Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Data

Bifunctional synergistic mesoporous Silica Nanoparticles as catalysts for the *Tsuji-Trost* reaction – Tuning the reactivity of Silica Nanoparticles

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1 General Methods

^{1}H NMR, ^{13}C NMR spectra were recorded on a *Bruker DPX 300*. Chemical shifts δ in ppm are referenced to the residual solvent signal ($CHCl_3$: $\delta(^{1}H)$ = 7.26 ppm, $\delta(^{13}C)$ = 77.16 ppm), respectively. ^{13}C assignments were confirmed by DEPT-spectra when necessary. **Solid state NMR** measurements were carried out on Bruker Avance spectrometers (300 MHz and 400 MHz) equipped with 4 mm single and double resonance NMR probes. The resonance frequencies were 300 MHz (7.04 T) and 400 MHz (9.40 T) for ^{1}H and 75.433 MHz (7.04 T) and 100.577 MHz (9.40 T) for ^{13}C, respectively. Chemical shifts are reported relative to TMS, using adamantane ($\delta(^{13}C)$=38.56 ppm for the methylene resonance) as secondary reference. The $^{13}C\{^{1}H\}$ CP/MAS spectra were measured using typical ^{1}H 90° pulse lengths of 3.8-4.0 μs, a spinning frequency of 10-12 kHz and contact times of 250 μs, respectively. The number of accumulated scans as well as the recycle delay is give in the caption of the spectra. ^{1}H decoupling during the acquisition was achieved by applying the TPPM-15 decoupling scheme.

High resolution mass spectra (ESI) were recorded on *Bruker Daltonics MicroTof* or *Thermo Scientific Orbitrap LTQ XL* (Nanospray). **IR** spectra were measured on a *Varian FTS 4000* equipped with a MKII Golden Gate single reflection ATR System. Intensities in the IR are given as follows: *s* – strong, *m* – medium, *w* – weak, *br* – broad. **Flash chromatography** (FC) was carried out on *Merck* or *Fluka* silica gel 60 (40 – 63 μm) with an argon pressure of about 1.4-1.6 bar. **TLC** was carried out on *Merck* silica gel 60 F254 plates; detection by UV (254 nm) and $KMnO_4$ / Na_2CO_3 solution.

2 Chemicals and Solvents

Tetra(TEOS) (*Acros* 98 %), Cetyl trimethylammonium bromide (CTAB) (*Merck*), Sodium azide (*Aldrich* >99.5 %), L-Ascorbic acid sodium salt (*Acros* 99 %), *N*,*N*-Dimethylformamide (*Acros* 99.8 %), *p*-Toluenesulfonyl chloride (*Acros* 99 %), tetraethylene glycol (*Aldrich* 99 %), Prop-2-yn-1-ol (*Acros* 99 %), Hydrobromic acid (*Acros* 48 % solution in water), 4,4'-Dimethyl-2,2'-bipyridyl (*Acros*, 99 %), Sodium cyanoborohydride (*TCI* >95%), Sodium hydride (*Acros* 60 % dispersion in mineral oil), 5-Bromo-1-pentene (*TCI* >95 %), terephthalaldeheyde (*Acros* 97 %), Hydrobromic acid (*Acros* 33 wt% in glacial acidic acid), Lithium aluminium hydride (*Acros* 95 %), Sodium iodide (*Acros* 99+ %), Chlorotrimethylsilane (*Alfa Aesar* 98+ %), 5-Hexen-1-ol (*Alfa Aesar* 98 %), Copper (*Aldrich* 99 %), 4,4'-Di-*tert*-butyl-[2,2']-bipyridinyl (*Aldrich* 98 %), $Cu(OTf)_2$ (*Alfa Aesar* 99 %), 2-Chloropropane (*Aldrich* 99 %), Palladium(II) chloride (*Acros* 59 % Pd), Ethyl acetoactetate (*Alfar Aesar* 99+ %) and Allyl methyl carbonate (*TCI* >98 %) were used as received. The solvents for FC were distilled prior to use. THF was dried over potassium hydroxide, then distilled over sodium and then distilled from potassium. Et_2O was dried over potassium hydroxide, then distilled from potassium sodium alloy. DCM was dried over phosphorus pentoxide. EtOH was distilled from sodium hydroxide.

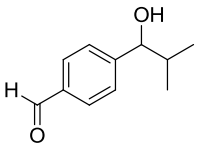
3 Abbreviations

aq.	aqueous
conc.	concentrated
CTAB	Cetyl trimethylammonium bromide
DCE	1,2-Dichloroethane
DCM	Dichloromethane
DMF	*N*,*N*-Dimethylformamide
EDCI	1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride
eq.	Equivalent
FC	flash chromatography
h	hour(s)
HOBT	1-Hydroxybenzotriazole
HRMS (ESI)	High resolution mass spectroscopy
MeCN	Acetonitrile
min	minute(s)
MTBE	*tert*-Butyl methyl ether
P	pentane
PEG	polyethylene glycol
ppm	parts per million
Pr	propyl
rt	room temperature
sat.	saturated
TEMPO	2,2,6,6-Tetramethylpiperidine-*N*-oxyl
Tf	Trifluoromethanesulfonyl
THF	tetrahydrofurane
TLC	thin layer chromatography
TMS	Trimethylsilyl
tosyl (Ts)	*p*-Toluenesulfonyl
UV	ultra violet

4 Experimental Section

4.1 The Synthesis of the triethoxysilanes 2 and 6 has been reported earlier.[1,2,3]

4.1.1 4-(1-Hydroxy-2-methylpropyl)-benzaldehyde

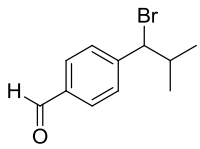


Following a procedure of *Studer* and coworkers[3] a solution of terephthaldehyde (20.8 g, 100 mmol, 1.0 eq.) in Et_2O (60 mL) was added to a solution of ^{i}PrMgCl, freshly prepared from magnesium (3.04 g, 125 mmol, 1.25 eq.) and 2-chloropropane (9.82 g, 125 mmol, 1.25 eq.) in Et_2O (40 mL). The reaction mixture was heated to 40 °C for 3 h. The reaction was stopped by addition of water (20 mL) followed by addition of HCl (6 M, 20 mL). Die aqueous layer was extracted with Et_2O and the organic layer was dried over $MgSO_4$, filtered and the solvents were removed *in vacuo*. Purification via FC (P-MTBE 10:1 → 1:1) afforded the desired aldehyde (16.0 g, 89.8 mmol, 90 %) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.99 (*s*, 1H, C*H*O), 7.85 (*d*, *J* = 8.2 Hz, 2 H, H_{Aryl}), 7.50 (*d*, *J* = 8.2 Hz, 2 H, CH_{Aryl}), 4.51 (*d*, *J* = 6.1 Hz, 1 H, C*H*OH), 2.41 (*s br*, 1 H, O*H*), 1.99 (*m*, 1 H, C*H*$(CH_3)_2$), 0.98 (*d*, *J* = 6.7 Hz, 3 H, CH_3), 0.86 (*d*, *J* = 6.7 Hz, 3 H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 192.2 (*C*HO), 150.9 (C_q), 135.7 (C_q), 129.7 (2 × *C*H), 127.2 (2 × *C*H), 79.3 (*C*HOH), 35.4 (*C*H$(CH_3)_2$), 19.0 (*C*H_3), 17.8 (*C*H_3).

The spectroscopic data are in accordance with those reported in the literature.[3]

4.1.2 4-(1-Bromo-2-methylpropyl)-benzaldehyde

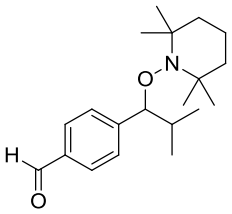


According to a procedure of *Studer* and coworkers[3] HBr (20.2 mL, 117 mmol, 33 % in AcOH, 1.30 eq.) was added to a solution of the alcohol (16.0 g, 89.8 mmol, 1.0 eq.) in DCM (100 mL) at 0°C. The reaction mixture was stirred for 14 h at rt. Purification via FC (P-MTBE 9-1) afforded the bromide (13.3 g, 55.2 mmol, 61 %) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.00 (*s*, 1 H, C*H*O), 7.85 (*d*, *J* = 8.1 Hz, 2 H, H_{Aryl}), 7.53 (*d*, *J* = 8.1 Hz, 2 H, H_{Aryl}), 4.72 (*d*, *J* = 8.4 Hz, 1 H, C*H*Br), 2.45-2.22 (*m*, 1 H, C*H*$(CH_3)_2$), 1.19 (*d*, *J* = 6.5 Hz, 3 H, CH_3), 0.87 (*d*, *J* = 6.8 Hz, 3 H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 189.6 (*C*HO), 146.2 (C_q), 134.0 (C_q), 127.9 (2 × *C*H), 126.6 (2 × *C*H), 60.5 (*C*HBr), 34.4 (*C*H$(CH_3)_2$), 19.3 (*C*H_3), 18.5 (*C*H_3).

The spectroscopic data are in accordance with those reported in the literature.[3]

4.1.3 4-[2-Methyl-1-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-propyl]-benzaldehyde

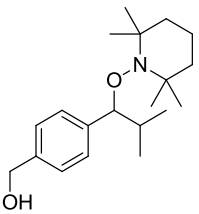


According to a method of *Matyjaszewski et al.*[4] the bromide (13.3 g, 55.2 mmol, 1.0 eq.) was dissolved in benzene (76 mL). Cu (3.683 g, 57.96 mmol, 1.15 eq.), $Cu(OTf)_2$ (200 mg, 0.552 mmol, 1 mol%), 4,4‘-di-*tert*-butyl-2,2‘-bipyridine (593 mg, 2.21 mmol, 4 mol%) and TEMPO (9.48 g, 60.7 mmol, 1.1 eq.) were added and the reaction mixture was heated to 80 °C for 28 h. The reaction mixture was filtered through a pad of celite. Purification via FC (P-MTBE 20:1) afforded the desired alkoxyamine (16.6 g, 52.3 mmol, 95 %) as a colorless oil.

IR (neat): 2966*w*, 2934*w*, 1700*m*, 1607*m*, 1305*w*, 1210*m*, 1168*w*, 1133*w*, 814*m*, 751*s*, 667*m*. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 9.93 (*s*, 1 H, C*H*O), 7.74 (*d*, *J* = 7.8 Hz, 2 H, H_{Aryl}), 7.32 (*d*, *J* = 7.8 Hz, 2 H,CH_{Aryl}), 4.56 (*d*, *J* = 5.3 Hz, 1 H, C*H*ON), 2.59-2.47 (*m*, 1 H, C*H*$(CH_3)_2$), 1.55-0.45 (*m*, 18 H, 3 × CH_2, 4 × CH_3), 0.74 (*d*, *J* = 6.7 Hz, 2 × CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 191.6 (*C*HO), 147.0 (C_q), 134.4 (C_q), 128.6 (2 × *C*H), 128.0 (2 × *C*H), 90.3 (*C*HON), 59.2 (2 × NC_q), 39.9 (2 × *C*H_2), 30.4 (*C*H, 2 × *C*H_3), 19.4 (2 × *C*H_3), 16.5 (*C*H_2), 15.2 (2 × *C*H_3).

The spectroscopic data are in accordance with those reported in the literature.[3]

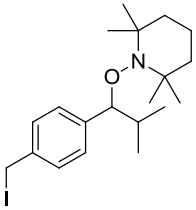
4.1.4 {4-[2-Methyl-1-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-propyl]-phenyl}-methanol



The aldehyde (3.00 g, 9.45 mmol, 1.0 eq.) was reduced in THF (100 mL) with $LiAlH_4$ (359 mg, 9.46 mmol, 1.0 eq.) for 1.5 h at rt. The reaction was stopped by addition of water (444 µL), stirred at rt for 5 min then NaOH (2 M, 444 µL) was added. The reaction was again stirred for approximately 5 min and water (888 µL) was added. The precipitate was filtered off and the solvents were removed *in vacuo* to afford the desired alcohol (2.875 g, 9.00 mmol, 95 %) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27-7.16 (*m*, 4 H, H_{Aryl}), 4.68 (*d*, *J* = 5.8 Hz, 2 H, CH_2OH), 4.54 (*d*, *J* = 5.3 Hz, 1 H, C*H*OH, 2.60-2.49 (*m*, 1 H, C*H*$(CH_3)_2$), 1.69-1.65 (*m*, 1 H, O*H*), 1.42-0.58 (*m*, 24 H, 3 × CH_2, CH(CH_3)$_2$, 2 × C_q(CH_3)$_2$). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 139.9 (C_q), 139.1 (C_q), 129.0 (2 × *C*H), 125.9 (2 × *C*H), 91.0 (*C*HON), 65.4 (*C*HOH), 59.9 (2 × NC_q), 40.7 (2 × *C*H_2), 31.2 (*C*H, 2 × *C*H_3), 20.2 (2 × *C*H_3), 17.25 (*C*H_2), 16.1 (2 × *C*H_3). **HRMS (ESI)**: m/z = 320.2584 calcd. for $C_{20}H_{33}NO_2H^+$ $[M+H]^+$; found: 320.2569. The spectroscopic data are in accordance with those reported in the literature.[3]

4.1.5 1-[1-(4-Iodomethyl-phenyl)-2-methyl-propoxy]-2,2,6,6-tetramethyl-piperidine



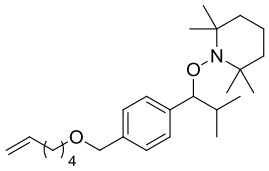
According to a procedure described in the literature[3] the alcohol (2.00 g, 6.26 mmol, 1.0 eq.) and NaI (2.82 g, 18.81 mmol, 3.0 eq.) were dissolved in MeCN (16 mL) and TMSCl (2.40 g, 22.09 mmol, 3.5 eq.) was added. The reaction was stirred for 6 h at rt and was stopped by addition of H_2O

and N_2SO_3 (sat., aq.). The aqueous layer was extracted with Et_2O and the combined organic layers were dried over $MgSO_4$ and filtered. The iodide was dried *in vacuo* and was isolated as a yellowish solid (2.69 g, >99 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 (*d*, *J* = 8.0 Hz, 2 H, H_{Aryl}), 7.15 (*d*, *J* = 8.0 Hz, 2 H, H_{Aryl}), 4.52 (*d*, *J* = 5.5 Hz, 1 H, C*H*ON), 4.48 (*s*, 2 H, CH_2I), 2.63-2.39 (*m*, 1 H, C*H*$(CH_3)_2$), 1.62-0.51 (*m*, 24 H, 3 × CH_2, 6 × CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 138.1, 135.2, 127.0, 125.4, 88.7, 57.7, 38.4, 28.9, 24.8, 18.0, 15.0, 14.0, 4.0. **HRMS (ESI):** m/z = 430.16013 calcd. for $C_{20}H_{32}INOH^+$ $[M+H]^+$; found: 430.15845.

The spectroscopic data are in accordance with those reported in the literature.[3]

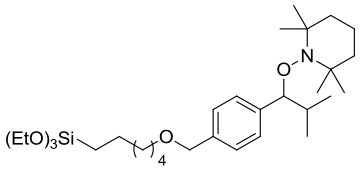
4.1.6 1-(1-(4-((Hex-5-ene-1-yloxy)methyl)phenyl)-2-methylpropoxy)-2,2,6,6-tetramethyl piperidine



5-Hexene-1-ol (2.51 g, 25.0 mmol, 4.00 eq.) in THF (200 mL) was treated with NaH (1.00 g, 60 % in mineral oil, 25.0 mmol, 4.00 eq.). The reaction mixture was stirred at 70 °C for 2 h and the iodide (2.70 g, 6.26 mmol, 1.0 eq.) was added. The reaction mixture was heated at 70 °C for additional 30 h. The solvents were removed *in vacuo*. Purification via FC (P-MTBE 40:1 → 10:1) afforded the desired ether (2.41 g, 6.00 mmol, 96 %) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23 (*d*, *J* = 8.1 Hz, 2 H, H_{Aryl}), 7.16 (*d*, *J* = 8.1 Hz, 2 H, H_{Aryl}), 5.96-5.59 (*m*, 1 H, $CH_2CHC_4H_8$), 5.06-4.88 (*m*, 2 H, $CH_2CHC_4H_8$), 4.51 (*d*, *J* = 5.4 Hz, 1 H, C*H*ON), 4.47 (*s*, 2 H, OCH_2C_q), 4.11 (*q*, *J* = 7.1 Hz, 6 H, 3 × $SiOCH_2$), 3.47 (*t*, *J* = 6.5 Hz, 2 H, CH_2CH_2O), 1.75-0.34 (*m*, 4 × CH_3, 6 × CH_2) 1.19 (*t*, *J* = 7.1 Hz, 9 H, 3 × $SiOCH_2CH_3$), 0.72 (*m*, 6 H, $CH(CH_3)_2$). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 139.7 (C_q), 136.9 (CH_2CH), 134.9 (C_q), 126.9 (2 × *C*H), 124.5 (2 × *C*H), 112.6 (CH_2CH), 89.1 (*C*HON), 71.0 (OCH_2), 68.4 (OCH_2), 58.5 (2 × NC_q), 58.0 (3 × $SiOCH_2$) , 38.7 (2 × CH_2), 31.6, 29.2, 27.3, 23.6, 19.1, 18.3, 15.3, 14.2, 12.3. **HRMS (ESI)**: m/z = 402.33666 calcd. for $C_{26}H_{43}NO_2H^+$ $[M+H]^+$; found: 402.33676.

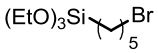
4.1.7 2,2,6,6-Tetramethyl-1-(2-methyl-1-(4-(((6-(triethoxysilyl)hexyl)oxy)methyl)-phenyl)-propoxy)piperidine [6]



In a sealed tube the olefin (3.42 g, 8.51 mmol, 1.0 eq.) was reacted with triethoxysilane (1.54 g, 9.37 mmol, 1.10 eq.) and *Karstedt*-catalyst (350 µL, ~2-2.4 %Pt, 0.5 mol%), which was added in three portions every 5 min. The reaction mixture was stirred at 50 °C for 6 h. Excess of silane was removed *in vacuo*. Purification via FC (P-MTBE 40:1) afforded the triethoxysilane (4.34 g, 7.67 mmol, 90 %) as a colorless oil.

IR (neat): 2972*m*, 2929*m*, 1461*w*, 1361*w*, 1216*w*, 1101*s*, 1077*s*, 956*m*, 789*s*. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.24 (*d*, *J* = 8.4 Hz, 2 H, H_{Aryl}), 7.17 (*d*, *J* = 8.4 Hz, 2 H, H_{Aryl}), 4.51 (*d*, *J* = 5.3 Hz, 1 H, C*H*ON), 4.47 (*s*, 2 H, OCH_2), 3.81 (*q*, *J* = 7.0 Hz, 6 H, 3 × SiOCH_2), 3.46 (*t*, *J* = 6.6 Hz, 2 H, OCH_2), 2.62-2.44 (*m*, *J* = 6.6 Hz, 1 H, C*H*(CH_3)$_2$), 1.67-0.44 (*m*, 28 H, 8 × CH_2, 4 × CH_3), 1.22 (*t*, *J* = 7.0 Hz, 9 H, 3 × SiOCH$_2$CH_3), 0.82-0.77 (*m*, 6 H, CH(CH_3)$_2$). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 139.7 (C_q), 136.9 (C_q), 128.9 (2 × *C*H), 126.5 (2 × *C*H), 91.2 (*C*HON), 73.0 (*C*H$_2$O), 70.7 (O*C*H$_2$), 60.0 (2 × N*C*$_q$), 58.4 (3 × SiO*C*H$_2$), 49.6, 40.8 (2 × *C*H$_2$), 34.3 (*C*H), 33.1 (2 × *C*H$_2$), 31.3, 29.8, 27.1, 26.0, 22.9, 22.5, 20.3, 18.4, 17.3, 16.2, 14.2, 10.5. **HRMS (ESI)**: m/z = 588.40547 calcd. for $C_{32}H_{59}NO_5SiNa^+$ $[M+Na]^+$;found: 588.40501.

4.1.8 (5-Bromopentyl)triethoxysilane

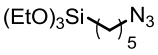


According to a procedure described by *Pinchon et al.*[5] 5-Bromopentene (3.15 mL, 3.98 g, 20 mmol, 1.0 eq.) was reacted with triethoxysilane (4.36 mL, 3.62 g, 22.0 mmol, 1.1 eq.) and *Karstedt*-catalyst (600 µL, ~2-2.4 % Pt, 0.3 mol%), which was added in three portions every 5 min. The reaction mixture was stirred for 5 h in the dark at 50 °C. FC (P-acetone 19 : 1) afforded the desired triethoxysilane (4.95 g, 18.0 mmol, 90 %) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.80 (*t*, *J* = 7.0 Hz, 6 H, 3 × OCH_2), 3.36 (*t*, *J* = 6.9 Hz, 2 H, CH_2Br), 1.82 (*quin*, *J* = 6.9 Hz, BrCH$_2$CH_2), 1.48-1.35 (*m*, 4 H, 2 × CH_2), 1.18 (*t*, 7.0 Hz, 9 H, 3 × CH_3), 0.64-0.52 (*m*, 2 H, SiCH_2). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 58.4 (3 × O*C*H$_2$), 34.0 (Br*C*H$_2$), 32.6 (*C*H$_2$), 31.7 (*C*H$_2$), 22.2 (*C*H$_2$), 18.4 (3 × *C*H$_3$), 10.4 (Si*C*H$_2$).

The spectroscopic data are in accordance with those reported in the literature.[2]

4.1.9 (5-Azidopentyl)triethoxysilane [2]



According to a procedure described by *Pichon et al.*[2] (5-Bromopentyl)triethoxysilane (3.10 g, 9.89 mmol, 1.0 eq.) and sodium azide (1.61 g, 24.7 mmol, 2.50 eq.) were stirred in acetonitrile (30 ml) at 80 °C for 48 h. FC (P-MTBE 20:1) afforded the desired azide (2.47 g, 8.98 mmol, 91 %) as a colorless liquid.

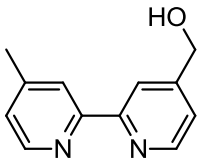
^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.79 (*q*, *J* = 7.0 Hz, 6 H, 3 × OC*H*$_2$), 3.22 (*t*, *J* = 6.9 Hz, 2 H, N_3C*H*$_2$), 1.67-1.50 (*m*, 2 H, C*H*$_2$), 1.46-1.32 (*m*, 4 H, 2 × C*H*$_2$), 1.20 (*t*, *J* = 7.0 Hz, 9 H, 3 × C*H*$_3$), 0.66-0.55 (*m*, 2 H, SiC*H*$_2$). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 58.4 (3 × O*C*H$_2$), 51.5 (N_3*C*H$_2$), 30.2 (*C*H$_2$), 28.6 (*C*H$_2$), 22.5 (*C*H$_2$), 18.3 (3 × *C*H$_3$), 10.4 (N_3*C*H$_2$). **HRMS (ESI):** m/z = 298.1557 calcd. for $C_{11}H_{25}N_3O_3SiNa^+$ $[M+Na]^+$; found: 298.1566.

The spectroscopic data are in accordance with those reported in the literature.[2]

4.2 Synthesis of the bipyridyl-ligand

Parts of the synthesis of the ligand have been reported earlier.[6]

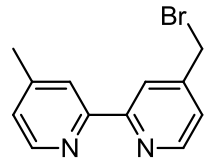
4.2.1 4-Hydroxymethyl-4'-methyl-2,2'-bipyridine



To a stirred suspension of 4,4'-Dimethyl-2,2'-bipyridine (2.0 g, 11 mmol) in 1,4-dioxane (100 mL) was added SeO_2 (2.0 g, 18 mmol). The mixture was heated at reflux for 24 h. After cooling to room temperature, the mixture was filtered, and the solvent was removed *in vacuo*. The resulting pink solid was dissolved in chloroform, and the suspension was filtered to remove selenium-containing by-products. After three successive dissolution and filtration treatments, crude product (1.4 g) was obtained. The resulting solid was suspended in methanol (15 mL), and sodium borohydride (0.3 g, 7.93 mmol) in NaOH (0.2 M, 2.5 mL, 5 mmol) was added dropwise at 0 °C. The mixture was stirred at room temperature for an additional hour and the methanol was then removed *in vacuo*. The remaining aqueous suspension was diluted with Na_2CO_3 (sat., aq., 6 mL) and extracted with chloroform. The organic phase was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by column chromatography and 4-Hydroxymetyl-4'-methyl-2,2'-bipyridine was obtained as a white solid (1.75 g, 79 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.62 (*d*, *J* = 5.0 Hz, 1 H), 8.52 (*d*, *J* = 4.9 Hz, 1 H), 8.34 (*d*, *J* = 0.8 Hz, 1 H), 8.22 (*d*, *J* = 0.8 Hz, 1 H), 7.32 (*dd*, *J* = 4.6, 1.4 Hz, 1 H), 7.18–7.10 (*m*, 1 H), 4.80 (*s*, 2 H, OC*H*$_2$), 2.44 (*s*, 3 H, C*H*$_3$). **HRMS (ESI):** calculated for $[M+H]^+$: 201.1022; found: 201.1019.

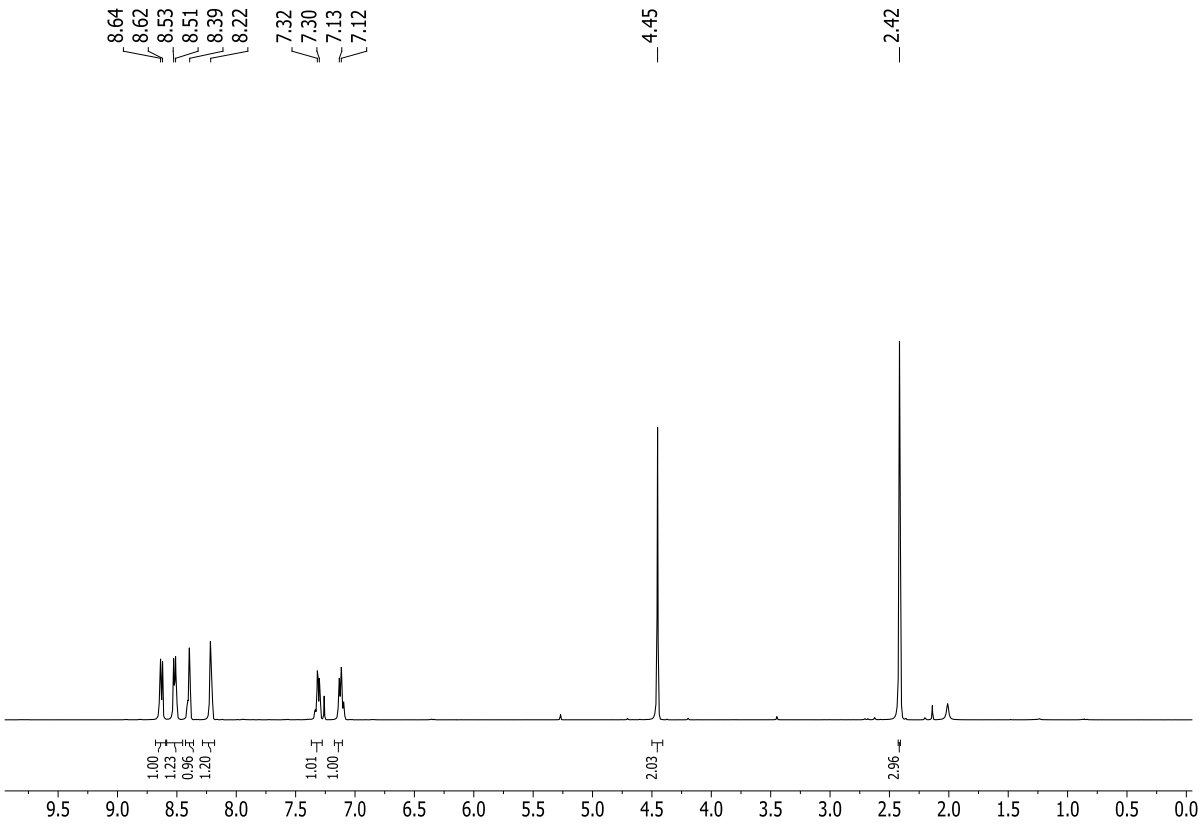
4.2.2 4-Bromomethyl-4'-methyl-2,2'-bipyridine

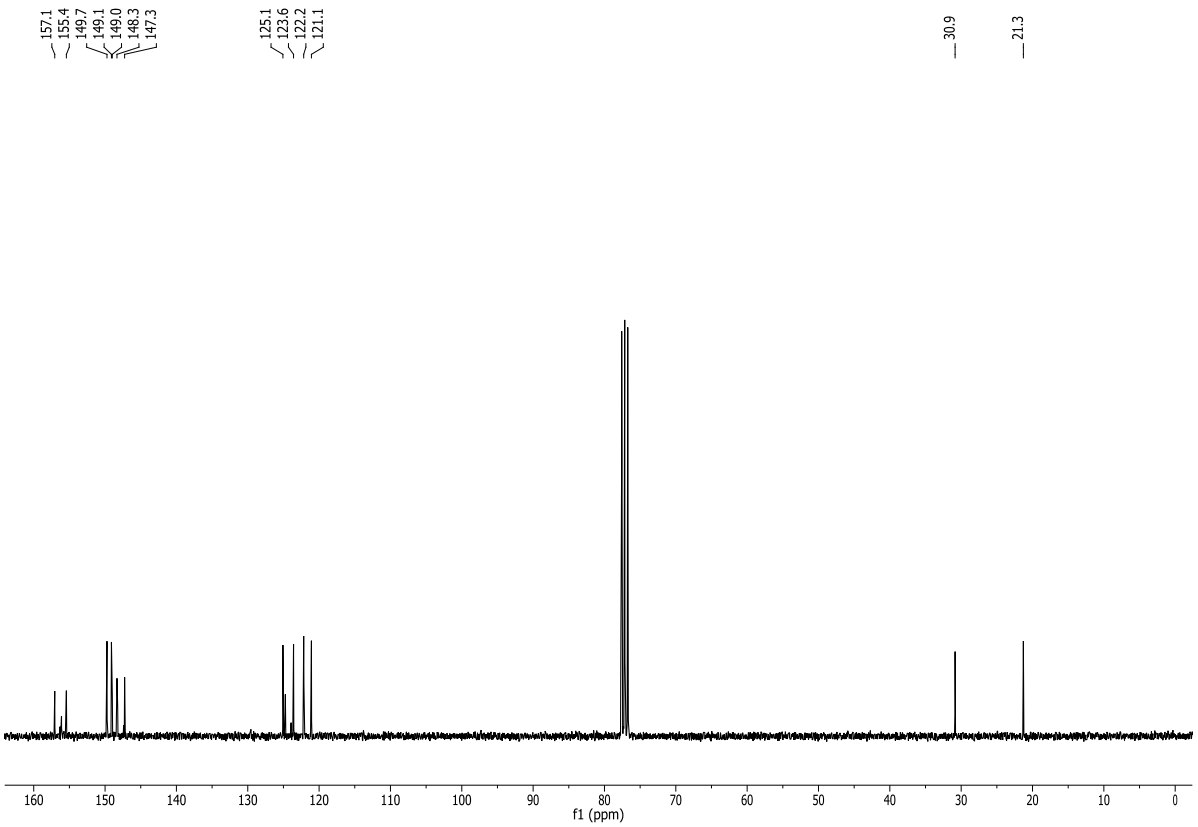


4-Hydroxymethyl-4'-methyl-2,2'-bipyridine (1.62 g, 8.09 mmol) was dissolved in HBr (aq., 48 %, 30 mL), and H_2SO_4 (conc., 3 mL) was added to the solution. The red solution was heated at 100 °C until all the starting material was consumed (monitored by TLC). After 6 h H_2O (13 mL) and DCM (13 mL) were added. The aqueous layer was brought to pH 8 by adding Na_2CO_3 (aq., sat.) and the aqueous layer was extracted with DCM until the organic layer was colourless. The combined organic layers were dried over $MgSO_4$ and the DCM removed *in vacuo* to yield 4-Bromomethyl-4'-methyl-2,2'-bipyridine (690 mg, 32 % yield).

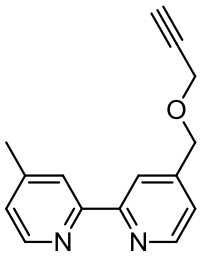
^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.63 (*d*, *J* = 5.3 Hz, 1 H), 8.52 (*d*, *J* = 5.3 Hz, 1 H), 8.40 (*d*, *J* = 2.4 Hz, 1 H), 8.22 (*d*, *J* = 1.8 Hz, 1 H), 7.31 (*dd*, *J* = 5.0 Hz, 1.8 Hz, 1 H), 7.21 - 7.00 (*m*, 1 H), 4.45 (s, 2 H), 2.42 (*s*, 3 H). **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 157.1, 155.4, 149.7, 149.1, 149.0, 148.3, 147.3, 125.1, 123.6, 122.2, 121.1, 30.9, 21.9.

Spectroscopic data are in accordance with those reported in the literature.[7]



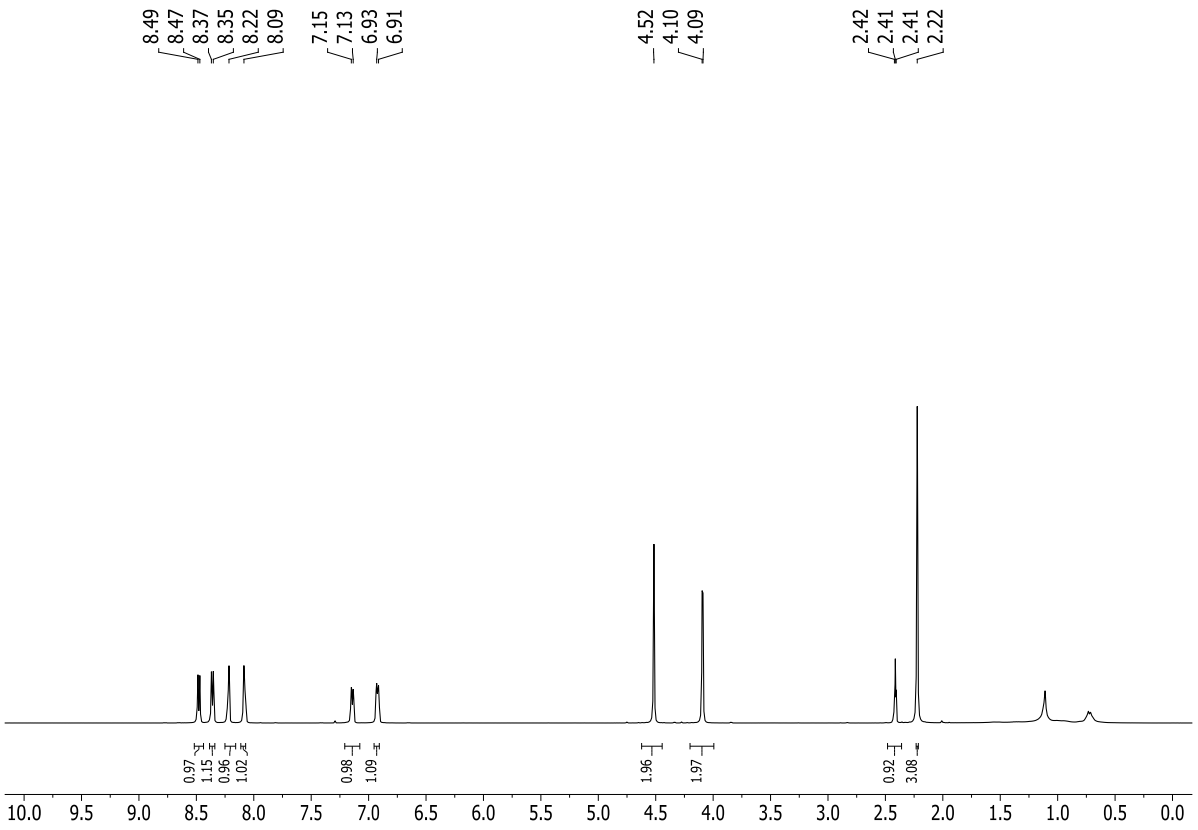


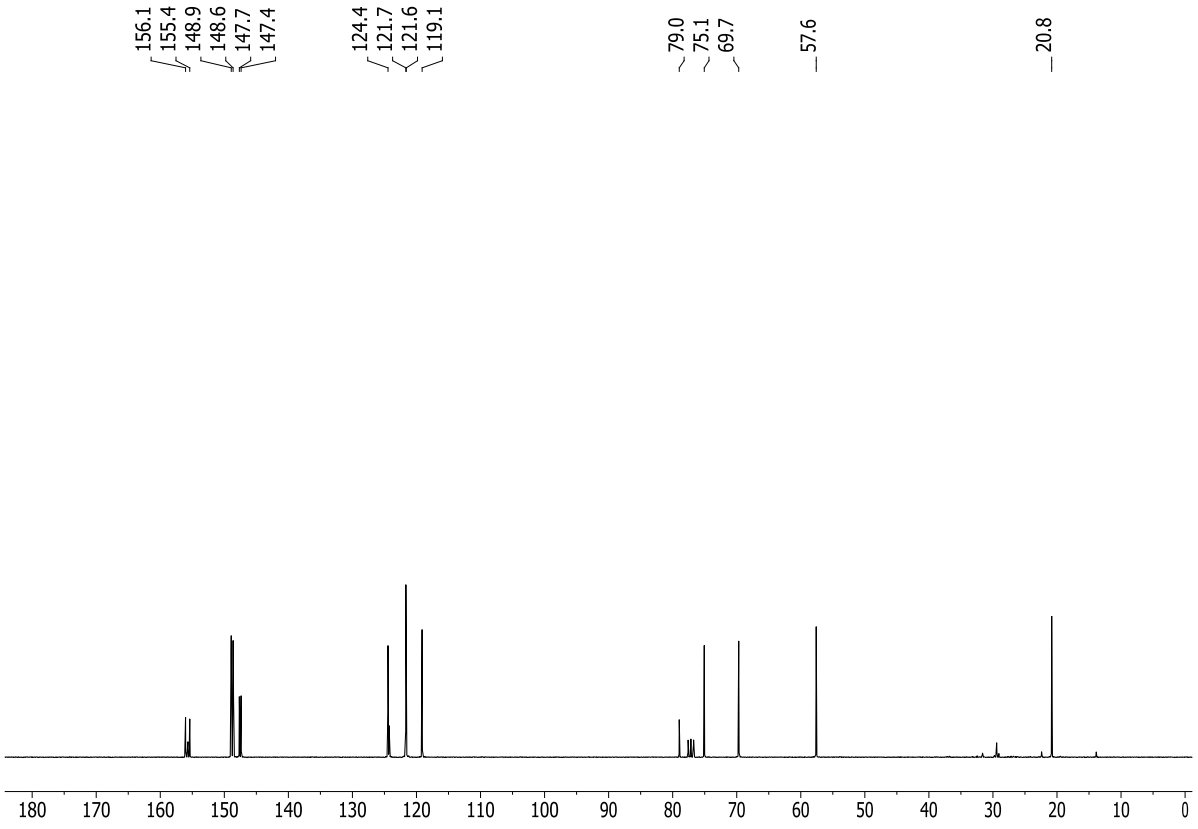
4.2.3 4-Methyl-4'-((prop-2-yn-1-yloxy)methyl)-2,2'-bipyridine



Prop-2-yn-1-ol (175 µL, 2.96 mmol, 1.2 eq.) was dissolved in THF (10 mL) and NaH (118 mg, 60 % in mineral oil, 2.96 mmol, 1.2 eq.) was added. Subsequently the bromide (650 mg, 2.47 mmol) was added and the reaction mixture was stirred at rt over night. The reaction was stopped by adding water (10 mL) and extracted with EtOAc. The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The desired product was obtained as a white solid (573 mg, 97 %).

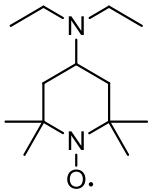
IR: 3294*m*, 2922*m*, 2853*m*, 1712*m*, 1597*s*, 1556*m*, 1460*s*, 1092*s*, 992*m*, 822*s*, 670*m*. **^{1}H NMR (300 MHz, $CDCl_3$):** δ = 8.48 (*d*, *J* = 5.0 Hz, 1 H), 8.39 – 8.34 (*m*, 1 H), 8.22 (*d*, *J* = 1.1 Hz, 1 H), 8.09 (*s*, 1 H), 7.19 – 7.11 (*m*, 1 H), 6.92 (*dd*, *J* = 4.8 Hz, 2.0 Hz, 1 H), 4.52 (*s*, 2 H, OC*H*$_2$), 4.09 (*d*, *J* = 2.4 Hz, 2 H, CC*H*$_2$), 2.41 (t, *J* = 2.4 Hz, 1 H, CC*H*), 2.22 (*s*, 3 H, C*H*$_3$). **^{13}C NMR (75 MHz, $CDCl_3$):** δ = 156.1 (C_q), 155.4 (C_q), 148.9 (CH), 148.6 (CH), 147.7 (C_q), 147.4 (C_q), 124.4 (CH), 121.7 (CH), 121.6 (CH), 119.1 (CH), 79.0 ($C_{q,\ alkyne}$), 75.1 ($C_{q,\ alkyne}$), 69.7 ($CH_{2,\ benzylic}$), 57.6 (OCH_2), 20.8 (CH_3). **HRMS (ESI):** calculated for $[M+H]^+$: 239.1179; found: 239.1188.


8.49
8.47
8.37
8.35
8.22
8.09
7.15
7.13
6.93
6.91
4.52
4.10
4.09
2.42
2.41
2.41
2.22
0.97
1.15
0.96
1.02
0.98
1.09
1.96
1.97
0.92
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


156.1
155.4
148.9
148.6
147.7
147.4
124.4
121.7
121.6
119.1
79.0
75.1
69.7
57.6
20.8
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

4.3 Synthesis oft the nirtoxides for exchange reaction

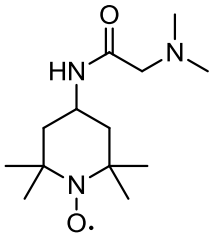
4.3.1 4-(Diethylamino)-2,2,6,6-tetramethylpiperidin-1-yloxy radical



4-Oxo-TEMPO (1.16 g, 6.82 mmol) was dissolved in Ti(O^iPr)$_4$ (2.45 mL, 8.18 mmol). After 20 min of stirring at rt diethylamine (1.40 mL, 13.6 mmol) was added and the reaction was stirred for additional 2 h at rt. Subsequently EtOH (5.8 mL) and $NaCNBH_3$ (514 mg, 8.18 mmol) was added carefully and the resulting solution was stirred 12 h at rt. The reaction was quenched by adding water (10 mL) and the aqueous layer was extracted with EtOAc. The organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo*. Purification via FC afforded the desired Nitroxide (1.51 g, 99 %) as a red oily solid.

IR (film): 3330*br m*, 2975*m*, 2940*m*, 2779*m*, 1658*s*, 1514*s*, 1459*m*, 1243*m*, 1178*m*, 1044*m*, 864*m*, 732*m*. **HRMS (ESI):** calculated for $[M+H]^+$: 228.2196; found: 228.2207.

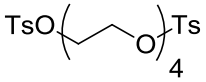
4.3.2 2-(Dimethylamino)-*N*-(1-yloxy-2,2,6,6-tetramethylpiperidin-4-yl)acetamide



To a solution of 4-Amino-TEMPO (752 mg, 4.40 mmol) in DCM (35 mL) was added HOBT (712 mg. 5.27 mmol, 1.2 eq.), *N*-Methylmorpholine (965 µL, 8.80 mmol, 2.0 eq.), EDCI (1.01 g, 5.27 mmol, 1.2 eq.) and *N.N*-dimethylglycine (612 mg, 4.40 mmol, 1.0 eq.) was added and the reaction mixture was stirred for 12 h. The crude reaction mixture was washed with Na_2CO_3 (sat., aq.). The combined aqueous layer was extracted with DCM and the solvent was removed *in vacuo*. Purification via FC (Acetone:P - 3:10) afforded the desired Nitroxide (1.05 g, 93 %) as a red oily solid.

IR (film): 2971*s*, 2934*m*, 2811*w*, 1724*w*, 1467*m*, 1362*s*, 1243*m*, 1202*s*, 1059*m*, 777*m*, 675*m*. **HRMS (ESI):** calculated for $[M+H]^+$: 257,2098; found: 257.2095.

4.3.3 ((Oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl) bis(4-methylbenzene-sulfonate)

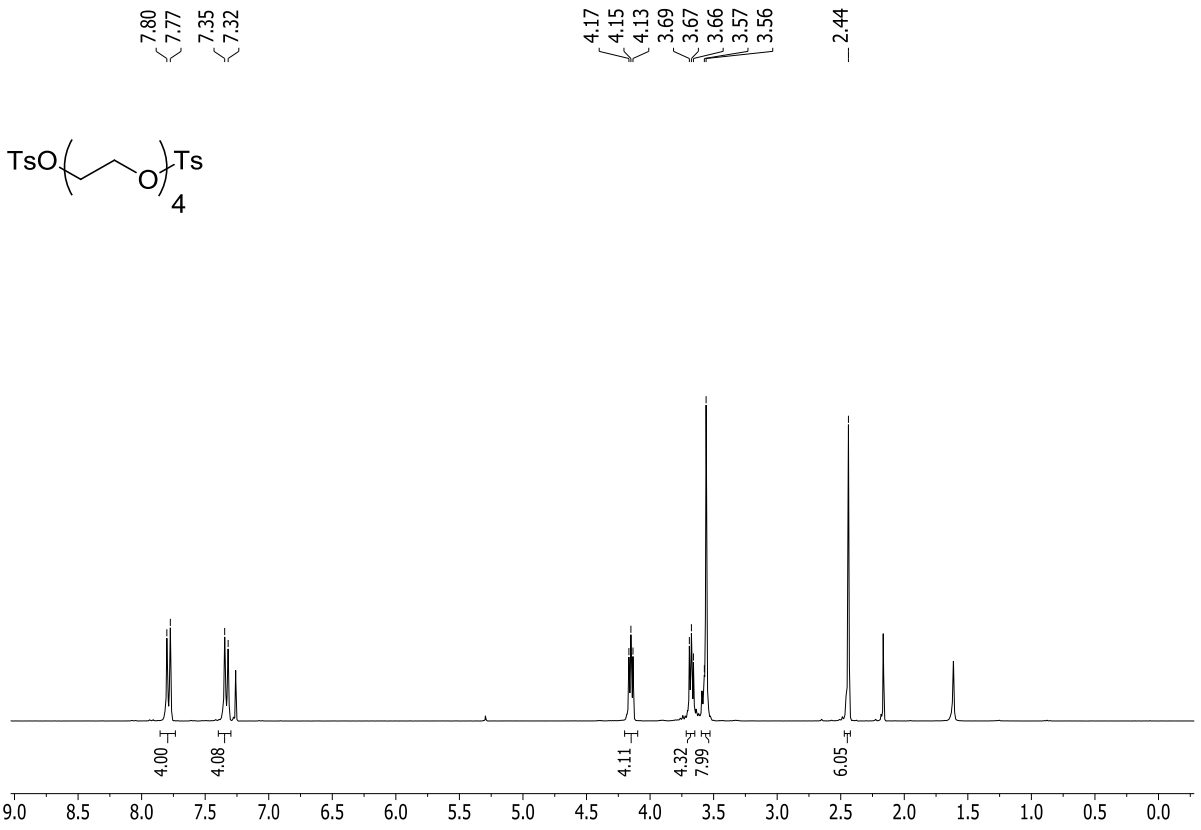


Tetraethylene glycol (1.94 g, 10.0 mmol, 1.0 eq.) was dissolved in DCM (20 mL) followed by addition of NEt_3 (2.78 mL, 20 mmol, 2.0 eq.) and tosylchloride (4.19 g, 22.0 mmol, 2.2 eq.). The reaction mixture was stirred for 3 d at rt. The solvents were removed *in vacuo*. Purification via FC (P-acetone 2:1) afforded bistosylate (3.75 g, 7.46 mmol, 75 %) as a colorless oil.

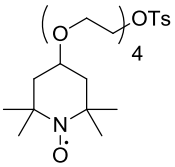
^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.85 (*d*, *J* = 2.5 Hz, 2 H), 2.72 (*t*, *J* = 2.5 Hz, 1 H).7.78 (*d*, *J* = 8.0 Hz, 4 H, H_{Aryl}), 7.34 (*d*, *J* = 8.0 Hz, 4 H, H_{Aryl}), 4.20-4.14 (*m*, 4 H, TsOCH_2), 3.70-3.65 (*m*, 4 H, OCH_2), 3.60-3.53 (m, 8 H, 4 × OCH_2), 2.44 (*s*, 6 H, 2 × CH_3).

The spectroscopic data are in accordance with those reported in the literature.[8]

^{1}H NMR of ((oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl) bis(4-methylbenzenesulfonate).



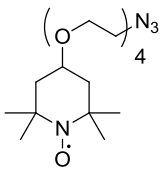
4.3.4 2-(2-(2-(2-((2,2,6,6-Tetramethylpiperidin-4-yl-*N*-oxyl)oxy)ethoxy)ethoxy)-ethoxy)ethyl 4-methylbenzenesulfonate



4-Hydroxy-TEMPO (688 mg, 4.00 mmol, 1.0 eq.) was dissolved in DMF (40 mL) and treated with NaH (168 mg, 60 % in mineral oil, 4.20 mmol, 1.05 eq.). The reactions mixture was stirred at 60 °C for 30 min followed by addition of bistosylglycol (2.01 g, 4.00 mmol, 1.0 eq.). The solution was stirred for additional 4 h at 60 °C and the reaction was stopped by addition of HCl (2 M, 20 mL). The aqueous layer was extracted with EtOAc and the combined organic layers were washed with $NaHCO_3$ (sat., aq.) and dried over $MgSO_4$, filtered and the solvents were removed *in vacuo*. Purification via FC (P-acetone 4:1) afforded the desired nitroxide (1.82 g, 3.97 mmol, 99 %) as a red oil.

IR (film): 2935*m*, 1723*m*, 1462*m*, 1352*m*, 1176*s*, 1096*s*, 920*m*, 817*m*, 774*m*, 734*m*, 663*m*. **HRMS (ESI):** m/z = 525.2367 calcd. for $C_{24}H_{40}NO_8SNa^+$ $[M+Na]^+$; found: 525.2370.

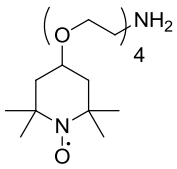
4.3.5 4-(2-(2-(2-(2-Azidoethoxy)ethoxy)ethoxy)ethoxy)-2,2,6,6-tetramethylpiperidine-*N*-oxyl



The tosylated alkoxyamine (1.82 g, 3.97 mmol, 1.0 eq.) was dissolved in MeCN (14 mL) in a flame dried sealed tube. Sodiumazide (650 mg, 10 mmol, 2.5 eq.) was added and the reaction mixture was stirred for 48 h at 80 °C. The solvent was removed *in vacuo*. Purification via FC (P-acetone 4:1) afforded the desired alkoxyamine (504 mg, 1.34 mmol, 34 %) as red oil.

IR (film): 2868*m*, 2098*s*, 1724*w*, 1462*m*, 1349*m*, 1285*m*, 1100*s*, 937*m*, 852*w*, 734*w*, 666*w*.
HRMS (ESI): m/z = 396.2343 calcd. for $C_{17}H_{33}N_4O_5Na^+$ $[M+Na]^+$; found: 396.2352.

4.3.6 2-(2-(2-(2-((2,2,6,6-Tetramethylpiperidine-4-yl)oxy)ethoxy)ethoxy)ethoxy)-ethanamine

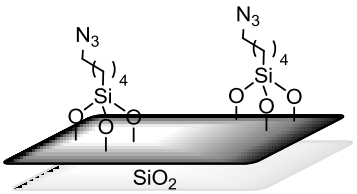


The azide (504 mmol, 1.34 mmol, 1.0 eq.) and PPh_3 (391 mg, 1.49 mmol, 1.1 eq.) was dissolved in DCM (5 mL) in a flame dried sealed tube. The reaction mixture was stirred at rt for 18 h followed by quenching with water. Purification via FC (P-acetone 4:1) afforded the desired amine (428 mg, 1.23 mmol, 91 %) as red oil.

IR (film): 3465*br*, 2870*w*, 1676*m*, 1438*m*, 1351*w*, 1178*m*, 1118*s*, 1094*s*, 937*m*, 712*s*, 695*s*.
HRMS (ESI): m/z = 348.2619 calcd. for $C_{17}H_{35}N2O_5H^+$ $[M+H]^+$; found: 348.2611.

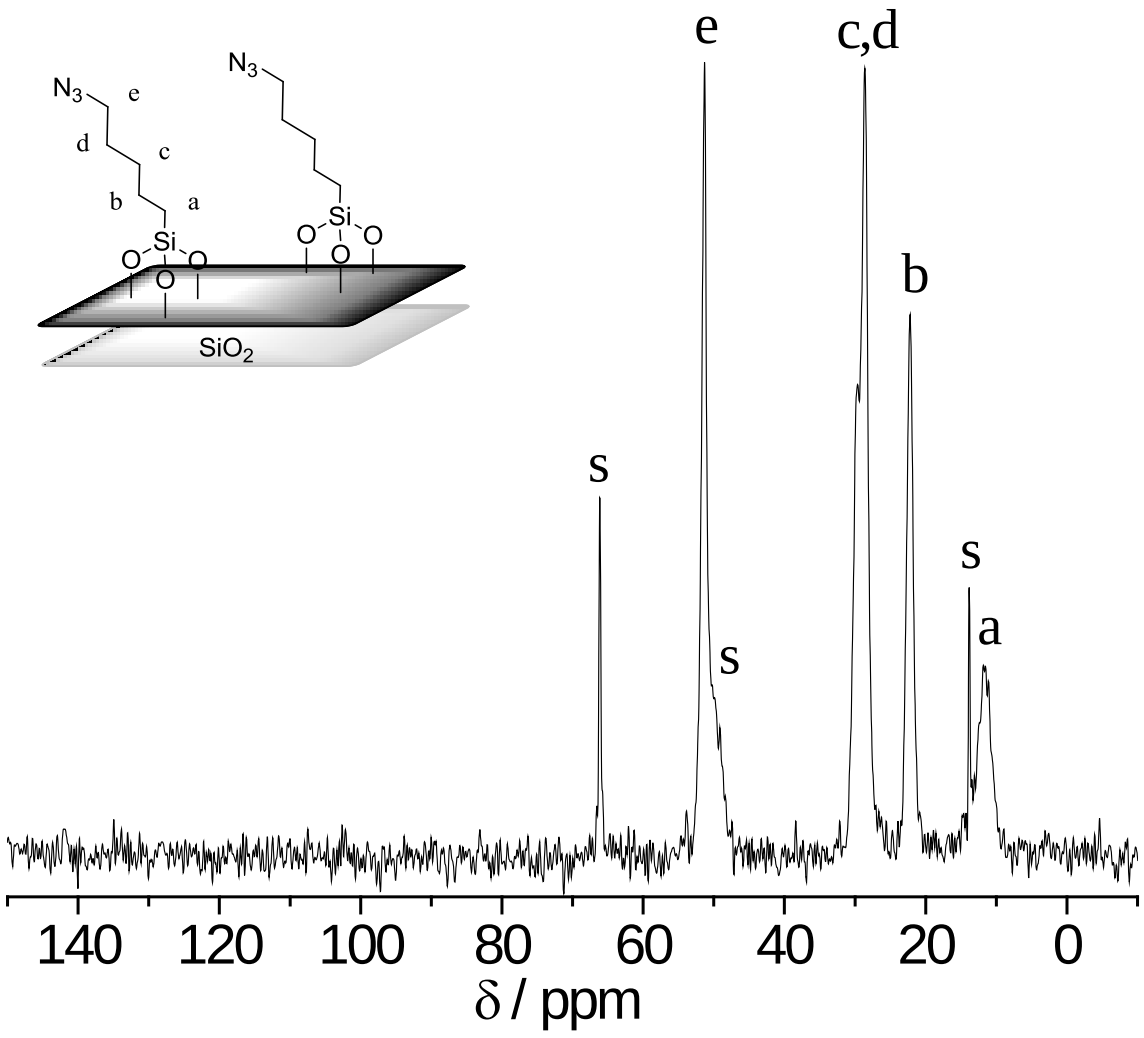
4.4 Synthesis of the nanoparticles

4.4.1 Azide functionalized particles [3]

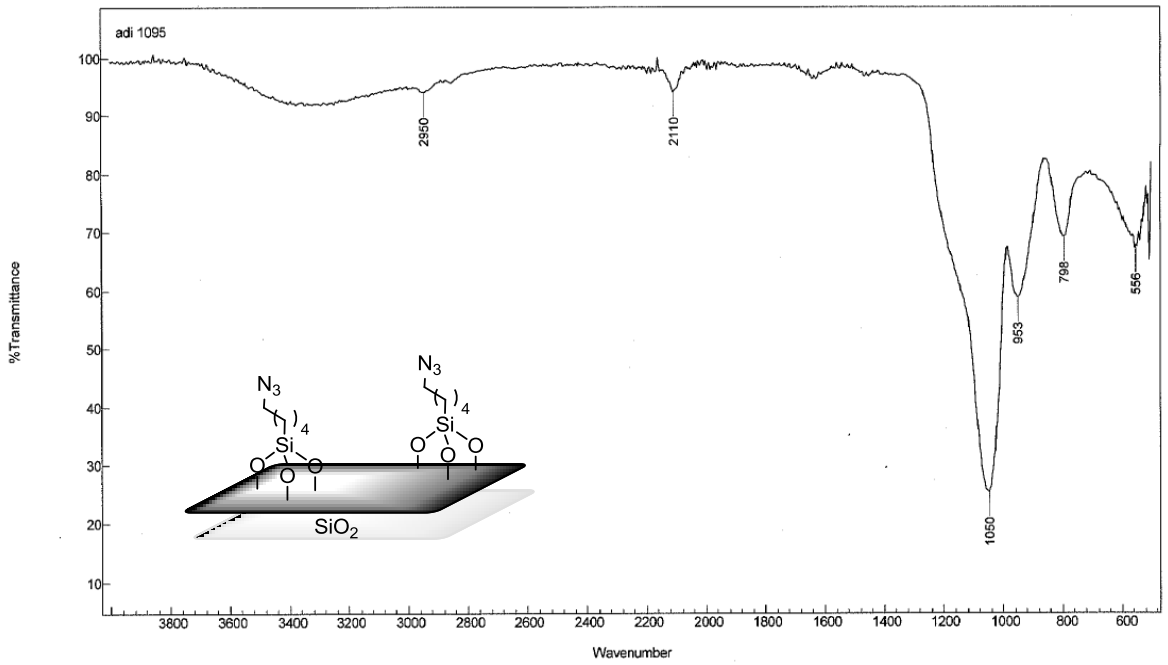


According to a procedure described by *Huh et al.*[9] Cetyl trimethylammonium bromide (CTAB, 2.0 g, 5.49 mmol) and NaOH (7.00 mL, 2 M, 14.0 mmol) in H_2O (480 mL) were stirred for 30 min at 80 °C. Subsequently Tetraethyl orthosilicate **1** (TEOS) (10.0 mL, 44.8 mmol, 10.0 eq.) and the corresponding azide (1.23 g, 4.46 mmol, 1.0 eq.) were added all at once and the reaction was stirred for additional 2 h at 80 °C. The white precipitate was filtered off and washed with copious amounts of water and MeOH. To remove the CTAB the particles were once again dissolved in MeOH (~100 mL per 1 g) and HCl (conc. 300 µL per 1 g) was added and the suspension was heated for another hour at 60 °C. Drying under high vacuum afforded the mesoporous silica nanoparticles (MSNs) as white solid (~2.5 g).

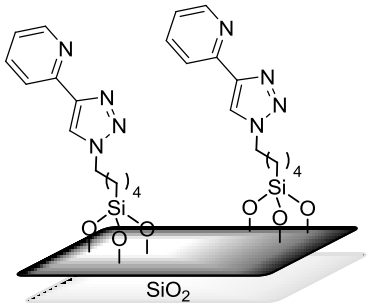
Elemental Anal.: C:14.76; H: 3.62; N: 9.16.



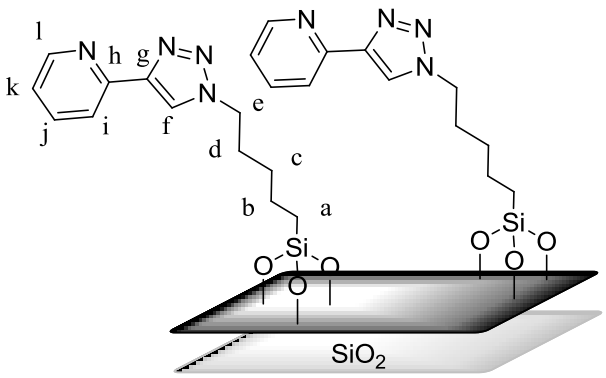
$^{13}C\{^{1}H\}$CPMAS-NMR spectrum of **3**.S marks signals of residual solvent. 5120 scans were accumulated using a recycle delay of 5 s.

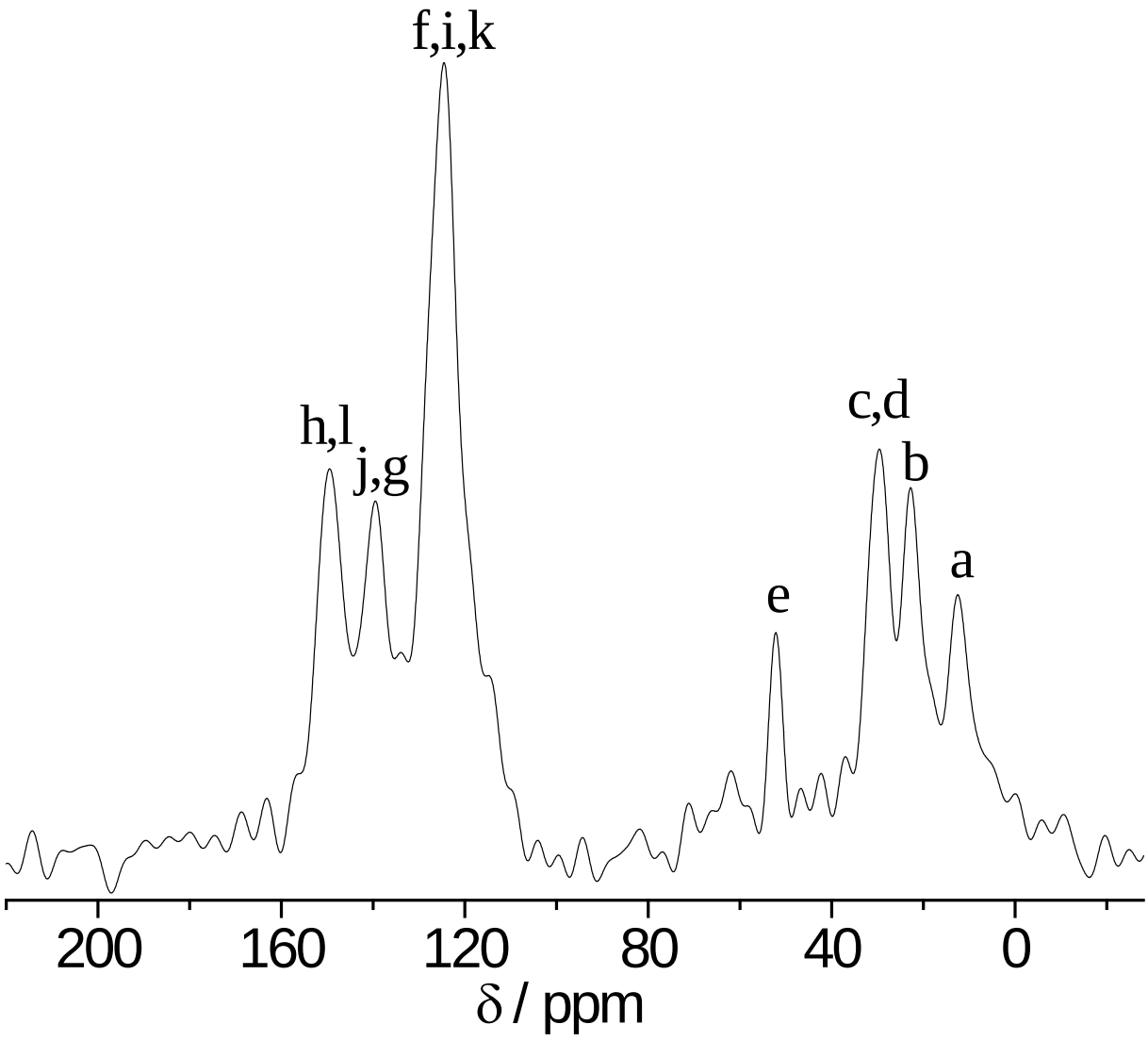


4.4.2 Pyridyl-functionalized particles [4]

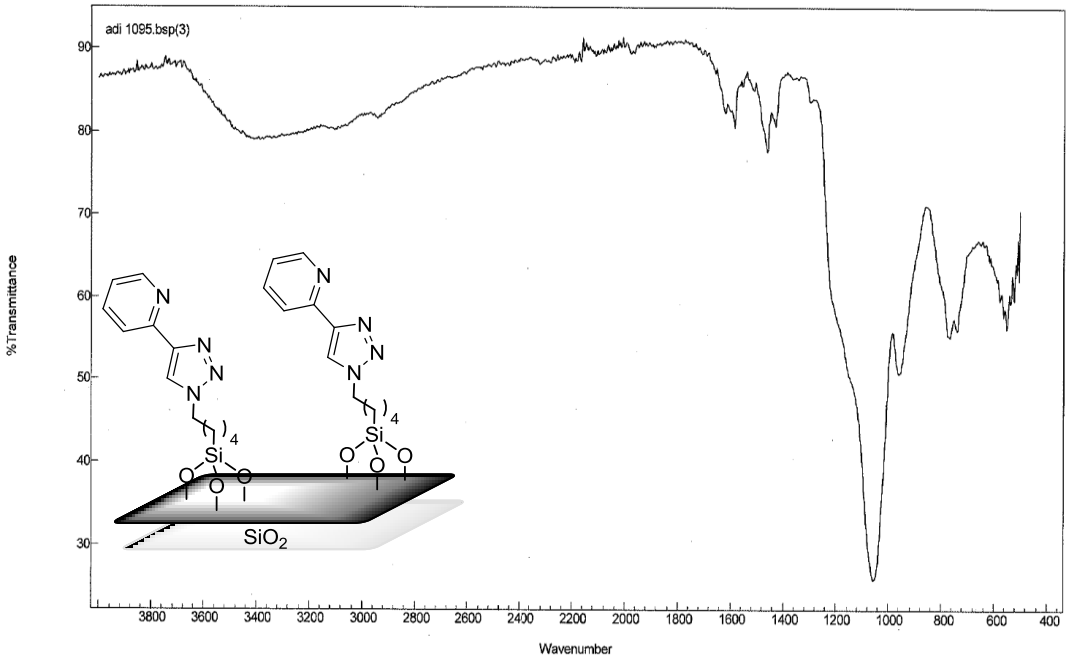


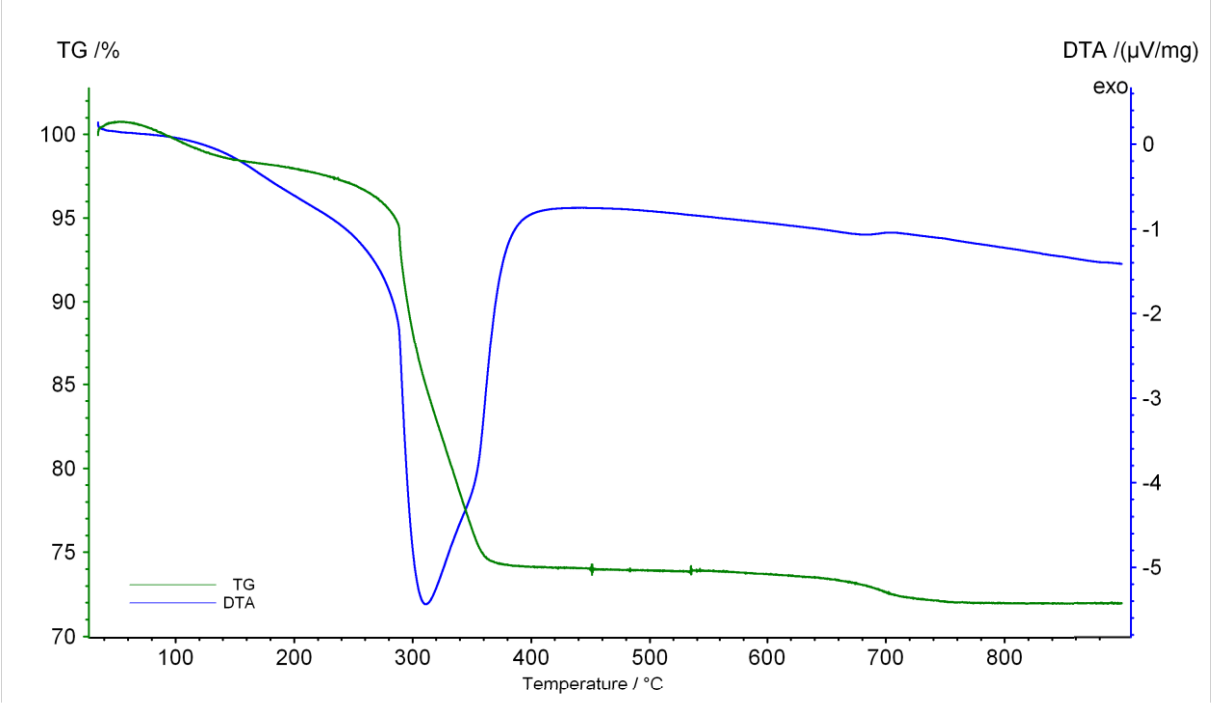
Azide functionalized particles **3** (2.0 g) were suspended in EtOH-H_2O (2-1, 45 mL) and $CuSO_4$ (200 mg, 1.25 mmol) and L-Ascorbic acid sodium salt (280 mg, 1.41 mmol) were added. Subsequently to the addition of 2-Ethynylpyridine (2.00 g, 19.4 mmol) the suspension was stirred at 90 °C for 8 h. The silica particles were filtered through a glass frit (Por.4) and washed with MeOH, DCM and Et_2O and subsequently dried *in vacuo*. The desired product was obtained as a brown powder.



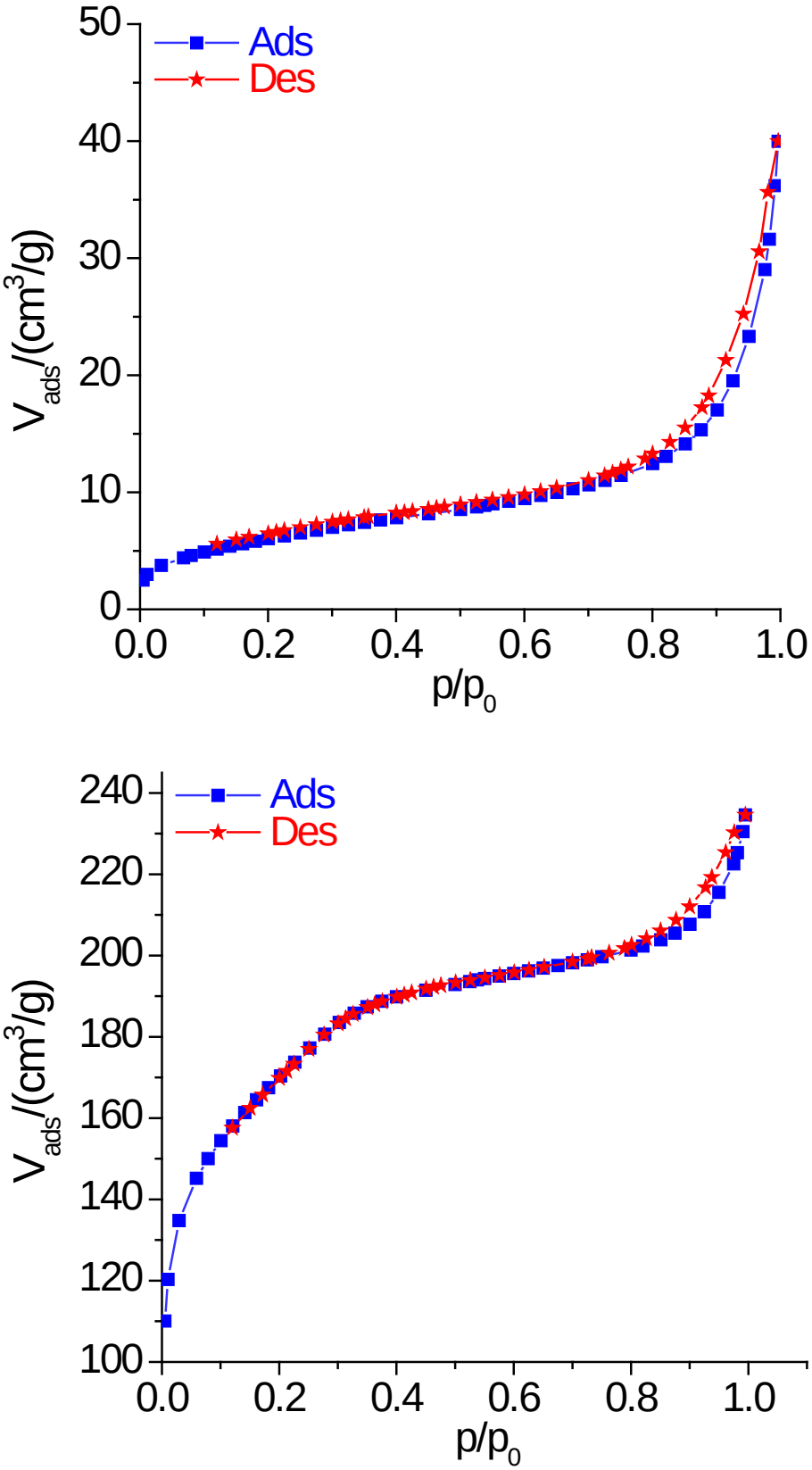


$^{13}C\{^{1}H\}$CPMAS-NMR spectrum of **4**. 14336 scans were accumulated using a recycle delay of 0.5 s.

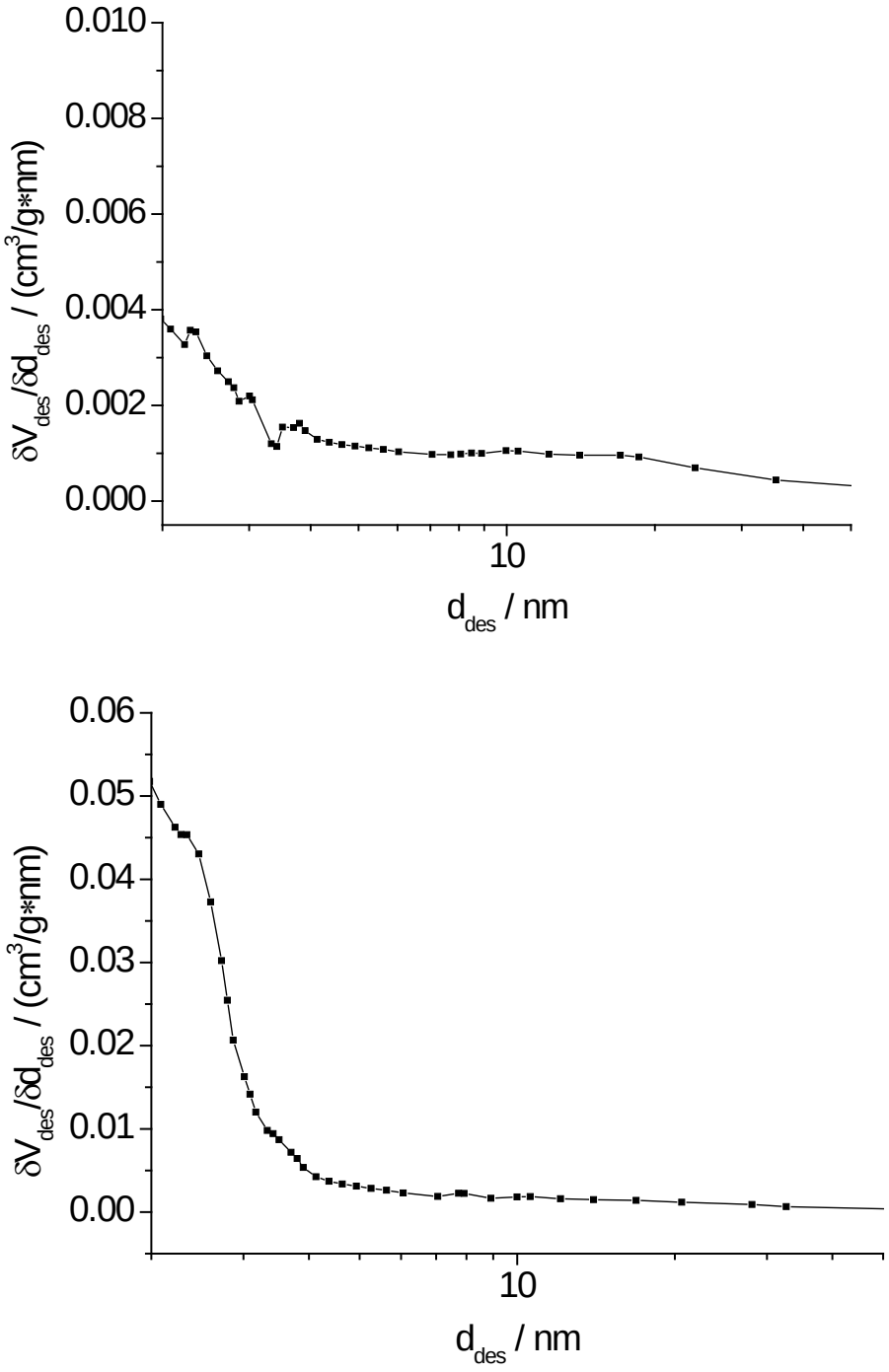




Thermogravimetric analysis of **4**.



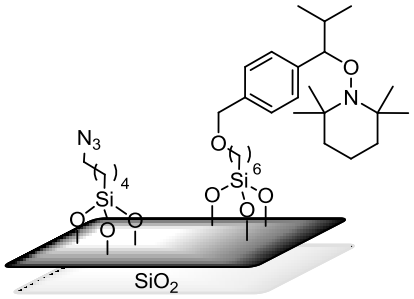
BET isotherms of **4** before (top) and after (bottom) 24 h calcination at 400 °C.



BJH plots of **4** before (top) and after (bottom) 24 h calcination at 400 °C.

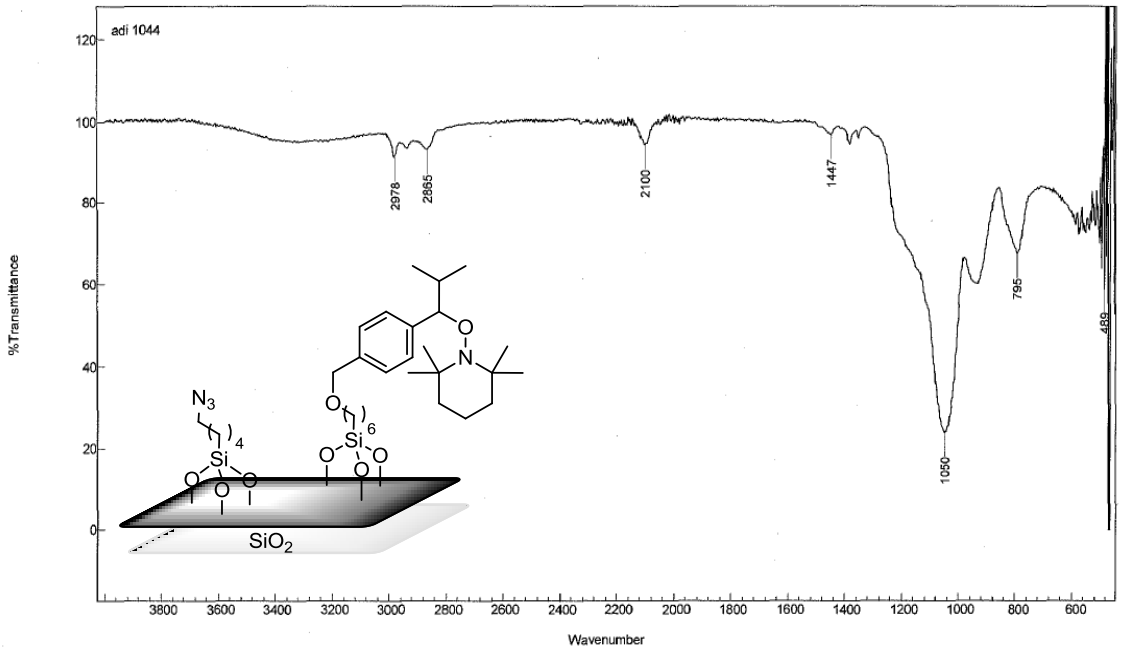
BET-Surface area: 22.7 m^2g^{-1} (before calcination) and 592.5 m^2g^{-1} (after calcination)

4.4.3 Azide-Alkoxyamine functionalized particles [7]

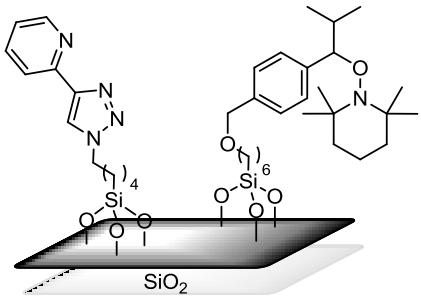


According to a procedure described by *Huh et al.*9 Cetyl trimethylammonium bromide (CTAB, 1.50 g, 4.12 mmol) and NaOH (5.25 mL, 2 M, 10.5 mmol) in H_2O (360 mL) were stirred for 30 min at 80 °C. Subsequently Tetraethyl orthosilicate **1** (TEOS) (6.64 mL, 30.0 mmol, 8.0 eq.), the corresponding azide (3.75 mmol, 1.0 eq.) and the corresponding alkoxyamine (3.75 mmol, 1.0 eq.) were added all at once and the reaction was stirred for additional 2 h at 80 °C. The white precipitate was filtered off and washed with copious amounts of water and MeOH. To remove the CTAB the particles were once again dissolved in MeOH (~100 mL per 1 g) and HCl (conc. 300 µL per 1 g) was added and the suspension was heated for another hour at 60 °C. Drying under high vacuum afforded the mesoporous silica nanoparticles (MSNs) as white solid (~2.5 g).

Elemental Anal.: C:12.49; H: 3.11; N: 3.10.

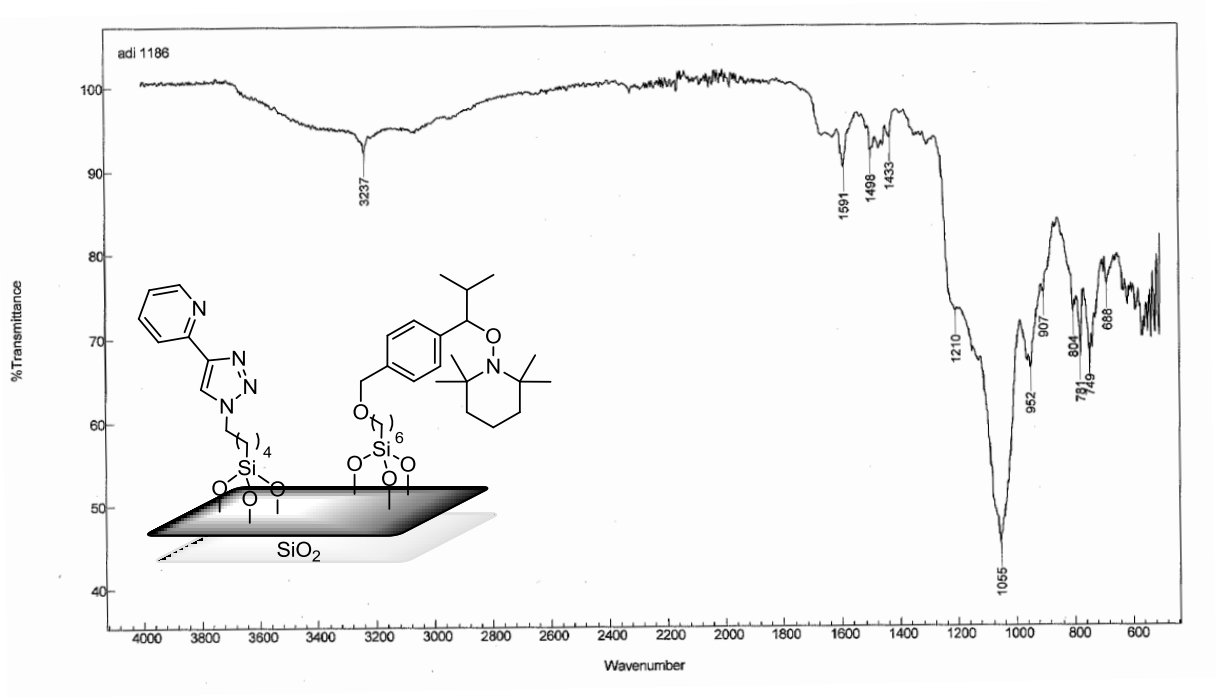


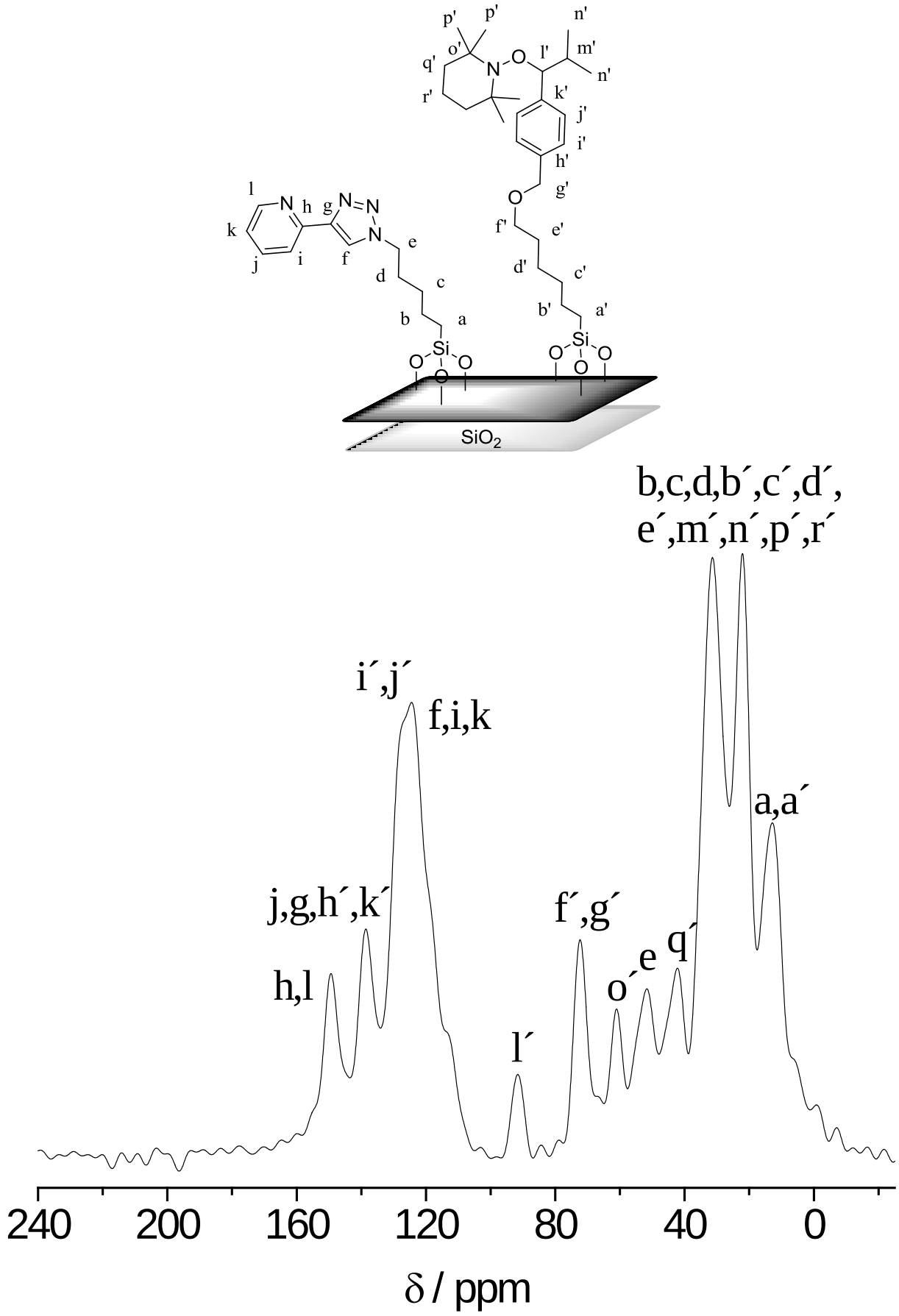
4.4.4 Pyridyl-Alkoxyamine functionalized particles [8]



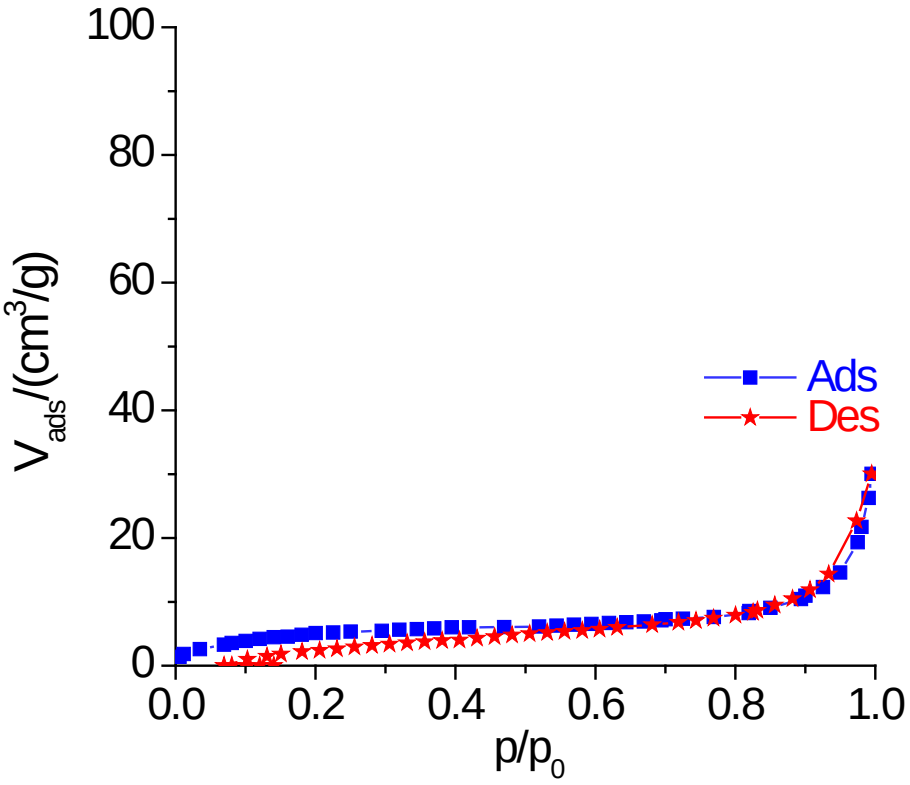
Azide-Alkoxyamine functionalized particles (500 mg) were suspended in EtOH-H_2O (2-1, 10 mL) and $CuSO_4$ (30 mg, 0.19 mmol) and L-ascorbic acid sodium salt (35 mg, 0.18 mmol) were added. After addition of 2-Ethynylpyridin (245 µL, 250 mg, 2.42 mmol) the suspension was stirred at 90 °C for 8 h. The silica particles were filtered through a glass frit (Por.4) and washed with MeOH, DCM and Et_2O and subsequently dried *in vacuo*. The desired product was obtained as a brown powder.

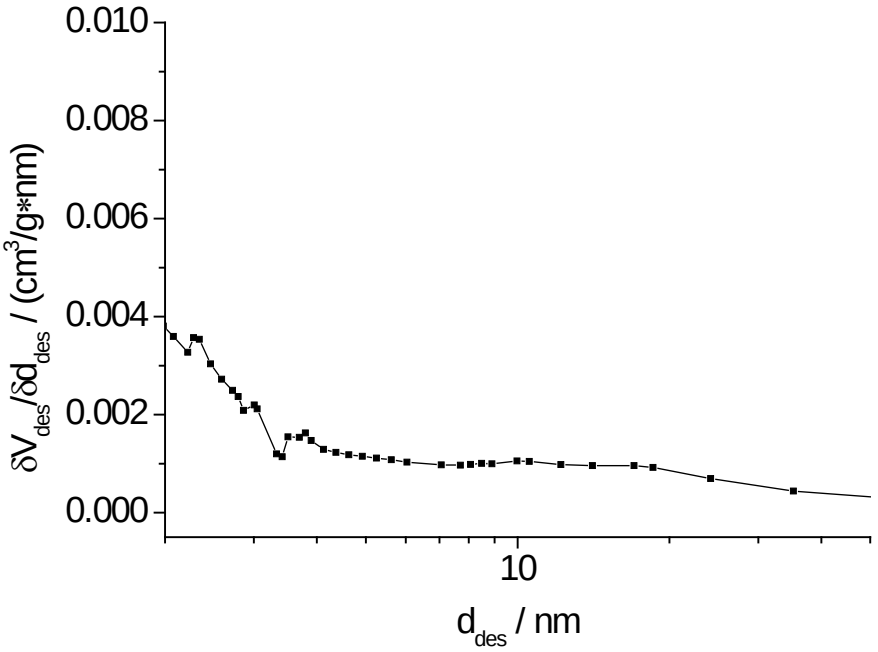
Elemental Anal.: C:22.48; H: 3.51; N: 3.68.





$^{13}C\{^{1}H\}$CPMAS-NMR spectrum of **8**. 107520 scans were accumulated using a recycle delay of 0.5 s.



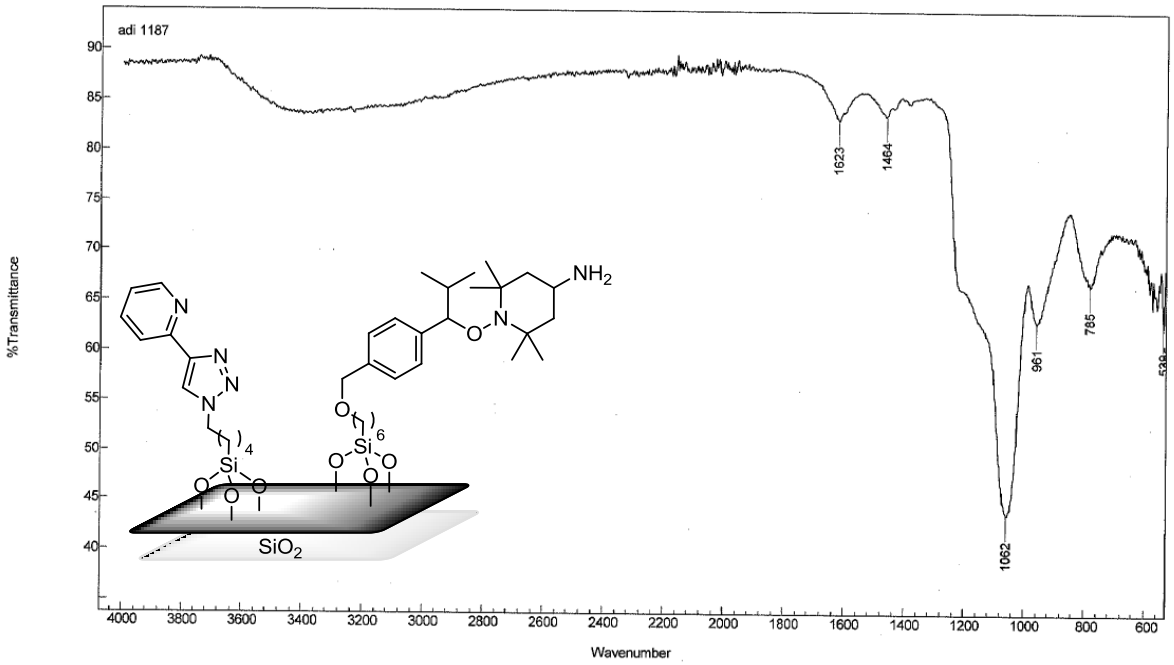


BET-Surface area: 28.5 m^2g^{-1}

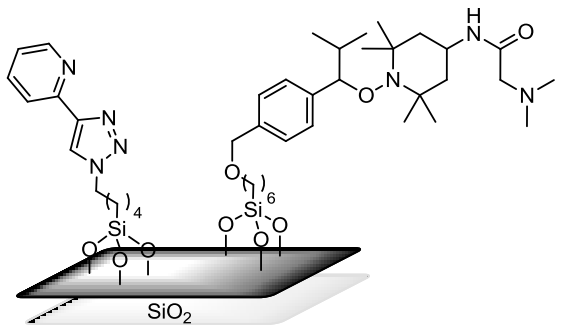
4.4.5 Pyridyl-Amino-TEMPO functionalized particles

Pyridyl-Alkoxyamine functionalized particles (120 mg) were suspended in DCE (5 mL) and mit 4-Amino-2,2,6,6-tetramethylpiperidin-*N*-oxyl (120 mg, 0.701 mmol) was added. Subsequently the reaction mixture was stirred in a pressure resistant Schlenktube at 125 °C for 24 h. The silica particles were filtered through a glass frit (Por.4) and washed with MeOH, DCM and Et_2O and subsequently dried *in vacuo*. The desired product was obtained as a brown powder.

Elemental Anal.: C:25.27; H: 3.88; N: 5.95.

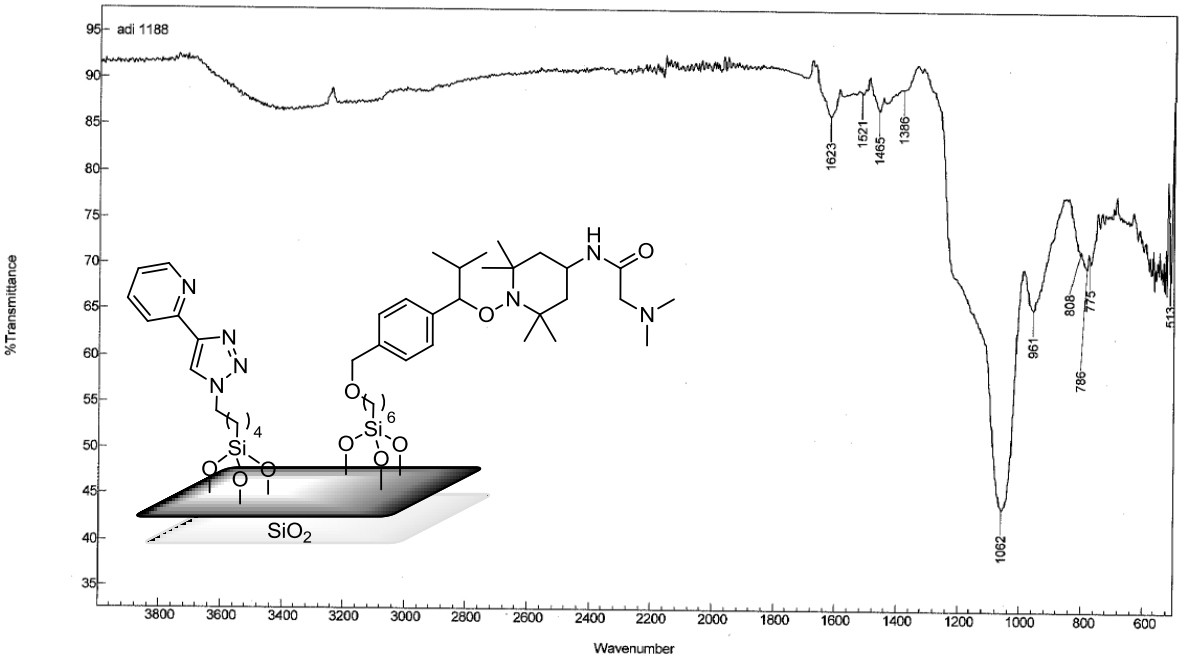


4.4.6 Pyridyl-Dimethylamine functionalized particles

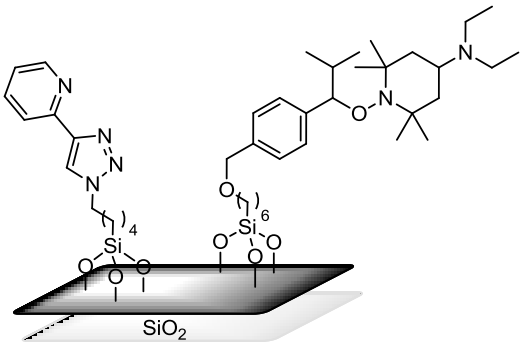


Pyridyl-Alkoxyamine functionalized particles (500 mg) were suspended in DCE (10 mL) and 2-(Dimethylamino)-*N*-(1-oxy-2,2,6,6-tetra-methylpiperidine-4-yl)acetamide (500 mg, 2.26 mmol) was added. Subsequently the reaction mixture was stirred in a pressure resistant Schlenktube at 125 °C for 24 h. The silica particles were filtered through a glass frit (Por.4) and washed with MeOH, DCM and Et_2O and subsequently dried *in vacuo*. The desired product was obtained as a brown powder.

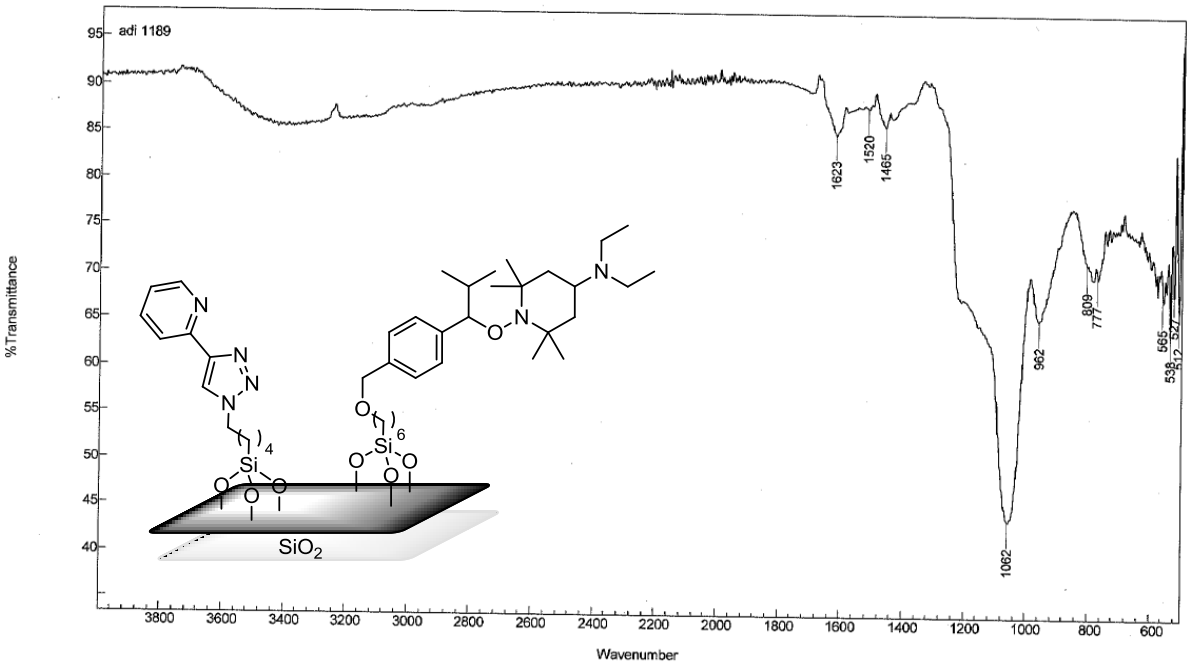
Elemental Anal.: C:23.23; H: 3.80; N: 4.46.



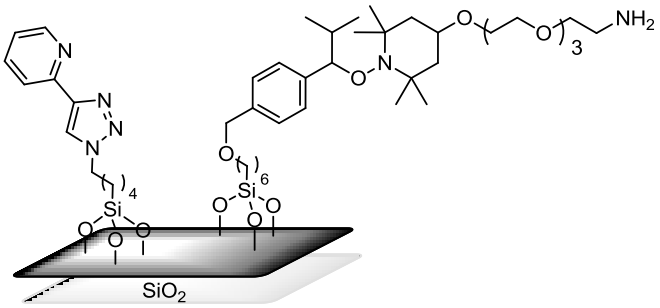
4.4.7 Pyridyl-Diethylamin functionalized particles



Pyridyl-Alkoxyamine functionalized particles (160 mg) were suspended in DCE (6 mL) and *N*,*N*-diethylamino-TEMPO (160 mg, 0.704 mmol) was added. Subsequently the reaction mixture was stirred in a pressure resistant Schlenktube at 125 °C for 24 h. The silica particles were filtered through a glass frit (Por.4) and washed with MeOH, DCM and Et_2O and subsequently dried *in vacuo*. The desired product was obtained as a brown powder.



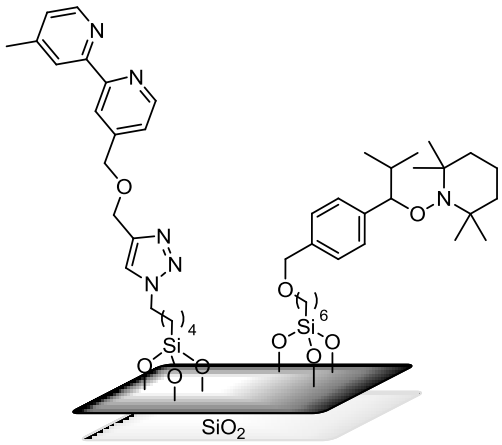
Pyridyl-PEGamine functionalized particles



Pyridyl-Alkoxyamine functionalized particles (120 mg) were suspended in DCE (5 mL) and PEG-Amino-TEMPO (120 mg, 0.330 mmol) was added. Subsequently the reaction mixture was stirred in a pressure resistant Schlenktube at 125 °C for 24 h. The silica particles were filtered through a glass frit (Por.4) and washed with MeOH, DCM and Et_2O and subsequently dried *in vacuo*. The desired product was obtained as a brown powder.

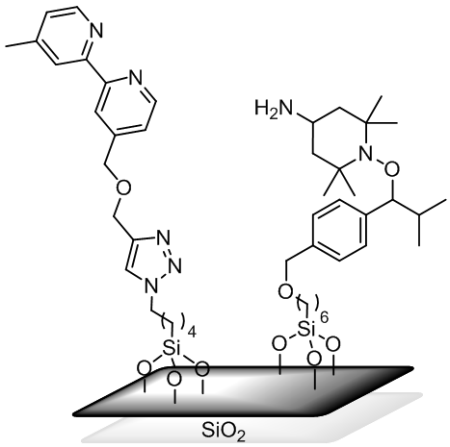
Elemental Anal.: C:27.15; H: 3.87; N: 4.30.

4.4.8 Bipyridyl-Alkoxyamine functionalized particles



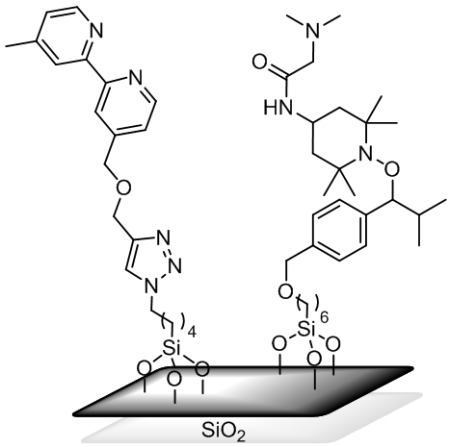
Azide-Alkoxyamine functionalized particles (120 mg) were suspended in EtOH-H_2O (2-1, 4 mL) and $CuSO_4$ (30 mg, 0.19 mmol) and L-ascorbic acid sodium salt (35 mg, 0.18 mmol) were added. After addition of the alkyne (120mg, 0.504 mmol) the suspension was stirred at 90 °C for 8 h. The silica particles were filtered through a glass frit (Por.4) and washed with H_2O, HCl (aq., 2 M) MeOH, DCM and Et_2O and subsequently dried *in vacuo*. The desired product was obtained as a brown powder.

4.4.9 Bipyridyl-Amino-TEMPO particles



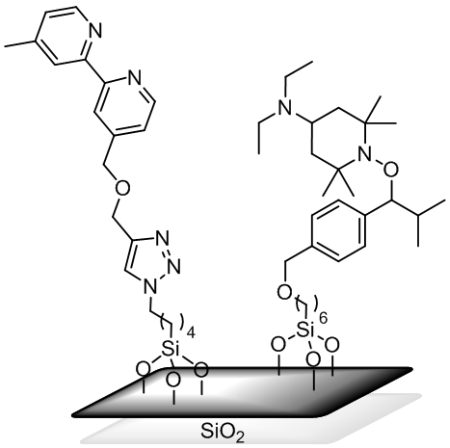
Bipyridyl-Alkoxyamine functionalized (50 mg) particles were suspended in DCE (3 mL) and Amino-TEMPO (50 mg, 0.27 mmol) was added. Subsequently the reaction mixture was stirred in a pressure resistant Schlenktube at 125 °C for 24 h. The silica particles were filtered through a glass frit (Por.4) and washed with MeOH, DCM and Et_2O and subsequently dried *in vacuo*. The desired product was obtained as a brown powder.

4.4.10 Bipyridyl-Dimethylamino-TEMPO particles



Bipyridyl-Alkoxyamine functionalized (86 mg) particles were suspended in DCE (2 mL) and 2-(Dimethylamino)-*N*-(1-oxy-2,2,6,6-tetra-methyl-piperidine-4-yl)acetamid (50 mg, 0.195 mmol) was added. Subsequently the reaction mixture was stirred in a pressure resistant Schlenktube at 125 °C for 24 h. The silica particles were filtered through a glass frit (Por.4) and washed with MeOH, DCM and Et_2O and subsequently dried *in vacuo*. The desired product was obtained as a brown powder.

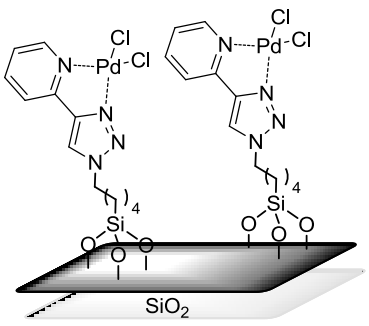
4.4.11 Bipyridyl-Diethylamino-TEMPO particles



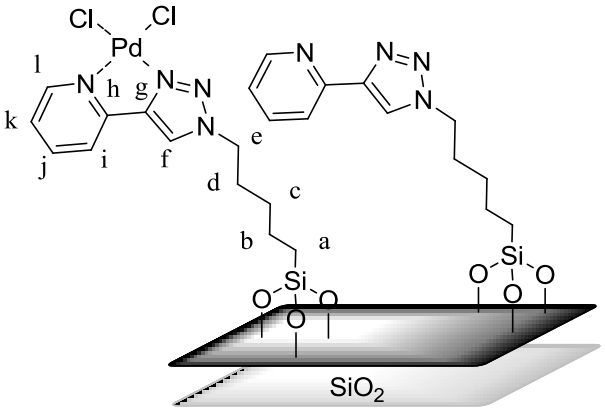
Bipyridyl-Alkoxyamine functionalized (86 mg) particles were suspended in DCE (2 mL) and Diethylamino-TEMPO (86 mg, 0.35 mmol) was added. Subsequently the reaction mixture was stirred in a pressure resistant Schlenktube at 125 °C for 24 h. The silica particles were filtered through a glass frit (Por.4) and washed with MeOH, DCM and Et_2O and subsequently dried *in vacuo*. The desired product was obtained as a brown powder.

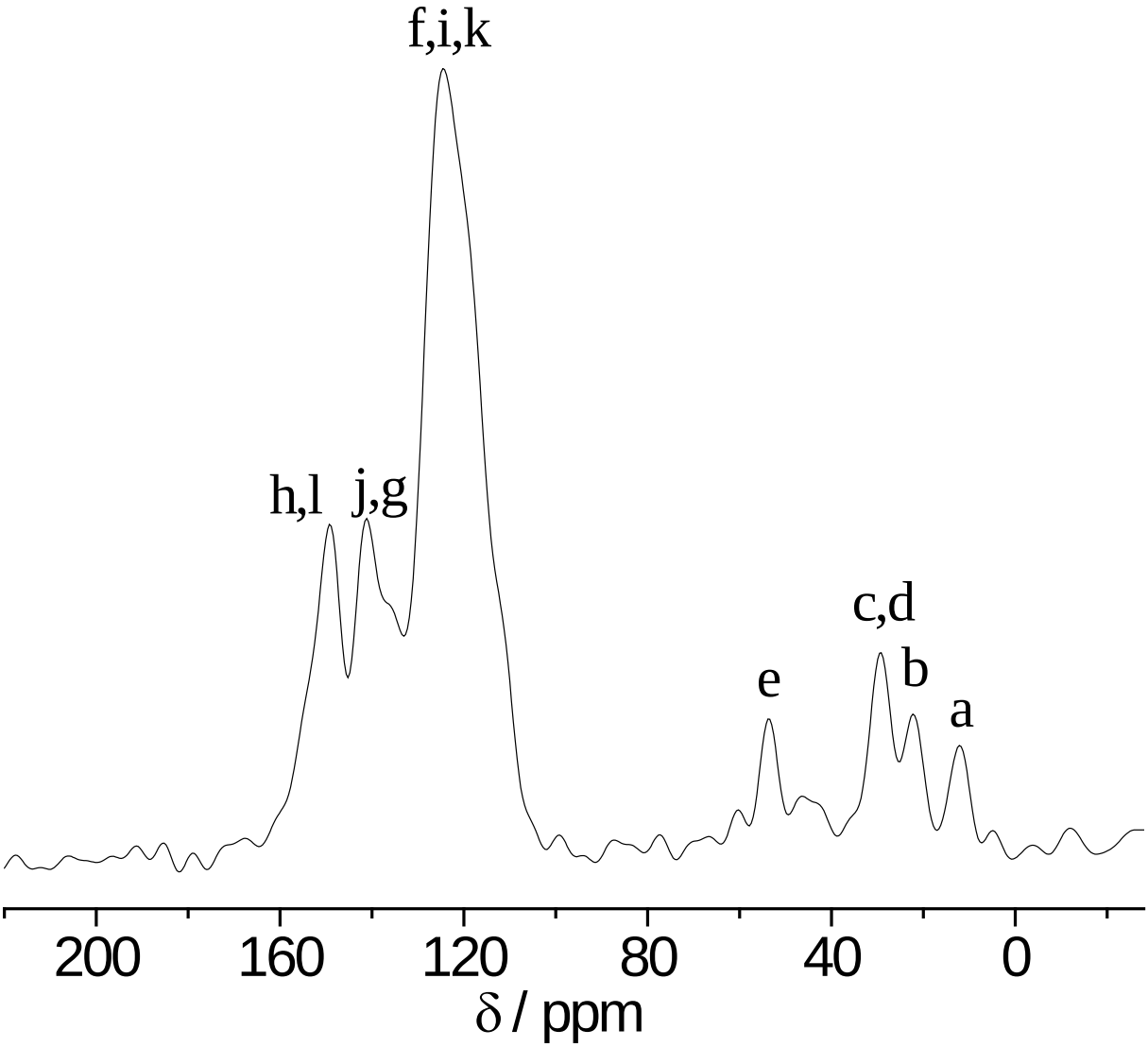
4.5 Synthesis of the palladium-loaded particles for catalysis

4.5.1 Palladium-functionalized particles [5]

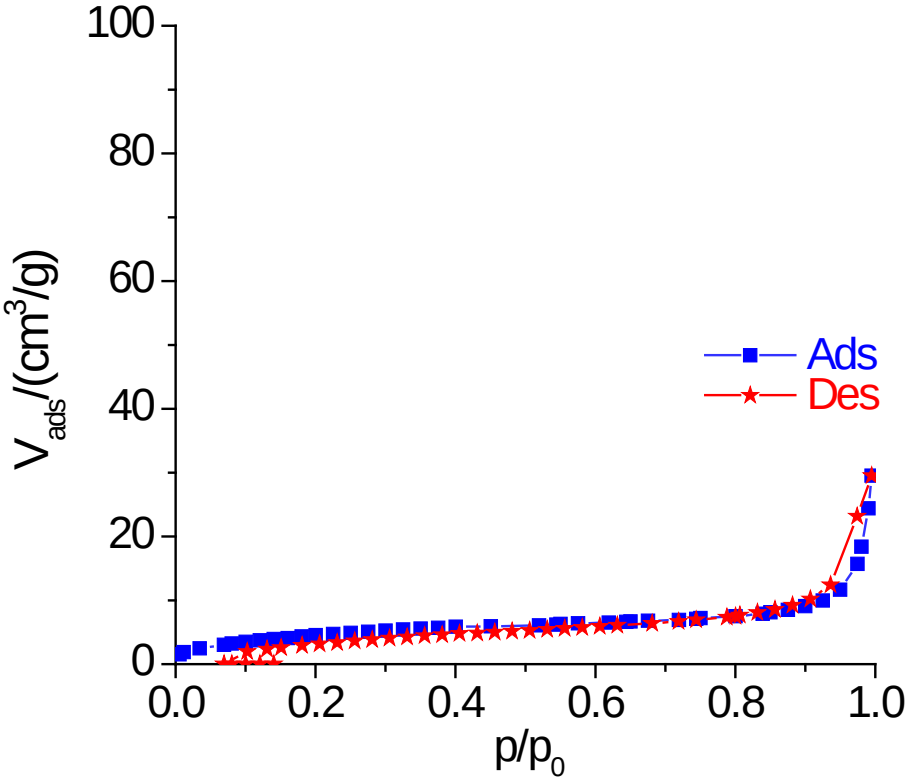


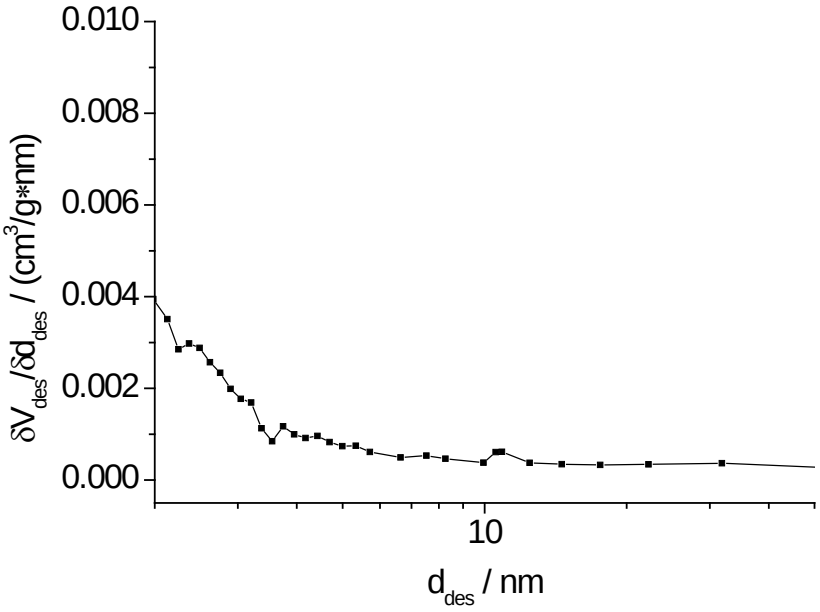
Pyridyl-functionalized particles (100 mg) were suspended in EtOH-H_2O (2-1, 4 mL) and $PdCl_2$ (100 mg, 0.565 mmol) was added. Subsequently the suspension was stirred at rt for 2 h and ultrasonicated for 15 min. The silica particles were filtered through a glass frit (Por.4) and washed with MeOH, DCM and Et_2O and subsequently dried *in vacuo*. The desired product **5** was obtained as a black powder and used for catalysis.





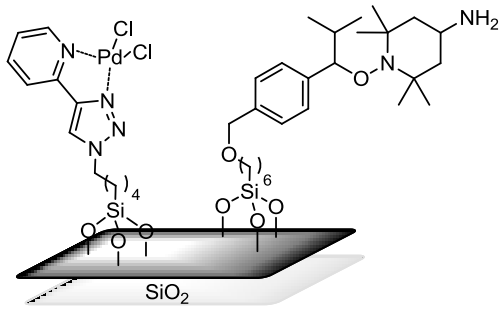
$^{13}C\{^{1}H\}$CPMAS-NMR spectrum of **5**. 55296 scans were accumulated using a recycle delay of 0.5 s.





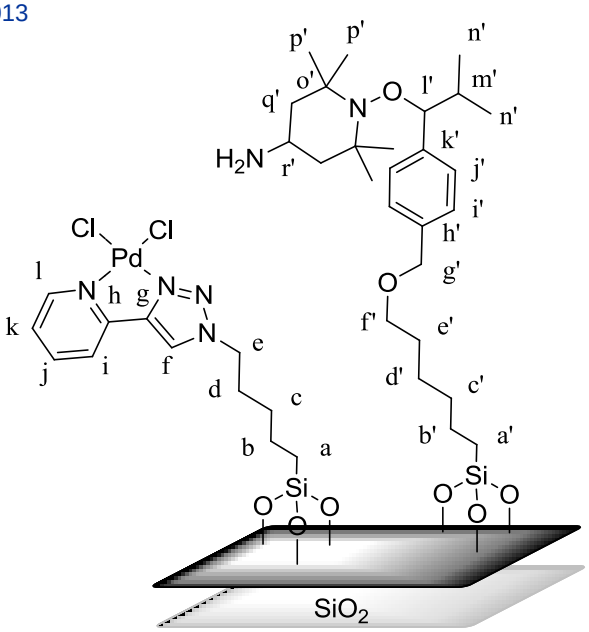
BET-Surface area: 17.8 m^2g^{-1}

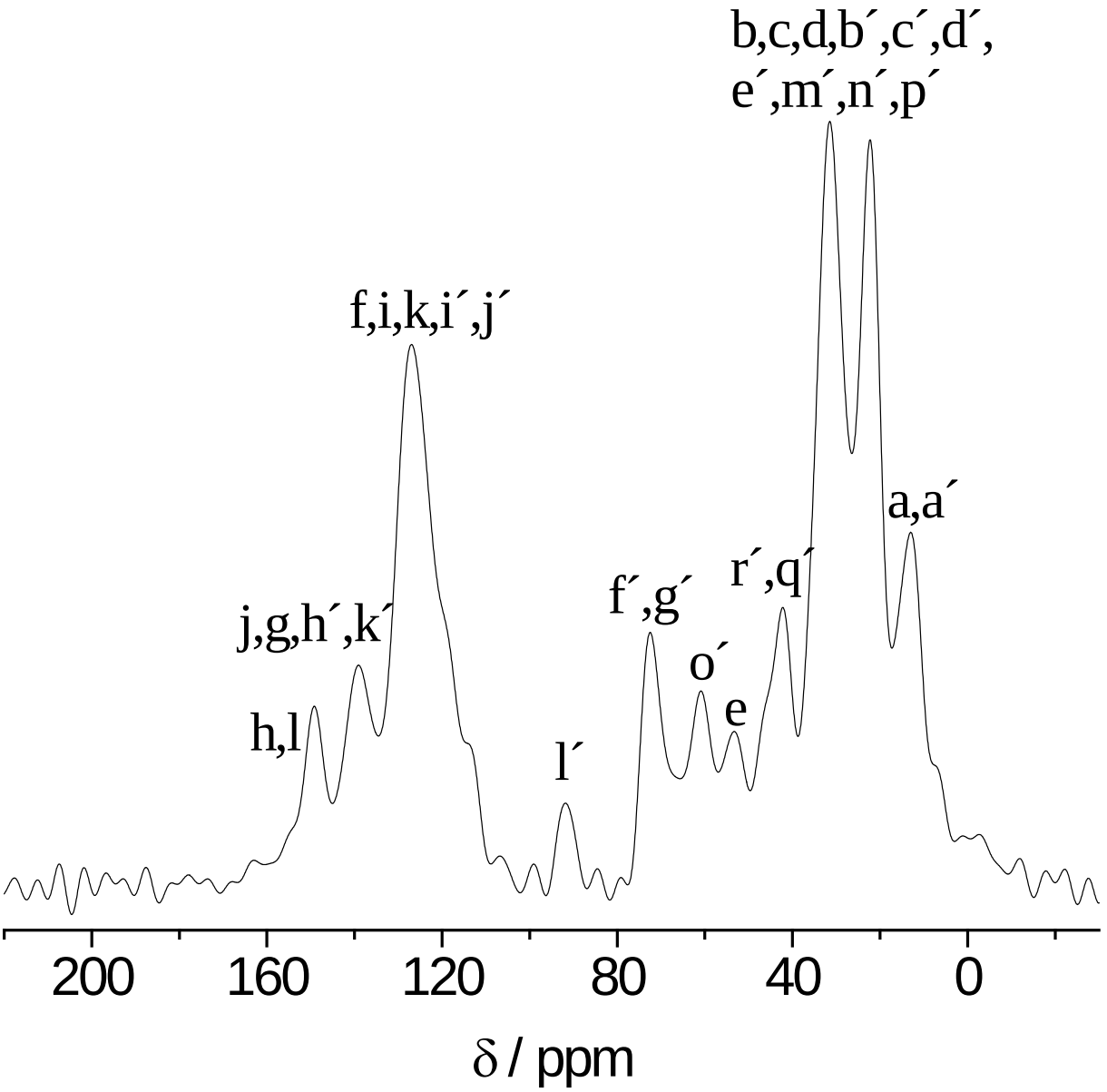
4.5.2 Palladium-Amino-TEMPO functionalized particles [9]



Pyridyl-Amino-TEMPO functionalized particles (80 mg) were suspended in EtOH-H_2O (2-1, 4 mL) and $PdCl_2$ (80 mg, 0.45 mmol) was added. Subsequently the suspension was stirred at rt for 2 h and ultrasonicated for 15 min. The silica particles were filtered through a glass frit (Por.4) and washed with MeOH, DCM and Et_2O and subsequently dried *in vacuo*. The desired product was obtained as a black powder and used for catalysis.

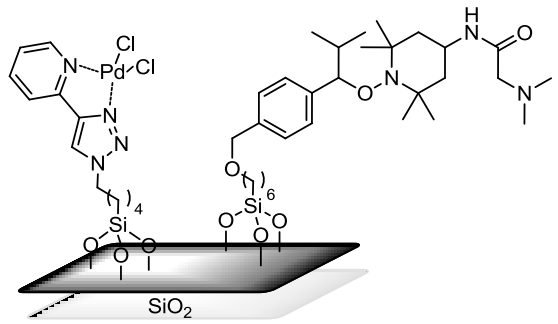
Elemental Anal.: C:13.92; H: 1.99; N: 3.20.





$^{13}C\{^{1}H\}$CPMAS-NMR spectrum of **9**. 49152 scans were accumulated using a recycle delay of 0.5 s.

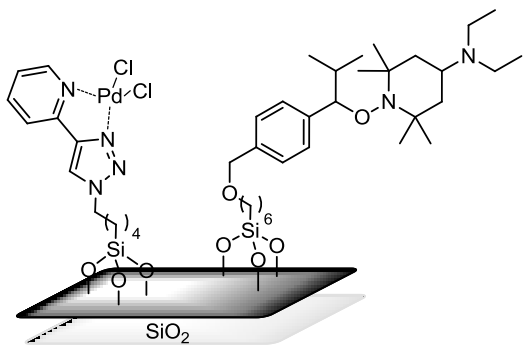
4.5.3 Palladium-Dimethylamin functionalized particles [10]



Pyridyl-Dimethylamine functionalized particles (400 mg) were suspended in EtOH-H_2O (2-1, 10 mL) and $PdCl_2$ (400 mg, 2.26 mmol) was added. Subsequently the suspension was stirred at rt for 2 h and ultrasonicated for 15 min. The silica particles were filtered through a glass frit (Por.4) and washed with MeOH, DCM and Et_2O and subsequently dried *in vacuo*. The desired product was obtained as a black powder and used for catalysis.

Elemental Anal.: C:14.51; H: 2.04; N:2.39.

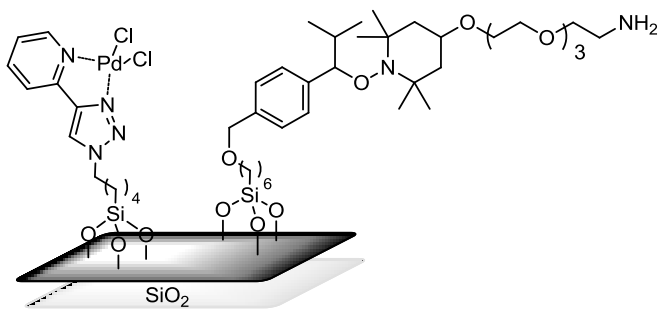
4.5.4 Palladium-Diethylamine functionalized particles [11]



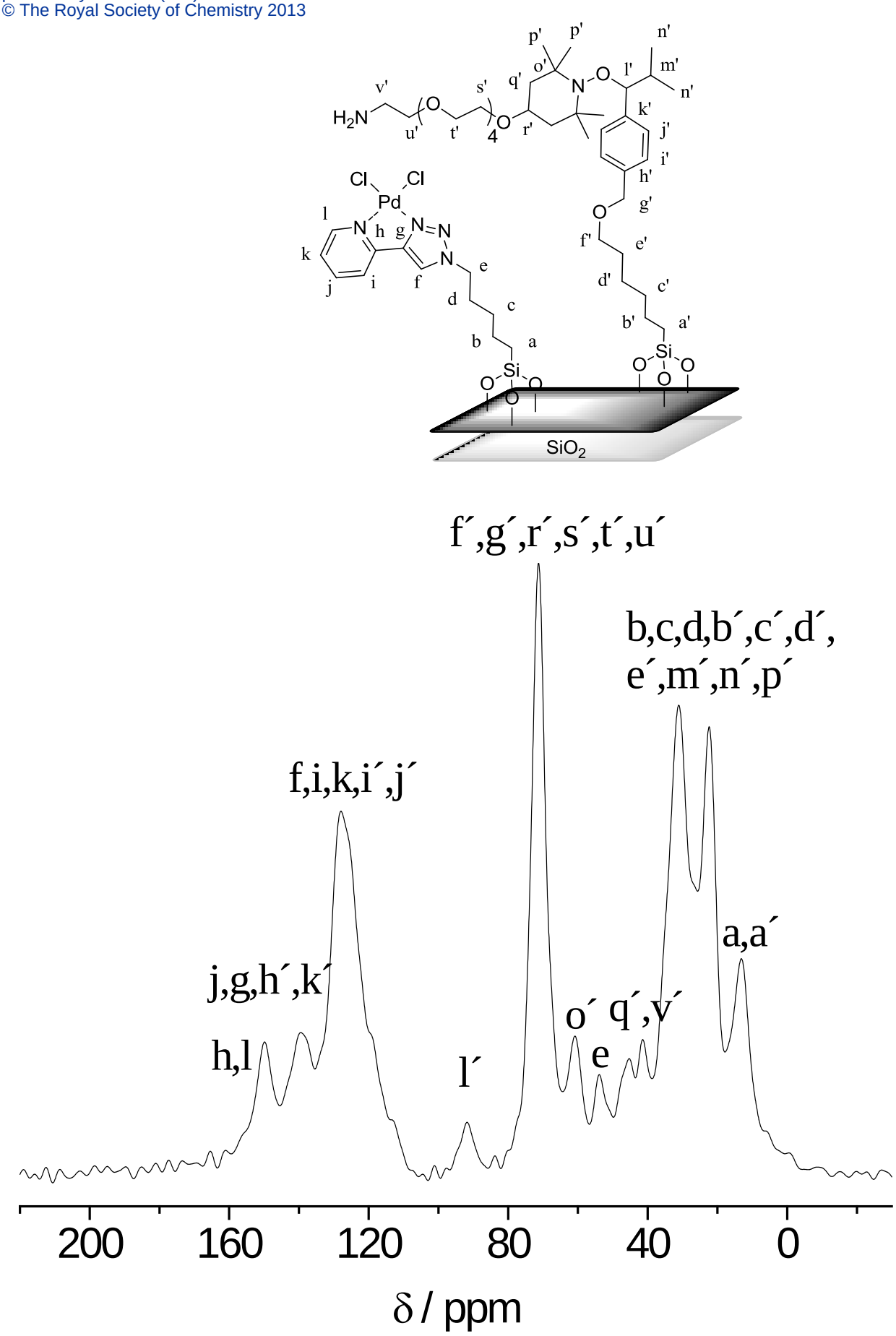
Pyridyl-Diethylamine functionalized particles (90 mg) were suspended in EtOH-H_2O (2-1, 2 mL) and $PdCl_2$ (90 mg, 0.51 mmol) was added. Subsequently the suspension was stirred at rt for 2 h and ultrasonicated for 15 min. The silica particles were filtered through a glass frit (Por.4) and washed with MeOH, DCM and Et_2O and subsequently dried *in vacuo*. The desired product was obtained as a black powder and used for catalysis.

Elemental Anal.: C:14.08; H: 1.76; N: 2.32.

4.5.5 Palladium-PEGamine functionalized particles [12]

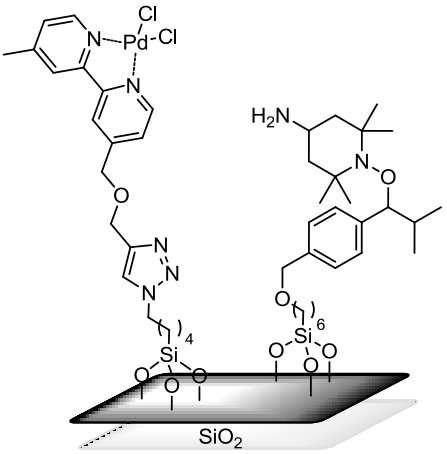


Pyridyl-PEGamine functionalized particles (80 mg) were suspended in EtOH-H_2O (2-1, 2 mL) and $PdCl_2$ (80 mg, 0.45 mmol) was added. Subsequently the suspension was stirred at rt for 2 h and ultrasonicated for 15 min. The silica particles were filtered through a glass frit (Por.4) and washed with MeOH, DCM and Et_2O and subsequently dried *in vacuo*. The desired product was obtained as a black powder and used for catalysis.

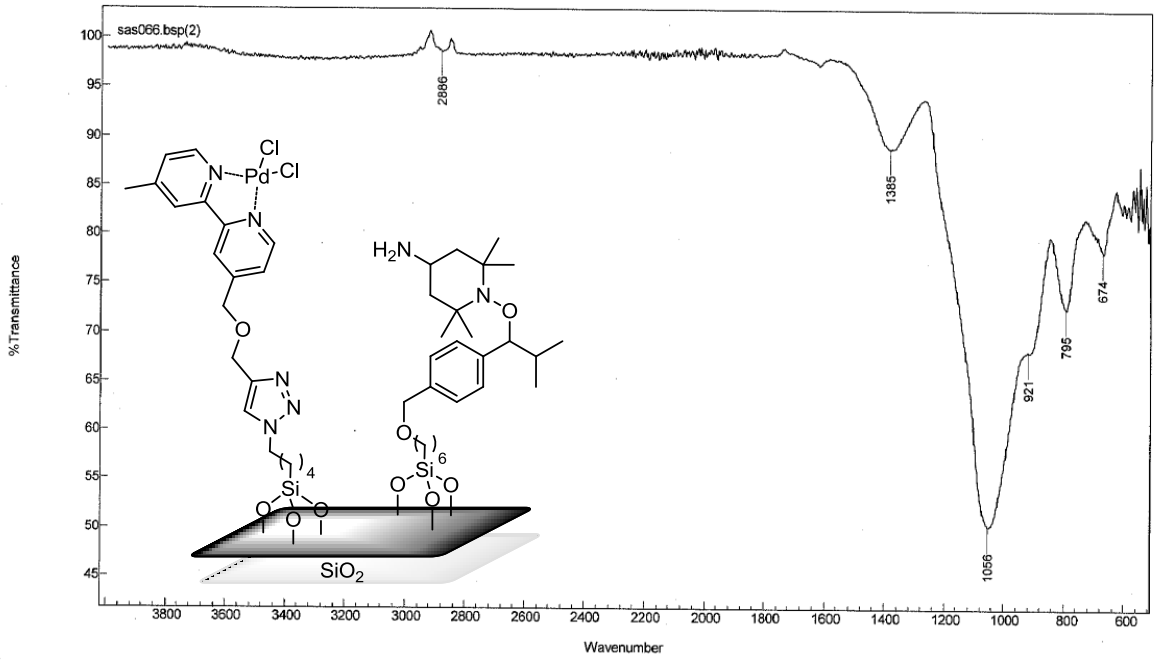


$^{13}C\{^{1}H\}$CPMAS-NMR spectrum of **12**. 106469 scans were accumulated using a recycle delay of 0.5 s.

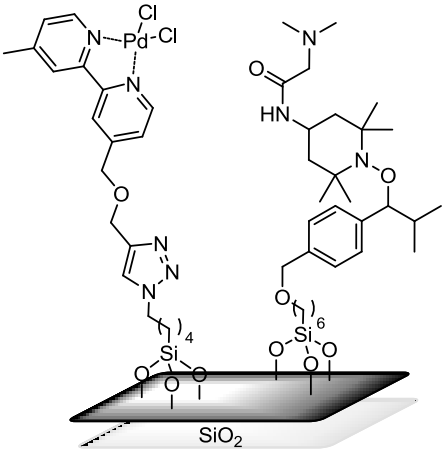
4.5.6 Bipyridyl-Palladium-Amino-TEMPO functionalized particles [16]



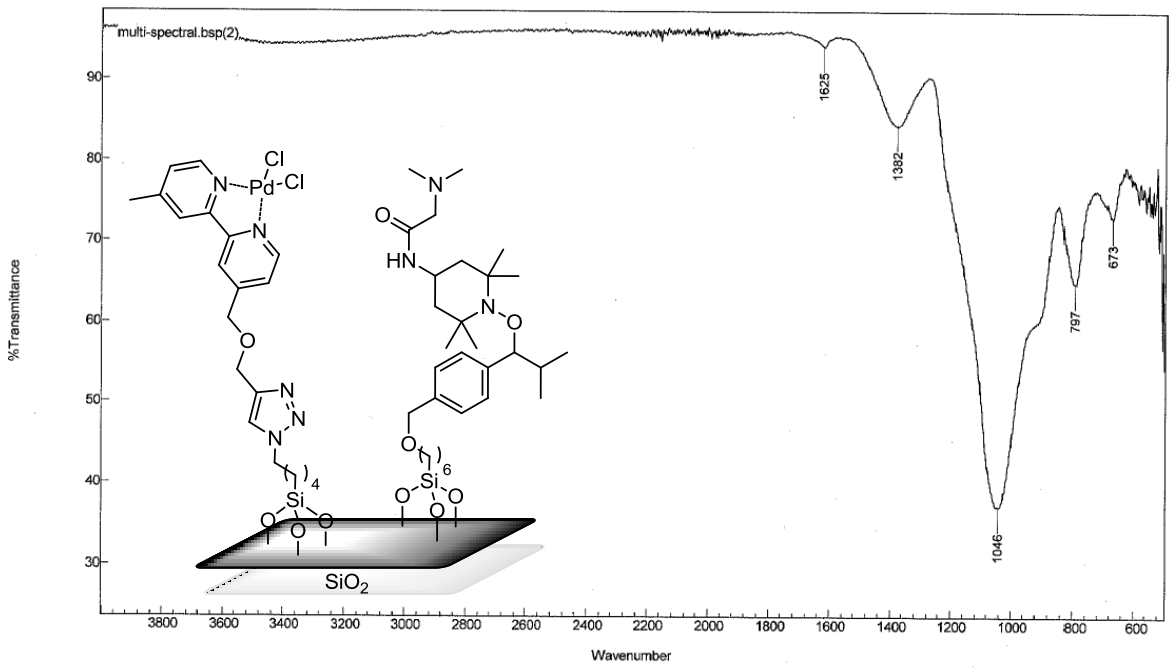
Bipyridyl-Amino-TEMPO functionalized particles (40 mg) were suspended in EtOH-H_2O (1-1, 2 mL) and $PdCl_2$ (40 mg, 0.23 mmol) was added. Subsequently the suspension was stirred at rt for 2 h and ultrasonicated for 15 min. The silica particles were filtered through a glass frit (Por.4) and washed with MeOH, DCM and Et_2O and subsequently dried *in vacuo*. The desired product was obtained as a black powder and used for catalysis.



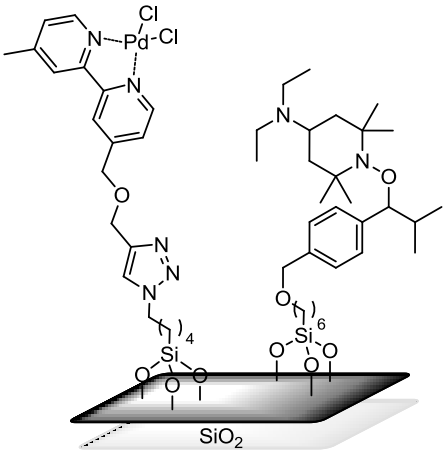
4.5.7 Bipyridyl-Palladium-Dimethylamino-TEMPO functionalized particles [17]



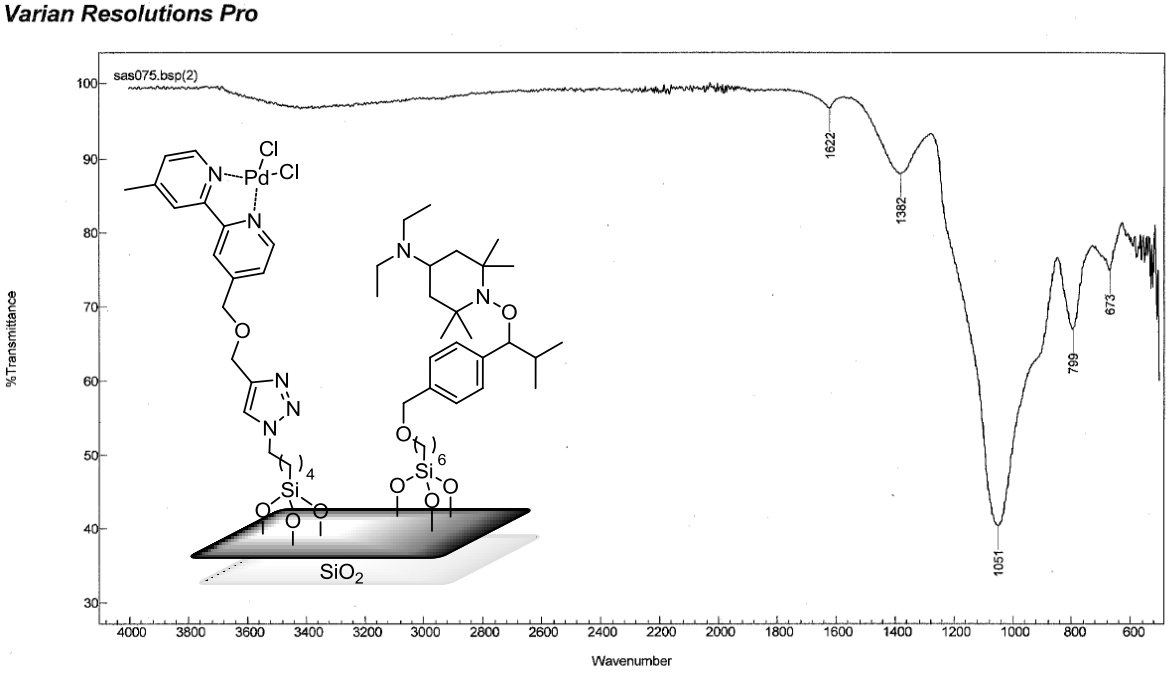
Bipyridyl-Dimethylamino-TEMPO functionalized particles (40 mg) were suspended in EtOH-H_2O (1-1, 2 mL) and $PdCl_2$ (40 mg, 0.23 mmol) was added. Subsequently the suspension was stirred at rt for 2 h and ultrasonicated for 15 min. The silica particles were filtered through a glass frit (Por.4) and washed with MeOH, DCM and Et_2O and subsequently dried *in vacuo*. The desired product was obtained as a black powder and used for catalysis.



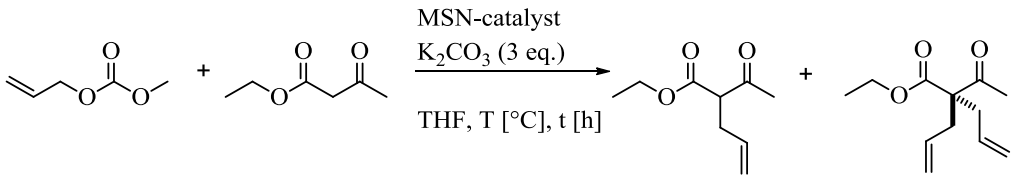
4.5.8 Bipyridyl-Palladium-Diethylamino-TEMPO functionalized particles [18]



Bipyridyl-Diethylamino-TEMPO functionalized particles (40 mg) were suspended in EtOH-H_2O (1-1, 2 mL) and $PdCl_2$ (40 mg, 0.23 mmol) was added. Subsequently the suspension was stirred at rt for 2 h and ultrasonicated for 15 min. The silica particles were filtered through a glass frit (Por.4) and washed with MeOH, DCM and Et_2O and subsequently dried *in vacuo*. The desired product was obtained as a black powder and used for catalysis.



4.6 Conduction of the *Tsuji-Trost* reaction using the bifunctional Palladium-Amine functionalized particles



12 **13** **14** **15**

In a heatgun dried Schlenktube bifunctionalized particles (50 mg or 25 mg respectively) and K_2CO_3 (365 mg or 183 mg, 2.64 mmol or 1.37 mmol) were suspended in THF (2 mL or 1 mL). Subsequently allyl methyl carbonate (283 µL or 142 µL, 289 mg or 130 mg, 2.50 mmol or 1.25 mmol) and ethyl acetoacetate (126 µL or 63 µL, 130 mg or 65 mg, 1.00 mmol or 0.50 mmol) were added. The reaction mixture was stirred at variable temperatures. Isolation of the product was conducted by filtration of the particles and extraction with DCM. For additional catalytic cycles the particles were washed with H_2O, MeOH, DCM and Et_2O and used again.

5 References

[1] A. T. Dickschat, F. Behrends, M. Bühner, J. Ren, M. Weiß, H. Eckert and A. Studer, *Chem. Eur. J.* DOI: 10.1002/chem.201200499.

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