Supporting Information

Ionic Liquid Brush as an Efficient and Reusable Heterogeneous Catalytic Assembly for Tosylation of Phenols and Alcohols in Neat Water

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1. General information

Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. Melting points were uncorrected. Reaction progress was monitored by TLC using Merck silica gel 60 F-254 with detection by UV and/or by GC analysis on an Agilent 6890N Gas Chromatography. Flash chromatography was performed using Merck silica gel 60 with freshly distilled solvents. ^{1}H NMR (300 MHz), ^{1}H NMR (400 MHz) spectra were recorded on a Bruker Avance spectrometers using $CDCl_3$ and DMSO-d_6 as a solvent. Chemical shifts (δ) are reported in ppm, using TMS as an internal standard. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, dd = doublet- doublet, m = multiplet), coupling constant J (Hz) and integration. The BET surface areas of the materials were measured by nitrogen adsorption Peking Pioneer-2002ST-03A. C, H and N elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. IR was recorded on a Brucker EQUINX55 Fourier transform Infrared Spectrometer (KBr pellet in the range 400-4000 cm^{-1}).

2. General procedures

2.1 General procedure for the synthesis of the brush.

1,4-Bis(imidazole-1-yl)butane was synthesized according to the literature.[1] mp. 61-63 °C, ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ 1.61 (m, 4H), 3.96 (m, 4H), 6.89 (s, 2H), 7.14 (s, 2H), 7.62 (s, 2H); ^{13}C NMR (300 MHz, DMSO-d_6, ppm) δ 28.1, 39.4, 39.6, 39.9, 40.2, 40.5, 45.7, 119.7, 128.9, 137.7. The silica modified by triethyl 3-chloropropanylsilicate was prepared according to the literature.[2] S_{BET} (m^2/g): 385. IR: (KBr disk) 2958, 2930, 2871 cm^{-1} ν(C-H, aliphatic).

1,4-Bis(imidazole-1-yl)butane (4.3 g, 22.5 mmol) was added to a suspension of modified silica (4.5 g) in 15 mL dry toluene and the mixture was refluxed for 24 h. The solid was then filtered and washed thoroughly with toluene followed by methanol in a Soxhlet' extractor. After dried in vacuum, 5.1 g of solid was obtained. S_{BET} (m^2/g): 231. IR: (KBr disk) 3155, 3120 cm^{-1}, ν(C-H, aromatic); 2947, 2871 cm^{-1}, ν(C-H, aliphatic); 1555, 1456 cm^{-1}, ν(C=N). Elemental analysis (%): found: C, 14.73; H, 2.567; N, 4.209, revealing that there are 1.50 mmol of imidazolium / g loaded on the brush.

The resulting silica bonding 1,4-Bis(imidazole-1-yl) butane (5 g, 7.50 mmol of imidazolium) was suspended in a solution of 1-chlorooctane (5 g, 34 mmol) in 20 mL of dry toluene and refluxed for 24 h under N_2 atmosphere. After the reaction mixture was cooled to room temperature, the solid was filtered, washed with toluene followed by ethanol in a Soxhlet extactor, and dried in vacuum, 5.4 g of solid was obtained. S_{BET} (m^2/g): 181. IR: (KBr disk) 3151, 3084 cm^{-1}, ν(C-H, aromatic); 2936, 2855 cm^{-1}, ν(C-H, aliphatic); 1568, 1458 cm^{-1}, ν(C=N). Elemental analysis: found (%): C, 14.11; H, 2.341; N, 3.540, revealing that the brush contains 1.27 mmol of imidazolium/g.

2.2 General procedure for tosylation of phenols or alcohols

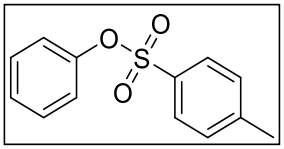
In a typical procedure, to a 25 mL flask was added a mixture of phenols or alcohols (2 mmol), *p*-toluenesulfonyl chloride (2.4 mmol), Na_2CO_3 (2 mmol), catalyst (2 mol% with respect to substrate) and 4 mL of water. The resulting mixture was stirred electromagnetically at room temperature until the substrate could not be detected by TLC. Then ethyl acetate (10 mL) was added to the reaction mixture. After the completion of the reaction, the catalyst was separated by filtration under reduced pressure, washed with ethyl acetate and water, and dried in vaccum. The organic layer of the filtrate

was separated and the aqueous layer was extracted by ethyl acetate (3 × 5 mL). The combined extracts was washed with saturated brine and dried by anhydrous sodium sulfate, the solvent was removed under reduced pressure to give crude product that was purified by silica gel column chromatography using petroleum ether-EtOAc as eluent.

2.3 Recycling of the brush catalyst

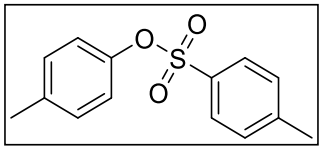
The reaction of phenol and *p*-TsCl was selected as the model reaction and was performed as described above, except for the separated catalyst was successively reused for the next reaction. For the next cycle was added successively phenol and *p*-TsCl in water and repeated the previous procedure. After 5 cycles, the spectral data (IR) of the ionic liquid brush was identical to the initial ionic liquid brush sample.

3. Characterization data of the products (Table x-y means Table x, entry y, e.g., Table 1-2 = Table 1, entry 2)



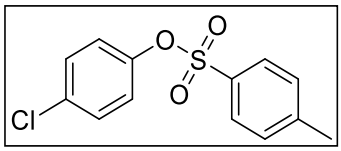
Phenyl *p*-toluenesulfonate[3] (Table 2-1): The reaction of phenol (0.188 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.491 g (99 %) of phenyl *p*-toluenesulfonate as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.45 (s, 3H), 6.98 (d, J = 7.2 Hz, 2H), 7.24-7.32 (m, 5H), 7.70 (d, J = 8.3 Hz, 2H).



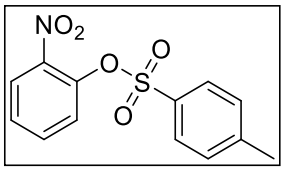
4-Totyl *p*-toluenesulfonate[3] (Table 2-2): The reaction of 4-methylphenol (0.216 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate(0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.493 g (94 %) of 4-totyl *p*-toluenesulfonate as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.30 (s, 3H), 2.44 (s, 3H), 6.84 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H).



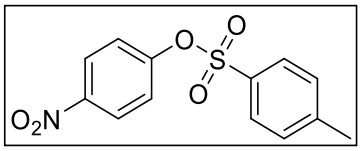
4-Chlorophenyl *p*-toluenesulfonate[3] (Table 2-3): The reaction of 4-chlorophenol (0.256 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.558 g (99 %) of 4-chlorophenyl *p*-toluenesulfonate as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.45 (s, 3H), 6.92 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.1 Hz, 2H).



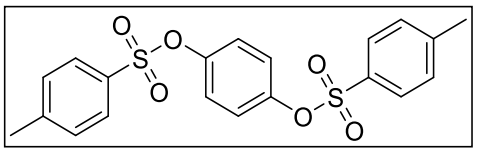
2-Nitrophenyl *p*-toluenesulfonate[3] (Table 2-4): The reaction of 2-nitrophenol (0.278 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.533 g (91 %) of 2-nitrophenyl *p*-toluenesulfonate as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.46 (s, 3H), 7.34 (d, J = 8.0 Hz, 2H), 7.39-7.44 (m, 2H), 7.59-7.63 (m, 1H), 7.76 (d, J = 8.1 Hz, 2H), 7.89 (d, J = 8.0 Hz, 1H).



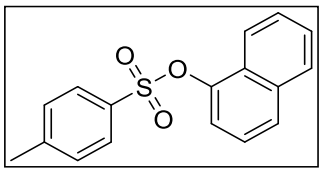
4-Nitrophenyl *p*-toluenesulfonate[3] (Table 2-5): The reaction of 4-nitrophenol (0.278 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.539 g (92 %) of 4-nitrophenyl *p*-toluenesulfonate as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.46 (s, 3H), 7.18 (d, J = 9.2 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 8.19 (d, J = 9.2 Hz, 2H).



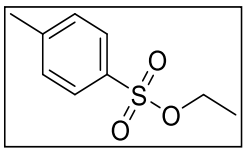
1,4-Phenylene bis(*p*-toluenesulfonate)[3] (Table 2-6): The reaction of hydroquinone (0.220 g, 2 mmol), *p*-toluenesulfonyl chloride (0.912 g, 4.8 mmol), sodium carbonate (0.424 g, 4 mmol) and the brush (0.064 g, 0.08 mmol) in H_2O (4 mL) produced 0.802 g (96 %) of 1,4-phenylene bis(*p*-toluenesulfonate) as a white solid.

^{1}H NMR (3 00 MHz, $CDCl_3$) δ (ppm): 2.46 (s, 6H), 6.90 (s, 4H), 7.31 (d, J = 8.1 Hz, 4H), 7.67 (d, J = 8.1 Hz, 4H).



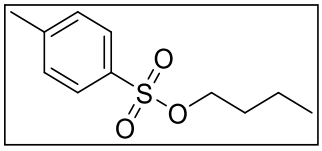
Naphthalen-1-yl *p*-toluenesulfonate[3] (Table 2-7): The reaction of 2-naphthol (0.288 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.560 g (94 %) of naphthalen-1-yl *p*-toluenesulfonate as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.31 (s, 3H), 7.12 (d, J = 7.6 Hz, 1H), 7.17 (d, J = 8.1 Hz, 2H), 7.25-7.29 (m, 1H), 7.33-7.39 (m, 2H), 7.63-7.75 (m, 4H), 7.82 (d, J = 8.2 Hz, 1H).



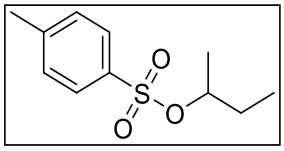
Ethyl *p*-toluenesulfonate[4] (Table 3-1): The reaction of ethanol (0.092 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.168 g (42 %) of ethyl *p*-toluenesulfonate as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.28 (t, J = 7.1 Hz, 3H), 2.43 (s, 3H), 4.09 (q, J = 7.1 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.1 Hz, 2H).



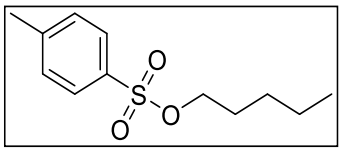
Butyl *p*-toluenesulfonate[5] (Table 3-2): The reaction of 1-butanol (0.148 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.260 g (57 %) of butyl *p*-toluenesulfonate as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.85 (t, J = 7.4 Hz, 3H), 1.29-1.38 (m, 2H), 1.60-1.63 (m, 2H), 2.44 (s, 3H), 4.02 (t, J = 6.5 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H).



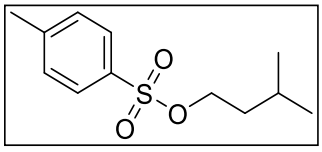
2-Butyl *p*-toluenesulfonate[6] (Table 3-3): The reaction of 2-butanol (0.148 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.246 g (54 %) of 2-butyl *p*-toluenesulfonate as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.60-0.67 (m, 3H), 1.07 (t, J = 5.7 Hz, 3H), 1.37-1.43 (m, 2H), 2.25 (s, 3H), 4.33-4.43 (m, 1H), 7.18 (d, J = 8.1 Hz, 2H), 7.63 (d, J = 8.2 Hz, 2H).



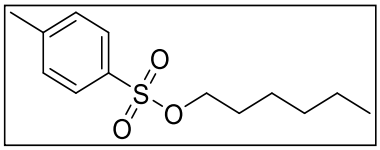
Pentyl *p*-toluenesulfonate[7] (Table 3-4): The reaction of 1-pentanol (0.176 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.334 g (69 %) of pentyl *p*-toluenesulfonate as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.85 (t, J = 8.0 Hz, 3H), 1.23-1.30 (m, 4H), 1.62-1.66 (m, 2H), 2.45 (s, 3H), 4.02 (t, J = 6.5 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.3 Hz, 2H).



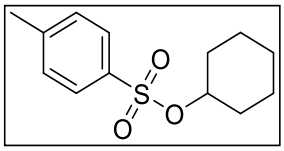
Isopentyl *p*-toluenesulfonate[5] (Table 3-5): The reaction of 3-methyl-1-butanol (0.177 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.320 g (66 %) of isopentyl *p*-toluenesulfonate as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.83 (d, J = 6.6 Hz, 6H), 1.49-1.54 (m, 2H), 1.64-1.71 (m, 1H), 2.45 (s, 3H), 4.05 (t, J = 6.6 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H).



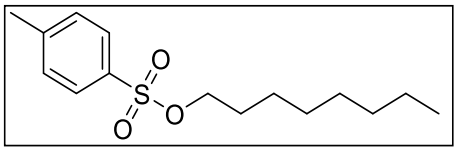
Hexyl *p*-toluenesulfonate[7] (Table 3-6): The reaction of 1-hexanol (0.204 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.405 g (79 %) of hexyl *p*-toluenesulfonate as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.84 (t, J = 6.8 Hz, 3H), 1.17-1.31 (m, 6H), 1.59-1.66 (m, 2H), 2.44 (s, 3H), 4.02 (t, J = 6.5 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 7.79 (d, J = 7.9 Hz, 2H).



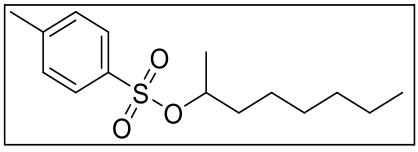
Cyclohexyl *p*-toluenesulfonate[4] (Table 3-7): The reaction of cyclohexanol (0.200 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.330 g (65 %) of cyclohexyl *p*-toluenesulfonate as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.22-1.29 (m, 3H), 1.43-1.54 (m, 3H), 1.66-1.78 (m, 4H), 2.42 (s, 3H), 4.48 (m, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H).



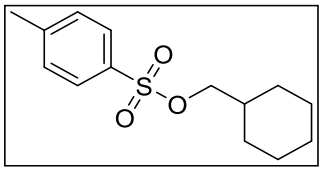
Octyl *p*-toluenesulfonate[4] (Table 3-8): The reaction of 1-octanol (0.260 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.517 g (91 %) of octyl *p*-toluenesulfonate as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.86 (t, J = 6.7 Hz, 3H), 1.21-1.27 (m, 10H), 1.58-1.66 (m, 2H), 2.43 (s, 3H), 4.01 (t, J = 6.5 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H).



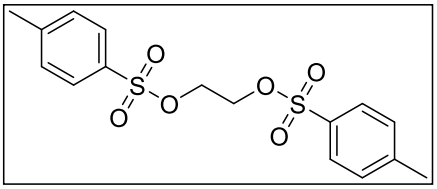
2-Octyl *p*-toluenesulfonate[4] (Table 3-9): The reaction of 2-octanol (0.260 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.466 g (82 %) of 2-octyl *p*-toluenesulfonate as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.75 (t, *J* = 6.9 Hz, 3H), 1.06-1.16 (m, 11H), 1.46-1.52 (m, 2H), 2.33 (s, 3H), 4.44-4.52 (m, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H).



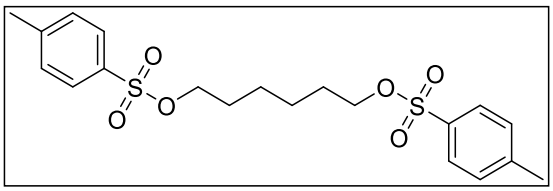
Cyclohexylmethyl *p*-toluenesulfonate[8] (Table 3-10): The reaction of cyclohexylmethanol (0.228 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.391 g (73 %) of cyclohexylmethyl *p*-toluenesulfonate as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm): 0.83-0.93 (m, 2H), 1.03-1.24 (m, 3H), 1.59-1.69 (m, 6H), 2.43 (s, 3H), 3.79 (d, *J* = 6.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H).



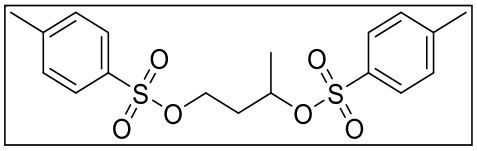
Ethane-1,2-diyl bis(*p*-toluenesulfonate)[9] (Table 3-11): The reaction of ethylene glycol (0.124 g, 2 mmol), *p*-toluenesulfonyl chloride (0.912 g, 4.8 mmol), sodium carbonate (0.424 g, 4 mmol) and the brush (0.064 g, 0.08 mmol) in H_2O (4 mL) produced 0.363 g (49 %) of ethane-1,2-diyl bis(*p*-toluenesulfonate) as a white crystal.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm): 2.46 (s, 6H), 4.19 (s, 4H), 7.34 (d, *J* = 8.0 Hz, 4H), 7.73 (d, *J* = 8.0 Hz, 4H).



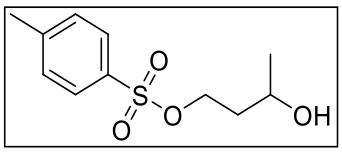
Hexane-1,6-diyl bis(*p*-toluenesulfonate)[10] (Table 3-12): The reaction of 1,6-hexandiol (0.236 g, 2 mmol), *p*-toluenesulfonyl chloride (0.912 g, 4.8 mmol), sodium carbonate (0.424 g, 4 mmol) and the brush (0.064 g, 0.08 mmol) in H_2O (4 mL) produced 0.668 g (66 %) of hexane-1,6-diyl bis(*p*-toluenesulfonate) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm): 1.27 (t, *J* = 6.4 Hz, 4H), 1.59 (m, *J* = 6.1 Hz, 4H), 2.45 (s, 6H), 3.98 (t, *J* = 6.4 Hz, 4H), 7.35 (d, *J* = 8.0 Hz, 4H), 7.77 (d, *J* = 8.1 Hz, 4H).



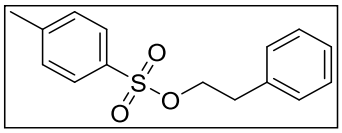
Butane-1,3-diyl bis(4-methylbenzenesulfonate) (Table 3-13): The reaction of 1,3-butanediol (0.182 g, 2 mmol), *p*-toluenesulfonyl chloride (0.912 g, 4.8 mmol), sodium carbonate (0.424 g, 4 mmol) and the brush (0.064 g, 0.08 mmol) in H_2O (4 mL) produced 0.391 g (49 %) of butane-1,3-diyl bis(4-methylbenzenesulfonate) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.23 (d, J = 6.3 Hz, 3H), 1.83-1.98 (m, 2H), 2.44 (s, 3H), 2.45 (s, 3H), 3.89-4.04 (m, 4H), 4.66-4.71 (m, 1H), 7.32-7.35 (m, 4H), 7.73-7.35 (m, 4H).



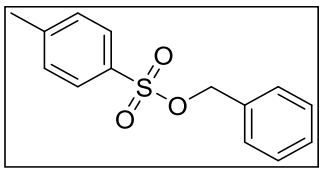
3-hydroxybutyl 4-methylbenzenesulfonate (Table 3-13): The reaction of 1,3-butanediol (0.182 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.298 g (61 %) of 3-hydroxybutyl 4-methylbenzenesulfonate as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.18 (d, J = 6.6 Hz, 3H), 1.66-1.73 (m, 2H), 1.80-1.84 (m, 1H), 2.45 (s, 3H), 3.94 (s, 1H), 4.08-4.26 (m, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H).



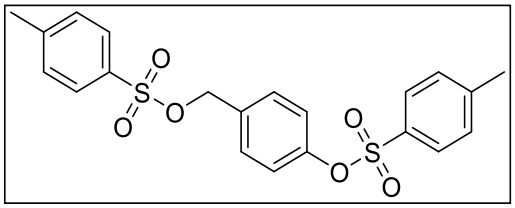
Phenethyl *p*-toluenesulfonate[8] (Table 3-14): The reaction of 2-phenylethanol (0.244 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.447 g (81 %) of phenethyl *p*-toluenesulfonate as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.35 (s, 3H), 2.87 (t, J = 7.1 Hz, 2H), 4.13 (t, J = 7.1 Hz, 2H), 7.02-7.04 (m, 2H), 7.13-7.21 (m, 5H), 7.60-7.62 (m, 2H).



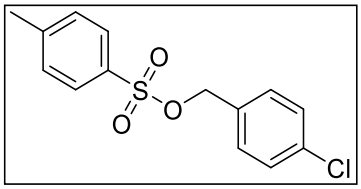
Benzyl *p*-toluenesulfonate[4] (Table 3-15): The reaction of benzyl alcohol (0.216 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.317 g (61%) of benzyl *p*-toluenesulfonate as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.38 (s, 3H), 4.96 (s, 2H), 7.17-7.19 (m, 1H), 7.23-7.31 (m, 6H), 7.73 (d, J = 8.0 Hz, 2H).



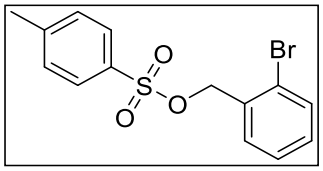
4-(Tosyloxy)benzyl *p*-toluenesulfonate (Table 3-16): The reaction of 4-hydroxybenzyl alcohol (0.248 g, 2 mmol), *p*-toluenesulfonyl chloride (0.912 g, 4.8 mmol), sodium carbonate (0.424 g, 4 mmol) and the brush (0.064 g, 0.08 mmol) in H_2O (4 mL) produced 0.821 g (95 %) of 4-(tosyloxy)benzyl *p*-toluenesulfonate as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.45 (s, 6H), 5.00 (s, 2H), 6.94 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 8.0 Hz, 4H), 7.69 (d, J = 8.5 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H).



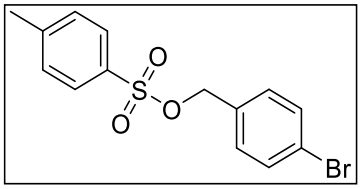
4-Chlorobenzyl *p*-toluenesulfonate[12] (Table 3-17): The reaction of 4-chlorobenzyl alcohol (0.284 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.456 g (77 %) of 4-chlorobenzyl *p*-toluenesulfonate as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.45 (s, 3H), 5.02 (s, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.27-7.34 (m, 4H), 7.78 (d, J = 8.0 Hz, 2H).



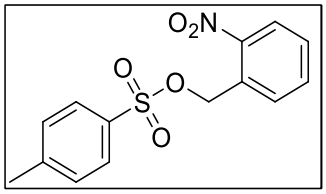
2-Bromobenzyl *p*-toluenesulfonate[13] (Table 3-18): The reaction of 2-bromobenzyl alcohol (0.372 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.544 g (80 %) of 2-bromobenzyl *p*-toluenesulfonate as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.44 (s, 3H), 5.14 (s, 2H), 7.16-7.20 (m, 1H), 7.27-7.30 (m, 1H), 7.33-7.34 (m, 2H), 7.38-7.40 (m, 1H), 7.50-7.50 (m, 1H), 7.82-7.84 (m, 2H).



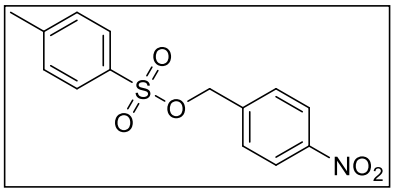
4-Bromobenzyl *p*-toluenesulfonate[12] (Table 3-19): The reaction of 4-bromobenzyl alcohol (0.372 g, 2mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.558 g (82 %) of 4-bromobenzyl *p*-toluenesulfonate as a white crystal.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.45 (s, 3H), 5.01 (s, 2H), 7.12 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H).



2-Nitrobenzyl *p*-toluenesulfonate[6] (Table 3-20): The reaction of 2-nitrobenzyl alcohol (0.307 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.547 g (89 %) of 2-nitrobenzyl *p*-toluenesulfonate as a white solid.

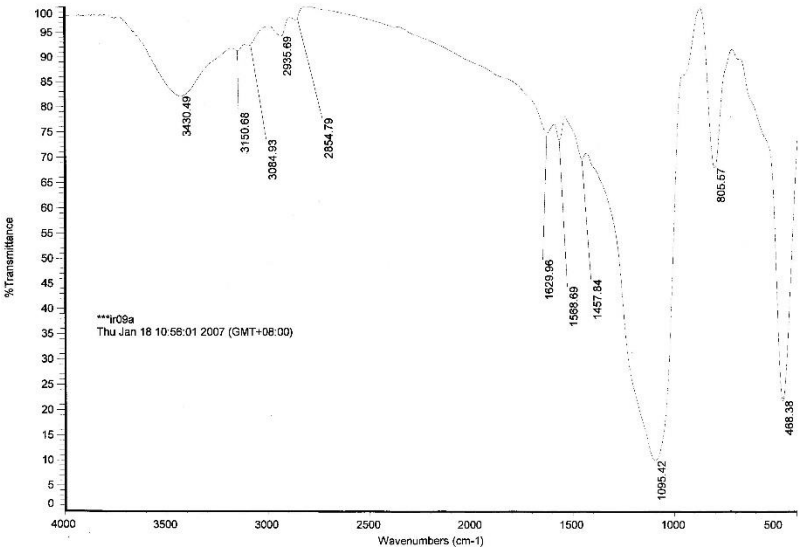
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.43 (s, 3H), 5.46 (s, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.49 (t, J = 7.7 Hz, 1H), 7.63-7.74 (m, 2H), 7.82 (d, J = 8.2 Hz, 2H), 8.08 (d, J = 8.1 Hz, 1H).



4-Nitrobenzyl *p*-toluenesulfonate[4] (Table 3-21): The reaction of 4-nitrobenzyl alcohol (0.307 g, 2 mmol), *p*-toluenesulfonyl chloride (0.456 g, 2.4 mmol), sodium carbonate (0.212 g, 2 mmol) and the brush (0.032 g, 0.04 mmol) in H_2O (4 mL) produced 0.565 g (92 %) of 4-nitrobenzyl *p*-toluenesulfonate as a yellow solid.

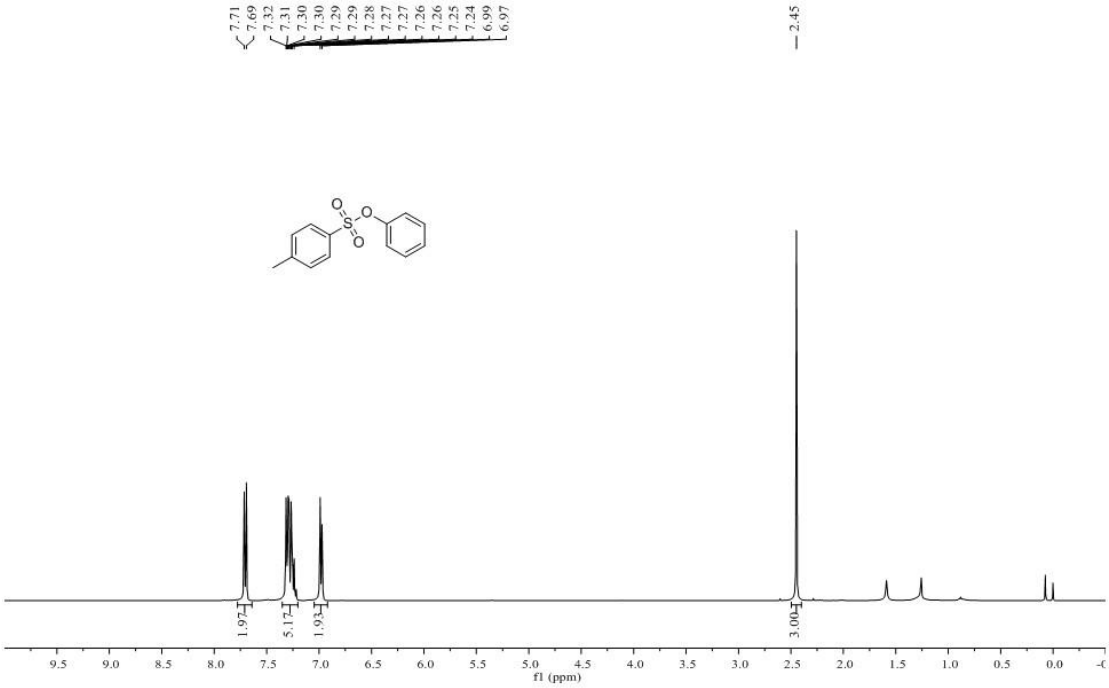
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.45 (s, 3H), 5.14 (s, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.1 Hz, 2H), 8.17 (d, J = 8.6 Hz, 2H).

4. IR spectrum of the ionic liquid brush

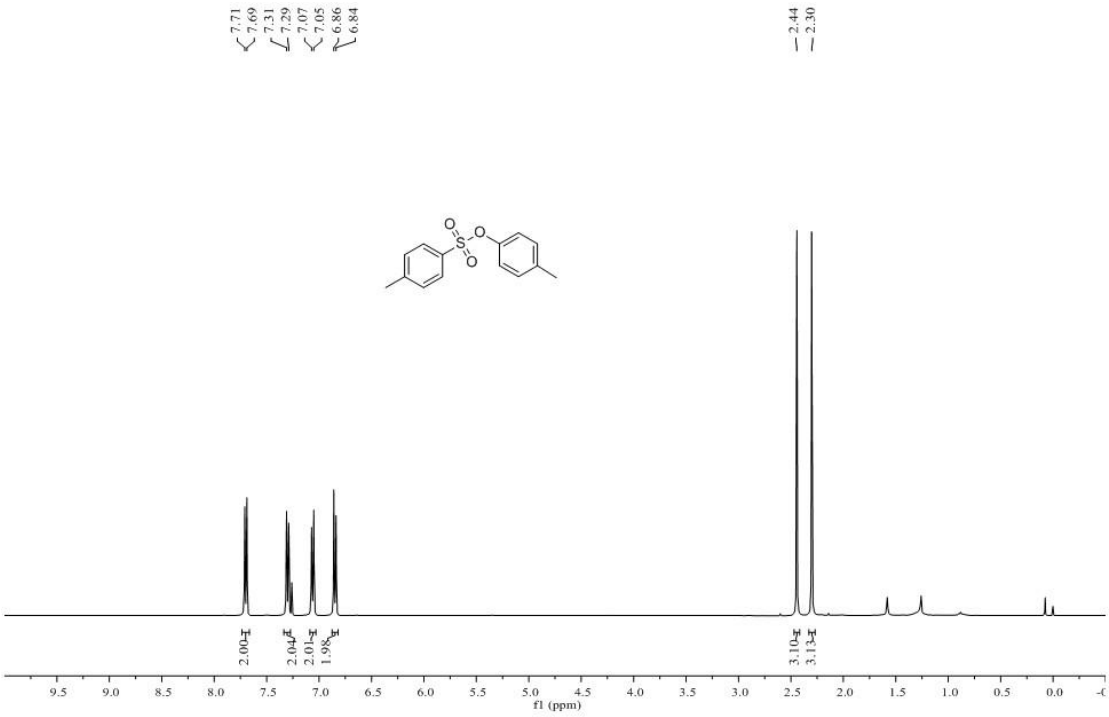


IR spectrum of the ionic liquid brush

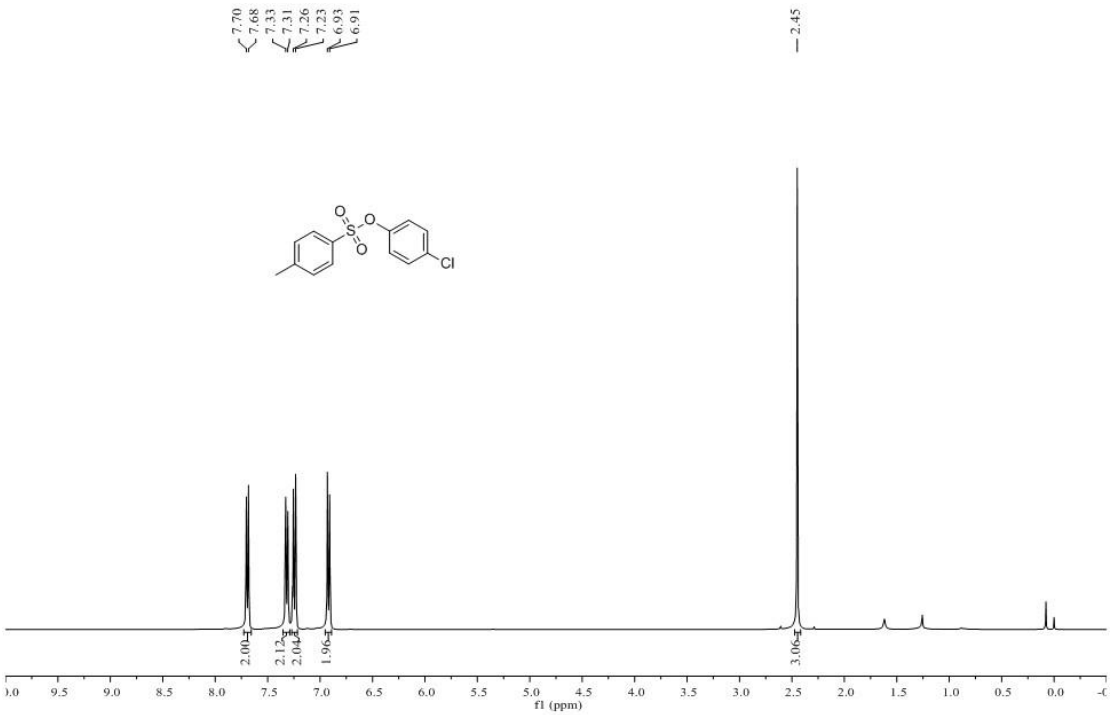
5. Copies of the ^{1}H NMR spectra of the products.



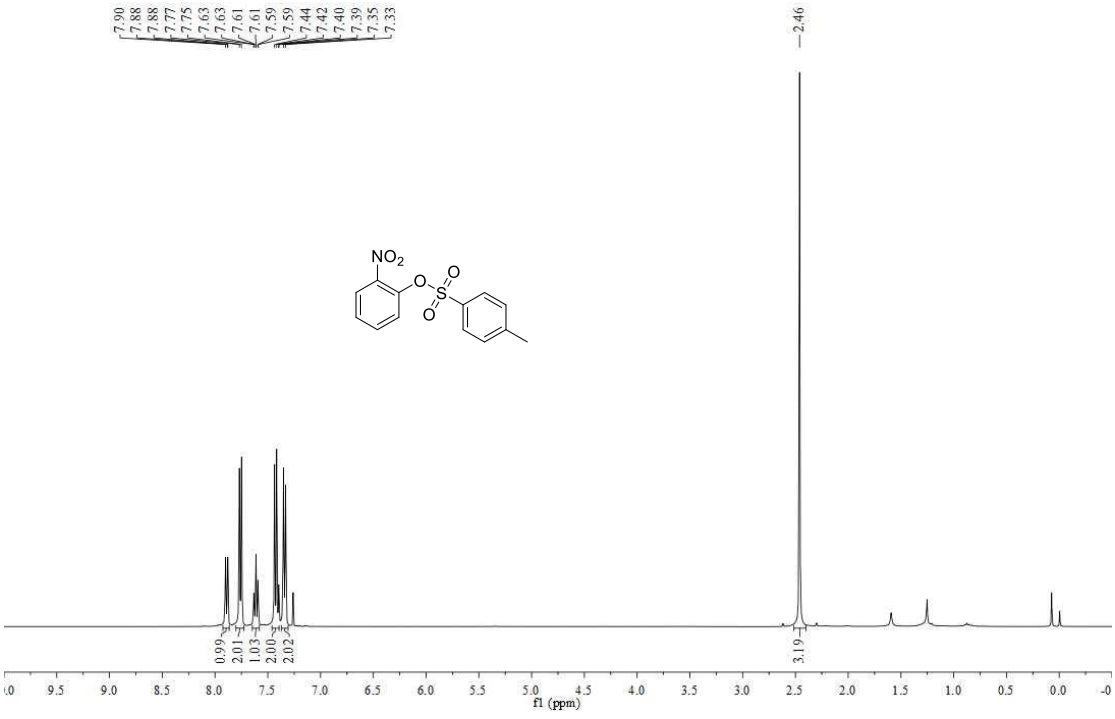
^{1}H NMR spectra of phenyl *p*-toluenesulfonate



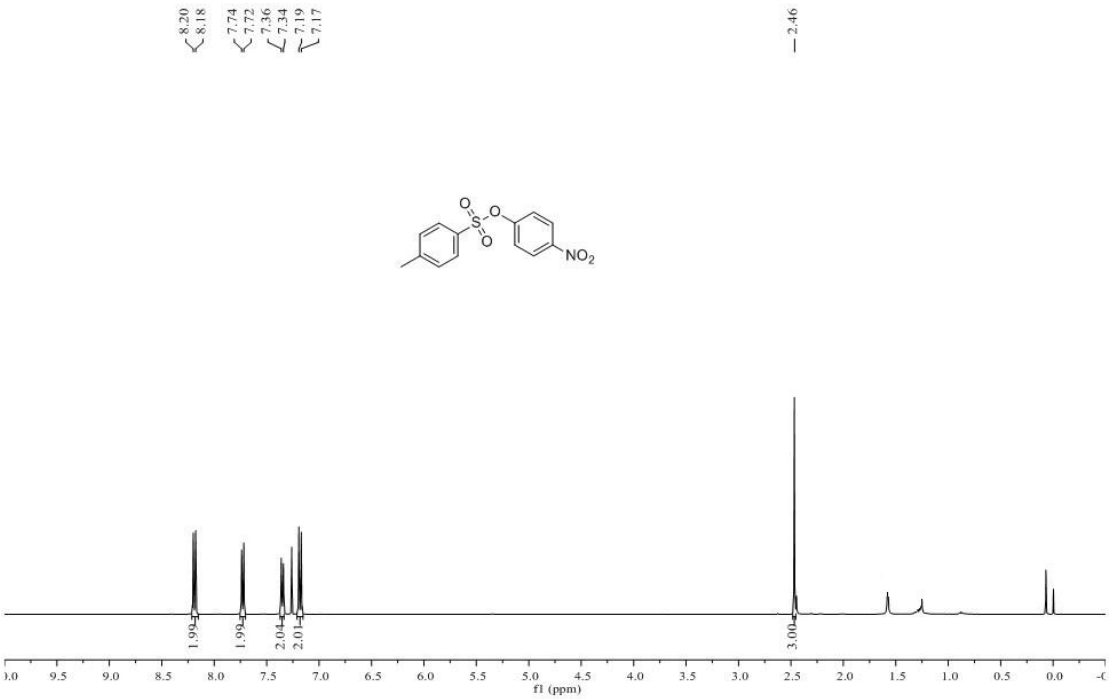
^{1}H NMR spectra of 4-totyl *p*-toluenesulfonate



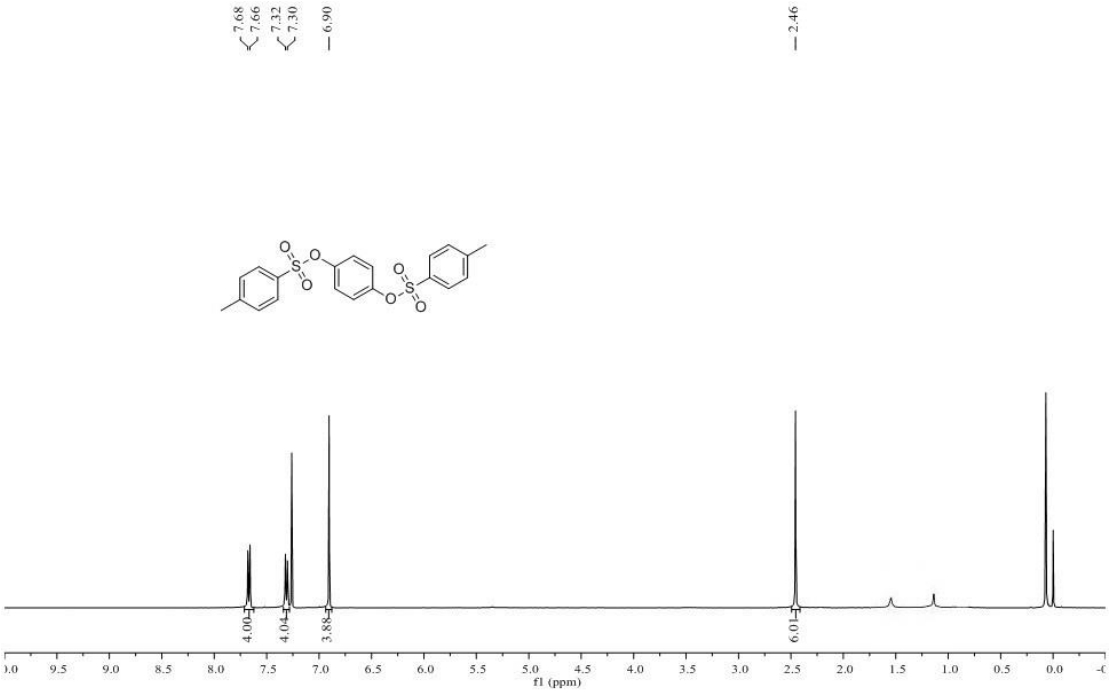
^{1}H NMR spectra of 4-chlorophenyl *p*-toluenesulfonate



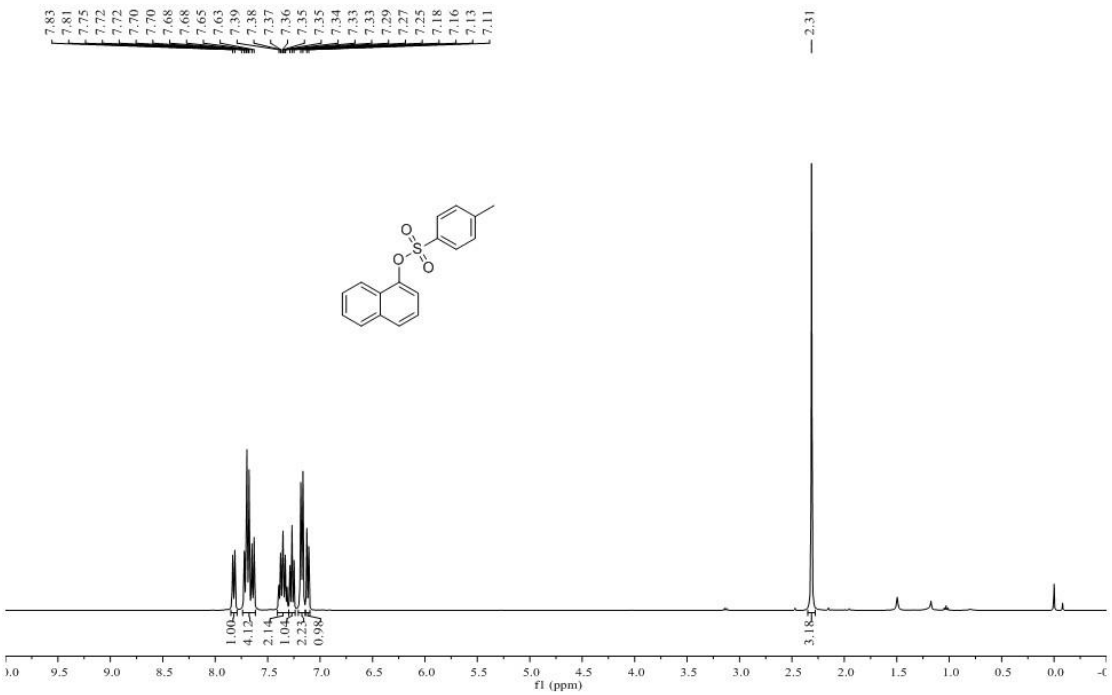
^{1}H NMR spectra of 2-nitrophenyl *p*-toluenesulfonate



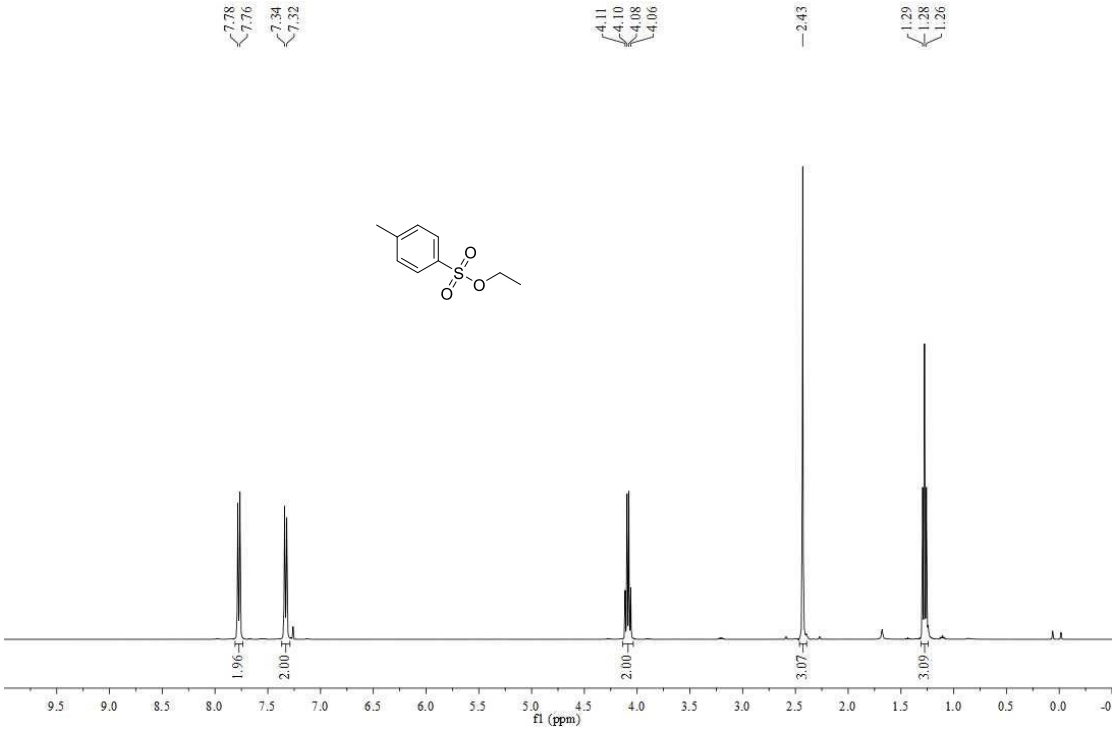
^{1}H NMR spectra of 4-nitrophenyl *p*-toluenesulfonate



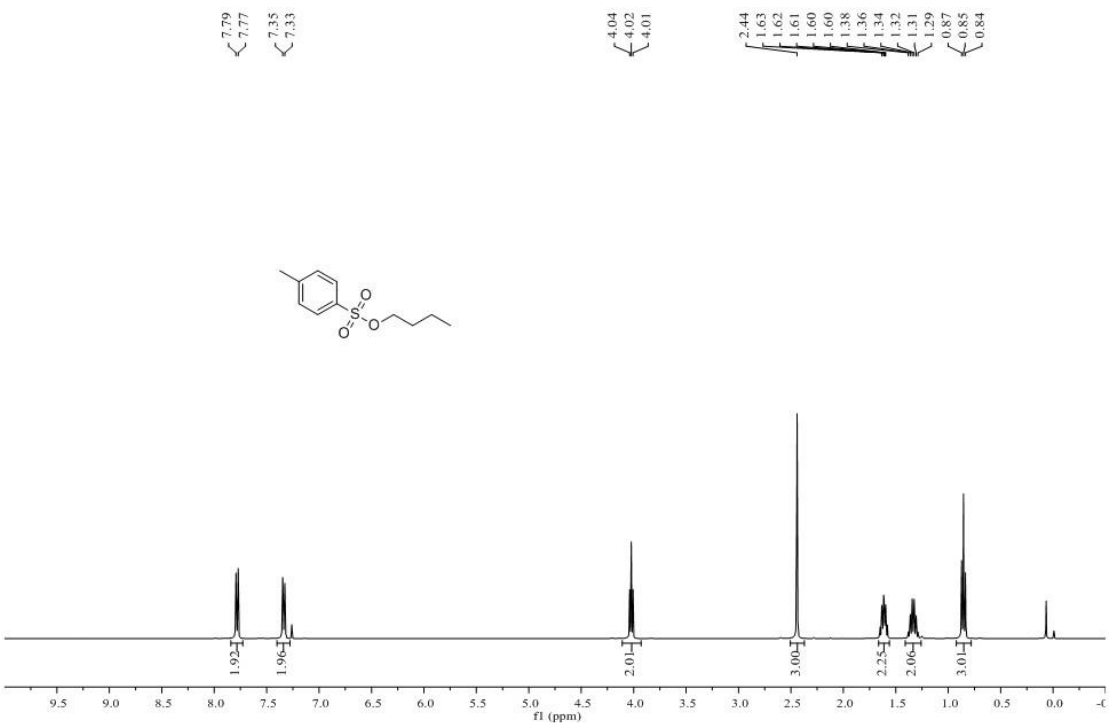
^{1}H NMR spectra of 1,4-phenylene bis(*p*-toluenesulfonate)



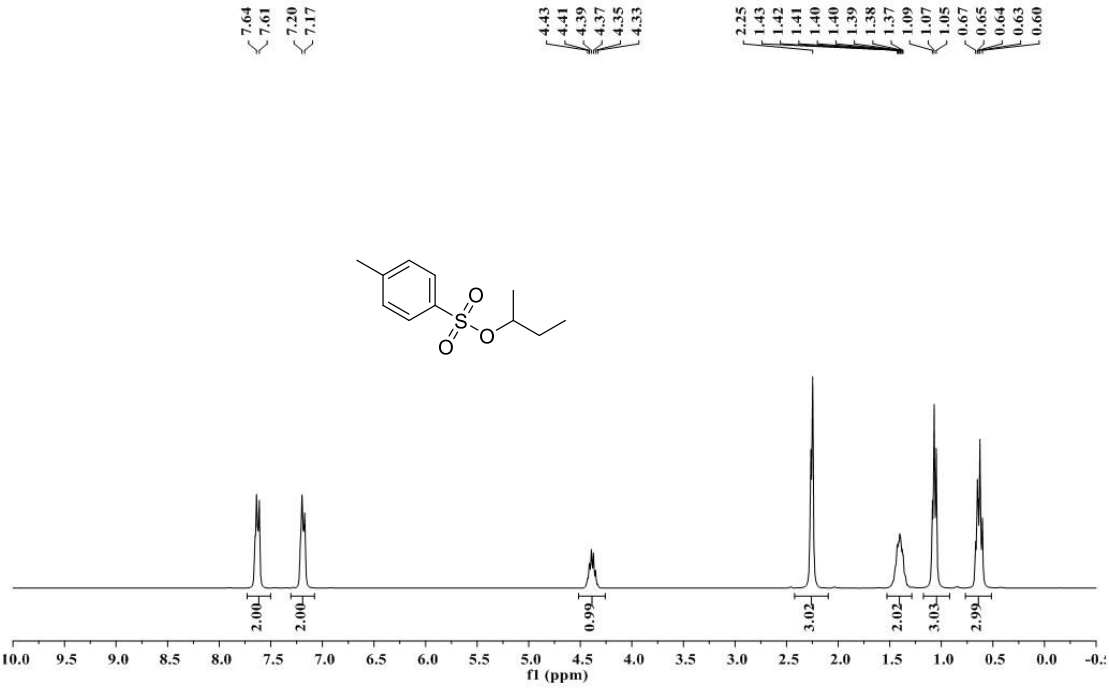
^{1}H NMR spectra of naphthalen-1-yl *p*-toluenesulfonate



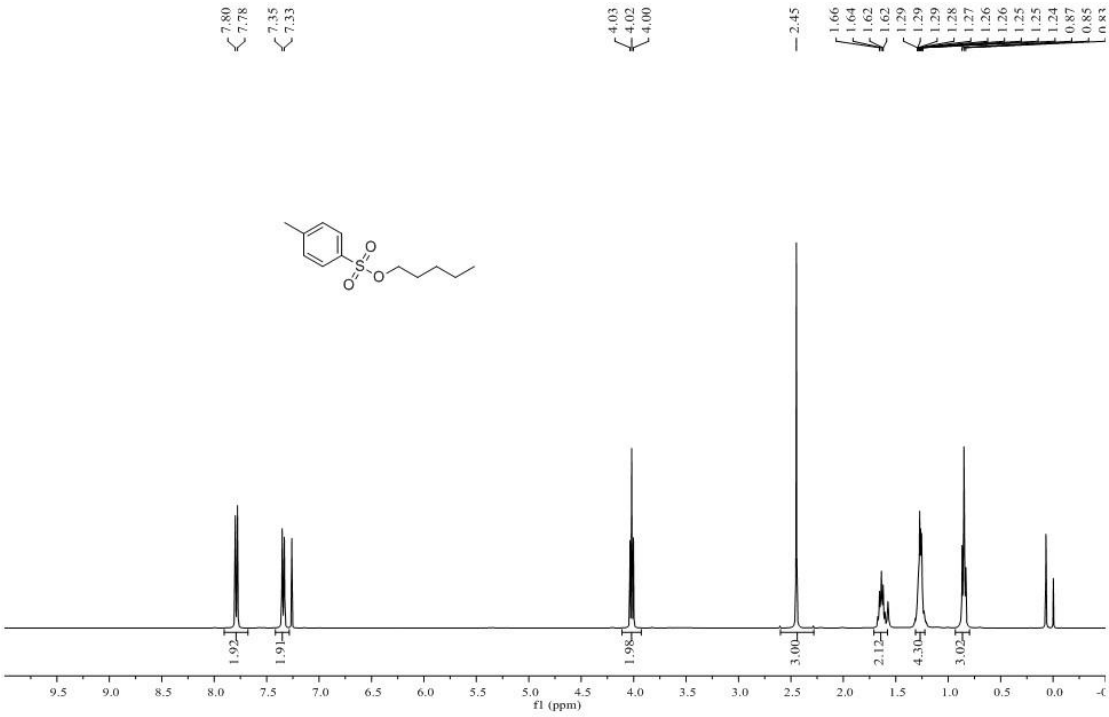
^{1}H NMR spectra of ethyl *p*-toluenesulfonate



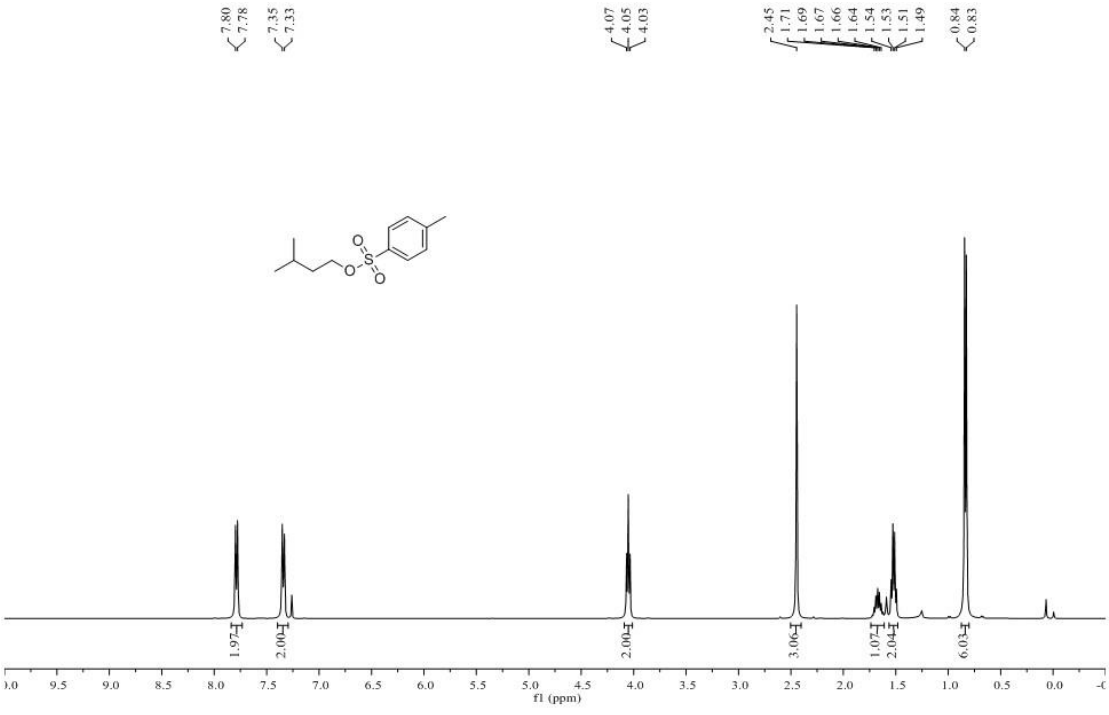
^{1}H NMR spectra of butyl *p*-toluenesulfonate



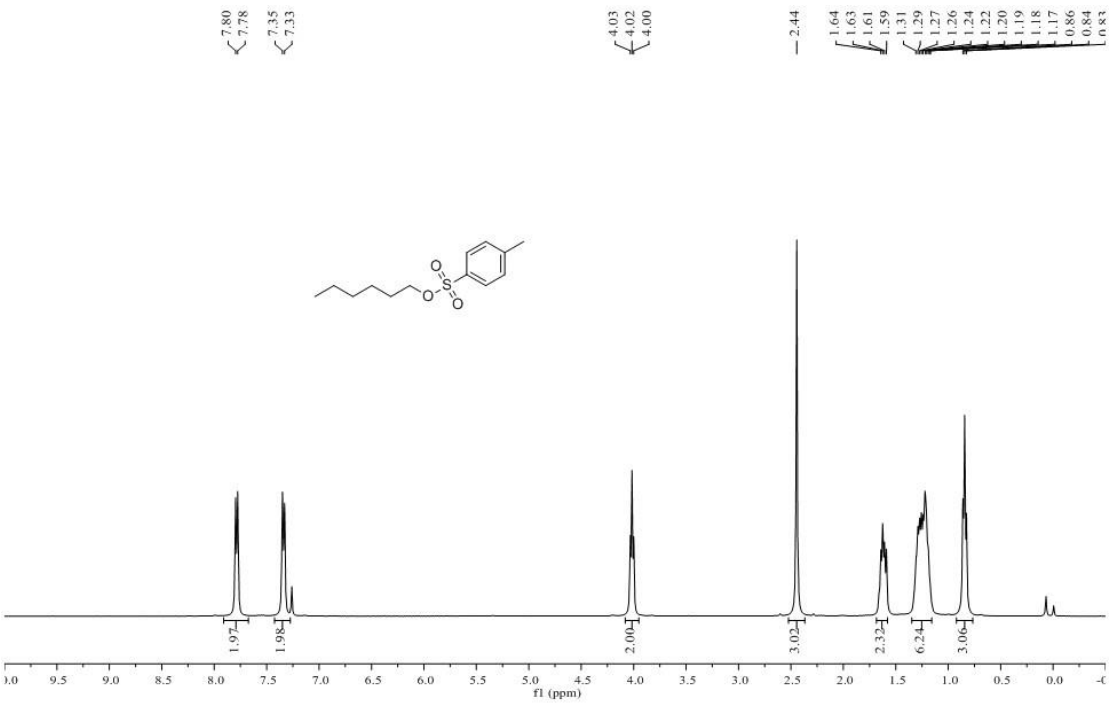
^{1}H NMR spectra of 2-butyl *p*-toluenesulfonate



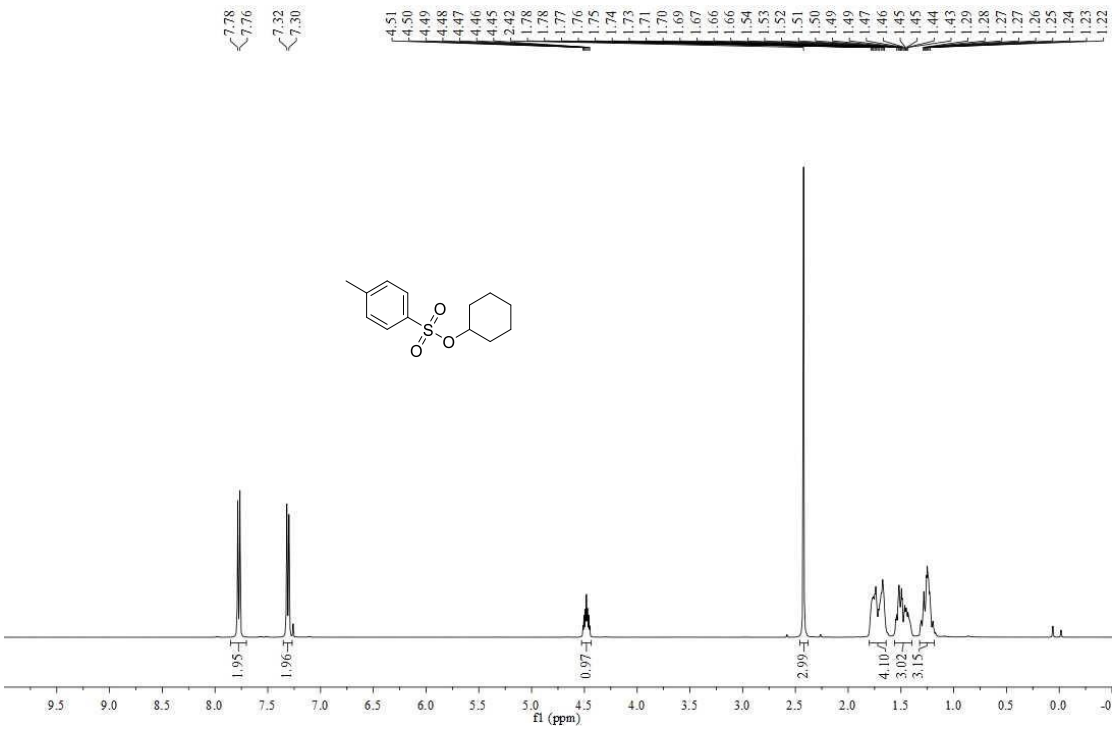
^{1}H NMR spectra of pentyl *p*-toluenesulfonate



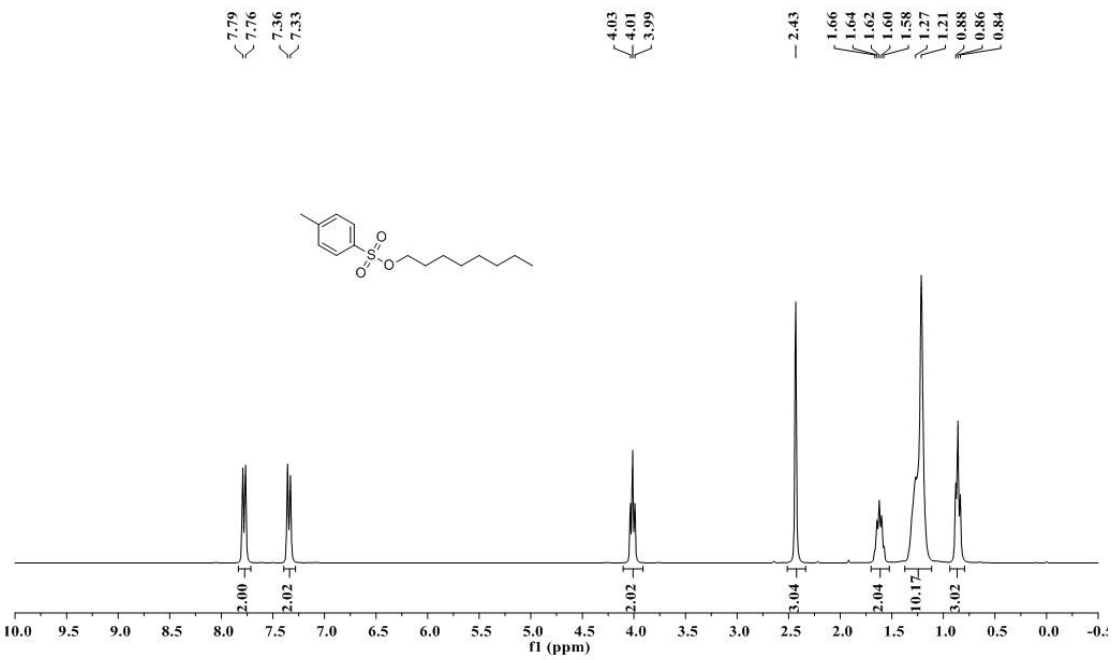
^{1}H NMR spectra of isopentyl *p*-toluenesulfonate



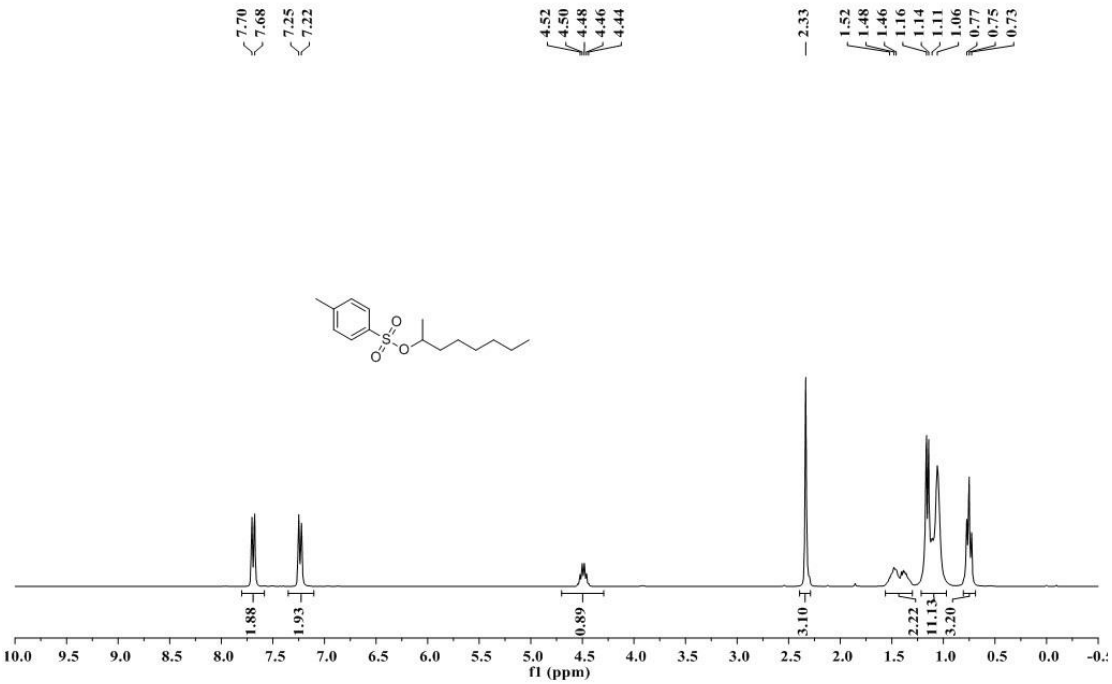
^{1}H NMR spectra of hexyl *p*-toluenesulfonate



^{1}H NMR spectra of cyclohexyl *p*-toluenesulfonate

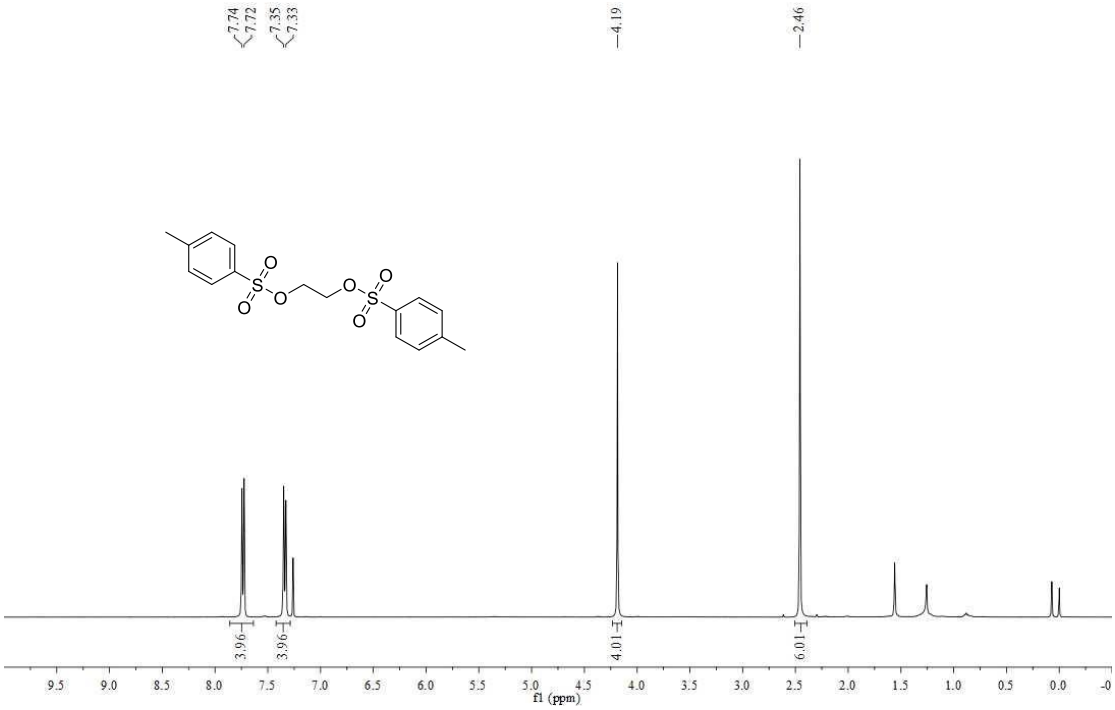


^{1}H NMR spectra of octyl *p*-toluenesulfonate



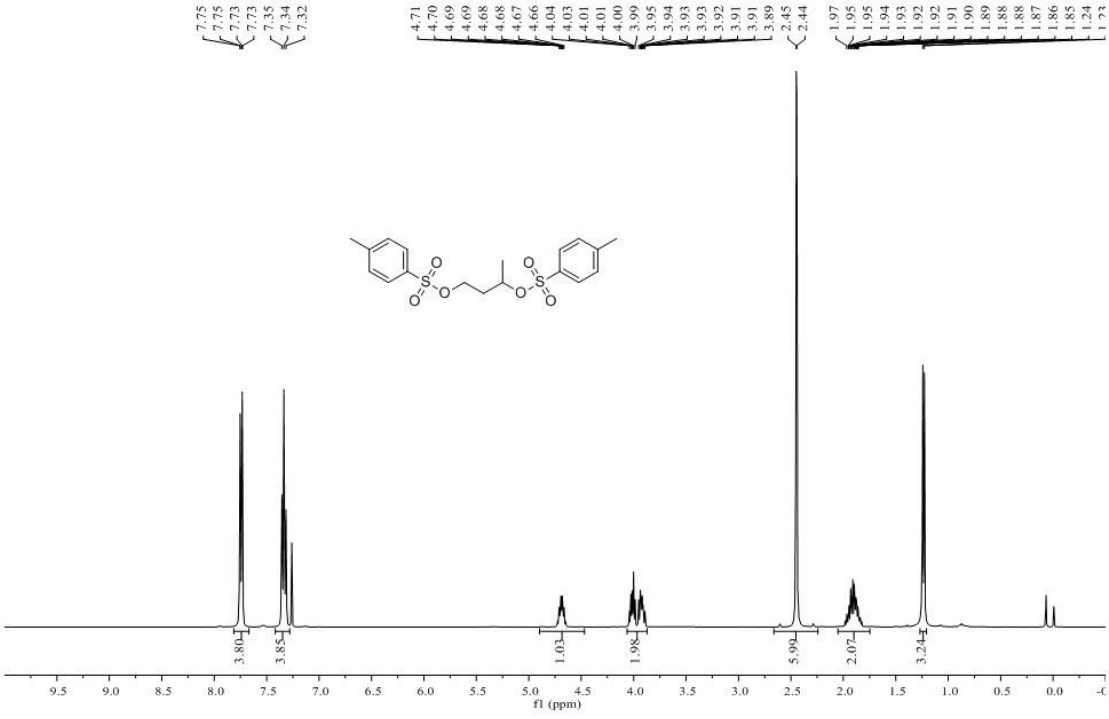
^{1}H NMR spectra of 2-octyl *p*-toluenesulfonate

^{1}H NMR spectra of cyclohexylmethyl *p*-toluenesulfonate

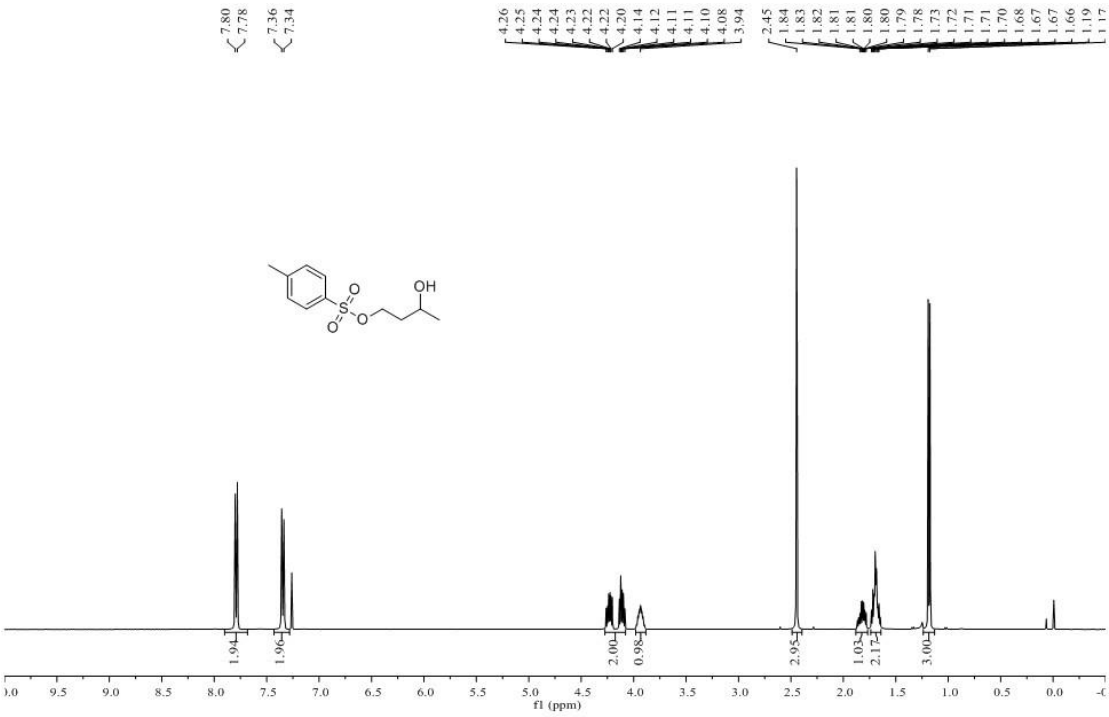


^{1}H NMR spectra of ethane-1,2-diyl bis(*p*-toluenesulfonate)

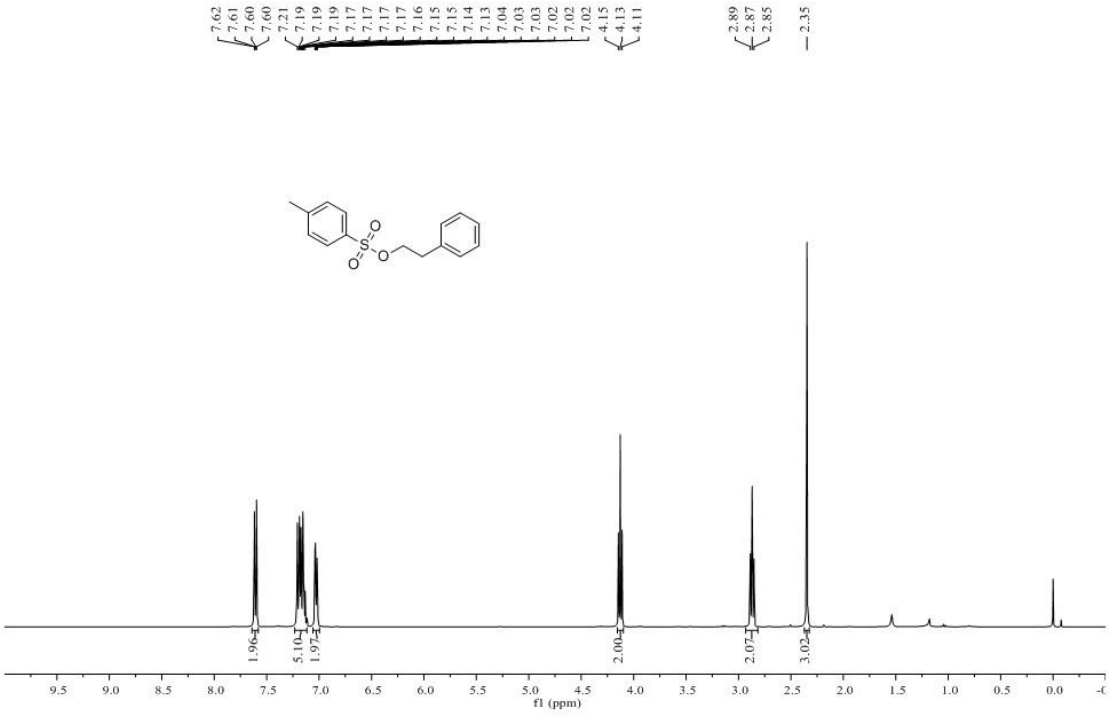
^{1}H NMR spectra of hexane-1,6-diyl bis(*p*-toluenesulfonate)



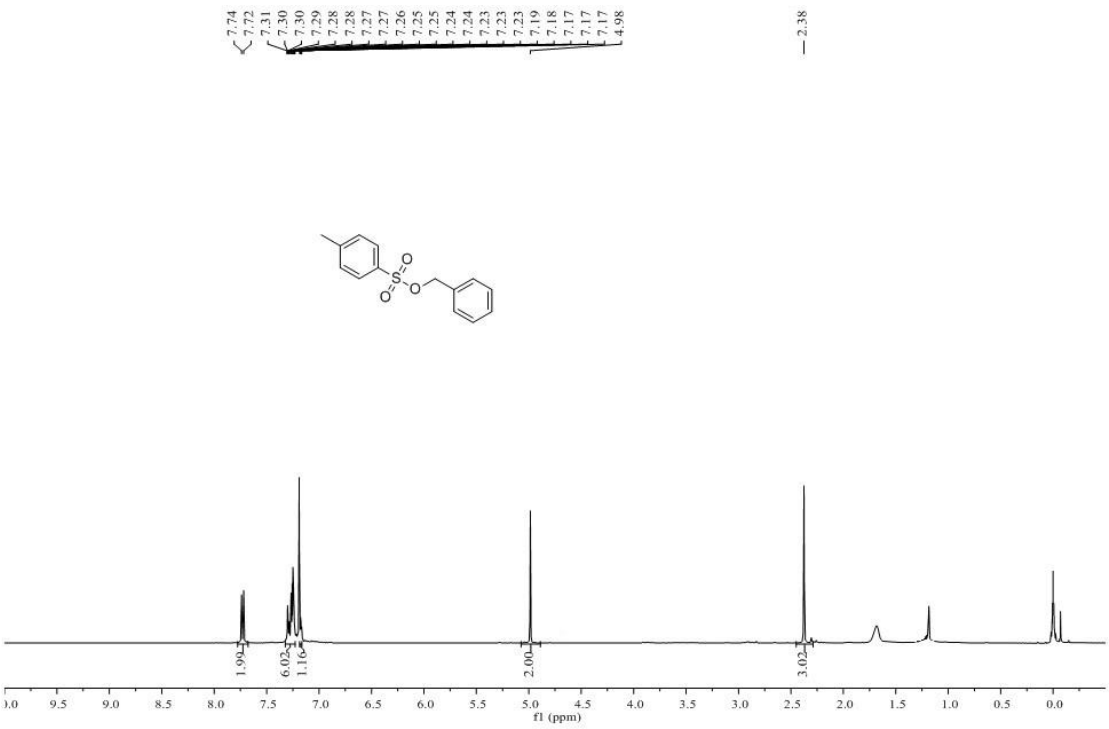
^{1}H NMR spectra of butane-1,3-diyl bis(4-methylbenzenesulfonate)



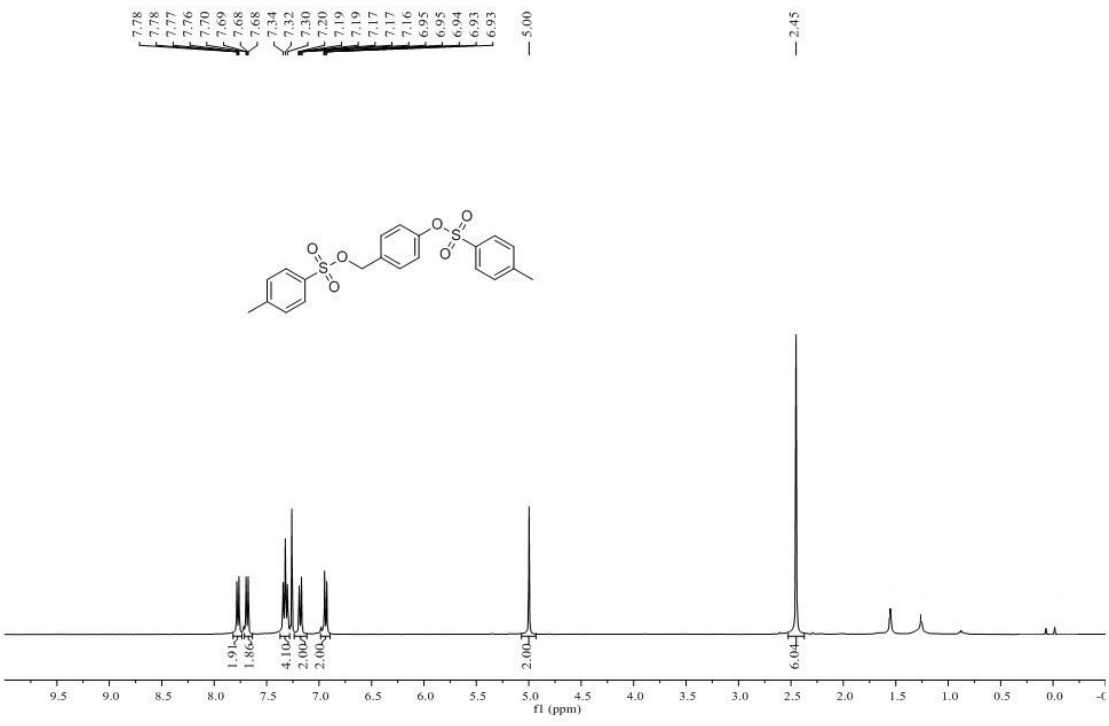
^{1}H NMR spectra of 3-hydroxybutyl 4-methylbenzenesulfonate



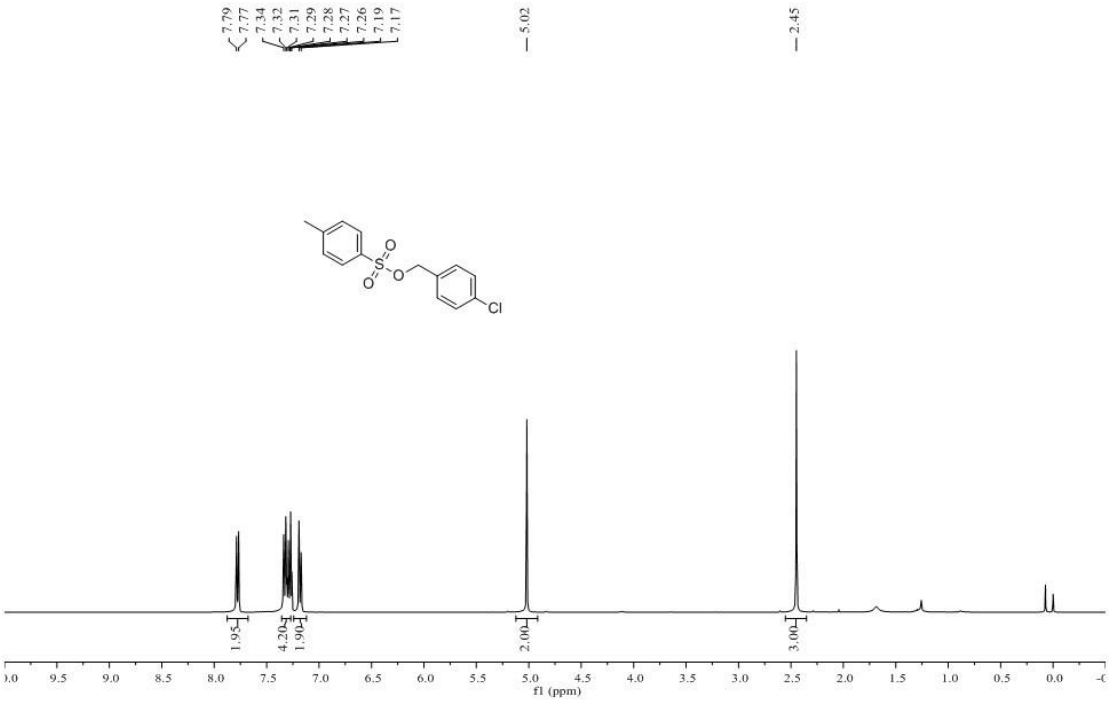
^{1}H NMR spectra of phenethyl *p*-toluenesulfonate



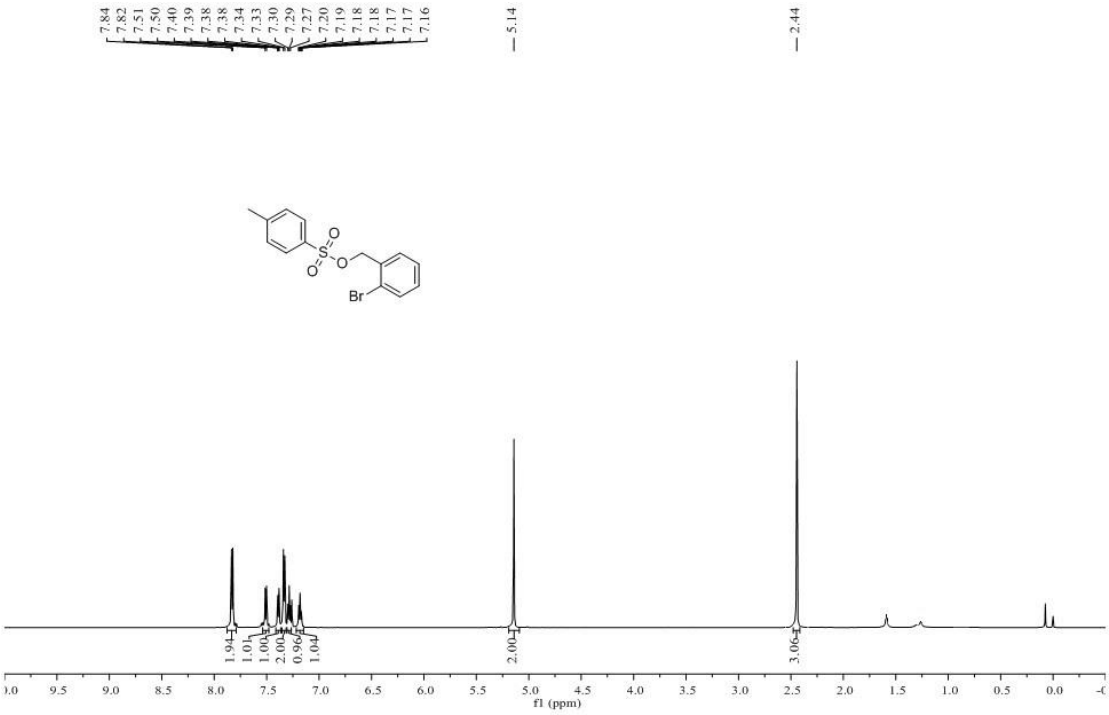
^{1}H NMR spectra of benzyl *p*-toluenesulfonate



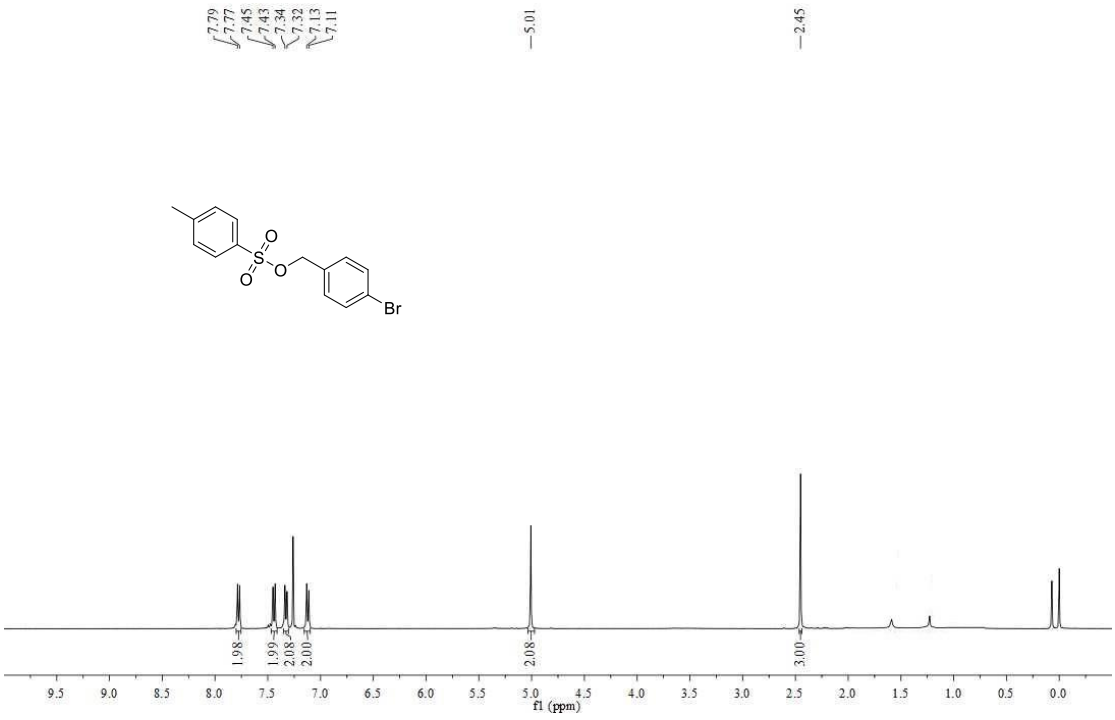
^{1}H NMR spectra of 4-(tosyloxy)benzyl *p*-toluenesulfonate



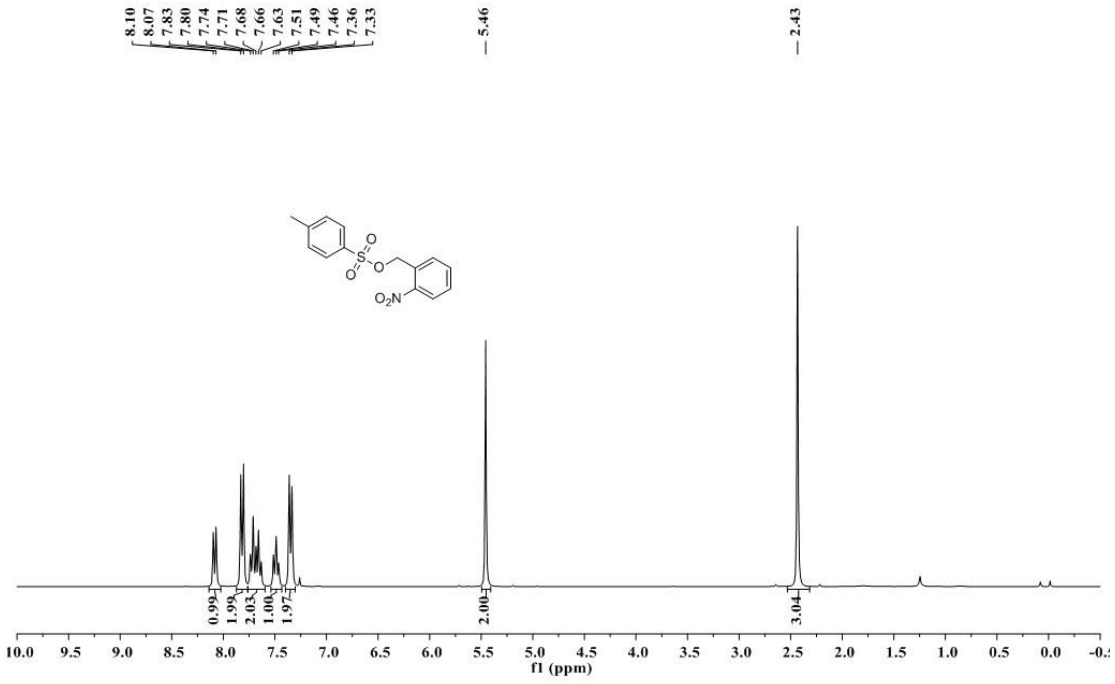
^{1}H NMR spectra of 4-chlorobenzyl *p*-toluenesulfonate



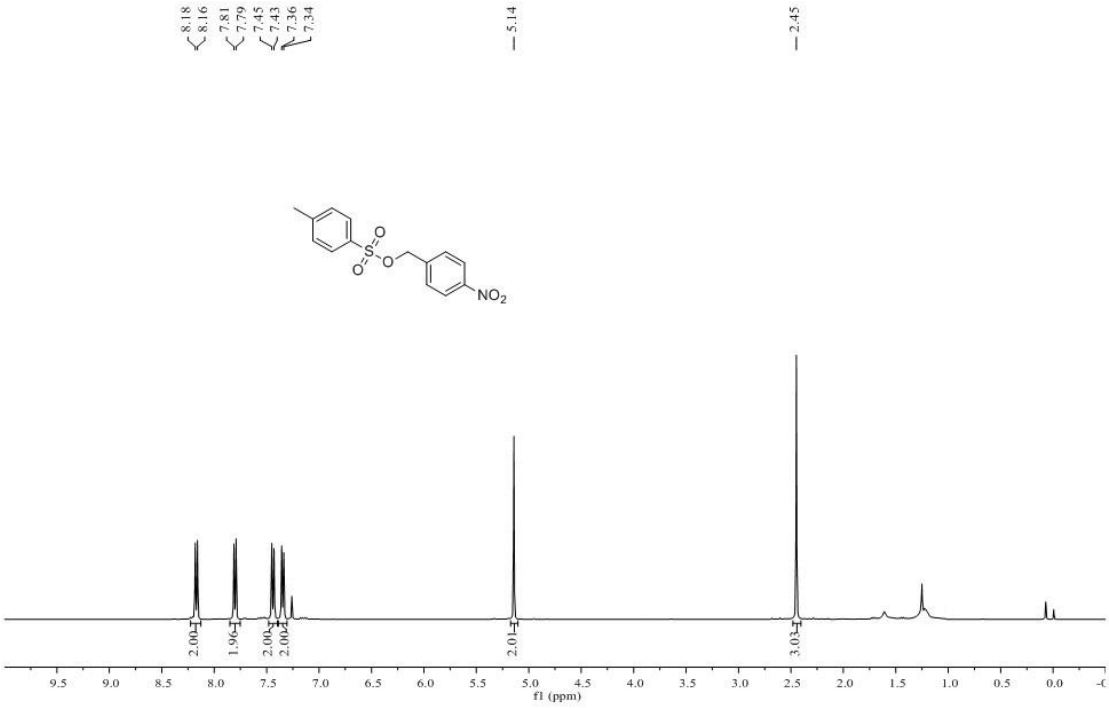
^{1}H NMR spectra of 2-bromobenzyl *p*-toluenesulfonate



^{1}H NMR spectra of 4-bromobenzyl *p*-toluenesulfonate



^{1}H NMR spectra of 2-nitrobenzyl *p*-toluenesulfonate



^{1}H NMR spectra of 4-nitrobenzyl *p*-toluenesulfonate

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