Electronic Supplementary Material (ESI) for ChemComm.

Mechanistic Studies of Reactive Oxygen Species Mediated Electrochemical Radical Reactions of Alkyl Iodides

Supporting Information

Experimental Procedures and ^{1}H NMR Spectra

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General Experimental Techniques

All reagents and solvents were used directly without further purification unless otherwise stated. Reaction progress was monitored by analytical thin layer chromatography (TLC) on silica gel coated aluminum oxide F254 plates (Merck KGaA). Developed TLC were visualized under UV light (254 nm). Flash column chromatography was performed using Biotage automatic column system (IS11579109). All ^{1}H NMR spectra were recorded at 400 MHz and 100 MHz respectively on Bruker Avance spectrometers at ambient temperature in $CDCl_3$ unless otherwise noted. NMR spectra were referenced to residual solvent peaks ($CDCl_3$: δ = 7.26 for ^{1}H NMR) and chemical shifts were reported in ppm. In ^{1}H NMR, the multiplicity of the signal is indicated as *s* (singlet), *d* (doublet), *t* (triplet) and m (multiplet), defined as all multipeak signals where overlap or complex coupling of signals makes definitive descriptions of peaks difficult. Coupling constants are defined as *J* and quoted in Hz to one decimal place. Electrochemical reactions were carried out using an Ivium Technologies Vertex model potentiostat operating in chronoamperometry mode. The fluorescence spectra and fluorescence intensity were measured with a Horiba FluoroMax-4 spectrofluorometer and the analytic sample was placed in a 1 mm length cuvette for these experiments.

Electrochemical Setup

For all reactions we used a divided 'H' cell as our reaction vessel (dimensions shown in **Figure S1**) with each chamber having a size B19 ground-glass neck and a total volume of 30 mL. A semiporous sintered glass divider sits between each chamber. All reactions were carried out using 15 mL of electrolyte solution in each. Where graphite electrodes were used for the working-electrode and counter electrode, rods of 5 mm diameter were used at a depth of 25 mm giving an effective area of 412 mm^2. A silver wire, which was 1 mm thick, was used as a quasi-reference electrode and was likewise placed into solution to a depth of 25 mm giving an effective area of 79 mm^2 . One graphite and the silver wire were placed into the same chamber to minimise the potential drop deriving from resistance and kept 10 mm apart. Another graphite was used as the counter-electrode and placed in the other chamber of the H cell. Reactions were run using an Ivium Technologies Vertex model potentiostat operating in chronoamperometry mode. This mode provides real-time charge over time and current over time graphs for measuring the total charges passed over the course of reaction.

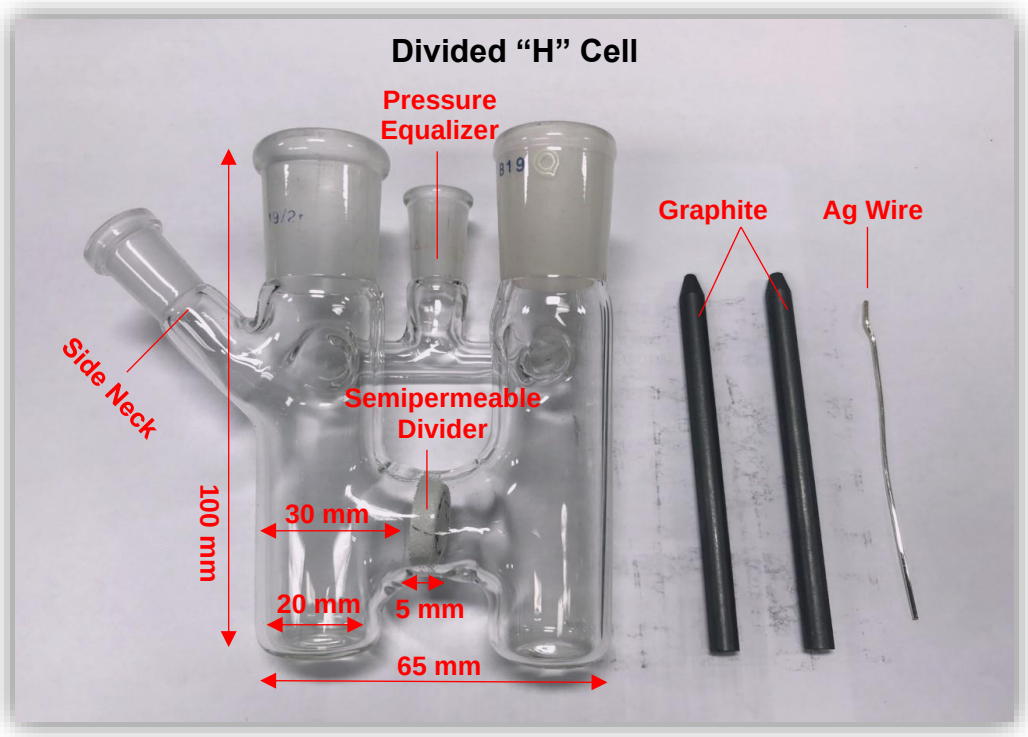
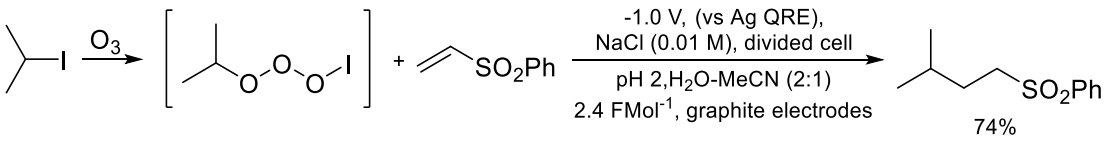


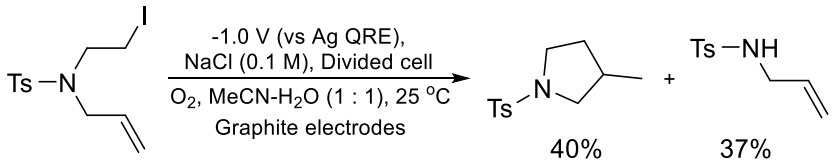
Figure S1. Image of divided H-cell and electrodes used with dimensions.

Electrochemical Radical Alkene Addition Reaction



Ozone was bubbled to a *i*-PrI (2 mL, 20.0 mmol) for 2 min and then purged with Ar for 5 min. The sample was stored under Ar for the following experiment. Two graphite electrodes (4.12 cm^2 area each) were placed into each chamber of the divided H cell and $HCl_{(aq)}$ (pH = 2, 10 mL), MeCN (5 mL) and NaCl (7 mol%) were added to each chamber and degassed with argon. Phenyl vinyl sulfone (200 mg, 1.19 mmol, 1.0 equiv.) and ozonized 2-iodopropane (0.142 mL, 1.43 mmol, 1.2 equiv.) were added to the cathodic chamber. The reaction mixture was stirred at room temperature under argon and a constant reductive potential (-1.0 V) applied to the cathode for 20 h. The reaction mixture was then diluted with water (10 mL) and phases were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was dried ($MgSO_4$), filtered, concentrated under reduced pressure and purified by column chromatography (cyclohexane : EtOAc 100 : 0 to 9 : 1) to yield 3-methylbutyl phenyl sulfone (187 mg, 0.88 mmol, 74 %) as colourless oil: $\mathbf{R_f}$ 0.30 (petroleum ether : EtOAc 9 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 2H), 7.70 – 7.63 (m, 1H), 7.60 – 7.54 (m, 2H), 3.11 – 3.05 (m, 2H), 1.66 – 1.54 (m, 3H), 0.86 (d, *J* = 6.3 Hz, 6H). The analytical data were in excellent agreement with those reported in the literature.[1]

Electrochemical Radical Reductive Cyclisation Reaction



Two graphite electrodes (4.12 cm^2 area each) were placed into each chamber of the divided H cell and sodium acetate buffer (pH = 3.6, 7.5 mL), MeCN (7.5 mL) and NaCl (88 mg, 1.51 mmol) were added to each chamber. *N*-Allyl-*N*-(2-iodoethyl)-4-methylbenzenesulfonamide (182 mg, 0.5 mmol) was added to the cathodic chamber and the reaction mixture was stirred at room temperature under a constant reductive potential (-1.0 V) applied to the cathode for 6 h. The reaction mixture was then diluted with aqueous $Na_2S_2O_3$ (1 M; 10 mL) and phases were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was dried ($MgSO_4$), filtered, concentrated under reduced pressure and purified by column chromatography (cyclohexane : EtOAc 100 : 0 to 4 : 1) to yield the corresponding pyrrolidine (40%) and *N*-allyltosylamide (37%).

3-Methyl-1-tosylpyrrolidine: $\mathbf{R_f}$ 0.33 (petroleum ether : EtOAc 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 3.42 (dd, *J* = 9.7, 7.2 Hz, 1H), 3.34 (ddd, *J* = 9.9, 8.2, 4.2 Hz, 1H), 3.22 (ddd, *J* = 9.8, 8.3, 7.3 Hz, 1H), 2.75 (dd, *J* = 9.7, 7.8 Hz, 1H), 2.43 (s, 3H), 2.12 (dq, *J* = 14.6, 7.1 Hz, 1H), 1.90 (dtd, *J* = 14.1, 6.9, 4.1 Hz, 1H), 1.35 (dd, *J* = 12.4, 8.4 Hz, 1H), 0.91 (d, *J* = 6.7 Hz, 3H). The analytical data were in excellent agreement with those reported in the literature.[2]

N-Allyl-4-methylbenzenesulfonamide: $\mathbf{R_f}$ 0.20 (petroleum ether : EtOAc 4 : 1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 5.72 (ddt, *J* = 17.1, 10.2, 5.8 Hz, 1H), 5.25 – 5.00 (m, 2H), 4.58 (s, 1H), 3.60 – 3.55 (m, 2H), 2.43 (s, 3H). The analytical data were in excellent agreement with those reported in the literature.[3]

Photoluminescence Spectroscopy

Fenton Reaction

$FeSO_4 \cdot 7H_2O$ (28 mg, 0.101 mmol), H_2O_2 (10 μL) and disodium terephthalate (21 mg, 0.100 mmol) were added to a mixture of sodium acetate buffer (pH = 3.6, 1 mL) and H_2O (6 mL) and the resulting mixture was stirred at room temperature for 30 min. An analytical sample of the reaction mixture (1 mL) was basified with aqueous NaOH (1 M, 0.1 mL). The fluorescence intensity was then measured at 431 nm with excitation at 310 nm.

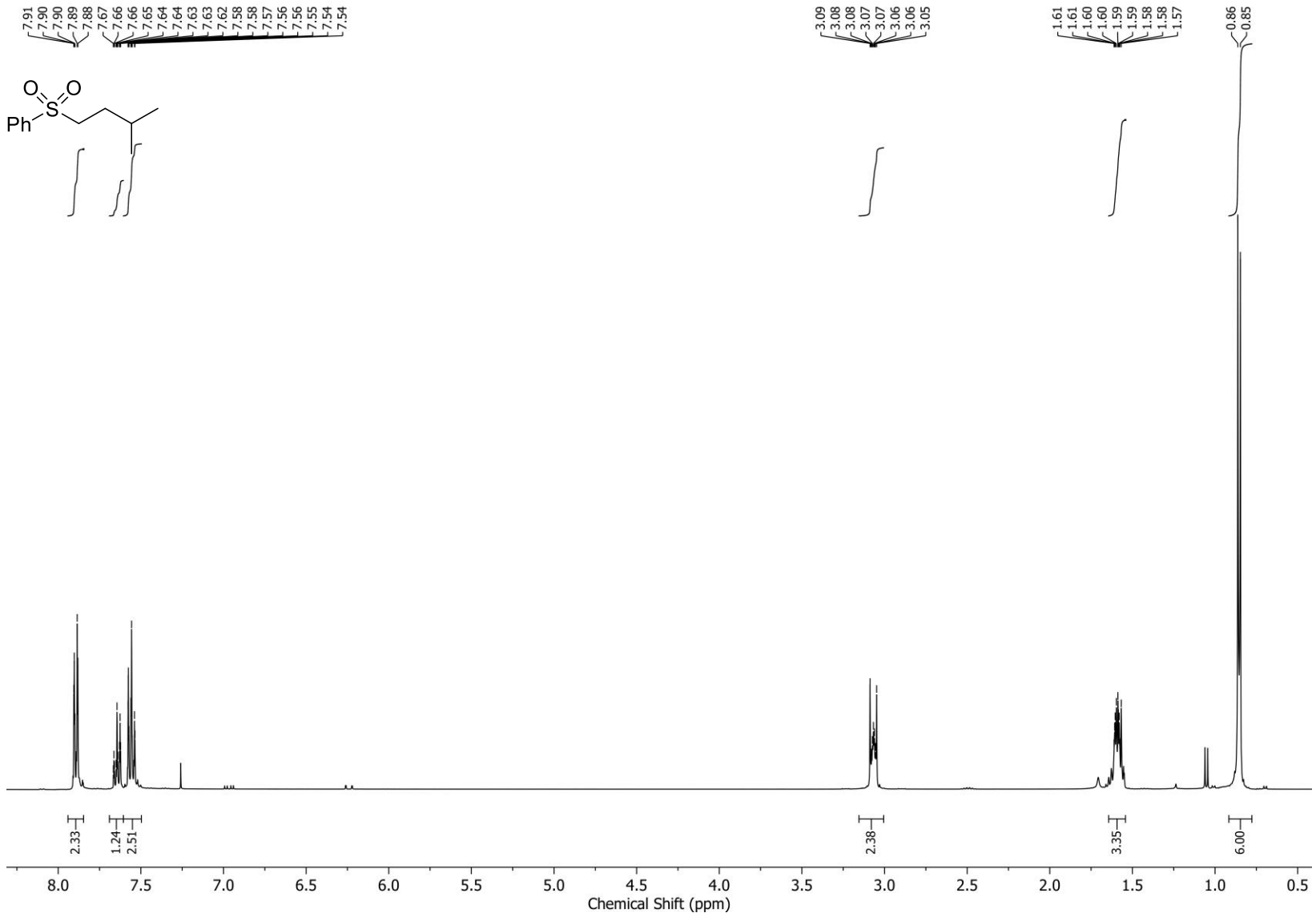
Reductive Cyclisation Reaction with Fluorescence Probe

Two graphite electrodes (4.12 cm^2 area each) were placed into each chamber of the divided H cell and sodium acetate buffer (pH = 3.6, 7.5 mL), MeCN (7.5 mL) and NaCl (88 mg, 1.51 mmol) were added to each chamber. *N*-Allyl-*N*-(2-iodoethyl)-4-methylbenzenesulfonamide (182 mg, 0.5 mmol) and disodium terephthalate (21 mg, 0.100 mmol) were added to the cathodic chamber and the reaction mixture was stirred at room temperature under a constant reductive potential (-1.0 V) applied to the cathode for 20 h. An analytical sample of the reaction mixture (1 mL) was basified with aqueous NaOH (2 M, 0.05 mL). The fluorescence intensity was then measured at 431 nm with excitation at 310 nm. A control experiment was performed with the sample procedure without the addition of *N*-allyl-*N*-(2-iodoethyl)-4-methylbenzenesulfonamide.

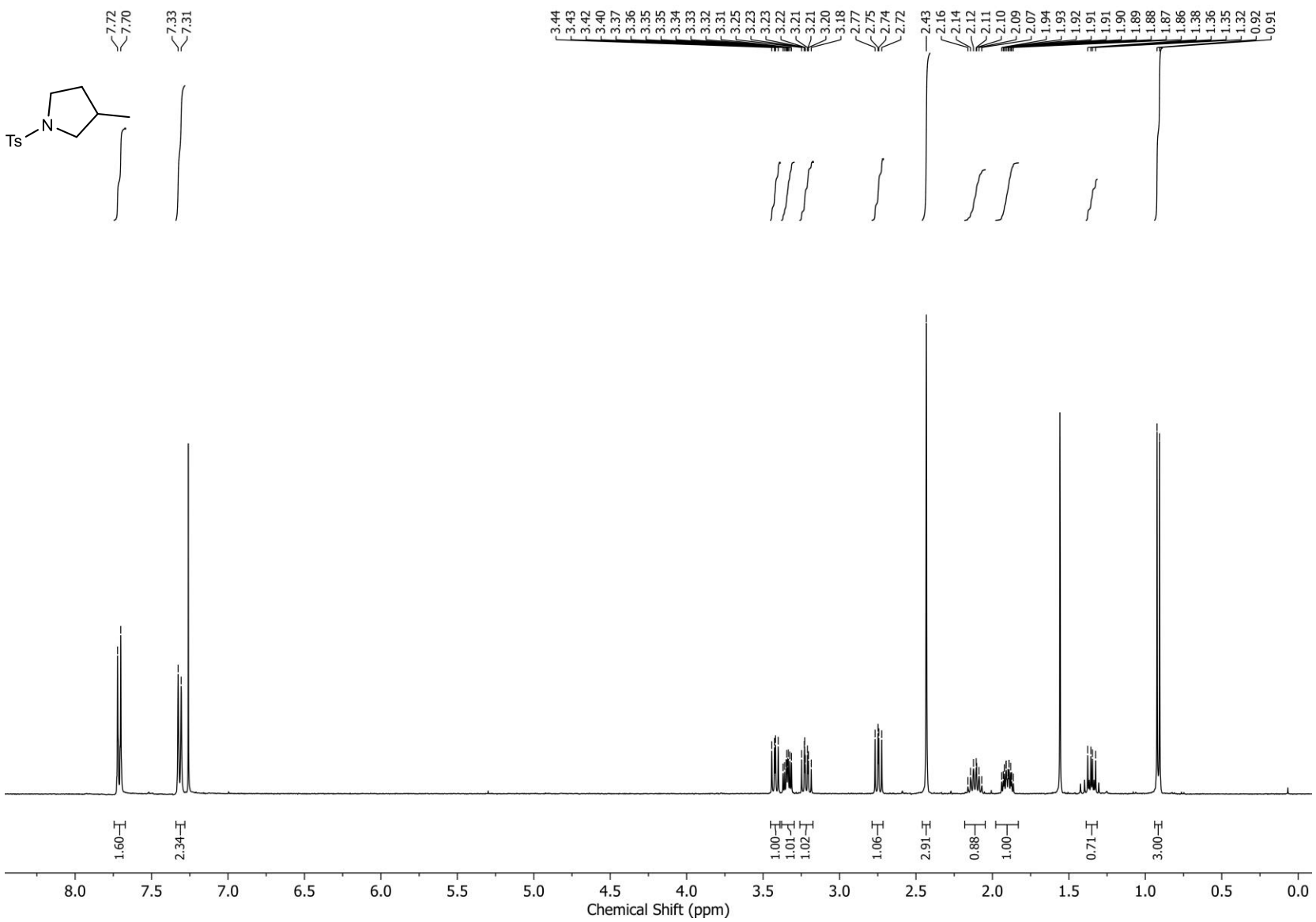
Detection of Hydroxyl Radicals in Anodic and Cathodic Chambers with Fluorescence Probe

Two graphite electrodes (4.12 cm^2 area each) were placed into each chamber of the divided H cell and disodium terephthalate (21 mg, 0.100 mmol), sodium acetate buffer (pH = 3.6, 7.5 mL), MeCN (7.5 mL) and NaCl (88 mg, 1.51 mmol) were added to each chamber. The reaction mixture was stirred at room temperature under a constant reductive potential (-1.0 V) applied to the cathode for 20 h. An analytical sample of the reaction mixture (1 mL) from each chamber was basified with aqueous NaOH (2 M, 0.05 mL). The fluorescence intensity was then measured at 431 nm with excitation at 310 nm.

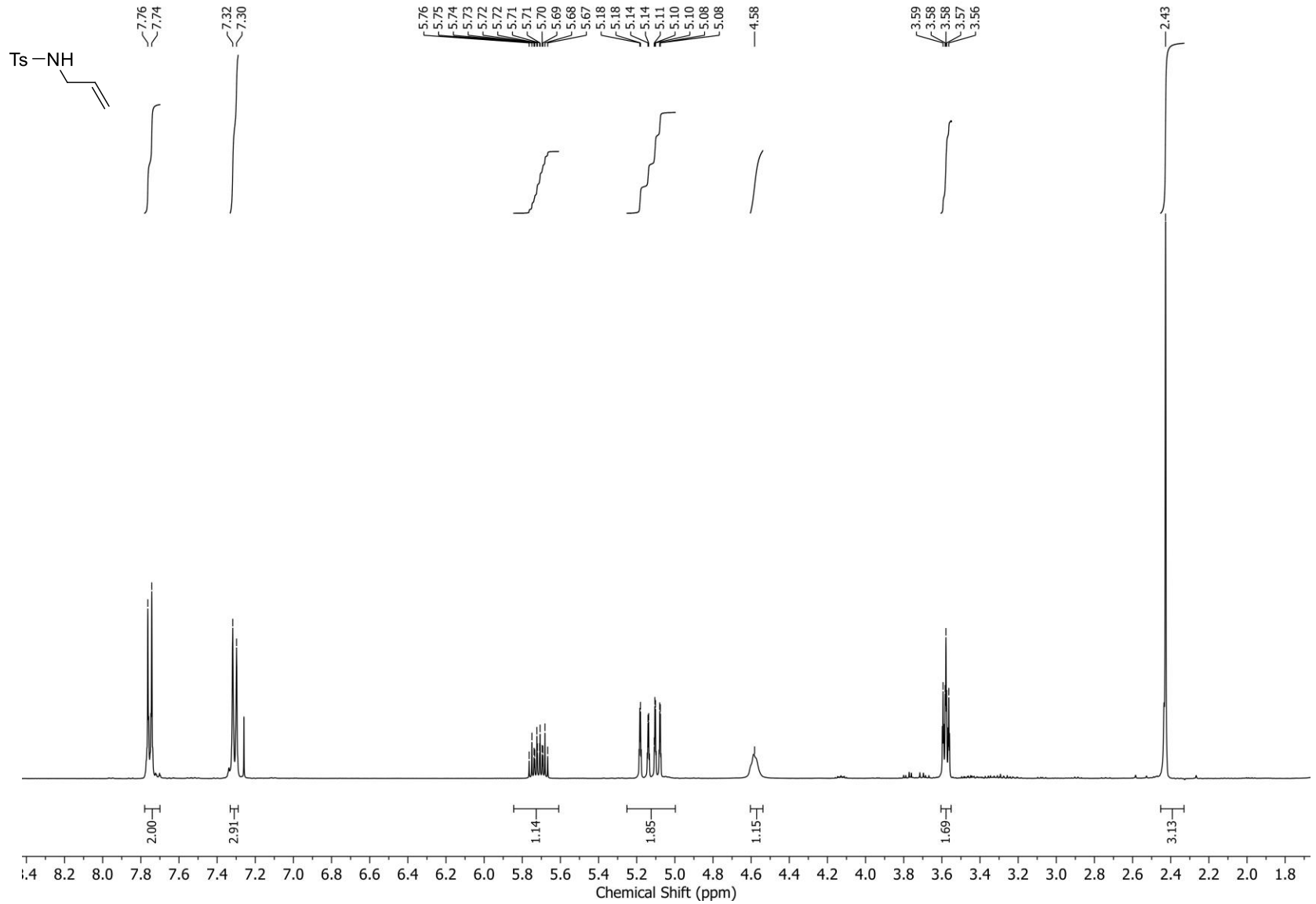
3-Methylbutyl phenyl sulfone ^{1}H NMR



3-Methyl-1-tosylpyrrolidine ^{1}H NMR



_N_-Allyl-4-methylbenzenesulfonamide ^{1}H NMR



References

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