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**Supporting Information for manuscript entitled:**

# Efficient and selective oxidation of sulphides in batch and continuous flow using styrene-based polymer immobilised ionic liquid phase supported peroxotungstates

S. Doherty, J. G. Knight, M. A. Carroll, A. R. Clemmet and J. R. Ellison T. Backhouse, N. Holmes and R. A. Bourne

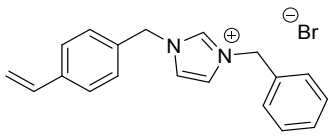
**Contents**

**Experimental**

**General Comments**. All reagents were purchased from commercial suppliers and used without further purification. $[NBu_4]_3[PO_4\{WO(O_2)_2\}_4]$[1] and 1-(4-vinylbenzyl)-1*H*-imidazole[2] were prepared as previously described and $H_3[PO_4\{WO(O_2)\}_4]$ was generated *in situ* immediately prior to use as previously described.[3] $^1H$ and $^{13}C\{^1H\}$ NMR spectra were recorded on JEOL LAMBDA-500 or ECS-400 instruments. Solid-state $^{31}P$ spectra were recorded at 161.87 MHz using a Varian VNMRS 400 spectrometer and a 4 mm (rotor o.d.) magic-angle spinning probe. They were obtained using cross-polarization with a 2 s recycle delay, 3 ms contact time, at ambient probe temperature (~25 °C) and at a sample spin-rate of 10 kHz. Between 1000 and 3600 repetitions were accumulated. Spectral referencing was with respect to an external sample of 85% phosphoric acid 85%. Solid-state $^{13}C$ spectra were recorded at 100.562 MHz using a Varian VNMRS 400 spectrometer. They were obtained using cross-polarization with a 10 s recycle delay, 1 ms contact time, at ambient probe temperature (~25 °C) and at a sample spin-rate of 6 kHz. Spectral referencing was with respect to an external sample of neat tetramethylsilane (carried out by setting the high-frequency signal from adamantane to 38.5 ppm). Thermogravimetric analysis (TGA) was performed using a TA TGA Q5000, at a heating rate of 10 °C $min^{-1}$. All samples were sealed in the glovebox into aluminium pans. The onset of the weight loss in each thermogram was used as a measure of the decomposition temperature. Gel permeation chromatography (GPC) was conducted on a Varian ProStar instrument (Varian Inc.) equipped with a Varian 325 UV-vis dual wavelength detector (254 nm), a Dawn Heleos II multi-angle laser light scattering detector (Wyatt Technology Corp.), a Viscotek 3580 differential RI detector, and a pair of PL gel 5 µm Mixed D 300 × 7.5 mm columns with guard column (Polymer Laboratories Inc.) in series. Near monodisperse polystyrene standards (Agilent Technologies) were used for calibration. Data collection was performed with Galaxie software (Varian Inc.) and chromatograms analysed with the Cirrus software (Varian Inc.) and Astra software (Wyatt Technology Corp.). SEM images were acquired on a Tescan Vega 3LMU scanning electron microscope with digital image collection. XPS measurements were carried out using a Theta Probe system (Thermo Scientific, UK) equipped with a microfocused monochromatic AlK$\alpha$ sourece. The X-ray source a soperated at 100 W and 15 kV. Flow reactions were performed using a Uniqsis FlowSyn Maxi all stainless steel platform with mandrels supplied by Uniqsis.

**Synthesis of 3-benzyl-1-(4-vinylbenzyl)-1*H*-imidazol-3-ium bromide (1a).**

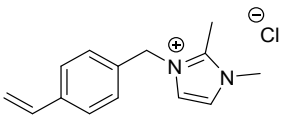
1-(4-Vinylbenzyl)-1*H*-imidazole (5.94 g, 32.2 mmol) was dissolved in MeCN (30 mL) and stirred. Benzyl



bromide (11.5 mL, 96.7 mmol) was added and the reaction mixture was stirred for 18 hours. The reaction mixture was added drop-wise in to $Et_2O$ (400 mL) while stirring rapidly upon which a white precipitate formed. The solvent was decanted off and the product was dissolved in MeCN (30 mL). The solvent was removed under reduced pressure to give the benzylated imidazole 30 as a white foam (11.33 g, 99%). $^1$H NMR (400 MHz, $CDCl_3$, δ): 10.81 (s, 1H, N-CH-N), 7.39 (m, 9H, Ar-H, N-CH=CH-N), 7.22 (m, 2H, Ar-H meta to vinyl), 6.64 (dd, *J* = 17.6, 10.9 Hz, 1H, $H_aC{=}CH_bH_c$), 5.72 (d, *J* = 17.5 Hz, 1H, $H_aC{=}CH_bH_c$), 5.52 (s, 4H, Ar-$CH_2$-N), 5.27 (d, *J* = 10.9 Hz, 1H, $H_aC{=}CH_bH_c$); $^{13}$C NMR (100 MHz, $CDCl_3$, *δ*): 138.9, 137.2, 135.8, 132.8, 132.1, 129.7, 129.6, 129.4, 129.1, 127.3, 121.9, 115.6, 53.6, 53.3; FT-IR (neat, $cm^{-1}$): $\nu$ = 3424, 3122, 3051, 2967, 2847, 1556, 1149, 914, 716. HRMS ($ESI^+$) exact mass calculated for $C_{19}H_{20}N_2$ $[M+H]^+$ *m/z* = 276.1626, found *m/z* = 276.1627; Anal. Calc. for $C_{19}H_{19}BrN_2$ (355.3): C, 64.23; H, 5.39; N, 7.89%. Found: C, 64.69; H, 5.66; N, 8.09%.

**Synthesis of 1,2-dimethyl-3-(4-vinylbenzyl)-1*H*-imidazol-3-ium chloride (1b).**

A flame dried three-neck round bottomed flask was charged with 1,2-dimethylimidazole (5.81 g, 60.5



mmol) and dry chloroform (50 mL). 4-Vinylbenzyl chloride (11.1 mL, 78.6 mmol) was added and the reaction mixture was heated to 50 °C and stirred for 18 hours. After this time, the solvent was removed under reduced pressure and the resulting residue washed with ethyl acetate (4 x 50 mL). The residual solvent was removed under reduced pressure to afford **2c** as a fine white powder (15.0 g, 100 %). $^1$H NMR (400 MHz, $CDCl_3$, *δ*): 7.72 (d, *J* = 2.1 Hz, 1H, N-CH=C*H*-N-$CH_3$), 7.69 (d, *J* = 2.1 Hz, 1H, N-C*H*=CH-N-$CH_3$), 7.36 (d, 2H, *J* = 8.2 Hz, Ar-H ortho to vinyl), 7.27 (d, 2H, *J* = 8.2 Hz, Ar-H meta to vinyl), 6.64 (dd, *J* = 17.6, 10.9

Hz, 1H, $H_a$C=CH$_b$H$_c$), 5.72 (d, *J* = 17.5 Hz, 1H, H$_a$C=C*H*$_b$H$_c$), 5.53 (s, 2H, Ar-CH$_2$-N), 5.26 (d, *J* = 10.9 Hz, 1H, H$_a$C=CH$_b$*H*$_c$), 3.94 (s, 3H, N-CH$_3$), 2.75 (s, 3H, N-C(C*H*$_3$)-N); $^{13}$C NMR (100 MHz, CDCl$_3$, *δ*): 144.3, 138.5, 135.8, 132.4, 128.6, 127.2, 123.0, 122.0, 115.4, 52.2, 35.9, 11.0; MP: 186-188 $^{o}$C; FT-IR (neat, cm$^{-1}$): ν = 3049, 3006, 2943, 1592, 1514, 1409, 1251, 1174, 826, 663; Anal. Calc. for $C_{14}H_{17}ClN_2$ (248.1): C, 67.60; H, 6.89; N, 11.26%. Found: C, 67.97; H, 7.11; N, 11.53%.

**Synthesis of 1-methyl-3-(4-vinylbenzyl)-1*H*-imidazol-3-ium chloride (1c).**

A flame-dried Schlenk flask was charged with 1-methylimidazole (2.6 mL, 30 mmol) in chloroform (27 mL). 4-Vinylbenzyl chloride (5.5 mL, 39 mmol) was added and the reaction mixture was stirred for 18 hours at 50 °C. The solvent was removed under reduced pressure and the resulting residue was washed with ethyl acetate (4 x 50 mL). The residual solvent was removed under reduced pressure to afford the imidazolium salt **1c** as a viscous orange oil (6.71 g, 95 %). $^{1}$H NMR (400 MHz, CDCl$_3$, *δ*): 10.9 (s, 1H, N-CH-N), 7.39 (dd, *J* = 14.8, 8.2 Hz, 4H, Ar-H), 7.36 (m, 1H, N-CH=C*H*-N-CH$_3$), 7.26 (m, 1H, N-C*H*=CH-N-CH$_3$), 6.65 (dd, *J* = 17.6, 10.9 Hz, 1H, $H_a$C=CH$_b$H$_c$), 5.73 (d, *J* = 17.5 Hz, 1H, H$_a$C=C*H*$_b$H$_c$), 5.54 (s, 2H, Ar-CH$_2$-N), 5.27 (d, *J* = 10.9 Hz, 1H, H$_a$C=CH$_b$*H*$_c$), 4.04 (s, 3H, Me); $^{13}$C NMR (100 MHz, CDCl$_3$, δ): 138.6, 137.1, 135.8, 132.7, 129.3, 128.9, 127.1, 126.6, 123.8, 122.0, 115.4, 52.9, 36.6; **FT-IR** (neat, cm$^{-1}$): *ν* = 3134, 3038, 2949, 2850, 1629, 1560, 1513, 1409, 1160, 994, 913, 830, 778, 622. Anal. Calc. for $C_{13}H_{15}ClN_2$ (234.7): C, 66.52; H, 6.44; N, 11.93%. Found: C, 66.94; H, 6.79; N, 12.31%.

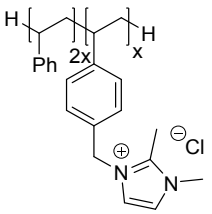
**Poly-3-Benzyl-1-(4-vinylbenzyl)-1*H*-imidazol-3-ium bromide-co-styrene (2a).**

A flame-dried Schlenk flask was charged with AIBN (0.81 g, 4.9 mmol, 5 mol %) followed by 3-benzyl-1-(4-vinylbenzyl)-1*H*-imidazol-3-ium bromide monomer **1a** (11.61 g, 32.8 mmol), styrene (6.8 mL, 66 mmol) and methanol (100 mL)

and styrene (6.8 mL, 66 mmol) and the resulting mixture degassed with five freeze/pump/thaw cycles. After reaching ambient temperature the flask was heated to 70 °C and stirred for 72 hours. After this time the solution was allowed to cool, the volume reduced by half and the resulting concentrate added drop-wise into diethyl ether (600 mL) with rapid stirring. The product was isolated by filtration, washed with $Et_2O$ (3 x 50 mL) and dried under reduced pressure to afford polymer **2a** as a white solid (14.0 g, 76 %). $^1$H NMR (400 MHz, $CDCl_3$, $\delta$): 9.67 (br, N-C*H*-N), 7.89 (br, Ar-*H*), 7.45 (br, Ar-*H*), 7.38 (br, Ar-*H*), 7.06 (br, Ar-*H*), 6.48 (br, Ar-*H*), 5.49 (br, Ar-C$H_2$-N), 5.38 (br, Ar-C$H_2$-N), 1.47 (br, C*H*C$H_2$, polymer backbone). FT-IR (neat, cm$^{-1}$): $\nu$ = 3406, 3057, 3025, 2925, 2850, 1601, 1558, 1493, 1452, 1149, 759, 700; Anal. Calc. for $C_{35}H_{35}BrN_2$ (563.6): C, 74.59; H, 6.26; N, 4.97%. Found: C, 71.69; H, 6.72; N, 5.03%.

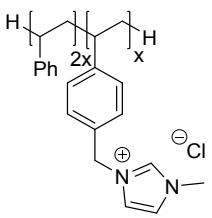
**Poly-1,2-dimethyl-3-(4-vinylbenzyl)-1*H*-imidazol-3-ium chloride-co-styrene (2b).**

Polymer **2b** was prepared and purified according to the procedure described above for **2a** and




isolated as a white powder in 79 % yield. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$): 7.75 (br, Ar-*H*), 7.06 (br, Ar-*H*), 6.48 (br, Ar-*H*), 5.37 (br, Ar-C$H_2$-N), 3.79 (br, N-C$H_3$), 2.56 (br, N-CHC$H_3$-N), 1.48 (br, C*H*C$H_2$, polymer backbone). FT-IR (neat, cm$^{-1}$): $\nu$ = 3290, 3026, 2923, 2850, 1587, 1536, 1513, 1493, 1452, 1034, 761, 701; Anal. Calc. for $C_{30}H_{33}ClN_2$ (457.1): C, 78.83; H, 7.28; N, 6.13%. Found: C, 73.52; H, 6.83; N, 6.57%.

**Synthesis of poly-1-methyl-3-(4-vinylbenzyl)-1*H*-imidazol-3-ium chloride-co-styrene (2c).**




Polymer **2c** was prepared and purified according to the procedure described above for **2a** and isolated as a white powder in 59% yield. $^1$H NMR (400 MHz, $CDCl_3$, $\delta$): 9.51 (br, N-C*H*-N), 7.75 (br, Ar-*H*), 7.06 (br, Ar-*H*), 6.49 (br, Ar-*H*), 5.36 (br, Ar-C$H_2$-N), 3.87 (br, N-C$H_3$), 1.67 (br, C*H*C$H_2$, polymer backbone), 1.42 (br, C*H*C$H_2$, polymer backbone). FT-IR (neat, cm$^{-1}$): $\nu$ = 3343, 3142, 3056, 3025, 2924, 2849,

1601, 1572, 1493, 1452, 1160, 1031, 760, 700, 619; Anal. Calc. for $C_{29}H_{31}ClN_2$ (443.0): C, 78.62; H, 7.05; N, 6.32%. Found: C, 74.65; H, 6.76; N, 6.29%.

**Synthesis of imidazole loaded Merrifield resin.[4]**

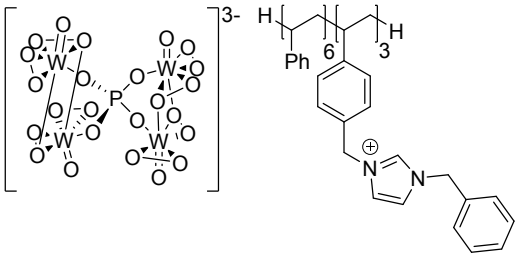
A flame-dried Schlenk flask was charged with Merrifield resin (2.0 g, 2.0 mmol) (1% divinylbenzene crosslinked, 1.0-1.3 mmol $g^{-1}$ Cl, 200- 400 mesh), imidazole (1.36 g, 20.0 mmol) and dry chloroform (30 mL) and the resulting mixture was heated to 50 $^{o}$C and stirred for 72 hours. After this time the reaction mixture was filtered and solid washed with chloroform (50 mL), water (50 mL), ethanol (50 mL) and diethyl ether (50 mL) and dried under reduced pressure to afford the desired product as a white solid in 82% yield (1.75 g). FT-IR (neat, $cm^{-1}$): $\nu$ = 3059, 3026, 2922, 2851, 1601, 1493, 1452, 1074, 1028, 755, 697; Anal. Calc. N, 2.72%. Found: C, 86.97; H, 8.54; N, 1.80%.

**Synthesis of imidazolium-decorated Merrifield resin (2e).**

A flame-dried Schlenk flask was charged with imidazole loaded Merrifield resin 41 (1.65 g) and benzyl bromide (2.38 mL, 20.0 mmol) in dry acetonitile (20 mL) and the reaction mixture was allowed to stir for 72 hours. The reaction mixture was filtered and washed with MeCN (50 mL) and Et2O (100 mL). The solvent was removed under reduced pressure to afford the benzylated imidazolium Merrifield resin **2e** as a white solid (1.15 g). FT-IR (neat, $cm^{-1}$): $\nu$ = 3059, 3025, 2922, 2850, 1601, 1493, 1452, 1151, 1028, 756, 697; CHN Anal. Calc. based on measured loading of imidazole in 41 N, 2.33%. Found: C, 80.68; H, 7.97; N, 1.43%. The nitrogen content corresponds to an imidazolium loading of 0.51 mmol $g^{-1}$.

**Synthesis of polymer supported peroxophosphotungstate 3a.**

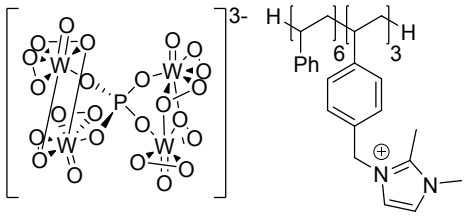
Aqueous hydrogen peroxide solution (35% w/w, 10.2 mL, 118 mmol) was added to a solution of



phosphotungstic acid (1.70 g, 600 µmol) in water (1 mL) and the resulting mixture stirred at room temperature for 30 minutes. After this time, a solution of **2a** (1.00 g, 1.80 mmol) in ethanol (50 mL) was added and the reaction mixture stirred for a further 30 minutes after which time it was added drop-wise into diethyl ether (500 mL) with rapid stirring. The product was isolated by filtration, washed with diethyl ether (3 x 50 mL) and dried under reduced pressure to afford **3a** as an off white solid (1.00 g, 37 %). FT-IR (neat, $cm^{-1}$): $\nu$ = 3140, 3061, 3026, 2925, 1712, 1640, 1602, 1558, 1494, 1453, 1148, 1029, 943, 887, 814, 756, 700; Anal. Calc. for $C_{105}H_{105}N_6O_{24}PW_4$ (2601.3) C, 48.48; H, 4.07; N, 3.23%. Found: C, 47.45; H, 4.25; N, 3.01 %; 32.3 wt% tungsten and a peroxotungstate loading of 0.414 mmol $g^{-1}$.

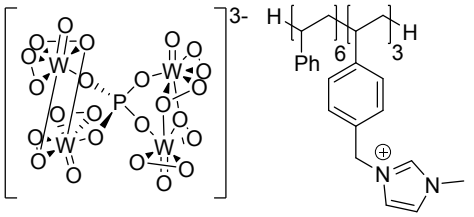
**Synthesis of polymer supported peroxophosphotungstate 3b.**

$[PO_4\{WO(O_2)_2\}_4]$@ImPIILP **3b** was prepared and purified according to the procedure described



above for **3a** and isolated as a white powder in 49 % yield. FT-IR (neat, $cm^{-1}$): $\nu$ = 3408, 3140, 3026, 2926, 1614, 1493, 1452, 1422, 1078, 949, 820, 759, 701; Anal. Calc. for $C_{90}H_{99}N_6O_{24}PW_4$ (2415.1) C, 44.76; H, 4.13; N, 3.48 %. Found: C, 41.29; H, 4.05; N, 3.38%; 33.9 wt% tungsten and a peroxotungstate loading of 0.464 mmol $g^{-1}$.

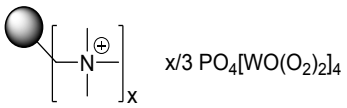
**Synthesis of polymer supported peroxophosphotungstate 3c.**



[$PO_4\{WO(O_2)_2\}_4$]@ImPIILP **3c** was prepared and purified according to the procedure described above for **3a** and isolated as a white powder in 29 % yield. FT-IR (neat, $cm^{-1}$): $\nu$ = 3411, 3149, 3026, 2925, 1633, 1602, 1562, 1493, 1452, 1425, 1159, 1080, 1029, 956, 869, 836, 756, 700; Anal. Calc. for $C_{87}H_{93}N_6O_{24}PW_4$ (2373.0): C, 44.03; H, 3.95; N, 3.54%. Found: C, 41.04; H, 3.99; N, 3.14%; 35.0 wt% tungsten and a peroxotungstate loading of 0.479 mmol $g^{-1}$.

**Synthesis of peroxophosphotungstate loaded Amberlite 3d.**

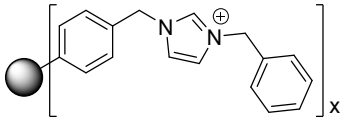
Aqueous hydrogen peroxide solution (35% w/w, 11.9 mL, 139 mmol) was added to a solution of



phosphotungstic acid (2.00 g, 700 µmol) in water (1.2 mL) and the resulting mixture stirred at room temperature for 30 minutes. After this time, the solution was passed through a narrow sinter funnel containing Amberlite IRA 900 chloride form (2.00 g). The Amberlite was then washed with water (50 mL) and $Et_2O$ (50 mL) and the solvent removed under reduced pressure to afford the functionalised Amberlite as white beads. FT-IR (neat, $cm^{-1}$): $\nu$ = 3401, 3030, 2928, 2362, 2343, 1636, 1614, 1476, 924, 885, 715; Found: C, 44.91; H, 7.66; N, 3.81%; 16.3 wt% tungsten and a peroxotungstate loading of 0.223 mmol $g^{-1}$.

**Synthesis of polymer supported Peroxophosphotungstate loaded imidazolium-decorated Merrifield resin (3e).**

Aqueous hydrogen peroxide solution (35% w/w, 4.5 mL, 52 mmol) was added to a solution of



phosphotungstic acid (0.75 g, 0.30 mmol) in water (0.5 mL) and the mixture was stirred at room temperature for 30 minutes. After this time, the solution was added to a suspension of 2e (0.9 g) in ethanol (47 mL) and the mixture was stirred for a further 30 minutes after which it was added drop-wise into diethyl ether (500 mL) with rapid stirring. The product was isolated by

filtration, washed with diethyl ether (3 x 50 mL) and finally dried under reduced pressure to afford **3e** as a white solid (1.2 g, 73 %). FT-IR (neat, $cm^{-1}$): $\nu$ = 3059, 3026, 2922, 2850, 1716, 1602, 1558, 1493, 1452, 1148, 1029, 960, 814, 755, 697; Anal. Calc. for $N_6O_{24}PW_4$ N, 1.86%. Found: C, 63.46; H, 6.16; N, 0.97%; 30.2 wt% tungsten and a peroxotungstate loading of 0.413 mmol $g^{-1}$.

**General procedure for catalytic sulfoxidation in batch.**

A flame-dried Schlenk flask was allowed to cool to room temperature and charged with sulfide (1.0 mmol), catalyst (0.56-0.58 mol %) and solvent (3 mL). The reaction was initiated by the addition of aqueous hydrogen peroxide (35% w/w, 0.21 mL, 2.5 mmol) and allowed to stir at room temperature for 15 minutes. The reaction mixture was diluted with dichloromethane (25 mL), washed with water (50 mL) and the organic extract dried over $MgSO_4$ filtered and the solvent removed under reduced pressure. The resulting residue was analysed by either $^1H$ or $^{13}C\{^1H\}$ NMR spectroscopy to quantify the composition of starting material and products; for each substrate tested an internal standard of 1,3-dinitrobenzene was initially employed to ensure mass balance.

**General procedure for the catalytic sulfoxidation recycle studies.**

A PTFE centrifuge tube containing a magnetic stirrer bar was placed in a flame-dried Schlenk flask. The tube was charged with **3a** (0.01146 mmol, 0.58 mol %), sulfide (2.0 mmol) and solvent (6 mL) and stirred for 2 minutes. The reaction was initiated by the addition of aqueous hydrogen peroxide (35% w/w, 0.43 mL, 5.0 mmol) and allowed to stir at room temperature for 5 minutes. After this time the solution was centrifuged (5 min, 14,000 rpm), decanted and the remaining PIILP catalyst washed with the reaction solvent (6 mL), re-centrifuged (5 min, 14,000 rpm) and the solvent decanted. The reaction solution was diluted with dichloromethane (25 mL), washed with water (50 mL) and the organic extract dried over $MgSO_4$ filtered and the solvent removed

under reduced pressure. The resulting residue was analysed by $^{1}$H NMR spectroscopy to quantify the composition of starting material and products. The residue in the centrifuge tube was re-suspended in solvent and reused without any further treatment.

**General procedure for the catalytic sulfoxidation kinetic studies.**

A flame-dried Schlenk flask was allowed to cool to room temperature and charged with sulfide (4.0 mmol), **3a** (0.02 mmol, 0.5 mol %) and solvent (12 mL). The reaction was initiated by the addition of aqueous hydrogen peroxide (35% w/w, 0.86 mL, 10.0 mmol) and the resulting mixture stirred at room temperature for 24 hours during which time 0.2 mL aliquots were removed for work-up (as above) and analysed by $^{1}$H NMR spectroscopy.

**General procedure for segmented and continuous flow catalytic sulfoxidations.**

Two reservoirs were charged with sulfide (5.0 mmol) dissolved in the appropriate solvent (25 mL, 0.2 M) and hydrogen peroxide (1.29 mL, 35%) in the same solvent (25 mL, 0.6 M). A Uniqsis FlowSyn reactor was used to pump 1.0 mL of each reagent at total flow rates that varied between 0.293 mL min$^{-1}$ and 8.8 mL min$^{-1}$ through a T-piece mixer to combine the two streams; in the case of segmented flow an additional reservoir of carrier solvent was also employed. The reaction stream was then flowed through a OMNIFIT® glass column reactor cartridge (10 mm id × 100 mm) packed with 0.1 g of $[PO_4\{WO\text{-}(O_2)_2\}_4]$@PIILP and 2.0 g of $SiO_2$ (Geduran® Si 60) and mounted in a FlowSyn column heater. The exiting stream was passed through a back pressure regulator (BPR) and 2 mL fractions were collected into separate vials followed by a 2 mL post-collect. Each sample was diluted with dichloromethane (10 mL), washed with water (ca. 15 mL), the organic extract dried over $MgSO_4$, the solvent removed under reduced pressure and the resulting residue analysed by $^{1}$H NMR spectroscopy to quantify the composition of starting material and products.

## Characterization Data

**Figure S1** $^{1}$H NMR spectrum of 3-benzyl-1-(4-vinylbenzyl)-1*H*-imidazol-3-ium bromide **(1a)**

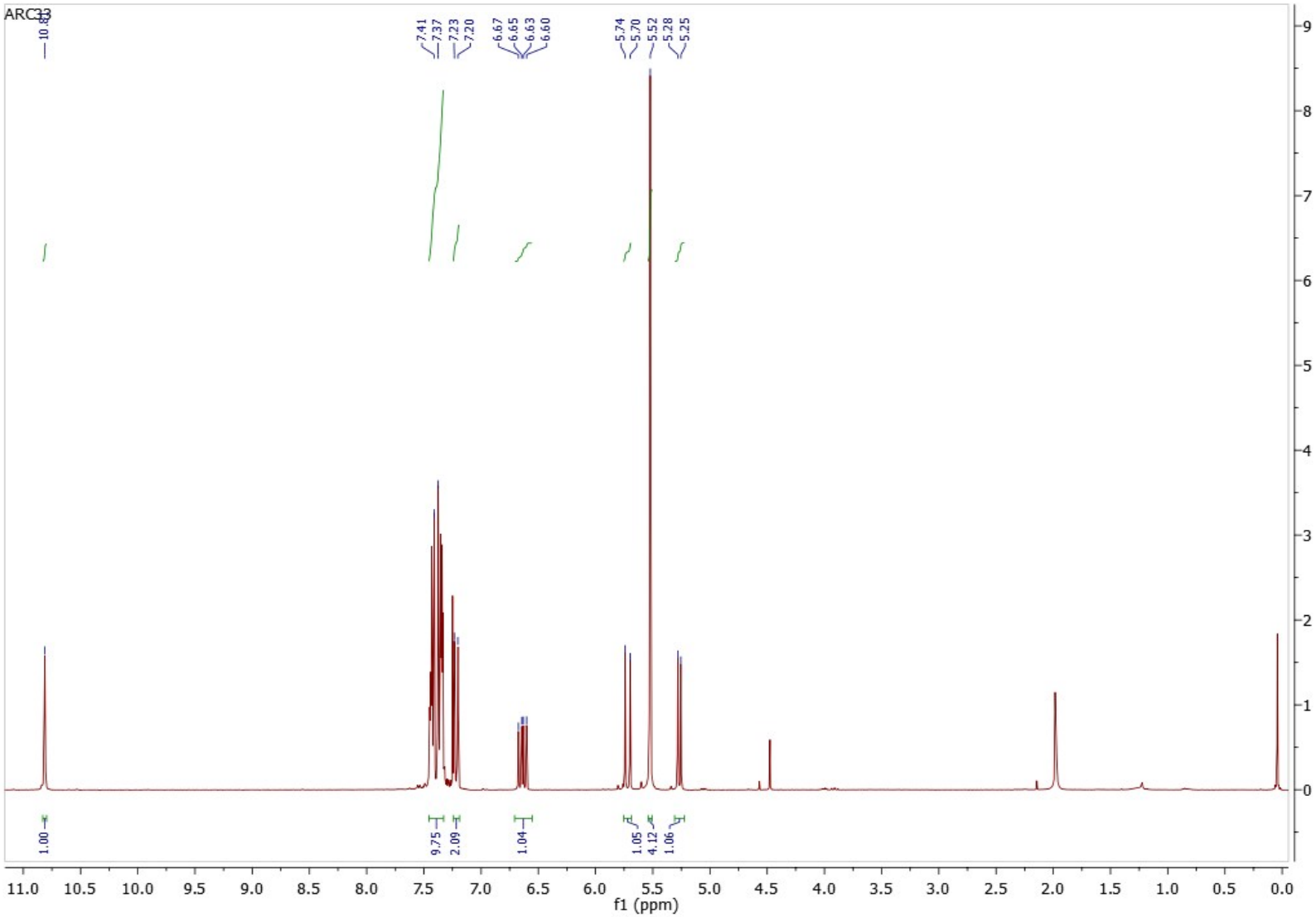


**Figure S2** $^{13}$C NMR spectrum of 3-benzyl-1-(4-vinylbenzyl)-1*H*-imidazol-3-ium bromide **(1a)**

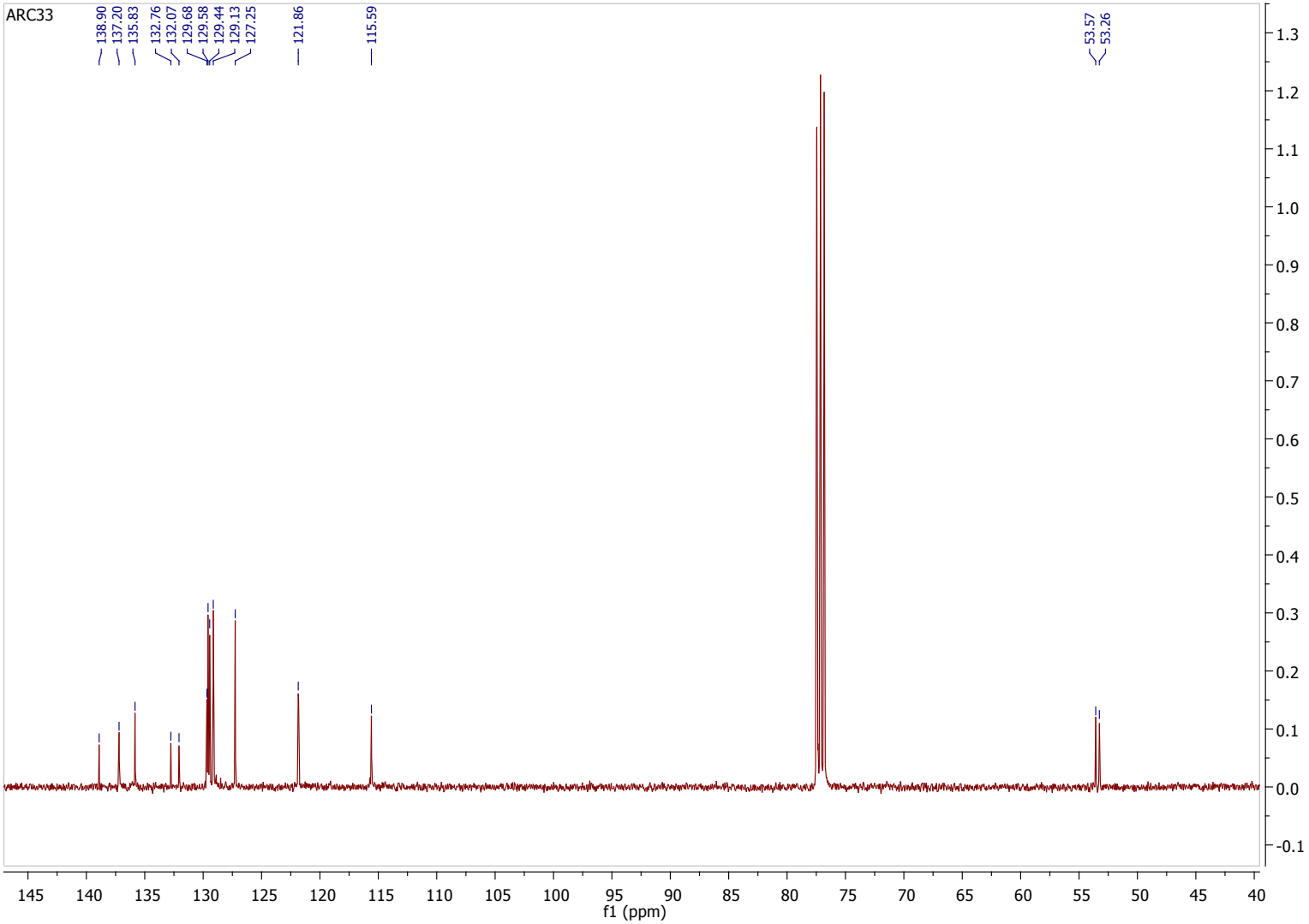


**Figure S3** $^{1}$H NMR spectrum of 1,2-dimethyl-3-(4-vinylbenzyl)-1*H*-imidazol-3-ium chloride (**1b**).

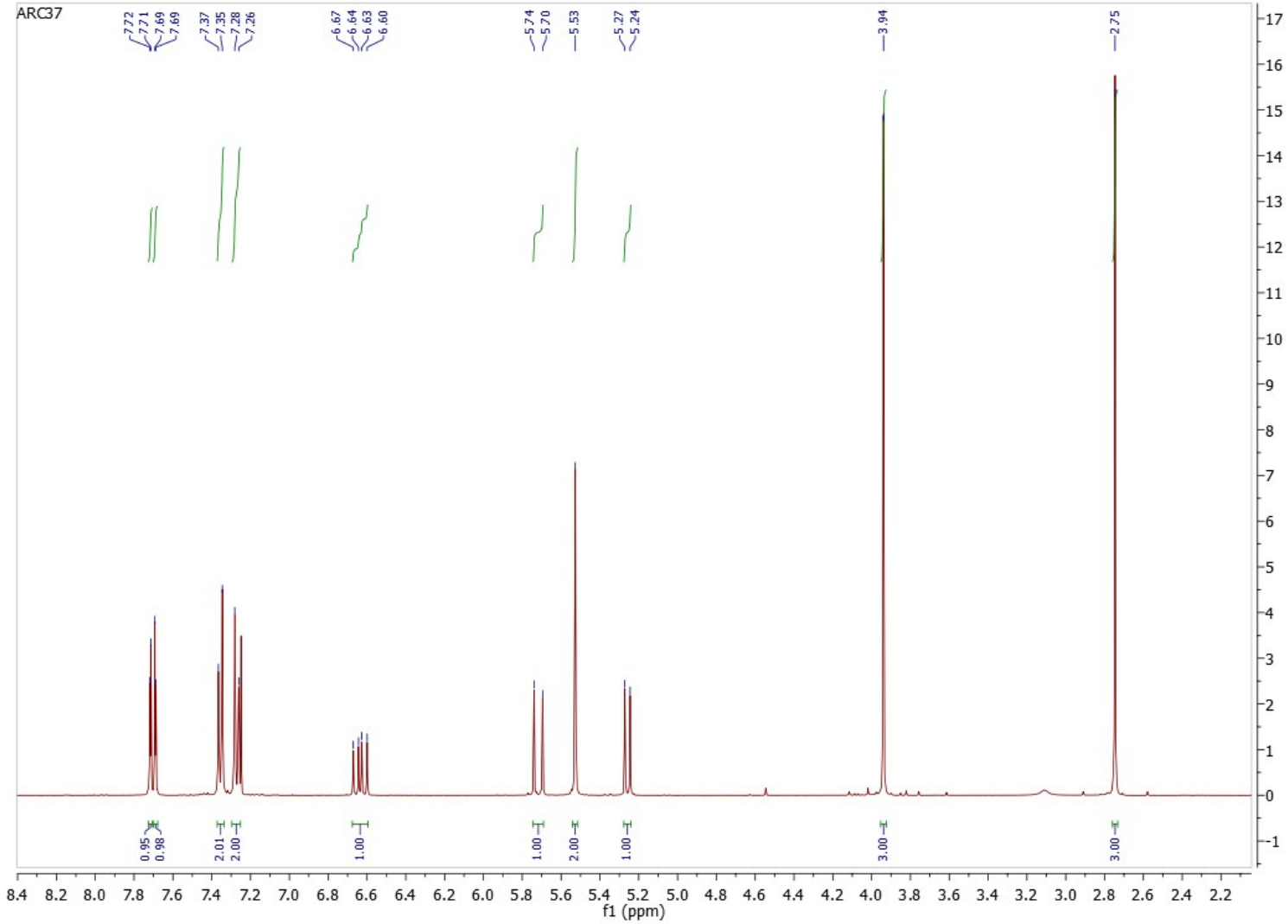


**Figure S4** $^{13}$C NMR spectrum of 1,2-dimethyl-3-(4-vinylbenzyl)-1*H*-imidazol-3-ium chloride (**1b**).

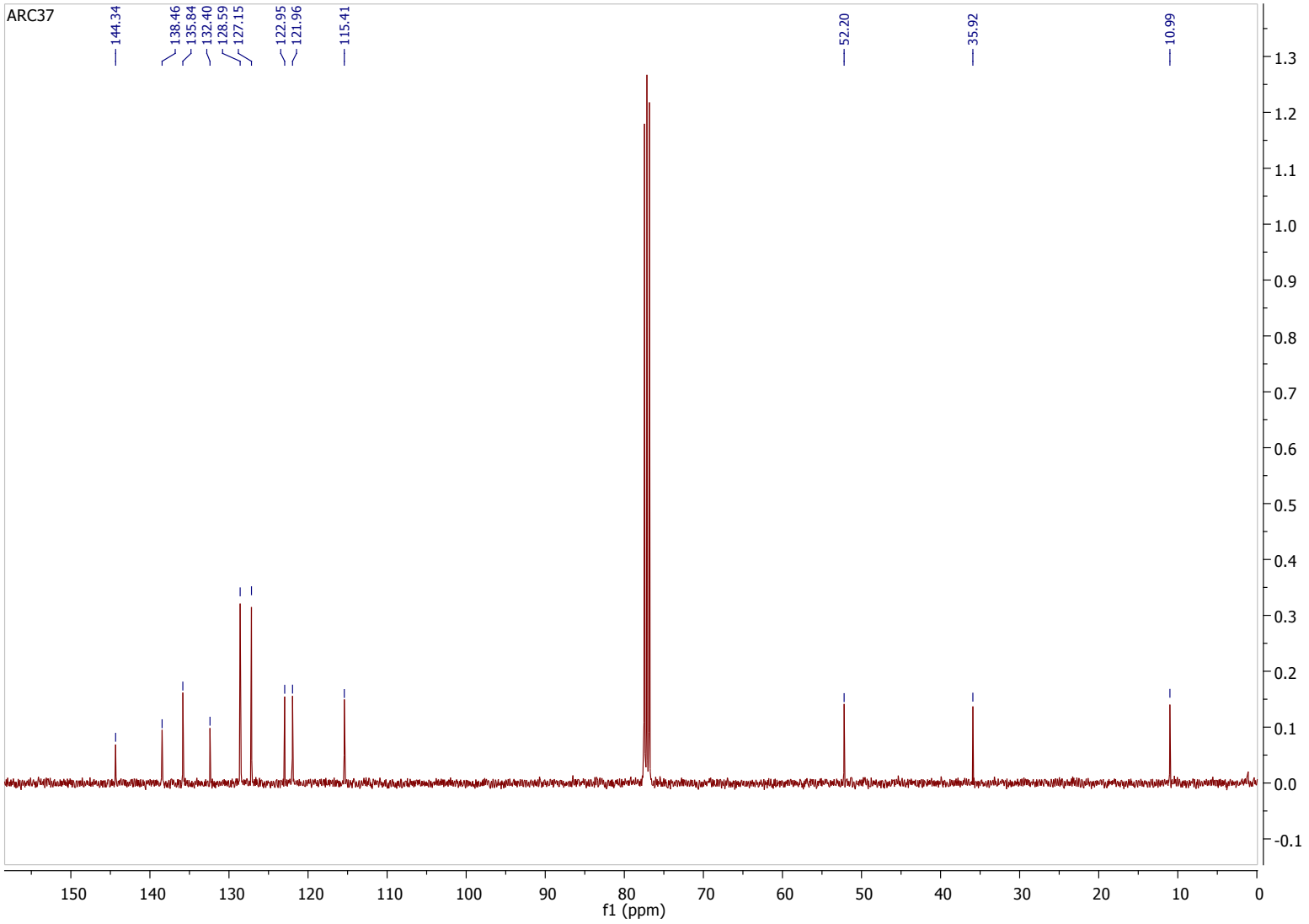


**Figure S5** $^{1}$H NMR spectrum of 1-methyl-3-(4-vinylbenzyl)-1*H*-imidazol-3-ium chloride (**1c**).

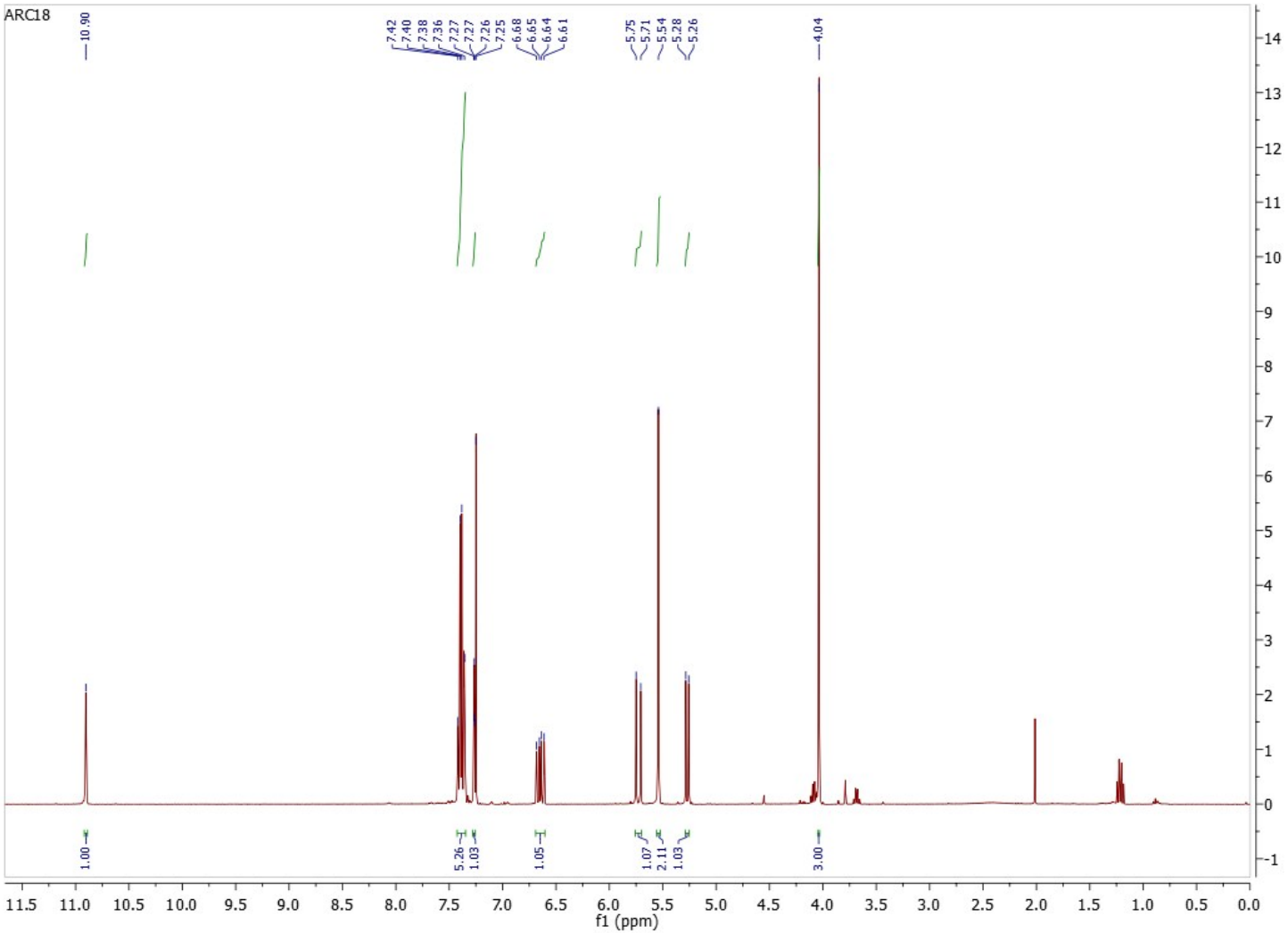


**Figure S6** $^{13}$C NMR spectrum of 1-methyl-3-(4-vinylbenzyl)-1*H*-imidazol-3-ium chloride (**1c**).

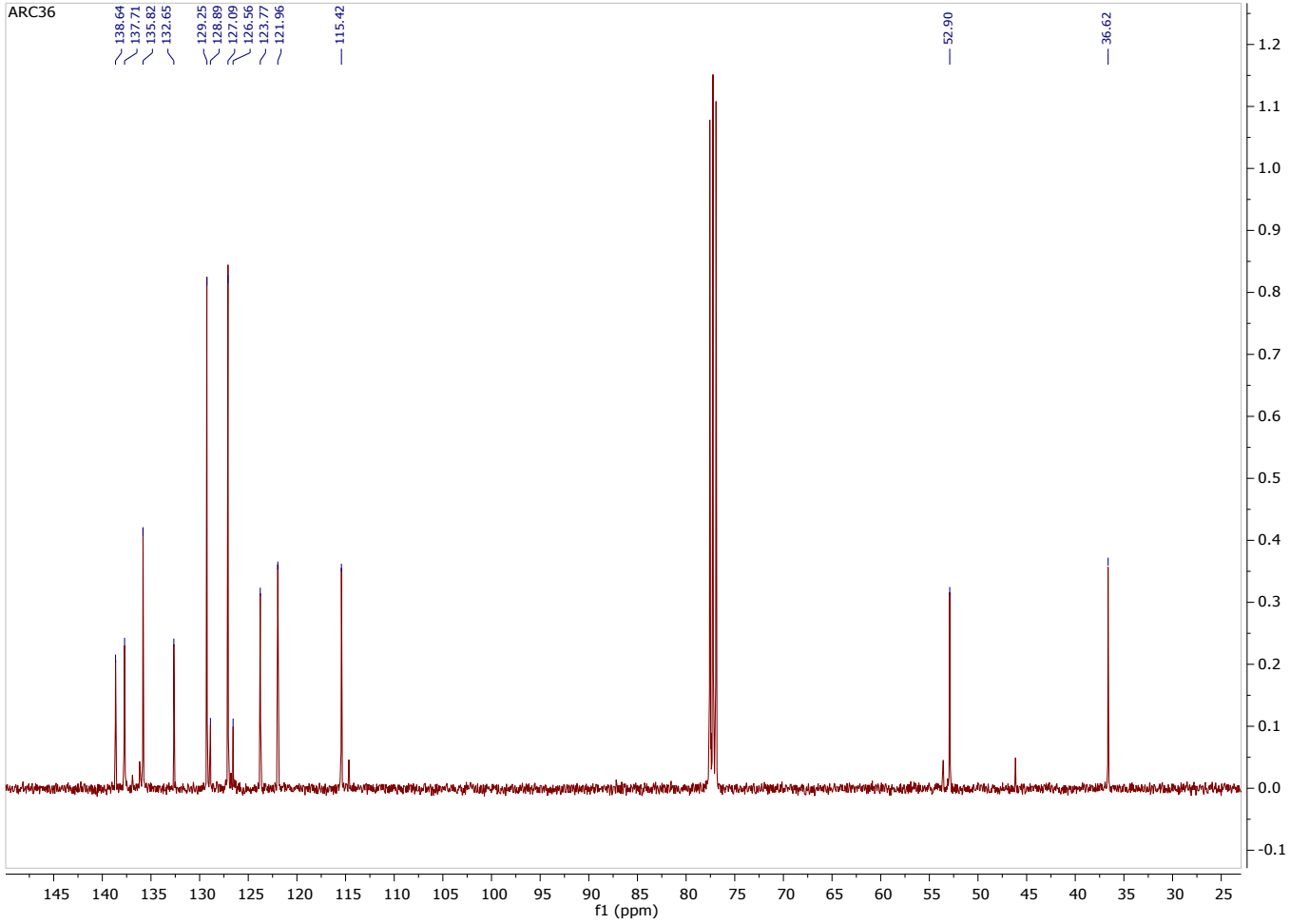


**Figure S7** $^{1}$H NMR spectrum of co-polymer **2a**

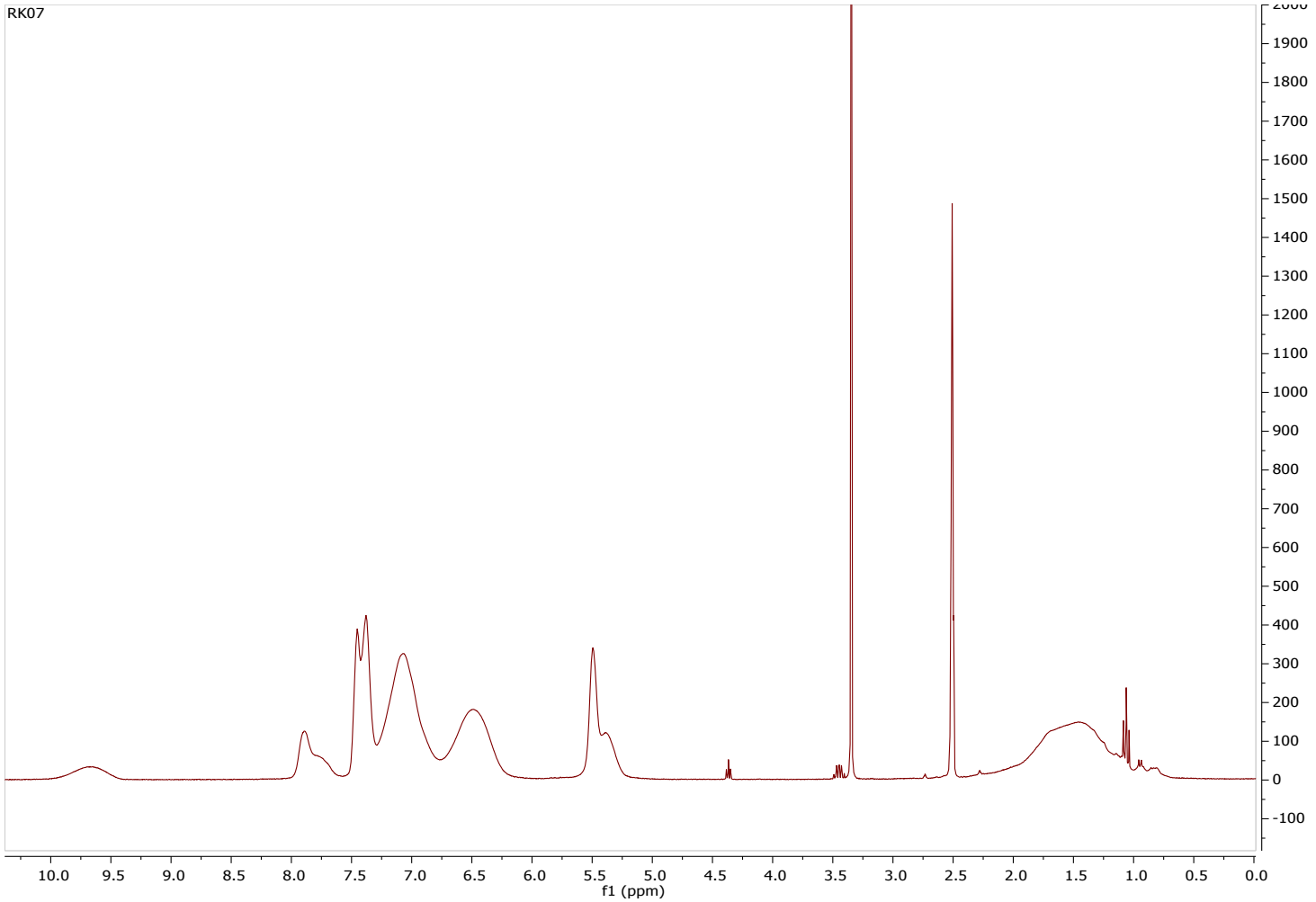


**Figure S8** Solid state $^{13}C$ NMR spectrum of co-polymer **2a**

Pairs of measurements we carried out. One is the full CP spectrum (dipolar dephasing with 0 µs delay) and one is the edited spectrum (missing the CH and $CH_2$ signals) with the 50 µs dephasing delay. There are spinning sidebands in the spectra. The aromatics give sidebands at 60 to 90 and 180 to 210 ppm but there should not be anything else in these ranges. There are some weaker, second order, sidebands around 10 and 25 ppm as well.

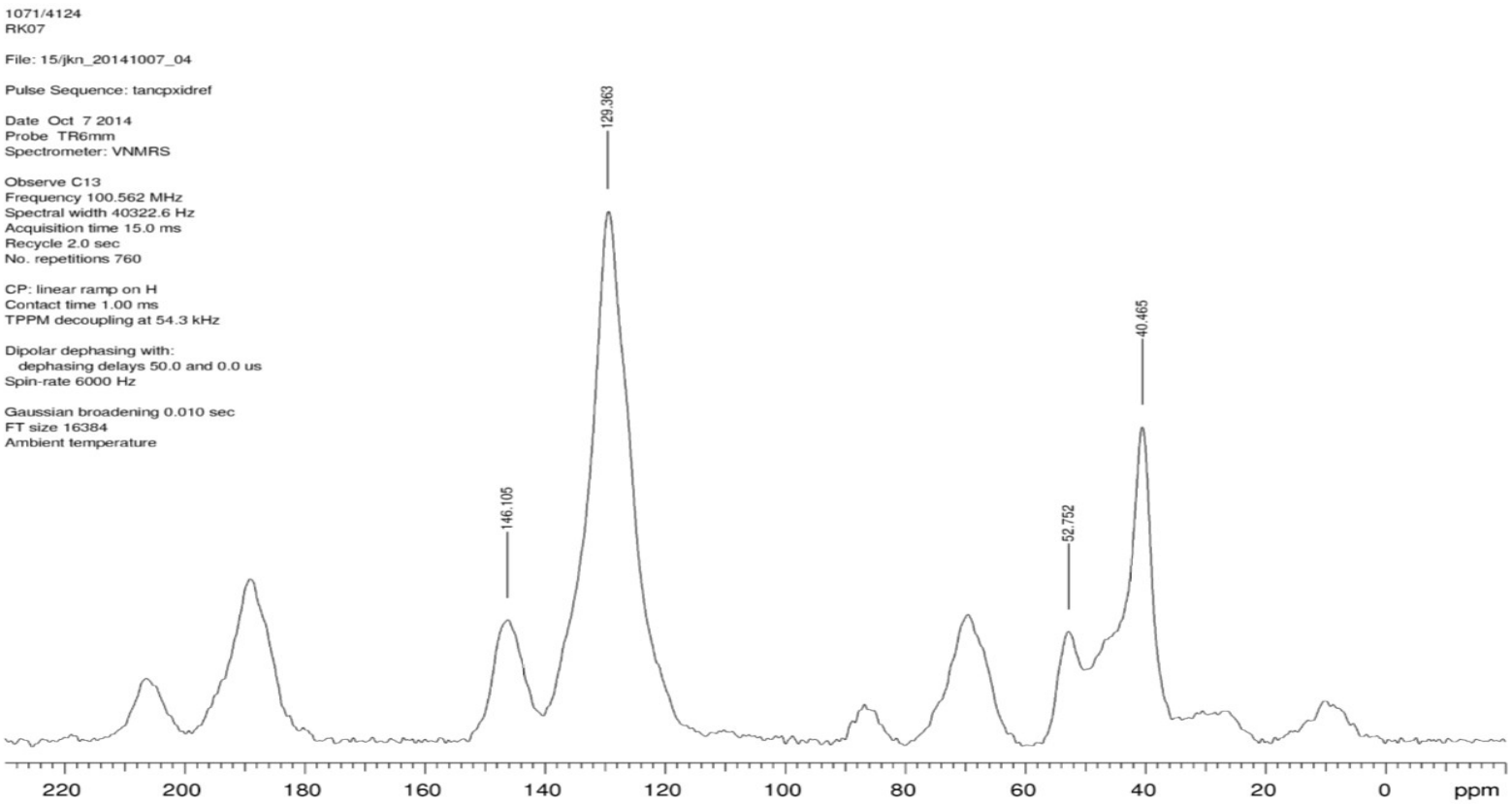


**Figure S9** Solid state $^{13}C$ NMR spectrum of co-polymer **2a**

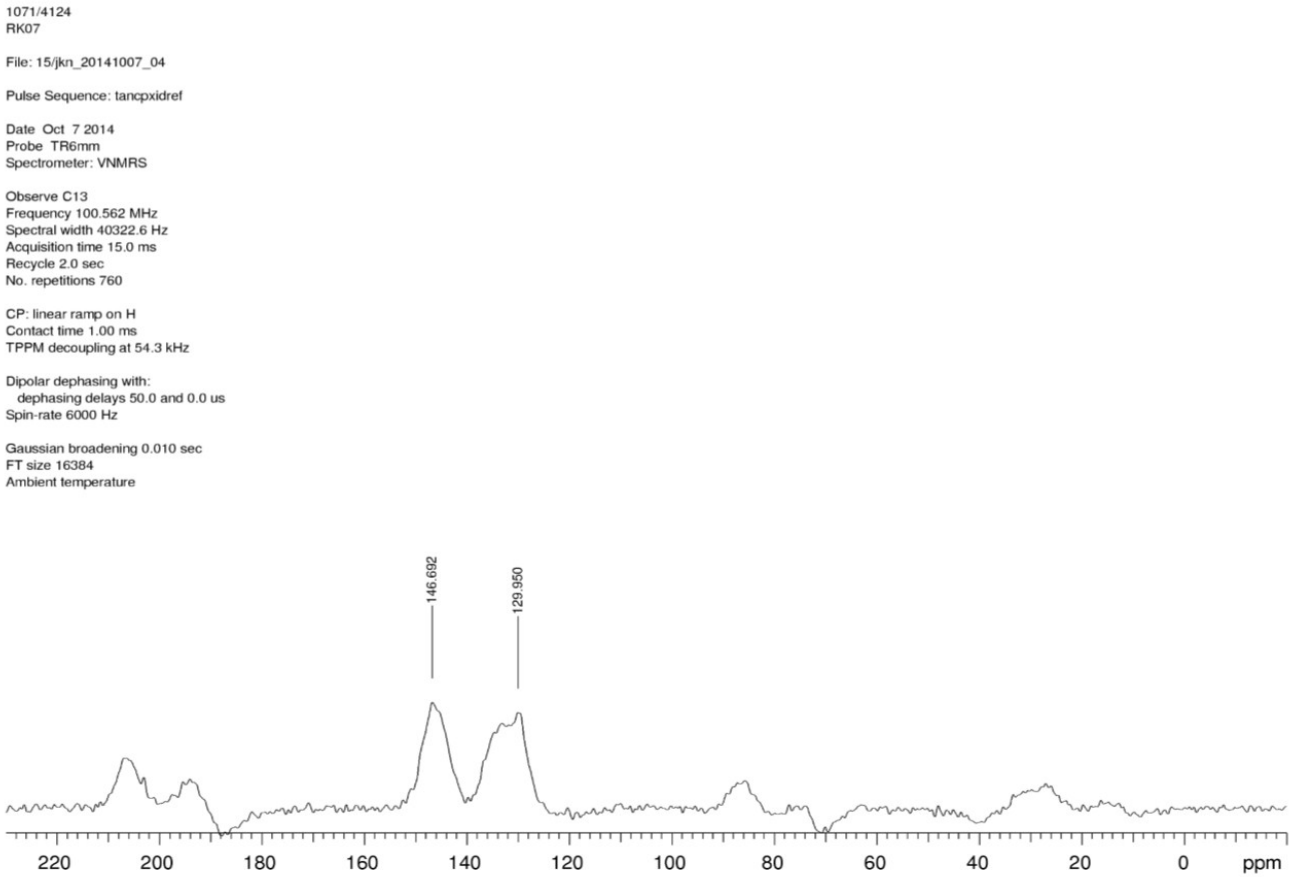


**Figure S10** FT-IR spectrum of co-polymer **2a**

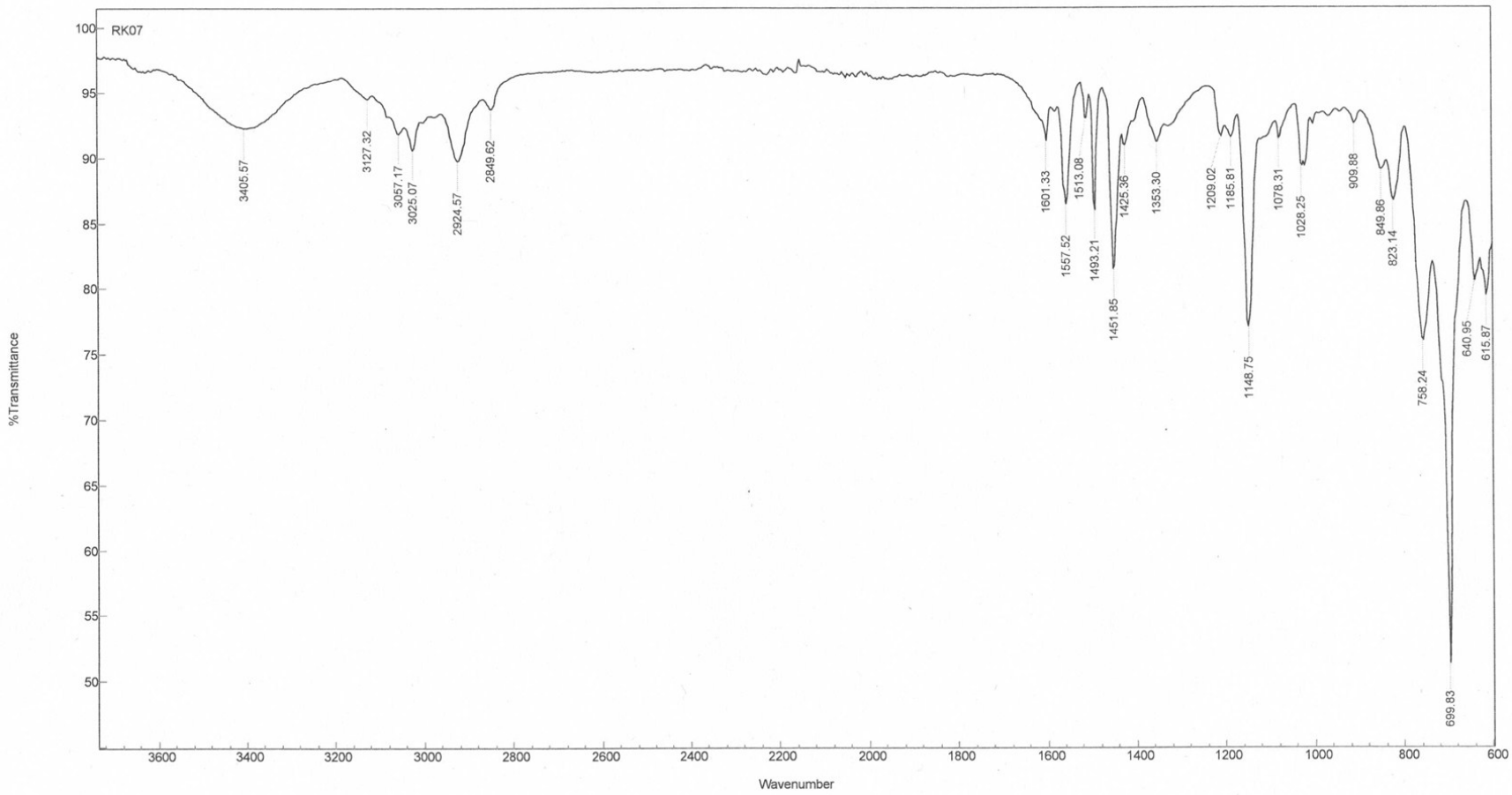
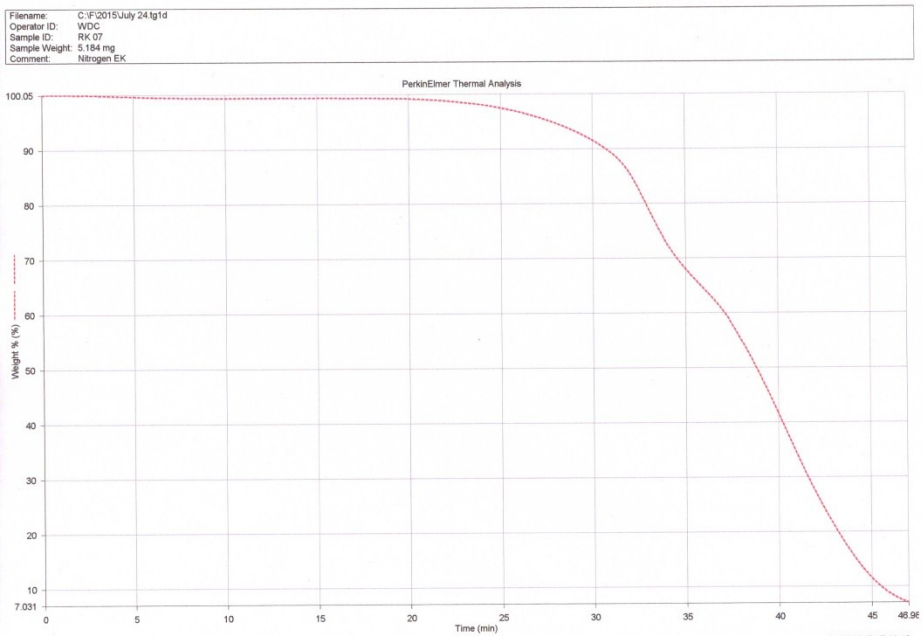


**Figure S11** TGA and DSC curves for co-polymer **2a,** (a) wt% v time and (b) wt% v temperature. Heating rate of 10 ºC $min^{-1}$

**(a)**




**(b)**

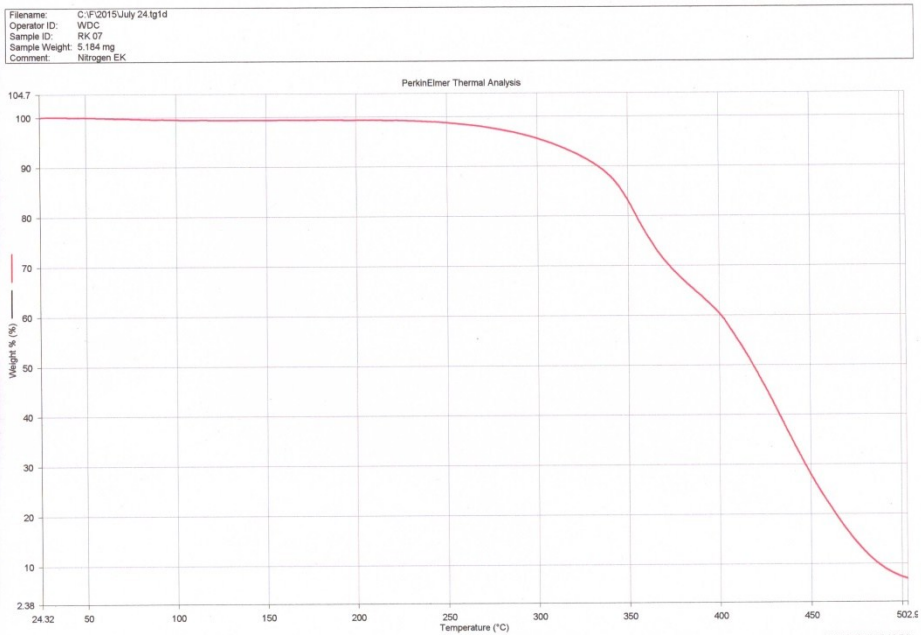


**Figure S12** DSC curve for co-polymer **2a.** The heating rate was 10 ºC $min^{-1}$

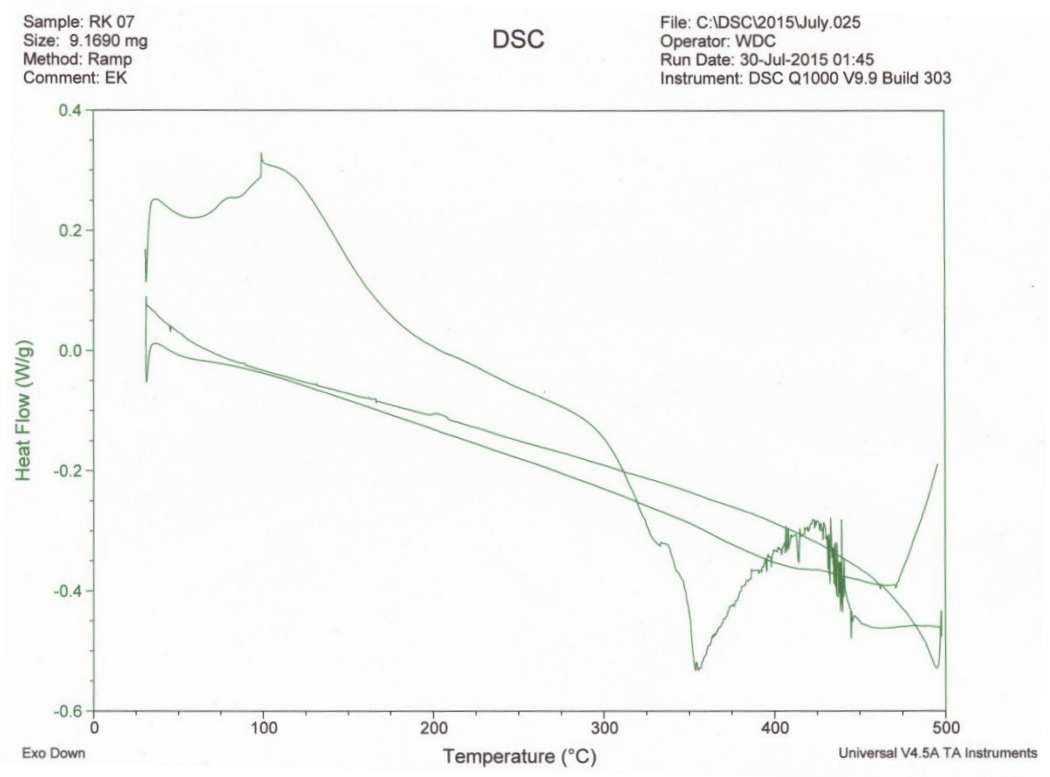
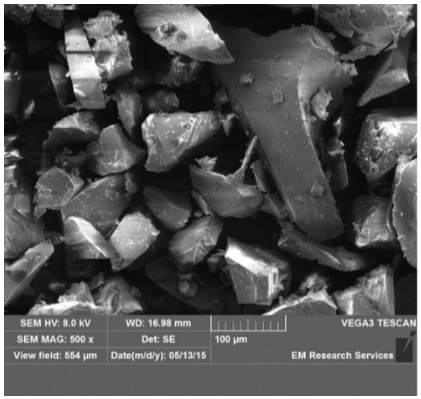
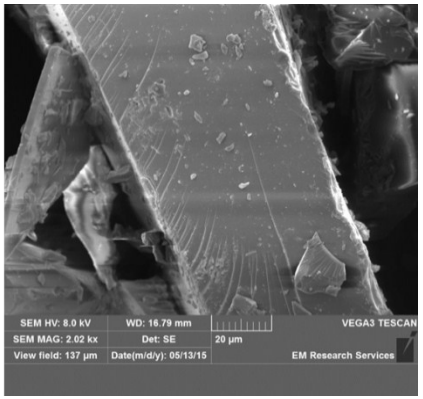
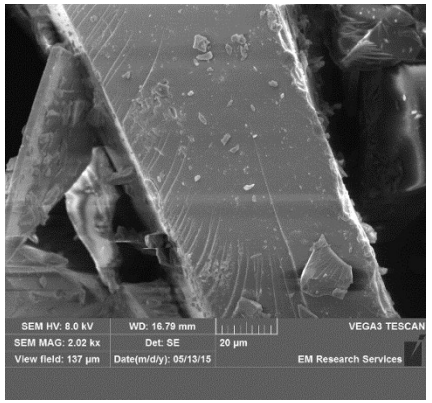
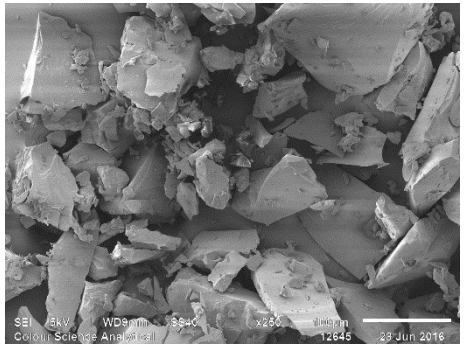


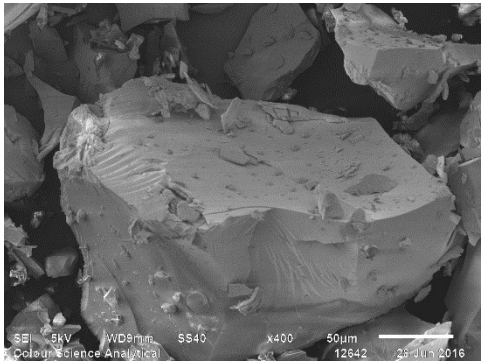
**Figure S13** SEM image of freshly prepared co-polymer **2a.**



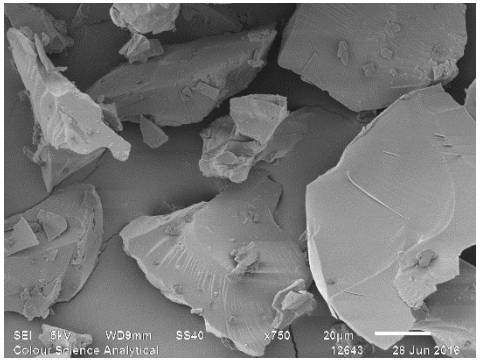



**Figure S14** Differential refractive index (dRI) GPC trace of polymer **2a** in DMF

**Cirrus GPC Sample Injection Report**

Generated by: Administrator — 18 May 2015 14:12
Workbook: C:\Cirrus Workbooks\dafgroupgpc\dafgroupgpc.plw

**Sample Details**
Sample Name: ARC-RK007 #1
Acquired: 18/05/2015 13:18:08 — By Analyst: Administrator
Batch Name: 18_05_2015
Filename: C:\Cirrus Workbooks\dafgroupgpc\18_05_2015-0002.cgrm
Concentration: 1.00 mg/ml — K of Sample: 14.1000
Injection Volume: 50.0 ul — Alpha of Sample: 0.7000
LIMS ID: — Bottle ID:

**Workbook Details**
Eluent: THF — Flow Rate: 1.00 ml/min
Column Set: PL Mixed D — Column Set Length: 0 mm
Detector: RI — Temperature: Ambient

ARC-007
10 g L⁻¹ DMF/LiBr eluent
(injected in same)
poor baseline.

**Analysis Using Method: Manual Analysis**
Comments: This method has processing switched on and is set so that you have to select the Peaks for Calibrants & Unknowns

Results File: C:\Cirrus Workbooks\dafgroupgpc\18_05_2015-0002.rst

**Calibration Used: 12/03/2015 16:01:12**
Calibration Type: Narrow Standard — Curve Fit Used: 1
Calibration Curve: y = 8.667926 - 0.165883x^1

High Limit MW RT: 20.17 mins — Low Limit MW RT: 36.17 mins
High Limit MW: 210190 — Low Limit MW: 466
K: 14.1000 — FRM Name:
Alpha: 0.7000 — Flow Marker RT: 0.00 mins
FRCF: 1.0000

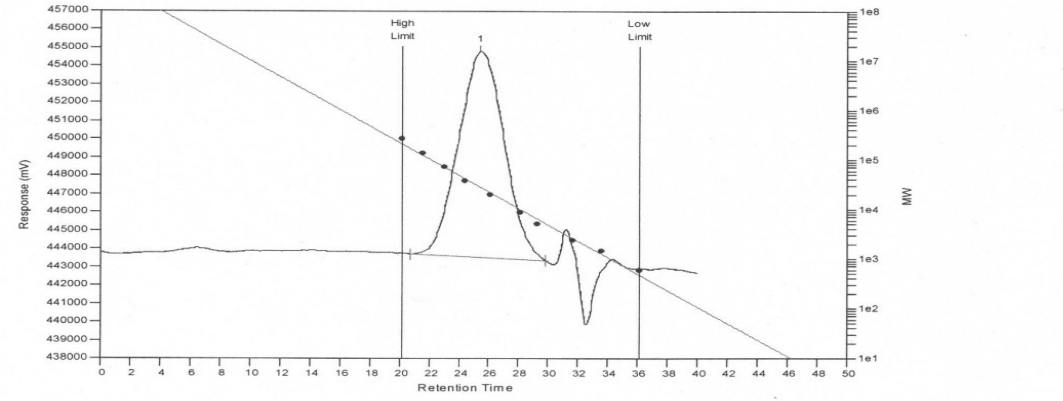


**Figure S15** $^{1}$H NMR spectrum of co-polymer **2b**

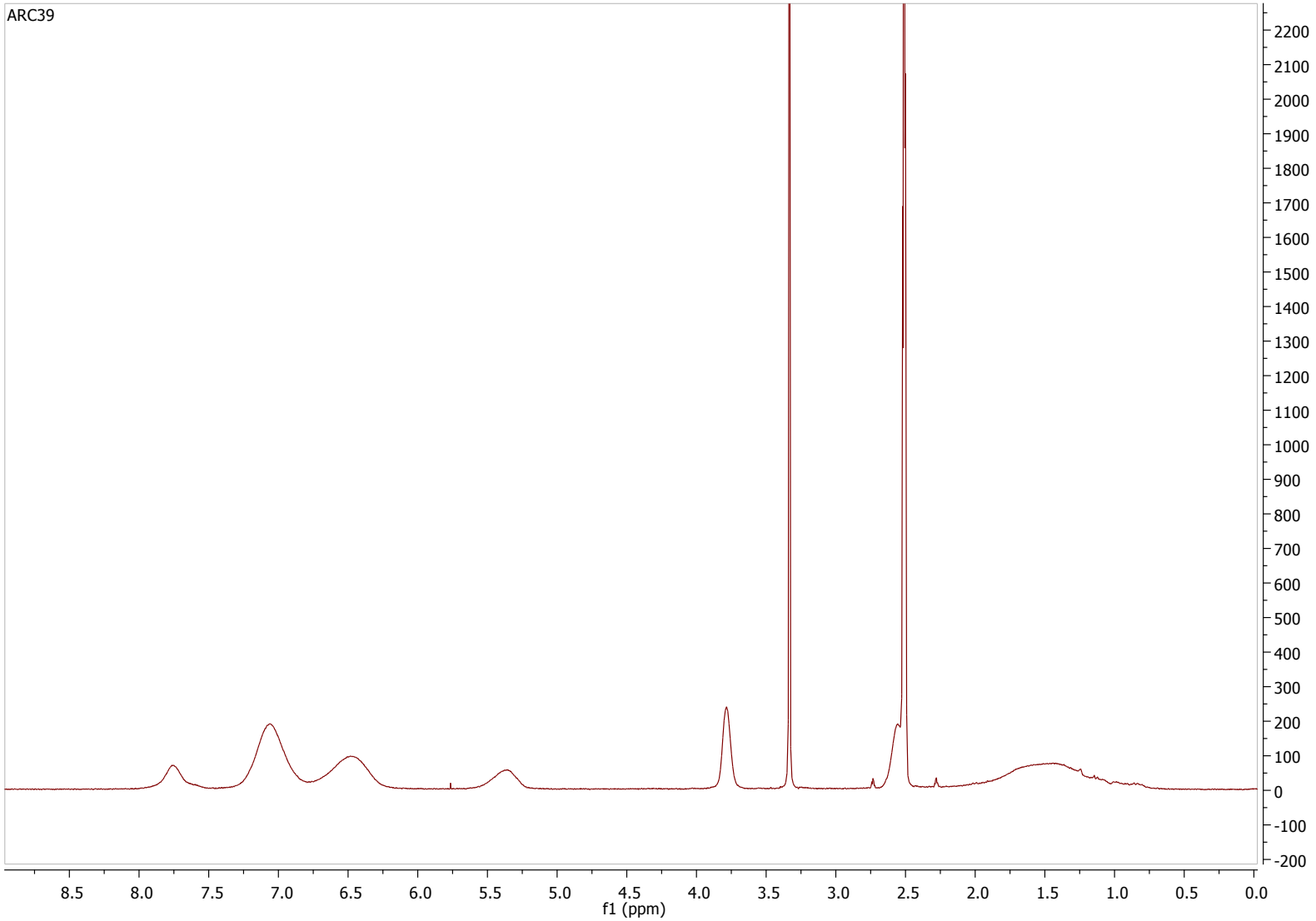


**Figure S16** Solid state $^{13}C$ NMR spectrum of co-polymer **2b**

Pairs of measurements we carried out. One is the full CP spectrum (dipolar dephasing with 0 µs delay) and one is the edited spectrum (missing the CH and $CH_2$ signals) with the 50 µs dephasing delay. There are spinning sidebands in the spectra. The aromatics give sidebands at 60 to 90 and 180 to 210 ppm but there should not be anything else in these ranges. There are some weaker, second order, sidebands around 10 and 25 ppm as well.

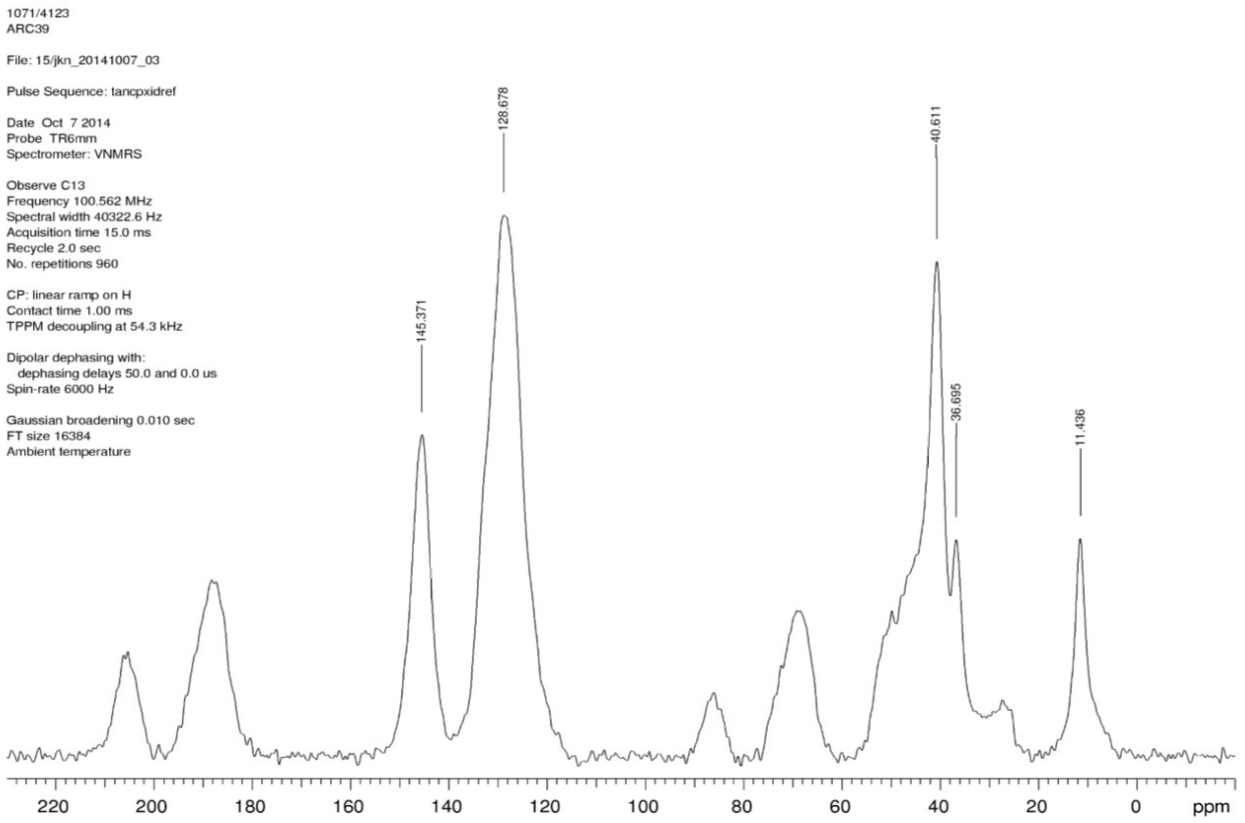


**Figure S17** Solid state $^{13}C$ NMR spectrum of co-polymer **2b**

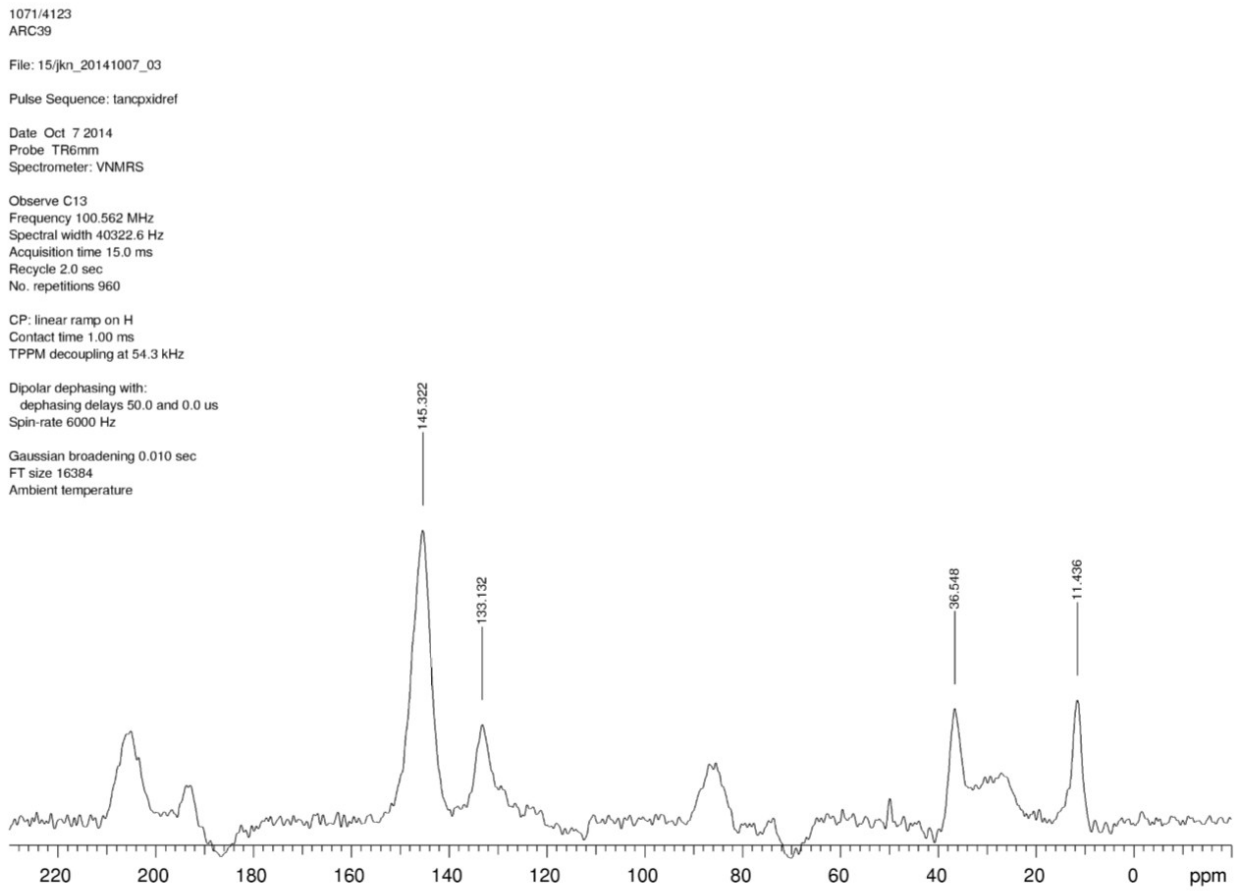


**Figure S18** FT-IR spectrum of co-polymer **2b**

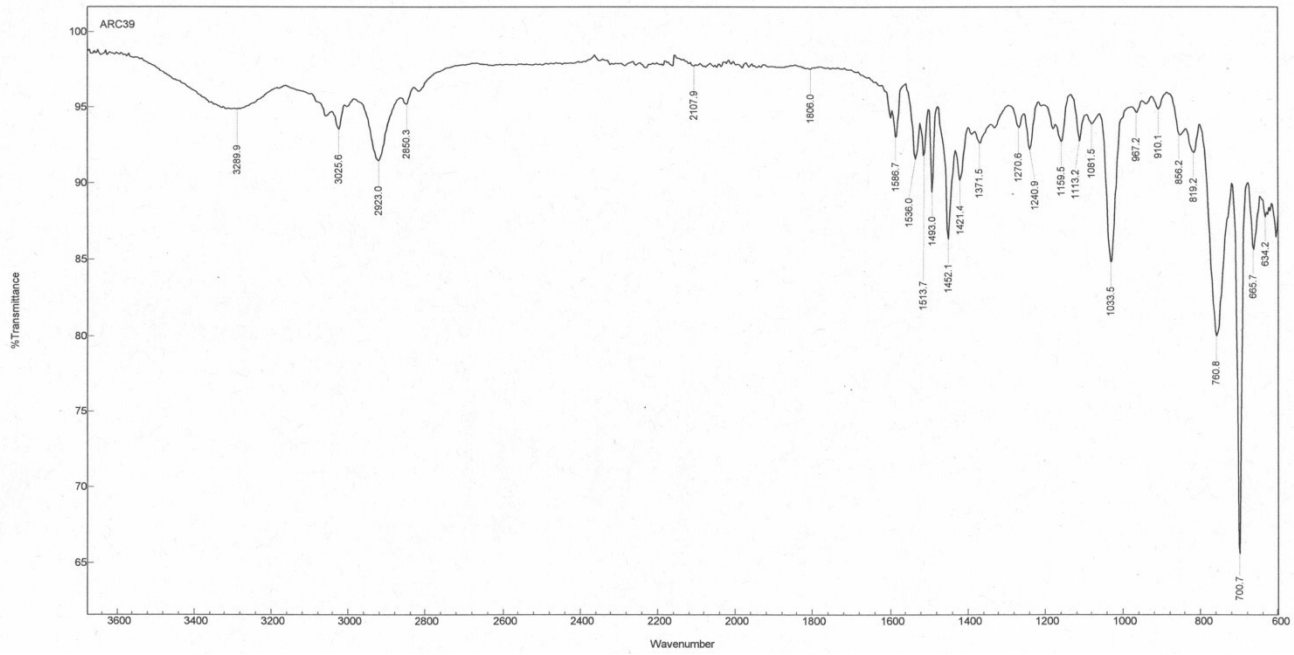
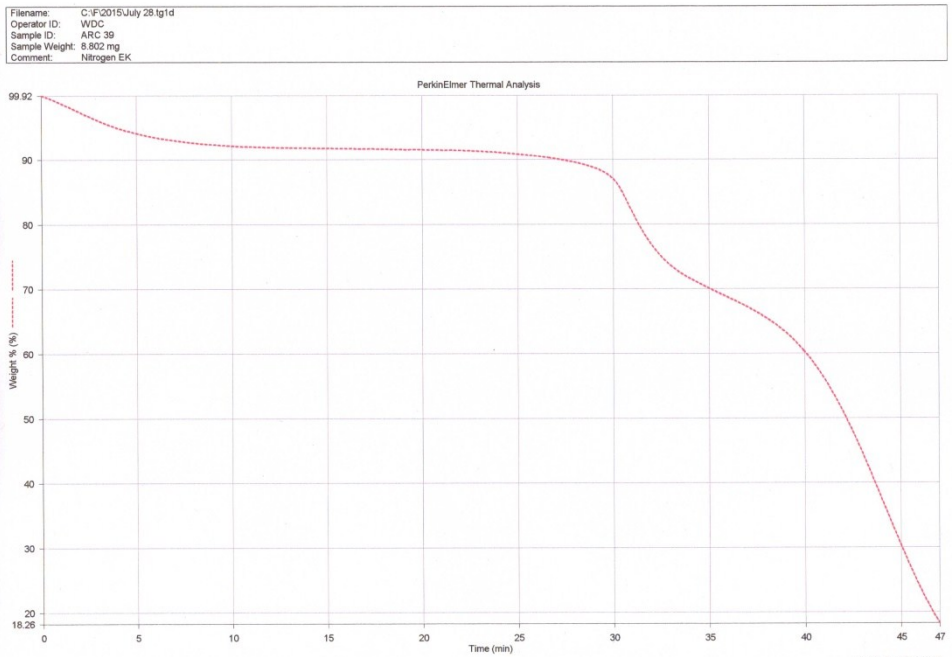


**Figure S19** TGA and DSC curves for co-polymer **2b,** (a) wt% v time and (b) wt% v temperature. Heating rate of 10 ºC $min^{-1}$

(a)




(b)

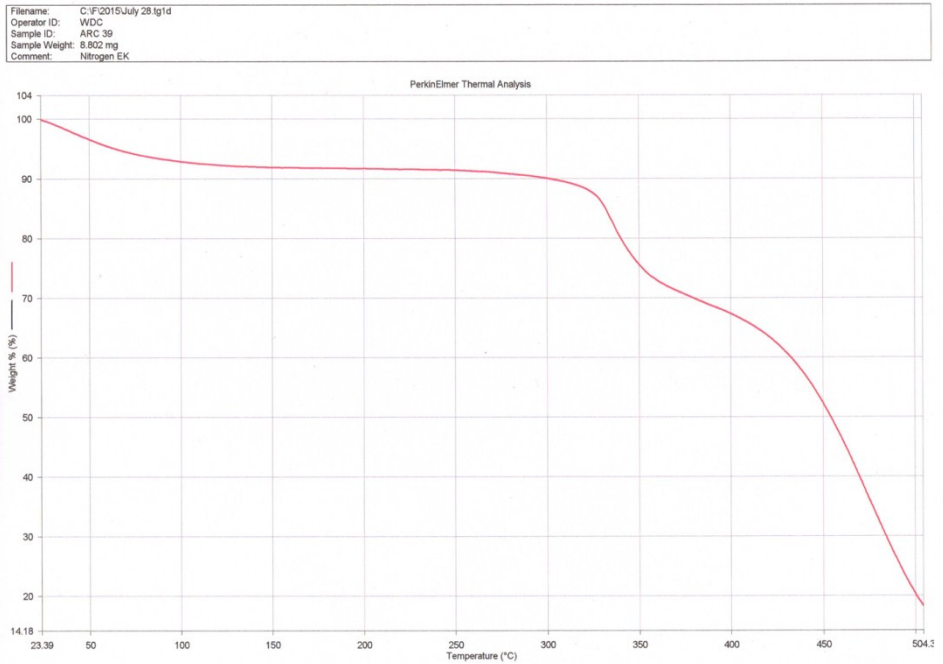


**Figure S20** DSC curve for co-polymer **2b.** The heating rate was 10 ºC min-

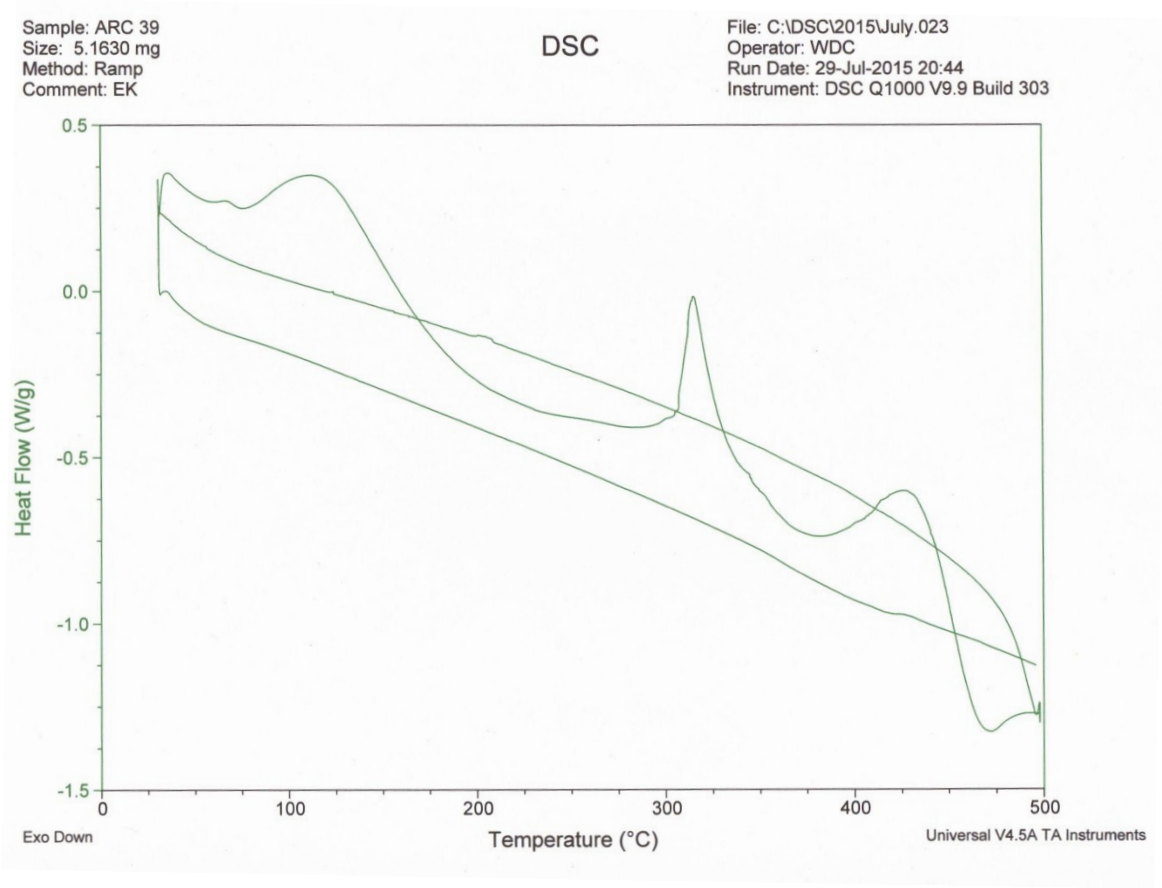
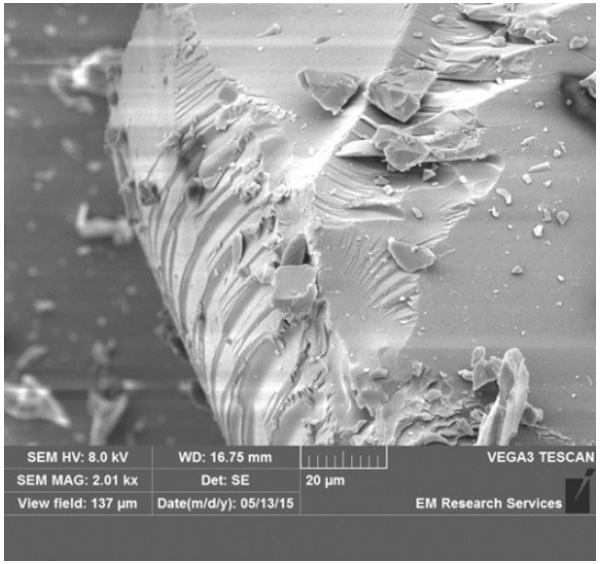


**Figure S21** SEM image of freshly prepared co-polymer **2b.**



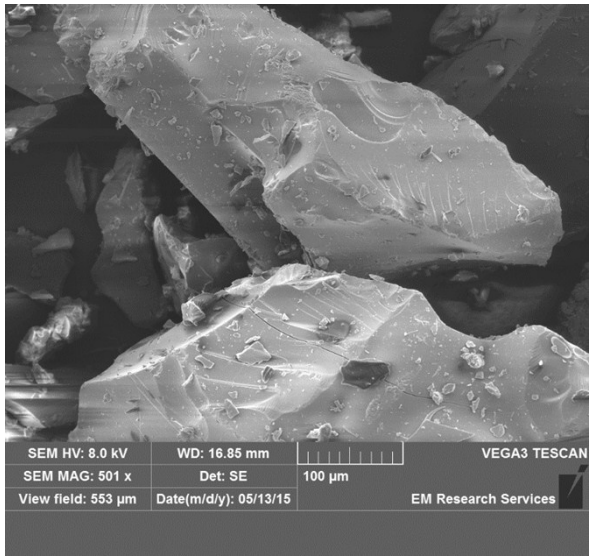
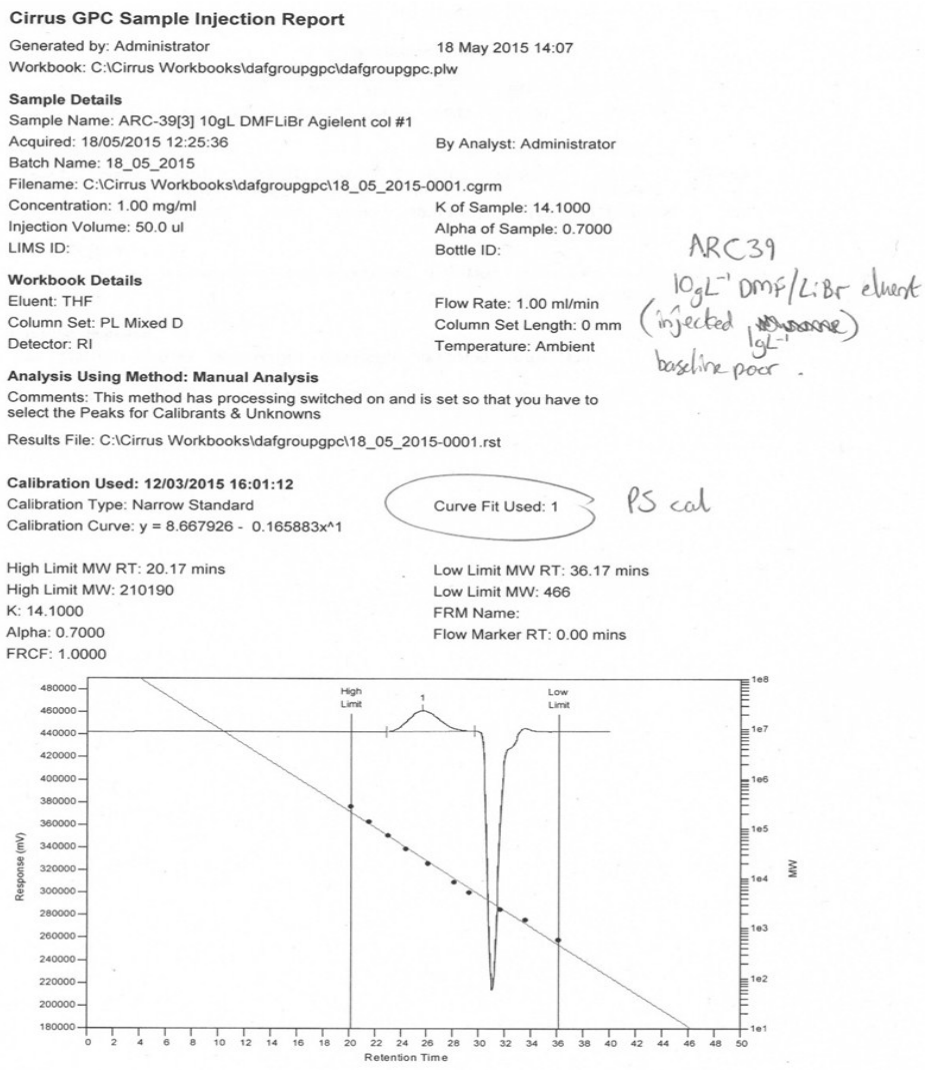



**Figure S22** Differential refractive index (dRI) GPC trace of polymer **2b** in DMF



**Cirrus GPC Sample Injection Report**

Generated by: Administrator — 18 May 2015 14:07
Workbook: C:\Cirrus Workbooks\dafgroupgpc\dafgroupgpc.plw

**Sample Details**
Sample Name: ARC-39[3] 10gL DMFLiBr Agielent col #1
Acquired: 18/05/2015 12:25:36 — By Analyst: Administrator
Batch Name: 18_05_2015
Filename: C:\Cirrus Workbooks\dafgroupgpc\18_05_2015-0001.cgrm
Concentration: 1.00 mg/ml — K of Sample: 14.1000
Injection Volume: 50.0 ul — Alpha of Sample: 0.7000
LIMS ID: — Bottle ID:

ARC39
$10gL^{-1}$ DMF/LiBr eluent
(injected $1gL^{-1}$)
baseline poor.

**Workbook Details**
Eluent: THF — Flow Rate: 1.00 ml/min
Column Set: PL Mixed D — Column Set Length: 0 mm
Detector: RI — Temperature: Ambient

**Analysis Using Method: Manual Analysis**
Comments: This method has processing switched on and is set so that you have to select the Peaks for Calibrants & Unknowns

Results File: C:\Cirrus Workbooks\dafgroupgpc\18_05_2015-0001.rst

**Calibration Used: 12/03/2015 16:01:12**
Calibration Type: Narrow Standard
Calibration Curve: y = 8.667926 - 0.165883x^1
Curve Fit Used: 1 — PS cal

High Limit MW RT: 20.17 mins — Low Limit MW RT: 36.17 mins
High Limit MW: 210190 — Low Limit MW: 466
K: 14.1000 — FRM Name:
Alpha: 0.7000 — Flow Marker RT: 0.00 mins
FRCF: 1.0000

**Figure S23** $^{1}$H spectrum of co-polymer **2c**

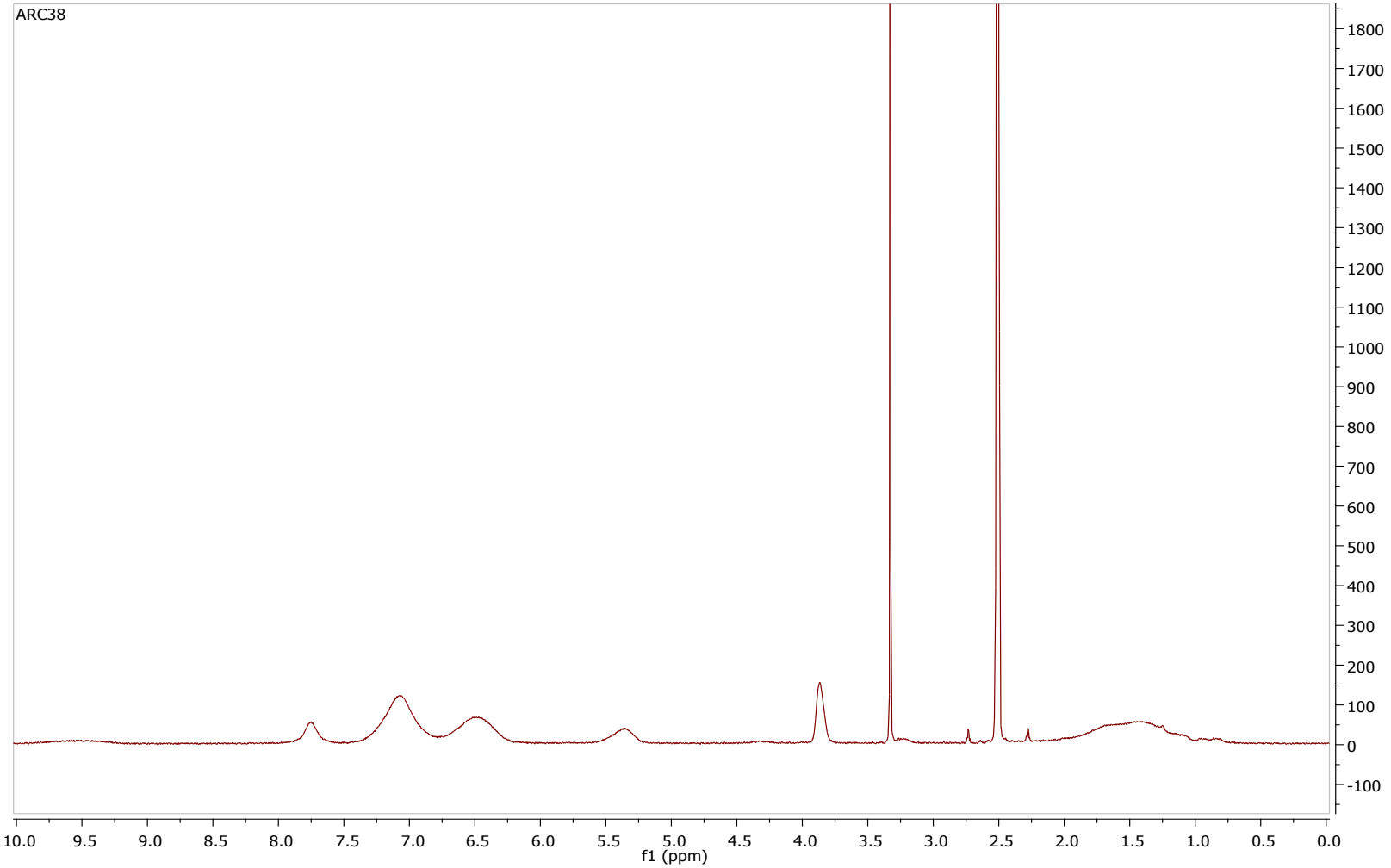


**Figure S24** Solid state $^{13}C$ NMR spectrum of co-polymer **2c**

Pairs of measurements were carrid out. One is the full CP spectrum (dipolar dephasing with 0 µs delay) and one is the edited spectrum (missing the CH and CH2 signals) with the 50 µs dephasing delay. There are spinning sidebands in the spectra. The aromatics give sidebands at 60 to 90 and 180 to 210 ppm but there should not be anything else in these ranges. There are some weaker, second order, sidebands around 10 and 25 ppm as well.

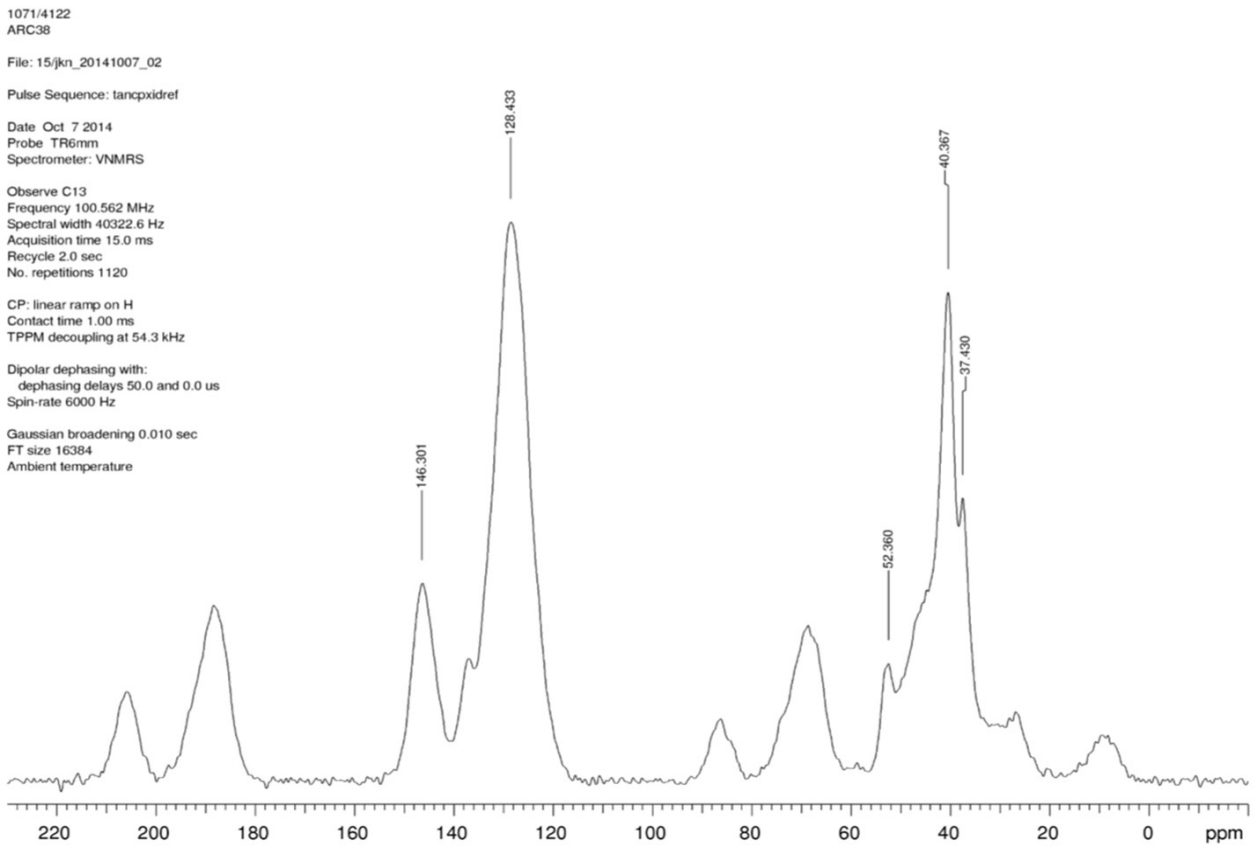


**Figure S25** Solid state $^{13}C$ NMR spectrum of co-polymer **2c**

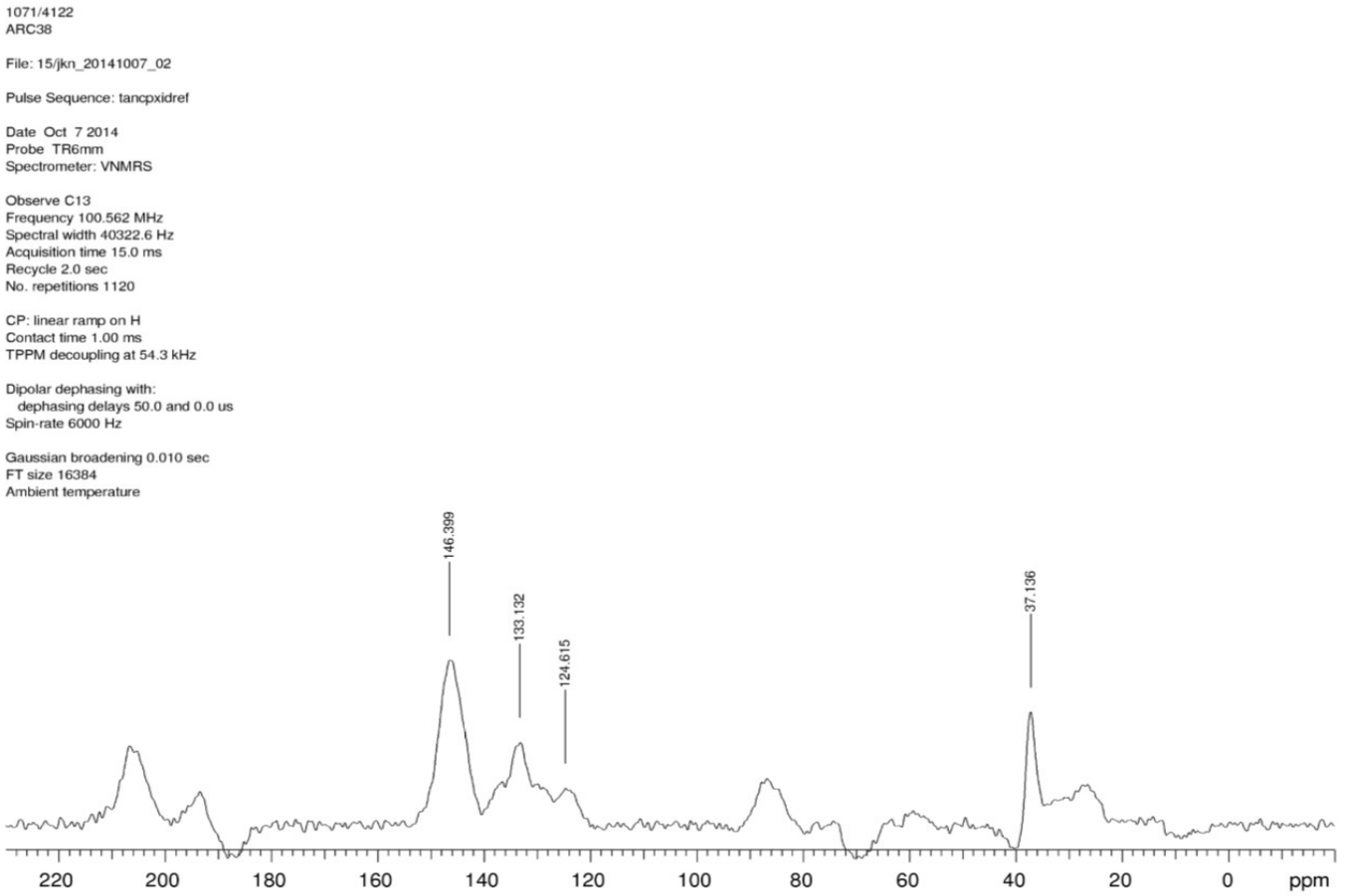


**Figure S26** FT-IR spectrm of co-polymer **2c**

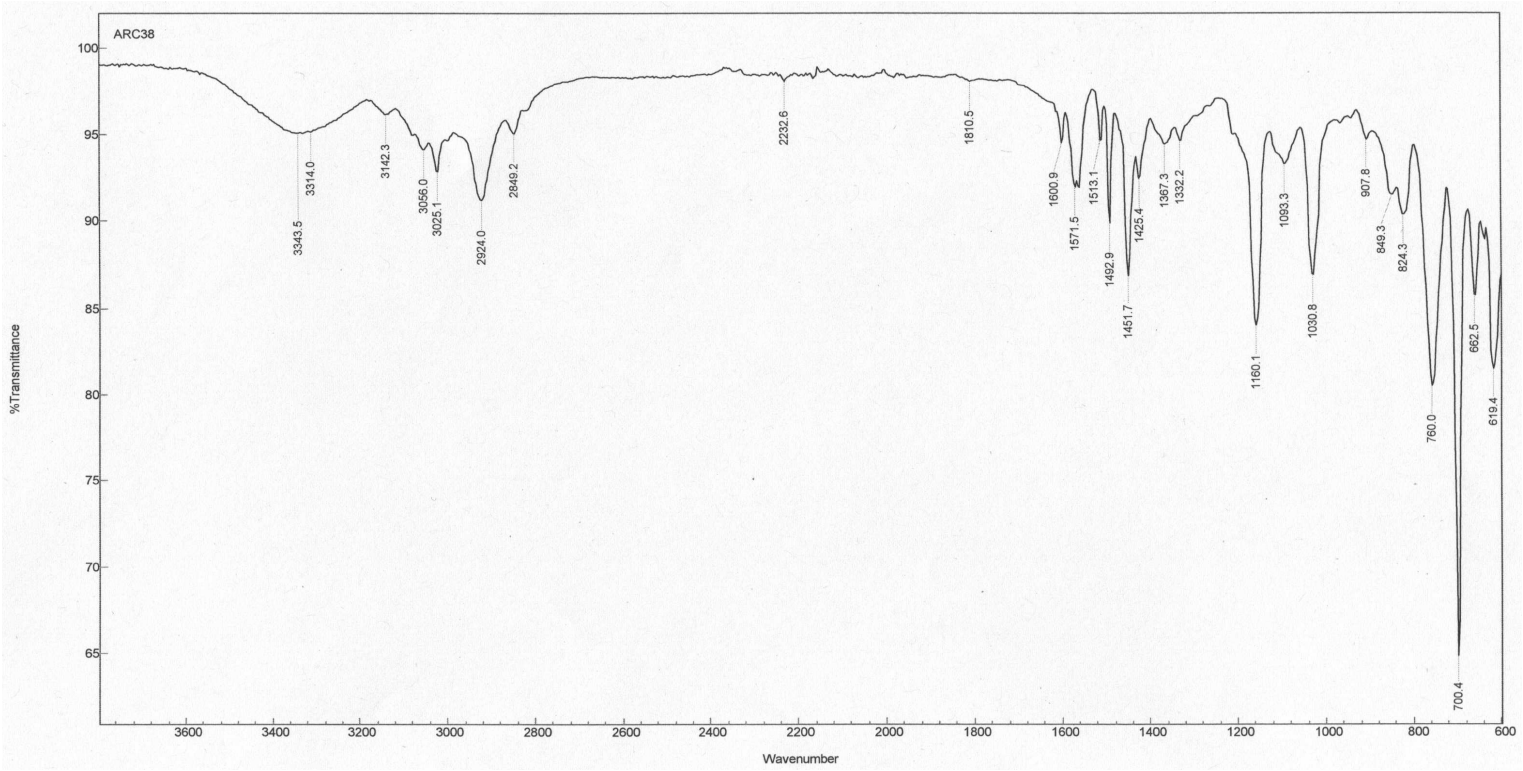
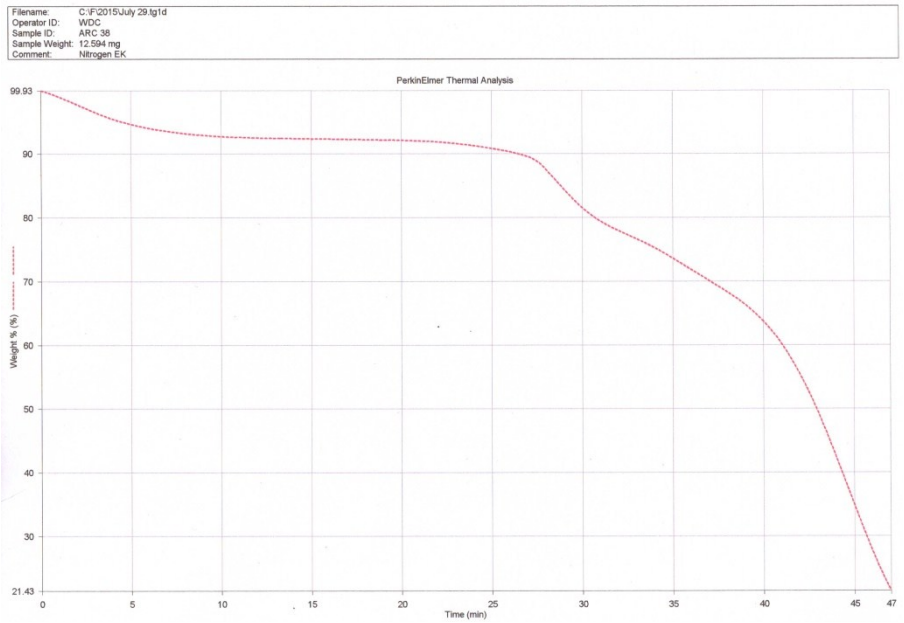


**Figure S27** TGA and DSC curves for co-polymer **2c**, (a) wt% v time and (b) wt% v temperature**.** Heating rate of 10 ºC $min^{-1}$

**(a)**




**(b)**

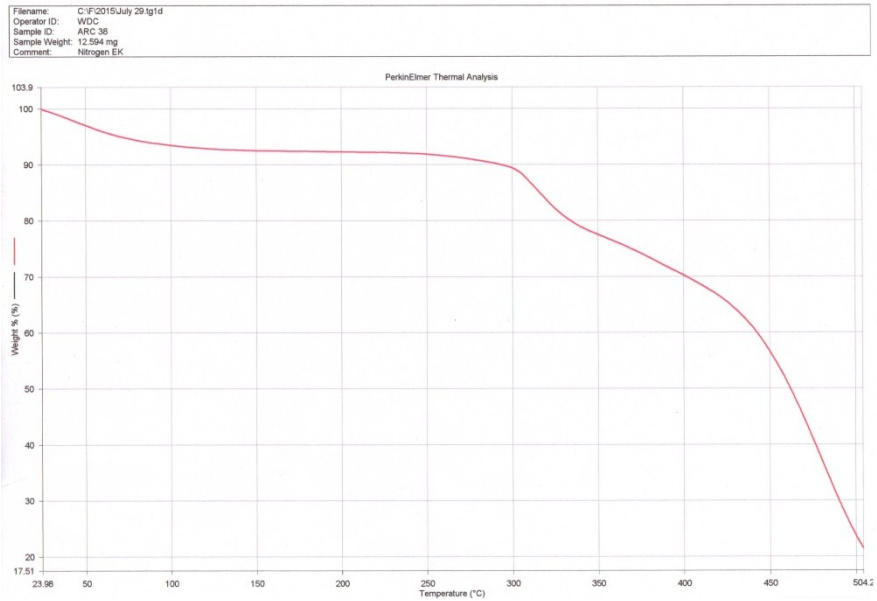


**Figure S28** DSC curve for co-polymer **2c.** The heating rate was 10 ºC $min^{-1}$

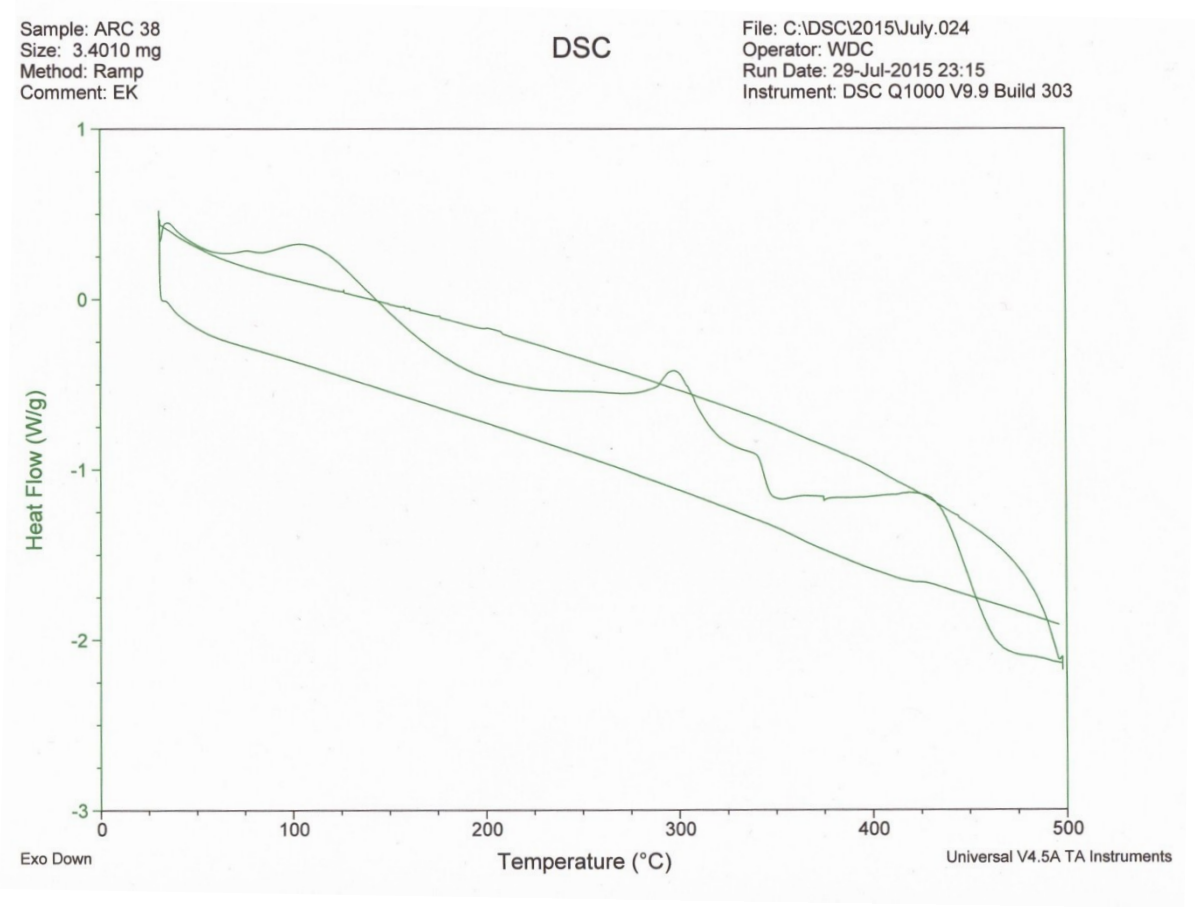
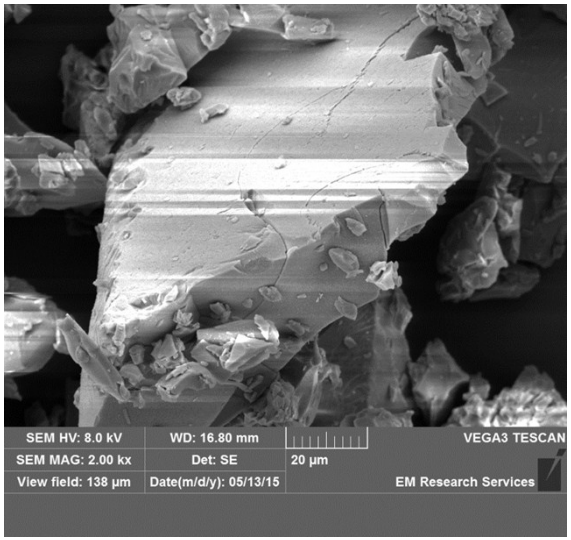


**Figure S29** SEM image of freshly prepared co-polymer **2c**



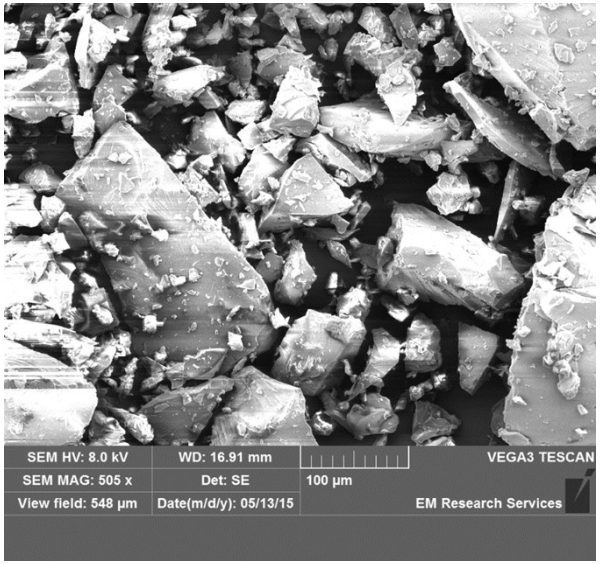
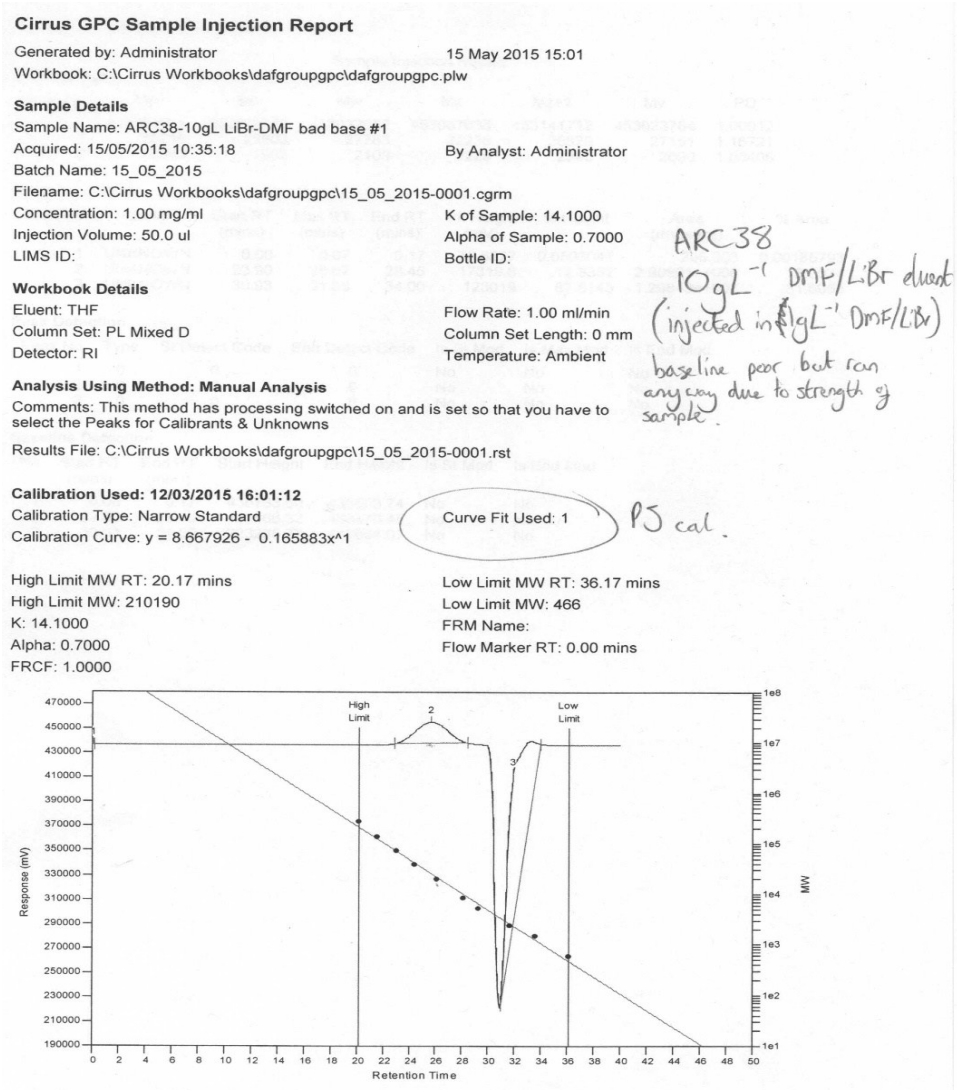



**Figure S30** Differential refractive index (dRI) GPC trace of polymer **2c** in DMF



**Cirrus GPC Sample Injection Report**

Generated by: Administrator — 15 May 2015 15:01
Workbook: C:\Cirrus Workbooks\dafgroupgpc\dafgroupgpc.plw

**Sample Details**
Sample Name: ARC38-10gL LiBr-DMF bad base #1
Acquired: 15/05/2015 10:35:18 — By Analyst: Administrator
Batch Name: 15_05_2015
Filename: C:\Cirrus Workbooks\dafgroupgpc\15_05_2015-0001.cgrm
Concentration: 1.00 mg/ml — K of Sample: 14.1000
Injection Volume: 50.0 ul — Alpha of Sample: 0.7000
LIMS ID: — Bottle ID:

ARC38
10gL$^{-1}$ DMF/LiBr eluent
(injected in 5gL$^{-1}$ DMF/LiBr)
baseline poor but ran anyway due to strength of sample.

**Workbook Details**
Eluent: THF — Flow Rate: 1.00 ml/min
Column Set: PL Mixed D — Column Set Length: 0 mm
Detector: RI — Temperature: Ambient

**Analysis Using Method: Manual Analysis**
Comments: This method has processing switched on and is set so that you have to select the Peaks for Calibrants & Unknowns

Results File: C:\Cirrus Workbooks\dafgroupgpc\15_05_2015-0001.rst

**Calibration Used: 12/03/2015 16:01:12**
Calibration Type: Narrow Standard — Curve Fit Used: 1
Calibration Curve: y = 8.667926 - 0.165883x^1

PS cal.

High Limit MW RT: 20.17 mins — Low Limit MW RT: 36.17 mins
High Limit MW: 210190 — Low Limit MW: 466
K: 14.1000 — FRM Name:
Alpha: 0.7000 — Flow Marker RT: 0.00 mins
FRCF: 1.0000

**Figure S31** FT-IR spectrum of freshly prepared polymer-supported peroxophosphotungstate **3a**

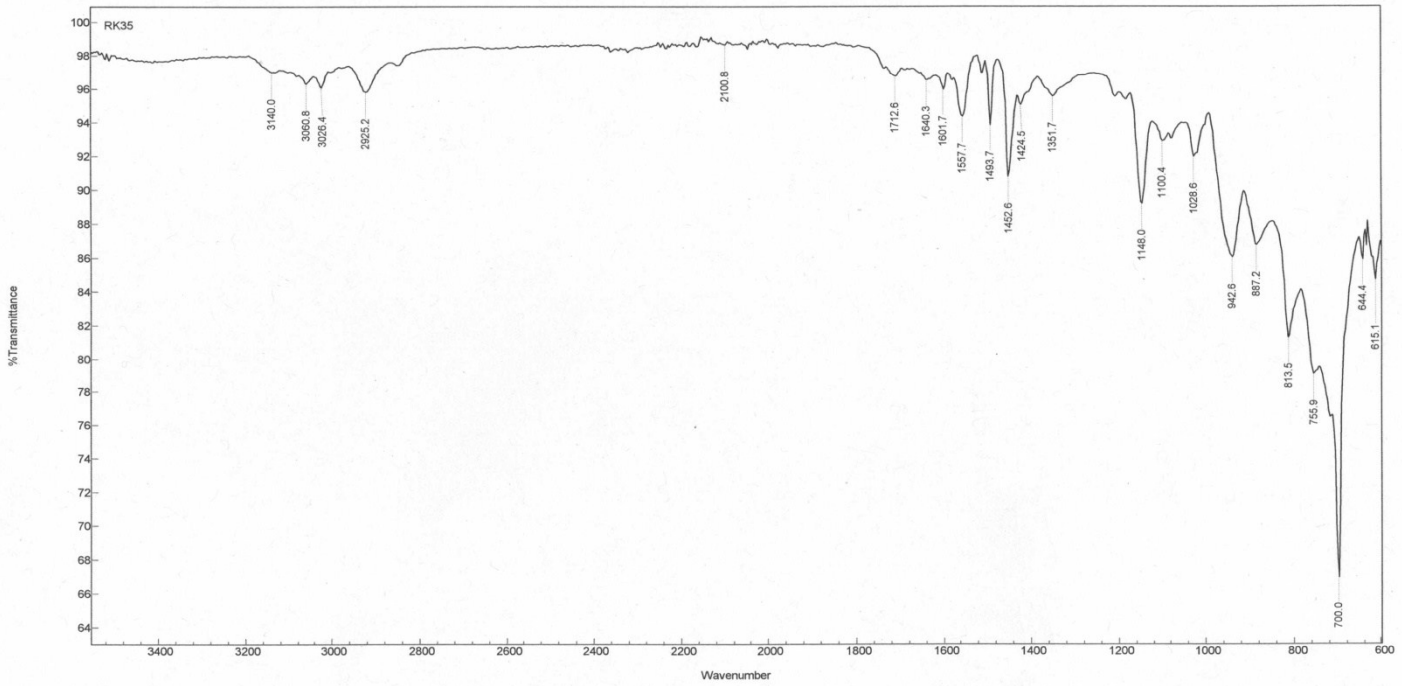


**Figure S32** XPS spectra of W ($4f_{7/2}$) and W ($4f_{5/2}$) peaks for freshly prepared polymer-supported peroxophosphotungstate **3a**

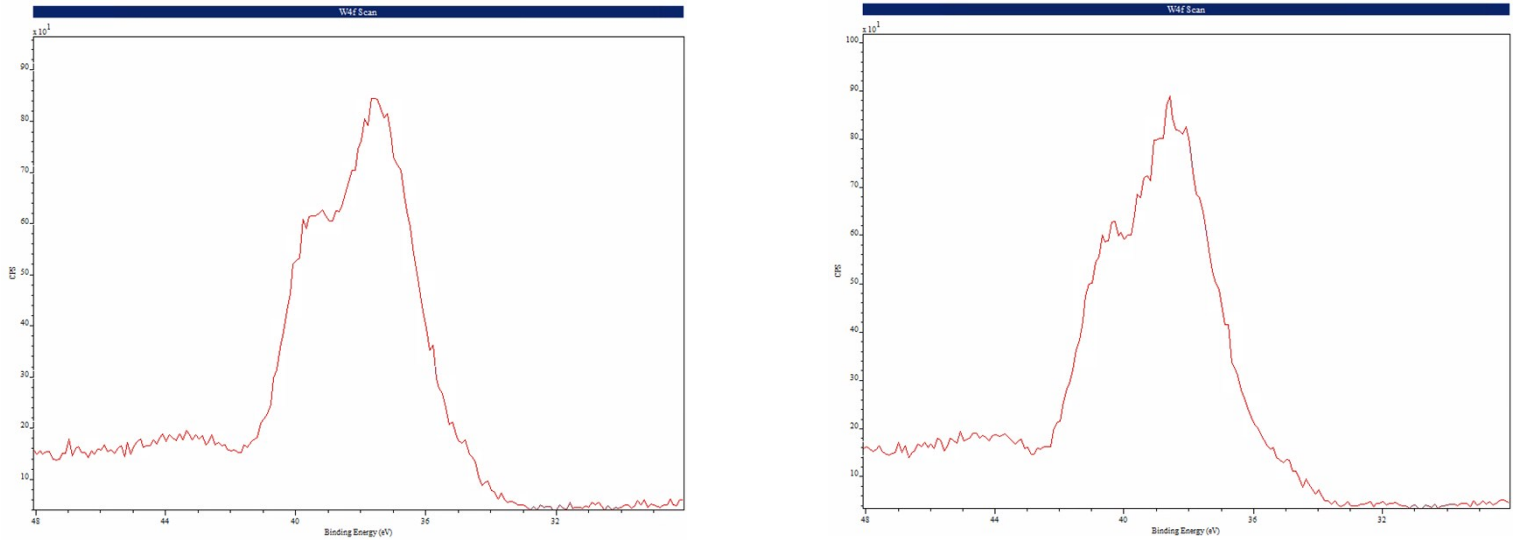


**Figure S33** Solid state $^{31}P$ NMR spectrum of freshly prepared polymer-supported peroxophosphotungstate **3a**

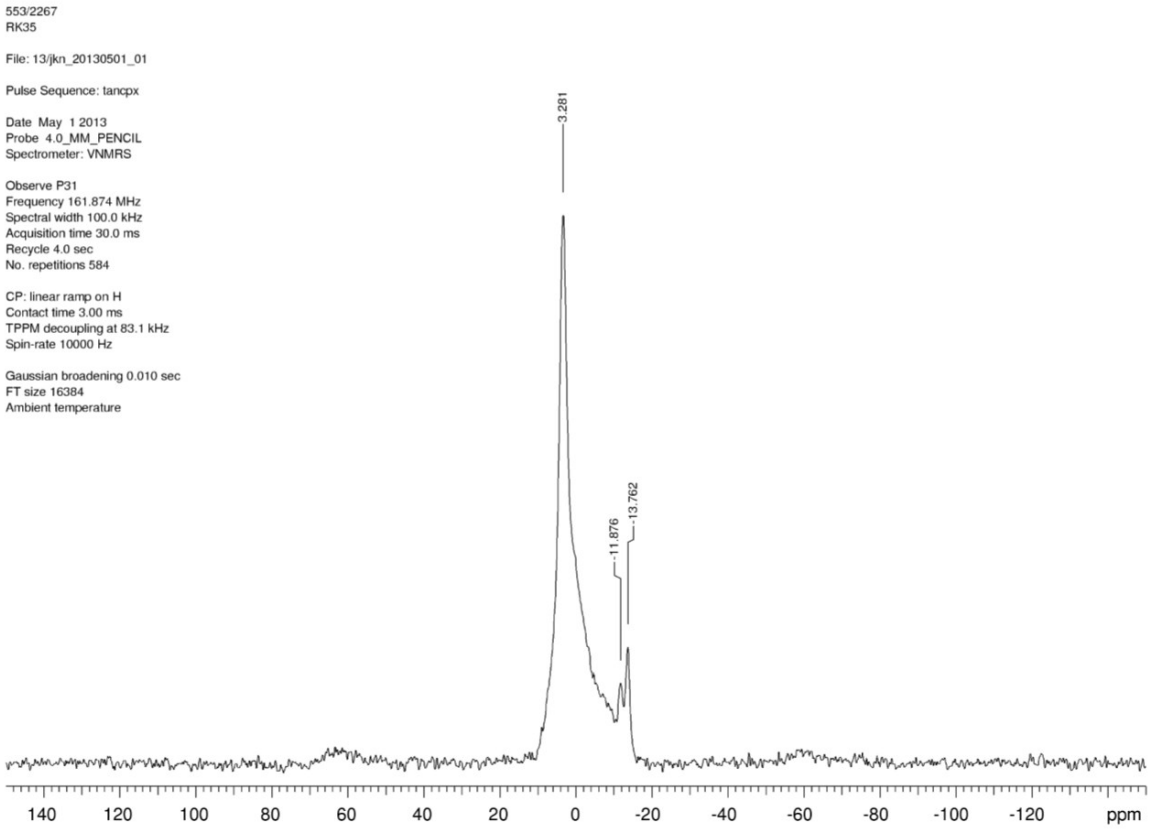


**Figure S34** Solid state $^{13}C$ NMR spectrum of freshly prepared polymer-supported peroxophosphotungstate **3a**

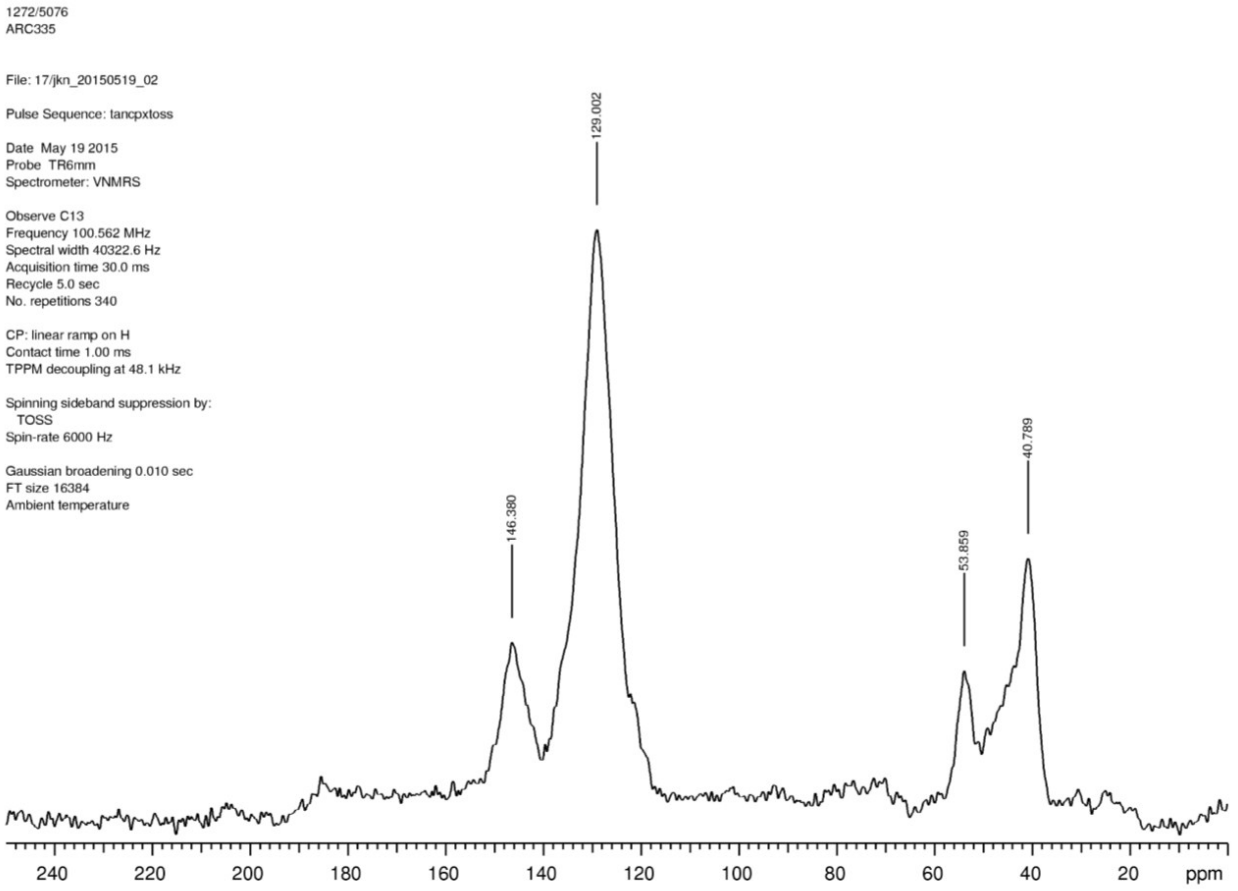
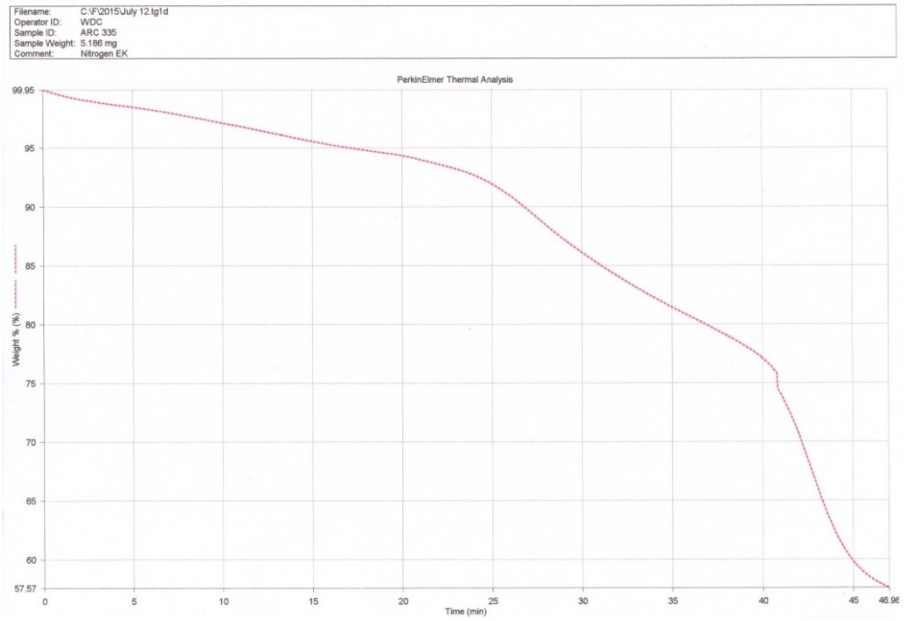


**Figure S35** TGA and DSC curves for polymer-supported peroxophosphotungstate **3a**, (a) wt% v time and (b) wt% v temperature**.** Heating rate of 10 ºC $min^{-1}$



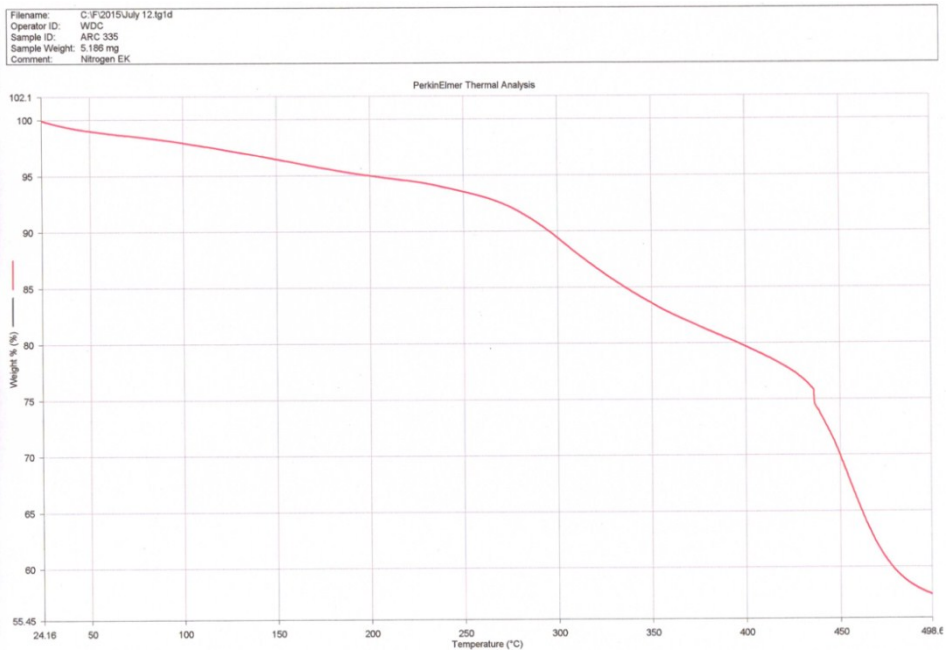



**Figure S36** DSC curve for polymer-supported peroxophosphotungstate **3a.** The heating rate was 10 ºC $min^{-1}$

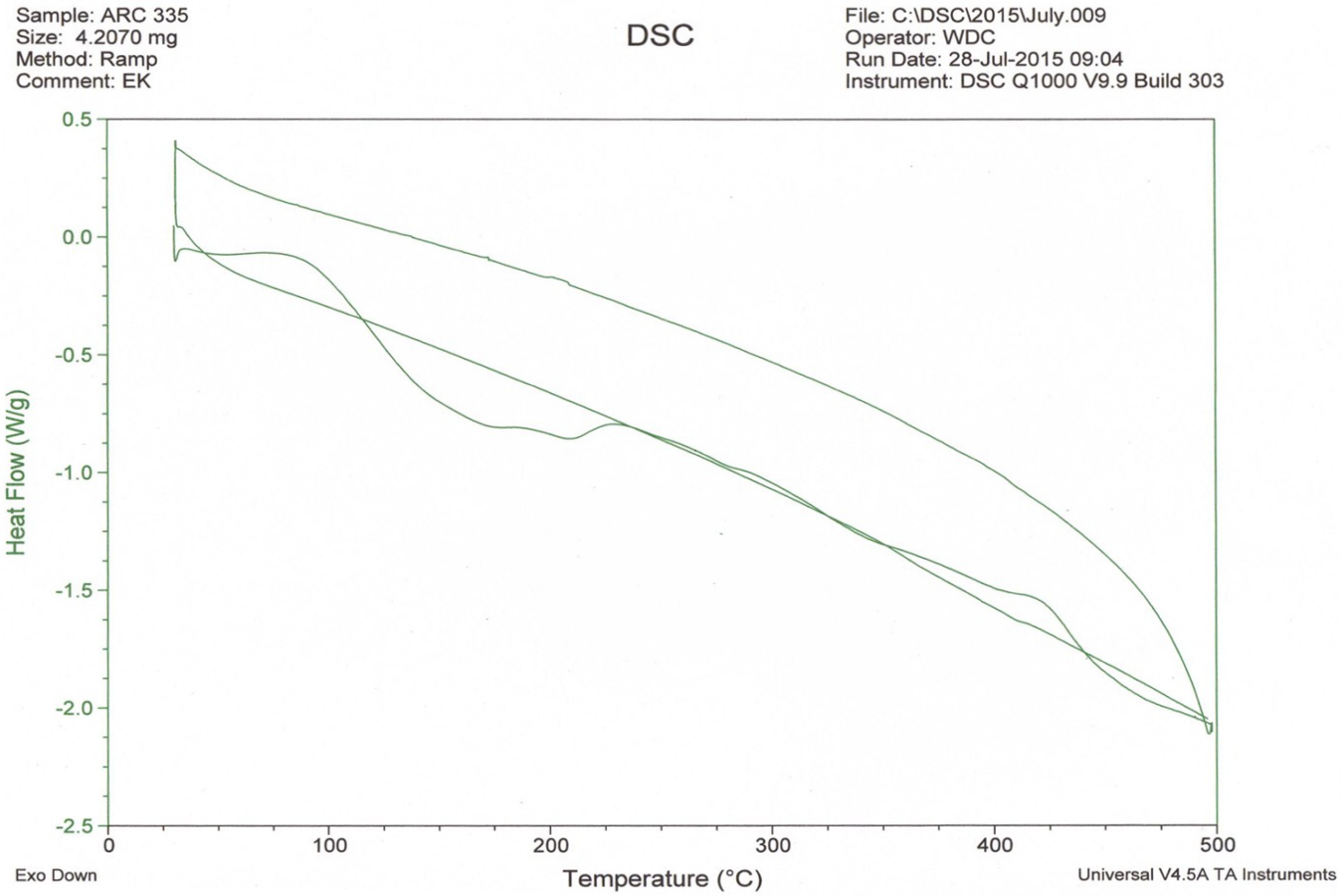
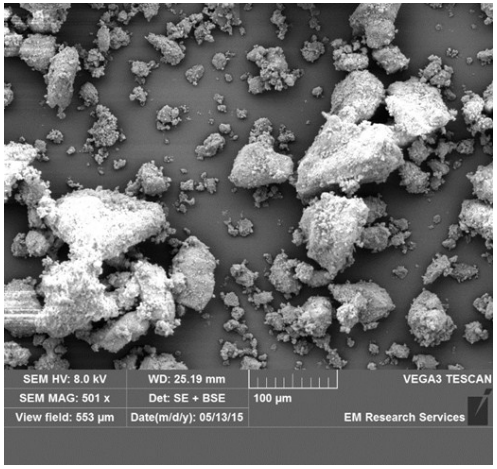
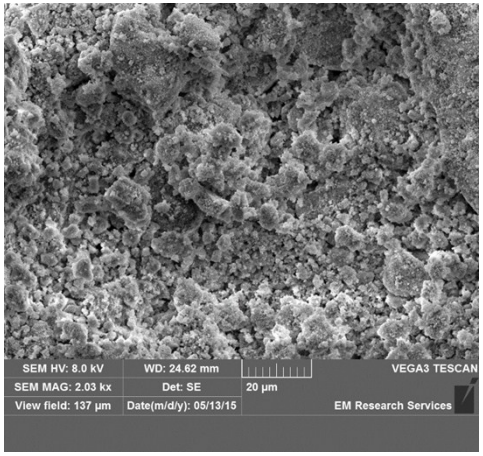
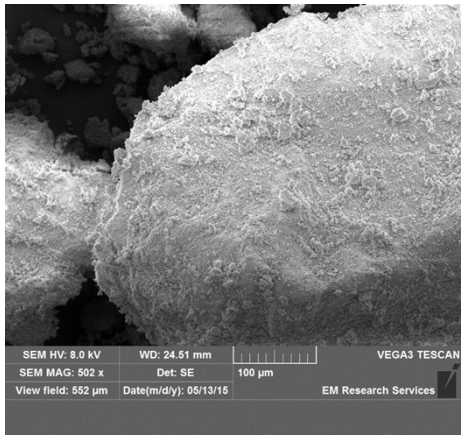
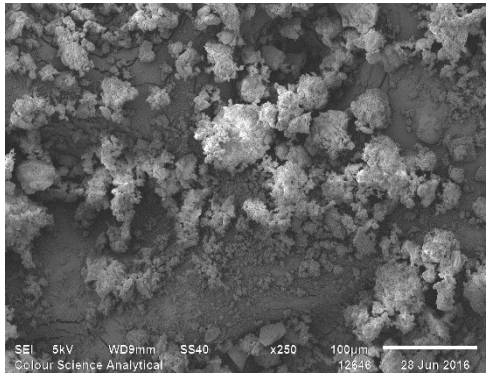


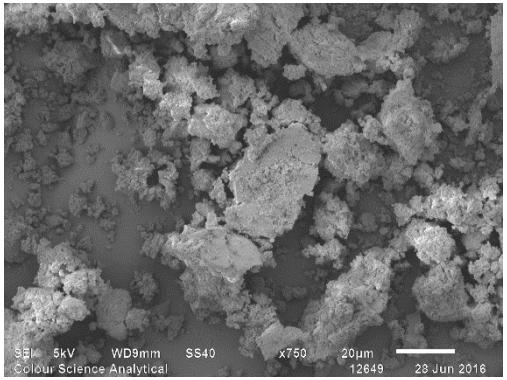
**Figure S37** SEM images of freshly prepared polymer-supported peroxophosphotungstate **3a**



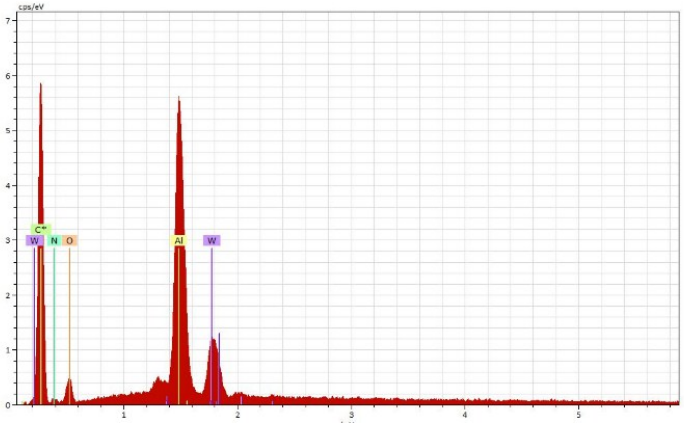



**Figure S38** FT-IR spectrum of freshly prepared polymer-supported peroxophosphotungstate **3b**

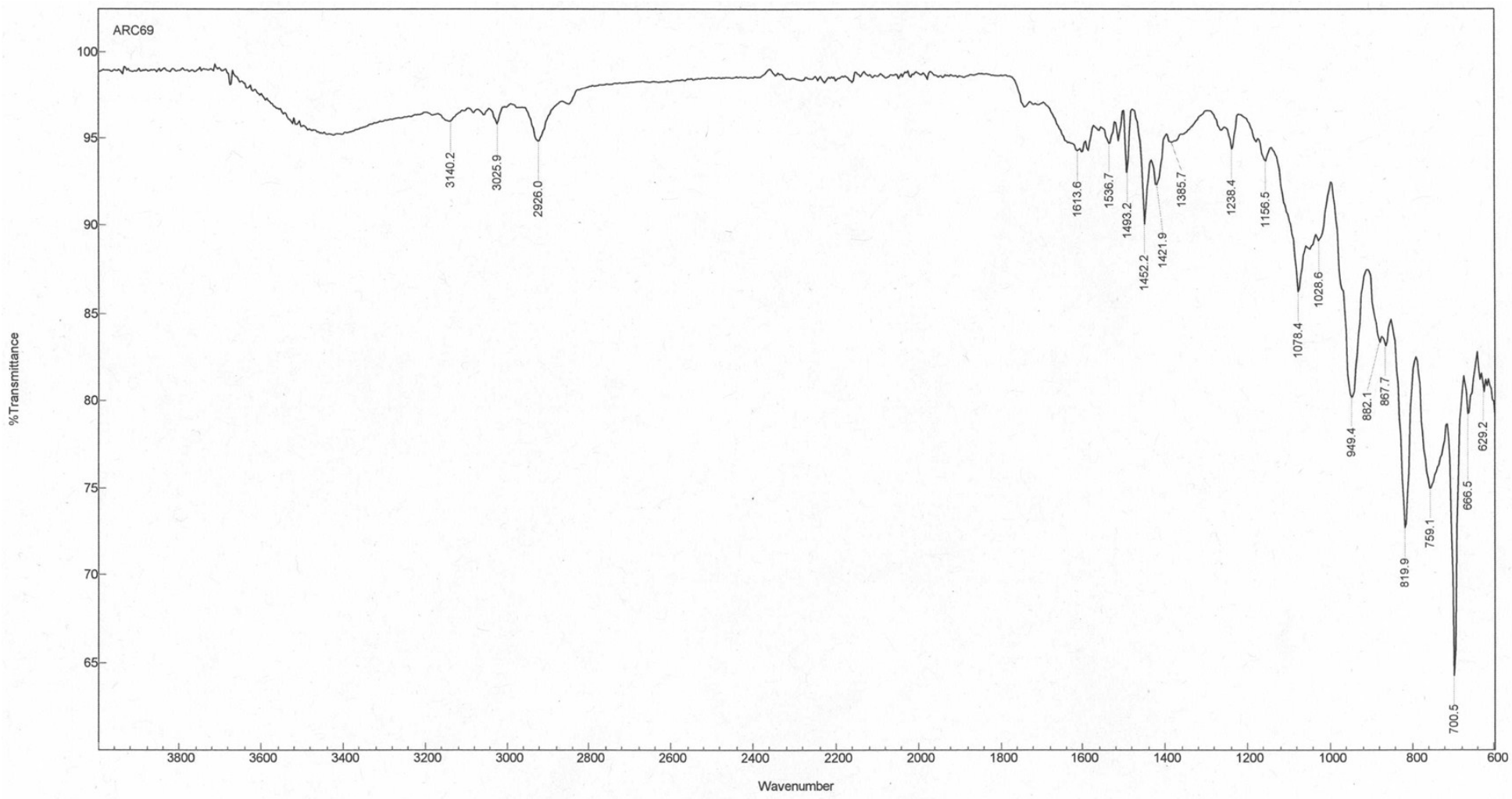


**Figure S39** XPS spectra of W ($4f_{7/2}$) and W ($4f_{5/2}$) peaks for freshly prepared polymer-supported peroxophosphotungstate **3b**

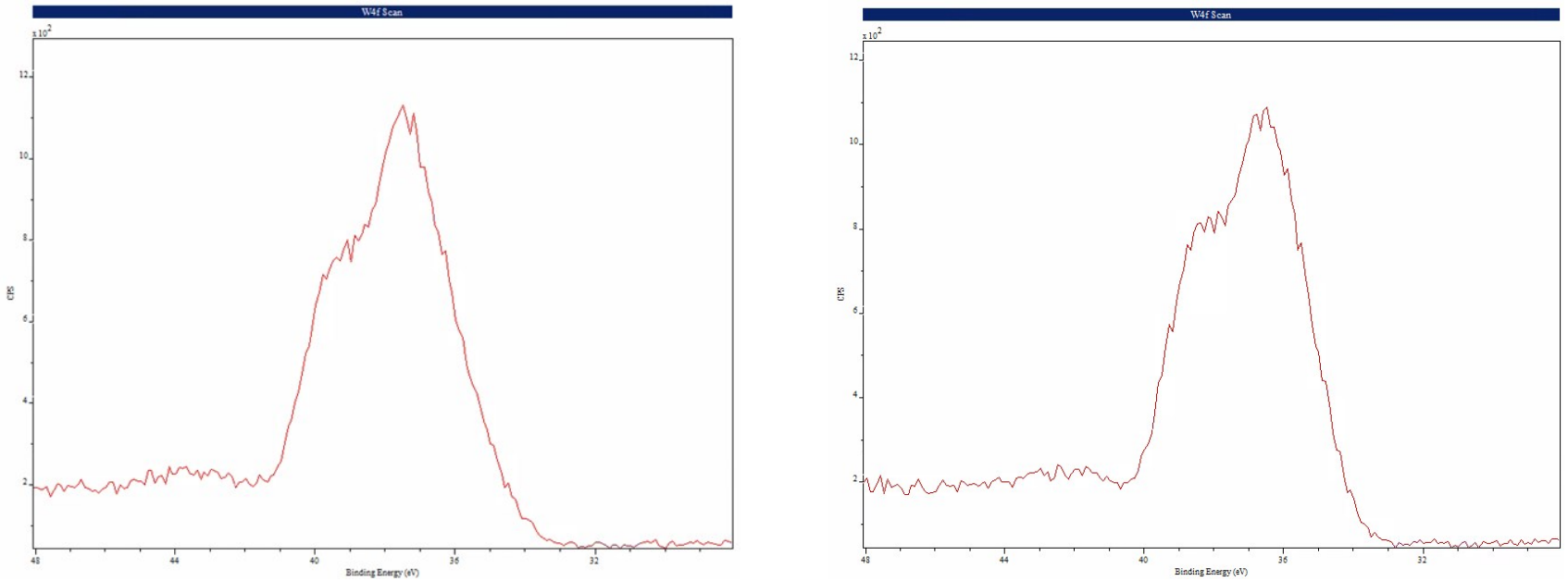


**Figure S40** Solid state $^{31}P$ NMR spectrum of freshly prepared polymer-supported peroxophosphotungstate **3b**

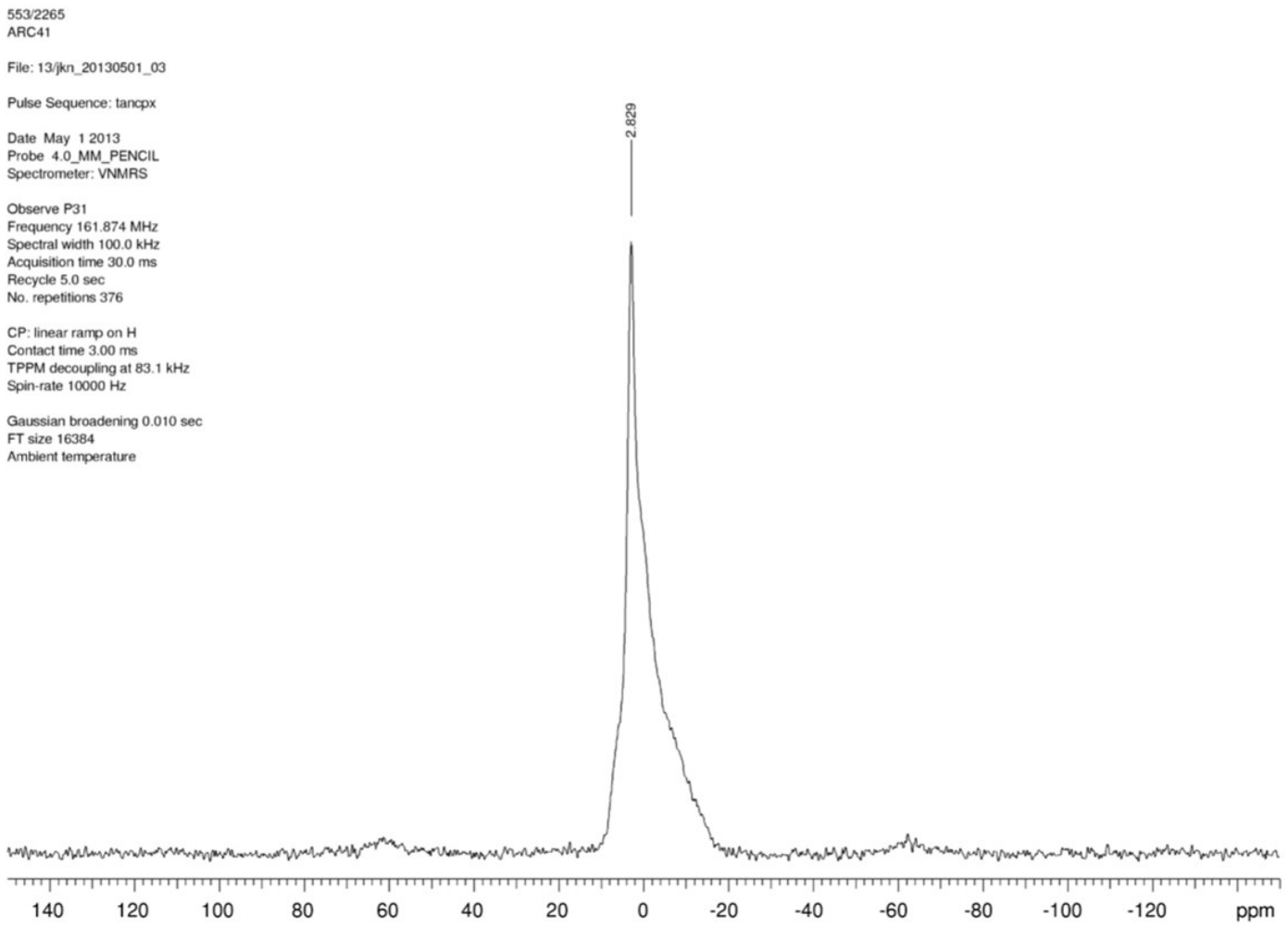


**Figure S41** Solid state $^{13}C$ NMR spectrum of freshly prepared polymer-supported peroxophosphotungstate **3b**

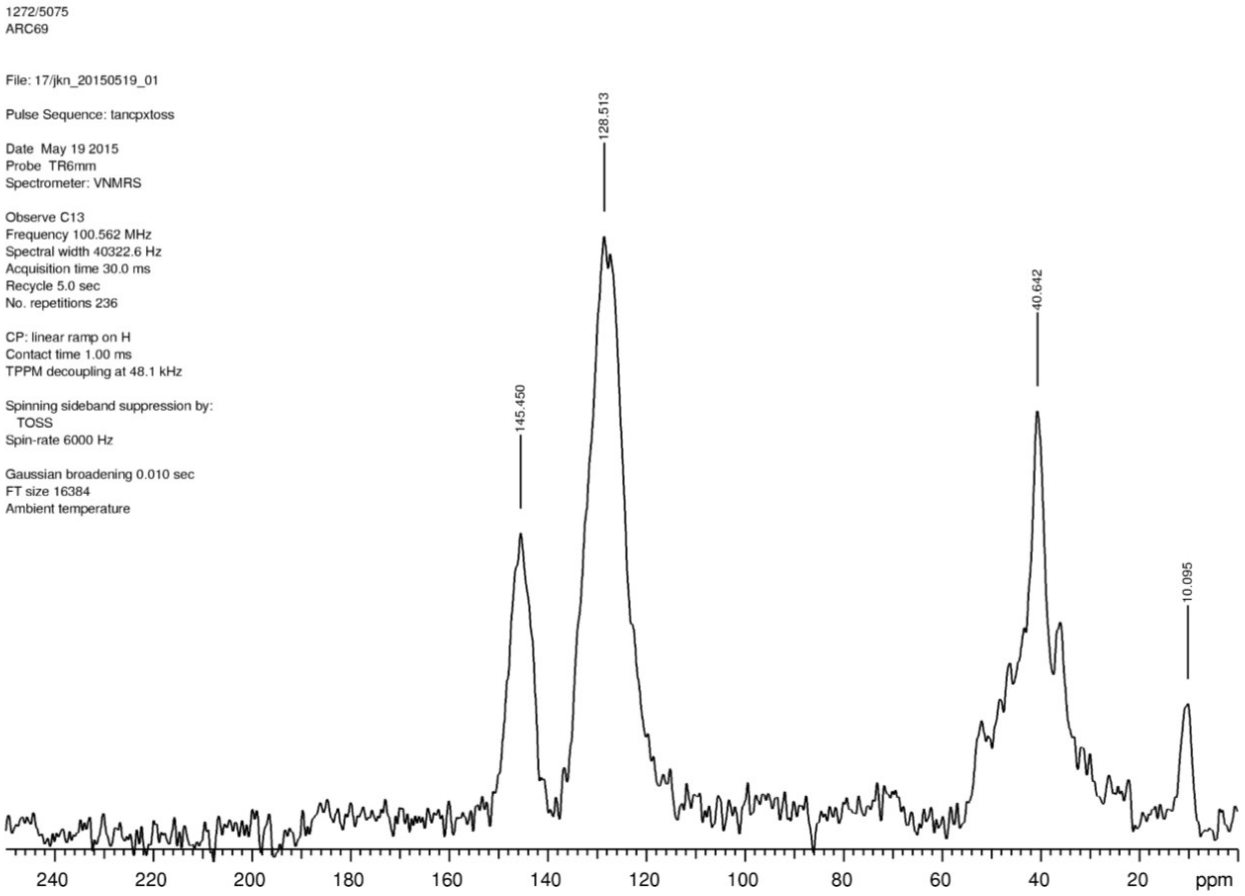
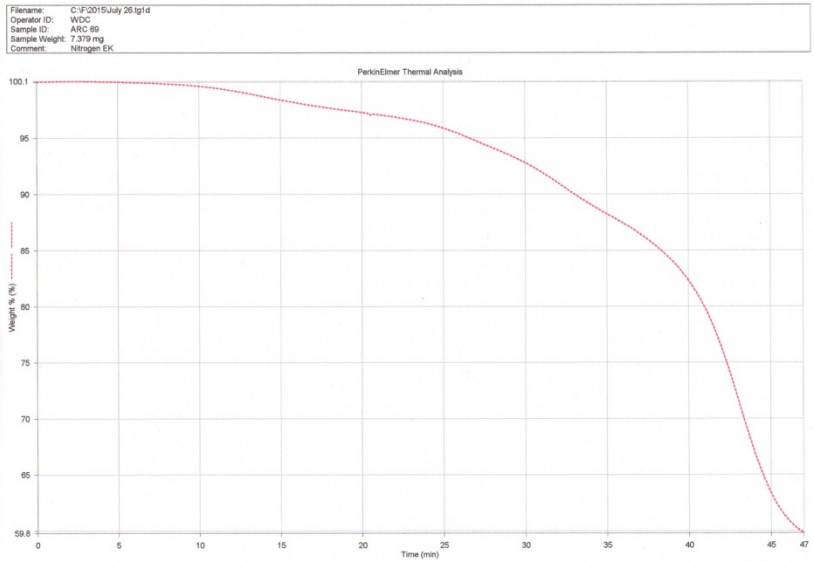


**Figure S42** TGA curves for polymer-supported peroxophosphotungstate **3b**, (a) wt% v time and (b) wt% v temperature**.** Heating rate of 10 ºC $min^{-1}$



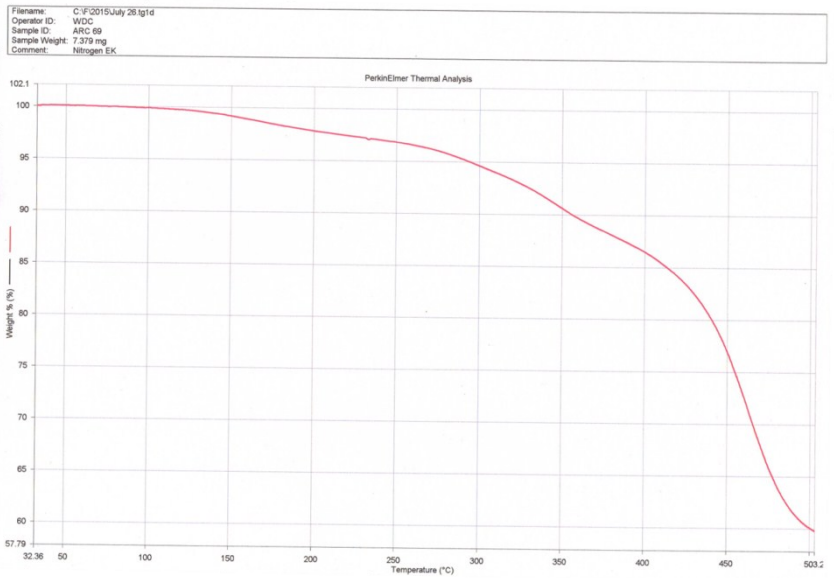



**Figure S43** DSC curve for polymer-supported peroxophosphotungstate **3b.** The heating rate was 10 ºC $min^{-1}$

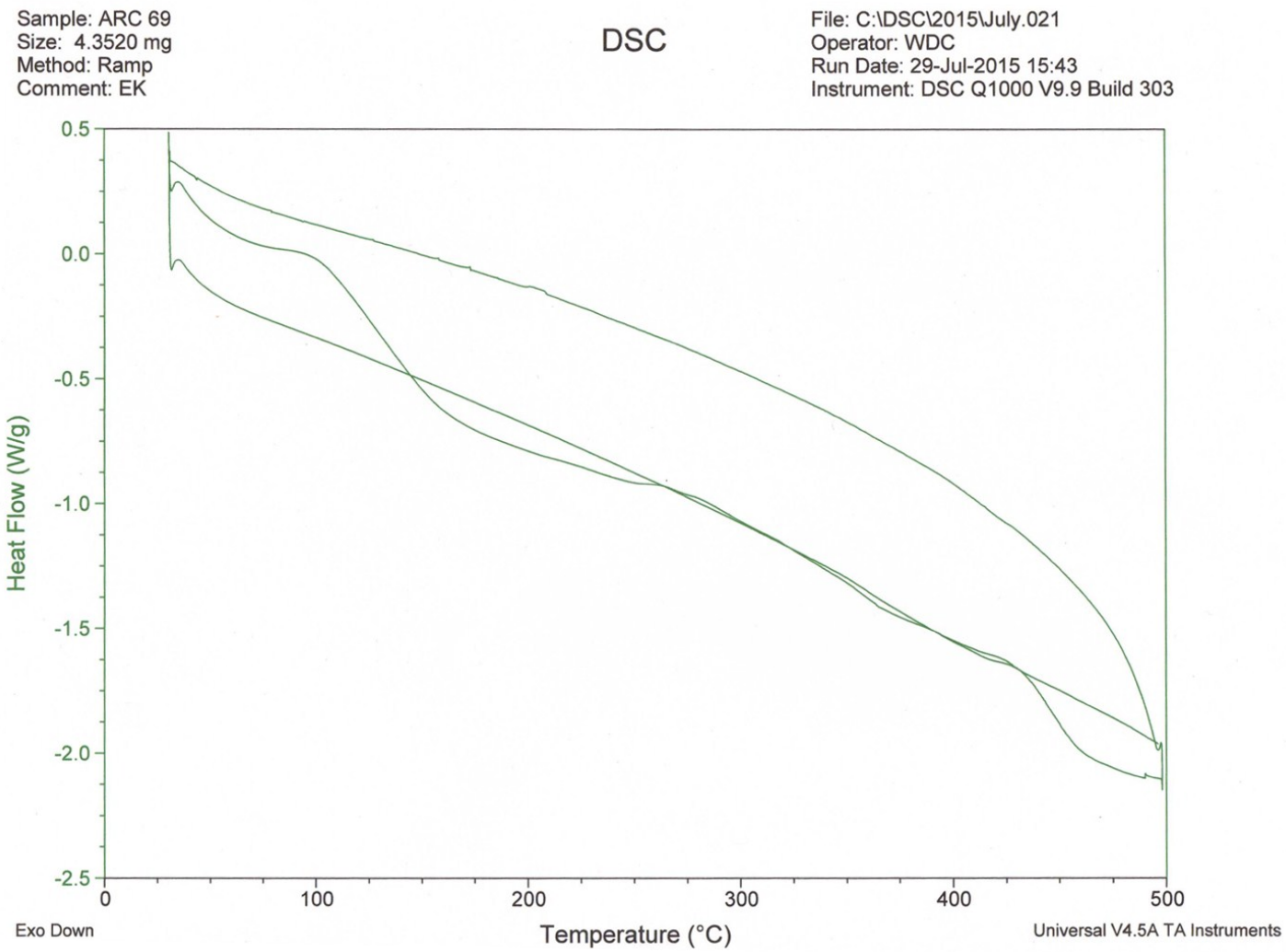
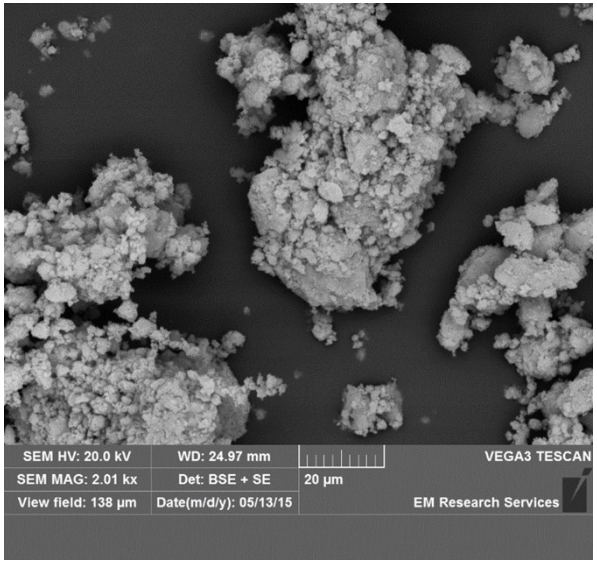
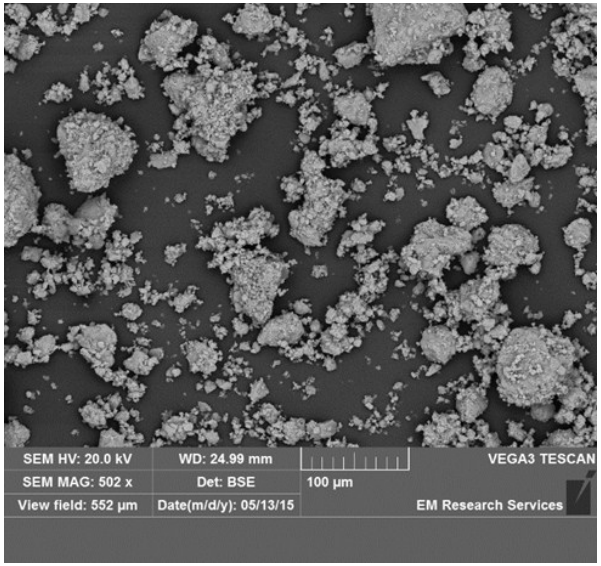


**Figure S44** SEM images of freshly prepared polymer-supported peroxophosphotungstate **3b**



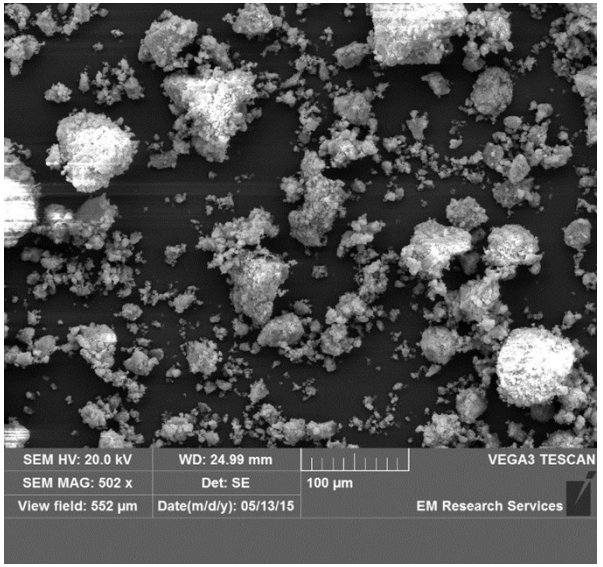



**Figure S45** FT-IR spectrum of freshly prepared polymer-supported peroxophosphotungstate **3c**

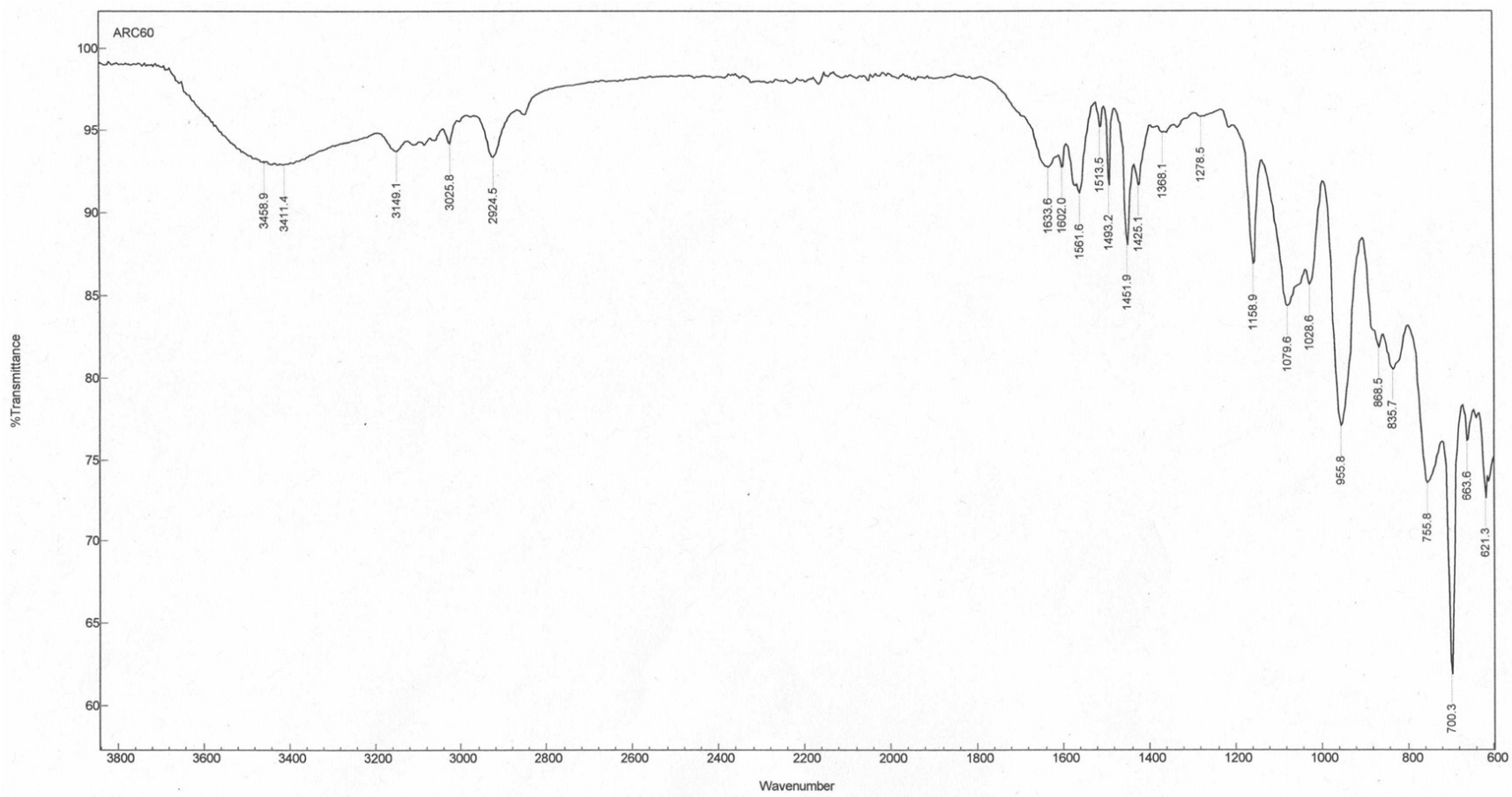
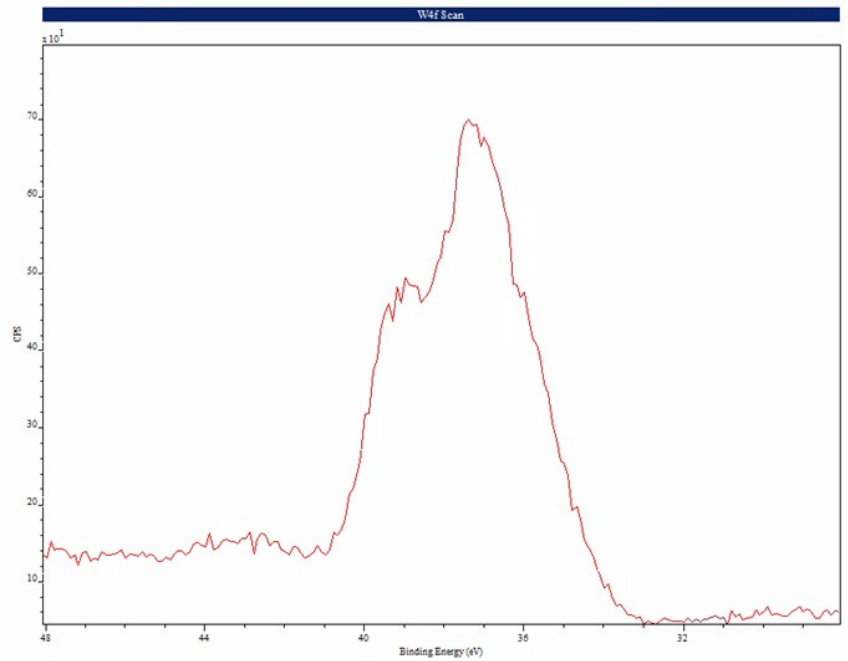


**Figure S46** XPS spectra of W ($4f_{7/2}$) and W ($4f_{5/2}$) peaks for freshly prepared polymer-supported peroxophosphotungstate **3c**



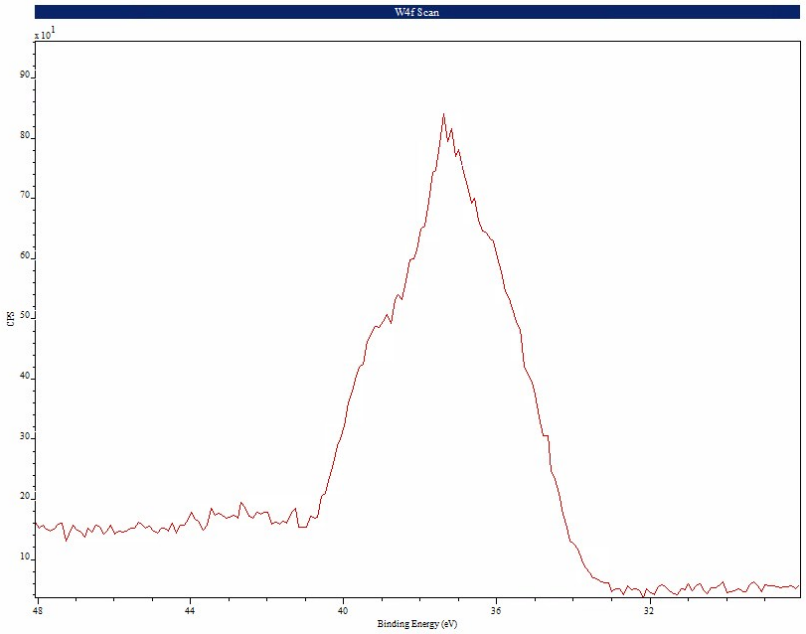



**Figure S47** Solid state $^{31}P$ NMR spectrum of polymer-supported peroxophosphotungstate **3c**

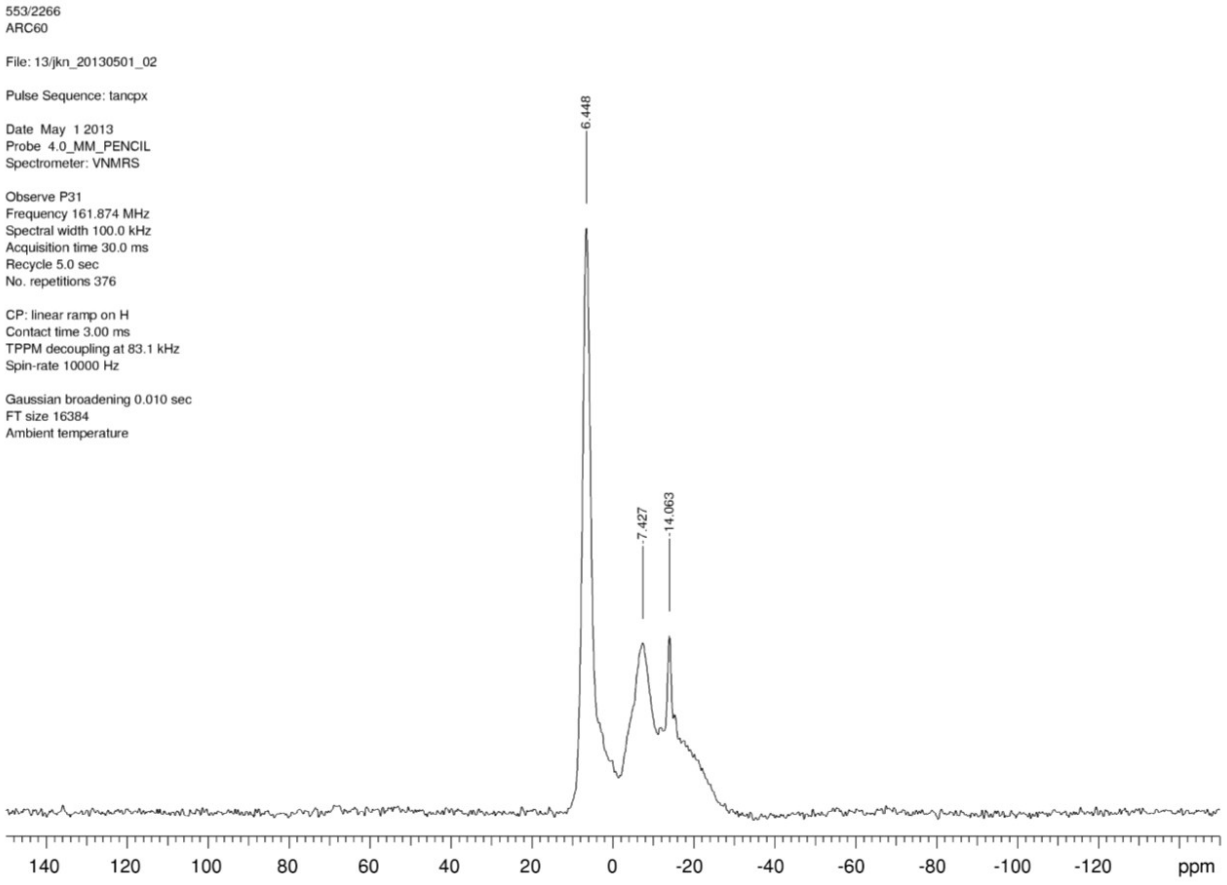


**Figure S48** Solid state $^{13}C$ NMR spectrum of freshly prepared polymer-supported peroxophosphotungstate **3c**

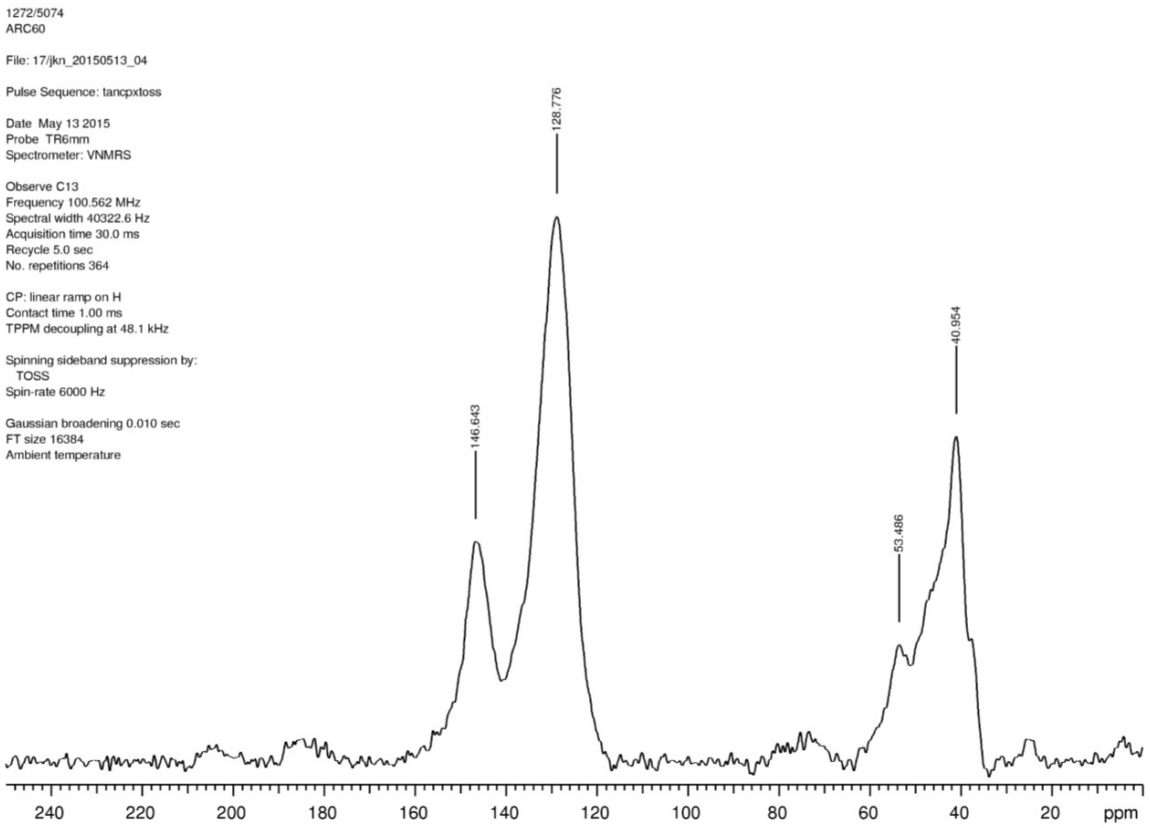
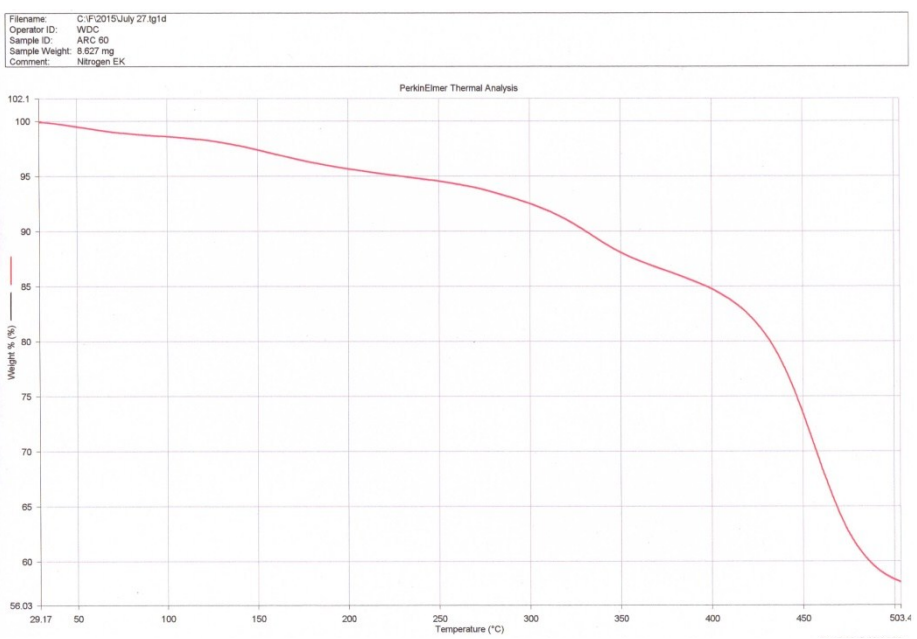


**Figure S49** TGA and DSC curves for polymer-supported peroxophosphotungstate **3c**, (a) wt% v time and (b) wt% v temperature**.** Heating rate of 10 ºC $min^{-1}$



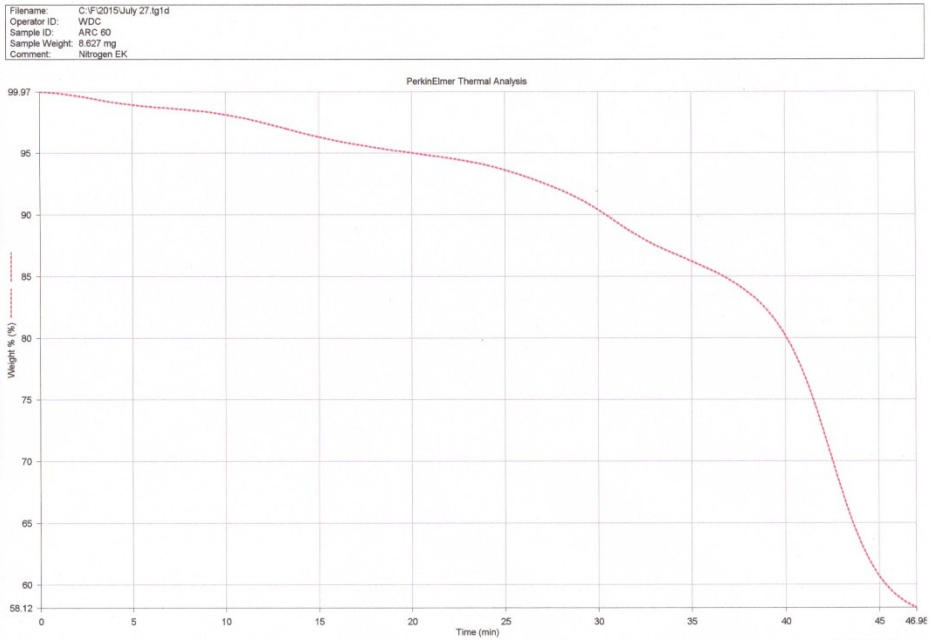



**Figure S50** DSC curve for polymer-supported peroxophosphotungstate **3c.** The heating rate was 10 ºC $min^{-1}$

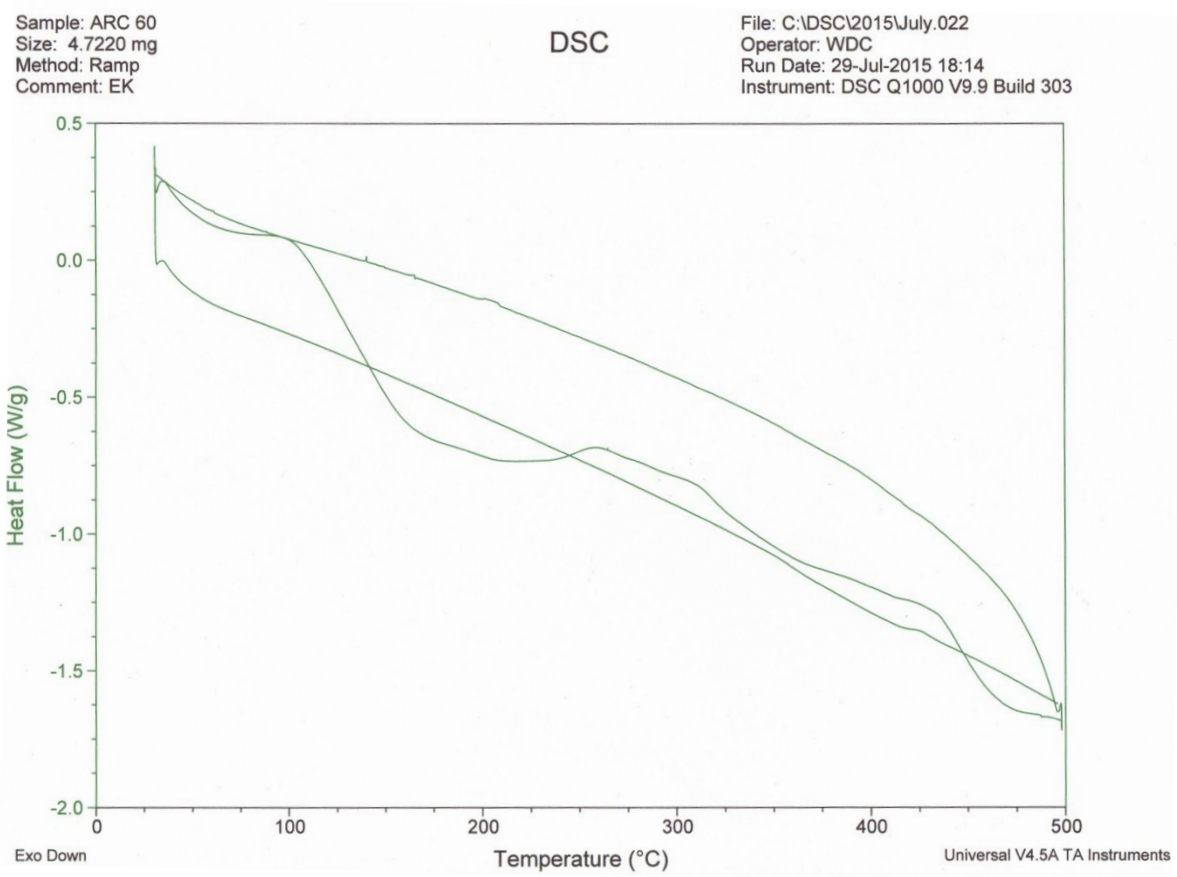
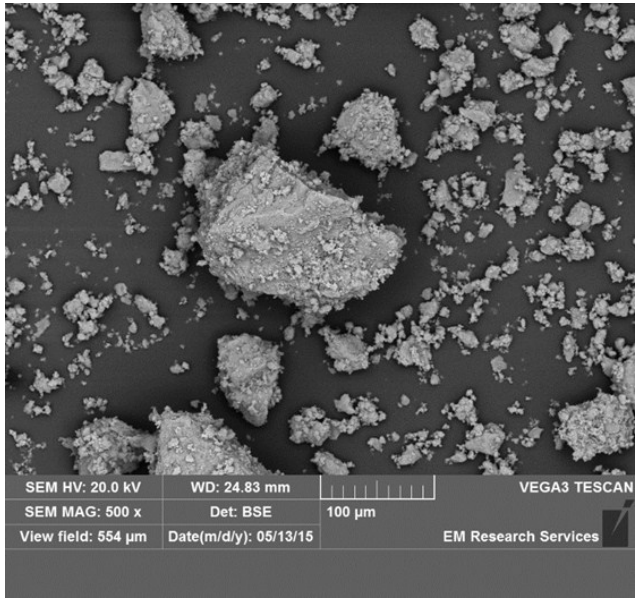


**Figure S51** SEM images of freshly prepared polymer-supported peroxophosphotungstate **3c**



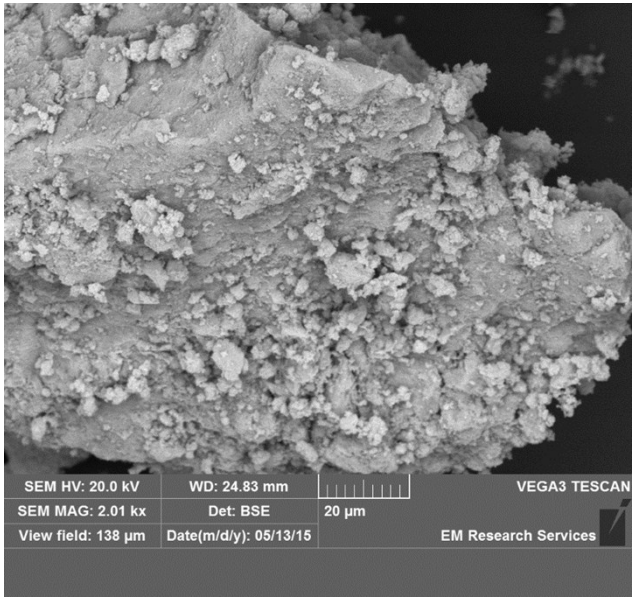



**Figure S52** FT-IR spectrum of freshly prepared polymer-supported peroxophosphotungstate **3d**

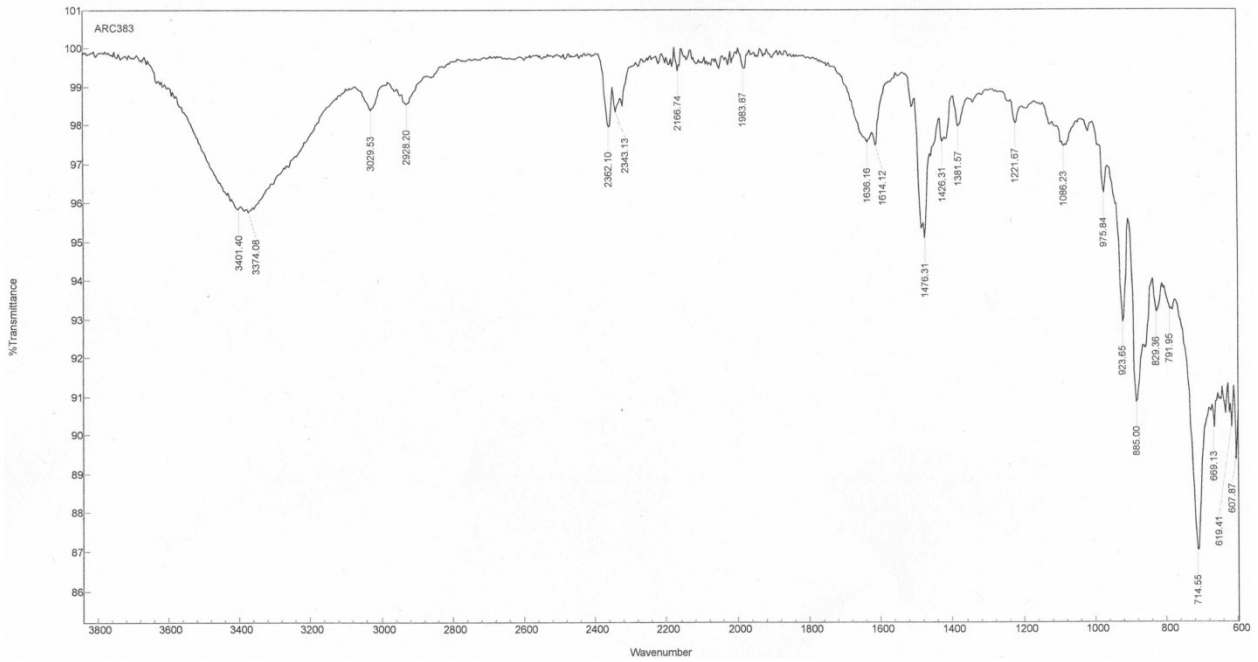


**Figure S53** Solid state $^{31}P$ NMR spectrum of freshly prepared polymer-supported peroxophosphotungstate **3d**

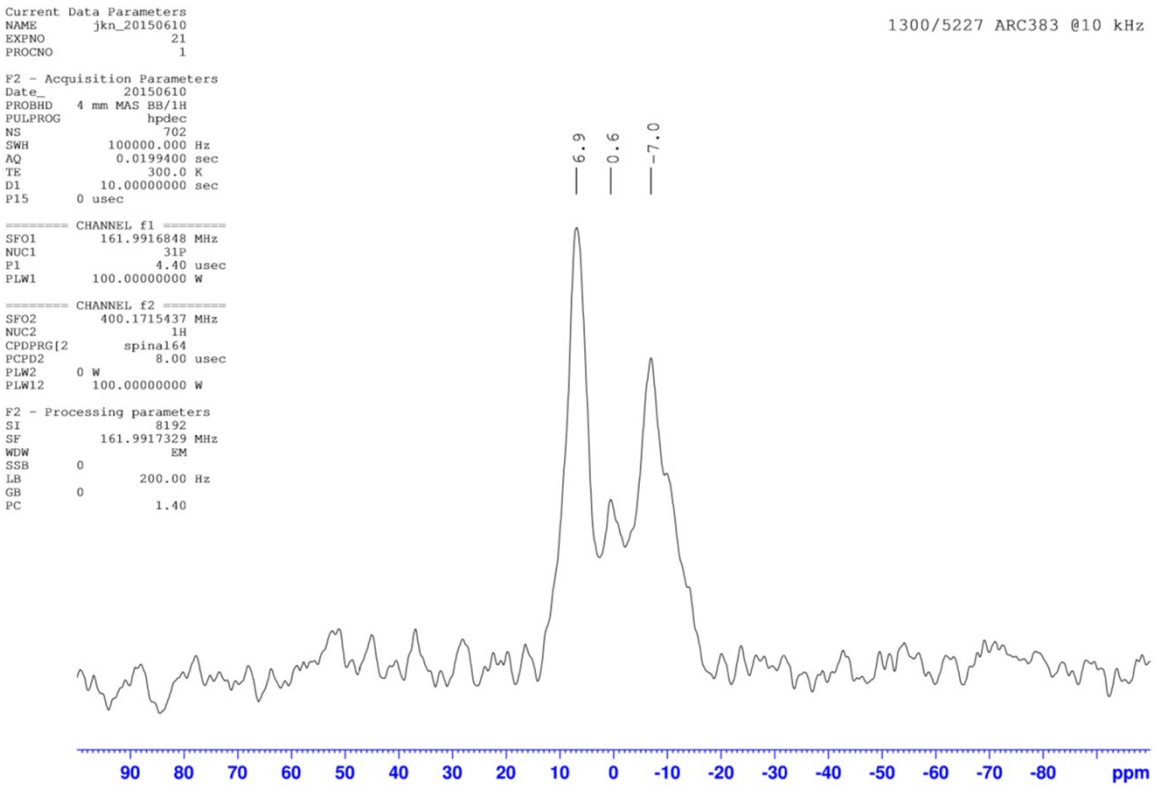


**Figure S54** Solid state $^{13}C$ NMR spectrum of freshly prepared polymer-supported peroxophosphotungstate **3d**

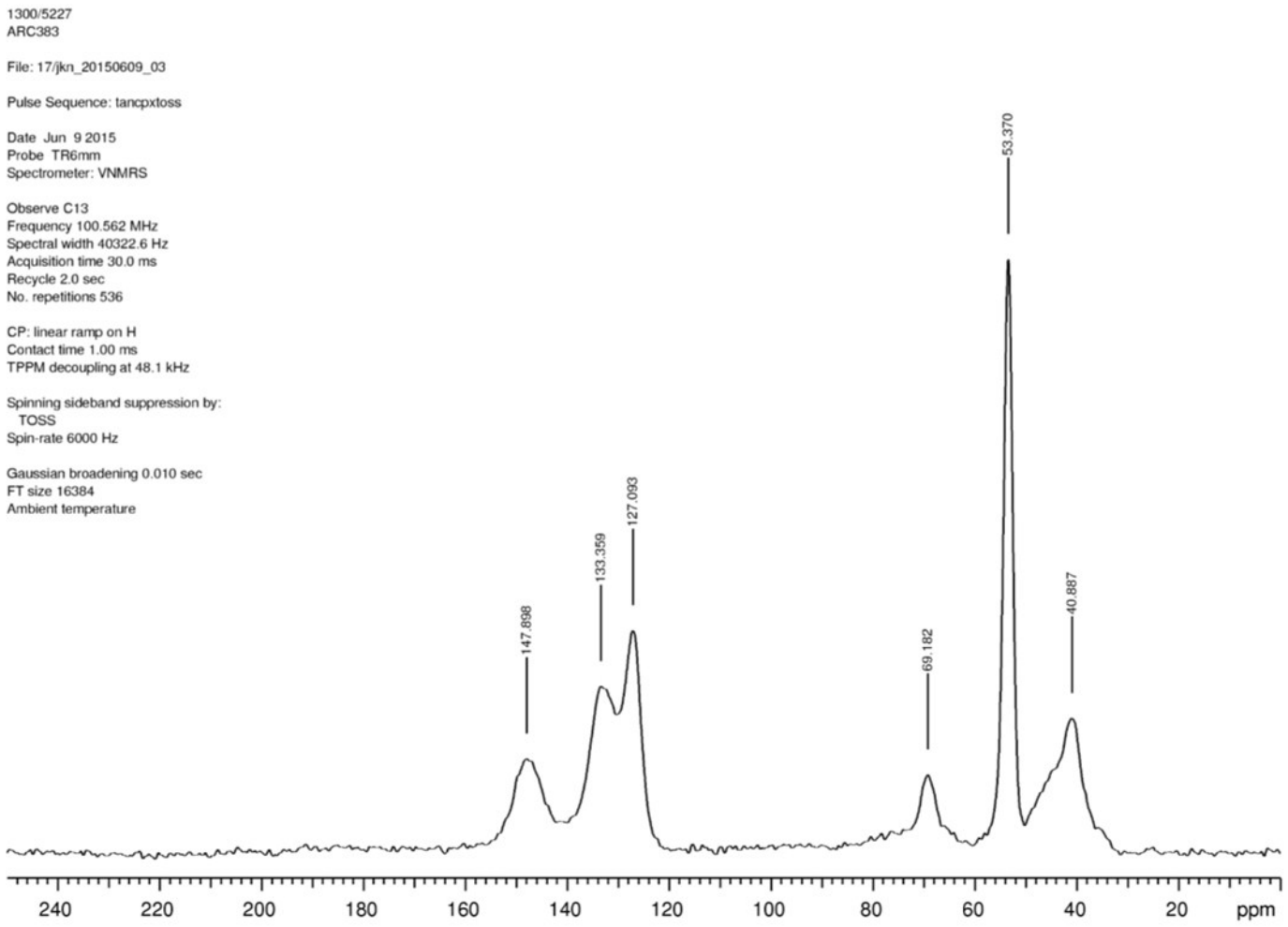
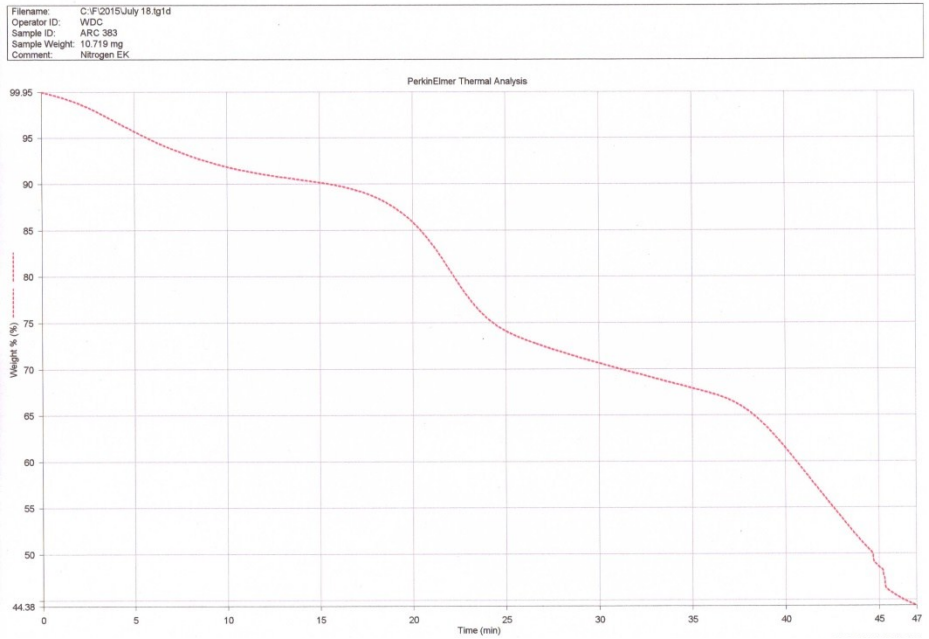


**Figure S55** TGA and DSC curves for polymer-supported peroxophosphotungstate **3d**, (a) wt% v time and (b) wt% v temperature**.** Heating rate of 10 ºC $min^{-1}$

(a)




(b)

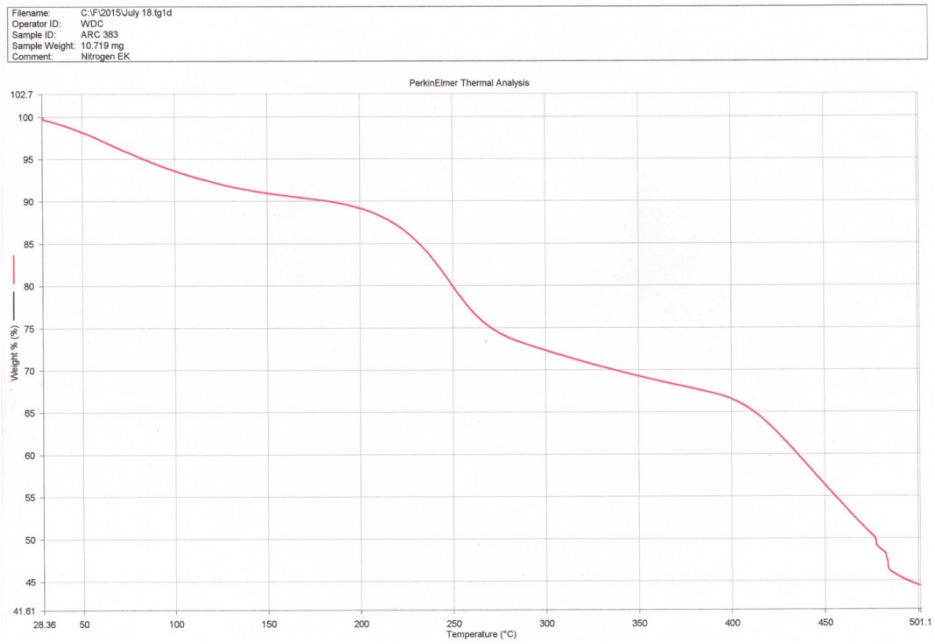


**Figure S56** DSC curve for polymer-supported peroxophosphotungstate **3d.** The heating rate was 10 ºC $min^{-1}$

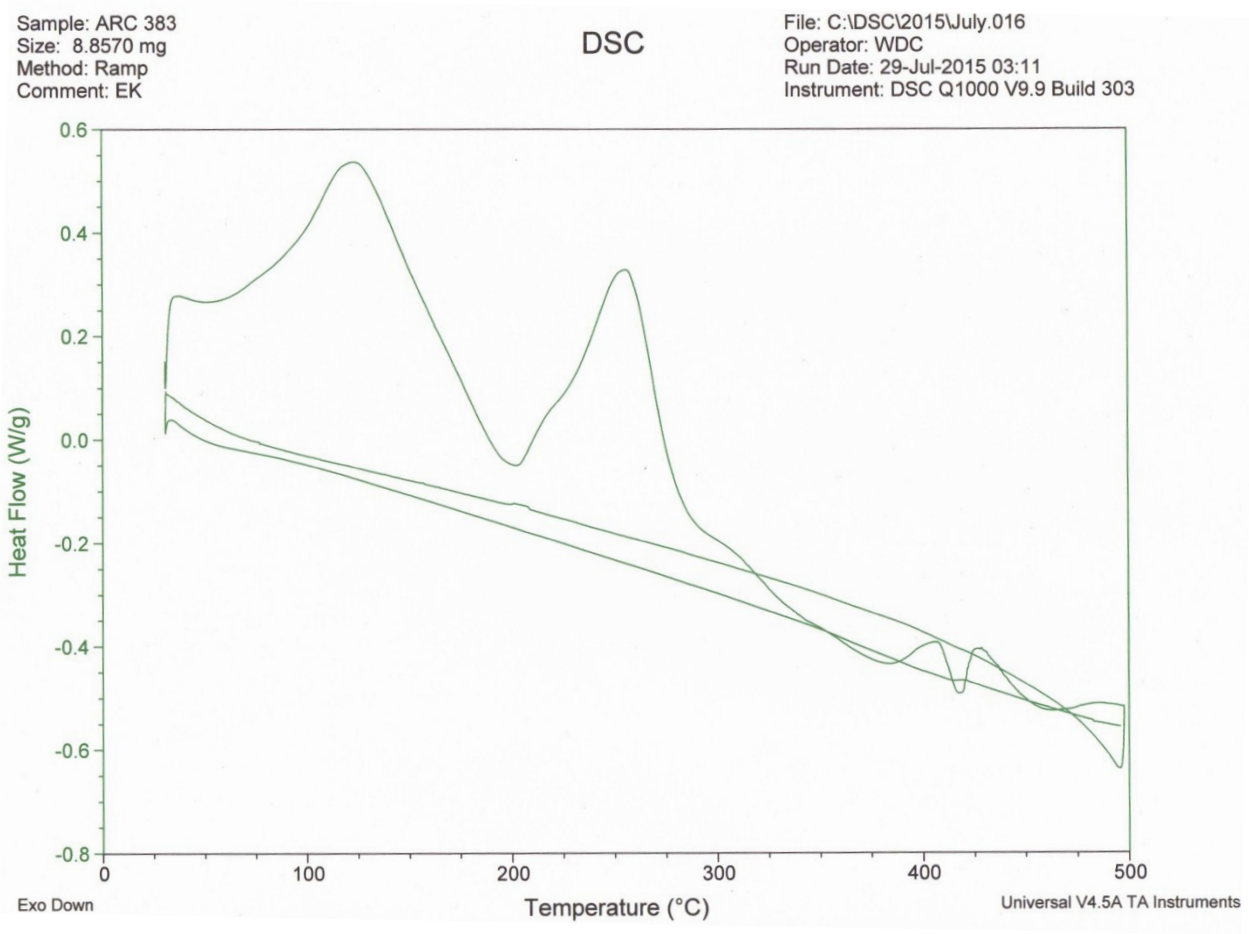
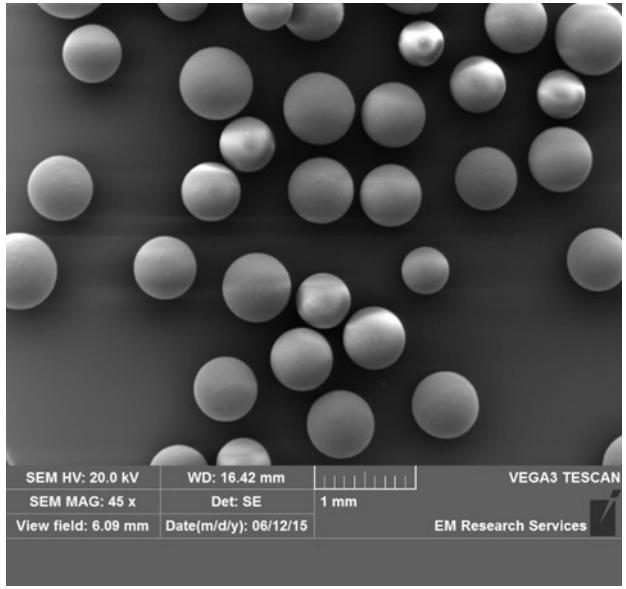


**Figure S57** SEM images of freshly prepared polymer-supported peroxophosphotungstate **3d**



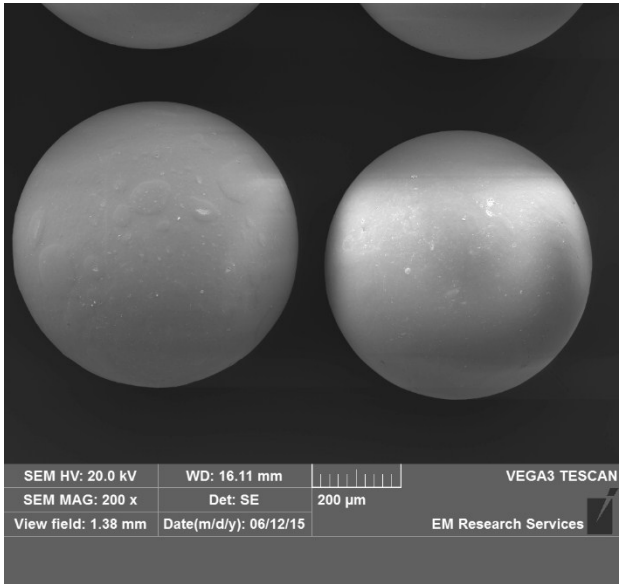



**Figure S58** FT-IR spectrum of freshly prepared polymer-supported peroxophosphotungstate **3e**

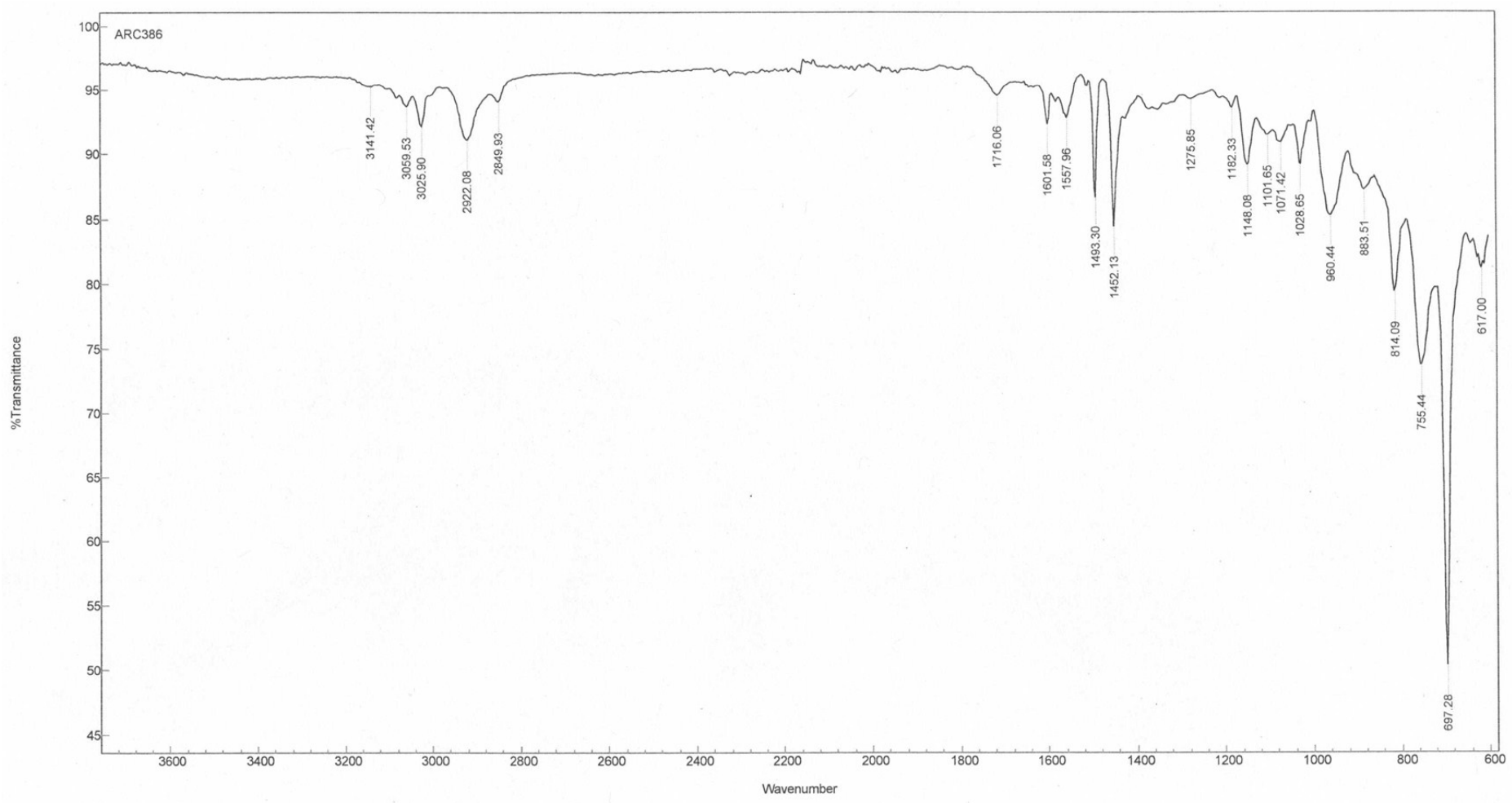


**Figure S59** Solid state $^{13}C$ NMR spectrum of freshly prepared polymer-supported peroxophosphotungstate **3e**

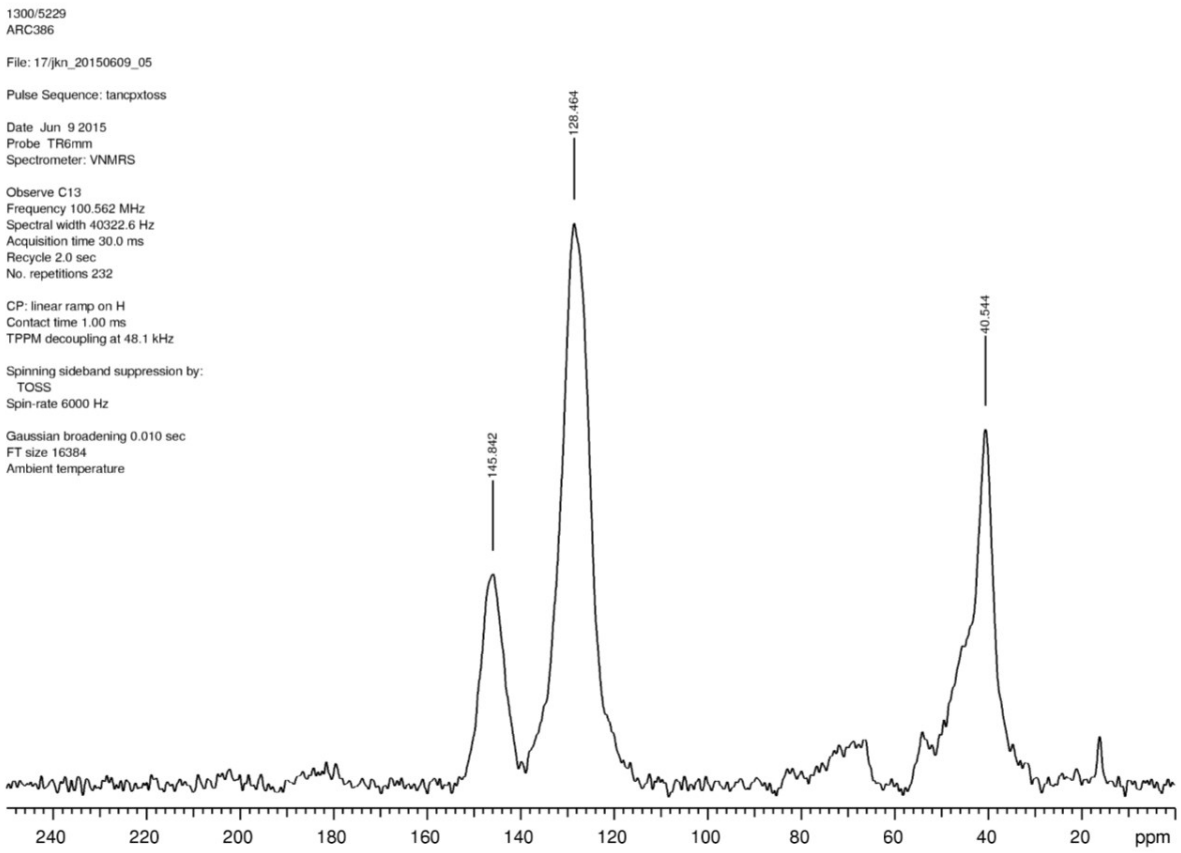
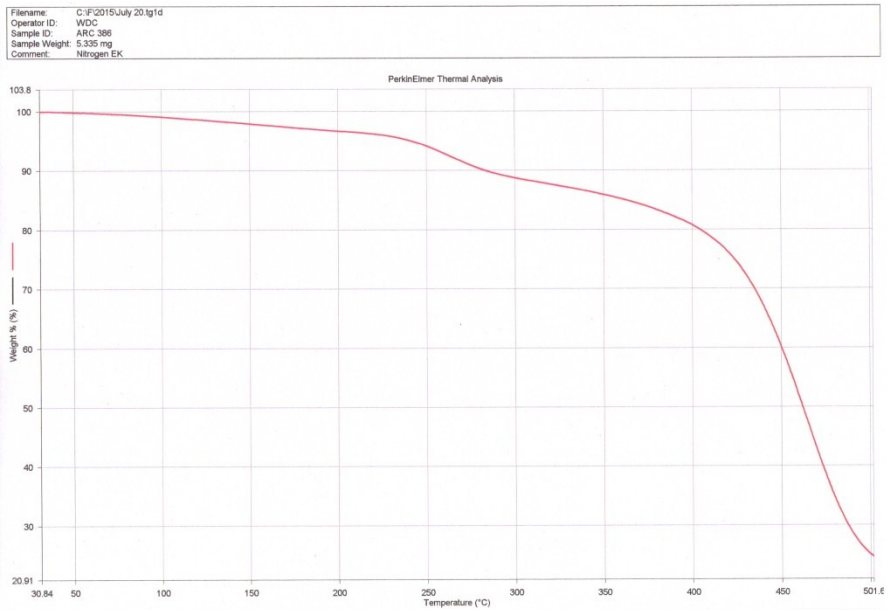


**Figure S60** TGA and DSC curves for polymer-supported peroxophosphotungstate **3e**, (a) wt% v time and (b) wt% v temperature**.** Heating rate of 10 ºC $min^{-1}$

(a)




(b)

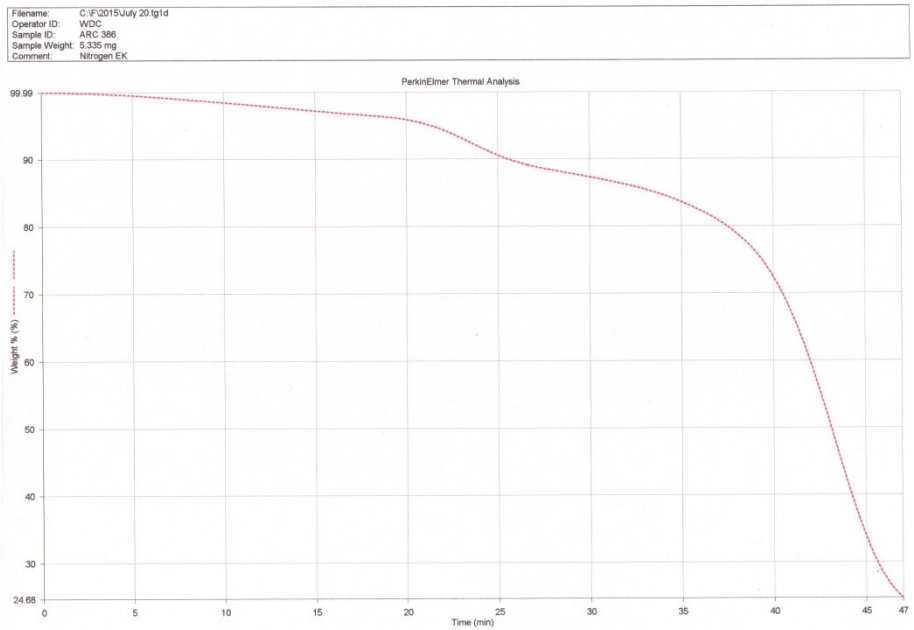


**Figure S61** DSC curve for polymer-supported peroxophosphotungstate **3e.** The heating rate was 10 ºC $min^{-1}$

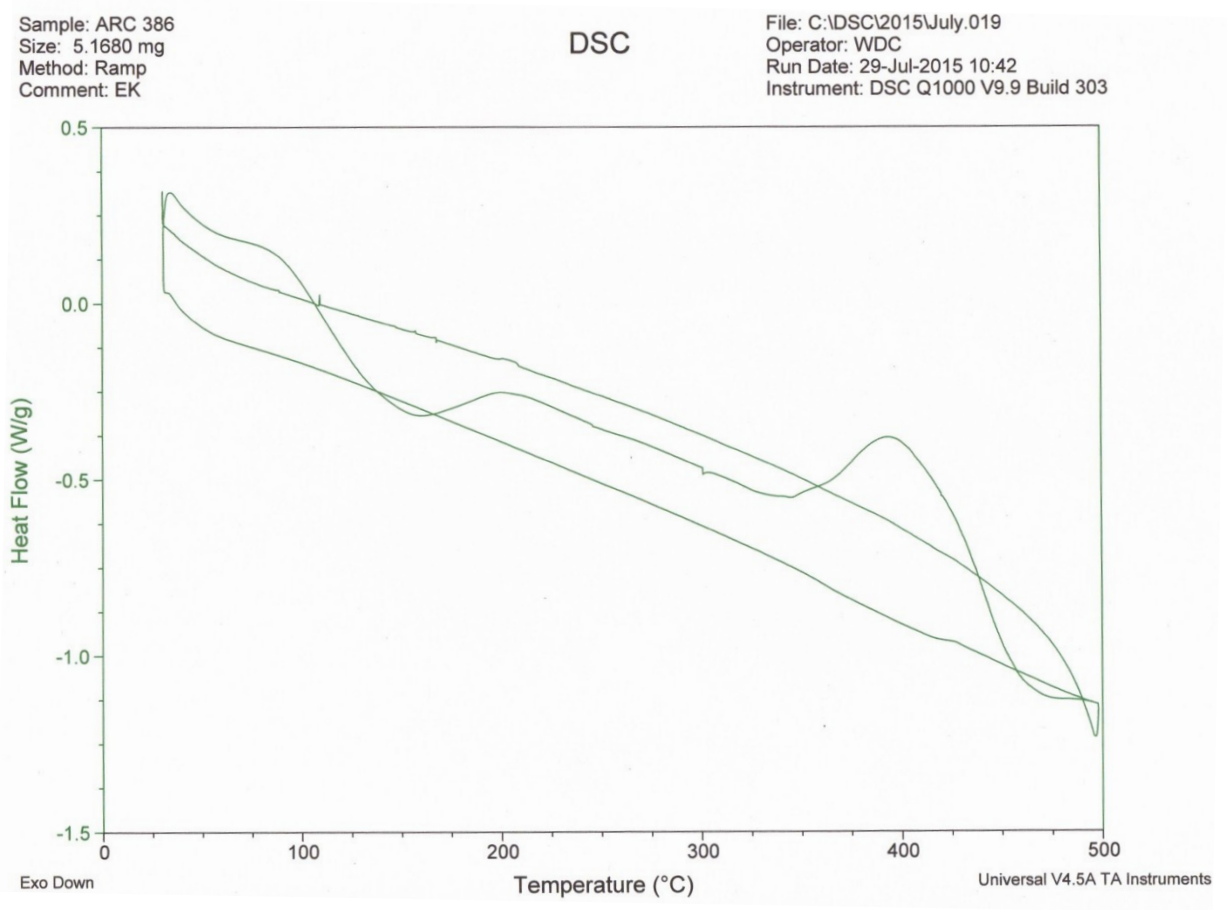
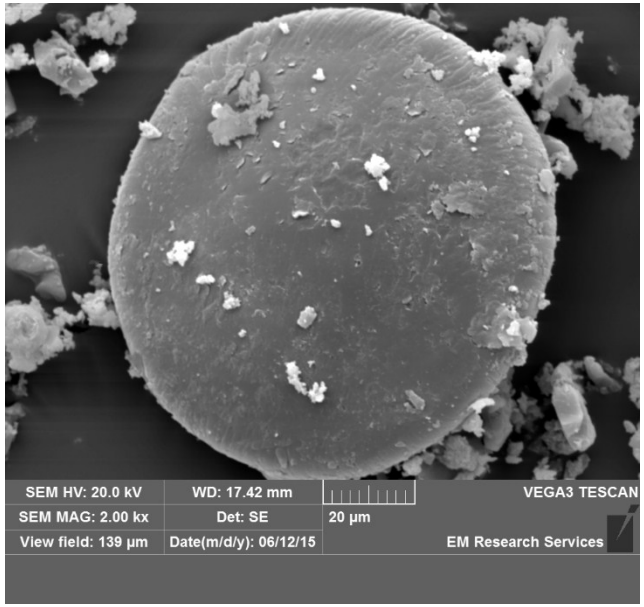
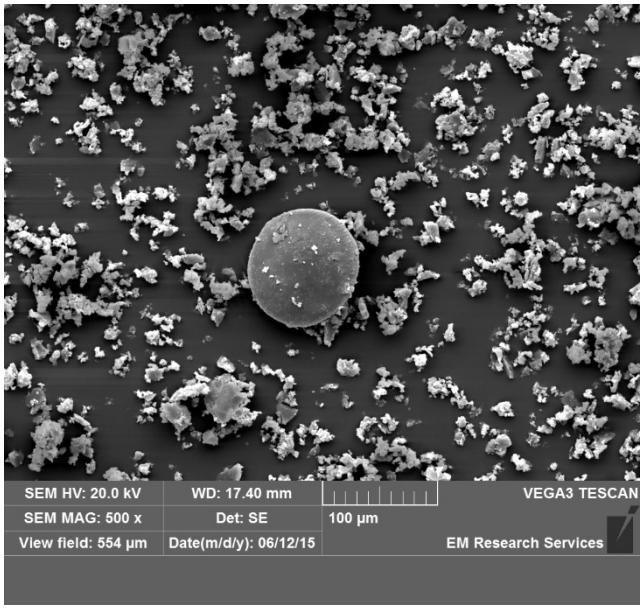


**Figure S62** SEM images of freshly prepared polymer-supported peroxophosphotungstate **3e**



**Characterisation data for sulfoxides and sulfones**

**Methyl phenyl sulfoxide.**[5]] $^{1}$H NMR (400 MHz, $CDCl_3$, $\delta$): 7.69-7.62 (m, 2H), 7.50-7.41 (m, 2H), 7.36-7.30 (m, 1H), 2.73 (s, 3H); $^{13}$C NMR (100.5 MHz, $CDCl_3$, $\delta$): 145.42, 130.95, 128.63, 123.54, 43.93; LRMS ($EI^+$) *m*/*z* 163 $[M+Na]^+$.

**Methyl phenyl sulfone**.[5] $^{1}$H NMR (400 MHz, $CDCl_3$, $\delta$): 7.95-7.87 (m, 2H), 7.71-7.61 (m, 2H), 7.59-7.52 (m, 1H), 3.02 (s, 3H); $^{13}$C NMR (100.5MHz, $CDCl_3$, $\delta$): 137.44, 133.21, 128.54, 126.23, 44.88; LRMS ($EI^+$) *m*/*z* 179 $[M+Na]^+$.

**Ethyl phenyl sulfoxide**.[5] $^{1}$H NMR (400 MHz, $CDCl_3$, $\delta$): 7.84-7.49 (m, 2H), 7.48-7.13 (m, 3H), 2.91 (q, 1H, *J* = 6.61 Hz), 2.78-2.69 (q, 1H, *J* = 6.61 Hz), 1.23 (t, 3H, *J* = 6.61 Hz); $^{13}$C NMR (100.5 MHz, $CDCl_3$, δ): 145.69, 131.47, 129.85, 125.42, 47.19, 10.39; LRMS ($EI^+$) *m*/*z* 177 $[M+Na]^+$.

**Ethyl phenyl sulfone**.[5] $^{1}$H NMR (400 MHz, $CDCl_3$, δ): 7.99 (m, 2H), 7.59 (m, 3H), 3.09 (q, 2H, *J* = 7.11 Hz), 1.30 (t, 3H, *J* = 7.11 Hz); $^{13}$C NMR (100.5MHz, $CDCl_3$, $\delta$): 138.31, 133.47, 128.92, 127.86, 50.28, 7.34; LRMS ($EI^+$) m/z 193 $[M+Na]^+$.

**Allyl phenyl sulfoxide.**[5] $^{1}$H NMR (400 MHz, $CDCl_3$, $\delta$): 7.64-7.60 (m, 2H), 7.39-7.36 (m, 2H), 7.31-7.26 (m, 1H), 5.44 (ddt, 1H, *J* = 7.11, 10.22, 17.10 Hz), 5.16 (dq, 1H, *J* = 1.12, 10.22 Hz), 5.01 (dq, 1H, *J* = 1.42, 17.10 Hz), 3.43 (dt, 2H, *J* = 7.11, 1.12 Hz); $^{13}$C NMR (100.5 MHz, $CDCl_3$, δ): 142.13, 131.24, 129.06, 125.09, 124.71, 117.93, 60.63; LRMS ($EI^+$) *m*/*z* 167 $[M+Na]^+$.

**Allyl phenyl sulfone**.[5] $^{1}$H NMR (400 MHz, $CDCl_3$, $\delta$): 7.95-7.91 (m, 2H), 7.69-7.62 (m, 2H), 7.37-7.44 (m, 1H), 5.63 (ddt, 1H, *J* = 7.19, 10.31, 17.21 Hz), 5.18 (dq, 1H, *J* = 1.22, 10.31 Hz), 5.02 (dq, 1H, *J* = 1.48, 17.21Hz), 3.91 (dt, 2H, *J* = 7.19, 1.22Hz); $^{13}$C NMR (100 MHz, $CDCl_3$, δ): 138.27, 133.74, 129.02, 128.88, 124.63, 117.51, 60.67; LRMS ($EI^+$) *m*/*z* 189 $[M+Na]^+$.

**Methyl 4-nitrophenyl sulfoxide.**[6] $^1$H NMR (400 MHz, $CDCl_3$, $\delta$): 8.39 (d, $J$ = 8.0 Hz, 2H), 7.90 (d, $J$ = 7.5 Hz, 2H), 2.85 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $\delta$): 152.4, 150.0, 126.2, 125.8, 43.5; LRMS ($EI^+$) $m/z$ 205 $[M+Na]^+$.

**Methyl 4-nitrophenyl sulfone.**[7] $^1$H NMR (400 MHz, $CDCl_3$, $\delta$): 8.43 (d, $J$ = 8.8 Hz, 2H), 8.16 (d, $J$ = 8.8 Hz, 2H), 3.12 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$, $\delta$): 150.9, 145.9, 129.0, 124.6, 44.3. LRMS ($EI^+$) $m/z$ 224 $[M+Na]^+$.

**Dibenzothiophene sulfoxide.**[5] $^1$H NMR (400M Hz, $CDCl_3$, $\delta$): 7.98-7.91 (m, 4H), 7.75-7.71 (m, 2H), 7.59-7.52 (m, 2H); $^{13}$C NMR (100.5 MHz, $CDCl_3$, $\delta$): 143.33, 132.67, 129.83, 126.37, 124.16, 123.45; LRMS ($EI^+$) $m/z$ 223 $[M+Na]^+$.

**Dibenzothiophene sulfone.**[5] $^1$H NMR (400 MHz, $CDCl_3$, $\delta$): 7.85-7.77 (m, 4H), 7.66-7.61 (m, 2H), 7.55-7.51 (m, 2H); $^{13}$C NMR (100.5 MHz, $CDCl_3$, δ): 137.62, 133.77, 131.53, 130.16, 121.97, 121.54; LRMS ($EI^+$) $m/z$ 239 $[M+Na]^+$.

**Homoallyl phenyl sulfoxide.**[8] $^1$H NMR (300 MHz, $CDCl_3$, $\delta$): 7.75-7.55 (m, 5H), 6.04-5.90 (m, 1H), 5.31-5.20 (m, 2H), 2.98-2.83 (m, 2H), 2.73-268 (m, 1H), 2.50-2.45 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$, δ): 135.4, 130.4, 129.0, 124.1, 117.0, 56.2, 26.3; LRMS ($EI^+$) $m/z$ 203 $[M+Na]^+$.

**Homoallyl phenyl sulfone.**[9] $^1$H NMR (400 MHz, $CDCl_3$, $\delta$): 7.89-7.87 (m, 2 H), 7.65-7.62 (m, 1H), 7.56-7.53 (m, 2 H), 5.73-5.64 (m, 1 H), 5.04-4.99 (m, 2 H), 3.15-3.11 (m, 2 H); 2.46-2.40 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$, δ) 138.9, 133.7, 133.6, 129.2, 128.0, 117.1, 55.3, 26.7; LRMS ($EI^+$) $m/z$ 219 $[M+Na]^+$.

**Benzyl phenyl sulfoxide**.[5] $^1$H NMR (400 MHz, $CDCl_3$, $\delta$): 7.55-7.42 (m, 2H), 7.36-7.17 (m, 3H), 7.11-6.63 (m, 5H), 3.98 (s, 2H); $^{13}$C NMR (100.5 MHz; $CDCl_3$, δ): 142.59, 130.83, 130.26, 128.87, 128.57, 128.24, 128.15, 124.21, 63.44; LRMS ($EI^+$) $m/z$ 239 $[M+Na]^+$.

**Benzyl phenyl sulfone.**[5] $^{1}$H NMR (400 MHz, $CDCl_3$, $\delta$): 7.74-7.65 (m, 2H), 7.41-7.32 (m, 3H), 7.14-7.06 (m, 5H), 4.41 (s, 2H); $^{13}$C NMR (100.5 MHz; $CDCl_3$, $\delta$): 137.49, 133.44, 130.53, 128.61, 128.47, 128.39, 128.31, 62.53; LRMS ($EI^+$) *m*/*z* 255 $[M+Na]^+$.

***n*-Decyl methyl sulfoxide.**[10] $^{1}$H NMR (300 MHz, $CDCl_3$, $\delta$): 2.71 (ddd, $J$ = 12.9, 8.7, 6.2 Hz, 1H), 2.62 (ddd, $J$ = 12.9, 9.0, 7.3 Hz) (s, 3H), 1.37 (s, 9H); 2.53 (s, 3H), 1.79–1.69 (m, 2H), 1.48–1.34 (m, 2H), 1.31–1.23 (m, 12H), 0.85 (t, $J$ = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz; $CDCl_3$, $\delta$): 54.73, 38.47, 31.80, 29.44, 29.30, 29.21, 29,14, 28,77, 22.57, 22.50, 14.02; LRMS ($EI^+$) *m*/*z* 227 $[M+Na]^+$.

**References**


[1] (a) C. Venturello, R. D'Aloisio, *J. Org. Chem*., 1998, **53**, 1553; (b) R. Neumann, A. M. Khenkin, *J. Org. Chem*., 1994, **59**, 7577; (c) A. L. Salles, C. Aubry, R. Thouvenot, F. Robert, C. Doremieux-Morin, G. Chottard, H. Ledon, Y. Jeannin, J.-M. Bregeault, *Inorg. Chem.,* 1994, **33**, 871; (d) D. C. Duncan, R. C. Chambers, E. Hecht, C. L. Hill, *J. Am. Chem. Soc.,* 1995, **117**, 681.

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[7] G. Yuan, J. Zheng, X. Gao, X. Li, L. Huang, H. Chen, H. Jiang, *Chem. Commun*. 2012, **48**, 7513-7515.

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[10 M. A. M. Capozzi, C. Cardellicchio , F. Naso and P. Tortorella, *J. Org. Chem*., 2000, **65**, 2843–2846.

**Figure S63** $^{1}$H NMR spectrum of the reaction mixture for the selective oxidation of thioanisole in ethanol at RT for 15 min**.**

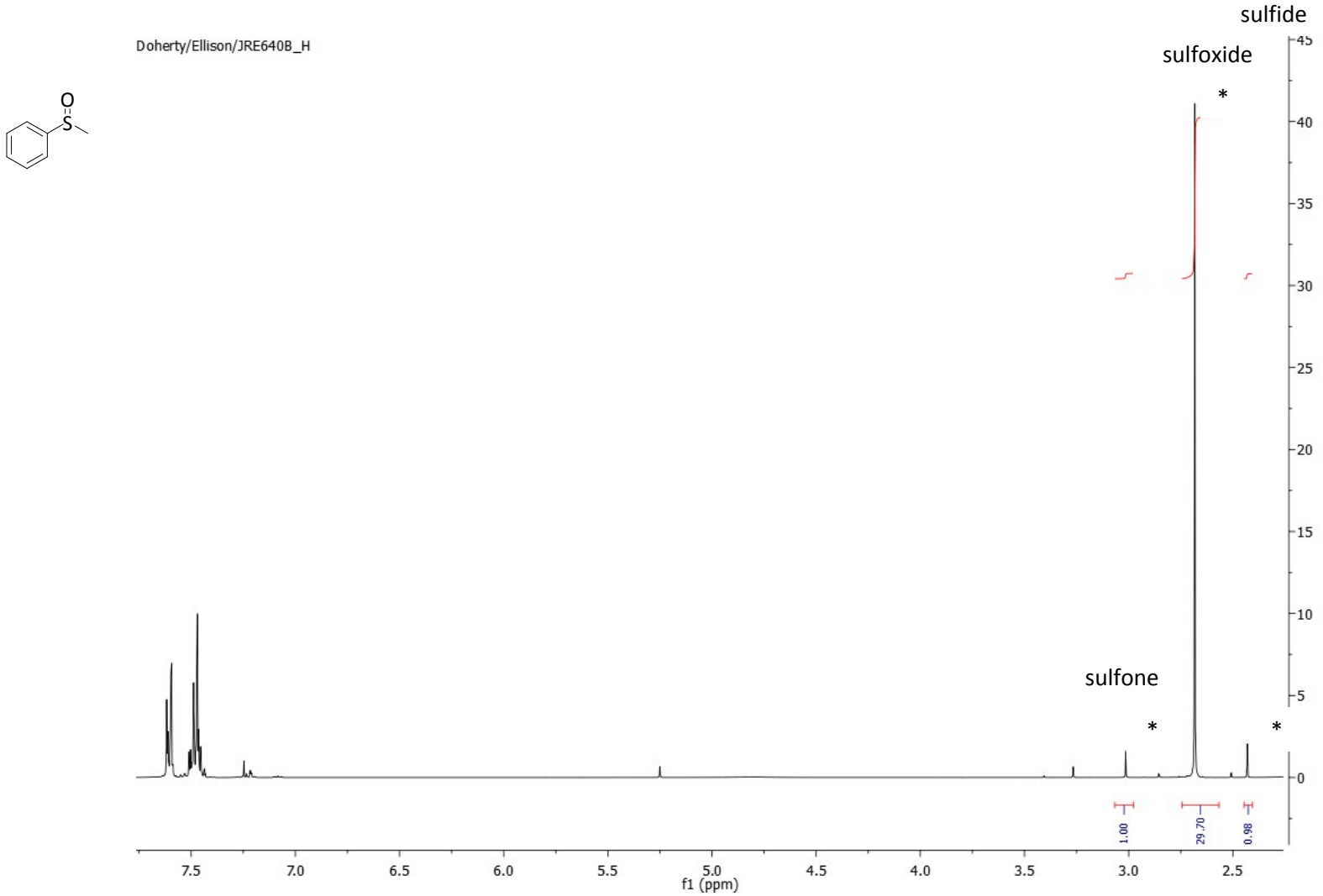
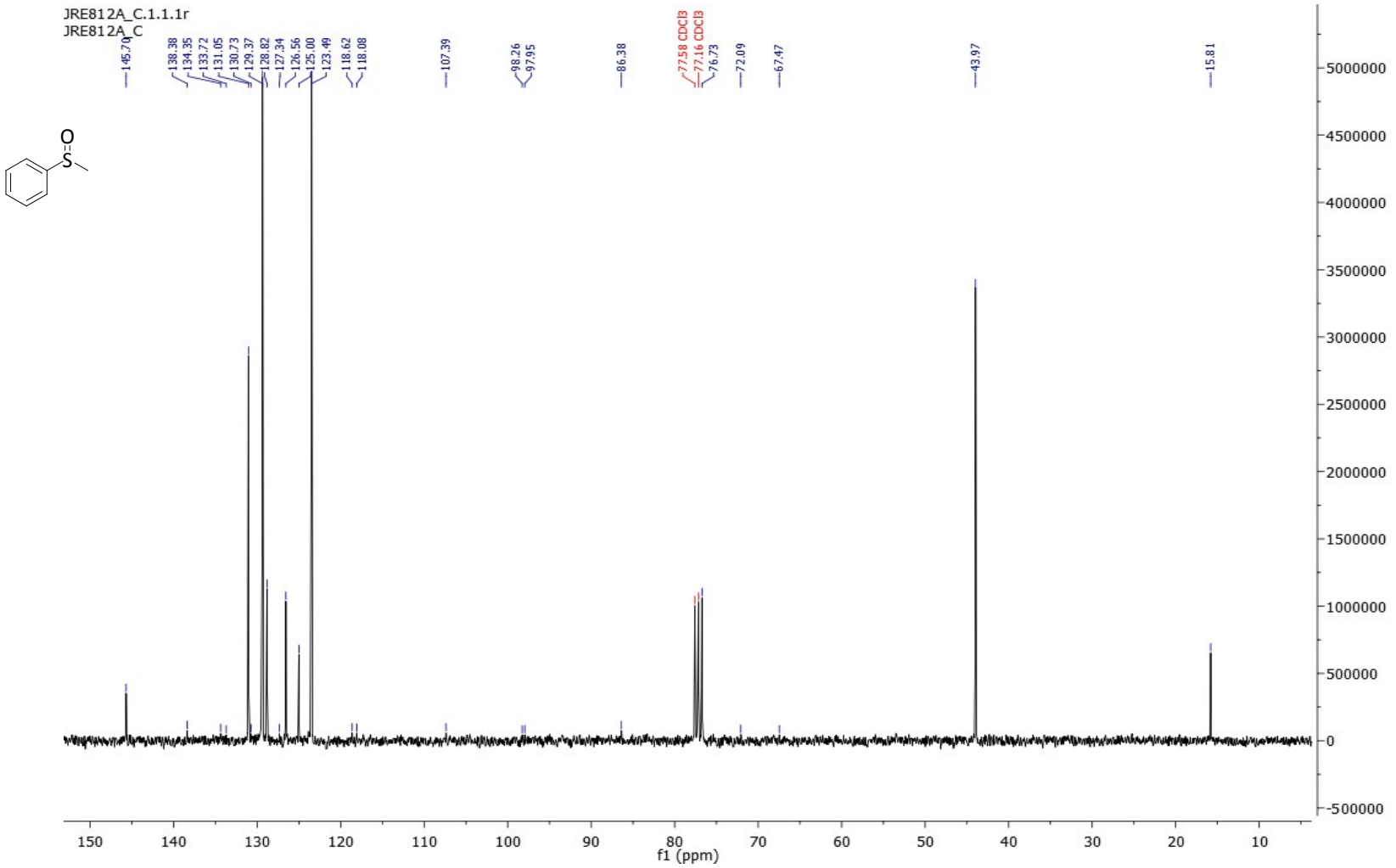
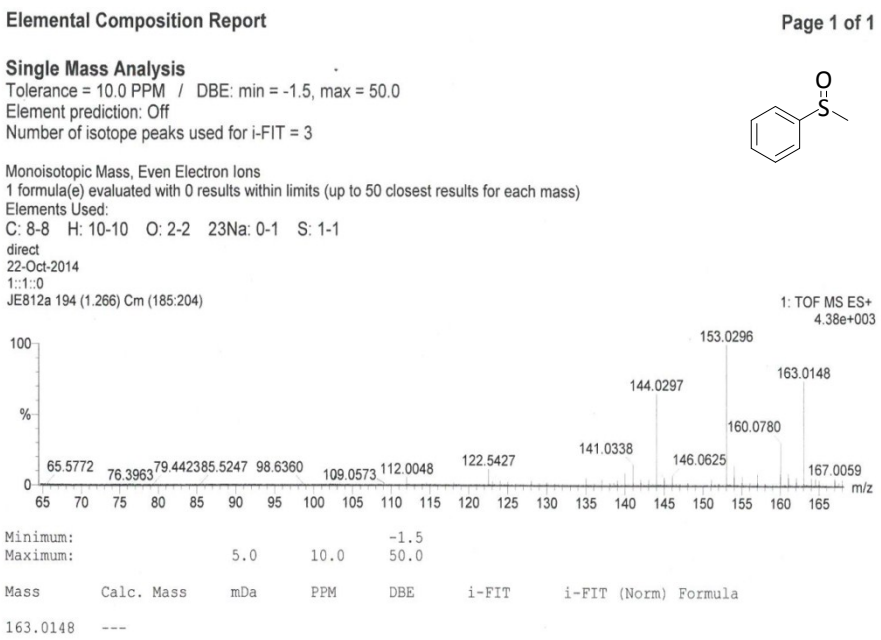


**Figure S64** $^{13}C\{^{1}H\}$ NMR spectrum of the reaction mixture for the selective oxidation of thioanisole in ethanol at RT for 15 min




sulfide

**Figure S65** Mass Spectra for methyl phenyl sulfoxide (left) and methyl phenyl sulfone (right)



Elemental Composition Report

Page 1 of 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 0 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 8-8 H: 10-10 O: 2-2 23Na: 0-1 S: 1-1
direct
22-Oct-2014
1::1::0
JE812a 194 (1.266) Cm (185:204)

1: TOF MS ES+
4.38e+003



| | | | | | | |
|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | |
| Maximum: | | 5.0 | 10.0 | 50.0 | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) Formula |
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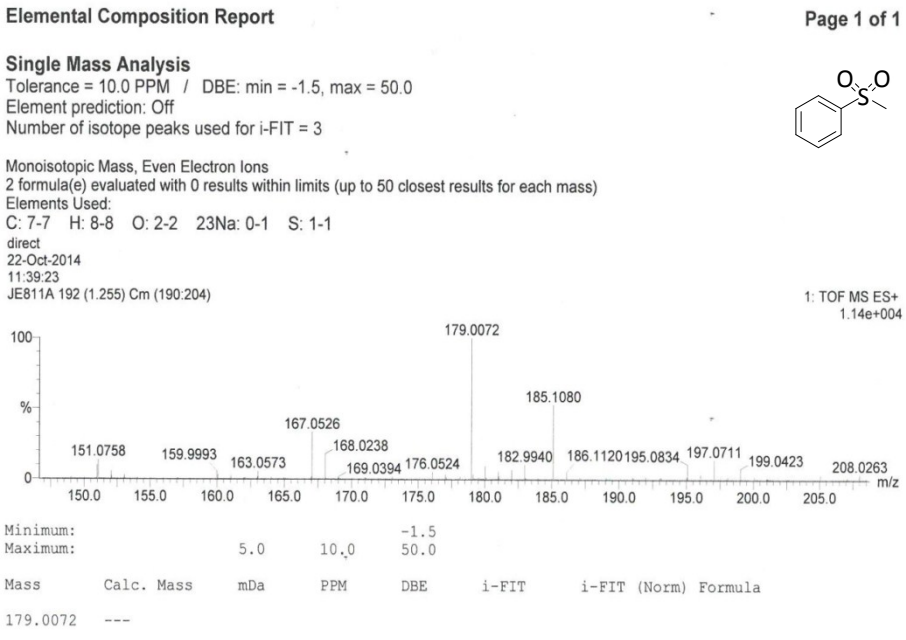

Elemental Composition Report

Page 1 of 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 0 results within limits (up to 50 closest results for each mass)
Elements Used:
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direct
22-Oct-2014
11:39:23
JE811A 192 (1.255) Cm (190:204)

1: TOF MS ES+
1.14e+004



| | | | | | | |
|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | |
| Maximum: | | 5.0 | 10.0 | 50.0 | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) Formula |
| 179.0072 | --- | | | | | |

**Figure S66** $^{1}$H NMR spectrum of the reaction mixture for the selective oxidation of ethyl phenyl sulfide in ethanol at RT for 15 min

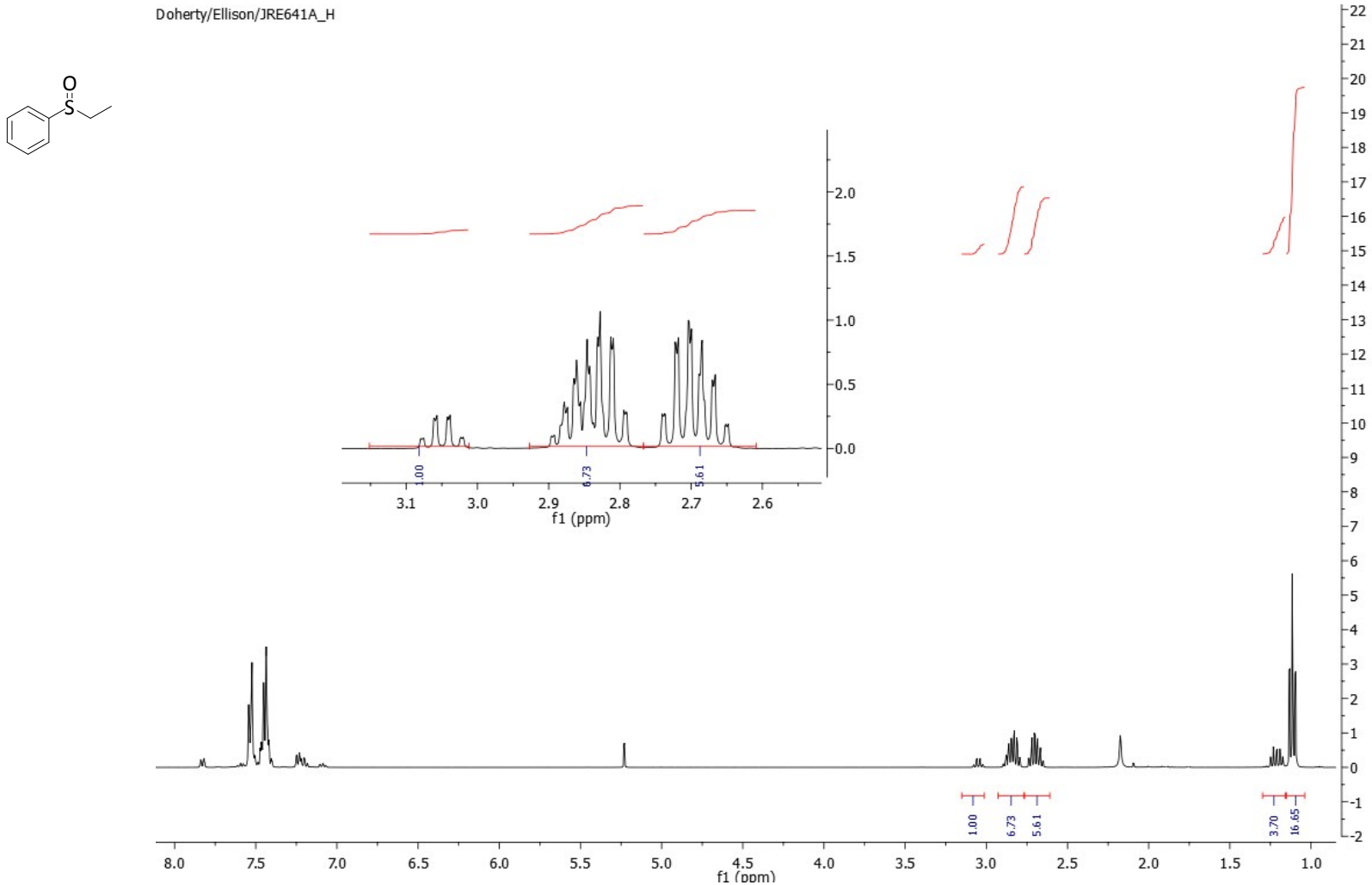


**Figure S67** $^{13}C\{^{1}H\}$ NMR spectrum of the reaction mixture for the selective oxidation of ethyl phenyl sulfide in ethanol at RT for 15 min

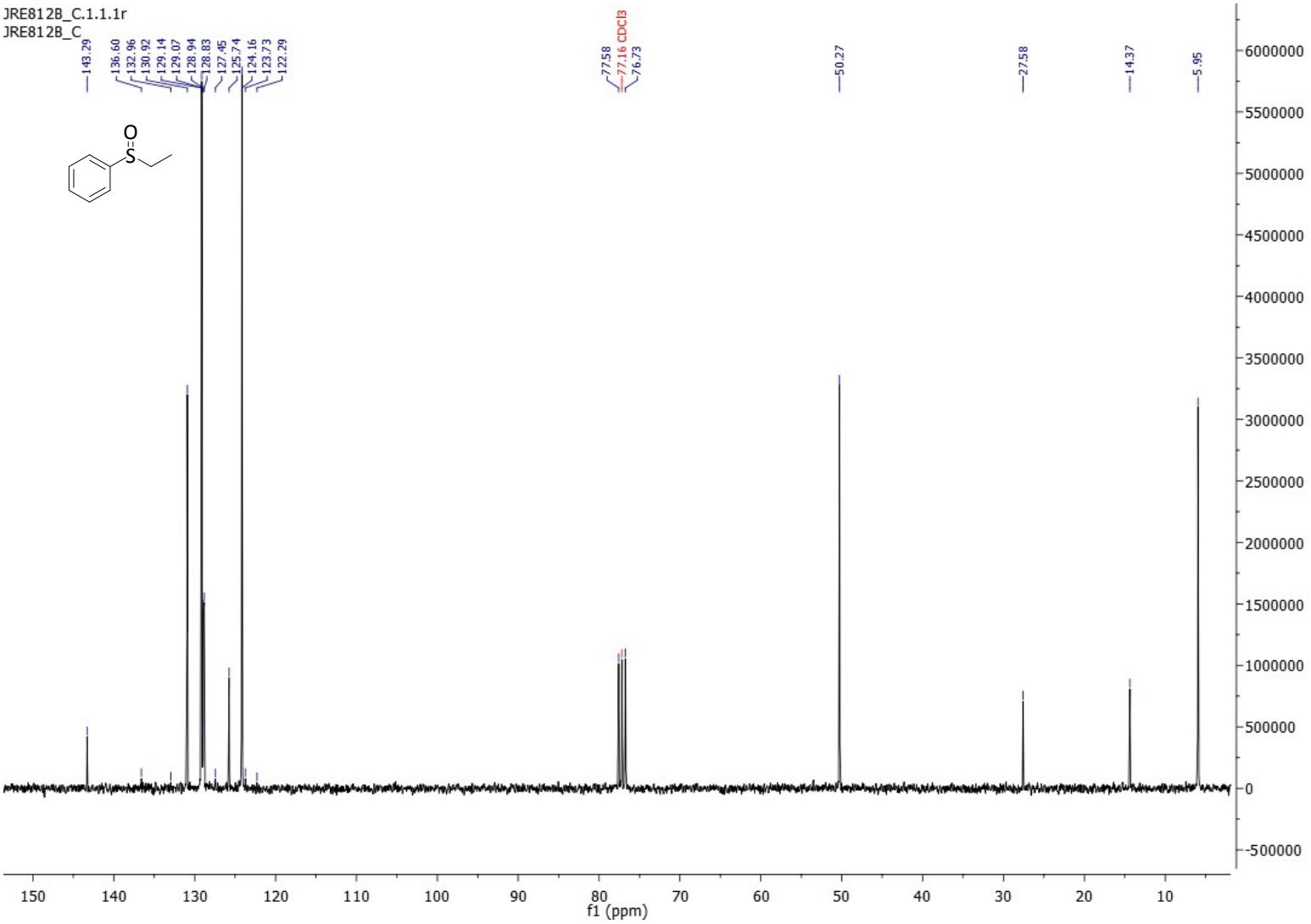
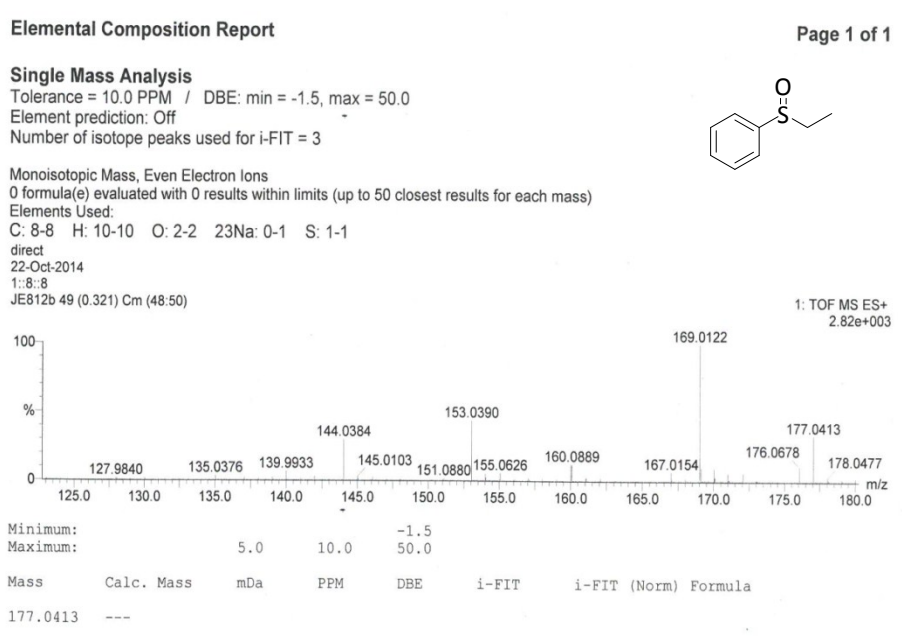


**Figure S68** Mass Spectra for ethyl phenyl sulfoxide (right) and ethyl phenyl sulfone (left)



Elemental Composition Report

Page 1 of 1

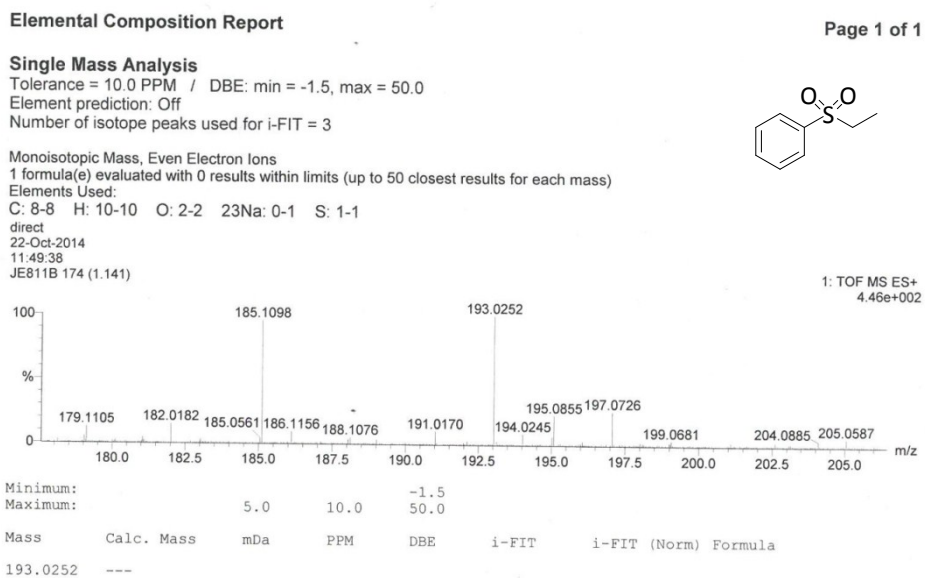
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
0 formula(e) evaluated with 0 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 8-8 H: 10-10 O: 2-2 23Na: 0-1 S: 1-1
direct
22-Oct-2014
1::8::8
JE812b 49 (0.321) Cm (48:50)

1: TOF MS ES+
2.82e+003



| | | | | | | |
|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | |
| Maximum: | | 5.0 | 10.0 | 50.0 | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) Formula |
| 177.0413 | --- | | | | | |



Elemental Composition Report

Page 1 of 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 0 results within limits (up to 50 closest results for each mass)
Elements Used:
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direct
22-Oct-2014
11:49:38
JE811B 174 (1.141)

1: TOF MS ES+
4.46e+002



| | | | | | | |
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| Minimum: | | | | -1.5 | | |
| Maximum: | | 5.0 | 10.0 | 50.0 | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) Formula |
| 193.0252 | --- | | | | | |

**Figure S69** $^{1}$H NMR spectrum of the reaction mixture for the selective oxidation of allyl phenyl sulfide in ethanol at RT for 15 min

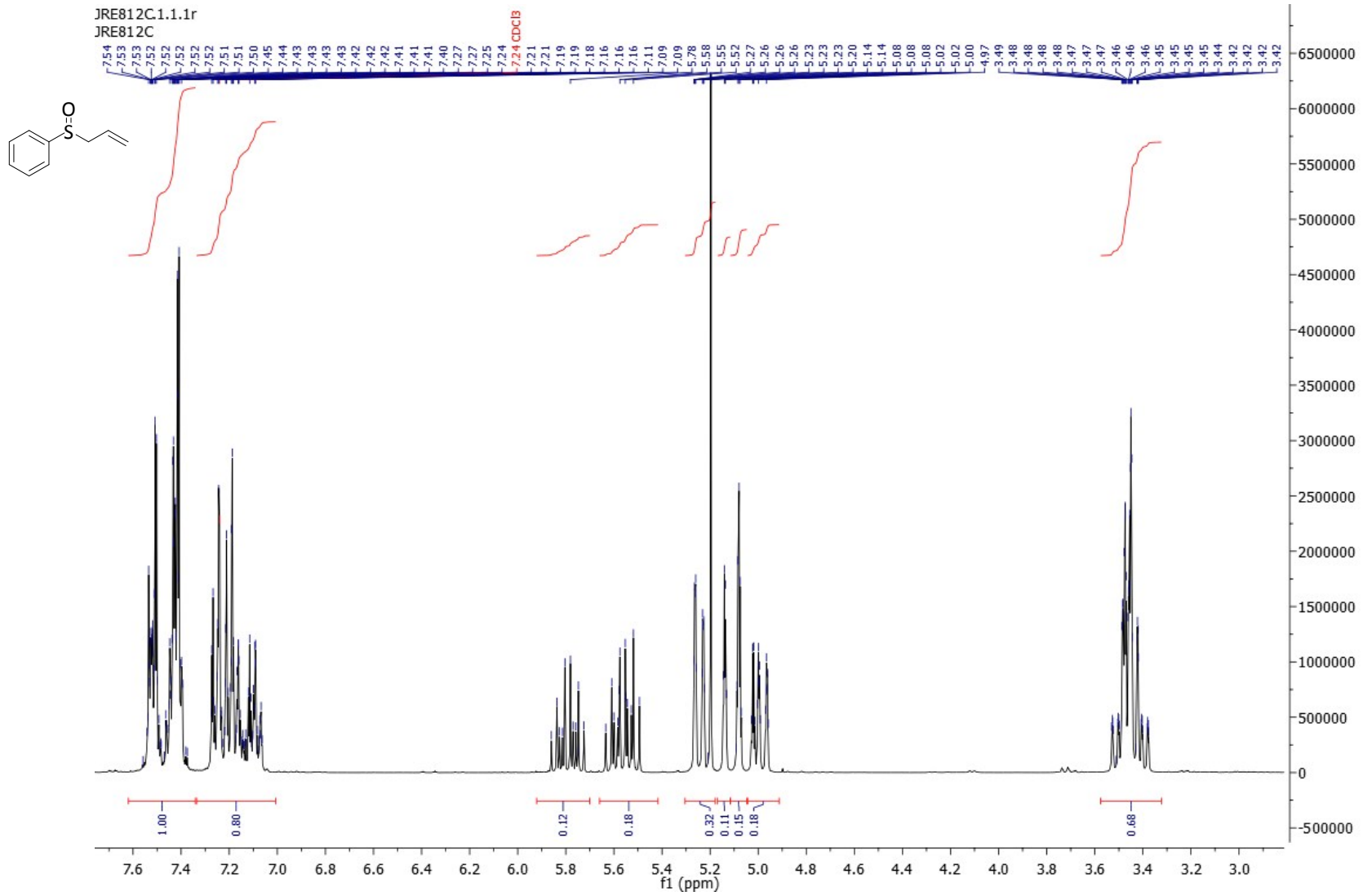


**Figure S70** $^{13}C\{^{1}H\}$ NMR spectrum of the reaction mixture for the selective oxidation of allyl phenyl sulfide in ethanol at RT for 15 min

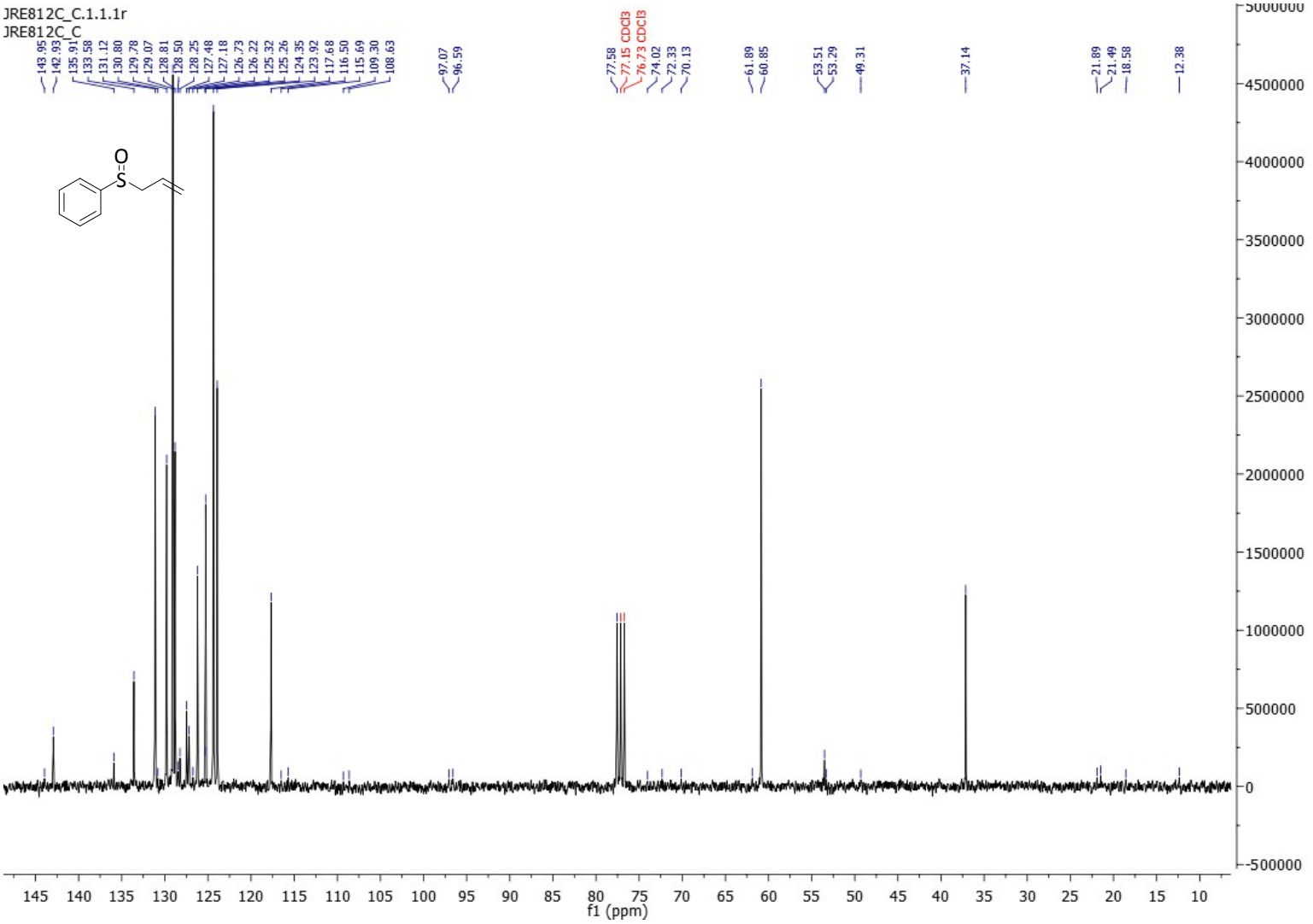
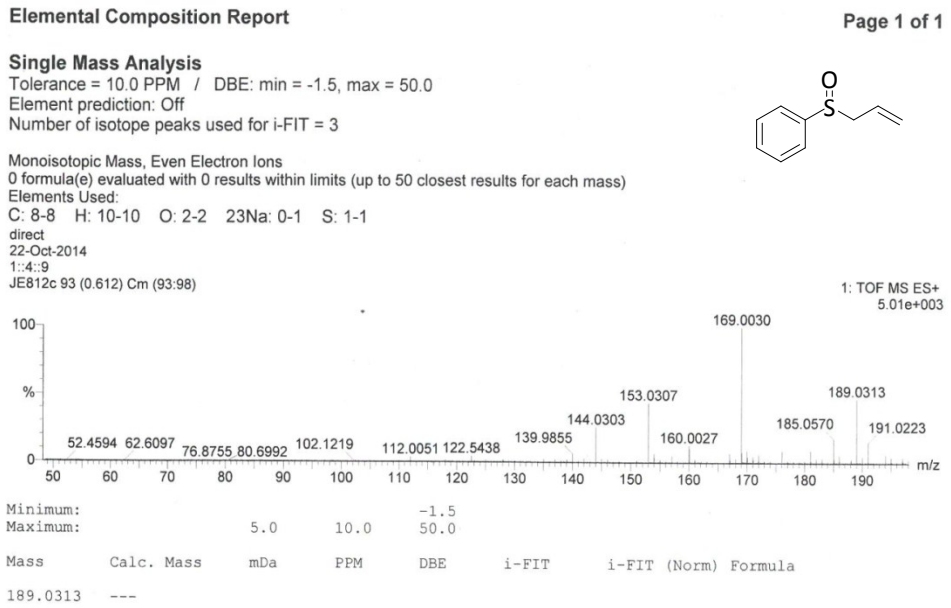


**Figure S71** Mass spectra for allyl phenyl sulfoxide (left) and allyl phenyl sulfone (right)



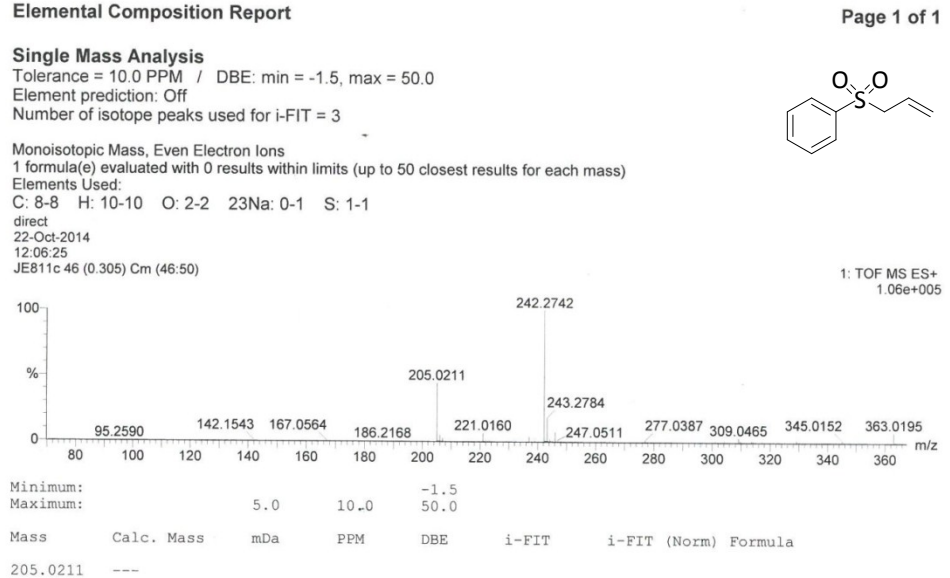



**Figure S72** $^{1}H$ NMR spectrum of the reaction mixture for the selective oxidation of 4-nitrothioanisole in ethanol at RT for 15 min

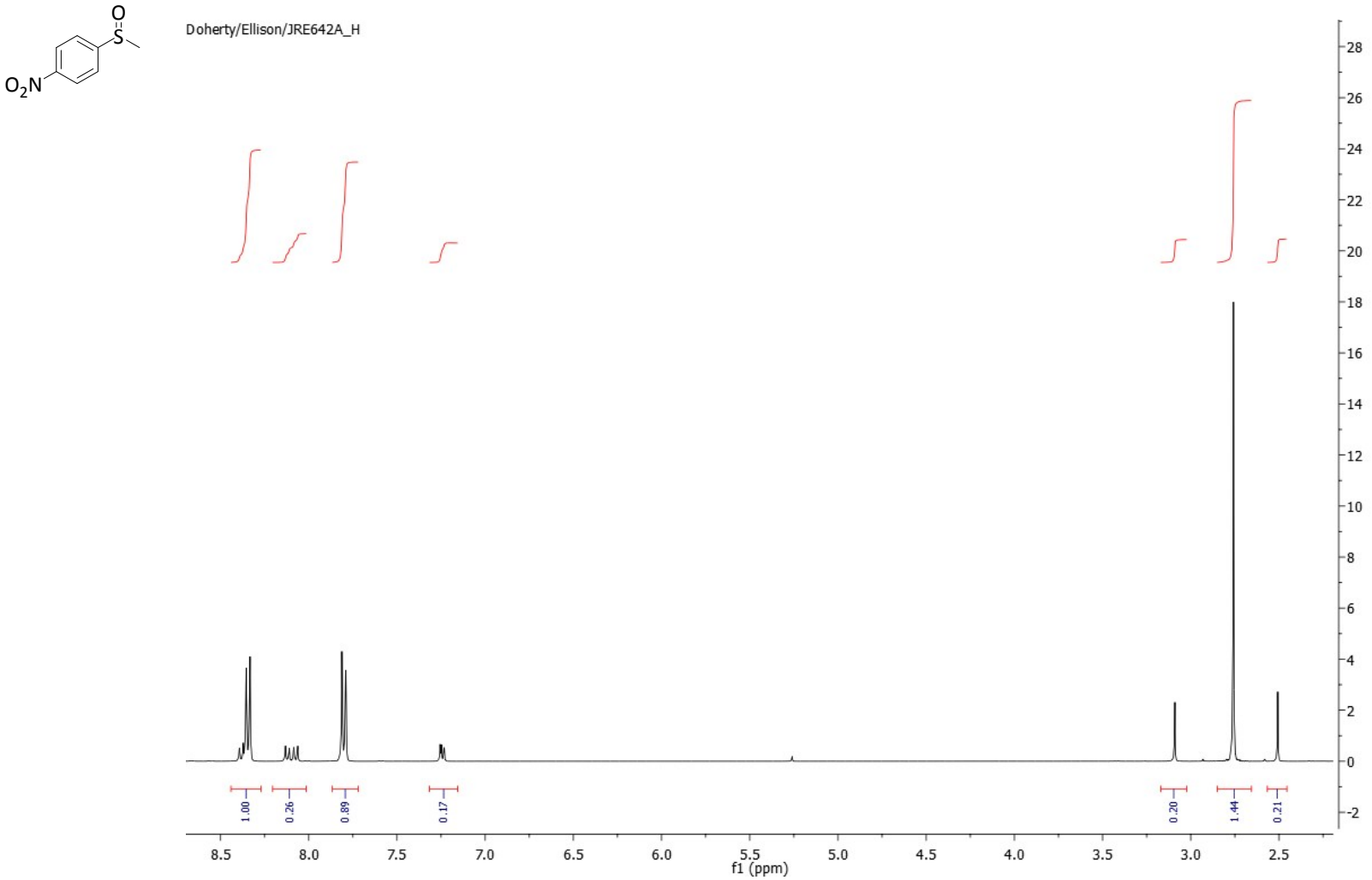


**Figure S73** $^{13}C\{^{1}H\}$ NMR spectrum of the reaction mixture for the selective oxidation of 4-nitrothioanisole in ethanol at RT for 15 min

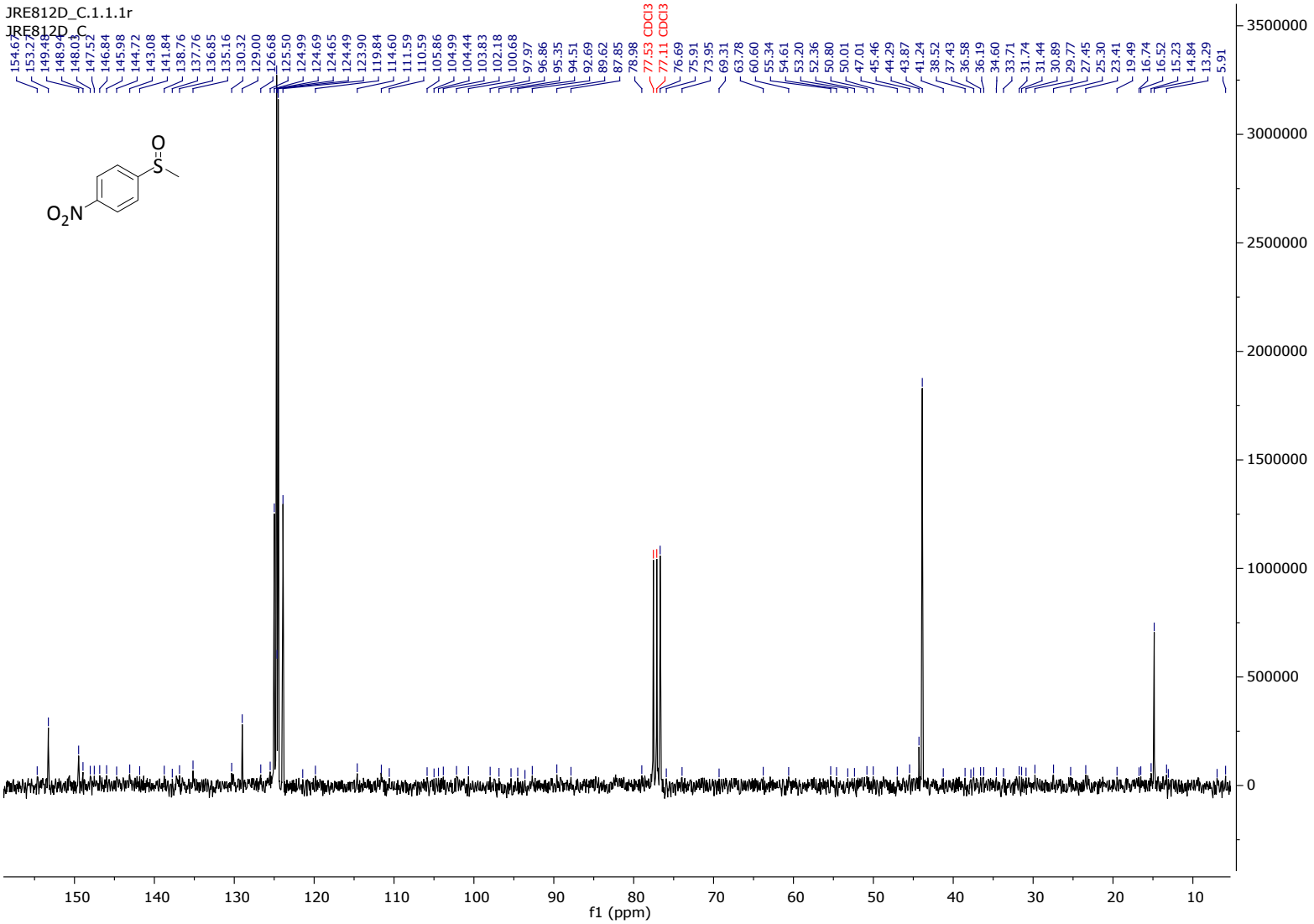
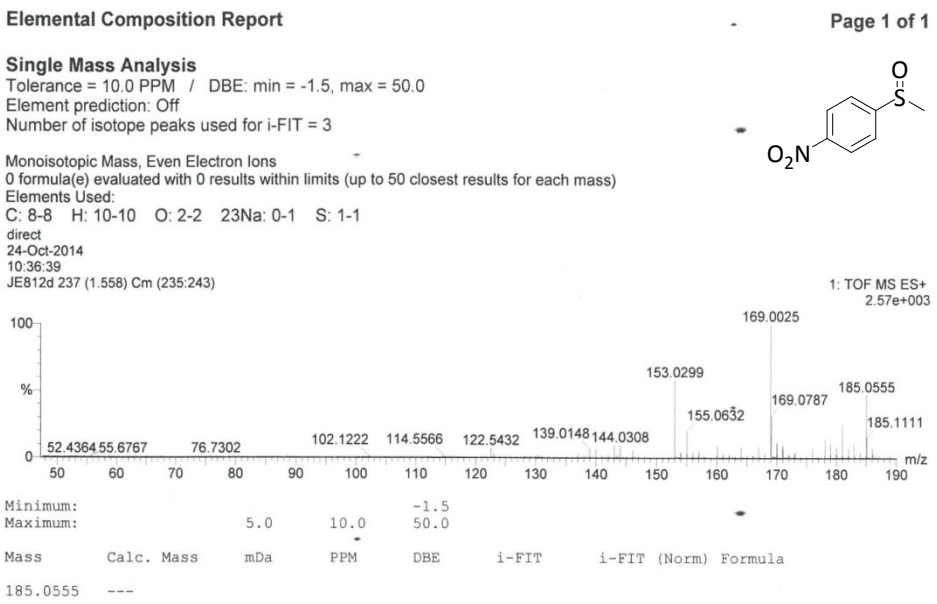


**Figure S74** Mass spectra for methyl 4-nitrophenyl sulfoxide (left) and methyl 4-nitrophenyl sulfone (right)



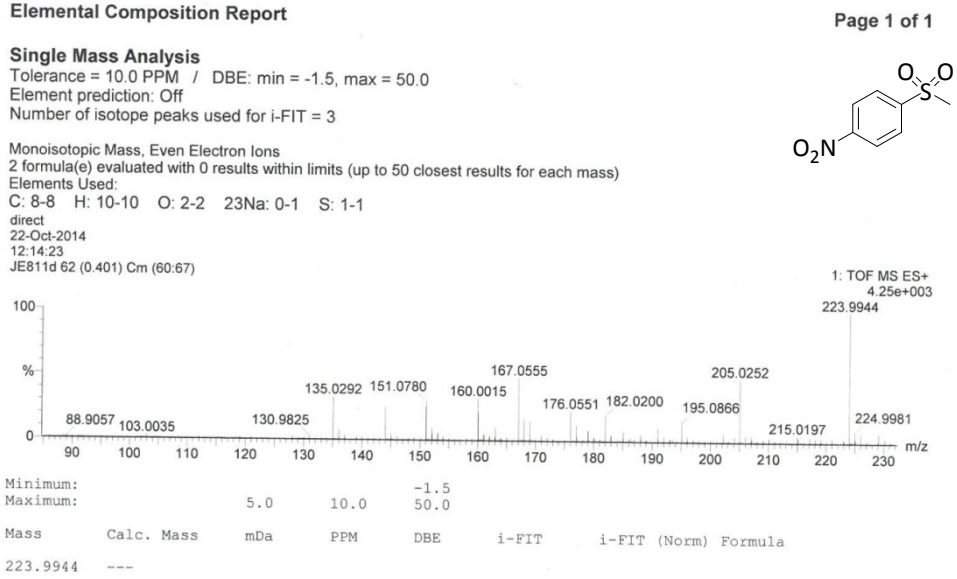



**Figure S75** $^{1}$H NMR spectrum of the reaction mixture for the selective oxidation of dibenzothiophene in ethanol at RT for 15 min

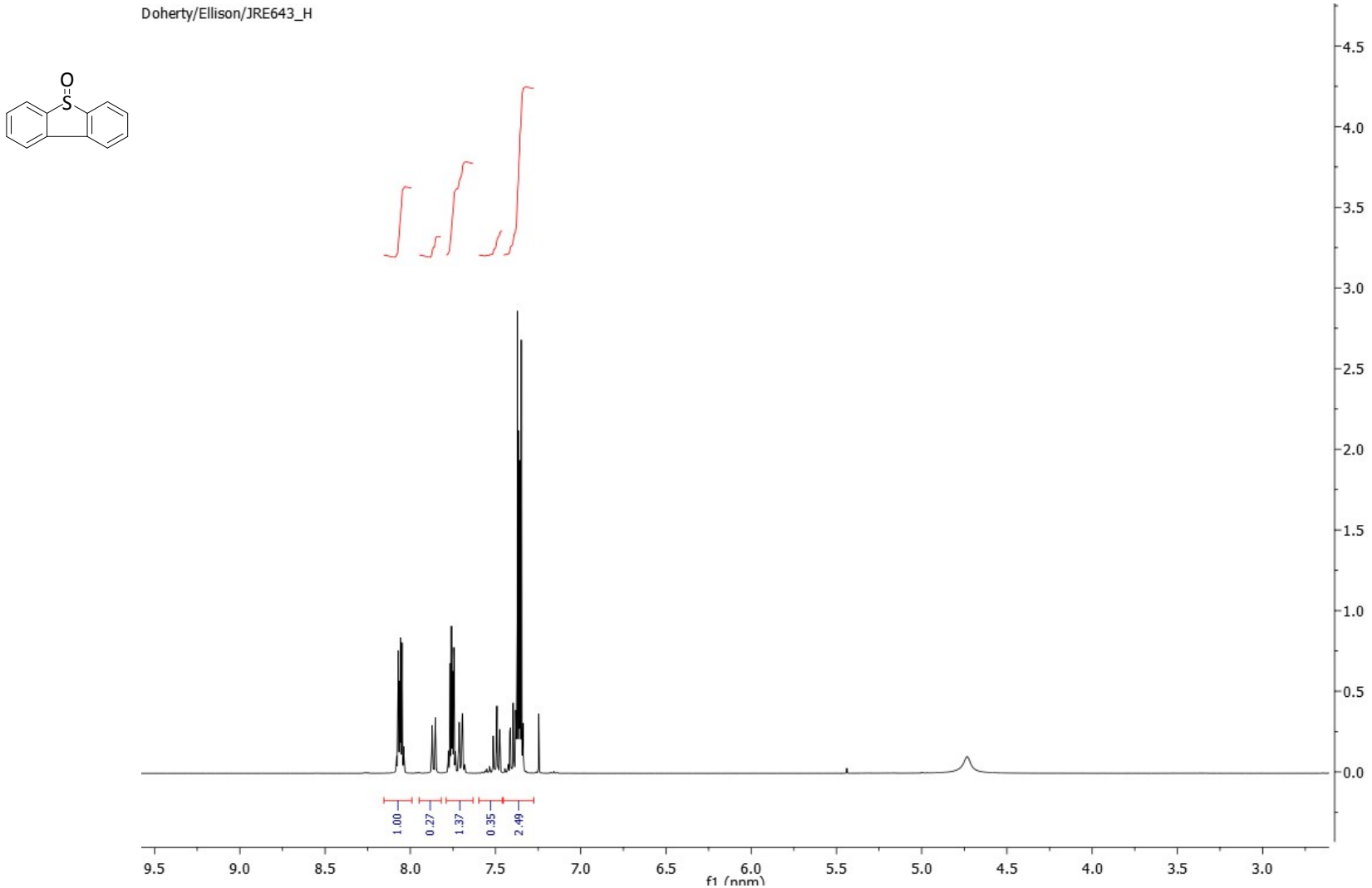


**Figure S76** $^{13}C\{^{1}H\}$ NMR spectrum of the reaction mixture for the selective oxidation of dibenzothiophene in ethanol at RT for 15 min

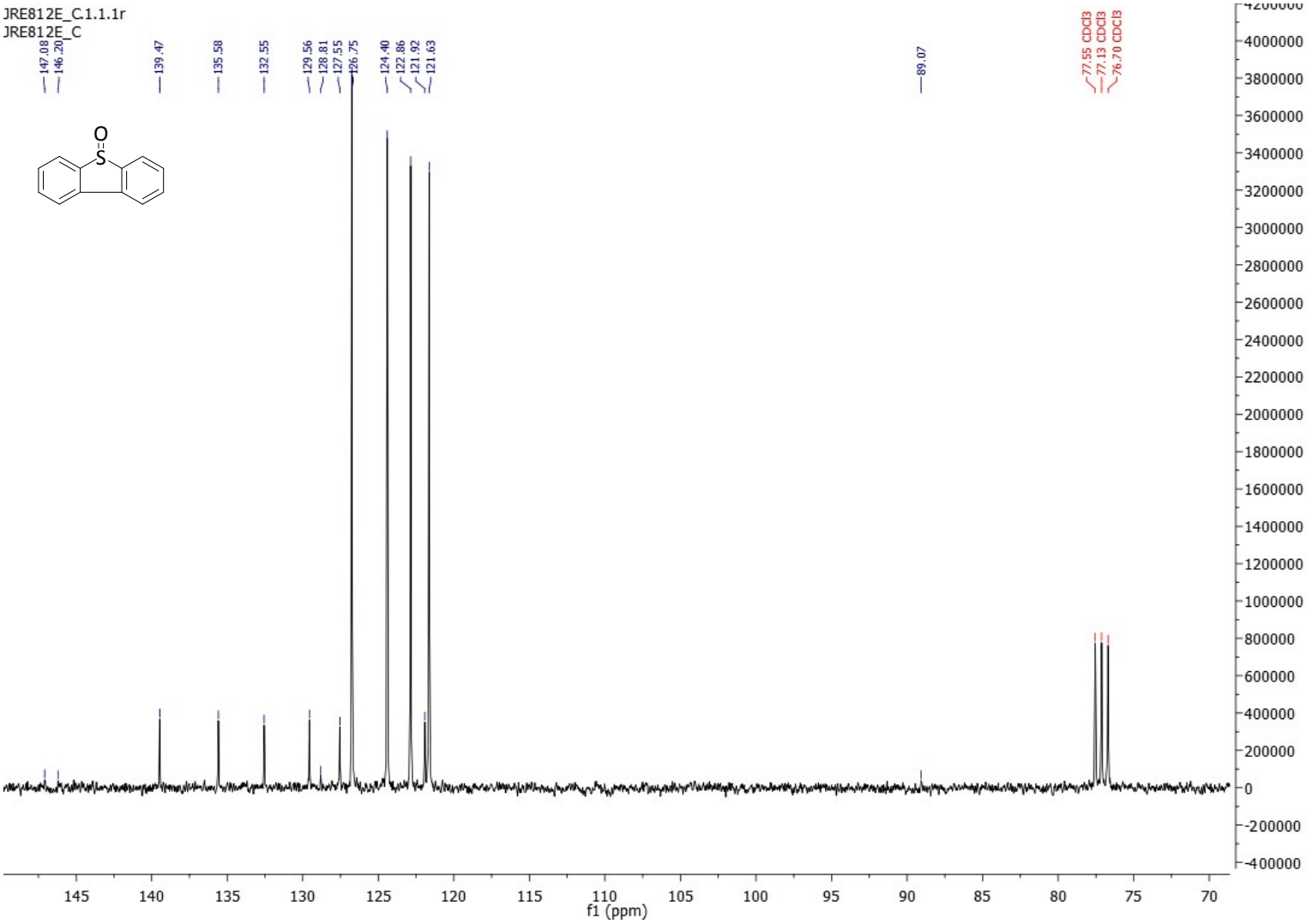
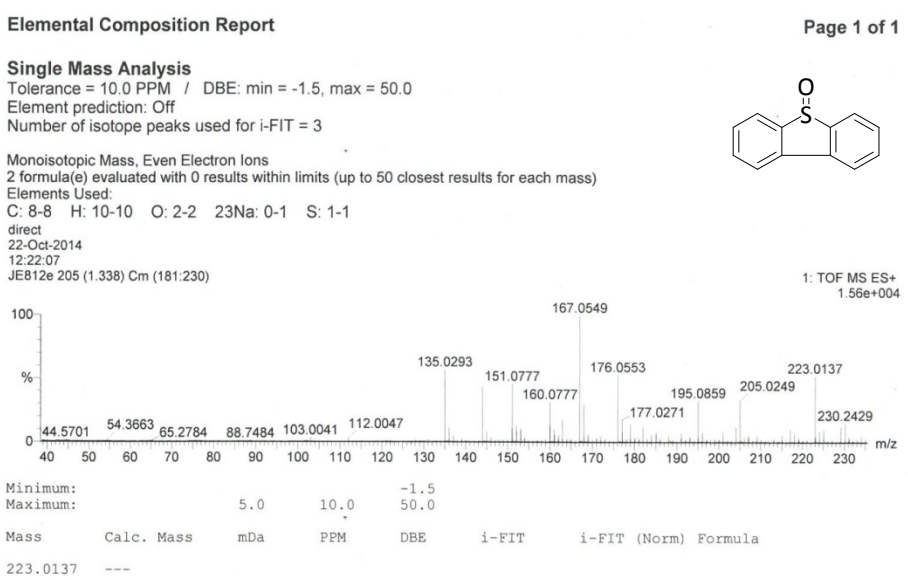


**Figure S77** Mass spectra for dibenzothiophene sulfoxide (left) and dibenzothiophene sulfone (right)



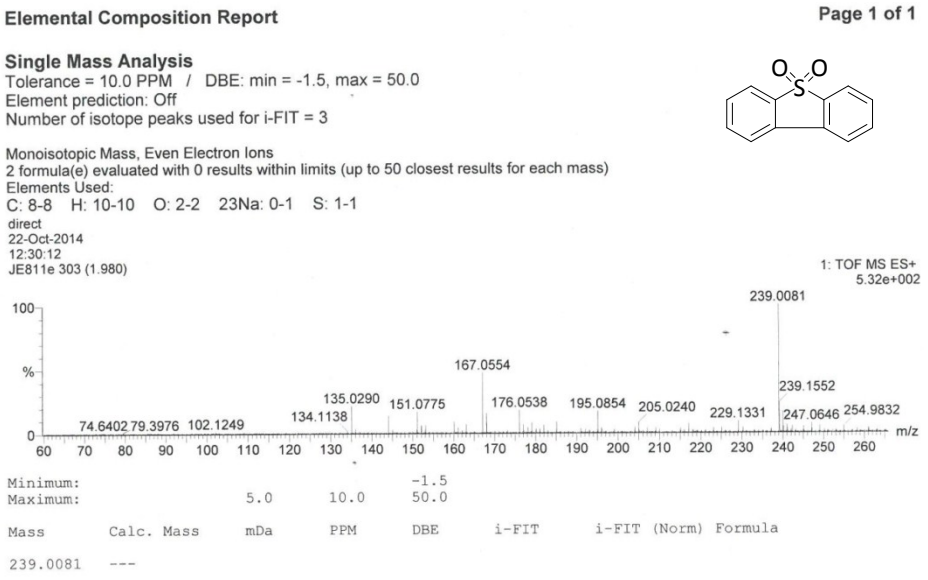



**Figure S78** $^{1}$H NMR spectrum of the reaction mixture for the selective oxidation of homoallyl phenyl sulfide ethanol at RT for 15 min

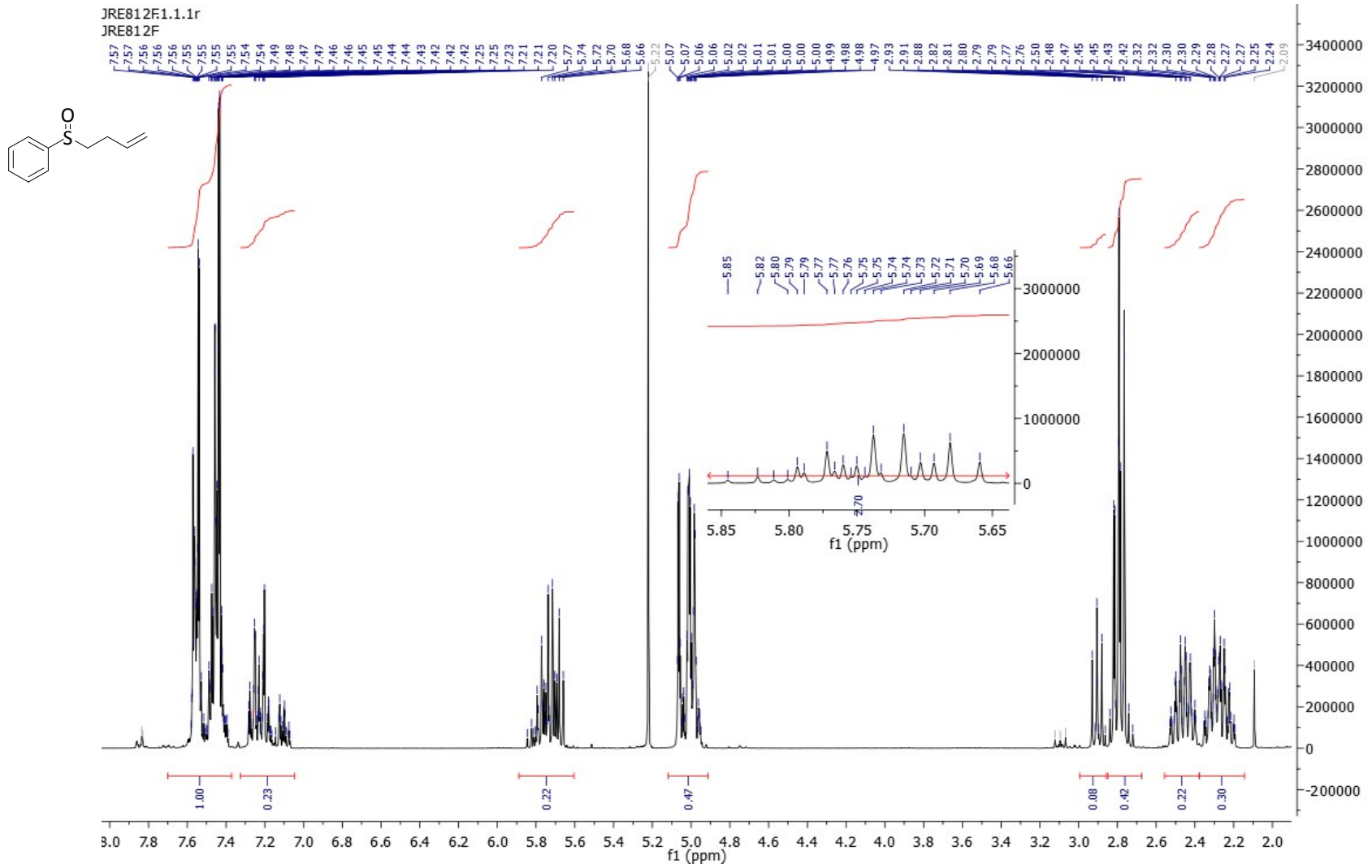


**Figure S79** $^{13}C\{^{1}H\}$ NMR spectrum of the reaction mixture for the selective oxidation of homoallyl phenyl sulfide in ethanol at RT for 15 min**.**

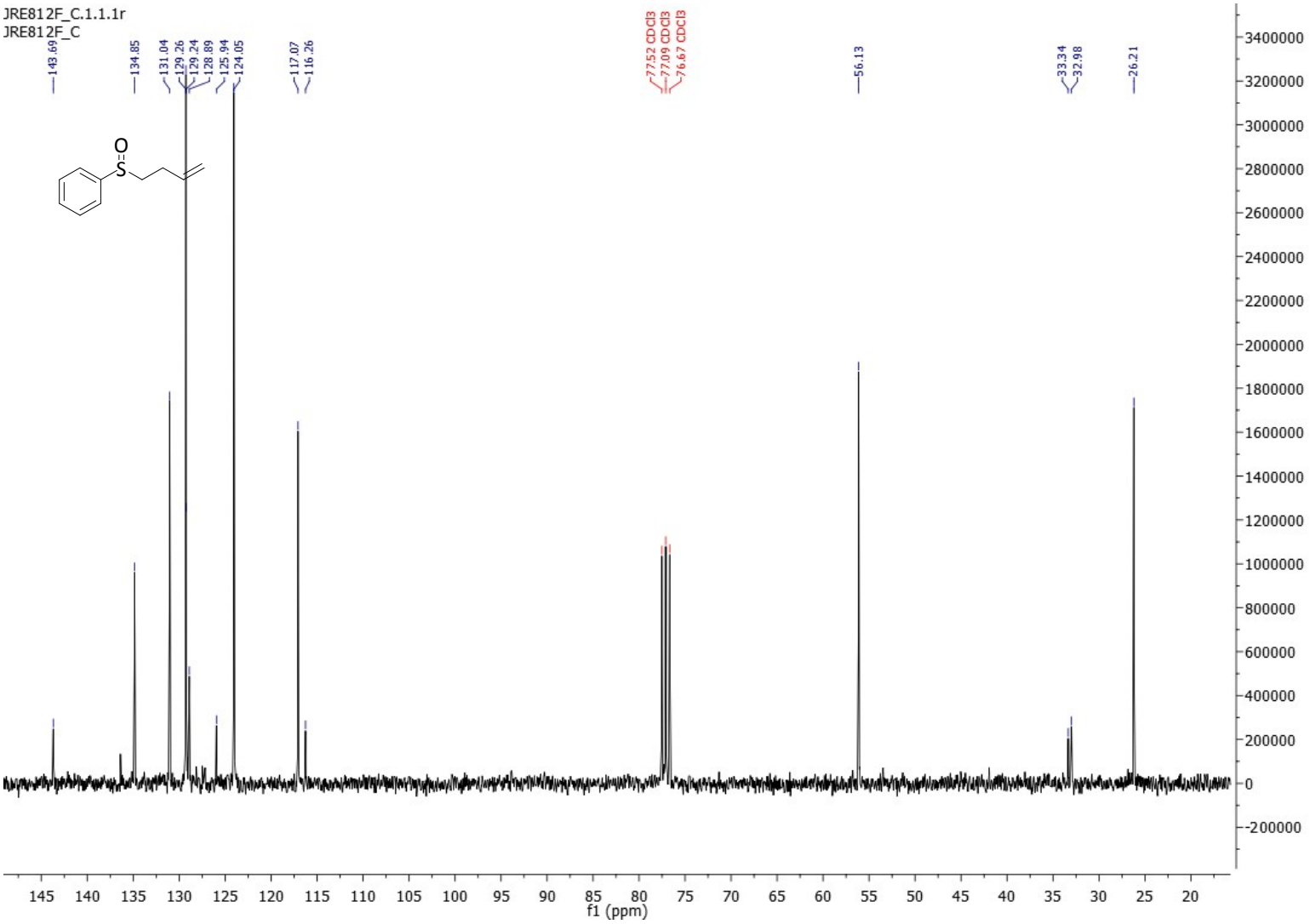
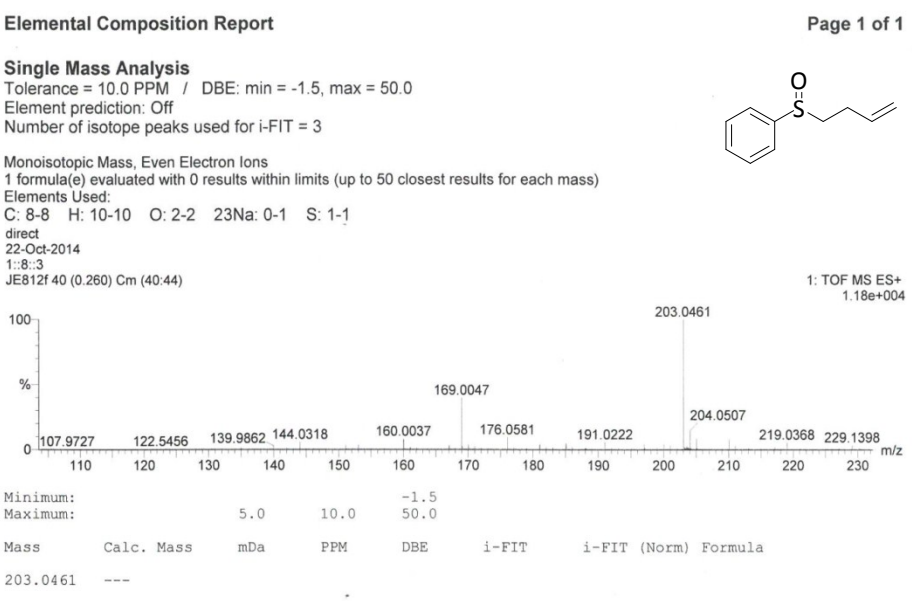


**Figure S80** Mass spectra for homoallyl phenyl sulfoxide (left) and homoallyl phenyl sulfone (right)



**Elemental Composition Report** Page 1 of 1

**Single Mass Analysis**
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
1 formula(e) evaluated with 0 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 8-8 H: 10-10 O: 2-2 23Na: 0-1 S: 1-1

direct
22-Oct-2014
1::8::3
JE812f 40 (0.260) Cm (40:44)

1: TOF MS ES+
1.18e+004



| | | | | | | | |
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| Maximum: | | 5.0 | 10.0 | 50.0 | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
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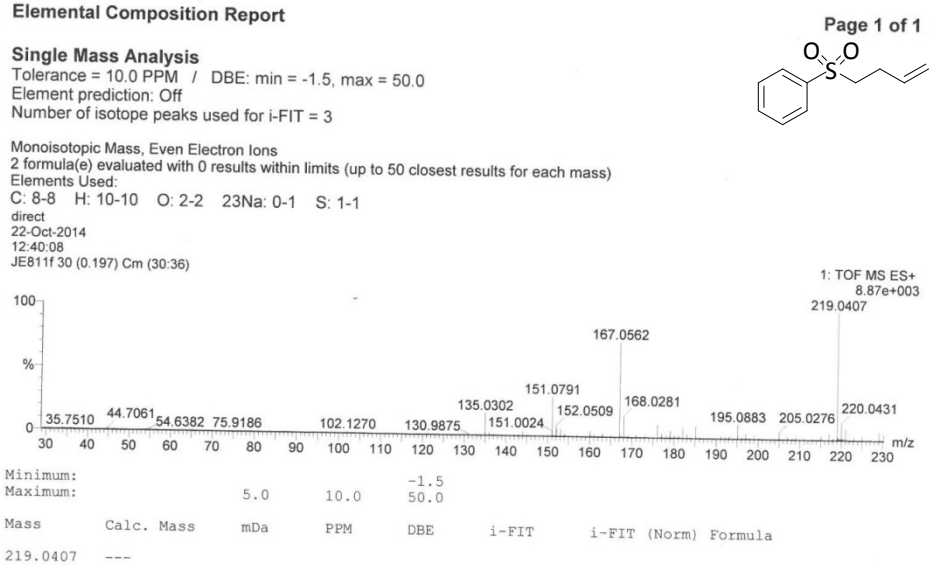


**Elemental Composition Report** Page 1 of 1

**Single Mass Analysis**
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 0 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 8-8 H: 10-10 O: 2-2 23Na: 0-1 S: 1-1

direct
22-Oct-2014
12:40:08
JE811f 30 (0.197) Cm (30:36)

1: TOF MS ES+
8.87e+003



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | |
| Maximum: | | 5.0 | 10.0 | 50.0 | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
| 219.0407 | --- | | | | | | |

**Figure S81** $^{1}$H NMR spectrum of the reaction mixture for the selective oxidation of benzyl phenyl sulfide in ethanol at RT for 15 min

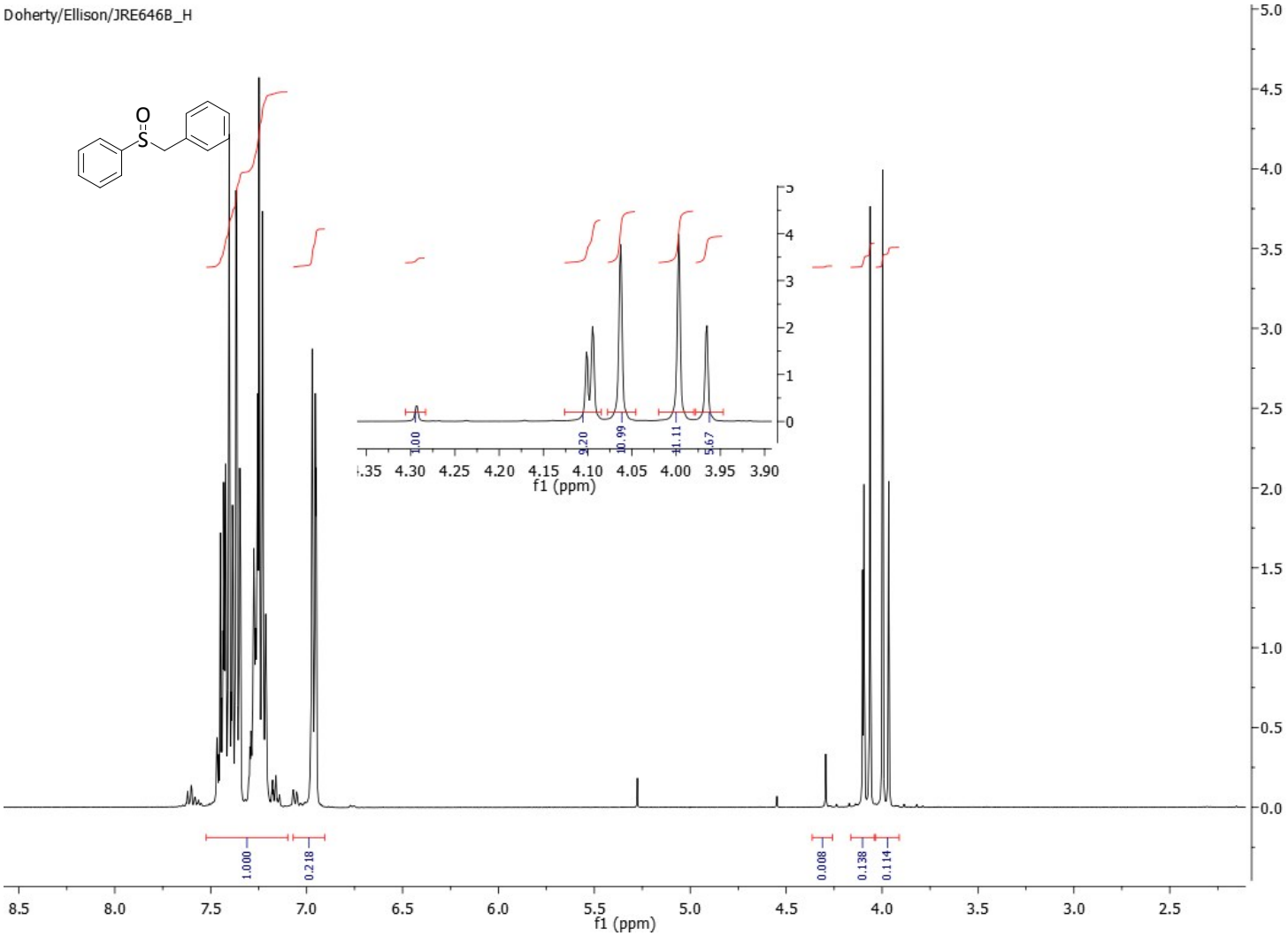


**Figure S82** $^{13}C\{^{1}H\}$ NMR spectrum of the reaction mixture for the selective oxidation of benzyl phenyl sulfide in ethanol at RT for 15 min

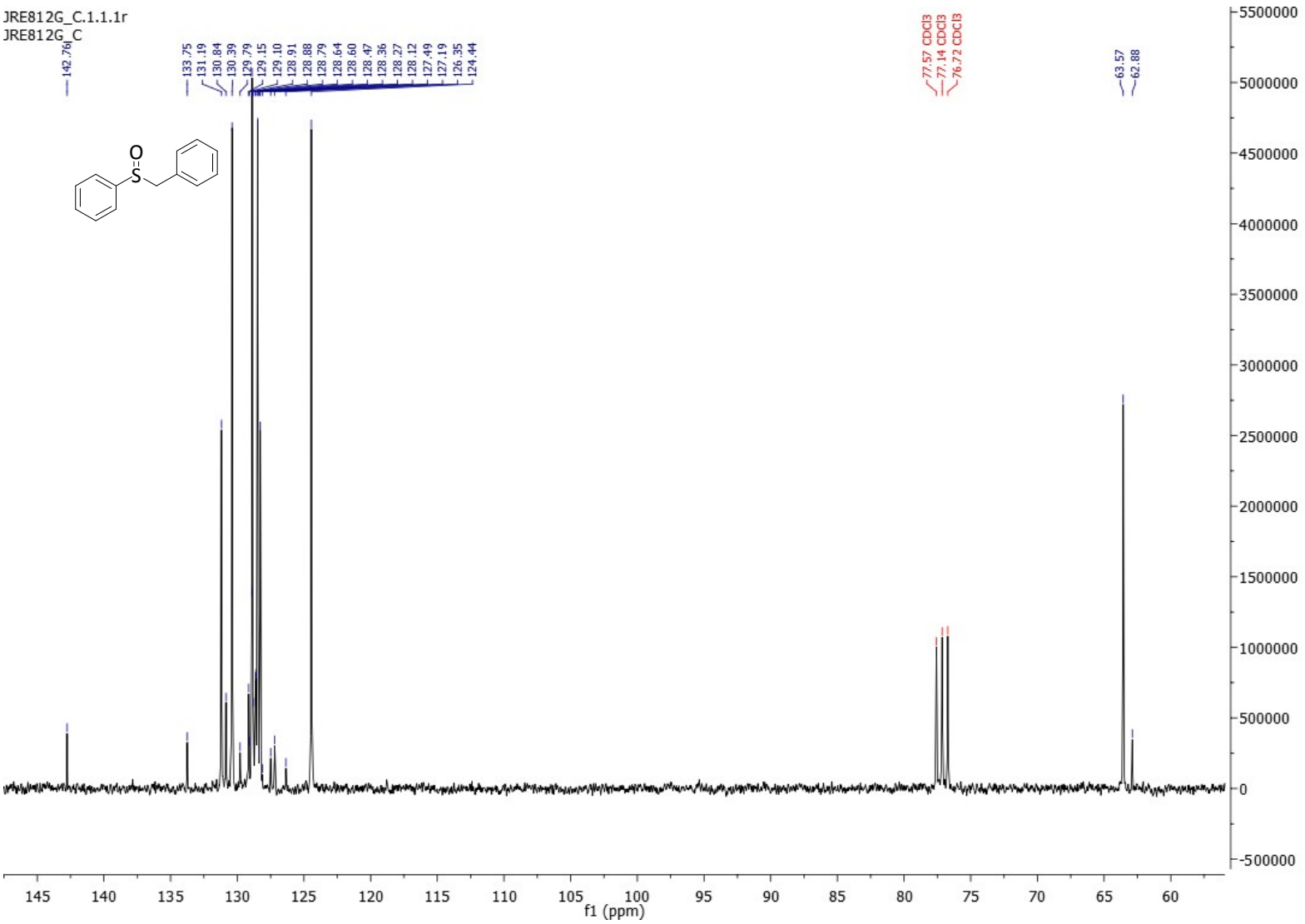
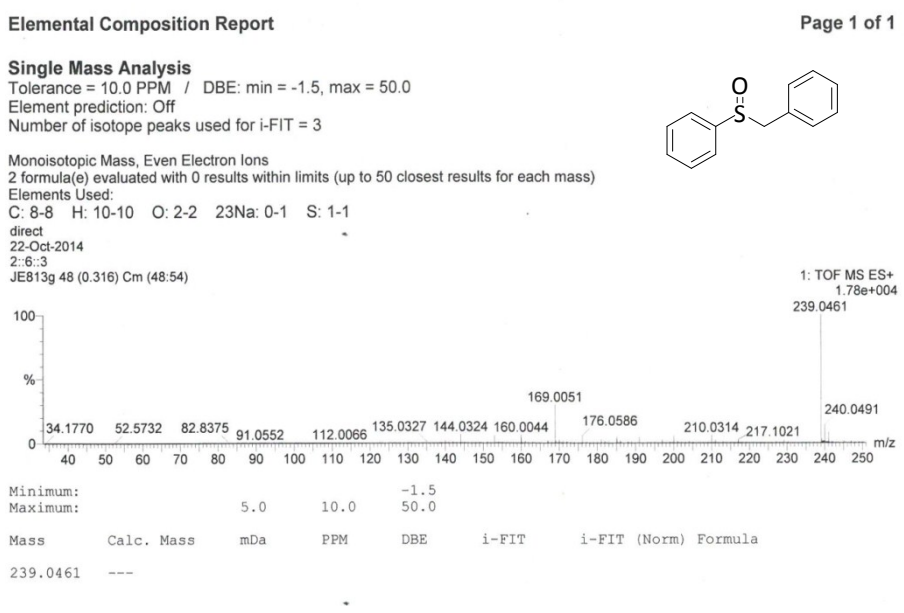


**Figure S83** Mass spectra for benzyl phenyl sulfoxide (left) and benzyl phenyl sulfone (right)



Elemental Composition Report Page 1 of 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 0 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 8-8 H: 10-10 O: 2-2 23Na: 0-1 S: 1-1
direct
22-Oct-2014
2::6::3
JE813g 48 (0.316) Cm (48:54)



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | |
| Maximum: | | 5.0 | 10.0 | 50.0 | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
| 239.0461 | --- | | | | | | |



Elemental Composition Report Page 1 of 1

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 0 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 8-8 H: 10-10 O: 2-2 23Na: 0-1 S: 1-1
direct
22-Oct-2014
12:47:11
JE811g 49 (0.322) Cm (43:53)



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | | |
| Maximum: | | 5.0 | 10.0 | 50.0 | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | i-FIT (Norm) | Formula |
| 255.0395 | --- | | | | | | |

**Figure S84** $^{1}$H NMR spectrum of the reaction mixture for the selective oxidation of *n*-decyl methyl sulfide in ethanol at RT for 15 min

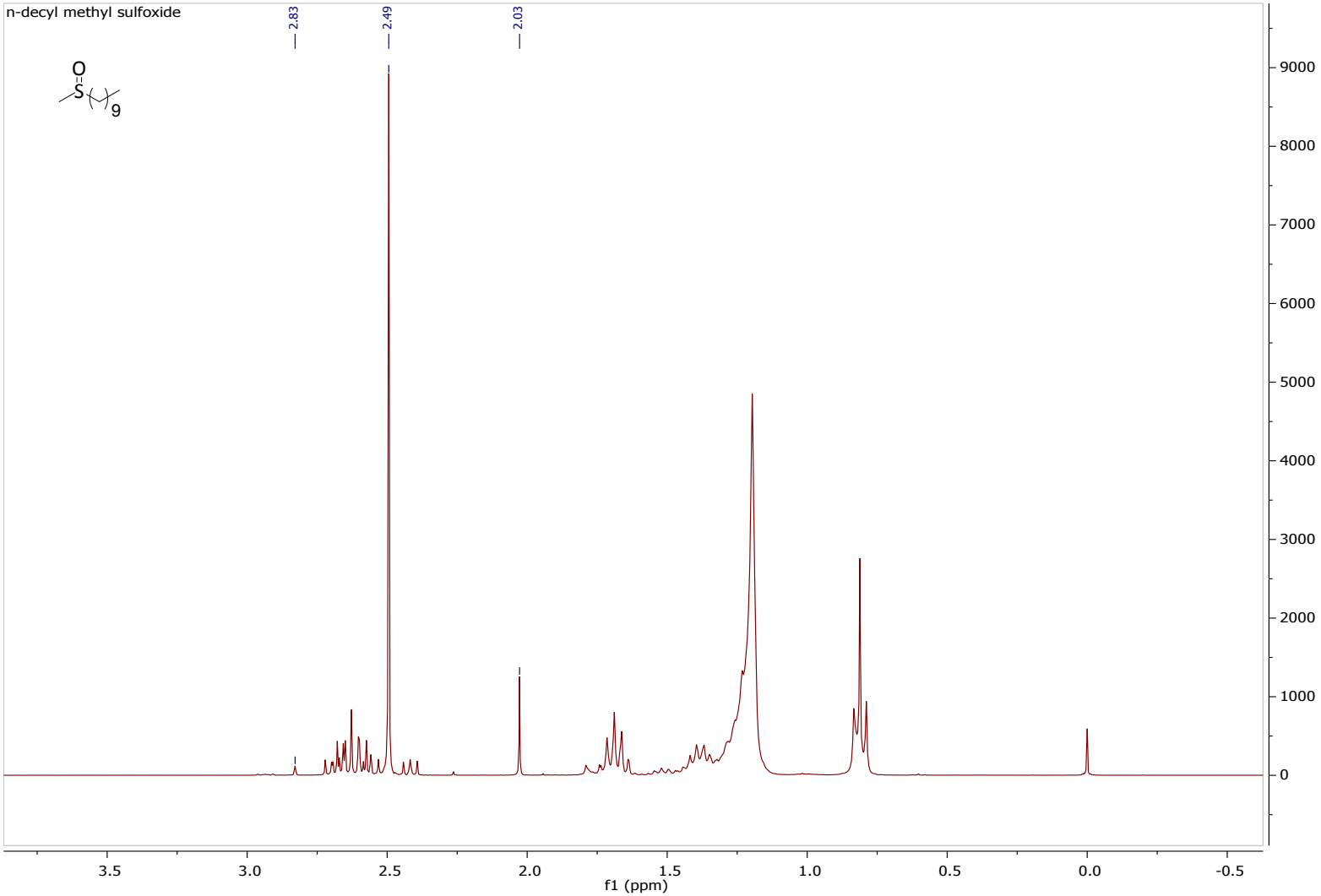


**Figure S85** $^{13}C$ NMR spectrum of the reaction mixture for the selective oxidation of *n*-decyl methyl sulfide in ethanol at RT for 15 min

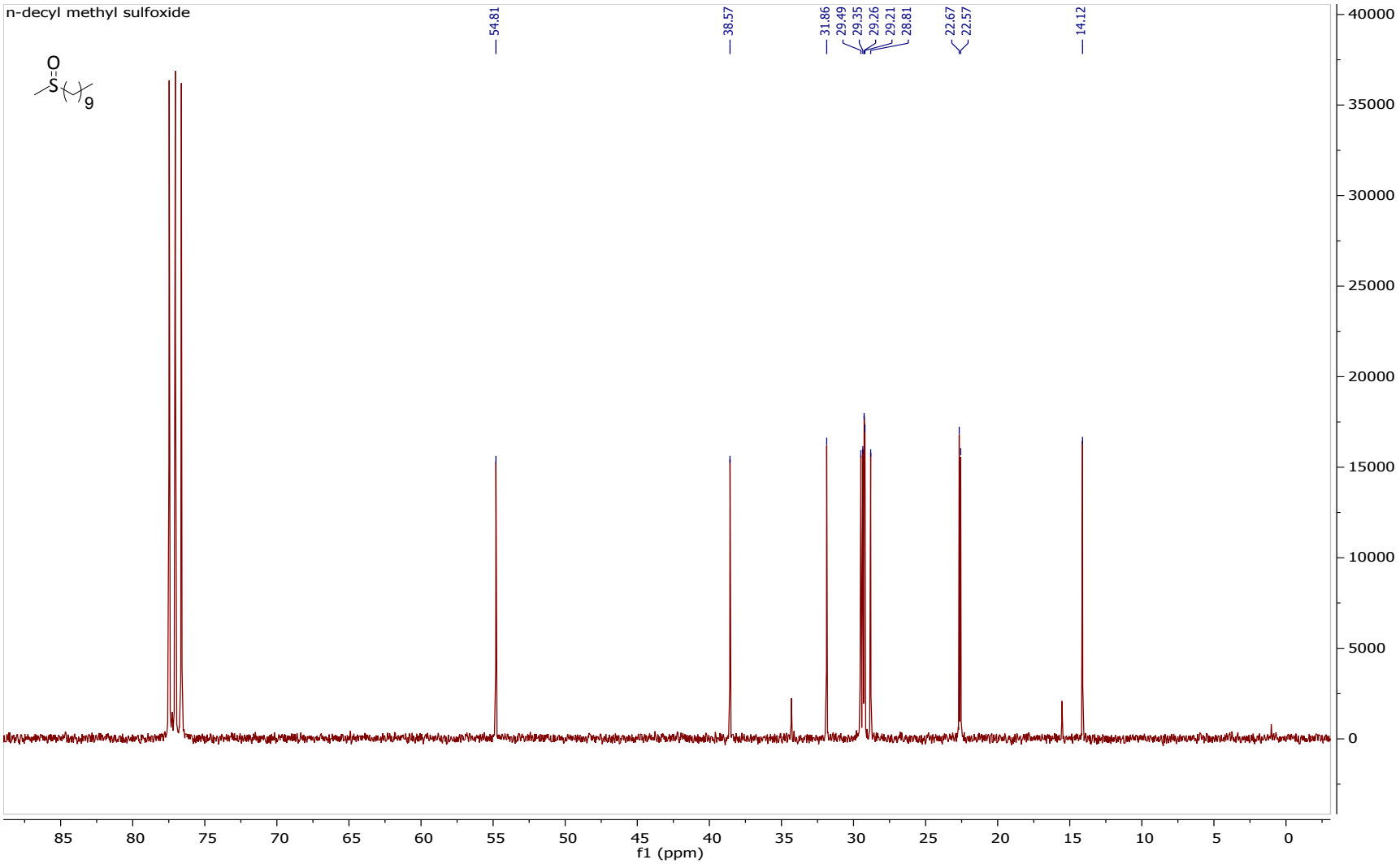


**Figure S86** Mass spectrum of *n*-decyl methyl sulfoxide

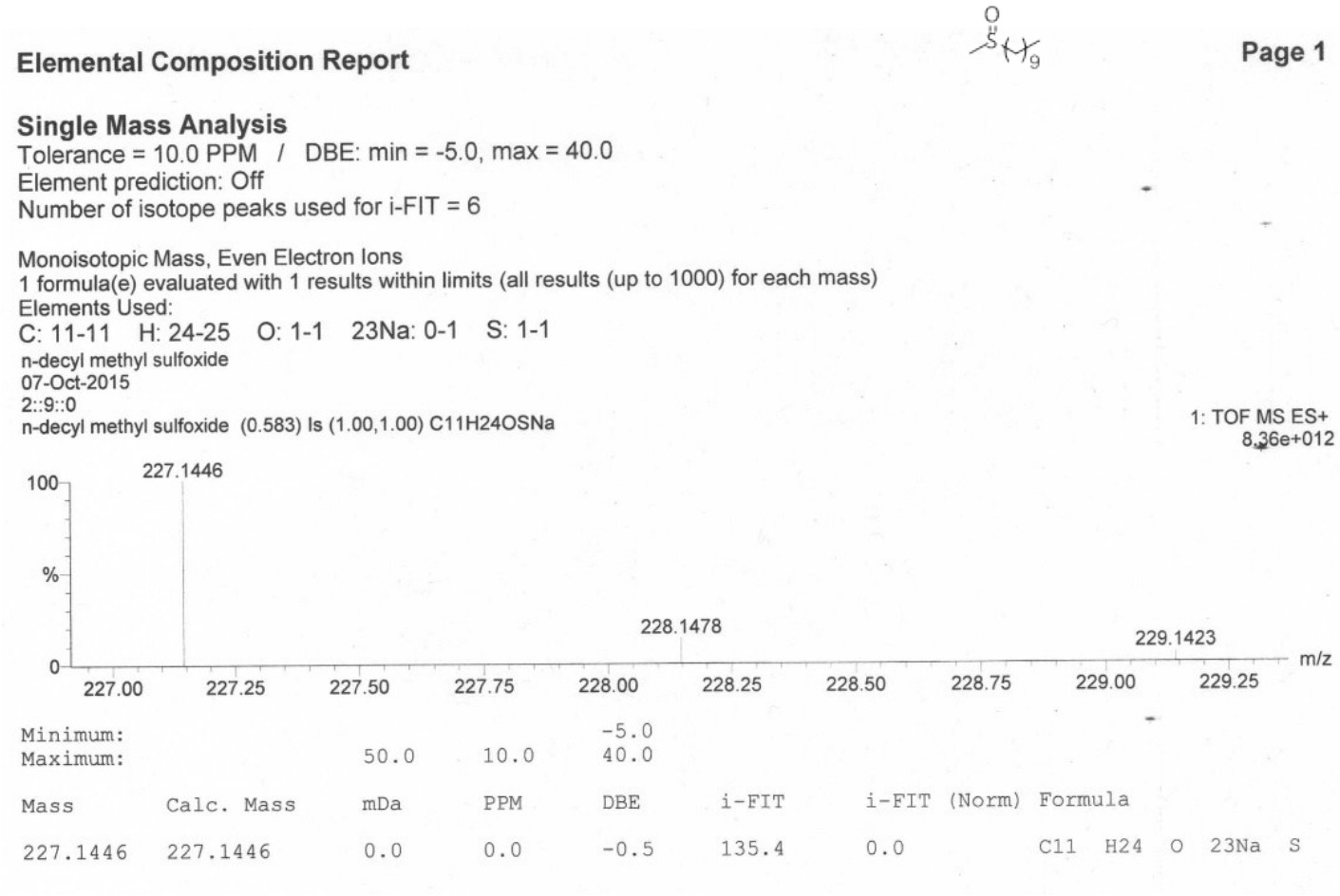
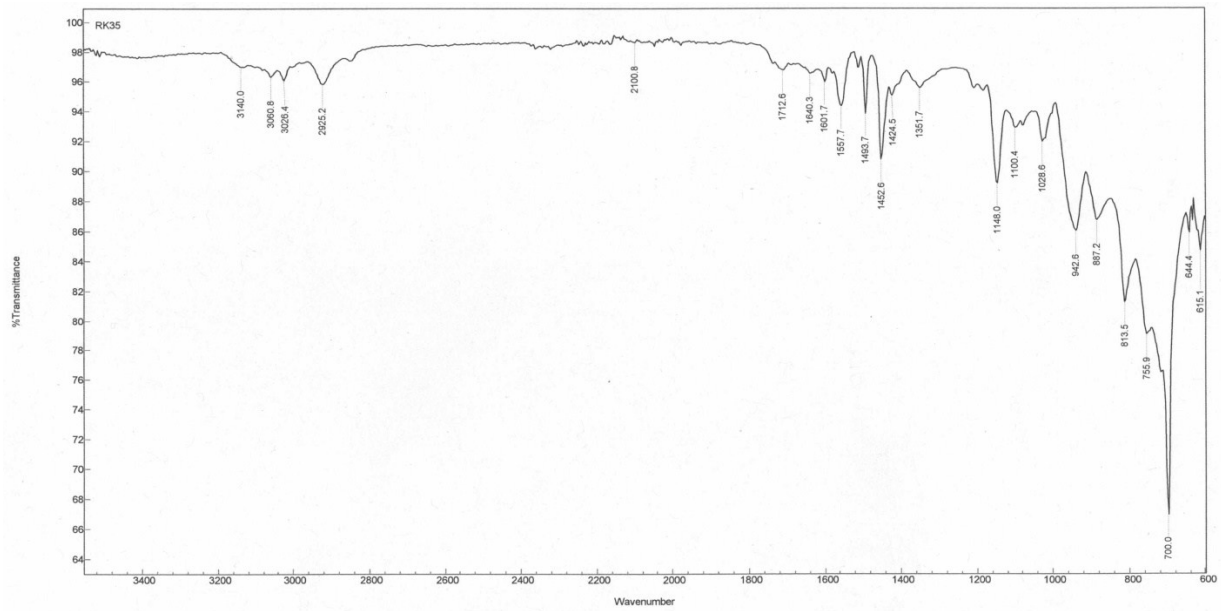


**Figure S87** FT-IR Spectra of (a) fresh polymer supported peroxotungstate **3a** and (b) catalyst isolated after the 5th run of an ethanol recycle experiment

(a)




(b)

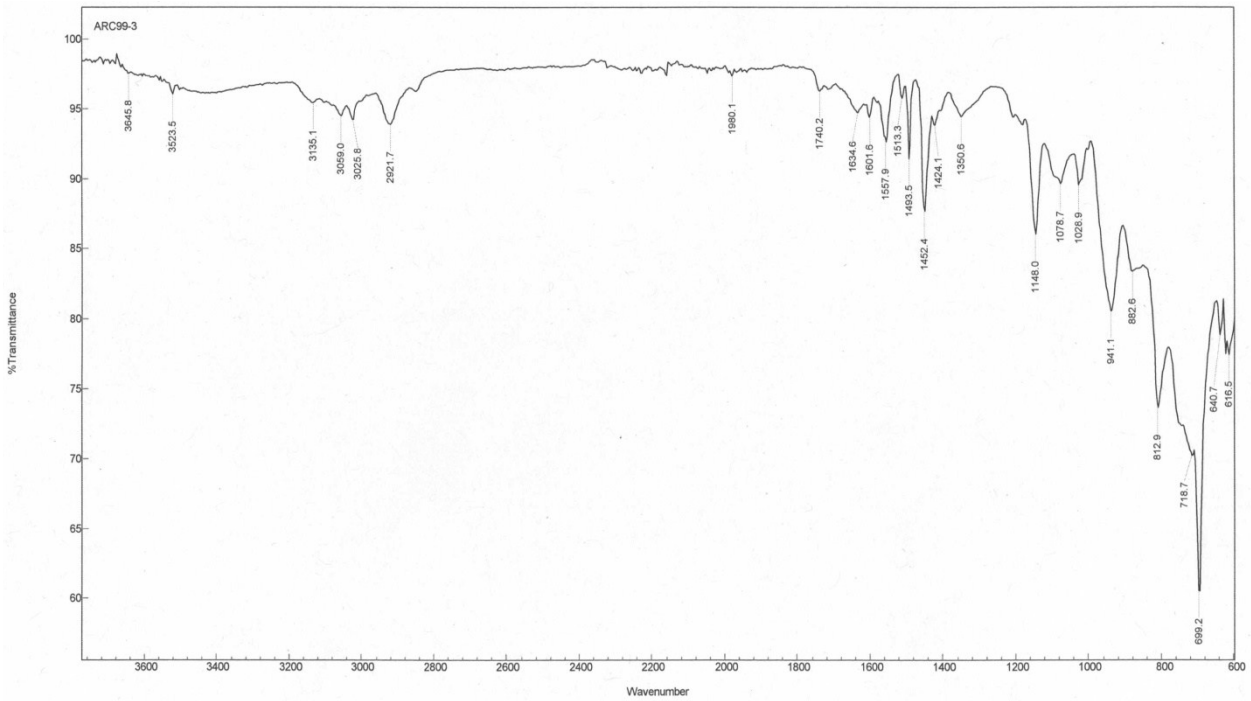
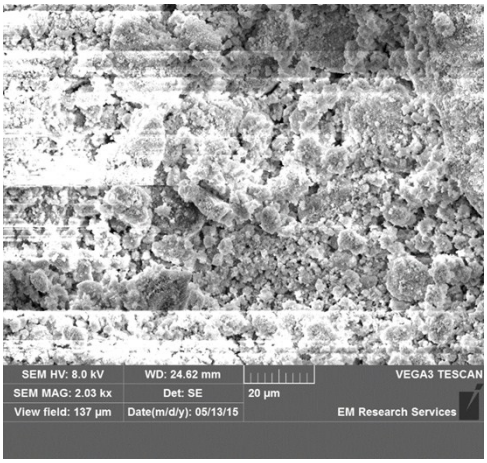


**Figure S88** SEM image of catalyst **3a** isolated after the 5th run of an ethanol recycle experiment.



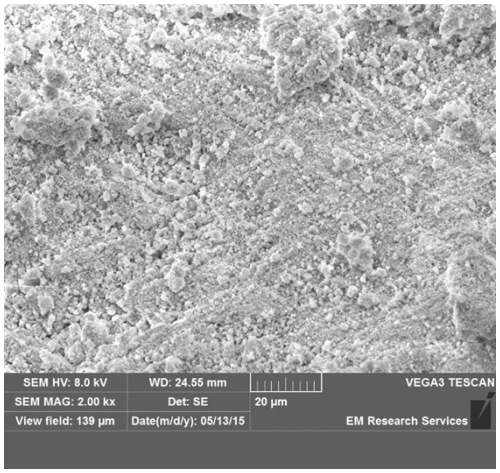
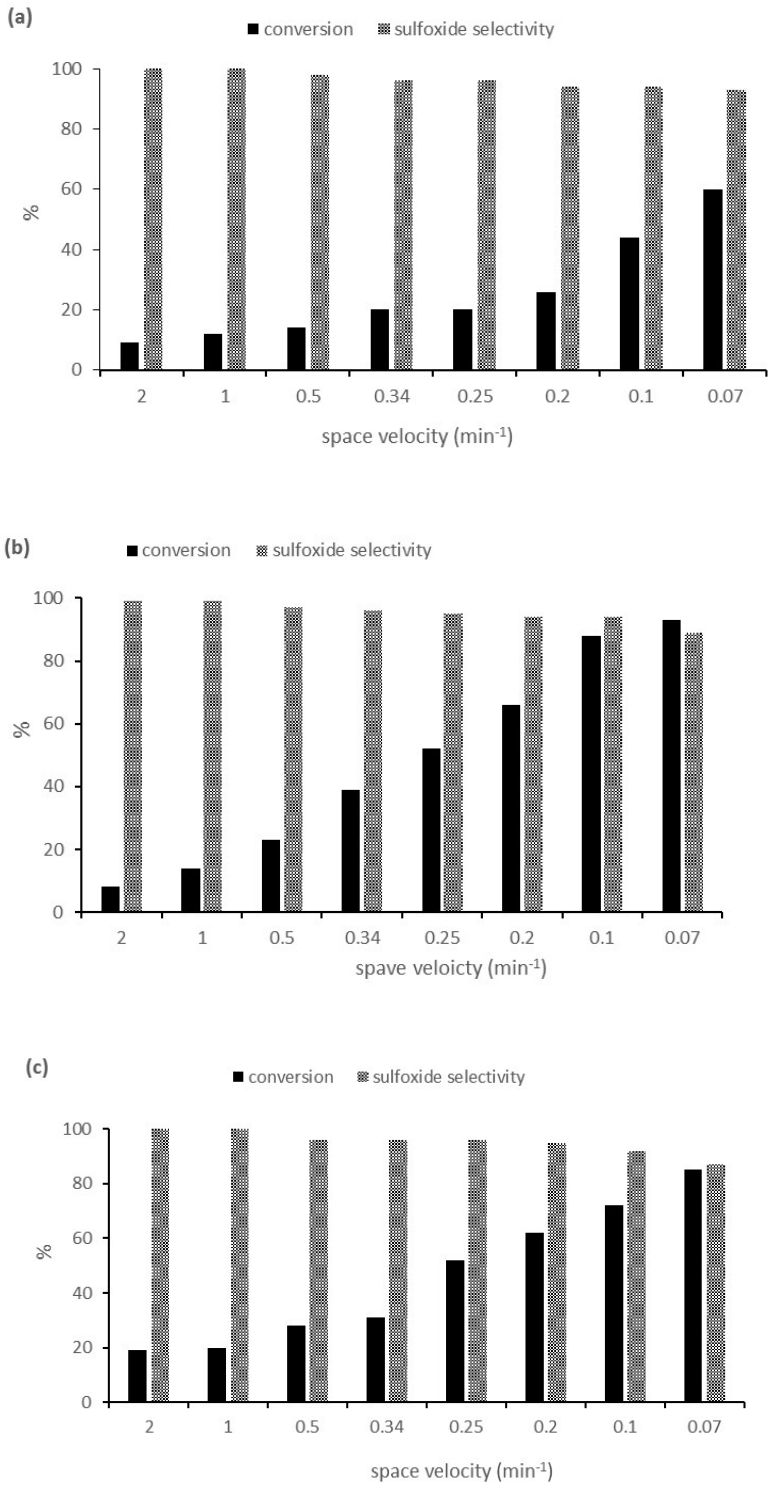
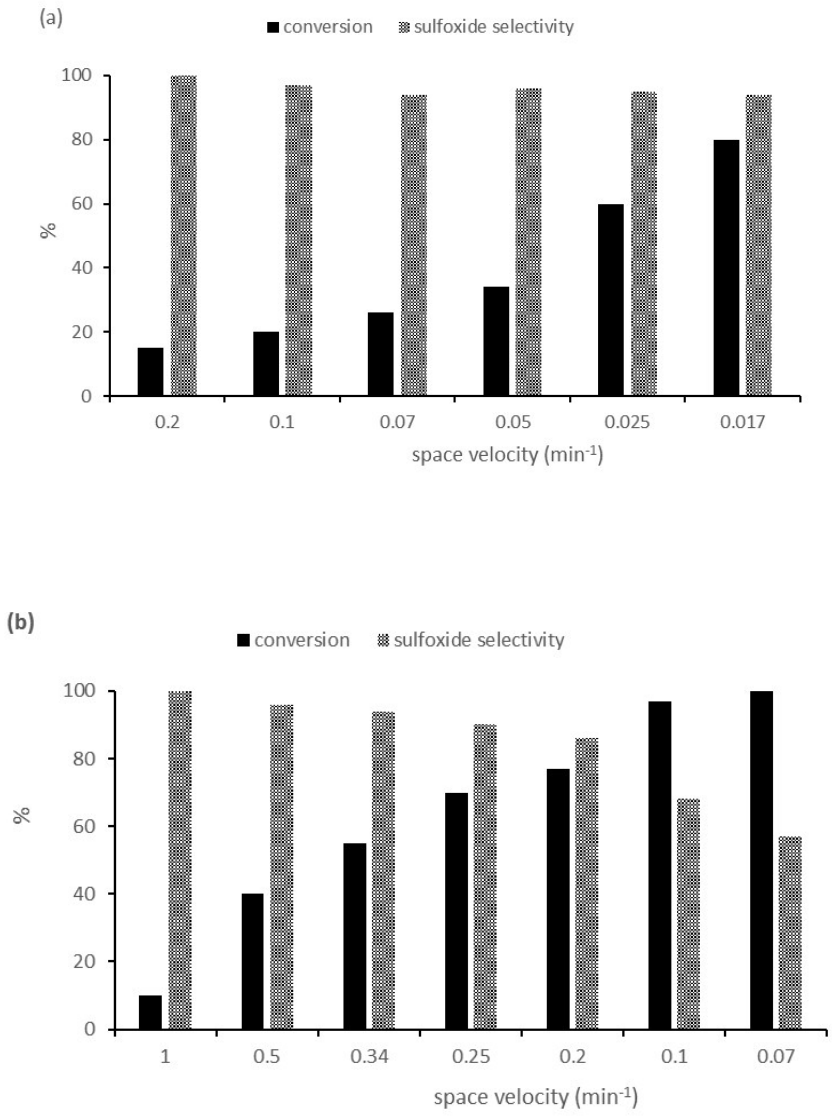



**Figure S89** Segmented flow oxidation of thioanisole as a function of hydrogen peroxide ratio catalyzed by **3a**.



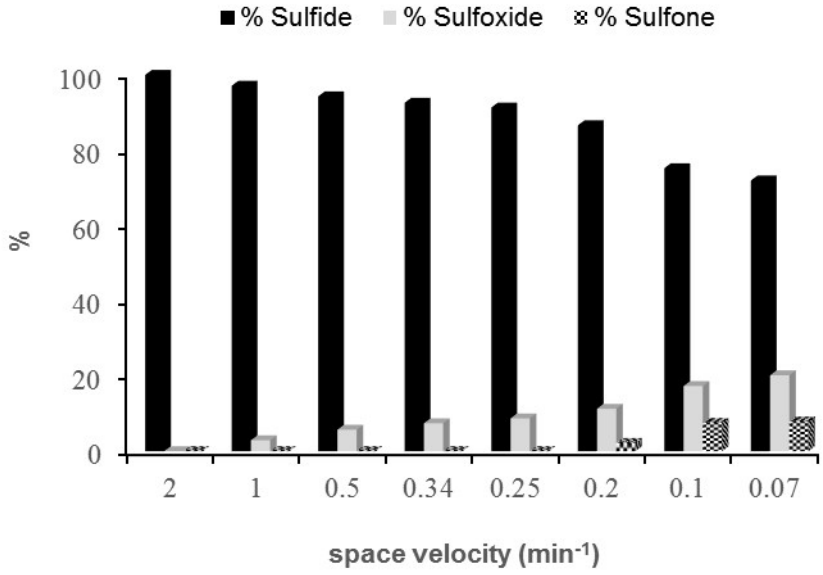

Conversion-selectivity profile as a function of space velocity (sv = volumetric flow rate/reactor volume) for the $[PO_4\{WO(O_2)_2\}_4]$@ImPIILP-catalysed sulfoxidation of thioanisole in ethanol using (a) 1.0, (b) 1.5 and (c) 2 equivalents of $H_2O_2$. Reaction conditions: 0.1 g catalyst/2.0 g silica, 1, 1.5 or 2 equiv. 35% $H_2O_2$, temp = 25 °C, space velocity 2.0–0.07 $min^{-1}$.

**Figure S90** Segmented flow oxidation of thioanisole as a function temperature catalyzed by **3a**.




Conversion-selectivity profile as a function of space velocity (sv = volumetric flow rate/reactor volume) for the $[PO_4\{WO(O_2)_2\}_4]$@ImPIILP-catalysed sulfoxidation of thioanisole in ethanol at (a) 10 °C and (b) 50 °C. Reaction conditions: 0.1 g catalyst/2.0 g silica, 1.5 equiv. 35% $H_2O_2$, space velocity (a) 0.2-0.017 $min^{-1}$ and (b) 1.0–0.07 $min^{-1}$.

**Figure S91** Segmented flow $[PO_4\{WO(O_2)_2\}_4]$@ImPIILP-catalysed sulfoxidation of dibenzothiophene at 25°C as a function of space velocity.




Conversion-selectivity profile as a function of space velocity (sv = volumetric flow rate/reactor volume) for the $[PO_4\{WO(O_2)_2\}_4]$@ImPIILP-catalysed sulfoxidation of dibenzothiophene in acetonitrile. Reaction conditions: 0.1 g catalyst/2.0 g silica, 3 equiv. 35% $H_2O_2$, MeCN, temp = 25 $^oC$, space velocity 2.0–0.07 $min^{-1}$.