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Synthesis of 4-[(1*R*,4*R*)-3-Oxo-*p*-menthan-2-ylidenemethyl]benzoic Acid and Its Esters

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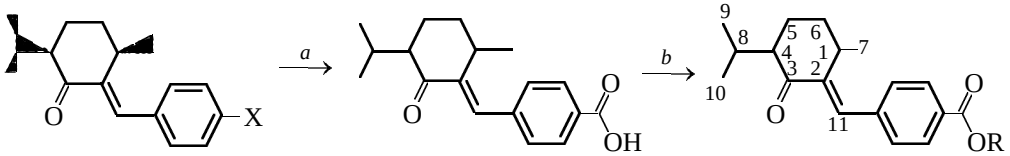
Abstract — Carbonylation of (*E*)-2-(4-halobenzylidene)-*p*-menthan-3-ones, catalyzed by $PdCl_2(PPh_3)_2$, gave a distereometric mixure of 4-[(1*R*,4*R*)- and (1*R*,4*S*)-3-oxo-*p*-menthan-2-ylidenemethyl]benzoic acids, whose reaction with phenols gave 1*R*,4*R* diastereomers of the corresponding esters.

4-Substituted 2-benzylidene-*p*-menthan-3-ones are effective chiral components of liquid crystalline materials used in the production of displays [1]. 4-[(1*R*,4*R*)-3-oxo-*p*-menthan-2-ylidenemethyl]benzoic acid esters, along with (1*R*,4*R*)-2-(4-hydroxybenzylidene)-*p*-menthan-3-one derivatives [2] are of particular importance, since the ester group imparts to these compounds enhanced solubility in ester liquid crystalline solvents that are employed in a number of practically important compositions. However, compounds like **I** proved to be difficult to synthesize [6, 7] by schemes involving crotonic or directed aldol condensation, that work well with other arylmethylene-*p*-menthan-3-ones (see, for example, [3–5]). Therefore, we chose another synthetic approach to (*E*)-4-[(1*R*,4*R*)-3-oxo-*p*-menthan-2-ylidenemethyl]benzoic acid (**II**) via carbonylation with carbon monoxide (**III**) of 2-(4-halobenzylidene)mentan-3-ones **IVa** and **IVb** on a palladium catalyst [scheme (1)]. This approach has been applied to success in the synthesis of *para*-substituted benzoic acids [8–12].



IVa, IVb **II** **Ia–Ij** (1)

a: CO, $[PdCl_2(PPh_3)_2]$ or $PdCl_2$; base (KOH or NaOH); H^+ (HCl or HAc);
b: ROH, *N*,*N*′-dicyclohexylcarbodiimide (**V**), 4-dimethylaminopyridine (**VI**);
I, R = CH_3 (**a**), C_6H_5 (**b**), *p*-$C_4H_9OC_6H_4$ (**c**), *p*-$C_5H_{11}OC_6H_4$ (**d**), *p*-$C_6H_{13}OC_6H_4$ (**e**), *p*-$C_7H_{15}OC_6H_4$ (**f**), *p*-$C_8H_{17}OC_6H_4$ (**g**), *p*-$C_9H_{19}OC_6H_4$ (**h**), *p*-$C_{10}H_{21}OC_6H_4$ (**i**), 4′-C_6H_{13}-(4-$C_6H_4C_6H_4$) (**j**); **IV**, X = I (**a**), Br (**b**).

The mechanism of the carbonylation of halobenzenes, catalyzed triphenylphosphine palladium(II) complexes **VII**, has been explored in detail by Grushin and Alper [9]. However, the cinnamoyl groups in compounds **IVa** and **IVb** can complicate their carbonylation. We could not find examples of successful carbonylations of such derivatives. At the same time, it is known that the double bond in certain alkenes, styrene, and cyclohexene is carbonylated at elevated pressures (7–20 atm) [13]. The carbonylation of cynnamoyl chloride, catalyzed by $[PdCl_2(PPh_3)_2]$, under 50 atm resulted in quantitative formation of 4-phenyl-3-butenoic acid [14].

According to [2, 15, 16], (1*R*,4*R*)-2-arylmethylene-*p*-menthan-3-ones, including **IVa** and **IVb**, can undergo both acid- or base-catalyzed and thermal epimerization (configuration inversion of the chiral C^4 center) via intermediate formation of dienol **VIII** [scheme (2)].

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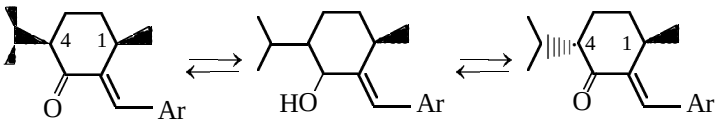

cis-1R,4*R* **VIII** *trans*-1*R*,4*R* (2)

Base-catalyzed epimerization of compounds **IVa** and **IVb** gives rise to an equilibrium mixture of (*E*)-(1*R*,4*R*)- (70–80%) and (*E*)-(1*R*,4*S*) diastereomers (30–20%) [15]. In this connection we considered it important to find out in the present work what is the ratio of the above diastereomers, formed in carbonylation of the 1*R*,4*R* isomers of compounds **IVa** and **IVb**.

In view of the data in [8–12], to find conditions for mild cabbonylation of compounds **IVa** and **IVb** (pressure 1 atm, temperature below 100°C), we tried three palladium catalysts: $[(Ph_3P)_2PdCl_2]$, $Pd(OAc)_2$, and $PdCl_2$. Attempted use of $Pd(OAc)_2$ under the conditions described in [8] has not met with success: No acid **II** was formed even when the reaction temperature was raised by 20°C.

The conditions and results of the $(Ph_3P)_2PdCl_2$- and $PdCl_2$-catalyzed carbonylations of compounds **IVa** and **IVb** are given in the table. The best results were obtained with $(Ph_3P)_2PdCl_2$ under conditions similar to those in [12]. The difference was that the reaction was performed in aqueous toluene with KOH instead of NaOH. Potassium hydroxide was preferred, since the potassium salt of acid **II** is better soluble than the sodium salt. As seen from the table, iodine derivative **IVa** reacts double as fast and at a lower temperature as bromine derivative **IVb** (see table, exp. nos. 1 and 4; 5, 7, and 8), which agrees with tendencies characteristic of other *para*-substituted aryl halides [11]. With triphenylphosphine as catalyst stabilizer, the reaction yield increases (exp. nos. 1 and 2). Decreased catalyst (0.2% per **IVa**) and KOH concentrations increase the reaction time (exp. nos. 2 and 10). At KOH concentrations above 16.8%, more by-products are formed [by HPLC data, 35% at a KOH concentration of 42.5%, exp. no. 3]. Therewith, isolation of the target esterificaion products is complicated.

The effects on the carbonylation reaction of such factors as triphenylphosphine and base concentrations, as well as temperature are similar to those described in [12], namely, the yield of the target reaction product increases in the presence of triphenylphosphine, the optimal concentration of KOH is 16.8%, and the reaction slows down at temperatures below 80°C with compound **IVa** and 85°C with compound **IVb**. Under the carbonylation conditions proposed in [10] (see table, exp. no. 10), the yield of acids **II** is as little as 10% lowed than in exp. no. 1, even though the reaction time is increased from 5 to 50 h. Nevertheless, such conditions are much more practical in terms of catalyst and base consumption. Note that compounds **IVa** and **IVb** exhibit reduced reactivity, and, therefore, they cannot be carbonylated in conditions suitable for carbonylation of aryl halides with electron-acceptor substituents, such as NO_2, CN, or Cl [solvent DMF–water, catalyst $Pd(OAc)_2$, 40–45°C] [8]. A possible explanation for this effect is that the electron-acceptor cinnamoyl substituent in the benzene ring of aryl halides **IVa** and **IVb** transforms in the basic medium into a strongly electron-acceptor group of dienolate **VIII** as an actual substrate [scheme (2)]. This suggestion is nicely consistent with the reported fact that *p*-iodoanisole is carbonylated in a much lower yield than iodobenzene in the same conditions [9].

We also performed carbonylation in the absence of an aromatic solvent by a procedure involving micellar catalysis [10] (see table, exp. no. 10, system BuOH–H_2O–sodium lauryl sulfonate–$PdCl_2$). However, with the system described in [10] we failed to obtain a microemulsion with haloarene **IVa**, which probably explains the unexpectedly low yield of the reaction product.

The ratio of the 1*R*,4*R* and 1*R*,4*S* isomers resulting from the carbonylation of compounds **IVa** (exp. no. 1) and **IVb** (exp. no. 4) was established by HPLC of the mixture of the reaction products extracted from the aqueous phase and esterified with methanol. It was earlier shown that (1*R*,4*R*)-2-(4-hydroxybenzylidene)-*p*-menthan-3-one is esterified under these conditions without appreciable configuration inversion of the C^4 chiral center [2]. As reference compounds in the analysis we used the individual diastereomers obtained previously by directed aldol condensation of 4-(methoxycarbonyl)benzaldehyde with (–)-menthone [6], whose structure was confirmed by ^1H NMR [17] and stereochemistry [(*E*)-(*R*,4*S*) isomer], by X-ray diffraction analysis [18].

Thus, it was shown that carbonylation of (*E*)-(*R*,4*S*)-2-(4-halobenzylidene)-*p*-mentan-3-ones **IVa** and **IVb** gives a mixture of the *E*-1*R*,4*R* and *E*-1*R*,4*S* diastereomers (~2.5 : 1). This ratio corresponds to that in the equilibrium mixture of the same diastereomers,

Carbonylation of 2-(4-halobenzylidene)-*p*-menthan-3-ones **IVa** and **IVb**[a]

Exp. no.	Substrate	Time, h (*t*, °C)	Solvent (v/v)	Catalyst (concentration)	Concentration of KOH in water, %	Yield of **II**, %
1	**IVa**	5 (79–80)	Toluene–water (75 : 25)	$[(Ph_3P)_2PdCl_2]$ 1 mol % per **IVa** + Ph_3P, 16 mol/mole Pd	16.8	55
2	**IVa**	5 (79–80)	Toluene–water (75 : 25)	$[(Ph_3P)_2PdCl_2]$ 1 mol % per **IVa**	16.8	46
3	**IVa**	4 (85–86)	Toluene–water (75 : 25)	Like in exp. no. 1	42.5	41
4	**IVb**	10 (85–86)	Toluene–water (75 : 25)	The same	16.8	34
5	**IVb**	4 (86–96)	*p*-Xylene–water (3 : 7)	$[(Ph_3P)_2PdCl_2]$ 1 mol % per **IVa** + Ph_3P, 2 mol/mole Pd	50[b]	20
6	**IVb**	9 (60–64)	*p*-Xylene–water (3 : 7)	Like in exp. no. 5	50	1
7[c]	**IVa**	5 (78–80)	Benzene–water (10 : 3)	Like in exp. no. 2	50	21
8[c]	**IVb**	10 (78–80)	Benzene–water (10 : 3)	The same	50	21
9[d]	**IVa**	30 (80–85)	BuOH–water (1 : 10)[e]	$PdCl_2$ (1 mol % per **IVa)**	2.1	19
10	**IVa**	50 (78–82)	Toluene–water (1 : 2)[e]	$[(Ph_3P)_2PdCl_2]$ 0.2 mol % per **IVa**	1.0	44

[a] In exp. nos. 1–6, Bu_4NI (5.6 mol % per **IV**) was used as phase-transfer catalyst. [b] NaOH was used instead of KOH. [c] As described in [9]. [d] As described in [10]. [e] Sodium lauryl sulfonate was added (0.5 g per 10 ml of water).

formed upon epimerization of 2-(4-phenylbenzylidene)-*p*-menthan-3-one in basic medium [15]. It is indubitable that the realization under the reaction conditions (basic medium) of the epimeric equilibrium according to scheme (2) (with the starting halo derivatives and, what is more important, with the resulting salt of acid **II**) is the main reason for the formation of the diastereomeric mixture. Similar thermal epimerization [19] (which evidently occurs in view of increased reaction temperature and long reaction time) can be considered as a certain additional factor.

Esterification of the diastereomeric mixture of acids **II** with methanol, phenol, and substituted phenols was performed in the presence of the system **V** + **VI** according to [20, 21]. Individual (1*R*,4*R*)-esters (98–99% pure) were isolated in 18–27% (per starting phenol) by double crystallization from 2-propanol. Thus prepared methyl benzoate **II** is identical to the major product of the directed aldol condensation of 4-(methoxycarbonyl)benzaldehyde with (–)-menthone with subsequent mild dehydration [6].

EXPERIMENTAL

The IR spectra were measured on a Specord M-82 instrument in KBr. The ^1H NMR spectra were obtained on Jeol JNM-LA-400FT-NMR (400 MHz) and Varian Mercury VX-200 (200 MHz) spectrometers in $CDCl_3$ and DMSO-d_6 (internal reference TMS). The mass spectra were taken on a Finnigan-MAT-1020 GC–MS system, ionizing energy 70 eV, direct sample inlet. The specific rotation of chiral compounds (α_D^{20}) [(deg ml) (g dm)$^{-1}$] was measured on an AA-10 automated polarimeter at λ 589 nm in chloroform (1–1.5 g sample/100 ml solvent).

High-performance liquid chromatography was performed on a Milikhrom-5 microcolumn chromatograph in the direct and reversed-phase modes on Silasorb-600 and Diasorb-C16T (5 μm), respectively. The eluents were 5% butyl acetate in heptane and acetonitrile–water (80 : 20, v/v). Detection was performed at λ 260, 280, and 330 nm.

(–)-Menthone was synthesized as described in [22], *p*-iodobenzaldehyde was prepared from 1-(bromomethyl)-4-iodobenzene by the Sommelet reaction [23]

and 1-(bromomethyl)-4-iodobenzene, by bromination of *p*-iodotoluene with *N*-bromosuccinimide [24].

***p*-(*n*-Alkoxy)phenols (n-$C_nH_{2n+1}OC_6H_4OH$, n = 4–10)** were synthesized by a procedure similar to that described in [25] and modified for alkylation of phenols [26], using, instead of sodium alcoholate, 28% aqueous KOH (15 ml), that was added dropwise over the course of 5 h to a boiling solution of 0.1 mol of hydroquinone and 0.1 mol of *n*-alkyl bromide in 25 ml of ethanol. Yield 15–25% (yield of n-$C_{10}H_{21}OC_6H_4OH$ 2%). n-$C_9H_{19}OC_6H_4OH$ and n-$C_{10}H_{21}OC_6H_4OH$ were isolated from the precipitate that, like in the synthesis of n-$C_8H_{17}O\cdot C_6H_4OH$, contains diester, after acidification and extraction with chloroform. The extract was dried over magnesium sulfate, the solvent was removed, and the residue was distilled in a vacuum [in the case of n-$C_9H_{19}OC_6H_4OH$, bp 186°C (8–10 mm)] and recrystallized from hexane. For further purification, n-$C_{10}H_{21}OC_6H_4OH$ was applied to Al_2O_3, washed with heptane until a negative Beilstein test of washings, eluted with 2-propanol and 5% acetic acid in 2-propanol, freed of the solvent, and dried in a vacuum (8–20 mm Hg).

n-$C_6H_{13}C_6H_4C_6H_4OH$ was synthesized as described in [27].

(*E*)-(1*R*,4*R*)-2-(4-iodobenzylidene)-*p*-menthan-3-one (**IVa**) was synthesized like bromo derivative **IVb** [5, 15] by condensation of *p*-iodobenzaldehyde with (–)-menthone in DMSO–$CsOH\cdot H_2O$ or DMSO–Bu_4NOH (30% aqueous) (0.1 mol base/mole menthone) at 18°C, yield 48% (after crystallization from ethanol), mp 87–88°C.

Synthesis of a mixture of diastereomeric oxomenthanylidenemethylbenzoic acids II from (*E*)-(1*R*,4*R*)-2-(4-iodobenzylidene)-*p*-menthan-3-one (IVa). To a solution of 4 g of compound **IVa** in 28 ml of toluene, 448 mg of triphenylphosphine, 224 mg of tetrabutylammonium iodide, 76 mg of dichlorobis-(triphenylphosphine)palladium (1 mol% per **IVa**), 8.2 ml of 16.8% aqueous KOH were added in succession. The system was purged with CO in triplicate and then heated with vigorous stirring at 79–80°C under CO until reaction completion (4–5 h, control by TLC). The layers were separated, and the aqueous layer was acidified with acetic acid to pH 4. The precipitate that formed was filtered off, washed with water and benzene, and dried at a temperature of no higher than 30°C, yield 55%. The reaction product was brought into esterification without further purification. Individual acid **II** was isolated from the resulting stereoisomeric mixture by crystallization from benzene, yield 14%, mp 169–170°C. ^{1}H NMR spectrum (DMSO-d_6, 200 MHz), δ, ppm: 0.899 d, 0.961 d (6H, C^9H_3, $C^{10}H_3$), 1.176 d (3H, C^7H_3), 1.865 d (4H, C^5H_2, C^6H_2), 2.251 m (1H, H^4), 2.543 m (1H, H^8), 3.373 m (1H, H^1), 7.088 s (1H, H^{11}), 7.427 d (2H, H_m), 8.105 d (2H, H_o), 9.490 s (1H, OH).

Synthesis of a mixture of diastereomeric oxomenthanylidenemethylbenzoic acids II from 2-(4-bromobenzylidene)-*p*-menthan-3-one (IVb). To a solution of 2 g of compound **IVb** in 15 ml of toluene, 257 mg of triphenylphosphine, 128 mg of tetrabutylammonium iodide, 43 mg of $[(Ph_3P)_2PdCl_2]$ (1 mol% per **IVb**), and 4.7 ml of 16.7% aqueous KOH were added in succession. The system was purged with CO in triplicate and then heated with vigorous stirring at 86°C under CO until reaction completion (8–10 h, control by TLC). Further workup was performed as described above. Yield 34%.

Esterification of 4-[(1*R*,4*R*)-3-oxo-*p*-menthan-2-ylidenemethyl]benzoic acid (II) with methanol. Stereoisomeric mixture **II** and 20 mg of compound **VI** were added to a solution of 0.06 ml of dry methanol in 7.5 ml of dry dichloromethane. After cooling to 0°C, diimide **V**, 317 mg, was added, and the mixture was stirred in moisture-proof conditions for 1 h at 0°C, for 6 h without cooling, left to stand for 14 h at room temperature, filtered through a bed (1 cm) of silica gel, and the solvent was removed by distillation. Individual methyl (*E*)-4-[(1*R*,4*R*)-3-oxo-*p*-menthan-2-ylidenemethyl]benzoate (**Ia**) was isolated by double crystallization from methanol; yield 19%, purity 99% (by HPLC). The melting point (73–74°C) and spectral data are consistent with those reported in [6].

Esterification of 4-[(1*R*,4*R*)-3-oxo-*p*-menthan-2-ylidenemethyl]benzoic acid (II) with phenols. A mixture of 2.3 mmol of stereisomeric mixture **II** and 0.25 mmol of compound **VI** were added to a solution of 2.3 mmol of phenol in 7.5 ml of dry dichloromethane. After cooling to After cooling to 0°C, diimide **V**, 2.53 mmol, was added, and the mixture was stirred in moisture-proof conditions for 1 h at 0°C, 6–8 h without cooling, left to stand for 14 h at room temperature, and filtered through a bed (1 cm) of silica gel. The solvent was removed from the filtrate ba distillation, and the residue was doubly crystallized from 2-propanol.

p-(Decyloxy)phenyl ester **Ii** was prepared from individual (1*R*,4*R*)-**II** and isolated by double crystallization from methanol–hexane (4:1).

Phenyl (*E*)-4-[(1*R*,4*R*)-3-oxo-*p*-menthan-2-ylidenemethyl]benzoate (Ib). Yield 21%, mp 129–130°C. IR spectrum, ν, cm^{-1}: 1727 (ester C=O), 1678 (ketone C=O), 1618; 1602 (aryl C=C). Mass spectrum,

m/z: 362 $[M]^+$, 269, 241, 227, 198, 183, 171, 155, 141, 128, 115, 94, 77, 65. α_D^{20} –118.45°. ^{1}H NMR spectrum, δ, ppm ($CDCl_3$, 400 MHz), δ, ppm: 0.981, 0.919 t (6H, C^9H_3, $C^{10}H_3$, *J* 6.8 Hz), 1.195 t (3H, C^7H_3, *J* 7.0 Hz), 1.784–1.960 m (4H, C^5H_2, C^6H_2), 2.269 m (1H, C^4H, *J* 12.3, 6.2, 3.4 Hz), 2.559 sept.d (1H, C^8H, *J* 6.8, 3.4 Hz), 3.407 m (1H, C^1H, *J* 7.0, 4.2, 2.2 Hz), 7.118 s (1H, ^{11}H), 7.218 d (2H, $H_{o'}$, *J* 8.5 Hz), 7.286 t (1H, $H_{p'}$), 7.446 t (2H, $H_{m'}$, *J* 8.5 Hz), 7.467 d (2H, H_o, *J* 8.5 Hz), 8.205 d (2H, H_m, *J* 8.5 Hz).

***p*-Butoxyphenyl (*E*)-4-[(1*R*,4*R*)-3-oxo-*p*-menthan-2-ylidenemethyl]benzoate (Ic).** Yield 33%, mp 108–109°C. ^{1}H NMR spectrum, δ, ppm (DMSO-d_6, 200 MHz), δ, ppm : 0.946 t (3H, CH_3), 0.964 d, 0.864 d (6H, C^9H_3, $C^{10}H_3$), 1.116 d (3H, C^7H_3), 1.445 m (4H, CH_2CH_2), 1.837 m (4H, C^5H_2, C^6H_2), 2.350 m (2H, C^4H, C^8H), 3.383 m (1H, C^1H), 3.995 t (2H, OCH_2), 6.997 d (2H, $H_{m'}$), 7.013 s (1H, $C^{11}H$), 7.184 d (2H, $H_{o'}$), 7.595 d (2H, H_m), 8.136 d (2H, H_o).

***p*-Pentyloxyphenyl (*E*)-4-[(1*R*,4*R*)-3-oxo-*p*-menthan-2-ylidenemethyl]benzoate (Id).** Yield 66%, purity 99% (by HPLC), mp 107–108°C. IR spectrum, ν, cm^{-1}: 1726 (ester C=O), 1675 (ketone C=O), 1599 (aryl C=C). Mass spectrum, *m/z*: 448 $[M]^+$, 269, 241, 227, 198, 171, 155, 141, 128, 115, 91, 81, 69. α_D^{20} –96.75°. ^{1}H NMR spectrum, δ, ppm ($CDCl_3$, 400 MHz), δ, ppm : 0.941 t (3H, CH_3, *J* 7.0 Hz), 0.980 d, 0.918 d (6H, C^9H_3, $C^{10}H_3$, *J* 6.8 Hz), 1.189 d (3H, C^7H_3, *J* 7.0 Hz), 1.426 m (4H, CH_2CH_2), 1.800 m (2H, CH_2, 1.866–1.937 m (4H, C^5H_2, C^6H_2), 2.267 m (1H, C^4H, *J* 12.3, 6.2, 3.4 Hz), 2.554 sept.d (1H, C^8H, *J* 6.8, 3.4 Hz), 3.400 m (1H, C^1H, *J* 7.0, 4.2, 2.2 Hz), 3.963 t (2H, OCH2, *J* 6.7 Hz), 6.931 d (2H, $H_{m'}$, *J* 8.5 Hz), 7.111 d (2H, $H_{o'}$, *J* 8.5 Hz), 7.114 s (1H, $C^{11}H$), 7.456 d (2H, H_o, *J* 8.5 Hz), 8.186 d (2H, H_m, *J* 8.5 Hz).

***p*-(Hexyloxy)phenyl (*E*)-4-[(1*R*,4*R*)-3-oxo-*p*-menthan-2-ylidenemethyl]benzoate (Ie).** Yield 21%, mp 96–97.5°C. IR spectrum, ν, cm^{-1}: 1730 (ester C=O), 1678 (ketone C=O), 1599 (aryl C=C). Mass spectrum, *m/z*: 462 $[M]^+$, 269, 241, 227, 198, 171, 155, 128, 115, 69. α_D^{20} –92.91. ^{1}H NMR spectrum, δ, ppm ($CDCl_3$, 400 MHz), δ, ppm : 0.911 t (3H, CH_3, *J* 6.9 Hz), 0.980 d, 0.917 d (6H, C^9H_3, $C^{10}H_3$), 1.188 d (3H, C^7H_3, *J* 7.0 Hz), 1.790 m (2H, CH_2), 1.865–1.937 m (4H, C^5H_2, C^6H_2), 2.265 m (1H, C^4H, *J* 12.3, 6.2, 3.4 Hz), 2.553 sept.d (1H, C^8H, *J* 6.8, 3.4 Hz), 1.343–1.504 m (6H, $CH_2CH_2CH_2$), 3.402 m (1H, C^1H, *J* 7.0, 4.2, 2.2 Hz), 3.961 t (2H, OCH_2, *J* 6.7 Hz), 7.110 d (2H, $H_{o'}$, *J* 8.5 Hz), 7.114 s (1H, $C^{11}H$), 7.456 d (2H, H_o, *J* 8.5 Hz), 7.930 d (2H, $H_{m'}$, *J* 8.5 Hz), 8.185 d (2H, H_m, *J* 8.5 Hz).

***p*-(Heptyloxy)phenyl (*E*)-4-[(1*R*,4*R*)-3-oxo-*p*-menthan-2-ylidenemethyl]benzoate (Id).** Yield 37%, mp 88–89°C. ^{1}H NMR spectrum, δ, ppm (DMSO-d_6, 200 MHz), δ, ppm : 0.879 t (3H, CH_3), 0.944 d, 0.862 d (6H, C^9H_3, $C^{10}H_3$), 1.112 d (3H, C^7H_3), 1.294 m (8H, (CH2)4), 1.726 m (2H, CH2), 1.824 m (4H, C^5H_2, C^6H_2), 2.338 m (2H, C^4H, C^8H), 3.379 m (1H, C^1H), 3.984 t (2H, OCH_2), 6.980 d (2H, $H_{m'}$), 7.016 s (1H, $C^{11}H$), 7.177 d (2H, $H_{o'}$), 7.590 d (2H, H_m), 8.135 d (2H, H_o).

***p*-(Octyloxy)phenyl (*E*)-4-[(1*R*,4*R*)-3-oxo-*p*-menthan-2-ylidenemethyl]benzoate (Ig).** Yield 28%, mp 79–80°C. IR spectrum, ν, cm^{-1}: 1725 (ester C=O), 1680 (ketone C=O), 1602 (aryl C=C). Mass spectrum, *m/z*: 490 $[M]^+$, 269, 241, 227, 198, 171, 155, 141, 128, 115, 69. δ_D^{20} –56.46. ^{1}H NMR spectrum, δ, ppm (DMSO-d_6, 400 MHz), δ, ppm : 0.883 t (3H, CH_3), 0.944 d, 0.948 d (6H, C^9H_3, $C^{10}H_3$), 1.120 d (3H, C^7H_3), 1.297 m [10H, $(CH_2)_5$], 1.725 m (2H, CH_2), 1.828 m (4H, C^5H_2, C^6H_2), 2.355 m (2H, C^4H, C^8H), 3.387 m (1H, C^1H), 3.988 t (2H, OCH_2), 6.990 d (2H, $H_{m'}$), 7.024 s (1H, $C^{11}H$), 7.182 d (2H, $H_{o'}$), 7.595 d (2H, H_m), 8.140 d (2H, H_o).

***p*-(Nonyloxy)phenyl (*E*)-4-[(1*R*,4*R*)-3-oxo-*p*-menthan-2-ylidenemethyl]benzoate (Ih).** Yield 42%, mp 76–78°C. ^{1}H NMR spectrum, δ, ppm (DMSO-d_6, 200 MHz), δ, ppm : 0.870 t (3H, CH_3), 0.946 d, 0.964 d (6H, C^9H_3, $C^{10}H_3$), 1.117 d (3H, C^7H_3), 1.288 m [12H, $(CH_2)_6$], 1.727 m (2H, CH_2), 1.830 m (4H, C^5H_2, C^6H_2), 2.356 m (2H, C^4H, C^8H), 3.383 m (1H, C^1H), 3.982 t (2H, OCH_2), 6.982 d (2H, $H_{m'}$), 7.020 s (1H, $C^{11}H$), 7.178 d (2H, $H_{o'}$), 7.594 d (2H, H_m), 8.137 d (2H, H_o).

***p*-(Decyloxy)phenyl (*E*)-4-[(1*R*,4*R*)-3-oxo-*p*-menthan-2-ylidenemethyl]benzoate (Ii).** Yield 55%, mp 78–79°C. ^{1}H NMR spectrum, δ, ppm (DMSO-d_6, 200 MHz), δ, ppm : 0.865 t (3H, CH_3, *J* 6.5 Hz), 0.948 d, 0.867 d (6H, C^9H_3, $C^{10}H_3$, *J* 6.9 Hz), 1.120 d (3H, C^7H_3, *J* 7.0), 1.272 m [14H, $(CH_2)_7$], 1.713 m (2H, CH_2), 1.658–1.856 m (4H, C^5H_2, C^6H_2), 2.354 m (2H, C^4H, C^8H), 3.384 m (1H, C^1H), 3.984 t (2H, OCH_2, *J* 6.4 Hz), 6.981 d (2H, $H_{m'}$, *J* 8.5 Hz), 7.023 s (1H, $C^{11}H$), 7.185 d (2H, $H_{o'}$, *J* 8.5 Hz), 7.596 d (2H, H_m, *J* 8.5 Hz), 8.137 d (2H, H_o, *J* 8.5 Hz).

***p*-[*p*-(Hexylphenyl]phenyl (*E*)-4-[(1*R*,4*R*)-3-oxo-*p*-menthan-2-ylidenemethyl]benzoate (Ij).** Yield 22%, mp 104–172°C (meso phase). ^{1}H NMR spectrum ($CDCl_3$, 200 MHz), δ, ppm : 0.898 t (3H, CH_3), 0.978 d, 0.916 d (6H, C^9H_3, $C^{10}H_3$), 1.193 d (3H, C^7H_3), 1.330 m [6H, (CH2)3], 1.622 m (2H, CH2), 1.885 m (4H, C^5H_2, C^6H_2), 2.270 m (1H, C^4H), 2.560 m (1H, C^8H), 2.649 t (2H, CH_2), 3.411 m (1H,

C^1H), 7.120 s (1H, $C^{11}H$), 7.477 d (2H, $H_{m'}$), 7.507 d (2H, H_m), 7.633 d (2H, $H_{o'}$), 8.221 d (2H, H_o).

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