Palladium–catalyzed synthesis of 2,3-dihydro-2-substituted-2-vinyl-1,4-benzodioxins

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Dedicated to Professor Marcial Moreno-Mañas on the occasion of his 60th birthday
(received 28 Dec 01; accepted 11 Mar 02; published on the web 19 Mar 02)

Abstract
Various 2,3-dihydro-2-substituted-2-vinyl-1,4-benzodioxins 6 are obtained by alkylation of the methyl carbonate of 2,3-dihydro-1,4-benzodioxin-2-ylideneethanol 5 with various carbon nucleophiles in the presence of a palladium complex. Altough the yields in alkytion products are good in the case of a non–bulky nucleophile, formation of the diene 7 was generally observed when a bulky nucleophile was used.

Keywords: Substituted 2-vinyl-benzodioxins, condensation, palladium, alkylation

Introduction

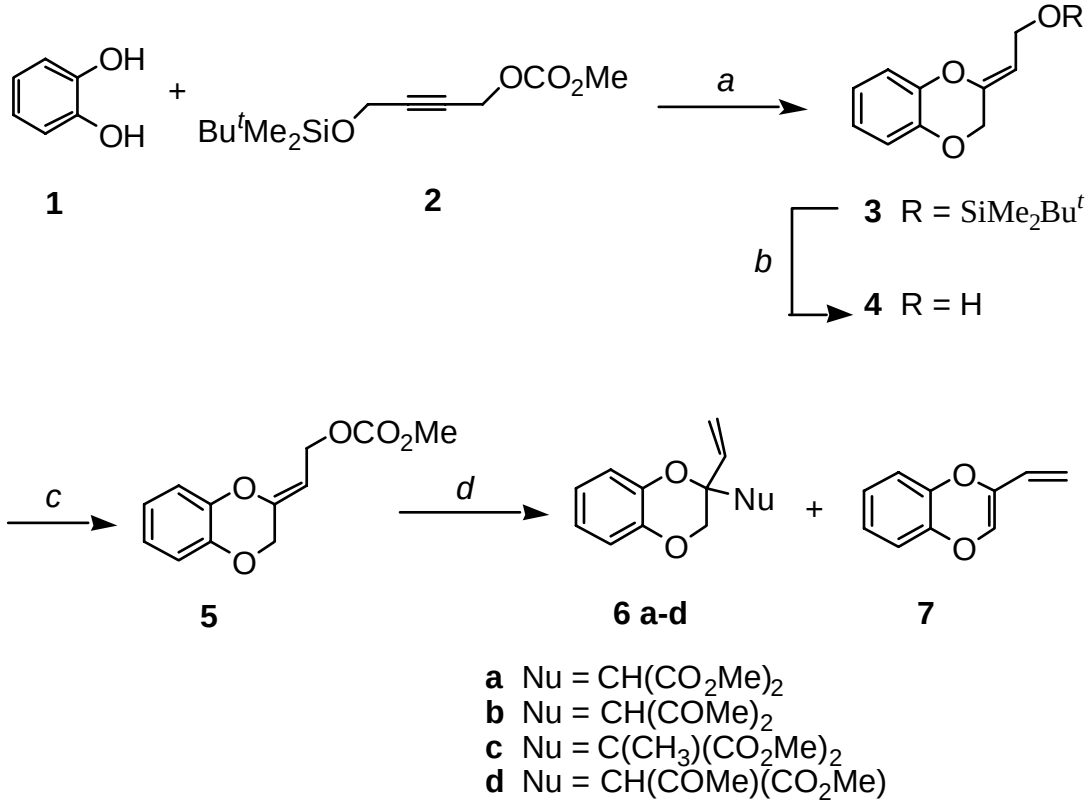
Compounds containing 1,4-benzodioxin and 1,4-benzodioxan structures have attracted considerable interest in recent years. This is mainly due to the interesting properties of these compounds. Some of them act as α- or β-blocking agents and could be used in antidepression or antihypertension therapy.[1–5] Others have antihyperglycemic properties[6] or act as inhibitors of 5-lipoxygenase.[7] The 1,4-benzodioxan frame is also found in a variety of biological active natural products.[8–11] It is also to be noticed that these compounds are useful intermediates in a variety of synthetic transformations.[12–14]

There are many approaches for the synthesis of substituted 1,4-benzodioxins,[15–20] even in an asymmetric way.[20,21] We have recently described the preparation of various 2,3-dihydro-2-ylidene-1,4-benzodioxins *via* a palladium–catalyzed condensation of benzene-1,2-diol with different propargylic carbonates.[22] Among the prepared heterocyclic compounds, we expected that *tert*-butyldimethyl-[(2,3-dihydro-1,4-benzodioxin-2-ylidene)ethoxy]silane **3**, obtained by palladium condensation of benzene-1,2–diol **1** with propargylic carbonate **2**, could be a valuable

starting material for the preparation of 2,3-dihydro-2-substituted-2-vinyl-1,4-benzodioxins. We described in this paper preliminary results in this field.

Results and Discussion

Cyclization of benzene-1,2-diol **1** with carbonate **2**[23] was performed in THF at room temperature in the presence of 2.5 mol% $Pd_2(dba)_3$ and 10 mol % dppb or 1,4-bis(diphenylphosphino)butane to afford after column chromatography 2,3-dihydro-1,4-benzodioxin derivative **3** in 67% yield (Scheme 1). Desilylation of compound **3** performed in THF as the solvent in the presence of tetrabutylammonium bromide trihydrate gave 2,3-dihydro-1,4-benzodioxin-2-ylideneethanol **4** in 95% yield after column chromatography. Carbonate **5** was obtained in 95% yield after column chromatography by condensation of this alcohol **4** with methyl chloroformate in CH_2Cl_2 in the presence of pyridine and dimethylaminopyridine.



(a) $Pd_2(dba)_3$, THF, 20 h; (b) $Bu_4NBr.3H_2O$, THF; (c) $ClCO_2Me$, DMAP, C_5H_5N, CH_2Cl_2; (d) $Pd_2(dba)_3$, NuH, THF.

Scheme 1

The reaction of various nucleophiles with this carbonate **5** was performed in THF at room temperature in the presence of 2.5 mol % $Pd_2(dba)_3$ and 10 mol % dppb. The results are summarized in Table 1.

Table 1. Palladium–catalyzed reaction of NuH with allylic carbonate **5**

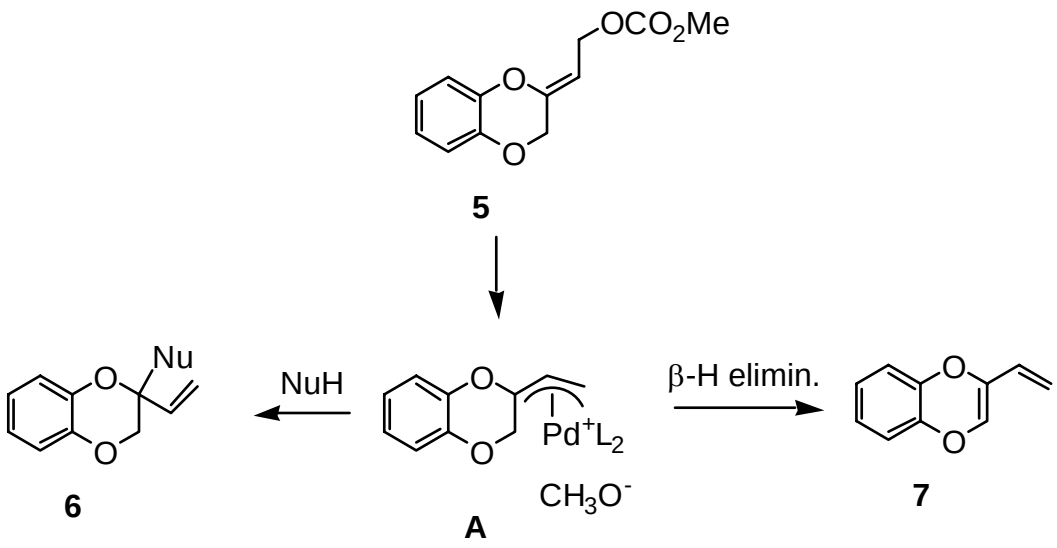
Entry	Nucleophile NuH	Yield % compound **6**	Yield % compound **7**
1	$CH_2(CO_2CH_3)_2$	67	11
2	$CH_2(COCH_3)_2$	53	33
3	$CH(CH_3)(CO_2CH_3)_2$	6	15
4	$CH_2(COCH_3)(CO_2C_2H_5)$	61	18
5	$C(NHCOCH_3)(CO_2CH_3)_2$	0	24

Dimethyl malonate (Table 1, entry 1) and acetylacetone (Table 1, entry 2) reacted with carbonate **5** to give after column chromatography the alkylated 2,3-dihydro-2-vinyl-benzo-1,4-dioxins **6a** and **6b** in 67 and 53% yield, respectively. The formation of 2-vinylbenzo-1,4-dioxine **7** was also observed in 11 and 33% yield, respectively. When dimethyl methylmalonate was used as the nucleophile (Table 1, entry 3), the formation of the alkylated compound **6c** was observed in quite low yield (6%) together with diene **7** (15%). The use of dimethyl acetamidomalonate as the nucleophile (Table 1, entry 5) afforded only the unsaturated compound **7** in 24% yield, with no trace of the corresponding alkylated compound.

Finally reaction of carbonate **5** with ethyl acetoacetate as the nucleophile gave the alkylated product **6d** in 61% yield as a mixture of the two diastereoisomers in a ratio 66:34, together with the diene **7** in 18% yield (Table 1, entry 4).

The formation of compounds **6** and **7** could be explained according to Scheme 2. The first step is the formation of the η^3-allyl intermediate **A** by oxidative addition of the palladium complex on compound **5**. One possibility is the generation of the nucleophile by abstraction of a hydrogen from Nu-H by CH_3O^-. The attack of the nucleophile on the η^3-allyl intermediate **A** occured not at the less hindered termini, but at the more electrophilic termini of this intermediate affording compound **6** bearing a quaternary carbon center. This regioselectivity is in agreement with previous studies on η^3-allyl intermediates bearing an oxygen atom on one of the termini of the η^3-allyl system.[24–26] It is to be noticed that this alkylation reaction is very sensitive to the bulkiness of the nucleophile; the more bulky the nucleophile is (dimethyl methylmalonate, dimethyl acetamidomalonate), the lowest is the chemical yield in the alkylated product.

The formation of the diene **7** could be explained by a β-hydrogen elimination from the intermediate **A**, leading to compound **7** and the formation of $H(CH_3O)Pd(dppb)$, affording Pd(dppb) *via* a reductive elimination of CH_3OH.[27] It seems that there is a competition between these two pathways.



Scheme 2

Mechanism of formation of compounds **6** and **7**

Conclusions

In conclusion, we have shown that various 2,3-dihydro-2-substituted-2-vinyl-1,4-benzodioxins **6** bearing a quaternary carbon could be very easily obtained from ***tert***-butyldimethyl-[(2,3-dihydro-1,4-benzodioxin-2-ylidene)ethoxy]silane **4** *via* a palladium– catalyzed alkylation reaction of the corresponding carbonate with various carbon– nucleophiles. However the chemical yields are strongly dependent on the bulkiness of the nucleophile, with the preferential formation of a diene when this nucleophile is too bulky. Work is actually in progress in our group in order to prepare chiral 2,3-dihydro-2-substituted-2-vinyl-1,4-benzodioxins **6** *via* the use of chiral ligands.

Experimental Section

General Procedures. All manipulations involving palladium catalysis were performed in Schlenk tubes under a nitrogen atmosphere. Unless otherwise stated, the materials were commercial samples; propargylic carbonate **2** was prepared as previously described.[23] All organic solvents were of analytical quality and used as purchased. Solvents mixtures are defined by volume ratios (v/v). Tetrahydrofuran was distilled from sodium/benzophenone. All ^{1}H– and ^{13}C–NMR spectra were recorded on a Brücker AM 300 spectrometers in $CDCl_3$. Chemical shifts are reported on the δ scale with the reference to tetramethylsilane or $CDCl_3$ as the internal standard and the coupling constants *J* are given in Hz. The IR–spectra were recorded on a Perkin–Elmer 681 instrument. Tin–layer chromatography was performed using Merck silica gel 60 F_{254} precoated aluminium plates, 0.2 mm thickness. Visualisation was by UV or by spraying

with 10% sulphuric acid and then heating. Column chromatography was carried out using Merck silica gel (Kieselgel 60, 70–230 mesh).

***(Z)-tert*-Butyldimethyl-[(2,3-dihydro-1,4-benzodioxin-2-ylidene)ethoxy]silane (3).** A mixture of $Pd_2(dba)_3$ (20.8 mg, 2.2 x 10^{-2} mmol), in THF (7 mL), was stirred under a nitrogen atmosphere at room temperature for 30 min. This catalyst solution was added to a mixture of benzene-1,2-diol **1** (100 mg, 0.9 mmol) and carbonate **2** (284 mg, 1.1 mmol). The resulting solution was stirred at room temperature for 24 h. The solvent was evaporated and the residue chromatographed over silica (R_f = 0.24, petroleum ether/EtOAc 100:1) to give 196 mg of **3** as an oil (yield 67%);^{1}H–NMR δ 7.10–6.80 (4H, m, H_{arom}), 4.91 (1H, t, *J* = 6.3, =C*H*-CH_2), 4.47 (2H, s, 3–H), 4.47 (2H, d, *J* = 6.3, =CH-C*H*$_2$), 0.88 (9H, s, CH_3), 0.12 (6H, s, CH_3); ^{13}C–NMR δ 144.0 (2–C), 143.2 (C_{arom}), 142.6 (C_{arom}), 122.3 (C_{arom}), 122.2 (C_{arom}), 117.4 (C_{arom}), 116.6 (C_{arom}), 107.7 (=*C*H-CH_2), 65.1 (3–C), 56.6 (CH_2OSi), 26.1 (C*Me*$_3$), 18.4 (*C*Me$_3$), –5.1 (SiMe); IR ν 3060, 3040, 2950, 2920, 2880, 2850, 1690, 1590, 1480, 1460, 1250 cm^{-1}. Anal. Calcd for $C_{16}H_{24}O_3Si$: C, 65.72; H, 8.28. Found: C, 65.39; H, 8.61.

***(Z)*-2,3-Dihydro-1,4-benzodioxin-2-ylideneethanol (4).** A solution of compound **3** (2.57 g, 9 mmol) and $Bu_4NBr.3H_2O$ (4.60 g, 18 mmol) in tetrahydrofuran (80 mL) was stirred at 25 °C for 1 h. After evaporation of the solvent, the residue was diluted with diethyl ether (100 mL), and the ethereal solution was washed three times with a saturated aqueous solution of sodium chloride (3x40 mL), and dried over sodium sulfate. Chromatography (R_f = 0.24, petroleum ether/EtOAc 4:3) of the residue obtained after evaporation of the solvent gave 1.49 g of compound **4** (yield 95%); oil; ^{1}H–NMR δ 7.10–6.80 (4H, m, H_{arom}), 4.93 (1H, t, *J* = 7.0, =C*H*-CH_2), 4.44 (2H, s, 3–H), 4.38 (2H, d, *J* = 7.0, =CH-C*H*$_2$), 2.65 (1H, bs, OH); ^{13}C–NMR δ 144.5 (2–C), 143.9 (C_{arom}), 142.4 (C_{arom}), 122.5 (C_{arom}), 122.4 (C_{arom}), 117.4 (C_{arom}), 116.6 (C_{arom}), 106.7 (=*C*H-CH_2), 65.9 (3–C), 56.8 (CH_2OH); IR ν 3350, 3060, 3040, 2940, 2920, 2850, 1690, 1590, 1490, 1250 cm^{-1}. These values are in agreement with the literature.[28]

Carbonic acid *(Z)*-(2-benzo[1,4]dioxin-2-ylidenethyl) ester methyl ester (5). To a stirred solution of the alcohol **4** (360 mg, 2 mmol), dimethylaminopyridine (50 mg, 0.4 mmol), and pyridine (632 mg, 8 mmol), in CH_2Cl_2 (10 mL) at 0 °C under argon was slowly added methyl chloroformiate (756 g, 8 mmol). After being stirred for 24 h at room temperature, the solution was hydrolyzed with a saturated aqueous solution of copper sulfate (10 mL), and extracted three times with diethyl ether (3x20 mL). The ethereal solution was washed with a saturated aqueous solution of copper sulfate (10 mL), and dried over sodium sulfate. Evaporation of the solvent followed by column chromatography (R_f = 0.66, petroleum ether/EtOAc 4:1) of the residue gave 448 mg of compound **5** as an oil (yield 95%); ^{1}H–NMR δ 7.10–6.80 (4H, m, H_{arom}), 5.00–4.87 (3H, m, =C*H*-CH_2, =C*H*-), 4.45 (2H, s, 3–H), 3.80 (3H, s, CH_3); ^{13}C–NMR δ 155.8 (CO), 147.0 (2–C), 143.9 (C_{arom}), 142.2 (C_{arom}), 122.7 (C_{arom}), 122.4 (C_{arom}), 117.4 (C_{arom}), 116.7 (C_{arom}), 100.7 (=*C*H-CH_2), 64.8 (3–C), 61.0 (=CH_2*C*H_2O), 54.8 (CH_3); IR ν 3060, 3040, 3020, 2990, 2950, 2890, 2850, 1750, 1690, 1590, 1490, 1450, 1250 cm^{-1}. Anal. Calcd for $C_{12}H_{12}O_5$: C, 60.00; H, 5.12. Found: C, 60.63; H, 5.16.

Alkylation of carbonic acid *(Z)*-(2-benzo[1,4]dioxin-2-ylidenethyl) ester methyl ester. To a stirred solution of carbonate **5** (104 g, 0.44 mmol) and nucleophile (0.53 mmol) in THF (7 mL) at 25 °C under argon was added the catalyst solution obtained by stirring under argon for 0.5 h $Pd_2(dba)_3$ (10.4 mg, 1.1 x 10^{-2} mmol) and dppb (19.4 mg, 4.6 x 10^{-2} mmol) in THF (7 mL). After being stirred for 24 h at room temperature, the solvent was evaporated and the residue purified by column chromatography to give the alkylated compound **6**.

2-(2,3-Dihydro-2-vinyl-1,4-benzodioxin-2-yl)malonic acid dimethyl ester (6a). Oil; yield 69%; R_f = 0.20 (petroleum ether/AcOEt 15:1); ^{1}H–NMR δ 7.00–6.80 (4H, m, H_{arom}), 6.26 (1H, dd, *J* = 17.3, 11.0, -CH=), 5.49 (1H, dd, *J* = 17.3, 0.7, =CH_2), 5.38 (1H, dd, *J* = 11.0, 0.7, =CH_2), 4.56 (1H, d, *J* = 11.4, 3–H), 4.15 (1H, d, *J* = 11.4, 3–H), 4.01 (1H, s, -CH<), 3.76 (3H, s, CH_3), 3.72 (3H, s, CH_3); ^{13}C–NMR δ 166.9 (CO), 166.5 (CO), 142.5 (C_{arom}), 141.7 (C_{arom}), 133.6 (-CH=), 122.2 (C_{arom}), 121.8 (C_{arom}), 118.9 (=CH_2), 117.7 (C_{arom}), 117.2 (C_{arom}), 76.1 (2–C), 68.1 (3–C), 55.5 (-CH<), 52.8 (CH_3), 52.6 (CH_3); IR ν 3080, 3040, 3020, 2950, 2920, 2870, 2840, 1750, 1645, 1595, 1490, 1430, 1255 cm^{-1}. Anal. Calcd for $C_{15}H_{16}O_6$: C, 61.62; H, 5.52. Found: C, 61.89; H, 5.55.

3-(2,3-Dihydro-2-vinyl-1,4-benzodioxin-2-yl)pentane-2,4-dione (6b). Oil; yield 53%; R_f = 0.24 (petroleum ether/AcOEt 10:1); ^{1}H–NMR δ 7.00–6.80 (4H, m, H_{arom}), 6.25 (1H, dd, *J* = 17.3, 11.0, -CH=), 5.51 (1H, dd, *J* = 17.3, 1.1, =CH_2), 5.35 (1H, dd, *J* = 11.0, 1.1, =CH_2), 4.36 (1H, d, *J* = 11.6, 3–H), 4.30 (1H, s, -CH<), 3.95 (1H, d, *J* = 11.6, 3–H), 2.29 (3H, s, CH_3), 2.21 (3H, s, CH_3); ^{13}C–NMR δ 202.9 (CO), 202.7 (CO), 143.0 (C_{arom}), 141.6 (C_{arom}), 133.8 (-CH=), 122.8 (C_{arom}), 122.4 (C_{arom}), 118.9 (=CH_2), 118.0 (C_{arom}), 117.8 (C_{arom}), 77.5 (2–C), 69.2 (3–C), 68.0 (-CH<), 32.8 (CH_3), 32.5 (CH_3); IR ν 3080, 3030, 2990, 2950, 2910, 2870, 1720, 1640, 1590, 1490, 1460, 1250 cm^{-1}. Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.20; H, 6.20. Found: C, 69.43; H, 6.22.

2-(2,3-Dihydro-2-vinyl-1,4-benzodioxin-2-yl)-2methylmalonic acid dimethyl ester (6c). Oil; yield 6%; R_f = 0.30 (petroleum ether/AcOEt 15:1); ^{1}H–NMR δ 7.30–6.80 (4H, m, H_{arom}), 6.07 (1H, dd, *J* = 17.1, 10.9, -CH=), 5.29 (1H, dd, *J* = 10.9, 1.0, =CH_2), 5.20 (1H, dd, *J* = 17.1, 1.0, =CH_2), 4.80 (1H, d, *J* = 11.2, 3–H), 4.32 (1H, d, *J* = 11.2, 3–H), 3.73 (3H, s, CH_3), 3.71 (3H, s, CH_3), 3.09 (3H, s, CH_3); IR ν 3040, 2950, 2880, 1750, 1645, 1600, 1450, 1430, 1255 cm^{-1}.

2-(2,3-Dihydro-2-vinyl-1,4-benzodioxin-2-yl)-3-oxobutyric acid methyl ester (6d). As an oily mixture of two diastereoisomers 66:34; yield 61%; R_f = 0.30 (petroleum ether/AcOEt 15:1); ^{1}H–NMR δ 6.96–6.86 (4H, m, H_{arom}), 6.32 (0.66H, dd, *J* = 17.2, 11.1, -CH=), 6.18 (0.34H, dd, *J* = 17.3, 10.9, -CH=), 5.52 (0.66H, dd, *J* = 17.2, 1.1, =CH_2), 5.45 (0.34H, dd, *J* = 17.3, 1.1, =CH_2), 5.39 (0.66H, dd, *J* = 11.1, 1.1, =CH_2), 5.34 (0.34H, dd, *J* = 10.9, 1.1, =CH_2), 4.50 (0.66H, d, *J* = 11.5, 3–H), 4.37 (0.34H, d, *J* = 11.5, 3–H), 4.28 (0.34H, d, *J* = 11.5, 3–H), 4.26–4.15 (2H, m, O*C*H_2CH$_3$), 4.09 (0.66H, s, -CH<), 4.06 (0.34H, s, -CH<), 3.96 (0.66H, d, *J* = 11.5, 3–H), 2.33 (3H, s, CH_3), 2.24 (3H, s, CH_3), 1.26 (1.98H, t, *J* = 7.1, CH_3), 1.25 (1.02H, t, *J* = 7.1, CH_3); ^{13}C–NMR δ 201.7 (CO), 143.0 (C_{arom}), 142.1 (0.34 C_{arom}), 141.7 (0.66 C_{arom}), 134.5 (0.34 -CH=), 133.5 (0.66 -CH=), 122.8 (0.66 C_{arom}), 122.5 (0.34 C_{arom}), 122.4 (0.66 C_{arom}), 122.1 (0.34 C_{arom}), 119.1 (0.66 =CH_2), 119.0 (0.34 =CH_2), 118.1 (0.66 C_{arom}), 117.9 (0.34 C_{arom}), 117.8 (0.66 C_{arom}), 117.6 (0.34 C_{arom}), 77.2 (0.34 2-C), 76.9 (0.66 2-C), 69.4 (0.66 3–C), 68.2 (0.34 3–C), 62.1 (0.34

O*C*H$_2$CH$_3$), 62.0 (0.66 O*C*H$_2$CH$_3$), 63.2 (0.34 –CH<), 61.4 (0.66 –CH<), 32.3 (0.66 CH$_3$), 32.2 (0.34 CH$_3$), 14.4 (CH$_3$); IR ν 3080, 3040, 2980, 2930, 2880, 1745, 1715, 1595, 1490, 1255 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_5$: C, 66.18; H, 6.25. Found: C, 66.01; H, 6.32.

2-Vinyl-1,4-benzodioxin (7). R_f = 0.85 (petroleum ether/AcOEt 15:1); ^{1}H–NMR δ 6.90–6.30 (4H, m, H$_{arom}$), 5.95 (1H, bs, 3–H), 5.90 (1H, dd, *J* = 17.0, 11.0, -CH=), 5.42 (1H, dd, *J* = 17.0, 0.8, =CH$_2$), 5.02 (1H, dd, *J* = 11.0, 0.8, =CH$_2$); IR ν 3040, 2950, 2880, 1750, 1645, 1600, 1490, 1430, 1255 cm^{-1}. These values are in agreement with those published in the litterature.[12]

Acknowledgements

J. R. L. thanks the MENRT for a fellowship.

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