Straightforward Immobilization of Phosphonic Acids and Phosphoric Acid Esters on Mesoporous Silica and their Application in an Asymmetric Aldol Reaction

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Supplementary Material

Synthesis of SBA-15 silica:

Pluronic P-123 (16.0 g, M_n~5800 g mol^{-1}, Sigma-Aldrich) was dissolved in deionized water (480.0 mL) and hydrochloric acid (48.0 mL, 37 %, Stockmeier). After the addition of TEOS (37.0 mL) the mixture was stirred at 35 °C for 24 h, transferred to a glass-lined autoclave and hydrothermally treated at 80 °C for 24 h. The precipitate was filtered, washed with deionized water and dried at 120 °C prior calcination in a tube furnace at 550 °C for 5 h with a heating ramp of 2.5 °C min^{-1} in air.

Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredricksen, G.H.; Chmelka, B.F.; Stucky, G.D. Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores. *Science* **1998**, *279*, 548-552.

Synthesis of MCM-41 silica:

Cetyltrimethylammonium bromide (9.6 g, Sigma-Aldrich) was dissolved in deionized water (480.0 mL) and an ammonia solution (41.0 mL, 25 %) and stirred for 5 min. After the addition of TEOS (40.0 mL) the mixture was stirred at room temperature for 24 h, filtered off, washed with deionized water and dried at 120 °C. Calcination was done in a tube furnace at 550 °C for 5 h with a heating ramp of 2.5 °C min^{-1} in air.

Kumar, D.; Schumacher, K.; du Fresne von Hohenesche, C.; Grün, M.; Unger, K. K. MCM-41, MCM-48 and Related Mesoporous Adsorbents: Their Synthesis and Characterisation. *Colloids Surf., A* **2001**, 109-116.

Synthesis of silica monolith:

Polyethylene glycol (0.616 g, PEG, 35000 g mol^{-1}, Sigma-Aldrich) was dissolved in deionized water (6.0 mL) and nitric acid (0.389 g, 30 %, Stockmeier). After the addition of tetraethyl orthosilicate (5.0 mL, TEOS, Sigma-Aldrich) the mixture was stirred until a clear solution was obtained. The H_2O : HNO_3 : TEOS : PEG molar ratio of the sol was 14.7 : 0.25 : 1.05 : 7.8·10^{-4}. The solution was transferred to a 96-well microplate, covered and aged for 72 h at 40 °C. Afterwards, the monoliths were transferred to a one molar ammonia solution (Stockmeier) at 90 °C for 24 h, followed by washing with deionized water and drying for 48 h between 40-80 °C. Calcination was carried out in a tube furnace at 550 °C for 5 h with a heating ramp of 0.5 °C min^{-1} in air. Before functionalization the monoliths were grinded.

Smått, J.-H.; Schunk, S.; M. Lindén, M. Versatile Double-Templating Synthesis Route to Silica Monoliths Exhibiting a Multimodal Hierarchical Porosity. *Chem. Mater.* **2003**, *15*, 2354-2361.

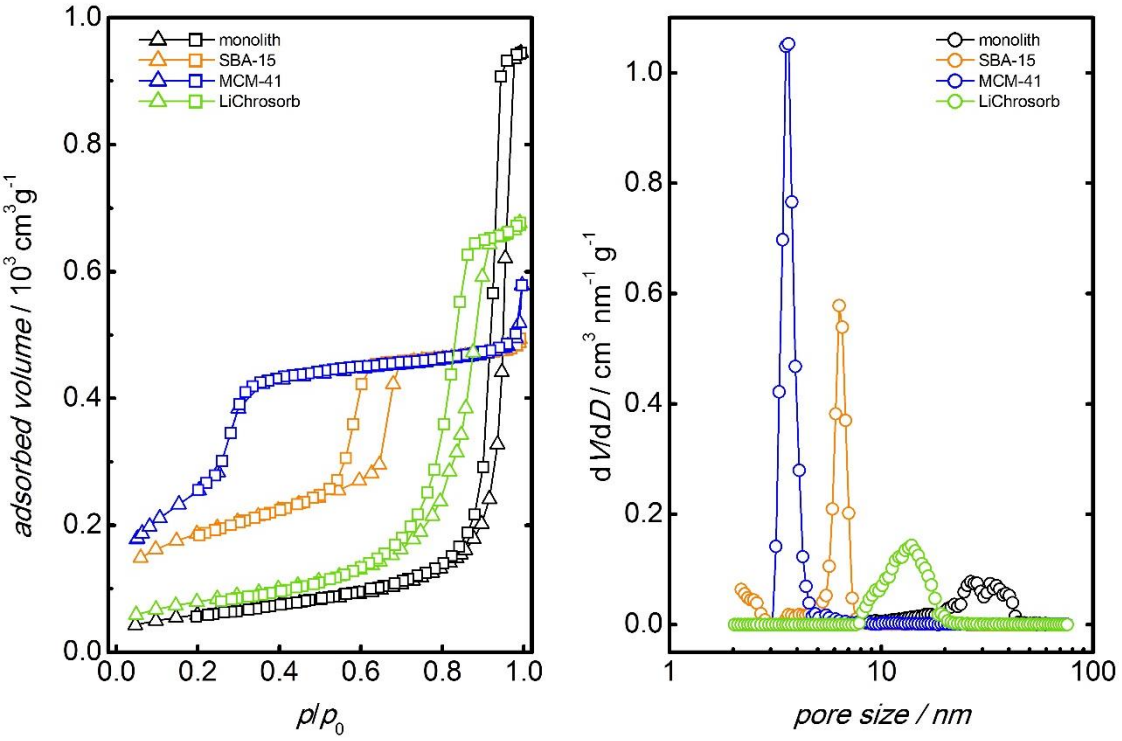

Figure S1. N_2 physisorption isotherms of the monolith, SBA-15, MCM-41 and LiChrosorb.

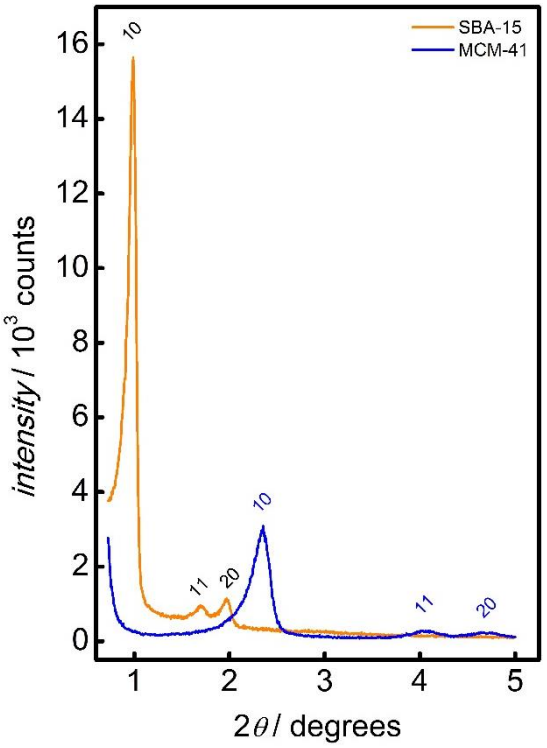

Figure S2. Low angle X-ray diffraction of of SBA-15 and MCM-41.

Functionalization with trimethoxyphenylsilane. LiChrosorb SI 100 (dried): IR (KBr): ν = 3442, 2921, 2850, 2381, 1635, 1101, 804, 471 cm^{-1}. Elemental analysis: 4.05 % C. Loading related to m_C: 0.562 $mmol \cdot g_{SiO2}^{-1}$. **Monolith (dried):** IR (KBr): ν = 3428, 2965, 2363, 2339, 1633, 1094, 808, 740, 700, 468 cm^{-1}. Elemental analysis: 5.60 % C. Loading related to m_C: 0.777 $mmol \cdot g_{SiO2}^{-1}$. **SBA-15 (dried):** IR (KBr): ν = 3425, 2363, 1631, 1080, 805, 700, 462 cm^{-1}. Elemental analysis: 3.66 % C. Loading related to m_C: 0.508 $mmol \cdot g_{SiO2}^{-1}$.

Functionalization with phenylphosphonic acid (PPA) (1). LiChrosorb SI 100 (dried): IR (KBr): ν = 3433, 2362, 2340, 1631, 1440, 1098, 806, 751, 717, 694, 467 cm^{-1}. Elemental analysis: 5.35 % C. Loading related to m_C: 0.742 $mmol \cdot g_{SiO2}^{-1}$. **Monolith:** IR (KBr): ν = 3435, 2960, 2920, 2853, 1630, 1180, 1096, 806, 467 cm^{-1}. Elemental analysis: 3.80 % C. Loading related to m_C: 0.527 $mmol \cdot gSiO_2$ [1]. **SBA-15:** IR (KBr): ν = 3468, 2961, 2926, 2855, 1639, 1439, 1385, 1193, 1101, 808, 748, 717, 692, 469 cm^{-1}. Elemental analysis: 4.04 % C. Related to m_C: 0.561 $mmol \cdot g_{SiO2}$ [1]. **MCM-41:** IR (KBr): ν = 3431, 2966, 2361, 2342, 1635, 1082, 810, 668, 459 cm^{-1}. Elemental analysis: 0.07 % C. Loading related to m_C: 0.01 $mmol \cdot g_{SiO2}^{-1}$.

Functionalization with adenosine monophosphate (AMP) (2). LiChrosorb SI 100: IR (KBr): ν = 3431, 3254, 3124, 3045, 2977, 2921, 2359, 2341, 1697, 1643, 1505, 1460, 1418, 1386, 1101, 987, 879, 808, 766, 722, 714, 628, 542, 471 cm^{-1}. Elemental analysis: 6.59 % N, 12.43 % C. Loading related to m_C: 1.035 $mmol \cdot g_{SiO2}^{-1}$. Loading related to m_N: 0.941 $mmol \cdot g_{SiO2}^{-1}$. **Monolith:** IR (KBr): ν = 3394, 3251, 3124, 3047, 2977, 2922, 2362, 2342, 1697, 1643, 1595, 1505, 1461, 1421, 1385, 1320, 1196, 1143, 1061, 1036, 988, 971, 956, 900, 878, 820, 807, 766, 723, 711, 675, 630, 540, 502, 433 cm^{-1}. Elemental analysis: 15.39 % N, 26.98 % C. Loading related to m_C: 2.489 $mmol \cdot g_{SiO2}^{-1}$. Loading related to m_N: 2.197 $mmol \cdot g_{SiO2}^{-1}$. **SBA-15:** IR (KBr): ν = 3435, 3254, 3124, 3049, 2977, 1699, 1639, 1505, 1460, 1422, 1318, 1081, 987, 973, 901, 819, 808, 714, 628, 542, 463 cm^{-1}. Elemental analysis: 6.24 % N, 12.00 % C. Loading related to m_C: 0.999 $mmol \cdot g_{SiO2}^{-1}$. Loading related to m_N: 0.891 $mmol \cdot g_{SiO2}^{-1}$. **MCM-41:** IR (KBr): ν = 3443, 3266, 2921, 2854, 1697, 1643, 1505, 1464, 1418, 1382, 1081, 973, 901, 808, 766, 714, 632, 542, 463 cm^{-1}. Elemental analysis: 6.97% N, 12.60% C. Loading related to m_C: 1.049 $mmol \cdot g_{SiO2}^{-1}$. Loading related to m_N: 0.995 $mmol \cdot g_{SiO2}^{-1}$.

Functionalization with n-dodecylphosphonic acid (DPA) (3). LiChrosorb SI 100: IR (KBr): ν = 3442, 2925, 2854, 2539, 2341, 1633,1468, 1101, 804, 471 cm^{-1}. Elemental analysis: 9.16 % C. Loading related to m_C: 0.636 $mmol \cdot g_{SiO2}^{-1}$. **SBA-15:** IR (KBr): ν = 3442, 2925, 2854, 1633, 1081, 812, 459 cm^{-1}. Elemental analysis: 8.18 % C. Loading related to m_C: 0.568 $mmol \cdot g_{SiO2}^{-1}$. **MCM-41:** IR (KBr): ν = 3438, 2925, 2854, 2363, 2341, 1633, 1081, 965, 804, 459 cm^{-1}. Elemental analysis: 6.72 % C. Loading related to m_C: 0.466 $mmol \cdot g_{SiO2}^{-1}$.

Functionalization with di-n-butylphosphoric acid (DBP) (4). LiChrosorb SI 100®: IR (KBr): ν = 3450, 2963, 2926, 2852, 633, 1100, 977, 805 471 cm^{-1}. Elemental analysis: 4.52 % C. Loading related to m_C: 0.470 $mmol \cdot g_{SiO2}^{-1}$. **SBA-15:** IR (KBr): ν = 3431, 2966, 2361, 2342, 1635, 1082, 810, 668, 459 cm^{-1}. Elemental analysis: 4.05 % C. Loading related to m_C: 0.422 $mmol \cdot g_{SiO2}^{-1}$. **MCM-41:** IR (KBr): ν = 3453, 2967, 2925, 1635, 1239, 1081, 969, 804, 459 cm^{-1}. Elemental analysis: 2.54 % C. Loading related to m_C: 0.264 $mmol \cdot g_{SiO2}^{-1}$.

Functionalization with (4*R*)-4-phosphonooxy-L-proline (5). LiChrosorb SI 100: IR (KBr): ν = 3450, 2921, 2850, 2359, 2341, 1745, 1635, 1097, 800, 467 cm^{-1}. Elemental analysis: 1.20 % N, 7.41 % C. Loading related to mc: 1.234 $mmol \cdot g_{SiO2}^{-1}$. Loading related to m_N: 0.857 $mmol \cdot g_{SiO2}^{-1}$. **SBA-15:** IR (KBr): ν = 3453, 2925, 2854, 1635, 1081, 965, 804, 463 cm−1. Elemental analyis: 0.62 % N, 6.98 % C. Loading related to m_C: 1.162 $mmol \cdot g_{SiO2}^{-1}$. Loading related to m_N: 0.514 $mmol \cdot g_{SiO2}^{-1}$.

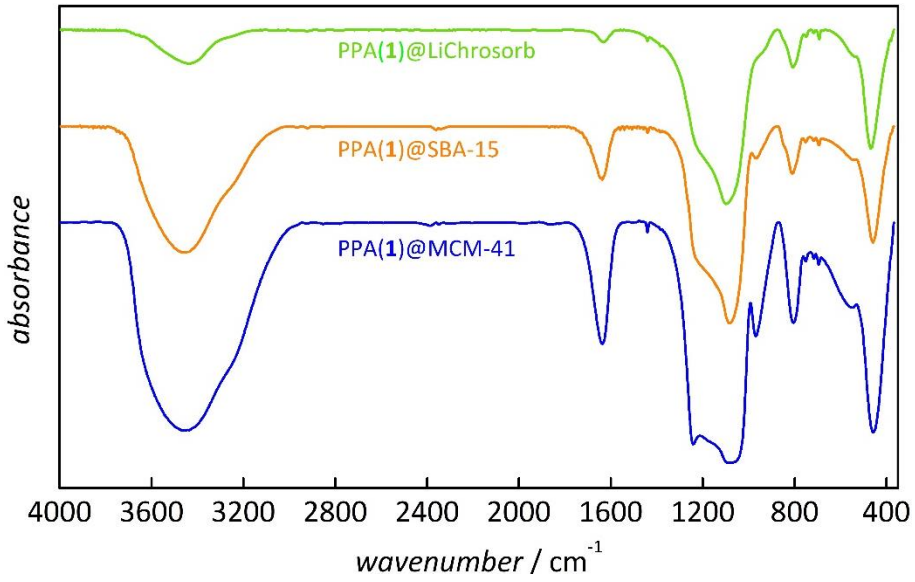

Figure S3. FTIR spectra of PPA(**1**)-functionalized silica (LiChrosorb, SBA-15, MCM-41).

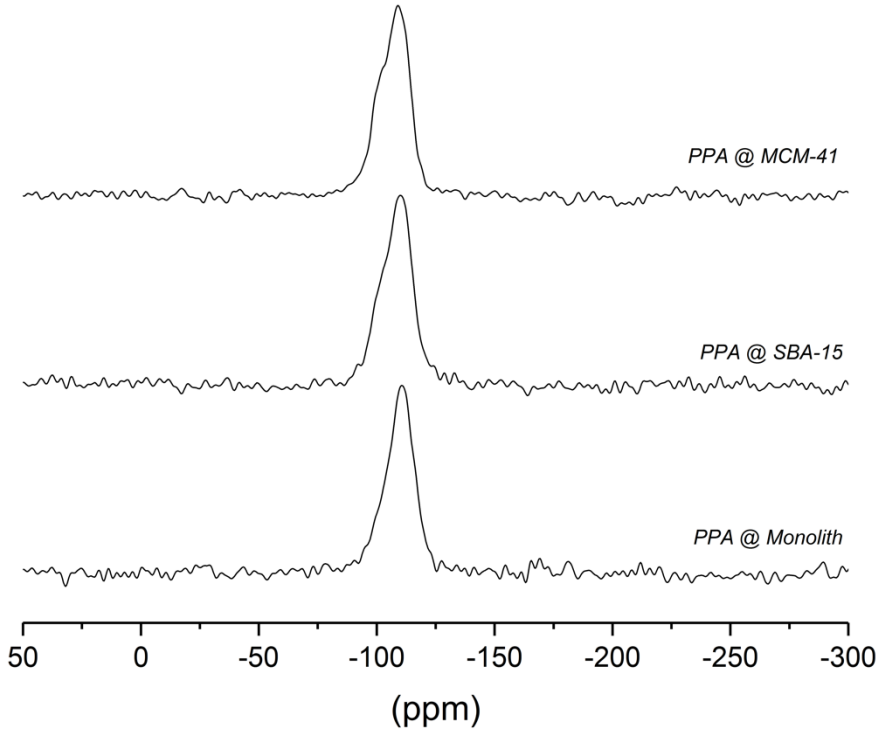

Figure S4. ^{29}Si MAS NMR spectra of PPA (**1**)-functionalized silica (MCM-41, SBA-15 and monolith).

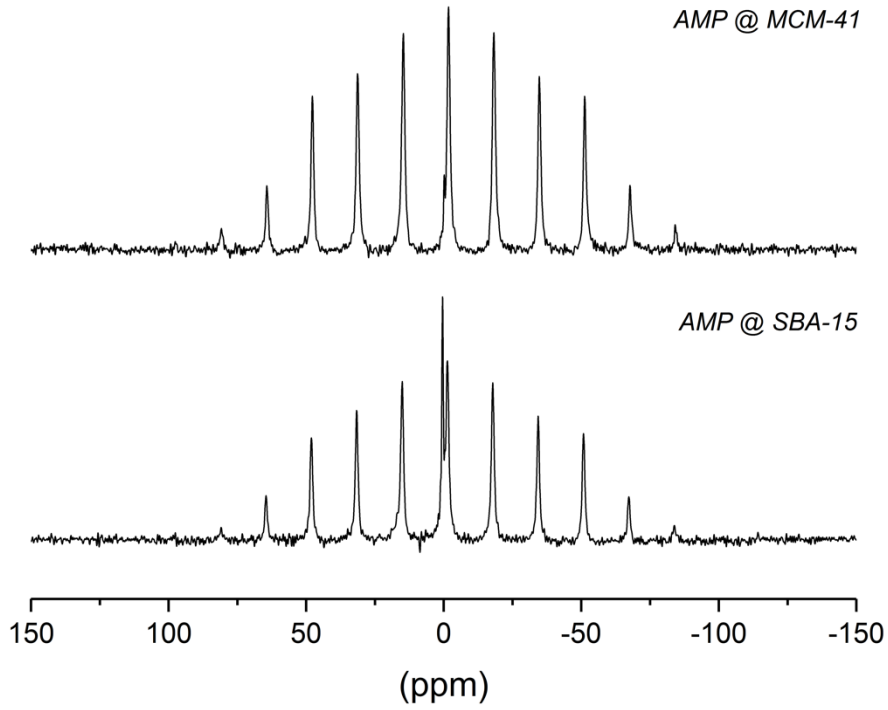

Figure S5. ^{31}P MAS NMR spectra of AMP (**2**)-loaded silica (MCM-41 and SBA-15).

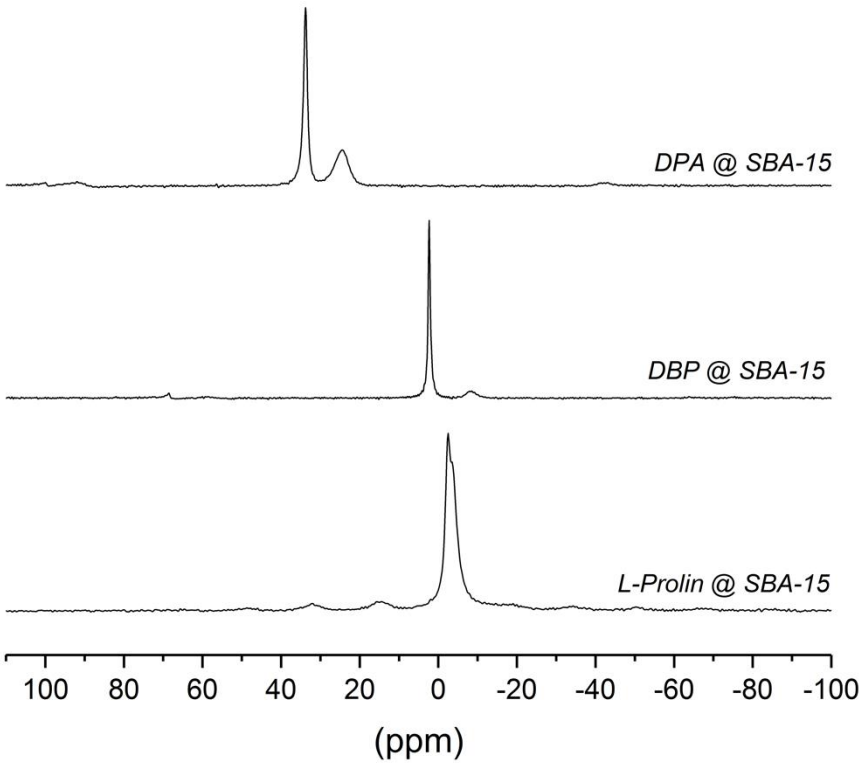

Figure S6. ^{31}P MAS NMR spectra of SBA-15-functionalized with DPA (**3**), DBP (**4**) and (4R)-4-phosphono-oxy