

# SYNTHESIS AND STEREOCHEMISTRY OF SOME NEW CHIRAL BROMINATED 1,3-DIOXANE DERIVATIVES

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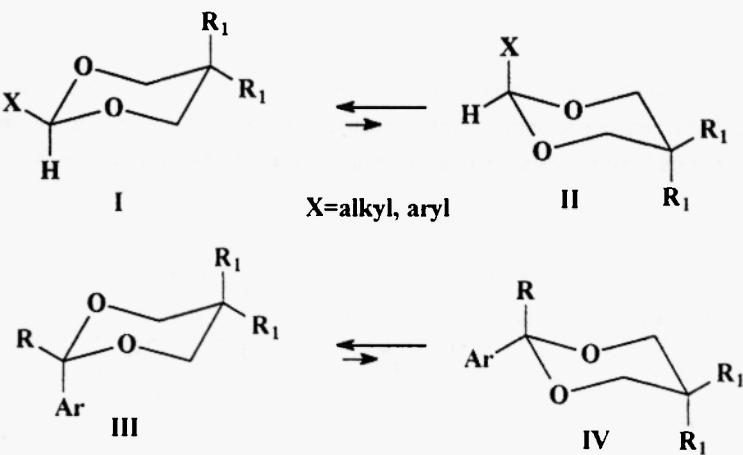
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**Abstract:** The stereochemistry of some new chiral brominated 1,3-dioxane derivatives is investigated by NMR methods. The anancomeric structure of the compounds and the diastereotopicity of the homomorphous groups are revealed. An influence through space of the chiral center at a distance of eight bonds have been observed.

## INTRODUCTION

The investigations<sup>1-11</sup> on the stereochemistry of 2-alkyl (or aryl)-1,3-dioxane and of 2-aryl-2-alkyl-1,3-dioxane derivatives revealed anancomeric structures (Scheme 1). In 2-aryl-1,3-dioxanes the aromatic group exhibits an equatorial orientation being "holding group" (A-value for the phenyl group 3.12 kcal/mol)<sup>1,2,10</sup>, whereas in 2-alkyl-2-aryl-1,3-dioxane derivatives the aromatic group shows an axial orientation.<sup>1,2,7-9,11</sup>



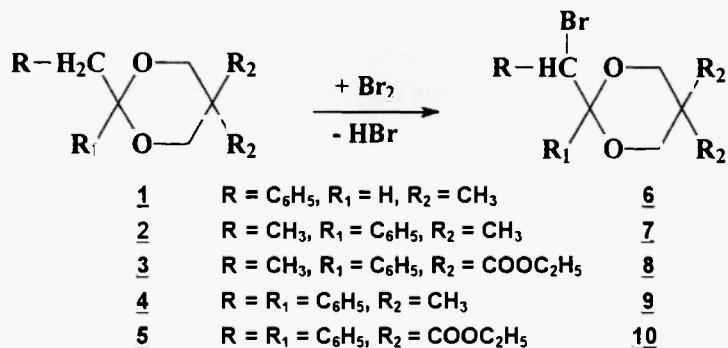
Scheme 1

In compounds bearing both alkyl and aryl substituents in the ketal part of the molecule the aryl group displays a considerably higher preference for the axial orientation as it is suggested by the simple addition of the A values of the two groups (e.g.  $\Delta A_{Me-Ph} = 0.86$  kcal/mol and the experimentally determined conformational free enthalpy in 2-methyl-2-phenyl-1,3-dioxane is about three times higher  $\Delta G^{\circ}_{Me-Ph} = 2.41$  kcal/mol).

The investigations by NMR on the stereochemistry of chiral 1,3-dioxanes revealed interesting aspects. The molecular chirality induces the diastereotopicity of the homomorphic groups increasing in the NMR spectra the number of the recorded signals in comparison with the spectra obtained for similar achiral 1,3-dioxane derivatives. NMR proved to be an efficient instrument to investigate molecular chirality. Thus, the peculiar axial and helical chirality in spiro compounds with six-membered rings<sup>12-13</sup> and the axial chirality on some 2-methyl-2-aryl-1,3-dioxane derivatives exhibiting disymmetric axial aryl groups (o-nitrophenyl, m-nitrophenyl,  $\alpha$ -naphthyl and  $\beta$ -naphthyl)<sup>8,9</sup> have been revealed by the complexity of NMR spectra due to the diastereotopicity of homomorphic groups. The configurational diastereoisomers determined by the presence of more chiral elements in some dibrominated-1,3-dioxane derivatives (*meso* and *d,l* forms)<sup>14</sup> and in some dispiro-1,3-dioxanes (*syn* and *anti* isomers)<sup>15</sup> have been identified on the basis of the different steric relations of the homomorphic groups in the different diastereoisomers.

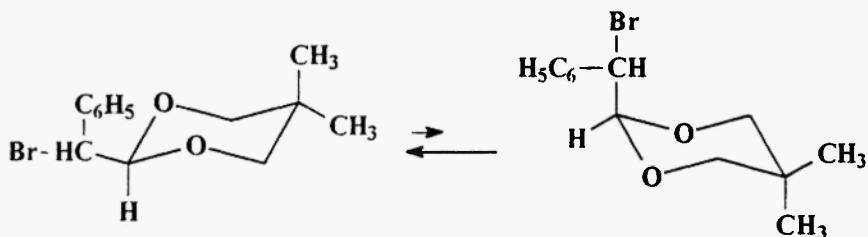
## RESULTS AND DISCUSSION

New brominated 1,3-dioxane derivatives have been obtained by the usual reaction of cyclic acetals<sup>16</sup> with bromine (Scheme 2)

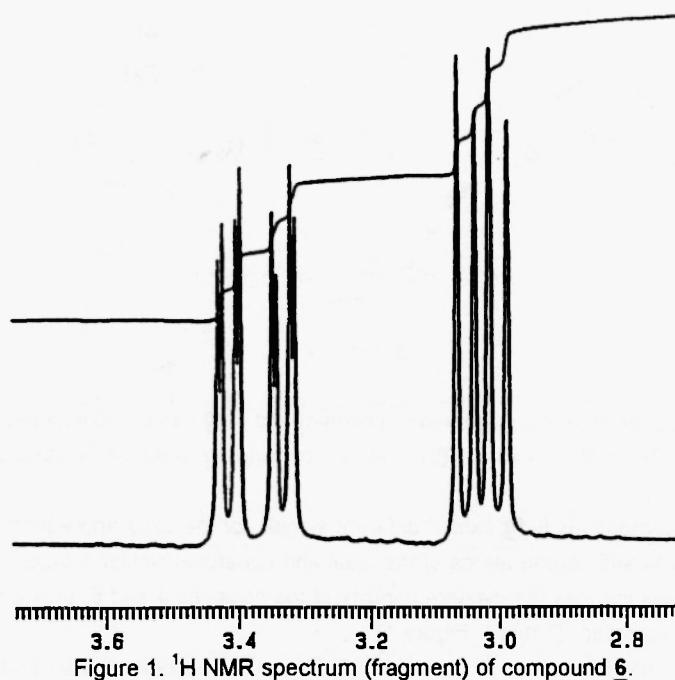


Scheme 2

Compounds 6-10 exhibit anancomeric structures. For compound 6 the characteristic conformational equilibrium (Scheme 3) is shifted toward the conformer showing the substituent in position 2 in equatorial orientation, whereas the preferred conformer of compounds 7-10 exhibits the phenyl group in axial orientation (Scheme 4).

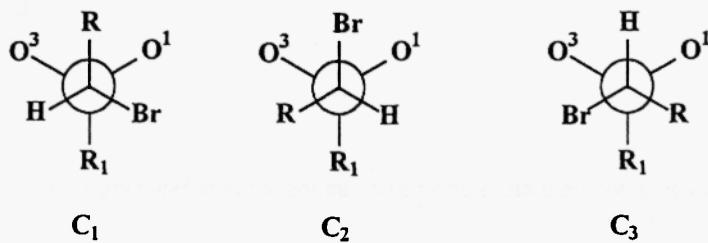


Scheme 3

Figure 1.  $^1\text{H}$  NMR spectrum (fragment) of compound 6.

The differences between the  $\delta$  values of axial and equatorial protons of positions 4 and 6 in compounds **7-10** are smaller than usual. This fact is due to the influence through space of the axial orthogonal aromatic group in position 2. The equatorial protons of the heterocycle are in the shielding area of the aromatic substituent.<sup>17</sup> Coincidentally, in compound **7**, the axial and equatorial protons of position 4 exhibit the same chemical shift.

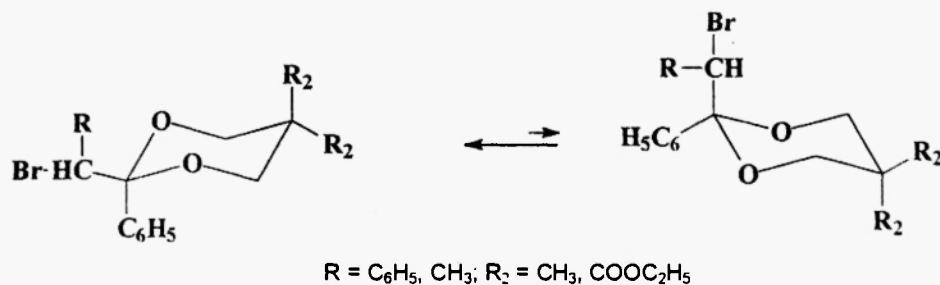
The diastereotopics of the protons of positions 4 and 6 show usual values and they are determined by the different populations of the conformers of the chiral substituent (Scheme 5). It has to be underline the recording of different signals for the diastereotopic methylene protons of the axial ester group of position 5 in compound **10**. In this case it is remarkable the influence of the chiral center at a distance of eight bonds. The diastereotopicity of the similar protons of the equatorial ester group could not be observed, so an influence through space for the axial group has to be taken into account.



Scheme 5

## CONCLUSIONS

New chiral brominated 1,3-dioxanes have been synthetized in good yields by reaction of cyclic acetals with bromine. NMR investigations showed an ancomeric structures. The influence through space of the chiral center and of the



Scheme 4

The axial preference of the aromatic substituent in compounds **7-10** can be considered taking into account that a substituted methyl group [as  $\text{Me}-\text{CH}(\text{Br})$ - or  $\text{Ph}-\text{CH}(\text{Br})$ - can be considered] have an A-value somewhat higher than an unsubstituted methyl group.<sup>1</sup>

The NMR spectra of compounds **6-10** exhibit different signals for the axial and equatorial protons of positions 4 and 6, as well as for the protons and carbon atoms of the axial and equatorial similar groups of position 5 (Tables 1 and 2). The chirality of the molecules induces the diastereotopicity of the positions 4 and 6, thus different signals for the four protons of these positions are recorded. (Table 1, Figure 1)

As an example the  $^1\text{H}$  NMR spectrum of compound **6** (Figure 1) shows for the protons of positions 4 and 6 two AB systems, one of them involving the axial and equatorial protons of position 4 and the other one pertaining to the protons of position 6 ( $\delta_{4e} = 3.33$ ,  $\delta_{4a} = 3.00$ ,  $\delta_{6e} = 3.41$ ,  $\delta_{6a} = 3.05$  ppm). The equatorial protons exhibit a further splitting due to the long range coupling between the equatorial protons of positions 4 and 6 made possible by the W disposition of the bonds  $\text{H}_e-\text{C}_4-\text{C}_5-\text{C}_6-\text{H}_e$  ( $J = 2.8$  Hz).

Table 1. NMR data ( $\delta$  ppm) for the protons and carbon atoms of positions 4 and 6 of compounds **6-10**.

Compound	$^1\text{H}$						$^{13}\text{C}$		
	4e	6e	$\Delta\delta_{6-4}$	4a	6a	$\Delta\delta_{6-4}$	4	6	$\Delta\delta_{6-4}$
<b>6</b>	3.33	3.41	0.08	3.00	3.05	0.05	76.69		-
<b>7</b>	3.25	3.26	0.01	3.25	3.33	0.08	71.97	71.92	0.05
<b>8</b>	4.865	4.872	0.007		4.08	-	64.08	64.21	0.13
<b>9</b>	3.505	3.52	0.015		3.44	-	-	71.66	-
<b>10</b>	4.93	4.97	0.04	4.086	4.090	0.004	65.19		-

Table 2. NMR data ( $\delta$  ppm) for the protons and carbon atoms of the substituents in position 5 of compounds **6-10** [ $5-(\text{COOCH}_2)\text{CH}_3$ ].

Compound	$^1\text{H}$				$^{13}\text{C}$					
	$-\text{CH}_3(\text{e})$	$-\text{CH}_3(\text{a})$	$-\text{CH}_2(\text{e})-$	$-\text{CH}_2(\text{a})-$	$-\text{CH}_3(\text{e})$	$-\text{CH}_3(\text{a})$	$-\text{CH}_2(\text{e})-$	$-\text{CH}_2(\text{a})-$	$-\text{COO-(e)}$	$-\text{COO-(e)}$
<b>6</b>	0.22	1.07	-	-	20.82	22.61	-	-	-	-
<b>7</b>	0.09	1.28	-	-	21.48	23.24	-	-	-	-
<b>8</b>	0.64	1.03	3.59	4.15	13.28	13.80	61.34	61.73	166.24	167.31
<b>9</b>	0.09	1.34	-	-	21.14	22.90	-	-	-	-
<b>10</b>	0.63	1.09	3.58	4.16 and 4.19	14.29	14.88	62.39	62.90	167.32	168.15

axial aromatic ring on the  $\delta$  values of the protons of the heterocycle and of the axial substituent of position 5 has been revealed.

## EXPERIMENTAL

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at room temperature, using  $\text{CDCl}_3$  as solvent in 5 mm tubes, on a Brucker AM 400 (Varian Gemini) Fourier transform NMR spectrometer, equipped with a dual  $^1\text{H}$ - $^{13}\text{C}$  (multinuclear) head, operating at 400 MHz (300 MHz) for protons and 100 MHz (75 MHz) for carbon atoms.

M.ps were measured with Electrothermal melting point apparatus and are uncorrected.

The synthesis and stereochemistry of compounds **1-5** have been reported previously.<sup>18</sup>

**Compounds 6-10, general procedure.** -The 1,3-dioxane compound (**1-5**; 0.1 mol) and dry diethyl ether or dichloromethane (100 ml) were introduced in a four-necked flask equipped with a reflux condenser, a mechanical stirring system, a thermometer and a dropping funnel. Bromine (0.1 mol) was added dropwise to this stirred mixture cooled in an ice-bath at 0-5 °C, the ensuing reaction being monitored initially by the fading of the solution colour. After the addition of bromine, the ice-bath was removed and the stirring was continued for 1h, the contents in the flask being allowed slowly to reach room temperature (20-25 °C). The mixture was evaporated *in vacuo* (10-15 mm col.Hg) and the residue was crystallized from ethanol or distilled at 0.5-1 mm col.Hg.

### 2- $\alpha$ -Bromobenzyl-5,5-dimethyl-1,3-dioxane **6**.

Solid, m.p.=63-64 °C. Yield 63%. Anal. Calcd. for  $\text{C}_{13}\text{H}_{17}\text{BrO}_2$ : C, 54.75; H, 6.01; Br, 28.02. Found: C, 54.61; H, 5.89; Br, 28.25.  $^1\text{H-NMR}$   $\delta$  ( $\text{C}_6\text{D}_6$ ) 0.22[3H, s, 5- $\text{CH}_3$ (eq)], 1.07[3H, s, 5- $\text{CH}_3$ (ax)], 3.00(1H, d,  $J=11.0$  Hz, 4- $\text{H}_{\text{ax}}$ ), 3.05(1H, d,  $J=11.0$  Hz, 6- $\text{H}_{\text{ax}}$ ), 3.33(1H, dd,  $J=11.0$  Hz,  $J'=2.8$  Hz, 4- $\text{H}_{\text{eq}}$ ), 3.41(1H, dd,  $J=11.0$  Hz,  $J'=2.8$  Hz, 6- $\text{H}_{\text{eq}}$ ), 4.58[1H, d,  $J=4.4$  Hz, 2- $\text{CH}(\text{Br})\text{C}_6\text{H}_5$ ], 4.97(1H, d,  $J=4.4$  Hz, 2- $\text{H}_{\text{ax}}$ ), 7.02[1H, t,  $J \approx J'=7.3$  Hz, overlapped peaks, aromatic proton (p)], 7.09[2H, t,  $J \approx J'=7.3$  Hz, overlapped peaks, aromatic protons (m)] and 7.16 ppm[2H, d,  $J=7.3$  Hz, aromatic protons (o)].  $^{13}\text{C-NMR}$   $\delta$  ( $\text{C}_6\text{D}_6$ ) 20.82[5- $\text{CH}_3$ (eq)], 22.61[5- $\text{CH}_3$ (ax)], 29.5( $\text{C}^5$ ), 53.47[2- $\text{CH}(\text{Br})\text{C}_6\text{H}_5$ ], 76.69( $\text{C}^{4,6}$ ), 101.72( $\text{C}^2$ ), 128.06, 128.15, 129.28(tertiary aromatic carbon atoms) and 138.26 ppm(quaternary aromatic carbon atoms).

### 2- $\alpha$ -Bromoethyl-5,5-dimethyl 2-phenyl-1,3-dioxane **7**.

Liquid, b.p.=127-9 °C (0.5 mm colHg). Yield 52%. Anal. Calcd. for  $\text{C}_{14}\text{H}_{19}\text{BrO}_2$ : C, 56.20; H, 6.40; Br, 26.71. Found: C, 56.33; H, 6.54; Br, 26.58.  $^1\text{H-NMR}$   $\delta$  ( $\text{C}_6\text{D}_6$ ) 0.09[3H, s, 5- $\text{CH}_3$ (eq)], 1.28[3H, s, 5- $\text{CH}_3$ (ax)], 1.58[3H, d,  $J=6.93$  Hz, 2- $\text{CH}(\text{Br})\text{CH}_3$ ], 3.25(2H, d,  $J=11.26$  Hz, 4- $\text{H}_{\text{ax, eq}}$ , overlapped peaks), 3.26(1H, dd,  $J=11.26$  Hz,  $J'=2.06$  Hz, 6- $\text{H}_{\text{eq}}$ , overlapped peaks), 3.33(1H, d,  $J=11.26$  Hz, 6- $\text{H}_{\text{ax}}$ ), 4.13[1H, q,  $J=6.93$  Hz, 2- $\text{CH}(\text{Br})\text{CH}_3$ ] and 7.15 ppm(5H, overlapped peaks, aromatic protons).  $^{13}\text{C-NMR}$   $\delta$  ( $\text{C}_6\text{D}_6$ ) 20.57[2- $\text{CH}(\text{Br})\text{CH}_3$ ], 21.48[5- $\text{CH}_3$ (eq)], 23.24[5- $\text{CH}_3$ (ax)], 30.00( $\text{C}^5$ ), 56.19[2- $\text{CH}(\text{Br})\text{CH}_3$ ], 71.92( $\text{C}^4$ ), 71.97( $\text{C}^6$ ), 127.06, 127.91, 128.30(tertiary aromatic carbon atoms) and 139.70 ppm(quaternary aromatic carbon atom).

### 2- $\alpha$ -Bromoethyl-5,5-bis(ethyloxycarbonyl)- 2-phenyl-1,3-dioxane **8**.

Solid, m.p.=85-87 °C. Yield 55.5 %. Anal Calcd. for  $\text{C}_{18}\text{H}_{23}\text{BrO}_6$ : C, 52.06; H, 5.58; Br, 19.24. Found: C, 51.88; H, 5.74; Br, 19.44.  $^1\text{H-NMR}$   $\delta$  ( $\text{C}_6\text{D}_6$ ) 0.64[3H, t,  $J=7.0$  Hz, 5-COOCH<sub>2</sub>CH<sub>3</sub>(eq)], 1.03[3H, t,  $J=7.0$  Hz, 5-COOCH<sub>2</sub>CH<sub>3</sub>(ax)], 1.54[3H, d,  $J=6.9$  Hz, 2-CH(Br)-CH<sub>3</sub>], 3.59[2H, q,  $J=7.0$  Hz, 5-COOCH<sub>2</sub>CH<sub>3</sub>(eq)], 4.07[1H, q,  $J=6.9$  Hz, 2-CH(Br)-CH<sub>3</sub>], 4.08(2H, d,  $J=11.1$  Hz, 4,6- $\text{H}_{\text{ax}}$ ), 4.15[2H, q,  $J=7.0$  Hz, 5-COOCH<sub>2</sub>CH<sub>3</sub>(ax)], 4.865(1H, dd,  $J=11.1$  Hz,  $J'=2.1$  Hz, 4- $\text{H}_{\text{eq}}$ ), 4.872(1H, dd,  $J=11.1$  Hz,  $J'=2.1$  Hz, 6- $\text{H}_{\text{eq}}$ ), 7.05-7.15 and 7.35-7.40 ppm(5H, overlapped peaks, aromatic protons).  $^{13}\text{C-NMR}$   $\delta$  ( $\text{C}_6\text{D}_6$ ) 13.28[5-COOCH<sub>2</sub>CH<sub>3</sub>(eq)], 13.80[5-COOCH<sub>2</sub>CH<sub>3</sub>(ax)], 19.85[2-CH(Br)-CH<sub>3</sub>], 53.20( $\text{C}^5$ ), 54.83[2-CH(Br)-CH<sub>3</sub>], 61.34[5-COOCH<sub>2</sub>CH<sub>3</sub>(eq)], 61.73[5-COOCH<sub>2</sub>CH<sub>3</sub>(ax)], 64.08( $\text{C}^4$ ), 64.21( $\text{C}^6$ ), 101.09( $\text{C}^2$ ), 128.76, 128.71, 128.38(tertiary aromatic carbon atoms), 134.49(quaternary aromatic carbon atom), 166.24[5-COOCH<sub>2</sub>CH<sub>3</sub> (eq) and 167.31 ppm[5-COOCH<sub>2</sub>CH<sub>3</sub> (ax)].

**2- $\alpha$ -Bromobenzyl-5,5-dimethyl-2-phenyl-1,3-dioxane 9.**

Solid, m.p.=96-98 °C. Yield 59.5 %. Anal. Calcd. for  $C_{19}H_{21}BrO_2$ : C, 63.17; H, 5.86; Br, 22.12. Found: C, 63.02; H, 5.69; Br, 22.39.  $^1H$ -NMR  $\delta$  (C<sub>6</sub>D<sub>6</sub>) 0.09[3H, s, 5-CH<sub>3</sub>(eq)], 1.34[3H, s, 5-CH<sub>3</sub>(ax)], 3.30(4H, d, 4,6-H<sub>ax</sub>, eq, overlapped peaks), 5.01[1H, s, 2-CH(Br)C<sub>6</sub>H<sub>5</sub>] and 6.91-7.26 ppm(10H, overlapped peaks, aromatic protons).  $^1H$ -NMR  $\delta$  (CDCl<sub>3</sub>) 0.58[3H, s, 5-CH<sub>3</sub>(eq)], 1.36[3H, s, 5-CH<sub>3</sub>(ax)], 3.44(2H, d, J=10.5 Hz, 4,6-H<sub>ax</sub>), 3.505(1H, dd, J=10.5 Hz, J'=1.5 Hz, 4-H<sub>eq</sub>, overlapped peaks), 3.52(1H, dd, J=10.5 Hz, J'=1.5 Hz, 6-H<sub>eq</sub>, overlapped peaks), 4.90[1H, s, 2-CH(Br)C<sub>6</sub>H<sub>5</sub>] and 7.267 ppm(10H, overlapped peaks, aromatic protons).  $^{13}C$  NMR  $\delta$  (C<sub>6</sub>D<sub>6</sub>) 21.14[5-CH<sub>3</sub>(eq)], 22.90[5-CH<sub>3</sub>(ax)], 29.60(C<sup>5</sup>), 61.63[2-CH(Br)C<sub>6</sub>H<sub>5</sub>], 71.66(C<sup>4,6</sup>), 101.05(C<sup>2</sup>), 127.22, 128.23, 128.87, 130.39 (tertiary aromatic carbon atoms) and 135.76, 137.76 ppm (quaternary aromatic carbon atoms).

**2- $\alpha$ -Bromobenzyl-5,5-bis(ethyloxycarbonyl)-2-phenyl-1,3-dioxane 10.**

Solid, m.p.=89-90 °C. Yield 55.94 %. Anal. Calcd. for  $C_{23}H_{25}BrO_6$ : C, 57.87; H, 5.28; Br, 16.74. Found: C, 57.66; H, 5.19; Br, 16.93.  $^1H$ -NMR  $\delta$  (C<sub>6</sub>D<sub>6</sub>) 0.63[3H, t, J=7.2 Hz, 5-COOCH<sub>2</sub>CH<sub>3</sub>(eq)], 1.04[3H, t, J=7.2 Hz, 5-COOCH<sub>2</sub>CH<sub>3</sub>(ax)], 3.58[2H, q, J=7.2 Hz, 5-COOCH<sub>2</sub>CH<sub>3</sub>(eq)], 4.086(1H, d, J=11.4 Hz, 4-H<sub>ax</sub>), 4.090(1H, d, J=11.4 Hz, 6-H<sub>ax</sub>), 4.19[2H, dq, J=7.2 Hz, J'=15.0 Hz, 5-COOCH<sub>2</sub>CH<sub>3</sub>(ax), overlapped peaks], 4.93(1H, dd, J=11.4 Hz, J'=2.7 Hz, 4-H<sub>eq</sub>), 4.97(1H, dd, J=11.4 Hz, J'=2.7 Hz, 6-H<sub>eq</sub>), 4.97[2H, s, 2-CH(Br)C<sub>6</sub>H<sub>5</sub>] and 6.95-7.15 ppm(10H, overlapped peaks, aromatic protons).  $^{13}C$  NMR  $\delta$  (C<sub>6</sub>D<sub>6</sub>) 14.29[5-COOCH<sub>2</sub>CH<sub>3</sub>(eq)], 14.88[5-COOCH<sub>2</sub>CH<sub>3</sub>(ax)], 54.14(C<sup>5</sup>), 61.84[2-CH(Br)C<sub>6</sub>H<sub>5</sub>], 62.39[5-COOCH<sub>2</sub>CH<sub>3</sub>(eq)], 62.90[5-COOCH<sub>2</sub>CH<sub>3</sub>(ax)], 65.19(C<sup>4,6</sup>), 102.38(C<sup>2</sup>), 127.43, 128.06, 128.34, 128.55, 128.91, 130.06(tertiary aromatic carbon atoms), 135.40, 138.41(quaternary aromatic carbon atoms), 167.32[5-COOCH<sub>2</sub>CH<sub>3</sub>(eq)] and 168.15 ppm[5-COOCH<sub>2</sub>CH<sub>3</sub>(ax)].

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