A Convenient Synthesis of *p*-Aminobenzyl-tris(hydroxymethyl)methane as Precursor of Solid-Supported Tripodal Ligands

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Received 25 July 2001; revised 12 October 2001

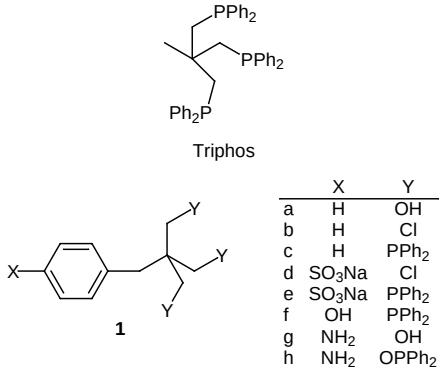
Abstract: *p*-Aminobenzyl-tris(hydroxymethyl)methane has been prepared in 5 steps from diethylmalonate and *p*-nitrobenzyl bromide, with an overall yield of 23%. This compound could be grafted on silica previously derivatized with 3-isocynatopropyltriethoxysilane.

Key words: tris(hydroxymethyl)methane derivatives, tripodal ligands, amino alcohols, solid-phase synthesis

Solid-supported reagents[1,2] are increasingly used in organic synthesis with a view of promoting clean and safe chemistry, making easier the purification steps and developing parallel or combinatorial chemistry. In this context, several organometallic catalysts have been bound to polymers[3–5] and silica.[6–8]

The usual ligands of transition metals are phosphorous derivatives,[9] particularly tripodal phosphines,[10] as well illustrated by Triphos[11–13] and the related aryl derivative **1c** (Scheme 1). Recent developments in the field of polypodal phosphorous ligands involve the synthesis of chiral ligands on the one hand,[14] and water-soluble ligands on the other hand.[15,16] Bianchini et al. synthesized an interesting new ligand belonging to this last family, called Sulphos (Scheme 1, structure **1e**).[17] This compound allowed the preparation of rhodium and ruthenium catalysts working in liquid biphasic systems,[17,18] or in solid heterogeneous systems after immobilization on silica via unique hydrogen bonding;[19,20] these catalysts were used under reductive conditions (hydrogenation and hydroformylation reactions).

We are interested in the development of homogeneous ruthenium catalysts for alcohol oxidation that could be covalently fixed on a solid support (heterogenization of homogeneous catalysis).[21] For that purpose, the phenyl substituent of ligand **1** should be equipped with a functional group X susceptible to make stable bonding at the support surface. One representative of such ligands, compound **1f** (X = OH)[22] has been prepared and fixed on a Merrifield resin via phenolic ether bonds. Here we considered the amine function (X = NH_2) as a more versatile anchorage point, allowing to create stable amide or urea linkages, either on organic polymers, or on (derivatized) silica. Accordingly, we selected the corresponding nitrobenzene derivative (X = NO_2) as a suitable precursor. We previously established that phosphinite ligands are more appropriate to fulfill our objective than the traditional phosphine ligands, which are too easily oxidizable.[23] Therefore, we designed the tripodal phosphinite ligand **1h** (Scheme 1) as synthetic target. In this paper, we describe the preparation of the triol precursor **1g** and its fixation on silica.



	X	Y
a	H	OH
b	H	Cl
c	H	PPh_2
d	SO_3Na	Cl
e	SO_3Na	PPh_2
f	OH	PPh_2
g	NH_2	OH
h	NH_2	$OPPh_2$

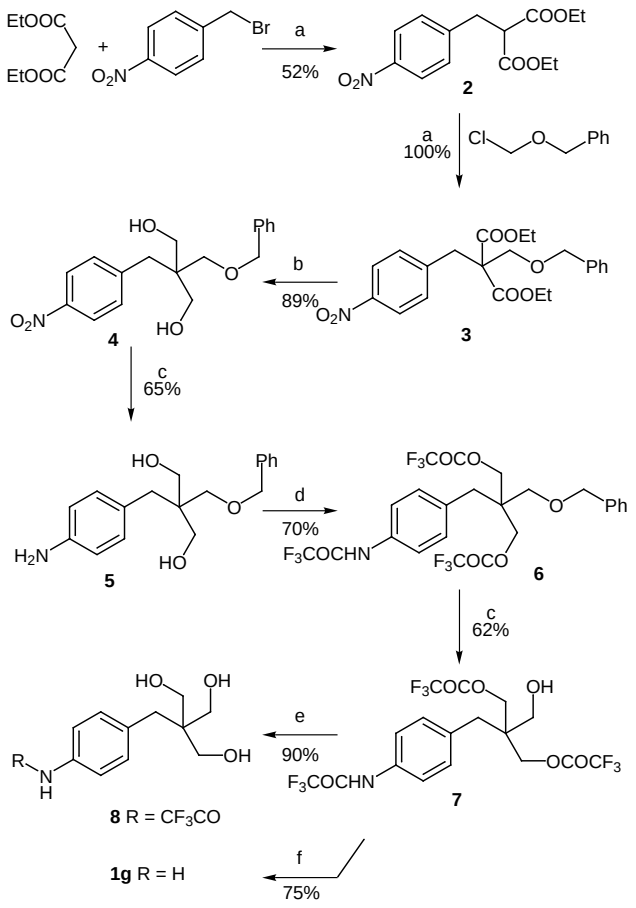
Scheme 1

We first examined a strategy similar to that of Bianchini[17] which uses the known unsubstituted aryl precursor **1a**[24] as the starting material; the sulfonyl substituent was introduced by treatment of tris(chloromethyl) derivative **1b** with hot concentrated sulfuric acid and sodium chloride. The resulting **1d** was then transformed into **1e** by substitution with potassium diphenylposphide. Several attempts to perform the nitration of **1b** with nitric acid failed [HNO_3–H_2SO_4 (1:3), HOAc, 120 °C]. Using ammonium nitrate and trifluoroacetic anhydride[25] [NH_4NO_3–TFAA (1:3), CH_2Cl_2, reflux, 24 h], we recovered a mixture of *o*- and *p*-nitrobenzyl-tris(chloromethyl)methane. Therefore, we preferred to prepare the target molecule from diethyl malonate and *p*-nitrobenzyl bromide (Scheme 2).

Diethyl 2-(*p*-nitrobenzyl)malonate (**2**) was obtained in 52% yield and further alkylated with chloromethyl benzyl ether.[26] The crude product **3** was reduced with sodium borohydride to furnish the diol **4** in 89% yield. Treatment of **4** by catalytic hydrogenation transformed the nitro function into the desired amine function **5**, without affecting the benzyl ether moiety. We found that the deprotection of this ether by hydrogenolysis could be performed

Synthesis 2002, No. 1, 28 12 2001. Article Identifier:
1437-210X,E;2002,0,01,0039,0042,ftx,en;E14901SS.pdf.

ISSN 0039-7881

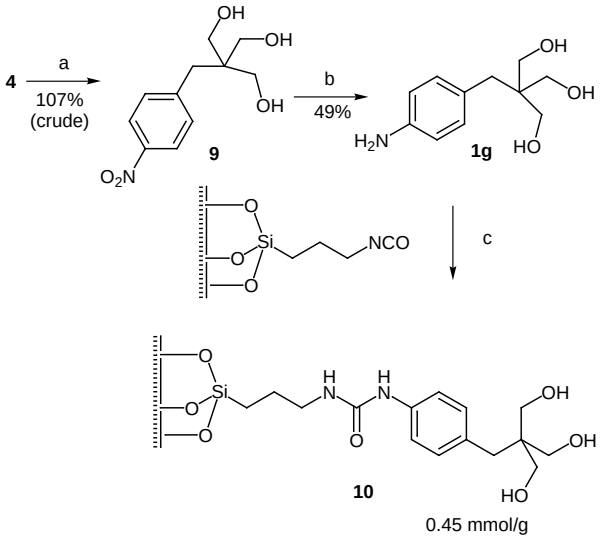


Scheme 2 *Reagents and conditions*: (a) NaH, THF, 20 °C to reflux; (b) $NaBH_4$, EtOH, reflux; (c) H_2, Pd–C, EtOAc; (d) $(CF_3CO)_2O$, pyridine; (e) H_2O–MeCN; (f) HCl, H_2O–MeCN

after masking the polar functions of **5** by acylation with trifluoroacetic anhydride in pyridine to form **6**. Catalytic hydrogenation of **6** gave now the mono-alcohol **7**, the two other hydroxyl functions of which could be unmasked by smooth hydrolysis to give **8**. Prolonged acidic hydrolysis of **7** furnished the final compound **1g**. This first synthetic scheme was shortened by changing the method of deprotection of the benzyl ether moiety from **4** (Scheme 3): nucleophilic displacement with trimethylsilyl iodide afforded the triol **9**; reduction of the nitro function by catalytic hydrogenation conducted to **1g** with an overall yield of 23% for five steps.

The possibility of grafting **1g** (and derivatives) on a solid support has been illustrated with silica derivatized by 3-isocyanatopropyltriethoxysilane. Such silica reacted with aniline **1g** to furnish the support **10** well characterized by elemental analysis. The heterogeneous phosphinite ligand of ruthenium (II), was obtained by reacting **10** with chlorodiphenylphosphine and triethylamine. The corresponding homogeneous ligands could be similarly prepared from **8** or **9**.

Thus, the amino-functionalized triol **1g** is readily accessible, as such, totally protected (**6**), or partially protected (**4**,**5**,**7**–**9**). These compounds are valuable precursors for the elaboration of phosphine and phosphinite tripodal ligands of transition metals, with a possibility of solid-support.



Scheme 3 *Reagents and conditions*: (a) TMSCl, NaI; (b) H_2, Pd–C, H_2O–acetone; (c) THF, reflux

Solvents were dried prior to use. Reagents and solvents (Aldrich or Acros) were used as purchased. Melting points (uncorrected) were determined on an electrothermal apparatus. ^{1}H (200 MHz or 300 MHz) and ^{13}C (50 MHz or 75 MHz) NMR spectra were recorded on Varian Gemini 200 or 300 spectrometers. Chemical shifts are reported as δ values downfield from TMS. The mass spectra (FAB, APCI or CI modes) were obtained on a Finnigan MAT TSQ-70 instrument. HRMS (CI mode) spectrum was performed on a VG-Autospec-Q apparatus. IR spectra were obtained using Biorad FTS 135 spectrometer calibrated with polystyrene. Thermogravimetric analysis (TGA) were performed on a Mettler Toledo TGA SDTA851 apparatus. TLC were carried out using silica gel 60 F_{254} (Merck) and spots were visualized by UV. Silica gel 60 mesh size 0.04–0.063 mm (Merck) was used for column chromatography.

Diethyl 2-[(4-Nitrophenyl)methyl]propanedioate (2)

To a suspension of NaH (60% in oil, 2.08 g, 0.05 mol) in THF (30 mL), under Ar, was added dropwise diethyl malonate (12 mL, 0.078 mol). The mixture was stirred 30 min at 20 °C, then cooled to 0 °C (ice bath). A solution of *p*-nitrobenzyl bromide (10.1 g, 46 mmol) in THF (30 mL) was added dropwise. After the addition was complete, the mixture was refluxed for 3 h. The mixture was concentrated under vacuum, the residue was dissolved in Et_2O (100 mL), the Et_2O layer was washed with H_2O (3 × 30 mL) and dried ($MgSO_4$). The excess of diethyl malonate was removed by horizontal distillation (3 h, 70 °C, 0.005 mbar). The yellow solid residue (9.97 g containing mono- and dialkylation products) was purified by column chromatography on silica gel (cyclohexane–EtOAc, 90:10) to furnish pure **2** as white crystals; yield: 7.11 g (52%); R_f 0.17; mp 60.5–62 °C.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 8.15 (d, 2 H_{arom}, *J* = 8.7 Hz), 7.39 (d, 2 H_{arom}, *J* = 8.7 Hz), 4.18 (q, 4 H, *J* = 7.2 Hz, CH_3CH_2O), 3.66 [t, 1 H, *J* = 7.8 Hz, $CH(CO_2Et)_2$)], 3.32 (d, 2 H, *J* = 7.8 Hz, $PhCH_2$), 1.22 (t, 6 H, *J* = 7.2 Hz, CH_3CH_2O).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 168.2 [$CH(CO_2Et)_2$], 147.0 (C_{arom}), 145.7 (C_{arom}), 128.8 (C_{arom}), 123.7 (C_{arom}), 61.8 (CH_3CH_2O), 53.2 [$CH(COOEt)_2$], 34.4 ($PhCH_2$), 14.0 (CH_3CH_2O).

IR (KBr): 3055, 2987, 1731, 1523 cm^{-1}.

MS (FAB): *m*/*z* (%) = 296.1 (100), 249.9 (10), 203.9 (32).

Anal. Calcd for $C_{14}H_{17}NO_6$: C 56.94; H 5.80; N 4.74. Found: C 57.29; H 5.80; N 4.62.

Diethyl 2-(Benzyloxymethyl)-2-[(4-nitrophenyl)methyl]-propanedioate (3)

To a suspension of NaH (60% in oil, 1.06 g, 26 mmol) in THF (30 mL), under Ar, was added dropwise a solution of **2** (7.06 g, 24 mmol) in THF (30 mL). After 10 min, chloromethyl benzyl ether[26] (3 mL, 29 mmol) was added and the mixture was refluxed for 5 h. Aq NH_4Cl (5%, 50 mL) was added and the aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic phases were dried ($MgSO_4$) and concentrated to give crude **3** as a yellow solid; yield: 10.3 g (~100%). An analytically pure sample was obtained by column chromatography on silica gel neutralized with NEt_3 (cyclohexane –EtOAc, 90:10); R_f 0.29; mp 53.2–55.1°C.

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 8.05 (d, 2 H_{arom}, *J* = 8.8 Hz), 7.4–7.3 (m, 5 H_{arom}), 7.19 (d, 2 H_{arom}, *J* = 8.8 Hz), 4.53 (s, 2H, PhC*H*$_2$O), 4.19 (q, 4 H, *J* = 7.1 Hz, CH_3CH_2O), 3.69 (s, 2 H, CCH_2O), 3.46 (s, 2 H, PhC*H*$_2$C), 1.23 (t, 6 H, *J* = 7.1 Hz, C*H*$_3$$CH_2O$).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 168.9 (*C*O_2Et), 147.1, 144.1, 137.2, 130.9, 128.4, 127.9, 127.8, 123.3 (C_{arom}), 73.4 (Ph*C*H_2O), 68.4 (C*C*H_2O), 61.7 (CH_3CH_2O), 59.4 (PhCH_2*C*), 36.0 (Ph*C*H_2C), 14.0 (*C*H_3CH_2O).

IR (KBr): 3055, 2986, 1731, 1524, 1349 cm^{-1}.

MS (FAB): *m*/*z* (%) = 416.1 (95), 91 (100).

Anal. Calcd for $C_{22}H_{25}NO_7$: C 63.9; H 6.06; N 3.37. Found: C 64.14; H 6.17; N 3.38.

2-(Benzyloxymethyl)-2-[(4-nitrophenyl)methyl]propan-1,3-diol (4)

To a suspension of $NaBH_4$ (17.1 g, 442 mmol) in EtOH (200 mL), under Ar, was added dropwise a solution of **3** (14.8 g, 30 mmol) in EtOH (100 mL) and the mixture was refluxed for 16 h. After addition of aq NH_4Cl in small portions (5%,150 mL), the crude solution was distilled under vacuum to remove EtOH. CH_2Cl_2 (200 mL) was added and the mixture filtered. The two layers were separated, the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL), the combined organic phases were washed with aq $NaHCO_3$ (5% 100 mL), dried ($MgSO_4$) and concentrated under vacuum. Crude **4** was isolated as an orange solid; yield; 8.8 g (89%). An analytically pure sample was obtained by column chromatography on silica gel (cyclohexane–EtOAc, 60:40); R_f 0.28; mp 85.5–86.7 °C.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.09 (d, 2 H_{arom}, *J* = 8.8 Hz), 7.36 (d, 2 H_{arom}, *J* = 8.8 Hz), 7.4–7.3 (m, 5 H_{arom}), 4.50 (s, 2 H, PhC*H*$_2$O), 3.61 and 3.53 (ABq, 4 H, *J* = 10.9, 11 Hz, C*H*$_2$OH), 3.31 (s, 2 H, CCH_2O), 2.85 (s, 2 H, PhC*H*$_2$C).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 147.5, 145.5, 137.8, 131.3, 128.6, 128.0, 127.8, 123.2 (C_{arom}), 73.7 (Ph*C*H_2O), 72.1 (C*C*H_2O), 65.1 (*C*H_2OH), 44.9 (PhCH_2*C*), 35.3 Ph*C*H_2C).

IR (KBr): 3616, 3501, 3055, 2985, 1521, 1348, 1098 cm^{-1}.

MS (FAB): *m*/*z* (%) = 332 (20), 91 (100).

Anal. Calcd for $C_{18}H_{21}NO_5$: C 65.24; H 6.39; N 4.23. Found: C 64.90; H 6.28; N 4.14.

2-(Benzyloxymethyl)-2-[(4-aminophenyl)methyl]propan-1,3-diol (5)

A solution of **4** (0.234 g, 0.710 mmol) in EtOAc (10 mL) was hydrogenated in a Parr apparatus (2750 mbar H_2), with 10% Pd/C as the catalyst (0.023 g, 0.02 mmol), for 3 h. The mixture was filtered and concentrated under vacuum, crude **5** was recovered as a yellow oil; yield: 0.132 g (65%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.3 (m, 5 H_{arom}), 6.9 (d, 2 H_{arom}, *J* = 8 Hz), 6.6 (d, 2 H_{arom}, *J* = 8 Hz), 4.5 (s, 2 H, PhC*H*$_2$O), 3.6 (s, 4 H, OH), 3.4 (s, 2 H CC*H*$_2$O), 2.6 (s, 2 H, PhC*H*$_2$C).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 144.4, 138.0, 131.0, 128.2, 127.4, 127.3, 126.8, 114.8 (C_{arom}), 73.3, 72.5 (CH_2OCH_2), 65.3 (*C*H_2OH), 44.0 (Ph*C*H_2C), 34.9 (PhCH_2*C*).

IR (KBr): 3457, 3382, 3052, 2923, 2871 cm^{-1}.

MS (FAB): *m*/*z* (%) = 301 (35, M; $C_{18}H_{23}NO_3$), 196 (100), 106 (45), 91 (60).

2-(Benzyloxymethyl)-2-{[4-(2,2,2-trifluoroacetamido)-phenyl]-methyl}-1,3-di(2,2,2-trifluoroacetoxy)propane (6)

To a solution of **5** (0.90 g, 3.0 mmol) in pyridine (5 mL) at 0 °C was added Ac_2O (2 mL, 14 mmol) over 10 min. The mixture was stirred at 20 °C for 20 h. CH_2Cl_2 (20 mL) was added, the solution was washed with dil HCl (1 mol/L, 5 × 15 mL), dried ($MgSO_4$) and concentrated under vacuum. Crude **6** was purified by column chromatography on silica gel (cyclohexane–EtOAc 85:15) to furnish a product still contaminated with partially deprotected derivatives; yield: 1.18 g (70%); R_f 0.23.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.2 (s, 1 H, NH), 7.5 (d, 2 H_{arom}, *J* = 8.7 Hz), 7.4–7.3 (m, 5 H_{arom}), 7.1 (d, 2 H_{arom}, *J* = 8.7 Hz), 4.5 (s, 2 H, PhC*H*$_2$O), 4.3 (s, 2 H, C*H*$_2$OCOCF_3), 3.5 (s, 2 H, C*H*$_2$OH), 3.3 (s, 2 H, CCH_2O), 2.7 (s, 2 H, PhC*H*$_2$C).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 137.1, 134.4, 132.7, 131.2, 128.6, 128.1, 127.8, 120.7 (C_{arom}), 73.7 (PhC*H*$_2$O), 67.8 (C*C*H_2O), 67.0 (*C*H_2OCOCF_3), 43.0 (Ph*C*H_2C), 34.9 (PhCH_2*C*) (CF_3CO not visible).

IR (KBr): 3412, 3055, 2987, 1786, 1734, 1168 cm^{-1}.

MS (FAB): *m*/*z* (%) = 588 (100, M-1; $C_{24}H_{20}NO_6F_9$), 492 (35), 396 (2), 113 (55).

2-(Hydroxymethyl)-2-{[4-(2,2,2-trifluoroacetamido)-phenyl]-methyl}-1,3-di(2,2,2-trifluoroacetoxy)propane (7)

A solution of **6** (2.74 g, 5.6 mmol) in EtOAc (50 mL) was stirred for 5 h at 50 °C under an atmosphere of H_2 with 10% Pd/C (1.06 g, 1.0 mmol) as catalyst. The mixture was filtered and concentrated under vacuum. Crude **7** was purified by column chromatography on silica gel (cyclohexane–EtOAc, 50:50); yield: 1.39 g (62%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.5 (br s, 1 H, NH), 7.5 (d, 2 H_{arom}, *J* = 8.4 Hz), 7.2 (d, 2 H_{arom}, *J* = 8.4 Hz), 3.7 (s, 4 H, CH_2O), 3.5 (s, 2 H, CH_2O), 2.7 (s, 2 H, PhC*H*$_2$).

^{13}C NMR ($CDCl_3$, 50 MHz): δ = 135.0, 133.7, 131.1, 120.5 (C_{arom}), 64.8, 62.3 (C*H*$_2$O), 38.2 (Ph*C*H_2), 36.3 (PhCH_2*C*) (CF_3CO not visible).

MS (FAB): *m*/*z* (%) = 306 (36, $C_{13}H_{16}F_3NO_4$), 236 (24), 188 (100).

3-(4-Nitrophenyl)-2-(hydroxymethyl)propan-1,3-diol (9)

To a solution of **4** (3.0 g, 9.1 mmol) and Et_3N (1.4 mL, 19 mmol) in MeCN (50 mL) was added trimethylsilyl chloride (9.5 mL, 73 mmol) and the mixture was refluxed for 90 min, NaI (8.30 g, 55 mmol) was then added and the mixture was further refluxed for 20 h. CH_2Cl_2 (20 mL) was added, the mixture was filtered and concentrated under vacuum. The brown solution was washed with aq $(NH_4)_2SO_3$ (5%, 3 × 25 mL), which caused decoloration. The organic phase was further extracted with H_2O (5 × 25 mL). Evaporation of H_2O under vacuum furnished crude **9** as a yellow solid (2.36 g, 107%).

^{1}H NMR (D_2O, 300 MHz): δ = 8.1 (d, 2 H_{arom}, *J* = 8 Hz), 7.4 (d, 2 H_{arom}, *J* = 8 Hz), 3.4 (s, 6 H, C*H*$_2$OH), 2.8 (s, 2 H, PhC*H*$_2$).

^{13}C NMR (D_2O, 75 MHz): δ = 146.2, 131.5, 123.4 (C_{arom}), 61.8 (*C*H_2OH), 45.1 (Ph*C*H_2), 34.7 (PhCH_2*C*) (quat C_{arom} not visible).

MS (APCI): *m*/*z* (%) = 242 (100, M; $C_{11}H_{15}NO_5$), 206 (45), 188 (37), 176 (17), 142 (15).

3-(4-Aminophenyl)-2-(hydroxymethyl)propan-1,3-diol (1g)

From **7**: A solution of **7** (0.45 g, 0.9 mmol) in a H_2O–acetone (2:1) mixture (15 mL) was stirred at 20 °C for 4 h with concd HCl (2.5 mL). The solution was concentrated under vacuum, CH_2Cl_2 (15 mL) was added, the organic phase was extracted with H_2O (3 × 10 mL) and the water evaporated under vacuum, **1g** was recovered from the aqueous phase as a yellow oil (0.188 g, 75%). If acid was omitted, **8** was recovered instead of **1g**.

8

^{1}H NMR (D_2O, 200 MHz): δ = 10.2 (br s, 1 H, NH), 7.6 (d, 2 H_{arom}, *J* = 9 Hz), 7.4 (d, 2 H_{arom}, *J* = 9 Hz), 3.5 (s, 6 H, C*H*$_2$OH), 2.3 (s, 2 H, PhC*H*$_2$).

^{13}C NMR (aceton-d_6, 50 MHz): δ = 132.2, 121.2 (C_{arom}), 64.8 (*C*H$_2$OH), 45.5 (Ph*C*H$_2$), 35.0 (PhCH$_2$*C*) (CF_3CO and quat. C_{arom} not visible).

From **9**: A solution of **9** in a H_2O–acetone (5:1) mixture (30 mL) was hydrogenated in a Parr apparatus (2000 mbar H_2) for 15 h with Pd 10% on charcoal (0.023 g, 0.02 mmol) as catalyst. The mixture was filtered, concentrated under vacuum and **1g** was obtained; yield: 0.037 g (49%).

^{1}H NMR (D_2O, 200 MHz): δ = 7.3 (d, 2 H_{arom}, *J* = 9 Hz), 7.1 (d, 2 H_{arom}, *J* = 9 Hz), 3.3 (s, 6 H, C*H*$_2$OH), 2.5 (s, 2 H, PhC*H*$_2$).

^{13}C NMR (D_2O, 50 MHz): δ = 138, 135, 134, 124 (C_{arom}), 65 (*C*H$_2$OH), 47 (Ph*C*H$_2$), 36 (PhCH$_2$*C*).

MS (APCI): *m*/*z* (%) = 212 (98), 195 (19), 194 (100), 177 (14), 166 (15)

HRMS (CI): *m*/*z* calcd for $C_{11}H_{18}NO_3$: 212.1287, Found: 212.1294

Silica Grafted with (Propyl)[3-phenyl-2,2-di(hydroxymethyl)-propan-1-ol]urea (10)

Silica Merck type 10184, 70–230 mesh (2 g, 5 mmol of silanol functions) was washed with MeOH in a Soxhlet apparatus for 2 d, dried under vacuum (0.005 mbar) at 70 °C for 5 h and reacted with 3-isocyanatopropyltriethoxysilane (1.52 g, 6.2 mmol) in THF (60 mL) at 20 °C for 3 h and then refluxed for 20 h. (The modified silica was filtered, washed with THF (10 mL) and immediately introduced in the next step.

Functionalization, 1.2 mmol/g of modified silica as measured by TGA: To a suspension of silica grafted with propylisocyanate (2 g, ca 2.4 mmol isocyanate function) in THF (50 mL) was added a solution of **1g** (0.27 g, 1.3 mmol) in pyridine (3 mL). The mixture was refluxed for 2 d. After filtration, crude **10** was washed with CH_2Cl_2 for 24 h in a Soxhlet apparatus to furnish **10** as a yellow powder.

Functionalization, 0.45 mmol/g of modified silica as measured by TGA: weight loss = 13.36%.

IR (KBr): 2944, 1517 cm^{-1}.

Anal. Calcd for $(SiO_2)_nC_{15}H_{23}N_2O_4{\cdot}3H_2O$: C 6.55; H 1.06; N 1.02. Found: C 6.38; H 1.13; N 0.76.

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