Electronic supplementary information for

Rate Enhancement for Hexose Sugar Oxidation on an Ethynylpyridine-Functionalized Pt/Al_2O_3 Catalyst with Induced Chirality

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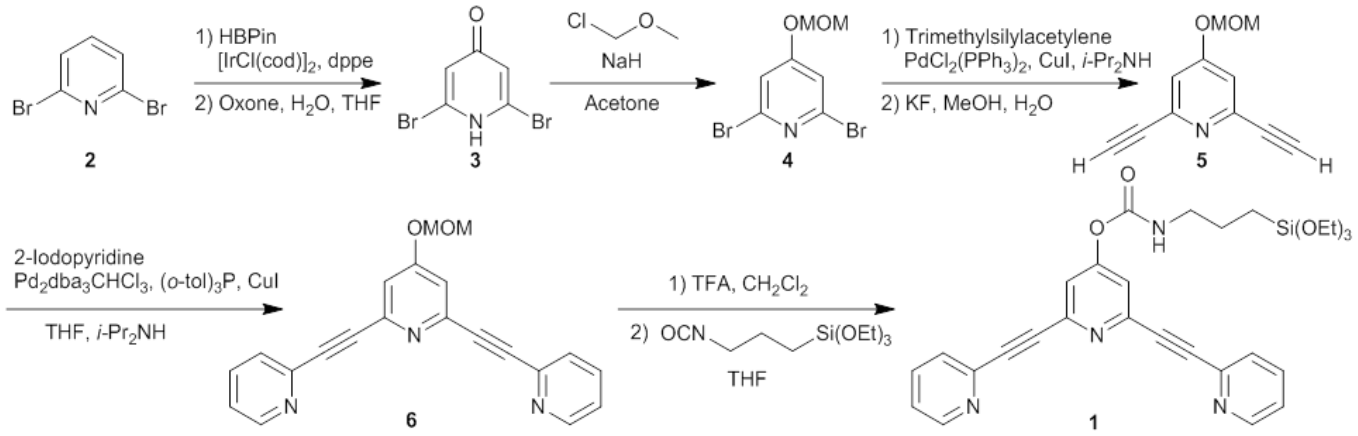
Contents

Experimental Section

General

All reagents and solvents were commercially available and used without further purification. ^{13}C cross-polarization (CP) magic-angle spinning (MAS) NMR measurements were respectively performed at 100.6 MHz at a sample spinning frequency of 8 kHz using a JEOL JNM-ECX-400 spectrometer with a 6 mm zirconia rotor. For the ^{13}C CP MAS NMR measurements, the repetition delay was 1 s, the contact time was 5 ms, and the pulse width was 5.4 μs (^{1}H 90° pulse). IR spectra were collected on a JASCO FT-IR4200 spectrometer. UV/vis and CD spectra were obtained using JASCO V-670 and J-820 spectrometers using integrated spheres, respectively.

Synthesis



2,6-Diethynyl-4-methoxymethoxypyridine (5): This compound was synthesized according to previous literature.[1]

2,6-Bis(2-pyridylethynyl)-4-methoxymethoxypyridine (6): To a mixture solution of *i*-Pr_2NH (50 mL) and THF (50 mL) was added **5** (1.24 g, 6.6 mmol), 2-iodopyridine (2.7 g, 13.2 mmol), $Pd_2dba_3{\cdot}CHCl_3$ (0.14 g, 0.13 mmol), (*o*-Tol)$_3$P (0.16 g, 0.53 mmol), CuI (0.05 g, 0.26 mmol). The mixture was stirred under N_2 at 343 K overnight. The resulting mixture was filtered to remove insoluble salt, and evaporated. The residue was purified by silica-gel column chromatography (eluent: AcOEt) to give **6** (1.22 g, 54%). IR (KBr): ν_{max} 2976, 2929, 2889, 2273, 1703, 1533, 1457 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.47 (3 H, s), 5.23 (2 H, s), 7.26-7.28 (2 H, m), 7.29 (2 H, m), 7.61 (2 H, *J* = 1.2, 7.8 Hz, dd), 7.69(2 H, *J* = 1.6, 7.8 Hz, dt), 8.63 (2 H, *J* = 0.8, 4.8 Hz, td); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.1, 65.4, 90.0, 90.4, 95.3 112.6, 118.9, 122.4, 129.1, 134.1, 135.4, 140.2, 151.0. ESI-HRMS *m/z* calcd. for $C_{21}H_{15}N_3NaO_2$ $(M+Na)^+$: 364.1062; found: 364.1056.

2,6-Bis(2-pyridylethynyl)-4-pyridone: To a CH_2Cl_2 (10 mL) solution of **6** (0.2 g, 0.59 mmol) was added CF_3COOH (1.5 g, 13.5 mmol). After stirring for 2 h at room temperature, the resulting mixture was quenched by adding aqueous $NaHCO_3$. The residue was extracted with CH_2Cl_2/H_2O. The organic layer was dried over $MgSO_4$, and concentrated to obtain 2,6-bis(2-pyridylethynyl)-4-pyridone. IR (KBr): ν_{max} 3079, 3047, 2992, 2961, 2941, 2916, 2831, 1582, 1553, 1463, 1153, 1135, 1014 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.22 (2 H, s), 7.29-7.33 (2 H, s), 7.58 (2 H, *J* = 8.0 Hz, d), 7.73 (2 H, *J* = 4.0, 8.0 Hz, dt), 8.59 (2 H, *J* = 4.0 Hz, d); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 90.0, 90.3 113.8 119.1, 122.6, 129.6, 133.6, 133.7, 153.8. ESI-HRMS *m/z* calcd. for $C_{19}H_{12}N_3O$ $(M+H)^+$: 298.0982; found: 298.0992.

2,6-Bis(2-pyridylethynyl)-4-[{(3-triethoxysilylpropyl)carbamoyl}oxy]pyridine (1): To a THF (10 mL) solution of 2,6-bis(2-pyridylethynyl)-4-pyridone was added 3-(triethoxysilyl)propyl isocyanate (0.22 g, 0.88 mmol). The resulting mixture was stirred at 60 ^{o}C for 15 h, and then concentrated by an evaporator. The mixture was added hexane, filterd to remove an insoluble matter and concentrated. The residue was purified by silica-gel column chromatography (eluent: AcOEt) to obtain **1** (0.17 g, 52% in 2 steps). IR (KBr): ν_{max} 3087, 2979, 2925, 2674, 2569, 2459, 2227, 1684, 1594, 1562, 1469, 1196, 1138 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.68 (2 H, *J* = 7.8 Hz, t), 1.22 (9 H, *J* = 7.0 Hz, t), 1.72 (2 H, *J* = 7.3 Hz, p), 3.28 (2 H, *J* = 6.8 Hz, q), 3.82 (6 H, *J* = 7.0 Hz, q), 5.82 (1 H, *J* = 5.8 Hz, t), 7.27 (2 H, *J* = 5.2 Hz, dd), 7.46 (2 H, s), 7.59 (2 H, 1.2, *J* =8.0 Hz, d), 7.68 (2 H, *J* = 1.6, 7.7 Hz, dt), 8.61 (2 H, *J* = 4.4 Hz, d); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 7.8, 18.4, 22.9, 43.7, 58.7, 87.1, 88.5, 120.1, 123.7, 128.0, 136.4, 142.4, 144.3, 150.3, 152.1, 158.5. ESI-HRMS *m/z* calcd. for $C_{25}H_{25}N_4O_5Si$ $(M+H)^+$: 489.1589; found: 489.1192. (Two ethoxy groups on silicon in **1** were hydrolyzed under the ionization condition during MS measurement.)

Attachment of EPy ligand 1 on Pt/Al_2O_3: To a toluene (40 mL) solution was added EPy ligand **1** (0.01 mmol, 5 mg) and Pt/Al_2O_3 (1.0 g, Pt: 5 wt%), and stirred at 373 K for 24 h under N_2. Followed by Sohxlet extraction with toluene for 24 h to remove the unreacted **1**, EPy/Pt/Al_2O_3 was obtained after drying under vacuum. The amounts of the binding EPy ligand (17 wt%) were measured by elemental analysis, assuming that the detected nitrogen was originated from the EPy ligand. EPy/Pt/Al_2O_3 catalysts with different loading of **1** were prepared in a similar way.

UV/vis titration experiment for EPy/Pt/Al_2O_3: A CH_2Cl_2 (20 mL) dispersion of EPy/Pt/Al_2O_3 (EPy: 17 wt%) (2 mg) was prepared. To this dispersion was added a CH_2Cl_2 solution of octyl β-D-glucopyranoside (Oct-β-D-Glc) at the concentrations of 0.8, 1.6, 2.4, and 3.2 × 10^{-3} M. UV/vis spectra of resulting dispersion were measured at a transmission mode by spectrometer attached with an integrating sphere unit at room temperature.

UV/vis titration experiment for MOM-protected ethynylpyridine 6: A CH_2Cl_2 solution of **6** (1.0 × 10^{-4} M) was prepared in a quartz cell. Then, a CH_2Cl_2 solution of Oct-β-D-Glc was added at the concentrations of 0.8, 1.6, 2.4, and 3.2 × 10^{-3} M. UV/vis spectra of solution were measured at each concentrations of Oct-β-D-Glc.

CD measurement[2]**:** A CH_2Cl_2 dispersion (5 mL) of EPy/Pt/Al_2O_3 (EPy: 17 wt%) (1.0 mg) was prepared in a quartz cell. Then, Oct-β-D-Glc or octyl β-L-glucopyranoside (58 mg, 0.02 mmol) was added to this dispersion. CD spectra of the dispersion with and without glucopyranoside were measured at a transmission mode by spectrometer attached with an integrating sphere unit at room temperature.

Catalytic reactions for the oxidation of hexose sugars: Catalyst (EPy/Pt/Al_2O_3 (Pt: 5 wt%, EPy: 0.2 wt%) or Pt/Al_2O_3 (Pt: 5 wt%)) (0.10 g), methyl α-D-glucopyranoside (Me-α-D-Glc) (or methyl-α-D-galactopyranoside and methyl-α-D-mannopyranoside) (1.0 mmol), and $NaHCO_3$ (0.71 mmol, 0.06 g) was suspended in H_2O (3 mL) under oxygen atmosphere. Oxidation reactions were carried out at 353 K for 2, 5, and 9 h. After that, the resulting mixture was subjected with ion-exchange resin to adjust pH into acidity. Amount of reactant and product were analyzed by ^{13}C NMR measurement. The molar ratio of them can be calculated from the average of the integrated intensities of the signals for the C2–C5 carbon atoms of each sugar in ^{13}C NMR.[3]

Catalytic reactions for the oxidation of cyclohexanemethanol: Catalyst (EPy/Pt/Al_2O_3 (Pt: 5 wt%, EPy: 0.2 wt%) or Pt/Al_2O_3 (Pt: 5 wt%)) (0.05 g) and $NaHCO_3$ (0.36 mmol, 0.031 g) was suspended in H_2O (1.5 mL) under oxygen atmosphere. Cyclohexanemethanol (0.5 mmol) was added and the mixture was stirred vigorously at 353 K for 1 h. After the system was cooled to room temperature, a few drops of conc. HCl aq. were added to acidify the pH of the solution. Then CH_2Cl_2 (1.5 mL) was added to the resulting mixture and the mixture was stirred vigorously for 10 min. to extract the organic compounds to CH_2Cl_2 phase. The amount of the reactant and product was monitored by GC (Shimadzu GC-14B, CHIRALDEX B-DM column), and the conversion of cyclohexanemethanol was determined by using a peak area ratio between the reactant and CH_2Cl_2. The extraction efficiencies of cyclohexanemethanol, cyclohexanealdeylde, and cyclohexanecarboxylic acid from aqueous phase to CH_2Cl_2 phase under the current catalytic condition were quantitative as determined by the GC peak areas of these compounds with respect to the peak area of CH_2Cl_2.

References for supporting information

1 H. Abe, H. Machiguchi, S. Matsumoto, M. Inouye, *J. Org. Chem.*, 2008, **73**, 4650–4661.

2 *Circular Dichroism: Principles and Applications*, Ed. N. Berova, K. Nakanishi, and R. W. Woody, Wiley-VCH, New York, 2nd edn, 2000.

3 (a) D. J. Wilbur, C. Williams, A. Allerhand, *J. Am. Chem. Soc.*, 1977, **99**, 5450–5452; (b) M. Waki, H. Abe, and M. Inouye, *Angew. Chem. Int. Ed.*, 2007, **46**, 3059-3061.

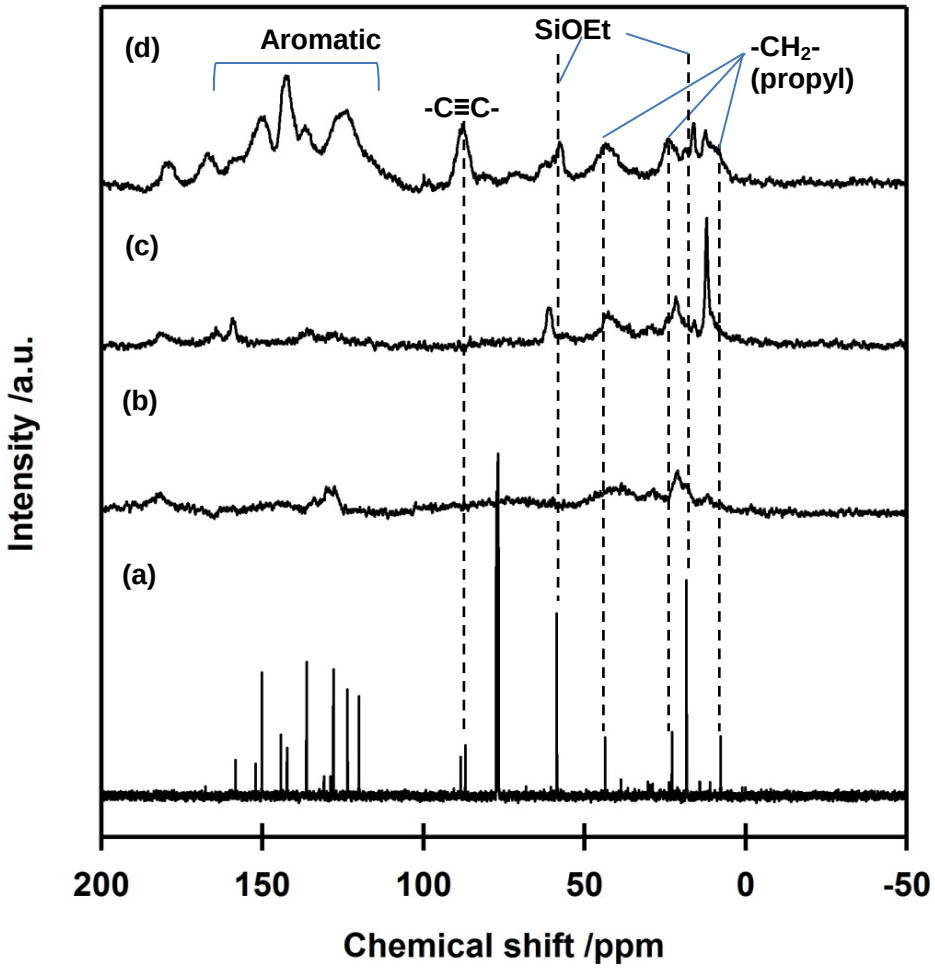


Fig. S1 ^{13}C liquid-state NMR spectrum of (a) **1** in $CDCl_3$, and ^{13}C solid-state CP MAS NMR spectra of EPy/Pt/Al_2O_3 (EPy: (b) 0.2 wt%, (c) 1.7 wt%, and (d) 17 wt%).

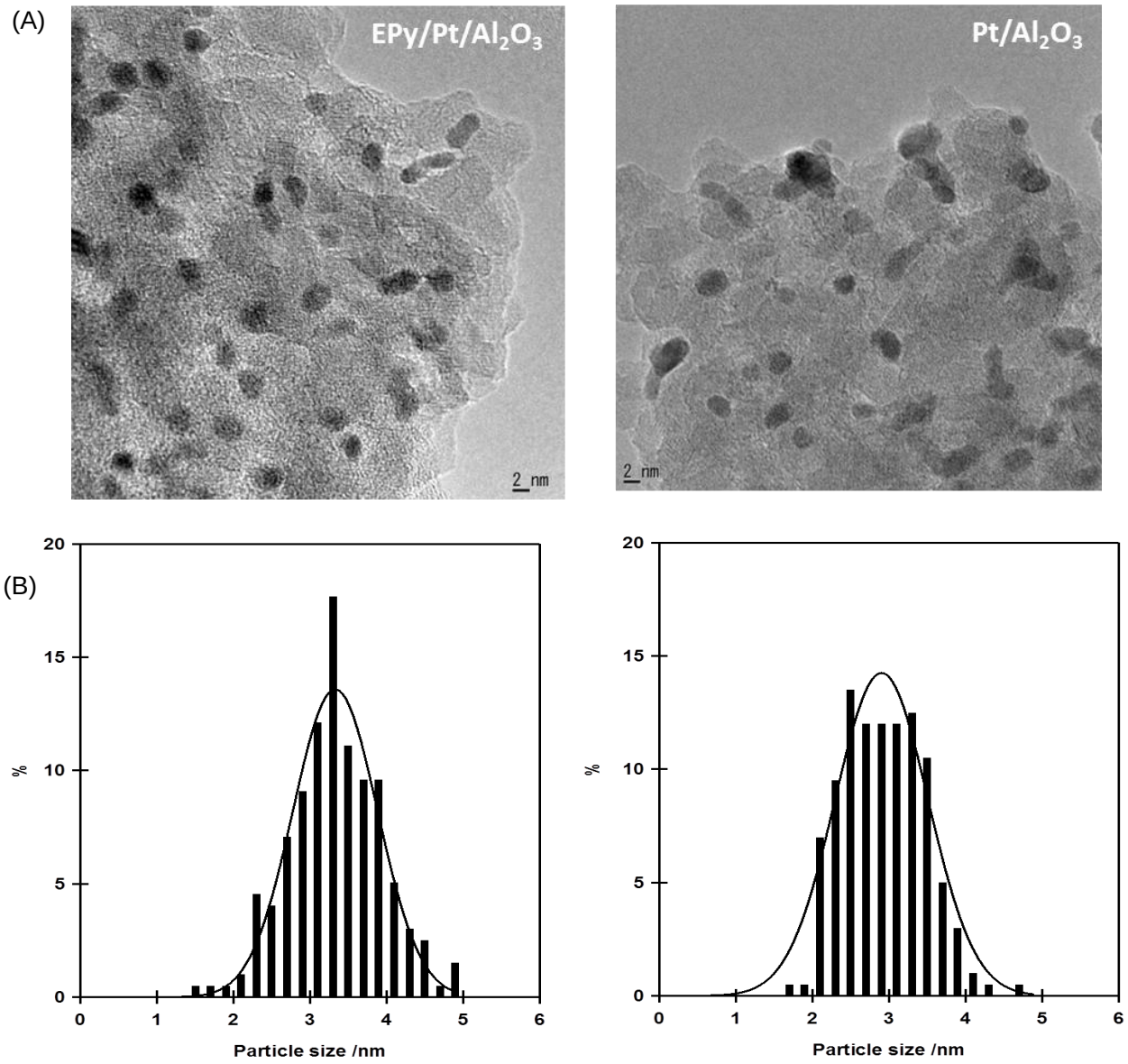


Fig. S2 (A) TEM images of EPy/Pt/Al_2O_3 (EPy: 0.2 wt%, Pt: 5wt%) and Pt/Al_2O_3 (Pt: 5 wt%). (B) Size distribution of Pt nanoparticles calculated by TEM images. The average diameters of the Pt particles on EPy/Pt/Al_2O_3 and Pt/Al_2O_3 were 3.3 ± 0.6 nm and 2.9 ± 0.7 nm, respectively.

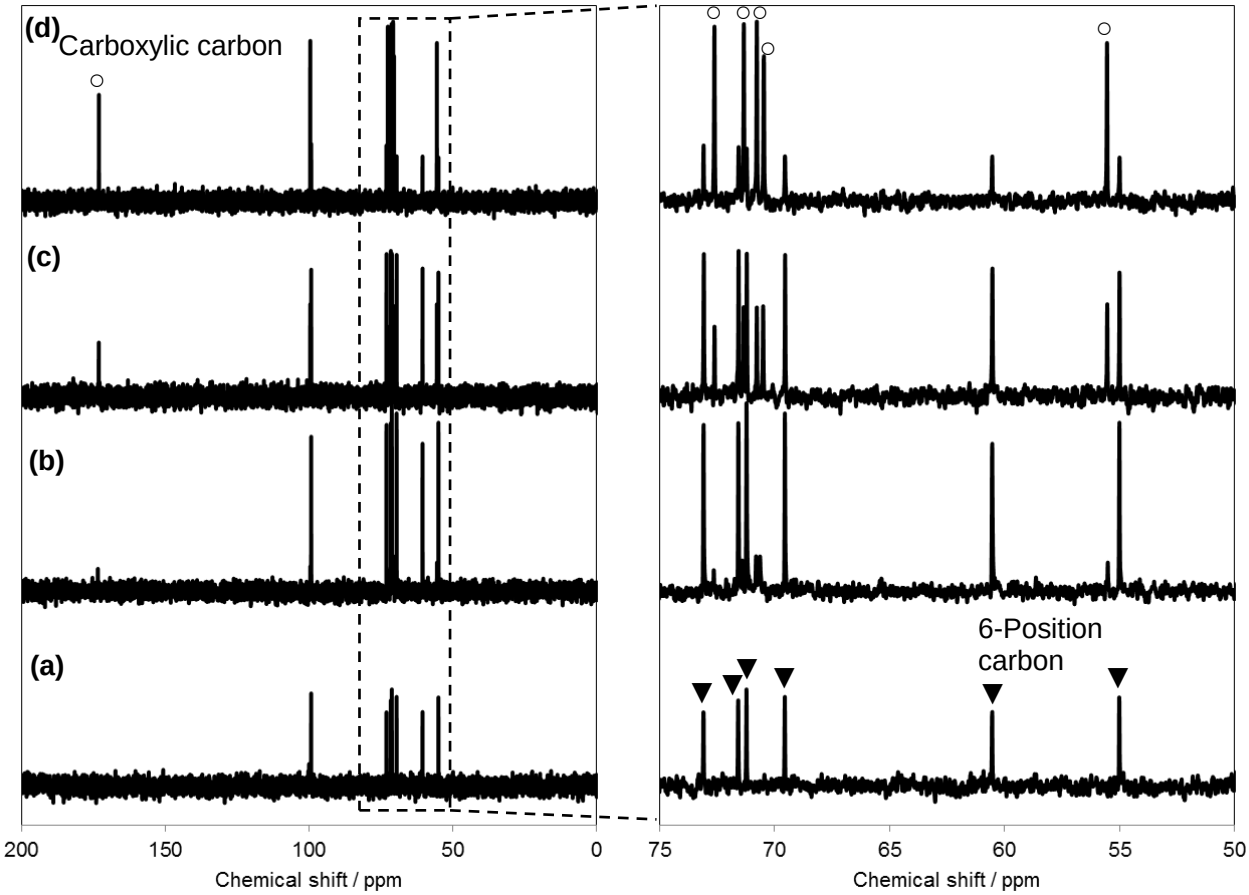


Fig. S3 ^{13}C NMR spectra of Me-α-D-Glc (▼) and methyl α-D-glucuronic acid (○) during the oxidation reaction of Me-α-D-Glc on EPy/Pt/Al_2O_3 (EPy: 0.2 wt%, Pt: 5 wt%) for (a) 0 h, (b) 2 h, (c) 5 h, and (d) 9 h.

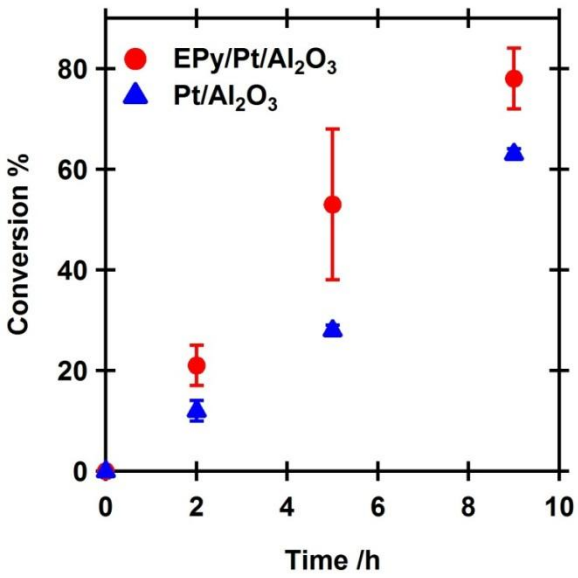


Fig. S4 Conversion of the selective oxidation of Me-α-D-Glc on the EPy/Pt/Al_2O_3 (EPy: 0.2 wt%, Pt: 5 wt%) and Pt/Al_2O_3 (Pt: 5 wt%) catalysts. Error bars were estimated by the repetition of the oxidation reactions.

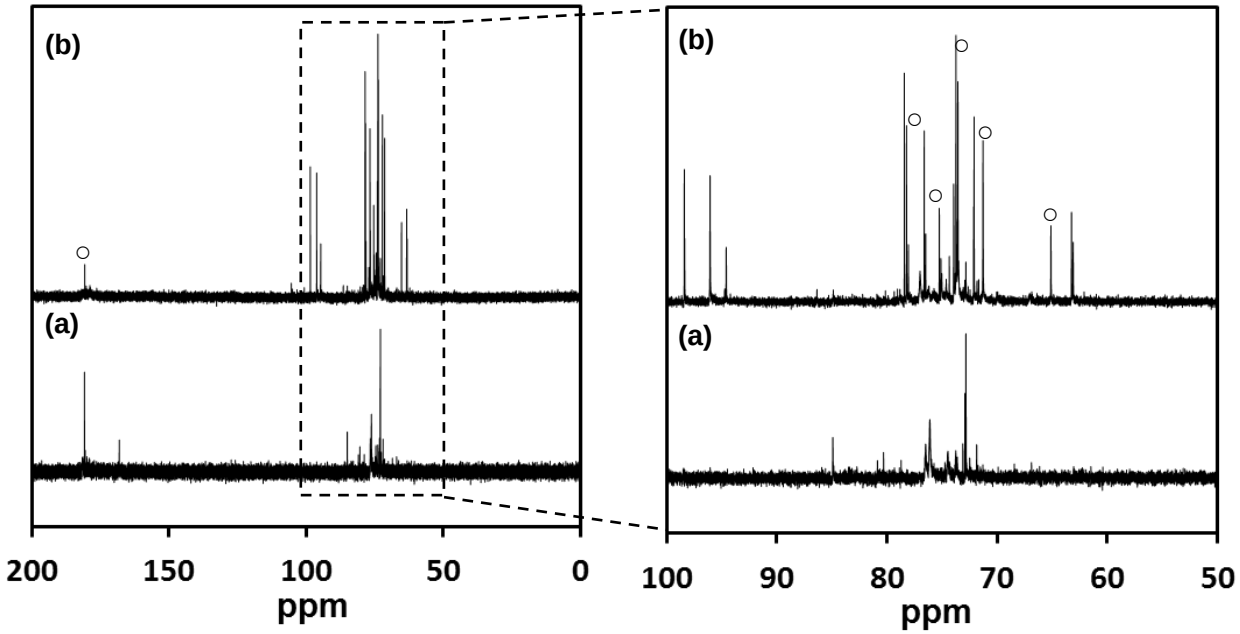


Fig. S5 ^{13}C NMR spectra for the oxidation of D-glucose on (a) Pt/Al_2O_3 (Pt: 5 wt%) and (b) EPy/Pt/Al_2O_3 (Pt: 5 wt%) for 12 h. (a) D-Glucose was comsumed, and several oxidized products were observed. (b) Unreacted D-glucose was mainly observed in the spectrum, and characteristic signals (○) were assigned to gluconic acid.

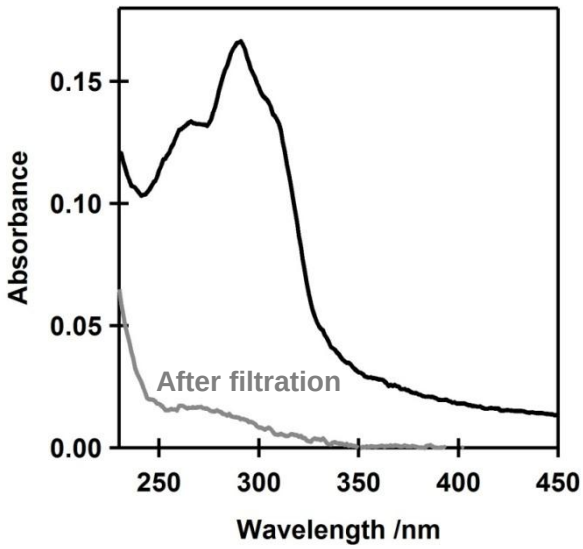


Fig. S6 UV/vis absorption spectra of a CH_2Cl_2 suspension of EPy/Pt/Al_2O_3 (EPy: 17 wt%) before and after the filtration of the solid catalyst using a syringe filter (0.2 μm).

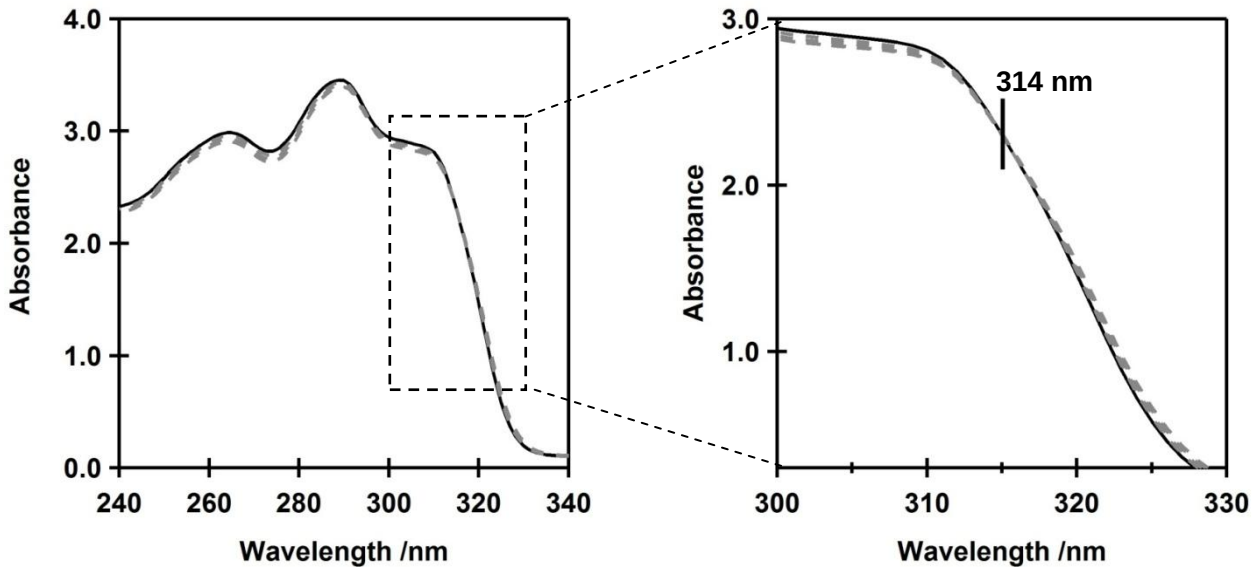


Fig. S7 Changes in UV/vis spectra of **6** in CH_2Cl_2 upon titration with Oct-β-D-Glc (0 - 3.2 × 10^{-3} M). Solid line: before titration .

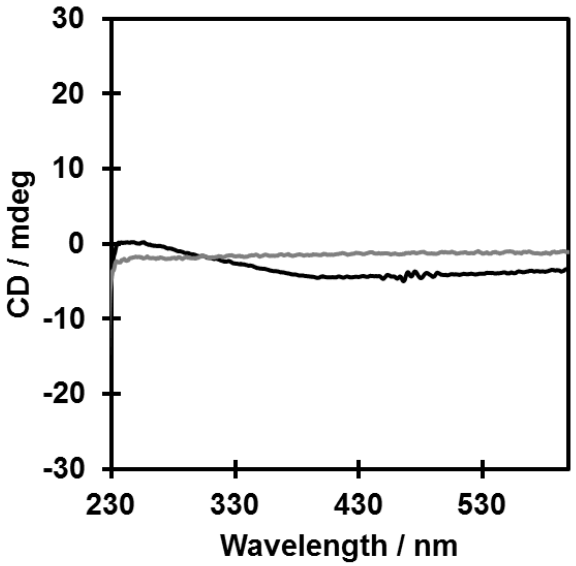
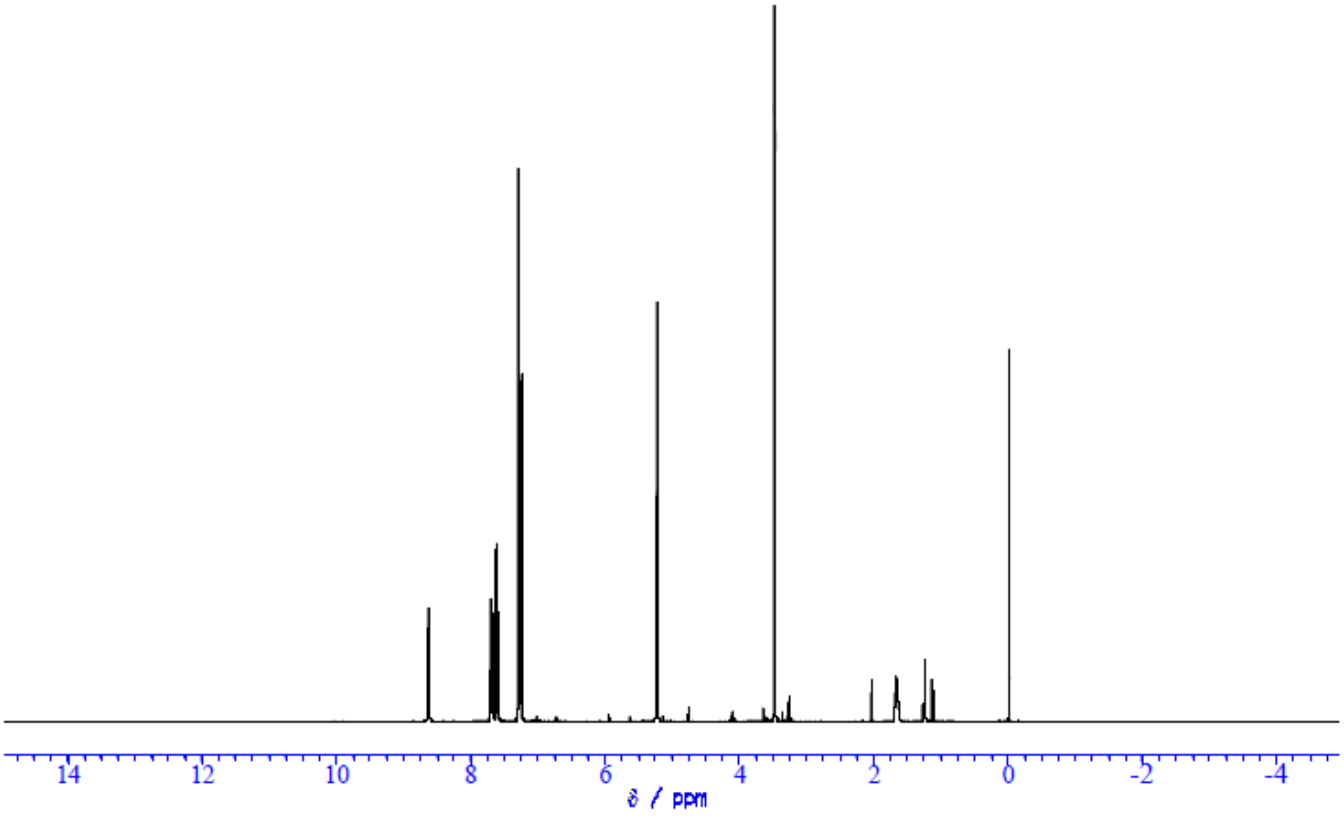
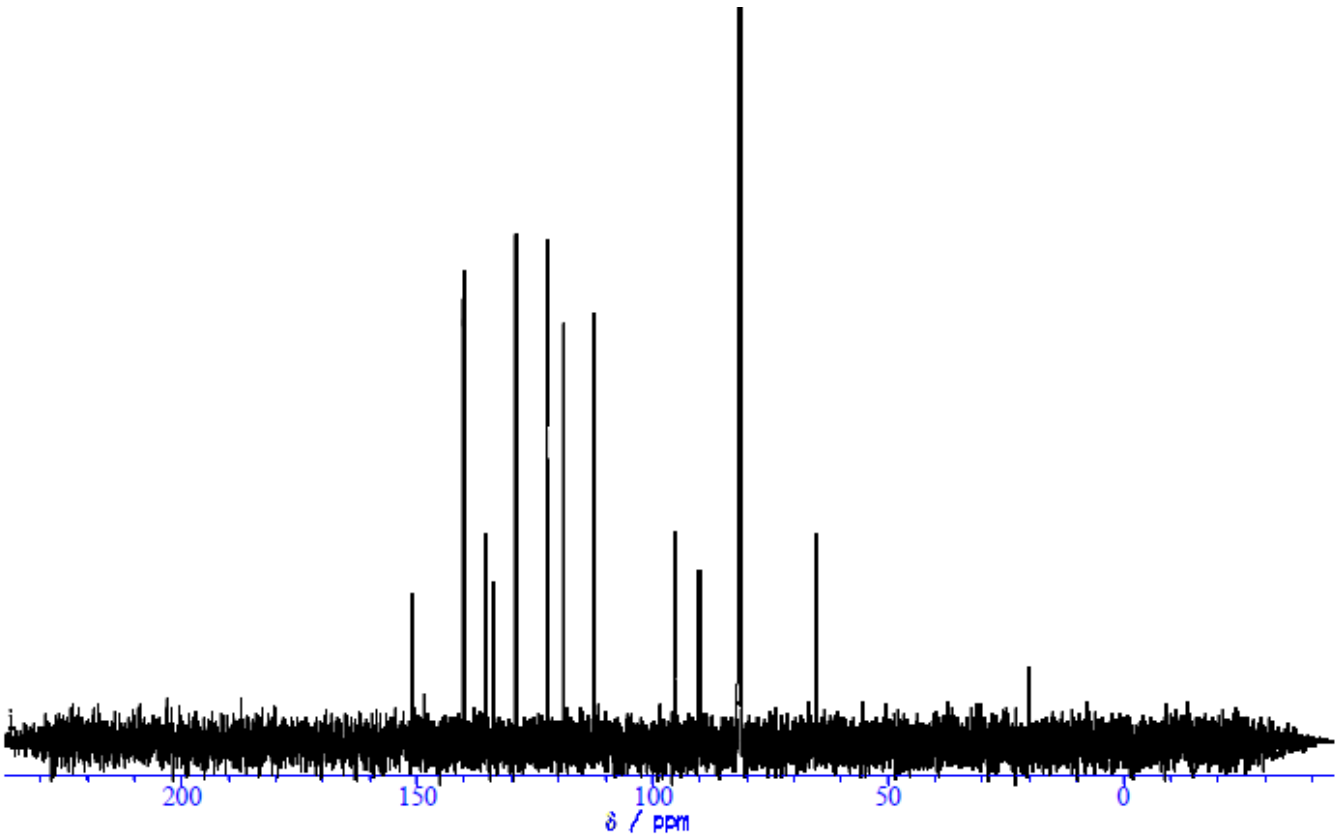


Fig. S8 The CD spectra of the suspension of EPy/Pt/Al_2O_3 (EPy: 1.7 wt%) (black) in CH_2Cl_2 and that after the addition of Oct-β-D-Glc (gray). There was no active CD signal observed.

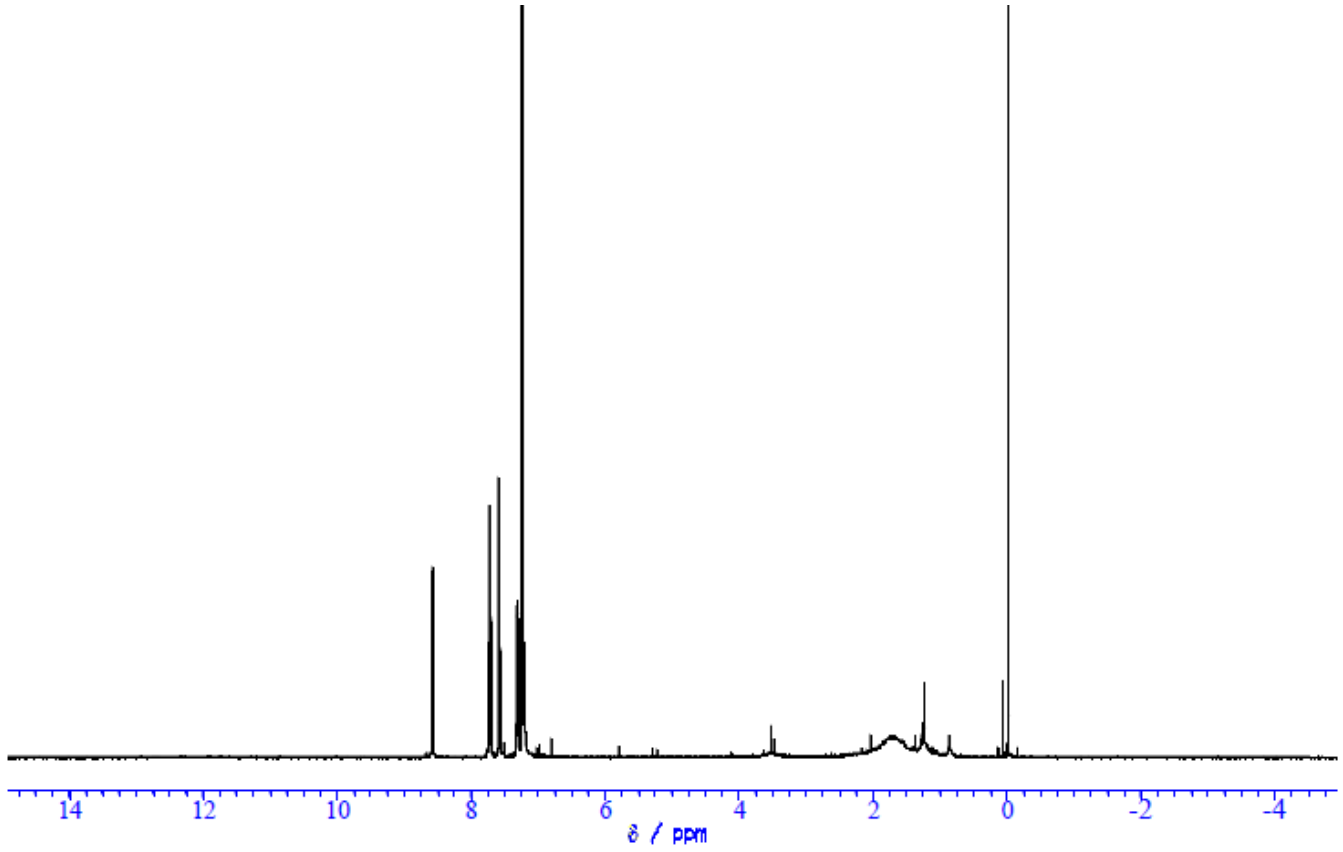
^{1}H NMR spectrum for **2,6-bis(2-pyridylethynyl)-4-methoxymethoxypyridine** (**6**)



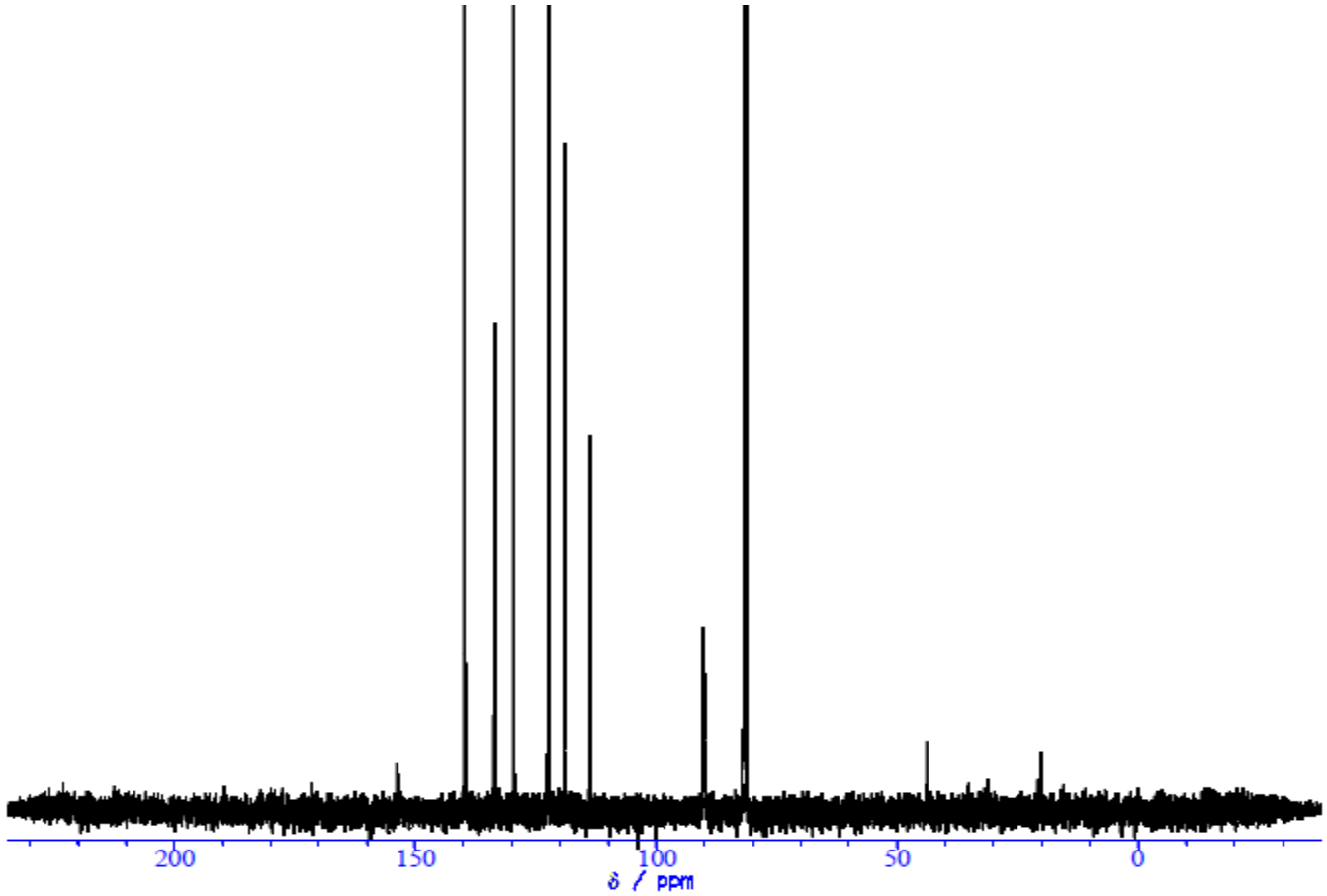
^{13}C NMR spectrum for **2,6-bis(2-pyridylethynyl)-4-methoxymethoxypyridine** (**6**)



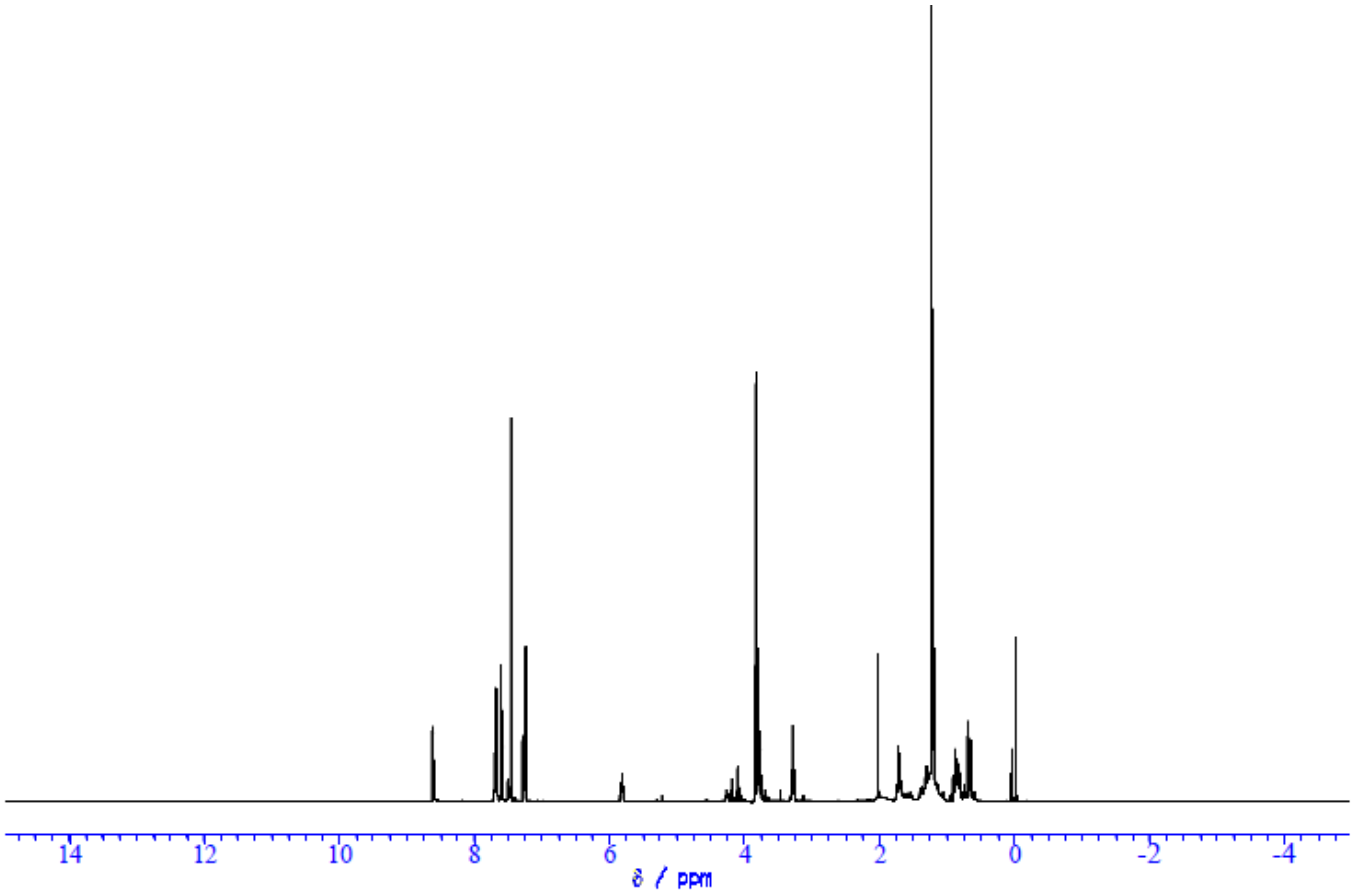
^{1}H NMR spectrum for **2,6-bis(2-pyridylethynyl)-4-pyridone**



^{13}C NMR spectrum for**2,6-bis(2-pyridylethynyl)-4-pyridone**



^{1}H NMR spectrum for **2,6-bis(2-pyridylethynyl)-4-[{(3-triethoxysilylpropyl)carbamoyl}oxy]pyridine** (**1**)



^{13}C NMR spectrum for **2,6-bis(2-pyridylethynyl)-4-[{(3-triethoxysilylpropyl)carbamoyl}oxy]pyridine** (**1**)