Diastereoselective Domino Heck–Suzuki Reaction: Synthesis of Substituted Methylenetetrahydrofurans

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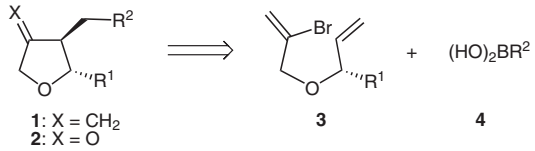
Abstract: In a palladium-catalyzed reaction of dienyl ethers with boronic acids, a diastereoselective cyclization occurs to give methylenetetrahydrofurans. They can be obtained as pure enantiomers and their conversion into dihydro-3(2*H*)-furanones and dioxanones is demonstrated.

Key words: palladium, catalysis, cyclizations, stereoselectivity, chirality



Scheme 1 Retrosynthetic approach of a diastereoselective domino Heck–Suzuki reaction

Domino reactions have developed into an exceptionally efficient tool in organic synthesis by taking advantage of the fact that two or more bonds can be formed in a consecutive manner without isolating the intermediate products. In the individual steps of domino reactions, different mechanisms can be combined in various transformations. Transition-metal-mediated, particularly palladium-catalyzed conversions are increasingly used in domino reactions.[1] Especially the Heck reaction has been applied in multifold consecutive carbon–carbon bond formations.[2] When a different palladium-catalyzed conversion is planned to succeed the Heck reaction, the intermediate palladium species has to be trapped in order to avoid the final β-elimination.[3–7] A very useful carbon–carbon bond formation will result if boronic acids serve as trapping agents. However, this sequence, a domino Heck–Suzuki reaction, has been realized rarely and was applied in syntheses of several carbocyclic and heterocyclic compounds only recently.[8] In none of those, however, the problem of stereoselective formation of contiguous chiral centers has been addressed.

In this communication, we describe the first diastereoselective domino Heck–Suzuki reaction. It permits to obtain 2,3-disubstituted 4-methylenetetrahydrofurans **1** and 3(2*H*)-dihydrofuranones **2** from readily accessible ethers **3** and boronic acids **4** according to retrosynthetic Scheme 1. It involves a disconnection of the 3,4-bond in the heterocyclic ring and the 1′,2′-bond in the side chain.[9]

The precursors of the conceived domino sequence, racemic dienes **3a**–**c**, were obtained from a Williamson etherification of 2,3-dibromopropene (**5**) with allylic alcohols (*rac*)-**6a**–**c** through the corresponding alkoxides. In an analogous manner, (*R*)-**3a** was prepared form commercially available allylic alcohol (*R*)-**6a**. The palladium-catalyzed coupling with boronic acids **4a**–**e**, which were present in the reaction mixture from the beginning, along with cesium carbonate, gave the heterocyclic five-membered products **1aa**–**1ca** (Table 1).

Both tetrakis(triphenylphosphino)palladium [$Pd(Ph_3P)_4$] and Herrmann's catalyst[10] generated from palladium acetate and tri-*o*-tolylphosphane were found to be suitable to bring about the domino sequence. The latter catalyst provided slightly higher yields, as shown in Table 2 (entries 1 vs. 2 and 7 vs. 8). Fair yields were usually obtained from substrate **1a** when coupled with arylboronic acids **4a**–**c** (entries 1–4). The protocol could also be applied to vinyl and alkyl boronic acids **4d** and **4e**; however, the products **1ad** and **1ae** were formed in moderate yields only (entries 5 and 6). Substrates **3b** and **3c** also underwent the domino reaction and gave methylenetetrahydrofurans **1ba**, **1bb**, **1bc**, and **1ca** (entries 7–11). Minor amounts (15–25%) of noncyclized products arising from a direct Suzuki coupling as well as dienes originating from final β-elimination could be removed by column chromatography.

In view of the formation of a second stereogenic carbon center in the course of the domino Heck–Suzuki reaction of ethers **3**, the problem of diastereoselectivity was addressed. It turned out that the cyclization reactions of phenyl-substituted ethers **3a** occurred with remarkably high stereoselectivity, giving in each case essentially a single diastereomer **1aa**–**1ae**. The NMR spectra and GC-MS detection of the crude products revealed diastereomeric ratios up to >98:2, as shown in Table 2 (entries 1–6). Lager amounts of the *cis*-isomer were found in the product **1ab** (entry 3). For substrates **3b**,**c**, which have a methyl or isopropyl residue at the stereogenic carbon center, lower diastereoselectivity was also obtained (entries 7–11). In some cases, the diastereomeric purity could be enhanced by column chromatography of the crude cyclization product. Thus, tetrahydrofuran **1aa** was obtained as a pure diastereomer (entries 1, 2, and 12). The ^{13}C

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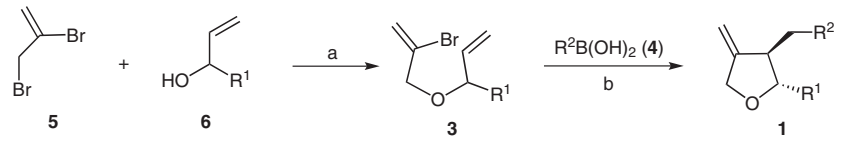
Table 1 Synthesis of Ethers **3** and Diastereoselective Cyclization to Methylenetetrahydrofurans **1**[a]



3, **6**	R^1	**4**	R^2	**1**	R^1	R^2
3a, **6a**	Ph	**4a**	Ph	**1aa**	Ph	Ph
3b, **6b**	Me	**4b**	4-$MeSC_6H_4$	**1ab**	Ph	4-$MeSC_6H_4$
3c, **6c**	*i*-Pr	**4c**	4-ClC_6H_4	**1ac**	Ph	4-ClC_6H_4
		4d	(*E*)-*n*-HexCH=CH	**1ad**	Ph	(*E*)-*n*-HexCH=CH
		4e	*i*-Pr	**1ae**	Ph	*i*-Pr
				1ba	Me	Ph
				1bb	Me	4-$MeSC_6H_4$
				1bc	Me	4-ClC_6H_4
				1ca	*i*-Pr	Ph

[a] Reaction conditions: (a) NaH, THF, reflux, **3a**: 93%, **3b**: 59%, **3c**: 36%; (b) $[Pd(PPh_3)_4]$ (3 mol%) or $(2\text{-}MeC_6H_4)_3P$ (2.5 mol%), $Pd(OAc)_2$ (2.5 mol%); (c) Cs_2CO_3 (150 mol%), EtOH, 25 °C, 24 h.

NMR spectroscopy served for the determination of the relative configuration in the products **1aa**–**1ca**. In diastereomeric 2,3-disubstituted tetrahydrofurans, the chemical shifts of carbon atoms 2 and 3 differ in a characteristic manner: both carbon atoms appear at lower field in the *trans*-diastereomers, whereas the resonances are high-field-shifted in the *cis*-diastereomers.[11] This assignment of the configuration, illustrated for *trans*- and *cis*-**1ba** in Figure 1, also applies to the other methylenetetrahydrofurans **1**. In accordance with reported data[7], the vicinal 2-H,3-H coupling constants are substantially smaller in the *cis*-diastereomers compared with the *trans*-diastereomers. As a result, the main products formed by the domino Heck–Suzuki protocol turned out to be *trans* configured. This is also in accordance with the stereochemical outcome in nickel-mediated Heck carbonylation sequences of **3a** that deliver *trans* products albeit with moderate diastereoselectivty.[7]

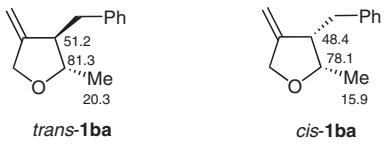


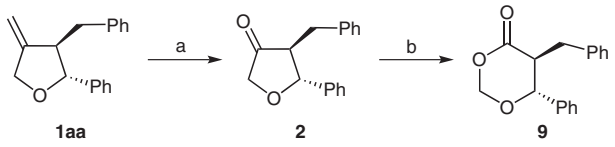
Figure 1 Relevant ^{13}C shift values in diastereomeric methylenetetrahydrofurans *trans*-**1ba** and *cis*-**1ba**

The predominant formation of the *trans*-diastereomers is plausibly explained by considering the transition state models **7a** and **7b**, as outlined in Scheme 2. In the diastereoselectivity determining step of the domino sequence, cyclization of **7a** and **7b** occurs to give the alkyl palladium intermediates *trans*-**8** and *cis*-**8**, respectively. It seems to be plausible that the chairlike transition state **7a** is favored compared with the boatlike **7b**. During the final coupling of the diastereomers **8** with boronic acids **4**, a competing β-elimination accounts for the formation of dienes as byproducts.[12] Thus, there are, aside from the direct Suzuki reaction without cyclization, altogether four

Table 2 Diastereoselective Domino Heck–Suzuki Reaction of Ethers **3** to 2,3-Disubstituted 4-Methylenetetrahydrofurans **1**

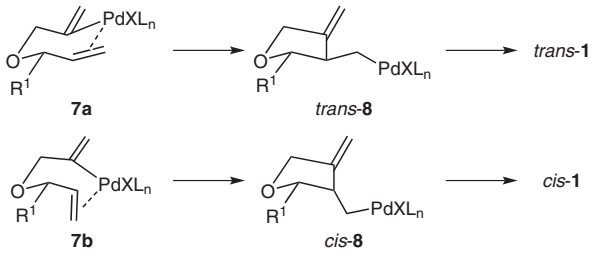
Entry	Substrate **3**	Boronic acid **4**	Product **1**	Yield (%)[a]	dr (*trans*-**1**/*cis*-**1**)[d]
1	**3a**	**4a**	**1aa**	54[b]	98:2 (>99:1)[e]
2	**3a**	**4a**	**1aa**	61[c]	98:2 (>99:1)[e]
3	**3a**	**4b**	**1ab**	52[c]	83:17 (89:11)[e]
4	**3a**	**4c**	**1ac**	51[c]	97:3
5	**3a**	**4d**	**1ad**	32[c]	96:4
6	**3a**	**4e**	**1ae**	31[c]	>98:2
7	**3b**	**4a**	**1ba**	28[b]	83:17 (88:12)[e]
8	**3b**	**4a**	**1ba**	48[c]	83:17
9	**3b**	**4b**	**1bb**	52[c]	89:11
10	**3b**	**4c**	**1bc**	31[c]	83:17
11	**3c**	**4a**	**1ca**	51[c]	82:18
12	(*R*)-**3a**	**4a**	(2*R*,3*R*)-**1aa**	54[c]	98:2 (>99:1)[e]

[a] Isolated products, purified by column chromatography.
[b] Catalyst: $[Pd(Ph_3P)_4]$.
[c] Catalyst: $(2\text{-}MeC_6H_4)_3P$, $Pd(OAc)_2$.
[d] Determined in the crude product.
[e] Values in parentheses: *trans*/*cis* ratio after column chromatography.



Scheme 3 Conversion of methylenetetrahydrofuran **1aa** into furanone **2** and dioxanone **9**. *Reagents and conditions*: (a) O_3, CH_2Cl_2, –78 °C; 60%; (b) 3-chloroperbenzoic acid, Li_2CO_3, CH_2Cl_2, 0–25 °C, 51%.

competing reactions with different rate constants. This easily explains that products from an individual bromoalkene **3** and different boronic acids **4** form in not equal diastereomeric ratios (entries 1–6 and 7–10). If, for example, the reaction of the boronic acid with *trans*-**8** is slow compared with that of *cis*-**8**, the former may undergo β-elimination to a higher degree, so that a higher amount of the *cis*-configured Heck–Suzuki product results (entries 3 vs. 2 or 8 vs. 9).



Scheme 2 Transition-state models **7a** and **7b** and rationale of the diastereoselective formation of *trans*-**1** in the Heck–Suzuki reaction

In order to demonstrate the synthetic significance of the diastereoselective domino Heck–Suzuki reaction, it was applied to enantiomerically pure ether (*R*)-**3**. As a result, methylenetetrahydrofuran (2*R*,3*R*)-**1aa** was obtained as a single stereoisomer (Table 2, entry 12). The exocyclic double bond can be used for further transformations (Scheme 3). Thus, ozonolysis of (2*R*,3*R*)-**1aa** gave 3-furanone **2** in 60% yield. Its CD spectrum displays a characteristic positive Cotton effect at 289 nm. When ketone **2** was submitted to a Baeyer–Villiger oxidation with 3-chloroperbenzoic acid, dioxanone **9** resulted in a completely regioselective manner.[13] It can be considered as a protected form of a 2,3-disubstituted 3-hydroxypropanoic acid, which, under retrosynthetic aspects, originates from a C-1–C-2 carbon–carbon bond disconnection and a C-1′–C-2′ disconnection of the side chain attached in 2-position, thus being complementary to the aldol transform.[14] The heterocyclic derivatives **2** and **9** are also obtained as pure enantiomers and diastereomers.

In summary, a protocol for a diastereoselective cyclization has been elaborated that leads to the formation of novel methylenetetrahydrofurans[15,16] from readily available starting materials, the allylic alcohols **6** and commercially available dibromide **5**. For the first time, a domino Heck–Suzuki reaction has been applied that permits to build up contiguous stereogenic carbon centers in the heterocyclic compounds **1**. By using enantiomerically pure allylic alcohols, the protocol readily leads to tetrahydrofurans **1**, dihydro-3-furanone **2**, and dioxanone **9** that form as single stereoisomers.

Acknowledgment

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(15) **Typical Procedure for the Preparation of Compound 1aa**
To a stirred solution of **3a** (0.253 g, 1.00 mmol) in EtOH (10 mL) under an argon atmosphere were added $PhB(OH)_2$ (**4a**, 0.183 g, 1.50 mmol), Cs_2CO_3 (0.489 g, 1.5 mmol), $Pd(OAc)_2$ (5.5 mg, 0.0025 mmol), and tri-*o*-tolylphosphane (5.1 mg, 0.0025 mmol). After stirring for 24 h at 25 °C, the solvent was removed in a rotary evaporator. The residue was dissolved in a mixture of Et_2O (40 mL) and deionized H_2O (40 mL). The aqueous layer was separated and extracted with three 20 mL portions of Et_2O. The combined organic layers were dried with anhyd $MgSO_4$, and the solvent was evaporated under reduced pressure. The yellow-brown crude product was purified by column chromatography on SiO_2 (hexane–EtOAc, 6:1) to give yellowish, oily **1aa** (0.153 g, 61%).

(16) **Spectroscopic Data**
Compound **1aa**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.38 (m, 2 H, CH_2Ph), 2.93 (m, 1 H, 3-H), 4.41 (dq, J_d = 13.16 Hz, J_q = 2.13 Hz, 1 H, 5-H), 4.54 (dt, J_d = 13.24 Hz, J_t = 1.66 Hz, 1 H, 5-H), 4.61 (d, *J* = 6.31 Hz, 1 H, 2-H), 4.75 (q, *J* = 2.36 Hz, 1 H, C=CH*H*), 4.90 (q, *J* = 2.05 Hz, 1 H, C=C*H*H), 7.19 (m, 10 H, arom. H). This *cis*-diastereomer differs in δ = 4.63 (d, *J* = 1.90 Hz, 1 H, 2-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 38.7, 53.0, 71.9, 86.4, 105.5, 115.7, 121.1, 126.6, 126.7, 128.0, 128.7, 129.6, 130.1, 139.7, 141.8, 151. 3. GC-MS (t_R = 9.71 min): *m/z* (%) = 250 (2) $[M]^+$, 158 (43), 129 (100).
Compound (2*R*,3*R*)-**1aa**: $[\alpha]_D^{20}$ –3.1 (*c* 1, $CHCl_3$).
Compound **1ab**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.80 (m, 2 H, CH_2Ar), 2.89 (m, 1 H, 3-H), 4.40 (m, 1 H, 5-H), 4.53 (m, 1 H, 5-H), 4.57 (d, *J* = 6.31 Hz, 1 H, 2-H), 4.76 (q, *J* = 2.21 Hz, 1 H, C=C*H*H), 4.90 (q, *J* = 1.26 Hz, 1 H, C=CH*H*), 7.22 (m, 9 H, arom. H). This *cis*-diastereomer differs in δ = 4.61 (d, *J* = 1.58 Hz, 1 H, 2-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.57, 32.94, 41.62, 71.83, 85.27, 105.52, 125.82, 126.77, 127.35, 128.73, 129.57, 130.08, 131.97, 130.06, 144.22, 152.99. GC-MS [t_R = 12.06 min(*trans*); t_R = 12.10 min(*cis*)]: *m/z* (%) = 296 (23) $[M]^+$, 158 (50), 137 (100).
Compound **1ac**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.90 (m, 2 H, CH_2Ar), 2.98 (m, 1 H, 3-H), 4.50 (m, 1 H, 5-H), 4.64 (m, 1 H, 5-H), 4.65 (d, *J* = 6.0 Hz, 1 H, 2-H), 4.84 (d, *J* = 1.89 Hz, 1 H, C=C*H*H), 5.01 (d, *J* = 1.58 Hz, 1 H, C=CH*H*), 7.09 (d, *J* = 8.20 Hz, 2 H, *m*-ArCl), 7.28 (m, 7 H, arom. H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.02, 27.96, 31.83, 35.68, 69.25, 86.53, 101.37, 124.51, 127.04, 129.65, 130.51, 141.74, 154.69. GC-MS (t_R = 10.70 min): *m/z* (%) = 284 (5) $[M]^+$, 158 (72), 143 (100).
Compound **1ad**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.81 (m, 3 H, CH_3), 1.21 (m, 10 H, CH_2), 1.87 (m, 1 H, CHC*H*H), 2.33 (m, CHCH*H*), 2.58 (m, 1 H, 3-H), 4.35 (dq, J_d = 13.24 Hz, J_q = 2.21 Hz, 1 H, 5-H), 4.54 (m, 1 H, 5-H), 4.92 (q, *J* = 2.05 Hz, 1 H, 2-H), 5.27 (m, 2 H, C=C*H*H, C*H*=CH), 5.41 (m, 2 H, C=CH*H*, CH=C*H*), 7.27 (d, *J* = 4.10 Hz, 2 H, *o*-arom. H), 7.38 (t, *J* = 7.72 Hz, 2 H, *m*-arom. H), 7.53 (dd, *J* = 1.10, 8.35 Hz, 1 H, *p*-arom. H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.0, 21.2, 24.4, 27.9, 31.5, 33.1, 34.7, 58.1, 70.5, 90.3, 109.6, 125.0, 126.1, 127.6, 129.2, 130.0, 136.5, 149.9. GC-MS (t_R = 10.70 min): *m/z* (%) = 284 (32) $[M]^+$, 269 (38), 172 (45), 158 (100).
Compound **1ae**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.25 (d, *J* = 6.31 Hz, 6 H, CH_3), 1.29 (m, 2 H, CH_2Ph), 1.38 (m, 1 H, C*H*CH_3), 2.94 (q, *J* = 7.25 Hz, 1 H, 3-H), 4.75 (m, 2 H, 5-H), 5.13 (d, *J* = 10.40 Hz, 1 H, 2-H), 5.27 (t, *J* = 1.42 Hz 1 H, C=CH*H*), 5.30 (t, *J* = 1.42 Hz, 1 H, C=C*H*H), 7.25 (m, 5 H, arom. H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.02, 27.96, 31.83, 35.68, 69.25, 86.53, 101.37, 124.51, 127.04, 129.65, 130.51, 141.74, 154.69. GC-MS (t_R = 10.70 min): *m/z* (%) = 165 (10) $[M - C_4H_3]^+$, 139 (12), 123 (85), 97 (100).
Compound **1ba**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.93 (d, *J* = 6.31 Hz, 3 H, CH_3), 2.63 (m, 2 H, CH_2Ph), 2.87 (m, 1 H, 3-H), 3.68 (quint, *J* = 6.46 Hz, 1 H, 2-H), 4.21 (dq, J_d = 13.24 Hz, J_q = 2.21 Hz, 1 H, 5-H), 4.35 (dt, J_d = 13.24 Hz, J_t = 1.42 Hz, 1 H, 5-H), 4.79 (q, *J* = 2.21 Hz, 1 H, C=CH*H*), 4.78 (q, *J* = 2.05 Hz, 1 H, C=C*H*H), 7.17 (m, 5 H, arom. H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.87 (*cis*), 20.30 (*trans*), 38.58, 51.75, 70.78, 81.29, 104.65, 115.70, 126.64, 128.81, 129.44, 130.05, 140.08, 152.57. GC-MS [t_R = 10.70 min(*trans*), 6.71 min(*cis*)]: *m/z* (%) = 188 (5) $[M]^+$, 143 (17), 129 (100), 97 (70).
Compound **1bb**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.96 (d, *J* = 6.31 Hz, 3 H, CH_3), 2.41 (s, 3 H, SCH_3), 2.58 (dd, *J* = 14.03, 8.04 Hz, 2 H, CH_2Ar), 2.81 (dd, *J* = 14.19, 6.13 Hz, 1 H, 3-H), 3.66 (quint, *J* = 6.38 Hz, 1 H, 2-H), 4.19 (q, *J* = 2.21 Hz, 1 H, 5-H), 4.21 (q, *J* = 2.21 Hz, 1 H, 5-H), 4.78 (q, *J* = 2.36 Hz, 1 H, C=CH*H*), 4.87 (q, *J* = 2.21 Hz, 1 H, C=C*H*H), 7.13 (m, 4 H, arom. H.). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.12, 21.17, 38.03, 44.76, 70.85, 79.92, 114.87, 127.57, 128.73, 130.37, 138.39, 149.53. GC-MS [t_R = 10.70 min, 9.09 min(*trans*), 9.30 min(*cis*)]: *m/z* (%) = 234 (12) $[M]^+$, 137 (100), 122 (8).
Compound **1bc**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.96 (d, *J* = 6.31 Hz, 3 H, CH_3), 2.41 (m, 1 H, C*H*HPh), 2.59 (m, 1 H, CH*H*Ph), 2.81 (dd, *J* = 14.03, 6.46 Hz, 1 H, 3-H), 3.66 (quint, *J* = 6.31 Hz, 1 H, 2-H), 4.20 (dq, J_d = 13.24 Hz, J_q = 2.21 Hz, 1 H, 5-H), 4.34 (dt, J_d = 13.03 Hz, J_t = 1.85 Hz, 1 H, 5-H), 4.76 (q, *J* = 2.21 Hz, 1 H, C=CH*H*), 4.78 (q, *J* = 2.21 Hz, 1 H, C=C*H*H), 7.07 (m, 2 H, *o*-arom. H), 7.19 (m, 2 H, *m*-arom. H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.33, 37.92, 51.69, 70.81, 81.07, 104.89, 128.92, 130.77, 132.92, 138.55, 153.58. GC-MS [t_R = 7.75 min(*trans*), 7.98 min(*cis*)]: *m/z* (%) = 222 (1) $[M]^+$, 143 (70), 125 (100), 97 (75).
Compound **1ca**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.71 (d, *J* = 6.94 Hz, 3 H, CH_3), 0.78 (d, *J* = 6.94 Hz, 3 H, CH_3), 1.48 (m, 1 H, C*H*CH_3), 2.71 (m, 2 H, CH_2Ph), 3.39 (m, 1 H, 3-H), 3.42 (m, 1 H, 2-H), 4.26 (m, 2 H, 5-H), 4.67 (d, *J* = 2.21 Hz,

1 H, C=CH*H*), 4.83 (d, *J* = 1.58 Hz, 1 H, C=C*H*H), 7.23 (m, 5 H, arom. H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.93, 19.60, 31.63, 40.89, 48.30, 70.88, 89.81, 105.17, 126.57, 127.66, 128,68, 129.65, 140.31, 141.65, 152.27. GC-MS [t_R = 7.21 min(*trans*), 7.31 min(*cis*)]: *m/z* (%) = 216 (7) $[M]^+$, 173 (15), 155 (45), 143 (45), 129 (85), 91 (100).
Compound **2**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.73 (m, 1 H, 3-H), 2.92 (m, 2 H, CH_2Ph), 3.84 (d, *J* = 17.34 Hz, 1 H, 5-H), 4.25 (d, *J* = 16.08 Hz, 1 H, 5-H), 4.73 (d, *J* = 9.48 Hz, 1 H, 2-H), 7.30 (m, 10 H, arom. H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 32.58, 56.36, 72.13, 84.00, 126.80, 127.07, 129.07, 129.76, 130.25, 131.88, 140.08, 142.04, 216.12. GC-MS (t_R = 9.91 min): *m/z* (%) = 252 (1) $[M]^+$, 193 (10), 161 (100).
Compound **9**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.68 (m, 2 H, CH_2Ph), 3.28 (m, 1 H, 5-H), 4.55 (d, *J* = 10.09 Hz, 1 H, 6-H), 5.18 (d, *J* = 5.67 Hz, 1 H, 2-H), 5.35 (d, *J* = 5.67 Hz, 1 H, 2-H), 7.22 (m, 10 H, arom. H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 33.30, 49.61, 80.49, 93.20, 127.34, 127.81, 129.11, 129.41, 129.76, 129.99, 137.93, 137.97, 170.04. GC-MS (t_R = 10.82 min): *m/z* (%) = 268 (13) $[M]^+$, 238 (13), 193 (22) [M], 176 (72), 91 (100).