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The (*S*)-Proline/Polyelectrolyte System: An Efficient, Heterogeneous, Reusable Catalyst for Direct Asymmetric Aldol Reactions

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A direct asymmetric aldol reaction between unmodified aldehydes and ketones was achieved using the (*S*)-proline/poly(diallyldimethylammonium) hexafluorophosphate heterogeneous catalytic system with enantioselectivities and yields comparable to those obtained in the (*S*)-proline-catalyzed reactions performed under homogeneous conditions. Recycling of the catalyst was possible at least six times without loss of activity and enantioselectivity.

Introduction

Homogeneous asymmetric catalysis is widely used in organic chemistry for the synthesis of fine chemicals and natural compounds.[1] Yet, recovery of expensive chiral homogeneous catalysts from the reaction solution remains a difficult and so far unsolved problem.[2] To facilitate the separation of homogeneous catalysts from the reaction mixture, they are immobilized on solid supports; however, reactions catalyzed by the supported catalysts are usually less selective than the corresponding reactions in solutions.[3]

A direct asymmetric aldol reaction between unmodified aldehydes and ketones is one of the most general and simple methods of forming carbon–carbon bonds. This reaction plays an important role in nature as a source of carbohydrates[4] and is used for the synthesis of chiral β-hydroxy carbonyl compounds, which are valuable intermediates in organic synthesis.[5] Native amino acid (*S*)-proline[5] and its amides[6,7] are efficient catalysts of the asymmetric aldol reaction. The reaction was performed in acetone,[6b,6c,7a–7c] DMSO,[5a,5b,7d,8] DMF,[7e] CH_2Cl_2,[7b,7d,9] $CHCl_3$,[7f] toluene,[7d] PEG,[10] and ionic liquids.[6a,11] The catalyst solution in anionic liquid can be recovered and reused. Yet, the application of ionic liquids in the industrial syntheses of fine chemicals is still problematic because of the relatively high cost of these solvents.[12]

The asymmetric aldol reaction was performed under the action of (*S*)-proline adsorbed on silica gel.[5b] The authors managed to recover the catalyst, though the *ee* of the products were lower. Good yields and *ee* values, compared to those obtained using nonsupported proline, were obtained when the aldol reaction was catalyzed by silica-supported (*S*)-proline modified by 1,2,3-trimethylimidazolium cations.[13] The modifier was covalently attached to the silica surface by the C–Si–O spacer. BF_4^- anions were used as counteranions. Yet, according to our data, the thereby prepared catalyst quickly lost its catalytic activity. The aldol yield became 30–40% lower after the catalytic system was used twice, possibly because of spacer cleavage.

Presumably, polymer supports in which ionic fragments are linked with the polymer chain by hydrolytically stable chemical bonds, in particular carbon-chained polyelectrolytes bearing the ionic moiety within each monomer unit, should have higher supporting ability and chemical resistance. It was reported that Rh and Ru chiral complexes immobilized in a mixture of a 20% water (or methanol) solution of poly(diallyldimethylammonium) chloride and the ionic liquid could be used as recoverable catalysts for enantioselective hydrogenation reactions of olefins and ketones.[14] The polyelectrolyte prevented leaching of the complexes and thus ensured the multiple use of the catalysts.

Here we report the first example of a direct asymmetric aldol reaction catalyzed by the heterogeneous, recoverable catalytic system consisting of (*S*)-proline supported on solid poly(diallyldimethylammonium) salts.

Results and Discussion

We investigated poly(diallyldimethylammonium) salts of different molecular mass [100.000–200.000 Da (**a**) and 400.000–500.000 Da (**b**)] containing Cl^- (**1**), BF_4^- (**2**), and PF_6^- (**3**) anions. Solid poly(diallyldimethylammonium) chloride **1b** was obtained from a commercially available (Aldrich) 20% aqueous solution of the corresponding polymer. Poly(diallyldimethylammonium) tetrafluoroborate **2b** and hexafluorophosphates **3a**,**b** were prepared by mixing polymer **1a** or **1b** (20%) with HBF_4 (50%) or HPF_6 (60%).

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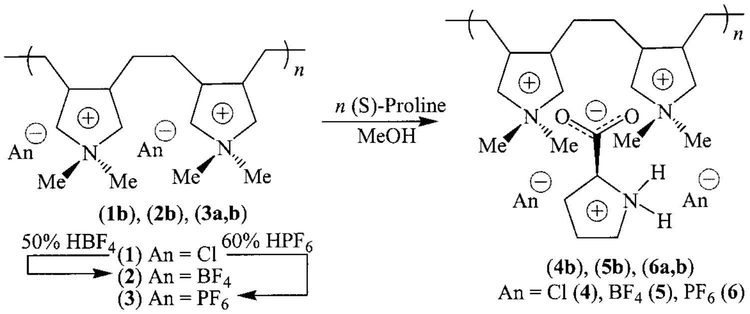
Polyelectrolytes **2b**, **3a**, and **3b**, which were poorly soluble in water, precipitated from the reaction mixture. They were identified by ^{31}P- and ^{19}F NMR spectroscopy and microanalysis data. We were not able to detect the tetrafluoroborate **2b** by ^{19}F NMR spectroscopy because of its poor solubility in [D$_6$]DMSO.

(*S*)-Proline was supported on polyelectrolytes **1b**, **2b**, **3a**, and **3b** by mixing each polymer solution (suspension) in CH_3OH with the organocatalyst solution in the same solvent. To achieve better (*S*)-proline adsorption, the amino acid/polymer ratio was chosen in such a way that each (*S*)-proline molecule would interact with two pyrrolidine moieties. Evaporation of the solvent under reduced pressure afforded the corresponding supported catalysts **4b**, **5b**, **6a**, and **6b** as colorless solids in quantitative yield (Scheme 1). IR spectra of the prepared catalysts contained signals at 1556–1564, 1624, and 2400–3000 cm^{-1}, which could be attributed to the C=O, NH, and OH groups of the proline molecules immobilized on the polymer surface.

First we studied the catalytic activities of the heterogeneous catalysts **4b**, **5b**, **6a**, and **6b** in the asymmetric aldol reaction between benzaldehyde (**7a**) and acetone (**8**). The reaction was carried out in a 30-fold excess of acetone at 25 °C for 15 h. The (*S*)-proline amount in the added catalyst was 15 mol-% with respect to the aldehyde. After completion of the reaction, the solid catalysts **4b**, **5b**, **6a**, and **6b** were filtered off, and a mixture of aldol **9a** and elimination product **10a** was isolated from the filtrate. According to ^{1}H NMR spectroscopic data, the aldol **9a** content in the mixture was 83–96% depending on the catalyst. Aldol **9a** was isolated from the mixture in a pure state by column chromatography on silica gel. The yield of product **9a** was 55–59%, *ee* 66–69%, $[\alpha]_D^{20} = +48 \pm 2$ ($c = 1.41$, $CHCl_3$) (Table 1).

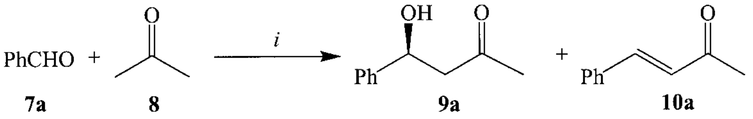
Next we investigated the recoverability of catalytic systems **4b**, **5b**, **6a**, and **6b** in the aldol reaction between compounds **7a** and **8**. Each catalyst was used twice without reduction of the *ee* values of aldol **9a**. The yield of aldol **9a** was found to decrease significantly in the second cycle in the reactions catalyzed by systems **4b** and **5b** bearing the anions Cl^- and BF_4^- (25% and 36%, respectively). Doubled reaction time (30 h) was required to obtain **9a** in the yield (50%) comparable with that in the first cycle (Table 1, entry 2). In the case of chloride **4b**, the amount of elimination product **10a** increased by a factor of 3.5 when the catalyst was used repeatedly. On the other hand, in the reactions catalyzed by hexafluorophosphates **6a**, and **6b**, the yield of aldol **9a** and the ratio **9a/10a** remained nearly the same when the recovered catalyst was used.

System **6b** was further studied in asymmetric aldol reactions between substituted aromatic aldehydes **7b**–**g** and acetone (**8**). The reactions were carried out under the same



Scheme 1. (*S*)-Proline-supported poly(diallyldimethylammonium) salts.

Table 1. Asymmetric aldol reaction between benzaldehyde (**7a**) and acetone (**8**) catalyzed by the (*S*)-proline/polyelectrolyte systems **4b**, **5b**, **6a**,and **6b**.[a]



Entry	Catalyst	Cycle	**9a/10a**[b]	Yield **9a** [%][c]	*ee* **9a** [%][d]
1	**4b**	1	10:2	55 (62[5b], 51[13], 58[11a])	67 (60[5b], 64[13], 71[11a])
2	**4b**	2	10:7(11:7[e])	25 (50[e])	67
3	**5b**	1	9:1	59	66
4	**5b**	2	9:1	36	67
5	**6a**	1	15:1	53	69
6	**6a**	2	12:1	52	67
7	**6b**	1	10:1	55	69
8	**6b**	2	10:1	54	67

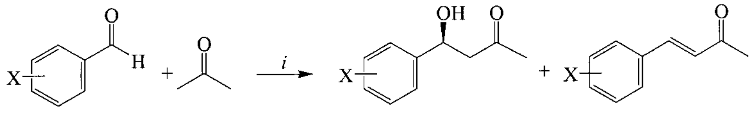
[a] Reagents and conditions: *i* **7a** (0.5 mmol), **8** (1 mL), **4b** (33.6 mg) or **5b** (40.6 mg) or **6a**,**b** (49.2 mg), 25 °C, 15 h. [b] Determined by ^{1}H NMR spectroscopy. [c] Isolated yield. [d] Determined by ^{1}H NMR spectroscopy in $CDCl_3$ by using Eu(facam)$_3$ and by comparing the specific optical rotation $[\alpha]_D^{20}$ of reaction product **9a** with literature data.[6b] [e] $T = 30$ h.

conditions. Addition products (AP) **9b–g** were obtained in 58–98% yields. A small amount (4%) of the elimination by-product (EP) formed along with the major compound **9e** (^{1}H NMR spectroscopy) only in the case of *p*-chlorobenzaldehyde (**7e**). The reaction of aldehyde **7g** with acetone (**8**) proceeded with participation of one of the two aldehyde groups, despite the donor excess, affording aldol **9g** (Table 2). 4-Methoxybenzaldehyde reacted sluggishly with acetone (**8**) under the studied conditions to give the corresponding aldol in only 10% yield (^{1}H NMR spectroscopic data).

The *ee* values for aldols **9b–e** were determined by ^{1}H NMR spectroscopy by using Eu(facam)$_3$ and by comparing the product-specific optical rotations with the literature data.[6b] The values obtained were comparable to those reported for the reactions catalyzed by modified silica-supported (*S*)-proline[13] and by (*S*)-proline–solvent {DMSO,[5b] PEG,[10] and ionic liquid (bmim)[PF$_6$][11a,11b]} systems. The advantage of the (*S*)-proline/polyelectrolyte system **6b** was its better recoverability. The catalyst that is filtered off and washed with acetone can be used in the aldol reaction at least six times without a decrease in product yields and enantioselectivities.

The extent of the catalytic system **6b** was estimated in asymmetric aldol reactions between aromatic aldehydes **7a–c** and cyclic ketones **11** and **12**. The reactions were per-

Table 2. Asymmetric aldol reaction between substituted aromatic aldehydes **7b–g** and acetone (**8**) catalyzed by the (*S*)-proline/poly(diallyldimethylammonium) hexafluorophosphate system **6b**.[a]



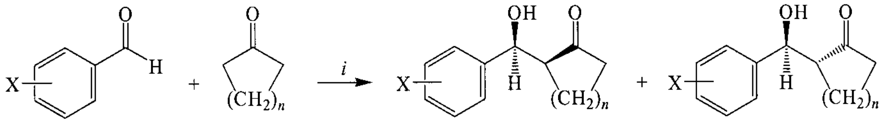
7b-g (ST) **8** **9b-g (AP)** **(EP)**

X = *m*-NO$_2$ (**b**); *p*-NO$_2$ (**c**); *o*-Cl (**d**); *p*-Cl (**e**); *p*-CO$_2$Me (**f**), *p*-CHO (**g**)

Entry	ST/AP/EP[b]	9	Yield [%][c] (cycle)	*ee* [%][d] (cycle)	$[\alpha]_D^{20}$, *c* = 1.00, CHCl$_3$[e]
1	<1:98:<1	**b**	97 (1), 98 (2), 95(3), 96(4), 97(5), 96(6) (88[10], 94[11b])	72 (1), 73 (2), 72 (3), 70 (4),72(5), 71 (6) (70[10],[11b])	+51.4 (+62.1; c 0.35)
2	<1:98:<1	**c**	98 (1), 97 (2), 95 (3), 94(4), 97 (5), 97 (6) (68[5b],[11b], 85[13])	70 (1), 68 (2), 71 (3), 72 (4),70 (5), 69 (6) (76[5b], 65[11b], 66[13])	+46.4 (+61.6; c 0.51)
3	<1:98:<1	**d**	97 (94[5b], 88[10])	65 (69[5b], 60[10])	+66.2 (+97.0; c 0.34)
4	19:77:4	**e**	65 (75[f], 74[g], 72[h])	62 (70[f], 65[g], 67[h])	+41.2 (+62.7; c 0.48)
5	<1:98:<1	**f**	96	62	+30.5
6	<1:98:<1	**g**	58	62	+49.9

[a] Reagents and conditions: *i* **7b–g** (0.5 mmol), **8** (1 mL), **6b** (49.2 mg), 25 °C, 15 h. [b] Determined by ^{1}H NMR spectroscopy. [c] Isolated yield. [d] Determined by ^{1}H NMR spectroscopy in CDCl$_3$ by using Eu(facam)$_3$. [e] Literature data[6b] for the corresponding compounds (*ee* 85–93%) are given in parentheses. [f] Data for the reaction of *p*-bromobenzaldehyde with acetone in the catalytic system (*S*)-proline-modified silica gel.[13] [g] Data for the reaction of *p*-bromobenzaldehyde with acetone in DMSO.[5b] [h] Data for the reaction of *p*-bromobenzaldehyde with acetone in (bmim)[PF$_6$].[11a]

Table 3. Asymmetric aldol reaction between aldehydes **7a–c** and cycloalkanones **11**, **12** catalyzed by the catalytic system **6b**.[a]



7a-c (ST) **11, 12** **AP**$_{syn}$ **13a-c, 14b,c** **AP**$_{anti}$

Reagents	X	*n*	AP	Yield [%][b]	*ee* [%][c]
7a, **11**	H	2	**13a** *syn*	50 (51[11a])	20 (n.d.[11a])
			13a *anti*	20 (32[11a])	71 (n.d.[11a])
7b, **11**	*m*-NO$_2$	2	**13b** *syn*	65 (47[d])	31 (86[d])
			13b *anti*	25 (47[d])	69 (32[d])
7c, **11**	*p*-NO$_2$	2	**13c** *syn*	70 (27[5b])	52 (63[5b])
			13c *anti*	28 (46[5b])	n.d. (69[5b])
7b, **12**	*m*-NO$_2$	3	**14b** *syn*	23 (4[d])	78
			14b *anti*	67 (87[d])	91 (93[d])
7c, 12	*p*-NO$_2$	3	**14c** *syn*	18(24[5b])	n.d (67[5b])
			14c *anti*	80(41[5b])	78 (89[5b])

[a] Reagents and conditions: *i* **7a–c** (0.5 mmol), **11** or **12** (1 mL), **6b** (49.2 mg), 20 °C, 15 h. [b] Determined by ^{1}H NMR spectroscopy. [c] Determined by ^{1}H NMR spectroscopy by using Eu(facam)$_3$. [d] Data for reactions of *p*-(trifluoromethyl)benzaldehyde with cyclopentanone and cyclohexanone in (bmim)[PF$_6$].[11b]

formed in excess ketone. Aldehydes **7a**–**c** were found to react with cycloalkanones **11** and **12** under the above-mentioned conditions to yield aldols **13a**–**c** and **14b**,**c**, respectively, as a mixture of *syn*- and *anti* isomers (Table 3).

The *syn*/*anti* isomer ratio in the reaction products was determined on the basis of integral ratios of protons located at the α-position with respect to the hydroxy group in the ^{1}H NMR spectra of each isomer. α-Protons were assigned to particular isomers on the basis of their chemical shifts δ and coupling constants $^3J^1{}_{\mathrm{H}-}{}^1{}_{\mathrm{H}}$ with the vicinal cycloalkanone proton (δ = 5.31–5.48 ppm, J = 2–3 Hz in *syn* isomers, δ = 4.71–4.91 ppm, J = 8–9 Hz in *anti* isomers).

It is worth mentioning that the *syn* isomers of aldols **13a**–**c** predominated in the reactions of aldehydes **7a**–**c** with cyclopentanone (**11**). However, the *anti* isomers of aldols **14b**,**c** were the major products of the corresponding reactions with cyclohexanone (**12**). The *syn*/*anti* isomer ratio was not influenced by the reaction time (15–48 h) or the structure of the aldehyde.

Conclusions

A new stable and recoverable heterogeneous catalytic system, (*S*)-proline/poly(diallyldimethylammonium) hexafluorophosphate, was developed for the direct asymmetric aldol reaction between unmodified aldehydes and ketones. A range of this and other supported polyelectrolyte systems as chiral catalysts for enantioselective reactions of organic compounds is now being studied.

Experimental Section

General Remarks: ^{1}H NMR spectra were recorded with Bruker AM 300 (300.13 MHz {^{1}H}) and Bruker DRX 500 (500.13 {^{1}H}, 125.76 {^{13}C}, 470.4 {^{19}F}, 202.4 MHz {^{31}P}) instruments in $CDCl_3$ and [D$_6$]DMSO. ^{1}H-, ^{13}C-, ^{19}F-, and ^{31}P chemical shifts were recorded relative to Me_4Si, $CDCl_3$, $CFCl_3$, and H_3PO_4, respectively. IR spectra (KBr pellets) were recorded with a Specord M82 instrument. Specific optical rotations $[\alpha]_D^{20}$ were measured with a Jasco DIP-360 instrument at 589 nm. Silica gel 0.060–0.200 nm (Acros) was used for column chromatography. Solvents were purified by standard methods.

Poly(diallyldimethylammonium) Chloride (1b): Methanol (40 mL) was added to a water solution of poly(diallyldimethylammonium) chloride (MM 400.000–500.000 Da) (4.00 g, 20%). The mixture obtained was poured into stirred diethyl ether (100 mL). The solvents were decanted; the residue was washed with diethyl ether (3 × 25 mL) and refluxed with anhydrous benzene (50 mL) in a Dean-Stark apparatus until the remaining water was completely removed (1 h). The solvent was evaporated, and the residue was dried in vacuo (3 Torr) at 25 °C for 1 h to afford **1b** (0.56 g, 70%) as a colorless powder. $(C_8H_{16}ClN)_{2n}$ $(161.67)_{2n}$: calcd. C 59.43, H 9.98, N 8.66; found C 59.20, H 9.76, N 8.79.

Poly(diallyldimethylammonium) Tetrafluoroborate (2b) and Hexafluorophosphates (3a,b). General Procedure: HBF_4 (3.20 g, 50%) [for **2b**] or HPF_4 (4.40 g, 60%) [for **3a**,**b**] was gradually added to a stirred water solution of poly(diallyldimethylammonium) chloride (MM 100.000–200.000 Da for **3a**, 400.000–500.000 Da for **2b** and **3b**) (10.0 g, 20%). The upper aqueous layer was decanted, the residue was thoroughly washed with distilled water until washings had pH 7 and dried with P_2O_5 in vacuo (3 Torr) at 60 °C for 2 h to afford the corresponding polymers **2b**, **3a**, and **3b** as colorless powders.

Poly(diallyldimethylammonium) Tetrafluoroborate (2b): Yield 2.48 g (94%). $(C_8H_{16}BF_4N)_{2n}$ $(213.02)_{2n}$: calcd. C 45.11, H 7.57, N 6.58; found C 45.19, H 7.47, N 6.63.

Poly(diallyldimethyl ammonium) Hexafluorophosphate (3a): Yield 3.18 g (95%). ^{19}F NMR ([D$_6$]DMSO): δ = –68.60 (d, $^1J_{P,F}$ = 713 Hz) ppm. ^{31}P NMR: δ = –41.21 (sept, $^1J_{P,F}$ = 714 Hz) ppm. $(C_8H_{16}F_6NP)_{2n}$ $(271.18)_{2n}$: calcd. C 35.43, H 5.95, N 5.17; found C 35.37, H 5.84, N 5.21.

Poly(diallyldimethylammonium) Hexafluorophosphate (3b): Yield 3.22 g (96%). ^{19}F NMR ([D$_6$]DMSO): δ = –69.00 (d, $^1J_{P,F}$ = 712 Hz) ppm. ^{31}P NMR: δ = –41.30 (sept, $^1J_{P,F}$ = 713 Hz) ppm. $(C_8H_{16}F_6NP)_{2n}$ $(271.18)_{2n}$: calcd. C 35.43, H 5.95, N 5.17; found C 35.39, H 5.98, N 5.12.

S-Proline/Poly(diallyldimethylammonium) Salt Catalysts 4b, 5b, 6a, 6b. General Procedure: A solution of (*S*)-proline (8.6 mg, 0.075 mmol) in CH_3OH (5 mL) was added to stirred solution (suspension) of polymer **1b** (24 mg), **2b** (32 mg), or **3a**,**b** (40 mg) in the same solvent (10 mL). The mixture was stirred at 20 °C for 0.5 h, the solvent was evaporated under reduced pressure, and the residue was dried in vacuo (3 Torr) at 25 °C for 1 h to afford the corresponding supported catalysts **4b**, **5b**, **6a**,**b** as colorless powders.

Catalyst 4b: Yield 33 mg (100%). IR (KBr): $\tilde{\nu}$ = 644, 796, 852, 916, 948, 984, 1036, 1084, 1172, 1256, 1296, 1320, 1380, 1408, 1452, 1564, 1624, 2348, 2956, 3056 (br), 3420 (br) cm^{-1}.

Catalyst 5b: Yield 41 mg (100%). IR (KBr): $\tilde{\nu}$ = 644, 796, 852, 916, 948, 1036, 1084, 1168, 1256, 1296, 1320, 1380, 1408, 1452, 1564, 1624, 2400, 2984, 3008, 3048 (br), 3430 (br) cm^{-1}.

Catalyst 6a: Yield 49 mg (100%). IR (KBr): $\tilde{\nu}$ = 644, 796, 852, 948, 984, 1036, 1088, 1168, 1256, 1296, 1320, 1380, 1408, 1452, 1556, 1624, 2348, 2984, 3048 (br), 3420 (br) cm^{-1}.

Catalyst 6b: Yield 49 mg, (100%). The IR spectrum was identical to that of the compound **6a**.

Aldol Reaction between Unmodified Aldehydes 7a-g and Ketones 8, 11, and 12 Catalyzed by S-Proline/Poly(diallyldimethylammonium) Salt Catalysts 4b, 5b, 6a,b. General Procedure: A mixture of aldehyde **7a**–**g** (0.5 mmol), the corresponding ketone **8**, **11**, or **12** (1 mL), and catalyst **4b** (33.6 mg), **5b** (40.6 mg) or **6a**,**b** (49.2 mg) was stirred at 25 °C for 15 h. The catalyst was filtered off, washed with acetone (2 × 0.5 mL), dried in vacuo (3 Torr) at 25 °C for 1 h and used in the reaction between fresh portions of the aldehyde and the ketone. The combined filtrates were evaporated under reduced pressure. The corresponding aldols **9a**–**g**, **13a**–**c**, and **14b**,**c** were isolated from the residue by column chromatography on silica gel (eluent: *n*-hexane/ethylacetate, 3:1). ^{1}H NMR spectra of known compounds **9a**–**e**, **13a**–**c**, and **14b** were in accordance with literature.[6b]

4-Hydroxy-4-(4′-methoxycarbonylphenyl)-butan-2-one (9f): M.p. 65–66 °C. $[\alpha]_D^{20}$ = +30.5 (c = 1.00, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 2.12 (s, 3 H, CH_3), 2.80 (m, 2 H, CH_2), 3.60 (br. s, 1 H, OH), 3.85 (s, 3 H, OCH_3), 5.16 (dd, J^1 = 8.5 Hz, J^2 = 4.0 Hz, 1 H, CH), 7.36 (d, 8.1 Hz, 2 H, H-Ar), 7.92 (d, 8.1 Hz, 2 H, H-Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 30.7 (C–CH_3), 51.7 (CH_2), 52.1 (OCH_3), 69.4 (CH–OH), 125.5 (CH-Ar), 129.3 (C-Ar), 129.8 (CH-Ar), 148.0 (C-Ar), 166.8 (CO_2Me), 208.7 (C=O) ppm. $C_{12}H_{14}O_4$ (222.24): calcd. C 64.85, H 6.35; found C 64.86, H 6.58.

4-Hydroxy-4-(4′-formylphenyl)-butan-2-one (9g): Colorless oil. $[\alpha]_D^{20}$ = +49.9 (c = 1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 2.21 (s, 3 H, CH_3), 2.84 (m, 2 H, CH_2), 3.55 (br. s, 1 H, OH), 5.21 (dd, J^1 = 7.5 Hz, J^2 = 4.8 Hz, 1 H, CH), 7.49 (d, 8.0 Hz, 2 H, H-Ar), 7.81 (d, 8.0 Hz, 2 H, H-Ar), 9.96 (s, 1 H, CH=O) ppm. ^{13}C NMR ($CDCl_3$): δ = 30.8 (C–CH_3), 51.7 (CH_2), 69.3 (CH–OH), 126.2 (CH-Ar), 130.0 (C-Ar), 135.7 (CH-Ar), 149.7 (C-Ar), 192.0 (CH=O), 208.7 (C=O) ppm. $C_{11}H_{12}O_3$ (192.21): calcd. C 68.74, H 6.29; found C 68.82, H 6.44.

Acknowledgments

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