Addition and Correction to Supporting Information for "Toward an Artificial Aldolase" (10.1021/ol702901z)

Daniel Font, Sonia Sayalero, Amaia Bastero, Ciril Jimeno, Miquel A. Pericàs*

*Institute of Chemical Research of Catalonia (ICIQ), Av. Països
Catalans, 16. E-43007 Tarragona, Spain, and Departament de
Química Orgànica, Universitat de Barcelona (UB), E-08028 Barcelona, Spain.*

mapericas@iciq.es

Preparation and characterization of Polystyrene resin 2 (PS-PEG derived resin)	S2
Preparation and characterization of Polystyrene resin 3 (ArgoPore™ derived resin)	S5
Preparation and characterization of Polystyrene resin 4 (Merrifield derived resin)	S8
Spectroscopic data of <i>tert</i> -butyl (2 <i>S</i> ,4 <i>S</i>)- <i>N</i> -Boc-4-bromoprolinate and <i>tert</i> -butyl (2 <i>S</i> ,4 <i>R</i>)- <i>N</i> -Boc-4-azidoprolinate.....	S12
General procedure for the asymmetric aldol reaction in water catalyzed by resin 4	S16
¹ H NMR and chromatographic data of the aldol products	S17
Recycling experiments of resin 4	S25
Aldol reaction at different temperatures using resin 4	S25
Procedure and characterization of the self-aldol addition of propanal in water catalyzed by resin 4	S26
Atomic Coordinates for Proline-triazole model with two water molecules	S28
References	S30

Preparation and characterization of Polystyrene resin **2** (PS-PEG derived resin):

a) Reaction of PS-PEG-Br with sodium azide

Sodium azide (0.114 g, 51 mmol) was added to a mixture of 1.4 g of NovaBioSynTM resin (Br-PEG-PS, $f = 0.25$ mmol/g) in 10 mL of DMSO, and heated at 60 °C for 18 h. After cooling, the suspension was filtered off and the resin was washed with H_2O , THF, THF-MeOH, MeOH and THF. The solid was dried *in vacuo* for 24 h at 40 °C

IR (ATR): 3045, 2865, 2100, 1638, 1452 cm⁻¹

Elemental analysis (%): C, 64.95; H, 9.62; N, 1.06.

$f = 0.25$ mmol/g

b) Cycloaddition of *tert*-butyl (2*S*,4*R*)-*N*-Boc-4-propargyloxyprolinate with N₃-PEG-PS

tert-Butyl (2*S*,4*R*)-*N*-Boc-4-propargyloxyprolinate (0.46 g, 1.2 mmol), [SI] *N,N*-diisopropylethylamine (0.60 mL, 4.2 mmol) and copper iodide (0.005g, 0.003 mmol) were added to a suspension of N₃-PEG-PS (1 g, *f* = 0.25 mmol/g) in DMF:THF 1:1 at 35°C and shaken for 24 h. When the IR-signal of the azido group had completely disappeared, the reaction mixture was filtered off and the resin was washed with THF (250 mL), water (250 mL), THF (250 mL), THF-MeOH 1:1 (250 mL), MeOH (250 mL) and THF (250 mL). The solid was dried *in vacuo* for 24 hours at 40 °C.

IR (ATR): 3045, 2864, 1736, 1699, 1452, 1398 cm⁻¹

Elemental analysis (%): C, 64.94; H, 9.69; N, 1.10.

f = 0.19 mmol/g

c) Deprotection

The doubly protected resin (1 g, $f = 0.19$ mmol/g) was swollen in CH_2Cl_2 (5 mL). After 10 minutes, trifluoroacetic acid (10 mL) was added and the reaction mixture was shaken at room temperature. When the IR-signals of the *t*Bu and carbonyl moieties in the protecting groups had completely disappeared, the reaction mixture was filtered off, and the polymer-supported proline **2** was washed with THF (containing 2% of Et_3N , 250 mL), water (250 mL), THF (250 mL), THF-MeOH 1:1 (250 mL), MeOH (250 mL) and THF (250 mL). The solid was dried *in vacuo* for 24 h at 40 °C.

IR (ATR): 3504, 3042, 2904, 2871, 1639, 1452, 1348 cm⁻¹

Elemental analysis (%): C, 64.86; H 9.10; N, 0.98.

$f = 0.17$ mmol/g

Preparation and characterization of Polystyrene resin **3** (ArgoPore™ derived resin):

a) Synthesis of (azidobenzyl)polystyrene

Sodium azide (1.07 g, 16.5 mmol) was added to a mixture of 3 g of (chlorobenzyl)polystyrene (ArgoPore™, $f = 0.6\sim 1.1$ mmol/g) in 30 mL of DMSO. The mixture was heated for 18 h at 60°C . After cooling, the suspension was filtered off and the solid washed with H_2O , THF, THF-MeOH, MeOH and THF. The solid was dried *in vacuo* for 24 h at 40°C .

IR (ATR): 3042, 2921, 2096, 1492, 1451 cm^{-1}

Elemental analysis (%): C, 86.05; H, 8.14; N, 4.44.

$f = 0.79$ mmol azido/g

b) Cycloaddition of *tert*-butyl (2*S*,4*R*)-*N*-Boc-4-propargyloxyprolinate with (azidobenzyl)polystyrene resin

(2*S*,4*R*)-*N*-Boc-4-propargyloxyprolinate (0.46 g, 1.2 mmol), [51] *N,N*-diisopropylethylamine (0.60 mL, 4.2 mmol) and copper iodide (0.005g, 0.003 mmol) were added to a suspension of (azidobenzyl)polystyrene (1 g, $f = 0.79$ mmol/g) and DMF:THF 1:1 at 35°C and shaken for 24 h. When the IR-signal of the azido group had completely disappeared, the reaction mixture was filtered off and the resin was washed with THF (250 mL), water (250 mL), THF (250 mL), THF-MeOH 1:1 (250 mL), MeOH (250 mL) and THF (250 mL). The solid was dried *in vacuo* for 24 hours at 40 °C.

IR(ATR): 3041, 2922, 1698, 1686, 1600, 1450, 1400, 1366 cm^{-1}

Elemental analysis (%): N, 4.55; C, 81.88; H, 9.96.

$f = 0.81$ mmol/g

c) Deprotection

The protected proline-functionalized resin obtained in the previous step (1 g, $f = 0.81$ mmol/g) was swollen in CH_2Cl_2 (5 mL). After 10 minutes, trifluoroacetic acid was added (10 mL) and the reaction mixture was shaken at r.t. When the IR-signals of *t*Bu and

carbonyl groups had completely disappeared, the reaction mixture was filtered off, and polymer-supported proline **3** was washed with THF (containing 2% of Et₃N, 250 mL), water (250 mL), THF (250 mL), THF-MeOH 1:1 (250 mL), MeOH (250 mL) and THF (250 mL). The solid was dried *in vacuo* for 24 hours at 40 °C.

IR(ATR): 3450, 2921, 1672, 1600, 1492, 1450 cm⁻¹

Elemental analysis (%): N, 4.54; C, 79.55; H, 7.09.

$f = 0.81$ mmol/g

Preparation and characterization of Polystyrene resin 4:

a) Preparation of propargyloxymethyl polystyrene

In a flame-dried flask, propargyl alcohol (0.237 mL, 4 mmol) was added dropwise to a suspension of sodium hydride in DMF (5 mL) at -20°C, and was stirred for 20 min at this temperature. Then, the reaction mixture was heated at room temperature, and transferred *via canula* to a suspension of Merrifield resin (3 g, 1 % DVB, $f = 0.8\sim 1$ mmol Cl/g) in THF. The reaction mixture was shaken at room temperature for 12 h. Then, MeOH (5 mL) was added, the reaction mixture was filtered off, and the resin washed sequentially with THF, H₂O, THF, THF-MeOH 1:1, MeOH and THF. The solid was dried *in vacuo* for 24 h at 40 °C.

IR (ATR): 3298, 3059, 3025, 2918, 2848, 1601, 1492, 1451cm⁻¹.

b) Preparation and characterization of *tert*-butyl (2*S*,4*R*)-*N*-Boc-4-azidoprolinate

Sodium azide (2.00 g, 30.8 mmol) was added to a solution of *tert*-butyl (2*S*,4*S*)-*N*-Boc-4-bromoprolinate[S2] (1.80 g, 5.1 mmol) in 50 mL of DMF. The reaction mixture was heated at 70 °C overnight, allowed to cool to room temperature and then diluted with water (30 mL). The organic phase was extracted with EtOAc (3 x 30 mL), washed with brine, dried (MgSO₄) and concentrated under reduced pressure. Purification of the residue by flash chromatography on silica gel (Hexanes/EtOAc 8:2) gave 1.23 g (77% yield) of (2*S*,4*R*)-*N*-Boc-4-azido-L-proline *tert*-butyl ester as a colorless oil.

¹H-NMR (400 MHz, CDCl₃, rotamers) δ: 1.35 – 1.55 (m, 18H), [2.12 (t, *J* = 6.05 Hz), 2.16 (t, *J* = 6.05 Hz), 1H], 2.22 – 2.41 (m, 1H), [3.44 (dd, *J* = 3.65, 11.35 Hz), 3.58 (dd, *J* = 2.65, 11.55 Hz), 1H], 3.63 – 3.71 (m, 1H), 4.10 – 4.19 (m, 1H), [4.21 (dd, *J* = 6.50, 8.10 Hz), 4.29 (dd, *J* = 6.10, 8.10 Hz), 1H] ppm.

¹³C-NMR (100 MHz, CDCl₃, rotamers) δ: [26.1, 27.9, 28.2, 28.3 (CH₃)], [35.3, 36.3 (CH₂)], [51.2, 51.3 (CH₂)], [58.3, 58.5 (CH)], 59.1 (CH), [80.3, 80.4 (C)], [81.5, 81.6 (C)], 153.6 (C=O), 171.4 (C=O) ppm.

IR (ATR): 2971; 2101 (N₃); 1739, 1702 (C=O); 1391, 1366, 1228, 1148 (C-O) cm⁻¹.

HRMS (ESI⁺) *m/z* = 335.1696 found, calcd. for C₁₄H₂₄N₄ONa [M+ Na]⁺: 335.1695
[α]_D²⁵ = – 62.5 (*c* 1.08, MeOH)

c) Cycloaddition of *tert*-butyl (2*S*,4*R*)-*N*-Boc-4-azidoprolinate with propargyloxymethyl polystyrene

tert-Butyl (2*S*,4*R*)-*N*-Boc-4-azidoprolinate (500 mg, 1.60 mmol), *N,N*-diisopropylethylamine (2.0 ml, 13.8 mmol) and copper iodide (5 mg, 0.026 mmol) were added to a suspension of propargyloxymethyl polystyrene (1.33 g, 1.06 mmol propargyl

groups) in DMF:THF 1:1. The mixture was stirred at 35°C for 24 h, the reaction progress being monitored by FTIR. When the IR bands of the C≡CH groups had completely disappeared, the reaction mixture was filtered off, and the resin was sequentially washed with THF (250 mL), water (250 mL), THF (250 mL), THF-MeOH 1:1 (250 mL), MeOH (250 mL) and THF (250 mL). The solid was dried *in vacuo* for 24 hours at 40 °C.

IR(ATR): 3025, 2974, 2922, 2851, 1737, 1701, 1393, 1366, 1061, 1492, 1453 cm⁻¹

d) Deprotection

Proline protected resin (1 g) was swollen in CH₂Cl₂ (5 mL). After 10 minutes, trifluoroacetic acid was added (10 mL), and the reaction mixture was shaken at room temperature. When the IR bands of the *t*Bu and carbonyl moieties in the protecting groups had completely disappeared, the reaction mixture was filtered off, and the resin was sequentially washed with THF (with 2% of Et₃N, 250 mL), water (250 mL), THF (250 mL), THF-MeOH 1:1 (250 mL), MeOH (250 mL) and THF (250 mL). The solid was dried *in vacuo* for 24 h at 40 °C.

IR(ATR): 3450, 3048, 2904, 1628, 1600, 1492, 1451 cm⁻¹

Elemental analysis (%): N, 3.16; C, 84.17; H, 8.30.

$f = 0.56$ mmol/g

Spectroscopic data of *tert*-butyl (2*S*,4*S*)-*N*-Boc-4-bromoproline and *tert*-butyl (2*S*,4*R*)-*N*-Boc-4-azidoproline

(2*S*,4*S*)-*N*-Boc-4-bromo-L-proline *tert*-Butyl Ester

$[\alpha]_D^{25} = -30.4$ (*c* 1.10, CHCl₃)

Lit. [*S*2] $[\alpha]_D = -38.1$ (*c* 1.00, CHCl₃)

(2S,4R)-N-Boc-4-azido-L-proline *tert*-Butyl Ester

General procedure for the asymmetric aldol reaction in water catalyzed by resin **4**:

Polystyrene-supported proline **4** (10% mol) was added to a suspension of aldehyde (0.4 mmol) and cyclohexanone (2.0 mmol) in water (0.14 mL). The reaction mixture was stirred at r.t. for 24 hours. Then 2 mL of ethyl acetate were added, the mixture was filtered off, the resin was washed with ethyl acetate (4 x 2 mL) and the combined liquid phases were concentrated *in vacuo*. Purification by silica gel column chromatography (Eluting with hexane/EtOAc 8:2) gave the corresponding aldol product.

The diastereomeric ratio was determined by ^1H NMR of the crude samples after removal of resin catalyst **4** by filtration and evaporation of the solvents.

The enantiomeric excess was determined by HPLC on a chiral stationary phase, after flash chromatography on silica gel.

^1H NMR and chromatographic data of the aldol products:

(2S,1'R)-2-(Hydroxy(phenyl)methyl)cyclohexan-1-one:

Chiralcel OD-H column (99:1 Hexane:2-propanol), 1 mL/min; $\lambda = 213$ nm; major enantiomer $t_r = 26.3$ min, minor enantiomer $t_r = 40.2$ min. All the spectroscopic data matched with literature. [S3]

5-214

(2S,1'R)-2-(Hydroxy(naphtyl)methyl)cyclohexan-1-one:

Enantiomeric excess was determined by HPLC with a Chiralcel AS column (98:2 Hexane:2-propanol), 1 mL/min; λ = 254 nm; major enantiomer t_r = 32.5 min, minor enantiomer t_r = 39.5 min.

All the spectroscopic data matched with literature. [S3]

(2*S*,1'*R*)-2-(Hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one:

Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (80:20 Hexane:2-propanol), 1 mL/min; $\lambda = 254$ nm; major enantiomer $t_r = 24.1$ min, minor enantiomer $t_r = 31.8$ min.

All the spectroscopic data matched with literature. [S4]

5-248

(2*S*,1'*R*)-2-(Hydroxy(4-methoxyphenyl)methyl)cyclohexan-1-one:

Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (95:5 Hexane:2-propanol), 0.25 mL/min; $\lambda = 254$ nm; major enantiomer $t_r = 77.7$ min, minor enantiomer $t_r = 110.6$ min.

All the spectroscopic data matched with literature. [S5]

(2*S*,1'*R*)-2-(Hydroxy(4-bromophenyl)methyl)cyclohexan-1-one:

Enantiomeric excess was determined by HPLC with a Chiralcel AS column (88:12 Hexane:2-propanol), 0.5 mL/min; $\lambda = 254$ nm; major enantiomer $t_r = 13.2$ min, minor enantiomer $t_r = 18.5$ min.

All the spectroscopic data matched with literature. [S6]

5-225

(2*S*,1'*R*)-2-(Hydroxy(-2-furylmethyl)cyclohexan-1-one:

Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (95:5 Hexane:2-propanol), 1 mL/min; $\lambda = 220$ nm; major enantiomer $t_r = 28.9$ min, minor enantiomer $t_r = 30.3$ min.

All the spectroscopic data matched with literature. [S7]

5-226

(2*S*,1'*R*)-2-(Hydroxy(4-trifluoromethylphenyl)methyl)cyclohexan-1-one:

Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (95:5 Hexane:2-propanol), 1 mL/min; $\lambda = 213$ nm; major enantiomer $t_r = 11.0$ min, minor enantiomer $t_r = 13.4$ min.

All the spectroscopic data matched with literature. [S8]

5-227

(2S,1'R)-2-(Hydroxyphenylmethyl)cyclopentan-1-one:

Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (90:10 Hexane:2-propanol), 1 mL/min; $\lambda = 213$ nm; major enantiomer $t_r = 11.6$ min, minor enantiomer $t_r = 14.0$ min

All the spectroscopic data matched with literature. [S3]

5-229

Recycling experiments of resin 4:

After performing the general procedure for the aldol reaction of cyclohexanone with benzaldehyde, resin **4** was separated by filtration and rinsed with AcOEt (4x2 ml), dried *in vacuo* at 40 °C for 24 h, and reused in the next run. Results have been collected in the following table:

Cycle	Yield (%) ^a	d.r. ^b	ee <i>anti</i> (%) ^c
1	75	96:4	98
2	74	96:4	98
3	75	97:3	98
4	75	97:3	98
5	75	97:3	98

^a Isolated Yield. ^b Determinated by ¹H NMR. ^c Determined by chiral HPLC.

Aldol reaction at different temperatures using resin 4:

The aldol reaction of cyclohexanone and benzaldehyde mediated by resin **4** was performed at different temperatures following the general procedure described above. Results have been collected in the following Table:

entry	T (°C)	Time (h)	Yield (%) ^a	d.r. ^b	ee <i>anti</i> (%) ^c
1	25	24	74	96:4	98
2	40	12	70	93:7	97
3	60	6	55	85:15	92

^a Isolated Yield. ^b Determinated by ¹H NMR. ^c Determined by chiral HPL

Procedure for the self-aldol addition of propanal in water catalyzed by resin

4.[S9]

Propionaldehyde (0.6 mL, 8 mmol) was added to resin **4** (71 mg, 1 mol%, $f=0.56$ mmol/g) in a vial with 2.87 mL of water (20 equiv.). The mixture was stirred at r.t. for 24 h. A sample was analyzed by ¹H-NMR, and showed total conversion (no propionaldehyde could be detected). Then the resin was removed by filtration, and rinsed with CH₂Cl₂. The solution containing the crude product was treated with a cooled suspension of NaBH₄ (0.45 g, 12 mmol) in EtOH (20 mL) at 0 °C. After 1 hour the reaction was diluted with water (20 mL) and extracted with CH₂Cl₂ (3 x 20 mL). After drying with Na₂SO₄, solvents were removed *in vacuo*. ¹H-NMR of the crude product showed a diastereomeric ratio of diols of anti:syn 4:1. After purification by flash chromatography on silica gel, 100 mg of the diol were isolated as a mixture of diastereomers (21% yield). The spectroscopic data matched with the literature data.[S9] Note that dehydration products also appeared after chromatography.

The diol was derivatized as monobenzoyl ester, purified by flash chromatography on silica gel, and analyzed by HPLC (Chiralpak IA, hexane:IPA 99:1, 1 mL/min, 230 nm): t_R = 29.4 and 36.3 min (*syn*), and 39.8 and 42.8 min (*anti*, 97% ee).

Atomic Coordinates for Proline-triazole model with two water molecules

Computed with Gaussian 03 Revision-C.02, with an ONIOM method at the MP2 level for the inner set of atoms involving hydrogen bonding, and at the PM3 level for the outer atoms (ONIOM (MP2-FC/6-31G(d,p):PM3/ZDO)):

Most stable conformer (E = -677.68809314 a.u., number of imaginary frequencies=0)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-2.943895	1.928499	-2.455909
2	6	-3.928997	0.234537	-0.472333
3	6	-3.278167	0.614008	-2.765698
4	6	-3.102714	2.396764	-1.156120
5	6	-3.593676	1.553052	-0.165321
6	6	-3.771226	-0.231209	-1.778337
7	1	-3.161113	0.246406	-3.790399
8	1	-2.843098	3.432092	-0.911378
9	1	-3.718436	1.927063	0.857649
10	1	-4.041022	-1.265281	-2.021430
11	6	-4.493376	-0.670856	0.586185
12	1	-4.731380	-0.107774	1.510613
13	1	-5.420964	-1.151697	0.226198
14	8	-3.685484	-1.800181	0.864005
15	6	-2.654433	-1.616676	1.814263
16	1	-2.982959	-0.974821	2.656310
17	1	-2.519690	-2.645922	2.196292
18	6	-1.383528	-1.128715	1.222903
19	6	-0.773872	-1.513433	0.042821
20	1	-1.058781	-2.196290	-0.738167
21	7	0.364066	-0.773308	0.010597
22	7	0.489046	0.021176	1.102162
23	7	-0.591669	-0.200752	1.843024
24	6	1.427474	-0.816385	-1.038299
25	6	1.881883	0.601370	-1.456131
26	7	3.026741	0.942816	-0.561946
27	6	3.581844	-0.325033	-0.004090
28	6	2.719853	-1.476971	-0.502100
29	1	1.004253	-1.382987	-1.900950
30	1	1.085580	1.367705	-1.413717
31	1	2.254182	0.585806	-2.499055
32	1	3.571071	-0.279896	1.092546
33	1	2.532083	-2.227959	0.288059
34	1	3.213596	-2.035799	-1.322077
35	1	2.725033	1.537848	0.219296
36	6	5.045039	-0.511644	-0.454494
37	8	5.721447	-1.469331	-0.128070
38	8	5.489194	0.495771	-1.220654
39	1	4.702502	1.094213	-1.287202
40	1	3.413920	2.411982	2.563986
41	8	2.657529	2.317020	1.978231
42	1	1.935733	2.006092	2.557084
43	1	-0.020743	2.454140	3.616401

44	8	0.530158	1.673035	3.732248
45	1	0.025292	0.965528	3.292664
46	1	-2.561787	2.595305	-3.235799

Less stable conformer (E = -677.67570510 a.u., number of imaginary frequencies=0)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	6	-3.756162	-0.839196	0.303208
2	7	-2.685905	-1.729587	0.825336
3	6	-1.718945	-1.943843	-0.285441
4	6	-1.780148	-0.647184	-1.134579
5	6	-3.236858	-0.158265	-0.968832
6	1	-3.996931	-0.084951	1.059607
7	1	-0.710971	-2.199223	0.089987
8	1	-2.065556	-2.807557	-0.886240
9	1	-1.537729	-0.849957	-2.204380
10	1	-3.823941	-0.450663	-1.862141
11	1	-3.330108	0.944492	-0.910756
12	1	-2.185766	-1.230751	1.554312
13	6	-5.035869	-1.623397	-0.041132
14	8	-5.055075	-2.818794	-0.252280
15	8	-6.142420	-0.860598	-0.136267
16	7	-0.782098	0.359499	-0.658338
17	6	0.415939	0.635689	-1.233793
18	1	0.746830	0.166024	-2.143313
19	6	0.980599	1.577543	-0.390672
20	7	0.120529	1.828500	0.640957
21	7	-0.959980	1.074608	0.482431
22	6	2.294191	2.262636	-0.516527
23	1	2.359219	3.153056	0.135220
24	1	2.449059	2.583915	-1.565971
25	8	3.378130	1.493859	-0.042394
26	6	3.809429	0.465821	-0.928849
27	1	2.969577	-0.220718	-1.158435
28	1	4.143184	0.911861	-1.887332
29	6	4.926283	-0.266870	-0.245343
30	6	6.999370	-1.642854	1.009013
31	6	4.642061	-1.232623	0.720566
32	6	6.252222	0.010517	-0.577861
33	6	7.285100	-0.678835	0.048047
34	6	5.677933	-1.917811	1.345491
35	1	3.601694	-1.444618	0.990641
36	1	6.480925	0.774401	-1.329641
37	1	8.325018	-0.459222	-0.214783
38	1	5.452159	-2.673187	2.105223
39	1	7.813960	-2.183355	1.501937
40	8	-5.712715	1.780304	0.428203
41	8	-3.317544	2.337623	1.706678
42	1	-3.135234	2.294335	2.650068
43	1	-4.895900	2.045328	0.895519
44	1	-2.540621	1.931293	1.282832
45	1	-6.435977	2.169577	0.928453
46	1	-5.948887	0.084206	0.068110

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