, R.; Arai, T.; Yanagisawa, A. *Org. Lett.* **2006**, *8*, 1721.
16. Ecke, G. G.; Napolitano, J. P. *J. Am. Chem. Soc.* **1955**, *77*, 6373.
17. Malosh, C. F.; Ready, J. M. *J. Am. Chem. Soc.* **2004***, 126*, 10240.
18. Carnduff; J.; Leppard, D. G. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1325.