Supporting Information

Facile Synthesis of Optically Active Helical Poly(phenyl isocyanide)s Brushes on Silicon Surface and Their Chiral Resolution Ability

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General consideration. The ^{1}H, ^{13}C NMR spectra were recorded using a Bruker 600 or 400 MHz spectrometer {H},Size exclusion chromatography (SEC) was performed on Waters 1515 pump and Waters 2414 differential refractive index (RI) detector (set at 40 °C) using a series of linear Styragel HR1, HR2 and HR4 columns. Molecular weight (M_n) and polydispersity (M_w/M_n) data are reported relative to polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 0.3 mL/min. FT-IR spectra were recorded on Perkin-Elmer Spectrum BX FT-IR system. ATR-FTIR spectra was performed on the surface of the diamond ATR crystal. UV-vis spectra were performed on a UNIC 4802 UV/VIS double beam spectrophotometer in 1.0 cm length quartz cell. Circular dichroism (CD) spectra were obtained in a 1.0 mm quartz cell at 25 °C using a JASCO J1500 spectropolarimeter. The polymer concentration was calculated on the basis of the repeated units and was 0.2 mg/mL. The optical rotations were measured in $CHCl_3$ at room temperature using a 10.0 cm quartz cell on a WZZ-2B polarimeter. Analytical high performance liquid chromatography (HPLC) was carried out on SHIMADZU LC-20AT equipment using chiral OD-H column. Atomic force microscopy (AFM) images were acquired in tapping mode with a Digital instruments dimension 3100 scanning probe microscope performed at room temperature. X-Ray photoelectron spectroscopy (XPS) characterization was performed on a Thermo ESCALAB250XI spectrometer using AlKa radiation (1486.6 eV) operated at 150 W. The spectra were calibrated by adjusting the binding energy of C_{1s} to 284.6 eV. XPS spectra were analyzed using XPS Peak 4.1 software. Data were analyzed using SCA20-U software. Specific rotations were measured on an Autopol I-Rudolph digital polarimeter with a halogen lamp as the light source at room temperature. The Filmetrics were performed on F20-UV, and the data are reported relative to polystyrene standards. The contact angle (CA) was determined by the sessile drop technique using a CA goniometer (Model: OCA 15EC, Dataphysics, input power: 55 W, Line voltage: 12V

DC; Fuses 6.3AT) with deionized water as the liquid at least on five different locations. CA measurements were carried out with an OCA15 video-based automatic contact angle measuring instrument which was installed in a temperature-controlled, dust-free room at 25 °C.

All solvents were purchased from Sinopharm Co. Ltd. and were purified by standard procedures before used. All chemicals were obtained from Aladdin, Sinopharm, and Sigma-Aldrich Chemical Co. Ltd. and were used as received without further purification otherwise denoted. Monomer L-**1**, D-**1**, TEOS-Pd(II), HO-poly-L-$\mathbf{1}_{100}$, HO-poly-D-$\mathbf{1}_{100}$, poly-L-$\mathbf{1}_{100}$-TEOS, and poly-D-$\mathbf{1}_{100}$-TEOS were prepared according to the reported literatures and the structures were confirmed by ^{1}H NMR.[1,2]

Synthesis of HO@Si: This compound was synthesized followed the reported literatures with slight modifications.[3] Silicon (100) wafers, single-polished, n type, phosphorus doped, 3−6 Ω cm, with a native oxide layer ca. 1.5 nm thick, purchased from Ultrasil Corporation, were cut into substrates (ca. 0.5 × 0.5 cm^2) and cleaned by immersion in a 3:1 v/v mixture of 98% sulfuric acid and 30% hydrogen peroxide ("piranha solution") at 100 °C for 1 h, rinsed extensively with water, and dried with a nitrogen stream. ATR-FTIR: 3350 ($\nu_{\mathrm{O-H}}$), 1100 ($\nu_{\mathrm{Si-O}}$), 800 ($\nu_{\mathrm{Si-O-Si}}$), 465 ($\nu_{\mathrm{Si-O}}$).

Synthesis of Si-Pd(II): Several pieces of prepared HO@Si was immersed in a 10 mM TEOS-Pd(II) initiator solution in anhydrous toluene (1.5 mL), first for 3 h at 50 °C and then overnight at 30 °C, eventually washed and gently sonicated with toluene, acetone, and ethanol, and dried with a nitrogen stream. The amount of TEOS-Pd(II) in the reaction system was about 10.2 mg. After the reaction completed, about 6.9 mg of unreacted TEOS-Pd(II) was removed, therefore 3.3 mg TEOS-Pd(II) (0.0049 mmol) was anchored onto the Si surface. The functionalized substrates were stored at room temperature until use. ATR-FTIR: 2130 ($\nu_{\mathrm{C\equiv C}}$), 1720 ($\nu_{\mathrm{C=O}}$), 1100 ($\nu_{\mathrm{Si-O}}$).

*Synthesis of Si-poly-*L*-**1**$_{100}$ via "grafting from" strategy*: Several Si-Pd(II) wafers were placed in a nitrogen-purged Schlenck flask which contained 0.0049 mmol TEOS-Pd(II). Then a solution of monomer L-**1** (100.0 mg, 0.49 mmol) in $CHCl_3$ (4.90 mL) was added ([L-**1**]$_0$/[Pd(II)]$_0$ = 100/1). The reaction flask was then immersed into a preheated oil bath at 55 °C and stirred for 72 h. After polymerization, the crude Si-poly-L-**1**$_{100}$ brushes were treated by Soxhlet extractor for overnight, which was further rinsed extensively with $CHCl_3$, gently sonicated in the same solvent, and dried under a nitrogen stream, afforded the expected Si-poly-L-**1**$_{100}$. ATR-FTIR: 2960 ($\nu_{C–H}$), 2930 ($\nu_{C–H}$), 2860 ($\nu_{C–H}$), 1720 ($\nu_{C=O}$), 1600 ($\nu_{C=N}$), 1100 ($\nu_{Si–O}$).

Si-poly-D-**1**$_{100}$ was prepared followed the same procedure. ATR-FTIR: 2960 ($\nu_{C–H}$), 2930 ($\nu_{C–H}$), 2860 ($\nu_{C–H}$), 1720 ($\nu_{C=O}$), 1630 ($\nu_{C=N}$), 1100 ($\nu_{Si–O}$).

*Procedure for cleavage poly-*L*-**1**$_{100}$ from Si-poly-*L*-**1**$_{100}$.* Polymer brush Si-poly-L-**1**$_{100}$ was put in $CHCl_3$ (4.0 mL) in a 10 mL plastic vial. Hydrofluoric acid (HF, ~50% aq., 2.0 mL) was added to the stirring solution. The mixture was stirred at room temperature overnight. After a half of the solvent was removed by evaporation under reduced pressure, it was precipitated into a large amount of methanol. The precipitated solid was isolated via filtration, washed with methanol, and dried in vacuum, afforded poly-L-**1**$_{100}$ as a light yellow solid. SEC: $M_n = 3.20 \times 10^4$ Da, M_w/M_n =1.17. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.86−8.51 (br, ^{1}H, COHN), 6.87−6.80 (br, ^{1}H, aromatic), 4.45–4.30 (brs, H, CH), 4.41−3.96 (br, 2H, OCH_2), 1.62−0.78 (br, 19H, CH_2 and CH_3). FT-IR (KBr, 25 °C, cm^{-1}): 2964 ($\nu_{C–H}$), 2922 ($\nu_{C–H}$), 2855 ($\nu_{C–H}$), 1745 ($\nu_{C=O}$), 1630 ($\nu_{C=N}$).

*Synthesis of poly-*L*-**1**$_{100}$-Si via "grafting to" strategy*: The HO@Si and poly-L-**1**$_{100}$-TEOS[4-6] (0.10 g), was placed in a nitrogen-purged 10 mL Schlenck flask. Then anhydrous toluene (1.0 mL) was added via a syringe at 25 °C. The mixture was stirred at 50 °C for 12 h. After cooled to room temperature. The unreacted materials was extracted by Soxhlet extractor with THF. The poly-L-**1**$_{100}$-Si was rinsed extensively with toluene, gently sonicated in the same solvent, and dried under a nitrogen stream. ATR-FTIR: 2960 ($\nu_{\mathrm{C-H}}$), 2930 ($\nu_{\mathrm{C-H}}$), 2860 ($\nu_{\mathrm{C-H}}$), 1720 ($\nu_{\mathrm{C=O}}$), 1630 ($\nu_{\mathrm{C=N}}$), 1538 ($\nu_{\mathrm{N-H}}$), 1100 ($\nu_{\mathrm{Si-O}}$).

Poly-D-**1**$_{100}$-Si was prepared followed the same procedure. ATR-FTIR: 2960 ($\nu_{\mathrm{C-H}}$), 2930 ($\nu_{\mathrm{C-H}}$), 2860 ($\nu_{\mathrm{C-H}}$), 1720 ($\nu_{\mathrm{C=O}}$), 1630 ($\nu_{\mathrm{C=N}}$), 1538 ($\nu_{\mathrm{N-H}}$), 1100 ($\nu_{\mathrm{Si-O}}$).

Procedure for surface chiral discrimination: A solution of racemic methyl benzyl alcohol (*R*/*S*-**5**) in THF (5×10^{-4} mol/mL, 1 mL) was added to a screw-capped sample bottle containing the polymer brush. The CD and UV-vis spectroscopies of the free analyte in solution was measured at appropriate time intervals in a 1.0 mm quartz cell at 25 °C. After the appropriate time, the absorbed enantiomer the surface of the poly-L-**1**$_{100}$-Si brush was washed off by dichloromethane and subjected to HPLC analysis.

References

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Table S1. The element contents of polymer brushes composites and precursor.

Entry (Atomic %)	Si (%)	C (%)	O (%)	N (%)	Pd (%)
Si	69.5	9.3	22.2	/	/
HO@Si	44.4	16.6	39	/	/
Si-Pd(II)	17.6	56.0	22.5	2.6	1.3
Si-poly-L-**1**$_{100}$	18.2	52.3	29.5	3.9	0.1
poly-L-**1**$_{100}$-Si	29.4	43.1	24.2	3.2	0.1

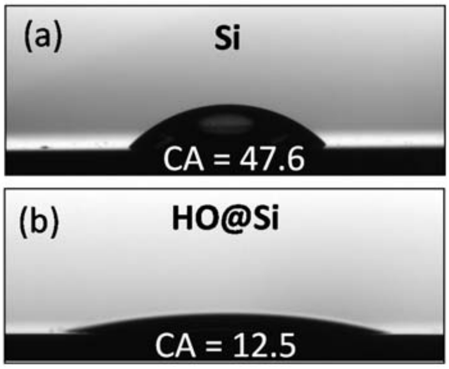

Figure S1. Contact angle of the bare Si substrate (a) and hydroxyl functionalization HO@Si (b).

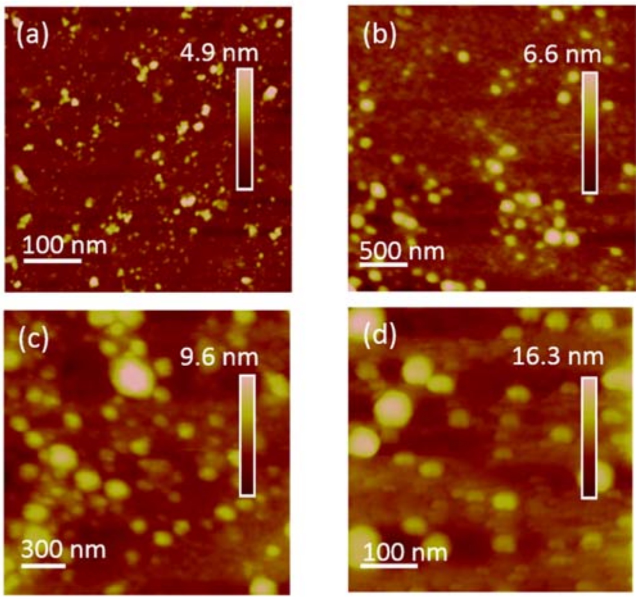

Figure S2. AFM height image of Si-poly-L-**1**$_m$ brushes obtained at different polymerization stages using Si-Pd(II) as the initiator: (a) 6 h; (b) 12 h; (c) 24 h; (d) 40 h.

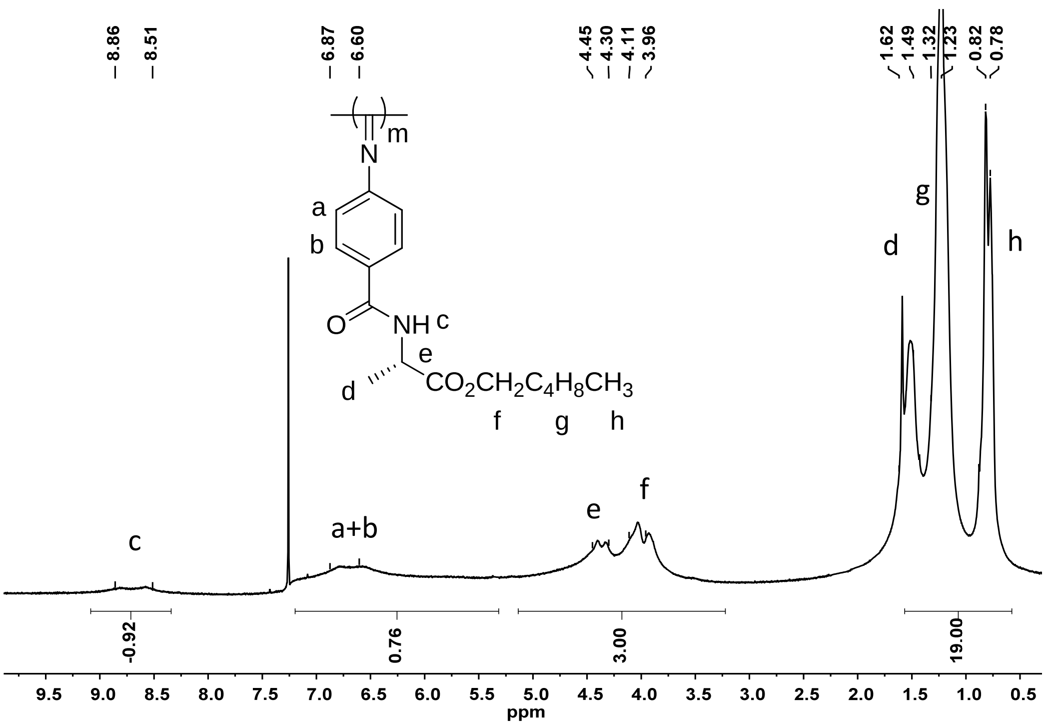

Figure S3. ^{1}H NMR (600 MHz) of etched poly-L-**1**$_{100}$ recorded in $CDCl_3$ at 25 °C.

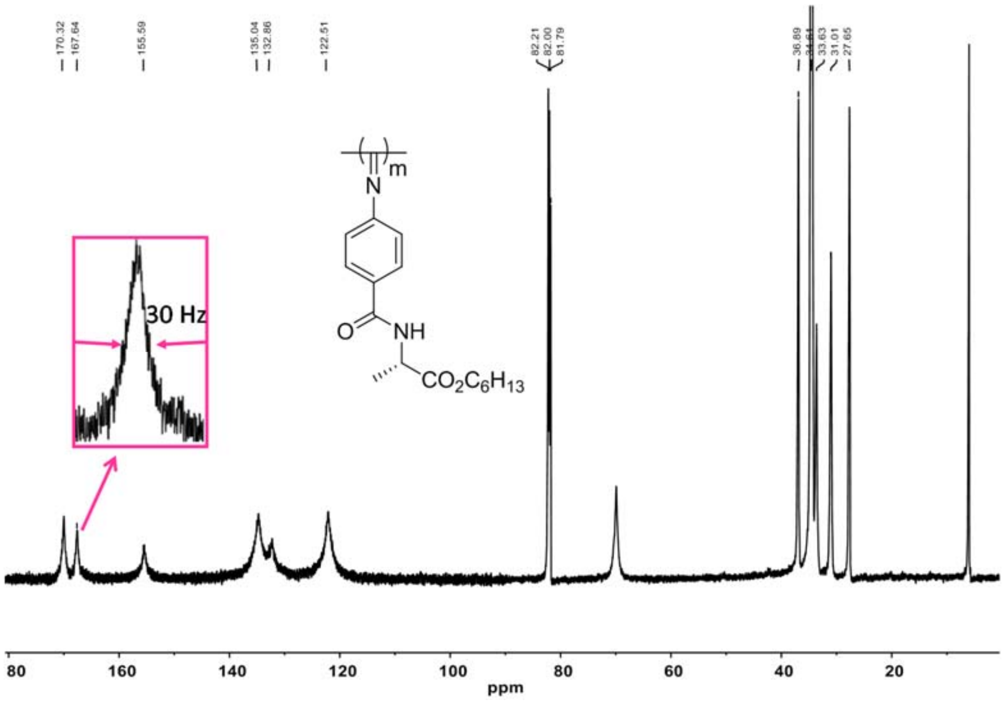

Figure S4. ^{13}C NMR (150 MHz) of etched poly-L-$\mathbf{1}_{100}$ recorded in $CDCl_3$ at 25 °C.

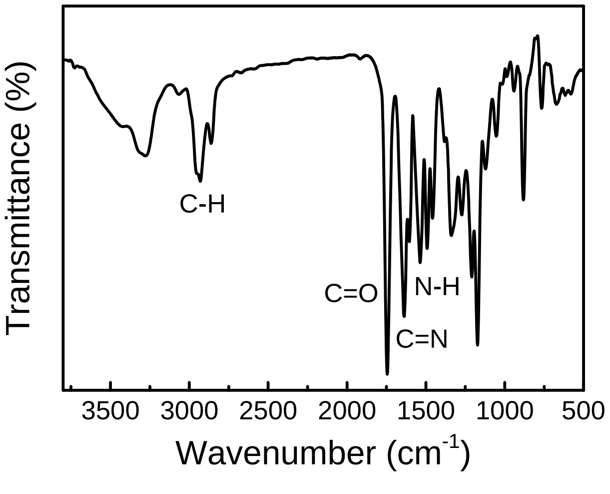

Figure S5. FT-IR spectra of etched poly-L-$\mathbf{1}_{100}$ measured at 25 °C using KBr pellets.

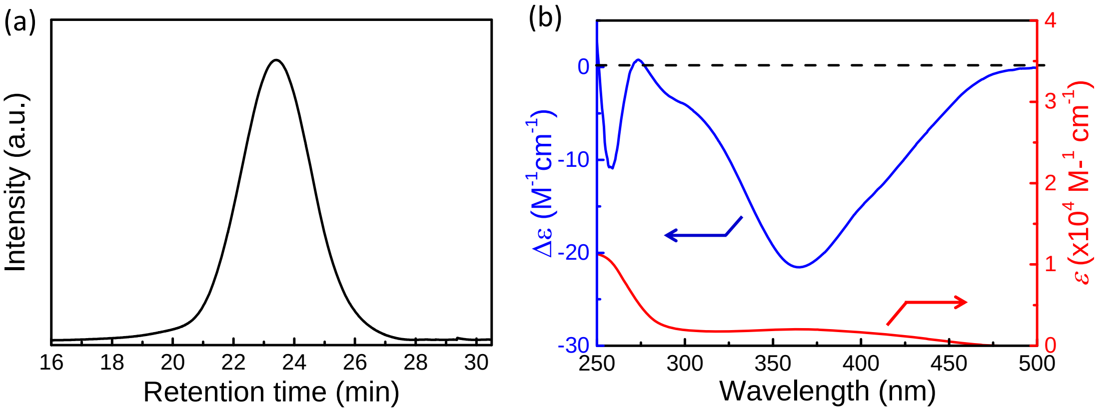

Figure S6. (a) Size exclusion chromatograms of poly-L-**1**$_{100}$-OH. SEC conditions: eluent = THF, temperature = 40 °C. (b) CD and UV-vis spectra of poly-L-**1**$_{100}$-OH in THF at 25 °C (c = 0.2 g/L).

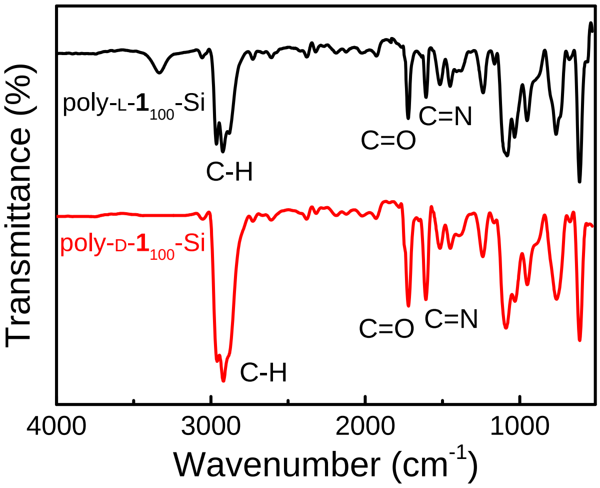

Figure S7. ATR-FTIR spectra of poly-L-**1**$_{100}$-Si and poly-D-**1**$_{100}$-Si.

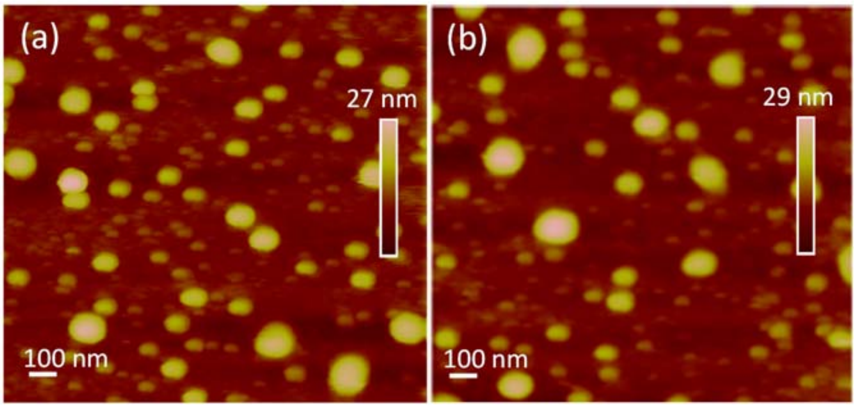

Figure S8. AFM height image of poly-L-**1**$_{100}$-Si (a) and poly-D-**1**$_{100}$-Si (b).

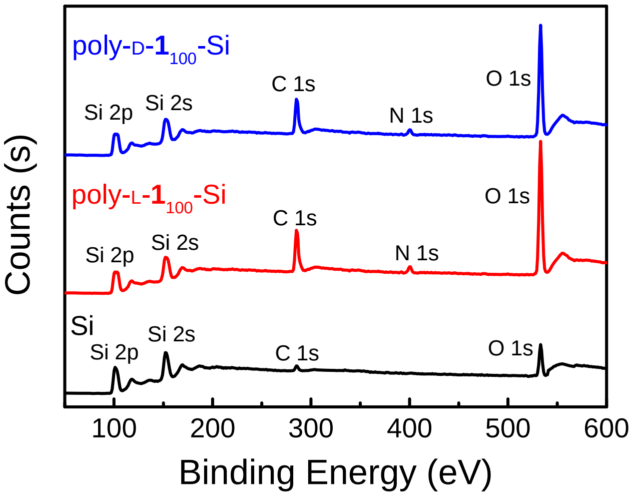

Figure S9. XPS spectra of Si, poly-L-**1**$_{100}$-Si and poly-D-**1**$_{100}$-Si.

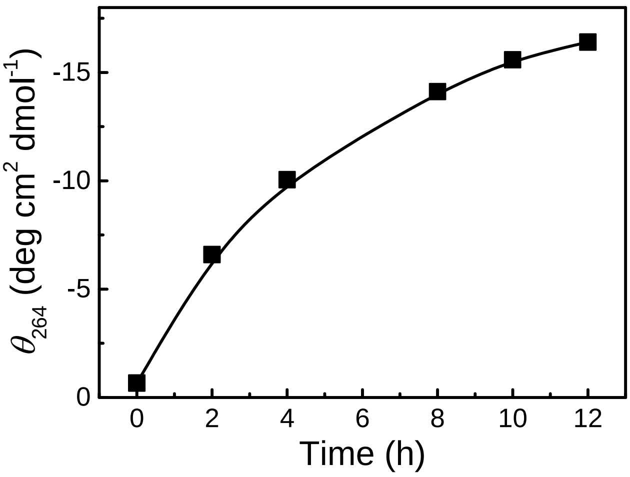

Figure S10. The θ_{264} changes of *R/S*-**5** with the incubation time of poly-L-$\mathbf{1}_{100}$-Si.

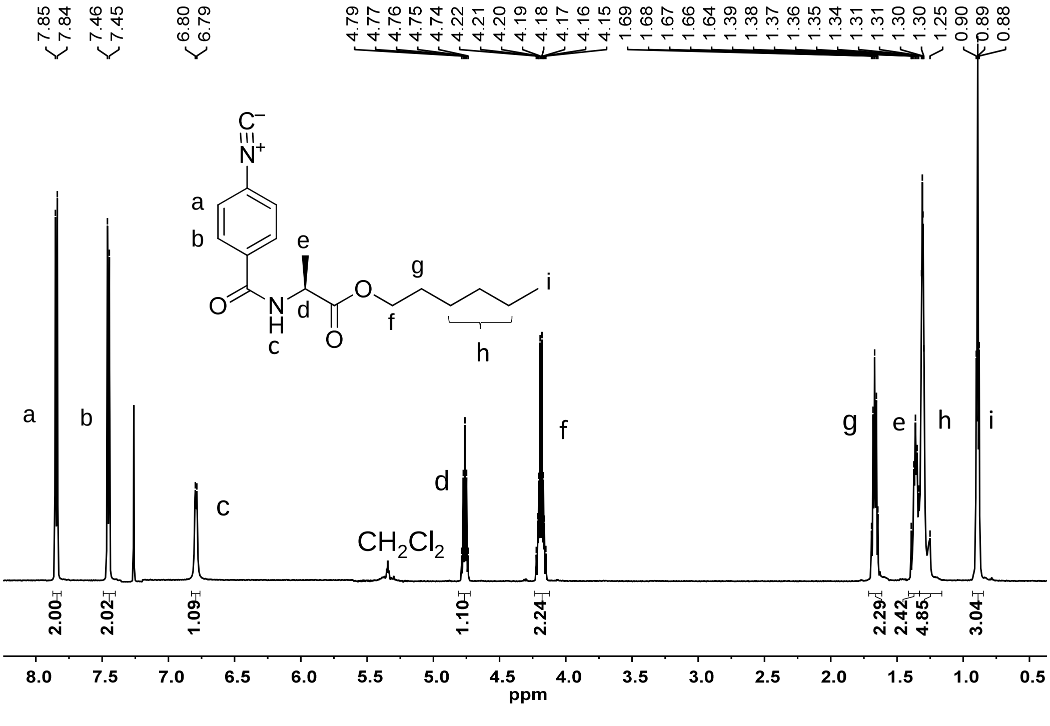

Figure S11. ^{1}H NMR (600 MHz) spectrum of L-**1** measured in $CDCl_3$ at 25 °C.

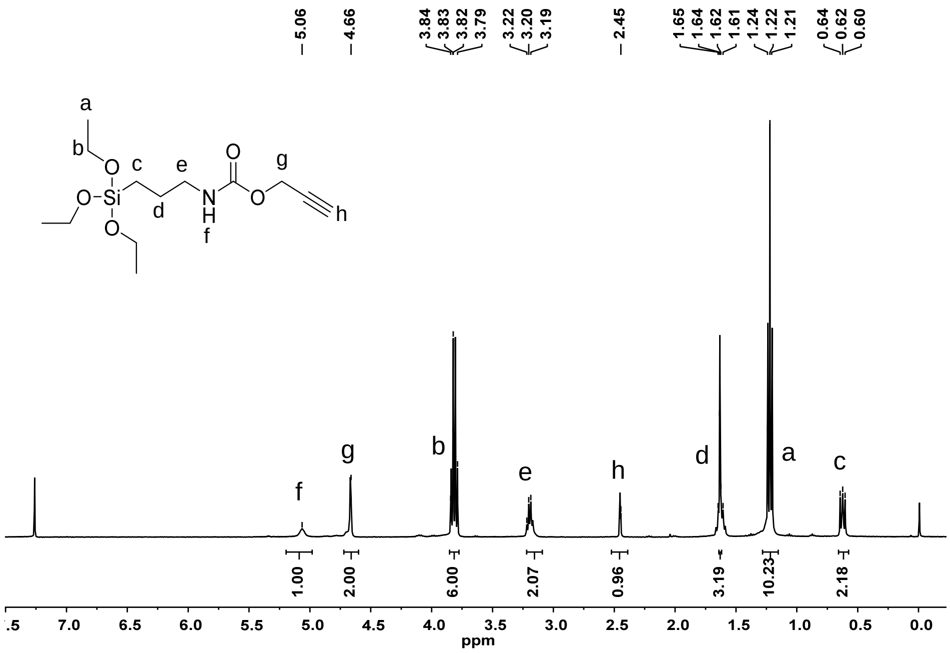

Figure S12. ^{1}H NMR (600 MHz) spectrum of TEOS-alkyne measured in $CDCl_3$ at 25 °C.

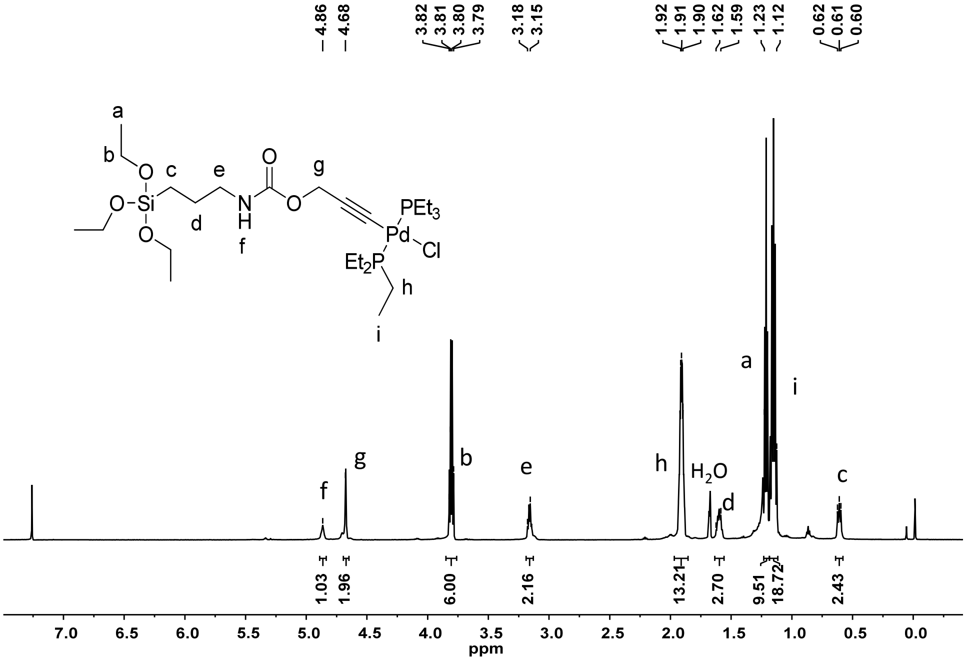

Figure S13. ^{1}H NMR (600 MHz) spectrum of TEOS-Pd(II) measured in $CDCl_3$ at 25 °C.