Baeyer–Villiger oxidation of norbornan-7-ones: long-range substituent effects on regioselectivity

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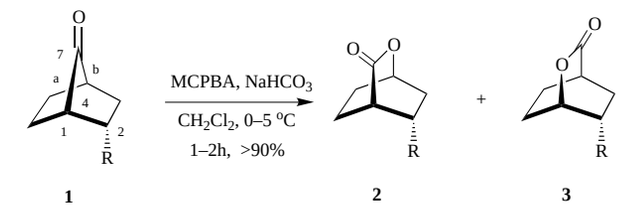
The regioselectivity of the Baeyer–Villiger oxidation of norbornan-7-ones can be steered by the distal 2-*endo*-substituents present. Hydrolysis of the resulting bicyclic lactones provides a stereospecific route to functionalized cyclohexanes.

Baeyer–Villiger (BV) oxidation is a commonly employed reaction for the transformation of ketones into esters/lactones by organic peroxy acids or hydrogen peroxide.[1] The BV reaction is extensively used since when it is suitably juxtaposed in a synthetic sequence, it can lead to the shortening of carbon chains, amplification of functionality in carbocyclic rings and chains, and transformation of carbocycles into heterocycles. Mechanistically, the reaction involves migration of one of the groups flanking the carbonyl to the adjacent electron-deficient oxygen atom in a concerted manner with retention of configuration.[1d,e] The migratory aptitude appears to be related to the ability of the group to support the developing positive charge in the transition state and this determines the regioselectivity of the reaction. Thus, the regiochemical outcome in BV oxidations is mainly governed by the nature of the α-substituent on the ketone although steric and conformational effects also play a role in some instances.[1d] Distal substituents, on the β or γ position to the carbonyl, have little influence on the regioselectivity. However, one example in the literature[9] reports that regioselectivity in the BV oxidation of some 8-oxabicyclo[3.2.1]octan-3-ones is subject to long-range substituent effects. In connection with an ongoing project on the synthesis of carba-sugars,[3] it was of interest to investigate the BV oxidation of several 2-*endo*-substituted norbornan-7-ones **1** to give stereospecific access to trisubstituted cyclohexanes. During these studies, we have encountered a profound effect of the distal C(2)-*endo*-substituents on the migratory preferences of the apparently equivalent C(1)–C(7) and C(4)–C(7) bonds. Since this long-range steering of regioselectivity has potential synthetic utility and is governed by some subtle stereoelectronic effects, our observations are briefly reported here.

The 2-*endo*-substituted norbornan-7-ones **1a**–**h** were synthesized according to the procedures previously described by us[4] and subjected to BV oxidation with *m*-chloroperbenzoic acid to furnish the lactones **2a**–**h** (migration of back-bond 'b') and **3a**–**h** (migration of bond 'a') in 85–95% yield (Scheme 1). The ratios of the two regioisomeric pair of lactones **2a**–**h** and **3a**–**h** were determined through ^{1}H NMR integration of bridgehead protons at C(1) and C(4), which were well separated at 200 MHz (see Scheme 1).

The structural identity of the lactones **2** and **3** was secured through base hydrolysis and diazomethane esterification to furnish the regioisomeric cyclohexane derivatives **4a**–**h** and **5a**–**h**, respectively, which were separated and fully characterized (^{1}H and ^{13}C NMR, MS see Experimental section). The unambiguous evidence that enabled differentiation between the stereospecifically trifunctionalized cyclohexane **4a**–**h** and **5a**–**h** was deduced from the ^{1}H-^{1}H COSY spectra. There are three downfield signals due to H_A, H_B and H_C in the ^{1}H NMR spectra of **4** and **5** (Scheme 2) while in the regioisomers **4a**–**h**, there is no coupling between H_A and H_B or H_C; the adjacent protons H_B and H_C are coupled. In a complementary way, in the series



1

1a R = CN
b R = CO_2Me
c R = OMe
d R = Ph
e R = C_6H_4OMe-*p*
f R = O_6H_4F-*p*
g R = $C_6H_4NO_2$-*o*
h R = $C_6H_4NO_2$-*p*

2

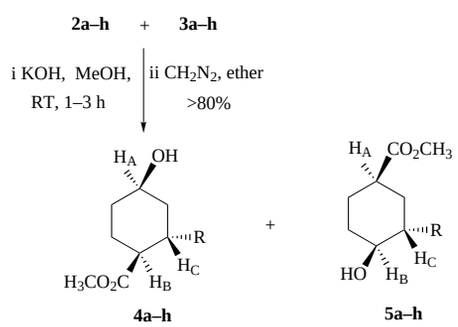
3

a (100:0)
b (>90:10)
c (77:23)
d (51:49)
e (39:61)
f (52:48)
g (70:30)
h (75:25)

Scheme 1

5a–**h**, there is coupling between H_B and H_C but not between H_A and H_B or H_C.

The results presented in Scheme 1 indicate that the electron-withdrawing substituents (*e.g.* CN, CO_2Me, OMe, *etc.*) at the C-2 *endo*-position significantly diminish the propensity of the C(1)–C(7) bond to migrate *vs.* the C(4)–C(7) bond to the extent that in the case of **1a** (R = CN) only the regioisomer **2a** is



4a–h **5a–h**

Scheme 2

formed with no trace of **3a** being detected. In the case of **1b** (R = CO_2Me), formation of the lactone **2b** is overwhelmingly favoured over **3b**. In the case of **1c**, the 2-methoxy substituent exerts a somewhat moderate preference for the formation of **2c** *vs.* **3c**. These results can be understood in terms of the strong inductive effect exerted by the C-2-electron-withdrawing substituent, which is relayed to the C(1)–C(7) bond 'a' through the C(1)–C(2) bond. While the inductive effects of the α-substituents on the regioselectivity of BV oxidations are well documented, this is a rare example of dominant effect of the β-substituent on the migratory preferences.

The regioselectivity exhibited by the 2-*endo*-aryl derivatives **1d**–**h** are also quite interesting, wherein the substituents in the remote phenyl ring lead to fine-tuning of the regioselectivity in a subtle manner. Surprisingly, the 2-*endo*-phenylnorbornan-7-

one **1d** exhibits no regioselectivity and the lactones **2d** and **3d** are formed in near equal amounts. However, introduction of the electron-withdrawing substituent on the phenyl ring as in **1f**–**h** leads to preference for the formation of **2f**–**h** as compared to **3f**–**h**. On the other hand, the electron-donating methoxy group on the phenyl ring leads to a 'reversal' in regioselectivity with modest preference for the formation of **3e**. The absence of any migratory preference in the case of **1d** bearing an inductively electron-withdrawing phenyl group is quite unusual at first sight. We believe that the 2-*endo*-phenyl group acts as a through-bond σ-electron acceptor and a through-space π-donor into the C(1)–C(2) σ-bond of **1d**. Thus, the two effects are neutralized and the C(1)–C(2) bond is rendered equivalent to the C(3)–C(4) bond. Consequently, no regioselectivity is observed in the case of **1d**. However, in the case of the *o*-nitrophenyl **1g** and *p*-nitrophenyl **1h** derivatives, the σ-bond acceptor ability is amplified but the through-space π-donor capacity is diminished. This renders the C(1)–C(2) bond electron deficient and, in turn, reduces the migratory propensity of the C(1)–C(7) bond. Thus, regioisomers **2g**,**h** predominate over **3g**,**h**.

The norbornan-7-one derivatives, with the 2-*endo*-substituent located on the 'blind side' of the carbonyl group, are so constituted that steric and conformational effects have no bearing on the regioselectivity, which is a consequence of the through-bond electronic effects exerted by the substituent. These findings are fully concordant with our earlier interpretation[5] of the origin of face-selectivities in nucleophilic additions to *endo*-substituted norbornan-7-ones and more recent observations on regioselectivity during diazomethane ring-expansion.[6] The key element in these interpretations is the ability of the C(1)–C(2) bond to respond to the electron demand made by the C-2 substituent and transmit the same onto the stereo-induction centre at C-7 through the C(1)–C(7) bond.

In summary, the regioselectivities in the BV oxidation of norbornan-7-ones can be profoundly influenced by the 2-*endo*-substituent. In the case of 2-*endo*-substituted norbornan-7-one derivatives **1a**–**h**, steric and conformational effects are non-determinants of regioselectivity. In these compounds, the regioselectivities are wholly controlled by the electronic effects of the distal substituents. Our results indicate that long-range electronic control of BV oxidation regioselectivity is a much more general occurrence than has been recognized so far. In the case of the norbornan-7-ones **1a**–**g**, BV oxidation and hydrolysis provides a stereospecific route to a range of trisubstituted cyclohexanes.

Experimental

Baeyer–Villiger oxidation of 1d: general procedure

To a solution of **1a** (17 mg, 0.0914 mmol) in CH_2Cl_2 (5 cm^3) was added $NaHCO_3$ (9 mg, 0.107 mmol) and *m*-CPBA (70%; 46 mg, 0.186 mmol) at 0–5 °C. After complete consumption of the starting material the reaction mixture was diluted with CH_2Cl_2 (20 cm^3) and then washed with 10% aqueous Na_2SO_3, saturated aqueous $NaHCO_3$ and brine, dried (Na_2SO_4) and evaporated under reduced pressure. Filtration of the residue through a silica gel pad (hexane–ethyl acetate, 8:2) afforded a mixture of the bicyclic lactones **2d** and **3d** (18 mg, 97%) in a ratio of 51:49 (^{1}H NMR and HPLC: Shimadzu Shimpack, HRC-SIL column, hexane–ethyl acetate, 8:2 eluent).

Hydrolysis of the lactones 2d and 3d: general procedure

To a stirred solution of each of the above lactones (14 mg, 0.069 mmol) in MeOH–H_2O (4:1; 4 cm^3) was added KOH (~6 mg, 0.1386 mmol). The resulting solution was stirred at room temp. for 3 h after which MeOH was removed under reduced pressure and the residue was acidified with 5% hydrochloric acid and extracted with ethyl acetate (3 × 15 cm^3). The combined extracts were concentrated *in vacuo* and the residue was dissolved in ether–MeOH (9:1; 2 cm^3) to which an excess of ethereal diazomethane was added at 0 °C until a yellow colour persisted. Excess of diazomethane was destroyed by the addition of acetic acid to the mixture which was then evaporated. The residue was chromatographed over silica gel (hexane–ethyl acetate, 8:2) to afford **4d** and **5d** (83%). *Methyl* (1S*,2S*,4R*)-4-*hydroxy*-2-*phenylcyclohexanecarboxylate* **4d**, mp 125–126 °C; ν_{max}(KBr)/cm^{-1} 3279 (OH) and 1726 (ester); δ_H(200 MHz; $CDCl_3$) 7.31–7.17 (5H, m, ArH), 4.24–4.22 (1H, m), 3.42 (3H, s), 3.38–3.22 (1H, m), 2.69–2.54 (1H, m), 2.13–1.56 (6H, series of m); δ_C(50.0 MHz; $CDCl_3$) 175.27, 143.94, 128.40 (2C), 127.35 (2C), 126.49, 65.70, 51.26, 49.93, 40.26, 39.78, 31.61 and 23.83; *m*/*z* (EI) 234 (M^+, 11%), 216 ($M^+ - 18$, 15) and 156 (100) (Found: 72.27; H, 7.54. $C_{14}H_{18}O_3$ requires C, 71.77; H, 7.74%).

Methyl (4S*,1R*,3R*)-4-*hydroxy*-3-*phenylcyclohexanecarboxylate* **5d**, ν_{max}(neat)/cm^{-1} 3437 (OH) and 1730 (ester); δ_H(200 MHz; $CDCl_3$) 7.35–7.25 (5H, m, ArH), 3.75 (3H, s, OCH_3), 3.68 (1H, dd, *J* 10, 4), 2.78–2.63 (2H, m), 2.37–2.30 (2H, m), 2.07–2.0 (1H, m) and 1.81–1.52 (3H, series of m); δ_C(50.0 MHz; $CDCl_3$) 174.80, 142.68, 128.69 (2C), 127.92 (2C), 126.84, 73.61, 51.67, 48.95, 39.12, 33.79, 31.09 and 26.01; *m*/*z* (EI) 216 ($M^+ - 18$, 14%), 156 (26), 104 (100) and 91 (38).

Baeyer–Villiger oxidation of 1a and hydrolysis to 4a

The reaction performed as described above, furnished lactone **2a** in quantitative yield. The lactone was hydrolysed to give **4a** (>95%). *Methyl* (1S*,2S*,4R*)-2-*cyano*-4-*hydroxycyclohexanecarboxylate* **4a**, ν_{max}(neat)/cm^{-1} 3450 (OH), 2243 (nitrile) and 1736 (ester); δ_H(200 MHz; $CDCl_3$) 4.15 (1H, m), 3.77 (3H, s), 3.33 (1H, td, *J* 9.8, 4.1), 2.64 (1H, td, *J* 9.6, 4.9), 2.14–1.49 (6H, series of m); δ_C(50.0 MHz; $CDCl_3$) 172.59, 121.17, 64.21, 52.33, 44.74, 34.93, 31.24, 25.91 and 22.73; *m*/*z* (EI) 184 ($M^+ + 1$, 11%), 183 (M^+, 11), 154 (9), 138 (23), 124 (41), 80 (74) and 40 (100).

Baeyer–Villiger oxidation of 1b and hydrolysis to 4b

The reaction performed as described above, furnished the lactones **2b**:**3b** (>90:10; 98.5%) which on hydrolysis gave **4b** (90%). *Dimethyl* (1S*,2S*,4R*)-4-*hydroxycyclohexane*-1,2-*dicarboxylate* **4b**, ν_{max}(neat)/cm^{-1} 3447 (OH) and 1736 (ester); δ_H(200 MHz; $CDCl_3$) 4.13 (1H, br s), 3.67 (6H, s), 3.12 (1H, m), 2.66 (1H, m), 2.10–2.04 (1H, m) and 1.90–1.58 (5H, series of m); δ_C(50.0 MHz; $CDCl_3$) 175.53, 174.92, 64.85, 51.80 (2C), 44.14, 39.17, 35.08, 31.60, 30.14 and 22.60; *m*/*z* (EI) 216 (M^+, 1%), 184 ($M^+ - 32$, 38), 138 (51), 97 (61) and 79 (100).

Baeyer–Villiger oxidation of 1c and hydrolysis to 4c and 5c

The reaction performed as described above, furnished the bicyclic lactones **2c**:**3c** (77:23; 86%) which upon hydrolysis yielded **4c** and **5c** (70%). *Methyl* (1S*,2S*,4R*)-4-*hydroxy*-2-*methoxycyclohexanecarboxylate* **4c**, ν_{max}(neat)/cm^{-1} 3420 (OH) and 1736 (ester); δ_H(200 MHz; $CDCl_3$) 4.2–4.1 (1H, m), 3.88–3.76 (1H, m), 3.69 (3H, s), 3.31 (3H, s), 2.42 (1H, td, *J* 9.4, 4) and 2.18–1.4 (6H, series of m); δ_C(50.0 MHz; $CDCl_3$) 174.72, 76.19, 66.48, 56.59, 51.63, 48.20, 36.50, 31.66 and 22.55; *m*/*z* (EI) 188 (M^+, 12%), 173 (9), 155 (16), 110 (33) and 87 (100); (HRMS [$M^+ - CH_3$], Found: 173.0820. $C_8H_{13}O_4$ requires *M*, 173.0814).

Methyl (3S*,4S*,1R*)-4-*hydroxy*-3-*methoxycyclohexanecarboxylate* **5c**, ν_{max}(neat)/cm^{-1} 3435 (OH) and 1732 (ester); δ_H(200 MHz; $CDCl_3$) 3.70 (3H, s), 3.6–3.5 (1H, m), 3.41 (3H, s), 3.29–3.18 (1H, m), 2.75 (1H, quintet, *J* 4), 2.40–2.28 (2H, m), 2.15–1.86 (2H, m) and 1.60–1.43 (2H, m); δ_C(50.0 MHz; $CDCl_3$) 175.04, 80.73, 71.43, 56.62, 51.63, 38.49, 28.56, 28.46 and 24.34; *m*/*z* (EI) 188 (M^+, 15%), 156 (60), 130 (88) and 111 (100).

Baeyer–Villiger oxidation of 1e and hydrolysis to 4e and 5e

The reaction performed as described above, furnished the bicyclic lactones **2e**:**3e** (39:61; quant. yield). The lactones were hydrolysed and chromatographed to give **4e** and **5e** (79%).

Methyl (1S*,2S*,4R*)-4-*hydroxy*-2-(4-*methoxyphenyl*)*cyclohexanecarboxylate* **4e**, $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3431 (OH) and 1732 (ester); δ_H(200 MHz; $CDCl_3$) 7.12 (2H, d, *J* 8.5), 6.82 (2H, d, *J* 8.7), 4.24 (1H, m), 3.77 (3H, s), 3.44 (3H, s), 3.24 (1H, td, *J* 11.8, 2.9), 2.59 (1H, td, *J* 11.7, 3.4) and 2.11–1.62 (6H, series of m); δ_C(50.0 MHz; $CDCl_3$) 175.12, 158.24, 136.04, 128.25 (2C), 113.87 (2C), 65.92, 55.17, 51.17, 50.29, 40.48, 38.97, 31.68 and 23.84; *m*/*z* (EI) 264 (M^+, 33%), 246 ($M^+ - H_2O$, 44), 186 (100) and 121 (83).

Methyl (4S*,1S*,3R*)-4-*hydroxy*-3-(4-*methoxyphenyl*)*cyclohexanecarboxylate* **5e**, ν_{max}(neat)/cm^{-1} 3445 (OH) and 1730 (ester); δ_H(200 MHz; $CDCl_3$) 7.19 (2H, d, *J* 8.1), 6.89 (2H, d, *J* 7.9), 3.80 (3H, s), 3.74 (3H, s), 3.70–3.59 (1H, m), 2.76 (1H, br s), 2.62 (1H, m), 2.34–2.25 (2H, m), 2.06–1.98 (1H, m) and 1.77–1.50 (3H, series of m); δ_C(50.0 MHz; $CDCl_3$) 174.80, 158.70, 134.32, 128.78 (2C), 114.34 (2C), 73.80, 55.27, 51.62, 48.18, 39.22, 33.90, 30.96 and 26.04; *m*/*z* (EI) 264 (M^+, 5%), 246 ($M^+ - H_2O$, 51), 135 (90) and 121 (100); (HRMS [M^+], Found: 264.1363. $C_{15}H_{20}O_4$ requires *M*, 264.1362).

Baeyer–Villiger oxidation of 1f and hydrolysis to 4f and 5f

The reaction performed as described above, furnished the lactones **2f**:**3f** (52:48; quant. yield) which on hydrolysis and chromatography gave **4f** and **5f** (92%). *Methyl* (1S*,2S*,4R*)-4-*hydroxy*-2-(4-*fluorophenyl*)*cyclohexanecarboxylate* **4f**, mp 132–133 °C, $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3422 (OH) and 1732 (ester); δ_H(200 MHz; $CDCl_3$) 7.19–7.10 (2H, m, ArH), 7.0–6.90 (2H, ArH), 4.23–4.19 (1H, m), 3.43 (3H, s, OCH_3), 3.29 (1H, td, *J* 12.1, 3.6), 2.55 (1H, td, *J* 11.6, 3.6) and 2.17–1.57 (6H, series of m); δ_C(50.0 MHz; $CDCl_3$) 175.09, 161.51 ($^1J_{CF}$ 242.6), 139.60, 128.78 (2C, $^3J_{CF}$ 7.75), 115.20 (2C, $^2J_{CF}$ 21), 65.71, 51.36, 50.14, 40.28, 39.08, 31.61 and 23.78; *m*/*z* (EI) 252 (M^+, 2%), 234 (M^+ −18, 100) and 175 (80); (HRMS [M^+], (Found: 252.1162. $C_{14}H_{17}O_3F$ requires *M*, 252.1165).

Methyl (4S*,1R*,3R*)-4-*hydroxy*-3-(4-*fluorophenyl*)*cyclohexanecarboxylate* **5f**, ν_{max}(neat)/cm^{-1} 3425 (OH) and 1730 (ester); δ_H(200 MHz; $CDCl_3$) 7.25–7.19 (2H, m, ArH), 7.07–6.98 (2H, m, ArH), 3.73 (3H, s), 3.70–3.58 (1H, m), 2.77–2.66 (2H, m), 2.34–2.21 (2H, m), 2.05–1.97 (1H, m) and 1.74–1.49 (3H, series of m); δ_C(50.0 MHz; $CDCl_3$) 176.77, 161.33 ($^1J_{CF}$ 244.7), 138.15, 129.28 (2C, $^3J_{CF}$ 7.8), 115.59 (2C, $^2J_{CF}$ 21.29), 73.92, 51.79, 48.23, 39.08, 33.90, 31.12 and 26.01; *m*/*z* (EI) 252 (M^+, 2%), 234 ($M^+ - 18$, 6), 174 (100) and 109 (62).

Baeyer–Villiger oxidation of 1g and hydrolysis to 4g and 5g

The reaction performed as described above, furnished the bicyclic lactones **2g**:**3g** (70:30; 90%) which upon hydrolysis and chromatography gave **4g** and **5g** (82%). *Methyl* (1S*,2S*,4R*)-4-*hydroxy*-(2-*nitrophenyl*)*cyclohexanecarboxylate* **4g**, ν_{max}(neat)/cm^{-1} 3447 (OH) and 1730 (ester); δ_H(200 MHz; $CDCl_3$) 7.72–7.27 (4H, series of m), 4.27 (1H, m), 3.95–3.82 (1H, m), 3.43 (3H, s, OCH_3) 2.74 (1H, td, *J* 11.6, 3.6), 2.38 (1H, br s, exchangeable) and 2.24–1.58 (6H, series of m); δ_C(50.0 MHz; $CDCl_3$) 174.15, 150.53, 138.23, 132.43, 128.02, 127.07, 124.05, 65.40, 51.56, 49.12, 40.15, 34.07, 31.46 and 24.14; *m*/*z* (EI) 280 ($M^+ + 1$, 1%), 262 ($M^+ - H_2O$, 3), 233 ($M^+ - NO_2$, 100); (HRMS [$M^+ - 33$], Found: 233.1178. $C_{14}H_{17}O_3$ requires *M*, 233.1182).

Methyl (4S*,1R*,3R*)-4-*hydroxy*-3-(2-*nitrophenyl*)*cyclohexanecarboxylate* **5g**, $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3437 (OH) and 1726 (ester); δ_H(200 MHz; $CDCl_3$) 7.76–7.38 (4H, series of m), 3.78 (3H, s), 3.8–3.75 (1H, m), 3.31–3.20 (1H, m), 2.78 (1H, m), 2.47–2.32 (3H, series of m) and 2.09–2.05 (2H, m); δ_C(50.0 MHz; $CDCl_3$) 169.18, 151.82, 136.88, 134.61, 131.40, 127.86, 127.28, 73.58, 51.88, 49.10, 42.96, 38.88, 32.19 and 25.96; *m*/*z* (EI) 233 ($M^+ - NO_2$, 100%).

Baeyer–Villiger oxidation of 1h and hydrolysis to 4h and 5h

The reaction performed as described above, furnished the lactones **2h**:**3h** (75:25; 93%) which on hydrolysis and chromatography gave **4h** and **5h** (82%). *Methyl* (1S*,2S*,4R*)-4-*hydroxy*-2-(4-*nitrophenyl*)*cyclohexanecarboxylate* **4h**, mp 131–132 °C; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3455 (OH) and 1732 (ester); δ_H(200 MHz; $CDCl_3$) 8.05 (2H, d, *J* 8), 7.29 (2H, d, *J* 8), 4.22–4.17 (1H, m), 3.46–3.34 (1H, m), 3.36 (3H, s, OCH_3), 2.56 (1H, td, *J* 11.6, 3.6) and 2.12–1.52 (6H, series of m); δ_C(50.0 MHz; $CDCl_3$) 174.48, 151.92, 146.76, 127.28 (2C), 123.74 (2C), 65.27, 51.48, 49.32, 39.94, 39.75, 31.67 and 23.72; *m*/*z* (EI) 79 (M^+, 11%), 261 ($M^+ - 18$, 15), 201 (98), 149 (49) and 116 (100); (HRMS [M^+], Found: 279.1102. $C_{14}H_{17}NO_5$ requires *M*, 279.1106).

Methyl (4S*,1R*,3R*)-4-*hydroxy*-3-(4-*nitrophenyl*)*cyclohexanecarboxylate* **5h**, ν_{max}(KBr)/cm^{-1} 3524 (OH) and 1722 (ester); δ_H(200 MHz; $CDCl_3$) 8.12 (2H, d, *J* 8, ArH), 7.36 (2H, d, *J* 8, ArH), 3.68 (3H, s), 3.72–3.65 (1H, m), 2.88–2.72 (2H, m), 2.33–2.18 (2H, m), 2.01–1.94 (1H, m) and 1.70–1.33 (3H, series of m); δ_C(50.0 MHz; $CDCl_3$) 174.48, 150.75, 147.02, 128.72 (2C), 123.87 (2C), 73.48, 51.86, 48.79, 38.82, 33.66, 31.72, 26.03; *m*/*z* (EI) 279 (M^+, 10%), 261 (8), 201 (100), 149 (28), 128 (31) and 116 (85).

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